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Heteropolymetallic complexes of 1,1′-bis(diphenylphosphino)ferrocene (dppf)

VI *. Synthesis and crystal structure of [Rh(dppf)(η^6-C_6H_5)B(C_6H_5)$_3$]

Bruno Longato [a], Giuseppe Pilloni [b], Rodolfo Graziani [b] and Umberto Casellato [c]

[a] *Centro di Studio Sulla Stabilità e Reattività dei Composti di Coordinazione, CNR, Via Marzolo 1, 35131 Padova (Italy)*
[b] *Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova, Via Loredan 4, 35131 Padova (Italy)*
[c] *Istituto di Chimica e Tecnologia dei Radioelementi, CNR, Corso Stati Uniti 4, 35100 Padova (Italy)*

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Abstract

The complex [Rh(COD)(dppf)]ClO_4 (COD = 1,5-cyclooctadiene; dppf = Fe((η^5-C_5H_4)P(C_6H_5)$_2$)$_2$) has been prepared by removal of the chloride ligand from [RhCl(COD)]$_2$ by $AgClO_4$ in acetone, followed by addition of one equivalent of 1,1′-bis(diphenylphosphino)ferrocene. Reaction of [Rh(COD)(dppf)]ClO_4 with dihydrogen in the presence of $NaBPh_4$ affords the neutral complex [Rh(dppf)(η^6-C_6H_5)B(C_6H_5)$_3$], which has been characterized by single crystal X-ray analysis. The Rh(dppf)$^+$ ion interacts strongly with the tetraphenylborate anion, one of the C_6H_5 groups being η^6-coordinated to the metal. The plane defined by the two P atoms of the chelated bisphosphine and the Rh atom is almost perpendicular to the mean plane containing the η^6-bonded phenyl group. The ^{1}H and ^{31}P NMR spectra of the isolated complexes are also discussed.

Introduction

We have recently reported the characterization of the cationic complexes [M(dppf)$_2$]$^+$ (M = Rh, Ir) containing the bisphosphine ligand 1,1′-bis(diphenylphosphino)ferrocene (dppf) [1]. In the course of the purification of the rhodium derivative stabilized by the tetraphenylborate ion, [Rh(dppf)$_2$](BPh_4), we isolated a few crystals of a new product whose elemental analysis was consistent with the formulation [Rh(dppf)BPh_4]. The known ability of BPh_4^- ion to bind a metal center through the coordination of one of its phenyl groups [2] suggested for the new complex a structure analogous to that of the bisphosphino complex [Rh(dppe)(η^6-

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* For Part V see ref. 1.

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Table 1

Fractional coordinates for [Rh(dppf)(η^6-C_6H_5)B(C_6H_5)$_3$] with isotropic or equivalent isotropic thermal parameters (Å^2)

Atom	x	y	z	$U_{iso/eq}$ [a]
Rh(1)	0.23220(4)	0.10415(5)	0.04508(4)	0.0332(3)
Fe(1)	0.17198(8)	−0.03800(9)	−0.07971(7)	0.0389(5)
P(1)	0.2838(1)	0.0173(2)	0.0027(1)	0.039(1)
P(2)	0.1432(1)	0.0535(2)	0.0355(1)	0.034(1)
B(1)	0.2565(6)	0.1621(6)	0.1980(5)	0.034(4)
C(1)	0.3392(4)	0.0592(5)	−0.0433(4)	0.054(5)
C(2)	0.3193(4)	0.1069(5)	−0.0828(4)	0.062(6)
C(3)	0.3595(4)	0.1380(5)	−0.1189(4)	0.081(7)
C(4)	0.4196(4)	0.1214(5)	−0.1155(4)	0.09(1)
C(5)	0.4396(4)	0.0736(5)	−0.0760(4)	0.12(1)
C(6)	0.3994(4)	0.0426(5)	−0.0399(4)	0.083(7)
C(7)	0.3284(4)	−0.0408(5)	0.0471(3)	0.042(4)
C(8)	0.3565(4)	−0.1006(5)	0.0256(3)	0.056(5)
C(9)	0.3942(4)	−0.1410(5)	0.0583(3)	0.065(6)
C(10)	0.4038(4)	−0.1216(5)	0.1126(3)	0.076(7)
C(11)	0.3757(4)	−0.0618(5)	0.1341(3)	0.073(7)
C(12)	0.3380(4)	−0.0214(5)	0.1014(3)	0.050(5)
C(13)	0.2525(4)	−0.0485(4)	−0.0453(3)	0.040(4)
C(14)	0.2158(4)	−0.1069(4)	−0.0310(3)	0.042(4)
C(15)	0.1989(4)	−0.1420(4)	−0.0799(3)	0.049(5)
C(16)	0.2251(4)	−0.1053(4)	−0.1245(3)	0.055(5)
C(17)	0.2582(4)	−0.0475(4)	−0.1031(3)	0.046(5)
C(18)	0.1236(4)	0.0293(4)	−0.0342(3)	0.039(4)
C(19)	0.0881(4)	−0.0285(4)	−0.0520(3)	0.042(4)
C(20)	0.0875(4)	−0.0282(4)	−0.1100(3)	0.052(5)
C(21)	0.1226(4)	0.0298(4)	−0.1281(3)	0.052(5)
C(22)	0.1450(4)	0.0653(4)	−0.0812(3)	0.043(5)
C(23)	0.0823(4)	0.1153(4)	0.0529(3)	0.035(4)
C(24)	0.0683(4)	0.1278(4)	0.1075(3)	0.049(5)
C(25)	0.0226(4)	0.1747(4)	0.1210(3)	0.061(6)
C(26)	−0.0090(4)	0.2090(4)	0.0797(3)	0.062(6)
C(27)	0.0050(4)	0.1964(4)	0.0251(3)	0.069(6)
C(28)	0.0506(4)	0.1496(4)	0.0117(3)	0.054(5)
C(29)	0.1219(3)	−0.0266(5)	0.0740(4)	0.040(4)
C(30)	0.1659(3)	−0.0715(5)	0.0942(4)	0.055(5)
C(31)	0.1503(3)	−0.1347(5)	0.1203(4)	0.061(5)
C(32)	0.0907(3)	−0.1530(5)	0.1261(4)	0.080(7)
C(33)	0.0467(3)	−0.1080(5)	0.1059(4)	0.065(6)
C(34)	0.0623(3)	−0.0449(5)	0.0798(4)	0.050(5)
C(35)	0.3151(3)	0.1173(4)	0.2206(3)	0.037(4)
C(36)	0.3097(3)	0.0561(4)	0.2523(3)	0.043(4)
C(37)	0.3603(3)	0.0226(4)	0.2727(3)	0.053(5)
C(38)	0.4163(3)	0.0504(4)	0.2613(3)	0.069(6)
C(39)	0.4217(3)	0.1116(4)	0.2296(3)	0.068(6)
C(40)	0.3711(3)	0.1450(4)	0.2092(3)	0.053(5)
C(41)	0.1923(4)	0.1243(4)	0.2157(4)	0.037(4)
C(42)	0.1492(4)	0.1624(4)	0.2443(4)	0.050(5)
C(43)	0.0962(4)	0.1295(4)	0.2592(4)	0.075(8)
C(44)	0.0863(4)	0.0585(4)	0.2456(4)	0.081(7)
C(45)	0.1294(4)	0.0205(4)	0.2170(4)	0.065(6)
C(46)	0.1824(4)	0.0534(4)	0.2021(4)	0.046(4)
C(48)	0.2042(5)	0.1941(6)	0.1026(5)	0.036(4)

Table 1 (continued)

Atom	x	y	z	$U_{iso/eq}$ [a]
C(49)	0.2027(7)	0.2193(6)	0.0491(6)	0.053(5)
C(50)	0.2556(8)	0.2198(7)	0.0163(6)	0.067(6)
C(51)	0.3056(6)	0.1878(7)	0.0406(6)	0.049(5)
C(52)	0.3060(6)	0.1646(7)	0.0951(5)	0.046(5)
C(47)	0.2557(5)	0.1718(6)	0.1297(5)	0.035(4)
C(54)	0.2869(4)	0.2493(4)	0.2766(4)	0.076(6)
C(55)	0.2890(4)	0.3150(4)	0.3029(4)	0.100(8)
C(56)	0.2629(4)	0.3743(4)	0.2787(4)	0.069(6)
C(57)	0.2347(4)	0.3679(4)	0.2282(4)	0.059(5)
C(58)	0.2325(4)	0.3022(4)	0.2020(4)	0.053(5)
C(53)	0.2586(4)	0.2429(4)	0.2262(4)	0.041(4)
C(59) [b]	0.6214(5)	0.2273(6)	0.0887(5)	0.039(3)
C(60) [b]	0.5161(8)	0.137(1)	0.0961(8)	0.093(6)
C(61) [b]	0.446(1)	0.323(2)	0.274(1)	0.07(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. [b] Isotropic.

$C_6H_5)B(C_6H_5)_3]$ (dppe = 1,2-bis(diphenylphosphino)ethane), which was characterized by single crystal X-ray analysis [3]. Interestingly, in the absence of BPh_4^-, the same bisphosphine dppe acts as bridging ligand to form the dinuclear complex $[Rh_2(dppe)_2]^{2+}$ in which one of the phosphorus phenyl substituents is η^6-coordinated to the metal center [4].

In view of our interest in the ligating ability of ferrocenylbisphosphine [5], we have optimized the procedure for the synthesis of $[Rh(dppf)BPh_4]$; the compound has been characterized in solution by ^1H and ^{31}P NMR spectroscopy and in the solid by X-ray crystallography. We report here also the synthesis of the precursor complex $[Rh(dppf)(COD)]ClO_4$ (COD = 1,5-cyclooctadiene).

Experimental

General procedures and materials

Syntheses and manipulations of solutions were performed under nitrogen by standard Schlenk-line techniques. All solvents were dried by standard procedures. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a JEOL 90 Q spectrometer equipped with a variable temperature probe and were referenced to internal $SiMe_4$ and external H_3PO_4, (85% w/w), respectively. 1,1′-Bis(diphenylphosphino)ferrocene (dppf) was from Strem Chemicals and was used as received. The complex $[RhCl(COD)]_2$ was prepared by published methods [6].

Preparation of $[Rh(dppf)(COD)]ClO_4$

A solution of $AgClO_4$ (245 mg, 1.18 mmol) in acetone (20 mL) was added to a suspension of $[RhCl(COD)]_2$ (276 mg, 1.12 mmol Rh) in acetone (20 mL). Precipitation of AgCl was immediately observed. The suspension was stirred at room temperature for a few minutes and the precipitate was removed by filtration. The filtrate was added to a solution of dppf (624 mg, 1.12 mmol) in toluene (40 mL), and within a few minutes a yellow orange precipitate had formed. The suspension was concentrated under vacuum to ca. 40 mL and precipitation completed by addition of pentane. The yield of isolated solid, $[Rh(dppf)(COD)]ClO_4$ was 840 mg

(86%). Elemental analysis. Found: C, 57.62; H, 4.65. $C_{42}H_{40}ClFeO_4P_2Rh$ calc.: C, 58.33; H, 4.66%. ^1H NMR (90 MHz, 27 °C, CD_2Cl_2): δ 8.0–7.5 (complex multiplet, C_6H_5); 4.35 and 4.28 (s, C_5H_4); 2.25 (br s, COD). $^{31}P\{^1H\}$NMR (36.23 MHz, 27 °C, $CDCl_3$): δ 22.0 (d, J(Rh–P) = 150 Hz).

Preparation of [Rh(dppf)(η^6-C_6H_5)B(C_6H_5)$_3$]

An equimolar solution of [Rh(dppf)(COD)]ClO_4 (352 mg, 0.4 mmol) and $NaBPh_4$ in CH_2Cl_2 (20 mL) and EtOH (20 mL) was treated with dihydrogen (1 atm) at room temperature. A red-brown precipitate was formed during ca. 1 h. The solid was filtered off and recrystallized from CH_2Cl_2/C_2H_5OH. The yield of red-brown crystals was 375 mg. The product contained trace amounts of CH_2Cl_2 of crystallization, as determined by ^1H NMR spectroscopy. Elemental analysis: Found: C, 70.49; H, 5.12. $C_{58}H_{48}BFeP_2Rh$. Calc.: C, 71.34; C, 4.95%.

X-ray data for [Rh(dppf)(η^6-C_6H_5)B(C_6H_5)$_3$]

Suitable crystals were obtained by slow evaporation of a CH_2Cl_2/C_2H_5OH solution. A crystal of maximum dimensions 0.2 mm was used for the X-ray measurements. Intensity data were recorded on a Philips diffractometer with the Mo-K_α radiation in the limits $4 < 2\theta < 50°$. Cell dimensions were determined by least-squares refinement of 25 medium-angle settings. Crystal $C_{58}H_{48}BFeP_2Rh$, Rh(dppf)BPh_4, FW = 976.5, orthorhombic, *Pbcn*, a = 22.556(4), b = 18.833(4), c = 24.489(4) Å, V = 10403 Å^3, D_c = 1.24 g cm^{-3} for Z = 8, μ(Mo-K_α) = 6.3 cm^{-1}. The crystal was stable under irradiation and of a total of 8882 unique reflections measured, whose intensities were corrected for Lp and for absorption [7], 4117 with $I > 3\sigma(I)$ were considered as observed and used in subsequent calculations. Solution of the structure was achieved by Patterson and Fourier methods alternated with cycles of least-squares refinement of the atomic parameters. Phenyl and cyclo-

Table 2

Selected bond lengths (Å) and angles (°) for [Rh(dppf)(η^6-C_6H_5)B(C_6H_5)$_3$] [a]

Rh···M	1.83(1)	Fe···Cp_2	1.64(1)
Rh–P(1)	2.260(3)	P(1)–C(1)	1.86(1)
Rh–P(2)	2.235(3)	P(1)–C(7)	1.84(1)
B–C(35)	1.67(2)	P(1)–C(13)	1.85(1)
B–C(41)	1.67(2)	P(2)–C(18)	1.82(1)
B–C(47)	1.75(2)	P(2)–C(23)	1.85(1)
B–C(53)	1.67(2)	P(2)–C(29)	1.84(1)
Fe···Cp_1	1.64(1)		
M···Rh–P(1)	132.0(4)		
M···Rh–P(2)	131.6(4)	C(1)–P(1)–C(7)	104.0(4)
P(1)–Rh–P(2)	96.0(1)	C(1)–P(1)–C(13)	99.1(4)
Rh–P(1)–C(1)	108.5(3)	C(7)–P(1)–C(13)	100.7(4)
Rh–P(1)–C(7)	116.0(3)	C(18)–P(2)–C(23)	101.1(4)
Rh–P(1)–C(13)	125.6(3)	C(18)–P(2)–C(29)	102.2(4)
Rh–P(2)–C(18)	115.0(3)	C(23)–P(2)–C(29)	101.8(4)
Rh–P(2)–C(29)	122.0(3)	Rh–P(2)–C(23)	112.0(3)

[a] M is the centroid of the η-bonded phenyl group. Rh···C distances are in the range 2.27–2.39 Å. Cp_1 and Cp_2 are the centroids of the η-bonded Cp groups. Angles at B are in the range 106.4–112.8° with a mean value of 109.5°.

pentadienyl groups were refined as rigid bodies (C–C = 1.395 and 1.420 Å, respectively, C–H = 1.08 Å), but the carbons of the η-bonded phenyl were refined as individual atoms in order to see whether the planarity of the aromatic cycle was maintained after coordination. At convergence, the residual conventional R factor was 0.063, based on the observed reflections. The function minimized was $\Sigma w(\Delta F)^2$ with $w = 1$. The SHELX programs package [8] and its scattering factors were used in the calculations; scattering factors for Rh were those of Ref. 9 and were corrected for the anomalous dispersion. Final atomic parameters are listed in Table 1 and selected bond lengths and angles in Table 2. Tables of hydrogen atom coordinates, anisotropic thermal parameters, and final structure factors are available from the authors.

Supplementary material available. Table A, listing of anisotropic thermal parameters (2 pages) of $[Rh(dppf)(\eta^6\text{-}C_6H_5)B(C_6H_5)_3]$.

Results and discussion

Preparation of $[Rh(dppf)(\eta^6\text{-}C_6H_5)B(C_6H_5)_3]$

The removal of the chloride ligand from $[RhCl(COD)]_2$ with silver perchlorate in acetone, followed by the addition of one equivalent of ferrocenylbisphosphine, gave the new complex $[Rh(COD)(dppf)]ClO_4$, which was isolated and characterized by elemental analysis and ^{31}P NMR spectroscopy. In the ^{31}P NMR spectrum of a CD_2Cl_2 solution the phosphorus resonance occurs as a sharp doublet at δ 22.0 ppm with $J(RhP) = 149$ Hz. The strictly related norbornadiene (NBD) derivative, $[Rh(NBD)(dppf)]ClO_4$, exhibits a similar spectrum, with the ^{31}P resonance at somewhat higher field (δ_P 14.8) and with a larger coupling constant ($J(RhP)$ 161 Hz) [10]. Thus, the ^{31}P NMR parameters of the coordinated ferrocenylbisphosphine appear to be quite sensitive to the nature of the diolefin in the *trans* position.

As the coupling constant value observed for the cation $[Rh(COD)(dppf)]^+$ is in the range observed for related Rh^I complexes containing chelated bisphosphine *trans* to a COD ligand [11], we suggest for the new complex a square planar geometry with the chelated ferrocenylbisphosphine and diolefin ligands symmetrically coordinated to the metal center. This suggestion is in line with the reactivity of this complex towards dihydrogen. When a solution of $[Rh(COD)(dppf)]ClO_4$ in $CDCl_3$ is saturated with dihydrogen at 1 atm a slow reaction occurs at room temperature. Within ca. 30 min a new doublet develops at δ 44.9 ppm ($J(RhP) = 213$ Hz) in the ^{31}P NMR spectrum of the reaction mixture. After ca. 24 h the intensity of the original resonance is reduced to 60% of its original value. The appearance of the doublet at δ 44.9 ppm ($J(RhP) = 213$ Hz) is concomitant with the formation of cyclooctane, detected by ^1H NMR spectroscopy (singlet at δ 1.58). The absence of any resonance in the high field region of the ^1H NMR spectrum of the reaction mixture indicates that the obtained complex is a rhodium(I) species, probably a perchlorato or a solvento complex, formed as result of a slow oxidative addition of hydrogen to the metal center, followed by the reductive elimination of the hydrogenated diolefin. Since the bisphosphine contains phenyl substituents, another possible reaction product is the dinuclear species $[Rh_2(dppf)_2]^{2+}$ in which the two $[Rh(dppf)]^+$ moieties are symmetrically linked through one of its phosphine phenyl groups. This coordination mode of a phenyl substituted bisphosphine has a precedent in the complex $[Rh_2(dppe)_2](BF_4)_2$ [4]. However, the involvement of the ClO_4^-

or solvent molecules in the coordination sphere of the metal seems preferable on the ground of their facile substitution. Thus, addition of a few % of ethanol to an hydrogenated solution of $[Rh(COD)(dppf)]ClO_4$ in $CDCl_3$, causes the immediate, although not complete, replacement of the ^{31}P NMR resonance at δ 44.9 by a new doublet centred at δ 53.8 ($J(RhP) = 215$ Hz). Moreover, the further addition of 1 equivalent of $NaBPh_4$ in ethanol brings about the quantitative coordination of the tetraphenylborate ion, as shown by the complete replacement of the ^{31}P resonances by a doublet at δ 43.0 ($J(RhP)$ 212 Hz) due to the formation of $[Rh(dppf)B(C_6H_5)_4]$.

This complex can be conveniently prepared by direct hydrogenation of the diolefin precursor in $CH_2Cl_2/EtOH$ solution, in the presence of the tetraphenylborate ion. In this procedure the overall reaction occurs in a few minutes and the adduct separates in virtually quantitative yield. The product is quite soluble in chlorinated solvents and appears to be air stable as a solid and in solution. The complex was characterized by single crystal X-ray analysis.

Structure of $[Rh(dppf)(\eta^6\text{-}C_6H_5)B(C_6H_5)_3]$

As shown in Fig. 1, the Rh atom is directly bonded to the P atoms of the bidentate dppf ligand and, via π-interaction, to one of the phenyl groups of the BPh_4^- anion.

If one coordination site is assigned to the phenyl group, the metal ion can be considered as being three-coordinate trigonal planar, with a displacement of only 0.06 Å from the plane defined by the two P atoms and by the centroid M of the

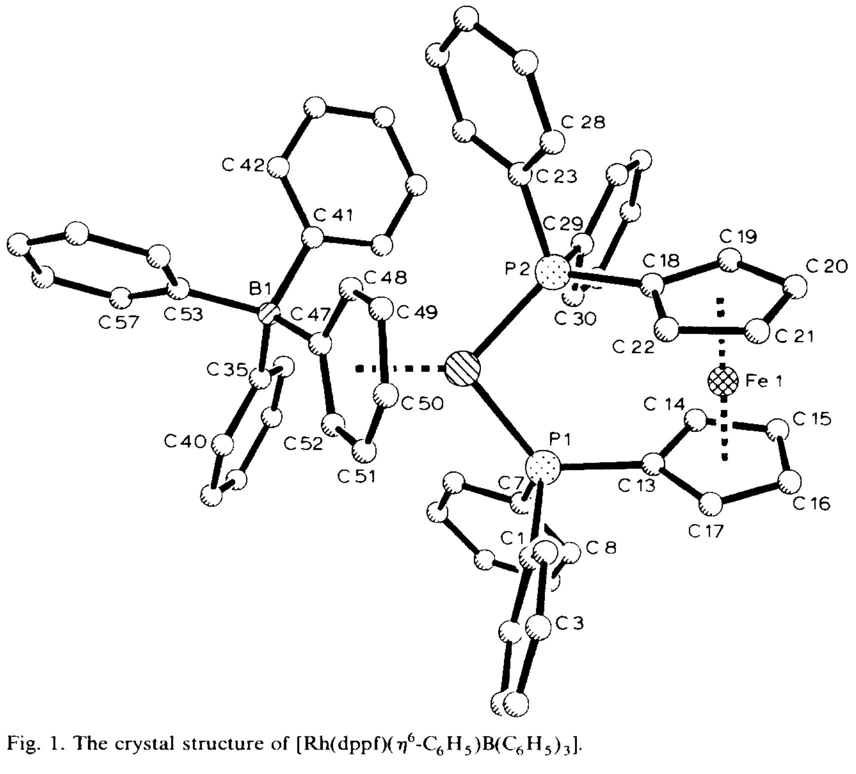

Fig. 1. The crystal structure of $[Rh(dppf)(\eta^6\text{-}C_6H_5)B(C_6H_5)_3]$.

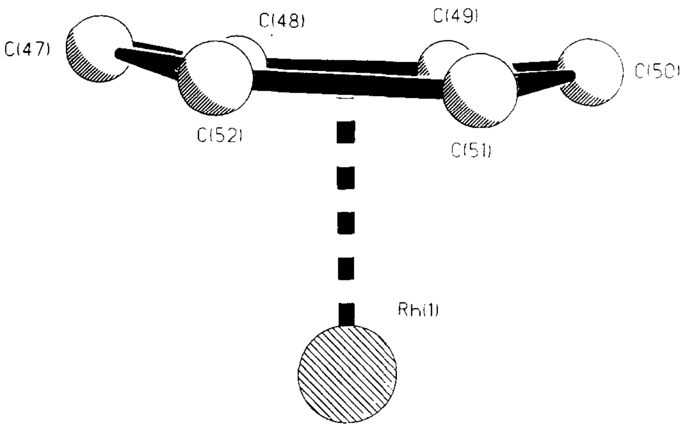

Fig. 2. Boat configuration of the η^6-coordinated phenyl group in the [Rh(dppf)(η^6-C_6H_5)B$(C_6H_5)_3$] complex.

η^6-bonded phenyl. As expected, the M · · · Rh–P angles (mean 131.8°) are significantly larger than the P–Rh–P one (96.0°). The fact that the Rh · · · M direction and the perpendicular to the phenyl are quasi-coincident (they form an angle of 3.5°) indicates that the η-bonded phenyl is quasi, but not exactly, symmetrically coordinated. This is confirmed by the fact that the Rh–C bond distances vary over the range 2.325–2.397 Å. Examination of the B–C distances shows that the B–C bond of the same phenyl (1.75(2) Å) is lengthened with respect to the others (1.67(2) Å), apparently as a result of coordination. A mean plane calculation through the six carbon atoms of the η-bonded phenyl ring shows that the atoms are not coplanar. Inspection of the deviations (Å) of the atoms from the plane [C(47) −0.058, C(48) 0.046, C(49) 0.008, C(50) −0.060, C(51) 0.034, C(52) 0.036, Rh (atom not included in the plane calculation) 1.867] clearly shows that four atoms are essentially coplanar and displaced [by about 0.03 Å] on the same side of the metal atom, while two atoms, namely C(47) and C(50), which occupy opposite positions in the phenyl hexagon, are significantly displaced (by about 0.06 Å) on the other side. A mean plane was then calculated through the four "coplanar" carbon atoms and deviations were calculated with respect to this plane.

As shown in Fig. 2, where the η^6-bonded phenyl is viewed in a suitable projection, four atoms are quasi coplanar (within 0.009 Å), whereas C(47) and C(50) are displaced by 0.07 and 0.11 Å, respectively, from this plane. A similar distortion of the phenyl to the boat configuration was previously observed in Rh[P(OMe)$_3$]$_2$-(BPh_4) [2] and in Rh(diphos)(BPh_4) [3], although in this last compound the position of the boat is inverted with respect to the metal.

The Rh–P bonds (mean 2.247 Å) are slightly shorter than the sum of the covalent and also of the atomic radii, suggesting the presence of some double bond character. These distances are significantly shorter than those in [Rh(NBD)(dppf)]ClO_4 [12]. The two Cp rings are staggered and the Fe atom is equidistant from the two centroids.

Solution properties of [Rh(dppf)(η^6-C_6H_5)B$(C_6H_5)_3$]

The ^{31}P NMR spectrum of the complex [Rh(dppf)B$(C_6H_5)_4$] in $CDCl_3$ solution exhibits a sharp doublet at δ 43.3 (J(RhP) = 212 Hz) that is temperature independent between 300 and 208 K. The corresponding ^{1}H NMR spectrum, at room temperature, shows in addition to a complex multiplet in the usual range for the phenyl protons, a clearly resolved first-order pattern (δ 5.76, doublet, J(HH) 6 Hz; 4.43, triplet, J(HH) 6 Hz) attributable to the *ortho*- and *meta*-protons, respectively, of the coordinated phenyl group. The expected triplet due to the *para*-proton is not detectable, probably being hidden by the intense resonance at δ 6.8–7.4 of uncoordinated phenyl protons.

By contrast, the cyclopentadienyl phosphino protons, at 27 ° C, exhibit a single broad signal centred at δ 4.23 which becomes resolved into sharp signals (δ 3.79 (2 H), 4.11 (2 H), 4.42 (2 H) and 4.52 (2H)) when the temperature is lowered at 208 K. Although the dynamic process responsible for the chemical equivalence of the cyclopentadienyl protons at room temperature was not investigated in detail, it is probably related to an inversion process at the phosphorus atoms and/or mutual twisting of the cyclopentadienyl ring in the chelating bisphosphine [10,13].

The coordination of the phenyl group of the $B(C_6H_5)_4^-$ anion to the rhodium atom seems to be particularly effective. Preliminary experiments carried out in $CDCl_3$ solution by ^{31}P NMR spectroscopy indicate that $[Rh(dppf)B(C_6H_5)_4]$ reacts with added dppf to form the cationic complex $[Rh(dppf)_2]^+$ to only a minor extent.

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