Pentamethylcyclopentadienyl-rhodium and -iridium Complexes. Part 19.[1] Preparation and Reactions of Azido-, Cyanato-, Thiocyanato-, Nitrito-, and Nitrato-rhodium Complexes

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Metathesis reactions of $[Rh_2(C_5Me_5)_2Cl_4]$ (1) with NaX give $[Rh_2(C_5Me_5)_2X_4]$ [X = N_3 (2), NCO (9), or SCN (14)]. The dimeric azido-complex (2) is cleaved by unidentate ligands [L = PPh_3, $P(OR)_3$, CNR, py, *etc.*] to give monomeric adducts $[Rh(C_5Me_5)(N_3)_2L]$ (3); 1,10-phenanthroline gives $[Rh(C_5Me_5)(N_3)(phen)][N_3]$ and 2,2′-bipyridyl gives $[Rh(C_5Me_5)(N_3)(bipy)][Rh(C_5Me_5)(N_3)_3]$. The azido-complexes undergo carbonylation: (2) gives first $[Rh_2(C_5Me_5)_2(NCO)_3(N_3)]$ (containing a bridging azide and a bridging cyanate ligand) and then (9), which is cleaved by PPh_3 to give $[Rh(C_5Me_5)(NCO)_2(PPh_3)]$ (12). Complex (12) is also obtained by carbonylation of $[Rh(C_5Me_5)(N_3)_2(PPh_3)]$ (3a). Equilibrium constants have been determined for the reactions of (2) and (9) with pyridine to give $[Rh(C_5Me_5)X_2(py)]$ (X = N_3 or NCO). Complex (3a) reacts with CS_2 to give (14) *via* $[\{Rh(C_5Me_5)(N_3CS_2)_2\}_n]$; $[Rh(C_5Me_5)(SCN)_2(PPh_3)]$ is obtained by reaction of (3a) with Na[NCS] or by reaction of (14) with PPh_3. Complex (2) reacts with hexafluorobut-2-yne to give first $[Rh_2(C_5Me_5)_2\{N_3C_2(CF_3)_2\}_2(N_3)_2]$ (containing two bridging azide ligands) and then $[Rh_2(C_5Me_5)_2[N_3C_2(CF_3)_2]_3(N_3)]$ (18, containing one bridging azide and one bridging and two terminally bonded triazolate ligands). Similarly, (2) reacts with CF_3CN to give $[Rh_2(C_5Me_5)_2(N_4CCF_3)_3(N_3)]$ (containing one bridging azide and one bridging and two terminally bonded tetrazolate ligands). These results show that terminal azide ligands are very much more reactive than bridging ones. Reaction of complex (1) with sodium (or potassium) nitrite gives $M[Rh(C_5Me_5)(NO_2)_3]$ which, with PPh_3, gives $[Rh(C_5Me_5)(NO_2)_2(PPh_3)]$; this complex could also be obtained from $[Rh(C_5Me_5)Cl_2(PPh_3)]$ and $Ag[NO_2]$. Reaction of complex (2) with N_2O_4 gives monomeric $[Rh(C_5Me_5)(NO_3)_2]$ (24), but reaction of (1) with $Ag[NO_3]$ gives the ionic isomer $[Rh_2(C_5Me_5)_2(NO_3)_3][NO_3]$ (25). Complex (24) gives $[Rh(C_5Me_5)(NO_3)_2(PPh_3)]$ with PPh_3, but (25) does not react. Structures for these complexes are proposed on the basis of i.r. and ^1H, ^{13}C, ^{19}F, and ^{31}P n.m.r. spectroscopic studies. The structure of complex (18) has been confirmed by a single-crystal *X*-ray determination which also showed that both rhodiums are bonded to N(1) of the bridging azide ligand.

EARLIER papers of this series have reported metathetical reactions in which the labile chlorines in di-μ-chloro-bis[chloro(pentamethylcyclopentadienyl)rhodium] (1) were exchanged for bromide,[2] iodide,[2] carboxylate,[3] hydroxide,[4] and even hydride [5] ligands. The Rh–C_5Me_5 bond is quite stable to such reactions and is retained throughout. We now discuss metathetical reactions of (1) with azide, cyanate, thiocyanate, nitrite, and nitrate and the further reactions of the resulting complexes. In particular, the azido-complexes show a large number of reactions in which the Rh–N_3 group acts as a 1,3-dipolar reagent.

RESULTS AND DISCUSSION

Azido-complexes.—The dichloride dimer (1) reacted with sodium azide in acetone to give the wine-red diazido-complex (2) in 95% yield. This complex was stable in air and showed no tendency to detonate (and decomposed only to a small extent) even after heating for some hours at 100 °C. Complex (2) was dimeric in solution and the i.r. spectrum showed two bands (both in the solid as a Nujol mull and in chloroform solution, Table 1), one in the region characteristic of terminal azide ligands (2 015—2 030 cm^{-1}) and one in the region characteristic of bridging azide ligands (2 045—2 060 cm^{-1}).[5-7] We propose the structure shown, with a *trans*-arrangement of the C_5Me_5 ligands [as has been found in (1) and its iridium analogue [8]]; although the i.r. data alone cannot establish the mode of attachment of the bridging azide ligands,[5] on the basis of other published structures of transition-metal complexes containing bridging azides [5,7,9] we suggest that both metals are attached to the same nitrogen [see also the structure of complex (18) discussed below].

The azide bridges in (2) were easily cleaved by a variety of unidentate ligands (L) to give the monomeric adducts (3a)—(3m) (Scheme 1), the i.r. spectra of which showed the presence only of terminal azide ligands. The equilibria (i) were well over to the right-hand side for all

$$(2) + 2L \rightleftharpoons 2(3) \qquad \text{(i)}$$

the complexes except those with pyridine or a methylpyridine as ligand. The adducts (3k)—(3m) did not dissociate in the solid but in solution both the ^1H n.m.r. and the i.r. spectra showed the presence of (2) indicating that some dissociation was occurring. Equilibrium constants (K_i) for equation (i) were calculated from the relative intensities of the C_5Me_5 resonances of (2) and (3) in the ^1H n.m.r. spectra of solutions of (3k)—(3m) as follows: (3k), 6 (34 °C); (3l), 40 (34 °C); (3m), 33 (50 °C), 75 (34 °C), 580 (10 °C), and 3 300 (−10 °C) $dm^3 mol^{-1}$. These values clearly reflect the relative nucleophilicities of the ligands and show that the strength of binding to RhC_5Me_5 is in the order 4-methylpyridine > 3-methylpyridine > pyridine.

The dimeric diazido-complex (2) also reacted with 1,10-phenanthroline (phen) and 2,2′-bipyridyl (bipy), but in these cases ionic products were formed. The orange complex (4) derived from addition of 1 equivalent of phen per rhodium showed the presence of two types of azide in the i.r. spectrum; one peak at 2 023 cm^{-1} is clearly due to a terminal ligand but the other, at 1 997 cm^{-1}, must be assigned to the azide anion. In acetonitrile solution the complex had a molar conductivity in the appropriate range for a 1 : 1 electrolyte; further proof that (4) was ionic was obtained from its reaction with $[NH_4][PF_6]$ which gave the hexafluorophosphate salt (5).

The product from reaction of (2) with bipy was formulated as the ionic complex (6) on the following grounds. (*a*) Both the ^1H and the ^{13}C n.m.r. spectra showed the presence of two inequivalent C_5Me_5 resonances of equal intensity and a bidentate, symmetrically co-ordinated bipy. These spectra did not vary with temperature. (*b*) The i.r. spectrum showed two bands (at 2 014 and 2 026 cm^{-1}) which must be assigned to $\nu(N_3)$ of two different types of terminal azide ligand.

If complex (1) and sodium azide were allowed to react in a 1 : 1 ratio (based on rhodium) then complex (7) which contained one azide and one chloride ligand per rhodium was obtained. The i.r. spectra were the same in the solid and in solution and showed the presence of only one type of (bridging) azide ligand [$\nu(N_3)$ at 2 045 cm^{-1}]; the presence of only one type of structure was confirmed by the temperature-invariant ^1H n.m.r. spectrum which showed the C_5Me_5 resonance as a singlet. The azide ligands must therefore be bridging and the chlorines must be terminal in (7); clearly the azide

TABLE 1

		Microanalytical data (%)						^1H N.m.r. (δ/p.p.m., in C^2HCl_3; J in Hz) [b]	
	Complex	C	H	N	Others	M [a]	I.r. (cm^{-1}, Nujol mull)	C_5Me_5	Other
(2)	$[Rh_2(C_5Me_5)_2(N_3)_4]$	37.2 (37.3)	4.7 (4.7)	26.0 (26.1)		623 (644)	$\nu(N_3)$ 2 023, 2 048 (2 029, 2 054 $CHCl_3$)	1.67	
(3)	$[Rh(C_5Me_5)(N_3)_2L]$								
(3a)	L = PPh_3	57.8 (57.5)	5.1 (5.1)	14.3 (14.4)		616 (584)	2 016	1.46 (d) [4]	7.41 (m, Ph)
(3b)	$P(OMe)_3$	35.2 (35.0)	5.5 (5.4)	18.6 (18.8)		460 (446)	2 014	1.7 (d) [5]	3.81 (d, MeO) [12]
(3c)	$P(OEt)_3$	39.5 (39.3)	6.2 (6.2)	17.2 (17.2)		480 (488)	2 022	1.67 (d) [6]	4.14 (dq, $-CH_2O-$), 1.29 (t, Me), J(H–H) = 7
(3d)	$P(OPr^i)_3$	43.3 (43.0)	6.7 (6.8)	15.8 (15.9)		613 (530)	2 020	1.69 (d) [5]	4.80 (m, $CHO-$), 1.33 (d, Me), J(H–H) = 6
(3e)	$P(OPh)_3$	53.2 (53.2)	5.0 (4.8)	12.5 (13.3)			2 023	1.58 (d) [6]	7.22 (m, Ph)
(3f)	$AsPh_3$	53.2 (53.5)	5.0 (4.8)	13.7 (13.4)		598 (628)	2 014	1.59	7.42 (m, Ph)
(3g)	$CNBu^t$	44.4 (44.5)	6.1 (6.0)	24.0 (24.2)		411 (405)	2 014, $\nu(NC)$ 2 190	1.74	1.61 (br s, Bu^t)
(3h)	CNMe	39.6 (39.7)	5.0 (5.0)	26.0 (27.0)			2 018, $\nu(NC)$ 2 222	1.72	3.56 (Me)
(3i)	CNC_6H_4Me-*p*	43.9 (44.4)	4.4 (4.1)	21.0 (21.3)	Cl 7.8 7.7		2 015, $\nu(NC)$ 2 051	1.74	7.49, 7.84 (dd, Ph)
(3j)	$NH_2NHC_6H_4Me$-*p*	45.3 (46.0)	5.7 (5.6)	25.6 (25.3)		396 (444)	2 028	1.68	6.73, 7.05 [dd, J(H–H) = 8, Ph], 6.15 (br, NH), 3.90 (br, NH_2), 2.26 (Me)
(3k)	py	44.7 (44.9)	5.0 (5.0)	24.2 (24.4)		379 (401)	2 029 (2 029, 2 052 $CHCl_3$)	1.58 [c]	7.31, 7.72, 8.59 (m, py)
(3l)	$3-MeC_5H_4N$	46.2 (46.3)	5.3 (5.3)	23.5 (23.6)		380 (415)	2 025 (2 028, 2 051 $CHCl_3$)	1.58 [c]	7.23, 7.52, 8.39 (m, py), 2.34 (Me)
(3m)	$4-MeC_5H_4N$	46.1 (46.3)	5.2 (5.3)	23.5 (23.6)		375 (415)	$\nu(N_3)$ 2 021 (2 029, 2 052 $CHCl_3$)	1.60 [c]	7.22, 8.41 [dd, J(H–H) = 8, py], 2.42 (Me)
(4)	$[Rh(C_5Me_5)(N_3)(phen)][N_3]$	52.2 (52.6)	4.5 (4.6)	22.0 (22.3)		*d*	1 997, 2023	1.7	8.19 (m), 8.83 (d), 9.29 (d) 8.23 (s) } (phen)
(5)	$[Rh(C_5Me_5)(N_3)(phen)][PF_6]$	43.3 (43.6)	3.8 (3.8)	11.4 (11.6)		*e*	2 020	1.86	8.28 (m), 8.97 (d), 9.52 (d) 8.33 (s) } (phen)
(6)	$[Rh(C_5Me_5)(N_3)(bipy)]$- $[Rh(C_5Me_5)(N_3)_3]$	45.3 (45.0)	4.6 (4.8)	24.6 (24.5)			2 014, 2 026	1.70 [f] 1.67	7.80 (m), 8.33 (m), 8.62 (m) (bipy)
(7)	$[Rh_2(C_5Me_5)_2Cl_2(N_3)_2]$	38.0 (38.0)	4.8 (4.8)	13.3 (13.3)	Cl 11.1 (11.3)	616 (631)	2 045 (2 051 $CHCl_3$)	1.66	
(8a)	$[Rh(C_5Me_5)Cl(N_3)\{P(OMe)_3\}]$	35.8 (35.5)	5.6 (5.5)	9.4 (9.6)	Cl 8.1 (8.1)	420 (439)	2 023 (2 029 $CHCl_3$)	See Experimental section	
(9)	$[Rh_2(C_5Me_5)_2(NCO)_4]$	44.4 (44.7)	4.8 (4.7)	8.5 (8.7)		681 (644)	$\nu(NCO)$ 2 166, 2 223	1.63	
(10)	$[Rh_2(C_5Me_5)_2(NCO)_3(N_3)]$	42.9 (42.9)	4.7 (4.7)	13.4 (13.0)		687 (644)	2 166, 2 221 $\nu(N_3)$ 2 051, (2 166, 2 218, 2 053 $CHCl_3$)	1.65	
(11)	$[Rh(C_5Me_5)(NCO)(N_3)(PPh_3)]$	59.2 (59.6)	5.1 (5.1)	10.3 (9.6)		560 (584)	2 184 2 012	1.46 (m)	7.44 (m, Ph)
(12)	$[Rh(C_5Me_5)(NCO)_2(PPh_3)]$	61.9 (61.6)	4.9 (5.1)	4.6 (4.8)		584 (584)	2 183	1.43 (d) [4]	7.49, 7.67 (m, Ph)
(13)	$[Rh(C_5Me_5)(NCO)_2(py)]$	50.8 (50.9)	5.1 (5.0)	10.1 (10.5)			2 194 (2 200, 2 166 $CHCl_3$)	1.55 [g]	7.44, 7.84, 8.69 (m, py)
(14)	$[Rh_2(C_5Me_5)_2(SCN)_4]$	40.3 (40.7)	4.3 (4.2)	7.6 (7.9)	S 18.4 (18.1)	750 (708)	$\nu(SCN)$ 2 100, 2 137	1.72	
(15)	$[Rh(C_5Me_5)(SCN)_2(PPh_3)]$	57.6 (58.4)	4.6 (4.9)	4.3 (4.6)	S 9.9 (10.4)	603 (616)	2 130	1.56 (d) [6]	7.45 (m, Ph)
(16)	$[Rh(C_5Me_5)(N_3CS_2)_2\}n]$	31.5 (30.4)	3.4 (3.2)	16.8 (17.7)	S 25.6 (27.0)		n.o.		
(17)	$[Rh_2(C_5Me_5)_2(N_3C_4F_6)_2(N_3)_2]$	34.5 (34.7)	3.0 (3.1)	17.1 (17.4)			$\nu(N_3)$ 2 061	1.52	
(18)	$[Rh_2(C_5Me_5)_2(N_3C_4F_6)_3(N_3)]$	33.6 (34.0)	2.4 (2.7)	14.6 (14.9)		1 071 (1 130)	2 061	1.37, 1.38	
(19)	$[Rh(C_5Me_5)(N_3C_4F_6)_2(PPh_3)]$	47.4 (47.6)	3.5 (3.3)	9.4 (9.3)		935 (908)	n.o.	1.36 (d) [3]	7.27 (m, Ph)
(20)	$[Rh_2(C_5Me_5)_2(N_4C_2F_3)_3(N_3)]$	33.5 (33.6)	2.9 (3.2)	22.6 (22.6)		972 (929)	2 058	1.44	
(21)	$[Rh(C_5Me_5)(CNBu^t)(N_4CBu^t)$- $(N_3)]$	50.7 (49.2)	7.7 (6.8)	20.3 (23.0)		516 (488)	2 059 $\nu(NC)$ 2 182	1.29	1.47, 1.80 (2 × Bu^t)
(22a)	$Na[Rh_2(C_5Me_5)(NO_2)_3]$	30.0 (30.1)	3.6 (3.8)	10.5 (10.5)		*h*	$\nu(NO_2)$ 1 026	1.58	
(22b)	$K[Rh(C_5Me_5)(NO_2)_3]$	29.4 (28.9)	4.0 (3.6)	9.8 (10.1)		*i*	1 027	1.57	
(23)	$[Rh(C_5Me_5)(NO_2)_2(PPh_3)]$	56.2 (56.8)	4.9 (5.1)	5.0 (4.7)		609 (592)	1 030	1.41 (d) [6]	7.45 (m, Ph)
(24)	$[Rh(C_5Me_5)(NO_3)_2]$	33.3 (33.2)	4.1 (4.1)	7.6 (7.7)		372 (362)	$\nu(NO_3)$ 1 241, 1 280, 1 390 1 468, 1 522 (all s)	1.76	
(25)	$[Rh_2(C_5Me_5)_2(NO_3)_3][NO_3]$	33.3 (33.2)	4.2 (4.1)	7.4 (7.7)		*j*	1 278 (m), 1 385 (vs), 1 460 (sh)	1.78 [k]	
(26)	$[Rh(C_5Me_5)(NO_3)_2(PPh_3)]$	54.0 (53.9)	5.1 (4.8)	4.1 (4.5)		646 (624)	1 270 (s), 1 385 (m), 1 470 (m)	1.42 (d) [4.4]	7.50 (m, Ph)

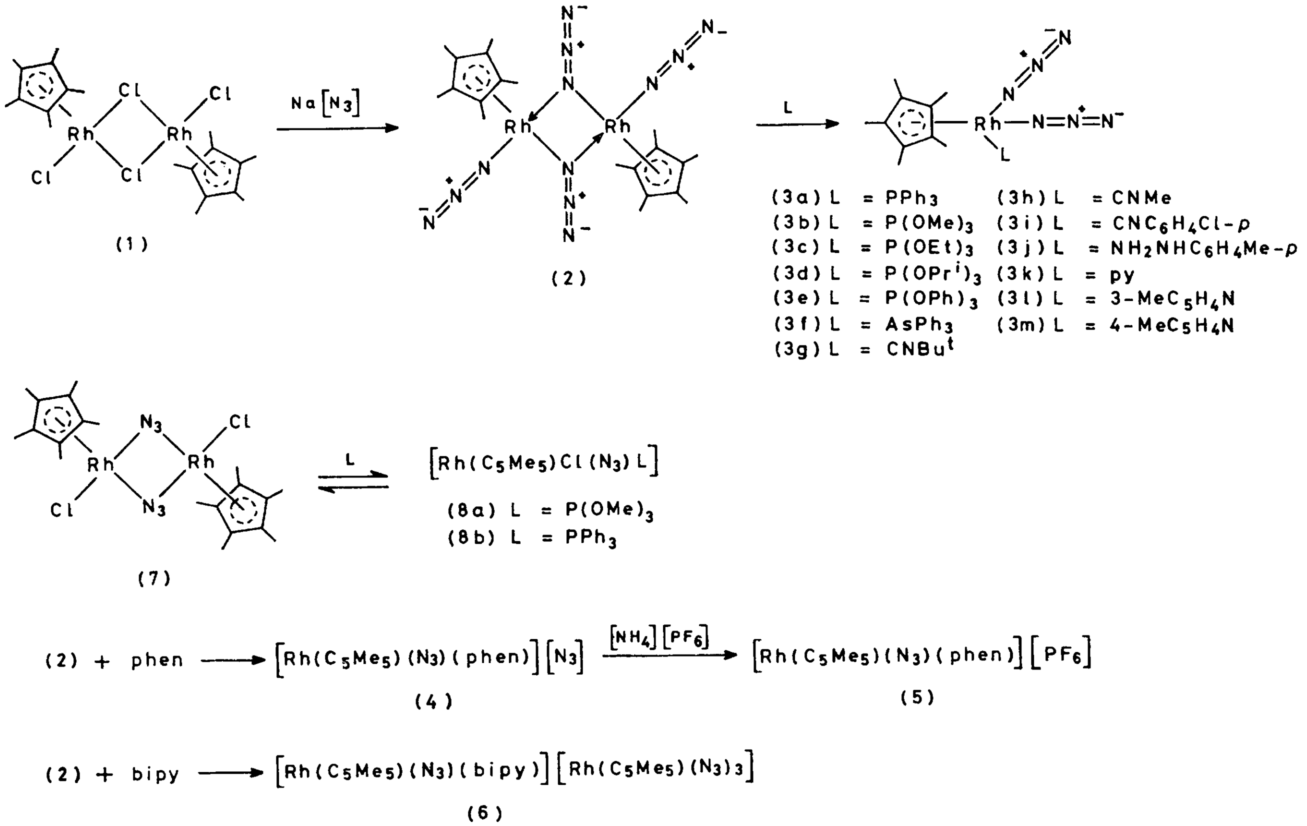
[a] Calculated values are given in parentheses. [b] J(H–P)/Hz given in square brackets. [c] This complex also shows a resonance at δ 1.67 p.p.m. due to complex (2) and arising from equilibrium (i) (see text); δ values at 34 °C. [d] Molar conductivity (Λ) = 129 S cm^2 mol^{-1}, in acetonitrile solution. [e] Λ = 128 S cm^2 mol^{-1} in acetonitrile solution. [f] In $C^2H^2Cl_2$. [g] This complex also shows a resonance at δ 1.61 p.p.m. due to complex (9) and arising from equilibrium (iv) (see text). [h] Λ = 93 S cm^2 mol^{-1}. [i] Λ = 122 S cm^2 mol^{-1}. [j] Λ = 381 S cm^2 mol^{-1}. [k] In [$^2H_6$]acetone.

ligand is extremely effective at bridging rhodium atoms.

Complex (7) was cleaved by trimethyl phosphite to give the adduct [8a; L = $P(OMe)_3$]; however, the ^1H and the ^{31}P n.m.r. spectra both showed the presence of three compounds in the ratio of 2 : 12 : 2 (see Experimental section). We ascribe this to the occurrence of the disproportionation (ii) in solution, which in this case

$$\underset{(8a)}{2[Rh(C_5Me_5)Cl(N_3)L]} \rightleftharpoons [Rh(C_5Me_5)Cl_2L] + \underset{(3)}{[Rh(C_5Me_5)(N_3)_2(L)]} \qquad \text{(ii)}$$

gave a non-statistical distribution with $K_{ii} = 0.03$. The triphenylphosphine adduct (8b; L = PPh_3) could also be made but could not be purified. The existence of a similar equilibrium was shown by the ^1H and the ^{31}P n.m.r. spectra; in this case, however, a statistical distribution was observed with $K_{ii} = 0.25$.



Scheme 1

Cyanato-complexes.—Reaction of the diazido-complex (2) with CO (1 atm, 20 °C)* in dichloromethane gave the dimeric dicyanato-complex (9); this was also obtained by reaction of complex (1) with sodium cyanate. Two ν(CN) bands at 2 166 and 2 223 cm^{-1} were observed in the i.r. spectrum of (9) which, following the assignments proposed by Norbury,[10] are assigned to the bridging and the terminal NCO ligands respectively and the structure shown is suggested for (9). When the reaction of (2) with carbon monoxide was carried out in acetone, the three-quarters carbonylated complex (10) was obtained which showed bands in the i.r. spectrum due to both bridging and terminal NCO (2 166 and 2 221 cm^{-1}) and to a bridging azide ligand (2 051 cm^{-1}). Since the i.r. spectrum was the same in solution as in the solid and since the ^1H n.m.r. spectrum was temperature invariant and showed only a single C_5Me_5 resonance, the symmetrical structure, with one N_3 and one NCO bridging and two NCO terminal, is proposed. The carbonylation of azido- to cyanato-complexes is a well known reaction which has been demonstrated to occur readily for a number of metal complexes.[5,7,11]

The dimeric dicyanato-complex (9) was cleaved by triphenylphosphine to give (12), which could also be obtained by carbonylation of (3a) in dichloromethane. When complex (3a) was carbonylated in acetone only one of the two azide ligands reacted and the mixed complex (11) was obtained; in dichloromethane this also gave (12) on reaction with CO. The ^1H n.m.r. spectrum of complex (11) showed a multiplet for the C_5Me_5 resonances, suggesting that it disproportionated in solution. This was confirmed by the ^{31}P n.m.r. spectrum of a 1 : 1 mixture of the di-azido- and the dicyanato-(triphenylphosphine) complexes (3a) and (12)

$$2(11) \rightleftharpoons (3a) + (12) \qquad \text{(iii)}$$

which showed, in addition to the resonances of equal intensity due to (3a) and (12), a further resonance of

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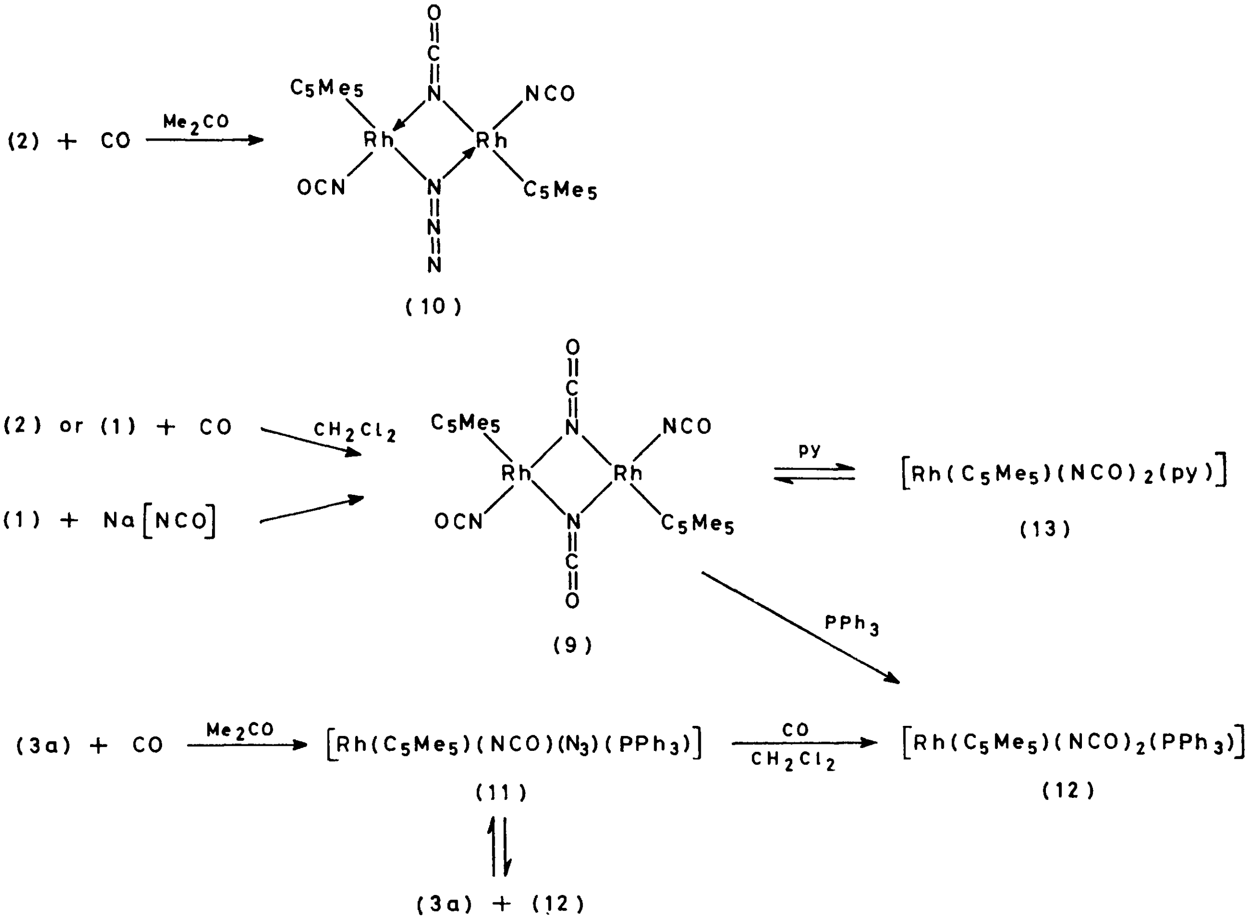
* Throughout this paper: 1 atm = 101 325 Pa.

relative intensity 2, which is ascribed to (11). This experiment shows that the equilibrium (iii) is statistically determined, with $K_{iii} = 0.25$.

The dicyanato-dimer (9) reacted with pyridine to form an adduct (13); however, in solution the i.r. spectrum showed that complex (13) was disproportionating, a conclusion which was supported by the ^{1}H n.m.r. spectrum which showed two C_5Me_5 resonances arising from equilibrium (iv).

$$(9) + 2\text{py} \rightleftharpoons 2(13) \qquad \text{(iv)}$$



SCHEME 2

Thiocyanato-complexes.—When the diazido-complex (2) was treated with CS_2 in acetone the dimeric orange dithiocyanato-complex (14) was obtained; the same complex was obtained by metathesis of the chloro-complex (1) with sodium thiocyanate (Scheme 3). The i.r. spectrum showed two ν(CN) bands at 2 100 and 2 137 cm^{-1} which we assign to the bridging and terminal SCN ligands respectively. On cleavage of the dimer with PPh_3 the product, (15), shows only the higher-frequency band (at 2 130 cm^{-1}) due to the terminal SCN ligand. On the basis of the assignments suggested by Norbury[10] [ν(CN) for M–NCS at 2 050—2 100 and M–SCN at 2 085—2 130 cm^{-1}], we suggest that the terminal thiocyanate ligands are *S*- rather than *N*-bonded in (15) and also in (14).

The monomeric diazido(triphenylphosphine) complex (3a) also reacted with sodium thiocyanate to give (15), but with CS_2 a more complex reaction occurred to give (14), together with sulphur and PPh_3S, according to equation (v). An intermediate in this reaction was isolated on one occasion; this material was very unstable but an analysis corresponded reasonably closely

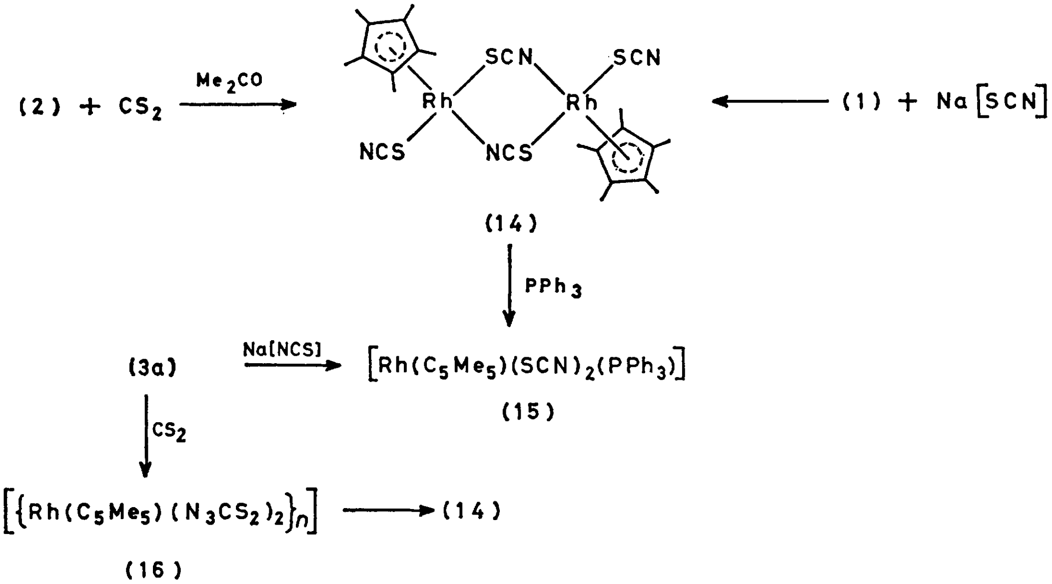
$$\underset{(3a)}{2[Rh(C_5Me_5)(N_3)_2(PPh_3)]} + 4CS_2 \longrightarrow$$
$$\underset{(14)}{[Rh_2(C_5Me_5)_2(SCN)_4]} + 2PPh_3S + 4N_2 + \tfrac{1}{4}S_8 \qquad \text{(v)}$$

to that required by (16) and since there were no strong bands in the i.r. spectrum due to ν(CN) or ν(N_3) we suggest that this is a 1,2,3,4-thiatriazole-5-thiolato-complex of rhodium. In acetone solution the complex (16) decomposed to give the dithiocyanato-complex (14). Analogous 1,2,3,4-thiatriazole-5-thiolato-complexes have been obtained by 1,3-dipolar addition of CS_2 to azides of Pd, Pt,[11,12] Cu, Ag, and Au[13] and it has been shown that they are intermediates in the formation of thiocyanato-complexes, as is the case here.

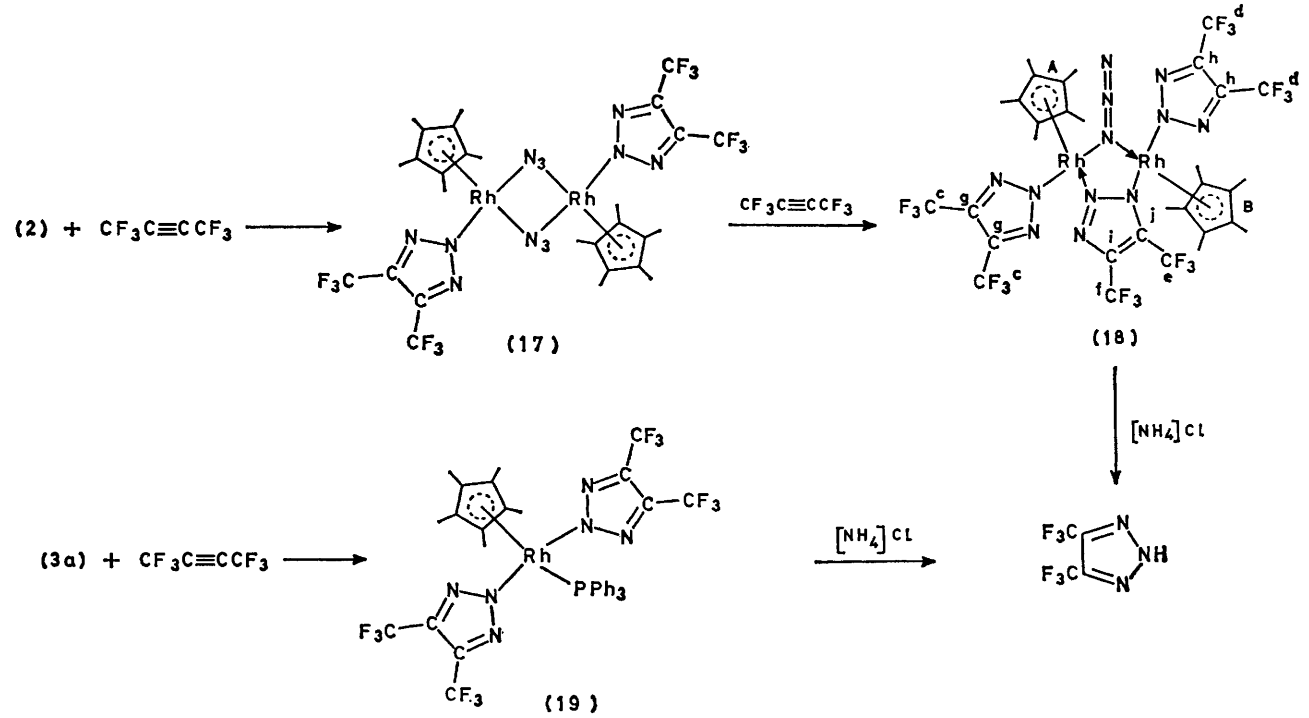
The above reaction of (3a) with CS_2 in acetone also revealed another interesting reaction and we found that PPh_3 could be conveniently removed from the adducts (3a) and (15) simply by reaction with elemental sulphur

$$2[Rh(C_5Me_5)X_2(PPh_3)] + S_8 \longrightarrow [Rh_2(C_5Me_5)_2X_4] + 2PPh_3S \quad (vi)$$

in acetone. Reaction (vi) (X = N_3 or SCN) appears to be one of the few reported wherein a tertiary phosphine can be cleanly removed from a transition-metal complex in high yield.



SCHEME 3



SCHEME 4

Reaction of the Diazido-complex (2) *with Hexafluorobut-2-yne.*—Organic azides undergo 1,3-dipolar addition reactions to olefins and acetylenes;[14] reactions of metal azides with dimethyl acetylenedicarboxylate to give 1,2,3-triazolatometal complexes have also been reported.[12,15]

Neither but-2-yne nor diphenylacetylene reacted with complex (2) at 20 °C; reaction did occur between (2) and dimethyl acetylenedicarboxylate or tetrafluoroethylene but in neither case was it possible to isolate pure products. However, hexafluorobut-2-yne reacted readily with (2) in dichloromethane at 20 °C to give, first, a complex (17) in which two of the four azide ligands in (2) had reacted. When the reaction was left for longer periods of time a second complex (18) was obtained in which three of the four azide ligands had reacted (Scheme 4).

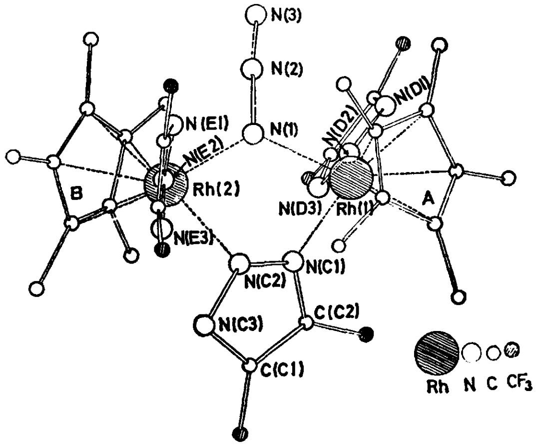
The molecular weight of complex (18) showed that it was binuclear and the i.r. spectrum indicated the presence of a bridging azide ligand. Since the C_5Me_5 ligand gave two resonances in both the ^1H and the ^{13}C-$\{^1H\}$ n.m.r. spectra the molecule is not a symmetrical dimer and the structure shown is proposed (Scheme 4). This is also in agreement with the ^{19}F n.m.r. spectrum which shows the presence of two coupled inequivalent CF_3 groups (e, f) and two pairs of inequivalent but uncoupled CF_3 groups (c, d); the ^{13}C-$\{^{19}F\}$ spectrum also shows the presence of four different $-N=C=CF_3$ carbons. In order to accommodate these data we presume there to be essentially free rotation of the terminal 1,2,3-triazolate ligands about the Rh–N bonds.

The *X*-ray crystal-structure determination of (18) (Figure) completely substantiates these conclusions and shows the molecule to contain one bridging azide and one bridging and two terminal bis(trifluoromethyl)-triazolate ligands, with a Rh–Rh distance of 2.739 Å. The crystal structure also shows that our assumption concerning the mode of bonding of the bridging azide ligand is correct; both rhodiums are bonded to the same nitrogen with Rh-N 2.11 and 2.13(1) Å. The two C_5Me_5 ligands are *trans* to each other.

Complex (17) again shows a bridging $\nu(N_3)$ in the i.r. spectrum but in this case the symmetrical nature of the molecule is shown by the presence of only one type of C_5Me_5 in the ^1H and one type of CF_3 in the ^{19}F n.m.r. spectrum. The structure shown is proposed for (17).

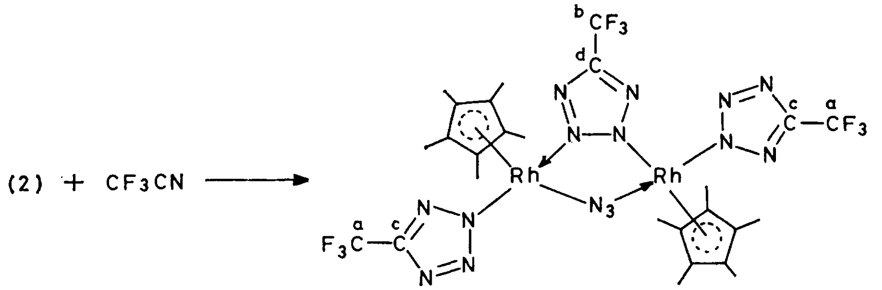
Complex (3a) also reacted with hexafluorobut-2-yne to give complex (19) in which both azide ligands have reacted. The ^{13}C-$\{^{19}F\}$ n.m.r. spectrum showed only one type of $N=C-CF_3$ grouping to be present and hence indicated the symmetrical binding of the triazole ring through N(2) as shown.

Confirmation that the complexes contain the 4,5-bis(trifluoromethyl)-1,2,3-triazolate ligand came from the reactions of (18) or (19) with ammonium chloride to yield the parent triazole and (1) or $[Rh(C_5Me_5)Cl_2(PPh_3)]$ respectively.



The structure of complex (18) (fluorines and hydrogens omitted for clarity). Bond lengths (Å; estimated standard deviations in parentheses): Rh(1)–Rh(2) 3.739(2), Rh(1)–N(1) 2.13(1), Rh(2)–N(1) 2.11(1), N(1)–N(2) 1.22(1), N(2)–N(3) 1.14(1), Rh(1)–N(C1) 2.15(1), Rh(2)–N(C2) 2.13(1), N(C1)–N(C2) 1.33(1), Rh(1)–N(D2) 2.08(1), Rh(2)–N(E2) 2.08(1), Rh(1)–C_5Me_5(A) 2.17(1) (average), Rh(2)–C_5Me_5(B) 2.161() (average). Bond angles (°; estimated standard deviations in parentheses): Rh(1)–N(1)–Rh(2) 123.9(3), Rh(1)–N(1)–N(2) 115.4(6), Rh(2)–N(1)–N(2) 120.6(6), N(1)–N(2)–N(3) 179(1), Rh(1)–N(C1)–N(C3) 118.3(5), Rh(2)–N(C2)–N(C1) 123.9(5), N(1)–Rh(1)–N(C1) 82.2(3), N(1)–Rh(2)–N(C2) 82.0(3)

Reaction of the Diazido-complex (2) *with Trifluoroacetonitrile and t-Butyl Isocyanide*.—Trifluoroacetonitrile reacted with complex (2), in a similar manner to the reaction with hexafluorobutyne, to give the binuclear complex (20) in which three of the four azide ligands had reacted and where the remaining one was bridging the two rhodiums. The n.m.r. spectra were much simpler than those of (18) and suggested a more symmetric structure, probably centrosymmetric as shown. For example, the ^{19}F spectrum showed only two types of (uncoupled) CF_3 groups in the ratio of 1 : 2 and the ^{13}C-$\{^{19}F\}$ spectrum also showed two types of CF_3 and two types of N=C carbons. Parallel reactions of other azido-complexes with nitriles to give co-ordinated tetrazoles have been reported,[11e,16] and it was found that electron-withdrawing groups on the nitrile facilitate reaction with electron-rich azides. Again, a very distinctive feature of the reaction discussed here is the



(20)

pronounced greater lability of terminal by comparison with bridging azides; the last bridging azide is indeed so inert that it frequently does not react at all.

The t-butyl isocyanide adduct (3g) slowly reacted with excess of Bu^tNC in acetone at 56 °C. However, the reaction was difficult to reproduce since it appeared to be photosensitive and the product (21) was difficult to purify. The i.r. spectrum of (21) showed the presence of a co-ordinated isocyanide and a band which was apparently due to a bridging azide; however, from its molecular weight the complex appeared to be mononuclear. The ^1H n.m.r. spectrum indicated the presence of one C_5Me_5 and two different t-butyl groups in the molecule and we very tentatively suggest that complex (21) may contain a t-butyltetrazolate ligand as well as co-ordinated azide and isocyanide.

No reaction was observed between complex (3h) and methyl isocyanide in acetone at 56 °C.

Nitrito-complexes.—Reaction of $[Rh_2(C_5Me_5)_2Cl_4]$ (1) with either sodium or potassium nitrite gave the anionic tris(nitrito)-complexes (22a) or (22b). Reaction of these complexes with PPh_3 afforded the neutral mononuclear complex (23) which could also be prepared by reaction of $[Rh(C_5Me_5)Cl_2(PPh_3)]$ with silver nitrite. Reaction of (22) with HCl regenerated (1).

$$\begin{tikzcd}
(1) + M[NO_2] \arrow[r] & \begin{array}{l} M[Rh(C_5Me_5)(NO_2)_3] \\ (22a)\ M = Na \\ (22b)\ M = K \end{array} \arrow[d, "PPh_3"] \\
{[Rh(C_5Me_5)Cl_2(PPh_3)] + Ag[NO_2]} \arrow[r] & \begin{array}{c} [Rh(C_5Me_5)(NO_2)_2(PPh_3)] \\ (23) \end{array}
\end{tikzcd}$$

Basolo and Hammaker[17] noted that *O*-bonded nitritorhodium complexes absorbed at *ca.* 1 060 cm^{-1} whereas *N*-bonded nitro-complexes had no bands in the region 900—1 100 cm^{-1}. Complexes (22a), (22b), and (23) exhibited bands at *ca.* 1 026 cm^{-1} and presumably are therefore best regarded as containing *O*-bonded nitrite groups, but whether all the NO_2 groups are bonded in this way is not known.

Nitrato-complexes.—Reaction of the dimeric diazido-complex (2) with N_2O_4 gave *monomeric* $[Rh(C_5Me_5)(NO_3)_2]$ (24); by contrast, reaction of $[Rh_2(C_5Me_5)_2Cl_4]$ with silver nitrate in acetone gave an ionic complex (25), isomeric with (24), which we suggest to contain the tri-μ-nitrato-bis[(pentamethylcyclopentadienyl)rhodium] cation. While (25) reacts with $[NH_4][PF_6]$ in acetone to give the hexafluorophosphate salt of the cation, (24) is inert to this reagent under the same conditions.

The two complexes were differentiated by their i.r. spectra; while (24) shows five strong bands between 1 240 and 1 520 cm^{-1}, (25) and the $[PF_6]^-$ salt both only show one very broad and intense band in this region (1 385 cm^{-1}). Unfortunately, the i.r. spectra in this region are not very reliable guides to the structures;[18] if these complexes are indeed simple mono- and binuclear complexes then presumably (24) contains one uni- and one bi-dentate NO_3, and (25) contains three bridging NO_3 ligands and one $[NO_3]^-$ anion.

$$\begin{tikzcd}
\begin{array}{c} [Rh_2(C_5Me_5)_2(N_3)_4] \\ (2) \end{array} \arrow[r, "N_2O_4"] & \begin{array}{c} [Rh(C_5Me_5)(NO_3)_2] \\ (24) \end{array} \arrow[d, "PPh_3"] \\
& \begin{array}{c} [Rh(C_5Me_5)(NO_3)_2(PPh_3)] \\ (26) \end{array} \\
\begin{array}{c} [Rh_2(C_5Me_5)_2Cl_4] \\ (1) \end{array} \arrow[r, "Ag{[NO_3]}"] & \begin{array}{c} [Rh_2(C_5Me_5)_2(NO_3)_3][NO_3] \\ (25) \end{array} \arrow[d, "{[NH_4][PF_6]}"] \\
& {[Rh_2(C_5Me_5)_2(NO_3)_3][PF_6]}
\end{tikzcd}$$

Complex (24), but *not* complex (25), reacts with PPh_3 to give the monomeric dinitrato(monophosphine) adduct (26). This shows a strong broad band at 1 270 cm^{-1} but only a medium-intensity band at 1 385 cm^{-1}.

EXPERIMENTAL

Analytical and molecular weight, i.r., and ^1H n.m.r. data are collected in Table 1. Microanalytical data were obtained by the University of Sheffield Microanalysis Laboratory, molecular weights were determined osmometrically in chloroform, and conductivities were carried out at 25 °C in acetonitrile using a Philips conductivity bridge. N.m.r. spectra were recorded on Perkin-Elmer R-12B (60 MHz), Varian HA-100 (100 MHz), Perkin-Elmer R-34 (220 MHz) (for ^1H), or JEOL PFT-100 spectrometers (for ^{13}C, ^{19}F, or ^{31}P). Tetramethylsilane was used as internal reference for ^1H and ^{13}C spectra, $CFCl_3$ as internal standard for ^{19}F, and H_3PO_4 as external standard for ^{31}P n.m.r. spectra. Spectra were recorded for C^2HCl_3 solutions unless otherwise stated. I.r. spectra were recorded on a Perkin-Elmer PE-180 spectrometer as Nujol mulls on Polythene plates. All reactions were carried out under nitrogen and solvents were degassed before use; the vast majority of complexes prepared were not, however, appreciably sensitive to air.

$[Rh_2(C_5Me_5)_2(N_3)_4]$ (2).—A suspension of $[Rh_2(C_5Me_5)_2Cl_4]$ (1) (2.00 g, 3.11 mmol) and $Na[N_3]$ (1.2 g, 18.7 mmol) in acetone (150 cm^3) was stirred for 18 h; during this time the colour changed from dark to bright red. The solvent was removed *in vacuo* and the product was dissolved in dichloromethane. The solution was then filtered to remove NaCl and unchanged $Na[N_3]$ and the product crystallised as wine-red crystals on addition of di-isopropyl ether, yield 2.00 g (95%). ^{13}C-{^1H} N.m.r.: δ 8.0 (C_5*Me*$_5$) and 93.4 p.p.m. [*C*$_5Me_5$, d, *J*(C–Rh) = 7.7 Hz].

$[Rh(C_5Me_5)(N_3)_2(PPh_3)]$ (3a).—Complex (2) (0.20 g, 0.31 mmol) and PPh_3 (0.16 g, 0.62 mmol) were stirred in acetone (30 cm^3) for 1 h. The solvent was then removed *in vacuo* and the product crystallised from dichloromethane–di-isopropyl ether to afford bright red crystals, yield 0.34 g (94%). ^{13}C-{^1H} N.m.r.: δ 8.4 (C_5*Me*$_5$), 98.9 [d, *C*$_5Me_5$, *J*(C–Rh) = 9.2 Hz], 128.7 [Ph–C(3), *J*(C–P) = 10.7], 130.0 [Ph–C(4)], 131.4 [Ph–C(2), *J*(C–P = 19.9], and 134.4 p.p.m. [Ph–C(1), *J*(C–P) = 10.7]. ^{31}P-{^1H} N.m.r.: δ 33.7 p.p.m. [d, *J*(P–Rh) = 147 Hz].

The complexes $[Rh(C_5Me_5)(N_3)_2L]$ (3b)—(3m) were prepared and purified by the same method: (3b), 90%, red

(^{31}P-{^{1}H} n.m.r.: δ 122.3 p.p.m. [d, *J*(P–Rh) = 227 Hz]); (3c), 81%, orange; (3d), 96%, red; (3e), 44%, orange; (3f), 84%, dark red; (3g), 88%, bright red [^{13}C-{^{1}H} n.m.r.: δ 8.9 ($C_5\mathit{Me}_5$), 30.6 ($C\mathit{Me}_3$), 58.9 ($\mathit{C}Me_3$), 98.8 (C_5Me_5), and 126.0 p.p.m. ($Bu^tN\mathit{C}$)]; (3h), 61%, yellow; (3i), 70%, dark red; (3j), 86%, bright red; (3k), 79%, bright red; (3l), 70%, red; (3m), 68%, bright red.

$[Rh(C_5Me_5)(N_3)(phen)][N_3]$ (4).—A solution of (2) (0.20 g, 0.31 mmol) and 1,10-phenanthroline (0.11 g, 0.62 mmol) in acetone (30 cm^3) was stirred for 6 h; during this time an orange powder was precipitated. This was filtered off and crystallised from dichloromethane–di-isopropyl ether, yield 0.25 g (79%).

$[Rh(C_5Me_5)(N_3)(phen)][PF_6]$ (5).—A solution of (4) (0.20 g, 0.40 mmol) and an excess of $[NH_4][PF_6]$ (0.50 g) in methanol (20 cm^3) was stirred for 1 h. The solvent was removed *in vacuo* and the product was dissolved in dichloromethane. The solution was then filtered to remove $[NH_4]Cl$ and $[NH_4][PF_6]$ and the product was crystallised as bright orange microcrystals on addition of di-isopropyl ether, yield 0.20 g (81%).

$[Rh(C_5Me_5)(N_3)(bipy)][Rh(C_5Me_5)(N_3)_3]$ (6).—A solution of (2) (0.20 g, 0.31 mmol) and 2,2′-bipyridyl (0.05 g, 0.31 mmol) in acetone (20 cm^3) was stirred for 2 h; during this time a bright red powder was precipitated. This was filtered off and crystallised from dichloromethane–di-isopropyl ether to afford bright red crystals, yield 0.22 g (90%). ^{13}C-{^{1}H} N.m.r. ($C^2H_2Cl_2$): δ 8.1 ($C_5\mathit{Me}_5$ anion), 8.8 ($C_5\mathit{Me}_5$ cation), 92.0 [d, *J*(C–Rh) = 9 Hz, C_5Me_5 anion], 97.3 [d, *J*(C–Rh) = 9 Hz, C_5Me_5 cation], 125.0, 128.7, 141.2, 150.9, and 154.9 p.p.m. (all s, bipy).

$[Rh_2(C_5Me_5)_2Cl_2(N_3)_2]$ (7).—A suspension of (1) (1.00 g, 1.62 mmol) and $Na[N_3]$ (0.21 g, 3.24 mmol) in acetone (40 cm^3) was stirred for 15 h. The solvent was removed *in vacuo* and the product was dissolved in dichloromethane (15 cm^3). The solution was filtered to remove NaCl and the product was crystallised as rust-coloured crystals on addition of di-isopropyl ether, yield 0.84 g (82%). ^{1}H N.m.r.: δ 1.7 p.p.m. (s, C_5Me_5). ^{13}C-{^{1}H} N.m.r.: δ 9.7 ($C_5\mathit{Me}_5$) and 93.6 p.p.m. [d, *J*(C–Rh) = 9 Hz, C_5Me_5].

$[Rh(C_5Me_5)Cl(N_3)\{P(OMe)_3\}]$ (8a).—Trimethyl phosphite (0.12 g, 0.95 mmol) and (7) (0.30 g, 0.48 mmol) in acetone (30 cm^3) were stirred for 6 h. The solvent was then removed *in vacuo* and the product crystallised from dichloromethane–di-isopropyl ether to afford bright red crystals, yield 0.37 g (88%). ^{1}H N.m.r.: δ 1.66, 1.69, 1.72 [all d, *J*(H–P) = 5 Hz, C_5Me_5, relative intensity 2 : 11 : 2], 3.83, 3.84, 3.85 p.p.m. [all d, *J*(H–P) = 12 Hz, $P(OMe)_3$, relative intensity 1 : 6 : 1]. ^{31}P-{^{1}H} N.m.r.: 119.6 [d, *J*(P–Rh) = 217 Hz], 121.2 [d, *J*(P–Rh) = 225 Hz], and 122.3 p.p.m. [d, *J*(P–Rh) = 230 Hz], relative intensity 1 : 6 : 1.

The red-brown complex $[Rh(C_5Me_5)Cl(N_3)(PPh_3)]$ (8b) was obtained analogously [79%, ν(N_3) at 2 033 cm^{-1}]; owing to disproportionation, this complex could not be purified. ^{1}H N.m.r.: δ 1.41 (m, C_5Me_5) and 7.48 p.p.m. (br m, Ph). ^{31}P-{^{1}H} N.m.r.: δ 30.6 [d, *J*(P–Rh) = 147 Hz], 32.0 [d, *J*(P–Rh) = 147 Hz], and 33.7 p.p.m. [d, *J*(P–Rh) = 144 Hz]; relative intensity 1 : 2 : 1.

$[Rh_2(C_5Me_5)_2(NCO)_4]$ (9).—A solution of (2) (0.20 g, 0.31 mmol) in dichloromethane (40 cm^3) was treated with CO (1 atm, 20 °C) for 6 h; during this time the colour lightened from red to orange. The solvent was removed *in vacuo* and the product was crystallised from dichloromethane–di-isopropyl ether to afford orange-red crystals, yield 0.18 g (89%). The same product (93%) was obtained when carbon monoxide was bubbled through a solution of $[\{Rh(C_5Me_5)(NCO)\}_2(NCO)(N_3)]$ in dichloromethane, and (92%) by reaction of complex (1) with sodium cyanate in acetone according to the method described for the synthesis of (2).

$[\{Rh(C_5Me_5)(NCO)\}_2(NCO)(N_3)]$ (10).—A solution of (2) (0.20 g, 0.31 mmol) in acetone (30 cm^3) was treated with CO (20 °C, 1 atm) for 3 h; during this time an orange-red powder was precipitated. This was filtered off and crystallised from dichloromethane–di-isopropyl ether to afford bright red crystals, yield 0.16 g (81%).

$[Rh(C_5Me_5)(NCO)(N_3)(PPh_3)]$ (11).—A solution of (3a) (0.20 g, 0.34 mmol) in acetone (30 cm^3) was treated with CO (20 °C, 1 atm) for 1 h; during this time a red solid was precipitated. This was filtered off, washed with diethyl ether (2 × 20 cm^3), and dried, to give a bright red powder, yield 0.18 g (90%).

The ^{31}P-{^{1}H} n.m.r. spectrum of a 1 : 1 mixture of complex (3a) and complex (12) showed, in addition to the equal-intensity resonances of (3a) (δ 33.7 p.p.m., d) and (12) (δ 33.6 p.p.m., d), a resonance of relative intensity 2 [δ 33.2 p.p.m., d, *J*(P–Rh) = 139 Hz] which is ascribed to complex (11).

$[Rh(C_5Me_5)(NCO)_2(PPh_3)]$ (12).—*Method* (*a*). A solution of (9) (0.20 g, 0.31 mmol) and PPh_3 (0.16 g, 0.62 mmol) in acetone (30 cm^3), was stirred for 1 h. The solvent was then removed *in vacuo* and the product crystallised from dichloromethane–di-isopropyl ether to afford orange microcrystals, yield 0.31 g (88%). ^{31}P-{^{1}H} N.m.r.: δ 33.6 p.p.m. [d, *J*(P–Rh) = 132 Hz]. The analogous complex $[Rh(C_5Me_5)(NCO)_2(py)]$ (13) was obtained in a similar fashion as a bright yellow powder, yield 74%.

Method (*b*). Carbon monoxide was bubbled through a solution of (11) (0.20 g, 0.34 mmol) in dichloromethane (30 cm^3) for 3 h. The solvent was removed *in vacuo* and the product (0.18 g, 88%) was then crystallised from dichloromethane–di-isopropyl ether.

Method (*c*). Complex (12) was also obtained (92%) when (3a) was treated with CO in dichloromethane.

$[Rh_2(C_5Me_5)_2(SCN)_4]$ (14).—A solution of (2) (0.20 g, 0.31 mmol) in acetone (10 cm^3) and carbon disulphide (10 cm^3) was stirred for 40 h. The solvent was removed *in vacuo* and the product crystallised from dichloromethane-di-isopropyl ether to afford an orange powder, yield 0.18 g (82%). The complex was also obtained (80%) by the reaction of (1) with sodium thiocyanate. ^{13}C-{^{1}H} N.m.r.: δ 9.3 ($C_5\mathit{Me}_5$) and 98.8 p.p.m. [d, *J*(C–Rh) = 7.6 Hz, C_5Me_5].

$[Rh(C_5Me_5)(SCN)_2(PPh_3)]$ (15).—A suspension of (3a) (0.20 g, 0.34 mmol) and $Na[NCS]$ (0.14 g, 1.70 mmol) in acetone (30 cm^3) was stirred for 6 h. The solvent was then removed *in vacuo* and the product was dissolved in dichloromethane. The solution was then filtered to remove $Na[N_3]$ and unchanged $Na[NCS]$ and the product (15) was crystallised as yellow crystals on addition of di-isopropyl ether, yield 0.19 g (86%). This complex was also obtained (89%) from (14) by the method (*a*) used to prepare (12).

$[\{Rh(C_5Me_5)(N_3CS_2)_2\}_n]$ (16).—A suspension of (3a) (0.20 g, 0.34 mmol) in carbon disulphide (15 cm^3) was stirred for 15 h. The solvent was removed *in vacuo* and the residue washed with diethyl ether (3 × 10 cm^3); it was then crystallised from dichloromethane–di-isopropyl ether to afford dark red needles, yield 0.11 g (69%). **CAUTION: this compound may detonate** The combined diethyl ether washings were evaporated *in vacuo* to leave an off-white solid, which was crystallised from diethyl ether–n-hexane to afford PPh_3S as white crystals, yield 0.05 g (47%).

Degradation of $[\{Rh(C_5Me_5)(N_3CS_2)_2\}_n]$.—A solution of (16) (0.02 g, 0.02 mmol) in acetone (10 cm^3) was stirred for 15 h. The solvent was then removed *in vacuo* and the residue crystallised from dichloromethane–di-isopropyl ether to afford $[Rh_2(C_5Me_5)_2(SCN)_4]$, yield 0.01 g (60%).

Reaction of $[Rh(C_5Me_5)(N_3)_2(PPh_3)]$ *and of* $[Rh(C_5Me_5)(SCN)_2(PPh_3)]$ *with Sulphur.*—Complex (3a) (0.02 g, 0.34 mmol) and sulphur (0.44 g, 1.70 mmol) in acetone (20 cm^3) were stirred for 4 h. The solvent was then removed *in vacuo*. The product was dissolved in dichloromethane and the solution filtered; $[Rh_2(C_5Me_5)_2(N_3)_4]$ (2) crystallised as red crystals on addition of di-isopropyl ether, yield 0.10 g (91%). The reaction of (15) (0.20 g, 0.32 mmol) and sulphur (0.41 g, 1.60 mmol) under the same conditions gave the corresponding product $[Rh_2(C_5Me_5)_2(NCS)_4]$ (14), yield 0.09 g (86%).

$[Rh_2(C_5Me_5)_2(N_3C_4F_6)_2(N_3)_2]$ (17).—Gaseous hexafluorobut-2-yne was bubbled through a solution of (2) (0.40 g, 0.62 mmol) in dichloromethane (10 cm^3) for 10 min at 20 °C. An orange solid precipitated from the wine-red solution which was filtered off and crystallised from dichloromethane–di-isopropyl ether to afford bright orange microcrystals, yield 0.52 g (88%). ^{19}F N.m.r.: δ 56.0 p.p.m. (s, CF_3).

$[Rh_2(C_5Me_5)_2(N_3C_4F_6)_3(N_3)]$ (18).—Hexafluorobut-2-yne (an excess) and (2) (0.60 g, 0.93 mmol) in dichloromethane (40 cm^3) were shaken in a sealed glass tube for 18 h; during this time an orange solid [presumably complex (17)] precipitated from the wine-red solution and slowly redissolved to give an orange-red solution. The solvent was removed *in vacuo* and the product crystallised from dichloromethane–di-isopropyl ether to afford bright red crystals, yield 0.75 g (71%). The complex was also obtained (72%) by an extended reaction of (17) with hexafluorobut-2-yne in a sealed tube. ^{19}F N.m.r.: δ 56.4, 59.6 [2 × q, CF_3(e), CF_3(f), J(F–F) = 6 Hz], 58.7, 58.8 p.p.m. [2 × s, CF_3(c), CF_3(d)]. ^{13}C-{^{1}H} N.m.r.: 7.6, 8.3 [2 × s, $C_5\mathit{Me}_5$ (A,B)], 97.6, 98.1 p.p.m. [2 × d, J(C–Rh) = 7 Hz, C_5Me_5 (A,B)]. ^{13}C-{^{19}F} N.m.r.: 7.6, 8.2 [2 × q, J(C–H) = 130 Hz, $C_5\mathit{Me}_5$ (A,B)], 98.1 [br m, C_5Me_5 (A,B)], 119.8, 121.8 [2 × s, N=*C* (g,h)], 120.7, 121.9 [2 × s, N=*C* (i,j), 135.5, 138.2 [2 × s, $\mathit{C}F_3$ (c,d)], 138.1, 140.4 p.p.m. [2 × s, $\mathit{C}F_3$ (e,f)].

$[Rh(C_5Me_5)(N_3C_4F_6)_2(PPh_3)]$ (19).—Complex (3a) (0.60 g, 1.0 mmol) and hexafluorobut-2-yne (an excess) in dichloromethane (40 cm^3) were shaken in a sealed glass tube for 6 h at 20 °C; during this time the orange-red solution became lighter in colour. The solvent was removed *in vacuo* and the product crystallised from dichloromethane–di-isopropyl ether to afford orange-yellow crystals, yield 0.83 g (90%). ^{19}F N.m.r.: δ 60.2 p.p.m. (s, CF_3). ^{13}C-{^{1}H} N.m.r.: δ 8.8 ($C_5\mathit{Me}_5$), 102.3 [d, J(C–Rh) = 5 Hz], 127.9 (d), 128.4 (s), 130.4 (d), 134.1 p.p.m. (d) (phenyls). ^{13}C-{^{19}F} N.m.r.: δ 8.8 [q, J(C–H) = 130 Hz, $C_5\mathit{Me}_5$], 102.2 (m, C_5Me_5), 121.0 (s, N=*C*), 136.6 (s, $\mathit{C}F_3$), 124.7, 131.1, and 137.1 p.p.m. (br m, phenyls).

Degradation of $[Rh_2(C_5Me_5)_2(N_3C_4F_6)_3(N_3)]$ (18).—Finely ground (18) (0.30 g, 0.27 mmol) and $[NH_4]Cl$ (1.00 g, an excess) were mixed thoroughly and placed in a two-neck round-bottomed flask (50 cm^3). The solid-state reactants were then heated to 100 °C, under a stream of nitrogen. A white solid sublimed and was collected in a U-tube at −78 °C. The solid was then extracted with chloroform (20 cm^3) and the solvent removed *in vacuo* to leave $HN_3C_4F_6$ as a white powder (0.05 g, 28%). Mass spectrum: parent ion at *m/e* 205. The solid remaining in the flask was (20 cm^3) and the solvent was removed *in vacuo* to leave $HN_3C_4F_6$ as a white powder (0.05 g, 28%). Mass spectrum: parent ion at *m/e* 205. The solid remaining in the flask was extracted with CH_2Cl_2 to give complex (1) (0.16 g, 97%).

Degradation of $[Rh(C_5Me_5)(N_3C_4F_6)_2(PPh_3)]$ (19).—A finely ground solid mixture of (19) (0.30 g, 0.33 mmol) and $[NH_4]Cl$ (1.00 g, an excess) was treated in the same manner as described above. This afforded $HN_3C_4F_6$ as a white powder, yield 0.02 g (11%), and $[Rh(C_5Me_5)Cl_2(PPh_3)]$ as an orange-red powder, yield 0.17 g (91%).

$[Rh_2(C_5Me_5)_2(N_4C_2F_3)_3(N_3)]$ (20).—Complex (2) (0.60 g, 0.93 mmol) and trifluoroacetonitrile (an excess) in dichloromethane (40 cm^3) was shaken in a sealed glass tube for 15 h; during this time the red solution became orange. The solvent was then removed *in vacuo* and the product crystallised from dichloromethane–di-isopropyl ether to afford bright orange crystals, yield 0.67 g (77%). ^{19}F N.m.r.: δ 62.9, 63.5 p.p.m. [2 × s, CF_3 (a,b)]. ^{13}C-{^{1}H} N.m.r.: δ 7.9 ($C_5\mathit{Me}_5$) and 97.4 p.p.m. [d, J(C–Rh) = 7 Hz]. ^{13}C-{^{19}F} N.m.r.: δ 7.8 [q, J(C–H) = 131 Hz, $C_5\mathit{Me}_5$], 97.4 (br m, C_5Me_5), 119.3, 120.4 [2 × s, *C*=N) c,d)], and 157.2, 159.4 p.p.m. [2 × s, $\mathit{C}F_3$ (a,b)].

$[Rh(C_5Me_5)(CNBu^t)(Bu^tN_4C)(N_3)]$ (21).—An acetone solution (50 cm^3) of $[Rh(C_5Me_5)(CNBu^t)(N_3)_2]$ (0.20 g, 0.49 mmol) and Bu^tNC (1 cm^3, an excess) was refluxed for 2 h; during this time the red solution became yellow. The solvent was then removed *in vacuo* and the product was crystallised from diethyl ether–n-hexane to afford orange-yellow crystals, yield 0.16 g (66%).

$[M][Rh(C_5Me_5)(NO_2)_3]$ (22a), (22b).—A suspension of (1) (2.00 g, 3.24 mmol) and $Na[NO_2]$ (2.23 g, 32.4 mmol) in acetone (200 cm^3) was refluxed for 15 h, during which time the colour changed from red to yellow. The precipitate was filtered off, washed with acetone (3 × 20 cm^3), and the acetone solutions were combined. The solvent was removed *in vacuo* and the product obtained from the residue by crystallisation from acetone–di-isopropyl ether as orange-yellow crystals, yield 2.35 g (91%). The salt $[K][Rh(C_5Me_5)(NO_2)_3]$ was prepared in the same manner as yellow crystals (86%), crystallised from acetone–n-hexane.

$[Rh(C_5Me_5)(NO_2)_2(PPh_3)]$ (23).—A solution of (22a) (0.20 g, 0.50 mmol) and PPh_3 (0.13 g, 0.50 mmol) in acetone (30 cm^3) was stirred for 3 h. The solvent was then removed *in vacuo* and the residue washed with water (2 × 5 cm^3), to remove $Na[NO_2]$, then acetone (1 × 2 cm^3), and dried. The product was crystallised from acetone–di-isopropyl ether to afford bright orange crystals, yield 0.28 g (96%). ^{31}P-{^{1}H} N.m.r.: δ 94.3 p.p.m. [d, J(P–Rh) = 146.5 Hz]. ^{13}C-{^{1}H} N.m.r.: δ 9.0 ($C_5\mathit{Me}_5$), 101.0 [d, J(C–Rh) = 9.1 Hz, C_5Me_5], 128.5 (d), 131.0, and 134.9 p.p.m. (d) (Ph).

A suspension of $[Rh(C_5Me_5)Cl_2(PPh_3)]$ (0.20 g, 0.35 mmol) and $Ag[NO_2]$ (0.14 g, 0.70 mmol) in acetone (30 cm^3) was stirred for 6 h. The precipitate was then filtered off and the solvent removed *in vacuo*. The residue was crystallised from acetone–di-isopropyl ether, affording the product as orange crystals, yield 0.18 g (89%).

$[Rh(C_5Me_5)(NO_3)_2]$ (24).—A suspension of (2) (0.20 g, 0.31 mmol) in dinitrogen tetra-oxide (5 cm^3) was stirred at 0 °C for 2 h. The solvent was then removed *in vacuo* and the residue washed with diethyl ether (2 × 20 cm^3) and crystallised from dichloromethane–di-isopropyl ether to afford orange crystals, yield 0.19 g (86%).

$[Rh_2(C_5Me_5)_2(NO_3)_3][NO_3]$ (25).—A suspension of (1) (0.20 g, 0.32 mmol) and $Ag[NO_3]$ (0.20 g, 1.29 mmol) in acetone (30 cm^3) was stirred for 3 h, during which time the colour changed from dark red to orange. The solution was then filtered and the solvent removed *in vacuo*. The residue was crystallised from acetone–di-isopropyl ether giving the product as orange microcrystals, yield 0.18 g (82%). $^{13}C-\{^1H\}$ N.m.r. ($C^2H_2Cl_2$): δ 9.5 (C_5Me_5) and 94.3 p.p.m. [d, $J(C-Rh)$ = 9.2 Hz, C_5Me_5].

TABLE 2

Atomic co-ordinates [$\times 10^4$, except Rh(01) and Rh(02) $\times 10^5$]

Atom	x	y	z
Rh(01)	33 821(3)	65 037(6)	21 184(4)
Rh(02)	17 505(3)	38 048(7)	8 153(5)
F(01)	1 959(4)	8 569(8)	4 249(6)
F(02)	2 710(3)	7 391(7)	4 256(4)
F(03)	1 497(4)	6 248(9)	4 967(5)
F(04)	245(4)	7 685(10)	2 724(8)
F(05)	−360(4)	5 394(10)	3 147(9)
F(06)	271(5)	6 761(17)	4 201(7)
F(07)	3 422(6)	1 199(10)	5 059(8)
F(08)	4 405(5)	3 233(16)	4 778(13)
F(09)	3 600(8)	2 698(13)	6 117(7)
F(10)	1 176(6)	2 072(20)	5 418(12)
F(11)	1 688(9)	878(12)	5 694(15)
F(12)	1 854(10)	2 413(23)	6 403(9)
F(13)	7 056(9)	417(10)	2 274(10)
F(14)	8 161(7)	1 667(16)	2 347(12)
F(15)	7 307(8)	1 612(12)	3 459(6)
F(16)	5 781(5)	2 143(10)	3 056(9)
F(17)	5 947(6)	4 321(12)	2 749(7)
F(18)	6 567(5)	3 778(13)	3 828(6)
N(01)	2 895(3)	4 592(7)	1 243(5)
N(02)	3 310(4)	3 906(8)	1 043(6)
N(03)	3 701(5)	3 272(11)	871(9)
C(01)	4 386(4)	7 722(9)	838(6)
C(02)	3 941(4)	8 623(9)	1 057(7)
C(03)	3 986(4)	8 990(9)	2 138(7)
C(04)	4 420(4)	8 291(9)	2 607(7)
C(05)	4 660(4)	7 463(9)	1 810(6)
C(06)	4 542(5)	7 171(12)	−183(7)
C(07)	3 547(5)	9 155(11)	253(8)
C(08)	3 697(6)	10 085(11)	2 602(9)
C(09)	4 621(6)	8 378(12)	3 699(8)
C(10)	5 184(5)	6 643(12)	1 931(9)
C(11)	1 008(6)	2 035(11)	−67(9)
C(12)	521(5)	2 363(10)	777(9)
C(13)	705(5)	1 983(10)	1 799(9)
C(14)	1 325(6)	1 478(10)	1 588(9)
C(15)	1 510(6)	1 512(10)	452(9)
C(16)	983(8)	2 253(17)	−1 225(11)
C(17)	−128(6)	2 896(14)	606(13)
C(18)	313(7)	2 070(15)	2 857(10)
C(19)	1 715(8)	996(13)	2 405(13)
C(20)	2 101(8)	984(15)	−133(13)
NC(01)	2 159(3)	6 181(7)	2 418(5)
NC(02)	1 701(3)	5 594(7)	1 692(5)
NC(03)	1 010(4)	5 671(8)	1 903(5)
CC(01)	1 019(5)	6 323(10)	2 797(7)
CC(02)	1 733(4)	6 641(9)	3 134(6)
CC(03)	1 984(5)	7 198(11)	4 153(7)
CC(04)	298(6)	6 529(14)	3 260(10)
ND(01)	2 377(4)	4 080(9)	3 987(6)
ND(02)	3 094(4)	4 850(7)	3 411(5)
ND(03)	3 642(4)	4 462(8)	3 725(6)
CD(01)	3 255(5)	3 396(10)	4 567(7)
CD(02)	2 471(5)	3 174(11)	4 716(7)
CD(03)	3 684(7)	2 659(13)	5 127(9)
CD(04)	1 796(7)	2 225(16)	5 516(10)
NE(01)	2 852(4)	5 207(8)	−1 207(6)
NE(02)	2 275(4)	5 333(7)	−560(5)
NE(03)	2 056(5)	6 385(9)	−915(6)
CE(01)	2 518(5)	6 976(10)	−1 848(7)
CE(02)	3 014(5)	6 242(10)	−2 037(6)
CE(03)	2 462(7)	8 258(13)	−2 487(9)
CE(04)	3 664(7)	6 488(13)	−2 915(7)

A solution of (25) (0.20 g, 0.27 mmol) and $[NH_4][PF_6]$ (0.50 g, an excess) in acetone (20 cm^3) was stirred for 2 h. The solvent was then removed *in vacuo* and the residue washed with water (2 × 5 cm^3) and methanol (1 × 5 ml) to remove $[NH_4]Cl$ and $[NH_4][PF_6]$. The residue was crystallised from acetone–di-isopropyl ether to afford bright red $[Rh_2(C_5Me_5)_2(NO_3)_3][PF_6]$ (0.20 g, 90%). ^1H N.m.r.: δ 1.67 p.p.m. (s, C_5Me_5).

$[Rh(C_5Me_5)(NO_3)_2(PPh_3)]$ (26).—A solution of (24) (0.20 g, 0.55 mmol) and PPh_3 (0.14 g, 0.55 mmol) in acetone (20 cm^3) was stirred for 30 min, during which time the colour changed from orange to red. The solvent was then removed *in vacuo* and the product obtained from the residue by crystallisation from acetone–di-isopropyl ether as red flaky crystals, yield 0.32 g (92%).

X-Ray Crystal-structure Determination of $[Rh_2(C_5Me_5)_2\{N_3C_2(CF_3)_2\}_3(N_3)]$ (18).—A crystal was selected from a batch prepared as described above.

Crystal data. $C_{32}H_{30}F_{18}N_{12}Rh_2$, M = 1 130.45, Triclinic, a = 18.64(2), b = 9.61(1), c = 12.81(5) Å, α = 87.01(4), β = 82.75(4), γ = 114.38(1)°, U = 2 058.13 Å^3, D_c = 1.824 g cm^{-3}, Z = 2, space group $P\bar{1}$, crystal size 0.057 × 0.049 × 0.061 cm, μ = 9.15 cm^{-1}, Mo-K_α radiation, λ = 0.710 69 Å. Cell constants were determined from a least-squares fit to the setting angles of 34 reflections centred manually. The Delaunay cell (a = 12.805, b = 18.645, c = 19.568 Å; α = 131.882, β = 120.567, γ = 97.250°) was not used for the calculations.

Three-dimensional X-ray data were collected with the crystal mounted along the c axis using a Stoe STADI-2 diffractometer in the stationary-counter–moving-crystal mode. Scans of variable width were measured with a background count at each end of the scan. 5 020 Independent reflections with $I_{obs.} \geqslant 3\sigma(I_{obs.})$ and $6.5 < 2\theta < 50°$ were obtained; Lorentz and polarisation corrections were applied but no allowance was made for absorption or extinction. The structure was solved using Patterson and Fourier methods, and is shown in the Figure. Block-diagonal least-squares refinement has reduced R to 0.050, with anisotropic thermal parameters for all non-hydrogen atoms.

Atomic scattering factors were taken from ref. 19. Calculations were performed on the University of Sheffield ICL 1906S computer with programs from the Sheffield X-ray System. Atomic co-ordinates are given in Table 2. Tables of observed and calculated structure factors, thermal parameters, and complete bond-length and bond-angle data for the structure are listed in Supplementary Publication No. SUP 22393 (78 pp.).*

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