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Some Organo-isothiocyanate Complexes of Iron(0)

H. C. ASHTON and A. R. MANNING*

Department of Chemistry, University College, Belfield, Dublin 4, Ireland

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[Fe(PPh$_3$)$_2$(CO)$_2$(RNCS)] complexes have been prepared by the reaction of [Fe(PPh$_3$)$_3$(CO)$_2$] with RNCS when R = Ph or Me, but not C$_6$H$_{11}$, but they cannot be obtained from [Fe$_2$(CO)$_9$], Ph$_3$P and RNCS in tetrahydrofuran. They are not stable and decompose spontaneously to other species even in the solid state. Their i.r. spectra are reported and assigned and it is proposed that the RNCS ligands are η^2-(CS) bonded to the metal atom so that the bent NCS moiety lies in the Fe(CO)$_2$ plane with the Ph$_3$P ligands above and below that plane. As well as ligand-to-metal electron donation and metal-to-ligand back donation involving CS π and π^* orbitals respectively, it is suggested that there may be further metal-to-ligand electron transfer into the vacant S 3d and CN π^* orbitals. Consequently organo-isothiocyanates are powerful electron-withdrawing ligands. It is possible to replace one Ph$_3$P ligand by trisorganophosphites, but Ph$_3$P ligand lability is not as marked as in the related [Fe(PPh$_3$)$_2$(CO)$_2$(η^2-CS$_2$)] derivatives so that it is possible to isolate [Fe(PPh$_3$){P(OPh)$_3$}(CO)$_2$(RNCS)] but not to replace RNCS by CO under mild conditions. Although [4-FC$_6$H$_4$NN][BF$_4$] displaces the RNCS ligand from these complexes to give [Fe(PPh$_3$)$_2$(CO)$_2$(NNC$_6$H$_4$F-4)][BF$_4$], their usual reaction with electrophiles, E, is to give [Fe(PPh$_3$)$_2$(CO)$_2${R(E)NCS}] derivatives with N→E bonds (E = H$^+$, Me$^+$, Et$^+$, AsCl$_3$, AsI$_3$, 2SbCl$_3$ or 2BiCl$_3$). These adducts are quite stable in solution and indefinitely stable in the solid state towards spontaneous further reactions. Their i.r. spectra are reported and discussed.

Introduction

Organo-isothiocyanates, RNCS, and carbon disulfide, CS$_2$, are structurally related. The latter forms a wide range of stable complexes with transition metals [1]. Usually it coordinates in a η^2-(CS) fashion, but it may also act as a η^1-(C), an η^2-(S) or a bridging ligand. In this last mode it usually bonds η^2-(CS) to one metal atom and η^1-(S) to another, but it may be η^1-(C) bonded to one metal and act as a mono- or bidentate ligand through sulphur atoms to the other [2, 3]. A characteristic but relatively limited reaction of these M–CS$_2$ complexes is sulphur redistribution to give M–CS and MS$_2$CS derivatives in which the thiocarbonyl and trithiocarbonate ligands may be bonded to the same metal atom. In contrast sulphur redistribution reactions are very common when attempts are made to use RNCS as ligands. Dithiocarbimate, RNCS$_2$, complexes are often obtained together with free or ligated RNC, and often without the detection of intermediate RNCS derivatives [4].

Among the RNCS complexes which have been reported are those of Pd(0) and Pt(0), [M(PPh$_3$)$_2$(RNCS) [5, 6], and Rh(1) and Ir(1), [M′{P(C$_6$H$_{11}$)$_3$}$_2$(Cl)(RNCS)] [7] (R = Ph, 4-MeC$_6$H$_4$, Me, allyl or EtCO). In all of these there appears to be a η^2-(CS)-RNCS ligand, and there is a marked tendency for them to react further, either with free RNCS or by the sulphur transfer processes discussed above. More relevant to our work are the [M(PPh$_3$)$_2$(CO)$_2${η^2-(CS)-RNCS}] derivatives of M = Ru and Os prepared from RNCS and [Ru(PPh$_3$)$_3$(CO)$_2$] (R = Ph, Me or Et) [4], PhNCS and [Os(PPh$_3$)$_2$(CO)$_2$(C$_2$H$_4$)] [8], or [Os(PPh$_3$)$_2$(CO)$_2$(Cl)(CNC$_6$H$_4$Me-4)] and [SH]$^-$ [8]. The ruthenium (0) derivatives are not particularly stable and with excess RNCS they form [Ru(PPh$_3$)$_2$(CO)(CNR)(S$_2$CNR)] [4].

Here we report studies on the related [Fe(PPh$_3$)$_2$(CO)$_2${η^2-(CS)-RNCS}] (R = Ph or Me) derivatives. This is a continuation of earlier work on [Fe(PR$_3$)$_2$(CO)$_2$(η^2-CS$_2$)] complexes [9].

Experimental

Literature methods were used to prepare [Fe$_2$(CO)$_9$] [10], [Fe(PPh$_3$)$_3$(CO)$_2$] [11], MeNCS [12]

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*Author to whom correspondence should be addressed.

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MeNC [13], and [$4\text{-}FC_6H_4NN$] [BF_4] [14]. Other chemicals were purchased.

Unless it is stated otherwise, all reactions were carried out at room temperature under an atmosphere of nitrogen. All solvents were dried and deoxygenated by refluxing over calcium hydride and were distilled prior to use.

Infrared spectra were measured on a Perkin-Elmer 337 spectrometer between 1500 and 2100 cm^{-1} and calibrated with CO and water vapour [15] so that peak positions on this region are accurate to ±2 cm^{-1}. They were also measured on a Perkin-Elmer 283 B spectrometer between 200 and 4000 cm^{-1} and calibrated with polystyrene [15] so that peak positions are only accurate to ±4 cm^{-1}. N.m.r. spectra were run on a Perkin Elmer R12 n.m.r. spectrometer. They are quoted in ppm downfield from the Me_4Si used as an internal standard.

Elemental analyses were carried out in the Analytical Laboratory, University College, Dublin.

Preparation of [Fe(PPh₃)₂(CO)₂(RNCS)]

[$Fe_2(CO)_9$] (1 g), Ph_3P and RNCS (R = Ph or Me; mole ratio 1:2:1) in tetrahydrofuran (50 ml) gave only [$Fe(CO)_5$], [$Fe(PPh_3)(CO)_4$] and [$Fe(PPh_3)_2(CO)_3$].

[$Fe(PPh_3)_3(CO)_2$] (1 g) was added to a solution of RNCS (R = Ph or Me; mole ratio 1:1) in tetrahydrofuran (50 ml). The mixtures were stirred until all of [$Fe(PPh_3)_3(CO)_2$] had been consumed. They were then filtered, the solvents removed at reduced pressures, and the residues recrystallised from dichloromethanehexane mixtures to give [$Fe(PPh_3)_2(CO)_2(RNCS)$] complexes (R = Ph or Me) in *ca.* 50% yield.

There was spectroscopic evidence for the formation of the $C_6H_{11}NCS$ derivative but the reaction did not go to completion.

Reaction of [Fe(PPh₃)₂(CO)₂(RNCS)] with (R′O)₃P (R,R′ = Ph or Me) and Other Nucleophiles

[$Fe(PPh_3)_2(CO)_2(MeNCS)$] (1 g) was dissolved in C_6H_6 (40 ml) and $(R'O)_3P$ added (R′ = Ph or Me; mol ratio 1:1). After 2 hr replacement of one Ph_3P ligand was complete. The mixtures were filtered and the solvent removed at reduced pressure. The residues were recrystallised from toluene-hexane mixtures. No pure product could be isolated when R′ = Me, but when R′ = Ph a 35% yield of [$Fe(PPh_3)\{P(OPh)_3\}(CO)_2(MeNCS)$] was obtained. The addition of a five-fold excess of $(R'O)_3P$ gave no further substitution.

[$Fe(PPh_3)_2(CO)_2(PhNCS)$] (0.5 g) was dissolved in benzene (50 ml) and MeNC added. A reaction took place, and within 30 min the reaction mixtures showed no absorption bands due to ν(CO) vibrations. However, no identifiable products could be isolated.

When CO was bubbled through a solution of [$Fe(PPh_3)_2(CO)_2(PhNCS)$] (0.5 g) in toluene (40 ml) in the dark or in the prevailing laboratory illumination, no reaction took place even after 6 hr. The substrate was recovered in 90% yield.

Reaction of [Fe(PPh₃)₂(CO)₂(PhNCS)] with [4-FC₆H₄NN][BF₄]

[$Fe(PPh_3)_2(CO)_2(PhNCS)$] (0.25 g) was dissolved in toluene (30 ml) and [$4\text{-}FC_6H_4NN$] [BF_4] added (mol ratio 1:1). After 10 mins an orange solid precipitated. It was recrystallised from methanol to give [$Fe(PPh_3)_2(CO)_2(NNC_6H_4F\text{-}4)$] [$BF_4$]. Yield = 82%; m.p. 208–211 °C. *Anal.* found (calculated) C = 62.0 (62.4), H = 3.8(4.0), N = 3.0(3.3), S = 0(0)%; I.R. spectra ν(NN) = 1712 cm^{-1}, ν(CO) = 1977 and 2027 cm^{-1} ($CHCl_3$ solution).

Reaction of [Fe(PPh₃)₂(CO)₂(MeNCS)] with MeCO₂H

Glacial acetic acid (5 ml) was added to a solution of [$Fe(PPh_3)_2(CO)_2(MeNCS)$] (0.5 g) in benzene (30 ml). After 2 hr the solution was filtered, the solvent removed at reduced pressure, and the residue recrystallised from tetrahydrofuran. Yellow crystals of [$Fe(PPh_3)_2(CO)_2\{Me(H)NCS\}$] [$MeCO_2$] were obtained (yield 75%).

Reaction of [Fe(PPh₃)₂(CO)₂(RNCS)] with R′SO₃F (R = Ph or Me; R′ = Me or Et)

To a solution of [$Fe(PPh_3)_2(CO)_2(RNCS)$] (1 g) in benzene (50 ml) was added $R'SO_3F$ (mol ratio 1:1). Orange crystals of [$Fe(PPh_3)_2(CO)_2\{R(R')NCS\}$] [$SO_3F$] precipitated and were recrystallised from acetone–methanol mixtures (yields 60%).

Anion exchange to give [$Fe(PPh_3)_2(CO)_2\{R(R')NCS\}$] [$BPh_4$] was brought about by recrystallising the above salts from methanol (50 ml) containing $NaBPh_4$ (1 g).

Reaction of [Fe(PPh₃)₂(CO)₂(PhNCS)] with MX₃ (M = As, Sb or Bi; X = Cl or I)

Equimolar amounts of [$Fe(PPh_3)_2(CO)_2(PhNCS)$] (0.25 g) and MX_3 in toluene (30 ml) were stirred. Orange crystals of [$Fe(PPh_3)_2(CO)_2(PhNCS)(AsCl_3)$], and [$Fe(PPh_3)_2(CO)_2(PhNCS)(MCl_3)_2$] (M = Sb or Bi) precipitated. They were filtered off, washed with hexane and dried. AsI_3 gave a dark brown reaction mixture in tetrahydrofuran which deposited dark brown crystals of [$Fe(PPh_3)_2(CO)_2(PhNCS)(AsI_3)$] at –20 °C. Yields of 1:1 adducts were *ca.* 70–80%, those of the 1:2 adducts were lower at *ca.* 30%.

The compounds prepared are listed in Table I together with their melting points, analyses and i.r. spectra.

TABLE I. Melting Points, Analyses and I.R. Spectra of Some Compounds Described in the Text.

Compound[a]	M.p. (°C)[d]	Analyses (%)[b]					I.r. spectra[d]		
		C	H	N	S	X	ν(CO)	ν(CO)	ν(CN)
[M(PhNCS)]	124–126	70.6(70.1)	4.8(4.5)	1.6(1.8)	4.1(4.2)		1935(10)	1980(9.1)	1627(3.6)
[M(MeNCS)]	104(d)	68.2(67.7)	4.6(4.6)	1.9(2.0)	4.2(4.5)		1932(10)	1979(9.0)	1624(3.6)
[M'(MeNCS)]	106(d)	62.8(63.4)	4.8(4.4)	1.9(1.8)	3.8(4.2)		1948(10)	2001(9.0)	1626(3.5)
[M{Me(H)NCS}] [CH_3CO_2]	110–112	65.3(65.5)	5.1(4.8)	1.4(1.8)	4.5(4.2)		1978(10)	2032(9.1)	1521(2.9)
[M{Me_2NCS}] [SO_3F]	128–130	59.5(59.8)	4.2(4.4)	1.6(1.7)	3.4(3.8)	F = 2.1(2.3)	1972(10)	2028(8.8)	1541(3.4)
[M{Me_2NCS}] [BPh_4]	124–126	74.9(74.8)	5.2(5.4)	1.2(1.3)	3.5(3.1)		1972(10)	2023(8.7)	1542(3.5)
[M{Me(Et)NCS}] [BPh_4]	154(d)	76.2(75.0)	5.6(5.5)	1.3(1.3)	3.4(3.0)		1973(10)	2024(8.8)	1542(3.0)
[M(PhNCS)$AsCl_3$]	130–132	58.5(58.6)	4.2(3.8)	1.3(1.5)	3.2(2.7)	Cl = 11.2(11.5)	1979(10)	2028(8.4)	1541(3.1)
[M(PhNCS)AsI_3]	108(d)	45.1(45.2)	2.9(2.9)	1.1(1.2)		I = 32.3(31.9)	1979(10)	2028(8.4)	1542(3.3)
[M(PhNCS)($SbCl_3$)$_2$]	120–123	43.5(43.9)	2.7(2.8)	1.0(1.1)		Cl = 16.9(17.3)	1980(10)	2029(9.1)	1542(2.9)
[M(PhNCS)($BiCl_3$)$_2$]	108–110	39.9(39.4)	3.0(2.6)	0.9(1.0)		Cl = 14.8(15.5)	1979(10)	2028(8.9)	1541(2.9)

[a] M = $Fe(PPh_3)_2(CO)_2$ and M' = $Fe(PPh_3)\{P(OPh)_3\}(CO)_2$. [b] Found with calculated values in parentheses. [c] Peak positions (cm^{-1}) with relative peak heights in parentheses. Measured in $CHCl_3$ solution. The ν(CN) bands are broad. [d] (d) = melts with decomposition.

Results and Discussion

It is well-known that one Ph_3P ligand in [$Fe(PPh_3)_3(CO)_2$] is labile [16] and so it is not surprising that it is replaced by RNCS (R = Ph or Me) to give [$Fe(PPh_3)_2(CO)_2$(RNCS)] derivatives. A similar reaction has been reported for [$Ru(PPh_3)_3(CO)_2$] [4]. The phosphine lability is probably a consequence of steric crowding about the metal atom; therefore it is possible that the failure to prepare [$Fe(PPh_3)_2(CO)_2(C_6H_{11}NCS)$] is a consequence of the greater bulk of the cyclohexyl group. The failure to obtain [$Fe(PPh_3)_2(CO)_2$(RNCS)] from [$Fe_2(CO)_9$], Ph_3P and RNCS (mol ratio 1:2:1) in tetrahydrofuran is rather surprising. This reaction is very effective for the preparation of [$Fe(PPh_3)_2(CO)_2(CS_2)$] and [$Fe(PPh_3)_2(CO)_2$(PhNSO)] derivatives if RNCS is replaced respectively by CS_2 [9] or PhNSO [17].

The [$Fe(PPh_3)_2(CO)_2$(RNCS)] complexes are pale red crystalline solids which are soluble in organic solvents but insoluble in water. They do not appear to be oxidised by air, but on standing they decompose to other species. This reaction takes place slowly in the solid state, and more rapidly in solution. Consequently it proved difficult to obtain high yields of the pure [$Fe(PPh_3)_2(CO)_2$(RNCS)] derivatives.

I.r. spectra, structure and bonding of [$Fe(PPh_3)_2(CO)_2$(RNCS)] complexes.

The i.r. spectra of the [$Fe(PPh_3)_2(CO)_2$(RNCS)] complexes show two absorption bands, *ca.* 1935 and 1980 cm^{-1}. These are due respectively to the asymmetric and symmetric ν(CO) vibrations of the $Fe(CO)_2$ moieties. Their frequencies and relative intensities are very similar to those of the corresponding absorption bands in the spectrum of [$Fe(PPh_3)_2(CO)_2(CS_2)$] which points to a very similar structure for the $Fe(PPh_3)_2(CO)_2$ fragments in both instances and suggests that RNCS, like CS_2, is a very powerful electron-withdrawing ligand. The presence of strong absorption bands at 1630 cm^{-1} which may be attributed to ν(C=N) and the absence of others at *ca.* 2300 cm^{-1} (due to a N=C=S unit) or *ca.* 1150 cm^{-1} (attributable to ν(C=S)) is consistent with a η^2-(CS)-bonded RNCS ligand. Thus, by analogy with the crystallographically characterised [$Fe(PPh_3)(PMe_3)(CO)_2(\eta^2\text{-}CS_2)$] [18], we propose the structure shown in Fig. 1 for the [$Fe(PPh_3)_2(CO)_2$(RNCS)] and the [$Fe(PPh_3)\{P(OPh)_3\}(CO)_2$(RNCS)] derivatives mentioned below. Similar structures have been proposed for [$Ru(PPh_3)_2(CO)_2$(RNCS)] [4] and their Os counterparts [8]. In all, the bent SCNR moiety coordinated to Fe via C and S lies in the $Fe(CO)_2$ plane with the Ph_3P ligands above and below that plane.

The bonding between the RNCS ligand and the metal atom is probably similar to that proposed for η^2-CS_2 [9] involving (a) donation of electrons from

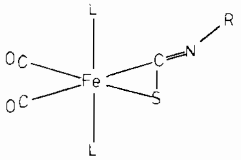

Fig. 1. Proposed structure of the $[Fe(L)_2(CO)_2(\eta^2$-CS)–RNCS)] derivatives L = Ph_3P or $(PhO)_3P$.

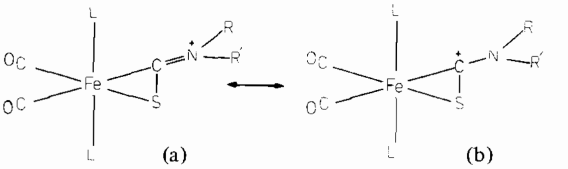

Fig. 2. Proposed structure and resonance forms of the $[Fe(L)_2(CO)_2\{\eta^2$-(CS)–R(R′)NCS}]$^+$ cations.

the filled C–S π-orbital into a vacant metal $3d_{x^2-y^2}$, $4p_x$, or $4p_y$ orbitals or a combination thereof (the z-axis lie perpendicular to the $Fe(CO)_2(NCS)$ plane), (b) back-donation from the filled metal $3d_{xy}$ orbital into the vacant C–S π* orbital, (c) donation of electrons from suitable filled metal orbitals into vacant 3d orbitals on the coordinated sulphur atom and (d) donation of electrons from filled metal $3d_{xz}$ or $3d_{yz}$ orbitals into the C=N π* orbital which lies above and below the xy-plane. The metal orbital involved in (b) is also that responsible for the extensive metal-to-ligand electron transfer in $[Fe(PPh_3)_2(CO)_2\{\eta^1$-(S)-$SO_2$}] [19], $[Fe(PPh_3)_2(CO)_2\{\eta^2$-(NS)-PhNSO}] [17], and related compounds. The preference of the RNCS ligand for η^2-(CS) as opposed to η^2-(CN) coordination to transition metals is probably a consequence of the reduced p_π–p_π overlap and hence a higher energy π and lower energy π* orbital for C=S as compared with C=N. This would render the former probably the better electron donor and, perhaps more importantly, the better electron acceptor, and the preferred site of ligation.

Reactions with Nucleophiles and Electrophiles

The Ph_3P ligands in $[Fe(PPh_3)_2(CO)_2(CS_2)]$ are readily replaced by other phosphorus(III) ligands, L, to give mixtures of the substrate with $[Fe(L)_2(CO)_2(CS_2)]$ and $(Fe(PPh_3)(L)(CO)_2(CS_2))$ (ref. 9 and references therein). The position of this equilibrium appears to depend on both the size and basicity of L [9]. In some instances it is possible to isolate all three complexes involved in the equilibria, but for others, *e.g.* L = $(PhO)_3P$, the mixed-ligand derivatives cannot be obtained [9]. In contrast to this behaviour, $[Fe(PPh_3)_2(CO)_2(RNCS)]$ are relatively inert when R = Ph or Me. Both $(PhO)_3P$ and $(MeO)_3P$ will replace one Ph_3P ligand, but not a second, to give $[Fe(PPh_3)\{P(OR)_3\}(CO)_2(RNCS)]$ which may be isolated when R′ = Ph but could only be identified spectroscopically when R′ =Me. Furthermore, unlike its CS_2 counterpart, $[Fe(PPh_3)_2(CO)_2(PhNCS)]$ does not react with CO by replacement of PhNCS or Ph_3P and PhNCS. This may be correlated with the relative inertness of its Ph_3P ligand towards replacement as it has been suggested that the initial product from the $[Fe(PPh_3)_2(CO)_2(CS)_2]$/CO reaction is $[Fe(PPh_3)(CO)_3(CS_2)]$. In this the CS_2 ligand is very labile and is readily replaced by CO or Ph_3P [9].

The reactions of our isothiocyanate complexes with electrophiles are generally similar to those of their carbon disulphide counterparts [9] except that it is possible to prepare $[Fe(PPh_3)_2(CO)_2\{R(H)NCS\}]^+$ but not $[Fe(PPh_3)_2(CO)_2\}C(S)SH\}]^+$ salts. Thus the diazonium cation $[4\text{-}FC_6H_4NN]^+$ displaces the PhNCS ligand to give $[Fe(PPh_3)_2(CO)_2(NNC_6H_4\text{-}F\text{-}4)][BF_4]$, whilst $R'SO_3F$ alkylate is to give $[Fe(PPh_3)_2(CO)_2\}R(R')NCS\}]^+$ salts, and neutral Lewis acids form 1:1 (*e.g.* $AsCl_3$ or AsI_3) or 1:2 adducts (*e.g.* $SbCl_3$ or $BiCl_3$) with it. These adducts are stable in air and much more resistant towards further reactions than the substrates from which they were obtained.

It is quite clear that in all of these adducts the Lewis acid, E is bonded to the N atom of the η^2-(CS)-RNCS ligand as is shown in Fig. 2 (*cf.* $[Ru(PPh_3)_2(CO)_2\{C(S)SMe\}]^+$ [20] and ref. 21). The evidence for this may be summarised as follows: (a) The frequencies and relative intensities of the absorption bands due to the ν(CO) vibrations of the adducts (Table I) are virtually independent of E which implies a similar structure in all cases, whilst the increase in the ν(CO) frequencies of the substrates on adduct formation are as expected (*cf.* ref. 9). (b) The marked decrease of the frequencies of the ν(CN) vibrations on adduct formation is consistent with electrophilic attack on the RNCS ligand. Direct attack on the metal atom and formation of a M → E bond would be expected to bring about an increase in the frequencies of such vibrations due to a reduction in the metal-to-isothiocyanate π-bonding, or to leave them virtually unchanged. The implied lowering of the C–N bond order points to greater contributions of canonical structures such as that illustrated in Fig. 2(b) towards the bonding in the adducts as compared with the substrates. (c) The appearance of an absorption band at 3244 cm^{-1} in the i.r. spectrum of $[Fe(PPh_3)_2(CO)_2Me(H)NCS][MeCO_2]$ due to a ν(NH) vibration and the absence of others due to ν(SH) or ν(MH). (d) The ^1H n.m.r. spectra of $[Fe(PPh_3)_2(CO)_2(RNCS)]$ show a multiplet at 7.1 ppm when R = Ph, and when R = Me a singlet at 3.0 ppm and a multiplet at 7.02 ppm (intensity ratio 3:30). $[Fe(PPh_3)_2(CO)_2(Me_2NCS)][SO_3F]$ exhibits a singlet at 3.0 ppm and a multiplet at 7.2 ppm (intensity ratio 6:30).The signals at *ca.* 3 and 7 ppm are due to methyl and aromatic group protons respectively. Similar alkylated species in which Ru or Os replace Fe have been reported [8].

The adducts of $[Fe(PPh_3)_2(CO)_2(PhNCS)]$ with the neutral Lewis acids $AsCl_3$, $2SbCl_3$ and $2BiCl_3$ conduct electricity when dissolved in $MeNO_2$ (respectively Λ_o = 44, 60 and 58 Ω^{-1} mol^{-1} cm^{-1}). As their i.r. spectra are so similar, it seems probable that all contain similar cations and are best formulated as $[Fe(PPh_3)_2(CO)_2\{Ph(X_2M)NCS\}]^+[Y]^-$ (MX_3 = $AsCl_3$, AsI_3, $SbCl_3$ or $BiCl_3$) where Y^- = X^- in the 1:1 adducts and MX_4^- in the 1:2 adducts. The actual values for Λ_o suggests that ionization is largely complete in the 1:2 adducts, but is more limited in the 1:1 adducts with, perhaps, tight ion-pair formation.

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