

# New Synthetic Routes to Face-to-face and Open-book Triazenide-bridged Dirhodium Bipyridyl Complexes with the $[\text{Rh}_2]^{4+}$ Core\*

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The iodide-abstraction reaction of  $[\{\text{Rh}_2(\mu\text{-I})(\text{CO})(\text{bipy})(\mu\text{-RNNNR})_2\}_2][\text{PF}_6]_2$  **1** (bipy = 2,2'-bipyridyl, R = *p*-tolyl) with  $\text{AgPF}_6$  in MeCN gave  $[\text{Rh}_2(\text{CO})(\text{NCMe})_2(\text{bipy})(\mu\text{-RNNNR})_2][\text{PF}_6]_2$  **2** which slowly decarbonylated at room temperature to  $[\text{Rh}_2(\text{NCMe})_3(\text{bipy})(\mu\text{-RNNNR})_2][\text{PF}_6]_2$  **3**. The crystal structure of **3** shows a Rh–Rh single bond [2.534(2) Å] and one of the three terminal nitrile ligands axially attached to the bipy-bound rhodium atom. Complex **3** reacts with  $\text{Na}[\text{S}_2\text{CNMe}_2]\cdot 2\text{H}_2\text{O}$  to give  $[\text{Rh}_2(\text{NCMe})(\text{S}_2\text{CNMe}_2)(\text{bipy})(\mu\text{-RNNNR})_2][\text{PF}_6]$  **4**. In  $\text{CH}_2\text{Cl}_2$ , the iodide-abstraction reaction of **1** affords a green solution containing a carbonyl complex  $[\text{Rh}_2(\text{CO})(\text{solv})_2(\text{bipy})(\mu\text{-RNNNR})_2]^{2+}$  **A** (solv =  $\text{CH}_2\text{Cl}_2$ ), an analogue of **2**. Complex **A** (solv =  $\text{CH}_2\text{Cl}_2$ ) reacted with neutral chelating ligands to give the carbonyl-bridged complexes  $[\text{Rh}_2(\mu\text{-CO})(\text{L-L})(\text{bipy})(\mu\text{-RNNNR})_2][\text{PF}_6]_2$  [L–L = bipy **5**, 4,4'-dimethyl-2,2'-bipyridyl (dmbipy) **6**, 1,10-phenanthroline (phen) **7**, di-2-pyridylamine (dpa) **8**, or  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$  (dppe) **9**] the last of which undergoes reduction with  $\text{NaBH}_4$  to give paramagnetic  $[\text{Rh}_2(\text{CO})(\text{dppe})\text{-P}(\text{bipy})(\mu\text{-RNNNR})_2][\text{PF}_6]$  **11** having a face-to-face structure with a monodentate dppe ligand. With  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$  (dppm), **A** (solv =  $\text{CH}_2\text{Cl}_2$ ) afforded  $[\text{Rh}_2(\mu\text{-CO})(\text{dppm})(\text{bipy})(\mu\text{-RNNNR})_2][\text{PF}_6]_2$  **10a**. X-ray studies on which, as a  $\text{CH}_2\text{Cl}_2$  solvate, reveal a carbonyl-bridged open-book structure with a Rh–Rh distance of 3.179(2) Å and a large Rh–C(O)–Rh angle of 108.3°. Complex **10a** equilibrates with the face-to-face, terminal carbonyl isomer  $[\text{Rh}_2(\text{CO})(\text{dppm})(\text{bipy})(\mu\text{-RNNNR})_2][\text{PF}_6]_2$  **10b** in solution. The electronic structures of the two isomers have been probed by extended-Hückel molecular-orbital calculations on the model compound  $[\text{Rh}_2\text{H}_4(\text{CO})_6]$ . These show (i) the absence of metal–metal bonding in **10a** while **10b** has a Rh–Rh  $\sigma$  bond, and (ii) that the CO in **10a** is best viewed as more ketonic than a typical bridging carbonyl. The reaction of complex **A** (solv =  $\text{CH}_2\text{Cl}_2$ ) with neutral chelating ligands also gives low yields of  $[\{\text{Rh}_2(\text{CO})(\text{O}_2\text{PF}_2)(\mu\text{-O}_2\text{PF}_2)(\text{bipy})(\mu\text{-RNNNR})_2\}_2]$  **12** the crystal structure of which shows two dirhodium fragments [Rh–Rh 2.505(4) Å] linked by two  $\text{O}_2\text{PF}_2$  groups bridging across axial and equatorial sites in different  $[\text{Rh}_2]^{4+}$  moieties. The reaction of **A** (solv =  $\text{CH}_2\text{Cl}_2$ ) with N–SH ligands yields  $[\text{Rh}_2(\text{CO})(\text{N-S})(\text{bipy})(\mu\text{-RNNNR})_2][\text{PF}_6]$  (N–S = 1-methyl-2-sulfanylimidazolate **13**, 2-sulfanylpurimidinate **14**, 2-sulfanylthiazolinate **15**, or 2-sulfanylbenzimidazolate **16**), and NaX gives  $[\text{Rh}_2(\text{CO})\text{X}_2(\text{bipy})(\mu\text{-RNNNR})_2]$  (X = Cl or  $\text{NO}_2$ ).

We have previously shown<sup>1</sup> that  $[\text{Rh}_2(\text{CO})_2(\text{bipy})(\mu\text{-RNNNR})_2]$  (bipy = 2,2'-bipyridyl, R = *p*-tolyl) is activated towards carbonyl substitution by one-electron oxidation, the resulting paramagnetic monocation  $[\text{Rh}_2(\text{CO})_2(\text{bipy})(\mu\text{-RNNNR})_2]^+$  acting as the precursor to a wide variety of  $[\text{Rh}_2]^{3+}$ - and  $[\text{Rh}_2]^{4+}$ -containing complexes in which two square-planar rhodium centres are retained in a face-to-face arrangement. We now give details<sup>2</sup> of how the halide-abstraction reactions of one such  $[\text{Rh}_2]^{4+}$  complex, namely  $[\{\text{Rh}_2(\mu\text{-I})(\text{CO})(\text{bipy})(\mu\text{-RNNNR})_2\}_2][\text{PF}_6]_2$  (R = *p*-tolyl), lead to a considerable expansion of the range of redox-active dirhodium complexes and, in particular, to novel carbonyl-bridged complexes with an 'open-book' rather than face-to-face  $[\text{Rh}_2]^{4+}$  core.

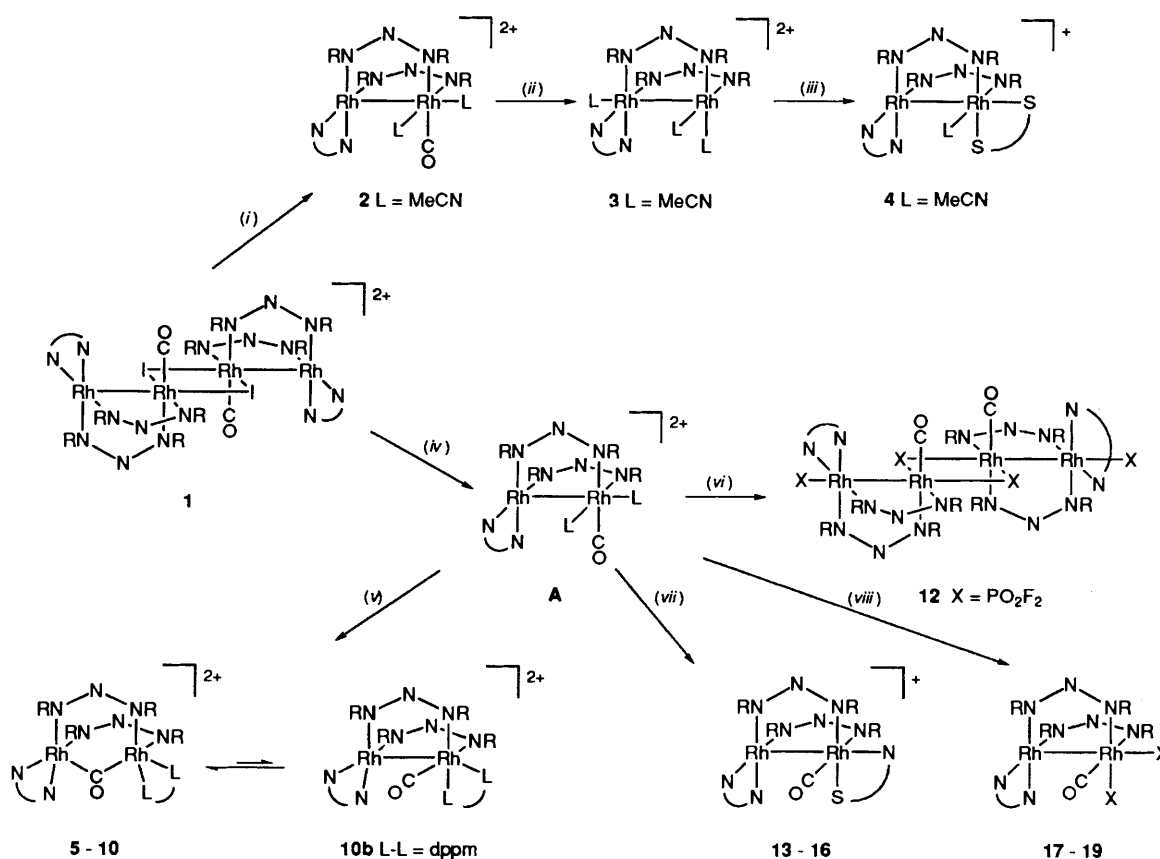
## Results and Discussion

The addition of  $\text{AgPF}_6$  to  $[\{\text{Rh}_2(\mu\text{-I})(\text{CO})(\text{bipy})(\mu\text{-RNNNR})_2\}_2][\text{PF}_6]_2$  **1** (R = *p*-tolyl) in acetonitrile results in

the precipitation of AgI and the formation of an orange solution from which green  $[\text{Rh}_2(\text{CO})(\text{NCMe})_2(\text{bipy})(\mu\text{-RNNNR})_2][\text{PF}_6]_2$  **2** (better prepared in a purer form by the route described below) may be isolated on addition of diethyl ether. The structure of complex **2** (Scheme 1) was deduced from the elemental analysis (Table 1), from the observation of one carbonyl band in the IR spectrum (at 2086  $\text{cm}^{-1}$ ), and from the <sup>1</sup>H NMR spectrum (Table 2) which showed the presence of two inequivalent pyridyl rings (of the bipy ligand), two inequivalent nitrile ligands (one axial and one equatorial with respect to the rhodium–rhodium bond), and three different methyl resonances associated with the tolyl substituents of the triazenide bridges. The two nitrile ligands are assumed to be co-ordinated to the same rhodium atom, by comparison with the structure<sup>1</sup> of the precursor **1** (but see below).

Once formed, complex **2** reacts further in MeCN. The reaction is slow at room temperature but more rapid in boiling acetonitrile; after 12 h the reaction mixture shows no carbonyl band in the IR spectrum, indicating complete loss of co-ordinated CO. Addition of diethyl ether to the acetonitrile solution gave the product **3** as an air-stable green powder in good yield. The C, H and N analyses (Table 1) were consistent with the formulation  $[\text{Rh}_2(\text{NCMe})_3(\text{bipy})(\mu\text{-RNNNR})_2]$ -

\* Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.



**Scheme 1** N-N = bipy, R = *p*-tolyl. (i) AgPF<sub>6</sub> in MeCN; (ii) MeCN, heat; (iii) Na[S<sub>2</sub>CNMe<sub>2</sub>]; (iv) AgPF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub>; (v) L-L = bipy, dppe, etc.; (vi) water; (vii) N-S = msim, etc.; (viii) NaX, X = Cl or NO<sub>2</sub>

**Table 1** Analytical data for dirhodium triazenide complexes (R = *p*-tolyl)

| Complex  | Yield (%) | Colour | $\tilde{\nu}(\text{CO})^a/\text{cm}^{-1}$ | Analysis (%) <sup>b</sup> |           |                          |
|--|-----------|--------|---|---------------------------|-----------|--------------------------|
|  |           |        |   | C                         | H         | N                        |
| 2 [Rh <sub>2</sub> (CO)(NCMe) <sub>2</sub> (bipy)(μ-RNNNR) <sub>2</sub> ][PF <sub>6</sub> ] <sub>2</sub>     | 60        | Green  | 2090                                      | 42.3 (42.7)               | 3.6 (3.5) | 11.4 (11.6)              |
| 3 [Rh <sub>2</sub> (NCMe) <sub>3</sub> (bipy)(μ-RNNNR) <sub>2</sub> ][PF <sub>6</sub> ] <sub>2</sub>         | 82        | Green  | —   | 42.9 (43.2)               | 3.7 (3.7) | 12.4 (12.6)              |
| 4 [Rh <sub>2</sub> (NCMe)(S <sub>2</sub> CNMe <sub>2</sub> )(bipy)(μ-RNNNR) <sub>2</sub> ][PF <sub>6</sub> ] | 77        | Brown  | —   | 45.9 (46.3)               | 3.9 (4.1) | 12.1 (12.5)              |
| 5 [Rh <sub>2</sub> (μ-CO)(bipy) <sub>2</sub> (μ-RNNNR) <sub>2</sub> ][PF <sub>6</sub> ] <sub>2</sub>         | 53        | Green  | 1769                                      | 46.0 (45.8)               | 4.0 (3.4) | 10.4 (10.1)              |
| 6 [Rh <sub>2</sub> (μ-CO)(dmbipy)(bipy)(μ-RNNNR) <sub>2</sub> ][PF <sub>6</sub> ] <sub>2</sub>               | 74        | Green  | 1777                                      | 46.5 (46.6)               | 3.8 (3.7) | 10.5 (10.7)              |
| 7 [Rh <sub>2</sub> (μ-CO)(phen)(bipy)(μ-RNNNR) <sub>2</sub> ][PF <sub>6</sub> ] <sub>2</sub>                 | 72        | Green  | 1777 <sup>c</sup>                         | 46.8 (46.8)               | 3.7 (3.4) | 10.5 (10.7)              |
| 8 [Rh <sub>2</sub> (μ-CO)(dpa)(bipy)(μ-RNNNR) <sub>2</sub> ][PF <sub>6</sub> ] <sub>2</sub>                  | 68        | Green  | 1774 <sup>d</sup>                         | 46.0 (46.1)               | 3.9 (3.9) | 11.3 (11.4) <sup>e</sup> |
| 9 [Rh <sub>2</sub> (μ-CO)(dppe)(bipy)(μ-RNNNR) <sub>2</sub> ][PF <sub>6</sub> ] <sub>2</sub>                 | 79        | Green  | 1760 <sup>c</sup>                         | 51.0 (51.1)               | 3.9 (3.9) | 7.3 (7.3)                |
| 10 [Rh <sub>2</sub> (μ-CO)(dppm)(bipy)(μ-RNNNR) <sub>2</sub> ][PF <sub>6</sub> ] <sub>2</sub>                | 76        | Green  | 1758s,<br>2070mw                          | 49.5 (49.8)               | 3.8 (3.8) | 7.3 (7.2) <sup>f</sup>   |
| 11 [Rh <sub>2</sub> (CO)(dppe- <i>P</i> )(bipy)(μ-RNNNR) <sub>2</sub> ][PF <sub>6</sub> ]                    | 80        | Brown  | 2016                                      | 55.3 (55.2)               | 4.7 (4.3) | 7.8 (7.9) <sup>f</sup>   |
| 13 [Rh <sub>2</sub> (CO)(msim)(bipy)(μ-RNNNR) <sub>2</sub> ][PF <sub>6</sub> ]                               | 71        | Green  | 2065                                      | 47.0 (47.1)               | 3.7 (3.7) | 12.7 (12.8)              |
| 14 [Rh <sub>2</sub> (CO)(spym)(bipy)(μ-RNNNR) <sub>2</sub> ][PF <sub>6</sub> ]                               | 74        | Green  | 2067                                      | 46.0 (45.9)               | 3.7 (3.5) | 12.0 (12.3) <sup>g</sup> |
| 15 [Rh <sub>2</sub> (CO)(stz)(bipy)(μ-RNNNR) <sub>2</sub> ][PF <sub>6</sub> ]                                | 70        | Green  | 2064                                      | 45.8 (45.8)               | 3.6 (3.6) | 11.2 (11.4)              |
| 16 [Rh <sub>2</sub> (CO)(sbzim)(bipy)(μ-RNNNR) <sub>2</sub> ][PF <sub>6</sub> ]                              | 77        | Green  | 2065                                      | 47.6 (47.5)               | 3.9 (3.5) | 11.7 (11.9) <sup>f</sup> |
| 17 [Rh <sub>2</sub> (CO)Cl <sub>2</sub> (bipy)(μ-RNNNR) <sub>2</sub> ]                                       | 71        | Green  | 2038                                      | 51.6 (51.5)               | 4.2 (4.0) | 12.1 (12.3)              |
| 19 [Rh <sub>2</sub> (CO)(NO <sub>2</sub> ) <sub>2</sub> (bipy)(μ-RNNNR) <sub>2</sub> ]                       | 70        | Brown  | 2043                                      | 50.0 (50.4)               | 3.8 (3.9) | 15.0 (15.1)              |

<sup>a</sup> In CH<sub>2</sub>Cl<sub>2</sub> unless stated otherwise; s = strong, mw = medium weak. <sup>b</sup> Calculated values in parentheses. <sup>c</sup> In MeCN. <sup>d</sup> In MeNO<sub>2</sub>. <sup>e</sup> Calculated for a 0.75 OEt<sub>2</sub> solvate (confirmed by <sup>1</sup>H NMR spectroscopy). <sup>f</sup> Calculated for a 0.5 CH<sub>2</sub>Cl<sub>2</sub> solvate. <sup>g</sup> Calculated for a 0.5 CH<sub>2</sub>Cl<sub>2</sub> solvate (confirmed by <sup>1</sup>H NMR spectroscopy).

[PF<sub>6</sub>]<sub>2</sub> and both the <sup>1</sup>H and <sup>13</sup>C NMR spectra (Table 2) show the presence of three acetonitrile ligands in the ratio 2:1. The <sup>1</sup>H signals for the methyl groups of the triazenide bridges occur as two singlets, in a 1:1 ratio, and those for the C<sub>6</sub>H<sub>4</sub> groups appear as pseudo-triplets (each due to the overlapping of two doublets). The signals for the bipyridyl protons are observed in the ratio 2:2:2:2 showing the pyridyl groups to be equivalent.

Taken together, these data are consistent with a structure for **3** having a mirror plane including the Rh-Rh axis and bisecting the planes of the two triazenide bridges. However, the NMR spectra do not define which axial site the third nitrile ligand occupies. An X-ray diffraction study was therefore carried out on crystals grown by slow diffusion of diethyl ether into an acetonitrile solution of **3**.

The structure of the dication of complex **3** is shown in Fig. 1 and selected bond lengths and angles are listed in Table 3. The X-ray diffraction study confirms the presence of three coordinated acetonitriles. However, the structure differs from that of **1** in that although two of the nitrile ligands are equatorially

bound to Rh(2) the third is axially bound to Rh(1) (*i.e.* the rhodium atom also bearing the bipy ligand). Both rhodium atoms have near-planar equatorial co-ordination, with a greater mean deviation from the plane at Rh(2) (0.0283 Å) than at Rh(1) (0.0178 Å). The smaller deviation at Rh(1) is possibly

**Table 2** Proton and  $^{13}\text{C}$  NMR spectroscopic data for dirhodium triazenide complexes<sup>a</sup>

| Compound | $^1\text{H}$   | $^{13}\text{C}$   |
|----------|--|---|
|          |  |   |
| <b>2</b> | 1.81 (3 H, s, MeCN), 2.07 (3 H, s, MeCN), 2.27 (3 H, s, $\text{C}_6\text{H}_4\text{Me}$ ), 2.28 (3 H, s, $\text{C}_6\text{H}_4\text{Me}$ ), 2.35 (6 H, s, $\text{C}_6\text{H}_4\text{Me}$ ), 7.12–7.42 (16 H, $\text{C}_6\text{H}_4\text{Me}$ ), 8.00 (2 H, m, $\text{H}^2$ ), 8.49 (2 H, m, $\text{H}^3$ ), 8.73 [1 H, d, $J(\text{H}^4\text{H}^3)$ 7, $\text{H}^4$ or $\text{H}^4$ ], 8.76 [1 H, d, $J(\text{H}^4\text{H}^3)$ 7, $\text{H}^4$ or $\text{H}^4$ ], 9.13 [1 H, d, $J(\text{H}^1\text{H}^2)$ 5, $\text{H}^1$ or $\text{H}^1$ ], 9.20 [1 H, d, $J(\text{H}^1\text{H}^2)$ 5, $\text{H}^1$ or $\text{H}^1$ ] <sup>b</sup>   | 3.3, 3.4 (MeCN), 21.0, 21.1 ( $\text{C}_6\text{H}_4\text{Me}$ ), 122.0, 123.0, 124.5, 125.2 ( <i>m</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 122.4, 126.4 (MeCN), 126.4, 127.0 ( $\text{C}^4$ ), 128.9, 129.5 ( $\text{C}^2$ ), 129.7, 129.9, 130.4, 130.7 ( <i>o</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 137.2, 138.1, 138.4 ( <i>p</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 142.4, 142.8 ( $\text{C}^3$ ), 146.4, 146.7, 147.0, 147.9 ( <i>ipso</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 153.5, 154.0 ( $\text{C}^1$ ), 157.4, 157.6 ( $\text{C}^5$ ), 179.7 [d, $J(\text{C}^{103}\text{Rh})$ 61, CO] <sup>c</sup>  |
| <b>3</b> | 1.80 (3 H, s, MeCN), 2.06 (6 H, s, MeCN), 2.28 (6 H, s, $\text{C}_6\text{H}_4\text{Me}$ ), 2.32 (6 H, s, $\text{C}_6\text{H}_4\text{Me}$ ), 7.13 (8 H, d, $J$ 9, <i>o</i> -H of $\text{C}_6\text{H}_4\text{Me}$ ), 7.36 (8 H, t, $J$ 9, <i>m</i> -H of $\text{C}_6\text{H}_4\text{Me}$ ), 7.90 [2 H, t, $J(\text{H}^2\text{H}^3)$ 8, $J(\text{H}^2\text{H}^1)$ 6, $\text{H}^2$ ], 8.41 [2 H, t, $J(\text{H}^3\text{H}^2)$ 8, $\text{H}^3$ ], 8.68 [2 H, d, $J(\text{H}^4\text{H}^3)$ 8, $\text{H}^4$ ], 8.98 [2 H, d, $J(\text{H}^1\text{H}^2)$ 6, $\text{H}^1$ ] <sup>b</sup>   | 2.8 (MeCN), 4.0 (MeCN), 21.4 ( $\text{C}_6\text{H}_4\text{Me}$ ), 120.4 (MeCN), 124.4, 125.9 ( <i>m</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 126.3 ( $\text{C}^4$ ), 126.6, 126.7 (MeCN), 129.7 ( $\text{C}^2$ ), 130.8, 131.2 ( <i>o</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 138.2, 138.3 ( <i>p</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 143.0 ( $\text{C}^3$ ), 149.4, 149.7 ( <i>ipso</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 155.6, 155.7 ( $\text{C}^1$ ), 159.3 ( $\text{C}^5$ ) <sup>b</sup>  |
| <b>4</b> | 1.83 (3 H, s, MeCN), 2.26 (12 H, m, $\text{C}_6\text{H}_4\text{Me}$ ), 2.77 (3 H, s, $\text{S}_2\text{CNMe}_2$ ), 3.02 (3 H, s, $\text{S}_2\text{CNMe}_2$ ), 7.08 (18 H, m, $\text{C}_6\text{H}_4\text{Me}$ , $\text{H}^2$ ), 8.13 (2 H, m, $\text{H}^3$ ), 8.29 [1 H, d, $J(\text{H}^1\text{H}^2)$ 5, $\text{H}^1$ or $\text{H}^1$ ], 8.38 [1 H, d, $J(\text{H}^1\text{H}^2)$ 5, $\text{H}^1$ or $\text{H}^1$ ], 8.40 [1 H, d, $J(\text{H}^4\text{H}^3)$ 8, $\text{H}^4$ or $\text{H}^4$ ], 8.46 [1 H, d, $J(\text{H}^4\text{H}^3)$ 8, $\text{H}^4$ or $\text{H}^4$ ]   | 3.6 (MeCN), 20.7 ( $\text{C}_6\text{H}_4\text{Me}$ ), 37.9, 38.3 ( $\text{S}_2\text{CNMe}_2$ ), 123.2, 123.5 ( <i>m</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 124.2 (MeCN), 127.2, 127.6 ( <i>o</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 129.1 ( $\text{C}^4$ ), 129.5 ( $\text{S}_2\text{CNMe}_2$ , $\text{C}^2$ ), 139.1, 139.2 ( <i>p</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 140.3 ( $\text{C}^3$ ), 152.2, 153.4 ( <i>ipso</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 157.6, 157.7 ( $\text{C}^1$ ), 158.0 ( $\text{C}^5$ )  |
| <b>5</b> | 2.27 (12 H, s, $\text{C}_6\text{H}_4\text{Me}$ ), 7.09 [8 H, dd, $J(\text{HH})$ 8, $J(\text{HRh})$ 2, <i>o</i> -H of $\text{C}_6\text{H}_4\text{Me}$ ], 7.21 [8 H, dd, $J(\text{HH})$ 8, $J(\text{HRh})$ < 1, <i>m</i> -H of $\text{C}_6\text{H}_4\text{Me}$ ], 7.49 [2 H, ddd, $J(\text{HH})$ 9, 6, 1.5, $\text{H}^2$ ], 8.21 [2 H, ddd, $J(\text{HH})$ 9, 8, 1.5, $\text{H}^3$ ], 8.24 [2 H, d, $J(\text{H}^1\text{H}^2)$ 6, $\text{H}^1$ ] <sup>d</sup>   | 20.9 ( $\text{C}_6\text{H}_4\text{Me}$ ), 123.8 ( <i>m</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 125.9 ( $\text{C}^4$ ), 128.9 ( $\text{C}^2$ ), 130.9 ( <i>o</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 138.5 ( <i>p</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 142.6 ( $\text{C}^3$ ), 146.8 ( <i>ipso</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 153.3 ( $\text{C}^1$ ), 157.7 ( $\text{C}^5$ ), 186.0 [t, $J(\text{C}^{103}\text{Rh})$ 48, CO] <sup>c,d</sup>  |
| <b>6</b> | 2.27 (12 H, s, $\text{C}_6\text{H}_4\text{Me}$ ), 2.52 (6 H, s, Me of dmbipy), 7.08 [8 H, dd, $J(\text{HH})$ 8, $J(\text{HRh})$ < 1, <i>m</i> -H of $\text{C}_6\text{H}_4\text{Me}$ ], 7.19 [8 H, dd, $J(\text{HH})$ 8, $J(\text{HRh})$ 2, <i>o</i> -H of $\text{C}_6\text{H}_4\text{Me}$ ], 7.30 [2 H, d, $J(\text{H}^7\text{H}^6)$ 6, $\text{H}^7$ ], 7.49 [2 H, ddd, $J(\text{HH})$ 9, 7, 1.5, $\text{H}^2$ ], 8.05 [2 H, d, $J(\text{H}^6\text{H}^7)$ 6, $\text{H}^6$ ], 8.20 [2 H, ddd, $J(\text{HH})$ 9, 8, 1.5, $\text{H}^3$ ], 8.23 [2 H, d, $J(\text{H}^1\text{H}^2)$ 7, $\text{H}^1$ ], 8.26 (2 H, s, $\text{H}^9$ ), 8.41 [2 H, dd, $J(\text{HH})$ 8, 1, $\text{H}^4$ ] <sup>d</sup>  | 21.4, 22.1 ( $\text{C}_6\text{H}_4\text{Me}$ ), 124.3 ( <i>m</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 126.7 ( $\text{C}^4$ ), 127.3 ( $\text{C}^9$ ), 130.3 ( $\text{C}^7$ ), 132.0 ( <i>o</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 139.8 ( <i>p</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 143.5 ( $\text{C}^3$ ), 147.6 ( <i>ipso</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 153.3, ( $\text{C}^1$ ), 154.2 ( $\text{C}^6$ ), 157.1 ( $\text{C}^5$ ), 158.1, 158.7 ( $\text{C}^8$ , $\text{C}^{10}$ ), 182.1 [t, $J(\text{C}^{103}\text{Rh})$ 46, CO] <sup>b</sup>  |
| <b>7</b> | 2.27 (6 H, s, $\text{C}_6\text{H}_4\text{Me}$ ), 2.28 (6 H, s, $\text{C}_6\text{H}_4\text{Me}$ ), 7.10 [8 H, d, $J(\text{HH})$ 8, <i>m</i> -H of $\text{C}_6\text{H}_4\text{Me}$ ], 7.26 [8 H, dd, $J(\text{HH})$ 8, $J(\text{HRh})$ 1.5, <i>o</i> -H of $\text{C}_6\text{H}_4\text{Me}$ ], 7.47 [2 H, ddd, $J(\text{HH})$ 8, 5, 1.5, $\text{H}^2$ ], 7.80 [2 H, dd, $J(\text{HH})$ 8, 5, $\text{H}^7$ ], 8.16 [2 H, td, $J(\text{HH})$ 8, 1.5, $\text{H}^3$ ], 8.19 (2 H, s, $\text{H}^{11}$ ), 8.26 [2 H, d, $J(\text{H}^1\text{H}^2)$ 5, $\text{H}^1$ ], 8.34 [2 H, d, $J(\text{H}^4\text{H}^3)$ 8, $\text{H}^4$ ], 8.54 [2 H, td, $J(\text{HH})$ 5, 1, $\text{H}^6$ ], 8.77 [2 H, dd, $J(\text{HH})$ 8, 1, $\text{H}^8$ ] <sup>b</sup> | 21.4 ( $\text{C}_6\text{H}_4\text{Me}$ ), 124.4, 124.6 ( <i>m</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 126.6 ( $\text{C}^4$ ), 128.0 ( $\text{C}^7$ ), 129.9 ( $\text{C}^2$ ), 132.1 ( <i>o</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 133.6 ( $\text{C}^9$ ), 139.9, 140.0 ( <i>p</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 142.6 ( $\text{C}^{11}$ ), 143.5 ( $\text{C}^3$ ), 147.6 ( <i>ipso</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 148.9 ( $\text{C}^6$ ), 154.2, 154.3 ( $\text{C}^{10}$ ), 155.1 ( $\text{C}^1$ ), 158.1 ( $\text{C}^5$ ), 181.6 [t, $J(\text{C}^{103}\text{Rh})$ 49, CO] <sup>b</sup>   |
| <b>8</b> | 2.24 (6 H, s, $\text{C}_6\text{H}_4\text{Me}$ ), 2.28 (6 H, s, $\text{C}_6\text{H}_4\text{Me}$ ), 6.92 [8 H, d, $J(\text{HH})$ 8, <i>m</i> -H of $\text{C}_6\text{H}_4\text{Me}$ ], 7.06 [10 H, m, <i>o</i> -H of $\text{C}_6\text{H}_4\text{Me}$ , $\text{H}^7$ ], 7.35 [2 H, d, $J(\text{H}^9\text{H}^8)$ 8, $\text{H}^9$ ], 7.73 [2 H, d, $J(\text{H}^6\text{H}^7)$ 6, $\text{H}^6$ ], 7.80 [2 H, ddd, $J(\text{HH})$ 8, 6, 1, $\text{H}^2$ ], 7.90 [2 H, td, $J(\text{HH})$ 8, < 1, $\text{H}^8$ ], 8.41 [2 H, td, $J(\text{HH})$ 8, 1, $\text{H}^3$ ], 8.66 [2 H, d, $J(\text{H}^4\text{H}^3)$ 8, $\text{H}^4$ ], 8.73 [2 H, d, $J(\text{H}^1\text{H}^2)$ 6, $\text{H}^1$ ], 9.27 (1 H, s, NH) <sup>b</sup>                           | 21.4 ( $\text{C}_6\text{H}_4\text{Me}$ ), 117.2, 123.2 ( $\text{C}^7$ , $\text{C}^9$ ), 124.1 ( <i>m</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 127.0 ( $\text{C}^4$ ), 130.1, ( $\text{C}^2$ ), 131.1 ( <i>o</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 139.7, 139.9 ( <i>p</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 143.8, 144.1 ( $\text{C}^3$ , $\text{C}^8$ ), 147.0, 147.4 ( <i>ipso</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 153.3 ( $\text{C}^1$ ), 153.8 ( $\text{C}^6$ ), 159.0 ( $\text{C}^5$ , $\text{C}^{10}$ ), 184.7 [t, $J(\text{C}^{103}\text{Rh})$ 48, CO] <sup>b</sup>   |
| <b>9</b> | 2.15 (6 H, s, $\text{C}_6\text{H}_4\text{Me}$ ), 2.34 (6 H, s, $\text{C}_6\text{H}_4\text{Me}$ ), 3.00 (4 H, m, $\text{CH}_2$ of dppe), 6.71 [4 H, d, $J(\text{HH})$ 8], 6.86 [4 H, dd, $J(\text{HH})$ 8, 12], 6.93 [8 H, d, $J(\text{HH})$ 8], 7.13–7.37 (20 H, m) ( $\text{C}_6\text{H}_4\text{Me}$ and <i>o</i> -, <i>m</i> -H of PPh), 7.56 (4 H, m, $\text{H}^2$ , $\text{H}^4$ ), 8.23 [2 H, td, $J(\text{HH})$ 8, 2, $\text{H}^3$ ], 8.38 [2 H, d, $J(\text{H}^4\text{H}^3)$ 8, $\text{H}^4$ ]  | 21.4, 21.6 ( $\text{C}_6\text{H}_4\text{Me}$ ), 28.8 [d, $J(\text{C}^{31}\text{P})$ 45, $\text{CH}_2$ of dppe], 124.7, 126.2 ( <i>m</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 126.3 ( $\text{C}^4$ ), 128.9 [d, $J(\text{C}^{31}\text{P})$ 52, <i>ipso</i> -C of $\text{C}_6\text{H}_5\text{P}$ ], 130.0 ( $\text{C}^2$ ), 131.1 ( <i>ipso</i> -C of $\text{C}_6\text{H}_5\text{P}$ ), 131.3, 131.4, 131.7, 131.8, 133.9, 134.4, 134.6, 134.7, 134.8 ( <i>o</i> -, <i>m</i> -, <i>p</i> -C of $\text{C}_6\text{H}_5\text{P}$ ; <i>o</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 140.2 ( <i>p</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 143.5 ( $\text{C}^3$ ), 147.0, 148.7 ( <i>ipso</i> -C of $\text{C}_6\text{H}_4\text{Me}$ ), 154.1 ( $\text{C}^1$ ), 158.1 ( $\text{C}^5$ ) <sup>b</sup> |

Table 2 (continued)

| Compound | <sup>1</sup> H  | <sup>13</sup> C   |
|----------|---|---|
| 10       | 2.19 (6 H, s, C <sub>6</sub> H <sub>4</sub> Me), 2.36 (6 H, s, C <sub>6</sub> H <sub>4</sub> Me), 4.56 (1 H, ddd, br, CH <sub>2</sub> of dppm), 4.90 (1 H, ddd, br, CH <sub>2</sub> of dppm), 6.86 [4 H, dd, J(HH) 8, 12], 7.04 (8 H, m), 7.15 [4 H, d, J(HH) 8], 7.30–7.66 (20 H, m and H <sup>2</sup> ) (C <sub>6</sub> H <sub>4</sub> Me and PPh), 8.00 [2 H, d, J(H <sup>1</sup> H <sup>2</sup> ) 5, H <sup>1</sup> ], 8.34 [2 H, td, J(HH) 8, 1, H <sup>3</sup> ], 8.52 [2 H, d, J(H <sup>4</sup> H <sup>3</sup> ) 8, H <sup>4</sup> ] <sup>b</sup>  | 21.4, 21.6 (C <sub>6</sub> H <sub>4</sub> Me), 39.3 [t, J(C <sup>31</sup> P) 30, CH <sub>2</sub> of dppm], 124.7, 125.3 ( <i>m</i> -C of C <sub>6</sub> H <sub>4</sub> Me), 126.6 (C <sup>4</sup> ), 127.8 [d, J(C <sup>31</sup> P) 53, <i>ipso</i> -C of C <sub>6</sub> H <sub>5</sub> P], 130.0 (C <sup>2</sup> ), 131.1 ( <i>ipso</i> -C of C <sub>6</sub> H <sub>5</sub> P), 131.4, 131.5, 131.9, 132.1, 134.4, 134.6 ( <i>o</i> -, <i>m</i> -C of C <sub>6</sub> H <sub>5</sub> P, <i>o</i> -C of C <sub>6</sub> H <sub>4</sub> Me), 133.5, 133.6 ( <i>p</i> -C of C <sub>6</sub> H <sub>5</sub> P), 140.0, 140.1 ( <i>p</i> -C of C <sub>6</sub> H <sub>4</sub> Me), 143.8 (C <sup>3</sup> ), 147.6, 149.3 ( <i>ipso</i> -C of C <sub>6</sub> H <sub>4</sub> Me), 154.4 (C <sup>1</sup> ), 158.1 (C <sup>5</sup> ) <sup>b,c</sup> |
| 13       | 2.15 (3 H, s, C <sub>6</sub> H <sub>4</sub> Me), 2.24 (6 H, s, C <sub>6</sub> H <sub>4</sub> Me), 2.41 (3 H, s, C <sub>6</sub> H <sub>4</sub> Me), 3.06 (3 H, s, NMe), 5.79 [1 H, d, J(H <sup>6</sup> H <sup>7</sup> ) 2, H <sup>6</sup> ], 5.97 [1 H, d, J(H <sup>7</sup> H <sup>6</sup> ) 2, H <sup>7</sup> ], 6.72 (4 H, m), 6.98 [2 H, d, J(HH) 8], 7.05 [2 H, d, J(HH) 8], 7.24 [2 H, d, J(HH) 8], 7.26 [2 H, d, J(HH) 8], 7.31 [2 H, d, J(HH) 8] (C <sub>6</sub> H <sub>4</sub> Me), 7.51 (3 H, m, <i>o</i> -H of C <sub>6</sub> H <sub>4</sub> Me, H <sup>2</sup> ), 7.58 [1 H, ddd, J(HH) 8, 6, 1, H <sup>2</sup> ], 8.22 (1 H, m, H <sup>3</sup> or H <sup>3</sup> ), 8.27 (1 H, m, H <sup>3</sup> or H <sup>3</sup> ), 8.31 [1 H, d, J(H <sup>1</sup> H <sup>2</sup> ) 6, H <sup>1</sup> or H <sup>1</sup> ], 8.42 [1 H, d, J(H <sup>1</sup> H <sup>2</sup> ) 6, H <sup>1</sup> or H <sup>1</sup> ], 8.44 [1 H, d, J(H <sup>4</sup> H <sup>3</sup> ) 8, H <sup>4</sup> or H <sup>4</sup> ], 8.49 [1 H, d, J(H <sup>4</sup> H <sup>3</sup> ) 8, H <sup>4</sup> or H <sup>4</sup> ]   | 20.6, 20.8 (C <sub>6</sub> H <sub>4</sub> Me), 31.3 (NMe), 115.8 (C <sup>6</sup> ), 129.5 (C <sup>7</sup> ), 121.4, 122.5, 122.8, 124.0 ( <i>m</i> -C of C <sub>6</sub> H <sub>4</sub> Me), 124.1, 124.6 (C <sup>4</sup> , C <sup>4</sup> ), 127.8, 128.4 (C <sup>2</sup> ), 128.3, 129.7, 129.8, 130.0 ( <i>o</i> -C of C <sub>6</sub> H <sub>4</sub> Me), 135.2, 135.8, 136.6 ( <i>p</i> -C of C <sub>6</sub> H <sub>4</sub> Me), 140.5, 141.1 (C <sup>3</sup> , C <sup>3</sup> ), 147.7, 148.2, 148.5, 148.7 ( <i>ipso</i> -C of C <sub>6</sub> H <sub>4</sub> Me), 152.7, 153.7 (C <sup>1</sup> , C <sup>1</sup> ), 154.2 (C <sup>8</sup> ), 157.4, 158.2 (C <sup>5</sup> , C <sup>5</sup> ), 184.4 [d, J(C <sup>103</sup> Rh) 60, CO] <sup>c</sup>   |
| 14       | 2.12 (3 H, s, C <sub>6</sub> H <sub>4</sub> Me), 2.23 (6 H, s, C <sub>6</sub> H <sub>4</sub> Me), 2.41 (3 H, s, C <sub>6</sub> H <sub>4</sub> Me), 6.33 [1 H, t, J(H <sup>7</sup> H <sup>6</sup> ) 5, H <sup>7</sup> ], 6.75 [2 H, d, J(H <sup>6</sup> H <sup>7</sup> ) 5, H <sup>6</sup> ], 6.80 [2 H, d, J(HH) 8], 6.91 [2 H, d, J(HH) 8], 7.02 [2 H, d, J(HH) 8], 7.12 [2 H, d, J(HH) 8], 7.39 [2 H, d, J(HH) 8], 7.50 [2 H, d, J(HH) 8], 7.62 [4 H, d, J(HH) 8] (C <sub>6</sub> H <sub>4</sub> Me), 7.64 (1 H, m, H <sup>2</sup> ), 7.72 [1 H, t, J(HH) 8, H <sup>2</sup> ], 8.1 (2 H, br, H <sup>6</sup> and H <sup>6</sup> ), 8.31 [1 H, t, J(HH) 8, H <sup>3</sup> or H <sup>3</sup> ], 8.37 [1 H, t, J(HH) 8, H <sup>3</sup> or H <sup>3</sup> ], 8.42 [1 H, d, J(H <sup>1</sup> H <sup>2</sup> ) 6, H <sup>1</sup> or H <sup>1</sup> ], 8.55 [1 H, d, J(H <sup>1</sup> H <sup>2</sup> ) 6, H <sup>1</sup> or H <sup>1</sup> ], 8.58 [1 H, d, J(H <sup>4</sup> H <sup>3</sup> ) 8, H <sup>4</sup> or H <sup>4</sup> ], 8.62 [1 H, d, J(H <sup>4</sup> H <sup>3</sup> ) 8, H <sup>4</sup> or H <sup>4</sup> ] <sup>b</sup>   | 20.6, 20.7, 20.8 (C <sub>6</sub> H <sub>4</sub> Me), 114.6 (C <sup>7</sup> ), 121.9, 122.7, 123.3, 124.0 ( <i>m</i> -C of C <sub>6</sub> H <sub>4</sub> Me), 124.1, 124.8 (C <sup>4</sup> , C <sup>4</sup> ), 127.9, 128.4 (C <sup>2</sup> , C <sup>2</sup> ), 129.0, 129.7, 130.0, 130.4 ( <i>o</i> -C of C <sub>6</sub> H <sub>4</sub> Me), 135.6, 136.2, 136.3, 137.0 ( <i>p</i> -C of C <sub>6</sub> H <sub>4</sub> Me), 140.7, 141.2 (C <sup>3</sup> , C <sup>3</sup> ), 147.2, 147.9, 148.3, 148.5 ( <i>ipso</i> -C of C <sub>6</sub> H <sub>4</sub> Me), 151.6, 158.1 (C <sup>6</sup> , C <sup>6</sup> ), 152.5, 153.8 (C <sup>1</sup> , C <sup>1</sup> ), 157.4, 158.3 (C <sup>5</sup> , C <sup>5</sup> ), 184.4 [d, J(C <sup>103</sup> Rh) 59, CO], 184.9 (C <sup>8</sup> )  |
| 15       | 2.08 [1 H, q, J(HH) 10, H <sup>6</sup> ], 2.24 (6 H, s, C <sub>6</sub> H <sub>4</sub> Me), 2.27 (3 H, s, C <sub>6</sub> H <sub>4</sub> Me), 2.39 (3 H, s, C <sub>6</sub> H <sub>4</sub> Me), 2.54 [1 H, ddd, J(HH) 8, 4, 9, H <sup>6</sup> ], 2.78 [1 H, ddd, J(HH) 8, 4, 12, H <sup>7</sup> ], 3.43 [1 H, ddd, J(HH) 8, 4, 13, H <sup>7</sup> ], 7.00 [4 H, d, J(HH) 8, <i>m</i> -H of C <sub>6</sub> H <sub>4</sub> Me], 7.02 [4 H, d, J(HH) 8, <i>o</i> -H of C <sub>6</sub> H <sub>4</sub> Me], 7.23 [4 H, d, J(HH) 8, <i>m</i> -H of C <sub>6</sub> H <sub>4</sub> Me], 7.30 [2 H, d, J(HH) 8, <i>o</i> -H of C <sub>6</sub> H <sub>4</sub> Me], 7.39 [2 H, d, J(HH) 8, <i>o</i> -H of C <sub>6</sub> H <sub>4</sub> Me], 7.46 [1 H, t, J(H <sup>2</sup> H <sup>1</sup> ) 8, 6, H <sup>2</sup> ], 7.57 [1 H, t, J(H <sup>2</sup> H <sup>1</sup> ) 8, 6, H <sup>2</sup> ], 8.20 [1 H, td, J(HH) 8, < 1, H <sup>3</sup> or H <sup>3</sup> ], 8.28 [1 H, td, J(HH) 8, < 1, H <sup>3</sup> or H <sup>3</sup> ], 8.25 [1 H, d, J(H <sup>1</sup> H <sup>2</sup> ) 6, H <sup>1</sup> or H <sup>1</sup> ], 8.35 [1 H, d, J(H <sup>1</sup> H <sup>2</sup> ) 6, H <sup>1</sup> or H <sup>1</sup> ], 8.46 [1 H, d, J(H <sup>3</sup> H <sup>4</sup> ) 8, H <sup>4</sup> or H <sup>4</sup> ], 8.51 [1 H, d, J(H <sup>3</sup> H <sup>4</sup> ) 8, H <sup>4</sup> or H <sup>4</sup> ] | 20.6, 20.7, 20.8 (C <sub>6</sub> H <sub>4</sub> Me), 30.2 (C <sup>7</sup> ), 56.2 (C <sup>6</sup> ), 121.4, 122.5, 122.9, 124.2 ( <i>m</i> -C of C <sub>6</sub> H <sub>4</sub> Me), 124.1, 124.8 (C <sup>4</sup> , C <sup>4</sup> ), 127.9, 128.5 (C <sup>2</sup> , C <sup>2</sup> ), 129.0, 129.8, 129.9, 130.0 ( <i>o</i> -C of C <sub>6</sub> H <sub>4</sub> Me), 135.4, 136.0, 136.3, 136.8 ( <i>p</i> -C of C <sub>6</sub> H <sub>4</sub> Me), 140.7, 141.3 (C <sup>3</sup> , C <sup>3</sup> ), 147.9, 148.4, 148.7 ( <i>ipso</i> -C of C <sub>6</sub> H <sub>4</sub> Me), 152.5, 153.5 (C <sup>1</sup> , C <sup>1</sup> ), 157.5, 158.2 (C <sup>5</sup> , C <sup>5</sup> ), 184.4 [d, J(C <sup>103</sup> Rh) 59, CO], 188.3 (C <sup>8</sup> )   |
| 16       | 1.76 (3 H, s, C <sub>6</sub> H <sub>4</sub> Me), 2.23 (3 H, s, C <sub>6</sub> H <sub>4</sub> Me), 2.24 (3 H, s, C <sub>6</sub> H <sub>4</sub> Me), 2.48 (3 H, s, C <sub>6</sub> H <sub>4</sub> Me), 5.29 [1 H, d, J(H <sup>8</sup> H <sup>7</sup> ) 8, H <sup>8</sup> ], 6.68 [1 H, t, J(HH) 8, H <sup>7</sup> ], 6.88 [1 H, d, J(HH) 8, H <sup>8</sup> ], 6.89 [1 H, m, J(HH) 8, H <sup>7</sup> ], 6.40 [2 H, d, J(HH) 8], 6.99 [2 H, d, J(HH) 8], 7.05 [2 H, d, J(HH) 8], 7.23 [2 H, d, J(HH) 8], 7.31 (6 H, m), 7.49 [1 H, t, J(HH) 8, 6, H <sup>2</sup> ], 7.59 (3 H, m and H <sup>2</sup> ), (C <sub>6</sub> H <sub>4</sub> Me), 8.18 [1 H, t, J(HH) 8, H <sup>3</sup> or H <sup>3</sup> ], 8.23 [1 H, t, J(HH) 8, H <sup>3</sup> or H <sup>3</sup> ], 8.35 [1 H, d, J(H <sup>1</sup> H <sup>2</sup> ) 6, H <sup>1</sup> ], 8.41 [1 H, d, J(H <sup>4</sup> H <sup>3</sup> ) 8, H <sup>4</sup> or H <sup>4</sup> ], 8.46 [1 H, d, J(H <sup>4</sup> H <sup>3</sup> ) 8, H <sup>4</sup> or H <sup>4</sup> ], 8.47 [1 H, d, J(H <sup>1</sup> H <sup>2</sup> ) 6, H <sup>1</sup> ], 9.24 (1 H, s, NH)   | 20.3, 20.7, 20.8 (C <sub>6</sub> H <sub>4</sub> Me), 110.3 (C <sup>7</sup> ), 112.4 (C <sup>6</sup> ), 115.2 (C <sup>8</sup> ), 121.4, 123.1, 123.2, 123.3 ( <i>m</i> -C of C <sub>6</sub> H <sub>4</sub> Me), 123.4, 124.5 (C <sup>4</sup> , C <sup>4</sup> ), 127.9, 129.4 (C <sup>2</sup> , C <sup>2</sup> ), 128.5, 129.8, 130.0, 130.3 ( <i>o</i> -C of C <sub>6</sub> H <sub>4</sub> Me), 135.3, 136.3, 136.9 ( <i>p</i> -C of C <sub>6</sub> H <sub>4</sub> Me), 140.7, 141.2 (C <sup>3</sup> , C <sup>3</sup> ), 147.4, 148.1, 148.4, 149.9 ( <i>ipso</i> -C of C <sub>6</sub> H <sub>4</sub> Me), 152.5, 153.9 (C <sup>1</sup> , C <sup>1</sup> ), 157.8, 158.2 (C <sup>5</sup> , C <sup>5</sup> ), 162.3 (C <sup>9</sup> ), 184.9 [d, J(C <sup>103</sup> Rh) 59, CO]  |
| 17       | 2.24 (3 H, s, C <sub>6</sub> H <sub>4</sub> Me), 2.25 (3 H, s, C <sub>6</sub> H <sub>4</sub> Me), 2.33 (6 H, s, C <sub>6</sub> H <sub>4</sub> Me), 7.0–7.5 (16 H, C <sub>6</sub> H <sub>4</sub> Me), 7.41 (1 H, m, H <sup>2</sup> or H <sup>2</sup> ), 7.51 (1 H, m, H <sup>2</sup> or H <sup>2</sup> ), 7.95 [1 H, td, J(HH) 5, 8, 2, H <sup>3</sup> or H <sup>3</sup> ], 8.02 [1 H, td, J(HH) 5, 8, 2, H <sup>3</sup> or H <sup>3</sup> ], 8.10 [1 H, d, J(H <sup>4</sup> H <sup>3</sup> ) 8, H <sup>4</sup> or H <sup>4</sup> ], 8.18 [1 H, d, J(H <sup>4</sup> H <sup>3</sup> ) 8, H <sup>4</sup> or H <sup>4</sup> ], 8.79 [1 H, d, J(H <sup>1</sup> H <sup>2</sup> ) 6, H <sup>1</sup> or H <sup>1</sup> ], 8.88 [1 H, d, J(H <sup>1</sup> H <sup>2</sup> ) 6, H <sup>1</sup> or H <sup>1</sup> ]   | 21.0, 21.1 (C <sub>6</sub> H <sub>4</sub> Me), 122.5, 123.1, 123.7 ( <i>m</i> -C of C <sub>6</sub> H <sub>4</sub> Me), 125.9, 126.2 (C <sup>4</sup> , C <sup>4</sup> ), 128.6, 128.8 (C <sup>2</sup> , C <sup>2</sup> ), 126.7, 127.1, 129.4, 129.8 ( <i>o</i> -C of C <sub>6</sub> H <sub>4</sub> Me), 135.1, 136.1, 139.2, 139.8 ( <i>p</i> -C of C <sub>6</sub> H <sub>4</sub> Me), 135.9, 136.2 (C <sup>3</sup> , C <sup>3</sup> ), 148.0, 148.1, 149.1, 149.2 ( <i>ipso</i> -C of C <sub>6</sub> H <sub>4</sub> Me), 153.8, 155.1 (C <sup>1</sup> , C <sup>1</sup> ), 157.2, 158.6 (C <sup>5</sup> , C <sup>5</sup> ) <sup>c</sup>   |
| 19       | 2.23 (3 H, s, C <sub>6</sub> H <sub>4</sub> Me), 2.28 (3 H, s, C <sub>6</sub> H <sub>4</sub> Me), 2.36 (6 H, s, C <sub>6</sub> H <sub>4</sub> Me), 7.06–7.39 (16 H, C <sub>6</sub> H <sub>4</sub> Me), 7.63 (2 H, m, H <sup>2</sup> ), 8.09 (4 H, m, H <sup>3</sup> and H <sup>4</sup> ), 8.73 [1 H, d, J(H <sup>1</sup> H <sup>2</sup> ) 6, H <sup>1</sup> or H <sup>1</sup> ], 8.99 [1 H, d, J(H <sup>1</sup> H <sup>2</sup> ) 6, H <sup>1</sup> or H <sup>1</sup> ]  |   |

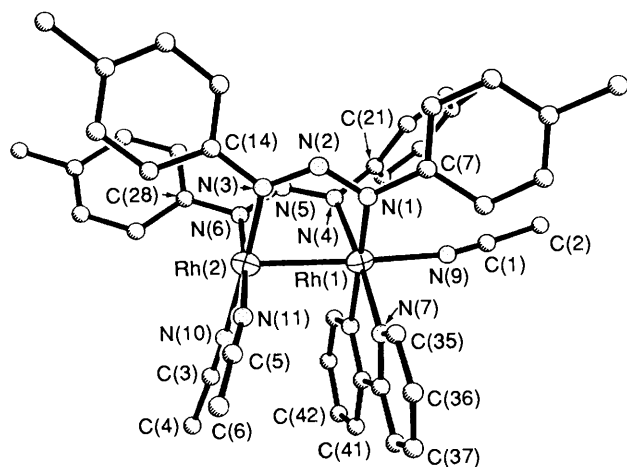
<sup>a</sup> *J* values are in Hz; 270 MHz spectra, in CD<sub>2</sub>Cl<sub>2</sub> unless stated otherwise. <sup>b</sup> In CD<sub>3</sub>NO<sub>2</sub>. <sup>c</sup> 400 MHz spectrum. <sup>d</sup> In CD<sub>3</sub>CN.

due to the greater rigidity of the bipyridyl ligand. The Rh–Rh distance of 2.534(2) Å is comparable with that of the dication [Rh<sub>2</sub>(μ-I)(CO)(bipy)(μ-RNNNR)<sub>2</sub>]<sub>2</sub><sup>2+</sup> [Rh–Rh 2.544(1) Å] and indicates a single M–M bond. The *trans* influence of the M–M bond is seen in the Rh–N distance of 2.080(9) Å for the axially co-ordinated acetonitrile. This is significantly longer than the Rh–N distances for the equatorially bound groups [2.032(8) and 2.011(8) Å respectively]. Similar dimensions for the Rh–Rh and Rh–N distances have recently been observed<sup>3</sup> in the closely related tetrakis(acetonitrile) dication [Rh<sub>2</sub>(NCMe)<sub>4</sub>(bipy)(μ-O<sub>2</sub>CMe)<sub>2</sub>]<sub>2</sub><sup>2+</sup> which has two axial acetonitrile ligands but is otherwise similar to the dication in **3** [Rh–Rh 2.540(1), Rh–NCMe<sub>ax</sub> 2.209, Rh–N<sub>eq</sub> 1.984 Å].

Elsewhere<sup>1</sup> we have presented a frontier-orbital rationale for the observed tendency for face-to-face complexes containing the [Rh<sub>2</sub>]<sup>4+</sup> core to co-ordinate additional ligands *trans* to the Rh–Rh bond (*i.e.* in an axial site). The structure of **3**, however, differs from that of [Rh<sub>2</sub>(μ-I)(CO)(bipy)(μ-RNNNR)<sub>2</sub>]<sub>2</sub><sup>2+</sup>, the only other [Rh<sub>2</sub>]<sup>4+</sup> complex so far structurally characterised in the triazenide-bridged series, in that the latter has the axial ligand, *i.e.* the bridging iodide, bound to Rh(2) (the rhodium atom *not* carrying the bipyridyl ligand). The preference for co-ordination at one axial site rather than the other most likely results from electronic rather than steric factors; ligand addition will occur at the more electron-deficient site. In all previous complexes in this class prepared to date Rh(2) carried at least one equatorial carbonyl ligand, the strong π-acceptor

**Table 3** Selected bond lengths (Å) and angles (°) for complex **3**

|                   |           |                  |           |                   |           |                  |           |
|-------------------|-----------|------------------|-----------|-------------------|-----------|------------------|-----------|
| Rh(1)–Rh(2)       | 2.534(2)  | P(2)–F(10)       | 1.598(15) | N(10)–C(3)        | 1.112(14) | N(7)–C(39)       | 1.351(12) |
| N(4)–C(21)        | 1.446(11) | N(1)–N(2)        | 1.289(12) | P(1)–F(2)         | 1.583(8)  | Rh(2)–N(6)       | 2.014(7)  |
| Rh(1)–N(7)        | 2.039(7)  | N(3)–C(14)       | 1.409(14) | P(1)–F(5)         | 1.578(12) | N(9)–C(1)        | 1.083(16) |
| N(7)–C(35)        | 1.319(13) | N(4)–N(5)        | 1.279(13) | P(2)–F(8)         | 1.575(9)  | P(1)–F(1)        | 1.558(8)  |
| Rh(2)–N(3)        | 2.009(8)  | Rh(1)–N(4)       | 2.053(7)  | P(2)–F(11)        | 1.543(14) | P(1)–F(3)        | 1.537(13) |
| N(8)–C(44)        | 1.339(13) | N(6)–C(28)       | 1.416(14) | N(1)–C(7)         | 1.432(14) | P(1)–F(6)        | 1.487(13) |
| Rh(2)–N(11)       | 2.011(8)  | Rh(1)–N(9)       | 2.080(9)  | Rh(1)–N(1)        | 2.060(8)  | P(2)–F(9)        | 1.531(14) |
| N(11)–C(5)        | 1.106(14) | N(8)–C(40)       | 1.337(11) | N(5)–N(6)         | 1.296(11) | P(2)–F(12)       | 1.545(12) |
| P(1)–F(4)         | 1.532(14) | Rh(2)–N(10)      | 2.032(8)  | Rh(1)–N(8)        | 2.047(8)  | N(2)–N(3)        | 1.300(13) |
| P(2)–F(7)         | 1.555(10) |                  |           |                   |           |                  |           |
| Rh(2)–Rh(1)–N(1)  | 86.1(3)   | Rh(1)–N(1)–C(7)  | 125.7(7)  | Rh(2)–Rh(1)–N(4)  | 83.3(2)   | N(2)–N(1)–C(7)   | 111.3(8)  |
| N(1)–Rh(1)–N(4)   | 88.3(3)   | N(1)–N(2)–N(3)   | 116.8(8)  | Rh(2)–Rh(1)–N(7)  | 93.6(3)   | Rh(2)–N(3)–N(2)  | 128.2(7)  |
| N(1)–Rh(1)–N(7)   | 95.2(3)   | Rh(2)–N(3)–C(14) | 118.0(7)  | N(4)–Rh(1)–N(7)   | 175.1(3)  | N(2)–N(3)–C(14)  | 113.8(8)  |
| Rh(2)–Rh(1)–N(8)  | 91.3(2)   | Rh(1)–N(4)–N(5)  | 126.5(6)  | N(1)–Rh(1)–N(8)   | 174.3(3)  | Rh(1)–N(4)–C(21) | 122.4(7)  |
| N(4)–Rh(1)–N(8)   | 96.4(3)   | N(5)–N(4)–C(21)  | 110.7(7)  | N(7)–Rh(1)–N(8)   | 79.9(3)   | N(4)–N(5)–N(6)   | 116.1(7)  |
| Rh(2)–Rh(1)–N(9)  | 172.3(2)  | Rh(2)–N(6)–N(5)  | 125.1(7)  | N(1)–Rh(1)–N(9)   | 97.0(3)   | Rh(2)–N(6)–C(28) | 119.7(6)  |
| N(4)–Rh(1)–N(9)   | 89.8(3)   | N(5)–N(6)–C(28)  | 113.2(7)  | N(7)–Rh(1)–N(9)   | 93.1(3)   | Rh(1)–N(7)–C(35) | 126.1(6)  |
| N(8)–Rh(1)–N(9)   | 86.1(3)   | Rh(1)–N(7)–C(39) | 115.0(6)  | Rh(1)–Rh(2)–N(3)  | 83.0(3)   | C(35)–N(7)–C(39) | 119.0(8)  |
| Rh(1)–Rh(2)–N(6)  | 85.5(3)   | Rh(1)–N(8)–C(40) | 114.8(6)  | N(3)–Rh(2)–N(6)   | 87.3(3)   | Rh(1)–N(8)–C(44) | 125.2(6)  |
| Rh(1)–Rh(2)–N(10) | 99.9(3)   | C(40)–N(8)–C(44) | 120.0(8)  | N(1)–Rh(2)–N(10)  | 177.0(4)  | Rh(1)–N(9)–C(1)  | 167.1(8)  |
| N(6)–Rh(2)–N(10)  | 93.3(3)   | Rh(2)–N(10)–C(3) | 176.4(9)  | Rh(1)–Rh(2)–N(11) | 99.8(3)   | Rh(2)–N(11)–C(5) | 167.3(12) |
| N(3)–Rh(2)–N(11)  | 92.7(3)   | N(9)–C(1)–C(2)   | 177.1(13) | N(6)–Rh(2)–N(11)  | 174.7(4)  | N(10)–C(3)–C(4)  | 179.0(12) |
| N(10)–Rh(2)–N(11) | 86.5(3)   | N(11)–C(5)–C(6)  | 178.7(14) | Rh(1)–N(1)–N(2)   | 121.8(7)  |                  |           |

**Fig. 1** The molecular structure of the dication of complex **3** showing the labelling scheme. All hydrogen atoms have been omitted for clarity; the rhodium atoms are shown as ellipsoids enclosing 50% probability density

ligand therefore making Rh(2) relatively electron poor. With complete decarbonylation, the ligand set Rh(2)(NCMe)<sub>2</sub> is more electron rich than Rh(1)(bipy) and axial co-ordination occurs at the latter site.

The cyclic voltammogram of complex **3** shows one diffusion-controlled, reversible reduction wave at 0.06 V and an ill defined oxidation wave at 1.29 V. These electron-transfer processes most likely involve the formation of [Rh<sub>2</sub>]<sup>3+</sup> and [Rh<sub>2</sub>]<sup>5+</sup>-containing complexes respectively. However, in common with the other new species described herein, the chemical and electrochemical oxidation and reduction reactions of **3** are complicated and the results of these studies will be detailed elsewhere.

Nitrile ligands are generally regarded as substitutionally labile, [Rh<sub>2</sub>(NCMe)<sub>6</sub>(μ-O<sub>2</sub>CMe)<sub>2</sub>]<sup>2+</sup> reacting<sup>4</sup> with bipy or 1,10-phenanthroline (phen) at room temperature to give, for example, [Rh<sub>2</sub>(NCMe)<sub>4</sub>(phen)(μ-O<sub>2</sub>CMe)<sub>2</sub>]<sup>2+</sup>. In this reaction initial substitution occurs at adjacent axial-equatorial positions but over a period of 48 h the diequatorially substituted isomer is formed. The axial nitrile ligands of [Rh<sub>2</sub>(NCMe)<sub>6</sub>(μ-O<sub>2</sub>CMe)<sub>2</sub>]<sup>2+</sup> are weakened by the *trans* effect of the Rh–Rh

bond, and are substitutionally labile whereas the equatorial ligands are fairly inert. Somewhat surprisingly, then, the reactivity of **3** is limited. Substitution with neutral ligands such as bipy does not occur, either at room temperature or thermally, and reaction was readily observed only with Na[S<sub>2</sub>CNMe<sub>2</sub>]<sub>2</sub>·2H<sub>2</sub>O in acetonitrile, giving [Rh<sub>2</sub>(NCMe)(S<sub>2</sub>CNMe<sub>2</sub>)(bipy)(μ-RNNNR)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> **4** (Tables 1 and 2) as a brown powder in good yield. The <sup>1</sup>H NMR spectrum of **4** is consistent with the asymmetric structure shown in Scheme 1 and is similar to that proposed<sup>1</sup> for [Rh<sub>2</sub>(CO)(S<sub>2</sub>CNMe<sub>2</sub>)(bipy)(μ-RNNNR)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> rather than to that determined for **3**. The methyl resonances for the tolyl groups of the triazenide bridges occur as a complex multiplet centred at δ 2.26 and the pyridyl rings of the bipy ligand are also inequivalent. In addition, the signals for the methyl groups of the dithiocarbamate ligand occur as two singlets at δ 2.77 and 3.02 suggesting S<sub>2</sub>CNMe<sub>2</sub> is bound to Rh(2) at one axial and one equatorial site.

Although complex **3** proved to be relatively inert, the halide-abstraction reaction of [{Rh<sub>2</sub>(μ-I)(CO)(bipy)(μ-RNNNR)<sub>2</sub>]<sup>2+</sup> **1** in CH<sub>2</sub>Cl<sub>2</sub> provided a more reactive precursor to a wide range of novel dirhodium complexes. Thus, the reaction with AgPF<sub>6</sub> gave a deep green solution which, after filtration to remove precipitated AgI, showed one carbonyl band in the IR spectrum [ν(CO) 2087 cm<sup>-1</sup>]; the similarity in energy of this band to that of **2** suggests the presence of a weakly solvated species *e.g.* [Rh<sub>2</sub>(CO)(solv)<sub>2</sub>(bipy)(μ-RNNNR)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> **A** (solv = CH<sub>2</sub>Cl<sub>2</sub>). During the reaction IR spectroscopy showed the initial formation of an intermediate with one carbonyl band at 2046 cm<sup>-1</sup>; though not isolable, it is most likely the monoiodide cation [Rh<sub>2</sub>I(CO)(solv)(bipy)(μ-RNNNR)<sub>2</sub>][PF<sub>6</sub>].

Complex **A** (solv = CH<sub>2</sub>Cl<sub>2</sub>) may be used *in situ* in CH<sub>2</sub>Cl<sub>2</sub>. Alternatively, removal of the solvent from the reaction mixture and treatment of the residue with tetrahydrofuran (thf) or methanol gave species which react in the same way, presumably **A** (solv = thf or MeOH). These solvated species could not be isolated though they are moderately stable in solution under nitrogen. However, treatment of the residue with MeCN, followed by precipitation with diethyl ether, provides the best synthetic route to pure [Rh<sub>2</sub>(CO)(NCMe)<sub>2</sub>(bipy)(μ-RNNNR)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> **2** (see above). All of the complexes **A** (solv = CH<sub>2</sub>Cl<sub>2</sub>, thf or MeOH) act as precursors to isolable, [Rh<sub>2</sub>]<sup>4+</sup>-containing species. Although the CH<sub>2</sub>Cl<sub>2</sub> solvento

complex has been most routinely used, the use of methanol and thf can provide advantages in the synthesis of neutral products (see below).

The addition of an equimolar quantity of a neutral bidentate N-donor ligand [ $L-L = \text{bipy}$ , 4,4'-dimethyl-2,2'-bipyridyl (dmbipy), phen, or di-2-pyridylamine (dpa)] to **A** (solv =  $\text{CH}_2\text{Cl}_2$ ) in  $\text{CH}_2\text{Cl}_2$ , and storage of the mixture at  $0^\circ\text{C}$  overnight, gave in each case a green microcrystalline precipitate which could be purified from acetonitrile-diethyl ether to give the product in 50–75% yield. Though elemental analysis (C, H and N) was consistent with the formula  $[\text{Rh}_2(\text{CO})(L-L)(\text{bipy})-(\mu\text{-RNNNR})_2][\text{PF}_6]_2$ , *i.e.* with a face-to-face structure related to that of  $[\text{Rh}_2(\text{CO})(\text{S}_2\text{CNMe}_2)(\text{bipy})(\mu\text{-RNNNR})_2][\text{PF}_6]_2$  **1** and **4** above, IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy (Tables 1 and 2) revealed the formation of the novel carbonyl-bridged compounds  $[\text{Rh}_2(\mu\text{-CO})(L-L)(\text{bipy})(\mu\text{-RNNNR})_2][\text{PF}_6]_2$  **5** ( $L-L = \text{bipy}$  **5**, dmbipy **6**, phen **7** or dpa **8**) with the structure shown in Scheme 1. Each complex shows one IR carbonyl band in the range  $1770\text{--}1780\text{ cm}^{-1}$  and the  $^1\text{H}$  NMR spectrum of **5** shows only one signal for the methyl groups of the two triazenide ligands, two doublets ( $\delta$  7.09 and 7.21) for the *ortho*- and *meta*-protons of the  $\text{C}_6$  rings, and three signals for the bipy ligands in the ratio 1:2:1. The 400 MHz  $^{13}\text{C}$  NMR spectrum shows a triplet at  $\delta$  186 for the bridging carbonyl carbon atom [ $J(^{13}\text{C}^{103}\text{Rh})$  48 Hz], one signal for the four methyl groups of the triazenide ligands and two equivalent pyridyl rings. For each of the compounds **6–8** the  $^1\text{H}$  NMR spectrum shows two signals for the RNNNR methyl groups. As the two halves of the bipyridyl ligand are equivalent the ligands  $L-L$  must chelate one rhodium atom, binding in *trans* positions to the two nitrogen atoms of the *cis*-bridging triazenide ligands. As with **5**, each complex **6–8** exhibits a triplet signal in the  $^{13}\text{C}$  NMR spectrum at  $\delta$  *ca.* 180, with a coupling to rhodium of *ca.* 50 Hz, corresponding to the bridging carbonyl ligand.

The reaction of 1 equivalent of dppe with complex **A** (solv =  $\text{CH}_2\text{Cl}_2$ ) in  $\text{CH}_2\text{Cl}_2$  is similar to those with the N–N ligands described above, resulting in an intense green solution from which a green solid was isolated after filtration, reduction of the solvent volume, and addition of diethyl ether or hexane as precipitant; recrystallisation from  $\text{CH}_2\text{Cl}_2$ -diethyl ether gave microcrystals of  $[\text{Rh}_2(\mu\text{-CO})(\text{dppe})(\text{bipy})(\mu\text{-RNNNR})_2][\text{PF}_6]_2$  **9** (Tables 1 and 2). The IR spectrum is similar to those of complexes **5–8** with one absorption in the bridging carbonyl region at  $1760\text{ cm}^{-1}$ . Similarly, the  $^1\text{H}$  NMR spectrum shows two resonances for the four *p*-tolyl methyl groups, and equivalent pyridyl groups for the bipy ligand. The  $^{13}\text{C}$  NMR spectrum shows two resonances, at  $\delta$  21.4 and 21.6, for the methyl groups of the triazenide bridges, and two signals for the *o*- and *m*-carbons of the  $\text{C}_6\text{H}_4$  groups, also indicating inequivalent ends to the two triazenide bridges. The  $^{31}\text{P}$  NMR spectrum showed a doublet at  $\delta$  58.0 [ $J(^{31}\text{P}^{103}\text{Rh})$  127 Hz], indicating equivalent phosphorus atoms, again in accord with the carbonyl-bridged structure in Scheme 1. However, the  $^{13}\text{C}$  signal for the bridging carbonyl carbon atom was not observed.

The reaction between complex **A** (solv =  $\text{CH}_2\text{Cl}_2$ ) and  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$  (dppm) is again similar to that with bipy, with a green solid isolated in good yield. Once again the elemental analysis was consistent with the formula  $[\text{Rh}_2(\text{CO})(\text{dppm})(\text{bipy})(\mu\text{-RNNNR})_2][\text{PF}_6]_2$  **10** and the Nujol-mull IR spectrum showed a bridging carbonyl absorption at  $1756\text{ cm}^{-1}$ . However, in  $\text{CH}_2\text{Cl}_2$ , the IR spectrum unexpectedly showed two bands ( $2070\text{m}$  and  $1758\text{s cm}^{-1}$ ) indicating the presence in solution of a second isomer **10b** with a terminal carbonyl ligand, in addition to  $[\text{Rh}_2(\mu\text{-CO})(\text{dppm})(\text{bipy})(\mu\text{-RNNNR})_2][\text{PF}_6]_2$  **10a** the analogue of **9**. Neither the  $^1\text{H}$  nor  $^{13}\text{C}$  NMR spectrum of **10** provided evidence for the nature of the second species. The signals for the triazenide  $\text{C}_6\text{H}_4$  and dppm phenyl protons are, however, broader than those observed for **9**, suggesting interconversion between the major, carbonyl-bridged isomer **10a** and the minor terminal form **10b**. The  $^{13}\text{C}$  NMR spectrum also shows no evidence for the terminally bound carbonyl

species **10b** although a doublet of triplets was observed for the carbonyl group of **10a** at  $\delta$  187.5 [ $J(\text{C}^{103}\text{Rh})$  124,  $J(\text{C}^{31}\text{P})$  7]. By contrast,  $^{31}\text{P}$  NMR spectroscopy provided good evidence both for the terminal isomer **10b** and for its equilibration with **10a**.

The room-temperature  $^{31}\text{P}$  NMR spectrum of complex **10** in  $(\text{CD}_3)_2\text{CO}$  (50%) showed only one broad signal ( $\delta$   $-25.5$ ) (apart from the well resolved heptet of the  $[\text{PF}_6]^-$  anion) suggesting, by comparison with the well defined spectrum of **9**, the occurrence of a rapid fluxional process. At  $-80^\circ\text{C}$  the spectrum is well resolved, showing not only a doublet [ $\delta$   $-23.5$ ,  $J(^{31}\text{P}^{103}\text{Rh})$  110.7 Hz] which can be assigned to the two equivalent phosphorus atoms of the carbonyl-bridged isomer **10a**, but also a doublet [ $\delta$   $-11.5$ ,  $J(^{31}\text{P}^{103}\text{Rh})$  92.7 Hz] and a doublet of doublets [ $\delta$   $-90.4$ ,  $J(^{31}\text{P}^{103}\text{Rh})$  58.3 and 64.3 Hz] due to the second, minor component **10b**. The latter resonances may be assigned to an equatorial phosphorus atom (coupled to one Rh atom), and an axial phosphorus atom (coupled to both Rh atoms, the second coupling *via* the *trans* M–M bond) respectively, as in the structure shown in Scheme 1.

Although the spectroscopic data show the presence of two species in solution, an X-ray crystallographic study on **10** revealed only the unusual carbonyl-bridged isomer **10a** in the solid state (as implied by the Nujol-mull IR spectrum). Crystals of the dichloromethane solvate of **10a** were grown by the slow diffusion of hexane into a  $\text{CH}_2\text{Cl}_2$  solution. The structure is shown in Fig. 2 and important molecular bond lengths and angles are listed in Table 4. The structural study of **10a**· $2\text{CH}_2\text{Cl}_2$  confirms the presence of a bridging carbonyl in the dication, and is in agreement with the molecular structure suggested by the spectroscopic results. The Rh...Rh distance of 3.179(2) Å is very long in comparison with other dirhodium(II) triazenide-bridged complexes [*cf.* 2.534(2) for **3** and 2.544(1) for **1**] suggesting little or no direct interaction between the two metal atoms. The angle of  $108.3(11)^\circ$  for Rh(1)–C(1)–Rh(2) is much greater than is common for  $\text{Rh}_2(\mu\text{-CO})$  species, for which the mean value is  $84.5^\circ$ .<sup>5</sup> The local geometry at each rhodium atom may be considered as square pyramidal with the Rh–C(1) interaction at the apex of the pyramid. Geometries such as this are well known for rhodium(III) acyl complexes such as  $[\text{RhCl}\{\text{C}(\text{O})\text{Me}\}(\text{PMe}_2\text{Ph})_3][\text{PF}_6]$ . For this species<sup>6</sup> the values of  $\nu(\text{CO})$  ( $1720\text{ cm}^{-1}$ ) and the Rh–C–Me angle [ $112.2(4)^\circ$ ] are comparable with  $\nu(\text{CO})$  ( $1758\text{ cm}^{-1}$ ) and the Rh–C–Rh angle [ $108.3(11)^\circ$ ] found for **10a**. The inference to be drawn is that the  $\mu\text{-CO}$  ligand in **10a** may be usefully viewed as a metallated formyl ligand, or more simply as a ketonic ( $\text{CO}^{2-}$ ) carbonyl.

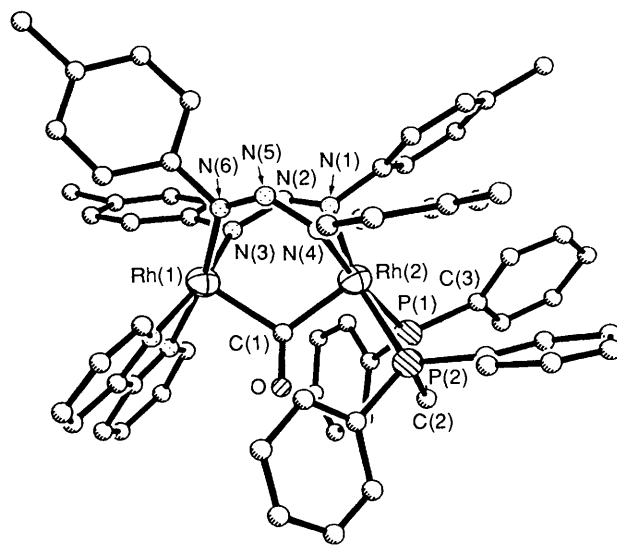


Fig. 2 The molecular structure of the dication of complex **10a** showing the labelling scheme. Other details as in Fig. 1

**Table 4** Selected bond lengths (Å) and angles (°) for complex **10a**·2CH<sub>2</sub>Cl<sub>2</sub>

|                  |           |                  |           |                  |           |                  |           |
|------------------|-----------|------------------|-----------|------------------|-----------|------------------|-----------|
| Rh(1)···Rh(2)    | 3.179(2)  | N(1)–C(27)       | 1.433(22) | P(3)–F(6)        | 1.478(29) | P(1)–C(2)        | 1.833(19) |
| Rh(1)–N(7)       | 2.086(15) | N(4)–N(5)        | 1.262(21) | P(4)–F(9)        | 1.556(24) | P(2)–C(2)        | 1.828(20) |
| Rh(2)–P(1)       | 2.303(6)  | N(6)–C(48)       | 1.423(24) | P(4)–F(12)       | 1.540(25) | P(3)–F(1)        | 1.453(32) |
| Rh(2)–N(4)       | 2.110(15) | N(8)–C(60)       | 1.248(23) | O–C(1)           | 1.192(26) | P(3)–F(4)        | 1.465(26) |
| P(1)–C(3)        | 1.791(18) | Rh(1)–N(3)       | 2.019(14) | N(2)–N(3)        | 1.291(19) | P(4)–F(7)        | 1.473(22) |
| P(2)–C(15)       | 1.854(20) | Rh(1)–N(8)       | 2.054(15) | N(4)–C(41)       | 1.460(26) | P(4)–F(10)       | 1.571(22) |
| P(3)–F(2)        | 1.508(24) | Rh(2)–P(2)       | 2.327(6)  | N(7)–C(55)       | 1.353(30) | Cl(1)–C(65)      | 1.714(36) |
| P(3)–F(5)        | 1.467(25) | Rh(2)–C(1)       | 1.929(20) | N(8)–C(64)       | 1.331(29) | N(1)–N(2)        | 1.296(24) |
| P(4)–F(8)        | 1.496(22) | P(1)–C(9)        | 1.797(20) | Rh(1)–N(6)       | 2.075(15) | N(3)–C(34)       | 1.456(26) |
| P(4)–F(11)       | 1.479(23) | P(2)–C(21)       | 1.805(23) | Rh(1)–C(1)       | 1.992(22) | N(5)–N(6)        | 1.275(23) |
| Cl(2)–C(65)      | 1.540(44) | P(3)–F(3)        | 1.483(23) | Rh(2)–N(1)       | 2.150(15) | N(7)–C(59)       | 1.372(27) |
| Rh(2)–Rh(1)–N(3) | 79.6(4)   | P(1)–Rh(2)–C(1)  | 86.5(7)   | Rh(2)–Rh(1)–N(6) | 72.2(4)   | P(2)–Rh(2)–C(1)  | 88.4(7)   |
| N(3)–Rh(1)–N(6)  | 88.1(6)   | N(1)–Rh(2)–C(1)  | 100.0(8)  | Rh(2)–Rh(1)–N(7) | 111.8(5)  | N(4)–Rh(2)–C(1)  | 99.6(7)   |
| N(3)–Rh(1)–N(7)  | 168.6(6)  | Rh(2)–P(1)–C(2)  | 93.3(6)   | N(6)–Rh(1)–N(7)  | 95.4(6)   | Rh(2)–P(1)–C(3)  | 116.1(7)  |
| Rh(2)–Rh(1)–N(8) | 118.3(4)  | Rh(2)–P(1)–C(9)  | 124.0(6)  | N(3)–Rh(1)–N(8)  | 95.2(6)   | Rh(2)–P(2)–C(2)  | 92.7(6)   |
| N(6)–Rh(1)–N(8)  | 169.3(5)  | Rh(2)–P(2)–C(15) | 119.1(7)  | N(7)–Rh(1)–N(8)  | 79.4(6)   | Rh(2)–P(2)–C(21) | 123.9(7)  |
| Rh(2)–Rh(1)–C(1) | 35.2(6)   | Rh(2)–N(1)–N(2)  | 131.1(11) | N(3)–Rh(1)–C(1)  | 97.5(7)   | Rh(2)–N(1)–C(27) | 112.4(12) |
| N(6)–Rh(1)–C(1)  | 102.8(7)  | Rh(1)–N(3)–N(2)  | 128.1(13) | N(7)–Rh(1)–C(1)  | 92.2(7)   | Rh(1)–N(3)–C(34) | 118.0(10) |
| N(8)–Rh(1)–C(1)  | 86.8(8)   | Rh(2)–N(4)–N(5)  | 125.9(14) | Rh(1)–Rh(2)–P(1) | 112.6(2)  | Rh(2)–N(4)–C(41) | 120.1(11) |
| Rh(1)–Rh(2)–P(2) | 119.4(1)  | Rh(1)–N(6)–N(5)  | 134.6(12) | P(1)–Rh(2)–P(2)  | 73.4(2)   | Rh(1)–N(6)–C(48) | 110.3(12) |
| Rh(1)–Rh(2)–N(1) | 72.4(4)   | Rh(1)–N(7)–C(55) | 125.7(13) | P(1)–Rh(2)–N(1)  | 96.6(4)   | Rh(1)–N(7)–C(59) | 112.2(14) |
| P(2)–Rh(2)–N(1)  | 166.6(4)  | Rh(1)–N(8)–C(60) | 113.7(14) | Rh(1)–Rh(2)–N(4) | 76.5(4)   | Rh(1)–N(8)–C(64) | 123.3(12) |
| P(1)–Rh(2)–N(4)  | 169.9(5)  | Rh(1)–C(1)–Rh(2) | 108.3(11) | P(2)–Rh(2)–N(4)  | 98.6(5)   | Rh(1)–C(1)–O     | 122.2(14) |
| N(1)–Rh(2)–N(4)  | 90.4(6)   | Rh(2)–C(1)–O     | 129.3(17) | Rh(1)–Rh(2)–C(1) | 36.5(7)   |                  |           |

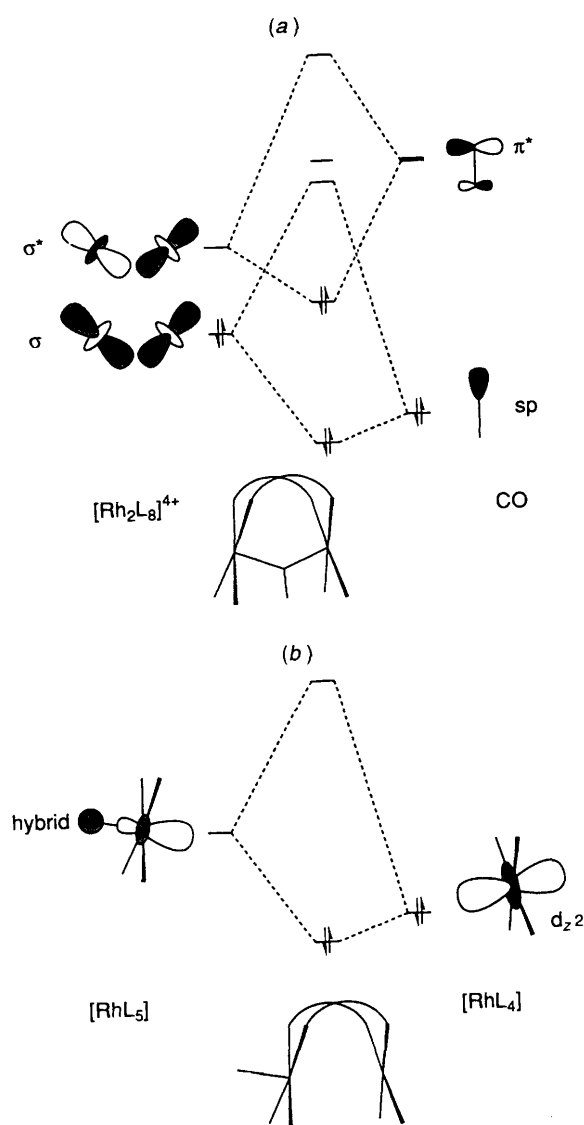
A corollary is that the rhodium atoms of **10a** are formally Rh<sup>III</sup>.

In order to assess these suggestions, and to probe the bonding in these species, extended-Hückel molecular-orbital (EHMO) calculations<sup>7</sup> were carried out on simple models of complex **10** as both the carbonyl-bridged **10a** and unbridged **10b** isomers (*i.e.* on [Rh<sub>2</sub>H<sub>4</sub>(CO)<sub>5</sub>] in which hydride ligands replace the triazenide ligands, and CO replaces the others, of **10**). Idealised geometries were employed [all bond angles at rhodium = 90 or 180°, Rh–C–O 180°, Rh–H 1.60, Rh–Rh 3.20–2.50, Rh–C(O) 1.808, C–O 1.152 Å]; Hückel parameters were taken from the literature.<sup>8</sup> The calculated total energies for the two isomers of [Rh<sub>2</sub>H<sub>4</sub>(CO)<sub>5</sub>] are similar [within 1 eV ( $\approx$ 96 kJ mol<sup>-1</sup>)] without geometry optimisation. Given the crudeness of the model this is in reasonable accord with the experimental evidence above. The Rh···Rh overlap population for the bridged isomer with Rh···Rh distance 3.20 Å is slightly negative (–0.051) indicating no direct Rh···Rh bonding (*cf.* 0.129 for the non-bridged isomer at the same Rh···Rh distance). The general form of the major interactions between the Rh<sub>2</sub> unit and the  $\mu$ -CO ligand is indicated in Fig. 3(a). The occupancy of both  $\sigma$  and  $\sigma^*$  Rh···Rh orbitals arises in the bridged isomer because of the stabilisation of the latter orbitals by interaction with the in-plane CO  $\pi^*$  orbital. As a consequence the Rh–Rh bond order is formally zero in the carbonyl-bridged isomer {and unity in the non-carbonyl-bridged isomer, *cf.* [Rh<sub>2</sub>( $\mu$ -O<sub>2</sub>CR)<sub>4</sub>L<sub>2</sub>] adducts<sup>9</sup>}. The lowest unoccupied molecular orbitals (LUMOs) are Rh( $\mu$ -CO) antibonding in character which is in agreement with the observed Rh– $\mu$ -CO bond cleavage on reduction of **10** to **11** (see below). In accord with the suggestion that the  $\mu$ -CO has ketonic character we calculate a build-up of negative charge on the oxygen of this group (–0.98 e, *cf.* –0.76 e for terminal carbonyls in the model for **10a**). It is notable that in the crystal structure of **10a**·2CH<sub>2</sub>Cl<sub>2</sub> the shortest intermolecular contact involving O is a C–H···O hydrogen bond to an acidic hydrogen of the ordered dichloromethane [O···H(65b) 2.46 Å, O···H(65b)–C(65) 173, C(1)–O···H(65b) 167°], consistent with significant negative charge at O. The calculations on the unbridged isomer of [Rh<sub>2</sub>H<sub>4</sub>(CO)<sub>5</sub>] analogous to **10b** showed that the addition of one axial ligand brings about substantial charge redistribution such that the rhodium with the axial CO ligand carries the *higher* fractional charge (+1.29,

*cf.* +0.28 for the other rhodium and +0.97 e for each rhodium in the bridged isomer). The implication is that the [Rh<sub>2</sub>]<sup>4+</sup> unit may be usefully viewed as consisting of a square-planar rhodium(i) centre interacting with a square-pyramidal rhodium(III) centre *via* a donor–acceptor metal–metal bond [see Fig. 3(b)]. In this bond the hybrid orbital arising from interaction of the axial CO lone pair and rhodium p<sub>z</sub> and d<sub>z<sup>2</sup></sub> [labelled hybrid in Fig. 3(b)] is the acceptor orbital and lies at high energy relative to the donor d<sub>z<sup>2</sup></sub> on the other rhodium atom. As a consequence the pair of electrons in the metal–metal  $\sigma$ -bond orbital is more localised on the rhodium without the axial carbonyl and the charge disparity noted above results.

The electrochemistry of complexes **9** and **10** appears deceptively simple. In CH<sub>2</sub>Cl<sub>2</sub> the cyclic voltammogram of each complex shows one oxidation wave (1.51 and 1.44 V respectively) and two reduction waves (–0.20 and –0.53, and 0.04 and –0.56 V respectively) all of which appear to be fully reversible. However, the chemical reduction is far from straightforward. On addition of 1 equivalent of NaBH<sub>4</sub> to **9** in thf a good yield was obtained of the paramagnetic, [Rh<sub>2</sub>]<sup>3+</sup>-containing complex [Rh<sub>2</sub>(CO)(dppe-*P*)(bipy)( $\mu$ -RNNNR)<sub>2</sub>][PF<sub>6</sub>]**11**, characterised by elemental analysis (Table 1) and by the close similarity of its spectroscopic and voltammetric properties to those of [Rh<sub>2</sub>(CO)(PPh<sub>3</sub>)(bipy)( $\mu$ -RNNNR)<sub>2</sub>][PF<sub>6</sub>].<sup>1</sup> Thus, it shows one IR carbonyl band at 2016 cm<sup>-1</sup>, an anisotropic ESR spectrum at 77 K (in a 2:1 thf:CH<sub>2</sub>Cl<sub>2</sub> glass) with g<sub>1</sub> = 2.254, g<sub>2</sub> = 2.223 and g<sub>3</sub> = 2.014 and hyperfine coupling to the two inequivalent rhodium atoms [A<sub>3</sub> = 27.1 and 8.0 G (8  $\times$  10<sup>-4</sup> T)], and a cyclic voltammogram with a reversible oxidation wave at 0.85 V and a reversible reduction wave at –0.51 V. Thus, when **9** undergoes one-electron reduction the bridging carbonyl reverts to a terminal position. Moreover, the dppe ligand becomes monodentate since the face-to-face structure does not favour axial site co-ordination in the [Rh<sub>2</sub>]<sup>3+</sup> state.

On treatment of complex **9** with 2 equivalents of [Co(cp)<sub>2</sub>] (cp =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) an air-sensitive green powder can be isolated which shows one carbonyl band at 1949 cm<sup>-1</sup> and which reacts with air or [Fe(cp)<sub>2</sub>]<sup>+</sup> to form **11**. Though the green species could not be further characterised it is most likely the neutral [Rh<sub>2</sub>]<sup>2+</sup> complex [Rh<sub>2</sub>(CO)(dppe-*P*)(bipy)( $\mu$ -RNNNR)<sub>2</sub>]. Though the formation of **11** from **9** would seem to involve a straightforward one-electron process the relationship between the cyclic voltammograms of the two species is not



**Fig. 3** Schematic diagrams: (a) the metal-( $\mu$ -CO) interactions in an open-book  $[\text{Rh}_2]^{4+}$  unit with a bridging CO ligand, based on EHMO calculations on  $[\text{Rh}_2\text{H}_4(\text{CO})_4(\mu\text{-CO})]$ ; (b) the metal-metal interactions in a face-to-face  $[\text{Rh}_2]^{4+}$  unit with an axial CO ligand, based on EHMO calculations on  $[\text{Rh}_2\text{H}_4(\text{CO})_5]$

clear; the first reduction of **9** occurs at  $-0.20$  V whereas the oxidation wave for **11** is at  $0.85$  V. Moreover, we have shown that the addition of a catalytic amount of reductant to **9** causes isomerisation to a second  $[\text{Rh}_2]^{4+}$  complex in which the two triazenide ligands are *cis* bound to one rhodium atom and *trans* bound to the second.<sup>10</sup> A more detailed study of the electrochemistry of **9** and the other carbonyl-bridged dirhodium complexes described above will be reported elsewhere.

During studies of the synthesis of complexes **5–10** from **A** (solv =  $\text{CH}_2\text{Cl}_2$ ) variable but small quantities of a second complex could occasionally be isolated. For example, after removing **6** from the reaction mixture formed from **A** (solv =  $\text{CH}_2\text{Cl}_2$ ) and *dm*bipy, addition of hexane to the mother-liquors gave a green-brown powder **12** in 11% yield. Better yields (40–50%) could be obtained by allowing **1** and  $\text{AgPF}_6$  to react together in  $\text{CH}_2\text{Cl}_2$  for prolonged periods but the product was usually contaminated by small amounts of other species which were difficult to separate from **12**. The IR spectrum of **12** showed one terminal carbonyl band at  $2062\text{ cm}^{-1}$  in  $\text{CH}_2\text{Cl}_2$  but the complex could not be further characterised spectroscopically. Crystals of **12** were therefore grown, from hexane- $\text{CH}_2\text{Cl}_2$ , and the structure of its solvate determined by X-ray crystallography.

The best refined model for the solvent incorporated a total of seven carbon atoms per  $\text{Rh}_2$  unit and the formula quoted reflects this. However, hexane seems the more likely solvent of crystallisation.

The X-ray diffraction study showed complex **12** to be neutral and tetranuclear, *i.e.*  $[\{\text{Rh}_2(\text{CO})(\text{O}_2\text{PF}_2)(\mu\text{-O}_2\text{PF}_2)(\text{bipy})(\mu\text{-RNNNR})_2\}_2]$ ; its molecular structure is shown in Figs. 4 and 5 and selected bond lengths and angles are listed in Table 5. The complex consists of two  $\text{Rh}_2(\text{CO})(\text{O}_2\text{PF}_2)(\text{bipy})(\mu\text{-RNNNR})_2$  fragments linked by two bridging  $\text{O}_2\text{PF}_2$  ligands, with the entire dimer having exact crystallographic  $C_2$  symmetry. Each bridging  $\text{O}_2\text{PF}_2$  ligand occupies an axial site, *trans* to the Rh–Rh vector, on one dirhodium moiety and an equatorial site, *trans* to a triazenido nitrogen atom, on the other. The remaining equatorial site on this rhodium [Rh(2)] is occupied by a terminal carbonyl ligand. The other rhodium atom [Rh(1)] carries a terminal  $\text{O}_2\text{PF}_2$  ligand in the axial site with the bipy ligand occupying the equatorial sites *trans* to the triazenido nitrogen atoms. The Rh(1)–Rh(2) distance [ $2.505(4)\text{ \AA}$ ] lies at the high end of the usual range<sup>9</sup> for  $\text{Rh}^{\text{II}}\text{–Rh}^{\text{II}}$  single bonds in  $\text{Rh}_2\text{L}_{10}$  species where the six-co-ordinate rhodium atoms carry axial ligands. The formation of the  $\{[\text{Rh}_2]^{4+}\}_2$  dimer by ligand bridging across axial and equatorial sites in different  $\{[\text{Rh}_2]^{4+}\}$  moieties is reminiscent of a similar structure in **1** in which iodide rather than  $\text{O}_2\text{PF}_2$  is the bridging ligand. In this case the carbonyl ligands are *cisoid* and lie on the same side of the  $\text{Rh}_2(\mu\text{-O}_2\text{PF}_2)_2$  ring. In contrast, in **1** the carbonyl ligands are *transoid*, lying on the opposite sides of the  $\text{Rh}_2(\mu\text{-I})_2$  ring. Other notable features of the structure of **12** include the variation in Rh–O( $\text{POF}_2$ ) distances, with those in axial sites being substantially longer [Rh(1)–O(1)  $2.23(2)$ , Rh(2)–O(2)  $2.382(14)$ , *vs.* Rh(2)–O(3)  $2.11(2)\text{ \AA}$ ], *cf.* similar behaviour in **3** above. The  $\text{O}_2\text{PF}_2$  ligands show considerable flexibility in the P–O–Rh bond angles with the terminal ligand at Rh(1) having a value intermediate between those for the bridging ligand [P(1)–O(1)–Rh(1)  $145.2(11)$ , P(2)–O(2)–Rh(2)  $165.4(11)$ , P(2a)–O(3)–Rh(2)  $130.8(10)^\circ$ ]. The monoanionic  $\text{O}_2\text{PF}_2$  ligands presumably arise by partial hydrolysis<sup>11</sup> of  $[\text{PF}_6]^-$ .

The reactions of anionic ligands with complexes **A** give products rather different from those formed with the neutral ligands described above. Complexes of chelating anionic N–S ligands can be prepared either using the thiols 1-methyl-2-sulfanylimidazole (*Hmsim*), 2-sulfanyl-pyrimidine (*Hspym*), -thiazoline (*Hstz*) or -benzimidazole (*Hsbzim*) directly or the corresponding sodium thiolates (prepared from the thiol and NaH in *thf*). Thus, addition of an equimolar quantity of the appropriate ligand to **A** (solv =  $\text{CH}_2\text{Cl}_2$ ), or of the sodium salt of the ligand to **A** (solv = *thf*), gave green solutions from which the green salts  $[\text{Rh}_2(\text{CO})(\text{N-S})(\text{bipy})(\mu\text{-RNNNR})_2][\text{PF}_6]$  (N–S = *msim* **13**, *spym* **14**, *stz* **15** or *sbzim* **16**) were readily isolated and characterised by elemental analysis and by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR and IR spectroscopy (Tables 1 and 2). The complexes **13–16** differ from **5–9** and **10a** in showing one carbonyl absorption band in the IR spectrum at *ca.*  $2065\text{ cm}^{-1}$ , indicative of a terminal CO ligand. The  $^{13}\text{C}$  NMR spectrum provides further evidence for such a CO ligand, with a doublet at  $\delta$  *ca.*  $185$  [ $J(^{13}\text{C}^{103}\text{Rh})$  *ca.*  $59\text{–}60\text{ Hz}$ ], showing coupling to only one rhodium atom. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are otherwise complicated, showing all of the bipyridyl protons and carbons and all of the methyl groups of the bridging triazenides to be inequivalent and therefore that the complexes are highly asymmetric.

The spectroscopic data are consistent with the structure shown in Scheme 1. In the absence of structural data (none of the complexes could be crystallised despite repeated attempts) it is not known if the N–S ligands are mono- or bi-dentate though the loss of the sulfur proton on co-ordination suggests the latter is more likely, with the metal chelated by the sulfur and nitrogen atoms. The inequivalence of the two halves of the bipyridyl ligand suggests that the N–S ligands occupy axial and



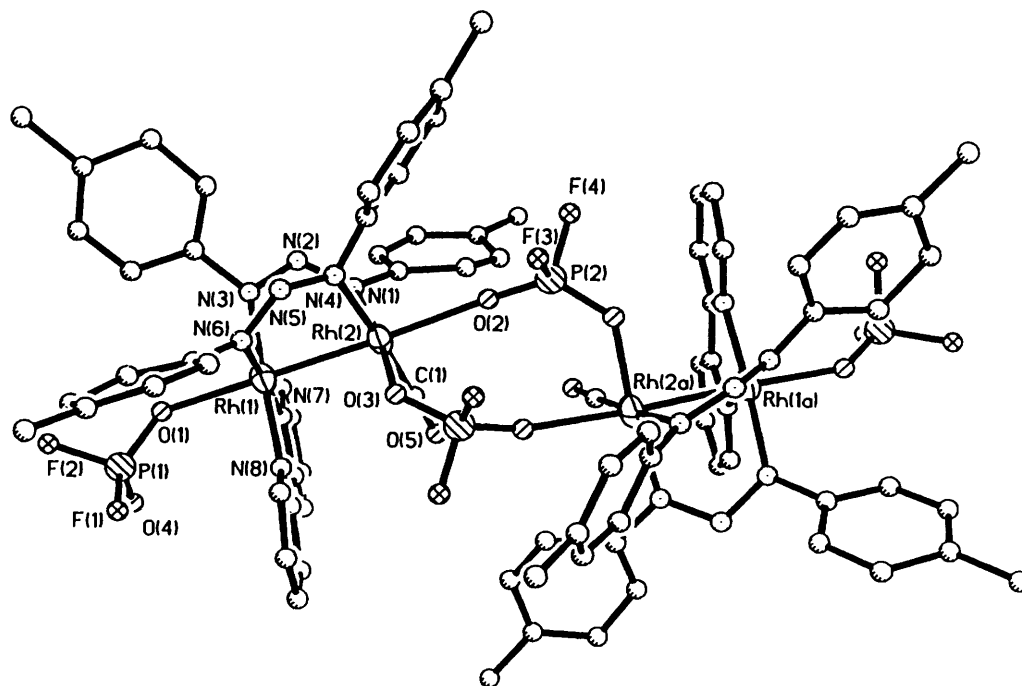


Fig. 4 Molecular structure of the dimer **12** showing the labelling scheme. Other details as in Fig. 1

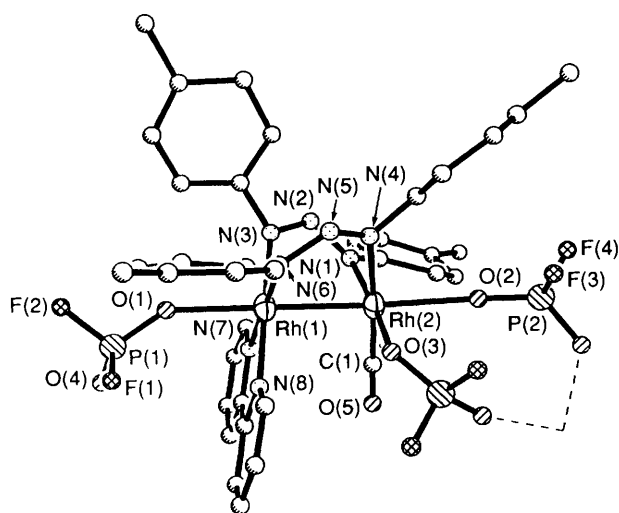


Fig. 5 Molecular structure of one half of complex **12** showing the labelling scheme. Dashed lines indicate bonds to Rh(2a) in the second half of the molecule. Other details as in Fig. 1

equatorial positions on one of the rhodium atoms although, again, it is not known which of the two donor atoms takes up which of the two positions. The proposed structure, containing an axial ligand, is similar to those of other known  $[\text{Rh}_2]^{4+}$  species. The preference for this structure over the  $\mu\text{-CO}$  form found for **5–9** and **10a** may be tentatively attributed to the anionic nature of the chelating ligand in these species. It is possible that the anionic ligand better stabilises the higher formal charge separation in the unbridged isomer noted in the EHMO calculations described above.

Each of the cyclic voltammograms of complexes **13–16** in  $\text{CH}_2\text{Cl}_2$  shows one diffusion-controlled oxidation wave at *ca.* 1.2 V; the waves for **14** and **16** are fully reversible and those for **13** and **15** become reversible at scan rates greater than  $500 \text{ mV s}^{-1}$ . The rather positive values for  $E^\circ$ , and the irreversible nature of the waves for **13** and **15** at slow scan rates, suggest that unstable products are formed on oxidation. Each of the cyclic voltammograms of **13–16** also shows two reduction waves at *ca.*

$-0.36$  and  $-1.13$  V respectively. For compounds **13–15** the waves are ill defined, only becoming reversible at scan rates greater than  $500 \text{ mV s}^{-1}$ . Complex **16** shows one irreversible reduction wave at  $-0.35$  V, with an associated product wave at  $-0.22$  V. A further product reduction wave is observed at  $-1.05$  V which becomes reversible only at scan rates greater than  $500 \text{ mV s}^{-1}$ . Again, further chemical studies of these oxidation and reduction processes will be reported later.

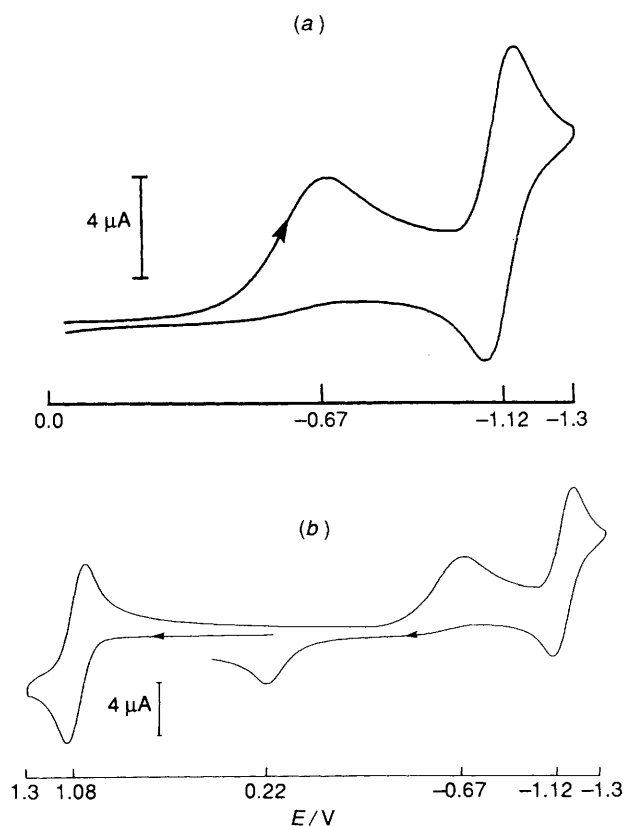
Complex **A** also reacts with salts of simple monoanions to give products with terminal carbonyl ligands. The addition of an excess of  $\text{NaCl}$  to **A** (solv =  $\text{MeOH}$ ) gave, after evaporation of the reaction mixture to dryness and extraction into  $\text{CH}_2\text{Cl}_2$ , high yields of  $[\text{Rh}_2(\text{CO})\text{Cl}_2(\text{bipy})(\mu\text{-RNNNR})_2]$  **17** as green, air-stable microcrystals. The neutral complex was characterised by elemental analysis (Table 1), by IR and NMR spectroscopy (Table 2), and by the mass spectrum which showed a parent ion at  $m/z$  910. The diiodide analogue of **17**, namely  $[\text{Rh}_2(\text{CO})\text{I}_2(\text{bipy})(\mu\text{-RNNNR})_2]$  **18**, has been prepared directly from  $[\text{Rh}_2(\text{CO})_2(\text{bipy})(\mu\text{-RNNNR})_2]$  and iodine<sup>1</sup> but is considerably less stable in the solid state. Moreover, the electrochemistry of **17** is far better defined than that of **18**.

The cyclic voltammogram of complex **17**, from 0.0 to 1.3 V, shows a fully reversible, diffusion-controlled oxidation wave centred at 1.08 V, corresponding to the formation of the  $[\text{Rh}_2]^{5+}$ -containing monocation  $[\text{Rh}_2(\text{CO})\text{Cl}_2(\text{bipy})(\mu\text{-RNNNR})_2]^+$ . On scanning from 0.0 to  $-1.3$  V [Fig. 6(a)] the voltammogram shows an irreversible reduction wave at *ca.*  $-0.67$  V followed by a second, fully reversible, product wave centred at  $-1.12$  V. The close similarity in potential of the product wave to that for the one-electron reduction of  $[\text{Rh}_2(\text{CO})\text{I}(\text{bipy})(\mu\text{-RNNNR})_2]^+$  ( $E^\circ = -1.07$  V)<sup>1</sup> strongly suggests that one-electron reduction of  $[\text{Rh}_2(\text{CO})\text{Cl}_2(\text{bipy})(\mu\text{-RNNNR})_2]$  to  $[\text{Rh}_2(\text{CO})\text{Cl}_2(\text{bipy})(\mu\text{-RNNNR})_2]^-$  (at *ca.*  $-0.67$  V) is followed by rapid loss of chloride ion to give  $[\text{Rh}_2(\text{CO})\text{Cl}(\text{bipy})(\mu\text{-RNNNR})_2]$  {which is reversibly reduced to  $[\text{Rh}_2(\text{CO})\text{Cl}(\text{bipy})(\mu\text{-RNNNR})_2]^-$ }. Further evidence for such a process is shown by scanning from 0.0 to 1.3 to  $-1.3$  to 0.0 V [Fig. 6(b)]. A second product wave at *ca.* 0.22 V appears only after scanning through the wave at  $-0.67$  V and corresponds to the oxidation of  $[\text{Rh}_2(\text{CO})\text{Cl}(\text{bipy})(\mu\text{-RNNNR})_2]$  to  $[\text{Rh}_2(\text{CO})\text{Cl}(\text{bipy})(\mu\text{-RNNNR})_2]^+$  {*cf.*

**Table 5** Selected bond lengths (Å) and angles (°) for complex 12·2.3C<sub>6</sub>H<sub>14</sub>

|                  |          |                  |           |                  |          |                  |           |
|------------------|----------|------------------|-----------|------------------|----------|------------------|-----------|
| Rh(1)–N(8)       | 1.99(2)  | N(5)–N(6)        | 1.36(2)   | O(3)–P(2a)       | 1.46(2)  | P(1)–O(4)        | 1.42(2)   |
| Rh(1)–N(7)       | 2.08(2)  | N(7)–C(35)       | 1.34(2)   | N(1)–C(2)        | 1.44(3)  | P(1)–F(1)        | 1.55(2)   |
| Rh(2)–C(1)       | 1.80(3)  | Rh(1)–N(3)       | 2.01(2)   | N(4)–N(5)        | 1.30(2)  | P(2)–F(4)        | 1.49(2)   |
| Rh(2)–O(3)       | 2.11(2)  | Rh(1)–O(1)       | 2.23(2)   | N(6)–C(23)       | 1.37(2)  | O(5)–C(1)        | 1.18(3)   |
| P(1)–O(1)        | 1.47(2)  | Rh(2)–N(1)       | 2.00(2)   | N(8)–C(30)       | 1.29(3)  | N(2)–N(3)        | 1.35(2)   |
| P(2)–O(2)        | 1.45(2)  | Rh(2)–O(2)       | 2.38(1)   | Rh(1)–N(6)       | 2.06(2)  | N(4)–C(16)       | 1.41(3)   |
| P(2)–F(3)        | 1.49(2)  | P(1)–F(2)        | 1.52(2)   | Rh(1)–Rh(2)      | 2.505(4) | N(7)–C(39)       | 1.29(3)   |
| N(1)–N(2)        | 1.31(2)  | P(2)–O(3a)       | 1.46(2)   | Rh(2)–N(4)       | 2.04(2)  | N(8)–C(34)       | 1.37(3)   |
| N(3)–C(9)        | 1.44(3)  |                  |           |                  |          |                  |           |
| N(8)–Rh(1)–N(3)  | 174.9(8) | O(3)–Rh(2)–O(2)  | 81.9(6)   | N(8)–Rh(1)–N(7)  | 79.0(8)  | C(1)–Rh(2)–Rh(1) | 93.5(7)   |
| N(3)–Rh(1)–N(6)  | 85.6(8)  | N(1)–Rh(2)–Rh(1) | 81.8(6)   | N(6)–Rh(1)–N(7)  | 178.0(8) | N(4)–Rh(2)–Rh(1) | 83.0(5)   |
| N(3)–Rh(1)–N(7)  | 96.1(8)  | O(3)–Rh(2)–Rh(1) | 92.6(4)   | N(3)–Rh(1)–O(1)  | 95.6(7)  | O(2)–Rh(2)–Rh(1) | 171.6(4)  |
| N(8)–Rh(1)–O(1)  | 85.1(7)  | P(1)–O(1)–Rh(1)  | 145.2(11) | N(7)–Rh(1)–O(1)  | 80.2(6)  | P(2)–O(2)–Rh(2)  | 165.4(11) |
| N(6)–Rh(1)–O(1)  | 98.7(7)  | P(2a)–O(3)–Rh(2) | 130.8(10) | N(3)–Rh(1)–Rh(2) | 82.7(6)  | N(2)–N(1)–Rh(2)  | 122(2)    |
| N(8)–Rh(1)–Rh(2) | 96.3(5)  | C(2)–N(1)–Rh(2)  | 123(2)    | N(7)–Rh(1)–Rh(2) | 95.8(5)  | N(2)–N(3)–Rh(1)  | 123(2)    |
| N(6)–Rh(1)–Rh(2) | 85.3(5)  | C(9)–N(3)–Rh(1)  | 128(2)    | C(1)–Rh(2)–N(1)  | 91.0(10) | N(5)–N(4)–Rh(2)  | 123(2)    |
| O(1)–Rh(1)–Rh(2) | 175.5(4) | C(16)–N(4)–Rh(1) | 124(2)    | N(1)–Rh(2)–N(4)  | 90.0(7)  | N(1)–N(6)–Rh(1)  | 119.7(14) |
| C(1)–Rh(2)–N(4)  | 176.2(9) | C(23)–N(6)–Rh(1) | 129(2)    | N(1)–Rh(2)–O(3)  | 172.0(7) | C(39)–N(7)–Rh(1) | 126(2)    |
| C(1)–Rh(2)–O(3)  | 95.0(9)  | C(35)–N(7)–Rh(1) | 116(2)    | C(1)–Rh(2)–O(2)  | 93.3(8)  | C(30)–N(8)–Rh(1) | 126(2)    |
| N(4)–Rh(2)–O(3)  | 83.7(7)  | C(34)–N(8)–Rh(1) | 116(2)    | N(4)–Rh(2)–O(2)  | 90.1(6)  | O(5)–C(1)–Rh(2)  | 178(2)    |
| N(1)–Rh(2)–O(2)  | 103.1(7) | N(8)–Rh(1)–N(6)  | 99.3(8)   |                  |          |                  |           |

Symmetry transformation used to generate equivalent atoms:  $a -x + 2, y, -z + \frac{1}{2}$ .



**Fig. 6** Cyclic voltammogram of complex 17 (a) from 0.0 to  $-1.3$  V and (b) from 0.0 to 1.3 to  $-1.3$  to 0.0 V

the oxidation of  $[\text{Rh}_2(\text{CO})\text{I}(\text{bipy})(\mu\text{-RNNNR})_2]$  to  $[\text{Rh}_2(\text{CO})\text{I}(\text{bipy})(\mu\text{-RNNNR})_2]^+$  ( $E^\circ = 0.21$  V).

The reaction between complex A (solv = MeOH) and  $\text{NaNO}_2$  gave  $[\text{Rh}_2(\text{CO})(\text{NO}_2)_2(\text{bipy})(\mu\text{-RNNNR})_2]$  19 as a brown precipitate (Tables 1 and 2). The cyclic voltammogram of 19 is qualitatively similar to that of 17, with an ill defined, irreversible reduction peak at *ca.*  $-0.74$  V accompanied by product waves at *ca.*  $-1.0$  (reversible) and  $0.32$  V, probably due

to the formation of  $[\text{Rh}_2(\text{CO})(\text{NO}_2)_2(\text{bipy})(\mu\text{-RNNNR})_2]^-$  and the subsequent loss of nitrite ion to give  $[\text{Rh}_2(\text{CO})(\text{NO}_2)(\text{bipy})(\mu\text{-RNNNR})_2]$ .

### Conclusion

The halide-abstraction reactions of  $[\{\text{Rh}_2(\mu\text{-I})(\text{CO})(\text{bipy})(\mu\text{-RNNNR})_2\}_2][\text{PF}_6]_2$  in  $\text{CH}_2\text{Cl}_2$  or MeCN give the labile solvates  $[\text{Rh}_2(\text{CO})(\text{solv})_2(\text{bipy})(\mu\text{-RNNNR})_2]^{2+}$ , versatile precursors to a wide range of complexes containing the  $[\text{Rh}_2]^{4+}$  core. Of particular interest are the open-book, carbonyl-bridged complexes  $[\text{Rh}_2(\mu\text{-CO})(\text{L-L})(\text{bipy})(\mu\text{-RNNNR})_2][\text{PF}_6]_2$  which, for L-L = dpmm, is in equilibrium in solution with the face-to-face, terminal carbonyl isomer  $[\text{Rh}_2(\text{CO})(\text{dpmm})(\text{bipy})(\mu\text{-RNNNR})_2][\text{PF}_6]_2$ .

### Experimental

The preparation, purification and reactions of the complexes described were carried out under an atmosphere of dry nitrogen, using dried, distilled and deoxygenated solvents. Unless otherwise stated, products were (i) purified by dissolution in  $\text{CH}_2\text{Cl}_2$ , filtration, addition of hexane, and partial evaporation *in vacuo* to induce precipitation, and are (ii) air-stable solids, dissolving in polar solvents such as  $\text{CH}_2\text{Cl}_2$  to give moderately air-sensitive solutions. The complexes  $[\{\text{Rh}_2(\mu\text{-I})(\text{CO})(\text{bipy})(\mu\text{-RNNNR})_2\}_2][\text{PF}_6]_2$  1 and  $[\text{Rh}_2(\text{CO})\text{I}_2(\text{bipy})(\mu\text{-RNNNR})_2]$  18 were prepared by published methods.<sup>1</sup> The salt  $\text{AgPF}_6$  was obtained from Fluorochem Ltd. and 2,2'-bipyridyl, 4,4'-dimethyl-2,2'-bipyridyl, 1,10-phenanthroline, 2-sulfanylpurimidine, 2-sulfanylbenzimidazole, 1-methyl-2-sulfanylimidazole, and 2-sulfanylthiazoline were obtained from Aldrich Chemical Co.

The IR spectra were recorded on Nicolet MX5 or 5ZDX FT spectrometers, X-band ESR spectra on a Bruker ESP 300E instrument and calibrated against a solid sample of the diphenylpicrylhydrazyl (dpph) radical, <sup>1</sup>H and <sup>13</sup>C NMR spectra on JEOL GX270 or GX400 spectrometers and calibrated against  $\text{SiMe}_4$  as an internal reference, <sup>31</sup>P NMR spectra on a JEOL FX90Q instrument using 85%  $\text{H}_3\text{PO}_4$  as an external reference and FAB mass spectra at the SERC Mass Spectrometry Service Centre at the University College of Swansea. Electrochemical studies were carried out using an EG&G model 273 potentiostat in conjunction with a three-

Table 6 Structure analyses

|   | 3  | 10a-2CH <sub>2</sub> Cl <sub>2</sub>   | 12-2.3C <sub>6</sub> H <sub>14</sub>   |
|---|--|--|--|
| Formula   | C <sub>44</sub> H <sub>45</sub> F <sub>12</sub> N <sub>11</sub> P <sub>2</sub> Rh <sub>2</sub> | C <sub>66</sub> H <sub>60</sub> Cl <sub>4</sub> F <sub>12</sub> N <sub>8</sub> OP <sub>4</sub> Rh <sub>2</sub> | C <sub>92</sub> H <sub>104</sub> F <sub>8</sub> N <sub>16</sub> O <sub>10</sub> P <sub>4</sub> Rh <sub>4</sub> |
| <i>M</i>  | 1223.6   | 1680.8   | 2249.2   |
| Crystal system  | Triclinic  | Monoclinic   | Monoclinic   |
| Space group (no.)   | <i>P</i> 2 <sub>1</sub> / <i>c</i> (14)  | <i>P</i> 2 <sub>1</sub> / <i>n</i> (14)  | <i>C</i> 2/ <i>c</i> (15)  |
| <i>a</i> /Å   | 10.267(3)  | 15.013(5)  | 22.820(17)   |
| <i>b</i> /Å   | 14.009(6)  | 18.406(6)  | 17.162(13)   |
| <i>c</i> /Å   | 18.687(6)  | 27.991(8)  | 27.148(25)   |
| $\alpha$ /°   | 95.31(4)   | 90   | 90   |
| $\beta$ /°  | 95.25(3)   | 103.85(5)  | 110.92(6)  |
| $\gamma$ /°   | 104.31(4)  | 90   | 90   |
| <i>U</i> /Å <sup>3</sup>  | 2567(2)  | 7510(4)  | 9931(14)   |
| <i>Z</i>  | 2  | 4  | 4  |
| <i>D<sub>c</sub></i> /g cm <sup>-3</sup>  | 1.57   | 1.49   | 1.53   |
| $\mu$ (Mo-K $\alpha$ )/mm <sup>-1</sup>   | 0.78   | 0.81   | 0.80   |
| <i>F</i> (000)  | 1228   | 3512   | 4660   |
| Crystal size/mm   | 0.05 × 0.32 × 0.5  | 0.15 × 0.25 × 0.7  | 1.0 × 0.5 × 0.75   |
| 2 $\theta$ range/°  | 4–45   | 4–45   | 3–40   |
| Scan width, $\omega$ /°   | 1.5  | 0.6  | 0.7  |
| Scan method   | Wyckoff, $\omega$  | Wyckoff, $\omega$  | Wyckoff, $\omega$  |
| Total data  | 7227   | 12 055   | 10 634   |
| Unique data   | 6737   | 11 636   | 4630   |
| 'Observed' data   | 4242   | 4677   | 2306   |
| [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>N<sub>o</sub></i> |  |  |  |
| Least-squares variables, <i>N<sub>v</sub></i>   | 420  | 567  | 311  |
| <i>R</i> <sup>a</sup>   | 0.057  | 0.093  | 0.109 ( <i>R</i> 1) <sup>b</sup>   |
| <i>R'</i> <sup>a</sup>  | 0.051  | 0.083  | 0.188 ( <i>wR</i> 2) <sup>b</sup>  |
| <i>S</i> <sup>a</sup>   | 1.51   | 1.88   | 1.35 <sup>b</sup>  |
| Weights <sup>a</sup>  | 0.0003 (g)   | 0.0005 (g)   | 0.05( <i>a</i> ), 15( <i>b</i> ) <sup>b</sup>  |
| Largest final difference map features e Å <sup>-3</sup>                               | +0.58, -0.55   | +0.82, -0.78   | +0.85, -0.61   |

<sup>a</sup>  $R = \Sigma |\Delta| / \Sigma |F_o|$ ;  $R' = (\Sigma w\Delta^2 / \Sigma wF_o^2)^{1/2}$ ;  $S = [\Sigma w\Delta^2 / (N_o - N_v)]^{1/2}$ ;  $\Delta = F_o - F_c$ ;  $w = [\sigma_c^2(F_o) + gF_o^2]^{-1}$ ;  $\sigma_c^2(F_o) = \text{variance in } F_o \text{ due to counting statistics}$ . <sup>b</sup> Residuals calculated for reflections with  $F^2 > 2\sigma(F^2)$ ;  $wR2 = [\Sigma w\Delta^2 / \Sigma wF_o^4]^{1/2}$ ;  $S = [\Sigma w\Delta^2 / (N - N_v)]^{1/2}$ ;  $R1 = \Sigma |F_o - F_c| / \Sigma |F_o|$ ;  $\Delta = F_o^2 - F_c^2$ ;  $N = N_o + \text{restraints}$ ;  $w = [\sigma_c^2(F_o^2) + (aP)^2 + bP]^{-1}$ ;  $\sigma_c^2(F_o^2) = \text{variance in } F_o^2 \text{ due to counting statistics}$ ;  $P = [\max(F_o^2, 0) + 2F_c^2] / 3$ .

electrode cell. For cyclic voltammetry the auxiliary electrode was a platinum wire and the working electrode a platinum disc. The reference was an aqueous saturated calomel electrode (SCE) separated from the test solution by a fine-porosity frit and an agar bridge saturated with KCl. Solutions were  $0.1 \times 10^{-3} \text{ mol dm}^{-3}$  in the test compound and  $0.1 \text{ mol dm}^{-3}$  in [NBu<sub>4</sub>][PF<sub>6</sub>] as the supporting electrolyte. Under these conditions the *E*<sup>o</sup> values for the couples [Fe( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]<sup>+</sup>–[Fe( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] and [Fe( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>]<sup>+</sup>–[Fe( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>] are 0.47 and -0.09 V respectively. Microanalyses were carried out by the staff of the microanalytical service of the School of Chemistry, University of Bristol.

*Bis*(acetonitrile)(2,2'-bipyridyl)carbonylbis( $\mu$ -di-*p*-tolyltriazenido-N<sup>1</sup>N<sup>3</sup>)dirhodium Bis(hexafluorophosphate), [Rh<sub>2</sub>(CO)(NCMe)<sub>2</sub>(bipy)( $\mu$ -RNNNR)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> **2** (*R* = *p*-tolyl).—To a stirred solution of [ $\{\text{Rh}_2(\mu\text{-I})(\text{CO})(\text{bipy})(\mu\text{-RNNNR})_2\}_2$ ][PF<sub>6</sub>]<sub>2</sub> (0.11 g, 0.05 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 cm<sup>3</sup>) was added AgPF<sub>6</sub> (0.026 g, 0.1 mmol). After 10 min the green solution was filtered through Celite to remove the precipitate of AgI. Acetonitrile (0.5 cm<sup>3</sup>) was then added to the filtrate to give an orange solution which was treated with hexane (15 cm<sup>3</sup>). The solvent was then reduced in volume *in vacuo*, giving an oil which solidified to an orange solid on stirring. Purification from CH<sub>2</sub>Cl<sub>2</sub>–hexane gave a green powder, yield 0.075 g (60%).

*Tris*(acetonitrile)(2,2'-bipyridyl)bis( $\mu$ -di-*p*-tolyltriazenido-N<sup>1</sup>N<sup>3</sup>)dirhodium Bis(hexafluorophosphate), [Rh<sub>2</sub>(NCMe)<sub>3</sub>(bipy)( $\mu$ -RNNNR)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> **3**.—To a stirred solution of [ $\{\text{Rh}_2(\mu\text{-I})(\text{CO})(\text{bipy})(\mu\text{-RNNNR})_2\}_2$ ][PF<sub>6</sub>]<sub>2</sub> (0.15 g, 0.07

mmol) in acetonitrile (30 cm<sup>3</sup>) was added AgPF<sub>6</sub> (0.033 g, 0.13 mmol). After 30 min the orange solution was filtered through Celite and then heated under reflux for 12 h. The orange solution was then filtered through Celite and the solvent was evaporated to low volume (*ca.* 5 cm<sup>3</sup>) *in vacuo*. Addition of diethyl ether precipitated a green powder which was purified from acetonitrile–diethyl ether, yield 0.135 g (82%).

*Acetonitrile*(2,2'-bipyridyl)(diethyldithiocarbamate)bis( $\mu$ -di-*p*-tolyltriazenido-N<sup>1</sup>N<sup>3</sup>)dirhodium Hexafluorophosphate, [Rh<sub>2</sub>(NCMe)(S<sub>2</sub>CNMe<sub>2</sub>)(bipy)( $\mu$ -RNNNR)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> **4**.—To a stirred solution of [Rh<sub>2</sub>(NCMe)<sub>3</sub>(bipy)( $\mu$ -RNNNR)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> (0.1 g, 0.082 mmol) in acetonitrile (30 cm<sup>3</sup>) was added Na[S<sub>2</sub>CNMe<sub>2</sub>] $\cdot$ 2H<sub>2</sub>O (0.014 g, 0.087 mmol). After 1 h the dark brown solution was filtered through Celite and the solvent evaporated to give a brown oil. Purification afforded the product as a brown powder, yield 0.071 g (77%).

*Bis*(2,2'-bipyridyl)( $\mu$ -carbonyl)bis( $\mu$ -di-*p*-tolyltriazenido-N<sup>1</sup>N<sup>3</sup>)dirhodium Bis(hexafluorophosphate), [Rh<sub>2</sub>( $\mu$ -CO)(bipy)<sub>2</sub>( $\mu$ -RNNNR)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> **5**.—To a stirred solution of [ $\{\text{Rh}_2(\mu\text{-I})(\text{CO})(\text{bipy})(\mu\text{-RNNNR})_2\}_2$ ][PF<sub>6</sub>]<sub>2</sub> (0.15 g, 0.07 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (25 cm<sup>3</sup>) was added AgPF<sub>6</sub> (0.034 g, 0.14 mmol). After 10 min the dark green solution was filtered through Celite to remove AgI. 2,2'-Bipyridyl (0.024 g, 0.15 mmol) was then added and the mixture stored at 0 °C for 12 h. The dark green microcrystalline precipitate was purified from acetonitrile–diethyl ether, yield 0.095 g (53%). The complexes [Rh<sub>2</sub>( $\mu$ -CO)(L–L)(bipy)( $\mu$ -RNNNR)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> (L–L = dmbipy **6**, phen **7**, or dpa **8**) were prepared similarly. The air-stable solids

**Table 7** Atomic coordinates ( $\times 10^4$ ) for complex 3

| Atom  | x          | y          | z        | Atom  | x          | y          | z        |
|-------|------------|------------|----------|-------|------------|------------|----------|
| Rh(1) | 10 144(1)  | 911(1)     | 2 723(1) | C(10) | 13 327(10) | -667(8)    | 810(6)   |
| Rh(2) | 9 603(1)   | 2 564(1)   | 2 614(1) | C(11) | 14 233(12) | -1 245(9)  | 469(6)   |
| P(1)  | 4 064(4)   | 8 325(4)   | 3 622(2) | C(12) | 12 530(10) | -221(8)    | 387(6)   |
| P(2)  | 7 674(6)   | 5 722(3)   | 4 028(3) | C(13) | 11 762(10) | 344(7)     | 692(5)   |
| F(1)  | 3 817(9)   | 7 822(7)   | 2 823(4) | C(14) | 9 686(10)  | 2 914(7)   | 1 082(5) |
| F(2)  | 4 321(9)   | 8 855(8)   | 4 428(4) | C(15) | 9 461(10)  | 2 575(8)   | 353(6)   |
| F(3)  | 5 487(10)  | 8 154(10)  | 3 724(5) | C(16) | 8 910(12)  | 3 100(9)   | -153(7)  |
| F(4)  | 2 797(10)  | 8 710(11)  | 3 502(5) | C(17) | 8 564(13)  | 3 929(10)  | 82(7)    |
| F(5)  | 4 849(12)  | 9 321(9)   | 3 353(5) | C(18) | 7 888(14)  | 4 471(11)  | -458(8)  |
| F(6)  | 3 349(18)  | 7 393(9)   | 3 892(6) | C(19) | 8 779(12)  | 4 282(10)  | 796(7)   |
| F(7)  | 8 569(11)  | 6 805(7)   | 4 087(6) | C(20) | 9 337(11)  | 3 782(9)   | 1 298(7) |
| F(8)  | 6 698(10)  | 4 616(6)   | 3 959(6) | C(21) | 7 825(9)   | -674(7)    | 1 801(5) |
| F(9)  | 8 876(12)  | 5 352(8)   | 3 800(7) | C(22) | 6 817(11)  | -1 308(8)  | 2 084(6) |
| F(10) | 6 431(12)  | 6 106(8)   | 4 286(9) | C(23) | 6 373(12)  | -2 303(9)  | 1 805(6) |
| F(11) | 7 144(17)  | 5 781(8)   | 3 236(7) | C(24) | 6 920(11)  | -2 656(9)  | 1 233(6) |
| F(12) | 8 178(11)  | 5 686(8)   | 4 829(5) | C(25) | 6 462(14)  | -3 733(10) | 924(7)   |
| N(1)  | 1 030(8)   | 1 118(6)   | 1 782(4) | C(26) | 7 915(12)  | -2 022(9)  | 945(6)   |
| N(2)  | 10 753(8)  | 1 731(6)   | 1 354(4) | C(27) | 8 380(10)  | -1 030(8)  | 1 219(5) |
| N(3)  | 10 101(8)  | 2 351(6)   | 1 605(4) | C(28) | 6 706(10)  | 2 236(7)   | 2 030(5) |
| N(4)  | 8 311(8)   | 358(6)     | 2 098(4) | C(29) | 5 664(10)  | 1 822(8)   | 1 489(5) |
| N(5)  | 7 399(8)   | 820(6)     | 1 977(4) | C(30) | 4 724(11)  | 2 363(8)   | 1 287(6) |
| N(6)  | 7 720(8)   | 1 752(6)   | 2 227(4) | C(31) | 4 780(10)  | 3 294(8)   | 1 628(6) |
| N(7)  | 11 884(7)  | 1 525(6)   | 3 403(4) | C(32) | 3 780(11)  | 3 843(9)   | 1 390(6) |
| N(8)  | 9 406(8)   | 828(6)     | 3 706(4) | C(33) | 5 827(11)  | 3 689(8)   | 2 154(6) |
| N(9)  | 10 311(8)  | -529(6)    | 2 792(4) | C(34) | 6 784(10)  | 3 177(8)   | 2 368(6) |
| N(10) | 9 092(8)   | 2 851(6)   | 3 625(4) | C(35) | 13 090(11) | 1 895(8)   | 3 204(6) |
| N(11) | 11 428(9)  | 3 486(7)   | 2 975(5) | C(36) | 14 234(13) | 2 292(9)   | 3 709(7) |
| C(1)  | 10 192(11) | -1 323(10) | 2 743(6) | C(37) | 14 086(13) | 2 278(9)   | 4 429(7) |
| C(2)  | 10 054(15) | -2 421(11) | 2 639(8) | C(38) | 12 835(11) | 1 926(8)   | 4 630(6) |
| C(3)  | 8 810(11)  | 3 055(8)   | 4 169(6) | C(39) | 11 744(10) | 1 543(7)   | 4 117(5) |
| C(4)  | 8 419(12)  | 3 323(9)   | 4 875(6) | C(40) | 10 339(9)  | 1 165(7)   | 4 282(5) |
| C(5)  | 12 301(14) | 4 083(11)  | 3 243(7) | C(41) | 9 983(10)  | 1 181(7)   | 4 983(5) |
| C(6)  | 13 488(15) | 4 876(11)  | 3 590(8) | C(42) | 8 639(11)  | 824(8)     | 5 064(6) |
| C(7)  | 11 761(10) | 488(7)     | 1 445(5) | C(43) | 7 676(12)  | 462(8)     | 4 487(6) |
| C(8)  | 12 555(10) | 36(7)      | 1 887(6) | C(44) | 8 104(10)  | 478(7)     | 3 800(5) |
| C(9)  | 13 330(11) | -540(8)    | 1 551(6) |       |            |            |          |

dissolve in acetonitrile or nitromethane to give brown solutions which decompose slowly in air.

(2,2'-Bipyridyl)[1,2-bis(diphenylphosphino)ethane] ( $\mu$ -carbonyl)bis( $\mu$ -di-*p*-tolyltriazenido- $N^1N^3$ )dirhodium Bis(hexafluorophosphate), [Rh<sub>2</sub>( $\mu$ -CO)(dppe)(bipy)( $\mu$ -RNNNR)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> **9**.—To a stirred solution of [Rh<sub>2</sub>( $\mu$ -I)(CO)(bipy)( $\mu$ -RNNNR)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> (0.15 g, 0.07 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (25 cm<sup>3</sup>) was added AgPF<sub>6</sub> (0.04 g, 0.16 mmol). After 10 min the dark green solution was filtered through Celite to remove AgI, and dppe (0.054 g, 0.14 mmol) added. After 30 min the intense green solution was filtered through Celite and reduced in volume *in vacuo*. Addition of diethyl ether gave a green powder which was purified from CH<sub>2</sub>Cl<sub>2</sub>-diethyl ether, yield 0.162 g (79%). The compound [Rh<sub>2</sub>( $\mu$ -CO)(dppm)(bipy)( $\mu$ -RNNNR)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> **10** was similarly prepared.

(2,2'-Bipyridyl)[1,2-bis(diphenylphosphino)ethane-*P*]carbonyl-bis( $\mu$ -di-*p*-tolyltriazenido- $N^1N^3$ )dirhodium Hexafluorophosphate, [Rh<sub>2</sub>(CO)(dppe-*P*)(bipy)( $\mu$ -RNNNR)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> **11**.—To a stirred solution of [Rh<sub>2</sub>( $\mu$ -CO)(dppe)(bipy)( $\mu$ -RNNNR)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> (0.105 g, 0.069 mmol) in thf (30 cm<sup>3</sup>) was added NaBH<sub>4</sub> (0.003 g, 0.079 mmol). After 1.5 h the brown solution was filtered through Celite and evaporated to low volume *in vacuo*. Addition of hexane precipitated a brown oily solid, and purification from CH<sub>2</sub>Cl<sub>2</sub>-hexane gave a brown powder, yield 0.076 g (80%).

(2,2'-Bipyridyl)carbonylbis( $\mu$ -di-*p*-tolyltriazenido- $N^1N^3$ )(1-methyl-2-sulfanylimidazolato)dirhodium Hexafluorophosphate, [Rh<sub>2</sub>(CO)(msim)(bipy)( $\mu$ -RNNNR)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> **13**.—To a stirred solution of [Rh<sub>2</sub>( $\mu$ -I)(CO)(bipy)( $\mu$ -RNNNR)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> (0.15 g, 0.065 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 cm<sup>3</sup>) was added AgPF<sub>6</sub> (0.035 g,

0.13 mmol). After 30 min the green solution was filtered through Celite and the filtrate evaporated to dryness. The residue was then dissolved in thf (5 cm<sup>3</sup>) and the solution added to a mixture of 1-methyl-2-sulfanylimidazole (0.05 g, 0.13 mmol) and NaH (3 mg, 0.13 mmol) in thf (5 cm<sup>3</sup>). The solvent was removed *in vacuo* and the residue extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>). Addition of hexane (10 cm<sup>3</sup>) and partial removal of the solvent *in vacuo* gave a green powder which was purified to give the green product, yield 0.105 g (71%).

(2,2'-Bipyridyl)carbonylbis( $\mu$ -di-*p*-tolyltriazenido- $N^1N^3$ )(2-sulfanylimidinato)dirhodium Hexafluorophosphate, [Rh<sub>2</sub>(CO)(spym)(bipy)( $\mu$ -RNNNR)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> **14**.—To a stirred solution of [Rh<sub>2</sub>( $\mu$ -I)(CO)(bipy)( $\mu$ -RNNNR)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> (0.1 g, 0.045 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (25 cm<sup>3</sup>) was added AgPF<sub>6</sub> (0.025 g, 0.1 mmol). After 10 min the dark green solution was filtered through Celite, and 2-sulfanylimidinate (0.01 g, 0.089 mmol) was added. After stirring for 1 h the green solution was filtered through Celite and reduced in volume *in vacuo*. Addition of hexane gave a green solid; purification from CH<sub>2</sub>Cl<sub>2</sub>-hexane gave a green powder, yield 0.073 g (74%).

The compounds [Rh<sub>2</sub>(CO)(N-S)(bipy)( $\mu$ -RNNNR)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> (N-S = msim **13**, stz **15**, or sbzim **16**) were similarly prepared.

(2,2'-Bipyridyl)carbonyldichlorobis( $\mu$ -di-*p*-tolyltriazenido- $N^1N^3$ )dirhodium [Rh<sub>2</sub>(CO)Cl<sub>2</sub>(bipy)( $\mu$ -RNNNR)<sub>2</sub>]**17**.—To a stirred solution of [Rh<sub>2</sub>( $\mu$ -I)(CO)(bipy)( $\mu$ -RNNNR)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> (0.11 g, 0.05 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 cm<sup>3</sup>) was added AgPF<sub>6</sub> (0.026 g, 0.1 mmol). After 10 min the green solution was filtered through Celite to remove the precipitate of AgI and the filtrate was evaporated to dryness *in vacuo*. The residue was then dissolved in MeOH (15 cm<sup>3</sup>), NaCl (0.03 g, 0.5

**Table 8** Atomic coordinates ( $\times 10^4$ ) for complex **10a**-2CH<sub>2</sub>Cl<sub>2</sub>

| Atom   | x          | y         | z         | Atom  | x         | y          | z         |
|--------|------------|-----------|-----------|-------|-----------|------------|-----------|
| Rh(1)  | 4 722(1)   | 10 626(1) | 1 819(1)  | C(16) | 3 467(16) | 7 871(12)  | 2 639(8)  |
| Rh(2)  | 5 462(1)   | 9 952(1)  | 2 887(1)  | C(17) | 2 623(17) | 7 692(15)  | 2 377(8)  |
| P(1)   | 6 493(4)   | 9 022(3)  | 2 897(2)  | C(18) | 1 966(16) | 8 185(13)  | 2 189(8)  |
| P(2)   | 4 784(4)   | 8 904(3)  | 3 101(2)  | C(19) | 2 094(16) | 8 888(13)  | 2 270(8)  |
| P(3)   | 7 153(7)   | 8 246(5)  | -119(3)   | C(20) | 3 016(14) | 9 129(12)  | 2 549(7)  |
| P(4)   | 4 871(6)   | 5 954(4)  | 2 572(4)  | C(21) | 4 688(15) | 8 703(11)  | 3 718(8)  |
| Cl(1)  | 2 775(10)  | 7 786(8)  | 1 007(5)  | C(22) | 5 446(17) | 8 551(12)  | 4 082(8)  |
| Cl(2)  | 4 562(11)  | 7 432(10) | 1 018(6)  | C(23) | 5 445(20) | 8 390(14)  | 4 570(10) |
| Cl(3)* | 9 862(16)  | 8 906(14) | 1 274(9)  | C(24) | 4 526(19) | 8 367(14)  | 4 633(11) |
| Cl(4)* | 10 243(15) | 7 407(13) | 1 020(8)  | C(25) | 3 788(17) | 8 541(12)  | 4 293(8)  |
| Cl(5)* | 9 423(20)  | 963(17)   | 312(11)   | C(26) | 3 848(16) | 8 720(12)  | 3 830(8)  |
| Cl(6)* | 9 459(23)  | 1 617(18) | -290(13)  | C(27) | 7 025(14) | 10 985(10) | 3 255(7)  |
| Cl(7)* | 10 228(39) | 1 697(32) | 1 024(20) | C(28) | 6 725(14) | 11 217(10) | 3 643(7)  |
| Cl(8)* | 8 875(31)  | 277(27)   | 582(17)   | C(29) | 7 364(15) | 11 308(11) | 4 089(8)  |
| Cl(9)* | 9 889(37)  | 1 762(39) | -836(25)  | C(30) | 8 281(16) | 11 216(11) | 4 138(8)  |
| F(1)   | 7 924(21)  | 7 776(18) | 93(13)    | C(31) | 8 600(16) | 10 993(12) | 3 744(8)  |
| F(2)   | 6 737(17)  | 8 099(9)  | 312(7)    | C(32) | 7 964(14) | 10 878(10) | 3 290(7)  |
| F(3)   | 7 508(15)  | 8 363(10) | -564(7)   | C(33) | 8 990(18) | 11 301(15) | 4 630(9)  |
| F(4)   | 6 336(15)  | 8 651(17) | -373(11)  | C(34) | 6 359(14) | 11 353(10) | 1 595(7)  |
| F(5)   | 7 491(20)  | 8 950(13) | 96(8)     | C(35) | 7 326(15) | 11 387(11) | 1 634(8)  |
| F(6)   | 6 755(26)  | 7 560(15) | -351(9)   | C(36) | 7 601(17) | 11 671(12) | 1 224(8)  |
| F(7)   | 5 724(13)  | 5 587(10) | 2 534(9)  | C(37) | 6 983(16) | 11 889(12) | 830(8)    |
| F(8)   | 5 324(16)  | 6 669(10) | 2 535(10) | C(38) | 6 070(15) | 11 869(11) | 794(7)    |
| F(9)   | 4 526(18)  | 5 910(14) | 2 002(8)  | C(39) | 5 754(13) | 11 595(9)  | 1 197(6)  |
| F(10)  | 4 442(16)  | 5 197(10) | 2 649(9)  | C(40) | 7 296(18) | 12 252(14) | 379(9)    |
| F(11)  | 5 092(16)  | 6 132(19) | 3 102(7)  | C(41) | 4 085(13) | 10 666(10) | 3 417(6)  |
| F(12)  | 3 894(14)  | 6 182(16) | 2 591(14) | C(42) | 3 116(13) | 10 794(10) | 3 326(7)  |
| O      | 4 758(10)  | 9 127(7)  | 2 022(5)  | C(43) | 2 754(16) | 10 713(12) | 3 734(8)  |
| N(1)   | 6 370(11)  | 10 823(8) | 2 805(5)  | C(44) | 3 252(17) | 10 528(13) | 4 195(9)  |
| N(2)   | 6 559(11)  | 11 103(8) | 2 416(6)  | C(45) | 4 215(15) | 10 385(11) | 4 266(8)  |
| N(3)   | 6 020(9)   | 11 010(8) | 1 986(5)  | C(46) | 4 620(14) | 10 463(11) | 3 860(7)  |
| N(4)   | 4 469(10)  | 10 712(8) | 2 986(6)  | C(47) | 2 808(17) | 10 471(14) | 4 628(9)  |
| N(5)   | 4 266(11)  | 11 298(9) | 2 750(6)  | C(48) | 4 356(13) | 12 073(11) | 2 130(7)  |
| N(6)   | 4 428(10)  | 11 356(7) | 2 325(5)  | C(49) | 3 791(13) | 12 242(11) | 1 658(7)  |
| N(7)   | 3 361(10)  | 10 338(8) | 1 515(6)  | C(50) | 3 722(15) | 12 930(12) | 1 484(8)  |
| N(8)   | 4 866(10)  | 10 029(9) | 1 223(5)  | C(51) | 4 221(16) | 13 455(13) | 1 746(8)  |
| C(1)   | 4 965(13)  | 9 707(13) | 2 205(7)  | C(52) | 4 820(13) | 13 319(11) | 2 192(7)  |
| C(2)   | 5 659(12)  | 8 317(10) | 2 948(7)  | C(53) | 4 930(13) | 12 622(10) | 2 391(7)  |
| C(3)   | 7 450(14)  | 8 991(10) | 3 421(7)  | C(54) | 4 113(16) | 14 212(13) | 1 533(9)  |
| C(4)   | 8 217(15)  | 8 563(12) | 3 412(8)  | C(55) | 2 628(15) | 10 550(12) | 1 684(8)  |
| C(5)   | 8 937(16)  | 8 547(12) | 3 832(8)  | C(56) | 1 758(18) | 10 400(13) | 1 452(9)  |
| C(6)   | 8 910(18)  | 8 919(14) | 4 270(10) | C(57) | 1 612(21) | 10 054(15) | 996(10)   |
| C(7)   | 8 148(15)  | 9 336(12) | 4 256(8)  | C(58) | 2 372(16) | 9 829(12)  | 800(9)    |
| C(8)   | 7 424(14)  | 9 381(11) | 3 851(7)  | C(59) | 3 255(15) | 9 989(12)  | 1 072(8)  |
| C(9)   | 6 976(12)  | 8 797(10) | 2 388(6)  | C(60) | 4 122(15) | 9 832(10)  | 949(7)    |
| C(10)  | 6 803(15)  | 8 161(13) | 2 133(8)  | C(61) | 4 063(17) | 9 935(13)  | 504(8)    |
| C(11)  | 7 189(18)  | 8 048(16) | 1 742(10) | C(62) | 4 917(17) | 9 263(13)  | 405(9)    |
| C(12)  | 7 735(16)  | 8 547(13) | 1 606(9)  | C(63) | 5 730(17) | 9 445(12)  | 718(8)    |
| C(13)  | 7 937(15)  | 9 195(12) | 1 839(8)  | C(64) | 5 676(15) | 9 853(11)  | 1 140(8)  |
| C(14)  | 7 524(13)  | 9 297(12) | 2 245(7)  | C(65) | 3 886(24) | 7 648(21)  | 1 329(13) |
| C(15)  | 3 647(14)  | 8 621(11) | 2 724(7)  |       |           |            |           |

\* Partial occupancy (in range 0.19–0.74) disordered atom.

mmol) added, and the mixture stirred for 1 h. The solvent was then removed *in vacuo* and the residue extracted with CH<sub>2</sub>Cl<sub>2</sub> (15 cm<sup>3</sup>). Addition of hexane and partial removal of the solvent *in vacuo* gave the green microcrystalline product, yield 0.065 g (71%).

(2,2'-Bipyridyl)carbonylbis(μ-di-p-tolyltriazenido-N<sup>1</sup>N<sup>3</sup>)-dinitrodiorrhodium [Rh<sub>2</sub>(CO)(NO<sub>2</sub>)<sub>2</sub>(bipy)(μ-RNNNR)<sub>2</sub>] **19**.—To a stirred solution of [{Rh<sub>2</sub>(μ-I)(CO)(bipy)(μ-RNNNR)<sub>2</sub>}]<sub>2</sub>[PF<sub>6</sub>]<sub>2</sub> (0.25 g, 0.11 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (60 cm<sup>3</sup>) was added AgPF<sub>6</sub> (0.06 g, 0.22 mmol). After 10 min the green solution was filtered through Celite to remove the precipitate of AgI and the filtrate was evaporated to dryness *in vacuo*. The residue was then dissolved in MeOH (15 cm<sup>3</sup>) and NaNO<sub>2</sub> (0.031 g, 0.45 mmol) was added to give a brown precipitate after 5 min. After a further 30 min the volume of the solvent was

reduced *in vacuo*. The brown solid was then filtered off and washed with MeOH (2 × 4 cm<sup>3</sup>), yield 0.150 g (70%).

*Crystal Structure Determinations of* [Rh<sub>2</sub>(NCMe)<sub>3</sub>-(bipy)(μ-RNNNR)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> **3**, [Rh<sub>2</sub>(μ-CO)(dppm)(bipy)(μ-RNNNR)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub>·2CH<sub>2</sub>Cl<sub>2</sub> **10a**·2CH<sub>2</sub>Cl<sub>2</sub> and [{Rh<sub>2</sub>(CO)(O<sub>2</sub>PF<sub>2</sub>)(μ-O<sub>2</sub>PF<sub>2</sub>)(bipy)(μ-RNNNR)<sub>2</sub>}]<sub>2</sub>·2.3C<sub>6</sub>H<sub>14</sub> **12**·2.3C<sub>6</sub>H<sub>14</sub>.—Many of the details of the structure analyses carried out on the complexes are listed in Table 6. X-Ray diffraction measurements were made at room temperature using Siemens four-circle P3m diffractometers on single crystals mounted in thin-walled glass capillaries with graphite-monochromated Mo-K<sub>α</sub> X-radiation ( $\lambda = 0.710 73 \text{ \AA}$ ). Cell dimensions for each analysis were determined from the setting angles of 25, 44 and 43 centred reflections respectively.

For each structure analysis, intensity data were collected for

**Table 9** Atomic coordinates ( $\times 10^4$ ) for complex **12**·2.3C<sub>6</sub>H<sub>14</sub>

| Atom  | x         | y         | z         | Atom  | x          | y         | z         |
|-------|-----------|-----------|-----------|-------|------------|-----------|-----------|
| Rh(1) | 8 811(1)  | 2 076(1)  | 3 673(1)  | C(15) | 7 000(12)  | 2 888(15) | 2 780(10) |
| Rh(2) | 9 077(1)  | 2 331(1)  | 2 869(1)  | C(16) | 8 326(12)  | 3 793(15) | 2 376(10) |
| P(1)  | 8 782(4)  | 1 446(5)  | 4 905(3)  | C(17) | 8 378(13)  | 4 599(16) | 2 367(12) |
| P(2)  | 9 564(4)  | 3 201(5)  | 1 784(3)  | C(18) | 8 191(13)  | 5 061(18) | 1 906(12) |
| F(1)  | 9 312(11) | 1 988(13) | 5 252(7)  | C(19) | 7 859(13)  | 4 704(17) | 1 408(11) |
| F(2)  | 8 278(10) | 1 658(11) | 5 129(7)  | C(20) | 7 629(15)  | 5 137(19) | 908(13)   |
| F(3)  | 9 551(12) | 4 049(11) | 1 894(11) | C(21) | 7 796(14)  | 3 932(18) | 1 419(12) |
| F(4)  | 9 073(8)  | 3 216(15) | 1 246(7)  | C(22) | 7 986(12)  | 3 461(16) | 1 871(11) |
| O(1)  | 8 551(8)  | 1 757(9)  | 4 363(6)  | C(23) | 8 813(10)  | 3 740(13) | 4 122(8)  |
| O(2)  | 9 335(7)  | 2 770(10) | 2 139(6)  | C(34) | 8 578(13)  | 3 526(16) | 4 495(10) |
| O(3)  | 9 838(7)  | 3 062(10) | 3 286(6)  | C(25) | 8 711(14)  | 3 988(17) | 4 981(12) |
| O(4)  | 8 968(11) | 654(12)   | 5 009(8)  | C(26) | 9 037(13)  | 4 733(16) | 5 015(11) |
| O(5)  | 9 873(9)  | 906(11)   | 3 018(7)  | C(27) | 9 111(14)  | 5 234(16) | 5 464(11) |
| N(1)  | 8 289(9)  | 1 718(11) | 2 525(8)  | C(28) | 9 195(12)  | 4 910(17) | 4 603(11) |
| N(2)  | 7 786(9)  | 1 817(11) | 2 646(8)  | C(29) | 9 111(12)  | 4 474(15) | 4 169(10) |
| N(3)  | 7 932(9)  | 2 070(12) | 3 147(8)  | C(30) | 10 046(12) | 2 558(16) | 4 411(10) |
| N(4)  | 8 555(8)  | 3 314(10) | 2 825(7)  | C(31) | 10 631(13) | 2 486(17) | 4 794(11) |
| N(5)  | 8 543(9)  | 3 680(12) | 3 240(8)  | C(32) | 10 871(16) | 1 712(19) | 4 918(13) |
| N(6)  | 8 702(8)  | 3 263(10) | 3 692(7)  | C(33) | 10 512(14) | 1 091(18) | 4 660(11) |
| N(7)  | 8 943(9)  | 879(10)   | 3 681(7)  | C(34) | 9 912(12)  | 1 243(14) | 4 297(9)  |
| N(8)  | 9 691(8)  | 1 985(11) | 4 173(7)  | C(35) | 9 503(11)  | 623(13)   | 4 001(9)  |
| C(1)  | 9 546(12) | 1 461(15) | 2 955(9)  | C(36) | 9 678(12)  | -126(14)  | 4 084(10) |
| C(2)  | 8 198(10) | 1 196(12) | 2 087(8)  | C(37) | 9 201(12)  | -635(15)  | 3 779(10) |
| C(3)  | 8 534(13) | 1 312(17) | 1 735(10) | C(38) | 8 665(12)  | -412(14)  | 3 466(9)  |
| C(4)  | 8 457(16) | 745(18)   | 1 369(13) | C(39) | 8 534(12)  | 375(14)   | 3 411(9)  |
| C(5)  | 7 972(14) | 218(17)   | 1 206(11) | C(40) | 437        | 6 564     | 1 357     |
| C(6)  | 7 849(15) | -284(18)  | 728(12)   | C(41) | 1 367      | 6 759     | 1 430     |
| C(7)  | 7 623(14) | 119(18)   | 1 520(12) | C(42) | 1 672      | 7 254     | 1 246     |
| C(8)  | 7 774(13) | 622(15)   | 1 963(11) | C(43) | 2 256      | 3 269     | 5 466     |
| C(9)  | 7 379(12) | 2 420(15) | 3 192(10) | C(44) | 2 336      | 3 226     | 5 013     |
| C(10) | 7 230(13) | 2 287(16) | 3 623(11) | C(45) | 2 500      | 2 500     | 5 000     |
| C(11) | 6 722(15) | 2 652(19) | 3 668(13) | C(46) | 0          | 6 196     | 2 500     |
| C(12) | 6 321(14) | 3 107(17) | 3 291(12) | C(47) | 82         | 6 217     | 2 045     |
| C(13) | 5 729(16) | 3 512(21) | 3 335(14) | C(48) | 761        | 6 871     | 1 241     |
| C(14) | 6 446(15) | 3 264(18) | 2 808(13) |       |            |           |           |

unique portions of reciprocal space to the limit of observable diffraction (rather low  $2\theta_{\max}$  in all three cases due to poor crystallinity). Corrections were applied for Lorentz, polarisation, and long-term intensity fluctuations, the latter on the basis of the intensities of three check reflections repeatedly measured during data collection. Corrections for X-ray absorption effects were applied on the basis of azimuthal scan data. The structures were solved by heavy-atom (Patterson or direct and Fourier difference) methods, and refined by full-matrix least squares against  $F$  and against  $F^2$  for **12**·2.3C<sub>6</sub>H<sub>14</sub>.<sup>12</sup> For **3** all rhodium, phosphorus, fluorine and nitrogen atoms were assigned anisotropic displacement parameters. For **10a**·2CH<sub>2</sub>Cl<sub>2</sub> all rhodium, phosphorus, fluorine, oxygen and nitrogen atoms and Cl(1), Cl(2), C(1) and C(2) were assigned anisotropic displacement parameters. For **12**·2.3C<sub>6</sub>H<sub>14</sub> all rhodium, phosphorus, fluorine and oxygen atoms and C(1) were assigned anisotropic displacement parameters. All other non-hydrogen atoms were assigned isotropic displacement parameters. All hydrogen atoms were constrained to ideal geometries with C–H 0.96 Å and assigned fixed isotropic displacement parameters. One of the two molecules of dichloromethane in **10a**·2CH<sub>2</sub>Cl<sub>2</sub> was severely disordered and was modelled with partial occupancy atom sites. The solvent in **12**·2.3C<sub>6</sub>H<sub>14</sub> is also severely disordered, about crystallographic  $\bar{1}$  and  $C_2$  sites. Nine carbon atom positions were assigned with total occupancy seven. A variety of models was refined all of which were unstable and had unrealistic geometries. The final model had atom positions and isotropic displacement parameters fixed at the values obtained in the best of these refinements. The model is therefore non-stoichiometric, corresponding to 2.33 hexanes of crystallisation per molecule of **12**. No hydrogen-atom positions were included in the refinement model for solvent molecules.

Final difference syntheses showed no chemically significant features, the largest maxima being close to the metal and solvent atoms. Refinements converged smoothly to residuals given in Table 6. Tables 7–9 report the positional parameters for these structure determinations. All calculations were made with programs of the SHELXTL PLUS<sup>12</sup> system and SHELXL 93.<sup>13</sup> Complex neutral-atom scattering factors were taken from ref. 14.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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