Rhodium(I) and Iridium(I) Carbonyl Complexes with Sulphur-donor Ligands; *X*-Ray Crystal Structure of $[Rh(CO)_2(Bu^tSCH{=}CHSBu^t)]ClO_4$ †

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The reactivity towards carbon monoxide of cationic complexes of Rh^I and Ir^I containing cyclo-octa-1,5-diene (cod) and sulphur-donor ligands has been studied. Mononuclear five-co-ordinated $[Ir(CO)_2(cod)L]ClO_4$ (L = tetrahydrothiophene, trimethylene sulphide, SMe_2, or SEt_2), binuclear four-co-ordinated $[(OC)_2Ir\{\mu\text{-}(L{-}L)\}_2Ir(CO)_2][ClO_4]_2$ [L–L = $Bu^tS(CH_2)_2SBu^t$ or 1,4-dithiacyclohexane (dtch)], and binuclear five-co-ordinated $[(cod)(OC)Ir\{\mu\text{-}(L{-}L)\}_2Ir(CO)(cod)][ClO_4]_2$ [L–L = $Bu^tS(CH_2)_2SBu^t$, dtch, or MeSSMe] have been prepared. Rhodium(I) cationic carbonyl complexes of formulation $[Rh(CO)_2(L{-}L)]_n[ClO_4]_n$ [L–L = dtch or $MeS(CH_2)_3SMe$] have been obtained from $[(OC)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$. When the ligand was $Bu^tS(CH_2)_2SBu^t$ the structure of the carbonyl complex obtained was determined by single-crystal *X*-ray diffraction. Surprisingly, the saturated ligand is found to be converted into $Bu^tSCH{=}CHSBu^t$ giving the complex $[Rh(CO)_2(Bu^tSCH{=}CHSBu^t)]ClO_4$. The crystals are orthorhombic, space group $Ccm2_1$. The rhodium is four-co-ordinated to two CO groups and two S atoms in a square-planar fashion. The five-membered chelate ring is planar.

It is well known that carbon monoxide reacts with four-co-ordinated cationic rhodium(I) complexes containing diolefins and nitrogen, phosphorus-, or oxygen-donor ligands (L) to give carbonyl derivatives of the type $[Rh(CO)_xL_2]^+$ (x = 2 or 3).[1,2] Cationic diolefin iridium(I) complexes have been studied to a lesser extent. The carbonylation of $[Ir(cod)\{P(C_6H_4Me\text{-}p)_3\}_2]BPh_4$ (cod = cyclo-octa-1,5-diene) leads to the formation of $[Ir(CO)_3\{P(C_6H_4Me\text{-}p)_3\}_2]BPh_4$.[3] The reaction of $[Ir(diolefin)(L{-}L)]ClO_4$ [L–L = 2,2′-bipyridyl (bipy) or 1,10-phenanthroline (phen)] complexes with carbon monoxide gives the corresponding five-co-ordinated adducts $[Ir(diolefin)(L{-}L)(CO)]ClO_4$, and slow displacement of diolefins leads to subsequent formation of tricarbonyl derivatives.[4] On the other hand, similarly carbonylated 1,10-phenanthroline complexes $[Ir(CO)_xL_2]^+$ (x = 2 or 3, L = P-donor ligands) have been isolated by different routes from $[\{Ir(CO)_3Cl\}_n]$ and *trans*-$[Ir(CO)ClL_2]$.[5,6]

Continuing our studies on complexes of Rh^I and Ir^I containing the diolefin cod and sulphur-donor ligands,[7–9] the reactivity of complexes previously reported[7,8] towards carbon monoxide has been studied. The formation of mononuclear five-co-ordinated and binuclear four- or five-co-ordinated iridium(I) carbonyl complexes together with carbonylated rhodium(I) complexes $[Rh(CO)_2(L{-}L)]_n[ClO_4]_n$ (L–L = bidentate sulphur-donor ligand) obtained from $[(OC)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$[10] is reported. The crystal structure of the complex obtained from the reaction with $Bu^tS(CH_2)_2SBu^t$ has been determined by *X*-ray analysis and shows the formation of an unexpected double bond in the ligand co-ordinated to Rh^I, *i.e.* $[Rh(CO)_2(Bu^tSCH{=}CHSBu^t)]ClO_4$.

Results and Discussion

Rhodium(I) *Carbonyl Complexes*.—(*i*) *Reactivity of* $[Rh(cod)L_2]ClO_4$ *and* $[(cod)Rh\{\mu\text{-}(L{-}L)\}_2Rh(cod)][ClO_4]_2$ *with carbon monoxide*. The bubbling of carbon monoxide at room temperature through dichloromethane solutions of $[Rh(cod)L_2]ClO_4$ [L = tetrahydrothiophene (tht), trimethylene sulphide (tms), SMe_2, or SEt_2; L_2 = $MeS(CH_2)_3SMe$] and $[(cod)Rh\{\mu\text{-}(L{-}L)\}_2Rh(cod)][ClO_4]_2$ [L–L = 1,4-dithiacyclohexane (dtch) or $Bu^tS(CH_2)_2SBu^t$] complexes brings about the formation of carbonylated species. Two ν(CO) bands characteristic of *cis*-dicarbonylrhodium(I) complexes[11] are detected in the 2 100—2 000 cm^{-1} region of the spectra of the solutions. However, attempts to isolate the solid carbonyl complexes have been unsuccessful because of the tendency of such complexes to form oil.

(*ii*) *Preparation of* $[Rh(CO)_2(L{-}L)]_n[ClO_4]_n$ *from* $[(OC)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$. Rhodium(I) carbonyl complexes with bidentate sulphur-donor ligands can be prepared by addition of the appropriate ligand to acetone solutions of $[Rh(CO)_2(Me_2CO)_x]ClO_4$[12] obtained by treating $[(OC)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$ with silver perchlorate [equation (i)]. Attempts to prepare complexes with unidentate sulphur-donor ligands

$$n\,[Rh(CO)_2(Me_2CO)_x]ClO_4 + n\,L{-}L \longrightarrow [Rh(CO)_2(L{-}L)]_n[ClO_4]_n + nx\,Me_2CO \qquad \text{(i)}$$

$$\begin{array}{ll} L{-}L = Bu^tS(CH_2)_2Bu^t, & L{-}L = Bu^tSCH{=}CHSBu^t, \\ \quad MeS(CH_2)_3SMe, & \quad MeS(CH_2)_3SMe, \\ \quad \text{or dtch} & \quad \text{or dtch} \end{array}$$

(L = tht, tms, SMe_2, or SEt_2) using the same route were unsuccessful since solid mixtures of complexes were obtained.

Addition of $Bu^tS(CH_2)_2SBu^t$ to acetone solutions of $[Rh(CO)_2(Me_2CO)_x]ClO_4$ leads to solutions from which a yellow crystalline solid can be isolated by adding diethyl

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† [1,2-Bis(t-butylthio)ethylene-*SS*′]dicarbonylrhodium(I) perchlorate.

Supplementary data available (No. SUP 56040, 8 pp.): thermal parameters, H-atom co-ordinates, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Analytical [a] and physical data for the rhodium(I) and iridium(I) carbonyl complexes

					Conductivity data		Analysis (%)		
Complex	Colour	M.p.[b] (°C)	Yield (%)	ν(CO)[c]/cm^{-1}	Λ_M/S cm^2 mol^{-1}	A[d]	C	H	S
(1) $[Ir(CO)_3(cod)]ClO_4$	Blue	135—140	65	2 070s, 2 095s, 2 135s	129	—	26.65 (27.25)	2.50 (2.50)	
(2) $[Ir(CO)_2(cod)(tht)]ClO_4$	Pink	125—130	80	2 040s, 2 090s	147	—	30.30 (30.85)	3.65 (3.65)	6.00 (5.90)
(3) $[Ir(CO)_2(cod)(tms)]ClO_4$	Pink	100—110	75	2 040s, 2 090s	141	—	28.80 (29.45)	3.15 (3.40)	6.35 (6.05)
(4) $[Ir(CO)_2(cod)(SMe_2)]ClO_4$	Pink	130—135	70	2 040s, 2 090s	152	—	28.50 (27.80)	3.65 (3.45)	5.90 (6.20)
(5) $[Ir(CO)_2(cod)(SEt_2)]ClO_4$	Pink	65—70	76	2 040s, 2 090s	148	—	31.05 (30.75)	4.25 (4.05)	5.60 (5.85)
(6) $[(cod)(OC)Ir\{\mu\text{-}Bu^tS(CH_2)_2SBu^t\}_2Ir(CO)(cod)][ClO_4]_2$	Yellow	135—140	86	1 980s	271	717	35.75 (35.95)	5.15 (5.35)	9.95 (10.10)
(7) $[(cod)(OC)Ir(\mu\text{-}dtch)_2Ir(CO)(cod)][ClO_4]_2$	Yellow	70—75	80	2 010s	284	896	28.05 (28.45)	3.80 (3.65)	11.95 (11.70)
(8) $[(cod)(OC)Ir(\mu\text{-}MeSSMe)_2Ir(CO)(cod)][ClO_4]_2$	Yellow	60—65	75	2 055s	—	—	24.70 (25.30)	3.70 (3.45)	11.70 (12.25)
(9) $[(OC)_2Ir\{\mu\text{-}Bu^tS(CH_2)_2SBu^t\}_2Ir(CO)_2][ClO_4]_2$	Orange	90—95	62	1 980s, 2 020s, 2 095s	267	567	25.40 (26.00)	4.15 (3.95)	11.25 (11.55)
(10) $[(OC)_2Ir(\mu\text{-}dtch)_2Ir(CO)_2][ClO_4]_2$	Yellow	60—65	78	2 040s, 2 100s, 2 150s	284	1 055	15.95 (15.40)	1.85 (1.70)	13.80 (13.70)
(11) $[Rh(CO)_2(Bu^tSCH{=}CHSBu^t)]ClO_4$	Yellow	84—87	70	2 045s, 2 098s [e]	140	—	31.50 (31.20)	4.60 (4.35)	13.50 (13.90)
(12) $[Rh(CO)_2(dtch)]_n[ClO_4]_n$	Yellow	105—108	79	2 005s, 2 050s, 2 103s	—	—	19.60 (19.05)	2.25 (2.15)	16.95 (16.95)
(13) $[Rh(CO)_2\{MeS(CH_2)_3SMe\}]_n[ClO_4]_n$	Brown	110—115	80	2 025s, 2 055s, 2 115s	—	—	20.95 (21.30)	2.90 (3.05)	16.45 (16.25)

[a] Required values are given in parentheses. [b] With decomposition. [c] Nujol mulls. [d] Slope of Onsager's equation measured in acetone solution. [e] Recorded in dichloromethane solution.

ether. The i.r. spectra show several bands in the ν(CO) region which could be assigned to solid-state effects as previously observed in related complexes,[13,14] since solutions of this complex show two ν(CO) bands in the 2 100—2 000 cm^{-1} region typical of *cis*-dicarbonyl mononuclear rhodium(I) complexes. The crystal structure of this reaction product has been determined by *X*-ray analysis and confirms the preparation of a dicarbonyl mononuclear cationic compound, but which has an unexpected double bond in the sulphur ligand $Bu^tSCH{=}CHSBu^t$ bonded to the metal. The structure was determined from a crystal grown from a CH_2Cl_2–Et_2O solution of the compound and repeated with crystals arising directly from the reaction in acetone [equation (i)]. The same results were achieved in both determinations, suggesting that the formation of the double bond occurs in the initial reaction, and could be related to the catalytic activity of rhodium(I) complexes. Studies of the $[Rh(CO)_2(Bu^tSCH{=}CHSBu^t)]ClO_4$ compound and its formation are currently in progress.

The same reaction with L–L = $MeS(CH_2)_3SMe$ or dtch leads to the precipitation of solids whose elemental analyses are in accordance with the $[Rh(CO)_2(L\text{–}L)]_n[ClO_4]_n$ formulation. The i.r. spectra of these show several bands in the ν(CO) region. However such complexes are sparingly soluble and their solutions unstable; therefore the i.r. spectra in solution could not be recorded and the nuclearity could not be established by measuring conductivities at various concentrations. Elemental analyses, ν(CO) data, and yields of the isolated complexes are summarized in Table 1.

Single-crystal *X*-ray analysis on the $[Rh(CO)_2(Bu^tSCH{=}CHSBu^t)]^+$ ion shows that it has C_s symmetry, which is also a crystallographic symmetry (Figure). The rhodium atom is located on a mirror plane and displays a square-planar co-ordination. The five-membered ring is planar, with atom C(1) showing high anisotropic thermal parameters normal to this plane. The bond lengths and angles (Table 2) are within three standard deviations of those obtained by Richter *et al.*[15] and the Rh–CO bond lengths are within one standard deviation of those obtained by Cowie and Dwight.[16] The structure consists of discrete ions linked by ionic and van der Waals forces. The shortest interionic distance is 3.66 Å between Rh and O(2′).

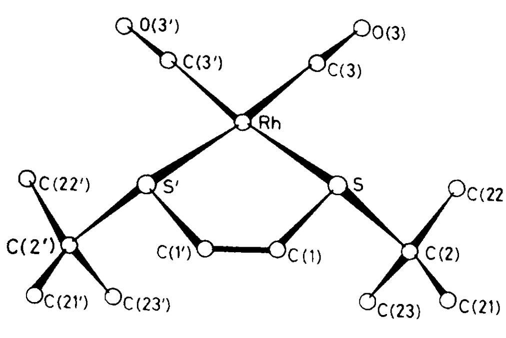

Figure 1. View of the crystal structure of $[Rh(CO)_2(Bu^tSCH{=}CHSBu^t)]^+$ with the atom numbering

Iridium(I) *Carbonyl Complexes*.—(*i*) *Five-co-ordinated mononuclear complexes*. We recently reported the preparation of $[Ir(cod)L_2]ClO_4$ (L = tht or tms) and $[(cod)Ir(\mu\text{-}L)_2Ir(cod)][ClO_4]_2$ (L = SMe_2 or SEt_2).[8] When carbon monoxide is bubbled at room temperature through dichloromethane solutions of these complexes five-co-ordinated dicarbonyl compounds are formed according to equations (ii) and (iii).

$$[\mathrm{Ir(cod)L_2]ClO_4} + 2\,\mathrm{CO} \longrightarrow [\mathrm{Ir(CO)_2(cod)L]ClO_4} + \mathrm{L} \quad \text{(ii)}$$

L = tht or tms

$$[\mathrm{(cod)Ir(\mu\text{-}L)_2Ir(cod)][ClO_4]_2} + 4\,\mathrm{CO} \longrightarrow 2\,[\mathrm{Ir(CO)_2(cod)L]ClO_4} \quad \text{(iii)}$$

$\mathrm{L = SMe_2}$ or $\mathrm{SEt_2}$

The i.r. spectra of these carbonylated complexes show two bands in the 2 100—2 000 $\mathrm{cm^{-1}}$ region characteristic of *cis*-dicarbonyl compounds (Table 1). The pink solids are relatively stable in air. The C, H, and S elemental analyses, molar conductivities in acetone, yields, melting points, and ν(CO) are listed in Table 1. Proton n.m.r. spectra of $\mathrm{CD_3Cl}$ solutions of $[\mathrm{Ir(CO)_2(cod)L]ClO_4}$ have been recorded (Table 3). The spectra show resonances corresponding to the vinyl and methylenic protons of cod, which have shifted downfield from the corresponding resonances of $[\mathrm{Ir(cod)L_2]ClO_4}$.[17] Analogously, the signals corresponding to the sulphur-donor ligands have also shifted downfield compared to those of the free ligands.

It is noteworthy that diolefin iridium(I) cationic complexes with sulphur-donor ligands show a different behaviour to that of $[\mathrm{Ir(cod)L_2]ClO_4}$ (L = P-donor ligand). The latter undergo diolefin displacement with carbon monoxide.[6] The formation of five-co-ordinated complexes $[\mathrm{Ir(CO)_2(cod)L]ClO_4}$ could be attributed to the tendency of $\mathrm{Ir^I}$ to form five-co-ordinated species [18] together with the presence of the sulphur ligand co-ordinated to the metal.

The time required for reactions (ii) and (iii) is a few seconds. When these reactions are carried out by bubbling CO over a long period some cod is displaced and mixtures with other products are obtained.

The reaction of the starting material $[\mathrm{Ir(cod)_2]ClO_4}$ [8] with carbon monoxide has been studied as well. When CO is bubbled through dichloromethane solutions of $[\mathrm{Ir(cod)_2]ClO_4}$ a decolouration of the solutions is observed and a carbonyl complex showing three i.r. bands in the 2 150—2 000 $\mathrm{cm^{-1}}$ region can be isolated. According to the i.r. spectra and elemental analyses (Table 1), the formation of $[\mathrm{Ir(CO)_3(cod)]ClO_4}$ is suggested.

Table 2. Interatomic distances (Å) and angles (°) for $[\mathrm{Rh(CO)_2(Bu^tSCH{=}CHSBu^t)]ClO_4}$

Rh–S	2.364(3)	C(2)–C(21)	1.49(2)
Rh–C(3)	1.86(1)	C(2)–C(22)	1.53(2)
S–C(1)	1.83(3)	C(2)–C(23)	1.51(3)
S–C(2)	1.86(1)	C(3)–O(3)	1.15(2)
C(1)–C(1)	1.23(7)		
C(3)–Rh–S	92.3(5)	C(2)–S–C(1)	105(1)
S–Rh–S	87.1(2)	C(21)–C(2)–S	108(1)
C(3)–Rh–C(3)	87.5(8)	C(22)–C(2)–S	108(1)
S–C(1)–C(1)	124(2)	C(23)–C(2)–S	107(1)
Rh–C(3)–O(3)	175(1)	C(22)–C(2)–C(21)	108(1)
C(1)–S–Rh	102(1)	C(23)–C(2)–C(21)	119(2)
C(2)–S–Rh	115.5(5)	C(23)–C(2)–C(22)	106(2)

(*ii*) *Binuclear complexes*. The carbonylation reactions of binuclear complexes of the type $[\mathrm{(cod)Ir\{\mu\text{-}(L{-}L)\}_2Ir(cod)][ClO_4]_2}$ [$\mathrm{L{-}L = Bu^tS(CH_2)_2SBu^t, MeS(CH_2)_3SMe}$, or MeSSMe] [8] gives different products depending on the bidentate ligand present and the time of reaction, as shown in equations (iv) and (v). The i.r. spectra of dichloromethane solutions of the tetracarbonylated complexes $[\mathrm{(OC)_2Ir\{\mu\text{-}(L{-}L)\}_2Ir(CO)_2][ClO_4]_2}$ show three ν(CO) bands in the 2 150—1 950 $\mathrm{cm^{-1}}$ region. Several previously reported tetracarbonylated binuclear compounds of $\mathrm{Rh^I}$ and $\mathrm{Ir^I}$ exhibit three similar CO stretching bands in solution.[19,20] The C, H, and S elemental analyses, conductivities in acetone, melting points, and yields of the isolated complexes are listed in Table 1. Measurements of the equivalent conductivities of the complexes in acetone solutions at different concentrations gave plots of the Onsager equation ($\Lambda_e = \Lambda_0 - A\sqrt{c}$) for which the A values were characteristic of 2 : 1 electrolytes.[21] In the case of $[\mathrm{(cod)(OC)Ir(\mu\text{-}MeSSMe)_2Ir(CO)(cod)][ClO_4]_2}$, attempts to establish the nuclearity using this method were unsuccessful because of the instability of the solutions, but by analogy with the related complexes a dimeric structure is suggested.

$$[\mathrm{(cod)Ir\{\mu\text{-}(L{-}L)\}_2Ir(cod)][ClO_4]_2} + 2\,\mathrm{CO} \longrightarrow [\mathrm{(cod)(OC)Ir\{\mu\text{-}(L{-}L)\}_2Ir(CO)(cod)][ClO_4]_2} \quad \text{(iv)}$$

$\mathrm{L{-}L = Bu^tS(CH_2)_2SBu^t}$, dtch, or MeSSMe; reaction time = 1 min

$$[\mathrm{(cod)Ir\{\mu\text{-}(L{-}L)\}_2Ir(cod)][ClO_4]_2} + 4\,\mathrm{CO} \longrightarrow [\mathrm{(OC)_2Ir\{\mu\text{-}(L{-}L)\}_2Ir(CO)_2][ClO_4]_2} + 2\,\mathrm{cod} \quad \text{(v)}$$

$\mathrm{L{-}L = Bu^tS(CH_2)_2SBu^t}$; reaction time = 1 h
$\mathrm{L{-}L}$ = dtch; reaction time = 2 h

The ^{1}H n.m.r. spectrum of $[\mathrm{(cod)(OC)Ir(\mu\text{-}dtch)_2Ir(CO)(cod)][ClO_4]_2}$ in $\mathrm{CDCl_3}$ solution shows resonances corresponding to the co-ordinated cod (Table 3). The methylenic protons from co-ordinated dtch give rise to two types of resonances in a 1 : 1 ratio at 3.42 and 3.80 p.p.m. which appear downfield compared to the free ligand. It should be noted that this spectrum shows resonances due to free dtch as well, which could indicate that one of the two bridging ligands is cleaved in solution giving the four-co-ordinated compound $[\mathrm{(cod)(OC)Ir(\mu\text{-}dtch)Ir(CO)(cod)][ClO_4]_2}$. The ^{1}H n.m.r. spectrum of the tetracarbonylated complex $[\mathrm{(OC)_2Ir\{\mu\text{-}Bu^tS(CH_2)_2\text{-}}$

Table 3. Proton n.m.r.[a] (δ/p.p.m.) data for some iridium(I) carbonyl complexes

	cod		Sulphur ligand				
Complex	CH=C	$\mathrm{CH_2{-}C}$	$\mathrm{CH_2{-}S}$	$\mathrm{CH_2{-}C}$	$\mathrm{CH_3{-}C}$	$\mathrm{CH_3{-}C}$	$\mathrm{Bu^t{-}S}$
(2)	4.90	2.63	3.37 (t)	2.17 (qnt)	—	—	—
(3)	4.84	2.59	3.83 (t)	3.10 (qnt)	—	—	—
(4)	4.50	2.50—2.80 (m)	—	—	2.85 (s)	—	—
(5)	4.87	2.63	3.11 (q)	—	—	1.41 (t)	—
(7) [b]	4.24	2.21—2.50 (m)	3.42, 3.80	—	—	—	—
(9)	—	—	3.53 (s)	—	—	—	1.66 (s)

[a] Recorded at 298 K in $\mathrm{CDCl_3}$ solutions, downfield from $\mathrm{SiMe_4}$; s = singlet, t = triplet, q = quartet, qnt = quintet, and m = multiplet.
[b] Also free dtch resonances at δ = 2.87 p.p.m.

$SBu^t\}_2Ir(CO)_2][ClO_4]_2$ in $CDCl_3$ solution shows signals corresponding to co-ordinated $Bu^tS(CH_2)_2SBu^t$ (Table 3).

Experimental

Materials.—All reactions were carried out at room temperature under dry nitrogen atmospheres using standard Schlenk techniques. Solvents were deoxygenated immediately before use.

Apparatus.—The C, H, and S analyses were carried out with a Perkin-Elmer 240B microanalyzer. I.r. spectra were recorded on a Beckman IR 4260 spectrophotometer using Nujol mulls between polyethylene sheets, ^1H n.m.r. spectra on a XL-200 Varian spectrometer using $CDCl_3$ as the solvent and $SiMe_4$ as the internal reference at room temperature. Conductivities were measured in acetone solutions, in the concentration range 1×10^{-4}—5×10^{-4} mol dm^{-3}, with a Red. Copenh. CDCM3 Radiometer conductimeter. Values of A in Onsager's equation were calculated from measurements in acetone at several concentrations in the range 5×10^{-3}—5×10^{-5} mol dm^{-3}. Melting points were determined with a Buchi 510 apparatus.

Preparation of Iridium(I) *Carbonyl Complexes.*—(*a*) Carbon monoxide was bubbled through dichloromethane solutions of the complexes $[Ir(cod)L_2]ClO_4$ (L = tht or tms), $[(cod)Ir(\mu\text{-}L)_2Ir(cod)][ClO_4]_2$ (L = SMe_2 or SEt_2), and $[(cod)Ir\{\mu\text{-}(L\text{-}L)\}_2Ir(cod)][ClO_4]_2$ [L-L = $Bu^tS(CH_2)_2SBu^t$, dtch, or MeSSMe] generated *in situ* as previously reported. After 1 min the starting solutions became colourless. Addition of Et_2O gave the corresponding $[Ir(CO)_2(cod)L]ClO_4$ (L = tht, tms, SMe_2, or SEt_2) and $[(cod)(OC)Ir\{\mu\text{-}(L\text{-}L)\}_2Ir(CO)(cod)][ClO_4]_2$ [L-L = $Bu^tS(CH_2)_2SBu^t$, dtch, or MeSSMe] which were filtered off, washed with Et_2O, and vacuum dried.

(*b*) When CO was bubbled through dichloromethane solutions of the complexes $[(cod)Ir\{\mu\text{-}(L\text{-}L)\}_2Ir(cod)][ClO_4]_2$ [L-L = $Bu^tS(CH_2)_2SBu^t$ or dtch] for 1 and 2 h respectively, a second and progressive colour change was observed in the solutions. The products $[(OC)_2Ir\{\mu\text{-}(L\text{-}L)\}_2Ir(CO)_2][ClO_4]_2$ [L-L = $Bu^tS(CH_2)_2SBu^t$ or dtch] were precipitated by addition of Et_2O, filtered off, washed with Et_2O, and vacuum dried.

Preparation of Rhodium(I) *Carbonyl Complexes.*—A stoicheiometric amount of $AgClO_4$ (0.26 mmol) was added to an acetone solution of $[(OC)_2Rh(\mu\text{-}Cl)_2Rh(CO)_2]$ (0.13 mmol). The mixture was stirred in the absence of light for 5 min and then a slight excess (0.27 mmol) of the appropriate ligand [L-L = $Bu^tS(CH_2)_2SBu^t$, $MeS(CH_2)_3SMe$, or dtch] was added. The solution was filtered through Kieselguhr to remove silver chloride and collected over Et_2O under a nitrogen atmosphere to give a precipitate of $[Rh(CO)_2(L\text{-}L)]_n[ClO_4]_n$ [L-L = $Bu^tSCH{=}CHSBu^t$, $MeS(CH_2)_3SMe$, or dtch] which was filtered off, washed with Et_2O, and vacuum dried.

X-Ray Data Collection, Structure Determination, and Refinement.—*Crystal data.* $C_{12}H_{20}ClORhS_2$, $M = 462.8$, orthorhombic, $a = 11.129(2)$, $b = 15.877(3)$, $c = 10.742(2)$ Å, $U = 1\,898.1(1)$ Å^3, space group $Ccm2_1$, $Z = 4$, $D_c = 1.62$ Mg m^{-3}, $F(000) = 936$, Mo-K_α radiation ($\lambda = 0.710\,69$ Å), μ(Mo-K_α) = 11.41 cm^{-1}.

A small crystal was selected and mounted on a Philips Pw-1100 four-circle diffractometer. The unit-cell parameters were determined from centring and subsequent refinement of 25 reflections ($4 \leqslant \theta \leqslant 9°$). Intensities were collected with monochromatized Mo-K_α radiation, using the ω-scan technique (scan speed 0.03° s^{-1} and scan range 1°). The crystal orientation and reflection intensity was monitored every 2 h, but no significant variation was observed. The number of measured intensities was 743 ($\theta \leqslant 25°$) with 734 considered as observed [$I \geqslant 2.5\sigma(I)$]. Lorentz, polarization, but not absorption, corrections were made.

Table 4. Atomic co-ordinates ($\times 10^4$) and occupancy factors (f) of the oxygen atoms of perchlorate ion in $[Rh(CO)_2(Bu^tSCH{=}CHSBu^t)]ClO_4$

Atom	X/a	Y/b	Z/c	f
Rh	1 435(1)	0(0)	0(0)	
S	2 358(4)	1 026(3)	1 277(4)	
C(1)	3 371(39)	389(27)	2 230(28)	
C(2)	3 341(14)	1 790(12)	454(19)	
C(21)	4 115(26)	2 213(21)	1 392(30)	
C(22)	4 158(26)	1 301(16)	−435(21)	
C(23)	2 531(25)	2 320(18)	−362(54)	
C(3)	565(14)	−811(10)	−869(19)	
O(3)	0(13)	−1 268(8)	−1 459(16)	
Cl	2 571(5)	0(0)	6 085(5)	
O(1)	3 197(44)	−568(27)	6 961(48)	0.76(10)
O(1′)	2 098(70)	−405(26)	5 088(81)	0.53(8)
O(2)	3 537(44)	0(0)	5 359(103)	0.37(7)
O(2′)	1 765(51)	−554(33)	6 707(38)	0.57(8)

The Rh and S atoms were located from an unsharpened Patterson map. The positions of the remaining, non-hydrogen and non-oxygen atoms linked to chlorine were obtained from a subsequent Fourier synthesis. Isotropic refinements were carried out with the SHELX 76 computer program.[22] A difference synthesis revealed several peaks for the oxygen atoms linked to chlorine, indicating a disorder. Isotropic and anisotropic refinements led to $R = 0.064$. A difference electron-density map revealed the location of the hydrogen atoms, which were refined with an overall isotropic thermal parameters, while the remaining atoms were refined anisotropically. The occupation factors for the oxygen atoms linked to chlorine atoms were treated as variables in the latter cycles. The final R was 0.035 for all observed reflections ($R' = 0.043$). The function minimized was $\Sigma_w ||F_o| - |F_c||^2$, where $w = [\sigma^2(F_o) + 0.0306|F_o|^2]^{-1}$. Final atomic co-ordinates are given in Table 4.

Acknowledgements

We thank Professor L. A. Oro for many helpful discussions. This work was partially sponsored by a grant from the University of Barcelona.

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Received 12th December 1983; *Paper* 3/2194