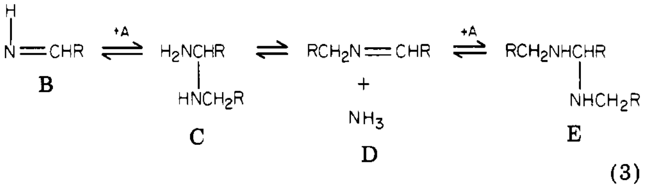
in the transformation shown in eq 3, but an organometallic species is needed to hydrogenate D to secondary amine. The ultimate hydrogen source in such a sequence comes from another amine, thus the reaction can be considered a transfer hydrogenation of sorts.



(3)

In conclusion this proposed mechanism should be contrasted with that proposed for the $Ru_3(CO)_{12}$ and Pd black H/D exchange studies on NEt_3.[25] In that case a mechanism is proposed whereby the α- and β-carbons can be metalated, and thus deuterated, because of the orientation of the ligated amine on the Ru_3 framework. Our mass spectral data, although not yet clearcut, does indicate a minor amount of multiple deuteration is occurring.[26] Thus, an alternate mechanism of H/D exchange may be operational outside the framework of our proposed mechanism. Such observations warrant further study.

We are currently actively pursuing the further intricasies of such catalyst systems in hopes of isolating further intermediates and unraveling further mechanistic details.

Acknowledgment. Our thanks to Dr. Clayton D. Wood and Dr. Horst G. Langer for mass spectral data and Dr. Richard M. Laine for helpful discussions.

Registry No. $RuCl_2(PPh_3)_2(ethylamine)_2$, 85565-62-4; $RuHCl(PPh_3)_2(ethylamine)_2$, 85565-63-5; $RuHCl(PBu_3)_3(decylamine)$, 85565-64-6; $[Ru_2Cl_3(PBu_3)_6]^+Ph_4B^-$, 85565-66-8; $RuCl_3$, 10049-08-8; PPh_3, 603-35-0; PBu_3, 998-40-3; $Ru(dppe)_2Cl_2$, 16594-81-3; decylamine, 2016-57-1.

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[25] Shvo, Y.; Thomas, D. W.; Laine, R. M. *J. Am. Chem. Soc.* **1981**, *103*, 2461.

[26] Unlike studies on NEt_3, mass spectral studies on our $HN(dec)_2$ system revealed deuteration of the chain could occur during fragmentation.[13] The chemical ionization spectrum of $DN(hexyl)_2$ in a methane plasma revealed a 114 peak due to $N(hexyl)Me^+$ and a 115 peak due to d_1-$N(hexyl)Me^+$. The CI mass spectrum for dihexylamine produced by the ruthenium/tributylphosphine catalyst system revealed d_0, 56.4%, d_1, 27.9%, d_2, 10.8%, and d_3, 3.1%, based on the 114 peak as d_0. Thus, although d_2 could come from incorporation of D into the backbone during fragmentation, vide infra, d_3 must come from multiple deuteration of the chain.

Reaction of $[(CO)_4FeC(O)OMe][C(NMe_2)_3]$ with $MeSO_3F$. Evidence for a Metal Alkylation

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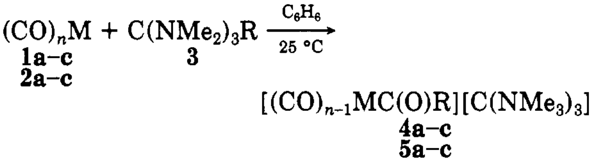
Summary: The reaction of $[(CO)_4FeC(O)OMe][C(NMe_2)_3]$ with $MeSO_4F$ at −78 °C results in the formation of $(CO)_4Fe(Me)C(O)OMe$ (**7**). At about 0 °C this complex decomposes to form methyl acetate and iron carbonyl species.

Some years ago we reported the synthesis of stable carbamoyl and alkoxycarbonyl complexes by addition of orthoamide derivatives $C(NMe_2)_3R$ to a carbonyl carbon atom of an appropriate metal carbonyl compound (eq 1).[1]



$$\underset{\substack{\mathbf{1a{-}c}\\ \mathbf{2a{-}c}}}{(CO)_nM} + \underset{\mathbf{3}}{C(NMe_2)_3R} \xrightarrow[25\ ^\circ C]{C_6H_6} \underset{\substack{\mathbf{4a{-}c}\\ \mathbf{5a{-}c}}}{[(CO)_{n-1}MC(O)R][C(NMe_3)_3]} \quad (1)$$

a, R = NMe_2, **b**, R = OMe, **c**, R = OEt; M = Fe for 1 and 4 (n = 5), M = Ni for 2 and 5 (n = 4)

High yields of 4 and 5 were obtained, and the equilibrium in reaction 1 lies far to the right. If a CS ligand is present, as in $(CO)_4FeCS$, the R group of **3a** is transferred preferentially to the more electrophilic thiocarbonyl carbon atom to yield a thiocarbamoyl complex. This on alkylation with $MeSO_3F$ gives the corresponding carbene complex.[2] Analogous reactions were carried out with the anion of **4a**.[3] This compound also behaves as a chelating ligand toward $NiBr_2$ to produce the covalent complex $[(CO)_4FeC(O)NMe_2]_2Ni$ with two iron–nickel bonds in a rare linear arrangement.[4] In contrast, **4b**, **4c**, and the corresponding thiocarbamoyl complex do not react with Ni^{2+} salts in this manner.

As an extension of our previous investigations concerning the reactivity of 4 and 5 toward various electrophiles, we report here an unusual metal (instead of O) alkylation of **4b** with $MeSO_3F$ and the thermal decomposition of the neutral alkylation product under very mild conditions to yield methyl acetate.

When **4b** is allowed to react with $MeSO_4F$ at −78 °C, a bright yellow crystalline powder can be isolated which is very soluble in pentane but decomposes slowly above −30 °C and rapidly at room temperature to give a brown, insoluble solid along with a volatile liquid.[5] The latter was identified as methyl acetate by comparison of its IR and ^1H NMR spectra and GC behavior with those of an authentic sample.

In contrast to similar experiments with **4a**,[3] the corresponding thiocarbamoyl complex[2] and various other anionic group 6B transition-metal complexes which give carbene complexes,[6] the spectroscopic data of the reaction product do not agree with the formation of the expected carbene complex **6**. However, all data are consistent with the formation of **7** as the result of methylation of the iron atom (eq 2). The increase of the coordination number from five to six may formally be considered as an oxidation of

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[1] (a) Petz, W. *J. Organomet. Chem.* **1976**, *105*, C19. (b) Petz, W. *Ibid.* **1975**, *90*, 223.

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[3] (a) Schmetzer, J.; Daub, J.; Fischer, P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 487. (b) Fischer, E. O.; Beck, H.-J.; Kreiter, C. G.; Lynch, J.; Muller, J.; Winkler, E. *Chem. Ber.* **1972**, *105*, 162.

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[5] Procedure: To a stirred solution of **4b** (0.95 g, 0.4 mmol) in CH_2Cl_2 at −78 °C is added an equimolar amount of CH_3SO_3F under an atmosphere of dry nitrogen. Immediately a dark orange-brown solution is formed which is stirred for about 10 min. The mixture is allowed to warm to about −30 °C, and the solvent is evaporated in vacuo. The dry residue is kept at low temperature and extracted with ca. 80 mL of cold pentane (−78 °C). The clear yellow pentane solution is decanted from insoluble material. Slow evaporation of the solvent at −78 °C results in the precipitation of 7 as a bright yellow crystalline powder. No analyses could be obtained because of the thermal instability of the compound. Recrystallization of the residue from the pentane extraction from hot water gave pure white $[C(NMe_2)_3]SO_3F$, identified by IR and NMR spectroscopy.

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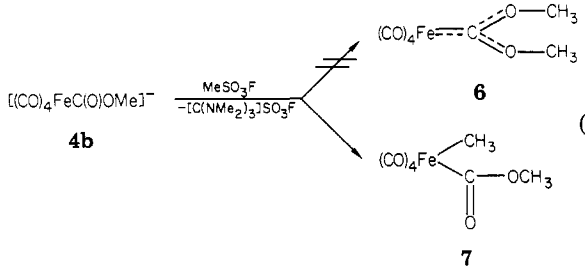
Table I. Comparison of Methyl ^{1}H NMR Shifts in Various Iron Complexes Containing Fe—Me, Fe—C(O)OMe, and Fe=C(OMe)$_2$ Bonds

compd	Fe—Me	Fe—C(O)OMe	Fe=C(OMe)$_2$
7[a]	0.72	3.34	
CpFe(CO)$_2$Me[b]	−0.10		
CpFe(CO)$_2$C(O)OMe[c]		3.39	
[(CO)$_4$FeC(O)OMe]$^-$ [d]		2.71	
(CO)$_2$(PMe$_3$)$_2$FeIMe[e]	0.36		
[CpFe(CO)$_2$C(OMe)$_2$]$^+$ [f]			4.42

[a] This work, in toluene-d_8. [b] Toluene.[10] [c] CS$_2$.[11] [d] CDCl$_3$.[1] [e] CD$_2$Cl$_2$.[9] [f] Acetone-d_6.[7] [g] All shifts in ppm relative to internal Me$_4$Si.

the metal atom. No CO evolution was observed during the reaction period.



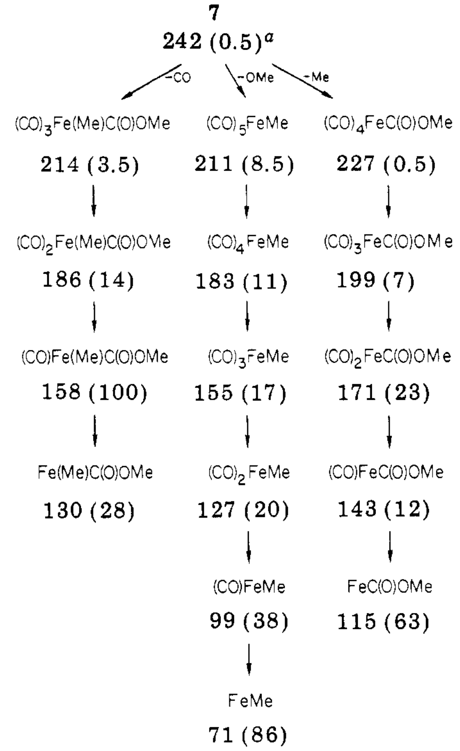
(2)

The ^{1}H NMR spectrum of 7 in toluene at −30 °C exhibits two sharp singlets at δ 0.72 and 3.34 ppm of equal intensity, indicating two types of methyl protons in different chemical environments. An alternate Z, E arrangement of the OCH$_3$ groups of the isomer **6** would also give rise to different methyl signals according to possible restricted rotation about the C$_{\text{carbene}}$–O axes, but all known dimethoxycarbene complexes of iron show only the average signal even at lower temperatures and the rotation barrier is found to be very low in such complexes.[7] In contrast, the isoelectronic NHMe group generates a high barrier as shown by NMR experiments.[8]

When an NMR sample of 7 is warmed from −30 °C to room temperature, the signals disappear without broadening and simultaneously two new signals grow in which are identical with those of MeCOOMe. This feature and the unusually large difference in chemical shifts of the two signals disagree with the formation of the isomeric carbene complex **6**. The ester is obtained in yields of ~70% by vacuum condensation if 7 is allowed to decompose at room temperature. The NMR experiments indicate a nearly quantiative formation by comparison of the relative peak intensities.

Table I summarizes, for comparison, NMR data of iron complexes with either Fe–Me or Fe–C(O)OMe bonds together with the shift of an authentic dimethoxycarbene complex. The high field signal is assigned to protons of a methyl group attached to the iron atom as proposed in structure 7 rather than to those of a methoxy group of a carbene ligand represented by **6**. No NMR data of a (CO)$_4$FeMe moiety has been reported, but the recently prepared complexes of type (CO)$_2$(PR$_3$)$_2$FeMeX (X = halogen) all display methyl resonances near the Me$_4$Si signal,[9] as does the Cp derivative of Wilkinson.[10] The shift of the "ester" methyl group of 7 is found to be identical with that of the corresponding cyclopentadienyl derivative.[11] There is no other molecule described in the literature with a Me and a C(O)OMe group attached to the same transition-metal atom.

Scheme I



[a] m/e (relative intensity).

Further evidence for the formation of the sixfold coordinated 7 is obtained by mass spectroscopy. The 70 eV spectrum shows the molecular ion at m/e 242, and no higher mass peaks due to a dimeric or oligomeric species can be detected. In contrast to a number of carbene complexes of the type (CO)$_4$FeL, which are characterized by consecutive loss of CO under electron-impact conditions to produce the FeL fragment, three parallel branches of fragmentation are observed, initiated by loss of either CO, Me, or OMe from the parent molecule. Further fragmentation steps are observable as outlined in Scheme I. Strong evidence for the proposed structure of 7 are the presence of mass peaks which can be assigned to the (CO)$_x$FeMe fragments and especially experiments with a deuterated starting material. When we examined the volatile part of the decomposition products of the reaction of [(CO)$_4$FeC(O)OCD$_3$]$^-$ (**4b-d$_3$**, obtained from Fe(CO)$_5$ and C(NMe$_2$)$_3$OCD$_3$) with MeSO$_3$F by NMR and mass spectroscopy, we found that only MeCOOCD$_3$ has formed. In contrast, equal amounts of CD$_3$COOMe and MeCOOCD$_3$ were expected from the decomposition of an intermediate carbene complex, (CO)$_4$FeC(OMe)(OCD$_3$). The key fragments (MeCOOCD$_3{}^+$) = 77, (COOCD$_3{}^+$) = 62, and (MeCO$^+$) = 43 were observed, and no peaks at m/e 59 (COOMe$^+$) and 46 (CD$_3$CO$^+$) could be detected.

The IR spectrum of 7, which could not be obtained free from the bands of the decomposition products, exhibits only absorptions of terminal CO groups at 2105 (m), 2040 (s), 2035 (s (sh)), 2010 (m (sh)), and 1990 cm^{-1}. A cis arrangement of the two noncarbonyl ligands can therefore be deduced. The absorption pattern is not typical for a

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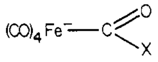
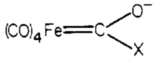
$(CO)_4Fe$ moiety bonded to a carbene ligand as expected for **6**.[12] A broad, medium intensity band at 1640 cm^{-1} can be assigned to the "ester" carbonyl group of **7**; a similar band appears in $CpFe(CO)_2COOMe$ at 1665 cm^{-1}.[11] The absorption bands of methyl acetate ($\nu(CO) = 1745\ cm^{-1}$) along with a band at 1815 cm^{-1} are already present as weak bands but grow to intense bands on a second run of the same sample, thus indicating ongoing decomposition of the initial complex. In the $\nu(CO)$ region the migration of the methyl group initiates a broad band centered at 2000 cm^{-1} along with an intense band at 1815 cm^{-1} due to bridging CO groups. $Fe_3(CO)_{12}$ was identified as a decomposition product of **7**, but the residue has not been studied further.

Anions of type **4** are basic and have two possible coordination sites for Lewis acids, one at the metal and the other at the alkoxycarbonyl or the carbamoyl oxygen atom. In contrast, the corresponding group 6B anions $M(CO)_5COOR^-$ (M = Cr, Mo, W) have only one site because two electrons at the metal are replaced by a CO group to achieve the rare-gas configuration. An attack of the electrophile at the metal is therefore not expected. The anion of **4b** may be compared with $S{=}C(O)OR^-$, in which S or O can be alkylated; similarities in chemical behavior of S and the $Fe(CO)_4$ group have been pointed out in a review.[13]

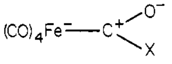
In spite of the two possible basic centers in **4**, the different behavior of **4a** and **4b** toward Me^+ is not fully understood. One explanation is that the replacement of the NR_2 group by OR causes a change in the basicity of the two sites. Considering the resonance structures A–D of the anion, it becomes apparent that a decreasing ability of X to back donation (going from X = NR_2 to X = OR) enhances the chance for an electrophile to react with the metal atom according to the minor contribution of form D.



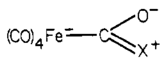
A



B



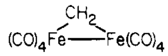
C



D

In contrast to this, a variety of salts of the type $[(CO)_4FeCOR]$ Li, mostly not isolated and used in situ, can be alkylated by $(Et_3O)BF_4$ to give the expected carbene complexes.[14] This communication reports the first example of the consecutive addition of a Lewis base and a Lewis acid to a binary transition-metal carbonyl that has not resulted in the formation of a Fischer-type carbene ligand.

The thermal decomposition of **7** via methyl group migration to the alkoxycarbonyl carbon atom to produce methyl acetate and iron carbonyl species can be regarded as a model reaction with respect to the chain growth sequence of the Fischer–Tropsch process.[15] A comparable methyl acetate formation has been observed by the reaction of the dinuclear complex **8** with MeOH at elevated temperatures; a μ-ketenyl complex was postulated as the reactive intermediate, generated by incorporation of a terminal CO group into the bridge.[16]



8

Homologation of a C_1 unit via rearrangement of a coordinated dimethoxycarbene ligand has not been reported. The free ligand, if generated from an organic source, dimerizes, and rearrangement to methyl acetate is only connected with special reaction conditions.[17] This feature and the spectroscopic data clearly indicate that the yellow alkylation product of **4b** has a structure as suggested for **7**. Further investigations concerning these systems are currently in progress.

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Registry No. 4b, 58411-26-0; 7, 85883-27-8.

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$W(\eta^5\text{-}C_5H_5)[C(Ph)C(CMe_3)C(Ph)]Cl_2$: A Molecule Having a Localized, Nonplanar, Fluxional Metallacyclobutadiene Ring

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Received April 13, 1983

Summary: The reaction between $W(\eta^5\text{-}C_5H_5)(CCMe_3)Cl_2$ and disubstituted acetylenes yields tungstenacyclobutadiene complexes that in some cases exhibit a signal for essentially only one type of ring carbon atom on the NMR time scale at room temperature. One of these is the product with the composition $W(\eta^5\text{-}C_5H_5)(CCMe_3)(PhC{\equiv}CPh)Cl_2$. It crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^5; No. 14] with a = 9.859 (4) Å, b = 10.821 (2) Å, c = 20.580 (11) Å, β = 92.88 (4)°, V = 2193 $Å^3$, and ρ(calcd) = 1.72 g cm^{-3} for Z = 4 and M_r = 567.2. Convergence was achieved with R_F = 3.1% and R_{wF} = 2.6% for all 2599 data with 2θ(Mo Kα) = 4.5–45.0°. The WC_3 ring conformation is approximately halfway between a planar and tungstenatetrahedrane form with localized, alternating double and single bonds ($W{=}C_\alpha$ = 1.943 (5) Å, $C_\alpha{-}C_\beta$ = 1.485 (7) Å, $C_\beta{=}C_\alpha'$ = 1.372 (8) Å, $C_\alpha'{-}W$ = 2.132 (5) Å); the two phenyl rings are found on the α-carbon atoms. It is proposed that the alkylidyne fragments are scrambled on the metal via a fluxional process involving formation of a tungsten(VI) metallatetrahedrane or, alternatively, a tungsten(IV) cyclopropenyl intermediate.

Recently we showed[2] that the reaction between $W(CCMe_3)Cl_3$(1,2-dimethoxyethane) and 1 equiv of di-

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(1) (a) State University of New York at Buffalo. (b) Massachusetts Institute of Technology.

(2) Pedersen, S. F.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1982**, *104*, 6808.

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