Cationic Complexes of Ruthenium(II)

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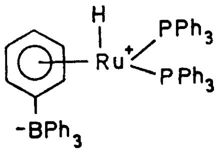
Summary Cationic hydrazine and substituted hydrazine salts of the type $[(\text{diene})Ru(N_2H_4)_4](BPh_4)_2$ and $[(C_8H_{12})Ru(H)L_3]BPh_4$ ($L = N_2H_4$, $N(CH_3)_2NH_2$) have been prepared and used as precursors for the formation of a series of ruthenium(II) salts.

THE preparations and catalytic properties of various cationic salts of rhodium(I) and iridium(I) have been reported.[1-3] Cyclo-octadiene compounds $[(C_8H_{12})MCl]_2$ (M = Rh or Ir) are useful starting materials for the formation of these salts but the insoluble nature of the diene–ruthenium complex $[(C_8H_{12})RuCl_2]_x$ ($x > 2$) has precluded its use in the preparation of cationic ruthenium(II) salts. We have found however that the polymers $[(\text{diene})\ RuCl_2]_x$ dissolve rapidly in warm methanol in the presence of hydrazine [diene = C_8H_{12} or norbornadiene (C_7H_8)] or *NN*-dimethylhydrazine (diene = C_8H_{12}), to give solutions from which cationic ruthenium(II) salts can be isolated. The lability of the ligands in these salts in solution, has promoted us to study their uses as intermediates in the formation of a series of ruthenium(II) salts by ligand exchange.

If suspensions of the complexes $[(\text{diene})RuCl_2]_x$(I) (diene = C_8H_{12} or C_7H_8) in methanol are warmed with anhydrous hydrazine, pale pink solutions are rapidly formed from which the salts $[(\text{diene})\text{Ru}(\text{N}_2\text{H}_4)_4](\text{BPh}_4)_2$(II) slowly precipitate on addition of the counteranion BPh_4^-. With the cycloheptatriene complex $[(\text{C}_7\text{H}_8)\text{RuCl}_2]_x$, no compound of composition (II) could be isolated under similar conditions. Over a period of 24 h, however, catalytic decomposition of the hydrazine occurs and the known salt $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)](\text{BPh}_4)_2$ is deposited from the solution. In fact small amounts of ammonia have been detected as a byproduct of all these reactions. Treatment of (I) (diene $= \text{C}_8\text{H}_{12}$) with *NN*-dimethylhydrazine in either cold or refluxing methanol gives only the hydride $[(\text{C}_8\text{H}_{12})\text{Ru(H)}\{\text{N(CH}_3)_2\text{NH}_2\}_3]\text{BPh}_4$(III) on addition of NaBPh_4. When this reaction is performed in refluxing ethanol a second isomer having the composition $[(\text{C}_8\text{H}_{12})\text{Ru(H)}\{\text{N(CH}_3)_2\text{NH}_2\}_3]\text{BPh}_4$(IV) is obtained. No salt of composition $[(\text{C}_8\text{H}_{12})\text{Ru}\{\text{N(CH}_3)_2\text{NH}_2\}_4](\text{BPh}_4)_2$ could be isolated for this disubstituted hydrazine ligand. The corresponding hydrazine hydride $[(\text{C}_8\text{H}_{12})\text{Ru(H)}(\text{N}_2\text{H}_4)_3]\text{BPh}_4$ is prepared by refluxing, for 2 h, the solution formed from (I) and anhydrous N_2H_4 in methanol and then adding NaBPh_4. All the salts isolated were characterised by analytical, n.m.r., and conductivity data, and all contained characteristic frequencies in their i.r. spectra between 3361—3160 cm^{-1} ν (N–H), 1621—1592 cm^{-1} δ (N–H)$_{\text{as}}$ and 930—898 ν (N–N).†

Complexes (II), (III), and (IV) decompose in air over a period of a few days and are reasonably stable in CH_2Cl_2 solutions over 24 h. In acetone solution an insoluble complex of composition $[(\text{C}_8\text{H}_{12})\text{RuBPh}_4]$(V) and of unknown stereochemistry is deposited from the solution after a few hours. Acetone–methanol solutions of (II), (III), or (IV) react with PPh_3 under reflux to give the neutral hydride $[\text{Ru(H)}(\text{PPh}_3)_2\text{BPh}_4]$ in high yield. Characteristic bands in the 1500—1300 cm^{-1} region in the i.r. indicate the stereochemistry of this compound to be an arene-bonded zwitterionic ruthenium(II) complex, (VI).



(VI)

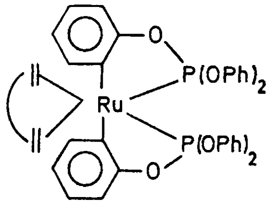
However other donor ligands, with low steric requirements react readily with (II), (III), or (IV) to give various salts depending upon the ligand and the reaction conditions. For instance, (II) (diene $= \text{C}_8\text{H}_{12}$) reacts with pyridine or 2,2′-bipyridyl in refluxing acetone solution to give the salts $[(\text{C}_8\text{H}_{12})\text{RuL}_4](\text{BPh}_4)_2$ (L = py or bipy) whereas similar treatment of (II) with P(OMe)_3 or γ-picoline produces only $[\text{RuL}_6](\text{BPh}_4)_2$ (L = P(OMe)_3 or γ-pic). The reaction of (II) with P(OEt)_3 in acetone–ethanol mixtures produces a salt of stoicheiometry $[\text{Ru}_2(\text{N}_2\text{H}_4)_3\text{L}_8](\text{BPh}_4)_4$ (VII) [L = P(OEt)_3]. The corresponding P(OMe)_3 product of (VII) [L = P(OMe)_3] is readily formed from (II) and excess P(OMe)_3 in refluxing methanol. Compound (VII) probably contains a single hydrazine ligand bridging two ruthenium atoms similar to that observed in the complexes $[\{\text{RhCl}_3(\text{PR}_3)_2\}_2\text{N}_2\text{H}_4]$.[4] Treatment of (III) with pyridine or γ-picoline in acetone–methanol mixtures gives the diene hydride $[(\text{C}_8\text{H}_{12})\text{RuHL}_3]\text{BPh}_4$(VIII) (L = py or γ-pic). Similar reactions of (III) with P(OEt)_3 or $\text{P(OMe)}_2\text{Ph}$, however produces only $[\text{Ru(H)L}_5]\text{BPh}_4$(IX) (L = P(OEt)_3 or $\text{P(OMe)}_2\text{Ph}$). Reactions of (II), (III), or (IV) with bulky phosphines or phosphites are inhibited by the steric requirements of the ligands and by the ready formation of (V). With P(OPh)_3, however, (III) gives, from acetone–methanol solution a neutral ruthenium complex of composition $[(\text{C}_8\text{H}_{12})\text{Ru}\{\text{P(OPh)}_3\}_2]$(XI) for which the following structure is proposed by analogy with the known[2] iridium–diene–phosphite complex reported recently.

TABLE

I.r. and n.m.r. data

Compound	ν (Ru–H) cm^{-1} [a]	Hydride resonance (τ)[b]
$[(\text{C}_8\text{H}_{12})\text{Ru(H)}\{\text{N(CH}_3)_2\text{NH}_2\}_3]\text{BPh}_4$	2000	12·87
$[(\text{C}_8\text{H}_{12})\text{Ru(H)}\{\text{N(CH}_3)_2\text{NH}_2\}_3]\text{BPh}_4$	2050	14·0
$[(\text{C}_8\text{H}_{12})\text{Ru(H)}(\text{N}_2\text{H}_4)_3]\text{BPh}_4$	2000	15·3
$[(\text{C}_8\text{H}_{12})\text{Ru(H)py}_3]\text{BPh}_4$	2062	13·0
$[(\text{C}_8\text{H}_{12})\text{Ru(H)}(\gamma\text{-pic})_3]\text{BPh}_4$	2070	12·87
$[\text{Ru(H)}(\text{P(OMe)}_2\text{Ph})_5]\text{BPh}_4$	1913	14·17 q 14·90 q[c]

[a] Nujol mulls; [b] Me_4Si as internal standard; q = quintuplet; [c] [*J*(P–H)*cis* 9 Hz; *J*(P–H)*trans* 43·8 Hz].



(XI)

Studies of further reactions of (II), (III), and (IV) with olefins and acetylenes are in progress. Treatment of (III) with NaBr in acetone has given a neutral diene ruthenium hydride complex from which a series of neutral diene hydrides of stoicheiometry *cis*-$[\text{C}_8\text{H}_{12}\text{RuHBrL}_2]$ (L = phosphine or phosphite) have been prepared.

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† Other relevant spectral data are summarised in the Table All compounds reported in this communication have been fully characterised.

[1] L. M. Haines, *Inorg. Chem.*, 1971, **10**, 1685, and references therein.
[2] L. M. Haines and E. Singleton, *J. Organometallic Chem.*, 1970, **25**, C83.
[3] J. R. Shapley, R. R. Schrock, and J. A. Osborn, *J. Amer. Chem. Soc.*, 1969, **91**, 2816.
[4] J. Chatt, N. P. Johnson, and B. L. Shaw, *J. Chem. Soc.*, 1964, 2508.