

Preparation and Reactivity of η -Cyclopentadienyl(thiocarbonyl)(triphenylphosphine)-rhodium(I) and -iridium(I): Formation of Methyl(methylthio)methylene Complexes

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The complexes $[M(\eta\text{-C}_5\text{H}_5)(\text{CS})(\text{PPh}_3)]$ [$M = \text{Rh}$ (1) or Ir (2)] have been synthesized from $[\text{MCl}(\text{CS})(\text{PPh}_3)_2]$ and sodium cyclopentadienide. The behaviour of the new thiocarbonyl complexes in their reactions with halogens or dry hydrogen chloride is similar to that observed for analogous carbonyl derivatives. The complexes $[\text{Rh}(\eta\text{-C}_5\text{H}_5)\text{X}(\text{CS})(\text{PPh}_3)]\text{X}$ ($\text{X} = \text{Cl, Br, or I}$) have been obtained by treating (1) with halogens at liquid-nitrogen temperature; on increasing the temperature these rearrange to $[\text{Rh}(\eta\text{-C}_5\text{H}_5)\text{X}_2(\text{PPh}_3)]$. The analogous cationic iridium(III) complexes are more stable and can be obtained at room temperature. Complex (1) reacts with dry HCl giving probably $[\{\text{RhCl}(\text{CS})(\text{PPh}_3)\}_2]$; in the same reaction (2) gives the cationic hydride $[\text{Ir}(\eta\text{-C}_5\text{H}_5)\text{H}(\text{CS})(\text{PPh}_3)]\text{Cl}$. The reactions of (1) and (2) with MeI afford the thiocarbene species $[\text{M}(\eta\text{-C}_5\text{H}_5)\{\text{CMe}(\text{SMe})\}(\text{PPh}_3)]\text{I}$ which has been isolated analytically pure only for the iridium derivative. The reactions of the complexes $[\text{MCl}(\text{CS})(\text{PPh}_3)_2]$ ($M = \text{Rh or Ir}$) with MeI have also been investigated. A possible mechanism of formation of the carbene species is proposed, and the influence of the metal-methyl σ -bond strength in the oxidative-addition product formed in the first step of this reaction is discussed. Complexes (1) and (2) react with HgCl_2 giving the adducts $[\text{M}(\eta\text{-C}_5\text{H}_5)(\text{CS})(\text{HgCl}_2)(\text{PPh}_3)]$. The i.r. and ^1H n.m.r. spectra of the complexes prepared are discussed.

An aspect of organotransition-metal chemistry in which there have recently been interesting developments concerns thiocarbonyl derivatives.¹ Thus, various synthetic routes to complexes of this type have been discovered²⁻⁸ and studies have been performed with the aim of comparing the reactivity of co-ordinated thiocarbonyl with that of carbonyl in analogous metal complexes.^{4,9} The interest in such comparisons arises from the fact that, although carbonyl and thiocarbonyl complexes display certain similarities in terms of electronic structure,¹⁰ in some cases nucleophilic attack at the carbon atom^{5,9a,11} and electrophilic attack at the sulphur^{12,13} of the co-ordinated thiocarbonyl ligand have been observed.

We have prepared new rhodium(I) and iridium(I) complexes $[\text{M}(\eta\text{-C}_5\text{H}_5)(\text{CS})(\text{PPh}_3)]$ ($M = \text{Rh or Ir}$) and studied their reactions with halogens, hydrogen chloride, methyl iodide, and Lewis acids. The results of these reactions might usefully be compared with the oxidative-addition reactions of the analogous carbonyl derivatives which have been well studied.¹⁴⁻¹⁶

RESULTS AND DISCUSSION

The complexes $[\text{Rh}(\eta\text{-C}_5\text{H}_5)(\text{CS})(\text{PPh}_3)]$ (1) and $[\text{Ir}(\eta\text{-C}_5\text{H}_5)(\text{CS})(\text{PPh}_3)]$ (2) are obtained by treating the known complexes $[\text{MCl}(\text{CS})(\text{PPh}_3)_2]$ ($M = \text{Rh or Ir}$) with sodium cyclopentadienide in refluxing benzene. Using tetrahydrofuran as solvent, in which the sodium cyclopentadienide was prepared, the products are obtained in lower yields owing to partial decomposition. A similar method, which implies the displacement of a phosphine ligand by the cyclopentadienyl π -electron system, was adopted in the preparation of $[\text{M}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)]$ ¹⁵ ($M = \text{Rh or Ir}$) and $[\text{Co}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)_2]$.¹⁷

Complexes (1) and (2) are orange solids, soluble in the common solvents including saturated hydrocarbons, and stable in the solid state and in solution. In the i.r. spectrum, $\nu(\text{CS})$ was observed at a lower wavenumber

than that of the starting rhodium(I) and iridium(I) complexes. In the ^1H n.m.r. spectrum the cyclopentadienyl resonance of (1) and (2) was observed at τ values similar to those reported for the analogous carbonyl derivatives.^{14,15} This indicates that the net result of the $\sigma + \pi$ synergistic interaction of the CS and the metal is very similar to that of CO in the analogous carbonyl derivatives. The C_5H_5 resonance was observed as a doublet owing to coupling of the protons of the η -cyclopentadienyl and the phosphorus; the size of this coupling is similar to that observed in related cyclopentadienyl-rhodium(I) and -iridium(I) complexes.^{14,15-18} For complex (1) the ^{103}Rh coupling to the cyclopentadienyl ring protons seems to be beyond the resolution of the spectrophotometer.

In the thiocarbonyl-rhodium(III) and -iridium(III) complexes, obtained by oxidative-addition reactions of (1) and (2) (see below), $\nu(\text{CS})$ is observed at higher wavenumber than the starting substrate owing to diminished back donation $d_{\pi}-p_{\pi}$ from the metal to the CS ligand; a deshielding of the C_5H_5 ring protons relative to the values for (1) and (2) is also observed. This is indicative of increased ring π -bond order resulting from a decrease in the metal-to-ring $d-\pi^*$ back bonding as a result of the lower electron density on the metal. The $J(\text{P}-\text{C}_5\text{H}_5)$ values are larger for the rhodium(III) and iridium(III) derivatives than for the starting materials (1) and (2) and the increase is of the same order of magnitude as that observed in the analogous carbonyl complexes.^{14,15}

Halogens readily react, at room temperature, with a pentane solution of (1) giving the derivatives $[\text{Rh}(\eta\text{-C}_5\text{H}_5)\text{X}_2(\text{PPh}_3)]$ ($\text{X} = \text{Cl, Br, or I}$); some of these have been obtained by different methods.^{14,19,20} At lower temperature, halogens react with (1), in dichloromethane, giving the derivatives $[\text{Rh}(\eta\text{-C}_5\text{H}_5)\text{X}(\text{CS})(\text{PPh}_3)]\text{X}$ ($\text{X} = \text{Cl, Br, or I}$); these readily lose the thiocarbonyl group and are converted into neutral dihalogeno-derivatives. The tetraphenylborate salts, obtained by rapid reaction at -80°C , in methanol, of $[\text{Rh}(\eta\text{-C}_5\text{H}_5)\text{X}(\text{CS})(\text{PPh}_3)]\text{X}$

with $\text{Na}[\text{BPh}_4]$, are more stable, but decompose over several hours at room temperature.

Pentane solutions of (2) react easily with iodine and bromine, at room temperature, to form the ionic derivatives $[\text{Ir}(\eta\text{-C}_5\text{H}_5)\text{X}(\text{CS})(\text{PPh}_3)]\text{X}$ ($\text{X} = \text{Br}$ or I), which are stable in the solid state for limited periods. Chlorine reacts similarly but the product decomposes slowly and smells of H_2S . The ionic nature of these complexes was confirmed by conductivity measurements in methanol, and by the formation of the corresponding tetraphenylborate salts on reaction, in methanol, with $\text{Na}[\text{BPh}_4]$.

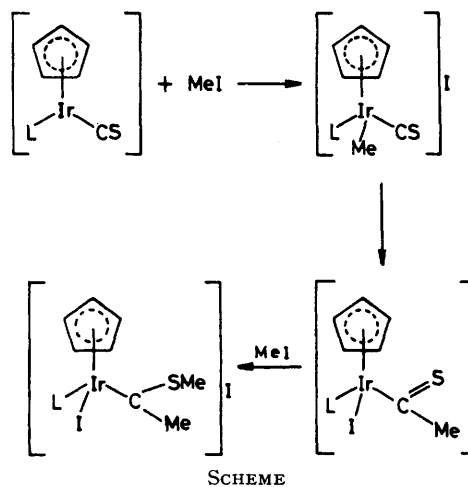
Complexes (1) and (2) react with dry hydrogen chloride giving different products. By bubbling HCl through a pentane solution of (1) a solid complex, which rapidly darkens, was obtained; even though this was not isolated in a pure form, spectral data suggest that it is $[\{\text{RhCl}(\text{CS})(\text{PPh}_3)_2\}]$. In fact, the i.r. spectrum shows $\nu(\text{CS})$ at $1\ 307\ \text{cm}^{-1}$ but no $\nu(\text{Rh-H})$ band, and the ^1H n.m.r. spectrum indicates that the complex does not contain the cyclopentadienyl ligand. The formulation as the chloride-bridged complex $[\{\text{RhCl}(\text{CS})(\text{PPh}_3)_2\}]$ has been confirmed by its reaction with PPh_3 which gave the well known $[\text{RhCl}(\text{CS})(\text{PPh}_3)_2]$. Thus the reaction of (1) with dry HCl seems to proceed in a similar way to the analogous reaction of the carbonyl derivative $[\text{Rh}(\eta\text{-C}_5\text{H}_5)(\text{CO})(\text{PPh}_3)]$.¹⁶ Also, in this case, a mechanism involving initial formation of a labile cationic hydrido-complex which undergoes hydrogen-ion migration on the cyclopentadienyl ring and co-ordination of the halide to the metal, leading to the formation of the final dimeric complex and free cyclopentadiene, seems reasonable.

A pentane solution of complex (2) reacts with dry hydrogen chloride giving immediately a white precipitate of $[\text{Ir}(\eta\text{-C}_5\text{H}_5)\text{H}(\text{CS})(\text{PPh}_3)]\text{Cl}$. The ^1H n.m.r. spectrum of the white solid shows the ring protons of the C_5H_5 resonance at $\tau\ 4.03$ (in CD_3OD) and in the i.r. spectrum the $\nu(\text{CS})$ band appears at $1\ 358\ \text{cm}^{-1}$; $\nu(\text{Ir-H})$ can be assigned at $2\ 160\ \text{cm}^{-1}$ {cf.²⁰ $[\text{Ir}(\eta\text{-C}_5\text{H}_5)\text{H}(\text{CO})(\text{PPh}_3)]\text{-}[\text{BPh}_4]$, $\nu(\text{Ir-H})$ at $2\ 142\ \text{cm}^{-1}$ } but its intensity decreases with time while a band at $2\ 045\ \text{cm}^{-1}$ appears. Rapid treatment of the protonated product, in methanol solution, with $\text{Na}[\text{BPh}_4]$ gave a white solid $[\text{Ir}(\eta\text{-C}_5\text{H}_5)\text{-H}(\text{CS})(\text{PPh}_3)]\text{[BPh}_4]$ for which the elemental analysis was satisfactory; for this complex the band at $2\ 045\ \text{cm}^{-1}$ is also present and it is more intense than that at $2\ 160\ \text{cm}^{-1}$. We are unable to explain the presence of two bands in the $\nu(\text{Ir-H})$ region because the limited solubility of the complex prevents the observation of variations in the hydridic region in the n.m.r.

Complex (2) and MeI react readily, at room temperature, giving red-orange crystals which analyze for $[\text{Ir}(\eta\text{-C}_5\text{H}_5)(\text{CS})(\text{PPh}_3)(\text{MeI})_2]$. Conductivity measurement, in methanol, indicates that the complex is a 1 : 1 electrolyte. Its ionic nature was confirmed by adding $\text{Na}[\text{BPh}_4]$ in methanol to a solution of the complex in the same solvent; a red solid, in which an iodine atom of the parent has been replaced by $[\text{BPh}_4]^-$, was obtained. On the basis of i.r. and ^1H n.m.r. spectral data, the

complex can be formulated as the thiocarbene $[\text{Ir}(\eta\text{-C}_5\text{H}_5)\{\text{CMe}(\text{SMe})\}\text{I}(\text{PPh}_3)]\text{I}$.^{*} In fact, the i.r. spectrum does not show the stretching band of the terminal thiocarbonyl group, and in the ^1H n.m.r. spectrum, besides peaks due to phenyl protons of PPh_3 and ring protons of C_5H_5 , singlets at $\tau\ 7.16$ and 6.32 , assignable respectively to CMe and SMe , were observed. A structure in which a methyl group is bonded to the iridium atom can be ruled out owing to the lack of a peak in the $\tau\ 8.5\text{--}9.8$ region.¹⁵ A downfield shift of the CMe and SMe groups was also observed for alkoxy-carbene complexes.²¹⁻²³

The mechanism of reaction proposed in the Scheme seems reasonable in the light of some aspects of the chemistry of cyclopentadienyl-rhodium(I) and -iridium(I) complexes and some reactions observed for metal thiocarbonyl derivatives. The first step involves oxidative addition of MeI to the iridium(I) substrate with formation of a labile cationic methyliridium(III) species which rearranges, *via* methyl transfer and co-



ordination of the iodide to the metal, to the neutral thioacyl derivative. This intermediate undergoes electrophilic attack at the sulphur atom by a second methyl iodide molecule with formation of the cationic thiocarbene complex. A similar mechanism has been recently proposed by us²⁴ for the reaction between $[\text{Ir}(\text{C}_6\text{F}_5)(\text{CS})(\text{PPh}_3)_2]$ and MeI ; in this case the $[\text{Ir}(\text{C}_6\text{F}_5)\{\text{CMe}(\text{SMe})\}\text{I}_2(\text{PPh}_3)_2]$ complex is the product. Some aspects of the proposed mechanism have been discussed previously.²⁴

The strength of the metal-carbon σ bond in the product formed in the oxidative addition, in the first step of the reaction, seems to be a determining factor of the reaction course, and the rearrangement process giving the thioacyl complex can only be observed when a weak metal-methyl σ bond is present. One has to take into account also that the carbon atom of co-ordinated CS in iridium(III) complexes is highly electrophilic,²⁴ and this, in the case of the intermediate $[\text{IrMe}(\eta\text{-C}_5\text{H}_5)\text{I}(\text{CS})(\text{PPh}_3)]\text{I}$, is enhanced by the charge on the complex.

* Note added at proof: The formulation of the complex has now been confirmed by single-crystal structure analysis.

The influence of the metal-carbon σ bond is clearly demonstrated by the following reactions. The product of the oxidative-addition reaction of ClCH_2CN to (2) is the cationic complex $[\text{Ir}(\text{CH}_2\text{CN})(\eta\text{-C}_5\text{H}_5)(\text{CS})(\text{PPh}_3)]^+$ which was isolated as its tetraphenylborate salt; in this case the high $\text{Ir}-\text{CH}_2\text{CN}$ bond strength (higher than $\text{Ir}-\text{Me}$ owing to the presence on the carbon atom of the electron-withdrawing CN group) prevents the rearrangement process and thus the formation of the thiocarbene species.

Also, in the reaction of $[\text{IrCl}(\text{CS})(\text{PPh}_3)_2]$ with MeI a product with an $\text{Ir}-\text{Me}$ σ bond, namely, $[\text{IrMe}(\text{Cl})\text{I}(\text{CS})(\text{PPh}_3)_2]$, was isolated; in fact the reaction product shows $\nu(\text{CS})$ at 1375 cm^{-1} , *i.e.* at higher wavenumber than the starting substrate, as observed in the oxidative-addition reaction products (the very low solubility of the complex prevents the recording of a satisfactory ^1H n.m.r. spectrum). A similar product was isolated in the reaction of $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ with MeI .²⁵ It is significant, also, that while the complex $[\text{Ir}(\text{C}_6\text{F}_5)(\text{CO})(\text{PPh}_3)_2]$ has been found²⁶ to be unreactive towards MeI , the analogous thiocarbonyl derivative, in the above reaction, gave the carbene complex $[\text{Ir}(\text{C}_6\text{F}_5)\{\text{CMe}(\text{SMe})\}\text{I}_2(\text{PPh}_3)_2]$;²⁴ in the light of the behaviour of the carbonyl derivative, the weakness of the $\text{Ir}-\text{Me}$ σ bond in the labile intermediate formed in the latter reaction, namely $[\text{IrMe}(\text{C}_6\text{F}_5)\text{I}(\text{CS})(\text{PPh}_3)_2]$, was to be expected.

It is well established that Rh^{III} is less effective than Ir^{III} in stabilizing metal-alkyl or -aryl σ bonds and this implies, for example, that carbonylmethylrhodium(III) complexes easily rearrange to acyl complexes^{27,28} *via* methyl transfer. This is reflected in the reactions of complex (1) and $[\text{RhCl}(\text{CS})(\text{PPh}_3)_2]$ with MeI ; these did not afford methylrhodium complexes but species which spectral data indicated to be $[\text{Rh}(\eta\text{-C}_5\text{H}_5)\{\text{CMe}(\text{SMe})\}\text{I}(\text{PPh}_3)]\text{I}$ and $[\text{Rh}\{\text{CMe}(\text{SMe})\}\text{ClI}_2(\text{PPh}_3)_2]$. In fact, in the i.r. spectrum, the $\nu(\text{CS})$ band of the terminal thiocarbonyl ligand is not observed and the n.m.r. spectrum shows peaks of CMe and SMe of the thiocarbene ligand at τ values very similar to those observed for the other thiocarbeneiridium(III) species. The rhodium(III) thiocarbene complexes formed are not very stable and satisfactory analyses have not been obtained.

Similarly to other cyclopentadienyl-cobalt(I), -rhodium(I), and -iridium(I) complexes,^{15,29-31} (1) and (2) react with the Lewis acid HgCl_2 to give well defined 1 : 1 adducts. In these reactions it is necessary that exactly equimolar amounts of reagents are used. The complexes obtained, $[\text{M}(\eta\text{-C}_5\text{H}_5)(\text{CS})(\text{HgCl}_2)(\text{PPh}_3)]$ ($\text{M} = \text{Rh}$, or Ir), are yellow solids, non-conducting in nitrobenzene solution, and nearly insoluble; in the i.r. spectrum $\nu(\text{CS})$ was observed at 1315 and 1340 cm^{-1} for the rhodium and iridium complex respectively, *i.e.* at higher wavenumber than that observed for the starting substrate, and $\nu(\text{Hg}-\text{Cl})$ at *ca.* 240 cm^{-1} , very similar to values found for analogous complexes.^{29,30} Thus these complexes may be regarded as Lewis acid-base adducts, and the possibility that the mercury halide adds at the sulphur of the CS ligand, as observed for the complex $[\text{W}(\text{CO})(\text{CS})(\text{dppe})_2]$ ¹² [$\text{dppe} = 1,2\text{-bis}(\text{diphenyl-}$

phosphino)ethane], can be ruled out; in the latter case a shift of $\nu(\text{CS})$ to lower wavenumber should have been observed. Only metal thiocarbonyl complexes with $\nu(\text{CS})$ absorption at *ca.* 1200 cm^{-1} have been found to be reactive toward electrophiles.¹³

EXPERIMENTAL

The starting materials $[\text{RhCl}(\text{CS})(\text{PPh}_3)_2]$ ³² and $[\text{IrCl}(\text{CS})(\text{PPh}_3)_2]$ ³³ were prepared by literature methods. Tetrahydrofuran (thf) was purified by allowing it to stand over sodium, and distillation from $\text{Li}[\text{AlH}_4]$ under nitrogen. Methyl iodide was distilled from sodium thiosulphate. Other reagents were used as obtained from commercial sources. Infrared spectra were recorded with a Perkin-Elmer 457 spectrometer using a polystyrene film for calibration. A Perkin-Elmer R 24B spectrometer was used to obtain ^1H n.m.r. spectra. Conductivity measurements were made with a WTW LBR conductivity meter. Elemental analyses were performed by Bernhardt Mikroanalytisches Laboratorium, Elbach, Germany and by the micro-analytical laboratory of the Organic Chemistry Institute of Milan. All the reactions were carried out under an atmosphere of oxygen-free nitrogen. Analytical and characteristic i.r. and ^1H n.m.r. data of the complexes prepared are reported in the Table.

η -Cyclopentadienyl(thiocarbonyl)(triphenylphosphine)-rhodium(I), (1).—A filtered solution of sodium cyclopentadienide in anhydrous thf (obtained from 1.5 cm^3 of cyclopentadiene and a sodium dispersion containing 0.8 g of the metal) was evaporated off; benzene (120 cm^3) and $[\text{RhCl}(\text{CS})(\text{PPh}_3)_2]$ (0.32 g , 0.46 mmol) were added and the mixture was heated under reflux for *ca.* 3 h . The solution was filtered, the solvent evaporated off, and the residue extracted with hexane until the solvent was colourless. The solution was concentrated and transferred to a hexane-packed column of basic alumina. Elution with hexane gave a fraction containing triphenylphosphine; elution with hexane-diethyl ether (2 : 1) then gave a yellow-orange fraction which, after evaporation of the solvent at reduced pressure and crystallization from pentane, gave the product as orange crystals (yield 65%). *η -Cyclopentadienyl(thiocarbonyl)(triphenylphosphine)iridium(I), (2),* was similarly prepared from $[\text{IrCl}(\text{CS})(\text{PPh}_3)_2]$ and $\text{Na}(\text{C}_5\text{H}_5)$ in benzene, and was obtained as orange crystals (yield 60%).

Reactions of (1) with Halogens.—A pentane solution of chlorine was added dropwise to (1) in dichloromethane and cooled to liquid-nitrogen temperature. The mixture was vigorously stirred and slowly warmed to -78°C . By adding pentane a yellow solid was formed. The solvent was removed and the yellow residue washed with pentane and dried while the temperature was close to -78°C . The solid, namely $[\text{Rh}(\eta\text{-C}_5\text{H}_5)\text{Cl}(\text{CS})(\text{PPh}_3)]\text{Cl}$, was rapidly converted into its tetraphenylborate salt by reaction with $\text{Na}[\text{BPh}_4]$ in methanol. The salt $[\text{Rh}(\eta\text{-C}_5\text{H}_5)\text{Cl}(\text{CS})(\text{PPh}_3)][\text{BPh}_4]$ has a limited stability and decomposes within hours. The complexes $[\text{RhBr}(\eta\text{-C}_5\text{H}_5)(\text{CS})(\text{PPh}_3)]\text{I}$ and $[\text{Rh}(\eta\text{-C}_5\text{H}_5)\text{I}(\text{CS})(\text{PPh}_3)]\text{I}$ were obtained similarly using the appropriate halogen.

Reactions of (2) with Halogens.—A pentane solution of bromine was added dropwise to a stirred solution of (2) in the same solvent. The orange solid $[\text{IrBr}(\eta\text{-C}_5\text{H}_5)(\text{CS})(\text{PPh}_3)]\text{Br}$ was obtained, collected, washed with pentane, and dried. Similarly, addition of iodine to (2) gave $[\text{Ir}(\eta\text{-C}_5\text{H}_5)\text{I}(\text{CS})(\text{PPh}_3)]\text{I}$. A pentane solution of chlorine

Analytical and characteristic i.r. and ¹H n.m.r. data

Complex	Colour	Analysis (%) ^a				$\bar{\nu}(\text{CS})$ ^b /cm ⁻¹	¹ H N.m.r. (τ) ^c	
		C	H	S	Halogen		C ₅ H ₅	Other
[Rh(η -C ₅ H ₅)(CS)(PPh ₃)]	Orange	60.9 (60.85)	4.35 (4.25)	6.70 (6.75)		1 268vs	4.88	
[Ir(η -C ₅ H ₅)(CS)(PPh ₃)]	Orange	51.1 (51.1)	3.60 (3.55)	5.65 (5.70)		1 292vs	4.96	
[Rh(η -C ₅ H ₅)Cl(CS)(PPh ₃)] [BPh ₄]	Orange					1 370vs	4.71	
[RhBr(η -C ₅ H ₅)(CS)(PPh ₃)] [BPh ₄]	Orange					1 365vs	4.65	
[Rh(η -C ₅ H ₅)I(CS)(PPh ₃)] [BPh ₄]	Orange					1 358vs	4.60	
[Ir(η -C ₅ H ₅)Cl(CS)(PPh ₃)]Cl	Yellow-orange					1 375vs	3.88 ^d	
[IrBr(η -C ₅ H ₅)(CS)(PPh ₃)]Br	Orange	39.8 (39.85)	2.80 (2.80)	4.30 (4.45)	22.15 (22.1)	1 373vs	3.85 ^d	
[Ir(η -C ₅ H ₅)I(CS)(PPh ₃)]I	Orange	35.35 (35.25)	2.50 (2.45)	3.90 (3.90)	31.2 (31.05)	1 370vs	3.79 ^d	
[[RhCl(CS)(PPh ₃)] ₂]	Brown					1 308s		
[Ir(η -C ₅ H ₅)H(CS)(PPh ₃)] [BPh ₄]	White	65.25 (65.2)	4.80 (4.65)	3.55 (3.60)		1 360vs ^e	4.03 ^d	
[Rh(η -C ₅ H ₅){CMe(SMe)}I(PPh ₃)]I	Brown						4.06	7.03 (CMe) 6.32 (SMe)
[Ir(η -C ₅ H ₅){CMe(SMe)}I(PPh ₃)]I	Red	36.8 (36.85)	3.15 (3.10)	3.75 (3.80)	29.85 (29.95)		4.05	7.16 (CMe) 6.57 (SMe)
[Ir(CH ₂ CN)(η -C ₅ H ₅)(CS)(PPh ₃)] [BPh ₄]	Yellow	65.15 (65.05)	4.65 (4.60)	3.40 (3.45)	1.47 ^f (1.50)	1 365vs ^g	<i>h</i>	
[Rh{CMe(SMe)}ClI ₂ (PPh ₃) ₂]	Brown							6.96 (CMe) 6.72 (SMe)
[IrMe(Cl)I(CS)(PPh ₃) ₂]	Ivory	48.4 (48.4)	4.10 (4.05)	3.40 (3.40)	13.5 ⁱ (13.45)	1 376vs	<i>h</i>	
[Rh(η -C ₅ H ₅)Cl ₂ (CS)(HgCl ₂)(PPh ₃)]	Yellow	38.7 (38.65)	2.75 (2.70)	4.30 (4.30)	9.50 (9.50)	1 315vs	4.52	
[Ir(η -C ₅ H ₅)Cl ₂ (CS)(HgCl ₂)(PPh ₃)]	Yellow	34.55 (34.5)	2.45 (2.40)	3.75 (3.85)	8.55 (8.50)	1 338vs	<i>h</i>	

^a Calculated values are given in parentheses. ^b Nujol mulls. ^c In CDCl₃ using SiMe₄ as internal standard; the $J(\text{P-C}_5\text{H}_5)$ values are 0.7 Hz for rhodium(I) and iridium(I) complexes and in the range 1.4–2.0 Hz for rhodium(III) and iridium(III) complexes. ^d In CD₃OD. ^e $\nu(\text{Ir-H})$ at 2 160w, and 2 045w cm⁻¹. ^f Referring to N. ^g $\nu(\text{CN})$ at 2 210w cm⁻¹. ^h Insoluble. ⁱ Referring to I.

seems to react similarly with (2), but the product smells of H₂S and cannot be isolated analytically pure.

The tetraphenylborate salts [Ir(η -C₅H₅)X(CS)(PPh₃)] [BPh₄] (X = Br or I) were prepared by adding Na[BPh₄] dissolved in methanol to a solution of the corresponding halide salt in the same solvent.

Reaction of (1) with Hydrogen Chloride.—Dry hydrogen chloride was bubbled through a pentane solution of (1). The yellow colour of the solution completely disappeared and a brown solid was formed. The solvent was removed and the residue washed with pentane and dried. Satisfactory analytical results for the product were not obtained. Addition of PPh₃ to a dichloromethane solution of the product gave a yellow solution; the solvent was partially evaporated and hexane was added. The yellow solid [RhCl(CS)(PPh₃)₂] was obtained, collected, washed with diethyl ether, and dried.

Reaction of (2) with Hydrogen Chloride.—A sample of (2) was dissolved in pentane and the resulting solution was cooled to -78 °C; hydrogen chloride was bubbled through this until the yellow colour disappeared and a white solid was formed. The solvent was removed and the white solid washed several times with pentane and dried to give [Ir(η -C₅H₅)H(CS)(PPh₃)]Cl (see Results and Discussion). Some of the product was dissolved in methanol and Na[BPh₄] in the same solvent was immediately added. The white precipitate formed was collected, washed with methanol, and dried.

η -Cyclopentadienyliodo[methyl(methylthio)methylene](triphenylphosphine)iridium(III) Iodide.—A mixture of MeI (4 cm³) and (2) (0.25 g, 0.44 mmol) was stirred, at room temperature, for 2 h. During this time the colour of the solution became red. The excess of MeI was partially

removed by evaporation, and on adding hexane the product was obtained as a red-orange solid. This was collected, washed several times with hexane, and dried. Some of the product was dissolved in methanol and, by adding Na[BPh₄] in the same solvent, the corresponding tetraphenylborate salt, [Ir(η -C₅H₅){CMe(SMe)}I(PPh₃)] [BPh₄], was obtained as a red solid. *η -Cyclopentadienyliodo[methyl(methylthio)methylene](triphenylphosphine)rhodium(III) iodide* was similarly formed but could not be obtained analytically pure.

(Cyanomethyl)(η -cyclopentadienyl)(thiocarbonyl)(triphenylphosphine)iridium(III) Tetraphenylborate.—To a hexane solution of (2) (0.28 g, 0.447 mmol) was added an excess of ClCH₂CN (0.8 cm³) and the mixture vigorously stirred at room temperature for ca. 4 h. A red oil was obtained on evaporation of the solvent. This was dissolved in methanol and by adding Na[BPh₄] in the same solvent the product was obtained as a yellow solid.

Chloroiodo(methyl)(thiocarbonyl)bis(triphenylphosphine)iridium(III).—A mixture of [IrCl(CS)(PPh₃)₂] (0.22 g, 0.27 mmol) and MeI (4 cm³) was stirred overnight at room temperature. The excess of MeI was evaporated off and the residue, after washing with pentane, gave the product as an ivory solid. The same product was also obtained by heating the mixture of [IrCl(CS)(PPh₃)₂] and MeI under reflux for 8 h.

η -Cyclopentadienyl(thiocarbonyl)(triphenylphosphine)rhodiumdichloromercury.—Mercury(II) chloride (0.060 g, 0.22 mmol) in ethanol (5 cm³) was added to a solution of (1) (0.104 g, 0.22 mmol) in dichloromethane (5 cm³). A rapid reaction occurred and the colour of the solution became yellow. The solvent was evaporated off and the yellow solid obtained was crystallized from dichloro-

methane-diethyl ether to give the pure product. η -Cyclopentadienyl(thiocarbonyl)(triphenylphosphine)iridium-dichloromercury was similarly obtained as a yellow solid.

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