Synthesis of the homoleptic rhodium(III) complex [Rh(C$_6$Cl$_5$)$_3$]. Molecular structures of [Rh(C$_6$Cl$_5$)$_3$] and [Rh(C$_6$Cl$_4$–C$_6$Cl$_4$)(C$_6$Cl$_5$)(SC$_4$H$_8$)$_2$]

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The arylation of [RhCl$_3$(SC$_4$H$_8$)$_3$] (SC$_4$H$_8$ = tetrahydrothiophene, tht) with the Grignard reagent MgCl(C$_6$Cl$_5$), under different reaction conditions, afforded the neutral rhodium(III) complexes [Rh(C$_6$Cl$_5$)$_3$] **1** and [Rh(C$_6$Cl$_4$–C$_6$Cl$_4$)(C$_6$Cl$_5$)(tht)$_2$] **2** as well as the paramagnetic rhodium(II) compound [Rh(C$_6$Cl$_5$)$_2$(tht)$_2$] **3**. The homoleptic complex **1** can also be obtained by treatment of [P(CH$_2$Ph)Ph$_3$][RhCl(C$_6$Cl$_5$)$_3$] with AgClO$_4$. The complexes are stable to the air and moisture in the solid state and moderately stable in deoxygenated solutions. The crystal structures of compounds **1** and **2** have been determined. They display distorted octahedral environments. All C$_6$Cl$_5$ groups in **1** or one C$_6$Cl$_5$ group in **2** act as chelating ligands being bonded through the *ipso*-C atom and one of the *ortho*-Cl atoms. Complex **2** additionally incorporates two tetrahydrothiophene ligands and a perchloro-2,2′-biphenylene ligand, formed by coupling of two pentachlorophenyl groups.

Introduction

The chemistry of perhalogenoaryl derivatives of rhodium and iridium has been a subject of our attention in recent years. In this area we have reported a variety of neutral, anionic, mono- and di-nuclear pentafluorophenyl complexes of rhodium and iridium in oxidation states III[1–5] and I.[6] Interestingly, the related, but less frequently used, pentachlorophenyl ligand has allowed the stabilisation of mononuclear rhodium and iridium complexes[7,8] in the rare oxidation state II, including the preparation of novel homoleptic complexes of formula [M^{II}(C$_6$Cl$_5$)$_4$]$^{2-}$ (M = Rh or Ir).[9,10] A relevant feature, recently observed for some rhodium pentachlorophenyl complexes such as [Rh^{III}(C$_6$Cl$_5$)$_4$]$^-$, is the capability of the pentachlorophenyl group to present two co-ordination modes, the conventional σ bond and the unusual chelating bonding through the C$_{ipso}$ atom and one of the *o*-Cl atoms.[10]

On the other hand, the preparation of aryl derivatives can be achieved by the reaction of the appropriate halogen starting metal complex with aryl-lithium or -magnesium compounds, but these reactions are very sensitive to the chosen conditions. For instance, the nature and yield of the products of the reactions of [RhCl$_3$(tht)$_3$] (tht = tetrahydrothiophene) with lithium derivatives depends on the experimental conditions and on the steric properties of the aryl or alkyl group used; so an excess of LiC$_6$Cl$_5$ leads[10] to the preparation of the arylated rhodium(II) dianion [Rh(C$_6$Cl$_5$)$_4$]$^{2-}$ and with Li(2,4,6-^{i}Pr$_3$C$_6$H$_2$) yields[11] the neutral square-planar complex [Rh$_2$(2,4,6-^{i}Pr$_3$C$_6$H$_2$)$_2$(tht)$_2$]. During these arylating reactions a one-electron reduction process has taken place. However, with LiC$_6$F$_5$ it gives[1] the square-pyramidal rhodium(III) dianion [Rh(C$_6$F$_5$)$_5$]$^{2-}$, while LiMe affords[12] the octahedral [RhMe$_6$]$^{3-}$. Quite likely, in these reactions radical processes are involved.

In general, organomagnesium compounds are less reactive than organolithium compounds, but they are also less basic and poorer one-electron reducing agents, and so less prone to side-reactions arising from these properties. For these reasons, and following our interest in the chemistry of the pentachloro-phenyl ligand, we have studied the arylation of [RhCl$_3$(tht)$_3$] with pentachlorophenylmagnesium chloride. We report here the synthesis and full characterisation of the new homoleptic [Rh^{III}(C$_6$Cl$_5$)$_3$] compound, which constitutes the first metal complex with three pentachlorophenyl groups acting as chelating ligands in a "RhC$_3$Cl$_3$" co-ordination environment, together with a related complex of formula [Rh^{III}(C$_6$Cl$_4$–C$_6$Cl$_4$)(C$_6$Cl$_5$)(tht)$_2$]. The latter complex is the result of the unusual coupling of two pentachlorophenyl groups.

Results and discussion

The previously reported arylation of [RhCl$_3$(tht)$_3$] with the lithium derivative LiC$_6$Cl$_5$ afforded[10] the paramagnetic rhodium(II) dianion [Rh(C$_6$Cl$_5$)$_4$]$^{2-}$. In contrast, the treatment of [RhCl$_3$(tht)$_3$] in THF with the Grignard reagent MgCl(C$_6$Cl$_5$) (1 : 6 ratio, 4 h reflux), work-up and column chromatography of the reaction product allow the preparation of the neutral homoleptic rhodium(III) complex [Rh(C$_6$Cl$_5$)$_3$] **1** (31% yield). The MS (FAB) of **1** shows the parent peak at *m/z* 851, together with the peak at *m/z* 601 corresponding to the [Rh(C$_6$Cl$_5$)$_2$] fragment. The IR spectrum exhibits only absorptions due to the C$_6$Cl$_5$ groups.[13] Its molecular geometry was established by an X-ray structural determination.

Trying to improve the yield in complex **1** in the Grignard reaction, the mixture of [RhCl$_3$(tht)$_3$] and MgCl(C$_6$Cl$_5$) was left at reflux temperature for 18 h. After work-up, in similar way to that before, the yield in complex **1** was smaller (around 10%) but a new fraction was collected from the column containing the complex [Rh(C$_6$Cl$_4$–C$_6$Cl$_4$)(C$_6$Cl$_5$)(tht)$_2$] **2** (15% yield). So the coupling of two C$_6$Cl$_5$ groups has taken place with the formation of a new C–C σ bond.[14] A similar process takes place when MCl$_4$ (M = Si or Ge) reacts with MgCl(C$_6$Cl$_5$).[15]

A coproduct in the above syntheses is the paramagnetic mononuclear rhodium(II) complex [Rh(C$_6$Cl$_5$)$_2$(tht)$_2$] **3**, formed in relatively small yield (about 20%) and easily separated from the column by elution with CH$_2$Cl$_2$. Complex **3** is paramagnetic and its X-band EPR spectrum at room temperature is analogous to those found for the neutral rhodium(II) complexes [Rh(C$_6$Cl$_5$)$_2$L$_2$] [L$_2$ = cycloocta-1,5-diene (cod), {P(OPh)$_3$}$_2$, {P(OMe)$_3$}$_2$, (PPh$_3$)$_2$, py$_2$, 1,2-bis(diphenylphosphino)ethane (dppe), bis(diphenylphosphino)methane (dppm)].[8] The values $g_x = 2.73$, $g_y = 2.60$ and $g_z = 1.95$ can be understood if the unpaired electron is mainly in a d_{z^2} orbital with the z axis perpendicular to the first co-ordination rhodium plane. No evidence of hyperfine structure has been found.
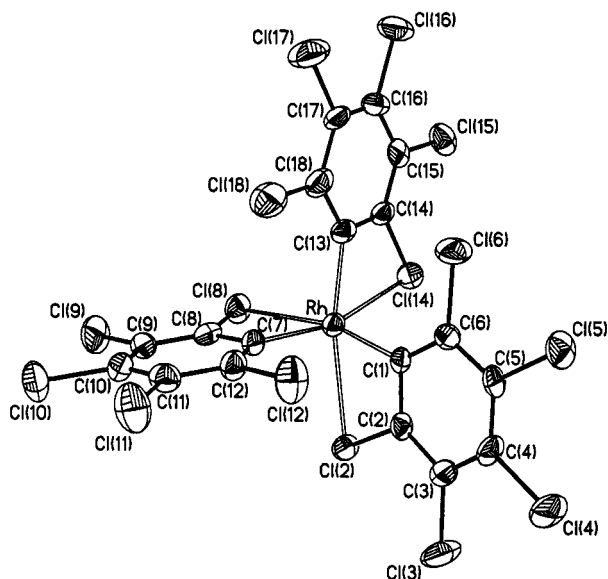
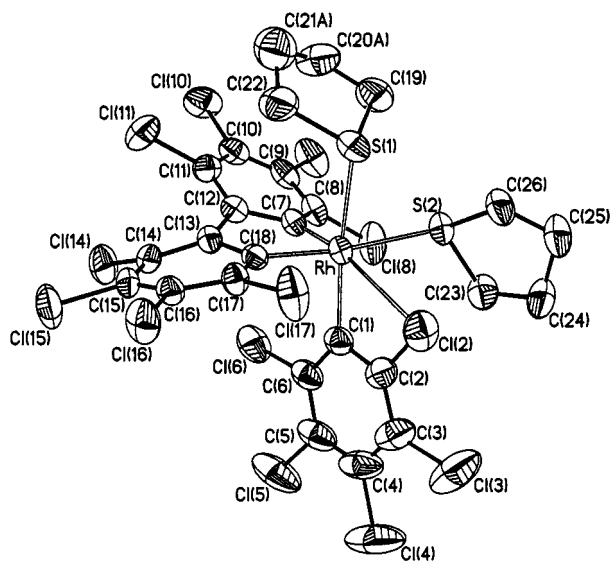**Fig. 1** Molecular diagram of the complex [Rh(C₆Cl₅)₃] **1**, together with the numbering scheme used.

Fig. 2 Molecular diagram of the complex [Rh(C₆Cl₄–C₆Cl₄)(C₆Cl₅)- (tht)₂] **2**, together with the numbering scheme used.

Complex **1** can also be obtained by reaction of [P(CH₂Ph)- Ph₃][RhCl(C₆Cl₅)₃] with AgClO₄; AgCl and [P(CH₂Ph)Ph₃]ClO₄ are separated and the solution provides [Rh(C₆Cl₅)₃] (72% yield).

Molecular structures of [Rh(C₆Cl₅)₃] 1 and [Rh(C₆Cl₄–C₆Cl₄)- (C₆Cl₅)(tht)₂] 2

The crystal structures of complexes **1**·½CH₂Cl₂ and **2** have been solved by single-crystal X-ray crystallography. The respective molecular structures of the complexes, including a conventional image of the displacement parameters, are presented in Figs. 1 and 2, together with the atomic labelling schemes used. Selected bond distances and angles are collected in Tables 1 and 2.

Although the complex **1** has only three ligands, the rhodium atom is in a distorted-octahedral environment formed by three Rh–C σ bonds from the three C₆Cl₅ ligands (in a *fac* disposition), and three Rh–Cl secondary bonds, each involving one *o*-chlorine of different pentachlorophenyl groups (Fig. 1). This arrangement of the perhalogenophenyl groups results in a helix structure with a pseudo-C_3 axis, making this complex chiral, but with both enantiomers present in the crystal struc-

Table 1 Selected bond lengths (Å) and angles (°) for [Rh(C₆Cl₅)₃] **1**

Rh–Cl(2)	2.6171(16)	Rh–C(1)	1.986(6)
Rh–Cl(8)	2.5889(17)	Rh–C(7)	1.993(7)
Rh–Cl(14)	2.6020(18)	Rh–C(13)	1.994(6)
Cl(2)–C(2)	1.764(6)	Cl(8)–C(8)	1.763(7)
Cl(14)–C(14)	1.764(6)	mean Cl–C[a]	1.722(3)
Cl(2)–Rh–Cl(8)	99.76(5)	C(1)–Rh–C(7)	100.4(3)
Cl(2)–Rh–Cl(14)	107.70(6)	C(1)–Rh–C(13)	100.8(2)
Cl(8)–Rh–Cl(14)	96.99(6)	C(7)–Rh–C(13)	100.8(3)
Cl(2)–Rh–C(1)	67.84(18)	Cl(8)–Rh–C(1)	164.56(19)
Cl(2)–Rh–C(7)	86.31(18)	Cl(8)–Rh–C(7)	68.64(19)
Cl(2)–Rh–C(13)	167.73(18)	Cl(8)–Rh–C(13)	92.17(18)
Cl(14)–Rh–C(1)	95.66(18)	Rh–Cl(2)–C(2)	73.2(2)
Cl(14)–Rh–C(7)	161.84(19)	Rh–Cl(8)–C(8)	73.3(2)
Cl(14)–Rh–C(13)	67.6(2)	Rh–Cl(14)–C(14)	73.4(2)
Rh–C(1)–C(2)	105.8(4)	Rh–C(1)–C(6)	138.0(5)
Rh–C(7)–C(8)	104.3(5)	Rh–C(7)–C(12)	137.9(5)
Rh–C(13)–C(14)	105.7(4)	Rh–C(13)–C(18)	136.3(5)

[a] Mean bond length of the non-co-ordinated chlorines.

Table 2 Selected bond lengths (Å) and angles (°) for [Rh(C₆Cl₄– C₆Cl₄)(C₆Cl₅)(tht)₂] **2**

Rh–S(1)	2.4275(12)	Rh–S(2)	2.4997(11)
Rh–Cl(2)	2.8682(14)	Rh–C(1)	2.046(4)
Rh–C(7)	1.990(4)	Rh–C(18)	2.020(4)
C(2)–Cl(2)	1.748(5)	mean Cl–C[a]	1.728(2)
C(12)–C(13)	1.472(5)		
S(1)–Rh–S(2)	82.11(4)	S(1)–Rh–Cl(2)	104.93(4)
S(1)–Rh–C(1)	167.74(14)	S(1)–Rh–C(7)	94.18(12)
S(1)–Rh–C(18)	90.86(11)	S(2)–Rh–Cl(2)	77.64(4)
S(2)–Rh–C(1)	97.47(12)	S(2)–Rh–C(7)	97.42(12)
S(2)–Rh–C(18)	172.76(11)	Cl(2)–Rh–C(1)	63.19(14)
Cl(2)–Rh–C(7)	159.24(12)	Cl(2)–Rh–C(18)	106.01(12)
C(1)–Rh–C(7)	98.02(18)	C(1)–Rh–C(18)	89.77(16)
C(7)–Rh–C(18)	81.31(16)	Rh–Cl(2)–C(2)	71.02(16)
Rh–C(1)–C(2)	109.5(3)	Rh–C(1)–C(6)	135.7(4)

[a] Mean bond length of the non-co-ordinated chlorines.

Table 3 Metal complexes containing chelating pentachlorophenyl ligands

	Number of C₆Cl₅ ligands			
Complex	Total	Chelating	σ-Bonded	Ref.
[Rh(C₆Cl₅)₃]	3	3	0	This work
[Rh(C₆Cl₄–C₆Cl₄)- (C₆Cl₅)(tht)₂]	1	1	0	This work
[Rh(C₆Cl₅)₄]⁻	4	2	2	10
[Rh(C₆Cl₅)₃Cl]⁻	3	2	1	10
[Rh{C(O)C₆Cl₅}₂- (C₆Cl₅)Cl]⁻	1	1	0	10
[Pt(C₆Cl₅)₄]	4	2	2	16
[Cr(C₆Cl₅)₄]⁻	4	2	2	17

ture. This chelating co-ordination mode of the pentachlorophenyl groups has previously been reported for the anionic rhodium complexes[10] [Rh(C₆Cl₅)₄]⁻, [Rh(C₆Cl₅)₃Cl]⁻ and [Rh{C(O)C₆Cl₅}₂(C₆Cl₅)Cl]⁻, for the platinum complex[16] [Pt(C₆Cl₅)₄] and, very recently, also for a chromium(III) complex[17] [Cr(C₆Cl₅)₄]⁻, but the present case is the first homoleptic one with all the C₆Cl₅ groups acting as chelate ligands (Table 3).

The deviation from a perfect octahedral co-ordination arises fundamentally from the chelating co-ordination of the pentachlorophenyl ligands, which form strained four-membered metallacycles. This distortion of the metal environment can be visualised in the Cl–Rh–C bite angles, 67.84(18), 68.64(19) and 67.6(2)°, and is the origin of an asymmetric co-ordination of the phenyl rings, which are tilted to permit the approach of the *o*-chlorine atoms to the metal centre. This tilting can be charac-

terised with the angles around the C_{ipso} carbons (see Table 1), or in terms of the value of the angle between the Rh–C bond and the C_{ipso}–C_{para} direction (the pseudo-2-fold axis of the ligand), 162.9, 160.9 and 162.9(4)° around C(1), C(7) and C(13), respectively.

The lengths observed for these Rh-*o*-Cl bonds [2.6171(16), 2.5889(17) and 2.6020(18) Å for Cl(2), Cl(8) and Cl(14), respectively] are, as expected, significantly longer than the usual Rh^{III}–Cl distances (mean value 2.374 Å),[18] but short enough to be considered as secondary bonds.[10] Furthermore, they are shorter than the secondary bonds described in the previously mentioned rhodium complexes [range 2.6277(11)–2.8863(9) Å]. Interestingly, in compound **1** all the chelating chlorines are *trans* disposed to the C_{ipso} atom of another C_6Cl_5 ring, as is also described for [Rh(C$_6$Cl$_5$)$_3$Cl]$^-$ and for the homoleptic complexes [M(C$_6$Cl$_5$)$_4$]$^-$ (M = Rh or Cr) and [Pt(C$_6$Cl$_5$)$_4$].

In compound **2** the metal centre also exhibits a distorted octahedral environment, completing the co-ordination sphere with three different type of ligands: two tetrahydrothiophene ligands, an octachlorobiphenylene chelating ligand and a C_6Cl_5 ring linked to the metal through a Rh–C σ bond and through a Rh–Cl secondary bond. In this complex the distortion is also due to the small bite angle of the C_6Cl_5 chelating group [63.19(14)°] and, to a lesser extent, of the perhalogeno-biphenylene ligand [81.31(16)°]. The tht ligands are in a *cis* disposition, the Rh-*o*-Cl bond being *trans* to a carbon atom of the perhalogenobiphenylene ligand.

The perchloro-2,2′-biphenylene group presents a considerable twist between the two phenyl rings [torsion angle C(11)–C(12)–C(13)–C(14) 36.3(7)°] due to the steric hindrance of Cl(11) and Cl(14). This conformation is similar to that reported for the compounds [M(C$_6$Cl$_4$–C$_6$Cl$_4$)(C$_6$Cl$_5$)$_2$] (M = Si or Ge)[15] with torsion angles of about 34°. The two Rh–C bond lengths in this ligand are slightly different [1.990(4) and 2.020(4) Å], probably due to the different *trans* atoms; the long one corresponds to the bond *trans* to the sulfur atom and is very similar to the Rh–C distance for the C_6Cl_5 group [2.046(4) Å], also *trans* to a tht ligand. The short distance, *trans* to an *o*-Cl, is equal to those calculated in **1** for Rh-C$_6$Cl$_5$ bonds, also *trans* to an *o*-chlorine.

The Rh–Cl bond [2.8682(14) Å] is longer than those observed for **1** [2.6171(16), 2.5889(17) and 2.6020(18) Å], but similar to those reported for [Rh{C(O)C$_6$Cl$_5$}$_2$(C$_6$Cl$_5$)Cl]$^-$ [2.8863(9) Å]. In fact there seems to be a correlation between the number of chelating C_6Cl_5 groups and the length of these Rh-*o*-Cl bonds. The shorter distances correspond to the compound with three chelating C_6Cl_5 rings (**1**, mean 2.603 Å), there are intermediate values in the complexes with two chelating C_6Cl_5 ligands {[Rh(C$_6$Cl$_5$)$_4$]$^-$, 2.6277 and 2.7521(11) Å; [Rh(C$_6$Cl$_5$)$_3$Cl]$^-$, 2.656 and 2.678(4) Å; mean value 2.688 Å} and longer distances in the compounds with one chelating C_6Cl_5 ligand (**2**, 2.8682(14) Å; [Rh{C(O)C$_6$Cl$_5$}$_2$(C$_6$Cl$_5$)Cl]$^-$, 2.8863(9) Å; mean value 2.881 Å).

Experimental

General

Analyses (C, H and S) and IR spectra (in Nujol suspension between polyethylene sheets) were obtained as described elsewhere.[8] Mass spectra were measured in a VG Autospec double-focusing mass spectrometer operating in the positive mode; ions were produced with the standard Cs$^+$ gun at *ca.* 30 kV; 3-nitrobenzyl alcohol was used as matrix; high-resolution FAB spectra are in accordance with the simulated isotopic pattern distribution. The starting rhodium(III) compound [RhCl$_3$(tht)$_3$] was prepared as described in the literature.[19] The compound MgCl(C$_6$Cl$_5$) was obtained by treating C$_6$Cl$_6$ with Mg, in tetrahydrofuran, using I$_2$ as the initiator, and keeping the mixture stirred at reflux temperature for 3 h; it was directly used without further isolation. Diethyl ether, THF, CH$_2$Cl$_2$ and hexane were distilled under nitrogen from the appropriate drying agents.

Preparations

[Rh(C$_6$Cl$_5$)$_3$] 1. *Method a.* Solid [RhCl$_3$(tht)$_3$] (0.500 g, 1.05 mmol) was added to a tetrahydrofuran solution (30 mL) of MgCl(C$_6$Cl$_5$) (6.33 mmol) and stirred for 4 h at reflux temperature. The mixture was slowly allowed to reach room temperature; the excess of Grignard compound was hydrolysed with aqueous diethyl ether and then evaporated till dryness. The residue was extracted with CH$_2$Cl$_2$ (50 mL), filtered and the filtrate concentrated to a few millilitres. Addition of diethyl ether caused the precipitation of a brown solid. This solid was chromatographed on a silica gel column (2.5 × 25 cm) using hexane as stationary phase. Elution with hexane afforded a yellow band; the hexane was evaporated till dryness and the residue dissolved in CH$_2$Cl$_2$; addition of methanol gave the yellow microcrystalline solid [Rh(C$_6$Cl$_5$)$_3$] **1** (31% yield). Elution with CH$_2$Cl$_2$ yield another yellow band, subsequently identified as [Rh(C$_6$Cl$_5$)$_2$(tht)$_2$] **3**.

Method b. To a CH$_2$Cl$_2$ solution of [P(CH$_2$Ph)Ph$_3$][RhCl-(C$_6$Cl$_5$)$_3$] (0.100 g, 0.08 mmol) was added solid AgClO$_4$ (16.6 mg, 0.08 mmol). The solution was stirred for 1 h under a nitrogen atmosphere and with exclusion of light to yield a white solid (AgCl and [P(CH$_2$Ph)Ph$_3$]ClO$_4$) which was removed by filtration through Kieselguhr. Concentration of the resulting solution under reduced pressure to a volume of 1 mL and addition of methanol (10 mL) afforded **1** as a yellow solid which was filtered off, washed with methanol and dried under vacuum. The compound was recrystallised from CH$_2$Cl$_2$–methanol (72% yield) (Found: C, 25.37. Calc. for C$_{18}$Cl$_{15}$Rh: C, 25.40%). IR (Nujol; cm^{-1}): *v*(C$_6$Cl$_5$) 1345, 1313, 1279, 831 (X-sensitive), 679, 637 [*v*(Rh–C)]. MS [FAB; *m/z* (%)]: 851 (39) [M$^+$, Rh(C$_6$Cl$_5$)$_3$], 601 (51) [Rh(C$_6$Cl$_5$)$_2$].

[Rh(C$_6$Cl$_4$–C$_6$Cl$_4$)(C$_6$Cl$_5$)(tht)$_2$] 2. The preparation and isolation of complex **2** was similar to that described for **1**, in Method a, but keeping the Grignard reaction at reflux temperature for 18 h. The silica gel column chromatography (2.5 × 25 cm) of the reaction product using hexane as stationary phase gave two yellow bands. Concentration of the hexane solutions provided complexes **1** and **2**. Data for **2**: yield 15% (Found: C, 32.38; H, 1.62; S, 6.40. Calc. for C$_{26}$H$_{16}$Cl$_{13}$RhS$_2$: C, 32.65; H, 1.69; S, 6.70%). IR (Nujol; cm^{-1}) *v*(C$_6$Cl$_5$) 1307, 1298, 1289, 1280, 795 and 674; MS [FAB; *m/z* (%)] 781 (30) [Rh(C$_6$Cl$_4$–C$_6$Cl$_4$)(C$_6$Cl$_5$)].

[Rh(C$_6$Cl$_5$)$_2$(tht)$_2$] 3. Elution of the column of the previous synthesis with CH$_2$Cl$_2$ gave an orange band; concentration of the CH$_2$Cl$_2$ solution and addition of methanol gave an orange solid identified as [Rh(C$_6$Cl$_5$)$_2$(tht)$_2$] **3**. Yield: 20% (Found: C, 30.95; H, 1.97; S, 8.20. Calc. for C$_{20}$H$_{16}$Cl$_{10}$RhS$_2$: C, 30.88; H, 2.07; S, 8.24%). IR (Nujol; cm^{-1}) *v*(C$_6$Cl$_5$) 1310, 1290, 820, 665 and 602.

Crystal structure determination of [Rh(C$_6$Cl$_5$)$_3$]·½CH$_2$Cl$_2$ 1·½CH$_2$Cl$_2$ and [Rh(C$_6$Cl$_4$–C$_6$Cl$_4$)(C$_6$Cl$_5$)(tht)$_2$] 2

A summary of crystal data and refinement parameters is reported in Table 4. Data were collected on a Siemens-Stoe AED-2 diffractometer with graphite-monochromated Mo-Kα radiation, using the ω–2θ scan method. Three standard reflections were monitored every 55 min throughout data collection; no important variations were observed. All data were corrected for Lorentz-polarisation effects, and for absorption using a semiempirical method (ψ scan);[20] minimum and maximum transmission factors are listed in Table 4. All structures were solved by direct methods (SIR 92)[21] and Fourier techniques, and refined by full-matrix least squares on F^2 (SHELXL 97).[22]

Table 4 Crystallographic data for [Rh(C$_6$Cl$_5$)$_3$]·$\frac{1}{2}$CH$_2$Cl$_2$ **1**·$\frac{1}{2}$CH$_2$Cl$_2$ and [Rh(C$_6$Cl$_4$–C$_6$Cl$_4$)(C$_6$Cl$_5$)(tht)$_2$] **2**

	1·$\frac{1}{2}$CH$_2$Cl$_2$	**2**
Crystal color and habit	Yellow, prismatic block	Orange, prismatic block
Crystal size/mm	0.14 × 0.21 × 0.35	0.16 × 0.21 × 0.45
Formula	C$_{18.5}$HCl$_{16}$Rh	C$_{26}$H$_{16}$Cl$_{13}$RhS$_2$
M	893.30	956.27
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)
T/K	233(2)	295(2)
a/Å	10.8207(11)	9.2192(5)
b/Å	10.8539(15)	32.660(2)
c/Å	14.0152(15)	11.3747(7)
a/°	108.608(5)	—
β/°	102.214(4)	105.805(6)
γ/°	106.976(6)	—
V/Å^3	1405.2(3)	3295.4(3)
Z	2	4
μ/mm^{-1}	2.142	1.721
θ range/°	1.6–23.0	1.9–25.0
Collected reflections	4173	6264
Unique reflections	3925 (R_{int} = 0.020)	5795 (R_{int} = 0.018)
Minimum, maximum transmission factors	0.8146, 1.0000	0.5147, 0.5625
Data/restraints/parameters	3925/7/329	5795/28/399
$R(F)$ [$F^2 > 2\sigma(F^2)$]^a	0.0472	0.0364
$wR(F^2)$ [all data]^b	0.1306	0.0913

^{a} $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, for 3261 and 4613 observed reflections, respectively. ^{b} $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$.

The function minimised was $\Sigma[w(F_o^2 - F_c^2)^2]$ with the weight defined as $w^{-1} = [\sigma^2(F_o^2) + (xP)^2 + yP]$ where $P = (F_o^2 + 2F_c^2)/3$. Atomic scattering factors, corrected for anomalous dispersion, were used as implemented in the refinement program.[22]

Complex 1·$\frac{1}{2}$CH$_2$Cl$_2$. Yellow prismatic crystals suitable for the X-ray diffraction study were obtained from a CH$_2$Cl$_2$–methanol solution of complex **1**. Anisotropic displacement parameters were used in the last cycles of refinement for all atoms, except for the dichloromethane solvent (one half per asymmetric unit), which was two-fold disordered and refined with geometrical restraints, free but complementary occupancy factors [0.277 and 0.224(5)], and two refined isotropic displacement parameters. The refinement converged to $R(F) = 0.0472$ [$F^2 > 2\sigma(F^2)$] and $wR(F^2) = 0.1306$ (all data), with weight parameters $x = 0.0787$ and $y = 3.6004$. Residual peaks in the final difference map were 1.74 and -0.99 e Å^{-3}.

Complex 2. Suitable crystals were obtained from a CH$_2$Cl$_2$–methanol solution. After refinement of all the non-hydrogen atoms with anisotropic displacement parameters, the hydrogen atoms of one tht ligand were introduced in calculated positions and refined riding on the corresponding carbon atoms; the hydrogens of the other tht ligand were not introduced because two carbons of this group were two-fold disordered [occupancy factors 0.53 and 0.47(3)]. The refinement converged to $R(F) = 0.0364$ and $wR(F^2) = 0.0913$, with weight parameters $x = 0.0334$ and $y = 4.3269$. Residual peaks in the final difference map were 0.45 and -0.34 e Å^{-3}.

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See http://www.rsc.org/suppdata/dt/1998/4211/ for crystallographic files in .cif format.

Acknowledgements

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