Two Analogous Azamacrocyclic Compounds of Cobalt(III) and Rhodium(III) Containing Pendent Metal–Carbon Bonds. Synthesis and Comparison by NMR and X-Ray Structure Determinations[†]
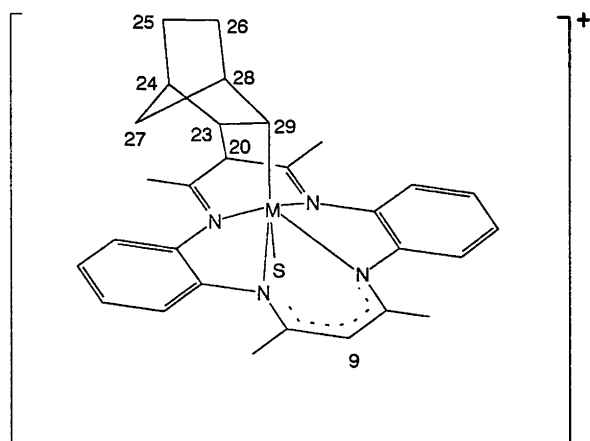
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The synthesis and characterisation by ^{1}H, ^{13}C and ^{59}Co NMR spectroscopy (the latter only for cation **A**), single-crystal X-ray crystallography and FAB mass spectrometry of two closely related pendent-arm macrocyclic complexes of cobalt(III) and rhodium(III), containing pendent metal–carbon bonds, are reported and compared {the tetraphenylborate salt of the six-coordinate [mono(acetone)(5,16-dihydro-16-(exo-norbornane-2,3-diyl-κC^2)-6,8,15,17-tetra-methyldibenzo[b,i][1,4,8,11]tetraazadecinato-$\kappa^4 N^{5,9,14,18}$)cobalt(III)] (cation **A**), and the hexafluorophosphate salt of the five-coordinate [5,16-dihydro-16-(exo-norbornane-2,3-diyl-κC^2)6,8,15,17-tetramethyldibenzo[b,i]-[1,4,8,11]tetraaza-decinato-$\kappa^4 N^{5,9,14,18}$)rhodium(III)] (cation **B**)}. The scalar one-bond coupling constants between the metal nucleus and the coordinating carbon atom are $^1J_{Rh-C} = 30.4$ Hz and $^1J_{Co-C} = 117 \pm 5$ Hz, the latter determined from the linewidths of the ^{13}C and ^{59}Co resonances.

The stability of organometallic compounds may often be related to lack of decomposition pathways such as β-elimination. Some unusual but stable compounds have
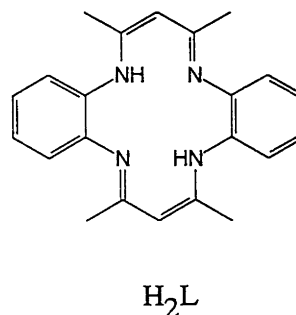

been made whose stability can be attributed to the difficulty of β-elimination due to strain. One such stabilised alkyl ligand is bridgehead 1-norbornyl, and it has been possible to prepare compounds like [Co(1-norborn-yl)₄].[2] Here we report cobalt(III) and rhodium(III) compounds with a pendent norbornyl group hanging from a tetraazamacrocycle and coordinating to the metal ion at the 2-position of norbornane (bicyclo[2.2.1]hept-ane) (cations **A** and **B**, respectively, Scheme 1).

These compounds are obtained by cycloaddition of the strained alkene norbornene (bicyclo[2.2.1]hept-2-ene) to

Scheme 1. (A) M = Co^{III}, S = acetone. (B) M = Rh^{III}, S = vacant site. Atomic numbering follows that adopted for the crystal structures of **A** (Ref. 1) and **B** (Figs. 1 and 2).

Scheme 2.

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† A Preliminary account of part of this work has been reported.[1]

the cobalt(II) complex or rhodium(II) complex of the macrocyclic tetraaza ligand H_2L ($H_2L = 5,14$-dihydro-6,8,15,17-tetramethyldibenzo-[b,i][1,4,8,11]tetraaza-cyclotetradecine, Scheme 2) in the presence of dioxygen. A similar cycloaddition of ethyne, giving an intramolecular vinylcobalt(III) compound, has been reported previously.[3] However, an attempt to prepare an analogous alkylcobalt(III) compound by cycloaddition of ethene was unsuccessful.[4] The structure of the six-coordinate cobalt(III) cation (**A**) was established previously by means of a crystal structure.[1] Here we report the crystal structure of the analogous five-coordinate rhodium(III) complex, and a comparison of these two closely related species as revealed by their crystal structures, and the multinuclear NMR and FAB mass spectral data of each.

Intramolecular alkylcobalt(III) compounds have interest as model compounds for coenzyme B_{12}. Systems with a planar tetradentate unsaturated ligand covalently bound to an axially coordinating alkyl group have been prepared,[5,6] while others have reported intramolecular Werner-type alkylcobalt(III) compounds.[7,8]

While a number of cobalt(III) complexes based on the macrocycle L^{2-} have been reported,[4] the chemistry of rhodium(III) complexes with this ligand is more sparse. The dinuclear metal–metal bonded $[Rh(L)]_2$ has been prepared, and ethylene insertion into the rhodium–rhodium bond to give a dinuclear organorhodium(III) compound has been reported.[9]

The coordination chemistry of L^{2-} has recently been reviewed.[10]

Experimental

Preparations

5,14-Dihydro-6,8,15,17-tetramethyldibenzo[b,i]*[1,4,8,11]-tetraazacyclotetradecine (H₂L)* was obtained as previously described by template condensation of 1,2-diamino-benzene and pentane-2,4-dione in the presence of Ni^{2+} ions, and subsequently stripping off the metal ion by gaseous HCl.[11]

[Mono(acetone) (5,16-dihydro-16-(exo-nornornane-2,3-diyl-κC²)-6,8,15,17-tetramethyldibenzo[b,i]*[1,4,8,11]tetra-azadecinato-κ⁴N⁵,⁹,¹⁴,¹⁸)cobalt(III)]* tetraphenylborate *([A][BPh₄])*. To a stirred slurry of H_2L (1.0 g, 2.9 mmol) and norbornene (bicyclo[2.2.1]hept-2-ene, 5.0 g, 53 mmol) in degassed dichloromethane (15 cm³) was added cobalt(II) acetate (0.73 g, 2.9 mmol) in degassed methanol (10 cm³) at 0°C. The red–brown [Co(L)] formed rapidly. After stirring the mixture for 5 min under nitrogen, the cobalt complex was slowly air oxidised for 8 h at 0°C. The green reaction mixture was stored overnight at −20°C. The solvent was removed under reduced pressure at temperatures not exceeding 0°C, and the solid was dissolved in ice-cold acetone and

applied to a column of Silica Gel 60 (Merck) (40 × 5.5 cm) cooled to approximately −5°C. The column was washed with acetone followed by methanol. **A** was eluted with 0.2% (w/w) potassium acetate in methanol. The blue–green solution of **A** was reduced to a volume of 20 cm³ under reduced pressure at temperatures not exceeding 0°C. A solution of potassium hexafluorophosphate (1.1 g, 6 mmol) in water (25 cm³) was added to obtain the hexafluorophosphate salt of **A** of analytical purity [S = vacant site (Scheme 1)]. ^1H NMR (CD_3CN, 300 K) δ 0.52 (1 H, d, J 10.5 Hz), 0.74 (1 H, d, J 10.5 Hz), 1.16 (3 H, m), 1.34 (1 H, dd, J 7.3 and 3.2 Hz), 1.45 (1 H, m), 1.98 (1 H, b), 2.11 (1 H, d, J 3.1 Hz), 2.32 (3 H, s), 2.34 (3 H, s), 2.54 (3 H, s), 2.57 (3 H, s), 3.70 (1 H, dd, J 7.3 and 1.0 Hz), 4.66 (1 H, d, J 3.2 Hz), 5.00 (1 H, s), 6.9–7.5 (8 H, m). ^{13}C NMR (CD_3CN, 300 K) δ 23.4, 23.7, 23.9, 26.7, 30.0, 31.9, 34.8, 42.9, 45.3, 45.8, 55.4, 71.8, 110.5, 122.0, 122.2, 122.2, 122.2, 122.5, 123.2, 129.2, 129.5, 145.4, 145.6, 150.8, 151.4, 159.2, 159.2, 175.7, 176.0.

To obtain the tetraphenylborate salt, the hexafluorophosphate salt was dissolved in a minimum volume of acetone, filtered, and a solution of sodium tetraphenylborate (1.5 g, 4.4 mmol) in water (30 cm³) added. The mixture was stored overnight at 5°C. The solid was filtered off, washed with water, and dried *in vacuo* at 5°C. Yield 2.3 g (90%) (Found: C, 76.5; H, 6.4; N, 6.5%. Calc. for $C_{56}H_{58}BCoN_4O$: C, 77.0; H, 6.7; N, 6.4%).

[5,16-Dihydro-16-(exo-norbornane-2,3-diyl-κC²)-6,8, 15,17-tetramethyldibenzo[b,i]*[1,4,8,11]tetraazadecinato-κ⁴N⁵,⁹,¹⁴,¹⁸) rhodium (III)] hexafluorophosphatedihydrate ([B][PF₆]·2H₂O).* The dinuclear $[Rh(L)]_2$ was prepared in ethanol using a published method.[9] A slurry of H_2L (0.85 g, 2.5 mmol) and rhodium(II) acetate dimer (0.5 g, 1.13 mmol) in absolute ethanol (60 cm³) was degassed at 0°C. The mixture was refluxed for 24 h under nitrogen. After cooling to 0°C, a solution of norbornene (10 g, 106 mmol) in ice-cold degassed dichloromethane (30 cm³) was added. The reaction mixture was stirred for 5 min under nitrogen. During the subsequent air oxidation the reaction mixture became red–violet. The mixture was stirred for 8 h in the presence of dioxygen and stored overnight at −20°C. **B** was purified by chromatography as in the method outlined for **A**, except that the red–violet solution of **B** was eluted with 0.5% (w/w) potassium acetate in methanol. The hexafluorophosphate salt of **B** was obtained by adding a solution of potassium hexafluorophosphate (1 g, 5.4 mmol) in water (25 cm³). The solid was dried *in vacuo* at 5°C. Yield 0.75 g (46%) (Found: C, 48.3; H, 4.8; N, 7.7%. Calc. for $C_{29}H_{36}F_6N_4O_2PRh$: C, 48.3; H, 5.0; N, 7.8%). [1] NMR (CD_3CN, 300 K) δ 0.61 (1 H, d, J 10.4 Hz), 0.69 (1 H, d, J 10.4 Hz), 1.08 (2 H, m), 1.39 (2 H, m), 1.74 (1 H, dd, J 8.2 and 3.2 Hz), 2.05 (1 H, b), 2.13 (1 H, b), 2.34 (6 H, s), 2.63 (3 H, s), 2.67 (3 H, s), 2.71 (1 H, ddd, J 8.2 and 3.7 and 1.3 Hz), 4.65 (1 H, d, J 3.2 Hz), 4.84 (1 H, s), 6.9–7.6 (8 H, m). ^{13}C NMR (CD_3CN, 300 K) δ 23.5, 24.5, 24.5, 26.8, 31.3 ($^3J_{Rh-C}$ 1.7 Hz), 32.1, 34.9, 42.3, 42.7, 44.4,

($^1J_{Rh-C}$ 30.4 Hz), 52.3, 76.8 ($^3J_{Rh-C}$ 6.5 Hz), 110.8 ($^3J_{Rh-C}$ 1.7 Hz), 122.1, 122.3, 122.3, 122.4, 123.5, 124.2, 129.8, 130.0, 144.2, 144.3, 150.4, 150.9, 157.1, 157.2, 174.0, 174.9.

NMR spectra were measured at 5.87 T with a Bruker ACF 250 NMR spectrometer equipped with a 5 mm broadband tuneable probe. Deuterated solvents were used to provide a deuterium lock. Quadrature detection and quadrature phase cycling were always used.

^{13}C DEPT NMR spectra[12] were used to achieve differentiation of the CH, CH$_2$ and CH$_3$ groups. ^{13}C and ^{1}H chemical shift values (δ) are reported relative to tetramethylsilane (TMS; $\delta = 0$ ppm).

^{59}Co NMR spectra were obtained with a 166 667 Hz spectral window using the RIDE (ring-down elimination) pulse sequence[13] to suppress probe ringing. ^{59}Co chemical shift values (δ) are reported in ppm relative to an external aqueous solution of K$_3$[Co(CN)$_6$] ($\delta = 0$ ppm), using replacement of the sample.

X-Ray crystallography. Crystals (well formed purple plates) of the rhodium(III) complex of formula [C$_{29}$H$_{32}$N$_4$Rh]$^+$ [PF$_6$]$^-$ ·CH$_2$Cl$_2$ (H$_2$O), $M = 684 + 84.9$, were grown from a saturated solution in dichloromethane/heptane at 253 K; triclinic, space group $P1$, $a = 10.197(5)$, $b = 11.360(5)$, $c = 14.046(6)$ Å, $\alpha = 81.95(3)$, $\beta = 70.84(4)$, $\gamma = 77.69(4)°$, $U = 1\,555.8$ Å^3, $Z = 2$, $D_c = 1.64$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 0.84 mm^{-1}, $T = 290$ K, $R = 0.065$ for 4109 unique observed [$I/\sigma(I) \geqslant 2.0$] reflections.

Data were collected with a Siemens R3m four-circle diffractometer in the ω–2θ mode. Maximum 2θ was 50° with scan range $\pm 0.75°$ (ω) around the $K_{\alpha1}$–$K_{\alpha2}$ angles, scan speed 2.5–15° (ω) min^{-1}, depending on the intensity of a 2 s pre-scan; backgrounds were measured at each end of the scan for 0.25 of the scan time. *hkl* ranges were: 0/12; −12/13; −16/16. Three standard reflections were monitored every 200 reflections, and showed a slight decrease (3%) during data collection. The data were rescaled to correct for this. Unit-cell dimensions and standard deviations were obtained by least-squares fit to 15 reflections (16 < 2θ < 21°). Reflections were processed using profile analysis to give 5431 unique reflections, of which 4109 were considered observed [$I/\sigma(I) \geqslant 2.0$]. These were corrected for Lorentz, polarisation and absorption effects, the last by the Gaussian method; minimum and maximum transmission factors were 0.82 and 0.93. The crystal had bounding faces $\pm 1\,0\,0$ ($d = 0.044$ mm); $\pm(1\,1\,0)(0.08$ mm); $0\,0 \pm 1(0.103$ mm); $\pm(3\,1\,5)$ (0.107 mm). There were no systematic reflection conditions; space group $P\bar{1}$ was selected and shown to be correct by satisfactory refinement. Heavy atoms were located by the Patterson interpretation section of SHELXTL, and the light atoms then found by E-map expansion, and successive Fourier syntheses, including one dichloromethane of solvation. An isolated residual peak (1.5 e Å^{-3}) was attributed to a partly occupied adventitious water molecule (refined with 0.25 occu-

pancy); the thermal parameters indicate that the dichloromethane is also partly disordered, but no special modelling was adopted for it. Anisotropic thermal factors were used for all non-H atoms (except the part-occupied oxygen). Hydrogen atoms were given fixed isotropic temperature factors, $U = 0.08$ Å^2. Those defined by molecular geometry were inserted at calculated positions and not refined; methyl groups were treated as rigid CH$_3$ units, with their initial orientation based on a staggered configuration. Final refinement was on F by least-squares methods refining 401 parameters. Largest positive and negative peaks on a final difference Fourier synthesis were of height ± 1.3 e Å^{-3}, all near Rh. A weighting scheme of the form $W = 1/[\sigma^2(F) + gF^2]$ with $g = 0.0016$ was used and shown to be satisfactory by weight analysis. Final $R = 0.065$, $R_w = 0.083$, $S = 1.47$; R(all reflections) = 0.083.

Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters (in Å$^2 \times 10^3$) for [C$_{29}$H$_{32}$N$_4$Rh]PF$_6$.

Atom	x	y	z	U_{eq}[a]
Rh(1)	1541.1(6)	2707.8(5)	1499.5(4)	32(1)
P(1)	2498(2)	4692(2)	6026(2)	55(1)
F(1)	3836(6)	4524(6)	6495(4)	80(3)
F(2)	1140(6)	4859(6)	5574(4)	89(3)
F(3)	3158(10)	3664(10)	5384(7)	181(6)
F(4)	1778(8)	5665(8)	6708(6)	142(4)
F(6)	2035(10)	3706(9)	6822(7)	161(5)
F(5)	2981(10)	5625(11)	5230(8)	184(6)
N(1)	1387(6)	4422(5)	1741(4)	35(2)
N(2)	2329(6)	3297(5)	173(4)	38(2)
N(3)	1564(6)	1027(5)	1266(5)	39(2)
N(4)	667(6)	2145(5)	2831(4)	37(2)
C(1)	1390(7)	5187(6)	841(5)	37(3)
C(2)	839(8)	6410(6)	742(6)	46(3)
C(3)	823(8)	7053(7)	−166(7)	50(3)
C(4)	1360(8)	6470(8)	−974(7)	53(3)
C(5)	1890(8)	5225(7)	−903(6)	47(3)
C(6)	1932(7)	4565(6)	−0(5)	36(2)
C(7)	3060(8)	2493(7)	−424(5)	43(3)
C(8)	3938(10)	2911(9)	−1339(7)	71(4)
C(9)	3133(8)	1242(7)	−194(6)	45(3)
C(10)	2436(8)	540(7)	515(6)	45(3)
C(11)	2720(9)	−824(7)	461(7)	64(4)
C(12)	598(8)	506(6)	1952(6)	42(3)
C(13)	4(9)	−443(7)	1792(8)	57(4)
C(14)	−1040(10)	−786(8)	2502(8)	67(4)
C(15)	−1513(9)	−208(8)	3288(8)	63(4)
C(16)	−950(9)	751(8)	3449(7)	58(3)
C(17)	94(8)	1115(6)	2792(6)	42(3)
C(18)	815(8)	2625(7)	3565(5)	40(3)
C(19)	385(10)	2232(8)	4609(6)	63(4)
C(20)	1719(8)	3591(7)	3356(5)	40(3)
C(21)	1437(7)	4670(6)	2603(5)	39(3)
C(22)	1472(10)	5888(7)	2872(7)	61(4)
C(23)	3151(8)	2818(7)	3079(6)	46(3)
C(24)	4362(9)	3473(8)	2888(6)	56(3)
C(25)	5626(9)	2463(9)	2995(7)	59(4)
C(26)	5772(8)	1812(9)	2082(7)	58(4)
C(27)	4573(9)	3812(8)	1787(7)	59(4)
C(28)	4602(8)	2526(8)	1547(6)	50(3)
C(29)	3309(8)	2207(7)	2125(6)	47(3)
C(001)	4052(12)	−1988(10)	3989(9)	91(5)
Cl(1)	4690(7)	−801(5)	4178(6)	228(5)
C1(2)	2606(4)	−1508(4)	3466(4)	133(2)
O(001)[b]	8385(38)	2354(33)	8448(27)	121(13)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor. [b] Occupancy 0.25.

Table 2. Selected bond lengths (in Å) in $[C_{29}H_{32}N_4Rh]^+$ (**B**).

Rh(1)-N(1)	1.992(6)	Rh(1)-N(2)	1.980(6)
Rh(1)-N(3)	1.977(6)	Rh(1)-N(4)	2.006(6)
Rh(1)-C(29)	2.080(9)	N(1)-C(1)	1.430(9)
N(1)-C(21)	1.293(10)	N(2)-C(6)	1.409(9)
N(2)-C(7)	1.340(9)	N(3)-C(10)	1.354(10)
N(3)-C(12)	1.416(10)	N(4)-C(17)	1.426(11)
N(4)-C(18)	1.277(11)	C(1)-C(2)	1.381(9)
C(1)-C(6)	1.428(10)	C(2)-C(3)	1.379(12)
C(3)-C(4)	1.365(10)	C(4)-C(5)	1.399(11)
C(5)-C(6)	1.382(10)	C(7)-C(8)	1.511(11)
C(7)-C(9)	1.402(11)	C(9)-C(10)	1.379(11)
C(10)-C(11)	1.524(11)	C(12)-C(13)	1.405(13)
C(12)-C(17)	1.413(11)	C(13)-C(14)	1.404(13)
C(14)-C(15)	1.327(15)	C(15)-C(16)	1.396(15)
C(16)-C(17)	1.375(11)	C(18)-C(19)	1.488(11)
C(18)-C(20)	1.545(12)	C(20)-C(21)	1.516(10)
C(20)-C(23)	1.550(10)	C(21)-C(22)	1.494(12)
C(23)-C(24)	1.539(13)	C(23)-C(29)	1.562(12)
C(24)-C(25)	1.546(12)	C(24)-C(27)	1.529(13)
C(25)-C(26)	1.537(14)	C(26)-C(28)	1.543(12)
C(27)-C(28)	1.538(13)	C(28)-C(29)	1.507(11)

Table 3. Selected bond angles (in °) in $[C_{29}H_{32}N_4Rh]^+$ (**B**).

N(1)-Rh(1)-N(2)	83.0(2)	N(1)-Rh(1)-N(3)	176.3(3)
N(2)-Rh(1)-N(3)	98.2(3)	N(1)-Rh(1)-N(4)	96.4(2)
N(2)-Rh(1)-N(4)	177.6(4)	N(3)-Rh(1)-N(4)	82.3(2)
N(1)-Rh(1)-C(29)	90.4(3)	N(2)-Rh(1)-C(29)	99.1(3)
N(3)-Rh(1)-C(29)	92.9(3)	N(4)-Rh(1)-C(29)	83.2(3)
Rh(1)-N(1)-C(1)	109.8(5)	Rh(1)-N(1)-C(21)	119.7(5)
Rh(1)-N(2)-C(6)	110.6(4)	Rh(1)-N(2)-C(7)	119.2(5)
Rh(1)-N(3)-C(10)	119.4(5)	Rh(1)-N(3)-C(12)	111.3(5)
Rh(1)-N(4)-C(17)	110.1(5)	Rh(1)-N(4)-C(18)	119.4(5)
Rh(1)-C(29)-C(23)	110.9(5)	Rh(1)-C(29)-C(28)	118.4(6)
C(24)-C(23)-C(29)	102.7(6)	C(23)-C(29)-C(28)	103.3(7)
C(29)-C(28)-C(27)	104.0(6)	C(27)-C(24)-C(23)	104.3(8)
C(24)-C(27)-C(28)	94.3(7)	C(26)-C(28)-C(27)	99.9(8)
C(26)-C(28)-C(29)	106.6(6)	C(25)-C(26)-C(28)	104.2(7)
C(24)-C(25)-C(26)	102.4(7)	C(25)-C(24)-C(27)	100.6(7)

Maximum shift/error in the final cycle was 0.15. Computing was performed with SHELXTL PLUS[14] on a DEC Microvax II. Scattering factors in the analytical form and anomalous dispersion factors were taken from Ref. 15. Final atomic coordinates are in Table 1, and selected bond lengths and angles are in Tables 2 and 3 respectively.[†]

$[C_{29}H_{32}N_4Co]^+[PF_6]^- \cdot CH_2Cl_2$ (H_2O) is isomorphous and apparently isostructural with $[C_{29}H_{32}N_4Rh]^+$ $[PF_6]^- \cdot CH_2Cl_2$ (H_2O) (for the cobalt(III) complex, unit cell: $a = 10.435(4)$, $b = 10.962(7)$, $c = 13.936(7)$ Å, $\alpha = 81.29(4)$, $\beta = 77.54(3)$, $\gamma = 77.65(4)°$, $U = 1511.3$ Å^3), but the Co complex suffered from a rapid fall-off in intensity during data collection, and the structure could not be refined below $R = 0.10$. Its broad features appear

[†] Additional data available from the Cambridge Crystallographic Centre comprise H-atom coordinates, thermal parameters and full bond lengths and angles.

to be identical to those of the rhodium(III) complex, including the presence of a solvent dichloromethane molecule.

Results and discussion

Syntheses and spectroscopy. The macrocyclic tetra-aza ligand H_2L is readily obtained as described. We measured the ^{13}C NMR spectrum of H_2L in acetonitrile-d_3 at 300 K. It shows resonances at $\delta = 21.1$ (CH_3), 98.7 (CH), 124.0 (aromatic CH), 124.3 (aromatic CH), 139.3 (aromatic C) and 160.4 ppm (imine carbon). As the organometallic adducts reported in this paper can be regarded as derivatives of norbornane (bicyclo[2.2.1]-heptane), we also measured for comparison the ^{13}C NMR spectrum of norbornane in acetonitrile-d_3 at 300 K. It shows resonances at $\delta = 30.3$ (CH_2), 37.3 (CH), and 39.0 ppm (CH_2, 7-position of norbornane).

In the presence of oxygen and excess norbornene [Co(L)] is oxidised to give the diamagnetic cation **A** in good yield. Fast atomic bombardment (FAB) mass spectrometry in *o*-nitrobenzyl alcohol shows peaks at m/z 495 (parent ion) and at m/z 401 corresponding to elimination of norbornene. It is also evident from the integrated ^{1}H NMR spectrum that this compound is a 1 : 1 adduct (Table 4). The ^{1}H NMR resonances of **A** are broad, showing many unresolved splittings, as is often the case for such rigid ring systems. The four methyl groups have different ^{1}H resonance frequencies owing to the two chiral carbon atoms, C23 and C29. The ^{1}H resonances at δ 5.00 and 4.66 ppm may be assigned to the protons at C9 and C20, respectively. The splitting of the latter ($J = 3.2$ Hz) demonstrates that the norbornyl group is covalently bound to the macrocycle. The resonance at δ 3.70 ppm may be assigned to the proton attached to the cobalt-bound carbon atom (C29). This resonance is a broad doublet of doublets ($J = 7.3$ and 1.0 Hz). We suggest that the larger coupling constant is due to coupling to the proton at C23, as the dihedral angle is close to zero, while the smaller coupling constant is due to coupling to the bridgehead (C28) proton. From the magnitude of the coupling constants (Table 4) the doublet of doublets at $\delta = 1.34$ ppm may be assigned to the proton at C23, although this implies that coupling to the bridgehead (C24) proton is too small to be observed.

The proton-decoupled ^{13}C NMR spectrum of **A** is well resolved (Table 5). The ^{13}C resonance of the cobalt-bound carbon atom (C29, $\delta = 45.3$ ppm) in acetonitrile-d_3 at 300 K has a linewidth at half height, $\Delta v_{1/2} = 46$ Hz, giving this resonance a rather poor signal to noise ratio (for comparison the other ^{13}C resonances have a linewidth of about 0.5 Hz). Owing to its broadness this resonance is partially overlapping with the resonance at $\delta = 45.8$ ppm. In CD_2Cl_2 this broad resonance is at $\delta = 40.0$ ppm and has $\Delta v_{1/2} = 15.5$ Hz (otherwise there is very little difference between the ^{13}C NMR spectra in CD_3CN and CD_2Cl_2).

The ^{59}Co NMR spectrum of the hexafluorophosphate

Table 4. ^{1}H NMR data for the hexafluorophosphate salts of $[C_{29}H_{32}N_4Co]^+$ (**A**) and $[C_{29}H_{32}N_4Rh]^+$ (**B**) in acetonitrile-d$_3$ at 300 K.

A				B			
δ/ppm	Integral	Multiplicity	J/Hz	δ/ppm	Integral	Multiplicity	J/Hz
0.52	1	d	10.5	0.61	1	d	10.4
0.74	1	d	10.5	0.69	1	d	10.4
1.16	3	m		1.08	2	m	
1.34	1	dd	7.3, 3.2	1.39	2	m	
1.45	1	m		1.74	1	dd	8.2, 3.2
1.98	1	b		2.05	1	b	
2.11	1	d	3.1	2.13	1	b	
2.32	3	s		2.34	6	s	
2.34	3	s					
2.54	3	s		2.63	3	s	
2.57	3	s		2.67	3	s	
3.70	1	dd	7.3, 1.0	2.71	1	ddd	8.2, 3.7, 1.3
4.66	1	d	3.2	4.65	1	d	3.2
5.00	1	s		4.84	1	s	
6.9–7.5	8	m^a		6.9–7.6	8	m^a	

^{a}Aromatic protons. (s) singlet; (d) doublet; (dd) doublet of doublet; (ddd) doublet of doublet of doublets; (m) multiplet; (b) broad.

Table 5. ^{13}C NMR data for the hexafluorophosphate salts of $[C_{29}H_{32}N_4Co]^+$ (**A**) and $[C_{29}H_{32}N_4Rh]^+$ (**B**) in aceto-nitrile-d$_3$ at 300 K.

A		B		
δ/ppm	Group	δ/ppm	Group	J/Hz
23.4	CH$_3$	23.5	CH$_3$	
23.7	CH$_3$	24.5	CH$_3$	
23.9	CH$_3$	24.5	CH$_3$	
26.7	CH$_3$	26.8	CH$_3$	
30.0	CH$_2$	31.3	CH$_2$	$^3J_{Rh-C} = 1.7$ Hz
31.9	CH$_2$	32.1	CH$_2$	
34.8	CH$_2$	34.9	CH$_2$	
42.9	CH	42.3	CH	
45.3	CH^c	42.7	CH	
45.8	CH	44.4	CH	$^1J_{Rh-C} = 30.4$ Hz
55.4	CH	52.3	CH	
71.8	CH	76.8	CH	$^3J_{Rh-C} = 6.5$ Hz
110.5	CH	110.8	CH	$^3J_{Rh-C} = 1.7$ Hz
122.0	CH^a	122.1	CH^a	
122.2	CH^a	122.3	CH^a	
122.2	CH^a	122.3	CH^a	
122.2	CH^a	122.4	CH^a	
122.5	CH^a	123.5	CH^a	
123.2	CH^a	124.2	CH^a	
129.2	CH^a	129.8	CH^a	
129.5	CH^a	130.0	CH^a	
145.4	C^a	144.2	C^a	
145.6	C^a	144.3	C^a	
150.8	C^a	150.4	C^a	
151.4	C^a	150.9	C^a	
159.2	C^b	157.1	C^b	
159.2	C^b	157.2	C^b	
175.7	C^b	174.0	C^b	
176.0	C^b	174.9	C^b	

^{a}Aromatic carbon. ^{b}Imine group. $^c\Delta v_{1/2} = 46$ Hz due to scalar coupling to ^{59}Co; see text.

salt of **A** in acetonitrile-d$_3$ at 300 K was obtained using the RIDE pulse sequence. It shows a single resonance at $\delta = 5560$ ppm ($\Delta v_{1/2} = 6250$ Hz). This resonance frequency is within the range typical for organo-cobalt(III) compounds with unsaturated ligands.[16] The relaxation of the ^{59}Co nucleus is dominated by quadrupole interaction, and the spin–lattice relaxation time $T_{1,Co}$ can safely be determined from a measurement of the linewidth of the resonance. This gives a value of $T_{1,Co} = 5.09 \times 10^{-5}$ s.

The lineshape of the resonance of a spin $S = 1/2$ nucleus which has scalar coupling to a spin $I = 7/2$ can be calculated using a relaxation matrix treatment developed by Pyper, if the $I = 7/2$ nucleus relaxes solely due to quadrupole interaction.[17] The lineshape of the $S = 1/2$ nucleus can also be calculated assuming relaxation of the $I = 7/2$ nucleus by magnetic dipole interactions by a similar relaxation matrix treatment.[18] However, if the spin–lattice relaxation rate of the cobalt nucleus is large compared to the coupling constant (i.e. $1/T_{1,Co} \gg J_{Co-C}$) for the ^{59}Co nucleus, the resonance becomes a Lorentzian with a spin–spin relaxation time T_2 given by eqn. (1).[19]

$$1/T_{2X} = (4\pi^2 J_{AX}^2/3)\, I(I+1)$$

$$\times [T_{2A}/(1 + (\omega_X - \omega_A)^2\, T_{2A}^2) + T_{1A}] \qquad (1)$$

The nucleus X has spin $S = 1/2$ and the nucleus A has spin I. The scalar coupling constant J is in Hz and the resonance frequency ω is in angular frequency units (rad s^{-1}). It has been shown numerically[18] that for a nucleus of spin $1/2$ coupled to a spin $I = 7/2$, eqn. (1) is valid for $J_{Co-C} T_{1,Co} < 0.01$. This criterion is fulfilled in the present case. From the lineshape of the cobalt-bound ^{13}C resonance, and the spin–lattice relaxation time of the ^{59}Co

nucleus, the cobalt–carbon coupling constant may be calculated using eqn. (1), despite the absence of a direct splitting. Such a calculation yields $^1J_{Co-C} = 117 \pm 5$ Hz. This value is somewhat larger than other values for cobalt–carbon coupling constants for sigma-bonded complexes. However, the directly observed rhodium–carbon coupling constant ($^1J_{Rh-C} = 30.4$ Hz, Table 5) is similarly large, and that gives a ratio $^1J_{Co-C}/^1J_{Rh-C}$ of about 3.8 as found previously.[7]

This value of the cobalt–carbon coupling constant also explains why a ^{59}Co resonance of the hexafluorophosphate salt of **A** in CD_2Cl_2 could not be observed. For $\Delta\nu_{1/2} = 15.5$ Hz for the C29 carbon nucleus application of eqn. (1) yields $T_{1,Co} = 1.72 \times 10^{-5}$ s, which will give a line with a width at half height of more than 18 kHz. This difference in the magnitude of $T_{1,Co}$ reflects a difference in the electric field gradient at the site of the ^{59}Co nucleus caused presumably by coordination of the solvent in the case of acetonitrile. The difference in solvent viscosity should give the opposite effect from that observed.

In the presence of oxygen and an excess of norbornene $[Rh(L)]_2$ is oxidised to give the diamagnetic cation **B** in moderate yield. FAB mass spectrometry in *o*-nitrobenzyl alcohol shows peaks at m/z 539 (parent ion) and at m/z 445 corresponding to elimination of norbornene.

Integration of the ^1H NMR spectrum of **B** clearly shows that this compound is a 1 : 1 adduct. No evidence has been found for a 2 : 1 adduct analogous to that of ethene.[9] This is probably due to the bulkiness of the norbornyl group. That the norbornyl group is covalently bound to the macroxycle is demonstrated by the scalar coupling ($J = 3.2$ Hz) to the proton at C20. That means that the two adducts of norbornene are analogous, as confirmed by the X-ray crystallography (q.v.).

The ^1H NMR spectrum of **B** shows scalar two-bond coupling to ^{103}Rh ($I = 1/2$). We can assign the resonance at δ 2.71 ppm to the proton of C29. This resonance shows an additional splitting compared to the corresponding resonance at δ 3.70 ppm for the cobalt(III) compound.
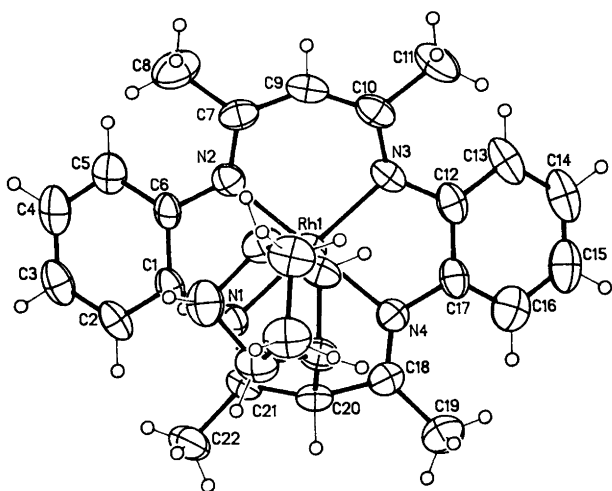

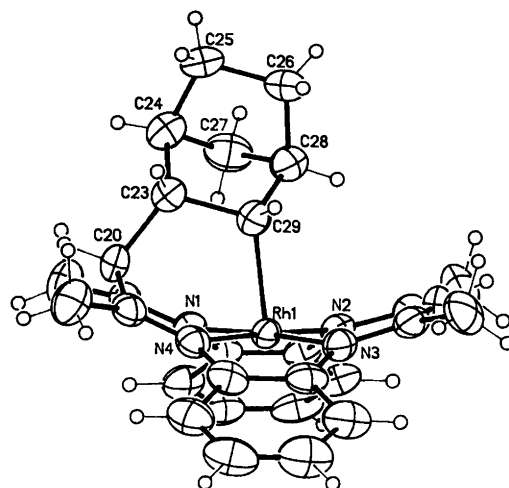*Fig. 2.* View of cation **B** along the macrocyclic plane, showing atomic numbering for the pendent norbornyl group.

The ratio $^1J_{Rh-C}/^2J_{Rh-H}$ is approximately 9 for bis-(dimethylglyoximato)methylrhodium(III) complexes, when the sixth ligand in a *trans*-position to the methylrhodium(III) is a relatively weak neutral ligand such as water or imidazole.[20] If this holds also for compound **B** the coupling constant of 3.7 Hz of the resonance at δ 2.71 ppm may be assigned to coupling to the rhodium nucleus. This leaves two coupling constants of this resonance at values close to that found for the cobalt(III) compound (Table 4). It has formerly been observed for analogous alkyl compounds of the two metal ions that the resonance frequency of the proton attached to the metal-bound carbon atom is lower for the rhodium(III) compound compared to the cobalt(III) compound.[20,21]

The ^{13}C NMR spectrum of **B** shows a number of splittings due to coupling to ^{103}Rh. In particular the resonance at $\delta = 44.4$ ppm (CH) shows a coupling with $J = 30.4$ Hz,
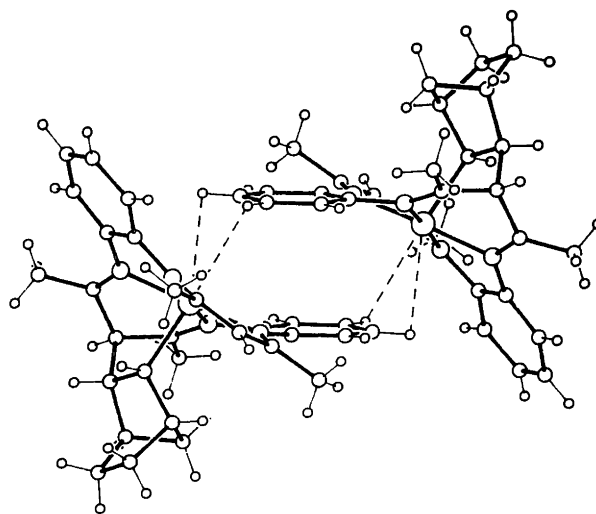

Fig. 1. Structure of cation **B** showing the atomic numbering.

Fig. 3. View of the two cations edge-on, showing the π–π stacking interactions. The dashed lines indicate the closest Rh–H contacts (2.9–3.1 Å).

and may thus be assigned to C29. A smaller coupling ($J = 1.7$ Hz) is observed for a CH_2 group, which implies that this must be a three-bond coupling. Because of the low frequency of this CH_2 group (31.3 ppm) we assign this resonance of C26, by comparison with norbornane. The CH groups at δ 76.8 ppm and 110.8 ppm we assign to C20 and C9, respectively, by comparison with H_2L. These assignments imply that some three-bond coupling constants, but no two-bond coupling constants between ^{13}C and ^{103}Rh, are observed.

At higher temperatures both compounds A and B are unstable, and eliminate norbornene (β-elimination) in dichloromethane or acetonitrile solution as shown by ^1H NMR.

Crystal structures. The structure of the five-coordinate rhodium(III) cation B (hexafluorophosphate salt) is shown in Fig. 1 and 2. It is broadly similar to that found for the analogous six-coordinate cobalt(III) cation A (tetraphenylborate salt),[1] but unlike the Co complex, there is no coordinated solvent molecule in the *trans*-position to the pendent coordinated norbornyl arm. The Rh lies 0.05 Å out of the N_4-plane in the direction of C(29). Selected bond lengths and angles for A and B are compared in Table 6. Although the cobalt crystal was rather poorly diffracting, leading to somewhat larger errors for the bond lengths and angles, it can be seen from Table 6 that the two structures are very similar. In B, comparison of the N(3)–C(10) and N(2)–C(7) bond lengths [average 1.35(1) Å] of the delocalised N–C–C–C–N fragment with N(4)–C(18) and N(1)–C(21) [average 1.29(1) Å] of the other N–propyl–N linkage (that carrying the pendent norbornyl arm) clearly shows the localised nature of the imine bonds of the latter [N–C(aromatic) bond lengths average 1.42(1) Å]. In the delocalised N–propyl–N ring,

C–C distances [average 1.39(1) Å] are also significantly shorter than in the localised ring [C–C average 1.53(1) Å]. The metal–nitrogen distances are on average 0.11 Å larger for the Rh compared with the Co complex, whereas the metal–C(29) distance is only 0.04 Å larger for the former, indicating that the Rh–C(29) bond is stronger than the Co–C(29) bond, as expected. This could account in part for the absence of a coordinated solvent molecule in a *trans*-position to the pendent arm, since strengthening of the Rh–C bond would result in a weaker bond to the *trans*-ligand. However, this is probably only part of the reason for B being five-coordinate, and lattice forces almost certainly contribute to the stabilisation of B. As can be seen from Fig. 3, the molecules stack in pairs, with clear π–π interactions between one of the phenyl rings and its counterpart across a centre of symmetry. The inter-plane distance is 3.45 Å, but the rings are slightly offset, such that the centroid–centroid distance is 3.64 Å. In the solid this π–π stacking blocks the vacant site on the Rh, although it is doubtful if this is maintained in donor solvents. The nature of the counter-anion may well be important in stabilising the six-coordinate cation A (solid tetraphenylborate salt), since the hexafluorophosphate salt of A was found to be isomorphous and probably isostructural with B.

Table 6. Comparison of selected bond lengths (in Å) and bond angles (in °) in the cations A (M = Co) and B (M = Rh).

	M = Co	M = Rh
M–C(29)	2.04(2)	2.080(9)
M–O(1)	2.30(2)	—
M–N(1)	1.87(2)	1.992(6)
M–N(2)	1.88(2)	1.980(6)
M–N(3)	1.86(2)	1.977(6)
M–N(4)	1.90(1)	2.006(6)
N(3)–C(10)	1.33(2)	1.354(10)
C(9)–C(10)	1.37(3)	1.379(11)
N(4)–C(18)	1.28(2)	1.277(11)
C(18)–C(20)	1.52(3)	1.545(12)
C(20)–C(23)	1.59(3)	1.550(10)
C(23)–C(29)	1.52(2)	1.562(12)
C(29)–M–N(4)	84.6(7)	83.2(3)
C(23)–C(29)–M	111(1)	110.9(5)
C(20)–C(23)–C(29)	113(2)	113.5(7)
C(18)–C(20)–C(21)	117(2)	120.6(7)
C(7)–C(9)–C(10)	128(2)	134.0(7)

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