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Chemistry of Thiocarbonyl Complexes of the Type π-$(C_5H_5)Fe(CO)(CS)(L)^+$

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Cationic thiocarbonyl complexes of the type π-$(C_5H_5)Fe(CO)(CS)(L)^+$ *have been prepared from* π-$(C_5H_5)Fe(CO)_2(CS)^+$ *and various group VA ligands. The loss of CO in the substitution reaction suggests that the strength of the Fe–(CS) bond is greater than that of the Fe–(CO) bond. The* ^{13}C *n.m.r. spectra of these new thiocarbonyl derivatives indicate that the deshielding of the thiocarbonyl resonance increases as the infrared stretching force constant of the CS group decreases; the shielding of the carbonyl resonance of* π-$(C_5H_5)Fe(CO)(CS)(P(C_6H_5)_3)^+$ *relative to the* π-$(C_5H_5)Fe(CO)_2(P(C_6H_5)_3)^+$ *is attributed to the increased* π*-acceptor ability of CS relative to CO. The reactions of* π-$(C_5H_5)Fe(CO)(CS)(L)^+$ *with various nucleophiles such as* NH_2R, CH_3O^-, N_3^-, NH_2NH_2 *have been studied; in all the cases reported the nucleophilic addition occurs, at the carbon of the thiocarbonyl group, in line with the* ^{13}C *n.m.r. chemical shift of the thiocarbonyl which indicates a large deshielded carbon resonance. The nucleophilic reactions studied can be summarized as follows: reaction with* NH_2R *with formation of* π-$(C_5H_5)Fe(CO)(L)(CNR)^+$*; reaction with* N_3^- *and* NH_2NH_2 *leading to* π-$(C_5H_5)Fe(CO)(L)(NCS)$*; reaction with* CH_3O^- *yielding thiocarbonyl derivatives* π-$(C_5H_5)Fe(CO)(L)(C(S)OCH_3)$*.*

Introduction

Several studies have shown that the thiocarbonyl group is one of the best π-bonding ligands. Infrared studies of iron[1], manganese[2] and rhodium[3] thiocarbonyl complexes have supported this idea. Also Mössbauer data for the cationic complexes, π-$(C_5H_5)Fe(CO)_2(CS)^+$ and π-$(C_5H_5)Fe(CO)_3{}^+$, indicate that CS is a more effective π-acceptor than CO[4]. Recent kinetic measurements on reactions of the type:

$$\pi\text{-}(C_5H_5)Mn(CO)(CS)(C_8H_{14}) + P(C_6H_5)_3 \rightarrow \rightarrow \pi\text{-}(C_5H_5)Mn(CO)(CS)(P(C_6H_5)_3) \quad (1)$$

$(C_8H_{14} = cis\text{-cyclooctene})$

indicate that olefin dissociation occurs more rapidly in π-$(C_5H_5)Mn(CO)(CS)(C_8H_{14})$ than in π-$(C_5H_5)Mn(CO)_2(C_8H_{14})$[5]. This too supports greater π-bonding for the CS ligand as compared to CO.

More recently it has been shown thant under photochemical conditions the substitution reaction of π-$(C_5H_5)Mn(CO)_2(CS)$[6] and π-$(RC_6H_5)Cr(CO)_2(CS)$[7] with Group VA donor ligands takes place by replacement of carbon monoxide, indicating that the strength of the M–CS bond is higher than that of the M–CO bond.

Although strong π-bonding from metal to the CS group stabilizes thiocarbonyl complexes, other studies suggest that the carbon atom of the CS ligand is quite susceptible to attack by nucleophiles such as OCH_3^- and amines. In the few cases studied, except for $Ir(CO)_2(CS)L_2{}^+$[8], the nucleophile attacks the CS ligand in preference to CO ligands in the complexes. Reported reactions of the CS ligand follow:

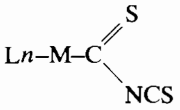
$$\pi\text{-}(C_5H_5)Fe(CO)_2(CS)^+ + OCH_3^- \rightarrow \pi\text{-}(C_5H_5)Fe(CO)_2C(S)OR^{9} \quad (2)$$

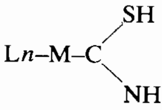
$$W(CO)_5(CS) + H_2NCH_3 \rightarrow W(CO)_5(C{\equiv}N\text{–}CH_3) + H_2S^{10} \quad (3)$$

$$\pi\text{-}(C_5H_5)Fe(CO)_2(CS)^+ + N_3^- \rightarrow \pi\text{-}(C_5H_5)Fe(CO)_2NCS + N_2{}^{9} \quad (4)$$

$$\pi\text{-}(C_5H_5)Fe(CO)_2(CS)^+ + NCS^- \rightarrow \pi\text{-}(C_5H_5)Fe(CO)_2CN + CS_2{}^{9} \quad (5)$$

The mechanisms of reactions (3), (4) and (5) are postulated to involve unstable intermediates of the type:





which rearrange to give M–CN or M–CNR derivatives.

We have now examined the reactions of the thiocarbonyl cation π-$(C_5H_5)Fe(CO)_2(CS)^+$ with various Group VA ligands (L) to ascertain whether CO or CS was preferentially substituted in order to: (i) have indication of the relative Fe–CO and Fe–CS bond strengths and (ii) if the products were the π-$(C_5H_5)Fe(CO)(CS)(L)^+$, to carry out reactions with amines and other nucleophiles such as CH_3O^-, N_3^- and NH_2–NH_2. It was hoped that this study would give us an indication on the factors influencing the reactivity of thiocarbonyl complexes toward nucleophiles.

Experimental

The complex [π-(C_5H_5)Fe$(CO)_2$(CS)]PF_6 was prepared by the published procedure[1–11]. Absolute methanol was dried and purified by distillation after refluxing over $Mg(OCH_3)_2$. Dichloromethane was dried over molecular sieves. Acetone was distilled after refluxing over $KMnO_4$ and dried with K_2CO_3. Liquid amines were freshly distilled prior to use; phenyl isonitrile was prepared following the method of Ugi[12]; the phosphines and all other chemicals were used as commercial products without further purification. All reactions were carried out under nitrogen atmosphere.

Infrared spectra were recorded on a Perkin–Elmer model 177 spectrometer; ^{13}C n.m.r. spectra were recorded on a Bruker-HX-90 operating in the Fourier transform mode; ^{1}H n.m.r. spectra were measured on a Jeol T-60 spectrometer; conductivity measurements were carried out with a LKB 5300 B conductivity bridge.

General preparative methods are given below and analytical data for the compounds prepared are in Table I.

[π-(C_5H_5)Fe(CO)(CS)(L)]PF_6 (L = P$(C_6H_4F)_3$, P$(C_6H_{11})_3$, P$(C_6H_4OCH_3)_3$, P$(C_6H_5)_3$, As$(C_6H_5)_3$, Sb$(C_6H_5)_3$)

[π-(C_5H_5)Fe$(CO)_2$(CS)]PF_6 (1 mmol) was dissolved in dry acetone and treated with an excess (1:4) of the appropriate ligand. The solution was then stirred until no further reaction took place, as evidenced by the disappearance in the ν(CO) region of the i.r. spectrum of the carbonyl stretching absorptions of the starting thiocarbonyl derivative. After evaporation of the solvent under reduced pressure the residue was washed with light petroleum and purified by several crystallizations until no π-C_5H_5Fe$(CO)_2L^+$ was present in the final product. The various solvent systems are collected in Table I. All the products were dried *in vacuo* (20–50% yields).

[π-(C_5H_5)Fe(CS)$(CNC_6H_5)_2$]PF_6

The complex [π-(C_5H_5)Fe$(CO)_2$(CS)]PF_6 (1 mmol) was dissolved in 30 ml of dry acetone and treated with 2 mmol of phenyl isonitrile; the solution turned red–brown and was stirred for 24 hr. After removal of the solvent under reduced pressure the residue was washed with diethyl ether, dissolved in dichloromethane and filtered; on addition of diethyl ether and cooling at –78° C a yellow crystalline precipitate was obtained (35% yield).

π-(C_5H_5)Fe(CO)(P$(C_6H_5)_3$)(C(S)OCH_3)

A solution of 0.3 gr (0.5 mmol) of [π-(C_5H_5)Fe(CO)(CS)(P$(C_6H_5)_3$)]PF_6 dissolved in 50 ml of dry methanol was treated, with stirring, with an excess of Na_2CO_3 for 6 hr. During this time the clear solution became cloudy. The mixture was filtered and the residue washed with 20 ml of dichloromethane. The resulting solution was evaporated to dryness, the solid dissolved with dichloromethane and filtered; on concentrating the solution under reduced pressure a yellow crystalline solid was obtained (34% yield).

π-(C_5H_5)Fe$(CNC_6H_5)_2$(C(S)OCH_3)

A solution of 0.258 gr (0.5 mmol) of [π-(C_5H_5)Fe$(CNC_6H_5)_2$(CS)]PF_6 dissolved in 50 ml of dry methanol was treated under stirring with an excess of anhydrous Na_2CO_3 for 12 hr. The resulting yellow solution was filtered and evaporated to dryness under reduced pressure. The residue, extracted with dichloromethane (20 ml), was filtered and the solution concentratd to 2 ml. Chromatography of this solution on a alumina column, with CH_2Cl_2 as eluent, gave a yellow band which was collected and evaporated under reduced pressure leaving a yellow oil, which was dried under high vacuum.

[π-(C_5H_5)Fe(CO)($CNCH_3$)(P$(C_6H_5)_3$)]PF_6

Methylamine was slowly bubbled into a stirred suspension of 0.5 mmol of [π-(C_5H_5)Fe(CO)(CS)(P$(C_6H_5)_3$)]PF_6 in 30 ml of dry diethyl ether saturated with nitrogen. After 15 min the reaction was stopped and the solvent removed with a stream of nitrogen. The residue was dissolved with 20 ml of CH_2Cl_2 and the solution was filtered. The yellow crystalline [π-(C_5H_5)Fe(CO)($CNCH_3$)(P$(C_6H_5)_3$)]PF_6 was obtained by addition of diethyl ether (20 ml) and on cooling the solution to –15° C (65% yield).

[π-(C_5H_5)Fe(CO)($CNCH_3$)(P$(p\text{-}FC_6H_4)_3$)]PF_6

The title compound was prepared in ~60% yield by the procedure described above and was crystallized from dichloromethane–hexane.

[π-(C_5H_5)Fe(CO)($CNCH_3$)(P$(C_6H_{11})_3$)]PF_6

To a suspension of 0.309 gr (0.5 mmol) of [π-(C_5H_5)Fe(CO)(CS)(P$(C_6H_{11})_3$)]PF_6 in 20 ml of dry diethyl ether were added 30 ml of diethyl ether saturated with methylamine. The solution was stirred for 5 days and the solvent was removed under reduced pressure. The residue was dissolved with 20 ml of CH_2Cl_2 and filtered. Addition of hexane give the light yellow product in ~65% yield.

[π-(C_5H_5)Fe(CO)(CNC_6H_{11})(P$(C_6H_5)_3$)]PF_6

To a solution of 0.300 gr (0.5 mmol) of [π-(C_5H_5)Fe(CO)(CS)(P$(C_6H_5)_3$)]PF_6 in 20 ml of CH_2Cl_2 were added 1.0 ml of cyclohexylamine. The reaction mixture was stirred for 4 hr and by addition of hexane a yellow–brown precipitate was obtained which was filtered, dissolved in 10 ml of dichloromethane and crystallized by slow addition of hexane (64% yield).

TABLE I. Analytical Data.

Compound	Reaction Time,[a] hr	Crystallized[b] from	Colour	Λ_M[c] Ω^{-1} cm^2 mol^{-1}	Analysis, found (calcd.)			
					C	H	N	S
$[\pi\text{-}(C_5H_5)Fe(CNC_6H_5)_2(CS)]PF_6$	24		Brown	121	46.9 (46.5)	3.0 (2.9)	5.0 (5.4)	7.1 (6.2)
$[\pi\text{-}(C_5H_5)Fe(CO)(CS)(P(C_6H_4F)_3)]PF_6$	48	d/e	Pale Yellow	129	46.3 (45.9)	2.6 (2.6)	–	4.4 (4.9)
$[\pi\text{-}(C_5H_5)Fe(CO)(CS)(P(C_6H_{11})_3)]PF_6$	2	d/e	Yellow	131	49.2 (48.5)	6.4 (6.1)	–	4.1 (5.2)
$[\pi\text{-}(C_5H_5)Fe(CO)(CS)(P(C_6H_4OCH_3)_3)]PF_6$	60	d/e	Yellow	–				
$[\pi\text{-}(C_5H_5)Fe(CO)(CS)(P(C_6H_5)_3)]PF_6$	24	a/h	Yellow	127	51.0 (50.0)	3.4 (3.3)	–	4.2 (5.3)
$[\pi\text{-}(C_5H_5)Fe(CO)(CS)(Sb(C_6H_5)_3)]PF_6$	70	a/e	Yellow		44.1 (43.4)	3.2 (2.9)	–	4.9 (4.6)
$[\pi\text{-}(C_5H_5)Fe(CO)(CS)(As(C_6H_5)_3)]PF_6$	70	d/e	Yellow	95				
$[\pi\text{-}(C_5H_5)Fe(CO)(CNCH_3)(P(C_6H_4F)_3)]PF_6$	0.5		Yellow		48.2 (47.9)	3.3 (3.1)	2.3 (2.1)	–
$[\pi\text{-}(C_5H_5)Fe(CO)(CNCH_3)(P(C_6H_{11})_3)]PF_6$	50		Yellow–Brown	117	50.7 (50.7)	6.7 (6.7)	2.4 (2.3)	–
$[\pi\text{-}(C_5H_5)Fe(CO)(CNCH_3)(P(C_6H_5)_3)]PF_6$	0.25		Pale Yellow		53.1 (52.3)	4.9 (3.9)	2.5 (2.3)	–
$[\pi\text{-}(C_5H_5)Fe(CO)(CNC_6H_{11})(P(C_6H_5)_3)]PF_6$	4		Yellow–Brown		56.2 (55.9)	4.8 (4.7)	1.9 (2.1)	–
$\pi\text{-}(C_5H_5)Fe(CO)(P(C_6H_5)_3)(C(S)OCH_3)$	6		Yellow	–	65.2 (64.2)	5.0 (4.7)	–	5.9 (6.6)
$\pi\text{-}(C_5H_5)Fe(CNC_6H_5)_2(C(S)OCH_3)$	12		Yellow	–	63.5 (62.7)	4.8 (4.5)	6.3 (7.0)	7.6 (8.0)
$\pi\text{-}(C_5H_5)Fe(CO)(P(C_6H_5)_3)NCS$[d]	–		Red	–	64.2 (64.0)	4.5 (4.3)	3.2 (3.0)	6.7 (6.8)
$\pi\text{-}(C_5H_5)Fe(CO)(P(C_6H_{11})_3)NCS$[e]	–		Red	–	62.3 (61.6)	7.6 (7.8)	3.2 (2.9)	6.7 (6.6)

[a] Taken at the disapperance of the νCO absorption of the starting complex. [b] Abbreviations used: d = dichloromethane; e = diethylether; a = acetone; h = n-hexane. [c] Acetone solvent. [d] Data obtained for the complex prepared using $NH_2\text{–}NH_2$. [e] Using N_3^-.

[π-(C_5H_5)Fe(CO)(CNC_6H_5)($P(C_6H_5)_3$)]PF_6

The complex was prepared by the same procedure described above by reacting [π-(C_5H_5)Fe(CO)(CS)($P(C_6H_5)_3$)]PF_6 with excess of aniline (1:5) in dichloromethane solution. The reaction is very slow and after 20 days an i.r. spectrum of the reaction mixture shows together with the ν(CO) of the starting complex an additional band at 1998 cm^{-1} attributable to the terminal CO stretching frequency of the title compound, which can be isolated by chromatography of the CH_2Cl_2 solution on Al_2O_3 followed by crystallization from CH_2Cl_2/diethyl ether.

π-(C_5H_5)Fe(CO)(L)(NCS) (L = $P(C_6H_5)_3$, $P(C_6H_{11})_3$)

From NaN_3

To a solution of 0.5 mmol of [π-(C_5H_5)Fe(CO)(CS)(L)]PF_6 in 30 ml of dry acetone was added 0.5 mmol of NaN_3 dissolved in 1 ml of water. Nitrogen was rapidly evolved, and the solution turned from yellow to red. After stirring for 20 min at room temperature, the acetone was removed in a rotatory evaporator and 15 ml of water were added to the residue. The resulting mixture was shaken with 20 ml of $CHCl_3$ and the organic layer dried over $CaCl_2$. The resulting solution was chromatographed in a alumina column using CH_2Cl_2 as eluent and the red band which contained the thiocyanate complex was collected; after evaporation of the solvent to 5 ml followed by addition of 50 ml of hexane the red π-(C_5H_5)Fe(CO)(L)(NCS) was collected in a 50% yield; m.p.: L = $P(C_6H_5)_3$, 164 °C; L = $P(C_6H_{11})_3$, 120 °C.

From NH_2–NH_2

A mixture of 0.5 mmol of [π-(C_5H_5)Fe(CO)(CS)(L)]PF_6 and 0.05 ml (1 mmol) of NH_2–NH_2 in CH_2Cl_2 was allowed to react at room temperature under nitrogen with stirring. The reaction mixture turned red immediately. After 30 min the solvent was evaporated off under vacuum and the residue treated with 15 ml of water and 20 ml of $CHCl_3$. The organic layer was dried over $CaCl_2$ and evaporated to dryness; the residue was dissolved in 2 ml of CH_2Cl_2 and chromatographed on alumina collecting the red band from which the red π-(C_5H_5)Fe(CO)(L)(NCS) derivative was purified as described above (35% yield).

Results and Discussion

Substitution Reactions

The π-(C_5H_5)Fe$(CO)_2$(CS)$^+$ complex reacts with Group VA donor ligands to give substitution products of the CO group according to the equation:

$$[\pi\text{-}(C_5H_5)Fe(CO)_2(CS)]PF_6 + L \rightarrow [\pi\text{-}(C_5H_5)Fe(CO)(CS)(L)]PF_6 + CO \quad (6)$$

where L = $P(C_6H_{11})_3$, $P(C_6H_5)_3$, $P(C_6H_4F)_3$, $P(C_6H_4OCH_3)_3$, $As(C_6H_5)_3$, $Sb(C_6H_5)_3$

All these reactions were carried out in dry acetone with an excess of the appropriate ligand. The reaction time is very markedly dependent on the nature of the ligand L; with L = $P(C_6H_{11})_3$ the reaction takes about 2 hr to go to completion while with L = $P(C_6H_5)_3$ it takes about 24 hr. The i.r. spectra of the crude products of the reaction (6) show, together with the terminal CO stretching frequency of the π-(C_5H_5)Fe(CO)(CS)(L)$^+$ complex, two additional side bands due to thiocarbonyl substituted products, π-(C_5H_5)Fe$(CO)_2$(L)$^+$. When L = $P(C_6H_5)_3$, these bands fall at 2070 and 2017 cm^{-1} in agreement with that reported in literature for the π-(C_5H_5)Fe$(CO)_2$($P(C_6H_5)_3$)$^+$ complex[13,14]. The small amounts (<5%) of the observed π-(C_5H_5)Fe$(CO)_2$(L)$^+$ complex could be well interpreted as due to a CO substitution from the π-(C_5H_5)Fe$(CO)_3^+$, not present in the starting thiocarbonyl complex, but formed in the reaction mixture. Another possible explanation for the formation of the π-(C_5H_5)Fe$(CO)_2$(L)$^+$ complex is that the CS group must be substituted in the reactions with the L ligands. In any event, it should be emphasized that the main products of the reaction (6) are the thiocarbonyl complexes π-(C_5H_5)Fe(CO)(CS)(L)$^+$ which can be purified by several crystallizations from dichloromethane–ether.

The i.r. and n.m.r. spectra of the new derivatives are presented in Table II. As expected, one ν(CO) absorption (2037–2020 cm^{-1}) and one ν(CS) absorption (1325–1315 cm^{-1}) are observed for the π-(C_5H_5)Fe(CO)(CS)(L)$^+$ complexes. The ν(CS) stretching modes decrease as the basicity of the ligand L increases indicating that the ν(CS) follows the same trend with change of L as observed for the carbonyl complexes.

The π-(C_5H_5)Fe$(CO)_2$(CS)$^+$ reacts with a 10fold excess of CNC_6H_5 according to the equation:

$$\pi\text{-}(C_5H_5)Fe(CO)_2(CS)^+ + 2\,CNC_6H_5 \rightarrow \pi\text{-}(C_5H_5)Fe(CNC_6H_5)_2(CS)^+ + 2\,CO \quad (7)$$

The isocyanide complex was characterized from its i.r. and n.m.r. spectra (see Table II). If the reaction is carried out with the stoichiometric amount of the phenyl isocyanide, the i.r. spectrum of the reaction product shows together with the bands due to the π-(C_5H_5)Fe$(CNC_6H_5)_2$(CS)$^+$ additional bands at 2130, 2030, 1330 cm^{-1} attributable to a ν(C≡N), a ν(C=O) and a ν(C≡S) of the π-(C_5H_5)Fe(CO)(CS)(CNC_6H_5)$^+$, respectively. The reaction with CNC_6H_5 probably proceeds by successive substitution of the carbonyl groups in the π(C_5H_5)Fe$(CO)_2$(CS)$^+$ complex.

It should be pointed out that the π-(C_5H_5)Fe$(CO)_2$(CS)$^+$ does not yield π-(C_5H_5)Fe(CS)$(L)_2^+$ on reacting with Group VA donors, even in the presence of large excess of ligand, in agreement with the lower labilising effect of the phosphines with respect to the CNR ligand[15].

The substitution reactions investigated in this study indicate–in line with the molecular orbital calculations

TABLE II. Infrared and Proton N.m.r. Spectra.

Compound	ν_{CO}[a], cm^{-1}	ν_{CS}[a], cm^{-1}	ν_{CN}[a], cm^{-1}	C_5H_5,[c] τ	Other Resonances
$[\pi\text{-}(C_5H_5)Fe(CO)_2(CS)]PF_6$	2093, 2064 (s)	1348 (s)	–	3.82[d]	
$[\pi\text{-}(C_5H_5)Fe(CNC_6H_5)_2(CS)]PF_6$	–	1310[b] (s)	2180, 2140[b] (s)	4.56[e]	≈ 2.4 (m) (C_6H_5)
$[\pi\text{-}(C_5H_5)Fe(CO)(CS)(P(C_5H_4F)_3)]PF_6$	2037 (s)	1325 (s)	–	4.32[d]	≈ 2.5 (m) (C_6H_4)
$[\pi\text{-}(C_5H_5)Fe(CO)(CS)(P(C_6H_{11})_3)]PF_6$	2037 (s)	1315 (s)	–	4.50[e]	≈ 8.3 (m) (C_6H_{11})
$[\pi\text{-}(C_5H_5)Fe(CO)(CS)(P(C_6H_4OCH_3)_3)]PF_6$	2030 (s)	1310 (s)	–	4.80[e]	6.13 (CH_3), ≈ 2.7 (m)(C_6H_4)
$[\pi\text{-}(C_5H_5)Fe(CO)(CS)(P(C_6H_5)_3)]PF_6$	2035 (s)	1320 (s)	–	4.31[d,f]	2.17 (m) (C_6H_5)
$[\pi\text{-}(C_5H_5)Fe(CO)(CS)(Sb(C_6H_5)_3)]PF_6$	2033 (s)	1321 (s)	–	–	–
$[\pi\text{-}(C_5H_5)Fe(CO)(CS)(As(C_6H_5)_3)]PF_6$	2030 (s)	1325 (s)	–	–	–
$[\pi\text{-}(C_5H_5)Fe(CO)(CNCH_3)(P(C_6H_4F)_3)]PF_6$	1996 (s)	–	2195 (m)	5.06[e]	6.78 (CH_3), ≈ 2.7 (m)(C_6H_4)
$[\pi\text{-}(C_5H_5)Fe(CO)(CNCH_3)(P(C_6H_{11})_3)]PF_6$	1990 (s)	–	2190 (m)	4.94[e]	6.48 (CH_3), ≈ 8.4 (C_6H_{11})
$[\pi\text{-}(C_5H_5)Fe(CO)(CNCH_3)(P(C_6H_5)_3)]PF_6$	1999[b] (s)	–	2194[b] (m)	4.90[d]	6.86 (CH_3), ≈ 3.00 (m) (C_6H_5)
$[\pi\text{-}(C_5H_5)Fe(CO)(CNC_6H_{11})(P(C_6H_5)_3)]PF_6$	1997 (s)	–	2184 (m)	5.00[e]	≈ 2.4 (m) (C_6H_5), ≈ 8.5 (m)(C_6H_{11})
$[\pi\text{-}(C_5H_5)Fe(CO)(CNC_6H_5)(P(C_6H_5)_3)]PF_6$	1998[b] (s)	–	2140[b] (s)	–	–
$\pi\text{-}(C_5H_5)Fe(CO)(P(C_6H_5)_3)(C(S)OCH_3)$	1950 (s)	1260 (s)	–	5.61[g]	6.60 (CH_3), ≈ 2.8 (m) (C_6H_5)
$\pi\text{-}(C_5H_5)Fe(CNC_6H_5)_2(C(S)OCH_3)$	–	–	2110, 2060 (s)	5.37[g]	5.97 (CH_3), ≈ 2.72 (m) (C_6H_5)
$\pi\text{-}(C_5H_5)Fe(CO)(P(C_6H_5)_3)NCS$	1960 (s)	815 (m)	2120 (s)	–	–
$\pi\text{-}(C_5H_5)Fe(CO)(P(C_6H_{11})_3)NCS$	1955 (s)	820 (m)	2105 (s)	–	–

[a] Nujol mull except as noted. [b] CH_2Cl_2 solvent. [c] Singlets except as noted. [d] Acetone-d_6 solvent. [e] Chloroform-d_1 solvent. [f] Doublet due to coupling with ^{31}P; J = 1.5 Hz. [g] CS_2 solvent.

TABLE III. ^{13}C N.m.r. Chemical Shifts (ppm)^{a}, $^{2}J_{^{13}C^{31}P}$ Coupling Constants and Force Constants (mdyn/Å) for the Thiocarbonyl Mode in π-$(C_5H_5)Fe(CO)(CS)(L)^+$ Derivatives.

Complex	C_5H_5	CO	$^{2}J_{^{13}C^{31}P}$	CS	$^{2}J_{^{13}C^{31}P}$	Solvent	k_{CS}^{b}
$[\pi$-$(C_5H_5)Fe(CO)_2(CS)]PF_6$^{c}	–92.1	–203.3	–	–307.9	–	Acetone-d_6	9.35
$[\pi$-$(C_5H_5)Fe(CO)(CS)(P(C_6H_4F)_3)]PF_6$	–91.1	–209.1	34	–316.4	27	Acetone-d_6	9.03
$[\pi$-$(C_5H_5)Fe(CO)(CS)(P(C_6H_5)_3)]PF_6$	–91.5	–209.0	35	–317.4	26	Acetone-d_6	8.96
$[\pi$-$(C_5H_5)Fe(CO)_2(P(C_6H_5)_3)]PF_6$^{c}	–90.8	–210.5	24	–	–	Acetone-d_6	–
$[\pi$-$(C_5H_5)Fe(CO)(CS)(P(C_6H_{11})_3)]PF_6$	–90.2	–211.9	23	–320.0	27	CD_3CN/CH_2Cl_2	8.90
$[\pi$-$(C_5H_5)Fe(CS)(CNC_6H_5)_2]PF_6$	–88.7	–	–	–320.1	–	$CDCl_3$	8.83

^{a} Chemical Shifts in ppm downfield from TMS as internal standard. ^{b} Calculated from the equation, $\lambda = \mu \cdot k$. ^{c} Data taken from G. M. Bodner, *Inorg. Chem., 13,* 2563 (1974).

which predicted that CS should be a better σ-donor ligand and a better π-acceptor than CO–that the strength of the Fe–(CS) bond is greater than that of the Fe–(CO) bond in similar organometallic complexes.

Carbon-13 N.m.r. Spectra

Previous reports of ^{13}C n.m.r. spectra of transition carbonyl complexes have indicated a linear correlation between the ^{13}C n.m.r. carbonyl chemical shifts and the stretching frequencies or force constants of the CO mode[16, 17]. In these studies it has been pointed out that the sign of the correlation is opposite to that expected on the basis of the model which predicts the stretching force constant to be directly proportional to the positive character of the carbonyl carbon[18]. In Table III are collected the ^{13}C n.m.r. data for some of the thiocarbonyl complexes reported in this work. The n.m.r. analysis was limited to only four complexes because of the low solubility of the starting derivatives; the spectra were recorded in presence of Me_4Si as internal chemical shift reference and of $Cr(acac)_3$ ($\sim$0.05M) as shiftless relaxation reagent[19].

The data in Table III indicate that the infrared stretching force constant of the CS group decreases as the deshielding of the thiocarbonyl resonance increases as observed by Bodner[16] for the ^{13}C n.m.r. chemical shifts of a series of π-$(C_5H_5)M(CO)_2L$ derivatives ($M = Cr^-, Mn^0, Fe^+$).

The ^{13}C thiocarbonyl chemical shifts follow the same trend as the ^{13}C carbonyl chemical shifts and, since it is well established that the latter is proportional to the electron density on the transition metal, it follows that also the ^{13}C n.m.r. thiocarbonyl chemical shift is proportional to the electron density on the transition metal and therefore a good measure of the relative σ-basicity/π-acidity of ligands in substituted metal thiocarbonyl complexes. The data presented in Table III suggest that the order of increasing electron density at the metal in π-$(C_5H_5)Fe(CO)(CS)(L)^+$ complexes is: $CO < P(C_6H_4F)_3 < P(C_6H_5)_3 < P(C_6H_{11})_3 \lesssim CNC_6H_5$.

The *deshielding* of the thiocarbonyl resonance in π-$(C_5H_5)Fe(CS)(CNC_6H_5)_2^+$ relative to π-$(C_5H_5)Fe(CO)_2(CS)^+$ reflects an increase of electron density at the metal that might arise from the well established poor π-acceptor ability of the CNC_6H_5 group, whereas *shielding* of the carbonyl resonance of π-$(C_5H_5)Fe(CO)(CS)(P(C_6H_5)_3)^+$ relative to the π-$(C_5H_5)Fe(CO)_2(P(C_6H_5)_3)^+$ could be due to the increased π-acidity of the CS group relative to the CO group.

Addition Reactions

Nucleophilic attacks at the carbonyl carbon in transition metal carbonyl complexes are rather common and widely studied[20]. It has been suggested that the driving force of these reactions is the electrophilic character of the carbonyl carbon which is estimated by the C–O stretching force constants of the coordinated CO group[21], *e.g.*, the higher the force constant, the higher the positive charge on the carbon.

This correlation is rather good in predicting the reactivity toward nucleophiles of carbonyl complexes but it seems not so good in predicting the reactivity of complexes which contain other sites susceptible of nucleophilic attack such as CNR or $CH_2{=}CH_2$[22, 23]. This appears to be also the case of the π-$(C_5H_5)Fe(CO)_2(CS)^+$ in which both the carbonyl and thiocarbonyl carbons are available sites of nucleophile addition and, in spite of the high CO force constant (17.4 mdyn/Å), the reactions with different nucleophiles (NH_2R, RO^-, N_3^-) proceed *via* attack at the thiocarbonyl carbon[9]. Since nucleophilic additions at the coordinated CO group are sensitive to the electron density on the metal (*vide supra*) we have investigated the reactions of the new π-$(C_5H_5)Fe(CO)(CS)(L)^+$ complexes here reported with various nucleophiles such as NH_2R, CH_3O^-, N_3^-, NH_2–NH_2 in order to have information on the influence of the phosphine ligands in these reactions.

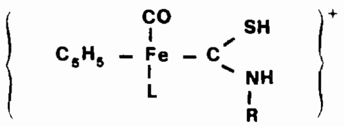
Primary amines react with the π-$(C_5H_5)Fe(CO)(CS)(L)^+$ to form isocyanide complexes according to equation (8):

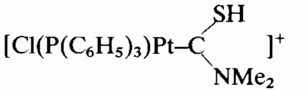
$$\pi\text{-}(C_5H_5)Fe(CO)(CS)(L)^+ + NH_2R \rightarrow \pi\text{-}(C_5H_5)Fe(CO)(CNR)(L)^+ + H_2S \quad (8)$$

$L = P(C_6H_5)_3 \qquad R = CH_3, C_6H_{11}, C_6H_5$
$L = P(C_6H_{11})_3, P(p\text{-}FC_6H_4)_3 \qquad R = CH_3$

The spectroscopic properties of the isocyanide derivatives are collected in Table II and those for the π-$(C_5H_5)Fe(CO)(CNCH_3)(P(C_6H_5)_3)^+$ are in agreement with that reported for the same complex prepared from π-$(C_5H_5)Fe(CO)(P(C_6H_5)_3)CN$ and CH_3I[22,24]. Earlier π-$(C_5H_5)Fe(CO)_2(CS)^+$ was reported to react with methylamine giving the thiocarbamoyl complex π-$(C_5H_5)Fe(CO)_2C(S)NHCH_3$[9]. Further work on this reaction has indicated the formation of the isocyanide derivative π-$(C_5H_5)Fe(CO)_2(CNCH_3)^+$ according to equation (8) where L = CO[25].

The isocyanide complexes are produced within few minutes when $L = P(C_6H_5)_3$ or $P(p\text{-}FC_6H_4)_3$ and $R = CH_3$; with a more basic phosphine such as $P(C_6H_{11})_3$ the reaction is slower; the same effect is obtained as the basicity of the reacting amines decrases: *e.g.* when $L = P(C_6H_5)_3$ and $R = C_6H_5$ the reaction takes about 20 days to go to completion. These results of decreasing reactivity are probably due to a lower rate of amine attack on the thiocarbonyl carbon atom, which forms the carbene intermediate

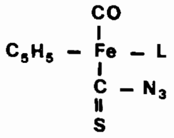


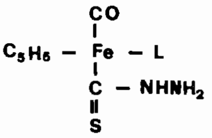
similar to those of the type  $[Cl(P(C_6H_5)_3)Pt\text{-}C\overset{\diagup SH}{\underset{\diagdown NMe_2}{}}]^+$ recently isolated by Angelici[26], which rapidly rearrange to isocyanide by eliminating hydrogen sulphide. Owing to the higher reactivity of CS relative to CO, the isocyanide derivatives can be obtained from reaction (8) even if the starting thiocarbonyl complexes are contaminated with π-$(C_5H_5)Fe(CO)_2(L)^+$ as indicated by the absence of the ν(CO) stretch at 1560 cm^{-1}, in the reaction mixture, due to the carboxamido group C(O) NHR eventually formed by nucleophilic attack of the amine on the coordinated CO[27].

Reaction (8) can be followed by the disappearance of the reactant infrared bands at 2030–2037 (CO stretch) and 1315–1325 cm^{-1} (CS stretch) and the appearance of the product absorptions at 1996–1999 (CO) and 2140–2190 cm^{-1} (C≡NR).

It has been shown recently that the π-$(C_5H_5)Fe(CO)(P(C_6H_5)_3)(CNR)^+$ reacts with NH_2CH_3 to give the amidinium complex π-$(C_5H_5)Fe(CO)(P(C_6H_5)_3)(C(NHCH_3)_2)^+$; in the nucleophilic addition with the thiocarbonyl complexes here reported no carbene derivative has been found in the reaction mixture under the conditions reported in the experimental section, suggesting that the reaction of amines with coordinated CS group is much more rapid than those with isocyanide as in the case of mixed carbonyl isocyanide complexes[28].

Like the π-$(C_5H_5)Fe(CO)_2(CS)^{+}$[9] the π-$(C_5H_5)Fe(CO)(CS)(L)^+$ reacts with N_3^- and hydrazine to form the N-bonded thiocyanate complex π-$(C_5H_5)Fe(CO)(L)(NCS)$ *via* reactive intermediates of the type





which rearrange eliminating nitrogen or ammonia.

Finally the π-$(C_5H_5)Fe(CNC_6H_5)_2(CS)^+$ reacts with CH_3O^- in anhydrous methanol to give the thiocarboxyl derivative π-$(C_5H_5)Fe(CNC_6H_5)_2(C(S)OCH_3)$. This isocyanide derivative is important in that it underlines the difference in reactivity of CO and CS bonded to similar organometallic complexes; in fact whereas the ν-$(C_5H_5)Fe(CO)(CNCH_3)_2^+$ gives the amidinium complex π-$(C_5H_5)Fe(CO)(CNCH_3)(C(NHCH_3)_2)^+$ by reacting with methylamine[22], preliminary results on the reaction of π-$(C_5H_5)Fe(CNC_6H_5)_2(CS)^+$ with $C_6H_{11}NH_2$ in CH_2Cl_2 indicate the formation of π-$(C_5H_5)Fe(CNC_6H_5)_2(CNC_6H_{11})^+$ (ν_{CN} 2178, 2125, 2128 cm^{-1}) which can be isolated by chromatography from the reaction mixture containing amidinium derivatives (ν_{CN} 1525 cm^{-1}) formed by successive nucleophilic attack on the carbon of the coordinated isonitrile.

The results discussed above on the electrophilic reactivity of these new thiocarbonyl complexes indicate that despite its greater character of π-acceptor relative to CO, the CS group is *always* the reactive site in the reaction with nucleophiles whatever the nucleophile used and the change in the charge distribution on the central metal; this would indicate a strong electrophilic character for the CS carbon atom which is consistent with the observed deshielding of the thiocarbonyl resonance in the ^{13}C n.m.r. spectra. On the other hand, it should be pointed out that the nucleophilic addition on the CS ligand occcurs at a rate substantially faster than for the CO ligand[9], suggesting a strong stabilization of the transition state probably due to the liberation of small molecules (*cf.* reactions (3), (5)).

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