Second-sphere Co-ordination of Cationic Rhodium Complexes $[Rh(L)(NH_3)_2]^+$ by Dibenzo-3*n*-crown-*n* Ethers [*n* = 6—12; L = cyclo-octa-1,5-diene (cod) or norbornadiene (nbd)]. Solution ^1H Nuclear Magnetic Resonance Spectroscopic Studies and *X*-Ray Crystal Structures of $[Rh(cod)(NH_3)_2{\cdot}db\text{-}21\text{-}c\text{-}7][PF_6]$, $[Rh(cod)(NH_3)_2{\cdot}db\text{-}24\text{-}c\text{-}8][PF_6]$, $[Rh(cod)(NH_3)_2{\cdot}db\text{-}30\text{-}c\text{-}10][PF_6]$, $[Rh(nbd)(NH_3)_2{\cdot}db\text{-}24\text{-}c\text{-}8][PF_6]$, and $[\{Rh(cod)(NH_3)_2\}_2{\cdot}db\text{-}36\text{-}c\text{-}12][PF_6]_2$ *

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Cationic rhodium(I) complexes of the form $[Rh(L)(NH_3)_2][PF_6]$ [L = cyclo-octa-1,5-diene (cod) or norbornadiene (nbd)] are solubilised in halocarbon solvents by the addition of equimolar quantities of crown ethers such as 18-crown-6 (18-c-6) or dibenzo-3*n*-crown-*n* (*n* = 6—12) ethers (db-3*n*-c-*n*). Solubilisation is a result of the formation of stable, highly structured, second-sphere co-ordination complexes in which a macrocyclic polyether interacts with the ammine ligands on rhodium *via* multiple hydrogen-bond formation. ^1H N.m.r. spectroscopic investigations in CD_2Cl_2 show that the resonances of protons associated with the diene ligands (L) undergo significant upfield shifts ($\Delta\delta$ values of up to 0.75 p.p.m.) when certain of the db-3*n*-c-*n* ethers (*n* = 7—10) are used in preference to 18-c-6, suggesting that the dienes are experiencing anisotropic ring-current shielding by the crown ether benzo rings. The close proximity of co-ordinated diene and db-3*n*-c-*n* ether aromatic rings, which this shielding requires, is confirmed by single-crystal *X*-ray studies of the isolated 1 : 1 adducts. $[Rh(cod)(NH_3)_2{\cdot}db\text{-}21\text{-}c\text{-}7][PF_6]$ is monoclinic, space group $P2_1/c$, a = 9.121(1), b = 23.405(2), c = 16.705(3) Å, β = 96.30(1)°, Z = 4, R = 0.047. $[Rh(cod)(NH_3)_2{\cdot}db\text{-}24\text{-}c\text{-}8][PF_6]$ is monoclinic, $P2_1/c$, a = 9.195(3), b = 29.380(9), c = 13.900(6) Å, β = 93.04(3)°, Z = 4, R = 0.043. $[Rh(cod)(NH_3)_2{\cdot}db\text{-}30\text{-}c\text{-}10][PF_6]$ is monoclinic, $P2_1/c$, a = 9.268(2), b = 34.335(7), c = 13.421(3) Å, β = 93.92(2)°, Z = 4, R = 0.034. $[Rh(nbd)(NH_3)_2{\cdot}db\text{-}24\text{-}c\text{-}8][PF_6]$ is orthorhombic, *Pbca*, a = 15.427(3), b = 18.739(3), c = 25.458(5) Å, Z = 8, R = 0.047. In all these supramolecular structures the crown ether adopts a V-shaped conformation with the ammine ligands forming hydrogen bonds to ether oxygens and with the co-ordinated diene sandwiched between the benzo rings of the db-3*n*-c-*n* ethers. In addition to electrostatic stabilisation, there are also a large number of other longer range contacts (C ··· H, Rh ··· C, Rh ··· O) at about van der Waals' distances which probably make a small contribution to the binding energy and possibly help to define the structures of the adducts. In contrast to the 2 : 1 adducts, the 2 : 1 adduct, $[\{Rh(cod)(NH_3)_2\}_2{\cdot}db\text{-}36\text{-}c\text{-}12][PF_6]_2$ [triclinic, $P\bar{1}$, a = 9.020(2), b = 12.241(3), c = 14.196(3) Å, α = 100.20(2), β = 99.00(2), γ = 98.11(2)°, Z = 1, R = 0.040] has a relatively flat structure in which a complex ion is hydrogen bonded to each face of the crown ether.

Macrocyclic polyethers (crown ethers) are known to afford crystalline adducts with a variety of transition metal complexes as a result of multiple hydrogen bond formation from protic ligands such as ammonia,[1] ethylenediamine,[1,2] acetonitrile,[3] and water[4] to crown ether oxygen atoms as evidenced by *X*-ray crystallographic studies in the solid state and by i.r. and n.m.r. spectroscopy in solution. In some cases, the adducts derive additional stability from other non-covalent interactions, including aromatic π–π charge transfer between electron-rich and electron-deficient π-systems present[5] in crown and complex, respectively.

The formation of a highly structured stable 'supercomplex' or adduct, which is dependent for its existence not only on strong covalent or ionic bonds, but also on the additive effect of a large number of weak interactions between ligands in the first and second co-ordination spheres of a metal, provides a potentially valuable tool for the investigation of non-covalent bonding in general. There seems no reason why the whole range of secondary bonding forces, including polarisation and dispersion forces, should not be as important in second-sphere co-ordination[6] as they are, for example, in solvation and crystal packing.

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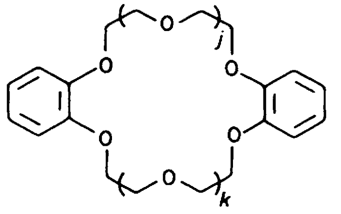
* Diammine(η^4-cyclo-octa-1,5-diene)rhodium(I) hexafluorophosphate 6,7,9,10,17,18,20,21,23,24-decahydrodibenzo[*b,k*][1,4,7,10,13,16,19]-heptaoxacyclohenicosin, –6,7,9,10,12,13,20,21,23,24,26,27-dodecahydrodibenzo[*b,n*][1,4,7,10,13,16,19,22]-octaoxacyclotetracosin, –6,7,9,10,12,13,15,16,23,24,26,27,29,30,32,33-hexadecahydrodibenzo[*b,q*]-[1,4,7,10,13,16,19,22,25,28]-decaoxacyclotriacontin, diammine(η^4-bicyclo[2.2.1]hepta-1,5-diene)rhodium(I) hexafluorophosphate–6,7,9,10,12,13,20,21,23,24,26,27-dodecahydrodibenzo[*b,n*][1,4,7,10,13,16,19,22]-octaoxacyclotetracosin, and bis[diammine(η^4-cyclo-octa-1,5-diene)rhodium(I)] bis(hexafluorophosphate)–6,7,9,10,12,13,15,16,18,19,26,27,29,30,32,33,35,36-octadecahydrodibenzo[*b,t*][1,4,7,10,13,16,19,22,25,28,31,34]-dodecaoxacyclohexatriacontin.

Supplementary data available (No. SUP 56508, 20 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

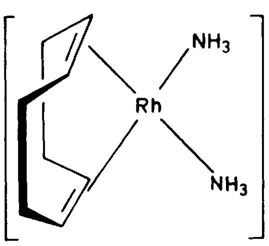


db-3*n*-c-*n*	*n*	*j*	*k*
db-18-c-6	6	1	1
db-21-c-7	7	2	1
db-24-c-8	8	2	2
db-27-c-9	9	3	2
db-30-c-10	10	3	3
db-33-c-11	11	4	3
db-36-c-12	12	4	4

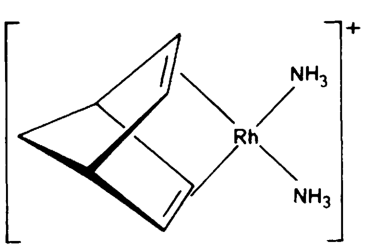
We now describe an extensive study of the interactions between a range of dibenzo-3*n*-crown-*n* ethers [7] where *n* = 6—12* and the novel rhodium(I) ammines $[Rh(L)(NH_3)_2]^+$ [L = cyclo-octa-1,5-diene (cod) or norbornadiene (nbd)]. It was anticipated that the [N–H ··· O] hydrogen bonding might not by itself provide the main driving force for adduct formation, but that the allylic methine hydrogen atoms and electron-deficient co-ordinated double bonds of the dienes might provide additional sites for weak non-covalent binding to the macrocyclic ligands. Part of this investigation and developments from it have already been communicated in preliminary forms.[8,9]

Results and Discussion

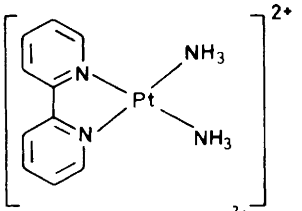
The rhodium(I) ammines were prepared by dissolving the corresponding chloride-bridged dimers,[10] $[\{Rh(L)Cl\}_2]$ in a slight excess of dilute aqueous ammonia, followed by precipitation of the crystalline hexafluorophosphate salts, $[Rh(L)(NH_3)_2][PF_6]$. The pale yellow complexes were insoluble in hydrocarbon and halocarbon solvents. However, on additon of an equimolar amount of crown ether [18-crown-6 or one of the db-3*n*-c-*n* ethers (*n* = 6—12)], they dissolved readily in dichloromethane. The ^1H n.m.r. spectra of the complexes in CD_2Cl_2 solutions, containing equimolar amounts of the db-3*n*-c-*n* ethers, particularly db-21-c-7 and db-24-c-8, revealed marked upfield shifts (Δδ of up to 0.75 p.p.m.) of resonances associated with the diene ligands, relative to their chemical shifts when 1 mol equiv. of 18-crown-6 was used as the solubilising agent. These data (δ and Δδ), which are listed in Tables 1 and 2 for $[Rh(cod)(NH_3)_2\cdot$db-3*n*-c-*n*]$[PF_6]$ and $[Rh(nbd)(NH_3)_2\cdot$db-3*n*-c-*n*]$[PF_6]$ respectively, strongly suggest that 1:1 adduct formation in solution results in the diene ligands being positioned within the aromatic ring-current shielding zone of one or both of the catechol-derived units of the db-3*n*-c-*n* ethers. This is known to be the case for the 2,2′-bipyridyl ligand (bipy) of $[Pt(bipy)(NH_3)_2]^{2+}$ in its 1:1 crystalline adducts [5] with db-24-c-8 and db-30-c-10, and also for the bipyridinium portion of diquat^{2+} in its 1:1 crystalline complexes with db-30-c-10 [7] and derivatives.[11] In agreement with this proposal, the resonances arising from the equatorial methylene protons (H_e) of the cyclo-octadiene ligand and the bridging methine protons (H_b) of the norbornadiene ligand are shifted to a rather greater extent than are the resonances for the other ligand protons. This observation can be anticipated if the aromatic rings of the db-3*n*-c-*n* ethers are assumed to approach these ligands face-on along the sterically unhindered *z* axis of the complexes as shown in Figure 1, *i.e.* perpendicular to the co-ordination plane of the metal.



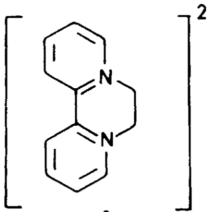
$[Rh(cod)(NH_3)_2]^+$



$[Rh(nbd)(NH_3)_2]^+$



$[Pt(bipy)(NH_3)_2]^{2+}$



diquat^{2+}

Further evidence of a close association between the aromatic systems of the db-3*n*-c-*n* ethers and the cyclo-octadiene ligand was provided by a series of double-resonance experiments with $[Rh(cod)(NH_3)_2\cdot$db-24-c-8$][PF_6]$ in which positive through-space nuclear Overhauser effects (n.O.e.) were observed (Figure 2) for H_e (δ 1.62) and H_o (δ 3.54) though *not* for H_a (δ 1.41) on irradiation at the aromatic proton frequency (δ 7.03). Corresponding n.O.e. enhancement of the aromatic signal intensity was observed on irradiation at the H_e and H_o frequencies, but, as anticipated, not on irradiation of the H_a frequency.

As indicated by inspection of Figure 3, the upfield shifts of cod and nbd proton signals on adduct formation attain a maximum with db-24-c-8 as do the modest *downfield* shifts observed for the aromatic protons of the db-3*n*-c-*n* ethers. Thus, it would appear that db-24-c-8 permits the closest possible approach, with this type of receptor, of the arene and diene moieties. We therefore attempted to obtain crystalline 1:1 adducts of $[Rh(cod)(NH_3)_2][PF_6]$ and $[Rh(nbd)(NH_3)_2][PF_6]$ with db-24-c-8 for full crystallographic characterisation of the solid-state structure. Suitable crystals were obtained from solutions containing equimolar amounts of the complexes and db-24-c-8 in dichloroethane by addition of diethyl ether. They were found, by elemental analysis and ^1H n.m.r. spectroscopy (Tables 1 and 2), to have the anticipated 1:1 stoicheiometry. I.r. spectra of the solid adducts showed marked shifts to lower frequencies of bands in the ν(N–H) region compared with the values observed for the free ammines. This observation is consistent [12] with hydrogen bond formation between the co-ordinated ammonia ligands and oxygen atoms in the db-3*n*-c-*n* ethers.

The solid-state structures of the cationic adducts, $[Rh(cod)(NH_3)_2\cdot$db-24-c-8$]^+$ and $[Rh(nbd)(NH_3)_2\cdot$db-24-c-8$]^+$, are shown respectively in Figures 4 and 5 as framework diagrams, with the corresponding space-filling representations portrayed in Figure 6. Selected adduct contact distances and relevant hydrogen contact distances and angles in order of increasing N ··· O distances are listed in Tables 3 and 4. Torsional angles are shown with the relevant bonds in Figures 4 and 5. The conformation of the db-24-c-8 receptor is very different from that adopted by the free macrocycle where a relatively extended conformation is found.[13] It also differs from those observed in

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* In this paper we employ the widely accepted notation of letters and numbers to identify the different dibenzo-crown ethers. Thus, in the general descriptor db-3*n*-c-*n*, db represents fused dibenzo rings, the first number (3*n*) represents the size of the macrocyclic ring, c, the crown ether constitution of repeating unit –OCCO–, and the second number (*n*), the number of oxygen atoms in the ring.

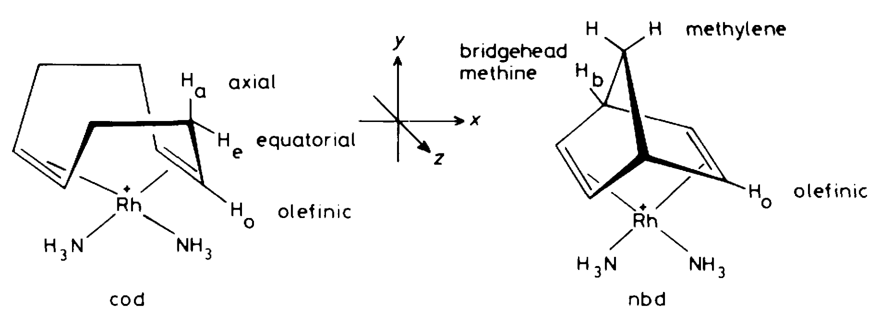

Figure 1. The cyclo-octa-1,5-diene (cod) and norbornadiene (nbd) ligands with respect to a Cartesian frame of reference

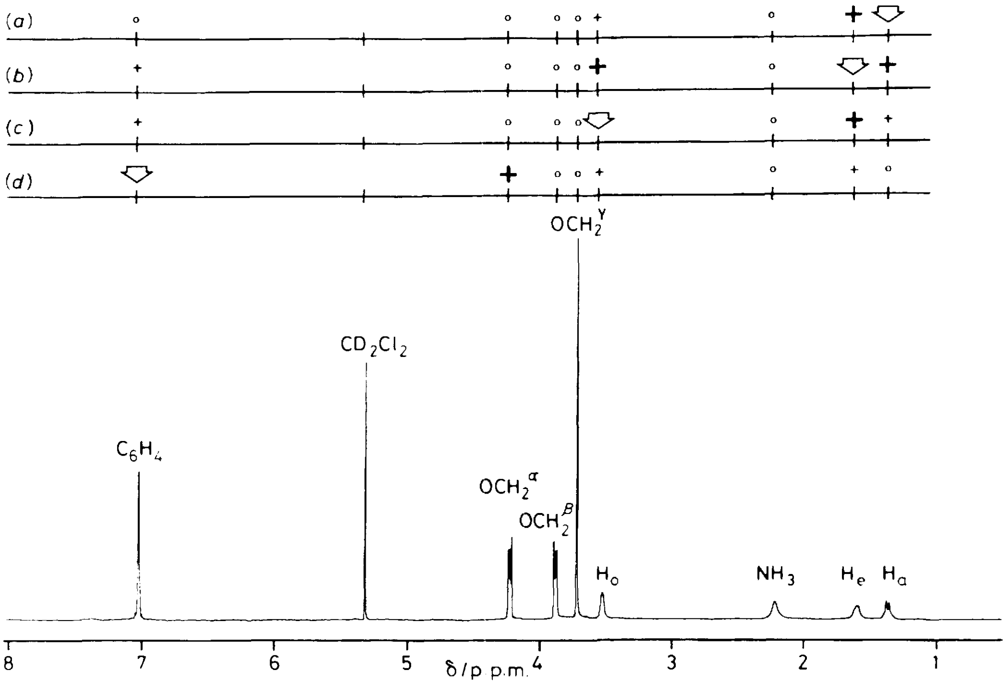

Figure 2. The results of n.O.e. experiments carried out on the ^1H n.m.r. spectrum of $[Rh(cod)(NH_3)_2{\cdot}db\text{-}24\text{-}c\text{-}8][PF_6]$ in CD_2Cl_2. The arrows indicate the signals that were irradiated in four separate experiments, (*a*)—(*d*). A large positive sign indicates a large signal intensity enhancement; a small positive sign indicates a small signal intensity enhancement; a zero indicates no noticeable change in signal intensity

the alkali-metal ion complexes $2KSCN{\cdot}db\text{-}24\text{-}c\text{-}8$ [14] and $2Na(OC_6H_4NO_2\text{-}o){\cdot}db\text{-}24\text{-}c\text{-}8$,[15] and in the Ba^{2+} complexes, $Ba(C_6H_2N_3O_7)_2{\cdot}db\text{-}24\text{-}c\text{-}8$ ($C_6H_2N_3O_7$ = picrate)[16] and $Ba(ClO_4)_2{\cdot}db\text{-}24\text{-}c\text{-}8$,[17] where extended,* and occasionally slightly twisted, conformations are observed rather than the V-shaped conformations adopted by db-24-c-8 in $[Rh(cod)(NH_3)_2{\cdot}db\text{-}24\text{-}c\text{-}8][PF_6]$ and $[Rh(nbd)(NH_3)_2{\cdot}db\text{-}24\text{-}c\text{-}8][PF_6]$. This conformation was also observed [5] in the 1 : 1 adduct $[Pt(bipy)(NH_3)_2{\cdot}db\text{-}24\text{-}c\text{-}8][PF_6]_2$, although, in this last case, there are some differences of detail as a consequence of π–π charge-transfer interactions between the bipyridyl ligand and one of the benzo rings of the dibenzo-crown ether. Nevertheless, it now seems probable that a transition-metal complex containing two *cis* ammine ligands will normally induce in db-24-c-8 a V-shaped conformation on binding. However, there are slight differences between the two adducts. The receptor adopts a more open V-shape in the adduct with $[Rh(cod)(NH_3)_2]^+$ than it does in the corresponding adduct with $[Rh(nbd)(NH_3)_2]^+$. This presumably is a result of the greater steric requirement of the cyclo-octadiene ligand. This point is highlighted in the space-filling representations of these superstructures as shown in Figure 6. It is also reflected in the differences in torsional angles about C(8)–C(9), C(9)–O(10), O(10)–C(11), C(12)–O(13), and O(19)–C(20) (*cf.* Figures 4 and 5). There is a notable departure from their customary coplanarity [18] with their associated benzo rings of one of the four phenolic oxymethylene units. The C(9)–O(10) bond is twisted out of plane in both structures and clearly facilitates the formation of a hydrogen bond to one of the *cis* ammine ligands with an approximately trigonal approach to the oxygen atom. The pattern of hydrogen bonding in both 1 : 1 adducts is essentially the same. As in the platinum adduct,[5] $[Pt(bipy)(NH_3)_2{\cdot}db\text{-}24\text{-}c\text{-}8]^{2+}$, one ammine ligand is bound within the macrocycle while the other is oriented over one edge and lies slightly outside the macrocycle. Hydrogen bond

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* It has been shown recently (H. M. Colquhoun, S. M. Doughty, J. F. Stoddart, A. M. Z. Slawin, and D. J. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1986, 253) by *X*-ray crystallography that db-24-c-8 adopts an extended conformation in the 2 : 1 crystalline complex formed between picric acid and db-24-c-8.

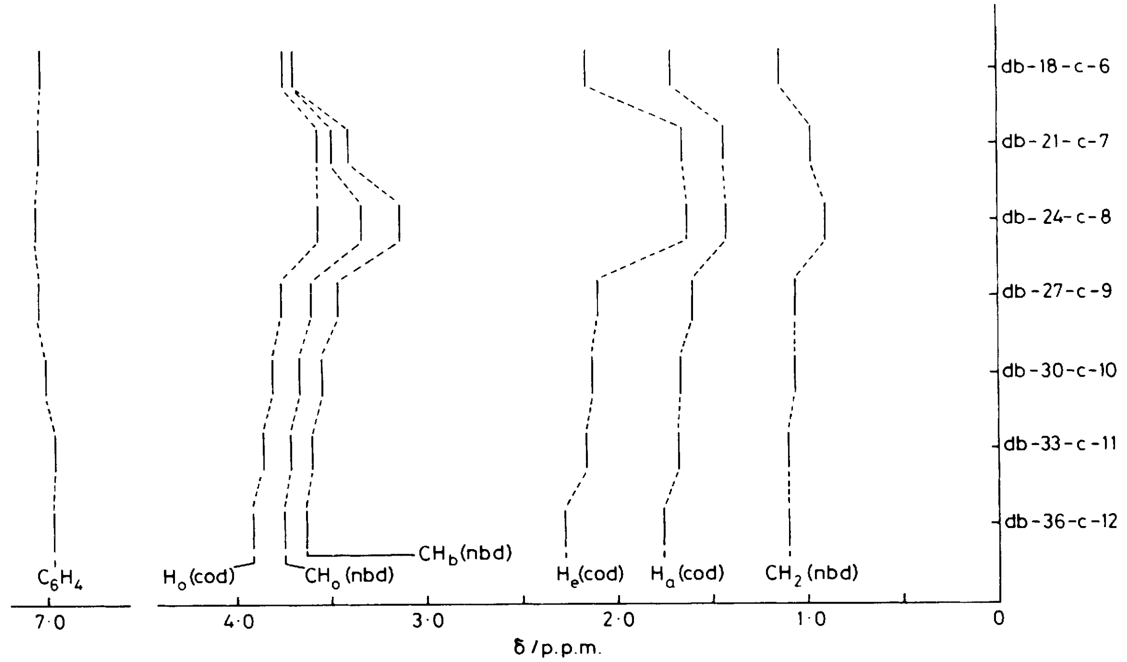

Figure 3. The partial ^1H n.m.r. line spectra for the complexes $[Rh(cod)(NH_3)_2{\cdot}db\text{-}3n\text{-}c\text{-}n][PF_6]$ and $[Rh(nbd)(NH_3)_2{\cdot}db\text{-}3n\text{-}c\text{-}n][PF_6]$. The ligand protons are designated in Figures 1 and 6 and the signals (singlets) for the benzo protons refer to $[Rh(cod)(NH_3)_2{\cdot}db\text{-}3n\text{-}c\text{-}n][PF_6]$ only

Table 1. Selected ^1H n.m.r. chemical shifts (δ)[a] for the 1:1 adducts $[Rh(cod)(NH_3)_2{\cdot}db\text{-}3n\text{-}c\text{-}n][PF_6]$ in CD_2Cl_2

	$[Rh(cod)(NH_3)_2]^+$				db-3*n*-c-*n*[b]	
Crown	H_o	H_e	H_a	$(NH_3)_2$	$(C_6H_4)_2$	$CH_2OC_6H_4OCH_2$
18-crown-6	4.06	2.39	1.86	2.39		
db-18-c-6	3.70	2.13	1.68	2.21	6.97	4.19
	(−0.36)	(−0.26)	(−0.18)		(+0.09)	(+0.05)
db-21-c-7	3.55	1.64	1.41	2.29	7.04	4.31, 4.19
	(−0.51)	(−0.75)	(−0.45)		(+0.14)	(+0.16, +0.04)
db-24-c-8	3.54	1.62	1.38	2.22	7.02	4.25
	(−0.52)	(−0.77)	(−0.48)		(+0.14)	(+0.12)
db-27-c-9	3.73	2.06	1.62	2.35	6.98	4.27
	(−0.33)	(−0.33)	(−0.24)		(+0.11)	(+0.13)
db-30-c-10	3.80	2.10	1.66	2.38	6.96	4.23
	(−0.26)	(−0.29)	(−0.20)		(+0.08)	(+0.11)
db-33-c-11	3.86	2.13	1.67	2.36	6.94	4.20
	(−0.20)	(−0.26)	(−0.19)		(+0.05)	(+0.06)
db-36-c-12	3.88	2.14	1.67	2.33	6.95	4.19
	(−0.18)	(−0.25)	(−0.19)		(+0.05)	(+0.07)
db-36-c-12[c]	3.91	2.27	1.75	2.10	6.96	4.18
	(−0.14)	(−0.15)	(−0.11)		(+0.06)	(+0.06)

[a] Unless otherwise stated, the spectra were recorded at room temperature on a 220-MHz spectrometer (Perkin-Elmer R34) using $SiMe_4$ as internal standard and lock. Some of the δ values in this Table are plotted against *n* in Figure 3. The values (Δδ) in parentheses indicate the extent to which the respective signals in the 1:1 adducts are shifted relative either to those for $[Rh(cod)(NH_3)_2{\cdot}18\text{-crown-}6][PF_6]$ or to those for the free db-3*n*-c-*n* ethers. The resonances for H_e and H_a on the cod ligand (Figure 1) were assigned on the basis of n.O.e. difference spectra obtained (Figure 2) for $[Rh(cod)(NH_3)_2{\cdot}db\text{-}24\text{-}c\text{-}8][PF_6]$. [b] See refs. 5 and 11 for the δ values for these protons in the free db-3*n*-c-*n* ethers. [c] These δ values for $[\{Rh(cod)(NH_3)_2\}_2{\cdot}db\text{-}36\text{-}c\text{-}12][PF_6]_2$ were obtained by dissolving crystals of the 2:1 adduct in CD_2Cl_2 and recording the ^1H n.m.r. spectrum on a Bruker WH400 spectrometer.

distances are comparable with those reported[1] for other metal–ammine–crown ether adducts. We have chosen, somewhat arbitrarily, to define the criteria for hydrogen bonds[12] as $[N \cdots O] < 3.4$ Å, $[H \cdots O] < 2.5$ Å, and $N\text{–}H \cdots O > 140°$. On this basis, each adduct contains only four well-defined hydrogen bonds (Tables 3 and 4 and Figures 4 and 5). The formally square planar Rh^I ion is potentially capable of interacting with donor atoms, particularly along the sterically unhindered *z* axis (Figure 1). In fact, there are several contacts in this direction at about the van der Waals distance [estimating the van der Waals' radius of Rh^I to be 2.2 Å and assuming those of O and aromatic C to be 1.4 and 1.7 Å, respectively] between the aromatic O–C–C–O units and the rhodium atoms. In $[Rh(cod)(NH_3)_2{\cdot}db\text{-}24\text{-}c\text{-}8]^+$, there are $Rh \cdots C$ contacts of 3.87, 3.87, 4.06, and 4.12 Å (*cf.* 3.9 Å for the calculated sum of van der Waals' radii of Rh and C) and $Rh \cdots O$ distances of

Table 2. Selected ^1H n.m.r. chemical shifts (δ)[a] for the 1:1 adducts $[Rh(nbd)(NH_3)_2\cdot db\text{-}3n\text{-}c\text{-}n][PF_6]$ in CD_2Cl_2

	$[Rh(nbd)(NH_3)_2]^+$				db-3*n*-c-*n*[b]	
Crown	H_a	H_b	CH_2	$(NH_3)_2$	$(C_6H_4)_2$	$CH_2OC_6H_4OCH_2$
18-Crown-6	4.04	3.87	1.29	2.17		
db-18-c-6	3.67	3.67	1.13	1.93	6.94	4.17
	(−0.37)	(−0.20)	(−0.16)		(+0.06)	(+0.03)
db-21-c-7	3.47	3.28	0.97	2.09	6.95	4.18
	(−0.57)	(−0.59)	(−0.33)		(+0.05)	(+0.03)
db-24-c-8	3.32	3.12	0.90	1.88	7.08	4.22
	(−0.72)	(−0.75)	(−0.39)		(+0.20)	(+0.09)
db-27-c-9	3.57	3.44	1.02	2.10	7.01	4.32, 4.26
	(−0.47)	(−0.43)	(−0.27)		(+0.14)	(+0.18, +0.12)
db-30-c-10	3.70	3.54	1.08	2.11	6.97	4.23
	(−0.34)	(−0.33)	(−0.21)		(+0.09)	(+0.11)
db-33-c-11	3.72	3.60	1.10	2.17	6.95	4.20
	(−0.32)	(−0.27)	(−0.19)		(+0.06)	(+0.06)
db-36-c-12	3.75	3.62	1.10	2.16	6.96	4.21
	(−0.29)	(−0.25)	(−0.19)		(+0.06)	(+0.09)

[a] Unless otherwise stated, the spectra were recorded at room temperature on a 220-MHz spectrometer (Perkin-Elmer R34) using $SiMe_4$ as internal standard and lock. Some of the δ values in this Table are plotted against *n* in Figure 3. The values (Δδ) in parentheses indicate the extent to which the respective signals in the 1:1 adducts are shifted relative either to those for $[Rh(nbd)(NH_3)_2\cdot 18\text{-}crown\text{-}6][PF_6]$ or to those for the free db-3*n*-c-*n* ethers. The protons of H_a, H_b, and CH_2 in the nbd ligand are defined in Figure 1. [b] See refs. 5 and 11 for the δ values for these protons in the free db-3*n*-c-*n* ethers.

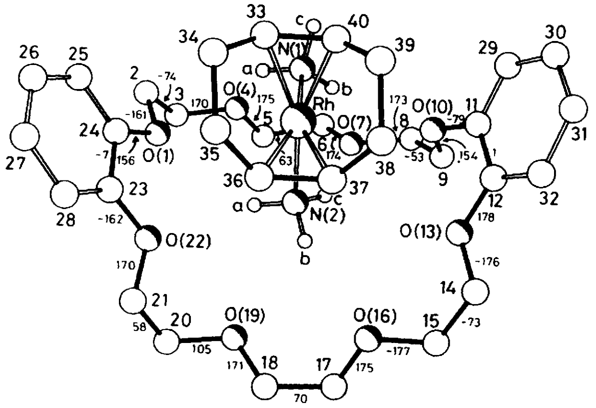

Figure 4. The supramolecular structure of $[Rh(cod)(NH_3)_2\cdot db\text{-}24\text{-}c\text{-}8]^+$ with atomic numbering scheme and torsional angles (°) (O–C–C–O and C–C–O–C) associated with the 24-membered ring. Shortest Rh ··· O(catechol) distances (Å): O(1), 3.65; O(10), 3.59. Distance between centroids of benzo rings: 9.00 Å. 'Cleft angle' between planes of benzo rings: 70°. No significant N–H ··· F contacts

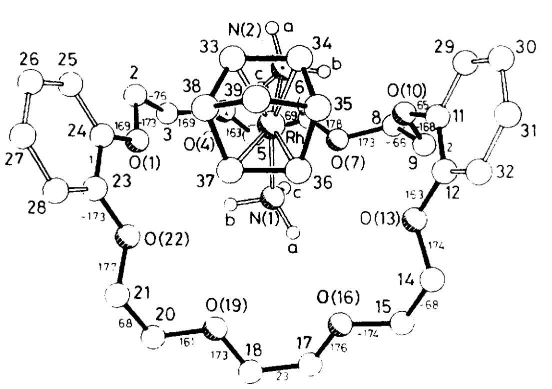

Figure 5. The supramolecular structure of $[Rh(nbd)(NH_3)_2\cdot db\text{-}24\text{-}c\text{-}8]^+$ with atomic numbering scheme and torsional angles (°) (O–C–C–O and C–C–O–C) associated with the 24-membered ring. Shortest Rh ··· O(catechol) distances (Å): O(1), 3.74; O(10), 3.50. Distance between centroids of benzo rings: 8.66 Å. 'Cleft angle' between planes of benzo rings: 59°. No significant N–H ··· F contacts

3.59, 3.65, 4.01, and 4.07 Å (*cf.* 3.6 Å for the calculated sum of van der Waals radii of Rh and O). The corresponding norbornadiene complex adduct, $[Rh(nbd)(NH_3)_2\cdot db\text{-}24\text{-}c\text{-}8]^+$, shows Rh ··· C contacts of 3.68, 3.86, 3.86, and 4.06 Å and Rh ··· O distances of 3.50, 3.74, 3.78, and 4.08 Å.

Two additional adducts, $[Rh(cod)(NH_3)_2\cdot db\text{-}21\text{-}c\text{-}7][PF_6]$ and $[Rh(cod)(NH_3)_2\cdot db\text{-}30\text{-}c\text{-}10][PF_6]$, with supramolecular structures closely related to that of $[Rh(cod)(NH_3)_2\cdot db\text{-}24\text{-}c\text{-}8][PF_6]$, have been characterised both spectroscopically (Table 1) and crystallographically. Crystals suitable for *X*-ray investigation were obtained from solutions containing equimolar amounts of either db-21-c-7 or db-30-c-10 and $[Rh(cod)(NH_3)_2][PF_6]$ in 1,2-dichloroethane by addition of diethyl ether. Both $[Rh(cod)(NH_3)_2\cdot db\text{-}21\text{-}c\text{-}7]^+$ and $[Rh(cod)(NH_3)_2\cdot db\text{-}30\text{-}c\text{-}10]^+$ adopt supramolecular structures very similar to those already described for the db-24-c-8 adducts, *i.e.* with the metal complex bound in a V-shaped cavity, the *cis* ammine ligands straddling one of the polyether chains, and the Rh(cod) fragment sandwiched between the two aromatic rings of the receptor molecules. Their structures are shown in Figures 7 and 8 and hydrogen-bond distances and angles and selected N ··· O contact distances are given in Tables 5 and 6. Torsional angles are shown with the relevant bonds in Figures 7 and 8. Figure 7 shows the first *X*-ray crystal structure of an adduct with a transition-metal complex containing a constitutionally unsymmetrical dibenzo-crown ether receptor. The conformation of the bound db-30-c-10 in $[Rh(cod)(NH_3)_2\cdot db\text{-}30\text{-}c\text{-}10]^+$ in Figure 8 is very different from the extended conformation adopted by this receptor in its free state.[19] It also differs markedly from the contorted conformations assumed by the receptor in crystalline KI·db-30-c-10,[19] RbSCN·db-30-c-10·H_2O,[20] and 2NaSCN·db-30-c-10·H_2O.[21] On account of stabilising charge-transfer interactions with $[Pt(bipy)(NH_3)_2]^{2+}$ and diquat^{2+}, db-30-c-10 adopts a U-shaped

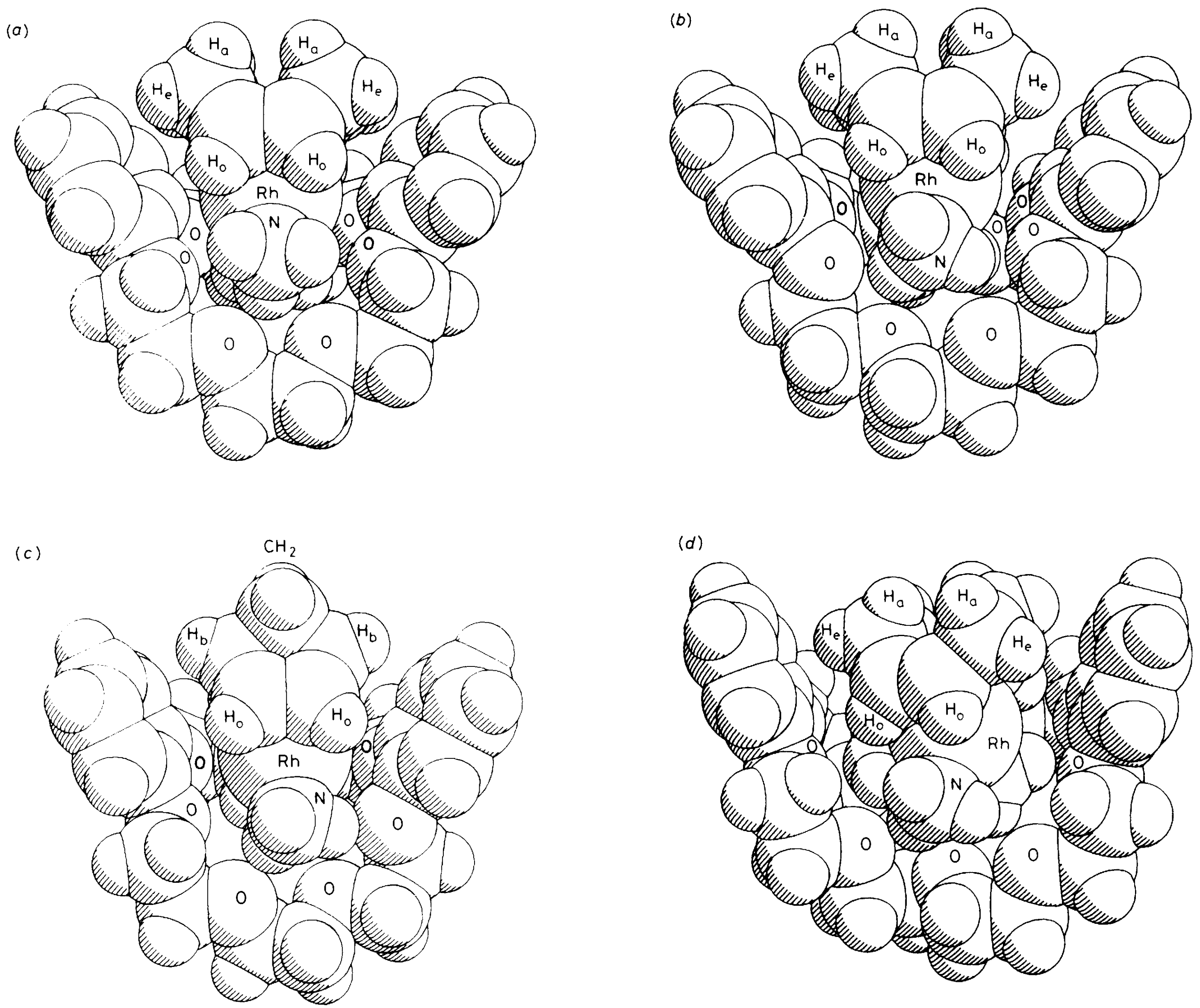

Figure 6. Space-filling representations of the solid-state structures of (*a*) [Rh(cod)$(NH_3)_2$·db-21-c-7]$^+$, (*b*) [Rh(cod)$(NH_3)_2$·db-24-c-8]$^+$, (*c*) [Rh(nbd)$(NH_3)_2$·db-24-c-8]$^+$, and (*d*) [Rh(cod)$(NH_3)_2$·db-30-c-10]$^+$

Table 3. Selected adduct contact distances and relevant hydrogen contact distances and angles in order of increasing N · · · O distance for [Rh(cod)(NH$_3$)$_2$·db-24-c-8][PF$_6$]

N–H · · · O or N · · · O	R(N · · · O)[a]/ Å	R(H · · · O)[b]/ Å	θ[c]/°	φ_H[d]/°	φ_N[e]/°
N(1)–H$_a$ · · · O(4)	3.03	2.16	150	20	18
N(1)–H$_b$ · · · O(10)	3.13	2.31	143	11	3
N(1) · · · O(7)	3.19				
N(2) · · · O(19)	3.20				
N(2)–H$_a$ · · · O(22)	3.21	2.43	138	21	33
N(2)–H$_b$ · · · O(16)	3.34	2.42	161	40	45
N(2) · · · O(1)	3.41				
N(2) · · · O(10)	3.43				
N(1) · · · O(1)	3.45				
N(2) · · · O(7)	3.46				
N(2) · · · O(13)	3.50				

[a] Estimated standard deviation (e.s.d.) 0.02 Å. [b] E.s.d. 0.2 Å. [c] N–H · · · O angles at H atoms; e.s.d. 5°. [d] Angles between COC planes and HO vectors; e.s.d. 5°. [e] Angles between COC planes and NO vectors; e.s.d. 1°.

Table 4. Selected adduct contact distances and relevant hydrogen contact distances and angles in order of increasing N · · · O distance for [Rh(nbd)(NH$_3$)$_2$·db-24-c-8][PF$_6$]

N–H · · · O or N · · · O	R(N · · · O)[a]/ Å	R(H · · · O)[b]/ Å	θ[c]/°	φ_H[d]/°	φ_N[e]/°
N(2)–H$_b$ · · · O(10)	2.95	2.07	152	8	16
N(2)–H$_c$ · · · O(4)	3.01	2.07	166	12	7
N(2) · · · O(7)	3.23				
N(1) · · · O(19)	3.24				
N(1)–H$_a$ · · · O(16)	3.27	2.35	171	43	45
N(1) · · · O(13)	3.30				
N(1)–H$_b$ · · · O(22)	3.38	2.45	164	40	44
N(1) · · · O(7)	3.41				
N(1) · · · O(1)	3.46				

[a–e] See footnotes to Table 3.

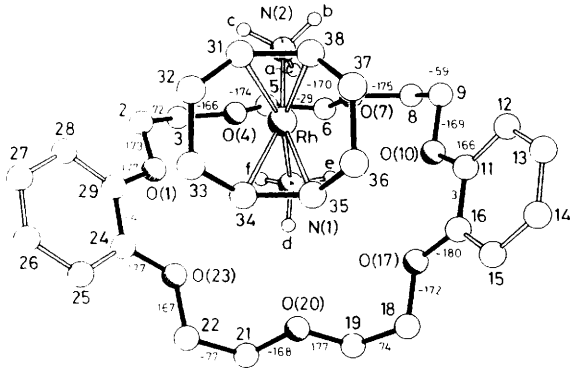

Figure 7. The supramolecular structure of [Rh(cod)(NH$_3$)$_2$·db-21-c-7]$^+$ with atomic numbering scheme and torsional angles (°) (O–C–C–O and C–C–O–C) associated with the 21-membered ring. Shortest Rh · · · O(catechol) distances (Å): O(1), 3.87; O(10), 3.80. Distance between centroids of benzo rings: 8.78 Å. 'Cleft angle' between planes of benzo rings: 82°. There is one N–H · · · F contact of 3.16 Å between N(2)–H$_b$ and F(2) with an N–H · · · F angle of 164°

Table 5. Selected adduct contact distances and relevant hydrogen contact distances and angles in order of increasing N · · · O distance for [Rh(cod)(NH$_3$)$_2$·db-30-c-10][PF$_6$]

N–H · · · O or N · · · O	R(N · · · O)[a]/ Å	R(H · · · O)[b]/ Å	θ[c]/°	φ_H[d]/°	φ_N[e]/°
N(1)–H$_c$ · · · O(7)	2.96	2.06	155	42	37
N(1)–H$_b$ · · · O(28)	3.16	2.37	139	45	52
N(2)–H$_a$ · · · O(19)	3.18	2.29	155	40	39
N(2) · · · O(22)	3.18				
N(1)–H$_a$ · · · O(22)	3.19	2.30	154	3	7
N(1) · · · O(4)	3.20				
N(1) · · · O(25)	3.26				
N(1) · · · O(1)	3.30				
N(2) · · · O(25)	3.35				

[a] E.s.d. 0.01 Å. [b] E.s.d. 0.1 Å. [c] N–H · · · O angles at H atoms; e.s.d. 3°. [d] Angles between COC planes and HO vectors; e.s.d. 3°. [e] Angles between COC planes and NO vectors; e.s.d. 1°.

Table 6. Selected adduct contact distances and relevant hydrogen contact distances and angles in order of increasing N · · · O distance for [Rh(cod)(NH$_3$)$_2$·db-21-c-7][PF$_6$]

N–H · · · O	R(N · · · O)[a]/ Å	R(H · · · O)[b]/ Å	θ[c]/°	φ_H[d]/°	φ_N[e]/°
N(2)–H$_a$ · · · O(4)	3.04	2.15	154	6	8
N(1)–H$_f$ · · · O(10)	3.12	2.39	133	30	37
N(1)–H$_b$ · · · O(10)	3.12	2.45	127	26	37
N(2)–H$_a$ · · · O(7)	3.17	2.45	132	26	30
N(1)–H$_d$ · · · O(20)	3.19	2.26	162	50	55
N(1)–H$_f$ · · · O(7)	3.19	2.39	141	33	25
N(1)–H$_c$ · · · O(23)	3.20	2.26	167	48	45
N(1)–H$_e$ · · · O(1)	3.22	2.32	155	45	50
N(1)–H$_b$ · · · O(17)	3.23	2.31	159	38	44
N(1)–H$_a$ · · · O(4)	3.31	2.41	157	49	47

[a–e] See footnotes to Table 3.

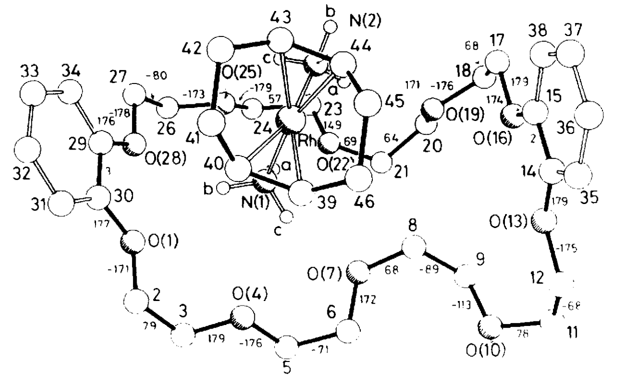

Figure 8. The supramolecular structure of [Rh(cod)(NH$_3$)$_2$·db-30-c-10]$^+$ with atomic numbering scheme and torsional angles (°) (O–C–C–O and C–C–O–C) associated with the 30-membered ring. Shortest Rh · · · O(catechol) distances (Å): O(16), 4.84; O(28), 4.13. Distance between centroids of benzo rings: 10.24 Å. 'Cleft angle' between planes of benzo rings: 36°. No significant N–H · · · F contacts

conformation[5,7] in fulfilling its receptor properties in [Pt(bipy)(NH$_3$)$_2$·db-30-c-10·0.6H$_2$O]$^{2+}$ and [diquat·db-30-c-10]$^{2+}$, respectively.

In both [Rh(cod)(NH$_3$)$_2$·db-21-c-7]$^+$ and [Rh(cod)(NH$_3$)$_2$·db-30-c-10]$^+$, the customary coplanarity[18] of the phenolic oxymethylene units with their associated benzo rings is observed. Adopting the same criteria for hydrogen bonds as enuniciated previously, the 1 : 1 adduct with db-30-c-10 contains four well defined hydrogen bonds (Table 5) with a fifth possible much weaker (N–H · · · O) hydrogen bond between N(2) and O(25) (N · · · O 3.35 Å). In [Rh(cod)(NH$_3$)$_2$·db-21-c-7]$^+$, it should be noted that for one of the ammine ligands [N(1)] there are two discrete orientations for the three ammine hydrogen

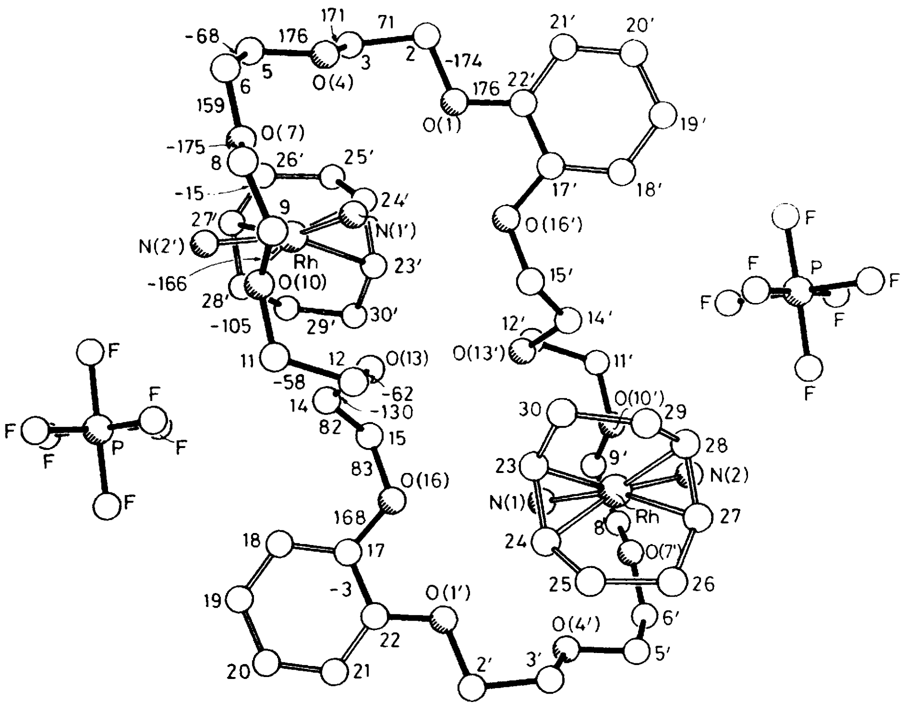

Figure 9. The supramolecular structure of $[\{Rh(cod)(NH_3)_2\}_2 \cdot db\text{-}36\text{-}c\text{-}12][PF_6]_2$ with atomic numbering scheme and torsional angles (°) (O–C–C–O and C–C–O–C) associated with the 36-membered ring

Table 7. Selected adduct contact distances and relevant hydrogen contact distances and angles in order of increasing N ··· O distance for $[\{Rh(cod)(NH_3)_2\}_2 \cdot db\text{-}36\text{-}c\text{-}12][PF_6]_2$

N–H ··· O or N ··· O	R(N ··· O)[a]/ Å	R(H ··· O)[b]/ Å	θ[c]/°	φ_H[d]/°	φ_N[e]/°
N(1)–H_a ··· O(16)	3.05	2.14	158	21	25
N(2)–H_b ··· O(7′)	3.07	2.15	160	20	22
N(1) ··· O(1′)	3.13				
N(1)–H_b ··· O(7′)	3.14	2.33	141	42	35
N(1)–H_b ··· O(4′)	3.20	2.38	143	72	76
N(1) ··· O(10′)	3.22				
N(2) ··· O(10′)	3.22				
N(1)–H_c ··· O(13′)	3.24	2.34	155	61	56

[a–e] See footnotes to Table 3.

atoms. Both orientations of $N(1)H_3$ experience two single and one bifurcated hydrogen bonds to the polyether chains, while $N(2)H_3$ is involved in only one bifurcated hydrogen bond, to O(4) and O(7). Whereas in $[Rh(cod)(NH_3)_2 \cdot db\text{-}21\text{-}c\text{-}7]^+$, there are Rh ··· O distances of less than 4 Å (*i.e.* 3.80 and 3.87 Å), in $[Rh(cod)(NH_3)_2 \cdot db\text{-}30\text{-}c\text{-}10]^+$, because of the larger ring size of the macrocycle, there are no contacts of less than 4 Å between the aromatic O–C–C–O units and the rhodium atom.

It is noticeable and possibly significant that in all four crystalline 1 : 1 adducts discussed in this paper the diene ligands are invariably sandwiched between the two aromatic rings of the crown so that, as predicted by ^1H n.m.r. spectroscopic studies (Tables 1 and 2), a number of allylic and vinylic C–H groups are brought into close proximity with the π-arene systems of the dibenzo-crown ethers. It is possible that these contacts enhance the stability of the adducts to a significant extent since the distances from the hydrogen atoms to the planes of the aromatic rings lie in the range 2.6—3.3 Å and thus differ only slightly from a calculated van der Waals' contact distance of 2.9 Å. In this context, it should be remembered that the polarisation and dispersion forces between molecules at the van der Waals' distance in molecular crystals are normally attractive in nature and provide a substantial fraction of the crystal packing and solvation energies for systems of low polarity.[22] Indeed, much evidence for a specific CH ··· arene interaction of this type has been presented in the literature[23] on the basis of conformational studies, *X*-ray crystallography, gas–liquid chromatography, and molecular mechanics calculations on the whole range of different systems containing both aromatic and aliphatic units. In addition to the known, attractive, dipole-induced–dipole interactions between phenyl and 1,3-dioxane rings,[24] it is clear that stabilising interactions occur between aromatic rings which are oriented with their planes orthogonal to one another.[25] In particular, the most stable geometry of benzene dimer is found, from long-range perturbation theory, to be 'perpendicular' or 'T-shaped'.[26] The binding energy of 3.5 kcal mol^{-1} for this dimer is derived almost entirely from dispersion forces between the CH groups of one ring and the carbon atoms of the other. Moreover, at the equilibrium ring centre–ring plane separation of 5.0 Å, the closest H-ring–plane contacts are in the range 2.5—3.7 Å, just as observed in this paper.

The crystalline adduct obtained after layering diethyl ether on a dichloromethane solution containing equimolar amounts of dibenzo-36-crown-12 and $[Rh(cod)(NH_3)_2][PF_6]$ proved unexpectedly to have 2 : 1 (metal complex : crown) stoicheiometry. As shown in Table 1 and Figure 2, the positions of ^1H resonances of the diene ligands were virtually unchanged relative to their chemical shifts when 18-crown-6 was used as the solubilising agent. This observation is readily explained in terms of the supramolecular structure indicated by the *X*-ray analysis (Figure 9 and Table 7) of the 2 : 1 adduct. It reveals a flattened, slightly S-shaped conformation for the macrocycle with two $[Rh(cod)(NH_3)_2]^+$ cations each bound *via* three long (> 3.0 Å) [N–H ··· O] hydrogen bonds. The planes of the aromatic rings of the receptor are virtually parallel and do not even begin to approach the metal complex, consistent with the virtual absence

Table 8. Crystal data and summary of intensity data refinement and structural refinement

	$[Rh(cod)(NH_3)_2\cdot$ db-24-c-8][PF_6]	$[Rh(nbd)(NH_3)_2\cdot$ db-24-c-8][PF_6]	$[Rh(cod)(NH_3)_2\cdot$ db-21-c-7][PF_6]	$[Rh(cod)(NH_3)_2\cdot$ db-30-c-10][PF_6]	$[\{Rh(cod)(NH_3)_2\}_2\cdot$ db-36-c-12][$PF_6]_2$
Molecular formula	$C_{32}H_{50}F_6N_2O_8PRh$	$C_{31}H_{46}F_6N_2O_8PRh$	$C_{30}H_{46}F_6N_2O_7PRh$	$C_{36}H_{58}F_6N_2O_{10}PRh$	$C_{48}H_{84}F_{12}N_4O_{12}P_2Rh_2$
M	839	823	795	927	1 405
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Triclinic
a/Å	9.195(3)	15.427(3)	9.121(1)	9.268(2)	9.020(2)
b/Å	29.380(9)	18.739(3)	23.405(2)	34.335(7)	12.241(3)
c/Å	13.900(6)	25.458(5)	16.705(3)	13.421(3)	14.196(3)
α/°					100.20(2)
β/°	93.04(3)		96.30(1)	93.92(2)	99.00(2)
γ/°					98.11(2)
U/Å^3	3 750	7 360	3 545	4 261	1 501
Space group	$P2_1/c$	$Pbca$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
Z	4	8	4	4	1
D_c/g cm^{-3}	1.49	1.49	1.50	1.45	1.56
Observed data[a]	3 401	2 984	3 110	3 915	3 864
Absorption correction	Empirical	Empirical	Empirical	Empirical	Numerical
μ/cm^{-1}	49	49	51	44	59
$\theta_{max.}$/°	50	50	50	50	58
R	0.043	0.047	0.047	0.034	0.040
R'[b]	0.049	0.047	0.049	0.037	0.045
g	0.0004	0.0003	0.0006	0.0003	0.0005

[a] Unique observed reflections $|F_o| > 3\sigma(|F_o|)$. [b] $w^{-1} = \sigma^2(F) + gF^2$.

Table 9. Atomic co-ordinates (× 10^4) for $[Rh(cod)(NH_3)_2\cdot$db-24-c-8][PF_6]

Atom	x	y	z
Rh	1 919(1)	1 304(1)	2 157(1)
P	4 762(2)	1 295(1)	7 009(1)
F(1)	6 475(5)	1 297(2)	6 968(3)
F(2)	4 900(7)	1 295(2)	8 118(3)
F(3)	3 060(5)	1 308(2)	7 017(4)
F(4)	4 649(6)	1 306(2)	5 884(3)
F(5)	4 710(6)	1 827(2)	7 030(4)
F(6)	4 716(8)	774(2)	6 954(4)
O(1)	−79(5)	886(1)	4 176(3)
C(2)	−304(9)	1 152(2)	4 994(5)
C(3)	−1 718(8)	1 390(2)	4 814(5)
O(4)	−1 551(4)	1 747(1)	4 137(3)
C(5)	−2 870(7)	1 937(3)	3 798(5)
C(6)	−2 676(7)	2 323(2)	3 178(5)
O(7)	−1 995(5)	2 193(2)	2 361(3)
C(8)	−1 938(8)	2 561(2)	1 701(5)
C(9)	−1 075(14)	2 429(4)	928(8)
O(10)	169(5)	2 277(1)	1 054(3)
C(11)	1 220(6)	2 310(2)	392(4)
C(12)	1 182(7)	2 013(2)	−378(4)
O(13)	61(4)	1 708(1)	−428(3)
C(14)	−15(8)	1 413(2)	−1 224(4)
C(15)	−1 359(8)	1 137(2)	−1 175(4)
O(16)	−1 208(4)	802(1)	−423(3)
C(17)	−2 415(7)	519(3)	−390(5)
C(18)	−2 243(8)	152(3)	317(5)
O(19)	−2 241(5)	299(1)	1 238(3)
C(20)	−2 288(8)	−52(2)	1 926(5)
C(21)	−976(8)	−143(2)	2 460(5)
O(22)	−436(5)	236(1)	2 963(3)
C(23)	708(7)	185(2)	3 631(4)
C(24)	899(6)	533(2)	4 272(4)
C(25)	2 016(7)	513(2)	4 981(4)
C(26)	2 933(8)	147(3)	5 027(5)
C(27)	2 760(7)	−191(2)	4 392(5)
C(28)	1 648(7)	−179(2)	3 686(5)
C(29)	2 321(7)	2 618(2)	521(5)
C(30)	3 438(8)	2 631(3)	−101(6)
C(31)	3 396(8)	2 333(3)	−863(6)
C(32)	2 285(7)	2 030(2)	−1 017(4)
C(33)	3 975(6)	1 284(2)	2 904(4)
C(34)	4 593(7)	812(2)	2 930(5)
C(35)	3 940(7)	493(2)	2 209(5)
C(36)	2 595(6)	649(2)	1 696(4)
C(37)	2 574(7)	952(2)	936(4)
C(38)	3 928(9)	1 161(3)	565(5)
C(39)	4 761(8)	1 463(3)	1 213(6)
C(40)	4 026(6)	1 580(2)	2 147(4)
N(1)	1 183(5)	1 837(1)	3 026(3)
N(2)	−328(5)	1 177(2)	1 799(4)

of ring-current shifts in the ^1H n.m.r. spectrum. The structure has a crystallographic centre of symmetry. It is strongly reminiscent of the disodium and dilithium complexes $2NaPF_6\cdot$db-36-c-12[27] and $2Li(C_6H_2N_3O_7)\cdot$db-36-c-12$\cdot 2H_2O$[28] respectively, in which the sodium or lithium ions are bound in essentially the same positions as the two symmetry related ammine ligands which are oriented towards the opposite sides of the macrocycle in $[\{Rh(cod)(NH_3)_2\}_2\cdot$db-36-c-12$]^{2+}$. Once again, the *cis* ammine ligands of both the $[Rh(cod)(NH_3)_2]^+$ complexes straddle the polyether chains of db-36-c-12.

It is clear that transition metal complexes containing *cis* ammine ligands can induce *via* hydrogen-bond formation and other stabilising electrostatic interactions a previously unknown V-shaped conformation in db-3*n*-c-*n* ethers when $n = 7$—10. This conformation is retained both in solution as well as in the solid state and may be stabilised by additional non-covalent attractive interactions between the benzo groups of the db-3*n*-c-*n* ($n = 7$—10) ethers and the transition-metal complex. This conformation is not accessible to db-3*n*-c-*n* ethers when $n = 6$ (by ^1H n.m.r. spectroscopy as shown in Figure 9). The situation when $n = 11$ is uncertain, since, although modest upfield shifts are observed upon adduct formation, crystals suitable for *X*-ray structural analysis could not be obtained.

The primary binding force between db-3*n*-c-*n* ($n = 7$—10)

Table 10. Atom co-ordinates (× 10^4) for $[Rh(nbd)(NH_3)_2{\cdot}db\text{-}24\text{-}c\text{-}8][PF_6]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh	2 355(1)	1 176(1)	1 395(1)	C(25)	576(4)	1 583(4)	2 759(3)
O(1)	1 075(3)	393(2)	2 503(2)	C(26)	22(4)	2 144(4)	2 676(3)
C(2)	1 578(4)	357(3)	2 965(2)	C(27)	−556(4)	2 107(4)	2 273(3)
C(3)	1 996(5)	−365(4)	2 972(3)	C(28)	−599(4)	1 517(4)	1 955(3)
O(4)	2 690(3)	−387(2)	2 613(2)	C(29)	4 926(4)	1 331(4)	670(3)
C(5)	3 023(6)	−1 078(3)	2 520(3)	C(30)	4 980(5)	1 833(4)	281(3)
C(6)	3 883(6)	−1 039(4)	2 280(3)	C(31)	4 429(4)	1 772(4)	−139(3)
O(7)	3 809(3)	−776(2)	1 760(2)	C(32)	3 840(4)	1 230(4)	−184(3)
C(8)	4 616(5)	−751(4)	1 502(3)	C(33)	2 198(4)	2 251(3)	1 613(3)
C(9)	4 514(5)	−390(4)	980(3)	C(34)	2 867(4)	2 198(3)	1 256(3)
O(10)	4 298(3)	325(2)	1 068(2)	C(35)	2 454(4)	2 301(3)	720(3)
C(11)	4 337(4)	780(3)	644(3)	C(36)	1 944(4)	1 617(4)	672(2)
C(12)	3 794(4)	726(4)	203(3)	C(37)	1 274(4)	1 660(4)	1 038(2)
O(13)	3 225(3)	163(2)	224(2)	C(38)	1 380(4)	2 374(4)	1 306(3)
C(14)	2 831(5)	−43(4)	−250(3)	C(39)	1 730(4)	2 837(4)	851(3)
C(15)	2 314(5)	−692(4)	−183(3)	N(1)	2 023(3)	85(3)	1 293(2)
O(16)	1 596(3)	−557(3)	128(2)	N(2)	3 279(3)	868(3)	1 965(2)
C(17)	1 021(6)	−1 088(4)	183(4)	P	2 265(1)	2 480(1)	−1 157(1)
C(18)	269(6)	−991(5)	456(4)	F(1)	2 056(4)	2 407(3)	−564(2)
O(19)	199(3)	−483(3)	818(2)	F(2)	2 465(3)	2 567(3)	−1 759(2)
C(20)	−557(4)	−474(4)	1 124(3)	F(3)	2 506(4)	1 679(3)	−1 171(2)
C(21)	−673(4)	235(4)	1 372(3)	F(4)	1 978(4)	3 285(3)	−1 144(2)
O(22)	−14(3)	333(2)	1 746(2)	F(5)	3 197(3)	2 705(3)	−993(2)
C(23)	−40(4)	956(3)	2 039(2)	F(6)	1 312(3)	2 279(3)	−1 321(2)
C(24)	562(4)	986(3)	2 445(3)				

Table 11. Atom co-ordinates (× 10^4) for $[Rh(cod)(NH_3)_2{\cdot}db\text{-}30\text{-}c\text{-}10][PF_6]$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh	9 770(1)	−1 397(1)	−1 539(1)	O(28)	11 868(4)	−2 319(1)	−97(2)
O(1)	12 024(3)	−1 812(1)	1 294(2)	C(29)	10 749(6)	−2 323(1)	515(3)
C(2)	12 177(6)	−1 511(1)	2 028(3)	C(30)	10 847(5)	−2 052(1)	1 288(3)
C(3)	13 408(5)	−1 256(1)	1 770(4)	C(31)	9 771(7)	−2 033(1)	1 959(3)
O(4)	12 907(3)	−1 001(1)	989(2)	C(32)	8 602(7)	−2 279(2)	1 837(4)
C(5)	14 004(5)	−742(2)	705(3)	C(33)	8 494(7)	−2 538(2)	1 074(4)
C(6)	13 392(5)	−465(1)	−56(3)	C(34)	9 557(6)	−2 563(1)	408(4)
O(7)	13 090(3)	−665(1)	−956(2)	C(35)	7 809(5)	322(1)	−2 837(3)
C(8)	12 310(5)	−443(1)	−1 723(3)	C(36)	6 419(5)	230(1)	−3 210(3)
C(9)	13 178(5)	−115(1)	−2 109(3)	C(37)	6 215(5)	−73(1)	−3 860(3)
O(10)	13 040(3)	234(1)	−1 555(2)	C(38)	7 370(4)	−287(1)	−4 150(3)
C(11)	12 330(5)	546(1)	−2 071(4)	C(39)	9 422(4)	−954(1)	−483(3)
C(12)	10 730(5)	511(1)	−2 181(3)	C(40)	9 038(4)	−1 307(1)	−82(3)
O(13)	10 389(3)	195(1)	−2 839(2)	C(41)	7 504(5)	−1 441(1)	−2(3)
C(14)	8 972(4)	118(1)	−3 131(3)	C(42)	6 929(5)	−1 673(2)	−905(4)
C(15)	8 756(4)	−192(1)	−3 788(3)	C(43)	7 579(4)	−1 553(2)	−1 859(4)
O(16)	9 986(3)	−380(1)	−4 026(2)	C(44)	7 762(4)	−1 176(2)	−2 188(3)
C(17)	9 823(5)	−695(1)	−4 701(3)	C(45)	7 254(5)	−827(2)	−1 670(3)
C(18)	11 285(5)	−827(1)	−4 942(3)	C(46)	8 379(5)	−655(1)	−922(3)
O(19)	12 026(3)	−1 000(1)	−4 092(2)	N(1)	11 959(3)	−1 472(1)	−1 006(3)
C(20)	13 460(5)	−1 100(2)	−4 319(4)	N(2)	10 368(4)	−1 643(1)	−2 901(3)
C(21)	14 296(5)	−1 217(2)	−3 394(4)	P	3 065(2)	1 519(1)	5 976(1)
O(22)	13 783(3)	−1 557(1)	−2 923(2)	F(1)	2 755(5)	1 536(1)	4 822(2)
C(23)	13 968(6)	−1 904(2)	−3 437(4)	F(2)	3 368(4)	1 498(1)	7 139(2)
C(24)	14 191(6)	−2 232(2)	−2 731(4)	F(3)	4 698(4)	1 608(1)	5 872(3)
O(25)	13 012(3)	−2 257(1)	−2 110(2)	F(4)	3 386(5)	1 080(1)	5 864(3)
C(26)	13 194(5)	−2 563(1)	−1 419(4)	F(5)	1 468(4)	1 428(2)	6 101(3)
C(27)	11 861(6)	−2 608(1)	−867(3)	F(6)	2 750(5)	1 963(1)	6 083(3)

ethers and the rhodium *cis* diammines undoubtedly arises from hydrogen-bond formation and associated electrostatic interactions. However, there also exists a large number of other longer range contacts (C ··· H, Rh ··· C, Rh ··· O) at about van der Waals' distances which may provide additional binding and perhaps even contribute to the overall stabilisation of these novel supramolecular adducts.

Experimental

Materials and Methods.—Literature procedures were used to prepare the dimers $[\{Rh(L)Cl\}_2]$ (L = nbd[10] or cod[29]). 18-Crown-6, db-18-c-6, and db-24-c-8 were commercial samples obtained from the Aldrich Chemical Company. The other crown ether derivatives, db-3*n*-c-*n* (*n* = 7, 9—12) were synthesised from catechol monobenzyl ether[30] using standard

Table 12. Atom co-ordinates (× 10^4) for $[Rh(cod)(NH_3)_2\cdot db\text{-}21\text{-}c\text{-}7][PF_6]$

Atom	*x*	*y*	*z*
Rh	1 757(1)	1 168(1)	2 076(1)
N(1)	4 069(5)	1 305(2)	2 290(3)
N(2)	2 157(6)	607(2)	1 122(3)
O(1)	3 938(6)	2 141(2)	755(2)
C(2)	3 694(11)	1 843(3)	13(4)
C(3)	4 965(11)	1 462(3)	−59(4)
O(4)	4 974(5)	1 003(2)	471(2)
C(5)	6 267(9)	696(4)	585(5)
C(6)	6 287(9)	194(4)	1 060(4)
O(7)	5 408(6)	160(2)	1 630(3)
C(8)	5 660(10)	−302(3)	2 144(5)
C(9)	4 541(11)	−333(3)	2 718(5)
O(10)	4 482(6)	132(2)	3 176(3)
C(11)	3 671(9)	116(3)	3 816(5)
C(12)	2 663(9)	−297(3)	3 955(5)
C(13)	1 983(10)	−274(4)	4 656(6)
C(14)	2 259(9)	152(4)	5 193(5)
C(15)	3 254(9)	577(4)	5 049(5)
C(16)	3 951(8)	561(3)	4 357(4)
O(17)	4 946(5)	968(2)	4 153(3)
C(18)	5 273(9)	1 434(3)	4 692(4)
C(19)	6 200(8)	1 859(3)	4 301(4)
O(20)	5 321(5)	2 152(3)	3 698(2)
C(21)	6 104(8)	2 581(3)	3 326(4)
C(22)	5 032(9)	2 943(3)	2 826(4)
O(23)	4 542(5)	2 651(2)	2 100(2)
C(24)	3 326(8)	2 862(3)	1 627(4)
C(25)	2 476(9)	3 309(3)	1 832(4)
C(26)	1 247(11)	3 473(4)	1 333(6)
C(27)	907(11)	3 181(4)	632(6)
C(28)	1 759(9)	2 730(4)	402(4)
C(29)	2 974(8)	2 571(3)	906(4)
C(31)	−466(7)	1 275(3)	1 591(4)
C(32)	−1 059(10)	1 841(4)	1 805(7)
C(33)	−140(9)	2 170(3)	2 396(5)
C(34)	1 277(7)	1 905(3)	2 750(4)
C(35)	1 393(8)	1 439(3)	3 249(4)
C(36)	102(8)	1 127(4)	3 531(4)
C(37)	−814(11)	813(5)	2 919(5)
C(38)	−373(7)	806(3)	2 094(4)
P	−387(2)	1 092(1)	−1 269(1)
F(1)	−1 129(8)	1 441(3)	−1 958(4)
F(2)	349(11)	739(4)	−592(4)
F(3)	−682(10)	1 509(3)	−625(4)
F(4)	−187(10)	639(3)	−1 890(3)
F(5)	1 045(7)	1 364(4)	−1 398(4)
F(6)	−1 887(7)	846(4)	−1 174(4)

Table 13. Atom co-ordinates (× 10^4) for $[\{Rh(cod)(NH_3)_2\}_2\cdot db\text{-}36\text{-}c\text{-}12][PF_6]_2$

Atom	*x*	*y*	*z*
Rh	3 159(1)	1 812(1)	2 540(1)
N(1)	781(4)	1 800(3)	2 279(2)
N(2)	2 835(5)	987(4)	3 716(3)
O(1)	−10 044(4)	−4 100(2)	8 170(2)
C(2)	−10 500(6)	−5 049(4)	7 375(3)
C(3)	−11 473(6)	−4 713(4)	6 555(3)
O(4)	−10 545(4)	−3 961(3)	6 152(2)
C(5)	−11 352(8)	−3 732(5)	5 278(4)
C(6)	−10 304(9)	−2 878(5)	4 962(4)
O(7)	−10 048(5)	−1 844(3)	5 625(3)
C(8)	−8 748(7)	−1 110(6)	5 637(5)
C(9)	−8 438(8)	−136(6)	6 345(7)
O(10)	−9 321(7)	261(4)	6 833(4)
C(11)	−8 996(8)	1 369(5)	7 386(5)
C(12)	−8 542(7)	1 416(4)	8 460(4)
O(13)	−9 627(4)	790(3)	8 858(3)
C(14)	−11 049(7)	1 166(5)	8 801(4)
C(15)	−11 527(6)	1 311(4)	9 773(3)
O(16)	−10 846(4)	2 357(2)	10 417(2)
C(17)	−11 496(5)	3 287(4)	10 307(3)
C(18)	−12 576(6)	3 340(4)	9 516(3)
C(19)	−13 156(7)	4 324(4)	9 473(4)
C(20)	−12 625(7)	5 248(4)	10 197(4)
C(21)	−11 549(6)	5 208(4)	10 985(4)
C(22)	−10 993(5)	4 232(3)	11 052(3)
C(23)	3 351(6)	2 017(4)	1 113(3)
C(24)	3 589(6)	3 071(4)	1 712(3)
C(25)	5 122(7)	3 806(5)	2 089(4)
C(26)	6 051(8)	3 475(7)	2 888(7)
C(27)	5 503(5)	2 357(5)	3 125(4)
C(28)	5 315(6)	1 329(5)	2 512(4)
C(29)	5 721(8)	1 223(9)	1 508(5)
C(30)	4 582(7)	1 450(5)	754(4)
P	−5 612(2)	−2 218(1)	3 554(1)
F(1)	−6 084(6)	−2 711(4)	4 414(3)
F(2)	−5 904(6)	−3 416(3)	2 928(3)
F(3)	−3 909(4)	−2 247(4)	3 957(4)
F(4)	−5 143(6)	−1 712(5)	2 688(3)
F(5)	−7 299(5)	−2 158(5)	3 165(4)
F(6)	−5 314(7)	−999(4)	4 182(4)

procedures.[7] I.r. spectra were determined using Perkin-Elmer PE197 and PE580 instruments. ^1H N.m.r. spectra were obtained on JEOL FX100, Perkin-Elmer R34, and Bruker WH400 spectrometers at 100, 220, and 400 MHz, respectively. Elemental analyses were performed by the Microanalytical Departments of I.C.I. Mond Division and Sheffield University. Melting points were determined in air using a hot-stage microscope and are uncorrected.

Diammine(η^4-*cyclo-octa*-1,5-*diene*)*rhodium*(I) *Hexafluorophosphate*.—The $[\{Rh(cod)Cl\}_2]$ dimer[29] (3.0 g) was suspended in water (100 cm^3) and stirred whilst aqueous ammonia (specific gravity 0.88) was added dropwise until dissolution of the dimer was *just* complete (excess of ammonia leads to a reduction in yield). A filtered solution of ammonium hexafluorophosphate (3.0 g) in water (20 cm^3) was added to the filtered solution of the rhodium complex. Bright yellow crystals formed immediately and were filtered off, washed with water (2 × 30 cm^3), and diethyl ether (2 × 20 cm^3), and dried *in vacuo* for 1 h. The *product*, $[Rh(cod)(NH_3)_2][PF_6]$, was collected as very fine bright yellow crystals (3.5 g, 73%), m.p. 209—215 °C (decomp.) (Found: C, 24.6; H, 4.8; N, 7.3. $C_8H_{18}F_6N_2PRh$ requires C, 24.6; H, 4.7; N, 7.2%). I.r. (Nujol): 3 400s and 3 300s (N–H str.), 1 625s (N–H def.), and 850br cm^{-1} (P–F str.).

Diammine (η^4-*bicyclo*[2.2.1]*hepta*-1,5-*diene*)*rhodium*(I) *Hexafluorophosphate*.—The dimer $[\{Rh(nbd)Cl\}_2]$[10] (1.5 g) was suspended in water (15 cm^3) and aqueous ammonia (s.g. 0.88) was added dropwise until dissolution of the orange product was complete. A filtered solution of ammonium hexafluorophosphate (1.5 g) in water (10 cm^3) was added to this filtered solution. Bright yellow crystals of the *product*, $[Rh(nbd)(NH_3)_2][PF_6]$, precipitated within a few minutes, and were filtered off, washed with water (30 cm^3) and diethyl

Table 14. Selected bond lengths (Å) and angles (°) for [Rh(cod)$(NH_3)_2$·db-24-c-8][PF_6]

Rh–C(33)	2.110(5)	Rh–C(36)	2.130(5)
Rh–C(37)	2.102(6)	Rh–C(40)	2.101(5)
Rh–N(1)	2.114(4)	Rh–N(2)	2.132(4)
C(33)–Rh–C(36)	81.7(2)	C(33)–Rh–C(37)	95.5(2)
C(36)–Rh–C(37)	38.1(2)	C(33)–Rh–C(40)	37.9(2)
C(36)–Rh–C(40)	93.6(2)	C(37)–Rh–C(40)	83.2(2)
C(33)–Rh–N(1)	92.6(2)	C(36)–Rh–N(1)	161.7(2)
C(37)–Rh–N(1)	160.2(2)	C(40)–Rh–N(1)	92.3(2)
C(33)–Rh–N(2)	160.4(2)	C(36)–Rh–N(2)	93.9(2)
C(37)–Rh–N(2)	92.4(2)	C(40)–Rh–N(2)	161.5(2)
N(1)–Rh–N(2)	85.8(2)	Rh–C(33)–C(40)	70.7(3)
Rh–C(33)–C(34)	111.5(4)	Rh–C(36)–C(35)	112.8(4)
Rh–C(36)–C(37)	69.8(3)	Rh–C(37)–C(38)	110.7(4)
Rh–C(37)–C(36)	72.1(3)	Rh–C(40)–C(33)	71.4(3)
Rh–C(40)–C(39)	111.5(4)		

Table 15. Selected bond lengths (Å) and angles (°) for [Rh(nbd)$(NH_3)_2$·db-24-c-8][PF_6]

Rh–C(33)	2.102(6)	Rh–C(34)	2.101(6)
Rh–C(36)	2.116(6)	Rh–C(37)	2.104(6)
Rh–N(1)	2.123(5)	Rh–N(2)	2.114(5)
C(33)–Rh–C(34)	38.3(3)	C(33)–Rh–C(36)	79.7(3)
C(34)–Rh–C(36)	67.0(3)	C(33)–Rh–C(37)	67.0(3)
C(34)–Rh–C(37)	80.3(3)	C(36)–Rh–C(37)	38.6(2)
C(33)–Rh–N(1)	157.9(2)	C(34)–Rh–N(1)	161.3(2)
C(36)–Rh–N(1)	101.4(2)	C(37)–Rh–N(1)	99.9(2)
C(33)–Rh–N(2)	99.2(2)	C(34)–Rh–N(2)	96.4(2)
C(36)–Rh–N(2)	154.9(2)	C(37)–Rh–N(2)	161.6(2)
N(1)–Rh–N(2)	89.0(2)	Rh–C(33)–C(34)	70.8(4)
Rh–C(33)–C(38)	96.1(4)	Rh–C(34)–C(35)	96.3(4)
Rh–C(34)–C(33)	70.9(4)	Rh–C(36)–C(37)	70.3(4)
Rh–C(36)–C(35)	96.0(4)	Rh–C(37)–C(36)	71.2(4)
Rh–C(37)–C(38)	95.8(4)		

Table 16. Selected bond lengths (Å) and angles (°) for [Rh(cod)$(NH_3)_2$·db-30-c-10][PF_6]

Rh–C(39)	2.118(4)	Rh–C(40)	2.135(4)
Rh–C(43)	2.115(4)	Rh–C(44)	2.139(4)
Rh–N(1)	2.121(3)	Rh–N(2)	2.122(4)
C(39)–Rh–C(40)	37.9(1)	C(39)–Rh–C(43)	97.5(2)
C(40)–Rh–C(43)	82.1(2)	C(39)–Rh–C(44)	81.4(2)
C(40)–Rh–C(44)	90.0(2)	C(43)–Rh–C(44)	37.9(2)
C(39)–Rh–N(1)	92.7(1)	C(40)–Rh–N(1)	93.7(1)
C(43)–Rh–N(1)	157.0(2)	C(44)–Rh–N(1)	165.1(2)
C(39)–Rh–N(2)	157.4(1)	C(40)–Rh–N(2)	164.7(2)
C(43)–Rh–N(2)	91.6(2)	C(44)–Rh–N(2)	93.5(2)
N(1)–Rh–N(2)	86.6(1)	Rh–C(39)–C(40)	71.7(2)
Rh–C(39)–C(46)	110.5(3)	Rh–C(40)–C(41)	112.5(3)
Rh–C(40)–C(39)	70.4(2)	Rh–C(43)–C(42)	109.3(3)
Rh–C(43)–C(44)	72.0(3)	Rh–C(44)–C(45)	113.0(3)
Rh–C(44)–C(43)	70.1(3)		

ether (30 cm^3), and then dried under vacuum (0.7 g, 28%), m.p. 159—164 °C (decomp.) (Found: C, 22.4; H, 3.9; N, 7.4. $C_7H_{14}F_6N_2PRh$ requires C, 22.5; H, 3.8; N, 7.5%). I.r. (Nujol): 3 380s and 3 290s (N–H str.), 1 615s (N–H def.), and 840br cm^{-1} (P–F str.).

Table 17. Selected bond lengths (Å) and angles (°) for [Rh(cod)$(NH_3)_2$·db-21-c-7][PF_6]

Rh–N(1)	2.125(5)	Rh–N(2)	2.126(5)
Rh–C(31)	2.114(6)	Rh–C(34)	2.132(6)
Rh–C(35)	2.120(6)	Rh–C(38)	2.123(7)
N(1)–Rh–N(2)	88.3(2)	N(1)–Rh–C(31)	159.9(2)
N(2)–Rh–C(31)	91.3(2)	N(1)–Rh–C(34)	92.6(2)
N(2)–Rh–C(34)	163.2(2)	C(31)–Rh–C(34)	82.1(3)
N(1)–Rh–C(35)	93.0(2)	N(2)–Rh–C(35)	159.2(2)
C(31)–Rh–C(35)	94.4(3)	C(34)–Rh–C(35)	37.6(3)
N(1)–Rh–C(38)	162.0(2)	N(2)–Rh–C(38)	89.8(2)
C(31)–Rh–C(38)	38.0(3)	C(34)–Rh–C(38)	94.3(3)
C(35)–Rh–C(38)	82.5(3)	Rh–C(31)–C(38)	71.4(4)
Rh–C(31)–C(32)	111.9(5)	Rh–C(34)–C(33)	110.2(4)
Rh–C(34)–C(35)	70.7(4)	Rh–C(35)–C(36)	110.5(4)
Rh–C(35)–C(34)	71.7(4)	Rh–C(38)–C(31)	70.6(4)
Rh–C(38)–C(37)	110.6(5)		

Table 18. Selected bond lengths (Å) and angles (°) for [{Rh(cod)$(NH_3)_2$}$_2$·db-36-c-12][PF_6]$_2$

Rh–N(1)	2.116(3)	Rh–N(2)	2.134(4)
Rh–C(23)	2.116(5)	Rh–C(24)	2.128(5)
Rh–C(27)	2.112(5)	Rh–C(28)	2.115(6)
N(1)–Rh–N(2)	87.5(2)	N(1)–Rh–C(23)	92.6(2)
N(2)–Rh–C(23)	159.3(2)	N(1)–Rh–C(24)	92.9(2)
N(2)–Rh–C(24)	162.7(2)	C(23)–Rh–C(24)	38.0(2)
N(1)–Rh–C(27)	160.0(2)	N(2)–Rh–C(27)	91.8(2)
C(23)–Rh–C(27)	95.0(2)	C(24)–Rh–C(27)	81.9(2)
N(1)–Rh–C(28)	162.2(2)	N(2)–Rh–C(28)	91.6(2)
C(23)–Rh–C(28)	82.0(2)	C(24)–Rh–C(28)	93.2(2)
C(27)–Rh–C(28)	37.8(2)	Rh–C(23)–C(24)	71.4(3)
Rh–C(23)–C(30)	111.6(4)	Rh–C(24)–C(25)	112.2(4)
Rh–C(24)–C(23)	70.5(3)	Rh–C(27)–C(26)	110.5(4)
Rh–C(27)–C(28)	71.2(3)	Rh–C(28)–C(29)	112.0(4)
Rh–C(28)–C(27)	71.0(3)		

Diammine(η^4-*cyclo-octa*-1,5-*diene*)*rhodium*(I) *Hexafluorophosphate–Dibenzo*-21-*crown*-7, [Rh(cod)$(NH_3)_2$·db-21-c-7][PF_6].—A solution of dibenzo-21-crown-7 (30.3 mg, 0.75 mmol) in 1,2-dichloroethane (3 cm^3) was used to dissolve [Rh(cod)$(NH_3)_2$][PF_6] (29.3 mg, 0.75 mmol). The solution was filtered and diethyl ether was layered in dropwise until a faint permanent precipitate was evident. After 18 h, the 1:1 *adduct* had crystallised as bright yellow needles. The yield was 42 mg (68%), m.p. 150—160 °C (Found: C, 46.0; H, 5.9; N, 3.7. $C_{30}H_{46}F_6N_2O_7PRh$ requires C, 45.4; H, 5.8; N, 3.5%).

Diammine(η^4-*cyclo-octa*-1,5-*diene*)*rhodium*(I) *Hexafluorophosphate–Dibenzo*-24-*crown*-8, [Rh(cod)$(NH_3)_2$·db-24-c-8][PF_6].—A solution of dibenzo-24-crown-8 (112 mg, 0.25 mmol) in 1,2-dichloroethane (3 cm^3) was used to dissolve [Rh(cod)$(NH_3)_2$][PF_6] (97.5 mg, 0.25 mmol). The solution was filtered and diethyl ether was allowed to diffuse into it from the vapour phase. After 16 h, the 1:1 *adduct* had crystallised as long rectangular yellow needles. The yield was 120 mg (58%), m.p. 135—145 °C (Found: C, 45.7; H, 6.3; N, 3.3. $C_{32}H_{50}F_6O_8PRh$ requires C, 45.8; H, 6.0; N, 3.2%).

Diammine(η^4-*cyclo-octa*-1,5-*diene*)*rhodium*(I) *Hexafluorophosphate–Dibenzo*-30-*crown*-10, [Rh(cod)$(NH_3)_2$·db-30-c-10][PF_6].—A solution of dibenzo-crown-10 (134 mg, 0.25 mmol) in 1,2-dichloroethane (3 cm^3) was used to dissolve [Rh(cod)$(NH_3)_2$][PF_6] (97.5 mg, 0.25 mmol). The solution was filtered and diethyl ether was allowed to diffuse into it slowly from the vapour phase. After 12 h, the 1:1 *adduct* had crystallised as bright yellow needles. The yield was 63 mg (27%), m.p. 95—100 °C (Found: C, 46.9; H, 6.9; N, 3.0. $C_{36}H_{58}F_6N_2O_{10}PRh$ requires C, 46.7; H, 6.3; N, 3.0%).

Bis[diammine(η^4-*cyclo-octa*-1,5-*diene*)*rhodium*(I)] *Bis*(*hexafluorophosphate*)-*Dibenzo*-36-*crown*-12, $[\{Rh(cod)(NH_3)_2\}_2\cdot$db-36-c-12$][PF_6]_2$.—A solution of dibenzo-36-crown-12 (160 mg, 0.26 mmol) in dichloromethane (4 cm^3) was used to dissolve $[Rh(cod)(NH_3)_2][PF_6]$ (100 mg, 0.26 mmol). The solution was filtered and diethyl ether was layered in dropwise until a faint permanent precipitate was evident. After 24 h, the 2:1 *adduct* had crystallised as long bright yellow needles. The yield was 82 mg (23%), m.p. 124—131 °C (Found: C, 41.1; H, 6.1; N, 4.1. $C_{48}H_{84}F_{12}O_{12}P_2Rh_2$ requires C, 41.0; H, 6.0; N, 4.0%).

Diammine(η^4-*bicyclo*[2.2.1]*hepta*-1,5-*diene*)*rhodium*(I) *Hexafluorophosphate*–*Dibenzo*-24-*crown*-8, $[Rh(nbd)(NH_3)_2\cdot$db-24-c-8$][PF_6]$.—A solution of dibenzo-24-crown-8 (112 mg, 0.25 mmol) in dichloromethane (5 cm^3) was used to dissolve $[Rh(nbd)(NH_3)_2][PF_6]$ (94 mg, 0.25 mmol). The solution was filtered and diethyl ether was layered in dropwise until a faint permanent precipitate was evident. After 16 h, the 1:1 *adduct* crystallised as bright yellow crystals. The yield was 29 mg (14%), m.p. 118—129 °C (Found: C, 44.1; H, 5.5; N, 3.4. $C_{31}H_{46}F_6N_2O_8PRh$ requires C, 45.3; H, 5.6; N, 3.4%).

X-*Ray Data Collections, Structure Solutions, and Refinements*.—Data for all the structures listed in Table 8 were measured on a Nicolet *R3m* diffractometer with graphite-monochromated Cu-K_α radiation (λ = 1.541 78 Å) and using ω-scans. Structure solution was by the heavy-atom method in each case and all the non-hydrogen atoms were refined anisotropically. The ammine hydrogen atom positions were in all cases derived from ΔF maps and the groups were refined as idealised rigid bodies and, with the exception of $[Rh(cod)(NH_3)_2\cdot$db-21-c-7$][PF_6]$, were assigned the thermal parameters $U(H) = 1.2\ U_{eq}(N)$. In this adduct, one of the NH_3 groups has two orientations of occupancy *ca.* 0.3 and 0.7. In this instance, group thermal parameters were refined for each orientation. All the other hydrogen atoms in the adducts were idealised (C–H 0.96 Å), assigned isotropic thermal parameters $U(H) = 1.2U_{eq}(C)$, and allowed to ride on their parent carbon atoms. Refinement was by block-cascade full-matrix least-squares methods using the SHELXTL program system.[31] Computations were carried out on an Eclipse S140 computer. The crystal data and refinement parameters are summarised in Table 8 and the atomic co-ordinates for the five structures are listed in Tables 9—13. Selected bond lengths and angles are recorded in Tables 14—18.

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