the low frequency side, could easily mask a weak bridging CO stretch. In any case, the data clearly indicate a terminal-to-bridge CO rearrangement.[17]

Acknowledgments. We appreciate the support of this research by the NSF through Grant GP-28878. J. S. Kristoff acknowledges an NDEA Fellowship.

Registry No. $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot BF_3$, 41666-88-0; $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot BCl_3$, 43198-12-5; $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2\cdot BBr_3$, 41666-89-1; $[(\pi\text{-}C_5H_5)Fe(CO)]_4\cdot BF_3$, 39466-88-1; $[(\pi\text{-}C_5H_5)Fe(CO)]_4\cdot 2BF_3$, 39334-03-7; $[(\pi\text{-}C_5H_5)Fe(CO)]_4\cdot BCl_3$, 39334-00-4; $[(\pi\text{-}C_5H_5)Fe(CO)]_4\cdot 2BCl_3$, 39334-01-5; $[(\pi\text{-}C_5H_5)Fe(CO)]_4\cdot BBr_3$, 39333-98-7; $[(\pi\text{-}C_5H_5)Fe(CO)]_4\cdot 2BBr_3$, 39333-99-8; $[(\pi\text{-}C_5H_5)Fe(CO)]_4\cdot AlBr_3$, 39466-84-7; $[(\pi\text{-}C_5H_5)Fe(CO)]_4\cdot 2AlBr_3$, 39466-85-8; $[(\pi\text{-}C_5H_5)Fe(CO)]_4\cdot 3AlBr_3$, 39466-86-9; $[(\pi\text{-}C_5H_5)Fe(CO)]_4\cdot 4AlBr_3$, 39466-87-0; $Co_2(CO)_8\cdot AlBr_3$, 40964-38-3; $Fe_2(CO)_9\cdot AlBr_3$, 49564-14-9; $Ru_3(CO)_{12}\cdot AlBr_3$, 39466-83-6; $Fe_3(CO)_{12}\cdot AlBr_3$, 39466-82-5.

(17) As an incidental point, we note that $Mn_2(CO)_{10}$ does not form an adduct under similar conditions.

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Alkylation and Substitution Reactions of Metal Carbonyl Acylate and Carbene Complexes

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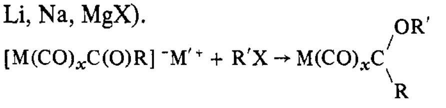
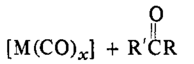
Alkylation reactions of *trans*-$LFe(CO)_3C(O)R^-Li^+$, where L = CO, PPh_3, $P(n\text{-}Bu)_3$, $P(OMe)_3$, and $P(OPh)_3$ and R = Ph, Me, and benzyl, employing as alkylating agents MeI, $MeOSO_2F$, $THFMe^+SO_3F^-$, and $Et_3O^+BF_4^-$, have been investigated. Alkoxonium salts react exclusively at the acyl oxygen yielding carbene complexes; ketones and products of $[LFe(CO)_3]$ are obtained from reaction of the acylate with MeI and $MeOSO_2F$. The rate of MeI reaction with $LFe(CO)_3C(O)R^-Li^+$ is ligand dependent with $P(n\text{-}Bu)_3 > PPh_3 > P(OPh)_3$. MeI is found to react with metal carbonyl carbene complexes also to yield ketone, however too slowly to suggest intermediacy of carbene complex in the ketone synthesis directly from the acylate complex. Alkoxycarbene ligands as well as the acyl ligand (lithiooxycarbene) were found to labilize ligands trans to themselves, *i.e.*, for X = Li or Et, the reaction is $LFe(CO)_3C(OX)R + L' \rightarrow L + L'Fe(CO)_3C(OX)R$. Mechanistic implications for the ketone synthesis based on the observation of ligand-exchange processes at both L and acyl sites ($LFe(CO)_3C(O)R^-Li^+ + L' \rightarrow LFe(CO)_3L' + [Li^+C(O)R^-]$) are discussed.

Introduction

Alkylation reactions of metal carbonyl acylates yield products according to eq 1 and 2 (M = transition metal; M' = Li, Na, MgX).



$$[M(CO)_xC(O)R]^-M'^+ + R'X \rightarrow M(CO)_xC\begin{matrix}\diagup OR'\\ \diagdown R\end{matrix} \tag{1}$$



$$\rightarrow [M(CO)_x] + R'\overset{\overset{O}{\|}}{C}R \tag{2}$$

Equation 1 represents the basis of Fischer's *in situ* preparation of the novel carbene ligand and is most successful with group VIb transition metal carbonyl complexes.[1] On the other hand Fischer and others have had difficulty alkylating analogous iron acylates.[2] Attempted methylation of $Fe(CO)_4[C(O)Ph]^-Li^+$ with $Me_3O^+BF_4^-$ in CH_2Cl_2 led to formation of $Fe_3(CO)_{12}$ and $Fe_2(CO)_9$ as major reaction products with μ-diphenylmethylene-octacarbonyldiiron in <0.5% yield; $Fe(CO)_4C(OMe)Ph$ was not observed. Alkylation of iron tetracarbonyl acylates by $Et_3O^+BF_4^-$ according to eq 1 in CH_2Cl_2 at −60° was observed only when R was a very electron-withdrawing group such as C_6F_5, C_6Cl_5, or $N(CH_3)_2$.[3]

The anionic acylates generated either by reaction of organolithium reagents with $Fe(CO)_5$[4,5] or by reaction of alkyl halides with $Na_2Fe(CO)_4$[6,7] have received much attention due to their usefulness in organic synthesis. Initial investigations into the mechanism of (2) and the isolation of alkyliron carbonylates prompts Collman and coworkers[8-10] to suggest a reductive elimination of the proposed (alkylacyl)iron carbonyl intermediate (formed by two successive oxidative additions of R^+ to $Fe(CO)_4^{2-}$) rather than a nucleophilic reaction by the acyl carbon on the alkyl halide as is most likely the case with main group metal acylates.[11,12]

We have recently completed a kinetic study of the reaction of benzylmagnesium chloride with monosubstituted iron carbonyl derivatives to give chloromagnesium salts of the metal carbonyl acylate.[13] These acylates may be readily characterized by reaction with Meerwein's salt, triethoxonium tetrafluoroborate, in tetrahydrofuran (THF) at room temperature to form the carbene derivative (eq 1). Characteristic CO stretching frequencies for the isolated carbene derivatives may be found in Table I.

Since methyl iodide alkylates at the acyl oxygen in group VIb metal carbonyl acylates[14] but yields ketones with iron carbonyl acylates, further studies on the dependence of site of alkylation on the metal carbonyl residue were undertaken. In particular, we were interested in examining (1) the possible intermediacy of a metal carbene complex in the ketone preparation according to eq 2, (2) the fate of the

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(1) R. Aumann and E. O. Fischer, *Angew. Chem.*, 79, 900 (1967); *Angew. Chem., Int. Ed. Engl.*, 6, 878 (1967).

(2) E. O. Fischer and V. Kiener, *J. Organometal. Chem.*, 23, 215 (1970).

(3) E. O. Fischer, H. J. Beck, C. G. Kreiter, J. Lynch, J. Muller, and E. Winkler, *Chem. Ber.*, 105, 162 (1972).

(4) M. Ryang, I. Rhee, and S. Tsutsumi, *Bull. Chem. Soc. Jap.*, 38, 330 (1965).

(5) M. Ryang, *Organometal. Chem. Rev., Sect. A*, 5, 67 (1970).

(6) I. Rhee, M. Ryang, and S. Tsutsumi, *J. Organometal. Chem.*, 9, 361 (1967).

(7) M. P. Cooke, *J. Amer. Chem. Soc.*, 92, 6080 (1970).

(8) J. P. Collman, S. R. Winter, and D. R. Clark, *J. Amer. Chem. Soc.*, 94, 1788 (1972).

(9) W. O. Siegl and J. P. Collman, *J. Amer. Chem. Soc.*, 94, 2517 (1972).

(10) J. P. Collman, J. N. Cawse, and J. I. Brauman, *J. Amer. Chem. Soc.*, 94, 5905 (1972).

(11) I. I. Lapkin, G. Y. Anvarova, and T. N. Povarnitsyna, *J. Gen. Chem. USSR*, 36, 1945 (1966).

(12) D. Seebach, *Angew. Chem., Int. Ed. Engl.*, 8, 639 (1969).

(13) M. Y. Darensbourg, H. L. Conder, D. J. Darensbourg, and C. Hasday, *J. Amer. Chem. Soc.*, 95, 5919 (1973).

(14) E. O. Fischer and A. Maasbol, *Chem. Ber.*, 100, 2445 (1967).

Table I. Carbonyl Stretching Frequencies of *trans*-$LFe(CO)_3L'$ in Tetrahydrofuran

L	L′	ν_{CO}, cm^{-1}	Assignment
Ph_3P	CO	2046 m, 1970 w, 1939 s	$A_1^{(2)}$, $A_1^{(1)}$, E
Ph_3P	Ph_3P	1887.5 s	E
Ph_3P	$(PhO)_3P$	1906 br	E
Ph_3P	C(OLi)Ph	1861 s, 1848 s	E (split)
Ph_3P	C(OEt)Ph	1905 s, 1893 s	E (split)
Ph_3P	C(OEt)Me	1895 br	E
Ph_3P	C(OMe)Ph	1905 s, 1891.5 s	E
n-Bu_3P	CO	2041 m, 1964 w, 1929 s	$A_1^{(2)}$, $A_1^{(1)}$, E
n-Bu_3P	*n*-Bu_3P	1865 s	E
n-Bu_3P	C(OLi)Ph	1848 s, 1838 s	E (split)
n-Bu_3P	C(OEt)Ph	1894 s, 1884 s	E (split)
n-Bu_3P	C(OEt)Me	1882 s	E
$(PhO)_3P$	CO	2063 m, 1990 w, 1958 s	$A_1^{(2)}$, $A_1^{(1)}$, E
$(PhO)_3P$	$(PhO)_3P$	1925 br	E
$(PhO)_3P$	C(OLi)Ph	1886 s, 1869 s	E (split)
$(PhO)_3P$	C(OEt)Ph	1925 s, 1908 s	E (split)
$(PhO)_3P$	C(OEt)Me	1917 s, 1907 s	E (split)
CO	CO	2015 m, 1994 s	A_1', A_2''
CO	C(OLi)Ph	2016 m, 1929 m	$A_1^{(2)}$, $A_1^{(1)}$
		1910 s, 1894 s	E (split)
CO	C(OEt)Ph	2050 m, 1980 m	$A_1^{(2)}$, $A_1^{(1)}$
		1958 s, 1942 s	E (split)

metal moiety of reduced coordination number produced simultaneously with ketone (eq 2), (3) yield and product distribution dependence of the metal carbene and/or ketone on the electronic properties of the trans-substituent ligand in the reactant, and (4) the dependence of reactions 1 and 2 on alkylating agent, R′X.

Experimental Section

All reactions and transferals were performed under N_2 or Ar atmosphere; extensive use was made of syringe and "pop-bottle" techniques.

Materials. Tetrahydrofuran, purified by distillation from sodium benzophenone dianion and flushed with argon, was used as solvent throughout these studies. Methyl iodide was freshly distilled from $CaCl_2$ prior to use. Triethoxonium tetrafluoroborate was prepared by Meerwein's method.[15] Methyl fluorosulfonate was used as purchased from Aldrich Chemical Co. Iron pentacarbonyl was purchased from Pressure Chemical Co. The following ligands were gifts of the sources cited and were generally used as received without further purification: tri-*n*-butylphosphine and triphenylphosphine (M & T Chemical Co.), trimethyl phosphite (Mobil Chemical Co.). Triphenyl phosphite was purchased from Strem Chemical Co. PhLi and MeLi were purchased from Alfa Inorganics and Lithium Corp., respectively. BzlLi was prepared from Bzl_2Hg.

Preparations. $LFe(CO)_4$ complexes were prepared by combinations of reflux and irradiation of the respective ligand in pure $Fe(CO)_5$. Detailed preparative and purification procedures are presented in a separate report.[16] All complexes prepared in this manner were isolated in 60-80% yield.

Solutions of $LFe(CO)_3C(O)R^-Li^+$ acylates were prepared in general by dissolving the appropriate amount of $LFe(CO)_4$ (0.10 mmol in 10 ml THF if the reaction was to be run on infrared scale) and then adding nearly stoichiometric amounts of RLi solution dropwise *via* a syringe.

The substituted iron carbonyl carbene derivatives were obtained by adding small amounts of the extremely hygroscopic ethoxonium salt under an N_2 atmosphere to THF solutions of the acylates until acid to litmus. Alternatively a solution of $MeOSO_2F$ in THF was similarly added to prepare the methoxycarbene complexes. This carbene complex solution (generally deep red) was quickly added to 100-150 ml of water and extracted into 50 ml hexane. Solid complexes ($Ph_3PFe(CO)_3C(OEt)Ph$, red, mp 124-126°, and $Ph_3PFe(CO)_3$-C(OEt)Me, yellow, dec pt 90°) were recrystallized from hexane at −78° several times yielding 30-66% of the respective carbene complexes analytically pure. Liquids ($(PhO)_3PFe(CO)_3C(OEt)Ph$, (*n*-$Bu_3P)Fe(CO)_3C(OEt)Me$, $Fe(CO)_4C(OEt)Ph$; all were red oils) were chromatographed on a 2-in. silica gel column with hexane as eluent. The solvent was removed *in vacuo*.

Analytical results for $Ph_3PFe(CO)_3C(OEt)Ph$ and for $Ph_3PFe(CO)_3C(OEt)Me$ follow. *Anal.* Calcd for $FePC_{30}H_{25}O_4$: C, 67.25; H, 4.66; mol wt 535.8. Found: C, 67.53; H, 4.82; mol wt 530. Calcd for $FePC_{25}H_{23}O_4$: C, 63.30; H, 4.85; mol wt 474. Found: C, 63.83; H, 5.26; mol wt 474.

Nmr parameters are all similar and analogous to other oxycarbene complexes. Spectra were recorded in acetone-*d* on a Jeolco MH100 and showed for the ethoxycarbene complexes the CH_2 quartet between 5.06 and 5.15 ppm and the CH_3 triplet between 1.54 and 1.62 ppm. The phenyl proton multiplet of the phenylalkoxycarbene ligand is centered at 7.38 ppm; the methyl singlet of the methylalkoxycarbene ligand is found at 3.05 ppm.

trans-$Ph_3PFe(CO)_3P(OPh)_3$ was prepared by refluxing 1.0 g (2.08 mmol) of $(PhO)_3PFe(CO)_4$ and 1.24 g (4.70 mmol) of Ph_3P in 5 ml of freshly distilled cyclohexanol for 12 hr. Pentane (100 ml) was added with stirring to the cooled solution producing a yellow precipitate. Recrystallization from CH_2Cl_2-heptane yielded 0.53 g (36% based on Fe) of *trans*-$Ph_3PFe(CO)_3P(OPh)_3$, mp 181.5-183°. *Anal.* Calcd for $FeP_2C_{39}H_{30}O_6$: C, 65.75; H, 4.22; mol wt 711.8. Found: C, 65.61; H, 4.25; mol wt 717.

Reactions. All reactions were followed using a Perkin-Elmer 521 grating spectrophotometer, equipped with a linear absorbance potentiometer and calibrated in the CO stretching region with CO and H_2O vapor. NaCl cells (0.1 mm) were used for THF solution spectra; 1.0 mm cells were used for hexane solution spectra. Carbonyl-containing products were identified by comparison of their infrared spectra with authentic samples. The carbonyl stretching frequencies of all complexes used in this study are presented in Table I. Yields were determined from Beer's law plots of isolated authentic samples.

Reaction of $LFe(CO)_3C(O)R^-Li^+$ and $MeOSO_2F$. THF solutions of the respective acylates were prepared as described above (10^{-2} *M*). A 0.1-ml (1.3-mmol) sample of $MeOSO_2F$ syringed into this 10 ml of the acylate solution yielded deep red solutions. Infrared spectra were taken 60 sec after mixing. Observed products were $LFe(CO)_4$, $L_2Fe(CO)_3$, $LFe(CO)_3C(OCH_3)R$, and $CH_3C(=O)R$. For R = Ph and L = *n*-Bu_3P, Ph_3P, and $(PhO)_3P$ the yield of carbene product was 19, 42, and 54%, respecitvely, based on starting acylate concentration. The numerical values of these per cent yields vary according to starting acylate concentration; however relative order (dependence on L) is constant and completely reproducible. All solutions jelled within 30 min.

A 1.5-ml sample of a 1.5 *M* solution of $MeOSO_2F$ in THF was added to 10 ml of THF 0.01 *M* in $Ph_3PFe(CO)_3C(O)Ph^-Li^+$. No ketone was produced and a 75-80% yield of $Ph_3PFe(CO)_3C(OMe)Ph$ was obtained.

A 0.1-mmol amount of $Ph_3PFe(CO)_3C(O)Ph^-Li^+$, produced in and isolated from THF, was dissolved in 10 ml of CH_2Cl_2 and 1.3 mmol of $MeOSO_2F$ was added. Acetophenone, $Ph_3PFe(CO)_4$, and $(Ph_3P)_2Fe(CO)_3$ were the only observed products; reaction time was <3 min.

Reaction of $Ph_3PFe(CO)_3C(OEt)Ph$ with $MeOSO_2F$ and $Et_3O^+BF_4^-$. A 0.1-ml (1.3-mmol) sample of $MeOSO_2F$ or ~0.2 g (~1 mmol) of $Et_3O^+BF_4^-$ was added to 10 ml of THF solution of carbene complex (~10^{-2} *M*). The only observed products were $Ph_3PFe(CO)_4$ and $(Ph_3P)_2Fe(CO)_3$.

Reaction of $LFe(CO)_3C(O)Ph^-Li^+$ and MeI. Freshly distilled MeI was injected into 10^{-2} *M* solutions of $LFe(CO)_3C(O)R^-Li^+$ at 25° and the reactions were monitored by infrared spectroscopy.

Reaction of $Ph_3PFe(CO)_3C(OEt)R$ and MeI. A 0.10-mmol sample of the respective carbene complex (R = Me, Ph) was dissolved in 10-15 ml of THF, rigorously excluding air. A 1-ml (0.016-mol) amount of MeI was added and the reaction mixture was maintained at 50° for the ~16 hr necessary for completion of reaction. Products were identified by comparison of spectral properties (nmr and ir) with those of known samples and found to be $Ph_3PMe^+I^-$, $Fe(CO)_4C(OEt)R$, and ketone. High-resolution infrared spectroscopy with an accuracy of 0.5 cm^{-1} shows a 2.5-cm^{-1} difference (scale expansion 5 cm^{-1}/cm) in propiophenone and acetophenone. On the basis of band position, band shape, and mixed infrared spectra the predominant ketone produced here is acetophenone with the possibility of a small (<10%) amount of propiophenone also being present. No other ketones were observed.

Reaction of $Ph_3PFe(CO)_3C(OEt)Ph$ and $(PhO)_3P$. Under conditions identical with those described above a 100-fold molar excess of $(PhO)_3P$ was added to $Ph_3PFe(CO)_3C(OEt)Ph$. Infrared spectral studies, *i.e.*, band area measurements, indicated a quantitative conversion of the starting carbene complex to $(PhO)_3PFe(CO)_3C(OEt)Ph$ with a half-life of 106.4 min in THF or 36.2 min in heptane at 50°.

Reaction of $LFe(CO)_3C(O)Ph^-Li^+$ and L′. Ten- to fifty-fold

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(15) H. Meerwein, *Org. Syn.*, 46, 113 (1966).

(16) H. L. Conder and M. Y. Darensbourg, *J. Organometal. Chem.*, in press.

molar excesses of L′ (L′ = $(PhO)_3P$, Ph_3P, n-Bu_3P) were added to THF solutions of $LFe(CO)_3C(O)Ph^-Li^+$ (~1 × 10^{-2} *M*: L = CO, Ph_3P, n-Bu_3P) prepared as indicated above. Reactions were monitored by infrared analysis and products were identified by comparison of infrared spectra with those of known compounds. Product distributions and per cent yields were based on initial acylate concentration and determined from Beer's law plots of isolated, known compounds.

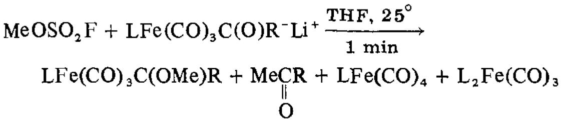
Photochemical Decomposition of $Ph_3PFe(CO)_3C(OEt)Ph$. Solutions of 10^{-2} *M* carbene complex in THF were placed in Pyrex tubes and positioned 10 cm from a 450-W Hanovia mercury arc lamp. Samples were removed periodically and the reaction was monitored by infrared spectroscopy. $Ph_3PFe(CO)_4$ was the only carbonyl-containing product in THF. *trans*-$(Ph_3P)_2Fe(CO)_3$ decomposed under these photochemical conditions.

Results and Discussion

$LFe(CO)_3C(O)R^-M'^+$ (M′ = Li, MgX) reacts instantaneously with $Et_3O^+BF_4^-$ in THF to yield the substituted iron carbonyl carbene complexes in nearly quantitative amounts. The carbene complexes thus formed were readily isolated; however a slow ($t_{1/2}$ from 15 to 30 min) secondary reaction of the alkylating agent with the carbene complex to yield $LFe(CO)_4$, $L_2Fe(CO)_3$, and unidentified organic products was observed. This secondary reaction is ligand dependent with rates decreasing in the order $(n\text{-}Bu)_3P > Ph_3P > (MeO)_3P > (PhO)_3P$. Detailed studies of this system were hampered due to solidification of the reaction mixture within 20-30 min.

Upon addition of $MeOSO_2F$ to the iron acylate dissolved in CH_2Cl_2, methyl ketone and products of $[LFe(CO)_3]$ (eq 2) are observed; no carbene complex is formed. Hence, in CH_2Cl_2, $MeOSO_2F$ behaves as does MeI toward iron acylates. If however $MeOSO_2F$ is previously mixed with THF before addition to the iron acylate, no ketone is produced and carbene complex is obtained instantaneously in high yields. Since $MeOSO_2F$ is known to form oxonium salts with THF,[17] carbene production is most likely resulting from alkylation by a THF-methoxonium agent. (Complete conversion of $MeOSO_2F$ to the THF-methoxonium salt requires about 15 min.)

Both the carbene derivative and ketone are observed as *initial* reaction products of methyl fluorosulfate added to THF solutions of the iron acylates (eq 3). Yields (determined for 1 min of reaction) of carbene derivative, of mono-, and of disubstituted L–Fe derivatives are typically 30, 20, and 45%, respectively, based on acylate, thus accounting for approximately all of the substituent phosphine or phosphite.


$$MeOSO_2F + LFe(CO)_3C(O)R^-Li^+ \xrightarrow[\text{1 min}]{\text{THF, 25°}} LFe(CO)_3C(OMe)R + Me\underset{\underset{O}{\|}}{C}R + LFe(CO)_4 + L_2Fe(CO)_3 \qquad (3)$$

L = $(n\text{-}Bu)_3P$, Ph_3P, $(PhO)_3P$; R = Ph, Me

The yield of the carbene complex, determined under identical conditions in all cases, was found to be dependent on the electronic character of the substituent L, the less electron-donating phosphite ligands promoting higher yields of carbene complex. Making the assumption that increased electronic charge in going from triphenyl phosphite to tri-*n*-butylphosphine is distributed over the acyl group as well as the terminal carbonyl groups (whose electron density is monitored by the frequency shifts found in Table I), the carbene yield dependence is most reasonably attributed to the competition between acylate complex and THF for $MeOSO_2F$. This study suggests the less electron-rich acylates to compete less effectively for $MeOSO_2F$ thus allowing for formation of $THFMe^+$ from which the carbene complex is produced.

Table II. Half-Lives (min) of Reactions of $LFe(CO)_3C(O)Ph^-Li^+$ [a] with MeI in THF at 25.0°.

L	[MeI],[b] *M* 0.20	0.40	2.0
$(PhO)_3P$	90	49	1
Ph_3P	10	5.5	*c*
n-Bu_3P	2.5	0.5	*c*

[a] $[LFe(CO)_3C(O)Ph^-Li^+] = 1.0 \times 10^{-2}$ *M*. [b] Approximate concentrations as discussed in text. [c] Instantaneous reactions.

The reaction of isolated analytically pure $Ph_3PFe(CO)_3C(OEt)Ph$ in THF with $MeOSO_2F$ is slow ($t_{1/2}$ = ~15 min) yielding as iron-containing products $Ph_3PFe(CO)_4$ and $(Ph_3P)_2Fe(CO)_3$. Reaction at the carbene ligand site is thus indicated although the nature of the organic products was not established. Since the longer reaction time permits formation of $THFMe^+$, the similarity between this reaction and the ethoxonium salt reaction with carbene complex is not surprising. It is clear however that the reaction of $MeOSO_2F$ with acylate under conditions leading to both ketone and carbene complex formation is so rapid (~1 min) that it is unlikely that the carbene complex is an intermediate in the production of ketone according to eq 3. Two separate fast reactions are occurring when $MeOSO_2F$ is added to THF solutions of acylates. These are according to eq 2 with $MeOSO_2F$ acting directly on the acyl moiety and according to eq 1 with $MeOSO_2F$ reacting as an alkoxonium compound, $THFMe^+SO_3F^-$.

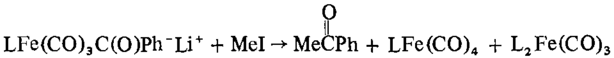
$MeOSO_2F$ reacts with $Ph_3PFe(CO)_3C(O)Ph^-Li^+$ in the presence of added free phosphine, 100-fold excess, to yield the carbene complex, ketone, and only $(Ph_3P)_2Fe(CO)_3$; the production of $Ph_3PFe(CO)_4$ is completely suppressed. The reaction mode of $[LFe(CO)_3]$ proposed in eq 4 is analogous

$$[LFe(CO)_3] \rightarrow L + Fe + 3CO \xrightarrow{[LFe(CO)_3]} LFe(CO)_4 + L_2Fe(CO)_3 \qquad (4)$$

to the pathway operative for $[LMo(CO)_4]$, the coordinately unsaturated intermediate produced in the first-order decomposition of $LL'Mo(CO)_4$ (L = PPh_3; L′ = NC_5H_5, NC_5H_{11}).[18]

The tetracoordinate $[LFe(CO)_3]$ moiety may also be produced by the photochemical decomposition of $Ph_3PFe(CO)_3C(OEt)Ph$. Irradiation of a THF solution of $Ph_3PFe(CO)_3C(OEt)Ph$ over a period of 8 hr leads to the production of $Ph_3PFe(CO)_4$ as the only carbonyl-containing species. No disubstituted product was observed; however a separate experiment showed $(Ph_3P)_2Fe(CO)_3$ to be photochemically unstable.

$LFe(CO)_3C(O)Ph^-Li^+$ reacts with MeI giving good yields of methyl phenyl ketone and shows no carbene complex formation (eq 5). The intermediacy of the $[LFe(CO)_3]$ species is again suggested by the iron-containing products, $LFe(CO)_4$ and $L_2Fe(CO)_3$. Plots of ln *A* of the iron acylate *vs.* time were linear over several reaction half-lives. Due to the possible presence of varying small amounts of excess phenyllithium, the rate law dependence on MeI concentration could not be established with certainty. However the dependence


$$LFe(CO)_3C(O)Ph^-Li^+ + MeI \rightarrow Me\overset{\overset{O}{\|}}{C}Ph + LFe(CO)_4 + L_2Fe(CO)_3 \qquad (5)$$

L = $(n\text{-}Bu)_3P$, Ph_3P, $(MeO)_3P$, $(PhO)_3P$

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(17) R. W. Alder, G. H. James, M. L. Sinnott, and M. C. Whiting, *Chem. Commun.*, 1533 (1968).

(18) C. L. Hyde and D. J. Darensbourg, *Inorg. Chem.*, 12, 1286 (1973).

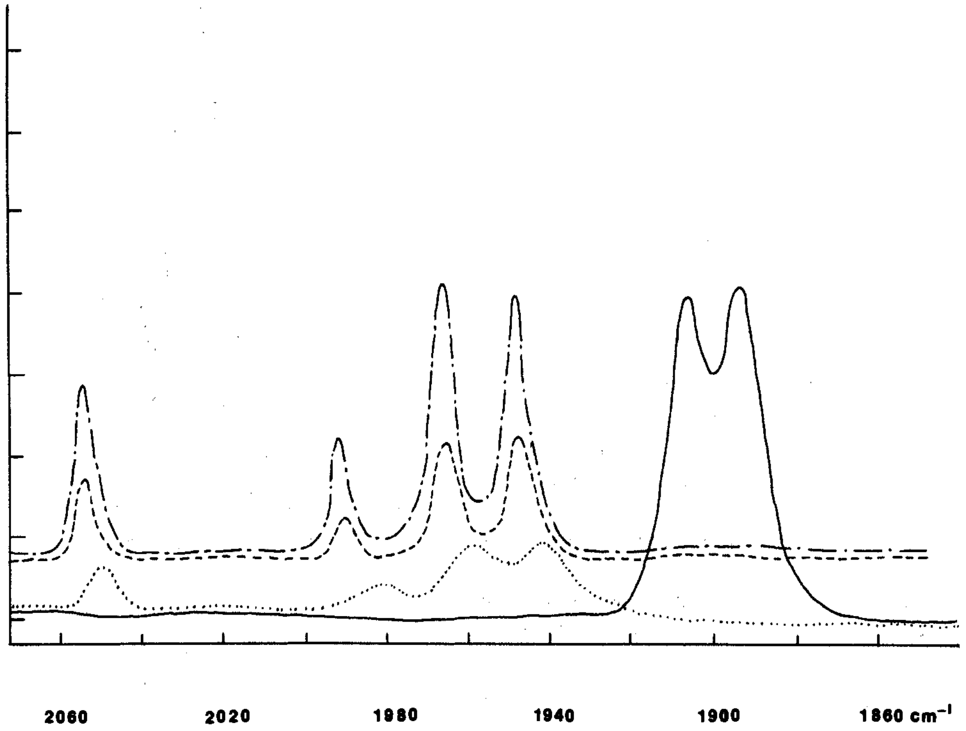

Figure 1. Nature of the infrared spectral changes as *trans*-$Ph_3PFe(CO)_3C(OEt)Ph$ reacts with MeI in THF according to eq 6: —, $Ph_3PFe(CO)_3C(OEt)Ph$; · · · ·, reaction mixture 16 hr after addition of MeI; - - -, reaction products in hexane; — · ·, pure $Fe(CO)_4C(OEt)Ph$ in hexane.

of reaction half-life on approximate MeI concentrations is shown in Table II. Rates of reaction 5 are ligand dependent, 10-fold decreases in $t_{1/2}$ being observed in going from $(PhO)_3P$ to Ph_3P to n-Bu_3P (MeI in 40-fold molar excesses). Approximately 20% of L from the starting acylate was accounted for in the carbonyl-containing products $LFe(CO)_4$ and $L_2Fe(CO)_3$. The other observed product, acetophenone, was produced in highest yields (90%) from the $(MeO)_3P$ acylate derivative; lowest yields of ketone (36%) were obtained from reaction of the Ph_3P derivative.

Methyl iodide reacts with pure $Ph_3PFe(CO)_3C(OEt)Ph$ extremely slowly (at 50°, 16 hr is required for complete reaction) yielding the products shown in eq 6. Although

$$Ph_3PFe(CO)_3C(OEt)Ph + MeI \xrightarrow[16\ hr]{THF,\ 50^\circ} Ph_3PMe^+I^- +$$
$$Me\overset{\overset{O}{\|}}{C}Ph + Fe(CO)_4C(OEt)Ph + Fe(CO)_5\ (trace) \qquad (6)$$

acetophenone is observed as one of the reaction products, the very slow rate of reaction indicates no possibility of a carbene complex intermediate in the methyl iodide–iron carbonyl acylate ketone synthesis. The nature of the infrared spectral changes observed as reaction 6 proceeds is shown in Figure 1.

Since it is unlikely that MeI would react with coordinated triphenylphosphine, production of the phosphonium salt in eq 6 implies that the carbene ligand is labilizing Ph_3P. MeI does not react with $Ph_3PFe(CO)_4$ or $(Ph_3P)_2Fe(CO)_3$ under the above conditions; the lability of Ph_3P in the carbene complexes depends on some specific property of the carbene ligand heretofore not expected.[19] Further investigations into the equilibrium given by eq 7 show that 100-

$$Ph_3PFe(CO)_3C(OEt)Ph \rightleftharpoons Ph_3P + [Fe(CO)_3C(OEt)Ph] \qquad (7)$$

fold molar excesses of $(PhO)_3P$ completely convert $Ph_3PFe(CO)_3C(OEt)Ph$ to the phosphite derivative within ~8 hr in THF at 50° (Figure 2). Initial kinetic results[20] show the substitution reaction to be first order in starting carbene complex and insensitive to the concentration or nature of the incoming ligand. The rate of reaction 7 in THF is significantly slower than the rate in heptane ($t_{1/2}$ = 106.4 min in THF and 36.2 min in heptane at 50°).

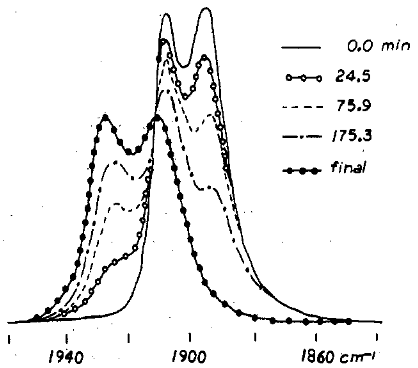

Figure 2. Infrared spectral changes with time for reaction of *trans*-$Ph_3PFe(CO)_3C(OEt)Ph$ with 100-fold molar excesses of $(PhO)_3P$ in THF, 50°: —, $Ph_3PFe(CO)_3C(OEt)Ph$; ●-●, $(PhO)_3PFe(CO)_3C(OEt)Ph$.

Substituted iron carbonyl acylates were also found to undergo ligand exchange (eq 8), however more slowly than

$$L\,Fe(CO)_3C(O)Ph^-Li^+ + L' \rightleftharpoons L'Fe(CO)_3C(O)Ph^-Li^+ + L \qquad (8)$$
$$L = Ph_3P;\ L' = n\text{-}Bu_3P,\ (PhO)_3P$$

their alkoxycarbene counterparts. Plots of ln A (E mode of carbonyl acylate) *vs.* time are linear over at least 4 half-lives (Figure 3). Reaction rates are independent of incoming ligand concentration (L′ in 10- to 50-fold molar excesses) as well as the nature of the incoming ligand. Thus a dissocia-

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(19) M. Y. Darensbourg and D. J. Darensbourg, *Inorg. Chem.*, 9, 32 (1970).

(20) D. J. Darensbourg and H. L. Conder, *Inorg. Chem.*, 13, 374 (1974).

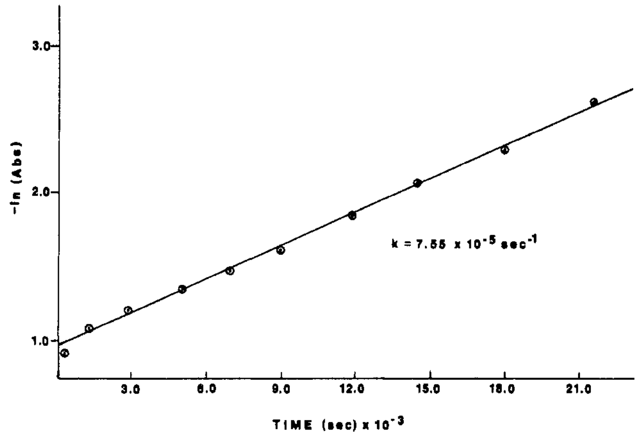

Figure 3. Pseudo-first-order rate plot for reaction of $Ph_3PFe(CO)_3C(O)Ph^-Li^+$ with n-Bu_3P in THF (10- or 50-fold molar excesses) at 70°.

tion process analogous to that found for the ethoxycarbene complexes is suggested.

With longer reaction periods the acyl moiety may also be replaced by L′ (eq 9). Thus a 10-molar excess of n-Bu_3P

$$LFe(CO)_3C(O)Ph^-Li^+ + L' \rightarrow \rightarrow L'_2Fe(CO)_3 + \text{undetermined products} \qquad (9)$$

reacts with $Ph_3PFe(CO)_3C(O)Ph^-Li^+$ in THF to give n-$Bu_3PFe(CO)_3C(O)Ph^-Li^+$ with $t_{1/2} = 3$ hr at 70° and further to give $(n\text{-}Bu_3P)_2Fe(CO)_3$ with $t_{1/2} = 23$ hr. Figure 4 shows the nature of the infrared spectral changes with time for the overall reaction. A 50-molar excess of n-Bu_3P undergoes initial ligand exchange also with $t_{1/2} = 3$ hr and acyl displacement with $t_{1/2} = 19$ hr. The reaction which results in replacement of the acyl moiety by L′ is found to obey no simple rate expression.

The dependence of acyl displacement on both L and L′ was indicated by the following experiments. n-Bu_3P displaces the acyl moiety of n-$Bu_3PFe(CO)_3C(O)Ph^-Li^+$ with $t_{1/2} = 19$ hr. Under identical conditions (50-molar excesses of L, 70°) $Ph_3PFe(CO)_3C(O)Ph^-Li^+$ reacts with Ph_3P to give disubstituted product extremely slowly; less than 10% reaction occurs within 19 hr. $(PhO)_3P$ (10-molar excess) reacts with $Ph_3PFe(CO)_3C(O)Ph^-Li^+$ at 65° to yield $Ph_3PFe(CO)_3P(OPh)_3$ exclusively and quantitatively within 12 hr. At 50°, 20 hr is required to bring the reaction to completion with a product distribution of 80% (based on parent acylate) $Ph_3PFe(CO)_3P(OPh)_3$ and 20% $(PhO)_3PFe(CO)_3C(O)Ph^-Li^+$. At 26° the initial ligand exchange dominates acyl displacement and within 24 hr the final product distribution of 70% $(PhO)_3PFe(CO)_3C(O)Ph^-Li^+$ and 30% $Ph_3PFe(CO)_3P(OPh)_3$ is attained. *No* $[(PhO)_3P]_2Fe(CO)_3$ *is ever observed although excess* $(PhO)_3P$ *is present.* This latter observation indicates acyl displacement or reactivity is totally suppressed by the presence of trans phosphite ligand, thus establishing the dependence of acyl activity on L in the parent acylate, n-$Bu_3P > Ph_3P > (PhO)_3P$.

The greater temperature dependence of the $(PhO)_3P$-acyl displacement over the $(PhO)_3$-Ph_3P exchange indicates a higher activation energy for the acyl displacement process. Since the ligand-ligand exchange itself is a high-energy bond-breaking process,[20] one might assume the acyl displacement also to involve bond breaking, possibly *via* prior formation of an L′-acyl adduct.[21,22] Subsequent dissociation yields $[LFe(CO)_3]$ which in the presence of excess L′ leads to $LFe(CO)_3L'$. The data show the proposed L′-acylate adduct to be most easily formed when the incoming ligand (L′) is the least nucleophilic, $(PhO)_3P$.

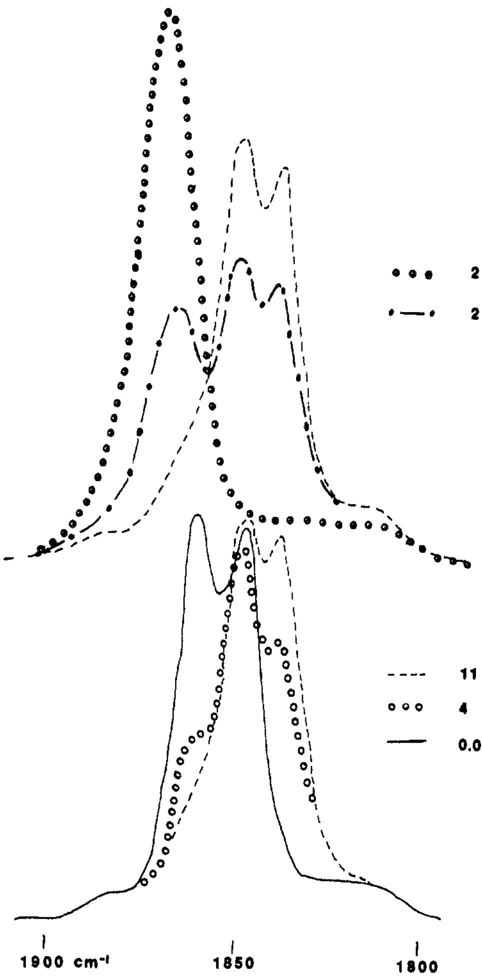

Figure 4. Infrared spectral changes with time for the reaction of *trans*-$Ph_3PFe(CO)_3C(O)Ph^-Li^+$ with n-Bu_3P in THF at 70°: —, $Ph_3PFe(CO)_3C(O)Ph^-Li^+$; - - -, n-$Bu_3PFe(CO)_3C(O)Ph^-Li^+$; o o o, *trans*-$(n\text{-}Bu_3P)_2Fe(CO)_3$.

In 1967, Schollkopf and Gerhart reported attempts to stabilize diethylcarbamoyllithium ($Li^+C(O)NEt_2^-$) by complexation with a heavy metal.[23] Thus the preparation of mercury-bound diethylcarbamoyllithium (or, diethylaminolithiooxycarbene) from reaction of n-BuLi and bis(diethylcarbamoyl)mercury was reported. This "complex" as well as acylberyllium halides (RC(O)BeX) exhibit the expected reactions of acyl anions.[11,12]

The reactions reported here certainly indicate the acyllithium moiety is similar in reactivity properties to alkoxycarbene ligands, *viz.*, trans-ligand labilizing ability and reaction with "soft" alkylating agent (MeI) to yield ketones, and may approximately be termed as a lithiooxycarbene complex.[24] On the other hand definitive experiments illustrating the necessity of alkylation at iron prior to alkyl addition to acyl carbon did not result from this work and to our knowledge have not been performed.

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(21) Adducts of tertiary or secondary alkylphosphines and alkoxycarbenepentacarbonyl complexes of chromium(0) and tungsten(0) have been isolated at low temperatures.[22] Such adducts are formulated as ylide derivatives, $(CO)_5M[C(PR_3)(OMe)R']$, and undergo thermal isomerization to $(CO)_5M[PR_2(C(R)(OMe)R')]$.

(22) F. R. Kreissl, E. O. Fischer, C. G. Kreiter, and H. Fischer, *Chem. Ber.*, 106, 1262 (1973).

(23) U. Schollkopf and F. Gerhart, *Angew. Chem., Int. Ed. Engl.*, 6, 805, 970 (1967).

Acknowledgments. The authors are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for a postdoctoral fellowship to H. L. C. and for support of this research. We are also appreciative to the Research Corp. for a Cottrell Research Grant to D. J. Darensbourg and M. Y. D. for the purchase of a Perkin-Elmer 521 infrared spectrophotometer. We wish to acknowledge the helpful suggestions of D. J. Darensbourg and E. J. Panek of Tulane University.

Registry No. *trans*-$Ph_3PFe(CO)_3C(OLi)Ph$, 49655-04-1; *trans*-$(n\text{-}Bu)_3PFe(CO)_3C(OLi)Ph$, 49655-05-2; *trans*-$(PhO)_3PFe(CO)_3C(OLi)Ph$, 49655-06-3; *trans*-$Fe(CO)_4C(OLi)Ph$, 49655-07-4; *trans*-$Ph_3PFe(CO)_3C(OLi)Me$, 49655-08-5; *trans*-$(n\text{-}Bu)_3PFe(CO)_3C(OLi)Me$, 49655-09-6; *trans*-$Ph_3PFe(CO)_3C(OEt)Ph$, 42947-52-4; *trans*-$Ph_3PFe(CO)_3C(OEt)Me$, 42947-54-6; *trans*-$Ph_3PFe(CO)_3C(OMe)Ph$, 49634-48-2; *trans*-$(n\text{-}Bu)_3PFe(CO)_3C(OEt)Ph$, 49634-49-3; *trans*-$(n\text{-}Bu)_3PFe(CO)_3C(OEt)Me$, 42947-57-9; *trans*-$(PhO)_3PFe(CO)_3C(OEt)Ph$, 42947-53-5; *trans*-$(PhO)_3PFe(CO)_3C(OEt)Me$, 42947-55-7; *trans*-$Fe(CO)_4C(OEt)Ph$, 49634-53-9; *trans*-$Ph_3PFe(CO)_4$, 49655-10-9; *trans*-$(Ph_3P)_2Fe(CO)_3$, 49655-11-0; *trans*-$Ph_3PFe(CO)_3P(OPh)_3$, 49655-12-1; *trans*-$(n\text{-}Bu)_3PFe(CO)_4$, 49655-13-2; *trans*-$[(n\text{-}Bu)_3P]_2Fe(CO)_3$, 49655-14-3; *trans*-$(PhO)_3PFe(CO)_4$, 49655-15-4; *trans*-$[(PhO)_3P]_2Fe(CO)_3$, 49655-16-5; *trans*-$Fe(CO)_5$, 13463-40-6; $MeOSO_2F$, 421-20-5; $Et_3O^+BF_4^-$, 368-39-8; MeI, 74-88-4; $THFMe^+SO_3F^-$, 49655-17-6; $(n\text{-}Bu)_3P$, 998-40-3; $(PhO)_3P$, 101-02-0; *trans*-$(PhO)_3PFe(CO)_3C(OLi)Me$, 49655-18-7; Ph_3P, 603-35-0.

[24] We would suggest that the most negative site in the acylate complex is the acyl oxygen which is ion paired with, in our studies, Li^+. Such ion pairing has been invoked to explain HMPA (hexamethylphosphoramide) inhibition of the cation-assisted alkyl to carbonyl migration reaction of the $RFe(CO)_4^-$ conversion to $LFe(CO)_3\text{-}C(O)R^-$.[9] Only the very strong alkylating agents Et_3O^+ and $THF\text{-}Me^+$ are capable of displacing the Li^+, forming the carbene complexes. Softer or weaker alkylating agents, MeI or $MeOSO_2F$, react at the next most negative site, either the iron, the acyl carbon, or most likely the iron-acyl carbon-acyl oxygen electron sink, centering at acyl carbon.

Contribution from the Department of Chemistry,
University of Alberta, Edmonton, Alberta, Canada

Silicon-Transition Metal Chemistry. VII.[1]
Metal Carbonyl Derivatives of 1,2-Bis(dimethylsilyl)ethane

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The reaction of 1,2-bis(dimethylsilyl)ethane with $Fe(CO)_5$, $Ru_3(CO)_{12}$, or $Os_3(CO)_{12}$ affords the chelate compounds $(OC)_4\text{-}\overline{MSiMe_2CH_2CH_2Si}Me_2$ [M = Fe (I), Ru (II), and Os (III)]. The product with $Co_2(CO)_8$ is $(OC)_4CoSiMe_2CH_2CH_2Me_2SiCo(CO)_4$, IV. Carbonyl stretching frequencies and proton and carbon-13 magnetic resonance spectra are reported.

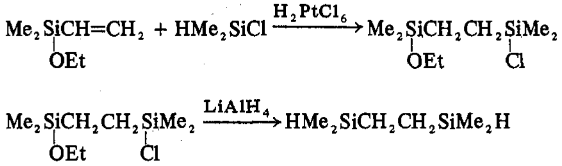
Introduction

Recent reports from this laboratory have described the remarkable stereospecific carbon monoxide exchange that takes place in *cis*-$Ru(CO)_4(SiCl_3)_2$ [2a] and the nonrigid character of $Os(CO)_4(SiMe_3)_2$,[2b,3] for which cis and trans isomers interconvert rapidly in a nondissociative process. To further our understanding of such systems, it was of interest to prepare analogs in which the silyl groups were linked so that they would be constrained to cis positions. In such chelated derivatives, for example, the possibility of interchange of axial and equatorial carbonyls without passing through a trans-octahedral form could be investigated.

The reaction of silicon-hydrogen bonds with metal carbonyls has proven to be of great utility,[4] and it was accordingly decided to utilize the silane $HMe_2SiCH_2CH_2SiMe_2H$ as a starting material. This paper describes a convenient synthesis of this useful ligand and its reactions with $Fe(CO)_5$, $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, and $Co_2(CO)_8$.

Results and Discussion

The silane starting material has been prepared in an overall yield of 56% from commercially available organosilicon compounds using the sequence of reactions

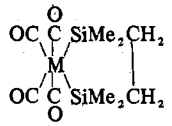


$$\underset{\text{OEt}}{\text{Me}_2\text{Si}}\text{CH=CH}_2 + \text{HMe}_2\text{SiCl} \xrightarrow{\text{H}_2\text{PtCl}_6} \underset{\text{OEt}}{\text{Me}_2\text{Si}}\text{CH}_2\text{CH}_2\underset{\text{Cl}}{\text{SiMe}_2}$$

$$\underset{\text{OEt}}{\text{Me}_2\text{Si}}\text{CH}_2\text{CH}_2\underset{\text{Cl}}{\text{SiMe}_2} \xrightarrow{\text{LiAlH}_4} \text{HMe}_2\text{SiCH}_2\text{CH}_2\text{SiMe}_2\text{H}$$

The intermediate in this preparation, 1-(dimethylethoxysilyl)-2-(dimethylchlorosilyl)ethane, was not isolated, but was reduced directly with $LiAlH_4$ to yield 1,2-bis(dimethylsilyl)ethane. This silane has been prepared before by the $LiAlH_4$ reduction[5] of the somewhat less readily available 1,2-bis(dimethylchlorosilyl)ethane.[6]

In general, the silane reacted either with heat or with ultraviolet irradiation with carbonyls of the iron group to produce the anticipated chelate complexes I-III. These have been fully characterized by analysis, mass spectrometry, and in-



I, M = Fe
II, M = Ru
III, M = Os

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[1] Part VI: A. J. Hart-Davis and W. A. G. Graham, *J. Amer. Chem. Soc.*, 93, 4388 (1971).

[2] (a) R. K. Pomeroy, R. S. Gay, G. O. Evans, and W. A. G. Graham, *J. Amer. Chem. Soc.*, 94, 272 (1972); (b) R. K. Pomeroy and W. A. G. Graham, *ibid.*, 94, 274 (1972).

[3] Throughout this paper, the methyl group is abbreviated as Me, and the ethyl group as Et.

[4] C. S. Cundy, B. M. Kingston, and M. F. Lappert, *Advan. Organometal. Chem.*, 11, 253 (1973).

[5] V. F. Mironov, V. P. Kozyukov, and V. D. Sheludyakov, *Dokl. Akad. Nauk SSSR*, 179, 600 (1968); *Dokl. Chem.*, 179, 261 (1968).

[6] W. A. Piccoli, G. G. Haberland, and R. L. Merker, *J. Amer. Chem. Soc.*, 82, 1883 (1960); M. Ishikawa, M. Kumada, and H. Sakurai, *J. Organometal. Chem.*, 23, 63 (1970); H. Sakurai, K. Tominaga, T. Watanabe, and M. Kumada, *Tetrahedron Lett.*, 5493 (1966).