

dinates were refined with a constraint on the isotropic thermal parameter shift until a criteria for a satisfactorily completed analysis were met.

Registry No. 6e, 112549-07-2; 8, 87322-31-4; 12, 112549-04-9; 13, 112549-03-8; 14, 112549-01-6; 15, 112549-02-7; 20, 112549-05-0; 20-naphthalene, 112549-06-1; C₆H₅PCl₂, 644-97-3; FeCl₂, 7758-94-3;

[CpFe(CO)₂]₂, 12154-95-9; Mn₂(CO)₁₀, 10170-69-1; ZrCl₄, 10026-11-6; 2-butyne, 503-17-3.

Supplementary Material Available: A listing of anisotropic thermal parameters and hydrogen atomic coordinates (2 pages); tables of observed and calculated structure factor amplitudes (23 pages). Ordering information is given on any current masthead page.

Metal-Hydride and Metal-Alkyl Bond Strengths: The Influence of Electronegativity Differences

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Relative metal-alkyl and metal-hydride bond strengths are analyzed in terms of the electronegativity differences between the metal center and carbon or hydrogen. The greater strength of transition metal-hydride bonds in most complexes reflects a high effective electronegativity of the metal center. Arguments are presented that as the effective electronegativity of the metal center decreases (i.e. as the metal center becomes more electropositive), $D(M-H) - D(M-CH_3)$ also decreases.

There has been considerable recent interest in establishing trends in metal-ligand bond strengths^{1,2} with a primary goal of developing predictive power for assessing the viability of catalytic reaction cycles. A question of primary importance is the relative strengths of the L_nM-H and L_nM-C bonds, a crucial factor in the energetics of processes such as hydrogenation and the activation of the C-H and C-C bonds of hydrocarbons. It is generally recognized that the L_nM-H bond is stronger than the L_nM-alkyl bond by an amount estimated to fall within the range of 15-25 kcal·mol⁻¹. The reason for this difference is not clear. Halpern has suggested that steric factors contribute to weakening the metal-alkyl bond² and points to the fact that for the binary, ligand-free neutral or cationic species [M-R]^{0/+} (R = H, CH₃, etc.), the metal-alkyl bond is generally as strong as or stronger than M-H.³

An observation which at first sight appears to be consistent with the above is the apparent one-to-one correspondence between L_nM-X and H-X bond energies: for a variety of transition-metal compounds (L_nM-X = (η⁵-C₅Me₅)(PMe₃)₂Ru-X, (Ph₂PCH₂CH₂PPh₂)(CH₃)Pt-X, (η⁵-C₅Me₅)₂Sc-X, etc.) good linear correlations are obtained for plots of the bond energies for H-X against those for the corresponding L_nM-X (in the absence of M-X multiple bonding), with the exception of the point for X = H, which consistently falls off the line in the direction of stronger L_nM-H.⁴ In these cases the implied "extra" stability of the L_nM-H bond is 5-10 kcal·mol⁻¹, again suggesting that there is some factor which makes the M-H bond particularly strong in such complexes. On the other hand, plots of the bond energies for H-X versus those for R-X show exactly the same trend (see Figure 1 for R = CH₃); the point for X = H is displaced in the direction of stronger R-H from an otherwise linear correlation for a range of different R's (hydrocarbyl, halogen, etc.). Since it is difficult to justify that the R-H bond is anomalously strong for all such R's, it occurred to us that the correlation may fail at X = H because the H-H bond strength is in

fact anomalously weak! H-H is the only homonuclear bond in these plots, so that a possible explanation is that all other bonds enjoy a larger ionic contribution due to electronegativity differences,⁵ causing H-H to be weaker relative to R-H than all other H-X relative to R-X. A closer examination of the data reveals that the difference in R-X (R = alkyl) and H-X bond energies increases with increasing electronegativity for X.

We have thus attempted to relate L_nM-H and L_nM-C bond strengths to effective electronegativity differences. The original Pauling equation relating bond strength and electronegativity is given in (1).⁶ When this formula is

$$D(A-B) = \frac{1}{2}\{D(A-A) + D(B-B)\} + a(\chi_A - \chi_B)^2 \quad (1)$$

applied to the difference between A-H and A-CH₃ bond strengths (Δ), the expression in (2) is obtained. Thus a

$$\Delta \equiv D(A-H) - D(A-CH_3) = 2a(\chi_C - \chi_H)\chi_A + \frac{1}{2}\{D(H-H) - D(CH_3-CH_3)\} + a\{\chi_H^2 - (\chi_C)^2\} \quad (2)$$

plot of Δ versus χ_A should be linear, with A-H becoming relatively stronger than A-CH₃ as A becomes more electronegative. This conclusion follows from the fact that the

(1) Bulls, A. R.; Manriquez, J. M.; Thompson, M. E.; Bercaw, J. E. *Polyhedron*, in press and references cited therein; see also other articles in this issue which is devoted to this topic.

(2) Halpern, J. *Inorg. Chim. Acta* 1985, 100, 41-48. Data presented in this review show strong evidence for steric weakening of Co-C bonds involving bulky, substituted alkyl groups.

(3) Schilling, J. B.; Goddard, W. A., III; Beauchamp, J. L. *J. Am. Chem. Soc.* 1987, 109, 5573-80 and references cited therein.

(4) Bryndza, H. E.; Fong, L. K.; Paciello, R. A.; Tam, W.; Bercaw, J. E. *J. Am. Chem. Soc.* 1987, 109, 1444-56.

(5) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University: Ithaca, NY, 1960; pp 88-91.

(6) The value of the empirical constant (a) is 23 kcal·mol⁻¹ in the original Pauling relationship. Revised values of electronegativities utilized a geometric mean of homonuclear bond energies and a constant of 30 kcal·mol⁻¹, but these values do not differ substantially from the original ones (see ref 5). A reviewer has pointed out that Pauling's approach to bond strengths is an approximation which in some cases can fail completely (see, for example: Pearson, R. G. *J. Chem. Soc., Chem. Commun.* 1968, 65). While this criticism has some validity, the good correlation represented by Figure 2 demonstrates that in the present case this method is applicable at least to some degree.

† Contribution No. 7730.

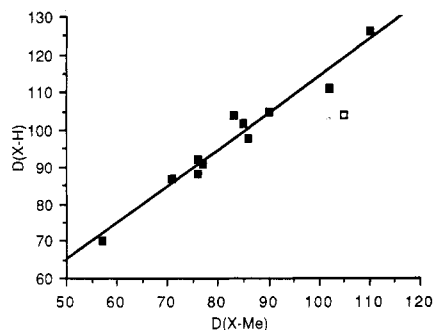


Figure 1. Plot of $D(\text{H-X})$ versus $D(\text{H}_3\text{C-X})$ ($\text{kcal}\cdot\text{mol}^{-1}$) for $\text{X} = \text{CH}_3, \text{CH}_2\text{CH}_3, \text{CH}_2\text{C}_6\text{H}_5, \text{C}_6\text{H}_5, \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{OCH}_3, \text{SCH}_3, \text{N}(\text{CH}_3)_2$ (filled), and H (open).

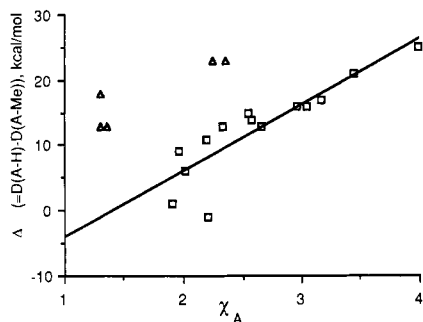


Figure 2. Plot of Δ versus Pauling electronegativity for main-group (open squares) and transition-metal (open triangles) compounds; data from Table I. The least-squares line corresponds to the main-group compounds only.

coefficient of χ_A is positive (CH_3 is more electronegative than H). Indeed, as shown in Table I and Figure 2, a reasonably good linear correlation does obtain for main-group A , with Δ largest for $\text{A} = \text{F}$ and near zero for $\text{A} = \text{SiMe}_3$.

Why, then, are $\text{L}_n\text{M-H}$ bonds so much stronger than $\text{L}_n\text{M-C}$, even for compounds of the electropositive early transition metals such as $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sc-R}$ and $(\eta^5\text{-C}_5\text{Me}_5)_2(\text{H})\text{Hf-R}$?¹ One might answer that the effective electronegativity of metal centers in such complexes is in fact quite high. Such a conclusion has been reached from ab initio calculations which point to a quite nonpolar Sc-H bond in $\text{Cl}_2\text{Sc-H}$ (and by extension in $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sc-R}$; $\text{R} = \text{H}, \text{alkyl}, \text{etc.}$),⁷ in contrast to the strongly polarized $\text{Sc}^+\text{-C}^-$ usually assumed for early-transition-metal alkyls. From the value of $\Delta \approx 13 \text{ kcal}\cdot\text{mol}^{-1}$ in the Sc system,¹ we conclude that the $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sc}$ fragment is similar in electronegativity to a methyl group! Although this likeness would at first sight seem absurd, the nonpolar character of the Sc-C bond may be understood on the basis that the two electronegative $(\eta^5\text{-C}_5\text{Me}_5)$ ancillary ligands⁸ bond principally via the $4s$ valence orbital of Sc , relegating the scandium orbital of the Sc-R bond to essentially pure $3d$ character. Bare M-R neutrals or cations (e.g. $[\text{Sc-H}]^+$ and $[\text{Sc-CH}_3]^+$),³ in this picture, are quite different, since these mono- or divalent metal centers use principally their $4s$ valence orbitals in M-R bonding. Hence these metal centers are extremely electropositive, as the various methods for estimating electronegativity imply,⁹ and exhibit low or negative values for Δ (i.e. the M-CH_3 bond

Table I. Pauling Electronegativities, Bond Energies, and Δ Values

A	χ_A^a	$D(\text{A-H})^{b,c}$	$D(\text{A-CH}_3)^{b,c}$	Δ^b
H	2.2	104	105	-1
H_3C	2.55	105	90	15
Me_3Si	1.90	90	89	1
Me_3Ge	2.01			6 ^d
Me_3Sn	1.96			9 ^d
Me_3Pb	2.33			13 ^d
Me_2N	3.04	92	76	16
Me_2P	2.19			11 ^e
MeO	3.44	104	83	21
MeS	2.58	91	77	14
F	3.98	135	110	25
Cl	3.16	102	85	17
Br	2.96	87	71	16
I	2.66	70	57	13
$(\eta^5\text{-C}_5\text{Me}_5)_2\text{Sc}$	1.36			$\approx 13^f$
$(\eta^5\text{-C}_5\text{Me}_5)_2(\text{H})\text{Hf}$	1.3			$\approx 18^f$
$(\eta^5\text{-C}_5\text{Me}_5)_2(\text{R})\text{Th}$	1.3			$\approx 13^f$
$(\eta^5\text{-C}_5\text{H}_5)_2(\text{R})\text{Mo}$	2.24			$\approx 23^g$
$(\eta^5\text{-C}_5\text{H}_5)_2(\text{R})\text{W}$	2.36			$\approx 23^g$

^a Pauling electronegativity of bonding atom, from ref 9. It might appear more appropriate to use a group electronegativity value for CH_3 rather than the Pauling value for carbon; since group electronegativities are not available for the other polyatomic substituents in this table, it seemed better to use the latter for consistency. In any case, as the electronegativities estimated for CH_3 are all greater than that for H (ref 9, p 156), the conclusions reached would not be altered. ^b In $\text{kcal}\cdot\text{mol}^{-1}$. ^c Data from: McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* 1982, 33, 493-532. ^d Data from: Jackson, R. A. *J. Organomet. Chem.* 1979, 166, 17-9. ^e Approximate value from mean bond energies; cf.: Maier, L. In *Organic Phosphorus Compounds*; Maier, L.; Kosolapoff, Eds.; Wiley: New York, 1972; Vol. 1, p 95. Experimental data for direct comparisons, e.g., ΔH_f° of PMe_2H , are not available (Frenking, G.; Goetz, H.; Marschner, F. *J. Am. Chem. Soc.* 1978, 100, 5295-6). ^f Based on the measured relative bond energies of M-H versus M-propyl , 18 (Sc) and 23 (Hf) $\text{kcal}\cdot\text{mol}^{-1}$ (ref 1), and the fact that A-Me bonds are typically about 5 $\text{kcal}\cdot\text{mol}^{-1}$ stronger. ^g These are not true single bond dissociation values but are based on the mean bond strengths in L_nMH_2 and $\text{L}_n\text{M}(\text{CH}_3)_2$ species. $\text{M} = \text{Th}$: Bruno, J. W.; Marks, T. J.; Morss, L. R. *J. Am. Chem. Soc.* 1983, 105, 6824-32. $\text{M} = \text{Mo}$ and W : data from ref 13.

energies may even exceed the M-H bond energies).³ By contrast, $[\text{L}_n\text{M}]$ fragments with strong π -acceptor ligands behave as though they are quite electronegative; the values² of $\Delta \approx 25 \text{ kcal}\cdot\text{mol}^{-1}$ for $\text{A} = [\text{Mn}(\text{CO})_5]^{10}$ and $[\text{Co}(\text{CO})_4]$ suggest that they resemble fluorine! Such an analogy would be consistent with (i) the strongly acidic nature of these "hydrides"¹¹ and (ii) the large values of $^1J_{\text{CH}}$ in $\text{CH}_3\text{Mn}(\text{CO})_5$ and related species, which are more typical of electronegatively substituted methanes such as CH_3OH than of methyl-metal species such as $(\text{CH}_3)_4\text{Si}$.¹²

One might contend that these arguments border on being circular, since according to the Pauling relationship electronegativity and bond energies are interdependent. Nonetheless, to the extent that the two properties of the $\text{L}_n\text{M-R}$ bond ($\text{R} = \text{H}, \text{hydrocarbyl}$) are accurately related by eq 1, we assert that one can be used to infer the other. Hence, the polarity of metal-alkyl and metal-hydride

(7) Steigerwald, M. L.; Goddard, W. A., III *J. Am. Chem. Soc.* 1984, 106, 308-11.

(8) The electron affinities of cyclopentadienyl radical and Cl^\cdot are comparable, so that the $\text{Sc}-(\eta^5\text{-C}_5\text{Me}_5)$ bond, like the Sc-Cl bond, is expected to be very polar.

(9) Huheey, J. E. *Inorganic Chemistry*, 2nd ed.; Harper & Row: New York, 1978; pp 162-4.

(10) An experimental value of $\Delta = 15 \text{ kcal}\cdot\text{mol}^{-1}$ has been reported for $\text{R-Mn}(\text{CO})_5$ ($\text{R} = \text{H}, \text{CH}_3$) (Connor, J. A.; Zafarani-Moattar, M. T.; Bickerton, J.; El Sayed, N. I.; Suradi, S.; Carson, R.; Al Takhin, G.; Skinner, H. A. *Organometallics* 1982, 1, 1166-74); however, this result has been somewhat controversial, with larger values for both $D(\text{Mn-H})$ and Δ considered more appropriate.² A reviewer notes that use of a revised value for ΔH_f° for $\text{Mn}(\text{CO})_5$ based on gas-phase studies (Martinho Simoes, J. A.; Schultz, J. C.; Beauchamp, J. L. *Organometallics* 1985, 4, 1238-42) would indeed result in a higher calculated value for $D(\text{Mn-H})$ (and $D(\text{Mn-R})$; Δ would remain unchanged).

(11) For a discussion of metal hydride acidity in terms of electronegativities see: Pearson, R. G. *Chem. Rev.* 1985, 85, 41-9.

(12) Labinger, J. A. *J. Organomet. Chem.* 1980, 187, 287-96.

bonds of transition-metal compounds could possibly be deduced from the magnitude of Δ . Similarly, differing ligand sets and metal oxidation states (even for the same transition metal) may result in greatly different relative metal-hydride and metal-alkyl bond strengths due to variations in the *effective* electronegativity of the metal center.¹³ Standard values of electronegativity will not generally give accurate pictures of bond polarity and

consequent relative bond strengths for transition-metal complexes, as is readily apparent from Figure 2. The most commonly cited values around 25 kcal·mol⁻¹ should only be ascribed to L_nM fragments with strongly π -withdrawing ligand sets and, hence, are probably at the upper end of the range. One might also infer a strategy for designing an alkane-activating metal center: relatively strong M-C bonding should be favored by a relatively electropositive [L_nM] which by inference uses much metal s character in the M-C bonding.

(13) Limited data demonstrate that this is also true for main-group compounds; e.g. for A = SiMe₃, SiMe₂Cl, and SiMeCl₂, $\Delta = 1, 2,$ and 7 kcal mol⁻¹ respectively (calculated from data in: Pilcher, G.; Skinner, H. A. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1982; Vol. 1, pp 43-90).

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Syntheses of the Ruthenium(VI) Alkyl Complexes [Ru(N)R_{4-x}Cl_x]⁻ (R = Me, CH₂SiMe₃) and the X-ray Crystal Structure of [N-*n*-Bu₄][Ru(N)Me₄]

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Anionic nitridoruthenium(VI) alkyl complexes [Ru(N)Me₄]⁻ and [Ru(N)(CH₂SiMe₃)₄]⁻ have been prepared by the alkylation of [Ru(N)(OSiMe₃)₄]⁻ with AlMe₃ or with Mg(CH₂SiMe₃)₂, respectively. The structure of one of these, [N-*n*-Bu₄][Ru(N)Me₄]⁻, was determined by single-crystal X-ray diffraction: $a = 9.359$ (3) Å, $b = 18.368$ (4) Å, $c = 15.193$ (5) Å; $V = 2519$ (1) Å³; $Z = 4$; $\beta = 105.31$ (2)°; $\rho_{\text{calcd}} = 1.101$ g/cm³, monoclinic space group $P2_1/n$. Mixed alkyl-chloro complexes, [Ru(N)R_{4-x}Cl_x]⁻ (R = CH₂SiMe₃, $x = 1-2$; R = Me, $x = 1-3$), result from the reaction of HCl(g) with the alkyl complexes. The gold(I) chloro complex Au(PPh₃)Cl reacts in a manner analogous to HCl and converts [Ru(N)Me₄]⁻ to [Ru(N)ClMe₃]⁻ with formation of Au(PPh₃)Me. In contrast to the related osmium complexes, both Lewis acid adducts of the ruthenium nitrides and (alkylimido)tetraalkylruthenium complexes are thermally unstable.

Introduction

Alkyl complexes of early transition elements in high oxidation states are now well-known but only recently have similar complexes of the platinum metals in high oxidation states been prepared. The homoleptic osmium(IV) alkyl complexes Os(*c*-C₆H₁₁)₄ and Os(*o*-MeC₆H₄)₄ were prepared and structurally characterized.¹ The first ruthenium(IV) alkyl complexes, (1-3:6,7:10-12- η -C₁₂H₁₈)RuIme and (1-3:6,7:10-12- η -C₁₂H₁₈)RuMe₂, were reported in 1985.² Cyclopentadienylrhodium and -iridium alkyl complexes in the +4 and +5 oxidation states were prepared.^{3,4} Series of nitrido-⁵ and (alkylimido)⁶osmium(VI) alkyl complexes were synthesized and the oxoosmium(VI) alkyl complexes Os(O)(CH₂SiMe₃)₄,⁷ Os(O)R₄ (R = Me, CH₂SiMe₃, CH₂Ph, and Ph),⁸ and OsO₂(2,4,6-Me₃C₆H₂)₂⁹ were also prepared. Prior to this work, however, no ruthenium(VI) alkyl complexes had been reported.

An investigation of the reaction chemistry of ruthenium(VI) alkyl complexes has implications to the catalytic oxidation and ammoxidation of organic molecules. Ruthenium tetraoxide and other complexes of ruthenium have been used as stoichiometric and catalytic oxidants.¹⁰⁻¹⁴ It has been proposed that some of these oxidants form intermediate high oxidation state organometallic complexes in their reactions with unsaturated organic molecules.^{15,16}

An investigation of reactions occurring at the heteroatom ligand are especially important. There is a possibility for protic acids and other electrophiles to react with nitrido-tetraalkylruthenium(VI) complexes at the nitrido nitrogen atom, at the d² metal center, or at a metal-carbon bond. There is precedent for each of these reactions. Molybdenum nitrides can be protonated^{17,18} the d⁰ alkyl complexes of metals of the titanium triad are directly cleaved

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