Table I. Parameters Used in the Extended Hückel Calculations

orbital	H_{ii}, eV	ξ_1	ξ_2	$C_1{}^a$	$C_2{}^a$
Rh 4d	−12.50	4.29	1.97	0.5807	0.5685
5s	−8.09	2.135			
5p	−4.57	2.10			
P 3s	−18.60	1.75			
3p	−14.00	1.30			
C 2s	−21.40	1.625			
2p	−11.40	1.625			
O 2s	−32.30	2.275			
2p	−14.80	2.275			
H 1s	−13.60	1.30			

[a] Contraction coefficients used in the double-ζ expansion.

LUMO in PT. Since π^* is doubly occupied in TT^{2-}, the formal Rh–Rh bond order is reduced to one. In our calculations the Rh–Rh overlap population drops from 0.319 in TT to 0.144 in TT^{2-} (where the Rh–Rh distance was kept identical with that in **3**). A geometric consequence of this is that the Rh–Rh bond length in **4**[8d] is elongated to 2.84 Å. Reference back to the contour plot of π^* in Figure 5 shows that considerable electron density in TT^{2-} will be accumulated on the carbonyl ligands, as well as the two metal atoms. The replacement of CO by other auxillary ligands, e.g., phosphines, should cause especially the second reduction potential to increase and may even influence the stability of TT^{2-}. This is a topic which we shall pursue in the future.

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Appendix

All calculations were performed with the extended Hückel method[11] using the modified Wolfsberg–Helmholz formula.[17] The H_{ii}'s and orbital exponents listed in Table I were taken from previous work.[7] All Rh–C, C–O, and P–H distances were set at 1.87, 1.14, and 1.41 Å, respectively. The C–Rh–C angles at the square-planar and tetrahedral geometries were fixed at 90.0° and 111.6°, respectively. A uniform variation of the C–Rh–C angle was assumed for intermediate geometries. The H–P–H angles were set at 106.0°.

Registry No. $Rh_2(CO)_4(PH_2)_2$, 94904-44-6.

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A Theoretical Study on the Proton Affinity of Some Mononuclear d^8 and d^{10} Metal Carbonyls by the Hartree–Fock–Slater Transition-State Method

Tom Ziegler

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

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Hartree–Fock–Slater calculations are reported on the protonation energies for the d^8 pentacarbonyls $M(CO)_5$ (M = Fe, Ru, Os), $M(CO)_5^-$ (M = Mn, Tc, Re), $Cr(CO)_5^{2-}$, and $Co(CO)_5^+$ as well as the d^{10} tetracarbonyls $M(CO)_4^-$ (M = Co, Rh, Ir), $M(CO)_4$ (M = Ni, Pd, Pt), $Fe(CO)_4^{2-}$, and $Cu(CO)_4^+$. The calculated protonation energies were decomposed into electrostatic ($\Delta E°$), electronic (ΔE_{elec}), and relativistic (ΔE_R) contributions as well as contribution (ΔE_{prep}) from the rearrangement of the $M(CO)_5$ and $M(CO)_4$ frameworks on formation of the hydrides. The electronic term ΔE_{elec} was calculated to increase vertically down a triad and decrease along a transition series with increasing nuclear charge on the metal. A possible explanation for the calculated trends in ΔE_{elec} is given in terms of simple perturbational molecular orbital (PMO) theory, and it is suggested that the trends in ΔE_{elec} calculated for the electrophile H^+ apply to other electrophiles as well.

Introduction

The ability of a metal in a low-valent complex to act as a good nucleophile is of crucial importance in several key-step catalytic processes, and there has as a consequence been considerable interest[1] in a quantitative characterization of the nucleophilicity of such complexes as a function of the metal atom as well as the coligands.

Much of our knowledge on the trends in nucleophilicity with respect to different metal centers comes from experimental solution studies[2] on the Brønsted acidity of transition-metal hydrides or the protonation basicity of transition-metal complexes. Such experimental studies are in part hampered by the air sensitivity of some transition-metal hydrides as well as the difficulty in finding a common suitable solvent for a variety of different hydrides. It is in addition difficult to gauge the difference in nucleophilicity between various metal centers from protonation/deprotonation solution studies alone, since the acidity of a transition-metal hydride, HML_n, in solution

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(1) (a) Vaska, L. *Acc. Chem. Res.* **1968**, *1*, 335. (b) Tolman, C. A. *Chem. Soc. Rev.* **1972**, *1*, 337.

(2) (a) Vidal, J. L.; Walker, W. E. *Inorg. Chem.* **1981**, *20*, 249. (b) King, R. B. *J. Am. Chem. Soc.* **1966**, *88*, 5121. (c) Walker, H. W.; Kresge, C. T.; Ford, P. C.; Pearson, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 7428 and references therein.

0276-7333/85/2304-0675$01.50/0

depends on the nucleophilicity of the metal center as well as the solvation energy of the ML_n^- anion. Thus, although $HCo(CO)_4$ in most solvents is a stronger acid than $HMn(CO)_5$, one can not conclude that $Mn(CO)_5^-$ is a stronger nucleophile than $Co(CO)_4^-$, since the solvation energies of the two anions might be different. The influence of the solvent can however be eliminated by measuring the proton affinity of metal complexes in the gas phase, as it has been done recently by Beauchamp et al.[3] The scope of proton affinities obtained from the gas phase is however still limited.

We felt that it might be of interest to supplement the experimental work with theoretical calculations on the proton affinity of several metal carbonyls such as $M(CO)_5^-$ (M = Mn, Tc, Re), $M(CO)_5$ (M = Fe, Ru, Os), $M(CO)_4^-$ (M = Co, Rh, Ir), and $M(CO)_4$ (M = Ni, Pd, Pt), where the systems have been chosen in such a way that it would be possible to examine variations in the metal nucleophilicity within a transition series as well as triad of congeners.

Computational Details

We have applied the LCAO–HFS method by Baerends et al.[4] The molecular orbitals were expanded in a triple-ζ STO basis set.[5] The exchange scaling factor α was given the standard value of $\alpha = 0.7$. All energies were calculated by the generalized transition-state method,[6] and relativistic effect were included for complexes of the 5d elements according to the scheme of Snijders et al.[7]

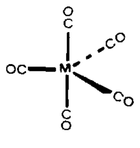
A bond length of 1.13 Å was adopted for CO in all the metal carbonyls. The metal to carbon distance R_{MC} as well as the metal to hydrogen distance R_{MH} have been taken[8] as Cr [1.85, 1.60], Mn [1.85, 1.60], Tc [2.01, 1.66], Re [2.01, 1.66], Fe [1.82, 1.60], Ru [2.00, 1.65], Os [2.01, 1.67], and Co [1.82, 1.60] for the $HM(CO)_5^{(1-n)+}$ (n = 2, 1, 0, −1) systems and as Fe [1.76, 1.56], Co [1.76, 1.56], Rh [1.99, 1.60], Ir [1.99, 1.64], Ni [1.84, 1.56], Cu [1.84, 1.56], Pd [1.98, 1.60], and Pt [1.98, 1.60] for the $HM(CO)_4^{(1-n)+}$ (n = 2, 1, 0, −1) systems, where the first entry refers to R_{MC} and the second entry to R_{MH}, with both distances in angstroms.

The bond angles[8] in the model systems $HM(CO)_5^{(1-n)+}$ and $HM(CO)_4^{(1-n)+}$ were taken from the known structures of $HMn(CO)_5$ and $HCo(CO)_4$, respectively, with the same R_{MC} distance for axial (apical) and equatorial (basal) CO groups.

Protonation of $M(CO)_5$ (M = Fe, Ru, Os) and $M(CO)_5^-$ (M = Mn, Tc, Re) as well as $Cr(CO)_5^{2-}$ and $Co(CO)_5^+$

We consider first the protonation of the d^8 pentacoordinated bipyramidal 1 metal carbonyls $M(CO)_5$ (M = Fe, Ru, Os) and $M(CO)_5^-$ (M = Mn, Tc, Re).

The protonation of $Mn(CO)_5^-$ and $Re(CO)_5^-$ affords hydride complexes 2 in which the $M(CO)_5$ framework has a square-pyramidal conformation 3, and we shall assume that the protonation of $Tc(CO)_5^-$ as well as $M(CO)_5$ (M = Fe, Ru, Os) also results in hydride complexes with the structure 2; see Computational Details.



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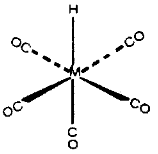

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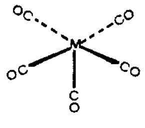

3

The bonding between H^+ and $M(CO)_5^{n-}$ in the hydride complexes $HM(CO)_5^{(1-n)+}$ as well as the factors of importance for the protonation energy

$$\Delta E_P = E[M(CO)_5^{n-}] - E[HM(CO)_5^{(1-n)+}] \qquad (1)$$

where $E[M(CO)_5^{n-}]$ is the energy of $M(CO)_5^{n-}$ in conformation 1 and $E[HM(CO)_5^{(1-n)+}]$ the energy of $HM(CO)_5^{(1-n)+}$ in conformation 2, can be studied conveniently by considering the protonation process

$$M(CO)_5^{n-} + H^+ = HM(CO)_5^{(1-n)+} - \Delta E_P \qquad (2)$$

in a sequence of three steps.

The $M(CO)_5^{n-}$ fragment is deformed in the first step from its ground-state geometry 1 to the conformation 3 it will have in the combined hydride complex 2. The contribution to ΔE_P from this deformation is refered to as ΔE_{prep}. The $M(CO)_5^{n-}$ fragment 3 as well as H^+ are in the second step given the positions they will take up in the combined hydride complex 2. The electron pairs on $M(CO)_5^{n-}$ of conformation 3 are however confined to the orbitals they occupied in the separate $M(CO)_5^{n-}$ fragment 3. Thus in the second step we only allow for an electrostatic interaction between H^+ and $M(CO)_5^{n-}$ and define the contribution to ΔE_P from this interaction as $\Delta E°$. The occupied and unoccupied orbitals of $M(CO)_5^{n-}$ in conformation 3 are allowed in the third step to interact with the unoccupied orbitals of H^+, that is, we carry out a full nonrelativistic HFS calculation on $HM(CO)_5^{(1-n)+}$. The contribution to ΔE_P from the third step is refered to as the electronic contribution ΔE_{elec}. The term ΔE_{elec} can further, since it has contributions from each of the symmetry representations corresponding to the C_{4v} point group of 2, be written as $\Delta E_{elec} = \Delta E_{A_1} + \Delta E_{A_2} + \Delta E_{B_1} + \Delta E_{B_2} + \Delta E_E$. A detailed account of the decomposition scheme used here has been given in ref 9.

We introduce finally as a separate term the contribution to the protonation energy from relativistic effects, ΔE_R. We have found from a previous study,[10] where ΔE_R is fully defined, that relativity only influences the strength of bonds in which 5d transition metals or even heavier elements are involved, and ΔE_P will accordingly only be evaluated for M = Re and Os in this section.

Calculated energies for the protonation of $M(CO)_5^-$ (M = Mn, Tc, Re) and $M(CO)_5$ (M = Fe, Ru, Os) are given in Table I, decomposed into the various component defined above. We have calculated the d^8 fragments $M(CO)_5^{n-}$ to be between 27 and 32 kJ mol^{-1} more stable in the bipyramidal conformation 1 than in the square-pyramidal conformation 3, and the contribution from ΔE_{prep} to ΔE_P is as a consequence negative (destabilizing). The structure 1 is according to our analysis favored over 3 by steric as well as electronic factors. We shall not provide any details

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(4) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, 2, 41.

(5) (a) The triple-ζ STO basis set was generated according to the method given in ref 5c and taken from ref 5b. Three metal (n + 1)p STO's were added to the atomic basis with the same experiments as the (n + 1)s metal STO's. The three STO exponents for 1s on H were 0.76, 1.00, and 1.57, respectively. (b) Snijders, G. J.; Baerends, E. J.; Vernooijs, P. Internal Report, Free University, Amsterdam, 1981. (c) Snijders, G. J.; Baerends, E. J.; Vernooijs, P. *At. Data Nucl. Data Tables* **1982**, *26*, 483.

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(8) Teller, R. G.; Bau, P. *Struct. Bonding (Berlin)* **1981**, *44*, 1 and references therein.

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

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

Table I. A Decomposition of Calculated Protonation Energies (in kJ mol^{-1}) for $M(CO)_5^-$ (M = Mn, Tc, Re) and $M(CO)_5$ (M = Fe, Ru, Os) as well as $Cr(CO)_5^{2-}$ and $Co(CO)_5^+$

$M(CO)_5^{n-}$	ΔE_{prep}	ΔE°	ΔE_{elec}	ΔE_{A_1}	$\Delta E_{elec} - \Delta E_{A_1}$	ΔE_R	ΔE_P
$Mn(CO)_5^-$	−30.0	403.8	843.5[b]	754.2	89.3		1217.3[a]
$Tc(CO)_5^-$	−30.7	356.1	934.9	839.3	95.6		1260.3
$Re(CO)_5^-$	−31.8	360.2	955.9	882.9	73.0	34.4	1318.7
$Fe(CO)_5$	−27.1	46.8	796.3	687.0	109.3		816.0
$Ru(CO)_5$	−26.3	33.1	833.8	713.5	120.3		840.6
$Os(CO)_5$	−31.9	24.7	860.9	771.6	89.3	28.9	882.6
$Cr(CO)_5^{2-}$	−29.2	941.7	890.7	819.6	71.2		1803.2
$Co(CO)_5^+$	−27.8	−496.6	702.7	581.1	121.6		178.3

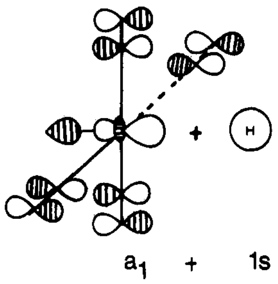
[a] The total protonation energy ΔE_P is given by $\Delta E_P = \Delta E_{prep} + \Delta E^\circ + \Delta E_{elec} + \Delta E_R$. [b] $\Delta E_{elec} = \Delta E_{A_1} + \Delta E_{A_2} + \Delta E_{B_1} + \Delta E_{B_2} + \Delta E_E$.

of this analysis here since the influence of electronic factors on the energy difference between 1 and 3 already have been discussed by Burdett[11] as well as Rossi and Hoffmann.[12] We note, however, that Demuynck et al.[13] have carried out ab initio calculations on the energy difference between the bipyramidal and square-pyramidal structures of $Mn(CO)_5^-$ and $Fe(CO)_5$. They found the bipyramidal conformation to be more stable than the square-pyramidal conformation by 3 kJ mol^{-1} for $Mn(CO)_5^-$ as well $Fe(CO)_5$.

The contribution to ΔE_P from ΔE° is, not surprisingly, calculated to be large (positive and stabilizing) for the protonation of $M(CO)_5^-$ (M = Mn, Tc, Re) where the electrostatic interaction ΔE° is between the positive proton H^+ and the negatively charged fragment $M(CO)_5^-$; see Table I. The contribution to ΔE_P from ΔE° is on the other hand modest for the protonation of $M(CO)_5$ (M = Fe, Ru, Os), where the electrostatic interaction ΔE° is between H^+ and the neutral fragment $M(CO)_5$. The stabilizing contribution to ΔE_P from the electrostatic interaction ΔE° is seen in Table I to decrease along the two triads M = Mn, Tc, and Re and M = Fe, Ru, and Os. We explain this trend by observing that $M(CO)_5^{n-}$ of the heavier transition elements has a more diffuse (extended) electron density around the metal center M than $M(CO)_5^{n-}$ of the 3d elements and that the more diffuse electron density is less effective in shielding the positively charged metal nucleus from the repulsive interaction with H^+.

The electronic term ΔE_{elec} represents the contribution to ΔE_P from the change in the occupied orbitals and the associated total density, as $HM(CO)_5^{(1-n)+}$ is formed from $M(CO)_5^{n-}$ and H^+. The change in electron density can further be written as $\Delta\rho = \Delta\rho_{A_2} + \Delta\rho_{B_1} + \Delta\rho_{B_2} + \Delta\rho_E$ and ΔE_{elec} as $\Delta E_{elec} = \Delta E_{A_1} + \Delta E_{A_2} + \Delta E_{B_1} + \Delta E_{B_2} + \Delta E_E$, where ΔE_Γ represents the contribution to ΔE_P from the change in the occupied orbitals of Γ symmetry with the associated change in density $\Delta\rho_\Gamma$. It is clear from Table I that ΔE_{elec} is the dominating term in thee decomposition $\Delta E_P = \Delta E_{prep} + \Delta E^\circ + \Delta E_{elec} + \Delta E_R$. Thus the major part of the protonation energy arises from the relaxation of the electron density after H^+ and $M(CO)_5^{n-}$ have been combined, rather than from the pure electrostatic interaction between H^+ and $M(CO)_5^{n-}$.

The change in density is most pronounced inthe a_1 representation where the HOMO a_1 of $M(CO)_5^{n-}$, a d_{z^2} metal orbital that is antibonding with respect to the ρ orbital on the apical CO ligand and bonding with respect to the π^* orbitals on the basal CO ligands, in $HM(CO)_5^{(1-n)+}$ will form a bonding orbital with 1s on H^+ through the donor–acceptor interaction 4. The change in density $\Delta\rho_{A_1}$, primarily representing the donation of charge from $M(CO)_5^{n-}$ to H^+ due to 4, is depicted in Figure 1a. The energy term ΔE_{A_1} corresponding to $\Delta\rho_{A_1}$ is given in Table I.



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The proton does not have orbitals of low energy available that can interact with $M(CO)_5^{n-}$ fragment orbitals of a_2, b_1, b_2, or e symmetry in a way similar to 4. Occupied and unoccupied $M(CO)_5^{n-}$ fragment orbitals within each symmetry representation will however mix as $HM(CO)_5^{(1-n)+}$ is formed, in response to the change in Coulomb potential felt by each electron. The corresponding change in density, $\Delta\rho_{A_2} + \Delta\rho_{B_1} + \Delta\rho_{B_2} + \Delta\rho_E$, is depicted in Figure 1b, whereas the contribution from the density change to the protonation energy ΔE_P is shown in Table I as $\Delta E_{elec} - \Delta E_{A_1}$. It follows from Table I that ΔE_{A_1} is the dominating part of ΔE_{elec}, whereas $\Delta E_{elec} - \Delta E_{A_1} = \Delta E_{A_2} + \Delta E_{B_1} + \Delta E_{B_2} + \Delta E_E$ is 1 order of magnitude smaller.

The last part of ΔE_P is the contribution to the protonation energy from relativistic effects, ΔE_R. Relativistic effects will primarily influence the strength of bonds in which the $(n + 1)$s orbital[14a] of a heavy element is involved. The participation from $(n + 1)$s in the HOMO a_1 of $M(CO)_5^{n-}$, and thus in the bonding between $M(CO)_5^{n-}$ and H^+, is however modest and ΔE_R as a consequence small compared to ΔE_{elec}; see Table I.

Estimates[2] on the order of nucleophilicity within a triad, from protonation studies or kinetic measurements on a homologous series of complexes, invariably have the 5d element as more nucleophilic than its 3d and 4d congeners, whereas the relative nucleophilicity of the 3d and 4d elements might vary. The calculated protonation energies in Table I give for each of the two triads M = Mn, Tc, and Re and M = Fe, Ru, and Os the order of proton affinity as 5d > 4d > 3d with the 4d metal intermediate between its 3d and 5d congeners. It is in addition clear from the

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(11) Burdett, J. K. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1599.

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

(13) Demuynck, J.; Strich, A.; Veillard, A. *Nouv. J. Chim.* **1977**, *1*, 217.

(14) (a) The *n*d, $(n + 1)$s, $(n + 1)$p orbitals are with n = 3–5 the valence orbitals in the first, second, and third transition series, respectively, and the index n should not be confused with the use of n in $M(CO)_5^{n-}$ and $M(CO)_5H^{(1-n)+}$. (b) The constant k in eq 3.3 is according to the angular overlap method of ref 14c given by $k = \epsilon(1s)^*\epsilon(1s)$ and thus independent of the metal center involved. The approximate expression for ΔE_{A_1} given in eq 3 was only used in the qualitative discussion whereas ΔE_{A_1} and ΔE° as well as ΔE_{elec} given in Tables I and II all were evaluated quantitatively according to the method given in ref 9. (c) Burdett, J. K.; "Molecular Shapes"; Wiley-Interscience: New York, 1980; p 31.

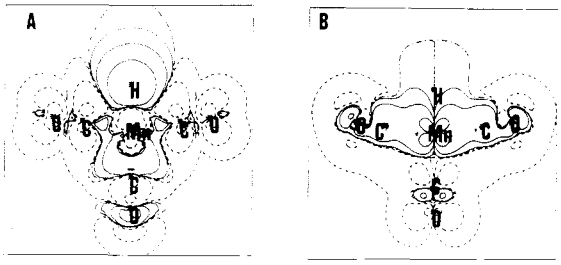


Figure 1. (A) Density plot of $\Delta\rho_{A_1}$ for $HMn(CO)_5$: positive contours, solid lines (—); negative contours, dashed lines (- - -). The zero contour is represented by (-•-). The positive contours represent a build up of charge on formation of $HMn(CO)_5$ from H^+ and $Mn(CO)_5^-$. Contours: 10^{-2}, 10^{-3}, 10^{-4}, -10^{-2}, -10^{-3}, -10^{-4}, and 0 e/au^3. (B) Density plot of $\Delta\rho_{A_2} + \Delta\rho_{B_1} + \Delta\rho_{B_2} + \Delta\rho_E$ for $HMn(CO)_5$ (same contour values as in A).

elaborate decomposition of ΔE_P given in Table I that the order of proton affinity 5d > 4d > 3d primarily is due to ΔE_{A_1}, for which we calculate an increase along both of the triads M = Mn, Tc, and Re and M = Fe, Ru, and Os.

The term ΔE_{A_1} and the strength of the donor–acceptor interaction 4 depend on the overlap $\langle 1s|a_1\rangle$ between the LUMO 1s of the incoming electrophile H^+ and the donor orbital a_1 on $M(CO)_5^{n-}$. The dependence is given in a approximate form[14b] based on perturbation theory by

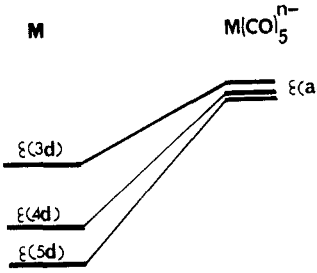
$$\Delta E_{A_1} = \frac{k\langle 1s|a_1\rangle^2}{\epsilon(1s) - \epsilon(a_1)} \qquad (3)$$

where k is a positive constant.[14c]

We have calculated $\langle 1s|a_1\rangle$ for the different metals as Mn (0.4756), Tc (0.5043), Re (0.5181), and Fe (0.4518), Ru (0.5006), and Os (0.5098) and can thus relate the increase in prooton affinity (and nucleophilicity) along each of the triads to a similar increase in the donor–acceptor integral $\langle 1s|a_1\rangle$. The more favorable overlap $\langle 1s|a_1\rangle$ for the 5d elements compared to the 3d elements reflects in fact that $\langle 1s|a_1\rangle$ largely depends on the σ overlap $\langle nd_{z^2}|1s\rangle$ and that such σ overlaps are smaller for the relatively contracted 3d orbitals than for the more extended 5d orbitals.

The order of proton affinity within each of the series $M(CO)_5$ (M = Fe, Ru, Os) and $M(CO)_5^-$ (M = Mn, Tc, Re) depends of course, in addition to the trends in $\langle 1s|a_1\rangle$, also on variations in the energy $\epsilon(a_1)$, through the denominator $\epsilon(1s) - \epsilon(a_1)$ of eq 3 representing the positive HOMO – LUMO gap in the donor–acceptor interaction 4. We have however calculated $\epsilon(a_1)$ within $M(CO)_5^-$ (M = Mn, Tc, Re) to vary by less than 0.2 eV and find a similar small spread in $\epsilon(a_1)$ for $M(CO)_5$ (M = Fe, Ru, Os). The small spread in $\epsilon(a_1)$ within each of the two homologous series $M(CO)_5$ (M = Fe, Ru, Os) and $M(CO)_5^-$ (M = Mn, Te, Re) is perhaps not surprising when we note that all nd_{z^2}-based a_1 orbitals of $M(CO)_5^{n-}$, in spite of the bonding interaction between nd_{z^2} and the π^* orbitals on the four basal CO ligands, are destabilized compared to the parent nd_{z^2} orbitals of the free atoms by the antibonding interaction between nd_{z^2} and the σ orbital on the apical CO ligand and that the destabilization based on the overlap considerations given before follows the order 5d > 4d > 3d. Thus, although the parent nd_{z^2} orbitals in the free atoms are well separated in energy with $\epsilon(5d) > \epsilon(4d) > \epsilon(3d)$ as shown to the left in 5, the nd_{z^2}-based orbitals in $M(CO)_5^{n-}$ will be closer in energy due to the different degree of destabilization as shown to the right in 5.

We have in step with experimental findings[2] calculated the 5d complex within $M(CO)_5$ (M = Fe, Ru, Os) as well as $M(CO)_5^-$ (M = Mn, Tc, Re) to have the largest proton affinity (and nucleophilicity). Our energy decomposition scheme, Table I, in conjunction with the qualitative considerations given above, leads us further to suggest that the 5d member within each of the two homologous series is the better nucleophile because the corresponding $5d_{z^2}$-based a_1 donor orbital has the better overlap $\langle 1s|a_1\rangle$ with the LUMO of the incoming electrophiles H^+. We will, if this analysis is correct, in general expect for a homologous series of complexes ML_n, with all three members of a traid, that the 5d member is the better nucleophile, even if H^+ is replaced by other electrophiles, provided that the donor orbital on ML_n is d based and interacts in a σ fashion with the LUMO of the electrophile, as in the case of a_1 on $M(CO)_5^{n-}$.



5

We have added $Cr(CO)_5^{2-}$ and $Co(CO)_5^+$ to the list of pentacarbonyls in Table I in order to study how the various components of ΔE_P will change along the homologous series $Cr(CO)_5^{2-}$, $Mn(CO)_5^-$, $Fe(CO)_5$, and $Co(CO)_5^+$ and possibly make predictions about the trend in nucleophilicity within a group of homologous complexes, with metal centers from the same transition series, toward other electrophiles than H^+. The term $\Delta E°$ is seen to decrease along M = Cr, Mn, Fe, and Co as the electrostatic interaction between $M(CO)_5^{n-}$ and H^+ becomes more repulsive with increasing nuclear charge on the metal. Perhaps more interesting is the steady decrease in ΔE_{elec} and ΔE_{A_1} with the nuclear charge on M along M = Cr, Mn, Fe, and Co. This trend can readily be explained by observing that the increase in nuclear charge will cause the 3d-based donor orbital a_1 on $M(CO)_5^{n-}$ to contract around the metal center, thus reducing the HOMO – LUMO overlap $\langle a_1|1s\rangle$ as well as ΔE_{A_1}; see eq 3. We calculate in fact $\langle a_1|1s\rangle$ for the different metals as Cr (0.4836), Mn (0.4756), Fe (0.4518), and Co (0.4138). The increase in nuclear charge will also lower $\epsilon(a_1)$, thus further diminishing ΔE_{A_1} and ΔE_{elec}. We expect in general, for a homologous family of complexes ML_n with metal centers from the same transition series, that ΔE_{elec}, corresponding to the interaction between an electrophile and ML_n, will decrease with increasing nuclear charge on M, provided that the donor orbital on the metal complexes is d based and interacts with the LUMO of the electrophile in a σ fashion. For charged electrophiles $\Delta E°$ will in addition increase for negatively charged electrophiles and decrease for positively charged electrophiles, with increasing nuclear charge on the metal.

We note finally in closing this section that the calculated protonation energy of 816 kJ mol^{-1} for $Fe(CO)_5$ is in fair agreement with the value of 853 kJ mol^{-1} reported by Beauchamp et al.[3] from gas-phase experiments.

Protonation of $M(CO)_4^-$ (M = Co, Rh, Ir), $M(CO)_4$ (M = Ni, Pd, Pt), $Fe(CO)_4^{2-}$, and $Cu(CO)_4^+$

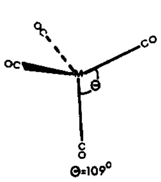
Protonation of the d^{10} tetracarbonylmetal anions $M(CO)_4^-$ (M = Co, Rh, Ir) and $Fe(CO)_4^{2-}$, all with a tetrahedral ground-state geometry 6, affords the metal hydrides $HM(CO)_4$ (M = Co, Rh, Ir) and $HFe(CO)_4^-$, where hydrogen takes up one of the axial positions in a slightly destorted bipyramidal structure[8] 7, whereas the $M(CO)_4$

Table II. A Decomposition of Calculated Protonation Energies (in kJ mol^{-1}) for $M(CO)_4$ (M = Ni, Pd, Pt) and $M(CO)_4^-$ (M = Co, Rh, Ir) as well as $Fe(CO)_4^{2-}$, $Cu(CO)_4^+$, and $Co(CO)_3(PH_3)^-$

$M(CO)_3L^{n-}$	ΔE_{prep}	$\Delta E°$	ΔE_{elec}	ΔE_{A_1}	$\Delta E_{A_2} + \Delta E_E$	ΔE_R	ΔE_P
$Co(CO)_4^-$	−30.2	475.3	747.1[b]	638.4	108.7		1192.2[a]
$Rh(CO)_4^-$	−35.1	462.4	777.6	671.5	106.1		1204.9
$Ir(CO)_4^-$	−29.8	441.4	812.3	702.2	110.1	23.1	1247.0
$Ni(CO)_4$	−32.3	−46.0	569.1	550.7	108.4		580.8
$Pd(CO)_4$	−39.2	−56.5	697.9	608.9	89.0		602.2
$Pt(CO)_4$	−27.3	−71.9	721.7	632.1	89.6	23.9	646.4
$Fe(CO)_4^{2-}$	−29.1	967.2	799.4	704.3	95.1		1735.5
$Cu(CO)_4^+$	−26.3	−599.3	594.3	498.7	95.6		−31.3
$Co(CO)_3(PH_3)^-$	−34.8	481.1	775.2	670.2	105.1		1221.5

[a] The total protonation energy ΔE_P is given by $\Delta E_P = \Delta E_{prep} + \Delta E° + \Delta E_{elec} + \Delta E_R$. [b] $\Delta E_{elec} = \Delta E_{A_1} + \Delta E_{A_2} + \Delta E_E$.

framework constitutes a destorted tetrahedron 8 where three of the CO–M–CO angles (θ) have been changed from 109.45° to ~98°, 8. Although protonation studies have been carried out on $M(PR_3)_4$ (M = Ni, Pd, Pt),[15] little is known about the proton affinity of $Ni(CO)_4$ or the extremely unstable complexes $Pd(CO)_4$, $Pt(CO)_4$, and $Cu(CO)_4^+$. We shall assume that $HM(CO)_4^+$ (M = Ni, Pd, Pt) and $HCu(CO)_4^{2+}$ all have the structure 7; see Computational Details.



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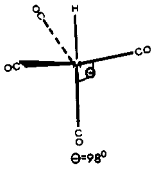

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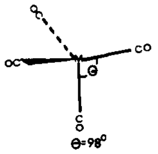
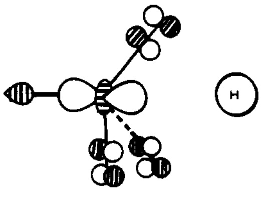


8

The energies, ΔE_P, calculated for the protonation of $M(CO)_4^{n-}$ (n = 2, 1, 0, −1) are given in Table II decomposed into ΔE_{prep}, $\Delta E°$, ΔE_{elec}, and ΔE_R. The term ΔE_{prep}, corresponding to the differnce in energy between 6 and 8, was calculated to be in the range −26 kJ mol^{-1} to −39 kJ mol^{-1} with 6 more stable than 8. The electronic term ΔE_{elec} can for $HM(CO)_4^{(1-n)+}$, with D_{3v} point group symmetry, be written as $\Delta E_{elec} = \Delta E_{A_2} + \Delta E_E$, and we note that ΔE_{A_1}, representing the donor–acceptor interaction 9, is the dominating term in ΔE_{elec}, just as in the case of $HM(CO)_5^{(1-n)+}$. The HOMO a_1 on $M(CO)_4^{n-}$, which serves as the donor orbital in 9, in quite similar to a_1 of $M(CO)_5^{n-}$, as it too consists of a d_{z^2} metal orbital bonding with respect to the π^* orbitals on the equatorial CO ligands and antibonding with respect to the σ orbital on the axial CO ligand.



$a_1 + 1s$

9

The trends gleaned from the calculations on $M(CO)_5^{n-}$ in Protonation of $M(CO)_5$ and $M(CO)_5^-$ as well as $Cr(CO)_5^{2-}$ and $Co(CO)_5^+$ are seen in Table II to apply for the $M(CO)_4^{n-}$ systems as well. Thus, the proton affinity increases along each of the triads M = Ni, Pd, and Pt and M = Co, Rh, and Ir and ΔE_{A_1} decreases with increasing nuclear charge in the homologous series $Fe(CO)_4^{2-}$ $Co(CO)_4^-$, $Ni(CO)_4$, and $Cu(CO)_4^+$ representing different metal centers from the same transition series.

One might perhaps were expected that the d^{10} $M(CO)_4^{n-}$ complexes in general would be better donors with a larger ΔE_{elec} than the d^8 $M(CO)_5^{n-}$ complexes, since $M(CO)_4^{n-}$ formally has a more electron-rich metal center than $M(CO)_5^{n-}$. This expectation is however not born out experimentally. We have[16] for instance that $HCo(CO)_4$ with $K_a \approx 1$ is a much stronger acid than $HMn(CO)_5$ with $K_a = 8 \times 10^{-8}$. from our calculations, Tables I and II, we find in fact that ΔE_{elec} is influenced very little by the formal oxidation state (d^8 or d^{10}), and thus for $Fe(CO)_4^{2-}$ we have ΔE_{elec} = 799 kJ mol^{-1} with ΔE_{elec} = 796 kJ mol^{-1} for $Fe(CO)_5$. The electronic term ΔE_{elec} is on the other hand for $M(CO)_4^{n-}$ as well as $M(CO)_5^{n-}$ strongly influenced by the nuclear charge on M as ΔE_{elec} for a group of metals from the same transition series decrease with increasing nuclear charge, and $Mn(CO)_5^-$ is according to our analysis a better base (donor) than $Co(CO)_4^-$ because Mn with the smaller nuclear charge has the largest ΔE_{elec}; see Tables I and II. If we assume that the difference in K_a between $HMn(CO)_5$ and $HCo(CO)_4$ is due solely to a difference in the protonation energies of $Mn(CO)_5^-$ and $Co(CO)_4^-$, thus neglecting variations in ΔS as well as the solvation energies, we find that ΔE_P for $Mn(CO)_5^-$ should be 37 kJ mol^{-1} larger than for $Co(CO)_4^-$, the calculated value is 25 kJ mol^{-1}.

Vidal and Walker[2a] have studied the basicity of $Co(CO)_4^-$, $Rh(CO)_4^-$, and $Ir(CO)_4^-$, experimentally. They were not able to obtain K_a values for the three acids $HCo(CO)_4$, $HRh(CO)_4$, and $HIr(CO)_4$ in the same solvent but found the qualitative order of basicity Ir > Co > Rh which differs from the order Ir > Rh > Co given in Table II with respect to Co and Rh. The calculated difference in ΔE_P between $Co(CO)_4^-$ and $Rh(CO)_4^-$ is only 13 kJ mol^{-1}, and it is thus possible that solvation effects might account for the discrepancy between the results in Table II and the observations by Vidal and Walker. A quantitative determination of K_a for the three acids $HM(CO)_4$ (M = Co, Rh, Ir) in the same solvent would clearly be of considerable interest as would the measurement of protonations energies for $M(CO)_4^-$ (M = Co, Rh, Ir) in the gas phase.

We shall finally, after the extensive discussion of how a metal center can influence the proton affinity and nucleophilicity of a complex, touch briefly on the role played by the coligands. This subject has recently been dealt with by Bursten[17] and Gatter, who considered a wide scope of different ligands, and we shall here only treat the case where the axial CO in $HCo(CO)_4$ of conformation 7 as well as $Co(CO)_4^-$ of conformation 8 is substituted by the model phosphine PH_3.

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Substitution of CO by PH_3 in $Co(CO)_4^-$ is seen from Table II to enhance the strength (ΔE_{A_1}) of the donor–acceptor interaction **9**. The protonation energy ΔE_P is as a result calculated to by 29 kJ mol^{-1} larger for $Co(CO)_3(PH_3)^-$ than for $Co(CO)_4^-$, and this is in line with experimental findings,[16] since $HCo(CO)_4$ with $K_a \approx 1.0$ is observed to be a stronger acid than $Co(CO)_3(PPh_3)$ with $K_a = 10^{-7}$. We note with reference to eq 3 that $\langle 1s|a_1\rangle$ is influenced very little by the substitution, $\langle 1s|a_1\rangle = 0.4648$ for $Co(CO)_4^-$ and $\langle 1s|a_1\rangle = 0.4624$ for $Co(CO)_3(PH_3)$, whereas $\epsilon(a_1)$ is raised by 0.8 eV on substitution. The higher energy of a_1 in $Co(CO)_3(PH_3)^-$ compared to $Co(CO)_4^-$ reflects an increase in the antibonding interaction between the axial σ orbital and $3d_{z^2}$ as CO is substituted by PH_3. The stronger antibonding interaction is brought about by a better overlap, $\langle \sigma_{PH3}|3d_{z^2}\rangle = 0.2134$ and $\langle \sigma_{CO}|3d_{z^2}\rangle = 0.1834$, as well as a considerable higher energy of σ_{PH_3} compared to σ_{CO}.

We hope, by means of our decomposition scheme, further to delineate the role played by the coligands in determining the nucleophilicity of a metal complex in a forthcoming communication.

Concluding Remarks

Orders of nucleophilicity have been established experimentally and rationalized theoretically, for numerous series of organic molecules. We have in the present study discussed the possible order of nucleophilicity for a homologous and isoelectronic series of metal complexes ML_n with respect to the position of the transition-metal M in the periodic table, based on an analysis of the calculated protonation energies for some d^8 and d^{10} metal carbonyls. Our calculations are approximate due to the limitations of the HFS method as well as the use of standard structural parameters rather than optimized geometries. We believed however that more involved calculations too would find that ΔE_{elec} from the interaction between ML_n and an electrophile increases with respect to M vertically down a triad and decreases along a transition series with increasing nuclear charge on M.

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$Cp_6Ni_2Zn_4$—An Unusually Electron-Rich Octahedral Cluster

P. H. M. Budzelaar, J. Boersma,* and G. J. M. van der Kerk

Department of Organic Chemistry, University of Utrecht, 3522 AD Utrecht, The Netherlands

A. L. Spek and A. J. M. Duisenberg

Department of Structural Chemistry, University of Utrecht, 3508 TB Utrecht, The Netherlands

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The title compound was prepared by heating Cp_2Zn and $Ni(COD)_2$ in benzene. It is surprisingly stable and can be heated to 250 °C without decomposition. Its structure was determined by a single-crystal X-ray diffraction study. The compound forms tetragonal crystals, space group $P4_2/mnm$, with two molecules in a cell of dimensions a = 9.352 (5) Å and c = 16.32 (1) Å. The molecule consists of an octahedron with apical nickel atoms and equatorial zinc atoms, each carrying an η^5-bound Cp group. The octahedron is compressed along the Ni–Ni axis, giving eight Ni–Zn bonds of 2.398 (2) Å, one long Ni–Ni bond of 2.571 (1) Å, and four nonbonded Zn–Zn distances of 2.86 Å (average). The formation of the compound is discussed in terms of the insertion of coordinatively unsaturated Ni into Cp–Zn bonds. $Cp_6Ni_2Zn_4$ is unusually electron-rich for an octahedral cluster. The electronic structure is discussed in a qualitative way.

Introduction

Although many zinc–transition-metal compounds are known, the compounds described in the literature are largely confined to derivatives of group 6 and 7 metals[17] and those of the iron and cobalt groups. In particular, no nickel–zinc compounds have been reported, although nickel–cadmium and nickel–mercury compounds are known.[1] In this paper, we describe the preparation and characterization of a nickel–zinc cluster compound and discuss its electronic structure. [For a preliminary account, see ref 2.]

Experimental Section

General Remarks. All manipulations were carried out in an atmosphere of dry, oxygen-free nitrogen. All solvents were dried and distilled under nitrogen prior to use. NMR spectra were recorded on Varian EM-390 and Bruker WP-200 spectrometers. $Ni(COD)_2$[3] and Cp_2Zn[4] were prepared according to literature methods.

Preparation of $Cp_6Ni_2Zn_4$. A mixture of 5 g of Cp_2Zn and 4 g of $Ni(COD)_2$ in 100 mL of benzene was heated in the course of 1 h from 20 to 75 °C. Initially, the solution was light yellow with white, suspended Cp_2Zn. Upon warming, the solution turned light green while the solid became orange. From about 50 °C on, the solution became deep green and dark green crystals of $Cp_6Ni_2Zn_4$ began to separate; the orange color of the solid disappeared. The reaction mixture was stirred for another hour at 75 °C, and the benzene was removed in vacuo. The residue was washed three times with 30 mL of pentane (from these washings, ca. 0.5 g of Cp_2Ni can be recovered by concentrating the solution and cooling to −40 °C). The green product was washed twice with 20 mL of a 3:1 diethyl ether–THF mixture to remove the excess of Cp_2Zn and dried in vacuo to yield 3.7 g (67%) of dark green $Cp_6Ni_2Zn_4$. NMR data (C_6D_6, δ in ppm relative to internal Me_4Si):

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