(Bicyclo[2.2.1]hepta-2,5-diene)carbonyltrihalogenoruthenate(II) Complexes

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The preparation of the first anionic ruthenium(II) diene complexes M[$RuX_3CO(C_7H_8)$] {M = $Ph_3(PhCH_2)P^+$ or Cs^+; X = Cl or Br; C_7H_8 = bicyclo[2.2.1]hepta-2,5-diene (norbornadiene)} *via* cleavage of [$RuCl_2CO(C_7H_8)$]$_n$ with halide ion are reported. Detailed ^1H n.m.r. and homonuclear decoupling studies indicate a structure with the carbonyl and a halide group co-ordinated *cis* to the diene. Reaction of the complex [$RuCl_2CO(C_7H_8)$]$_n$ with Ph_4AsCl,HCl in acetone gives a mixture of inseparable products, but when heated under reflux only *cis*-$(Ph_4As)_2$[$RuCl_4(CO)_2$] is isolated.

ALTHOUGH extensive investigations of the chemistry of rhodium(I) diene complexes have been reported,[1] relatively few studies on ruthenium(II) diene complexes have been published. The complexes [RuX_2(diene)]$_n$ {X = Cl, Br, or I; diene = bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) or cyclo-octa-1,5-diene (C_8H_{12})} were the first to be synthesised from '$RuCl_3,xH_2O$' and the diene.[2] Cleavage reactions of these with *p*-toluidine and pyridine (py) to give respectively [RuX_2(diene)(*p*-toluidine)$_2$] and *trans*-[$RuX_2(py)_4$] have also been reported.[2] Recent papers have described carbonylation reactions of the complex [$RuCl_2$(diene)]$_n$ giving, for example, *cis*-[$Ru(OH)_2(CO)_2(C_7H_8)$] [3] and also their reaction with hydrazine giving the first cationic ruthenium(II) diene complexes, *e.g.* [Ru(diene)$(N_2H_4)_4$]$(BPh_4)_2$.[4] From these a range of other cationic diene complexes, such as [Ru(diene)L_4]$^{2+}$ (L = py, *etc.*), have been prepared. (h^6-Benzene)cyclohexa-1,3-dieneruthenium(II) cations are also cited in a recent paper by Zelonka and Baird.[5]

The neutral diene complexes [$RuX_2(PPh_3)_2$(diene)] and [Ru(H)Cl$(PPh_3)_2$(diene)] have been prepared by reaction of [$RuX_2(PPh_3)_{3\text{ or }4}$] [6] {or [$RuX_3(PPh_3)_2$-MeOH] [7]} and [Ru(H)Cl$(PPh_3)_3$] [8] respectively with diene (X = Cl, Br; diene = bicyclo[2.2.1]hepta-2,5-diene). Treatment of the complex [$RuCl_2$(diene)]$_n$ with allylmagnesium chloride produced [Ru(allyl)$_2$(diene)] which, when diene = C_8H_{12}, underwent further reaction with allyl halides giving the dimeric complex [Ru_2X_2(allyl)$_2(C_8H_{12})_2$].[9] Finally, by reaction of dienes with the well known 'carbonyl-containing' red solution (*i.e.* $RuCl_3,xH_2O$ in refluxing ethanol treated with CO for 5 h), the first carbonyl diene complexes of ruthenium [RuX_2CO(diene)]$_n$, were isolated (X = Cl, Br; diene = bicyclo[2.2.1]hepta-2,5-diene, cyclo-octa-1,5-diene).[6]

Here, we present full details of the reactions of the complex [$RuCl_2CO(C_7H_8)$]$_n$ with chloride ion in the presence of various large cations from which, in some instances, the first anionic diene complexes of ruthenium(II) have been successfully prepared.[10]

RESULTS AND DISCUSSION

Earlier work,[6] has shown that [$RuCl_2CO(C_7H_8)$]$_n$ (C_7H_8 = bicyclo[2.2.1]hepta-2,5-diene) does not undergo simple bridge-splitting reactions with neutral ligands, since the severe conditions apparently required for bridge cleavage also cause displacement of the diene. Thus, in neat pyridine, [$RuCl_2CO(py)_3$] is obtained.[6] However, if a suspension of [$RuCl_2CO(C_7H_8)$]$_n$ in acidified degassed acetone is shaken with a large excess of benzyl(triphenyl)phosphonium chloride or caesium chloride for several days, slow conversion to the complexes M[$RuCl_3CO(C_7H_8)$] [M = $Ph_3(PhCH_2)P^+$ or Cs^+] occurs. These diamagnetic complexes exhibit, in their i.r. spectra, a single carbonyl band at 2 009 cm^{-1} (Nujol), a strong band characteristic of norbornadiene at 1 303 (M = $Ph_3PhCH_2P^+$) or 1 309 cm^{-1} (M = Cs^+), and, for M = $Ph_3(PhCH_2)P^+$, the many bands associated with this cation. Treatment of a suspension of the latter complex in acetone with an excess of lithium bromide gave a brown solution from which [$Ph_3(PhCH_2)P$][$RuBr_3CO(C_7H_8)$] could be extracted. All these complexes are 1 : 1 electrolytes (see Experimental section) and remarkably stable to oxidation in solution. Furthermore, none of the complexes shows any tendency to undergo isomerisation in solution; *e.g.*, the sharp ν(CO) band at 2 011 cm^{-1} in the i.r. spectrum of a dichloromethane solution of the benzyl(triphenyl)phosphonium chloro-salt was unchanged in position even after setting aside for 24 h or heating to *ca.* 323 K.

There are two possible geometrical isomers for the [$RuX_3CO(C_7H_8)$]$^-$ anion containing either *trans* (I) or *cis* (II) dissymmetry with respect to the diene group. A comparison of the far i.r. spectra for the chloro- and bromo-complexes (see Experimental section) does *not* enable a distinction to be made between these two possible isomers. However, close examination of the ^1H n.m.r. spectra leads to unequivocal assignment of the stereochemistry. Earlier work with the square-planar

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[1] See. R. R. Schrock and J. A. Osborn, *J. Amer. Chem. Soc.*, 1971, **93**, 2397 and references therein.

[2] M. A. Bennett and G. Wilkinson, *Chem. and Ind.*, 1959, 1516; E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 1959, 3178.

[3] R. B. King and P. N. Kapoor, *Inorg. Chem.*, 1972, **11**, 336.

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

[5] R. A. Zelonka and M. C. Baird, *Canad. J. Chem.*, 1972, **50**, 3063.

[6] S. D. Robinson and G. Wilkinson, *J. Chem. Soc. (A)*, 1966, 300.

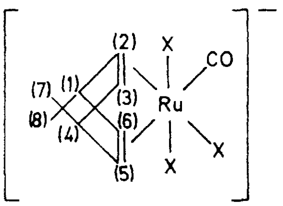
[7] E. S. Switkes, L. Ruiz-Ramirez, T. A. Stephenson, and (in part) J. Sinclair, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 593; *J.C.S. Dalton*, 1973, 1770.

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

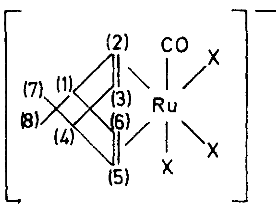
[9] J. Powell and B. L. Shaw, *J. Chem. Soc. (A)*, 1968, 159.

[10] Preliminary communication, T. A. Stephenson and E. S. Switkes, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 805.

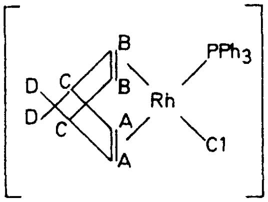
rhodium(I) diene complex $[RhCl(C_7H_8)(PPh_3)]$ (III) illustrates the effect of *trans*-asymmetry on the norbornadiene proton resonances. Four magnetically inequivalent sets of protons are found (A—D) with the two sets of olefin protons A and B assigned at τ 4·66 and 7·00 respectively, well separated because of the large *trans*-effect difference between triphenylphosphine and chloride.[11] Similar spectra would be expected if the ruthenium complexes had configuration (I). However, the ^1H n.m.r. spectra of all the complexes show *five* diene resonances (Table 1), which is consistent with configuration (II) since H(1) and H(4) will be magnetically inequivalent. Furthermore, the smaller separation between the H(2), H(6) and H(3),H(5) olefin protons is consistent with *cis*-asymmetry. The detailed assignments have been confirmed by homonuclear decoupling experiments (Table 2) and the coupling constants obtained from these measurements are also shown in Table 2.



(I)



(II)



(III)

Table 1

^1H N.m.r. chemical shifts and coupling constants for the complexes $M[RuX_3CO(C_7H_8)]$

M = $Ph_3(PhCH_2)P^+$		M = Cs^+			
X = Cl τ [b]	X = Br τ [b]	X = Cl τ [c]	Relative intensity	Fine structure	Assignment [a]
2·38 2·90	2·52 2·90		20	Multiplet	Phenyl
4·80	4·90		2	Doublet	Methylene [d]
4·78	4·80	4·35	2	Triplet [e]	H(2) and H(6)
5·48	5·62	4·60	2	Triplet [e]	H(3) and H(5)
5·80	5·90	5·54	1	Broad multiplet	H(1)
6·34	6·36	5·87	1	Broad multiplet	H(4)
8·71	8·78	8·20	2	Triplet	H(7) and H(8)

[a] See configuration (II). [b] Measured in $CDCl_3$. [c] Measured in D_2O. [d] J_{PH} 14·0 Hz. [e] Shown by double-resonance experiments to be overlapping doublet of doublets.

In support of the i.r. observations, no change in the ^1H n.m.r. spectrum was observed on heating a deuteriochloroform solution of the $Ph_3(PhCH_2)P^+$ salt to *ca.* 323 K and, unlike the rhodium complexes, addition of an excess of diene or chloride ion produced no change in the diene resonance positions, even after setting aside for 3 days. Thus, it appears that these diene anions are formed stereospecifically and are of high kinetic stability, undergoing neither ligand exchange, isomerisation, nor oxidation under the conditions studied. However, the nature of the product is sensitive to the reaction conditions and, in particular, to *which* large cation is used. With $Ph_3(PhCH_2)PCl$ and CsCl, the only product isolated was the acetone-insoluble $M[RuCl_3CO(C_7H_8)]$. However, with Ph_4AsCl,HCl, reaction with $[RuCl_2CO(C_7H_8)]_n$ in acetone at room temperature gave a mixture of acetone-soluble products which unfortunately proved impossible to separate satisfactorily. In addition, the reaction was irreproducible, leading to different product mixtures (i.r. and analytical evidence) under, ostensibly, the same reaction conditions.*

Table 2

Double-resonance experiment on $Ph_3(PhCH_2)P[RuCl_3CO(C_7H_8)]$

Irradiated at τ	Resonance observed τ	Assignment	Fine structure observed on irradiation
6·34 H(4)	**4·78**	H(2), H(6)	Double doublet
	5·48	H(3), H(5)	Doublet
	5·80	H(1)	No change
	8·71	H(7), H(8)	Doublet
5·80 H(1)	**4·78**	H(2), H(6)	Doublet
	5·48	H(3), H(5)	Double doublet
	6·34	H(4)	No change
	8·71	H(7), H(8)	Doublet
5·48 H(3) and H(5)	**4·78**	H(2), H(6)	Doublet
	5·80	H(1)	No change
	6·34	H(4)	Sharpens to triplet
4·78 H(2) and H(6)	**5·48**	H(3), H(5)	Doublet
	5·80	H(1)	Sharpens
	6·34	H(4)	No change

$J_{[H(7),H(8)-H(1)]}$ 1·25 Hz; $J_{[H(7),H(8)-H(4)]}$ 1·50 Hz; $J_{[H(2)-H(3)]} = J_{[H(6)-H(5)]}$ 4·5 Hz; $J_{[H(1)-H(2)]} = J_{[H(1)-H(6)]}$ 3·0 Hz; $J_{[H(4)-H(3)]} = J_{[H(4)-H(5)]}$ 3·5 Hz.

If, however, Ph_4AsCl,HCl and $[RuCl_2CO(C_7H_8)]_n$ were gently heated under reflux in acetone for *ca.* 1 h, a single product was obtained which analysed closely for *cis*-$(Ph_4As)_2[RuCl_4(CO)_2]$. In support of this formulation, the complex has a conductivity in dichloromethane characteristic of a 2 : 1 electrolyte [Λ(0·001M) 46 Ω cm^2 mol^{-1}] and its i.r. spectrum shows two ν(CO) bands at 2 030 and 1 940 cm^{-1} (Nujol), very close to those reported earlier for *cis*-$Cs_2[RuCl_4(CO)_2]$ [ν(CO) 2 036 and 1 935 cm^{-1}).[12] No evidence for norbornadiene was found in the i.r. or n.m.r. spectra. The mechanism by which a dicarbonyl monomer is obtained from a complex containing only one carbonyl ligand per ruthenium atom

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* Interested readers are referred to Table 8, E. S. Switkes, Ph.D. Thesis, Massachusetts Institute of Technology, 1972, in which i.r. spectra of the products from six separate reactions are listed.

[11] K. Vrieze, H. C. Volger, and A. P. Praat, *J. Organometallic Chem.*, 1968, **15**, 195 and earlier references.

[12] R. Colton and R. H. Farthing, *Austral. J. Chem.*, 1967, **20**, 1283; M. J. Cleare and W. P. Griffith, *J. Chem. Soc.* (*A*), 1969, 372.

is not understood at present. The extra carbonyl group may arise from the solvent (*cf.* the synthesis of $[Ru(H)Cl(CO)(PPh_3)_3]$ [13]) or from some intramolecular-rearrangement process. It is of interest that Robinson and Wilkinson [6] also isolated a dicarbonyl complex *trans*-$[RuCl_2(CO)_2(quinoline)_2]$ by reaction of $[RuCl_2CO(C_7H_8)]_n$ with an excess of quinoline in ethanol.

EXPERIMENTAL

Microanalyses were undertaken by A. Bernhardt, West Germany, and the University of Edinburgh Chemistry Department. I.r. spectra were recorded in the region 4 000—200 cm^{-1} on a Perkin-Elmer grating spectrometer using Nujol mulls on caesium iodide plates. Solution spectra were run in potassium bromide cells. ^1H N.m.r. spectra were obtained on a Varian Associates HA-100 spectrometer equipped with a variable-temperature probe. Conductivity measurements were made on a model 310 Portland Electronics conductivity bridge. Melting points were determined with a Kofler hot-stage microscope and are uncorrected.

Benzyl(triphenyl)phosphonium (Bicyclo[2.2.1]*hepta*-2,5-*diene)carbonyltrichlororuthenate*(II).—A suspension of the complex $[RuCl_2CO(C_7H_8)]_n$ (ref. 6) (0·40 g) was shaken in degassed acetone (50 cm^3) for 5 days with an excess of benzyl(triphenyl)phosphonium chloride (1·10 g) and concentrated hydrochloric acid (0·50 cm^3). The resulting orange *solid* was filtered, washed free of acid and excess of benzyl(triphenyl)phosphonium chloride with warm water, then with acetone, and recrystallised from dichloromethane–heptane (62%); m.p. 177—180 °C (Found: C, 57·8; H, 4·4; Cl, 15·8; O, 2·5; P, 4·7. Calc. for $C_{33}H_{30}Cl_3OPRu$: C, 58·2; H, 4·5; Cl, 15·6; O, 2·4; P, 4·6%). Λ(0·001M) 16·5 Ω cm^2 mol^{-1} in CH_2Cl_2. Far i.r. spectrum (400—200 cm^{-1}): 385m; 350w; 330m; 314w; 303w; 283vs; 268s; 250vs; 224m, and 202m cm^{-1}.

Benzyl(triphenyl)phosphonium (Bicyclo[2.2.1]*hepta*-2,5-*diene)tribromocarbonylruthenate*(II).—The salt $Ph_3(PhCH_2)P[RuCl_3CO(C_7H_8)]$ (0·20 g) was suspended in degassed acetone (100 cm^3) and shaken for *ca.* 6 h with an excess of lithium bromide (1·20 g). The resulting brown solution was concentrated to dryness, the residual solid leeched with dichloromethane, and the unreacted lithium bromide filtered off. The brown solution, now free of lithium bromide, was concentrated to dryness and acetone–diethyl ether addition then gave a brown microcrystalline *solid* (65%); m.p. 162 °C (Found: C, 48·4; H, 3·6; Br, 29·7. Calc. for $C_{33}H_{30}Br_3OPRu$: C, 48·7; H, 3·6; Br, 29·5%). Λ(0·001M) 25·4 Ω cm^2 mol^{-1} in CH_2Cl_2. Far i.r. spectrum (400—200 cm^{-1}): 385m; 350w; 330m; 318w; 303m; 281vs; 269w; 255w; 249s; 225s, and 203vs cm^{-1}.

Caesium (Bicyclo[2.2.1]*hepta*-2,5-*diene)carbonyltrichlororuthenate*(II).—A suspension of the complex $[RuCl_2CO(C_7H_8)]_n$ (0·50 g) was shaken with an excess of caesium chloride (1·0 g) and concentrated hydrochloric acid (0·50 cm^3) in degassed acetone (50 cm^3) for 6 days. The resulting yellow powder was decanted from the unreacted caesium chloride, filtered, washed with acetone, and recrystallised from hot methanol to give a yellow *powder* (80%); m.p. *ca.* 270 °C (decomp.) (Found: C, 21·2; H, 1·8; Cl, 22·8; O, 3·4. Calc. for $C_8H_8Cl_3CsORu$: C, 20·9; H, 1·8; Cl, 23·1; O, 3·5%). Λ(0·001M) 87·2 Ω cm^2 mol^{-1} in methanol. Far i.r. spectrum (400—200 cm^{-1}): 326m; 280s; and 260s cm^{-1}.

Bis(tetraphenylarsonium) cis-*Dicarbonyltetrachlororuthenate*(II).—The complex $[RuCl_2CO(C_7H_8)]_n$ (0·23 g) was heated under reflux gently, under an atmosphere of nitrogen, in degassed acetone (50 cm^3) with an excess of Ph_4AsCl,HCl (0·97 g) for *ca.* 1 h. The solution was filtered and then concentrated to dryness. The residue was washed with water to remove unreacted Ph_4AsCl and the yellow solid recrystallised from dichloromethane–light petroleum (b.p. 60—80 °C) (Found: C, 54·2; H, 3·7; Cl, 14·1. Calc. for $C_{50}H_{40}As_2Cl_4O_2Ru$: C, 56·3; H, 3·7; Cl, 13·3%).

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[13] L. Vaska and J. W. DeLuzio, *J. Amer. Chem. Soc.*, 1961, **83**, 1262.