

Transition Metal-Hydrogen and Metal-Carbon Bond Strengths: The Keys to Catalysis

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I. Introduction

"Organometallic thermochemistry is one of the growth areas in chemical investigation at the present time and has been so for the past two decades. The thermochemist is now presented with an area for investigation almost unexplored, challenging his technical skills and beginning to be met." This remark was made by Henry Skinner at the second Rossini Lecture in 1978.¹ Fourteen years earlier the same author wrote a similar comment in a review article entitled *The Strengths of Metal-to-Carbon Bonds*,² which is the first comprehensive and critical survey of organometallic thermochemistry. Although this area of research had not experienced a fast growth during the 1960s and the 1970s, a result mainly of the experimental difficulties faced by thermochemists, the number of studies devoted to organometallic complexes started to increase in the early 1970s, particularly after the groups of Wilkinson and Lappert independently reanalyzed the

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problem of kinetic versus thermodynamic stability of transition-metal compounds containing metal-carbon σ bonds.³ This problem was confronted by several thermochemists, who sought experimental evidence for the thermodynamic stability of transition metal-carbon bonds. Examples of articles in which this point is

mentioned as being the aim of the studies described therein are provided by Skinner and co-workers⁴ and by Ashcroft et al.⁵

The increasing application of homogeneous catalysis in industrial processes⁶⁻⁹ provides today the major incentive for thermochemical studies of organometallic compounds of the transition elements. A knowledge of metal-carbon and metal-hydrogen bond enthalpies is essential for the understanding of catalytic reaction mechanisms, which often involve the cleavage or the formation of those bonds.^{6,10-12} Moreover, as noted by Halpern 10 years ago, "developments in the fields of homogeneous catalysis and coordination chemistry have once again focused attention on free radical mechanisms and suggest that such mechanisms are more important and widespread than previously suspected".¹³

The recognition of the importance of transition metal-ligand bond enthalpies and, in particular, metal-hydrogen and metal-carbon σ -bond enthalpies in the above and in several other areas of current investigation, such as surface chemistry and biochemistry, has fostered research efforts devoted to thermochemistry. Although the number of those studies remains small in comparison to the overall level of activity in organometallic chemistry, the amount of relevant information presently available is not as scarce as a cursory search of the literature would lead one to believe. In addition, from theoretical models and a knowledge of periodic trends in thermochemical data, it is often feasible to estimate values with a fair degree of accuracy.

The aim of this review is to summarize the presently available information relating mainly to transition metal-carbon σ -bond enthalpies and transition metal-hydrogen bond enthalpies. Transition metal-olefin,¹⁴ metal-carbene, metal-carbyne, and metal-carbide bond enthalpies are also surveyed. When thermochemical values are determined from the enthalpies of formation of the parent molecules or from enthalpies of reaction in solution, special attention is given to the reliability of any assumptions involved in the analysis. In several instances reevaluation of experiments leads to values markedly different from the ones originally reported. In other words, this review intends also to be a critical analysis of the published data, by discussing the methods of calculation of bond enthalpies and the meaning of the two parameters usually considered as measuring "bond strengths".

Enthalpies of displacement reactions in solution are not extensively reviewed since they cannot yield bond enthalpy values without additional data. Many cases are, however, included in the discussion, particularly when it is thought that the solution studies provide approximate values for the bond enthalpies. Except for a few examples, transition metal-carbonyl, -arene, and -cyclopentadienyl bond enthalpies are not included in the discussion. Most of these data have been analyzed in a review by Pilcher and Skinner.¹⁵

Finally, it should be mentioned that the present survey covers the literature through the end of 1988, with a few references from 1989.

II. Experimental Methods

There are excellent reviews discussing experimental techniques for obtaining thermochemical data. The aim of the present section is therefore restricted to a brief

survey of those methods, emphasizing their advantages or drawbacks when applied to organometallic compounds.

Combustion calorimetry has been the more widely used technique to obtain enthalpies of formation of organic substances, which generally present few problems to the experimentalist. Several comprehensive reviews have dealt with combustion techniques, either discussing the final states (products) of combustion reactions or describing the more suitable combustion bombs to study a given class of substances.¹⁶⁻²¹ The stage of development of organic thermochemistry is reflected by the considerable number of organic molecules whose enthalpies of formation are known and also by the precision of the results.^{19,22,23}

The experimental situation is more difficult with molecules containing one or more transition-metal atoms. Among other problems, the formation of oxides having several stoichiometries or the presence of unoxidized metal after oxygen combustion can contribute to an ill-defined final state. Moreover, these problems are sometimes specific for each metal,²¹ requiring new techniques and new types of calorimeters, such as the rotating combustion bomb.^{19,24} Combustion calorimetry of some organometallic complexes demands so many tricks that Good and Scott noted that "control of the combustion reaction, in the present state of thermochemistry, is more an art than a science".²⁵ Although this comment was made in a 1962 review article, which is one of the first surveys on combustion calorimetry of organometallic compounds, it remains an important consideration.

Combustion calorimetry has two other important drawbacks when used for organometallic compounds. First, the amount of substance in each experiment is often larger than 1 g, which means that the study of a given compound requires a minimum of 5 g. This obviates the study of many interesting molecules. The second difficulty is caused by the spontaneous reaction of some organometallic complexes with oxygen. This means that the sample has to be protected inside the bomb (which contains oxygen at a pressure of about 30 atm), usually by using an impermeable container or by covering the substance with paraffin. Although the combustion energy of the protecting substance can be measured accurately, its value is often higher than the combustion energy of the sample.

Traditional versions of combustion calorimeters, which were widely and successfully used for organic molecules or even for some molecules containing main-group elements, did not prove suitable for studying many transition metal-organo complexes. This led to the development of new experimental approaches, including rotating minicombustion bombs, enabling the use of samples as small as a few milligrams.^{24,26} However, these bombs also present difficulties related to analysis of the combustion products of tiny amounts of material.

Reaction solution calorimetry, in its several forms, has been one major alternative to combustion studies of organometallic complexes. It is also a fairly standard technique, employing simple and inexpensive equipment, and can provide very accurate results.^{19,20,27-30} The major limitation is that the accuracy and the precision of the results are sometimes determined by

chemical factors, such as reaction yields, which are less than 100%. This disadvantage, together with the knowledge that high-quality results are obtained in the applications of combustion calorimetry to organic substances, explains why reaction solution calorimetry was not widely used in the past. However, organometallic thermochemistry is usually far less demanding in terms of accuracy and precision of results, mainly because the purity of many samples is unfortunately not comparable with the achievable purity for most organic compounds. The errors in solution calorimetric measurements are often determined by the purity of the samples rather than the completeness of reactions. Even if it is assumed that a given sample is 100% pure and that the yield of the reaction is about 95%, the final inaccuracy in the enthalpy of formation of the complex will seldom be more than a few kilojoules. This is, of course, a consequence of the usually low values of reaction enthalpies in comparison to combustion values, whose magnitude is on the order of several thousand kilojoules.

Although the enthalpy of formation of a compound can only be obtained by reaction calorimetry if the enthalpies of formation of the remaining reactants and products are available, which is often not the case, the enthalpy of reaction can provide direct information relating to individual bond enthalpies. Combustion experiments yield enthalpies of formation from which the total sum of bond enthalpies in a molecule can be evaluated. This important distinction, which is illustrated in sections III and IV, is also responsible for the growth in use of reaction solution calorimetry for the study of organometallic systems.

A second important alternative to combustion calorimetry has been provided by heat flux microcalorimetry.^{19,30-33} The application of this technique to organometallic complexes was developed by Skinner and co-workers around 1970.^{34,35} The quantities measured are enthalpies of either thermal decomposition or halogenation, which in turn yield enthalpies of formation of crystalline or liquid samples. Although the results obtained by this method are usually less accurate than the ones derived by solution calorimetry, this minor disadvantage is more than compensated by the fact that each experiment requires a small sample, on the order of 3-5 mg. A second advantage of heat flux microcalorimetry is that it can often be used for measuring the enthalpies of sublimation or vaporization of the organometallic complexes,³⁶ thus enabling the evaluation of their gas-phase enthalpies of formation.

Among the so-called methods of thermal analysis, differential scanning calorimetry (DSC)^{30,37-41} has been preferred for measuring enthalpies of decomposition of organometallic substances (see section IV). As in heat flux microcalorimetry, this technique makes use of very small samples and enables the determination of enthalpies of sublimation or vaporization.⁴² However, the experimental values it yields are generally considered less reliable than those obtained with a heat flux calorimeter.

One of the drawbacks of reaction calorimetry stems from the fact that chemical reactions seldom involve the formation or the cleavage of only one bond, and thus the measured enthalpies of reaction usually yield *differences* between unknown bond enthalpies. A different type of reaction solution calorimetry, called

"photoacoustic", has been developed in recent years and enables the study of the energetics of very rapid processes (e.g., radical-molecule reactions).^{43,44} In many cases the measured reaction enthalpies also reflect the cleavage and the formation of more than one bond, but often only one bond enthalpy is unknown. The use of photoacoustic calorimetry to study main-group element molecules has provided a significant amount of information on bonding energetics, but its application to transition-metal systems is more scarce. Several complicating factors can be expected in experiments involving these substances, including solvation effects in the coordinatively unsaturated complexes, lack of reliable values for quantum yields, and frequent possibility of competing reactions.⁴⁵

In addition to the "first law" methods mentioned above, enthalpies of reactions involving organometallic complexes have also been obtained through "second law" methods,¹⁹ both in solution and in the gas phase. These approaches make use of the van't Hoff equation, by plotting the logarithm of the measured equilibrium constants for a reaction against the inverse of absolute temperatures. The usual van't Hoff analysis treats reaction enthalpies as constants over the considered range of temperatures. Hence, the accuracy of the second law method is in principle smaller than the direct measurements by calorimetry. Nevertheless, the differences are usually inconsequential as far as organometallic thermochemistry is concerned, particularly when experimental conditions require narrow temperature ranges.

Arrhenius or Eyring plots of rate constant data have also provided very useful information on the energetics of metal-ligand bonds. However, the derived reaction enthalpies, in particular those obtained in solution, usually rely on a number of assumptions that are difficult to assess.⁴⁶

The isolation of organometallic species in the vapor phase makes it possible to employ a range of sophisticated techniques to study their properties and reactions in the absence of complicating solvation phenomena. These studies often yield direct measurements of bond dissociation enthalpies, and the considerable number of results obtained thus far merely presage the more extensive application of these techniques in the future. Included among newer experimental methods are ion cyclotron resonance spectroscopy,⁴⁷⁻⁵¹ high-pressure mass spectrometry,⁵²⁻⁵⁵ photoionization mass spectrometry,⁵⁶ photoelectron spectroscopy,⁵⁷⁻⁵⁹ ion beam studies of endothermic reactions,^{49,60-62} flowing afterglow,⁶³⁻⁶⁶ kinetic energy release distributions,⁶⁷⁻⁷⁰ and laser-powered homogeneous pyrolysis.⁷¹ The techniques generally employ some form of mass spectrometry to detect and study organometallic ions formed by ionization of neutral species.

Mass spectrometry has long been employed to analyze the effluents of Knudsen cells and thus characterize the vapor species in equilibrium with condensed phases.⁷² Knudsen cells are excellent sources of organometallic "fragments", such as metal carbides, which in addition to the equilibrium data can be further characterized using spectroscopic techniques.

Ion cyclotron resonance experiments use electric and magnetic fields to create an electromagnetic bottle in which charged particles can be stored for time periods

up to several seconds at pressures below 10^{-6} Torr.⁷³⁻⁷⁵ In a typical experiment, reactant ions are generated from a volatile precursor by a pulsed electron beam and stored for a suitable delay time or reaction period. In early versions of ion cyclotron resonance spectroscopy, ion concentrations and masses were determined by examining absorption of energy from a radiofrequency electric field at the cyclotron frequency of the detected ion. By varying the delay time, temporal profiles of ion concentration were obtained and analyzed to yield reaction rates and equilibrium constants for ion-molecule reactions. The application of Fourier transform methods has greatly improved the sensitivity and resolution of ion cyclotron resonance spectroscopy^{50,51} and, together with the development of associated techniques or experimental procedures, is responsible for a wealth of mechanistic and thermochemical data obtained for organometallic species in recent years. Newer experimental methodologies include the use of pulsed valves,⁷⁶ laser desorption,⁷⁷ collision-induced dissociation,^{78,79} and photodissociation.⁸⁰

High-pressure mass spectrometry⁵²⁻⁵⁵ and the related flow tube techniques provide data relating to the kinetics and equilibria of ion-molecule reactions at high pressures (usually 1–10 Torr), where clustering and ion solvation processes are more prevalent. Although they have considerable potential, these techniques have not yet been extensively used to study the thermochemistry of organometallic complexes.

Photoionization mass spectrometry provides accurate ionization thresholds for generating molecular and fragment ions from molecular species.⁵⁶ These data directly provide bond dissociation enthalpies in molecular ions and, with additional information relating to ionization energies of fragments, in neutral species as well. Photoelectron spectroscopy, including various coincidence techniques, yields accurate ionization energies for both parent molecules and molecular fragments.⁵⁷⁻⁵⁹

Ion beam studies of endothermic reactions have now provided a considerable body of information relating to metal-hydrogen and metal-carbon bond dissociation enthalpies in organometallic fragments.^{81,82} These experiments utilize an energy- and mass-selected ion beam, which is allowed to collide with reactant species under single-collision conditions. By monitoring the conversion of reactants to products, thresholds for endothermic processes can be determined, which directly yield bond dissociation enthalpies. The frequent presence of significant amounts of excited-state ions in the beam was a serious complication in some early experiments, but the problem has been overcome by "cooling" the ions through their collision with molecules of an argon bath gas maintained at room temperature.⁸³

Early ion beam studies utilized a simple collision cell, which provides cross-section data with limited quantitative significance. Armentrout's development of guided ion beam techniques, using a radiofrequency (rf) octopole for the collision cell, has greatly improved the quality of the experimental results.^{61,62,81-83} More recently, tandem mass spectrometric methods, usually involving triple quadrupole experiments, have been employed to determine metal-ligand bond dissociation energies.^{84,85} The quantitative analysis of these experiments is often plagued with problems arising from

broad ion translational and vibrational energy distributions.

A relatively new and powerful technique for obtaining information relating to potential energy surfaces and reaction thermochemistry for organometallic processes involves the determination of kinetic energy release distributions for the products of ionic fragmentation processes.⁶⁷⁻⁷⁰ Two distinct experiments have evolved. The majority of studies have comprised the examination of bimolecular processes leading to chemically activated intermediates whose internal energies are well-known.⁶⁸ In more recent developments, it has been shown that it is not necessary to precisely define the internal energy of the decomposing ion.⁷⁰ The instrument of choice for these studies is a VG ZAB-2F reversed-geometry double-focusing mass spectrometer, which is ideally suited for the precise determination of metastable ion kinetic energies.⁸⁶ In studies of chemically activated reaction intermediates, adducts of atomic metal ions with neutral reactants are extracted from a high-pressure ion source and mass analyzed on a magnetic sector. Translational energies of products formed by adduct dissociation in the second field-free region between the magnetic and electric sectors are determined from an analysis of the metastable peak shape obtained by scanning the electric sector.⁸⁶ Since many complex organometallic species are relatively involatile, techniques such as fast atom or ion bombardment and laser desorption can be used to generate interesting species for gas-phase studies. These processes generally yield ions with a broad distribution of internal energies, which is also characteristic of ions formed in electron impact fragmentation processes. Recent studies of kinetic energy release distributions for the latter have yielded useful data for reaction thermochemistry. While the systems studied thus far are relatively simple (determination of the first four carbonyl binding energies in $\text{Mn}(\text{CO})_6^+$),⁷⁰ the technique works best with large ions and there is now considerable promise for gas-phase studies of complex species.

Laser techniques are being used increasingly to activate and probe organometallic molecules. These studies are highlighted by the determination of the first CO bond dissociation enthalpy in a series of metal-carbonyl compounds by Lewis, Golden, and Smith.⁷¹ They used a pulsed CO_2 laser to heat a bath gas containing the metal-carbonyl compound and a standard with well-known activation parameters for thermal decomposition. The technique ensures homogeneous thermolysis since the walls of the reaction vessel remain cool. This is particularly important for organometallic species, where metallic deposits often catalyze decomposition at relatively low temperature.

III. Evaluation of Bond Enthalpies

The parameters usually regarded as measuring "bond strengths" are *bond dissociation enthalpies* (D), *mean bond dissociation enthalpies* (\bar{D}), and *bond enthalpy terms* (E) (see short definitions in the Appendix). These quantities have different meanings and seldom can be equated.

It is the purpose of the present section to show how these parameters can be evaluated from experimental data, such as enthalpies of formation, enthalpies of reaction in solution, enthalpies of decomposition in the

solid state, and also enthalpies of reaction in the gas phase. This is not a trivial matter, particularly in molecules as complex as organometallic compounds, where it is often necessary to "transfer" a bond enthalpy from one molecule to another in order to derive a "new" value. The importance of the *transferability* problem has been emphasized in an early review by Connor.⁸⁷

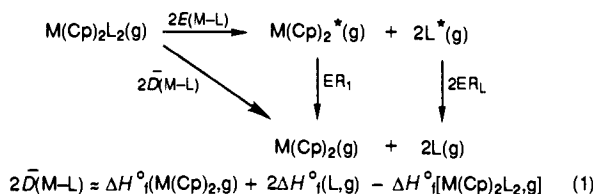
Although the following discussion deals with general ideas, applicable to any organometallic system, the quoted examples always involve transition metal-carbon or metal-hydrogen bonds, which are the focus of the present review. This discussion of methods used to calculate *E* and *D* serves as an introduction to section IV.

A. Bond Enthalpies from Enthalpies of Formation in the Gas Phase

The standard enthalpy of formation of a molecule is a measure of its enthalpy content. If the molecule has several atoms and bonds, the problem of assigning a value to the enthalpy of each bond can become rather difficult. This is particularly so when the central atom is surrounded by different polyatomic ligands and one wants to know the strength of a particular bond between that central atom and one of the ligands. As will be shown, experimental thermochemistry cannot, by itself, provide an answer to this problem.

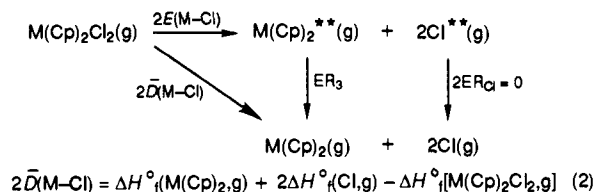
Consider, as an example, the molecule $M(\text{Cp})_2\text{L}_2$ (*M* is a transition-metal atom, *Cp* is $\eta^5\text{-C}_5\text{H}_5$, and *L* is a mono- or polyatomic ligand). If the gaseous enthalpies of formation of the complex, the $M\text{Cp}_2$ moiety, and the ligand *L* were available, a value for the mean bond dissociation enthalpy, $\bar{D}(M-L)$, could be obtained through Scheme 1 or eq 1. However, the enthalpy of

SCHEME 1



formation of $M(\text{Cp})_2$ is not available directly, and so one has to calculate it by using Scheme 2 or eq 2, where the specific example for *L* = Cl is considered.

SCHEME 2



One asterisk in Scheme 1 means that the fragments $M(\text{Cp})_2^*$ and L^* have the same structures they had in $M(\text{Cp})_2\text{L}_2$. Two asterisks in Scheme 2 mean that the fragment $M(\text{Cp})_2^{**}$ keeps the same configurations as in $M(\text{Cp})_2\text{Cl}_2$. ER_1 , ER_L , and ER_3 , called reorganization energies, are therefore the energy changes associated with the relaxation of $M(\text{Cp})_2^*$, L^* , and $M(\text{Cp})_2^{**}$ to their ground states, $M(\text{Cp})_2$ and *L*. These quantities help in discussing the problem of how to estimate a reliable value for $\bar{D}(M-Cl)$, so that $\Delta H_f^\circ(M(\text{Cp})_2, \text{g})$ can be obtained. Although this question is not crucial for

deriving *relative* *M-L* mean bond dissociation enthalpies in a series of complexes, i.e., all the values are anchored to the same $\bar{D}(M-Cl)$ value, it is obviously desirable to make a sensible assignment. What seems to be a reasonable approximation is to identify *M-Cl bond strengths* in the complex and in the homoleptic molecule $M\text{Cl}_n$, on the basis of similar bond lengths. The question is whether it should be assumed that $\bar{D}(M-Cl)$ in $M\text{Cl}_n$ is also equal to $\bar{D}(M-Cl)$ in the complex. This is a common procedure, and it was used in early studies of systems of this type.⁸⁸ However, it must be realized that similar bond lengths (or bond strengths) do not imply similar bond dissociation enthalpies because the reorganization energies of the fragments formed in the disruption process can be quite different. A better hypothesis is therefore to identify the *M-Cl* bond enthalpy terms in both molecules, since these quantities do not include the reorganization energies of the fragments. If it is also assumed that *ER* of an atom is zero, then

$$\begin{aligned}
 E(M-Cl) &= \bar{D}(M-Cl) \text{ in } M\text{Cl}_n \\
 &= E(M-Cl) \text{ in } M(\text{Cp})_2\text{Cl}_2 \quad (3)
 \end{aligned}$$

When assumption 3 is introduced in eq 2 and the result subtracted from eq 1, metal-ligand mean bond dissociation enthalpy is finally obtained by eq 4.

$$\begin{aligned}
 \bar{D}(M-L) &= E(M-Cl) + \Delta H_f^\circ(\text{L}, \text{g}) - \Delta H_f^\circ(\text{Cl}, \text{g}) - \\
 &\quad \{\Delta H_f^\circ[M(\text{Cp})_2\text{L}_2, \text{g}] - \Delta H_f^\circ[M(\text{Cp})_2\text{Cl}_2, \text{g}]\} / 2 + \\
 &\quad \text{ER}_3 / 2 \quad (4)
 \end{aligned}$$

An expression for the bond enthalpy term $E(M-L)$ also follows from Schemes 1 and 2 and eq 5.

$$\begin{aligned}
 E(M-L) &= E(M-Cl) + \Delta H_f^\circ(\text{L}^*, \text{g}) - \Delta H_f^\circ(\text{Cl}, \text{g}) - \\
 &\quad \{\Delta H_f^\circ[M(\text{Cp})_2\text{L}_2, \text{g}] - \Delta H_f^\circ[M(\text{Cp})_2\text{Cl}_2, \text{g}]\} / 2 + \\
 &\quad (\text{ER}_3 - \text{ER}_L) / 2 \quad (5)
 \end{aligned}$$

The above discussion illustrates some cautions that should be taken when bond enthalpy values are derived from thermochemical data, particularly if bond enthalpies are transferred from one molecule to another. "Correct" values for $\bar{D}(M-L)$ and $E(M-L)$ can only be obtained if ER_1 , ER_3 , $\Delta H_f^\circ(\text{L}, \text{g})$, and $\Delta H_f^\circ(\text{L}^*, \text{g})$ are available.

If the fragments $M(\text{Cp})_2^*$ and $M(\text{Cp})_2^{**}$ have identical structures, then $\text{ER}_3 \approx \text{ER}_1$. This is indeed what happens for many $M(\text{Cp})_2\text{L}_2$ complexes. In others, however, there are large variations of *Cp-M-Cp* centroid angles. For example, it is known that when the ligand *L* is a strong σ donor or a weak π acceptor, the *Cp-M-Cp* angles are considerably larger in $M(\text{Cp})_2\text{L}_2$ than in $M(\text{Cp})_2\text{Cl}_2$.⁸⁹ For these cases, it seems unwise to use eq 5 and make $\text{ER}_3 = \text{ER}_1$. In fact, extended Hückel molecular orbital calculations reveal that the energy change associated with the rearrangement of $M(\text{Cp})_2$ fragments from an angle *Cp-M-Cp* = 130.5° (in $\text{Mo}(\text{Cp})_2\text{Cl}_2$)⁹⁰ to 145.8° (in $\text{Mo}(\text{Cp})_2\text{H}_2$)⁹¹ is about -66 kJ/mol (see Figure 1b), which implies that the correcting term in eq 5 can amount to -33 kJ/mol.

ER_3 can also be derived from curves similar to Figure 1, although in this case the obtained values are certainly less reliable than the differences $\text{ER}_3 - \text{ER}_1$. Note that, in the case of titanium (Figure 1a), the most stable geometry, which should correspond to the reorganized fragment, is achieved with *Cp-M-Cp* \approx 140°. According to the extended Hückel calculations,⁹² this result is a consequence of the fact that the Ti(II) atom has two

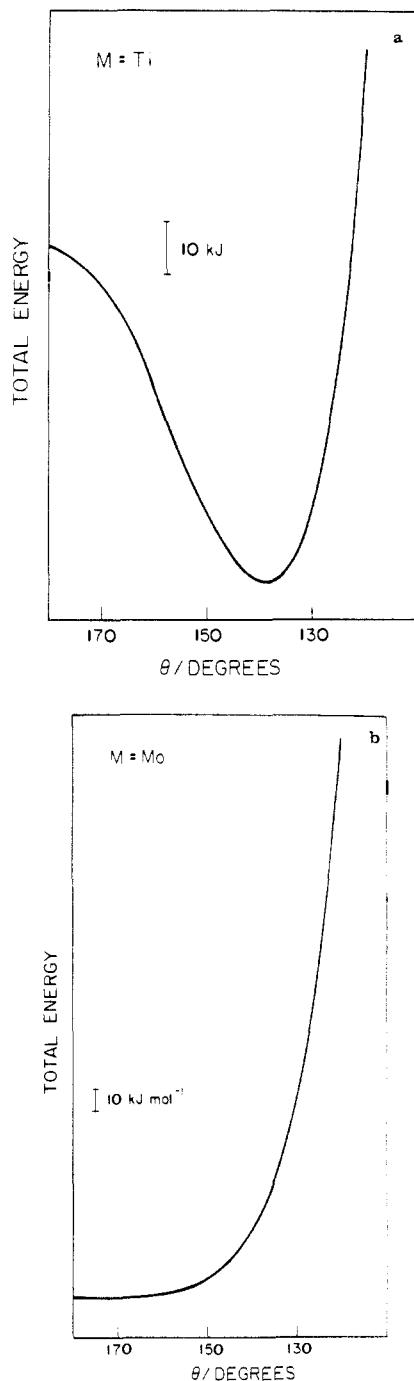


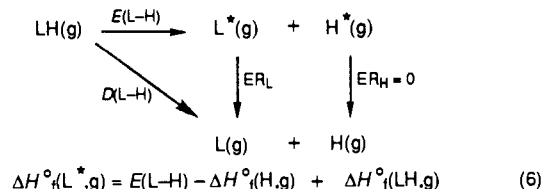
Figure 1. Total energies of $M(\text{Cp})_2$ fragments as a function of the centroid angle Cp-M-Cp (θ): (a) $M = \text{Ti}$; (b) $M = \text{Mo}$. The following bond lengths were used in the calculations (pm): C-C, 140; C-H, 109; Ti-Cp, 207; Ti-C, 238.8; Mo-Cp, 200; Mo-C, 232.8. See: Reference 92. Calhorda, M. J. Unpublished results.

d electrons and so the total energy of the system closely follows a low-energy occupied b_2 level, the HOMO (a_1) remaining mostly nonbonding as the distortion proceeds. The presence of further d electrons would favor the configuration corresponding to $\theta = 180^\circ$ because they would occupy the b_2 level, which is destabilized with bending due to the steric repulsion between the cyclopentadienyl rings. This effect contributes more to the total energy than the stabilization of b_2^* , and so the more stable configuration for $\text{Mo}(\text{Cp})_2$ and $\text{W}(\text{Cp})_2$ fragments, where metals have four d electrons, corresponds to 180° .^{89,92} This makes the correction term ER_3 very large in the case of molybdenum and tungsten complexes, as compared to the same term for the tita-

niun analogues, because the Cp-M-Cp angle is not far from 130° in most $M(\text{Cp})_2L_2$ compounds.⁹⁰

The remaining correction term that deserves a brief discussion is $\Delta H^\circ_f(L^*,g)$ in eq 5. If L is an atom, then, according to the assumption above, $\Delta H^\circ_f(L^*,g) = \Delta H^\circ_f(L,g)$. However, when L is a polyatomic species, the difference between these quantities must be estimated. In many cases the structure of L is identical in the $M(\text{Cp})_2L_2$ complex and in the molecule LH .⁹³ Assuming this as a general feature,⁹⁴ $\Delta H^\circ_f(L^*,g)$ can be derived from Scheme 3 or eq 6. The problem now is

SCHEME 3

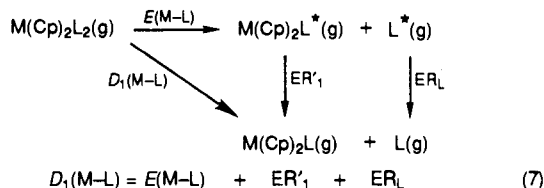


the evaluation of $E(\text{L-H})$. An ideal analysis of Scheme 3 would employ potential energy surfaces, generated from spectroscopic data and theoretical calculations, to provide accurate values for ER_L , the reorganization energy of the fragments as they relax to their most stable form from the structures they had in the molecule LH . Although a growing body of data is available for simple radicals,^{95,96} it would be premature to employ it in the present review. There are three less exact, but readily applied, approaches that can be used to evaluate $E(\text{L-H})$: (1) Sanderson's method,⁹⁷⁻¹⁰⁰ (2) correlations between bond enthalpy terms and bond distances,^{15,101} and (3) use of Laidler parameters.^{19,102} These alternatives have been discussed,^{93,103} and the Laidler scheme seems the best choice. Unfortunately, it is not always possible to use this scheme, as, for example, in $\text{Ti}(\text{Cp})_2\text{Fc}_2$ (Fc = ferrocenyl), presented in section IV.A. $E(\text{Fc-H})$ was derived by using a correlation of the quantities $E(\text{C-H})/r(\text{C-H})$.^{93,104} It must be noted that the use of Laidler parameters, which are defined in a self-consistent fashion to reproduce hydrocarbon enthalpies of formation,¹⁹ may lead to reorganization energies that do not have a simple physical interpretation. If "true" reorganization energies were available, they would always be negative since $\text{L}^*(g)$ must be higher in energy than $\text{L}(g)$. A perusal of the data in the Appendix indicates that this is the case for benzyl [$ER(\text{Bz}) = -43 \text{ kJ/mol}$], where the resonance energy becomes available only after the system relaxes. Phenyl and methyl, however, have reorganization energies equal to 44 and 24 kJ/mol, respectively. These positive values are a consequence of the way in which the Laidler parameters are defined.^{19,102} Reasonable estimates of bond dissociation enthalpies in organometallic compounds result from the self-consistent application of this analysis.

As pointed out before, the present discussion shows that the procedure of evaluating bond enthalpies should be carefully considered and not regarded as a mere exercise of using thermochemical data. "Correct" bond enthalpy terms and mean bond dissociation enthalpies may also rely upon structural data and theoretical calculations. The meaning of each of these parameters is also of importance. For example, bond enthalpy terms seem to be the right parameters to correlate with force constants, bond lengths, or solid cone angles, since

bond dissociation enthalpies contain the energies of reorganization of the fragments. An exception is made, of course, when these reorganization energies are approximately constant in a given series of molecules. $E(M-L)$ values can also be more useful than $D(M-L)$ if one needs to estimate a new bond enthalpy value (see section IV), and they can provide a basis for establishing a set of bond terms, consistent with schemes used for organic compounds, such as the Laidler scheme.^{19,102} Finally, they enable estimation of metal-ligand stepwise bond dissociation enthalpies by using a simple extension of the method described above.¹⁰⁵ The first bond dissociation enthalpy, $D_1(M-L)$, is calculated by eq 7, derived from Scheme 4, where the symbols have the

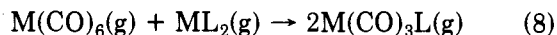
SCHEME 4



usual meaning. As $E(\text{M-L})$ is transferred from eq 5, $D_1(\text{M-L})$ in eq 7 is independent from the value ascribed to $E(\text{L-H})$. The reorganization energy ER'_1 can be estimated through the extended Hückel approximation.¹⁰⁵ The second metal-ligand bond dissociation enthalpy, $D_2(\text{M-L})$, is simply the difference between $2\bar{D}(\text{M-L})$ and $D_1(\text{M-L})$.

$\text{M(Cp)}_2\text{L}_2$ complexes were chosen to illustrate the above discussion not only because there is a considerable body of thermochemical data but also because they provide a good example of some difficulties that arise when bond enthalpies are derived. It must be stressed, however, that any conclusions derived from the method described must be regarded as semiquantitative, particularly when the reorganization energies are obtained by the extended Hückel approach.

Another good example to show how the uncritical assumption of bond transferability can cause some problems is provided by the complexes M(CO)_6 , $\text{M(CO)}_3\text{L}$ and ML_2 ($\text{M} = \text{Cr, Mo, W}$; $\text{L} = \text{arene}$). To obtain $D(\text{M-L})$ in $\text{M(CO)}_3\text{L}$, equal $\bar{D}(\text{M-CO})$ values in this complex and in the hexacarbonyl complex were assumed. If, on the other hand, it was valid to transfer $\bar{D}(\text{M-L})$ from ML_2 to $\text{M(CO)}_3\text{L}$, then the enthalpy of reaction 8, calculated from the enthalpies of formation



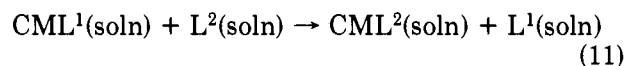
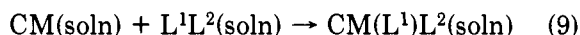
of product and reactants, should be zero. In several reported examples for $\text{M} = \text{Cr}$ and $\text{L} = 1,2,3,4,4a,8a-\eta$ -naphthalene, benzene, η -1,3,5-trimethylbenzene, and η -hexamethylbenzene, $\Delta H^\circ(8)$ falls within the range of -16 ± 20 to -99 ± 29 kJ/mol.¹⁰⁶ These values are discussed by Connor, Skinner, and co-workers, and the exothermicity of reaction 8 seems to be caused mainly by the fact that metal-carbonyl bonds are stronger in the heteroleptic complex than in chromium hexacarbonyl. If the subject were discussed by using bond enthalpy terms and if these were correlated with bond lengths, then it should be expected that $E(\text{Cr-L})$ would decrease from CrL_2 to $\text{Cr(CO)}_3\text{L}$ and that $E(\text{Cr-CO})$ would increase from Cr(CO)_6 to $\text{Cr(CO)}_3\text{L}$.

Although outside the scope of the present review, the studies on the thermochemistry of metal-metal bonds

that have been made by the group of Skinner, Pilcher, and Connor, at Manchester, are worth mentioning.¹⁵ More than in any other case, the concept of the bond enthalpy term plays an essential role when metal-metal bond enthalpies are derived from thermochemical data.

B. Bond Enthalpies from Enthalpies of Reaction in Solution

A considerable portion of the bond enthalpy data presented in section IV is derived directly from enthalpies of reaction in solution, obtained through calorimetric, equilibrium, or kinetic measurements. These studies usually involve one of three types of reactions: (1) oxidative addition (or the inverse process, reductive elimination), (2) dissociation, and (3) ligand-exchange reactions, exemplified in reactions 9–11, respectively, where CM is a transition-metal complex and L^1 and L^2 are poly- or monoatomic additional ligands.



In order to derive bond enthalpy data from the experimental reaction enthalpies, it is necessary to use some convenient assumptions. To analyze these assumptions, it is helpful to consider eqs 12–14, which give the enthalpy change of reactions 9–11, respectively, but with all the products and reactants in their standard gaseous state, ΔH°_g .

$$\begin{aligned}
 \Delta H^\circ_g(9) = & \Delta H^\circ(9) + \{\Delta H^\circ_{\text{soln}}(\text{CM}, \text{s}) - \\
 & \Delta H^\circ_{\text{soln}}[\text{CM}(\text{L}^1)\text{L}^2, \text{s}] + \Delta H^\circ_{\text{soln}}(\text{L}^1\text{L}^2, \text{s/l})\} + \\
 & \{\Delta H^\circ_{\text{s}}[\text{CM}(\text{L}^1)\text{L}^2] - \Delta H^\circ_{\text{s}}(\text{CM}) - \Delta H^\circ_{\text{s/v}}(\text{L}^1\text{L}^2)\} \quad (12)
 \end{aligned}$$

$$\begin{aligned}
 \Delta H^\circ_g(10) = & \Delta H^\circ(10) + [\Delta H^\circ_{\text{soln}}(\text{CML}^1, \text{s}) - \\
 & \Delta H^\circ_{\text{soln}}(\text{CM}, \text{s}) - \Delta H^\circ_{\text{soln}}(\text{L}^1, \text{s/l})] + [\Delta H^\circ_{\text{s}}(\text{CM}) - \\
 & \Delta H^\circ_{\text{s}}(\text{CML}^1) + \Delta H^\circ_{\text{s/v}}(\text{L}^1)] \quad (13)
 \end{aligned}$$

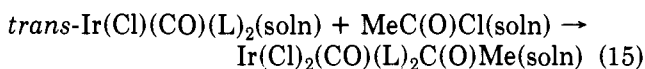
$$\begin{aligned}
 \Delta H^\circ_g(11) = & \Delta H^\circ(11) + [\Delta H^\circ_{\text{soln}}(\text{CML}^1, \text{s}) - \\
 & \Delta H^\circ_{\text{soln}}(\text{CML}^2, \text{s}) + \\
 & \Delta H^\circ_{\text{soln}}(\text{L}^2, \text{s/l}) - \Delta H^\circ_{\text{soln}}(\text{L}^1, \text{s/l})] + [\Delta H^\circ_{\text{s}}(\text{CML}^2) - \\
 & \Delta H^\circ_{\text{s}}(\text{CML}^1) + \Delta H^\circ_{\text{s/v}}(\text{L}^1) - \Delta H^\circ_{\text{s/v}}(\text{L}^2)] \quad (14)
 \end{aligned}$$

When these equations were written, it was considered that the reference state at 298 K for the complexes is the solid state and that L^1 , L^2 , or L^1L^2 are solid or liquid, yielding either sublimation or vaporization enthalpies ($\Delta H^\circ_{\text{s/v}}$). If L^1 , L^2 , or L^1L^2 is a gas, $\Delta H^\circ_{\text{s/v}}$ will vanish.

Even though enthalpies of solution, $\Delta H^\circ_{\text{soln}}$, are usually very easy to obtain by standard calorimetric techniques or when L^1 , L^2 , and L^1L^2 are gases, also from solubility data, studies where bond enthalpy values are directly derived from the enthalpies of reaction in solution, without making use of eqs 12–14, are abundant. This procedure implies that several conditions have to be fulfilled; namely, the solution and the vaporization or sublimation enthalpies must cancel. It is usually taken for granted that the enthalpies of sublimation of the organometallic complexes in reactions 9–11 are approximately equal so that $\Delta(\Delta H^\circ_{\text{s}}) \approx 0$.^{107–111} Considering the difficulty of obtaining experimental values

for enthalpies of sublimation of most organometallic compounds, this assumption is very often necessary and fortunately not unreasonable. There are no reliable methods of estimating enthalpies of sublimation, although there are some semiquantitative guidelines that can be used, based, e.g., on the molecular weight and the polarity of the molecule. For example, it could be expected that $\Delta H^\circ_s(\text{CML}^2) > \Delta H^\circ_s(\text{CML}^1)$ if both L^1 and L^2 are nonpolar and the molecular weights are $L^2 > L^1$. Estimates can be accurate to about ± 10 kJ/mol if, for example, the enthalpy of sublimation of a similar complex is known or, even better, if one is looking for differences between ΔH°_s of two similar complexes.

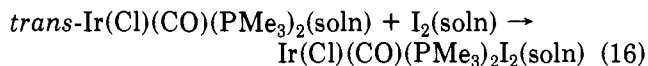
As stated above, the assumption $\Delta(\Delta H^\circ_s) \approx 0$ for reactant and product complexes in reactions 9–11 seems reasonable (see also section III.C). This has been confirmed for one important system in a study by Blake et al.¹¹² on the thermochemistry of oxidative addition processes involving iridium, reaction 15. By using a



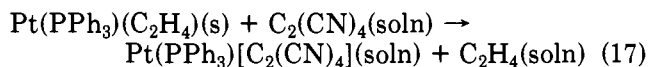
Knudsen cell, the authors arrived at $\Delta H^\circ_s[\text{Ir}(\text{Cl})(\text{CO})(\text{PMe}_3)_2] = 67.4 \pm 15.5$ kJ/mol, $\Delta H^\circ_s[\text{Ir}(\text{Cl})_2(\text{CO})(\text{PMe}_3)_2\text{C}(\text{O})\text{Me}] = 67.4 \pm 8.4$ kJ/mol, $\Delta H^\circ_s[\text{Ir}(\text{Cl})(\text{CO})(\text{PEt}_3)_2] = 79.5 \pm 9.6$ kJ/mol, and $\Delta H^\circ_s[\text{Ir}(\text{Cl})_2(\text{CO})(\text{PEt}_3)_2\text{C}(\text{O})\text{Me}] = 71.6 \pm 0.8$ kJ/mol. Hence, for this system, $\Delta(\Delta H^\circ_s) \approx 0$ within the limits of experimental uncertainties, for both $L = \text{PMe}_3$ and PEt_3 .

Another possible assumption concerning the enthalpies of sublimation and vaporization in eqs 12 and 13 is simply to say that their summation vanishes because $\Delta H^\circ_s[\text{CM}(\text{L}^1)\text{L}^2] \approx \Delta H^\circ_s(\text{CM}) + \Delta H^\circ_{s/v}(\text{L}^1\text{L}^2)$ or $\Delta H^\circ_s(\text{CML}^1) \approx \Delta H^\circ_s(\text{CM}) + \Delta H^\circ_{s/v}(\text{L}^1)$. Available data indicate, however, that this assumption often lacks validity. In the case discussed above, i.e., reaction 15, $\Delta H^\circ_v(\text{MeCOCl}) = 30.1 \pm 0.4$ kJ/mol and $\Delta(\Delta H^\circ_s) \approx 0$. Of course, one may have a different situation in eq 14. For example, if L^1 and L^2 are nonpolar molecules with similar boiling points, it is possible to make $\Delta H^\circ_v(\text{L}^1) \approx \Delta H^\circ_v(\text{L}^2)$, and by taking $\Delta H^\circ_s(\text{CML}^1) \approx \Delta H^\circ_s(\text{CML}^2)$, the last four terms in that equation can be neglected.

When it is ascertained that the solution enthalpies in eqs 12–14 are small, it is possible to neglect these terms without causing serious errors in ΔH°_g .^{111,112} However, this is not without exception. For example, in reaction 16, failure to account for the large enthalpy



of solution of iodine in 1,2-dichloroethane (23.1 ± 0.5 kJ/mol) would yield a large error in $\Delta H^\circ_g(16)$.¹¹¹ Even in the favorable case represented by reaction 17, studied



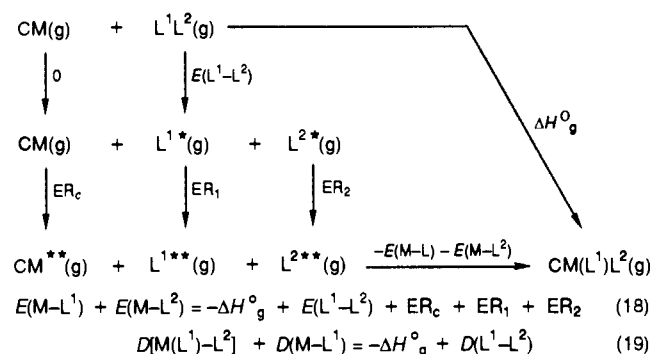
by solution calorimetry by breaking ampoules of the crystalline complex in a tetrahydrofuran solution of tetracyanoethylene, neglecting the solution enthalpies will increase $\Delta H^\circ_g(17)$ by about 10 kJ/mol.¹⁰⁷

From the many cases known in the literature, illustrated by the two preceding examples, it may be con-

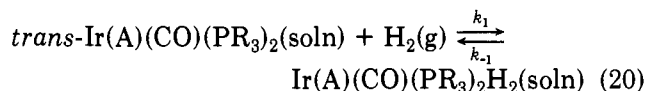
cluded that enthalpies of solution are necessary to derive *reliable* ΔH°_g values. A perfectly valid option is, of course, reporting bond enthalpy data in solution, since these are more relevant for many practical applications than gas-phase values. Nevertheless, comparisons between solution- and gas-phase values should be made with caution.

The evaluation of metal–ligand bond enthalpy terms or bond dissociation enthalpies when ΔH°_g values are known follows from an analysis identical with the one described in section III.A. This can be illustrated by examining Scheme 5 and eqs 18 and 19, which were obtained by considering reaction 9 with all the reactants and products in their standard gaseous state. In Scheme 5 the two asterisks mean that the fragments have the same structure as in the complex $\text{CM}(\text{L}^1)\text{L}^2$ and one asterisk means that the structure of L^1 or L^2 did not change after the L^1 – L^2 bond was broken.

SCHEME 5



The use of eq 18 requires the bond enthalpy term, $E(\text{L}^1\text{-L}^2)$, and the three reorganization energies, ER_c , ER_1 , and ER_2 . Methods for evaluating these quantities were discussed in section III.A. To simplify matters, assume that L^1 and L^2 are both monoatomic species. Then $E(\text{L}^1\text{-L}^2) = D(\text{L}^1\text{-L}^2)$ and $\text{ER}_1 = \text{ER}_2 = 0$. The only "correction" term remaining in eq 18 is therefore ER_c . An example of the extent to which this reorganization enthalpy may affect $E(\text{M-L}^1) + E(\text{M-L}^2)$ is given in a remarkable paper published almost 20 years ago by Vaska and Werneke on the activation of molecular hydrogen by metal complexes.¹¹³ These authors obtained the enthalpy of reaction 20 in chlorobenzene

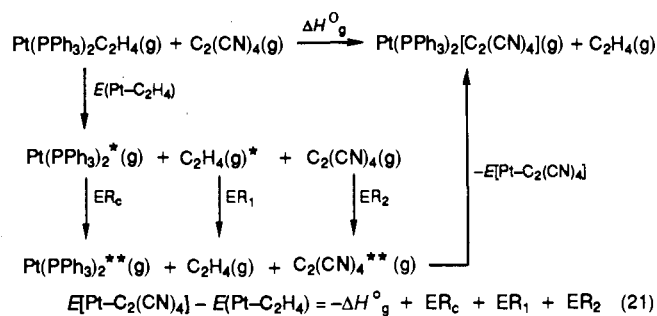


for several ligands A (e.g., Cl, Br, and I) and with A = Cl for a variety of tertiary phosphines (PR_3). Vaska and Werneke assumed $\Delta H^\circ(20) \approx \Delta H^\circ_g(20)$ and derived a relationship similar to eq 18 with $\text{ER}_1 = \text{ER}_2 = 0$.¹¹⁴ This left the problem of evaluating ER_c , which was overcome through a kinetic study of reaction 20. They observed that the activation enthalpy for dehydrogenation, ΔH^\ddagger_{-1} , is almost independent of A and PR_3 . However, this was not the case for ΔH^\ddagger_1 . For example, ΔH^\ddagger_{-1} is about 107 kJ/mol for both chloride and iodide, while ΔH^\ddagger_1 is 50 kJ/mol for chloride and 25 kJ/mol for iodide (when PR_3 is triphenylphosphine). Therefore, the enthalpy of reaction 20, $\Delta H^\circ_g(20) = \Delta H^\ddagger_1 - \Delta H^\ddagger_{-1}$, varies according to ΔH^\ddagger_1 . These and other facts led Vaska and Werneke to suggest that $\text{ER}_c \approx \Delta H^\ddagger_1$, enabling the evaluation of $E(\text{Ir-H}) \approx 271$ kJ/mol, a constant value for a series of different A and PR_3 ligands.¹¹⁵

Iridium-hydrogen mean bond dissociation enthalpies were also obtained by Vaska and Werneke by using eq 19. The values are in the range 239–258 kJ/mol for 11 Ir(A)(CO)L₂ complexes with different A and L. As noted above, this contrasts with the constancy of the iridium-hydrogen bond enthalpy terms, 271 kJ/mol, a number that can be considered as $\langle E(\text{Ir-H}) \rangle$ for the complexes studied.

As noted by Vaska and Werneke, the fact that iridium-hydrogen "bond strengths" are fairly similar could be predicted from the constancy of Ir-H stretching frequencies in the complexes. This shows how valuable bond enthalpy terms can be for measuring a bond strength, but it also stresses how careful one needs to be when using bond dissociation enthalpy data for the same purpose. This point has also been recognized by Evans, Mortimer, and Puddephatt.^{107,108} In their thermochemical study of reaction 17, they have obtained a value for $D[\text{Pt-C}_2(\text{CN})_4] - D(\text{Pt-C}_2\text{H}_4)$ (see Table 12). However, they were aware that the carbon-carbon bond lengths in the complexed and in the uncomplexed ligands are rather different, and they correctly interpreted the result as being a lower limit of $E[\text{Pt-C}_2(\text{CN})_4] - E(\text{Pt-C}_2\text{H}_4)$. Scheme 6 and eq 21 show why this is the case.

SCHEME 6



The carbon-carbon bond lengths increase when the olefins are complexed. Therefore, one should have $\text{ER}_1 < 0$ and $\text{ER}_2 > 0$. Furthermore, that increase is about 9 pm for C₂H₄ and 17 pm for C₂(CN)₄, suggesting that $|\text{ER}_2| > |\text{ER}_1|$. The platinum-phosphine bond length is fairly constant in both complexes (~227–229 pm). The dihedral angle between the planes P-Pt-P and C-Pt-C changes from 1.6° in the ethylene complex to 8.3° in the tetracyanoethylene complex, suggesting $\text{ER}_c > 0$.

As a last note, it is useful to stress that thermochemical studies based on ligand-exchange reactions, such as reactions 11 and 17, always give *differences* between metal-ligand bond enthalpies. When L¹ = L² in oxidative addition reactions such as reaction 20, *absolute* bond enthalpy terms or mean bond dissociation enthalpies can be obtained. This is also true in the case of decomposition reactions exemplified by reaction 10.

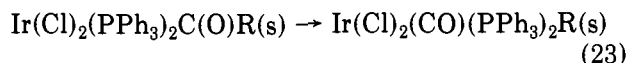
C. Bond Enthalpies from Enthalpies of Reaction of the Crystalline Complexes

Some complexes undergo partial decomposition in the solid state, as illustrated in reaction 22. If $\Delta H^\circ(22)$ is measured, it will provide a direct value for $D(\text{CM-L}^1)$ once it is assumed that $\Delta H^\circ_{\text{g}}(\text{CM}) - \Delta H^\circ_{\text{g}}(\text{CML}^1) \approx 0$ ^{5,116-119} and L¹ is in the standard gaseous state. The quantity $E(\text{CM-L}^1)$ can be evaluated by methods sim-

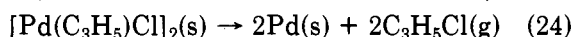
ilar to those described above.



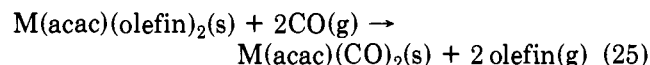
Although solution enthalpies are not needed to obtain $\Delta H^\circ_{\text{g}}$ in the case of reaction 22, other data are required to calculate bond enthalpies at 298 K. In fact, most of the complexes studied in a calorimeter decompose at temperatures well above 298 K, and therefore the measured ΔH° has to be corrected by heat capacity values. However, as these data are seldom available, it is usually assumed^{5,116-119} that $\Delta H^T \approx \Delta H^{298}$, which seems reasonable, particularly when T is not too high. In one example, quoted from a communication by Blake et al.,¹²⁰ the correction terms, $\sim \Delta C_p(T - 298)$, for reaction 23, with $T \approx 445$ K, are very small, ca. 0.08



kJ/mol for R = CF₃ and 0.01 kJ/mol for R = *p*-NO₂C₆H₄CH₂. In this case, however, the crystalline complex is the only product of the reaction, and therefore small ΔC_p values could be expected. Another example, which gives a feeling for the ΔC_p correction, is provided by reaction 24,¹²¹ where $\Delta H^{298}(24) = 105.0 \pm 1.7$ kJ/mol and $\Delta H^{450}(24) = 100.8 \pm 1.7$ kJ/mol.



An interesting example concerning the evaluation of bond enthalpies from thermochemical studies of the crystalline complexes refers to reaction 25, where M =

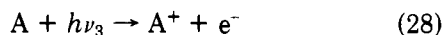
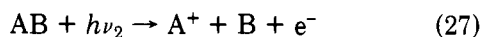
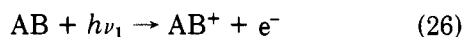


Rh or Ir and acac = acetylacetonate.¹²² Vrieze and co-workers have shown that the assumption $\Delta(\Delta H^\circ_{\text{g}}) \approx 0$ applied to the evaluation of $\Delta H^\circ_{\text{g}}(25)$ yields errors in the range of -9 to +35 kJ/mol. This means that $\Delta(\Delta H^\circ_{\text{g}})$ may provide a significant contribution to $D(\text{M-olefin}) - D(\text{M-CO})$, e.g. 18 kJ/mol in the case of M = Rh and olefin = vinyl acetate. On the other hand, ΔC_p corrections are shown to be small and thus can be neglected; e.g., for M = Rh and olefin = ethylene, $\Delta H^{298}(25) - \Delta H^{203}(25) \approx 0.2$ kJ/mol. A very important point is illustrated by this example. It has been stated in the present review that the assumption $\Delta(\Delta H^\circ_{\text{g}}) \approx 0$ should be reasonable for many cases; i.e., it should not change significantly the magnitudes and especially the trends found for metal-ligand bond enthalpies. However, Vrieze and co-workers tried to compare metal-olefin bond enthalpies for different olefins with the same metal and interpreted the trend by using the Dewar-Chat-Duncanson model.^{123,124} The differences between pairs were so small that this trend might be different if the enthalpies of sublimation were not taken into account (see section IV). Studies of this type cannot rely on assumptions like $\Delta(\Delta H^\circ_{\text{g}}) \approx 0$ if the correct trends are to be derived.

D. Bond Enthalpies from Gas-Phase Studies

The determination of bond enthalpies from ionization threshold measurements follows from an analysis of the general processes 26–28, where for the purpose of discussion photoionization studies are considered. Monoenergetic electron impact investigations provide similar results,¹²⁵ although the sensitivity in determining

onsets is not as good as with photoionization due to less favorable threshold ionization laws.⁵⁶



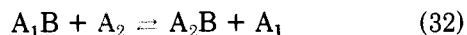
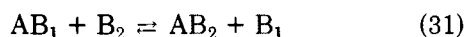
If the molecule AB is in its ground vibrational and rotational state and the products can be detected at the exact threshold for their production in the ground states, then the bond dissociation enthalpies $D(A^+-B)$ and $D(A-B)$ are given by eqs 29 and 30, respectively,

$$D(A^+-B) = h\nu_2 - h\nu_1 \quad (29)$$

$$D(A-B) = h\nu_2 - h\nu_3 \quad (30)$$

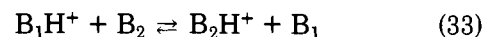
at 0 K. This situation is never realized in practice. The molecules AB are usually at ambient temperature, and their thermal energy content may lower the ionization energy $h\nu_1$ (hot-band ionization) and contribute to the total energy available for dissociation in AB^+ , giving a lower apparent threshold $h\nu_2$. Dissociation at threshold implies a zero rate constant for fragmentation. Dissociation at a finite rate, determined by the time scale for ion detection, requires internal energy in excess of threshold. This is often referred to as the *kinetic shift*.¹²⁶ Experimental methods using ion trapping have been designed to extend the time scale for ion detection and thus reduce the kinetic shift.¹²⁷ In addition, schemes based on an RRKM analysis of dissociation rates have been employed to account for kinetic shifts. While these are purported to yield accurate thermochemical data,¹²⁶⁻¹²⁹ there is still not general agreement as to the best approach.¹³⁰ Photoelectron-photoion coincidence experiments detect ions in coincidence with energy-selected electrons, allowing the internal energy of the ion to be more precisely defined. Kinetics of dissociation above threshold must be consistent with activation parameters which, in turn, are often directly related to bond dissociation enthalpies.^{128,129} These experiments are not straightforward, however, and eqs 29 and 30 are often used directly to derive bond dissociation enthalpies that are assumed to be valid at 298 K. In part, this approach derives advantage from the fact that effects due to the thermal energy content of the parent neutral and the kinetic shift act in opposite directions and partially cancel. Bond dissociation enthalpies derived in this fashion are likely to be accurate to ± 10 kJ/mol, which is quite useful since the technique gives individual rather than average values. Differences in bond dissociation enthalpies can usually be derived with greater accuracy than absolute values. The energies $h\nu_1$ and $h\nu_3$ can be accurately determined by photoelectron spectroscopy.^{57-59,131} Studies of transient species, such as free radicals, are quite useful in this regard.¹³¹

The analysis of equilibrium constants measured by ion cyclotron resonance spectroscopy¹³²⁻¹³⁷ and high-pressure mass spectrometry^{55,138-142} has provided a wealth of data relating to the acid-base properties of molecules. The processes most often studied are generalized in acid-base equilibria 31 and 32. The equi-



librium indicated by eq 31 yields the relative Gibbs energy of binding two bases B_1 and B_2 to a reference acid A. Similarly, eq 32 quantifies the relative acidity of A_1 and A_2 toward a reference base B.

Not surprisingly, the proton has been the reference acid most often considered in gas-phase studies. The measured Gibbs energy change for reaction 33 is con-

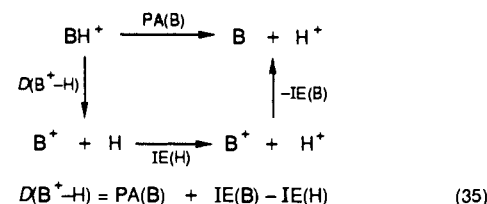


verted to an enthalpy change by measuring or estimating the small entropy change for the process.^{132,141,142} This directly provides the difference in proton affinities, defined by eq 34, for the two bases B_1 and B_2 . Nu-

merous measurements provide absolute proton affinities that can be used to determine values for other species from measured differences.¹⁴³ Scheme 7 relates PA(B)

$$PA(B) = D(B-H^+) = \Delta H_f^\circ(B) + \Delta H_f^\circ(H^+) - \Delta H_f^\circ(BH^+) \quad (34)$$

SCHEME 7

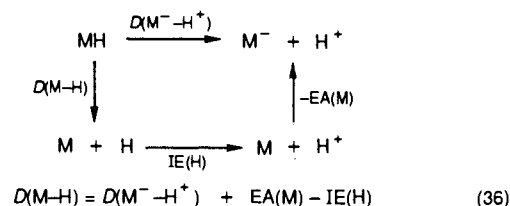


to the homolytic bond dissociation enthalpy $D(B^+-H)$, as indicated by eq 35. Ion cyclotron resonance studies have provided proton affinities for a large number of organometallic complexes¹³⁶ that protonate on basic metal centers. These data yield metal-hydrogen homolytic bond dissociation enthalpies, using eq 35 with $IE(B)$ measured by photoelectron spectroscopy.⁵⁷⁻⁵⁹ The major error in these measurements can often be attributed to the reference data used to calibrate the proton affinity scale (± 10 kJ/mol).¹⁴³

The use of Me^+ as a reference acid yields methyl cation affinities,¹⁴⁴ which, in analogy with proton affinity results, can be combined with ionization energy data to determine metal-carbon bond dissociation enthalpies. No studies of the methyl cation affinities of organometallic compounds have been reported.

Studies of proton-transfer reactions between anions have yielded acidities of neutral metal hydrides, $D(M-H^+)$.^{137,145} Scheme 8 relates the acidities to other

SCHEME 8

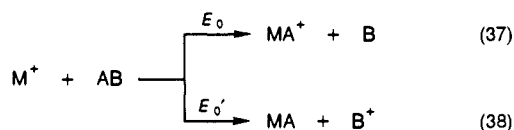


fundamental parameters as indicated in eq 36.¹³⁴ Acidities of neutral metal hydrides thus yield data relating to the electron affinity of M and the metal-hydrogen homolytic bond dissociation enthalpy in the neutral species.

The general equation (31) has also been applied in determining binding enthalpies of n -donor and π -donor bases to metal ion centers.¹⁴⁶ The analysis of these data, in which cationic transition metal centers serve as the

reference Lewis acid, is similar to that presented for the proton.

Ion beam studies of endothermic reactions have mainly considered reactions of atomic transition-metal ions with small molecules leading to an ionic (eq 37) or



neutral (eq 38) organometallic fragment.¹⁴⁷ Measurement of the threshold energies E_0 and E_0' for reactions 37 and 38 allows the bond dissociation enthalpies $D(M^+-A)$ and $D(M-A)$ to be calculated from eqs 39 and 40, respectively. Note that if E_0 and E_0' can both be

$$D(M^+-A) = D(A-B) - E_0 \quad (39)$$

$$D(M-A) = D(A-B) - E_0' = D(A-B) - E_0 + IE(B) - IE(MA) \quad (40)$$

determined, they yield the ionization energy of the organometallic fragment. The main difficulty in these experiments involves extracting true thresholds from variation of the reaction cross-section with relative kinetic energy. Thorough discussions of the assumptions and theoretical models used to analyze the data appear elsewhere.^{60,61,148,149} Bond dissociation enthalpies accurate to better than ± 10 kJ/mol are provided by this analysis. Care must be taken to avoid contributions from excited states in the beam, since they can have thresholds shifted to lower energies (by the excitation energy) from the true thermodynamic threshold.

An intriguing feature of the ion beam experiments is the ease with which the metal can be varied to examine periodic trends in the thermochemistry of organometallic fragments such as metal hydrides and metal alkyls.^{49,81,82} In addition, the systems are simple enough to compare to the predictions of rigorous ab initio electronic structure calculations.¹⁵⁰⁻¹⁵³ It has also been possible to generate organometallic fragments^{154,155} and metal cluster ions¹⁵⁶ as reactant species. For example, deprotonation of metal hydride ions yields metal atom proton affinities and the corresponding metal-hydrogen bond dissociation enthalpies.¹⁵⁴

Since the ion beam experiments focus on thresholds for endothermic reactions to provide thermochemical data, they are unable to provide similar quantitative results for the many exothermic reactions occurring at transition-metal centers without activation energies in the gas phase. Fortunately, complementary studies involving the determination of product kinetic energy release distributions are often able to provide enthalpies of reaction in just these instances.⁶⁷⁻⁷⁰ The success of the phase-space theory in fitting kinetic energy release distributions for exothermic reactions involving no barrier for the reverse reaction has led to the use of this analysis as a tool for deriving thermochemical data for species that would otherwise be difficult to characterize.⁶⁸⁻⁷⁰

To illustrate how the amount of energy released to product translation may reflect specific details of the potential energy surface, including the overall enthalpy of reaction, consider the two hypothetical surfaces for a chemically activated species in Figure 2. The interaction of a metal ion M^+ with a neutral molecule A can result in the formation of an adduct MA^+ con-

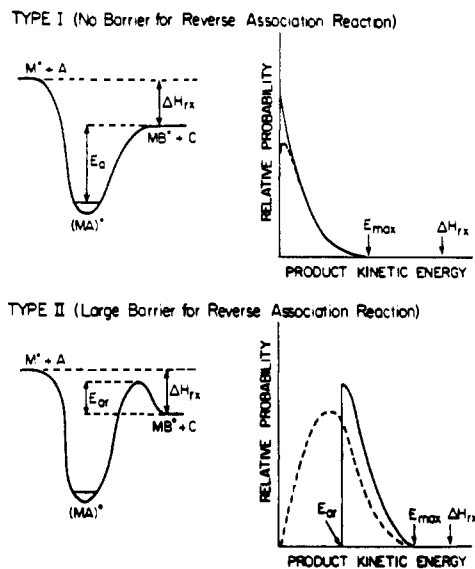


Figure 2. Characteristic shapes of kinetic energy release distributions for different model potential energy surfaces. For type I surfaces, E_{\max} is normally much less than the enthalpy change for the reaction. With high barriers in the exit channel, E_{\max} may approach ΔH° , for type II surfaces (adapted from ref 68).

taining internal energy E^* . In the absence of collisions, the internal excitation in this chemical activation process may be utilized for molecular rearrangement and subsequent fragmentation. In Figure 2, adduct MA^+ is depicted fragmenting to MB^+ and C along two different potential energy surfaces designated type I and type II. For a reaction occurring on a type I surface, it is assumed that there is no barrier to the reverse association reaction. The transition state resembles very loosely associated products, and very little interaction occurs between products after the transition state has been passed. Phase-space theory has been successfully used in modeling translational energy release distributions for reactions occurring on this type of potential energy surface.⁶⁸ A central assumption of these theories is that the statistical partitioning of energy between the reaction coordinate and all internal degrees of freedom at the transition state will be retained as the products separate. A consequence of this assumption is that the probability of a given energy being partitioned to relative product translation will decrease rapidly with increasing energy, as shown in the upper right-hand portion of Figure 2.

As shown in Figure 2, a type II surface involves a barrier with activation energy (E_{ar}) for the reverse association reaction. This type of surface is often associated with complex reactions, which involve the simultaneous rupture and formation of several bonds in the transition state. In the absence of coupling between the reaction coordinate and other degrees of freedom after the molecule has passed through the transition state, all of the reverse activation energy would appear as translational energy of the separating fragments. Accordingly, the translational energy release would be shifted from zero by the amount E_{ar} . In practice, broad distributions such as the one indicated by the dashed line in the lower right half of Figure 2 are often observed and attributed to exit channel effects that distort the translational energy distribution of the products.^{67,68}

As an example of the use of kinetic energy release distributions to determine metal-carbon bond disso-

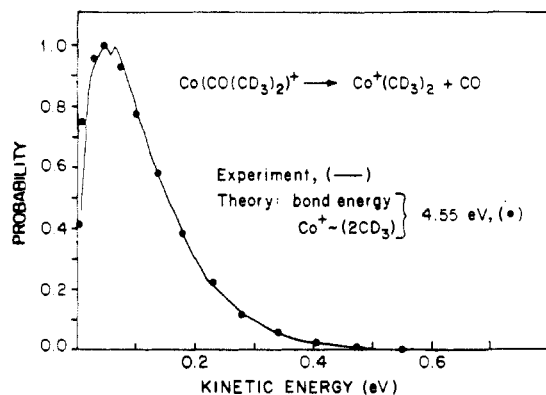


Figure 3. Comparison of experimental kinetic energy release distribution to phase-space calculations for decarbonylation of acetone by Co^+ . The sum of the first and second metal-carbon bond dissociation enthalpies is 4.55 eV (439 kJ/mol) at 0 K; this corresponds to 460 kJ/mol at 298 K.⁶⁸

ciation enthalpies, consider the reaction of acetone with Co^+ . This yields two products in which either CO or C_2H_6 is eliminated. Decarbonylation process 41 leads



to the formation of the dimethylcobalt ion as a product. The kinetic energy release distribution for this process (Figure 3) can be fit with phase-space theory using a sum of the first and second metal-methyl bond dissociation enthalpies of 4.55 eV at 0 K (4.77 eV or 460 kJ/mol at 298 K).⁶⁸ From Table 16, the first bond dissociation enthalpy is 255 kJ/mol, giving a somewhat smaller second bond enthalpy of 205 kJ/mol. Significantly, the sum of the two bond enthalpies is substantially greater than typical C-C bond dissociation enthalpies in saturated hydrocarbons, and insertion of Co^+ into a C-C bond is exothermic by 105 kJ/mol! The fact that the reaction is exothermic does not guarantee that the process will be observed.

The phase-space calculations are mainly sensitive to the reaction exothermicity and not to choices for the structures and vibrational frequencies of the reactants and products. If the reaction exothermicity increases, then the kinetic energy release increases in proportion. In most cases the reaction exothermicity is not known and the matching of the experimental and theoretical distributions can be used to derive product thermochemistry. In general, any process involving the elimination of an n-donor or π -donor base from a metal center should have little or no barrier for the reverse process and thus should exhibit a statistical kinetic energy release. Possible exceptions might result from changes in spin multiplicity accompanying ligand loss, but no examples of such complications have yet been observed.⁷⁰

As is the case for studies of endothermic reactions, thermochemical data for neutral organometallic fragments can also be derived from an analysis of kinetic energy release distributions. The reactions of Co^+ with trimethyl- and tetramethylsilane, respectively, yield CoH and CoMe as neutral products, and statistical distributions are observed for both reactions.¹⁵⁷

A note of caution must be offered in attempts to use kinetic energy release distributions to determine organometallic thermochemistry. In numerous cases distributions have been observed that appear statistical but are narrower than predicted by phase-space theory.

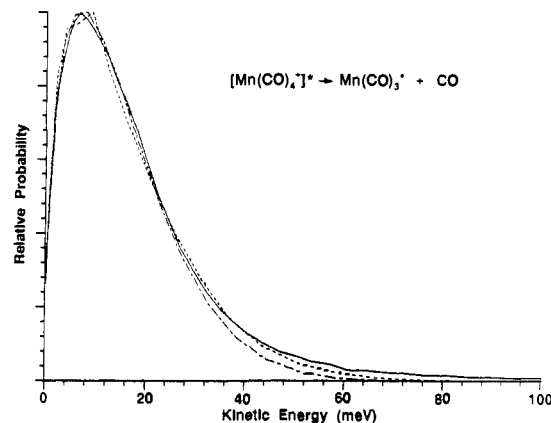


Figure 4. Comparison of theoretical kinetic energy release distributions to the experimental distribution (solid line) for the loss of CO from vibrationally excited $\text{Mn}(\text{CO})_6^+$. The short dashed line corresponds to $\log A = 13.0$ and $D_0^\circ[\text{Mn}(\text{CO})_5^+ - \text{CO}] = 71$ kJ/mol; the short-long dashed line corresponds to $\log A = 15.3$ and $D_0^\circ[\text{Mn}(\text{CO})_5^+ - \text{CO}] = 96$ kJ/mol.⁷⁰

This can occur when intrinsic barriers exist in the potential energy surface with energy near the energy of the reactants.¹⁵⁸ The collision partners may pass over the centrifugal barrier in the entrance channel only to be reflected by the effective potential associated with the intrinsic barrier. Typically this shows up in the form of a "cold" product translational energy distribution and a small reaction cross-section. While the example given above does not exhibit this complication, careful examination of each system is necessary. Another caution involves making certain that excited states do not contribute to the measured distributions. This typically will lead to an excess kinetic energy release and the inference that products are more stable (bond energies will be too high).

The above analysis assumes that the chemical activation process used to generate the reactant ions yields a relatively narrow range of internal energies for the decomposing species. It is possible, however, to derive thermochemical data from studies of kinetic energy release distributions even when ions are generated with a broad internal energy distribution by processes such as electron impact or desorption from surfaces by atom or ion bombardment. Rates of unimolecular reactions increase with increasing internal energy, giving rise to a corresponding broad range of dissociation rates. Fragment ions are detected only when decomposition occurs in the second field free region between the magnetic and electric sectors. Typically, ions reach this region in 10^{-5} s. As a result, the experiment selects those ions decomposing with a rate constant of 10^5 s^{-1} . This dissociation rate corresponds to a narrow range of internal energies that can be calculated by RRKM theory. Once the internal energies of the decomposing ions are specified, distributions can be analyzed by phase-space theory as described above, yielding reaction thermochemistries. This has recently been applied to determine individual $D_0^\circ[\text{Mn}(\text{CO})_{x-1}^+ - \text{CO}]$ values (kJ/mol): $x = 6, 134 \pm 21$; $x = 5, 67 \pm 13$; $x = 4, 84 \pm 13$; $x = 3, 130 \pm 25$; $x = 2, <105$; $x = 1, >29$.⁷⁰ A fit of the experimental distribution to phase-space theory is shown in Figure 4 for $n = 6$. The major source of uncertainty in this analysis results from having to estimate the A factor for the unimolecular reaction. The two calculations shown in Figure 4 represent $\log A$ values

TABLE 1. Metal-Carbonyl First Bond Dissociation Enthalpies (D_1) and Mean Bond Dissociation Enthalpies (\bar{D})

compd	E_a , kJ/mol	log A	D_1 , ^a kJ/mol	\bar{D} , ^b kJ/mol
Cr(CO) ₆	147.7	15.5	154 ± 13	107 ± 1
Mo(CO) ₆	163.2	15.6	170 ± 13	152 ± 1
W(CO) ₆	186.2	15.6	192 ± 13	178 ± 1
Fe(CO) ₅	167.4	15.8	174 ± 13 ^c	118 ± 2

^aReference 71. ^bReference 15. ^cAn activation barrier of 17 kJ/mol has been assumed for the recombination reaction Fe(CO)₄ + CO → Fe(CO)₅; Walsh, R. NATO Advanced Workshop on the Design, Activation and Transformation of Organometallics into Common and Exotic Materials, Montpellier, France, 1986. This would lower D_1 (Fe-CO) to 157 kJ/mol.

of 15.3 and 13.0. Fortunately, the results are not overly sensitive to the assumed values.

When a reaction of interest is the lowest energy decomposition pathway available to an organometallic complex in the gas phase, the laser-driven thermal activation experiments of Lewis et al.⁷¹ represent an important experimental methodology to determine reaction thermochemistry. For example, the determination of individual metal-carbonyl bond dissociation enthalpies follows in a straightforward manner. Arrhenius parameters are extracted from comparative rate measurements, using dicyclopentadiene decomposition as a standard. The activation parameters and derived bond dissociation enthalpies are summarized in Table 1. Inherent in the analysis of these experiments is the assumption that the kinetic bond dissociation enthalpies also represent thermodynamic values and there is no barrier to recombination. This assumption is probably valid for the group 6 metal carbonyls, which dissociate cleanly to square-pyramidal singlet ground-state products.⁷¹ Fe(CO)₄, however, is known to be a ground-state triplet, but the similarity in A factors suggests that dissociation is also to a singlet state, which would make the derived bond dissociation enthalpy an upper limit to the thermodynamic value.

The data in Table 1 are presented separately to allow their comparison with the *mean* metal-carbonyl bond dissociation enthalpies,¹⁵ which are also included. Keeping in mind the possible difficulty with the value for Fe(CO)₅, the \bar{D} values are all lower than the measured first bond dissociation enthalpies. With second- and third-row metals the difference is not great. In the first row, the substitution of mean values for the first bond dissociation enthalpy may lead to significant errors. The first bond dissociation enthalpy in Cr(CO)₆, 154 ± 13 kJ/mol, is close to the value of 134 ± 21 kJ/mol for the isoelectronic cation.⁷⁰

IV. Bond Enthalpy Values

A. Neutral Organometallic Complexes

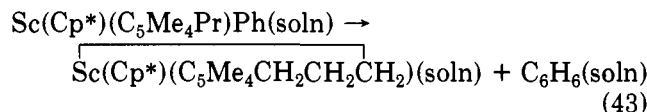
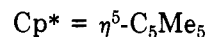
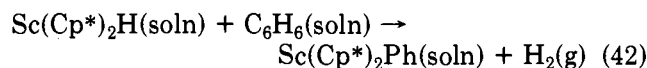
The available metal-hydrogen and metal-carbon bond enthalpies (see short definitions in Appendix) are presented in Tables 2-5, 8, 10, and 12. All values are given in kilojoules per mole at $T = 298$ K and were calculated by using, to the extent possible, a consistent set of auxiliary data. This option led to some differences between values originally reported and those given in tables. Unless noted otherwise, the enthalpies of formation of elements and inorganic compounds were quoted from NBS Tables¹⁵⁹ and the enthalpies of for-

mation of organic molecules were taken from the compilation by Pedley and Rylance.^{22,160} The selected enthalpies of formation of radicals are presented in the Appendix, together with bond dissociation enthalpies, bond enthalpy terms, and reorganization energies. The enthalpies of formation of the organometallic complexes considered in this review were all taken from a recent survey,¹⁶¹ but most can be found in the review by Pilcher and Skinner.¹⁵

All but a few results in the tables are *enthalpies*. For those that should be called *bond energies*, the correction terms are much smaller than their accuracy or their precision, and so they were also handled as *bond enthalpies*.¹⁶²

1. Group 3 and Actinides

a. Scandium. The available bond enthalpy data for group 3 organometallic complexes containing metal-carbon σ bonds are still very scarce. The values shown in Table 2 were calculated (eqs 44 and 45) from the



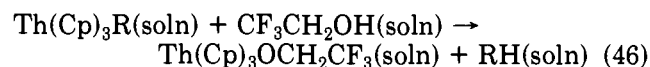
$$D(\text{Sc-Ph}) - D(\text{Sc-H}) = -\Delta H^\circ(42) + D(\text{Ph-H}) - D(\text{H-H}) \quad (44)$$

$$D(\text{Sc-C}) - D(\text{Sc-Ph}) = -\Delta H^\circ(43) + D(\text{C-H}) - D(\text{Ph-H}) \quad (45)$$

reported enthalpies of reactions 42 and 43 in benzene,^{163,164} by assuming that the solvation enthalpies cancel and that $D(\text{C}_5\text{Me}_4\text{CH}_2\text{CH}_2\text{CH}_2\text{-H}) \approx D(\text{Pr-H})$ with data from the Appendix. $\Delta H^\circ(42)$ and $\Delta H^\circ(43)$ were obtained from van't Hoff plots over the temperature ranges 279-353 and 323-373 K, respectively. The trend $D(\text{Sc-H}) \approx D(\text{Sc-Ph}) > D(\text{Sc-C})$ seems reasonable, despite the polymeric nature of the scandium hydride complex in solution.¹⁶³

b. Thorium. A large number of thermochemical studies on thorium and uranium organometallic complexes have been reported in the last 8 years by the group of T. Marks. With few exceptions, the technique used was either titration or batch reaction solution calorimetry,¹⁶⁵ and the experimental procedure involved the measurement of enthalpies of alcoholysis of the complexes in toluene.

The method can be illustrated by reaction 46, whose enthalpy was measured for R = Me, *i*-Pr, CH₂CMe₃, CH₂SiMe₃, and Bz.¹⁶⁶ In order to derive bond enthalpy data from $\Delta H^\circ(46)$, several assumptions are required.



First, the ubiquitous question of the solvation enthalpies is considered. The authors have measured the solution enthalpies needed to calculate the enthalpy of reaction 46 with all reactants and products in standard reference states (i.e., crystalline complexes, liquid alcohol, and liquid or gaseous RH). However, although the enthalpies of vaporization of the alcohol and RH

TABLE 2. Group 3 and Actinides M-H and M-C Bond Enthalpies

molecule	method/ ref ^a	<i>D</i> , kJ/mol	<i>E</i> , kJ/ mol
Sc(Cp*) ₂ H	ES/163	<i>D</i> ^b	
Sc(Cp*) ₂ Ph	ES/163	<i>D</i> 1 - (5 ± 8)	
Sc(Cp*)(C ₆ Me ₄ CH ₂ CH ₂ CH ₂)	ES/164	<i>D</i> 1 - (67 ± 12)	
Th(Cp*) ₂ (OR)H	RSC/168 ^c		
R = CH(<i>t</i> -Bu) ₂		389 ± 6	389
R = 2,6-(<i>t</i> -Bu) ₂ C ₆ H ₃		384 ± 6	384
[Th(Cp*) ₂ H ₂] ₂	RSC/165 ^d	390	
Th(Cp*) ₃ R	RSC/166 ^c		
R = Me		375 ± 9	351
R = <i>i</i> -Pr		350 ± 15	351
R = CH ₂ CMe ₃		333 ± 15	326
R = CH ₂ SiMe ₃		369 ± 12	365
R = Bz		315 ± 12	358
Th(Cp*) ₂ R ₂	RSC/165 ^c		
R = Me		339 ± 5	315
R = Et		318 ± 8	308
R = Bu		307 ± 9	300
R = CH ₂ CMe ₃		302 ± 17	295
R = CH ₂ SiMe ₃		335 ± 7	331
R = Ph		372 ± 10	328
Th(Cp*) ₂ (OBu- <i>t</i>)R	RSC/165 ^c		
R = Me		349 ± 6	326
R = Et		330 ± 8	320
R = Bu		316 ± 15	309
R = CH ₂ CMe ₃		321 ± 17	314
R = CH ₂ SiMe ₃		345 ± 7	341
R = Ph		387 ± 9	343
Th(Cp*) ₂ [OCH(<i>t</i> -Bu) ₂]Bu	RSC/168 ^c	347 ± 15	340
Th(Cp*) ₂ (Cl)R	RSC/165 ^c		
R = Et		313 ± 8	303
R = Ph		374 ± 10	330
R = Bz		285 ± 7	328
Th(Cp*) ₂ [(CH ₂) ₂ CMe ₂]	RSC/165 ^c	274 ± 12	
Th(Cp*) ₂ [(CH ₂) ₂ SiMe ₂]	RSC/165 ^c	318 ± 8	
Th(Cp*) ₂ (C ₄ H ₆)	RSC/169 ^d	209 ± 9	
Th(Cp*) ₂ [CH ₂ (CMe) ₂ CH ₂]	RSC/169 ^d	188 ± 9	
Th(Cp*) ₂ (OR)[C(O)H]	ES/170 ^c		
R = CH(<i>t</i> -Bu) ₂		345 ± 8	396
R = 2,6-(<i>t</i> -Bu) ₂ C ₆ H ₃		351 ± 10	402
Th(Cp*) ₂ (CHCH ₂ CH ₂) ₂	RSC/169 ^d	368 ± 21	
U(Cp*) ₂ [OSi(<i>t</i> -Bu)Me ₂]R	RSC/168 ^c		
R = H		342 ± 5	
R = Me		317 ± 6	293
U(Cp*) ₂ R ₂	RSC/168 ^{d,e}		
R = Me		300 ± 11	276
R = Bz		244 ± 8	287
R = CH ₂ SiMe ₃		307 ± 8	303
U(Cp*) ₂ (Cl)R	RSC/168 ^c		
R = Me		312 ± 8	288
R = Ph		358 ± 11	314
R = Bz		263 ± 12	306
U(Me ₃ SiC ₅ H ₄) ₃ R	RSC/171		
R = Me		185 ± 2	161
R = Bu		152 ± 8	145
R = CH ₂ SiMe ₃		168 ± 8	164
R = Bz		149 ± 8	192
R = CHCH ₂		223 ± 10	185
R = CCPH		(363)	

^aKey: ES = equilibrium studies in solution; RSC = reaction solution calorimetry. ^b*D*1 = *D*(Sc-H). ^cData rely on *D*(Th-O) = 518.8 kJ/mol. ^dMean bond dissociation enthalpies. ^eData rely on *D*(U-O) = 481.2 kJ/mol.

are available or can be easily estimated, $\Delta H^\circ_g(46)$ cannot be experimentally derived because the enthalpies of sublimation of the complexes are unknown. It is likely that $\Delta H^\circ_g[\text{Th}(\text{Cp})_3\text{OCH}_2\text{CF}_3]$ exceeds $\Delta H^\circ_g[\text{Th}(\text{Cp})_3\text{R}]$, and so the assumption $\Delta(\Delta H^\circ_g) \approx 0$ may be less reasonable than simply considering that the measured solution data are close to the gas-phase values. In other words, it is expected that the bracketed terms in eq 14 nearly cancel. This option, used by T. Marks and co-workers,¹⁶⁶ is also favored in the present review (see also discussion below).

The second assumption necessary to calculate Th-R bond data concerns the value assigned to *D*(Th-O). As there are no thermochemical data for homoleptic thorium alkoxides, that bond dissociation enthalpy was estimated on the basis of eq 47,¹⁶⁵ a relationship that

$$\bar{D}(\text{M}'\text{-OR})/\bar{D}(\text{M-OR}) \approx \bar{D}(\text{M}'\text{-X})/\bar{D}(\text{M-X}) \quad (47)$$

holds within ca. 5% for M, M' = Ti, Zr and X = Cl, F. In addition, data for thorium and zirconium fluorides^{159,167} suggest that $\bar{D}(\text{M-F}) \approx D_1(\text{M-F})$ and so an average value, $\bar{D}(\text{Th-O}) \approx D_1(\text{Th-O}) \approx 518.8$ kJ/mol, was used by authors. Although the uncertainty assigned to this estimate is probably no less than ca. ± 20 kJ/mol, the error will not be included in the bond enthalpy data in Table 2, since it has no effect on the observed trends for *D*(Th-R) and *E*(Th-R), calculated through eqs 48 and 49, respectively. Note that eq 49 does not contain

$$D(\text{Th-R}) = \Delta H^\circ(46) + D(\text{Th-O}) - D(\text{CF}_3\text{CH}_2\text{O-H}) + D(\text{R-H}) \quad (48)$$

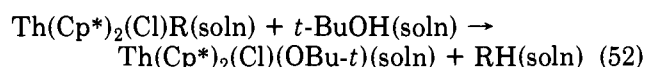
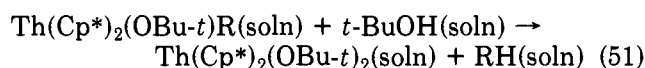
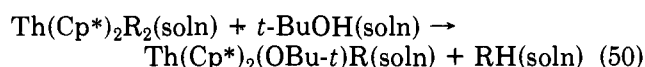
$$E(\text{Th-R}) = D(\text{Th-R}) - ER_R \quad (49)$$

the reorganization energy of the organometallic fragment, which is not available, but only the reorganization energies of the organic radicals (Appendix). *D*(CF₃CH₂O-H) was assumed to be equal to *D*(EtO-H) but with an error bar of ± 8 kJ/mol.

An interesting feature emerges from the data in Table 2 for the Th(Cp)₃R complexes. While *D*(Th-R) values span a range of 60 kJ/mol, *E*(Th-R) values are remarkably constant, with exception of the one for neopentyl, where steric effects are expected. This suggests that an average thorium-carbon (sp³) bond enthalpy term, 356 ± 6 kJ/mol, can be used to predict new Th-R bond dissociation enthalpies by simply subtracting the reorganization energy of R from that number. In other words, since the reorganization energies used in this survey merely reflect differences between *D*(R-H) and *E*(R-H), the constancy in *E*(Th-R) implies that *D*(Th-R) and *D*(R-H) follow nearly parallel trends (see section V).

An additional fact favoring the assumption of canceling solvation enthalpies in reaction 46 versus $\Delta(\Delta H^\circ_g) \approx 0$ for the complexes is that the use of this hypothesis would lead, for example, to *D*(Th-CH₂SiMe₃) > *D*(Th-Me) by about 15 kJ/mol, which does not seem reasonable.

Bond enthalpy data for complexes Th(Cp*)₂R₂, Th(Cp*)₂(OBu-*t*)R, and Th(Cp*)₂(Cl)R are also presented in Table 2 and were derived from the measured enthalpies of reactions 50-52.^{165,168} The method and the



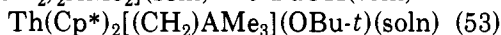
assumptions were the same as those described above. *D*(Th-R) and *E*(Th-R) values were calculated through equations similar to eqs 48 and 49, but where $\Delta H^\circ(46)$ was replaced by $\Delta H^\circ(50)$, $\Delta H^\circ(51)$, or $\Delta H^\circ(52)$ and *D*(*t*-BuO-H) was used in place of *D*(CF₃CH₂O-H).

Comparisons between $D(\text{Th-R})$ in $\text{Th}(\text{Cp})_3\text{R}$, $\text{Th}(\text{Cp}^*)_2\text{R}_2$, $\text{Th}(\text{Cp}^*)_2(\text{OBu-}t)\text{R}$, and $\text{Th}(\text{Cp}^*)_2(\text{Cl})\text{R}$ can be misleading, because all values rely on the same number for $D(\text{Th-O})$, 518.8 kJ/mol, and this bond dissociation enthalpy may vary. For example, it could be said that $D_1(\text{Th-R})$ in $\text{Th}(\text{Cp}^*)_2\text{R}_2$ are smaller than in $\text{Th}(\text{Cp}^*)_2(\text{OBu-}t)\text{R}$, but it is also possible that $D(\text{Th-O})$ in this complex is strengthened as compared with the same bond in $\text{Th}(\text{Cp}^*)_2(\text{OBu-}t)_2$.

The trends in $D(\text{Th-R})$ for the three families of complexes are essentially similar to that observed for $\text{Th}(\text{Cp})_3\text{R}$. The $D(\text{Th-CH}_2\text{SiMe}_3)$ values are also very close to $D(\text{Th-Me})$ for the complexes $\text{Th}(\text{Cp}^*)_2\text{R}_2$ and $\text{Th}(\text{Cp}^*)_2(\text{OBu-}t)\text{R}$. If the assumption $\Delta(\Delta H^\circ_s) \approx 0$ had been used, the trend would also be reversed, i.e., $D(\text{Th-CH}_2\text{SiMe}_3) > D(\text{Th-Me})$.

In the case of complexes $\text{Th}(\text{Cp}^*)_2(\text{Cl})\text{R}$ ($\text{R} = \text{Et, Ph}$), the alcoholysis reaction has also been studied with $\text{CF}_3\text{CH}_2\text{OH}$,¹⁶⁶ leading to $D(\text{Th-Me}) = 309 \pm 12$ kJ/mol and $D(\text{Th-Ph}) = 382 \pm 18$ kJ/mol, both values being in good agreement with those shown in Table 2.

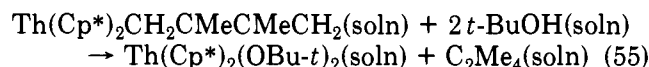
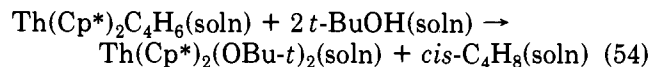
The thermochemistry of the metallacycle complexes $\text{Th}(\text{Cp}^*)_2[(\text{CH}_2)_2\text{CMe}_2]$ and $\text{Th}(\text{Cp}^*)_2[(\text{CH}_2)_2\text{SiMe}_2]$ was examined by the methods described above, i.e., reaction with $t\text{-BuOH}$ in toluene, reaction 53,¹⁶⁵ and $\text{Th}(\text{Cp}^*)_2[(\text{CH}_2)_2\text{AME}_2](\text{soln}) + t\text{-BuOH}(\text{soln}) \rightarrow$



A = C, Si

$D(\text{Th-C})$ were obtained by the usual procedure (Table 2). The weak thorium-carbon bond for A = C, $D(\text{Th-C}) = 274$ kJ/mol, as compared to $D(\text{Th-C}) = 318$ kJ/mol for A = Si, reflects the expected larger strain in the carbon-only metallacycle.

Bond data for two other thorium metallacycles, $\text{Th}(\text{Cp}^*)_2\text{L}$ ($\text{L} = \text{C}_4\text{H}_6, \text{CH}_2\text{CMeCMeCH}_2$), are presented in Table 2. Those data were derived, in both cases, from the measured enthalpies of reaction with $t\text{-BuOH}$ in toluene, yielding mixtures of isomers LH_2 and $\text{Th}(\text{Cp}^*)_2(\text{OBu-}t)_2$.¹⁶⁹ As a quantitative analysis of the reaction products was reported, it is possible to estimate the enthalpies of reactions 54 and 55, in which $\text{cis-C}_4\text{H}_8$



and C_2Me_4 are the only organic products, $\Delta H^\circ(54) = -294.4 \pm 15.8$ and $\Delta H^\circ(55) = -330.6 \pm 15.8$ kJ/mol. This was made by using tabulated enthalpies of formation to derive the isomerization enthalpies in the gas phase and by assuming that the values are identical in solution.²² The corrections are quite small, less than ca. 6 kJ/mol. The thorium-carbon mean bond dissociation enthalpies for the above two ligands (Table 2) were calculated by using an equation similar to eq 48, but where the enthalpy of reaction appears divided by 2 and $D(\text{R-H})$ is replaced by the carbon-hydrogen mean bond dissociation enthalpy. The values of $\bar{D}(\text{C-H})$ were obtained from the gaseous enthalpies of formation²² of 1,3-butadiene and cis-2-butene , $\bar{D}(\text{C-H}) = 276.9 \pm 0.5$ kJ/mol, and of 2,3-dimethyl-1,3-butadiene and tetramethylethylene, $\bar{D}(\text{C-H}) = 274.6 \pm 0.6$ kJ/mol. The results in Table 2 are small relative to other thorium-carbon σ bonds. However, comparisons between D -

(Th-R) and $\bar{D}(\text{Th-R})$ are not straightforward.¹⁶⁹ Also, both complexes can be formulated as $\text{Th}(\text{Cp}^*)_2(\eta^4\text{-L})$, in which case the thorium-diene bond dissociation enthalpies are twice the values shown in Table 2.

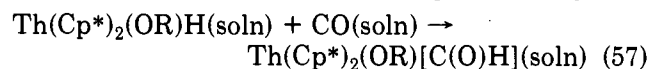
The first three entries in Table 2 for thorium compounds refer to thorium-hydrogen bond dissociation enthalpies. In the case of the complexes $\text{Th}(\text{Cp}^*)_2(\text{OR})\text{H}$, the experimental method and the procedure to derive $D(\text{Th-H})$ values were as described above, except that $t\text{-BuOH}$ has been replaced by MeOH .¹⁶⁸ The calculation of the mean thorium-hydrogen bond dissociation enthalpy in the dimer $[\text{Th}(\text{Cp}^*)_2\text{H}_2]_2$, from the enthalpy of its reaction with $t\text{-BuOH}$, yielding $\text{Th}(\text{Cp}^*)_2(\text{OBu-}t)_2$ and H_2 , was made through eq 56. Here,

$$\Delta H^\circ_r = 5\bar{D}(\text{Th-H}) + 4D(t\text{-BuO-H}) - 4\bar{D}(\text{Th-O}) - 4D(\text{H-H}) \quad (56)$$

it was assumed that the total bond enthalpy of each of the two bridging hydrogens is $1.5\bar{D}(\text{Th-H})$ of a terminal hydrogen. Although this procedure seems somewhat arbitrary, the obtained $\bar{D}(\text{Th-H})$ value is in the range of those calculated for $\text{Th}(\text{Cp}^*)_2(\text{OR})\text{H}$ complexes.

The thorium-hydrogen bond dissociation enthalpy values in Table 2 are best compared with $D(\text{Th-R})$ in $\text{Th}(\text{Cp}^*)_2(\text{OBu-}t)\text{R}$ complexes. It is seen that $D(\text{Th-H}) - D(\text{Th-Me}) \approx 40$ kJ/mol and $D(\text{Th-H}) \approx D(\text{Th-Ph})$ (recall the case of scandium complexes). A comparison is also provided by another $D(\text{Th-R})$ entry in Table 2. The enthalpy of reaction of the complex $\text{Th}(\text{Cp}^*)_2[\text{OCH}(t\text{-Bu})_2]\text{Bu}$ (alcoholysis with methanol)¹⁶⁸ led to $D(\text{Th-Bu}) = 347$ kJ/mol. This value is unexpectedly higher than $D(\text{Th-Bu})$ in $\text{Th}(\text{Cp}^*)_2(\text{OBu-}t)\text{Bu}$ (by about 30 kJ/mol) and it places the difference $D(\text{Th-H}) - D(\text{Th-alkyl})$ in the range of 40–60 kJ/mol.

Thorium-formyl bond dissociation enthalpies in complexes $\text{Th}(\text{Cp}^*)_2(\text{OR})[\text{C}(\text{O})\text{H}]$ rely on equilibrium studies in toluene of the carbonyl insertion reaction 57.¹⁷⁰ Equation 58 shows how $D[\text{Th-C}(\text{O})\text{H}]$ were



$$D[\text{Th-C}(\text{O})\text{H}] = -\Delta H^\circ(57) + D(\text{Th-H}) - D(\text{OC-H}) \quad (58)$$

calculated. Using $D(\text{OC-H}) = 62.5 \pm 4.0$ kJ/mol [from the value in Appendix for $\Delta H^\circ_f(\text{HCO})$] and $D(\text{Th-H}) = 389 \pm 6$ kJ/mol, the values displayed in Table 2 for $D[\text{Th-C}(\text{O})\text{H}]$ are obtained. They are quite high, in the range of $D(\text{Th-alkyl})$ in analogous complexes. $E[\text{Th-C}(\text{O})\text{H}]$, calculated by subtracting the reorganization enthalpy of formyl radical to $D[\text{Th-C}(\text{O})\text{H}]$, exceeds $E(\text{Th-alkyl})$ by more than 60 kJ/mol. This is in keeping with the high affinity of thorium for oxygen, causing η^2 -coordination of the formyl moiety to the metal.

The last thorium-carbon mean bond dissociation enthalpy in Table 2 was directly quoted from the literature and relies on the alcoholysis of $\text{Th}(\text{Cp}^*)_2(\text{CHCH}_2\text{CH}_2)_2$ with $t\text{-BuOH}$.¹⁶⁹

c. Uranium. Uranium-carbon and -hydrogen bond enthalpies in Table 2 were also determined from recent thermochemical studies by T. Marks and co-workers. The experimental technique (reaction solution calorimetry, alcoholysis reactions in toluene), the assumptions, and the method used to derive $D(\text{U-R})$ and \bar{E} -

(U-R), eqs 59 and 60, were usually the same as for the thorium complexes. $D(U-O)$ was obtained as 481.2 kJ/mol,¹⁶⁸ by using the method described for $D(Th-O)$.

$$D(U-R) = \Delta H^\circ_r + D(U-O) - D(RO-H) + D(R-H) \quad (59)$$

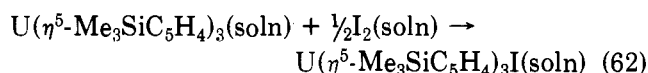
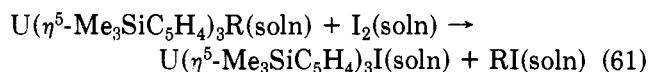
$$E(U-R) = D(U-R) - ER_R \quad (60)$$

Uranium-hydrogen and -carbon bond dissociation enthalpies in the complexes $U(Cp^*)_2[OSi(t-Bu)Me_2]R$ ($R = H, Me$) (Table 2) were obtained from the enthalpies of their reactions with methanol.¹⁶⁸ It is noted that $D(U-H) - D(U-Me) = 25$ kJ/mol is only slightly smaller than the corresponding difference for thorium complexes and also that $D(U-R) < D(Th-R)$ by 30–40 kJ/mol.

Uranium-carbon mean bond dissociation enthalpies in the molecules $U(Cp^*)_2R_2$ are presented in Table 2 for $R = Me, Bz,$ and CH_2SiMe_3 .¹⁶⁸ They were calculated from the enthalpies of reaction with $t-BuOH$, by using eq 59 (with ΔH°_r replaced by $\Delta H^\circ_r/2$). The trend $\bar{D}(U-Me) < \bar{D}(U-CH_2SiMe_3)$ looks surprising, but the uncertainty intervals should be considered. If the assumption concerning cancellation of enthalpies of sublimation of the complexes $U(Cp^*)_2R_2$ and $U(Cp^*)_2(OBu-t)_2$ had been invoked, $\bar{D}(U-CH_2SiMe_3)$ would exceed $\bar{D}(U-Me)$ by 24 kJ/mol.

The enthalpies of reaction of $U(Cp^*)_2(Cl)R$ with $t-BuOH$ were reported in the same paper by Marks and co-workers,¹⁶⁸ enabling derivation of $D(U-R)$ by the usual method (Table 2).

The measured enthalpy of reaction 61 (in toluene) for a series of ligands, together with the enthalpy of reaction 62, led to the uranium-carbon bond data shown in Table 2 for the sterically crowded complexes $U(\eta^5-$



$Me_3SiC_5H_4)_3R$.¹⁷¹ $D(U-R)$ were calculated from eq 63, by using data in Appendix, and $E(U-R)$ were obtained as described above (eq 60). The striking feature about

$$D(U-R) = \Delta H^\circ(61) - \Delta H^\circ(62) + D(R-I) - 0.5D(I-I) \quad (63)$$

the set of $D(U-R)$ values in Table 2 is their magnitude as compared with $D(U-R)$ in other families of complexes. This point has been extensively discussed by the authors,¹⁷¹ and the difference was attributed mainly to strong nonbonded interligand repulsions, which destabilize $D(U-R)$ in $U(\eta^5-Me_3SiC_5H_4)_3R$. The fact that these latter bond dissociation enthalpies are *absolute*, whereas the remaining $D(U-R)$ in Table 2 rely on an estimated value for $D(U-O)$, could suggest that the value assigned to the "anchor" is affected by a large error. However, the differences between $D(U-R)$ values for the complex $U(\eta^5-Me_3SiC_5H_4)_3R$ and those for the other families are too large to be due only to a wrong assignment to $D(U-O)$.

2. Group 4

a. Titanium. The mean bond dissociation enthalpies for the homoleptic compounds TiR_4 (Table 3) were calculated from reassessed values of their enthalpies of

TABLE 3. Group 4 M-H and M-C Bond Enthalpies

molecule	method/ ref ^a	D , kJ/mol	E , kJ/ mol
TiR_4	RSC/172 ^b		
R = CH_2CMe_3		198	191
R = CH_2SiMe_3		253	249
R = Bz		201	244
$Ti(Cp)_2R_2$	RSC/178 ^{b,c}		
R = Me		298 ± 6	274
R = Ph		332 ± 10	288
R = 3-MeC ₆ H ₄		343 ± 10	299
R = 4-MeC ₆ H ₄		342 ± 10	298
R = 4-CF ₃ C ₆ H ₄		341 ± 10	297
R = 4-MeOC ₆ H ₄		350 ± 10	306
R = Fc ^d			278
$Ti(Cp)_2Bz_2$	SB/173 ^{b,c}	237 ± 9	280
$Ti(Cp)_2(Cl)R$	RSC/178 ^c		
R = Me			293
R = Ph			291
$Ti(Cp)_2(Cl)Et$	KSL/179	(150)	
$Ti(Cp^*)_2R_2$	RSC/180		
R = Me		281 ± 8	257
R = Ph		280 ± 19	236
$Ti(Cp^*)(C_5Me_4CH_2)$	RSC/185	$D_2 + 200^e$	
$Ti(Cp^*)(C_5Me_3CH_2CH_2)$	RSC/185	$D_2 + 324^e$	
ZrR_4	RSC/172 ^b		
R = CH_2CMe_3		249	242
R = CH_2SiMe_3		310	306
R = Bz		263	306
$Zr(Cp)_2Me_2$	RSC/186 ^{b,f}	285 ± 2	261
$Zr(Cp)_2Ph_2$	SB/187 ^{b,f}	300 ± 10	256
$Zr(Cp^*)_2R_2$	RSC/186 ^f		
R = H		339 ± 2 ^b	339
R = Me		284 ± 2 ^b	260
R = Ph		312 ± 10	268
$Zr(Cp^*)_2H_2$	RSC/186 ^f	326 ± 8	326
$Zr(Cp^*)_2(OPh)H$	RSC/186 ^f	372 ± 9	372
$Zr(Cp^*)_2H_2$	RSC/186 ^f	317 ± 10	317
$Zr(Cp^*)_2(OC_6F_5)H$	RSC/186 ^f	357 ± 10	357
$Zr(Cp^*)_2H_2$	RSC/186 ^f	318 ± 8	318
$Zr(Cp^*)_2(OCH_2CF_3)H$	RSC/186 ^f	347 ± 8	347
$Zr(Cp^*)_2(OBu-t)H$	RSC/186 ^f	363 ± 13	363
$Zr(Cp^*)_2(Ph)H$	RSC/186 ^f	335 ± 10	335
$Zr(Cp^*)_2(OPh)Me$	RSC/186 ^f	299 ± 2	275
$Zr(Cp^*)_2CH_2(CHEt)_2CH_2$	RSC/186 ^f	261 ± 10	
$Zr(Cp^*)_2CH_2CH_2C_6H_4-o$	RSC/186 ^f	282 ± 8	
$Zr(Cp^*)Me_3$	RSC/186 ^f	276 ± 10	252
$Zr(Cp^*)(OC_6F_5)Me_2$	RSC/186 ^f	289 ± 11	265
$Zr(Cp^*)(OC_6F_5)_2Me$	RSC/186 ^f	310 ± 11	286
$Zr(Cp^*)(C_5Me_4CH_2)Ph$	RSC/186	$D_3 + (195 \pm 13)^g$	
$Hf(CH_2CMe_3)_4$	RSC/172 ^b	266	259
$Hf(Cp^*)_2R_2$	RSC/186 ^{b,h}		
R = H		346 ± 7	346
R = Me		306 ± 7	282
R = Bu		274 ± 10	267
$Hf(Cp^*)_2H_2$	RSC/186 ^b	326 ± 10	326
$Hf(Cp^*)(H)Ph$	ES/164 ^h	350 ± 11	306
$Hf(Cp^*)Me_3$	RSC/186 ^b	294 ± 10	270
$Hf(Cp^*)(OC_6F_5)Me_2$	RSC/186 ^b	300 ± 10	276
$(Hf(Cp^*)(OC_6F_5)_2)Me$	RSC/186 ^b	309 ± 11	285
$Hf(Cp^*)(C_5Me_4CH_2CH_2CH_2)H$	ES/164 ^h	243 ± 13	
$Hf(Cp^*)(C_5Me_3CH_2C_6H_4-o)H$	ES/164 ^h	320 ± 13	
$Hf(Cp)_2(Me)C(O)Me$	ES/187 ^h	298 ± 10	366

^a Key: KSL = kinetic studies in the solid phase; ES = equilibrium studies in solution; RSC = reaction solution calorimetry; SB = static bomb combustion calorimetry. ^b Mean bond dissociation enthalpies. ^c Data rely on $E(Ti-Cl) = 430.5 \pm 1.3$ kJ/mol. ^d Fc = $(\eta^5-C_5H_4)Fe(\eta^5-C_5H_5)$. ^e $D_2 = D(Ti-Cp^*)$. ^f Data rely on $E(Zr-Cl) = 491.4 \pm 0.7$ kJ/mol. ^g $D_3 = D(Zr-Cp^*)$. ^h Data rely on $E(Hf-Cl) = 497.6$ kJ/mol.

formation.^{161,172} The titanium-carbon bond enthalpy terms were derived by using the reorganization energies given in Appendix. The steric effects in the neopentyl molecule are evidenced by the low $\bar{D}(Ti-C)$ and $E(Ti-C)$ values.

The $Ti(Cp)_2R_2$ complexes listed in Table 3 were studied either by combustion calorimetry or by reaction solution calorimetry.^{173,174} $\bar{D}(Ti-C)$ and $E(Ti-C)$ were

derived through eqs 4 and 5, respectively, by using the reported enthalpies of formation of the complexes in the gas phase,¹⁷⁴ which rely, in most cases, on estimates of sublimation enthalpies. It is not expected, however, that the accuracy of the bond enthalpies is significantly affected by those estimates.¹⁷⁴ The correction terms $ER_3/2$ and $(ER_3 - ER_1)/2$ were not included in the calculations (see discussion in section III.A). In any case, it is predicted by the extended Hückel method that those corrections are small. For example, the available molecular structures of the complexes $Ti(Cp)_2Ph_2$ and $Ti(Cp)_2Fc_2$ [$Fc = (\eta^5-C_5H_5)Fe(\eta^5-C_5H_5)$],^{175,176} together with Figure 1a, lead, respectively, to $(ER_3 - ER_1)/2 \approx -5$ and -1 kJ/mol. This reflects the fact that their Cp-Ti-Cp angles (135.9° and 131.2°, respectively), are close to the same angle in $Ti(Cp)_2Cl_2$, 131.0°.¹⁷⁷ ER_3 is also negligible (-5 kJ/mol).

All $\bar{D}(Ti-C)$ and $E(Ti-C)$ values for the $Ti(Cp)_2R_2$ complexes rely upon $E(Ti-Cl) = 430.5 \pm 1.3$ kJ/mol, derived from $TiCl_4$.¹⁷³ This assumption (see eq 3) is discussed below.

$\Delta H_f^\circ(R^*,g)$ were evaluated from the appropriate Laidler terms (Appendix), except in the case of $Ti(Cp)_2Fc_2$, where an $E(C-H)/r(C-H)$ curve was used.^{93,104} The enthalpies of formation of the radicals RC_6H_4 ($R = 4-CF_3, 3-Me, 4-Me, 4-MeO$) were estimated by assuming $D(RC_6H_4-H) \approx D(Ph-H)$.

Titanium-methyl and titanium-phenyl bond enthalpy terms in the complexes $Ti(Cp)_2(Cl)R$ were calculated through eq 64, derived from schemes similar to 4.¹⁷⁸ ER'_{13} , the reorganization energy of the fragment

$$E(Ti-R) = E(Ti-Cl) + \Delta H_f^\circ(R^*,g) - \Delta H_f^\circ(Cl,g) - \{\Delta H_f^\circ[Ti(Cp)_2(Cl)R,g] - \Delta H_f^\circ[Ti(Cp)_2Cl_2,g]\} - (ER'_3 - ER'_{13}) \quad (64)$$

$Ti(Cp)_2Cl$ from $Ti(Cp)_2(Cl)R$, was assumed to be equal to ER'_3 , the reorganization energy of the same fragment from $Ti(Cp)_2Cl_2$. Identical values for $E(Ti-Ph)$ are observed for the complexes $Ti(Cp)_2Ph_2$ and $Ti(Cp)_2(Cl)Ph$, but $E(Ti-Me)$ seems strengthened in $Ti(Cp)_2(Cl)Me$, relative to $Ti(Cp)_2Me_2$. However, both values rely on the same number for $E(Ti-Cl)$. If the titanium-chlorine bond is also stronger in $Ti(Cp)_2(Cl)Me$, then the two $E(Ti-Me)$ values will be closer to each other.

Estimates of $D(Ti-R)$ in $Ti(Cp)_2(Cl)R$ can be made by using the extended Hückel result for ER'_3 , ca. -41 kJ/mol,¹⁰⁵ together with eq 65. The values, $D(Ti-Me)$

$$D(Ti-R) = E(Ti-Cl) + \Delta H_f^\circ(R,g) - \Delta H_f^\circ(Cl,g) - \{\Delta H_f^\circ[Ti(Cp)_2(Cl)R,g] - \Delta H_f^\circ[Ti(Cp)_2Cl_2,g]\} - ER'_3 \quad (65)$$

$= 276$ kJ/mol and $D(Ti-Ph) = 294$ kJ/mol, can be compared with the values estimated through the same method (see Scheme 4 and eq 7) for the *first* Ti-R bond dissociation enthalpy in $Ti(Cp)_2Me_2$ and $Ti(Cp)_2Ph_2$, 287 and 291 kJ/mol, respectively [$ER'_1 = -11$ kJ/mol for $Ti(Cp)_2Me$ and -41 kJ/mol for $Ti(Cp)_2Ph$;¹⁷⁴ $E(Ti-Me)$ and $E(Ti-Ph)$ from Table III]. According to the extended Hückel results, therefore, the Ti-Me *first* bond dissociation enthalpy in $Ti(Cp)_2Me_2$ is higher than $D(Ti-Me)$ in $Ti(Cp)_2(Cl)Me$ due to a larger reorganization energy of $Ti(Cp)_2Cl$ as compared to $Ti(Cp)_2Me$. In the case of the Ti-Ph bond, the corresponding dissociation enthalpies have the same magnitude, not only because $E(Ti-Ph)$ are similar (Table 3) but also because

the reorganization energies of $Ti(Cp)_2Ph$ and $Ti(Cp)_2Cl$ are predicted to be comparable.

The value presented in Table 3 for $D(Ti-Et)$ is an estimate, based on measurement of the activation energy of the thermal decomposition reaction of $Ti(Cp)_2(Cl)Et$, yielding $Ti(Cp)_2Cl$ and the ethyl radical.¹⁷⁹ This activation energy was identified with the bond dissociation enthalpy $D(Ti-Et)$, by assuming that the activation energy for recombination of the trivalent titanium complex with the alkyl radical is close to zero.¹⁷⁹ Although the value seems too low, it is qualitatively in line with the above comments; i.e., it suggests a large reorganization energy of $Ti(Cp)_2Cl$ fragment.

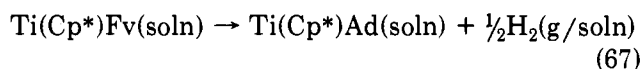
The titanium-methyl *first* bond dissociation enthalpy in the complex $Ti(Cp^*)_2Me_2$, $D_1(Ti-Me) = 281 \pm 8$ kJ/mol (Table 3), was calculated directly from the reported enthalpies of formation of the crystalline complexes $Ti(Cp^*)_2Me_2$ and $Ti(Cp^*)_2Me$,¹⁸⁰ assuming that their sublimation enthalpies are identical. The value is in good agreement with $D_1(Ti-Me)$ in $Ti(Cp)_2Me_2$ estimated above, 287 kJ/mol. A similar exercise for the complex $Ti(Cp^*)_2Ph_2$ led to $D_1(Ti-Ph) = 280 \pm 19$ kJ/mol. Although the uncertainty is large, due to the fact that, in this case, the enthalpy of formation of the Ti(IV) complex had to be estimated, the value is also close to $D_1(Ti-Ph)$ in $Ti(Cp)_2Ph_2$, 294 kJ/mol. However, this agreement is probably fortuitous, since the difference between $D_1(Ti-Ph) - D_1(Ti-Me)$ should be no less than ca. 20 kJ/mol. The "experimental" value quoted in Table 3 is probably a lower limit *relative* to $D_1(Ti-Me)$ (see discussion below).

A disturbing feature emerging from the data in Table 3 discussed so far, is that $E(Ti-Me)$ and $E(Ti-Bz)$ in $Ti(Cp)_2R_2$ seem too high as compared to $E(Ti-CH_2SiMe_3)$ and $E(Ti-Bz)$ in TiR_4 . Recall that all the values in the dicyclopentadienyl complexes rely on $E(Ti-Cl)$ from $TiCl_4$ and this would suggest that, in the absence of steric constraints, $E(Ti-R)$ should be similar in both families of compounds. This hypothesis can be tested for other $Ti(Cp)_2L_2$ and TiL_4 molecules. For example, the enthalpies of formation of alkoxytitanium compounds, $Ti(OR)_4$,^{161,181,182} where R ranges from ethyl to *tert*-pentyl, yield an average value $\langle E(Ti-OR) \rangle \approx 466$ kJ/mol, which is in the range of $\langle E(Ti-O) \rangle \approx 452$ kJ/mol in several $Ti(Cp)_2L_2$ complexes ($L = OCOPh, OCOCF_3, OCOCl_3, OPh, o-, m-,$ and $p-OC_6H_4Me, o-OC_6H_4Cl$).¹⁷⁴ On the other hand, $E(Ti-I) = 298$ kJ/mol in $Ti(Cp)_2I_2$ compares with $E(Ti-I) = 294$ kJ/mol in TiI_4 .¹⁸³ Although some of these comparisons are not entirely satisfactory because they rely on different ligands in TiL_4 and $Ti(Cp)_2L_2$, they emphasize the usefulness of bond enthalpy terms to test the consistency of data and suggest that the values for $E(Ti-C)$ in the two families of compounds should be closer.

While the examples above indicate that $E(Ti-R)$ in $Ti(Cp)_2R_2$ and TiR_4 should be more similar, the *trends* in bond enthalpy data for the $Ti(Cp)_2R_2$ complexes look sensible. For example, the differences $\bar{D}(Ti-Ph) - \bar{D}(Ti-Me) = 34$ kJ/mol and $\bar{D}(Ti-Me) - \bar{D}(Ti-Bz) = 61$ kJ/mol are in the range of the values observed for other transition-metal compounds (see, e.g., Tables 2 and 5) and close to the differences between carbon-hydrogen bond dissociation enthalpies in the corresponding hydrocarbons. A reasonable trend is, however, also observed for the TiR_4 compounds. For example, $\bar{D}(Ti-$

$\text{CH}_2\text{SiMe}_3 - \bar{D}(\text{Ti}-\text{Bz}) = 52 \text{ kJ/mol}$ compares with $D(\text{Me}_3\text{SiCH}_2-\text{H}) - D(\text{Bz}-\text{H}) = 47 \text{ kJ/mol}$. Accepting the values for the homoleptic compounds as being more accurate will probably imply a downward adjustment of $\text{Ti}(\text{Cp})_2\text{R}_2$ data in Table 3 by ca. 25 kJ/mol (see discussion for the zirconium complexes). Incidentally, two early combustion results for $\text{Ti}(\text{Cp})_2\text{Me}_2$ ^{173,184} lead to $\bar{D}(\text{Ti}-\text{Me}) = 305 \pm 7$ and $257 \pm 7 \text{ kJ/mol}$ [or $E(\text{Ti}-\text{Me}) = 281$ and 233 kJ/mol]. If the last (and more recent) value is accepted, the comparison with the data for TiR_4 improves but the trend in the dicyclopentadienyl complexes looks unreasonable [e.g., $\bar{D}(\text{Ti}-\text{Me}) - \bar{D}(\text{Ti}-\text{Ph}) = 75 \text{ kJ/mol}$]. Another literature value for $\bar{D}(\text{Ti}-\text{Ph})$ in $\text{Ti}(\text{Cp})_2\text{Ph}_2$, 430 kJ/mol, also derived from static bomb combustion experiments,¹⁸⁴ is unacceptable. In summary, although the values in Table 3 seem to be in the correct range (within ca. 25 kJ/mol) and follow a reasonable trend, only a reassessment of their thermochemistry will solve the above contradictions.

The last two values in Table 3 for titanium complexes refer to the differences $D(\text{Ti}-\text{C}_5\text{Me}_4\text{CH}_2) - D(\text{Ti}-\text{Cp}^*)$ and $D(\text{Ti}-\text{C}_5\text{Me}_4\text{CH}_2\text{CH}_2) - D(\text{Ti}-\text{Cp}^*)$ and are based on the enthalpies of reactions 66 and 67 (Fv = fulvene, $\text{Ti}(\text{Cp}^*)_2\text{Me}(\text{soln}) \rightarrow$

$$\text{Ti}(\text{Cp}^*)\text{Fv}(\text{soln}) + \text{CH}_4(\text{g}/\text{soln}) \quad (66)$$


Ad = allyl diene), 29.5 ± 7.3 and $-67.9 \pm 6.4 \text{ kJ/mol}$, respectively.¹⁸⁵ The bond dissociation enthalpies are estimates and aimed to help probing the bonding of the fragments Fv and Ad. For example, the large difference $D(\text{Ti}-\text{Cp}^*) - D(\text{Ti}-\text{Fv})$ may suggest that the fulvene complex contains a strained titanium-carbon σ bond in addition to the η^5 coordination.¹⁸⁵

b. Zirconium. Zirconium-carbon mean bond dissociation enthalpies in the compounds ZrR_4 (Table 3) were derived from their enthalpies of formation.^{161,172} It is noted that they are higher (by ca. 50 kJ/mol) than the corresponding values for the titanium analogues but follow the same trend.

The zirconium-methyl mean bond dissociation enthalpy (Table 3) in $\text{Zr}(\text{Cp})_2\text{Me}_2$ was derived from the measured enthalpy of reaction 68 in toluene, by as-

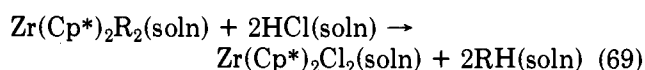
$$\text{Zr}(\text{Cp})_2\text{Me}_2(\text{soln}) + 2\text{I}_2(\text{soln}) \rightarrow \text{Zr}(\text{Cp})_2\text{I}_2(\text{soln}) + 2\text{MeI}(\text{soln}) \quad (68)$$

suming that the solvation enthalpies of products and reactants cancel.¹⁸⁶ It relies on data in the Appendix and on $E(\text{Zr}-\text{I}) = \bar{D}(\text{Zr}-\text{I}) = 343.6 \pm 0.7 \text{ kJ/mol}$, a value assumed to be equal to $E(\text{Zr}-\text{I}) = \bar{D}(\text{Zr}-\text{I})$ in the analogous $\text{Zr}(\text{Cp}^*)_2\text{I}_2$ complex (see below).

Static bomb combustion experiments on $\text{Zr}(\text{Cp})_2\text{Me}_2$, $\text{Zr}(\text{Cp})_2\text{Ph}_2$, and $\text{Zr}(\text{Cp})_2\text{Cl}_2$, together with measured enthalpies of sublimation,^{15,161,187} led to the enthalpies of formation of these molecules, from which $\bar{D}(\text{Zr}-\text{Me}) = 282 \pm 3 \text{ kJ/mol}$ and $\bar{D}(\text{Zr}-\text{Ph}) = 300 \pm 10 \text{ kJ/mol}$ are derived, by using the methods described for the titanium compounds and $E(\text{Zr}-\text{Cl}) = 491.4 \pm 0.7 \text{ kJ/mol}$.¹⁶⁷ The agreement of $\bar{D}(\text{Zr}-\text{Me})$ with the reaction solution result is excellent, but $\bar{D}(\text{Zr}-\text{Ph})$ seems a bit too low.

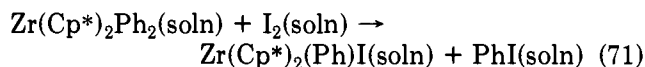
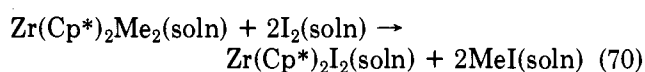
The remaining data for zirconium complexes in Table 3 have origin in a recent calorimetric work by Schock

and Marks.¹⁸⁶ The values for $\bar{D}(\text{Zr}-\text{R})$ in the complexes $\text{Zr}(\text{Cp}^*)_2\text{R}_2$ (R = H, I) were obtained from the enthalpies of reaction 69 in toluene, by assuming that the



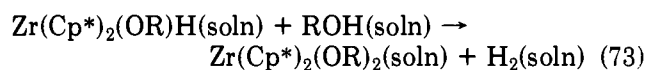
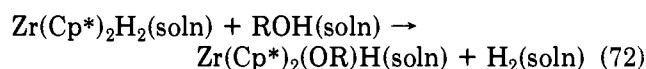
solvation enthalpies cancel. These mean values rely on $E(\text{Zr}-\text{Cl}) = \bar{D}(\text{Zr}-\text{Cl}) = 491.4 \pm 0.7 \text{ kJ/mol}$.¹⁶⁷ The "anchor" chosen by authors was only about 7 kJ/mol lower: They have used $D_1(\text{Zr}-\text{Cl}) = 484.1 \text{ kJ/mol}$ in ZrCl_4 . The most recently recommended value for this quantity is $D_1(\text{Zr}-\text{Cl}) = 467 \pm 21 \text{ kJ/mol}$.¹⁶⁷ While the choice of the anchor is somewhat a matter of personal taste, a procedure similar to the one described for thorium, uranium, and titanium compounds is preferred in the present survey. $\bar{D}(\text{Zr}-\text{I}) = 344 \pm 1 \text{ kJ/mol}$ (not quoted in Table 3) compares with $\bar{D}(\text{Zr}-\text{I})$ in ZrI_4 , $348.2 \pm 2.1 \text{ kJ/mol}$.¹⁶⁷

The value obtained for zirconium-iodine mean bond dissociation enthalpy was then used to derive bond data for the methyl and phenyl complexes, from the enthalpies of reactions 70 and 71 (in toluene). Note that



in the case of the phenyl complex the reaction enthalpy reflects $D_1(\text{Zr}-\text{Ph}) - \bar{D}(\text{Zr}-\text{I})$, but the value quoted in Table 3 relies on $\bar{D}(\text{Zr}-\text{I}) = 344 \pm 1 \text{ kJ/mol}$. The iodolysis reaction of the dihydride complex, yielding the diiodide complex and hydrogen, was also used by the authors to confirm the value of $\bar{D}(\text{Zr}-\text{H})$ from reaction 69 (Table 3). $\bar{D}(\text{Zr}-\text{H}) = 319 \pm 2 \text{ kJ/mol}$ is obtained. Although the difference is 20 kJ/mol, the agreement is not bad, given the difficulties involved in studying the thermochemistry of these complexes and also the assumption about canceling solvation enthalpies.

A series of values of zirconium-hydrogen bond dissociation enthalpies in complexes $\text{Zr}(\text{Cp}^*)_2\text{H}_2$ and $\text{Zr}(\text{Cp}^*)_2(\text{OR})\text{H}$ (Table 3) were calculated from the enthalpies of alcoholysis reactions illustrated by reactions 72 and 73 (OR = OPh, OC_6F_5 , OCH_2CF_3).¹⁸⁶ These



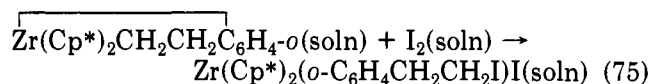
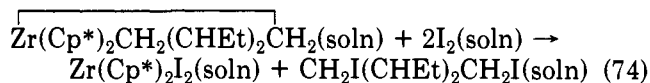
values rely on $\bar{D}(\text{Zr}-\text{OPh}) = 384 \pm 8 \text{ kJ/mol}$, $\bar{D}(\text{Zr}-\text{OC}_6\text{F}_5) = 387 \pm 10 \text{ kJ/mol}$, and $\bar{D}(\text{Zr}-\text{OCH}_2\text{CF}_3) = 427 \pm 8 \text{ kJ/mol}$, which were obtained from the enthalpies of reaction of the $\text{Zr}(\text{Cp}^*)_2(\text{OR})_2$ complexes with HCl (similar to reaction 69),¹⁸⁶ and are thus "consistent" with the anchor chosen. It is noted that the zirconium-hydrogen bond dissociation enthalpies are higher in the alkoxy-containing complexes by ca. 30 kJ/mol. Recall, however, that the zirconium-oxygen bonds may also be strengthened in $\text{Zr}(\text{Cp}^*)_2(\text{OR})\text{H}$ compounds, in which case those differences are upper limits. It is also possible to derive three independent values for $\text{Zr}-\text{H}$ mean bond dissociation enthalpy in $\text{Zr}(\text{Cp}^*)_2\text{H}_2$ from the three sets of results [i.e., from $\Delta H^\circ(72) + \Delta H^\circ(73)$], 349, 337, and 333 kJ/mol, respectively for OR = OPh, OC_6F_5 , and OCH_2CF_3 . The agreement is good and the

values are also close to $\bar{D}(\text{Zr-H})$ obtained from the study of reaction 69, 339 kJ/mol (Table 3).

Zirconium-hydrogen bond dissociation enthalpies in the complexes $\text{Zr}(\text{Cp}^*)_2(\text{L})\text{H}$ ($\text{L} = t\text{-BuO}$, Ph) are also presented in Table 3. They were calculated from the enthalpies of reaction of the complexes with $\text{C}_6\text{F}_5\text{OH}$,¹⁸⁶ yielding $\text{Zr}(\text{Cp}^*)_2(\text{L})(\text{OC}_6\text{F}_5)$ and H_2 , and are based on $\bar{D}(\text{Zr-OC}_6\text{F}_5) = 387 \pm 10$ kJ/mol (see above). Although, as discussed before, it is not straightforward to draw conclusions from these trends, the values seem to indicate that $D(\text{Zr-H})$ values in complexes $\text{Zr}(\text{Cp}^*)_2(\text{L})\text{H}$ are higher for $\text{L} = \text{alkoxy}$ than for $\text{L} = \text{H}$ or Ph .

The influence of alkoxy groups in Zr-Me bond dissociation enthalpy may be smaller, as suggested by the value displayed in Table 3 in the case of $\text{Zr}(\text{Cp}^*)_2(\text{OPh})\text{Me}$, 299 ± 2 kJ/mol, as compared to $\bar{D}(\text{Zr-Me}) = 284 \pm 2$ kJ/mol in $\text{Zr}(\text{Cp}^*)_2\text{Me}_2$. The former value is based on the enthalpy of reaction of the complex with HCl , the products being $\text{Zr}(\text{Cp}^*)_2\text{Cl}_2$, phenol, and methane.¹⁸⁶ It relies also on $\bar{D}(\text{Zr-OPh})$ and $\bar{D}(\text{Zr-Cl})$ given above.

Zirconium-carbon bond enthalpies in the metallacycles $\text{Zr}(\text{Cp}^*)_2\text{CH}_2(\text{CHEt})_2\text{CH}_2$ and $\text{Zr}(\text{Cp}^*)_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{-o}$ were calculated from the enthalpies of reactions 74 and 75, respectively,¹⁸⁶ by using eqs 76 and 77. The main difficulty in these cases is to



$$\bar{D}(\text{Zr-C}) = \Delta H^\circ(74)/2 + \bar{D}(\text{Zr-I}) - D(\text{I-I}) + \bar{D}(\text{C-I}) \quad (76)$$

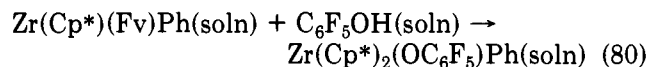
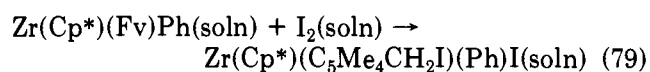
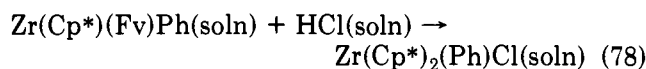
$$D(\text{Zr-C}) = \Delta H^\circ(75) + D(\text{Zr-I}) - D(\text{I-I}) + D(\text{C-I}) \quad (77)$$

estimate the values for $D(\text{C-I})$. The option in the present review was to identify both these quantities with alkyl-iodine dissociation enthalpy, 237 ± 8 kJ/mol (Appendix). This, together with the Zr-I bond enthalpy value given above, led to the results shown in Table 3, 261 and 282 kJ/mol, respectively for the metallacycles of reactions 74 and 75. Although these values are not strictly comparable, since $\bar{D}(\text{Zr-I})$ in $\text{Zr}(\text{Cp}^*)_2\text{I}_2$ can be different from $D(\text{Zr-I})$ in $\text{Zr}(\text{Cp}^*)_2(\text{L})\text{I}$, they seem to indicate a small amount of strain in the zirconacyclopentane metallacycle. It must be small because it is expected that $D(\text{Zr-alkyl})$ is less than the value for $\bar{D}(\text{Zr-Me})$ in Table 3, 284 kJ/mol. On the same basis, no strain is observed in the zirconaindan metallacycle. However, as stated above, the conclusions may change if different values are assigned to $D(\text{C-I})$ in eqs 76 and 77.¹⁸⁶

The enthalpies of successive substitution of methyl groups by $\text{C}_6\text{F}_5\text{O}$ in the complex $\text{Zr}(\text{Cp}^*)\text{Me}_3$ were also measured in toluene by Schock and Marks¹⁸⁶ and led to the respective Zr-Me bond dissociation enthalpies. As usual, these were calculated on the basis of a constant $D(\text{Zr-OC}_6\text{F}_5)$, and so the increase observed in the values of Table 3 may be offset if those zirconium-oxygen bond dissociation enthalpies also increase. In any case, the average value for the three substitution reactions, $\bar{D}(\text{Zr-Me}) = 292 \pm 10$ kJ/mol, is close to $D(\text{Zr-}$

$\text{Me})$ in $\text{Zr}(\text{Cp}')_2\text{Me}_2$ complexes ($\text{Cp}' = \text{Cp}$, Cp^*).

The last value for zirconium complexes in Table 3 refers to the difference $D(\text{Zr-C}_5\text{Me}_4\text{CH}_2) - D(\text{Ti-Cp}^*)$ and is based on the enthalpies of reactions 78-80.¹⁸⁶



Each of these reactions affords an independent value for the difference, namely 187 ± 8 , 208 ± 9 , and 190 ± 17 kJ/mol, respectively. The agreement is good, given the uncertainties affecting the auxiliary data, in particular $D(\text{C}_5\text{Me}_4\text{CH}_2\text{-H})$ (reactions 78 and 80) and $D(\text{C}_5\text{Me}_4\text{CH}_2\text{-I})$ (reaction 79), which were identified with $D(\text{Bz-H})$ and $D(\text{Bz-I})$ (Appendix). The value quoted in Table 3, the average of those results, 195 kJ/mol, is very close to the one derived for titanium, supporting the existence of strained metal-carbon σ bonds in both fulvene complexes.

The comparison between bond enthalpy data in $\text{Ti}(\text{Cp})_2\text{R}_2$ and TiR_4 compounds indicated that the values given in Table 3 for the dicyclopentadienyl complexes are probably too high. The same exercise for the analogous zirconium molecules (including Cp and Cp^* compounds) may lead to the opposite conclusion! For example, it is unexpected that $\bar{D}(\text{Zr-CH}_2\text{SiMe}_3)$ is higher than $\bar{D}(\text{Ti-Me})$ in $\text{Ti}(\text{Cp})_2\text{Me}_2$ by about 25 kJ/mol. Clearly, more experimental work is needed in these systems, to improve the accuracy of data. The trend $\bar{D}(\text{Ti-Me}) > \bar{D}(\text{Zr-Me})$ is unacceptable and is not likely to be entirely due to unreasonable assumptions on transferability of bond enthalpies. The fact that the trends within each family look reasonable suggests that a systematic error is affecting all values of one or more families.

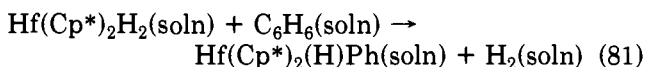
c. Hafnium. Most data for hafnium-hydrogen and hafnium-carbon bond enthalpies in Table 3 were also reported by Schock and Marks.¹⁸⁶ One exception refers to the homoleptic neopentyl compound, whose enthalpy of formation was determined by Lappert, Patil, and Pedley¹⁷² and the value reassessed elsewhere.¹⁶¹

$\bar{D}(\text{Hf-Me})$ and $\bar{D}(\text{Hf-I})$ in the complexes $\text{Hf}(\text{Cp}^*)_2\text{R}_2$ were calculated from the enthalpies of their reactions with HCl in toluene (see reaction 69), under the assumptions discussed for the zirconium analogues. In the present case, values rely on $E(\text{Hf-Cl}) = \bar{D}(\text{Hf-Cl}) = 497.6$ kJ/mol in HfCl_4 .¹⁵⁹ The results obtained were $\bar{D}(\text{Hf-I}) = 352 \pm 6$ kJ/mol and $\bar{D}(\text{Hf-Me}) = 317 \pm 2$ kJ/mol (not quoted in Table 3). The hafnium-iodine value was then used to derive $\bar{D}(\text{Hf-R})$ in the same family of complexes ($\text{R} = \text{H}$, Me , Bu) whose enthalpies of reaction with iodine in toluene have been reported.¹⁸⁶ For $\text{R} = \text{Me}$ and Bu , these reactions are similar to reaction 68, and for $\text{R} = \text{H}$, 1 mol of I_2 yields the diiodide complex and H_2 . The mean bond dissociation enthalpies and the bond enthalpy terms [calculated by the usual method, i.e., subtracting the reorganization energy of the radical to $\bar{D}(\text{Hf-R})$] are presented in Table 3. It is noted that $\bar{D}(\text{Hf-Me})$ is only slightly lower than the value given above (calculated through the reaction with HCl), but $\bar{D}(\text{Hf-Bu})$ seems too low. Although the un-

certainty interval should be considered, it is perhaps unexpected that $\bar{D}(\text{Hf-Me}) - \bar{D}(\text{Hf-Bu})$ is as large as 32 kJ/mol.

The measured enthalpy for the reaction between $\text{Hf}(\text{Cp}^*)_2\text{H}_2$ and $\text{C}_6\text{F}_5\text{OH}$ in toluene (see reaction 72)¹⁸⁶ enabled the calculation of $D(\text{Hf-H})$ on the basis of $\bar{D}(\text{Hf-OC}_6\text{F}_5) = 395 \pm 10$ kJ/mol. This mean bond dissociation enthalpy in $\text{Hf}(\text{Cp}^*)_2(\text{OC}_6\text{F}_5)_2$ was obtained from the enthalpy of reaction of this complex with HCl in toluene.¹⁸⁶ The value in Table 3 for $D(\text{Hf-H})$ is about 20 kJ/mol lower than $\bar{D}(\text{Hf-H})$, also given in the table. This trend, together with a word of caution, had been noted for the zirconium compounds.

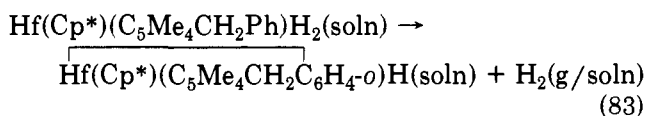
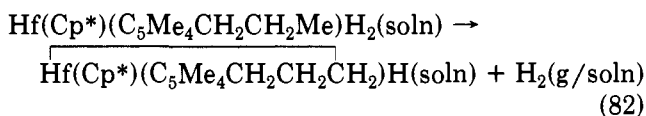
A comparison between Hf-H and Hf-Ph bond dissociation enthalpies is provided by the enthalpy of reaction 81, obtained from equilibrium studies in benzene, in the temperature range 373–444 K.¹⁶⁴ Assuming that



the solvation enthalpies cancel and using data in Appendix, $D(\text{Hf-Ph}) - D(\text{Hf-H}) = 4 \pm 8$ kJ/mol is obtained. The value shown in Table 3 for $D(\text{Hf-Ph})$ relies on this difference and on $\bar{D}(\text{Hf-H}) = 346 \pm 7$ kJ/mol. As remarked by Schock and Marks,¹⁸⁶ note that for all the systems described so far, metal-hydrogen bond dissociation enthalpies are similar or higher than metal-phenyl bond dissociation enthalpies, in contrast to $D(\text{Ph-H}) - D(\text{H-H}) = 29$ kJ/mol.

As in the case of zirconium complexes, the enthalpies of successive substitution of methyl groups by $\text{C}_6\text{F}_5\text{O}$ in the complex $\text{Hf}(\text{Cp}^*)\text{Me}_3$ were also measured in toluene by Schock and Marks.¹⁸⁶ The respective Hf-Me bond dissociation enthalpies, calculated on the basis of a constant $D(\text{Hf-OC}_6\text{F}_5) = 395 \pm 10$ kJ/mol, are given in Table 3 and show a trend similar to Zr; i.e., there is an increase in $D(\text{Hf-Me})$ when the number of alkoxy ligands also increases (see, however, the comment made for the zirconium complexes). The average value for the three substitution reactions, $\bar{D}(\text{Hf-Me}) = 301 \pm 9$ kJ/mol, is close to $\bar{D}(\text{Hf-Me})$ in $\text{Hf}(\text{Cp}^*)_2\text{Me}_2$.

The enthalpies of reactions 82 and 83 in benzene were obtained from van't Hoff plots in the temperature ranges 343–387 and 332–386 K, respectively,¹⁶⁴ and lead, (eq 84) to differences $D(\text{Hf-H}) - D(\text{Hf-C})$ by assuming



$$D(\text{Hf-H}) - D(\text{Hf-C}) = \Delta H^\circ_r - D(\text{C-H}) + D(\text{H-H}) \quad (84)$$

that the solvation enthalpies cancel and by estimating values for $D(\text{C-H})$. In the case of reaction 82, $D(\text{C-H})$ was identified with $D(\text{Pr-H})$ and, for reaction 83, with $D(\text{Ph-H})$. The difference obtained for $D(\text{Hf-H}) - D[\text{Hf-C}(\text{sp}^3)]$, 83 ± 8 kJ/mol, is surprisingly large and indicates a considerable strain in the metallacycle. $D(\text{Hf-H}) - D[\text{Hf-C}(\text{sp}^2)] = 6 \pm 9$ kJ/mol is in the range of the differences found for $D(\text{M-H}) - D(\text{M-Ph})$. The values quoted in Table 3 refer to $D(\text{Hf-C})$ and were

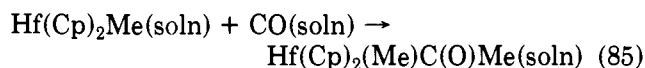
TABLE 4. Groups 5 and 6 M-H and M-C Bond Enthalpies

molecule	method/ref ^a	D , kJ/mol	E , kJ/mol
TaMe ₅	RSC/189 ^b	261 ± 5	237
Cr(Cp)(CO) ₃ H	CMC, ES/190, 191	258 ± 3	258
Mo(Cp) ₂ R ₂	RSC/174, 178, 197 ^{b,c}		
R = H		257 ± 8	
R = Me		166 ± 8	142
R = Et		156 ± 9	146
R = Bu		154 ± 12	147
Mo(Cp) ₂ (C ₂ H ₄)	RSC/197 ^c	59 ± 20	
Mo(Cp) ₂ (C ₂ Ph ₂)	RSC/197 ^c	120 ± 27	
Mo(Cp)(CO) ₃ H	RSC/190, 198, 199	273 ± 9	
Mo(Cp)(CO) ₃ R	RSC/200–202		
R = H		282 ± 6	282
R = Me		203 ± 8	179
R = Et		185 ± 11	175
R = C ₂ H ₅		147 ± 10	195
R = Bz		154 ± 10	197
WMe ₆	RSC/189 ^b	160 ± 6	136
W(Cp) ₂ R ₂	RSC/174, 178 ^{b,d}		
R = H		311 ± 4	311
R = Me		221 ± 3	197
W(Cp) ₂ (I)H	RSC/174, 178 ^d		273
W(Cp)(CO) ₃ H	RSC/190	339 ± 5	339
W(CO) ₃ [P(c-C ₆ H ₁₁) ₃] ₂ (H ₂)	RSC/207	40 ± 2	
W(CO) ₅ [C(OMe)Ph]	CMC/210	359 ± 18	

^aKey: CMC = Calvet microcalorimetry; ES = equilibrium studies in solution; RSC = reaction solution calorimetry. ^bMean bond dissociation enthalpies. ^cData rely on $E(\text{Mo-Cl}) = 303.8 \pm 7.1$ kJ/mol. ^dData rely on $E(\text{W-Cl}) = 347.3 \pm 0.8$ kJ/mol.

derived by taking $D(\text{Hf-H}) = 326$ kJ/mol.

The last value in Table 3 was calculated from the enthalpy of carbonyl insertion reaction 85, obtained from a van't Hoff plot in toluene.¹⁸⁸ $D[\text{Hf-C}(\text{O})\text{Me}] - D(\text{Hf-Me})$ was calculated as -8 ± 7 kJ/mol through eq 86, by using the enthalpies of formation of Me and



$$D[\text{Hf-C}(\text{O})\text{Me}] - D(\text{Hf-Me}) = -\Delta H^\circ(85) - D(\text{OC-Me}) \quad (86)$$

MeCO (Appendix) to derive $D(\text{OC-Me}) = 60.7 \pm 1.8$ kJ/mol. The high value for $D[\text{Hf-C}(\text{O})\text{Me}]$ reflects, as in the case of thorium, the donating character of the oxygen, yielding a strong η^2 bond with the metal atom (for comparison, $D[\text{MeC}(\text{O})\text{-H}] - D(\text{Me-H}) = -80.4 \pm 2.0$ kJ/mol). The value shown in Table 3 relies on $D(\text{Hf-Me}) = 306$ kJ/mol.

3. Group 5

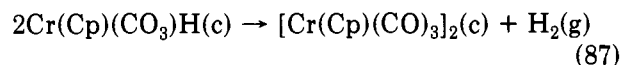
The only group 5 transition metal-carbon σ bond whose mean bond dissociation enthalpy is reported in the literature^{15,189} refers to Ta-Me in the compound TaMe₅. The enthalpy of formation in the gas phase leads to the values shown in Table 4, where the bond enthalpy term was obtained under the usual assumption, i.e., that the structures of Me in the complex and in methane are similar, and by using the reorganization energy of methyl radical (Appendix).

4. Group 6

The available thermochemical data for group 6 metal-hydrogen and metal-carbon σ bonds are presented in Table 4.

a. Chromium. Microcalorimetric and differential scanning calorimetry experiments led to the enthalpy

of reaction 87,¹⁹⁰ from which the difference $2D(\text{Cr-H}) - D(\text{Cr-Cr})$ can be estimated (eq 88) as 450 ± 6 kJ/mol



$$2D(\text{Cr-H}) - D(\text{Cr-Cr}) = \Delta H^\circ(87) + D(\text{H-H}) \quad (88)$$

by assuming that $\Delta H^\circ_s[\text{Cr}(\text{Cp})(\text{CO})_3]_2 \approx 2\Delta H^\circ_s[\text{Cr}(\text{Cp})(\text{CO})_3\text{H}]$. Another recent study involving the measurement of the enthalpy for the equilibrium dimer-monomers (van't Hoff plot in toluene over the temperature range 208–368 K)¹⁹¹ leads to $D(\text{Cr-Cr}) \approx 66 \pm 1$ kJ/mol and to $D(\text{Cr-H}) = 258$ kJ/mol. According to the discussion in section III.B (after eqs 12–14), the relationship $\Delta H^\circ_s[\text{Cr}(\text{Cp})(\text{CO})_3]_2 \approx 2\Delta H^\circ_s[\text{Cr}(\text{Cp})(\text{CO})_3\text{H}]$ can be expected, since the ratio of molecular weights of the complexes is about 2.

A mention is made to several kinetic studies in water, involving the evaluation of activation enthalpies of chromium-carbon bond cleavage in the cations $[\text{Cr}(\text{H}_2\text{O})_5\text{R}]^{2+}$.^{192–195} These activation enthalpies are identified with $D(\text{Cr}^{2+}-\text{R})$ by assuming negligible activation barriers for the reverse reactions and by neglecting solvation effects. While the trends obtained in these studies are quite valuable, a comparison with “gas-phase” data is not straightforward.

Photoacoustic calorimetry studies have yielded the difference $D[\text{Cr}(\text{CO})_5-\text{CO}] - D[\text{Cr}(\text{CO})_5-\text{heptane}] = 112.9 \pm 1.0$ kJ/mol.¹⁹⁶ The enthalpy of the weak chromium-hydrocarbon bond, 41 ± 13 kJ/mol, was derived by taking $D[\text{Cr}(\text{CO})_5-\text{CO}]$ from Table 1.

b. Molybdenum. Values of $\bar{D}(\text{Mo-R})$ and $E(\text{Mo-R})$ in the complexes $\text{Mo}(\text{Cp})_2\text{R}_2$ were calculated from their enthalpies of formation in the gas phase,^{174,197} by using eqs 4 and 5. Once again, the analysis required transferring bond enthalpy terms. $E(\text{Mo-Cl})$ was assumed to be identical in $\text{Mo}(\text{Cp})_2\text{Cl}_2$ and MoCl_6 , 303.8 ± 7.1 kJ/mol.¹⁷³ Unfortunately, not as many data are available to test this assignment as in the case of titanium- or zirconium-dicyclopentadienyl complexes (see, however, discussion for tungsten analogues).

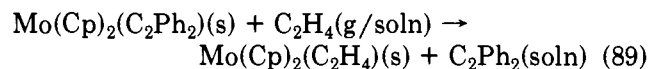
The values presented in Table 4 are not affected by the reorganization energies ER_1 and ER_3 (see eqs 4 and 5). As stated in section III.A, $|ER_3|$, the reorganization energy of the $\text{M}(\text{Cp})_2$ fragment from $\text{M}(\text{Cp})_2\text{Cl}_2$, is much smaller for $\text{M} = \text{Ti}$ than for $\text{M} = \text{Mo}$ or W . The Cp-Mo-Cp angle in $\text{Mo}(\text{Cp})_2\text{Cl}_2$ is 130.5° ,⁹⁰ giving (Figure 1b) $ER_3 \approx -82$ kJ/mol. This suggests that the $\bar{D}(\text{Mo-R})$ values in Table 4 are upper limits (if, of course, the assignment of $E(\text{Mo-Cl})$ is accurate). A discussion of the bond enthalpy terms is less speculative since the differences $ER_3 - ER_1$ are considered. The only pertinent molecular structural data available refers to $\text{Mo}(\text{Cp})_2\text{H}_2$, showing a Cp-Mo-Cp angle of 145.8° ,⁹¹ which results in $ER_3 - ER_1 \approx -66$ kJ/mol (see Figure 1b and section III.A). The molecular structure of $\text{Mo}(\text{Cp})_2\text{Me}_2$ is not known, and so it is not possible to estimate a correction for $E(\text{Mo-Me})$. However, as methyl groups are electron σ donors, it may be expected that the Cp-M-Cp angles will be slightly wider in $\text{Mo}(\text{Cp})_2\text{Me}_2$ than in $\text{Mo}(\text{Cp})_2\text{Cl}_2$ complexes,⁸⁹ yielding negative $ER_3 - ER_1$ terms and a small decrease of $E(\text{Mo-Me})$ value presented in Table 4.

Extended Hückel calculations and eq 7 suggest that the molybdenum-chlorine first bond dissociation enthalpy in $\text{Mo}(\text{Cp})_2\text{Cl}_2$ is substantially smaller than the

second, due to a large reorganization energy of $\text{Mo}(\text{Cp})_2\text{Cl}$ fragment (-65 kJ/mol).¹⁰⁵ In the case of the dimethyl and the dihydride complexes, these energies are smaller (-17 and -11 kJ/mol, respectively),¹⁰⁵ indicating that the first bond dissociation enthalpies will be closer to $\bar{D}(\text{Mo-R})$.

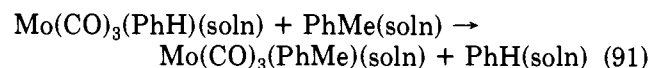
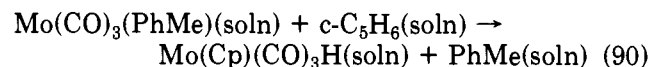
The trend observed for molybdenum-alkyl mean bond dissociation enthalpies in Table 4 could be anticipated; i.e., they nearly parallel $D(\text{alkyl-H})$. The larger uncertainty in the case of the butyl molecule is due to an estimated enthalpy of sublimation. It is also observed that $\bar{D}(\text{Mo-H}) - \bar{D}(\text{Mo-Me}) = 91$ kJ/mol is larger than $\bar{D}(\text{Zr-H}) - \bar{D}(\text{Zr-Me}) = 55$ kJ/mol (Table 3; see section V).

The values presented in Table 4 for the ethylene and phenylacetylene complexes reflect the cleavage of these ligands; i.e., they represent $\text{Mo-C}_2\text{H}_4$ and $\text{Mo-C}_2\text{Ph}_2$ bond dissociation enthalpies.¹⁹⁷ They were calculated through the method described above. $D(\text{Mo-C}_2\text{H}_4)$ and $D(\text{Mo-C}_2\text{Ph}_2)$ are both quite small, probably due to the large reorganization energies of ethylene and phenylacetylene (see discussion for late transition metals). The large uncertainties were caused by the assigned errors in the estimated enthalpies of sublimation of the complexes. The trend $D(\text{Mo-C}_2\text{H}_4) < D(\text{Mo-C}_2\text{Ph}_2)$ is, however, more reliable. The enthalpy of reaction 89,



calculated from the enthalpies of reaction of the complexes with iodine in toluene, is $\Delta H^\circ(89) = 56.6 \pm 2.5$ kJ/mol. If the sublimation plus the solution enthalpies cancel, which is not unlikely, then the above value will be a better “gas-phase” measure of the difference than the one drawn from Table 4.

Information on molybdenum-hydrogen and molybdenum-carbon bond enthalpies in the complexes $\text{Mo}(\text{Cp})(\text{CO})_3\text{R}$ is shown in Table 4. These data have been obtained by Hoff and co-workers from calorimetric enthalpies of reaction.^{198–202} A certain number of estimates concerning enthalpies of solution have occasionally been made by authors, but it is thought that those approximations have a small influence on the bond enthalpy values. An example is provided by $D(\text{M-H})$ in $\text{Mo}(\text{Cp})(\text{CO})_3\text{H}$, which can be derived from the measured enthalpies of reaction 90 in tetrahydro-



furan, $\Delta H^\circ(90) = -43.1 \pm 3.3$ kJ/mol,¹⁹⁹ and of reaction 91 in dichloromethane, $\Delta H^\circ(91) = -8.4 \pm 3.8$ kJ/mol.¹⁹⁸ In order to determine $\Delta H^\circ(91)$, some reasonable assumptions concerning cancellation of solution enthalpies were made. The combined enthalpies of reactions 90 and 91 lead to the bond enthalpy balance shown in eq 92, by neglecting the differences in solution en-

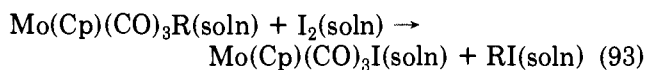
$$\Delta H^\circ(90) + \Delta H^\circ(91) = D(\text{Mo-PhH}) + D(\text{Cp-H}) - D(\text{Mo-Cp}) - D(\text{Mo-H}) \quad (92)$$

thalpies and also by considering that the solvation en-

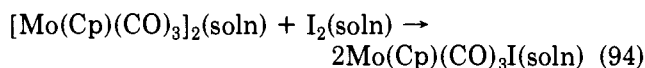
thalpies cancel. As stated above, the effect of this interminable series of assumptions on the final result (i.e., eq 92) must be small. The real problem is estimating the difference $D(\text{Mo-PhH}) - D(\text{Mo-Cp})$. Hoff has chosen the value 126 ± 21 kJ/mol by using reported data for $\text{Cr}(\text{Cp})_2$ and $\text{Cr}(\text{PhH})_2$. While the most recent surveys^{15,161} that include the enthalpies of formation of these two molecules yield a higher value, ca. 169 kJ/mol, it seems too speculative to transfer that *mean* bond dissociation enthalpy difference to $D(\text{Mo-Cp}) - D(\text{Mo-PhH})$ in eq 92. Thus, the lower value was postulated, yielding $D(\text{Mo-H}) = 273 \pm 24$ kJ/mol.

The enthalpy of reaction 87 for the analogous molybdenum complexes was obtained by Landrum and Hoff¹⁹⁰ and enabled them to derive $D(\text{Mo-H})$ by using the method described for the chromium compounds (eq 88). The value obtained, 273 ± 9 kJ/mol, matches the one above! It relies on the activation enthalpy for Mo-Mo cleavage in the dimer, 136 ± 2 kJ/mol,^{203,204} which is identified with $D(\text{Mo-Mo})$. As in the case of the chromium complexes, it can be expected that $\Delta H^\circ_s[\text{Mo}(\text{Cp})(\text{CO})_3]_2 \approx 2\Delta H^\circ_s[\text{Mo}(\text{Cp})(\text{CO})_3\text{H}]$ (see also discussion below).

The enthalpy of reaction 93 in tetrahydrofuran was determined by Hoff and co-workers²⁰⁰ for $\text{R} = \text{H}$ and Me and enabled them to derive $D(\text{Mo-H}) - D(\text{Mo-I}) = 63 \pm 3$ kJ/mol and $D(\text{Mo-Me}) - D(\text{Mo-I}) = -16 \pm$



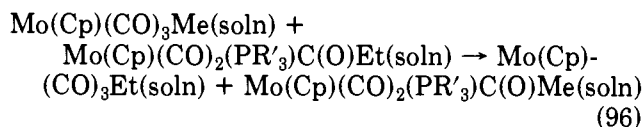
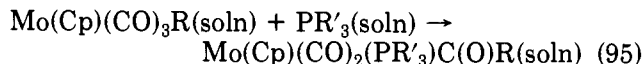
6 kJ/mol by assuming that the solvation enthalpies cancel. A value for molybdenum-iodine bond dissociation enthalpy, $D(\text{Mo-I}) = 219 \pm 5$ kJ/mol, was then calculated from the enthalpy of reaction 94,²⁰⁰ also by



assuming the cancellation of solvation terms and taking the above kinetic result for $D(\text{Mo-Mo})$, 136 ± 2 kJ/mol. This led to the results in Table 4 for $\text{Mo}(\text{Cp})(\text{CO})_3\text{R}$. The value for $\text{R} = \text{H}$ is in good agreement with the ones derived above, indicating that the assumption related to the sublimation enthalpies, $\Delta H^\circ_s[\text{Mo}(\text{Cp})(\text{CO})_3]_2 \approx 2\Delta H^\circ_s[\text{Mo}(\text{Cp})(\text{CO})_3\text{H}]$, must hold. In any case, the trend $D(\text{Mo-H}) - D(\text{Mo-Me}) = 79 \pm 10$ kJ/mol is independent of those assumptions. Note also that the difference is in the range of the one observed for the dicyclopentadienyl complexes. In this regard, it is of interest to add that the enthalpies of reactions of $\text{Mo}(\text{Cp})(\text{CO})_3\text{H}$ with CCl_4 and CBr_4 (yielding the chloride and the bromide complexes, respectively) were also determined by authors,²⁰⁰ affording $D(\text{Mo-Cl}) - D(\text{Mo-H}) = 27 \pm 4$ kJ/mol and $D(\text{Mo-Br}) - D(\text{Mo-H}) = -22 \pm 9$ kJ/mol.²⁰⁵ The corresponding differences in the case of dicyclopentadienyl complexes are $D(\text{Mo-Cl}) - D(\text{Mo-H}) = 47 \pm 11$ kJ/mol and $D(\text{Mo-Br}) - D(\text{Mo-H}) = -15 \pm 13$ kJ/mol.¹⁷⁴

The enthalpies of iodination reaction 93 were also measured by Hoff and co-workers for $\text{R} = \text{C}_3\text{H}_5$ and Bz ,²⁰¹ leading to the values presented in Table 4, by using $D(\text{Mo-I}) = 219 \pm 5$ kJ/mol.

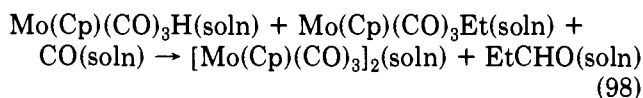
The enthalpies of reaction 95 for $\text{R} = \text{Me}$, Et , and several phosphine or phosphites yielded an average value for reaction 96 and the difference $D(\text{Mo-Me}) - D(\text{Mo-Et}) = 18 \pm 7$ kJ/mol²⁰² (eq 97), on the basis of



$$\Delta H^\circ(96) = D(\text{Mo-Me}) - D(\text{Mo-Et}) + D[\text{Mo-C}(\text{O})\text{Et}] - D[\text{Mo-C}(\text{O})\text{Me}] + D(\text{OC-Et}) - D(\text{OC-Me}) \quad (97)$$

canceling solvation enthalpies, $D[\text{Mo-C}(\text{O})\text{Et}] - D[\text{Mo-C}(\text{O})\text{Me}] \approx D[\text{EtC}(\text{O})-\text{H}] - D[\text{MeC}(\text{O})-\text{H}] = 7 \pm 4$ kJ/mol, and by taking $D(\text{OC-Me}) - D(\text{OC-Et}) = 12 \pm 6$ kJ/mol. The value of $D(\text{Mo-Et})$ shown in Table 4 is in the expected range.

Hoff and co-workers have also derived the enthalpy of reaction 98,²⁰¹ from which the sum $D(\text{Mo-H}) + D(\text{Mo-Et}) = 431 \pm 8$ kJ/mol is calculated, by using $D(\text{Mo-Mo})$ given above and $D(\text{OC-Et}) = 49 \pm 6$ kJ/mol



(Appendix). Taking $D(\text{Mo-H})$ from Table 4, one obtains $D(\text{Mo-Et}) = 149 \pm 10$ kJ/mol, a value that seems too low when compared to $D(\text{Mo-Me})$.

The enthalpy of reaction 95 was also measured for $\text{R} = \text{Bz}$ and a number of phosphines or phosphites (in acetonitrile)²⁰¹ and, together with the reaction data for $\text{R} = \text{Me}$ and an equation similar to eq 97 (Et replaced by Bz), gives an average $D(\text{Mo-Me}) - D(\text{Mo-Bz}) = 6 \pm 4$ kJ/mol. This value must be, however, a very low limit (compare with the difference in Table 4), since the $\text{Mo-C}(\text{O})\text{R}$ and OC-R terms in eq 97 have been neglected (the enthalpy of formation of BzCO radical is not available).

c. Tungsten. The tungsten-methyl bond enthalpies in the homoleptic compound WMe_6 , calculated from its enthalpy of formation in the gas phase,^{15,189} led to the values shown in Table 4. Note that $E(\text{W-Me})$ is quite low as compared to $E(\text{W-Me})$ in the dicyclopentadienyl complex, presented in the same table, but the difference is likely to be due, at least in part, to steric effects in WMe_6 .¹⁸⁹

The bond data for the $\text{W}(\text{Cp})_2\text{R}_2$ complexes rely on their enthalpies of formation¹⁷⁴ and on the calculation method described earlier. $E(\text{W-Cl})$ was taken as 347.3 ± 0.8 kJ/mol.¹⁷³ As before, reorganization energies ER_1 and ER_3 were not included in the calculations, although, as in the case of the molybdenum complexes, the extended Hückel approach suggests that they are not negligible (e.g., ER_3 has been estimated as -103 kJ/mol).^{174,178} The trend $D(\text{W-H}) - D(\text{W-Me}) = 90$ kJ/mol is similar to the one found for the analogous molybdenum compounds.

Some comments about the W-H bond enthalpy term in $\text{W}(\text{Cp})_2(\text{I})\text{H}$ are necessary. Its calculation was made by using an equation similar to eq 64 (with $\text{ER}'_{13} = \text{ER}'_3$), but where the "reference" molecule was replaced by $\text{W}(\text{Cp})_2\text{I}_2$ and $E(\text{W-I})$ was taken as 268 kJ/mol (note that this number itself relies on $E(\text{W-Cl}) = 347.3$ kJ/mol). The fact that $E(\text{W-H})$ in $\text{W}(\text{Cp})_2(\text{I})\text{H}$ is about 38 kJ/mol lower than $E(\text{W-H})$ in $\text{W}(\text{Cp})_2\text{H}_2$ may be caused by the fact that this last bond term has not been corrected with the difference $(\text{ER}_3 - \text{ER}_1)/2$ (eq 5),

TABLE 5. Group 7 M-H and M-C Bond Enthalpies

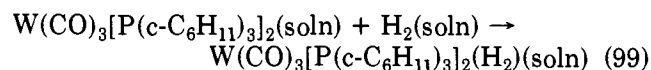
molecule	method/ ref ^a	D^b , kJ/mol	E , kJ/mol
Mn(CO) ₅ H	CMC/212	245 ± 10	245
Mn(CO) ₅ Me	CMC/212	187 ± 4	163
	PIMS/137	192 ± 11	168
Mn(CO) ₅ Ph	CMC/212	207 ± 11	163
Mn(CO) ₅ Bz	CMC/212	129 ± 10	172
Mn(CO) ₅ CH ₂ F	PIMS/137	139 ± 11	(130) ^c
Mn(CO) ₅ CHF ₂	PIMS/137	144 ± 11	(141) ^c
Mn(CO) ₅ CF ₃	PIMS/137	182 ± 11	(156) ^c
	CMC/212	203 ± 6	(177) ^c
Mn(CO) ₅ C(O)Me	CMC/212	160 ± 10	228
Mn(CO) ₅ C(O)Ph	CMC/212	127 ± 12	193
Mn(CO) ₅ C(O)CF ₃	CMC/212	176 ± 14	222
Mn(CO) ₅ C(O)R	ES/230		
R = Me		182	250
R = Et		181	242
R = Pr		175	236
R = Ph		131	197
Mn(CO) ₅ C(O)Me	RSC/231	185 ± 8	253
Mn(CO) ₄ (L)(CH ₂ C ₆ H ₄ OMe- <i>p</i>) ^d	KS/232	105	
Re(CO) ₅ Me	CMC/4, 15	220 ± 11	196

^aKey: CMC = Calvet microcalorimetry; ES = equilibrium studies in solution; KS = kinetic studies in solution; PIMS = photoionization mass spectrometry; RSC = reaction solution calorimetry. ^bValues for Mn complexes rely on $D(\text{Mn-Mn}) = 159 \pm 21$ kJ/mol and for Re complexes on $D(\text{Re-Re}) = 187 \pm 15$ kJ/mol. The uncertainty intervals in table do not include errors in $D(\text{M-M})$. ^cEstimated value. ^dL = P(C₆H₄OMe-*p*)₃.

which is estimated to be -37 kJ/mol.¹⁷⁸ As stated elsewhere,¹⁷⁴ the agreement may be fortuitous, but it illustrates the importance of reorganization energies when transferring bond enthalpy terms.

The tungsten-hydrogen bond dissociation enthalpy in $\text{W}(\text{Cp})(\text{CO})_3\text{H}$ in Table 4 was derived from the enthalpy of a reaction¹⁹⁰ similar to eq 87 and relies on $D(\text{W-W}) = 234 \pm 4$ kJ/mol, obtained by equilibrium studies in the gas phase²⁰⁶ (see eq 88). As before, it can be expected that $\Delta H^\circ_{\text{f}}[\text{W}(\text{Cp})(\text{CO})_3]_2 \approx 2\Delta H^\circ_{\text{f}}[\text{W}(\text{Cp})(\text{CO})_3\text{H}]$.

An average value of the enthalpy of reaction 99 in toluene and tetrahydrofuran, -40 ± 2 kJ/mol, was determined from several calorimetric experiments.²⁰⁷



$-\Delta H^\circ(99)$ measures the tungsten-(η^2)dihydrogen bond dissociation enthalpy, by assuming that the solvation enthalpies cancel. As remarked by Hoff and co-workers,²⁰⁷ $D(\text{W-H}_2)$ contains the reorganization of the fragments, in particular the formation of an *agostic*²⁰⁸ bond between the tungsten atom and a cyclohexyl moiety. This agostic interaction was estimated as ca. 42 kJ/mol, by using the photoacoustic value for $D(\text{Cr-heptane})$ (see above), implying that $E(\text{W-H}_2)$ is at least 82 kJ/mol. The small value for $D(\text{W-H}_2)$ explains the reversibility of hydrogen addition²⁰⁹ to the complex $\text{W}(\text{CO})_3[\text{P}(\text{c-C}_6\text{H}_{11})_3]_2$: the ΔS term is estimated as -146 ± 42 J/(mol K), leading to $\Delta G \approx 4$ kJ/mol.²⁰⁷

The last value in Table 4 refers to tungsten-carbene bond dissociation enthalpy in the complex $\text{W}(\text{CO})_5[\text{C}(\text{OMe})\text{Ph}]$, and it was calculated from its enthalpy of formation in the gas phase,²¹⁰ together with $\Delta H^\circ_{\text{f}}[\text{C}(\text{OMe})\text{Ph}, \text{g}] = 320 \pm 5$ kJ/mol (Appendix) and $\Delta H^\circ_{\text{f}}[\text{W}(\text{CO})_5, \text{g}] = -581 \pm 13$ kJ/mol, this obtained by using $D_1(\text{W-CO})$ in $\text{W}(\text{CO})_6$ (Table 1) and $\Delta H^\circ_{\text{f}}[\text{Cr}(\text{CO})_6, \text{g}]$.^{15,161}

A final mention is made to recent time-resolved infrared spectroscopy studies on the equilibrium between

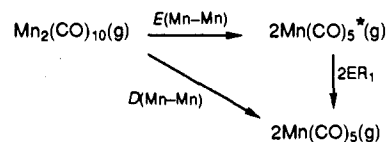
$\text{W}(\text{CO})_5$ and ethane, leading to $D[\text{W}(\text{CO})_5\text{-ethane}] = 41 \pm 13$ kJ/mol.²¹¹ This value is very close to $D(\text{Cr-heptane})$ mentioned above.

5. Group 7

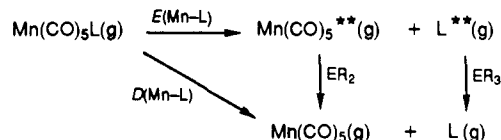
a. Manganese. The first 10 $\text{Mn}(\text{CO})_5\text{L}$ complexes presented in Table 5 were studied by two different methods: iodination, bromination or simple thermal decomposition reactions in a Calvet microcalorimeter,²¹² and photoionization mass spectrometry.¹³⁷ These studies overlap in three compounds, with L = H, Me, and CF₃.

The bond dissociation enthalpies and the bond enthalpy terms, which refer to the calorimetric studies, were derived by using Schemes 9 and 10 and eqs 100 and 101, where the asterisks have the usual meaning; i.e., they indicate nonreorganized species.

SCHEME 9



SCHEME 10



$$D(\text{Mn-L}) = \frac{1}{2}D(\text{Mn-Mn}) + \frac{1}{2}\Delta H^\circ_{\text{f}}[\text{Mn}_2(\text{CO})_{10}, \text{g}] + \Delta H^\circ_{\text{f}}[\text{L}, \text{g}] - \Delta H^\circ_{\text{f}}[\text{Mn}(\text{CO})_5\text{L}, \text{g}] \quad (100)$$

$$E(\text{Mn-L}) = D(\text{Mn-L}) - \text{ER}_2 - \text{ER}_3 \quad (101)$$

Both $D(\text{Mn-L})$ and $E(\text{Mn-L})$ rely on the value of $D(\text{Mn-Mn})$, which itself depends upon the enthalpy of formation of pentacarbonylmanganese radical. On the other hand, "correct" values for $E(\text{Mn-L})$ can be obtained only if ER_2 and ER_3 are known.

ER_3 values were derived by the usual method, i.e., by assuming identical structures for L in LH and $\text{Mn}(\text{CO})_5\text{L}$ and by using L-H Laidler terms (Appendix) or bond enthalpy/bond length correlations. Although, as referred in section III.A, this assumption can be dangerous in certain cases, it is probably the best approach when the molecular structures or supporting theoretical calculations are not available. In the case of L = CF₃, the structures of $\text{Mn}(\text{CO})_5\text{CF}_3$ and CHF₃ are available,^{213,214} showing that C-F bond length is about 4 pm longer in the complex (137.0 ± 0.3 pm) than in the organic molecule (133.2 ± 0.8 pm) and suggesting that $E(\text{Mn-CF}_3)$ presented in Table 5 is a lower limit.

There are no theoretical calculations for ER_2 . Therefore, all the $E(\text{Mn-L})$ values are affected by an error which, however, may be considered constant if the structures of fragments $\text{Mn}(\text{CO})_5^{**}$ are identical for different L. This can be assessed from Table 6, where available structural data for $\text{Mn}(\text{CO})_5\text{L}$ complexes are summarized. All the relevant parameters (i.e., Mn-CO_{eq}, Mn-CO_{ax}, and C-O bond lengths and the angle C_{ax}-Mn-C_{eq}) are similar in the three complexes where L = H, Me, and CF₃, particularly when the more recent electron diffraction data for $\text{Mn}(\text{CO})_5\text{H}$ ²¹⁵ are considered. The only exception is Mn-CO_{ax} in the case of L = Me, but this is an assumed value.

TABLE 6. Structural Data of Some $\text{Mn}(\text{CO})_5\text{L}$ Complexes^a

	L			
	$\text{Mn}(\text{CO})_5$	H^b	Me^c	CF_3^d
Mn-L	$292.3 \pm 0.3 \text{ X}^e$	$160.1 \pm 1.6 \text{ N}^f$	$218.5 \pm 1.1 \text{ E}$	$205.6 \pm 0.5 \text{ E}$
	$291 \pm 2 \text{ E}^g$	$(150 \pm 2) \text{ E}^h$		
	$297.7 \pm 1.1 \text{ E}^i$	$157.6 \pm 1.8 \text{ E}^j$		
Mn- CO_{eq}	$183.1 \pm 0.9 \text{ X}^e$	$185.3 \pm 0.7 \text{ X}^f$	$186.0 \pm 0.4 \text{ E}$	$186.4 \pm 0.3 \text{ E}$
	$186 \pm 1 \text{ E}^g$	$185.3 \pm 1.2 \text{ N}^f$		
	$187.3 \pm 0.5 \text{ E}^i$	$186.5 \pm 0.2 \text{ E}^h$		
		$185.6 \pm 0.6 \text{ E}^j$		
Mn- CO_{ax}	$179.2 \pm 1.4 \text{ X}^e$	$182.4 \pm 1.7 \text{ X}^f$	(182.0)	$187.4 \pm 0.7 \text{ E}$
	$182 \pm 2 \text{ E}^g$	$182.2 \pm 1.2 \text{ N}^f$		
	$180.3 \pm 1.6 \text{ E}^i$	$184.0 \pm 0.2 \text{ E}^h$		
		$185.4 \pm 3.0 \text{ E}^j$		
C-O	$115.6 \pm 0.7 \text{ X}^e$	$112.3 \pm 1.3 \text{ X}^f$	$114.1 \pm 0.2 \text{ E}$	$114.3 \pm 0.2 \text{ E}$
	$112 \pm 1 \text{ E}^g$	$113.4 \pm 0.4 \text{ N}^f$		
	$114.7 \pm 0.2 \text{ E}^i$	$113.9 \pm 0.2 \text{ E}^h$		
		$114.02 \pm 0.3 \text{ E}^j$		
$\text{C}_{\text{ax}}\text{-Mn-}\text{C}_{\text{eq}}$	93.8 X^e	96.7 X^f	$94.7 \pm 1.0 \text{ E}$	$92.1 \pm 0.2 \text{ E}$
	$93.4 \pm 0.5 \text{ E}^i$	97.2 N^f		
		$96.4 \pm 0.5 \text{ E}^h$		
		$94.5 \pm 0.8 \text{ E}^j$		

^a Bond lengths are in picometers and angles in degrees. CO_{eq} and CO_{ax} mean equatorial and axial carbonyl groups, respectively. X, N, and E indicate that data were obtained by X-ray, neutron, or electron diffraction, respectively. ^b Neutron and X-ray diffraction data refer to $\beta\text{-Mn}(\text{CO})_5\text{H}$. Available values for $\alpha\text{-Mn}(\text{CO})_5\text{H}$ (La Placa, S. J.; Hamilton, W. C.; Ibers, J. A. *Inorg. Chem.* 1964, 3, 1491) are similar to those obtained by X-ray diffraction given in the table. The value in parentheses is not considered to be reliable (see note h). ^c Seip, H. M.; Seip, R. *Acta Chem. Scand.* 1970, 24, 3431. The value in parentheses was assumed by the authors. ^d Reference 213. ^e Dahl, L. F.; Rundle, R. E. *Acta Crystallogr.* 1963, 16, 419. ^f La Placa, S. J.; Hamilton, W. C.; Ibers, J. A.; Davidson, A. *Inorg. Chem.* 1969, 8, 1928. ^g Gapotchenko, N. I.; Alekseev, N. V.; Anisimov, K. N.; Kolobova, N. E.; Ronova, I. A. *Zh. Strukt. Khim.* 1968, 9, 892. ^h Robiette, A. G.; Sheldrick, G. M.; Simpson, R. N. F. *J. Mol. Struct.* 1969, 4, 221. ⁱ Almendinger, A.; Jacobsen, G. G.; Seip, H. M. *Acta Chem. Scand.* 1969, 23, 685. ^j Reference 215.

The third term needed to obtain $E(\text{Mn-L})$ is $D(\text{Mn-L})$, calculated through eq 100. Unfortunately, it is not simple to decide what value should be used for $D(\text{Mn-Mn})$, as evidenced by Table 7. It has been argued that since the rate recombination of the $\text{Mn}(\text{CO})_5$ radicals is diffusion-controlled and is independent of the non-polar solvent used, it is unlikely that there is any contribution to the activation enthalpy from solvation or from the geometric rearrangement of the $\text{Mn}(\text{CO})_5$ radical.^{216,217} The low mass spectrometry value for $D(\text{Mn-Mn})$ would imply a "totally unreasonable" low value of the entropy of activation for the homolytic fission process.²¹⁸ It is not clear whether or not this should be accepted, with the implication of a "high value" for $D(\text{Mn-Mn})$ in the gas phase. As pointed out by Connor et al.,²¹² a value obtained by equilibrium studies, 96 kJ/mol,²¹⁹ compares with independent electron impact measurements, such as the one by Junk and Svec,²²⁰ 104 kJ/mol. It is noted, however, that the ionization and appearance energies of $\text{Mn}(\text{CO})_5$ quoted in Table 7 are probably too high, as indicated by comparison between the value for the adiabatic ionization energy of $\text{Mn}_2(\text{CO})_{10}$ ²¹² and those derived from earlier studies. On the other hand, experiments on the mechanism of ligand substitution in $\text{Mn}_2(\text{CO})_{10}$ also suggest that $D(\text{Mn-Mn})$ is probably greater than the early mass spectrometric values.²²¹ Further kinetic studies by Marcomini and Poë led to the conclusion that the early kinetic value in solution (154 kJ/mol) is even a lower limit for $D(\text{Mn-Mn})$.^{222,223} Although the mechanism suggested by these authors for the Mn-Mn fission has been challenged,²²⁴ the "high" value seems to be confirmed by an electron impact and a photoelectron study of the complex $\text{Mn}(\text{CO})_5\text{Bz}$, from which $\Delta H^\circ_f[\text{Mn}(\text{CO})_5\text{g}]$ could be derived, yielding $D(\text{Mn-Mn}) \approx 171$ kJ/mol,²²⁵ and by a photoacoustic calorimetry study of $\text{Mn}_2(\text{CO})_{10}$ that led to $D(\text{Mn-Mn}) = 159 \pm 21$

TABLE 7. Literature Values for $D(\text{Mn-Mn})$ in $\text{Mn}_2(\text{CO})_{10}$ ^a

year	method ^b	IE[$\text{Mn}_2(\text{CO})_{10}$]	$\text{Mn}(\text{CO})_5$		$D(\text{Mn-Mn})$
			AE	IE	
1960	TE ^c				142 ± 54
1966	EI ^d		9.26 ± 0.03	8.44 ± 0.03	79 ± 4
1966	KS ^e				154
1967	EI ^f	8.58	9.40	8.44 ^g	93
1968	EI ^h		9.4	8.2	116
1970	EI ⁱ	8.46 ± 0.03	9.40 ^j	8.32 ^k	104 ± 3
1970	EI ^l	8.42 ± 0.1	9.26 ± 0.1	8.44 ± 0.10	79 ± 14
1970	E/EI ^m				96 ± 13^a
1982	TE ⁿ	7.69 ± 0.01^p			94
1982	PIMS ^q		10.3 ± 0.1^r	7.8 ± 0.2	(159 ± 21)
1984	KS ^s				≥ 154
1985	EI/PES ^t				171
1986	PAC ^u				159 ± 21
1988	LP ^v				≥ 176

^a Ionization and appearance energies are in electronvolts and $D(\text{Mn-Mn})$ in kilojoules per mole. ^b Key: E/EI = equilibrium studies using electron impact mass spectrometry; EI = electron impact mass spectrometry; KS = kinetic studies in solution; LP = laser pyrolysis; PAC = photoacoustic calorimetry; PES = photoelectron spectroscopy; PIMS = photoionization mass spectrometry; TE = thermochemical estimate. ^c Cotton, F. A.; Monchamp, R. R. *J. Chem. Soc.* 1960, 533. ^d Pyrolysis of $\text{Mn}_2(\text{CO})_{10}$; Bidinosti, D. R.; McIntyre, N. S. *J. Chem. Soc., Chem. Commun.* 1966, 555. ^e Reference 216. ^f Svec, H. J.; Junk, G. A. *J. Am. Chem. Soc.* 1967, 89, 2836. ^g Value quoted from the reference given in note d. ^h Pyrolysis of $\text{Mn}(\text{CO})_5\text{Cl}$; Svec, H. J.; Junk, G. A. *Inorg. Chem.* 1968, 7, 1688. ⁱ Reference 220. ^j Value quoted from the reference given in note f. ^k Average value from the references given in notes d and h. ^l Pyrolysis of $\text{Mn}_2(\text{CO})_{10}$; Reference 219. ^m Reference 219. ⁿ Value corrected to 298 K. Authors give $D(\text{Mn-Mn}) = 88 \pm 13$ kJ/mol at 0 K. ^o Reference 212. ^p Adiabatic IE from the photoelectron spectrum of $\text{Mn}_2(\text{CO})_{10}$. ^q Reference 137. ^r AE from $\text{Mn}(\text{CO})_5\text{H}$. This value, taken with the assumed $D(\text{Mn-Mn}) \approx 159 \pm 21$ kJ/mol, leads to $\text{IE}[\text{Mn}(\text{CO})_5] \approx 7.8 \pm 0.2$ eV. ^s References 222 and 223. ^t Reference 225. ^u Reference 226. ^v Reference 229.

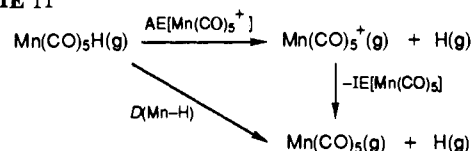
kJ/mol.²²⁶ These results are supported by photolysis experiments involving $\text{Mn}_2(\text{CO})_{10}$, consistent with a value in the range 134–171 kJ/mol,²²⁷ and also by recent electrochemical measurements in solution.²²⁸ Finally, laser pyrolysis studies of $\text{Mn}_2(\text{CO})_{10}$ enabled estimation

of a lower limit for $D(\text{Mn-Mn})$, 176 kJ/mol.²²⁹

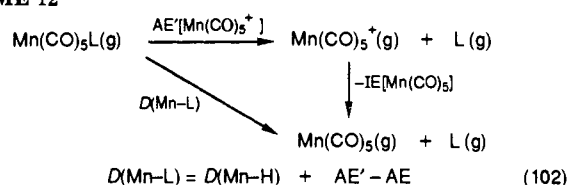
In the present review the photoacoustic value of $D(\text{Mn-Mn}) = 159 \pm 21$ kJ/mol was chosen, leading to $\Delta H^\circ_f[\text{Mn}(\text{CO})_5\text{g}] = -713 \pm 11$ kJ/mol.

The bond dissociation enthalpy data from Table 5 obtained by photoionization mass spectrometry were evaluated¹³⁷ by using Schemes 11 and 12 or eq 102.

SCHEME 11



SCHEME 12



Each $D(\text{Mn-L})$ value is directly given by the difference between the appearance energies of pentacarbonylmanganese ion from $\text{Mn}(\text{CO})_5\text{H}$ and from $\text{Mn}(\text{CO})_5\text{L}$ (see Table 20), plus a constant, $D(\text{Mn-H}) = 245 \pm 10$ kJ/mol (Table 5). Therefore, the PIMS data rely also on the same chosen value for $D(\text{Mn-Mn})$.

$E(\text{Mn-CH}_n\text{F}_m)$ ($n + m = 3$) values were determined by assuming identical structures of CH_nF_m in the organometallic complex and in $\text{CH}_{n+1}\text{F}_m$ and by using $\text{CH}_n\text{F}_m\text{-H}$ bond enthalpy terms derived from a curve $E(\text{C-H})/r(\text{C-H})$,⁹³ since there are no Laidler parameters for these cases.

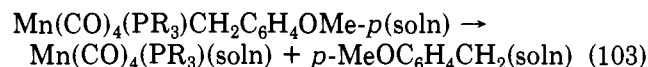
The general trend for $D(\text{Mn-L})$ in Table 5 is as expected, and the calorimetric values are in fair agreement with the photoionization data. An exception is, perhaps, the fact that $D(\text{Mn-CF}_3) \approx D(\text{Mn-Me})$ or $E(\text{Mn-CF}_3) < E(\text{Mn-Me})$. The manganese-carbon bond length is about 13 pm shorter in the CF_3 complex than in the Me complex (Table 6), suggesting $E(\text{Mn-CF}_3) > E(\text{Mn-Me})$. The calorimetric value is in better agreement with this prediction, although the observed difference seems smaller than might be expected for the 13-pm difference in bond lengths. A previously recommended value for $\Delta H^\circ_f[\text{Mn}(\text{CO})_5\text{Me,g}]$, -730 ± 9 kJ/mol,^{4,212} gives $D(\text{Mn-Me}) = 164$ kJ/mol. However, the new value for the enthalpy of formation of the complex was preferred by Connor et al.,²¹² and indeed it does yield bond enthalpy data close to the values obtained by PIMS.

Another interesting feature of the data in Table 5 results from the large negative reorganization enthalpies of the acetyl, benzoyl, and trifluoroacetyl radicals (Appendix). The manganese-carbon bond dissociation enthalpies in those three complexes are smaller than some values in the table such as $D(\text{Mn-Me})$ and $D(\text{Mn-Ph})$, but their bond enthalpy terms are larger. This suggests that Mn-C(O)R bond lengths are shorter than Mn-Me , Mn-Ph , or $\text{Mn-CH}_n\text{F}_m$. An opposite conclusion would be drawn if the bond dissociation enthalpies were identified with "bond strengths".

Mn-C(O)R bond data for $\text{R} = \text{Me}$, Et , Pr , and Ph can also be derived from the reported enthalpies of carbonyl insertion in the complexes $\text{Mn}(\text{CO})_5\text{R}$ (see reaction 85 and eq 86), which were obtained from van't Hoff plots in 2,2'-diethoxydiethyl ether.²³⁰ $D(\text{Mn-Me}) - D[\text{Mn-}$

$\text{C(O)R}] = 8, 9, 15,$ and 59 kJ/mol for R in the above order. These values, together with $D(\text{Mn-Me}) = 190 \pm 6$ kJ/mol (average between the calorimetric and PIMS results) led to the bond enthalpy data in Table 5. Shown in the table is another value for $D[\text{Mn-C(O)Me}]$, also obtained from the enthalpy of carbonyl insertion in $\text{Mn}(\text{CO})_5\text{Me}$, measured by reaction solution calorimetry (using a high-pressure cell), in tetrahydrofuran.²³¹ It is noted that the "solution" results are in excellent agreement with, but are about 25 kJ/mol higher than, the calorimetric gas-phase result. However, if the enthalpy of carbonyl insertion in solution (under the assumption that the solution enthalpies cancel) is calculated from the enthalpies of formation of the crystalline complexes, and this value is used to derive $D[\text{Mn-C(O)Me}]$, one obtains 183 ± 10 kJ/mol, also in agreement with the above results. This example emphasizes the precautions that should be taken when solution- and gas-phase bond enthalpies are compared, even when "reasonable" assumptions concerning solvation enthalpies are claimed.

The last manganese-carbon bond dissociation enthalpy listed in Table 5 was derived from kinetic studies of reaction 103 in benzene²³² (R stands for $p\text{-MeOC}_6\text{H}_4$).



The value obtained for the activation enthalpy of this reaction, 115 ± 2 kJ/mol, was considered an upper limit to $D(\text{Mn-C})$. By assuming that the radical recombination is diffusion-controlled, implying a small activation enthalpy for this recombination reaction (8–10 kJ/mol),²³³ Halpern and co-workers recommended the result presented in Table 5, 105 kJ/mol. This value cannot easily be compared with the other manganese-carbon data since it may be affected by unknown solvation enthalpies.

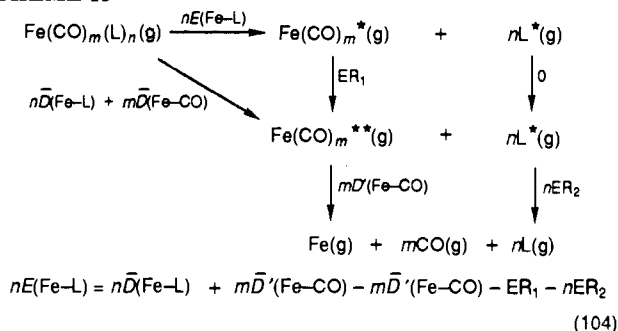
b. Rhenium. The only available rhenium-carbon bond dissociation enthalpy is also presented in Table 5. $D(\text{Re-Me})$ and $E(\text{Re-Me})$ rely on the enthalpy of formation of the complex in the gas phase²³⁴ and were calculated by using the method described for the manganese analogues. In this case the kinetic value for $D(\text{Re-Re})$ in $\text{Re}_2(\text{CO})_{10}$, 166 kJ/mol,^{203,223} is lower than the mass spectrometry result, 187 ± 5 kJ/mol.²²⁰ The option was to use the higher value (with an error bar of 15 kJ/mol). This, together with the enthalpy of formation of $\text{Re}_2(\text{CO})_{10}$,²³⁴ led to $\Delta H^\circ_f[\text{Re}(\text{CO})_5\text{g}] = -686 \pm 9$ kJ/mol. The value in Table 5 is only about 30 kJ/mol higher than $D(\text{Mn-Me})$, which suggests that the number quoted for $D(\text{Re-Re})$ may be too low.

6. Group 8

a. Iron. To calculate the iron-olefin bond enthalpy terms presented in Table 8, it was necessary to transfer $E(\text{Fe-CO})$ from $\text{Fe}(\text{CO})_5$ to each one of the listed complexes.^{235,236} This method is described by Scheme 13 or by eq 104.

One and two asterisks mean that the fragment has the same structure it had in $\text{Fe}(\text{CO})_m(\text{L})_n$ and in $\text{Fe}(\text{CO})_5$, respectively. $\bar{D}(\text{Fe-CO})$ is the mean bond dissociation enthalpy in pentacarbonyliron, 117.7 ± 1.6 kJ/mol, obtained from the enthalpy of formation of gaseous $\text{Fe}(\text{CO})_5$.¹⁵ On the other hand, the sum $n\bar{D}(\text{Fe-L}) + m\bar{D}(\text{Fe-CO})$ can be evaluated from ΔH°_f

SCHEME 13

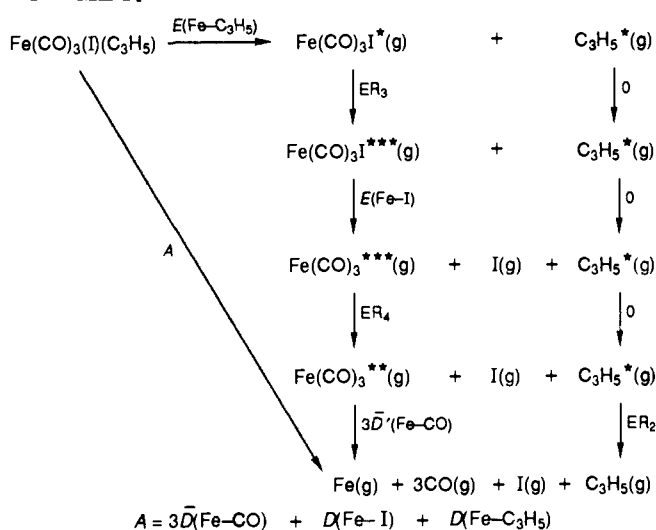


$[\text{Fe(CO)}_m(\text{L})_n, \text{g}]$.¹⁵ When these bond dissociation enthalpies are written in terms of enthalpies of formation of the complexes and the result introduced in eq 104, one obtains eq 105, from which $E(\text{Fe-L})$ can be estimated.

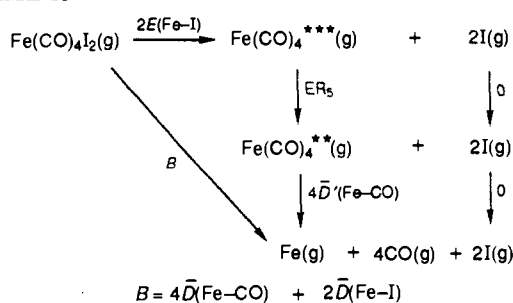
$$\begin{aligned}
 E(\text{Fe-L}) = & \Delta H_f^\circ(\text{L}, \text{g}) + [(5-m)/5n]\Delta H_f^\circ(\text{Fe}, \text{g}) - \\
 & (1/n)\Delta H_f^\circ[\text{Fe(CO)}_m(\text{L})_n, \text{g}] + \\
 & (m/5n)\Delta H_f^\circ[\text{Fe(CO)}_5, \text{g}] - \text{ER}_1/n - \text{ER}_2 \quad (105)
 \end{aligned}$$

In the case of $\text{Fe(CO)}_3(\text{I})(\text{C}_3\text{H}_5)$, the method is more complicated because it is also necessary to transfer $E(\text{Fe-I})$ from $\text{Fe(CO)}_4\text{I}_2$. Equation 106 was obtained from Schemes 14 and 15, where three asterisks indicate the structure of $\text{Fe(CO)}_4\text{I}_2$.

SCHEME 14



SCHEME 15



$$\begin{aligned}
 E(\text{Fe-C}_3\text{H}_5) = & 0.3\Delta H_f^\circ(\text{Fe}, \text{g}) + \Delta H_f^\circ(\text{C}_3\text{H}_5, \text{g}) + \\
 & 0.2\Delta H_f^\circ[\text{Fe(CO)}_5, \text{g}] - \Delta H_f^\circ[\text{Fe(CO)}_3(\text{I})(\text{C}_3\text{H}_5), \text{g}] + \\
 & 0.5\Delta H_f^\circ[\text{Fe(CO)}_4\text{I}_2, \text{g}] - \text{ER}_2 - \text{ER}_3 - \text{ER}_4 + \text{ER}_5/2 \quad (106)
 \end{aligned}$$

When A and B are expressed in terms of the enthalpies of formation of the complexes, eq 106 is derived

TABLE 8. Group 8 M-H and M-C Bond Enthalpies

molecule ^a	method/ref ^b	D , kJ/mol	E , kJ/mol
$\text{Fe(CO)}_4\text{H}_2$	137	272 ^c	244
$\text{Fe(CO)}_4(\text{C}_2\text{H}_4)$	CMC/235	152 ± 18	96 ± 12
$\text{Fe(CO)}_3(1,3\text{-C}_4\text{H}_6)_2$	CMC/235		178 ± 5
$\text{Fe(CO)}_3(1,3\text{-C}_4\text{H}_6)$	CMC/235		200 ± 10
$\text{Fe(CO)}_3(1,3\text{-c-C}_6\text{H}_8)_2$	CMC/235		194 ± 5
$\text{Fe(CO)}_3(\text{I})(\text{C}_3\text{H}_5)$	CMC/236		170 ± 13
$\text{Fe(CO)}_3(\text{cot})$	CMC/236		179 ± 13
$\text{Fe(CO)}_3(\text{C}_2\text{H}_4)_2$	KG/239	$\geq 113 \pm 25$	
$\text{Ru(Cp}^*)(\text{PMe}_3)_2\text{L}$	ES/241		
L = OH		$D4^d$	
L = H		$D4 - 38$	
L = CPh		$D4 + 59$	
L = CH_2COMe		$D4 - 86$	
Ru(oepp)Et_2	KS/242	91 ± 6	
$\text{Os}_3(\text{CO})_{11}(\text{C}_2\text{Ph}_2)$	KS/244	$D5 - 39^e$	

^a Key: cot = 1,3,5,7-cyclooctatetraene; oep = 2,3,7,8,12,13,17,18-octaethylporphyrinato anion. ^b Key: CMC = Calvet microcalorimetry; ES = equilibrium studies in solution; KG = kinetic studies in the gas phase; KS = kinetic studies in solution. ^c Mean bond dissociation enthalpy estimated in ref 137 from data by: Pearson, R. G.; Mauermann, H. *J. Am. Chem. Soc.* 1982, 104, 500. Sweany, R. L. *J. Am. Chem. Soc.* 1981, 103, 2410. ^d $D4 = D(\text{Ru-OH})$. ^e $D5 = D(\text{Os-CO})$ in $\text{Os}_3(\text{CO})_{12}$.

and $E(\text{Fe-C}_3\text{H}_5)$ can be obtained.

The reorganization energies $\text{ER}_1\text{--ER}_5$ are not available, and therefore the values presented in Table 8 are approximations. Furthermore, it is not possible to say that all the values are affected by a constant error as was measured for $\text{Mn(CO)}_5\text{L}$ complexes. While in that case there was a "constant" moiety, Mn(CO)_5 , fairly similar in all the molecules, the iron complexes have different arrangements of the ligands around the iron atom. However, an idea of the correction for each bond enthalpy term in Table 8 can be gleaned from the bond length data for the iron complexes in Table 9.

The iron-carbon and carbon-oxygen bond distances are similar in Fe(CO)_5 and $\text{Fe(CO)}_4(\text{C}_2\text{H}_4)$, suggesting that $\text{ER}_1 \approx 0$. As far as ER_2 is concerned, it certainly is negative, since the 133.7-pm^{214} C-C bond length in the free olefin increases to 146 ± 6 pm in the complex.²³⁷ This increase of 12 pm is explained in terms of the Dewar-Chart-Duncanson model,^{123,124} which considers a σ bond formed by the filled π orbital of the olefin with an empty σ -type orbital of the metal and a π back-bond where metal d electrons are donated to an antibonding π^* orbital of the olefin. This back-donation weakens the carbon-carbon bond. In the case under discussion, if a curve $E(\text{C-C})/r(\text{C-C})$ is used,⁹³ the reorganization energy ER_2 is close to -140 kJ/mol, making $E(\text{Fe-C}_2\text{H}_4) \approx 230$ kJ/mol. Although this value is only approximate, it provides the order of magnitude of correction to $E(\text{Fe-C}_2\text{H}_4)$ in Table 8 when ER_2 is considered.

A similar discussion could be made for each of the $\text{Fe(CO)}_m(\text{L})_n$ complexes. For some of them the bond length data are not reliable, but as a general feature it can be expected that ER_2 will make the largest contribution to $E(\text{Fe-L})$.

The structural parameters for $\text{Fe(CO)}_3(\text{I})(\text{C}_3\text{H}_5)$ are not very precise,²³⁸ and so the data for $\text{Fe(CO)}_3\text{-Br(C}_3\text{H}_5)$ are also included in Table 9. On the other hand, since we are not aware of the structure of $\text{Fe(CO)}_4\text{I}_2$, it was assumed that the relevant bond distances in this complex and in $\text{Fe(CO)}_4\text{H}_2$ are identical. It is noticed that Fe-CO and C-O bond lengths are similar in $\text{Fe(CO)}_4\text{H}_2$, $\text{Fe(CO)}_3(\text{Br})(\text{C}_3\text{H}_5)$, and Fe(CO)_5 , suggesting small values for ER_3 , ER_4 , and ER_5 . Therefore,

TABLE 9. Bond Length Data (pm) for Some Iron Carbonyls

molecule	method ^a	Fe-CO ^b	C-O ^b	Fe-L ^c
Fe(CO) ₅	E ^d	182.1 ± 0.1	115.3 ± 0.1	
	E ^{d,e}	182.8 ± 0.3	114.8 ± 0.2	
	X ^f	179 ± 2	112 ± 2	
Fe(CO) ₄ (C ₂ H ₄)	E ^g	182 ± 4	114.6 ± 1.0	212 ± 3
Fe(CO) ₃ (1,3-C ₄ H ₆)	E ^g	180 ± 1.5	113.5 ± 1.0	208 ± 1.5
	X ^h	176 ± 5	115 ± 5	206 ± 6
Fe(CO)(1,3-C ₄ H ₆) ₂	X ⁱ	194 ± 2	102 ± 3	209 ± 1
Fe(CO)(1,3-c-C ₆ H ₈) ₂	X ^j	174.7 ± 0.3	113.8 ± 0.4	203.6 ± 0.5
Fe(CO) ₃ (C ₃ H ₅)I	X ^k	180 ± 2	119 ± 3	209 ± 2
Fe(CO) ₃ (C ₃ H ₅)Br	X ^k	179 ± 1	114 ± 1	206 ± 1
Fe(CO) ₃ (cot) ^l	X ^m	179	113	205 ± 3
Fe(CO) ₄ H ₂	E ⁿ	182 ± 1	114.5 ± 0.3	155.6 ± 2.1 ^o

^aKey: E = electron diffraction; X = X-ray diffraction. ^bAverage values. ^cApproximate distance between the iron atom and the closest carbon of the olefin. ^dBeagley, B.; Schmidling, D. G. *J. Mol. Struct.* 1974, 22, 466. ^eAlmendinger, A.; Haaland, A.; Wahl, K. *Acta Chem. Scand.* 1969, 23, 2245. ^fDonohue, J.; Carson, A. *Acta Crystallogr.* 1964, 17, 663. ^gReference 237. ^hMills, O. S.; Robinson, G. *Acta Crystallogr.* 1963, 16, 758. ⁱWhiting, D. A. *Cryst. Struct. Commun.* 1972, 1, 379. ^jKruger, C.; Tsay, Yi-Hung. *J. Organomet. Chem.* 1971, 33, 59. ^kReference 238. ^lcot = 1,3,5,7-cyclooctatetraene. ^mDickens, B.; Lipscomb, W. N. *J. Am. Chem. Soc.* 1961, 83, 4862; *J. Chem. Phys.* 1962, 37, 2084. ⁿReference 215. ^oFe-H bond length.

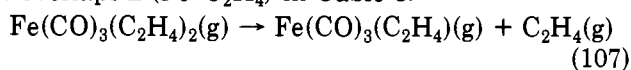
in this case ER₂ should also provide the largest correction for $E(\text{Fe}-\text{C}_3\text{H}_5)$.

Connor, Skinner, and co-workers^{235,236} implicitly assumed the cancellation of all the reorganization energies in eq 105 and 106. If $-\text{ER}_1/n - \text{ER}_2$ has similar values for each of the olefin complexes, then their main conclusion remains; i.e., the iron-diene bond enthalpy terms are relatively constant. Although more accurate structural data and also some theoretical work are desirable, the values for iron-olefin bond lengths in Table 9 seem to confirm that expectation.

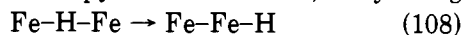
The iron-ethylene bond dissociation enthalpy presented in Table 8 was calculated from $D[\text{Fe}(\text{CO})_4-\text{CO}]$ (Table 1), which yields $\Delta H^\circ_f[\text{Fe}(\text{CO})_4, \text{g}] = -441 \pm 15$ kJ/mol. As discussed above, it is not possible at the present stage to compare the values for $D(\text{Fe}-\text{C}_2\text{H}_4)$ and $E(\text{Fe}-\text{C}_2\text{H}_4)$ in the absence of the reorganization terms in Scheme 13.

Values for $D[\text{Fe}(\text{CO})_4-\text{H}]$ and $E[\text{Fe}(\text{CO})_4-\text{H}]$ are also shown in Table 8. The mean bond dissociation enthalpy was estimated¹³⁷ from the activation enthalpy for the thermal decomposition in solution (109 ± 8 kJ/mol), yielding Fe(CO)₄ and H₂, and from the activation enthalpy of the oxidative addition of H₂ to Fe(CO)₄ (~0 kJ/mol). Assuming that these values also apply for the gas phase, $\Delta H^\circ_f[\text{Fe}(\text{CO})_4\text{H}_2, \text{g}] \approx -549$ kJ/mol can be derived by using $\Delta H^\circ_f[\text{Fe}(\text{CO})_4, \text{g}]$ given above. Equation 104 leads to $E(\text{Fe}-\text{H}) \approx 244$ kJ/mol (not including ER₁ and ER₂).

Recent kinetic studies led to a value for the activation enthalpy of reaction 107 in the gas phase, 113 ± 25 kJ/mol.²³⁹ This value should be a lower limit for D_1 - $(\text{Fe}-\text{C}_2\text{H}_4)$ in the complex Fe(CO)₃(C₂H₄). Indeed, note it overlaps $D(\text{Fe}-\text{C}_2\text{H}_4)$ in Table 8.

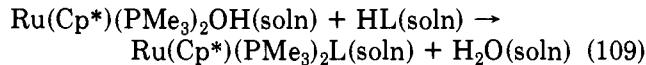


A mention is also made of equilibrium studies in benzene that enabled estimation of the iron-hydrogen bond enthalpy term for a bridging hydrogen, $E(\text{Fe}-\text{H}-\text{Fe}) \approx 356$ kJ/mol, in the cluster Fe₃(CO)₉(μ₂-H)₃(μ₃-CMe).²⁴⁰ This can be used to make a very crude prediction of the enthalpy of reaction 108,²⁴⁰ by using



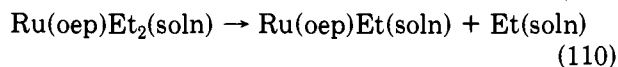
$E(\text{Fe}-\text{H})$ in Table 8 and $E(\text{Fe}-\text{Fe}) = 81$ kJ/mol.¹⁵ One obtains $\Delta H^\circ(108) = 31$ kJ/mol, indicating that the bridged structure will be thermodynamically more stable. Note, however, that the use of bond enthalpy terms to estimate reaction enthalpies is not linear. In addition, the overall uncertainty affecting the value obtained for $\Delta H^\circ(108)$ is not easy to assess.

b. Ruthenium. Bercaw and co-workers measured the equilibrium constants of reaction 109 in tetrahydrofuran ($T \sim 300$ K) for a series of ligands L.²⁴¹



Assuming that the solvation enthalpies cancel and entropic terms are negligible, metal-ligand bond dissociation enthalpies relative to $D(\text{Ru}-\text{OH})$ (Table 8) can be derived from the values of $\Delta G^\circ(109)$, by using the data in the Appendix. The last assumption has been shown to be reasonable by comparing, for L = NPh₂, $\Delta G^\circ(109) = 13.4 \pm 2.5$ kJ/mol in tetrahydrofuran with $\Delta H^\circ(109) = 5.0$ kJ/mol, obtained from a van't Hoff plot in benzene. The trend evidenced by the ruthenium-ligand bond dissociation enthalpies is as expected, i.e., $D[\text{Ru}-\text{C}(\text{sp}^3)] < D[\text{Ru}-\text{C}(\text{sp})]$, and reflects the carbon-hydrogen bond dissociation enthalpies in the hydrocarbons (see also section V).

Kinetic studies in benzene led to the activation enthalpy for the cleavage of a ruthenium-ethyl bond, reaction 110.²⁴² By assuming that the activation barrier for radical recombination is diffusion-controlled, au-



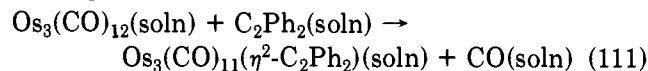
oe =

2,3,7,8,12,13,17,18-octaethylporphyrinato dianion

thors estimated $\Delta H^\ddagger_{-1} \approx 8$ kJ/mol and gave 91 ± 6 kJ/mol for $D(\text{Ru}-\text{Et})$. Being reasonable to consider that solvation effects are small, the authors suggested that this low value for the bond dissociation enthalpy is probably due to a large trans effect of the second ethyl ligand.

A reference is made to a recent paper where equilibrium studies in solution involving ruthenium and osmium clusters (similar to the one mentioned above for iron) enabled estimation of several M-C-M and M-H-M bond enthalpies (M = Ru, Os).²⁴³

c. Osmium. Poë et al. measured the enthalpy of reaction 111 in decalin, as 39 ± 12 kJ/mol, and suggested that this value is equal to $D(\text{Os}-\text{CO}) - D(\text{Os}-\text{C}_2\text{Ph}_2)$.²⁴⁴ Indeed, for a ligand substitution reaction like this, it seems reasonable to assume that the solvation enthalpies cancel.



7. Group 9

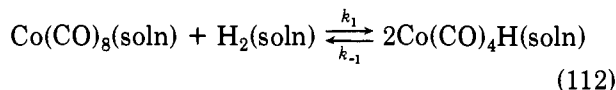
a. Cobalt. The Co-H, Co-CCl, and Co-CBr bond enthalpies were derived from the enthalpies of formation of the respective complexes,^{15,161,245,246} by transferring $E(\text{Co}-\text{CO})$ from the radical Co(CO)₄.

For the Co(CO)₄H complex, the method is similar to the one described for manganese compounds and $E(\text{Co}-\text{H})$ is affected by the same sort of errors since the reorganization energy equivalent to ER₂ (see Scheme 10 or eq 100) is also unknown.

$D(\text{Co-H})$ relies on $D(\text{Co-Co})$ in $\text{Co}_2(\text{CO})_8$, which has been determined by Bidinosti and McIntyre by gas-phase equilibrium studies,²¹⁹ under the assumption that the complex contains no bridging carbonyls. This assumption is not entirely supported by other gas-phase studies of $\text{Co}_2(\text{CO})_8$, which show predominance of binuclear fragments produced under electron impact.²⁴⁷ Furthermore, although electron diffraction data are not available, the crystalline structure of the complex reveals the existence of two bridging carbonyls.²⁴⁸ This matter was discussed by Gardner et al.,²⁴⁶ who concluded that as far as bond enthalpies are concerned the assumption of either bridged or nonbridged structure is irrelevant since the enthalpy difference between both forms is quite small,²⁴⁹ ca. 5 kJ/mol (to be divided among at least nine bonds).

In the present review a value of $D(\text{Co-Co}) = 64$ kJ/mol was used, after Connor⁸⁷ and Pilcher and Skinner.¹⁵ This is close to the values obtained from independent experiments by Bidinosti and McIntyre,²¹⁹ and it leads to the $D(\text{Co-H})$ and $E(\text{Co-H})$ results presented in Table 10, by using equations similar to eqs 100 and 101.

Besides the work by Bronshtein et al.,²⁴⁵ there are two more studies^{250,251} where Co-H bond enthalpy data in $\text{Co}(\text{CO})_4\text{H}$ are reported, both using van't Hoff plots to derive the enthalpy of reaction 112 in heptane.



Ungvary²⁵⁰ obtained $\Delta H^\circ(112) = 13.4$ kJ/mol, while Alemdaroglu et al.²⁵¹ arrived at $\Delta H^\circ(112) = 27.6$ kJ/mol. This difference was attributed²⁵¹ to the fact that in Ungvary's work the concentrations of $\text{Co}_2(\text{CO})_8$ and $\text{Co}(\text{CO})_4\text{H}$ were determined indirectly at ambient temperature and pressure, whereas Alemdaroglu et al. measured those concentrations by means of in situ infrared spectroscopy. Alemdaroglu et al. point out that Ungvary's technique can lead to misinterpretation due to the reaction taking place on sampling. On the other hand, the measured activation enthalpies,²⁵¹ $\Delta H^\ddagger_1(112)$ and $\Delta H^\ddagger_{-1}(112)$, yield $\Delta H^\circ(112) = 26.4$ kJ/mol, in good agreement with the above higher value. In any case, as far as bond enthalpy data are concerned, the difference between the two reported values is insignificant.

In both papers it is implicitly assumed that the solvation enthalpies cancel in reaction 112. With this in mind, $D(\text{Co-H}) = 243$ ²⁵⁰ or 236 ²⁵¹ kJ/mol are obtained through eq 113, by using $D(\text{Co-Co})$ given previously.

$$D(\text{Co-H}) = [-\Delta H^\circ(112) + D(\text{Co-Co}) + D(\text{H-H})]/2 \quad (113)$$

It is noticed that both values are in fair agreement with $D(\text{Co-H})$ presented in Table 10, particularly the one obtained by Alemdaroglu et al. This also suggests that the above assumption is quite reasonable. As remarked for reaction 87, the cancellation of the sublimation enthalpies makes some sense if the discussion in section III.B is recalled, and it is noticed that the ratio of the molecular weights $\text{Co}_2(\text{CO})_8/\text{Co}(\text{CO})_4\text{H}$ is about 2. A similar case is provided by $\text{Mn}_2(\text{CO})_{10}$ and $\text{Mn}(\text{CO})_5\text{H}$, whose enthalpies of vaporization^{13,212} show a ratio of 2.4 (it would probably be closer to 2 if the enthalpy of melting of $\text{Mn}(\text{CO})_5\text{H}$ was considered). As far as the solution enthalpies are concerned, the cancellation of

their small values can be expected.

The evaluation of Co-CCl and Co-CBr is slightly more difficult than the previous ones because it also involves the transfer of Co-Co and C-X bond enthalpies (X = Cl, Br).

Bond length data for some cobalt carbonyls is presented in Table 11. It may be noticed that Co-Co distances are relatively constant, although the one for $\text{Co}_2(\text{CO})_8$ is about 4 pm longer than the average. In the absence of reorganization energy data, the best thing to do is probably to assume they are similar. In fact, this has been the usual procedure, concerning not only cobalt-cobalt bond enthalpies but also cobalt-carbonyl (bridging and terminal) bond enthalpies.^{15,87} The availability of better structural data and theoretical calculations would probably change this picture, as suggested, e.g., by the large difference in the C-O bond lengths in $\text{Co}_2(\text{CO})_8$ and in $\text{Co}_4(\text{CO})_{12}$. Meanwhile, the transferability principle must be accepted, even when the magnitude of the errors that it causes is ignored.

$E(\text{Co-Co})$ and $E(\text{Co-CO})_t$ (terminal carbonyl) were obtained as 88.0 and 135.9 kJ/mol, respectively, by using the method described by Connor⁸⁷ and Pilcher and Skinner¹⁵ and the enthalpies of formation of $\text{Co}_2(\text{CO})_{10}$ and $\text{Co}_4(\text{CO})_{12}$ in the gas phase.¹⁵ Those values can now be introduced in eq 114, which gives the sum of Co-CX and C-C bond enthalpy terms (X = Cl, Br). The right-hand side of this equation is 691 kJ/mol for X = Cl and 700 kJ/mol for X = Br.

$$3E(\text{Co-CX}) + E(\text{C-X}) = 3\Delta H^\circ_f(\text{Co}_3\text{g}) + \Delta H^\circ_f(\text{C,g}) + \Delta H^\circ_f(\text{X,g}) + 9\Delta H^\circ_f(\text{CO,g}) - \Delta H^\circ_f[\text{Co}_3(\text{CO})_9(\text{CX})_g] - 3E(\text{Co-Co}) - 9E(\text{Co-CO})_t \quad (114)$$

The complexes $\text{Co}_3(\text{CO})_9(\text{CX})$ have no bridging carbonyls (Table 11), as evidenced by eq 114. Otherwise the term $E(\text{Co-CO})_b = 62.1$ kJ/mol would also be considered.

We are now left with the second problem, i.e., the evaluation of $E(\text{C-Cl})$ and $E(\text{C-Br})$. Gardner et al.²⁴⁶ assumed that these bond terms match $E(\text{C-X})$ in CCl_4 and CBr_4 , respectively, although they recognized that this presumption can be flawed because there is evidence for electron delocalization over the three cobalt-carbon and carbon-halogen bonds in the complexes. In fact, the C-Cl bond length in $\text{Co}_3(\text{CO})_9(\text{CCl})$, 170.7 pm,²⁵² is shorter than the one in CCl_4 (176.6 ± 0.3 pm),²¹⁴ suggesting a higher value for $E(\text{C-Cl})$ in the complex. We are not aware of the structure of $\text{Co}_3(\text{CO})_9(\text{CBr})$, but a similar trend can be expected.

By taking Gardner's assumption, maximum values for $E(\text{Co-CX})$ should therefore be obtained. $E(\text{C-Cl}) = 325 \pm 1$ kJ/mol, derived from $\Delta H^\circ_f(\text{CCl}_4\text{g})$,²² leads to $E(\text{Co-CCl}) = 122$ kJ/mol. $E(\text{C-Br}) = 270 \pm 1$ kJ/mol, calculated from $\Delta H^\circ_f(\text{CBr}_4\text{g})$,²⁵³ gives $E(\text{Co-CBr}) = 143$ kJ/mol.

$E(\text{C-Cl})$ and $E(\text{C-Br})$ can also be calculated from the enthalpies of formation of the diatomic molecules CCl and CBr, it being noted that these values are controversial. JANAF tables¹⁶⁷ recommend $\Delta H^\circ_f(\text{CCl,g}) = 502 \pm 20$ kJ/mol, implying $D(\text{C-Cl}) = E(\text{C-Cl}) = 336$ kJ/mol. A value of $\Delta H^\circ_f(\text{CCl,g}) = 464$ kJ/mol ($D = 374$ kJ/mol), obtained from a Birge-Spencer extrapolation, is also mentioned in those tables but is considered a lower limit; i.e., $D(\text{C-Cl})$ is a high value. On the other hand, Kerr and Trotman-Dickenson²¹⁴ quote $D(\text{C-Cl})$

= 397 ± 29 kJ/mol. C-Cl equilibrium bond length in CCl₄ is 164 pm,¹⁶⁷ indicating that $D(\text{C-Cl})$ should be higher than $E(\text{C-Cl})$ in the organometallic complex and in CCl₄. The difference between the JANAF value and $E(\text{C-Cl})$ in CCl₄, 11 kJ/mol, seems too small to account for the change in the bond lengths. Thus, we prefer to accept the Birge-Sponer result, which agrees, within their error limits, with Kerr and Trotman-Dickenson's value. The resulting $E(\text{Co-CCl}) \approx 106$ kJ/mol is, of course, a minimum.

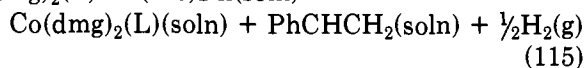
JANAF tables give 510 ± 63 kJ/mol for the enthalpy of formation of CBr (or 319 kJ/mol for the bond dissociation enthalpy), while Kerr and Trotman-Dickenson quote $D(\text{C-Br}) = 280 \pm 21$ kJ/mol. Accepting the first value, we are led to the lower limit $E(\text{Co-CBr}) \approx 127$ kJ/mol.

From the above discussion, it may be concluded that results for both cobalt-carbon bond enthalpy terms lie in a narrow range: 106–122 kJ/mol for $E(\text{Co-CCl})$ and 127–143 kJ/mol for $E(\text{Co-CBr})$. The mean values, presented in Table 10, can be compared with $E(\text{Co-H})$ in Co(CO)₄H. Differences $E(\text{Co-H}) - E(\text{Co-CX})$ are in the expected range. It should, however, be emphasized that the two values calculated for $E(\text{Co-CX})$ rest on some assumptions whose validity may be questioned.

A number of kinetic, equilibrium, and calorimetric studies in solution, aiming to probe the energetics of cobalt-alkyl bonds, have been reported in the last 10 years.^{254–271} The kinetic method, which dominates the set of results obtained so far, relies on the measurement of activation enthalpies for reactions in which the cleavage of cobalt-alkyl bond is the rate-determining step. These activation enthalpies are then identified with the enthalpies of reaction, by assuming that the radical recombinations are diffusion-controlled, implying small activation barriers (ΔH^\ddagger_{-1}) for these reverse processes. In addition, if the results are to be compared with gas-phase data, it is also presumed that the net solvation effect of the homolytic cleavage is negligible.

It has been shown that for main-group elements (e.g., organic, organosilicon, and organotin compounds), the enthalpies of homolytic cleavages in solution are comparable to gas-phase data.^{44,272} As pointed out in section II, considerable solvation effects may, however, be expected when an unsaturated transition-metal complex is formed in solution. This point has recently been addressed by Koenig, Hay, and Finke,⁴⁶ together with a detailed discussion on how activation enthalpy data in solution should be properly handled to yield "gas-phase" bond enthalpies. Unfortunately, a thorough testing and use of their model requires experimental information that are still not available. Nevertheless, the data discussed below must have at least the merit of providing *trends* that can be extrapolated to the gas phase.

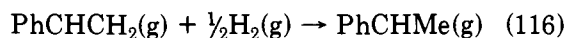
Co-H(Me)Ph bond dissociation enthalpies in several complexes were calculated from the enthalpies of reaction 115, obtained by equilibrium studies in acetone

$$\text{Co}(\text{dmg})_2(\text{L})\text{CH}(\text{Me})\text{Ph}(\text{soln}) \rightarrow$$


dmgH = dimethylglyoxime

(for L = pyridine, also in toluene), in the temperature range 283–310 K.^{254,255} Each $D(\text{Co-C})$ was derived by

adding $\Delta H^\circ(115)$ to the enthalpy of reaction 116, $\Delta H^\circ(116)$. For $\Delta H^\circ(116)$, Halpern et al. have obtained -9.2 kJ/mol, based on $\Delta H^\circ_f(\text{PhCHMe}, \text{g}) = 138$ kJ/



mol.²⁷³ If, however, a more recent value for this enthalpy of formation is accepted (see Appendix), $\Delta H^\circ(116)$ will become 22 ± 6 kJ/mol. The five $D[\text{Co-CH}(\text{Me})\text{Ph}]$ presented in Table 10 were calculated by using the modern value for $\Delta H^\circ(116)$.

Kinetic studies of reaction 115 in acetone and toluene were also made by Halpern et al.²⁵⁵ The activation enthalpies (Table 10), regarded as upper limits of $D[\text{Co-CH}(\text{Me})\text{Ph}]$,^{233,254–256} are only 8–9 kJ/mol higher than the original $D(\text{Co-CHMePh})$ equilibrium values, reported in ref 255. This consistency is not observed with respect to the equilibrium values in Table 10, since these are ca. 30 kJ/mol higher than Halpern's, due to the different auxiliary value used to calculate $\Delta H^\circ(116)$. We are unable to reconcile this contradiction, but it may well be possible that the reported activation enthalpies in solution are affected by noncanceling solvation terms or that the most recent value for $\Delta H^\circ_f(\text{PhCHMe}, \text{g})$ is too high.

The calculation of cobalt-carbon bond enthalpy terms, $E[\text{Co-CH}(\text{Me})\text{Ph}]$, would require the energy differences between Co(dmg)₂L* [from the Co(III) complexes] and Co(dmg)₂L and also the reorganization energy of PhCHMe. If it is assumed that this fragment has similar structures in the Co(III) complexes and in ethylbenzene, then its ER will be about -50 kJ/mol (Appendix), close to the ER of benzyl radical, suggesting that $E[\text{Co-CH}(\text{Me})\text{Ph}] > D[\text{Co-CH}(\text{Me})\text{Ph}]$.

Also shown in Table 10 are the Co-CH(Me)Ph bond dissociation enthalpies in the same family of complexes, but where L is a phosphine. The values were also obtained by Halpern and co-workers, using the kinetic method (solvent acetone) and the assumption that the activation enthalpies for the recombination reactions are ca. 8 kJ/mol.²⁵⁷ Leaving aside the question of the *absolute* accuracy of these values, it is interesting to note the decrease in $D(\text{Co-C})$ for bulkier phosphines. The influence of steric effects has been quantified by a linear correlation between $D(\text{Co-C})$ and the phosphine cone angle.²⁵⁷

More kinetically derived cobalt-carbon bond dissociation enthalpies are presented in Table 10, including data for the families of complexes Co(dmg)₂(L)CH-(CH₂X)COOMe (solvent cyclohexanone),²⁵⁸ Co(dmg)₂(L)Bz and Co(oep)(L)Bz (toluene),²⁵⁹ and Co(saloph)(py)R (pyridine).²⁶⁰ All these results rely on the same estimated value for the activation enthalpy of radical recombination, 8 kJ/mol. The trends are discussed in detail by the authors. For example, the steric effects caused by the phosphine are also apparent in the Co-Bz dissociation enthalpies, both for the dimethylglyoxime and for the octaethylporphyrin complexes. In the saloph (*N,N'*-bis(salicylidene)-*o*-phenylenediamine) family, the smaller values for isopropyl and neopentyl also attest to the importance of steric effects in these complexes.²⁶⁰ It is interesting to note that the activation enthalpies of the reactions involving some of the complexes Co(dmg)₂(L)Bz (L = PEtPh₂, P(c-C₆H₁₁)₃, PPh₃) and Co(oep)(L)Bz (L = PMe₂Ph) were also determined in ethylene glycol.²⁶¹ The values were ca. 20–35 kJ/mol higher than those derived in toluene. According to

TABLE 10. Group 9 M-H and M-C Bond Enthalpies

molecule ^a	method/ref ^b	D, kJ/mol	E, kJ/mol	molecule ^a	method/ref ^b	D, kJ/mol	E, kJ/mol
Co(CO) ₄ H	EG/245	227 ^c	227	Rh(acac)L	RSC/277		
Co ₃ (CO) ₉ (CCl)	RSC/246		114	L = cot		D7 ^f	
Co ₃ (CO) ₉ (CBr)	RSC/246		135	L = cod		D7 + 18	
Co(dmgl) ₂ (L)CH(Me)Ph	ES/254, 255			Rh(acac)L ₂	DSC/122		
L = pyridine		113 ± 7		L = C ₂ H ₄		D8 ^g	
L = pyridine		117 ± 7 ^d		L = MeCHCH ₂		D8 + (4 ± 3)	
L = 4-methylpyridine		115 ± 7		L = CH ₂ CHCl		D8 - (13 ± 5)	
L = 4-aminopyridine		120 ± 7		L = va		D8 + (1 ± 5)	
L = 4-cyanopyridine		106 ± 7		L = ma		D8 + (12 ± 4)	
L = imidazole		118 ± 7		Rh(acac)L ₂	RSC/276		
Co(dmgl) ₂ (L)CH(Me)Ph	KS/255			L = C ₂ H ₄		D8 ^g	
L = pyridine		<90 ± 2		L = MeCHCH ₂		D8 - (7.8 ± 0.2)	
L = pyridine		<89 ± 2 ^d		L = CH ₂ CHCl		D8 - (7.8 ± 0.2)	
L = methylpyridine		<91 ± 2		L = va		D8 - (6.8 ± 0.2)	
L = 4-aminopyridine		<97 ± 2		L = ma		D8 - (4.6 ± 0.2)	
L = 4-cyanopyridine		<84 ± 2		L = CH ₂ CHPh		D8 - (8.7 ± 0.2)	
L = imidazole		<96 ± 2		Rh(oep)H	ES/284	259	259
Co(dmgl) ₂ (L)CH(Me)Ph	KS/257			Rh(oep)C(O)H	ES/283	249	300
L = PMe ₂ Ph		100		Rh(oep)CH(Bu)OH	ES/286	187	
L = PBu ₃		87		Rh(Cl)(B)[P(4-tolyl) ₃] ₂ H ₂	ES/288	242 ± 2 ^h	242
L = PEtPh ₂		81		Rh(Cp*)(PR ₃)(H)R	KS/289, 291		
L = PPh ₃		73		R = Ph		D9 ⁱ	
L = P(CH ₂ CH ₂ CN) ₃		85		R = Me		D9 - 55	
Co(dmgl) ₂ (L)Bz	KS/259			R = Pr		D9 - 83	
L = PMe ₂ Ph		128	171	Rh(NC ₃ H ₃ C ₆ H ₅ CO)(Cl)(py)-	KS/292	128	
L = PBu ₃		121	164	C(Ph)(OMe)H			
L = PEtPh ₂		113	156	Ir(X)(CO)(PPh ₃) ₂ H ₂	ES/113 ^h		
L = PPh ₃		108	151	X = Cl		247	272
L = P(c-C ₆ H ₁₁) ₃		96	139	X = Br		253	
Co(oep)(L)Bz	KS/259			X = I		258	270
L = PMe ₂ Ph		114	157	Ir(Cl)(CO)(PPh ₃) ₂ (Cl)H	RSC/293	245	271
L = PBu ₃		123	166	Ir(Cl)(CO)(PPh ₃) ₂ (Br)H	RSC/293	237	262
L = PEtPh ₂		110	153	Ir(Cl)(CO)(PMePh ₂) ₂ (Cl)H	RSC/293	266	291
L = PPh ₃		100	143	Ir(Cl)(CO)(PMe ₃) ₂ (I)R	RSC/110, 111		
L = P(c-C ₆ H ₁₁) ₃		124	167	R = H		D10 + (109 ± 15) ^j	E10 + 109 ^k
Co(dmgl) ₂ (L)CH(CH ₂ X)-	KS/258			R = Me		D10 + (6 ± 11)	E10 - 18
COOMe				R = Et		D10 - (4 ± 10)	E10 - 14
L = pyridine, X = H		120		R = Pr		D10 - (4 ± 11)	E10 - 11
L = 4-methylpyridine,		123		R = <i>i</i> -Pr		D10 - (23 ± 15)	E10 - 22
X = H				R = Bz		D10 - (29 ± 14)	E10 - 14
L = 4-cyanopyridine,		118		R = C(O)Me		D10 - (5 ± 10)	E10 + 63
X = H				R = C(O)Ph		D10 + (18 ± 16)	E10 + 74
L = pyridine, X = COOMe		139		Ir(Cl)(CO)(PR ₃) ₂ H ₂	ES/294 ^h		
Co(dmgl) ₂ (py)R	RSC/274			PR ₃ = PEt ₃		243	268
R = Me		138 ± 3	114	PR ₃ = P(c-C ₆ H ₁₁) ₃		246	271
R = <i>i</i> -Pr		98 ± 9	99	Ir(X)(CO)(PR ₃) ₂ H ₂	ES/297 ^h		
R = Bz		136 ± 9	179	X = Cl, PR ₃ = P(<i>i</i> -Pr) ₃		240	265
Co(saloph)(py)R	KS/260			X = Cl, PR ₃ = PBuPh ₂		242	267
R = Pr		105	98	X = Cl, PR ₃ = PPh ₃		251	276
R = <i>i</i> -Pr		83	84	X = Cl, PR ₃ = P(c-C ₆ H ₁₁) ₃		240	265
R = CH ₂ CMe ₃		77	70	X = Cl, PR ₃ = PBz ₃		249	274
R = Bz		91	134	X = Cl, PR ₃ = P(<i>p</i> -tolyl) ₃		246	271
Co[C ₂ (DO)(DOH) _{pn}](I)R	KS/262			X = Cl, PR ₃ = P(OPh) ₃		244	269
R = CH ₂ CMe ₃		127	120	X = Br, PR ₃ = P(<i>i</i> -Pr) ₃		245	270
R = Bz		109	152	X = Br, PR ₃ = PPh ₃		235	260
Co(dmglBF ₂) ₂ (H ₂ O)Bz	KS/263	99	142	X = Br, PR ₃ = P(c-C ₆ H ₁₁) ₃		244	269
Co(14-aneN ₄)(H ₂ O)Bz ²⁺	KS/264	98	141	X = Br, PR ₃ = P(OPh) ₃		238	263
[cobinamide]R	KS/265			X = I, PR ₃ = P(<i>i</i> -Pr) ₃		227	252
R = <i>i</i> -Pr		110	111	X = I, PR ₃ = PPh ₃		229	254
R = CH ₂ CMe ₃		126	119	X = I, PR ₃ = (c-C ₆ H ₁₁) ₃		256	281
R = Bz		105	148	X = I, PR ₃ = P(OPh) ₃		224	249
[cobinamide]Ado	KS/266	144		Ir(Cl) ₂ (CO)(L) ₂ C(O)Me	RSC/112		
B ₁₂ R	KS/265			L = PMe ₃		492 - D11 ^l	>237
R = <i>i</i> -Pr		79	80	L = PEt ₃		496 - D12 ^m	>241
R = <i>i</i> -Bu		104	95	Ir(Cl) ₂ (CO)(L) ₂ C(O)Me	RSC/112		
R = CH ₂ CMe ₃		90	83	L = PMe ₃		462 - D13 ⁿ	
R = Bz		95	138	L = PEt ₃		460 - D13	
B ₁₂ R	KS/271			L = PMe ₂ Ph		464 - D13	
R = CH ₂ CMe ₃		99	92	L = PMePh ₂		453 - D13	
R = CH ₂ C ₃ H ₉		99		L = P(<i>t</i> -Bu) ₃		431 - D13	
B ₁₂ Ado	KS/267	112		L = P(<i>p</i> -tolyl) ₃		445 - D13	
B ₁₂ Ado	KS/268	125		L = PBz ₃		415 - D13	
B ₁₂ Ado	KS/269	131		L = P(OPh) ₃		411 - D13	
Rh(Cp)(C ₂ H ₄) ₂	KG/280	<130		Ir(Cl) ₂ (CO)(PMe ₂ Ph) ₂ C(O)Ph	RSC/112	453 - D13	
Rh ₂ (Cl) ₂ [P(OPh) ₃] ₂ L	RSC/277						
L = cot		D6 ^e					
L = nbd		D6 + 11					
L = cod		D6 + 8					
L = dcpd		D6 - 5					

TABLE 10 (Continued)

molecule ^a	method/ref ^b	D, kJ/mol	E, kJ/mol	molecule ^a	method/ref ^b	D, kJ/mol	E, kJ/mol
Ir(Cl) ₂ (CO)(PPh) ₃ R	DSC/295, 296			Ir(Cp*)(PMe ₃)Me ₂	RSC/301 ^a	243 ± 3	219
R = Me			E14 ^c	Ir(Cp*)(PMe ₃)(Br)C ₂ H ₅	RSC/301	326 ± 10	288
R = CH ₂ F			E14 + 19	Ir(X)(CO)(PPh ₃) ₂ L	DSC/117, 302		
R = CHF ₂			E14 + 39	X = F, L = C ₂ F ₄		79	
R = CF ₃			E14 + 57	X = F, L = C ₄ F ₆		99	
R = CH ₂ Cl			E14 + 32	X = Cl, L = C ₂ F ₄		67	
R = CH ₂ OPh			E14 + 4	X = Cl, L = C ₄ F ₆		96	
R = C(O)OEt			E14 + 19	X = Br, L = C ₂ F ₄		41	
R = <i>p</i> -MeC ₆ H ₄ CH ₂			E14 - 13	X = Br, L = C ₄ F ₆		79	
R = <i>p</i> -MeOC ₆ H ₄ CH ₂			E14 - 14	X = I, L = C ₂ F ₄		57	
R = <i>p</i> -NO ₂ C ₆ H ₄ CH ₂			E14 - 11	X = I, L = C ₄ F ₆		82	
Ir(Cp*)(PMe ₃)H ₂	KS/RSC/ PAC/300	310 ± 18	310	Ir(acac)L ₂	DSC/122		
Ir(Cp*)(PMe ₃)(R)H	RSC/300 ^p			L = C ₂ H ₄		D15 ^q	
R = Ph		337 ± 15	293	L = MeCHCH ₂		D15 - (8 ± 4)	
R = <i>c</i> -C ₆ H ₁₁		209 ± 7	216	L = CH ₂ CHCl		D15 + (2 ± 5)	
Ir(Cp*)(PMe ₃)(H)R	ES/298, 299			L = va		D15 - (12 ± 4)	
R = <i>c</i> -C ₅ H ₉		215		L = ma		D15 - (6 ± 5)	
R = C ₅ H ₁₁		244		Ir(acac)L ₂	RSC/276		
R = Ph		321	277	L = C ₂ H ₄		D15 ^q	
R = <i>c</i> -C ₆ H ₁₁		218	225	L = CH ₂ CHCl		D15 - (4.2 ± 0.2)	
R = 2,3-Me ₂ Bu		240	237	L = va		D15 - (5.3 ± 0.2)	
R = CH ₂ CMe ₂ Et		<233		L = ma		D15 - (3.6 ± 0.2)	
				L = CH ₂ CHPh		D15 - (9.1 ± 0.2)	

^aKey: acac = acetylacetonate; 14-aneN₄ = 1,4,8,11-tetraazacyclotetradecane; B₁₂Ado = 5'-deoxyadenosylcobalamine; C₂(DO)(DOH)_{pn} = 11-hydroxy-2,10-diethyl-3,9-dimethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraen-1-olato; cobinamide = B₁₂ without the axial base and the phosphoribosyl groups; cod = 1,5-cyclooctadiene; cot = 1,3,5,7-cyclooctatetraene; dcpd = dicyclopentadiene; dmgH = dimethylglyoxime; ma = methyl acrylate; nbd = 2,5-norbornadiene; oep = octaethylporphyrin; py = pyridine; salophH = *N,N'*-bis(salicylidene)-*o*-phenylenediamine; va = vinyl acetate. ^bKey: DSC = differential scanning calorimetry; EG = equilibrium studies in the gas phase; ES = equilibrium studies in solution; KG = kinetic studies in the gas phase; KS = kinetic studies in solution; PAC = photoacoustic calorimetry; RSC = reaction solution calorimetry. ^cData rely on $D(\text{Co-Co}) = 64 \text{ kJ/mol}$. ^dExperimental measurements in toluene. The remaining values for the same family of complexes were obtained in acetone. ^e $D6 = D(\text{Rh-cot})$. ^f $D7 = D(\text{Rh-cot})$. ^g $D8 = D(\text{Rh-C}_2\text{H}_4)$. ^hMean bond dissociation enthalpies. ⁱ $D9 = D(\text{Rh-Ph})$. ^j $D10 = D(\text{Ir-I})$ in $\text{Ir}(\text{Cl})(\text{CO})(\text{PMe}_3)_2\text{L}_2$. ^k $E10 = E(\text{Ir-I})$. ^l $D11 = D(\text{Ir-Cl})$ in $\text{Ir}(\text{Cl})_2(\text{CO})(\text{PMe}_3)_2$. ^m $D12 = D(\text{Ir-Cl})$ in $\text{Ir}(\text{Cl})_2(\text{CO})(\text{PEt}_3)_2$. ⁿ $D13 = D(\text{Ir-Cl})$ in $\text{Ir}(\text{Cl})_2(\text{CO})(\text{PR}_3)_2$. ^o $E14 = E(\text{Ir-Me})$. ^pThe uncertainties do not include the error in $D(\text{Ir-H})$. ^q $D15 = D(\text{Ir-C}_2\text{H}_4)$.

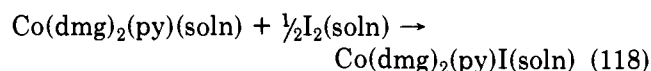
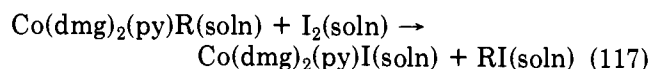
TABLE 11. Bond Length Data (pm) for Some Cobalt Carbonyls^a

molecule	Co-Co	Co-CO _b	Co-CO _t ^c	C-O	Co-L
Co ₂ (CO) ₈ , X ^d	252.4 ± 0.2	192 ± 1	180 ± 1	118 ± 3	
Co ₄ (CO) ₁₂ , X ^e	249.2	204.3	193.4	107	
Co(CO) ₄ H, E ^f			180	114	155.6 ± 1.8
Co ₃ (CO) ₉ (CCL), X ^g	248.0 ± 0.5		179 ± 2	114	189
Co ₃ (CO) ₉ (CMe), X ^h	247		180	110	190
Co ₃ (CO) ₉ [C(OH)], X ⁱ	247.8		181.1 ± 0.8	113 ± 1	192.8 ± 0.8

^aExcept for Co-Co in Co₂(CO)₈ and for Co-H, all the bond lengths are mean values. Key: X = X-ray diffraction; E = electron diffraction. ^bBridging cobalt-carbonyl bond length. ^cTerminal cobalt-carbonyl bond length. ^dReference 248. ^eCarré, F. H.; Cotton, F. A.; Frenz, B. A. *Inorg. Chem.* **1976**, *15*, 380. ^fReference 215. ^gReference 252. ^hSutton, P. W.; Dahl, L. F. *J. Am. Chem. Soc.* **1967**, *89*, 261. ⁱAdams, H.-N.; Fanchinetti, G.; Strähle, J. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 125.

Geno and Halpern,²⁶¹ these differences are only due to the much higher viscosity of ethylene glycol, as compared to toluene, which leads to higher activation enthalpies for recombination (17–25 kJ/mol). $D(\text{Co-C})$ values should thus be nearly solvent-independent.

Recent calorimetric determinations of the enthalpies of reactions 117 (in bromoform) and 118 (in toluene),²⁷⁴ enabled derivation of the values shown in Table 10 for



$D(\text{Co-R})$ (R = Me, Bz, *i*-Pr) on the assumption of canceling solvation enthalpies. As discussed before, this hypothesis seems quite reasonable for reaction 117 but is less likely for eq 118, although, as claimed by authors, toluene must be a poor solvating molecule for the Co(II) system. $D(\text{Co-I}) = 144 \pm 3 \text{ kJ/mol}$ was calculated from $\Delta H^\circ(118)$ and used to derive $D(\text{Co-R})$ from eq 119. As $D(\text{Co-R}) = \Delta H^\circ(117) + D(\text{Co-I}) - D(\text{I-I}) + D(\text{R-I})$ (119)

pointed out by Toscano et al., the surprising feature of the values in Table 10 is the very high $D(\text{Co-Bz})$ as compared to $D(\text{Co-Me})$.²⁷⁴ Keeping in mind the effect of the axial ligand L on cobalt-alkyl bond dissociation enthalpy, the calorimetric value for $D(\text{Co-Bz})$ is close to the one observed in $\text{Co}(\text{dmg})(\text{PMe}_2\text{Ph})\text{Bz}$, although much higher than in $\text{Co}(\text{saloph})(\text{py})\text{Bz}$.

The activation enthalpies for cobalt-benzyl bond cleavage are also low in the complexes $\text{Co}[\text{C}_2(\text{DO})(\text{DOH})_{\text{pn}}](\text{IR})$ (solvent *o*-dichlorobenzene),²⁶² $\text{Co}(\text{dmgBF}_2)_2(\text{H}_2\text{O})\text{Bz}$ (water),²⁶³ $\text{Co}(14\text{-aneN}_4)(\text{H}_2\text{O})\text{Bz}^{2+}$ (water),²⁶⁴ [cobinamide]R (water),²⁶⁵ and B₁₂R (water).²⁶⁵ In the dimethylglyoxime compound, however, the value assumed for the activation enthalpy of the recombination reaction was higher, 21 kJ/mol.²⁶³

It is appropriate to recall at this stage that the considerable interest in the energetics of cobalt-carbon σ bonds is justified by the fact that coenzyme B₁₂ contains one such bond. Moreover, it is thought that the cleavage of that bond is an important step in several types of biological processes.²⁷⁵ The structure of an alkylcobalamin is presented in Figure 5. In coenzyme B₁₂ the group R is an adenosyl (Ado) moiety. Cobin-

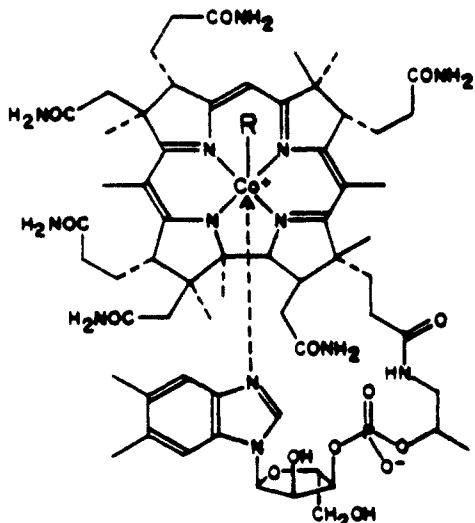


Figure 5. Structure of alkylcobalamins in the base-on form. The axial base and the phosphoribosyl moieties are not present in cobinamides.²⁶⁵

amides lack the axial base and the phosphoribosyl moieties. Most of the studies mentioned above dealt with model compounds. Some models are rather similar to coenzyme B₁₂, in particular the compounds [cobinamide]R, B₁₂R, and [cobinamide]Ado, and recently several values have been reported for the cobalt-adenosyl bond dissociation enthalpy in the coenzyme itself (Table 10).^{267–269}

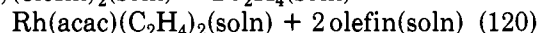
The influence of the axial base can be ascertained through the values presented in Table 10 for [cobinamide]R and B₁₂R, obtained by Schrauzer and Grate in anaerobic aqueous solution.²⁶⁵ In both cases the recombination barrier was taken as 8 kJ/mol. It is noticed that bond dissociation enthalpies for cobinamide complexes are higher than those for cobalamine. This weakening of Co–C bonds caused by the axial base is also observed when the values for [cobinamide]Ado are compared with those for B₁₂Ado. Moreover, the first of these values (obtained from experiments in water at pH 7)²⁶⁶ was derived assuming 13 kJ/mol for the activation enthalpy of radical recombination.

There is some polemic around the value for $D(\text{Co-Ado})$. Halpern and co-workers (experiments in water, pH 4.3)²⁶⁷ obtained $D(\text{Co-Ado}) \approx 112$ kJ/mol, a value that relies on 8 kJ/mol for the activation enthalpy of radical recombination (ΔH^{\ddagger}_{-1}). Finke and Hay arrived at $D(\text{Co-Ado}) = 131$ kJ/mol (ethylene glycol; $\Delta H^{\ddagger}_{-1} = 13$ kJ/mol)²⁶⁹ or $D(\text{Co-Ado}) = 125$ kJ/mol (water, pH 7.0; $\Delta H^{\ddagger}_{-1} = 13$ kJ/mol)²⁶⁸ and claimed that the discrepancy with Halpern's result is mainly due to a large contribution of heterolysis reaction that occurs at low pH. In their recent review,²⁷⁰ Hay and Finke proposed a 126–144 kJ/mol range for $D(\text{Co-Ado})$, by discussing results obtained under different solvents and the model to derive $D(\text{Co-C})$. Geno and Halpern, on the other hand, attributed the discrepancy in the results in water (pH 4) and in ethylene glycol only to different solvent viscosities.²⁶¹ More recently, Halpern and co-workers obtained identical values for $D(\text{Co-C})$ in the complexes B₁₂R (R = neopentyl, cyclopentylmethyl) (Table 10).²⁷¹ The experiments were made in water, at pH 6.8 and 5.0, respectively, and ΔH^{\ddagger}_{-1} was taken as 13 kJ/mol. The activation enthalpy in the case of neopentyl was also measured in ethylene glycol, and the value found was

about 26 kJ/mol higher than in water. The difference was also attributed to the higher viscosity of this solvent, leading to a higher ΔH^{\ddagger}_{-1} .

Another important detail about the experiments involving the cobalamin complexes must be mentioned. As coenzyme B₁₂ exists in solution as an equilibrium between at least two forms, so-called "base-on" and "base-off" (meaning that the axial imidazole base is or is not bonded to cobalt), a correction on the experimentally derived activation enthalpy has to be made in order to obtain the value corresponding to the base-on form. This correction is not negligible (ca. 10–26 kJ/mol); it is solvent-dependent,^{267–271} and it may be expected that its estimates have also some weight in the accuracy of $D(\text{Co-C})$ values.

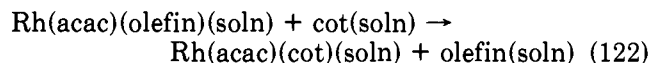
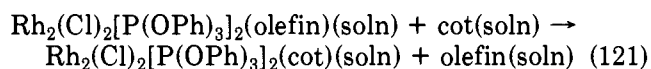
b. Rhodium. The rhodium–olefin bond enthalpy data listed in Table 10 were obtained through calorimetric methods, except in the case of Rh(Cp)(C₂H₄)₂. The aim of these studies was to gain insight into the nature of the metal–olefin bond, by comparing the enthalpies of displacement reactions, illustrated in section III.B by reaction 11 and eq 14, where L¹ and L² are two different olefins. The main difficulty with studies of this type was pointed out in section III.C, by using reaction 25 as an example. The values of those displacement reactions in solution (or with the complexes in the solid state) are usually very small, sometimes even smaller than the assigned uncertainty limits. Therefore, any assumption concerning the cancellation of sublimation and/or solution enthalpies may lead to wrong conclusions about the trend of gas-phase displacement enthalpies, which, as stated above, was the main goal of the investigation. A good example of this point is provided by rhodium–olefin bond dissociation enthalpies in Rh(acac)(olefin)₂, presented in Table 10. Jesse et al. have used differential scanning calorimetry¹²² or reaction solution calorimetry²⁷⁶ to obtain several displacement enthalpies, yielding $D(\text{Rh-olefin}) - D(\text{Rh-C}_2\text{H}_4)$. The DSC values are based on reaction 25 and also on measurements of the sublimation enthalpies of the complexes. As no assumptions were required, it might be expected that these measurements would provide reliable values for $D(\text{Rh-olefin}) - D(\text{Rh-C}_2\text{H}_4)$. However, in the most recent paper,²⁷⁶ the authors reevaluated these differences by using reaction solution calorimetric measurements, which led to the enthalpies of reaction 120 in heptane. The enthalpies



of reaction in the gas phase were then calculated by assuming the cancellation of all solvation terms, giving the values quoted in Table 10, which show bad agreement with the DSC data. Jesse et al. justify the discrepancies by noting that the DSC measurements are dependent not only on the accuracy of the apparatus but also on some assumptions that have been made in the evaluation of the data, such as stoichiometry, Kirchoff's corrections, and definition of the base line for each peak. However, they also note that the approximation of equal solvation enthalpies can yield significant errors, as demonstrated by enthalpies of solvation (sublimation plus solution) in the case of Rh(acac)(va)₂: $\Delta H^{\circ}_{\text{soln}}[\text{Rh}(\text{acac})(\text{va})_2] + 2\Delta H^{\circ}_{\text{soln}}(\text{C}_2\text{H}_4) = -98 \pm 4$ kJ/mol and $\Delta H^{\circ}_{\text{soln}}[\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2] + 2\Delta H^{\circ}_{\text{soln}}(\text{va}) = -127 \pm 4$ kJ/mol.²⁷⁶ If these corrections are applied to

$D(\text{Rh}-\text{va})$ in Table 10, a value of $D8 + (8 \pm 3)$ kJ/mol will be obtained and the trend will be reversed, i.e., $D(\text{Rh}-\text{va}) > D(\text{Rh}-\text{C}_2\text{H}_4)$, in keeping with the DSC results.

The work by Partenheimer and Hoy²⁷⁷ deals also with solution measurements, giving the enthalpies of reactions 121 and 122 in dichloromethane. Once again, the

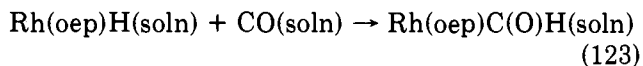


authors assumed that the solvation enthalpies cancel and so $\Delta H^\circ(121)$ and $\Delta H^\circ(122)$ are close to gas-phase values. However, there are not available sublimation, vaporization, and solution enthalpies to check this hypothesis. Additional examples of measurements in solution in which relative values of rhodium-olefin bond dissociation enthalpies can be estimated are abundant.^{14,277-279}

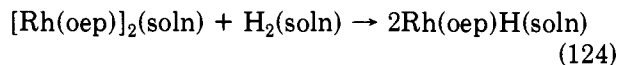
Cramer studied the pyrolysis of $\text{Rh}(\text{Cp})(\text{C}_2\text{H}_4)_2$ in the gas phase and derived the activation enthalpy for the cleavage of one rhodium-ethylene bond, 130 kJ/mol.²⁸⁰ This value was considered an upper limit for $D(\text{Rh}-\text{C}_2\text{H}_4)$, with the activation enthalpy for the reverse reaction being nonzero, but probably small.

Rhodium-olefin bond enthalpy terms could be evaluated through a method similar to the one described for Scheme 6. It may be expected that the reorganization energies equivalent to ER_1 and ER_2 provide a significant contribution to $E(\text{Rh}-\text{olefin})$ values, as suggested by the available X-ray structure for $\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2$ and $\text{Rh}(\text{acac})(\text{cod})$.^{281,282} Both cases show differences between the structures of complexed and free olefins.

Data on rhodium-hydrogen and rhodium-carbon bond enthalpies have only recently become available. Van't Hoff plots of the equilibrium constant of reaction 123 in benzene over the 298-335 K temperature range



led to $\Delta H^\circ(123) = -53 \pm 5$ kJ/mol.²⁸³ The difference $D(\text{Rh}-\text{H}) - D[\text{Rh}-\text{C}(\text{O})\text{H}] = 10 \pm 6$ kJ/mol was calculated from an equation similar to eq 58, by assuming cancellation of the solvation enthalpies. This difference is extremely small, as compared to the one observed for thorium complexes (about 40 kJ/mol). Moreover, the formyl moiety is η^1 -bonded to the rhodium center! An absolute value for $D[\text{Rh}-\text{C}(\text{O})\text{H}]$ (Table 10) can be calculated as follows. The enthalpy of reaction 124 was

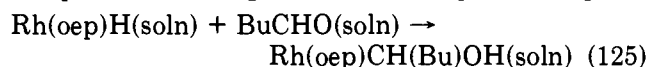


also obtained in benzene by Wayland and co-workers,²⁸⁴ leading to $D(\text{Rh}-\text{Rh}) - 2D(\text{Rh}-\text{H}) = -449 \pm 4$ kJ/mol. An estimate for $D(\text{Rh}-\text{Rh})$ in the dimer, 69 kJ/mol, has been made by the authors, on the basis of the measured activation enthalpy for metal-metal cleavage and a negligible barrier for radical recombination.²⁸⁴ This value yields $D(\text{Rh}-\text{H}) = 259$ kJ/mol and $D[\text{Rh}-\text{C}(\text{O})\text{H}] = 249$ kJ/mol.

Estimates of rhodium-acyl bond dissociation enthalpies in the complexes $(\text{oe})\text{RhC}(\text{O})\text{Rh}(\text{oe})$ and $(\text{oe})\text{RhC}(\text{O})\text{C}(\text{O})\text{Rh}(\text{oe})$ were made by Wayland and

co-workers, based on the measured enthalpies of carbonyl insertion in the dimer $[\text{Rh}(\text{oe})]_2$.²⁸⁵ The values rely on a number of approximations, but they are lower (by ca. 43 and 25 kJ/mol, respectively) than the result quoted in Table 10. Steric effects were invoked to account for the differences.²⁸⁵

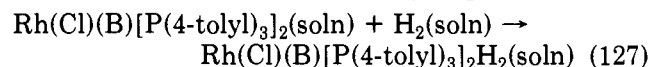
The enthalpy of reaction 125, also reported by Wayland, enabled calculation of $D(\text{Rh}-\text{C})$ in the complex $\text{Rh}(\text{oe})\text{CH}(\text{Bu})\text{OH}$,²⁸⁶ by using the usual assumption concerning solvation enthalpies and eq 126.



$$\Delta H^\circ(125) = D(\text{Rh}-\text{H}) + \Delta H^\circ_f[\text{C}(\text{Bu})(\text{OH})\text{H}_g] - \Delta H^\circ_f(\text{H}_g) - \Delta H^\circ_f(\text{BuCHO}_g) - D(\text{Rh}-\text{C}) \quad (126)$$

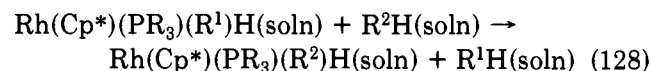
The result obtained, 187 kJ/mol, relies on the above value for $D(\text{Rh}-\text{H})$, data in the Appendix, and the enthalpies of formation of pentanal and pentanol.²² This low value for rhodium-carbon bond dissociation enthalpy was attributed to steric effects. While this is likely, it is noted that carbon-hydrogen bonds are considerably weakened when hydroxyl groups are bonded to the carbon center; e.g., $D[\text{C}(\text{Me})(\text{H})(\text{OH})-\text{H}] - D(\text{Et}-\text{H}) \approx 21$ kJ/mol.²⁸⁷ $D(\text{Rh}-\text{C})$ in $\text{Rh}(\text{oe})\text{CH}_2\text{Bu}$ can therefore be estimated as ca. 208 kJ/mol, only 51 kJ/mol lower than $D(\text{Rh}-\text{H})$.

The enthalpy of oxidative addition reaction 127 in benzene was determined by Drago et al.²⁸⁸ and enabled the calculation of the rhodium-hydrogen mean bond



dissociation enthalpy shown in Table 10. The value quoted is an average between the results of $\Delta H^\circ(127)$ for $\text{B} = \text{P}(4\text{-tolyl})_3$ and tetrahydrothiophene. Note that it is in the same range as $D(\text{Rh}-\text{H})$ in the octaethylporphyrin complex.

Kinetic and mechanistic studies in solution involving complexes of the type $\text{Rh}(\text{Cp}^*)(\text{PR}_3)(\text{R})\text{H}$ have been reported by Jones and Feher.²⁸⁹⁻²⁹¹ These studies led to Gibbs energy diagrams for some alkane and arene activation reactions, which obviously contain information on metal-carbon bond dissociation enthalpies. For example, if in reaction 128



the entropy change is neglected, i.e., $\Delta H^\circ(128) \approx \Delta G^\circ(128)$, then $D(\text{Rh}-\text{Ph}) - D(\text{Rh}-\text{Me}) \approx 55$ kJ/mol and $D(\text{Rh}-\text{Ph}) - D(\text{Rh}-\text{Pr}) \approx 83$ kJ/mol.^{289,291} The striking feature of these results is the large difference between rhodium-phenyl and rhodium-alkyl bond dissociation enthalpies as compared, e.g., to $D(\text{Ph}-\text{H}) - D(\text{alkyl}-\text{H})$. The entropic factor is not a likely explanation, and the cancellation of solvation enthalpies seems reasonable in the case of reaction 128.

A final mention for rhodium complexes is made to a kinetic estimate of $D[\text{Rh}-\text{C}(\text{Ph})(\text{OMe})\text{H}]$ in the complex $\text{Rh}(\text{NC}_3\text{H}_3\text{C}_6\text{H}_3\text{CO})(\text{Cl})(\text{py})\text{C}(\text{Ph})(\text{OMe})\text{H}$ (Table 10).²⁹² This low value was derived by assuming 8 kJ/mol for the radical recombination reaction.

c. Iridium. Iridium-hydrogen mean bond dissociation enthalpies and bond enthalpy terms in $\text{Ir}(\text{X})(\text{CO})(\text{PPh}_3)_2\text{H}_2$ complexes ($\text{X} = \text{halogen}$) were determined by Vaska and Werneke,¹¹³ as discussed in section

III.B, and are presented in Table 10.

Blake and co-workers have also carried out thermochemical studies leading to Ir-H and Ir-C bond enthalpies in Vaska's type of complexes.^{110-112,293-296} In one of these studies,¹¹¹ the enthalpies of reaction 129 $\text{trans-Ir}(\text{Cl})(\text{CO})(\text{PMe}_3)_2(\text{soln}) + \text{RI}(\text{soln}) \rightarrow \text{Ir}(\text{Cl})(\text{CO})(\text{PMe}_3)_2(\text{I})\text{R}(\text{soln})$ (129)

were obtained by titration calorimetry (R = I, Me, Et, Pr, *i*-Pr, Bz, C(O)Me, C(O)Ph). These data, together with measured solution enthalpies, literature sublimation or vaporization enthalpies for RI, and the assumption of equal $\Delta H^\circ_{\text{g}}$ for both complexes in reaction 129, led to gas-phase values for $\Delta H^\circ(129)$, from which the bond values reported in Table 10 were evaluated.

Yoneda and Blake used the reaction with R = I to derive differences $D(\text{Ir-R}) - D(\text{Ir-I})$ through eq 130, which can be obtained from two equations similar to eq 19 (see also Scheme 5), one for $\text{L}^1\text{L}^2 = \text{RI}$ and the other for $\text{L}^1\text{L}^2 = \text{I}_2$. $\Delta H^\circ_{\text{g}}(129)$ refers to $\text{L}^1\text{L}^2 = \text{I}_2$; $D(\text{Ir-R}) - D(\text{Ir-I}) = \Delta H^\circ_{\text{g}}(129) - \Delta H^\circ_{\text{g}}(129) + D(\text{R-I}) - D(\text{I-I})$ (130)

$D(\text{R-I})$ and $D(\text{I-I})$ are the bond dissociation enthalpies of RI and I_2 . Note that $D(\text{Ir-I})$ is the bond dissociation enthalpy in the complex $\text{Ir}(\text{Cl})(\text{CO})(\text{PMe}_3)_2\text{I}_2$ and not in $\text{Ir}(\text{Cl})(\text{CO})(\text{PMe}_3)_2(\text{I})\text{R}$. The mean value $\bar{D}(\text{Ir-I})$ for the dissociation of both iodines was obtained from $\Delta H^\circ_{\text{g}}(129)$ as 189 ± 4 kJ/mol. $D(\text{Ir-R})$ values reported in Table 10 were therefore calculated through eq 130 by making $D(\text{Ir-I}) = \bar{D}(\text{Ir-I})$.

Evaluation of $E(\text{Ir-R})$ values uses two schemes similar to Scheme 5, or two equations similar to eq 18, one for $\text{L}^1\text{L}^2 = \text{RI}$ and the other for $\text{L}^1\text{L}^2 = \text{I}_2$. Assuming $E(\text{Ir-I}) \approx E'(\text{Ir-I})$ and $\text{ER}_c \approx \text{ER}'_c$, eq 131 is obtained, $E(\text{Ir-R}) - E(\text{Ir-I}) = \Delta H^\circ_{\text{g}}(129) - \Delta H^\circ_{\text{g}}(129) + E(\text{R-I}) - D(\text{I-I}) + \text{ER}_1$ (131)

where ER_1 is the reorganization energy of R, when it goes from RH to the complex. If this energy difference is small, approximate values for $D(\text{Ir-R}) - E(\text{Ir-I})$ can be calculated from eq 131 after $E(\text{R-I})$ are known. The Laidler scheme provides just one value for $E(\text{C-I})$, 233.7 kJ/mol,¹⁹ which is fairly reliable for the iodoalkanes considered (i.e., it yields acceptable agreement between experimental and calculated enthalpies of formation) but not for BzI, PhC(O)I, and MeC(O)I. Methyl iodide is, of course, another exception as the Laidler scheme has no parameter for C-H in methane (Appendix). In these four cases $E(\text{R-I})$ were obtained from eq 132

$$E(\text{R-I}) = D(\text{R-I}) - \text{ER}_R \quad (132)$$

under the assumption that the reorganization energies of R from RI and RH are identical (i.e., R has identical structures in RI and RH). $D(\text{R-I})$ and ER_R are listed in the Appendix. When this assumption is applied to the three iodoalkanes, the obtained values compare within 10 kJ/mol with the ones derived from the Laidler term.

The bond enthalpy terms calculated by the above method are displayed in Table 10, where $E10 = E(\text{Ir-I})$. They should be regarded as provisional results, intended to give approximate values for the differences $E(\text{Ir-R}) - E(\text{Ir-R}')$. A more accurate set of data will only be possible to obtain when the molecular structures

of the complexes are available.

In another paper²⁹³ Blake and co-workers report the enthalpies of several reactions similar to eq 133, where AB = HCl, HBr, Cl_2 , Br_2 , and I_2 . The gas-phase $\text{trans-Ir}(\text{Cl})(\text{CO})(\text{PPh}_3)_2(\text{soln}) + \text{AB}(\text{soln}) \rightarrow \text{Ir}(\text{Cl})(\text{CO})(\text{PPh}_3)_2(\text{A})\text{B}(\text{soln})$ (133)

action enthalpies were evaluated through an equation identical to eq 12, under the assumption that the solution and sublimation terms cancel, except $\Delta H^\circ_{\text{soln}}(\text{AB})$. In the cases of HCl, HBr, and Cl_2 , where the standard reference state is a gas, that assumption seems reasonable. However, in the cases of bromine and iodine, it may be necessary to consider their vaporization and sublimation enthalpies. Blake's values for $\Delta H^\circ_{\text{g}}(133)$ were therefore corrected in these two cases, and the consequences of the correction will be shown below.

Iridium-halogen mean bond dissociation enthalpies are easily calculated from eq 134 when A = B: $\bar{D}(\text{Ir-A}) = 298, 256, \text{ and } 178$ kJ/mol, for A = Cl, Br, and I, respectively. As far as $E(\text{Ir-A})$ values are concerned,

$$\bar{D}(\text{Ir-A}) = [-\Delta H^\circ_{\text{g}}(133) + D(\text{A-A})]/2 \quad (134)$$

once again we are not aware of the relevant molecular structures. Nevertheless, it may be assumed that the reorganization energy of the $\text{Ir}(\text{Cl})(\text{CO})(\text{PPh}_3)_2$ moiety in those complexes is similar to Vaska's ER_c for the same fragment from $\text{Ir}(\text{Cl})(\text{CO})(\text{PPh}_3)_2\text{H}_2$, ca. 50 kJ/mol (see Scheme 5 and the discussion in section III.B). By using eq 135, $E(\text{Ir-A})$ can thus be obtained: 323, 281, and 203 kJ/mol, for A = Cl, Br, and I, respectively.

$$E(\text{Ir-A}) = \bar{D}(\text{Ir-A}) + \text{ER}_c/2 \quad (135)$$

The two remaining reactions relate to HCl and HBr oxidative addition. $E(\text{Ir-H})$ can be derived in both cases if the above $E(\text{Ir-Cl})$ or $E(\text{Ir-Br})$ values are introduced in eq 136. The results are 271 kJ/mol for A = Cl and 262 kJ/mol for A = Br, in close agreement with Vaska's mean bond enthalpy term, $\langle E(\text{Ir-H}) \rangle = 271$ kJ/mol.

$$E(\text{Ir-H}) = -E(\text{Ir-A}) - \Delta H^\circ_{\text{g}}(133) + D(\text{A-H}) + \text{ER}_c \quad (136)$$

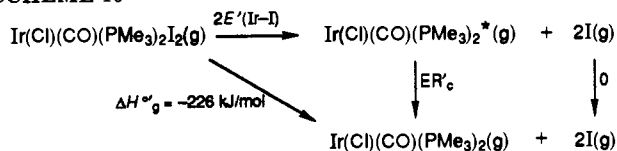
$D(\text{Ir-H})$ are now easily calculated by subtracting $\text{ER}_c/2$ from the bond enthalpy terms (see Scheme 5). The results are collected in Table 10.

The same procedure has been used to obtain iridium-hydrogen bond enthalpy data for the analogous complex $\text{Ir}(\text{Cl})(\text{CO})(\text{PMePh}_2)_2(\text{Cl})\text{H}$ (Table 10), although the value of ER_c can be different in this case. Indeed the relatively high $E(\text{Ir-H})$ suggests that ER_c will be smaller for the $\text{Ir}(\text{Cl})(\text{CO})(\text{PMePh}_2)_2$ fragment than for $\text{Ir}(\text{Cl})(\text{CO})(\text{PPh}_3)_2$.

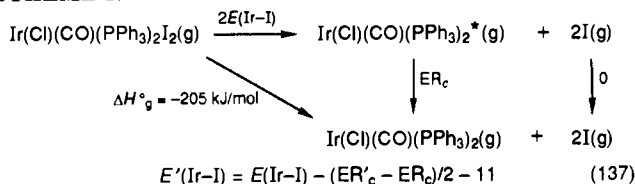
It is now possible to have an idea of the absolute values of $E(\text{Ir-R})$ in the complexes $\text{Ir}(\text{Cl})(\text{CO})(\text{PMe}_3)_2(\text{I})\text{R}$. Consider the gas-phase enthalpies of reaction 129 with R = I (-226.4 ± 7.9 kJ/mol)¹¹¹ and reaction 133 with AB = I_2 (-204.7 ± 4.1 kJ/mol)²⁹³ and also Schemes 16 and 17 or eq 137.

Since there are no values for ER_c and ER'_c , it is assumed, in a first approximation, that they are similar. Taking the value given above for $E(\text{Ir-I})$, $E10 = E'(\text{Ir-I}) \approx 192$ kJ/mol is obtained. This yields, for example (see Table 10), $E(\text{Ir-H}) = E10 + 109 \approx 301$ kJ/mol. If the uncertainty intervals are considered, it may be noticed

SCHEME 16



SCHEME 17



that this value is not far from the mean bond enthalpy term $\langle E(\text{Ir}-\text{H}) \rangle$ in $\text{Ir}(\text{Cl})(\text{CO})(\text{PPh}_3)_2\text{H}_2$ and $\text{Ir}(\text{Cl})(\text{CO})(\text{PPh}_3)_2(\text{X})\text{H}$ complexes. If it is imposed that $E'(\text{Ir}-\text{I}) = E(\text{Ir}-\text{I})$, then the value of $E10$ will be slightly higher, ca. 203 kJ/mol, leading to $E(\text{Ir}-\text{H}) \approx 312$ kJ/mol.

Further information on iridium-hydrogen mean bond dissociation enthalpies in the same family of complexes is also shown in Table 10. These data were derived from equilibrium studies of H_2 oxidative addition reactions in chlorobenzene²⁹⁴ or toluene²⁹⁷ (see reaction 20), under the assumption that solvation enthalpies cancel. Although the reported enthalpies of reaction do not include error bars, it can be seen that the average $E(\text{Ir}-\text{H})$ is not far from the value 271 kJ/mol suggested above.

Another paper by Blake and co-workers¹¹² deals with the thermochemical study of reaction 15. In this case, all the solvation enthalpies were available and the authors could derive $\Delta H^\circ_{\text{g}}(15)$ without the usual assumptions. For $\text{L} = \text{PMe}_3$ and PEt_3 , they obtained $\Delta H^\circ_{\text{g}}(15) = -152 \pm 17$ and -156 ± 12 kJ/mol, respectively.

Equations 138 and 139 can be derived from Scheme 5, giving $D[\text{Ir}-\text{C}(\text{O})\text{Me}]$ and $E[\text{Ir}-\text{C}(\text{O})\text{Me}]$. Estimates of $E[\text{Ir}-\text{C}(\text{O})\text{Me}]$ can be achieved if $E(\text{Ir}-\text{Cl})$ is transferred from $\text{Ir}(\text{Cl})(\text{CO})(\text{PPh}_3)_2\text{Cl}_2$ and if $E[\text{MeC}(\text{O})-\text{Cl}]$ is known. The Laidler scheme does not provide a term

$$E[\text{Ir}-\text{C}(\text{O})\text{Me}] = -\Delta H^\circ_{\text{g}}(15) - D(\text{Ir}-\text{Cl}) + D[\text{MeC}(\text{O})-\text{Cl}] \quad (138)$$

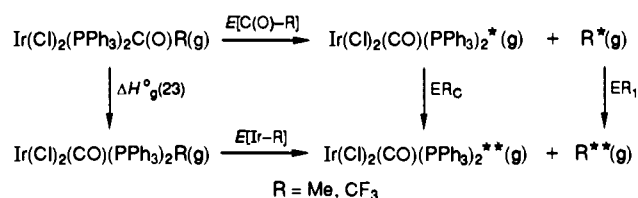
$$E[\text{Ir}-\text{C}(\text{O})\text{Cl}] = -\Delta H^\circ_{\text{g}}(15) - E(\text{Ir}-\text{Cl}) + E[\text{MeC}(\text{O})-\text{Cl}] + \text{ER}_c + \text{ER}_1 \quad (139)$$

for $E(\text{C}-\text{Cl})$ in acetyl chloride, and thus we have to apply an identical method to the one described above for acetyl iodide, i.e., to consider that the reorganization energy of MeCO is about -68 kJ/mol and use $D[\text{MeC}(\text{O})-\text{Cl}]$ (Appendix). ER_1 is expected to be small, but ER_c can contribute significantly to the iridium-carbon bond enthalpy terms and most probably will increase the $E[\text{Ir}-\text{C}(\text{O})\text{Me}]$ values quoted in Table 10.

$D[\text{Ir}-\text{C}(\text{O})\text{Me}]$ can be obtained as a function of $D(\text{Ir}-\text{Cl}) = D11$ for $\text{L} = \text{PMe}_3$ or $D(\text{Ir}-\text{Cl}) = D12$ for $\text{L} = \text{PEt}_3$. The results are also displayed in Table 10. As it is expected that $D11 \approx D12$, $D[\text{Ir}-\text{C}(\text{O})\text{Cl}]$ must be similar for both phosphines. A crude estimate of this value, 196 kJ/mol, can be made by using the $\text{Ir}-\text{Cl}$ mean bond dissociation given above (298 kJ/mol).

The effect of the phosphine (L) on $D[\text{Ir}-\text{C}(\text{O})\text{Me}]$ can be estimated from the enthalpies of oxidative addition reactions of $\text{MeC}(\text{O})\text{Cl}$ to *trans*- $\text{Ir}(\text{Cl})(\text{CO})(\text{L})$.¹¹² Al-

SCHEME 18



though these are solution data, it can be expected that the trend is not dramatically modified in the gas phase. For example, it is seen in Table 10 that the values for PMe_3 and PEt_3 are quite close to each other, as it is also the case for the gas-phase results discussed above. Note that a constant value for $D(\text{Ir}-\text{Cl}) = D13$ was also assumed to obtain the data in the table. The enthalpies of oxidative addition in solution of $\text{EtC}(\text{O})\text{Cl}$, *i*- $\text{PrC}(\text{O})\text{Cl}$, $\text{PhC}(\text{O})\text{Cl}$, $\text{CH}_2\text{ClC}(\text{O})\text{Cl}$, and $\text{CHCl}_2\text{C}(\text{O})\text{Cl}$ to *trans*- $\text{Ir}(\text{Cl})(\text{CO})(\text{PMe}_2\text{Ph})_2$ were also given in the same paper by Blake et al.¹¹² and could be used to derive relative $D[\text{Ir}-\text{C}(\text{O})\text{R}]$ values, but with exception of $\text{R} = \text{Ph}$, for which $D[\text{Ir}-\text{C}(\text{O})\text{Ph}] = 453 - D13$ kJ/mol is obtained, the auxiliary data are not available. It can, however, be predicted that these bond dissociation enthalpies are not strongly dependent on R .

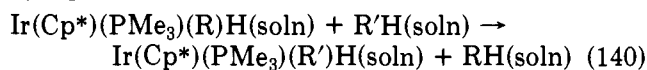
The data provided by Blake's group point to some interesting conclusions, even though extensions of the studies are clearly warranted, together with the determination of molecular structures and the theoretical calculations of the reorganization energies (particularly ER_c). In general, the $E(\text{Ir}-\text{L})$ and $D(\text{Ir}-\text{L})$ values are in the expected order, considering uncertainties. There are also some surprises, such as $D[\text{Ir}-\text{C}(\text{O})\text{Me}] - D[\text{Ir}-\text{C}(\text{O})\text{Ph}] \approx -23$ kJ/mol, compared to 33 kJ/mol for the manganese complexes. Nevertheless, it must be stressed that the data for $\text{Ir}(\text{Cl})(\text{CO})(\text{PMe}_3)_2(\text{I})\text{R}$ were derived on the basis of canceling sublimation enthalpies for the complexes in reaction 129 but using the vaporization enthalpies of RI . If these were not considered, i.e., if it were assumed that the enthalpy of the reaction in the gas phase is close to the enthalpy of reaction with reactants and products in their standard reference states, then a value of $D[\text{Ir}-\text{C}(\text{O})\text{Me}] - D[\text{Ir}-\text{C}(\text{O})\text{Ph}] \approx 0$ kJ/mol would be obtained. This stems from the fact that $\Delta H^\circ_{\text{v}}[\text{PhC}(\text{O})\text{I}] = 61.9$ kJ/mol whereas $\Delta H^\circ_{\text{v}}[\text{MeC}(\text{O})\text{I}] = 38.5$ kJ/mol.²² It also provides another example of how difficult it is to select the best assumption regarding enthalpies of sublimation. In the present case, however, the values in Table 10 are favored, after the discussion made in section III.B (reaction 15). Moreover, note that $D[\text{MeC}(\text{O})-\text{H}] - D[\text{PhC}(\text{O})-\text{H}] = -12$ kJ/mol.

Blake et al.^{120,295} have also made a calorimetric (DSC) study of reaction 23 for several R (CF_3 , CHF_2 , CH_2F , *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2$, *p*- $\text{MeC}_6\text{H}_4\text{CH}_2$, *p*- $\text{MeOC}_6\text{H}_4\text{CH}_2$). If the enthalpies of sublimation cancel for each pair of complexes, then $\Delta H^\circ_{\text{g}}(23) = -84 \pm 4$, -66 ± 8 , -46 ± 5 , -16 ± 1 , -14 ± 2 , and -13 ± 4 kJ/mol for R in the above order. By noticing that $\Delta H^\circ_{\text{g}}(23)$ for CH_nF_m ($n + m = 3$) varies linearly with n , the enthalpy change for the migration of methyl could be predicted by extrapolation to $n = 0$.²⁹⁵ The obtained value, -27 ± 5 kJ/mol, together with the one for CF_3 , yields $E(\text{Ir}-\text{CF}_3) - E(\text{Ir}-\text{Me}) \geq 57$ kJ/mol. This difference was calculated from two schemes similar to Scheme 18 by using the following assumptions: (1) the sum of the two reorganization

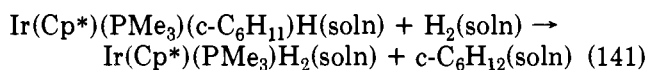
energies is identical in both schemes, and (2) $E[\text{C}(\text{O})-\text{CF}_3] \geq E[\text{C}(\text{O})-\text{Me}]$. The same assumptions were applied to the remaining ligands, giving the values presented in Table 10, where $E_{14} = E(\text{Ir}-\text{Me})$. The data for $\text{R} = \text{CH}_2\text{Cl}$, CH_2OPh , and $\text{C}(\text{O})\text{OEt}$ ²⁹⁶ were also obtained through the same method.

If it is accepted that differences $E(\text{M}-\text{CF}_3) - E(\text{M}-\text{Me})$ are close for different metals, then $E(\text{Ir}-\text{CF}_3) - E(\text{Ir}-\text{Me})$ is in contrast to $E(\text{Mn}-\text{CF}_3) - E(\text{Mn}-\text{Me})$ in $\text{Mn}(\text{CO})_5\text{L}$ complexes (Table 5), particularly if the PIMS data are considered. Although assumption 2 cannot be discussed because there are no reported structures for the molecules considered, it may be expected that the reorganization energies E_{r} do not contribute significantly to the difference $E(\text{Ir}-\text{CF}_3) - E(\text{Ir}-\text{Me})$. It is, however, emphasized that the relative values shown in Table 10 can be affected by an error of at least 10 kJ/mol. For example, it is unexpected that $D(\text{Ir}-\text{CH}_2\text{Cl}) > D(\text{Ir}-\text{CH}_2\text{F})$.

Bergman and co-workers have recently reported enthalpies of reaction 140, for several R and R', obtained by equilibrium studies in solution.^{298,299} The values

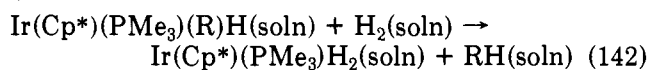


were calculated by assuming that the entropy changes of the reactions are negligible; i.e., $\Delta H^\circ(140) \approx \Delta G^\circ(140)$. If the net solvation effects are small, these enthalpies yield $D(\text{Ir}-\text{R}) - D(\text{Ir}-\text{R}')$, by using the carbon-hydrogen bond dissociation enthalpies in the Appendix. On the other hand, kinetic studies in solution afforded the activation enthalpy for the reductive elimination of RH in the case of $\text{R} = \text{c-C}_6\text{H}_{11}$, 149 ± 2 kJ/mol.²⁹⁹ By estimating a value of 21 kJ/mol for the activation of the reverse (oxidative addition) reaction, it is concluded that $D(\text{Ir}-\text{C}_6\text{H}_{11}) + D(\text{Ir}-\text{H}) \approx 528$ kJ/mol.²⁹⁹ The key to finding absolute $D(\text{Ir}-\text{R})$ values is therefore $D(\text{Ir}-\text{H})$. This has been measured as 305 ± 18 kJ/mol by photoacoustic calorimetry³⁰⁰ and confirmed in the same paper by determining the enthalpy of reaction 141 from reaction solution calorimetric



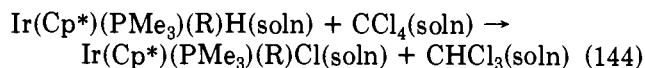
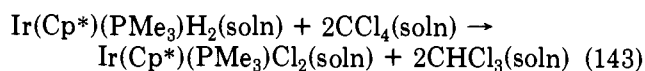
measurements. From $\Delta H^\circ(141) = -65 \pm 6$ kJ/mol, the difference $D(\text{Ir}-\text{H}) - D(\text{Ir}-\text{C}_6\text{H}_{11}) = 101 \pm 7$ kJ/mol is calculated. This and the above value for the sum of the two bond enthalpies, 528 kJ/mol, lead to $D(\text{Ir}-\text{H}) = 315$ kJ/mol. The data presented in Table 10 were derived on the basis of the average $D(\text{Ir}-\text{H}) = 310$ kJ/mol, as recommended by the authors.³⁰⁰

The enthalpies of reaction 142 in toluene for $\text{R} = \text{Ph}$ and $\text{c-C}_6\text{H}_{11}$ were determined in a recent reaction-solution calorimetry study.³⁰⁰ They also yield differences $D(\text{Ir}-\text{H}) - D(\text{Ir}-\text{R})$, by considering that the solvation enthalpies cancel. The $D(\text{Ir}-\text{R})$ results displayed in Table 10 rely also on the recommended value for $D(\text{Ir}-\text{H})$.

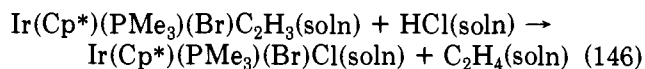
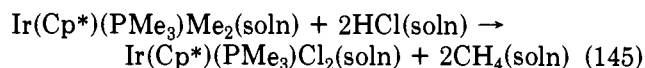


In the same paper Nolan et al. report values for iridium-halogen mean bond dissociation enthalpies, calculated from the enthalpies of reaction of the dihydride complex with CCl_4 , CBr_4 , and MeI :³⁰⁰ $\bar{D}(\text{Ir}-\text{Cl}) = 378 \pm 2$ kJ/mol, $\bar{D}(\text{Ir}-\text{Br}) = 317 \pm 3$ kJ/mol, and

$\bar{D}(\text{Ir}-\text{I}) = 265 \pm 5$ kJ/mol.²⁰⁵ These results rely again on $D(\text{Ir}-\text{H}) = 310$ kJ/mol. An important point was made about the reaction with CCl_4 , reaction 143.³⁰⁰ $\Delta H^\circ(143) = -347 \pm 3$ kJ/mol is about twice the measured enthalpies of reaction 144 for $\text{R} = \text{Cl}$, Ph , and $\text{c-C}_6\text{H}_{11}$ (-175 ± 3 , -171 ± 6 , -180 ± 6 kJ/mol), indicating that the effect of R in $D(\text{Ir}-\text{H})$ is small.

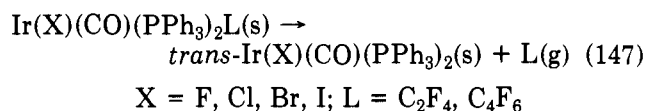


$D(\text{Ir}-\text{Cl}) \approx \bar{D}(\text{Ir}-\text{Cl}) = 378 \pm 5$ kJ/mol was used together with the calorimetric enthalpies of reactions 145 and 146 to calculate $\bar{D}(\text{Ir}-\text{Me})$ and $D(\text{Ir}-\text{C}_2\text{H}_3)$ (Table 10), under the usual assumption concerning solvation enthalpies.³⁰¹



The most surprising trend in the iridium family under discussion is $D(\text{Ir}-\text{Ph}) > D(\text{Ir}-\text{H})$. As recognized by the authors,³⁰⁰ there is no other example of such a trend. The difference $D(\text{Ir}-\text{Ph}) - D(\text{Ir}-\text{Me}) = 94$ kJ/mol is also extremely high, although in this case a mean bond dissociation enthalpy and a bond dissociation enthalpy are being compared. Recall that for the analogous rhodium family $D(\text{Rh}-\text{Ph}) - D(\text{Rh}-\text{Me}) = 55$ kJ/mol. The value for $D(\text{Ir}-\text{C}_2\text{H}_3) - D(\text{Ir}-\text{Me}) = 83$ kJ/mol is also very high, compared, for example, to $D(\text{C}_2\text{H}_3-\text{H}) - D(\text{Me}-\text{H}) = 22$ kJ/mol (Appendix). Additional thermochemical studies on this important family of complexes, aiming to confirm the above trends, are clearly warranted. In addition, some discrepancy between the calorimetric and the equilibrium values is apparent: while the former give $D(\text{Ir}-\text{Ph}) - D(\text{Ir}-\text{C}_6\text{H}_{11}) = 128$ kJ/mol, the latter yield 103 kJ/mol. Although this is not unreasonable, given the approximations considered, particularly in the equilibrium studies (zero entropy change for reaction 140), the calorimetric values are, in principle, more reliable.

The attention is now turned to iridium-olefin bond enthalpies. Mortimer and co-workers^{117,302} studied the thermochemistry of reactions 147. By assuming that the sublimation enthalpies are similar for both complexes, $\Delta H^\circ(147)$ can be identified with iridium-olefin bond dissociation enthalpies. The results are shown in Table 10.



The decomposition temperatures of these iridium complexes, i.e., the temperatures corresponding to the maximum rate of decomposition, are about 450 K. However, as discussed in section III.C, the reaction enthalpies at 298 K should be close to the reported value.

As pointed out by the authors, the Dewar-Chatt-Duncanson model^{123,124} predicts that for a given olefin the metal-olefin bond strength increases in the order $\text{F} < \text{Cl} < \text{Br} < \text{I}$ when π bonding is predominant and

TABLE 12. Group 10 M-H and M-C Bond Enthalpies

molecule ^a	method/ ref ^b	<i>D</i> , kJ/mol	<i>E</i> , kJ/ mol	molecule ^a	method/ ref ^b	<i>D</i> , kJ/mol	<i>E</i> , kJ/ mol
Ni(cod) ₂	RS/304 ^c	209		Pt(Cl) ₂ (L)CH ₂ CH ₂ CH ₂	DSC/118 ^c		
Ni[P(o-Tolyl) ₃] ₂ L	ES/306			L = (py) ₂		117	
L = C ₂ H ₄		D16 ± 14 ^d		L = (4-Mepy) ₂		113	
L = <i>trans</i> -(Me ₃ CCH) ₂		D16 - 23		L = bipy		121	
L = <i>trans</i> -(CHCN) ₂		D16 + 44					
[Pd(C ₃ H ₅)Cl] ₂	DSC/121		262	Pt(Br) ₂ (L)CH ₂ CH ₂ CH ₂	DSC/118 ^c		
<i>cis</i> -Pd(Cl) ₂ (cod)	CMC/312		344	L = (py) ₂		117	
Pd(Cl) ₂ L	RSC/313			L = (4-Mepy) ₂		114	
L = (CH ₂ NMe ₂) ₂		D17 ^e		L = bipy		124	
L = nbd		D17 - 70		Pt(PPh ₃) ₂ (dpcb)	RSC/324 ^{e,h}	150 ± 16	217
L = cod		D17 - 63		Pt(PPh ₃) ₂ (bcpd)	RSC/324 ^h		(217)
L = 1,5-C ₈ H ₁₀		D17 - 96		Pt(Ph ₂ PCH ₂) ₂ (Me)CH ₂ COMe	ES/241	D20 - 18 ⁱ	
L = dp		D17 - 82		Pt(PPh ₃) ₂ L	RSC/324 ^h		
L = cot		D17 - 92		L = C ₂ H ₄		152 ± 18	
L = dcpd		D17 - 95		L = PhCHCH ₂		169 ± 37	
Pd(Cl) ₂ (py)L	RSC/314			L = <i>cis</i> -C ₂ H ₂ Ph ₂		194 ± 37	
L = C ₂ H ₄		D18 ^f		L = <i>trans</i> -C ₂ H ₂ Ph ₂		210 ± 37	
L = <i>c</i> -C ₈ H ₁₄		D18 + 9		L = C ₂ Ph ₂		181 ± 17	
L = <i>cis</i> -(MeCH) ₂		D18 + 6		L = C ₂ (CN) ₄		277 ± 37	
L = <i>cis</i> -C ₇ H ₁₂		D18 + 5		L = pcbd		177 ± 27	
L = <i>c</i> -C ₈ H ₁₀		D18		Pt(Cl) ₂ (cod)	CMC/312 ^h	398 ± 24	
L = CH ₂ CHPh		D18 - 1		Pt(AsMe ₃)(X)(Me)L	DSC/116		
L = <i>c</i> -C ₅ H ₈		D18 - 2		X = Cl, L = C ₂ F ₄		52 ± 1	
Pd(I)(bipy)Me ₃	DSC/316 ^c	136 ± 6		X = Br, L = C ₂ F ₄		48 ± 1	
Pt(Cp)Me ₃	KG/317	163 ± 21		X = Cl, L = C ₄ F ₆		69 ± 2	
Pt(Cp)Me ₃	SB/173		(195)	X = Br, L = C ₄ F ₆		61 ± 2	
Pt(Cp) ₂ Me ₂	SB/173		(195)	Pt(AsMe ₂ Ph)(X)(Me)L	DSC/116		
<i>trans</i> -Pt(PEt ₃) ₂ Ph ₂	CMC/320	D19 - (87 ± 12) ^g	159 ^h	X = Cl, L = C ₄ F ₆		73 ± 1	
				X = Br, L = C ₄ F ₆		80 ± 1	
<i>cis</i> -Pt(PEt ₃) ₂ Me ₂	CMC/312 ^{e,h}	269 ± 11	245	Pt(Cl) ₂ (py)L	RSC/337		
<i>cis</i> -Pt(PEt ₃) ₂ (<i>o</i> -tolyl) ₂	CMC/312 ^{e,h}	298 ± 18	254	L = C ₂ H ₄		D21 ^k	
<i>cis</i> -Pt(PEt ₃) ₂ (Cl)Me	CMC/312 ^h	251 ± 30	227	L = <i>cis</i> - <i>c</i> -C ₈ H ₁₄		D21 - 2	
<i>cis</i> -Pt(PEt ₃) ₂ (Cl)(<i>o</i> -tolyl)	CMC/312 ^h	300 ± 34	256	L = <i>c</i> -C ₇ H ₁₂		D21 - 5	
<i>trans</i> -Pt(PPh ₃) ₂ (Cl)H	RSC/324 ^h	307 ± 37	307	L = <i>cis</i> -(MeCH) ₂		D21 - 10	
<i>cis</i> -Pt(PPh ₃) ₂ (I)Me	RSC/324 ^h	242 ± 38	218	L = CH ₂ CHPh		D21 - 19	
<i>trans</i> -Pt(PEt ₃) ₂ (Cl)Et	ES/326 ^h	206	196	L = <i>c</i> -C ₆ H ₈		D21 - 19	
Pt(PPh ₃) ₂ (Cl)C(O)Ph	DSC/5 ^h	>232	>288	L = CH ₂ CHC ₆ H ₄ NO ₂		D21 - 24	
Pt(PMe ₂ Ph) ₂ (Cl)(Me) ₂ C(O)Me	DSC/119	306 ± 4 ⁱ		L = <i>c</i> -C ₆ H ₁₀		D21 - 24	
Pt(X) ₂ CH ₂ CH ₂ CH ₂	DSC/118 ^c						
X = Cl		120					
X = Br		122					

^a Key: bcpd = platinum-benzocyclopentene-1,2-dione metallacycle; bipy = 2,2'-bipyridine; cod = 1,5-cyclooctadiene; cot = 1,3,5,7-cyclooctatetraene; dcpd = dicyclopentadiene; dp = dipentene; dpcb = platinum-diphenylcyclobutenone metallacycle; Mepy = methylpyridine; nbd = 2,5-norbornadiene; Otolyl = OC₆H₄Me; pcbd = 3-phenylcyclobutene-1,2-dione; py = pyridine. ^b Key: CMC = Calvet microcalorimetry; DSC = differential scanning calorimetry; ES = equilibrium studies in solution; KG = kinetic studies in the gas phase; RSC = reaction solution calorimetry; SB = static bomb combustion calorimetry. ^c Mean bond dissociation enthalpies. ^d D16 = *D*(Ni-P) in Ni[P(o-Tolyl)₃]₂. ^e D17 = *D*[Pd-(CH₂NMe₂)₂]. ^f D18 = *D*(Pd-C₂H₄). ^g D19 = *D*(Pt-Cl) in *trans*-Pt(PEt₃)₂(Ph)Cl. ^h Data rely on *E*(Pt-Cl) = 290 kJ/mol. ⁱ *D*(Pt-Me) + *D*(Pt-C(O)Me). ^j D20 = *D*(Pt-OMe) in Pt(Ph₂PCH₂)₂(Me)OMe. ^k D21 = *D*(Pt-C₂H₄).

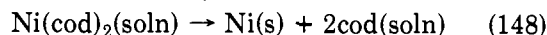
the trend is reversed when the σ -bonding component is more significant. If $E(\text{Ir-L})$ values parallel $D(\text{Ir-L})$ in Table 10, then these results imply a balance of both types of bonding, as suggested by the minimum for X = Br.

The final set of values presented in Table 10 for iridium complexes was obtained by Jesse et al.^{122,276} as described for the rhodium analogues. The discussion is also similar, and so are the conclusions. The listed iridium-olefin bond dissociation enthalpies lie in a narrow range, precluding the identification of trends due to substituent effects.

As in the case of rhodium, literature data from which values of iridium-olefin bond dissociation enthalpies in solution can be derived are abundant.^{14,294,303}

8. Group 10

a. Nickel. Tolman and co-workers³⁰⁴ measured the enthalpy change associated with reaction 148 by titration calorimetry. The decomposition of Ni(cod)₂ was achieved by adding catalytic amounts of carbon tetra-



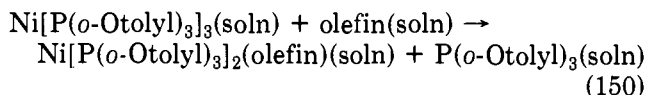
chloride to a toluene solution of the complex. The authors derived $\bar{D}(\text{Ni-cod})$ through eq 149, which implies the cancellation of the solution enthalpies and also $\Delta H^\circ_s[\text{Ni(cod)}_2] = 2\Delta H^\circ_s(\text{cod}) = 82.0 \pm 1.1 \text{ kJ/mol}$.²² The result is presented in Table 12.

$$\bar{D}(\text{Ni-cod}) = [\Delta H^\circ(148) + \Delta H^\circ_f(\text{Ni,g})]/2 \quad (149)$$

It is not possible to discuss the influence of the solvation terms on the value of $\bar{D}(\text{Ni-cod})$ as there are no available data. However, there is indirect evidence that the assumptions may be reasonable. Tolman et al. used this value to obtain several nickel-phosphorus bond dissociation enthalpies in Ni(PR₃)₄ complexes,³⁰⁴ the mean value, $\bar{D}(\text{Ni-PR}_3) \approx 149 \text{ kJ/mol}$, compares with $\bar{D}(\text{Ni-PF}_3) = 147 \pm 3 \text{ kJ/mol}$ in Ni(PF₃)₄, reported by Brown, Connor, and Skinner.³⁰⁵ Nevertheless, it must be realized that Tolman's $\bar{D}(\text{Ni-P})$ were also obtained by using the same kind of assumptions and are based on a transference of a bond dissociation enthalpy, not a bond enthalpy term. Thus, it may well be possible that some cancellation of errors occurs.

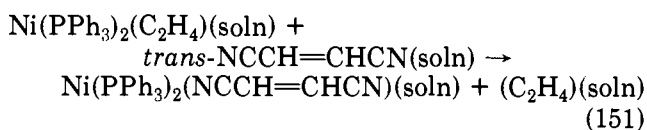
Tolman also reported some nickel-olefin bond dissociation enthalpies, determined from equilibrium

studies in solution of reaction 150, on the assumption that $\Delta G^\circ \approx \Delta H^\circ$.³⁰⁶ If the solvation enthalpies cancel,



$\Delta H^\circ(150)$ will be equal to the difference between $D(\text{Ni-P})$ in $\text{Ni}[\text{P}(o\text{-Otolyl})_3]_3$ and $D(\text{Ni-olefin})$. Three of these differences are presented in Table 12, where $D16 = D(\text{Ni-P})$. Tolman estimated $D16 \approx 126$ kJ/mol, but his more recent data for $\bar{D}(\text{Ni-P})$ indicate that this value must be too low.³⁰⁴ On the other hand, it can be expected that the dissociation enthalpy is different from the *mean* bond dissociation enthalpy, and therefore it is preferable not to assign a value to $D(\text{Ni-P})$.

The effect of the solvation terms and the assumption $\Delta G^\circ \approx \Delta H^\circ$ on the results in Table 12 is also unknown. This point is exemplified by a calorimetric study of reaction 151 in toluene.³⁰⁷ By using the same argu-



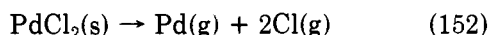
ments, i.e., that the solvation enthalpies cancel, $\Delta H^\circ(151)$ gives the difference between $D(\text{Ni-C}_2\text{H}_4)$ and $D[\text{Ni}-(\text{CHCN})_2]$, whose value should not be far from the one calculated from the data in Table 12, -30 kJ/mol. However, the result reported by Ittel, -63 kJ/mol, seems to be in poor agreement with Tolman's value.

Additional data for nickel-olefin bond dissociation enthalpies in solution can be found in the literature.^{304,306-309}

b. Palladium. A value for $E(\text{Pd-C}_3\text{H}_5)$ in the dimer $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$ was obtained by Ashcroft and Mortimer.¹²¹ Using a differential scanning calorimeter, they measured the enthalpy of reaction 24 at 452 K, which was corrected to 298 K (see section III.C), giving $\Delta H^\circ(24) = 105.0 \pm 1.7$ kJ/mol and enabling the calculation of the enthalpy of formation of the crystalline complex. This value depends on $\Delta H^\circ_f(\text{C}_3\text{H}_5\text{Cl}, \text{g})$, which has not been determined accurately. Ashcroft and Mortimer quoted -1.3 kJ/mol, and it is noticed that this result agrees with an estimate by using Benson's scheme,³¹⁰ which in turn yields values for the enthalpies of formation of allyl bromide and allyl iodide that agree within ca. 4 kJ/mol with the experimental results.²² Thus, in the present review we have also used $\Delta H^\circ_f(\text{C}_3\text{H}_5\text{Cl}, \text{g}) = -1.3$ kJ/mol with an error of ± 4 kJ/mol.

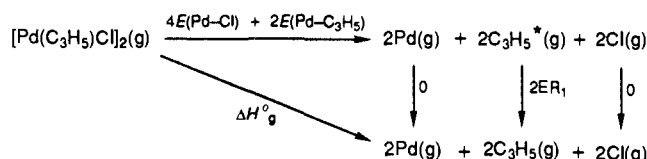
The authors have also measured the enthalpy of sublimation of the complex and calculated $\Delta H^\circ_f\{\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}\}_2(\text{g}) = 18 \pm 5$ kJ/mol, from which ΔH°_g in Scheme 19 can be obtained as 1308 ± 16 kJ/mol.

To evaluate $E(\text{Pd-C}_3\text{H}_5)$, Ashcroft and Mortimer considered that the bond strength between palladium and the bridging chlorine atoms is similar to $E(\text{Pd-Cl})$ in the chain $(\text{PdCl}_2)_n$ of crystalline PdCl_2 , ca. 196 kJ/mol. This value was obtained from the enthalpy of reaction 152^{159,311} and neglects the probably small interactions between the PdCl_2 chains.



On the other hand, as the authors also pointed out, it may be expected that $E(\text{Pd-Cl})$ in PdCl_2 exceeds

SCHEME 19

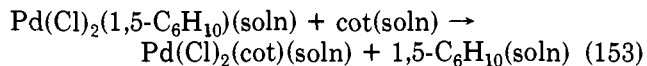


$E(\text{Pd-Cl})$ in the complex, as suggested by the palladium-chlorine bond lengths, 231 and 241 pm, respectively.¹²¹ Thus, the transferring process gives a high value for $E(\text{Pd-Cl})$ and a lower limit for $E(\text{Pd-C}_3\text{H}_5)$. However, as evidenced in Scheme 19, the reorganization energy of the allyl radical also has to be accounted for. ER_1 is most probably negative (see section III.B and also the discussion for iron and platinum complexes), giving a positive contribution to $E(\text{Pd-C}_3\text{H}_5)$. The net effect of the two sources of error is unknown. In addition, the enthalpy of formation of PdCl_2 is also controversial: A value of -198.7 kJ/mol is given in NBS tables,¹⁵⁹ while -163 ± 8 kJ/mol is recommended by Glushko and Medvedev.³¹¹ The latter was preferred in the calculations (see also below).

Skinner and co-workers determined the enthalpy of formation of the complex *cis*- $\text{Pd}(\text{Cl})_2(\text{cod})$ by measuring its enthalpy of decomposition, yielding gaseous cyclooctadiene and solid PdCl_2 .³¹² Their value also relies on the high result for $\Delta H^\circ_f(\text{PdCl}_2, \text{g})$.³¹¹ By using a scheme similar to Scheme 19 (i.e., breaking all the metal-ligand bonds in the molecule) and a value for $E(\text{Pd-Cl}) = 215$ kJ/mol (see discussion in ref 312), $E(\text{Pd-cod})$ shown in Table 12 is obtained. As in the case of $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$, this value has not been corrected with the reorganization energy of cod. On the other hand, it is dependent on the reliability of the value assigned to $E(\text{Pd-Cl})$. Interestingly (or, perhaps, fortuitously), the average palladium-carbon atom bond strengths are similar in $\text{Pd}(\text{Cl})_2(\text{cod})$ and $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$: $E(\text{Pd-C}_3\text{H}_5)/E(\text{Pd-cod}) \approx 3/4$.

Most of the available information about palladium-olefin bond enthalpies has been obtained by Parteneheimer and co-workers.^{313,314} Their reaction solution calorimetry data yield differences between palladium-olefin bond dissociation enthalpies, if it is assumed that the solvation terms cancel.

In the first paper of the series, this point was discussed and the solvation (vaporization + solution) enthalpies of the olefins were considered in the final results. For example, in reaction 153 (in dichloro-

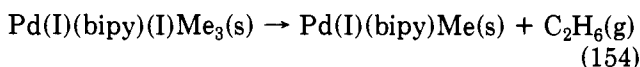


methane) the solvation enthalpies of 1,5-hexadiene and of cyclooctatetraene are about -28 and -42 kJ/mol, respectively. Thus, if this correction were not taken into account, $D(\text{Pd-1,5-hexadiene}) - D(\text{Pd-cot})$ would be affected by an error of -14 kJ/mol, which is larger than $\Delta H^\circ(153)$ for the same system, 10 kJ/mol. Similar examples could be given for other olefins,³¹³ showing once more the need for accurate data and the importance of avoiding less reliable assumptions in these kind of studies. Unfortunately, Parteneheimer's values presented in Table 12 ($D17 = D[\text{Pd}-(\text{CH}_2\text{NMe}_2)_2]$) do not contain the corrections due to the solvation enthalpies of the complexes $\text{Pd}(\text{Cl})_2(\text{olefin})$. Although it is claimed³¹³ that the contribution from those terms

should be negligible, it is difficult to predict whether even small contributions could not change a trend based on equally (and unknown) small differences. In the absence of such data, the solution results, though very useful, cannot be regarded as defining a trend in terms of bond dissociation enthalpies, except in the cases where the differences are particularly large.

The second paper by Partenheimer yields the data shown in Table 12 for the complexes $\text{Pd}(\text{Cl})_2(\text{py})\text{L}$.³¹⁴ These are also solution values and do not contain any correction for the solvation terms. Additional solution data leading to palladium-olefin bond dissociation enthalpies can be found in the two mentioned^{313,314} and other^{14,279,315} papers.

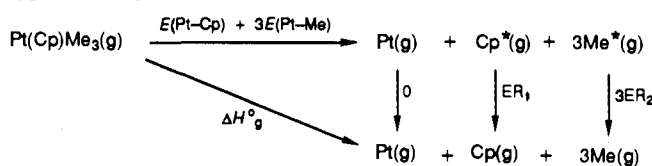
A very recent measurement of the enthalpy of reaction 154 by differential scanning calorimetry enabled estimation of a value for palladium-methyl mean bond dissociation enthalpy (Table 12), under the assumption of similar sublimation enthalpies for the complexes.³¹⁶



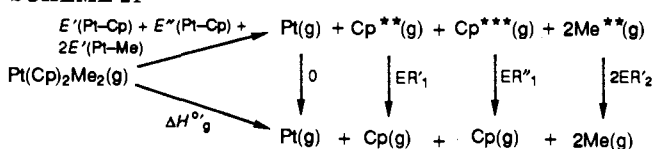
c. Platinum. The platinum-methyl bond dissociation enthalpy in the complex $\text{Pt}(\text{Cp})\text{Me}_3$ was obtained by kinetic studies of its thermal decomposition in the temperature range 388–438 K.³¹⁷ The activation enthalpy for splitting off methyl from the molecule was identified with $D(\text{Pt}-\text{Me})$ by assuming that the activation enthalpy for the recombination of the radicals is close to zero.

The same complex and also $\text{Pt}(\text{Cp})_2\text{Me}_2$ have been studied by static bomb combustion calorimetry.¹⁷³ The calculation of platinum-methyl bond enthalpy terms from the enthalpies of formation of the complexes¹⁵ is not possible at the present stage. The X-ray structure of $\text{Pt}(\text{Cp})\text{Me}_3$ shows that the cyclopentadienyl ring is nearly parallel to the plane of the three methyl carbon atoms, having an η^5 coordination to the metal.^{318,319} This enables definition of two different bond enthalpy terms, $E(\text{Pt}-\text{Me})$ and $E(\text{Pt}-\text{Cp})$. On the other hand, although the molecular structure of $\text{Pt}(\text{Cp})_2\text{Me}_2$ is not available, it may be expected that one of the rings is σ bonded to the metal atom, the other ring being probably η^5 coordinated. Therefore, in this case three different bond enthalpy terms should be defined: $E'(\text{Pt}-\text{Me})$, $E''(\text{Pt}-\text{Cp})$, and, for the σ -bonding ring, $E''(\text{Pt}-\text{Cp})$. Even if it is assumed that $E(\text{Pt}-\text{Me}) \approx E'(\text{Pt}-\text{Me})$ and $E(\text{Pt}-\text{Cp}) \approx E'(\text{Pt}-\text{Cp})$ and that all the reorganization energies are negligible or cancel (see Schemes 20 and 21 and eq 155), it is still not possible to calculate E -

SCHEME 20



SCHEME 21

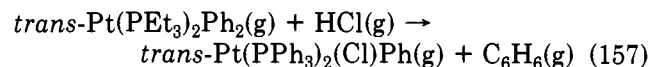


$$\begin{aligned} 6E(\text{Pt}-\text{Me}) - 2E''(\text{Pt}-\text{Me}) = \\ 2\Delta H^\circ_g - \Delta H^\circ'_g - 2E(\text{Pt}-\text{Cp}) + E'(\text{Pt}-\text{Cp}) + \\ E''(\text{Pt}-\text{Cp}) - (2ER_1 - ER'_1 - ER''_1) - (6ER_2 - 2ER'_2) \end{aligned} \quad (155)$$

(Pt-Me) because $E''(\text{Pt}-\text{Cp})$ is not available. A very crude estimate of a mean platinum-methyl bond enthalpy term in the two complexes can, however, be attempted by using some of the above assumptions and by considering $E(\text{Pt}-\text{Cp}) \approx E'(\text{Pt}-\text{Cp}) > E''(\text{Pt}-\text{Cp})$. $2\Delta H^\circ_g - \Delta H^\circ'_g$ is obtained from the enthalpies of formation of the gaseous complexes, of platinum, and of methyl radical, as 874 ± 11 kJ/mol. Making $2ER_1 \approx ER'_1 + ER''_1$ and $ER_2 \approx ER'_2$, eq 155 reduces to eq 156, where A represents the difference $E(\text{Pt}-\text{Cp}) - E(\text{Pt}-\text{Me}) \approx (2\Delta H^\circ_g - \Delta H^\circ'_g)/4 - ER_2 - A/4$ (156)

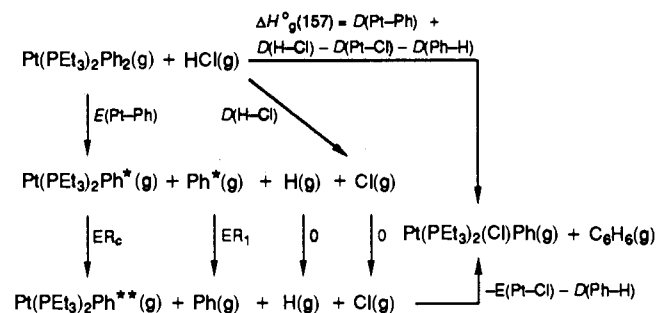
$E''(\text{Pt}-\text{Cp})$. With $ER_2 = 24$ kJ/mol (Appendix) and $A \approx 0$, one finally obtains $E(\text{Pt}-\text{Me}) \approx 195$ kJ/mol, a value that probably represents an upper limit for the platinum-methyl bond strength (note that the error in A is divided by 4).

The enthalpy of reaction 157 has been determined by Ashcroft and Mortimer, under the assumption that the complexes have the same enthalpy of sublimation within ± 6 kJ/mol.³²⁰ The reported value, -120 ± 13 kJ/mol, yields the difference between $D(\text{Pt}-\text{Ph})$ in $\text{Pt}(\text{PEt}_3)_2\text{Ph}_2$ and $D(\text{Pt}-\text{Cl}) = D19$ in $\text{Pt}(\text{PEt}_3)_2(\text{Ph})\text{Cl}$, as shown in Table 12.



The evaluation of bond enthalpy terms can be made through Scheme 22 or eq 158, but again the final results are affected by the lack of structural data and theoretical calculations of the reorganization enthalpies.

SCHEME 22



$$E(\text{Pt}-\text{Ph}) = \Delta H^\circ_g(157) + D(\text{Ph}-\text{H}) - D(\text{H}-\text{Cl}) + E(\text{Pt}-\text{Cl}) - ER_c - ER_1 \quad (158)$$

If the phenyl moiety has a similar structure in the initial complex and in benzene, then $D(\text{Ph}-\text{H}) - ER_1 = E(\text{Ph}-\text{H})$, which is given in the Appendix. For $E(\text{Pt}-\text{Cl})$ a value estimated by Skinner and co-workers will be used, 290 kJ/mol,³¹² which relies on the enthalpy of formation of PtCl_2 .³²¹⁻³²³

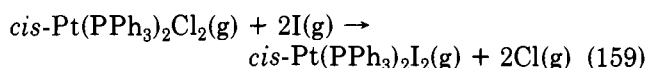
The result for $E(\text{Pt}-\text{Ph})$ shown in Table 12 is therefore affected by all these approximations and also by $ER_c = 0$. It is thought that this reorganization term makes a small contribution to platinum-phenyl bond enthalpy.

The enthalpies of formation of the complexes *cis*- $\text{Pt}(\text{PEt}_3)_2\text{Me}_2$, *cis*- $\text{Pt}(\text{PEt}_3)_2(o\text{-MeC}_6\text{H}_4)_2$, and *cis*- Pt -

(PEt₃)₂Cl₂ in the gas phase were obtained by Skinner and co-workers³¹² and enable derivation of platinum-carbon mean bond dissociation enthalpies and bond enthalpy terms, by using schemes similar to Schemes 1 and 2 and neglecting the reorganization energies associated with Pt(PR₃)₂ fragments. The same assumption and equations similar to eqs 64 and 65 were used to calculate $E(\text{Pt-R})$ and $D(\text{Pt-R})$ in the complexes *cis*-Pt(PEt₃)₂(Cl)Me and *cis*-Pt(PEt₃)₂(Cl)C₆H₄Me-*o*, whose enthalpies of formation in the gas phase were also determined by those authors.³¹² All values are given in Table 12 and rely on $E(\text{Pt-Cl}) = 290$ kJ/mol.

The enthalpy of formation of the complex *trans*-Pt(PPh₃)₂(Cl)H in the gas phase was derived by Mortimer³²⁴ and recalculated as 513 ± 31 kJ/mol.¹⁶¹ On the other hand, $\Delta H^\circ_f[\textit{cis}\text{-Pt}(\text{PPh}_3)_2\text{Cl}_2, \text{g}] = 448 \pm 21$ is also available,³¹² together with an estimate of the *cis* to *trans* isomerization enthalpy, -15 ± 2 kJ/mol,³²⁵ yielding the enthalpy of formation of the *trans* complex. This was used to calculate $E(\text{Pt-H})$ and $D(\text{Pt-H})$ (Table 12), by using once again equations similar to eqs 64 and 65 and $E(\text{Pt-Cl}) = 290$ kJ/mol.

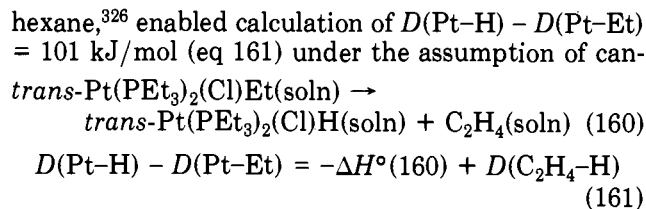
The calculation of platinum-methyl bond enthalpy data in the molecule *cis*-Pt(PPh₃)₂(I)Me, consistent with the above value for $E(\text{Pt-Cl})$, requires the evaluation of $E(\text{Pt-I})$ through the following method. As it is reasonable to assume constant Pt-PPh₃ bond terms in *cis*-Pt(PPh₃)₂X₂ (X = Cl, I), the enthalpy of reaction 159, 193 ± 32 kJ/mol, derived from the enthalpies of



formation of the gaseous complexes,^{312,324} can be identified with $2E(\text{Pt-Cl}) - 2E(\text{Pt-I})$ and yields $E(\text{Pt-I}) = 194$ kJ/mol. The above method (equations similar to eqs 64 and 65), together with $\Delta H^\circ_f[\textit{cis}\text{-Pt}(\text{PPh}_3)_2(\text{I-Me}), \text{g}] = 604 \pm 28$ kJ/mol and $\Delta H^\circ_f[\textit{cis}\text{-Pt}(\text{PPh}_3)_2\text{I}_2, \text{g}] = 611 \pm 25$ kJ/mol,^{161,324} led to the values shown in Table 12 for $D(\text{Pt-Me})$ and $E(\text{Pt-Me})$.

The trend evidenced by platinum-hydrogen, platinum-methyl, and platinum-aryl bond enthalpy data in the phosphine complexes is comparable to the one found for other transition metals. The large uncertainty intervals stem from the errors in the estimated sublimation enthalpies. They should be reduced to ca. ± 15 kJ/mol on a *relative* basis, i.e., if the trend is being analyzed. The only values that look discrepant refer to $D(\text{Pt-Ph})$ and $E(\text{Pt-Ph})$ in *trans*-Pt(PEt₃)₂Ph₂. $E(\text{Pt-Ph})$ in this case is rather small as compared to $E(\text{Pt-tolyl})$. The origin of the problem is the very exothermic value for $\Delta H^\circ(157)$, -120 kJ/mol. This value, which was determined for reaction 157 with both complexes in the solid state, can be compared with the enthalpy of the corresponding reaction involving the complexes *cis*-Pt(PEt₃)₂(*o*-tolyl)₂ and *cis*-Pt(PEt₃)₂(Cl)(*o*-tolyl), 9 kJ/mol, calculated from their enthalpies of formation.³¹² It is believed that the two reaction enthalpies should be similar and so the disagreement is not due to any unreliable assumption, but only to experimental data. The bond enthalpy results for the diphenyl complex in Table 12 are far too low, and a value for $E(\text{Pt-Ph}) = 255$ kJ/mol [or $D(\text{Pt-Ph}) = 299$ kJ/mol] is assigned in the present review.

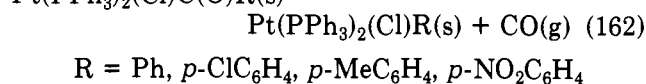
The enthalpy of β -elimination reaction 160 (50 kJ/mol), measured by equilibrium studies in cyclo-



celing solvation enthalpies and by quoting the enthalpy of formation of ethyl radical given in the Appendix. The values of $D(\text{Pt-Et})$ and $E(\text{Pt-Et})$ in Table 12 were derived by transferring $D(\text{Pt-H}) = 307$ kJ/mol. Independent differential scanning calorimetry studies of reaction 160 led to $\Delta H^\circ(160) = -66 \pm 3$ kJ/mol (with complexes in the crystalline state),³²⁷ in contrast to the above positive value. It is rather unlikely that such difference is due to solution effects. On the other hand, if it is assumed that the sublimation enthalpies of the complexes cancel (this should be valid within 15 kJ/mol), the negative value for $\Delta H^\circ(160)$ implies $D(\text{Pt-H}) - D(\text{Pt-Et}) = 217$ kJ/mol, which is too high.

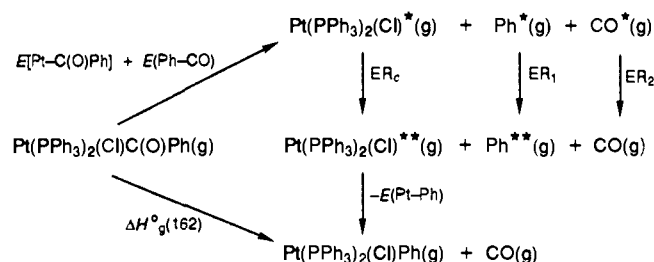
Recent kinetic studies in solution on the reductive elimination of H₂ from the complex *cis*-Pt(PMe₃)₂H₂ are worth mentioning.³²⁸ According to Packett and Trogler, the activation enthalpy for this reaction (84 kJ/mol in 2,2,5,5-tetramethyltetrahydrofuran) corresponds to the formation of an $\eta^2\text{-H}_2$ transition state. If solvation enthalpies are neglected, then the activation enthalpy provides an upper limit for $D(\text{Pt-H}_2)$.

In another paper by Ashcroft et al. on platinum-carbon bond enthalpies, the enthalpies of reaction 162 are reported ($T \sim 415\text{--}480$ K).⁵ These can be con-



sidered close to gas-phase data under the usual assumptions; i.e., the sublimation enthalpies cancel and the heat capacity corrections are negligible. For R = Ph it is possible to evaluate a minimum value of $E[\text{Pt-C}(\text{O})\text{Ph}]$, by using Scheme 23 or eq 163.

SCHEME 23



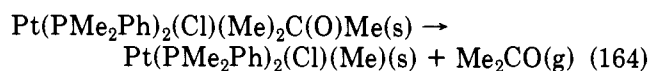
$$E[\text{Pt-C}(\text{O})\text{Ph}] = \Delta H^\circ_g(162) + E(\text{Pt-Ph}) - E(\text{Ph-CO}) - \text{ER}_c - \text{ER}_1 - \text{ER}_2 \quad (163)$$

Although relatively small values may be expected for ER_c and ER₁ (the structures of Pt(PPh₃)₂Cl and Ph must not change dramatically in the two complexes), ER₂ should make a larger contribution to $E[\text{Pt-C}(\text{O})\text{Ph}]$. A minimum value for |ER₂| is estimated by comparing the Laidler term for C-O in PhCHO (662 kJ/mol)¹⁹ with $E(\text{C-O})$ in free carbon monoxide (1076 kJ/mol). The difference, -414 kJ/mol, should be an upper limit to ER₂ because $E(\text{C-O})$ in the benzoyl complex must be even smaller than in benzaldehyde, as suggested by the C=O stretching frequencies in

these molecules, 1614 and 1701 cm^{-1} , respectively.^{5,329} The value of $E[\text{Pt}-\text{C}(\text{O})\text{Ph}]$ presented in Table 12 was then obtained through eq 163 by using $E(\text{Pt}-\text{Ph}) = 255$ kJ/mol (see discussion above) and by quoting the Laidler term (415 kJ/mol)¹⁹ for $E(\text{Ph}-\text{CO})$. As for the value of $D[\text{Pt}-\text{C}(\text{O})\text{Ph}]$, it has been derived simply by adding the reorganization energy of benzoyl radical (Appendix) to the bond enthalpy term.

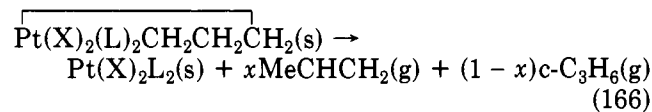
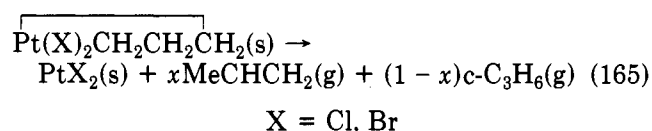
For $\text{R} = p\text{-ClC}_6\text{H}_4$, $p\text{-MeC}_6\text{H}_4$, and $p\text{-NO}_2\text{C}_6\text{H}_4$ in reaction 162 it is not possible to derive platinum-carbon bond enthalpy terms, mainly because the effect of the substituent on $E(\text{Pt}-\text{R})$ is not known. It can be expected, however, that $E[\text{Pt}-\text{C}(\text{O})\text{R}]$ and $D[\text{Pt}-\text{C}(\text{O})\text{R}]$ are close to the values shown in Table 12 for $\text{R} = \text{Ph}$ [$\Delta H^\circ(162)$ varies from 34 kJ/mol for $\text{R} = \text{Ph}$ to 19 kJ/mol for $\text{R} = p\text{-NO}_2\text{C}_6\text{H}_4$].

The sum of the bond dissociation enthalpies $D(\text{Pt}-\text{Me}) + D[\text{Pt}-\text{C}(\text{O})\text{Me}]$ can be calculated from the reported enthalpy of reaction 164, -33.6 ± 3.2 kJ/mol.¹¹⁹

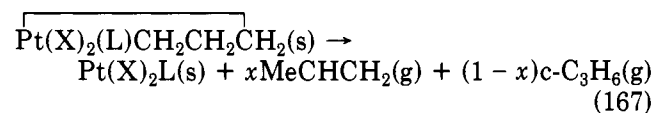


The value presented in Table 12, 306 ± 4 kJ/mol, is based on $D[\text{Me}-\text{C}(\text{O})\text{Me}]$ given in the Appendix and does not depend on any approximation other than the cancellation of the enthalpies of sublimation of the complexes. It is not possible to derive meaningful bond enthalpy terms since it may be expected that the unknown reorganization enthalpy (ER_c) associated with the process $\text{Pt}^{\text{IV}}(\text{PMe}_2\text{Ph})_2(\text{Cl})\text{Me}^* \rightarrow \text{Pt}^{\text{II}}(\text{PMe}_2\text{Ph})_2(\text{Cl})\text{Me}^{**}$ contributes significantly to the sum $E(\text{Pt}-\text{Me}) + E[\text{Pt}-\text{C}(\text{O})\text{Me}] = (363 \pm 9) - \text{ER}_c - \text{ER}_1 - \text{ER}_2$. The value 363 kJ/mol was obtained by taking the Laidler term $E[\text{Me}-\text{C}(\text{O})\text{Me}]$ from the Appendix. ER_1 and ER_2 refer to the reorganization of Me and MeCO from the Pt^{IV} complexes to 2-propanone and are thought to be small.

Another differential scanning calorimetry study that leads to platinum-carbon bond dissociation enthalpies relates to reactions 165–167.¹¹⁸ Reaction 165 was ac-



$\text{X} = \text{Cl}, \text{Br}; \text{L} = \text{pyridine}, 4\text{-methylpyridine}$

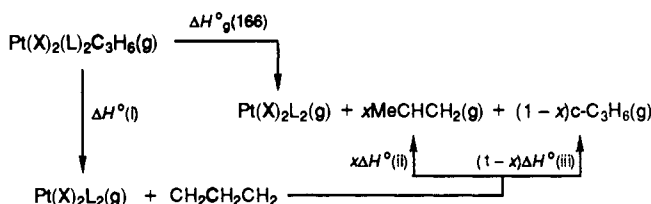


$\text{X} = \text{Cl}, \text{Br}; \text{L} = 2,2'\text{-bipyridyl}$

ually studied for the complexes $[\text{Pt}(\text{X})_2\text{C}_3\text{H}_6]_4$, but the reported enthalpies refer to the monomer. The evaluation of platinum-carbon bond enthalpies can be made through Scheme 24,¹¹⁸ which illustrates the method for $\text{Pt}(\text{X})_2(\text{L})_2\text{CH}_2\text{CH}_2\text{CH}_2$ complexes.

$\Delta H^\circ(\text{ii})$ and $\Delta H^\circ(\text{iii})$ were quoted from the literature by Hall et al.¹¹⁸ as -258.5 and -225.9 kJ/mol, respectively. Assuming that $\Delta H^\circ(\text{ii}) \approx \Delta H^\circ(\text{iii})$, it is possible to calculate $\bar{D}(\text{Pt}-\text{C})$ by using eq 168. The

SCHEME 24



$$\bar{D}(\text{Pt}-\text{C}) = [\Delta H^\circ(166) - x\Delta H^\circ(\text{ii}) - (1-x)\Delta H^\circ(\text{iii})]/2 \quad (168)$$

mole fractions x were measured in each case by gas chromatography. Note that the values presented in Table 12 are not Pt-C "bond strengths". As evidenced by the previous discussion, the reorganization of the $\text{Pt}(\text{X})_2\text{L}_2$ moiety from the initial complex, together with the reorganization of the biradical $\text{CH}_2\text{CH}_2\text{CH}_2$, are unknown quantities that cannot be neglected in this case. For example, a negative reorganization energy may be expected for the trimethylene fragment due to the strain in the metallocyclobutane ring.¹¹⁸ The only assumption that can eventually be accepted if one is interested in expressing the results as bond enthalpy terms is to consider that those two reorganization enthalpies are nearly constant for the complexes in reactions 165–167. In other words, it is possible that the pattern for $E(\text{Pt}-\text{C})$ values is close to the one shown in Table 12 for mean bond dissociation enthalpies.

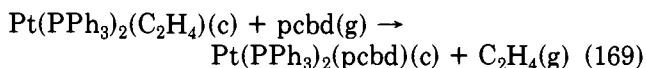
The reported enthalpy of formation of another complex containing a four-membered ring metallacycle (platinum diphenylcyclobutenone), $\text{Pt}(\text{PPh}_3)_2(\text{dpcb})$,³²⁴ enabled estimation of the Pt-C mean bond dissociation enthalpy. The method was similar to the one described for the dicyclopentadienyl complexes of groups 4 and 6 and has already been applied above for platinum compounds. The approximation was also identical: The reorganization enthalpy of the fragment $\text{Pt}(\text{PPh}_3)_2$ from the "reference" molecule $\text{cis-Pt}(\text{PPh}_3)_2\text{Cl}_2$ (analogous to ER_3 in eq 4) was ignored. Using $E(\text{Pt}-\text{Cl}) = 290$ kJ/mol and $\Delta H^\circ_f(\text{diphenylcyclopropanone}, \text{g}) = 552.3 \pm 0.5$ kJ/mol,³³⁰ one obtains the value in Table 12 for $\bar{D}(\text{Pt}-\text{C})$, 150 kJ/mol. This is quite low, as compared to $D(\text{Pt}-\text{Me})$, but it must be recalled that the reorganization energy of the organic fragment involves the formation of a strained carbon-carbon bond. Accepting a value estimated for this $D(\text{C}-\text{C})$, 133 kJ/mol,³²⁴ then $E(\text{Pt}-\text{C}) \approx D(\text{Pt}-\text{C}) + 133/2 = 217$ kJ/mol is obtained, suggesting a small strain in the metallacycle. Note, however, that this result has not been corrected for the energy difference between the organic fragment in the complex and in the diphenylpropanone biradical.

The enthalpy of formation of a five-membered metallacycle complex, platinum benzocyclopentene-1,2-dione, $\text{Pt}(\text{PPh}_3)_2(\text{bcpd})$, is not available. Yet, as remarked by Mortimer,³²⁴ the gas-phase enthalpy of reaction of this complex with $\text{trans-C}_2\text{H}_2\text{Ph}_2$ is only 12 kJ/mol higher than the same reaction involving the previous four-membered metallacycle. Although the enthalpies of sublimation were estimated, this result indicates a similar $E(\text{Pt}-\text{C})$ in the present case.

Several platinum-olefin bond enthalpies are reported in the literature, largely through the work of Mortimer, Puddephatt, and others.^{107,108,116,312,324,331-337} Enthalpies of formation are available for the following complexes:

Pt(PPh₃)₂L with L = C₂H₄, PhCHCH₂, *cis*-C₂H₂Ph₂, *trans*-C₂H₂Ph₂, C₂Ph₂, and C₂(CN)₄.^{161,324} As in the case of the metallacycles, it is possible to apply the method described for the groups 4 and 6 dicyclopentadienyl compounds to derive $D(\text{Pt-L})$, on the basis of $E(\text{Pt-Cl}) = 290$ kJ/mol. The enthalpies of formation of the gaseous ligands were quoted from NPL tables,²² except for the recently measured enthalpy of sublimation of diphenylacetylene, 99.9 ± 1.5 kJ/mol.¹⁹⁷ The $D(\text{Pt-L})$ values are shown in Table 12.

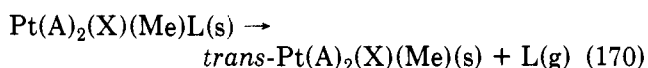
Although the enthalpy of formation of the olefin complex Pt(PPh₃)₂(pcbd) (pcbd = 3-phenylcyclobutene-1,2-dione) is not available, the enthalpy of reaction 169, -65 ± 4 kJ/mol, together with estimated



sublimation enthalpies of the complexes,³²⁴ leads to $D(\text{Pt-pcbd}) - D(\text{Pt-C}_2\text{H}_4) = 25$ kJ/mol and to the value in Table 12 for $D(\text{Pt-pcbd})$ by using the result for platinum-ethylene bond dissociation enthalpy.

Also presented in Table 12 is the Pt-olefin mean bond dissociation enthalpy for the molecule *cis*-Pt(Cl)₂(cod) (cod = cyclooctadiene). It was calculated from the enthalpy of formation of the complex,³¹² by using the same method as for the palladium analogue, and relies on $E(\text{Pt-Cl}) = 290$ kJ/mol.

Mortimer et al.¹¹⁶ have measured the enthalpies of the thermal decomposition reactions 170 by using a differential scanning calorimeter. By making the usual assumptions, i.e., the enthalpies of sublimation of the complexes cancel and $\Delta H^\circ(170)$ are temperature-independent, the authors identified these reaction enthalpies as platinum-olefin bond dissociation enthalpies. The results are given in Table 12.



X = Cl, Br; A = AsMe₃, AsMe₂Ph; L = C₂F₄, C₄F₆

The last set of platinum-olefin bond dissociation enthalpies presented in Table 12 was obtained by Parteneimer by reaction solution calorimetry.³³⁷ The trends $D(\text{M-C}_2\text{H}_4) - D(\text{M-olefin})$ are different for M = Pt and Pd and also for Ni. This is explained by the author in terms of the Dewar-Chat-Duncanson model,^{123,124} but, as stated for the palladium analogues, these are solution data and do not contain any correction for the solvation terms. In addition, the values lie in a narrow range. It is also believed that the Dewar-Chat-Duncanson model should be used to explain trends of E values and not D values. Reorganization energy differences $ER_1 + ER_2$ (see Scheme 6) can make large contributions to $D(\text{M-C}_2\text{H}_4) - D(\text{M-olefin})$, thus making it difficult to deduce the real trend in *bond strengths*.

Crude predictions of the reorganization energy of olefins are now illustrated. The reorganization energy of ethylene from Pt(PPh₃)₂(C₂H₄) can be estimated by considering the C=C bond length in the complex (143.4 ± 1.3 pm)³³⁸ and in free ethylene (133.9 ± 0.2 pm)³³⁹ and using an $E(\text{C-C})/r(\text{C-C})$ correlation.⁹³ The value obtained, -109 kJ/mol, leads to $E(\text{Pt-C}_2\text{H}_4) \approx 261$ kJ/mol (neglecting the reorganization energy of the Pt(PPh₃)₂ moiety). The same method has been used by Skinner and co-workers in the case of diphenylacetylene from

the complex Pt(PPh₃)₂(C₂Ph₂),³¹² and the result ($ER = -120$ kJ/mol) implies $E(\text{Pt-C}_2\text{Ph}_2) \approx 301$ kJ/mol. These two examples provide evidence that the reorganization energies cannot be ignored in a discussion of *bond strengths*, in particular if it involves metal-olefin bonds.

A relative value for a platinum-carbon σ -bond dissociation enthalpy is finally mentioned. Bercaw and co-workers reported $D(\text{Pt-CH}_2\text{COMe}) - D(\text{Pt-OMe}) = -18$ kJ/mol in the complexes Pt(Ph₂PCH₂)₂(Me)L.²⁴¹ This value was obtained from equilibrium studies in solution, by assuming $\Delta H^\circ \approx \Delta G^\circ$. It shows that for late-transition elements metal-oxygen and metal-carbon bond strengths are in the same range.

B. Organometallic Fragments and Ions

All the results presented in Tables 13–25 are given in kilojoules per mole and refer to 298 K, unless indicated otherwise. The designation *bond dissociation enthalpy* is again preferred because in the few cases where the word *energy* would be more correctly used, the difference between the two concepts is negligible when compared with the uncertainties assigned to the results.

1. Fragments ML, ML⁺, ML⁻, and M(L')L⁺

The diatomic transition-metal hydrides MH, MH⁺, and MH⁻ are of considerable interest since they are the simplest species that can be studied to better understand the nature and energetics of bonding in transition-metal compounds. The available data for $D(\text{M-H})$, $D(\text{M}^+\text{-H})$, and $D(\text{M}^-\text{-H})$, limited mainly to the first and second rows, are presented in Table 13. With a few exceptions, these values are the result of guided ion beam experiments performed by Armentrout and co-workers in the last 7 years,^{81,83,340–350} and are believed to be more accurate than those obtained by other methods. The results for $D(\text{M-H})$ and $D(\text{M}^+\text{-H})$ were derived mainly from the determination of thresholds for reactions 171 and 172, respectively, where RH is a hydrocarbon for which $\Delta H_f^\circ(\text{R}^+, \text{g})$ is well established. When deuterium was used in place of H₂, the results for $D(\text{M-H})$ and $D(\text{M}^+\text{-H})$ were corrected for zero point energy differences.



Ion beam results determined with a less sophisticated apparatus, using a collision cell rather than the guided ion beam, are given for $D(\text{Ru}^+\text{-H})$, $D(\text{U}^+\text{-H})$, $D(\text{Mo-H})$, $D(\text{Ru-H})$, $D(\text{Rh-H})$, and $D(\text{Pd-H})$.^{351–353} In each case of $D(\text{Mo-H})$, the number in Table 13 is the average between an ion beam result (222 ± 21 kJ/mol)³⁵³ and an ion cyclotron resonance spectroscopy value (193 ± 13 kJ/mol).¹⁴⁵ ICR data are also presented for $D(\text{Cr-H})$,¹⁴⁵ and Knudsen cell results are shown for $D(\text{Sc-H})$, $D(\text{Ag-H})$, and $D(\text{Au-H})$.^{354,355} The latter technique is thought to be quite reliable for the neutral hydrides. For example, the Knudsen cell values for $D(\text{Co-H})$, $D(\text{Ni-H})$, and $D(\text{Cu-H})$, 192 ± 4 , 252 ± 8 , and 248 ± 8 kJ/mol,^{354,355} respectively, are in good agreement with the ion beam values in Table 13. Data for $D(\text{Zn-H})$ and $D(\text{Cd-H})$ are also presented for comparison purposes.³⁵⁶

TABLE 13. Thermochemical Data for Transition-Metal Hydrides^a

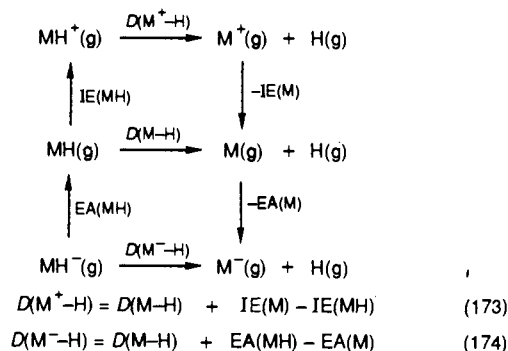
M	IE(M) ^b	EA(M) ^c	IE(MH) ^d	D(M-H)	D(M ⁺ -H)	D(M-H ⁺) ^e	D(M ⁻ -H) ^f	D(M-H ⁻) ^g	D(M ⁺ -H ⁻) ^h	D(M ⁻ -H ⁺) ⁱ
First Row										
Sc	6.56	0.19	6.18	202 ± 8 ^j	239 ± 9 ^k	918			762	1496
Ti	6.82	0.08	6.51	197 ^l	227 ± 11 ^m	881			782	1501
V	6.74	0.53	6.43	172 ± 17 ^l	202 ± 6 ⁿ	864			750	1433
Cr	6.77	0.67	7.14	172 ± 13 ^o	136 ± 9 ^p	795	162 ^q	153	752	1419
Mn	7.44	ns	6.64	126 ± 17 ^l	203 ± 14 ^r	797	>210 ^s	137	771	>1438
Fe	7.87	0.16	7.69	191 ± 13 ^t	208 ± 6 ^u	761	265 ^v	208	878	1488
Co	7.86	0.66	7.81	190 ± 10 ^w	195 ± 6 ^v	749	191 ^z	182	876	1438
Ni	7.64	1.16	8.44	243 ± 13 ^x	166 ± 8 ^y	741	177 ^{aa}	217	907	1443
Cu	7.73	1.23	9.42	255 ± 17 ^x	92 ± 13 ^y	658			928	1448
Zn	9.39	ns	7.89	86 ± 2 ^{bb}	231 ± 13 ^{cc}	637			919	>1398
Second Row										
Y	6.22	0.31			261 ± 6 ^k	973				
Zr	6.59	0.43			230 ± 13 ^{dd}	906				
Nb	6.59	0.89			226 ± 13 ^{dd}	902				
Mo	7.10	0.75	7.58	208 ± 15 ^{ee}	176 ± 13 ^{dd}	803		820	1448	
Ru	7.27	1.05	7.91	234 ± 21 ^{ff}	172 ± 13 ^{gg}	783		863	1445	
Rh	7.54	1.14	8.53	247 ± 21 ^{ff}	151 ± 13 ^l	736		902	1449	
Pd	8.34	0.56	8.72	234 ± 25 ^{ff}	197 ± 13 ^l	704		966	1492	
Ag	7.58	1.30	9.11	215 ± 8 ^{hh}	67 ± 13 ^{dd}	648		874	1402	
Cd	8.99	ns		69.0 ± 0.4 ^{bb}				864	>1380	
Third Row, Lanthanides, and Actinides										
La	5.58	0.5			243 ± 9 ^k	1017				
Au	9.23	2.31		292 ± 8 ^{hh}				1109	1381	
Pt	8.61	2.13		352 ± 38 ^{bb}				1110	1458	
Yb	6.25			159 ± 38 ^{bb}				689		
Lu	5.43				204 ± 15 ^k	992				
U	6.19				208 ± 19 ⁱⁱ	995				

^a Ionization energies and electron affinities are in electronvolts; bond dissociation enthalpies, kilojoules per mole. ^b Values from ref 159. ^c Values from: Mead, R. D.; Stevens, A. E.; Lineberger, W. C. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1984; Vol. III. ns = not stable. ^d Calculated from eq 173. ^e Calculated from eq 35, using IE(H) = 13.598 eV.¹⁵⁹ ^f Calculated from eq 174. ^g Calculated from eq 175, using EA(H) = 0.754 eV (reference given in note c). ^h Calculated from eq 176, using EA(H) = 0.754 eV (reference given in note c). ⁱ Calculated from eq 36, using IE(H) = 13.598 eV.¹⁵⁹ ^j Reference 354. ^k Reference 340. ^l Reference 348. ^m Reference 341. ⁿ Reference 342. ^o Reference 145. ^p Reference 343. ^q EA(CrH) = 0.56 ± 0.01 eV.³⁵⁹ ^r Reference 344. ^s EA(MnH) = 0.87 ± 0.01 eV.³⁵⁸ ^t Reference 349. ^u Reference 83. ^v EA(FeH) = 0.93 ± 0.01 eV. ^w Reference deleted on revision. ^x Reference 350. ^y Reference 345. ^z EA(CoH) = 0.67 ± 0.01 eV.³⁵⁹ ^{aa} EA(NiH) = 0.48 ± 0.01 eV.³⁵⁹ ^{bb} Reference 356. ^{cc} Reference 346. ^{dd} Reference 347. ^{ee} Average between values from ref 145 and 353. ^{ff} Reference 353. ^{gg} Reference 351. ^{hh} Reference 355. ⁱⁱ Reference 352.

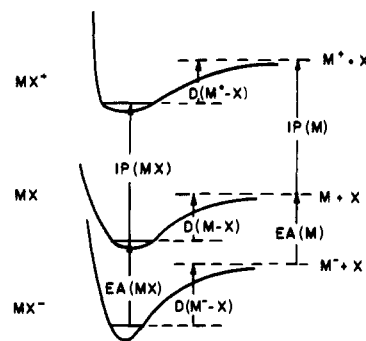
These were obtained from a Birge-Sponer extrapolation of the $v = 0-5$ vibrational levels and are thus considered accurate.³⁵⁷ The same cannot perhaps be said about $D(\text{Pt-H})$. However, for silver and gold the Birge-Sponer results, 226 ± 8 and 314 ± 10 kJ/mol, respectively,³⁵⁶ are in fair agreement with the Knudsen cell values. Finally, the value for $D(\text{Ti-H})$ in Table 13 is the result of a theoretical calculation, quoted from a recent review by Armentrout.³⁴⁸

The energetics of the species MH^+ , MH , and MH^- can be related through Scheme 25 and eq 173 and 174 (refer also to Figure 6). Values of $D(\text{M-H})$ can

SCHEME 25

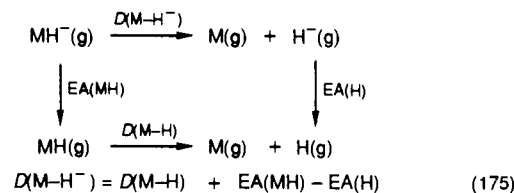


therefore be obtained if the electron affinities (EA) of MH are available. This is the case for $\text{M} = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co},$ and Ni ,^{358,359} and the results are displayed in Table 13. Values of $D(\text{M-H}^-)$, which are also shown for these

Figure 6. Potential energy curves for the species MX^- , MX , and MX^+ .

five metals, were calculated from eq 175, derived from Scheme 26.

SCHEME 26



Equation 173 can be used to evaluate the ionization energies of the bare metal hydrides MH (Table 13), which can be compared with the ionization energies of the metal atoms.

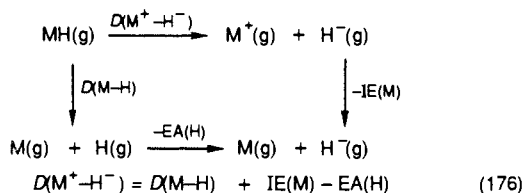
TABLE 14. Metal-Ligand Bond Dissociation Enthalpies, $D(M^+-L)$, in Fragments ML_n^+ ^a

M	L				
	H ^b	Me	CH ₂	CH	C
	First Row				
Sc	239 ± 9	247 ± 13 ^c	412 ± 22 ^d		
Ti	227 ± 11	226 ± 8 ^e	391 ± 15 ^f	508 ± 15 ^f	
V	202 ± 6	207 ± 8 ^g	335 ± 13 ^h	481 ± 8 ^g	383 ± 7 ^g
Cr	136 ± 9	126 ± 8 ⁱ	226 ± 17 ⁱ	314 ± 29 ⁱ	
Mn	203 ± 14	213 ± 8 ^e	297 ± 13 ^e		
Fe	208 ± 6	242 ± 10 ^j	347 ± 17 ^e	426 ± 30 ^k	397 ± 30 ^k
Co	195 ± 6	205 ± 15 ^j	326 ± 8 ^e	426 ± 30 ^k	384 ± 30 ^k
Ni	166 ± 8	188 ± 10 ^j	314 ± 8 ^e		
Cu	92 ± 13	124 ± 7 ^l	268 ± 8 ^e		
Zn	231 ± 13	296 ± 14 ^m			
	Second Row				
Y	261 ± 6	249 ± 5 ^d	398 ± 13 ^d		
Zr	230 ± 13				
Nb	226 ± 13		456 ± 29 ⁿ	610 ± 37 ⁿ	600 ± 20 ⁿ
Ru	172 ± 13	226 ± 21 ^o			
Rh	151 ± 13	198 ± 21 ^o	381 ± 21 ⁿ	431 ± 30 ⁿ	686 ± 67 ⁿ
Pd	197 ± 13	247 ± 21 ^o			
Ag	67 ± 13				
Cd		228 ± 3 ^p			
	Third Row and Lanthanides				
La	243 ± 9	231 ± 14 ^d	411 ± 6 ^d	524 ± 36 ⁿ	427 ± 30 ⁿ
Hg		285 ± 3 ^p			
Lu	204 ± 15	190 ± 20 ^d	≥240 ± 5 ^d		

^a Values in kilojoules per mole. ^b Values from Table 13. ^c Reference 360. ^d Reference 365. ^e Reference 348. ^f Reference 367. ^g Reference 361. ^h Reference 368. ⁱ References 362 and 363. ^j Reference 349. ^k Reference 370. ^l Reference 350. ^m Reference 364. ⁿ Reference 369. ^o Reference 351. ^p Reference 366.

The three remaining entries in Table 13 refer to the metal proton affinities, $D(M-H^+)$, the metal hydride acidities, $D(M^-H^+)$, and the hydride affinities of the metal cations, $D(M^+-H^-)$. The proton affinity values, which were calculated through eq 35 (making $B = M$), decrease when one goes across the first- and second-row elements, from left to right. An opposite behavior is noticed for $D(M^+-H^-)$, which were evaluated with use of Scheme 27 or eq 176. It is noted that metal hydride acidity values, $D(M^-H^+)$, determined from eq 36, vary in a relatively narrow range (ca. 80 kJ/mol).

SCHEME 27



The available bond dissociation enthalpies $D(M^+-Me)$, $D(M^+-CH_2)$, $D(M^+-CH)$, and $D(M^+-C)$ in fragments MMe^+ , MCH_2^+ , and MC^+ , respectively, are summarized in Table 14. For comparison, values of $D(M^+-H)$ in MH^+ are also included in the table. As in the case of metal hydride cations, MH^+ , almost all the results selected for $D(M^+-Me)$ were obtained through guided ion beam experiments by Armentrout and co-workers.^{348,349,360-365} The only exceptions are $D(M^+-Me)$ for $M = Ru, Rh,$ and Pd , determined with the ion beam apparatus incorporating a collision cell,³⁵¹ and for $M = Cd$ and Hg (included for comparison purposes), determined by photoionization mass spectrometry.³⁶⁶ The measurement of thresholds for processes such as reac-

TABLE 15. Metal-Methyl Bond Dissociation Enthalpies in MMe and MMe^+

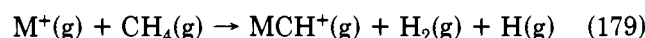
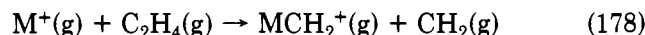
M	$D(Me^+-Me),^a$	$D(M-Me),$	IE(MMe), ^b eV
	kJ/mol		
	First Row		
Sc	247 ± 13	134 ± 29 ^c	5.39
Ti	226 ± 8	192 ± 29 ^c	6.47
V	207 ± 8	155 ± 38 ^c	6.20
Cr	126 ± 8	172 ± 29 ^c	7.25
Mn	213 ± 8	126 ± 17 ^c	6.54
Fe	242 ± 8	155 ± 29 ^c	6.97
Co	205 ± 15	191 ± 13 ^d	7.71
Ni	188 ± 10	231 ± 13 ^d	8.09
Cu	124 ± 7	243 ± 8 ^d	8.96
Zn	296 ± 14	80 ± 13 ^e	7.15
	Second and Third Rows		
Cd	228 ± 3	49 ± 17 ^f	7.13
Au		>113 ^g	
Hg	285 ± 3	6 ± 17 ^f	7.55

^a Values from Table 14. ^b Calculated values (see text). ^c Reference 348. ^d Reference 350. ^e Reference 364. ^f Reference 287. ^g Reference 371.

tion 177 were used to extract $D(M^+-Me)$ in the ion beam experiments.



Guided ion beam results have also yielded the majority of $D(M^+-CH_2)$ values in Table 14,^{348,362,363,365,367,368} with the exception of $M = Nb$ and Rh , which were obtained by ICR photodissociation or bracketing experiments.³⁶⁹ In the case of $D(M^+-CH)$, the values for $Ti, V,$ and Cr were obtained by the guided ion beam method^{361-363,367} and the remaining by ICR photodissociation.^{369,370} Finally, the results for $D(M^+-C)$ were determined by ICR photodissociation or bracketing experiments,^{369,370} except $D(V^+-C)$, measured with the guided ion beam instrument.³⁶¹ Reactions 178-180 illustrate some of the processes whose thresholds have been measured to obtain $D(M^+-CH_2)$, $D(M^+-CH)$, and $D(M^+-C)$.



The present overall picture of the energetics of fragments under discussion is completed by the data in Tables 15-17. The first shows the metal-methyl bond dissociation enthalpies in the neutral species MMe in comparison with the values for the cations. Each pair of results permits evaluation of the ionization energies of MMe by using the method described for the hydrides (eq 173). Table 16, on the other hand, summarizes the stepwise bond dissociation enthalpies in the fragments $M(L')L$ ($L, L' = H, Me$). Finally, Table 17 collects the remaining data available for fragments ML_n^+ . It must be stressed that this last set of values is probably not comprehensive, since a large amount of estimates of upper or lower limits of $D(M^+-L)$ can be found in the literature, derived mainly from the assumption that reactions involving ML_n^+ species as products (or reactants) are exothermic. It is difficult, however, to assess the role of excited states in many of these studies, especially when the reactant ions are prepared by laser evaporation or electron impact fragmentation of an appropriate precursor.

TABLE 16. First and Second Bond Dissociation Enthalpies in $M(L')L^+$ Fragments (kJ/mol)

$M(L')L^+$	$D(L'M^+-L)$	$D(M^+-L)^a$	$D(L'M^+-L) + D(M^+-L')$
ScH ₂	244 ± 16	239 ± 9	483 ± 13 ^b
YH ₂	272 ± 9	261 ± 6	533 ± 7 ^c
LaH ₂	266 ± 12	243 ± 9	509 ± 8 ^c
GdH ₂			≤498 to 523 ^d
LuH ₂	207 ± 23	204 ± 15	411 ± 18 ^c
CoH ₂	209	195 ± 6	404 ^e
ScMe ₂	238 ± 15	247 ± 13	485 ± 8 ^f
YMe ₂			>464 ^g
GdMe ₂			>481 ^d
LaMe ₂			>464 ^g
TiMe ₂	268 ± 24	226 ± 8	494 ± 25 ^f
VMe ₂	203 ± 22	207 ± 8	410 ± 21 ^f
FeMe ₂	>160	242 ± 10	>402 ^h
RuMe ₂	>176	226 ± 21	>402 ⁱ
CoMe ₂	255 ± 20	205 ± 15	460 ± 13 ^j
RhMe ₂	>205	198 ± 21	>402 ⁱ
NiMe ₂	>214	188 ± 10	>402 ^e
PdMe ₂	>155	247 ± 21	>402 ⁱ
ZnMe ₂	115 ± 4	296 ± 14	411 ± 3 ^k
CdMe ₂	109 ± 3	228 ± 3	337 ± 4 ^l
HgMe ₂	96 ± 5	285 ± 3	381 ± 6 ^l
Sc(H)Me	263 ± 13	239 ± 9	502 ± 8 ^f
Gd(H)Me			≥521 ^d
V(H)Me	188 ± 25	202 ± 6	390 ± 25 ^f
Co(H)Me	182	195 ± 6	377 ^e

^a Values from Table 14. ^b Reference 360. ^c Reference 365. ^d Reference 376. ^e Reference 373. ^f Reference 348. ^g Reference 375. ^h Reference 374. ⁱ Reference 372. ^j Reference 68. ^k Reference 364. ^l Reference 366.

The data for $D(M-Me)$ stem from guided ion beam experiments,^{348,350,364} except the lower limit for $D(Au-Me)$, which was estimated by ICR results,³⁷¹ and $D(M-H)$ ($M = Cd, Hg$) quoted from McMillen and Golden's review.²⁸⁷ The stepwise bond dissociation enthalpies in Table 16 rely on values determined (or estimated) for the sum $D(L'M^+-L) + D(M^+-L')$, either by guided ion beam,^{348,360,364,365} ICR,^{374,375} kinetic energy release,⁶⁸ ion beam,^{372,373,376} or photoionization mass spectrometry experiments.³⁶⁶ Most of the values in Table 17 refer to metal-olefin bonds, but data for other bond dissociation enthalpies are also included, as for $D(Nb^{2+}-CH_2)$, $D(Co^+-SiH_2)$, $D(Ni^+-SiH_2)$, and $D(V^+-Et)$.^{68,80,349,360,361,372,375,377-392}

With reliable thermochemical data available for organometallic fragments involving most of the first- and second-row metals, as well as several of the third-row metals, it is now possible to formulate an overall picture of metal-hydrogen bond dissociation enthalpies for these species. Because of the simplicity of the systems involved, mainly due to the absence of spectator ligands, high-quality ab initio theoretical calculations have now been carried out for most of the species studied. It is of further interest to develop relationships, if they exist, between bond enthalpies in organometallic fragments and the values of $D(M-H)$ in closed-shell organometallic complexes. There is no a priori reason to expect any agreement between bond dissociation enthalpies for MnH or MnH^+ and $Mn(CO)_5H$.

A starting point for analysis is the comparison of experimental and theoretical bond dissociation enthalpies for first-, second-, and third-row transition-metal hydride ions shown in Figure 7. For brevity and consistency we have chosen to use the results obtained in collaborations between one of the authors and Professor W. A. Goddard at Caltech.^{150-153,393,394} Other

TABLE 17. Additional Thermochemical Data for Cationic Fragments ML_n^+ ($n = 1, 2$)

ML_n^+	method/ref ^a	$D(M^+-L)$, kJ/mol
ScL ⁺	GIB/360	
L = C ₂ H ₂		326 ± 10
L = C ₂ H ₄		≥147 ± 5
ScC ₂ H ₄ ⁺	ICR/377	167 ± 21
ScC ₆ H ₆ ⁺	ICR/378	222 ± 11
YL ⁺	ICR/375	
L = C ₂ H ₄		>138
L = C ₃ H ₄		>297
L = C ₃ H ₆		>126
L = C ₄ H ₆		>238
LaL ⁺	ICR/375	
L = C ₂ H ₄		>138
L = C ₃ H ₄		>297
L = C ₃ H ₆		>126
L = C ₄ H ₆		>238
TiC ₆ H ₆ ⁺	ICR/379	>205
VL ⁺	GIB/361	
L = C ₂		≥527 ± 14
L = C ₂ H		497 ± 8
L = C ₂ H ₂		212 ± 20
L = C ₂ H ₃		≥367 ± 19
L = C ₂ H ₄		209
L = Et		234 ± 13
VC ₃ H ₅ ⁺	ICR/380	427 ± 67
VC ₆ H ₆ ⁺	ICRp/80	260 ± 20
V(C ₆ H ₆) ₂ ⁺	ICRp/80	239 ± 20
NbCH ₂ ²⁺	ICR/392	819 ± 43
NbC ₆ H ₆ ⁺	ICRp/381	276 ± 29
TaC ₆ H ₆ ⁺	ICR/379	251 < D < (301 ± 21)
CrC ₆ H ₆ ⁺	ICR/379	222 ± 38
MoL ⁺	IB/382	
L = C ₂ H ₂		≥312
L = C ₂ H ₄		≥137
L = 1,3-C ₄ H ₆		≥245
L = C ₆ H ₆		≥250
FeC ₂ H ₄ ⁺	TE/383	142 ± 8
FeC ₂ H ₄ ⁺	TE/349	174 ± 39
Fe(C ₃ H ₅) ₂ ⁺	ICR/384	232 ^b
FeC ₃ H ₅ ⁺	ICR/383	155 ± 8
FeC ₄ H ₆ ⁺	ICRp/80	201 ± 21
FeCp ⁺	ICR/385	>(364 ± 21)
Fe(c-C ₅ H ₈) ⁺	ICRp/381	213 ± 21
FeC ₆ H ₆ ⁺	ICR, ICRp/386	318 ± 42
FeC ₆ H ₆ ⁺	ICRp/80	230 ± 21
RuC ₂ H ₄ ⁺	IB/372	>159
CoC ₂ H ₄ ⁺	IB/391	155 ± 8
CoC ₂ H ₄ ⁺	KERD/68	192 ± 33
CoC ₃ H ₅ ⁺	ICR/381	>301
CoC ₃ H ₅ ⁺	KERD/68	201 ± 13
CoC ₄ H ₆ ⁺	ICR/381	<218
Co(Cp)C ₄ H ₆ ⁺	ICR/381	>238
CoCp ⁺	ICR/387	356 ± 12
Co(Cp) ₂ ⁺	ICR/387	513 ± 42 ^c
Co(C ₆ H ₆) ⁺	ICRp/80	285 ± 21
Co(PhMe) ⁺	ICR/381	>201
CoSiH ₂ ⁺	ICR/388	271 ± 24
RhC ₂ H ₄ ⁺	IB/372	>159
RhC ₄ H ₆ ⁺	ICR/389	>236
RhC ₆ H ₆ ⁺	ICRp/381	276 ± 29
NiC ₂ H ₄ ⁺	TE/383	155 ± 8
Ni(C ₂ H ₄) ₂ ⁺	ICRp/80	180
NiC ₃ H ₅ ⁺	ICRp/80	243 ± 10
NiC ₆ H ₆ ⁺	ICR/379	285 ± 21
NiCF ₂ ⁺	IB/390	196 ± 29
NiSiH ₂ ⁺	IB/388	271 ± 24
CuC ₆ H ₆ ⁺	ICR/379	209 ± 38

^a Key: GIB = guided ion beam mass spectrometry; IB = ion beam mass spectrometry; ICR = ion cyclotron resonance spectroscopy; ICRp = ion cyclotron resonance spectroscopy (photodissociation); KERD = kinetic energy release distribution; TE = thermochemical estimate. ^b Mean bond dissociation enthalpy. ^c Recalculated value.

groups have also made significant contributions to understanding the electronic structure of organometallic

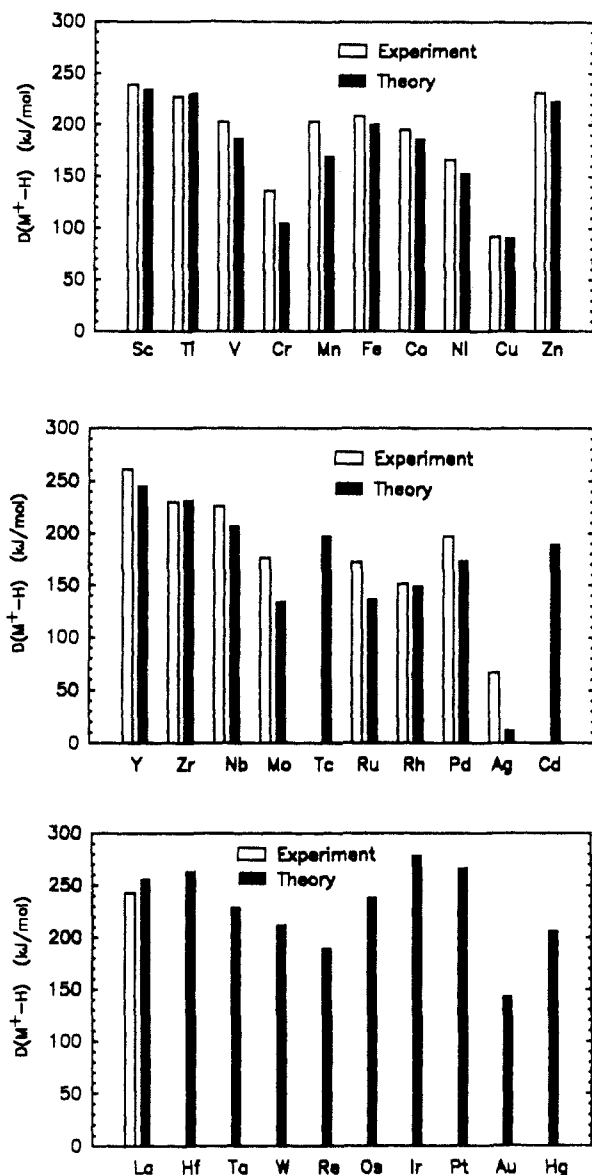


Figure 7. Comparison between experimental and theoretical values of transition metal-hydrogen bond dissociation enthalpies in cationic hydrides, MH^+ .

fragments.³⁹⁵⁻³⁹⁷ Considering that both the experimental and the theoretical results represent cutting edge science, the agreement is excellent.

Theoretical studies at Caltech have used the generalized valence bond (GVB) approach. In this description, there are two overlapping orbitals in the bond, each with one electron. The first is essentially a hydrogen 1s orbital localized near the proton, while the other is a mixture of valence s, d, and p character, centered near the metal. The best description yields a covalent bond (rather than $M^{2+}H^-$). The H 1s orbital remains nearly the same for all cases, with the metal orbital exhibiting systematic changes in hybridization that can be understood from the electronic structure of M^+ . Starting from the ground-state configuration of M^+ , electrons are distributed so as to reserve a singly occupied σ orbital for binding to the H while minimizing the number of other σ electrons. This idea provides an immediate explanation of the most striking features of the periodic trends in bond enthalpies shown in Figure 7. For the first-row metals, Cr^+ and Cu^+ have the weakest bonds. With stable half-filled (d^5) and filled

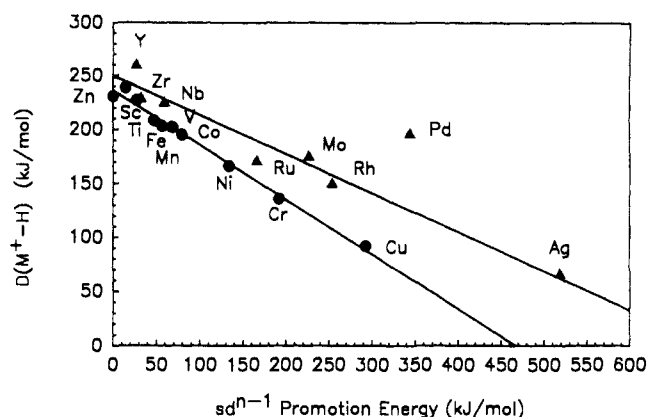


Figure 8. First-row (closed circles) and second-row (closed triangles) transition metal-hydrogen bond dissociation enthalpies in species MH^+ vs atomic metal ion promotion energies to sd^{n-1} spin-decoupled states appropriate for forming covalent single bonds.

(d^{10}) configurations giving rise to the 6S and 1S ground states, respectively, of the two ions, it is not surprising that promotion to a bonding configuration is energetically demanding.

Calculations show that the M^+-H bond pair involves a metal valence orbital that is a mixture of valence s and d orbitals, with minimal valence p character.³⁹⁴ In the first row the 4s orbital is much larger than 3d, making it dominant in bonding to H. Hybridization varies from 45% s for ScH^+ through CrH^+ , increasing to 75% s for MnH^+ through CuH^+ . The latter results from the presence of a σ nonbonding electron starting with manganese. In the second row, the 5s and 4d orbitals are more similar in size, leading to much larger d character in the bond orbitals. There is a gradual increase of d character from YH^+ (57%) to PdH^+ (93%) because the d^n configurations of the metal ions are particularly stable in late-second-row metals. The trend is smoother again in the third row, where HfH^+ to IrH^+ have about 60% d character, with an increase for PtH^+ and AuH^+ resulting from d^n configurations that give rise to the ground states of M^+ for these species.

Even before the extensive ab initio calculations described above were carried out, clues relating to the nature of the bonding were revealed in correlations of bond dissociation enthalpies with promotion energy, E_p , defined as the energy necessary to take the metal center in its ground state to an electron configuration where there is one electron in the s valence orbital.⁸¹ Loss of exchange energy involved in spin decoupling this electron from the valence d electrons must be included. E_p can be taken as the mean energy of the electronic states with sd^{n-1} configurations where the s electron is high-spin- and low-spin-coupled to the d electrons. Such correlations are shown in Figure 8 for first- and second-row metal hydride ions.⁸¹ If E_p is defined as excitation to a sd^{n-1} configuration, but the d- σ is the bonding orbital and is spin-decoupled, then a correlation almost as good as Figure 8 is obtained. The correlation thus does not distinguish the possibility of significant s and d participation, and it is better for the first row than the second, with Pd^+ exhibiting the largest deviation. The observations are rationalized by the insight provided by the ab initio calculations, which support the involvement of both s and d orbitals in the bonding and explain the unusual behavior of palladium.

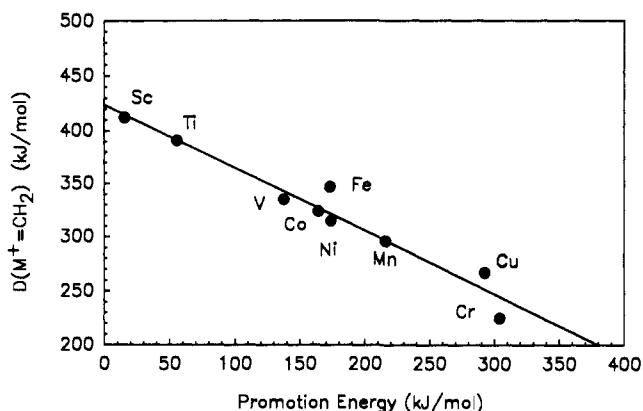


Figure 9. Metal-carbene bond dissociation enthalpies for first-row transition-metal ions vs atomic metal ion promotion energies to sd^{n-1} spin-decoupled states appropriate for forming covalent double bonds.

The intercept in Figure 8 gives what has been termed an "intrinsic" transition metal-hydrogen bond enthalpy, which is approximately 235 and 250 kJ/mol for first- and second-row metals, respectively. A similar plot of the neutral metal hydride bond dissociation enthalpies vs promotion energy gives a correlation that is not as good.⁸¹ The intercept for $E_p = 0$ is 238 kJ/mol. It has been suggested that these values should be representative of metal-hydrogen bond dissociation enthalpies in completely ligated closed-shell (18-electron) complexes. The metal-hydrogen bond dissociation enthalpies in the complexes $Mn(CO)_5H$, $Fe(CO)_4H_2$, and $Co(CO)_4H$ are 245, 272 and 227 kJ/mol, respectively, giving an average value of 248 kJ/mol, which is close to the intrinsic value of 235 kJ/mol.

The comparison of promotion energies with bond dissociation enthalpies has also been used to correlate metal-carbon dissociation enthalpies and to determine intrinsic bond enthalpies for metal-methyl, metal-carbene, and first-row transition metal-carbyne ions, 238, 422, and 544 kJ/mol, respectively.^{81,398} The successive increases of approximately 180 and 120 kJ/mol represent the additional bond strength associated with π bonding in proceeding from single to double and from double to triple bonds, respectively. The correlation for metal carbenes is shown in Figure 9.³⁹⁸ It is of interest to compare the intrinsic metal-carbene bond enthalpy of 422 kJ/mol to the value of 401 kJ/mol, derived for the coordinately saturated complex $Mn(CO)_5CH_2^+$ (see below). Due to steric effects and relaxation of the ligated organometallic fragment following metal-carbon bond cleavage, it may be appropriate to consider the intrinsic bond enthalpies as upper limits to compare with ligated complexes. In addition, comparisons are probably best made to complexes with a single metal-ligand σ bond.

The greatest curiosity to result from early studies of bond enthalpies in organometallic fragment ions was the observation that metal-methyl bond dissociation enthalpies were often *higher* than the corresponding metal-hydrogen bond dissociation enthalpies. In contrast, the data presented in part A of this section show that $D(M-H) > D(M-Me)$ in coordinatively saturated complexes. Halpern has recently suggested that steric effects may account for the weaker metal-methyl bonds in complexes.^{256,399}

One factor that cannot be overlooked in analyzing the results for cationic fragments is the increased polarizability of the methyl group compared to a hydrogen atom, which provides additional stabilization for the charge.¹⁵³ This effect alone, however, would certainly not contribute more than 25 kJ/mol toward explaining the fact that *transition metal-carbon bonds are strong!* For example, $D(Ni^+-Me)$ exceeds $D(Ni^+-H)$ by 22 kJ/mol. This difference is directly confirmed in the report that reaction 181 proceeds in the direction in-



indicated and is rapid at thermal energies.⁴⁰⁰ Since $D(Me-H)$ and $D(H-H)$ are approximately equal, the exothermicity of reaction 181 is determined by the higher metal-carbon bond dissociation enthalpy relative to metal-hydrogen bond dissociation enthalpy.

For metals of groups 8-12, the M^+-Me bonds are stronger than M^+-H bonds by ca. 30 kJ/mol. For Sc, Ti, Cr, and Mn the difference is negligible. The limited data for second-row metals suggest a similar trend. The possible role of agostic interactions, in which a C-H bonding pair interacts with an empty 3d π orbital in the M-C-H plane, has been considered.⁴⁰¹ If agostic interactions are important, they would be more so for the early metals and it would be necessary to infer that they *weaken* metal-methyl bond enthalpies, which seems an unlikely result.

Selected transition metal-methyl cations have been studied by ab initio GVB and configuration interaction methods.¹⁵³ Theory leads to similar M^+-H and M^+-Me bond dissociation enthalpies, with an average difference of 2 kJ/mol favoring the metal-carbon bonds. In all aspects, theoretical results show that the metal-methyl bonds are very similar to the σ bonds found in the corresponding metal hydrides.

The growing gas-phase data base for neutral metal hydrides and methyls makes it possible to more fully assess the influence of charge. The data in Tables 13 and 15 indicate that $D(M-H)$ exceeds $D(M-Me)$. This generally supports the notion that polarization effects favor stronger metal-carbon bonds in the ions. However, in view of the specific electronic requirements on each metal center, which manifests itself in the correlation of bond dissociation enthalpies with promotion energy, this is a naive comparison. The neutral metal atoms generally have ground states derived from the configuration $4s^23d^{n-2}$ (the metal ions are mainly $3d^n$). Covalent bond formation to the metal atom thus involves promotion of an electron from a filled 4s subshell, which is more energetically demanding than promotion from a d^n orbital of a metal ion with the same number of valence electrons. This leads to the expectation of weaker bonds for the neutral species.

While the metal-hydrogen and metal-carbon bond dissociation enthalpies in singly ligated organometallic fragments are of intrinsic interest, it is important to know both the *first* and *second* metal-ligand bond dissociation enthalpies in $M(L')L^+$, $D(L'M^+-L)$ and $D(M^+-L')$, respectively, in order to interpret the energetics of oxidative addition processes. These data are now available for several systems (Table 16). While first and second bond dissociation enthalpies are similar for Sc^+ , V^+ , and Co^+ , the values differ significantly for Zn^+ . In this case, the second bond dissociation enthalpy is high since there is an unpaired electron in a 4s orbital

($E_p = 0$). $D(\text{MeZn}^+-\text{Me})$ is low because it requires disruption of the filled $3d^{10}$ shell. Similar expectations would hold for Mn^+ , which should have a small $D(\text{L}^+\text{Mn}^+-\text{L})$ compared to $D(\text{Mn}^+-\text{L})$. Promotion energies for Co^+ and CoR^+ are 80 kJ/mol and approximately 109 kJ/mol,⁸¹ respectively, giving the expectation of comparable bond dissociation enthalpies with the first being somewhat smaller. The first bond is actually somewhat stronger (Table 16), an observation that holds for many of the first and second bond dissociation enthalpies presented in Table 16. The promotion energy for Sc^+ is only 15 kJ/mol and should be nearly zero for ScR^+ with only one valence electron. Hence, both first and second bonds are strong for this ion. Theoretical calculations provide additional insight into the bonding of ScH_2^+ ,⁴⁰² CrH_2^+ , and MoH_2^+ .³⁹³ The subtle differences in character for the bonding orbitals of the latter two species explain why molybdenum cations are able to activate C-H bonds while chromium is unreactive.⁴⁰³ The larger size of the d orbitals in the case of molybdenum cation reduces the d-d exchange energy and increases the σ -bond energies between the metal and carbon or hydrogen, allowing exothermic insertion into C-H bonds.

A large number of metal-olefin bond enthalpies in fragments ML^+ (Table 17) are now available, being derived mainly from studies (in what is most likely the decreasing order of reliability) of kinetic energy release distributions for statistical elimination processes in exothermic reactions, the determination of thresholds for endothermic reactions, and the determination of thresholds for photodissociation of metal-olefin complexes. The bond dissociation enthalpies for olefins, e.g., 155 ± 8 kJ/mol for the $\text{Co}^+(\text{C}_2\text{H}_4)$ fragment, are nearly 3 times larger than would be expected if the bonding were purely electrostatic. This binding enthalpy, which is the middle of the range of measured values for organometallic fragments, is very close to the metal-ethylene bond dissociation enthalpies in $\text{Fe}(\text{C}-\text{O})_4(\text{C}_2\text{H}_4)$ and $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$, both equal to 152 ± 18 kJ/mol. The available data are not sufficient to comment on periodic trends or the important features of the metal electronic structure to permit significant covalent interactions. The general notions of the Dewar-Chatto-Duncanson model^{123,124} for metal-olefin bonding are probably applicable. Strong bonds should be observed for those systems where an empty orbital is available on the metal center to accept electron density from the filled π orbital of the olefin and have, in addition, filled or partially filled orbitals on the metal center with appropriate symmetry to donate electron density to the π^* orbital of the olefin double bond.

Several groups have used ion cyclotron resonance techniques to measure equilibrium constants of ligand-exchange processes, exemplified by reaction 182.^{146,404-410} By assuming that the entropy changes are



negligible, the equilibrium constants yield $\Delta G^\circ_{\text{g}}(182) \approx \Delta H^\circ_{\text{g}}(182) = D(\text{M}^+-\text{L}) - D(\text{M}^+-\text{L}')$. The differences, which have always been reported relative to a given ligand [e.g., $D(\text{Mn}^+-\text{MeSH}) = 0$,⁴⁰⁴ $D(\text{Ni}^+-2\text{C}_2\text{H}_2) = 0$ ⁴⁰⁷] show good linear correlations with the proton affinities of the ligands, and therefore these correlations can be used to estimate new $D(\text{M}^+-\text{L})$ values.

TABLE 18. Nickel-Ligand Bond Dissociation Enthalpies, $D[\text{Ni}(\text{Cp})^+-\text{L}']$, and Proton Affinities of L' Relative to $\text{PA}(\text{NH}_3)$

L'	$D[\text{Ni}(\text{Cp})^+-\text{L}']$, kJ/mol	$\text{PA}(\text{L}')$, ^a kJ/mol
PH_3	190.4	-58.2
MeOH	190.8	-84.1
NO	192.0	-78 ^b
Me_2O	196.2	-49.8
MeCHO	196.7	-67.4
MeSH	197.1	-68.6
EtOH	198.7	-61.5
HCN	199.2	-109.2
EtCHO	201.3	-56.9
<i>i</i> -PrCHO	205.4	-49.0
$\text{C}_2\text{H}_3\text{CHO}$	206.3	-59.8 ^b
<i>i</i> -PrOH	207.1	-43.9 ^b
<i>t</i> -BuCHO	207.5	-52.3 ^b
Me_2CO	212.1	-32.6
<i>i</i> -BuOH	212.5	-41.8
MeOAc	213.0	-41.4 ^b
Et_2O	213.0	-19.2
Me_2S	213.8	-18.0
NH_3	218.8	0
MeCN	222.6	-59.0
MeNH_2	231.0	38.1
NMe_3	236.0	80.8
Me_2NH	237.7	64.9
AsMe_3	239.3	36.4
MeNC	241.0	-26.4 ^b
PMe_3	241.0	86.6

^a Data from ref 133 unless indicated otherwise. ^b Reference 146.

Relative bond enthalpies involving transition metals are available for Mn^+ ,^{404,410} FeBr^+ ,⁴⁰⁵ Co^+ ,⁴⁰⁶ Ni^+ ,⁴⁰⁷ and Cu^+ .⁴⁰⁸ For nontransition elements, data are limited to Li^+ ,⁴¹¹ Mg^+ ,⁴¹² and Al^+ .⁴¹³ A correlation for NiCp^+ has also been reported,¹⁴⁶ and in this case it is possible to obtain absolute metal-ligand bond dissociation enthalpies. Photoionization mass spectrometry studies of the complex corresponding to ML^+ in reaction 182, $\text{Ni}(\text{Cp})\text{NO}$, afforded $\text{IE}[\text{Ni}(\text{Cp})\text{NO}] = 8.21 \pm 0.03$ eV and $\text{AE}(\text{NiCp}^+) = 10.20 \pm 0.03$ eV, values enabling the calculation of $D[\text{Ni}(\text{Cp})^+-\text{NO}]$ as 192 ± 4 kJ/mol.⁴¹⁴ $D(\text{M}^+-\text{L}')$ can therefore be obtained for a variety of ligands, as shown in Table 18.

A brief summary of the trends that are apparent from $D[\text{Ni}(\text{Cp})^+-\text{L}']$ is as follows.¹⁴⁶ Bond dissociation enthalpies generally increase with increasing substitution of alkyl groups for H on the basis site ($\text{PMe}_3 > \text{PH}_3$, $\text{Me}_2\text{O} > \text{MeOH} > \text{H}_2\text{O}$, $\text{Me}_2\text{S} > \text{MeSH} > \text{H}_2\text{S}$) and with increasing alkyl substitution on carbon remote to the basic site (*t*-BuCHO > *i*-PrCHO > EtCHO > MeCHO); $D[\text{Ni}(\text{Cp})^+-\text{L}']$ is greater for second-row n-donor ligands than for first-row species ($\text{PMe}_3 > \text{NMe}_3$, $\text{Me}_2\text{S} > \text{Me}_2\text{O}$).

For comparison, the proton affinities of the ligands relative to $D(\text{NH}_3-\text{H}^+)$ ¹⁴³ are also presented in Table 18. As noted above, good correlations between $D(\text{M}^+-\text{L}')$ and $D(\text{L}'-\text{H}^+)$ are usually found, enabling the prediction of new metal-ligand bond dissociation enthalpies. However, in the case of NiCp^+ some exceptions to the observed correlation are found, particularly for ligands that must have a substantial π -bonding ability, such as HCN, MeCN, MeNC, and AsMe_3 . As seen in Table 18, these molecules exhibit a greater preference for bonding to NiCp^+ than predicted by their proton affinity.¹⁴⁶

Studies of Staley and co-workers for $\text{M}^+ = \text{Co}^+$, Ni^+ , and Cu^+ revealed some interesting synergistic effects

TABLE 19. Stabilization Enthalpies for Two Ligand-Metal Ion Complexes^a (kJ/mol)

M	L ^b	L' ^c	$2\bar{D}(M^+-L') - 2\bar{D}(M^+-L)$	δ^d
Co	EtOH	EtCH=CH ₂	2	6
Co	Me ₂ O	EtCH=CH ₂	2	7
Co	PrOH	Me ₂ C=CH ₂	2	6
Co	Me ₂ C=CH ₂	EtCHO	2	6
Ni	MeCH=CH ₂	Me ₂ O	7	11
Ni	Me ₂ C=CH ₂	PrOH	2	10
Ni	Me ₂ O	EtCH=CH ₂	0	10
Ni	CH ₂ =C=CH ₂	MeOH	3	9
Cu	Me ₂ C=CH ₂	PrCHO	2	6
Cu	MeCH=CH ₂	Me ₂ O	6	10

^aData from ref 409. ^b σ -Donor ligand. ^c π -Acceptor ligand. ^dEstimated uncertainty ± 2 kJ/mol.

exhibited by two ligand-metal fragments. The measured equilibrium constants for these systems refer to reactions 183 and 184. If there is no interaction be-



tween the ligands L and L', eq 185 is verified. However, when $\Delta H^\circ_{\text{g}}(183)$ is different from $\Delta H^\circ_{\text{g}}(184)$, a synergistic effect occurs and the difference $\delta = \Delta H^\circ_{\text{g}}(184) - \Delta H^\circ_{\text{g}}(183) = [D(\text{L}'\text{M}^+-\text{L}) - D(\text{L}'\text{M}^+-\text{L}') - [D(\text{LM}^+-\text{L}) - D(\text{LM}^+-\text{L}')] = 0$

$$D(\text{L}'\text{M}^+-\text{L}') - [D(\text{LM}^+-\text{L}) - D(\text{LM}^+-\text{L}')] = 0 \quad (185)$$

(184) - $\Delta H^\circ_{\text{g}}(183)$ may be considered as a direct measurement of that effect. Some δ values are presented in Table 19, together with differences $2\bar{D}(M^+-L') - 2\bar{D}(M^+-L)$ obtained from the known equilibrium constants of reactions 186. It may be noticed that the



metal-ligand bond enthalpies are higher in the mixed complexes. As Kappes, Jones, and Staley remark,⁴⁰⁹ this observation is in agreement with the theories of "trans effect" that consider that unlike trans ligands having different degrees of π bonding cause a synergistic enhancement due to asymmetric distortion of the metal orbitals involved in bonding. Quoting an example given by the same authors, a pure σ -donor/ π -acceptor ligand pair implies a distortion of the empty metal σ orbital toward the σ -donor ligand and a distortion of an occupied metal d orbital toward the empty ligand π -acceptor orbital. With $L = L'$, a symmetric structure results, giving no enhancement.

Note that in the case under discussion the δ values in Table 19 can be regarded as being direct measurements of synergistic effects although they are not bond enthalpy terms. In fact, it may be expected that the reorganization energies of L from LML^+ and LML'^+ are quite similar, the same occurring with L' from $\text{L}'\text{ML}'^+$ and LML'^+ . Therefore, the sum of these reorganization energies must be close to zero, and δ values in Table 19 are a good approximation of the "correct" bond strength differences.

2. Transition-Metal Complexes

Metal-carbene bond dissociation enthalpies in organometallic complex ions are comparable to $D(\text{M}^+-\text{CH}_2)$ in the bare carbene ions, although the available values are limited to three $\text{Mn}(\text{CO})_5\text{CXY}$ molecules:

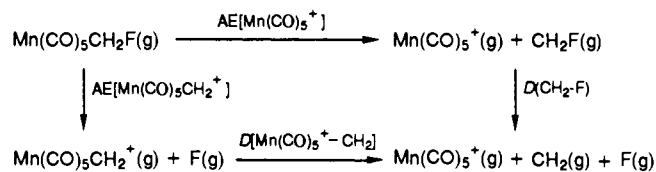
TABLE 20. Ionization Energies and Appearance Energies Determined by Photoionization Mass Spectrometry for $\text{Mn}(\text{CO})_5\text{L}^{137}$

molecule	ion	AP, eV	IE[$\text{Mn}(\text{CO})_5\text{L}$], eV
$\text{Mn}(\text{CO})_5\text{H}$	$\text{Mn}(\text{CO})_5^+$	10.3 ± 0.1	8.52 ± 0.03
$\text{Mn}(\text{CO})_5\text{Me}$	$\text{Mn}(\text{CO})_5^+$	9.75 ± 0.05	8.33 ± 0.03
$\text{Mn}(\text{CO})_5\text{CH}_2\text{F}$	$\text{Mn}(\text{CO})_5^+$	9.20 ± 0.05	8.35 ± 0.03
$\text{Mn}(\text{CO})_5\text{CHF}_2$	$\text{Mn}(\text{CO})_5\text{CH}_2^+$	10.2 ± 0.3^a	
	$\text{Mn}(\text{CO})_5^+$	9.25 ± 0.05	8.65 ± 0.03
$\text{Mn}(\text{CO})_5\text{CF}_3$	$\text{Mn}(\text{CO})_5\text{CHF}^+$	10.0 ± 0.2^a	
	$\text{Mn}(\text{CO})_5^+$	9.65 ± 0.05	8.90 ± 0.03
	$\text{Mn}(\text{CO})_5\text{CF}_2^+$	10.0 ± 0.1	

^aSelected value based on F⁻-transfer reactions.

$D[\text{Mn}(\text{CO})_5^+-\text{CH}_2] = 401 \pm 31$ kJ/mol, $D[\text{Mn}(\text{CO})_5^+-\text{CHF}] = 356 \pm 25$ kJ/mol, and $D[\text{Mn}(\text{CO})_5^+-\text{CF}_2] = 332 \pm 12$ kJ/mol. Each one of these results was derived from the appearance energies of $\text{Mn}(\text{CO})_5^+$ and $\text{Mn}(\text{CO})_5\text{CXY}^+$ (Table 20), which were obtained by photoionization mass spectrometry.¹³⁷ Scheme 28 and eq 187 exemplify the method of calculation in the case of $\text{Mn}(\text{CO})_5\text{CH}_2^+$. $D(\text{CXY}-\text{F})$ values are listed in the Appendix.

SCHEME 28

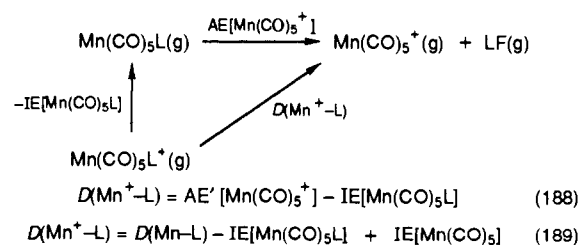


$$D[\text{Mn}(\text{CO})_5^+-\text{CH}_2] = \text{AE}[\text{Mn}(\text{CO})_5^+] - \text{AE}[\text{Mn}(\text{CO})_5\text{CH}_2^+] + D(\text{CH}_2-\text{F}) \quad (187)$$

The observed decrease of metal-carbene bond dissociation energies by successive fluorine substitution could be expected after the discussion presented in part A of the present section concerning metal-olefin bond enthalpies. The electronegative fluorine atom weakens the π bonding between the metal and the carbon atom. This effect is also observed in the bare carbenes NiCH_2^+ and NiCF_2^+ , where $D(\text{Ni}^+-\text{CH}_2)$ is 118 kJ/mol higher than $D(\text{Ni}^+-\text{CF}_2)$ (Tables 14 and 17).

The appearance energies of $\text{Mn}(\text{CO})_5^+$, together with $D(\text{Mn}-\text{L})$ values shown in Table 5, enable calculation of bond dissociation energies $D(\text{Mn}^+-\text{L})$ by using Schemes 12 and 29, summarized in eq 188 and 189.

SCHEME 29



$D(\text{Mn}^+-\text{L})$ values are collected in Table 21, together with the differences $D(\text{Mn}-\text{L}) - D(\text{Mn}^+-\text{L})$. Note that eqs 188 or 189 yield $D(\text{Mn}^+-\text{L})$ values independently of any assumption concerning $D(\text{Mn}-\text{Mn})$ in $\text{Mn}_2(\text{CO})_{10}$ [with exception of $D(\text{Mn}^+-\text{Mn})$].

Connor et al.²¹² have remarked that $\Delta D = D(\text{M}-\text{L}) - D(\text{M}^+-\text{L})$ are generally positive and increase with the

TABLE 21. Homolytic Bond Dissociation Enthalpies, $D(\text{Mn}^+-\text{L})$, in $\text{Mn}(\text{CO})_5\text{L}$ (kJ/mol)

$\text{Mn}(\text{CO})_5\text{L}$	$D(\text{Mn}^+-\text{L})^a$	$D(\text{Mn}-\text{L}) - D(\text{Mn}^+-\text{L})^b$
$\text{Mn}(\text{CO})_5\text{H}$	172 ± 10	73 ± 14
$\text{Mn}(\text{CO})_5\text{Me}$	137 ± 6	55 ± 14
	132 ± 15 ^c	55 ± 14
$\text{Mn}(\text{CO})_5\text{CH}_2\text{F}$	82 ± 6	57 ± 14
$\text{Mn}(\text{CO})_5\text{CHF}_2$	58 ± 6	86 ± 14
$\text{Mn}(\text{CO})_5\text{CF}_3$	72 ± 6	110 ± 14
	93 ± 15 ^c	110 ± 14
$\text{Mn}(\text{CO})_5\text{Bz}$	153 ± 17 ^{c,d}	-24 ± 14
$\text{Mn}_2(\text{CO})_{10}$	166 ^e	-7

^aThe values are based on $D(\text{Mn}-\text{Mn}) = 159$ kJ/mol, which implies $D(\text{Mn}-\text{H}) = 245$ kJ/mol (see Table 5). This result, together with $\text{AP}[\text{Mn}(\text{CO})_5^+]$ from $\text{Mn}(\text{CO})_5\text{H}$, gives $\text{IE}[\text{Mn}(\text{CO})_5] = 749 \pm 14$ kJ/mol. See note b, Table 5. ^bSee note b, Table 5. ^cValue based on the calorimetric result in Table 5. ^d $\text{IE}[\text{Mn}(\text{CO})_5\text{Bz}] = 7.51 \pm 0.02$ eV²²⁵ from the He I photoelectron spectrum of the complex. ^e $\text{IE}[\text{Mn}_2(\text{CO})_{10}] = 7.69 \pm 0.01$ eV.²¹²

electronegativity of group L.⁴¹⁵ This appears to be confirmed if the series $\text{L} = \text{Me}, \text{CH}_2\text{F}, \text{CHF}_2$, and CF_3 is considered. For $\text{L} = \text{Cl}, \text{Br}$, and I , ΔD also shows the same type of correlation.²¹² Noticeable exceptions are found for $\text{L} = \text{Bz}$ and $\text{Mn}(\text{CO})_5$. These negative results for ΔD are consequence of the low ionization energies of $\text{Mn}(\text{CO})_5\text{Bz}$, 7.51 ± 0.02 eV,²²⁵ and $\text{Mn}_2(\text{CO})_{10}$, 7.69 ± 0.01 eV,²¹² as compared with other $\text{IE}[\text{Mn}(\text{CO})_5\text{L}]$ listed in Table 20. Note that although ΔD values rely on $D(\text{Mn}-\text{Mn}) = 159$ kJ/mol, the trend shown in Table 21 is independent of this assignment, as evidenced by eq 189.

Interestingly, the value chosen for $D(\text{Mn}-\text{Mn})$ could be confirmed by determining the adiabatic ionization energy of $\text{Mn}(\text{CO})_5$. This value would enable the calculation of $\Delta H_f^\circ[\text{Mn}(\text{CO})_5, \text{g}]$ since $\Delta H_f^\circ[\text{Mn}(\text{CO})_5^+, \text{g}]$ is fairly established as 38 ± 14 kJ/mol (average value, obtained by considering the appearance energy data for $\text{Mn}(\text{CO})_5\text{H}$ and $\text{Mn}(\text{CO})_5\text{Me}$ in Table 20 and the enthalpies of formation of the complexes in the gas phase).²¹² It is important to stress that $\Delta H_f^\circ[\text{Mn}(\text{CO})_5^+, \text{g}]$ does not depend on any assumption regarding $D(\text{Mn}-\text{Mn})$, as shown by eq 190.

$$\Delta H_f^\circ[\text{Mn}(\text{CO})_5^+, \text{g}] = \text{AE}[\text{Mn}(\text{CO})_5^+, \text{g}] + \Delta H_f^\circ[\text{Mn}(\text{CO})_5\text{L}, \text{g}] - \Delta H_f^\circ[\text{L}, \text{g}] \quad (190)$$

Most transition metal-hydrogen bond dissociation enthalpies, $D(\text{M}^+-\text{H})$, in organometallic complexes have been obtained through ion cyclotron resonance spectroscopy studies, by measuring the proton affinities of the complexes B and by using literature values for the adiabatic ionization energies of B, together with $\text{IE}(\text{H}) = 13.598$ eV.¹⁵⁹ The available data not shown in Table 22, and the calculation method is typified by Scheme 7 or eq 35.

The usual situation in proton-transfer reactions, generalized in eq 33, is for proton transfer from B_1 to B_2 to occur when $\text{PA}(\text{B}_2) \geq \text{PA}(\text{B}_1)$. For example, the onset of reaction 191 establishes the proton affinity of

$$\text{Mn}(\text{CO})_5\text{Me}(\text{g}) + \text{BH}^+(\text{g}) \rightarrow \text{Mn}(\text{CO})_5(\text{Me})\text{H}^+(\text{g}) + \text{B}(\text{g}) \quad (191)$$

$\text{Mn}(\text{CO})_5\text{Me}$, 775 kJ/mol, as shown in Table 22.⁴¹⁶ However, as remarked in section III.D, these proton affinity values were derived by assuming negligible

TABLE 22. Metal-Hydrogen Homolytic Bond Dissociation Enthalpies in Transition-Metal Compounds^a

molecule (B)	$\text{PA}(\text{B}),^b$ kJ/mol	$\text{IE}(\text{B}),^c$ eV	$D(\text{B}^+-\text{H}),$ kJ/mol
$\text{V}(\text{CO})_6$	813 ± 10	7.45 ± 0.1	220 ± 14
$\text{Cr}(\text{CO})_6$	756 ± 10	8.142 ± 0.017	230 ± 10
$\text{Cr}(\text{CO})_2(\text{Cp})\text{NO}$	824 ± 10	7.2 ± 0.1	207 ± 14 ^d
$\text{Cr}(\text{CO})_2(\text{Cp})\text{Me}$	861 ± 11	7.2 ± 0.2	244 ± 22 ^d
$\text{Cr}(\text{CO})_3\text{Bz}$	858 ± 12	7.0 ± 0.1	221 ± 15
$\text{Mo}(\text{CO})_6$	778 ± 9	8.227 ± 0.011	260 ± 9
$\text{W}(\text{CO})_6$	774 ± 9	8.242 ± 0.006	257 ± 9
$\text{Mn}(\text{CO})_5\text{H}$	839 ± 10	8.52 ± 0.03 ^e	349 ± 11
$\text{Mn}(\text{CO})_5\text{Me}$	775 ± 10	8.33 ± 0.03 ^e	267 ± 11
$\text{Mn}(\text{CO})_3(\text{MeC}_5\text{H}_4)$	837 ± 8	7.86 ± 0.1	283 ± 13
$\text{Mn}_2(\text{CO})_{10}$	774 ± 13	7.69 ± 0.01 ^e	204 ± 13 ^f
$\text{Re}(\text{CO})_5\text{Me}$	786 ± 9	8.5 ± 0.1	294 ± 13
$\text{Re}_2(\text{CO})_{10}$	805 ± 5	7.80 ± 0.05 ^e	246 ± 7 ^f
$\text{MnRe}(\text{CO})_{10}$	794 ± 6	8.14 ± 0.01 ^g	<267 ± 7 ^g
$\text{Fe}(\text{CO})_5$	841 ± 15	7.98 ± 0.01	299 ± 15
$\text{Fe}(\text{Cp})_2$	879 ± 19	6.72 ± 0.1	215 ± 21
$\text{Fe}(\text{Cp})_2$	862 ± 6	6.72 ± 0.1	198 ± 11 ^h
$\text{Fe}(\text{Cp})_2$	866 ± 4	6.72 ± 0.1	202 ± 10 ⁱ
$\text{Fe}(\text{CO})_2(\text{Cp})\text{Me}$	798 ± 10	7.5 ± 0.1	210 ± 14
$\text{Ru}(\text{Cp})_2$	908 ± 12	7.0 ± 0.1 ^j	271 ± 15
$\text{Co}(\text{CO})_2(\text{Cp})$	854 ± 12	7.29 ± 0.02 ^k	245 ± 12
$\text{Rh}(\text{CO})_2(\text{Cp})$	883 ± 12	7.42 ± 0.02 ^k	287 ± 12
$\text{Ni}(\text{CO})_4$	757 ± 9	8.32 ± 0.01	248 ± 9
$\text{Ni}(\text{Cp})_2$	929 ± 9	6.2 ± 0.1	215 ± 13 ^d
$\text{Ni}(\text{Cp})\text{NO}$	835 ± 13	8.21 ± 0.03	315 ± 14 ^d

^aData recalculated from ref 136, unless indicated otherwise.

^bValues relative to $\text{PA}(\text{NH}_3) = 854 \pm 8$ kJ/mol. ^cAdiabatic ionization energies. Values were quoted from ref 136, unless indicated otherwise. ^dProtonation on the ligand. All the remaining values refer to protonation on the metal center. ^eValues from Table 20 except $\text{IE}[\text{Mn}_2(\text{CO})_{10}]$ (ref 212) and $\text{IE}[\text{Re}_2(\text{CO})_{10}]$ (Hall, M. B. *J. Am. Chem. Soc.* 1975, 97, 2057). ^fValue recalculated from the proton affinity reported in ref 417 by using the adiabatic ionization energy of the complex. ^gValue from ref 417. This must be an upper limit since the value for $\text{IE}[\text{MnRe}(\text{CO})_{10}]$ is the vertical ionization energy, measured by electron impact mass spectrometry: Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data* 1977, 9, Suppl. No. 1. ^hProton affinity from ref 141. ⁱProton affinity from ref 142. A value of $\text{IE}[\text{Fe}(\text{Cp})_2] = 6.81 \pm 0.07$ eV, measured by charge-transfer equilibria, is reported in this reference. ^jValue estimated from the published photoelectron spectrum in ref 59. ^kLichtenberger, D. L. Private communication.

entropy effects for reaction 33. Relatively small corrections are thus expected if the entropy changes are accounted for. This is observed in the case of ferrocene, where two recent high-pressure mass spectrometry studies led to values of $\text{PA}[\text{Fe}(\text{Cp})_2]$ that are about 15 kJ/mol lower than the ICR result (see Table 22).^{141,142}

Some periodic trends emerge from the data in Table 22. For example, on proceeding from a first-row compound to its second-row homologue, the metal-hydrogen bond increases, while it seems that on proceeding from a second- to a third-row metal the bond dissociation enthalpies are nearly constant. However, the latter trend is only shown for $\text{Mo}(\text{CO})_6$, $\text{W}(\text{CO})_6$, and somewhat indirectly for $\text{Mn}(\text{CO})_5\text{Me}$, $\text{Re}(\text{CO})_5\text{Me}$ ¹³⁶ and $\text{Mn}_2(\text{CO})_{10}$, $\text{Re}_2(\text{CO})_{10}$.⁴¹⁷

Within a "homologous" series of compounds, the homolytic bond energy $D(\text{B}^+-\text{H})$ remains constant.¹³⁶ On the other hand, compounds with higher oxidation states of the same metal atom have weaker metal-hydrogen bonds. The formation of several σ bonds causes changes in the electron density and orbital hybridization of the metal center, which result in weaker bonds with increasing oxidation state, even in the absence of stereochemical factors. This widely recognized feature has also been pointed out by Connor.⁸⁷ The iron com-

TABLE 23. Gas-Phase Acidities of Metal Carbonyl Hydrides

complex [M(L) _n H]	$D(L_nM^+H^+)$, kJ/mol	$EA[M(CO)_n]$, kJ/mol
Mn(CO) ₅ H	1331 ± 13	≤245
Fe(CO) ₄ H ₂	1334 ± 21	232 ± 29 ^a
Co(CO) ₄ H	≤1314	≥227
Fe(CO) ₄ H	≥1335 ± 21	232 ± 29 ^a

^a Reference 418.

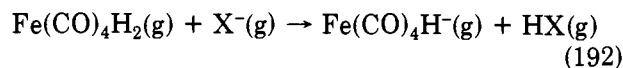
plexes presented in Table 22 illustrate this behavior; namely, $D(Fe^+-H)$ in $Fe^0(CO)_5$ is stronger than $D(Fe^+-H)$ in $Fe^{II}(Cp)_2$. Nevertheless, an exception may also be noticed in the case of manganese complexes, where $D[Mn(CO)_5Me^+H]$ is about 80 kJ/mol weaker than $D[Mn(CO)_5H^+H]$.

It is also interesting to compare $D[Mn(CO)_5H^+H] = 349$ kJ/mol (Table 22) with $D[Mn(CO)_5^+H] = 172$ kJ/mol (Table 21). The fact that the manganese-hydrogen *first* bond dissociation enthalpy in $Mn(CO)_5H_2^+$ is about 180 kJ/mol stronger than the *second* may suggest that the dihydrogen complex has an η^2-H_2 bond, whose dissociation enthalpy can be calculated as 85 kJ/mol by using the above values and $D(H-H)$.

Finally, it may be noticed from the data in Tables 13 and 22 that $D(M^+H)$ are stronger in organometallic complexes than in the bare hydrides. Recall that this ligand effect is not observed for $D(M^+-CH_2)$, although the available data for metal-carbene bond dissociation enthalpies in organometallic compounds are too scarce to define a general trend.

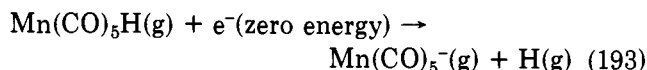
Data for gas-phase acidities or organometallic complexes are not abundant, despite the fact that these values can provide useful information about several problems of current interest. For example, a comparison between gas-phase results and solution data will improve our understanding of solvation and substituent effects.¹³⁵ Also, the determination of gas-phase acidities can afford other interrelated thermochemical parameters as evidenced by Scheme 8 or eq 36.

The gas-phase acidities of three organometallic complexes, $Mn(CO)_5H$, $Fe(CO)_4H_2$, and $Co(CO)_4H$, have been obtained from ICR studies involving reactions between each of these complexes and anions such as CF_3CO^- , Cl^- , Br^- , and I^- .¹³⁷ The method used is typified in reaction 192 for the iron complex. The reaction oc-



curs with $X^- = Cl^-$ and Br^- but not with $X^- = I^-$. This brackets the acidity of $Fe(CO)_4H^-$ between $D(I^-H^+) = 1315.0 \pm 0.8$ kJ/mol and $D(Br^-H^+) = 1353.9 \pm 1.3$ kJ/mol.^{135,137} The average value, 1334 ± 21 kJ/mol, was assigned to $D[Fe(CO)_4H^-H^+]$.

The results obtained for the three above complexes (Table 23) were checked by examining their reactions with zero-energy electrons. For example, the fact that reaction 193 was not observed indicates that $\Delta H_g^\circ(193)$



≥ 0 or that $D[Mn(CO)_5-H] \geq EA[Mn(CO)_5]$. This affords an upper limit of 245 kJ/mol for $EA[Mn(CO)_5]$ by using the value quoted in Table 5. On the other hand, eq 194 shows that $D[Mn(CO)_5^+H^-] \geq IE(H) =$

TABLE 24. Hydride Affinities of Carbonyl Complexes and Metal-Formyl Bond Dissociation Enthalpies (kJ/mol)

molecule	HA ^a	$EA[M(CO)_{n-1}]$	$D[M(CO)_{n-1}-CHO]$
Cr(CO) ₆	184 ± 17	≥201 ^a	≤147
Mo(CO) ₆	184 ± 17	≥192 ^a	≤172
W(CO) ₆	184 ± 17	≥192 ^a	≤194
Fe(CO) ₅	235 ± 17	232 ± 29 ^b	187 ± 36

^aData from refs 419 and 420. ^bReference 418.

1312 kJ/mol, in agreement with the result shown in Table 23.

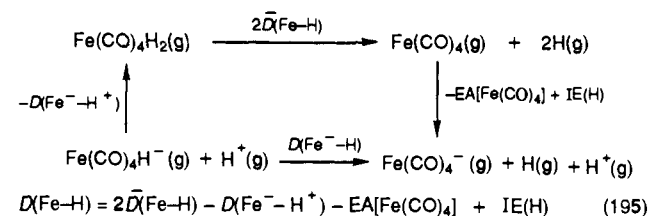
$$\Delta H_g^\circ(193) = D[Mn(CO)_5-H] - EA[Mn(CO)_5] = D[Mn(CO)_5^+H^-] - IE(H) \quad (194)$$

The occurrence of a reaction similar to eq 193 but involving the cobalt complex yields the lower limit $EA[Co(CO)_5] \geq D[Co(CO)_4-H] = 227$ kJ/mol (Table 10). For the iron complex, the observation of $Fe(CO)_4^-$ by attachment of zero-energy electrons to $Fe(CO)_4H_2$, giving $Fe(CO)_4^-$ and H_2 , indicates $EA[Fe(CO)_4] \geq 2\bar{D}[Fe(CO)_4-H] - D(H-H) = 108$ kJ/mol (see Table 8). This lower limit can be compared with the adiabatic $EA[Fe(CO)_4]$, which was determined as 232 ± 29 kJ/mol.⁴¹⁸

The values in Table 33 show that the transition-metal carbonyl hydrides are extremely strong acids in the gas phase, mainly as a consequence of the weak metal-hydrogen bonds.¹³⁷ An interesting feature that may become apparent when more $D(L_nM^+H^+)$ are available is the relatively small dependence of the acidity on the nature of the metal. This point has already been noted for the bare metal hydrides (Table 13), and a similar pattern may emerge for organometallic complexes, as suggested by the few available values in Table 23.

The acidity of $Fe(CO)_4H_2$ and the electron affinity of $Fe(CO)_4$ enable the comparison of metal-hydrogen bond dissociation enthalpies in the isoelectronic series $Fe(CO)_4H^-$, $Co(CO)_4H$, and $Ni(CO)_4H^+$. $D[Fe(CO)_4-H]$ can be calculated through Scheme 30 or eq 195, with

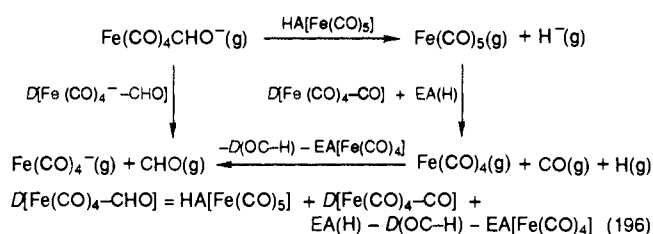
SCHEME 30



data from Tables 8 and 23 and $IE(H) = 13.598$ eV.¹⁵⁹ $D[Co(CO)_4-H]$ and $D[Ni(CO)_4^+H]$ are given in Tables 10 and 22, respectively. The values, 290 kJ/mol for iron, 227 kJ/mol for cobalt, and 248 kJ/mol for nickel, do not show an obvious periodic trend. The value for iron has the greatest uncertainty and might have been expected to be weaker.

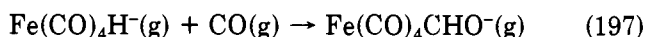
The experimental methods and most of the available anion affinity data for transition-metal complexes were analyzed in a recent review by Squires.⁶⁶ When the anion is H^- , these values may lead to metal-hydrogen bond dissociation enthalpies if the hydrogen binds to the metal center. In the molecules shown in Table 24, however, the hydride attachment yields formyl complexes,^{419,420} as shown by Scheme 31. If the electron affinities of $M(CO)_{n-1}$ are known, $D[M(CO)_{n-1}-CHO]$ can be calculated by using this scheme or eq 196, illustrated

SCHEME 31



for $\text{Fe}(\text{CO})_5$. The results are displayed in Table 24. They rely on the metal-carbonyl bond dissociation enthalpies in Table 1, on $\text{EA}(\text{H}) = 0.754 \text{ eV}$,¹⁵⁹ and on $D(\text{OC-H}) = 63 \pm 4 \text{ kJ/mol}$. Their accuracies are determined by the electron affinities of the unsaturated molecules $\text{M}(\text{CO})_{n-1}$ (see Table 24).

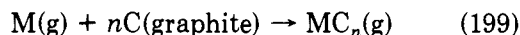
As remarked by Squires,⁴²⁰ the values of $D[\text{M}(\text{CO})_{n-1}\text{-CHO}]$ can be used to predict the enthalpies of carbonyl insertion in the metal-hydrogen bonds (reaction 197). From $D[\text{Fe}(\text{CO})_4\text{-H}] = 290 \text{ kJ/mol}$ and $D(\text{OC-H}) = 63 \text{ kJ/mol}$ given above, eq 198 led to $\Delta H^\circ_{\text{g}}(197) \approx 40 \text{ kJ/mol}$.



$$\Delta H^\circ_{\text{g}}(197) = D[\text{Fe}(\text{CO})_4\text{-H}] - D(\text{OC-H}) - D[\text{Fe}(\text{CO})_4\text{-CHO}] \quad (198)$$

3. Fragments MC and MC_2

The thermochemistry of metal carbides, MC_n , has been studied by high-temperature Knudsen cell mass spectrometry techniques,⁴²¹ which enable the determination of equilibrium constants of reactions 199 at



several temperatures. The use of van't Hoff plots or, more commonly, third-law equations, yields $\Delta H^\circ_{\text{g}}(199)$, from which the enthalpies of formation and atomization (cleavage of all bonds in the molecule) of $\text{MC}_n(\text{g})$ can be obtained.

With $n = 1$, the atomization enthalpy of the carbide equals $D(\text{M-C})$; for $n > 1$, $D(\text{M-C}_n)$ is calculated by subtracting $\Delta H^\circ_{\text{atom}}(\text{C}_n, \text{g})$ from the atomization enthalpy of MC_n . This implies that a structure M-C-C_{n-1} is assumed.

The enthalpies of formation of gaseous polyatomic carbides are difficult to determine, and so the uncertainties affecting $D(\text{M-C}_n)$ are large, of the order of $\pm 50 \text{ kJ/mol}$ for $n = 2$.⁴²¹ At the present stage, the values for the bond dissociation enthalpies in the diatomic molecules are the most reliable. The available data for $D(\text{M-C})$ and $D(\text{M-C}_2)$ are collected in Table 25.^{356,421-427} For comparison purposes, values of $D(\text{M-O})$ in diatomic oxides are also included in the table.⁴²⁸

Several authors⁷² have correlated $D(\text{M-C}_2)$ and $D(\text{M-O})$ by considering that the bonding in a metal dicarbide can be described as an ionic bond between M^{2+} and C_2^{2-} . As Gupta and Gingerich remarked,⁴²¹ this concept of the pseudo-oxygen character for the C_2 group has been applied successfully in interpreting the M-C_2 and M-O bond enthalpies for groups 3 and 4 (note, however, the very large uncertainties). The relationship $D(\text{M-O}) > D(\text{M-C}_2)$, which is easily explained as a consequence of the higher electronegativity of oxygen as compared to C_2 , also holds for groups 5 and 6. However, for group

9 an opposite trend is observed, suggesting an enhanced covalent character of M-C_2 bonds. The C_2 group, with its delocalized π electrons, is expected to form stronger covalent bonds than the oxygen atom.⁴²¹

Gupta and Gingerich have also provided some other interesting conclusions about the trends of $D(\text{M-C}_2)$ and $D(\text{M-O})$ in Table 25: (1) $D(\text{M-O}) - D(\text{M-C}_2)$ decreases from left to right; (2) both $D(\text{M-C}_2)$ and $D(\text{M-O})$ are nearly constant for metals in groups 3-5 but decrease from group 6 onward. This last conclusion may be explained in terms of an increasing metal electronegativity, which implies a decrease of the ionic character of M-C_2 and M-O bonding. The first supports the interpretation given above for the relationship $D(\text{M-C}_2) > D(\text{M-O})$ observed in the case of group 9 molecules.

Bearing in mind the errors assigned to $D(\text{M-C})$ values in Table 25 and also the fact that some of them are upper limits, it is interesting to compare those results with $D(\text{M-C}_2)$. The differences $D(\text{M-C}_2) - D(\text{M-C})$ seem to decrease from left to right and are negative for groups 8-10 carbides. This trend can be interpreted as for $D(\text{M-O}) - D(\text{M-C}_2)$. M-C bonding is less ionic than M-C_2 bonding, since the carbon atom is less electronegative than C_2 . However, with increasing metal electronegativity the covalent bonding becomes more and more important, a situation in which the carbon atom has a clear advantage over C_2 . The importance of covalent metal-carbon bonds in the diatomic molecules is also stressed by the fact that $D(\text{M-C})$ does not decrease on going from group 3 to group 10, in opposition to the behavior found for $D(\text{M-C}_2)$ and $D(\text{M-O})$.

The nature of metal-carbon bonding in MC has been discussed by Gingerich and co-workers, either by noting a correlation between $D(\text{M-C})$ and $D(\text{M-M})$ in diatomic molecules M_2 , for groups 5 and 6,⁴²¹ or through theoretical calculations involving, e.g., the molecule PdC .⁴²⁷ The correlation with $D(\text{M-M})$ suggests that metal-carbon bonding in transition-metal monocarbides is predominantly multiply covalent, particularly for metals with higher electronegativity. Ab initio calculations show the existence of two σ bonds and one π bond in palladium carbide.

V. Concluding Remarks

The data compiled and analyzed in previous sections exemplify the growing body of information relating to the strengths of transition metal-hydrogen and metal-carbon bonds. These results dispel the notion, sometimes claimed, that reliable bond strength values are virtually nonexistent. Nevertheless, it is also true that a significant fraction of these data were published recently, in the last decade, mainly as a result of the stimulus provided by the growing fields of organometallic chemistry and homogeneous catalysis and the increased use of new techniques applied to gas-phase organometallic species. There is every expectation that this growth will continue unabated in the near future. Many values are still needed to define trends more reliably and enable more accurate estimates.

The concept of "bond enthalpy term" can be used to predict enthalpies of formation of new complexes and can also afford reasonable estimates of bond dissociation enthalpies if the correction parameters, the so-

TABLE 25. Metal-Carbide and Metal-Oxygen Bond Dissociation Enthalpies in MC, MC₂, and MO^{a,b} (kJ/mol)

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
M-C	444 ± 21 ^{c,d}	423 ± 30	423 ± 24 ^e							
M-C ₂	572	573	578	451						
M-O	681 ± 11	672 ± 9	625 ± 19	429 ± 29	403 ± 42	390 ± 17	384 ± 13	381 ± 17	270 ± 21	271 ± 42 ^f
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
M-C	418 ± 63	561 ± 25	568 ± 13 ^e	482 ± 16 ^e	564 ± 29 ^f	648 ± 13	580 ± 4 ^g	436 ± 20 ^{c,h}		
M-C ₂	638	581	656	500		519	433			
M-O	719 ± 11	776 ± 13	769 ± 25	560 ± 21	(548)	528 ± 42	405 ± 42	(381)	221 ± 21	(236)
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
M-C	463 ± 20 ⁱ	540 ± 25				649 ± 13 ^j	631 ± 5 ^k	610 ± 5 ^k		
M-C ₂	659	674				569	555 ^k	557 ^k		
M-O	801 ± 11	801 ± 13	799 ± 13	672 ± 42	(627)	(598)	414 ± 42	391 ± 42	223 ± 21	(213)

^a $D(M-C)$ and $D(M-C_2)$ were taken from refs 356 and 421, respectively, unless indicated otherwise. $D(M-O)$ were quoted from ref 428. Values in parentheses are estimates by the authors in ref 428. ^b Values reported at 0 K were corrected to 298 K by adding $1.5RT$. ^c Upper limit. ^d Reference 422. ^e Reference 421. ^f Reference 423. ^g Reference 424. ^h Reference 427. ⁱ Reference 425. ^j Reference 72. ^k Reference 426.

called reorganization energies, are available. However, as noted before, most of the bond enthalpy terms derived in the present survey should only be regarded as an extension of Laidler terms. Reliable theoretical calculations of *real* reorganization energies would allow the evaluation of absolute bond strength values.

Other methods for estimating the energetics of reactions involving organometallic compounds have been reported in recent years. One of these methods makes use of linear relationships between the enthalpies of formation of crystalline organometallic complexes of a given family and the enthalpies of formation of the organic ligands bonded to the metal atoms.⁴²⁹⁻⁴³¹ Since the latter quantities are usually known, the enthalpy of formation of *one* complex may provide the enthalpies of formation of other complexes from the same family. This connection between organometallic systems and the respective organic ligands has also been explored by linear plots of metal-ligand bond dissociation enthalpies versus ligand-hydrogen bond dissociation enthalpies.^{241,432} Indeed, it can be observed that this parallel trend is followed by many of the values discussed in section IV.A.

The two previous methods, which in essence are equivalent,⁴³⁰ are probably the best present way of predicting new data, but other empirical approaches, such as the Drago equation,^{433,434} or one that relies on the chemical hardness concept,⁴³⁵ should also be mentioned. In addition, it is likely that correlations between enthalpies of formation and electronegativity values based on the "unshielded core potential" of atoms,⁴³⁶ will be used in the near future to estimate bond dissociation enthalpies in transition-metal organometallic systems.

The experimental methods that have been applied in thermochemical studies of organometallic complexes and fragments were discussed in section II. It is expected that gas-phase techniques such as laser pyrolysis, photoionization mass spectrometry, ion cyclotron resonance (ICR, FT-ICR), high-pressure mass spectrometry, flowing-afterglow, guided ion beam, and kinetic energy release experiments will play an increasingly important role in studies of metal-ligand energetics. Also, photoacoustic calorimetry is likely to become an important source of data for transition-metal complexes. All these experimental techniques may yield absolute values of bond dissociation enthalpies, while the direct information obtained with older calorimetric techniques is often limited to enthalpies of formation

or relative values of bond dissociation enthalpies. Both types of data have their own interest and application ranges, and it can be said that, in many ways, the new and the old techniques complement each other.

As discussed in section IV.B, ab initio calculations have provided very useful insight into the nature of metal-hydrogen and metal-carbon bonds and have afforded M-H and M-C bond dissociation enthalpies that were occasionally mentioned in the present review. Their agreement with experimental values is usually good. These theoretical calculations have mainly been restricted to small molecules, but the evolution of computing methods and hardware will probably enable the accurate study of more complex systems in the future. For these species, a number of relevant results within the scope of the present review have recently been reported by several groups.^{396,437-459} The extended Hückel method, despite being placed "on the low end of a quality scale of approximate molecular orbital calculations",⁴⁶⁰ has been applied to estimate some reorganization energies when the molecular structures are available.

It is somewhat frustrating to have a large amount of carefully assessed data at hand and not use it to explore the thermochemical changes attending a wide range of interesting organometallic reactions. The goal of the present review was, however, to provide a critically evaluated data bank, by emphasizing the advantages and limitations of the experimental methods and the assumptions used to derive each "bond strength". It is hoped that this goal has been accomplished.

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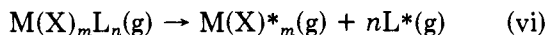
VII. Appendix

The bond enthalpy values derived in the present review rely on thermochemical data for organic free radicals. While this area of research has also been subject to considerable development in the last decade, the enthalpies of formation of many "basic" radicals are still

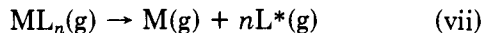
in the initial complex (*nonreorganized* fragments).



$$\Delta H^\circ(v) = E(M-L)$$



$$\Delta H^\circ(vi)/n = E(M-L)$$



$$\Delta H^\circ(vii)/n = E(M-L)$$

As described in section III, the bond enthalpy terms are related to the bond dissociation enthalpies through the *reorganization or relaxation energies of the fragments*. In the case of atoms, the reorganization (promotion) energies are taken as zero, meaning that the bond enthalpy terms used in the present review are not *intrinsic bond enthalpies*. Nevertheless, as also explained in section III, they should correlate better with other structural parameters, such as bond lengths or force constants, than bond dissociation enthalpies. In other words, *bond strengths* are better described by bond enthalpy terms, $E(M-L)$, than by bond dissociation enthalpies, $D(M-L)$ or $\bar{D}(M-L)$.

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