

Preparation and Some Reactions of (σ -Aryl)(thiocarbonyl)bis(triphenylphosphine)-rhodium(I) and -iridium(I): A Comparative Study with the Analogous Carbonyl Derivatives

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Complexes of the type $[\text{MR}(\text{CS})(\text{PPh}_3)_2]$ [$\text{M} = \text{Rh}$, $\text{R} = \text{C}_6\text{F}_5$ (1a) or C_6Cl_5 (2a); $\text{M} = \text{Ir}$, $\text{R} = \text{C}_6\text{F}_5$ (1b) or C_6Cl_5 (2b)] have been prepared from $[\text{MCl}(\text{CS})(\text{PPh}_3)_2]$ and the corresponding aryl-lithium reagents or aryl-magnesium halides. None of the prepared complexes gives a dioxygen adduct. Complexes (1b) and (2b) react with hydrochloric acid to give six-co-ordinate hydrido-iridium(III) species; the reaction is reversible and, by refluxing the adducts in ethanol, the starting iridium(I) complexes are regenerated. Complexes (1a) and (2a) react with HCl giving $[\text{RhCl}(\text{CS})(\text{PPh}_3)_2]$. The halogens react with (1b) and (2b) giving, in some cases, well defined adducts. The iridium(III) adduct $[\text{Ir}(\text{C}_6\text{F}_5)(\text{CS})\text{I}_2(\text{PPh}_3)_2]$ reacts with *p*-toluidine to give the isocyanide complex $[\text{Ir}(\text{C}_6\text{F}_5)(\text{CNC}_6\text{H}_4\text{Me-}p)\text{I}_2(\text{PPh}_3)_2]$ by nucleophilic attack of the amine on the carbon atom of CS. Complex (1b) reacts with MeI giving the thiocarbene $[\text{Ir}(\text{C}_6\text{F}_5)\{\text{CMe}(\text{SMe})\}\text{I}_2(\text{PPh}_3)_2]$; the mechanism of this reaction is discussed. Mercury(II) chloride reacts with (1b) to give $[\text{Ir}(\text{C}_6\text{F}_5)\text{Cl}(\text{CS})(\text{HgCl})(\text{PPh}_3)_2]$. The i.r. and ^1H n.m.r. spectra of the complexes are discussed.

ALTHOUGH carbonyl and thiocarbonyl complexes display some similarity in terms of electronic structure, several studies on thiocarbonyl metal complexes have indicated that CS is a better σ donor and π acceptor than CO.¹⁻³ Furthermore, in some cases, metal thiocarbonyls have been observed to undergo nucleophilic attack at the carbon atom and electrophilic attack at sulphur of the co-ordinated thiocarbonyl ligand.² Such properties are of interest in a comparative study of carbonyl and thiocarbonyl derivatives.

This paper reports the formation, stabilization, and some reactions of σ -bonded aryl derivatives of rhodium(I) and iridium(I) containing the thiocarbonyl ligand; the analogous carbonyl derivatives have recently been studied in detail.⁴⁻¹⁰

RESULTS AND DISCUSSION

New σ -aryl derivatives of the type $[\text{MR}(\text{CS})(\text{PPh}_3)_2]$ [$\text{M} = \text{Rh}$, $\text{R} = \text{C}_6\text{F}_5$ (1a) or C_6Cl_5 (2); $\text{M} = \text{Ir}$, $\text{R} = \text{C}_6\text{F}_5$ (1b) or C_6Cl_5 (2b)] have been prepared from the

reactions of $[\text{MCl}(\text{CS})(\text{PPh}_3)_2]$ and the corresponding aryl-lithium reagents or arylmagnesium halides, in tetrahydrofuran solution. The pentachlorophenyl and pentafluorophenyl derivatives are red solids which can be handled in air or in solution for long periods without evident decomposition.

Selected i.r. spectral data of the complexes are listed in the Table. It is interesting that, for the $[\text{MR}(\text{CS})(\text{PPh}_3)_2]$ complexes, $\nu(\text{CS})$ lies below that of $[\text{MCl}(\text{CS})(\text{PPh}_3)_2]$; for the carbonyl σ -pentafluorophenyl-rhodium(I) and -iridium(I) complexes $\nu(\text{CO})$ lies above that of $[\text{MCl}(\text{CO})(\text{PPh}_3)_2]$ ($\text{M} = \text{Rh}$ or Ir) and, since the inductive electron-withdrawing effect of the C_6F_5 group is less than that of chlorine, an efficient π overlap has been assumed to occur when this group is σ -bonded to a metal.^{6,7} Structural data indicate an almost pure σ bond between the iridium and the carbon of the C_6F_5 ligand in the complex $[\text{Ir}(\text{C}_6\text{F}_5)(\text{CO})(\text{PPh}_3)_2]$.¹¹ Infrared spectral data of the prepared complexes confirm this observation. For the rhodium(III) and iridium(III)

Analytical data and characteristic i.r. bands

Complex	Colour	Analysis (%) ^a				I.r. bands (cm^{-1}) ^b	
		C	H	S	Halogen	$\nu(\text{CS})$	Others
$[\text{Rh}(\text{C}_6\text{F}_5)(\text{CS})(\text{PPh}_3)_2]$	Red	61.65 (61.60)	3.65 (3.60)	3.80 (3.80)	11.20 (11.30)	1 277vs	
$[\text{Rh}(\text{C}_6\text{Cl}_5)(\text{CS})(\text{PPh}_3)_2]$	Red	56.10 (56.10)	3.30 (3.30)	3.40 (3.50)	19.20 (19.25)	1 278vs	
$[\text{Ir}(\text{C}_6\text{F}_5)(\text{CS})(\text{PPh}_3)_2]$	Red	55.75 (55.65)	3.30 (3.25)	3.50 (3.45)	10.30 (10.25)	1 300vs	
$[\text{Ir}(\text{C}_6\text{Cl}_5)(\text{CS})(\text{PPh}_3)_2]$	Red	51.0 (51.10)	3.05 (3.00)	3.20 (3.15)	17.60 (17.55)	1 302vs	
$[\text{Ir}(\text{C}_6\text{F}_5)\text{Cl}(\text{H})(\text{CS})(\text{PPh}_3)_2]$	White	53.60 (53.55)	3.20 (3.25)	3.30 (3.30)		1 358vs	2 218w $\nu(\text{Ir-H})$ 275m $\nu(\text{Ir-Cl})$
$[\text{Ir}(\text{C}_6\text{Cl}_5)\text{Cl}(\text{H})(\text{CS})(\text{PPh}_3)_2]$	White	49.45 (49.35)	3.05 (3.00)	3.00 (3.05)		1 356vs	2 240w $\nu(\text{Ir-H})$ 278m $\nu(\text{Ir-Cl})$
$[\text{IrBr}_2(\text{C}_6\text{F}_5)(\text{CS})(\text{PPh}_3)_2]$	Yellow	47.40 (47.50)	2.80 (2.80)	2.85 (2.95)		1 362vs	
$[\text{Ir}(\text{C}_6\text{F}_5)(\text{CS})\text{I}_2(\text{PPh}_3)_2]$	Yellow	43.65 (43.70)	2.60 (2.55)	2.70 (2.70)		1 355vs	
$[\text{Ir}(\text{C}_6\text{F}_5)(\text{CNC}_6\text{H}_4\text{Me-}p)\text{I}_2(\text{PPh}_3)_2]^c$	Pale yellow	47.60 (47.85)	2.90 (2.95)				2 175s $\nu(\text{CN})$
$[\text{Ir}(\text{C}_6\text{F}_5)\{\text{CMe}(\text{Me})\}\text{I}_2(\text{PPh}_3)_2]$	Yellow	44.60 (44.60)	3.00 (3.00)	2.60 (2.65)	21.0 ^d (20.95)		
$[\text{Ir}(\text{C}_6\text{F}_5)\text{Cl}(\text{CS})(\text{HgCl})(\text{PPh}_3)_2]$	White	43.05 (43.05)	2.60 (2.50)	2.65 (2.65)	6.05 ^e (5.90)	1 335vs	

^a Calculated values are given in parentheses. ^b Nujol mull. ^c N, 1.20 (1.10%). ^d Referring to I. ^e Referring to Cl.

adducts $\nu(\text{CS})$ is at higher wavenumber than for the starting species, in agreement with the increased formal oxidation state of the metal. The *trans* disposition of the PPh_3 ligands in the σ -aryl complexes, as well as in their adducts, was confirmed in some cases by the method of Kubota and Loeffler.¹² For the pentafluorophenyl derivatives, bands associated with the presence of the C_6F_5 group are observable at 1 495 s, 1 040s, 940vs, and 770s cm^{-1} and for the pentachlorophenyl derivatives the bands of the C_6Cl_5 are at 1 320m, 1 315s, 1 288s, 1 230m, and 660m cm^{-1} .

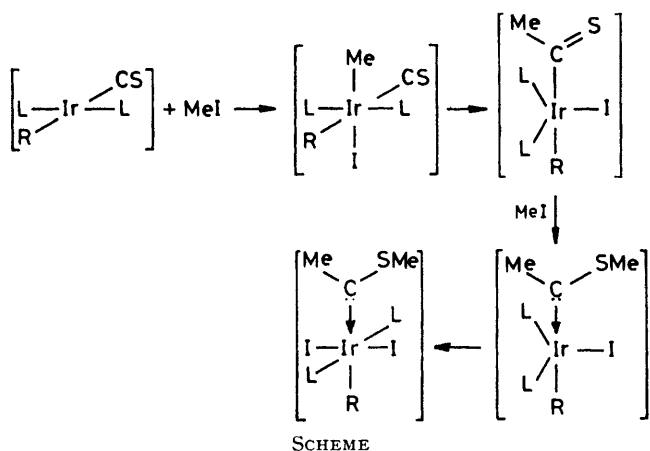
We have carried out a comparative study of the reactivity of the new σ -aryl(thiocarbonyl) derivatives and the analogous carbonyl complexes. As observed for the carbonyl complexes, the rhodium(I) derivatives are less reactive towards oxidative addition than those of iridium(I),^{13,14} and pentachlorophenyl derivatives are less reactive than pentafluorophenyl derivatives in these reactions.^{6,7} In some cases we observe substantial variations in reactivity of the thiocarbonyls in oxidative-addition reactions compared to the well known carbonyl complexes.

Complexes (1b) and (2b) react with hydrochloric acid, at room temperature, giving the hydrides $[\text{IrR}(\text{Cl})\text{H}(\text{CS})(\text{PPh}_3)_2]$ ($\text{R} = \text{C}_6\text{F}_5$ or C_6Cl_5) as white solids, but while the pentafluoro-complex reacts almost immediately the pentachloro-derivative requires *ca.* 3 d to complete reaction. When heated in ethanol, the HCl adducts readily lose hydrogen chloride to give the starting iridium(I) derivatives. A similar behaviour was observed for the analogous carbonyl σ -perhalogenoaryl complexes.⁷ The hydrogen chloride adducts showed $\nu(\text{CS})$ at 1 355 cm^{-1} ; the $\nu(\text{Ir-H})$ at *ca.* 2 230 cm^{-1} and $\nu(\text{Ir-Cl})$ at 275 cm^{-1} indicate that the hydride ligand is *trans* to Cl in these complexes.¹⁵ Complexes (1a) and (2a) when treated with HCl produce $[\text{RhCl}(\text{CS})(\text{PPh}_3)_2]$. The reaction probably proceeds with formation of a labile rhodium(III) adduct intermediate of lower stability than analogous iridium(III) adducts; reductive elimination of $\text{C}_6\text{F}_5\text{H}$ or $\text{C}_6\text{Cl}_5\text{H}$ then yields the product $[\text{RhCl}(\text{CS})(\text{PPh}_3)_2]$.

The halogens Br_2 and I_2 react readily, at room temperature, with (1b) giving the adducts $[\text{IrX}_2(\text{C}_6\text{F}_5)(\text{CS})(\text{PPh}_3)_2]$ ($\text{X} = \text{Br}$ or I) as yellow solids. Complex (2b) probably reacts similarly with halogens [a shift to higher wavenumbers was observed for $\nu(\text{CS})$ in the i.r. spectrum] but no satisfactory elementary analyses were obtained.

The CS carbon atom in iridium(III) complexes exhibits electrophilic character not observed in the parent iridium(I) derivatives. Thus, while (1b) does not react with *p*-toluidine, the iodine adduct $[\text{Ir}(\text{C}_6\text{F}_5)\text{I}_2(\text{CS})(\text{PPh}_3)_2]$ readily gives the isocyanide complex $[\text{Ir}(\text{C}_6\text{F}_5)\text{I}_2(\text{CNC}_6\text{H}_4\text{Me-}p)(\text{PPh}_3)_2]$. Very similar reactions could probably be observed between other σ -arylium(III) substrates and nucleophiles. Attack at co-ordinated CS by primary amines has sometimes been observed and this probably proceeds through formation of labile aminomercaptocarbene species which give the final isocyanide complex by elimination of H_2S .¹⁶⁻¹⁸

The complex $[\text{Ir}(\text{C}_6\text{F}_5)(\text{CO})(\text{PPh}_3)_2]$ has been found to be unreactive towards MeI.⁶ Surprisingly, we observed that the analogous thiocarbonyl derivative (1b) reacts with MeI within a few minutes on refluxing the solution or after *ca.* 12 h at room temperature, giving a neutral yellow solid which analyzes for $[\text{Ir}(\text{C}_6\text{F}_5)(\text{MeI})_2(\text{CS})(\text{PPh}_3)_2]$. Infrared and ^1H n.m.r. spectral data suggest that the complex is the thiocarbene $[\text{Ir}(\text{C}_6\text{F}_5)\{\text{CMe}(\text{SMe})\text{I}_2(\text{PPh}_3)_2\}]$; the i.r. spectrum does not show the stretching frequency of the terminal thiocarbonyl group, and in the ^1H n.m.r. spectrum singlets at τ 7.19 and 6.98, assignable respectively to CMe and SMe, were observed. In addition, the ^1H n.m.r. spectrum does not show the peak characteristic of a methyl group bonded to a metal. The $\nu(\text{CS})$ of the thiocarbene complex could not be assigned because this region is obscured by absorption bands of the other ligands. The considerable downfield shift of the CMe and SMe groups was expected and it is similar to that observed in alkoxy-carbene complexes.¹⁹⁻²¹



We suggest that the reaction of (1b) with MeI proceeds with initial formation of a six-co-ordinate iridium(III) adduct which rearranges, *via* methyl transfer, to a five-co-ordinate iridium(III) thioacetyl complex. In this transient intermediate, the sulphur atom is a nucleophilic centre and can undergo electrophilic attack by a second methyl iodide molecule with formation of a labile cationic complex which in turn undergoes a fast rearrangement involving co-ordination of the halogen to the metal and formation of the neutral six-co-ordinate thiocarbene complex (Scheme). Spectral data are not sufficient to establish the structure of the final product and in the Scheme the C_6F_5 group has been arbitrarily placed in a *trans* position to the thiocarbene ligand. The first steps of the proposed mechanism can be related to the known rearrangement process of carbonyl(methyl) and acyl complexes, *via* methyl transfer.²²⁻²⁴ Rearrangement processes of carbonyl(methyl) to acyl complexes are well known for rhodium(III)²² but are also observed, in some cases, for iridium(III) complexes;²⁵ such a process is however favoured in the presence of a very weak Ir-Me bond. One has also to take into account

that the carbon atom of CS in iridium(III) complexes probably has a higher electrophilic character than a CO group. The fact that $[\text{Ir}(\text{C}_6\text{F}_5)(\text{CO})(\text{PPh}_3)_2]$ has been found to be unreactive toward MeI could indicate that the first steps of the reaction described occur when the position of equilibrium is well over to the left and that the attack of MeI on thioacetyl iridium(III) species is the factor determining the reaction. A mechanism involving, as a first step, electrophilic attack of the alkyl group at the sulphur atom of a co-ordinated thiocarbonyl ligand in an iridium(I) complex can be ruled out. Thus (i) only metal thiocarbonyl complexes having $\nu(\text{CS})$ at $< ca. 1\,200\text{ cm}^{-1}$ have been found to be reactive toward electrophiles,^{26,27} and (ii) no reaction occurs between MeI and (2b) for which $\nu(\text{CS})$ indicates a nucleophilic character of the sulphur similar to that in complex (1b).

Complex (1a) probably reacts with MeI in a similar way to (1b), but satisfactory analyses were not obtained; the i.r. and ^1H n.m.r. spectral data of the product are very similar to that of $[\text{Ir}(\text{C}_6\text{F}_5)(\text{CMe}(\text{SMe}))\text{I}_2(\text{PPh}_3)_2]$.

The reaction of (1b) with an equimolar amount of HgCl_2 gives the adduct $[\text{Ir}(\text{C}_6\text{F}_5)\text{Cl}(\text{CS})(\text{HgCl})(\text{PPh}_3)_2]$ as a white solid. The complex is a non-electrolyte in nitrobenzene and displays a $\nu(\text{CS})$ band at $1\,335\text{ cm}^{-1}$; this indicates oxidative addition of mercury(II) chloride to the metal. In thiocarbonyl complexes in which the sulphur atom exhibits nucleophilic character, addition of mercury(II) halides has been observed to occur at the sulphur of the CS ligand²⁶ and consequently a shift of $\nu(\text{CS})$ to lower frequency was observed. The lower stability of rhodium(III) with respect to iridium(III) adducts prevents the isolation of $[\text{Rh}(\text{C}_6\text{F}_5)\text{Cl}(\text{CS})(\text{HgCl})(\text{PPh}_3)_2]$; decomposition takes place *via* elimination of $\text{Hg}(\text{C}_6\text{F}_5)\text{Cl}$, which was identified,²⁸ and $[\text{Rh}(\text{CS})\text{Cl}(\text{PPh}_3)_2]$ was isolated as the final product.

EXPERIMENTAL

The complexes $[\text{RhCl}(\text{CS})(\text{PPh}_3)_2]$ ²⁹ and $[\text{IrCl}(\text{CS})(\text{PPh}_3)_2]$ ³⁰ were prepared by literature methods. Tetrahydrofuran (thf) was purified by allowing it to stand over sodium and then by distillation from $\text{Li}[\text{AlH}_4]$ under nitrogen. Diethyl ether was purified by drying over CaCl_2 and distillation under nitrogen from sodium. Benzene was purified by distillation under nitrogen from calcium hydride. Methyl iodide was distilled from sodium thiosulphate. Other reagents were used as obtained from commercial sources. Infrared spectra were recorded in a Perkin-Elmer 457 spectrometer, ^1H n.m.r. spectra with a Perkin-Elmer R 24B spectrometer. A WTW LBR conductivity meter was used for conductivity measurements. Elemental analyses were by Bernhardt Mikroanalytisches Laboratorium, Elbach, Germany. All the reactions were carried out under an atmosphere of oxygen-free nitrogen.

σ -Pentafluorophenyl(thiocarbonyl)bis(triphenylphosphine)-rhodium(I), (1a).—To a solution of pentafluorophenylmagnesium bromide [obtained from bromopentafluorobenzene (0.741 g, 3.0 mmol) and magnesium (0.073 g) in anhydrous thf (20 cm^3)] was added $[\text{RhCl}(\text{CS})(\text{PPh}_3)_2]$ (0.741 g, 1.0 mmol) and the mixture was left at room temperature for *ca.* 40 h. The solvent was evaporated off and the residue dissolved in benzene (3 cm^3) and transferred to a hexane-

packed column of basic alumina. Elution with hexane-benzene (1 : 1) gave a red band which, after evaporation of the solvent, gave a red solid; this was washed with diethyl ether and dried, yield 60%.

σ -Pentafluorophenyl(thiocarbonyl)bis(triphenylphosphine)-iridium(I), (1b). was prepared in the same way from $[\text{IrCl}(\text{CS})(\text{PPh}_3)_2]$ and $\text{MgBr}(\text{C}_6\text{F}_5)$ and was obtained as red crystals, yield 62%. The reaction time was *ca.* 3 d.

σ -Pentachlorophenyl(thiocarbonyl)bis(triphenylphosphine)-rhodium(I), (2a).—To a thf solution of pentachlorophenylmagnesium chloride [prepared by the method of Rosenberg *et al.*³¹ from hexachlorobenzene (0.855 g, 3.0 mmol) and dry magnesium (0.073 g) in anhydrous thf (30 cm^3)] was added $[\text{RhCl}(\text{CS})(\text{PPh}_3)_2]$ (0.713 g, 1.0 mmol) and the mixture left at room temperature for *ca.* 3 d. The solvent was evaporated off under reduced pressure and the residue treated with anhydrous benzene (2 cm^3) and transferred to a hexane-packed column of basic alumina. Eluting with hexane, fractions containing hexachlorobenzene and pentachlorobenzene were separated. Elution with hexane-benzene (1 : 1) gave a red fraction which, after evaporation of the solvent at reduced pressure and crystallization from benzene-hexane, gave the product as red crystals, yield 42%.

σ -Pentachlorophenyl(thiocarbonyl)bis(triphenylphosphine)-iridium(I), (2b). was similarly prepared from $[\text{IrCl}(\text{CS})(\text{PPh}_3)_2]$ and $\text{Mg}(\text{C}_6\text{Cl}_5)\text{Cl}$ and was obtained as red crystals, yield 45%.

Addition of HCl to (1b) and (2b).—Concentrated HCl was added dropwise to a solution of (1b) or (2b) in benzene. The initial red colour of the solution became colourless [in a few minutes in the case of (1b) and 3 d in the case of (2b)] and a white solid was formed. This was filtered off and washed several times with benzene. By boiling the adducts in ethanol for *ca.* 15 min, the reaction mixture became red and, by evaporation of the solvent, the starting materials (1b) and (2b) were obtained.

Reaction of HCl with (1a) and (2a).—Hydrogen chloride was bubbled through a dichloromethane solution of (1a) or (2a). The red solution rapidly became yellow. By adding diethyl ether to the concentrated solution, the yellow solid $[\text{RhCl}(\text{CS})(\text{PPh}_3)_2]$ was obtained. Using concentrated hydrochloric acid the same product was obtained.

Addition of Halogens to (1b).—A solution of the halogen in benzene was added dropwise to a solution of (1b) in the same solvent until the colour changed from red to yellow. The solution was concentrated by partial evaporation of the solvent and, by adding hexane, a solid was formed. This was separated and recrystallized from dichloromethane-diethyl ether to give the adduct in an analytically pure form.

Preparation of Di-iodo[methyl(methylthio)methylene]-(σ -pentafluorophenyl)bis(triphenylphosphine)iridium.—A mixture of MeI (4 cm^3) and (1b) (0.46 g, 0.5 mmol) was left overnight at room temperature with vigorous stirring. The colour of the solution became yellow. The solvent was evaporated off at reduced pressure and the yellow solid obtained was washed with hexane and dried, yield 85%. A mixture of (1b) and MeI gave the same product (yield 87%) when heated under reflux for *ca.* 8 min.

Under the same experimental conditions, MeI and (1a) react similarly, but the product was not obtained in an analytically pure form.

Reaction of HgCl_2 with (1b).—To a benzene solution of (1b) (0.35 g, 0.37 mmol) was added a solution of HgCl_2 (0.102 g, 0.37 mmol) in ethanol. The mixture was left at

room temperature, with vigorous stirring, for ca. 5 min. The red solution became colourless. The solvent was evaporated off at reduced pressure and the white solid obtained washed with diethyl ether to give $[\text{Ir}(\text{C}_6\text{F}_5)\text{Cl}(\text{CS})-(\text{HgCl})(\text{PPh}_3)_2]$, yield 95%.

Reaction of HgCl_2 with (1a).—To a benzene solution of (1a) (0.21 g, 0.25 mmol) was added a solution of HgCl_2 (0.068 g, 0.25 mmol) in ethanol and the mixture left at room temperature until the colour of the solution became yellow. The solvent was evaporated off and the residue, washed with methanol, gave $[\text{RhCl}(\text{CS})(\text{PPh}_3)_2]; \text{Hg}(\text{C}_6\text{F}_5)\text{Cl}$ was isolated from the methanol solution and identified.²⁸

Preparation of Di-iodo(σ -pentafluorophenyl)(p -tolyl isocyanide)bis(triphenylphosphine)iridium.—To a dichloromethane solution of $[\text{Ir}(\text{C}_6\text{F}_5)_2(\text{CS})(\text{PPh}_3)_2]$ was added an excess of p -toluidine and the mixture gently warmed for ca. 1 h and then left at room temperature for 20 h. Some of the solvent was evaporated and by adding diethyl ether the product was obtained as a pale yellow solid, yield 68%.

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