

Preliminary communication

Structure of (*meso-cis*-2,10-diphenyl-6-aza-*kN*-2,10-diphospho-*k*²*P*-bicyclo[9.4.0]pentadeca-11(1),12,14-triene)-(bicyclo[2.2.1]heptadiene)rhodium(I) hexafluorophosphate

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Abstract

The structure of the title compound has been determined. All three donor atoms in the macrocycle are coordinated to the metal center to form a novel penta-coordinated rhodium(I) species. The N–Rh distance is 2.317(4) Å, slightly longer than normal ones.

Introduction

Recently, due to the research interest in the field of asymmetric catalytic hydrogenation [1], the structural analyses of rhodium(I) complexes have received considerable attention [1,2,3]. Whereas many tetra-coordinated rhodium(I) complexes are known, few penta-coordinated species are reported [4]. Here, we would like to present the structure of an unusual square-pyramidal rhodium(I) compound.

Results and discussion

A solution of (NBD)₂RhPF₆ (NBD = norbornadiene) in dichloromethane was added under nitrogen to a solution of the macrocyclic ligand [5] in dichloromethane. Crystals of the yellow complex were grown from the above solution with addition of a small portion of ethanol. The ORTEP plot of the title complex is shown in Fig. 1 *. Selected bond distances and angles are listed in Table 1. As shown in Fig. 1 the rhodium center is surrounded in a plane by two phosphorus atoms and two double bonds (assuming that each double bond occupies a single coordination site), since the nitrogen atom is apical with respect to the plane, the rhodium metal is in square-pyramidal geometry. The rhodium–phosphorus distances (2.233(2) and

* Crystal data: C₃₁H₃₅F₆NP₃Rh CH₂Cl₂, *M* = 816.4, monoclinic, *P*2₁/*c*, *a* 12.878(2), *b* 14.874(8), *c* 17.725(2) Å, β 97.02(1)°, *V* 3369.71 Å³, *Z* = 4, *D*_x 1.61 Mg m⁻³, *D*_m 1.60 Mg m⁻³, μ 0.70 mm⁻¹, λ(Mo-K_α) 0.7107 Å, *F*(000) = 1516, *T* 300 K, *R* = 0.048 for 4748 observed reflections.

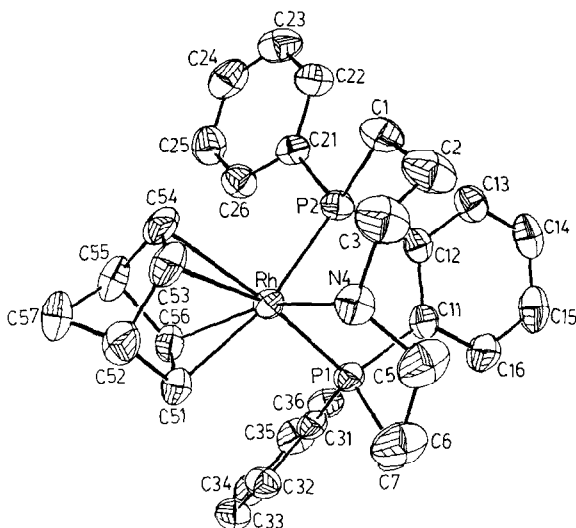


Fig. 1. ORTEP Plot of the cation of the rhodium(I) complex.

2.296(2) Å), as well as the P2–Rh–P1 angle (85.39(5)°) are similar to those reported in [(PPFA)Rh(NBD)]⁺ (PPFA = α -(2-diphenylphosphinoferrocenyl)ethyldimethylamine) (2.28(1) Å) and [(*S,S*-chiraphos)Rh(COD)]⁺ (*S,S*-chiraphos = (2*S*,3*S*)-2,3-bis(diphenylphosphino)butane; COD = 1,5-cyclooctadiene) (2.275(1) and 2.266(1) Å, 83.82(6)°) [2a,3].

Although both double bonds are in *trans* position to phosphorus atoms, their distances to metal center appear to be unequal. The Rh–C distances are 2.125(5) and 2.103(5) Å for one double bond and 2.275(5) and 2.282(5) Å for the other (i.e.,

Table 1

Selected bond lengths (Å) and bond angles (°)

Rh–P1	2.2326(15)	Rh–P2	2.2959(15)
Rh–N4	2.317(4)		
Rh–C53	2.275(5)	Rh–C54	2.282(5)
Rh–C56	2.103(5)	Rh–C51	2.125(5)
P1–C7	1.822(6)	P2–C1	1.820(6)
P1–C31	1.822(5)	P2–C21	1.832(5)
P1–C11	1.828(5)	P2–C12	1.839(5)
C1–C2	1.525(9)	C2–C3	1.465(10)
C3–N4	1.486(8)	N4–C5	1.458(8)
C5–C6	1.462(10)	C6–C7	1.539(9)
P1–Rh–P2	85.39(5)	P1–Rh–N4	90.18(12)
P2–Rh–N4	90.51(12)	N4–Rh–C56	148.15(19)
Rh–P1–C7	114.00(19)	Rh–P2–C1	114.64(20)
Rh–P2–C12	108.62(17)	Rh–N4–C3	114.9(3)
Rh–N4–C5	119.6(3)	C3–N4–C5	111.9(5)
N4–C5–C6	114.1(5)	C5–C6–C7	117.4(6)
P1–C7–C6	114.7(4)	C2–C3–N4	117.8(5)
P2–C1–C2	112.5(4)	C1–C2–C3	117.9(6)

Table 2

Selected torsional angles ($^{\circ}$)

P2-Rh-N4-C3	39.5	P1-Rh-N4-C5	-12.5
Rh-N4-C3-C2	-64.0	Rh-N4-C5-C6	-41.9
N4-C3-C2-C1	78.0	N4-C5-C6-C7	84.3
C3-C2-C1-P2	-64.5	C5-C6-C7-P1	-46.9
C2-C1-P2-Rh	46.7	C6-C7-P1-Rh	-18.3
C1-P2-Rh-N4	-32.0	C7-P1-Rh-N4	37.8

the distances of Rh to double bonds are 1.992 and 2.176 Å, respectively). Such unequal metal-olefin distances have been reported in many systems, such as $([\eta^5\text{-}(t\text{-Bu})_2\text{P}(\text{C}_3\text{H}_4)]_2\text{Fe})\text{Rh}(\text{NBD})$ cation [2b], but the difference of 0.18 Å in our complex is somewhat larger than that previously reported (see below).

Another unique feature of this structure is that the distance of the nitrogen atom to metal is 2.317(4) Å, indicating the bonding between these two atoms. Although the distance is slightly longer than the reported value 2.26(3) Å in $[(\text{PPFA})\text{Rh}(\text{NBD})]^+$ species, this longer distance is probably due to the influence of its position as an axial group.

Focusing on the 6-membered ring, it is noteworthy that the torsional angles around the Rh, P2, C1, C2, C3, N4 atoms have the typical +g, -g alternation, characteristic for a chair conformation (Table 2). The other ring with four negative and two positive torsional angles is attributed to a twist-boat conformation. The conformations of the two six-membered chelate rings are similar to those in the NiCl_2 analog [5], due to the "flagpole" interactions between H2B and H6B. Additionally, such an arrangement can also explain the unequal distances between rhodium and carbons in the crystal structure. The H3B-H53 distance is 2.26 Å for this particular conformational arrangement. Inspection of the Dreiding model of this complex with equal Rh-C distances indicates that the H3B-H53 distance becomes relatively close, thus the increase in this distance relieves the interaction. However, this unequal behavior in crystal structure is not observed in CDCl_3 solution by NMR spectroscopy. The ^{31}P NMR spectrum only shows a doublet at 56.0 ppm with $J(\text{Rh-P})$ 121 Hz.

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References

- (a) J. Halpern *Pure Appl. Chem.*, 55 (1983) 99; (b) W.S. Knowles *Acc. Chem. Res.*, 16 (1983) 106.
- (a) W.R. Cullen, F.W.B. Einstein, C.-H. Huang, A.C. Willis, E.-S. Yeh *J. Am. Chem. Soc.*, 102 (1980) 988; (b) W.R. Cullen, T.-J. Kim, F.W.B. Einstein, T. Jones *Organometallics*, 2 (1983) 714, (c) W.R. Cullen, T.-J. Kim, F.W.B. Einstein, T. Jones, *ibid.*, 4 (1985) 346, and ref. therein.
- R.G. Ball, N.C. Payne *Inorg. Chem.*, 16 (1977) 1187.
- F.A. Cotton, G. Wilkinson *Advanced Inorganic Chemistry*, 4th edit., 1980. John-Wiley & Son, New York.
- E.P. Kyba, R.E. Davis, S.-T. Liu, K.A. Hassett, S.B. Larson, *Inorg. Chem.*, 24 (1985) 4629.