Rhodium Complexes of a Chelating Bisphosphoniobenzophospholide Cation

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The 1-(diphenyl(2-diphenylphosphinoethyl)phosphonio)-3-triphenylphosphoniobenzo[*c*]-phospholide cation **1** reacts with $[RhCl(C_2H_4)_2]_2$ to form a dinuclear chelate complex, $[RhCl(\kappa^2\text{-}P(\sigma^2),P'(\sigma^3)\text{-}\mathbf{1})]_2$ (**5**). Treatment of **5** with PPh_3 affords mononuclear $[RhCl(PPh_3)(\kappa^2\text{-}P(\sigma^2),P'(\sigma^3)\text{-}\mathbf{1})]$ (**8**), whereas reaction with 1,5-cyclooctadiene proceeds via cleavage of the Cl bridges to give $[RhCl(cod)(\kappa\text{-}P(\sigma^3)\text{-}\mathbf{1})]$ (**6**). The chelating binding mode of **1** can be reconstituted by abstraction of chloride with TlOTf to give the dicationic complex $[Rh(cod)(\kappa^2\text{-}P(\sigma^2),P'(\sigma^3)\text{-}\mathbf{1})]^{2+}$ (**7**). All complexes have been characterized by ^1H, ^{31}P, and ^{103}Rh NMR spectroscopy, and $\mathbf{5}[BPh_4]_2$ was characterized as well by single-crystal X-ray diffraction. The structural parameters and metal NMR data confirm the different electronic properties of the two types of phosphorus centers in **1** and support in particular the assumption of distinct π-acceptor character for the σ^2-P atom, which should render the complexes potentially interesting precatalysts for hydroformylation. In accord with this hypothesis, complexes $\mathbf{5}[BPh_4]_2$ and $\mathbf{7}[BPh_4]_2$ display good activities and chemoselectivities as catalysts for the hydroformylation of 1-hexene at room temperature, even though the regioselectivities for *n*-aldehydes are low.

Introduction

Rhodium complexes of phosphorus-based ligands are of considerable importance as (pre)catalysts in hydroformylation reactions, which, since their discovery nearly 60 years ago, have developed into one of the most important homogeneous catalytic processes.[1] Intensive studies of hydroformylation chemistry have provided some basic understanding of reaction mechanisms, and it is now well recognized that both reactivity and selectivity of a catalyst system benefit from increased π-acceptor ability of the phosphorus ligands.[2] However, despite considerable efforts that have been made toward a rational catalyst design, many aspects still remain in the dark, and a precise control of both reactivity and selectivity is still a major challenge.[2]

Among the different classes of phosphorus auxiliaries used, unsymmetric bidentate ligands which allow a chelating binding mode and at the same time an electronic differentiation of the two binding sites appear to be of great importance if one attempts to optimize selectivity.[3] A recent advantage in this field involved the utilization of phosphabenzene ligands whose low-lying π*-orbitals provide for π-acceptor qualities that are comparable to those of phosphites.[4] In the course of our studies of the coordination chemistry of phosphonio-substituted benzophospholides[5] we recently succeeded in the synthesis of the phosphine-functionalized bisphosphoniobenzo[*c*]phospholide **1**, which features two phosphorus centers with notably different electronic properties.[6] The disposition of **1** to act as a $\kappa^2\text{-}P(\sigma^2),P'(\sigma^3)$-coordinating chelate ligand was demonstrated by the synthesis of complexes **2** and **3** (Scheme 1), whose spectroscopic data suggested that the two coordinate phosphorus centers should be electronically similar to a phosphite.[6] Taking these criteria into account, we became interested in exploring the synthesis of rhodium complexes of **1** and their propensity to act as precatalysts in hydroformylation reactions. Here, we report on the preparation as well as spectroscopic and structural characterization of such complexes and a study of their

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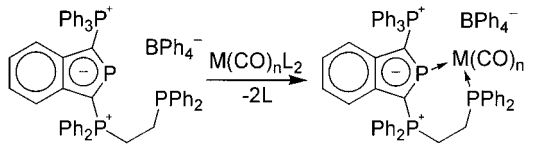
Scheme 1



1[BPh_4] **2**[BPh_4] (M = Ni, n = 2)
3[BPh_4] (M = Fe, n = 3)

use as precatalysts in the hydroformylation of hexene under mild conditions.

Results and Discussion

Synthesis of Rh Complexes. A standard method for the synthesis of rhodium phosphine complexes involves treatment of a dinuclear complex [RhCl(olefin)$_2$]$_2$ with a phosphine L. Depending on the stoichiometry and the nature of L, the reaction proceeds either via displacement of the olefins to give [RhCl(L)$_2$]$_2$, via cleavage of the halide bridges to afford a mononuclear complex [RhCl(olefin)$_2$(L)], or a combination of both to give [RhCl(L)$_3$] or [Rh(L)$_4$]Cl, respectively.[7,8] We found that **1**[X] (X = BPh_4, OTf) reacted with half an equivalent of [RhCl(C_2H_4)$_2$]$_2$ (**4a**; Rh:P = 1:2) via selective displacement of C_2H_4, to give a quantitative yield (according to a ^{31}P NMR spectroscopic assay) of the dinuclear complexes **5**[X]$_2$ (Scheme 2). The products precipitated from the solution as deep red crystals and were isolated in good yield by filtration. Characterization was achieved by analytic and spectroscopic techniques, and an X-ray crystal structure determination of **5**[BPh_4]$_2$.

Investigation of the reaction of **1**[X] with other rhodium olefin complexes revealed that [RhCl(cyclooctene)$_2$]$_2$ (**4b**) behaved similarly to **4a**, whereas only low yields of **5**[X]$_2$ were obtained when [RhCl(cod)$_2$]$_2$ (**4c**; cod = 1,5-cyclooctadiene) was used as the starting material. NMR spectra of the reaction mixtures showed that in this case besides **5**[X]$_2$ a second species had formed, which was subsequently identified (see below) as complex **6**[X] arising from cleavage of the halide bridges in **4c** by the Ph_2P group of **1**. Integration of the NMR signals indicated **6**[X] to be the major product. Addition of cod in excess to the reaction mixture resulted in quantitative conversion of **5**[X]$_2$ into **6**[X]; the same reaction was likewise observed upon treatment of isolated **5**[X]$_2$ with cod. The displacement of a coordinated phosphine moiety by cod is known for rhodium complexes of monodentate phosphines,[7,8] but unprecedented for a chelate complex, and the observed reaction behavior of **5** thus suggests that the bond to the benzophospholide phosphorus atom must be rather weak. Reconstitution of a chelating binding mode of ligand **1** was achieved by subsequent reaction of **6**[X] with thallium triflate, which afforded a precipitate of TlCl together with the salt **7**[OTf]$_2$ (Scheme 2). Pure **6**[BPh_4] and **7**[OTf]$_2$ were isolated after precipitation with hexane as microcrystalline, light yellow solids and were characterized by analytical and spectroscopic techniques.

Ligand displacement was further observed upon addition of PPh_3 to **5**[X]$_2$. In contrast to the previously described cases, this reaction proceeded via specific cleavage of the halide bridges to afford the monomeric trisphosphine rhodium chloride **8**[X], which can be regarded as an analogue of Wilkinson's complex. Isolation of the product as dark red crystals was feasible after precipitation with hexane. Remarkably, no ligand displacement was observed when **5**[X]$_2$ was treated with an excess of **1**[X]. Presumably, attachment of a second unit of **1** to the same metal, which is known in other cases,[6] is here prevented by steric overcrowding.

Spectroscopic Investigations. Composition and constitution of the prepared complexes followed unequivocally from elemental analyses and spectroscopic (NMR, FAB-MS) data. Whereas the presence of OTf and BPh_4 anions was generally disclosed by appropriate ^{19}F and ^{1}H NMR signals, the diagnostically most relevant information for the determination of the constitution of the cations came from ^{31}P{^{1}H} NMR spectra (Table 1). The spectra of **5**[X]$_2$−**7**[X]$_2$ displayed the expected signals of the four chemically inequivalent phosphorus nuclei of ligand **1**, whose assignment was unequivocally feasible based on the observed chemical shifts and the characteristic intraligand coupling patterns. Coordination of one (**6**) or two phosphorus atoms (**5**, **7**, **8**) was indicated by additional splittings due to $^1J_{RhP}$ couplings. The spectra of complexes **5** and **7**, which feature a chelating binding mode of the ligand **1**, showed further an additional splitting due to $^2J_{PMP}$, whose magnitude indicates a *cis*-arrangement of the coordinated phosphorus nuclei.[9] The spectrum of **8**[X] displayed an additional resonance for the PPh_3 ligand. The significantly different magnitudes of the two $^2J_{PMP}$ couplings from this site to the nuclei in the PPh_2 ($^2J_{PMP}$ = 386 Hz) and benzophospholide units ($^2J_{PMP}$ = 51 Hz) reveal a mutual *trans*-alignment of the two phosphine centers on one hand and the chloride and benzophospholide moieties on the other hand.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **5**, **7**, and **8** revealed the chemical inequivalence of all methylene hydrogen atoms and phenyl substituents in the side chain of coordinated **1** and of all carbon and hydrogen atoms in the diolefin moiety of **7**. These findings indicate a molecular C_1-symmetry, which implies the presence of a nonplanar, seven-membered chelate ring whose conformational inversion is slow on the NMR time scale.[10] Consequently, the spectra of **6**, which lacks such a chelate ring, reveal the pairwise chemical equivalence of the corresponding hydrogen and carbon nuclei and are compatible with effective C_s-symmetry.

To obtain further insight into the mechanism of interconversion between **5** and **6**, solutions containing mixtures of both complexes together with a small excess of cod were investigated by VT ^{1}H and ^{31}P NMR spectroscopy. The spectra disclosed besides **5**, **6**, and cod

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(10) For **7**[BPh_4]$_2$, slow inversion of the chelate ring at ambient temperature was proven by the appearance of cross-peaks in two-dimensional ^{1}H EXSY NMR spectra connecting the resonances of the diastereotopic protons in CH_2 and HC=CH moieties.

Scheme 2

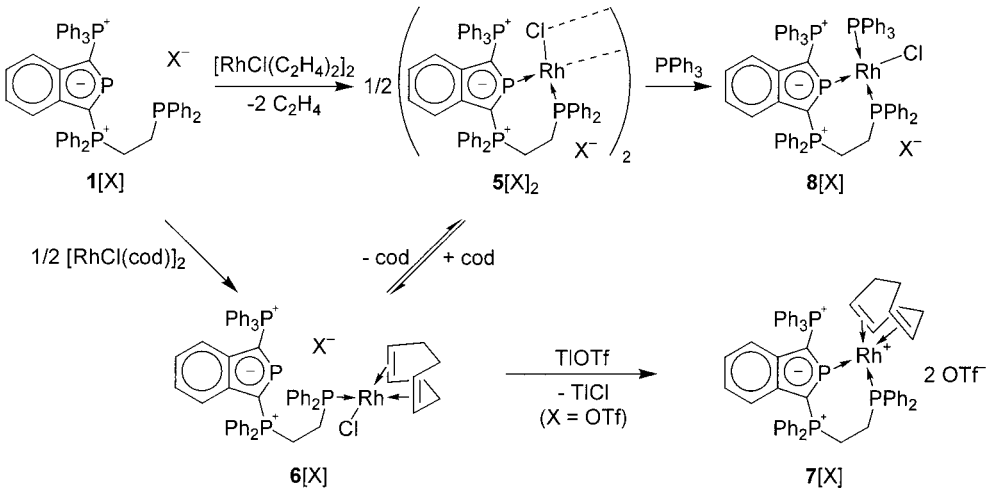
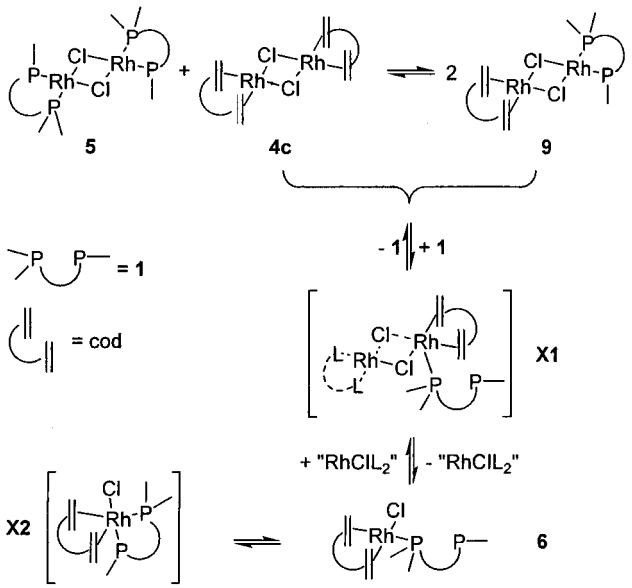


Table 1. ^{31}P NMR Data of Rhodium Complexes 5−8 (at 30 °C, in CD_2Cl_2)

	$\delta^{31}P^a$ (−P−)	$\Delta\delta(P^a)$	$\delta^{31}P^b$ (PPh_2)	$\Delta\delta(P^b)$	$\delta^{31}P^c$ (−PPh_2−)	$\delta^{31}P^d$ (−PPh_3)	J_{PP} (Hz)	$J_{Rh,P}$ (Hz)
5[a]	226.6	−7.5	51.6	+63.6	15.6	15.1	65.2 (P^aP^b), 65.7 (P^aP^c), 64.8 (P^aP^d), 9.5 (P^bP^c), 6.4 (P^cP^d)	232.8 (Rh,P^a), 172.0 (Rh,P^b)
6	233.9		27.2	+39.2	17.4	16.1	83.0 (P^aP^c), 91.9 (P^aP^d), 51.7 (P^bP^c), 8.1 (P^cP^d)	152.9 (Rh,P^b)
7	186.8	−47.3	30.2	+42.2	16.9	16.0	56.3 (P^aP^b), 62.6 (P^aP^c), 67.7 (P^aP^d), 6.9 (P^bP^c), 5.9 (P^cP^d)	162.4 (Rh,P^a), 134.0 (Rh,P^b)
8[b]	236.7	+2.6	32.4	+34.4	15.7	15.3	65.6 (P^aP^b), 62.9 (P^aP^c), 70.0 (P^aP^d), 6.5 (P^bP^c), 6.6 (P^cP^d)	205.2 (Rh,P^a), 130.0 (Rh,P^b)

[a] Data obtained from iteration of the spectrum as an $[ADMNX]_2$ spin system; further coupling constants (abs values): $^4J_{PaPa'} = 3.2$ Hz, $^4J_{PaPb'} = 1.6$ Hz, $^3J_{PaRh'} = 5.3$ Hz, $^4J_{PbPb'} = 2.2$ Hz, $^3J_{PbRh'} = 4.7$ Hz, $^2J_{Rh'Rh'} = 1.7$ Hz. [b] $\delta P^e(PPh_3)$: 22.3, $^2J_{PePa}$ 51.4 Hz, $^2J_{PePb}$ 286.0 Hz, $^1J_{Rh,\,Pe}$ 125.0 Hz.

Scheme 3. Schematic Representation of Postulated Dynamic Exchange Pathways between Complexes 4c, 5, and 6



the presence of small amounts of $[RhCl(cod)]_2$ (**4c**), **1**, and a further species tentatively formulated as a "mixed" dinuclear complex **9** (Scheme 3).[11] Temperature-dependent line shape variations in the ^{31}P NMR spectra revealed mutual interconversion of **5** and **9**; two-dimensional ^{1}H-EXSY NMR spectra (Figure 1a) proved further the presence of chemical exchange between **4c**, **6**, and **9**, and the absence of any exchange between coordinated and free cod. In addition, the 2D-EXSY spectra revealed a further *intramolecular* exchange between the coordinated double bonds in *cis*- and *trans*-position to the Ph_2P ligand in **6** which occurred with preservation of interligand $^2J_{PMC}$ and $^3J_{PMCH}$ couplings across the metal. This process can be described in terms of a formal rotation of the cod moiety and persisted at higher dilution when intermolecular exchange was negligible (Figure 1b). Altogether, the observed spectrosocpic data are compatible with a reaction sequence displayed in Scheme 3, which resembles previously established reaction mechanisms for substitution reactions of other rhodium diolefin complexes with phosphorus ligands.[8] A likely mechanism for the rotation of the coordinated cod in **6** involves the intermediate formation of a pentaccordinate complex **X2**, followed by pseudorotation of the diolefin, and subsequent decomplexation of the benzophospholide moiety.

Analysis of trends in $^1J_{RhP}$ couplings revealed that in all chelate complexes the coupling to the two-coordinate σ^2-phosphorus atoms exceeds that to the σ^3-phosphorus atoms in phosphine moieties by 30−60 Hz. This effect is attributable to the different formal hybridization (sp^2 vs sp^3) of the donor atoms. Coordination shifts ($\Delta\delta = \delta$(complex) − δ(**1**)) for the nuclei in Ph_2P moieties are around +40 ppm in mononuclear **7** and **8** and +64 ppm in the dinuclear complex **5**. The small coordination shifts for the endocyclic phosphorus atoms in **5** and **8** ($|\Delta\delta| <$

(11) $^{31}P\{^1H\}$ NMR data of **9**: P^a, 229.3 (dddd, $^1J_{Rh,P} = 231.1$, $^2J_{PaPb} \approx {}^2J_{PaPc} \approx {}^2J_{PaPd} \approx 68$ Hz); P^b, 50.6 (ddd, $^1J_{Rh,P} = 174.5$ Hz, $^2J_{PaPb} = 69$ Hz, $^3J_{PbPc} = 4.8$ Hz); signals of P^c and P^d were obscured by those of complexes **5** and **6**.

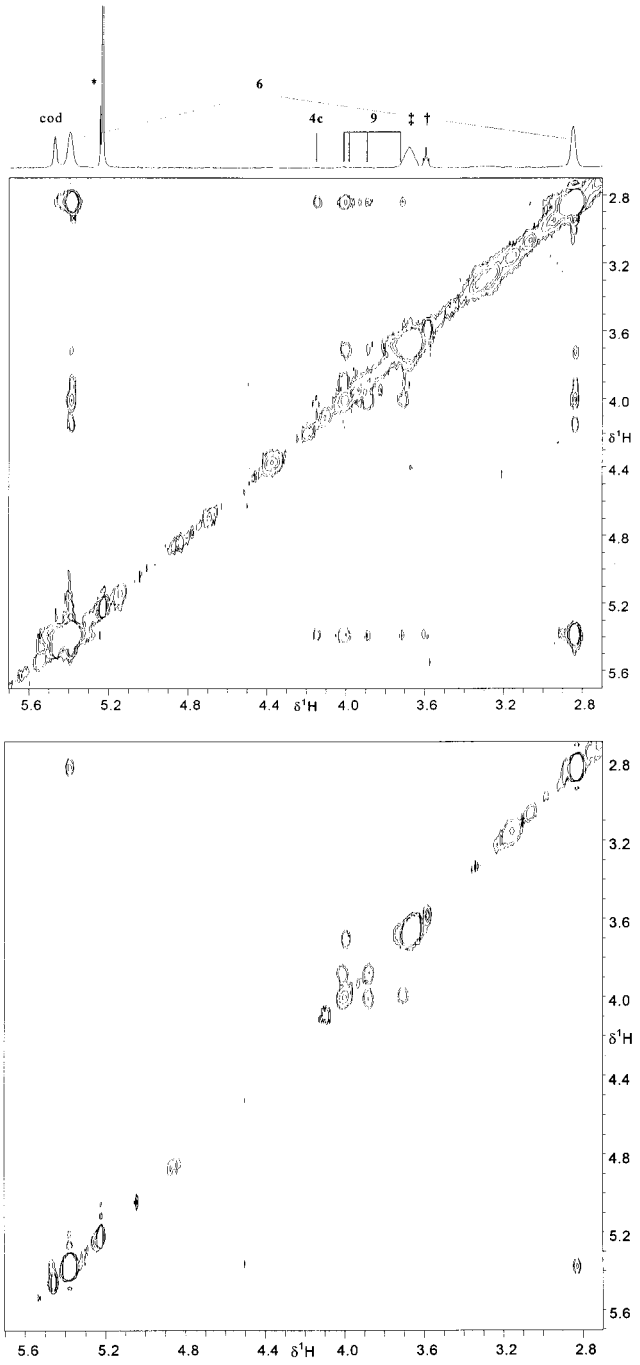


Figure 1. (a) Expansion of the gradient-enhanced two-dimensional ^{1}H EXSY NMR spectrum (500 MHz, mixing time 500 ms, 25 °C, in CD_2Cl_2, only positive contour levels shown) of a 4:1 mixture of **6**[BPh_4] and cod, showing the region containing olefinic protons and one of the PCH_2 signals of **6** (‡) with the assignment of the olefinic protons of **6** (2 signals), **4c** and **9** (4 signals), free cod, and residual solvent resonances (* = $CHDCl_2$, † = thf) being marked in the 1D spectrum given as projection on the top. The visible cross-peaks indicate intermolecular chemical exchange between the three cod complexes, but the absence of exchange between free and coordinated cod. (b) Spectrum of the same sample after 4-fold dilution. Peaks indicating intermolecular reactions are no longer visible; the remaining cross-peaks are attributable to intramolecular exchange processes: pairwise mixing between the four different CH sites in **9** arises from inversion of the chelate ring, and mixing between the two sites in **6** from pseudorotation of the coordinated cod moiety.

Table 2. ^{103}Rh NMR Data of 5−8 (at 25 °C, in CD_2Cl_2) and Selected Reference Compounds (Data from Ref 14)

	δ^{103}Rh			
	$[RhCl(P)_2]_2$	[RhCl(P)(cod)]	$[Rh(P)_2(cod)]^+$	$[RhCl(P)_2(P')]$
2P = **1**, P′ = PPh_3	46 (**5**)	357 (**6**)	−76 (**7**)	32 (**8**)
P = P′ = PPh_3	−85	393	−145	−81
P = P′ = PPh_2Me		348	−267	
2P = dppe			−505	

10) are of similar magnitude as in the carbonyl complexes **2** and **3**.[6] The corresponding resonance of the dication **7** shows a significant negative coordination shift ($\Delta\delta = -46$).

In addition to NMR studies of nuclei in coordinated ligands, metal NMR spectroscopy has recently received increasing attention since it has been shown that trends in metal chemical shifts may disclose information related to the reactivities of the complexes.[12] In pioneering studies, the group of von Philipsborn has demonstrated that under favorable circumstances even information on catalytic activities may be available.[13] These findings stimulated us to determine the ^{103}Rh chemical shifts of complexes **5**[X]$_2$−**8**[X] from two-dimensional ^{1}H or ^{31}P detected ^{1}H,^{103}Rh or ^{31}P{^{1}H},^{103}Rh shift correlations. Comparison of the results with known metal chemical shifts[14] for phosphine complexes of similar composition (see Table 2) reveals that δ^{103}Rh in the chelate complexes **5**, **7**, and **8** is generally deshielded with respect to the reference compounds by some hundred ppm, whereas **6** displays a value similar to that of the corresponding Ph_2PMe complex. The deshielding effects can be related in the light of systematic investigations on the origin of ^{103}Rh chemical shifts[12,15] to a combination of electronic (increased π-acceptor ability of **1** as compared to two $MePPh_2$ or PPh_3 ligands) and steric influences (geometric distortions of metal coordination polyhedra, see below) even though the small number of available data prevents a more detailed analysis. In view of the findings of von Philipsborn et al., who noted that deshieldings of metal nuclei following the variation of a controller-ligand are frequently associated with enhanced reactivities,[12,13] these results suggest that the complexes **5**[X]$_2$−**8**[X] might display catalytic activities competitive with the reference complexes listed in Table 2.

Crystal Structure Determination of 5[BPh_4]$_2$. Crystals of **5**[BPh_4]$_2$·5CH_2Cl_2·thf suitable for a single-crystal X-ray structure determination were obtained by recrystallization from CH_2Cl_2/thf. The crystals consist of discrete cations and anions which lack any unusually short distances. The cations come close to C_2-symmetry. A representation of the molecular structure of one-half of the cation and of the whole P_4Rh_2Cl core of the

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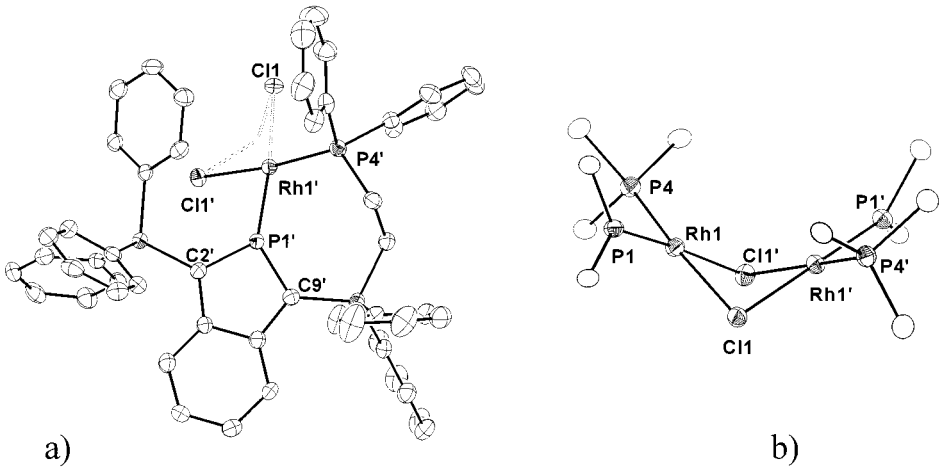

Figure 2. ORTEP-style representation of the molecular structure (a) of one-half of the cation in crystalline **5**$[BPh_4]_2$ and (b) the $Rh_2Cl_2P_4$ core of **5** with surrounding atoms. Thermal ellipsoids are drawn at the 50% probability level, and H atoms in (a) have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh(1)−P(1) 2.1677(11), Rh(1′)−P(1′) 2.1746(11), Rh(1)−P(4) 2.1880(11), Rh(1′)−P(4′) 2.1953(11), Rh(1)−Cl(1) 2.4374(10), Rh(1′)−Cl(1′) 2.4342(10), Rh(1)−Cl(1′) 2.3764(9), Cl(1)−Rh(1′) 2.3802(9), Rh(1)−Rh(1′) 3.1248(3), P(1)−C(2) 1.723(4), P(1′)−C(2′) 1.733(4), P(1)−C(9) 1.739(4), P(1′)−C(9′) 1.739(4), P(1)−Rh(1)−P(4) 95.66(4), P(1′)−Rh(1′)−P(4′) 96.43(4), P(4)−Rh(1)−Cl(1′) 89.02(3), P(4′)−Rh(1′)−Cl(1) 89.76(3), P(1)−Rh(1)−Cl(1) 93.71(4), P(1′)−Rh(1′)−Cl(1′) 92.28(4), Cl(1′)−Rh(1)−Cl(1) 81.62(2), Cl(1)−Rh(1′)−Cl(1′) 81.61(2), C(2)−P(1)−C(9) 93.5(2), C(2′)−P(1′)−C(9′) 93.3(2).

dimeric unit is given in Figure 2 together with important bond distances and angles.

The rhodium atoms adopt distorted square-planar coordination geometries (sum of bond angles 360°), with the angles involving the σ^2-phosphorus atom (P1−Rh1−P4/P1′Rh1′−P4′ 95.66(4)°/96.43(4)° and P1−Rh1−Cl1/P1′−Rh1′−Cl1′ 93.71(4)°/92.28(4)°) being larger and the remaining angles smaller than 90°. The fold angle (118°) between the two coordination planes and the Rh−Rh′ distance (3.1248(3) Å) are close to the lower end of the known ranges of interplanar angles (115−180°[16]) and Rh−Rh distances (3.03−3.80 Å[16]) in Cl-bridged dimers. The Rh1−P1/Rh1′−P1′ bonds (2.1677(11)/2.1746(11) Å) to the σ^2-phosporus atoms lie between the values of *SP4*−Rh(I) complexes with σ-coordinated phosphaalkenes (Rh−P 2.11−2.13 Å[17]) and phosphaarenes (Rh−P 2.16−2.29 Å[4b,18]) and are likewise shorter than the Rh1−P4/Rh1′−P4′ distances (2.1880(11)/2.1953(11) Å). The Rh−Cl bonds *trans* to the benzophospholide moiety (Rh1−Cl 1′ 2.3764(9), Rh1′−Cl1 2.3802(9) Å) are slightly, but significantly, shorter than the ones in *cis*-position (Rh1−Cl1 2.4374(10), Rh1′−Cl1′ 2.4342(10) Å). The coordination geometry at the ring phosphorus atoms P1 and P1′ is nearly planar (sum of bond angles 358°). The bond lengths and angles in the benzophospholide moieties display no peculiarities and are, apart from a slight increase of the endocyclic C2−P1−C9/C2′−P1′−C9′ angle (93.5(2)°/93.3(2)°), comparable to corresponding values in noncoordinated cations.[5,6] The seven-membered chelate rings display as expected a nonplanar twist conformation.

On the whole, the small angle between the metal coordination planes and the distortion from regular square-planar geometry around each metal center are presumably attributable to steric factors such as the extraordinary bulk of the ligand **1** or conformational strain in the seven-membered chelate ring. The difference in Rh−Cl bond lengths can be ascribed to the different electronic influence of the *trans*-ligands: owing to its weaker σ-donor and stronger π-acceptor ability as compared to a phosphine, a bisphosphoniobenzophospholide enhances Cl(σ) → M charge transfer and reduces the repulsion between the Cl(π)-orbitals and filled metal d-orbitals, and thus gives rise to a synergistic strengthening of the M−Cl bond in *trans*-position. In light of this argument, the shortening of the Rh−P(σ^2) with respect to the Rh−P(σ^3) bonds should reflect primarily the difference in covalence radii between sp^2- and sp^3-hybridized phosphorus atoms, rather than a change in bond orders. This view is in accord with the observed selective substitution of the σ^2-phosphorus atom during the reaction of **5** with cod, which seems to confirm that the Rh−P(σ^2) bond is in fact weaker than the Rh−P(σ^3) bond.

Study of Catalytic Hydroformylations. As a test reaction, we investigated the hydroformylation of hexene under mild conditions (20 °C), using complexes **5**$[BPh_4]_2$, **7**$[OTf]_2$, or **8**$[BPh_4]$ as precatalysts. Analogous reactions with **6**[X] were not studied since it was considered that under the reaction conditions the same catalytically active species as from **5**$[X]_2$ should be formed. In a typical reaction, 3.0 mL (25 mmol) of hexene and 1.00 mL of mesitylene (internal standard) were added to a solution containing 0.025 mmol of the appropriate complex in 10 mL of CH_2Cl_2. The solution was transferred to a stainless steel autoclave and the hydroformylation started by pressurizing with carbon monoxide (20 bar) and hydrogen (20 bar). The reaction mixture was stirred magnetically under these conditions for 24 h and, after depressurizing the autoclave, analyzed by GC. The results are given in Table 3.

(16) Results of a quest in the CSD database for complexes containing the fragment $Rh_2(\mu\text{-}Cl)_2$ and *SP4*-coordination geometry at the metal atoms.

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Table 3. Results of Rhodium-Catalyzed Hydroformylation Reactions

	catalyst	substrate	T (°C)	p^a (bar)	t (h)	conv^b (%)	l:b ratio	TON^c	TOF^c (h^{-1})
1	0.10 mol % **5**$[BPh_4]_2$	1-hexene	20	40	24	85	1.6	850	35
2	0.10 mol % **7**$[OTf]_2$	1-hexene	20	40	24	27	2.7	270	11.2
3	0.10 mol % **8**[OTf]	1-hexene	20	40	24	<1	3	<10	<0.4
4^d	0.36 mol % $[Rh(CO)_2acac]$ 7.2 mol % PPh_3	styrene	20	50	22	31	3.88×10^{-2}		3.9^e
5^d	0.36 mol % $[Rh(CO)_2acac]$ 0.72 mol % 2,6-Me_2-4-Ph-phosphabenzene	styrene	20	50	22	80	3.76×10^{-2}		10.2^e
6^f	0.36 mol % $[Rh(CO)_2acac]$ 1.79 mol % 2,4,6-Ph_3-phosphabenzene	styrene	25	20	3	30.8	5.0×10^{-2}		28.7^e

^{a} CO/H_2, 1:1. ^{b} Conversion to linear and branched aldehydes as determined by GC. ^{c} TON (turnover number) was calculated as (mol produced aldehyde) × (mol catalyst)$^{-1}$; TOF (turnover frequency) was calculated as TON × $(t/h)^{-1}$. ^{d}Data from ref 4c. ^{e} Based on Rh. ^{f} Data from ref 46.

None of the reactions gave rise to the formation of hexane, showing that the used complexes were under the chosen conditions inactive as hydrogenation catalysts. Complex **5**$[BPh_4]_2$ gave a conversion of hexene to the corresponding hydroformylation products of 85% and was thus approximately three times as active as complex **7**$[OTf]_2$, although at the cost of a lower regioselectivity for the formation of the desired *n*-aldehyde. The trisphosphine complex **7**$[BPh_4]$ displayed negligible catalytic activity. Regarding that rhodium complexes containing more than two phosphorus-based ligands (L) perform frequently very poorly as hydroformylation catalysts,[2d] it can be assumed that the mild reaction conditions apparently disfavor the cleavage of one of the phosphorus-based ligands which is required for the generation of a catalytically highly active species of the type $[Rh(L)_2(CO)_2H]$.[2]

A comparison of the observed results with literature data is rendered difficult by the absence of standardized reaction conditions. Hydroformylation of 1-hexene is generally carried out at elevated temperatures (80−100 °C) so that conversion rates are not directly comparable with our results.[2] Recently, Breit et al. reported on investigations of the hydroformylation of styrene with phosphabenzene-rhodium catalysts which were carried out under conditions (50 bar H_2/CO, 25 °C) similar to our studies.[4] Regarding that Wilkinson et al. have shown that the hydroformylation of styrene with $RhH(CO)(PPh_3)_3$ as catalyst proceeds at a rate about 1.23 times as fast as that of 1-hexene,[19] the performance of **5**$[BPh_4]_2$ can be considered better than that of the reference system $[Rh(CO)_2(acac)]/PPh_3$ (1:5) (Table 3, entry 4) and roughly similar to that of complexes of monodentate 2,6-disubstituted phosphabenzenes (Table 3, entries 5, 6). In contrast to the good chemoselectivity and activity, however, the low l:b ratios obtained with both **5**$[BPh_4]$ and **7**$[BPh_4]_2$ indicate poor regioselectivities for *n*-aldehydes, which are inferior as compared to other catalysts[2,4] and make further optimization of the catalyst system mandatory.

Conclusions

The bisphosphoniobenzo[*c*]phospholide cation **1** forms a variety of rhodium complexes in which it is coordinated either as a κ-$P(\sigma^3)$-monodentate or a κ^2-*P*,*P*′-chelating ligand. The observed dynamic interconversion between both coordination modes in the system **5**$[BPh_4]_2$/**6**$[BPh_4]$/cod suggests the Rh−P(σ^2) bond to be weaker than the Rh−P(σ^3) bond and awards cation **1** some hemilabile[20] character. A study of the use of the new complexes as precatalysts in the hydroformylation of 1-hexene revealed the catalytic performance to be highly dependent on the co-ligands; in particular, the presence of a further phosphine ligand lead to severe inhibition of catalytic activity. Complexes **5**$[BPh_4]_2$ and **7**$[OTf]_2$, which contain no additional phosphorus donors, are active catalysts and allow the hydroformylation of 1-hexene at room temperature and with high chemoselectivity to aldehydes but poor l:b regioselectivity.

Experimental Section

General Comments. All manipulations were carried out under dry argon. Solvents were dried by standard procedures. NMR spectra: Bruker AMX300 (^{1}H 300.1 MHz, ^{31}P 121.5 MHz, ^{13}C 75.4 MHz, ^{103}Rh 9.4 MHz) and Bruker DRX500 (^{19}F 470.4 MHz, ^{103}Rh 15.7 MHz) in CD_2Cl_2 at 30 °C if not stated otherwise; two-dimensional ^{1}H,^{103}Rh and ^{31}P{^{1}H},^{103}Rh HMQC spectra were recorded using published pulse sequences;[12,15] chemical shifts referenced to external TMS (^{1}H,^{13}C), 85% H_3PO_4 (Ξ = 40.480747 MHz, ^{31}P), Ξ = 3.16 MHz (^{103}Rh); positive signs of chemical shifts denote shifts to lower frequencies; coupling constants are given as absolute values. Unequivocal assignment of ^{1}H NMR signals was derived from COSY and ^{1}H,^{31}P and ^{1}H,^{13}C HMQC spectra; owing to the severe overlap in the aromatic region of the ^{13}C{^{1}H} NMR spectra, no attempts toward assignment of other signals but those of the cod ligands in **6** and **7** were made. MS: Kratos Concept 1H, Xe-FAB, m-NBA matrix. Elemental analyses: Heraeus CHNO-Rapid. Melting points were determined in sealed capillaries. The amount of cocrystallized solvents was verified by integration of suitable ^{1}H NMR signals. ^{31}P and ^{103}Rh NMR data are given in Table 2.

Hydroformylation reactions were carried out in a 100 mL stainless steel autoclave equipped with a magnetic stirrer which was charged with a solution prepared from 0.025 mmol of the appropriate catalyst, 3.00 mL (25 mmol) of 1-hexene, 1.00 mL of mesitylene, and 10 mL of CH_2Cl_2 and pressurized with CO (20 bar) and H_2 (20 bar). The resulting mixture was stirred for 24 h at 25 °C, depressurized, and subjected to GC analysis (Hewlett-Packard 5890 Ser. IIen gas chromatograph, 0.2 mm × 50 m capillary column, stat. phase 5% cross-linked phenyl methyl silicone, FID). Quantification and identification of the products were achieved by comparison of peak integrals and retention times with those of actual samples. Furthermore, the assignments were cross-checked by GC−MS analysis.

Bis[μ-chloro-κ^2-*P*,*P*′-{1-(diphenyl(2-diphenylphosphinoethyl)phosphonio)-3-triphenylphosphoniobenzo[*c*]phospholide}rhodium(I)]Bistetraphenylborate (5[$BPh_4]_2$). A mixture of **1**$[BPh_4]$ (1.00 g, 0.90 mmol) and $[RhCl(C_2H_4)_2]_2$

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(**4a**, 0.18 g, 0.46 mmol) was dissolved in 25 mL of thf. After stirring for 30 min, the solution was concentrated in vacuo to approximately 20 mL and stored overnight at 4 °C. The formed dark red precipitate was filtered off, washed with a little cold thf, and dried in vacuo to give 0.97 g (0.39 mmol, 87%) of **5**$[BPh_4]_2$ × thf, mp 194 °C (dec). Compound **5**$[OTf]_2$ was accessible following the same procedure starting from **1**[OTf]. Anal. Calcd for $C_{152}H_{126}B_2Cl_2P_8Rh_2$ (2498.8) × thf: C 72.88; H 5.25. Found: C 72.11; H 5.48. ^{1}H NMR: δ 4.64 (m, 2H), 2.79 (m, 2H), 2.37 (m, 2H), 2.17 (m, 2H) [PCH_2], 6.6−6.8 (m, 8H) [C_6H_4], 6.8−7.9 (m, 110H) [H_{phenyl}]. MS ((+)-Xe-FAB, mNBA) *m/e* (%): 2179 (5) [(**5**·BPh_4)$^+$]; 1860 (5) [(**5** − H)$^+$] 929 (75) [(RhCl + **1** − H)$^+$]; 893 (100) [(Rh + **1** − H)$^+$].

[Chloro-κ^2-*P,P'*-{1-(diphenyl(2-diphenylphosphinoethyl)phosphonio)-3-triphenylphosphoniobenzo[*c*]-phospholide}(triphenylphosphine)rhodium(I)] Tetraphenylborate (8[BPh_4]). A mixture of **5**$[BPh_4]_2$ × thf (400 mg, 0.156 mmol) and PPh_3 (82 mg, 0.310 mmol) was dissolved in 20 mL of CH_2Cl_2 and stirred for 5 h. Evaporation of the dark red solution in vacuo and drying in high vacuum afforded 480 mg (0.31 mmol, 100%) of **8**$[BPh_4]$ × thf, mp 197 °C. Compound **8**[OTf] was accessible following the same procedure starting from **1**[OTf]. Anal. Calcd for $C_{94}H_{78}BClP_5Rh$ (1583.8) × thf: C 74.32; H 5.47. Found: C 74.04; H 5.77. ^{1}H NMR (d_8-THF): δ 5.03 (m, 1H), 2.98 (m, 1H), 2.85 (m, 1H), 2.49 (m, 1H) [CH_2], 6.5−6.85 (m, 4H) [C_6H_4] 6.85−7.85 (m, 70H) [H_{phenyl}]. MS ((+)-Xe-FAB, mNBA) *m/e* (%): 1191 (10) [(**8**)$^+$], 929 (100) [(RhCl + **1** − H)$^+$], 893 (50) [(Rh + **1** − H)$^+$].

[Chloro-η^4-(1,5-cyclooctadiene)-κ^2-*P,P'*-{1-(diphenyl(2-diphenylphosphinoethyl)phosphonio)-3-triphenylphospho-niobenzo[*c*]phospholide}rhodium(I)] Tetraphenylborate or Trifluoromethane Sulfonate (6[BPh_4], 6[OTf]). (a) Cod (500 mg) was added to a suspension of **5**$[BPh_4]_2$ (400 mg, 0.156 mmol) in thf (7 mL) and CH_2Cl_2 (8 mL). The resulting mixture was stirred for 15 h and then concentrated in a vacuum to approximately one-third of the original volume. Addition of hexane (15 mL) produced a light yellow precipitate, which was filtered off, washed with hexane, and dried in high vacuum to afford 390 mg (0.29 mmol, 95%) of **6**$[BPh_4]$ of mp 166 °C (dec). Anal. Calcd for $C_{84}H_{75}BClP_4Rh$ (1357.6) × thf: C 73.93; H 5.85. Found: C 73.33; H 5.63. ^{1}H NMR: δ 6.60−7.00 (m, 4H) [C_6H_4], 7.00−8.24 (m, 35H) [H_{phenyl}], 5.50 (m, 2H), 2.95 (m, 2H) [cod-C*H*]; 3.79 (m, 2H), 2.71 (m, 2H) [PCH_2]; 2.32 (m, 2H), 2.28 (m, 2H), 2.10 (m, 2H), 1.91 (m, 2H) [cod-CH_2]. ^{13}C{^{1}H} NMR: δ 108.59 (dd, $^1J_{RhC}$ = 12.2 Hz, $^2J_{PC}$ = 7.2 Hz), 73.37 (d, $^1J_{RhC}$ = 13. 4 Hz) [cod-*C*H]; 34.79 (d, $^3J_{PC}$ = 2.3 Hz), 30.68 (s) [cod-*C*H_2]; 25.44 (m, J_{PC} = 61.4, 9. 2, 3.2 Hz), 24.15 (dm, $^1J_{PC}$ = 26.7 Hz), P*C*H_2]. MS ((+)-Xe-FAB, mNBA) *m/e* (%): 1079 (50) [((**1**)RhOTf)$^+$], 1037 (50) [((**1**)Rh(cod))$^+$], 929 (10) [((**1**)RhCl)$^+$], 893 (80) [((**1**)Rh − H)$^+$]; 791 (100) [**1**$^+$].

(b) To a solution of **1**[OTf] (500 mg, 0.47 mmol) and [RhCl-(cod)]$_2$ (**4c**, 120 mg, 0.47 mmol) in 20 mL of thf were added 200 mg of cod, and the resulting mixture was stirred for 5 h. Addition of Et_2O (5 mL) and hexane (10 mL) to the light red solution afforded a yellow precipitate, which was filtered off, washed thoroughly with hexane, and dried in high vacuum to give 480 mg (0.41 mmol, 87%) of **6**[OTf], mp 164 °C (dec). Compound **6**$[BPh_4]$ was accessible analogously from **1**$[BPh_4]$. The isolated salts gave identical ^{31}P and ^{1}H (apart from signals of the anions) NMR spectra as the product prepared as described in (a). ^{19}F NMR: δ −78.2.

[η^4-(1,5-Cyclooctadiene)-κ^2-*P,P'*-{1-(diphenyl(2-diphenylphosphinoethyl)phosphonio)-3-triphenylphosphoniobenzo[*c*]phospholide}rhodium(I)] Bistrifluormethanesulfonate (7[OTf]$_2$). A mixture of **1**[OTf] (190 mg, 0.20 mmol) and [RhCl(cod)]$_2$ (**4c**, 50 mg, 0.10 mmol) was dissolved in CH_2Cl_2 (10 mL). The resulting solution was stirred for 45 min, TlOTf (70 mg, 0.20 mmol) added, and the reaction mixture stored for 3 h at 4 °C. A second batch of TlOTf (70 mg) was added, and the mixture stirred for a further 2 h at ambient temperature. The formed precipitate was then filtered off and the filtrate evaporated to dryness. The red residue was recrystallized from CH_2Cl_2/Et_2O to afford a red crystalline solid, which was filtered off and dried in high vacuum to give 180 mg (0.16 mmol, 80%) of **7**$[OTf]_2$, mp 172 °C. No satisfactory elemental analysis could be obtained owing to varying solvent content and the hygroscopic nature of the product. ^{1}H NMR: δ 7.2−7.7 (m, 4H) [C_6H_4]; 8.1−7.6 (m), 7.0−6.8 (m, 35H) [H_{phenyl}]; 5.29 (m, 1H), 4.83 (m, 1H), 4.64 (m, 1H), 3.87 (m, 1H) [cod-C*H*]; 4.76 (m, 1H), 4.57 (m, 1H), 3.49 (m, 1H), 2.93 (m, 1H) [PCH_2]; 2.5−1.8 (7H), 1.5264 (m, 1H) [cod-CH_2]. ^{13}C{^{1}H} NMR: δ 106.32 (dd, J = 7.2, 6.9 Hz), 105.26 (dd, J = 9.3, 8.6 Hz), 102.59 (dd, J = 7.6, 8.8 Hz), 100.18 (dd, J = 6.5, 11.8 Hz) [cod-*C*H]; 34.41 (s), 33.10 (dd, J = 1.1, 3.4 Hz), 28.27 (s), 27.14 (s) [cod-*C*H_2], 27.17 (ddd, $J_{P,C}$ = 57.5, 9.8, 3.5 Hz), 20.44 (dm, $^1J_{PC}$ = 32.8 Hz) [P*C*H_2]. ^{19}F NMR: δ −78.2. MS ((+)-Xe-FAB, mNBA) *m/e* (%): 1151 (10) [((**1**)(cod)RhOTf)$^+$], 893 (50) [((**1**)-Rh − H)$^+$], 791 (100) [**1**$^+$], 501 (50) [((**1**)(cod)Rh)$^{2+}$].

Crystallography. Crystals of composition **5**$[BPh_4]_2$ × 5CH_2-Cl_2 × thf were obtained as red plates from CH_2Cl_2/thf (1:1). The crystal structure determinations were performed on a Nonius KappaCCD diffractometer at 123(2) K. Crystal data, data collection parameters, and results of the analyses are listed in Table 4. The structures were solved by direct methods (SHELXS-97[21]) and refined anisotropically by blocked cycle full-matrix least-squares on F^2 using all data (SHELXL-97[22]) without absorption correction, H atoms with a riding model.

Table 4. Crystallographic Data and Summary of Data Collection and Refinement for 5[BPh_4]$_2$

formula	$C_{152}H_{126}B_2Cl_2P_8Rh_2$ × 5CH_2Cl_2 × thf, red plates
fw	2995.36
cryst size	0.25 × 0.15 × 0.05 mm
unit cell dimens	a = 15.3048(3) Å, α = 86.909(1)°
b = 15.7930(3) Å, β = 79.200(1)°	
c = 30.8106(5) Å, γ = 80.170(1)°	
volume	7206.0(2) Å^3
Z, ρ_{calc}	2, 1.380 Mg m^{-3}
temperature	123(2) K
radiation	Mo Kα (λ = 0.71073 Å), graphite monochromated
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
μ	0.59 mm^{-1}
max. and min. transmn	0.9709 (theor) and 0.8658 (theor)
abs corr	none
diffractometer	Nonius KappaCCD
max. 2θ	25°
limiting indices	$-18 \le h \le 18$, $-18 \le k \le 18$, $-36 \le l \le 36$
no. of reflns collected/unique	77265/25169 [R(int) = 0.042]
no. of data/restraints/params	25169/330/1663
goodness-of-fit on F^2	1.044
R1 [$I > 2\sigma(I)$]	0.051
wR2 (all data)	0.151
largest diff peak and hole	1.781 and −1.429 e A^{-3}

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Supporting Information Available: Tables of atom parameters, anisotropic temperature factors, and all bond distances and angles of **5**$[BPh_4]_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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