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Nonplanar Rh(I) in Rh$(PMe_2Ph)_4^+$: Magnitude and Origin of the Distortion

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Abstract

The crystal and molecular structure of $Rh(PMe_2Ph)_4BF_4 \cdot 0.5$(tetrahydrofuran) has been determined at −144 °C. Space group $P\bar{1}$ with a = 11.416(2), b = 14.501(2), c = 11.195(2) Å, α = 96.53(1)°, β = 102.78(1)°, γ = 85.70(1)° and Z = 2. $R(F)$ = 0.0497, $R_w(F)$ = 0.0519. The BF_4^- and THF do not interact with the $Rh(PMe_2Ph)_4^+$ cation, which shows marked distortion from square planar towards tetrahedral geometry: transoid P–Rh–P angles are 150.77(8) and 150.01(8)°. Analysis of space-filling representations, and comparison to other related structures permits the conclusion that such distortions originate in the need to interleave the 12 R groups in $Rh(PR_3)_4^+$ species.

Introduction

During the course of work directed towards the generation of unsaturated polyalkyl tris-phosphine complexes of Rh(III), we have seen evidence for reductive elimination of alkane, with the resulting Rh(I) species scavenging phosphine ligands to generate, for example, $Rh(PMe_2Ph)_4BF_4$. The perchlorate and hexafluorophosphate analogs have been reported previously [1, 2]. We have confirmed our spectroscopic identification of our product by the X-ray diffraction study we report here. Comparison of these structural results to prior related structural studies permits some conclusions about the origin of the unusual deformation of the coordination geometry in $Rh(PMe_2Ph)_4^+$.

Experimental

All manipulations were carried out using standard Schlenk and glove box procedures under prepurified nitrogen or vacuum. Solvents were dried and deoxygenated by NaK/benzophenone (THF, pentane) or P_2O_5 (CH_2Cl_2, CD_2Cl_2). ^1H and ^{31}P NMR were recorded on a Nicolet 360 MHz spectrometer (25 °C) at 360 and 146 MHz, respectively. C_2H_4 (C.P. Grade, Matheson) was used as received.

$Rh(PMe_2Ph)_4BF_4$

To a degassed CH_2Cl_2 solution (10 ml) containing 0.26 mmol of $RhMe_2P_3BF_4$† was added excess (one atm) ethylene. After stirring for one hour, CH_2Cl_2 was removed under vacuum yielding an orange powder. Dissolving this material in a 2:1 THF/CH_2Cl_2 solution (3 ml total) followed by layering with 0.5 ml of pentane produces, after two days, a good yield of dark orange crystals. ^1H NMR (360 MHz, 25 °C, CD_2Cl_2) δ: 1.05 (br s, P-Me); 7.35–7.45 (m, P-Ph). $^{31}P\{^1H\}$ NMR (146 MHz, 25 °C, CD_2Cl_2) δ: −3.0 (d, J_{P-Rh} = 136 Hz). Both the ^1H NMR and $^{31}P\{^1H\}$ NMR spectra in CD_2Cl_2 show no changes upon cooling to −80 °C.

Crystal Structure Determination on [$Rh(PMe_2Ph)_4$]$BF_4 \cdot 0.5$THF

The crystal selected for study was mounted using silicone grease and was transferred to a goniostat where it was cooled to −144 °C for characterization and data collection [3]. A systematic search of a limited hemisphere of reciprocal space group revealed no symmetry and no systematic absences. Space group $P\bar{1}$ was assigned and was later confirmed by the successful solution of the structure. Characteristics of the data collection (6° < 2θ < 45°) processing and refinement are given in Table 1. The crystal was lost before its size could be accurately measured and consequently no correction was made for absorption. Since the crystal size was less than 1/4 mu = 0.36 cm, this was not considered a serious problem.

The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques. After the non-hydrogen atoms had been located for the cation and anion, a difference map revealed a THF molecule disordered about a center of symmetry. An attempt to refine hydrogen atoms on the cation was unsuccessful. Hydrogen atoms were subsequently placed in fixed calculated positions to improve the refinement of the non-hydrogen atoms. No attempt was made to include hydrogens on the disordered THF, which was modeled as three carbon atoms in the asymmetric unit. The final dif-

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†The complex $RhMe_2(PMe_2Ph)_3BF_4$ is produced by protonation of *fac*-$RhMe_3(PMe_2Ph)_3$. The details of this preparation will be published elsewhere.

TABLE 1. Crystal Data for $[Rh(PMe_2Ph)_4]BF_4 \cdot 0.5THF$

Empirical formula	$C_{32}H_{44}BF_4P_4Rh \cdot 0.5C_4H_8O$
Color	orange
Crystal dimensions (mm)	0.15 × 0.2 × 0.3
Space group	$P\bar{1}$
Cell dimensions (at −144 °C; 92 reflections)	
a (Å)	11.416(2)
b (Å)	14.501(2)
c (Å)	11.195(2)
α (°)	96.53(1)
β (°)	102.78(2)
γ (°)	85.70(1)
Molecules/cell	2
Volume (Å^3)	1793.15
Calculated density (gm/cm^3)	1.45
Wavelength (Å)	0.71069
Molecular weight	782.37
Linear absorption coefficient (cm^{-1})	6.88
No. unique intensities	4697
No. with $F > 0.0$	4512
No. with $F > 2.33\sigma(F)$	4237
R for averaging of 449 intensities observed more than once	0.058
Final residuals	
$R(F)$	0.0497
$R_w(F)$	0.0519
Goodness of fit for the last cycle	2.32
Maximum Δ/σ for last cycle	0.09

ference map was essentially featureless, the largest peak being 0.84 e/Å^3. The results of the refinement are given in Tables 2 and 3 and Figs. 1 and 2.

Results and Discussion

The sample used in the X-ray study was synthesized by slow crystallization of solution A, whose origin is shown in eqn. (1). This ethylene-induced

$$RhMe_2(PMe_2Ph)_3BF_4 + C_2H_4 \xrightarrow{-C_2H_6} A \qquad (1)$$

reductive elimination of ethane would be expected to produce a $Rh(PMe_2Ph)_3(C_2H_4)_nBF_4$ species, which evidently redistributes ligands. The crystalline product isolated from solution A by recrystallization from CH_2Cl_2/THF/pentane shows ^1H and ^{31}P NMR spectra similar to those reported for $Rh(PMe_2Ph)_4X$ ($X = ClO_4$ and PF_6). We have also isolated this same compound by treatment of $Rh(PMe_2Ph)_3Cl$ with $LiBF_4$ in CH_2Cl_2. To confirm that identification, we determined the structure of our material, which crystallizes with complete formula $Rh(PMe_2Ph)_4BF_4 \cdot 0.5THF$.

TABLE 2. Fractional Coordinates[a] and Isotropic Thermal Parameters[b] for $[Rh(PMe_2Ph)_4]BF_4 \cdot 0.5THF$

Atom	x	y	z	$10B_{iso}$
RH(1)	7656(1)	2535.2(4)	7334(1)	13
P(2)	5959(2)	3180(1)	6134(2)	18
C(3)	5638(8)	4398(6)	6674(9)	27
C(4)	5625(9)	3243(7)	4475(9)	30
C(5)	4660(7)	2647(6)	6447(9)	22
C(6)	3679(8)	2312(6)	5549(9)	27
C(7)	2753(9)	1920(7)	5939(11)	36
C(8)	2795(9)	1871(7)	7152(10)	31
C(9)	3737(9)	2190(7)	8040(10)	32
C(10)	4662(8)	2575(7)	7680(10)	30
P(11)	8777(2)	3783(1)	7350(2)	17
C(12)	10393(8)	3470(7)	7674(9)	29
C(13)	8720(8)	4898(6)	8284(8)	24
C(14)	8570(8)	4116(6)	5785(8)	21
C(15)	8202(8)	5008(6)	5465(8)	24
C(16)	7983(9)	5182(6)	4222(9)	27
C(17)	8135(10)	4475(7)	3324(9)	33
C(18)	8528(10)	3585(7)	3637(9)	33
C(19)	8742(9)	3408(6)	4854(9)	27
P(20)	8724(2)	2125(1)	9210(2)	15
C(21)	9138(8)	3119(6)	10353(8)	22
C(22)	10124(7)	1420(6)	9449(8)	21
C(23)	7779(7)	1518(6)	9966(7)	16
C(24)	6928(8)	2022(6)	10528(8)	24
C(25)	6172(9)	1577(8)	11056(9)	34
C(26)	6268(9)	615(9)	11026(10)	38
C(27)	7106(10)	105(7)	10469(9)	33
C(28)	7858(8)	559(6)	9947(8)	23
P(29)	7137(2)	1038(1)	6588(2)	16
C(30)	6620(8)	886(6)	4919(8)	25
C(31)	6011(8)	407(6)	7034(9)	26
C(32)	8473(7)	240(6)	6749(7)	17
C(33)	8508(8)	9347(6)	7076(8)	20
C(34)	9552(8)	−1228(6)	7135(8)	25
C(35)	10566(8)	−906(6)	6881(8)	25
C(36)	10537(8)	−18(6)	6540(8)	24
C(37)	9506(8)	555(6)	6478(8)	21
B(38)	2860(10)	2722(8)	1729(11)	29
F(39)	3595(6)	3460(5)	2095(7)	57
F(40)	3495(7)	1911(5)	2041(10)	74
F(41)	1928(7)	2853(5)	2347(7)	59
F(42)	2382(8)	2746(7)	506(6)	80
C(43)	6026(12)	5316(8)	182(11)	46
C(44)	6136(14)	4335(9)	203(12)	57
C(45)	5105(12)	4228(11)	483(13)	65

[a] Fractional coordinates are $\times 10^{-4}$. [b] Isotropic values for those atoms refined anisotropically are calculated using the formula given in ref. 4.

The X-ray study shows solid $[Rh(PMe_2Ph)_4]BF_4$ to be comprised of cations and anions, with neither the THF molecule nor the BF_4^- coordinated to rhodium. The cation (Fig. 1) has a geometry which is distinctly distorted from square planar (expected to be preferred for a four-coordinate d^8 species), but quite distinct as well from tetrahedral; this is most evident in the pseudo-*trans* angles, which are both approximately 150°. This

TABLE 3. Selected Bond Distances (Å) and Angles (°) for [Rh(PMe$_2$Ph)$_4$]BF$_4$·0.5THF

Rh(1)	P(2)	2.3015(22)		Rh(1)	P(11)	C(12)	112.0(3)
Rh(1)	P(11)	2.2886(21)		Rh(1)	P(11)	C(13)	126.6(3)
Rh(1)	P(20)	2.3008(21)		Rh(1)	P(11)	C(14)	109.7(3)
Rh(1)	P(29)	2.3076(21)		C(12)	P(11)	C(13)	101.8(5)
P(2)	C(3)	1.838(9)		C(12)	P(11)	C(14)	100.2(4)
P(2)	C(4)	1.823(9)		C(13)	P(11)	C(14)	103.3(4)
P(2)	C(5)	1.839(9)		Rh(1)	P(20)	C(21)	113.7(3)
P(11)	C(12)	1.833(9)		Rh(1)	P(20)	C(22)	125.1(3)
P(11)	C(13)	1.829(9)		Rh(1)	P(20)	C(23)	110.70(26)
P(11)	C(14)	1.831(9)		C(21)	P(20)	C(22)	100.7(4)
P(20)	C(21)	1.831(9)		C(21)	P(20)	C(23)	100.9(4)
P(20)	C(22)	1.816(9)		C(22)	P(20)	C(23)	102.7(4)
P(20)	C(23)	1.836(8)		Rh(1)	P(29)	C(30)	113.2(3)
P(29)	C(30)	1.824(9)		Rh(1)	P(29)	C(31)	125.7(3)
P(29)	C(31)	1.817(9)		Rh(1)	P(29)	C(32)	110.82(26)
P(29)	C(32)	1.833(8)		C(30)	P(29)	C(31)	99.7(4)
F(39)	B(38)	1.378(13)		C(30)	P(29)	C(32)	99.3(4)
F(40)	B(38)	1.373(14)		C(31)	P(29)	C(32)	104.6(4)
F(41)	B(38)	1.383(13)		P(2)	C(5)	C(6)	125.2(7)
F(42)	B(38)	1.361(14)		P(2)	C(5)	C(10)	116.7(7)
P(2)	Rh(1)	P(11)	93.51(8)	P(11)	C(14)	C(15)	123.6(7)
P(2)	Rh(1)	P(20)	150.77(8)	P(11)	C(14)	C(19)	117.3(7)
P(2)	Rh(1)	P(29)	92.84(8)	P(20)	C(23)	C(24)	119.8(6)
P(11)	Rh(1)	P(20)	94.35(8)	P(20)	C(23)	C(28)	121.4(6)
P(11)	Rh(1)	P(29)	150.01(8)	P(29)	C(32)	C(33)	124.2(6)
P(20)	Rh(1)	P(29)	94.26(8)	P(29)	C(32)	C(37)	117.1(6)
Rh(1)	P(2)	C(3)	112.5(3)	F(39)	B(38)	F(40)	109.9(9)
Rh(1)	P(2)	C(4)	128.0(3)	F(39)	B(38)	F(41)	108.5(10)
Rh(1)	P(2)	C(5)	107.0(3)	F(39)	B(38)	F(42)	107.2(9)
C(3)	P(2)	C(4)	100.5(5)	F(40)	B(38)	F(41)	108.2(9)
C(3)	P(2)	C(5)	99.8(4)	F(40)	B(38)	F(42)	114.9(11)
C(4)	P(2)	C(5)	105.4(4)	F(41)	B(38)	F(42)	108.0(10)

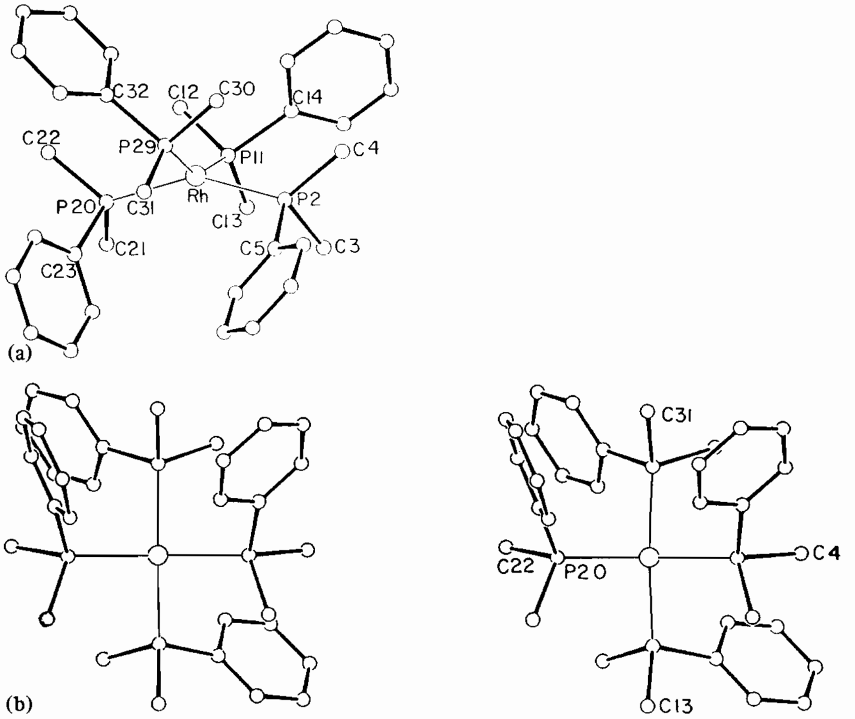

Fig. 1(a) ORTEP drawing of Rh(PMe$_2$Ph)$_4^+$ showing atom labeling. Hydrogen atoms have been omitted. (b) Stereo ORTEP drawing of Rh(PMe$_2$Ph)$_4^+$ viewed perpendicular to the best RhP$_4$ plane, showing the rotational conformation about Rh–P bonds.

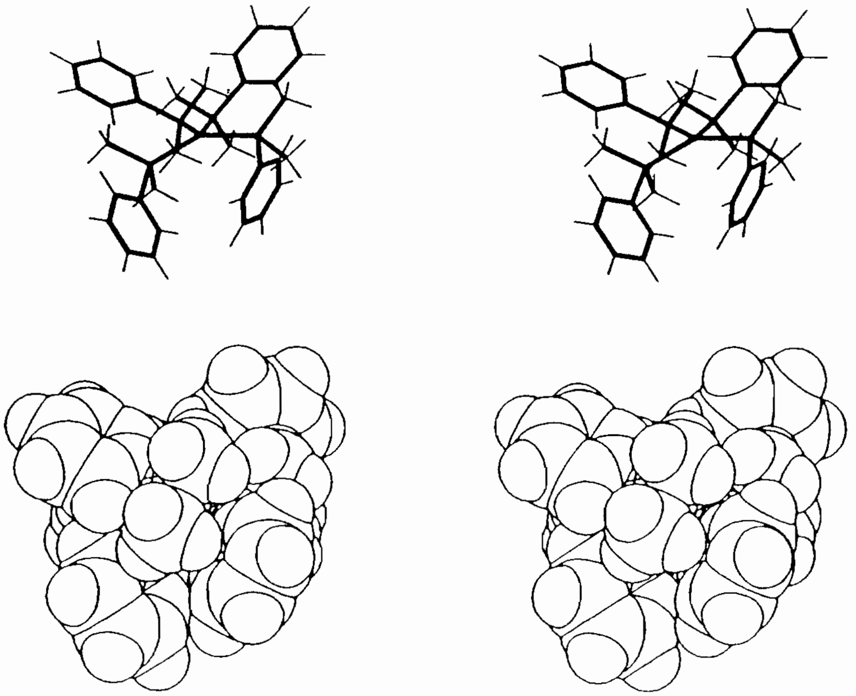

Fig. 2. Stereo stick figure and space-filling drawings of $Rh(PMe_2Ph)_4^+$, with hydrogens placed with $d(C-H) = 1.05$ Å.

out-of-plane distortion is very symmetric (compare the similarity of all pseudo-*cis* P–Rh–P angles at 93 ± 1°). We suggest that the out-of-plane distortion of the RhP_4 unit originates from interactions between organic substituents on the four PMe_2Ph groups. It is clear from stereo space-filling drawings (Fig. 2) that the packing of four of these groups is quite 'tight'. Since $Rh(PMe_3)_4^+$ has P–Rh–P angles and Rh–P distances nearly identical [5] to those of $Rh(PMe_2Ph)_4^+$ the packing cannot be specific to the phenyl rings, but instead more generally due to packing together four three-fold rotors (PR_3). This conclusion is reinforced by the observation that both $Rh(PR_3)_4^+$ cations adopt torsional angles about all P–Rh bonds which gives a planar W conformation of the transoid C–P–Rh–P–C units (Fig. 1b). In $Rh(PMe_2Ph)_4^+$, these groups are always methyl groups (C4, C13, C22, C31). This directs the two remaining substituents on a given phosphorus into the octants 'vacated' by the bending of the two adjacent phosphorus centers away from a mutual angle of 180° to 150° (Fig. 1). Although this gives distinctly different environments to the phosphine substituents, all P–C distances are equal to within 2σ. The Rh–P–C angles show marked differences however. For each PMe_2Ph group, one methyl, the one in the transoid RhP_2 plane, has a large Rh–P–C angle (125.1–128.0) while the other has a small angle (112.0–113.7). The phenyl *ipso* carbon then has the smallest Rh–P–C angle (107.0–110.8). Also noteworthy is the fact that the phenyl group on P20 destroys what would otherwise be S_4 symmetry of phenyl substituent placement. This irregular placement of phenyl rings reinforces the conclusion above that the phenyl rings occupy no special place in the packing problem in $Rh(PMe_2Ph)_4^+$. Likewise, there is no graphitic (face-to-face) stacking of phenyl rings within the cation.

One Rh–P distance differs from the other three by about 5σ (2.289 *versus* 2.304 Å), but there is no (spectrosocpic) evidence for persistence of this effect in solution, and we suggest it is not chemically (even if statistically) significant. Metric parameters within the phenyl rings and the BF_4^- ion show no noteworthy features.

Several $Rh(chelate)_2^+$ structures have been reported, where 'chelate' is a bidentate phosphine. While those with a short chelate 'bite' (intraligand P–Rh–P angle) approach planarity of the RhP_4 unit [6–8], those with a larger bite [9, 10] also show considerable out-of-plane distortion towards the angular pattern of a tetrahedron. The latter thus have an intrachelate P–M–P angle large enough to exhibit the effect of interligand steric repulsion, and thus display the same distortions as do $Rh(PMe_3)_4^+$ and $Rh(PMe_2Ph)_4^+$.

The cation $Ir(PMePh_2)_4^+$ in its BF_4 salt [11] (two crystallographically independent cations) is also distorted towards a tetrahedron (transoid P–Ir–P angles 150.5 to 151.0°) and has Ir–P rotational angles which give the W conformation described above. Here, all phenyl rings exhibit intracation graphitic stacking, and steric shielding has been cited as the reason this cation fails to react with O_2. In this regard, the structural results reported here nicely account for the lack of addition of (or even rapid ligand exchange between) $Rh(PMe_2Ph)_4^+$ and added PMe_2Ph [2].

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