Cationic Ruthenium(II) Systems. Part 1. The Preparation and Reactivity of Diene(hydrazine)ruthenium(II) Cations, and the Formation of Amino-bonded Hydrazone Complexes

By **Terence V. Ashworth, Eric Singleton,*** and **Johannes J. Hough,** National Chemical Research Laboratory, Council for Scientific and Industrial Research, Pretoria 0001, Republic of South Africa

The polymeric species $[\{RuCl_2(diene)\}_n]$ (1; $n > 2$) and the appropriate hydrazine have been used to prepare the salts $[Ru(diene)(N_2H_4)_4][BPh_4]_2$ {2; diene = bicyclo[2.2.1]hepta-2,5-diene(nbd) or cyclo-octa-1,5-diene(cod)} $[Ru(cod)(NH_2NHMe)_4][PF_6]_2$, and $[RuH(cod)(NH_2NRR')_3]X$ [R = R′ = Me, X = BPh_4 (3) or X = PF_6 (4); R = H, R′ = H or Me, X = BPh_4 (5)]. Solutions of (2; diene = cod) in refluxing acetone–ethanol mixtures give a complex of stoicheiometry $[Ru(BPh_4)(cod)]$ (6) and, in the presence of ligands L, $[Ru(cod)L_4][BPh_4]_2$ [L = pyridine (py), Me_2SO (dmso), or MeCN], $[RuL_6][BPh_4]_2$ (L = 4Me-py or dmso), and the hydrazone-containing salts $[Ru(NH_2NCMe_2)_2L_4][BPh_4]_2$ {7; L = $P(OMe)_3$, $P(OEt)_3$, $P[(OCH_2)_3CR]$ (R = Me or Et), and $PPh(OMe)_2$}. Treatment of $[Ru(cod)(NH_2NHMe)_4][PF_6]_2$ with $PPh(OMe)_2$ in acetone produces $[Ru(NH_2NHMe)_2\{PPh(OMe)_2\}_4][PF_6]_2$. Substitution reactions of (3) give $[RuH(cod)L_3]^+$ [L = py, 4Me-py, or MeCN] and $[RuHL_5]^+$ [L = $PPh(OMe)_2$, $P(OEt)_3$, or $PPh(OEt)_2$], while the neutral complexes $[\{RuXH(cod)\}_2NH_2NMe_2]$ (8) have been prepared from (3) and LiX (X = Cl or Br) in methanol or acetone solutions. Complex (8) may be converted into $[RuXH(PPh_3)_3]$ and $[RuXH(cod)(PMePh_2)_2]$ (X = Cl or Br) with PPh_3 and $PMePh_2$ respectively.

THE growing interest in the synthesis and reactivity of cationic ruthenium(II) complexes during the past few years has provided a fairly extensive series of stable ruthenium(II) salts containing a wide variety of ligands which co-ordinate *via* carbon,[1,2] oxygen,[3,4] nitrogen,[5,6] or phosphorus atoms.[7] These complexes have been prepared by a number of procedures including halide-ion displacement by neutral ligands in the presence of large counter ions,[8,9] abstraction of hydride[10] or an η-allyl ligand[5] by H^+ or $[CPh_3]^+$, substitution reactions of suitable readily available starting materials, *e.g.* $RuCl_3 \cdot xH_2O$,[11] chemical modification of a co-ordinated ligand into a non- or weakly binding form,[12] and, more recently, substitution followed by reduction of ruthenium(III) precursors.[13] In general these procedures have led to a specific and limited range of products and, as yet, suitable general precursors which lead by direct substitution reactions to an extensive variety of cationic complexes have not been reported. In contrast, a wide range of very reactive cationic rhodium(I) and iridium(I) complexes have been obtained[14] in this laboratory from substitution reactions of the readily available $[\{MCl(cod)\}_2]$ (M = Rh or Ir, cod = cyclo-octa-1,5-diene) with neutral ligands. These reactions occur *via* a rapid initial solvolysis step in alcohol solvents, but the insoluble nature of the corresponding ruthenium complex $[\{RuCl_2(cod)\}_n]$ (1; $n > 2$) has to date precluded solvolysis as a route to cationic ruthenium(II) systems. However, a few salts have been prepared[15] from the polymer with phosphites and related ligands under more extreme conditions but the range was limited.

We have now found that suspensions of (1) in methanol or ethanol rapidly react with hydrazines to produce clear solutions from which salts containing dienehydrazine-ruthenium(II) cations can be isolated on addition of a suitable counter anion. These complexes are highly labile in solution making them ideal precursors for an extensive range of new ruthenium(II) salts as well as for many known ruthenium(II) complexes. We report here the preparation of these hydrazine salts, their characterization together with i.r. and ^1H n.m.r. data, and some representative reactions to demonstrate their usefulness. Part of this work has been briefly reported[16] together with other notes[17-19] on new highly reactive species that have been synthesized *via* these complexes by simple substitution reactions.

RESULTS AND DISCUSSION

Treatment of a suspension of [1; diene = cod or norbornadiene (nbd)] in methanol with anhydrous hydrazine rapidly gave pale red solutions from which the salts $[Ru(diene)(N_2H_4)_4][BPh_4]_2$ (2; diene = cod or nbd) were isolated in high yield on addition of an aqueous solution of $Na[BPh_4]$. Tetraphenylborate was the only counter anion that effected precipitation and attempts to

---

[1] M. L. H. Green, L. C. Mitchard, and M. G. Swanwick, *J. Chem. Soc.* (*A*), 1971, 794.

[2] D. J. Doonan and A. L. Balch, *Inorg. Chem.*, 1974, **13**, 921.

[3] D. F. Christian and W. R. Roper, *J. Organometallic Chem.*, 1974, **80**, C35.

[4] R. J. Young and G. Wilkinson, *J.C.S. Dalton*, 1976, 719.

[5] R. R. Schrock, B. F. G. Johnson, and J. Lewis, *J.C.S. Dalton*, 1974, 951.

[6] P. C. Ford, *Co-ordination Chem. Rev.*, 1970, **5**, 75.

[7] J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 1961, 896; M. S. Lupin and B. L. Shaw, *J. Chem. Soc.* (*A*), 1968, 741.

[8] T. Blackmore, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 2376.

[9] G. M. Bancroft, M. J. Mays, B. E. Prater, and F. P. Stefanini, *J. Chem. Soc.* (*A*), 1970, 2146.

[10] J. R. Sanders, *J.C.S. Dalton*, 1973, 743.

[11] P. W. Armit, A. S. F. Boyd, and T. A. Stephenson, *J.C.S. Dalton*, 1975, 1663 and refs. therein.

[12] S. A. Adfyemi, E. C. Johnson, F. J. Miller, and T. J. Meyer, *Inorg. Chem.*, 1973, **12**, 2371.

[13] L. Ruiz-Raminz and T. A. Stephenson, *J.C.S. Dalton*, 1975, 2244.

[14] L. M. Haines, *Inorg. Chem.*, 1970, **9**, 1517; 1971, **10**, 1685; L. M. Haines and E. Singleton, *J.C.S. Dalton*, 1972, 1891.

[15] D. A. Couch and S. D. Robinson, *Inorg. Chim. Acta*, 1974, **9**, 39; *Inorg. Chem.*, 1974, **13**, 456.

[16] J. J. Hough and E. Singleton, *J.C.S. Chem. Comm.*, 1972, 371.

[17] T. V. Ashworth and E. Singleton, *J.C.S. Chem. Comm.*, 1976, 204.

[18] T. V. Ashworth and E. Singleton, *J.C.S. Chem. Comm.*, 1976, 705.

[19] T. V. Ashworth, E. Singleton, and M. Laing, *J.C.S. Chem. Comm.*, 1976, 875.

isolate the cations of (2) with other anions, *e.g.* $[BF_4]^-$ and $[PF_6]^-$, were unsuccessful. The i.r. and ^1H n.m.r. evidence and the variation of the C, H, and N analytical data obtained for different samples indicated varying and non-stoicheiometric quantities of water of crystallization in the crude product, and recrystallization from mixtures of anhydrous solvents gave crystalline products which always contained solvent of crystallization. The filtrate from the above reactions yielded a further crop of crystals over 24 h which contained a mixture of products which were extremely difficult to separate. These products were therefore not further investigated. Under similar conditions the cyclohepta-1,3,5-triene (cht) complex $[\{RuCl_2(cht)\}_n]$ ($n > 2$) gave the known[20] salt $[Ru(NH_3)_5(N_2)][BPh_4]_2$ as the only isolable product. A suspension of (1; diene = cod) in methanol dissolved on addition of NH_2NHMe to give a dark red-brown solution from which the salt $[Ru(cod)(NH_2NHMe)_4][PF_6]_2$ was isolated on addition of an aqueous solution of $[NH_4][PF_6]$.

In contrast, when a suspension of (1; diene = cod) was heated in a 1 : 1 mixture of methanol and aqueous *NN*-dimethylhydrazine (90%) for 15 min a dark brown solution was formed from which the hydride $[RuH(cod)(NH_2NMe_2)_3][BPh_4]$ (3) precipitated in two crystalline forms (plates and needles) with $Na[BPh_4]$, depending only on the water : methanol ratio. Thus additions of an aqueous solution of $Na[BPh_4]$ effected precipitation in plate form [ν(Ru–H) at 2 050 cm^{-1}] while the needle form of (3) [ν(Ru–H) at 2 000 cm^{-1}] crystallized on addition of methanol solutions of $Na[BPh_4]$. However, the ^1H n.m.r. spectra of the two forms were identical and, since the difference in the i.r. absorption frequencies of the metal hydride can be ascribed to differences in crystal packing, there is no unequivocal evidence that two geometrical isomers of (3) exist in the solid state as was originally proposed.[16] The salt $[RuH(cod)(NH_2NMe_2)_3][PF_6]$ (4) was also isolated from the above dark brown solutions but, because of its higher solubility, better yields were obtained by concentrating the solution under reduced pressure after adding an aqueous solution of $[NH_4][PF_6]$.

Other hydrazinehydrido-cations were prepared from the salts (3) by ligand exchange. For example the salts $[RuH(cod)(NH_2NHR)_3][BPh_4]$ (5; R = H or Me) were obtained by treating a suspension of (3) in methanol under reflux with NH_2NHR (R = H or Me). Complex (5; R = H) also formed directly from (1; diene = cod), after several hours, on heating under reflux a solution of (1) in a 1 : 1 mixture of aqueous hydrazine (60%) and methanol.

All of the above complexes decompose in air, moisture, or light over a period of *ca.* 1 week and are best kept in the dark and under a dry inert atmosphere.

The i.r. spectra of complexes (2)—(5) have characteristic bands in the 3 100—3 360 regions [ν(N–H)], 1 590—1 640 (asymmetric N–H bending), and 915—930 cm^{-1} [ν(N–N)] regions. The ν(N–N) frequency has been used previously[21] to indicate the type of hydrazine co-ordination since it is reported to increase from 875 cm^{-1} in free hydrazine to *ca.* 930 cm^{-1} in complexes containing unidentate hydrazine ligands and to 948—985 cm^{-1} in complexes with bridging hydrazine ligands. Thus the values for ν(N–N) (see Table 1) suggest that all the hydrazine ligands are unidentate in the above complexes.

Surprisingly the ^1H n.m.r. spectra of (2)—(5) contained reasonably well defined resonances attributable to protons directly attached to the nitrogen atoms of the co-ordinated hydrazine and substituted hydrazine ligands. The spectra reported here represent to our knowledge the first examples of proton resonances being observed in the ^1H n.m.r. of metal hydrazine complexes as exchange reactions and the ^{14}N nuclear-quadrupole moment[22] tend to broaden proton resonances in hydrazine compounds to such a degree that they become unobservable. No $^{14}N(I = 1)$–^1H spin–spin couplings were discernible in any of these spectra, due probably to the rapid relaxation of the ^{14}N quadrupole moment. Relevant proton spectra of (2; diene = cod) recorded in CD_3CN contained weak bands at τ 3.9 and 5.3 (4 H) and a strong resonance at τ 6.3 (16 H). Shaking the solution with D_2O caused the resonances at τ 3.9 and 5.3 to collapse and the signal at τ 6.3 to sharpen, whereas CF_3CO_2H additions shifted part of the resonance at τ 6.3 (12 H) revealing a very broad olefinic proton resonance at τ 6.2—6.9 (4 H). Thus we assign the resonances at τ 3.9 and 5.3 to NH_2 protons of the co-ordinated nitrogen, and part of the resonance at τ 6.3 to protons on the unco-ordinated NH_2 ends. These latter integration ratios further confirm the stoicheiometry as $[Ru(cod)(NH_2NH_2)_4][BPh_4]_2$ and exclude the presence of bridging hydrazine ligands. The integration of only 4 H for the resonances at τ 3.9 and 5.3 could be a consequence of ligand-exchange reactions.

The ^1H n.m.r. spectra of $[Ru(cod)(NH_2NHMe)_4][PF_6]_2$ contained weak broad resonances in the τ 2.0—4.6 region which are assigned to NH protons, and singlets at τ 6.7 and 7.48 for the NMe protons. It was not possible to determine whether all the methylhydrazine groups were bonded through the NH_2 end in this complex.

The ^1H n.m.r. spectra of the hydrido-salts (3) and (4) contained resonances at τ 4.03 (br, 2 H) and 5.48 (centre of an 'AB quartet',[23] 4 H) for (3) and at τ 3.83 (br, 2 H) and 5.10 (centre of an 'AB quartet', 4 H) for (4) which are assigned to NH_2 protons from D_2O exchanges. The methyl protons were observed at τ 7.48 (6 H) and 7.80 (12 H) for (3) and at τ 7.25 (6 H) and 7.57 (12 H) for (4), whilst the diene protons occurred in the range τ 6.6—8.8 for both salts. The upfield chemical shifts observed in the resonances of these cations on changing the anion from $[PF_6]^-$ to $[BPh_4]^-$ may be due in part to anisotropic shielding effects of the phenyl groups on the tetraphenyl-

---

[20] A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Amer. Chem. Soc.*, 1967, **89**, 5595.

[21] D. Nicholls, M. Rowley, and R. Swindells, *J. Chem. Soc.* (*A*), 1966, 950; D. Nicholls and R. Swindells, *Inorg. Chem.*, 1968, **7**, 2211.

[22] J. A. Pople, W. G. Schneider, and H. J. Bernstein, 'High-resolution Nuclear Magnetic Resonance,' McGraw-Hill, 1959, p. 226.

[23] Ref. 22, p. 119.

TABLE 1

Melting points and i.r. and analytical data for new ruthenium complexes

		Analyses (%) [b]			I.r. data [c] (cm^{-1})				
						δ(NH)			
Complex	M.p.[a] (θ_c/°C)	C	H	N	ν(NH)	asym	sym	ν(NN)	Other
$[Ru(cod)(N_2H_4)_4][BPh_4]_2$	160—165	68.4 (68.9)	7.1 (7.0)	11.2 (11.5)	3 100— 3 360m	1 612 (sh), 1 606s	1 140m, 1 149m	920m	
$[Ru(nbd)(N_2H_4)_4][BPh_4]_2$	230—240	68.8 (68.8)	6.9 (6.7)	11.4 (11.7)	3 318m, 3 270m, 3 160m	1 609s	1 145w, 1 120w	930m	
$[Ru(cod)(NH_2NHMe)_4][PF_6]_2$	140—145	20.9 (21.1)	4.9 (5.3)	15.9 (16.4)	3 330m, 3 310m, 3 260w	1 620m	1 135m	Obscured	840s ν(PF), 560s δ(PF)
$[RuH(cod)(NH_2NMe_2)_3][BPh_4]$	148	64.5 (64.3)	8.1 (8.1)	11.6 (11.8)	3 205s, 3 198 (sh)	1 601s	1 142 (sh) 898w	921m,	2 050m ν(RuH), also 2 020m (see text)
$[RuH(cod)(NH_2NMe_2)_3][PF_6]$	115	31.4 (31.5)	6.9 (6.8)	15.5 (15.7)	3 235s, 3 060s	1 600m	1 160m, 1 145m	915m	2 040m ν(RuH), 840s ν(PF), 560s δ(PF)
$[RuH(cod)(N_2H_4)_3][BPh_4]$	230	61.2 (61.4)	7.2 (7.3)	13.4 (13.4)	3 160— 3 360m	1 621 (sh), 1 608s	1 120m	924s, 908 (sh)	2 000m ν(RuH)
$[RuH(cod)(NH_2NHMe)_3][BPh_4]$	148—150	63.2 (63.0)	7.3 (7.7)	12.5 (12.6)	3 270m, 3 220m, 3 120 (sh)	1 620m, 1 605m	1 120m, 1 140m	900w	2 020m ν(RuH)
$[Ru(NH_2NCMe_2)_2L_4][BPh_4]_2$:									
L = $P(OMe)_3$	209	57.0 (57.4) P 9.1 (9.0)	6.8 (6.7)	4.1 (4.1)	3 280w	*d*			1 640w [e]
$P(OEt)_3$	163—170	59.1 (60.5)	7.3 (7.1)		3 280w	*d*			1 640w [e]
$P[(OCH_2)_3CMe]$	195—198	60.4 (60.2)	6.3 (6.3)	5.4 (3.8)	3 265w	*d*			1 650w [e]
$P[(OCH_2)_3CEt]$	200—201	61.0 (61.1)	6.6 (6.6)	4.2 (3.7)	3 250w	*d*			1 640w [e]
$PPh(OMe)_2$ [f]	170	63.7 (63.6) Cl 4.4 (4.3)	6.4 (6.2) P 7.8 (7.5)	3.0 (3.4)	3 280w	*d*			1 650w [e]
$[Ru(NH_2NHMe)_2\{PPh(OMe)_2\}_4][PF_6]_2$	162—165	35.1 (35.0)	5.0 (4.9)	4.9 (4.8)	3 330m 3 270m,	1 580m			
$[\{RuClH(cod)\}_2NH_2NMe_2]$	165	39.6 (39.2) Cl 13.5 (12.9)	6.4 (6.2)	4.8 (5.1)	3 245w, 3 120w,	1 570m		→	2 055m, 2 035m ν(RuH); 995m, 970w, 955w, 920w [g]
$[\{RuBrH(cod)\}_2NH_2NMe_2]$	190	33.6 (33.8) Br 24.6 (25.0)	5.4 (5.4)	4.4 (4.4)	3 260w, 3 140w	1 560m		→	2 060m, 2 030m ν(RuH); 990m, 975w, 950w, 920w [g]
$[Ru(BPh_4)(cod)]$	200	73.0 (72.9) B 2.3 (2.1)	5.9 (5.9)		1 580m, 1 485m, 1 450m, 1 430m, 1 396m (bands associated with $[BPh_4]$ [h])				
$[Ru(cod)(py)_4][BPh_4]_2$	175	78.1 (78.4)	6.0 (6.3)	5.3 (4.8)	1 619m, 1 600m ν(CN) or ν(CC) of pyridine				
$[Ru(cod)(dmso)_4][BPh_4]_2$	160	65.9 (66.3) S 11.4 (11.1)	6.7 (6.6)		920—950s ν(SO) *O*-bonded,[i] 1 425s δ_d (CH), 1 040 ρ_r(CH), 980s ρ_r(CH)				
$[Ru(cod)([^2H_6]dmso)_4][BPh_4]_2$					2250m, 2130m ν(CD); 1015m δ_d(CD), 825m ρ_r(CD), 765(sh) ρ_r(CD)				
$[Ru(4Me\text{-}py)_6][BPh_4]_2$	200	77.4 (77.6)	6.4 (6.6)	6.3 (6.5)	1 620m ν(CN), ν(CC) of 4Me-py				
$[Ru(dmso)_6][BPh_4]_2$ [j]		58.8 (57.9) S 18.2 (17.5)	6.4 (6.4)		1 120br, s, ν(SO) *S*-bonded;[i] 930s ν(SO) *O*-bonded;[i] 1 425m, 1 315m δ_d(CH); 1 030m, 1 010m, 990m, 980m, 920 (sh) ρ_r(CH)				
$[Ru([^2H_6]dmso)_6][BPh_4]_2$					1 015m, 945 (sh), δ_d(CD); 835m, 827m, 815m, 810 (sh), 780w, 765w ρ_r(CD); 2 280m, 2 270m, 2 265m, 2 135m ν(CD)				
$[RuH(cod)(4Me\text{-}py)_3][BPh_4]$	150	74.3 (74.3)	6.6 (6.7)	5.1 (5.2)	2 070m ν(RuH), 1 620m ν(CN), ν(CC) of 4Me-py				
$[RuH(cod)(py)_3][BPh_4]$	147	72.9 (73.6)	6.1 (6.3)	5.2 (5.5)	2 060w ν(RuH), 1 600m ν(CN), ν(CC) of py				

[a] In air. All the complexes decomposed on melting. [b] Calculated values are in parentheses. [c] Nujol mulls unless otherwise stated. [d] Not observed; possibly obscured by band at 1 580 cm^{-1} due to $[BPh_4]$, *e.g.* see $[Ru(NH_2NHMe)_2\{PPh(OMe)_2\}_4][PF_6]_2$. [e] ν(C=N). [f] Calculated with 1 mol of CH_2Cl_2 per mol of complex. [g] In the region for ν(NN). [h] KBr disc. [i] Assigned from comparison of spectra of $[^2H_6]$dmso analogues. [j] Calculated with 1 mol of dmso solvent per mol of complex.

borate anion.[24] The ^1H n.m.r. spectra of the corresponding salts $[RuH(cod)(NH_2NHR)_3][BPh_4]$ (R = H or Me) in $[^2H_6]$dimethyl sulphoxide and CD_3CN respectively contained broad unresolved resonances in the τ 3.0—6.0 region and a singlet for the methyl protons at τ 7.05. It thus seems in this latter case that a rapid intra- or intermolecular exchange process is occurring in solution to equilibrate the methyl protons. In the case of (3) and (4) this process is evidently slow enough to allow a magnetic distinction to be made between the two NH_2 protons (there is no plane of symmetry along the Ru–N bond) on two equivalent hydrazine ligands.

TABLE 2

Hydrogen-1 n.m.r. data for new ruthenium complexes

Complex	Solvent	^1H N.m.r. data (τ [a])
$[Ru(cod)(N_2H_4)_4][BPh_4]_2$	CD_3CN	3.96 (br) [b] (NH_2, 2 H), 5.28 (br) [b] (NH_2, 2 H), 5.8—6.7 (br) [c,d] (CH and NH_2, 4 + 12 H), 7.9 (br) (CH_2, 8 H)
$[Ru(nbd)(N_2H_4)_4][BPh_4]_2$	$(CD_3)_2CO$	6.7—8.2 (protons of nbd), hydrazine protons not observed
$[Ru(cod)(NH_2NHMe)_4][PF_6]_2$	CD_3CN	2.0—5.0 (br) [b] (NH or NH_2), 5.3—8.2 (br) [c,d] (NH, NH_2, and cod protons), 6.70 (s), 7.48 (s) [d] (NMe)
$[RuH(cod)(NH_2NMe_2)_3][BPh_4]$	CD_2Cl_2	4.03 (br) [b] (NH_2, 2 H), 5.48 [e] (τ_A 5.14,[b] τ_B 5.79,[b] J 10.0,[f] NH_2, 4 H), 7.48 [d] (6 H), 7.80 [d] (12 H, NMe_2), 6.5—8.8 (cod, 12 H), 15.70 (RuH)
$[RuH(cod)(NH_2NMe_2)_3][PF_6]$	CD_2Cl_2	3.83 (br) [b] (NH_2, 2 H), 5.10 [e] (τ_A 4.83,[b] τ_B 5.37,[b] J 10.25,[f] NH_2, 4 H), 7.27 [d] (6 H), 7.55 (12 H, NMe), 6.5—9.0 (cod, 12 H), 15.57 (RuH)
$[RuH(cod)(N_2H_4)_3][BPh_4]$	$(CD_3)_2SO$	3.6—4.1 (br) [b] (NH_2), 4.8—5.5 (br) [b] (NH_2), 5.9—8.9 (br) [c] (NH_2 and cod), 15.5 (RuH)
$[RuH(cod)(NH_2NHMe)_3][BPh_4]$	CD_3CN	4.1 (br) [b], 5.7 (br) [b] (NH or NH_2), 6.1—8.8 (NH, NH_2, and cod), 7.55 (s) (NMe), 15.5 (br) (RuH)
$[Ru(NH_2NCMe_2)_2L_4][BPh_4]_2$:		
L = $P(OMe)_3$	CD_3CN	6.14 (m) (OMe, 36 H), 8.25 (N=CMe_2, 12 H)
$P(OEt)_3$	CD_2Cl_2	5.7—6.3 (br) (OCH_2, 24 H), 8.16 (N=CMe_a, 6 H), 8.33 (N=CMe_b, 6 H), 9.7 (t) (J 9.5,[f] OCH_2CH_3, 36 H)
$P[(OCH_2)_3CMe]$	CD_2Cl_2	5.91 (m) (OCH_2, 24 H), 8.22 (N=CMe_a, 6 H), 8.50 (N=CMe_b, 6 H), 9.38 (CMe, 12 H)
$P[(OCH_2)_3CEt]$	CD_2Cl_2	5.87 (m) (OCH_2, 24 H), 8.20 (N=CMe_a, 6 H), 8.50 (N=CMe_b, 6 H), 7.9—9.5 (m) (CH_2CH_3, 20 H)
$PPh(OMe)_2$	CD_2Cl_2	6.5—7.0 (m) (OMe, 24 H), 8.30 (N=CMe_a, 6 H), 8.55 (N=CMe_b, 6 H)
$[Ru(NH_2NHMe)_2\{PPh(OMe)_2\}_4][PF_6]_2$	CD_2Cl_2	6.05 (NH_2, 4 H), 6.59 (m) (OMe, 24 H), 7.58 (NMe, 6 H)
$[Ru(cod)(py)_4][BPh_4]_2$	$(CD_3)_2CO$	1.45 (d) (protons of py), 6.8—8.3 (protons of cod)
$[Ru(cod)(dmso)_4][BPh_4]_2$	CD_3NO_2	5.2—5.8 [CH and CD_3NO_2 (τ 5.7)], 7.09 (6 H), 7.16 (dmso, 6 H), 7.5 (free dmso), 7.6—7.85 (CH_2 of cod), 7.93 (dmso, 12 H)
$[Ru(4Me\text{-}py)_6][BPh_4]_2$	CD_2Cl_2	1.95 (d) (part of 'AB quartet' due to 4Me-py [g]), 7.65 (Me of 4Me-py)
$[Ru(dmso)_6][BPh_4]_2$	CD_3NO_2	6.76 (s) (*S*-bonded dmso), 7.07 (s) (*O*-bonded dmso), ratio 1 : 1
$[RuH(cod)(py)_3][BPh_4]$	$(CD_3)_2CO$	6.0—8.5 (br) (protons of cod), hydride resonance not observed
$[RuH(cod)(4Me\text{-}py)_3][BPh_4]$	$(CD_3)_2CO$	1.50 (d), 1.67 (d) (protons of 4Me-py), 7.66 (s) (3 H), 7.75 (6 H, Me of 4Me-py), 12.9 (RuH)

[a] Relative to $SiMe_4$. Resonances due to aromatic protons were found in the τ 2.5—3.5 region unless otherwise stated. Assignment and integration values are in parentheses. [b] Disappeared on treatment with D_2O. [c] Sharpened on treatment with D_2O. [d] Position shifted on addition of CF_3CO_2H. [e] Centre of an 'AB quartet.'[23] [f] Coupling constants in Hz. [g] Second doublet obscured by $[BPh_4]^-$ resonances.

The cations in (3) and (4) have recently been shown[25] to have the configuration (I), as anticipated from simple thermodynamic arguments involving antisymbiosis effects.[26]

The reactivity of salts (2) was specifically studied in acetone solutions. Condensations that occur between the hydrazine ligands and the solvent, producing weakly bonding hydrazones[27] or perhaps azines, will have the effect of forming highly labile dieneruthenium(II) species in solution. Attempts to isolate the product formed from dissolving (2; diene = cod) in acetone gave only a complex of formula $[Ru(BPh_4)(cod)]$, but when MeCN, dimethyl sulphoxide (dmso), or pyridine (py) were added to the acetone solutions stable salts of formula $[Ru(cod)L_4][BPh_4]_2$ (L = MeCN, dmso, or py) were obtained. In neat dmso, $[Ru(cod)(dmso)_4][BPh_4]_2$ was converted into $[Ru(dmso)_6][BPh_4]_2$ after several hours. When (2; diene = cod) was heated under reflux in acetone with 4-methylpyridine $[Ru(4Me\text{-}py)_6][BPh_4]_2$ was formed. It is interesting to note that whereas the i.r. and ^1H n.m.r. spectra of $[Ru(dmso)_6]^{2+}$ indicated the presence of both *O*- and *S*-bonded dmso groups,[28] the i.r. spectrum of $[Ru(cod)(dmso)_4]^{2+}$ and that of the deuteriated analogue indicated only *O*-bonded dmso ligands (see Tables 1 and 2).

We are as yet unsure of the structure of the insoluble complex which precipitates slowly in high yield (69%) from boiling acetone–ethanol mixtures of (2) and for which a stoicheiometry of $[Ru(BPh_4)(cod)]$ (6) is inferred from microanalytical data. The complex appears to contain an arene-bonded BPh_4 from the characteristic additional aromatic vibrations observed at 1 450 and 1 396 cm^{-1} in its i.r. spectrum.[29] Zwitterionic complexes of general formula $[RuH(BPh_4)L_2]$ (L = bulky phosphine)

---

[24] T. V. Ashworth, R. H. Reimann, E. Singleton, and E. v.d. Stok, unpublished work.

[25] T. V. Ashworth, M. J. Nolte, and E. Singleton, unpublished work.

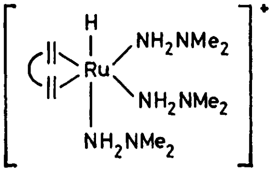
[26] R. G. Pearson, *Inorg. Chem.*, 1973, **12**, 712.

[27] C. H. Stapfer, R. W. D'Andrea, and R. H. Herber, *Inorg. Chem.*, 1971, **10**, 1224; 1972, **11**, 204.

[28] I. P. Evans, A. Spencer, and G. Wilkinson, *J.C.S. Dalton*, 1973, 204 and refs. therein.

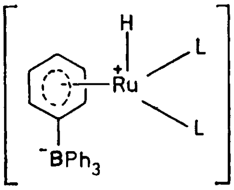
[29] R. R. Schrock and J. A. Osborn, *Inorg. Chem.*, 1970, **9**, 2339.

[structure (II)] have been characterized from reactions of (2) with a series of neutral phosphines in acetone–ethanol mixtures,[30] but a similar formulation for (6; L = $\frac{1}{2}$ cod) is precluded because of the absence of terminal ν(M–H) bonds in the i.r. and because of the unreactivity of this complex towards phosphines. The structure (III) involving an η-allylic dieneruthenium(II) species fits in with the analytical data but this formulation is only tentative. An *X*-ray structural determination of this complex is at present underway.



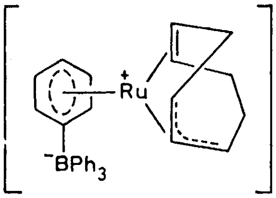
(I)

When a solution of (2) in refluxing acetone was treated with a 6 : 1 molar ratio of phosphites or phosphonites, bis(hydrazone) salts of formula $[Ru(NH_2NCMe_2)_2L_4][BPh_4]_2$ {7; L = $P(OMe)_3$, $P[(OCH_2)_3CMe]$, $P[(OCH_2)_3CEt]$, $P(OEt)_3$, or $PPh(OMe)_2$} were rapidly formed in high yield. Similar reactions with a range of other ligands including phosphinites produced unstable species which could not be characterized or isolated. The i.r. spectra of these complexes all contained a characteristic azomethine band of medium intensity in the 1 635—1 648 cm^{-1} region and N–H stretching and deformation vibrations were observed in the 3 200—3 300 cm^{-1} region. The asymmetric NH bending vibrations are obscured by $[BPh_4]^-$ bands. The ^{1}H n.m.r. spectra of (7) contained no resonances in the region expected for acetone methyl groups, but all contained two singlets located upfield from free acetone and only consistent with asymmetric methyl groups bonded to a rigid azomethine-containing ligand. Except for {7; L = $P[(OCH_2)_3CMe]$} where the broad resonance at τ 5.13 was assigned to NH_2 protons, no evidence of NH_2 protons was found in the ^{1}H n.m.r. spectra of (7). Infrared spectra of the complexes or the proton resonance of the groups attached to the phosphorus atoms of (7) were not useful in definitely assigning one of the possible isomers to these complexes. The methylene and the methyl resonances of the constrained phosphite in {7; L = $P[(OCH_2)_3CMe]$} indicated that the phosphite ligands were co-ordinated in an equatorial plane but the methyl resonances in [7; L = $P(OMe)_3$ and $PPh(OMe)_2$] were not characteristic[31] of an equatorial-planar arrangement but tended towards the type of multiplet observed for a pair of adjacent sets of *facial* $P(OMe)_3$ and $PPh(OMe)_2$ groups. In order to resolve the stereochemistry of the hydrazones and to try to determine the factors affecting the unusual stability of these salts in solution, the *X*-ray structure of [7; L = $P(OMe)_3$] was determined. This showed[32] the complex to have structure (IV), containing the first confirmed amine-bonded hydrazone ligands.

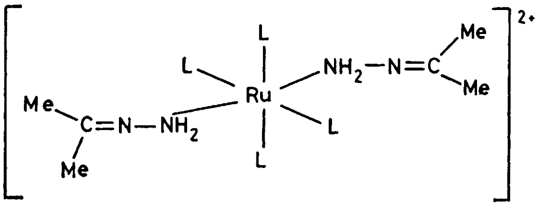


(II)

Other metal hydrazone complexes characterized[33] to date are either square planar or tetrahedral and contain the hydrazone ligands bonded through the imino-nitrogen. However, the ligands used in these earlier studies have relatively bulky groups attached to the amino-nitrogen and consequently the co-ordination may be determined by steric effects. Certainly, in the octahedral complexes (7) bonding *via* the imino-nitrogen would be prevented by interligand repulsions. Large deviations from ideal tetrahedral symmetry around the phosphorus atoms and short (mean 2.84 Å) O · · · N distances were attributed to strong hydrogen bonding occurring between the NH_2 moiety and an O atom of a phosphite group. This strong hydrogen bonding thus accounts for the inertness of these complexes in solution to further substitution reactions, and the non-symmetrical phosphite methyl resonances and doublet hydrazone methyl resonance observed in the ^{1}H n.m.r. It also explains why no stable products were formed with small phosphines since no hydrogen bonding is possible with these ligands. In the case of phosphinites, however, it is probable that steric interactions of these larger ligands with the hydrazones become a dominant factor in destabilizing complexes of type (7) containing these groups.



(III)



(IV) L = $P(OMe)_3$

---

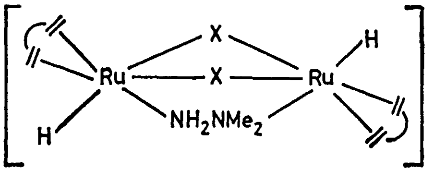
[30] T. V. Ashworth, R. H. Reimann, and E. Singleton, unpublished work.

[31] Last two publications given in ref. 14.

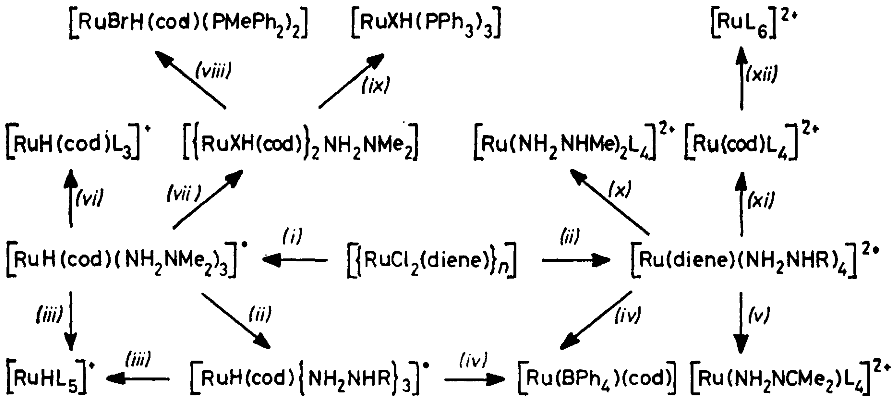
[32] M. J. Nolte and E. Singleton, *J.C.S. Dalton*, 1974, 2406.

[33] P. Braunstein, J. Dehand, and M. Pfeffer, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 521; F. Gaspanini, D. Misiti, and E. Cernia, *Inorg. Chim. Acta*, 1976, **17**, L3; N. Bresciani Pahor, M. Calligaris, P. Delise, L. Randaccio, L. Maresca, and G. Natile, *ibid.*, **19**, 45.

In a single attempt to prepare other hydrogen-bonded ruthenium species we treated $[Ru(cod)(NH_2NHMe)_4][PF_6]_2$ with $PPh(OMe)_2$ in refluxing acetone and characterized the colourless crystalline stable salt $[Ru(NH_2NHMe)_2\{PPh(OMe)_2\}_4][PF_6]_2$ from the reaction solution. Infrared and ^1H n.m.r. data for this complex are given in Tables 1 and 2. A *trans*-hydrazine configuration is proposed for this salt by analogy.



(VI)



SCHEME Selected reactions of hydrazine-substituted ruthenium(II) cations. diene = Bicyclo[2.2.1]hepta-2,5-diene (nbd) or cycloocta-1,5-diene (cod). (*i*) NH_2NMe_2; (*ii*) NH_2NHR (R = H or Me); (*iii*) L = $PPh(OMe)_2$ or $P(OEt)_3$; (*iv*) Me_2CO–EtOH; (*v*) L = $P(OMe)_3$, $P[(OCH_2)_3CMe]$, $P[(OCH_2)_3CEt]$, $P(OEt)_3$, or $PPh(OMe)_2$, reflux in Me_2CO (R = H); (*vi*) L = 4Me-py, py, or MeCN; (*vii*) LiX (X = Cl or Br); (*viii*) $PMePh_2$; (*ix*) PPh_3; (*x*) L = $PPh(OMe)_2$, R = Me; (*xi*) L = py, MeCN, or dmso; (*xii*) L = 4Me-py or dmso

In contrast, the *NN*-dimethylhydrazine groups in (3) and (4) are all readily replaced in acetone solution and substitution reactions with nitrogen-donor ligands gave $[RuH(cod)L_3]^+$ (L = py, 4Me-py, or MeCN) (Tables 1 and 2) and the known salts $[RuHL_5]^+$ [L = $PPh(OMe)_2$,[10,16] $PPh(OEt)_2$,[10] and $P(OEt)_3$ [15]] were formed with phosphites. With tertiary phosphines and arsines, (4) gave a range of products, which in some cases are themselves highly reactive, and these systems will be described in detail in subsequent publications. Of relevance to this work, however, are the reactions of (3) or (4) with LiX (X = Cl and Br) in methanol or acetone solutions which produced red-brown insoluble complexes of stoicheiometry $[\{RuXH(cod)\}_2NH_2NMe_2]$ (8; X = Cl or Br). Only i.r. data are given for these complexes (Table 1) which were too insoluble for ^1H n.m.r. spectra to be recorded. Complexes (8) provide a route to a number of neutral hydridoruthenium(II) systems, namely $[RuXH(cod)(PMePh_2)_2]$ and $[RuXH(PPh_3)_3]$ (X = Cl or Br),[34] and also to the hydrido-cations $[RuHL_5]^+$ for a series of phosphorus-donor ligands. It was not possible to determine whether the dimethylhydrazine ligand was unidentate or bridging in (8) as a number of weak bonds were found in the bridging-hydrazine region of 900—980 cm^{-1} in their i.r. spectra. However, a plausible structure (VI) which satisfies the 18-electron rule and which is typical of ruthenium chemistry is a triply bridged dimer with two halogen atoms and the hydrazine ligand bridging the two metal centres. An *X*-ray structural determination of (8; X = Cl) is underway.

An outline of the reactions discussed above is given in the Scheme.

EXPERIMENTAL

The complexes $[\{RuCl_2(diene)\}_n]$ (1; diene = cod or nbd) were prepared as described previously [35] except that use of an excess of diene gave much higher yields in shorter reaction times. Hydrazine, methylhydrazine, and *NN*-dimethylhydrazine were obtained commercially and were not further purified. Melting points were obtained on a Kofler hot-stage apparatus, and i.r. spectra were recorded using a Perkin-Elmer model 457 grating spectrophotometer. The ^1H n.m.r. spectra were recorded with Varian A-60A and HA-100 instruments. Microanalyses were carried out in this laboratory. Physical and spectroscopic data for the complexes are presented in Tables 1 and 2 respectively.

Preparations.— *(Cyclo-octa-1,5-diene)tetrakis(hydrazine)-ruthenium bis(tetraphenylborate)*, (2; diene = cod). The complex $[\{RuCl_2(cod)\}_n]$ (2.0 g) was suspended in methanol (50 cm^3) and hydrazine (97%, 5 cm^3) was added. The solution obtained on shaking (*ca.* 30 s) was heated under reflux for 5 min, water (10 cm^3) was added, and the solution was filtered. Addition of a solution of $Na[BPh_4]$ (5.0 g) in methanol (25 cm^3) and cooling to 0 °C gave the product as colourless needles containing water of crystallization (5.5 g, yield 80%). Recrystallization from N_2H_4 and ethanol afforded colourless *prisms* containing ethanol of crystallization.

Tetrakis(hydrazine)(norbornadiene)ruthenium bis(tetraphenylborate), (2; diene = nbd). Hydrazine (97%, 10 cm^3) was added to a stirred suspension of $[\{RuCl_2(nbd)\}_n]$ (1.0 g) in degassed methanol (10 cm^3) under an atmosphere of nitro-

---

[34] P. S. Hallman, B. R. McGarvey, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1968, 3143.

[35] M. A. Bennett and G. Wilkinson, *Chem. and Ind.*, 1959, 1516.

gen. Sodium tetraphenylborate (2.5 g) in water (20 cm^3) was added to the resulting clear solution from which the product crystallized as colourless *plates* on cooling to -5 °C (1.2 g, yield 35%).

(*Cyclo-octa*-1,5-*diene*)*tetrakis*(N'-*methylhydrazine*)*ruthenium bis*(*hexafluorophosphate*). Methylhydrazine (10 cm^3) was added to a suspension of $[\{RuCl_2(cod)\}_n]$ (1.0 g) in methanol (20 cm^3) which was then heated on a steam-bath until a dark red-brown solution had formed (*ca.* 10 min). Ammonium hexafluorophosphate (2.5 g) in water (15 cm^3) was added to the cooled solution. Removal of the solvent under reduced pressure gave the product as a white *powder* (1.5 g, yield 60%).

(*Cyclo-octa*-1,5-*diene*)*tris*(N'N'-*dimethylhydrazine*)*hydridoruthenium tetraphenylborate*, (3). Anhydrous *NN*-dimethylhydrazine (25 cm^3) and water (5 cm^3) were added to a suspension of $[\{RuCl_2(cod)\}_n]$ (2.0 g) in methanol (25 cm^3). Boiling the suspension for 20 min produced a dark brown solution from which colourless needles precipitated over a period of 30 min on addition of $Na[BPh_4]$ (2.5 g) in methanol (15 cm^3). Addition of an aqueous solution of $Na[BPh_4]$ gave the precipitate as colourless *plates* (4.5 g, yield 90%). The product could be recrystallized from NH_2NMe_2, methanol, and water.

(*Cyclo-octa*-1,5-*diene*)*tris*(N'N'-*dimethylhydrazine*)*hydridoruthenium hexafluorophosphate*, (4). An aqueous solution (20 cm^3) of $[NH_4][PF_6]$ (2.0 g) was added to the dark brown solution obtained above. On removing the solvent under reduced pressure the required product precipitated as a white *powder*. An analytically pure sample was obtained by drying the crude material for several hours at 60 °C at low pressure (10^{-3} Torr) (1.8 g, yield 50%).*

(*Cyclo-octa*-1,5-*diene*)*tris*(*hydrazine*)*hydridoruthenium tetraphenylborate*, (5; R = H). *Method* (*a*). A suspension of $[\{RuCl_2(cod)\}_n]$ (0.5 g) in methanol (50 cm^3) and hydrazine (97%, 10 cm^3) was stirred until a clear solution was obtained, and then water (20 cm^3) was added and the solution was heated under reflux for 2.5 h. Addition of $Na[BPh_4]$ (0.5 g) in water (15 cm^3) to the resulting deep purple solution and cooling to -5 °C produced the required product as colourless *needles* over a period of several hours (0.58 g, yield 50%).

Method (*b*). Complex (3) (1.0 g) was dissolved in a mixture of N_2H_4 (10 cm^3) and methanol (10 cm^3) and the pale yellow solution was heated under reflux for 15 min. Water (*ca.* 5 cm^3) was slowly added to the hot solution until precipitation just began. On cooling to room temperature, colourless *needles* (0.7 g, 80%) precipitated. The product was recrystallized from N_2H_4, methanol, and water.

The complex $[RuH(cod)(NH_2NHMe)_3][BPh_4]$ (5; R = Me) was similarly obtained, using NH_2NHMe, as white *needles* (0.75 g, yield 80%).

(*Cyclo-octa*-1,5-*diene*)(*tetraphenylborato*)*ruthenium*, (6). A solution of (2; diene = cod) (1.0 g) in acetone–ethanol (1 : 1, 30 cm^3) was heated under reflux for 1 h during which a pale yellow *powder* formed (0.38 g, yield 70%). The product was slightly soluble in pyridine and insoluble in all the other common solvents.

The following preparations were carried out under an inert atmosphere.

$[Ru(cod)(py)_4][BPh_4]_2$. Pyridine (1 cm^3) was added to a solution of (2; diene = cod) (0.7 g) in acetone (15 cm^3) which was then heated under reflux for 2 h. The solvent was removed under reduced pressure and addition of methanol gave yellow *prisms* of the required product (0.5 g, yield 60%).

$[Ru(4Me\text{-}py)_6][BPh_4]_2$. An acetone solution (15 cm^3) of (2; diene = cod) (0.7 g) and 4-methylpyridine (1 cm^3) was heated under reflux for 2 h and the required product was obtained, after removal of the solvent and addition of methanol, as bright yellow *prisms* (0.7 g, yield 78%).

$[Ru(cod)(dmso)_4][BPh_4]_2$. A solution of (2; diene = cod) (2.5 g) in a mixture of dimethyl sulphoxide (10 cm^3) and acetone (30 cm^3) was heated under reflux for 1.5 h. The acetone was removed under reduced pressure and ethanol was added to afford a pale yellow *powder* (1.5 g, yield 52%). Recrystallization from dmso and ethanol gave dark orange *prisms* of the required product. Addition of ethanol to the filtrate gave a mixture of the above complex and $[Ru(dmso)_6][BPh_4]_2$.

$[Ru(dmso)_6][BPh_4]_2$. The complex $[Ru(cod)(dmso)_4][BPh_4]_2$ (0.5 g) was dissolved in dmso (5 cm^3) and the solution was stirred at 80 °C for 1 h. After cooling and addition of ethanol to the reaction solution, an off-white powder of the required product was obtained (0.4 g, yield 80%).

Bis(*acetone hydrazone*)*tetrakis*(*trimethyl phosphite*)*ruthenium bis*(*tetraphenylborate*), [7; L = $P(OMe)_3$]. An acetone solution (20 cm^3) of (2; diene = cod) (1.0 g) and $P(OMe)_3$ (0.72 g, 6.0 mmol) was heated under reflux for 15 min. Ethanol (20 cm^3) was added, and the solution was boiled to remove solvent and then allowed to cool when precipitation commenced (1.0 g, yield 70%). The product was recrystallized from dichloromethane and ethanol as colourless prisms.

Similarly prepared as colourless *prisms* were: $[Ru(NH_2NCMe_2)_2\{P[(OCH_2)_3CMe]\}_4][BPh_4]_2$ (70%), $[Ru(NH_2NCMe_2)_2\{P[(OCH_2)_3CEt]\}_4][BPh_4]_2$ (40%), $[Ru(NH_2NCMe_2)_2\{P(OEt)_3\}_4][BPh_4]_2$ (50%), $[Ru(NH_2NCMe_2)_2\{PPh(OMe)_2\}_4][BPh_4]_2$ (70%), and $[Ru(NH_2NHMe)_2\{PPh(OMe)_2\}_4][BPh_4]_2$ (yield 70%).

$[\{RuClH(cod)\}_2NH_2NMe_2]$ (8; X = Cl). Addition of LiCl (0.12 g) to a refluxing solution of (3) (0.7 g) in a mixture of acetone (5 cm^3) and methanol (15 cm^3) effected precipitation of red-brown *prisms* (0.38 g, yield 70%) over 15 min.

The complex $[\{RuBrH(cod)\}_2NH_2NMe_2]$ was similarly prepared using LiBr (0.15 g) and obtained as a red-brown *powder* (0.26 g, yield 40%).

[6/2298 *Received*, 20*th December*, 1976]

---

* Throughout this paper: 1 Torr = (101 325/760) Pa.