# Structure and Bonding of the Transition-Metal Carbonyl Complexes $M(CO)_5L$ (M = Cr, Mo, W) and $M(CO)_3L$ (M = Ni, Pd, Pt; L = CO, SiO, CS, $N_2$, $NO^+$, $CN^-$, $NC^-$, HCCH, $CCH_2$, $CH_2$, $CF_2$, $H_2$)[1]

Andreas W. Ehlers,[†] Stefan Dapprich, Sergei F. Vyboishchikov, and Gernot Frenking*

*Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse, D-35032 Marburg, Germany*

*Received September 6, 1995*[⊗]

Quantum mechanical ab initio calculations at the MP2 and CCSD(T) level of theory using effective core potentials (ECP) for the metals with a valence basis set of DZP quality and a 6-31G(d) all-electron basis set for the other elements are reported for the complexes $M(CO)_5L$ (M = Cr, Mo, W) and $M(CO)_3L$ (M = Ni, Pd, Pt) with ligands L = CO, SiO, CS, $N_2$, $NO^+$, $CN^-$, $NC^-$, HCCH, $CCH_2$, $CH_2$, $CF_2$, and $H_2$. The optimized geometries at MP2/II are in very good agreement with experiment. The theoretically predicted $(CO)_nM-L$ bond dissociation energies at CCSD(T)/II using MP2/II optimized geometries also agree quite well with experimental data. The $(CO)_nM-L$ bond is investigated using the charge decomposition analysis (CDA), which gives an interpretation of the donor−acceptor complexes in terms of charge donation, back-donation and repulsive polarization. The CDA results, which may be considered as a quantitative expression of the Dewar−Chatt−Duncanson model, are in agreement with the standard classification of the ligands.

## Introduction

Some 105 years after the accidental[2] synthesis of nickel tetracarbonyl by Mond, Langer, and Quincke,[3] transition-metal (TM) carbonyl complexes have become one of the most important classes of compounds in inorganic chemistry. Carbonyl complexes are not just of interest for synthesis in academic research;[4−6] they are also used by industry as important homogeneous and heterogeneous catalysts.[7] The conceptual framework of chemical bonding in TM carbonyls and related complexes given in modern textbooks of inorganic[8] and organometallic chemistry[9] is based on the classical picture of synergistic $\sigma$ donation and $\pi$ back-donation between the ligand and the metal, i.e. the Dewar−Chatt−Duncanson model.[10] The power of this model has been demonstrated by Hoffmann and co-workers, who showed that the structure and reactivity of many TM complexes can be understood and, to a certain extent, can even be predicted using the $\sigma$ donation/$\pi$ back-donation picture in conjunction with semiempirical calculations.[11,12] The problem with these studies is that only a qualitative insight into the structure and bonding of TM complexes can be given.

A pivotal question about the nature of different ligands in TM complexes is the relative strength of $\sigma$ donation and $\pi$ back-bonding. Numerous theoretical studies have been devoted to evaluating the relative contributions of the $\sigma$ and $\pi$ interactions.[13] There have also been attempts to correlate the amount of $\pi$ back-

---

[†] Present address: Afdeling Theoretische Chemie, Faculteit Scheikunde, Vrije Universiteit Amsterdam, Amsterdam, The Netherlands.

[⊗] Abstract published in *Advance ACS Abstracts*, November 1, 1995.

(1) Theoretical Studies of Organometallic Compounds. 19. Part 18: Reference 58.

(2) Obituary to L. Mond: Langer, C. *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 3671. See also: Herrmann, W. A. *Chem. Unserer Zeit* **1988**, *22*, 113.

(3) Mond, L.; Langer, C.; Quincke, F. *J. Chem. Soc.* **1890**, 749.

(4) Werner, H. *Angew. Chem.* **1990**, *102*, 1109; Angew. *Chem., Int. Ed. Engl.* **1990**, *29*, 1077.

(5) (a) Ellis, J. E. *Adv. Organomet. Chem.* **1990**, *31*, 1 and references therein. (b) Kündig, E. P.; Moskovits, M.; Ozin, G. A. *Angew. Chem.* **1975**, *87*, 314; *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 292 and references therein. (c) Ozin, G. A. *Acc. Chem. Res.* **1977**, *10*, 21 and references therein.

(6) Hurlburt, P. K.; Rack, J. J.; Luck, J. S.; Dec, S. F.; Webb, J. D.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1994**, *116*, 10003.

(7) (a) Solomon, E. I.; Jones, P. M.; May, J. A. *Chem. Rev.* **1993**, *93*, 2623. (b) Sen, A. *Acc. Chem. Res.* **1993**, *26*, 303. (c) Waugh, K. C. *Catal. Today* **1992**, *15*, 51. (d) Vannice, M. A. *Catal. Today* **1992**, *12*, 255. (e) Guczi, L., Ed. *Studies in Surface Science and Catalysis*; New Trends in CO Activation 64; Elsevier: Amsterdam, 1991. (f) Henrici-Olivé, G.; Olivé, S. *The Chemistry of the Catalyzed Hydrogenation of Carbon Monoxide*; Springer-Verlag, Berlin, 1983. (g) Ford, P. C., Ed. *Catalytic Activation of Carbon Monoxide*; ACS Symposium Series 152; American Chemical Society: Washington, DC, 1981.

(8) (a) Huheey, J. E. *Inorganic Chemistry: Principle of Structure and Reactivity*, 4th ed.; Harper Collins College Publishers: New York, 1993. (b) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980.

(9) Elschenbroich, Ch.; Salzer, A. *Organometallics*, 2nd ed.; VCH: Weinheim, Germany, 1992.

(10) (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C79. (b) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2929.

(11) (a) Hoffmann, R.; Chen, M. M. L.; Thorn, D. L. *Inorg. Chem.* **1977**, *16*, 503. (b) Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456. (c) Hoffmann, R. *Science* **1981**, *211*, 995. (d) Hoffmann, R.; Albright, T. A.; Thorn, D. L. *Pure Appl. Chem.* **1978**, *50*, 1 and references therein.

(12) Albright, T. A.; Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.

(13) (a) Yamamoto, S.; Kashiwagi, H. *Chem. Phys. Lett.* **1993**, *205*, 306 and references therein. (b) Blomberg, M. R. A.; Siegbahn, P. E. M.; Lee, T. L.; Rendell, A. P.; Rice, J. E. *J. Chem. Phys.* **1991**, *95*, 5898 and references therein. (c) Barnes, L. A.; Rosi, M.; Bauschlicher, C. W. *J. Chem. Phys.* **1991**, *94*, 2031 and references therein. (d) Smith, S.; Hillier, I. H.; von Niessen, W.; Guest, M. F. *Chem. Phys.* **1987**, *135*, 357. (e) Pierfoot, K.; Verhulst, J.; Verbeke, P.; Vanquickenborne, L. G. *Inorg. Chem.* **1989**, *28*, 3059 and references therein. (f) Williamson, R. L.; Hall, M. B. *Int. J. Quantum Chem.* **1987**, *21*, 503 and references therein.

0276-7333/96/2315-0105$12.00/0

bonding with experimental results. The lengthening of the AB multiple bond in the transition-metal complex $L_nM-AB$ is usually taken as evidence for electron donation from the metal into the $\pi^*$ orbital of AB. In particular, the C−O stretching frequency is used as a very sensitive probe of the metal−CO interaction in TM carbonyl complexes. Classical carbonyls have a slightly lower C−O stretching frequency than free CO, while nonclassical carbonyls have higher C−O wavenumbers.[6,14] The interpretation of the frequency shift is usually given in terms of $\sigma$ donation and $\pi$ back-donation between the metal and CO, although other explanations are also possible for this phenomenon.[6] The extent of $\pi$ back-bonding has also been probed using the results of Mössbauer spectroscopy.[15]

The model of orbital mixing between the metal and the ligand in TM carbonyl complexes has been critically examined in a recent theoretical study by Davidson et al.[16] These authors analyzed the bonding in $Cr(CO)_6$ using Hartree−Fock (HF) ab initio calculations in conjunction with the Morokuma partitioning scheme.[17] They found that $Cr(CO)_6$ is unbound at the HF level of theory relative to 6 CO and Cr in its $d^5s$ ($^7S$) electronic ground state. The total metal−CO bond energy of $Cr(CO)_6$ was found to be approximately equal to the correlation energy.[16] This makes any interpretation of the bonding in terms of orbital interactions questionable. The authors emphasized the importance of the atomic promotion energy from the ground state to the valence excited state for a qualitative correct understanding of the bond energy. They criticized the vocabulary of frontier orbital theory, which leads to the impression that the orbital overlap might be the driving force for the formation of a bond. This is not correct, because optimal orbitals can not be improved merely by mixing with other orbitals. Empty orbitals such as the $\pi^*$ MO on CO would disappear if a complete basis set were used. The authors pointed out that the true energy-lowering effect of HOMO−LUMO mixing is driven by the interactions between the nuclei and electrons, not by overlap of the occupied and unoccupied orbitals.[16]

We agree with the analysis of the chemical bonding in $Cr(CO)_6$ by Davidson et al.,[16] which is probably also true for related low-valent TM complexes. However, we think that the orbital-mixing model is very helpful for a qualitative interpretation, provided that it is not confused with a physical interpretation of the chemical bonding. The HOMO−LUMO concept in general[18] and the Dewar−Chatt−Duncanson model[10] in particular are not only proven as valuable tools for the interpretation of the structure and reactivity of molecules, they can also be rationalized by theoretical arguments.[11,12] It has been clearly shown by Davidson et al. that a large part of the stabilizing metal−ligand interactions in $Cr(CO)_6$ can be traced back to the relaxation energy of the individual orbitals.[16] If this part of the bond energy can be correlated with the total bond energy *and* can also be correlated with orbital properties of different ligands and metals, metal−ligand orbital interactions would be a solid basis for a chemical model. We want to point out that the strength of a good chemical model lies in the ability to explain and to predict *differences* in chemical behavior. The Dewar−Chatt−Duncanson model has been widely accepted in transition metal chemistry, because the large class of TM complexes can be easily classified and interpreted in terms of synergistic $\sigma$ donation and $\pi$ back-donation between the metal and the ligands.

The interpretation of the metal−ligand bonding in TM complexes in the past has been based mainly upon semiempirical MO calculations.[11,12] A more quantitative analysis using density functional theory was given by Ziegler.[19] It would be helpful if the analysis of the bonding situation in TM complexes could be based upon calculations which give accurate geometries and bond energies. We have shown in several studies that quantum mechanical ab initio methods using pseudopotentials for the metal atoms predict geometries and bond energies of heavy-atom molecules which are in good agreement with experimental results.[20,21] Standard levels of theory for calculating TM complexes have been suggested, which are summarized in a recent review.[22] The development of quantum-mechanical methods including density functional theory[23] has reached the point where accurate calculations of medium-size heavy-atom molecules of main-group elements and transition metals are possible.

It has been stated in the past that the results of accurate calculations are "difficult to interpret and understand in terms of simple qualitative concepts of bonding".[24] We disagree with this statement. On the contrary, we believe that only chemical models which are based on accurate quantum-mechanical methods

---

(14) (a) Hurlburt, P. K.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1991**, *113*, 6277. (b) Willner, H.; Schaebs, J.; Hwang, G.; Mistry, F.; Jones, R.; Trotter, J.; Aubke, F. *J. Am. Chem. Soc.* **1992**, *114*, 8972 and references therein.

(15) Morris, R. H.; Schlaf, M. *Inorg. Chem.* **1994**, *33*, 1725 and references therein.

(16) (a) Davidson, E. R.; Kunze, K. L.; Machado, F. B. C.; Chakravorty, S. J. *Acc. Chem. Res.* **1993**, *26*, 628. (b) Kunze, K. L.; Davidson, E. R. *J. Phys. Chem.* **1992**, *96*, 2129.

(17) Morokuma, K. *Acc. Chem. Res.* **1977**, *10*, 294 and references therein.

(18) (a) Fukui, K. *Acc. Chem. Res.* **1971**, *4*, 57. (b) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1976.

(19) (a) Li, J.; Schreckenbach, G.; Ziegler, T. *J. Am. Chem. Soc.* **1995**, *117*, 486. (b) Ziegler, T. *NATO ASI Ser.* **1992**, *No. C378*, 367. (c) Ziegler, T.; Tschinke, V.; Ursenbach, C. *J. Am. Chem. Soc.* **1987**, *109*, 4825. (d) Baerends, E. J.; Rozendaal, A. *NATO ASI Ser.* **1986**, *No. C176*, 159. (e) Ziegler, T. *NATO ASI Ser.* **1986**, *No. C176*, 189. (f) Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1.

(20) (a) Ehlers, A. W.; Frenking, G. *J. Chem. Soc., Chem. Commun.* **1993**, 1709. (b) Ehlers, A. W.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 1514. (c) Ehlers, A. W.; Frenking, G. *Organometallics* **1995**, *14*, 423.

(21) (a) Jonas, V.; Frenking, G. Reetz, M. T. *J. Comput. Chem.* **1992**, *13*, 919. (b) Stegmann, R.; Neuhaus, A.; Frenking, G. *J. Am. Chem. Soc.* **1993**, *115*, 11930. (c) Jonas, V.; Frenking, G. Reetz, M. T. *Organometallics* **1993**, *12*, 2111. (d) Veldkamp, A.; Frenking, G. *Organometallics* **1993**, *12*, 4613. (e) Veldkamp, A.; Frenking, G. *J. Am. Chem. Soc.* **1994**, *116*, 4937. (f) Böhme, M.; Frenking, G.; Reetz, M. T. *Organometallics* **1994**, *13*, 4237. (g) Neuhaus, A.; Veldkamp, A.; Frenking, G. *Inorg. Chem.* **1994**, *33*, 5278. (h) Dapprich, S.; Frenking, G. *Angew. Chem.* **1995**, *107*, 383; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 354.

(22) Frenking, G.; Antes, I.; Böhme, M.; Dapprich, S.; Ehlers, A. W.; Jonas, V.; Neuhaus, A.; Otto, M.; Stegmann, R.; Veldkamp, A.; Vyboishchikov, S. F. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH: New York, in press; Vol. 8.

(23) (a) Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964**, *136*, 864. (b) Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133. (c) Levy, L. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 6062. (d) Parr, R. G.; Yang, W., Eds. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1988. (e) Labanowski, J.; Andzelm, J., Eds. *Density Functional Methods in Chemistry*; Springer-Verlag: Heidelberg, Germany, 1991.

(24) Hofmann, P. In *Transition Metal Carbene Complexes*; Dötz, K. H., Fischer, H., Hofmann, P., Kreissl, F. R., Schubert, U., Weiss, K., Eds.; Verlag Chemie: Weinheim, Germany, 1983; p 118.

have the prospect of giving a sound understanding of chemical phenomena. The recently introduced charge-decomposition analysis (CDA) is a method for analyzing donor−acceptor interactions of a complex AB in terms of donation A→B, back-donation A←B, and repulsive polarization A↔B.[25] The CDA method can be used for ab initio calculations at the HF or any correlated level of theory. The CDA results may be used as a quantitative expression of the Dewar−Chatt−Duncanson model.[10]

In this paper we present and discuss the results of ECP calculations at correlated levels for the transition-metal complexes $M(CO)_5L$ ($M = Cr, Mo, W$) and $M(CO)_3L$ ($M = Ni, Pd, Pt$) with $L = CO, SiO, CS, N_2, NO^+, CN^-, NC^-, CCH_2, HCCH, CH_2, CF_2, H_2$. There are two goals of this study. One goal is to predict accurate metal−ligand bond lengths and $(CO)_nM-L$ bond dissociation energies. The exact determination of bond energies of TM complexes is difficult and remains a major challenge for theory and experiment.[26] The second goal is the interpretation of the different metal−ligand interactions in terms of $\sigma$ donation and $\pi$ back-donation using the CDA method. We want to demonstrate that transition-metal complexes can be calculated and interpreted by ab initio methods[27] with an accuracy comparable to that for light-atom molecules.[28]

## Methods

The geometry optimizations have been carried out at the HF and MP2[29] level of theory using an effective core potential (ECP) for the metals developed by Hay and Wadt.[30a] The ECPs are derived from nonrelativistic atom calculations of the first-row TM elements (Cr, Ni) and from relativistic calculations of the second- and third-row TM elements (Mo, W, Pd, Pt). A (441/2111/N1) split-valence basis set is used for the metals, which is derived from the $(55/5/N + 1)$ minimal basis set ($N =$ 4, 3, and 2 for Cr, Mo, and W, respectively).[30] The $(n - 1)s^2$ and $(n - 1)p^6$ electrons are treated explicitly as part of the valence space. A 6-31G(d) all-electron basis set is used for the ligand atoms of the second row. A 31G(p) basis set was employed for hydrogen.[31] A pseudopotential with a (31/31/1) valence basis set was used for Si and S.[30b] The d polarization functions have five spherical components. This basis set combination is our standard basis set II.[22] The dissociation energies are calculated using coupled-cluster theory[32] with singles and doubles and a noniterative estimate of triple substitutions (CCSD(T)).[33] The calculations have been carried out using the program packages TURBOMOLE,[34] ACES II,[35] and Gaussian 92.[36]

In the CDA method the (canonical or natural) molecular orbitals of the complex are expressed in terms of the MOs of appropriately chosen fragments. In the present case, the natural orbitals (NO) of the MP2/II wave function of $M(CO)_nL$ are formed by a linear combination of the MOs of $M(CO)_n$ and L in the geometry of $M(CO)_nL$. Charge donation $d_i$ from L to $M(CO)_n$ is then given by

$$d_i = \sum_{k}^{\text{occ,A}} \sum_{n}^{\text{vac,B}} m_i c_{ki} c_{ni} \langle \varphi_k | \varphi_n \rangle$$

Similarly, the back-donation $b_i$ from $M(CO)_n$ to L is given by

$$b_i = \sum_{l}^{\text{occ,B}} \sum_{m}^{\text{vac,A}} m_i c_{li} c_{mi} \langle \varphi_l | \varphi_m \rangle$$

Finally, the repulsive polarization $r_i$ between the occupied orbitals of $M(CO)_n$ and L is given by

$$r_i = \sum_{k}^{\text{occ,A}} \sum_{m}^{\text{occ,B}} m_i c_{ki} c_{mi} \langle \varphi_k | \varphi_m \rangle$$

$$A = L;\ B = M(CO)_n$$

$$m = \text{occupation number}$$

$$c = \text{fragment orbital coefficient}$$

$$\varphi = \text{fragment MO}$$

The sum of the orbital contributions $d_i$, $b_i$, and $r_i$ gives the total amount of donation, back-donation, and charge repulsion, respectively. The CDA calculations have been performed using the program CDA 2.1.[37]

## Geometries and Bond Energies

Table 1 shows the optimized bond lengths and calculated M−L bond dissociation energies of the $M(CO)_5L$ complexes for $M = Cr, Mo, W$. Experimental values are given in parentheses. The bond lengths and bond energies of the $M(CO)_3L$ complexes for $M = Ni, Pd, Pt$ are given in Table 2.

The theoretical results for the hexacarbonyls $M(CO)_6$ ($M = Cr, Mo, W$) and the tetracarbonyls $M(CO)_4$ ($M =$ Ni, Pt, Pd) have already been reported.[20] The calculated M−CO bond lengths of $Cr(CO)_6$ and $Ni(CO)_4$ are slightly

---

(25) Dapprich, S.; Frenking, G. *J. Phys. Chem.* **1995**, *99*, 9352.

(26) (a) Marks, T. J., Ed. *Bonding Energetics in Organometallic Compounds*; ACS Symposium Series 428; American Chemical Society: Washington, DC, 1990. (b) Simoes, J. A. M., Ed. *Energetics of Organometallic Species*; Kluwer: Dordrecht, The Netherlands, 1992. (c) Salahub, D. R., Zerner, M. C., Eds. *The Challenge of d and f Electrons: Theory and Computation*; ACS Symposium Series 349; American Chemical Society: Washington, DC, 1989.

(27) ECP calculations are not genuine ab initio methods, because the core electrons are not calculated explicitly. However, it has been recognized that for calculating valence properties such as geometries, bond energies, and vibrational frequencies, the error introduced by the well-parameterized ECP approximation is negligible compared with the inherent errors of the basis set truncation and the approximate calculation of the correlation energy.

(28) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(29) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229.

(30) (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299. (b) Bergner, A.; Dolg, M.; Küchle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431.

(31) (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (b) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (c) Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163.

(32) (a) Cizek, J. *J. Chem. Phys.* **1966**, *45*, 4256. (b) Cizek, J. *Adv. Chem. Phys.* **1966**, *14*, 35.

(33) (a) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem.* **1978**, *14*, 545. (b) Bartlett, R. J.; Purvis, G. D. *Int. J. Quantum Chem.* **1978**, *14*, 561. (c) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910. (d) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1987**, *86*, 7041.

(34) (a) Häser, M.; Ahlrichs, R. *J. Comput. Chem.* **1989**, *10*, 104. (b) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165. (c) Horn, H.; Weiss, H.; Häser, M.; Ehrig, M.; Ahlrichs, R. *J. Comput. Chem.* **1991**, *12*, 1058. (d) Häser, M.; Almlöf, J.; Feyereisen, M. W. *Theor. Chim. Acta* **1991**, *79*, 115.

(35) ACES II, an ab initio program system written by J. F. Stanton, J. Gauss, J. D. Watts, W. J. Lauderdale, and R. J. Bartlett; University of Florida, Gainesville, FL, 1991.

(36) Gaussian 92, Reversion C, by M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. A. Robb, J. S. Binkley, C. Gonzalez, R. Martin, D. J. Fox, D. J. DeFrees, J. Baker, J. J. P. Stewart, and J. A. Pople; Gaussian Inc., Pittsburgh, PA, 1992.

(37) CDA 2.1, by S. Dapprich and G. Frenking, Marburg, 1994. The program is available via anonymous ftp server: ftp.chemie.uni-marburg.de (/pub/cda).

**Table 1. Calculated Bond Lengths (MP2/II) (Å) and Bond Dissociation Energies $D_0$ (CCSD(T)/II//MP2/II) (kcal/mol) for the $(OC)_5M-L$ Bond (Experimental Values Given in Parentheses)**

| molecule | sym | $M-C_{cis}$[l] | $M-C_{trans}$ | $M-L_1$ | $L_1-L_2$ | $D_0$ |
|---|---|---|---|---|---|---|
| $Cr(CO)_5CO$ | $O_4$h | 1.861 (1.918[l]) | | | 1.168 (1.141[m]) | 43.2 (36.8 ± 2[p]) |
| $Mo(CO)_5CO$ | $O_h$ | 2.061 (2.063[l]) | | | 1.164 (1.145[m]) | 38.2 (40.5 ± 2[p]) |
| $W(CO)_5CO$ | $O_h$ | 2.060 (2.058[l]) | | | 1.166 (1.148[m]) | 45.7 (46.0 ± 2[p]) |
| CO | $C_{\infty v}$ | | | | 1.151 (1.115[a]) | |
| $Cr(CO)_5SiO$ | $C_{4v}$ | 1.851 | 1.831 | 2.190 | 1.542 | 38.6 |
| $Mo(CO)_5SiO$ | $C_{4v}$ | 2.0059 | 2.047 | 2.392 | 1.543 | 38.0 |
| $W(CO)_5SiO$ | $C_{4v}$ | 2.058 | 2.043 | 2.405 | 1.542 | 44.2 |
| SiO | $C_{\infty v}$ | | | | 1.542 (1.51[a]) | |
| $Cr(CO)_5CS$ | $C_{4v}$ | 1.860 | 1.920 | 1.804 (1.854) | 1.564 (1.565) | 63.6 (56 ± 4[e]) |
| $Mo(CO)_5CS$ | $C_{4v}$ | 2.066 | 2.119 | 1.985 | 1.564 | 59.2 (64 ± 14[e]) |
| $W(CO)_5CS$ | $C_{4v}$ | 2.063 | 2.094 | 2.006 (1.996) | 1.561 (1.556) | 68.8 (70 ± 8[e]) |
| CS | $C_{\infty v}$ | | | | 1.545 (1.534[b]) | |
| $Cr(CO)_5N_2$ | $C_{4v}$ | 1.870 | 1.803 | 1.936 | 1.144 | 23.2 |
| $Mo(CO)_5N_2$ | $C_{4v}$ | 2.060 | 1.996 | 2.164 | 1.139 | 20.6 |
| $W(CO)_5N_2$ | $C_{4v}$ | 2.057 | 2.013 | 2.126 | 1.143 | 24.8 |
| $N_2$ | $D_{\infty h}$ | | | | 1.131 (1.094[a]) | |
| $Cr(CO)_5NO^+$ | $C_{4v}$ | 1.900 | 2.055 | 1.761 | 1.193 | 105.4 |
| $Mo(CO)_5NO^+$ | $C_{4v}$ | 2.119 | 2.233 | 1.877 | 1.201 | 103.2 |
| $W(CO)_5NO^+$ | $C_{4v}$ | 2.107 | 2.178 | 1.891 | 1.197 | 108.6 |
| $NO^+$ | $C_{\infty v}$ | | | | 1.103 (1.062[c]) | |
| $Cr(CO)_5CN^-$ | $C_{4v}$ | 1.854 | 1.792 | 1.998 | 1.189 | 89.7 |
| $Mo(CO)_5CN^-$ | $C_{4v}$ | 2.045 | 2.004 | 2.207 | 1.190 | 87.3 |
| $W(CO)_5CN^-$ | $C_{4v}$ | 2.044 | 2.012 | 2.198 | 1.1900 | 97.7 |
| $Cr(CO)_5NC^-$ | $C_{4c}$ | 1.866 | 1.773 | 1.997 | 1.196 | 73.8 |
| $Mo(CO)_5NC^-$ | $C_{4v}$ | 2.052 | 1.982 | 2.183 | 1.196 | 74.8 |
| $W(CO)_5NC^-$ | $C_{4v}$ | 2.048 | 1.997 | 2.166 | 1.196 | 84.4 |
| $CN^-$ | $C_{\infty v}$ | | | | 1.201 (1.177[d]) | |
| $Cr(CO)_5CCH_2$[n] | $C_{2v}$ | 1.876/1.836 | 1.874 | 1.822 | 1.314 | 66.7 |
| $Mo(CO)_5CCH_2$[n] | $C_{2v}$ | 2.081/2.054 | 2.124 | 1.977 | 1.319 | 62.6 |
| $W(CO)_5CCH_2$[n] | $C_{2v}$ | 2.076/2.055 | 2.103 | 1.997 | 1.319 | 73.0 |
| $CCH_2$ | $C_{2v}$ | | | | 1.308 (1.300[f]) | |
| $Cr(CO)_5HCCH$[n] | $C_{2v}$ | 1.861/1.854 | 1.770 | 2.275 | 1.245 | 22.0 |
| $Mo(CO)_5HCCH$[n] | $C_{2v}$ | 2.055/2.061 | 2.005 | 2.368 | 1.255 | 21.9 |
| $W(CO)_5HCCH$[n] | $C_{2v}$ | 2.057/2.059 (2.040[h]) | 2.020 (1.97[h]) | 2.331 (2.37−2.40[h]) | 1.262 | 28.9 |
| HCCH | $D_{\infty h}$ | | | | 1.218 (1.203[g]) | |
| $Cr(CO)_5CH_2$[o] | $C_{2v}$ | 1.842 | 1.854 | 1.890 | 1.097 | 84.3 |
| $Mo(CO)_5CH_2$[o] | $C_{2v}$ | 2.098 | 2.196 | 2.028 | 1.098 | 84.2 |
| $W(CO)_5CH_2$[o] | $C_{2v}$ | 2.064 | 2.119 | 2.031 | 1.097 | 90.8 |
| $CH_2$ | $C_{2v}$ | | | | 1.109 (1.11) | |
| $Cr(CO)_5CF_2$[o] | $C_{2v}$ | 1.854 | 1.856 | 1.904 | 1.323 | 42.9[k] |
| $Mo(CO)_5CF_2$[o] | $C_{2v}$ | 2.093 | 2.128 | 2.074 | 1.330 | 38.6[k] |
| $W(CO)_5CF_2$[o] | $C_{2v}$ | 2.060 | 2.083 | 2.057 | 1.331 | 47.5[k] |
| $CF_2$ | $C_{2v}$ | | | | 1.315 (1.308) | |
| $Cr(CO)_5H_2$[n] | $C_{2v}$ | 1.864/1.859 | 1.787 | 1.745 | 0.814 | 15.9 (15.0 ± 1.3)[i] |
| $Mo(CO)_5H_2$[n] | $C_{2v}$ | 2.056/2.057 | 1.989 | 1.959 | 0.791 | 12.8 |
| $W(CO)_5H_2$[n] | $C_{2v}$ | 2.054/2.053 | 2.006 | 1.918 | 0.810 | 16.3 (≥16)[j] |
| $H_2$ | $D_{\infty h}$ | | | | 0.734 (0.742) | |

[a] Reference 73a. [b] Reference 73b. [c] Reference 73c. [d] Theoretical value (CEPA).[73d] [e] Reference 39. [f] Theoretical value (CCSD(T)).[73e] [g] Reference 73f. [h] Reference 52. [i] Reference 66. [j] Reference 67a. [k] Estimated using isostructural reactions; see text. [l] When two values are given, the first refers to the carbonyl group eclipsing the ligand L. [m] Reference 73g. [n] Eclipsed. [o] Staggered. [p] Reference 68.

too short, while the calculated metal−CO distances of the other carbonyls are in very good agreement with experimental results (Tables 1 and 2). The theoretically predicted first bond dissociation energy of $Cr(CO)_6$ is higher than the experimental value, but the bond strengths of the other carbonyls are predicted very accurately. This indicates that the geometries and bond energies of second- and third-row TM elements are calculated reliably at the CCSD(T)/II//MP2/II level of theory, while first-row TM elements are more difficult. The reason for this has been discussed before.[22] The d electrons of the first-row TM elements can penetrate deeper into the core region than the second- or third-row transition metals, because there is no lower lying shell of filled d orbitals. This induces a smaller HOMO−LUMO gap for compounds of the first-row transition metals than for the higher homologues, which makes the calculation of the former compounds using single-determinant-based methods more difficult.

Perhaps the most interesting ligand of this study is SiO. In his review about 100 years of transition-metal carbonyl complexes, Werner called silicon monoxide a prospective candidate among the yet unknown complex ligands, which are valence isoelectronic with CO.[4] Indeed, transition-metal complexes with SiO as ligands have recently been observed in matrix isolation studies.[38] The calculations predict that the $(CO)_5M-SiO$ bond strength is only slightly lower than the first M−CO dissociation energy in the corresponding hexacarbonyls (Table 1). Very similar bond strengths are also predicted for the $(CO)_3Ni-SiO$ bond ($D_0 = 20.3$ kcal/mol) and for $(CO)_3Ni-CO$ ($D_0 = 22.3$ kcal/mol). The $(CO)_3Pd-SiO$ and $(CO)_3Pt-SiO$ bonds, however, are calculated to be clearly more strongly bound than the

---

(38) (a) Mehner, T.; Köppe, R.; Schnöckel, H. *Angew. Chem.* **1992**, *104*, 653; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 638. (b) Mehner, T.; Schnöckel, H.; Almond, M. J.; Downs, A. J. *J. Chem. Soc., Chem. Commun.* **1988**, 117.

**Table 2. Calculated Bond Lengths (MP2/II) (Å) and Bond Dissociation Energies $D_0$ (CCSD(T)/II//MP2/II) (kcal/mol) for the $(OC)_3M-L$ Bond (Experimental Values Given in Parentheses)**

| molecule | sym | M−C[i] | M−L$_1$ | L$_1$−L$_2$ | $D_0$ |
|---|---|---|---|---|---|
| $Ni(CO)_3CO$ | $T_d$ | 1.801 (1.817[j]) | | 1.162 (1.127[k]) | 22.3 (25.0 ± 2[k]) |
| $Pd(CO)_3CO$ | $T_d$ | 2.013 | | 1.157 | 7.5 |
| $Pt(CO)_3CO$ | $T_d$ | 1.966 | | 1.160 | 10.9 |
| CO | $C_{\infty v}$ | | | 1.151 (1.115) | |
| $Ni(CO)_3SiO$ | $C_{3v}$ | 1.802 | 2.154 | 1.541 | 20.3 |
| $Pd(CO)_3SiO$ | $C_{3v}$ | 2.013 | 2.275 | 1.542 | 15.9 |
| $Pt(CO)_3SiO$ | $C_{3v}$ | 1.962 | 2.255 | 1.540 | 22.2 |
| SiO | $C_{\infty v}$ | | | 1.542 (1.51[a]) | |
| $Ni(CO)_3CS$ | $C_{3v}$ | 1.809 | 1.765 | 1.555 | 35.7 |
| $Pd(CO)_3CS$ | $C_{3v}$ | 2.017 | 1.941 | 1.551 | 18.0[i] |
| $Pt(CO)_3CS$ | $C_{3v}$ | 1.972 | 1.917 | 1.551 | 26.9 |
| CS | $C_{\infty v}$ | | | 1.545 (1.534[b]) | |
| $Ni(CO)_3N_2$ | $C_{3v}$ | 1.801 | 1.823 | 1.143 | 4.6[i] (10)[e] |
| $N_2$ | $D_{\infty h}$ | | | 1.131 (1.094[a]) | |
| $Ni(CO)_3NO^+$ | $C_{3v}$ | 1.933 | 1.760 | 1.203 | 68.9 |
| $Pd(CO)_3NO^+$ | $C_{3v}$ | 2.170 | 1.835 | 1.191 | 51.0[h] |
| $Pt(CO)_3NO^+$ | $C_{3v}$ | 2.060 | 1.834 | 1.187 | 45.7[h] |
| $NO^+$ | $C_{\infty v}$ | | | 1.103 (1.062[c]) | |
| $Ni(CO)_3CN^-$ | $C_{3v}$ | 1.774 | 1.930 | 1.191 | 60.4 |
| $Pd(CO)_3CN^-$ | $C_{3v}$ | 1.957 | 2.130 | 1.1900 | 44.9 |
| $Pt(CO)_3CN^-$ | $C_{3v}$ | 1.922 | 2.105 | 1.188 | 57.1 |
| $Ni(CO)_3NC^-$ | $C_{3v}$ | 1.781 | 1.937 | 1.196 | 47.1[h] |
| $Pd(CO)_3NC^-$ | $C_{3v}$ | 1.959 | 2.175 | 1.196 | 32.9 |
| $Pt(CO)_3NC^-$ | $C_{3v}$ | 1.920 | 2.159 | 1.196 | 38.7 |
| $CN^-$ | $C_{\infty v}$ | | | 1.201 (1.177[d]) | |
| $Ni(CO)_3CCH_2$ | $C_s$ | 1.793/1.801 | 1.800 | 1.307 | 38.8 |
| $Pd(CO)_3CCH_2$ | $C_s$ | 2.083/2.000 | 1.927 | 1.310 | 22.2 |
| $Pt(CO)_3CCH_2$ | $C_s$ | 2.007/1.957 | 1.907 | 1.312 | 33.5 |
| $CCH_2$ | $C_{2v}$ | | | 1.308 (1.300[f]) | |
| $Ni(CO)_3HCCH$ | $C_s$ | 1.803/1.791 | 2.168 | 1.243 | 5.4[h] |
| $Pd(CO)_3HCCH$ | $C_s$ | 2.008/1.971 | 2.513 | 1.231 | −2.1[h] |
| $Pt(CO)_3HCCH$ | $C_s$ | 1.954/1.931 | 2.414 | 1.242 | −2.5[h] |
| HCCH | $D_{\infty h}$ | | | 1.218 (1.203[g]) | |
| $Ni(CO)_3CH_2$ | $C_s$ | 1.782/1.799 | 1.861 | 1.097/1.096 | 49.2 |
| $Pd(CO)_3CH_2$ | $C_s$ | 2.147/1.971 | 1.948 | 1.098/1.097 | 35.6 |
| $Pt(CO)_3CH_2$ | $C_s$ | 2.038/1.939 | 1.940 | 1.094/1.094 | 51.4 |
| $CH_2$ | $C_{2v}$ | | | 1.109 | |
| $Ni(CO)_3CF_2$ | $C_s$ | 1.782/1.799 | 1.835 | 1.316/1.316 | 39.4 |
| $Pd(CO)_3CF_2$ | $C_s$ | 2.043/1.995 | 2.008 | 1.316/1.319 | 13.4 |
| $Pt(CO)_3CF_2$ | $C_s$ | 1.987/1.957 | 1.967 | 1.322/1.318 | 21.1 |
| $CF_2$ | $C_{2v}$ | | | 1.315 | |
| $Ni(CO)_3H_2$ | $C_s$ | 1.792/1.795 | 1.679 | 0.798 | −3.2 |
| $H_2$ | $D_{\infty h}$ | | | 0.734 | |

[a] Reference 73g. [b] Reference 73b. [c] Reference 73c. [d] Theoretical value (CEPA).[73d] [e] Reference 42c. [f] Theoretical value (CCSD(T)).[73e] [g] Reference 73f. [h] ZPE estimated. [i] When two values are given, the second refers to the two equivalent carbonyl groups. [j] Reference 73h. [k] Reference 73i.

respective metal−CO bonds (Table 2). A previous theoretical study of PdSiO and PdCO also reported a higher bond strength for the Pd−SiO bond (43.5 kcal/mol) than for the Pd−CO bond (38.7 kcal/mol).[38] It seems that the low stability of the silacarbonyl complexes is not because of the weak M−SiO bond but rather because of the high reactivity of the dicoordinated silicon.

The calculations suggest that the Si−O distance in the metal complexes should practically be the same as in isolated SiO, while the C−O distance in the hexacarbonyls is longer than in carbon monoxide (Tables 1 and 2). The theoretical result is supported by the experimentally observed vibrational spectra of PdSiO and PdCO, which show for PdSiO a small shift toward higher wavenumbers by 20 $cm^{-1}$, while for PdCO a shift toward lower frequencies by 88 $cm^{-1}$ is observed.[38]

The only complexes $M(CO)_5L$ other than the hexacarbonyls for which a complete set of experimental M−L bond energies is known are the thiocarbonyls $M(CO)_5CS$. Mass spectroscopic studies give M−CS bond dissociation energies of 56 ± 4 kcal/mol for $Cr(CO)_5CS$, 64 ± 14 kcal/mol for $Mo(CO)_5CS$, and 70 ± 8 kcal/mol for $W(CO)_5CS$.[39]

The calculated bond strengths for $Mo(CO)_5CS$ ($D_0 = 59.2$ kcal/mol) and $W(CO)_5CS$ ($D_0 = 68.8$ kcal/mol) are in excellent agreement with the experimental values (Table 1). The calculated Cr−CS bond strength of $Cr(CO)_5CS$ ($D_0 = 63.6$ kcal/mol) is higher than the experimental value. Also, the Cr−CO bond strength of $Cr(CO)_6$ has been calculated slightly too high.[20]

There are no direct experimental values for the geometries of the $M(CO)_5CS$ complexes available. An X-ray structure analysis of $Cr(CO)_5CS$ could not be resolved because of structural disorder.[40a] The $(CO)_5M-CS$ and $(CO)_5MC-S$ bond lengths in the chromium and tungsten compounds have been estimated using experimental bond lengths of other carbonyl and thiocarbonyl complexes as Cr−CS = 1.854 Å and CrC−S = 1.565 Å

---

(39) Michels, G. D.; Flesch, G. D.; Svec, H. J. *Inorg. Chem.* **1980**, *19*, 479.

(40) (a) Saillard, P. J.; Grandjean, D. *Acta Crystallogr.* **1978**, *B34*, 3318. (b) English, A. M.; Plowman, K. R.; Butler, I. S. *Inorg. Chem.* **1981**, *20*, 2553. (c) Saillard, J.-Y.; Le Borgne, G.; Grandjean, D. *J. Organomet. Chem.* **1975**, *94*, 409. (d) Bird, P .H.; Ismail, A. A.; Butler, I. S. *Inorg. Chem.* **1985**, *24*, 2911. (e) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3155, 3160. (f) Basolo, F.; Brault, A. T.; Poe, A. J. *J. Chem. Soc.* **1984**, *678*, (g) Woodard, S. S.; Jacobsen, R. A.; Angelici, R. J. *J. Organomet. Chem.* **1976**, *117*, C75.

for $Cr(CO)_5CS$ and W−CS = 1.996 Å and WC−S = 1.556 Å for $W(CO)_5CS$.[40b] The theoretical results shown in Table 1 are in very good agreement with the experimental estimate,[40b] with the exception of the Cr−CS bond, which is predicted as too short. The calculated M−CS bond lengths are 0.06−0.13 Å shorter than the M−CO bond lengths in $M(CO)_5CS$ (Table 1). The theoretical result is supported by experimental geometries for other mixed carbonyl−thiocarbonyl complexes, which show that the M−CS bond is typically 0.05−0.15 Å shorter than the M−CO bond.[40] The shorter M−CS bond is in agreement with the calculated bond strength of the thiocarbonyl ligand being higher than that of the M−CO bond (Table 1). The C−S bond length in the $M(CO)_5CS$ complexes is calculated as being longer than in isolated CS. Experimental studies of thiocarbonyl complexes show that the C−S bond length can be shorter[40e] or longer[40f] than in CS. The related compound *trans*-$W(CO)_4(CNC_6H_{11})(CS)$ has a C−S distance of 1.564 Å,[40g] which is in good agreement with the calculated value of 1.561 Å for $W(CO)_5CS$.

Although thiocarbonyl complexes of the nickel triad are known,[5] there is no experimental evidence for the existence of $M(CO)_3CS$ (M = Ni, Pd, Pt). The calculations predict that the $(CO)_3M$−CS bond should be stronger and shorter than the respective metal−CO bond in the tetracarbonyls (Table 2). In particular, $Ni(CO)_3CS$ might be a promising target for experimental studies, because the calculated bond energy $D_0 = 35.7$ kcal/mol for the Ni−CS bond is rather high.

The calculations predict that $N_2$ is significantly more weakly bonded than CO in $M(CO)_nL$ complexes. The calculated $(CO)_5M-N_2$ bond dissociation energies are only between 20.6 kcal/mol (M = Mo) and 24.8 kcal/mol (M = W). A very low $M-N_2$ bond energy ($D_0 = 4.6$ kcal/mol) is calculated for $Ni(CO)_3N_2$. $Pd(CO)_3N_2$ and $Pt(CO)_3N_2$ are not energy minima at the MP2/II level; the $N_2$ ligand dissociates during the geometry optimization. The predicted low stability of the $M-N_2$ bond is in agreement with experimental results. The first transition-metal dinitrogen complex reported in the literature was $(C_6H_6)Cr(CO)_2N_2$.[41] The parent dinitrogen carbonyl complex $Cr(CO)_5N_2$ is thermally stable only in solution of liquid xenon at −35 °C.[42a] The other analogues $Mo(CO)_5N_2$ and $W(CO)_5N_2$ have also been observed so far only in low-temperature matrices.[42b] The unstable species $Ni(CO)_3N_2$ was generated in solution by UV photolysis of $Ni(CO)_4$ in $N_2$-doped liquid Kr in a high-pressure cell.[42c] From kinetic measurements of the $N_2$ dissociation a $(CO)_3Ni-N_2$ bond dissociation energy of ∼10 kcal/mol has been estimated,[42c] which is somewhat higher than the calculated value $D_0 = 4.6$ kcal/mol. The thermal corrections at 298 °C are 2.1 kcal/mol.[43] This gives a theoretical prediction of 6.7 kcal/mol for the bond strength of $(CO)_3Ni-N_2$, which is in reasonable agreement with the experimental estimate ∼10 kcal/mol.[42c] More stable dinitrogen complexes have ligands other than CO as coligands at the metal. Phosphine ligands, in particular, stabilize $N_2$ complexes.[44] The observed $M-N_2$ bond lengths in zerovalent phosphine complexes of Cr, Mo, and W are significantly (0.05−0.15 Å)) shorter than calculated for $M(CO)_5N_2$.[44]

The most strongly bound ligand investigated in this study is $NO^+$. The calculated dissociation energies for the $M(CO)_5NO^+$ complexes are 105.4 kcal/mol for M = Cr, 103.2 kcal/mol for M = Mo, and 108.6 kcal/mol for M = W (Table 1). Strong metal−$NO^+$ bonds are also calculated for $Ni(CO)_3NO^+$ ($D_0 = 68.9$ kcal/mol), $Pd(CO)_3NO^+$ ($D_0 = 51.0$ kcal/mol), and $Pt(CO)_3NO^+$ ($D_0 = 45.7$ kcal/mol). It is notable that the heaviest of the group 10 elements, platinum, has the weakest M−$NO^+$ bond, while the heaviest of the group 6 transition metals, tungsten, has the strongest M−$NO^+$ bond.

It is well-known that $NO^+$ is significantly more strongly bound than CO in transition-metal complexes.[4,45a,b] The calculated N−O distance in the $M(CO)_5NO^+$ and $M(CO)_3NO^+$ complexes is clearly longer than in isolated $NO^+$ (Tables 1 and 2). This is in agreement with experimental evidence, which shows that the N−O bond length in transition-metal complexes is typically 1.16−1.20 Å, much longer than in isolated $NO^+$ (1.06 Å).[45] We want to point out that the observed metal−NO distances in neutral complexes are typically *shorter* than those calculated here for the metal cations. For example, the CpNi−NO distance is 1.60 Å,[45h] while the calculated $(CO)_3Ni-NO^+$ bond length is 1.760 Å. The reported Mo−NO distance in $Cp_2Mo(\eta^1\text{-}C_5H_5)NO$ is 1.75 Å;[45i] the calculated $(CO)_5Mo-NO^+$ bond length is 1.877 Å.

A strong metal−ligand bond is also calculated for the cyano ligand $CN^-$. Table 1 shows that the calculated bond strengths are between 87.3 kcal/mol (M = Mo) and 97.7 kcal/mol (M = W) when $CN^-$ is bound through the carbon atom. Strong M−$CN^-$ bonds are also calculated for the group 10 elements. The $(CO)_3Pt-CN^-$ bond is predicted to be even stronger ($D_0 = 57.1$ kcal/mol) than the $(CO)_3Pt-NO^+$ bond ($D_0 = 45.7$ kcal/mol). The M−NC bond of the isocyanide complexes is calculated to be 10−20 kcal/mol weaker than the respective M−CN bond of the cyanide complexes. It has been shown[46] that deprotonation of $M(CO)_5NCH$ (M = Cr, W) leads to the rearrangement $[M(CO)_5NC]^- \rightarrow [M(CO)_5CN]^-$, which indicates that the M−$CN^-$ bond is stronger than the

---

[41] Sellmann, D.; Maisel, G. *Z. Naturforsch.* **1972**, *27B*, 465.

[42] (a) Turner, J. J.; Simpson, M. B.; Poliakoff, M.; Maier, W. B.; Graham, M. A. *Inorg. Chem.* **1983**, *22*, 911. (b) Burdett, J. K.; Downs, A. J.; Gaskill, G. P.; Graham, M. A.; Turner, J. J.; Turner, R. F. *Inorg. Chem.* **1978**, *17*, 523. (c) Turner, J. J.; Simpson, M. B.; Poliakoff, M.; Maier, W. B. *J. Am. Chem. Soc.* **1983**, *105*, 3898.

[43] The thermal corrections at 298 °C for loss of $N_2$ include the work term $pV = RT$ (0.6 kcal/mol), three degrees of translation ($^3/_2RT$ = 0.9 kcal/mol), and two degrees of rotation ($RT$ = 0.6 kcal/mol) for 1 mol of $N_2$ produced in the reaction. The thermal corrections to the ZPE values were calculated as <0.1 kcal/mol.

[44] (a) Anderson, S. N.; Richards, R. L.; Hughes, D. L. *J. Chem. Soc., Dalton Trans.* **1986**, 245. (b) Dadkhah, H.; Dilworth, J. R.; Fairman, K.; Kan, C. T.; Richards, R. L.; Hughes, D. L. *J. Chem. Soc., Dalton Trans.* **1985**, 1523. (c) Carmona, E.; Galindo, A.; Poveda, M. L.; Rogers, R. D. *Inorg. Chem.* **1985**, *24*, 4033. (d) Carmona, E.; Marin, J. M.; Poveda, M. L.; Rogers, R. D.; Atwood, J. L. *J. Organomet. Chem.* **1982**, *238*, C63. (e) Salt, J. E.; Girolami, G. S.; Wilkinson, G.; Motevalli, M.; Thornton-Pett, M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1985**, 685. (f) Girolami, G. S.; Salt, J. E.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *J. Am. Chem. Soc.* **1983**, *105*, 5954. (g) Sato, M.; Tatsumi, T.; Kodama, T.; Hidai, M.; Uchida, T.; Uchida, Y. *J. Am. Chem. Soc.* **1978**, *100*, 4447.

[45] (a) Hedberg, L.; Hedberg, K.; Satija, S. K.; Swanson, B. I. *Inorg. Chem.* **1985**, *24*, 2766. (b) Hedberg, L.; Hedberg, K.; Hagen, K.; Ryan, R. R.; Jones, L. J. *Inorg. Chem.* **1985**, *24*, 2771. (c) Holl, M. M.; Hillhouse, G. L.; Folting, K.; Huffman, J. C. *Organometallics* **1987**, *6*, 1522. (d) Ardon, M.; Cohen, S. *Inorg. Chem.* **1993**, *32*, 3241. (e) Faller, J. W.; Chodosh, D. F.; Katahira, D. *J. Organomet. Chem.* **1980**, *187*, 227. (f) Atwood, J. L.; Shakir, R.; Malito, J. T.; Herberhold, M.; Kremnitz, W.; Bernhagen, W. P. E.; Alt, H. G. *J. Organomet. Chem.* **1979**, *165*, 65. (g) Lin, J. T.; Wang, S. Y.; Huang, P. S.; Hsiao, Y. M.; Wen, Y. S.; Yeh, S. K. *J. Organomet. Chem.* **1990**, *388*, 151. (h) Cox, A. P.; Thomas, L. F.; Sheridan, J. *Nature* **1958**, *181*, 1157. (i) Calderon, J. L.; Cotton, F. A.; Legzdins, P. *J. Am. Chem. Soc.* **1969**, *91*, 2528.

[46] Guttenberger, J.-F. *Chem. Ber.* **1968**, *101*, 403.

M−NC$^-$ bond. Structural data are available for hydrogen-bridged $[(CO)_5CrCN]_2H^-$ and $(CO)_5MoCNGeH_2(C_6H_5)$.[47] The experimental Cr−CN bond distance of the former complex is 2.012 Å.[47a] The Mo−CN distance of the latter complex is reported as 2.150 Å.[47b] The calculated M−CN$^-$ bond lengths are in reasonable agreement with the experimental data (Table 1).

The calculations predict that the vinylidene ligand is much more strongly bound than the acetylene ligand (Tables 1 and 2). The acetylene complexes $Pd(CO)_3HCCH$ and $Pt(CO)_3HCCH$ are shallow energy minima at MP2/II. The CCSD(T)/II calculations indicate that the molecules are not stable. $Ni(CO)_3HCCH$ is predicted as a weakly bound complex ($D_0 = 5.4$ kcal/mol). The calculations indicate that the metal−ligand bond strength of acetylene in the $M(CO)_5L$ complexes is comparable to that of $N_2$, while the bond strength of vinylidene is similar to that of CS (Tables 1 and 2). The theoretically predicted higher bond strengths of $CCH_2$ is supported by the experimentally observed high thermodynamic stability of vinylidene complexes.[4,48] There are many reports about reactions of TM complexes with alkynes which yield only the vinylidene complex as a stable product, although there are indications that the alkyne complex is formed as the primary product.[49,50] Therefore, it is difficult to find experimental geometries of TM alkyne complexes in low oxidation states.[51] The only example related to our work has recently been reported by Dötz et al.[52] They reported the result of an X-ray structure analysis of a tungsten tetracarbonyl alkyne carbene complex, where the alkyne ligand has two phenyl rings. The observed W−C(alkyne) distances are 2.37 and 2.40 Å.[52] These data are in good agreement with the calculated $(CO)_5W$−C(acetylene) distance of 2.331 Å (Table 1).

The calculated metal−C(vinylidene) bond lengths are also in good agreement with available experimental data for related complexes. The experimentally observed W−C(vinylidene)) distance in $W(CCHCO_2Me)(CO)_3(dppe)$ is 1.98 Å;[50] the calculated $(CO)_5W-CCH_2$ bond length is 1.997 Å. A Mo−C(vinylidene) distance of 1.917 Å has been reported for $Mo(CCHPh)Cp(Br)[P(OMe)_3]_2$; the calculated $(CO)_5Mo-CCH_2$ bond length is 1.977 Å. However, the experimental value refers to a Mo(II) complex, which should have a shorter bond length than a Mo(0) complex. Other reported vinylidene complexes have higher metal oxidation states and cannot directly be compared with the calculated values shown in Table 1.[48a,53] We suggest that the bond lengths predicted here should be used as standard values for metal−ligand bonds, except for those of chromium and nickel, which are probably slightly too short.

The calculated results for the carbene complexes $M(CO)_nCH_2$ and $M(CO)_nCF_2$ are interesting, because the latter molecules are predicted to have a longer and weaker metal−C(carbene) bond than the respective methylene complex. It is well-known that low-valent (Fischer-type) carbene complexes need a stabilizing $\pi$-donor substituent at the carbene carbon atom to become isolable.[53,54] The calculations provide clear evidence that the molecules are stable because the carbene carbon atom is electronically saturated by the $\pi$-donor substituent, while the metal−carbene bond becomes longer and weaker upon $\pi$ substitution.[55] The stability of the Fischer-type carbene complexes is directly related to the degree of electronic saturation of the carbene carbon p($\pi$) orbital. The same effect is responsible[56] for the novel class of Arduengo-type carbenes.[57]

The $(CO)_5M-CF_2$ bond energies could not be calculated at the CCSD(T)/II level for computational reasons (2 GB single file size limit). We estimated the bond energies using the isostructural[58] reaction (1).

$$M(CO)_6 + (^1A_1)CF_2 \rightarrow M(CO)_5CF_2 + CO + \Delta E_R \quad (1)$$

The sum of the reaction energies of reaction 1 calculated at the MP2/II level and the $(CO)_5M-CO$ bond energy calculated at the CCSD(T)/II level gives the estimated $(CO)_5M-CF_2$ bond energies shown in Table 1. Systematic studies have shown that isostructural reaction energies calculated at the MP2/II level give bond energies which are in good agreement with CCSD(T)/II results.[58]

Since the experimentally observed Fischer-type complexes have even better $\pi$-donor substituents than fluorine at the carbene center, the reported metal−carbene distances are somewhat longer than calculated for the $(CO)_5MCF_2$ complexes.[53,54] For example, the experimental $(CO)_5W-CPh_2$ distance is 2.15 Å; the calculated $(CO)_5W-CF_2$ bond length is 2.057 Å.[59] The metal−carbene distance can vary considerably, depending on the nature of the $\pi$-donor ligand at the carbene center. The reported $(CO)_5Cr-CXY$ distances are between 1.97 and 2.19 Å.[54] The experimental results indicate a significant trans effect of the degree of $\pi$-donation at the carbene center upon the trans CO group. The metal−CO bond length of the trans carbonyl becomes shorter when the M−C(carbene) bond is longer.[53,54] The same trend is predicted by the calcu-

---

[47] (a) Bär, E.; Fuchs, J.; Rieger, D.; Aguilar-Parilla, F.; Limbach, H.-H.; Fehlhammer, W. P. *Angew. Chem.* **1991**, *103*, 88. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 88. (b) Treichel, P. M.; Shaw, D. B.; Calabrese, J. C. *J. Organomet. Chem.* **1977**, *139*, 31.

[48] (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (b) Antonova, A. B.; Johansson, A. A. *Usp. Khim.* **1989**, *58*, 1197.

[49] (a) Kolobova, N. E.; Antonova, A. B.; Khitrova, O. M.; Antipin, M. Yu.; Struchkov, Yu. T. *J. Organomet. Chem.* **1977**, *137*, 69. (b) Bruce, M. I.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1471. (c) Berke, H.; Härter, P.; Huttner, G.; Zsolnai, L. *Z. Naturforsch.* **1981**, *36B*, 929.

[50] Birdwhistell, K. R.; Nieter Burgmayer, S. J.; Templeton, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 7789.

[51] There are many structures of high-valent TM alkyne complexes available. See for example: (a) Kersting, M.; El Kohli, A.; Müller, U.; Dehnicke, K. *Chem. Ber.* **1989**, *122*, 279. (b) Kersting, M.; Dehnicke, K.; Fenske, D. *J. Organomet. Chem.* **1988**, *346*, 201 and references therein.

[52] Dötz, K. H.; Schäfer, T.; Kroll, F.; Harms, K. *Angew. Chem.* **1992**, *104*, 1257; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1236.

[53] Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988.

[54] *Transition Metal Carbene Complexes*; Dötz, K. H., Fischer, H., Hofmann, P., Kreissl, F. R., Schubert, U., Weiss, K., Eds.; Verlag Chemie: Weinheim, Germany, 1983; p 118.

[55] Vyboishchikov, S. F.; Frenking, G. *J. Am. Chem. Soc.*, to be submitted for publication.

[56] (a) Heinemann, C.; Thiel, W. *Chem. Phys. Lett.* **1994**, *217*, 11. (b) Böhme, C.; Frenking, G. *J. Am. Chem. Soc.*, in press. For an alternative explanation see: (c) Cioslowski, J. *Int. J. Quantum. Chem., Quantum Chem. Symp.* **1993**, *27*, 309. (d) Arduengo, A. J.; Rasika Dias, H. V.; Dixon, D. A.; Harlow, R. L.; Klooster, W. T.; Koetzle, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 6812.

[57] (a) Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361. (b) Arguengo, A. J.; Rasika Dias, H. V.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1992**, *114*, 5530.

[58] Dapprich, S.; Pidun, U.; Ehlers, A. W.; Frenking, G. *Chem. Phys. Lett.* **1995**, *242*, 521.

[59] Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127.

lated geometries of the tungsten and molybdenum (CO)$_5$MCX$_2$ complexes (Table 1). The M−CO$_{trans}$ bonds of the (CO)$_5$MCF$_2$ complexes are clearly shorter than those of the (CO)$_5$MCH$_2$ molecules (M = Mo, W). The theoretical results for the chromium complexes do not show such a correlation. This may be due to the problems of MP2 optimizations of first-row TM complexes. The distinct trans effect of the ligands L in M(CO)$_5$L complexes upon the M−CO$_{trans}$ bond length is discussed below in the section about the bonding analysis.

Carbene complexes of the group 10 elements Ni, Pd, and Pt are also known, but carbene complexes with the formal oxidation state 0 have been reported only for nickel.[60] Carbene complexes of Pd and Pt are square-planar structures with a higher oxidation state.[54] (CO)$_3$NiCXY complexes are reported in the literature, but there is no experimental geometry known to us.[60] The M−C(carbene) distances of square-planar complexes of M(II) are 1.82−1.91 Å for M = Ni, 1.95−1.98 for M = Pd, and 1.92−2.05 Å for M = Pt.[54] Although these distances are in reasonable agreement with the calculated metal−C(carbene) bond lengths of (CO)$_3$MCF$_2$, a definite conclusion about the accuracy of the theoretically predicted bond lengths shall not be made because of the different types of complexes. It is interesting to note, however, that the (CO)$_3$Pt−CF$_2$ bond is much weaker ($D_0$ = 21.1 kcal/mol) than the (CO)$_3$Pt−CH$_2$ bond ($D_0$ = 51.4 kcal/mol), while the dissociation energies of the respective nickel complexes are less influenced by the $\pi$-donor substitution ($D_0$ = 39.4 kcal/mol for (CO)$_3$Ni−CF$_2$ and 49.2 kcal/mol for (CO)$_3$Ni−CH$_2$).

The results for the dihydrogen complexes (CO)$_5$MH$_2$ have been reported elsewhere.[21h] The calculated H−H distances are in good agreement with experimental results for related transition-metal dihydrogen complexes, which show a H−H distance of ca. 0.82 Å, despite widely varying ligand sets, central metals, and charges.[61,62] Also, the predicted metal−hydrogen distances compare favorably with experimental results. The Mo−H bond length in [Mo(CO)(H$_2$)(dppe)$_2$] (dppe = Ph$_2$PC$_2$H$_4$PPh$_2$) is reported as 1.92 Å.[61] Since the dppe ligand enforces the L$_n$M−H$_2$ bonding, the calculated Mo−H distance of 1.959 Å in [Mo(CO)$_5$H$_2$] appears to be reasonable. The calculated W−H distance in [W(CO)$_5$H$_2$] (1.918 Å) is in good agreement with the experimental values for the original Kubas complex [W(CO)$_3$(PiPr$_3$)$_2$(H$_2$)], which has been reported as 1.95 Å (X-ray) and 1.89 Å (neutron diffraction).[63,64] The Cr−H bond length of the chromium analogue [Cr(CO)$_3$(PiPr$_{)2}$(H$_2$)] has recently been determined by X-ray analysis (Cr−H = 1.70−1.80 Å).[65] The calculated value for the Cr−H distances in [Cr(CO)$_5$H$_2$] is 1.745 Å (Table 1).

The calculated (CO)$_5$Cr−H$_2$ bond energy ($D_0$ = 15.9 kcal/mol) is in excellent agreement with the recently reported dissociation energy 15.0 ± 1.3 kcal/mol.[66] The good agreement may appear to be surprising, because we mentioned that first-row TM complexes may not be calculated very accurately at this level of theory. It should be noted that a 10−15% error in the bond energy of the dihydrogen complex would be 1.5−2.5 kcal/mol, which is in the experimental error range.

The theoretical dissociation energy $D_0$ = 16.3 kcal mol$^{-1}$ for W(CO)$_5$H$_2$ concurs with the experimental estimate, >16 kcal mol$^{-1}$.[67a] The theoretically predicted value is also supported by the experimental W−L binding enthalpies of the complexes [W(CO)$_3$(PCy)$_2$L]. The measured values are $\Delta H$ = 9.9 kcal mol$^{-1}$ (L = H$_2$) and $\Delta H$ = 30.4 kcal mol$^{-1}$ (L = CO).[67b] The first CO dissociation energy of [W(CO)$_6$] is calculated as $D_0$ = 45.7 kcal mol$^{-1}$ (Table 2); the experimental value is 46.0 ± 2 kcal mol$^{-1}$.[68] Thus, the W−CO bond strength of [W(CO)$_6$] is stronger than in [W(CO)$_4$(PCy)$_2$] by a factor of 1.5. This factor gives an estimated bond strength of ca. 15 kcal mol$^{-1}$ for the W−H$_2$ bond in [W(CO)$_5$H$_2$], which is in good agreement with the calculated value of 16.3 kcal mol$^{-1}$. The calculations suggest that the tungsten complex has the strongest (CO)$_5$M−H$_2$ bond ($D_0$ = 16.3 kcal mol$^{-1}$) and the molybdenum complex has the weakest bond ($D_0$ = 12.8 kcal mol$^{-1}$). The chromium complex is slightly more weakly bound than the tungsten complex ($D_0$ = 15.9 kcal mol$^{-1}$). This theoretical result is in agreement with a correlation of properties of group 6 dihydrogen complexes, which shows the order W ≈ Cr > Mo for the M−H$_2$ bond strengths.[65] Also, the thermal stability of [Mo(CO)$_5$H$_2$] in liquid Xe is clearly lower than that observed for the W and Cr analogues.[69] Pd(CO)$_3$H$_2$ and Pt(CO)$_3$H$_2$ are not energy minima at the MP2/II level of theory. The nickel complex Ni(CO)$_3$H$_2$ is a minimum at MP2/II. However, energy calculations at CCDSD(T)/II give a negative bond energy, which means that Ni(CO)$_3$H$_2$ is probably not stable at higher levels of theory.

There can be different conformations of the M(CO)$_n$L complexes, where L = CCH$_2$, HCCH, CH$_2$, CF$_2$, and H$_2$. In M(CO)$_5$L the ligand L may have an eclipsed (e) or staggered (s) position with regard to the cis CO groups. The calculations showed that the two conformations are always very close in energy (<0.2 kcal/mol) except for L = HCCH, where the eclipsed conformation of the M(CO)$_5$(HCCH) complexes is 2−3 kcal/mol more stable than the staggered conformation at the MP2/II level of theory. In the M(CO)$_3$L complexes the ligand L may be in an eclipsing position with one CO group, or it may

---

[60] (a) Fischer, E. O.; Kreissl, F. R.; Winkler, E.; Kreiter, C. G. *Chem. Ber.* **1972**, *105*, 588. (b) Fraser, P. J.; Roper, W. R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1974**, 1827. (c) Lappert, M. F.; Rye, P. L. *J. Chem. Soc., Dalton Trans.* **1977**, 2172. (d) Dean, W. K.; Charles, R. S.; Van Derveer, D. G. *Inorg. Chem.* **1977**, *16*, 3328. (e) Ogura, K.; Wada, M.; Okawara, R. *J. Organomet. Chem.* **1978**, *159*, 417.

[61] Kubas, G. J.; Burns, C. J.; Eckert, J.; Johnson, S. W.; Larson, A. C.; Vergamini, P. J.; Unkefer, C. J.; Khalsa, G. R. K.; Jackson, S. A.; Eisenstein, O. *J. Am. Chem. Soc.* **1993**, *115*, 569.

[62] (a) Ricci, J. S.; Koetzle, T. F.; Bautista, M. T.; Hofstede, T. M.; Morris, R. H.; Sawyer, J. F. *J. Am. Chem. Soc.* **1989**, *111*, 8823. (b) Van Der Sluys, L. S.; Eckert, J.; Eisenstein, O.; Hall, J. H.; Huffman, J. C.; Jackson, S. A.; Koetzle, T. J.; Kubas, G. J.; Vergamini, P. J.; Caulton, K. G. *J. Am. Chem. Soc.* **1990**, *112*, 4831.

[63] (a) Kubas, G. J.; Ryan, R. R.; Swanson, B. J.; Vergamini, P. J.; Wassermann, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451. (b) Kubas, G. J.; Ryan, R. R.; Wroblewski, D. J. *J. Am. Chem. Soc.* **1986**, *108*, 1229. (c) Kubas, G. J.; Unkefer, C. J.; Swanson, B. J.; Fukushima, E. *J. Am. Chem. Soc.* **1986**, *108*, 7000.

[64] Sweany, R. L. *J. Am. Chem. Soc.* **1986**, *108*, 6986.

[65] Kubas, G. J.; Nelson, J. E.; Bryan, J. C.; Eckert, J.; Wisniewski, L.; Zilm, K. *Inorg. Chem.* **1994**, *33*, 2954.

[66] Wells, J. R.; House, P. G.; Weitz, E. *J. Phys. Chem.* **1994**, *98*, 8343.

[67] (a) Ishikawa, Y.-I.; Hackett, P. A.; Rayner, D. M. *J. Phys. Chem.* **1989**, *93*, 652. (b) Gonzalez, A. A.; Zhang, K.; Nolan, S. P.; Lopez de la Vega, R.; Mukerjee, S. L.; Hoff, C. D.; Kubas, G. J. *Organometallics* **1988**, *7*, 2429.

[68] Lewis, K. E.; Golden, D. M.; Smith, G. P. *J. Am. Chem. Soc.* **1984**, *106*, 3905.

[69] Upmacis, R. K.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 3645.

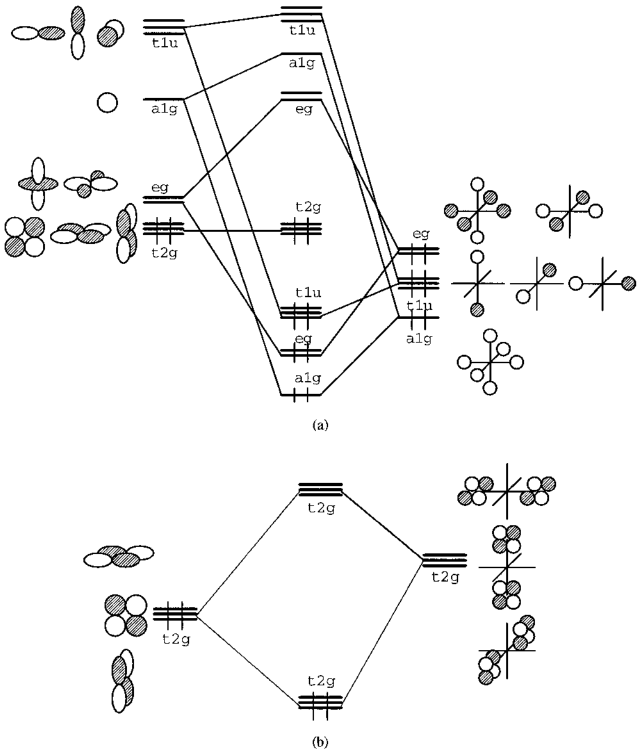

**Figure 1.** Orbital interaction diagram for octahedral complexes $ML_6$ with $d^6$ metals M: (a) $\sigma$ interactions; (b) $\pi$ interactions.

have a staggered conformation. Again, the energy differences were very low (<0.2 kcal/mol) for the two forms of the complexes for all ligands L.

## Bonding Analysis

In order to analyze the metal–ligand bonding of the $(CO)_nM-L$ complexes, we used the CDA method,[25] which has been described above. The CDA method is helpful for a comparison of the ligands in terms of electron donation and back-donation. The method can be used as a quantitative tool for the analysis of ab initio wave functions of molecules in terms of charge donation and back-donation between two closed-shell fragments. In particular, the CDA method can be used as a quantitative expression of the Dewar–Chatt–Duncanson model,[10] which has been proven to be very valuable for the interpretation of transition-metal complexes. The CDA results show the *relative* amount of charge donation and back-donation between the ligand and the remaining fragment. Thus, it is possible to classify different ligands with regard to their donating and back-donating strength. We want to emphasize that the extent of electron donation and back-donation is not directly related to the actual driving force for the formation of the bond.

We discuss first the CDA results for $W(CO)_6$ in detail, and then we give a comparison of the $M(CO)_5L$ complexes. Figure 1 shows a qualitative orbital interaction diagram between a $d^6$ metal and six CO ligands in an octahedral geometry. Donation from CO to the metal takes place via the $a_{1g}$, $e_g$, and $t_{1u}$ orbitals, while the back-donation occurs through the $t_{2g}$ orbitals. This is the standard model for qualitative orbital interactions in $ML_6$ complexes given in many textbooks.[8,9,12] The results of the CDA method for $W(CO)_6$ using the HF/6-31G(d) and MP2/6-31G(d) wave functions at the optimized geometries are shown in Table 3. They may be compared with Figure 1.

The CDA method shows that the dominant electron donation from CO to $W(CO)_5$ takes place via the $t_{1u}$ and $e_g$ orbitals, as expected from the qualitative model. The contribution from the $a_{1g}$ orbital is rather small. The HF orbitals show contributions from only one component of the degenerate $t_{1u}$ and $e_g$ orbitals, because the analysis is carried out between only one CO and the remaining fragment. Since the natural orbitals are a mixture of the HF orbitals, the CDA results at the MP2/6-31G(d) level show contributions from all components. Note that there is no direct correlation between a canonical MO (CMO) and a natural MO (NMO). The CMOs have energy eigenvalues, given by the diagonalization of the Fock matrix. The NMOs are given by the diagonalization of the first-order spinless reduced density matrix. There are no energy values associated with the NMOs. The CDA results for NMOs are ordered by an estimate of the shape similarity with the NMOs. At both levels, HF and MP2, the donation from CO to the metal is dominated by the $t_{1u}$ and $e_g$ orbitals. The total donation is slightly smaller at the MP2 (0.315 e) than at the HF level (0.354 e). The CDA result for the back-donation is also in agreement with Figure 1. The only sizable contribution is given by the $t_{2g}$ orbitals (Table 3).

The results of the CDA calculation for $W(CO)_6$ indicate that the donation of electronic charge from CO to $W(CO)_5$ is larger than the back-donation. *This must not be used as evidence that electron donation contributes more to the metal–carbonyl bond energy than back-donation*. The results[10] of a Morokuma analysis[17] of the ab initio wave function of $Cr(CO)_6$ and the generalized transition state method using DFT calculations.[19] for $W(CO)_6$ demonstrate clearly that the M→CO back-donation is more important for the M–CO bond strength than the OC→M back-donation. The CO→W donation is mainly due to the carbon lone-pair ($\sigma$) orbital, which penetrates deeply into the spd valence shell of tungsten. This leads to large repulsion between the carbon lone-pair MO and the occupied orbitals at W. In fact, the CDA method shows that there is a substantial repulsive polarization for the $t_{1u}$ and $e_g$ orbitals (Table 3). However, the repulsive polarization for the $t_{2g}$ orbitals is also large. It is interesting to note that the repulsive polarization of the $a_{1g}$ orbitals is positive. There is no information by the CDA about the importance of these charge contributions upon the energy. The conclusion is that the amount of donation and back-donation must not be used as a measure of the binding energy. The CDA results are, however, a measurement of the change in the electronic structure in terms of donation and back-donation. This is an important information, because the metal–ligand bond lengths and bond strengths are often classified with regard to the donation/back-donation strength of the ligands.

An important question about the results of the CDA calculations concerns the basis set superposition error (BSSE). A part of the orbital mixing between the ligand and the metal is caused by the truncated basis sets. We have studied the influence of the BSSE upon the CDA results.[25] It was found that larger basis sets beyond the DZP level give very similar results for the ratio between donation and back-donation, as predicted when

**Table 3. Results of the Charge Decomposition Analysis of $W(CO)_6$: Calculated HF/II (MP2/II) Donation *d*, Back-Donation *b*, and Repulsive Polarization *r***

| orb | occ | *d* | *b* | *r* |
|---|---|---|---|---|
| $a_{1g}$ | 2.0 (1.96) | +0.010 (−0.002) | −0.001 (−0.003) | +0.068 (+0.007) |
| $e_g$ | 2.0 (1.97) | 0.000 (−0.001) | −0.004 (−0.001) | −0.028 (−0.008) |
| $e_g$ | 2.0 (1.97) | 0.000 (−0.003) | 0.000 (−0.004) | 0.000 (−0.022) |
| $t_{1u}$ | 2.0 (1.95) | 0.000 (+0.001) | +0.001 (+0.004) | +0.001 (+0.010) |
| $t_{1u}$ | 2.0 (1.95) | 0.000 (+0.003) | +0.001 (+0.021) | +0.001 (−0.046) |
| $t_{1u}$ | 2.0 (1.95) | −0.002 (+0.004) | −0.003 (+0.025) | −0.020 (+0.056) |
| $a_{1g}$ | 2.0 (1.98) | +0.024 (+0.036) | −0.008 (−0.005) | +0.066 (+0.097) |
| $t_{2g}$ | 2.0 (1.95) | 0.000 (+0.013) | 0.000 (−0.004) | 0.000 (−0.071) |
| $t_{2g}$ | 2.0 (1.95) | +0.003 (+0.007) | +0.003 (−0.002) | +0.029 (−0.033) |
| $t_{2g}$ | 2.0 (1.95) | +0.003 (+0.005) | +0.003 (−0.002) | +0.029 (−0.018) |
| $t_{1u}$ | 2.0 (1.97) | +0.023 (+0.003) | −0.003 (+0.002) | +0.011 (−0.005) |
| $t_{1u}$ | 2.0 (1.97) | +0.003 (+0.013) | +0.001 (−0.002) | +0.023 (−0.034) |
| $t_{1u}$ | 2.0 (1.97) | +0.003 (+0.011) | +0.001 (−0.001) | +0.023 (−0.029) |
| $e_g$ | 2.0 (1.96) | 0.000 (+0.048) | 0.000 (+0.008) | 0.000 (−0.018) |
| $e_g$ | 2.0 (1.96) | +0.143 (+0.102) | +0.015 (+0.016) | −0.079 (−0.037) |
| $t_{2u}$ | 2.0 (1.95) | 0.000 (+0.001) | 0.000 (−0.002) | 0.000 (−0.006) |
| $t_{2u}$ | 2.0 (1.95) | 0.000 (+0.001) | 0.000 (−0.002) | −0.004 (−0.006) |
| $t_{2u}$ | 2.0 (1.95) | 0.000 (0.000) | 0.000 (0.000) | −0.004 (0.000) |
| $t_{1g}$ | 2.0 (1.95) | 0.000 (0.000) | 0.000 (0.000) | 0.000 (−0.003) |
| $t_{1g}$ | 2.0 (1.95) | +0.002 (+0.001) | 0.000 (−0.003) | −0.015 (−0.018) |
| $t_{1g}$ | 2.0 (1.95) | +0.002 (+0.001) | 0.000 (−0.002) | −0.015 (−0.017) |
| $t_{1u}$ | 2.0 (1.96) | 0.000 (+0.130) | +0.004 (−0.003) | −0.020 (−0.113) |
| $t_{1u}$ | 2.0 (1.96) | 0.000 (+0.015) | +0.004 (+0.004) | −0.020 (+0.001) |
| $t_{1u}$ | 2.0 (1.96) | +0.169 (+0.021) | −0.014 (+0.004) | −0.226 (−0.005) |
| $t_{2g}$ | 2.0 (1.91) | 0.000 (−0.003) | 0.000 (+0.050) | 0.000 (−0.034) |
| $t_{2g}$ | 2.0 (1.91) | −0.008 (−0.006) | +0.093 (+0.086) | −0.048 (−0.058) |
| $t_{2g}$ | 2.0 (1.91) | −0.008 (−0.005) | +0.093 (+0.073) | −0.048 (−0.050) |
| $\sum a_{1g}$ | | +0.033 (+0.023) | −0.011 (−0.008) | +0.138 (+0.145) |
| $\sum e_g$ | | +0.133 (+0.111) | +0.009 (+0.015) | −0.105 (−0.071) |
| $\sum t_{1u}$ | | +0.195 (+0.166) | −0.009 (+0.044) | −0.224 (−0.139) |
| $\sum t_{2g}$ | | −0.010 (+0.011) | +0.188 (+0.191) | −0.037 (−0.184) |
| $\sum t_{2u}$ | | 0.000 (−0.004) | 0.000 (−0.004) | −0.007 (−0.007) |
| $\sum t_{1g}$ | | +0.003 (+0.002) | 0.000 (−0.005) | −0.027 (−0.022) |
| $\sum$ | | +0.354 (+0.315) | +0.177 (+0.233) | −0.262 (−0.278) |
| $\sum$ | HF//MP2 | +0.342 | +0.177 | −0.307 |
| $\sum$ | TZ2P | +0.376 (+0.316) | +0.156 (+0.184) | −0.274 (−0.305) |

basis set II is used. For example, the donation and back-donation of $W(CO)_6$ at MP2/TZ2P are 0.316 and 0.184 e, respectively.[25]

The total contributions of the charge donation, back-donation, and repulsive polarization calculated at MP2/II for the $M(CO)_5L$ complexes are shown in Table 4. There is a significant charge donation and back-donation for L = CO in the three $M(CO)_6$ complexes. This is in agreement with the C−O stretching frequency observed for $M(CO)_6$ being lower than that for CO, which is explained by the charge donation from the metal into the $\pi^*$ orbital of CO.[6,14] The CDA indicates that SiO has also a substantial back-donation from the metal. The donation and back-donation of SiO are slightly smaller than those of CO (Table 4). Also, CS shows a large donation and a back-donation, which are larger than those of CO. The back-donation is always larger than the donation, opposite to what is calculated for CO. This is in agreement with the general classification of CS as a stronger $\pi$ acceptor than CO.[9] Also, $N_2$ is predicted by the CDA to be a stronger $\pi$ acceptor than a donor. The same conclusion about the nature of the $N_2$ ligand was made using the analysis of the Mössbauer spectra of several dinitrogen complexes.[70] The CDA results indicate that $N_2$ is a weaker $\sigma$ donor *and* a weaker $\pi$ acceptor than CO, which is in agreement with the common classification of the two ligands.[8] The CDA results also show higher metal→ligand back-donation than ligand→metal donation for $NO^+$ (Table 4). This should be expected, because the positive charge lowers the orbital energies of the ligand, which increases the acceptor strength and decreases the donor strength.

The ligand behavior opposite to that for $NO^+$ is calculated for $CN^-$ and $NC^-$. The CDA results show clearly that the negatively charged ligands are nearly exclusively donors; the amount of back-donation is negligible compared with the donation (Table 4). Also, the acetylene ligand has a larger donation than back-donation in $M(CO)_5(HCCH)$. This is an interesting result because the sizes of the ($\pi$) donor and ($\pi^*$) acceptor orbitals of HCCH are the same.[71] The isomeric vinylidene ligand $CCH_2$ is also a stronger donor than acceptor. The same holds true for the carbene ligands $CH_2$ and $CF_2$. The CDA results indicate that $CF_2$ is a stronger donor and a stronger acceptor than $CH_2$ in the $Cr(CO)_5$−carbene complexes, although $CH_2$ is more strongly bound than $CF_2$ (Tables 1 and 4). This indicates clearly that the amount of charge donation and back-donation should not be used as a measure of the bond strength.

The results of the CDA calculations for the $M(CO)_5H_2$ complexes have already been reported.[21h] The barrier to rotation about the metal−$H_2$ axis suggests that $d(\pi)\rightarrow\sigma^*$ back-bonding is important in these compounds.[61] Previous theoretical studies indicate that both $H_2$→metal $\sigma$ bonding and metal→$H_2$ $\pi$ back-

---

[70] (a) Morris, R. H.; Schlaf, M. *Inorg. Chem.* **1994**, *33*, 1725. (b) Bancroft, G. M.; Mays, M. J.; Prater, B. E.; Stefanini, F. P. *J. Chem. Soc. A* **1970**, 2146.

[71] The labelling of $\sigma$ and $\pi$ symmetry of the complexes is made in regard to the metal−ligand axis. In some cases a $\sigma$-symmetric orbital in a complex has $\pi$ symmetry for the ligand. For example, the $\pi$ orbital of acetylene has $\sigma$ symmetry in the complex.

**Table 4. Results of the Charge Decomposition Analysis of M(CO)$_5$L Complexes: Calculated (MP2/II) Donation *d*, Back-Donation *b*, and Repulsive Polarization *r* of the Ligands L**

| molecule | sym | *d* | *b* | *r* |
|---|---|---|---|---|
| Cr(CO)$_6$ | $O_h$ | 0.460 | 0.314 | −0.266 |
| Mo(CO)$_6$ | $O_h$ | 0.342 | 0.244 | −0.255 |
| W(CO)$_6$ | $O_h$ | 0.315 | 0.233 | −0.278 |
| Cr(CO)$_5$SiO | $C_{4v}$ | 0.299 | 0.208 | −0.374 |
| Mo(CO)$_5$SiO | $C_{4v}$ | 0.138 | 0.231 | −0.254 |
| W(CO)$_5$SiO | $C_{4v}$ | 0.214 | 0.213 | −0.239 |
| Cr(CO)$_5$CS | $C_{4v}$ | 0.310 | 0.345 | −0.426 |
| Mo(CO)$_5$CS | $C_{4v}$ | 0.292 | 0.337 | −0.373 |
| W(CO)$_5$CS | $C_{4v}$ | 0.259 | 0.308 | −0.387 |
| Cr(CO)$_5$N$_2$ | $C_{4v}$ | 0.166 | 0.173 | −0.214 |
| Mo(CO)$_5$N$_2$ | $C_{4v}$ | 0.028 | 0.094 | −0.206 |
| W(CO)$_5$N$_2$ | $C_{4v}$ | 0.027 | 0.107 | −0.252 |
| Cr(CO)$_5$NO$^+$ | $C_{4v}$ | 0.152 | 0.326 | −0.274 |
| Mo(CO)$_5$NO$^+$ | $C_{4v}$ | 0.108 | 0.386 | −0.313 |
| W(CO)$_5$NO$^+$ | $C_{4v}$ | 0.119 | 0.378 | −0.318 |
| Cr(CO)$_5$CN$^-$ | $C_{4v}$ | 0.604 | 0.089 | −0.206 |
| Mo(CO)$_5$CN$^-$ | $C_{4v}$ | 0.499 | 0.043 | −0.211 |
| W(CO)$_5$CN$^-$ | $C_{4v}$ | 0.488 | 0.024 | −0.241 |
| Cr(CO)$_5$NC$^-$ | $C_{4v}$ | 0.482 | 0.038 | −0.188 |
| Mo(CO)$_5$NC$^-$ | $C_{4v}$ | 0.358 | 0.005 | −0.219 |
| W(CO)$_5$NC$^-$ | $C_{4y}$ | 0.361 | 0.002 | −0.252 |
| Cr(CO)$_5$HCCH | $C_{2v}$ | 0.516 | 0.186 | −0.372 |
| Mo(CO)$_5$HCCH | $C_{2v}$ | 0.301 | 0.191 | −0.354 |
| W(CO)$_5$HCCH | $C_{2v}$ | 0.315 | 0.213 | −0.419 |
| Cr(CO)$_5$CCH$_2$ | $C_{2v}$ | 0.364 | 0.322 | −0.380 |
| Mo(CO)$_5$CCH$_2$ | $C_{2v}$ | 0.420 | 0.349 | −0.344 |
| W(CO)$_5$CCH$_2$ | $C_{2v}$ | 0.404 | 0.324 | −0.348 |
| Cr(CO)$_5$CH$_2$ | $C_{2v}$ | 0.331 | 0.238 | −0.375 |
| Mo(CO)$_5$CH$_2$ | $C_{2v}$ | 0.318 | 0.300 | −0.355 |
| W(CO)$_5$CH$_2$ | $C_{2v}$ | 0.314 | 0.282 | −0.370 |
| Cr(CO)$_5$CF$_2$ | $C_{2v}$ | 0.494 | 0.264 | −0.237 |
| Mo(CO)$_5$CF$_2$ | $C_{2v}$ | 0.375 | 0.245 | −0.253 |
| W(CO)$_5$CF$_2$ | $C_{2v}$ | 0.369 | 0.219 | −0.289 |
| Cr(CO)$_5$H$_2$ | $C_{2v}$ | 0.393 | 0.143 | −0.147 |
| Mo(CO)$_5$H$_2$ | $C_{2v}$ | 0.315 | 0.105 | −0.117 |
| W(CO)$_5$H$_2$ | $C_{2v}$ | 0.349 | 0.129 | −0.105 |

bonding are important in the complexes.[62b,72] From the plot of isomer shift versus quadrupole splitting of the Mössbauer spectra of several iron complexes it was concluded that "$\pi$-bonding in transition metal dihydrogen complexes is very significant, more so than for N$_2$ or CO complexes".[70a] The results of the CDA calculation show that M→H$_2$ back-donation is important for the M(CO)$_5$H$_2$ complexes (Table 4). However, the H$_2$→M donation is clearly stronger than the $\pi$ back-donation! It follows that H$_2$ should be considered as a stronger donor than an acceptor in transition-metal complexes.

The calculated geometries of the M(CO)$_5$L complexes (Table 1) show that the lengths of the M−CO bonds cis and trans to M−L are in most cases very different. The M−L bond has a distinct influence upon the M−CO$_{\mathrm{trans}}$ bond length. In some case, M−CO$_{\mathrm{trans}}$ is clearly longer than M−CO$_{\mathrm{cis}}$, while the opposite is found in other cases. The longest M−CO$_{\mathrm{trans}}$ bonds are calculated for M(CO)$_5$NO$^+$, M(CO)$_5$CS, and the carbene complexes of Mo and W (Table 1). The CDA results classify these ligands as strong $\pi$ acceptors. The shortest M−CO$_{\mathrm{trans}}$ distances are calculated for M(CO)$_5$CN$^-$, M(CO)$_5$NC$^-$, M(CO)$_5$H$_2$, and M(CO)$_5$N$_2$. Although N$_2$ binds mainly through metal→N$_2$ back-bonding, the rather weak electron-withdrawing strength makes the M−CO$_{\mathrm{trans}}$ bond stronger. Figure 2a shows a plot between the calculated M−CO$_{\mathrm{trans}}$ bond length of M(CO)$_5$L and the calculated L→M donation. There is no correlation between the two sets of data. Figure 2b shows the analogous plot of the M−CO$_{\mathrm{trans}}$ bond length and the M→L back-donation. The plot demonstrates clearly that *ligands which are strong acceptors tend to increase the M−CO$_{trans}$ bond, while ligands which are poor acceptors tend to decrease the M−CO$_{trans}$ bond.*

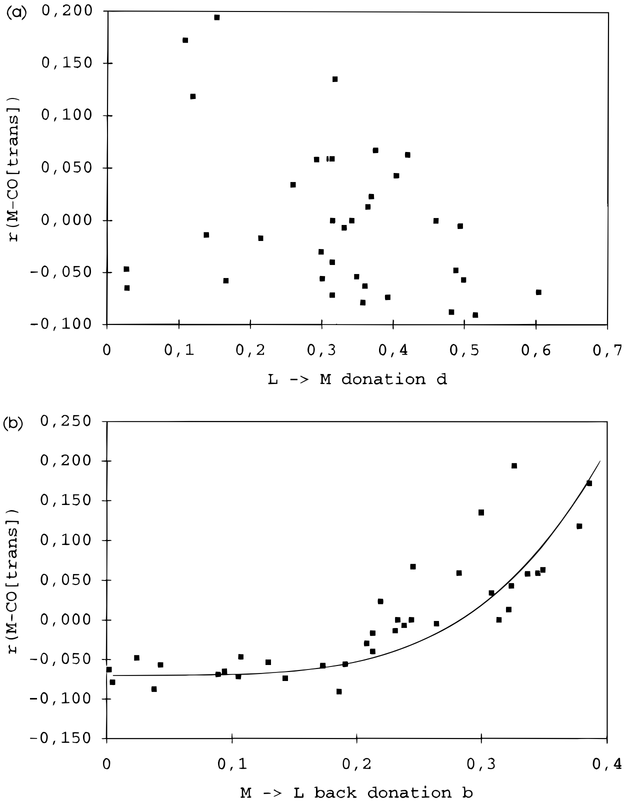

**Figure 2.** (a) Plot of the calculated L→M electron donation and the change of the M−CO$_{\mathrm{trans}}$ bond length relative to that in M(CO)$_6$. (b) Plot of the calculated M→L back-donation and the change of the M−CO$_{\mathrm{trans}}$ bond length relative to that in M(CO)$_6$. Negative values indicate that the M−CO$_{\mathrm{trans}}$ bond is shorter than in M(CO)$_6$.

Because the orbital interactions in tetrahedral ML$_4$ complexes are quite different from those in ML$_6$ complexes, we discuss the CDA results for Ni(CO)$_4$ in more detail before we present the analysis for the other M(CO)$_3$L complexes. Figure 3 shows a qualitative orbital interaction diagram between a d$^{10}$ metal and four CO ligands. The main difference from the ML$_6$ diagram shown in Figure 1 is that there is no empty metal d orbital in the tetrahedral ML$_4$ complex. It follows that electron donation from the $\sigma$ lone-pair orbital of CO into the metal d orbitals of an *unperturbed* (d$^{10}$) Ni atom is

---

(72) (a) Hay, P. J. *J. Am. Chem. Soc.* **1987**, *109*, 705. (b) Jean, Y.; Lledos, A.; Maouche, B.; Aiad, R. *J. Chim. Phys. Phys.-Chim. Biol.* **1987**, *84*, 805. (c) Maseras, F.; Duran, M.; Lledos, A.; Bertran, J. *J. Am. Chem. Soc.* **1991**, *113*, 2879. (d) Albinati, A.; Bakhmutov, V. I.; Caulton, K. G.; Clot, E.; Eckert, J.; Eisenstein, O.; Gusev, D. G.; Grushin, V. V.; Hauger, B. E.; Klooster, W. T.; Koetzle, T. F.; McMullan, R. K.; O'Loughlin, T. J.; Pelissier, M.; Ricci, R. S.; Sigalas, M. P.; Vymenits, A. B. *J. Am. Chem. Soc.* **1993**, *115*, 7300.

(73) (a) Herzberg, G. *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules*; Krieger: Malabar, 1989. (b) Mockler, R. C.; Bird, G. R. *Phys. Rev.* **1955**, *98*, 1837. (c) *International Tables of X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974. (d) Botschwina, P. *Chem. Phys. Lett.* **1985**, *114*, 58. (e) Gallo, M. M.; Hamilton, T. P.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1990**, *112*, 8714. (f) Harmony, M. D.; Laurie, V. W.; Kuezkowski, R. L.; Schwendenman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data Ser.* **1979**, *8*, 619. (g) Jost, A.; Rees, B. *Acta Crystallogr.* **1975**, *B31*, 2649. (h) Braga, D.; Grepioni, F.; Orpen, A. G. *Organometallics* **1993**, *12*, 1481. (i) Stevens, A. E.; Feigerle, C. S.; Lineberger, W. C. *J. Am. Chem. Soc.* **1982**, *104*, 5026.

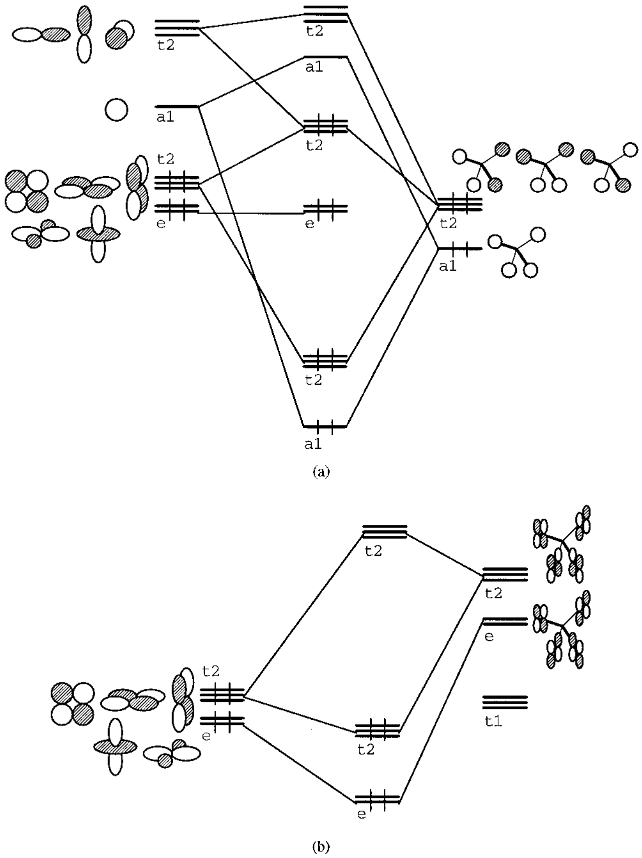

**Figure 3.** Orbital interaction diagram for tetrahedral complexes $ML_4$ with $d^{10}$ metals M: (a) $\sigma$ interactions; (b) $\pi$ interactions.

not possible. OC→M donation is possible, however, because the (*n*)s and (*n*)p valence orbitals of the metal are empty. Thus, d/p hybridization makes partial donation into the metal d orbitals possible. Figure 3 shows that the OC→M donation in $M(CO)_4$ should take place mainly via the $t_2$ and $a_1$ orbitals. The M→CO back-donation into the empty $\pi^*$ orbitals of CO is also shown in Figure 3. The eight $\pi^*$ valence orbitals of CO form three sets of orbitals with $t_2$, e, and $t_1$ symmetry. The empty $t_2$ and e orbitals of the ligands can interact with the occupied metal d orbitals of the same symmetry. Thus, the dominant M→CO back-donation should take place via the $t_2$ and e orbitals.

Table 5 shows that the CDA results for $Ni(CO)_4$ agree with the qualitative model exhibited in Figure 3. The OC→Ni donation takes place only through the $a_1$ and $t_2$ orbitals. The donation of the $t_2$ orbitals is clearly larger than that of the $a_1$ orbitals. The back-donation is dominated by the e and $t_2$ orbitals. There is a substantial charge polarization of the $t_2$ orbitals, as given by the *r* term (Table 5). This is reasonable, because there is significant repulsive interaction between the occupied orbitals with $t_2$ symmetry of the metal and the ligands. The total amount of charge donation at the MP2/II level is twice as large (0.394 e) as the back-donation (0.195 e).

The total amount of charge donation, back-donation, and repulsive polarization of the $M(CO)_3L$ complexes calculated at MP2/II is shown in Table 6. In general, the nature of the ligands is the same in $M(CO)_3L$ as in the $M(CO)_5L$ complexes, which should be expected. $CN^-$ and $NC^-$ are pure $\sigma$ donors. This is interesting, because it has been suggested that the driving force for the metal−CO bond in $M(CO)_6$ and $M(CO)_4$ complexes is mainly due to the metal→CO back-bonding.[16,19a−d] The CDA results suggest that for $CN^-$ and $NC^-$ the ligand→metal $\sigma$ bonding may be the dominant driving force for the bonding. Although there is no direct correlation between the donation and the bond strength, the near-absence of $\pi$ back-donation indicates that the contribution to the bond energy should be negligible. The other ligands have a substantial $\pi$-acceptor contribution in the $M(CO)_3L$ complexes. It is interesting to note that the CDA charge terms for $Ni(CO)_3H_2$ are rather large, although the $Ni-H_2$ bond is very weak.

**Table 5. Results of the Charge Decomposition Analysis of $Ni(CO)_4$: Calculated HF/II (MP2/II) Donation *d*, Back-Donation *b*, and Repulsive Polarization *r***

| orb. | occ | *d* | *b* | *r* |
|---|---|---|---|---|
| $a_1$ | 2.0 (1.976) | +0.038 (+0.084) | −0.014 (−0.019) | +0.072 (+0.123) |
| $t_2$ | 2.0 (1.888) | +0.006 (−0.008) | −0.001 (+0.047) | −0.010 (−0.030) |
| $t_2$ | 2.0 (1.888) | +0.008 (−0.017) | −0.001 (+0.018) | −0.013 (+0.003) |
| $t_2$ | 2.0 (1.888) | +0.003 (−0.006) | 0.000 (−0.052) | −0.005 (−0.036) |
| $a_1$ | 2.0 (1.966) | +0.046 (+0.009) | −0.025 (+0.013) | +0.106 (+0.011) |
| $t_2$ | 2.0 (1.966) | +0.001 (+0.043) | 0.000 (−0.002) | −0.001 (−0.053) |
| $t_2$ | 2.0 (1.966) | +0.056 (+0.019) | +0.006 (+0.009) | −0.032 (−0.008) |
| $t_2$ | 2.0 (1.966) | +0.029 (−0.004) | +0.003 (−0.003) | −0.017 (+0.009) |
| e | 2.0 (1.959) | +0.001 (+0.003) | +0.003 (+0.017) | +0.018 (+0.025) |
| e | 2.0 (1.959) | +0.001 (+0.003) | +0.003 (+0.017) | +0.018 (+0.025) |
| $t_2$ | 2.0 (1.952) | +0.002 (+0.004) | +0.002 (−0.001) | +0.022 (−0.013) |
| $t_2$ | 2.0 (1.952) | +0.002 (+0.008) | +0.001 (−0.003) | +0.014 (−0.065) |
| $t_2$ | 2.0 (1.952) | +0.002 (+0.003) | +0.002 (0.000) | +0.021 (−0.003) |
| $t_1$ | 2.0 (1.947) | 0.000 (0.000) | 0.000 (−0.002) | −0.011 (−0.012) |
| $t_1$ | 2.0 (1.947) | 0.000 (0.000) | 0.000 (−0.001) | −0.004 (−0.004) |
| $t_1$ | 2.0 (1.947) | 0.000 (0.000) | −0.001 (−0.003) | −0.014 (−0.016) |
| e | 2.0 (1.910) | −0.002 (−0.001) | +0.026 (+0.033) | −0.018 (−0.025) |
| e | 2.0 (1.910) | −0.002 (−0.001) | +0.026 (+0.033) | −0.018 (−0.025) |
| $t_2$ | 2.0 (1.969) | +0.009 (+0.007) | +0.054 (+0.012) | −0.053 (+0.007) |
| $t_2$ | 2.0 (1.969) | +0.009 (+0.131) | +0.054 (−0.019) | −0.052 (−0.155) |
| $t_2$ | 2.0 (1.969) | +0.141 (+0.024) | −0.009 (+0.008) | −0.319 (−0.015) |
| $\sum a_1$ |  | +0.088 (+0.123) | −0.039 (−0.020) | +0.179 (+0.168) |
| $\sum e$ |  | −0.002 (+0.004) | +0.058 (+0.100) | 0.000 (0.000) |
| $\sum t_1$ |  | 0.000 (0.000) | −0.001 (−0.006) | −0.029 (−0.032) |
| $\sum t_2$ |  | +0.269 (+0.267) | +0.117 (+0.121) | −0.434 (−0.333) |
| $\sum$ |  | +0.355 (+0.394) | +0.135 (+0.195) | −0.281 (−0.197) |

**Table 6. Results of the Charge Decomposition Analysis of $M(CO)_3L$ Complexes: Calculated (MP2/II) Donation *d*, Back-Donation *b* and Repulsive Polarization *r* of the Ligands L**

| molecule | sym | *d* | *b* | *r* |
|---|---|---|---|---|
| $Ni(CO)_4$ | $T_d$ | 0.394 | 0.195 | −0.197 |
| $Pd(CO)_4$ | $T_d$ | 0.401 | 0.198 | −0.165 |
| $Pt(CO)_4$ | $T_d$ | 0.294 | 0.243 | −0.200 |
| $Ni(CO)_3SiO$ | $C_{3v}$ | 0.456 | 0.170 | −0.138 |
| $Pd(CO)_3SiO$ | $C_{3v}$ | 0.352 | 0.253 | −0.230 |
| $Pt(CO)_3SiO$ | $C_{3v}$ | 0.309 | 0.281 | −0.296 |
| $Ni(CO)_3CS$ | $C_{3v}$ | 0.344 | 0.261 | −0.271 |
| $Pd(CO)_3CS$ | $C_{3v}$ | 0.382 | 0.266 | −0.198 |
| $Pt(CO)_3CS$ | $C_{3v}$ | 0.233 | 0.318 | −0.291 |
| $Ni(CO)_3N_2$ | $C_{3v}$ | 0.172 | 0.130 | −0.195 |
| $Ni(CO)_3NO^+$ | $C_{3v}$ | 0.217 | 0.273 | −0.153 |
| $Pd(CO)_3NO^+$ | $C_{3v}$ | 0.160 | 0.372 | −0.258 |
| $Pt(CO)_3NO^+$ | $C_{3v}$ | 0.067 | 0.396 | −0.326 |
| $Ni(CO)_3CN^-$ | $C_{3v}$ | 0.518 | 0.014 | −0.212 |
| $Pd(CO)_3CN^-$ | $C_{3v}$ | 0.545 | 0.038 | −0.101 |
| $Pt(CO)_3CN^-$ | $C_{3v}$ | 0.409 | 0.036 | −0.123 |
| $Ni(CO)_3NC^-$ | $C_{3v}$ | 0.421 | 0.005 | −0.186 |
| $Pd(CO)_3NC^-$ | $C_{3v}$ | 0.428 | 0.006 | −0.136 |
| $Pt(CO)_3NC^-$ | $C_{3v}$ | 0.357 | 0.007 | −0.180 |
| $Ni(CO)_3HCCH$ | $C_s$ | 0.347 | 0.138 | −0.201 |
| $Pd(CO)_3HCCH$ | $C_s$ | 0.270 | 0.083 | −0.183 |
| $Pt(CO)_3HCCH$ | $C_s$ | 0.331 | 0.105 | −0.279 |
| $Ni(CO)_3CCH_2$ | $C_s$ | 0.375 | 0.202 | −0.249 |
| $Pd(CO)_3CCH_2$ | $C_s$ | 0.450 | 0.290 | −0.218 |
| $Pt(CO)_3CCH_2$ | $C_s$ | 0.290 | 0.330 | −0.305 |
| $Ni(CO)_3CH_2$ | $C_s$ | 0.332 | 0.183 | −0.200 |
| $Pd(CO)_3CH_2$ | $C_s$ | 0.429 | 0.307 | −0.232 |
| $Pt(CO)_3CH_2$ | $C_s$ | 0.344 | 0.331 | −0.304 |
| $Ni(CO)_3CF_2$ | $C_s$ | 0.399 | 0.170 | −0.186 |
| $Pd(CO)_3CF_2$ | $C_s$ | 0.419 | 0.201 | −0.179 |
| $Pt(CO)_3CF_2$ | $C_s$ | 0.338 | 0.242 | −0.230 |
| $Ni(CO)_3H_2$ | $C_s$ | 0.379 | 0.119 | −0.068 |

## Summary

The theoretically predicted metal−ligand bond lengths of the $M(CO)_5L$ and $M(CO)_3L$ complexes at the MP2/II level of theory are in very good agreement with experimental data. This holds for strongly bound ligands such as CS in the $M(CO)_5CS$ complexes, and for $H_2$ in $Cr(CO)_5H_2$. The calculated $(CO)_nM{-}L$ bond dissociation energies at CCSD(T)/II using the MP2/II-optimized geometries concur also with reported results. The calculated geometries and bond energies may be used as a reliable data source for those complexes where experimental data are not available. The analysis of the ab initio wave function of the complexes using the CDA method gives insight into the interaction between the ligands and the metal fragment in terms of donation, back-donation, and repulsive polarization. The OC→metal charge donation is higher than the metal→CO back-donation. The CDA results show significantly stronger back-donation for CS, $NO^+$, and $CCH_2$ than for CO. This is in agreement with the calculated $M{-}CO_{trans}$ bond lengths of the $M(CO)_5L$ complexes, which are significantly longer than the $M{-}CO_{cis}$ bond lengths and longer than the M−CO bonds of $M(CO)_6$. Clearly stronger donation than back-donation is calculated for $CN^-$, $NC^-$, HCCH, and $H_2$. The respective $M(CO)_5L$ complexes have $M{-}CO_{trans}$ bonds which are *shorter* than the $M{-}CO_{cis}$ bonds and the M−CO bonds of $M(CO)_6$. $CH_2$ and $CF_2$ are strong donors *and* strong acceptors. $N_2$ is a substantially weaker $\sigma$ donor and $\pi$ acceptor than CO. The donor and acceptor strengths of SiO are only slightly weaker than those of CO. The CDA results agree with the standard textbook classification of the nature of the ligands. The advantage of the CDA results is that the classification of relative donor/acceptor strength can be based on very accurate ab initio wave functions, while the nature of the ligand is usually discussed in terms of an assumed correlation between electronic factors and observable quantities.

**Acknowledgment.** This work was supported by the Deutsche Forschungsgemeinschaft (Grant No. SFB 260 and Graduiertenkolleg Metallorganische Chemie) and the Fonds der Chemischen Industrie. S.F.V. thanks the Deutscher Akademischer Austauschdienst for a scholarship. Excellent service by the Hochschulrechenzentrum of the Philipps-Universität Marburg is gratefully acknowledged. Additional computer time was provided by the HHLRZ Darmstadt and the HLRZ Jülich.

OM950697A