Pentamethylcyclopentadienyl-rhodium and -iridium Complexes. Part 20.[1] Rhodium Complexes of Co-ordinated Hydrazines

By **William Rigby, Jon A. McCleverty, and Peter M. Maitlis,*** Department of Chemistry, The University, Sheffield S3 7HF

The monoadducts $[\mathrm{Rh(C_5Me_5)X_2(NH_2NR^1R^2)}]$ are formed by reaction of $\mathrm{NH_2NR^1R^2}$ with $[\mathrm{Rh_2(C_5Me_5)_2X_4}]$ (1) ($\mathrm{R^1 = R^2 = Me}$, X = Cl, Br, or I; $\mathrm{R^1 = H}$, $\mathrm{R^2 = Ph}$, $\mathrm{C_6F_5}$, or p-$\mathrm{MeC_6H_4}$, X = Cl; and $\mathrm{R^1 = Me}$, $\mathrm{R^2 = Ph}$, X = Cl); the bis complexes $[\mathrm{Rh(C_6Me_5)Cl(NH_2NHR)_2}][\mathrm{PF_6}]$ (R = Ph or p-$\mathrm{MeC_6H_4}$) are also obtained. All these complexes are very labile and lose the hydrazine readily. Methylhydrazine forms a 1 : 2 adduct with (1), $[\mathrm{Rh_2(C_5Me_5)_2X_4(NH_2NHMe)}]$, the n.m.r. spectra of which shows the existence of an exchange process. This is proposed to be due to an equilibrium between the neutral monohydrazine-bridged species $[\{\mathrm{Rh(C_5Me_5)X_2}\}_2\mathrm{(NH_2NHMe)}]$ and ionic species $[\{\mathrm{Rh(C_5Me_5)X(NH_2NHMe)}\}]_2{}^{2+}$ $2[\mathrm{Rh(C_5Me_5)X_3}]^-$. The reaction of (1; X = Cl) with a stoicheiometric amount of $\mathrm{N_2H_4}$ eventually leads to $[\mathrm{Rh(C_5Me_5)(N_2H_4)_3}]\mathrm{Cl_2}$; analogous ammine complexes $[\mathrm{Rh(C_5Me_5)(NH_3)_3}]^{2+}$ have also been obtained.

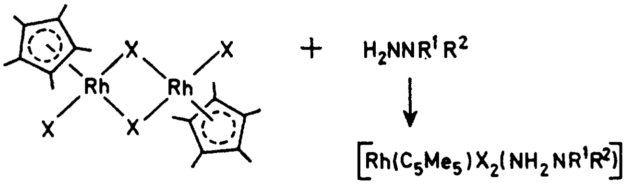
As part of our investigation of the complexes of pentamethylcyclopentadienylrhodium with nitrogen-based ligands we here report on complexes with a variety of substituted hydrazines. As we have shown, many ligands will act as bridging groups between two $\mathrm{Rh(C_5Me_5)}$ units[1-4] and this was, therefore, an interesting area to explore in view of our interest in modifying the reactivity of hydrazines by bidentate co-ordination to either one or two metal atoms.[5] The complexes formed by hydrazines with transition metals have been reviewed by Bottomley.[6]

	Complex	Microanalytical data(%) [a]				M [a]	^{1}H N.m.r. (δ/p.p.m., in C^{2}HCl$_3$)		^{13}C N.m.r. (δ/p.p.m., in C^{2}HCl$_3$) [b]		
		C	H	N	Halide		$\mathrm{C_5Me_5}$	Others	$\mathrm{C_5}\mathit{Me}_5$	$\mathit{C}_5\mathrm{Me_5}$	Others
(2a)	$[\mathrm{Rh(C_5Me_5)Cl_2(NH_2NMe_2)}]$	39.3 (39.0)	6.4 (6.2)	7.3 (7.6)	19.2 (19.2)	434 (369)	1.69	2.60 ($\mathrm{Me_2N}$), 4.30 (v br, $\mathrm{NH_2}$)	9.2 [c]	94.3 [c] [9.2]	50.2 [c] ($\mathrm{Me_2N}$)
(2b)	$[\mathrm{Rh(C_5Me_5)Br_2(NH_2NMe_2)}]$	31.7 (31.4)	5.1 (5.0)	6.3 (6.1)	35.1 (34.9)	487 (458)	1.81	2.70 ($\mathrm{Me_2N}$), 3.76 (v br, $\mathrm{NH_2}$)	9.8	94.9 [7.7]	50.1 ($\mathrm{Me_2N}$)
(2c)	$[\mathrm{Rh(C_5Me_5)I_2(NH_2NMe_2)}]$	25.0 (25.3)	3.9 (3.6)	2.6 (2.7)	48.5 (48.7)	948 (1 044)	1.99	2.58 ($\mathrm{Me_2N}$), 3.55 (v br, $\mathrm{NH_2}$)			
(3a)	$[\mathrm{Rh(C_5Me_5)Cl_2(NH_2NHPh)}]$	45.7 (46.0)	5.7 (5.5)	6.3 (6.7)	16.5 (17.0)	434 (417)	1.74	7.14 (m, Ph)	9.3 [c]	94.6 [c] [9.2]	115.2, 122.4, 129.5, 149.8 [c]
(4a)	$[\mathrm{Rh(C_5Me_5)Cl_2(NH_2NMePh)}]$	47.5 (47.3)	6.1 (5.8)	6.9 (6.5)	16.2 (16.5)	398 (431)	1.63	3.11 (MeN), 7.17 (m, Ph)	9.3	94.2 [9.2]	44.7 (MeN), 115.9, 121.9, 129.5, 151.1 (Ph)
(5a)	$[\mathrm{Rh(C_5Me_5)Cl_2(NH_2NHC_6F_5)}]$	38.2 (37.9)	3.9 (3.6)	5.5 (5.5)	Cl 14.1 (14.0)	548 (507)	1.69	5.45 (v br, $\mathrm{NH_2}$), 6.50 (v br, NH)			
(6a)	$[\mathrm{Rh(C_5Me_5)Cl_2(NH_2NHC_6H_4Me}$-$p)]$	45.9 (47.3)	6.0 (5.8)	6.3 (6.5)	17.4 (16.5)	434 (431)	1.73	2.25 (Me), 5.21 (v br, NH), 6.89, 7.05 [dd, J (H–H) = 8 Hz, aryl]			
(7)	$[\mathrm{Rh(C_5Me_5)Cl(NH_2NHPh)_2}]\mathrm{Cl}$	49.3 (50.3)	6.1 (5.9)	9.9 (10.7)	14.3 (13.5)						
(8)	$[\mathrm{Rh(C_5Me_5)Cl(NH_2NHPh)_2}][\mathrm{PF_6}]$	42.6 (41.6)	5.0 (4.9)	9.2 (8.8)	5.3 (5.6)		1.76	5.18, 5.63, 6.00 (br, NH), 7.12 (m, Ph)			
(9)	$[\mathrm{Rh(C_5Me_5)Cl(NH_2NHC_6H_4Me}$-$p)_2][\mathrm{PF_6}]$	43.2 (43.5)	5.3 (5.3)	8.7 (8.5)	5.5 (5.4)		1.74	2.23 (Me), 6.82, 7.08 [dd, J (H–H) = 8 Hz, aryl]			
(10a)	$[\mathrm{Rh_2(C_5Me_5)_2Cl_4(NH_2NHMe)}]$	38.3 (38.0)	5.5 (5.4)	4.2 (4.2)	21.2 (21.4)			See text	9.5 [d] (br)	94.2 [d] [9.2] 94.4 [d] [7.7] 95.4 [d] (9.2] 95.6 [d] [9.2]	46.7 [d] (br) 44.4 (br) MeN
(10b)	$[\mathrm{Rh_2(C_5Me_5)_2Br_4(NH_2NHMe)}]$	30.2 (29.9)	4.4 (4.3)	3.0 (3.3)	37.9 (38.0)		1.74 [e] 1.86 [e]	2.95 [e], 3.79 [e] (br, NMe) (NH not observed)			
(10c)	$[\mathrm{Rh_2(C_5Me_5)_2I_4(NH_2NHMe)}]$	24.7 (24.5)	3.7 (3.5)	2.7 (2.7)	46.9 (46.3)			See text	11.2 [f] 11.4 [f] 11.7 [f]	95.4 [f] [7.7] 96.5 [f] [9.2] 97.5 [f] [7.6] 97.8 [f] [7.7]	43.4 [f] (s, NMe)
(11)	$[\mathrm{Rh_2(C_5Me_5)_2Cl_3(NH_2NHMe)}][\mathrm{PF_6}]$	32.5 (32.6)	4.6 (4.7)	3.4 (3.6)	Cl 13.8 (13.8)		1.63 1.68	3.17 (d, J = 6 Hz, NMe), 5.05 (d, br, J = 6 Hz, NH), 6.21 (dd, br, NH), 6.70 (m, br, NH)	9.5 [g]	96.7 [g] [9.2] 96.8 [g] [9.2]	47.1 [g] (s, NMe)
(13)	$[\mathrm{Rh(C_5Me_5)(N_2H_4)_3}]\mathrm{Cl_2{\cdot}H_2O}$	28.2 (28.4)	6.5 (6.9)	19.5 (19.9)	17.0 (16.8)		1.68 [h]				
(14)	$[\mathrm{Rh(C_5Me_5)(NH_3)_3}]\mathrm{Cl_2}$	33.2 (33.2)	6.6 (6.7)	11.8 (11.7)	18.5 (19.7)		1.76 [i]	2.66 (v br, $\mathrm{NH_3}$)			
(15)	$[\mathrm{Rh(C_5Me_5)(NH_3)_3}][\mathrm{PF_6}]_2$ [k]	21.9 (20.7)	4.3 (4.2)	7.1 7.3			1.83 [j]	3.30 (v br, $\mathrm{NH_3}$)			

[a] Calculated values are given in parentheses. [b] J (C–Rh)/Hz is given in square brackets. [c] In C^{2}H$_2$Cl$_2$ at − 30°C. [d] In C^{2}H$_2$Cl$_2$ at −40°C. [e] In C^{2}HCl$_3$ at −20°C. [f] In C^{2}H$_2$Cl$_2$ at −50°C. [g] In C^{2}H$_3$CN. [h] In C^{2}H$_3$O^{2}H. [i] In liquid SO$_2$ at −30°C. [j] In [^{2}H$_6$]acetone. [k] Λ_M = 240 S cm^2 mol^{-1} (nitromethane).

RESULTS AND DISCUSSION

Mononuclear Complexes of Substituted Hydrazines.—The halide bridges in (1a)—(1c) are readily cleaved by a variety of mono- or 1,1-di-substituted hydrazines to give the monomeric adducts; in this sense these hydrazines behave in the same way as unidentate ligands.[2] Analytical and spectroscopic data (Table) agree with the proposed structures and we suggest that in each case the hydrazine binds to the metal at the unsubstituted nitrogen for steric reasons.



(1a) X = Cl
(1b) X = Br
(1c) X = I

(2a)-(2c) $R^1 = R^2 = Me$
(3a) $R^1 = H, R^2 = Ph$
(4a) $R^1 = Me, R^2 = Ph$
(5a) $R^1 = H, R^2 = C_6F_5$
(6a) $R^1 = H, R^2 = p\text{—}MeC_6H_4$

Complexes (2)—(6) were very labile; for example, with acetone they rapidly regenerated the parent complex (1), presumably together with the appropriate acetone hydrazone. Similarly, attempts to protonate the uncoordinated N of the hydrazine were unsuccessful and led to decomposition with the formation of the tri-μ-halogeno-cations $[Rh_2(C_5Me_5)_2X_3]^+$. Attempts to cause the hydrazine in (2a) to become bidentate by creating a vacant site at the metal by removal of chloride with $Tl[PF_6]$ were unsuccessful; the hydrazine was lost and $[Rh_2(C_5Me_5)_2Cl_3][PF_6]$ was isolated.

Only mono- and 1,1-di-substituted hydrazines were found to react; the reaction with hydrazine itself is discussed below.

When (1a) was dissolved in phenylhydrazine reaction occurred to give the hygroscopic ionic chloride (7) which was converted into the more stable hexafluorophosphate

$$\text{(1a)} + RNHNH_2 \longrightarrow \underset{(7)\ R = Ph}{[Rh(C_5Me_5)Cl(NH_2NHR)_2]Cl}$$

$$\downarrow$$

$$\begin{array}{ll}(8)\ R = Ph & \\ (9)\ R = p\text{-}MeC_6H_4 & [Rh(C_5Me_5)Cl(NH_2RNH)_2][PF_6]\end{array}$$

salt (8); (9) was obtained analogously. Neither 1,1-dimethyl- nor 1-methyl-1-phenyl-hydrazine formed bis-complexes under these conditions, and even complexes (7)—(9) were rather labile. Acetone displaced the hydrazine in each case, with formation of (1a) from (7) and $[Rh_2(C_5Me_5)_2Cl_3][PF_6]$ from (8) or (9).

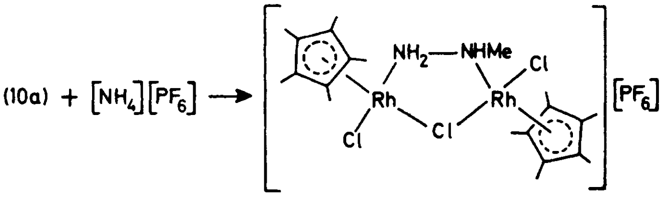
Binuclear Complexes from Methylhydrazine.—In contrast to the reaction with mono-aryl-, 1,1-dimethyl-, and 1-methyl-1-phenyl-hydrazines, which gave 1 : 1 adducts with (1a), the smaller methylhydrazine gave a 1 : 2 adduct $[Rh_2(C_5Me_5)_2Cl_4(NH_2NHMe)]$ (10a). Analogous complexes [(10b), (10c)] were obtained from the bromo- or iodo-complexes (1b), (1c).

Reaction of (10a) with $[NH_4][PF_6]$ in dichloromethane gave a good yield of the ionic $[Rh_2(C_5Me_5)_2Cl_3(NH_2NHMe)][PF_6]$ (11) together with 10% of $[Rh_2(C_5Me_5)_2Cl_3][PF_6]$. However, when the same reaction was attempted with the iodide (10c) the major product (71%) was $[Rh_2(C_5Me_5)_2I_3][PF_6]$ and only a small amount of the (presumed) iodo-analogue of (11) could be detected.

The n.m.r. spectra of (10a)—(10c) varied with temperature and showed that an exchange process was occurring. Thus, for example, the ^1H spectrum of (10a) at —40 °C showed two C_5Me_5 and two NMe resonances and six NH resonances, which could be grouped into two sets in the intensity ratio *ca.* 2 : 1. The peaks were assigned as discussed below on the basis of selective decoupling experiments; the NH resonances were also easily identified since they disappeared after exchanging with ^2H_2O. At higher temperatures the ^1H spectra became broader and coalesced; however, no sharp high-temperature limiting spectrum could be achieved below the decomposition temperature. A very similar series of ^1H spectra were obtained for the iodo-complex (10c), but in that case one species predominated to a much greater extent (*ca.* 1 : 4) at the limiting low temperature (—50 °C).

$$(1) + H_2NNHMe \longrightarrow [\{Rh(C_5Me_5)\}_2X_4(NH_2NHMe)]$$

(10a) X = Cl
(10b) X = Br
(10c) X = I

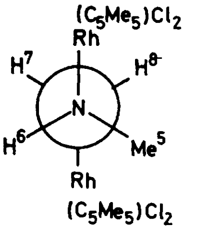


(11)

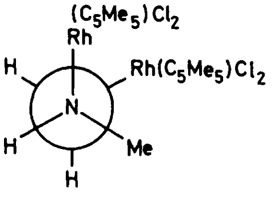
The ^{13}C spectrum of (10a) was also broad at 25 °C but sharpened at lower temperatures (—40 °C) when the C_5Me_5 resonances were observed as four doublets (arising from coupling to ^{103}Rh, $I = \frac{1}{2}$), implying the presence of four different RhC_5Me_5 groups, in the intensity ratio *ca.* 2 : 2 : 1 : 1. Again, the iodo-complex showed very similar behaviour.

By contrast, the ^1H and ^{13}C spectra of the ionic complex (11) were temperature invariant and showed the presence of two inequivalent RhC_5Me_5 units and the absence of a plane or centre of symmetry in the molecule. We accordingly suggest the structure shown for (11) with the methylhydrazine and one chlorine bridging two RhC_5Me_5 units.

Both the ^1H and the ^{13}C n.m.r. spectra of (11) were quite different to those found for (10a) at low temperature and we may therefore assume that the cation of (11) is not present in solutions of (10a). We can also exclude the existence of any significant amounts of mononuclear complexes in solutions of (10a). The ^1H spectrum clearly shows that the *N*-bonded hydrogens in both species present are all coupled and hence each hydrazine must have a rigid structure. If a hydrazine were unidentate free rotation about the N–N bond would be possible and vicinal couplings would collapse. We also discount the existence of an equilibrium between two monobridged rotamers (A and B) in order to explain the low-temperature spectra since molecular models indicate that the bulk of the $Rh(C_5Me_5)Cl_2$ groups is so great that the cisoid rotamer (B) would be energetically extremely unfavourable.

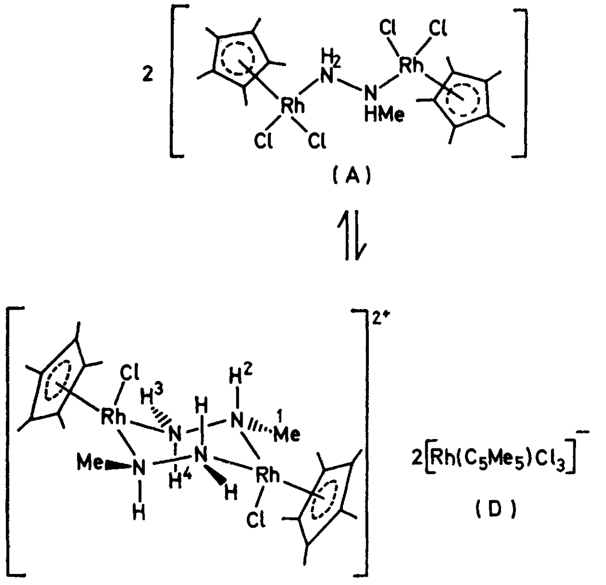


transoid, (A)



cisoid, (B)

In order to account for the n.m.r. spectra we suggest an equilibrium between the monobridged transoid form (A) and a dimeric dication (C) and its associated anion (D). The −40 °C 220-MHz ^1H n.m.r. spectrum of (10a) showed that the group (i) of one NMe and three NH bands of relative intensity 2 was at significantly lower field than the group (ii) of one NMe and three NH bands of relative intensity 1. We therefore assign the bands of group (i) to the dicationic complex (10aC) and the bands of group (ii) to the transoid neutral complex (10aA).



(C)

Molecular models indicate that steric repulsions are minimised if the centrosymmetric six-membered $Rh_2(NH_2NHMe)_2$ ring in (C) has the chair conformation with the N-methyls (Me^1) equatorial, as shown. The four resonances of group (i) were observed at δ 3.43 (d, $J = 7$ Hz, Me^1), 5.54 (dd, $J = J = 8$ Hz, H^4), 6.70 (m, H^2), and 8.75 p.p.m. (d, $J = 8$ Hz, H^3). Selective decoupling showed that H^2 was coupled to Me^1 and that the geminal hydrogens (H^3, H^4) were coupled. The remaining coupling of 8 Hz was between H^2 and H^3 or H^4. From the model it is clear that the dihedral angle between NH^2 (axial) and NH^3 (equatorial) is *ca.* 90° while that between NH^2 and NH^4 (axial) is *ca.* 150°. Although the Karplus relation for vicinal H–H coupling constants is normally only applied to carbon systems, we may note that it predicts a coupling close to 0 for dihedral angles of 90° and 7—12 Hz for an angle of 150°.[7] If we assume that such a relationship also holds for the rigid $Rh_2(NH_2NHMe)_2$ ring in (10aC) then clearly we would expect $J(H^2\text{–}H^3) = 0$ and therefore the 8 Hz coupling observed must be $J(H^2\text{–}H^4)$, arising from interaction of the two vicinal axial hydrogens.

The four resonances of group (ii) which we assign to $MeNHNH_2$ in (10aA) were observed at δ 2.90 (d, $J = 7$ Hz, Me^5), 3.13 (m, H^7), 4.38 (dd, $J = J = 7$ Hz, H^8), and 7.15 p.p.m. (m, $J = J = 7$ Hz, H^6). Once again, the NMe*H*, H^6, is easily assigned since it is coupled to Me^5, and the other two hydrogens H^7, H^8 are coupled to each other. One additional 7 Hz coupling was observed between H^6 and the resonances at δ 4.38 p.p.m.; which we therefore suggest to be H^8. Although it could not be resolved, the breadth of the peaks at δ 3.13 and 7.15 p.p.m. suggested the presence of a further small coupling ($\leqslant 3$ Hz) between them. These results are again entirely consistent with a rigid (at −40 °C) transoid structure (A) if a version of the Karplus relation also holds.

Associated with these $NHMeNH_2$ resonances are two C_5Me_5 signals (δ 1.60 and 1.81 p.p.m., ratio 2 : 1) the first of which is slightly broadened, probably due to the accidental near-equivalence of more than one peak. The ^{13}C n.m.r. spectrum (at −40 °C) shows the $C_5\mathit{Me}_5$ as a broad single resonance but the C_5Me_5 appear as four distinct doublets, as expected for a mixture of (10aA), (10aC), and (10aD). The two RhC_5Me_5 units are equivalent in the centrosymmetric form (C) but are inequivalent in (A); since each (C) dication is associated with two (D) anions the observation that the C_5Me_5 doublets are found to be in a 2 : 2 : 1 : 1 ratio is consistent with the ^1H n.m.r. spectra of the $NHMeNH_2$ ligands and indicates that $K = 33$ dm^3 mol^{-1} for the equilibrium, $2A \rightleftharpoons CD_2$.

The iodo-complex (10c) appeared to behave very similarly to (10a) but the 220-MHz ^1H spectrum at −50 °C was more difficult to analyse owing to difficulties in resolution. Nevertheless, it was clear that again two types of co-ordinated NH_2NHMe ligands were present: a group (ii) of intensity *ca.* 4 arising from (10cA) [δ 1.80, 1.95 (2 × s, $C_5\mathit{Me}_5$), 2.50 (d, Me, $J = 7$ Hz), 3.67 (m, H, $J = 7$ Hz), and 4.25 p.p.m. (m, H)] and a group (i) of intensity *ca.* 1 arising from (10cC) [δ 1.85 ($C_5\mathit{Me}_5$), 2.82 (d, Me, $J = 7$ Hz), and 4.75 p.p.m. (m, H, $J = 7$ Hz)].

Hydrazine Complexes.—When complex (1a) was treated with an excess of hydrazine complete decomposition with the formation of metal occurred. However, a stoicheiometric reaction of (1a) with N_2H_4 (1 equivalent per rhodium) gave an orange solution which yielded an unstable orange material that, largely on the basis of its ^1H n.m.r. spectrum in C^2HCl_3, we suggest to be the 1 : 1 adduct $[Rh(C_5Me_5)Cl_2(N_2H_4)]$ (12). When the orange solution was allowed to stand for a longer time it turned red and a yellow precipitate was formed. The red solution yielded only complex (1a) while the yellow precipitate was characterised as the tris(hydrazine) complex (13).

$$\underset{(1a)}{[Rh_2(C_5Me_5)_2Cl_4]} + 2N_2H_4 \longrightarrow \underset{(12)}{[Rh(C_5Me_5)Cl_2(N_2H_4)]}$$

$$(12) \longrightarrow \underset{(13)}{[Rh(C_5Me_5)(N_2H_4)_3]Cl_2} + (1a)$$

Tris(ammine) Complexes.—In order to compare ammonia and hydrazine as ligands, complex (1a) dissolved in dichloromethane was treated with liquid ammonia. An immediate reaction occurred as shown by the colour change from red to yellow. From the solution a very insoluble and hygroscopic complex, characterised as $[Rh(C_5Me_5)(NH_3)_3]Cl_2$ (14), was isolated. The more soluble hexafluorophosphate salt $[Rh(C_5Me_5)(NH_3)_3][PF_6]_2$ (15) was obtained by treatment of a suspension of (1a) and $Ag[PF_6]$ in dichloromethane with liquid ammonia.

EXPERIMENTAL

Analytical and ^1H and ^{13}C n.m.r. data are collected in the Table. Analyses were determined by the University of Sheffield Microanalytical Service. ^1H N.m.r. spectra were run on Perkin-Elmer R12B (60 MHz) or R-34 (220 MHz) spectrometers, ^{13}C n.m.r. spectra on a JEOL PFT-100 spectrometer. Tetramethylsilane was used as reference. All reactions were carried out under a nitrogen atmosphere.

$[Rh(C_5Me_5)Cl_2(NH_2NMe_2)]$ (2a).—A solution of $[Rh_2(C_5Me_5)_2Cl_4]$ (0.40 g, 0.65 mmol) and Me_2NNH_2 (0.08 g, 1.3 mmol) in dichloromethane (40 cm^3) was stirred for 3 h; during this time the colour changed from dark red to orange-red. The solvent was then removed *in vacuo* and the product was crystallised as orange-red crystals from dichloromethane–di-isopropyl ether, yield 0.44 g (92%). The following complexes (yields in parentheses) were made by the same route from the appropriate dihalogeno-complex and hydrazine: (2b), bright red (80); (2c), purple (84); (3a), red (71); (4a), red (89); (5a), bright red (86); and (6a), orange-brown (86%).

Reaction of complexes (2a), (3a), or (4a) with HBF_4 in dichloromethane gave only $[Rh_2(C_5Me_5)_2Cl_3][BF_4]$; this complex was also obtained (93%) from the reaction of $[Rh_2(C_5Me_5)_2Cl_4]$ with HBF_4 in dichloromethane (Found: C, 35.5; H, 4.6; Cl, 15.7. $C_{20}H_{30}BCl_3F_4Rh_2$ requires C, 35.9; H, 4.5; Cl, 15.9%). ^1H N.m.r. (C^2HCl_3): δ 1.65 p.p.m. ^{13}C N.m.r. ($C^2H_2Cl_2$): δ 9.5 ($C_5\mathit{Me}_5$) and 96.6 p.p.m. [d, J(C–Rh) = 10.6 Hz, C_5Me_5].

$[Rh(C_5Me_5)Cl(NH_2NHPh)_2]Cl$ (7).—A suspension of $[Rh_2(C_5Me_5)_2Cl_4]$ (0.20 g, 0.32 mmol) in phenylhydrazine (5 cm^3) was stirred for 15 h. Addition of diethyl ether (100 cm^3) to the now orange-yellow viscous solution caused a bright yellow solid to precipitate. The precipitate was filtered off and crystallised from dichloromethane–diethyl ether to afford an orange-yellow powder, yield 0.31 g (91%). Reaction of (7) with acetone (1 h, 20 °C) gave $[Rh_2(C_5Me_5)_2Cl_4]$ (98%).

$[Rh(C_5Me_5)Cl(NH_2NHR)_2][PF_6]$ [R = Ph (8) *or* p-MeC_6H_4 (9)].—A suspension of $[Rh_2(C_5Me_5)_2Cl_4]$ (0.20 g, 0.32 mmol) and $[NH_4][PF_6]$ (0.50 g, an excess) in $RNHNH_2$ (5 cm^3) was stirred for 15 h. Addition of diethyl ether (100 cm^3) to the viscous solution caused a pale yellow solid to precipitate. The solid was filtered off and then dissolved in dichloromethane (20 cm^3); the solution was filtered to remove $[NH_4]Cl$ and $[NH_4][PF_6]$ and the product was crystallised to afford orange crystals on addition of di-isopropyl ether [yield 82% for (8), 79% for (9)]. Reaction of (8) or (9) in acetone (1 h) (20 °C) gave $[Rh_2(C_5Me_5)_2Cl_3][PF_6]$ (Found: C, 33.4; H, 4.4; Cl, 13.9. $C_{20}H_{30}Cl_3F_6PRh$ requires C, 33.0; H, 4.2; Cl, 14.6%). This complex was also obtained when (2a) was reacted with $Tl[PF_6]$ in CH_2Cl_2.

$[Rh_2(C_5Me_5)_2Cl_4(NH_2NHMe)]$ (10a).—A solution of $[Rh_2(C_5Me_5)_2Cl_4]$ (0.40 g, 0.65 mmol) and $MeHNNH_2$ (0.03 g, 0.65 mmol) in dichloromethane (20 cm^3) was stirred for 3 h. The solvent was removed *in vacuo* and the product crystallised from dichloromethane–di-isopropyl ether to afford orange microcrystals, yield 0.39 g (90%). The complexes (10b; red, 66%) and (10c; maroon, 84%) were obtained analogously. When complex (10a) was dissolved in acetone (20 °C, 1 h) $[Rh_2(C_5Me_5)_2Cl_4]$ (91%) was obtained.

$[Rh_2(C_5Me_5)_2Cl_3(NH_2NHMe)][PF_6]$ (11).—A suspension of $[NH_4][PF_6]$ (0.50 g, an excess) and (10a) (0.20 g, 0.30 mmol) in dichloromethane (20 cm^3) was stirred for 1 h. The solution was filtered to remove $[NH_4]Cl$ and $[NH_4][PF_6]$ and the solvent was removed *in vacuo*. The product was crystallised from dichloromethane–di-isopropyl ether to afford dark red crystals, yield 0.19 g (80%). A by-product from this reaction was identified as $[Rh_2(C_5Me_5)_2Cl_3][PF_6]$ (10%) and complex (11) could be converted (91%) into this complex on stirring in acetone.

Reaction of $[Rh_2(C_5Me_5)_2I_4(NH_2NHMe)]$ *with* $[NH_4][PF_6]$.—When complex (11c) was treated with $[NH_4][PF_6]$ as described above only a small amount (10%) of $[Rh_2(C_5Me_5)_2I_3(NH_2NHMe)][PF_6]$ could be detected. The major product (71%) was $[Rh_2(C_5Me_5)_2I_3][PF_6]$ (Found: C, 23.8; H, 3.0; I, 38.3. $C_{20}H_{30}F_6I_3PRh$ requires C, 24.0; H, 3.0; I, 38.0%).

Reaction of $[Rh_2(C_5Me_5)_2Cl_4]$ *with* N_2H_4.—A solution of $[Rh_2(C_5Me_5)_2Cl_4]$ (0.20 g, 0.23 mmol) and anhydrous hydrazine (0.02 g, 0.65 mmol) in dichloromethane (10 cm^3) was stirred for 10 min. The solvent was removed *in vacuo* from the orange solution to leave an orange residue (12) which was unstable and could not be purified. ^1H N.m.r. ($CDCl_3$): δ 1.80 (s, br, C_5Me_5), 3.44, 6.41 p.p.m. (v br, NH). I.r.: ν(NH) at 3 000—3 200vs,br cm^{-1}.

A solution of $[Rh_2(C_5Me_5)_2Cl_4]$ (0.20 g, 0.32 mmol) and anhydrous hydrazine (0.02 g, 0.65 mmol) in dichloromethane (10 cm^3) was stirred for 15 h; during this time a yellow solid was precipitated while the colour of the solution changed back from orange to dark red. The precipitate was filtered off, washed with diethyl ether (2 × 10 cm^3), and dried to afford $[Rh(C_5Me_5)(N_2H_4)_3]Cl_2\cdot H_2O$ (13) as a bright yellow powder, yield 0.05 g (19%). The dark red solution was also collected and the solvent removed *in vacuo*. The residue was washed with diethyl ether (2 × 10 cm^3) and dried, to afford $[Rh_2(C_5Me_5)_2Cl_4]$ as a brick-red powder, yield 0.12 g (60%).

$[Rh(C_5Me_5)(NH_3)_3][Cl_2]$ (14).—A solution of $[Rh_2(C_5Me_5)_2Cl_4]$ (0.20 g, 0.32 mmol) in dichloromethane (10 cm^3) was added to liquid ammonia (30 cm^3); an immediate colour change occurred, from red to pale yellow. The reaction was stirred for 3 h; during this time the liquid ammonia evaporated off to leave a yellow suspension. The precipitate was filtered off, washed with acetone (20 cm^3), chloroform (20 cm^3), and diethyl ether (20 cm^3), and dried to give a pale yellow powder, yield 0.22 g (96%).

$[Rh(C_5Me_5)(NH_3)_3][PF_6]_2$ (15).—Liquid ammonia (20 cm^3) was added to a suspension of $[Rh_2(C_5Me_5)_2Cl_4]$ (0.20 g, 0.32 mmol) and $Ag[PF_6]$ (0.33 g, 1.29 mmol) in dichloromethane (10 cm^3). The suspension was then stirred for 2 h while the ammonia was allowed to evaporate off to leave a yellow suspension. The solvent was removed *in vacuo* and the residue dissolved in acetone (10 cm^3). The solution was filtered to remove AgCl and the product was crystallised as bright yellow crystals on addition of di-isopropyl ether, yield 0.29 g (78%).

We thank Mr. P. Tyson and Dr. B. F. Taylor for running n.m.r. spectra, and the S.R.C. for support.

[8/990 *Received*, **26*th May*, 1978**]

REFERENCES

[1] Part 19, W. Rigby, P. M. Bailey, J. A. McCleverty, and P. M. Maitlis, preceding paper.

[2] J. W. Kang, K. Moseley, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1969, **91**, 5970.

[3] J. W. Kang and P. M. Maitlis, *J. Organometallic Chem.*, 1971, **30**, 127.

[4] C. White, A. J. Oliver, and P. M. Maitlis, *J.C.S. Dalton*, 1973, 1901.

[5] N. A. Bailey, P. D. Frisch, J. A. McCleverty, N. W. Walker, and J. Williams, *J.C.S. Chem. Comm.*, 1975, 350.

[6] F. Bottomley, *Quart. Rev.*, 1970, **24**, 617 and refs. therein.

[7] S. Sternhell, *Quart. Rev.*, 1969, **23**, 236.