Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

A NEW SYNTHETIC ROUTE TO $[C_5H_5Fe(CO)_2(CS)][BPh_4]$

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(Received April 11th, 1969)

Thiocarbonyl compounds of transition metals and complexes in which carbon disulfide acts as a simple donor ligand or as a "π-bonded" ligand have been recently prepared[1-4]. In a preliminary communication[1] we reported the preparation of $[C_5H_5Fe(CO)_2(CS)]^+$ by reaction of $[C_5H_5Fe(CO)_2]^-$ with $ClC(S)OC_2H_5$, followed by treatment with HCl. In the present paper we report greatly improved yields by using $ClC(S)OCH_3$. The reaction sequence is shown in eqn. (1):

$$\underset{(I)}{[C_5H_5Fe(CO)_2]^-} + ClC(S)OCH_3 \rightarrow \underset{(IV)}{C_5H_5Fe(CO)_2C(S)OCH_3} \xrightarrow{HCl}$$

$$\underset{(V)}{[C_5H_5Fe(CO)_2(CS)]^+} + CH_3OH \qquad (1)$$

The thio-ester (IV) has been isolated and characterized. Its infrared spectrum shows terminal CO stretching absorptions at 2024 s and 1993 s cm^{-1} and the $-C{=}S$ stretching absorption at 1223 m cm^{-1}. The position and intensity of the C=S absorption are in good agreement with those of many organic compounds containing the C=S group[5]. Reaction of (IV) with HCl in benzene solvent yields (V) which is isolated as the tetraphenylborate salt, $[C_5H_5Fe(CO)_2(CS)]BPh_4$.

We have also found an entirely new route to the thiocarbonyl complex (V) via the reaction of $[C_5H_5Fe(CO)_2]^-$ with CS_2. This route is shown in eqn. (2):

$$\underset{(I)}{[C_5H_5Fe(CO)_2]^-} + CS_2 \rightarrow \underset{(II)}{[C_5H_5Fe(CO)_2CS_2]^-} \xrightarrow{CH_3I}$$

$$\underset{(III)}{C_5H_5Fe(CO)_2C(S)SCH_3} \xrightarrow{HCl} \underset{(V)}{[C_5H_5Fe(CO)_2(CS)]^+}Cl^- + CH_3SH \qquad (2)$$

Attempts to isolate (II) as the tetraphenylarsonium salt were unsuccessful. Likewise, we were unable to isolate the dithiomethyl ester complex (III), but after treatment with CH_3I the reaction mixture gives an infrared spectrum which shows strong terminal C–O stretching absorptions at 2088 s and 2062 s cm^{-1}, and a C=S stretching absorption at 1193 m cm^{-1}. Although the positions of these bands are shifted significantly from those of the thioester, $C_5H_5Fe(CO)_2C(S)OCH_3$, their general location and relative intensities are similar to those of (IV) and suggest that the dithioester complex (III) is indeed produced in the reaction.

By treating (III) with hydrogen chloride in benzene solution a brown oil is obtained. On adding an excess of $Na[BPh_4]$ in acetone the complex $[C_5H_5Fe(CO)_2(CS)]\,[BPh_4]$ was isolated as a yellow crystalline product. Its infrared spectrum, taken in a hexachlorobutadiene mull, exhibits a strong C–S stretching at 1343 cm^{-1}, in good agreement with 1348 cm^{-1} for the same compound prepared by a different method[1]. This value may also be compared with 1299 cm^{-1} for *trans*-$RhCl(CS)[P(C_6H_5)_3]_2$, 1362 cm^{-1} for $RhCl_3(CS)[P(C_6H_5)_3]_2$[3], 1305 cm^{-1} for $[Ir(CS)(\pi\text{-}CS_2)(PPh_3)_2]^+$ and with 1289 cm^{-1} $[Rh(CS)(\pi\text{-}CS_2)(PPh_3)_2]^{+}$[4]. The CO stretching frequencies of the $[C_5H_5Fe(CO)_2(CS)][B(C_6H_5)_4]$ (2095 and 2071 cm^{-1}) are significantly higher than those of analogous complexes of the type $[C_5H_5Fe(CO)_2L]^+$ [$L = C_2H_4$[6], $P(C_2H_5)_3$[7], CH_3CN and pyridine[8]], suggesting a decreased back-donation from filled metal orbitals to the carbonyl groups. It might reasonably be inferred that the CS group is a remarkably good π-bonding ligand.

EXPERIMENTAL

Materials

The compound $[C_5H_5Fe(CO)_2]_2$ was synthesized as described in the literature*. The ligand $ClC(S)OCH_3$ was prepared from thiophosgene and absolute methyl alcohol and distilled under nitrogen[10,11]. Boiling point 104–105°. Tetrahydrofuran was dried over $LiAlH_4$ and benzene was dried over sodium.

Infrared spectra were recorded with a Perkin–Elmer 621 spectrophotometer.

Preparation of $C_5H_5Fe(CO)_2C(S)OCH_3$

A mixture of $Na[C_5H_5Fe(CO)_2]$ (from 7.08 g, 0.02 mole, of cyclopentadienyliron dicarbonyl dimer and excess 1% sodium amalgam[12]) and methyl chlorothioformate (4.42 g, 0.04 mole) in 80 ml of freshly distilled tetrahydrofuran was stirred under nitrogen for 12 h. Removal of the solvent at room temperature (20 mm), extraction of the residue with 100 ml of benzene in 5–20 ml portions and filtration through celite filter aid were followed by evaporation of the solvent. The residue was dissolved in dichloromethane (15 ml) and the red-brown $C_5H_5Fe(CO)_2C(S)OCH_3$ was precipitated by adding hexane on cooling in a dry ice/acetone bath. Yield 43%. The IR spectrum in hexane solution shows two CO stretching absorptions at 2024 s and 1993 s cm^{-1} and a strong C=S stretching absorption at 1193 cm^{-1}. (Found: C, 43.01; H, 3.51; S, 12.83. $C_9H_8FeO_3S$ calcd.: C, 42.88; H, 3.20; S, 12.72%.)

Preparation of $[C_5H_5Fe(CO)_2(CS)]\,[BPh_4]$

The compound has been prepared following two methods.

(*i*). The benzene solution containing $C_5H_5Fe(CO)_2C(S)OCH_3$ obtained as described above {from 0.02 mole of $[C_5H_5Fe(CO)_2]_2$ and 0.04 mole of $ClC(S)OCH_3$}

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* See procedures described in ref. 9.

was treated with hydrogen chloride. After 20 min a brown oil was obtained. By adding an acetone solution of $NaBPh_4$ to the reaction mixture the yellow crystalline $[C_5H_5Fe(CO)_2(CS)][BPh_4]$ was obtained. After washing with acetone and ether the yield was 45%. (Found: C, 71.20; H, 4.80; S, 5.89. $C_{32}H_{25}FeO_2SB$ calcd.: C, 71.14; H, 4.66; S, 5.93%.)

(*ii*). A mixture of $Na[C_5H_5Fe(CO)_2]$ (from 7.08 g, 0.02 mole of $[C_5H_5Fe(CO)_2]_2$ and excess 1% sodium amalgam) and 50 ml of CS_2 in 100 ml of freshly distilled tetrahydrofuran was stirred under nitrogen for 5 h. To the resulting solution 5.68 g (0.04 mole) of CH_3I were added dropwise. After 12 h the solution was evaporated the residue dissolved in 50 ml of benzene and filtered through alumina. After evaporation of the solvent the oily red-brown $C_5H_5Fe(CO)_2C(S)SCH_3$ was characterized by its infrared spectrum in pentane solvent. The cationic compound $[C_5H_5Fe(CO)_2(CS)]$-BPh_4 was obtained and characterized as described above. Yield 16%.

ACKNOWLEDGEMENT

This work has been partially supported by the National Science Foundation and partially by the National Council of Research (C.N.R. – Rome).

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