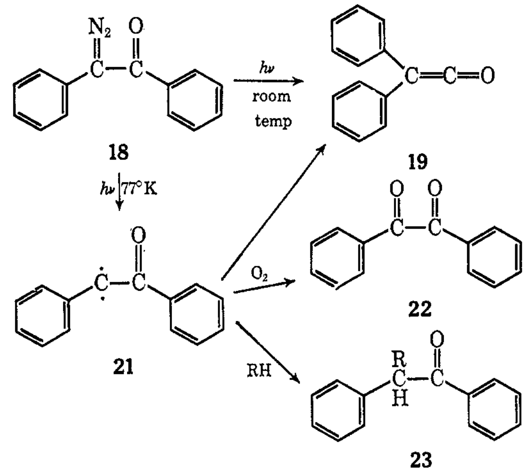
Scheme VI



When the glass was warmed, the benzoylphenylmethylene was free to react. The products obtained from warming an irradiated solution in methylcyclohexane or tetrahydro-2-methylfuran were benzil (**22**) (0–12%), deoxybenzoin (**23**) (74–80%) (or solvent-substituted deoxybenzoin), and only a very small amount of diphenylketene (0–12%), the Wolff rearrangement product (Scheme VI). These compounds were observed by their characteristic phosphorescence spectrum[36] and gas chromatographic retention time. The amount of benzil which was found depended upon how much oxygen was initially present. The formation of benzil from the ground-state **21** is analogous to the formation of benzophenone from diphenylmethylene.[25] The formation of **23** probably occurs by hydrogen abstraction from the solvent.

When the photolyses of azibenzil were performed at room temperature, the product distributions were quite different from those obtained in the low-temperature experiments. Diphenylketene (**19**), the usual Wolff rearrangement product, was the major component (85–90%), as judged from phosphorescence and gas chromatographic analysis.

The results obtained indicate that the triplet ground-state species **21** does not undergo the Wolff rearrangement efficiently, if at all, but that it does behave as a free-radical species (hydrogen abstraction, reaction with oxygen). Further extrapolation would suggest that, since **21** does not rearrange to **19** upon warming from 77°K, it is probably not the reactive intermediate in the room-temperature Wolff rearrangement of **18** to **19**.

My interest in arylmethylenes began as a fruitful collaboration with Dr. Robert W. Murray in the area of dicarbenes. Our subsequent collaboration with Dr. Edel Wasserman and William A. Yager, each a pioneer in epr spectroscopy, greatly enlarged the scope of the research. Dr. William A. Gibbons brought his talent and skill in low temperature photochemistry to the problem of the optical spectroscopy of arymethylenes, and Mrs. Susan R. Fahrenholtz applied some of the spectral measurements to the photochemical Wolff rearrangement. I am pleased to acknowledge the contributions of these colleagues. In addition, I thank Dr. L. C. Snyder and Professors C. A. Hutchison, Jr., and G. L. Closs for several helpful discussions and W. Delavan and R. M. R. Cramer for their aid in obtaining some of the epr spectra.

Reversible Activation of Covalent Molecules by Transition Metal Complexes. The Role of the Covalent Molecule[1]

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The reactions of metals or their compounds with small gaseous[2] molecules play a vital role in life and industry. Oxygen transport by hemoglobin (Hb) (eq 1) and the catalytic hydrogenation of olefins over metal surfaces (eq 2) are two prominent examples among a vast variety of these reactions.

$$Hb_4 \underset{-O_2}{\overset{+O_2}{\rightleftarrows}} Hb_4O_2 \underset{-O_2}{\overset{+O_2}{\rightleftarrows}} Hb_4O_4 \underset{-O_2}{\overset{+O_2}{\rightleftarrows}} Hb_4O_6 \underset{-O_2}{\overset{+O_2}{\rightleftarrows}} Hb_4O_8 \qquad (1)$$

A fundamental step in these chemical processes is the initial combination of the reacting molecule with the metal.

$$\underline{M} + C_2H_4 \rightleftarrows \underline{M}\text{–}C_2H_4 \qquad (2a)$$

$$\underline{M} + H_2 \rightleftarrows H\underline{M}H \qquad (2b)$$

$$H\underline{M}H + \underline{M}\text{–}C_2H_4 \rightleftarrows H\underline{M}\text{–}C_2H_5 \qquad (2c)$$

$$H\underline{M}\text{–}C_2H_5 \longrightarrow \underline{M} + C_2H_6 \qquad (2d)$$

($\underline{M}$ = metal surface, not necessarily an individual surface atom)

The step is usually reversible; it is called the *activation* of the reactant (eq 1, 2a, 2b). *An understanding of the over-all reaction requires a knowledge of this primary interaction: its stoichiometry, mechanism, energetics, and the nature of the bonding in and the structure of the activated*

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[1] Presented in part at the Tenth International Conference on Coordination Chemistry (10.I.C.C.C.), Tokyo and Nikko, Sept 12–16, 1967; L. Vaska, "Proceedings of the 10.I.C.C.C.," K. Yamasaki, Ed., The Chemical Society of Japan, Tokyo, 1967, p 132.

[2] The work reviewed here deals with the activation of small covalent molecules, most of which are gases at ordinary temperatures, thus the brief and convenient synonyms "gas" and "gaseous molecule," although most of the reactions described are those of solutions of gases in liquids. It should be also noted that the types of reactions which are presented and interpreted are not limited to "small" or "gaseous" molecules (see, *e.g.*, Table III).

adduct.[3] Yet, in spite of the many and remarkable recent advances in heterogeneous[4] and enzymatic[5-7] catalysis, the long history of these sciences has been able to give only partial or indirect answers to most of these basic questions, owing to the very nature of the catalytic reactions at large: they are either very fast or very complex, usually both, and their reactive intermediates have been generally inaccessible to direct or reliable observation. For the examples cited above (eq 1, 2) it suffices to mention that the mechanism of hemoglobin oxygenation (eq 1) is still obscure,[5,6] not to speak of the factors which determine the reversibility of oxygenation, and no definite electronic or geometric information is available for the activated adducts[3] formulated in eq 2.[4,8]

The development of coordination chemistry of the transition metals during the past two decades has greatly helped to clarify some of these fundamental questions. The discoveries of the reversible activation of molecular hydrogen and oxygen by metal complexes in solution by Calvin and others[9] mark the beginning of a new branch of science which has grown to the broad, diversified, and very active field of homogeneous catalysis[10] today. It was not until 1962, however, that it became possible to directly observe the electronic *and* stereochemical properties of a metal–gas activated adduct, and thereby to inquire, on a rational basis, into the factors which determine the reversible activation of small covalent molecules by transition metal complexes. A synthetic complex of iridium[11] was discovered to yield reversible but isolable and relatively stable adducts with hydrogen (eq 3),[12] oxygen,[13] and numerous other "inert" covalent

$$[IrCl(CO)((C_6H_5)_3P)_2] + H_2 \rightleftarrows [H_2IrCl(CO)((C_6H_5)_3P)_2] \quad (3)$$

molecules.[12] Furthermore, it was found that some of these adducts (*e.g.*, eq 3) are intimately related to some analogous but well-established chemical compounds,[14] and they thus became exposed to direct and conventional observations of their chemical and physical properties.

An immediate fruit of these observations was that the reactants (eq 3) could be characterized as a reductant or base (metal complex) and as an oxidant or acid (covalent gas). This simple and general interpretation, originally suggested by spectroscopic and chemical evidence,[12] and the unusual reactivity of our model compound ($[IrCl(CO)((C_6H_5)_3P)_2]$) to undergo simple addition reactions,[12] gave the impetus which has resulted in an intensive and widespread research activity with this and related d^8 (and also d^{10}, d^7, and d^6) complexes. In this account, however, we are not concerned with the large number and variety of addition and substitution reactions of and homogeneous catalysis with $[IrCl(CO)((C_6H_5)_3P)_2]$ and its analogs which have been studied in this and other laboratories.[18] Our intent here is to summarize some quantitative data obtained in recent years on a few representative reversible reactions, mainly with hydrogen,[12,19,20] oxygen,[13,21,22] sulfur dioxide,[23,24] carbon monoxide,[25,26] ethylene,[19,27] and substituted ethylenes,[27] and to present a general hypothesis for these metal complex–gas interactions.

I. Experimental Approach to the Problem

Equations 4 and 5 refer to our experimental studies.

$$ML_i + XY \underset{k_{-1}}{\overset{k_2}{\rightleftarrows}} (XY)ML_i \quad (4)$$

$$M = \text{central metal atom};\ L_i = \text{ligands};$$

$$XY = \text{addendum: } H_2, O_2, CO, SO_2, C_2H_4, \text{etc.}$$

$$K_{eq} = [(XY)ML_i]/[ML_i][XY] \quad (5)$$

ML_i represents various derivatives of our model compound, $[IrA(CO)L_2]$ (A = univalent anionic ligand,

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[3] The term "activated adduct" refers to a reversible reaction *intermediate* or *product* composed of an "activated molecule(s) or radical(s)" and a metal complex or metal. It does not indicate or imply any type of bond or structure; it is simply a collective and shorthand name for species containing the reacting molecule in a new form, and it is to be distinguished from the "activated complex" (in the usual sense). The term "adduct" is used in the same sense except that it is a more general one and does not necessarily imply reversibility.

[4] Some recent volumes on chemisorption and heterogeneous catalysis: (a) D. O. Hayward and B. M. W. Trapnell, "Chemisorption," Butterworth and Co. (Publishers) Ltd., London, 1964; (b) G. C. Bond, "Catalysis by Metals," Academic Press, New York, N. Y., 1962; (c) *Advan. Catal.*, **17** (1967).

[5] "Hemes and Hemoproteins," B. Chance, R. W. Estabrook, and T. Yonetani, Ed., Academic Press, New York, N. Y., 1966.

[6] "Oxygen, Proceedings of a Symposium Sponsored by the New York Heart Association," Little, Brown and Co., Boston, Mass., 1967.

[7] R. H. Burris, *Ann. Rev. Plant Physiol.*, **17**, 155 (1966); W. D. P. Stewart, *Science*, **158**, 1428 (1967).

[8] Equations 2 represent one of the several suggested schemes for this catalytic hydrogenation.[4b]

[9] (a) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice Hall, Inc., Englewood Cliffs, N. J., 1952, Chapter 8, and references quoted; (b) L. H. Vogt, H. M. Faigenbaum, and S. E. Wiberley, *Chem. Rev.*, **63**, 269 (1963); (c) J. Halpern, *Ann. Rev. Phys. Chem.*, **16**, 103 (1965); (d) S. Fallab, *Angew. Chem. Intern. Ed. Engl.*, **6**, 496 (1967).

[10] Some recent reviews are: (a) ref 9c; (b) G. N. Schrauzer, *Advan. Organometal. Chem.*, **2**, 1 (1964); (c) J. P. Collman, *Transition Metal Chem.*, **2**, 1 (1966); (d) J. Kwiatek, *Catal. Rev.*, **1**, 37 (1967); (e) E. W. Stern, *ibid.*, **1**, 73 (1967); (f) C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Academic Press, New York, N. Y., 1967.

[11] L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, **83**, 2784 (1961).

[12] L. Vaska and J. W. DiLuzio, *ibid.*, **84**, 679 (1962).

[13] L. Vaska, *Science*, **140**, 809 (1963).

[14] For example, the hydrogen adduct (eq 3) is an "authentic" dihydride (see ref 12, 15, and Figure 1), and the oxygen adduct $[O_2IrCl(CO)((C_6H_5)_3P)_2]$ can be classified as a peroxo-type complex (see ref 13, 16, 17, and Figure 1).

[15] A. P. Ginsberg, *Transition Metal Chem.*, **1**, 111 (1965).

[16] J. A. Connor and E. A. V. Ebsworth, *Advan. Inorg. Chem. Radiochem.*, **6**, 279 (1964).

[17] S. J. La Placa and J. A. Ibers, *J. Am. Chem. Soc.*, **87**, 2581 (1965).

[18] Many of these reactions have been cited or summarized in the following recent reviews: (a) L. Malatesta, "Alfred Werner Commemoration Volume," Verlag Helvetica Chimica Acta, Basel 1967, p 147; (b) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967; (c) W. P. Griffith, "The Chemistry of Rarer Platinum Metals (Os, Ru, Ir and Rh)," Interscience Publishers, New York, N. Y., 1967; (d) ref 10c.

[19] L. Vaska and R. E. Rhodes, *J. Am. Chem. Soc.*, **87**, 4970 (1965).

[20] L. Vaska and M. F. Werneke, in preparation.

[21] L. Vaska, in preparation.

[22] L. Vaska, C. V. Senoff, and L. S. Chen, in preparation.

[23] L. Vaska and S. S. Bath, *J. Am. Chem. Soc.*, **88**, 1333 (1966).

[24] L. Vaska, and J. Peone, Jr., in preparation.

[25] L. Vaska, *Science*, **152**, 769 (1966).

[26] L. Vaska and A. A. A. Gerges, unpublished results.

[27] L. Vaska and M. F. Werneke, in preparation.

L = monodentate neutral ligand), and, to a lesser extent, some isostructural complexes of rhodium, [RhA(CO)L_2]. For most of the reactions discussed in this paper, A = Cl; L = triphenylphosphine, $(C_6H_5)_3P$.

In order to study the controlling factors for these reversible addition reactions (eq 4), we have carried out two series of comparative and interrelated experiments. (i) In the first of these, the objective was to determine the role of the reacting gas by investigating a series of reactions of *one metal complex* (ML_t) with a variety of *different addenda* (XY) and by comparing the kinetic (eq 4), equilibrium (eq 5), and thermochemical data of these different reactions and the electronic and geometric properties of the corresponding adducts ((XY)-ML_t). The discussion of these data is the subject of the present account. (ii) The aim of the second series of experiments was to identify the role of the metal complex by comparing the results (as above) of the reactions of *one addendum* (*e.g.*, H_2) with *different ML_t;* a subsequent article will summarize these observations.

II. Information from Vibrational Spectra

The formally univalent d^8 complexes [IrCl(CO)($(C_6H_5)_3P)_2$] and [RhCl(CO)($(C_6H_5)_3P)_2$], and their substituted derivatives ([IrA(CO)L_2] and [RhA(CO)L_2]) are unique in that they contain a single coordinated carbon monoxide, the stretching frequency (ν_{CO}) of which responds sensitively to any changes in the environment of the central atom.[12,23] Since the stoichiometry of the reactions considered here (eq 6, M = Ir or Rh) is that of a simple addition reaction, any difference

$$[\mathrm{MA(CO)L_2}] + \mathrm{XY} \underset{k_{-1}}{\overset{k_2}{\rightleftharpoons}} [\mathrm{(XY)MA(CO)L_2}] \qquad (6)$$

between the ν_{CO} of the starting material and that of its adduct must *originate* exclusively from the added molecule XY. Also, the adducts with different XY are expected to exhibit different ν_{CO} and this is, of course, what is actually observed. (The same is true for adducts with different M, A, and L.) Table I displays the ν_{CO}'s of a selected series of complexes, *i.e.*, the adducts of *one complex* with *different XY*, arranged in the order of increasing ν_{CO}.

We first note that all of the stretching frequencies given are higher than that of the starting complex (but see Tables II and III), and this is readily interpretable as an indication that Ir carries a higher positive charge in these adducts than in [IrCl(CO)($(C_6H_5)_3P)_2$]. (This observation conforms with the usual experience with transition metal carbonyl complexes: electron-withdrawing groups shift the ν_{CO} to a higher frequency, and this is interpreted as resulting from a diminished back-donation from the metal to the antibonding orbitals (π^*) of the CO and from a synergic decrease in the σ donation from the CO to the central atom.) Accordingly, these addition reactions (eq 6, Table I) emerge as oxidations of the univalent complex by the various molecules, including molecular hydrogen (eq 3).[12,28]

Table I

Carbonyl Stretching Frequencies (ν_{CO}) and Relative Oxidation States of Iridium in the Adducts of [IrCl(CO)($(C_6H_5)_3P)_2$] with Some Covalent Molecules (XY)

Adduct stability[a]	Addendum, XY[b]	ν_{CO}, cm^{-1} in $CHCl_3$	Relative oxidn state[c]
		1967[d]	*1.00*[c]
"Easily reversible"	O_2	2015	1.89
	SO_2	2021	2.00
	D–D[e]	2034	2.24
"Stable, reversible"	H–Cl	2046	2.46
	CH_3–I	2047	2.48
	C_2F_4	2052	2.57
	$C_2(CN)_4$	2057	2.67
	BF_3	2067[f]	2.85
"Stable, irreversible"	I–I	2067	2.85
	Br–Br	2072	2.95
	Cl–I	2074	2.98
	Cl–Cl	2075	*3.00*[c]

[a] Refers to eq 6 as written; see text. [b] Molecular formula (*e.g.*, O_2) indicates that the addendum remains associated (molecular) in the adduct (types II, III, IV of Figure 1, and graph A of Figure 3); hyphenated formula (*e.g.*, H–Cl) refers to the adduct type of dissociated (radical) addendum (type I of Figure 1 and graph B of Figure 3). [c] Defined and explained in text. [d] The ν_{CO} of the parent compound, [IrCl(CO)($(C_6H_5)_3P)_2$]. [e] Deuterium.[28,29] [f] In benzene (R. N. Scott, D. F. Shriver, and L. Vaska, *J. Am. Chem. Soc.*, **90,** 1079 (1968)).

Next we observe that the CO stretching frequency increases almost *continuously* as we descend the third column in Table I. If we now assume that the ν_{CO} is a linear function of the electron density on the metal, and if we further—in conformity with the usual chemical convention—*define* the oxidation state of Ir in [IrCl(CO)($(C_6H_5)_3P)_2$] as I (1+) and that in [$IrCl_3$(CO)($(C_6H_5)_3P)_2$] as III (3+), we obtain a series of relative and fractional oxidation states for the adducts, shown in the last column of Table I. This procedure implies that the fractional charges are localized on the central atom, while in a more realistic model they will reflect the polarity of the appropriate molecular orbital(s). Be that as it may, it is certainly reasonable to consider that as a first approximation, and within the limits of the above definition, the fractional oxidation state is a rough measure of the relative extent of electron loss by the central atom and electron gain by the addendum.

The concept of fractional oxidation states as defined above is obviously only a working hypothesis which does not aspire to theoretical heights. It is at variance with the conventional view of "fractional charges and integral oxidation states," although the difference is mainly in terminology rather than in substance. Our fractional numbers (Table I) are derived from a periph-

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(28) The CO stretching frequency of the deuterium adduct, [D_2IrCl(CO)($(C_6H_5)_3P)_2$], is given instead of the ν_{CO} of the hydrogen adduct, [H_2IrCl(CO)($(C_6H_5)_3P)_2$], because of a H–CO resonance interaction in the latter (giving a misleading ν_{CO} value); see ref 29. Thus, for the spectroscopic part, D_2 stands for H_2 in Tables I and II and in Figure 3, while the structural kinetic, etc., data are those of H_2. The D_2 and H_2 adducts are isostructural[12,29] and the kinetic isotope effect is relatively small (*e.g.*, k_2: H_2/D_2 = 1.2).

(29) L. Vaska, *J. Am. Chem. Soc.*, **88,** 4100 (1966).

eral vibrational frequency only[30] and are consequently dependent on the symmetry of the complexes (discussed in the subsequent section) which places a definite (in some cases, severe) limitation to their usefulness. The concept is introduced here mainly to emphasize that the oxidation of Ir(I) by the different molecules is apparently a gradual one and not stepwise (see also Figure 3), and also because such a model is a necessary introduction to our interpretation of metal-gas interactions as generalized acid-base reactions. Further, it is meant to demonstrate that there is no use for the traditional notion which makes a pointed distinction between "negative" and "neutral" ligands in the assignment of (integral) oxidation states to metals in their complexes. For example, the latter view would formulate the O_2 and HCl adducts as containing ter- or bivalent iridium, while in the complexes with some substituted ethylenes and BF_3 the metal would retain its univalency (which, according to the data in Table I, is, of course, untenable). It also seem unreasonable to assign a single oxidation state—or even two or more *integral* ones—to Ir in the adducts given in Table III.

Our further problem is to find a correlation between the CO stretching frequency or the relative oxidation state and an electron-accepting property of the addendum. As anticipated, but with some notable exceptions, the increase in ν_{CO} corresponds *qualitatively* to an increasing "electronegativity," acidity, or oxidizing power of the XY. Perhaps surprisingly, however, there is no satisfactory quantitative correlation between the ν_{CO} and the common electronegative (EN) values[33a] for even those addenda (for which EN values are available) which otherwise stand in the expected sequence (*e.g.*, $Cl_2 > HCl > D_2$). Furthermore, the order of some molecules (*e.g.*, $D_2 > O_2$),[28] and especially the "low" position of oxygen in the series, contradict the "usual laboratory experience" with these species. These apparent discrepancies are related to the differences in the symmetry of the adducts (section III; see also footnote *b* to Table I), and they appear to be rooted mainly in the inherent electronic properties of the activator complex, $[IrCl(CO)((C_6H_5)_3P)_2]$.

The first column in Table I refers to the stability of the adducts as estimated from qualitative observations on the synthesis and general behavior of the complexes. The three broad and rather arbitrary categories contain exceptions (*e.g.*, the HCl and CH_3I adducts should be in the last category), but the general trend is unmistakably clear: the stability appears to parallel the extent of electron transfer from the metal to the addendum. This all-important preliminary observation gave the impetus to carry out quantitative measurements of the kinetics and equilibria, and it became the basis for the formulation of some important factors which determine the reversibility of the activation of covalent molecules by metal complexes.

Finally, we note that there are other types of complexes which undergo addition reactions similar to those of $[MA(CO)L_2]$ (eq 6) but which do not possess such an informative label as the ν_{CO} in the latter. For example, the adducts of $[M(L\text{-}L)_2]Cl$ (M = Ir, Rh; L-L = chelating diphosphine, etc.)[34,35] and $[RhClL_3]$ (L = tertiary phosphine, -arsine or -stibine)[36] with different XY are thus not easily comparable with one another in the manner reported here.[37]

III. Symmetry Factors. The Structures of the Activated Adducts[3]

The preceding discussion was based essentially on a single property of the complexes (ν_{CO}), and it was intended to show that this property alone can yield some valuable information on the nature of metal complex-gas interactions. A further interpretation of these reactions (or any reaction, for that matter), however, requires an analysis of the structures of the principal species involved.

Figure 1 depicts the molecular configurations of *trans*-$[IrCl(CO)((C_6H_5)_3P)_2]$ and its adducts with H_2, O_2, CO, and SO_2; shown are only the unique symmetry planes which bisect the $(C_6H_5)_3P\text{-}Ir\text{-}(C_6H_5)_3P$ axes (not shown) perpendicular to these planes (of paper). A diagram showing all coordinated atoms and illustrating the probable mechanism of a *cis* addition is given in Figure 2. The structures of $[O_2IrCl(CO)((C_6H_5)_3P)_2]$[17] and $[(SO_2)IrCl(CO)((C_6H_5)_3P)_2]$[38] (II and IV)[39] have been determined by X-ray diffraction techniques. The configuration of the dihydride I[39] rests on nmr and infrared evidence,[15,29] and the probable structure of the CO adduct III[39] has been derived from infrared and other data.[25] The parent compound is known to have a planar *trans*-$((C_6H_5)_3P)_2$ structure.[11,19] Spectroscopic data show that the coordinational geometry of each of the complexes in Figure 1 is the same in crystal form and in the solutions where the reversible reactions have been studied.

The four structures I-IV[39] can be considered as prototypes for many other XY adducts of $[MA(CO)L_2]$ thus far found. Type I represents complexes in which the addendum is dissociated and the two frag-

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[30] Of the other vibrational frequencies in $[(XY)IrCl(CO)((C_6H_5)_3P)_2]$ (and its analogs), the Ir-CO stretch is probably of greater value than the ν_{CO}, but the former has been recognized only in a relatively few examples; the ν_{IrP}'s are difficult to detect in the $(C_6H_5)_3P$ complexes, and the ν_{IrCl}, while important in the assignment of structures,[31,32] appears to be nondiagnostic in the context of the present analysis.[31]

[31] L. Vaska, *J. Am. Chem. Soc.*, **88**, 5325 (1966).

[32] M. A. Bennett, R. J. H. Clark, and D. L. Milner, *Inorg. Chem.*, **6**, 1647 (1967).

[33] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience Publishers, New York, N. Y., 1967: (a) pp 100-104; (b) p 33.

[34] Unpublished results.

[35] L. Vaska and D. L. Catone, *J. Am. Chem. Soc.*, **88**, 5324 (1966).

[36] J. T. Mague and G. Wilkinson, *J. Chem. Soc., A*, 1736 (1966), and references cited.

[37] There are, of course, numerous other known or potential spectroscopic facets (vibrational,[30] electronic, nmr, Mössbauer) of these and related complexes which could or should provide information of the type presented here or perhaps a more accurate and truthful appraisal of the electronic interactions under consideration, but these have not yet been studied in detail.

[38] S. J. La Placa, and J. A. Ibers, *Inorg. Chem.*, **5**, 405 (1966).

[39] The roman numerals refer to the structures or reactions in Figure 1.

ments (atoms or groups) are individually bonded to the central atom. This type is displayed by the complexes with halogens and pseudohalogens (X = Y) and their various derivatives (X ≠ Y), *e.g.*, interhalogens, hydrogen, alkyl, and mercuric halides, etc.,[18] that is, with saturated molecules of X–Y bond order equal to 1.

The configuration of the oxygen complex II can be taken as another prototype, characterized by a symmetrical addendum (X = Y), retention of XY association in the adduct, and C_{2v} symmetry of the metal–(XY) group. The complexes with ethylene, acetylene, and their symmetrical derivatives are expected to exhibit these features by analogy with their established relatives in transition metal chemistry.[40] The tetracyanoethylene and tetrafluoroethylene adducts, $[C_2(CN)_4IrBr(CO)((C_6H_5)_3P)_2]$[41] and $[C_2F_4IrI(CO)((C_6H_5)_3P)_2]$,[42] have been reported to generally conform to these expectations, but unlike the structures depicted in Figures 1 and 2, in these complexes the two triphenylphosphines are *cis* to each other, *i.e.*, there is a P_2IrC_2 plane perpendicular to the halogen–Ir–CO axis.

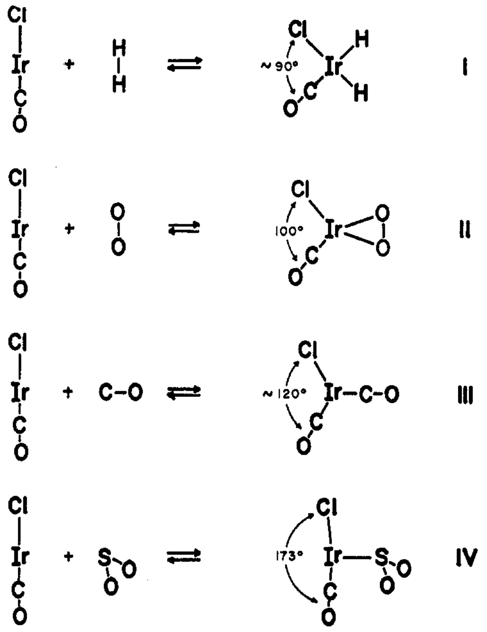

Figure 1. Two-dimensional diagrams representing the addition reactions of H_2, O_2, CO, and SO_2 to planar *trans*-$[IrCl(CO)((C_6H_5)_3P)_2]$. The two *trans*-$(C_6H_5)_3P$ groups, not shown in the diagrams, are normal to the plane of the paper. The lines connecting the atoms do not refer to bond orders. For references, see text.

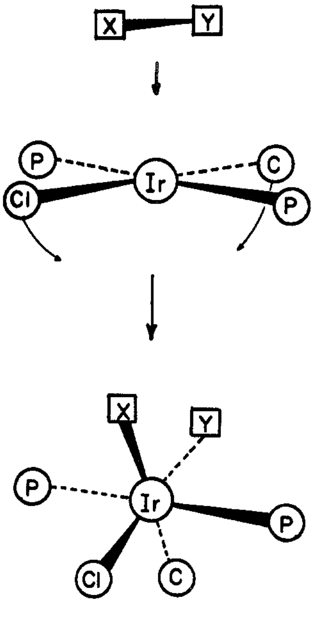

Figure 2. Proposed mechanism for a *cis* addition of a diatomic molecule (XY) to planar *trans*-$[IrCl(CO)((C_6H_5)_3P)_2]$. The diagrams show only the immediate coordinational configuration of Ir.

The carbon monoxide and sulfur dioxide adducts III and IV represent further types of structures in which the addendum remains associated (as in II), but here the XY coordinates to the metal through one of its atoms only. Analogous structures may be expected for the adducts with NO,[34] boron halides,[43] and related molecules.

In the light of these structural data (Figure 1), the "anomalies" in the correlation of the CO stretching frequency with the electron-accepting properties of the addendum (cited above, section II) become understandable. On the one hand, the ν_{CO} is dependent not only on the nature and identity of the other ligands present but also on the total stereochemistry of the complex (*trans* effects, etc.). On the other hand, and more importantly, the electron-attracting power or acidity of the reacting molecule XY is a function not only of its inherent electronic and symmetric properties but also of those of the particular metal complex, *i.e.*, of the type and extent of the metal–(XY) orbital overlap. At the moment we are dealing with one activator complex, $[IrCl(CO)((C_6H_5)_3P)_2]$, and it is obvious that a meaningful comparison of its activated adducts can be possible only within groups of adducts exhibiting closely related symmetries. This is borne out in Figure 3 where the ν_{CO} is plotted against the electron affinity (EA) of the addendum. Clearly, there are (at least) two distinct regions in this figure, graphs A and B, one comprising the adducts with molecular addenda (structures types II, III, and IV and the other which includes six-coordinated complexes (structure type I).

Although there appears to be no unambiguous theoretical justification for the correlations shown in Figure 3 (and space prohibits an adequate discussion of the problem here), the results are remarkably informative in several respects. (1) As noted above, the correlations testify to the importance of the symmetry factors. (2) In each group of adducts (A and B), the relative oxidation state of iridium is proportional to an electron-accepting property of the addendum. Furthermore,

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[41] J. A. McGinnety and J. A. Ibers, *Chem. Commun.*, 235 (1968).

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[43] R. N. Scott, D. F. Shriver, and L. Vaska, *J. Am. Chem. Soc.*, **90**, 1079 (1968).

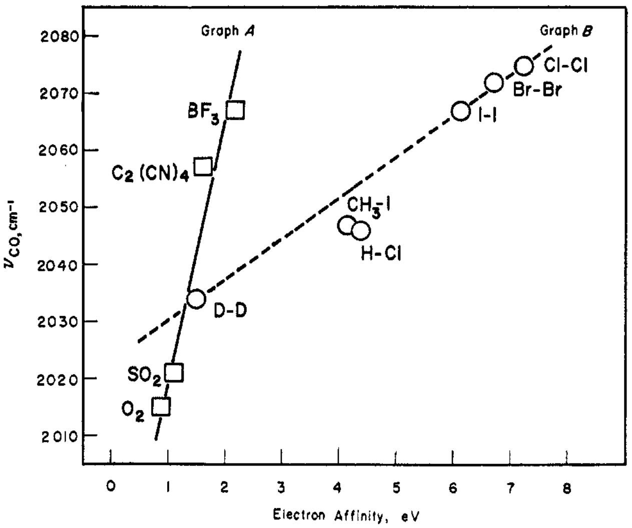

Figure 3. A relation between the CO stretching frequency of $[(XY)IrCl(CO)((C_6H_5)_3P)_2]$, in chloroform solution (see Table I), and the electron affinity (EA) of the atoms or molecules XY: A, ---□---, EA of molecules;[43] B, ---○---, sums of EA of atoms or groups,[33b,43] *e.g.*, $EA_{CH_3-I} = EA_{CH_3} + EA_I$. For deuterium (D–D), the EA of hydrogen is used.[28]

the data in Figure 3 support the earlier qualitative observation that the oxidation of Ir(I) by the various XY is a continuum (see also Table III), that is to say that integral oxidation states are not meaningful in this system or at least they cannot be defined. (3) Finally, the rough relation between the relative oxidation state and the qualitative stability of the adducts (Table I) acquires some refinement: as would be expected, the adducts with molecular addenda (graph A) are generally more readily reversible than the six-coordinated complexes (graph B). A strictly analogous correlation as in Figure 3 has been found also for $[RhCl(CO)((C_6H_5)_3P)_2]$ and its adducts with SO_2 and $C_2(CN)_4$ (A) and halogens and pseudohalogens (B) (eq 6), which shows that this phenomenon is not restricted to one particular series of complexes; the slopes of the graphs in Figure 3 are nearly identical with the corresponding ones for the rhodium complexes.

In the foregoing discussion the four structures of Figure 1 were at first considered as representing four different types of configurations, and then, with reference to Figure 3, they were viewed as two broad categories, differentiated by the criterion of whether the XY dissociates upon its activation (I) or retains its molecular image in the adduct (II, III, and IV). A closer look reveals, however, that all four of them have some common basic features, and that their differences are only gradual and not in kind. First of all, we note that the addition of the covalent molecule to $[IrCl(CO)((C_6H_5)_3P)_2]$ produces a "bending back" of the Cl and CO ligands from their original *trans* positions in order to accommodate the incoming group. According to the resulting Cl–Ir–C angle, the dihydride I has an octahedral structure, and the configurations of the CO (III) and SO_2 (IV) adducts are based on trigonal bipyramid and tetragonal pyramid, respectively. The oxygen complex II, however, has no regular structural countertype, and its coordination number cannot be defined in terms of an integral number. This structure can be thought of as being an intermediate between the six-coordinated I and the five-coordinated III, but it is considerably closer to the former with respect to the Cl–Ir–C and Ir–X–Y angles.[44] In fact, structures I and II differ, in essence, only in the X–Y distance (and the consequent bond angles in the symmetry plane), and it is quite realistic to postulate a potential series of intermediate forms bridging the two. It seems that both the hydrogen and the oxygen complexes can perform this function. The question of bond or no bond between the X and Y seems to be only a relative one, and it should be no obstacle to this analysis. For example, assuming the mechanism as in eq I (Figure 1; see also Figure 2), the kinetic activated complex in the addition of molecular hydrogen is likely to have a configuration intermediate between those of "collected but isolated" reactants and the product, *i.e.*, with the H–H bond partially cleaved and a relatively long Ir–(H_2) distance. For the oxygen complexes, rather widely different O–O distances have in fact been found,[17,41,45] and these appear to suggest that the oxygen adducts can, in principle, exhibit structures extending gradually from a peroxo (or "molecular" oxygen) type (II) to a six-coordinated dioxo type structure (I) (*i.e.*, with two *cis* Ir=O bonds).[46] A close relation between structures I and II emerges also from the kinetic and equilibrium studies on the activation of these two gases (section IVA).

The principal difference between structures II and III lies in the Ir–X–Y angle (72 and 180°, respectively), and this is obviously a function of the symmetry and electronic properties of the coordinated molecule. The adducts with carbon disulfide[47] and substituted unsymmetrical olefins and acetylenes, for example, are likely to show ∠Ir–X–Y values between those of II and III, and such complexes would provide a link between the two types. Finally, although structures III and IV bear different names (trigonal bipyramid and tetragonal pyramid), their main difference is only in the Cl–Ir–C angle which apparently depends on the Ir–(XY) bond length (the longer the bond, the wider the angle) which, in turn, is related to the particular XY. As before, intermediate structures appear entirely feasible, for example, of the adducts with BF_3, NO_2, NO, SO, CS, etc.

In summary, we conclude that the adducts of $[IrA(CO)L_2]$ with covalent molecules exhibit a series of

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(44) ∠Ir–H–H ~45°; ∠Ir–O–O 72°.[17]

(45) J. A. McGinnety, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 2243 (1967).

(46) A different view, proposing discrete electronic states for the covalently bonded oxygen (and other small molecules), that is, a discontinuous series of structures, has been advanced in a recent note by R. Mason, *Nature*, **217**, 543 (1968).

(47) (a) M. Baird, G. Hartwell, Jr., R. Mason, A. I. M. Rae, and G. Wilkinson, *Chem. Commun.*, 92 (1967); (b) M. Baird and G. Wilkinson, *J. Chem. Soc., A*, 865 (1967).

Table II

Kinetic,[a] Equilibrium, Thermochemical,[a] and Infrared Data for Homogeneous Reversible Activation of Some Covalent Molecules by $[IrCl(CO)((C_6H_5)_3P)_2]$ in Chlorobenzene[b] at 30°

$$[IrCl(CO)((C_6H_5)_3P)_2] + XY \underset{k_{-1}}{\overset{k_2}{\rightleftharpoons}} [(XY)IrCl(CO)((C_6H_5)_3P)_2]$$

XY	k_2, sec^{-1} l. mol^{-1}	k_{-1}, sec^{-1}	K_{eq}, l. mol^{-1}	$\Delta\nu_{CO}$,[c] cm^{-1}	ΔH_2^*, kcal mol^{-1}	ΔS_2^*, eu	$\Delta H_2°$, kcal mol^{-1}	$\Delta S_2°$, eu	$\Delta F_2°$, kcal mol^{-1}	XY
C_2H_4[d]	0.051	4.5×10^{-2}	1.1	−21[e]	11.3	−21	−11.8	−39	−0.1	C_2H_4[d]
CO[f,g]	(>1)	($>10^{-3}$)	1,250	(−6)[h]			−10.8	−22	−4.3	CO[f,g]
SO_2[g]	($>10^4$)	(>10)	1,320	+54			−10.1	−19	−4.3	SO_2[g]
O_2	0.060	3.5×10^{-6}	17,100	+48	9.3	−33	−17.1	−37	−5.9	O_2
H_2	1.2	3.8×10^{-5}	32,200	+67[i]	11.5	−20	−15.0	−29	−6.2	H_2

[a] Subscript 2 on the kinetic and thermodynamic symbols refers to the forward reactions, subscript −1 to the reverse reactions. The thermodynamic data have been calculated from the rate and/or equilibrium constants measured at different temperatures, 0–60°. The following constants were determined from direct measurements: (C_2H_4) k_2, K_{eq}; (CO) K_{eq}, (k_2, k_{-1}); (SO_2) K_{eq}, (k_2, k_{-1}); (O_2 and H_2) k_2, k_{-1}. [b] 10^{-3} to 10^{-5} *M* in metal complex and severalfold to hundredfold molar excess of the gas. [c] The increase (+) or decrease (−) in the ν_{CO} from the ν_{CO} of the parent complex to that of the adduct ($CHCl_3$ solution data; see Table I); there is no essential difference between the spectra in $CHCl_3$ and C_6H_5Cl. [d] Reaction with the iodide, $[IrI(CO)((C_6H_5)_3P)_2]$.[48] [e] Measured in Nujol at *ca.* −60°; the solid is not stable at higher temperatures and the solutions lack adequate concentrations of the adduct. [f] The kinetic and equilibrium data as reported in ref 25 are in error due to a faulty measurement of CO solubility. [g] The rate data are preliminary and indicate approximate orders of magnitude. [h] Average value of two frequencies (A_1 and B_2).[25] [i] See ref 28.

interrelated structures and that these include configurations (II, and the potential ones suggested above) which do not fit under customary geometric labels, which are clearly intermediates between certain regular structure types, and which can therefore be viewed as involving *relative and fractional coordination numbers of the metal.* These observations are presented here as another necessary preliminary to the interpretation of the reactions under discussion.

The structural diagrams in Figure 1 show also probable over-all mechanisms for these reversible addition reactions. According to these schemes, the kinetic activated complexes can be described in terms of the Cl–Ir–C angle, the Ir–(XY) distance, and the X–Y bond order (see above for the activation of hydrogen). For instance, it is logical to suggest that in the activated complex the Cl–Ir–C angle is larger than in the products but smaller than 180°.

IV. Information from Kinetic and Stability Data

Our early qualitative observations on stability and its relation to some other properties of the various activated adducts (see above and Table I) prompted a study of the kinetics and equilibria (eq 4–6) which, in the meantime, has developed into a comprehensive and long-range program in the author's laboratory. Although only a small fraction of the "total objective" has been attained thus far, and the available data are in part preliminary, these results appear to be of considerable significance to merit an appraisal at this time. Some pertinent data are summarized in Tables II and III and they have, for the most part, not been published previously; full experimental details will appear elsewhere.[20,22,24,26,27] The reaction rates and equilibria have been determined in dilute solutions of the reactants mainly by spectroscopic (electronic and/or vibrational) methods. The forward reactions with hydrogen, oxygen, and carbon monoxide (eq 6, Table II) have been found to obey the second-order rate law (rate = $k_2[IrA(CO)L_2][XY]$,[50] and the reverse reactions the first-order law (rate = $k_{-1}[(XY)IrA(CO)L_2]$); for the orders of the reactions with ethylene and sulfur dioxide only incomplete data are presently available, but they appear to conform with those cited above.

A. Comparison of the Reversible Activation of Molecular Hydrogen, Oxygen, Carbon Monoxide, Ethylene, and Sulfur Dioxide. Table II gives a comparative summary of the reactions of *trans*-chlorocarbonylbis(triphenylphosphine)iridium(I) with some common gases. The data are arranged in the order of increasing equilibrium constants (K_{eq}, eq 5) for the addition reactions at 30°. Except for sulfur dioxide, this order coincides with that of increasing relative oxidation states of iridium in the respective adducts as reflected by the $\Delta\nu_{CO}$ (section II, Table I). The CO and C_2H_4 complexes, which were omitted from Table I and Figure 3 because no strictly comparable infrared data are available for these compounds (see footnotes *d*, *e*, and *h* of Table II), show a *decrease* in the ν_{CO} which implies a *reduction* of the formally univalent $[IrA(CO)((C_6H_5)_3P)_2]$ by the two molecules (see further in section IVB). We thus enlarge on our earlier preliminary comments (sections II and III) by observing that, within a group of complexes with not greatly different symmetries (see below), the thermodynamic stability of the adducts is proportional to the manifested acidity

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(48) There is no measurable uptake of ethylene by $[IrCl(CO)((C_6H_5)_3P)_2]$ under normal conditions, which implies that the K_{eq} is much smaller for this reaction than for the reaction of the iodide with ethylene. Since the chloride catalyzes ethylene hydrogenation,[19,49] its reaction with ethylene must be postulated.

(49) G. G. Eberhardt and L. Vaska, *J. Catalysis*, **8**, 183 1967.

(50) Since the commencement of our kinetic and thermochemical studies some 6 years ago, a report has appeared[51] on the kinetics of the uptake of hydrogen and oxygen by $[Ir(Cl,Br,I)(CO)((C_6H_5)_3P)_2]$. These results are in general agreement with ours, although they differ somewhat in detail which may be attributed to the different methods of measurements used. The authors describe only the forward reactions and give no interpretation for their results.

(51) P. B. Chock and J. Halpern, *J. Am. Chem. Soc.*, **88**, 3511 (1966).

of the addendum or the positive oxidation state of the metal, M^{n+}, that is to say, that an electron donation in the opposite direction, (XY)→ML_i, tends to decrease the stability.

The exceptional position of SO_2 in the sequence (Table II) can be reconciled by recalling that (a) we presently compare the activation of different types of molecules and that (b) the structure of the sulfur dioxide complex stands out as being considerably more different from those of the other adducts than the latter from each other (see the Cl–Ir–C angles in Figure 1). The relatively low stability of $[(SO_2)IrCl(CO)((C_6H_5)_3P)_2]$ is consistent with the relatively long Ir–SO_2 bond length[38] and the consequent essential retention of the symmetry of $[IrCl(CO)((C_6H_5)_3P)_2]$ in the adduct.

The sequence of the stability constants (K_{eq} in Table II) for the different complexes as a function of XY holds approximately also for some other derivatives of $[(XY)IrA(CO)L_2]$ for which quantitative data have been obtained, and the same appears roughly to be true of some additional examples of low-valent and "unsaturated" (low coordination number) complexes of group VIII metals, *e.g.*, $[Ir(L\text{–}L)_2]A$.[34,35] But the sequence is not, of course, of "universal" relevance, and two strongly qualifying comments are in order. (1) Although in the present discussion we are attempting to define the role of the covalent molecule, this role, as pointed out above, is obviously not separable from that of the metal complex. For example, in the system on hand, hydrogen seems to be the strongest acid of the five gases under comparison, but its position in the series may change when a different type of activator complex (*e.g.*, a more basic one) is used. (2) The second comment concerns another obvious but a more critical hazard: a comparison of the stability constants of different though related reactions at any one single temperature. For the reactions given in Table II, changes in the order of K_{eq}'s are not found in the temperature range of measurements, 0–60°, but for some other groups of reactions they have actually been observed.[24]

This brings us to the comparison and evaluation of the enthalpy changes, which is a complicated task since this energy term is related to several others and these are mostly of unknown magnitudes. The heat of the reaction includes the sum of the energies of (a) the change in the X–Y bond order (ΔB_{XY}), that is from the B_{XY} value in the free molecule to that in the adduct, (b) the formation of the metal–(XY) bond(s) ($D_{M(XY)}$ = M–(XY) dissociation energy), as well as the rehybridization of the metal or the ML_i unit (R_{ML_i}) which includes the electronic promotion energy for the central atom. Except for ΔB_{HH}, which is the dissociation energy of the hydrogen molecule, the values of none of these terms (ΔB_{XY} and R_{ML_i}) are presently available (*i.e.*, readily calculable) for any of these reactions, and the important question of the relation of the enthalpy change to the Ir–(XY) bond energy ($D_{M(XY)}$) can thus be answered—approximately—only for the hydrogen adducts.

As expected for simple bimolecular associative reactions (*i.e.*, without large or complicated changes in solvation), the standard entropy changes ($\Delta S_2°$) are highly negative. The individual differences in the $\Delta S_2°$ values can, to some extent, be related to the corresponding differences in the structures (Figure 1). For example, the entropy changes for the reactions with oxygen and ethylene are *ca.* 20 eu more negative than those with carbon monoxide and sulfur dioxide, and one can almost intuitively conclude that the type II complexes (O_2 and C_2H_4 adducts) are more constrained than the CO and SO_2 adducts.

The relative order of the rates of the several reversible reactions can in part be understood by considering only the structural changes involved, *i.e.*, by assuming the simple mechanisms as depicted in Figures 1 and 2, and suggested above (section III). Thus we find that both the addition and reverse reactions of sulfur dioxide proceed much faster than those of the other gases compared in Table II. Of course, the electronic factors also play an important role in determining the sequence of the rates under discussion. In fact, this role can probably override all structural differences when the electronic differences are large. For example, halogens and hydrogen halides react with $[IrA(CO)L_2]$—producing type I complexes—apparently orders of magnitude faster than any of the molecules (except SO_2) shown in Table II.

It is worthy of note that hydrogen reacts about 20 times faster than oxygen, but that the ratio of the reverse rate constants (k_{-1}) for the two reactions is only one-half of this value. Also, the "π-bonded" addenda of type II (O_2, C_2H_4) show about equal reactivity, but the corresponding reverse reactions differ in their rate constants by four orders of magnitude! The uptake of oxygen and ethylene is considerably slower than that of other molecules given in Table II, but some highly electronegative substituted ethylenes (section IVB) react "instantly" with $[IrA(CO)L_2]$.[27,34]

The activation energies for both the forward (ΔH_2^*) and the reverse (ΔH_{-1}^*, implied in Table II) reactions are of about the same magnitude for the three cases cited, the ΔH_{-1}^* values being *ca.* twice as large as the ΔH_2^* values, in accordance with the nature of these reversible processes. The entropies of activation also follow the general interpretation as advanced above, *i.e.*, their values agree with the mechanism which postulates an activated complex with an over-all resemblance to the product but possessing more motional freedom (section III).

The kinetic results and their discussion above underline the well-known but frequently ignored danger of concluding anything about the thermodynamics of a reaction from one-sided or one-directional rate and activation data alone. They also point to the futility of attempting to separate the electronic and stereochemical factors in the analysis of a chemical reaction, factors which sometimes yield to a phenomenological separation but not to a substantial one.

B. Comparison of Molecules with Related Sym-

Table III

Equilibrium and Infrared Data for the Reactions of $[IrA(CO)((C_6H_5)_3P)_2]$ with Some Unsaturated Molecules, C_2R_4, in Chlorobenzene at 30°

A = Cl			A = I	
$\Delta\nu_{CO}$, cm^{-1} [a,b]	K_{eq},[c] l. mol^{-1}	C_2R_4	K_{eq},[c] l. mol^{-1}	$\Delta\nu_{CO}$, cm^{-1} [a,b]
	<1[d]	$H_2C{=}CH_2$	1.1	−21 (0.7)[e]
+57 (1.9)	1.2	$H_2C{=}CH(CN)$	0.4[f]	−6 (1.2)[g]
+70 (2.2)	1,500	$(CN)HC{=}CH(CN)$	87	+62 (2.2)
+91 (2.6)		$F_2C{=}CF_2$	(>100)	+82 (2.6)
+96 (2.7)	140,000[h]	$(CN)_2C{=}C(CN)_2$		+87 (2.7)

[a] The increase (+) or decrease (−) in the ν_{CO} from the ν_{CO} of the parent complex to that of the adduct measured in chloroform; the spectra in $CHCl_3$ and C_6H_5Cl are essentially the same. [b] Relative oxidation state of Ir is given in parentheses; it is defined and explained in section II (Table I). Oxidation state 3.0 for the iodide is defined as that of Ir in $[Cl_2IrI(CO)((C_6H_5)_3P)_2]$, ν_{CO} 2074 cm^{-1}. [c] Equilibrium constant, eq 4–6. [d] See ref 48. [e] In Nujol. [f] In toluene. [g] In acrylonitrile. [h] In THF.

metries. **Reversible Activation of Ethylene and Substituted Ethylenes.** The data and discussions presented thus far have abundantly demonstrated that an unequivocal understanding of the role of small covalent molecules in their activation by a metal complex will require (1) a quantitative comparison of a group of reactions showing identical or closely related (a) mechanisms and (b) symmetries of the reactants and products, and (2) a subsequent comparison of several *different* groups of such reactions. While the accomplishment of this total task lies in the future, much can be learned from the study of even one or two different series of reactions. Olefin complexes are appropriate for these studies, and we have investigated equilibria in the reactions of $[IrA(CO)L_2]$ with some ethylenes, C_2R_4 (R = H, F, CN) and have compared these data with the basic or acidic properties of the addenda (C_2R_4). Some results, in part preliminary, are summarized in Table III.

Although the data are less extensive than is desirable, the anticipated trends are, in general, present, and this enforces our previous observations on the relation of thermodynamic stability to electronic properties, *i.e.*, $-\Delta F_2° \propto M^{n+}$, $\propto$ XY acidity, ($\propto$ 1/basicity), the qualifying comments cited above (section IVA) being naturally applicable also here.

Several other important aspects are evident from Table III, some of which limit the intended value of the comparison. So far we have implicitly assumed that the structures of the complexes are approximately the same, but this is obviously not the case. The adducts with acrylonitrile may not even be expected to conform with the configurations of the other complexes (see discussion in section III), but they have been included to again demonstrate the importance of the symmetry factors: both the chloro and iodo complexes show much lower stabilities than might have been expected on the basis of the changes in the ν_{CO}, and this is reminiscent of the respective properties of the SO_2 adduct discussed above (Table II). For the rest of the complexes it appears safe to assume that they represent type II complexes (Figure 1) *as far as the* IrC_2 symmetry is concerned, but the configuration of the $IrA(CO)P_2$ unit is probably different in some of the examples given (see section III).

A fundamental question about the nature of the metal–olefin association is that of bond polarity, that is, the *direction* and extent of *net* electron transfer between the metal and the unsaturated molecule. For complexes with strongly electronegative or acidic substituted olefins, the direction of electron donation is usually obvious and its relative extent can sometimes be estimated from measurements such as shown in Table III, but for metal complexes containing simple alkenes or ethylene itself there is, in my opinion, no simple or general answer to these questions. The measured carbon–carbon bond lengths and stretching frequencies, which always show a lower C–C bond order in the coordinated olefin (as compared with that in the free molecule), are nondiagnostic with respect to the metal–olefin bond polarity, since the generally accepted $\sigma\pi$ model of Dewar–Chatt–Duncanson[40] always predicts this C–C bond weakening, *i.e.*, regardless of the relative magnitudes of the σ and π contributions.

At least an indirect contribution to the understanding of the nature of the metal–C_2H_4 bond is found in the infrared data of Table III. Accordingly, and remembering the assumptions in our interpretation of the CO stretching frequencies (section II), the ethylene acts as a *weak base* toward the particular iridium complex (iodide) (and, incidentally, one can therefore call this reaction a "reductive addition" (with respect to the metal) rather than an "oxidative addition," a term which, following our first communication on the subject,[12] has become fashionable in recent years for characterizing the types of reactions reviewed in this article). Previous evidence about the metal–ethylene bond polarity has been available apparently only for some platinum complexes for which also a small electron transfer (0.25 electron?) toward the metal has been reported on the basis of dipole moment data.[40] It was perhaps this important study by Chatt which has led to what seems to be a "universal belief" in the basicity of ethylene and other simple olefins. In the context of the results and their interpretation given in this paper, the existence of the opposite type of metal–olefin complexes (*i.e.*, $M{\rightarrow}C_2H_4$) cannot be precluded. They appear to be possible with very basic metal complexes, and even in the present example, $[C_2H_4IrI(CO)((C_6H_5)_3P)_2]$ (Table III), the question of Ir–C_2H_4 bond polarity is not entirely clear. The least we can say is that this question is still imperfectly understood and that the traditional formulation, metal←olefin, is misleading in that it implies general validity. It is obvious, of course, that the problem discussed above is not only of fundamental significance but also of great practical importance for the selection and design of metal complexes as catalysts for the various reactions of olefins.

We conclude this brief account by noting that only some of the pertinent data could be discussed here and none of them in adequate detail. Even so, the discussion raised perhaps more questions than could be answered. One important result of our inquiry into the role of the covalent molecule—apparently the first of its kind—is that it points to the many properties which need be considered and the interdependence of these properties. The main result, however, is the discovery that the acidity or oxidizing power of the covalent molecule is the principal factor which, other things being equal or nearly so, determines the reversibility of the metal complex–gas reactions. The main limitation, inherent in the type of our inquiry, is the obvious fact that the "other things" are never exactly equal for different molecules, not even in the homologous series of ethylenes (Table III).

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The Critical Locus Curve and the Phase Behavior of Mixtures

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The locus of the critical points of a system of mixtures defines the upper limit in temperature and pressure of the heterogenous region. It therefore exerts a great influence on the form of the phase diagram. By the determination of the critical locus curves of a series of binary systems composed of a common component with the members of an homologous series of compounds, the development of the phase diagram from the relatively simple to the more complex form is revealed. These changes are related to the size, shape, and difference in chemical family of the component molecules.

The critical point of a liquid, whether it be a single compound or a mixture, is a property of considerable practical as well as theoretical importance. This is because the critical point defines the temperature and pressure where the liquid and vapor phases have identical properties and is, therefore, a key point in the construction of the phase diagram as well as in the development of a theory of the liquid state. Also, for the engineer, a knowledge of the critical temperature and pressure makes possible, by van der Waals' theorem of corresponding states, the prediction of the thermodynamic properties of the compound when these properties have not been determined experimentally.

Evidence for the existence of a critical point was first presented in 1822 by de la Tour,[1] who observed that a liquid when heated in a hermetically sealed glass tube is reduced to vapor in a space from two to four times the original volume of the sample. However, it was not until the quantitative measurements of Andrews on carbon dioxide[2] that the nature of the transition was understood. Andrews was the first to apply the term "critical point" to the phenomenon associated with the liquid–vapor transition. The first reliable experimental investigation of the critical state of liquid mixtures began with the work of Kuenen,[3] who used a magnetic stirrer to establish equilibrium between the liquid and vapor as the sample, confined over mercury in narrow glass capillaries, was compressed and heated. Kuenen showed that, unless the sample was well stirred, the observations could not be reproduced. Interest in the critical region of a mixture in the period 1876–1914 was heightened by the theoretical and experimental studies of van der Waals and his associates at the Universities of Amsterdam and Leiden. After World War I research on the phase behavior of mixtures was superseded by an interest in the atomic structure of matter. More recently, the increased use of high pressures in the chemical and petroleum industries has emphasized the paucity of accurate P–V–T data on pure substances and mixtures and the need for a better understanding of the phase behavior of liquid mixtures above atmospheric pressure. This has led to a resurgence of interest in the

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[1] C. de la Tour, *Ann. Chim.*, (3) **21**, 127 (1822).

[2] (a) T. Andrews, *Phil. Trans.*, **159**, 575 (1869); (b) *Proc. Roy. Soc.* (London), **18**, 42 (1869).

[3] (a) J. P. Kuenen, *Commun. Phys. Lab. Univ. Leiden*, No. 4B, 7 (1892); (b) *Koninkl. Akad. Wetenschapp. Amsterdam, Versl. Van Vergrad.*, **1**, 15 (1892); (c) *ibid.*, **3**, 90 (1894); (d) *Arch. Neerl. Sci.*, (ii) **1**, 331 (1898).