

**Bimetallic Cyano-bridged Cations: Preparation and Hydride Reduction of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}(\mu\text{-CN})\text{ML}'_2(\eta^5\text{-C}_5\text{H}_5)]\text{PF}_6$  [ $\text{L}_2, \text{L}'_2 = (\text{PPh}_3)_2, \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ;  $\text{M} = \text{Ru}$  or  $\text{Fe}$ ]. Formation of  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_3]$  and X-Ray Crystal Structure of  $[(\eta^5\text{-C}_5\text{H}_5)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Ru}(\mu\text{-CN})\text{Ru}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]\text{PF}_6^+$**

Gordon J. Baird, Stephen G. Davies,\* Steven D. Moon, and Stephen J. Simpson

The Dyson Perrins Laboratory, South Parks Road, Oxford OX1 3QY

Richard H. Jones

Chemical Crystallography Laboratory, 9 Parks Road, Oxford OX1 3PD

The cyano-complexes  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)_2\text{L}_2(\text{CN})]$  [(1)  $\text{L} = \text{PPh}_3$  and (2)  $\text{L}_2 = \text{dppe}$  ( $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ )] react with the corresponding chlorides (3) and (4) and with  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Br}]$  (9) to give the diruthenium cyano-bridged cations  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{L}_2\text{Ru}(\mu\text{-CN})\text{RuL}'_2(\eta^5\text{-C}_5\text{H}_5)]^+$  [ $\text{L} = \text{L}' = \text{PPh}_3$  (5);  $\text{L} = \text{PPh}_3, \text{L}'_2 = \text{dppe}$  (6);  $\text{L}_2 = \text{dppe}, \text{L}' = \text{PPh}_3$  (7);  $\text{L}_2 = \text{L}'_2 = \text{dppe}$  (8)] and the mixed iron-ruthenium cation  $[(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Ru}(\mu\text{-CN})\text{Fe}(\text{dppe})(\eta^5\text{-C}_5\text{H}_5)]^+$ . An X-ray crystal structure of complex (7) shows the  $\text{Ru-C}\equiv\text{N-Ru}$  bridge to be essentially linear. Hydride reduction of these cyano-bridged cations results in the breakage of the metal-nitrogen bond to regenerate the original cyano-complexes (1) and (2) together with the required hydrido-complexes  $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{H}]$  [ $\text{M} = \text{Ru}$  (11) or  $\text{Fe}$  (12)] or  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{H}]$  (13). For those reductions giving (13), the novel ruthenium trihydride  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_3]$  (14) was also isolated. Reduction of chloride (3) with sodium methoxide exclusively gave the monohydride (13), whereas reduction with lithium aluminium hydride in tetrahydrofuran gave a 1 : 4 mixture of the monohydride (13) and the trihydride (14). The mechanism for the formation of the trihydride (14) is discussed.

As a model for the reductive polymerisation of carbon monoxide we have recently reported the sequential reduction of co-ordinated carbon monoxide in mononuclear transition-metal cations.<sup>1</sup> Species other than C-terminal co-ordinated carbon monoxide may well be important in heterogeneous systems.<sup>2</sup> Of particular interest is the isocarbonyl linkage where carbon monoxide is co-ordinated at carbon and oxygen bridging two metal centres. Reduction of the isocarbonyl linkage might be expected to be especially facilitated if the metal co-ordinating oxygen were cationic, *i.e.*,  $\text{M-C}\equiv\text{O-M}^+ \longleftrightarrow \text{M}^+=\text{C}\equiv\text{O-M}$ .

There are presently no examples of stable isocarbonyl cations in the literature. Tilley and Andersen<sup>3</sup> have recently reported several mixed transition metal-lanthanide metal neutral isocarbonyl complexes and Merola *et al.*<sup>4</sup> have structurally characterised a tetrametallic, dimolybdenum-dititanium complex containing four isocarbonyl bridges. In contrast, the bridging cyanide group  $\text{M-C}\equiv\text{N-M}$ , occurs more widely.<sup>5</sup>

As models for the reduction of bridging isocarbonyl ligands we describe here the synthesis of some dimetallic cationic bridging cyano-complexes and an investigation of their reduction by hydride. We have previously reported<sup>6</sup> that the cyano-ligand in the compound  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{CN})]$  (1) is nucleophilic, undergoing reaction with weak electrophiles such as alkyl halides ( $\text{RX}$ ) to give the corresponding isonitrile cations  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{CNR})]^+$ . It was anticipated that this nucleophilicity could be utilised to provide a general route to cationic dinuclear cyano-bridged complexes by interaction of (1) with suitable organometallic halogeno-compounds. For

example, the halides  $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{PR}_3)_2\text{X}]$  ( $\text{M} = \text{Fe}$  or  $\text{Ru}$ ,  $\text{X} = \text{Cl}$  or  $\text{Br}$ ) are known to dissociate readily in methanol.<sup>7</sup>

## Results

The cyano-complexes  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{CN})]$  (1) and  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})(\text{CN})]$  (2) ( $\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ) were prepared as described previously by reaction of the corresponding chlorides (3) and (4), respectively, with potassium cyanide in methanol under reflux.<sup>6</sup> Treatment of these cyano-complexes with the chlorides (3) and (4) in the presence of ammonium hexafluorophosphate in methanol under reflux resulted in the formation of the crystalline diruthenium cyano-bridged cations (5)–(8). Under similar conditions (2) reacted with  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Br}]$  (9) to give the mixed iron-ruthenium cyano-bridged cation (10).

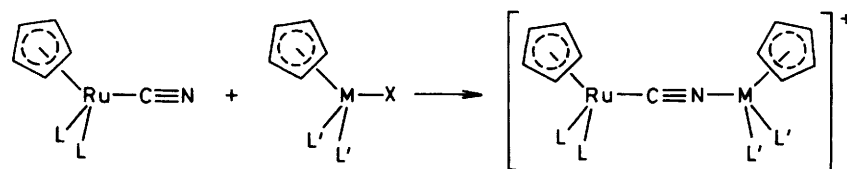
The new dimetallic cations (5)–(8) and (10) were characterised by  $^1\text{H}$  and  $^{31}\text{P}$  n.m.r. spectroscopy, field-desorption mass spectrometry, and elemental microanalysis. They all exhibit an i.r. band at *ca.*  $2\,090\text{ cm}^{-1}$  assignable to  $\nu(\text{C}\equiv\text{N})$  which differs little in frequency from the parent mononuclear cyano-complexes (1) [ $\nu(\text{C}\equiv\text{N})\ 2\,080\text{ cm}^{-1}$ ] and (2) [ $\nu(\text{C}\equiv\text{N})\ 2\,070\text{ cm}^{-1}$ ]. Cations (5)–(8) and (10) were found to be stable with respect to dissociation and cyano-bridge linkage isomerisation in solution at  $20^\circ\text{C}$ . For example, on monitoring an equimolar mixture of (2) and (5) in dichloromethane by  $^{31}\text{P}\{^1\text{H}\}$  n.m.r. spectroscopy over a period of 7 d, no trace of (1) or (7) could be found.

Treatment of the cations (6), (8), and (10) with lithium aluminium hydride in tetrahydrofuran at  $20^\circ\text{C}$  overnight led to displacement of the metal-nitrogen bond to produce the corresponding metal-hydride with the regeneration of the original mononuclear cyano-complex. Treatment of cation (6) with lithium aluminium deuteride gave  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{D}]$  with none of the corresponding hydride (11) being observed.

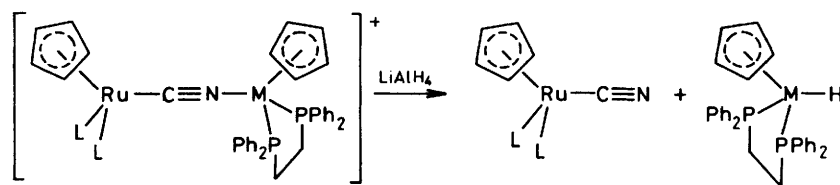
Reduction of cations (5) and (7), which both contain an N-bound bis(triphenylphosphine)ruthenium moiety gave the

<sup>†</sup> 2-[1,2-Bis(diphenylphosphino)ethane-PP']- $\mu$ -cyano- $\text{C}(\text{Ru}^2)\text{N}(\text{Ru}^1)$ -1,2-bis( $\eta^5$ -cyclopentadienyl)-1,1-bis(triphenylphosphine)diruthenium-(II,II) hexafluorophosphate.

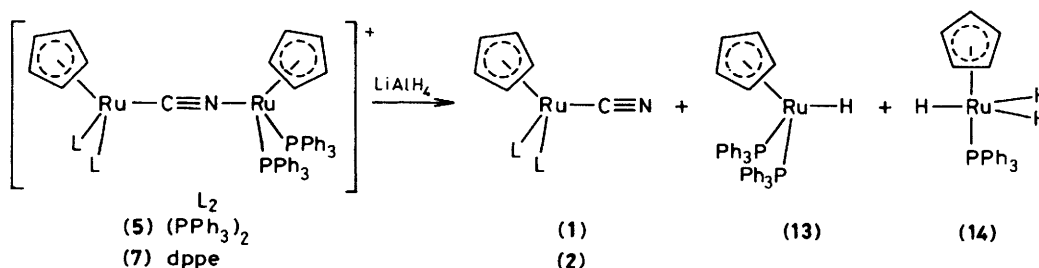
Supplementary data available (No. SUP 56216, 17 pp.): anisotropic and isotropic thermal parameters, full list of bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii–xix. Structure factors are available from the editorial office.



L <sub>2</sub>	M	X	L' <sub>2</sub>
(1) (PPh <sub>3</sub> ) <sub>2</sub>	(3) Ru	Cl	(PPh <sub>3</sub> ) <sub>2</sub> (5)
(1) (PPh <sub>3</sub> ) <sub>2</sub>	(4) Ru	Cl	dppe (6)
(2) dppe	(3) Ru	Cl	(PPh <sub>3</sub> ) <sub>2</sub> (7)
(2) dppe	(4) Ru	Cl	dppe (8)
(2) dppe	(9) Fe	Br	dppe (10)



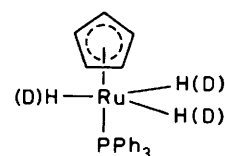
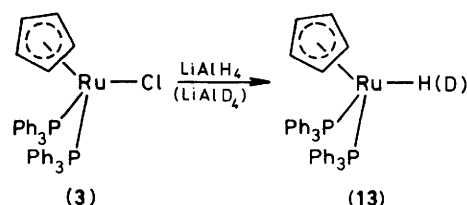
M	L	M
(6) Ru	(PPh <sub>3</sub> ) <sub>2</sub>	(1) + (11) Ru
(8) Ru	dppe	(2) + (11) Ru
(10) Fe	dppe	(2) + (12) Fe



L <sub>2</sub>	(1)	(13)	(14)
(5) (PPh <sub>3</sub> ) <sub>2</sub>			
(7) dppe			

cyano-complexes (1) and (2) respectively and unexpectedly a mixture of the monohydride (13) and the trihydride (14). The novel trihydride (14) was fully characterised and synthesised independently (see below).

Treatment of  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{Cl}]$  (3) with sodium methoxide in methanol gave the yellow complex  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{H}]$  (13) in 78% yield.<sup>8</sup> The monohydride (13), characterised by a high-field triplet ( $\delta -11.1$ ,  $J$  34 Hz) in the  $^1\text{H}$  n.m.r. spectrum, has been previously reported from the reaction of (3) with lithium aluminium hydride in diethyl ether.<sup>9</sup> In our hands this reaction consistently gave only very poor yields of a mixture of hydride compounds. Reduction of (3) with lithium aluminium hydride in tetrahydrofuran gave a mixture of the monohydride (13) and the trihydride (14) in a 1:4 ratio. The colourless major product (14) was sparingly soluble in diethyl ether and could be easily separated from (13) as colourless needles by crystallisation. Characterisation of (14) by  $^1\text{H}$  and  $^{31}\text{P}$  n.m.r. spectroscopy, mass spectrometry, and elemental analysis led to its formulation as  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_3\text{H}_3]$ . The presence of three hydride ligands was confirmed by obtaining a  $^{31}\text{P}$  n.m.r. spectrum with selective decoupling of the phenyl protons only, a sharp quartet being observed consistent with phosphorus coupling to three equivalent protons. The  $^1\text{H}$  n.m.r. spectrum of (14) was invariant from  $-80$  to  $70^\circ\text{C}$  and the i.r.



(14) [(15)]

spectrum consisted of two absorptions attributable to  $\text{Ru}-\text{H}$  at  $2040$  and  $1995\text{ cm}^{-1}$ . Reaction of (3) with lithium aluminium deuteride in tetrahydrofuran using  $\text{D}_2\text{O}$  in the work-up led cleanly to the trideuteride  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_3\text{D}_3]$  (15).

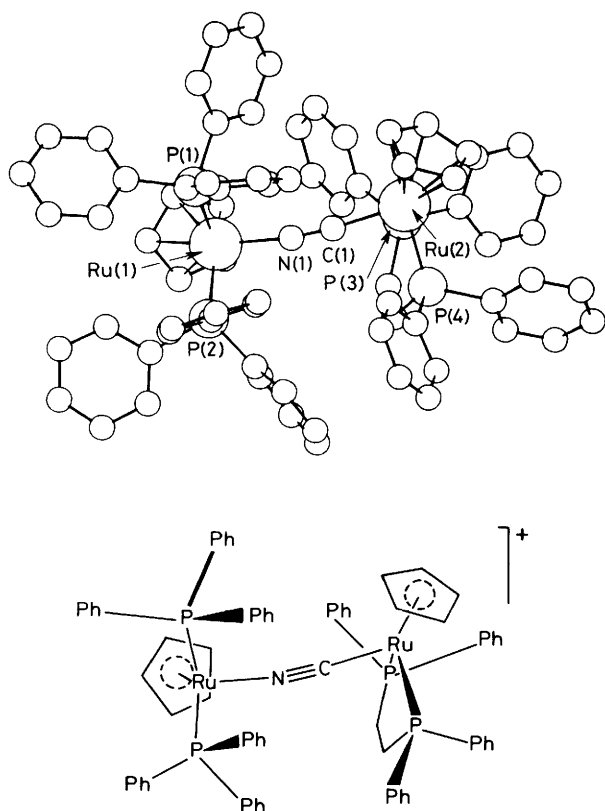
Examination of (15) by  $^2\text{H}$  n.m.r. spectroscopy showed a

**Table 1.** Atomic co-ordinates ( $\times 10^4$ ), with estimated standard deviations (e.s.d.s) in parentheses, for (7)

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Ru(1)	2 526.1(8)	1 797.7(3)	1 989.9(8)	C(195)	3 624(10)	-116(3)	5 172(10)
Ru(2)	969.0(9)	695.1(3)	2 155.7(9)	C(196)	3 586(10)	143(3)	4 557(9)
P(1)	569(3)	1 976(1)	1 285(3)	C(101)	2 658(10)	70(3)	1 649(6)
P(2)	3 250(3)	1 780(1)	499(3)	C(102)	2 035(10)	-95(4)	2 225(9)
P(3)	2 522(3)	686(1)	3 624(3)	C(103)	2 250(10)	-403(4)	2 401(9)
P(4)	2 377(3)	483(1)	1 447(4)	C(104)	3 097(11)	-550(3)	2 006(6)
C(1)	1 623(11)	1 109(4)	1 911(10)	C(105)	3 682(10)	-388(4)	1 349(9)
N(1)	1 941(9)	1 350(3)	1 819(8)	C(106)	3 462(10)	-76(4)	1 167(8)
C(2)	4 253(11)	1 981(4)	2 858(8)	C(202)	1 732(11)	-140(4)	1 352(8)
C(3)	3 364(12)	2 204(4)	2 828(8)	C(203)	1 950(11)	-448(4)	1 530(9)
C(4)	2 584(12)	2 085(4)	3 371(9)	C(205)	4 029(11)	-343(4)	2 384(8)
C(5)	2 960(11)	1 792(4)	3 740(8)	C(206)	3 810(11)	-32(4)	2 205(8)
C(6)	4 012(12)	1 733(4)	3 403(9)	C(111)	2 202(10)	537(2)	39(10)
C(7)	-454(8)	355(4)	2 343(12)	C(112)	2 962(10)	364(2)	-424(13)
C(8)	-625(8)	423(3)	1 287(11)	C(113)	2 821(11)	389(2)	-1 512(13)
C(9)	-896(8)	735(4)	1 105(13)	C(114)	1 931(11)	584(2)	-2 112(11)
C(10)	-881(8)	856(4)	2 085(13)	C(115)	1 166(10)	739(2)	-1 641(13)
C(11)	-618(8)	636(4)	2 829(14)	C(116)	1 302(10)	715(2)	-568(13)
C(12)	3 965(12)	712(4)	3 230(11)	C(212)	3 106(11)	676(2)	-345(13)
C(13)	3 813(12)	653(3)	2 110(11)	C(213)	2 971(11)	699(2)	-1 423(14)
C(21)	473(9)	1 845(3)	71(9)	C(215)	1 005(11)	465(2)	-1 733(13)
C(22)	-1 024(9)	2 032(4)	-741(9)	C(216)	1 140(11)	442(2)	-658(14)
C(23)	-1 919(11)	1 913(5)	-1 604(11)	P(5)	2 569(3)	-1 112(1)	4 591(3)
C(24)	-2 223(11)	1 615(5)	-1 614(12)	F(1)	1 836(9)	-1 416(2)	4 431(8)
C(25)	-1 666(11)	1 430(4)	-813(12)	F(2)	3 347(9)	-814(2)	4 760(8)
C(26)	-787(11)	1 543(4)	33(11)	F(3)	3 557(9)	-1 270(3)	5 473(10)
C(31)	-472(9)	1 902(3)	2 105(9)	F(4)	1 621(9)	-961(3)	3 685(10)
C(32)	-202(11)	1 697(2)	2 913(9)	F(5)	1 894(11)	-1 009(3)	5 409(10)
C(33)	-1 020(12)	1 633(3)	3 505(10)	F(6)	3 280(11)	-1 215(3)	3 790(10)
C(34)	-2 103(12)	1 774(3)	3 280(11)	H(2)	4 956(11)	2 003(4)	2 545(8)
C(35)	-2 397(11)	1 981(3)	2 472(11)	H(3)	3 305(12)	2 408(4)	2 483(8)
C(36)	-1 596(11)	2 045(3)	1 880(10)	H(4)	1 854(12)	2 188(4)	3 489(9)
C(41)	529(7)	2 396(3)	1 163(9)	H(5)	2 552(11)	1 654(4)	4 145(8)
C(42)	184(8)	2 583(4)	1 858(10)	H(6)	4 504(12)	1 543(4)	3 538(9)
C(43)	229(10)	2 890(4)	1 754(14)	H(7)	-255(8)	152(4)	2 679(12)
C(44)	620(10)	3 020(4)	968(15)	H(8)	-557(8)	274(3)	733(11)
C(45)	970(9)	2 834(5)	261(13)	H(9)	-1 060(8)	848(4)	427(13)
C(46)	926(8)	2 520(4)	344(10)	H(10)	-1 051(8)	1 072(4)	2 228(13)
C(51)	2 203(11)	1 770(4)	-814(10)	H(11)	-551(8)	660(4)	3 594(14)
C(52)	2 098(11)	2 011(4)	-1 505(11)	H(12)	4 288(12)	923(4)	3 386(11)
C(53)	1 234(14)	2 000(5)	-2 445(12)	H(13)	4 550(12)	563(4)	3 648(11)
C(54)	498(14)	1 756(6)	-2 688(12)	H(14)	3 888(12)	850(3)	1 751(11)
C(55)	590(11)	1 510(4)	-2 015(13)	H(15)	4 468(12)	512(3)	2 037(11)
C(56)	1 455(12)	1 520(4)	-1 055(11)	H(22)	-790(9)	2 251(4)	-728(9)
C(61)	4 217(10)	2 106(5)	359(7)	H(23)	-2 311(11)	2 053(5)	-2 189(11)
C(62)	3 847(13)	2 389(5)	507(7)	H(24)	-2 858(11)	1 531(5)	-2 214(12)
C(63)	4 421(13)	2 652(4)	310(8)	H(25)	-1 894(11)	1 211(4)	-829(12)
C(64)	5 443(16)	2 606(6)	-53(8)	H(26)	-384(11)	1 405(4)	618(11)
C(65)	5 873(13)	2 328(7)	-210(8)	H(32)	600(11)	1 593(2)	3 074(9)
C(66)	5 265(12)	2 074(5)	-6(7)	H(33)	-798(12)	1 484(3)	4 095(10)
C(71)	4 268(8)	1 459(2)	444(9)	H(34)	-2 695(12)	1 728(3)	3 699(11)
C(72)	4 924(11)	1 322(3)	1 374(9)	H(35)	-3 199(11)	2 085(3)	2 313(11)
C(73)	5 780(10)	1 098(3)	1 360(9)	H(36)	-1 825(11)	2 192(3)	1 286(10)
C(74)	5 979(8)	1 011(2)	409(10)	H(42)	-88(8)	2 489(4)	2 447(10)
C(75)	5 392(11)	1 165(3)	-525(9)	H(43)	-24(10)	3 024(4)	2 271(14)
C(76)	4 526(11)	1 389(3)	-511(6)	H(44)	657(10)	3 246(4)	909(15)
C(172)	4 109(11)	1 262(3)	-426(9)	H(45)	1 250(9)	2 928(5)	-324(13)
C(173)	4 968(12)	1 037(3)	-440(9)	H(46)	1 172(8)	2 386(4)	-178(10)
C(175)	6 081(10)	1 191(3)	1 299(9)	H(52)	2 634(11)	2 193(4)	-1 330(11)
C(176)	5 225(11)	1 415(3)	1 318(9)	H(53)	1 140(14)	2 172(5)	-2 955(12)
C(81)	3 613(11)	980(2)	4 600(9)	H(54)	-128(14)	1 749(6)	-3 370(12)
C(82)	1 582(12)	1 104(2)	4 766(10)	H(55)	47(11)	1 330(4)	-2 203(13)
C(83)	1 607(15)	1 306(3)	5 583(11)	H(56)	1 542(12)	1 347(4)	-551(11)
C(84)	2 691(15)	1 382(3)	6 247(10)	H(62)	3 108(13)	2 410(5)	771(7)
C(85)	3 744(14)	1 259(3)	6 091(11)	H(63)	4 088(13)	2 855(4)	428(8)
C(86)	3 712(13)	1 060(6)	5 291(10)	H(64)	5 891(16)	2 789(6)	-200(8)
C(91)	2 654(8)	351(2)	4 464(7)	H(65)	6 620(13)	2 308(7)	-463(8)
C(92)	3 410(10)	345(3)	5 482(10)	H(66)	5 594(12)	1 871(5)	-128(7)
C(93)	3 454(10)	84(3)	6 103(10)	H(82)	790(12)	1 050(2)	4 277(10)
C(94)	2 735(9)	-168(3)	5 698(8)	H(83)	845(15)	1 396(3)	5 685(11)
C(95)	1 996(10)	-162(3)	4 701(11)	H(84)	2 731(15)	1 525(3)	6 842(10)
C(96)	1 955(9)	97(3)	4 086(10)	H(85)	4 536(14)	1 314(3)	6 575(11)
C(192)	1 736(10)	297(3)	4 952(10)	H(86)	4 476(13)	969(3)	5 197(10)
C(193)	1 774(10)	37(3)	5 568(9)				

**Table 2.** Selected bond lengths (Å) and angles (°), with e.s.d.s in parentheses, for (7)

Ru(1)–P(1)	2.337(3)	Ru(2)–P(3)	2.276(4)
Ru(1)–P(2)	2.327(3)	Ru(2)–P(4)	2.265(4)
Ru(1)–N(1)	2.07(1)	Ru(2)–C(1)	2.03(2)
C(1)–N(1)	1.14(2)		
P(1)–Ru(1)–P(2)	100.8(1)	P(3)–Ru(2)–P(4)	82.0(4)
P(1)–Ru(1)–N(1)	91.4(1)	P(3)–Ru(2)–C(1)	84.9(4)
P(2)–Ru(1)–N(1)	92.9(4)	P(4)–Ru(2)–C(1)	88.5(4)
Ru(1)–N(1)–C(1)	168(1)	Ru(2)–C(1)–N(1)	175(1)

**Figure.** Molecular structure of  $[(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Ru}(\mu\text{-CN})\text{Ru}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$  (7)

complete absence of deuterium in the triphenylphosphine and cyclopentadienyl ligands. Treatment of (3) with  $\text{LiAlD}_4$  in tetrahydrofuran using  $\text{H}_2\text{O}$  in the work-up gave a product whose high-field  $^1\text{H}$  n.m.r. spectrum showed it to be a mixture of the isotopomers of (14) with by far the major component being the dideuteriomonohydride ( $14\text{-D}_2$ ). Spectra obtained at both 300 and 500 MHz consisted of a well resolved doublet of 1:1:1 triplets for ( $14\text{-D}_1$ ) and a doublet of 1:2:3:1 pentets for ( $14\text{-D}_2$ ). Analysis of the spectra gave  $^2J_{\text{HD}} = 2.78$  Hz, and secondary isotopic shifts as follows:  $\sigma_{\text{H}}^{\text{a}}(\text{RuH}_2\text{D}) - \sigma_{\text{H}}^{\text{a}}(\text{RuH}_3) = 0.023$  p.p.m.,  $\sigma_{\text{H}}^{\text{a}}(\text{RuHD}_2) - \sigma_{\text{H}}^{\text{a}}(\text{RuH}_3) = 0.046$  p.p.m. The observation of this large isotopic shift enabled us to demonstrate that pure (14) does not undergo H/D exchange with neutral  $\text{D}_2\text{O}$ , toluene-*p*-sulphonic acid- $\text{D}_2\text{O}$ , or  $\text{NaOD-D}_2\text{O}$  at 300 K in  $[\text{C}_6\text{H}_6]$ benzene. The monohydride (13) does not convert to the trihydride (14) in tetrahydrofuran or benzene solution and transforms only very slowly in tetrahydrofuran containing  $\text{LiAlH}_4$  at 60 °C, giving for example a mixture of (13)

and (14) in a 1:3 ratio after 48 h. Reaction of  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Cl}]$  (4) with  $\text{LiAlH}_4$  in tetrahydrofuran leads cleanly to  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{H}]$  (11), characterised by  $^1\text{H}$  and  $^{31}\text{P}$  n.m.r. spectroscopy, mass spectrometry, and elemental analysis. The hydride  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{H}]$  (13) does not react with dppe in toluene under reflux to give (11), in contrast to the reaction of the chloride (3) to give (4).<sup>10</sup>

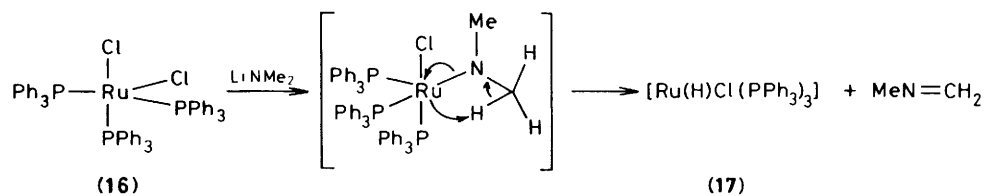
**X-Ray Structure Analysis of  $[(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Ru}(\mu\text{-CN})\text{Ru}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]\text{PF}_6$  (7).**—The Figure shows the *X*-ray crystal structure of (7). Final atomic positional co-ordinates are listed in Table 1 and selected bond lengths and bond angles are given in Table 2.

The disposition of the bridging cyano-ligand is such that the four atoms Ru(1), N(1), C(1), and Ru(2) are almost collinear with an angle of 168° at nitrogen and 175° at carbon and a dihedral angle of 42°. This situation is commonly encountered in metal-isonitrile compounds, e.g.  $[\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2\text{-(CNC}_6\text{H}_4\text{Cl-}p)]\cdot\text{EtOH}$  where RuCN and CNC(aryl) are 176 and 165° respectively,<sup>11</sup> and  $[\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{CNBu}^t)]$  where MnCN and CNC(Bu<sup>t</sup>) are 177 and 172° respectively.<sup>12</sup> However, in an organic analogue, *N*-(2,6-dimethylphenyl)-acetonitrilium tetrafluoroborate,<sup>13</sup> these angles are 179.2 and 177.4° respectively. The neutral cyano-bridged compound  $[(\text{NC})_5\text{Co}(\mu\text{-CN})\text{Co}(\text{NH}_3)_5]$  possesses a *syn* disposition of metal atoms about a bent Co–N–C–Co system with angles of 172.4 and 159.8° at carbon and nitrogen respectively.<sup>14</sup> The Ru(2)–C(1) bond length of 2.03(2) Å is longer than that found in ruthenium-isonitrile complexes, for example  $[\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2(\text{CNC}_6\text{H}_4\text{Cl-}p)]\cdot\text{EtOH}$ , 1.94 Å,<sup>11</sup> and  $[\text{RuI}_2(\text{CO})(\text{PPh}_3)_2\{\text{CH}(\text{NMe})\text{C}_6\text{H}_4\text{Me-}p\}(\text{CNBu}^t)]$ , 1.998 Å,<sup>15</sup> whilst the Ru(1)–N(1) bond length, 2.07(1) Å, is shorter than that found in typical ruthenium N-donor systems, for example  $[\text{Ru}(\eta^4\text{-C}_8\text{H}_{12})\text{Cl}_2(\text{CO})(\text{NCMe})]$ , 2.165 Å;<sup>16</sup> this supports the charge distribution  $\text{Ru-C}\equiv\text{N-Ru}^+$  with the positive charge being localised on the metal bearing nitrogen. The CN bond length, 1.14(2) Å, is in agreement with this, comparing favourably with 1.14 Å for  $[\text{RuCl}_2(\text{CO})(\text{PPh}_3)_2(\text{CNC}_6\text{H}_4\text{Cl-}p)]\cdot\text{EtOH}$ <sup>14</sup> and 1.132 Å in *N*-(2,6-dimethylphenyl)acetonitrilium tetrafluoroborate.<sup>13</sup> The ruthenium-phosphorus bond lengths are also consistent with the above neutral and cationic Ru moieties  $[\text{Ru}(\text{dppe})]$  systems, ref. 17a,  $[\text{Ru}(\text{PPh}_3)]$  systems, ref. 17b]. In conclusion, (7) contains an essentially linear cyano-bridge linking a carbon-bound neutral and a nitrogen-bound cationic cyclopentadienyl ruthenium bis(phosphine) fragment.

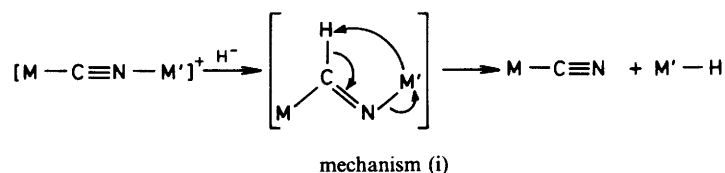
## Discussion

The halides (3), (4), and (9) readily ionize in methanol solution.<sup>7</sup> In the presence of the nucleophilic cyano-complexes (1) and (2),<sup>6</sup> the solvated cationic intermediates thus produced are trapped to yield the cyano-bridged cations (5)–(8) and (10). The spectroscopic properties of the cations (5)–(8) and (10) are unexceptional; the  $^1\text{H}$  n.m.r. spectra for each cation contain two cyclopentadienyl singlets. The stretching frequencies of the cyano-bridges are 10–30  $\text{cm}^{-1}$  higher than that of the cyano-ligands in the precursors (1) and (2). In general, the absorption of bridging cyano-groups is 50–100  $\text{cm}^{-1}$  higher than that of the parent mononuclear cyano-complexes and a force-field argument has been proposed to explain this.<sup>18</sup> The reduction of the binuclear cations (6), (8), and (10) regenerated the initial mononuclear cyano-complexes together with the appropriate monohydrides (11) and (12). Two mechanisms for these reductions can be ruled out. Prior dissociation of the dinuclear cations to give the neutral cyano-complex and 16-electron cations which are then attacked directly at the metal centre by hydride is incompatible with their observed stability towards dissociation and cyano-bridge linkage isomerisation in





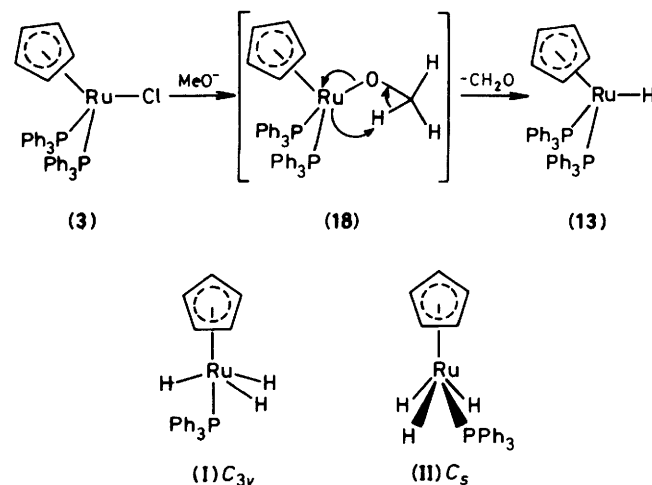
solution. Initial attack *exo* onto the cyclopentadienyl ligand followed by *endo* hydrogen migration to the metal is inconsistent with the formation of the ruthenium deuteride  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{D}]$  as the sole product on reduction of cation (6) with lithium aluminium deuteride. In accordance with the experimental results and by analogy with our previous work on carbon monoxide reduction we propose the mechanism (i)



for the reduction of the dinuclear cyano-bridged cations. Initial attack on the carbon of the cyano-bridge generates a bridging iminoformyl which then undergoes  $\beta$ -elimination to generate the observed products.

Stable ruthenium iminoformyls have been isolated<sup>19</sup> but never where decomposition *via*  $\beta$ -elimination was possible. Monitoring the reactions of cations (6) or (10) with lithium aluminium hydride, from  $-60$  to  $30^\circ\text{C}$  by  $^1\text{H}$  n.m.r. spectroscopy, provided no evidence for an iminoformyl intermediate which would have been expected to exhibit a characteristic resonance at *ca.*  $\delta$  10–11 for the iminoformyl proton.<sup>19</sup> Presumably the  $\beta$ -elimination is too rapid to allow observation of the intermediate. An analogy, (16)  $\rightarrow$  (17), to the proposed  $\beta$ -elimination mechanism has been reported.<sup>20</sup>

Reduction of cations (5) and (7) proceeds similarly to give the neutral cyano-complexes and monohydride (13) but with additional formation of trihydride (14) from further reduction of (13). In our hands the most efficient synthesis of the monohydride (13) is from methoxide treatment of the chloride (3), presumably *via*  $\beta$ -elimination of intermediate (18). Treatment of monohydride (13) with lithium aluminium hydride slowly generates trihydride (14).



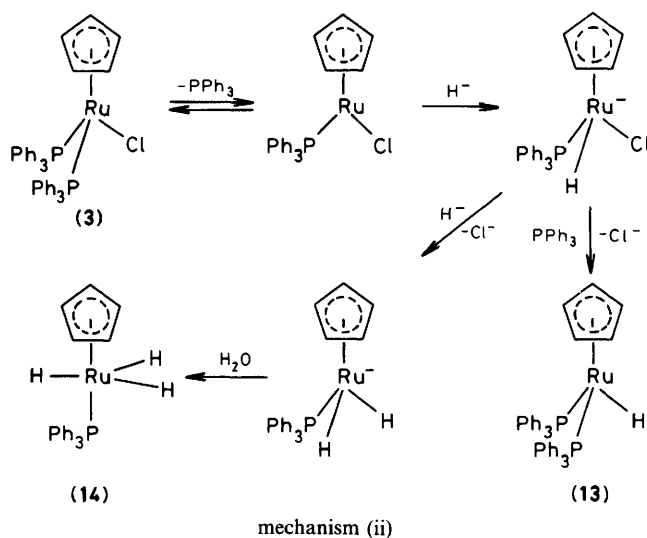
Reduction of the chloride (3) with lithium aluminium hydride in tetrahydrofuran gave the yellow monohydride (13) together with the novel, colourless trihydride (14). There are two possible idealised structures for the seven-co-ordinate trihydride (14); the capped octahedron ( $C_{3v}$ ) (I) and the tetragonal base-trigonal base structure ( $C_s$ ) (II).

The structure (I) should exhibit two i.r.-active Ru–H stretch-

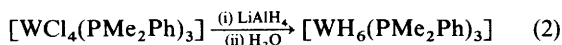
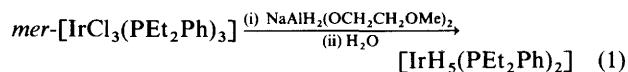
ing modes ( $A_1 + E$ ) while structure (II) should exhibit three i.r.-active modes ( $2A' + A''$ ). The trihydride (14) possesses two absorptions at 2 040 and 1 995  $\text{cm}^{-1}$ . The  $^1\text{H}$  n.m.r. spectrum of (14) consists of a sharp doublet ( $\delta$   $-9.8$ ,  $J = 19.8$  Hz) in the high-field region and is unchanged down to  $-80^\circ\text{C}$ . The coupling constant is characteristic of a *cis* relationship between phosphine and hydride ligands on ruthenium; the *trans* arrangement would lead to a coupling constant of 120–160 Hz depending on precise geometry.<sup>21</sup> The recently reported  $[\text{Os}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})\text{H}_3]$ <sup>22</sup> is fluxional giving a doublet and a triplet at  $-50^\circ\text{C}$  in the high-field  $^1\text{H}$  n.m.r. spectrum and a broad singlet at  $25^\circ\text{C}$  and thus presumably has the  $C_s$  structure [*e.g.* (II)] found crystallographically in the related tribromide  $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})\text{Br}_3]$ .<sup>23</sup> The spectroscopic data for (14) are consistent with the  $C_{3v}$  structure (I) which is presumably favoured by the steric requirement of the bulky triphenylphosphine ligand. The measured coupling constant ( $^2J_{\text{HD}} = 2.78$  Hz) for the isotopomers of (14) leads to a value of  $^2J_{\text{HH}} = 18$  Hz, which is a much larger value than those usually found, 0–10 Hz.<sup>24</sup> The secondary isotopic shift found for the  $\text{RuH}_3$  system in (14) of 0.023 p.p.m. is comparable to that found for  $\text{CH}_3$  systems;<sup>25</sup> this appears to be the first report of this parameter in an organometallic system.  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_3]$  (14) is stable in solution to *ca.*  $100^\circ\text{C}$ , but solutions rapidly become green in sunlight presumably losing hydrogen. This thermal stability is in marked contrast to other neutral ruthenium polyhydrides;<sup>26</sup> however, Werner and Kletzin<sup>27</sup> have reported some stable cationic trihydrides,  $[\text{Ru}(\eta^6\text{-arene})(\text{PR}_3)_3]^+$  ( $\text{R} = \text{Me, Ph, or Pr}^i$ ).

The isolation of the trideuteride (15) from the reaction of (3) with lithium aluminium deuteride followed by  $\text{D}_2\text{O}$  work-up and the absence of deuterium in the cyclopentadienyl or triphenylphosphine ligands rules out the intermediacy of *ortho*-metallated species in the reaction leading to (14). Use of  $\text{H}_2\text{O}$  in place of  $\text{D}_2\text{O}$  in this reaction gave predominantly (14- $\text{D}_2$ ). The trihydride (14) does not undergo exchange with  $\text{D}_2\text{O}$  under neutral, weakly acidic or basic conditions in benzene solution. Consideration of these results in addition to the very slow reaction of (13) with  $\text{LiAlH}_4$  in tetrahydrofuran to give (14) suggests mechanism (ii) for the conversion of (3) into (13) and (14).

The dissociation of triphenylphosphine from (I) has been



observed previously in solvents of low dielectric constant.<sup>28</sup> We note that increase of co-ordination number is common on reaction of metal chloride compounds containing bulky phosphine ligands with complex hydride reducing agents, *e.g.*, equations (1) and (2).<sup>29</sup>



The straightforward reaction of the chloride  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Cl}]$  (4) with lithium aluminium hydride in tetrahydrofuran to yield only the monohydride (11) rather than a trihydride analogous to (14) can be rationalised on the grounds of phosphine loss from the bidentate system being unfavourable.

## Experimental

All reactions and purifications were performed under a nitrogen atmosphere using standard vacuum line and Schlenk-tube techniques.<sup>30</sup> Tetrahydrofuran and toluene were dried over sodium diphenylketyl and distilled. Diethyl ether and light petroleum (b.p. 40–60 °C) were dried over sodium wire and distilled. Dichloromethane was dried over calcium hydride and distilled. Methanol was dried over magnesium methoxide and distilled. Infrared spectra were recorded on a Perkin-Elmer 297 instrument and calibrated against polystyrene film. Nuclear magnetic resonance spectra were recorded on Bruker AM250 (101.26 MHz <sup>31</sup>P, 62.90 MHz <sup>13</sup>C), Bruker WH 300 (300.13 MHz <sup>1</sup>H, 46.07 MHz <sup>2</sup>H, 75.47 MHz <sup>13</sup>C, 121.49 MHz <sup>31</sup>P), and Bruker AM 500 (500.13 MHz <sup>1</sup>H) spectrometers. Mass spectra were obtained by field desorption (f.d.) and fast-atom bombardment (f.a.b.) methods using a V.G. Micromass ZAB-1F instrument. Elemental analyses were performed by Dr. F. B. Strauss of this department. Melting points were determined in capillaries sealed under nitrogen and are uncorrected. The compounds  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Br}]$ ,<sup>31</sup>  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{X}]$  (X = Cl<sup>10</sup> or CN<sup>6</sup>), and  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{X}]$  (X = Cl<sup>10</sup> or CN<sup>6</sup>) were prepared by published procedures.

$[(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{Ru}(\mu\text{-CN})\text{Ru}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]\text{PF}_6$  (5).—A suspension of  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{Cl}]$  (3) (0.44 g, 0.61 mmol),  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{CN})]$  (1) (0.44 g, 0.61 mmol), and  $\text{NH}_4\text{PF}_6$  (0.50 g, 3.1 mmol) in distilled methanol (25 cm<sup>3</sup>) was stirred at 50 °C for 2 h, then at 20 °C for 12 h. Filtration and

drying under reduced pressure gave yellow microcrystals (0.7 g, 74%). I.r. (Nujol):  $\nu_{\text{max}}$  2 080 s cm<sup>-1</sup> (CN). <sup>1</sup>H N.m.r. (CDCl<sub>3</sub>):  $\delta$  7.05 (m, 60 H, Ph), 4.19 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.05 (s, 5 H, C<sub>5</sub>H<sub>5</sub>). <sup>31</sup>P-{<sup>1</sup>H} N.m.r. (CDCl<sub>3</sub>):  $\delta$  47.3 (s), 41.6 (s). *M/z* (f.a.b.): 1 410 [*M*]<sup>+</sup>. M.p. 178–180 °C.

$[(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Ru}(\mu\text{-CN})\text{Ru}(\text{dppe})(\eta^5\text{-C}_5\text{H}_5)]\text{PF}_6$  (6).—A suspension of  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{CN})]$  (1) (0.2 g, 0.28 mmol),  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Cl}]$  (4) (0.18 g, 0.3 mmol), and  $\text{NH}_4\text{PF}_6$  (0.25 g, 1.5 mmol) in distilled methanol (15 cm<sup>3</sup>) was stirred for 3 h at 50 °C then for 12 h at 20 °C. Filtration, drying under reduced pressure, and recrystallisation (dichloromethane–light petroleum) gave yellow plates (0.25 g, 63%) (Found: C, 56.65; H, 4.30; N, 0.85; P, 9.45. C<sub>73</sub>H<sub>64</sub>F<sub>6</sub>NP<sub>5</sub>Ru<sub>2</sub>·2CH<sub>2</sub>Cl<sub>2</sub> requires C, 56.40; H, 4.25; N, 0.85; P, 9.70%). I.r. (Nujol):  $\nu_{\text{max}}$  2 090 s cm<sup>-1</sup> (CN). <sup>1</sup>H N.m.r. (CDCl<sub>3</sub>):  $\delta$  7.5–6.7 (m, 50 H, Ph), 5.2 (s, 4 H, CH<sub>2</sub>Cl<sub>2</sub>), 4.48 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 3.76 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 2.8–2.0 (m, 4 H, CH<sub>2</sub>). <sup>31</sup>P-{<sup>1</sup>H} N.m.r. (CDCl<sub>3</sub>):  $\delta$  78.05 (s, Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>), 47.4 (s, PPh<sub>3</sub>). *M/z* (f.d.) 1 282 [*M*]<sup>+</sup>. M.p. 190–192 °C.

$[(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Ru}(\mu\text{-CN})\text{Ru}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]\text{PF}_6$  (7).—A suspension of  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{Cl}]$  (3) (0.22 g, 0.30 mmol),  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})(\text{CN})]$  (2) (0.165 g, 0.28 mmol), and  $\text{NH}_4\text{PF}_6$  (0.25 g, 1.5 mmol) in distilled methanol (20 cm<sup>3</sup>) was stirred at 50 °C for 3 h, then at 20 °C for 12 h. Filtration, drying under reduced pressure, and recrystallisation (dichloromethane–light petroleum) gave yellow plates (0.25 g, 63%) (Found: C, 61.30; H, 4.80; N, 1.15; P, 10.55. C<sub>73</sub>H<sub>64</sub>F<sub>6</sub>NP<sub>5</sub>Ru<sub>2</sub> requires C, 61.55; H, 4.50; N, 1.00; P, 10.90%). I.r. (Nujol):  $\nu_{\text{max}}$  2 090 s cm<sup>-1</sup> (CN). <sup>1</sup>H N.m.r. (CDCl<sub>3</sub>):  $\delta$  7.5–6.8 (m, 50 H, Ph), 4.7 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 3.6 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 2.7–2.4 (m, 4 H, CH<sub>2</sub>). <sup>31</sup>P-{<sup>1</sup>H} N.m.r. (CDCl<sub>3</sub>):  $\delta$  81.6 (s, Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>), 41.6 (s, PPh<sub>3</sub>). *M/z* (f.d.): 1 282 [*M*]<sup>+</sup>. M.p. 184–188 °C.

$[(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Ru}(\mu\text{-CN})\text{Ru}(\text{dppe})(\eta^5\text{-C}_5\text{H}_5)]\text{PF}_6$  (8).—A suspension of  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})(\text{CN})]$  (2) (0.165 g, 0.28 mmol),  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Cl}]$  (4) (0.18 g, 0.30 mmol), and  $\text{NH}_4\text{PF}_6$  (0.25 g, 1.5 mmol) in distilled methanol (15 cm<sup>3</sup>) was stirred at 50 °C for 2 h, then at 20 °C for 12 h. Filtration, drying under reduced pressure, and recrystallisation (dichloromethane–light petroleum) gave lemon yellow crystals (0.15 g, 41%) (Found: C, 56.20; H, 4.55; N, 1.15. C<sub>63</sub>H<sub>58</sub>F<sub>6</sub>NP<sub>5</sub>Ru<sub>2</sub> requires C, 58.20; H, 4.45; N, 1.10%). I.r. (Nujol):  $\nu_{\text{max}}$  2 110 s cm<sup>-1</sup> (CN). <sup>1</sup>H N.m.r. (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.5–6.7 (m, 40 H, Ph), 4.35 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 4.17 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 2.5–1.8 (m, 8 H, CH<sub>2</sub>). <sup>31</sup>P-{<sup>1</sup>H} N.m.r. (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  82.1 (s), 79.7 (s). *M/z* (f.d.): 1 156 [*M*]<sup>+</sup>.

$[(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Ru}(\mu\text{-CN})\text{Fe}(\text{dppe})(\eta^5\text{-C}_5\text{H}_5)]\text{PF}_6$  (10).—A suspension of  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})(\text{CN})]$  (2) (0.165 g, 0.28 mmol),  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Br}]$  (9) (0.18 g, 0.33 mmol), and  $\text{NH}_4\text{PF}_6$  (0.25 g, 1.5 mmol) in distilled methanol (15 cm<sup>3</sup>) was stirred at 20 °C for 24 h. Evaporation, extraction with dichloromethane (2 × 10 cm<sup>3</sup>), concentration and crystallisation by addition of diethyl ether gave dark red needles (0.20 g, 57%) (Found: C, 60.05; H, 4.50; N, 1.20; P, 11.75. C<sub>63</sub>H<sub>58</sub>F<sub>6</sub>FeNP<sub>5</sub>Ru requires C, 60.25; H, 4.60; N, 1.10; P, 12.35%). I.r. (Nujol):  $\nu_{\text{max}}$  2 095 s cm<sup>-1</sup> (CN). <sup>1</sup>H N.m.r. (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  7.8–6.8 (m, 40 H, Ph), 4.44 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 3.83 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 2.0 (m, 4 H, CH<sub>2</sub>), 1.4 (m, 4 H, CH<sub>2</sub>). <sup>31</sup>P-{<sup>1</sup>H} N.m.r. (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  95.8 (s), 81.8 (s). *M/z* (f.d.): 1 110 [*M*]<sup>+</sup>. M.p. > 235 °C.

**Reduction of (5) with LiAlH<sub>4</sub>.**—LiAlH<sub>4</sub> (50 mg, 1.3 mmol) was added to a suspension of (5) (0.35 g, 0.23 mmol) in thf (20 cm<sup>3</sup>) at –78 °C and the mixture stirred at 20 °C for 18 h. Hydrolysis at –78 °C and evaporation gave a yellow solid. Extraction with toluene (2 × 10 cm<sup>3</sup>) and evaporation yielded a

yellow solid (60 mg) identified by  $^1\text{H}$  and  $^{31}\text{P}$  n.m.r. as a 1:1 mixture of  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{H}]$  (13) and  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{H}_3]$  (14). Further extraction of the toluene-insoluble material with dichloromethane (10  $\text{cm}^3$ ) and evaporation yielded a yellow solid (40 mg) identified as  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{CN})]$  (1) by  $^1\text{H}$  n.m.r. and i.r. spectroscopy.

**Reaction of (6) with  $\text{LiAlH}_4$ .**— $\text{LiAlH}_4$  (50 mg, 1.3 mmol) was added to a suspension of (6) (0.3 g, 0.21 mmol) in thf (20  $\text{cm}^3$ ) at  $-78^\circ\text{C}$  and the mixture stirred at  $20^\circ\text{C}$  for 18 h to give a yellow solution. Hydrolysis of excess  $\text{LiAlH}_4$  and evaporation gave a yellow solid. Extraction with toluene (2  $\times$  10  $\text{cm}^3$ ) gave a yellow solid (50 mg) identified as  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{H}]$  (11) by  $^1\text{H}$  and  $^{31}\text{P}$  n.m.r. spectroscopy. Extraction of the toluene-insoluble material with  $\text{CH}_2\text{Cl}_2$  (10  $\text{cm}^3$ ) and evaporation gave a yellow solid (30 mg) identified as  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2(\text{CN})]$  (1) by  $^1\text{H}$  n.m.r. and i.r. spectroscopy.

Repeating the reaction using  $\text{LiAlD}_4$  in place of  $\text{LiAlH}_4$  and hydrolysis using  $\text{H}_2\text{O}$  gave (1) and  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{D}]$ , identified by  $^1\text{H}$  and  $^2\text{H}$  n.m.r. spectroscopy. There was no detectable metal-hydride resonance in the  $^1\text{H}$  n.m.r. spectrum.

**Reaction of (7) with  $\text{LiAlH}_4$ .**— $\text{LiAlH}_4$  (50 mg, 1.3 mmol) was added to a suspension of (7) (0.3 g, 0.21 mmol) in thf (20  $\text{cm}^3$ ) at  $-78^\circ\text{C}$  and the mixture stirred at  $20^\circ\text{C}$  for 18 h to give a yellow solution. Hydrolysis and evaporation gave a yellow solid. Extraction with toluene (2  $\times$  10  $\text{cm}^3$ ) and evaporation gave a yellow solid (100 mg) identified by  $^1\text{H}$  and  $^{31}\text{P}$  n.m.r. and i.r. spectroscopy as a 1:1 mixture of  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{H}]$  (13) and  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{H}_3]$  (14). Further extraction of the toluene-insoluble material with  $\text{CH}_2\text{Cl}_2$  (10  $\text{cm}^3$ ) and evaporation gave a yellow solid identified as  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})(\text{CN})]$  (2) by  $^1\text{H}$  n.m.r. and i.r. spectroscopy.

**Reaction of (8) with  $\text{LiAlH}_4$ .**— $\text{LiAlH}_4$  (100 mg, 2.6 mmol) was added to a suspension of (8) (0.4 g, 0.31 mmol) in thf (20  $\text{cm}^3$ ) at  $-78^\circ\text{C}$  and the mixture stirred at  $20^\circ\text{C}$  for 18 h to give a yellow-green solution. Hydrolysis of excess  $\text{LiAlH}_4$  and evaporation gave a yellow solid. Extraction with toluene (10  $\text{cm}^3$ ) and evaporation gave a yellow solid (100 mg) identified as  $[\text{Ru}(\eta\text{-C}_5\text{H}_5)(\text{dppe})\text{H}]$  (11) by  $^1\text{H}$  and  $^{31}\text{P}$  n.m.r. spectroscopy. Further extraction of the toluene-insoluble material with  $\text{CH}_2\text{Cl}_2$  (10  $\text{cm}^3$ ) and evaporation gave a yellow solid (20 mg) identified as  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})(\text{CN})]$  (2) by  $^1\text{H}$  n.m.r. and i.r. spectroscopy.

**Reaction of (10) with  $\text{LiAlH}_4$ .**— $\text{LiAlH}_4$  (20 mg, 0.52 mmol) was added to a red solution of (10) (0.25 g, 0.12 mmol) in thf (20  $\text{cm}^3$ ) at  $-78^\circ\text{C}$  and the mixture stirred at  $20^\circ\text{C}$  for 18 h to give a yellow-orange solution. Hydrolysis and evaporation gave an orange solid. Extraction with toluene (5  $\text{cm}^3$ ) and evaporation gave  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{H}]$  (12) (50 mg).  $^1\text{H}$  N.m.r. ( $\text{C}_6\text{D}_6$ ):  $\delta$  8.0—7.0 (m, 20 H, Ph), 4.2 (t,  $J_{\text{PH}} = 1.5$  Hz, 5 H,  $\text{C}_5\text{H}_5$ ), 2.2—1.7 (m, 4 H,  $\text{CH}_2$ ),  $-16.2$  (t,  $J_{\text{PH}} = 72$  Hz, 1 H, FeH). Further extraction of the toluene-insoluble material with  $\text{CH}_2\text{Cl}_2$  (10  $\text{cm}^3$ ) and evaporation gave a yellow solid identified as  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})(\text{CN})]$  (2) by  $^1\text{H}$  n.m.r. and i.r. spectroscopy.

**$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{H}]$  (13).**— $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{Cl}]$  (3) (0.2 g, 0.28 mmol) and sodium methoxide (0.2 g, 4.8 mmol) were stirred as a suspension in methanol (40  $\text{cm}^3$ ) at  $20^\circ\text{C}$  for 18 h. Evaporation, extraction with diethyl ether (2  $\times$  10  $\text{cm}^3$ ), and removal of solvent under reduced pressure gave a yellow solid (0.15 g, 78%).  $^1\text{H}$  N.m.r. ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.9—7.1 (m, 30 H, Ph), 4.5 (s, 5 H,  $\text{C}_5\text{H}_5$ ),  $-11.1$  (t,  $J_{\text{PH}} = 34$  Hz, 1 H, RuH).  $^{13}\text{C}$ - $\{^1\text{H}\}$  N.m.r. ( $\text{C}_6\text{D}_6$ ):  $\delta$  141.6 (ABX,  $^1J_{\text{PC}} + ^3J_{\text{PC}} = 37$ ,  $C_{\text{ipso}}$ ), 134.1 (ABX,  $^2J_{\text{PC}} + ^4J_{\text{PC}} = 11$ ,  $C_{\text{ortho}}$ ), 128.2 (s,  $C_{\text{para}}$ ), 127.2 (ABX,

$^3J_{\text{PC}} + ^5J_{\text{PC}} = 9$  Hz),  $C_{\text{meta}}$ ), 82.0 (s,  $\text{C}_5\text{H}_5$ ).  $^{31}\text{P}$ - $\{^1\text{H}\}$  N.m.r. ( $\text{C}_6\text{D}_6$ ):  $\delta$  67.45 (s). M.p. 136—138  $^\circ\text{C}$ .

**$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{H}_3]$  (14).**— $\text{LiAlH}_4$  (50 mg, 1.3 mmol) was added to a suspension of  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{Cl}]$  (3) (0.3 g, 0.41 mmol) in thf (20  $\text{cm}^3$ ) at  $-78^\circ\text{C}$  and the mixture stirred at  $20^\circ\text{C}$  for 7 h. Hydrolysis with water (10 drops), evaporation, extraction with toluene (3  $\times$  10  $\text{cm}^3$ ) and removal of solvent under reduced pressure gave a yellow solid.  $^1\text{H}$  N.m.r. ( $\text{C}_6\text{D}_6$ ) indicated a 1:4 mixture of  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{H}]$  (13) and another hydride species [ $\delta$  4.8 (s, 5 H),  $-9.8$  (d,  $J_{\text{PH}} = 18$  Hz, 3 H)]. Fractional crystallisation (toluene-diethyl ether) gave white needles of  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{H}_3]$  (14) (0.08 g, 45%) (Found: C, 64.40; H, 5.50; P, 8.00.  $\text{C}_{23}\text{H}_{23}\text{PRu}$  requires C, 64.05; H, 5.35; P, 7.20%). I.r. (Nujol):  $\nu_{\text{max}}$  2 040m (RuH), 1 995s  $\text{cm}^{-1}$  (RuH).  $^1\text{H}$  N.m.r. ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.8—7.0 (m, 15 H, Ph), 4.8 (s, 5 H,  $\text{C}_5\text{H}_5$ ),  $-9.8$  (d,  $J_{\text{PH}} = 19.8$  Hz, 3 H, RuH).  $^{13}\text{C}$ - $\{^1\text{H}\}$  N.m.r. ( $\text{C}_6\text{D}_6$ ):  $\delta$  141.5 (d,  $J_{\text{PH}} = 48.4$ ,  $C_{\text{ipso}}$ ), 133.6 (d,  $J_{\text{PC}} = 11.2$ ,  $C_{\text{ortho}}$ ), 129.2 (s,  $C_{\text{para}}$ ), 127.8 (d,  $J_{\text{PC}} = 10$  Hz,  $C_{\text{meta}}$ ), 83.4 (s,  $\text{C}_5\text{H}_5$ ).  $^{31}\text{P}$  N.m.r. ( $\text{C}_6\text{D}_6$ ):  $\delta$  73.12 (s, fully  $^1\text{H}$  decoupled; q,  $J_{\text{PH}} = 19.8$  Hz, phenyl protons decoupled).  $M/z$  (f.d.): 432  $[M]^+$ . M.p. 143—146  $^\circ\text{C}$  (decomp.).

The procedure above for (14) was repeated using  $\text{LiAlD}_4$  (50 mg, 1.2 mmol) and  $\text{D}_2\text{O}$  in the work-up procedure. Fractional crystallisation yielded  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{D}_3]$  (15) (0.06 g, 33%). I.r. (Nujol):  $\nu_{\text{max}}$  1 435vs  $\text{cm}^{-1}$  (RuD).  $^1\text{H}$  N.m.r. ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.7—6.9 (m, 15 H, Ph), 4.9 (s, 5 H,  $\text{C}_5\text{H}_5$ ).  $^2\text{H}$ - $\{^1\text{H}\}$  N.m.r. ( $\text{C}_6\text{H}_6$ ):  $\delta$   $-9.8$  (d,  $J_{\text{PD}} = 3$  Hz, RuD).

Using  $\text{LiAlD}_4$  and  $\text{H}_2\text{O}$  in the work-up procedure gave a material which was examined by  $^1\text{H}$  n.m.r. spectroscopy at 300 and 500 MHz. Three species were present:  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{H}_3]$  (ca. 15%),  $\delta$   $-9.811$  (d,  $J_{\text{PH}} = 19.8$  Hz);  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{H}_2\text{D}]$  (ca. 25%),  $\delta$   $-9.834$  (dt,  $J_{\text{PH}} = 19.8$ ,  $J_{\text{HD}} = 2.78$  Hz); and  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{HD}_2]$  (ca. 60%),  $\delta$   $-9.875$  (d of pent,  $J_{\text{PH}} = 19.8$ ,  $J_{\text{HD}} = 2.78$  Hz).

**Reaction of  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{H}]$  (13) with  $\text{LiAlH}_4$ .**— $\text{LiAlH}_4$  (100 mg, 2.63 mmol) was added to a solution of (13) (100 mg, 0.14 mmol) in thf (15  $\text{cm}^3$ ) at  $-78^\circ\text{C}$  and the mixture stirred at  $60^\circ\text{C}$  for 48 h. Hydrolysis of excess  $\text{LiAlH}_4$  with water (10 drops), evaporation, extraction with diethyl ether (20  $\text{cm}^3$ ) and evaporation gave a yellow solid, indicated by  $^1\text{H}$  n.m.r. spectroscopy to be a 3:1 mixture of  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{H}_3]$  (14) and (13).

Observation of a sample of (13) in the presence of thf alone showed no change over 48 h at  $20^\circ\text{C}$ . No phosphine exchange could be seen on observing a sample of (13) in the presence of dppe by  $^1\text{H}$  n.m.r. over a period of 48 h at  $20^\circ\text{C}$  and 8 h at  $60^\circ\text{C}$ .

**$[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{H}]$  (11).**— $\text{LiAlH}_4$  (70 mg, 1.8 mmol) was added to a solution of  $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Cl}]$  (4) (0.3 g, 0.5 mmol) in thf (20  $\text{cm}^3$ ) at  $-78^\circ\text{C}$ . Stirring for 24 h at  $20^\circ\text{C}$  followed by hydrolysis of excess  $\text{LiAlH}_4$  with water (10 drops) at  $-78^\circ\text{C}$  and evaporation gave a yellow solid. Extraction with diethyl ether (3  $\times$  10  $\text{cm}^3$ ) and crystallisation by concentration gave yellow plates (0.15 g, 53%) (Found: C, 65.80; H, 5.35; P, 10.35.  $\text{C}_{31}\text{H}_{30}\text{P}_2\text{Ru}$  requires C, 65.85; H, 5.30; P, 10.95%). I.r. (Nujol):  $\nu_{\text{max}}$  1 955m (RuH), 1 910m  $\text{cm}^{-1}$  (RuH). I.r. ( $\text{C}_6\text{H}_6$ ):  $\nu_{\text{max}}$  1 920m  $\text{cm}^{-1}$  (RuH).  $^1\text{H}$  N.m.r. ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.3 (m, 20 H, Ph), 4.8 (s, 5 H,  $\text{C}_5\text{H}_5$ ), 2.0 (m, 4 H,  $\text{CH}_2$ ),  $-12.9$  (t,  $J_{\text{PH}} = 34.2$  Hz, 1 H, RuH).  $^{31}\text{P}$ - $\{^1\text{H}\}$  N.m.r. ( $\text{C}_6\text{H}_6$ ):  $\delta$  91.0 (s).  $M/z$  (f.d.): 566  $[M]^+$ . M.p. 113—117  $^\circ\text{C}$ .

**X-Ray Structure Analysis of  $[(\eta^5\text{-C}_5\text{H}_5)(\text{dppe})\text{Ru}(\mu\text{-CN})\text{Ru}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]\text{PF}_6$  (7).**—A crystal of dimensions ca.  $0.30 \times 0.33 \times 0.15$  mm was mounted on an Enraf-Nonius CAD-4 diffractometer. Cell dimensions were determined from the setting angles of 25 high  $\theta$  angle reflections. Reflection intensities



were measured in the  $\omega/2\theta$  scan mode using graphite monochromated Mo- $K_\alpha$  ( $\lambda = 0.71069 \text{ \AA}$ ) radiation, with  $\omega$  scan angles of  $(1.0 + 0.35 \tan \theta)$ , and scan speed varying from 1.4 to  $6.7^\circ \text{ min}^{-1}$ . 10 923 Reflections were scanned in the range  $0 < 2\theta < 47^\circ$ . The standard reflections showed no appreciable variation in intensity or orientation with time.

Lorentz, polarisation, and empirical<sup>32</sup> absorption corrections (relative transmission factors 1.00–1.08) were applied. The equivalent reflections were merged to give 9 271 unique reflections ( $R_m = 0.019$ ). 4 935 Reflections [ $I > 2.5\sigma(I)$ ] were considered to be observed but 52 strong reflections with markedly unsymmetrical backgrounds were not used in the structure analysis, leaving 4 883 observed reflections which were used in subsequent calculations.

Crystal data  $C_{73}H_{64}F_6NP_5Ru_2$ ,  $M = 1426.17$ , monoclinic,  $a = 11.472(3)$ ,  $b = 44.022(9)$ ,  $c = 13.225(4) \text{ \AA}$ ,  $\beta = 104.75(2)^\circ$ ,  $U = 6458.8 \text{ \AA}^3$ ,  $Z = 4$ ,  $D_c = 1.467 \text{ Mg m}^{-3}$ ,  $F(000) = 2904$ ,  $\mu(\text{Mo-}K_\alpha) = 6.45 \text{ cm}^{-1}$ , space group  $P2_1/n$  (alt.  $P2_1/c$  no. 14).

The structure was solved by Patterson and electron-density methods. Refinement was by a cascade procedure. Four of the phenyl groups are rotationally disordered and two orientations for each ring were determined from difference syntheses and 50% occupancy of each orientation was confirmed by the least-squares refinement.

All positional parameters were refined, except for hydrogen atoms which had been geometrically placed and were subsequently allowed to 'ride' on their respective carbon atoms. Anisotropic thermal parameters were used for all non-hydrogen atoms except for the carbon atoms of the cyclopentadienyl ring [C(7)—C(11)] and the disordered phenyl rings which were refined isotropically. In order to achieve convergence extensive use was made of restraints.<sup>33</sup> Planarity restraints were applied to all the aromatic rings, geometrical restraints to the C(7)—C(11) ring and to the disordered rings. The thermal motion of the  $PF_6^-$  group was assumed to be centrosymmetric and restraints were applied to the P—F bond lengths. Refinement converged at  $R = 0.071$  ( $R' = 0.086$ ). The weighting scheme used a two-term Chebyshev series  $w = [15.2t_0(x) + 9.7t_1(x)]^{-1}$  where  $x = F_o/F_{\text{max}}$ .<sup>34</sup> Data reduction, structure refinement, and geometry calculations were performed using CRYSTALS<sup>35</sup> on a VAX 11/750 computer in the Chemical Crystallography Laboratory. The Figure was drawn using CHEMGRAF.

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