but in such a way that the equality of chemical potentials of the reactants is preserved. This results in a transfer of the charge described by eq 19 or 22. The amount of charge transferred is now having strong dependence on the structure and orientation of the reactants.

Thus eq 3 and 19 illuminate different aspects of the acid-base reaction. The difference is reflected in different expressions for the numerator in eq 3 and 19. The common aspect of the equations is reflected by their denominator. Both equations show that soft-soft interaction facilitates the electron transfer, thus predicting covalent character for the bonding.

Acknowledgment. Discussions with Professors R. G. Parr, M. Levy, and J. L. Templeton and Mr. Weitao Yang have been very helpful. I am thankful to Dr. Tachibana for explaining to me his ideas on the hard-soft acid-base principle.[11] This research has been aided by a grant from the National Institutes of Health.

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(11) Tachibana, A., private communication.

Thermal Stability and Kinetic Lability of the Metal-Carbonyl Bond. A Theoretical Study on $M(CO)_6$ (M = Cr, Mo, W), $M(CO)_5$ (M = Fe, Ru, Os), and $M(CO)_4$ (M = Ni, Pd, Pt)

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Abstract: Molecular orbital calculations based on density functional theory have been carried out on the intrinsic mean bond energy D(M-CO) of $Mn(CO)_m$ between M in the d^n valence configuration and m CO ligands, as well as the first CO ligand dissociation energy ΔH of $M(CO)_m$. The calculated values for D(M-CO), all in kJ mol^{-1}, were D(Cr-CO) = 211, D(Mo-CO) = 178, D(W-CO) = 210 for $M(CO)_6$, D(Fe-CO) = 216, D(Ru-CO) = 163, D(Os-CO) = 177 for $M(CO)_5$, and D(Ni-CO) = 179, D(Pd-CO) = 44, D(Pt-CO) = 59 for $M(CO)_4$. The calculated values for the intrinsic mean bond energy revealed the ordering second row < third row < first row, for a series of homologous $M(CO)_m$ systems with metal centers from the same triad. The ordering for D(M-CO) without the inclusion of relativistic effects was third row < second row < first row. The same trends were found in the calculated values for ΔH with $\Delta H_{Cr} = 147$, $\Delta H_{MO} = 119$, $\Delta H_{W} = 142$ for $M(CO)_6$, $\Delta H_{Fe} = 185$, $\Delta H_{Ru} = 92$, $\Delta H_{Os} = 99$ for $M(CO)_5$, and $\Delta H_{Ni} = 106$, $\Delta H_{Pd} = 27$, $\Delta H_{Pt} = 38$ for $M(CO)_4$. The π-back-donation was found to be more important for the stability of the $M(CO)_m$ systems than the σ-donation. The π-back-donation is largest for the first row elements whereas σ-donation is largest for second and third row elements. The repulsive interactions between occupied nd metal orbitals and occupied σ_{CO} orbitals were found to weaken the M-CO bonds for the second and third row elements in the pentacarbonyls and tetracarbonyls compared to the homologous systems of the first row elements. Calculations are also presented on the M-CO bond strength in $V(CO)_6^-$, $Mn(CO)_6^+$ as well as the Ni-L bond strength in $Ni(CO)_3L$ for L = CS, N_2, PH_3, PF_3, $N(CH_3)_3$, $P(CH_3)_3$, and $As(CH_3)_3$.

I. Introduction

The extensive use of coordinatively saturated mononuclear metal carbonyls as starting materials in organometallic chemistry, along with their volatility and high molecular symmetry, has prompted numerous experimental[1-3] and theoretical[4,5] studies on their structure and reactivity. Special attention has been given to the degree of σ-donation and π-back-donation in the synergic[4k] M-CO bond, and now, after some controversy,[4j] it seems well-established[4b-g,5a,5e] that π-back-donation is more pronounced in the M-CO bond than σ-donation.

There is, however, in spite of many experimental[2] investigations still a lack of basic data on the thermal stability and kinetic lability of the M-CO bond in essential metal carbonyls such as $M(CO)_6$ (M = Cr, Mo, W), $M(CO)_5$ (M = Fe, Ru, Os), and $M(CO)_4$ (M = Ni, Pd, Pt), in particular with respect to the carbonyls of the second- and third-row metals.

Theoretical methods have begun to play a role in determining the energetics of organometallics[5g] and ab initio type methods have recently been applied to calculation on the M-CO bond strength of $Cr(CO)_6$,[5d-e] $Fe(CO)_5$,[5a-c,f] and $Ni(CO)_4$,[5a,f] but not yet to the M-CO bond strengths of their second- and third-row homologues.

We shall here present calculations on the intrinsic mean bond energy D(M-CO) and first CO dissociation energy ΔH of $Cr(CO)_6$, $Fe(CO)_5$, and $Ni(CO)_4$ as well as their second- and third-row homologues. Our calculations are based on the LCAO program system of Baerends et al.[6] as well as a new density

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(1) (a) Kettle, S. F. A. *Curr. Top. Chem.* **1977**, *71*, 111. (b) Braterman, P. S. In *Metal Carbonyl Spectra*; Academic Press: London, 1975. (c) Mingos, D. M. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; 1982; Vol. 3, p 1.

(2) (a) Lewis, K. E.; Golden, D. M.; Smith, G. P. *J. Am. Chem. Soc.* **1984**, *106*, 3906. (b) Bernstein, M.; Simon, J. D.; Peters, J. D. *Chem. Phys. Lett.* **1983**, *100*, 241. (c) Connor, J. A. *Curr. Top. Chem.* **1977**, *71*, 71.

(3) (a) Rees, B.; Mitschler, A. *J. Am. Chem. Soc.* **1976**, *98*, 7918. (b) Beagley, B.; Schmidling, D. G. *J. Mol. Struct.* **1974**, *22*, 466. (c) Hedberg, L.; Lijima, T.; Hedberg, K. *J. Chem. Phys.* **1979**, *70*, 3224. (d) Jones, L. J.; McDowell, R. S.; Boldblatt, M. *Inorg. Chem.* **1969**, *8*, 2349.

(4) (a) Guenzburger, D.; Saitovitch, E. M. B.; De Paoli, M. A.; Manela, J. *J. Chem. Phys.* **1984**, *80*, 735. (b) Baerends, E. J.; Ros, P. *Mol. Phys.* **1975**, *30*, 1735. (c) Heijser, W.; Baerends, E. J.; Ros, P. *J. Mol. Struct.* **1980**, *19*, 1805. (d) Bursten, B. E.; Freier, D. G.; Fenske, R. F. *Inorg. Chem.* **1980**, *19*, 1804. (e) Demuynk, J.; Veillard, A. *Theor. Chim. Acta* **1973**, *28*, 241. (f) Caulton, K. G.; Fenske, R. F. *Inorg. Chem.* **1968**, *7*, 1273. (g) Hubbard, J. L.; Lichtenberger, J. *J. Am. Chem. Soc.* **1982**, *104*, 2132. (h) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058. (i) Saddei, D.; Freund, H. J.; Hohlneicher, G. *Chem. Phys.* **1981**, *55*, 1981. (j) Johnson, J. B.; Klemperer, W. G. *J. Am. Chem. Soc.* **1977**, *99*, 7132. (k) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939. (l) Hillier, I. H.; Saunders, V. R. *Mol. Phys.* **1971**, *22*, 1025. (m) Vanquickenborne, L. G.; Verhulst, J. *J. Am. Chem. Soc.* **1977**, *99*, 7132. (n) Ford, P. C.; Hillier, I. H.; Pope, S. A.; Guest, M. F. *Chem. Phys. Lett.* **1983**, *102*, 555. (o) Burdett, J. K. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1599. (p) Penzak, D. A.; McKinney, R. J. *Inorg. Chem.* **1979**, *18*, 3407. (q) Osman, R.; Ewig, C. S.; Van Wazer, J. R. *Chem. Phys. Lett.* **1978**, *54*, 392. (r) Serafini, A.; Barthelat, J. C.; Durand, P. *Mol. Phys.* **1978**, *36*, 1341. (s) Sakai, T.; Huzinaga, J. *Chem. Phys.* **1982**, *76*, 2552.

(5) (a) Bauschlicher, C. W.; Bagus, P. S. *J. Chem. Phys.* **1984**, *81*, 5889. (b) Luthi, H. P.; Siegbahn, P. E. M.; Almlof, J. *J. Phys. Chem.* **1985**, *89*, 2156. (c) Daniel, C.; Benard, M.; Dedieu, A.; Wiest, R.; Veillard, A. *J. Phys. Chem.* **1984**, *88*, 4805. (d) Sherwood, D. E.; Hall, M. B. *Inorg. Chem.* **1983**, *22*, 93. (e) Baerends, E. J.; Rozendaal, A. *NATO ASI* **1986**, *Series C, 176*, 159. (f) Rösch, N.; Jorg, H.; Dunlap, B. I. *NATO ASI* **1986**, *Series C, 176*, 179. (g) Veillard, A., Ed. *NATO ASI* **1986**, Series C. (h) Rolfing, C. M.; Hay, P. J. *J. Chem. Phys.* **1985**, *83*, 4641.

0002-7863/87/1509-4825$01.50/0

functional theory[7] which previously has been applied to metal–metal bond strengths in transition-metal dimers and binuclear complexes[8a] as well as the strengths of the M–H and M–CH_3 bonds involving middle to late transition metals.[8b]

The LCAO program system by Baerends[6] et al. has, in conjunction with the generalized transition-state method,[9] the distinct advantage of providing a breakdown of the calculated bonding energy[10] between M and CO in terms of steric factors as well as electronic contributions from σ-donation and π-back-donation. The relativistic extension of the LCAO program due to Snijders et al.[11] makes it, in addition, possible to analyze[12] the contribution from relativistic effects to the M–CO bond energy.

The objective of this study has been, by way of the analysis provided by the generalized transition-state method, to discuss how trends in the M–CO bond strength within the series of hexa-, penta-, and tetracarbonyls are influenced by changes in steric factors, σ-donation, and π-back-donation as well as relativistic effects.

II. Computational Details

The Hartree–Fock–Slater (HFS) or Xα method[13] has been used frequently in calculations on transition-metal complexes. The HFS method is, however, an approximation to the density functional theory of Kohn and Sham[14] in much the same way as ab initio Hartree–Fock–Slater theory is an approximation to many-body theories including configuration interaction, since both methods neglect the correlation between electrons of different spins.[15] Recent advances[16] in density functional theory, which in many ways parallels the development of post-HF methods, have led to remedies for the lack of correlation between electrons of different spins and other short-comings of the HFS method by including two corrections to the HFS-energy expression E_{HFS} in order to obtain the new energy expression

$$E_{\mathrm{BS}} = E_{\mathrm{HFS}} + E_{\mathrm{C}} + E_{\mathrm{X}}{}^{\mathrm{NL}} \qquad (1)$$

The first correction term E_{C} proposed by Stoll et al.[17] represents the correlation between electrons of different spins, whereas the second correction term $E_{\mathrm{X}}{}^{\mathrm{NL}}$, due to Becke,[7] represents a nonlocal correction[13] to the local HFS-exchange energy E_{X}. All calculations presented here were based on the LCAO-HFS program system due to Baerends et al.[6] or its relativistic extension due to Snijders et al.[11] with only minor modifications to allow for Becke's nonlocal exchange correction[7] as well as the correlation between electrons of different spins in the formulation by Stoll et al.[17] based on Vosko's[18] parametrization from electron gas data. The SCF part of the calculations, as well as the optimization of geometrical parameters, included, of the two correction terms in eq 1, only E_{C} corresponding to the correlation between electrons of different spins. The wave functions generated from this type of SCF calculation were used to calculate Becke's nonlocal exchange correction $E_{\mathrm{X}}{}^{\mathrm{NL}}$ at the optimized or assumed geometries, in order to evaluate E_{BS} of eq 1. Bond energies were evaluated by the generalized transition-state method[9] or its relativistic extension.[12]

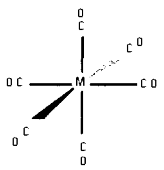
The molecular orbitals were expanded in an uncontracted triple-ζ STO basis set[19] augmented by a single STO d-orbital ($\zeta^{\mathrm{C}}{}_{3d} = 2.5$, $\zeta^{\mathrm{N}}{}_{3d} = 2.2$, $\zeta^{\mathrm{O}}{}_{3d} = 2.0$, $\zeta^{\mathrm{S}}{}_{3d} = 2.0$, $\zeta^{\mathrm{P}}{}_{3d} = 1.3$, $\zeta^{\mathrm{As}}{}_{4d} = 1.6$) on the ligand atoms, with the exception of H where a 2p polarization STO function of $\zeta^{\mathrm{H}}{}_{2p} = 1.0$ was used. A set of auxilliary s, p, d, f, and g STO functions,[20] centered on all nuclei, was used in order to fit the molecular density and present the Coulomb and exchange potentials accurately in each SCF cycle. The orbitals in the upper ns, np, nd, $(n + 1)$s, and $(n + 1)$p shells on the metals and the upper ns, np shells on the ligands were considered as valence whereas orbitals in shells of lower energies were considered as core and frozen according to the procedure by Baerends et al.[6]

Geometrical parameters for the ligands were taken as those of free CO, CS, N_2, PH_3, PF_3, $N(CH_3)_3$, and $As(CH_3)_3$ molecules, respectively. The M–C bond distances were given experimental values in $M(CO)_6$ (M = Cr, Mo, W)[3a] and $Ni(CO)_4$.[3c] The M–C bond distances for $M(CO)_4$ (M = Pd, Pt) were those of ref 21. All other bond distances were optimized.

Bond energies derived from optimized structures differ usually only by a few kJ mol^{-1} from those derived from experimental geometries.[25] The optimized M–C bond distances in metal carbonyls are between 0.05 and 0.02 Å shorter than the bond lengths obtained experimentally.[5e,f]

III. $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$

The hexacarbonyls of chromium, molybdenum, and tungsten **1** were all synthesized early on in this century. They are, primarily as a result of their stability and volatility, among the best characterized and most widely used organometallic compounds. The high molecular symmetry (O_h) of **1** has further facilitated numerous theoretical studies on the electronic structure of $M(CO)_6$ (M = Cr, Mo, W).[4j,5d,e]



1

The bonding in **1**, between the d^6 metal center with a t_{2g}^6 electronic valence configuration and the CO ligands, has been accounted for successfully[1c,5d,e] in terms of donation of charge **2a** from linear combinations of the carbon-based σ_{CO} lone-pair orbitals of octahedral e_g symmetry to the empty e_g d-orbitals on the metal

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(6) (a) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 71. (b) Baerends, E. J.; Ros, P. *Int. J. Quant. Chem.* **1978**, *S12*, 169. (c) Baerends, E. J.; Snijders, J. G.; de Lange, C. A.; Jonkers, G. In *Local Density Approximations in Quantum Chemistry and Solid State Physics*; Dahl, J. P., Avery, J., Eds.; Plenum: New York, 1984.

(7) Becke, A. *J. Chem. Phys.* **1986**, *84*, 4524.

(8) (a) Ziegler, T.; Tschinke, V.; Becke, A. *Polyhedron*, in press. (b) Ziegler, T.; Tschinke, V.; Becke, A. *J. Am. Chem. Soc.*, in press.

(9) Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1. The generalized transition state procedure is not only applicable to the HFS method but can be extended by any energy density functional such as the one by Becke in ref 7.

(10) Many other suitable decomposition schemes are available, see: (a) Wolfe, S.; Mitchell, D. J.; Wangbo, M.-H. *J. Aa. Chem. Soc.* **1978**, *100*, 1936. (b) Bernardi, F.; Bottoni, A.; Manhini, A.; Tonachini, G. *J. Mol. Struct.* (*THEOCHEM*) **1981**, *86*, 163. (c) Stone, A. J.; Erskine, R. W. *J. Am. Chem. Soc.* **1980**, *102*, 7158. (d) Fujimoto, H.; Osamura, Y.; Minato, T. *J. Am. Chem. Soc.* **1978**, *100*, 2954. (e) Kitaura, K.; Morokuma, K. *Int. J. Quant. Chem.* **1976**, *10*, 325.

(11) Snijders, G. J.; Baerends, E. J.; Ros, P. *Mol. Phys.* **1979**, *38*, 1909.

(12) Ziegler, T.; Snijders, G. J.; Baerends, E. J. *J. Chem. Phys.* **1981**, *74*, 1271.

(13) Slater, J. C. *Adv. Quant. Chem.* **1972**, *6*, 1.

(14) Kohn, W.; Sham, L. *J. Phys. Rev.* **1965**, *140*, A1133.

(15) Ziegler, T.; Rauk, A.; Baerends, E. J. *Theor. Chim. Acta* **1977**, *46*, 1.

(16) (a) Dreizler, R. M., da Providencia, J., Eds. *Local Density Approximations in Physics*; Plenum: New York, 1985. (b) Avery, J., Dahl, J. P., Eds. *Local Density Approximations in Quantum Chemistry and Solid State Physics*; Plenum: New York, 1984. (c) Erdahl, R. M., Smith, V. H., Jr., Eds. *Density Matrices and Density Functionals*; D. Reidel: Dordrecht, in press.

(17) Stoll, H.; Golka, E.; Preuss, H. *Theor. Chim. Acta* **1980**, *55*, 29.

(18) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(19) (a) Snijders, G. J.; Baerends, E. J.; Vernooijs, P. *At. Nucl. Data. Tables* **1982**, *26*, 483. (b) Vernooijs, P.; Snijders, G. J.; Baerends, E. J. *Slater type basis functions for the whole periodic system*; Internal report, Free University: Amsterdam, The Netherlands, 1981.

(20) Krijn, J.; Baerends, E. J. *Fit functions in the HFS-method*; Internal Report (in Dutch), Free University: Amsterdam, The Netherlands, 1984.

(21) Ziegler, T. *Organometallics* **1985**, *4*, 675.

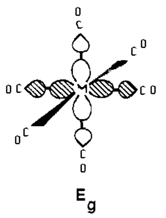
(22) Kirtley, S. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; 1983; p 783.

(23) (a) Angelici, R. J. *Organomet. Chem. Rev. A* **1968**, *3*, 173. (b) Covey, W. D.; Brown, T. L. *Inorg. Chem.* **1973**, *12*, 2820. (c) Centini, G.; Gambino, O. *Atti. Acad. Sci. Torino I* **1963**, *97*, 757, 1197. (d) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 930. (e) Graham, J. R.; Angelici, R. J. *Inorg. Chem.* **1967**, *6*, 2082. (f) Werner, H.; Prinz, R. *Chem. Ber.* **1960**, *99*, 3582. (g) Werner, H.; Prinz, R. *J. Organomet. Chem.* **1966**, *5*, 79.

(24) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1558.

(25) The contributions to $D(\mathrm{Mo{-}CO})$ and $D(\mathrm{Cr{-}CO})$ from ΔE_{Rel} were less than 1 kJ mol^{-1}. Contributions to M–L bond energies from ΔE_{Rel} will roughly increase as Z^4 with the atomic number Z of the metal M.

center, as well as back-donation **2b** from the t_{2g} metal d-orbitals to linear combinations of vacant π^*_{CO} orbitals with t_{2g} symmetry. More elaborate bonding schemes include, in addition, donation of charge **2c** from the linear combination of σ_{CO} orbitals with a_{1g} symmetry to the $(n + 1)$s metal orbitals, as well as donation to the $(n + 1)$p metal orbitals from linear combination of respectively σ_{CO} (**2d**) and π_{CO} (**2e**) orbitals of t_{2u} symmetry. For a recent comprehensive discussion of the bonding in $Cr(CO)_6$ see Baerends et al.[5e]



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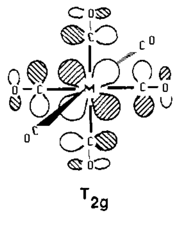

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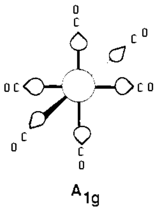

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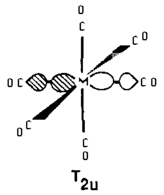

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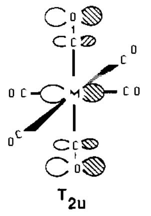


2e

We shall here be concerned with periodic trends in the strength of the M–CO bonding interaction within the triad M = Cr, Mo, W. We will, as measures for the M–CO bonding interaction in the hexacarbonyls, consider the intrinsic mean bond energy D(M–CO) between M (in its t_{2g}^6 valence state) and the six CO ligands as well as the bond energy ΔH between $M(CO)_5$ and CO.

There are two sets of experimental data with a bearing on the M–CO bond strength in $M(CO)_6$, namely, the mean bond energy E corresponding to the process

$$M(CO)_6(g) \rightarrow M(g) + 6CO(g) - 6E \qquad (2a)$$

and the first bond dissociation energy ΔH corresponding to the process

$$M(CO)_6 \rightarrow M(CO)_5 + CO - \Delta H \qquad (2b)$$

The mean bond energy E has been measured[2c] with considerable accuracy as E_{Cr} = 108 kJ mol^{-1}, E_{Mo} = 151 kJ mol^{-1}, and E_W = 179 kJ mol^{-1} for chromium, molybdenum, and tungsten, respectively. It is, however, important to note the E is given by

$$E = D(\text{M–CO}) - \tfrac{1}{6}\Delta E_{prep} \qquad (3)$$

where ΔE_{prep} is the energy required to promote the metal atom from its high-spin electronic ground state to the t_{2g}^6 valence configuration. One can, as a consequence, not conclude from the order $E_{Cr} < E_{Mo} < E_W$ that the M–CO bonding interaction, as represented by D(M–CO), will increase through the triad (M = Cr, Mo, W), since ΔE_{prep} might differ significantly for the three elements. Experimental data on the promotion energy ΔE_{prep} are unfortunately not available, although ΔE_{prep} in principle can be measured, and it is thus not possible, presently, to deduce the ordering of the M–CO interaction in group 6 from the average bond energies E_{Cr}, E_{Mo}, and E_W.

The first bond dissociation energy ΔH is on the other hand a direct measure for the strength of the M–CO bond interaction. It is further an extremely important kinetic parameter, since the dissociation process 2b is assumed to be a key step in the large volume of kinetically useful substitution reactions[22]

$$M(CO)_6 + L \rightarrow M(CO)_5L + CO \qquad (4)$$

where L is introduced into the coordination sphere of M by replacing one carbonyl ligand.

Table I. Calculated Mean Bond Energies, E, and M–CO Force Constants, k(M–CO), for $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$, Compared to Experimental Values

	E (kJ mol^{-1})		k(M–CO) (mdyn Å^{-1})	
$M(CO)_6$	calcd	exptl[a]	calcd	exptl[b]
$Cr(CO)_6$	107	110	2.2[d]	2.08
$Mo(CO)_6$	126	151	2.0	1.96
$W(CO)_6$	156	179	2.6 (2.0)[c]	2.36

[a] Reference 2c. [b] Reference 3d. [c] Nonrelativistic results in parentheses. [d] Based on calculations without E_X^{NL}.

The first bond dissociation energy ΔH has been measured for three elements M = Cr, Mo, and W by two independent techniques with quite different results as far as the ordering of ΔH_{Cr}, ΔH_{Mo}, and ΔH_W is concerned. Lewis, Golden, and Smith[2a] find in a recent laser pyrolysis study the following order: $\Delta H_W > \Delta H_{Mo} > \Delta H_{Cr}$, with ΔH_{Cr} = 153.8 kJ mol^{-1}, ΔH_{Mo} = 169.3 kJ mol^{-1}, and ΔH_W = 193.3 kJ mol^{-1}, respectively, for the three hexacarbonyls.

Kinetic studies[23] on the substitution reaction 4, for which (2b) is assumed to be a rate-determining step, afford, on the other hand, invariably, the order $\Delta H_W \sim \Delta H_{Cr} > \Delta H_{Mo}$. This order is, provided that (2b) in fact is a rate-determining step in (4) for all three metals, in harmony with the experimental observation that the substitution reaction 4 is more facile for $Mo(CO)_6$ than for $Cr(CO)_6$ or $W(CO)_6$.

We found that it might be of interest, as a supplement to the experimental studies on the periodic trends in the M–CO bond strength among d^6 hexacarbonyls, to undertake a theoretical investigation, and we shall in the next sections provide estimates of D(M–CO) as well as ΔH along with an analysis of the various steric and electronic contributions to the M–CO bond strength.

(a) Average M–CO Interaction Energies in d^6 Hexacarbonyls. We compare in Table I our calculated mean bond energies in $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ with the experimental data on E. The calculated values differ by as much as 25 kJ mol^{-1} from the experimental energies, but they follow otherwise the experimentally observed ordering: $E_W > E_{Mo} > E_{Cr}$.

We have in an effort to understand the ordering $E_W > E_{Mo} > E_{Cr}$ in more detail decomposed the mean bond energy, E, into a number of terms by considering the formation of $M(CO)_6$ from M (in its high-spin electronic ground state) and six CO ligands in a sequence of steps. The metal atom is in the first step promoted from its high-spin electronic ground state to the d^6 valence state with the t_{2g}^6 configuration. The promotion energy required for the first step is ΔE_{prep}. The metal atom M, now in its t_{2g}^6 valence state, is in the second step brought together with the six CO ligands to the positions they will have in $M(CO)_6$, while confining the electrons to the orbitals they occupied in the free states of CO and $M(t_{2g}^6)$, respectively. Thus after this step the system is described by the normalized and antisymmetrical product wave function

$$\Psi^\circ = A(\Psi_M{}^*\Psi_{CO_1}, ..., {}^*\Psi_{CO_6}) \qquad (5)$$

where Ψ_M is the wave function for $M(t_{2g}^6)$ and Ψ_{CO_n} the wave function of one of the CO ligands (n = 1, 6). The energy required in the second step, ΔE°, is given by

$$\Delta E^\circ = E^\circ - E(M) - 6E(CO) \qquad (6)$$

where E° is the energy corresponding to Ψ°, whereas E(CO) is the energy of a CO ligand and E(M) the energy of $M(t_{2g}^6)$. The energy ΔE°, which we shall refer to as the steric interaction energy, has two components. The first is the pure electrostatic interaction, E_{elst}, between M and CO (as well as between different CO ligands), and the second the exchange repulsion, ΔE_{exrp}, from the destabilizing two-orbital four-electron interactions between occupied orbitals on M and the CO ligands (as well as between occupied orbitals on different CO ligands). Thus

$$\Delta E^\circ = \Delta E_{exrp} + E_{els} \qquad (7)$$

The principal contribution to ΔE_{exrp} comes in the hexacarbonyls

Table II. Decomposition of the Mean Bond Energy, E, and Intrinsic Mean Bond Energy, D(M–CO), in $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$

	$^1/_6\Delta E_{prep}$	$^1/_6\Delta E^\circ$	$^1/_6\Delta E(a_{1g})$	$^1/_6\Delta E(e_g)$	$^1/_6\Delta E(t_{2g})$	$^1/_6\Delta E(t_{2u})$	$^1/_6\Delta E_{rel}$	E^a	D(M–CO)^b
$Cr(CO)_6$	100.7	142.5	−1.9	−79.1	−237.4	−35.2		110	211
$Mo(CO)_6$	51.6	147.2	−3.2	−108.1	−189.3	−23.9		126	178
$W(CO)_6$	54.4	155.0	−2.1	−122.1	−186.4	−19.4	−35.2	156	210

[a] The mean bonding energy E is given as $E = -^1/_6[\Delta E_{prep} + \Delta E^\circ + \Delta E(a_{1g}) + \Delta E(e_g) + \Delta E(t_{2g}) + \Delta E(t_{2u}) + \Delta E_{rel}]$. [b] The internal bond energy D(M–CO) is given as $D(\text{M–CO}) = -^1/_6[\Delta E^\circ + \Delta E(a_{1g}) + \Delta E(e_g) + \Delta E(t_{2g}) + \Delta E(t_{2u}) + \Delta E_{rel}]$.

from the interaction between the σ_{CO} orbitals on the ligands and the fully occupied ns, np orbitals on the metal.

In the third step we allow the density to relax to that of $M(CO)_6$ by performing a full SCF calculation. We will, in this step, have an energy contribution, $\Delta E(t_{2g})$, from the back-donation **2b** in the t_{2g} representation as well as the energy contributions, $\Delta E(a_{1g})$, $\Delta E(e_g)$, and $\Delta E(t_{2u})$, from the donations **2a**, **2c**, **2d**, and **2e** in the a_{1g}, e_g, and t_{2u} representations, respectively.

Collecting the various terms and taking into account contributions from relativistic effects as a separate term, ΔE_R, provide the following expression for the mean bond energy

$$E = -\tfrac{1}{6}[\Delta E_{prep} + \Delta E^\circ + \Delta E(a_{1g}) + \Delta E(t_{2g}) + \Delta E(e_g) + \Delta E(t_{2u}) + \Delta E_R] \quad (8)$$

The reader is referred to ref 24 for a more detailed account of the decomposition scheme outlined here.

The intrinsic bond energy D(M–CO), which does not depend on the promotion energy ΔE_{prep} of the first step but otherwise compromises all contributions from step 2 and step 3 of our decomposition scheme, is further given by

$$D(\text{M–CO}) = -\tfrac{1}{6}[\Delta E^\circ + \Delta E(a_{1g}) + \Delta E(t_{2g}) + \Delta E(e_g) + \Delta E(t_{2u}) + \Delta E_R] \quad (9)$$

It follows from Table II, where E and D(M–CO) as well as their components are presented for $M(CO)_6$ (M = Cr, Mo, and W), that the mean bond energy E and the intrinsic mean bond energy D(M–CO) follow quite different trends through the triad. Thus, whereas E is increasing down the triad, the intrinsic mean bond energy D(M–CO) has the following ordering: D(Mo–CO) < D(Cr–CO) ~ D(W–CO), with the weakest bonding interaction between $M(t_{2g}^6)$ and CO for molybdenum. The different trends in E and D(M–CO) are related to variations in the promotion energy ΔE_{prep}, see Table II, as the promotion energy is seen to be much larger for M = Cr than for M = Mo, W. That the promotion energy is largest for chromium is perhaps not unexpected since ΔE_{prep} depends on exchange integrals that in general are larger for the relatively contracted 3d-orbitals of chromium than for the more diffuse 4d- and 5d-orbitals of molybdenum and tungsten.

The relativistic correction, ΔE_R, which only is of importance[25] for M = W, is seen to strengthen the W–CO bond considerably (Table II). In fact, the intrinsic bond energy D(W–CO) would be comparable to D(Mo–CO) without the relativistic contribution ΔE_{rel}. Thus, the fact that the M–CO bond is weakest for molybdenum, at least according to our calculations, is indirectly a relativistic effect, since our calculations suggest that the M–CO bond without relativity would be even weaker for tungsten.

We note, in turning next to the electronic terms $\Delta E(a_{1g})$, $\Delta E(e_g)$, $\Delta E(t_{2g})$, and $\Delta E(t_{2u})$ as well as the steric interaction energy ΔE°, that the contribution to E and D(M–CO) from the steric interaction energy, $-^1/_6\Delta E^\circ$, is destabilizing (negative) due to the four-electron two-orbital interactions represented by ΔE_{exrp} of eq 7, whereas all the electronic terms have stabilizing (positive) contributions to E and D(M–CO). The back-donation **2b** from d_π to π_{CO}^* is seen for all three metals to be more important for the stability of $M(CO)_6$ than the donation **2a** from σ_{CO} to d_σ, as $-^1/_6\Delta E(t_{2g})$ is larger than $-^1/_6\Delta E(e_g)$ throughout the triad, see Table II. There is, however, a clear distinction between $Cr(CO)_6$ on the one hand and $Mo(CO)_6$ and $W(CO)_6$ on the other, in that the contribution to D(M–CO) from the back-donation, $-^1/_6\Delta E(t_{2g})$, is larger for M = Cr than for M = Mo, W, whereas the contribution to D(M–CO) from the donation, $-^1/_6\Delta E(e_g)$, is larger for M = Mo, W than for M = Cr.

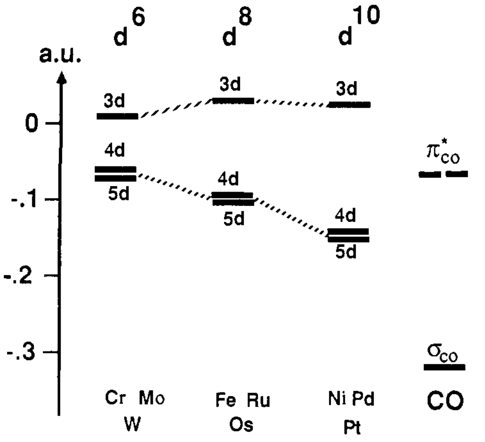


Figure 1. Orbital energy levels for M and CO. The average energies of the d-orbitals for Cr, Mo, and W in the d^6 configuration, for Fe, Ru, and Os in the d^8 configuration, as well as Ni, Pd, and Pt in the d^{10} configuration are shown relative to the σ_{CO} HOMO and π_{CO}^* LUMO of CO.

The stronger σ-bonding interaction in **2a** for $Mo(CO)_6$ and $W(CO)_6$ compared to $Cr(CO)_6$ is in the first place the result of better overlaps between d_σ and σ_{CO} in the case of the relatively diffuse $4d_\sigma$ and $5d_\sigma$ orbitals of molybdenum and tungsten, respectively, compared to the case of the rather contracted $3d_\sigma$ orbital of chromium. Thus, the group overlaps S_σ in **2a** were calculated as 0.38, 0.48, and 0.50 for M = Cr, Mo, and W, respectively. The 4d and 5d orbitals are moreover seen to have a better energy match with σ_{CO} than 3d (Figure 1) as they are of lower energy. The better energy match will further enhance the σ-bonding interaction **2a** in $Mo(CO)_6$ and $W(CO)_6$ compared to $Cr(CO)_6$. The 4d- and 5d-orbitals are of lower energies than 3d since the d–d repulsion is smaller for the diffuse 4d- and 5d-orbitals than the contracted 3d-orbitals.

The group overlaps S_π in the π-interaction **2b**, calculated as 0.41, 0.47, and 0.48 for M = Cr, Mo, and W, respectively, would tend to render $Mo(CO)_6$ and $W(CO)_6$ a stronger π-interaction than $Cr(CO)_6$. However, the 3d-orbital of chromium has, on the other hand, the more favorable energy match with π_{CO}^* as it is of higher energy than the 4d- and 5d-orbitals of molybdenum and tungsten, respectively (Figure 1). The more favorable energy match in the case of the 3d-orbital is the prevailing factor for the π-interaction **2b** according to our quantitative calculations (Table II), where $-^1/_6\Delta E(t_{2g})$ is calculated to be larger for M = Cr than for M = Mo and W. The role of (n + 1)p and in particular (n + 1)s as acceptor orbitals is seen to be modest in $M(CO)_6$, see $-\Delta E(t_{2u})$ and $-\Delta E(a_{1g})$ of Table II, respectively. The 4p-orbital of chromium forms somewhat stronger overlaps with σ_{CO} and π_{CO} than the 5p- and 6p-orbitals of the heavier elements, and is thus better able to interact with σ_{CO} in **2d** or π_{CO} in **2e**. The contribution from $-\Delta E(t_{2u})$ to D(M–CO) is as a result marginally larger for M = Cr than for M = Mo, W. The steric interaction energy ΔE°, the final term in our energy decomposition scheme, is quite similar for the three hexacarbonyls with a spread of only 10 kJ mol^{-1} in favor of $Cr(CO)_6$. The hexacarbonyls do not have any contribution to ΔE° from σ-interactions between occupied nd- and σ_{CO}-orbitals. We shall see later, in connection with our discussion of the $M(CO)_4$ and $M(CO)_5$ systems, that such interactions have a strongly destabilizing effects on the M–CO bond, in particular for the heavier 4d and 5d elements.

Each of the components in D(M–CO) depends, as it is shown in Figure 2 for the leading terms ΔE°, $\Delta E(e_g)$, and $\Delta E(t_{2g})$,

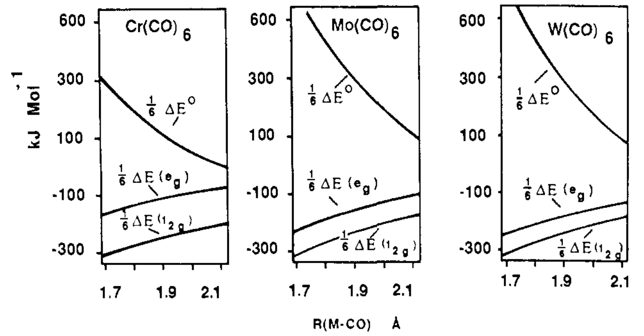


Figure 2. Steric and electronic contributions to D(M–CO) in M(CO)$_6$ (M = Cr, Mo, W) as a function of R(M–CO). The three major components in the decomposition of the intrinsic mean bond energy D(M–CO) of M(CO)$_6$, the steric interaction energy $^1/_6\Delta E°$, the σ-donation energy $^1/_6\Delta E(e_g)$, and π-back-donation energy $^1/_6\Delta E(t_{2g})$, are given as a function of R(M–CO) for M = Cr, Mo, and W.

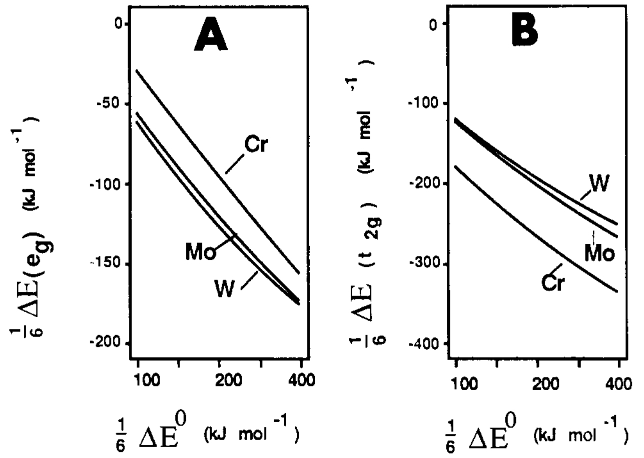


Figure 3. (A) The σ-donation energy $^1/_6\Delta E(e_g)$ as a function of the steric interaction energy $^1/_6\Delta E°$ in M(CO)$_6$ (M = Cr, Mo, W). (b) The π-back-donation energy $^1/_6\Delta E(t_{2g})$ as a function of the steric interaction energy $^1/_6\Delta E°$ in M(CO)$_6$ (M = Cr, Mo, W).

strongly on the M–CO distance, more so actually than D(M–CO). It is possible in fact, as it can be seen in Figure 2, to enhance the σ-donation **2a** as well as the π-back-donation **2b** considerably for any of the hexacarbonyls by decreasing the M–CO distance, but *not* without increasing at the same time the steric interaction energy $\Delta E°$. What is of importance then for the relative strength of the M–CO bonds in M(CO)$_6$ is the dependence of $\Delta E(e_g)$ and $\Delta E(t_{2g})$ on $\Delta E°$, that is, the stability gained from $\Delta E(e_g)$ and $\Delta E(t_{2g})$ for a certain value of $\Delta E°$. The dependence of $\Delta E(e_g)$ and $\Delta E(t_{2g})$ on $\Delta E°$ is depicted in Figure 3, where it can be seen that $\Delta E(e_g)$ renders more stability to Mo(CO)$_6$ and W(CO)$_6$ than to Cr(CO)$_6$ for the same value of $\Delta E°$, whereas the opposite is the case for $\Delta E(t_{2g})$.

We have finally found, in an extension of our study on the d^6 hexacarbonyls to V(CO)$_6^-$ and Mn(CO)$_6^+$, that D(V–CO) and D(Mn–CO) bracket D(Cr–CO), with D(V–CO) = 297 kJ mol^{-1} and D(Mn–CO) = 135 kJ mol^{-1}, respectively. The ordering D(V–CO) > D(Cr–CO) > D(Mn–CO) is, as one would expect, caused by a decrease in the back-bonding interaction (**2b**) through the series M = V, Cr, Mn.

We note, in summarizing our analysis, that the intrinsic bond energy D(M–CO) in the nonrelativistic limit is larger for Cr(CO)$_6$ than for either Mo(CO)$_6$ or W(CO)$_6$, primarily as a result of a stronger π-interaction in **2b** for M = Cr compared to M = Mo, W. Relativistic effects will, however, change the ordering to D(Mo–CO) < D(Cr–CO) ~ D(W–CO) by enhancing the strength of the W–CO bond. The experimentally observed ordering $E_{Cr} < E_{Mo} < E_W$ for the mean bonding energies is further seen to reflect differences in the energy required to promote the metal atoms from there electronic ground states to the t_{2g}^6 valence configuration, rather than trends in the M–CO bond strength.

Table III. Calculated Values for the First Ligand Dissociation Energy ΔH in Cr(CO)$_6$, Mo(CO)$_6$, W(CO)$_6$, Mn(CO)$_6^+$, and V(CO)$_6^-$ Compared to Experimental Data

	ΔH (kJ mol^{-1})			
M(CO)$_6$	calcd	exptl[a]	exptl[b]	exptl[c]
Cr(CO)$_6$	147	162	155	154
Mo(CO)$_6$	119	126	142	169
W(CO)$_6$	142	166	159	192
Mn(CO)$_6^+$	92			
V(CO)$_6^-$	171			

[a] Kinetic data from ref 23. [b] Photochemical data from ref 2b. [c] Laser pyrolysis data from ref 2a.

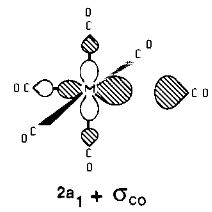
The calculated mean bond energies, E, are as already mentioned in reasonable agreement with experimental data. We expect the major part of the error in our theoretical values to come from calculations on the promotion energy ΔE_{prep}. The calculated intrinsic mean energies should thus be more accurate than the mean energies.

(b) First Ligand Dissociation Energy in d^6 Hexacarbonyls. Calculated values of the first ligand dissociation energy, ΔH, for M(CO)$_6$ (M = Cr, Mo, W) are compared in Table III with experimental data from different sources. Our calculated ordering for the first ligand dissociation energy, given as $\Delta H_{Mo} < \Delta H_W \sim \Delta H_{Cr}$, is in line with the data from solution kinetics[23] as well as Bernsteins[2b] results based on a photochemical study, but differs from the ordering $\Delta H_{Cr} < \Delta H_{Mo} < \Delta H_W$ obtained by Lewis et al.[2a] in their laser pyrolysis work.

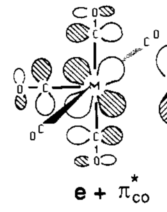
The first ligand dissociation energy can be decomposed in a way similar to the mean bond energy, ΔE, as

$$\Delta H = -[\Delta E_{prep} + \Delta E° + \Delta E(a_1) + \Delta E(e) + \Delta E_R] \qquad (10)$$

Here $\Delta E°$ is the steric interaction energy between CO and the M(CO)$_5$ fragment whereas $\Delta E(a_1)$ represents the contribution to ΔH due to the donation **3a** from σ_{CO} to the LUMO or M(CO)$_5$, and ΔE(e) is the contribution to ΔH due to the back-donation **3b** from the HOMO of M(CO)$_5$ to the π_{CO}*-orbital of CO. The contribution from relativistic effects is given as ΔE_R. There is no electronic promotion energy required in the interaction between M(CO)$_5$ and CO, but ΔE_{prep} should, in principle, have a contribution from the energy required to relax the geometry of free M(CO)$_5$ to that of the M(CO)$_5$ framework in M(CO)$_6$. We have not included such a relaxation energy in the present work. Thus ΔH of Table III is with respect to CO and a square-pyramidal M(CO)$_5$ fragment of the same geometry as the M(CO)$_5$ framework in M(CO)$_6$. We expect, however, the relaxation energy to be small since both experimental[26] and theoretical[1c,4h] studies indicate that d^6 pentacarbonyls have a square-pyramidal ground-state conformation.



3a



3b

It can be seen from Table IV, where ΔH is decomposed into its various components, that the steric interaction energy $\Delta E°$ and the term $\Delta E(a_1)$, representing the donation **3a**, are quite similar for the three hexacarbonyls, whereas ΔE(e), from the back-donation **3b**, is more important for Cr(CO)$_6$ than for either Mo(CO)$_6$ or W(CO)$_6$. The back-donation **3b** is thus in the nonrelativistic limit responsible for ΔH_{Cr} being larger than ΔH_{Mo} or ΔH_W. Relativity will, however, strengthen the W–CO bond to the extent where ΔH_W becomes similar to ΔH_{Cr}, Table IV, just as in the case

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(26) Burdett, J. K. *Coord. Chem. Rev.* **1978**, *27*, 1.

Table IV. Decomposition of the First Ligand Dissociation Energy, ΔH, in $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$

$M(CO)_6$	ΔE° [b]	$\Delta E(a_1)$ [b]	$\Delta E(e)$ [b]	ΔE_R [b]	ΔH [a]
$Cr(CO)_6$	193	−163	−177		147
$Mo(CO)_6$	197	−165	−148	−3	119
$W(CO)_6$	197	−160	−154	−25	142

[a] The first bond dissociation energy ΔH is given by the following: $\Delta H = -[\Delta E^{\circ} + \Delta E(a_1) + \Delta E(e) + \Delta E_R]$. [b] kJ mol^{-1}.

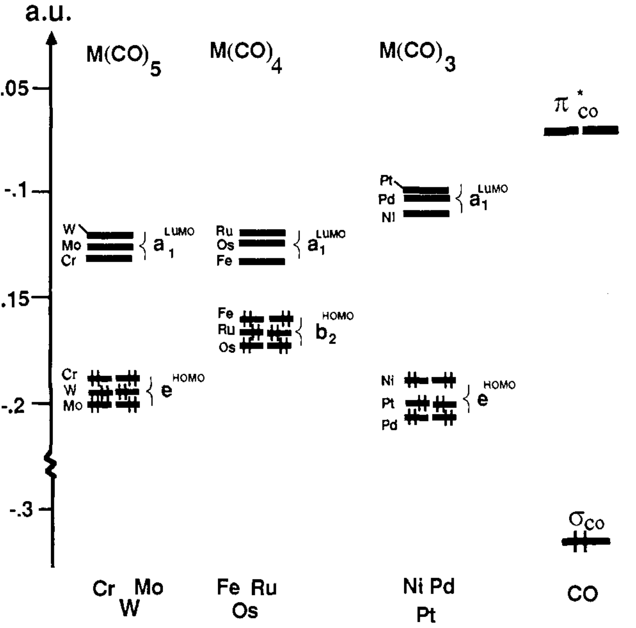

Figure 4. Energies of the HOMOs and LUMOs in $M(CO)_n$ relative to σ_{CO} and π_{CO}* of CO.

of the intrinsic mean bond energies discussed in the previous section.

The HOMOs of $M(CO)_5$, involved in the back-donation interaction **3b**, are in-phase combinations between metal nd_{π}-orbitals and the π_{CO}-orbitals on the five CO ligands. These orbitals have, in contrast to their parent d-orbitals, nearly the same energy in the three $M(CO)_5$ fragments (Figure 4) since the higher energy of 3d (Figure 1) is offset by a stronger π-interaction in $Cr(CO)_5$ compared to $Mo(CO)_5$ and $W(CO)_5$. The difference in the strength of **3b**, between M = Cr on the one side and M = Mo, W on the other, can as a consequence, not be explained in terms of variations in the energy match between π_{CO} and the HOMOs of $M(CO)_5$. Nor can it be explained in terms of a significant difference in the overlaps between π_{CO} and the HOMOs, as the overlaps were calculated to be 0.18, 0.19, and 0.19 for M = Cr, Mo, and W, respectively.

The back-donation interaction **3b** constitute a delocalization of charge from the metal center to the π_{CO}*-orbital, and it is a favorable process as it reduces the electron–electron repulsion around the metal center. The electron–electron repulsion is, however, stronger for chromium, with the relatively contracted 3d-orbitals, than it is for molybdenum and tungsten, with their more diffuse 4d- and 5d-orbitals, and the delocalization **3b** is, as a consequence, more favorable for M = Cr than for M = Mo and W.

We have here in our theoretical study found that the intrinsic bond energy D(M–CO), as well as the first ligand dissociation energy ΔH, in the nonrelativistic limit follows the ordering Cr > Mo ∼ W, through the triad, primarily as a result of a stronger back-bonding interaction in $Cr(CO)_6$ compared to $Mo(CO)_6$ and $W(CO)_6$. Relativistic effects will, however, strengthen the M–CO bond to the extent where the ordering for ΔH and D(M–CO) becomes Mo < Cr ∼ W.

The finding here, that the Mo–CO bond is weaker than either the Cr–CO or W–CO bonds, has also been inferred from kinetic data,[23] but it is at variance with recent direct measurements of ΔH by Lewis et al.[2a] in which the ordering $\Delta H_{Cr} < \Delta H_{Mo} < \Delta H_W$ was obtained. We are not able to give a rational[27] for the different conclusions reached by the various experimental techniques (Table III) nor can we exclude that our theoretical results are misleading due to the approximations inherent in the theoretical method. We would, however, like to point out that there are several other examples where the 4d member of a homologous series of metal fragments appears to have a weaker interaction with a strong π-accepting ligand than its 3d and 5d congeners, and we shall in the next sections discuss some more possible examples among mononuclear metal carbonyls.

It has been pointed out[22] that the ordering of the observed k(M–CO) force constants for $M(CO)_6$ (Table III) correlates with the ordering for ΔH inferred from kinetic experiments.[23] We have calculated the k(M–CO) force constant to be smaller for M = Mo than for M = Cr and W (Table III) after the inclusion of relativistic effects. The two force constants k(W–CO) and k(Mo–CO) are on the other hand similar in the nonrelativistic limit and both smaller than k(Cr–CO) (Table III). The relation between bond energies and force constants is unfortunately not a simple one, and it is, as a consequence, not possible from the relative magnitudes of the observed k(M–CO) force constants conclusively to predict the trend in the first CO-dissociation energy ΔH.

The calculated first ligand dissociation energies for the d^6 hexacarbonyls $Mn(CO)_6^+$ and $V(CO)_6^-$ (Table III) are, as one might expect, respectively smaller and larger than ΔH of $Cr(CO)_6$. The ordering $\Delta H_{Mn} < \Delta H_{Cr} < \Delta H_V$ is a reflection of the increase in back-donation through the series $Mn(CO)_6^+$, $Cr(CO)_6$, and $V(CO)_6^-$.

IV. Tetrahedral d^{10} Complexes

$Ni(CO)_4$ appears, among the d^{10} tetracarbonyls $Ni(CO)_4$, $Pd(CO)_4$, and $Pt(CO)_4$ of the platinum triad, to be more stable than the two homologues $Pt(CO)_4$ and $Pt(CO)_4$. Thus $Ni(CO)_4$ is stable at ambient temperatures, whereas $Pt(CO)_4$ and $Pd(CO)_4$ only have been isolated in a low-temperature matrix.[28] Accurate experimental values are available on the mean bond energy,[2c] E, as well as the first ligand dissociation energy,[2a] ΔH, for $Ni(CO)_4$. The apparent instability at room temperature of $Pt(CO)_4$ and $Pd(CO)_4$ has on the other hand to data precluded any thermochemical measurements on the Pt–CO and Pd–CO bond strengths, and the relative stabilities of the two bonds are at present unknown. For other π-accepting ligands, notably L = PF_3 and $P(OEt)_3$, where d^{10} ML_4 complexes are stable for all three members of the platinum triad, one observes,[29] however, that the 4d member has a more labile M–L bond than the 3d and 5d congeners, just as in the case of the hexacarbonyls.[23]

There is according to the traditional qualitative bonding scheme for d^{10} tetracarbonyls (Figure 5) a strong destabilization of $M(CO)_4$ in the σ-framework due to the repulsive interaction **4c** between the fully occupied σ_{CO}- and nd-orbitals in the t_2 representation. Some stabilization in the σ-framework is, however, rendered by the interactions between the σ_{CO}-orbitals and the empty metal acceptor orbitals $(n + 1)$s (**4a**) or $(n + 1)$p (**4b**). The interactions in the π-framework (Figure 5) are stabilizing and include π-back-donations to π_{CO}* from d-orbitals of e symmetry (**5a**) or t_2 symmetry (**5b**) as well as a donation (polarization) of charge from σ_{CO} to π_{CO}* (**5c**). There have been several theoretical studies on $Ni(CO)_4$,[4] including the very recent work by Bauschlicher and Bagus,[5a] where it was stressed that the acceptor ability of the π_{CO}* ligand orbitals is more important for the stability of $Ni(CO)_4$ than the acceptor abilities of the 4s and 4p metal orbitals.

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(27) Two activation energies of 45.5 and 35.3 kJ mol^{-1}, respectively, were obtained in ref 2a for the first CO dissociation in $Cr(CO)_6$, with the smaller value of 35.3 kJ mol^{-1} being adopted in the final evaluation of ΔH. If the larger value of 45.5 kJ mol^{-1} had been adopted the ordering for ΔH would, in agreement with other experimental data as well as our calculation, have been $\Delta H_{Mo} < \Delta H_{Cr} \sim \Delta H_W$.

(28) Kundig, E. P.; McIntosh, D.; Moskovits, M.; Ozin, G. A. *J. Am. Chem. Soc.* **1973**, *95*, 7234.

(29) Meler, M.; Basolo, F.; Pearson, R. G. *Inorg. Chem.* **1969**, *9*, 795.

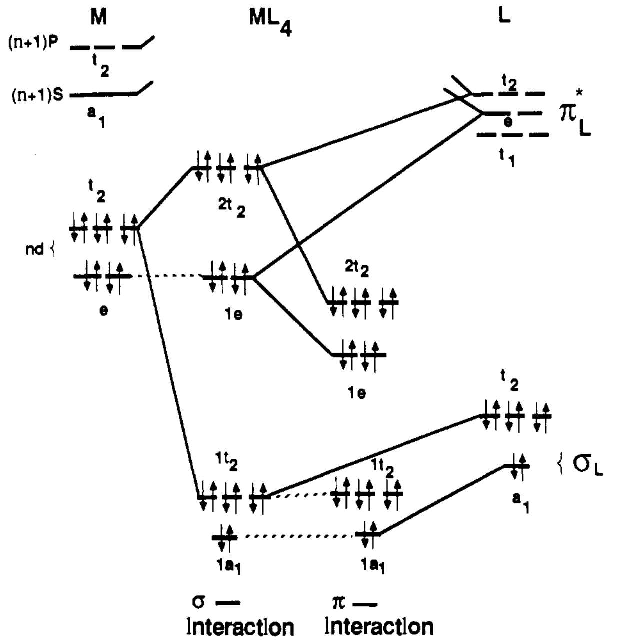
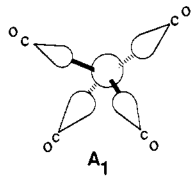
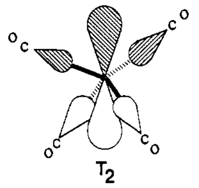


Figure 5. The σ-interactions and π-interactions between M(d^{10}) and L in ML_4.

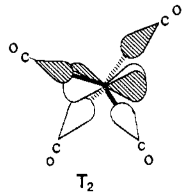
The $Pd(CO)_4$ and $Pt(CO)_4$ tetracarbonyls have not been investigated in any details by theoretical methods.



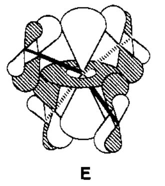
4a



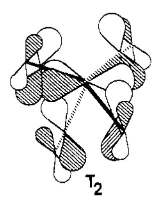
4b



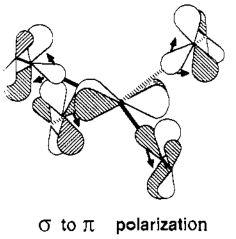
4c



5a



5b



5c

We shall, in the next sections, discuss how the σ-donations, **4a** and **4b**, and π-back donations, **5a** and **5b**, as well as the interactions, **4c** and **5c**, influence the relative strengths of the M–CO bonds in $M(CO)_4$ (M = Ni, Pd, and Pt). Both the intrinsic mean bond energy D(M–CO) between M, with the d^{10} valence configuration, and four CO ligands, as well as the first CO dissociation energy, ΔH, will be considered as measures for the M–CO bond strength. We shall further, for the d^{10} metal centers, compare the M–CO bond strength to the strength of M–L bonds involving other π-accepting ligands L. For the ML_4 systems mentioned here calculations on the M–L bond strength have previously only been carried out on $Ni(CO)_4$[5a,f,h] and $M(CO)_4$ (M = Pd, Pt).[5h]

(a) The Intrinsic Mean Bond Energies in $M(CO)_4$ and $M(PF_3)$ for M = Ni, Pd, and Pt. The calculated intrinsic mean bond energies, D(M–L), for $M(CO)_4$ (M = Ni, Pd, Pt) and $M(PF_3)$ (M = Ni, Pd, Pt) are given in Table V along with the experimental values for $Ni(CO)_4$ and $Ni(PF_3)_4$. The experimental values were deduced from the observed mean energies,[2c] E, and spectroscopic data on the energy[30] ΔE_{prep} (176 kJ mol^{-1}) required to promote Ni from its ^3F ground state with the $3d^84s^2$ configuration to the ^1S valence state with the $3d^{10}$ configuration as $D(\text{Ni–L}) = E + {}^1/_4\Delta E_{prep}$. The calculated and experimental values for D(M–L) differ by 13 and 3 kJ mol^{-1} for $Ni(CO)_4$ and $Ni(PF_3)_4$, respectively, and we find, in accordance with qualitative observations, that the 3d systems form considerably stronger M–L bonds than the 4d and 5d homologues (Table V). The tetrakis(trifluorophosphine) complexes of palladium and platinum are further, again in accordance with qualitative observations, calculated to be considerably more stable than the corresponding tetracarbonyls. We have finally found, as for the hexacarbonyls, that the M–L bonds, with L = PF_3 and CO, are weakest in the case of the 4d member of the triad (i.e., M = Pd) (Table V).

Table V. Intrinsic Mean Bond Energies, D(M–L), for $M(CO)_4$ and $M(PF_3)_4$ with M = Ni, Pd, and Pt

	D(M–L) (kJ mol^{-1})			D(M–L) (kJ mol^{-1})	
ML_4	calcd	exptl	ML_4	calcd	exptl
$Ni(CO)_4$	178.9	191[a]	$Ni(PF_3)_4$	193.3	191[a]
$Pd(CO)_4$	43.9		$Pd(PF_3)_4$	95.6	
$Pt(CO)_4$	58.8		$Pt(PF_3)_4$	104.2	

[a] Reference 2c.

It is possible to decompose D(M–L) of ML_4 in a way similar to D(M–CO) of the hexacarbonyls as

$$D(\text{M–L}) = -{}^1/_4[\Delta E^\circ + \Delta E(a_1) + \Delta E(e) + \Delta E_1(t_2) + \Delta E_2(t_2) + \Delta E_R] \quad (11)$$

Here ΔE° is the sum of the steric interaction energies between the ligands as well as M(d^{10}) and L, whereas $\Delta E(a_1)$, $\Delta E(e)$, and ΔE_R represent contribution from **4a**, **5a**, and relativistic effects, respectively. There are three stabilizing interactions in the t_2 representation, namely, **4b** involving the $(n + 1)$p orbitals and **5b** involving nd as well as **5c**. The combined contribuion to D(M–L) from the three interactions **4b**, **5b**, and **5c** is given as $\Delta E(t_2)$. We have estimated the respective contributions to $\Delta E(t_2)$ from **4b** on the one hand and **5b** as well as **5c** on the other by performing calculations on ML_4 with and without $(n + 1)$p-orbitals. Thus in eq 11 $\Delta E_1(t_2)$ corresponds to **4b** and $\Delta E_2(t_2)$ to **5b** and **5c**. We did not try to determine the individual contributions to D(M–L) from the two interactions **5b** and **5c** which both involve donation of charge to $\pi_{CO}*$.

Table VI displays the different terms in D(M–L) according to eq 11. We find for the tetracarbonyls that the low stability of $Pd(CO)_4$ and $Pt(CO)_4$, compared to $Ni(CO)_4$, largely is caused by a stronger repulsive steric interaction in the case of M = Pd and Pt than in the case of M = Ni, ΔE° of Table VI. The differential in ΔE° between M = Pd and Pt on the one hand and M = Ni on the other is primarily due to the destabilizing σ-interaction **4c** between the fully occupied nd- and σ_{CO}-orbitals (see Figure 5). This interaction is stronger for the 4d and 5d members than for the 3d member since the group overlaps in **4c** increase down the triad as 0.19, 0.24, and 0.27 for M = Ni, Pd, and Pt, respectively. The 4d- and 5d-orbitals are closer in energy to σ_{CO} than 3d (Figure 1).

The contributions to D(M–CO) from the metal acceptor orbitals $(n + 1)$s (**4a**) and $(n + 1)$p (**4b**), represented by $-{}^1/_4\Delta E(a_1)$ and $-{}^1/_4\Delta E_1(t_2)$, respectively, are rather modest and do not add much to the stability of the M–CO bond in spite of the fact that the combined occupation of $(n + 1)$s and the three $(n + 1)$p orbitals is close to 1.0 (Table VII). The role of $\pi_{CO}*$ as an acceptor orbital is on the other hand crucial for the M–CO bond strength both in **5a**, with the contribution $-{}^1/_4\Delta E(e)$, and in particular in **5b** and **5c**, with the combined contribution $-{}^1/_4\Delta E_2(t_2)$. The interactions **5b** and **5c** serve primarily to relieve the destabilizing interaction **4c** by donating density to $\pi_{CO}*$ from both nd and σ_{CO} (Table VII).

The π-acceptor interactions **5a**, **5b**, and **5c** are somewhat stronger for M = Ni than for M = Pd, Pt as one might expect from 3d being closer in energy to $\pi_{CO}*$ than 4d and 5d (Figure 1). Relativistic effects are further seen to increase the Pt–CO

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(30) Moore, C. E. In *Atomic Energy Levels* **1952**, NBS C 467.

Table VI. Decomposition of Intrinsic Mean Bond Energies, D(M–L), in $M(CO)_4$ and $M(PF_3)_4$ for M = Ni, Pd, and Pt

ML_4	$^1/_4\Delta E°$	$^1/_4\Delta E(a_1)$	$^1/_4\Delta E(e)$	$^1/_4\Delta E_2(t_2)$	$^1/_4\Delta E_1(t_2)$	$^1/_4\Delta E_R$	D(M–L)[a]
$Ni(CO)_4$	165.5	-3.1	-74.1	-247.4	-19.8		178.9
$Pd(CO)_4$	269.9	-2.8	-58.6	-232.1	-14.1	-6.2	43.9
$Pt(CO)_4$	305.5	-2.4	-58.6	-237.6	-14.6	-50.9	58.8
$Ni(PF_3)_4$	118.4	-6.3	-81.6	-195.6	-28.2		193.3
$Pd(PF_3)_4$	186.8	-8.7	-64.6	-176.3	-24.8	-8.3	95.6
$Pt(PF_3)_4$	213.8	-7.8	-59.6	-189.1	-23.8	-37.7	104.2

[a] The intrinsic mean bond energy D(M–L) is given as $D(M–L) = -^1/_4[\Delta E° + \Delta E(a_1) + \Delta E(e) + \Delta E_1(t_2) + \Delta E_2(t_2) + \Delta E_R]$.

Table VII. Mulliken Population Changes in Metal and Ligand Symmetry Orbitals of $M(CO)_4$ and $M(PF_3)_4$ for M = Ni, Pd, and Pt

	changes in Mulliken population of[a] each metal symmetry orbital				changes in Mulliken population of each[b] ligand symmetry orbital			
ML_4	$(n + 1)$s	$(n + 1)$p	d(e)	e(t_2)	$\sigma_L(a_1)$	$\sigma_L(t_2)$	$\pi_L^*(e)$	$\pi_L^*(t_2)$
$Ni(CO)_4$	0.20	0.17	-0.19	-0.29	-0.20	-0.21	0.19	0.33
$Pd(CO)_4$	0.16	0.20	-0.20	-0.30	-0.16	-0.21	0.21	0.31
$Pt(CO)_4$	0.18	0.23	-0.19	-0.35	-0.18	-0.22	0.19	0.34
$Ni(PF_3)_4$	0.28	0.20	-0.24	-0.25	-0.28	-0.30	0.24	0.35
$Pd(PF_3)_4$	0.22	0.28	-0.27	-0.30	-0.22	-0.30	0.27	0.32
$Pt(PF_3)_4$	0.21	0.29	-0.24	-0.34	-0.21	-0.30	0.24	0.35

[a] The d orbitals of e symmetry are designated d(e) whereas the d orbitals of t_2 symmetry are designated d(t_2). [b] The σ_L orbtials span the a_1 and t_2 symmetries as $\sigma_L(a_1)$ and $\sigma_L(t_2)$ combinations, respectively, whereas the π_L^* orbitals span the e and t_2 representations as $\pi_L^*(e)$ and $\pi_L^*(t_2)$, respectively.

bond strength sufficiently to make it stronger than the Pd–CO bond, but not enough to bring it on a par with the Ni–CO bond strength (Table VI). Rolfing and Hay[5h] also found the order of stability as Ni ≥ Pt > Pd in $M(CO)_4$ systems. They did not, however, discuss specifically the role of relativity although relativistic effects were included in their calculations.

We have, as already mentioned, calculated the tetrakis(trifluorophosphine) complexes $M(PF_3)_4$ to be more stable than the corresponding tetracarbonyls, in particular for M = Pd and Pt (Table V). This is in line with experimental observations since $M(PF_3)_4$ is stable at ambient temperatures for all three members of the platinum triad, whereas $Ni(CO)_4$ as the only tetracarbonyl is stable at room temperature.

The bonding in the $M(PF_3)_4$ molecules of T_d symmetry is qualitatively similar to that in the tetracarbonyls since PF_3 has σ- and π^*-orbitals corresponding to σ_{CO} and π_{CO}^*, respectively, and we can, as a consequence, use the same decomposition scheme for $D(M–PF_3)$ as for D(M–CO) (Table VI and eq 11). There is, in going from L = CO to PF_3, an enhancement in the energy contributions to D(M–L) from the σ-interactions **4a** and **4b** as well as the π-back-donation interaction **5a** (Table VI), but these enhancements are not large enough to account for the $M–PF_3$ bond being much stronger than the M–CO bond in the cases of M = Pd and Pt. The determining factor is instead seen to be the steric interaction energy, $\Delta E°$, which is consistently smaller in the tetrakis(trifluorophosphine) systems than in the corresponding tetracarbonyls. This difference reflects first of all a weaker repulsive interaction between nd and σ_L (**4c**) for L = PF_3 than for L = CO, as a consequence of the σ_L orbitals forming smaller overlaps with nd in the case of $M(PF_3)_4$ compared to $M(CO)_4$. Thus, in the case of L = CO we have for the overlaps in **4c** 0.19, 0.24, and 0.27, with M = Ni, Pd, and Pt, respectively, whereas the corresponding overlaps for L = PF_3 are 0.16, 0.20, and 0.22, respectively. The reduction in the steric interaction energy, in going from $M(CO)_4$ to $M(PF_3)_4$, is to some degree offset by a corresponding reduction in $-^1/_4\Delta E_2(t_2)$ from the two interactions **5b** and **5c**, instrumental in reducing the repulsive interaction **4c** (Table VI). We had originally expected that part of the difference in $\Delta E°$ between $M(PF_3)_4$ and $M(CO)_4$ might stem from a difference in the L–L steric interaction energies. We have, however, found that the contributions to $-^1/_4\Delta E°$ from the L–L steric interactions, 32 and 35 kJ mol^{-1} for L = CO and PF_3, respectively, are quite similar for $M(PF_3)_4$ and $M(CO)_4$.

We conclude that the acceptor ability of π_L^* is more important for the stability of the $M(CO)_4$ and $M(PF_3)_4$ systems than the acceptor abilities of the $(n + 1)$s and $(n + 1)$p metal orbitals. Variations in the intrinsic mean bond energy D(M–L), with respect to both M and L, are in addition determined largely by the repulsive interaction **4c** between nd and σ_L (Figure 5).

Table VIII. Calculated Values for the First Ligand Dissociation Energy, ΔH, in $Ni(CO)_4$, $Pd(CO)_4$, $Pt(CO)_4$, and $Ni(CO)_3(N_2)$ Compared to Experimental Data

	ΔH (kJ mol^{-1})			ΔH (kJ mol^{-1})	
$M(CO)_3L$	calcd	exptl	$M(CO)_3L$	calcd	exptl
$Ni(CO)_4$	106	104[a]	$Pt(CO)_4$	38 (-14)	
$Pd(CO)_4$	27 (20)		$Ni(CO)_3(N_2)$	71	42[b]

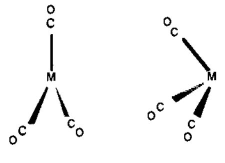
[a] Reference 2a. [b] Reference 35.

(b) The First Ligand Dissociation Energy of $Ni(CO)_4$, $Pd(CO)_4$, and $Pt(CO)_4$. The calculated values for the first ligand dissociation energy, ΔH, in $Ni(CO)_4$, $Pd(CO)_4$, and $Pt(CO)_4$ are given in Table VIII. The ordering within the triad, $\Delta H_{Ni} \gg \Delta H_{Pt} > \Delta H_{Pd}$, is the same as that for D(M–CO). The first ligand dissociation energy, ΔH, is known experimentally[2a] only for $Ni(CO)_4$, and it can be seen from Table VIII that the experimental and theoretical values differ by only 2 kJ mol^{-1}.

The first ligand dissociation energy can be decomposed as

$$\Delta H = -[\Delta E_{prep} + \Delta E° + \Delta E(a_1) + \Delta E(e) + \Delta E_R] \qquad (12)$$

where ΔE_{prep} represents the energy required to deform $M(CO)_3$ from its trigonal planar equilibrium geometry **6a** to the trigonal pyramidal conformation **6b** of the $M(CO)_3$ framework in $M(CO)_4$, whereas $\Delta E°$ is the steric interaction energy between CO and $M(CO)_3$ of conformation **6b**. The two terms $\Delta E(a_1)$ and $\Delta E(e)$ are the electronic contributions to ΔH from the a_1 and e representations as $M(CO)_4$ is formed from $M(CO)_3$ and CO under C_{3v} constraints.



6a **6b**

The HOMO (**7b**) of $M(CO)_3$, 3e of Figure 6, is a metal based nd-orbital with out-of-phase contributions from σ_{CO} and in-phase contributions from π_{CO}^*. At somewhat lower energy is another metal based nd orbital (**7a**) of e symmetry, 2e of Figure 6, with in-phase contributions from π_{CO}^*. Both 3e and 2e can interact with π_{CO}^* of the incoming CO ligand. The interactions between 3e of $M(CO)_3$ and π_{CO}^* (**7b**) will result in the formation of two

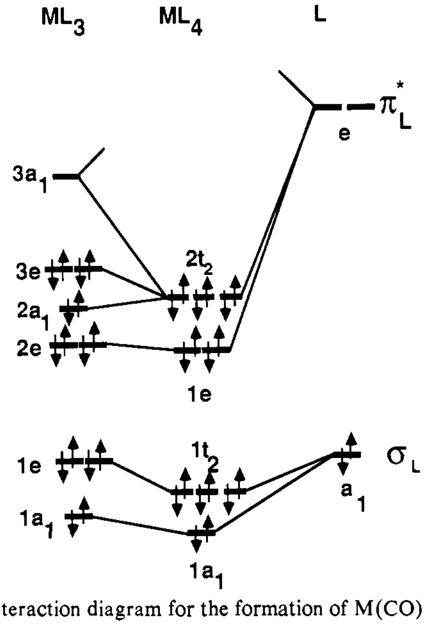
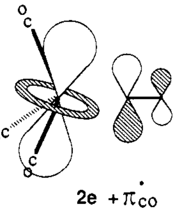
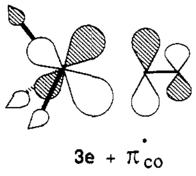


Figure 6. Interaction diagram for the formation of $M(CO)_3L$ from d^{10} $M(CO)_3$ and L.

of the $2t_2$ orbitals in $M(CO)_4$ (Figure 6) and the interaction between 2e of $M(CO)_3$ and π_{CO}^* (**7a**) in the formation of the two 1e orbitals of $M(CO)_4$. The combined contributions from **7a** and **7b** are represented by $\Delta E(e)$ in eq 12.

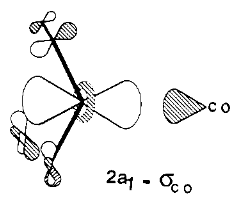


7a

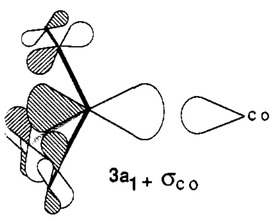


7b

The LUMO (**8b**) of $M(CO)_3$, $3a_1$ of Figure 6, is a metal based (d,s,p)-hydride orbital with in-phase contributions from π_{CO}^*. At lower energy is another $M(CO)_3$ orbital (**8a**) of a_1 symmetry, namely the metal based *n*d-orbital $2a_1$, with out-of-phase contributions from σ_{CO} and in-phase contributions from π_{CO}^*. The σ_{CO}-orbital of the incoming ligand will interact repulsively with $2a_1$ (**8a**), and this interaction will contribute significantly to $\Delta E°$. There will, in addition in the a_1 representation, be a stabilizing interaction (**8b**) between $3a_1$ and the σ_{CO} orbital of the incoming ligand in which density is donated from σ_{CO} to $3a_1$. This interaction serves, together with a certain amount of polarization of charge from $2a_1$ of $M(CO)_3$ to $3a_1$ of $M(CO)_3$, to reduce the repulsive interaction in **8a** and leads further to the formation the third $2t_2$ orbital in $M(CO)_4$ (Figure 6). The contribution from **8b** as well as the $2a_1$ to $3a_1$ polarization is given in eq 12 as $\Delta E(a_1)$.



8a



8b

It can be seen from Table IX that the nonrelativistic ordering for ΔH in $M(CO)_4$, $\Delta H_{Ni} \gg \Delta H_{Pd} > \Delta H_{Pt}$, is the result of an increase in the steric interaction energy $\Delta E°$ through the triad, primarily due to an increase in the repulsive interaction **8a** as the overlap in **8a** is larger for M = Pd and Pt than for M = Ni. The π-interactions **7a** and **7b** are further seen to enhance ΔH_{Ni} compared to ΔH_{Pd} and ΔH_{Pt}, $\Delta E(e)$ of Table IX. Relativistic effects will, in the by now familiar pattern, strengthen the Pt–CO bond compared to the Pd–CO bond. The trend for the first ligand dissociation energy in the relativistic limits is as a consequence $\Delta H_{Ni} \gg \Delta H_{Pt} > \Delta H_{Pd}$.

Table IX. Decomposition of the First Ligand Dissociation Energy, ΔH, in $Ni(CO)_4$, $Pd(CO)_4$, and $Pt(CO)_4$

$M(CO)_4$	ΔE_{prep}[b]	$\Delta E°$[b]	$\Delta E(a_1)$[b]	$\Delta E(e)$[b]	ΔE_R[b]	ΔH[a]
$Ni(CO)_4$	9.2	169.3	−145.3	−138.9		105.7
$Pd(CO)_4$	11.3	225.1	−143.2	−113.4	−7.1	27.3
$Pt(CO)_4$	10.6	261.1	−145.6	−112.6	−51.5	38.0

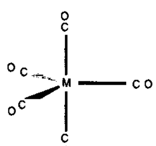
[a] The first ligand bond dissociation energy ΔH is given by $\Delta H = [\Delta E_{prep} + \Delta E° + \Delta E(a_1) + \Delta E(e) + \Delta E_R]$. [b] kJ mol^{-1}.

(c) The Ni–L Bond Strength in $Ni(CO)_3L$ for L = CO, CS, N_2, $P(CH_3)_3$, $N(CH_3)_3$, and $As(CH_3)_3$. We have carried out exploratory calculations on the Ni–L bond strength in $Ni(CO)_3L$ for a number of ligands in order to assess how different degrees of σ-donor abilities and π-acceptor abilities can influence the Ni–L bond strength. The calculated bond energies are shown in Table X along with the occupations of the σ_L HOMO and π_L^* LUMOs of L. In a comparison between two ligands the stronger π-acceptor will have the higher value for the occupation of π_L^* and the stronger σ-donor the smaller value for the occupation of σ_L.

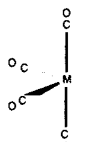
The CS ligand, a better σ-donor and π-acceptor than CO, has the largest Ni–L bond energy in the series. The PF_3 ligand, a relatively strong π-acceptor and modest σ-donor, and $P(CH_3)_3$, $N(CH_3)_3$, and $As(CH_3)_3$, all good σ-donors but weak π-acceptors, have a somewhat stronger Ni–L bond than CO. The N_2 ligand on the other hand, which is a poorer σ-donor and π-acceptor than CO, has a weaker Ni–L than CO. It is interesting that PH_3 has a considerably weaker Ni–L bond than $P(CH_3)_3$ although the two ligands in terms of charge seem to be equally good σ-donors and equally poor π-acceptors (Table X). The $P(CH_3)_3$ ligand forms a stronger N–L bond than PH_3 since its σ_L orbital is of higher energy[31] and thus has a better energy match with the $3a_1$ LUMO of $Ni(CO)_3$. The better bonding ability of $P(CH_3)_3$ compared to PH_3 has been observed experimentally by Corderman and Beauchamp[32] in $CpNiL^+$ where the $CpNi^+$–L bond strength was found to be 50 kJ mol^{-1} larger for L = $P(CH_3)_3$ than for L = PH_3. We have previously[33] calculated the Ni–L bond strength in $Ni(CO)_3L$ with the $X\alpha$ method for a number of different ligands. It is, however, by now well established that the $X\alpha$ method overestimates bond energies[5f,34] and the theoretical values in ref 33 are for this reason too high. The present density functional method provides on the other hand, Table IX, in the cases of L = CO and N_2, where experimental data are available, values in reasonable accord with experiment.

V. The Pentacarbonyls $Fe(CO)_5$, $Ru(CO)_5$, and $Os(CO)_5$

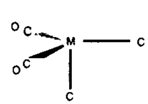
The three pentacarbonyls $Fe(CO)_5$, $Ru(CO)_5$, and $Os(CO)_5$ all have a trigonal-pyramidal structure **9a** as determined in the case of $Fe(CO)_5$ by X-ray or electron diffraction studies[3b] and in the cases of $Ru(CO)_5$ and $Os(CO)_5$ from IR spectroscopy.[36]



9a



9b



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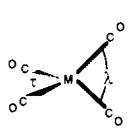

9d

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(31) The orbital energy of σ_L was calculated to be 1.9 eV higher in energy in $P(CH_3)_3$ than in PH_3.

(32) Corderman, R. R.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 3994.

(33) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1755.

(34) Ziegler, T.; Tschinke, V.; Versluis, L. *NATO ASI* **1986**, *Series C, 176*, 189.

(35) Turner, J. J.; Simpson, M. B.; Paliakoff, M.; Maier, W. B. *J. Am. Chem. Soc.* **1983**, *105*, 3998.

(36) Calderazzo, F.; Eplattenier, L. *Inorg. Chem.* **1967**, *6*, 1220.

Table X. Calculated Values for the Ni-L Bond Energy, ΔH, in $Ni(CO)_3L$ as well as the Occupations $Q(\sigma_L)$ and $Q(\pi_L^*)$ for the σ_L HOMO and π_L^* LUMO of L, with L = CO, CS, N_2, PF_3, PH_3, $P(CH_3)_3$, $As(CH_3)_3$, and $N(CH_3)_3$

	CO	CS	N_2	PF_3	PH_3	$P(CH_3)_3$	$N(CH_3)_3$	$As(CH_3)_3$
ΔH^a	106	186	71	133	85	146	138	135
R(Ni-L)^b	1.82	1.81		2.09	2.15	2.17	1.96	2.35
$Q(\sigma_L)^c$	1.69	1.56	1.89	1.84	1.59	1.54	1.62	1.59
$Q(\pi_L^*)^d$	0.20	0.22	0.11	0.19	0.09	0.09	0.02	0.05

[a] The Ni-L bond energy in kJ mol^{-1}. [b] Optimized Ni-L bond distance in Å. [c] Occupation of the σ_L donor orbitals of L. [d] Occupation for each of the two π_L^* acceptor orbitals of L.

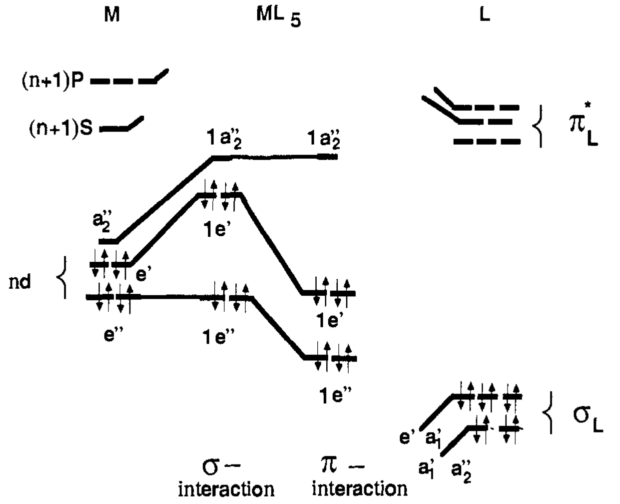
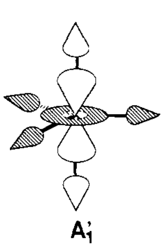


Figure 7. The σ-interactions and π-interactions in $M(CO)_5$ (M = Fe, Ru, Os) between orbitals on the metal center M with a d^8 configuration and symmetry combinations (D_{3h}) of the σ_{CO} HOMO and π_{CO}^* LUMO orbitals of the five CO ligands. Only the upper valence levels are shown.

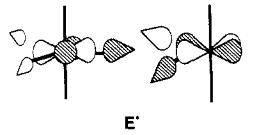
Accurate data on the mean bond energy[2d] E and first ligand dissociation energy[2a] ΔH are available for $Fe(CO)_5$ but not for $Ru(CO)_5$ and $Os(CO)_5$. Qualitative observations indicate, however, that $Ru(CO)_5$, although thermally more robust than $Pd(CO)_4$, is thermally less stable than $Fe(CO)_5$ and $Os(CO)_5$, whereas the thermal stability of $Os(CO)_5$ is comparable to that of $Fe(CO)_5$ and $W(CO)_6$. One[37] finds in addition, as for the d^6 hexacarbonyls $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ as well as the d^{10} ML_4 systems with M = Ni, Pd, and Pt, that the M-L bond in d^8 ML_5 complexes involving M = Fe, Ru, or Os is kinetically more labile for the second-row metal than for the first- and third-row metals.

The M-L bond in FeL_5 complexes is kinetically rather inert, not only in comparison to the M-L bonds in RuL_5 and OsL_5 but also in comparison to M-L bonds in NiL_4 and CrL_6. Thus, in the first transition series one[37] finds for the M-L bond the following order of lability: $FeL_6 < CrL_6 < NiL_4$. The lability order for the M-L bond in the second and third transition series seems[37] on the other hand to be given by $ML_6 \ll ML_5 < ML_4$, with the M-CO bonds being considerably more labile in $Ru(CO)_5$ and $Os(CO)_5$ than in $Mo(CO)_6$ and $W(CO)_6$, respectively. The reason for the apparent change in the order of lability for the M-L bonds among ML_6, ML_5, and ML_4 systems in going from the first transition series to the second and third transition series is not known with certainty. There have been several theoretical studies on $Fe(CO)_5$; Rossi[38] and Hoffmann have outlined the bonding for pentacoordinated complexes in general and $Fe(CO)_5$ in particular using the extended Hückel method, whereas Bauschlicher[5a] and Bagus have provided an elegant, and clear-cut, analysis of the bonding in $Fe(CO)_5$ based on ab initio HF calculations. The $Fe(CO)_5$ complex has further been the subject of one of the largest configuration interaction ab initio[5b] calculations ever undertaken on an organometallic system. There have only been a few calculations on $Ru(CO)_5$ and $Os(CO)_5$.

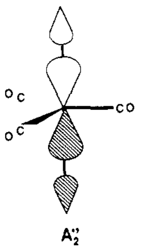
The interactions in $M(CO)_5$ of conformation **9a**, between M in its d^8 valence configuration, with one vacant $d(z^2)$ orbital pointing along the axial CO-M-CO bonds, and five CO ligands are presented schematically in Figure 7. There are, in the σ-framework, two strongly repulsive interactions (**10b**) between occupied σ_{CO} orbitals on the equatorial ligands and occupied nd orbitals of e′ symmetry as well as one strongly bonding interaction (**10a**) between the vacant $d(z^2)$-orbital and σ_{CO}-orbitals primarily centered on the axial ligands. The two predominant interaction types in the σ-framework, **10a** and **10b**, would tend to destabilize the equatorial M-CO bonds relative to the axial M-CO bonds.



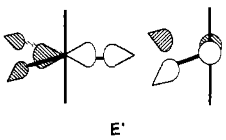
10a



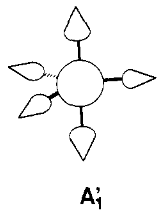
10b



10c

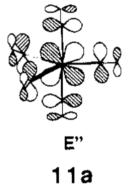


10d

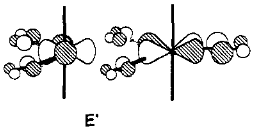


10e

There is in addition in the σ-framework the possibility for σ-donations from σ_{CO} to $(n + 1)$s, **10e**, or from σ_{CO} to $(n + 1)$p, **10c** or **10d**. The interactions in the π-framework, Figure 7, involve π-back-donation **11b** from occupied nd metal orbitals of e′ symmetry to π_{CO}^*-orbitals on the equatorial ligands as well as π-back-donation **11a** from occupied nd metal orbitals of e″ symmetry to π_{CO}^*-orbitals on equatorial and axial ligands. The more recent studies[5a,b] on $Fe(CO)_5$ have found that π-back-donation, in particular **11b** which serves to alleviate the repulsive interactions in **10b**, is more important for the stability of $Fe(CO)_5$ than σ-donation. We shall, in the next sections, discuss the influence of σ-donation and π-back-donation, as well as the interactions **10b**, on the relative strength of the M-CO bonds in $M(CO)_5$ (M = Fe, Ru, and Os). Both the intrinsic mean bond energy D(M-CO), between M(d^8) and five CO ligands, and the first CO dissociation energy ΔH will be considered as measures for the M-CO bond strength. Correlations, in conjunction with the results presented in previous sections, will also be given between M-CO bond strengths in hexa-, penta- and tetracarbonyls involving metals from the same transition series.



11a



11b

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(37) Atwood, J. D. In *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole: Monterey, 1985.

(38) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.

Table XI. Calculated Intrinsic Mean Bond Energies, *D*(M–CO), and Equatorial CO Dissociation Energies, ΔH_e, as well as Optimized Axial and Equatorial M–CO Bond Distances, R_a(M–CO) and R_e(M–CO), for $Fe(CO)_5$, $Ru(CO)_5$, and $Os(CO)_5$

$M(CO)_5$[e]	*D*(M–CO) calcd	ΔH_e calcd	ΔH exptl	R_a(M–CO) calcd	R_a(M–CO) exptl	R_e(M–CO) calcd	R_e(M–CO) exptl
$Fe(CO)_5$	216.8	185	176[b]	1.77	1.81[d]	1.79	1.83[e]
$Ru(CO)_5$	162.8 (157)[a]	92 (86)[a]	117[c]	1.95		1.96	
$Os(CO)_5$	176.7 (130)[a]	99 (41)[a]		1.98		1.99	

[a] Nonrelativistic results in parentheses. [b] Reference 2a. [c] Reference 41. [d] Reference 36. [e] The bond energies are in kJ mol^{-1} and the bond distance in Å.

(a) The Intrinsic Mean Bond Energies of $Fe(CO)_5$, $Ru(CO)_5$, and $Os(CO)_5$. The calculated bond energies and bond distances for the pentacarbonyls are compiled in Table XI. The intrinsic mean bond energy *D*(M–CO) of the pentacarbonyls is seen to follow the familiar trend already encountered among the hexacarbonyls and tetracarbonyls. Thus, the ordering in the nonrelativistic limit is *D*(Fe–CO) > *D*(Ru–CO) > *D*(Os–CO), whereas the ordering after the inclusion of relativistic effects is *D*(Fe–CO) > *D*(Os–CO) > *D*(Ru–CO).

The intrinsic mean bond energy can, as it is done in Table XII, be decomposed according to

$$D(\text{M–CO}) = -\tfrac{1}{5}[\Delta E^\circ + \Delta E_1(\text{a}'_1) + \Delta E_2(\text{a}'_1) + \Delta E_1(\text{e}') + \Delta E_2(\text{e}') + \Delta E(\text{a}''_2) + \Delta E(\text{e}'') + \Delta E_\text{R}] \quad (13)$$

where $\Delta E_1(\text{a}'_1)$ represents the σ-donation **10e** to $(n + 1)$s, $\Delta E(\text{a}''_2)$ and $\Delta E_1(\text{e}')$ the σ-donations, respectively **10c** and **10d**, to $(n + 1)$p, and $\Delta E_2(\text{a}'_1)$ the σ-donation **10a** to the vacant nd(z^2) metal orbital, whereas $\Delta E(\text{e}'')$ corresponds to the π-back-donation **11a** and $\Delta E_2(\text{e}')$ to the π-back-donation **11b**, including as well some σ_{CO} to π_{CO}* polarization.

The π-acceptor ability of π_{CO}*, $\Delta E_2(\text{e}')$ and $\Delta E(\text{e}'')$ of Table XII, is seen for all three pentacarbonyls to be more important for the M–CO bond strength than the σ-acceptor abilities of *n*d(z^2) and in particular $(n + 1)$s and $(n + 1)$p, $\Delta E_2(\text{a}'_1)$, $\Delta E_1(\text{a}'_1)$, $\Delta E_2(\text{e}'_1)$, and $\Delta E(\text{a}''_2)$, respectively, of Table XII. We find further, for reasons already discussed in connection with the hexacarbonyls, that the π-back-donation is stronger for M = Fe than for M = Ru, Os, whereas the σ-donation **10a** is more important for M = Ru, Os than for M = Fe. The trend setting term along the triad for *D*(M–CO) is the steric interaction energy ΔE°, which is more destabilizing for M = Ru and Os than for M = Fe. This is primarily so since the 4d- and 5d-orbitals, in comparison with the 3d-orbital, form stronger group overlaps in **10b** and thus, as in the case of the tetracarbonyls, are engaged in stronger two-orbital four-electron repulsive interactions with the σ_{CO} orbitals.

We have seen that electronic factors, represented by π-back-donation to π_{CO}* and σ-donations to vacant *n*d orbitals, as well as steric factors, dominated by repulsive interactions between occupied *n*d and σ_{CO} orbitals, are of primary importance for the M–CO bond strength in metal carbonyls. A comparison of the results presented in Tables II, VI and XII indicates that electronic factors are most favorable for the M–CO bond strength among the pentacarbonyls where *both* π-back-donation and σ-donation are important, whereas the steric interactions are most favorable for the M–CO bond among the hexacarbonyls, where repulsive interactions between occupied *n*d and σ_{CO} orbitals are absent. For first-row transition metals, where the repulsive interactions between occupied *n*d- and σ_{CO}-orbitals still are modest, electronic factors will make the intrinsic mean bond energy *D*(M–CO) larger for $Fe(CO)_5$ than for $Cr(CO)_6$ (Figure 8a). The steric factors will, on the other hand, in carbonyls of 4d or 5d elements, where repulsive interactions between occupied *n*d and σ_{CO} orbitals are considerable, cause the M–CO bonds in $Ru(CO)_5$ and $Os(CO)_5$ to be weaker than in $Mo(CO)_6$ and $W(CO)_6$, respectively, Figure 8a. The tetracarbonyls, in which all interactions between the *n*d- and σ_{CO}-orbitals are repulsive, have, in each of the transition series, weaker M–CO bonds than the corresponding hexacarbonyls and pentacarbonyls (Figure 8a).

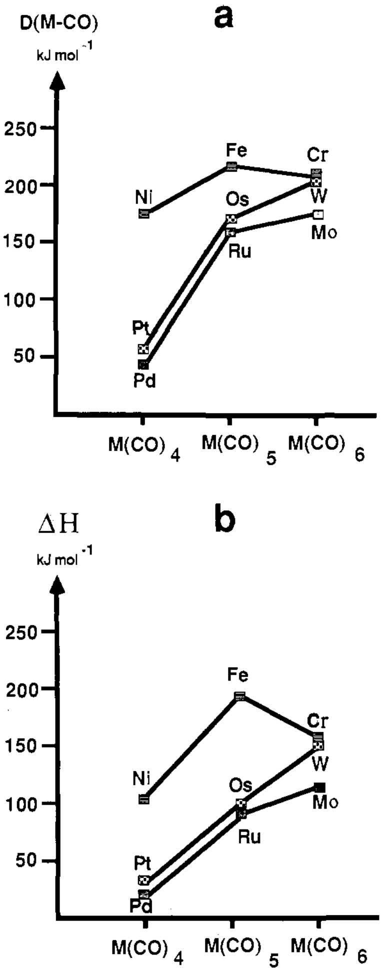


Figure 8. Calculated bond energies for $M(CO)_6$ (M = Cr, Mo, W), $M(CO)_5$ (M = Fe, Ru, Os), and $M(CO)_4$ (M = Ni, Pd, Pt): (a) intrinsic mean bond energies *D*(M–CO); (b) first CO dissociation energies ΔH.

We have for $Fe(CO)_5$, where a mean Fe–CO bond energy *E* of 117 kJ mol^{-1} has been measured, calculated *E* by evaluating the experimentally unknown energy difference ΔE_prep between the d^8 valence state of Fe and its ^{5}D ground state corresponding to the d^6s^2 electron configuration. We calculate, with ΔE_prep = 492.1 kJ mol^{-1} and $E = D(\text{Fe–CO}) - {}^1/_5\Delta E_\text{prep}$, the mean energy *E* to be 118.4 kJ mol^{-1}.

(b) Ligand Dissociation Energies for $Fe(CO)_5$, $Ru(CO)_5$, and $Os(CO)_5$. Dissociation of the first CO ligand in the pentacarbonyls $Fe(CO)_5$, $Ru(CO)_5$, and $Os(CO)_5$ can take place from either an axial or an equatorial position **9a** with a simultaneous or subsequent relaxation of respectively **9c** or **9b** to the equilibrium conformation **9d** of $M(CO)_4$. A previous theoretical study[39] has

Table XII. Decomposition of the Intrinsic Mean Bond Energy, *D*(M–CO), in $Fe(CO)_5$, $Ru(CO)_5$, and $Os(CO)_5$[b]

$M(CO)_5$	$k\Delta E^\circ$	$k\Delta E_1(\text{a}'_1)$	$k\Delta E_2(\text{a}'_1)$	$k\Delta E_1(\text{e}')$	$k\Delta E_2(\text{e}')$	$k\Delta E(\text{a}''_2)$	$k\Delta E(\text{e}'')$	$k\Delta E_\text{R}$	*D*(M–CO)
$Fe(CO)_5$	210.8	−3.1	−53.7	−14.7	−211.8	−12.8	−131.5		216.8
$Ru(CO)_5$	250.5	−2.0	−93.2	−10.8	−187.1	−9.4	−105.0	−5.8	162.8
$Os(CO)_5$	288.8	−2.3	−95.2	−11.3	−195.5	−9.5	−105.1	−46.6	176.7

[a] The intrinsic mean bond energy is given by $D(\text{M–CO}) = -k[\Delta E^\circ + \Delta E_1(\text{a}'_1) + \Delta E_2(\text{a}'_1) + \Delta E_1(\text{e}') + \Delta E_2(\text{e}') + \Delta E(\text{a}''_2) + \Delta E(\text{e}'') + \Delta E_\text{R}]$ with $k = 1/5$. [b] Energy components in kJ mol^{-1}.

Table XIII. Calculated Equatorial Ligand Dissociation Energies, ΔH, for $Fe(CO)_5$, $Ru(CO)_5$, and $Os(CO)_5$

$M(CO)_5$	ΔE_{prep}	$\Delta E°$	$\Delta E(a_1)$	$\Delta E(b_1)$	$\Delta E(b_2)$	ΔE_R	ΔH^a
$Fe(CO)_5$	10.3	212.6	−205.1	−129.3	−73.3		184.9
$Ru(CO)_5$	16.2	324.1	−234.9	−120.4	−71.2	−6.2	92.4
$Os(CO)_5$	16.8	399.5	−263.2	−120.9	−71.7	−58.9	98.4

[a] The first equatorial bond dissociation energy ΔH is given by $\Delta H = -[\Delta E_{prep} + \Delta E° + \Delta E(a_1) + \Delta E(b_1) + \Delta E(b_2) + \Delta E_R]$. [b] All energies in kJ mol^{-1}.

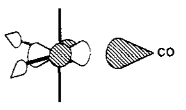
indicated that $Ru(CO)_4$, and this is probably also the case for $Os(CO)_4$, has a low-spin singlet ground state. The dissociation from either an axial or an equatorial position in the two closed shell pentacarbonyls $Ru(CO)_5$ and $Os(CO)_5$ should thus be a spin-allowed process. The $Fe(CO)_4$ species on the other hand has been determined experimentally[40] to have a high-spin triplet ground state. The dissociation of the closed-shell pentacarbonyl $Fe(CO)_5$ into CO and triplet $Fe(CO)_4$ would thus correspond to a spin-forbidden process.[5c] The experimentally[2a] determined value for the first ligand dissociation energy ΔH in $Fe(CO)_5$ pertains, however, to the spin-allowed dissociation of $Fe(CO)_5$ into CO and $Fe(CO)_4$ in its first excited singlet state.

We shall here, where we primarily are interested in periodic trends in the M–CO bond strength for the iron triad, restrict ourselves to the dissociation of one CO ligand from the equatorial position. We shall further consider the dissociation in which $M(CO)_4$ attains a singlet state for all three metals.

The energy ΔH required for the spin-allowed equatorial CO dissociation process can, as it is done in Table XIII, be decomposed according to

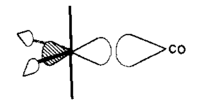
$$\Delta H = -[\Delta E_{prep} + \Delta E° + \Delta E(a_1) + \Delta E(b_1) + \Delta E(b_2) + \Delta E_R] \quad (14)$$

The first term ΔE_{prep} in eq 14 represents the energy required to deform $M(CO)_4$ from its singlet equilibrium conformation **9d** to conformation **9b**. The $M(CO)_4$ species in the singlet state were found to be nonrigid with equilibrium structures **9d** of D_{2d} symmetries at $\lambda = \tau = 162°$, 154°, and 154° for M = Fe, Ru, and Os, respectively. A distortion of $M(CO)_4$ to the C_{2v} structure **9b** ($\lambda = 120°$, $\tau = 180°$) requires less than 20 kJ mol^{-1} (Table XIII).



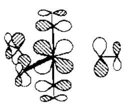
$1a_1 - \sigma_{CO}$

12a



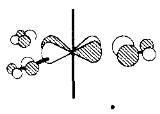
$2a_1 + \sigma_{CO}$

12b



$1b_2 + \pi^*_{CO}$

12c



$1b_1 + \pi^*_{CO}$

12d

There is, as $M(CO)_5$ is formed from CO and $M(CO)_4$ under C_{2v} constraints, a strong repulsive interaction **12a** between the incoming occupied σ_{CO}-orbital and the occupied metal based $1a_1$-orbitals of $M(CO)_4$ which will contribute strongly to the steric interaction energy $\Delta E°$ of eq 14. The repulsive interaction can be reduced by donation of charge **12b** from σ_{CO} to the $2a_1$ LUMO of $M(CO)_4$ as well as a polarization of charge from the occupied $1a_1$ orbital on $M(CO)_4$ to the $2a_1$ LUMO of $M(CO)_4$ (Figure 9). The two types of interaction will contribute with $-\Delta E(a_1)$ to ΔH.

The π_{CO}*-orbitals of the incoming CO ligand can interact with the occupied b_1 (**12d**) and b_2 (**12c**) orbitals of $M(CO)_4$ to form (Figure 9) respectively one of the 1e′ (**11b**) and 1e″ (**11a**) orbitals of $M(CO)_5$. The two π-back-donation interactions **12d** and **12c** will contribute to ΔH or eq 14 with $-\Delta E(b_1)$ and $-\Delta E(b_2)$, respectively. The $1b_1$ orbital (**12d**) is of higher energy than $1b_2$ (**12c**) and is thus better able to interact with the incoming π_{CO}*-orbital (Table IX). The contribution $-\Delta E(b_1)$ from **12d** is for this reason somewhat larger than the contribution $-\Delta E(b_2)$ from **12c** (Table XIII).

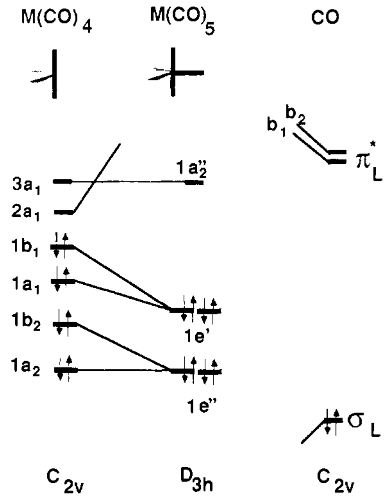


Figure 9. Diagram for the interaction between $M(CO)_4$ in conformation **9b** with C_{2v} symmetry and CO. Only the upper valence levels are shown.

It is clear from Table XIII that the ligand dissociation energy ΔH is much smaller for $Ru(CO)_5$ and $Os(CO)_5$ than for $Fe(CO)_5$ as the second- and third-row pentacarbonyls have a larger steric interaction energy $\Delta E°$ than $Fe(CO)_5$, primarily as a result of stronger repulsive interactions for M = Ru and Os than for M = Fe in **12a**. The sum of the two contributions $-\Delta E(b_2)$ and $-\Delta E(b_1)$ from the π-back-bonding interactions **12c** and **12d** is larger for $Fe(CO)_5$ than for $Ru(CO)_5$ and $Os(CO)_5$, whereas the opposite is the case for the contribution $-\Delta E(a_1)$ due to the σ-donation **12b**. The relativistic contribution is further instrumental in stabilizing the Os–CO bond compared to the Ru–CO bond (Table XIII).

We have summarized the results presented in Tables IV, IX, and XIII on the first ligand dissociation energies ΔH for the $M(CO)_6$, $M(CO)_5$, and $M(CO)_4$ systems in Figure 8b. A comparison with Figure 8a shows that D(M–CO) and ΔH follow the same trends although D(M–CO) for each $M(CO)_n$ systems is somewhat larger than the corresponding ΔH value. The rationals given for the variations in D(M–CO) can further be used to explain the trends in ΔH (Tables IV, IX, and XIII).

The calculated values for the equatorial dissociation energies in $Fe(CO)_5$ and $Ru(CO)_5$ compare well with experimental values for the first CO dissociation energies of the two pentacarbonyls given in Table XI. Also given in Table XI are the optimized axial and equatorial M–CO bond distances. The axial and equatorial bonds are calculated to be nearly equidistant, as they are observed to be in $Fe(CO)_5$. The calculated M–CO bond distances are too short by 0.05 Å in comparison with experiment.

VI. Concluding Remarks

We have here provided an analysis of the first ligand dissociation energy ΔH as well as the intrinsic mean energy D(M–CO) in a number of mononuclear metal carbonyls. Our analysis was based on a decomposition of ΔH and D(M–CO) into contributions from steric factors, σ-donation, π-back-donation, and relativistic effects. We have found, in particular for the $M(CO)_4$ and $M(CO)_5$ systems, that the repulsive (steric) four-electron two-orbital interactions between occupied orbitals on the metal center and the occupied σ_{CO} lone-pair orbitals on the carbonyl ligands considerably destabilize the M–CO bonds in carbonyls of 4d and 5d transition metals. This destabilization, in conjunction with a stronger π-back-donation in carbonyls of 3d metals, is responsible

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(39) Ziegler, T. *Inorg. Chem.* **1986**, *24*, 2721.

(40) Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1974**, *70*, 93.

(41) Huq, R.; Poe, A. J.; Chawla, S. *Inorg. Chim. Acta* **1979**, *38*, 121.

for the calculated ordering 3d > 4d > 5d for the M–CO bond strength in the nonrelativistic limit. Four-electron two-orbital interactions, including those encountered in the metal carbonyls between occupied metal orbitals and σ_{CO} orbitals, are, as already mentioned, destabilizing. The destabilization is in part due to an increase in the electronic kinetic energy caused by the node in the out-of-phase combination from the two-orbital interaction. Relativistic effects can, as it is explained in ref 12, to some degree reduce the electronic kinetic energy by increasing the electronic mass through the socalled mass–velocity term. The stabilizing relativistic effect will be larger for carbonyls of 5d metals than for carbonyls of 4d metals. The calculated ordering of the M–CO bond strength is as a result, after relativistic effects have been included, 3d > 5d > 4d.

We have attempted as well to assess the relative importance of σ-donation and π-back-donation for the strength of the synergic M–CO bond. The conclusions from such an assessment depend on the operative definition of σ-donation and π-back-donation. It depends, in addition, on whether one considers ΔH or D(M–CO) as a measure for the M–CO bond strength. We conclude, based on the definition for σ-donation and π-back-donation given in this work, that π-back-donation is the more important factor in D(M–CO), whereas both σ-donation and π-back-donation are of importance for ΔH. It should, however, be noted that σ_{CO} largely has a repulsive role in metal carbonyls and that σ-donation only serves to reduce the repulsive role. The $\pi_{CO}{}^*$ orbitals on the other hand serve exclusively to stabilize the M–CO bond.

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A Versatile New Synthesis of Organic Compounds with Chiral Methyl Groups: Stereochemistry of Protolytic Rhenium–Carbon Bond Cleavage in Chiral Alkyl Complexes (η^5-C_5H_5)Re(NO)(PPh_3)(R)

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Abstract: Reaction of (η^5-C_5H_5)Re(NO)(PPh_3)(CO_2CH_3) (**1**) with (3,5-dimethoxyphenyl)magnesium iodide gives 3,5-dimethoxybenzoyl complex (η^5-C_5H_5)Re(NO)(PPh_3)(CO(3,5-$C_6H_3(OCH_3)_2$)) (**2**, 97%). Reaction of **2** with BH_3·THF gives 3,5-dimethoxybenzyl complex (η^5-C_5H_5)Re(NO)(PPh_3)(CH_2(3,5-$C_6H_3(OCH_3)_2$)) (**3**, 86%). Reaction of **3** with $Ph_3C^+PF_6^-$ at –80 °C gives a 62:38 mixture of the *sc* and *ac* Re=C geometric isomers (**4k**, **4t**) of 3,5-dimethoxybenzylidene complex [(η^5-C_5H_5)Re(NO)(PPh_3)(=CH(3,5-$C_6H_3(OCH_3)_2$))]$^+PF_6^-$; workup gives **4t** (89%). Reaction of **4t** with Li$(C_2H_5)_3$BD or $NaBD_4$ gives addition product (*SS*,*RR*)-**3**-α-d_1. Optically active (+)-(*S*)-**1** and (–)-(*R*)-**1** (≥98% ee) are similarly treated with (3,5-dimethoxyphenyl)magnesium iodide, BD_3·THF, and $Ph_3C^+PF_6^-$ to give (+)-(*S*)- and (–)-(*R*)-**4t**-α-d_1. Addition of $NaBT_4$ gives (+)-(*SS*)- and (–)-(*RR*)-**3**-α-d_1t_1. Reaction with HBr gives (*S*)- and (*R*)-dimethoxytoluene-α-d_1t_1, and (+)-(*R*)- and (–)-(*S*)-(η^5-C_5H_5)Re(NO)(PPh_3)(Br) (retention of configuration at carbon and rhenium). The former are treated with O_3 to give chiral acetate salts (*S*)- and (*R*)-CHDTCOO$^-$Na$^+$ of 93% and 86% ee, as established by an enzymatic assay. The mechanisms of these transformations, and the utility of this route to chiral acetic acid, are discussed.

Asymmetric organic synthesis has evolved in sophistication to the stage where several classes of chiral molecules are now easily synthesized in optically pure form. Both chemical and enzymatic methodologies have been developed, and the former, which are often more amenable to laboratory study, have provided important insights into the mechanisms of biological stereogenesis. In this paper, we describe a versatile, convenient, metal-mediated synthesis of molecules containing the most fundamental unit of organic asymmetry, the chiral methyl group, –CHDT.[3] Such chiral-by-isotopic-substitution derivatives of proprochiral compounds have seen practical use in the elucidation of enzymatic reaction mechanisms and are also of value, as illustrated below, in the study of abiological reaction mechanisms.[3,4]

The first preparations of compounds containing chiral methyl groups were reported in landmark communications by Cornforth and Arigoni in 1969.[5a,6a] Since then, additional elegant syntheses have been developed. These include purely chemical routes,[5] and ones involving enzymatic steps.[6] Most have been directed at the preparation of chiral acetic acid (CHDTCOOH), for which an

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(1) University of Utah.

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(3) Floss, H. G.; Tsai, M.-D.; Woodward, R. W. *Top. Stereochem.* **1984**, *15*, 253.

(4) (a) Lowe, G. *Acc. Chem. Res.* **1983**, *16*, 244. (b) Buchwald, S. L.; Pliura, D. H.; Knowles, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 4916.

(5) See, inter alia: (a) Cornforth, J. W.; Redmond, J. W.; Eggerer, H.; Buckel, W.; Gutschow, C. *Nature* (*London*) **1969**, *221*, 1212. (b) Townsend, C. A.; Scholl, T.; Arigoni, D. *J. Chem. Soc., Chem. Commun.* **1975**, 921. (c) Kajiwara, M.; Lee, S.-F.; Scott, A. I.; Akhtar, M.; Jones, C. R.; Jordan, P. M. *Ibid.* **1978**, 967. (d) Fryzuk, M. D.; Bosnich, B. *J. Am. Chem. Soc.* **1979**, *101*, 3043. (e) Caspi, E.; Piper, J.; Shapiro, S. *J. Chem. Soc., Chem. Commun.* **1981**, 76. (f) Townsend, C. A.; Neese, A. S.; Theis, A. B. *Ibid.* **1982**, 116. (g) Kobayashi, K.; Jadhav, P. K.; Zydowsky, T. M.; Floss, H. G. *J. Org. Chem.* **1983**, *48*, 3510. (h) Caspi, E.; Aranachalam, T.; Nelson, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 6987. (i) Kobayashi, K.; Kakinuma, K.; Floss, H. G. *J. Org. Chem.* **1984**, *49*, 1290. (j) Coates, R. M.; Kock, S. C.; Hegde, S. *J. Am. Chem. Soc.* **1986**, *108*, 2762. (k) Zydowsky, T. M.; Courtney, L. F.; Frasca, V.; Kobayashi, K.; Shimizu, H.; Yuen, L.-D.; Matthews, R. G.; Benkovic, S. J.; Floss, H. G. *Ibid.* **1986**, *108*, 3152.

(6) See, inter alia: (a) Lüthy, J.; Rétey, J.; Arigoni, D. *Nature* (*London*) **1969**, *221*, 1212. (b) Rose, I. A. *J. Biol. Chem.* **1970**, *245*, 6052. (c) Creighton, D. F.; Rose, I. A. *Ibid.* **1976**, *251*, 61. (d) Altman, L. J.; Han, C. Y.; Bertolino, A.; Handy, G.; Laungaini, D.; Muller, W.; Schwartz, S.; Shanker, D.; de Wolf, W. H.; Yang, F. *J. Am. Chem. Soc.* **1978**, *100*, 3235. (e) Rozell, J. D., Jr.; Benner, S. A. *J. Org. Chem.* **1983**, *48*, 1190.

0002-7863/87/1509-4837$01.50/0