DALTON

Preparation, crystal structure and mechanism of formation of a novel dinuclear carbopentazane complex, $[Rh_2(PPh_3)_4\{(NH_2NH)_2CH_2\}][NO_3]_2$

Brian T. Heaton,*[a] Chacko Jacob,[a] Gary L. Monks,[a] Michael B. Hursthouse,*†[b] Indira Ghatak,[b] Richard G. Somerville,[b] William Heggie,[c] Philip R. Page[c] and Ivan Villax[c]

[a] *Department of Chemistry, University of Liverpool, PO Box 147, Liverpool L69 3BX, UK*

[b] *Department of Chemistry, Queen Mary and Westfield College, Mile End Road, London E1 4NS, UK*

[c] *Research Laboratories, Hovione Sociedade Quimica SA, 2670 Loures, Portugal*

The reaction of $Rh(NO_3)_3\cdot 2H_2O$ with PPh_3 and $N_2H_4\cdot H_2O$ in MeOH gave the dinuclear carbopentazane complex $[Rh_2(PPh_3)_4\{(NH_2NH)_2CH_2\}]^{2+}$ **1**, which has been characterised by multinuclear NMR measurements and X-ray diffraction. It is a dipositive, dinuclear cation in which the two bis(triphenylphosphine)rhodium units are bridged by the tetradentate carbopentazane ligand. The rhodium atoms have the expected square-planar geometry, with Rh–P and Rh–N distances of 2.225(3)–2.253(3) and 2.130(6)–2.166(6) Å respectively. A series of experiments, aimed at elucidating the mechanism of formation of **1**, indicated that the formation of the NCH_2N linkage occurs *via* acid-catalysed nucleophilic addition of free N_2H_4 to the CH_2 group of an $NH_2N{=}CH_2$ ligand co-ordinated to Rh^I, and unambiguous multinuclear NMR (^{13}C, ^{15}N and ^{31}P) and mass spectrometric evidence has been obtained for the monomeric complex $[Rh(PPh_3)_2(NH_2NHCH_2NHNH_2)]^+$, which readily rearranges to form **1**. Related experiments have also provided evidence for the formation of $[Rh(PPh_3)_2(NH_2NHCHMeNHNH_2)]^+$, which also rearranges to give a dinuclear complex, $[Rh_2(PPh_3)_4\{(NH_2NH)_2CHMe\}]^{2+}$.

In a recent publication[1] the crystal structure and NMR data for $[Rh(PPh_3)_3(ONO_2)]$ **2**, obtained from the reaction of $Rh(NO_3)_3\cdot 2H_2O$ with PPh_3 in MeOH, was reported. Its reaction with $N_2H_4\cdot H_2O$ in CH_2Cl_2 has been shown[2] to give $[Rh_2(PPh_3)_4(\mu\text{-}N_2H_4)_2][NO_3]_2$ **3** and $[Rh(PPh_3)_2(N_2H_4)_2]NO_3$ **4**, whereas in CH_2Cl_2–MeOH (1:1) the analogous reaction gave $[Rh(PPh_3)_3(N_2H_4)]NO_3$ **5**; all these complexes have been characterised by NMR spectroscopy and $[Rh_2(PPh_3)_4(N_2H_4)_2][NO_3]_2$ by X-ray crystallography.[3]

We now report a detailed study of the reaction of $Rh(NO_3)_3\cdot 2H_2O$ with PPh_3, $N_2H_4\cdot H_2O$ and MeOH which gives rise to the unusual dinuclear complex $[Rh_2(PPh_3)_4\{(NH_2NH)_2CH_2\}][NO_3]_2$ **1**.[3] This contains the unusual carbopentazane ligand which is bridging and quadridentate and we now describe reactions designed to elucidate the sequential mechanism of the formation of **1**, together with its X-ray crystallographic characterisation. The discussion includes the spectroscopic characterisation of a range of inorganic and organic intermediates, together with the precursor to **1**, a monomeric complex containing the carbopentazane acting as a bidentate ligand.

Experimental

All preparations and manipulations were carried out under an oxygen-free nitrogen atmosphere. All solvents were dried using standard techniques and distilled under nitrogen prior to use. The NMR spectra were recorded on Bruker WM200, AC200 and AMX400 spectrometers; ^{13}C, ^{15}N and ^{31}P NMR chemical shift data are relative to external $SiMe_4$, $MeNO_2$ and 85% H_3PO_4, respectively. The ^{13}C NMR data are given in the Experimental section and ^{31}P and ^{15}N NMR data are summarised in Tables 1 and 2, respectively. Fast atom bombardment (FAB) mass spectra were obtained on a VG Analytical 7070E instrument and the matrix used was 3-nitrobenzyl alcohol.

Crystallography

Crystals of complex **1** used for X-ray analysis were sealed under argon in thin-walled glass capillaries. Unit-cell and intensity data were obtained using an Enraf-Nonius CAD4 diffractometer operating in the ω–2θ mode with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å), following standard procedures. Structure determination and refinement was achieved *via* standard heavy-atom procedures, with refinement by blocked-matrix least squares. The first sample chosen suffered considerable decay during data collection and although suitable corrections were made the structure refinement was unsatisfactory, leading only to an *R* value of 0.10. The analysis indicated the presence of at least one molecule of methanol of solvation, loss of which presumably caused the crystal decay. Both nitrate ions were severely disordered also, but the structure of the cation was quite clear. In order to obtain a better refinement a second crystal, from a new preparation, was sealed in an atmosphere of argon, and a new set of data recorded. For this sample slightly different cell dimensions were obtained. Structure solution and refinement showed the sample to be of the same compound but with less solvent of crystallisation, and this time the crystal remained stable during data collection. No absorption correction was made in view of the low value of and the equidimensional nature of the crystal used. In view of the large number of atoms, refinement was made in blocks, with the atoms of the bridging $(NH_2NH)_2CH_2$ core refined at all times, and one rhodium, the attached pair of phosphines plus one nitrate in separate blocks. Phenyl rings were refined with idealised geometry (C–C 1.395, C–H 0.96 Å). Hydrogens in the carbopentazane ligand were all experimentally located and refined isotropically. One common U_{iso} was refined for all hydrogens. One of the nitrate groups and what is probably a fraction of a molecule of methanol of

† *Present address:* Department of Chemistry, University Wales, College of Cardiff, PO Box 78, Cardiff CF1 1XL, UK.

solvation were severely disordered and each was represented by clusters of atoms with partial occupancies.

Crystal data. $[Rh_2(PPh_3)_4\{(NH_2NH)_2CH_2\}][NO_3]_2 \cdot x$MeOH, $M = 1471.13$ ($x = 0.5$), monoclinic, space group $P2_1/n$, $a = 22.269(3)$, $b = 23.311(3)$, $c = 13.838(2)$ Å, $\beta = 100.51(2)°$, $U = 7062.96$ Å^3, $F(000) = 3020$, $Z = 4$, $D_c = 1.37$ g cm^{-3}, crystal dimensions 0.25 × 0.35 × 0.40 mm, $\mu = 5.38$ cm^{-1}, $R = 0.041$, $R' = 0.056$ for 7529 observed data ($F_o > 3\sigma F_o$) from 9820 unique measured data and 784 parameters. The refinement of the structure {SHELX 80,[4] $w = [\sigma^2(F_o) + 0.0038F_o^2]^{-1}$} was improved since that reported previously.[3] Final atomic coordinates are given in Table 3.

The proportion of methanol used for crystal data calculation was based on the sums of the occupancies of the disordered component atoms.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Preparations

$[Rh_2(PPh_3)_4\{(NH_2NH)_2CH_2\}][NO_3]_2$ 1. Addition of MeOH (58 cm^3) to a mixture of $Rh(NO_3)_3 \cdot 2H_2O$ (0.187 g, 0.575 mmol) and PPh_3 (1.06 g, 4.04 mmol) produced an orange suspension. After stirring for 15 min, $N_2H_4 \cdot H_2O$ (0.084 cm^3, 1.73 mmol) was added which caused the suspension to turn yellow. After stirring for 30 min and standing for 16 h the yellow solid was filtered off and the product obtained by evaporation of the yellow filtrate to dryness followed by removal of $OPPh_3$ and PPh_3 by washing with MeOH (3 × 10 cm^3) and Et_2O (3 × 10 cm^3) respectively and drying *in vacuo*. Yield 0.423 g (50%). The complex had identical NMR spectroscopic data to the product prepared previously[3] and characterised by X-ray analysis (see Tables 3 and 4) and $\delta(CH_2)$ 73.1, $^1J(^1H-^{13}C) = 156$ Hz. FAB mass spectrum: m/z 1392, $[M + NO_3]^+$.

$[PPh_3(CH_2OH)]NO_3$. Addition of formaldehyde (0.62 cm^3, 7.6 mmol) to a solution of PPh_3 (2.00 g, 7.6 mmol) in MeOH (90 cm^3), followed by stirring for 5 min and addition of concentrated HNO_3 (0.48 cm^3, 7.6 mmol), resulted in a colourless solution, which on removal of solvent *in vacuo* gave a white solid. This was dissolved in CH_2Cl_2 and addition of Et_2O gave a white powder, which was filtered off, washed with Et_2O and dried *in vacuo*. Yield 2.00 g (74%) (Found: C, 64.35; H, 5.00; N, 3.80. $C_{19}H_{18}NO_4P$ requires C, 64.20; H, 5.10; N, 3.95%). FAB mass spectrum: m/z 293 (M^+). ^{13}C NMR (−30 °C, MeOH): δ 57.4 [CH_2, $^1J(^{31}P-^{13}C)$ 64, $^1J(^1H-^{13}C)$ 151], 117.9 [C_3PCH_2, $^1J(^{31}P-^{13}C)$ 84 Hz] and 128–136 (other aryl C).

CH_3OCH_2OH. A solution of formaldehyde (0.25 cm^3) in MeOH (24.75 cm^3) gave only CH_3OCH_2OH, which was identified by comparison of $^{13}C-\{^1H\}$ NMR data with previously published values.[5] Further support for this assignment came from non-^1H-decoupled ^{13}C NMR measurements which gave values of $^1J(^1H-^{13}C)$ of 140 and 162 Hz for the methyl and methylene resonances, respectively.

NH_2NHCH_2OH. To a solution of CH_3OCH_2OH (2.5 cm^3, 0.31 mmol) prepared as above was added $N_2H_4 \cdot H_2O$ (0.06 cm^3, 1.2 mmol). ^{13}C NMR (MeOH, −30 °C): δ 76.1 [$^1J(^1H-^{13}C)$ 153 Hz].

This compound was also prepared at high concentration in an NMR tube from the reaction of neat formaldehyde (0.59 cm^3, 7.2 mmol) with neat $N_2H_4 \cdot H_2O$ (1.41 cm^3, 29.0 mmol) at −30 °C and shaking for 30 s. The $^{13}C-\{^1H\}$ NMR spectrum at −30 °C showed the presence of NH_2NHCH_2OH and the ^{15}N spectrum at −30 °C consisted of two equally intense singlets, δ −323.2 and −301.7, with no visible coupling to ^1H, presumably because of fast hydrogen exchange.

$NH_2N{=}CH_2$. To a solution of CH_3OCH_2OH (2.5 cm^3, 0.31 mmol) prepared as above was added concentrated HNO_3 (0.04 cm^3, 0.6 mmol) followed by $N_2H_4 \cdot H_2O$ (0.060 cm^3, 1.2 mmol). The ^{13}C NMR data (MeOH, −30 °C) were consistent with the formation of $NH_2N{=}CH_2$: δ 133.2 [dd, $^1J(^1H-^{13}C)$ 160 and 184 Hz]. This compound was also formed by allowing a solution of NH_2NHCH_2OH, in the absence of acid, to stand at room temperature for 45 min. It was also prepared with

Table 1 Phosphorus-31 NMR data at −30 °C

Compound	δ(^{31}P)	$^1J(^{103}Rh-^{31}P)$/Hz	$^2J(^{31}P-^{31}P)$/Hz
1[a]	46.8 (ABX)	176	50
	47.5 (ABX)	175	50
$[PPh_3(CH_2OH)]NO_3$[b]	18.6 (s)	—	—
6[a]	46.9 (dd)	177	49
	49.0 (dd)	173	49
7[a]	47.4 (ABX)	178	49
	47.8 (ABX)	174	49
8[a]	43.5 (dd)	175	51
	45.3 (dd)	173	51
	50.2 (dd)	180	51
	50.9 (dd)	177	51
PPh_3[b]	−5.8 (s)	—	—
$OPPh_3$[b]	34.3 (s)	—	—

[a] In CD_2Cl_2. [b] In MeOH.

Table 2 $\{^1H\}-^{15}N$ INEPT NMR data for di- and mono-nuclear rhodium(I) complexes containing the carbopentazane ligand in $CD_2Cl_2-CH_2Cl_2$ (1:4). Chemical shifts are in ppm and coupling constants in Hz

Compound	T/°C	δ(^{15}N)	Assignment	$^1J(^{103}Rh-^{15}N)$	$^2J(^{31}P_{trans}-^{15}N)$	$^1J(^1H-^{15}N)$
1	−30	−307.2	NH_2	12	30	73
		−308.8	NH	13	29	74
6	−55	−317.4	N_aH_2	12	33	69
		−310.7	N_bH	—	—	72
		−304.5	N_cH	13	32	76
		−306.8	N_dH_2	—	—	66

Table 3 Fractional atomic coordinates (× 10^4) for $[Rh_2(PPh_3)_4\{NH_2NH)_2CH_2\}]^{2+}$ **1**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh(1)	1866.4(2)	880.8(2)	3054.4(3)	C(314)	−934(2)	1338(1)	4724(3)
Rh(2)	1209.9(2)	1734.4(2)	4990.6(3)	C(315)	−366(2)	1610(1)	4878(3)
N(11)	1151(2)	637(2)	3843(3)	C(31)	−268(2)	2078(1)	4297(3)
N(12)	736(2)	1130(2)	3942(3)	C(321)	1002(2)	2553(1)	2840(3)
N(21)	1821(2)	1011(2)	5180(3)	C(322)	1078(2)	2817(1)	1966(3)
N(22)	2277(2)	1071(2)	4533(3)	C(323)	723(2)	3292(1)	1616(3)
C(1)	1454(3)	503(2)	4839(4)	C(324)	292(2)	3503(1)	2140(3)
P(1)	1306(1)	501(1)	1683(1)	C(325)	215(2)	3240(1)	3015(3)
C(111)	15(2)	467(1)	1655(3)	C(32)	571(2)	2765(1)	3365(3)
C(112)	−547(2)	736(1)	1635(3)	C(331)	−85(2)	3039(2)	5839(3)
C(113)	−594(2)	1331(1)	1540(3)	C(332)	−168(2)	3519(2)	6402(3)
C(114)	−79(2)	1657(1)	1465(3)	C(333)	206(2)	3999(2)	6397(3)
C(115)	483(2)	1388(1)	1485(3)	C(334)	663(2)	3999(2)	5828(3)
C(11)	530(2)	793(1)	1580(3)	C(335)	746(2)	3519(2)	5265(3)
C(121)	1591(2)	−539(1)	2653(2)	C(33)	372(2)	3039(2)	5270(3)
C(122)	1563(2)	−1133(1)	2766(2)	P(4)	1722(1)	2263(1)	6208(1)
C(123)	1196(2)	−1463(1)	2051(2)	C(411)	845(2)	2025(1)	7286(3)
C(124)	856(2)	−1199(1)	1222(2)	C(412)	463(2)	2111(1)	7968(3)
C(125)	884(2)	−606(1)	1110(2)	C(413)	490(2)	2625(1)	8491(3)
C(12)	1252(2)	−276(1)	1826(2)	C(414)	899(2)	3053(1)	8332(3)
C(131)	1953(1)	300(2)	178(2)	C(415)	1280(2)	2967(1)	7649(3)
C(132)	2044(1)	282(2)	−793(2)	C(41)	1253(2)	2453(1)	7126(3)
C(133)	1595(1)	492(2)	−1547(2)	C(421)	2372(2)	1690(2)	7892(2)
C(134)	1056(1)	719(2)	−1331(2)	C(422)	2880(2)	1405(2)	8418(2)
C(135)	965(1)	738(2)	−360(2)	C(423)	3404(2)	1337(2)	8011(2)
C(13)	1414(1)	528(2)	394(2)	C(424)	3421(2)	1554(2)	7076(2)
P(2)	2693(1)	1158(1)	2478(1)	C(425)	2914(2)	1838(2)	6549(2)
C(211)	2095(1)	1811(2)	904(3)	C(42)	2389(2)	1906(2)	6957(2)
C(212)	2050(1)	2232(2)	177(3)	C(431)	2410(2)	3299(2)	6505(2)
C(213)	2561(1)	2557(2)	78(3)	C(432)	2726(2)	3751(2)	6169(2)
C(214)	3117(1)	2462(2)	705(3)	C(433)	2737(2)	3805(2)	5168(2)
C(215)	3162(1)	2041(2)	1432(3)	C(434)	2431(2)	3406(2)	4503(2)
C(21)	2651(1)	1716(2)	1531(3)	C(435)	2115(2)	2953(2)	4840(2)
C(221)	3134(2)	54(2)	2518(3)	C(43)	2105(2)	2899(2)	5841(2)
C(222)	3456(2)	−408(2)	2223(3)	N(1)	123(2)	240(2)	6262(3)
C(223)	3766(2)	−346(2)	1439(3)	O(11)	−394(2)	350(2)	6470(3)
C(224)	3753(2)	179(2)	950(3)	O(12)	242(2)	−251(2)	6015(3)
C(225)	3431(2)	640(2)	1245(3)	O(13)	503(2)	637(2)	6300(3)
C(22)	3122(2)	578(2)	2029(3)	N(2)*	2826(20)	159(17)	6306(38)
C(231)	3178(1)	2038(1)	3761(3)	O(21)*	3024(16)	−197(17)	4918(24)
C(232)	3604(1)	2292(1)	4501(3)	O(22)*	2490(6)	183(5)	6682(8)
C(233)	4124(1)	1990(1)	4934(3)	O(23)*	3263(12)	−149(11)	7043(21)
C(234)	4219(1)	1433(1)	4627(3)	O(24)*	3090(7)	196(8)	5601(16)
C(235)	3793(1)	1178(1)	3887(3)	O(25)*	2938(15)	−601(16)	6420(24)
C(23)	3273(1)	1480(1)	3454(3)	O(1)*	5400(6)	20(6)	3736(10)
P(3)	496(1)	2408(1)	4530(1)	O(2)*	1352(12)	4300(11)	46(17)
C(311)	−737(2)	2274(1)	3563(3)	C(2)*	1920(14)	3985(12)	337(18)
C(312)	−1305(2)	2002(1)	3409(3)	C(3)*	2365(16)	4411(15)	106(20)
C(313)	−1403(2)	1535(1)	3990(3)				

* Atom in disordered groups with partial occupancies and a common U_{iso}.

nitrogen-15 enrichment as follows. To a solution of $[^{15}N_2H_6]SO_4$ (33 mg, 0.25 mmol) and KOH (28 mg, 0.50 mmol) in water (0.33 cm^3) was added MeOH (1.16 cm^3) and CD_3OD (0.50 cm^3) which resulted in precipitation of K_2SO_4. The white suspension was then added to a solution of CH_3OCH_2OH (0.51 cm^3, 0.063 mmol) prepared as above and after mixing for 30 s the resulting suspension was left to stand for 45 min. The NMR data for the resulting colourless solution were: $^{13}C\text{-}\{^1H\}$ (−30 °C), δ 134.8 [d, $^1J(^{15}N\text{–}^{13}C)$ 5]; ^{15}N (inverse gated decoupling), δ −269 [d, $^1J(^{15}N\text{–}^{15}N)$ 11, $CH_2{=}^{15}N^{15}NH_2$] and −42.9 [d, $^1J(^{15}N\text{–}^{15}N)$ 11 Hz, $CH_2{=}^{15}N^{15}NH_2$].

$[Rh(PPh_3)_2(NH_2NHCH_2NHNH_2)]NO_3$ 6. To a suspension of $[Rh(PPh_3)_3(ONO_2)]$ **2** (0.111 g, 0.117 mmol) in MeOH (3.1 cm^3) was added formaldehyde (0.076 cm^3, 0.94 mmol) and then $N_2H_4{\cdot}H_2O$ (0.18 cm^3, 3.7 mmol). The mixture was heated to reflux to obtain a clear solution. Upon refrigeration at −30 °C for 7 d yellow crystals were formed. These were filtered off, washed with MeOH and Et_2O and dried *in vacuo*. Yield 63 mg (71%) (Found: C, 57.95; H, 5.55; N, 8.50. $C_{37}H_{38}N_5O_3P_2Rh$ requires C, 58.05; H, 5.00; N, 9.15%). FAB mass spectrum: *m/z* 703, M^+. NMR: ^{13}C (−30 °C, CH_2Cl_2), δ 72.9 [CH_2, $^1J(^1H\text{–}^{13}C)$ 150 Hz] and 128–135 (aryl C), ^{31}P and ^{15}N in Tables 1 and 2, respectively.

$[Rh(PPh_3)_2(NH_2NHCHMeNHNH_2)]^+$ 7. Complex **2** was generated *in situ* by the reaction of $Rh(NO_3)_3{\cdot}2H_2O$ (0.651 g, 2.0 mmol) with PPh_3 (3.68 g, 14.0 mmol) in EtOH (81 cm^3). After stirring this mixture for 45 min, CH_3CHO (1.12 cm^3, 20 mmol) was added and stirring continued for 5 min, followed by addition of $N_2H_4{\cdot}H_2O$ (2.92 cm^3, 60.1 mmol), stirring for 5 min and addition of concentrated HNO_3 (0.25 cm^3, 4 mmol). The resulting mixture was stirred for 5 min, and then stored at −30 °C for 60 d whereupon yellow crystals of the product were formed. These were filtered off, washed with cold EtOH and Et_2O and dried *in vacuo*, but could not be obtained analytically pure. Nevertheless, NMR and mass spectrometric data (FAB mass spectrum: *m/z* 717) are fully consistent with the formulation. NMR: ^{31}P (see Table 1); ^{13}C (−30 °C, CH_2Cl_2), δ

Table 4 Selected bond lengths (Å) and angles (°) for $[Rh_2(PPh_3)_4\{(NH_2NH)_2CH_2\}]^{2+}$ **1**

N(11)–Rh(1)	2.166(6)	N(22)–Rh(1)	2.130(6)	C(11)–P(1)	1.838(5)	C(12)–P(1)	1.829(5)
P(1)–Rh(1)	2.253(3)	P(2)–Rh(1)	2.231(3)	C(13)–P(1)	1.844(6)	C(21)–P(2)	1.837(6)
N(12)–Rh(2)	2.155(6)	N(21)–Rh(2)	2.152(6)	C(22)–P(2)	1.828(6)	C(23)–P(2)	1.849(5)
P(3)–Rh(2)	2.242(3)	P(4)–Rh(2)	2.225(3)	C(31)–P(3)	1.841(6)	C(32)–P(3)	1.848(6)
N(12)–N(11)	1.497(7)	C(1)–N(11)	1.454(7)	C(33)–P(3)	1.842(6)	C(41)–P(4)	1.840(6)
N(22)–N(21)	1.478(7)	C(1)–N(21)	1.467(8)	C(42)–P(4)	1.847(5)	C(43)–P(4)	1.829(6)
N(22)–Rh(1)–N(11)	78.3(3)	P(1)–Rh(1)–N(11)	88.6(2)	C(23)–P(2)–Rh(1)	111.6(2)	C(23)–P(2)–C(21)	99.8(3)
P(1)–Rh(1)–N(22)	164.9(1)	P(2)–Rh(1)–N(11)	170.9(1)	C(23)–P(2)–C(22)	102.1(3)	C(211)–C(21)–P(2)	118.7(3)
P(2)–Rh(1)–N(22)	92.6(2)	P(2)–Rh(1)–P(1)	100.3(2)	C(215)–C(21)–P(2)	121.3(3)	C(221)–C(22)–P(2)	116.7(4)
N(21)–Rh(2)–N(12)	77.9(2)	P(3)–Rh(2)–N(12)	91.8(2)	C(225)–C(22)–P(2)	123.3(4)	C(231)–C(23)–P(2)	118.5(3)
P(3)–Rh(2)–N(21)	169.3(1)	P(4)–Rh(2)–N(12)	172.6(1)	C(235)–C(23)–P(2)	121.5(3)	C(31)–P(3)–Rh(2)	110.0(2)
P(4)–Rh(2)–N(21)	96.7(2)	P(4)–Rh(2)–P(3)	93.8	C(32)–P(3)–Rh(2)	113.0(2)	C(32)–P(3)–C(31)	105.2(3)
N(12)–N(11)–Rh(1)	111.5(4)	C(1)–N(11)–Rh(1)	106.0(4)	C(33)–P(3)–Rh(2)	124.8(2)	C(33)–P(3)–C(31)	101.7(3)
C(1)–N(11)–N(12)	105.4(5)	N(11)–N(12)–Rh(2)	109.2(4)	C(33)–P(3)–C(32)	99.9(3)	C(311)–C(31)–P(3)	122.4(4)
N(22)–N(21)–Rh(2)	110.0(4)	C(1)–N(21)–Rh(2)	106.9(4)	C(315)–C(31)–P(3)	117.6(3)	C(321)–C(32)–P(3)	118.3(3)
C(1)–N(21)–N(22)	106.6(5)	N(21)–N(22)–Rh(1)	109.9(4)	C(325)–C(32)–P(3)	121.7(4)	C(331)–C(33)–P(3)	120.8(4)
N(21)–C(1)–N(11)	105.5(5)	C(11)–P(1)–Rh(1)	106.8(2)	C(335)–C(33)–P(3)	119.2(4)	C(41)–P(4)–Rh(2)	112.3(2)
C(12)–P(1)–Rh(1)	109.6(2)	C(12)–P(1)–C(11)	107.2(2)	C(42)–P(4)–Rh(2)	115.1(2)	C(42)–P(4)–C(41)	102.7(3)
C(13)–P(1)–Rh(1)	130.6(1)	C(13)–P(1)–C(11)	101.5(3)	C(43)–P(4)–Rh(2)	116.1(2)	C(43)–P(4)–C(41)	110.3(3)
C(13)–P(1)–C(12)	99.2(3)	C(111)–C(11)–P(1)	124.5(3)	C(43)–P(4)–C(42)	98.8(3)	C(411)–C(41)–P(4)	113.9(4)
C(115)–C(11)–P(1)	115.4(3)	C(121)–C(12)–P(1)	119.2(3)	C(415)–C(41)–P(4)	126.1(4)	C(421)–C(42)–P(4)	121.9(4)
C(125)–C(12)–P(1)	120.8(3)	C(131)–C(13)–P(1)	117.7(3)	C(425)–C(42)–P(4)	118.1(4)	C(431)–C(43)–P(4)	123.7(4)
C(135)–C(13)–P(1)	122.2(4)	C(21)–P(2)–Rh(1)	121.5(2)	C(435)–C(43)–P(4)	116.2(4)		
C(22)–P(2)–Rh(1)	115.1(2)	C(22)–P(2)–C(21)	104.1(3)				

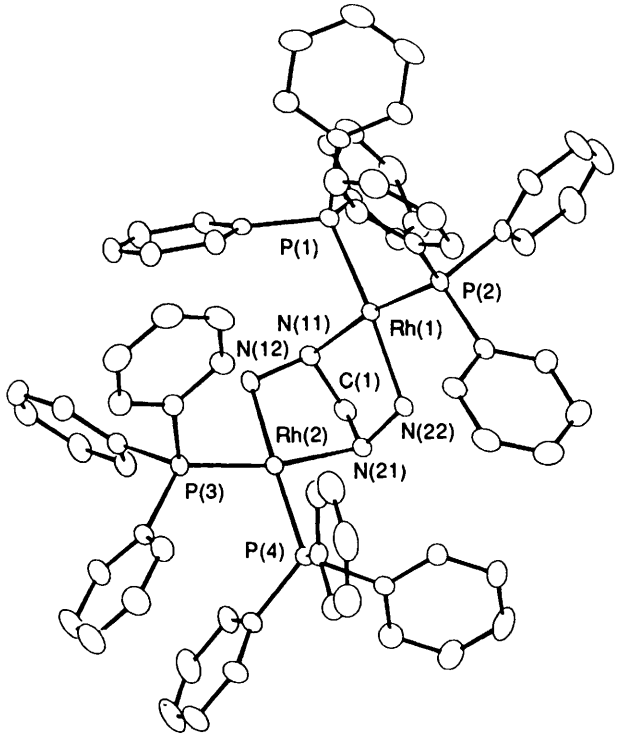


Fig. 1 Molecular structure of $[Rh_2(PPh_3)_4\{(NH_2NH)_2CH_2\}]^{2+}$ **1**

78.9 [$CHCH_3$, $^1J(^1H–^{13}C)$ 146] and 18.3 [$CHCH_3$, $^1J(^1H–^{13}C)$ 127 Hz].

In situ NMR measurements to monitor the formation of complex 1 from 2

2 + NH_2NHCH_2OH + $N_2H_4·H_2O$. The compound NH_2N-HCH_2OH was generated *in situ* by the addition of $N_2H_4·H_2O$ (0.0055 cm^3, 0.11 mmol) to a 0.123 mol dm^{-3} solution of CH_3OCH_2OH (0.23 cm^3, 0.028 mmol). The resulting solution was immediately added to a solution of complex **2** (27 mg, 0.028 mmol) in CH_2Cl_2–MeOH (1 : 1, 2 cm^3) in an NMR tube. The ^{31}P-$\{^1H\}$ NMR spectrum was monitored with time at room temperature and showed the immediate formation of $[Rh_2(PPh_3)_4(\mu\text{-}N_2H_4)_2][NO_3]_2$ **3** which was completely converted into **1** after 30 min.

2 + $NH_2N{=}CH_2$ + $N_2H_4·H_2O$. The compound $NH_2N{=}CH_2$ was formed by allowing a solution of NH_2NHCH_2OH to stand for 45 min as described above. This solution was then added to a solution of complex **2** in CH_2Cl_2–MeOH (1 : 1) as described above. Similar ^{31}P NMR spectra were observed but the formation of **1** was complete within 20 min.

2 + $NH_2N{=}CH_2$ + $N_2H_4·H_2O$ + HNO_3. As above, except that concentrated HNO_3 (0.0035 cm^3, 0.056 mmol) was added prior to the addition of $N_2H_4·H_2O$. The ^{31}P NMR spectrum in this case showed the immediate formation of **1** only.

Results and Discussion

Structural and spectroscopic characterisation of complex 1

A diagram of the dinuclear cation, **1**, is shown in Fig. 1 and selected bond lengths and angles are given in Table 4. The Rh–P and Rh–N distances each show some variation, but there is no correlation with the slightly different character of the two types of nitrogen, NH_2 and NHR. The P_2RhN_2 units are both reasonably planar (maximum deviation 0.08 Å), although there are considerable differences in the distribution of angles in the square planes. In particular, the P–Rh–P angles differ by more than 6°. These differences are presumably due to packing effects.

The ^{31}P-$\{^1H\}$ NMR spectrum at 81 MHz of a solution of complex **1** in CD_2Cl_2 (Fig. 2) shows the characteristic AB component of an ABX spin system (X = ^{103}Rh) and the ^{13}C-$\{^1H\}$ NMR spectrum contains a singlet at δ 73.1, which with proton coupling becomes a triplet due to $^1J(^1H–^{13}C)$ 156 Hz. The refocused ^1H-decoupled $\{^1H\}$-^{15}N INEPT (insensitive nuclei enhanced by polarisation transfer) spectrum consists of two resonances which are both doublets of doublets due to $^1J(^{103}Rh–^{15}N)$ and $^2J(^{31}P_{trans}–^{15}N)$. The ^1H-coupled INEPT spectrum shows that the resonance at δ −307.2 is due to the NH_2 group, whereas that at δ −308.8 is due to the NH group; these data are summarised in Table 2 and are entirely in accord with the crystal structure for **1**. The ^{15}N NMR measurements using the INEPT pulse sequence, as well as direct ^{15}N NMR measurements, were carried out as described previously.[6]

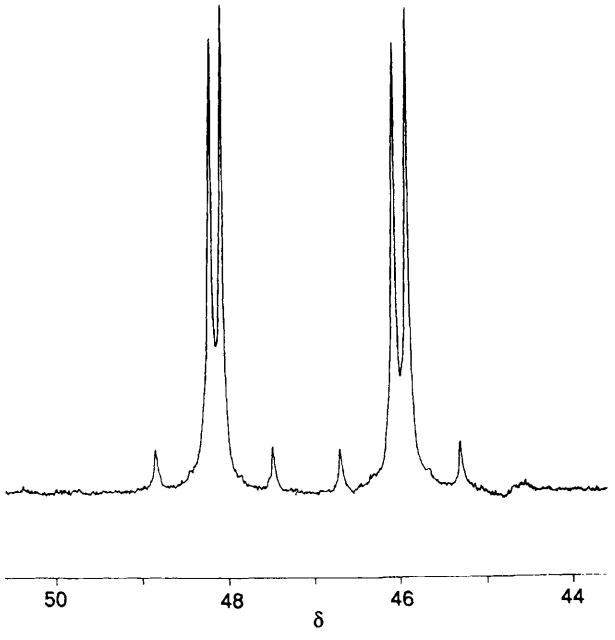


Fig. 2 The $^{31}P-\{^1H\}$ NMR spectrum (81 MHz) of $[Rh_2(PPh_3)_4\{(NH_2NH)_2CH\}]^{2+}$ **1** at −30 °C in CD_2Cl_2

Mechanism of formation of complex 1

In order to gain insight into the mechanism of formation of complex **1** from the reaction of $Rh(NO_3)_3{\cdot}2H_2O$, PPh_3 and $N_2H_4{\cdot}H_2O$ in MeOH, we have separately investigated reactions involving different combinations of the individual components.

A solution of $Rh(NO_3)_3{\cdot}2H_2O$ in MeOH gives CH_3OCH_2OH which has identical ^{13}C NMR resonances to those found for a sample prepared *via* the addition of HCHO to MeOH as described in the Experimental section. This oxidation of MeOH by Rh^{III} is in keeping with the formation of rhodium(I) complexes [equation (1)].

$$2MeOH + Rh^{III} \longrightarrow CH_3OCH_2OH + Rh^{I} + 2H^{+} \quad (1)$$

Addition of MeOH to a mixture of $Rh(NO_3)_3{\cdot}2H_2O$ and PPh_3 (1:5) at room temperature results in the formation of an orange solution together with a little yellow precipitate. The $^{31}P-\{^1H\}$ NMR spectrum of the orange solution showed the presence of $[Rh(PPh_3)_3(ONO_2)]$ **2**, PPh_3, $OPPh_3$ and a singlet resonance at δ 18.6 which has been indentified as due to $[PPh_3(CH_2OH)]NO_3$ by comparison with an authentic sample prepared as described in the Experimental section. The appearance of this compound is rather unexpected but both it [equation (2)] and CH_3OCH_2OH [equation (1)] act as

$$PPh_3 + CH_3OCH_2OH + HNO_3 \longrightarrow [PPh_3(CH_2OH)]NO_3 + MeOH \quad (2)$$

reservoirs for HCHO which is the source of the CH_2 group in **1**, see below.

It has been proposed that PPh_3 acts as a reducing agent in the formation of $[Rh(PPh_3)_3Cl]$ starting from $RhCl_3{\cdot}3H_2O$ and PPh_3.[7] However, no spectroscopic evidence has been presented to substantiate this, but on carrying out this reaction in EtOH we do find evidence for the intermediate formation of Ph_3PCl_2 [$\delta(^{31}P)$ 62.5] before hydrolysis (15 min) occurs to give $OPPh_3$. It is thus reasonable to assume that analogous reactions [equations (3) and (4)] occur on reaction of Rh-

$$Rh(NO_3)_3{\cdot}2H_2O + 4PPh_3 \longrightarrow \underset{\mathbf{2}}{[Rh(PPh_3)_3(ONO_2)]} + Ph_3P(ONO_2)_2 \quad (3)$$

$$Ph_3P(ONO_2)_2 + H_2O \longrightarrow 2HNO_3 + OPPh_3 \quad (4)$$

$(NO_3)_3{\cdot}2H_2O$ with PPh_3 in MeOH *in the absence of* N_2H_4. However, we have no spectroscopic evidence for the formation of $Ph_3P(ONO_2)_2$ [equation (3)] and $OPPh_3$ is only formed in trace amounts. As a result, the reduction of Rh^{III} in the reaction of $Rh(NO_3)_3{\cdot}2H_2O$ with PPh_3 in MeOH *in the absence of* N_2H_4 occurs predominantly *via* equation (1) rather than *via* (3). Complex **2** then results according to equation (5).

$$Rh^{I}(NO_3) + 3PPh_3 \longrightarrow \underset{\mathbf{2}}{[Rh(PPh_3)_3(ONO_2)]} \quad (5)$$

In order to understand the effect of hydrazine, we have sequentially investigated the reaction of hydrazine with the products from equations (1), (2) and (5).

The reaction of CH_3OCH_2OH with $N_2H_4{\cdot}H_2O$ (1:4) is very dependent on the acidity of the solution and the concentration of hydrazine present. In the absence of acid as described in the Experimental section, NH_2NHCH_2OH is formed which slowly eliminates water to give $NH_2N{=}CH_2$ [equation (6)]. When acid

$$CH_3OCH_2OH + N_2H_4 \xrightarrow{-MeOH} NH_2NHCH_2OH \xrightarrow{-H_2O} NH_2N{=}CH_2 \quad (6)$$

is present, the latter is formed immediately (see Experimental section).

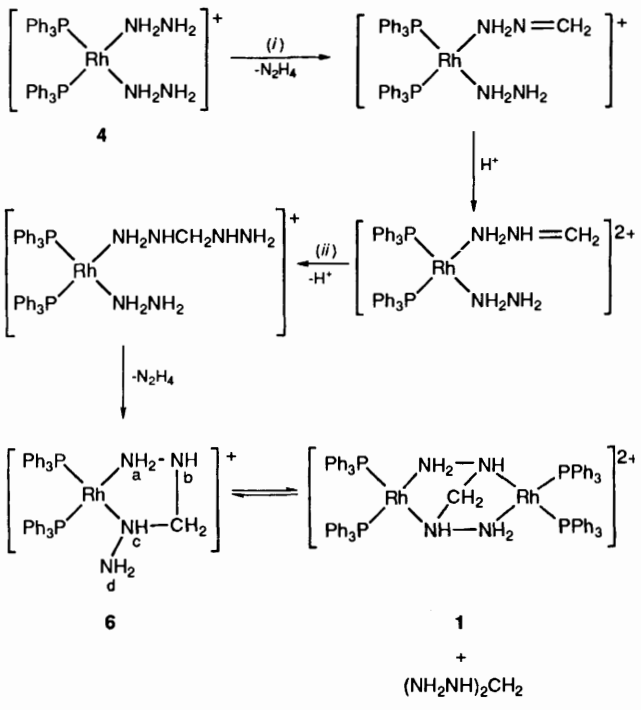
Although no NMR data for NH_2NHCH_2OH and $NH_2N{=}CH_2$ have previously been reported, the variations in their ^{13}C chemical shift data and those of other homologues, $NH_2NHCRR'OH$ (R = Me; R' = H, Me, Et or CH_2Ph) and $NH_2N{=}CRR'$ (R = Me; R' = Et or CH_2Ph),[8] are entirely consistent with the formulations given. If the ratio of $CH_3OCH_2OH:N_2H_4$ is increased (2:1), then a white insoluble product is obtained which appears to be polymeric. However, this has not been further investigated since the optimum formation of **1** occurs in the presence of an excess of hydrazine.

It has been shown by monitoring ^{31}P and ^{13}C NMR spectra that addition of an excess of $N_2H_4{\cdot}H_2O$ to $[PPh_3(CH_2OH)]NO_3$ in MeOH results in an immediate reaction, (7) followed by (6).

$$[PPh_3(CH_2OH)]NO_3 + N_2H_4 \xrightarrow{MeOH} PPh_3 + CH_3OCH_2OH + [N_2H_5][NO_3] \quad (7)$$

Previous NMR measurements have shown that a solution of pure $[Rh(PPh_3)_3(ONO_2)]$ in the presence of hydrazine can be converted into $[Rh(PPh_3)_3(N_2H_4)]^{+}$ **5** in CH_2Cl_2–MeOH (1:1) and sequentially to $[Rh_2(PPh_3)_4(\mu\text{-}N_2H_4)_2]^{2+}$ **3** and $[Rh(PPh_3)_2(N_2H_4)_2]^{+}$ **4** in CH_2Cl_2.[2] Addition of $N_2H_4{\cdot}H_2O$ at low temperature to a solution of $Rh(NO_3)_3{\cdot}2H_2O$ and PPh_3 in MeOH, followed by variable-temperature ^{31}P NMR measurements, show the presence of all of these species in the reaction solution, together with a new species $[Rh(PPh_3)_2(NH_2NHCH_2NHNH_2)]NO_3$ **6** which appears to be a key intermediate in the formation of **1** (see Scheme 1). Complex **6** is also formed on reaction of $[Rh(PPh_3)_3(ONO_2)]$ in methanol solution with an excess of hydrazine in the presence of a moderate excess (8 mol) of HCHO. X-Ray-quality crystals of it have not yet been obtained, but the structure has been deduced from spectroscopic data (see Experimental section).

It is difficult to establish whether the formation of complex **6** involves an acid-catalysed, inter- or intra-molecular process,



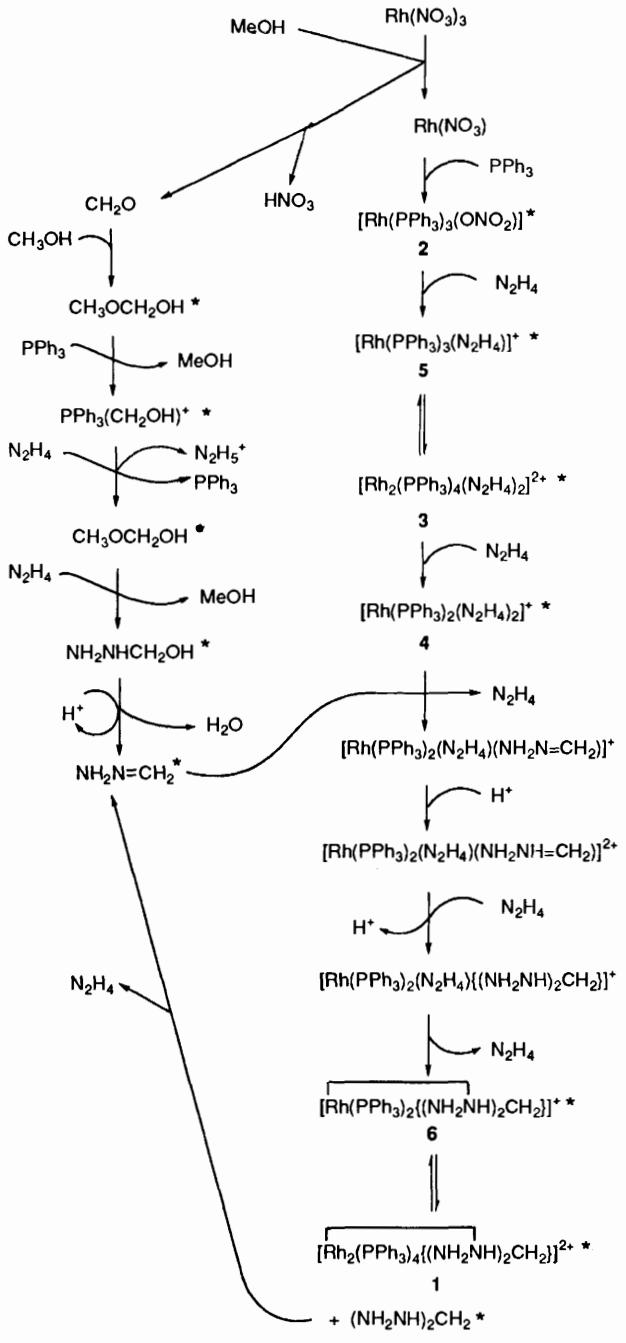
Scheme 1 Mechanism of formation of the $-NHCH_2NH-$ linkage in complex **1**. (*i*) $NH_2N{=}CH_2$; (*ii*) N_2H_4

but we presently favour the intermolecular mechanism shown in Scheme 1. This should be preferred because of the higher nucleophilicity of free rather than complexed hydrazine. Having formed **6**, then formation of the dinuclear complex **1** is straightforward and it should be noted that dissolution of **6** in CH_2Cl_2–MeOH (1:1) at room temperature results in the clean formation of **1** (from ^{31}P NMR spectra) and another species, $\delta(^{13}C)$ (at −30 °C) 68.1, which we believe to be free $(NH_2NH)_2CH_2$. The preparation of the latter has been previously reported,[9] but the compound was not well characterised due to its instability. The resonance at δ 68.1 attributed to it quickly disappears with a possible mode of decomposition being as shown in Scheme 2.

In an attempt to mimic the reaction conditions used for the formation of complex **1** in order to produce complexes containing the methyl-substituted carbopentazane ligand, we found that the reaction of $[Rh(PPh_3)_3(ONO_2)]$ **2** with an excess of MeCHO and an excess of N_2H_4 in EtOH, in the presence of HNO_3, gave yellow crystals which could not be obtained analytically pure, but nevertheless provided excellent spectroscopic evidence for the formation of the desired products. Thus, NMR and mass spectra of the first-formed product were entirely consistent with the formation of the monomeric complex $[Rh(PPh_3)_2(NH_2NHCHMeNHNH_2)]^+$ **7** (see Table 1 and Experimental section). A solution of **7** in CH_2Cl_2 slowly gives $[Rh_2(PPh_3)_4\{(NH_2NH)_2CHMe\}]^{2+}$ **8** and, consistent with this formulation, the ^{31}P NMR spectrum of **8** showed the presence of four equally intense doublets of doublets due to the four inequivalent PPh_3 (see Table 1). This reinforces the validity of the mechanism of formation of **1** shown in Scheme 2.

Conclusion

This research provides strong evidence that the mechanism of formation of complex **1** is as shown in Schemes 1 and 2. The formation of the $NHCH_2NH$ linkage is of particular interest since this must involve a metal-mediated reaction of a hydrazone with hydrazine which has not previously been reported. Significant new multinuclear NMR spectroscopic



Scheme 2 Summary of the mechanism of formation of complex **1** from $Rh(NO_3)_3{\cdot}2H_2O$, PPh_3 and $N_2H_4{\cdot}H_2O$ in MeOH. Spectroscopic evidence has been obtained for sequential formation of all the asterisked compounds and **1**–**3** have been crystallographically characterised

data for formaldehyde derivatives and for carbopentazane derivatives, *i.e.*, **1**, **6**–**8**, have been obtained and this work clearly illustrates the power of *in situ* multinuclear variable-temperature NMR studies as a spectroscopic technique for mechanistic investigations.

The complexes containing $NH_2N{=}CH_2$ are clearly important reactive intermediates. Whereas most hydrazone complexes involve co-ordination *via* the imino-N atom,[10] the formation of **1** (Schemes 1 and 2) is observed to be acid catalysed which strongly suggests that co-ordination of $NH_2N{=}CH_2$ is *via* the amino-N and not the imino-N atom. Little research has been carried out on the co-ordination of simple hydrazones. Our studies in this area are continuing.

Acknowledgements

We thank the SERC for a studentship (to G. L. M.).

References

1 B. T. Heaton, J. A. Iggo, C. Jacob, H. Blanchard, M. B. Hursthouse, I. Ghatak, M. E. Harman, R. G. Somerville, W. Heggie, P. R. Page and I. Villax, *J. Chem. Soc., Dalton Trans.*, 1992, 2533.
2 B. T. Heaton, C. Jacob, G. L. Monks, J. Ratnam, M. B. Hursthouse, I. Ghatak, H. Lieberman, R. G. Somerville, W. Heggie, P. R. Page and I. Villax, unpublished work.
3 W. Heggie, P. R. Page, I. Villax, I. Ghatak and M. B. Hursthouse, *Eur. Pat.*, 0 283 616, 1987.
4 G. M. Sheldrick, SHELX 80, enlarged version of SHELX 76, University of Cambridge, 1976.
5 B. Tomita and S. Hatono, *J. Polym. Sci.*, 1978, **16**, 2509.
6 B. T. Heaton, C. Jacob, W. Heggie, P. R. Page and I. Villax, *Magn. Reson. Chem.*, 1991, **29**, S21.
7 J. A. Osborn and G. Wilkinson, *Inorg. Synth.*, 1967, **10**, 67.
8 J. A. Chudek, R. Foster and D. Young, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1285.
9 E. Fluck and H. Schultheiss, *Liebigs Ann. Chem.*, 1974, 1851.
10 M. J. Prendergast, M.Sc. Thesis, University of Liverpool, 1987.

Received 8*th June* 1995; *Paper* 5/03702F