Next, we studied the $\mathrm{Cr{\equiv}C}$ triple bond in the cationic and neutral metal carbyne complexes, $\mathrm{(CO)_5Cr{\equiv}CH^+}$ and $\mathrm{Cl(CO)_4Cr{\equiv}CH}$, respectively, which show different reactivities for nucleophiles. The nature of the $\mathrm{Cr{\equiv}C}$ bond studied by the orbital-correlation diagram is similar to that of the $\mathrm{M{=}C}$ bond in the Fischer-type carbene complexes. The polarization of the $\mathrm{Cr{\equiv}C}$ bond is calculated to be $\mathrm{Cr(1.06+)}$—$\mathrm{C(0.31-)}$ for $\mathrm{(CO)_5Cr{\equiv}CH^+}$ and $\mathrm{Cr(0.90+)}$—$\mathrm{C(0.42-)}$ for $\mathrm{Cl(CO)_4Cr{\equiv}CH}$. Just as the Fischer-type carbene complex, the carbyne carbon atom is negatively charged in contradiction with the idea of the charge-controlled reactivity. The reactivity of the carbyne complexes can be explained clearly by the frontier orbital theory. The differences in the reactivity between the cationic and neutral carbyne complexes are explained from the existence of the nearly degenerate LUMO and next LUMO in the frontier MO region of the neutral complex. They would never be explained by the charge-controlled mechanism.

Thus, the nature of the metal–carbon multiple bonds in the Fischer-type and Schrock-type carbene complexes and in the carbyne complex has been clarified theoretically by the previous[12] and present studies. The reactivities of these metal–carbon multiple bonds are understood in a unified form on the basis of the frontier orbital theory.

Acknowledgment. For the SCF calculations we have used a slightly modified version of the HONDOG program by King, Dupuis, and Rys whom the author would like to acknowledge. Calculations were carried out with the HITAC M-200H computer at the Institute for Molecular Science and with the FACOM M-382 computer at the Data Processing Center of Kyoto University. Part of this study was supported by the Japan Society for the Promotion of Science.

Registry No. $\mathrm{H_2(CH_3)Nb{=}CH_2}$, 91711-58-9; $\mathrm{(CO)_5Cr{\equiv}CH^+}$, 91711-56-7; $\mathrm{Cl(CO)_4Cr{\equiv}CH}$, 91711-57-8.

Theoretical Study of Multiple Metal–Metal Bonds in Binuclear Complexes of Group 6D and Group 7D Transition Elements with the General Formula $\mathrm{M_2Cl_4(PH_3)_4}^{n+}$ (n = 0, 1, 2) by the Hartree–Fock–Slater Transition-State Method

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Abstract: Hartree–Fock–Slater calculations are reported on $\mathrm{M_2Cl_4(PH_3)_4}^{n+}$ for M = Mn, Tc, Re with n = 0, 1, 2, as well as for M = Mo with n = 0, 1 and M = Cr, W with n = 0. The calculated metal–metal bond energies for n = 0 are $D(\mathrm{Cr}\overset{4}{-}\mathrm{Cr})$ = 153 kJ mol^{-1}, $D(\mathrm{Mo}\overset{4}{-}\mathrm{Mo})$ = 524 kJ mol^{-1}, and $D(\mathrm{W}\overset{4}{-}\mathrm{W})$ = 428 kJ mol^{-1}, respectively. The calculated bond strengths in $\mathrm{M_2Cl_4(PH_3)_4}$ for M = Mn, Tc, and Re were $D(\mathrm{Mn}\overset{4}{-}\mathrm{Mn})$ = 295 kJ mol^{-1}, $D(\mathrm{Tc}\overset{4}{-}\mathrm{Tc})$ = 599 kJ mol^{-1}, and $D(\mathrm{Re}\overset{4}{-}\mathrm{Re})$ = 562 kJ mol^{-1}, respectively. An energy-decomposition analysis provided a possible explanation for the relative strength of the metal–metal bond between 3d, 4d, and 5d elements. The analysis indicated further that the δ bond is rather weak. The contribution from relativistic effects to the metal–metal bond in the binuclear complexes of 5d elements was calculated to be small.

I. Introduction

The number of well-characterized binuclear complexes[1] of the general formula $\mathrm{M_2(X)_m(L)_{8-m}}^{n+}$, where X represents halides and L phosphines, has grown considerably over the past 20 years, following the recognition[2] of a quadrupole bond in $\mathrm{Re_2Cl_8}^{2-}$. It is now known[1] that W, Mo, Re, and to some extent Tc can form binuclear complexes of the type $\mathrm{M_2(X)_m(L)_{8-m}}^{n+}$ in which the metal–metal bond order is 3, 3.5, and 4, whereas $\mathrm{M_2(X)_m(L)_{8-m}}^{n+}$ systems of either Cr or Mn are unknown.

Cotton[2] described in 1965 the quadrupole bond of $\mathrm{Re_2Cl_8}^{2-}$ in terms of one σ bond, two π bonds, and one δ bond. The essence of this bonding scheme has since been confirmed by SCF-Xα-SW calculations[3] on several $\mathrm{M_2(X)_m(L)_{8-m}}^{n+}$ systems. However, a number of recent theoretical works[4] have shown that a simple molecular orbital picture is inadequate for a quantitative description of the weak δ bond.

Theoretical investigations to date have concentrated mainly on the assignment of electronic spectra. There has been much less emphasis on an evaluation of the metal–metal bond strength.[5] This is in a way unfortunate since it has proven difficult experimentally[1a] to assess metal–metal bond energies. There is as a consequence not a clear understanding of how the σ component, the two π components, and the δ component contribute in relative terms to the bond strength. Lack of experimental and theoretical data has also made it difficult to evaluate[1b] variations in the bond strength between 3d, 4d, and 5d elements.

The Xα method as implemented by Baerends[6] et al. (LCAO-HFS method) has previously, in connection with the generalized

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(1) (a) Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982. (b) Cotton, F. A. *Chem. Soc. Rev.* **1983**, *12*, 35.

(2) Cotton, F. A. *Inorg. Chem.* **1965**, *4*, 334.

(3) (a) Norman, J. G., Jr.; Kolari, H. J. *J. Am. Chem. Soc.* **1975**, *97*, 33. (b) Mortala, A. P.; Moskowitz, J. W.; Rosch, N.; Cowan, C. D.; Gray, H. B. *Chem. Phys. Lett.* **1975**, *32*, 283. (c) Cotton, F. A.; Hubbard, J. L.; Lichtenberger, D. L.; Shim, I. *J. Am. Chem. Soc.* **1982**, *104*, 679. (d) Bursten, B. E.; Cotton, F. A.; Fanwick, P. E.; Stanley, G. G. *J. Am. Chem. Soc.* **1983**, *105*, 3082. (e) Bursten, B. E.; Cotton, F. A.; Fanwick, P. E.; Stanley, G. G.; Walton, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 2606.

(4) (a) Benard, M.; Veillard, A. *Nouv. J. Chim.* **1977**, *1*, 97. (b) Guest, M. F.; Hillier, I. H.; Garner, C. D. *Chem. Phys. Lett.* **1977**, *48*, 587. (c) Hay, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 2897. (d) Correa de Mello, P.; Edwards, W. D.; Zerner, M. C. *J. Am. Chem. Soc.* **1982**, *104*, 1440. (e) Hay, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 7007. (f) Hall, M. B. *J. Am. Chem. Soc.* **1980**, *102*, 2104.

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(6) (a) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41. (b) Baerends, E. J.; Ros, P. *Int. J. Quantum Chem.* **1978**, *S12*, 169.

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transition-state method,[7] proved to be useful in calculating[8] the metal bond strengths of Au_2 and Hg_2^{2+} as well as[5b] Cr_2L_6, Mo_2L_6, and W_2L_6. We present here similar calculations on some $M_2Cl_4(PH_3)_4^{n+}$ model systems.

The calculated energies of the triple bonds in $Mn_2Cl_4(PH_3)_4$, $Tc_2Cl_4(PH_3)_4$, and $Re_2Cl_4(PH_3)_4$ are given in section V.1, decomposed into the various contributions from the σ, π, and δ components, along with the optimized metal–metal bond distances. The quadrupole-bonded systems $Cr_2Cl_4(PH_3)_4$, $Mo_2Cl_4(PH_3)_4$, and $W_2Cl_4(PH_3)_4$ are analyzed in a similar way in section V.2. The difference in strength between the triple metal–metal bond and the quadrupole metal–metal bond is studied further in section V.3 by calculations on the $M_2Cl_4(PH_3)_4^{n+}$ model systems of M = Mn, Tc, Re with $n = 0, 1, 2$. Calculations on various excited states of $Mo_2Cl_4(PH_3)_4^+$ are finally used in section V.4 to demonstrate the extent to which a change in the occupation of the σ-, π-, and δ-metal-bonding orbitals can change the metal–metal bond distance.

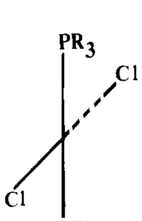
II. Computational Details

1. Basis Set and Computational Procedures. The calculations were based on the HFS method as implemented by Baerends et al.[6] The molecular orbitals were calculated as linear combinations of atomic orbitals (LCAO). The 3s, 3p valence shells on Cl and P as well as the *n*s, *n*p, *n*d, $(n + 1)$s, $(n + 1)$p valence shells on the metal were all represented by a triple-ζ STO-basis set.[9] The core electrons of lower energy were described in the frozen core approximation according to the procedure by Baerends et al.[6] Two 3d STO orbitals were added to each P atom as polarization functions. Three 1s STO's were used on each H atom. The total electron density was fitted in each SCF iteration by s, p, d STO's on H, Cl, P and s, p, d, f, g STO's on the metal atoms, in order to represent the Coulomb and exchange potentials accurately. A standard exchange factor of $\alpha = 0.7$ was used for all the molecules.

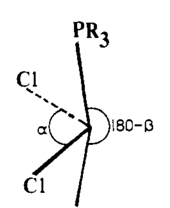
2. Geometries. The metal-to-metal bond distances were optimized for all the binuclear complexes. The additional geometrical parameters were as follows. The geometrical parameters for $Re_2Cl_4(PH_3)_4^{n+}$ were those given by Bursten[3e] et al. for $Re_2Cl_4(PH_3)_4$. The geometries for $Mo_2Cl_4(PH_3)_4$ and $W_2Cl_4(PH_3)_4$ were those given by Cotton[3c] et al. The Mn–Cl and Cr–Cl distances were taken to be 2.29 Å, and the Mn–P and Cr–P distances were taken to be 2.43 Å in $Mn_2Cl_4(PH_3)_4^{n+}$ and $Cr_2Cl_4(PH_3)_4$. This is in both cases 0.12 Å shorter than the known Mo–Cl and Mo–P distances in $Mo_2Cl_4(PR_3)_4$. All other parameters in $Mn_2Cl_4(PH_3)_4^{n+}$ and $Cr_2Cl_4(PH_3)_4$ were the same as in $Mo_2Cl_4(PH_3)_4$. The model systems $Tc_2Cl_4(PH_3)_4^{n+}$ were given the same geometries as in $Mo_2Cl_4(PH_3)_4$.

III. Electronic Structure of the $MCl_2(PH_3)_2$ Fragment

It is convenient to consider the binuclear complex $M_2Cl_4(PH_3)_4$ as a dimer of the $MCl_2(PH_3)_2$ fragment and begin a discussion of the metal–metal bond by looking briefly at the orbitals of the $MCl_2(PH_3)_2$ unit.[10] The $MCl_2(PR_3)_2$ fragments in $M_2Cl_4(PR_3)_4$ are somewhat distorted away from an ideal pseudo-square-planar conformation **1** by reductions in the Cl–M–Cl angle α and the P–M–P angle β from 180° to 130° and 160°, respectively, ,2.



1



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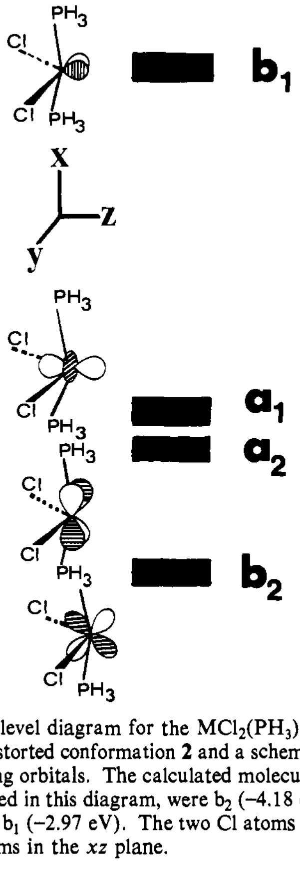


Figure 1. Orbital level diagram for the $MCl_2(PH_3)_2$ fragment of C_{2v}-symmetry in the distorted conformation **2** and a schematic representation of the corresponding orbitals. The calculated molecular orbital energies of $TcCl_2(PH_3)_2$, used in this diagram, were b_2 (−4.18 eV), a_2 (−3.84 eV), a_1 (−3.74 eV), and b_1 (−2.97 eV). The two Cl atoms are in the *yz* plane and the two P atoms in the *xz* plane.

Calculations on $MnCl_2(PH_3)_2$, $TcCl_2(PH_3)_2$, and $ReCl_2(PH_3)_2$ in conformation **1** as well as conformation **2** showed that the distortion from the pseudo-square-planar conformation **1** to **2** required 10 kJ mol^{-1} or less.

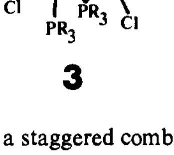
Figure 1 presents the four highest occupied orbitals of the $MCl_2(PH_3)_2$ fragment in conformation **2**. All four orbitals are metal-ligand antibonding of primarily d character. The orbitals $b_1(d_{yz})$ and $b_2(d_{xz})$ both have π symmetry with respect to the C_2 axis of the fragment, whereas $a_1(d_{z^2})$ and $a_2(d_{xy})$ are of σ symmetry and δ symmetry, respectively. The four orbitals in Figure 1 are in energy within 1 eV of each other. The b_1 orbital is highest in energy since[10] d_{yz} in the distorted conformation **2** with $\alpha = 130°$ has a large antibonding interaction with the σ-ligand orbitals on the two Cl atoms.

The $MCl_2(PH_3)_2$ unit has C_{2v} symmetry in conformation **1** as well as conformation **2**. The d^5 fragments $MnCl_2(PH_3)_2$, $TcCl_2(PH_3)_4$, and $ReCl_2(PH_3)_2$ were in both **1** and **2** calculated to have the high-spin ground-state configuration $(a_2)^2(a_1)^1(b_1)^1(b_2)^1$ corresponding to the symmetry term $^4A_2$.

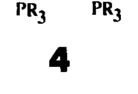
The d^4 fragments $MnCl_2(PH_3)_2^+$, $TcCl_2(PH_3)_2^+$, $ReCl_2(PH_3)_2^+$, $CrCl_2(PH_3)_2$, $MoCl_2(PH_3)_2$, and $WCl_2(PH_3)_2$ all had a $(a_1)^1(a_2)^1(b_1)^1(b_2)^1$ high-spin ground-state configuration of $^5A_1$ symmetry.

IV. Electronic Structure of $M_2Cl_4(PH_3)_4^{n+}$

1. General Considerations. The observed[1] structure of $M_2Cl_4(PR_3)_4$ for M = Mo, W, Re is that of two deformed $MCl_2(PR_3)_2$ fragments **2** combined into a staggered conformation **3** of D_{2d} symmetry, as opposed to an eclipsed arrangement **4**, or



3



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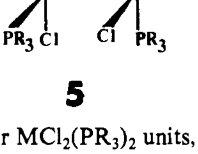

5

a staggered combination of two square-planar $MCl_2(PR_3)_2$ units,

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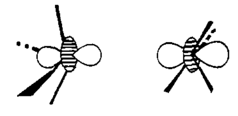
[7] Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1.

[8] Ziegler, T.; Snijders, J. G.; Baerends, E. J. *J. Chem. Phys.* **1981**, *74*, 1271.

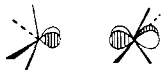
[9] Snijders, G. J.; Baerends, E. J.; Vernooijs, P. *At. Nuc. Data Tables* **1982**, *26*, 483; and private communication.

[10] Dedieu, A.; Albright, T. A.; Hoffman, R. *J. Am. Chem. Soc.* **1979**, *101*, 3141.

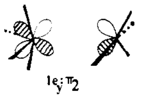
5. Calculations on $Tc_2Cl_4(PH_3)_4$ showed **4** to be 230 kJ mol^{-1} higher in energy than **3**, and **5** to be unstable with respect to the two $M(Cl)_2(PH_3)_2$ fragments. An energy decomposition along the lines described in section IV.3 revealed that **4** as well as **5** are destabilized compared to **3** by repulsive steric interactions between electron pairs on ligands attached to different metals, whereas the electronic contributions to the metal–metal bond are comparable for the three geometries. We shall in the following restrict the discussion of $M_2Cl_4(PH_3)_4$ to the observed staggered geometry **3** of D_{2d} symmetry. The four fragment orbitals of Figure 1 on each $MCl_2(PH_3)_2$ unit can be combined into metal–metal bonding and metal–metal antibonding orbital combinations. The in phase combination of $d_{z^2}(a_1)$ on each fragment gives rise to a σ-bonding orbital of a_1 symmetry, **6**, whereas b_1 on one fragment, see Figure 1, with b_2 on another fragment afford a degenerate set of π-bonding orbitals with e symmetry, **7a** and **7b**. We have further from the d_{xy} set a δ-bonding orbital, **8a**, and an δ-antibonding orbital, **8b**.



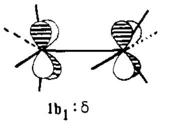
6



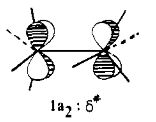
7a



7b



8a



8b

The two orbitals in **8a** and **8b** are of b_1 symmetry and a_2 symmetry, respectively. All studied $M_2Cl_4(PH_3)_4$ systems had the orbital energies of the upper occupied levels in the order $\epsilon_{1a_1} \sim \epsilon_{1e} < \epsilon_{1b_1} < \epsilon_{1a_2}$ or $\epsilon_\sigma \sim \epsilon_\pi < \epsilon_\delta < \epsilon_\delta{}^*$. The calculated orbital energy diagram for $Tc_2Cl_4(PH_3)_4$ is presented in Figure 2. It follows from Figure 2 that the antibonding σ^* orbital, $1b_2$, as well as the two antibonding π^* orbitals, 2e, are of considerable higher energy (3 eV) than the corresponding bonding orbitals $1a_1$ and 1e. Both $1b_2$ and 2e are unoccupied for the $M_2Cl_4(PH_3)_4$ systems under consideration here and need not concern us any further. The two δ orbitals of **8** closely resemble the actual calculated occupied orbital of highest energy with b_1 symmetry (δ) and a_2 symmetry (δ^*), respectively. The symmetrical in-phase combination **6** constitutes in all cases more than 80% of the actual calculated occupied orbital of highest energy with a_1 symmetry (σ), and the lowest unoccupied orbital of b_2 symmetry is the corresponding out-of-phase combination (σ^*). The highest set of occupied orbitals with e symmetry (π) are linear combinations of the b_1 orbitals on one fragment, see Figure 1, with the b_2 orbital on the other fragment as shown in **7**. The contribution from b_2 (60%) is larger than the contribution from b_1 (40%) since $\epsilon_{b_2} < \epsilon_{b_1}$ (see Figure 1). The set of lowest unoccupied orbitals of e symmetry (π^*) is represented by the corresponding out-of-phase combination with the largest amplitude on b_1.

2. Representation of the Many-Electron Wave Function. The d^5–d^5 systems $Mn_2Cl_4(PH_3)_4$, $Tc_2Cl_4(PH_3)_4$, and $Re_2Cl_4(PH_3)_4$ all have the ground-state configuration $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2$ with the state symmetry $^1A_1$. The ground-state configuration for the d^5–d^4 systems $Mn_2Cl_4(PH_3)_4{}^+$, $Tc_2Cl_4(PH_3)_4{}^+$, and $Re_2Cl_4(PH_3)_4{}^+$ is $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1$ with $^2A_2$-state symmetry. It is clear from Figure 2 that the ground-state configurations for d^5–d^5 systems as well as d^5–d^4 systems are well separated in energy from other configurations of similar symmetries. The many-electron wave functions can as a consequence for both systems by represented adequately by a single Slater determinant, and the total energy evaluated by the corresponding statistical energy expression used in connection with the HFS method. The d^4–d^4 systems $Cr_2Cl_4(PH_3)_4$, $Mo_2Cl_4(PH_3)_4$, $W_2Cl_4(Ph_3)_4$, $Mn_2Cl_4(Ph_3)_4{}^{2+}$, $Tc_2Cl_4(PH_3)_4{}^{2+}$, and $Re_2Cl_4(PH_3)_4{}^{2+}$ all have the ground-state configuration $(\sigma)^2(\pi)^4(\delta)^2$ with the state symmetry $^1A_1$. The δ overlaps between the two d_{xy} orbitals in $1a_2$, **8b**, and $1b_1$, **8a**, are small, so that the energy separation between δ and δ^* is modest, see Figure 2. One is as a consequence forced to consider $(\sigma)^2(\pi)^4(\delta^*)^2$ in addition to the ground-state configuration and represent the ground-state many-electron wave function for d^4–d^4 systems by two Slater determinants as

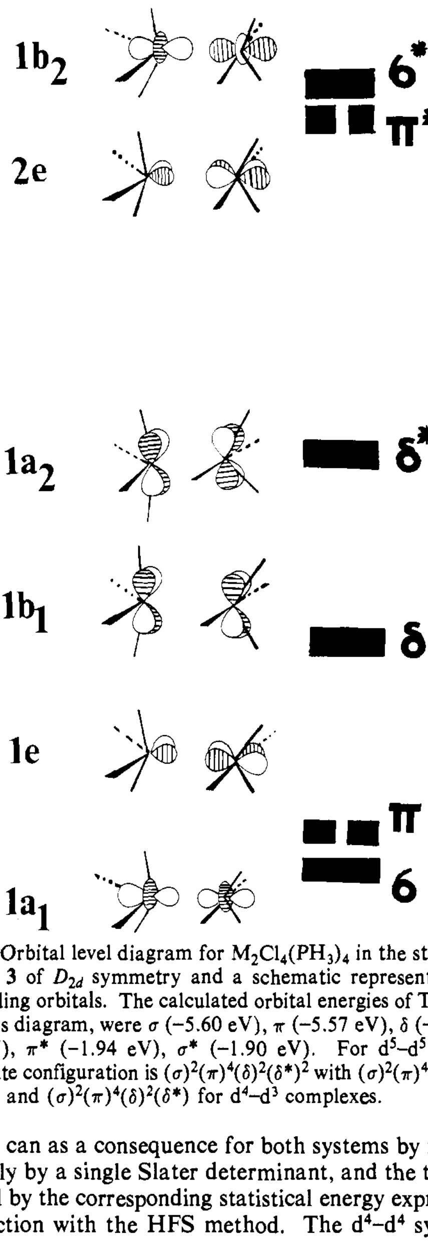


Figure 2. Orbital level diagram for $M_2Cl_4(PH_3)_4$ in the staggered conformation **3** of D_{2d} symmetry and a schematic representation of the corresponding orbitals. The calculated orbital energies of $Tc_2Cl_4(PH_3)_4$, used in this diagram, were σ (−5.60 eV), π (−5.57 eV), δ (−4.67 eV), δ^* (−3.82 eV), π^* (−1.94 eV), σ^* (−1.90 eV). For d^5–d^5 systems the ground-state configuration is $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2$ with $(\sigma)^2(\pi)^4(\delta)^2$ for d^4–d^4 complexes and $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)$ for d^4–d^3 complexes.

$$\Psi = c_1|\overset{+}{\sigma}\overset{-}{\sigma}\overset{+}{\pi}_1\overset{-}{\pi}_1\overset{+}{\pi}_2\overset{-}{\pi}_2\overset{+}{\delta}\overset{-}{\delta}| + c_2|\overset{+}{\sigma}\overset{-}{\sigma}\overset{+}{\pi}_1\overset{-}{\pi}_1\overset{+}{\pi}_2\overset{-}{\pi}_2\overset{+}{\delta}{}^*\overset{-}{\delta}{}^*| \qquad \text{(IV.2.1)}$$

Noodleman et al.[11] have recently shown how a wave function of the form given in eq IV.2.1 as well as the corresponding energy can be evaluated within the HFS scheme, and this method has been used for the d^4–d^4 systems in the present work. The use of spin-unrestricted and symmetry-broken calculations in connection with the evaluation of Ψ in eq IV.2.1 has been described in details for M_2L_8 systems in ref 11b.

3. Decomposition of the Metal–Metal Bonding Energy. The total metal–metal bonding energy

$$\Delta E_{\mathrm{MM}} = -E(M_2L_8) + 2E(ML_4) \qquad \text{(IV.3.1)}$$

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[11] (a) Noodleman, L. *J. Chem. Phys.* **1981**, *74*, 5737. (b) Noodleman, L.; Norman, J. G., Jr. *J. Chem. Phys.* **1979**, *70*, 4903.

Table I. Optimized Metal–Metal Bond Distances, and Decomposition of Calculated Bonding Energies, for $M_2Cl_4(PH_3)_4$ with M = Mn, Tc, and Re

$M_2Cl_4(PH_3)_4$	R_{MM}, Å	E, kJ mol^{-1}					
		ΔE_{MM}	ΔE°	ΔE_σ	ΔE_π	ΔE_δ	ΔE_R
$Mn_2Cl_4(PH_3)_4$	1.92	294.8	376.5	−246.3	−423.8	−1.2	
$Tc_2Cl_4(PH_3)_4$	2.16	598.7	319.6	−331.4	−584.3	−2.6	
$Re_2Cl_4(PH_3)_4$	2.27	562.1	256.0	−303.6	−503.9	−1.1	−9.2[a]

[a] Contributions to the bonding energy from relativistic effects are given by $-\Delta E_R$. The total bonding energy is given as $\Delta E_{MM} = -\Delta E^\circ - \Delta E_\sigma - \Delta E_\pi - \Delta E_\delta - \Delta E_R$.

where $E(M_2L_8)$ is the total energy of M_2L_8 and $E(ML_4)$ the total energy of ML_4, can be decomposed into various contributions as

$$\Delta E_{MM} = -\Delta E^\circ - \Delta E_\sigma - \Delta E_\pi - \Delta E_\delta \qquad (IV.3.2)$$

Here ΔE°, the steric interaction energy, is the energy required to bring together two ML_4 units to the position they will have in the M_2L_8 complex, while keeping all the upper valence electrons unpaired. That is, the electrons are confined to the orbitals they occupied in the separate fragments. The wave function for such a system in the d^4–d^4 case would be:

$$\Psi^\circ = |^+a_{1L}{}^+a_{2L}{}^+b_{1L}{}^+b_{2L}{}^-a_{1R}{}^-a_{2R}{}^-b_{1R}{}^-b_{2R}| \qquad (IV.3.3)$$

where a_{1L}, a_{1R}, etc., are orbitals on the two different fragments (see Figure 1). With the energy corresponding to Ψ° given by E°, we have for the steric interaction energy,

$$\Delta E^\circ = E^\circ - 2E(ML_4) \qquad (IV.3.4)$$

The electronic contributions ΔE_σ, ΔE_π, ΔE_δ represent the additional energy gained when the electrons pair up in orbitals of σ symmetry (ΔE_σ), π symmetry (ΔE_π), and δ symmetry (ΔE_δ), respectively. A more detailed account of the decomposition scheme has been given in ref 12. The total energy of the M_2L_8 complex is according to eq IV.3.1 given by

$$E(M_2L_8) = \Delta E + 2E(ML_4) = -\Delta E_{MM} + 2E(ML_4) = \Delta E^\circ + \Delta E_\sigma + \Delta E_\pi + \Delta E_\delta + 2E(ML_4) \qquad (IV.3.5)$$

The contribution to the total energy from the steric interaction (ΔE°) is in most cases positive (repulsive), whereas the σ-bonding interaction (ΔE_σ), the π-bonding interaction (ΔE_π), and the δ-bonding interaction (ΔE_δ) all have negative (attractive) contributions. With the metal–metal bond energy defined as $\Delta E_{MM} = -\Delta E$, a positive value of ΔE_{MM} corresponding to a stable metal–metal bond. The contribution to the bonding energy from the steric interaction ($-\Delta E^\circ$) is now negative (repulsive), whereas the contributions from the σ-bonding interaction ($-\Delta E_\sigma$), the π-bonding interaction ($-\Delta E_\pi$), and the δ-bonding interaction ($-\Delta E_\delta$) now all are positive (attractive).

V. Strength of the Metal-Metal Bond

We shall now discuss the strength of the metal–metal bond as a function of the d-electron count and the metal atom involved in the bonding.

1. $Mn_2Cl_4(PH_3)_4$, $Tc_2Cl_4(Ph_3)_4$, and $Re_2Cl_4(PH_3)_4$. The calculated metal–metal bonding energies, ΔE_{MM}, for $Mn_2Cl_4(PH_3)_4$, $Tc_2Cl_4(PH_3)_4$, and $Re_2Cl_4(PH_3)_4$ are given in Table I along with the optimized metal–metal bond distances, R_{MM}.

Rhenium[1] is known to form binuclear complexes with a formal bond order of 4 as well as 3.5 and 3. The chemistry of technetium[1b] is less developed in this field due to the radioactive nature of the element. To date binuclear complexes of Tc are only known in a few cases where the formal bond order is either 4($Tc_2Cl_8^{2-}$) or 3.5($Tc_2Cl_8^{3-}$). It is, however, expected that $Tc_2(PR_3)_4Cl_4$ with a bond order of 3 should have a metal–metal bond similar in strength to that of the well-known $Re_2Cl_4(PR_3)_4$ systems. The HFS calculations on the two-model systems $Tc_2Cl_4(PH_3)_4$ and $Re_2Cl_4(PH_3)_4$, with $D(Tc\overset{4}{-}Tc)$ = 598 kJ mol^{-1} and $D(Re\overset{4}{-}Re)$ = 562 kJ mol^{-1}, indicate in fact that Tc might form marginally stronger metal–metal triple bonds than Re. There are few experimental estimates of the bond-dissociation energy for binuclear complexes of either Tc or Re with a multiple metal–metal bond. Trogler[13] et al. have, based on the Birge-Sponer procedure, estimated the dissociation energy of the quadrupole bonds in $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$ to be $D(Re\overset{4}{-}Re)$ = 635 ± 80 kJ mol^{-1} and $D(Re\overset{4}{-}Re)$ = 580 ± 100 kJ mol^{-1}, respectively. The metal–metal bond distance in $Re_2Cl_4(PH_3)_4$ is calculated to be R_{MM} = 2.27 Å in reasonable agreement with an observed[14] bond distance of 2.24 Å in $Re_2Cl_4(PMe_2Ph)_4$. The calculated distance for $Tc_2Cl_4(PH_3)_4$ at R_{MM} = 2.16 Å is further in line with the general observation[1] that multiple metal–metal bonds of 4d elements are ~0.1-Å shorter than the corresponding bonds of 5d elements.

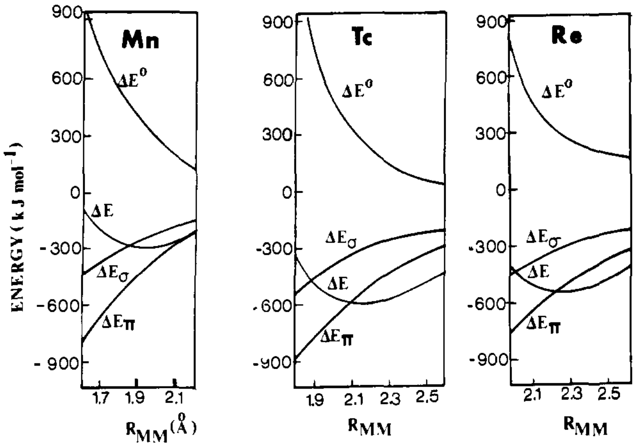

Figure 3. A plot of $\Delta E = -\Delta E_{MM}$, ΔE_σ, ΔE_π, and ΔE° as a function of the metal–metal bond distance R_{MM}. The metal–metal bonding energy is given as $\Delta E_{MM} = -\Delta E = \Delta E^\circ - \Delta E_\sigma - \Delta E_\pi$.

Manganese[1] has so far not been shown to form binuclear complexes with multiple metal–metal bonds, in contrast to its heavier congeners and neighboring 3d elements. We predict, Table I, that $Mn_2(PR_3)_4Cl_4$ should have a rather short bond distance ($R_{MM} \simeq$ 1.9 Å) with a metal–metal bond energy close to 300 kJ mol^{-1}. The calculated properties of $Mn_2Cl_4(PH_3)_4$ are close to those observed for dichromium complexes with a "supershort" quadrupole bond. One might thus expect that it should be possible to synthesize binuclear complexes of Mn, homologous to those of Cr, Tc, and Re.

The variation of $\Delta E = -\Delta E_{MM}$, as well as ΔE°, ΔE_σ, and ΔE_π, is depicted in Figure 3 for $Mn_2Cl_4(PH_3)_4$, $Tc_2Cl_4(PH_3)_4$, and $Re_2Cl_4(PH_3)_4$ as a function of R_{MM}.

The steric contribution to the bonding energy, $-\Delta E^\circ$, is increasingly repulsive as the metal–metal bond is shortened. The repulsion comes from the interactions between an occupied orbital on one fragment with an occupied orbital on the other fragment (4-electron-destabilizing interactions), as well as from the interactions between the partly filled orbitals a_1, a_2, b_1, b_2 (see Figure 1) on one fragment with the occupied orbitals on the other fragment (3-electron-destabilizing interactions). The major part of the 4-electron repulsion is due to electron pairs on the two metal centers, in particular electrons in *n*s and *n*p. The repulsion between electron pairs on ligands attached to different metal centers has on the other hand been greatly reduced by the distortion of the two ML_4 units, as discussed in section IV.1.

The stabilizing contributions to ΔE_{MM} come from $-\Delta E_\sigma$ and $-\Delta E_\pi$. The relative importance of the σ interaction as compared to the π interaction depends somewhat on R_{MM}. The term $-\Delta E_\sigma$ is at the calculated equilibrium distance slightly larger than $-{}^1/_2\Delta E_\pi$ (see Table I), thus making the σ bond somewhat stronger than each of the π bonds.

The contribution from the δ interaction is not shown in Figure 3. It is negligible (see Table I), since both the δ orbital as well as the δ^* orbital are fully occupied.

The calculated order of stability for the binuclear complexes, $D(Tc\overset{4}{-}Tc) > D(Re\overset{4}{-}Re) \gg D(Mn\overset{4}{-}Mn)$, can be rationalized by the aid of Figure 4, where we depict ΔE° as a function of ΔE_σ

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

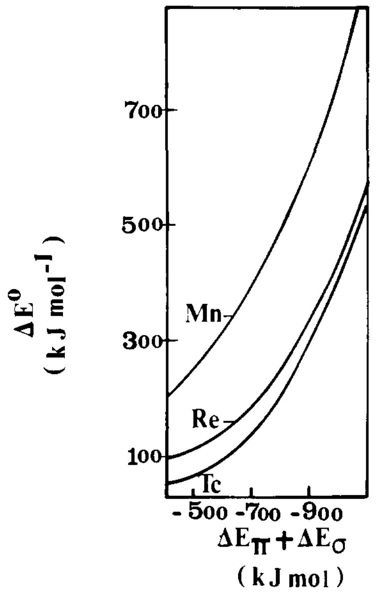

Figure 4. The steric interaction energy, $\Delta E°$, of $M_2Cl_4(PH_3)_4$ with M = Mn, Tc, or Re, as a function of $\Delta E_\sigma + \Delta E_\pi$.

+ ΔE_π for each of the three binuclear systems.

The difference in $\Delta E°$, for a given value of $\Delta E_\sigma + \Delta E_\pi$, between the three metals (Mn, Tc, Re), correlates directly with the calculated trend in the metal–metal bonding energies. The 3d orbitals on Mn are more contracted than either 4d on Tc or 5d on Re. The two Mn atoms must as a consequence come very close together in order to acquire the same bonding interaction ($\Delta E_\sigma + \Delta E_\pi$) as the heavier metals. At such a close range the 4-electron-destabilizing interactions are substantial, in particular between the occupied 3p orbitals of nearly the same radial distribution as 3d. The ratio between $\Delta E°$ and $-(\Delta E_\sigma + \Delta E_\pi)$ is for this reason larger for Mn than for Tc and Re, and the metal–metal bond as a consequence is weaker in $Mn_2Cl_4(PH_3)_4$ than in either $Tc_2Cl_4(PH_3)_4$ or $Re_2Cl_4(PH_3)_4$.

Both Tc and Re have sufficiently diffuse d orbitals to acquire good bonding overlaps ($\Delta E_\sigma + \Delta E_\pi$) at distances where 4-electron-destabilizing interactions still are modest. The major contribution to $\Delta E°$ now comes from the 3-electron-destabilizing interactions between the partly filled d orbitals (Figure 1) on one fragment with the occupied orbitals on the other fragment. This interaction is, for a give value of $\Delta E_\sigma + \Delta E_\pi$, largest for Re with the most diffuse d orbitals. The metal–metal bond in $Re_2Cl_4(PH_3)_4$ is as a consequence marginally weaker than in $Tc_2Cl_4(PH_3)_4$.

Relativistic effects[8] can have a considerable influence on the stability of metal–metal bonds between 5d elements. Calculations on Cr_2L_6, Mo_2L_6, and W_2L_6 showed that relativistic effects ($-\Delta E_R$) stabilized the triple bond in W_2L_6 to the point where $D(\mathrm{W}\overset{4}{-}\mathrm{W}) > D(\mathrm{Mo}\overset{4}{-}\mathrm{Mo})$, whereas nonrelativistic calculations gave $D(\mathrm{Mo}\overset{4}{-}\mathrm{Mo}) > D(\mathrm{W}\overset{4}{-}\mathrm{W})$. We have used the relativistic HFS method by Snijders[15] et al. to calculate the influence of relativity ($-\Delta E_R$) on the strength of the metal–metal bond in $Re_2Cl_4(PH_3)_4$ (see Table I). The influence in the case of $Re_2Cl_4(PH_3)_4$ is modest, and $-\Delta E_R$ is not large enough to invert the nonrelativistic order of stability, $D(\mathrm{Tc}\overset{4}{-}\mathrm{Tc}) > D(\mathrm{Re}\overset{4}{-}\mathrm{Re})$. The small contribution to the metal–metal bond of $Re_2Cl_4(PH_3)_4$ from $-\Delta E_R$ reflects the modest participation of the 6s orbital on Re in the triple bond. Such a participation is necessary for a sizable contribution from $-\Delta E_R$, as discussed in ref 8.

Table II. Optimized Metal–Metal Bond Distances, and Decomposition of Calculated Bonding Energies, for $M_2Cl_4(PH_3)_4$ with M = Cr, Mo, and W

	R_{MM},	E, kJ mol^{-1}					
$M_2Cl_4(PH_3)_4$	Å	ΔE_{MM}	$\Delta E°$	ΔE_σ	ΔE_π	ΔE_δ	ΔE_R
$Cr_2Cl_4(PH_3)_4$	1.89	152.9	498.5	−222.6	−420.7	−8.1	
$Mo_2Cl_4(PH_3)_4$	2.18	523.5	389.5	−288.6	−591.6	−32.8	
$W_2Cl_4(PH_3)_4$	2.28	428.3	430.5	−285.8	−540.2	−25.2	−7.2[a]

[a] The total bonding energy is given as $\Delta E_{MM} = -\Delta E° - \Delta E_\sigma - \Delta E_\pi - \Delta E_\delta - \Delta E_R$.

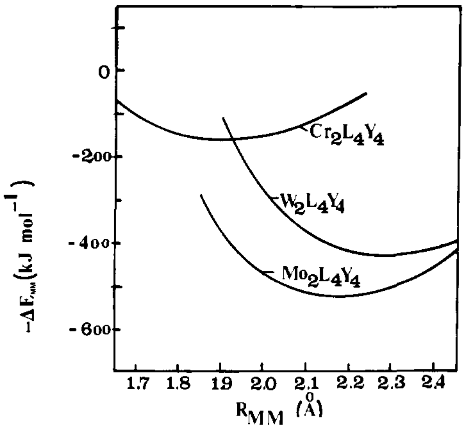

Figure 5. A plot of ΔE_{MM}, where ΔE_{MM} is the metal–metal bonding energy, as a function of the metal–metal bond distance R_{MM} for $M_2Cl_4(PH_3)_4$ with M = Cr, Mo, or W.

2. $Cr_2Cl_4(PH_3)_4$, $Mo_2Cl_4(PH_3)_4$, and $W_2Cl_4(PH_3)_4$. The calculated bonding energies, decomposed into the various contributions ($-\Delta E°$, $-\Delta E_\sigma$, $-\Delta E_\pi$, $-\Delta E_\delta$, $-\Delta E_R$), are shown in Table II for $Cr_2Cl_4(PH_3)_4$, $Mo_2Cl_4(PH_3)_4$, and $W_2Cl_4(PH_3)_4$ along with the optimized metal–metal bond distances.

The two known systems[16] $Mo_2Cl_4(PR_3)_4$ and $W_2Cl_4(PR_3)_4$ have two valence electrons less than $Re_2Cl_4(PR_3)_4$.[14] The configuration is then $(\sigma)^2(\pi)^4(\delta)^2$, corresponding to a formal bond order of 4.

The relative bond strength, Figure 5 and Table II, for the three quadruple bonds is calculated as $D(\mathrm{Cr}\overset{4}{-}\mathrm{Cr}) \ll D(\mathrm{W}\overset{4}{-}\mathrm{W}) < D(\mathrm{Mo}\overset{4}{-}\mathrm{Mo})$ and follows the same order of stability with respect to the 3d, 4d, and 5d elements as the triple bonds in section V.1. It is further clear from Table II that the contributions to $D(\mathrm{W}\overset{4}{-}\mathrm{W})$ from relativistic effects (ΔE_R) are small.

One might have expected that the energy of the triple bond in $Re_2Cl_4(PH_3)_4$ and the energy of the quadrupole bond in $W_2Cl_4(PH_3)_4$ would be related simply by

$$D(\mathrm{W}\overset{4}{\equiv}\mathrm{W}) \cdot D(\mathrm{Re}\equiv\mathrm{Re}) - \Delta E_\delta \qquad (\mathrm{V}.2.1)$$

where $-\Delta E_\delta$ is the contribution to $D(\mathrm{W}\overset{4}{-}\mathrm{W})$ from the δ bond of $W_2Cl_4(PH_3)_4$. Such a simple relationship as expressed in eq V.2.1 would, in addition to $D(\mathrm{W}\overset{4}{-}\mathrm{W}) > D(\mathrm{Re}\overset{4}{-}\mathrm{Re})$, imply that the metal–metal bond distance should be somewhat smaller in $W_2Cl_4(PH_3)_4$ than in $Re_2Cl_4(PH_3)_4$. It is assumed in eq V.2.1 that any change in either $\Delta E°$ or $\Delta E_\sigma + \Delta E_\pi$ between the $Re_2Cl_4(PH_3)_4$ and $W_2Cl_4(PH_3)_4$ is small compared to $-\Delta E_\delta$, although some variation must be expected due to the different size of the core and d orbitals on Re and W, respectively.

A comparison between Table I and Table II shows that $-\Delta E_\delta$ in fact is smaller than the change in $\Delta E°$ and of the same order of magnitude (25 kJ mol^{-1} for $W_2Cl_4(PH_3)_4$) as the change in $\Delta E_\sigma + \Delta E_\pi$. It is for this reason not possible to assess the importance of the δ bond by looking at differences in observed (or calculated) properties between $W_2Cl_4(PR_3)_4$ and $Re_2Cl_4(PR_3)_4$. The calculated order of stability between the triple bonds, Table I, and the quadrupole bonds, Table II, is in fact $D(\mathrm{Mn}\overset{4}{-}\mathrm{Mn}) > D(\mathrm{Cr}\overset{4}{-}\mathrm{Cr})$, $D(\mathrm{Tc}\overset{4}{-}\mathrm{Tc}) > D(\mathrm{Mo}\overset{4}{-}\mathrm{Mo})$, and $D(\mathrm{Re}\overset{4}{-}\mathrm{Re}) > D(\mathrm{W}\overset{4\ \sigma\mathrm{tbW}).}{-}$ and

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[13] Trogler, W. C.; Cowman, C. D.; Gray, H. B.; Cotton, F. A. *J. Am. Chem. Soc.* **1977**, *99*, 2993.

[14] Cotton, F. A.; Dunbar, K. R.; Falvello, R. L.; Tomas, M.; Walton, R. A. *J. Am. Chem. Soc.* **1983**, *105*, 4950.

[15] (a) Snijders, J. G.; Baerends, E. J. *Mol. Phys.* **1978**, *36*, 1789. (b) Snijders, J. G.; Baerends, E. J.; Ros, P. *Mol. Phys.* **1979**, *38*, 1909.

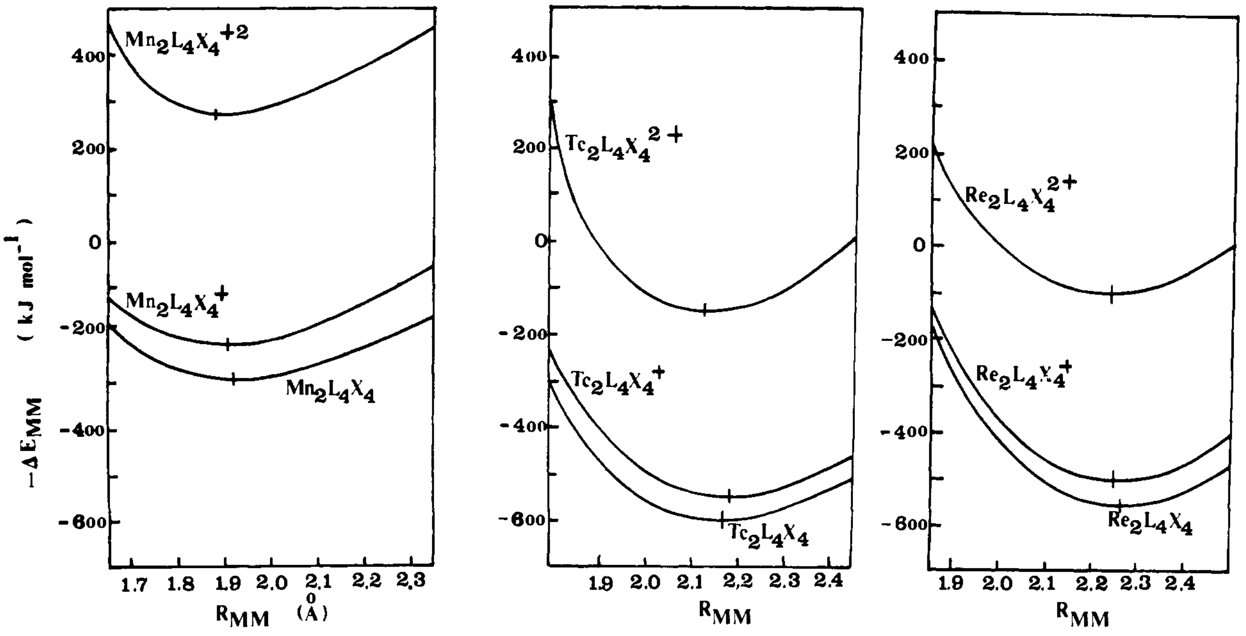


Figure 6. A plot of $-\Delta E_{MM}$ as a function of the metal-metal bond distance R_{MM} for $M_2Cl_4(PH_3)_4^{n+}$ with $n = 0, 1, 2$ and M = Mn, Tc, or Re. The bond distances (Å) and bond energies (kJ mol^{-1}) were calculated as Mn($n = 0$) [1.92, 295], Mn($n = 1$) [1.91, 232], Mn ($n = 2$) [1.90, 267], Tc($n = 0$) [2.16, 599], Tc($n = 1$) [2.18, 532], Tc($n = 2$) [2.12, 142], Re($n = 0$) [2.27, 562], Re($n = 1$) [2.25, 499], Re($n = 2$) [2.24, 87].

this order is primarily influenced by $\Delta E°$, Tables I and Table II. Contributions to $-\Delta E°$ from 4-electron-destabilizing interactions as well as 3-electron-destabilizing interactions are largest in the case of Cr, Mo, and W since those elements have more diffuse core and d orbitals than Mn, Tc, and Re, respectively, due to the smaller nuclear charge.

The calculated quadrupole bond distances of $Cr_2Cl_4(PH_3)_4$, $Mo_2Cl_4(PH_3)_4$, and $W_2Cl_4(PH_3)_4$ are similar to the corresponding triple bond distances in $Mn_2Cl_4(PH_3)_4$, $Tc_2Cl_4(H_3)_4$, and $Re_2Cl_4(PH_3)_4$, respectively, and we note that the observed quadrupole bond distance[16] in $W_2Cl_4(PMe_3)_4$ (2.26 Å) is larger than the observed[14] triple bond distance (2.24 Å) in $Re_2Cl_4(PMe_2PH)_4$.

For the d^4–d^4 systems use was made of the simplest possible wave function, eq IV.2.1, adequate to describe the weakly coupled electron pair in the δ bond. The simple wave function allowed for the occupation of the δ orbital as well as the δ^* orbital. The occupation of the two orbitals for the three different metal centers was as follows: W, $[(\delta)^{1.82}(\delta^*)^{0.18}]$; Mo, $[(\delta)^{1.79}(\delta^*)^{0.21}]$; and Cr, $[(\delta)^{1.46}(\delta^*)^{0.54}]$. It is not surprising that $Cr_2Cl_4(PH_3)_4$ has the highest occupation of δ^*, and thus the weakest δ bond, since the overlap between d orbitals of δ symmetry on the two Cr atoms is smaller than the corresponding overlaps between d orbitals on either Mo or W.

We note further that a calculated quadrupole bond energy of $D(\mathrm{Cr}\overset{4}{-}\mathrm{Cr})$ = 153 kJ mol^{-1} probably is too small to suggest that $Cr_2Cl_4(PH_3)_4$ might be isolated. The rather modest strength of the quadruple bond in $Cr_2Cl_4(PH_3)_4$ is surprising in view of previous calculations[5b] on Cr_2L_6 systems (L = H, Cl, CH_3, OH, NH_2) where the Cr–Cr triple bond energy was calculated to be in the range of 300 to 250 kJ mol^{-1}. We hope to persue this point further by calculations on known binuclear complexes of chromium with a quadrupole bond.

We shall now, in connection with a recent paper by Cotton,[1b] turn to a discussion on the influence of metal-metal bond order on the metal-metal bond length.

3. $Mn_2Cl_4(PH_3)_4^+$, $Mn_2Cl_4(PH_3)^{2+}$, $Tc_2Cl_4(PH_3)_4^+$, $Tc_2Cl_4(Ph_3)_4^{2+}$, $Re_2Cl_4(PH_3)_4^+$, and $Re_2Cl_4(PH_3)_4^{2+}$,. The dication $Re_2Cl_4(PH_3)_4^{2+}$ is isoelectronic with $W_2Cl_4(PH_3)_4$, and it might be more realistic to estimate the influence of the δ bond by comparing the properties of $Re_2Cl_4(PH_3)_4$ and $Re_2Cl_4(PH_3)_4^{2+}$.

Cotton et al.[14] have synthesized and characterized the series $Re_2Cl_4(PMe_2Ph)_4^{n+}$ for $n = 0, 1, 2$, where the metal-metal bond is observed to contract (~0.02 Å) with increasing bond order through $n = 0, 1, 2$.

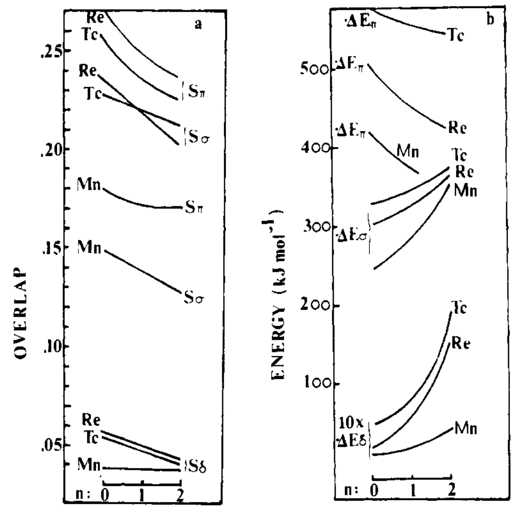


Figure 7. (a) Overlaps[18] between orbitals on the two $MCl_2(PH)_4^{n+}$ ($n = 0, 1$) fragments of σ symmetry (S_σ), 6; π symmetry (S_π), 7; and δ symmetry (S_δ), 8, for $M_2Cl_4(PH_3)_4^{n+}$ with $n = 0, 1$, or 2 and M = Mn, Tc, or Re. The following metal-metal bond distances were used: Mn 1.92 Å ($n = 0, 1, 2$), Tc 2.16 Å ($n = 0, 1, 2$), Re 2.27 Å ($n = 0, 1, 2$). (b) The σ-interaction energies ($-\Delta E_\sigma$), π-interaction energies ($-\Delta E_\pi$), and δ-interaction energies ($-\Delta E_\delta$) of $M_2Cl_4(PH_3)_4^{n+}$ with $n = 0, 1, 2$ and M = Mn, Tc, Re. The bond distances were the same as in part a.

We present in Figure 6 the calculated metal-metal bond energies for $M_2Cl_4(PH_3)_4^{n+}$ with $n = 0, 1, 2$ and M = Mn, Tc, Re. The bonding energy of $M_2(PH_3)_4Cl_4^+$ is with respect to the two fragments $MCl_2(PH_3)_2$ and $MCl_2(PH_3)_2^+$, whereas the bonding energy of $M_2Cl_4(PH_3)_4^{2+}$ is with respect to two $MCl_2(PH_3)_2^+$ units.

The energy required to bring together the two fragments into the combined complex without pairing the electrons, $\Delta E°$, is clearly larger for $M_2Cl_4(PH_3)_4^{2+}$ than for $M_2Cl_4(PH_3)_4$, since the electrostatic interaction between the two charged $MCl_2(PH_3)_2^+$ units is less favorable than the electrostatic interaction between two neutral $MCl_2(PH_3)_2$ fragments. The bonding energies of $M_2Cl_4(PH_3)_4^{2+}$, $M_2Cl_4(PH_3)_4^+$, and $M_2Cl_4(PH_3)_4$ differ for this reason in absolute terms, Figure 6.

The most important feature of Figure 6 is perhaps that the variation in ΔE_{MM} as a function of R_{MM} is nearly the same for the three species ($n = 0, 1, 2$) although they represent different formal bond orders. Thus, the dications with a quadruple bond

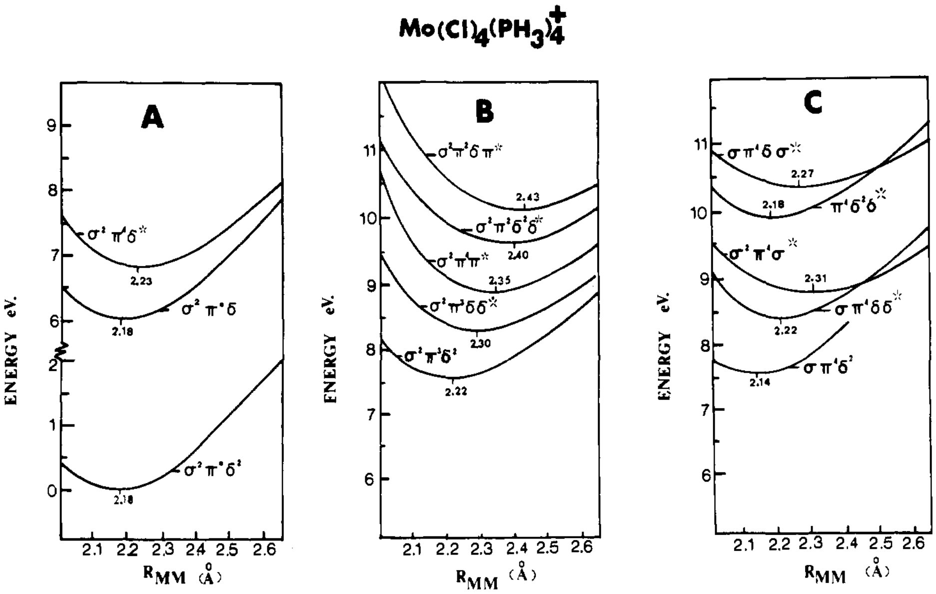
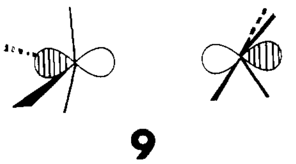


Figure 8. Energy plots of $Mo_2Cl_4(PH_3)_4^+$ in various excited states as a function of the metal–metal bond distance R_{MM}. All energies (eV) are with respect to $Mo_2Cl_4(PH_3)_4$ in its ground state at the optimized metal–metal bond distance (2.18 Å). The actual state used in connection with calculations on each configuration was in each case that of highest spin multiplicity.

do not have a substantially shorter metal–metal bond than the neutral complexes with a triple bond. Rather, ΔE_{MM} for the three binuclear complexes of the same metal, Figure 6, appears at first sight merely to differ by a constant energy term over a wide range of R_{MM}.

We do, however, as shown in Figure 6, calculate a small contraction of the metal–metal bond with increasing bond order through $n = 0, 1, 2$. This contraction correlates nicely with the small increase in $-\Delta E_\delta$ through $n = 0, 1, 2$ (see Figure 7b). A close analysis shows, however, that the rather drastic process, in which two electrons are ionized from the δ^* orbital, has a substantial influence on every term contributing to ΔE_{MM}. The influence on ΔE_π and δE_σ, illustrated in Figure 7a, is determined by two factors. The first factor is a reduction in the bonding overlaps of **6** and **7**, Figure 7a, as the d orbitals on $MCl_2(PH_3)_2^+$ (a_1, a_2, b_1, b_2 of Figure 1) are more contracted[14] than the d orbitals of $MCl_2(PH_3)_2$.

The second factor is an increasing participation of the in-phase combination between the two metal $(n + 1)p_z$ orbitals, **9**, in the σ bond, as the energy of **9** is lowered with increasing n. The result of the two opposing factors is an increase in $-\Delta E_\sigma$ ($n = 0, 1, 2$) whereas $-\Delta E_\pi$ is reduced by the first factor ($n = 0, 1, 2$), see Figure 7b. The contraction of the d orbitals in the charged binuclear complexes will in addition reduce the 3-electron-destabilizing interactions of $\Delta E°$.



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We conclude this section by pointing out that it probably is difficult to study the influence of the δ bond in a series such as $M_2Cl_4(PR_3)_4^{n+}$, where the bond order has been increased by ionization through $n = 0, 1, 2$. The ionization will induce changes in all contributing factors to ΔE_{MM} (and $R_{MM(opt)}$), and those changes might be larger than the weak contribution from the δ bond. It is in this respect interesting that[17] $Tc_2Cl_8^{2-}$ with a bond order of $4(\sigma^2\pi^4\delta^2)$ has a larger bond distance ($R_{MM} = 2.16$ Å) than $Tc_2Cl_8^{2-}$ (2.10 Å) with a bond order of 3.5.

4. $Mo_2Cl_4(PH_3)^+_4$. The change in the metal–metal bond distance as a function of the formal metal–metal bond order is illustrated in Figure 8, where we present the optimized bond distances for various excited states of $Mo_2Cl_4(PH_3)_4^+$. The ground-state configuration is $\sigma^2\pi^4\delta$, and $Mo_2Cl_4(PH_3)_4^+$ has here the same bond distance (2.18 Å) as $Mo_2Cl_4(PH_3)_4$ in $\sigma^2\pi^4\delta^2$, Figure 8A. The promotion of one electron from the δ orbital to the δ^* orbital results in a modest increase in the bond length to 2.23 Å.

The reduction in the π-bond order gave, as one might have expected, rise to a somewhat larger increase in the bond length, Figure 8B. Thus, the bond length of $Mo_2Cl_4(PH_3)_4^+$ in configuration $\sigma^2\pi^4\pi^*$ with a π-bond order of 1.5 was calculated to be 2.35 Å, whereas the configuration $\sigma^2\pi^3\sigma\ \pi^*$ with a π bond order of 1 gave $R_{MM} = 2.43$ Å, Figure 8B.

The σ bond is slightly stronger than the π bond, section V.1, and one might thus have expected that the promotion of one or two electrons from the σ orbital would increase the metal–metal bond distance considerably. Configurations in which one or two electrons are promoted from the σ orbital are in fact calculated, Figure 8C, to have nearly the same bond distance as the ground-state configuration, thus $\sigma\pi^4\delta^2$ have $R_{MM} = 2.14$ Å, with $R_{MM} = 2.22$ for $\sigma\pi^4\delta\delta^*$, Figure 8C. An analysis showed that $-\Delta E°$, positive and repulsive, is reduced substantially as electrons are removed from the σ orbitals, **6**, since such a removal will eliminate the 3-electron-destabilizing interactions between d_{z^2} on one fragment and the np_z, ns orbitals on the other fragment. The influence from the reduction in the σ-bond order on R_{MM} is as a consequence largely diminished by the decrease of $-\Delta E°$, as electrons are promoted from the σ orbital. The population of the σ^* orbital does on the other hand not result in a reduction of the 3-electron-destabilizing interaction discussed above. The configuration $\sigma^2\pi^4\sigma^*$, where the σ-bond order is 0.5, exhibits as a consequence a substantial increase in the bond length, Figure 8C, with $R_{MM} = 2.31$ Å. An increase in the bond length is also calculated for $\sigma\pi^4\delta\sigma^*$ with $R_{MM} = 2.27$ Å.

VI. Concluding Remarks

The present study on the relative stability of metal–metal bonds in the homologous binuclear complexes of the form $M_2(PH_3)_4Cl_4$ reveals, for the two triads M = Mn, Tc, Re and M = Cr, Mo, W, that the metal–metal bond energies $\Delta E_{MM}(3d)$, $\Delta E_{MM}(4d)$, $\Delta E_{MM}(5d)$ for three congeners follow the order $\Delta E_{MM}(3d) < \Delta E_{MM}(5d) < \Delta E_{MM}(4d)$ at variance with the trend $\Delta E_{MM}(3d) < \Delta E_{MM}(4d) < \Delta E_{MM}(5d)$ observed in studies[19] on metal bulk.

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We have found that nonrelativistic calculations on binuclear metal complexes uniformly afford the order ΔE_{MM}(5d) < ΔE_{MM}(4d). This order might, however, be reversed by relativistic effects, provided that the $(n + 1)$s metal orbitals have a substantial contribution to the metal–metal bond as in Ag_2 and Au_2[8] or Mo_2H_6 and W_2H_6.[5b] A modest participation from $(n + 1)$s in the metal–metal bond will on the other hand result in too small a contribution from the relativistic effects to reverse the nonrelativistic order ΔE_{MM}(5d) < ΔE_{MM}(4d), as in the case of the $M_2Cl_4(PH_3)_4$ systems.

We would expect that the contribution to the metal–metal bond from the relatively diffuse $(n + 1)$s orbital is considerably increased and the contribution from the more contracted *n*d orbitals decreased in metal–bulk compared to $M_2Cl_4(PH_3)_4$, since the metal–metal bond distance R_{MM} is much longer in bulk than in $M_2Cl_4(PH_3)_4$ (note that R_{MM} in Mo-bulk is 1 Å longer than in $M_2Cl_4(PH_3)_4$!) Our analysis above would thus suggest that the order ΔE_{MM}(4d) < ΔE_{MM} observed in bulk is a relativistic effect, brought about by the substantial contribution from the $(n + 1)$s orbital to the metal–metal bond in bulk.

It is hoped that additional theoretical calculations will provide a simple qualitative method by which the involvement of $(n + 1)$s in the metal–metal bond, and thus the order of ΔE_{MM}(4d) and E_{MM}(5d), can be predicted for any class of binuclear complexes.

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Registry No. $Mn_2Cl_4(PH_3)_4$, 91550-28-6; $Mn_2Cl_4(PH_3)_4^+$, 91550-29-7; $Mn_2Cl_4(PH_3)_4^{2+}$, 91550-30-0; $Tc_2Cl_4(PH_3)_4$, 91550-31-1; $Tc_2Cl_4(PH_3)_4^+$, 91550-32-2; $Tc_2Cl_4(PH_3)_4^{2+}$, 91550-33-3; $Re_2Cl_4(PH_3)_4$, 91604-62-5; $Re_2Cl_4(PH_3)_4^+$, 91550-34-4; $Re_2Cl_4(PH_3)_4^{2+}$, 91550-35-5; $Mo_2Cl_4(PH_3)_4$, 80485-12-7; $Mo_2Cl_4(PH_3)_4^+$, 91550-36-6; $Cr_2Cl_4(PH_3)_4$, 91550-37-7; $W_2Cl_4(PH_3)_4$, 80485-13-8.

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(18) The corresponding overlaps for $M_2Cl_4(PH_3)_4$ with M = Cr, Mo, W were the following: Cr [$S_\sigma = 0.168$, $S_\delta = 0.053$, $S_\pi = 0.212$] at $R_{MM} = 1.9$ Å; Mo [$S_\sigma = 0.256$, $S_\delta = 0.081$, $S_\pi = 0.301$] at 2.15 Å; W [$S_\sigma = 0.265$, $S_\delta = 0.075$, $S_\pi = 0.305$] at $R_{MM} = 2.28$ Å. The overlaps of Cr, Mo, and W are larger than the corresponding overlaps with Mn, Tc, and Re, respectively, since the d orbitals on Cr, Mo, and W are more diffuse than the corresponding d orbitals on Mn, Tc, and Re.

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Kinetics and Mechanism of Substitution Reactions of η^5-Cyclopentadienyldicarbonylrhodium(I) Derivatives. Rate Enhancement of Associative Substitution in Cyclopentadienylmetal Compounds[1]

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Abstract: The reactions of $Rh(\eta^5\text{-}C_9H_7)(CO)_2$, $Rh(\eta^5\text{-}C_9(CH_3)_7)(CO)_2$, $Rh(\eta^5\text{-}C_5H_4NO_2)(CO)_2$, and $[Rh(\eta^5\text{-}C_5H_4PPh_3)(CO)_2]^+$ with triphenylphosphine (PPh_3) take place readily to form monosubstituted products. These reactions proceed solely by a second-order process, first order in the metal complex and first order in PPh_3. The rates of reaction follow the order $Rh(\eta^5\text{-}C_9H_7)(CO)_2 > Rh(\eta^5\text{-}C_9(CH_3)_7)(CO)_2 > Rh(\eta^5\text{-}C_5H_4NO_2)(CO)_2 > [Rh(\eta^5\text{-}C_5H_4PPh_3)(CO)_2]^+$, and all are orders of magnitude greater than that of $Rh(\eta^5\text{-}C_5H_5)(CO)_2$. The reasons for this ordering are discussed in terms of the presumed transition states of these reactions, relative to the corresponding reaction of $Rh(\eta^5\text{-}C_5H_5)(CO)_2$.

In 1966 we reported[2] that the rates of reaction of $Rh(\eta^5\text{-}C_5H_5)(CO)_2$ with a variety of phosphine, phosphite, and isocyanide ligands are dependent on the concentration of both the rhodium complex and the incoming nucleophile. The associative nature of the substitution of this 18-electron compound was explained by transfer of an electron pair from rhodium to the cyclopentadienyl ligand, creating an empty orbital for nucleophilic attack. It seemed necessary at the time that some such process be involved, because it was known[3] that the pseudoisoelectronic $Fe(CO)_5$ undergoes CO substitution very slowly and by a dissociative process. Although our suggestion predated the Tolman[4] 16–18-electron rule, we recognized that formation of a 20-electron species, $Rh(\eta^5\text{-}C_5H_5)(CO)_2L$, was unfavored so that some process by which an 18-electron count at rhodium be maintained seemed appropriate. Since the fundamental difference between $Fe(CO)_5$ and the pseudoisoelectronic $Rh(\eta^5\text{-}C_5H_5)(CO)_2$ is the cyclopentadienyl ligand, it was felt that the cyclopentadienyl ligand allows an associative reaction at the 18-electron rhodium center by accepting an electron pair and creating a vacant low-energy metal orbital to accept a pair of electrons from the entering nucleophile.

Cramer and Seiwell[5] examined the kinetics of substitution for the analogous ethylene complex, $Rh(\eta^5\text{-}C_5H_5)(C_2H_4)_2$. Associative substitution was observed with certain nucleophiles, and they also felt that transfer of an electron pair from rhodium to the cyclpentadienyl ligand was essential in the substitution process. They

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