Aryl Compounds of Rhodium: Syntheses and X-Ray Crystal Structures†

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The interactions of *fac*-$RhCl_3(tht)_3$, tht = tetrahydrothiophene, with aryl-lithium or -magnesium bromide reagents, aryl = 2,4,6-$R_3C_6H_2$ (R = Me or Pr^i), 2,6-$Me_2C_6H_3$, or 2-MeC_6H_4, and also $Mg(PhCH_2)Br$, have been studied. With Li(2,4,6-$Pr^i_3C_6H_2$)(Et_2O) only the unique, square, paramagnetic rhodium(II) compound *trans*-Rh(2,4,6-$Pr^i_3C_6H_2$)$_2$(tht)$_2$ is obtained. This reacts with CO reversibly to give labile carbonyl species and with Bu^{t}NC to give the rhodium(I) σ-bonded iminoacyl Rh(CNBu^t)$_3$(2,4,6-$Pr^i_3C_6H_2C$=NBu^t). A similar mesityl (mes) compound is obtained from Rh(mes)$_3$ and Bu^{t}NC. Homoleptic rhodium(III) aryls Rh(aryl)$_3$ have been obtained for aryl = 2,6-$Me_2C_6H_3$ and 2,4,6-$Me_3C_6H_2$. The mesityl reacts with CO to give a carbonyl species that has a bridged acyl and a bridge in which a mesityl group σ-bonded to one Rh atom is bound η^6 to the other. It also reacts with PMe_2Ph to give Rh(mes)(PMe_2Ph)$_3$. The interaction of $RhCl_3(tht)_3$ with $Mg(PhCH_2)Br$ gives only the unsymmetric bridged species (tht)($PhCH_2$)$_2$Rh(μ-Cl)$_3$Rh(CH_2Ph)(tht)$_2$. The crystal structures of six compounds have been determined: *trans*-Rh(2,4,6-$Pr^i_3C_6H_2$)$_2$(tht)$_2$ is square with a two-fold axis of symmetry perpendicular to the molecular plane [Rh–C and Rh–S 2.11(1) and 2.291(5) Å]. The compounds Rh(CNBu^t)$_3$(σ-RC=NBu^t), (R = 2,4,6-$Me_3C_6H_2$ or 2,4,6-$Pr^i_3C_6H_2$) have similar structures in which the rhodium(I) centres are square [Rh–C (isocyanide) and Rh–C (imino) 1.88–1.94(2) and 2.08 and 2.06(2) Å]. The compound Rh_2(2,4,6-$Me_3C_6H_2CO$)(2,4,6-$Me_3C_6H_2$(CO)$_3$ contains two rhodium centres with quite different co-ordination: Rh(1) is square with bonds to two carbonyls [Rh–C 1.81(1) and 1.90(1) Å], an aryl [Rh–C 2.07(1) Å] and an oxygen from the aroyl ligand [Rh–O 2.08(1) Å]; Rh(2) is trigonal bipyramidal with the aryl σ-bonded to Rh(1) now η^6 bonded over two equatorial [Rh–C 2.33(1) and 2.34(1) Å] and one axial [Rh–C 2.44(1) Å] sites, the remaining axial and equatorial sites being occupied by the aroyl carbon [Rh–C 1.94(1) Å] and a carbonyl group [Rh–C 1.84(1) Å]. The compound Rh(2,4,6-$Me_3C_6H_2$)(PMe_2Ph)$_3$ has square rhodium(I) geometry [Rh–C 2.09(1) and Rh–P 2.304(4) Å (*trans* to the aryl) and 2.276(4) and 2.287(4) Å *trans* to each other]. The dimer $Rh_2(PhCH_2)_3Cl_3(tht)_3$ has a confacial bioctahedral structure with Rh–Cl, Rh–C and Rh–S distances showing considerable variations due to the differing *trans* influences of the three ligand types.

Neutral homoleptic aryl compounds of the platinum-group metals are known for Ru[1a] and Os;[1b] some redox and reaction chemistry[1c] of M(2-MeC_6H_4)$_4$, M = Ru or Os, has been described, including the synthesis of [Os(2-MeC_6H_4)$_4$]CF_3SO_3. Structural studies are summarized in a review.[2]

This paper expands on a preliminary report[3] in which the synthesis and X-ray crystal structure of tris(mesityl)rhodium(III) were described; reactions of the latter and of the rhodium(II) compound *trans*-Rh(2,4,6-$Pr^i_3C_6H_2$)$_2$(tht)$_2$ (tht = tetrahydrothiophene) are now given, together with synthesis of a benzyl complex. Although iridium analogues of none of these species have yet been made, the paramagnetic, tetrahedral tetramesityl, Ir(mes)$_4$ (mes = 2,4,6-$Me_3C_6H_2$), has been structurally characterized.[4] Analytical and physical data for new compounds are given in Table 1

Results and Discussion

The only productive rhodium starting material we have found for the aryl syntheses is the tht complex *fac*-$RhCl_3(tht)_3$, which was also used in the synthesis of [Li(tmen)]$_3$[$RhMe_6$], tmen = *N,N,N′,N′*-tetramethylethylenediamine, and [Rh(Me_3CCH_2)$_3$]$_2$(μ-O).[5] In these arylations the nature and yield of the product depends upon the conditions and upon the steric properties of the aryl group used; quite likely radical processes are involved.

trans-*Bis*(*tetrahydrothiophene*)*bis*(2,4,6-*triisopropylphenyl*)*rhodium*(II).—The interaction of the lithium aryl diethyl etherate with $RhCl_3(tht)_3$ in a 3:1 ratio in toluene at room temperature leads to a brown solution from which, on work-up, pale orange crystals of the air-sensitive rhodium(II) complex Rh(2,4,6-$Pr^i_3C_6H_2$)$_2$(tht)$_2$ **1** can be obtained from hexane in *ca.* 25% yield. While the aryl can also be obtained using Et_2O as solvent, when the reaction time is shorter, the product is difficult to purify from an accompanying black oil. No isolable product is obtained using the Grignard reagent.

A similar one-electron reduction process occurs in the reaction of $CrCl_3(thf)_3$ (thf = tetrahydrofuran) and Li(2,4,6-$Pr^i_3C_6H_2$)(Et_2O). If the reaction is carried out with a 1:3 stoichiometry deep blue solutions commonly found for Cr^{2+} are obtained. Further reaction of these blue solutions with PMe_3 gives Cr(2,4,6-$Pr^i_3C_6H_2$)$_2$(PMe_3)$_2$ as orange-red needles which were identified by comparison with an authentic sample prepared from $CrCl_2$, Mg(2,4,6-$Pr^i_3C_6H_2$)Br and PMe_3 (see Experimental section).

The structure of compound **1** as determined by X-ray diffraction is shown in Fig. 1; bond lengths and angles are given in Table 2. The molecule lies on a crystallographic two-fold rotation axis, which is perpendicular to the molecular plane.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Analytical and physical data for rhodium compounds[a]

Compound	Colour	M.p./°C	Analysis (%) C	H	N
1 $Rh(2,4,6\text{-}Pr^i{}_3C_6H_2)_2(tht)_2$	Pale orange	143–146 (decomp.)	66.4 (66.5)	9.2 (9.1)	
2 $Rh(CNBu^t)_3(2,4,6\text{-}Pr^i{}_3C_6H_2C{=}NBu^t)$	Yellow	172 (decomp.)	64.2 (65.8)	9.1 (9.2)	8.4 (8.7)
3 $Rh(CNBu^t)_3(2,4,6\text{-}Me_3C_6H_2C{=}NBu^t)$	Orange	134–136 (decomp.)	62.9 (62.8)	8.5 (8.5)	9.8 (10.1)
4 $Rh(2,6\text{-}Me_2C_6H_3)_3$	Orange	178–179 (decomp.)	68.8 (68.9)	6.5 (6.5)	
7 $Rh_2(2,4,6\text{-}Me_3C_6H_2CO)(2,4,6\text{-}Me_3C_6H_2)(CO)_3$	Light yellow	[b]	[b]		
8 $Rh(2,4,6\text{-}Me_3C_6H_2)(PMe_2Ph)_3$	Yellow	85–87 (decomp.)	62.6 (62.3)	7.1 (7.0)	
9 $Rh_2(PhCH_2)_3Cl_3(tht)_3$	Dark orange	89–91 (decomp.)	46.8 (46.6)	5.4 (5.3)	

[a] For $Rh(2,4,6\text{-}Me_3C_6H_2)_3$ **5** see ref. 3. [b] Too unstable to determine.

Table 2 Selected bond lengths (Å) and angles (°) for *trans*-$Rh(2,4,6\text{-}Pr^i{}_3C_6H_2)_2(tht)_2$ **1**

S(1)–Rh	2.291(5)	C(11)–Rh	2.109(10)
C(10)–S(1)	1.850(13)	C(40)–S(1)	1.842(12)
C(11)–Rh–S(1)	90.0(4)	S(1)–Rh–S(1B)	178.0(2)
S(1)–Rh–C(11B)	90.1(4)	C(11)–Rh–C(11B)	180.0(3)
C(10)–S(1)–Rh	113.0(6)	C(40)–S(1)–Rh	115.3(5)
C(12)–C(11)–Rh	122.7(7)	C(16)–C(11)–Rh	121.0(8)

Table 3 Selected bond lengths (Å) and angles (°) for $Rh(CNBu^t)_3(2,4,6\text{-}Pr^i{}_3C_6H_2C{=}NBu^t)$ **2** and $Rh(CNBu^t)_3(2,4,6\text{-}Me_3C_6H_2C{=}NBu^t)$ **3**

	Compound **2**	Compound **3**
C(1)–Rh	2.064(18)	2.080(10)
C(2)–Rh	1.884(19)	1.934(11)
C(3)–Rh	1.898(20)	1.930(13)
C(4)–Rh	1.939(20)	1.907(12)
C(2)–Rh–C(1)	95.5(8)	93.1(5)
C(3)–Rh–C(1)	176.4(9)	175.2(5)
C(2)–Rh–C(3)	85.4(9)	86.6(5)
C(4)–Rh–C(1)	93.5(7)	92.4(4)
C(4)–Rh–C(2)	169.9(8)	165.2(4)
C(4)–Rh–C(3)	86.0(9)	89.0(5)
C(11)–C(1)–Rh	112.2(13)	110.0(7)
N(1)–C(1)–Rh	138.0(17)	138.3(7)
N(2)–C(2)–Rh	167.3(20)	170.8(9)
N(3)–C(3)–Rh	175.9(20)	177.9(10)
N(4)–C(4)–Rh	171.8(16)	170.1(8)

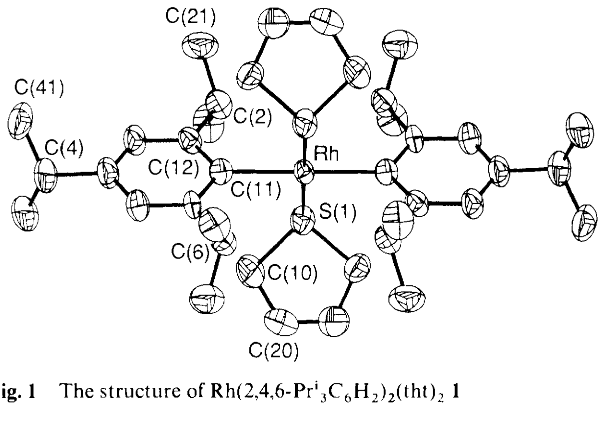


Fig. 1 The structure of $Rh(2,4,6\text{-}Pr^i{}_3C_6H_2)_2(tht)_2$ **1**

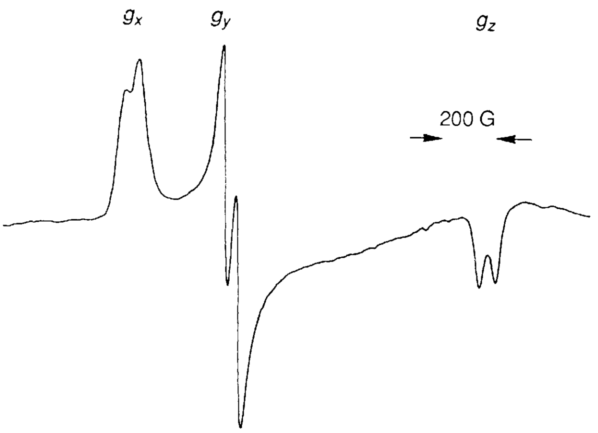


Fig. 2 The EPR X-band spectrum of $Rh(2,4,6\text{-}Pr^i{}_3C_6H_2)_2(tht)_2$ in frozen toluene at 78 K: $g_x = 2.96$, $A_x = 4.7 \times 10^{-3}$ cm, $g_y = 2.58$, $g_z = 1.85$, $A_y = A_z = 5.6 \times 10^{-3}$ cm (G = 10^{-4} T)

The rhodium(II) centre has a slightly distorted square geometry with the four ligands arranged in a propeller-like fashion. The Rh–C(aryl) distance, 2.11(1) Å, is some 0.14 Å greater than the distances in the tris-mesityl.[3] This is consistent with the difference in oxidation state and co-ordination number, both of which would lead to increases.

Compound **1** is paramagnetic and the X-band EPR spectrum at 293 K has a broad band, $g_{iso} = 2.456$. The spectrum in frozen toluene (77 K) is shown in Fig. 2; there are three distinct regions, each showing coupling of the single unpaired electron to the ^{103}Rh ($I = \frac{1}{2}$) nucleus giving doublets. Cyclic voltammetry of **1** in CH_2Cl_2, 0.1 mol dm^{-3} in $NBu^n{}_4PF_6$ as supporting electrolyte, shows a reversible one-electron reduction wave at $E_{\frac{1}{2}} = -1.10$ V *vs.* ferrocene–ferrocenium; attempts to isolate the rhodium(I) species using various chemical reductants (cobaltocene, Li, Na/Hg) were unsuccessful.

Although dimeric, diamagnetic rhodium(II) compounds are numerous and well established,[6] monomeric species are scarce. Examples include complexes of bulky phosphines such as the structurally characterized planar *trans*-$RhCl_2(PPh_3)_2$[7] and the pseudo-octahedral ion $[Rh\{P[C_6H_2(OMe)_3\text{-}2,4,6]_3\}_2]^{2+}$.[8] The dication[9] $[Rh(C_6Me_6)_2]^{2+}$ appears to be the only organometallic compound; it was not characterized structurally. Other cationic rhodium(II) complexes have been generated in solution by electrochemical means.[10]

Reactions of Compound **1**.—On passing a large excess of carbon monoxide through a hexane solution of compound **1** the colour immediately becomes pale yellow. Solution IR studies show two strong CO stretches at 2046 and 2042 and weaker

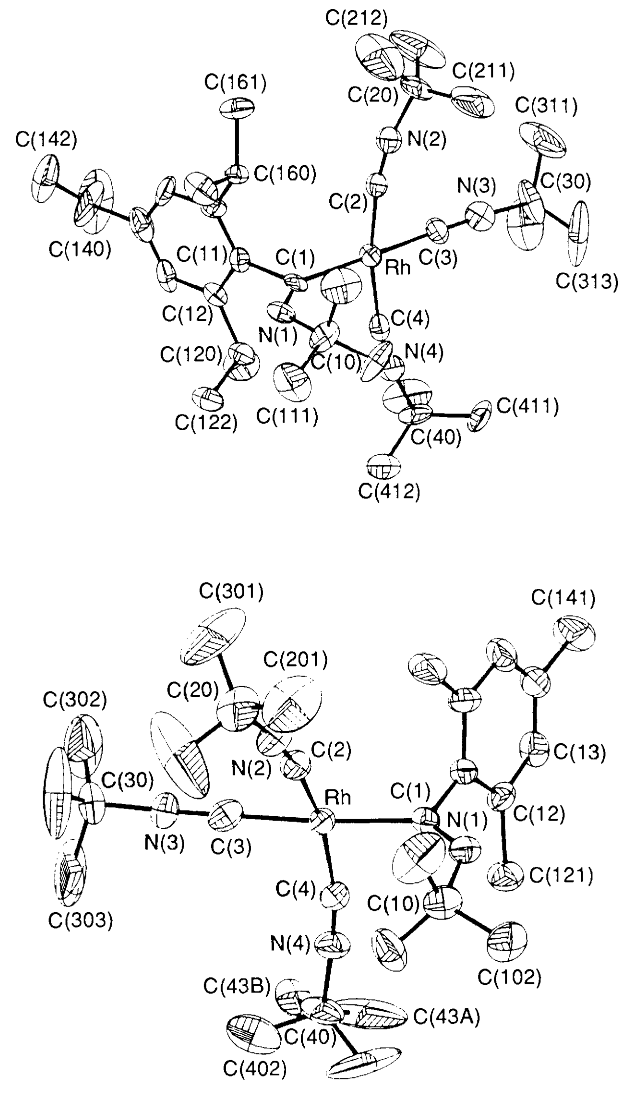


Fig. 3 The structure of $\mathrm{Rh(CNBu^t)_3(RC{=}NBu^t)}$ where R = 2,4,6-$\mathrm{Pr^i{}_3C_6H_2}$ **2** (top) or 2,4,6-$\mathrm{Me_3C_6H_2}$ **3** (bottom)

stretches at 2075 and 2025 cm^{-1}. It was found that the initial addition of CO gave rise to three signals in the IR spectrum at 2052, 2046 and 1991 cm^{-1}. On further addition of CO the signals at 2052 and 1991 cm^{-1} became weaker and are replaced by stronger stretches at 2046 and 2042 cm^{-1}. If the hexane solution is then exposed to vacuum (1 min) the signals at 2052 and 1991 cm^{-1} reappear and those at 2046 and 2042 cm^{-1} are no longer observed. The EPR spectrum of a hexane solution of **1** under a CO atmosphere at 77 K consists of several broad signals around $g = 2$ as well as a sharp signal at $g = 2.00$ which does not change with increasing microwave power; the latter may be due to localization of electron spin on the oxygen of CO. The reaction of **1** and CO in neat tht was also monitored by IR spectroscopy; again this showed terminally bonded CO stretches at 2045, 1983 and 1938 cm^{-1}.

Removal of most of the hexane solvent in vacuum and crystallization gives only compound **1** indicating that with CO there are reversible addition and tht displacement reactions giving a labile mixture of the species probably $\mathrm{RhR_2(tht)_2(CO)}$, $\mathrm{RhR_2(tht)(CO)_2}$ and $\mathrm{RhR_2(CO)_3}$ (R = 2,4,6-$\mathrm{Pr^i{}_3C_6H_2}$) that may have isomers. We have been unable to isolate any crystalline carbonyl product. Removal of volatile materials under a CO stream gave only an oily brown residue having two very weak CO stretches at 2064 and 2052 cm^{-1}. There was no evidence for CO insertion into the Rh–C(aryl) bonds, giving aroyls, using CO pressures up to 30 atm (*ca.* 3 × 10^6 Pa).

The only reported interactions of rhodium(II) monomeric species with CO are (*i*) that with tetramesitylporphyrinrhodium to give a paramagnetic monoadduct which dimerizes by C–C bond formation to give a diolyl bridge,[11a] (*ii*) that with $\mathrm{[Rh\{P[C_6H_2(OMe)_3\text{-}2,4,6]_3\}_2]^{2+}}$ noted above which is postulated to give unstable, undetected adducts with one and two CO groups which interact further with $\mathrm{[Rh\{P[C_6H_2(OMe)_3\text{-}2,4,6]_3\}_2]^{2+}}$ leading to isolable cationic species of $\mathrm{Rh^I}$ and $\mathrm{Rh^{III}}$.[11b]

Interaction of compound **1** and $\mathrm{Bu^tNC}$ in hexane gives light yellow solutions from which can be isolated the diamagnetic compound $\mathrm{Rh(CNBu^t)_3(2,4,6\text{-}Pr^i{}_3C_6H_2C{=}NBu^t)}$ **2** whose X-ray structure confirms that it is a rhodium(I) compound with a σ-bonded $\mathrm{Pr^i{}_3C_6H_2C{=}NBu^t}$ group. A similar compound $\mathrm{Rh(CNBu^t)_3(2,4,6\text{-}Me_3C_6H_2C{=}NBu^t)}$ **3** has been obtained from interaction of $\mathrm{Rh(mes)_3}$ and $\mathrm{Bu^tNC}$ (as discussed later) and the two structures are considered together and shown in Fig. 3; bond lengths and angles are in Table 3.

The two molecules are very similar and the metal atoms have a slightly distorted square geometry. The Rh–C distances to the $\mathrm{RC{=}NBu^t}$ ligands are similar, at 2.08(1) and 2.06(1) Å, and longer, as expected, than those to the isocyanides. In the mesityl compound **3** the Rh–C(isocyanide) distances do not show a consistent trend, with no clear difference between the bond *trans* to the organic ligand [1.93(1) Å] and those *trans* to each other [1.91(1) and 1.93(1) Å]. In compound **2**, however, there does seem to be a clear trend, with a difference of 0.05 Å between the unique bond and the two, more closely similar, Rh–C(isocyanide) bonds [1.88(1) and 1.90(1) Å]. The IR and NMR spectra are consistent with the structures in the solid state. It may be noted that compounds of the later transition metals often have σ-bonding of iminoacyl ligands.[12]

The reaction of **1** with $\mathrm{Bu^tNC}$ leading to reduction of $\mathrm{Rh^{II}}$ suggests the likelihood of a radical reaction (1) (R = 2,4,6-$\mathrm{Pr^i{}_3C_6H_2}$).

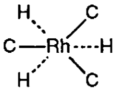
$$\mathrm{Rh^{II}R_2(tht)_2 + 4Bu^tNC \longrightarrow Rh^I(CNBu^t)_3(RC{=}NBu^t) + R^{\bullet}} \quad (1)$$

The aryl radical should give triisopropylbenzene on hydrogen abstraction from the solvent and this has been confirmed by carrying out the reaction in $[^2H_8]$toluene; gas chromatography–mass spectrometry GC–MS) analysis shows the presence of deuteriated triisopropylbenzene.

Compound **1** can be recovered unchanged after treatment with $\mathrm{PMe_3}$, pyridine, quinuclidine, and triethylamine; although reactions occur with NO, O_2 and $\mathrm{AgO_3SCF_3}$, we have been unable to identify the products.

Rhodium(III) *Aryls and their Reactions*.—The interaction of $\mathrm{RhCl_3(tht)_3}$ with MgRBr (R = 2,6-$\mathrm{Me_2C_6H_3}$ or 2,4,6-$\mathrm{Me_3C_6H_2}$) gives the respective tris aryls **4** and **5**.

The X-ray structure and NMR spectra of the mesityl **5** have been described.[3] The compound was found to have a quasi-octahedral structure **I**, with the three aryls σ-bonded to Rh in a



I

fac configuration and with the other three positions occupied by agostic hydrogen atoms of three of the *ortho* methyl groups on the aryl ligands. The IR spectra of both compounds in the solid state suggest similarity in structure.

A third aryl was also obtained as pale orange crystals using the *o*-tolyl Grignard, but the reaction was irreproducible and very sensitive to the conditions and the product, always formed in low yield, was often contaminated with a black oily substance. Crystals suitable for X-ray study could not be obtained but spectroscopic data suggest the formulation

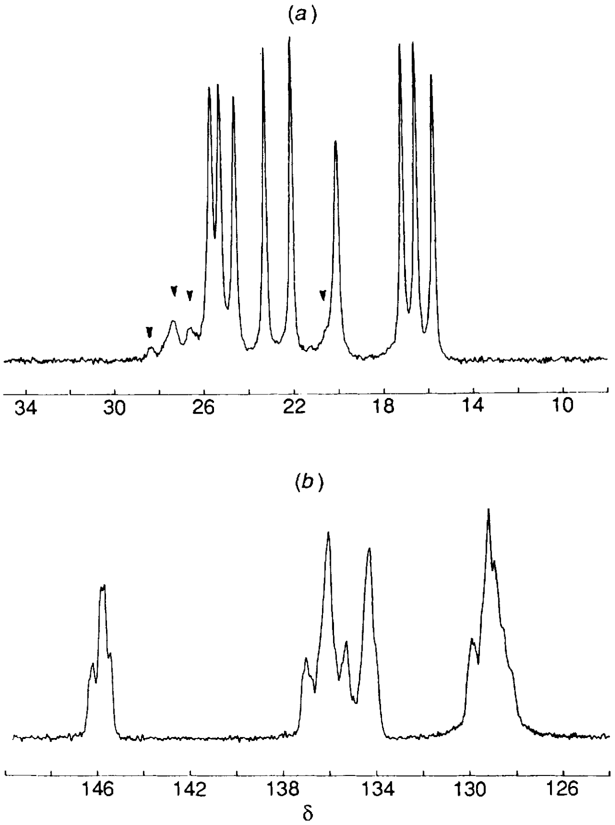


Fig. 4 Solid-state ^{13}C CP MAS NMR spectra of Rh(2,4,6-$Me_3C_6H_2)_3$: (*a*) the methyl region with marked peaks being second-order spinning sidebands of aromatic carbons (*b*) the aromatic region

as $Rh(2\text{-}MeC_6H_4)_3(tht)_2$ **6**. The solvation is presumably connected with the lower steric bulk of the aryl; with less bulky aryls or even with metals of larger atomic radius, solvates are often obtained.[2]

As noted previously[3] the ^1H and $^{13}C\text{-}\{^1H\}$ NMR and IR spectra of compound **5** in solution provide no evidence for agostic interaction. Further confirmation has been obtained from coupled ^{13}C NMR spectra in CD_2Cl_2 at low temperatures using the microprogram DEPTC/AUR on a Bruker AM-500 spectrometer. Although the resonances became sharper on cooling to 198 K there was no observable change in the initial, room-temperature, quartet pattern expected for the three equivalent protons on the *ortho* methyl carbon atoms on the mesityl ligands. The solution spectra thus confirm the absence of agostic interactions and it seems most likely that in solution **5** is trigonal planar. The synchronous rotation of the mesityl groups about the Rh–C bond was noted previously.[3]

Planar structures for tris-mesityl compounds have been confirmed by X-ray diffraction for trimesitylindium,[13] where the mesityl groups are crystallographically inequivalent, for trimesitylaluminium[14] where the three mesityls are disposed in a propeller-like fashion, and trimesitylgallium,[15] which is similar. The only transition-metal tris(mesityl) is the paramagnetic manganese(II) compound $[Li(thf)_4][Mn(mes)_3]$,[16] which also has the mesityl groups having dihedral angles with respect to the MC_3 plane and without any Mn ··· H or Mn ··· C contacts.

The low-temperature ^{13}C NMR spectra[13] of $In(mes)_3$ show a lowering of the coupling constant $J(^{13}C\text{–}^1H)$ from 124 to 102.0 Hz for the *ortho* methyl groups as well as an IR band at 2710 cm^{-1} (in Nujol) said to be supportive of agostic interactions observed in the X-ray structure, but distortions present in the solid state due to crystal-packing forces were not eliminated; the evidence for agostic hydrogens is hence tenuous. In contrast both $Al(mes)_3$[14] and $Ga(mes)_3$[15] do not have any close *ortho* methyl contacts with the metal in the solid state nor in the case of $Al(mes)_3$ in solution according to ^{13}C NMR data which show only one type of *ortho* methyl group with a normal $J(^{13}C\text{–}^1H)$ value of 123.9 Hz; ^{13}C NMR data for $Ga(mes)_3$ were not reported.

Additional information for $Rh(mes)_3$ is provided by solid-state ^{13}C NMR spectra which show (see Fig. 4) nine narrow signals (half width *ca.* 15 Hz) in the methyl region indicating crystallographic inequivalence of the methyl groups. There is no indication of any coupling of the *o*-CH_3 groups to ^{103}Rh as might have been expected for strong agostic C–H ··· Rh interaction (*cf.* X-ray data) and the line shapes of all CH_3 groups, including those *para*, are identical. However, couplings of less than 6 Hz would not be detected, thus putting an upper limit on the $^{13}C\text{–}^{103}Rh$ coupling. The aromatic carbons give rise to three sets of signals, each having fine structure due to crystallographic inequivalence, together with $^{13}C\text{–}^{103}Rh$ coupling.

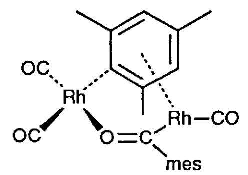
As an aid to spectral assignment the spectrum was recorded using non-quaternary suppression with the TOSS pulse sequence. This has the effect of removing spurious side bands as well as peaks due to carbons directly bonded to H atoms. Thus the signals at δ 128.2–129.9 are those of C^3 and C^5. From analogy with the ^{13}C NMR spectra in solution (see ref. 3 and additional data in Experimental section) the following assignments of the remaining signals could be made: δ 145.4–146.2, C^2 or C^6; 134.3, C^4; 136.1, C^2 or C^6; 136.2 (J_{RhC} = 128 Hz) C^1. It is to be noted that the value of J_{RhC} here is more than double that in solution which we consider strongly to support differences in bonding and in geometry of $Rh(mes)_3$ between the solid state and solution.

On available evidence we conclude that all tris-mesityls known so far are planar in solution.

Reactions of Tris(mesityl)rhodium.—The compound is stable in air both as a solid and in hexane or diethyl ether solution. It can be recovered unchanged from solutions after treatment with hydrogen, oxygen, sulphur dioxide, ethylene, $SiHPh_3$ and $Bu^tO_2Bu^t$ at ambient temperature and pressure. Interaction with neat pyridine occurred only at *ca.* 50 °C which led to decomposition.

Cyclic voltammetry of compound **5** in CH_2Cl_2 using $NBu^n{}_4PF_6$ as supporting electrolyte showed a reversible one-electron oxidation wave at +0.75 V *vs.* ferrocene–ferrocenium and a second, irreversible oxidation at a slightly higher potential. Attempts to oxidize **5** by $AgBF_4$ in CH_2Cl_2 were unsuccessful; no reaction occurred below 50 °C after which decomposition began. The 2,6-dimethylphenyl **4** showed two irreversible oxidation waves the first at *ca.* +0.94 V. No reduction wave was observed in either case and treatment of **4** and **5** with Na/Hg in thf gave only decomposition to black insoluble matter.

With carbon monoxide; compound **5** reacts cleanly to give the carbonyl complex **7**, **II**, and dimesityl ketone. In the solid state **7** is only moderately stable at room temperature and is unstable in solution in organic solvents even at low temperature on prolonged standing. Suitable crystals were obtained from hexane and the structure is shown in Fig. 5; bond lengths and angles are given in Table 4.



II

Both metal atoms can be assigned an oxidation state of +1; Rh(1) has a normal square geometry and a 16e configuration. Of particular note are the Rh–CO bond lengths where the bond *trans* to the Rh–C(aryl) bond is some 0.1 Å longer than that *trans* to the oxygen atom of the μ-OC(mesityl) group.[17] Since the σ-mesityl group on Rh(1) is acting as a η^6, 6e donor to Rh(2), and is considered to occupy three co-ordination sites, then Rh(2) can be assigned a trigonal-bipyramidal geometry and an 18e configuration. The aromatic ring occupies one axial and two equatorial sites and the other axial site is occupied by the carbon of the OC(mes) group. The Rh(2)–C(10) bond length of 1.94(1) Å is some 0.12 Å shorter than the Rh(1)–C(11) bond, which is clearly lengthened by the *trans* influence of the carbonyl bonding. The Rh(2)–C(4) equatorial bond length is intermediate between the lengths for the Rh(1)–carbonyl bonds and although the Rh(1) · · · C(η^6-mesityl) bond lengths, with Rh(2)–C(14) (axial) some 0.1 Å longer than Rh(2)–C(12,16) (equatorial and equal within experimental error), reflect the usual differences between trigonal-bipyramidal axial and equatorial bond lengths, restrictions due to the ligand geometry and bridging are also likely to affect the geometry here.

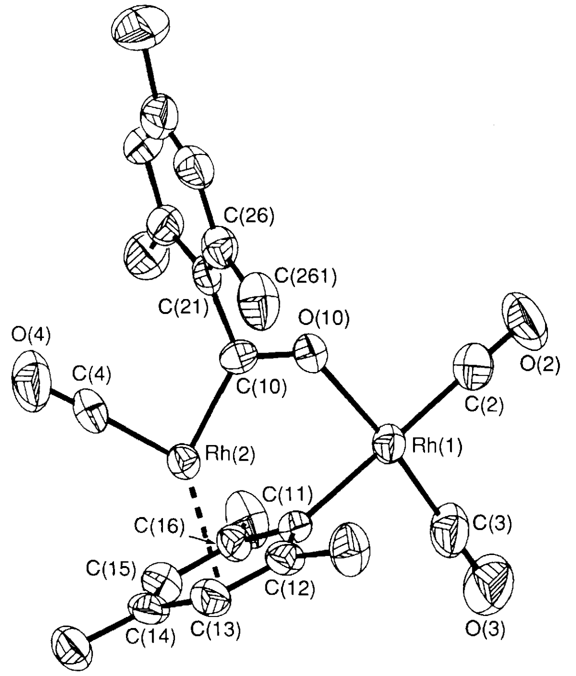


Fig. 5 The structure of $Rh_2(2,4,6\text{-}Me_3C_6H_2CO)(2,4,6\text{-}Me_3C_6H_2)(CO)_3$ **7**

Table 4 Selected bond lengths (Å) and angles (°) for $Rh_2(2,4,6\text{-}Me_3C_6H_2CO)(2,4,6\text{-}Me_3C_6H_2)(CO)_3$ **7**

C(2)–Rh(1)	1.899(13)	C(3)–Rh(1)	1.805(13)
O(10)–Rh(1)	2.075(8)	C(11)–Rh(1)	2.073(10)
C(4)–Rh(2)	1.840(11)	C(10)–Rh(2)	1.939(10)
C(11)–Rh(2)	2.247(10)	C(12)–Rh(2)	2.334(10)
C(13)–Rh(2)	2.403(10)	C(14)–Rh(2)	2.436(10)
C(15)–Rh(2)	2.422(10)	C(16)–Rh(2)	2.341(9)
Rh(2) · · · Rh(1)	3.579(5)		
C(3)–Rh(1)–C(2)	93.0(6)	O(10)–Rh(1)–C(2)	91.9(4)
O(10)–Rh(1)–C(3)	175.1(4)	C(11)–Rh(1)–C(2)	177.9(3)
C(11)–Rh(1)–C(3)	88.8(5)	C(11)–Rh(1)–O(10)	86.4(4)
O(2)–C(2)–Rh(1)	178.6(9)	O(3)–C(3)–Rh(1)	178.1(11)
O(4)–C(4)–Rh(2)	177.8(8)	C(10)–O(10)–Rh(1)	131.3(5)
C(21)–C(10)–Rh(2)	127.6(7)	O(10)–C(10)–Rh(2)	119.4(7)
Rh(2)–C(11)–Rh(1)	111.8(4)	C(10)–Rh(2)–C(4)	90.2(5)
C(11)–Rh(2)–C(4)	178.7(3)	C(11)–Rh(2)–C(10)	91.0(4)
C(12)–Rh(2)–C(4)	144.5(3)	C(12)–Rh(2)–C(10)	104.7(4)
C(13)–Rh(2)–C(4)	116.0(5)	C(13)–Rh(2)–C(10)	136.7(3)
C(14)–Rh(2)–C(4)	104.2(4)	C(14)–Rh(2)–C(10)	165.5(3)
C(15)–Rh(2)–C(4)	115.3(4)	C(15)–Rh(2)–C(10)	139.8(3)
C(16)–Rh(2)–C(4)	142.6(3)	C(16)–Rh(2)–C(10)	107.5(4)

Table 5 Selected bond lengths (Å) and angles (°) for $Rh(2,4,6\text{-}Me_3C_6H_2)(PMe_2Ph)_3$ **8**

P(1)–Rh	2.304(4)	P(2)–Rh	2.276(4)
P(3)–Rh	2.287(4)	C(10)–Rh	2.087(8)
P(2)–Rh–P(1)	94.0(2)	P(3)–Rh–P(1)	93.7(2)
P(3)–Rh–P(2)	171.9(1)	C(10)–Rh–P(1)	175.5(2)
C(10)–Rh–P(2)	86.5(3)	C(10)–Rh–P(3)	85.6(3)
C(11)–P(1)–Rh	112.3(2)	C(101)–P(1)–Rh	121.6(3)
C(102)–P(1)–Rh	120.8(3)	C(21)–P(2)–Rh	117.4(2)
C(201)–P(2)–Rh	115.5(4)	C(202)–P(2)–Rh	119.8(4)
C(41)–P(3)–Rh	116.2(3)	C(411)–P(3)–Rh	119.6(4)
C(412)–P(3)–Rh	115.7(4)	C(20)–C(10)–Rh	120.4(5)
C(60)–C(10)–Rh	123.4(5)		

Interaction of the tris-mesityl **5** with tertiary phosphines yields rhodium(I) compounds but only the PMe_2Ph derivative **8** has been structurally characterised, as shown in Fig. 6; bond lengths and angles are given in Table 5. In this complex Rh^I again has square geometry. The Rh–C distance is 2.09(1) Å and the Rh–P distances reflect the different environments, 2.304(4) Å *trans* to the aryl and 2.276(4) and 2.287(4) Å *trans* to each other. This difference is rather more distinctive than that found in the hydride $RhH(PPh_3)_3$[18a] and quite different to the situation in $RhCl(PPh_3)_3$,[18b] where the Rh–P distance *trans* to Cl is *shorter* than those *trans* to each other. The spectroscopic data for **8** are consistent with the structure as determined.

The few compounds of the type $RhR(PR_3')_3$ have been characterized only spectroscopically; for R = Ph or *o*-$MeOC_6H_4$, R′ = Me the compounds are stable[19a] but for R = R′ = Ph the compound was unstable and could not be obtained pure.[19b]

A similar reduction to Rh^I occurs with Bu^tNC to give $Rh(CNBu^t)_3(2,4,6\text{-}Me_3C_6H_2C{=}NBu^t)$ 3, noted earlier, where insertion to give the σ-iminoacyl has occurred as in the reaction with the rhodium(II) compound **1**.

Whilst reductive eliminations to give bimesityl are conceivable they are probably disfavoured on steric grounds. In

Table 6 Selected bond lengths (Å) and angles (°) for $Rh_2(PhCH_2)_3Cl_3(tht)_3$ **9**

Cl(1)–Rh(1)	2.582(6)	Cl(2)–Rh(1)	2.626(6)
Cl(3)–Rh(1)	2.411(5)	S(3)–Rh(1)	2.273(5)
C(2)–Rh(1)	2.069(12)	C(3)–Rh(1)	2.081(11)
Cl(1)–Rh(2)	2.366(5)	Cl(2)–Rh(2)	2.376(5)
Cl(3)–Rh(2)	2.607(5)	S(1)–Rh(2)	2.303(5)
S(2)–Rh(2)	2.324(5)	C(1)–Rh(2)	2.136(11)
Rh(2) · · · Rh(1)	3.262(4)		
Cl(2)–Rh(1)–Cl(1)	76.8(2)	Cl(3)–Rh(1)–Cl(1)	82.1(2)
Cl(3)–Rh(1)–Cl(2)	81.8(2)	S(3)–Rh(1)–Cl(1)	99.1(2)
S(3)–Rh(1)–Cl(2)	98.9(2)	S(3)–Rh(1)–Cl(3)	178.7(1)
C(2)–Rh(1)–Cl(1)	100.0(4)	C(2)–Rh(1)–Cl(2)	173.6(3)
C(2)–Rh(1)–Cl(3)	92.4(4)	C(2)–Rh(1)–S(3)	87.0(4)
C(3)–Rh(1)–Cl(1)	166.3(3)	C(3)–Rh(1)–Cl(2)	90.7(4)
C(3)–Rh(1)–Cl(3)	90.7(4)	C(3)–Rh(1)–S(3)	88.2(4)
C(3)–Rh(1)–C(2)	91.9(5)	Cl(2)–Rh(2)–Cl(1)	86.0(2)
Cl(3)–Rh(2)–Cl(1)	82.4(2)	Cl(3)–Rh(2)–Cl(2)	82.8(2)
S(1)–Rh(2)–Cl(1)	178.4(1)	S(1)–Rh(2)–Cl(2)	92.8(2)
S(1)–Rh(2)–Cl(3)	98.5(2)	S(2)–Rh(2)–Cl(1)	95.8(2)
S(2)–Rh(2)–Cl(2)	177.0(1)	S(2)–Rh(2)–Cl(3)	95.0(2)
S(2)–Rh(2)–S(1)	85.5(2)	C(1)–Rh(2)–Cl(1)	89.3(4)
C(1)–Rh(2)–Cl(2)	89.1(4)	C(1)–Rh(2)–Cl(3)	168.8(3)
C(1)–Rh(2)–S(1)	89.6(4)	C(1)–Rh(2)–S(2)	93.3(4)
Rh(2)–Cl(1)–Rh(1)	82.4(2)	Rh(2)–Cl(2)–Rh(1)	81.2(2)
Rh(2)–Cl(3)–Rh(1)	81.0(2)	C(61)–S(3)–Rh(1)	110.7(5)
C(64)–S(3)–Rh(1)	109.2(5)	C(41)–S(1)–Rh(2)	110.9(5)
C(44)–S(1)–Rh(2)	109.6(6)	C(51)–S(2)–Rh(2)	108.7(5)
C(54)–S(2)–Rh(2)	113.3(6)	C(11)–C(1)–Rh(2)	113.6(7)
C(21)–C(2)–Rh(1)	112.7(7)	C(31)–C(3)–Rh(1)	119.0(7)

contrast to the reaction of compound **1** with Bu^tNC in [$^2H_8$]toluene, GC–MS analysis of the products formed from the reaction of **5** with Bu^tNC in the same solvent shows only mesitylene and no deuteriated arene. This could be due to a reaction pathway not involving release of aryl radical or perhaps a transition state involving a cage complex which then allows the aryl radical preferentially to abstract a hydrogen atom from a Bu^tNC molecule. No evidence was found to support a reaction pathway involving double insertion of Bu^tNC into two Rh–mesityl bonds followed by reductive elimination of the imine, $(2,4,6\text{-}Me_3C_6H_2)_2C{=}NBu^t$, to give a rhodium(I) product. Several examples of Lewis base-promoted reductive eliminations of rhodium(III) organometallic compounds are known.[20]

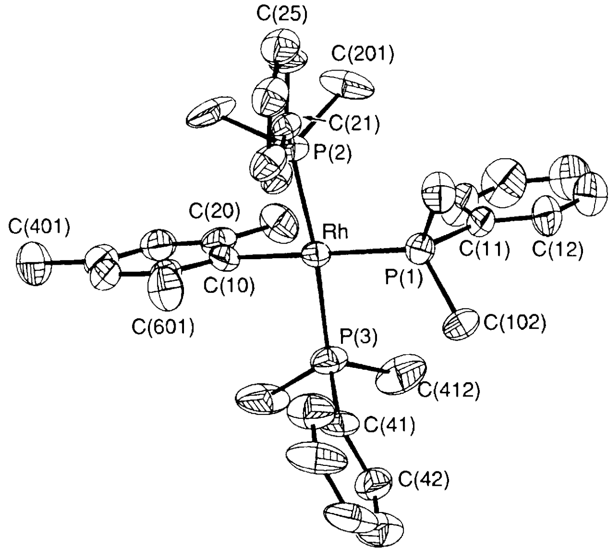


Fig. 6 The structure of $Rh(2,4,6\text{-}Me_3C_6H_2)(PMe_2Ph)_3$ **8**

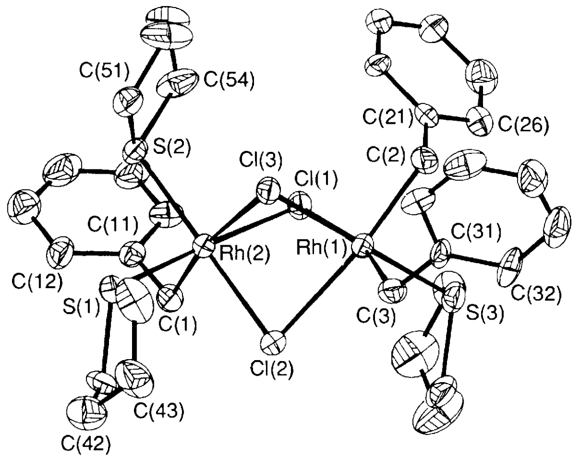


Fig. 7 The structure of $Rh_2(PhCH_2)_3Cl_3(tht)_3$ **9**

Interaction of $RhCl_3(tht)_3$ *with* $Mg(PhCH_2)Br$.—This interaction leads only to the triply halide-bridged unsymmetrical rhodium(III) compound **9**. The use of excess (4 mol equivalents) of the Grignard leads to intractable products. The structure is shown in Fig. 7; bond lengths and angles are given in Table 6.

The dimer consists of two confacially bridged rhodium(III) octahedra. The differing environments, $RhCl_3C_2S$ and $RhCl_3CS_2$, and *trans* influences of the tht and $PhCH_2$ ligands, lead to

Table 8 Fractional atomic coordinates (× 10^4) for compound **1**

Atom	*x*	*y*	*z*
Rh	2500	2500	0
S(1)	675(2)	2267(1)	−459(2)
C(10)	222(12)	1403(7)	−40(8)
C(20)	−34(23)	874(9)	−719(12)
C(30)	−175(16)	1189(10)	−1466(9)
C(40)	261(10)	1944(7)	−1487(6)
C(11)	2411(8)	2124(5)	1126(5)
C(12)	1955(7)	2553(5)	1628(5)
C(13)	1893(10)	2315(5)	2378(6)
C(14)	2316(10)	1608(6)	2646(6)
C(15)	2762(10)	1164(6)	2149(6)
C(16)	2819(8)	1414(5)	1406(5)
C(2)	1452(10)	3346(5)	1340(6)
C(4)	2282(13)	1285(7)	3466(7)
C(6)	3344(10)	898(5)	900(6)
C(21)	2008(14)	3961(6)	1941(8)
C(22)	234(12)	3339(7)	1224(7)
C(41)	2608(13)	1882(9)	4112(7)
C(42)	1232(13)	916(8)	3425(7)
C(61)	2763(12)	123(7)	770(8)
C(62)	4540(11)	772(7)	1249(8)

Table 7 Crystal data, details of intensity measurements and structure refinement

Compound	**1**	**2**	**3**	**7**	**8**	**9**
Formula	$C_{38}H_{56}RhS_2$	$C_{35}H_{57}N_4Rh$	$C_{30}H_{47}N_4Rh$	$C_{22}H_{23}O_4Rh$	$C_{33}H_{44}P_3Rh$	$C_{33}H_{45}Cl_3Rh_2S_3$
M	679.900	636.770	554.625	557.23	636.539	942.228
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Triclinic
a/Å	12.622(2)	12.072(2)	10.730(2)	9.581(3)	9.512(6)	11.481(2)
b/Å	17.782(3)	20.024(3)	13.385(2)	11.501(3)	17.056(7)	16.142(4)
c/Å	17.563(3)	16.330(1)	22.985(2)	19.672(7)	20.385(2)	11.373(4)
α/°	90	90	90	90	90	100.50(2)
β/°	103.681(3)	96.02(1)	90	96.50(3)	99.73(10)	91.74(2)
γ/°	90	90	90	90	90	86.06(2)
U/Å^3	3817	3928.81	3290.86	2155.45	3275.50	2067.53
Space group	$C2/c$	$P2_1/n$	$P2_12_12_1$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
Z	4	4	4	4	4	2
D_c/g cm^{-3}	1.183	1.077	1.119	1.717	1.291	1.514
μ/cm^{-1}	4.48	4.01	4.63	14.06	6.43	9.26
F(000)	1444	1366	1176	1108	1328	866
Total no. of reflections	12 370	17 001	3293	3476	4882	6083
No. of unique reflections	4729	6013	3267	2994	3552	5744
No. of reflections used [$F > 3\sigma(F)$]	1672	1792	2441	2165	2905	3613
No. of parameters	187	361	317	286	341	400
Weighting scheme parameter g in $w = 1/[\sigma^2(F) + gF^2]$	0.0002	0.0002	0.0002	0.0002	0.000 25	0.000 02
Final R	0.0582	0.0637	0.0504	0.0471	0.0456	0.0564
Final R'	0.0548	0.0653	0.0468	0.0535	0.0385	0.0449

Table 9 Fractional atomic coordinates (× 10^4) for compound **2**

Atom	*x*	*y*	*z*
Rh	331(2)	970(1)	3134(1)
C(1)	−660(18)	1369(7)	2147(10)
C(11)	−1928(18)	1205(9)	2181(10)
C(12)	−2630(19)	1652(9)	2590(10)
C(13)	−3756(19)	1507(12)	2617(12)
C(14)	−4267(23)	938(14)	2226(15)
C(15)	−3590(22)	498(12)	1834(14)
C(16)	−2434(21)	628(9)	1767(11)
C(160)	−1707(17)	185(8)	1269(10)
C(161)	−1962(19)	−551(8)	1394(12)
C(162)	−1913(21)	391(10)	354(11)
C(120)	−2046(20)	2314(9)	2956(11)
C(121)	−2546(19)	2479(10)	3787(12)
C(122)	−2324(19)	2885(9)	2305(12)
C(140)	−5487(26)	833(19)	2234(21)
C(141)	−5794(24)	771(19)	3006(20)
C(142)	−6054(23)	565(16)	1501(17)
N(1)	−534(13)	1716(7)	1488(9)
C(10)	609(20)	1917(10)	1284(14)
C(111)	343(23)	2481(12)	676(16)
C(112)	1389(22)	2151(14)	2018(13)
C(113)	1087(21)	1275(11)	882(16)
C(2)	523(17)	135(8)	2638(11)
N(2)	828(15)	−406(8)	2428(9)
C(20)	1359(25)	−1063(10)	2421(16)
C(211)	2530(25)	−1005(15)	2574(28)
C(212)	886(29)	−1479(12)	3080(20)
C(213)	994(37)	−1347(14)	1655(23)
C(3)	1160(18)	596(10)	4075(12)
N(3)	1738(16)	388(8)	4672(10)
C(30)	2370(25)	141(16)	5434(14)
C(311)	2389(34)	−592(14)	5403(17)
C(312)	1878(28)	441(15)	6155(13)
C(313)	3503(29)	462(21)	5409(21)
C(4)	385(17)	1797(9)	3753(11)
N(4)	485(15)	2252(8)	4203(10)
C(40)	778(22)	2776(10)	4831(12)
C(411)	2045(22)	2725(12)	5022(14)
C(412)	457(22)	3437(10)	4393(15)
C(413)	170(24)	2612(12)	5552(12)

Table 10 Fractional atomic coordinates (× 10^4) for compound **3**

Atom	*x*	*y*	*z*
Rh	8 225(1)	153(1)	9 448.5(3)
C(1)	8 092(9)	−5(6)	8 548(4)
C(11)	6 882(10)	−497(6)	8 390(3)
C(12)	6 787(11)	−1 542(6)	8 259(4)
C(13)	5 642(13)	−1 937(9)	8 118(5)
C(14)	4 556(12)	−1 428(9)	8 093(5)
C(15)	4 606(11)	−414(11)	8 196(5)
C(16)	5 757(9)	54(9)	8 358(4)
C(121)	7 984(11)	−2 158(8)	8 251(6)
C(141)	3 329(13)	−1 881(11)	7 906(6)
C(161)	5 802(14)	1 174(9)	8 458(6)
N(1)	8 747(7)	174(7)	8 100(4)
C(2)	8 201(12)	284(8)	10 287(5)
N(2)	8 190(10)	396(6)	10 801(4)
C(20)	8 103(16)	539(8)	11 428(5)
C(201)	8 417(38)	1 644(19)	11 504(8)
C(202)	6 847(20)	459(23)	11 612(8)
C(203)	9 080(39)	−69(32)	11 661(8)
C(3)	7 890(9)	1 573(7)	9 421(4)
N(3)	7 829(9)	2 434(6)	9 452(5)
C(30)	7 861(17)	3 500(8)	9 566(7)
C(301)	6 573(35)	3 696(15)	9 862(12)
C(302)	8 885(40)	3 656(13)	9 970(13)
C(303)	8 062(29)	4 021(11)	8 960(9)
C(10)	10 009(12)	616(9)	8 121(5)
C(101)	10 798(11)	329(14)	8 619(6)
C(102)	10 646(11)	347(11)	7 560(5)
C(103)	9 780(17)	1 793(13)	8 091(9)
C(4)	8 969(9)	−1 132(7)	9 536(4)
N(4)	9 548(8)	−1 862(6)	9 649(4)
C(40)	10 476(12)	−2 593(9)	9 833(7)
C(401)	11 457(22)	−2 663(18)	9 385(11)
C(402)	11 181(21)	−2 206(17)	10 332(9)
C(43A)	10 058(40)	−3 519(29)	9 595(46)
C(43B)	9 837(32)	−3 270(25)	10 292(13)

Table 11 Fractional atomic coordinates (× 10^4) for compound **7**

Atom	*x*	*y*	*z*
Rh(1)	3121(1)	1112(1)	1077.5(3)
Rh(2)	1231(1)	1152(1)	2544.6(3)
C(21)	4251(8)	1152(7)	3278(4)
C(22)	4697(8)	2204(8)	3583(4)
C(23)	5744(9)	2196(9)	4135(4)
C(24)	6280(11)	1136(11)	4404(5)
C(25)	5753(9)	125(9)	4129(4)
C(26)	4746(8)	108(8)	3561(4)
C(221)	4119(11)	3355(9)	3308(5)
C(241)	7491(14)	1154(15)	4979(6)
C(261)	4217(12)	−1034(8)	3275(5)
C(2)	4965(11)	1108(8)	810(5)
O(2)	6062(9)	1088(8)	640(4)
C(3)	2307(12)	1092(9)	204(5)
O(3)	1792(11)	1046(9)	−342(4)
C(4)	1269(9)	1232(7)	3482(5)
O(4)	1256(9)	1303(7)	4056(4)
O(10)	3888(6)	1146(5)	2107(3)
C(10)	3268(9)	1153(6)	2635(4)
C(11)	1136(8)	1077(7)	1400(4)
C(12)	563(8)	16(7)	1581(4)
C(13)	−628(8)	10(9)	1958(4)
C(14)	−1260(8)	1070(8)	2130(4)
C(15)	−740(8)	2119(8)	1901(4)
C(16)	442(7)	2140(7)	1535(4)
C(141)	−2478(10)	1051(9)	2530(5)
C(161)	917(10)	3282(9)	1279(5)
C(121)	1176(11)	−1120(7)	1398(5)

asymmetry in all three Rh–Cl–Rh bridges, although there is some consistency in respect of the *trans* arrangement. Thus the longest Rh–Cl bonds [2.58(1)–2.63(1) Å] are those *trans* to the benzyls; the lower *trans* influence of the tht ligands leads to Rh–Cl distances of 2.32(1)–2.41(1) Å. Both the Rh–C(benzyl) and Rh–S distances show variations which must reflect the particular metal environments since all tht ligands are *trans* to chlorines which are *trans* to benzyls. Thus Rh–C distances on Rh(1) are equal at 2.07(1) and 2.08(1) Å, but Rh(2)–C(1) is 2.14(1) Å, whilst Rh(2)–S distances are 2.303(5), 2.324(5) Å and Rh(1)–S(3) is 2.273(5) Å.

Experimental

Microanalyses were by Pascher, Remagen and University College, London, laboratories.

Instrumentation and techniques were as described previously.[21] The NMR data are in C_6D_6 referenced to $SiMe_4$ or for ^{13}P, 83% H_3PO_4 external. The ^{13}C cross-polarization magic-angle-spinning (CP MAS) NMR spectra were recorded on a Bruker MSL-300 spectrometer using a 5.1 μs 90° pulse length, 10 ms contact pulse, 8 s recycle delay and 4.1 kHz spinning speed.

All reactions and operations were carried out under purified N_2 or Ar or in vacuum; solvents were dried by standard methods and distilled before use. Commercial chemicals were from Aldrich.

trans-*Bis*(*tetrahydrothiophene*)*bis*(2,4,6-*triisopropylphenyl*)-*rhodium*(II) **1**.—A solution of Li(2,4,6-$Pr^i_3C_6H_2$)(Et_2O)[22] (0.54 g, 1.9 mmol in 20 cm^3 toluene) was added dropwise to a solution of *$RhCl_3(tht)_3$*[23] (0.3 g, 0.6 mmol) in toluene (30 cm^3) at −70 °C. The solution was allowed to warm to room temperature and stirred for 16 h. Evaporation under vacuum and extraction of the brown residue with hexane (3 × 15 cm^3) followed by concentration (to 10 cm^3) and cooling (−20 °C) gave pale orange crystals. Yield: 0.11 g, 26%.

Table 12 Fractional atomic coordinates (× 10^4) for compound **8**

Atom	x	y	z
Rh	467(1)	2202.8(3)	1608.1(3)
P(1)	−1321(2)	2733(1)	840(1)
P(2)	−935(2)	2073(1)	2403(1)
P(3)	2085(2)	2207(1)	895(1)
C(12)	−3466(5)	2170(2)	−182(2)
C(13)	−4235(5)	1581(2)	−554(2)
C(14)	−3896(5)	796(2)	−418(2)
C(15)	−2787(5)	601(2)	91(2)
C(16)	−2018(5)	1191(2)	463(2)
C(11)	−2358(5)	1975(2)	327(2)
C(101)	−2760(7)	3314(4)	1092(4)
C(102)	−907(7)	3404(4)	193(4)
C(22)	−876(4)	3671(2)	2662(2)
C(23)	−1294(4)	4363(2)	2938(2)
C(24)	−2433(4)	4357(2)	3290(2)
C(25)	−3154(4)	3659(2)	3364(2)
C(26)	−2736(4)	2967(2)	3087(2)
C(21)	−1597(4)	2973(2)	2736(2)
C(201)	−2552(8)	1488(4)	2166(4)
C(202)	−239(9)	1587(5)	3184(4)
C(10)	2049(6)	1638(4)	2269(3)
C(20)	2192(6)	804(4)	2252(3)
C(30)	3258(8)	433(5)	2686(4)
C(40)	4188(7)	823(5)	3162(4)
C(50)	4012(7)	1626(5)	3196(4)
C(60)	2986(6)	2031(3)	2762(3)
C(401)	5340(8)	401(5)	3642(4)
C(601)	2906(8)	2915(4)	2842(4)
C(200)	1228(7)	300(4)	1747(4)
C(42)	3098(5)	3291(3)	26(2)
C(43)	3510(5)	4038(3)	−145(2)
C(44)	3450(5)	4666(3)	287(2)
C(45)	2979(5)	4547(3)	890(2)
C(46)	2567(5)	3800(3)	1062(2)
C(41)	2626(5)	3172(3)	630(2)
C(411)	3833(8)	1772(6)	1152(5)
C(412)	1546(10)	1685(5)	110(4)

Tris(2,6-*dimethylphenyl*)*rhodium*(III) **4** *and tris*(2,4,6-*trimethylphenyl*)*rhodium*(III) **5**.—The method for the two compounds was the same except for the use of different Grignard reagents. The compound Mg(2,6-$Me_2C_6H_3$)Br (or the mesityl analogue) (0.3 mol dm^{-3} in thf, 14.1 cm^3) was added to $RhCl_3(tht)_3$ (0.5 g, 1.06 mmol) in Et_2O (45 cm^3) at −78 °C with vigorous stirring. The mixture was allowed to warm and was stirred for 3 h at room temperature, then filtered, the solvent removed under vacuum and the residue extracted with hexane (3 × 10 cm^3). Cooling the hexane extract (−30 °C) gave orange crystals. Yield: *ca.* 0.15 g, *ca.* 35% based on rhodium. NMR: **4**, ^1H, δ 1.85 (s, br, 3 H, *o*-CH_3), 2.01 (s, br, 3 H, *o*-CH_3), 6.40 (d, br, *J ca.* 7, 1 H, aromatic *m*-H), 6.80 (d, br, *J ca.* 7, 1 H, aromatic *m*-H) and 6.90 (pseudo t, *J ca.* 7.26 Hz, 1 H, aromatic *p*-H); **5** (see ref. 3), additional data, ^{13}C, δ 129.29 (d, J_{CH} = 153.08 Hz, C^5 or C^3).

The compound tris(2-methylphenyl)bis(tetrahydrothiophene)rhodium(III) was obtained in a similar manner but the yields were only a few % and the reaction was irreproducible for no obvious reasons. ^1H NMR: δ 1.16 [m, 8 H, $S(CH_2CH_2)_2$], 2.13 (s, 9 H, 2-MeC_6H_4), 2.31 [m, 8 H, $S(CH_2CH_2)_2$], 6.63 (d, 3 H, 2-MeC_6H_4), 6.95 (m, 6 H, 2-MeC_6H_4) and 7.66 (d, 3 H, 2-MeC_6H_4).

Tribenzyl-1κ^{2}C^1,2κC^1-*tri*-μ-*chloro*-*tris*(*tetrahydrothiophene*)-1κS,2κ^{2}S-*dirhodium*(III) **9**.—To a stirred suspension of $RhCl_3(tht)_3$ (0.5 g, 1.06 mmol) in thf–Et_2O (1:3 v/v, 50 cm^3) at −78 °C was added benzylmagnesium bromide (7.7 cm^3 of a 0.41 mol dm^{-3} solution in Et_2O). After warming and stirring at room temperature (3 h) the solution was evaporated, the residue washed with hexane and then extracted with Et_2O (2 × 25 cm^3). Cooling (−30 °C) of the extract gave dark orange crystals. Yield: 0.2 g, 45% based on Rh. X-Ray-quality crystals were obtained on recrystallization from Et_2O. ^1H NMR: δ 1.23 (s, br, 8 H), 1.79 and 1.95 (s, br, 16 H) (all C_4H_8S), 3.77 [d of d, J_{RhH} = 2.89, $J(H^1H^2)$ = 7.65, 2 H, CH_2Ph], 4.59 (d, J_{RhH} = 3.19, 2 H, CH_2Ph), 4.71 (d of d, J_{RhH} = 4.0, J = 7.65 Hz, 2 H, CH_2Ph) and 7–7.9 (complex m, 15 H, Ph).

Table 13 Fractional atomic coordinates (× 10^4) for compound **9**

Atom	x	y	z	Atom	x	y	z
Rh(1)	2700(1)	2467(1)	1874(1)	C(33)	5383(8)	2038(4)	−1684(7)
Rh(2)	765(1)	1905(1)	3567(1)	C(34)	5781(8)	1194(4)	−1764(7)
Cl(1)	2315(2)	2795(2)	4142(2)	C(35)	5131(8)	644(4)	−1277(7)
Cl(2)	413(2)	2660(2)	1969(2)	C(36)	4083(8)	939(4)	−711(7)
Cl(3)	2326(2)	1059(2)	2125(2)	C(31)	3685(8)	1783(4)	−631(7)
S(3)	3073(3)	3782(2)	1598(3)	C(41)	−2065(10)	1705(8)	2535(11)
S(1)	−777(3)	1071(2)	2998(3)	C(42)	−2534(14)	1164(9)	1414(13)
S(2)	1113(3)	1102(2)	5057(3)	C(43)	−1512(14)	826(12)	664(13)
C(1)	−384(9)	2809(6)	4648(9)	C(44)	−548(13)	465(10)	1443(13)
C(12)	−1149(6)	2256(5)	6384(8)	C(51)	1717(11)	45(7)	4369(11)
C(13)	−1099(6)	2194(5)	7592(8)	C(52)	3011(15)	29(12)	4844(17)
C(14)	−254(6)	2605(5)	8346(8)	C(53)	3121(15)	586(12)	5974(16)
C(15)	540(6)	3077(5)	7892(8)	C(54)	2389(13)	1405(9)	6012(12)
C(16)	489(6)	3139(5)	6684(8)	C(61)	2986(13)	4530(8)	3010(12)
C(11)	−355(6)	2728(5)	5930(8)	C(62)	1784(19)	4943(12)	3035(18)
C(2)	4489(9)	2206(8)	1902(9)	C(63)	1365(19)	5054(11)	1860(17)
C(22)	5048(6)	1963(4)	3968(7)	C(64)	1746(13)	4271(9)	926(13)
C(23)	5541(6)	2230(4)	5098(7)	C(71)	2783(26)	5737(12)	8627(20)
C(24)	6017(6)	3016(4)	5373(7)	C(72)	3817(27)	5200(23)	8751(29)
C(25)	6000(6)	3535(4)	4517(7)	C(73)	3989(30)	4552(24)	7835(42)
C(26)	5507(6)	3269(4)	3387(7)	C(74)	3324(30)	4377(16)	6903(29)
C(21)	5031(6)	2483(4)	3112(7)	C(75)	2302(24)	4919(19)	6775(26)
C(3)	2607(10)	2105(8)	23(9)	C(76)	2034(17)	5617(15)	7694(29)
C(32)	4336(8)	2333(4)	−1117(7)	C(711)	2695(25)	6444(16)	9623(24)

Interaction of Compounds **1** *and* **5** *with* Bu^{t}NC.—Rh(CNBu^t)$_3$(RC=NBu^t) **2** (R = 2,4,6-Pr$^i{}_3$C$_6$H$_2$). To a toluene (20 cm^3) solution of compound **1** (0.05 g, 0.01 mmol) was added 4 equivalents of Bu^{t}NC (0.6 cm^3 of a 0.5 mol dm^{-3} solution in toluene) when the colour changed to bright yellow. Volatiles were removed and the residue extracted with hexane (2 × 15 cm^3). Concentration of the extract and cooling (−20 °C) gave compound **2**. Yield 0.04 g, 87%. IR: 2156, 2097, and 2060 cm^{-1}. ^{1}H NMR: δ 0.89 [d, 18 H, (C*H*$_3$)$_3$CH, 1.11 (s, 27 H, Bu^{t}NC), 1.99 (s, 9 H, Bu^{t}N=C) and 7.23 (s, 2 H, Pr$^i{}_3$C$_6$*H*$_2$).

3 (R = 2,4,6-Me$_3$C$_6$H$_2$). Excess of Bu^{t}NC (0.15 cm^3) was added to compound **5** (0.06 g, 0.13 mmol) in Et$_2$O (20 cm^3) and the mixture stirred for 2 h. Removal of solvent left a residue which was washed with hexane, extracted into Et$_2$O (2 × 10 cm^3) reduced in volume (10 cm^3) and cooled to give orange crystals. Yield 0.09 g, 81%. IR: 2199, 2152, 2066, 1618, and 1567 cm^{-1}. ^{1}H NMR: δ 0.98 (s, 9 H, Bu^{t}N=C), 0.99 (s, 18 H, axial Bu^{t}NC), 2.06 (s, 9 H, equatorial Bu^{t}NC), 2.35 (s, 3 H, *p*-Me), 2.66 (s, 6 H, *o*-Me) and 6.98 (s, 2 H, aromatic *m*-H).

Tricarbonyl-1κ^{2}C,2κC-μ-2,4,6-*trimethylbenzoyl*-1κO:2κC-μ-2(η^6)-2,4,6-*triphenylmethyl*-1κC^1-*dirhodium*(I) **7**.—A solution of Rh(mes)$_3$ (0.1 g, 0.2 mmol) in Et$_2$O (10 cm^3) was treated with CO for *ca.* 0.5 h at −78 °C. After warming to room temperature and evaporation the residue was extracted with hexane (2 × 15 cm^3). Reduction in volume (to *ca.* 10 cm^3) and cooling (−30 °C) gave light yellow crystals of compound 7 (Yield *ca.* 40%) contaminated with some dimesityl ketone[24] which was removed by a quick wash with chilled ether. The ketone, separately isolated from the mother-liquors, was purified by chromatography on silica and identified by m.p. (137 °C), IR and NMR spectra. **7**, IR (hexane): 2069, 2001, 1999 [ν(RhCO)], and 1610 cm^{-1} {ν[(mes)CO]}. ^{1}H NMR: δ 1.35 (s, 3 H, *p*-Me), 2.04 (s, 6 H, *o*-Me), 2.07 (s, 3 H, *p*-Me), 2.659 (s, 3 H, *o*-Me), 2.664 (s, 3 H, *o*-Me), 5.93 (s, 2 H, aromatic H) and 6.63 (s, 2 H, aromatic H).

Tris(*dimethylphenylphosphine*)(2,4,6-*trimethylphenyl*)-*rhodium*(I) **8**.—To a solution of compound **5** (0.06 g, 0 13 mmol) in Et$_2$O (20 cm^3) was added excess of PMe$_2$Ph (0.25 cm^3) and the mixture stirred (1.5 h) at room temperature. Evaporation under vacuum with heating and extraction of the solid with hexane (20 cm^3) followed by reduction in volume (to 10 cm^3) and cooling (−30 °C) gave yellow crystals. Yield: 0.07 g, 84%. X-Ray-quality crystals were obtained from hexane. NMR: ^{1}H, δ 0.81 [d, *J*(P–CH) = 5.1, 6 H, PMe$_2$Ph], 1.06 [d of t, *J*(P–CH) = 2.6, *J*(Rh–CH) 1.3, 12 H, PMe$_2$Ph], 2.42 (s, 3 H, *p*-Me), 3.00 (s, 6 H, *o*-Me), and 6.71–7.62 (complex m, 17 H, PMe$_2$Ph + mesityl); ^{31}P-{^{1}H}, δ 0.6 (d of d, J_{PP} = 35.5, J_{RhP} = 158.3) and −4.7 (d of t, J_{PP} = 35.5, J_{RhP} = 117.7 Hz).

Bis(2,4,6-*triisopropylphenyl*)*bis*(*trimethylphosphine*)-*chromium*(II).—To a stirred suspension of CrCl$_2$ (0.1 g, 0.81 mmol) in thf (40 cm^3) at −78 °C was added 2 equivalents of Mg(2,4,6-Pr$^i{}_3$C$_6$H$_2$)Br (3.5 cm^3 0.47 mol dm^{-3} solution in thf) and the mixture allowed to warm to ambient temperature. After *ca.* 0.5 h, excess (0.2 cm^3) of PMe$_3$ was added and the solution stirred for 10 h. Removal of volatiles in vacuum, extraction of the residue with hexane (2 × 30 cm^3), concentration (*ca.* 40 cm^3) and cooling (−20 °C) gave orange-red crystals. Yield 0.33 g (66%), m.p. 153–156 (decomp.) Analysis: Found (Calc.) C, 70.6 (70.8); H, 10.5 (10.5)% The compound is similar to other paramagnetic monomeric chromium(II) aryls.[24, 25] It is EPR silent in liquid or frozen toluene but shifted and broadened ^{1}H NMR resonances are observed. On the basis of integration ratios, peaks can be assigned for the *para* isopropyl hydrogen at δ +37 ($w_{\frac{1}{2}}$ = 460 Hz), *para* isopropyl methyl hydrogen at δ +4 ($w_{\frac{1}{2}}$ = 20 Hz), *ortho* isopropyl methyl hydrogens at δ +21 ($w_{\frac{1}{2}}$ = 1220 Hz) and PMe$_3$ hydrogens at δ −30 ($w_{\frac{1}{2}}$ = 1260 Hz).

X-Ray Crystallography.—Crystals of all six compounds were sealed under argon in thin-walled glass capillaries for X-ray measurement. Cell dimensions and intensity data were obtained using a CAD4 diffractometer for compounds **3**, **7**, **8** and **9** and a FAST TV area detector for compounds **1** and **2** following procedures previously described.[26,27] Crystals of **1** and **2** were both small and gave very poor diffraction. As a result only very few acceptable reflections were obtained, in spite of the fact that the X-ray source of the FAST is higher in brightness than that of the CAD4. The structures were solved and developed *via* the heavy-atom method and refined by full-matrix least squares. An empirical absorption correction[28] was applied at the end on refinement in the isotropic approximation in each case. Non-hydrogen atoms were refined in the anisotropic mode; some or all hydrogens were included in compounds **7** (all), **8** (all) and **9** (ring H only). Crystal data and other experimental details are summarised in Table 7; final atomic coordinates are listed in Tables 8–13.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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