Structural Studies of Substituted Hydrazine Complexes. Part 3.[1] Crystal and Molecular Structure of Dichlorobis(η-cyclo-octa-1,5-diene)-(*NN*-dimethylhydrazine)dihydridodiruthenium, an Asymmetric Triply Bridged Dimer containing a Bidentate Bridging *NN*-Dimethylhydrazine Ligand

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

Crystals of the title complex are monoclinic, space group $P2_1/c$, with unit-cell dimensions a = 17.99(2), b = 7.46(2), c = 20.91(2) Å, and β = 133.8(1)°. A final R of 0.073 for 1 487 observed reflections has been obtained. The molecule is a highly distorted dimer with the two ruthenium atoms bridged by H^-, Cl^-, and NH_2NMe_2 ligands. Terminal chloride and hydride ligands are situated *trans* to, respectively, the bridging H^- and Cl^- ligands, and an η-cyclo-octa-1,5-diene is co-ordinated to each ruthenium atom. The methyl-substituted nitrogen is bonded to the ruthenium which carries the terminal H^- ligand. A unique structural feature is the bidentate bridging NH_2NMe_2 ligand: $Ru-NH_2$ 2.12, $Ru-NMe_2$ 2.24, and N–N 1.51 Å; $Ru-NH_2-N$ 115 and $Ru-NMe_2-N$ 103°. The Ru · · · Ru distance (2.91 Å) indicates the presence of a metal–metal bond of order one.

ALKYL or aryl substitution of hydrazine sterically inhibits the ligating ability of the substituted nitrogen atom, especially in the formation of octahedral metal complexes. This explains why, in general, the substituted hydrazines NH_2NHR or NH_2NR_2 function as unidentate ligands, co-ordinating *via* the less crowded NH_2 nitrogen atom.[2] The recent structural determination[3] of $[Mo(\eta\text{-}C_5H_5)I(NO)(NH_2NHPh)][BF_4]$ has shown, however, that, at least for monosubstituted hydrazines, the steric resistance to bonding *via* the substituted nitrogen atom can be overcome. For complexes containing *NN*-disubstituted hydrazine complexes, although co-ordination *via* a NMe_2 nitrogen atom has been proposed[4] in tetrahedral $[CoCl_2(NMe_2NH_2)_2]$, no *X*-ray crystal structures are at present available to clarify the bonding modes. If in fact co-ordination *via* the more bulky end of a hydrazine molecule were to occur, unusual ligand configurations may result from sterically induced rearrangements within the co-ordination sphere of the metal. During our studies on the reactivity of the cation $[RuH(cod)(NH_2NMe_2)_3]^+$ (cod = cyclo-octa-1,5-diene) we found[5] that acetone or methanol solutions of the complex in the presence of LiX produced complexes of unusual stoicheiometry, *viz.* $[\{RuX(H)(cod)\}_2(NH_2NMe_2)]$ (1; X = Cl or Br). Believing[5] these complexes to contain a unique example of a bidentate bridging NH_2NMe_2 ligand we undertook an *X*-ray crystallographic study of (1; X = Cl) to discover the parameters related to this unusual co-ordination mode. The unexpected molecular structure found for this complex demonstrates how an asymmetrically substituted hydrazine ligand, when co-ordinated *via* the substituted nitrogen atom, can impose an unusual ligand configuration on a complex.

EXPERIMENTAL

Preparation.—A method for preparing $[\{RuCl(H)(cod)\}_2(NH_2NMe_2)]$ has been described previously[5] and this procedure was modified as follows in order to obtain suitable crystals for the *X*-ray diffraction study. A recrystallized sample of $[RuH(cod)(NH_2NMe_2)_3][BPh_4]$ (2.1 g, 3 mmol) in acetone (25 cm^3) was added to a solution of LiCl (0.35 g, 8 mmol) in methanol (10 cm^3). After filtration and thorough mixing of the contents, the reaction flask was placed in a thermostatted water-bath at 44 °C. This gave suitable crystals (0.53 g, 67%) of the required product over 45 min.

Crystal Data.—$C_{18}H_{34}Cl_2N_2Ru_2$, M = 551.5, Monoclinic, space group $P2_1/c$, a = 17.99(2), b = 7.46(2), c = 20.91(2) Å, β = 133.8(1)°, U = 2 026.6 Å^3, D_m (by flotation) = 1.81, Z = 4, D_c = 1.81 g cm^{-3}, $F(000)$ = 1 112, Mo-K_α radiation (graphite monochromator), λ = 0.710 7 Å, μ(Mo-K_α) = 17.15 cm^{-1}.

A reddish brown needle-like crystal, dimensions 0.04 × 0.10 × 0.20 mm, was selected for the collection of 2 084 reflection intensities in the range θ 3—20°, using the Philips PW1100 four-circle single-crystal diffractometer of the N.P.R.L., C.S.I.R. The ω—2θ scan technique was used; each reflection was scanned for 33.3 s and the same time was taken to accumulate the background count. Standard reflections (211), ($50\bar{8}$), and ($\bar{9}010$), remeasured every hour, decreased respectively by 4.8, 5.4, and 5.3% during data collection (37 h). According to the criterion $I > 1.65\sigma(I)$, 1 487 reflections were classed as observed and were used in the structure determination. Lorentz-polarization corrections were applied, but no corrections were made for absorption, extinction, or decomposition.

Structure Solution and Refinement.—The structure was solved by heavy-atom methods. Computer programs from the '*X*-RAY' system[6] were used on an I.B.M. 360/65 computer. Full-matrix least-squares refinements were carried out with the Ru and Cl atoms anisotropic and the remaining non-hydrogen atoms isotropic. Unit weights were used.

---

[1] Part 2, T. V. Ashworth, M. J. Nolte, and E. Singleton, preceding paper.

[2] J. R. Dilworth, *Co-ordination Chem. Rev.*, 1976, **21**, 29.

[3] N. A. Bailey, P. D. Frisch, J. R. McCleverty, N. W. J. Walker, and J. Williams, *J.C.S. Chem. Comm.*, 1975, 350.

[4] D. Nicholls, M. Rowley, and R. Swindells, *J. Chem. Soc.* (*A*), 1966, 950.

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

[6] J. M. Stewart, G. J. Kruger, H. Ammon, C. H. Dickinson, and S. R. Hall, Technical Report TR-192, Computer Science Centre, University of Maryland.

A final difference electron-density map revealed a number of peaks, one of which appeared in a position suitable for a symmetrically bridging hydrogen atom. Peak heights amounted to $\leqslant 1.33$ e Å^{-3}. Following the method described by LaPlaca and Ibers,[7] another two difference electron-density maps were calculated using only low-angle reflections, cut off at $(\sin\theta)/\lambda = 0.42$ (1 193 reflections) and 0.32 Å^{-1} (549 reflections). The peak at the fractional co-ordinate position (0.77 −0.14 0.05) decreased by only 14% whereas all the other peak heights were diminished by 50% or more by this process. This peak was situated *ca.* 1.7 and 1.8 Å away from Ru(1) and Ru(2) respectively [Ru(1)–H–Ru(2) 112.3°]. However, all attempts[8] to refine the supposedly bridging hydride led to divergence of the H parameters. The reported atomic positional and thermal parameters, as well as structure factors, were obtained in the absence of any H atoms. The final R value for the observed intensities was 0.073. Scattering factors, corrected for anomalous dispersion, were those of Cromer and Mann.[9] Observed and calculated structure factors, as well as temperature factors, are listed in Supplementary Publication No. SUP 22278 (18 pp.).* Final atomic co-ordinates are listed in Table 1, bond lengths and angles in Tables 2 and 3. Figure 1, drawn by the program ORTEP,[10] gives the numbering scheme and Figure 2 is a diagram of the bridging co-ordination.

TABLE 1

Final atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*X*	*Y*	*Z*
Ru(1)	7 297(1)	−1 693(3)	−496(1)
Ru(2)	7 037(1)	446(3)	503(1)
Cl(1)	6 748(4)	1 500(8)	−777(4)
Cl(2)	5 648(5)	2 498(10)	22(4)
C(11)	8 670(16)	−596(31)	−139(14)
C(12)	8 930(16)	−2 179(31)	355(14)
C(13)	913(19)	−4 025(36)	175(17)
C(14)	8 295(19)	−4 661(36)	−763(17)
C(15)	7 231(17)	−3 815(31)	−1 232(14)
C(16)	6 882(16)	−2 194(30)	−1 719(14)
C(17)	7 491(18)	−1 013(34)	−1 825(16)
C(18)	8 570(19)	−568(36)	−937(16)
C(21)	7 164(16)	18(29)	1 597(13)
C(22)	7 617(15)	−1 473(30)	1 560(13)
C(23)	8 782(16)	−1 633(32)	2 195(14)
C(24)	9 328(17)	133(33)	2 295(15)
C(25)	8 657(16)	1 339(30)	1 475(13)
C(26)	8 036(17)	2 737(33)	1 338(15)
C(27)	7 931(19)	3 173(36)	1 989(17)
C(28)	7 730(18)	1 497(36)	2 282(15)
N(1)	5 742(12)	−2 305(24)	−1 011(11)
N(2)	5 706(14)	−1 153(27)	−438(12)
C(1)	5 639(26)	−4 101(49)	−822(22)
C(2)	4 857(23)	−1 705(44)	−1 934(20)

TABLE 2

Bond lengths (Å) with estimated standard deviations in parentheses

Ru(1)–Ru(2)	2.91(1)	Ru(2)–Cl(2)	2.47(1)
Ru(1)–Cl(1)	2.49(1)	Ru(2)–Cl(1)	2.47(1)
Ru(1)–N(1)	2.24(2)	Ru(2)–N(2)	2.12(2)
Ru(1)–C(11)	2.18(3)	Ru(2)–C(21)	2.16(3)
Ru(1)–C(12)	2.17(2)	Ru(2)–C(22)	2.20(2)
Ru(1)–C(15)	2.15(3)	Ru(2)–C(25)	2.21(2)
Ru(1)–C(16)	2.14(3)	Ru(2)–C(26)	2.20(2)
C(11)–C(12)	1.42(4)	C(21)–C(22)	1.41(4)
C(12)–C(13)	1.54(4)	C(22)–C(23)	1.52(3)
C(13)–C(14)	1.50(3)	C(23)–C(24)	1.57(4)
C(14)–C(15)	1.56(4)	C(24)–C(25)	1.53(3)
C(15)–C(16)	1.42(3)	C(25)–C(26)	1.41(4)
C(16)–C(17)	1.54(5)	C(26)–C(27)	1.53(6)
C(17)–C(18)	1.53(3)	C(27)–C(28)	1.54(5)
C(18)–C(11)	1.55(5)	C(28)–C(21)	1.51(3)
N(1)–C(1)	1.45(5)	N(1)–C(2)	1.49(3)
N(1)–N(2)	1.51(4)		

TABLE 3

Bond angles (°) with estimated standard deviations in parentheses

Cl(1)–Ru(1)–N(1)	85.5(5)	Cl(1)–Ru(2)–N(2)	85.3(8)
Cl(1)–Ru(1)–C(11)	83.8(7)	Cl(1)–Ru(2)–C(21)	168.9(6)
Cl(1)–Ru(1)–C(12)	166.5(6)	Cl(1)–Ru(2)–C(22)	153.3(9)
Cl(1)–Ru(1)–C(15)	136.0(7)	Cl(1)–Ru(2)–C(25)	93.2(8)
Cl(1)–Ru(1)–C(16)	97.6(6)	Cl(1)–Ru(2)–C(26)	93.3(9)
N(1)–Ru(1)–C(11)	168.6(7)	N(2)–Ru(2)–C(21)	97(1)
N(1)–Ru(1)–C(12)	153.2(9)	N(2)–Ru(2)–C(22)	90.7(8)
N(1)–Ru(1)–C(15)	94(1)	N(2)–Ru(2)–C(25)	161(1)
N(1)–Ru(1)–C(16)	95.9(9)	N(2)–Ru(2)–C(26)	161(1)
C(11)–Ru(1)–C(12)	38.0(9)	C(21)–Ru(2)–C(22)	38(1)
C(11)–Ru(1)–C(15)	91(1)	C(21)–Ru(2)–C(25)	88(1)
C(11)–Ru(1)–C(16)	81(1)	C(21)–Ru(2)–C(26)	81(1)
C(12)–Ru(1)–C(15)	80.6(9)	C(22)–Ru(2)–C(25)	82.2(9)
C(12)–Ru(1)–C(16)	96(1)	C(22)–Ru(2)–C(26)	98.5(9)
C(15)–Ru(1)–C(16)	38.5(9)	C(25)–Ru(2)–C(26)	37(1)
Ru(1)–N(1)–N(2)	103(1)	Ru(2)–N(2)–N(1)	114(2)
Ru(1)–N(1)–C(1)	114(2)	Cl(2)–Ru(2)–Cl(1)	88.1(3)
Ru(1)–N(1)–C(2)	115(2)	Cl(2)–Ru(2)–N(2)	78.2(7)
N(2)–N(1)–C(1)	103(3)	Cl(2)–Ru(2)–C(21)	81.8(7)
N(2)–N(1)–C(2)	105(2)	Cl(2)–Ru(2)–C(22)	117.0(9)
C(1)–N(1)–C(2)	114(2)	Cl(2)–Ru(2)–C(25)	120.4(7)
Ru(1)–Cl(1)–Ru(2)	71.9(2)	Cl(2)–Ru(2)–C(26)	83.3(8)
C(18)–C(11)–C(12)	122(3)	C(28)–C(21)–C(22)	126(2)
C(11)–C(12)–C(13)	126(3)	C(21)–C(22)–C(23)	121(1)
C(12)–C(13)–C(14)	114(2)	C(22)–C(23)–C(24)	114(2)
C(13)–C(14)–C(15)	112(3)	C(23)–C(24)–C(25)	114(2)
C(14)–C(15)–C(16)	122(3)	C(24)–C(25)–C(26)	124(3)
C(15)–C(16)–C(17)	126(2)	C(25)–C(26)–C(27)	123(2)
C(16)–C(17)–C(18)	113(3)	C(26)–C(27)–C(28)	113(2)
C(17)–C(18)–C(11)	114(3)	C(27)–C(28)–C(21)	114(3)

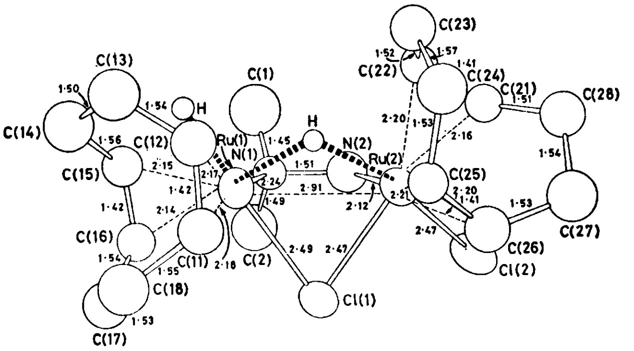

FIGURE 1 Atom-numbering system. The hydride atom is drawn in a hypothetical position to illustrate the complete co-ordination

RESULTS AND DISCUSSION

The molecular structure of $[\{RuCl(H)(cod)\}_2(NH_2NMe_2)]$ consists of an asymmetric dimer in which the two ruthenium atoms are linked by three different bridging ligands and a metal–metal bond of order one.

---

* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[7] S. J. LaPlaca and J. A. Ibers, *Acta Cryst.*, 1965, **18**, 511.

[8] S. W. Kirtley, J. P. Olsen, and R. Bau, *J. Amer. Chem. Soc.*, 1973, **95**, 4532.

[9] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[10] C. K. Johnson, Report ORNL TM 3794, Oak Ridge National Laboratories, Oak Ridge, Tennessee, 1965.

On the basis that metal-co-ordinated hydrogens occupy distinct sites at normal covalent bond distances,[11] the basic configuration of the complex can be considered as formed by the junction of two very distorted octahedra at a common face. The face is defined by a chlorine and hydrogen atom and a point between the nitrogen atoms of the hydrazine ligand. Thus, these chlorine and hydrogen atoms are co-ordinated to both rutheniums, whereas each nitrogen is bonded to a separate metal atom (see Figure 2). Octahedral co-ordination is completed around the Ru atoms by a Cl and H atom *trans* to the bridging H and Cl atoms respectively, and by a bidentate cyclo-octadiene ring co-ordinated to each metal. The dimethyl-substituted end of the hydrazine group N(1) is co-ordinated to the less sterically crowded Ru(1) atom carrying the terminal H.

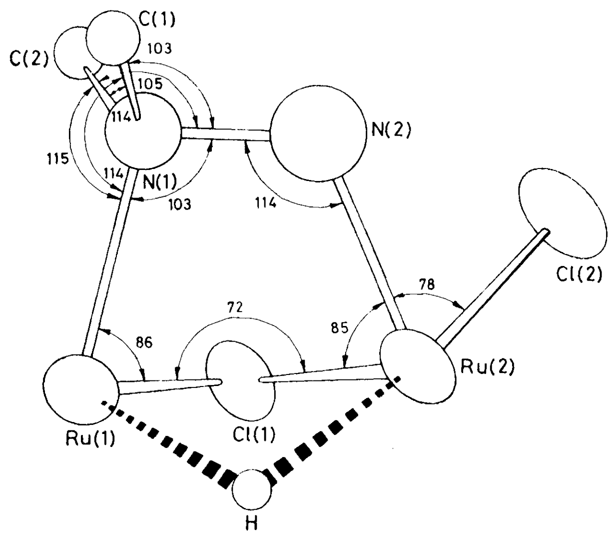

FIGURE 2 Bridging co-ordination. The hydride atom is depicted in a hypothetical position

The presence of both terminal and bridging chloride ligands necessitates a bridging and a terminal hydride ligand in order to satisfy the valency requirements of each ruthenium. Evidence for the terminal hydride comes from the medium-intensity i.r. bands at 2 055 and 2 035 cm^{-1} (Nujol mull *) [5] and this ligand can be readily located by the 'co-ordination void' on Ru(1). Crystallographic evidence for the bridging hydride comes from two sources: (*i*) the above residual peak which was found in the final difference electron-density map; and (*ii*) the overall configuration of the complex which resembles that of known [12] triply bridged dimers of Ru$^{\mathrm{II}}$.

The value of 2.91 Å observed for the Ru · · · Ru distance falls within the range (2.70—2.95 Å) found [13,14] for a single Ru–Ru bond. The title complex appears to be the first example of a confacial bioctahedron [15] in which a bridging hydride links two ruthenium(II) ions, so direct comparison of the Ru · · · Ru distance cannot at present be made. However, the shortening of the Ru · · · Ru distance and the compression of the Ru–Cl–Ru angle from the 'normal' values of 3.39 Å and 90° found [12] in $[\mathrm{Ru_2Cl_3L_6}]^+$ strongly suggest a substantial metal–metal interaction. A metal–metal bond would be expected, since the complex is rendered 'electron deficient' [16] by the bridging hydride ligand which has only one electron pair available for bonding. The close approach of the metal atoms to each other is thus in keeping with the metal–metal distances observed in other bent M(μ-H)M systems.[17] The Ru–Cl–Ru (71.9), Ru–$\mathrm{NMe_2}$–N (103), and Ru–$\mathrm{NH_2}$–$\mathrm{NMe_2}$ (114°) angles (a typical value [18] for an M–N–N angle is 117°) are all compressed suggesting that the chloride and dimethylhydrazine ligands play a negligible role in determining the metal–metal distance.

A unique structural feature in (1) is the presence of the bridging $\mathrm{NH_2NMe_2}$ ligand (Figure 2). The bond lengths Ru–$\mathrm{NH_2}$ (2.12) and Ru–$\mathrm{NMe_2}$ (2.24 Å) represent a significant distortion from the symmetrical arrangements found in structures containing bridging $\mathrm{NH_2NH_2}$ ligands.[18] If the covalent radii of Ru and N are taken as 1.42 (ref. 14) and 0.70 Å,[19] respectively, a Ru–N bond length of 2.12 Å is normal. In the present structure the two Ru–N bond distances differ significantly by 6σ and only the Ru–$\mathrm{NH_2}$ bond length can be considered normal. The lengthening of the Ru–$\mathrm{NMe_2}$ bond can be ascribed to the size of the two methyl groups bonded to N(1) which apparently prevents a closer approach to Ru(1). This is confirmed by the atoms C(1) and C(2) of the methyl groups being 3.52 and 3.37 Å from the olefinic carbon atoms C(15) and C(16) respectively. Both these distances are closer than the normal van der Waals distance (3.8 Å). Furthermore, since the two nitrogen atoms are each situated *trans* to an olefinic group, the discrepancy between the two Ru–N bond lengths cannot be ascribed to a structural *trans* influence.

The N–N bond length [1.51(4) Å] is marginally longer than the values usually found for N–N single bonds, *viz.* $\mathrm{N_2H_4}$ [1.46(2)],[20] $[\mathrm{N_2H_5}]^+$ (1.45),[21] complexes containing unidentate or bridging $\mathrm{N_2H_4}$ ligands (1.45—1.48),[22] $[\mathrm{RuH(cod)(NH_2NMe_2)_3}][\mathrm{PF_6}]$ (1.46—1.48),[1] $[\mathrm{Mo}(\eta\text{-}\mathrm{C_5H_5})\mathrm{I(NO)(NH_2NHPh)}][\mathrm{BF_4}]$ (1.43),[3] and $[\mathrm{PtCl(NH_2NHPh)(PEt_3)_2}][\mathrm{BF_4}]$ (1.44 Å).[23] The Ru–Cl bond lengths are unaffected by different substituents in the *trans* positions

---

* The complex was too insoluble to record a solution spectrum and the two bands must be ascribed to crystal-field splitting.

[11] H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, 1972, **72**, 280.

[12] M. Laing and L. Pope, *Acta Cryst.*, 1976, **B32**, 1547 and refs. therein.

[13] B. M. Mattson, J. R. Heiman, and L. H. Pignolet, *Inorg. Chem.*, 1976, **15**, 564.

[14] J. Howard and P. Woodward, *J.C.S. Dalton*, 1975, 59.

[15] F. A. Cotton, and D. A. Ucko, *Inorg. Chim. Acta*, 1972, **6**, 161.

[16] R. Mason and D. M. P. Mingos, *J. Organometallic Chem.*, 1973, **50**, 53.

[17] M. R. Churchill and S. A. Julis, *Inorg. Chem.*, 1977, **16**, 1488.

[18] A. Ferrari, A. Braibanti, G. Bigliardi, and A. M. Lanfredi, *Acta Cryst.*, 1965, **19**, 548.

[19] M. J. Bennett and R. Mason, *Nature*, 1965, **205**, 760.

[20] R. L. Collin and W. N. Lipscomb, *Acta Cryst.*, 1951, **4**, 10.

[21] G. Chiglien, J. Etienne, S. Joulmes, and P. Laruelle, *Acta Cryst.*, 1974, **B30**, 2229.

[22] F. Bottomley, *Quart. Rev.*, 1970, **24**, 617.

[23] S. D. Ittel and J. A. Ibers, *Inorg. Chem.*, 1975, **14**, 636.

(*viz.* H and two cod carbon atoms) or by the occupation of either bridging or terminal positions and vary between 2.47 and 2.49(1) Å {*cf.* [Cl(η-C_5Me_5)M(μ-Cl,μ-H)M(η-C_5Me_5)Cl] (M = Rh[24] or Ir[17])}. The two cyclooctadiene rings have the usual ' boat ' conformation with normal bond lengths.

Conclusion.—We anticipated[5] that two chlorine atoms would be in bridging positions since it seemed reasonable to assume that Cl^- would bridge in preference to H^- as complexes containing bridging hydride ligands and terminal halide ligands are rare.[17,24] The unsymmetrical distribution of the chloride and hydride ligands in bridging and terminal positions within the dimer can, however, be explained. Of the possible configurations that can be drawn for (1) the one adopted is the least crowded. Replacement of the bridging H^- ligand by the larger Cl^- 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[24]) hence forcing closer non-bonded contacts at the ruthenium atom carrying the NMe_2 group. Thus the unexpected geometry of the dimer appears to be a consequence of the size and shape of the asymmetrically substituted hydrazine ligand.

A remarkable aspect of the reactivity of (1; X = Cl or Br) is the ease with which bridge splitting occurs during substitution reactions, producing a range of neutral and cationic monomeric complexes.[25] This is in marked contrast to the reactivity[26] of other triply bridged dimers of Ru^{II}. The ligation of the NMe_2 end of the hydrazine ligand, which imposes strain on the Ru–N–N–Ru bridge, provides a tentative explanation for the remarkable reactivity of (1).

[7/1521 *Received, 23rd August,* 1977]

---

[24] M. R. Churchill, S. A. Julis, and F. J. Rotella, *Inorg. Chem.*, 1977, **16**, 1137.

[25] T. V. Ashworth, R. H. Reimann, and E. Singleton, *J.C.S. Dalton*, 1978, 1036.

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