

Journal of Organometallic Chemistry, 139 (1977) C73—C76
 © Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

X-RAY STRUCTURE OF *fac*-[RuH(1,5-cod)(NH₂NMe₂)₃][PF₆]: STABILIZATION OF COORDINATED SUBSTITUTED HYDRAZINES BY HYDROGEN BONDING

TERENCE V. ASHWORTH*, MAGRIET J. NOLTE and ERIC SINGLETON

*National Chemical Research Laboratory, Council for Scientific and Industrial Research,
 P.O. Box 395, Pretoria, 0001 (Republic of South Africa)*

(Received July 28th, 1977)

Summary

The structure of [RuH(cod)(NH₂NMe₂)₃][PF₆] has been solved by X-ray diffraction methods and shows the cation to contain a facial arrangement of *N,N*-dimethylhydrazine ligands, coordinated via the NH₂ nitrogen atoms, and held together by hydrogen bonds.

Few transition metal complexes containing alkyl-substituted hydrazine ligands have so far been reported and most of these are unstable and difficult to characterize [1]. Possible reasons for this instability are (i) the ease with which hydrazines undergo redox or deprotonation reactions [2] and (ii) steric effects which prevent bonding of the more basic [3] substituted nitrogen atom to the metal. We have recently isolated, however, a range of stable* ruthenium(II) complexes containing hydrazine ligands, viz. [Ru(cod)-(NH₂NHR)₃]²⁺ (I; R = H or Me), [RuH(cod)(NH₂NR¹R²)₃]⁺ (II; R¹ = R² = H; R¹ = H, R² = Me; or R¹ = R² = Me), and [RuHX(cod)₂(NH₂NMe₂)₂] (X = Cl⁻ or Br⁻) (cod = cycloocta-1,5-diene) which are ideal precursors for the synthesis of an extensive series of cationic and neutral ruthenium(II) complexes [4]. During this preparative study, we noticed that *N,N*-dimethylhydrazine behaved differently to the other hydrazines. For example, under the same conditions used for the preparation of the dications I, the ionic complex [RuCl(cod)(NH₂NMe₂)₃]Cl was the only product with NH₂NMe₂. However, in the presence of water the hydrido cation [RuH(cod)-(NH₂NMe₂)₃]⁺ was rapidly formed, whereas the analogous complexes (II; R¹ = R² = H, R¹ = Me, R² = H) could be isolated only after a much longer period. This difference in reactivity may be ascribed to either steric hindrance

*Sufficient for isolation and easy manipulation.

by an NMe_2 coordinated ligand, or to the weaker binding properties of NH_2NMe_2 which is the least basic of the hydrazines studied [5]. The cation $[\text{RuH}(\text{cod})(\text{NH}_2\text{NMe}_2)_3]^+$ is perhaps the most reactive of the complexes I and II, yet is stable enough in solution to provide the first example of the detection of NH_2 proton resonances of a hydrazine ligand in a metal complex [4]. Since the two relevant X-ray structural studies so far reported [6] on monosubstituted hydrazine derivatives are insufficient to elucidate all possible coordination modes of substituted hydrazines, we decided to carry out X-ray crystallographic analyses of the structures of certain of these derivatives. We were interested to discover (i) the conditions which stabilize coordination of hydrazines, and (ii) how alkyl or aryl groups affect the ligating ability of the substituted nitrogen atom and the configuration of the complex. We considered that the determination of the structure of the salt $[\text{RuH}(\text{cod})(\text{NH}_2\text{NMe}_2)_3][\text{PF}_6]$, in view of its manner of preparation, solution properties and high reactivity, would provide a suitable starting point in this programme. The structure represents the first structural characterization of an *N,N*-disubstituted hydrazine containing complex.

Crystal data

$[\text{RuH}(\text{cod})(\text{NH}_2\text{NMe}_2)_3][\text{PF}_6]$, mol. wt. 535.6, forms colourless crystals which are monoclinic, a 14.96(2), b 16.34(2), c 9.78(2) Å, β 92.6(1), U 2388.2 Å³, D_m 1.47, D_c 1.49 g cm⁻³, Z = 4, space group $P2_1/n$.

The intensities of 2195 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-monochromatized Mo- K_α radiation. The structure was determined by the heavy atom method and was refined by full-matrix least squares to a current R = 0.063 for 1780 observed reflections ($I > 3\sigma(I)$)*.

The coordination geometry of the cation is approximately octahedral with the six sites occupied by a facial configuration of *N,N*-dimethylhydrazine ligands, coordinated via their NH_2 nitrogen atoms, a bidentate cycloocta-1,5-diene ligand and a hydride ligand (unlocated) (Fig. 1). Two Ru–N bond lengths (2.17 and 2.20 Å) and the Ru–N–N angles (118, 118, 121°) are similar to the values found [7] in the bis-hydrazone ruthenium(II) complex $[\text{Ru}(\text{NH}_2\text{NCMe}_2)_2\{\text{P}(\text{OMe})_3\}_4][\text{BPh}_4]_2$, while the bond from Ru to the nitrogen atom situated *trans* to the hydride is significantly further away at 2.28 Å. The N–N distances (1.46, 1.47 and 1.48 Å) are in the range (1.45–1.48 Å) found previously in structures of complexes containing either unidentate or bridging NH_2NH_2 ligands [2]. A striking aspect of the structure is the evidence for strong hydrogen bonding between the hydrazine ligands as shown by (i) the small N–Ru–N angles (82, 84, 86°), (ii) the close non-bonded contacts (2.87, 2.89, 2.93 Å) between NH_2 nitrogen atoms and NMe_2 nitrogen atoms and (iii) the symmetrical arrangement of the hydrazine ligands (Fig. 2). The N–N–C and C–N–C angles (mean 109°) are all close ($\pm 1.5^\circ$) to the tetrahedral values.

The configuration adopted by the cation is thus the one which both maxi-

* A list of atomic coordinates is available from T.V.A.

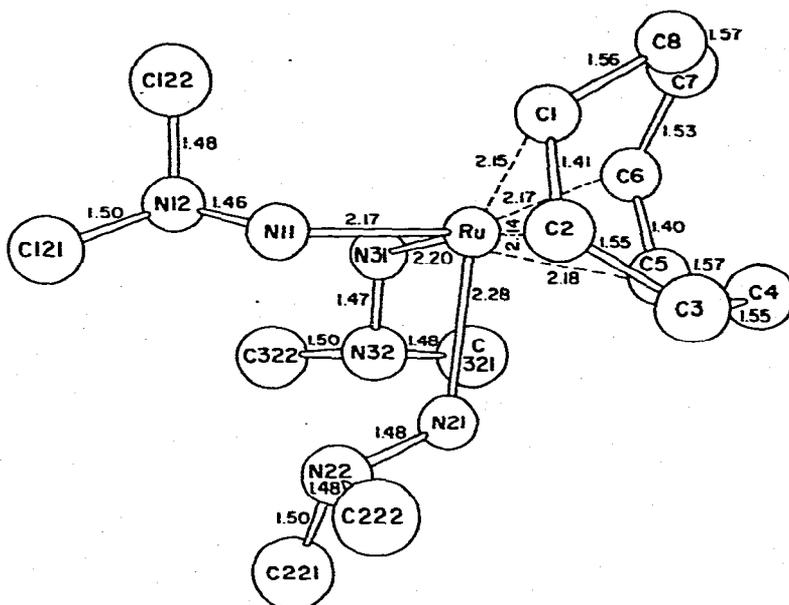


Fig. 1. Atom-numbering system. The hydrido ligand was not located but must occupy the "vacant" coordination site *trans* to N(21).

mizes hydrogen bonded contacts and minimizes the non-bonded contacts between the bulky NMe_2 ends of the hydrazine ligands. It is apparent that four N,N -dimethylhydrazine ligands would easily fit around the "(cod)Ru" moiety if bonded via the NH_2 nitrogen atoms, and hence it could be that in the ruthenium(II) systems studied [4], the electronic properties of the

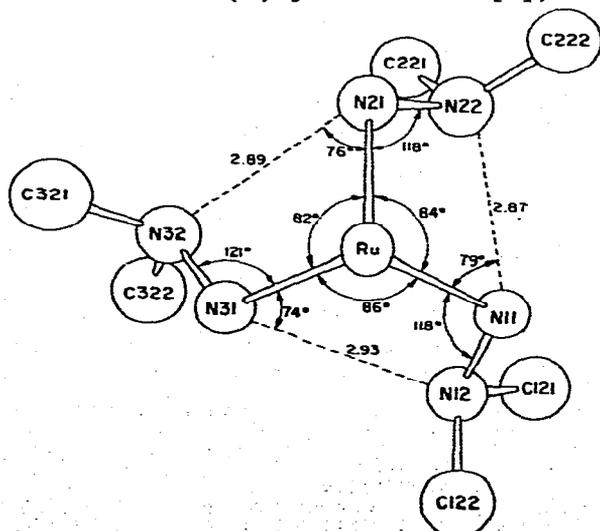


Fig. 2. A projection of part of the cation onto the plane defined by N(11), N(21) and N(31) to illustrate the hydrogen bonding.

hydrazine ligands are the dominant feature in determining the nature of the products.

The ^1H NMR spectrum of $[\text{RuH}(\text{cod})(\text{NH}_2\text{NMe}_2)_3][\text{PF}_6]$ exhibits an unusual feature, which can now be tentatively explained. Resonances at τ 3.83 (br, 2H) and 5.10 ppm (centre of an "AB quartet", 4H) were assigned to NH_2 protons from D_2O exchanges. The presence of an "AB quartet" [8] signifies that the two hydrogen atoms on each of the nitrogen atoms situated *trans* to the olefinic groups are nonequivalent (there is no plane of symmetry along these Ru—N bonds). This conditions can only be fulfilled if ligand exchange or rotation about the Ru—N bond is slow enough to allow a magnetic distinction to be made between the two NH_2 protons. A ready explanation for this phenomenon is that rotation or dissociation of the hydrazine ligands is hindered by their strong hydrogen bonding, which is shown to be present by the molecular structure determination.

The complex is, however, highly reactive towards substitution of the NH_2NMe_2 ligands by a wide range of nucleophiles [9]. It is evident from the long Ru—N distance that the bond to the nitrogen *trans* to the hydrido ligand is weakened and hence is possibly the first point of substitution. In any event, replacement of any one of the hydrazine ligands would break down the hydrogen bonding system and hence render the remaining two ligands more susceptible to substitution. The reactivity of $[\text{RuH}(\text{cod})(\text{NH}_2\text{NMe}_2)_3][\text{X}]$ (III; X = PF_6^- or IV, X = BPh_4^-) is further exemplified by (i) the reaction of III with PPh_3 under varying conditions which yielded $[\text{RuH}(\eta^6\text{-C}_6\text{H}_5\text{PPh}_2)(\text{PPh}_3)_2]^+$ [10], $[\text{RuH}_2(\text{CO})(\text{PPh}_3)_3]$ [11] and $[\text{RuH}(\text{O}_2\text{CMe})(\text{CO})(\text{PPh}_3)_2]$ [12] and (ii) the reaction with triaryl phosphites which produced the *ortho*-metallated derivatives $[\text{Ru}(\text{p-c})_2\{\text{P}(\text{OAr})_3\}_2]$ ($\text{p-c} = \text{P}(\text{OAr})_2(\text{OC}_6\text{H}_3\text{-o-X})$, X = H, Ar = Ph [13] or X = Me, Ar = *o*-tolyl). Under similar conditions IV gave the zwitterionic complexes $[\text{RuH}(\eta^6\text{-C}_6\text{H}_5\text{BPh}_3)(\text{PPh}_3)_2]$ [14] and $[\text{Ru}(\eta^6\text{-C}_6\text{H}_5\text{BPh}_3)(\text{p-c})\text{P}(\text{OAr})_3]$. We are currently investigating further reactions of III with a view to synthesizing cationic complexes of the type $[\text{RuH}(\text{arene})\text{L}_2]^+$ and $[\text{Ru}(\text{p-c})(\text{arene})\text{P}(\text{OAr})_3]^+$.

References

- 1 J.R. Dilworth, *Coordin. Chem. Rev.*, 21 (1976) 29.
- 2 F. Bottomley, *Quart. Rev.*, 24 (1970) 617, and ref. therein.
- 3 R.F. Evans and W. Kynaston, *J. Chem. Soc.*, (1963) 3151.
- 4 T.V. Ashworth, E. Singleton and J.J. Hough, *J. Chem. Soc. Dalton*, (1977) in press.
- 5 R.J. Hinman, *J. Org. Chem.*, 23 (1958) 1587.
- 6 N.A. Bailey, P.D. Frisch, J.R. McCleverty, N.W.J. Walker and J. Williams, *J. Chem. Soc. Chem. Commun.*, (1975) 350; S.D. Ittel and J.A. Ibers, *Inorg. Chem.*, 14 (1975) 636.
- 7 M.J. Nolte and E. Singleton, *J. Chem. Soc. Dalton*, (1974) 2406.
- 8 J.A. Pople, W.G. Schneider and H.J. Bernstein, *High-resolution Nuclear Magnetic Resonance*, McGraw-Hill, New York, 1959, p. 119.
- 9 T.V. Ashworth and E. Singleton, *J. Chem. Soc. Chem. Commun.*, (1976) 705; T.V. Ashworth, E. Singleton and M. Laing, *J. Organometal. Chem.*, 117 (1976) C113.
- 10 J.R. Sanders, *J. Chem. Soc. Dalton*, (1973) 743.
- 11 J.J. Sevison and S.D. Robinson, *J. Chem. Soc. A*, (1970) 2947.
- 12 S.D. Robinson and M.F. Uttley, *J. Chem. Soc. Dalton*, (1973) 1912.
- 13 M. Preece, S.D. Robinson and J.N. Wingfield, *J. Chem. Soc. Dalton*, (1976) 613.
- 14 J.J. Hough and E. Singleton, *J. Chem. Soc. Chem. Commun.*, (1972) 371.