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BIDENTATE, MONODENTATE AND BRIDGING THIOCARBOXAMIDO COMPLEXES OF RHODIUM AND IRIDIUM; THE X-RAY STRUCTURE DETERMINATION OF $[Ir(\eta^2\text{-}SCNMe_2)_2(CO)(PPh_3)]^+\ BF_4^-$

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Summary

$Me_2NC(S)Cl$ reacts with "$IrCl(PPh_3)_2$", $IrCl(CO)(PPh_3)_2$ and $IrH(CO)(PPh_3)_3$, to give *cis*- and *trans*-$IrCl_2(\eta^2\text{-}SCNMe_2)(PPh_3)_2$, *trans*-$[IrCl(\eta^2\text{-}SCNMe_2)(CO)(PPh_3)_2]^+\ Cl^-$ and *trans*-$[IrH(\eta^2\text{-}SCNMe_2)(CO)(PPh_3)_2]^+\ Cl^-$, respectively (with *cis* and *trans* referring to the relative position of the PPh_3 groups). Dehydrohalogenation of *trans*-$[IrH(\eta^2\text{-}SCNMe_2)(CO)(PPh_3)_2]^+\ Cl^-$ by Et_3N results in *trans*-$Ir(\eta^1\text{-}SCNMe_2)(CO)(PPh_3)_2$ and the dimeric $[Ir(\mu\text{-}SCNMe_2)(CO)(PPh_3)]_2$. Dehydrohalogenation of *trans*-$[IrH(\eta^2\text{-}SCNMe_2)(CO)(PPh_3)_2]^+\ Cl^-$ in the presence of $Me_2NC(S)Cl$ gives the bis(η^2-thiocarboxamido) complex $[Ir(\eta^2\text{-}SCNMe_2)_2(CO)(PPh_3)]^+\ Cl^-$.

In the reaction of $Me_2NC(S)Cl$ with $RhH(CO)(PPh_3)_3$ displacement of CO occurs and $RhCl(\eta^2\text{-}SCNMe_2)_2(PPh_3)_2$ is formed. This complex can also be prepared from $Me_2NC(S)Cl$ and $RhH(PPh_3)_4$.

The X-ray structure analysis of $[Ir(\eta^2\text{-}SCNMe_2)_2(CO)(PPh_3)]^+\ BF_4^-$ shows both $SCNMe_2$ ligands to be planar and coordinated via C and S, with bond distances and angles comparable to those in other η^2-$SCNMe_2$ complexes. As the C—Ir—S angles within both $IrSCNMe_2$ units are small (43°), the coordination geometry around the iridium is distorted octahedral.

Introduction

N,N-Dialkylthiocarboxamide ($SCNR_2$) [1,2] and dithioalkyl ester (SCSR) [3—7] complexes have been prepared in the last decade via several routes. For $SCNR_2$, coordination via C (η^1 coordination), coordination via C and S to give a three membered M—C—S ring (η^2 coordination), and bridging via C and S (μ coordination) have been reported. For SCSR, up to now only η^1 coordination and η^2 coordination have been found.

X-ray crystallographic data have been obtained for η^2-SCSMe [5], η^2-$SCNMe_2$ [8,9], η^2-$SCN(n\text{-}Pr)_2$ [10], and μ-$SCNMe_2$ [11]. The geometry of η^2-SCSR and

TABLE 1

ANALYTICAL DATA (theoretical values in parentheses)

Code	Compound	Analysis (Found (calcd.) (%))				Mol.Wt. [a]
		C	H	N	S	
trans-I	*trans*-$IrCl_2(\eta^2\text{-}SCNMe_2)(PPh_3)_2 \cdot 2\ CHCl_3$	44.5	3.4	1.3		
		(45.8)	(3.6)	(1.3)		
II(Cl^-)	*trans*-$[IrCl(\eta^2\text{-}SCNMe_2)(CO)(PPh_3)_2]^+ Cl^- \cdot C_6H_6$	56.1	4.2	1.9		
		(56.2)	(4.2)	(1.4)		
III(Cl^-)	*trans*-$[IrH(\eta^2\text{-}SCNMe_2)(CO)(PPh_3)_2]^+ Cl^-$	55.9	4.6	1.4		
		(55.3)	(4.3)	(1.6)		
V	$[Ir(\mu\text{-}SCNMe_2)(CO)(PPh_3)]_2$	47.5	4.0	2.1	5.4	1144 [b]
		(46.2)	(3.7)	(2.4)	(5.6)	(1141)
VII(BF_4^-)	$[Ir(\eta^2\text{-}SCNMe)_2(CO)(PPh_3)]^+ BF_4^-$	40.4	3.6	3.7		
		(40.3)	(3.6)	(3.8)		
IX	$RhCl(\eta^2\text{-}SCNMe_2)_2(PPh_3)CHCl_3$	43.1	4.0	3.9	9.3	710 [c]
		(43.1)	(4.0)	(4.0)	(9.2)	(696)

[a] Osmometric. [b] In C_6H_6 under N_2. [c] In $CHCl_3$.

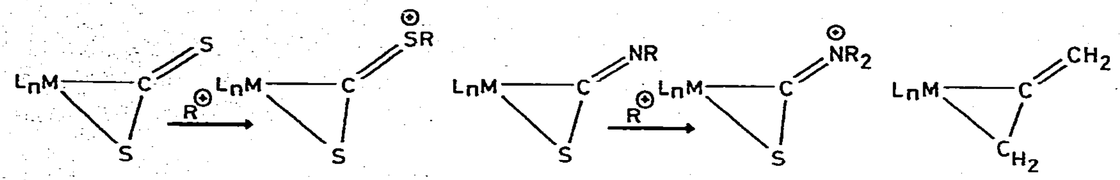

Fig. 1. η^2-Allene and the "pseudo-allenes" η^2-CS_2, η^2-SCSMe, η^2-SCNR and η^2-SCNRMe.

η^2-$SCNR_2$ is closely related to that observed for η^2-CS_2 complexes [12,13]. Methylation of η^2-CS_2 and η^2-SCNR complexes has been reported to give η^2-SCSMe and η^2-SCNRMe complexes [2,5,6] (Fig. 1).

η^2-CS_2 and η^2-SCNR, as well as their alkylated forms, can be called pseudo-allenes [37], because of the analogy of their coordination geometry to that of η^2-allene [38] (Fig. 1). In defining the oxidation state of the central metal, η^2-CS_2, η^2-SCSR, η^2-SCNR and η^2-$SCNR_2$ can be considered either as monodentate two electron π-donors {S=C=S, S=C=SR^+, S=C=NR, S=C=NR_2^+) or as bidentate four electron σ-donors ($\overline{S}$—$\overline{C}$=S^{2-}, $\overline{S}$—$\overline{C}$=SR^-, $\overline{S}$—$\overline{C}$=NR^{2-}, $\overline{S}$—$\overline{C}$=NR_2^-). The latter formalism is used for η^2-$SCNMe_2$ in this article.

In an attempt to find out how the mode of coordination of $SCNMe_2$ is influenced by the oxidation state of the central metal and the nature of the other ligands present, we prepared iridium(III) and iridium(II) $SCNMe_2$ complexes via oxidative addition of $Me_2NC(S)Cl$ to "$IrCl(PPh_3)_2$", $IrCl(CO)(PPh_3)_2$ and $IrH(CO)(PPh_3)_3$, and compared these with the products obtained from the reaction of $Me_2NC(S)Cl$ with $RhCl(PPh_3)_3$, $RhCl(CO)(PPh_3)_2$, $RhH(CO)(PPh_3)_3$ and $RhH(PPh_3)_4$. The coordination of $SCNMe_2$ in some of the complexes is compared with that in corresponding SCSR (R = Me, Et) complexes, reported before. The preparation and geometry of bis(η^2-$SCNMe_2$) complexes, not known for CS_2 or SCNR, is described.

A. Synthesis and characterization of the complexes

Experimental

IR spectra were obtained with Perkin—Elmer 257 and 283 spectrophotometers. ^{1}H NMR spectra were recorded on a Varian T-60 and a Bruker WH-90-FT NMR spectrometer. ^{31}P {^{1}H}NMR spectra were recorded on a Varian XL-100-FT. at 40.5 MHz, using the deuterated solvent as internal lock.

C, H and N analysis of the air sensitive $[Ir(\mu\text{-}SCNMe_2)(CO)PPh_3]_2$, S analyses and molecualr weight determinations were performed by Alfred Bernhardt, Microanalytisches Laboratorium, Elbach über Engelskirchen, W.-Germany. The other analyses were performed by the microanalytical department of this university. Table 1 summarizes the analytical data.

The starting complexes $RhH(PPh_3)_4$ [19], $RhH(CO)(PPh_3)_3$ [19], $[IrCl(C_8H_{14})_2]_2$ [20], $IrH(CO)(PPh_3)_3$ [19] and $IrCl(CO)(PPh_3)_2$ [36] were prepared according to literature procedures. $IrCl(PPh_3)_2$ was prepared in situ from $[IrCl(C_8H_{14})_2]_2$ and 4 PPh_3 [35]. $Me_2NC(S)Cl$ was prepared according to [21]. The synthesis of the $SCNMe_2$ complexes from the Rh^I and Ir^I complexes was performed under nitrogen.

Mono(η^2-SCNMe$_2$) complexes

cis-IrCl$_2$(η^2-SCNMe$_2$)(PPh$_3$)$_2$ (cis-I) *. 0.22 mmol $Me_2NC(S)CL$ was added to a solution of 0.10 mmol $[IrCl(C_8H_{14})_2]_2$ and 0.40 mmol PPh_3 in 25 ml of benzene. After 15 min a brown-yellow precipitate of *cis*-I began to form. After 2 h the precipitate was filtered off.

trans-IrCl$_2$(η^2-SCNMe$_2$)(PPh$_3$)$_2$ · 2 CHCL$_3$ (trans-I). Slow crystallisation of *cis*-I from chloroform/n-hexane gave red crystals of *trans*-I. The presence of $CHCl_3$ was confirmed by IR.

trans-[IrCl(η^2-SCNMe$_2$)(CO)(PPh$_3$)$_2$]$^+$ Cl$^-$ · C$_6$H$_6$ (II(Cl$^-$)). A solution of 0.17 mmol $Me_2NC(S)Cl$ and 0.15 mmol $IrCl(CO)(PPh_3)_2$ in 20 ml of benzene was refluxed for six hours. II precipitated spontaneously as a white powder. The presence of C_6H_6 was confirmed by ^1H NMR.

trans-[IrH(η^2-SCNMe$_2$)(CO)(PPh$_3$)$_2$]$^+$ Cl$^-$ (III(Cl$^-$)). 0.12 mmol $Me_2NC(S)Cl$ was added to a solution of 0.10 mmol $IrH(CO)(PPh_3)_3$ in 15 ml of benzene. Stirring for 12 h resulted in a white precipitate of III(Cl$^-$) which proved to be a mixture of two isomers, IIIA and IIIB (see Results and discussion).

trans-[IrH(η^2-SCNMe$_2$)(CO)(PPh$_3$)$_2$]$^+$ BF$_4^-$ (III(BF$_4^-$)). Addition of several drops of 40% aqueous fluoroboric acid to a suspension of IIIA(Cl$^-$) and IIIB(Cl$^-$) in acetone produced a colourless solution, from which the isomers IIIA and IIIB were precipitated as BF_4^- salts by addition of water. IIIA and IIIB were separated via fractional crystallisation from dichloromethane/n-hexane, from which IIIB(BF$_4^-$) crystallizes first.

(μ- and η^1-SCNMe$_2$) complexes

[Ir(μ-SCNMe$_2$)(CO)(PPh$_3$)]$_2$ (V) and Ir(η^1-SCNMe$_2$)(CO)(PPh$_3$)$_2$ (IV). Upon addition of a slight excess of Et_3N to a stirred suspension of 0.20 mmol of III(Cl$^-$) in 10 ml of benzene, the colour changed via yellow and orange-red to purple. After four hours III(Cl$^-$) has almost completely dissolved and Et_3NHCl has precipitated. Filtration, addition of n-hexane and cooling gave purple-brown crystals of V. The complex is air-sensitive both in solution and in the solid state.

If the same reaction is performed in the presence of 6 mol of additional PPh_3 per mol of Ir, a mixture of V and orange crystalline $Ir(\eta^1\text{-}SCNMe_2)(CO)(PPh_3)_2$ (IV) is isolated. The IR absorptions of η^1-SCNMe$_2$ in IV were obtained from the IR spectrum of this mixture.

Bis(η^2-SCNMe$_2$) complexes

[Ir(η^2-SCNMe$_2$)$_2$(CO)(PPh$_3$)]$^+$ BF$_4^-$ (VII(BF$_4^-$)). 0.25 mmol Et_3N and 0.22 mmol $Me_2NC(S)Cl$ were added successively to a suspension of 0.20 mmol of III(Cl$^-$) in 25 ml of benzene. After stirring for 1.5 h, Et_3NHCl was filtered off from the yellow solution. Addition of n-hexane resulted in a yellow precipitate, which was shown by IR to be a mixture of $IrCl(\eta^1\text{-}SCNMe_2)(\eta^2\text{-}SCNMe_2)(CO)(PPh_3)$ (VI) and $[Ir(\eta^2\text{-}SCNMe_2)_2(CO)(PPh_3)]^+ Cl^-$(VII(Cl$^-$)).

Addition of several drops of 40% aqueous fluoroboric acid to a suspension of the yellow precipitate in aceton produced a colourless solution, from which a white precipitate of VII(BF$_4^-$) was obtained by addition of water. If the reaction of III(Cl$^-$) with $Me_2NC(S)Cl$ and Et_3N was performed in benzene under reflux,

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* *cis* and *trans* indicate relative positions of PPh_3 groups.

partial displacement of CO occurred, and a mixture of VII(Cl^-) and $IrCl(\eta^2$-$SCNMe_2)_2(PPh_3)$ (VIII, identified by IR) was obtained.

$RhCl(\eta^2$-$SCNMe_2)_2(PPh_3) \cdot CHCl_3$ (IX). (a) 0.20 mmol Et_3N and 0.32 mmol $Me_2NC(S)Cl$ were added successively to a stirred solution of 0.15 mmol $RhH(PPh_3)_4$ in 15 ml of benzene. Et_3NHCl and a yellow powder of $RhCl(\eta^2$-$SCNMe_2)_2(PPh_3)$ precipitated simultaneously. After 2 h the precipitate was filtered off and washed with water (removal of Et_3NHCl). Recrystallization from chloroform/ n-hexane gave yellow crystals of IX. The presence of $CHCl_3$ was confirmed by IR. In the solid state under the influence of light the colour of IX changed from yellow to orange. The observed change in colour did not result in a change in the IR spectrum. Because of this sensitivity to light, X-ray structure determination was not possible.

(b) Upon addition of 0.42 mmol $Me_2NC(S)Cl$ to a solution of 0.20 mmol $RhH(CO)(PPh_3)_3$ in 15 ml of benzene, the colour of the solution changed from yellow to red and back to yellow again within 15 min and a yellow precipitate of $RhCl(\eta^2$-$SCNMe_2)_2(PPh_3)$ was formed spontaneously. $RhCl(CO)(PPh_3)_2$ could be isolated by addition of n-hexane.

Results and discussion

IR, ^1H NMR and $^{31}P\{^1H\}$ NMR parameters of the thiocarboxamido complexes are given in Tables 2 and 3.

$Me_2NC(S)Cl$ reacts with $IrCl(PPh_3)_2$ (prepared in situ; see Experimental) in benzene to *cis*-$IrCl_2(\eta^2$-$SCNMe_2)(PPh_3)_2$(*cis*-I). The *cis*-structure is indicated by the inequivalence of both PPh_3 groups in the ^{31}P NMR spectrum (Table 3). In a polar solvent like $CHCl_3$ or CH_2Cl_2 slow isomerisation to *trans*-$IrCl_2(\eta^2$-$SCNMe_2)(PPh_3)_2$ (*trans*-I) is observed. η^2-coordination of $SCNMe_2$, via C and S, in both isomers, is inferred from the similarity of its IR absorptions to the absorptions of the $SCNMe_2$ group in $RhCl[SC(S)NMe_2](\eta^2$-$SCNMe_2)PPh_3$ and $RhCl[PhNC(S)NMe_2](\eta^2$-$SCNMe_2)PPh_3$, for which η^2-coordination has been confirmed by X-ray structure analyses [8].

In the analogous reaction of $RhCl(PPh_3)_3$ with $Me_2NC(S)Cl$, *trans*-$RhCl_2(\eta^2$-$SCNMe_2)(PPh_3)_2$ is isolated (Tables 2 and 3). Corain et al. [15] have reported this complex (prepared by the same procedure) to be dimeric. Based on the IR absorptions of the $SCNMe_2$ group and the monomeric molecular weight found by us (in $CHCl_3$: found 909, calcd. 945), we think this complex to be isostructural to *trans*-I and the related $RhCl_2(\eta^2$-$SCSEt)(PPh_3)_2$ [4]. A *trans* position of the PPh_3 groups in all three complexes is indicated by the ^{31}P NMR spectrum (Table 3).

$Me_2NC(S)Cl$ reacts with $IrCl(CO)(PPh_3)_2$ to give *trans*-$[IrCl(\eta^2$-$SCNMe_2)(CO)(PPh_3)_2]^+ Cl^-$ (II) in benzene. The course of the reaction is different from that observed for $RhCl(CO)(PPh_3)_2$, where displacement of CO instead of Cl^- occurs to give *trans*-$RhCl_2(\eta^2$-$SCNMe_2)(PPh_3)_2$. The relative aptitude to displacement for Rh: CO > Cl^- and for Ir: Cl^- > CO appears to be a general phenomenon in the oxidative addition of $Me_2NC(S)Cl$ (see below). Interestingly, the II-related $[IrCl(\eta^2$-$SCSMe)(CO)(PPh_3)_2]^+$ has been reported to be formed in the absence of additional Cl^- [6], whereas, in the presence of additional Cl^-, $IrCl_2(\eta^1$-$SCSEt)(CO)(PPh_3)_2$ is found [4]. Therefore it seems that $SCNMe_2$ is able to become

(Continued on p. 88)

TABLE 2

IR ABSORPTION (cm^{-1})

Code	Compound [a]	SCNMe$_2$ absorptions (CsJ) mode	ν(C=N)	$\delta(CH_3)$			C–S / M	ν(CO) (CH_2Cl_2)	Others	
cis-I	*cis*-IrCl$_2$(η^2-SCNMe$_2$)(PPh$_3$)$_2$	η^2	1587s	1409m	1230m	918m	835m			
trans-I	*trans*-IrCl$_2$(η^2-SCNMe$_2$)(PPh$_3$)$_2$	η^2	1607s	1406m	1227m	917m	834m		305m	ν(Ir—Cl), CsJ
II(Cl$^-$)	*trans*-[IrCl(η^2-SCNMe$_2$)(CO)(PPh$_3$)$_2$]$^+$ Cl$^-$ · C$_6$H$_6$	η^2	1625s	1405m	1213m	911m	830m	2050vs	290m	ν(Ir—Cl), CsJ
III(BF$_4^-$)	*trans*-[IrH(η^2-SCNMe$_2$)(CO)(PPh$_3$)$_2$]$^+$BF$_4^-$	A [b] η^2	1610s	1405m	1215m	922m	848m	2040vs	2144m(br)	ν(Ir—H), CH$_2$Cl$_2$
		B [b] η^2	1608s	1410m	1215m	916m	817m	2027vs	1022m(br)	μ(Ir—H), CH$_2$Cl$_2$
IV	*trans*-Ir(η^1-SCNMe$_2$)(CO)(PPh$_3$)$_2$ [c]	η^1	1508m	1382m	1239w 1130m	940w	—	1953vs		
V	[Ir(μ-SCNMe$_2$)(CO)(PPh$_3$)]$_2$	μ	1503m	1382m	1237w 1129m	918w	—	1930vs		
VI	IrCl(η^1-SCNMe$_2$)(η^2-SCNMe$_2$)(CO)(PPh$_3$) [d]	η^1	1494m	1366m	1225m	945m	—	2030vs(CsJ)		
		η^2	1612s	1406m	1123m					
		η^2	1612s	1406m	1225m	922m	842m			
VII(BF$_4^-$)	[Ir(η^2-SCNMe$_2$)$_2$(CO)(PPh$_3$)]$^+$BF$_4^-$	η^2	1613s	1404s	1220m	919sh 914m	842m 829m	2030vs 2024vs(CsJ)		
VIII	IrCl(η^2-SCNMe$_2$)$_2$(PPh$_3$) [d]	η^2	1577s	1400s	1232m	921sh 914m	867m 834m			
IX	RhCl(η^2-SCNMe$_2$)$_2$(PPh$_3$)	η^2	1576s	1405s	1224m	924sh 917m	860m 819m		286m	ν(Rh—Cl), CsJ
	trans-RhCl$_2$(η^2-SCNMe$_2$)(PPh$_3$)$_2$ [e]	η^2	1608s	1400m	1220m	917m	826m			
	trans-PtCl[(η^1-SCNMe$_2$)(PPh$_3$)$_2$ [f]	η^1	1514m	1380m	1237m 1138m	952m	—			

[a] *cis* and *trans* indicate relative positions of PPh$_3$ groups. [b] Isomer A: H *trans* to S; Isomer B: H *trans* to C. [c] IR absorptions obtained from a mixture of IV and V (see [d] Experimental). [d] Characterized only by IR. [e] Prepared according to [15]. [f] Prepared according to [14].

TABLE 8

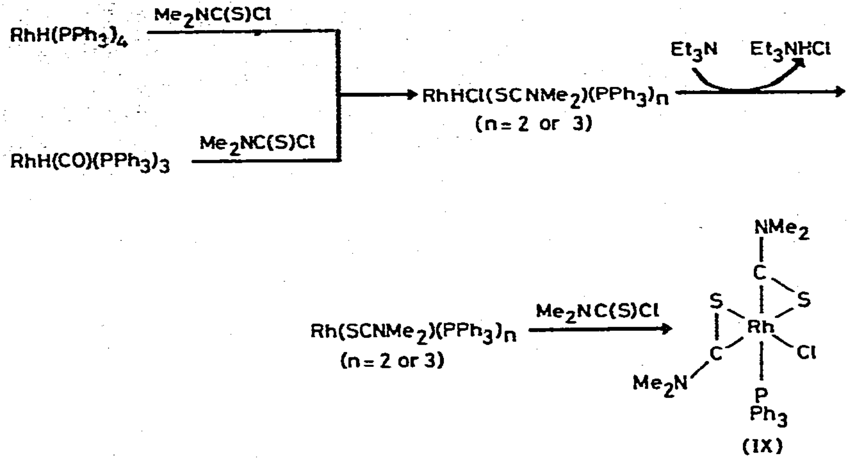
^1H NMR AND $^{31}P\{^1H\}$NMR PARAMETERS IN CD_2Cl_2

Code	Compound [d]	^1H NMR		^{31}P NMR		
		$\tau(NMe_2)$ [a,c] (ppm)	$\tau(Ir—H)$ [a] (ppm)	$\delta(^{31}P)$ [b] (ppm)	$^nJ(P—X)$ [c] (Hz)	
cis-I	*cis*-$IrCl_2(\eta^2\text{-}SCNMe_2)(PPh_3)_2$	7.96(3)		−2.2	9	$^2J(P^1—P^2)$cis
		7.53(3)		+20.9		
trans-I	*trans*-$IrCl_2(\eta^2\text{-}SCNMe_2)(PPh_3)_2$	7.68(3)		+14.4		
		7.81(3)				
II(Cl⁻)	*trans*-$[IrCl(\eta^2\text{-}SCNMe_2)(CO)(PPh_3)_2]^+ Cl^-$	6.20(3)		+5.4		
		6.43(3)				
III(BF_4^-)	*trans*-$[IrH(\eta^2\text{-}SCNMe_2)(CO)(PPh_3)_2]^+ BF_4^-$	A [f] 8.05(3)	+25.8	−1.4	14	$^2J(P—H)$*cis* [g]
		7.26(3)				
		B [f] 7.32(6)	+17.8	−6.1	14	$^2J(P—H)$*cis* [g]
IV	*trans*-$Ir(\eta^1\text{-}SCNMe_2)(CO)(PPh_3)_2$	7.51(3) [h]		−15.0		
		7.89(3) [h]				
V	$[Ir(\mu\text{-}SCNMe_2)(CO)(PPh_3)]_2$	6.09(3)		−11.6		
		6.81(3)				
VII(BF_4^-)	$[Ir(\eta^2\text{-}SCNMe_2)(CO)(PPh_3)]^+ BF_4^-$	6.23(3)		−2.6		
		6.61(3)				
		6.71(3)				
		6.82(3)				
IX	$RhCl(\eta^2\text{-}SCNMe_2)_2(PPh_3)$	6.50(3)		−35.1	175	$^1J(Rh—P)$
		6.85(3)				
		7.05(3)				
		7.69(3)				
	trans-$RhCl_2(\eta^2\text{-}SCNMe_2)(PPh_3)_2$	7.69(3)		−16.0	93	$^1J(Rh—P)$
		7.79(3)				
	trans-$RhCl_2(\eta^2\text{-}SCSEt(PPh_3)_2$ [i]	—		−15.8	92	$^1J(Rh—P)$

[a] Rel. to TMS int. ref. [b] Rel. to $O{=}P(OMe)_3$ (=TMP) int. ref. δ(TMP, int. ref) − δ(85% H_3PO_4, ext. ref) = +2.3 ppm, δ values ± 0.2 ppm. [c] *J* values: ±1 Hz. [d] *trans* and *cis* indicate relative positions of PPh_3 groups. [e] Between angles: number of protons determined from relative intensity to Ph resonances. [f] A and B are two different isomers. A: H *trans* to S, B: H *trans* to C. [g] From ^1H NMR. [h] Broadened singlets. [i] Prepared according to [4].

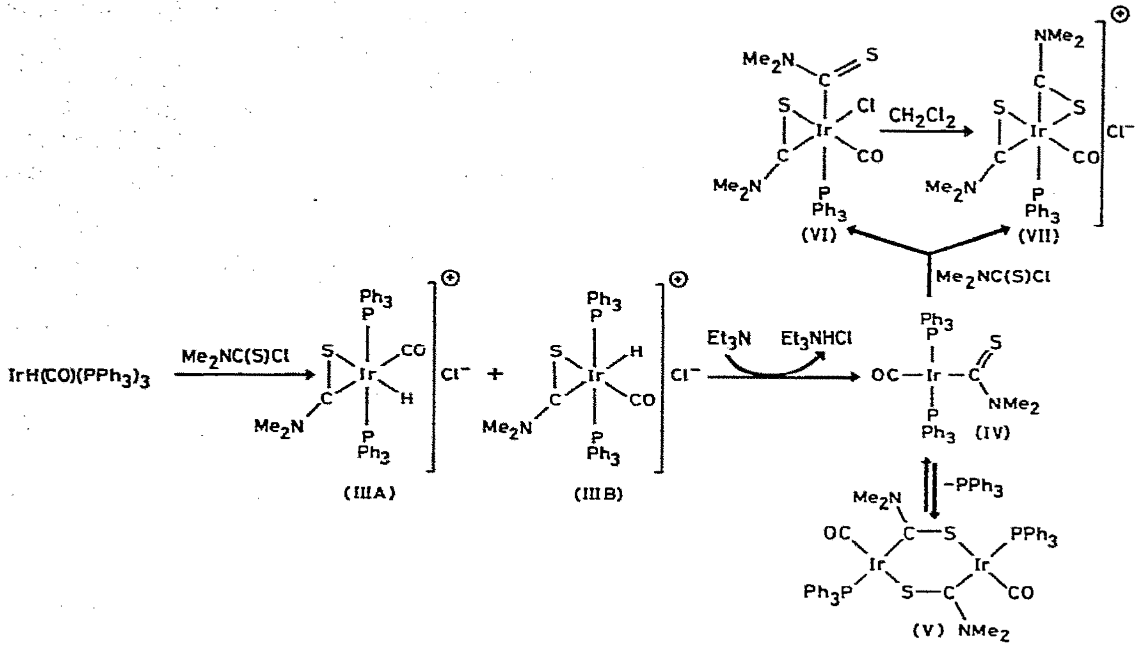
η^2-coordinated via displacement of Cl^- from iridium (III), whereas SCSMe is not. This higher tendency for η^2-coordination also has been observed for $Ru(CO)_2(\eta^2\text{-}SCX)(PPh_3)_2$ (X = SMe, N(*p*-tol)Me) [7], and has been ascribed to higher Lewis basicity of S in $SCNR_2$ caused by stronger dative p_π—p_π-interaction with the central C-atom of NR_2 compared to SR [9].

The product of the reaction of $Me_2NC(S)Cl$ with $RhH(PPh_3)_4$ or $RhH(O)(PPh_3)_3$ in the presence of Et_3N contains two η^2-$SCNMe_2$ groups, which suggests a reaction route via two successive oxidative additions of $Me_2NC(S)Cl$ to the Rh center (Scheme 1). CO displacement from $RhH(CO)(PPh_3)_3$ probably occurs in the oxidative addition of the first $Me_2NC(S)Cl$ molecule, as in the displacement of CO by $Me_2NC(S)Cl$ from $RhCl(CO)(PPh_3)_2$. If no Et_3N is present, reaction of $RhH(PPh_3)_4$ and $RhH(CO)(PPh_3)_3$ with HCl, eliminated after oxidative addition of the first $Me_3NC(S)Cl$ molecule, occurs as a side reaction. This is indicated by the formation of $RhCl_2(\eta^2\text{-}SCNMe_2)(PPh_3)_2$ (via $RhH_2Cl(PPh_3)_3$ and $RhCl(PPh_3)_3$) and $RhCl(CO)(PPh_3)_2$ (via $RhH_2Cl(CO)(PPh_3)_2$), respectively. $RhCl(CO)(PPh_3)_2$ reacts much slower with $Me_2NC(S)Cl$ than $RhCl(PPh_3)_3$ [15], so that no $RhCl_2(\eta^2\text{-}SCNMe_2)(PPh_3)_2$ is formed in the latter case. In the reaction of $Me_2NC(S)Cl$ with $RhH(PPh_3)_4$ as well as $RhH(CO)(PPh_3)_3$, attempts to isolate the intermediate hydridochlororhodium(III) complex, or the intermediate $Rh(SCNMe_2)(PPh_3)_n$, by keeping the concentration of $Me_2NC(S)Cl$ low, failed. The structural assignment of IX is based on analogy to $[Ir(\eta^2\text{-}SCNMe_2)_2(CO)(PPh_3)]^+$ (see below).



Scheme 1. The reaction of $Me_2NC(S)Cl$ with $RhH(PPh_3)_4$ and $RhH(CO)(PPh_3)_3$.

In the reaction of $Me_2NC(S)Cl$ with $IrH(CO)(PPh_3)_3$, in contrast to the analogous reaction involving $RhH(CO)(PPh_3)_3$, CO remains in the coordination sphere and the intermediate hydrido complex $[IrH(\eta^2\text{-}SCNMe_2)(CO)(PPh_3)_2]^+$ Cl^- (III) precipitates spontaneously in two isomeric forms (IIIA and IIIB, Scheme 2), which can be separated as BF_4^- salts (by fractional crystallization, see Experimental). In the analogous dithiomethylester complex, $IrClH(\eta^1\text{-}SCSMe)(CO)(PPh_3)_2$, η^1-coordination occurs and Cl^- is not displaced from the coordination sphere [6]. In III, the equivalence of both PPh_3 groups in the ^{31}P NMR spec-



Scheme 2. The reaction of $Me_2NC(S)Cl$ with $IrH(CO)(PPh_3)_3$.

trum and the observed ^2J(P—H) in the ^{1}H NMR spectrum indicate a *trans*-position of both PPh_3 groups (Table 3) (values ranging from 12--17 Hz have been reported for ^2J(P—H) *cis* [23,24]). The low values of ν(Ir—H) and τ(Ir—H) in isomer B suggest H to be *trans* to C of the η^2-$SCNMe_2$ group [25] (Tables 2 and 3). The relatively large *trans*-influence of this C-atom on ν(M—Cl) and the M—Cl distance has been reported before [1].

Reaction of III with Et_3N in benzene gives $[Ir(\mu\text{-}SCNMe_2)(CO)(PPh_3)]_2$ (V, Scheme 2) which can be isolated as brown-purple crystals. The assigned ν(C$\overset{\cdots}{=}$N) at 1503 cm^{-1} (m) is clearly at lower position and intensity than ν(C$\overset{\cdots}{=}$N) observed at 1613—1576 cm^{-1} in the η^2-$SCNMe_2Ir^{(III)}$ complexes. $\delta(CH_3)$ is lower also (1382 (m) compared to 1400—1410 cm^{-1} in η^2-$SCNMe_2$). A new absorption is found at 1129 cm^{-1}, and the absorption observed for the η^2-$SCNMe_2$ complexes in the range 817—867 cm^{-1} and tentatively assigned to a $\overline{C\text{—}S\text{—}M}$ vibration is absent in this case (Table 2). The ^{31}P NMR spectrum demonstrates the equivalence of both PPh_3 groups, in accordance with the proposed structure. The very low value of ν(CO), for a square planar iridium(I) complex [26], is in accordance with a position of CO *trans* to S of the μ-$SCNMe_2$ group. In $Ir(X)(CO)(PPh_3)_2$, ν(CO) is found at 1940—1950 cm^{-1} for X = SR and SAr [27], whereas for X = carbene, ν(CO) is observed at 1980 cm^{-1} [28]. The expected lowering *cis*-influence on ν(CO) of the carbenoid C-atom in V, which has been reported before in iridium(I) and rhodium(I) carbene complexes [28,29], makes the observed ν(CO) (1930 cm^{-1}) a reasonable value. The structure suggested for V, is comparable to that suggested for $[Pt(\mu\text{-}SCNMe_2)(PPh_3)_2]^{2+}$ and $[PdCl(\mu\text{-}SCNMe_2)$-

$P(OMe)_3]_2$. The latter has been shown by X-ray structure analysis to contain a six-membered $\overline{\text{Pd—S—C—Pd—S—C}}$ ring in the boat form [14].

If the reaction of III with Et_3N in benzene is performed in the presence of one equivalent of $Me_2NC(S)Cl$, no dimeric V is observed, but instead a mixture of $IrCl(\eta^1\text{-}SCNMe_2)(\eta^2\text{-}SCNMe_2)(CO)(PPh_3)$ (VI) and $[Ir(\eta^2\text{-}SCNMe_2)_2(CO)(PPh_3)]^+ Cl^-$ (VII) is formed (Scheme 2). As can be seen from the IR spectrum, upon dissolving the mixture in a polar solvent like CH_2Cl_2 immediately η^2-coordination and Cl^- displacement occurs in VI, so that only VII is observed (Scheme 2). In VI the IR absorptions of η^1-$SCNMe_2$ are clearly different from those of η^2-$SCNMe_2$. $\nu(C{=}N)$ of η^1-$SCNMe_2$ is lower in position and intensity than $\nu(C{=}N)$ of η^2-$SCNMe_2$ (1494m and 1612s cm^{-1}, respectively). $\delta(CH_3)$ is also somewhat lower for η^1-coordination (1366 and 1406 cm^{-1}). As for μ-$SCNMe_2$ in V, for η^1-$SCNMe_2$ in VI an absorption is observed at ~1130 cm^{-1} and no absorption in the range 817—867 cm^{-1}. The absorption at 945 cm^{-1} is assigned to $\nu(C{=}S)$, analogous to the assignment in $PtCl(\eta^1\text{-}SCNMe_2)(PPh_3)_2$ [14,30], and occurs at higher frequency than the absorption in the range for the η^2-$SCNMe_2$ complexes (924—911 cm^{-1}).

The formation of V and VII from IIIA and IIIB has been studied in CH_2Cl_2 into somewhat more detail. The ^{31}P NMR spectrum of a solution of III in CD_2Cl_2 shows the presence of IIIA and IIIB in a ratio 2/1. Upon addition of Et_3N, IIIA is immediately converted and the single resonance of V is observed (δ 11.6 ppm) together with a somewhat broadened resonance at δ —15.0 ppm, ascribed to the monomeric *trans*-$Ir(\eta^1\text{-}SCNMe_2)(CO)(PPh_3)_2$ (IV, Scheme 2). Also a resonance of PPh_3 is observed, broadened and somewhat shifted from its free resonance position, probably because of exchange with PPh_3 in IV ($\delta(PPh_3)$ rel. to TMP: unshifted: +7.7 ppm; observed: +6.4 ppm). IIIB is much slower dehydrohalogenated than IIIA to give the same products. If 2 mol of PPh_3 per mol of Ir are added before addition of Et_3N, almost no V is observed, suggesting the existance of an equilibrium between IV and V. If 4 mol of PPh_3 per mol of Ir are added to a concentrated solution of V in CD_2Cl_2, slow formation of IV is observed and after 2 h 75% of the dimer has been converted into IV. In the ^1H NMR the two broadened singlets observed for IV indicate hindered rotation around the $C{=}N$ bond as for V and the $(\eta^2\text{-}SCNMe_2)Ir^{III}$ complexes. In $PtCl(\eta^1\text{-}SCNMe_2)(PPh_3)_2$ also hindered rotation around the $C{=}N$ bond has been observed [14]. In the IR besides $\nu(CO)$ of V (1930 cm^{-1}) also $\nu(CO)$ of IV is observed (1950 cm^{-1}). The occurrence of a new absorption at 940 cm^{-1} ($\nu(C{=}S)$) suggests η^1-coordination of the $SCNMe_2$ group in IV. No other absorptions significantly different from those of V are observed. Upon addition of $Me_2NC(S)Cl$ to the CD_2Cl_2 solution of IV and V, IV is completely converted into VII within 1 h, whereas resonances of V are still observed in the ^1H and ^{31}P NMR spectrum at that time. If $Me_2NC(S)Cl$ is added to a solution of V in CD_2Cl_2, V has still not completely been converted after 2 h and, besides formation of VII, formation of other unidentified products is observed. So IV has been shown to be an intermediate in the reaction of $Me_2NC(S)Cl$ with $IrH(CO)(PPh_3)_3$ to VII (Scheme 2).

Conclusions

Starting from $Me_2NC(S)Cl$ and $IrH(CO)(PPh_3)_3$, products containing three different types of coordination for $SCNMe_2$ (η^2, η^1 and μ) have been observed.

Within $IrCl(\eta^1\text{-}SCNMe_2)(\eta^2\text{-}SCNMe_2)(CO)(PPh_3)$, η^1- and η^2-$SCNMe_2$ can clearly be distinguished by IR. The difference in IR absorption between μ-$SCNMe_2$ and η^1-$SCNMe_2$, coordinated to iridium(I) is less pronounced. The dimeric $[Ir(\mu\text{-}SCNMe_2)(CO)(PPh_3)]_2$ is unprecedented in iridium(I) chemistry, and its air-sensitivity makes investigation of its reactivity towards molecular oxygen worthwhile. Whereas η^2-coordination seems to be preferred by rhodium(III) and iridium(III), η^1 and μ-coordination in a square planar complex seem to be preferred by iridium(I). This is similar to the observed preference for η^1 and μ-coordination of palladium(II) and platinum(II) [14]. The isolated Rh^{III}—and Ir^{III}—$(\eta^2\text{-}SCNMe_2)_2$ complexes are the first examples in this category. In order to reveal the coordination geometry in these complexes, an X-ray structure analysis of $Ir(\eta^2\text{-}SCNMe_2)_2(CO)(PPh_3)]^+ BF_4^-$ was performed.

B. X-ray diffraction study of $[Ir(\eta^2\text{-}SCNMe_2)_2(CO)(PPh_3)]^+ BF_4^-$

Experimental

$[Ir(\eta^2\text{-}SCNMe_2)_2(CO)(PPh_3)]^+ BF_4^-$ was recrystallized from dichloromethane/methanol to give colourless crystals. A well formed crystal, with the dimensions 0.5 × 0.4 × 0.15 mm was selected for X-ray work. Weissenberg (Cu-K_α) photographs indicated that the cell was monoclinic, the space group being $P2_1/n$. Cell data, as determined from a least-square refinement of diffractometer readings for 24 reflections with $2\theta > 42°$, using Mo-K_α radiation (λ 0.71069 Å), are given in Table 4. Reflection data were collected on a NONIUS CAD-4 single crystal diffractometer employing monochromated Mo-K_α radiation. The "moving crystal, moving counter technique" was used. 6447 independent intensities were collected up to $\sin \theta/\lambda$ 0.65 Å^{-1}. 3858 reflections were more than 3 times the standard deviation. The intensities of four standard reflections, each measured after every 15 reflections, showed a linear decrease up to 30%, due to the occurrence of severe radiation damage. The data were corrected for the decrease in intensity, for Lorentz and polarization effects, and for absorption (μ 51.52 cm^{-1}, the absorption coefficients on the intensity were calculated in the range of 2.10—2.37).

Structure solution and refinement

The iridium atom was found from a three dimensional Patterson map. The remaining part of the structure was found by applying direct methods on normallised difference Fourier coefficients using the program DIRDIF.B [31]. The

TABLE 4

CELL DATA

Space group: $P2_1/n$
a 9.730(2) Å
b 21.151(3) Å
c 15.281(2) Å
β 112.01(2) Å
$Z = 4$
d(calcd.) 1.70 g cm^{-1}
d(obs.) 1.69 g cm^{-1}

resulting Fourier synthesis shows the positions of the sulfur, phosphorus and nine carbon atoms. The remaining non-hydrogen atoms were located on a difference Fourier map. The reflections with $I > 3\sigma$ were used in the refinement by full matrix least squares methods, allowing anisotropic vibration for iridium, sulfur, phosphorus and fluorine atoms. The quantity minimised was $\Sigma w(|F_o| - k|F_c|)^2$, with $w = [\sigma_F{}^2 + 0.002\,F_o{}^2]^{-1}$ and $\sigma_F = (F/2I)$. The hydrogen atoms were placed at calculated positions.

As demonstrated by the high value of their thermal parameters (Table 6), the fluorine atoms are disordered. A difference Fourier map did not give other possible positions for the fluorine atoms. All parameters shifts in the final cycle were smaller than their e.s.d.'s. The final conventional R-value was 0.052 (on 3858 reflections) *. The atomic scattering factors were those of the neutral atoms [32]. Those of Ir were corrected for the real and imaginary part of the anomalous dispersion. All calculations were carried out on an IBM 370/158 computer with the X-ray system of crystallographic programs [33].

Results and discussion

Positional and thermal parameters are listed in Tables 5 and 6. Structural parameters derived from the X-ray data are presented in Table 7. Because of the unreliability of the fluorine positions, the bond distances and angles of the BF_4^- ion are not given. The configuration of the $[Ir(\eta^2\text{-}SCNMe_2)_2(CO)(PPh_3)]^+$ ion is given in Fig. 2. The X-ray structure analysis confirms the η^2-coordination of both $SCNMe_2$ groups. In both $SCNMe_2$ moieties, the C—S and C—N distance, the S—C—N angle and the angles within the Ir—C—S ring are not significantly different from those in other η^2-$SCNMe_2$ groups, coordinated rhodium(III), molybdenum(IV) and manganese(I) [8—10]. The Ir—C distances observed for the $SCNMe_2$ groups fall at the low end of the range observed for Ir^{III}—C_{sp^2} bonds (1.98—2.06 Å) [16—18], and are significantly longer than the Ir—CO distance in the same complex. The Ir—S distances are longer than other Ir^{III}—S distances observed before, e.g. in $Ir(S_2CNEt_2)_2$ the average Ir—S distance is 2.36 Å [39].

Both $IrSCNMe_2$ units are virtually planar. The largest deviation from the least-squares plane through the atoms Ir, S(1), C(1), N(1), C(2), C(3) (plane I) is 0.07 Å for C(3), and the largest deviation from the least-squares plane through Ir, S(2), C(4), N(2), C(5) and C(6) (plane II) is 0.04 Å for C(4). Both $IrSCNMe_2$ units are oriented approximately perpendicular to each other (the angle between plane I and plane II is 85.5°) and roughly perpendicular to the least-squares plane through P, Ir, C(7) and O (plane III). The angle between the planes I and III is 74.3° and between the planes II and III 81.9°. The Ir—P bond is approximately situated in plane I (distance of P from this plane, 0.3 Å) and the carbonyl group is situated in plane II (distances from this plane, C(7) 0.02 Å; O 0.03 Å). The orientations of the $SCNMe_2$ groups in plane I and plane II relative to the Ir—P and the Ir—CO bond respectively are given in Fig. 3. We suggest to describe the observed geometry as octahedral, distorted by the ring-strain within both Ir—C—S rings.

The coordinating CS bond of $(SCNMe_2)_I$ is located beneath least-squares plane III (C(1) —0.81; S(1) —2.21 Å) and the CS bond of $(SCNMe_2)_{II}$ is located above this

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* A list of the structure factors can be obtained from the authors on request.

TABLE 5

FINAL ATOMIC COORDINATES FOR THE NON-HYDROGEN ATOMS WITH STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z
Ir	0.10648(4)	0.11478(2)	0.15255(3)
S(1)	—0.1600(3)	0.0981(2)	0.1164(3)
S(2)	0.1681(4)	0.0290(2)	0.0638(3)
P	0.2564(3)	0.0669(2)	0.2990(2)
O	0.1563(15)	0.2454(6)	0.2305(9)
N(1)	—0.1436(10)	0.1563(4)	—0.0372(6)
N(2)	0.3525(15)	0.1252(6)	0.0669(9)
C(1)	—0.0855(11)	0.1334(5)	0.0459(7)
C(2)	—0.0540(15)	0.1873(6)	—0.0824(9)
C(3)	—0.3063(16)	0.1517(7)	—0.0954(10)
C(4)	0.2492(13)	0.1006(5)	—0.919(8)
C(5)	0.4019(23)	0.1894(9)	0.0938(14)
C(6)	0.4198(25)	0.0892(10)	0.0109(15)
C(7)	0.1369(14)	0.1964(6)	0.2016(9)
C(81)	0.4356(11)	0.0440(5)	0.3019(7)
C(82)	0.5347(14)	0.0902(6)	0.2961(9)
C(83)	0.6656(17)	0.0757(7)	0.2906(10)
C(84)	0.7095(20)	0.0137(8)	0.2912(12)
C(85)	0.6143(18)	—0.0366(8)	0.2934(12)
C(86)	0.4729(16)	—0.0192(6)	0.3007(9)
C(91)	0.2906(12)	0.1163(5)	0.4026(8)
C(92)	0.1672(13)	0.1480(5)	0.4099(8)
C(93)	0.1828(15)	0.1831(6)	0.4891(9)
C(94)	0.3311(18)	0.1912(7)	0.5596(11)
C(95)	0.4438(16)	0.1613(7)	0.5510(10)
C(96)	0.4321(14)	0.1239(5)	0.4703(9)
C(101)	0.1704(12)	—0.0044(5)	0.3263(7)
C(102)	0.0665(14)	—0.0387(6)	0.2544(8)
C(103)	0.0044(16)	—0.0936(7)	0.2758(10)
C(104)	0.0400(23)	—0.1114(8)	0.3665(14)
C(105)	0.1485(20)	—0.0780(8)	0.4405(12)
C(106)	0.2137(20)	—0.0238(7)	0.4181(11)
B	0.722(2)	0.760(1)	0.180(2)
F(1)	0.671(3)	0.720(2)	0.109(2)
F(2)	0.868(2)	0.756(1)	0.196(3)
F(3)	0.688(3)	0.817(1)	0.167(2)
F(4)	0.729(3)	0.728(2)	0.255(2)

plane (C(4) +1.86 Å; S(2) +1.21 Å). The orientation of the two CS bonds relative to the plane defined by the metal and the two other donor atoms in the 18 electron Ir complex, is different from that observed for the two coordinating CC bonds in the 16 electron Rh complex, Rh(acac)(η^2-Me_2CCCMe_2)$_2$ [34]. In this complex the Rh(η^2-Me_2CCCMe_2) planes also are roughly perpendicular to each other and to the plane formed by Rh and the two donor atoms of the acetylacetonato ligand. But now each coordinating CC bond is intersected by this latter plane, so that for each coordinating CC bond one C atom is situated above and one below this plane. To define the structural difference: if η^2-SCNMe$_2$ and η^2-Me_2CCCMe_2 in the two complexes are both seen as bidentate, the 16 electron Rh complex is best described as distorted trigonal prismatic, whereas the 18 electron Ir complex is best described as distorted octahedral.

(Continued on p. 96)

TABLE 6

THERMAL PARAMETERS X10^2 FOR THE NON-HYDROGEN ATOMS

Thermal parameters are expressed in the form $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + U_{12}hka^*b^* + U_{13}hla^*c^* + U_{23}klb^*c^*)]$ where the U_{ij} values are in Å.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ir	3.82(3)	4.93(3)	4.03(3)	0.08(2)	1.31(2)	—0.22(2)
S(1)	4.3(2)	9.4(2)	6.2(2)	0.8(2)	2.4(2)	1.4(2)
S(2)	5.4(3)	7.4(2)	6.6(2)	0.3(2)	2.6(2)	—1.7(2)
P	3.7(2)	4.8(1)	4.3(2)	0.3(1)	1.3(1)	—0.1(1)
F(1)	17(2)	27(2)	16(2)	—4(2)	—2(2)	—4(2)
F(2)	9(2)	22(2)	43(4)	—2(2)	9(3)	5(2)
F(3)	20(2)	12(1)	33(3)	2(2)	—11(2)	6(2)
F(4)	40(4)	12(3)	12(3)	6(2)	11(2)	9(2)

Atom	U_{11}	Atom	U_{11}
O	10.2(4)	C(85)	8.8(4)
N(1)	5.4(2)	C(86)	7.0(3)
N(2)	7.5(3)	C(91)	5.0(3)
C(1)	4.8(2)	C(92)	5.7(3)
C(2)	6.7(3)	C(93)	6.8(3)
C(3)	7.6(3)	C(94)	8.0(4)
C(4)	5.8(3)	C(95)	7.6(4)
C(5)	10.2(5)	C(96)	6.0(3)
C(6)	11.4(6)	C(101)	5.0(2)
C(7)	6.5(3)	C(102)	6.1(3)
C(81)	4.9(2)	C(103)	7.4(3)
C(82)	6.3(3)	C(104)	9.7(5)
C(83)	7.6(4)	C(105)	9.2(5)
C(84)	8.7(4)	C(106)	8.4(4)
		B	9(1)

TABLE 7

BOND LENGTHS (Å) AND ANGLES (°) IN THE $[Ir(\eta^2\text{-}SCNMe_2)(CO)(PPh_3)]^+$ ION

Coordination of the iridium					
Ir—S(1)	2.465(3)	Ir—P	2.391(2)	Ir—C(4)	1.961(15)
Ir—S(2)	2.469(4)	Ir—C(1)	2.005(9)	Ir—C(7)	1.860(12)
S(1)—Ir—S(2)	102.9(1)	S(1)—Ir—C(7)	102.6(5)	P—Ir—C(4)	95.0(3)
S(1)—Ir—P	111.8(1)	S(2)—Ir—C(1)	92.4(3)	P—Ir—C(7)	93.8(4)
S(2)—Ir—P	90.8(1)	S(2)—Ir—C(4)	42.9(4)	C(1)—Ir—C(4)	105.0(5)
S(1)—Ir—C(1)	42.6(4)	S(2)—Ir—C(7)	150.2(5)	C(1)—Ir—C(7)	96.0(5)
S(1)—Ir—C(4)	138.1(3)	P—Ir—C(1)	154.1(4)	C(4)—Ir—C(7)	107.3(6)
The thiocarboxamido ligand $(SCNMe_2)_I$					
S(1)—C(1)	1.681(12)	N(1)—C(1)	1.28(2)	N(1)—C(2)	1.46(2)
N(1)—C(3)	1.50(2)	Ir—S(1)—C(1)	53.9(3)	Ir—C(1)—S(1)	83.5(4)
Ir—C(1)—N(1)	144(1)	S(1)—C(1)—N(1)	132.0(9)	C(1)—N(1)—C(2)	121.5(9)
C(1)—N(1)—C(3)	123(1)	C(2)—N(1)—C(3)	116(1)		
The thiocarboxamido ligand $(SCNMe_2)_{II}$					
S(2)—C(4)	1.688(11)	N(2)—C(4)	1.31(2)	N(2)—C(5)	1.45(2)
N(2)—C(6)	1.47(3)	Ir—S(2)—C(4)	52.3(5)	Ir—C(4)—S(2)	84.8(6)
Ir—C(4)—N(2)	146.6(9)	S(2)—C(4)—N(2)	128(1)	C(4)—N(2)—C(5)	120(2)
C(4)—N(2)—C(6)	121(2)	C(5)—N(2)—C(6)	119(2)		
Coordination of the phosphorus					
P—C(81)	1.80(2)	P—C(91)	1.82(2)	P—C(101)	1.85(2)
Ir—P—C(81)	112.6(4)	Ir—P—C(101)	112.9(3)	C(81)—P—C(101)	102.9(5)
Ir—P—C(91)	114.9(3)	C(81)—P—C(91)	105.9(5)	C(91)—P—C(101)	106.9(5)
Carbonyl					
C(7)—O	1.117(17)	Ir—C(7)—O	179(2)		

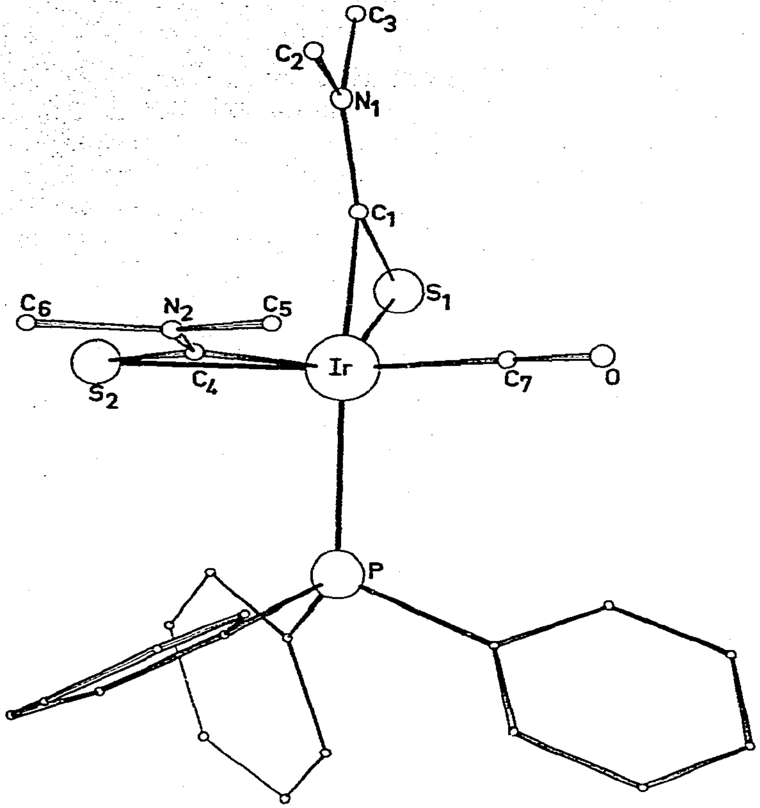

Fig. 2. The configuration of the $[Ir(\eta^2\text{-}SCNMe_2)_2(CO)(PPh_3)]^+$ ion.

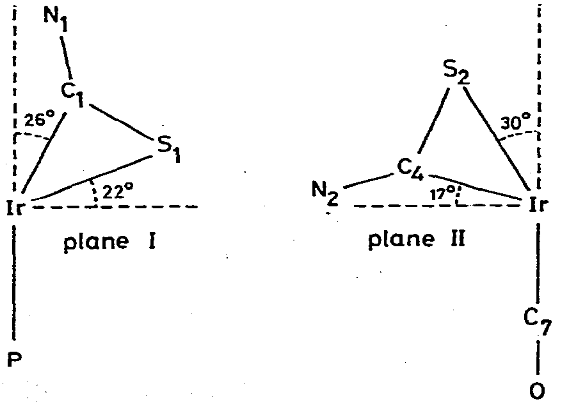

Fig. 3. The orientation of $(SCNMe_2)_I$ and $(SCNMe_2)_{II}$ in plane I and plane II relative to the Ir—P and the Ir—CO bond respectively.

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