Macrocyclic Organometallics. Part 2.[1] An organorhodium(III) Complex of a Macrocyclic Triamine†

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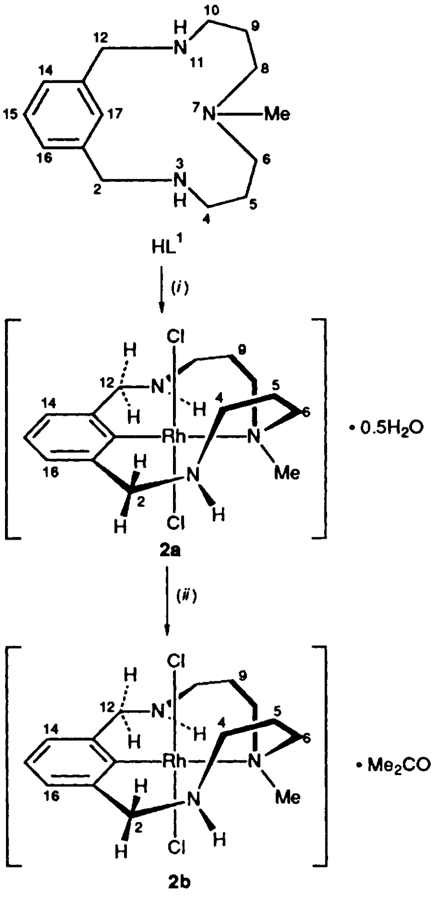
A novel macrocyclic organometallic, *trans*-dichloro(7-methyl-3,7,11-triazabicyclo[11.3.1]heptadeca-1(17),13,15-trien-17-yl)rhodium(III)–acetone(1/1), has been prepared from $RhCl_3 \cdot 3H_2O$ and the corresponding macrocyclic triamine in refluxing 2-methoxyethanol. X-Ray structural analysis shows that the crystals are monoclinic, space group $P2_1/c$, with a = 9.494(1), b = 20.480(4), c = 19.541(3) Å, β = 113.75(1)°, Z = 8 and R = 0.054 for 5999 observed reflections. The complex has *trans* chloride ligands, and the metallated macrocyclic triamine serves as a CN_3-type quadridentate ligand. The Rh–C(17) bond is the shortest rhodium(III)–aryl bond so far reported.

Organo-cobalt and -rhodium complexes containing a macrocyclic quadridentate ligand have been investigated extensively in connection with the chemistry of vitamin B_{12}.[2,3] A few organocobalt complexes which have an intramolecularly bridged methine-,[4] methylene-[5] or vinyl-metal bond[6] have been reported. Previously, we reported[1] the synthesis of $[PdL^1]ClO_4 \cdot H_2O$ [L^1 = 7-methyl-3,7,11-triazabicyclo[11.3.1]heptadeca-1(17),13,15-trien-17-yl] in which the macrocyclic triamine (HL^1) is deprotonated and metallated directly at aromatic carbon C(17) and serves as a CN_3-type quadridentate ligand. Recently, Markies *et al.*[7] prepared organomagnesium compounds of type $[Mg\{C_6H_3(CH_2OCH_2CH_2OCH_2)\text{-}1,3\}X]$ ($X = C_6H_5$ or Br). Such macrocyclic organometallics, in which one carbon of a multidentate macrocycle is bonded directly to the metal, are very rare. They are interesting from the viewpoints of their unique structure and reactivity. In this paper we describe the preparation and X-ray crystal structure analysis of the new macrocyclic organometallic *trans*-$[Rh(L^1)Cl_2] \cdot Me_2CO$.



Scheme 1 Synthesis of complex **2**. (*i*) $RhCl_3 \cdot 3H_2O$; (*ii*) acetone

Results and Discussion

Reactions of the Macrocyclic Triamine with $RhCl_3 \cdot 3H_2O$.—The macrocyclic triamine HL^1 was treated with $RhCl_3 \cdot 3H_2O$ in ethanol at room temperature to give an addition product, $RhCl_3(HL^1) \cdot 2H_2O$ **1**. Complex **1** was so poorly soluble in organic solvents that NMR data could not be obtained. On the basis of the poor solubility, **1** is suggested to have a bridge polymeric structure, involving co-ordination of the secondary amine moieties of HL^1. The macrocyclic triamine is not metallated.

The triamine HL^1 reacted with $RhCl_3 \cdot 3H_2O$ in refluxing 2-methoxyethanol (at *ca.* 125 °C) to give yellowish orange powders. The powders were separated by chromatography on Wakogel C-200 to afford two yellowish orange solids, *trans*-$[Rh(L^1)Cl_2] \cdot 0.5H_2O$ **2a** and **3**. The IR spectrum of **2a** showed three strong bands at 1060, 1040 and 980 cm^{-1}, ascribable to aromatic in-plane deformations, and two bands at 780 and 750 cm^{-1}, assignable to aromatic out-of-plane bendings. Each set of bands indicates the presence of a 1,2,3-trisubstituted phenyl moiety.

The ^1H NMR spectrum of complex **2a** exhibited a singlet at δ 2.67 (3 H, CH_3), two doublets at δ 3.85 and 4.27 (each 2 H, $^2J_{AB}$ = 12 Hz, aryl-CH_AH_B), and a slightly broad singlet near δ 6.87 (3 H, aryl-H), lacking H(17). The ^{13}C-{^1H} NMR spectrum

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

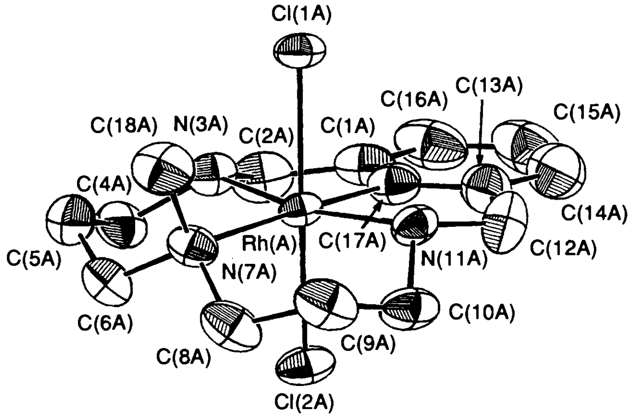

Fig. 1 Structure of *trans*-[Rh(L^1)Cl$_2$] with the numbering scheme adopted. Molecule A is shown (see text)

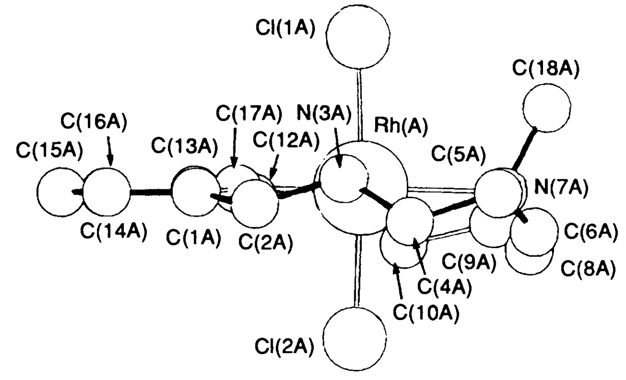

Fig. 2 Side-view of molecule A in complex **2b**

Table 1 Bond lengths (Å) for complex **2b***

Rh(A)–Cl(1A)	2.351(2)	Rh(B)–Cl(1B)	2.352(2)
Rh(A)–Cl(2A)	2.350(2)	Rh(B)–Cl(2B)	2.343(2)
Rh(A)–N(3A)	2.079(5)	Rh(B)–N(3B)	2.081(6)
Rh(A)–N(7A)	2.236(5)	Rh(B)–N(7B)	2.246(5)
Rh(A)–N(11A)	2.085(6)	Rh(B)–N(11B)	2.079(5)
Rh(A)–C(17A)	1.894(7)	Rh(B)–C(17B)	1.892(5)
N(3A)–C(2A)	1.500(8)	N(3B)–C(2B)	1.498(10)
N(3A)–C(4A)	1.472(10)	N(3B)–C(4B)	1.483(10)
N(7A)–C(6A)	1.495(11)	N(7B)–C(6B)	1.514(11)
N(7A)–C(8A)	1.498(9)	N(7B)–C(8B)	1.483(11)
N(7A)–C(18A)	1.508(10)	N(7B)–C(18B)	1.488(10)
N(11A)–C(10A)	1.475(8)	N(11B)–C(10B)	1.486(10)
N(11A)–C(12A)	1.493(10)	N(11B)–C(12B)	1.494(8)
C(1A)–C(2A)	1.481(13)	C(1B)–C(2B)	1.541(11)
C(4A)–C(5A)	1.514(9)	C(4B)–C(5B)	1.508(13)
C(5A)–C(6A)	1.545(10)	C(5B)–C(6B)	1.535(13)
C(8A)–C(9A)	1.552(12)	C(8B)–C(9B)	1.558(12)
C(9A)–C(10A)	1.495(11)	C(9B)–C(10B)	1.505(9)
C(12A)–C(13A)	1.549(11)	C(12B)–C(13B)	1.512(12)
C(13A)–C(14A)	1.381(11)	C(13B)–C(14B)	1.397(11)
C(14A)–C(15A)	1.381(12)	C(14B)–C(15B)	1.414(16)
C(15A)–C(16A)	1.427(16)	C(15B)–C(16B)	1.408(13)
C(1A)–C(16A)	1.384(11)	C(1B)–C(16B)	1.395(10)
C(17A)–C(1A)	1.416(10)	C(17B)–C(1B)	1.357(12)
C(17A)–C(13A)	1.348(13)	C(17B)–C(13B)	1.406(10)

* Numbers in parentheses are estimated standard deviations (e.s.d.s) in the least significant digits.

Table 2 Selected bond angles (°) for complex **2b***

Cl(1A)–Rh(A)–Cl(2A)	176.0(1)	Cl(1B)–Rh(B)–Cl(2B)	176.6(1)
Cl(1A)–Rh(A)–N(3A)	87.0(2)	Cl(1B)–Rh(B)–N(3B)	87.6(2)
Cl(1A)–Rh(A)–N(7A)	92.9(2)	Cl(1B)–Rh(B)–N(7B)	92.6(2)
Cl(1A)–Rh(A)–N(11A)	87.7(2)	Cl(1B)–Rh(B)–N(11B)	87.3(2)
Cl(2A)–Rh(A)–N(3A)	91.0(2)	Cl(2B)–Rh(B)–N(3B)	93.3(2)
Cl(2A)–Rh(A)–N(7A)	90.8(2)	Cl(2B)–Rh(B)–N(7B)	90.6(2)
Cl(2A)–Rh(A)–N(11A)	93.5(2)	Cl(2B)–Rh(B)–N(11B)	91.0(2)
C(17A)–Rh(A)–N(3A)	83.2(3)	C(17B)–Rh(B)–N(3B)	82.9(3)
C(17A)–Rh(A)–N(11A)	82.8(3)	C(17B)–Rh(B)–N(11B)	83.0(3)
N(3A)–Rh(A)–N(7A)	98.6(2)	N(3B)–Rh(B)–N(7B)	95.7(2)
N(3A)–Rh(A)–N(11A)	165.1(2)	N(3B)–Rh(B)–N(11B)	165.2(2)
N(7A)–Rh(A)–N(11A)	95.6(2)	N(7B)–Rh(B)–N(11B)	98.4(2)
Rh(A)–N(3A)–C(4A)	115.6(3)	Rh(B)–N(3B)–C(4B)	113.9(5)
N(3A)–C(4A)–C(5A)	111.8(6)	N(3B)–C(4B)–C(5B)	111.1(8)
C(4A)–C(5A)–C(6A)	115.9(7)	C(4B)–C(5B)–C(6B)	115.5(6)
C(5A)–C(6A)–N(7A)	114.0(6)	C(5B)–C(6B)–N(7B)	114.8(7)
C(6A)–N(7A)–Rh(A)	109.3(4)	C(6B)–N(7B)–Rh(B)	107.8(5)
Rh(A)–N(7A)–C(8A)	108.8(5)	Rh(B)–N(7B)–C(8B)	108.4(4)
N(7A)–C(8A)–C(9A)	113.8(6)	N(7B)–C(8B)–N(9B)	114.3(6)
C(8A)–C(9A)–C(10A)	116.7(6)	C(8B)–C(9B)–C(10B)	115.0(7)
C(9A)–C(10A)–N(11A)	111.5(6)	C(9B)–C(10B)–N(11B)	111.7(6)
C(10A)–N(11A)–Rh(A)	114.1(5)	C(10B)–N(11B)–Rh(B)	115.1(4)
Rh(A)–C(17A)–C(1A)	117.4(6)	Rh(B)–C(17B)–C(1B)	120.0(5)
Rh(A)–C(17A)–C(13A)	120.5(5)	Rh(B)–C(17B)–C(13B)	118.1(6)
Rh(A)–N(7A)–C(18A)	116.1(4)	Rh(B)–N(7B)–C(18B)	116.3(5)

* Numbers in parentheses are e.s.d.s in the least significant digits.

showed one doublet at δ 165.2 [^2J(CRh) = 19.8 Hz, C(17)] and eight singlets, implying that **2a** has C_s symmetry. These data indicate that the triamine is unambiguously metallated at C(17), serving as a CN$_3$-type quadridentate ligand in a similar fashion to that in [PdL^1]ClO$_4$·H$_2$O[1] (Scheme 1). It is noted that HL^1, which has two secondary amine moieties [N(3) and N(11)], was easily metallated at C(17), in sharp contrast with the fact that secondary benzylamines were not orthometallated by Li$_2$[PdCl$_4$].[8] Furthermore, some cyclometallated complexes of rhodium(III) were formed by direct reactions of RhCl$_3$·3H$_2$O with aryl-substituted nitrogen bases.[9–11]

The elemental analyses of the minor component, **3**, were similar to the corresponding data for **2a**. The ^{1}H NMR spectrum showed two singlets at δ 2.60 (2.4 H) and 2.67 (0.6 H), assignable to *N*-methyl protons. The latter singlet coincided completely with the corresponding one of **2a** (see above). These data indicate that **3** consisted of **2a** and its isomer, [Rh(L^1)Cl$_2$]·0.5H$_2$O **3a**, in a ratio of about 1:4. However, we failed to isolate the latter isomer in a pure state. Complex **3a** was tentatively ascribed to *cis*-[Rh(L^1)Cl$_2$]·0.5H$_2$O. Blake *et al.*[12] reported a *cis*-type iridium(III) complex [IrCl(H)(L^2)]PF$_6$ containing a macrocyclic tetraamine, 7-methyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (L^2).

Solid-state Structure of trans-[Rh(L^1)Cl$_2$]·Me$_2$CO **2b**.—Complex **2a** was recrystallized from acetone to give yellowish orange crystals of *trans*-[Rh(L^1)Cl$_2$]·Me$_2$CO **2b**. The molecular geometry and atomic numbering scheme are shown in Fig. 1, bond lengths and selected bond angles in Tables 1 and 2, respectively. The whole structure of **2b** is fairly similar to that of *trans*-[Rh(L^3)Cl$_2$]$^+$ (L^3 = 2,7,12-trimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene),[13] except for the Rh–C(17) bond in place of the Rh–N(17) bond and the two additional methyl groups at C(2) and C(12) in the latter complex.

There are two unique molecules both with a distorted-octahedral structure around the Rh atom and two *trans*-chlorine atoms. The Rh atom lies 0.026(1) Å above the least-squares plane defined by C(17)–N(3)–N(7)–N(11) in molecule A, but 0.035(1) Å below in molecule B. The side view of molecule A indicates that the zigzag N(3)–N(7)–N(11) chain is a little twisted (Fig. 2), although the molecule has C_s symmetry, as shown by NMR spectra in chloroform solution. We don't know why the Rh atoms lie at different positions in the two molecules and the chain is twisted; these may just have to do with the strain in the macrocyclic ring around the Rh atom. However, molecule B is omitted in Figs. 1 and 2 since the difference between A and B is small as a whole.

The geometry around the Rh–C(17)–N(3)–N(11) moiety in

Table 3 Positional parameters and their e.s.d.s for complex **2b**

Atom	x	y	z	Atom	x	y	z
Rh(A)	0.543 33(5)	0.080 79(2)	0.315 18(3)	Rh(B)	−0.020 30(5)	0.289 99(2)	0.237 76(3)
Cl(1A)	0.515 8(2)	0.192 33(7)	0.284 14(9)	Cl(1B)	0.026 8(2)	0.188 77(8)	0.299 82(9)
Cl(2A)	0.555 8(2)	−0.032 09(8)	0.338 5(1)	Cl(2B)	−0.079 2(2)	0.387 92(8)	0.170 09(9)
C(1A)	0.273 3(8)	0.051 0(4)	0.186 7(4)	C(1B)	−0.035 6(8)	0.219 8(4)	0.110 4(4)
C(2A)	0.212 3(8)	0.051 9(4)	0.245 5(4)	C(2B)	0.130 5(8)	0.246 0(5)	0.139 5(4)
N(3A)	0.323 8(5)	0.085 3(3)	0.314 3(3)	N(3B)	0.174 5(5)	0.273 3(3)	0.216 5(3)
C(4A)	0.311 3(7)	0.064 1(4)	0.383 6(4)	C(4B)	0.277 6(7)	0.330 7(4)	0.230 8(5)
C(5A)	0.424 5(8)	0.099 6(4)	0.451 4(4)	C(5B)	0.337 7(8)	0.351 1(4)	0.311 7(5)
C(6A)	0.593 1(8)	0.075 9(4)	0.480 5(4)	C(6B)	0.222 8(8)	0.387 9(4)	0.334 7(5)
N(7A)	0.679 3(6)	0.101 0(3)	0.436 6(3)	N(7B)	0.102 2(6)	0.345 3(3)	0.344 7(3)
C(8A)	0.826 2(8)	0.062 8(4)	0.462 5(4)	C(8B)	−0.008 9(9)	0.390 7(4)	0.355 4(4)
C(9A)	0.923 2(7)	0.075 8(4)	0.416 2(4)	C(9B)	−0.159 7(8)	0.357 6(4)	0.351 5(4)
C(10A)	0.867 6(7)	0.045 2(4)	0.340 4(4)	C(10B)	−0.278 2(7)	0.345 1(4)	0.273 7(4)
N(11A)	0.732 1(5)	0.079 7(3)	0.286 3(3)	N(11B)	−0.238 0(5)	0.287 3(3)	0.239 2(3)
C(12A)	0.687 4(9)	0.055 2(5)	0.208 4(4)	C(12B)	−0.354 0(7)	0.273 7(4)	0.161 9(4)
C(13A)	0.509 8(9)	0.052 2(4)	0.167 8(4)	C(13B)	−0.278 9(8)	0.233 8(4)	0.120 7(4)
C(14A)	0.431(1)	0.036 7(5)	0.093 2(5)	C(14B)	−0.351(1)	0.192 5(4)	0.059 6(5)
C(15A)	0.273(1)	0.030 1(5)	0.065 0(5)	C(15B)	−0.262(1)	0.164 4(5)	0.024 1(5)
C(16A)	0.191(1)	0.036 9(4)	0.111 8(5)	C(16B)	−0.104(1)	0.178 5(4)	0.049 1(4)
C(17A)	0.434 4(8)	0.059 9(3)	0.212 8(4)	C(17B)	−0.119 3(7)	0.244 0(3)	0.146 9(3)
C(18A)	0.718(1)	0.171 6(4)	0.457 6(4)	C(18B)	0.176(1)	0.305 3(4)	0.413 6(5)

complex **2b** is comparable with the Rh–C(1)–N(1)–N(2) one in $[RhCl_2\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(H_2O)]$ **4**[14] or $[RhMe\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}I]$ **5**.[15] The Rh–N(3) and Rh–N(11) bonds (2.079 and 2.085 Å) of **2b** are slightly shorter than the Rh–N bonds (2.118 and 2.160 Å) in **4**[14] and **5**.[15] It is noteworthy that the Rh–C(17) bonds (1.892 and 1.894 Å) in **2b** are the shortest of all the rhodium(III)–aryl bonds encountered so far.[14–17] This is possibly a combined result of the strong *trans* influence of the aryl group and the effect of the macrocyclic ligand. Accordingly, the Rh atom is displaced to the C(17) side from the centre of the octahedral structure, and the Rh–N(7) bond is long in comparison with both the two other Rh–N bonds in **2b** and the Rh–N bonds in **4**,[14] **5**[15] and $[RhCl_2(tmc)]PF_6$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane).[18] The long Rh–N(7) bond causes somewhat large Rh–N(3)–C(4), C(4)–C(5)–C(6), C(5)–C(6)–N(7), N(7)–C(8)–C(9), C(8)–C(9)–C(10) and C(10)–N(11)–Rh angles in the two six-membered chelates. The other characteristic feature of **2b** is that the Rh–N(7)–C(18) angle is larger than the normal angle (109°) for a tetrahedral structure. This is probably associated with the steric interaction between the *N*-methyl group and the Cl(1) atom.

The final Fourier difference map shows only a little electron density between the molecules, in a sort of channel, but we could not identify an acetone unit.

Experimental

The cyclic triamine HL^1 was prepared according to the literature.[1] The other procedures were almost the same as described previously.[19]

Reaction of HL^1 *with* $RhCl_3\cdot3H_2O$ *at Room Temperature.*—An ethanol solution (6 cm^3) containing $RhCl_3\cdot3H_2O$ (0.22 g) and HL^1 (0.28 g) was stirred at room temperature for 7 h. A small amount of a dark brown precipitate was filtered off. The resulting solution was evaporated to dryness to give a dark violet solid $RhCl_3(HL^1)\cdot2H_2O$ **1**. Yield 81%, m.p. 216 °C (Found: C, 36.7; H, 5.9; N, 7.7. $C_{15}H_{29}Cl_3N_3O_2Rh$ requires C, 36.6; H, 5.9; N, 8.5%). IR(KBr)/cm^{-1}: ν(NH) and ν(OH) 3440s (br), ν(CH_2) 2940s, ν(aromatic ring) 1605s, 1590m, δ(CH_2) and δ(CH_3) 1450s, 1380m, δ(aromatic in-plane deformation) 1150m, 1110m, 1040m, π(aromatic out-of-plane bending) 800m, 695m and ρ[$(CH_2)_3$ rocking] 740m.

Preparation of $[Rh(L^1)Cl_2]\cdot0.5H_2O$.—A red-brown suspension (60 cm^3) of 2-methoxyethanol containing HL^1 (3.63 mmol) and $RhCl_3\cdot3H_2O$ (0.48 g) was refluxed for 9 h. A small amount of a black precipitate was filtered off. The resulting solution was evacuated to dryness with a rotary evaporator. The residue was washed with water (10 cm^3) three times to afford 0.44 g of a yellowish orange powder, the crude complex $[Rh(L^1)Cl_2]\cdot0.5H_2O$. This was chromatographed on a column of Wakogel C-200 (13 × 260 mm). The first yellow band eluted with dichloromethane was dried under vacuum to give a yellowish orange solid, $[Rh(L^1)Cl_2]\cdot0.5H_2O$ **3**. Yield 8% (Found: C, 42.3; H, 5.8; N, 9.4. $C_{15}H_{25}Cl_2N_3O_{0.5}Rh$ requires C, 42.0; H, 5.9; N, 9.8%). ^1H NMR ($CDCl_3$, 293 K, 100 MHz): δ 1.52 (H_2O), 1.8–2.2 (br, $CH_2CH_2CH_2$, 4 H), 2.60 (s, CH_3, 2.4 H), 2.67 (s, CH_3, 0.6 H), 2.4–3.4 (br, NCH_2, 8 H), 3.7–4.4 (br, aryl–CH_2, 4 H) and 6.86 (br, C_6H_3, 3 H).

The second yellow fraction was eluted with an additional portion of dichloromethane and evacuated to dryness to give yellowish orange crystals of *trans*-$[Rh(L^1)Cl_2]\cdot0.5H_2O$ **2a**. Yield 52%, m.p. 294 °C (Found: C, 41.6; H, 5.6; N, 9.3. $C_{15}H_{25}Cl_2N_3O_{0.5}Rh$ requires C, 42.0; H, 5.9; N, 9.8%). IR(KBr)/cm^{-1}: ν(NH) 3240s, ν(aromatic CH) 3030w, ν(CH_2) 2920s, 2840m, ν(aromatic ring) 1570m, 1560w, δ(CH_2) 1470s, 1430s, δ(CH_3) 1455s, 1340m, δ(aromatic in-plane deformation) 1060s, 1040s, 980s; π(aromatic out-of-plane bending) 780m, 750s and ρ[$(CH_2)_3$ rocking] 720m. NMR ($CDCl_3$, 293 K): ^1H (100 MHz), δ 1.50 (H_2O), 1.6–2.2 (m, $CH_2CH_2CH_2$, 4 H), 2.3–2.9 (m, NCH_2, 4 H), 2.67 (s, CH_3, 3 H), 3.0–3.4 (m, NCH_2, 4 H), 3.85 (d, $^2J_{AB}$ = 12, aryl–CH_A, 2 H), 4.27 (d, $^2J_{AB}$ = 12, aryl–CH_B, 2 H), 4.5 (br, NH, 2 H) and 6.87 (br s, C_6H_3, 3 H); ^{13}C-$\{^1H\}$ (22.628 MHz), δ 26.7 (s, $CH_2CH_2CH_2$, 2 C), 45.8 (s, CH_3), 52.1 (s, aryl–CH_2, 2 C), 61.2 (s, NCH_2, 2 C) and 61.9 (s, NCH_2, 2 C), 119.5 [s, C(14) and C(16), 2 C], 122.7 [s, C(15)], 142.2 [s, C(1) and C(13), 2 C] and 165 [d, ^1J(CRh) = 19.8 Hz, C(17)].

Complex **2a** was recrystallized by gentle evaporation of the concentrated acetone solution to afford yellowish orange crystals of *trans*-$[Rh(L^1)Cl_2]\cdot Me_2CO$ **2b** (Found: C, 44.5; H, 6.2; N, 8.6. $C_{18}H_{30}Cl_2N_3ORh$ requires C, 45.2; H, 6.3; N, 8.8%). IR(KBr)/cm^{-1}: ν(C=O) 1705vs and δ(CH_3) 1370s; other bands almost the same as those of **2a**.

Crystal Structure Determination of Complex **2b**.—A yellowish orange rectangular crystal of complex **2b** with approximate dimensions 0.30 × 0.52 × 0.60 mm was mounted on a glass fibre and placed in a goniometer head on an Enraf-Nonius CAD4 computer-controlled κ axis diffractometer equipped with a graphite monochromator and Mo-Kα radiation (λ = 0.710 73 Å).

The unit-cell parameters and an orientation matrix for data collection were obtained by autoindexing and least-squares refinement of 22 reflections in the range $7 < \theta < 10°$.

Crystal data. $C_{18}H_{30}Cl_2N_3ORh$, monoclinic, space group $P2_1/c$, a = 9.494(1), b = 20.480(4), c = 19.541(3) Å, β = 113.75(1)°, U = 3478(2) Å^3, Z = 8, D_c = 1.66 g cm^{-3} and μ = 12.8 cm^{-1}. The space group was determined from the extinctions and subsequent least-squares refinement. A total of 7197 unique reflections were collected at a temperature of 25 ± 1 °C using the ω-scan technique to a maximum 2θ angle of 60.0°.

Data reduction. As a check on the crystal and electronic stability, three representative reflections were measured every 120 min. A linear decay correction was applied to the data. Lorentz and polarization corrections and an empirical absorption correction based on a series of ψ scans were made. Relative transmission coefficients ranged from 0.757 to 0.999 with an average value of 0.940.

Structure solution and refinement. The structure was solved with SHELXS 86[20] using the Patterson heavy-atom method which revealed the positions of six atoms. The remaining atoms were located in successive Fourier difference syntheses and least-square refinements. Hydrogen atoms were not included in the calculations. Anomalous dispersion effects were included in F_c;[21] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[22] Only 5999 reflections having $F_o > 3.0\ \sigma(F_o)$ were used in the refinements. The final cycle of least squares included 379 variables and converged with a maximum parameter shift e.s.d. of 0.00 and agreement factors of R 0.0540 and R' 0.0612, respectively. The standard deviation of an observation of unit weight was 2.39. The largest peak in the final Fourier difference map had a height of 0.53 e Å^{-3} with an estimated error based on ΔF of 0.12.[23] Plots of $\Sigma w(|F_o| - |F_c|)^2$ *versus* $|F_o|$, the reflection order in data collection, $\sin\theta/\lambda$, and various classes of indices showed no unusual trends. Scattering factors were taken from Cromer and Waber.[24] All calculations were performed on a MicroVAX II computer using SDP/VAX.[25] The final atomic coordinates are given in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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