Reaction of a Diazepine with Chlorodicarbonylrhodium(I) Dimer; the Molecular Structure of Chloro-*cis*-dicarbonyl-(3,5,7-triphenyl-4*H*-1,2-diazepine)rhodium(I)

By R. A. SMITH, D. P. MADDEN, and A. J. CARTY*
(*Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada*)
and GUS J. PALENIK
(*Department of Chemistry, University of Florida, Gainsville, Florida*)

Summary Chlorodicarbonylrhodium(I) dimer reacts with 3,5,7-triphenyl-4*H*-1,2-diazepine without cleavage of the N–N bond of the diazepine to yield chloro-*cis*-dicarbonyl (3,5,7-triphenyl-4*H*-1,2-diazepine)rhodium(I) in which the diazepine (in a twisted boat conformation) is co-ordinated to the rhodium(I) atom *via* only one nitrogen atom

THE reaction of $Fe_2(CO)_9$ with 3,5,7-triphenyl-4*H*-1,2-diazepine (diaz) proceeds *via* cleavage of the N–N bond with the formation of a novel nitrogen-bridged metallobicyclo-system.[1] 1-Substituted 1*H*-1,2-diazepines, including 1-methyl-3,5,7-triphenyl-1,2-diazepine yield diene-type iron tricarbonyl complexes with $Fe_2(CO)_9$.[2] In contrast, the reaction of $[Rh(CO)_2Cl]_2$ with (diaz) gives a $Rh(CO)_2Cl\cdot$(diaz) complex where only one nitrogen atom is co-ordinated and the diazepine ring is intact. These results indicate that substituted diazepines may be considerably more versatile as ligands than the related cycloheptatrienes.

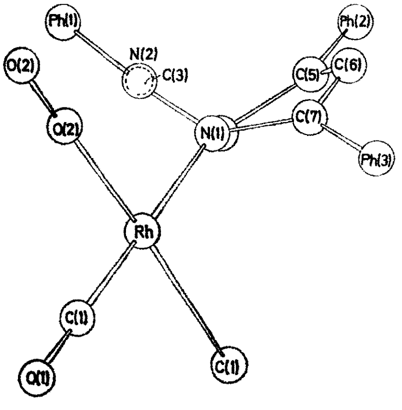

FIGURE. *View down the* N(2)–C(3) *bond of the diazepine ring illustrating the square-planar arrangement around the* Rh *atom and the conformation of the diazepine ring. Pertinent distances and angles are* Rh–Cl *of* 2·335(2) Å, Rh–Cl *of* 1·844(15) Å, Rh–C(2) *of* 1·865(15) Å, Rh–N *of* 2·127(7) Å, Cl–Rh–Cl of 89·4(5), Cl–Rh–C(2) *of* 90·3(7)°, C(2)–Rh–N(1) *of* 90·2(6)° *and* N(1)–Rh–Cl *of* 89·6(2)°.

Reaction of $[Rh(CO)_2Cl]_2$ with (diaz) in benzene yields yellow crystals (m.p. 144—147°) which give analyses consistent with the formula $Rh(CO)_2Cl$(diaz). The i.r. spectra in $CHCl_3$ show ν(C≡O) at 2086s and 2014s cm^{-1} and in the solid ν(Rh–Cl) at 313 cm^{-1} suggesting a square-planar Rh^I complex with *cis*-carbonyl groups. Similar frequencies were observed in a $Rh(CO)_2Cl$–fulvene complex for which a C=C co-ordinated to the Rh atom was suggested.[3] However, the appearance of a strong band at 725 cm^{-1} suggests either an *ortho*-substituted benzene and nitrogen co-ordination[4] or simply one nitrogen co-ordinated to the Rh^I atom. The latter possibility seemed most likely since the i.r. spectrum in the region 1650—1450 cm^{-1} and the 100 MHz n.m.r. spectrum [δ (C_6D_6) 7·80 (m, phenyl H), 7·03 (m, phenyl H), 6·20 (s, vinyl H), 4·13 (d) and 3·01 (d) (AB quartet, J_{AB} 12 Hz, CH_2) p.p.m.] are similar to that of the free ligand.[1] To resolve the structural question and to study a virtually unchanged diazepine system, the *X*-ray crystal structure was studied.

Crystal data: $(C_{23}H_{18}N_2)RhCl(CO)_2$, monoclinic, space group $P2_1/c$ (No. 14), $a = 12{\cdot}557(4)$, $b = 8{\cdot}237(2)$, $c = 21{\cdot}919(9)$ Å $\beta = 94{\cdot}03(4)°$, $D_m = 1{\cdot}49$ g cm^{-3}, $Z = 4$, $D_c = 1{\cdot}52$ g cm^{-3}.

X-Ray intensity data were collected on a G.E. automatic diffractometer using the stationary crystal–stationary counter method and Cu-K_α ($\lambda = 1{\cdot}54051$ Å) radiation; 4466 reflections were measured, of which 2687 were considered observed and used in the refinement. The structure was solved by the heavy atom technique and refined by least-squares methods using anisotropic thermal parameters to an *R* value of 0·076.

The co-ordination about the Rh atom is shown in the Figure, which is a view down the N(2)–C(3) bond. The Rh atom is in the centre of a square-planar arrangement consisting of two *cis*-carbonyl groups, a chlorine atom, and one nitrogen of the diazepine ring. The Rh–Cl bond [2·335(2) Å] is shorter and the Rh–C bonds [av. 1·855(15) Å] are longer than the distances reported in di-μ-bis(diphenylarsino)methane-bis[*trans*-chlorocarbonylrhodium(I)][5]: Rh–Cl, 2·372(2) Å and Rh–C, 1·797(10) Å. However, these differences probably reflect the different back-bonding requirements in the two compounds. The Rh–N(1) distance of 2·127(7) Å is long relative to the Rh–C distances, suggesting essentially a single bond with little or no back-bonding from Rh to the diazepine ligand. On this basis, using a N(sp^2) single bond radius of 0·720 Å,[6] the Rh^I covalent radius can be estimated as 1·407 Å. Further studies of other Rh^I complexes are required to support these hypotheses.

The heterocyclic ring is (see Figure) considerably distorted from planarity and is best described as a twisted boat form of the 4*H*-1,2-diazepine in agreement with n.m.r. studies of the uncomplexed form.[7] The N(1)–N(2) distance of 1·382(12) Å is close to the value [6,8] expected for an N–N single bond. The N(1)–C(7) and N(2)–C(3) distances [av. 1·292(13) Å] are close to the value for a C=N bond and the C(5)–C(6) distance of 1·332(15) Å is close to that expected for a C=C bond. Therefore, the diazepine ring appears to be a localized system of single and double bonds. Similar conclusions have apparently been drawn from the only other *X*-ray study of a 1,2-diazepine so far reported.[8] This result may be of importance in explaining the relatively large value of $\Delta G\ddagger$ for the interconversion of the two non-planar forms of (diaz).

The reaction of chlorodicarbonylrhodium dimer with (diaz) retains the N–N bond in the ring unlike the corresponding reaction with $Fe_2(CO)_9$ which leads to the insertion of an $Fe_2(CO)_6$ unit into the N–N bond. The products of the reactions of organo-nitrogen compounds containing N–N bonds with chlorodicarbonylrhodium dimer may therefore be different from the products of the corresponding reaction with iron carbonyls.

We thank the National Research Council of Canada for financial support.

(*Received, March* 15*th*, 1971; *Com.* 248.)

---

[1] A. J. Carty, D. P. Madden, M. Mathew, G. Palenik, and T. Birchall, *Chem. Comm.*, 1970, 1664.
[2] (a) J. Streith and J. M. Cassal, *Bull. Soc. chim. France*, 1969, 2175; (b) V. Snieckus, D. P. Madden, A. J. Carty, unpublished results.
[3] J. Altman and G. Wilkinson, *J. Chem. Soc.*, 1964, 5654.
[4] A. Kasahara, *Bull. Chem. Soc. Japan*, 1968, **41**, 1272.
[5] J. T. Mague, *Inorg. Chem.*, 1969, **8**, 1975.
[6] A. Camerman, *Canad. J. Chem.*, 1970, **48**, 179.
[7] O. Buchardt, C. L. Pedersen, U. Stanholm, A. M. Duffield, and A. T. Balaban, *Acta Chem. Scand.*, 1969, **23**, 3125.
[8] J. N. Brown, R. L. Towns, and L. M. Trefonas, *J. Amer. Chem. Soc.*, 1970, **92**, 7436.