Dimeric Ruthenium(II) Complexes with Bridging *NN*-Dimethylhydrazine Ligands: *X*-Ray Analysis of the Structure of [{RuHCl(cyclo-octa-1,5-diene)}$_2$NH$_2$NMe$_2$]

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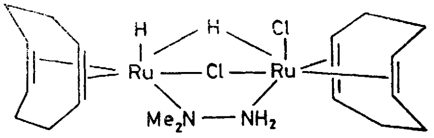
Summary An *X*-ray analysis of the structure of [{RuHCl(cyclo-octa-1,5-diene)}$_2$(NH$_2$NMe$_2$)] shows it to contain a unique example of a bidentate bridging alkyl-substituted hydrazine ligand which appears to cause the unexpected, asymmetric configuration adopted by the complex.

Alkyl or aryl substitution of hydrazine sterically inhibits the ligating ability of the substituted nitrogen atom, especially in the formation of octahedral metal complexes.[1] In fact, the only structurally verified example of co-ordination *via* this type of nitrogen atom is found[2] in the complex [Mo(η^5-C$_5$H$_5$)I(NO)(NH$_2$NHPh)][BF$_4$] in which the chelated NH$_2$NHPh ligand was synthesized on the metal. We now report the molecular structure of [(cod)ClRu{μ-(-NH$_2$NMe$_2$-)}(μ-Cl)(μ-H)RuH(cod)] (cod = cyclo-octa,-1,5-diene) which provides a unique example of a bidentate bridging *NN*-disubstituted hydrazine ligand, apparently formed in competition with free NH$_2$NMe$_2$.

Reaction of the salt [RuH(cod)(NH$_2$NMe$_2$)$_3$][BPh$_4$] (I) with 2·1 mol. equiv. of LiX in acetone–MeOH mixtures at 45 °C produced highly insoluble crystalline precipitates analysing for [{RuHX(cod)}$_2$NH$_2$NMe$_2$] [(II) X = Cl: ν(NH) 3254w and 3120w; ν(RuH) 2055m and 2035m cm^{-1}, or X = Br: ν(NH) 3260w and 3140w; ν(RuH) 2060m and 2030 cm^{-1}]. Crystals of (II; X = Cl) were suitable for an *X*-ray crystallographic study.



(II)

Crystal data: crystals of (II; X = Cl), M = 551·5, are red-brown, monoclinic, space group $P2_1/c$, a = 17·99(2), b = 7·46(2), c = 20·91(2) Å, β = 133·8(1)°, U = 2026·6 Å^3, D_m = 1·81, D_c = 1·81 g cm^{-3}, Z = 4.

The intensities of 2084 *X*-ray reflections were measured in the θ range 3—20° using the Philips PW 1100 diffractometer of the N.P.R.L., C.S.I.R., and graphite-monochromated Mo-K_α radiation. The structure was determined by the heavy-atom method and refined by full-matrix least squares to a current R of 0·073† for 1487 observed reflections [$I > 1·65\sigma(I)$]. The molecular structure is an unsymmetrical dimer with a triple bridge containing a hydride, chloride, and *NN*-dimethylhydrazine ligand, and two cod ligands, a hydride, and a chloride occupying the remaining terminal co-ordination sites (Figure 1).

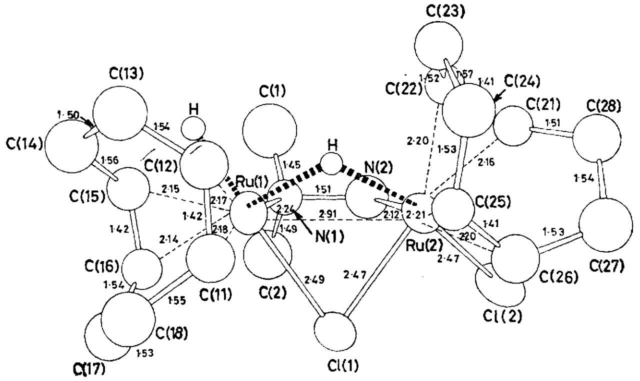


Figure 1. Structure of [{RuHCl(cyclo-octa-1,5-diene)}$_2$NH$_2$-NMe$_2$] (II), with atom-numbering system and bond lengths (in Å). The hydrogen atoms are drawn in hypothetical positions to illustrate the complete co-ordination.

A unique structural feature in (II) is the presence of the bridging NH$_2$NMe$_2$ ligand (Figure 2), the relevant parameters of which are; bond lengths Ru–NH$_2$, 2·12; Ru–NMe$_2$, 2·24, N–N, 1·51 Å; bond angles: Ru–NH$_2$–NMe$_2$, 115; Ru–NMe$_2$–NH$_2$, 103°. This represents a significant distortion from the symmetrical arrangements found[3] in structures containing bridging NH$_2$NH$_2$ ligands. The following additional features are noteworthy: i; The two nitrogen atoms are subjected to an equal structural *trans* influence. Hence the longer Ru–N bond to the substituted nitrogen atom is probably a consequence of the steric requirements of the methyl groups. ii; The methylated nitrogen atom is attached to the ruthenium atom with the less crowded ligand environment, *i.e.* that to which the terminal hydrido ligand is co-ordinated. iii; The other bridging ligands are a chloride and a hydride.‡ We expected[4] that two chlorine atoms would be in bridging positions since it seemed reasonable to assume that Cl$^-$ would bridge in preference to H$^-$. Complexes containing bridging hydrido ligands and terminal halide ligands are rare.[5] iv; The short Ru ⋯ Ru distance (2·91 Å) and the small Ru–Cl–Ru angle (72°; *cf.* the typical value of 90° found[6] in other triple bridged systems) suggest the presence of a metal–metal bond, which is required[7] since a bridging hydride makes the complex 'electron-deficient.'

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† The atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ The presence of a bridging hydride was inferred from the geometry of the molecule and from a residual peak at the expected position in the difference Fourier map.

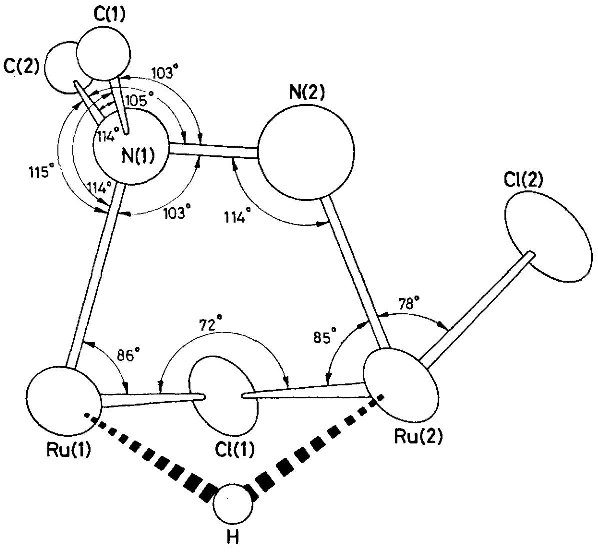

FIGURE 2. Bridging co-ordination in (II). The hydrogen atom is depicted in a hypothetical position.

v; There is a small, possibly significant, lengthening of the N–N bond compared to the values found[8] for monodentate NH_2NMe_2 ligands (1·46—1·48 Å).

Indications of steric strain within the *NN*-dimethylhydrazine ligand are evident from the fact that the methyl groups are angled at **114**(2)° from each other and from Ru(1), but **104**(2)° from N(2). This suggests a possible reason for the unsymmetrical distribution of the chloride and hydride ligands in bridging and terminal positions within the dimer. Of the possible configurations that can be drawn for (II), the one adopted is the least crowded. Replacement of the bridging H^- ligand by the larger Cl^- ligand would increase non-bonding repulsions within the bridge, while replacement of the bridging Cl^- ligand by H^- would effectively produce a shorter Ru · · · Ru distance (formally a double bond[7]) hence forcing closer non-bonded contacts at the ruthenium atom carrying the NMe_2 group. Thus the unexpected geometry of the dimer may be a consequence of the size and shape of the asymmetrically substituted hydrazine ligand.

Attempts to prepare complexes analogous to (II) using other hydrazines, or potentially bridging ligands such as $[Ph_2PCH_2]_2$ or ethylenediamine have so far been unsuccessful. However, a remarkable aspect of the reactivity of (II; X = Cl or Br) is the ease with which bridge splitting occurs during substitution reactions, producing a range of neutral and cationic monomeric complexes of the type $[(cod)RuHXL_2]$ (L = $PMePh_2$, $AsPh_3$, $SbPh_3$, or pyridine),[9] $[RuHXL_3]$ (L = PPh_3)[10] and $[RuHL_5]^+$ [L = $P(OMe)_3$ or $P(OMe)_2Ph$].[11] This is in marked contrast to the reactivity[12] of other triple-bridged dimers of Ru^{II}.

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