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ALKYLATION OF ORGANOIRON THIOLATE COMPLEXES

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Summary

The iron thiolate complexes $Fe(SPh)(CO)(L)(\eta\text{-}C_5H_5)$ ($L = PMe_3$, PPh_2Me, PPh_3, PPh_2OMe, $PPh(OMe)_2$, $P(OMe)_3$, $P(OPh)_3$) react with EtBr in $CHCl_3$ (21°C) to produce the cationic sulfide complexes, $[Fe(PhSEt)(CO)(L)(\eta\text{-}C_5H_5)]Br$. A study of the kinetics of these reactions shows that these reactions are first order in complex and in EtBr; however the rates are largely insensitive to the nature of L in the precursor. After prolonged periods of time, or upon heating, a further reaction ensues in which bromide ion displaces the sulfide ligand to yield $FeBr(CO)(L)(\eta\text{-}C_5H_5)$. Reactions between $Fe(SPh)(CO)_2(\eta\text{-}C_5H_5)$ and EtBr, and between $Fe(SPh)(CO)(PMe_3)(\eta\text{-}C_5Me_5)$ and EtBr, give $FeBr(CO)_2(\eta\text{-}C_5H_5)$ and $FeBr(CO)(PMe_3)(\eta\text{-}C_5Me_5)$ directly. These reactions presumably also occur via facile ligand loss from the intermediate sulfide complexes.

Broad research interests concerning reactions at coordinated ligands recently led our group to prepare a variety of iron thiolate complexes having formulae $Fe(SPh)(CO)_2(\eta\text{-}C_5H_5)$, $Fe(SPh)(CO)(L)(\eta\text{-}C_5H_5)$ and $Fe(SPh)(L)_2(\eta\text{-}C_5H_5)$ (L = various phosphorus(III) ligands and organic isocyanides). We have described studies on one-electron oxidations of these species which produce either paramagnetic iron(III) complexes [1,2] or diamagnetic iron(II) complexes having a bridging disulfide ligand [3]. These latter complexes are formed by coupling of two mononuclear species via a sulfur–sulfur bond.

Another project reported from this group involved a study of the acidity of $[Fe(PhSH)(CO)_2(\eta\text{-}C_5H_5)]BF_4$ [4].

In the organometallic area the alkylation of sulfur in the coordinated thiolate ligand has received little attention. We felt that such a study involving $Fe(SPh)(CO)(L)(\eta\text{-}C_5H_5)$ complexes might complement and extend our work in the area of organometallic thiolate chemistry. Specifically, we hoped to obtain information concerning the effect of different ligands on the rates of such reactions, assuming that the relative donor or acceptor capacity of L would influence the nucleophilicity of the sulfur atoms. This paper reports our study in this area.

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Experimental

The following starting materials were prepared by published procedures: $Fe(SPh)(CO)_2(\eta\text{-}C_5H_5)$ [5], $Fe(SPh)(CO)(L)(\eta\text{-}C_5H_5)$ ($L = PPh_3$, PPh_2Me, PMe_3, $P(OPh)_3$) [3], $Fe(SPh)(CO)(PMe_3)(\eta\text{-}C_5Me_5)$ [3]. The syntheses of several additional $Fe(SPh)(CO)(L)(\eta\text{-}C_5H_5)$ compounds by an analogous method is briefly described below. Solvents and other reagents were used as obtained. Petroleum ether refers to the commercial solvent Skelly B, a hydrocarbon mixture (b.p. 60–70°C) containing mostly hexanes.

The ^1H NMR spectral data were obtained on $CDCl_3$ solutions of these compounds using an IBM WP-200 spectrometer. Infrared spectra in $CHCl_3$ were recorded on a Beckman 4230 spectrophotometer and were calibrated against the 1944.5 cm^{-1} absorption of polystyrene. Mass spectra were obtained using an AEI-MS-902 mass spectrometer. Peak match data were sometimes used in place of elemental analyses; when so, purity was verified by a combination of IR and NMR data. Melting points were determined in sealed tubes. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

All manipulations were carried out under nitrogen as a precautionary measure. However, neither products nor reactants were noticeably sensitive to oxygen over a several hour time period.

Kinetic measurements

An ~ 0.1 mmol sample of $Fe(SPh)(CO)(L)(\eta\text{-}C_5H_5)$ ($L = PMe_3$, PPh_2Me, PPh_3, PPh_2OMe, $PPh(OMe)_2$, $P(OPh)_3$, $P(OMe)_3$) was dissolved in $CHCl_3$ in a 1.00 ml volumetric flask. Bromoethane (0.15 ± 0.01 ml) was added to the flask followed by more $CHCl_3$ to give 1.00 ml of solution. This produced a solution with concentrations of complex and bromoethane of ~ 0.1 and 2.0 ± 0.1 M respectively at $t = 0$, bromoethane being chosen in large excess to assure pseudo first-order conditions. The solutions were thermostated at 21 ± 1°C. Periodically, samples of the reaction mixture were removed from the reaction vessel using a syringe, placed in an infrared cell, and the absorption in the $\nu(CO)$ region recorded. These manipulations took about one minute with the sample in the spectrometer less than half of this time. Since the reaction temperature was very close to ambient temperature, and since the half lives of these reactions were generally on the order of several hours, we believe that this handling did not perturb the accuracy to a measurable extent. Concentrations of reactant and product in solution were determined from measurements of $\nu(CO)$ intensities; standard solutions of both product and reactant were used to establish the (Beer's Law) relationship of absorption and concentration. Data were collected over a period of several hours (~ 1 to 4 half lives). At longer times, problems were encountered because of a slow secondary reaction in which bromide ion displaces the sulfide (vide infra).

Analysis of the concentration-time data by standard methods showed a first order dependence on the metal complex. Pseudo-first order rate constants as a function of ligand identity are listed in Table 1 ([EtBr] = constant). These values are the average of results from at least three independent experiments and are believed accurate to $\pm 0.1 \times 10^{-4}$ sec^{-1}; since [EtBr] is held constant in these experiments these numbers are comparable.

Another series of experiments was performed using the complex Fe(SPh)-

TABLE 1

PSEUDO-FIRST ORDER RATE CONSTANTS FOR THE REACTION AT 21±1°C[a]

$Fe(SPh)(CO)(L)(\eta\text{-}C_5H_5)$ + excess EtBr → $[Fe(PhSEt)(CO)(L)(\eta\text{-}C_5H_5)]Br$

L	k' (×10^4) sec^{-1} [b]
PMe_3	1.8
PPh_2Me	1.5
PPh_3	1.6
PPh_2OMe	1.4
$PPh(OMe)_2$	5.2
$P(OMe)_3$	1.7
$P(OPh)_3$	1.0

[a] Reaction in $CHCl_3$, [EtBr] = 2.0±0.1 *M*. [b] Values are an average from three or more determinations, and are believed accurate to ±0.1×10^{-4}.

$(CO)[PPh(OMe)_2](\eta\text{-}C_5H_5)$ in which initial concentrations of bromoethane were chosen to be 1.00 ± 0.05 *M* and 0.50 ± 0.05 *M*. Initial rates of these reactions were calculated to be -1.9×10^{-5} mol $l^{-1}s^{-1}$ and -9.7×10^{-6} mol $l^{-1}sec^{-1}$, respectively. For the solution with [EtBr] = 2.0 ± 0.1 *M* the initial rate of reaction was 4.2×10^{-5} mol $l^{-1}sec^{-1}$. These data establish that this reaction is also first order in bromoethane.

Synthesis of other $Fe(SPh)(CO)(L)(\eta\text{-}C_5H_5)$ complexes

$Fe(SPh)(CO)(PPh_2OMe)(\eta\text{-}C_5H_5)$. Samples of $Fe(SPh)(CO)_2(\eta\text{-}C_5H_5)$ (3.0 g, 10.5 mmol) and PPh_2OMe (3.0 ml, 15 mmol) were dissolved in 50 ml toluene and heated (at reflux) for 3 h. The solution was then allowed to cool; filtration followed by evaporation of solvent under reduced pressure gave a red oil. This was dissolved in CH_2Cl_2; addition of petroleum ether followed by chilling at −20°C furnished red crystals of the product (2.0 g, 40% yield); m.p. 82–85°C.

Anal. by MS peak match: $^{12}C_{25}{}^{1}H_{23}{}^{56}Fe^{16}O_2{}^{31}P^{32}S$ calcd. 474.0500; found, 474.0508. IR: ν(CO) 1948 cm^{-1}. ^1H NMR: δ 3.50d ($J(POCH_3)$ 13 Hz) OCH_3; 4.54s, C_5H_5; 6.9–7.8m, δ SC_6H_5 and PC_6H_5.

$Fe(SPh)(CO)\{PPh(OMe)_2\}(\eta\text{-}C_5H_5)$. The same procedure was followed, except the product was recrystallized from toluene/petroleum ether; (93%), m.p. 111–114°C.

Anal. by MS peak match: $^{12}C_{20}{}^{1}H_{21}{}^{56}Fe^{16}O^{31}P^{32}S$: calcd. 428.0293; found, 428.0299. IR: ν(CO) 1958 cm^{-1}. ^1H NMR: δ 3.65d and 3.66d ($J(POCH_3)$ 12 Hz), diastereotopic $POCH_3$; 4.47d (J(PH) 1 Hz) C_5H_5, 6.8–7.9m δ SC_6H_5 and PC_6H_5.

$Fe(SPh)(CO)\{P(OMe)_3\}(\eta\text{-}C_5H_5)$. This compound was prepared in the same manner and recrystallized from petroleum ether (63%); m.p. 54–58°C.

Anal. by MS peak match: $^{12}C_{15}{}^{1}H_{19}{}^{56}Fe^{16}O_4{}^{31}P^{32}S$ calcd. 382.0086; found, 382.0092. IR: ν(CO) 1963 cm^{-1}; ^1H NMR: δ 3.65d ($J(POCH_3)$ 12 Hz), $POCH_3$; 4.68s, C_5H_5; 6.8–7.1 m, *meta* and *para* δ C_6H_5, and 7.5–7.7m δ $o\text{-}C_6H_5$.

Syntheses of $[Fe(PhSEt)(CO)(L)(\eta\text{-}C_5H_5)]Br$ complexes

$[Fe(PhSEt)(CO)(PPh_2Me)(\eta\text{-}C_5H_5)]Br$. A solution of $Fe(SPh)(CO)(PPh_2Me)(\eta\text{-}C_5H_5)$ (1.0 g, 2.2 mmol) and bromoethane (3 ml, ~ 16 mmol) in 25 ml of

$CHCl_3$ was stirred for 4 h at ambient temperature. The solution was filtered; addition of ethyl ether to the filtrate caused precipitation of the red crystalline product (0.82 g, 66%), m.p. 109–111°C.

Anal. Found: C, 56.92; H, 5.03. $C_{27}H_{28}BrFeOPS$ calcd.: C, 57.14; H, 4.94%. IR: $\nu(CO)$ 1975 cm^{-1}. ^1H NMR: δ 0.96t (J 7 Hz) CH_2CH_3; 2.22d (J(PH) 9 Hz) PCH_3; 2.94m, 3.17m, diastereotopic CH_2CH_3; 4.95d (J(PH) 1 Hz) C_5H_5; 7.3–7.6m, SC_6H_5 and PC_6H_5.

The following compounds were prepared similarly.

[Fe(PhSEt)(CO)(PPh₃)(η-C₅H₅)]Br. Orange-red powder (56%), m.p. 112–114°C. Anal. Found: C, 60.69; H, 4.93. $C_{32}H_{30}BrFeOPS$ calcd.: C, 61.05; H, 4.77%. IR: $\nu(CO)$ 1975 cm^{-1}. ^1H NMR: δ 1.00t (J 6 Hz) CH_2CH_3; 3.10m, 3.54m, diastereotopic CH_2CH_3; 4.97s C_5H_5; 7.1–7.8m SC_6H_5 and PC_6H_5.

[Fe(PhSEt)(CO)(PPh₂OMe)(η-C₅H₅)]Br. Red powder (70%); m.p. 116–118°C. Anal. Found: C, 55.70; H, 5.04. $C_{27}H_{28}BrFeO_2PS$ calcd.: C, 55.57; H, 4.80%. IR: $\nu(CO)$ 1986 cm^{-1}. ^1H NMR: δ 1.06t (J 7 Hz) CH_2CH_3; 2.85m CH_2CH_3; 3.47d (J(PH) 12 Hz) $POCH_3$; 4.89s, C_5H_5, 7.3–7.8m, SC_6H_5 and PC_6H_5.

[Fe(PhSEt)(CO){PPh(OMe)₂}(η-C₅H₅)]Br. Red crystals (41%); m.p. 102–104°C. Anal. Found: C, 49.16; H, 4.84, $C_{22}H_{26}BrFeO_3PS$ calcd.: C, 49.16; H, 4.84%. IR: $\nu(CO)$ 1986 cm^{-1}. ^1H NMR: δ 1.10t (J 8 Hz) CH_2CH_3; 3.05 m, 3.14 m, diastereotopic CH_2CH_3; 3.68 d, 3.84 d (J(PH) 12 Hz) diastereotopic $P(OCH_3)_2$; 4.82 d (J(PH) 1 Hz) C_5H_5; 7.3–7.5 m SC_6H_5 and PC_6H_5.

[Fe(PhSEt)(CO){P(OMe)₃}(η-C₅H₅)]Br. Red powder (18%); m.p. 83–84°C. Anal. Found: C, 41.72, H, 5.17. $C_{17}H_{24}BrFeO_4PS$ calcd.: C, 41.55; H, 4.89%. IR: $\nu(CO)$ 1990 cm^{-1}. ^1H NMR: δ 1.18t (J 7 Hz) CH_2CH_3; 3.15m, 3.25m, diastereotopic CH_2CH_3; 3.80d (J(PH) 11 Hz) $POCH_3$; 5.00d (J(PH) 1 Hz) C_5H_5; 7.35–7.65m, SC_6H_5.

[Fe(PhSEt)(CO){P(OPh)₃}(η-C₅H₅)]Br. Orange-red platelets (52%); m.p. 87–88°C. Anal. Found: C, 56.96; H, 4.66. $C_{32}H_{30}BrFeO_4PS$ calcd: C, 56.72; H, 4.43%. IR: $\nu(CO)$ 2000 cm^{-1}. ^1H NMR: δ 1.22t ($J = 7$ Hz) CH_2CH_3; 3.18m, 3.70m, diastereotopic CH_2CH_3; 4.82s C_5H_5, 7.1–7.9m SC_6H_5 and POC_6H_5.

A modification of this procedure was used to make $[Fe(PhSEt)(CO)(PMe_3)(\eta\text{-}C_5H_5)]Br$. The subsequent reaction of this complex in $CHCl_3$ to form $FeBr(CO)(PMe_3)(\eta\text{-}C_5H_5)$ was fairly rapid and this led to problems in yield and purity of the desired product. When toluene was used as solvent for this reaction the product precipitated and the subsequent reaction was avoided.

[Fe(PhSEt)(CO)(PMe₃)(η-C₅H₅)]Br. A sample of $Fe(SPh)(CO)(PMe_3)(\eta\text{-}C_5H_5)$ (0.50 g, 1.5 mmol) was dissolved in 25 ml of toluene. Bromoethane (3 ml, ~ 40 mmol) was added and the resulting solution was stirred at ambient temperature for 36 h, during this time the insoluble product precipitated. This solid was separated by filtration, washed with ethyl ether, and dried in vacuo (0.45 g, 68% yield); m.p. 88–90°C.

Anal. Found: C, 45.85; H, 5.35. $C_{17}H_{24}BrFeOPS$ calcd.: C, 46.05; H, 5.42%. IR: $\nu(CO)$ 1973 cm^{-1}. ^1H NMR: δ 1.26t (J 7 Hz) CH_2CH_3; 1.69d (J(PH) 9 Hz) PCH_3; 3.25m, CH_2CH_3; 5.03s C_5H_5; 7.35–7.65m C_6H_5.

In some of the kinetic runs, and in the preparation of $[Fe(PhSEt)(CO)(PMe_3)(\eta\text{-}C_5H_5)]Br$, the subsequent conversion to $FeBr(CO)(L)(\eta\text{-}C_5H_5)$ compounds was observed. Thus we decided to study further these reactions which occurred by bromide ion displacement of the sulfide ligand.

Preparation of $FeBr(CO)(L)(\eta\text{-}C_5H_5)$ complexes from $[Fe(PhSEt)(CO)(L)(\eta\text{-}C_5H_5)]Br$

$FeBr(CO)(PMe_3)(\eta\text{-}C_5H_5)$. A 0.25 g (0.56 mmol) sample of $[Fe(PhSEt)(CO)(PMe_3)(\eta\text{-}C_5H_5)]Br$ was dissolved in 25 ml $CHCl_3$. The solution was heated (at reflux) for 1 h, a change in color from red to green occurring in this period of time. The solution was allowed to cool and solvent was removed by evaporation at reduced pressure. The residue remaining was dissolved in CH_2Cl_2 and placed on an alumina chromatographic column. Elution with CH_2Cl_2 led to separation of the green product which could be recrystallized from CH_2Cl_2/hexane, 0.13 g (76%). The product, a known compound, [2] was identified from m.p., IR and NMR data.

This compound could also be obtained as the only product of the reaction of $Fe(SPh)(CO)(PMe_3)(\eta\text{-}C_5H_5)$ and bromoethane in $CHCl_3$ at 21°C, over prolonged time (~ 100 h).

$FeBr(CO)(PPh_2Me)(\eta\text{-}C_5H_5)$. It was necessary to heat the reaction mixture for 3 h, (25%) m.p. 115–118°C. Anal. by MS peak match: $^{12}C_{19}{}^{1}H_{18}{}^{79}Br^{56}Fe^{16}O^{31}P$ calcd. 427.9624. Found 427.9627. IR: $\nu(CO)$ 1961 cm^{-1}.

$FeBr(CO)(PPh_2OMe)(\eta\text{-}C_5H_5)$. The reaction mixture was heated 4 h, (32%); m.p. 135–136°C. Anal. by MS peak match: $^{12}C_{19}{}^{1}H_{18}{}^{79}Br^{56}Fe^{16}O_2{}^{31}P$ calcd. 443.9573. Found: 443.9576. IR: $\nu(CO)$ 1965 cm^{-1}.

$FeBr(CO)\{P(OPh)_3\}(\eta\text{-}C_5H_5)$. The reaction mixture was heated 15 h (76%); m.p. 132–133°C. Anal. by MS peak match: $^{12}C_{24}{}^{1}H_{20}{}^{79}Br^{56}Fe^{16}O_4{}^{31}P$ calcd. 537.9627. Found 537.9633. IR: $\nu(CO)$ 1991 cm^{-1} (lit. [6] 1990 cm^{-1}).

$FeBr(CO)(PPh_3)(\eta\text{-}C_5H_5)$. A solid sample of $[Fe(PhSEt)(CO)(PPh_3)(\eta\text{-}C_5H_5)]Br$ (0.15 g, 0.24 mmol) was heated at 120°C/1 torr for 2 h. A liquid distilled from the vessel und these conditions; this was identified as PhSEt using NMR data. The solid residue was extracted with several portions of toluene. After filtration and reduction of solvent volume, petroleum ether was added causing precipitation to the green product; this was identified by m.p., IR, and NMR data [7].

$FeBr(CO)\{PPh(OMe)_2\}(\eta\text{-}C_5H_5)$. This compound was prepared using the procedure just described, with the pyrolysis being carried out at 100°C for 40 min (18%); m.p. 121–122°C. Some decomposition was observed, and starting material was also present. Anal. by MS peak match: $^{12}C_{14}{}^{1}H_{16}{}^{79}Br^{56}Fe^{16}O_3{}^{31}P$ calcd. 397.9366. Found 397.9370. IR: $\nu(CO)$ 1974 cm^{-1}.

Experiments involving two related systems, $Fe(SPh)(CO)(PMe_3)(\eta\text{-}C_5Me_5)$ and $Fe(SPh)(CO)_2(\eta\text{-}C_5H_5)$, were also carried out. They provided slightly different results.

Reaction of $Fe(SPh)(CO)(PMe_3)(\eta\text{-}C_5Me_5)$ and EtBr to give $FeBr(CO)(PMe_3)(\eta\text{-}C_5Me_5)$

A solution (25 ml) containing the title compound (0.5 g, 1.2 mmol) and bromoethane (5.0 ml, ~ 70 mmol) was stirred at 21°C for 5.5 h. No substantial accumulation of the cationic species, $[Fe(PhSEt)(CO)(PMe_3)(\eta\text{-}C_5Me_5)]Br$, was detected during this period either by IR or by TLC on aliquots taken from the reaction mixture periodically. Evaporation of the solvent under reduced pressure produced a solid which was recrystallized from CH_2Cl_2/hexane giving 0.25 g (46%) of the product $FeBr(CO)(PMe_3)(\eta\text{-}C_5Me_5)$, m.p. 161–163°C.

Anal. by MS peak match: $^{12}C_{14}{}^{1}H_{24}{}^{79}Br^{56}Fe^{16}O^{31}P$ calcd. 374.0092. Found: 374.0099. IR: $\nu(CO)$ 1926 cm^{-1}.

Reaction of $Fe(SPh)(CO)_2(\eta\text{-}C_5H_5)$ and EtBr

A solution of $Fe(SPh)(CO)_2(\eta\text{-}C_5H_5)$ (0.50 g, 1.7 mmol) and bromoethane (3.0 ml, ~ 40 mmol) in 25 ml $CHCl_3$ was stirred at ambient temperature for 96 h. It was not possible to monitor this reaction either by color which did not change noticeably, or by IR since the $\nu(CO)$ frequencies for starting material and product were similar. After removal of the solvent under reduced pressure the residue was subjected to chromatography on alumina. Dichloromethane was used to elute the major product from the column. This fraction was concentrated; hexane addition led to precipitation of the product, $FeBr(CO)_2(\eta\text{-}C_5H_5)$, 0.22 g (50%). Identification of the product was based on m.p. and $\nu(CO)$ values.

Further elution of the chromatographic column with methanol gave a very small amount of the compound $[Fe(PhSEt)(CO)_2(\eta\text{-}C_5H_5)]Br$, identified by $\nu(CO)$ values of 2049 and 2004 cm^{-1}. Attempts to purify this compound by recrystallization were unsuccessful.

Preparation of $[Fe(PhSEt)(CO)_2(\eta\text{-}C_5H_5)]BF_4$

A 1.0 g (3.0 mmol) sample of $[Fe(THF)(CO)_2(\eta\text{-}C_5H_5)]BF_4$ [8] was dissolved in 20 ml CH_2Cl_2. Phenyl ethyl sulfide (1.0 ml, ~ 8 mmol) was added and the solution stirred at ambient temperature for 3 h. Solvent was next removed under reduced pressure, leaving a residue which was recrystallized from acetone/ethyl ether giving 0.6 g (50%) product; m.p. 91–93°C.

Anal. Found: C, 45.00; H, 3.84. $C_{15}H_{15}BF_4FeO_2S$ calcd.: C, 44.79; H, 3.76%. IR: $\nu(CO)$ 2058, 2013 cm^{-1}. ^1H NMR: δ 1.22t (J 7 Hz) CH_2CH_3; 3.19q (J 7 Hz) CH_2CH_3; 5.42s C_5H_5; 7.48bs δ, C_6H_5.

Reaction of $[Fe(PhSEt)(CO)_2(\eta\text{-}C_5H_5)]BF_4$ and $[Et_4N]Br$

A solution of the indicated iron complex (0.10 g, 0.25 mmol) and $[Et_4N]Br$ (0.05 g, 1.3 mmol) in acetone was heated for 2 h at reflux. After cooling, solvent was removed in vacuo and the residue chromatographed on alumina with a single product, $FeBr(CO)_2(\eta\text{-}C_5H_5)$ eluting. Workup, as described earlier, gave 0.24 g (40%) yield of this product.

No reaction was evident between these reactants in $CHCl_3$ at ambient temperature.

Discussion

Equations 1 and 2 identify the reactions carried out in this study:

$$Fe(SPh)(CO)(L)(\eta\text{-}C_5H_5) + EtBr \rightarrow [Fe(PhSEt)(CO)(L)(\eta\text{-}C_5H_5)]Br \qquad (1)$$

$$[Fe(PhSEt)(CO)(L)(\eta\text{-}C_5H_5)]Br \rightarrow FeBr(CO)(L)(\eta\text{-}C_5H_5) + PhSEt \qquad (2)$$

$(L = PMe_3, PPh_2Me, PPh_3, PPh_2OMe, PPh(OMe)_2, P(OPh)_3, P(OMe)_3)$

The compounds $Fe(SPh)(CO)_2(\eta\text{-}C_5H_5)$ and $Fe(SPh)(CO)(PMe_3)(\eta\text{-}C_5Me_5)$ react with EtBr in similar fashion but the intermediate sulfide complexes were not isolated since organic sulfide ligand displacement by bromide ion appears to be quite rapid (vide infra).

The reactions described by equation 1 were carried out in $CHCl_3$ at 21°C over several hours. Reactants and products are soluble in this solvent and the progress of these reactions can be followed by monitoring ν(CO) values of starting material and product which has a ν(CO) absorption at 30–40 cm^{-1} higher value. The red ionic complexes may be precipitated from solution on addition of diethyl ether and can be recrystallized from mixtures of $CHCl_3$ and Et_2O. Both ^1H NMR and IR data are in accord with the formula for these species.

The alkylation of a thiolate ligand group in a metal complex is not an unexpected reaction, although there is not extensive precedent for this process within the organometallic literature. Perhaps this is due to the limited number of organometallic complexes having terminal thiolate ligands. The single reference in the area coming to our attention is over 15 years old, and concerns the reaction of $Fe(SMe)(CO)_2(\eta\text{-}C_5H_5)$ and MeI to give $[Fe(SMe_2)(CO)_2(\eta\text{-}C_5H_5)]I$ [9]. Examples from the non-organometallic literature are much more abundant, with such reactions being known as far back as 1883. More recently, these reactions have proven useful in such projects as the formation of complexes having macrocyclic ligand systems [10].

At ambient temperatures, the alkylation of these thiolatoiron complexes is moderately slow. It was possible to obtain rate data on these reactions by monitoring the intensities of the ν(CO) absorptions of starting material and product. The reactions are first order in both complex and bromoethane. Earlier studies elsewhere [11] on the alkylation (benzylation) of several mercaptoethylaminenickel complexes have also shown second order kinetics for those reactions using low RBr concentrations.

We had hoped that the nucleophilicity of the thiolate sulfur in the complexes $Fe(SPh)(CO)(L)(\eta\text{-}C_5H_5)$ might vary with the nature of L. Such an effect could be steric or perhaps electronic in origin, good donors being expected to enhance the nucleophilicity. This proved not the case, however; the rates were largely insensitive to the nature of L. Rates for reactions of the mercaptoethylaminenickel complexes were found to vary by a factor of three depending on the substituent groups on the amino nitrogen. We suspect that the carbonyl ligand may largely compensate for any electronic effect introduced by L in these $Fe(SPh)(CO)(L)(\eta\text{-}C_5H_5)$ complexes; this could lead to similar results among the various complexes studied here.

The single exception in these rate data was the rate of the reaction of $Fe(SPh)(CO)\{PPh(OMe)_2\}(\eta\text{-}C_5H_5)$ and bromoethane; this was more than three times faster than the other rates. This result was reproduced accurately in three independent runs, using different samples of starting material, arguing in favor of its validity, but it is difficult to explain. There is no evidence in the literature suggesting that use of this ligand leads to unusual results.

When the reactions between $Fe(SPh)(CO)(L)(\eta\text{-}C_5H_5)$ and bromoethane were continued for periods longer than several half-lives (at 21°C), a subsequent reaction was detected. This reaction produces the green organoiron complexes $FeBr(CO)(L)(\eta\text{-}C_5H_5)$ and phenylethylsulfide and obviously occurs by displacement of the sulfide ligand by bromide ion. The reaction occurs more rapidly at a higher temperature; at the reflux temperature of the solvent ($CHCl_3$) 3–4 h are required to effect complete conversion. As an alternative procedure the solid salt $[Fe(PhSEt)(CO)(L)(\eta\text{-}C_5H_5)]Br$ can be heated in vacuum without solvent; using this technique PhSEt may then be collected and identified as a reaction product.

Reactions of $Fe(SPh)(CO)_2(\eta\text{-}C_5H_5)$ and $Fe(SPh)(CO)(PMe_3)(\eta\text{-}C_5Me_5)$ and bromoethane merit additional comment. Using conditions comparable to those described earlier (ambient temperature, several hours, $CHCl_3$ as solvent) the major products are halide complexes, $FeBr(CO)_2(\eta\text{-}C_5H_5)$ and $FeBr(CO)(PMe_3)(\eta\text{-}C_5Me_5)$. We presume that these reactions occur via an initial alkylation step to give the sulfide complexes; this reaction is apparently followed by a rather rapid displacement of the sulfide by bromide ion, so that there is little accumulation of the intermediate in the reaction system. The intriguing aspect of this result is that the two starting materials are electronically very different, $Fe(SPh)(CO)_2(\eta\text{-}C_5H_5)$ being the least electron rich and $Fe(SPh)(CO)(PMe_3)(\eta\text{-}C_5Me_5)$ the most electron rich of the complexes investigated. This point may bear further study.

Facile displacement of a sulfide ligand from an organometallic complex does have a precedent. Butler and Sawai [12] have described a kinetic study concerning the displacement of the sulfide ligand in $Mn(R_2S)(CO)_2(\eta\text{-}C_5H_5)$ complexes by phosphines and phosphites. These reactions are first order, proceeding by initial ligand dissociation. The rates are somewhat slower than the rates of reaction of analogous THF and olefin $Mn(L)(CO)_2(\eta\text{-}C_5H_5)$ ($L = THF$, C_8H_{14}) complexes. They are much more rapid than the rate of carbonyl displacement in $Mn(CO)_3(\eta\text{-}C_5H_5)$, however.

As an extension to this work we prepared the complex $[Fe(PhSEt)(CO)_2(\eta\text{-}C_5H_5)]BF_4$ by displacement of the THF from $[Fe(THF)(CO)_2(\eta\text{-}C_5H_5)]BF_4$ [8]. This complex reacts with $[Et_4N]Br$ in refluxing acetone to give $FeBr(CO)_2(\eta\text{-}C_5H_5)$. No reaction occurred in $CHCl_3$ at ambient conditions between these reagents. The fact that bromide ion displaces the sulfide lends some support to the assumption that $[Fe(PhSEt)(CO)_2(\eta\text{-}C_5H_5)]Br$ is an intermediate in the formation of $FeBr(CO)_2(\eta\text{-}C_5H_5)$ from $Fe(SPh)(CO)_2(\eta\text{-}C_5H_5)$ and bromoethane. The rates of these two reactions ($[Fe(PhSEt)(CO)_2(\eta\text{-}C_5H_5)]BF_4$ + $[NEt_4]Br$, and $[Fe(PhSEt)(CO)_2(\eta\text{-}C_5H_5)]Br$ degradation) appear to be considerably different, but the reactions themselves are different so these results should not really be compared.

References

1 P.M. Treichel, D.C. Molzahn, and K.P. Wagner, J. Organomet. Chem., 174 (1979) 191.
2 P.M. Treichel and D.A. Komar, J. Organomet. Chem., 206 (1981) 78.
3 P.M. Treichel and L.D. Rosenhein, J. Am. Chem. Soc., 103 (1980) 692; P.M. Treichel, L.D. Rosenhein, and M.S. Schmidt, Inorg. Chem., in press.
4 P.M. Treichel and L.D. Rosenhein, Inorg. Chem., 20 (1981) 942.
5 M. Ahmad, R. Bruce, and G.R. Knox, J. Organomet. Chem., 6 (1966) 1.
6 D.A. Brown, H.J. Lyons, A.R. Manning, and J.M. Rowley, Inorg. Chem. Acta, 3 (1969) 346.
7 P.M. Treichel, R.L. Shubkin, K.W. Barnett, and D. Reichard, Inorg. Chem., 5 (1966) 1177.
8 D.L. Reger and C.J. Coleman, J. Organomet. Chem., 131 (1977) 153.
9 R.B. King and M.B. Bisnette, Inorg. Chem., 4 (1964) 482.
10 S.G. Murray and F.R. Hartley, Chem. Rev., 81 (1981) 365.
11 E.L. Blinn and D.H. Busch, J. Am. Chem. Soc., 90 (1968) 4280.
12 I.S. Butler and T. Sawai, Inorg. Chem., 14 (1975) 2703.