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Are α-Alkoxyalkyl Complexes Special? ^{13}C-H Coupling Constant Evidence.

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Summary

Complexes of type $L_nMCH_2O_2CCMe_3$ exhibit relatively large values of $^1J_{CH}$ for the α-carbon; however, unexpectedly large values are also found for the methyl analogs, L_nMCH_3. Thus this technique does not provide evidence for any unusual interactions in the former. Cleavage of the ester linkage by MeLi proceeded cleanly only for L_nM = $CpMo(CO)_3$, leading to $CpMo(CO)_3^-$; with L_nM = $Mn(CO)_5$ or $CpFe(CO)_2$ electron transfer processes predominate. Such reactions are also observed for simple metal alkyls such as $CpFe(CO)_2CH_3$.

Introduction

Complexes of the form L_nMCH_2OR have attracted attention for several years, initially as precursors to carbene complexes (1);

$$L_nMCH_2OR + H^+ \longrightarrow L_nMCH_2^+ + ROH$$

and, more recently, as possible key intermediates (when R = H) in homogeneous CO reduction (2). There has been some speculation that this structure leads to special interactions not common to metal alkyls in general. Notably, the ^1H chemical shift of the α protons is well downfield of that in corresponding organic species $R'CH_2OR$, in contrast to the general tendency of MCH_2R to show upfield shifts (3). (Of course, inferences from chemical shifts are always suspect, especially when transition metals are involved.) More recently the crystal structure of $CpFe(CO)(PPh_3)$-(CH_2O-menthyl) was reported to exhibit short Fe-C_α and long C_α-O distances (by ca 0.1 and 0.05 Å respectively), suggesting some contribution of the carbene-like structure in the ground state (4):

$$Fe{-}CH_2{-}OR \longleftrightarrow Fe^+{=}CH_2\ ^-OR$$

Such a contribution would be consistent with the NMR observations.

We have been examining possible general routes for generation of L_nMCH_2OH, and prepared several complexes of the type $L_nMCH_2O_2CCMe_3$, in hopes that cleavage of the ester linkage followed by protonolysis would yield the desired species. (An attempted preparation of $(CO)_5MnCHPhOH$ by a closely related route has previously been reported (2a)). These complexes show the same ^1H NMR behavior previously noted, and we decided to examine the ^{13}C NMR spectra in hopes of shedding additional light on the nature of the bonding. In addition, the reactions of these complexes with methyllithium are described briefly.

Experimental

Manipulations were carried out under inert atmosphere, although the products appear to be air-stable, at least as solids. All reagents used are commercially available, including $(CH_3)_3CCO_2CH_2Cl$ (Fluka), and were used without additional preparation; carbonylmetallate anions were generated from the corresponding dimers (5); methyllithium solutions were standardized by double titration. Analyses were performed by Midwest Microlab, Indianapolis. Melting points were determined in sealed, evacuated capillaries and are uncorrected.

^{13}C NMR spectra were run on approximately 1 M solutions in $CDCl_3$ (at 25.2 MHz, Varian XL-100 spectrometer) <u>without</u> adding $Cr(acac)_3$; under these conditions carbonyl signals were not generally detected. ^{13}C-H coupling constants were obtained by gating off the broad-band proton decoupling during acquisition (with the exception of $CH_3Mn(CO)_5$, which *did not* give a good ^{13}C spectrum at all; $^1J_{CH}$ was obtained from satellite peaks in the ^{1}H spectrum).

<u>$CpFe(CO)_2CH_2O_2CC(CH_3)_3$ (Ia)</u>. A solution of 4.5 mmol $CpFe(CO)_2Na$ in 30 ml THF was treated with a slight excess of $(CH_3)_3CCO_2CH_2Cl$ at room temperature, resulting in an immediate color change from orange to yellow-brown and deposition of white solid. After stirring for several minutes, evaporation of solvent, extraction of the residue with 30 ml hexane, filtration, concentration of the filtrate to about $\frac{1}{4}$ its original volume and cooling to -78° afforded pale yellow crystals: 1.0 g (76%); mp 44-46°. Anal. Calcd. for $C_{13}H_{16}FeO_4$: C, 53.45; H, 5.52. Found: C, 53.45; H, 5.46. IR: ν_{CO} (Nujol) 2020, 1945, 1749 cm^{-1}. ^{1}H NMR: 1.10 (s, 9 H, $C(C\underline{H}_3)_3$); 4.85 (s, 5 H, Cp); 5.30 δ (s, 2 H, $FeC\underline{H}_2O$). ^{13}C NMR: 27.5 (quartet of septets: $^1J_{CH} = 126.8$, $^3J_{CH} = 4.5$ Hz; $C(\underline{C}H_3)_3$); 39.2 (m; $-\underline{C}(CH_3)_3$); 54.5 (t: $^1J_{CH} = 153.8$ Hz; $Fe\underline{C}H_2O$); 85.3 (doublet of quintets: $^1J_{CH} = 179.0$, $^2J_{CH} = {}^3J_{CH} = 6.6$ Hz; Cp).

Preparation of the other two compounds was entirely analogous except that alkylation of the anions is slower, so reaction mixtures were stirred overnight before workup.

<u>$(CO)_5MnCH_2O_2CC(CH_3)_3$ (Ib)</u> obtained as off-white microcrystals, mp 66-68°. Anal. Calcd. for $C_{11}H_{11}MnO_7$: C, 42.60; H, 3.58. Found: C, 42.18; H, 3.68. IR: ν_{CO} (Nujol) 2092, 2020, 1965,

1721 cm^{-1}. ^{1}H NMR: 1.20 (s, 9 H, C(C$\underline{H}_3$)$_3$); 4.75 δ (s, 2 H, MnC$\underline{H}_2$O). ^{13}C NMR: 27.3 (quartet of septets: $^1J_{CH}$ = 126.5, $^3J_{CH}$ = 4.4 Hz; C($\underline{C}$H$_3$)$_3$); 39.1 (m; $-\underline{C}$(CH$_3$)$_3$); 54.5 (t: $^1J_{CH}$ = 152.4 Hz; Mn$\underline{C}$H$_2$O).

<u>CpMo(CO)$_3$CH$_2$O$_2$CC(CH$_3$)$_3$ (Ic)</u> obtained as yellow plates, mp 67-71°. Anal. Calcd. for C$_{14}$H$_{16}$MoO$_5$: C, 46.68; H, 4.48. Found: C, 47.15; H, 4.63. IR: ν_{CO} (Nujol) 2016, 1984 (sh), 1908, 1709 cm^{-1}. ^{1}H NMR: 1.04 (s, 9 H, C(C$\underline{H}_3$)$_3$); 5.24 (s, 2 H, MoC$\underline{H}_2$O); 5.37 δ (s, 5 H, Cp). ^{13}C NMR: 27.5 (quartet of septets: $^1J_{CH}$ = 126.9, $^3J_{CH}$ = 4.4 Hz; C($\underline{C}$H$_3$)$_3$); 39.2 (m, $-\underline{C}$(CH$_3$)$_3$); 50.9 (t: $^1J_{CH}$ = 155.1 Hz; Mo$\underline{C}$H$_2$O); 92.7 (doublet of quintets: $^1J_{CH}$ = 177.8, $^2J_{CH}$ = $^3J_{CH}$ = 6.7 Hz; Cp).

<u>Reactions with methyllithium.</u> Solutions of the appropriate alkyl in ether were cooled to -78°, treated with an equivalent amount of an ether solution of MeLi, and allowed to warm until a color change occurred (for Ia, about -25°; Ib, about 0°; Ic, no color change) or to room temperature, then quenched with ethereal HCl or CH$_3$I. Volatiles were distilled off and examined by NMR and gas chromatography - mass spectrometry (DuPont DP-101 instrument), while the residue was redissolved in benzene or CDCl$_3$ and its NMR examined.

Results and Discussion

Synthesis and characterization of complexes L$_n$MCH$_2$O$_2$CC(CH$_3$)$_3$ was straightforward (6). Key NMR parameters for Ia-c and the corresponding methyl complexes, L$_n$MCH$_3$ (IIa-c) are listed in the Table. The upfield shifts observed for metal alkyls are generally considered to reflect the low electronegativity of a metal substituent, although as noted above, significant contributions from other factors such as magnetic anisotropy always make such correlations tenuous. In this context, however, the downfield shifts observed in the ^{1}H NMR for the α-protons of Ia-c appear striking, especially considering the fact that in a related main-group metal alkyl, $CH_3OCH_2Si(CH_3)_3$, the α-protons show the typical upfield shift (2.59 δ) (7).

$^1J_{CH}$ coupling constants have been suggested as better probes of effective hybridization and electronegativity of substituents; a linear correlation between these values and ^1H shifts has been drawn for species without substantial anisotropy contributions (8). In particular, the upfield shift of main group metal alkyls is reflected by $^1J_{CH}$ values smaller than those found for corresponding alkanes (9). Few $^1J_{CH}$ values have been reported for transition metal alkyls, aside from a series of platinum complexes (9). The value of $^2J_{HH}$ has been determined from $^2J_{HD}$ for a number of monodeuterated complexes L_nMCH_2D, including $CpFe(CO)_2CH_2D$. These values are greater (less negative) than for methane, consistent either with a high effective electronegativity for the metal group or π-donor ability of the latter (10). The second interpretation was preferred, again referring to the upfield chemical shift as an indication that such groups have low electronegativity.

$^1J_{CH}$ for **Ia-c** are indeed higher than for corresponding organic compounds, consistent with the downfield shift and apparently not inconsistent with resonance contributions of the form suggested by structural data above. However, the $^1J_{CH}$ values for **IIa-c** are similarly higher than for alkanes; indeed, the differences are even greater than in the α-alkoxy species. If the data for these compounds is plotted on the $^1J_{CH}$ vs. chemical shift graph mentioned above (8), compounds **IIa-c** come out far off the line; **Ia-c** while still somewhat off, are far closer.

The simplest conclusion to draw is that there is not any unusual interaction in **Ia-c** manifested in the NMR: the downfield shifts are consistent with the coupling constants, and it is the *methyl* compounds whose shifts appear anomalous. This appears to suggest that these transition metal groups are rela-

TABLE. NMR PARAMETERS FOR α-CARBON

	Ia	**Ib**	**Ic**	$R'OCH_2R$[a]	**IIa**	**IIb**	**IIc**	RCH_3[a]
^1H shift (δ, ± .05)	5.30	4.75	5.24	4.0	0.1	-0.1	0.2	1.0
^{13}C shift (ppm, ± .5)	54.4	54.5	50.9	60	-23.5	-19.3	-21.8	14
$^1J_{CH}$ (Hz, ± .5)	153.8	152.4	155.1	145	135.0	140 (±2)	137.8	125

[a] Approximate value for typical organic compound, cf. Ref. 12.

tively electronegative, in contrast to main-group metal-centered substituents such as $Si(CH_3)_3$. Substituent effects on $^1J_{CH}$ seem to be additive in these systems: values of $^1J_{CH}$ for complexes **II** and for CH_3OR predict (11) a value of 153 ± 4 Hz for complexes **I**, encompassing the observed value. While these arguments may be oversimplified in that they neglect other possible factors contributing to the magnitude of $^1J_{CH}$, generally the contact term (in which electronegativity effects are manifested) dominates (12). Still, it is possible that other factors might become important for transition metal alkyls; as noted earlier, $^1J_{CH}$ data on such compounds are rather sparse.

These results indicate that there is no need to invoke special interactions of the sort suggested by crystallographic results, in order to account for the NMR shifts. $^1J_{CH}$ coupling constants have been measured for several stable carbene complexes, including $Cp_2Ta(CH_3)(CH_2)$, 132 Hz (13), and $CpFe(CO)_2(CHPh)^+$, 146 Hz (1). These values, especially the latter which should be a fairly good model for the proposed resonance form contributing to **Ia**, show that substantial contributions of this type would not be inconsistent with the observed coupling constants. On the other hand, the above stable complexes show extreme downfield shifts for the α-protons, which should lead to strong deviations from the $^1J_{CH}$ vs. shift plot if there *were* important contributions from a carbene-like form. Since the deviations are relatively small (and on the *upfield* side), NMR data, at least, do not support the existence of these interactions.

The ^{13}C shifts of the α-carbons in **Ia-c** are upfield from corresponding organic species, although by a much smaller amount than observed for methyl complexes **IIa-c**. Detailed interpretation of ^{13}C shifts in transition metal complexes is notoriously difficult (14). Other ^{13}C parameters are listed in the Experimental section and appear unexceptional; of some note is the appearance of double quintets for the Cp carbons in Ia and Ic, indicating that ${}^2J_{CH} = {}^3J_{CH}$.

All complexes I react with methyllithium, but not by the same route. Ic requires an excess (> 2 equivalents) of MeLi for complete reaction; otherwise unreacted Ic remains. After neutralization the major organic product detected (NMR and GC-MS) is $(CH_3)_3CC(CH_3)_2OH$, while $CpMo(CO)_3H$ is the only organometallic product. This implies that the desired ester cleavage does occur as the first step, giving $CH_3COC(CH_3)_3$ which reacts with additional MeLi much faster than does Ia. The resulting anion, $CpMo(CO)_3CH_2O^-$, loses formaldehyde to give $CpMo(CO)_3^-$, which is subsequently protonated to give the stable hydride. (That loss of CH_2O occurs here rather than after protonation is shown by quenching instead with CH_3I, leading to virtually quantitative formation of IIc; the alternative would have led to stable (3) $CpMo(CO)_3CH_2OCH_3$. This behavior parallels that previously reported for $(CO)_5MnCHPhO^-$ (2a).

In contrast, addition of one equivalent of MeLi causes complete consumption of Ia or Ib, leading to deeply colored solutions and/or precipitates; NMR spectra suggest the presence of paramagnetic species. These reactions appear to include electron transfer rather than attack on the ester group, a mechanism which hence should not depend on the nature of the alkyl. Indeed, complexes $CpFe(CO)_2R$ (R = CH_3, $PhCH_2$, η^1-Cp) show completely similar behavior towards MeLi. It has long been known that, in many cases, the reaction of a transition metal halide (such as $CpFe(CO)_2X$) with an alkyllithium or Grignard reagent is a relatively poor preparative route (15), and these observations suggest a reason - excess reagent can consume desired product. It might be noted that $CpFe(CO)(PPh_3)R$ can be prepared in very good yield by this route (16); we find that $CpFe(CO)(PPh_3)CH_3$, in contrast to IIa, is inert to MeLi. Studies aimed at elucidating the nature and mechanism of these reactions are continuing.

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