

photooxidation in Cu(II) macrocycles are smaller than those determined for similar Ag(II) compounds. These Cu(II) complexes also undergo a significant photooxidation of axial ligands that we have not detected with Ag(II) homologues. Quantum yields, calculated from changes in the optical spectrum and from the concentration of free Ag(I), give an upper limit, $\phi \leq 10^{-2}$, for the axial ligand photooxidation, i.e. less than 1% of the total photochemical transformation, in spite of the existence of (axial ligand to metal) charge-transfer states at low energies. Insofar as flash photolysis shows the absence of slow back-electron-transfer reactions where Ag(I) macrocycles are reoxidized, the low value of the quantum yield must reflect rapid reoxidation within the solvent cage and/or a fast relaxation of the charge-transfer excited state. Consideration of the respective self-exchange rate constants of Cu(II)/Cu(I) and Ag(II)/Ag(I) complexes of the [14]aneN₄ macrocycle (Table II) casts doubt upon the first possibility, i.e. the reoxidation of Ag(I) in the solvent cage with a faster rate than in the case of Cu(I) complexes. Moreover, comparison of the wavelength-dependent low quantum yield photochemistry of the Cu(II) to the wavelength-independent high quantum yield photochemistry (relative to Cu(II)) of the Ag(II) complexes suggests that the CTTM_{N→Ag} reactive state or states in Ag(II) macrocycles are rapidly populated from states placed at higher energies in-

cluding those involving charge transfers from axial ligands. Although the role of metal-centered states in depopulating the reactive CTTM must still be investigated, one can propose that such a radiationless crossing, faster for Cu(II) than for Ag(II), can explain some of our experimental observations.¹ Evidence about this mechanism will be the subject of further work on the photochemistry of Ag(II) complexes.

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Registry No. Ni(Me₆[14]aneN₄)²⁺, 18444-38-7; Ni(Me₆[14]aneN₄)⁺, 47105-34-0; Ni(Me₆[14]dieneN₄)²⁺, 15079-51-3; Ni(Me₆[14]dieneN₄)⁺, 115303-92-9; Ni(Me₂pyo[14]trieneN₄)²⁺, 47023-95-0; Ni(Me₂pyo[14]trieneN₄)⁺, 116025-30-0; Ni(Me₆[14]-1,4,8,14-tetraeneN₄)²⁺, 18444-46-7; Ni(Me₆[14]-1,4,8,11-tetraeneN₄)⁺, 75400-04-3; Ag([14]aneN₄)³⁺, 48146-03-8; Ag([14]aneN₄)²⁺, 48146-02-7; Ag[14]aneN₄⁺, 116025-32-2; Cu(Me₆[14]dieneN₄)²⁺, 33727-13-8; Cu(Me₆[14]dieneN₄)⁺, 47105-27-1; Cu(Me₆[14]-1,3,8,10-tetraeneN₄)²⁺, 71170-97-3; Cu(Me₆[14]-1,3,8,10-tetraeneN₄)⁺, 80502-51-8; Cu(Me₂pyo[14]trieneN₄)²⁺, 21780-13-2; Cu(Me₂pyo[14]trieneN₄)⁺, 80502-45-0; Cu(Me₂pyo[14]eneN₄)²⁺, 116301-16-7; Cu(Me₂pyo[14]eneN₄)⁺, 116301-15-6; Ag(Me₆[14]aneN₄)²⁺, 47105-14-6; Ag(Me₆[14]aneN₄)⁺, 47105-13-5.

Contribution from the Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4, and Department of Theoretical Chemistry, Free University, Amsterdam, The Netherlands

Theoretical Study on the Difference in the Relative Strengths of Metal-Hydrogen and Metal-Methyl Bonds in Complexes of Early Transition Metals and Complexes of Middle to Late Transition Metals

Tom Ziegler,^{*,†} Wendan Cheng,^{†,§} Evert Jan Baerends,[‡] and Walter Ravenek[‡]

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Molecular orbital calculations based on density-functional theory have been carried out on the homolytic metal-hydrogen and metal-methyl bond energies in Cp₂MR (M = Sc, V, Mn), CpNi(CO)R, Co(CO)₄R, CpFe(CO)₂R, Mn(CO)₅R, and CpCr(CO)₃R for R = H and CH₃. The intrinsic M-H bond energies (the bond energies between H and the metal fragments ML_n in the same conformation as the ML_n framework in HML_n) are calculated to be remarkably similar (202–230 kJ mol⁻¹) for all the hydride complexes, irrespective of the vast differences in electronegativity between the metal centers. The calculated strengths of the metal-methyl bonds vary strongly from 220 kJ mol⁻¹ for the early transition metal Sc to between 100 and 170 kJ mol⁻¹ for the middle to late transition metals. It is shown that the electroneutral M-CH₃ bond in complexes of middle to late transition metals is weakened by repulsive interactions between occupied metal orbitals and the fully occupied (mainly) 2s_C orbital on CH₃, to the extent where the M-CH₃ bond becomes weaker than the corresponding M-H bond. The repulsive interaction between occupied metal orbitals and the fully occupied 2s_C orbital on CH₃ is reduced considerably in the polar M-CH₃ bond of Cp₂Sc(CH₃), and it is found for the early transition metal scandium that the M-CH₃ bond is as strong as the M-H bond. An extension of our study to Cp₂MR (M = Y, La, Tc, and Re) reveals, among the 4d and 5d elements, the same change in the stability order from M-H ~ M-CH₃ for the early transition metals to M-H > M-CH₃ for the middle transition metals. It is in addition found that the M-R bond energies increase on descending each of the two triads M = Sc, Y, La and M = Mn, Tc, Re. The increase is correlated to a corresponding increase in bonding overlaps.

Introduction

Thermochemical data on metal-ligand bonds constitute a much needed source of input in any estimate of the energetics for organometallic reaction steps. Of particular importance are data on the strength of M-R (R = H, alkyl) bonds, in view of the fact that M-R bond cleavage and M-R bond formation pervade most of the elementary reaction steps in organometallic chemistry. Nevertheless, the development of a thermochemistry for the metal-alkyl and metal-hydride bonds has been slow and painful.¹ The M-R bond strength (R = alkyl, H) has been studied in a number of ligand-free MR systems both experimentally² and theoretically.³ Experimental⁴ and theoretical⁵ data on M-R bond strengths in RML_n alkyl and hydride complexes are, however, often

insufficient for a rational approach to the synthesis of new organometallics based on quantitative estimates of reaction en-

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[†] University of Calgary.

[‡] Free University, Amsterdam.

[§] On leave from Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science, Fujian, Peoples Republic of China.

thalpies. Sufficient data on the strength of M-L single bonds are also lacking for other ligands (L), in spite of recent experimental^{4a,4c} and theoretical⁶ efforts.

We present here calculations on M-H and M-CH₃ bond energies in a number of representative RML_n complexes, encompassing early- as well as middle- to late-transition-metal centers. The main objective in this study has been to scan the spectrum of transition metals in search for the general periodic trends governing M-R (R = H, alkyl) bond strengths. In particular, we would like to understand why M-R bond strengths of early transition metals appear⁷ to be quite similar for R = H and R = alkyl, whereas the M-H bond seems^{1a} to be stronger than the corresponding M-alkyl bond for complexes of middle to late transition metals. The difference in M-H and M-alkyl bond strengths has important implications for the relative ease with which ligands can insert⁸ into the two types of bonds as well as the facility^{5a,7} with which H₂ can add oxidatively to a metal center in comparison with H-alkyl and alkyl-alkyl bonds.

All our calculations are based on Becke's density functional theory⁹ and the HFS-LCAO program system due to Baerends¹⁰ et al. The new density functional theory has been tested extensively on diatomics⁹ as well as polyatomic molecules¹¹ and applied in a number of calculations on metal-ligand¹² and metal-metal¹³ bond energies. We shall in conjunction with Becke's density functional theory apply the generalized transition state theory.¹⁴ The generalized transition state theory allows for a decomposition of the bond energies in terms of steric and electronic factors.

Computational Details

All calculations were based on the LCAO-HFS program system due to Baerends¹⁰ et al. or its relativistic extension due to Snijders¹⁵ et al. The density functional employed contained Becke's nonlocal exchange correction⁹ as well as Stoll's correlation potential¹⁶ for electrons of different spins based on Vosko's parametrization¹⁷ from electron gas data. Bond energies were evaluated by the generalized transition-state method^{14a} or its relativistic extension^{14c}.

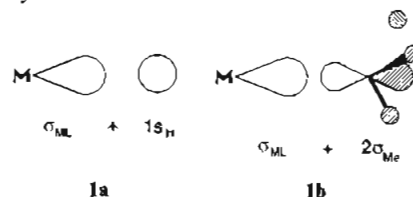
A triple- ζ -STO basis set¹⁸ was employed for the *ns*, *np*, *nd*, (*n* + 1)*s*, and (*n* + 1)*p* shells of the transition metals. The *ns* and *np* valence shells of the ligand atoms were represented by a double- ζ -STO basis set augmented by a single- ζ -STO 3d orbital, except for H where a 2p STO was used as a polarization function. The other shells of lower energy were considered as core and frozen according to the method of Baerends¹⁰ et al. In order to describe accurately the Coulomb and exchange potentials, extensive fits¹⁰ of the density were carried out by using a set of fit functions¹⁹ including *s*-, *p*-, *f*-, and *g*-type STO functions.

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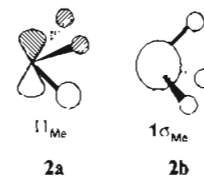
The Cp₂M fragments were given a standard Cp-M-Cp angle of 140° and the remaining geometrical parameters for M = Sc^{20a}, Y^{20b}, La^{20c}, V^{20d}, Mn^{20e}, Tc^{20f}, and Re^{20g} were taken from the literature. Standard geometrical parameters were adopted for CpNi(CO)^{21a}, Co(CO)₄^{21b}, CpFe(CO)₂^{21c}, Mn(CO)₅^{21d}, and CpCr(CO)₃^{21e}. The R(M-H) and R(M-CH₃) bond distances were 1.56 and 2.24 Å, respectively, for the 3d elements. The M-H and M-CH₃ distances for M = Tc and Re were taken from ref 5b. The M-H and M-CH₃ distances for M = Y and La were optimized at R(Y-H) = 1.80 Å, R(Y-CH₃) = 2.45 Å, R(La-CH₃) = 2.72 Å, and R(La-H) = 2.24 Å, respectively.

Qualitative Description of the M-H and M-CH₃ Bonds in RML_n (R = H, CH₃)

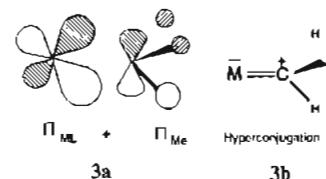
The only interaction (1a) of importance in a metal-hydrogen bond is between a singly occupied σ -type ML_n fragment orbital σ_{ML} and the singly occupied 1s_H orbital of hydrogen. The metal-alkyl bond can to a first approximation be described by a similar interaction (1b) between σ_{ML} and the singly occupied orbital 2 σ_{Me} on the methyl radical.



In contrast to the hydrogen atom, the methyl radical has three pairs of valence electrons. These valence electrons are situated in respectively the π_{Me} (2a) and 1 σ_{Me} (2b) orbitals.

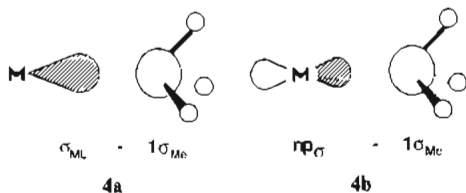


The influence of the occupied π_{Me} orbitals on the M-CH₃ bond is primarily stabilizing as electron density is donated (3a) from π_{Me} to empty orbitals on the ML_n fragment in what one might classify as a hyperconjugation interaction (3b).



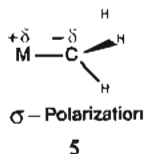
The occupied 1 σ_{Me} orbital of the methyl radical will on the other hand destabilize the M-CH₃ bond since 1 σ_{Me} is involved in a two-orbital-three-electron repulsive interaction²² (4a) with σ_{ML} as well as a two-orbital-four-electron repulsive interaction²² (4b) with the *ns* and *np_σ* core orbitals on the metal center of ML_n.

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There has been considerable interest^{1,4,5} in determining both the absolute and relative strengths of M-H and M-CH₃ bonds. The picture emerging^{1,4,5a} from the currently scanty experimental data^{1,4} seems to indicate that M-H bonds are stronger (~ 240 kJ mol⁻¹) than M-CH₃ bonds (~ 160 kJ mol⁻¹) for middle to late transition metals (groups 6-10), whereas the M-alkyl bond is equal^{4a,7} to (~ 240 kJ mol⁻¹) or even stronger than the M-H bond for early transition metals (groups 3 and 4).

For group 10 to group 6 metals we have previously^{5b} analyzed the relative strength of M-H and M-CH₃ bonds in terms of the simple bonding picture given above. We concluded in this analysis that M-CH₃ bonds are weaker than M-H bonds for middle to late transition metals as a result of the two-orbital-three-electron interaction **4a** between σ_{ML} and $1\sigma_{Me}$. We shall here try to understand how the M-R (R = H, CH₃) bond is modified by early transition metals in such a way that M-H and M-CH₃ bond strengths are nearly equalized. Our rationale will be based on the repulsive interaction **4a**, between σ_{ML} and $1\sigma_{Me}$, as well as the polarity **5** in the σ -bonding interactions **1a** and **1b**.



The interrelationship between the polarity **5** and the interaction in **4a** is illustrated in Figure 1. We have to the right in Figure 1 a simple two-electron picture of the M-CH₃ bond, in which a σ -bonding orbital ϕ_σ is formed from the interaction **1b** between σ_{ML} and $2\sigma_{Me}$. The σ -bonding orbital ϕ_σ can be written in terms of its components as

$$\phi_\sigma = C_1\sigma_{ML} + C_2[2\sigma_{Me}] \quad (1)$$

where a small value of $|C_1|$ ($|C_1| \ll 1/\sqrt{2}$) corresponds to a substantial polarization in **5** with a large δ . The simple two-electron picture of the M-CH₃ bond is modified when we in a full SCF calculation include the $1\sigma_{Me}$ lone-pair orbitals as illustrated to the left in Figure 1. The occupied $1\sigma_{Me}$ orbital will interact with ϕ_σ . In doing so $1\sigma_{Me}$ is stabilized by $-\Delta E_1$ (ΔE_1 positive) whereas ϕ_σ is destabilized by ΔE_2 (ΔE_2 positive). The interaction between ϕ_σ and $1\sigma_{Me}$ is four-electron destabilizing²² with $\Delta E_2 > \Delta E_1$, and the M-CH₃ bond is as a consequence destabilized by $\Delta E_2 - \Delta E_1$ from this interaction. It can readily be shown²³ that qualitatively

$$\Delta E_2 - \Delta E_1 \propto (1\sigma_{Me}|\phi_\sigma)^2 \quad (2)$$

where $(1\sigma_{Me}|\phi_\sigma)$ is the overlap between $1\sigma_{Me}$ and ϕ_σ . The expression in eq 2 is, however, reduced to

$$\Delta E_2 - \Delta E_1 \propto (1\sigma_{Me}|\sigma_{ML})^2[C_1]^2 \quad (3)$$

by observing that $1\sigma_{Me}$ and $2\sigma_{Me}$ have zero overlap and thus, to a first approximation, zero interaction.

It follows from eq 3 that the destabilizing influence of $1\sigma_{Me}$ on the M-CH₃ bond depends strongly on the polarity in **5**, since $\Delta E_2 - \Delta E_1$ will be smaller in a polar bond where $[C_1]^2$ is modest than in an electroneutral bond where $[C_1]^2 \sim 0.5$. In the next sections we shall present results from density functional calculations on M-H and M-CH₃ bond energies in a number of different metal hydrides and metal alkyl complexes. The qualitative analysis of our numerical results will be based on eq 3.

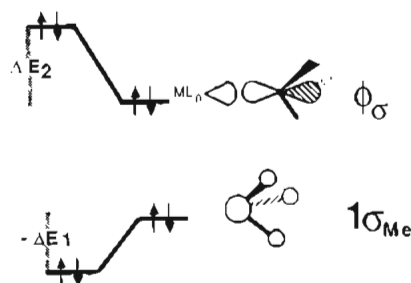


Figure 1. Destabilization of the M-CH₃ bond from the interaction between $1\sigma_{Me}$ and ϕ_σ . The M-CH₃ bonding orbital ϕ_σ , an in-phase bonding combination between the singly occupied $2\sigma_{Me}$ orbital on CH₃ and the singly occupied σ_{ML} orbital on the ML_n fragment (see **1b** of text), is involved in a repulsive two-orbital-four-electron interaction. The $1\sigma_{Me}$ orbital is stabilized by $-\Delta E_1$, and the ϕ_σ orbital is destabilized by ΔE_2 . The M-CH₃ bond is weakened by $\Delta E_2 - \Delta E_1$.

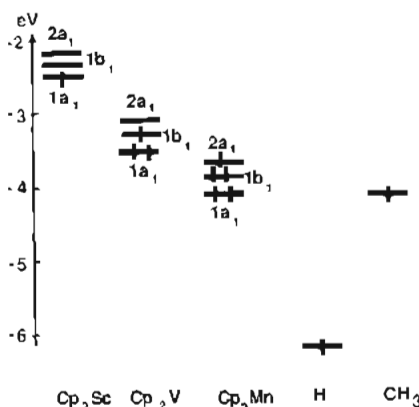


Figure 2. Energies of the three Cp_2M orbitals $1a_1$, $1b_1$, and $2a_1$ in comparison with the orbital energies of $1s_H$ and $2\sigma_{Me}$. The occupations correspond to the electronic groundstate configurations for the three Cp_2M ($M = Sc, V, Mn$) fragments. Orbital energies do not correspond to ionization potentials in the HFS theory.

Cp_2M-R (R = H, CH₃; M = Sc, V, Mn)

Experimental comparisons of M-R (R = H, CH₃) bond energies in RML_n fragments often differ in their coordination number and conformation as well as the nature of the coligand L. Such complicating factors are removed in the series of bent sandwich complexes (**6**) Cp_2M-R known to exist²¹ for both early ($M = Sc, La, Y$) and middle ($M = V, Re$) transition metals, and we shall here consider first the series Cp_2M-R ($M = Sc, V, \text{ and } Mn$).

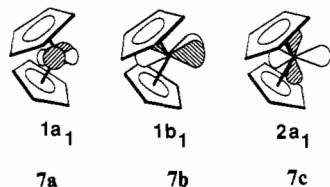


The Cp_2M fragment has the three characteristic²⁴ frontier orbitals $1a_1$ (**7a**), $1b_1$ (**7b**), and $2a_1$ (**7c**), of which $2a_1$ is ideally suited for a σ -bonding interaction (**1b**) with $2\sigma_{Me}$ (and $1s_H$). The orbital energies of $1a_1$, $1b_1$, and $2a_1$ are given in Figure 2 for all three metals $M = Sc, V, \text{ and } Mn$. We note, not surprisingly, that there is a steady decrease (of 2 eV) in the energies of the three orbitals as we proceed from the less electronegative Sc to the more electronegative Mn. The electronic ground state configurations for the fragments are $(1a_1)^1$, $(1a_1)^2(1b_1)^1$, and $(1a_1)^2(1b_1)^2(2a_1)^1$ for $M = Sc, V, \text{ and } Mn$, respectively.

It is useful in a discussion of the $D(M-R)$ (R = H, CH₃) bond energies, between R and the Cp_2M fragment of conformation **6b**

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(in its electronic ground state), to consider the formation of the M-R bond in a sequence of steps. In the first step the Cp_2M fragments of conformation **6b** are prepared for the formation of the combined complex Cp_2MR by electronic promotions. The Cp_2Sc fragment was promoted from the $(1a_1)^1$ ground state to the $(2a_1)^1$ valence configuration (promotional energy 40 kJ mol^{-1}), whereas Cp_2V was promoted from the $(1a_1)^2(1b_1)^1$ ground state to the $(1a_1)^2(2a_1)^1$ valence configuration (promotional energy 14 kJ mol^{-1}). The electronic promotions of Cp_2Sc and Cp_2V will not influence the calculated $D(Cp_2M-R)$ ($M = Sc, V$) bond energies since $-\Delta E_p$ will be taken properly into account in the evaluation of $D(M-R)$ (see eq 4, vide infra). The promotion will, however, make the discussion of the bonding in Cp_2M-R more uniform since the σ -bond formation now for all three metals involves the pairing of an electron in $2a_1$ with either $2\sigma_{Me}$ (**1a**) or $1s_H$ (**1b**). For the methyl complexes we add as an additional contribution to $-\Delta E_p$ the energy (25 kJ mol^{-1}) required to deform CH_3 from its trigonal-planar ground-state conformation to the trigonal-pyramidal ($H-C-H = 109^\circ$) geometry it will have in Cp_2MCH_3 .

In the second step we allow Cp_2M and R to interact by bringing the two fragments together to the positions they will take up in the combined complex. However, the interactions in the second step are restricted, since we confine the electrons to occupy the same orbitals as in the separate fragments. The contribution to the bond energy $D(M-R)$ from the second step, referred to as the steric interaction energy $-\Delta E_0$, is destabilizing (negative) since it involves two-orbital-three- (and four-) electron interactions of the type given in **4a** and **4b**.

The final step consists of a full SCF calculation in which we allow for the electron pairing in the σ -interactions **1a** and **1b** as well as a general relaxation of the electron density, including the π -back-donation in **3a**. The contribution to $D(M-R)$ from changes in the electron density due to the σ -interactions and π -back-donations are given by $-\Delta E_\sigma$ and $-\Delta E_\pi$, respectively. The total $D(M-R)$ bond energy is according to our decomposition scheme given by

$$D(M-R) = -[\Delta E_p + \Delta E_0 + \Delta E_\sigma + \Delta E_\pi + \Delta E_{Rel}] \quad (4)$$

where we have added the contribution from relativistic effects ΔE_{Rel} as a separate term. The contribution from ΔE_{Rel} is only of importance for 5d elements. A more detailed account of the bond energy decomposition scheme applied here is given in ref 25.

For the following discussion it is important to specify clearly how the various factors ΔE_0 , ΔE_σ , ΔE_π , etc. contribute to the expression for $\Delta E_2 - \Delta E_1$ given in eq 3, and we shall to this end rewrite eq 3 in the form

$$\Delta E_2 - \Delta E_1 \propto \frac{1}{2} \langle 1\sigma_{Me} | \sigma_{ML} \rangle^2 - [\frac{1}{2} - C_1^2] \langle 1\sigma_{Me} | \sigma_{ML} \rangle^2 \quad (5)$$

The first term is simply a measure of the repulsive interaction **4a** between $1\sigma_{Me}$ and σ_{ML} and constitutes as such a part of the steric interaction energy $-\Delta E_0$ with a (negative) contribution proportional to $-\frac{1}{2} \langle 1\sigma_{Me} | \sigma_{ML} \rangle^2$. The second part of eq 5 represents a correction term from the change (polarization) of the electron density upon formation of Cp_2MCH_3 from the Cp_2M and CH_3 fragments and belongs to $-\Delta E_\sigma$ with a stabilizing (positive) contribution proportional to $[\frac{1}{2} - C_1^2] \langle 1\sigma_{Me} | \sigma_{ML} \rangle^2$. Note that $\Delta E_2 - \Delta E_1$ is zero in the case of a complete polarization ($C_1 = 0$), whereas the last term is zero in an electroneutral bond with $C_1^2 = 0.5$.

The calculated $D(M-R)$ bond energies for Cp_2MR ($M = Sc, V, \text{ and } Mn$), decomposed into the various contributions, are given

Table I. Decomposition of $D(M-R)$ in Cp_2M-R ($R = H, CH_3$; $M = C, V, Mn$)

Cp_2M-R	energy, kJ mol^{-1}				$D(M-R)^a$
	$-\Delta E_0$	$-\Delta E_\sigma$	$-\Delta E_\pi$	$-\Delta E_p$	
Cp_2Sc-H	-74	323		-40	209
Cp_2Sc-CH_3	-304	571	18	-65	220
Cp_2V-H	-113	333		-18	202
Cp_2V-CH_3	-285	468	21	-43	161
Cp_2Mn-H	-105	315			210
Cp_2Mn-CH_3	-279	384	18	-25	98

^aThe total bonding energy $D(M-R)$ is given by $D(M-R) = -[\Delta E_0 + \Delta E_\sigma + \Delta E_\pi + \Delta E_p + \Delta E_{Rel}]$. The contribution from relativistic effects $-\Delta E_{Rel}$ can be neglected for 3d elements.

in Table I, where we see that the relative stability of the M-H and M- CH_3 bonds in the series Cp_2MR ($M = Sc, V, Mn$) follows the expected trend. Thus, for the middle transition metal manganese we find that $D(M-H)$ is much larger than $D(M-CH_3)$, whereas $D(M-CH_3)$ for the early transition metal scandium is slightly larger than $D(M-H)$. The Cp_2VR systems are seen to take up an intermediate position where $D(V-H)$ still is somewhat larger than $D(V-CH_3)$.

The major contributions to $D(M-R)$ for all the Cp_2MR systems come from $-\Delta E_0$ and $-\Delta E_\sigma$ (see Table I). The σ -bonding contributions $-\Delta E_\sigma$ from interactions **1a** and **1b** are, as we shall explain shortly, larger (Table I) for $R = CH_3$ than for $R = H$. The steric interaction energy $-\Delta E_0$ is on the other hand more repulsive for $R = CH_3$ than for $R = H$, due largely to interaction **4a** between $1\sigma_{Me}$ and σ_{ML} . This type of interaction is not present in the Cp_2MH hydrides.

The bond energies $D(M-H)$, as well as the contributions to $D(M-H)$ from the steric ($-\Delta E_0$) and electronic ($-\Delta E_\sigma$) factors, are remarkably constant through the hydride series Cp_2MH ($M = Sc, V, Mn$) (Table I). Thus, the M-H bond energy does not depend much on the nature of the 3d metal, and we shall in the next section give a possible explanation for this. We find on the other hand for the methyl series $Cp_2M(CH_3)$ ($M = Sc, V, Mn$) a pronounced increase in $-\Delta E_\sigma$ as we move from Mn toward Sc, whereas $-\Delta E_0$ is relatively constant. The increase in $-\Delta E_\sigma$ gives rise to a corresponding increase in $D(M-CH_3)$ with $D(Mn-CH_3) < D(V-CH_3) < D(Sc-CH_3)$.

A metal by metal comparison of the various factors responsible for the relative M-H and M- CH_3 bond strengths provides the following picture. The term $-\Delta E_\sigma$ is, in the case of the middle transition metal manganese, comparable for the two ligands H and CH_3 , and the order $D(M-CH_3) < D(Mn-H)$ is determined largely by the steric factor ($-\Delta E_0$) being more repulsive for $R = CH_3$ than for $R = H$ (Table I). The order of the bond energies for vanadium is also $D(V-H) > D(V-CH_3)$, again due to the steric factor $-\Delta E_0$. The term $-\Delta E_\sigma$ is, however, now much larger for $R = CH_3$ than for $R = H$ with the result that the M-H and M- CH_3 bond energies are much closer for V than for Mn. The steric factor ($-\Delta E_0$) is also more repulsive for $R = CH_3$ than for $R = H$ in the case of the early transition metal scandium. The trend set by $-\Delta E_0$ is, however, reversed by $-\Delta E_\sigma$, which is much larger for $R = CH_3$ than for $R = H$. One finds as a result that $D(Sc-CH_3) > D(Sc-H)$.

It should be clear from the discussion up to this point, that the change in the relative order of stability between M-H and M- CH_3 bonds, from $D(M-H) > D(M-CH_3)$ for middle (and late) transition metals to $D(M-CH_3) \sim D(M-H)$ for early transition metals, must be related to a steady increase in $-\Delta E_\sigma$, as we proceed from $M = Mn$ to $M = Sc$. Why does $-\Delta E_\sigma$ increase in the manner illustrated in Table I? It seems evident that the increase should be related to the difference in electronegativity between Sc, V, and Mn or equivalently to the increase in energy of the Cp_2M fragment orbitals $1a_1$, $1b_1$, and $2a_1$ through $M = Mn, V, \text{ and } Sc$ (Figure 2). The least electronegative element scandium is obviously going to form the more planar M- CH_3 σ -bond, and one could perhaps imagine that the higher polarity in the σ -interaction **1b** would enhance $-\Delta E_\sigma$. We do in fact, from a Mulliken population analysis of ϕ_σ , calculate the polarity δ of **5** to increase as

Table II. M–R Bond Energies in RCp_2M ($\text{M} = \text{Mn, Tc, Re, V, Sc, Y, La}$; $\text{R} = \text{H, CH}_3$) without $[D(\text{M–R})]$ and with $[E(\text{M–R})]$ the Cp_2M Relaxation Energy, ΔE_{relax}

M	energy, kJ mol ⁻¹					
	R = H			R = CH ₃		
	$D(\text{M–H})^a$	ΔE_{relax}	$E(\text{M–H})^b$	$D(\text{M–CH}_3)$	ΔE_{relax}	$E(\text{M–CH}_3)$
Sc	209	71	138	220	71	149
Y	280	83	197	276	83	193
La	285	83	202	272	83	189
V	202	92	110	161	92	69
Mn	210	162	48	98	162	-64
Tc	247	136	111	152	136	16
Re	250	136	114	156	136	20

^aThe bond energy $D(\text{M–R})$ does not take into account the relaxation of the Cp–M–Cp angle from 140 to 180° . ^bThe bond energy $E(\text{M–R})$ takes into account the relaxation of the Cp_2M fragment. The bond energy $E(\text{M–R})$ is given by $E(\text{M–R}) = D(\text{M–R}) - \Delta E_{\text{relax}}$, where ΔE_{relax} is the (positive) energy required to distort the Cp_2M fragment from its ground-state conformation with a Cp–M–Cp angle of 180° to the bent conformation with a Cp–M–Cp angle of 140° .

$$\delta_{\text{Mn}} = 0.07 < \delta_{\text{V}} = 0.29 < \delta_{\text{Sc}} = 0.43.$$

If $-\Delta E_\sigma$ is enhanced by the polarity of **1b** in the methyl systems, then one would expect a similar enhancement of $-\Delta E_\sigma$ in the hydride systems, where we likewise find δ of **5** to increase as $\delta_{\text{Mn}} = 0.13 < \delta_{\text{V}} = 0.24 < \delta_{\text{Sc}} = 0.52$. This is not the case. In fact, $-\Delta E_\sigma$ for H is seen in Table I to be nearly the same for $\text{M} = \text{Sc, V, and Mn}$.

There is, however, in the case of $\text{R} = \text{CH}_3$ (but not in the case of $\text{R} = \text{H}$) another contributing factor to $-\Delta E_\sigma$ aside from the σ -interactions of **1**, namely the last term in eq 5, where we express the destabilization $\Delta E_2 - \Delta E_1$ from the repulsive interaction between ϕ_σ and $1\sigma_{\text{Me}}$. The last term in eq 5 is nearly zero for the electroneutral Mn–CH_3 bond ($\delta_{\text{Mn}} = 0.07$) with $C_1^2 \sim 0.5$. The same term is on the other hand nonzero for the polar Sc–CH_3 bond ($\delta_{\text{Sc}} = 0.43$) where $C_1^2 = 0.23$. Its contribution to $-\Delta E_\sigma$ (proportional to $[1/2 - C_1^2](1\sigma_{\text{Me}}|\sigma_{\text{ML}})^2$) is further stabilizing (positive). We might conclude our analysis by observing that the repulsive interaction between ϕ_σ and $1\sigma_{\text{Me}}$ in the methyl complexes considerably destabilizes the M–CH_3 bond in the case of middle (and late) transition metals with the result that $D(\text{M–H}) > D(\text{M–CH}_3)$. The destabilization is reduced sizably in early-transition-metal systems, due to the polarity of the M–CH_3 bond, with the result that the M–H and M–CH_3 bonds are nearly equal in strength.

We have recently⁶ compared M–L bond strengths in the early-transition-metal complexes Cl_3TiL with the corresponding bond strengths in the late-transition-metal complexes $\text{LCo}(\text{CO})_4$ for $\text{L} = \text{OH, OCH}_3, \text{SH, NH}_2, \text{PH}_2, \text{and CN}$. All the ligands L had, in addition to a singly occupied σ -orbital $2\sigma_{\text{L}}$, a doubly occupied orbital $1\sigma_{\text{L}}$ similar to $1\sigma_{\text{Me}}$. It was evident from the calculations that all M–L bonds suffered a destabilization of the type illustrated in Figure 1 for $\text{L} = \text{CH}_3$. The destabilization was, however, much smaller for the polar Ti–L bonds than for the electroneutral Co–L bonds, and this was one of the reasons for the calculated order of stability $D(\text{Ti–L}) > D(\text{Co–L})$.

The study of $D(\text{M–H})$ and $D(\text{M–CH}_3)$ bond energies in the Cp_2MR complexes is extended in Table II to the 4d and 5d elements in the group 3 triad $\text{M} = \text{Sc, Y, La}$ as well as the group 7 triad $\text{M} = \text{Mn, Tc, Re}$. It follows from Table II that the change in the relative stabilities of M–H and M–CH_3 bonds in going from early to middle transition metals takes place for 4d and 5d elements as well as 3d elements. Furthermore in both triads there is an increase in the $D(\text{M–R})$ bond energies toward the heavier elements. This increase is primarily caused by a corresponding increase in the $\langle 2\sigma_{\text{Me}}|\sigma_{\text{ML}} \rangle$ and $\langle 1\sigma_{\text{H}}|\sigma_{\text{ML}} \rangle$ bonding overlaps. Relativistic effects were further found to stabilize the M–R bonds of the 5d elements by 20 and 2 kJ mol⁻¹ for Re and La, respectively.

The bond energy $D(\text{M–R})$ is well suited for a comparison of M–H and M–CH_3 bond strengths. However, it does not take into account the energy ΔE_{relax} related to a relaxation of the Cp_2M fragment from its bent conformation with $\Phi = 140^\circ$ (**6**) to its

Table III. Decomposition of the Bonding Energy $D(\text{M–R})$ in $\text{Cp}_2\text{Ni}(\text{CO})\text{R}$, $\text{Co}(\text{CO})_4\text{R}$, $\text{CpFe}(\text{CO})_2\text{R}$, $\text{Mn}(\text{CO})_5\text{R}$, and $\text{CpCr}(\text{CO})_3\text{R}$, with $\text{R} = \text{H, CH}_3$

Cp ₂ M–R	energy, kJ mol ⁻¹				$D(\text{M–R})^a$
	$-\Delta E_0$	$-\Delta E_\sigma$	$-\Delta E_\pi$	$-\Delta E_p$	
Cp ₂ Ni(CO)H	-107	317			210
Co(CO) ₄ H ^b	-111	341			230
CpFe(CO) ₂ H	-85	310			225
Mn(CO) ₅ H ^b	-110	335			225
CpCr(CO) ₃ H	-140	365			225
Cp ₂ Ni(CO)CH ₃	-188	363	24	-25	174
Cp(CO) ₄ CH ₃ ^b	-210	366	29	-25	160
Mn(CO) ₅ CH ₃ ^b	-202	360	20	-25	153
CpFe(CO) ₂ CH ₃	-190	370	25	-25	180
CpCr(CO) ₃ CH ₃	-284	398	33	-25	122

^aThe total bonding energy $D(\text{M–R})$ is given by $D(\text{M–R}) = -[\Delta E_0 + \Delta E_\sigma + \Delta E_\pi + \Delta E_p + \Delta E_R]$. The contribution from relativistic effects, $-\Delta E_R$, can be neglected for 3d elements. ^bFrom ref 5a.

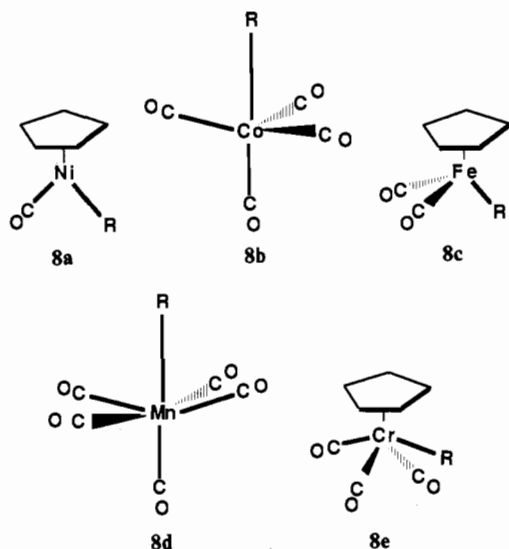
ground-state conformation with $\Phi = 180^\circ$. It follows from Lauher's and Hoffmann's²⁴ discussion of Cp_2M that the (positive) relaxation energy ΔE_{relax} is substantial. Consequently, one must take into account ΔE_{relax} by introducing the adiabatic bond energy $E(\text{M–R}) = D(\text{M–R}) - \Delta E_{\text{relax}}$. We display $D(\text{M–R})$ along with $E(\text{M–R})$ and ΔE_{relax} for the various Cp_2MR systems in Table II. It is evident from Table II that Cp_2MR complexes of the group 7 metals $\text{M} = \text{Mn, Tc, and Re}$ are rather unstable with respect to Cp_2M ($\Phi = 180^\circ$) and R, in spite of the sizable intrinsic bond strength $D(\text{M–R})$, as a result of the large relaxation energy ΔE_{relax} (130–160 kJ mol⁻¹). Given the data in Table III, it is in fact not surprising that the only well-characterized Cp_2MR complexes of group 7 metals are Cp_2TcH and Cp_2ReH . The corresponding complexes of the early transition metals $\text{M} = \text{Sc, Y, and La}$ have a stronger intrinsic $D(\text{M–CH}_3)$ bond energy and a smaller relaxation energy ΔE_{relax} . The adiabatic bond energies $E(\text{M–R})$ are as a consequence large enough for Cp_2MR to be stable for all three metals. In fact hydride and alkyl complexes of the form Cp_2MR are known²⁰ for all metals in the group 3 triad.

The Cp_2M systems are ideally suited for a comparison between M–R bond energies in complexes of early-transition-metal through middle-transition-metal complexes, since the fragment Cp_2M retains the same coligands and coordination number throughout the series $\text{M} = \text{Sc, V, and Mn}$. A further simplification comes from the fact that $2a_1$ (**7c**) is the only one of the three frontier orbitals (**7a**, **7c**, and **7e**) on Cp_2M that interacts effectively with $2\sigma_{\text{Me}}$. Thus, the $1b_1$ (**7b**) orbital is of the wrong symmetry and $1a_1$ (**7a**) has a negligible overlap (0.05) with $2\sigma_{\text{Me}}$. The Cp_2MR ($\text{R} = \text{H, CH}_3$) series is, however, somewhat limited and does not include late transition metals. Furthermore, not all the complexes are authentic, as discussed above. We shall as a consequence, in the next section, broaden the scope of our study by considering actual alkyl and hydride systems involving other metal fragments, some of which encompass late transition metals.

CpNi(CO)R, Co(CO)₄R, CpFe(CO)₂R, Mn(CO)₅R, and CpCr(CO)₃R

Table III displays calculated $D(\text{M–R})$ bond energies ($\text{R} = \text{H}$ and CH_3) for hydride and methyl complexes involving the ML_n metal fragments $\text{CpNi}(\text{CO})$ (**8a**), $\text{Co}(\text{CO})_4$ (**8b**), $\text{CpFe}(\text{CO})_2$ (**8c**), $\text{Mn}(\text{CO})_5$ (**8d**), and $\text{CpCr}(\text{CO})_3$ (**8e**). Each of the fragments is seen to encompass a different element in the first transition series, starting with the late transition metal Ni in group 10 and ending with the middle transition metal Cr in group 6.

The metal fragments in **8** all have a singly occupied σ -type orbital σ_{ML} suitable for bonding interactions with $2\sigma_{\text{Me}}$ (**1b**) and $1s_{\text{H}}$ (**1a**), as well as an empty π -type orbital capable of accepting electron density from π_{Me} (**3a**). Consequently, we can decompose the $D(\text{M–R})$ bond energies for the complexes in **8** according to eq 4, as is done in Table III. Note that the bond energies $D(\text{M–R})$ in all cases are defined with respect to R and a ML_n fragment (in its electronic ground state) of the same conformation as the ML_n framework in the combined RML_n complex. An electronic promotion of ML_n was not required in any of the complexes, as



ML_n in all cases had an electronic ground state with a singly occupied orbital suitable for a σ -interaction (1) with R. The only contribution to $-\Delta E_p$ comes as a consequence from the deformation (25 kJ mol⁻¹) of CH₃.

The $D(M-H)$ bond energies for the hydride complexes in Table III, as well as the corresponding steric ($-\Delta E_0$) and electronic ($-\Delta E_\sigma$) contributions, are all remarkably similar and resemble further the corresponding values for the Cp₂MH systems in Table I. It is somewhat surprising that $-\Delta E_0$ is so similar for the different hydrides, particularly in view of the fact that the energy gap between σ_{ML} and $1s_H$ varies by up to 4 eV, as shown in Figure 3. This point can perhaps be rationalized from the qualitative expression for $-\Delta E_\sigma$ given (for hydrides) by

$$-\Delta E_\sigma = -[2\epsilon(\phi_\sigma) - \epsilon(1s_H) - \epsilon(\sigma_{ML})] \quad (6a)$$

where $\epsilon(1s_H)$ and $\epsilon(\sigma_{ML})$ are the orbital energies of $1s_H$ and σ_{ML} respectively and $\epsilon(\phi_\sigma)$ is the orbital energy of the bonding orbital (1a) between $1s_H$ and σ_{ML} .

$$\phi_\sigma = C_1[\sigma_{ML}] + C_2[1s_H] \quad (6b)$$

As it stands the qualitative expression for $-\Delta E_\sigma$ in eq 6a is not very useful for our discussion. However, a substitution of eq 6b into eq 6a provides, with the aid of the approximate normalization condition $C_1^2 + C_2^2 = 1$, the following more informative expression:

$$-\Delta E_\sigma = -[C_2^2 - C_1^2][\epsilon(1s_H) - \epsilon(\sigma_{ML})] - 4C_1C_2(1s_H|H_{eff}|\sigma_{ML}) \quad (6c)$$

where $(1s_H|H_{eff}|\sigma_{ML})$ is the (negative) interaction matrix element between $1s_H$ and σ_{ML} .

Of the two terms in eq 6c, the last (covalent one) is the more important for hydride complexes (CpNi(CO)H, Co(CO)₄H, and Mn(CO)₅H) with an electroneutral M-H bond ($C_1^2 = C_2^2 \sim 0.5$) where there is a near perfect match (Figure 3) between the orbital energies of $1s_H$ and σ_{ML} , and $4C_1C_2$ as a consequence has a maximum value ($4C_1C_2 \sim 2.0$). The first (ionic) term is on the other hand for the same series of complexes nearly zero ($\epsilon(1s_H) - \epsilon(\sigma_{ML}) \sim 0$). The relative importance of the two terms in eq 6 is reversed somewhat for hydrides (Cp₂ScH and Cp₂VH) with a poor energy match between $1s_H$ and σ_{ML} where $\epsilon(\sigma_{ML}) - \epsilon(1s_H) > 0$ and the M-H bond polar ($C_1^2 < C_2^2$). The first (ionic) term in eq 6c, representing the energy contribution due to a transfer of charge from σ_{ML} to $1s_H$, is substantial for this type of complex since both $\epsilon(\sigma_{ML}) - \epsilon(1s_H)$ and $C_2^2 - C_1^2$ are larger than zero, whereas the second (covalent) term has been reduced, in comparison to that in hydrides with electroneutral M-H bonds, as $4C_1C_2 < 2$.

It is clear from our qualitative discussion based on eq 6c that any loss of covalent interaction energy (second term in eq 6c), associated with an increase in the energy gap $\epsilon(\sigma_{ML}) - \epsilon(1s_H)$, to some degree will be compensated for by an increase in the first (ionic) term of eq 6c. Of course the degree of compensation can

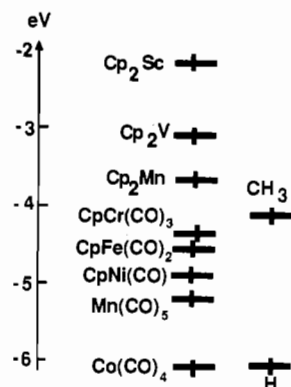


Figure 3. Orbital energies for the singly occupied σ_{ML} orbital on the ML_n metal fragments in comparison with the orbital energies of $1s_H$ and $2\sigma_{Me}$.

only be determined from quantitative calculations. The density functional results presented in Table III indicate in fact that there is a high degree of compensation.

The qualitative analysis given here should also serve as a caution against correlating M-H bond energies, or for that matter M-L bond energies of any ligand L, with a single factor such as bonding overlaps (1a), electronegativity of ML_n or electron affinity of ML_n . Thus, bonding overlaps put the emphasis squarely on the second term in eq 6c, whereas theories correlating bond strengths with electronegativity and electron affinities emphasize the first term in eq 6c.

In turning to the methyl complexes, we note next that the M-CH₃ bond energies for the systems (8) in Table III in all cases are weaker than the M-H bond energies among the corresponding hydrides. The primary factor responsible for the stability order $D(M-H) > D(M-CH_3)$ is seen (Table III), as for the Cp₂MR systems, to be the steric interaction energy $-\Delta E_0$, since $-\Delta E_\sigma$ is nearly the same for methyl and hydride complexes. The single most important factor responsible for the steric interaction energy $-\Delta E_0$ being more repulsive for R = CH₃ than for R = H is, as for the Cp₂MR systems, the destabilizing interaction (4a) between $1\sigma_{Me}$ and σ_{ML} . Other steric interactions between electron pairs on CH₃ and electron pairs on the Cp ring are also important, in particular for the crowded CpCr(CO)₃CH₃ complex (Table III). The importance of the π -back-donation (3a) for the M-CH₃ bond strength is relatively modest, both for the electron-rich late (to middle) transition metals (Table III) and electron-poor early transition metals (Table I). One might have expected that the degree of π -back-donation (3a) in the electron-poor early transition metals would have been extensive and largely responsible for the enhanced strength of the M-CH₃ bond. This is not the case according to our calculations, most likely because the π -accepting orbitals (2a) on an electropositive metal such as Sc are too high in energy (Figure 2). The π -back-donation (3a) is, as we have shown in a previous study,^{5b} more pronounced in positively charged methyl complexes.

The bond energies $D(M-R)$ in Table III are defined with respect to R and ML_n of the same conformation as the ML_n framework in RML_n . For a comparison with experimental bond energies one should take into account the relaxation of the ML_n framework to the geometry of the free ML_n fragment. We have not done this since it would require a full optimization of the experimentally unknown ML_n geometries. We do not expect the relaxation energy ΔE_{relax} to be as substantial ($\Delta E_{relax} < 20$ kJ mol⁻¹) as ΔE_{relax} of the Cp₂MR systems. The relaxation energies ΔE_{relax} will reduce the M-R bond energies without influencing the relative stabilities of the M-H and M-CH₃ bonds.

There have been several theoretical^{13,5b} and experimental² studies of the M-H and M-CH₃ bond strengths in the ligand-free complexes MR and MR⁺. The conclusions from such studies are, however, not directly transferable to RML_n complexes due to the high-spin multiplicity of M compared to ML_n as well as the relatively low energy of $(n+1)s$ in M compared to ML_n . Thus the $D(M-R)$ bond energies for ligand-free MR systems compared to RML_n complexes are more influenced by loss of spin mul-

tiplicities along a period^{3a} as well as variations in the participation^{3c} from the $(n + 1)s$ orbital in the M-R bond down a triad.^{3c}

Our calculated bond strengths are in fair agreement with the few available experimental data on $D(M-R)$ bond energies in RML_n complexes. Connor^{4c} et al. found for RMn(CO)₅ that $D(Mn-H) = 213 \text{ kJ mol}^{-1}$ and $D(Mn-CH_3) = 153 \text{ kJ mol}^{-1}$, respectively. Ungvary^{4d} has further measured $D(H-Co(CO)_4)$ as 238 kJ mol^{-1} , in close accord with our theoretical value of 230 kJ mol^{-1} . We expect the upper bound for the errors in the calculated M-H and M-CH₃ bond energies to be 50 kJ mol^{-1} . The errors in the calculated relative strengths of the M-H and M-CH₃ bonds should however be less.

Concluding Remarks

The main objective in the present investigation has been to reveal the factors governing the general periodic trends in relative M-H and M-CH₃ bond strengths across a transition series. We have found that the M-CH₃ bond is considerably weaker than the M-H bond for late to middle transition metals as a result of the repulsive interaction between the fully occupied (mainly) 2s_c orbital on CH₃ and the σ -bonding CH₃ML_n orbital ϕ_{σ} , where ϕ_{σ} is an in-phase combination between the singly occupied $2\sigma_{Me}$ and σ_{ML} orbitals on CH₃ and ML_n, respectively. The repulsive interaction between the fully occupied (mainly) 2s_c orbital on CH₃ and ϕ_{σ} is reduced in methyl complexes of early transition metals due to the high polarity of the M-CH₃ bond, with the result that M-H and M-CH₃ bonds become comparable in strength. The

intrinsic M-H bond energy $D(M-H)$ does not change noticeably across a transition series. The M-H bond as well as the M-CH₃ bond are strengthened on descending a triad due to an increase in the bonding overlap between $2\sigma_{Me}$ and σ_{ML} .

We do not expect that the main conclusions reached here will be changed by more accurate calculations including extensive geometry optimization. Studies are now under way on the relative M-H and M-CH₃ bond strengths in complexes of f-block elements. A comparison between M-H and M-L bond strengths for a number of one-electron ligands L, which in analogy with CH₃ have a singly occupied $2\sigma_L$ orbital and a fully occupied $1\sigma_L$ orbital, is given in ref 6.

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Registry No. Cp₂ScH, 116301-38-3; Cp₂ScCH₃, 116301-39-4; Cp₂VH, 116301-40-7; Cp₂VCH₃, 54111-39-6; Cp₂MnH, 116301-41-8; Cp₂MnCH₃, 116301-42-9; Cp₂YH, 116301-43-0; Cp₂LaH, 116301-44-1; Cp₂TcH, 12116-92-6; Cp₂ReH, 1271-32-5; Cp₂YCH₃, 116301-45-2; Cp₂LaCH₃, 116301-46-3; Cp₂TcCH₃, 116301-47-4; Cp₂ReCH₃, 72316-82-6; CpNi(CO)H, 116301-48-5; CpFe(CO)₂H, 35913-82-7; CpCr(CO)₃H, 36495-37-1; CpNi(CO)CH₃, 92476-37-4; CpFe(CO)₂CH₃, 12080-06-7; CpCr(CO)₃CH₃, 41311-89-1.

Contribution from the Department of Chemistry,
University of California, Santa Barbara, California 93106

Synthesis, Structure, Electrochemistry, and Photophysics of Methyl-Substituted Phenylpyridine Ortho-Metalated Iridium(III) Complexes

F. O. Garces, K. A. King, and R. J. Watts*

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Synthetic, structural, photophysical, and electrochemical characterizations of ortho-metalated [Ir(NC)₂Cl]₂ dimeric and [Ir(NC)₂NN]Cl monomeric complexes, where NC = 2-(*p*-tolyl)pyridine (ptpy) or 3-methyl-2-phenylpyridine (mppp) and NN = 2,2'-bipyridine (bpy), are described. Structural characterizations by ¹H and ¹³C nuclear magnetic resonance (NMR) indicate the presence of symmetry elements in these complexes. Proton resonances were assigned by two-dimensional homonuclear *J*-correlation spectroscopy (2D-COSY), and carbon resonances were elucidated by single-frequency off-resonance decoupling (SFORD) and attached proton test (APT) experiments. NMR data support a structural configuration for these complexes in which the Ir-N bonds from the pyridyl rings of the metalating ligands (i.e., ptpy, mppp) are mutually trans. The ultraviolet-visible absorption properties of these complexes are similar to those of the unsubstituted phenylpyridine (ppy) complexes, with the dimers showing low-energy charge-transfer bands ranging from 484 to 400 nm and the monomers displaying charge-transfer transitions ranging from 468 to 325 nm. The emission spectra are also similar to those of the unsubstituted ppy complexes; at room temperature the dimers show broad emission bands at 515 nm, and in 77 K glasses they show structured emissions at 494 and 528 nm. The emission spectra of the monomers indicate dual emissive states, as has been suggested for the unsubstituted [Ir(ppy)₂bpy]⁺ monomer. At room temperature in fluid solvents, an emission maximum is centered at 595 nm, but at low temperatures (77 K glasses), structured emissions with maxima centered at 527 and 550 nm are observed. Emission lifetimes are in the range 32–250 ns under ambient conditions and range from 4.4 to 5.2 μ s at 77 K. Cyclic voltammetric measurements reveal that these methyl-substituted complexes are easier to oxidize and harder to reduce relative to the unsubstituted ppy complexes. Cathodic shifts in the half-wave potentials ($\sim 100 \text{ mV}$) compared to the potential of the ppy complex suggest that the electron density around the iridium metal, which influences the reducing power of these complexes, may be controlled via inductive effects from the methyl group on the phenylpyridine ligands.

I. Introduction

Transition-metal complexes containing ligands with extended π -systems (e.g., pyridine, bipyridine) have generated tremendous interest because of their potential to participate as photocatalysts in solar-driven artificial photoconversion processes.¹⁻¹⁰ The classic

example of a molecule used as a photocatalyst in photoconversion systems is Ru(bpy)₃²⁺.^{3,4,5,11-15} The excited-state redox potentials of metal complexes such as Ru(bpy)₃²⁺ may be altered by several types of structural modifications. Potential modifications include (i) changing the central metal, (ii) replacing some or all of the

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