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Notes

Abstraction of Methyl from Neutral Fischer-Type Carbene Complexes: A New Site for Nucleophilic Attack

Laurence M. Toomey and Jim D. Atwood*

Department of Chemistry, University at Buffalo, State University of New York,
Buffalo, New York 14260-3000

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Summary: Reactions of Fischer-type carbene complexes, $M(CO)_5(C(OMe)Ph)$ ($M = Cr, W$), with metal carbonyl anions ($M'^- = CpFe(CO)_2^-$, $Re(CO)_5^-$, $Mn(CO)_4PPh_3^-$, $Co(CO)_3PPh_3^-$, $Cp^*Cr(CO)_3^-$, $CpMo(CO)_3^-$) result in demethylation of the carbene complexes. The products are $M(CO)_5C(O)Ph^-$ and $M'{-}Me$, characterized by infrared and NMR spectroscopy. A slower rate for reaction with $W(CO)_5(C(OEt)Ph)$ in comparison to the methyl analogue is consistent with nucleophilic attack of the metal carbonyl anion on the methyl of the methoxy group of the carbene. This is a new type of nucleophilic attack on a Fischer-type carbene.

Introduction

Transition-metal carbene complexes have received considerable attention for their involvement in reactions such as olefin metathesis, olefin cyclopropanation, and Fischer−Tropsch synthesis.[1] Among the many important reactions of carbene complexes is nucleophilic attack on the carbene. Alkoxycarbene complexes (Fischer-type carbene complexes) undergo nucleophilic attack at the carbene carbon.[2] This site of nucleophilic attack contradicts Mulliken population studies, which have indicated that the carbon atoms of the *cis*-carbonyl ligands carry the greatest positive charge.[3] The justification provided for the observed site of attack is that the lowest unoccupied molecular orbital (LUMO) is spatially and energetically localized on the carbene carbon; therefore, the nucleophilic attack is frontier-orbital-controlled and not simply charge-controlled.[3,4] Nucleophilic attack at the carbene carbon can be suppressed to the *cis*-carbonyl ligands by placing a formal negative charge at the carbene carbon as for anionic acyl metalates.[5] Hegedus recently reported that nucleophilic attack can be directed toward the *cis*-carbonyl ligands by deprotonation at the α-position, again resulting in formation of a formal negative charge at the carbene carbon.[6] Here, we report a series of reactions between transition-metal carbonyl anions and neutral alkoxycarbene complexes which result in transfer of the alkyl group of the alkoxy substituent to the metal carbonyl anion. This transfer most likely corresponds to nucleophilic attack directly at the alkyl portion of the alkoxy group of a neutral carbene and is the only example in which this is the observed site of attack. This system also represents an unusual example of oxygen-to-metal alkyl transfer; a similar example is decomposition of the heterodinuclear μ_2-alkoxycarbyne complex $Cp(CO)Fe(\mu\text{-}COR)(\mu\text{-}CO)Mn(CO)Cp'$ ($Cp' = \eta^5\text{-}C_5H_4Me$) described by Hersh.[7] A few examples of alkyl displacement from the alkoxy group of cationic carbene complexes have been reported.[8,9] An example is[8]

$$CpFe(CO)(PPh_3)({=}C(OEt)Me)^+ + I^- \rightarrow CpFe(CO)(PPh_3)(C(O)Me) + EtI \quad (1)$$

indicating that for such a cationic carbene the alkyl on the alkoxy group carries significant positive charge.

Experimental Section

Materials. $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $Cp_2Fe_2(CO)_4$, $Cp_2Mo_2(CO)_6$, $Co_2(CO)_8$, $W(CO)_6$, $Cr(CO)_6$, and $Fe(CO)_5$ were purchased from Strem Chemical Co. and used as received. [PPN][Cl] (PPN = bis(triphenylphosphine)nitrogen(1+)), C_6H_5Li, $(CH_3)_3OBF_4$, and $(CH_3CH_2)_3OBF_4$ were purchased from Aldrich Chemical Co. Solvents were dried and degassed prior to use.

Instrumental Measurements. Infrared spectra were recorded on a Mattson Polaris Fourier transform spectrometer using 0.5 mm NaCl solution cells or KBr disks. All spectra are reported in wavenumbers (cm^{-1}). ^1H NMR spectra were recorded on a Varian VXR-400, with the reference set to residual solvent peaks. All chemical shifts are reported in ppm, and all coupling constants (J) are reported in Hz.

Preparations. Syntheses were accomplished under an inert atmosphere of dry nitrogen or argon using glovebox, Schlenk, or high-vacuum techniques. The complexes [PPN]-

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Table 1. Characterization Data of the Methyl Products and Times of Reactions for Metal Carbonyl Anions and Methoxyphenylcarbene Complexes

anion (M′)	products	IR (ν_{CO}), cm^{-1}	^{1}H NMR (acetonitrile-d_3), ppm (J, Hz)	time[h]
$Fe(CO)_4^{2-}$	$CH_3Fe(CO)_4^{-}$ [c]	1922 (m), 1874 (s)[a]	0.13 (s)	a few seconds
$CpFe(CO)_2^-$	$CH_3CpFe(CO)_2$[d]	2014 (s), 1960 (s)[b]	0.10 (s), 4.85 (s)	a few seconds
$Re(CO)_5^-$	$CH_3Re(CO)_5$[d]	2127 (w), 2013 (s), 1978 (s)[b]	−0.26 (s)	1 h
$Mn(CO)_4PPh_3^-$	$CH_3Mn(CO)_4PPh_3$[e]	2056 (w), 1985 (m), 1969 (s), 1939 (m)[b]	−0.51 (d) (J_{Hz} = 7.6), 7.50 (mult)	14 h
$Co(CO)_3PPh_3^-$	$CH_3Co(CO)_3PPh_3$[f]	2039 (w), 1983 (w), 1966 (vs)[b]	0.90 (d) (J_{Hz} = 2.0), 7.50 (mult)	1.5 days
$CpMo(CO)_3^-$	$CH_3CpMo(CO)_3$[d]	2024 (m), 1941 (s)[b]	0.33 (s), 5.40 (s)	5 days
$Cp^*Cr(CO)_3^-$	$CH_3Cp^*Cr(CO)_3$[g]	1998 (s), 1925 (s), 1919 (sh)[b]	0.24 (s), 1.79 (s)	6 days
$Co(CO)_4^-$	no reacn			

[a] In THF. [b] In hexanes. [c] Arndt, L. W.; Bancroft, B. T.; Darensbourg, M. Y.; Janzen, C. P.; Kim, C. M.; Reibenspies, J.; Varner, K. E.; Youngdahl, K. A. *Organometallics* **1988**, *7*, 1302. [d] Davison, A.; McCleverty, J. A.; Wilkinson, G. *J. Chem. Soc.* **1963**, 1133. [e] Kraihanzel, C. S.; Maples, P. K. *J. Am. Chem. Soc.* **1965**, *22*, 5268. [f] King, R. B. *Adv. Organomet. Chem.* **1964**, *2*, 157. [g] Jaeger, T. J.; Baird, M. C. *Organometallics* **1988**, *7*, 2074. [h] The time quoted is the time required for half of the metal carbonyl anion to be consumed.

Table 2. Carbonyl Stretching Frequencies for Acyl Metalates Formed in Reactions in THF

acyl metalate	ν_{CO}, cm^{-1}
$[PPN][(CO)_5CrC(O)Ph)]$	2025 (w), 1895 (vs), 1861 (m)
$[PPN][(CO)_5WC(O)Ph)]$	2040 (w), 1895 (vs), 1861 (m)
$[Na][(CO)_5CrC(O)Ph)]$	2040 (w), 1895 (vs), 1880 (m)

$[CpFe(CO)_2]$,[8] $[PPN][Re(CO)_5]$,[10] $[PPN][Mn(CO)_4(PPh_3)]$,[10] $[PPN][Co(CO)_3(PPh_3)]$,[10] $[PPN][Co(CO)_4]$,[10] $[PPN][Cp^*Cr(CO)_3]$,[11] $[PPN][CpMo(CO)_3]$,[12] $Na_2Fe(CO)_4$,[13] $(CO)_5M{=}C(OCH_3)Ph$ (M = Cr, W),[14] and $(CO)_5W{=}C(OCH_2CH_3)Ph$[15] were prepared by literature procedures. The spectroscopic characterizations were in excellent agreement with those previously reported.[14,15] $(CO)_5W{=}C(OMe)Ph$: IR (hexane), 2070 (w), 1985 (w), 1950 (vs), and 1941 (vs) cm^{-1}; ^{1}H NMR (CD_3CN), 4.73 (s) and 7.50 (m) ppm. $(CO)_5W{=}C(OCH_2CH_3)Ph$: IR (hexane), 2070 (w), 1983 (w), 1954 (vs), and 1947 (vs) cm^{-1}; ^{1}H NMR (CD_3CN), 1.65 (t), 5.05 (q), and 7.46 (m) ppm. $(CO)_5Cr{=}C(OMe)Ph$: IR (hexane), 2064 (m), 1987 (w), 1964 (s), 1954 (vs), and 1943 (sh) cm^{-1}. The carbonyl stretching frequencies for the metal carbonyl anions are shown in Table S1 (Supporting Information).

Product Studies. For determination of products, equal volumes of 2×10^{-4} M THF solutions of metal carbonyl anion and transition-metal carbene complex were mixed at ambient temperature in an inert-atmosphere glovebox. The reactions were monitored using infrared spectroscopy for times varying from a few seconds to a week. After completion, the THF was removed *in vacuo* and the resulting solids were washed with hexane, extracting all neutral products. The residual ionic products were then extracted using either THF or diethyl ether. All product determinations were done by infrared and ^{1}H NMR spectroscopy (Tables 1 and 2).

Kinetic Studies. Reactions of $W(CO)_5(C(OR)Ph)$ (R = Me, Et) with $Mn(CO)_4PPh_3^-$ were studied kinetically. The reactions were followed by disappearance of $Mn(CO)_4PPh_3^-$ (1814 cm^{-1}) with the carbene in excess. Concentrations of $Mn(CO)_4PPh_3^-$ were in the range of $(5.0-6.0) \times 10^{-4}$ M, and the carbene concentrations were in the range of 5.0×10^{-3} M to 0.0201 M. For R = Me the k value was obtained as a plot of k_{obsd} versus $[W(CO)_5(C(OMe)Ph)]$. For R = Et k was determined by dividing the pseudo-first-order rate constant by the concentration of $W(CO)_5(C(OEt)Ph)$. Error limits in k and k_{obsd} are standard deviations.

Results

Monoanion Reactions. With the exception of $[PPN][Co(CO)_4]$, which did not react, all metal carbonyl anions investigated reacted with the neutral methoxyphenylcarbene complexes, resulting in transfer of the methyl substituent from the alkoxy oxygen to the metal carbonyl anion (reaction 2). The reactions and characterization data for the products formed in these reactions are listed in Tables 1 and 2. The metal carbonyl dimer M'_2 was not a product in any of the reactions.

$$(CO)_5M{=}C(OCH_3)Ph + [M']^- \rightarrow [(CO)_5MC(O)Ph]^- + M'CH_3$$

$$M = Cr, W$$

$$M' = CpFe(CO)_2, Re(CO)_5, Mn(CO)_4PPh_3, Co(CO)_3PPh_3, Cp^*Cr(CO)_3, CpMo(CO)_3 \quad (2)$$

The formation of the acyl metalate $M(CO)_5C(O)Ph^-$ was verified by reaction with 1 equiv of trimethyloxonium tetrafluoroborate, which regenerated the corresponding carbene in each instance (reaction 3).

$$[(CO)_5MC(O)Ph]^- + (CH_3)_3OBF_4 \rightarrow (CO)_5M{=}C(OCH_3)Ph \quad (3)$$

$$M = Cr, W$$

A low-temperature ^{1}H NMR spectroscopic examination of the reaction between $[PPN][Mn(CO)_4(PPh_3)]$ and $(CO)_5W{=}C(OCH_3)Ph$ indicates clean conversion to products. At −70 °C, the spectrum contained only peaks from the starting materials. Only at room temperature (18 °C) was there evidence of reaction, with the appearance of a new peak attributed to $CH_3Mn(CO)_4(PPh_3)$ (−0.51 (d) ppm (J_{P-H} = 7.6 Hz)). A gradual decrease in the methoxy peak of $(CO)_5W{=}C(OCH_3)Ph$ (4.87 (s) ppm) coupled with an increase in the new methyl signal was observed over a 5-day period.

For the anions investigated, the reactivity suggests that the rate of CH_3^+ transfer occurs in the order

$$Cp^*Cr(CO)_3^- < CpMo(CO)_3^- < Co(CO)_3(PPh_3)^- < Mn(CO)_4(PPh_3)^- < Re(CO)_5^- \ll CpFe(CO)_2^-$$

The time required for half of the reactants to be consumed ranged from 6 days for $Cp^*Cr(CO)_3^-$ to a few seconds for $CpFe(CO)_2^-$ (see Table 1), in reasonable agreement with the nucleophilicity of the metal carbonyl anion.[16] Only $Co(CO)_3PPh_3^-$ (faster than expected) was

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significantly different. The metal carbonyl anion $Co(CO)_4^-$, which is the weakest nucleophile, exhibited no reaction with the carbene complexes.

To determine the dependence on the alkyl group transferred, kinetic studies of the reactions of $W(CO)_5(C(OMe)Ph)$ and $W(CO)_5(C(OEt)Ph)$ with $PPNMn(CO)_4PPh_3$ were conducted. The methoxycarbene complex was studied fully, showing the rate law

$$\text{rate} = k[[\text{PPN}][\text{Mn(CO)}_4\text{PPh}_3]][\text{W(CO}_5)(\text{C(OMe)Ph})]$$

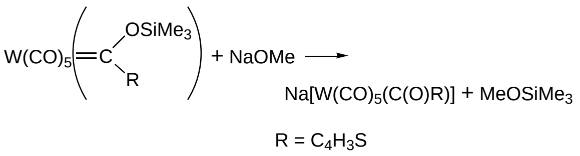
with $k = 0.14 \pm 0.01\ s^{-1}\ M^{-1}$ at 28 °C. For the ethoxycarbene the observed pseudo-first-order rate constant was divided by the concentration of the carbene complex, giving $k = (2.0 \pm 0.7) \times 10^{-3}\ s^{-1}\ M^{-1}$.

Reaction with Tetracarbonylferrate(2−). Reaction of $Na_2Fe(CO)_4$ with $(CO)_5W{=}C(OCH_3)Ph$ was also investigated and cleanly provides the products expected from a methyl transfer (reaction 4). The reaction was complete within seconds, consistent with the estimated nucleophilicity of $Na_2Fe(CO)_4$.[17]

$$\text{Fe(CO)}_4^{2-} + \text{(CO)}_5\text{W}{=}\text{C(OCH}_3\text{)Ph} \rightarrow \text{CH}_3\text{Fe(CO)}_4^{-} + \text{(CO)}_5\text{WC(O)Ph}^{-} \quad (4)$$

Discussion

The reaction under consideration is demethylation of the methoxy group of a neutral tungsten or chromium carbene complex (reaction 2) by a metal carbonyl anion. While this reaction is unprecedented, a desilylation has been reported:[18]



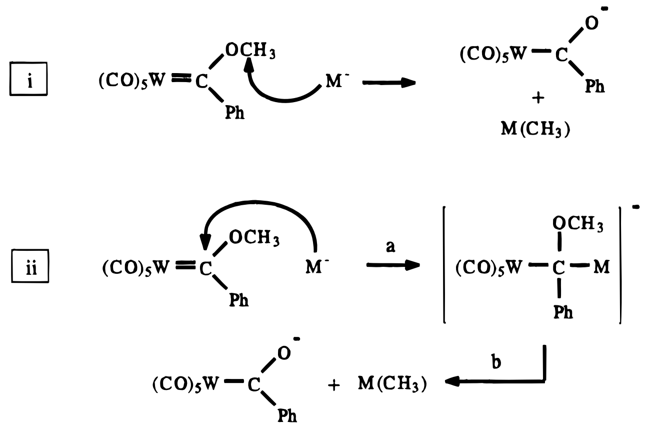
$$\text{W(CO)}_5\left(=\text{C}\begin{matrix}\text{OSiMe}_3\\ \text{R}\end{matrix}\right) + \text{NaOMe} \longrightarrow \text{Na[W(CO)}_5\text{(C(O)R)]} + \text{MeOSiMe}_3 \quad (5)$$

$R = C_4H_3S$

A similar reaction was observed with LiPh. Methanol and amines also attacked the silyl group, while PMe_3 attacked the carbene carbon. The discussion centered on $\pi_p - \pi_d$ bonding; similar reactions were not observed in the absence of the silyl group.[18] Cationic carbene complexes (reaction 1) have been dealkylated by I^-, phosphine ligands, and MeLi.[7−9] However, the nucleophilic attack by a metal carbonyl anion on the alkyl part of the alkoxy group (reaction 2) appears to be unprecedented.

Mechanism. The reactions described by reaction 2 involve transfer of the alkyl substituent from the alkoxy oxygen of the carbene to the metal carbonyl anion. Metal carbonyl anions react as nucleophilic or single-electron-transfer reagents.[19] Single-electron reactions invariably produce metal carbonyl dimers; no dimers were observed in the reactions represented by reaction 2. Thus, reaction 2 most likely proceeds through nucleophilic attack through two possible sites (Scheme 1): (i) nucleophilic attack by the metal anion directly at the alkyl substituent or (ii) nucleophilic attack of the metal anion at the carbene carbon followed by a subsequent methyl migration to the anion. Nucleophilic attack directly at the alkyl substituent should result in a large effect of the alkyl substituent being transferred on the rate.[20] The second potential mechanism (ii) would require that the initial nucleophilic attack at the carbon be rate-determining and the subsequent methyl migration to be rapid, since there was no evidence of the bridging carbene intermediate. We would also expect a much smaller dependence on the organic fragment transferred if the reaction followed pathway ii.

Scheme 1. Possible Sites for Nucleophilic Attack on Fischer-Type Carbenes



The methoxy complex $W(CO)_5(C(OMe)Ph)$ reacts with $Mn(CO)_4PPh_3^-$ 70 times more rapidly than the ethoxy complex $W(CO)_5(C(OEt)Ph)$. Such a slowing for C_2H_5 in comparison to CH_3 is typical for direct nucleophilic attack at carbon,[20] consistent with the mechanism shown as (i) in Scheme 1.

Nucleophilic attack at Fischer-type carbene complexes is well-known[1] and is a distinguishing feature for Fischer-type carbene complexes in comparison to early-transition-metal alkylidene complexes, which are susceptible to electrophilic attack. However, the reactions reported in this paper evidently represent the first examples of nucleophilic attack at the alkoxy carbon group. Calculations show that the alkoxy methyl carries a positive charge[3] but is the least likely of the three sites for nucleophilic attack. The significant rate dependence on the alkyl group is inconsistent with attack at the carbene carbon or at the *cis* carbonyl. Why then do metal carbonyl anions attack $(CO)_5M(C(OMe)Ph)$ exclusively at the methyl? Earlier studies on alkyl transfer reactions between metal carbonyl anions indicated transfer occurred when the reactant anion is more nucleophilic than the product anion. Evidently $M(CO)_5C(O)Ph^-$ is a weak nucleophile and a thermodynamic driving force for methyl transfer exists. It is likely that the relatively large metal carbonyl anions cannot access the carbene carbon or carbonyl carbon but can interact with the methyl which is further removed from the group 6 metal center.

Decomposition of $Cp(CO)Fe(\mu\text{-COR})(\mu\text{-CO})MnCp'(CO)(Cp' = \eta^5\text{-}C_5H_4Me)$ produces $MeFeCp(CO)_2$ and Cp′Mn-

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$(CO)_3$ in a transfer of an alkyl from a bridging carbyne to a metal.[7] While this provides precedent for alkyl transfer from an alkoxy on a carbene, it does not seem to be mechanistically related. Two reactions have been reported where nucleophilic attack by a metal carbonyl anion on a cationic carbene complex result in heterobimetallic complexes with bridging carbene groups:[21,22]

$$\mathrm{CpFe(CO)(PPh_3)({=}CH(OMe))^+ + CpFe(CO)_2^- \rightarrow Cp_2(CO)_2(\mu\text{-}CH(OMe))(\mu\text{-}CO)Fe_2 + PPh_3} \quad (6)$$

$$\mathrm{CpFe(CO)(CH_3CN)({=}C(SMe)_2)^+ + Co(CO)_4^- \rightarrow Cp(CO)Fe(\mu\text{-}C(SMe)_2)(\mu\text{-}CO)Co(CO)_3 + CH_3CN} \quad (7)$$

Reaction 7 is not easily compared to the reactions reported in this paper, but reaction 6 indicates attack by $CpFe(CO)_2^-$ at the carbene carbon. The similarity of the reactants in reactions 1 and 6 indicates that cationic carbene complexes are susceptible to attack by nucleophiles at either the carbon of the carbene or the alkyl of the alkoxy group on the carbene. The reactions reported in this paper (reaction 2) provide the first indication that neutral carbene complexes offer the same two sites, depending on the nucleophile.

Conclusion

Formally, one can consider the transfer of the alkyl group as a nucleophilic competition for R^+ between the acyl metalate and the metal anion. We can therefore estimate the nucleophilicity of the acyl metalates:

$$\mathrm{Fe(CO)_4^{2-} \approx CpFe(CO)_2^- > Re(CO)_5^- > Mn(CO)_4(PPh_3)^- > Co(CO)_3(PPh_3)^- > CpMo(CO)_3^- > Cp^*Cr(CO)_3^- > W(CO)_5(C(O)Ph)^- \approx Cr(CO)_5(C(O)Ph)^- > Co(CO)_4^-}$$

The reported reactions show a new site for nucleophilic attack on neutral Fischer-type carbene complexes.

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Supporting Information Available: A table of IR frequencies for metal carbonyl anions and absorbance vs time plots for the reaction of $W(CO)_5(C(OMe)Ph)$ with $[PPN][Mn(CO)_4PPh_3]$ and of $W(CO)_5(C(OEt)Ph)$ with $[PPN][Mn(CO)_4PPh_3]$ (5 pages). Ordering information is given on any current masthead page.

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