Formation of Acyliron Complexes CpFe(CO){P(OR')$_3$}COR' by Reaction of Silyliron Complexes CpFe(CO)$_2$SiR$_3$ with Alkylphosphites P(OR')$_3$

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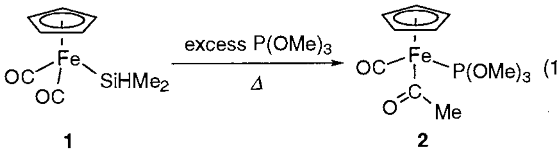
(Received November 2, 1998; CL-980835)

Heating a toluene solution of CpFe(CO)$_2$SiR$_3$ (R$_3$ = HMe$_2$, HEt$_2$, and FMe$_2$) and excess P(OR')$_3$ (R' = Me, Et, and Me-d_3) at 80 °C resulted in the formation of an acyliron complex CpFe(CO){P(OR')$_3$}COR' in 25 - 40% yield: Hence the alkyl group of phosphite is transferred to the carbon of a carbonyl ligand to give an acyl ligand during the reaction.

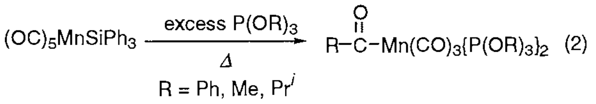
A number of transition-metal complexes containing both silyl and phosphite ligands have been synthesized by thermal or photochemical ligand exchange reactions of silyl(carbonyl) complexes with phosphites.[1] Silyliron complexes containing alkylphosphite ligands CpFe(CO)$_{2-n}${P(OR)$_3$}$_n$SiR$_3$ (n = 1, 2) have been prepared by photolysis of FpSiR$_3$ (Fp = CpFe(CO)$_2$) in the presence of alkylphosphites.[2] However, we found that the photochemical method cannot be applied for (hydrodimethylsilyl)iron complex FpSiHMe$_2$ (**1**). Photolysis of **1**[3] in the presence of alkylphosphite P(OR)$_3$ afforded a complex mixture of unidentified products. Thus, we attempted thermal ligand exchange reaction between FpSiHMe$_2$ (**1**) and P(OMe)$_3$. Surprisingly, this reaction did not give any phosphite-substituted silyliron complex, but, instead, gave the known acetyliron complex CpFe(CO){P(OMe)$_3$}COMe (**2**)[4] in moderate yield (eq 1).



(1)

1 **2**

In this paper, we report the reactions of silyliron complexes FpSiR$_3$ with alkylphosphites. So far only one reaction similar to eq 1 has been reported, in which an acylmanganese complex was formed by the reaction of a silylmanganese complex with a phosphite (eq 2).[5]



$$(OC)_5MnSiPh_3 \xrightarrow[\Delta]{\text{excess } P(OR)_3} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}Mn(CO)_3\{P(OR)_3\}_2 \quad (2)$$

R = Ph, Me, Pr^i

Ross and Dobson proposed that the reaction proceeds via an Arbuzov-type rearrangement.[6]

Reaction of FpSiHMe$_2$ (**1**) with a 10-fold excess of P(OMe)$_3$ was carried out at 80 °C in C$_6$D$_6$ and monitored by ^{1}H NMR spectroscopy. The signals of silyliron complex **1** gradually disappeared and new signals assignable to Cp and the acetyl group of **2** appeared at δ 4.35 and 2.73 ppm, respectively. The signals of **1** completely disappeared after 12 h. A large scale reaction was carried out at 80 °C in toluene for 12 h. Chromatographic purification afforded yellow crystals of **2** in 34% yield (eq 1).

When the reaction of **1** with P(OMe)$_3$ was carried out at lower temperature (50 - 60 °C) and monitored by ^{1}H and ^{13}C NMR spectroscopy, the formation of FpMe[7] was observed at the early stage of the reaction which gradually decreased with increase of **2**. It has been well known that alkyliron complexes containing carbonyl ligands are easily converted to the corresponding acyliron complexes by migratory insertion of the coordinated CO ligands in the presence of 2 electron donors.[8] Indeed, methyliron complex FpMe in C$_6$D$_6$ was converted quantitatively into acetyliron complex **2** in the presence of excess P(OMe)$_3$ at 80 °C for 10 h. Therefore, the acetyliron complex **2** is most likely formed by two consecutive processes, i.e., (1) formation of FpMe by the reaction of FpSiHMe$_2$ with trimethylphosphite and (2) conversion of FpMe into **2**.

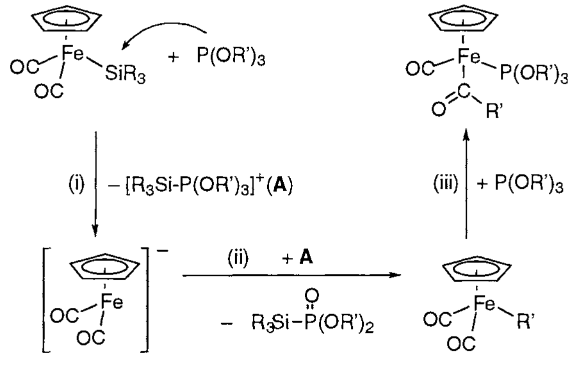
To determine the origin of the methyl group in the acetyl ligand in **2**, reactions between **1** and labeled phosphites were performed. When a toluene solution of **1** and a 10-fold excess of P(OMe-d_3)$_3$ or P(OEt)$_3$ was heated at 80 °C for 12 h, CpFe(CO){P(OMe-d_3)$_3$}COMe-d_3 (**2**-d_{12}) or CpFe(CO)-{P(OEt)$_3$}COEt (**3**)[4] was obtained in 29 or 40% yield, respectively (eq 3).

$$\underset{\mathbf{1}}{FpSiHMe_2} \xrightarrow[\substack{\text{excess } P(OR)_3 \\ R = Me\text{-}d_3,\ Et}]{\Delta} \underset{\substack{R = Me\text{-}d_3\ (\mathbf{2}\text{-}d_{12}) \\ R = Et\ (\mathbf{3})}}{CpFe(CO)\{P(OR)_3\}COR} \quad (3)$$

Similarly, the reaction of FpSiHEt$_2$ (**4**)[9] or FpSiFMe$_2$ (**5**)[10] with excess P(OMe)$_3$ in toluene under reflux or at 80 °C afforded **2** in 25 or 33% yield, respectively. These results clearly show that the alkyl group in the phosphites was transferred to the carbon of a carbonyl ligand to form an acyl ligand.

Interestingly, trimethylsilyliron complex FpSiMe$_3$[2a] does not react with P(OMe)$_3$ at all even after heating at 80 °C in C$_6$D$_6$ for 3 days. This suggests that the steric crowding around the silicon atom prevents the formation of acyliron complex and nucleophilic attack of phosphite on the silicon atom is an important step for the acyliron formation.

Scheme 1 shows a possible mechanism for the reaction of silyliron complexes with alkylphosphites to form acyliron complexes:[11] (i) Nucleophilic attack of phosphite on the silicon atom which results in heterolytic cleavage of the Fe-Si bond to give Fp$^-$ and a silylphosphonium ion [R$_3$Si-P(OR')$_3$]$^+$ (**A**),[13] (ii) nucleophilic attack of the Fp$^-$ fragment on the α-carbon of the OR' group of **A** to generate an alkyliron complex FpR', and (iii) reaction of FpR' with alkylphosphite which causes migratory insertion of a CO ligand into the Fe-R' bond to form a phosphite-substituted acyliron complex. Since the metal-silicon bond in FpSiR$_3$ is polarized as M$^{\delta-}$-Si$^{\delta+}$,[1,14] the occurrence of step (i) shown in Scheme 1 is understandable. This corresponds to Arbuzov-type reaction.[6] However, an alternative mechanism is also conceivable: An oxygen atom, not a phosphorus atom, in P(OR')$_3$ attacks the silicon atom to form Fp$^-$ and an oxonium ion [(R'O)$_2$P-O(R')-SiR$_3$]$^+$ (**B**) which is a structural isomer of **A**. If this is the case, an Arbuzov-type reaction is not involved in the mechanism. At present moment, we have no experimental data to distinguish between the intermediates **A** and **B**. For conversion of Fp$^-$ to FpR' (step (ii)), the alkyl group R' can be transferred not only from **A** but also from $P(OR')_3$ because we found that the reaction of NaFp with $P(OMe)_3$ at room temperature afforded FpMe in 23% yield.



Scheme 1.

The generation of the Fp^- as an intermediate is also supported by the fact that the yield of **2** dramatically increased (88%) when the reaction of **1** with $P(OMe)_3$ was carried out in the presence of excess MeI. In this case, the generated Fp^- is considered to be efficiently trapped to give FpMe which is then converted to the final product **2**.

According to the mechanism proposed in Scheme 1, the silylphosphonate $R_3Si\text{-}P(O)(OR')_2$ or silylphosphonium ion **A** must be formed in addition to the acyliron complex. The ^{29}Si NMR spectrum of the reaction mixture showed several peaks over the range of 0 to -20 ppm. This result indicates that several silyl compounds were produced. However we could not isolate and characterize these products.

References and Note

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9 $FpSiHEt_2$ (**4**) was prepared as follows: A solution of NaFp (2.00×10^{-3} mol) in THF (80 cm^3) was slowly added to a THF solution (80 cm^3) of Et_2SiHCl (2.12 g, 1.73×10^{-2} mol) with vigorous stirring at room temperature. After stirring for 5 h, volatiles were removed under reduced pressure. The red-brown residue was extracted with three 30 cm^3 portions of diethyl ether. The extracts were combined, filtered through a Celite pad, and concentrated under vacuum. Molecular distillation of the resulting dark-red oil (90 - 115 °C, 0.50 torr) gave an orange oil of **4**. Yield 2.41 g (57%). ^1H NMR (300 MHz, C_6D_6) δ 0.95-1.03 (m, 4H, $SiCH_2$), 1.17-1.22 (m, 6H, CH_3), 4.04 (s, 5H, Cp), 4.69 (quintet, $^3J_{HH} = 3.0$ Hz, 1H, SiH). ^{29}Si NMR (59.6 MHz, C_6D_6) δ 37.4. ^{13}C NMR (75.5 MHz, C_6D_6) δ 10.8 ($SiCH_2$), 11.2 (CH_3), 83.2 (Cp), 215.3 (CO). IR (C_6D_6 solution) 2054 (m, ν_{SiH}), 1992, 1938 (s, ν_{CO}) cm^{-1}. Mass (EI, 70 eV): *m/z* 264 (M^+, 5.3), 263 (M^+-H, 10), 236 (M^+-CO, 81), 206 (M^+-CO-Et, 92), 178 ($CpFeSiEt^+$, 100). Anal. Found: C, 49.71; H, 6.02%. Calcd for $C_{11}H_{16}FeO_2Si$: C, 50.01; H, 6.10%.

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11 A radical mechanism may not be operative in our particular reactions by the following reasons. Addition of a radical source AIBN (2,2'-azobisisobutyronitrile) or a radical scavenger duroquinone did not affect the reaction of silyliron complexes with phosphites. Baird et al. recently reported that the reaction of an iron-centered radical $\{(\eta\text{-}C_5Ph_5)Fe(CO)_2\}^\bullet$ with trialkylphosphite $P(OR)_3$ (R = Me and Et) in benzene resulted in the formation of $(\eta\text{-}C_5Ph_5)Fe(CO)_2R$, $(\eta\text{-}C_5Ph_5)Fe(CO)_2\{P(O)(OR)_2\}$, and $(\eta\text{-}C_5Ph_5)Fe(CO)\{P(OR)_3\}\{P(O)(OR)_2\}$.[12] This means that the reaction via radical mechanism gives iron complexes containing phosphonate ligands. In our system, we could not observe the corresponding phosphonate iron complexes at all.

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