

Journal of Organometallic Chemistry, 405 (1991) 393–402
 Elsevier Sequoia S.A., Lausanne
 JOM 21415

Synthesis and reactions of di, tri- and tetra-nuclear cationic complexes derived from bis(μ -methylene-pentamethylcyclopentadienyl)dirhodium: the crystal structure of tetranuclear $\{[(C_5Me_5Rh-\mu-CH_2)_2]_2(\mu-CN)_2\}(PF_6)_2$

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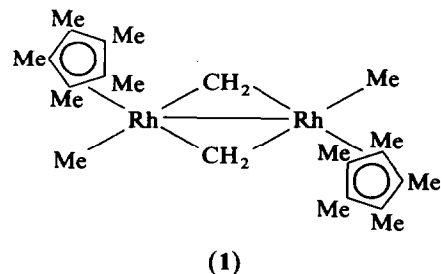
(Received August 31st, 1990)

Abstract

The new di- or tri-nuclear cationic complexes $[(C_5Me_5Rh-\mu-CH_2)_2(Me)(L)]PF_6$ ($L = Me_3P$, **2b**; $(MeO)_3P$, **2c**; $MeNC$, **2d**; $t-BuNC$, **2e**; $C_5Me_5Rh(CO)(Me)(4-C_5H_4N)$, **2f**; and $C_5Me_5Ir(CO)(Me)(4-C_5H_4N)$, **2g**), were made by displacement of acetonitrile by L in $[(C_5Me_5Rh-\mu-CH_2)_2(Me)(MeCN)]PF_6$, **2a**. Reaction of **2a** with $Hg(CN)_2$ gave $\{[(C_5Me_5Rh-\mu-CH_2)_2]_2(\mu-CN)_2\}(PF_6)_2$, **4**. A single crystal X-ray structure determination showed **4** to contain the unexpected feature of a tetranuclear cluster dication comprising two $\{(C_5Me_5Rh-\mu-CH_2)_2\}$ units, linked by two cyano ligands bridging two rhodiums. Reaction of $\{[(C_5Me_5Rh-\mu-CH_2)_2(Me)]_2\}$ with $Hg(CN)_2$ gave $\{(C_5Me_5Rh-\mu-CH_2)_2(Me)(CN)\}$.

Introduction

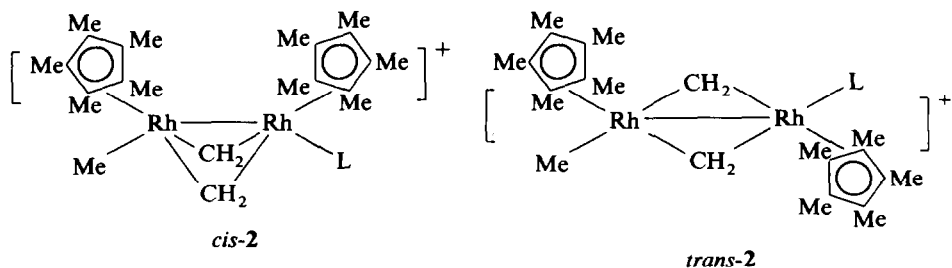
The syntheses and reactions of bis(μ -methylene-pentamethylcyclopentadienyl)dirhodium complexes derived from **1** have been presented in a number of papers from this Laboratory [1]. These include *cis*- and *trans*- $\{[(C_5Me_5Rh-\mu-CH_2)_2(Me)(L)]^+\}$, (**2**) [2] as well as complexes of the types *cis*- or *trans*- $\{[(C_5Me_5Rh-\mu-CH_2)_2(X)]_2\}$, [3] *trans*- $\{[(C_5Me_5Rh-\mu-CH_2)_2(L)]_2\}^{2+}$, [3], and *cis*- $\{[(C_5Me_5Rh-\mu-CH_2)_2(\mu-X)]^+\}$, [4] ($X =$ anionic, $L =$ neutral ligand). We now report further complexes of type (**2**) but with strongly bound ligands, such as PMe_3 , in place of the more labile $MeCN$ or CO , and a remarkable tetranuclear dicationic complex held together by two pairs of μ -methylene and one pair of μ -cyano ligands.



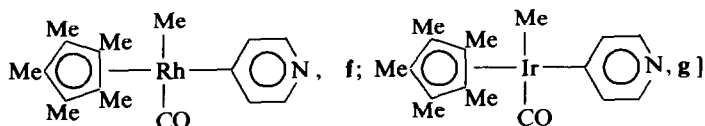
Results and discussion

Monomethyl salts, $[(C_5Me_5Rh-\mu-CH_2)_2(Me)(L)]PF_6$

The di- or tri-nuclear complexes $[(C_5Me_5Rh-\mu-CH_2)_2(Me)(L)]PF_6$ [$L = Me_3P$, **2b**; $(MeO)_3P$, **2c**; $MeNC$, **2d**; $t-BuNC$, **2e**; $C_5Me_5Rh(CO)(Me)(4-C_3H_4N)$, **2f**; and $C_5Me_5Ir(CO)(Me)(4-C_3H_4N)$, **2g**], were made by displacement of acetonitrile by L in $[(C_5Me_5Rh-\mu-CH_2)_2(Me)(MeCN)]PF_6$, (**2a**). The 4-metallopyridyl ligands used to make **2f** and **2g** have recently been described [5].



[$L = Me_3P$, **b**; $(MeO)_3P$, **c**; $MeNC$, **d**; $t-BuNC$, **e**;

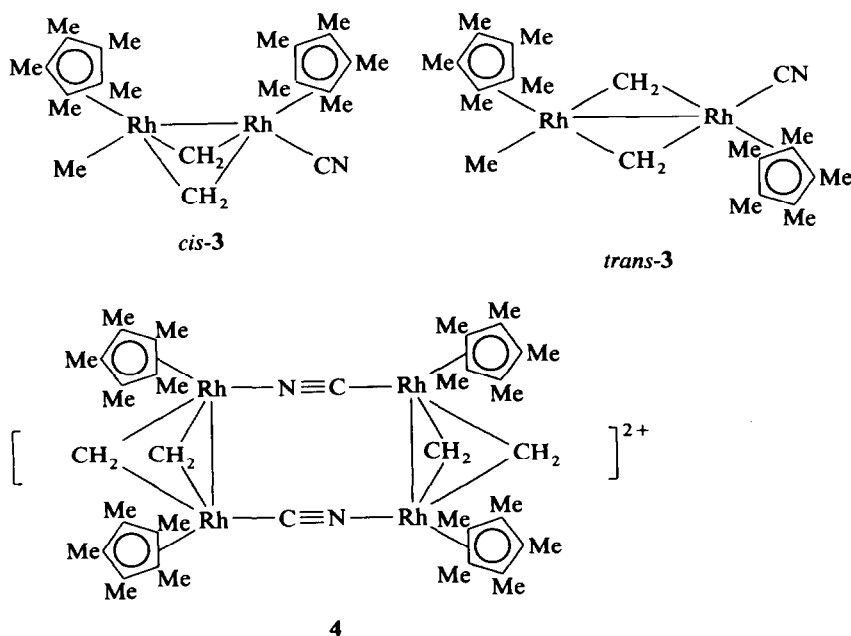


Each of the complexes **2** can have the C_5Me_5 rings either *cis*- or *trans*- to each other. In practice, the complexes **2b** and **2c** contained only one isomer, the *trans*-, while two isomers, *cis*- and *trans*- were present in **2d**, **2e**, **2f** and **2g**, the *trans*-predominating. The isomers were identified by their 1H NMR spectra: the methylens are related by a plane of symmetry [through the two Rh's and perpendicular to the $(Rh-\mu-CH_2)_2$ unit], but within each the hydrogens are diastereotopic. Thus each isomer shows two signals in the methylene region of the 1H spectrum. We have previously shown that for *trans*-complexes of type **2**, $\Delta\delta$, difference in chemical shift between the methylene resonances, is generally < 0.5 ppm, while for the *cis*-complex $\Delta\delta$ is usually > 0.5 ppm. This rule of thumb also works well here, and shows that the single isomer found for **2b** and **2c** was *trans*. The isomers for **2d**–**2g** could readily be distinguished; thus for example in **2d** the isomer assigned the *trans*-configuration has the methylenes at δ 8.24 and 8.29, while in the *cis*- they come at δ 8.14 and 9.29. The trinuclear $IrRh_2$ -pyridyl complex *trans*-**2g** showed the methylenes as four multiplets; this indicates the loss of the plane of symmetry and is probably due to restricted rotation of the $C_5Me_5Ir(CO)(Me)C_5H_4N-$, making one conformer preferred.

The ^{13}C NMR spectra of complexes **2** also showed two different C_5Me_5 rings, while the methylene carbons were observed as a double doublet for each isomer, arising from coupling to the two different rhodiums, with $J(Rh-C)$ typically 23 and 28 Hz respectively. It may also be noted that the Rh-methyls on the *trans*-isomers were significantly to lower field (δ 6–9) than in the *cis* ($\delta < 0$); $J(Rh-C)$ was similar in both cases, ca 32 Hz.

Cyano complexes: *cis*- and *trans*- $[(C_5Me_5Rh-\mu-CH_2)_2(Me)(CN)]$ and $[\{(C_5Me_5Rh-\mu-CH_2)_2\}_2(\mu-CN)_2](PF_6)_2$

Reaction of the dichloro-complex $[(C_5Me_5Rh-\mu-CH_2)_2Cl_2]$ with NaCN was shown to give the dicyano-complex, $[(C_5Me_5Rh-\mu-CH_2)_2(CN)_2]$ [3]. By contrast, reaction of **1**, in dichloromethane, with $Hg(CN)_2$ (ratio, 2:1) in methanol, gave a mixture of *cis*- and *trans*-isomers (ratio 12:1) of $[(C_5Me_5Rh-\mu-CH_2)_2(Me)(CN)]$, **3**, identified as described above. Both the red *cis*- and the yellow *trans*-isomers were separated pure by column chromatography; they showed $\nu(CN)$ bands at 2109 and 2110 cm^{-1} , respectively, due to the presence of terminal Rh-CN. The use of higher ratios of $Hg(CN)_2$ to **1** gave increasing amounts of $[(C_5Me_5Rh-\mu-CH_2)_2(CN)_2]$ in addition to **3**. The NMR spectra of crude reaction mixtures showed the presence of methyl-mercury species; hence great care must be taken in carrying out such reactions.



An unexpected ionic product was formed when **2a** was reacted with $Hg(CN)_2$; this was identified as the tetranuclear dication $[\{(C_5Me_5Rh-\mu-CH_2)_2\}_2(\mu-CN)_2](PF_6)_2$, **4**, spectroscopically and by an X-ray crystal structure determination. FAB mass spectrometry showed peaks at m/z 1060 and 1250, corresponding to $[\{(C_5Me_5Rh-\mu-CH_2)_2\}_2(\mu-CN)_2]$ and $[\{(C_5Me_5Rh-\mu-CH_2)_2\}_2(\mu-CN)_2](PF_6)$, with loss of two and one PF_6 respectively. The IR spectrum showed $\nu(CN)$ at 2155 cm^{-1} , higher than in **3** at 2110 cm^{-1} , and consistent with the presence of a $\mu-CN$ bridge between two rhodiums. The NMR spectra showed the presence of two different C_5Me_5 rings (one attached to Rh-NC-, the other to Rh-CN-), and one type of *cis*-(Rh- μ -CH₂)₂ unit.

The X-ray structure (Fig. 1; Table 1) shows that the dication comprises a centrosymmetric tetranuclear loose cluster in which each of the independent rhodiums carries an approximately symmetrically bonded $\eta^5-C_5Me_5$ (r.m.s. deviation of ring atoms from mean planes 0.005 and 0.001 Å; perpendicular distances of

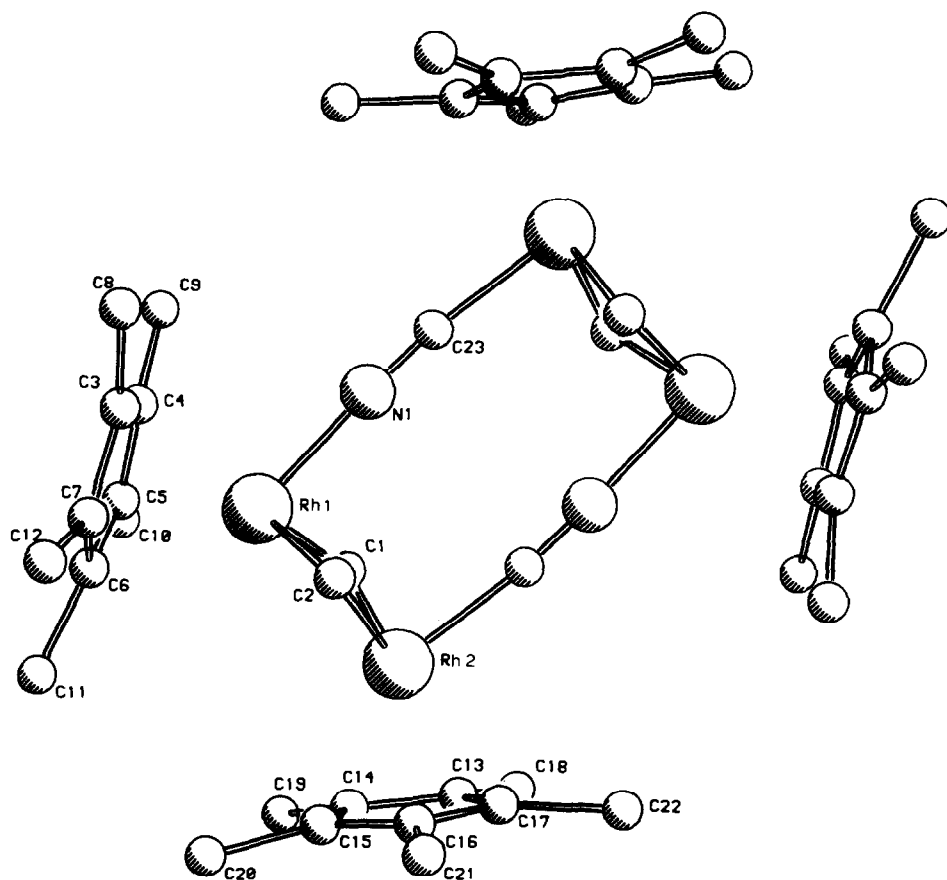


Fig. 1. The structure of the dication $[\{(C_5Me_5Rh-\mu-CH_2)_2(\mu-CN)_2\}]^{2+}$, **4**, hydrogens omitted.

Rh's 1.896, 1.898 Å). The methyls are all displaced away from the rhodium (0.12–0.32 Å). Adjacent Rh's are bridged alternately by two methylenes (mean Rh–C 2.04 Å) or a linear μ -CN; it is likely that the CN is disordered, end-for-end. The four rhodiums are necessarily coplanar.

Experimental

All reactions were carried out in Schlenk apparatus, under nitrogen; typical preparations are given. Yields, microanalytical and IR data are collected in Table 2, 1H and ^{13}C NMR spectra in tables 3 and 4. Microanalyses were carried out by the University of Sheffield microanalytical service; 1H and ^{13}C NMR spectra were run on a Bruker AM-250 spectrometer, and IR spectra on a Perkin Elmer 1710 FT spectrometer.

Synthesis of $[(C_5Me_5Rh-\mu-CH_2)_2(Me)(L)]PF_6$ ($L=PMe_3$)

Trimethylphosphine (0.1 cm³, 1 mmol) was added to a stirred solution of $[(C_5Me_5Rh-\mu-CH_2)_2(Me)(MeCN)]PF_6$, **2a**, (0.24 g, 0.34 mmol) in acetonitrile–di-

Table 1

Atomic coordinates ($\times 10^4$) and temperature factors ($\text{\AA}^2 \times 10^3$) for $[(C_5Me_5Rh-\mu-CH_2)_2(\mu-CN)_2](PF_6)_2$, **4**

| Atom | x | y | z | U_{eq}^a |
|-------|-----------|-----------|-----------|------------|
| Rh(1) | -1289(2) | 1007(1) | 842(1) | 40(1) |
| Rh(2) | -676(1) | 72(1) | 1992(1) | 36(1) |
| P(1) | 4528(7) | 1740(2) | 4948(4) | 73(2) |
| N(1) | -512(17) | 639(5) | -329(9) | 56(5) |
| C(1) | -2592(18) | 271(6) | 904(10) | 46(5) |
| C(2) | 808(19) | 718(7) | 1676(11) | 52(6) |
| C(3) | -1059(18) | 1906(6) | 373(11) | 46(5) |
| C(4) | -2648(21) | 1696(7) | -85(12) | 58(6) |
| C(5) | -3498(26) | 1585(8) | 666(15) | 74(8) |
| C(6) | -2468(30) | 1735(8) | 1574(15) | 80(9) |
| C(7) | -963(25) | 1928(7) | 1405(12) | 72(7) |
| C(8) | 177(26) | 2126(8) | -196(15) | 88(9) |
| C(9) | -3343(23) | 1666(8) | -1180(12) | 74(8) |
| C(10) | -5265(22) | 1417(10) | 524(20) | 109(12) |
| C(11) | -3027(36) | 1814(10) | 2537(16) | 137(15) |
| C(12) | 454(32) | 2183(8) | 2111(17) | 126(13) |
| C(13) | -1636(24) | -599(7) | 2881(10) | 60(7) |
| C(14) | -2098(17) | -32(8) | 3189(10) | 54(6) |
| C(15) | -692(20) | 280(7) | 3597(10) | 57(6) |
| C(16) | 676(18) | -67(7) | 3566(9) | 48(5) |
| C(17) | 64(22) | -595(7) | 3131(10) | 56(6) |
| C(18) | -2728(35) | -1086(11) | 2513(15) | 140(14) |
| C(19) | -3830(23) | 154(13) | 3153(15) | 119(13) |
| C(20) | -564(29) | 872(7) | 4117(13) | 87(9) |
| C(21) | 2393(21) | 70(12) | 4033(14) | 97(10) |
| C(22) | 1107(30) | -1132(8) | 3062(13) | 100(11) |
| C(23) | -129(17) | 403(5) | -970(8) | 33(4) |
| F(1) | 4056(23) | 1441(7) | 3893(11) | 149(9) |
| F(2) | 4064(25) | 2319(6) | 4418(14) | 172(10) |
| F(3) | 4910(25) | 2055(8) | 5937(11) | 177(10) |
| F(4) | 4938(24) | 1172(6) | 5422(15) | 178(10) |
| F(5) | 6261(18) | 1872(10) | 4806(14) | 179(11) |
| F(6) | 2739(18) | 1641(8) | 5032(13) | 148(9) |

^a Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

chloromethane (1 : 1, 5 cm³). The colour of the solution darkened immediately from red to deep red; the solution was stirred (15 min/20 °C), filtered, and reduced in volume to 2 cm³. On addition of diethyl ether (50 cm³) dark red microcrystals of **2b** (0.19 g, 75%) were obtained. The complex decomposed in air, especially in solution; the complexes **2c**–**2g** were prepared similarly but were appreciably less sensitive.

Synthesis of $[(C_5Me_5Rh-\mu-CH_2)_2(Me)CN]$

A solution of $[(C_5Me_5Rh-\mu-CH_2)_2Me_2]$, **1**, (0.5 g, 0.94 mmol) in CH₂Cl₂ (25 cm³) was added to a vigorously stirred solution of Hg(CN)₂ (0.118 g, 0.47 mmol) in methanol (25 cm³) at 20 °C. The mixture was stirred (4 h) and the solvent removed in vacuo to leave a red solid, shown by NMR to be a mixture of *cis*- and *trans*-**3**, yield, 0.380 g, 75%. [CAUTION: Highly toxic and possibly volatile methyl-mercury compounds are also formed in this reaction (¹H NMR δ 0.89, $J(^{199}Hg-H)$ 170 Hz).

Table 2

Yields, and microanalytical, mass-spectroscopic and IR spectral data

| Complex | Yield (%) | Microanalyses ^a | | | IR ^b (cm ⁻¹) | MS (m/z) | Isomer ratio <i>cis/trans</i> ^c |
|-------------------------|-----------|----------------------------|--------------|--------------|---------------------------------------|--|---|
| | | C | H | N | | | |
| 2b | 75 | 41.6 (42.2) | 6.4 (6.3) | | PF ₆ 844 s | | all <i>trans</i> |
| 2c | 80 | 39.2 (39.6) | 6.0 (5.9) | | PF ₆ 844 s | | all <i>trans</i> |
| 2d | 75 | 41.75 (42.6) | 5.5 (5.7) | 1.9 (2.0) | PF ₆ 852 s,br CN 2218 s | | 1/3 |
| 2e | 70 | 44.7 (45.0) | 6.6 (6.2) | 1.9 (1.9) | PF ₆ 844 s CN 2186 s | 602 (<i>M</i> - PF ₆) | 1/4 |
| 2f | 75 | 45.3 (46.9) | 5.6 (5.8) | 1.4 (1.4) | CO 2018 ^d | 878 (<i>M</i> - PF ₆) | 3/7 |
| 2g | 70 | 43.2 (43.2) | 5.3 (5.3) | 1.2 (1.3) | CO 1996 ^d | | 3/7 |
| <i>cis</i> - 3 | | 52.6 (52.9) | 6.9 (6.8) | 2.5 (2.6) | CN 2109 | 546 (<i>M</i> + 1) 530 (<i>M</i> - Me) | |
| <i>trans</i> - 3 | | 53.4 (52.9) | 7.0 (6.8) | 2.6 (2.6) | CN 2110 | | |
| 4 | 60 | 40.9 (40.9) | 5.1 (5.1) | 2.0 (2.1) | CN 2155 PF ₆ 849 s | 1205 (<i>M</i> - PF ₆) 1060 (<i>M</i> - 2 PF ₆) | |

^a Analysis. Found (calcd.) (%). ^b IR in Nujol mulls except where indicated. ^c *cis/trans* ratios by ¹H NMR spectra. ^d IR in CH₂Cl₂ solution.

All operations must therefore be carried out in a well-ventilated fume-cupboard in accordance with safety regulations.] The isomers were separated by chromatography in diethyl ether on deactivated neutral alumina (10 cm³ water to 100 cm³ alumina) to give the red *cis*- (0.35 g) and the yellow *trans*- (0.03 g) isomers.

Synthesis of $\{[(C_5Me_5Rh-\mu-CH_2)_2]_2(\mu-CN)_2\}(PF_6)$

$\{[(C_5Me_5Rh-\mu-CH_2)_2(Me)(MeCN)]PF_6\}$, **2a**, (0.15 g, 0.21 mmol) was added to a stirred solution of mercury cyanide (0.052 cm³, 0.21 mmol) in methanol (20 cm³). The colour of the solution slowly changed from red to orange and a yellow solid precipitated over 10 h. The volume of the solution was reduced (to 5 cm³), and the yellow solid **4** filtered off (yield 0.85 g, 60%) and recrystallised. [**Caution: Highly toxic methyl-mercury compounds are also formed in this reaction, and all operations must therefore be carried out in a well-ventilated fume-cupboard in accordance with safety regulations.**] The use of excess Hg(CN)₂ gave increasing amounts of $\{[(C_5Me_5Rh-\mu-CH_2)_2(CN)_2]\}$

*X-ray crystal structure of $\{[(C_5Me_5Rh-\mu-CH_2)_2]_2(\mu-CN)_2\}(PF_6)_2$, **4**.* A sample of complex **4** was crystallised from acetone–diethyl ether as orange plates. C₄₆H₆₈F₁₂N₂P₂Rh₄, *M* = 1350.61. Crystal dimensions 0.275 × 0.175 × 0.05 mm, monoclinic, *a* = 8.460(9), *b* = 23.151(21), *c* = 13.880(18) Å, β = 101.89(10)°, *U* = 2660(5) Å³; *D_c* = 1.686 g cm⁻³, *Z* = 2, space group *P*2₁/*c* (*C*_{2h}⁵, no. 14), Mo-*K*_α radiation (λ = 0.71069 Å), μ(Mo-*K*_α) = 13.33 cm⁻¹, *F*(000) = 1351.86.

Three dimensional, room temperature X-ray data were collected in the range 3.5 < 2θ < 50° on a Nicolet R3 4-circle diffractometer by the omega scan method. The 3120 independent reflections for which |*F*|/σ(|*F*|) > 3.0 were corrected for

Table 3

¹H NMR spectral data (δ , ppm) in CDCl₃ ^a

| Complex | C ₅ Me ₅ | μ -CH ₂ | Me | L |
|--------------------------|--------------------------------|------------------------|----------------|---|
| 2b | 1.74 | 7.88 dm (15) | -0.20 d [3] | PMe ₃ , 1.40 dd(10)[1] |
| | 1.82 d (3) | 8.52 m | | |
| 2c | 1.71d [1] | 8.29 dm (14) | -0.26 d [3] | P(OMe) ₃ 3.66 d (12) |
| | 1.80 d (5) | 8.53 m | | |
| <i>trans</i> - 2d | 1.70 | 8.24 br | -0.30 d [3] | MeNC 3.46 d [1] |
| | 1.83 | 8.29 ddd [3; 3]{1} | | |
| <i>cis</i> - 2d | 1.66 d [1] | 8.14 ddd [3; 2]{2} | -0.71 d [3] | MeNC 3.52d [1] |
| | 1.79 d [1] | 9.19 dd [3]{2} | | |
| <i>trans</i> - 2e | 1.71 | 8.18br | -0.28 d [3] | ¹ BuNC 1.46 |
| | 1.83 | 8.30 ddd [3; 3]{1} | | |
| <i>cis</i> - 2e | 1.68 | 8.26ddd [3; 2]{2} | -0.70 d [3] | ¹ BuNC 1.51 |
| | 1.80 | 9.29 dd [3]{2} | | |
| <i>trans</i> - 2f | 1.35 | 8.81 m | -0.74 d [3] | C ₅ Me ₅ , 1.71 Me, 0.35 d [2] |
| | 1.46 | 9.28 m | | 4-C ₃ H ₄ N 7.15-7.55 m |
| <i>cis</i> - 2f | 1.52 | 8.28 br | -0.91 d [3] | C ₅ Me ₅ , 1.71 Me, 0.43 d [2] |
| | 1.66 | 9.18 m | | 4-C ₃ H ₄ N 7.15-7.55 m |
| <i>trans</i> - 2g | 1.37 | 8.79m; 8.84 m | -0.74 d [3] | C ₅ Me ₅ , 1.81 Me, 0.40 |
| | 1.46 | 9.27 m; 9.30 m | | 4-C ₃ H ₄ N 7.1-7.5 m |
| <i>cis</i> - 2g | 1.53 | 8.28 br | -0.88 d [3] | C ₅ Me ₅ , 1.77 Me, 0.49 |
| | 1.71 | 9.18 m | | 4-C ₃ H ₄ N 7.1-7.5 m |
| <i>cis</i> - 3 | 1.72 d [1] | 8.01 ddd [3,1]{1} | -0.86 d [3] | |
| | 1.77 d [1] | 9.10 dd [3]{1} | | |
| <i>trans</i> - 3 | 1.71 d [1] | 8.21 m | 0.04 d [3] | |
| | 1.83 | | | |
| 4^b | 1.82 | 9.24 ddd [2; 2]{2} | | |
| | 1.93 | 9.77 dd [2]{2} | | |

^a [] *J*(Rh-H) in Hz; { } *J*(H-H) in Hz; () *J*(P-H) in Hz. ^b In (CD₃)₂CO.

Lorentz and polarisation effects, and for absorption by analysis of azimuthal scans. The structure was solved by Patterson and Fourier techniques and refined by blocked cascade least squares methods. Hydrogen atoms were included in calculated

Table 4

 $^{13}\text{C}\{^1\text{H}\}$ NMR spectral data (δ /ppm) in CDCl_3

| Complex | C_5Me_5 | C_5Me_5 | $\mu\text{-CH}_2$ | Me | L |
|-----------------------|-------------------------|--------------------------------------|--------------------------|----------------|---------------------------------------|
| <i>trans-2c</i> | 10.0 | 104.8 d [3] 105.8 dd [4]{4} | 163.6 dd [28; 25]{10} | 6.7 [33] | $\text{P}(\text{OMe})_3$, 53.7 d (9) |
| <i>trans-2d</i> | 9.7 | 103.2 104.0 [4] | 161.3 dd [29; 23] | 8.6 d [33] | <i>MeNC</i> , 30.5 |
| <i>cis-2d</i> | 9.0 | 103.2 | 167.4 dd [28; 22] | -0.2 d [32] | <i>MeNC</i> , 31.0 |
| | 10.1 | 104.3 d [4] | | | |
| <i>trans-2e</i> | 9.7 | 103.3 d [3] | 161.6 dd [28; 23] | 8.7 d [32] | $^t\text{BuNC}$, 30.1; 59.0 |
| | 9.8 | 104.0 d [4] | | | |
| <i>cis-2e</i> | 9.2 | 102.9 d [3] | 168.7 dd [28; 22] | -0.2 d [32] | $^t\text{BuNC}$, 30.7; 59.7 |
| | 10.3 | 104.7 d [4] | | | |
| <i>cis-3</i> | 9.1 | 101.7 d [4] | 163.4 dd [28; 24] | -2.6 d [33] | <i>CN</i> , 130.8 d [63] |
| | 10.1 | 101.9 d [5] | | | |
| <i>trans-3</i> | 9.6 | 101.6 d [3] | 158.4 dd [29; 24] | 7.7 d [32] | <i>CN</i> , 134.2 d [66] |
| | 9.9 | 101.8 d [5] | | | |
| 4 ^b | 10.3 | 105.1 d [5] | 176.5 dd [24] | | <i>CN</i> , 141.5 dd [72; 5] |
| | 10.5 | 106.5 d [4] | | | |

^a [] $J(\text{Rh}-\text{C})$ in Hz; { } $J(\text{P}-\text{C})$ in Hz. ^b In $(\text{CD}_3)_2\text{CO}$.

positions, with isotropic thermal parameters related to those of the supporting atoms. Refinement converged at a final R 0.0749, with allowance for the thermal anisotropy of all non-hydrogen atoms. Complex scattering factors were taken from ref. 6 and from the program package SHELXTL as implemented on the Data General Nova 3 computer. Unit weights were used throughout. Atomic coordinates and temperature factors are in Table 1, and selected bond lengths and angles are in Table 5.

Table 5

Table of bond lengths and bond angles for $[(C_5Me_5Rh-\mu-CH_2)_2(\mu-CN)_2KPF_6]_2$, **4**

| | | | |
|-------------------------------|-----------|-------------------------------|-----------|
| Rh(1)–Rh(2) | 2.676(3) | Rh(1)–N(1) | 2.058(14) |
| Rh(1)–C(1) | 2.040(15) | Rh(1)–C(2) | 2.023(14) |
| Rh(1)–C(3) | 2.201(14) | Rh(1)–C(4) | 2.217(16) |
| Rh(1)–C(5) | 2.271(21) | Rh(1)–C(6) | 2.300(22) |
| Rh(1)–C(7) | 2.267(15) | Rh(2)–C(1) | 2.027(13) |
| Rh(2)–C(2) | 2.058(16) | Rh(2)–C(13) | 2.238(18) |
| Rh(2)–C(14) | 2.257(16) | Rh(2)–C(15) | 2.283(15) |
| Rh(2)–C(16) | 2.271(12) | Rh(2)–C(17) | 2.207(15) |
| Rh(2)–C(23) ^a | 2.020(13) | P(1)–F(1) | 1.595(16) |
| P(1)–F(2) | 1.539(17) | P(1)–F(3) | 1.529(17) |
| P(1)–F(4) | 1.481(17) | P(1)–F(5) | 1.549(18) |
| P(1)–F(6) | 1.559(17) | N(1)–C(23) | 1.147(19) |
| C(3)–C(4) | 1.447(22) | C(3)–C(7) | 1.419(23) |
| C(3)–C(8) | 1.522(29) | C(4)–C(5) | 1.407(30) |
| C(4)–C(9) | 1.514(22) | C(5)–C(6) | 1.420(27) |
| C(5)–C(10) | 1.518(28) | C(6)–C(7) | 1.413(33) |
| C(6)–C(11) | 1.518(35) | C(7)–C(12) | 1.505(28) |
| C(13)–C(14) | 1.459(25) | C(13)–C(17) | 1.408(27) |
| C(13)–C(18) | 1.481(32) | C(14)–C(15) | 1.407(22) |
| C(14)–C(19) | 1.519(26) | C(15)–C(16) | 1.417(24) |
| C(15)–C(20) | 1.541(24) | C(16)–C(17) | 1.415(22) |
| C(16)–C(21) | 1.497(23) | C(17)–C(22) | 1.540(28) |
| N(1)–Rh(1)–C(1) | 87.2(6) | N(1)–Rh(1)–C(2) | 86.0(6) |
| C(1)–Rh(1)–C(2) | 96.8(6) | C(1)–Rh(2)–C(2) | 96.1(6) |
| C(1)–Rh(2)–C(23) ^a | 86.3(5) | C(2)–Rh(2)–C(23) ^a | 86.5(6) |
| F(1)–P(1)–F(2) | 87.0(9) | F(1)–P(1)–F(3) | 176.7(10) |
| F(2)–P(1)–F(3) | 90.1(10) | F(1)–P(1)–F(4) | 90.7(10) |
| F(2)–P(1)–F(4) | 177.7(11) | F(3)–P(1)–F(4) | 92.1(10) |
| F(1)–P(1)–F(5) | 91.9(11) | F(2)–P(1)–F(5) | 85.6(12) |
| F(3)–P(1)–F(5) | 89.4(11) | F(4)–P(1)–F(5) | 95.2(12) |
| F(1)–P(1)–F(6) | 86.6(10) | F(2)–P(1)–F(6) | 90.5(11) |
| F(3)–P(1)–F(6) | 91.8(11) | F(4)–P(1)–F(6) | 88.7(11) |
| F(5)–P(1)–F(6) | 175.9(10) | Rh(1)–N(1)–C(23) | 175.7(12) |
| Rh(1)–C(1)–Rh(2) | 82.3(5) | Rh(1)–C(2)–Rh(2) | 82.0(6) |
| C(4)–C(3)–C(7) | 108.0(15) | C(4)–C(3)–C(8) | 124.0(15) |
| C(7)–C(3)–C(8) | 127.6(14) | C(3)–C(4)–C(5) | 107.8(14) |
| C(3)–C(4)–C(9) | 126.1(16) | C(5)–C(4)–C(9) | 125.7(16) |
| C(4)–C(5)–C(6) | 107.4(18) | C(4)–C(5)–C(10) | 126.2(18) |
| C(6)–C(5)–C(10) | 125.9(22) | C(5)–C(6)–C(7) | 109.8(19) |
| C(5)–C(6)–C(11) | 124.4(23) | C(7)–C(6)–C(11) | 124.3(18) |
| C(3)–C(7)–C(6) | 106.9(15) | C(3)–C(7)–C(12) | 122.9(19) |
| C(6)–C(7)–C(12) | 129.8(18) | C(14)–C(13)–C(17) | 104.1(14) |
| C(14)–C(13)–C(18) | 126.9(19) | C(17)–C(13)–C(18) | 128.5(18) |
| C(13)–C(14)–C(15) | 108.9(14) | C(13)–C(14)–C(19) | 124.1(17) |
| C(15)–C(14)–C(19) | 126.7(18) | C(14)–C(15)–C(16) | 109.0(14) |
| C(14)–C(15)–C(20) | 128.0(17) | C(16)–C(15)–C(20) | 122.6(15) |
| C(15)–C(16)–C(17) | 105.9(14) | C(15)–C(16)–C(21) | 126.4(16) |
| C(17)–C(16)–C(21) | 127.2(17) | C(13)–C(17)–C(16) | 112.1(15) |
| C(13)–C(17)–C(22) | 123.3(15) | C(16)–C(17)–C(22) | 124.1(16) |
| N(1)–C(23)–Rh(2) ^a | 173.9(11) | | |

^a Symmetry operation is $[-x, -y, -z]$

Acknowledgements

We thank the SERC for supporting this work, Johnson Matthey for the loan of rhodium salts, the Royal Society for some instrumentation, and Dr B.F. Taylor for NMR spectra.

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