Preparation, Ligand-exchange Reactions, and Alkylation Reactions of Some Carbon Disulphide Derivatives of Iron

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A number of $[Fe(CO)_2L_2(\eta^2\text{-}CS_2)]$ complexes have been prepared from $[Fe_2(CO)_9]$ and L in CS_2 solution [L = PR_3, $P(OR)_3$, or CNR]. When L = $P(OMe)_3$ a second unstable product is isolated which may be polynuclear. When L = CNMe or $CNBu^t$ further reaction occurs to give $[Fe(CO)L_3(CS_2)]$ and then a carbonyl-free complex. Ligand-exchange reactions of the complexes where L = PPh_3 or $P(OPh)_3$ with the phosphorus(III) ligands L′ gives $[Fe(CO)_2L(L')(CS_2)]$ rapidly and then $[Fe(CO)_2L'_2(CS_2)]$ much more slowly. The extent of this reaction depends on ligand size and is more complete for the less bulky L′. However, ligand basicity is also very important so that L′ = $AsBu^n_3$ displaces only one L = $P(OPh)_3$ whilst with L′ = $SbEt_3$ even this reaction is incomplete. On the other hand the very bulky but basic L′ = PPr^i_3 will displace completely the less bulky but less basic L = $P(OPh)_3$. Where L′ = CNMe the reaction takes a different course with the formation of $[Fe(CO)_2L(CNMe)(CS_2)]$ and then $[Fe(CO)L(CNMe)_2(CS_2)]$. Reagents such as L′ = CO, SO_2, $[N_2Ph]^+$, and X_2 (halogen) will displace CS_2 to give $[Fe(CO)_2L_2(L')]$. The η^2-CS_2 complexes are alkylated readily at the unco-ordinated sulphur atom, S_u, forming $[Fe(CO)_2L_2(CS_2R)]^+$ salts which are relatively inert to exchange of L. Carbon disulphide is a powerful electron-withdrawing ligand. It is suggested that this is because it may accept electrons into (*a*) its $C-S_c\ \pi^*$ orbital as in olefin–metal bonding, (*b*) the vacant 3*d* orbitals on the co-ordinated sulphur atom S_c as in thioether–metal bonding, and (*c*) the $C-S_u\ \pi^*$ orbitals as in M–CS bonding with this last being particularly important. Also, it is suggested that, as a consequence of the importance of the metal-to-CS_2 backbonding, η^2-CS_2 complexes are only stable if the metal centre is relatively electron-rich. Thus phosphorus ligands which are very basic but bulky, *e.g.* PPr^i_3, will replace those which are less basic even if they are less bulky, *e.g.* $P(OPh)_3$.

THE iron(0) complexes $[Fe(CO)_2L_2(CS_2)]$ [L = PPh_3, $P(C_6H_4F\text{-}p)_3$, and $P(C_6H_4OMe\text{-}p)_3$] were first prepared over a decade ago by Baird *et al.*[1] However, when we started our work they had received little attention even though their ruthenium and osmium counterparts had been the subject of intense activity.[2] Our interest in these compounds stems from an alternative, but less convenient or general, route to them which we have discovered. This is the photolysis of $[Fe(CO)_3\{P(OR)_3\}_2]$ (R = aryl) and the subsequent reaction of the product with CS_2 which gives $[Fe(CO)_2\{P(OR)_3\}_2(CS_2)]$.[3] We report here the preparation of a wide variety of $[FeL_4(CS_2)]$ complexes (L = tertiary phosphites, phosphines, arsines, stibines, isocyanides, or CO), their reactions with other ligands including CO and SO_2, and their reactions with alkyl halides and other alkylating agents.

During the course of our work yet another route to these complexes was reported together with some ligand-exchange studies and the structure of one of the products, $[Fe(CO)_2(PMe_3)(PPh_3)(CS_2)]$.[4]

EXPERIMENTAL

Literature methods were used to prepare $[Fe_2(CO)_9]$,[5] tertiary phosphines,[6] arsines,[6] and stibines,[6] $P(OCH_2)_3CMe$,[7] CNMe,[8] and $CNBu^t$.[9] Other chemicals were purchased.

Reactions were carried out at room temperature in dried and deoxygenated solvents under an atmosphere of nitrogen unless it is stated otherwise.

A mixture of finely ground $[Fe_2(CO)_9]$ (*ca.* 1 g), the ligand L (mol ratio *ca.* 1 : 4), and CS_2 (50 cm^3) was heated to reflux for *ca.* 30 min, or stirred at room temperature where appropriate. The reactions were monitored by i.r. spectroscopy. When they were complete or had reached a suitable stage either the products were filtered off or the solvent was removed at reduced pressure. Product purification and/or separation where necessary was effected by recrystallization from tetrahydrofuran, methylene chloride, chloroform, or toluene–pentane mixtures, or by chromatography (alumina, benzene–hexane) followed by recrystallization.

Ligand-exchange studies were carried out in benzene, chloroform, or tetrahydrofuran using *ca.* 0.5 g of $[Fe(CO)_2L_2(CS_2)]$ and an appropriate amount of the free ligand L′. Carbon monoxide and SO_2 were bubbled through the solution. The reactions were monitored by i.r. spectroscopy, and were stopped as appropriate by removal of the solvent at reduced pressure. Product purification and isolation was carried out as described above.

The alkylation reactions between $[Fe(CO)_2L_2(CS_2)]$ (0.5 g) and the alkyl halide RX (2 cm^3) were carried out in benzene (*ca.* 50 cm^3). After *ca.* 24 h the reactions were complete. The products were filtered off and recrystallized from methanol–chloroform or acetone–diethyl ether mixtures. If RX was replaced by RSO_3F (0.2 cm^3; R = Me or Et) the reactions were more rapid and complete within *ca.* 30 min. The products were purified as above or crystallized from methanol solution containing $Na[BF_4]$ to bring about replacement of $[SO_3F]^-$ by $[BF_4]^-$.

The yields, melting points, analyses, and i.r. spectra of the products are summarized in Tables 1 and 2.

Infrared spectra were run on a Perkin-Elmer 337 spectrometer fitted with a Hitachi–Perkin-Elmer readout recorder. They were calibrated with DCl and water vapour (1 700—2 200 cm^{-1}), and polystyrene (1 000—1 250 cm^{-1}).[10] Proton n.m.r. spectra were obtained but were of no particular interest and are not included.

RESULTS AND DISCUSSION

Although Baird *et al.*[1] reacted only triarylphosphines, L, with finely ground $[Fe_2(CO)_9]$ in refluxing carbon disulphide to give $[Fe(CO)_2L_2(CS_2)]$ derivatives, we have found that other phosphorus(III) ligands may be used successfully. This particular route is more convenient than those involving (*a*) the photolysis of $[Fe(CO)_3\{P(OR)_3\}_2]$ (R = aryl) followed by reaction with

TABLE 1

Melting points, analyses, and i.r. spectra of some η^2-CS_2 complexes of iron

L_n	M.p.[a] (θ_c/°C)	Analysis (%)[b]				I.r. spectra (cm^{-1})[c]			
		C	H	N	S	ν(CO)[d]	ν(CO)[d]	ν(CN)[d]	ν(CS)[e]
(*a*) $[Fe(CO)_2L_2(CS_2)]$									
$\{P(OMe)_3\}_2$	69 (d)	24.6 (24.7)	4.4 (4.1)		14.8 (14.7)	1 954 (10)	2 014 (8.4)		1 160[f]
$\{P(OEt)_3\}_2$	60—61	34.1 (34.6)	5.7 (5.8)		12.4 (12.3)	1 949 (10)	2 011 (8.4)		1 150[f]
$\{P(OPh)_3\}_2$	68—69	58.2 (58.0)	3.5 (3.8)		9.1 (7.9)	1 963 (10)	2 022 (9.4)		1 152
$\{P(OC_6H_4Me\text{-}p)_3\}_2$	108—109	60.4 (60.5)	4.6 (4.7)		8.4 (7.2)	1 961 (10)	2 021 (10.0)		1 165[f]
$\{P(OC_6H_4Me\text{-}o)_3\}_2$	85—86	60.6 (60.5)	5.0 (4.7)		7.4 (7.2)	1 962 (10)	2 020 (9.2)		1 160[f]
$\{P(OMe)_3\}(PPh_3)$	d 95—100	50.2 (50.2)	4.1 (4.2)		11.5 (11.5)	1 943 (10)	2 001 (7.5)		1 149
$\{P(OPh)_3\}(AsBu^n{}_3)$	70—73	53.5 (53.2)	5.4 (5.6)		8.6 (8.6)	1 943 (10)	2 002 (9.4)		1 161, 1 145
$\{P(OPh)_3\}(SbEt_3)$	d 78—83	46.0 (45.8)	4.6 (4.2)		9.9 (9.1)	1 942 (10)	1 998 (9.6)		1 163, 1 141
$(PEt_3)_2$	85—87	42.5 (42.5)	7.2 (7.1)			1 920 (10)	1 981 (9.8)		1 119
$(PBu^n{}_3)_2$	69—71	54.4 (54.7)	8.9 (9.1)		10.9 (10.8)	1 919 (10)	1 979 (9.7)		1 126
$(PMe_2Ph)_2$	d 115	49.1 (49.1)	4.8 (4.7)		13.4 (13.8)	1 930 (10)	1 991 (8.5)		1 133
$(PMePh_2)_2$	d 138	59.4 (59.2)	4.7 (4.4)		11.8 (10.9)	1 930 (10)	1 991 (8.7)		1 140
$(PBu^sPh_2)_2$	d 115—120	62.7 (62.5)	6.1 (5.7)		10.5 (9.5)	1 918 (10)	1 979 (7.6)		1 140[f]
$(PPh_3)_2$	d 133	65.4 (65.5)	4.2 (3.8)		8.8 (9.0)	1 930 (10)	1 993 (7.7)		1 151
$\{P(C_6H_4Cl\text{-}p)_3\}_2$	d 105—108	53.3 (53.5)	3.7 (3.8)		Cl 21.5 (21.4)	1 932 (10)	1 981 (7.0)		1 168[f]
$(PPh_3)(CNMe)$	d 105	55.7 (56.2)	3.6 (3.7)	2.8 (2.8)	13.9 (13.0)	1 959 (9,9)[g]	2 017 (10)[g]	2 203 (4.3)[g]	1 153
$(CNMe)_2$	d 90	31.5 (31.1)	2.5 (2.2)	9.9 (10.4)		1 972 (10)[g]	2 028 (8.2)[g]	2 194 (7.5)[g]	1 155[f]
$(CNBu^t)_2$	d 90	44.6 (44.1)	5.2 (5.1)	7.9 (7.9)	17.6 (18.1)	1 970 (10)[g]	2 024 (9.2)[g]	2 158 (8.5)[g]	1 157
(*b*) $[Fe(CO)L_3(CS_2)]$									
$\{P(OPh)_3\}(CNMe)_2$	136—138	52.3 (52.2)	4.2 (3.8)	4.9 (5.1)	11.5 (11.6)	1 971 (8.7)		2 175 (10)	1 151
$\{P(OPh)_3\}(CNBu^t)_2$	111—115	56.2 (56.6)	5.2 (5.2)	4.2 (4.4)	10.6 (10.1)	1 975 (8.8)		2 152 (10)	1 161
$(PPh_3)(CNMe)_2$	d 120	56.7 (57.1)	4.4 (4.2)	5.3 (5.6)	12.5 (12.7)	1 950 (8.7)[g]		2 169 (10)[g]	1 132
$(CNMe)_3$	d 118	33.6 (33.9)	3.5 (3.2)	14.6 (14.8)	22.4 (22.6)	1 958 (10)[g]		2 171 (9.7 br)[g]	1 133
$(CNBu^t)_3$	d 120	50.0 (49.9)	7.0 (6.6)	10.0 (10.3)	16.0 (15.6)	1 957 (9.5)[g]		2 135 (10, br)[g]	1 136

[a] Measured in sealed tubes; d = decomposed. [b] Calculated values are given in parentheses. [c] Relative peak heights are given in parentheses. [d] Measured in CS_2 solution unless stated otherwise. [e] Measured in CH_2Cl_2 solution unless stated otherwise. [f] Measured in KBr discs. [g] Measured in tetrahydrofuran solution.

TABLE 2

Melting points, analytical data, and i.r. spectra of some $[Fe(CO)_2L_2(CS_2R)][X]$ complexes

L	R	X	M.p. (θ_c/°C)[a]	Analysis (%)[b]			I.r. spectra (cm^{-1})[c]		
				C	H	S	ν(CO)	ν(CO)	ν(CS)[d]
PPh_3	Me	I	98 (d)	54.7 (56.3)	3.8 (3.9)	I 15.1 (14.9)	1 975 (10)	2 029 (8.0)	1 132
	Me	BF_4[e]	145—146	59.1 (59.0)	4.3 (4.1)	8.1 (7.8)	1 975 (10)	2 029 (8.1)	1 132
	Me	SO_3F	143—144	56.2 (57.6)	4.0 (3.9)	12.4 (12.3)	1 975 (10)	2 029 (8.2)	1 132
	Et	BF_4[e]	172—174	58.1 (59.4)	4.4 (4.2)	9.5 (7.7)	1 975 (10)	2 029 (7.8)	1 140
$P(C_6H_4Cl\text{-}p)_3$	Me	SO_3F	147—148	46.3 (46.4)	2.8 (2.7)	9.2 (9.3)	1 974 (10)	2 029 (7.5)	1 148
	Et	SO_3F	155—156	46.6 (47.1)	3.1 (2.8)	9.2 (9.2)	1 974 (10)	2 029 (6.8)	1 140
$[Fe(CO)_2(PPh_3)_2(CS_2)]\cdot 2CI_4$[f]			d 95	27.7 (28.1)	2.2 (1.7)	3.7 (3.7)	1 937 (10)	2 021 (8.2)	
$[Fe(CO)Br(PPh_3)_2(CS_2CH_2Ph)]$			139—140	63.4 (63.2)	4.0 (4.3)	8.2 (7.5)	1 916		

[a] Measured in sealed tubes. [b] Calculated values are given in parentheses. [c] Relative peak heights are given in parentheses. Measured in $CHCl_3$ solution unless it is otherwise stated. [d] Measured for solid samples. [e] ν(BF_4) at 1 050 cm^{-1}. [f] I, 57.8 (58.0%).

CS_2,[3] (*b*) the replacement of $[Fe_2(CO)_9]$ by $[Fe_3(CO)_{12}]$ which gives various by-products that are difficult to remove, or (*c*) the reaction of $[Fe(CO)_3(bzac)]$ (bzac = benzylideneacetone) with L and CS_2.[4] We have used it to prepare complexes of the general type $[Fe(CO)_2L_2(CS_2)]$ where L is a tertiary phosphine or phosphite (Table 1). Under the same conditions, the very bulky $P(C_6H_4Me\text{-}o)_3$ ligand fails to react. When $L = P(OR)_3$ and with reaction times >30 min, the reaction mixtures are a deep green due to unidentified by-products, but they deposit yellow-red crystals of the $[Fe(CO)_2L_2(CS_2)]$ derivatives. These are quite stable in air, but tend to decompose when dissolved in most organic solvents. Trimethyl phosphite undergoes a reaction which is similar to the above, but apart from the rather low yield of $[Fe(CO)_2\{P(OMe)_3\}_2(CS_2)]$ a small amount of a second product was obtained as yellow unstable crystals which smelt of $P(OMe)_3$. Its i.r. spectrum was rather complicated [ν(CO) at 1 931 (10), 1 955 (3.5), 1 967 (2.6, sh), 1 973 (3.6), and 2 027 (8.4) cm^{-1} in carbon disulphide solution with relative peak heights in parentheses] which indicates either a polymeric structure or isomerism in solution. The analytical data (C, 25.9; H, 3.1; S, 11.7%) are consistent with an empirical formula such as $[Fe(CO)_2\{P(OMe)_3\}(CS)]$ (C, 25.7; H, 3.2; S, 11.6%) or $[Fe_2(CO)_5\{P(OMe)_3\}_2(CS)_2]$ (C, 26.5; H, 3.1; S, 10.9%). Unfortunately the very low yields of this potentially interesting compound prevented its further characterization. Triethyl phosphite also forms two products but the second could not be crystallized. The caged phosphite $P(OCH_2)_3CMe$ forms a product which could be identified spectroscopically as $[Fe(CO)_2(PO_3C_5H_9)_2(CS_2)]$, but it was too insoluble to purify.

Although $[Fe(CO)_2(CNMe)_2(CS_2)]$ was the only product which could be isolated when CNMe and $[Fe_2(CO)_9]$ were heated in refluxing CS_2 solution, other species appeared to be formed. Consequently we carried out the reaction with CNMe and $CNBu^t$ at 25—40 °C. The first products which we were able to detect by i.r. spectroscopy were $[Fe(CO)_2(CNR)_2(CS_2)]$ and these were slowly converted into $[Fe(CO)(CNR)_3(CS_2)]$. These were rather unstable, and difficult to purify so they did not give very good analyses. With a large excess of the isocyanide, red oils were obtained which contained no CO ligands. They would not crystallize. No reaction was observed if the $[Fe_2(CO)_9]$–CS_2 mixture was heated with pyridine, acetonitrile, or dimethyl sulphide.

Ligand Exchange.—One of the most noticeable properties of the $[Fe(CO)_2L_2(CS_2)]$ complexes where $L = P(OR)_3$ or PR_3 (R = aryl) is the ease with which they undergo ligand-exchange reactions.[1,4] Thus the addition of 1 equivalent of L′ to a chloroform solution of the complex [$L = PPh_3$ and $L' = P(OPh)_3$, or $L = P(OPh)_3$ and $L' = PPh_3$] brings about the rapid establishment of an equilibrium between $[Fe(CO)_2L_2(CS_2)]$, $[Fe(CO)_2L(L')(CS_2)]$, and $[Fe(CO)_2L'_2(CS_2)]$. The three components may be distinguished by their i.r. spectra in the ν(CO) region. A similar equilibrium is rapidly established when equimolar amounts of $[Fe(CO)_2L_2(CS_2)]$ and $[Fe(CO)_2L'_2(CS_2)]$ are mixed in solution. Due to the rapidity of this ligand-redistribution reaction we could not isolate the mixed-ligand derivative. These results suggest that the reaction proceeds *via* a dissociative pathway; this is consistent with the observation that both compounds are only stable in solution if excess of ligand is present.[1]

At room temperature in $CHCl_3$ solution, 1 equivalent of $P(OMe)_3$ and $P(OEt)_3$, L′, rapidly (<1 min) displace one PPh_3 ligand from $[Fe(CO)_2(PPh_3)_2(CS_2)]$ to give $[Fe(CO)_2(PPh_3)L'(CS_2)]$ as the sole product in approximately quantitative yield.[4] The somewhat more bulky $L' = P(OPr^i)_3$ gives this as the major product but small amounts of $[Fe(CO)_2(PPh_3)_2(CS_2)]$ and $[Fe(CO)_2\{P(OPr^i)_3\}_2(CS_2)]$ are also present. The displacement of the second PPh_3 ligand by $P(OMe)_3$ is a much slower process (>1 h) requiring an excess of ligand (*ca.* 3 equivalents). The yield of $[Fe(CO)_2\{P(OMe)_3\}_2(CS_2)]$ is approximately quantitative. In tetrahydrofuran solution, a large excess of $P(OMe)_3$ also brings about CO substitution and $[Fe(CO)\{P(OMe)_3\}_3(CS_2)]$ is obtained in low yield.

One equivalent of PBu^n_3 will react with $[Fe(CO)_2\{P(OPh)_3\}_2(CS_2)]$ to give $[Fe(CO)_2\{P(OPh)_3\}(PBu^n_3)(CS_2)]$ as the principal product, but small amounts of the symmetrical compounds are also present. An excess of PEt_3 or PBu^n_3 (*ca.* 5 equivalents) converts both $[Fe(CO)_2L_2(CS_2)]$ [$L = PPh_3$ or $P(OPh)_3$] into $[Fe(CO)_2(PBu^n_3)_2(CS_2)]$ or its PEt_3 counterpart in a quantitative reaction.

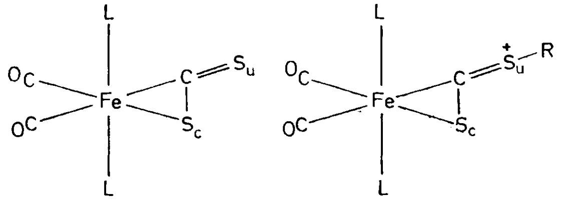
Replacing PBu^n_3 by $L' = AsBu^n_3$ or $AsMe_2Ph$ (3 equivalents) allows the displacement of only one $P(OPh)_3$ ligand to give $[Fe(CO)_2\{P(OPh)_3\}L'(CS_2)]$. The reaction is slow and almost quantitative with only traces of $[Fe(CO)_2(AsBu^n_3)_2(CS_2)]$ [ν(CO) at 1 917 (10) and 1 978 (10) cm^{-1} in CS_2 solution, *cf.* Table 1] and no $[Fe(CO)_2\{P(OPh)_3\}_2(CS_2)]$ in the reaction mixtures. With $SbEt_3$ (4 equivalents) the replacement of one $P(OPh)_3$ ligand is incomplete and $[Fe(CO)_2\{P(OPh)_3\}L'(CS_2)]$ [$L' = P(OPh)_3$ and $SbEt_3$] are in equilibrium after *ca.* 24 h.

The reaction of CNMe with $[Fe(CO)_2\{P(OPh)_3\}_2(CS_2)]$ in tetrahydrofuran solution at room temperature may be monitored by i.r. spectroscopy. The only species present after *ca.* 1 min has ν(CO) values which are between those of the starting complex and $[Fe(CO)_2(CNMe)_2(CS_2)]$ (Table 1). It is probably $[Fe(CO)_2\{P(OPh)_3\}(CNMe)(CS_2)]$. Further reaction (*ca.* 3 h) does not result in the loss of the second phosphite ligand. Instead CO is expelled and $[Fe(CO)\{P(OPh)_3\}(CNMe)_2(CS_2)]$ may be isolated from the reaction mixture. With $[Fe(CO)_2(PPh_3)_2(CS_2)]$ and CNMe in benzene solution, the reaction may be stopped at the first stage after 1 h, and $[Fe(CO)_2(PPh_3)(CNMe)(CS_2)]$ isolated. Further reaction (*ca.* 10 h) gives $[Fe(CO)(PPh_3)(CNMe)_2(CS_2)]$, but in refluxing tetrahydrofuran a very unstable compound is given which analyses as $[Fe(CO)_2(CNMe)_3]$.

The above reactions involve L or CO loss prior to CS_2 loss, and that was only observed in the last example where vigorous conditions were used. Consequently, it was surprising that CO gas displaced CS_2 rather than PPh_3 from $[Fe(CO)_2(PPh_3)_2(CS_2)]$ in acetone solution. Over a period of *ca.* 10 h near quantitative conversion into $[Fe(CO)_3(PPh_3)_2]$ took place. There was no evidence for the hoped for $[Fe(CO)_3(PPh_3)(CS_2)]$.

Another ligand which replaces CS_2 is SO_2, and the $[Fe(CO)_2L_2(SO_2)]$ [11] complexes were obtained in high yield. This provides a useful route to these potentially interesting compounds, and we are investigating their chemistry at present. Reactions with other electrophilic reagents such as $[N_2Ph][BF_4]$, and halogens, X_2, also resulted in CS_2 loss giving the known $[Fe(CO)_2L_2(N_2Ph)][BF_4]$ [12] and $[Fe(CO)_2L_2X_2]$ [13] derivatives respectively.

Alkylation.—Another characteristic reaction of these complexes derives from the well known basicity of the S atom in the CS_2 ligand.[2] Thus although dimethyl sulphate fails to react with $[Fe(CO)_2L_2(CS_2)]$ and related complexes, 1 : 1 adducts are formed in a slow reaction by MeI, EtI, and $PhCH_2Br$ and in a rapid reaction (<30 min) by $MeSO_3F$ and $EtSO_3F$. These adducts (Table 2) are formulated as $[Fe(CO)_2L_2(CS_2R)][X]$ salts. Where $L = PPh_3$ and RX = MeI or EtI they are difficult to purify, and where $[X]^- = [SO_3F]^-$ consistent analyses could not always be obtained. Then, anion exchange allowed isolation of the more tractable $[BF_4]^-$ salts.



Structures of $[Fe(CO)_2L_2(\eta^2-CS_2)]$ and $[Fe(CO)_2L_2(\eta^2-CS_2R)]^+$ complexes

Polybromo- and polyiodo-methanes react with $[Fe(CO)_2L_2(CS_2)]$ complexes. The i.r. spectra of the products suggest that they are also of the above type, but we were unable to purify them. The exception was the $[Fe(CO)_2(PPh_3)_2(CS_2)]$–$CI_4$ reaction which formed a 1 : 2 adduct.

In the $[Fe(CO)_2(PPh_3)_2(CS_2)]$–$PhCH_2Br$ reaction, as well as the salt, a second, covalent product was obtained. It appeared to be $[Fe(CO)Br(PPh_3)_2(CS_2CH_2Ph)]$ in which Br^- has displaced CO from the cation.

Unlike their precursors, the salts where $L = PPh_3$ or $P(OPh)_3$ are not particularly susceptible to replacement of L by other ligands. Thus $[Fe(CO)_2(PPh_3)_2(CS_2Me)][SO_3F]$ reacts only slowly (>3 d at room temperature) with MeNC. There is no evidence for PPh_3 loss and the only change observed in the i.r. spectrum was the slow growth of a single ν(CO) absorption band which may be a consequence of CO replacement. A similar reaction occurs between $[Fe(CO)_2(PPh_3)_2(CS_2CH_2Ph)]^+$ and Br^- (*cf.* ref. 14).

Structure.—It is probable that the structures of the $[Fe(CO)_2L(L')(CS_2)]$ complexes and the $[Fe(CO)_2L(L')(CS_2R)][X]$ salts are similar to those found for the related $[Fe(CO)_2(PMe_3)(PPh_3)(CS_2)]$ [4] and $[Ru(CO)_2(PPh_3)_2(CS_2Me)][ClO_4]$ [14] derivatives (Figure). In both, the co-ordination about the Fe atom may be regarded as quasi-trigonal bipyramidal. The CS_2 or $C(S_c)SR$ ligand adopts a η^2 mode of bonding to iron with one C–S_c bond (S_c is the sulphur atom co-ordinated to iron, S_u is not) occupying one of the equatorial co-ordination positions so that the CS_2 or CS_2R moiety lies almost in the equatorial plane of the complex. The i.r. spectra in the ν(CO) and ν(CS) regions are consistent with these proposals (Tables 1 and 2). However, although the $[Fe(CO)_2L_2(CS_2)]$ complexes are formally derivatives of Fe^0, their ν(CO) vibrations have much higher frequencies than do those of their $[Fe(CO)_3L_2]$ counterparts [$L = P(OPh)_3$, ν(CO) at 1 925 cm^{-1} in CS_2 solution]. The observed values are much closer to those exhibited by octahedral iron(II) complexes such as $[Fe(CO)_2\{P(OPh)_3\}_2D_2]$[ν(CO) at 1 977 and 2 029 cm^{-1}].[3] This may be rationalized in terms of the bonding between the iron atom and the carbon disulphide ligand which may be described as (*a*) of the metal–olefin type or (*b*) involving the formation of a heterometallocyclopropane. In (*a*) there is donation of electrons from one filled C=S_c orbital into suitable vacant orbitals on the trigonal-bipyramidal Fe^0, and back bonding into the vacant C–S_c π^* orbital. This involves only orbitals of the correct symmetry which lie in the equatorial plane of the molecule (the *xy* plane with P–Fe–P defining the *z* axis). In (*b*) a three-membered ring is formed with Fe–C, Fe–S_c, and C–S_c single bonds so that the iron atom is formally six-co-ordinate and in the +II oxidation state. The C–S_c bond length of 1.68 Å (ref. 4) is longer than that found in free CS_2 (1.55 Å) [15] but is shorter than the C–S bond length in thioether complexes (1.78—1.83 Å).[16] This implies a C–S bond order of between 1 and 2, and a description of the bonding which lies between the two extremes of (*a*) and (*b*). At the same time, there are vacant 3*d* orbitals on the S_c atom which are able to act as acceptor orbitals as they would in thioether complexes so that there is iron to sulphur d_π–d_π back bonding. Also, the vacant π^* orbital of the unco-ordinated C–S_u bond lies perpendicular to the *xy* plane. Therefore it is able to act as an acceptor orbital for electrons from the filled d_{xz},d_{yz} orbitals on the iron atom. The consequent presence of electrons in this π^* orbital would be expected to bring about a reduction of the C–S_u bond order and an increase in its bond length as observed,[4,†] and an increase in the nucleophilicity of S_u. Since the thiocarbonyl ligand is a very powerful π acceptor this effect is probably important. Thus carbon disulphide may act as an electron-acceptor ligand in three ways, and as a consequence it is a much more effective electron-withdrawing ligand than even carbon monoxide.

The considerable contribution that this metal-to-ligand electron transfer makes to the bonding between carbon disulphide and iron could be responsible for the unexpected ability of CO to displace CS_2 from $[Fe(CO)_2(PPh_3)_2(CS_2)]$. Since other σ-donor ligands such as the

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[†] Part of the observed increase to 1.61 Å may be a consequence of the increasing *p* character of the σ bonding about the C atom on co-ordination of the CS_2 molecule.

derivatives of phosphorus(III) or isocyanides replace PPh_3 and not CS_2, it is very probable that CO does likewise. However, PR_3 and CNR are stronger σ donors and poorer π acceptors than CO, and if they were replaced by it there would be a reduction in the electron density at the metal atom. This would be expected to result in a reduction of the Fe–(η^2-CS_2) bond strength, and an increased lability of the CS_2 ligand. The free PPh_3 in the reaction solution could then displace carbon disulphide from the first-formed $[Fe(CO)_3(PPh_3)(CS_2)]$ to give $[Fe(CO)_2(PPh_3)_2]$.

Also, on the basis of the same reasoning, carbon disulphide complexes of the transition metals would be expected to be most stable in those situations where the metal centre is relatively electron-rich. Consequently it is not surprising that derivatives such as $[Mo(CO)_5(\eta^2\text{-}CS_2)]$ are unknown,[2] and even though $[Fe(CO)_4(CS_2)]$ has been reported the CS_2 ligand is σ-bonded through sulphur.[1]

It has been suggested that the ease with which $[Fe(CO)_2L_2(CS_2)]$ complexes undergo ligand-exchange reactions is a function of the bulk of the ligands L and a consequence of the crowding about the iron atom.[4] Although this appears to be valid, it does not explain why $AsBu^n_3$ displaces only one L = $P(OPh)_3$ and that $SbEt_3$ does even this incompletely. Consequently ligand size is not the only important factor and ligand basicity must also be considered. It has been shown that the more bulky, but more basic, PMe_2Ph will displace $P(OMe)_3$ from $[Fe(CO)_2\{P(OMe)_3\}_2(CS_2)]$.[4] Our view of the Fe–$CS_2$ bonding may be used to rationalize this observation. Neither ligand is particularly bulky[17] and steric factors are unlikely to be overwhelmingly important. Consequently the stronger σ donor poorer π acceptor PMe_2Ph is preferred to $P(OMe)_3$ as a ligand since it gives rise to a greater electron density at the metal, and hence a stronger Fe-CS_2 bond. It is also consistent that, as we have found, the less bulky[17] but less basic[18] $P(OMe)_3$ ligand (cone angle *ca.* 107°) does not displace the more bulky[17] but more basic PBu^n_3 (cone angle *ca.* 130°) from $[Fe(CO)_2(PBu^n_3)_2(CS_2)]$.

As a test of the validity of our proposals, we treated a very bulky but basic[18] trialkylphosphine ligand PPr^i_3 (cone angle of *ca.* 160°)[17] with the complex of a less basic[18] and less bulky[17] ligand $[Fe(CO)_2\{P(OPh)_3\}_2(CS_2)]$ [$P(OPh)_3$ cone angle *ca.* 120°].[17] Using 2.8 equivalents of PPr^i_3 in chloroform solution at 25 °C brought about a reaction that was slower than that of PBu^n_3 (cone angle *ca.* 130°,[17] but basicity comparable[19] to that of PPr^i_3), but within 3 h all of the $[Fe(CO)_2\{P(OPh)_3\}_2(CS_2)]$ had been converted into $[Fe(CO)_2\{P(OPh)_3\}(PPr^i_3)(CS_2)]$ and this entirely to $[Fe(CO)_2(PPr^i_3)_2(CS_2)]$ after *ca.* 24 h.* This confirms that ligand basicity is very important and can often outweigh the consequences of ligand bulk. It lends support to our suggestions as to the nature of the M–CS_2 bond.

The electronic structure of the $[Fe(CO)_2L_2(\eta^2\text{-}CS_2R)]^+$ salts and the nature of the Fe-[η^2-$CS_c(S_uR)$] bonding may be rationalized in the same way as those of their covalent precursors. However, the co-ordination of S_u to an R^+ group caused an increase in the electron-withdrawing ability of the C–S_u bond (*cf.* $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3(CNR)]$ and $[Fe_2(\eta\text{-}C_5H_5)_2(CO)_3\{CN(R')R\}]^+$ salts[19]), an increase in the Fe-CS_2R back bonding, and an increase in the frequencies of the stretching vibrations of the CO ligands. The relative difficulty with which the ligands L = PPh_3 or $P(OPh)_3$ are replaced in these cations may well be a consequence of the increased electron-withdrawing ability of the $\overset{+}{CS_2}R$ ligand which brings about an increase in the L$\rightarrow$Fe σ bonding. Steric effects are not as important as for the covalent complexes even though the crowding about the iron atom for the two series of compounds cannot be very different.

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* The last compound cannot be isolated but may be identified unambiguously by its i.r. spectrum in the ν(CO) region, 1 925(10) and 1 985(9.4) cm^{-1}, *cf.* Table 1.

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