Cationic Ruthenium Systems. Part 4.[1] Bridge-splitting Reactions of the Triply Bridged Dimers Bis(η-cyclo-octa-1,5-diene)(*NN*-dimethylhydrazine)dihalogenodihydridodiruthenium with a Series of Neutral Donor Ligands

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

The triply bridged complexes $[\{RuX(H)(cod)\}_2(NH_2NMe_2)]$ (2; X = Cl or Br; cod = cyclo-octa-1,5-diene), containing H, X, and NH_2NMe_2 as bridging ligands, have been prepared from $[RuH(cod)(NH_2NMe_2)_3]A$ (1; A = PF_6 or BPh_4) and LiX in moderate yields from acetone–methanol mixtures. The mother liquors of these reactions produced $[Ru_3(CO)_{12}]$ and $[RuX(H)(PPh_3)_3]$ with CO and PPh_3 respectively. Complexes (2) undergo bridge-splitting reactions with a series of neutral donor ligands to produce $[RuX(H)(cod)L_2]$ [3; L = $PMePh_2$, $SbPh_3$, $AsPh_3$, or pyridine (py)], $[RuCl(H)(PPh_3)_3]$, $[RuH\{PPh(OMe)_2\}_5][PF_6]$, $[RuH(cod)L_3]^+$ (L = 4Me-py or NCMe), and $[RuCl_2(4Me\text{-}py)_4]$. Infrared and ^1H n.m.r. data for the complexes are discussed.

We have recently synthesised[2] the salts $[RuH(cod)(NH_2NMe_2)_3]A$ (1; cod = cyclo-octa-1,5-diene, A = PF_6 or BPh_4) the cation of which represents one of the very few stable *NN*-dimethylhydrazine complexes known. This stability has been attributed to hydrogen bonding between the three *facial* amino-bonded hydrazine groups from an *X*-ray structural determination of the hexafluorophosphate salt.[3] In solution this hydrogen bonding readily breaks down to give a very labile ruthenium(II) system which is the most versatile precursor known to date for a large range of neutral and cationic ruthenium(II) complexes.[2] For example, reactions of (1) under a variety of conditions have given the η-arene zwitterionic complexes $[Ru(\eta^6\text{-}C_6H_5BPh_3)(1\text{—}3,5,6\text{-}\eta\text{-}C_8H_{11})]$ and $[RuH(\eta^6\text{-}C_6H_5BPh_3)L_2]$ (L = phosphine; L_2 = diphosphine),[4] the hydrido-cations $[RuH(PMe_2Ph)_5]^+$,[5] and $[RuH(L_2)_2]^+$ (L_2 = diphosphine),[6] and the triply bridged

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[1] Part 3, T. V. Ashworth, E. Singleton, M. Laing, and L. Pope, preceding paper

[2] T. V. Ashworth, E. Singleton, and J. J. Hough, *J.C.S. Dalton*, 1977, 1809.

[3] T. V. Ashworth, M. J. Nolte, and E. Singleton, *J. Organometallic Chem.*, 1977, **139**, C73; *J.C.S. Dalton*, following paper.

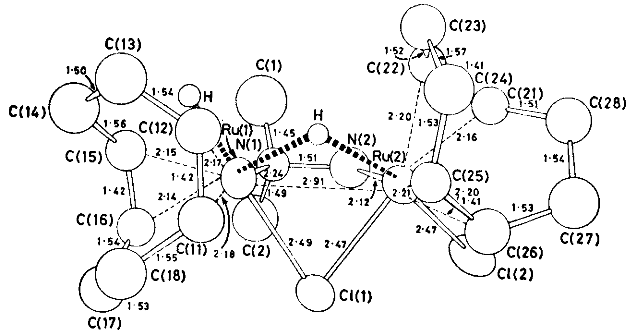
[4] T. V. Ashworth, M. J. Nolte, R. H. Reimann, and E. Singleton, *J.C.S. Chem. Comm.*, 1977, 937.

[5] T. V. Ashworth, M. Laing, M. J. Nolte, and E. Singleton, *J.C.S. Dalton*, 1977, 1816.

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

salts $[L_3RuX_3RuL_3]A$ (X = OH, SH, or SMe; L = phosphine or phosphinite).[7]

We have recently found that the interaction of (1) with Cl^- and Br^- gave the dimeric neutral complexes $[\{RuX(H)(cod)\}_2(NH_2NMe_2)]$ (2; X = Cl or Br) and the crystal and molecular structure of the chloride derivative was determined [8] (A) to confirm the presence of a triply bridged system in which the hydrazine ligand is bidentate bridging. It has been proposed [8] that the asymmetry of the triple bridge in this complex is a consequence of the size and shape of the hydrazine ligand, which causes a certain degree of strain within the molecule. It was thus of interest to see whether the strain imposed by co-ordination of the dimethylated nitrogen could induce reactivity in these bridged complexes, in contrast to the usual [9] inert nature of the tri-μ-halogeno-bridged salts. The results of this investigation are now presented.



(A)

RESULTS AND DISCUSSION

Preparation of $[\{RuX(H)(cod)\}_2(NH_2NMe_2)]$ (2; X = Cl *or* Br).—Addition of either LiCl or LiBr to a refluxing methanol–acetone solution of (1; $A = BPh_4$) resulted in the rapid deposition of (2) as a pale brown solid. The complex slowly decomposed to give a dark brown solution when reflux was continued beyond 30 min. The yields of (2) depended largely on the purity of the dimethylhydrazine precursor and optimum yields were obtained only by using freshly recrystallised samples. The nature of the impurity could not be ascertained but caused the reaction to give only dark brown solutions from which no ruthenium(II) complexes could be isolated. Complexes (2; X = Cl or Br) are very insoluble in all the common organic solvents.

The i.r. spectrum of (2) contained two bands at 2 060 and 2 030 cm^{-1} characteristic of terminal hydrides. The presence of two bands for each complex must be due to variations in site symmetry due to crystal packing. The complexes are too insoluble for their ^1H n.m.r. spectra to be recorded.

In cases where (2; X = Cl or Br) were isolated in low yield, it was not possible to deduce the nature of the complexes remaining in solution by adding donor ligands to the dark brown mother liquors. Addition of triphenylphosphine gave, after heating under reflux for 10 min, the known complex $[RuX(H)(PPh_3)_3]$.[10] Bubbling CO through the refluxing solution for 4 h gave, surprisingly, a low yield of the orange carbonyl $[Ru_3(CO)_{12}]$. This ready reduction of Ru^{II} to Ru^0 is most unusual and it is possible that the released dimethylhydrazine ligand acts as the reducing agent in this case.

No iodide or azide analogue of (2) could be prepared by analogous reactions of (1) with LiI or $Na[N_3]$. This could be a consequence of the bonding requirements of the $[N_3]^-$ ion, or the size of the I^- ion which prevents a close enough approach of the two Ru atoms for significant metal–metal interaction to occur. Reactions of (1) with Na[SCN] gave a golden brown microcrystalline product which analysed approximately for (2; X = SCN). Characterisation by further purification or by bridge-splitting reactions using $AsPh_3$ or $SbPh_3$ was not successful. It is probable in this complex that only one atom of the SCN ligand bridges the two ruthenium atoms. We are unable to say at this stage whether bonding occurs *via* the S or N atom, although the S atom may be favoured due to its similar size to Cl^-.

In order to confirm that the asymmetric shape of the dimethylhydrazine ligand in (2) is responsible for the unusual chlorohydrido-bridge, an attempt was made to prepare a complex of similar stoicheiometry to (2) containing NH_2NH_2. However, reactions of $[RuH(cod)(N_2H_4)_3][BPh_4]$ [11] with LiCl or LiBr gave only microcrystalline colourless precipitates which contained hydrazine but could not be unequivocally identified since they were extremely insoluble in organic solvents and could not be further purified. It was also not possible to selectively replace the bridging dimethylhydrazine ligand in (2) by direct reaction with other potentially bidentate ligands.

Bridge-splitting Reactions of (2; X = Cl *or* Br).—Reactions of (2; X = Cl or Br) with Lewis bases gave exclusively monomeric complexes *via* substitution of the bridging dimethylhydrazine ligand and asymmetric cleavage of the bridge. Thus the dimeric complexes are useful precursors to a range of mononuclear alkene-hydrido-derivatives of general formula $[RuX(H)(cod)L_2]$ [3; L = $PMePh_2$, $SbPh_3$, $AsPh_3$, or pyridine (py)]. These were prepared by heating (2; X = Cl or Br) under reflux in warm acetone or methanol with 4 mol equivalents of the respective ligand. The products precipitated rapidly as colourless to pale yellow solids either during the reaction or after cooling the reaction mixture. All were stable in the solid state but decomposed fairly rapidly in solution.

Terminal hydride-stretching frequencies were observed in the i.r. spectra of the complexes in the range 2 034—2 103 cm^{-1} and are characteristic of hydride *trans* to a

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[7] T. V. Ashworth, M. J. Nolte, and E. Singleton, *J.C.S. Chem. Comm.*, 1977, 936.

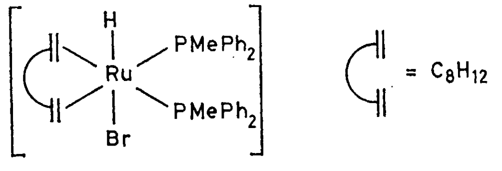
[8] T. V. Ashworth, M. J. Nolte, R. H. Reimann, and E. Singleton, *J.C.S. Chem. Comm.*, 1977, 757.

[9] P. W. Armit and T. A. Stephenson, *J. Organometallic Chem.*, 1973, **57**, C80.

[10] T. A. Stephenson and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1966, **28**, 945.

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

halogen ligand. The ^{1}H n.m.r. spectrum of (3; X = Br; L = $PMePh_2$) consists of a 1 : 2 : 1 hydride triplet at τ 20.21 [J(PH) 21 Hz] and a virtually coupled partial triplet for the ligand methyls. This is consistent with a stereochemistry in which two equivalent phosphorus ligands are in *cis* positions both to each other and to a hydride ligand and, together with the i.r. evidence, favours the stereochemistry given in (B). For (3; X = Cl, L = $PMePh_2$) the methyl resonances were virtually identical with those of the bromo-analogue but no hydride resonances were observed due to the less-soluble nature of the complex. No useful ^{1}H n.m.r. data were obtained from (3; X = Cl or Br; L = $AsPh_3$, $SbPh_3$, or py).



(B)

Analytical and spectroscopic data for the new complexes

Complex	M.p.[a] (θ_c/°C)	Analysis (%) [b] C	H	N	Halide	I.r. data [c] (cm^{-1}) ν(Ru–H)	^{1}H N.m.r. data (τ [d]) Ru–H	Other
[RuCl(H)(cod)($PMePh_2$)$_2$]	149—151	63.0 (63.2)	6.3 (6.1)		5.8 (5.5)	2 072		8.34 (pt, J^* 8.0, PCH_3)
[RuBr(H)(cod)($PMePh_2$)$_2$]		59.4 (59.1)	5.8 (5.7)		11.9 (11.6)	2 080	20.21 (t, J 21)	8.25 (pt, J^* 8.0, PCH_3)
[RuCl(H)(cod)($AsPh_3$)$_2$]	155—165	61.0 (61.6)	5.1 (5.1)		4.5 (4.1)	2 103	18.0 (s)	
[RuCl(H)(cod)($SbPh_3$)$_2$]	172—174	55.7 (55.2)	4.7 (4.6)		3.8 (3.7)	2 034	21.10 (s)	
[RuBr(H)(cod)($SbPh_3$)$_2$]	>178	53.1 (53.0)	4.2 (4.4)		10.2 (8.0)	2 035	16.40 (s)	
[RuCl(H)(cod)(py)$_2$]	>120	53.6 (53.5)	5.6 (5.7)	7.2 (6.9)	8.7 (8.8)	2 067	15.02 (s)	
[RuBr(H)(cod)(py)$_2$]	>130	48.3 (48.2)	5.3 (5.2)	6.3 (6.3)	18.2 (17.8)	2 068	15.05 (s)	
[$RuCl_2$(4Me-py)$_4$]	>250	52.8 (52.9)	5.1 (5.2)	10.4 (10.3)	13.4 (13.0)		*e*	
[$RuBr_2$(4Me-py)$_4$]	>230	45.3 (45.5)	4.6 (4.5)	8.6 (8.9)	25.6 (25.2)		*e*	
[RuH(cod)(NCMe)$_3$][BPh_4]	137—143	69.7 (69.9)	6.5 (6.5)	6.3 (6.4)		2 029 $\left.\begin{matrix}2\,321\\2\,293\end{matrix}\right\}\nu(C\equiv N)$	16.05 (s)	8.12 (s) and 8.35 (s) (CH_3CN)

[a] In air. All the complexes decomposed either on melting or without melting above the given temperatures. [b] Calculated values are in parentheses. [c] Nujol mulls. [d] Relative to $SiMe_4$. Coupling constants J,J^* in Hz. pt = Partial triplet, t = triplet, and s = singlet. Broad resonances due to the cod protons were observed in the usual positions but were not useful for assigning stereochemistry and are therefore omitted. [e] Too insoluble.

When (2; X = Cl) was treated with an excess of the more sterically demanding PPh_3 only [RuCl(H)(PPh_3)$_3$] [10] was isolated. The reaction may well proceed *via* [RuCl(H)(cod)(PPh_3)$_2$], followed by labilisation of the cyclo-octadiene ligand due to non-bonded steric repulsions caused by the bulky phenyl groups. With PPh(OMe)$_2$ the diene in (2; X = Cl or Br) was also displaced and the known [11,12] complex [RuH{PPh(OMe)$_2$}$_5$][PF_6] was isolated after addition of [NH_4][PF_6].

A suspension of (2; X = Cl or Br) in ethanol reacted with 4-methylpyridine to give a yellow solution after 2 h from which [RuH(cod)(4Me-py)$_3$][BPh_4] was isolated on addition of the [BPh_4]$^-$ anion. The labilisation of the halide ligands in these reactions contrasts with the similar reactions of pyridine which gave [RuX(H)(cod)(py)$_2$], and may be ascribed to the higher basicity of 4Me-py when compared with that of py. When the 4Me-py reaction solutions were heated under reflux for 20 h an orange solid precipitated which on recrystallisation from CH_2Cl_2–MeOH formed golden needles of [RuX_2(4Me-py)$_4$] (X = Cl or Br). The route by which the hydride ligand is lost from (2) cannot be defined at this stage. The complexes are analogous to the reported [13] [$RuCl_2$(py)$_4$] for which a structure with mutually *trans* chloride ligands was proposed on the basis of fine splitting in the far-i.r. spectrum.

Abstraction of the halide ligands from (2; X = Cl or Br) rapidly occurred with Ag[NO_3] in methyl cyanide solution. After filtration of the insoluble silver halide and addition of Na[BPh_4] to the filtrate, the complex [RuH(cod)(NCMe)$_3$][BPh_4] slowly precipitated from solution. The complex was, however, unstable in solution and had to be prepared analytically pure in preference to recrystallisation. The ^{1}H n.m.r. spectrum confirmed the presence of the hydride ligand (see Table) and the methyl cyanide protons were observed as two singlets at τ 8.12 and 8.35. Although the instability of the complex in solution resulted in broad cyclo-octadiene resonances which overlapped and prevented integration of the methyl cyanide singlets, an assignment was possible by analogy with studies made on a related complex. It has been established [14] for [Ru(cod)(NCMe)$_4$][BF_4]$_2$ that the mutually *trans* pair of MeCN

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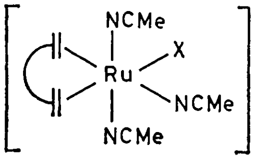
[12] D. A. Couch and S. D. Robinson, *Inorg. Chim. Acta*, 1974, **9**, 39.

[13] R. K. Poddar and V. Agarwala, *J. Inorg. Nuclear Chem.*, 1973, **35**, 567.

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

ligands resonates at τ 7.34 and the pair of MeCN ligands *trans* to cyclo-octadiene at τ 7.57. Therefore, the chemical-shift values of τ 7.38 and 7.60 observed for the MeCN protons of the salt $[RuCl(cod)(NCMe)_3][PF_6]$ [15] is consistent with the stereochemistry shown in (C; X = Cl).



(C)

The tetraphenylborate anion in $[RuH(cod)(NCMe)_3][BPh_4]$ can be expected [16] to cause an upfield shift in the resonances of the MeCN ligands both *cis* and *trans* to cyclo-octadiene, but again the lower-field singlet at τ 8.12 can be assigned to the two mutually *trans* MeCN ligands and the higher-field singlet at τ 8.35, of lower intensity, to the unique MeCN *trans* to cyclo-octadiene, thus establishing the stereochemistry to be as in (C; X = H). The resonance at τ 8.35 collapsed on addition of free CD_3CN, suggesting that the methyl cyanide ligand *trans* to cod is the most readily displaced. This result is also in accordance with previous observations.[14] The lability of the MeCN ligand suggests that $[RuH(cod)(NCMe)_3][BPh_4]$ is itself an excellent precursor to other hydrido-olefin complexes and reactions with donor ligands can be expected to give initially $[RuH(cod)L(NCMe)_2][BPh_4]$ with mutually *trans* methyl cyanide ligands.

Conclusion.—The limited series of reactions reported herein is sufficient to demonstrate the far greater reactivity of complexes (2) compared with that of the tri-μ-halogeno-bridged dimers of Ru^{II}.

EXPERIMENTAL

The complex $[RuH(cod)(NH_2NMe_2)_3][BPh_4]$ was prepared as described previously.[2] All the other reagents were obtained commercially and were not further purified. All the operations were carried out under an atmosphere of nitrogen since the majority of the mononuclear complexes were unstable in solution in air. Physical measurements were carried out as described previously [1] and the physical data for the complexes prepared are listed in the Table. Data for the complexes $[\{RuX(H)(cod)\}_2(NH_2NMe_2)]$ (X = Cl or Br) have already been reported.[2]

Preparations.— *Dichlorobis(η-cyclo-octa-*1,5-*diene)(NN-dimethylhydrazine)dihydridodiruthenium* (2; X = Cl). A solution of LiCl (0.35 g, 8.33 mmol) in methanol (10 cm^3) was added to a solution of $[RuH(cod)(NH_2NMe_2)_3][BPh_4]$ (2.00 g, 2.86 mmol) in acetone (25 cm^3) and the mixture was warmed to 45 °C without agitation. The complex began to precipitate almost immediately and was filtered off after 30 min as dark red *needles.* The yield was somewhat variable depending on the purity of the starting material and optimum yields were obtained by using samples freshly recrystallised from an NH_2NMe_2–H_2O mixture (optimum yield 0.53 g, 67%). The complex (2; X = Br) was similarly prepared using LiBr and obtained as dark red *needles* in 45% yield.

*Chloro(η-cyclo-octa-*1,5-*diene)hydridobis(methyldiphenylphosphine)ruthenium* (3; X = Cl, L = $PMePh_2$). Methyldiphenylphosphine (0.6 g, 3.00 mmol) was added to a suspension of (2; X = Cl) (0.4 g, 0.73 mmol) in refluxing acetone (15 cm^3). After 10 min the solvent was removed and ethanol (20 cm^3) was added. The resulting cream precipitate was recrystallised from dichloromethane–methanol to give the required product as colourless *prisms* (yield 0.28 g, 30%). The complex (3; X = Br, L = $PMePh_2$) was similarly prepared from (2; X = Br) as a yellow *powder* in 58% yield.

*Bromo(η-cyclo-octa-*1,5-*diene)hydridobis(triphenylstibine)ruthenium* (3; X = Br, L = $SbPh_3$). Addition of $SbPh_3$ (0.46 g, 1.3 mmol) to a suspension of (2; X = Br) (0.2 g, 0.31 mmol) in refluxing methanol resulted in the rapid deposition of a cream precipitate which was filtered off after 2 h. Recrystallisation from dichloromethane–methanol gave the required product as colourless prisms (yield 0.39 g, 62%). Similarly prepared from (2; X = Cl) and the respective ligand were (3; X = Cl, L = $AsPh_3$) as pale yellow *prisms* in 85% yield and (3; X = Cl, L = $SbPh_3$) as pale yellow *prisms* in 95% yield.

*Chloro(η-cyclo-octa-*1,5-*diene)hydridobis(pyridine)ruthenium* (3; X = Cl, L = py). Pyridine (0.3 g, 3.8 mmol) was added to a suspension of (2; X = Cl) (0.5 g, 9.1 mmol) in refluxing methanol (15 cm^3). After 2 h the yellow solution was filtered while hot and allowed to cool. The required product precipitated as large yellow *prisms* of analytical purity (yield 0.46 g, 63%). The complex (3; X = Br, L = py) was similarly prepared as yellow *prisms* in 85% yield.

*(η-Cyclo-octa-*1,5-*diene)hydridotris(*4-*methylpyridine)ruthenium tetraphenylborate.* 4-Methylpyridine (0.5 g, 5.38 mmol) was added to a suspension of (2; X = Br) (0.4 g, 0.63 mmol) in refluxing ethanol (20 cm^3). After 45 min the yellow solution was filtered while hot and a filtered solution of $Na[BPh_4]$ (0.51 g, 1.49 mmol) in ethanol (5 cm^3) was added. The required complex crystallised as cream *prisms* of analytical purity (yield 0.46 g, 45%).

*Dibromotetrakis(*4-*methylpyridine)ruthenium.* 4-Methylpyridine (0.6 g, 6.45 mmol) was added to a suspension of (2; X = Br) (0.4 g, 0.63 mmol) in refluxing methanol (20 cm^3). After 20 h the precipitate was filtered off and recrystallisation from hot acetone gave the required product as yellow *needles* (yield 0.12 g, 15%). The complex $[RuCl_2(4Me\text{-}py)_4]$ was similarly prepared from (2; X = Cl) as golden *needles* in 13% yield.

*(η-Cyclo-octa-*1,5-*diene) hydridotris (methyl cyanide)ruthenium tetraphenylborate.* Silver(I) nitrate (0.31 g, 1.82 mmol) was added to a suspension of (2; X = Cl) (0.5 g, 0.91 mmol) in acetonitrile (25 cm^3) and the mixture was stirred for 30 min at 25 °C. The solution was filtered to remove AgCl and a filtered solution of $Na[BPh_4]$ (0.68 g, 1.99 mmol) in ethanol (10 cm^3) was added. Concentration under reduced pressure gave the required product as cream *microcrystals* (yield 0.73 g, 62%). The product was also prepared in 56% yield from (2; X = Br) by a similar procedure.

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[15] T. V. Ashworth and E. Singleton, *J. Organometallic Chem.*, 1974, **77**, C31.

[16] T. V. Ashworth, R. H. Reimann, E. Singleton, and E. v.d. Stok, *Inorg. Chim. Acta*, 1977, **25**, L33.