Articles

Convenient Syntheses of $[IrCl(CS)(PPh_3)_2]$ and a Bis(thiocarbonyl) Complex of Iridium†

Anthony F. Hill*,‡ and James D. E. T. Wilton-Ely

Department of Chemistry, Imperial College of Science, Technology and Medicine, London SW7 2AY, U.K.

Received March 19, 1996⊗

Treating $[IrCl(CO)(PPh_3)_2]$ with ClC(=S)OR (R = C_6H_4Me-4) provides $[IrCl_2\{C(=S)OR\}(CO)(PPh_3)_2]$, which reacts with $NaBH_4$ to give $[IrHCl\{C(=S)OR\}(CO)(PPh_3)_2]$. The aryloxide group is cleaved by HCl to give $[IrHCl_2(CS)(PPh_3)_2]$, which is dehydrochlorinated by DBU to provide $[IrCl(CS)(PPh_3)_2]$ (overall yield for "Ir(CO)" → "Ir(CS)" 75%). Treating $[IrCl(CS)(PPh_3)_2]$ with ClC(=S)SPh provides $[IrCl_2\{C(=S)SPh\}(CS)(PPh_3)_2]$ (in equilibrium with $[IrCl(\eta^2\text{-SCSPh})(CS)(PPh_3)_2]Cl$) which reacts subsequently with I_2 or ICl to provide $[IrCl_2(CS)_2(PPh_3)_2]X$ (X = I_3, Cl). $[Ir(CS_2Ph)Cl_2(CO)(PPh_3)_2]$, however, reacts with I_2 to provide $[IrClI_2(CS)(PPh_3)_2]$. Reaction of $[IrHCl_2(CS)(PPh_3)_2]$ with $CNC_6H_3Me_2$-2,6 does not proceed *via* migratory insertion but, rather, leads to reduction of iridium and formation of the salt $[Ir(CNC_6H_3Me_2\text{-}2,6)_2(CS)(PPh_3)_2]Cl$.

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on September 3, 1996 on http://pubs.acs.org | doi: 10.1021/om960205+

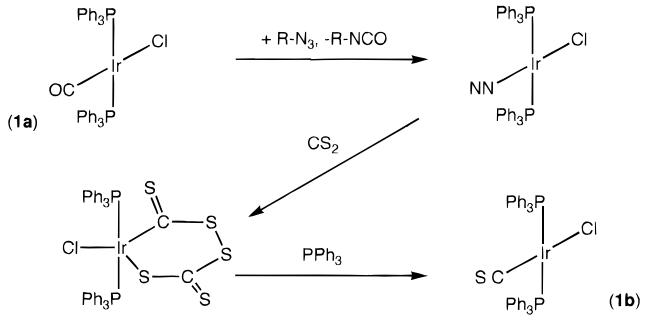
Introduction

Wilkinson's archetypal thiocarbonyl complex $[RhCl(CS)(PPh_3)_2]$ is conveniently obtained in good yield (ca. 80%) by treating $[RhCl(PPh_3)_3]$ with CS_2 and PPh_3 (reaction 1).[1] The preparation of the iridium analogue

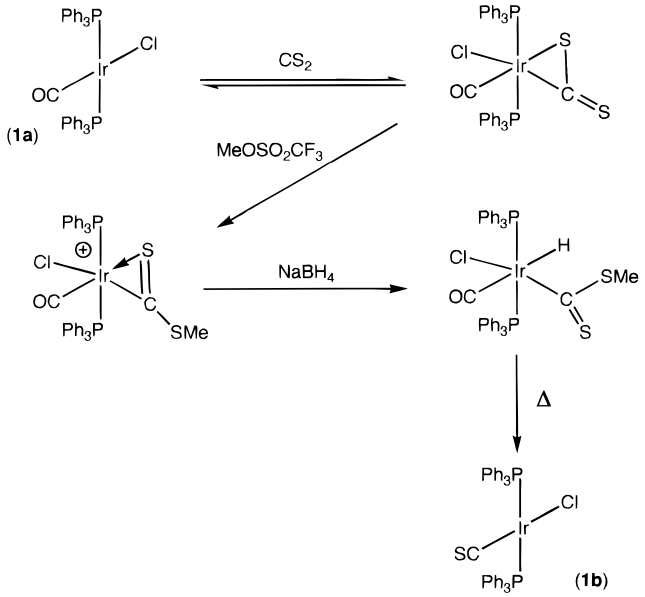
$$[RhCl(PPh_3)_3] + CS_2 \xrightarrow{PPh_3} \textit{trans}\text{-}[RhCl(CS)(PPh_3)_2] + SPPh_3 + \ldots \quad (1)$$

$[IrCl(CS)(PPh_3)_2]$ (**1b**)[2] is somewhat more problematical. Two routes for the conversion of $[IrCl(CO)(PPh_3)_2]$ (**1a**) to its thiocarbonyl analogue are currently available, each with their own attendant problems. The first (Scheme 1),[3] requiring anaerobic conditions, involves the initial conversion of Vaska's complex to $[IrCl(N_2)(PPh_3)_2]$ using an organic azide followed by treatment with carbon disulfide to provide an ill-defined metallacyclic species. This is then converted to (**1b**) by phosphine (overall yield 48%). The second route (Scheme 2)[4] offers the advantages of air-stable intermediates. Alkylation of "$IrCl(CS_2)(CO)(PPh_3)_2$" (generated *in situ* in CS_2) with methyl triflate to provide $[IrCl\{\eta^2\text{-SCSMe}\}(CO)(PPh_3)_2](O_3SCF_3)$ followed by triflate/hydride metathesis gives $[IrHCl\{C(=S)SMe\}(CO)(PPh_3)_2]$. Thermolysis then leads to elimination of methanethiol and carbon monoxide and formation of **1b**.

Scheme 1



Scheme 2



We were eager to investigate further the chemistry of $[IrCl(CS)(PPh_3)_2]$ but were somewhat discouraged by

† Dedicated to Professor Max Herberhold on the occasion of his 60th birthday.

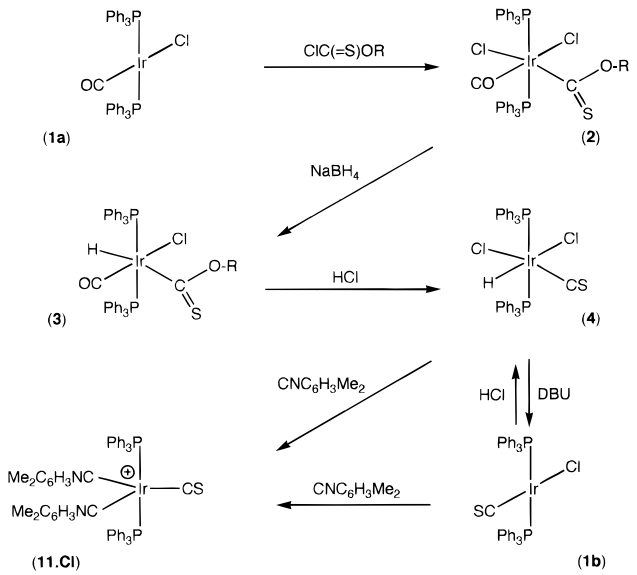
‡ Email: a.hill@ic.ac.uk.

⊗ Abstract published in *Advance ACS Abstracts,* August 1, 1996.

(1) Baird, M. C.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1966**, 267.
(2) Yagupsky, M. P.; Wilkinson, G. *J. Chem. Soc., A* **1968**, 2813.
(3) Kubota, M. *Inorg. Synth.* **1979**, *19*, 206. Kubota, M.; Carey, C. R. *J. Organomet. Chem.* **1970**, *24*, 491.
(4) Collins, T. J.; Roper, W. R.; Town, K. G. *J. Organomet. Chem.* **1976**, *121*, C41.

S0276-7333(96)00205-1 CCC: $12.00 © 1996 American Chemical Society

Scheme 3



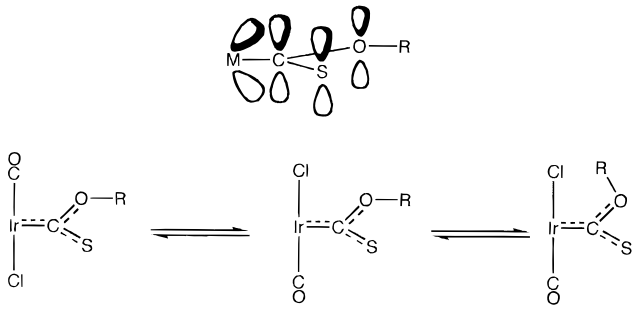
the associated problems with each of these approaches. We have therefore developed an alternative procedure, the advantages of which include (i) high overall yield, (ii) short process times, (iii) reagents which are all commercially available and cheap and have minimal health and safety criteria, (iv) intermediates that are all air-stable, and (v) the fact that the approach allows the introduction of a second thiocarbonyl ligand to give the first group 9 bis(thiocarbonyl) complex.

Results and Discussion

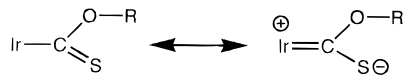
The chemistry described employs chlorothionoformate esters, ClC(=S)OAr (Ar = C_6H_5, C_6H_4Me-4), as source molecules for the thiocarbonyl ligand. The processes proceed equally well for both aryl substituents; however, those based on the 4-tolyl derivatives will be discussed, due to the spectroscopic advantages (^{1}H and ^{13}C NMR, IR). Treating **1a** with ClC(=S)OC_6H_4Me-4 (hereafter R = C_6H_4Me-4) in tetrahydrofuran provides the yellow complex [$IrCl_2${C(=S)OR}(CO)(PPh_3)$_2$] (**2**) in 95% yield. The identity of this complex follows unambiguously from spectroscopic data. The occurrence of an oxidative-addition process is indicated by the high-frequency shift in the ν(CO) IR absorption to 2074 and 2054 cm^{-1} (Nujol) (1961 cm^{-1} in the precursor). The stereochemistry at iridium (Scheme 3) follows from the appearance of two ν($IrCl_2$) absorptions at 317 and 271 cm^{-1}, a singlet resonance in the ^{31}P NMR spectrum (δ −16.1 ppm), and a triplet carbonyl resonance in the ^{13}C NMR spectrum (δ 156.4 ppm; $J(P_2C)$ = 7.2 Hz). The resonance derived from the (aryloxy)thiocarbonyl carbon appears to lower field, at δ 215.4 ppm, also as a triplet ($J(P_2C)$ = 5.4 Hz) and those due to the phosphine aryl groups appear as virtual triplets, further confirming the *trans* bis(phosphine) arrangement. In addition to confirming the gross molecular composition (M^+ at m/z 967) and revealing a range of ligand fragmentations, the FAB-mass spectrum also shows a peak due to "$[M - OR]^+$", which bodes well for the subsequent chemistry.

The splitting of the ν(CO)-associated absorption in the infrared spectrum (retained in solution) suggests the possibility of isomers which nevertheless interconvert within the NMR time scale. The most plausible origin

Scheme 4. Rotational Isomerism in Alkoxythiocarbonyl Complexes



Scheme 5



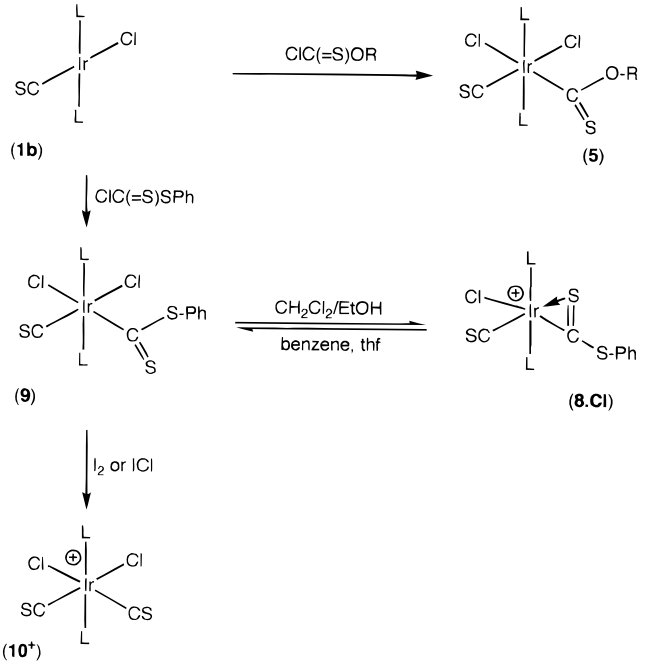
of such a process would be rotational isomerism about either the Ir−C or C−O bonds of the (aryloxy)thiocarbonyl ligand (Scheme 4). Both of these linkages can be expected to have a degree of multiple bonding, albeit small. Such rotational isomerism is a feature of related alkoxycarbene complexes.

The two chloride ligands of **2** show different chemical reactivities. Treating **2** with an excess of ethanolic sodium borohydride leads to replacement of only one chloride and formation of [IrHCl{C(=S)OR}(CO)(PPh_3)$_2$] (**3**). It is most likely that it is the chloride *trans* to the (aryloxy)thiocarbonyl ligand which is replaced, on the basis of chemical intuition (σ-organyls having a stronger *trans* effect than carbonyl ligands) and spectroscopic data for **3**. Most spectroscopic data for **3** are comparable to those for **2** and need no further discussion. Those associated with the hydride and (aryloxy)thiocarbonyl ligand are, however, noteworthy. First, the hydride ligand gives rise to a triplet resonance in the ^{1}H NMR spectrum at δ −11.0 (J(PH) = 14.5 Hz). Second, although the ^{13}C NMR resonance associated with the carbonyl ligand shows only a small shift to δ 161.8 ppm ($J(P_2C)$ = 8.1 Hz), that due to the (aryloxy)thiocarbonyl shows a dramatic shift to lower field to 268.5 ppm and is observed as two overlapping triplets. This presumably results from the coupling to the *trans* hydride being comparable to the *cis* PC coupling (*ca.* 7 Hz). The large shift may be due to the increase in carbene character which would be favored by a stronger *trans* donor ligand (Scheme 5). This is also supported by the apparent absence of rotational isomerism about the C−O bond of this ligand, which should have reduced multiple-bond character.

The aryloxide group of **3** is readily cleaved by Brønstead acids. Treating **3** with HCl leads to loss of both cresol and carbon monoxide to provide [$IrHCl_2$(CS)-(PPh_3)$_2$] (**4**) in high yield. The stereochemistry at iridium (Scheme 3) follows from the appearance of two ν($IrCl_2$) absorbances in the infrared spectrum (CsI) at 293 and 261 cm^{-1} and a singlet resonance in the ^{31}P-{^{1}H} NMR spectrum (δ 1.86 ppm). The thiocarbonyl ligand which results from the aryloxide abstraction gives rise to an intense IR absorption at 1358 cm^{-1}. The complex (**4**) is readily dehydrochlorinated by 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in a mixture of dichloromethane and ethanol (25 °C) to provide [IrCl-(CS)(PPh_3)$_2$] (**1b**), characterized by comparison of spec-

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on September 3, 1996 on http://pubs.acs.org | doi: 10.1021/om960205+

Scheme 6



troscopic data with those previously reported.[3,4] The multistep sequence for the conversion of **1a** to **1b** may be performed without isolation of the intermediates (see Experimental Section), giving yields in excess of 75% for the IrCO → IrCS conversion.

Bis(thiocarbonyl) Complexes. With access to **1b** we have extended the approach to the preparation of bis(thiocarbonyl) complexes. This class of complex remains rare,[5] due to the difficulties in the construction of the thiocarbonyl ligand within a coordination sphere. The three successful approaches previously employed involve the following. (i) Successive carbonyl photolabilization has been used to generate solvent-stabilized species which react with CS_2 and phosphine. This has been extended to a tris(thiocarbonyl) complex of manganese, albeit in low overall yield.[6] (ii) Reduction of $[OsCl_2(CS)(PPh_3)_3]$ to $[Os(CO)(CS)(PPh_3)_3]$ occurs *via* a multistep procedure, followed by coordination of CS_2 to provide $[Os(\eta^2\text{-SCS})(CO)(CS)(PPh_3)_2]$. Alkylation of the coordinated CS_2 ligand followed by thiol protonolysis with hydrohalic acids provides $[OsX_2(CS)_2(PPh_3)_2]$ (X = Cl, Br).[7] (iii) Reaction of $[OsCl_2(=CCl_2)(CS)(PPh_3)_2]$ with sodium hydrosulfide provides $[OsCl_2(CS)_2(PPh_3)_2]$. This last approach has also been extended to the mixed-chalcogenocarbonyl complex $[OsCl_2(CS)(CSe)(PPh_3)_2]$.[8]

The reaction of **1b** with ClC(=S)OR proceeds in a manner completely analogous to that of **1a** to provide $[IrCl_2\{C(=S)OR\}(CS)(PPh_3)_2]$ (**5**) (Scheme 6). Oxidation of the iridium(I) center is accompanied by a bathochromic shift in the thiocarbonyl infrared absorption (Nujol, 1365 cm^{-1}; CH_2Cl_2, 1369 cm^{-1}). Once again, bands are observed at 1113 and 999 cm^{-1} (*cf.* 1119 and 1008 for **2**) due to ν(C—O) and ν(C=S) vibrations of the (aryloxy)-thiocarbonyl ligand. Both thiocarbonyl carbon nuclei are observed to low field in the ^{13}C NMR spectrum as triplets (IrCS, δ 244.9 ppm, J(PC) = 8.0 Hz; OCS, δ 218.3 ppm, J(PC) = 5.4 Hz). The FAB mass spectrum of **5** differs slightly from that of **2** in that while the base peak for **2** corresponded to loss of chloride, such a fragmentation for **5** is not as strongly observed. Rather, the base peak is due to the molecular ion, with only minor peaks being observed for loss of phosphine (42%) followed by loss of chloride (12%). Presumably this reflects the more electron poor iridium center in **5** relative to **2**, which reduces the facility of iridium—halide ionization.

Table 1. Infrared Data (cm^{-1})[a] for the Complexes $[MClX(CS_2R)(AB)L_2]$ and $[MX(\eta^2\text{-SCSR})(AB)L_2]^+$ (MX(AB) = OsI (NO),[b] OsCl (NO),[b] IrCl (CO), IrCl (CS); L = PPh_3)

complex	ν(AB)	$\Delta\nu$(AB)	$\nu(CS_2)$	$\Delta\nu(CS_2)$
$[OsClI(CS_2Me)(NO)L_2]$	1843		991	
$[OsI(\eta^2\text{-SCSMe})(NO)L_2]^+$	1798	−45	1122	+131
$[OsCl(\eta^2\text{-SCSMe})(NO)L_2]^+$	1792	−51	1128	+137
$[IrCl_2(CS_2Ph)(CO)L_2]$	2069		1009	
$[IrCl(\eta^2\text{-SCSPh})(CO)L_2]^+$	2028	−41	1136	+137
$[IrCl_2(CS_2Ph)(CS)L_2]$	1363		1029	
$[IrCl(\eta^2\text{-SCSPh})(CS)L_2]^+$	1360	−3	1124	+95

[a] Data from Nujol mulls. [b] From ref 9.

Reaction of **1a** with $ClCS_2Ph$ provides $[IrCl(\eta^2\text{-SCSPh})(CO)(PPh_3)_2]Cl$ (**6**·Cl) or $[IrCl_2(CS_2Ph)(CO)(PPh_3)_2]$ (**7**), depending on the solvent combination used for recrystallization. From weakly polar or nonpolar solvent mixtures the isolated species is the neutral complex $[IrCl_2(CS_2Ph)(CO)(PPh_3)_2]$ (**7**; monodentate (phenylthio)-thiocarbonyl ligand), as indicated by the appearance of bands at 1009 s and 910 m cm^{-1}. The carbonyl absorption occurs at 2069 cm^{-1}. The salt $[IrCl(\eta^2\text{-SCSPh})(CO)(PPh_3)_2]Cl$ (**6**·Cl) has a ν(C—S) absorption at 1136 cm^{-1}. If the product is, however, crystallized from polar solvents, e.g., a mixture of dichloromethane and ethanol, the salt $[IrCl(\eta^2\text{-SCSPh})(CO)(PPh_3)_2]Cl$ (**6**·Cl) is obtained; alternatively, metathesis with NH_4PF_6 provides exclusively $[IrCl(\eta^2\text{-SCSPh})(CO)(PPh_3)_2]PF_6$ (**6**·PF_6). We have encountered similar behavior in the formally isoelectronic osmium compounds $[OsI(\eta^2\text{-SCSMe})(NO)(PPh_3)_2]Cl$ and $[OsClI(CS_2Me)(NO)(PPh_3)_2]$.[9] Notably, the conversion of a neutral nitrosyl or carbonyl complex to a cationic derivative is normally expected to result in a shift to higher frequency of ν(NO) or ν(CO); however, in both systems the ionization of the complexes and the adoption of η^2-*SC*SR coordination results in a decrease in ν(NO) and ν(CO). Table 1 summarizes the changes in infrared data for these two pairs of complexes in addition to the thiocarbonyl analogues of $\mathbf{6}^+$ and **7**, which show interconversion between the two forms (*vide infra*). These data indicate that the bidentate mode of (alkylthio)thiocarbonyl coordination results in a substantial transfer of electron density to the metal center relative to monodentate coordination. Upon σ-coordination the CS_2R ligand acts as a strong π-acid; however, η^2(SC) coordination renders it a strong donor ligand. These effects are presumably exaggerated by a stereochemistry at the metal center in which the sulfur donor ligates *trans* to the π-acid. Similar results are to be found for the analogous

(5) For a review of thiocarbonyl coordination chemistry see: Broadhurst, P. V. *Polyhedron* **1985**, *4*, 1801.
(6) Fenster, A. E.; Butler, I. S. *Inorg. Chem.* **1974**, *13*, 915.
(7) Collins, T. J.; Roper, W. R. *J. Organomet. Chem.* **1977**, *139*, C9.
(8) Clark, G. R.; Marsden, K.; Rickard, C. E. F.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1988**, *338*, 393.
(9) Herberhold, M.; Hill, A. F.; McAuley, N.; Roper, W. R. *J. Organomet. Chem.* **1986**, *310*, 95.

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on September 3, 1996 on http://pubs.acs.org | doi: 10.1021/om960205+

Table 2. $^{31}P\{^1H\}$ NMR Data[a] for Monodentate and Bidentate Complexes of Phenoxythiocarbonyl and (Phenylthio)thiocarbonyl and Thiocarbamoyl[b] Ligands

complex	δ (ppm)
$[IrCl_2(CS_2Ph)(CO)L_2]$	−17.3
$[IrCl_2(CS_2Ph)(CS)L_2]$	−13.0[c]
$[IrCl_2(CSOR)(CO)L_2]$	−16.1
$[IrCl_2(CSOR)(CS)L_2]$	−9.6
$[IrCl(\eta^2\text{-}SCSPh)(CO)L_2]^+$	−1.8
$[IrCl(\eta^2\text{-}SCSPh)(CS)L_2]^+$	1.6
$[IrCl(\eta^2\text{-}SCNMe_2)(CO)L_2]^+$	−2.4
$[IrCl(\eta^2\text{-}SCNMe_2)(CS)L_2]^+$	−0.7

[a] Data obtained from saturated solution in $CDCl_3$ at 25 °C; R = C_6H_4Me-4. [b] Data from ref 10. [c] In equilibrium with *ca.* 5% of **8**·Cl.

thiocarbamoyl complex $[IrCl(\eta^2\text{-}SCNMe_2)(CO)(PPh_3)_2]^+$.[10] In general the thiocarbamoyl ligand shows a greater propensity for bidentate coordination, being a stronger net donor than either the alkoxythiocarbonyl or (alkylthio)thiocarbonyl ligand.

A similar reaction of **1b** with $ClCS_2Ph$ provides the salt $[IrCl(\eta^2\text{−}SCSPh)(CS)(PPh_3)_2]Cl$ (**8**·Cl), which is in solvent-dependent equilibrium with $[IrCl_2(CS_2Ph)(CS)(PPh_3)_2]$ (**9**). As with $\mathbf{6}^+$ and **7** in nonpolar or weakly polar solvents, *e.g.,* tetrahydrofuran, the neutral species **9** predominates. However, in more polar solvents (e.g., dichloromethane−ethanol mixtures) ionization is favored, followed by bidentate coordination of the (alkylthio)thiocarbonyl ligand. This would appear to be in contrast to the alkoxythiocarbonyl complexes described above but is supported by the greater tendency of thiocarbamoyl ligands to adopt bidentate coordination modes. The bidentate mode of coordination appears to be increasingly favored with increasing π-dative capacity of the thiocarbonyl substituent. The salt $[IrCl(\eta^2\text{-}SCNMe_2)(CO)(PPh_3)_2]Cl$ shows no tendency toward monodentate thiocarbamoyl coordination in the presence of excess halide.[10] The compounds **8**·Cl and **9** provide similar FAB-mass spectra independent of the solvent of crystallization suggesting preionization to **8**·Cl in the nba matrix. The base peaks for the spectra correspond to the ion $[IrCl(\eta^2\text{-}SCSPh)(CS)(PPh_3)_2]^+$ ($\mathbf{8}^+$), with minor fragmentations due to loss of ClSPh (8%) and sequential loss of phosphine (24%) and chloride (5%). The exclusive isolation of $\mathbf{8}^+$ is achieved by Cl/PF_6 metathesis and fractional crystallization of $[IrCl(\eta^2\text{-}SCSPh)(CS)(PPh_3)_2]PF_6$ (**8**·PF_6). $^{31}P\{^1H\}$ NMR data for the complexes **9** and $\mathbf{8}^+$ also further confirm the nature of the two isomers when compared with the related complexes discussed above. These data are summarized in Table 2 in addition to data for carbamoyl analogues,[10] and show that for all the neutral η^1 examples of (aryloxy)thiocarbonyl and (arylthio)thiocarbonyl complexes, a singlet resonance is observed in the region δ −9.6 to −17.3 ppm. These data span a wider range of values than for the bidentate isomers, which give rise to peaks in the range δ +1.6 to −2.4 ppm.

The position of the ionization equilibrium does not interfere with the next step on the way to a bis(thiocarbonyl) complex. Roper has previously described the use of iodine to cleave a methylthio group (as ISMe) from a (methylthio)thiocarbonyl ligand: $[IrCl_2(CS_2Me)(CO)(PPh_3)_2]$ reacts with iodine to provide the salt $[IrCl_2(CO)(CS)(PPh_3)2]I_3$ and MeSI.[11] A similar reaction ensues between **8**·Cl/**9** and iodine to provide green $[IrCl_2(CS)_2(PPh_3)_2]I_3$ (**10**·I_3). Our interest in the complex $\mathbf{10}^+$ stems from its anticipated reactivity toward nucleophiles, and accordingly, the triiodide counteranion was considered inappropriate. Attempts to metathesize this with NH_4PF_6 in dichloromethane/ethanol mixtures were unsuccessful, due to the reaction of ethanol with one of the thiocarbonyl ligands to provide an as yet uncharacterized compound. An alternative preparation of $\mathbf{10}^+$ was therefore investigated, using iodine monochloride as the source of electrophilic iodine but providing the more "innocent" chloride counteranion. The reaction of **8**·Cl/**9** with ICl leads to clean formation of orange $[IrCl_2(CS)_2(PPh_3)_2]Cl$ (**10**·Cl) in high yield, indicating that the intense green color of the triiodide salt stems from the counteranion and not the metal complex. The stereochemistry at iridium is *cis,cis,trans,* as indicated by the appearance of a singlet resonance in the $^{31}P\{^1H\}$ NMR at δ −11.2 ppm for **10**·I_3 (δ −11.0 ppm for **10**·Cl). Two $\nu(IrCl_2)$ absorptions are observed (320, 300 cm^{-1}), indicating the *cis* $IrCl_2$ stereochemistry. Two ν(CS)-associated infrared absorptions are observed (KBr disc, 1425, 1357; CH_2Cl_2, 1438, 1369 cm^{-1}) to particularly high frequency, indicating both the electron-poor nature of the iridium center and the mutual *cis* disposition of the two thiocarbonyl ligands. These values may be compared with 1400 cm^{-1} for $[IrCl_2(CO)(CS)(PPh_3)_2]^+$ [11] and 1370 and 1260 cm^{-1} for $[OsCl_2(CS)_2(PPh_3)_2]$.[7,8] The complexes are formally isoelectronic, and spectroscopic data are comparable notwithstanding the perturbations associated with the more electron poor iridium centers (cationic Ir(III) *vs* neutral Os(II)). These changes are reflected in an increase of approximately 0.82 N m^{-1} of the thiocarbonyl Cotton−Kraihanzel force constants from 7.00 N m^{-1} for the osmium complex to 7.82 N m^{-1} for the iridium salt. Finally, the low-field region of the $^{13}C\{^1H\}$ NMR spectrum shows a triplet resonance at 232.4 ppm with a reduced coupling to phosphorus (J(PC) = 5.4 Hz) relative to that in, *e.g.,* **4**.

The facile cleavage of ISMe from $[IrCl_2(CS_2Me)(CO)(PPh_3)_2]$ by iodine to provide $[IrCl_2(CO)(CS)(PPh_3)_2]^+$ suggested that **7** should also serve as a precursor for this cationic complex. This proved not to be the case. Reaction of **7** with iodine provided the neutral iridium(III) thiocarbonyl complex $[IrClI_2(CS)(PPh_3)_2]$. The reasons for the different outcomes for the two iodination reactions remain obscure.

Preparation of $[Ir(CNC_6H_3Me_2\text{-}2,6)_2(CS)(PPh_3)_2]Cl$. One exciting aspect of thiocarbonyl chemistry to emerge in recent times is the tendency of this ligand to enter into migratory insertion reactions, even involving ligands with such negligible migratory aptitude as hydrides[12] and σ-silyls.[13] The complex **4**, with both a hydride and a thiocarbonyl ligand, might appear to be a suitable precursor for thioformyl complexes. Treating **4** with isonitriles might be expected to trap such a species, should it be in tautomeric equilibrium with **4**. Reaction of **4**, however, with excess $CNC_6H_3Me_2$-2,6

(10) Hill, A. F.; Wilton-Ely, J. D. E. T., manuscript in preparation.

(11) Roper, W. R.; Town, K. G. *J. Chem. Soc., Chem. Commun.* **1977**, 781.

(12) Collins, T. J.; Roper, W. R. *J. Organomet. Chem.* **1978**, *159*, 73.

(13) Rickard, C. E. F.; Roper, W. R.; Salter, D. M.; Wright, L. J. *Organometallics* **1992**, **11**, 2323.

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on September 3, 1996 on http://pubs.acs.org | doi: 10.1021/om960205+

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on September 3, 1996 on http://pubs.acs.org | doi: 10.1021/om960205+

leads not to the thioformyl complex $[IrCl_2\{C(=S)H\}(CNC_6H_3Me_2\text{-}2,6)(PPh_3)_2]$ but rather *via* reductive dehydrochlorination to the monovalent iridium salt $[Ir(CNC_6H_3Me_2\text{-}2,6)_2(CS)(PPh_3)_2]Cl$ (**11**·Cl), which may be metathesized with $NH_4[PF_6]$ to give **11**·PF_6. The geometry about iridium does not follow unambiguously from spectroscopic data, in that trigonal-bipyramidal structures with either *trans*-axial or *cis*-equatorial isocyanide ligands are plausible. The $^{31}P\{^1H\}$ NMR spectrum consists of a singlet (δ 7.53 ppm), while the ^1H NMR spectrum indicates that the four isonitrile methyl groups are equivalent (δ 1.80 ppm). The infrared spectrum shows three isonitrile bands both in the solid state (Nujol: 2171, 2141, 2112 cm^{-1}) and in solution (CH_2Cl_2: 2176, 2136, 2108 cm^{-1}), although there is only one resolvable ν(CS)-associated absorption (Nujol: 1283 cm^{-1}) in a region consistent with "CS" bound to monovalent cationic iridium. Two possibilities are considered. First, there may be an intramolecular Berry pseudorotation interconverting the two isomers, or second, the complex may be in dissociative equilibrium with the coordinatively unsaturated complex $[Ir(CNC_6H_3Me_2\text{-}2,6)(CS)(PPh_3)_2]^+$, with either of these processes occurring within the ^{31}P and ^1H NMR time scales. The peaks in the aryl region of the $^{13}C\{^1H\}$ NMR spectrum are somewhat broad; however, a virtual triplet due to the *ipso* carbon nuclei of the phosphine ligands is apparent, suggesting that the the *trans*-bis(phosphine) geometry is adopted. The salt **11**·Cl is also obtained from the reaction of preformed and isolated **1b** with excess $CNC_6H_3Me_2$-2,6; thus, it is not clear whether in the transformation **4** → **11**·Cl reversible dehydrochlorination occurs prior to isonitrile coordination or if intermediates of the form $[IrHCl(CNC_6H_3Me_2\text{-}2,6)(CS)(PPh_3)_2]Cl$ are involved.

Experimental Section

General Procedures. Unless otherwise indicated, all manipulations were carried out under aerobic conditions using solvents and reagents as received from commercial sources. Vaska's complex $[IrCl(CO)(PPh_3)_2]$ was prepared according to the method outlined in ref 14, with the exception that hexachloroiridic acid was used in place of iridium(III) chloride with no substantial compromise in yield. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a JEOL JNM EX270 NMR spectrometer and calibrated against internal Me_4Si (^1H), internal $CDCl_3$ (^{13}C), or external H_3PO_4 (^{31}P). Infrared spectra were recorded using a Perkin-Elmer 1720-X FT-IR spectrometer. Characteristic absorptions due to coordinated triphenylphosphine are omitted from the data below. FAB mass spectrometry was carried out using an Autospec Q mass spectrometer employing nitrobenzyl alcohol as matrix. Abundances are given for the major peak of isotopic envelopes confirmed by simulation. For salts, "M" refers to the cationic complex. Elemental microanalytical data were obtained from the ICSTM microanalytical service.

Synthesis of $[IrCl_2\{C(=S)OC_6H_4Me\text{-}4\}(CO)(PPh_3)_2]$ (2). A suspension of $[IrCl(CO)(PPh_3)_2]$ (3.70 g, 4.75 mmol) and $ClC(=S)OC_6H_4Me$-4 (0.80 cm^3, 0.98 g, 5.3 mmol) in tetrahydrofuran (10 cm^3) was stirred for 1 h, and then ethanol (20 cm^3) was added. Concentration under reduced pressure provided yellow crystals, which were isolated by filtration and washed with light petroleum ether. The complex is mildly light sensitive as a solid. Yield: 4.35 g (95%). IR (cm^{-1}) in Nujol, 2074, 2054 (ν(CO)), 1119, 1008 (ν(COC) and ν(C=S)), 821 ($\delta(C_6H_4)$); in CH_2Cl_2, 2076, 2061 (ν(CO)); in CsI, 317, 271 (*cis* $\nu(IrCl_2)$). NMR ($CDCl_3$, 25 °C): ^1H δ 2.21 [s, 3 H, CH_3], 5.68, 6.84 [(**AB**)$_2$, 4 H, J(**AB**) = 8.3 Hz, C_6H_4], 7.36, 8.01 [m × 2, 20 H, PC_6H_5] ppm; $^{13}C\{^1H\}$ δ 215.4 [t, J(PC) = 5.4 Hz, IrCSO], 156.4 [t, J(PC) = 7.2 Hz, IrCO], 153.9 [s, $C^1(OC_6H_4)$], 134.9, 130.8, 128.8, 127.9 [vt × 4, $C^{(3,5),4,(2,6)}(PC_6H_5)$], *ca.* 115.1 [s, $C^4(OC_6H_4)$], 128.8 [s, $C^{2,6}(OC_6H_4)$], 121.3 [s, $C^{3,5}(OC_6H_4)$], 20.7 [s, CH_3] ppm; $^{31}P\{^1H\}$:, −16.1 ppm. FAB-MS: *m*/*z* (% abundance) [assignment] 967 (2.4) $[M]^+$, 931 (100) $[M - Cl]^+$, 903 (9) $[M - Cl - CO]^+$, 859 (7) $[M - OR]^+$, 796 (5) $[M - CO - Cl - OR]^+$, 751 (3) $[M - Cl - CO - CSOR]^+$, 669 (5) $[M - Cl - PPh_3]^+$, 641 (36) $[M - Cl - CO - PPh_3]^+$, 605 (12) $[M - Cl_2 - CO - PPh_3]^+$, 497 (21) $[Ir(CS)(PPh_3)]^+$, 453 (10) $[Ir\text{-}PPh_3]^+$, 297 (61) $[Ph_3PHCl]^+$, 262 (32) $[PPh_3]$. Anal. Found: C, 54.8; H, 3.8. Calcd for $C_{45}H_{37}Cl_2IrO_2P_2S\cdot0.25CH_2Cl_2$: C, 55.0; H, 3.8. The solvent of crystallization was confirmed by NMR integration.

Synthesis of $[IrHCl\{C(=S)OC_6H_4Me\text{-}4\}(CO)(PPh_3)_2]$ (3). A magnetically stirred solution of **2** (4.30 g, 4.45 mmol) in tetrahydrofuran (100 cm^3) and ethanol (100 cm^3) was treated with a filtered solution of sodium borohydride (0.40 g, 10.5 mmol) in ethanol (30 cm^3). Stirring was continued for 60 min, during which time a pale green-yellow solid crystallized. The crystals were isolated by filtration, washed with ethanol (50 cm^3), and petroleum ether (50 cm^3) and dried *in vacuo*. The product could be recrystallized from a mixture of dichloromethane and ethanol; however, the crude material obtained above was of sufficent purity for spectroscopic and preparative purposes. Yield: 3.90 g (94%). IR (cm^{-1}) Nujol, 2051, 1992 (νCO), 1276, 1259, 1130, 1001, 946, 880, 825 in CH_2Cl_2, 2039 (ν(CO)); in CsI, 310 (ν(IrCl)). NMR ($CDCl_3$, 25 °C): ^1H, δ −11.0 [t, 1 H, J(PC) = 14.5 Hz, IrH], 2.22 [s, 3 H, CH_3], 5.72, 6.89 [(**AB**)$_2$, 4 H, J(**AB**) = 8.3 Hz], 7.4, 7.7 [m × 2, 30 H, PC_6H_5] ppm; $^{13}C\{^1H\}$, δ 268.5 [dt, J(HC) ≈ J(PC) ≈ 7 Hz, IrCSO], 161.8 [t, J(PC) = 8.1 Hz, IrCO], 155.6 [s, $C^1(OC_6H_4)$], 134.8, 131.0, 130.5, 128.2 [vt × 4, $C^{(3,5),4,(2,6)}(PC_6H_5)$], 134.4 [s, $C^4\text{-}(OC_6H_4)$], 129.0 [s, $C^{2,6}(OC_6H_4)$], 122.2 [s, $C^{3,5}(OC_6H_4)$], 20.9 [s, CH_3]; $^{31}P\{^1H\}$, δ −2.20. FAB-MS: *m*/*z* (% abundance) [assignment] 933 (24) $[M]^+$, 897 (4) $[M - Cl]^+$, 869 (3) $[M - Cl - CO]^+$, 825 (11) $[M - HOR]^+$, 781 (42) $[M - HCSOR]^+$, 745 (28) $[M - Cl - HCSOR]^+$, 635 (8) $[M - Cl - PPh_3]^+$, 483 $[Ir(CO)\text{-}(PPh_3)]^+$, 263 (100) $[HPPh_3]^+$. Anal. Found: C, 56.2; H, 4.1. Calcd for $C_{45}H_{38}ClIrO_2P_2S\cdot0.5CH_2Cl_2$: C, 56.1; H, 4.0. The solvent of crystallization was confirmed by NMR integration.

Synthesis of $[IrHCl_2(CS)(PPh_3)_2]$ (4). A solution of (**3**) (0.20 g, 0.22 mmol) in dichloromethane (10 cm^3) was treated with concentrated hydrochloric acid (1 cm^3). Ethanol (20 cm^3) was then added, and the total solvent volume was reduced to *ca.* 10 cm^3. The colorless microcrystals which formed were isolated by filtration, washed with ethanol (2 × 10 cm^3) and light petroleum ether (2 × 10 cm^3), and dried *in vacuo*. The complex was recrystallized from a mixture of dichloromethane and ethanol. Yield: 0.15 g (84%). A larger scale run (3.80 g) resulted in an improved yield [3.25 g (96%)]. IR (cm^{-1}): Nujol, 2022 (ν(IrH)), 1358 (ν(CS)); in CsI 1357 (ν(CS)), 293, 261 (*cis*-$IrCl_2$). NMR ($CDCl_3$, 25 °C):^1H, δ −13.9 [t, 1 H, J(PH) = 11.2 Hz, IrH], 7.39, 7.82 [m × 2, 30 H, PC_6H_5]; $^{13}C\{^1H\}$, insufficiently soluble in $CDCl_3$, $(CD_3)_2CO$, or CD_2Cl_2; $^{31}P\{^1H\}$, δ 1.86. FAB-MS: useful data not obtained. Anal. Found: C, 51.7; H, 3.6. Calcd for $C_{37}H_{31}Cl_2IrP_2S\cdot0.25CH_2Cl_2$: C, 51.5; H, 3.7.

Synthesis of $[IrCl(CS)(PPh_3)_2]$ (1b). (a) From 4. A solution of **4** (0.90 g, 1.1 mmol) in dichloromethane (50 cm^3) and ethanol (20 cm^3) was treated with DBU (0.5 cm^3). The mixture was stirred for 1 h, during which time bright orange crystals formed. The suspension was concentrated under reduced pressure to *ca.* 30 cm^3, and the orange *microcrystals* were isolated by filtration, washed with ethanol (2 × 10 cm^3) and light petroleum ether (10 cm^3), and dried *in vacuo*. Yield: 0.67 g (78%).

(b) From 1a. A suspension of **1a** (4.00 g, 5.13 mmol) in tetrahydrofuran (100 cm^3) was treated with $ClC(=S)OC_6H_4$-Me-4 (1.2 cm^3, 1.43 g, 7.67 mmol) and the mixture stirred for

(14) Vrieze, K.; Collman, J. P.; Sears, C. T., Jr.; Kubota, M. *Inorg. Synth.* **1968**, *11*, 101.

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on September 3, 1996 on http://pubs.acs.org | doi: 10.1021/om960205+

1 h. Ethanol (100 cm^3) was then added, followed by a filtered solution of sodium borohydride (0.50 g, 13 mmol, excess) in ethanol (50 cm^3), and the mixture was stirred for 60 min. The solvent was then removed under reduced pressure, the residue was extracted with dichloromethane, and the combined extracts were filtered through diatomaceous earth. To the resulting filtrate was added concentrated hydrochloric acid (*ca.* 5 cm^3), and the mixture was stirred for 20 min or until the solution was colorless. Ethanol (100 cm^3) was then added, the total solvent volume was reduced to *ca.* 80 cm^3, and the supernatant was decanted from the colorless precipitate. The precipitate was washed by decantation with ethanol (3 × 20 cm^3) and then suspended in dichloromethane (100 cm^3) and treated with DBU (4.0 cm^3, 3.93 g, 25.8 mmol) and stirred until all of the white solid had dissolved to give a bright orange solution (*ca.* 60 min). This solution was then diluted with ethanol and concentrated under reduced pressure to provide orange crystals of **1b**, which were washed with ethanol (4 × 20 cm^3) and light petroleum ether (20 cm^3) and dried *in vacuo*. Yield: 3.00 g (75% based on **1a**). IR and elemental microanalytical data for **1b** are comparable to those previously reported.[3] NMR ($CDCl_3$, 25 °C): $^{31}P\{^1H\}$ δ 8.0 ppm. FAB-MS: *m/z* (% abundance) [assignment] 796 (47) $[M]^+$.

Synthesis of [$IrCl_2${C(=S)OC_6H_4Me-4}(CS)(PPh_3)$_2$] (5). A suspension of [IrCl(CS)(PPh_3)$_2$] (0.28 g, 0.35 mmol) and ClC(=S)OC_6H_4Me-4 (0.06 cm^3, 0.07 g, 0.39 mmol) in tetrahydrofuran (10 cm^3) was stirred for 30 min, and then ethanol (30 cm^3) was added, followed by hexane (20 cm^3). Concentration under reduced pressure provided a precipitate of the crude material, which was crystallized from a mixture of dichloromethane and hexane. The compound is mildly light sensitive as a solid and is not amenable to chromatography. Yield: 0.25 g (72%). IR (cm^{-1}): in Nujol, 1365 (ν(CS)), 1113, 999 (ν(COC) and ν(C=S)), 820 ($\delta(C_6H_4)$); in CH_2Cl_2, 1369 (ν(CS)). NMR ($CDCl_3$, 25 °C): ^1H, δ 2.24 [s, 3 H, CH_3], 5.90, 6.92 [(**AB**)$_2$, 4 H, J(**AB**) = 8.4 Hz, C_6H_4], 7.34, 8.02 [m × 2, 20 H, PC_6H_5]; $^{13}C\{^1H\}$, δ 244.9 [t, J(PC) = 8.0 Hz, IrCS], 218.3 [t, J(PC) = 5.4 Hz, IrCSO], 154.3 [s, $C^1(OC_6H_4)$], 135.6, 130.7, 127.6 [vt × 3, $C^{(3,5),4,(2,6)}(PC_6H_5)$], 129.6 [vt + s, $C^1(PC_6H_5)$ and $C^{3,5}(OC_6H_4)$], 115.2 [s, $C^4(OC_6H_4)$], 20.8 [s, CH_3]; $^{31}P\{^1H\}$, δ −9.64. FAB-MS: *m/z* (% abundance) [assignment] 947 (100) $[M - Cl]^+$, 685 (41) $[M - PPh_3]^+$, 649 (13) $[M - HCl - PPh_3]^+$, 262 $[PPh_3]^+$. Anal. Found: C, 54.7; H, 3.8. Calcd for $C_{45}H_{37}Cl_2IrOP_2S_2$: C, 55.0; H, 3.8.

Synthesis of [$IrCl_2(CS_2Ph)(CO)(PPh_3)_2$] (7). Under an atmosphere of dry dinitrogen, a suspension of **1a** (0.50 g, 0.64 mmol) in dried and degassed tetrahydrofuran (30 cm^3) was treated with ClC(=S)SPh (0.10 cm^3, 0.13 g, 0.71 mmol), resulting in a deep orange solution being formed. The mixture was stirred for 1 h and then diluted with ethanol (30 cm^3). Concentration under reduced pressure provided crystals of the desired complex **7**, which were isolated by filtration, washed with ethanol (10 cm^3) and light petroleum ether (10 cm^3), and dried *in vacuo*. Yield: 0.60 g (95%). IR (cm^{-1}): in Nujol, 2069 (ν(CO)), 1009, 910 (ν(SCS)); in CH_2Cl_2, 2062 (ν(CO)). NMR ($CDCl_3$, 25 °C): ^1H, δ = 6.14 [d, 2 H, J(HH) = 7.3 Hz, $H^{2,6}(SC_6H_5)$], 7.10, 7.20 [t × 2, 3 H, J(HH) = 7.3 Hz, $H^{3-5}(SC_6H_5)$], 7.33−8.00 [m, 30 H, PC_6H_5]; $^{13}C\{^1H\}$ δ 232.6 [t(br), SCS, J(PC) not resolved], 156.0 [t(br), IrCO, J(PC) not resolved], 136.1 [s, $C^1(SC_6H_4)$], 135.3 , 130.8, 129.1, 127.9 [vt × 4, $C^{(3,5),4,(2,6)}(PC_6H_5)$], 133.7 [s, $C^{3,5}(SC_6H_4)$], 128.6 [s, $C^4(SC_6H_4)$], 128.4 [s, $C^{2,6}(SC_6H_4)$]; $^{31}P\{^1H\}$, δ −17.3 (br; peak half-height ≈ 1 ppm). FAB-MS: *m/z* (% abundance) [assignment] 933 (92) $[M - Cl]^+$, 905 (4) $[M - Cl - CO]^+$, 796 (6) $M - Cl - CO - SPh]^+$, 761 (3) $M - 2Cl - CO - SPh]^+$, 643 (82) $[M - Cl - CO - PPh_3]^+$, 607 (12) $[M - 2Cl - CO - PPh_3]^+$. N.B.: The major components of this spectrum correspond to those of **6**·PF_6, suggesting virtually complete ionization of **7** to $\mathbf{6}^+$ in the nba matrix. Anal. Found: C, 48.9; H, 3.3. Calcd for $C_{44}H_{35}Cl_2IrOP_2S_2$·$2CH_2Cl_2$: C, 48.6; H, 3.5.

Synthesis of [$IrCl(\eta^2$-SCSPh)(CO)(PPh_3)$_2$]PF_6 (6·PF_6). A solution of **7** (0.20 g, 0.21 mmol) in dichloromethane (20 cm^3) and ethanol (10 cm^3) was treated with a solution of $NH_4[PF_6]$ (0.10 g, 0.61 mmol, excess) in water (1 cm^3) and ethanol (30 cm^3). Slow concentration of the mixture under reduced pressure provides the salt **6**·PF_6 in quantitative yield. IR (cm^{-1}): in Nujol, 2028 (ν(CO)), 1136 (ν(SCS)); in CH_2Cl_2, 2047 (ν(CO)). NMR ($CDCl_3$, 25 °C): ^1H, δ 6.44 [d, 2 H, J(HH) = 7.3 Hz, $H^{2,6}(SC_6H_5)$], 7.24−7.97 [m, 33 H, PC_6H_5 and $H^{3-5}(SC_6H_5)$]; $^{13}C\{^1H\}$, δ 238.6 [t, SCS, J(PC) ≈ 3.6 Hz], 168.8 [t, IrCO, J(PC) = 8.9 Hz], 134.4−125.7 [C_6H_5]; $^{31}P\{^1H\}$ δ −1.77. FAB-MS: *m/z* (% abundance) [assignment] 933 (100) $[M]^+$, 905 (3) $[M - CO]^+$, 780 (2) $[M - CS_2Ph]^+$, 643 (53) $[M - CO - PPh_3]$. Anal. Found: C, 49.1; H, 3.1. Calcd for $C_{44}H_{35}ClF_6IrOP_3S_2$: C, 49.0; H, 3.3.

Synthesis of [$IrCl_2(CS_2Ph)(CS)(PPh_3)_2$] (9). A suspension of **1b** (0.20 g, 0.25 mmol) in benzene (10 cm^3) was treated with ClC(=S)SPh (0.03 cm^3, 0.04 g, 0.28 mmol), resulting in dissolution of **1b**. The mixture was stirred for 60 min and then freed of volatiles under reduced pressure. The residue was then crystallized from a mixture of tetrahydrofuran and cyclohexane to provide the desired complex **9**. Yield: 0.22 g (89%). IR (cm^{-1}): in Nujol, 1363 (ν(CS)), 1029 (ν(SCS)). NMR ($CDCl_3$, 25 °C):^1H, δ 6.35 [d, 2 H, J(HH) = 7.1 Hz, $H^{2,6}(SC_6H_5)$], 7.15, 7.24 [t × 2, 3 H, J(HH) = 7.1 Hz, $H^{3-5}(SC_6H_5)$], 7.30−8.09 [m, 30 H, PC_6H_5]; $^{13}C\{^1H\}$, δ 242.8 [t(br), IrCS, J(PC) ≈ 7.1 Hz], 136.4 [s, $C^1(SC_6H_4)$], 135.6, 130.6, 128.9 [vt(br) × 3, $C^{(3,5),4,1}(PC_6H_5)$], 133.7 [s, $C^{3,5}(SC_6H_4)$], 128.5 [s, $C^4(SC_6H_4)$], 127.6 [vt(br) + s, $C^{2,6}(PC_6H_5)$ and $C^{2,6}(SC_6H_4)$]; $^{31}P\{^1H\}$, δ 1.61 [20% intensity] (**8**$^+$), −13.0 [100% intensity] (**9**) (br; peak half-height ≈ 1 ppm). FAB-MS: *m/z* (% abundance) [assignment] 949 (92) $[M - Cl]^+$, 805 (5) $[M - ClSPh]^+$, 687 (18) $[M - PPh_3]^+$, 651 (4) $[M - Cl - PPh_3]^+$, 262 (32) $[PPh_3]^+$. Anal. Found: C, 54.6; H, 4.1. Calcd for $C_{44}H_{35}Cl_2IrP_2S_3$·$0.25C_6H_{11}$: C, 54.3; H, 3.8.

Synthesis of [$IrCl(\eta^2$-SCSPh)(CS)(PPh_3)$_2$]PF_6 (8.PF_6). A solution of **1b** (0.10 g, 0.13 mmol) in dichloromethane (20 cm^3) and ethanol (15 cm^3) was treated with ClC(=S)SPh (0.02 cm^3, 0.027 g, 0.14 mmol), causing an immediate color change to deep yellow. The mixture was stirred for 30 min and then treated with $K[PF_6]$ (0.05 g, 0.27 mmol), and stirring was continued for a further 1 h. The solvent was then removed under reduced pressure and the residue extracted with dichloromethane (2 × 10 cm^3), and the combined extracts were filtered through diatomaceous earth to remove KCl. The filtrate was then diluted with ethanol (10 cm^3). Slow concetration of the solution under reduced pressure provided crystals of **8**·PF_6 which were isolated by filtration, washed with ethanol (10 cm^3) and light petroleum ether (10 cm^3), and dried *in vacuo*. Yield: 0.13 g (91%). IR (cm^{-1}): in Nujol, 1360 (ν(CS)), 1124, 1042, 923. NMR ($CDCl_3$, 25 °C): ^1H, δ 6.35 [d, 2 H, J(HH) = 6.9 Hz, $H^{2,6}$(SPh)], 7.2−8.1 [m × 6, 33 H, H^{3-5}(SPh) and PPh]; $^{31}P\{^1H\}$, δ 1.61; $^{13}C\{^1H\}$, 250.9 [t, IrCS, J(PC) = 8.1 Hz], 241.5 [t, SCS, J(PC) ≈ 3.5 Hz], 135−124 [C_6H_5]. FAB-MS: *m/z* (% abundance) [assignment] 949 (100) $[M]^+$, 687 (18) $[M - PPh_3]^+$, 643 (2) $[M - PPh_3 - CS]^+$. Anal. Found: C, 48.2; H, 3.4. Calcd for $C_{44}H_{35}ClF_6IrP_3S_3$: C, 48.3; H, 3.2.

Synthesis of [$IrCl_2(CS)_2(PPh_3)_2$]I_3 (10·X). (a) **X = I_3: From 9.** A solution of **9** (0.10 g, 0.10 mmol) in tetrahydrofuran (5 cm^3) was treated with iodine (0.05 g, 2.0 mmol), and the mixture was stirred for 10 min, resulting in the precipitation of dark green crystals. These were isolated by filtration, washed with benzene (10 cm^3), and dried *in vacuo*. Yield: 0.075 g (61%). Comparable yields were obtained for runs based on 0.40 g of **9**.

(b) X = I_3: From 1b. A suspension of **1b** (1.05 g, 1.32 mmol) in tetrahydrofuran (30 cm^3) was treated with ClC(=S)-SPh (0.20 cm^3, 0.27 g, 1.43 mmol), resulting in dissolution of **1b**. The mixture was stirred for 2 h and then treated with iodine (0.68 g, 2.70 mmol) and stirred for a further 20 min. The green crystals which formed were isolated by filtration and washed with benzene (2 × 10 cm^3) and dried *in vacuo*. Yield: 1.46 g (88%).

IR (cm^{-1}): in KBr disk, 1425, 1357 (ν(CS)); in CH_2Cl_2, 1436,

1365 (ν(CS)). NMR (CH_2Cl_2, 25 °C): ^{1}H, δ 7.54, 8.04 [m × 2, 30 H, PC_6H_5]; $^{31}P\{^1H\}$, δ −11.2. FAB-MS: *m*/*z* (% abundance) [assignment] 875 (0.5) $[M]^+$. Anal. Found: C, 36.1; H, 2.5. Calcd for $C_{38}H_{30}Cl_2I_3IrP_2S_2$: C, 36.3; H, 2.4.

(c) X = Cl: From 1b. In a similar manner to that described in (b) above, a solution of **1b** (0.15 g, 0.19 mmol) in tetrahydrofuran (5 cm^3) was treated with ClC(=S)SPh (0.025 cm^3, 0.033 g, 0.20 mmol), stirred for 2 h, and then treated with iodine monochloride (0.035 g, 0.22 mmol). The resulting orange solution was stirred for a further 20 min, during which time orange crystals of the product formed, which were isolated by filtration, washed with benzene (10 cm^3), and dried *in vacuo*. A further crop of crystals could be obtained by concentration of the filtrate. Yield: 0.15 g (87%). IR (cm^{-1}): in Nujol, 1435, 1361 (ν(CS)); in CH_2Cl_2, 1438, 1369 (ν(CS)); in KBr, 1425, 1357 (ν(CS)), 320, 300 (*cis*-ν($IrCl_2$)). NMR ($CDCl_3$, 25 °C): $^{31}P\{^1H\}$, δ −11.0; $^{13}C\{^1H\}$, δ 232.4 [t, Ir(CS)$_2$, *J*(PC) = 5.4 Hz], 134.9 [t, $C^{3,5}$(PPh), *J*(PC) = 4.5 Hz], 132.6 [s, C^4(PPh)], 128.8 [t, $C^{2,6}$(PPh), *J*(PC) = 5.3 Hz], 126.8 [t, C^1(PPh), *J*(PC) = 30.3 Hz]. FAB-MS: *m*/*z* (% abundance) [assignment] 875 (100) $[M]^+$, 843 (9) $[M - S]^+$, 615 (8) $[M - PPh_3]^+$, 541 (2) $[M - 2Cl - PPh_3]^+$, 497 (10) $[M - 2Cl - CS - PPh_3]^+$, 297 (63) $[Ph_3PCl]^+$, 262 (72) $[PPh_3]^+$.

Synthesis of [Ir(CNC$_6$H$_3$Me$_2$-2,6)$_2$(CS)(PPh$_3$)$_2$]Cl (11·Cl). A solution of (**4**) (0.56 g, 0.67 mmol) in dichloromethane (20 cm^3) was treated with 2,6-dimethylphenyl isocyanide (0.18 g, 1.40 mmol), and the mixture was stirred for 1 h. The solvent was then removed under reduced pressure and the residue triturated with light petroleum ether to remove unreacted isocyanide. The remaining residue could be crystallized from a mixture of dichloromethane and hexane to provide **11**·Cl; alternatively, the chloride counteranion could be metathesized with ammonium hexafluorophosphate to provide the more crystalline salt **11**·PF_6. The residue was then dissolved in dichloromethane (20 cm^3), and this solution was treated with a solution of $NH_4[PF_6]$ (0.15 g, 0.92 mmol) in water (1 cm^3) and ethanol (20 cm^3). Slow concentration of the mixture under reduced pressure affected crystallization of **11**·PF_6. Yield of **11**·Cl: 0.65 g (83%). IR (cm^{-1}): in Nujol, 2171, 2141, 2112 (ν(CN)), 1283 (ν(CS)); in CH_2Cl_2, 2176, 2136, 2108 (ν(CN)), 1292 (ν(CS)). NMR ($CDCl_3$, 25 °C): ^{1}H, δ 1.80 [s, 12 H, CH_3], 6.93 [d, 4 H, *J*(HH) = 7.9 Hz, $H^4(C_6H_3)$], 7.07 [t, 4 H, *J*(HH) = 7.9 Hz, $H^{3,5}(C_6H_3)$], 7.39, 7.57 [m × 2, 30 H, PC_6H_5]; $^{13}C\{^1H\}$, δ 283.4 [t, *J*(PC) = 14.3 Hz, IrCS], 135.3−126.5 [C_6H_3 and C_6H_5 including 130.3 (vt, $J(P_2C)$ = 30.3 Hz) for $C^1(PC_6H_5)$], 18.2 [s, CH_3]; $^{31}P\{^1H\}$, 7.53 [7.69 ppm for **9**·PF_6]. FAB-MS (X = $C_6H_3Me_2$-2,6): *m*/*z* (% abundance) [assignment] = 1023 (12) $[M]^+$, 892 (89) $[M - CNX]^+$, 796 (9) $M - CNX + Cl]^+$, 761 (100) $[M - 2CNX]^+$, 717 (7) $[M - CS - CNX]^+$, 630 (14) $[M - PPh_3]^+$, 497 (17) $[M - PPh_3 - CNX]^+$. Anal. Found: C, 58.0; H, 4.5; N, 2.4. Calcd for $C_{55}H_{48}ClIrN_2P_2S$·1.25(CH_2Cl_2): C, 58.0; H, 4.4; N, 2.4. The solvent of crystallization was confirmed by NMR integration.

Acknowledgment. We wish to thank the Engineering and Physical Sciences Research Council (U.K.) for the award of a studentship (to J.D.E.T.W.-E.).

OM960205+

Downloaded by CARLI CONSORTIUM on June 30, 2009
Published on September 3, 1996 on http://pubs.acs.org | doi: 10.1021/om960205+