Synthesis and Basic Coordination Properties of Side-chain Functionalized Bis-phosphonio-benzophospholides

Dietrich Gudat*, Stefan Häp, Volker Bajorat, and Martin Nieger

Bonn, Institut für Anorganische Chemie der Rheinischen Friedrich-Wilhelms-Universität

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Dedicated to Professor Marianne Baudler on the Occasion of her 80th Birthday

Abstract. Salts containing bis-phosphonio-benzophospholide cations **2a–d** with an additional donor site in one of the phosphonio-moieties were synthesized either via quaternisation of the Ph_2P moiety in the neutral phosphonio-benzophospholide **3**, or via ring-closure of the functionalized bisphosphonium ion **6**. The Ph_2P-substituted cation **2d** formed chelate complexes $[M(\kappa^2 P,P'\text{-}\mathbf{2d})(CO)_n]^+$ with $M(CO)_n = Ni(CO)_2$, $Fe(CO)_3$, $Cr(CO)_4$. In the latter case, competition between formation of the chelate and a complex $[Cr(\kappa P\text{-}\mathbf{2d})_2(CO)_4]^{2+}$ was observed, and interpreted as a consequence of antagonism between the stabilizing chelate effect and destabilizing ligand–ligand repulsions. The formation of stable Pd^{II} and Pt^{II} complexes of **2d** suggests that the chelate effect may also overcome the kinetic inhibition which so far prevented isolation of complexes of these metals with bis-phosphonio-benzophospholides. The newly synthesized ligands and complexes were characterized by spectroscopic data, and an X-ray crystal structure analysis of **2a**[Br]. The reactivity of chelate complexes towards Ph_3P indicates that the ring phosphorus atom is a weaker donor than the pendant Ph_2P-group.

Keywords: Phosphorus heterocycles; Benzophospholides; Chelates

Synthese und grundlegende Koordinationseigenschaften seitenkettenfunktionalisierter Bis-phosphonio-benzophospholide

Inhaltsübersicht. Salze der Bis-phosphonio-benzophospholid-Kationen **2a–d**, die über eine zusätzliche Koordinationsstelle in einem der Phosphonio-Substituenten verfügen, werden entweder durch Quaternisierung der Ph_2P-Gruppe des neutralen Phosphonio-benzophospholids **3** oder über Ringschlußreaktion aus dem funktionalisierten Bis-phosphoniumion **6** dargestellt. Das Ph_2P-substituierte Kation **2d** bildet Chelatkomplexe $[M(\kappa^2 P,P'\text{-}\mathbf{2d})(CO)_n]^+$ mit $M(CO)_n = Ni(CO)_2$, $Fe(CO)_3$, $Cr(CO)_4$. Im letzten Fall wurde eine Konkurrenz zwischen der Chelatbildung und der Entstehung eines Komplexes $[Cr(\kappa P\text{-}\mathbf{2d})_2(CO)_4]^{2+}$ beobachtet und als Ausdruck eines Antagonismus zwischen dem stabilisierenden Chelateffekt und destabilisierenden Ligand–Ligand Abstoßungen interpretiert. Die Bildung stabiler Pd^{II}- und Pt^{II}-Komplexe von **2d** zeigt, daß durch den Chelateffekt auch die kinetische Hemmung überwunden werden kann, die bisher die Darstellung von Bis-phosphonio-benzophospholid-Komplexen mit diesen Metallen verhinderte. Die neu synthetisierten Liganden und Komplexe werden spektroskopisch und im Fall von **2a**[Br] durch eine Einkristallstrukturanalyse charakterisiert. Die Reaktivität der Chelatkomplexe gegenüber Ph_3P gibt Hinweise, daß das Phosphoratom im Ring ein schwächerer Donor als die periphere Ph_2P-Einheit ist.

Introduction

Phosphorus based ligands are of considerable importance because of their ability to act as σ-donor/π-acceptor ligands towards transition metals [1]. Only recently, this field gained new attention when it was pointed out that low coordinate phosphorus compounds in which the phosphorus atom is part of a multiple bond system may act as effective π-acceptor ligands via their energetically low lying π^*-orbitals [2]. Because of these properties, transition metal complexes containing σ(P)-coordinated phosphinines (phosphabenzenes) have been proven to be highly efficient hydroformylation catalysts [2a, 3].

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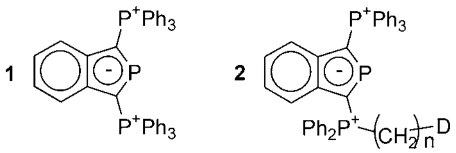
* Priv. Doz. Dr. Dietrich Gudat
Institut für Anorganische Chemie der Universität Bonn
Gerhard-Domagk-Str. 1
D-53121 Bonn
Fax: +49(0)2 28 73 53 27
E-mail: dgudat@uni-bonn.de

We have recently established that the bis-triphenylphosphonio-benzophospholide cation **1** forms stable complexes with univalent coinage metals [4]. Coordination occurs via the lone-pair at the ring phosphorus atom, and the bonding situation has been qualitatively described as superposition of dative L → M and retrodative L ← M contributions. The latter implies for **1** some π-acceptor character which owes presumably to inductive stabilization of the π*-orbitals by the phosphonio groups [5]. Even though this quality should make the cation **1** an interesting ligand for many applications, its use turned out to be severely restricted owing to steric protection of the coordination site by the bulky R_3P substituents (**I**, Fig. 1) which prevented bonding to metals with coordination geometries other than planar or linear [4, 5 b]. Looking for a strategy to circumvent this limitation, we became interested in side-chain functionalized bis-phosphonio-benzophospholides **II** with a further donor site in a peripheral phosphonio moiety. Upon complex formation, these species permit incorporation of one group R as active ligand into the metal coordination sphere and turn thus a former repulsive interaction between the metal fragment and an "innocent" R_3P group into an attractive interaction. Apart from thermodynamic stabilization of the formed complexes by the chelate effect, this approach should reduce the steric constraints in the vicinity of the ring phosphorus atom and make the ligand amenable to coordinate to metal fragments with a larger structural variety.



Scheme 1

We report here on the syntheses of bis-phosphonio-benzophospholides **2** featuring additional donor groups (D = $CH{=}CH_2$, CN, CO_2^-, PPh_2) in one of the pendant phosphonio groups. In order to assess the accessibility of the ring phosphorus atom for metal coordination, the formation of chelate complexes of **2 d** (n = 2, D = PPh_2) with metal carbonyl fragments of varying steric requirements ($Ni(CO)_2$, $Fe(CO)_3$, $Cr(CO)_4$) was studied. Regarding the importance of complexes of Pt and Pd in catalysis, reaction of **2 d** with $[PtCl_2(cod)]$ and $[PdCl_2(PhCN)_2]$ were also investigated.

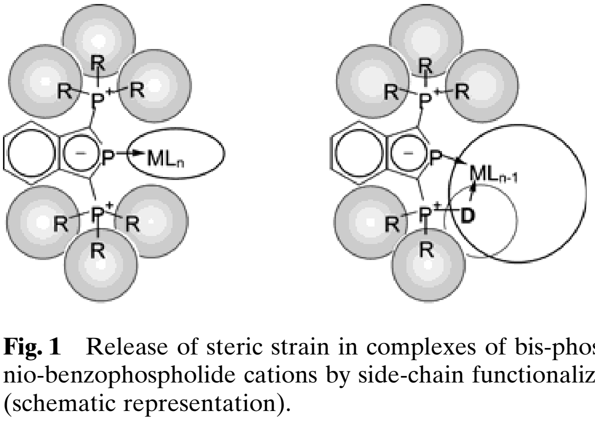
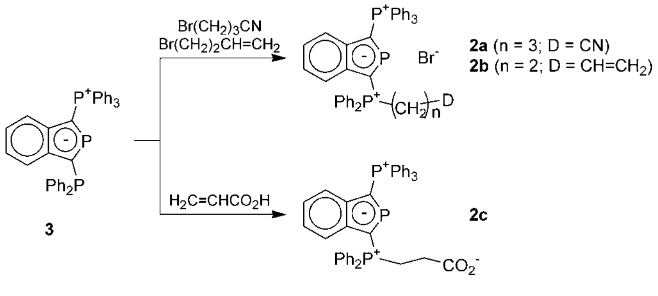


Fig. 1 Release of steric strain in complexes of bis-phosphonio-benzophospholide cations by side-chain functionalization (schematic representation).

Results and Discussion

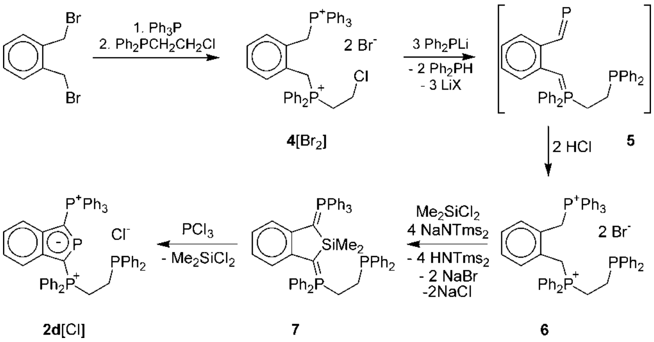
Ligand Syntheses

The assembly of cations of type **2** was achieved following two different strategies. The first approach involved quaternisation of the phosphino-substituent in the mono-phosphonio benzophospholide **3** [6] by appropriately functionalized alkyl bromides to afford bis-phosphonio-benzophospholides **2 a, b**[Br] with an additional olefine or nitrile moiety, or by addition of acrylic acid [7] to afford the zwitterion **2 c** with a pendant carboxylate group (scheme 2). A preliminary survey of the scope of this reaction [8] suggested that the quaternisation route tolerates a wide range of spacer units between the benzophospholide moiety and the pendant donor and can thus give access to bidentate ligands with a variety of bite angles. On the other hand, the choice of donor functions is limited by the tendency of ω-functionalized alkyl halides with strongly nucleophilic functional groups to undergo self quaternisation. As a consequence, cations of type **2** with pendant amine, phosphine, or pyridine moieties were unaccessible by this route.



Scheme 2 Synthesis of bis-phosphonio-benzophospholides by quaternisation of **3**.

In order to obtain phosphine-functionalized bis-phosphonio-benzophospholide ions which are particularly appealing ligands we developed an alternative synthetic strategy as outlined in scheme 3. α,α'-Dibromo-*ortho*-xylene was first converted via two subsequent quaternisation steps into the ω-chloroethyl-substituted bis-phosphonium salt **4**$[Br_2]$. The pendant Ph_2P-group was then introduced by reaction with three equivalents of $LiPPh_2$ and subsequent quenching of the formed transient bis-ylide **5** with ethereal hydrogen chloride to give the bis-phosphonium salt **6**[Cl_2]. Reaction of **6**[Cl_2] with Cl_2SiMe_2 and excess $NaN(SiMe_3)_2$ yielded the silaheterocycle **7** whose metathetis with PCl_3 finally gave the target compound **2d**[Cl]. Conversion into trifluoromethanesulfonate (OTf) or BPh_4 salts was easily possible by anion exchange with LiOTf or $NaBPh_4$, respectively.



Scheme 3 Synthesis of **2d**[Cl] (Tms = Me_3Si).

Formation of the cation **2d** was also observed when **6** was directly reacted with PCl_3/NEt_3 as originally reported by *Schmidpeter* et al. for the synthesis of **1** [9], but owing to decomposition during the aqueous work-up procedure only impure products were isolated and this protocol was therefore abandoned. By analogy to known reactions of β-functionalized phosphonium salts [7], the phosphination of the 2-chloroethyl-phosphonio moiety in **4** is thought to proceed via base ($LiPPh_2$) promoted dehydrochlorination to give first a transient vinylphosphonium species which is converted to the ylide **5** by addition of $HPPh_2$ and final deprotonation. A consequence arising from this special reaction mechanism is the unfeasibility to vary the length of the alkyl chain connecting the phosphorus atoms of the phosphonio and phosphine moieties, however, the nature of the pendant phosphine moiety should easily be modified by employing other phosphanide reagents than $LiPPh_2$.

Characterization of the salts **2a, b, d**[X] and the betain **2c** was unequivocally achieved from analytical and spectroscopic (NMR, FAB-MS) data and a single crystal X-ray structure analysis of **2a**[Br]. The ^{31}P NMR spectra of **2a–c** display ABX patterns with similar chemical shifts and coupling constants (see Table 1) as in the cation **1**. The ^{31}P NMR spectrum of **2d** reveals an AMNX-type splitting. The signal of the pendant Ph_2P-group displays a chemical shift in the typical range of alkyldiphenylphosphines ($\delta^{31}P = -14$ to -30 [10]) and is split into a doublet by coupling with the phosphorus atom of the adjacent phosphonio-group. The ^1H and ^{13}C spectra display no peculiarities apart from duplication of the signals with respect to symmetrically substituted bis-phosphonio-benzophospholide cations such as **1**, and chemical shifts and coupling patterns of all atoms in the fused ring system are similar as there.

Crystals of **2a**[Br] are composed of discrete anions and cations (Figure 2) which display no unusually short contacts and contain two additional solvent molecules (CH_2Cl_2) per asymmetric unit. The presence of two phosphonio-groups with different substitution pattern in the cation introduces no measurable asymmetric distortion of the fused ring system. All bond

Table 1 ^{31}P NMR data (in $CDCl_3$ at 30 °C) of cations **2a–d** and metal complexes **8–14**. P^A, P^M, P^N, P^X, P^Y denote nuclei of AMNX, $[AMNX]_2$, or AMNXY spin systems; $\Delta\delta^{coord} = \delta(\text{complex}) - \delta(\mathbf{2d})$

	P^A ($\Delta\delta^{coord}$)	P^M	P^N	P^X ($\Delta\delta^{coord}$)	J_{PP} and $J_{Pr,P}$ [Hz][b)]
2a	236.8	16.5	16.2	–	$J_{AM} = 84.7$, $J_{AN} = 91.9$, $J_{MN} = 8.1$
2b	235.2	16.1	15.9	–	$J_{AM} = 83.9$, $J_{AN} = 92.0$, $J_{MN} = 8.2$
2c	237.5	16.7	16.0	–	$J_{AM} = 85.8$, $J_{AN} = 92.2$, $J_{MN} = 8.3$
2d	234.1	17.4	16.4	–12.0	$J_{AM} = 83.8$, $J_{AN} = 91.7$, $J_{NX} = 44.6$, $J_{MN} = 8.1$
8	234.4	15.9	17.6	28.6	$J_{AM} = 91.9$, $J_{AN} = 82.5$, $J_{MN} = 8.0$, $J_{NX} = 54.2$
9	224.8 (–9.3)	14.6	19.7	32.7 (+44.7)	$J_{AM} = 74.7$, $J_{AN} = 75.1$, $J_{AX} = 7.6$, $J_{NX} = 10.1$, $J_{MN} = 7.1$, $J_{MX} = 1.4$
10[a)]	232.0 (–2.1)	13.9	18.8	71.9 (+83.9)	$J_{AM} = 68.7$, $J_{AN} = 69.9$, $J_{AX} = 84.6$, $J_{MN} = 7.0$, $J_{NX} = 4.5$ Hz
11[a)]	237.8 (+3.7)	15.7	20.7	56.4 (+68.4)	$J_{AM} = 65.0$, $J_{AN} = 63.4$, $J_{AX} = 26.8$, $J_{NM} = 7.0$, $J_{NX} = 12.5$
12[a)]	234.2[c)]	16.0	17.5	67.3 (+79.3)	$J_{AM} = 91.6$, $J_{AN} = 84.7$, $J_{AX} = 2.2$, $J_{MN} = 7.9$, $J_{NX} = 38.2$, $J_{NX'} = 0.4$, $J_{XX'} = 26.0$
	233.8[c)]	16.0	17.1	49.9	$J_{AM} = 91.8$, $J_{AN} = 83.2$, $J_{AX} = 2.3$, $J_{MN} = 7.9$, $J_{NX} = 31.2$, $J_{MX} = 0.7$, $J_{XX'} = 31.7$
13a	173.7 (–60.3)	14.7	16.6	27.4 (+39.4)	$J_{AM} = 61.0$, $J_{AN} = 58.8$, $J_{AX} = 30.1$, $J_{MN} = 4.9$, $J_{NX} = 7.9$
13b	156.8 (–77.3)	14.7	16.7	5.0 (+17.0)	$J_{AM} = 55.3$, $J_{AN} = 56.4$, $J_{AX} = 30.3$, $J_{MN} = 4.5$, $J_{NX} = 9.1$, $J_{Pt,A} = 4078$, $J_{Pt,X} = 3281$
14b[d)]	234.6	16.3	17.4	9.3 (+21.3)	$J_{AM} = 91.7$, $J_{AN} = 83.3$, $J_{MN} = 8.3$, $J_{NX} = 53.9$, $J_{XX'} = 15.4$, $J_{Pt,X} = 3649$
15a	156.8	15.9	16.9	28.9 (+40.9)[e)]	$J_{AM} = 91.3$, $J_{AN} = 84.5$, $J_{MN} = 8.0$, $J_{MX} = 49.9$, $J_{XY} = 4.0$ Hz
15b	234.1	15.8	17.1	11.3 (+23.3)[e)]	$J_{AM} = 92.5$, $J_{AN} = 84.7$, $J_{NX} = 55.2$, $J_{MN} = 9.1$, $J_{XY} = 16.8$, $1J_{Pt,X} = 5100$

[a)] in THF-d_8; [b)] absolute values given for all couplings; [c)] two data sets correspond to *cis*/*trans* isomers; [d)] $\delta^{195}Pt = 114$; [e)] $\delta^{31}P$ (P^Y) [PPh_3] = 32.1 (**15a**), 10.5 ($J_{Pt,Y} = 5090$ Hz) (**15b**)

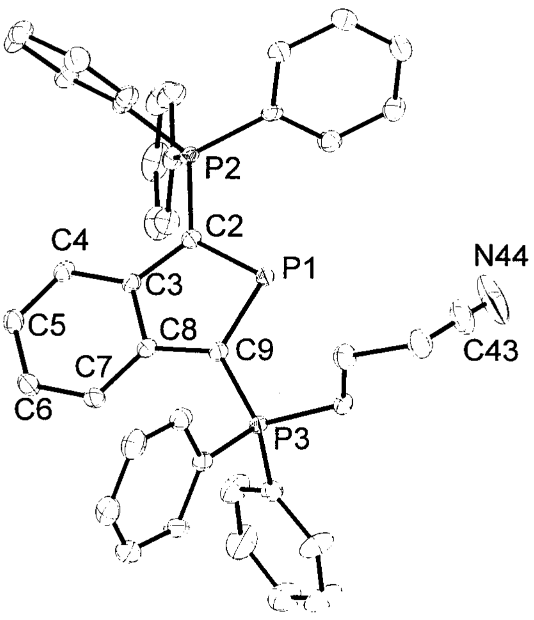


Fig. 2 Molecular structure of **2a** in the crystal, ORTEP view thermal ellipsoids are at the 50% probability level, H atoms omitted for clarity; selected bond distances/Å:

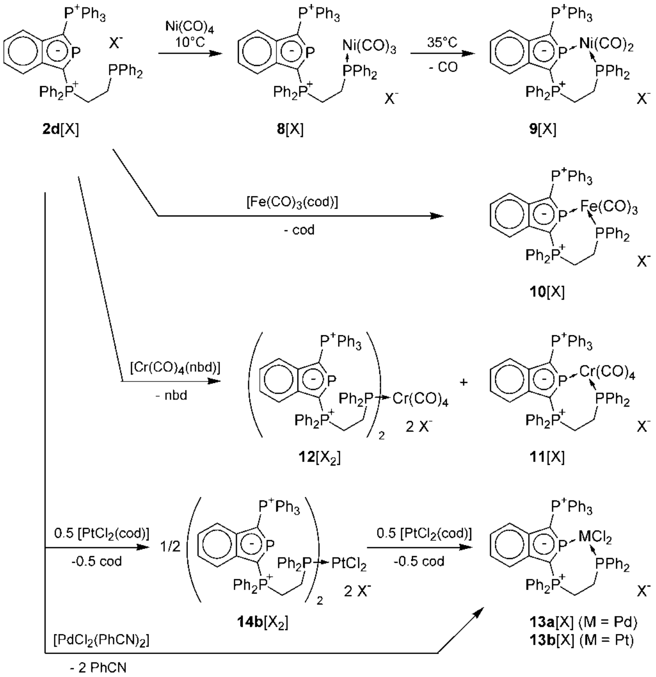
P(1)-C(2) 1.739(3), P(1)-C(9) 1.740(3), C(2)-C(3) 1.441(4), C(2)-P(2) 1.745(3), C(3)-C(4) 1.412(4), C(3)-C(8) 1.427(4), C(4)-C(5) 1.372(4), C(5)-C(6) 1.399(4), C(6)-C(7) 1.379(4), C(7)-C(8) 1.407(4), C(8)-C(9) 1.441(4), C(9)-P(3) 1.751(3).

distances and angles in the benzophospholide moiety match those of other structurally characterized bis-phosphonio-benzophospholides [4 a, 5].

Complexation properties of a phosphine-functionalized bis-phosphonio-benzophospholide

In order to survey to which extent side-chain functionalization in the cations **2** is successful in steric deprotection of the ring phosphorus atom, we carried out a systematic study of the reactions of **2d** with $Ni(CO)_4$, $[Fe(CO)_3(cod)]$, and $[Cr(CO)_4(nbd)]$ (nbd = norbornadiene; cod = cyclooctadiene). The substrates were chosen to permit the formation of chelate complexes $[M(\kappa^2P,P'\text{-}\mathbf{2d})(CO)_n]$ in which the steric demand of the $M(CO)_n$ fragment increases continuously with the change in metal coordination geometry from tetrahedral (Ni) over trigonal-bipyramidal (Fe) to octahedral (Cr). Further investigations of reactions of **2d** with $[PtCl_2(cod)]$ and $[PdCl_2(PhCN)_2]$ were stimulated by the observation that the cation **1** failed likewise to form complexes with Pd(II) or Pt(II) centers [5 b, 11]. Regarding that ligand substitution at square planar d^8-transition metal centers follows frequently an associative mechanism, we attribute this reluctance to kinetic inhibition due to sterically induced destabilization of a pentacoordinate transition state. Steric deprotection in connection with possible "pre-coordination" of a metal atom to the pendant Ph_2P group in **2d** was anticipated to overcome this effect and make chelate complexes readily available.

Addition of **2d**[X] (X = OTf, BPh_4) at low temperature to a CH_2Cl_2 solution of excess $Ni(CO)_4$ proceeded smoothly with gas evolution and coordination of the pendant phosphine moiety to give the complex **8**[X] which was identified by ^{31}P NMR spectroscopy. Attempts to isolate the product by removal of solvents and excess $Ni(CO)_4$ in vacuo resulted in loss of a second CO ligand and generation of the chelate complex **9**[X]. This compound was formed directly when the reaction of **2d**[X] and $Ni(CO)_4$ was carried out at 35 °C, and was isolated after removal of volatiles and recrystallization. The corresponding iron complex **10**[X] was likewise formed in a clean reaction from **2d**[X] and $[Fe(CO)_3(cod)]$ in THF and isolated after precipitation with ether. ^{31}P NMR studies gave no evidence for the occurrence of a similar intermediate as **8** in this case.



Scheme 4 Complexation reactions of **2d**[X] (X = OTf, BPh_4; cod = cyclooctadiene, nbd = norbornadiene).

Treatment of **2d**[X] with $[Cr(CO)_4(nbd)]$ afforded in contrast to the previous reactions a mixture of three phosphorus containing complexes. Even if all attempts to their separation by fractionating crystallization or chromatography failed and thus no pure compounds were isolated, one of the products was identified by its characteristic ^{31}P NMR spectrum (see below) as the expected chelate **11**[X]. The ^{31}P NMR signals of the remaining complexes displayed $[AMNX]_2$-type patterns which suggested coordination of the Ph_2P moieties of two molecules of **2d** to the same metal and were on this basis tentatively assigned as the *cis*-

and *trans*-isomers of **12**[X$_2$]. The product ratio **11** : **12** varied depending on the reaction conditions, with the formation of **11** (from 10 up to ca. 56%) being favored by the use of excess $Cr(CO)_4$(nbd), higher reaction temperatures, and lower reagent concentrations.

Finally, reaction of **2d**[X] with equimolar [$PdCl_2(PhCN)_2$] or [$PtCl_2$(cod)] proceeded straightforward with quantitative conversion into the complexes **13a, b**[X]. Performing the reactions under ^{31}P NMR spectroscopic control revealed the formation of the Pt-complex **13b** to occur according to a two-step mechanism: rapid reaction of two cations **2d** with a molecule of [$PtCl_2$(cod)] first gave a transient complex **14b** which then reacted slowly with a second equivalent of the starting material to afford **13b**.

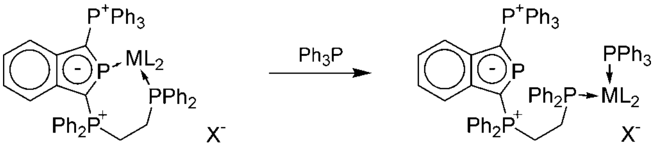
All obtained metal complexes constituted light yellow to orange solids which were readily soluble in polar aprotic organic solvents such as CH_2Cl_2 or CH_3CN, and insoluble in unpolar solvents (hexane, toluene). Complexes with zerovalent metals were moderately stable towards air and moisture, whereas **13a, b** displayed an enhanced sensitivity towards hydrolysis which had been previously noted for some complexes of **1** [4a, 11]. The constitution of all complexes followed unequivocally from analytical and spectroscopic data [12]. The ^{31}P NMR spectra of **8–11** and **13a, b** displayed AMNX-type patterns and those of the bis-phosphine-complexes **12** and **14b** more complicated [AMNX]$_2$ patterns. Comparison of the observed chemical shifts of all complexes with those of free **2d** (Table 1) revealed small negative or positive coordination shifts ($\Delta\delta^{\mathrm{coord}} = \delta(\mathrm{complex}) - \delta(\mathbf{2d})$) for the resonance of the ring phosphorus atom in chelate complexes, and positive coordination shifts for coordinated phosphorus atoms of pendant Ph_2P-moieties. Attachment of both coordination centers to the same metal in chelate complexes was indicated by additional splittings due to $^2J_{\mathrm{PMP}}$ couplings which were absent in the spectra of both free **2d** and complexes **8**, **12**, **14b** containing non-chelating cationic ligands, and a significantly reduced magnitude of $^3J_{\mathrm{PP}}$ attributable to the coupling of the two ^{31}P nuclei in the PCCP chain. The latter is attributable to the presence of a second coupling path in a chelate complex which corresponds to a ^4J interaction and is presumably of opposite sign than the ^3J coupling through the ligand backbone. Whereas the value of $^2J_{\mathrm{PMP}}$ allows no clear assignment of the *cis*- and *trans*-isomers of **12**, both the small magnitude of $^2J_{\mathrm{PMP}}$ and the values of $^1J_{\mathrm{Pt,P}}$ are indicative of a *cis*-arrangement of the two phosphorus ligands in **13b** and **14b** [13]. The difference in $^1J_{\mathrm{Pt,P}}$ values in **13b** is consistent with a higher degree of s-character in the Pt–P bond to the ring phosphorus atom and reflects the different formal hybridisation (sp^2 vs. sp^3) of the different donor atoms.

The IR spectra of the chelate complexes **9**, **10** display the expected number of νCO vibrations for Ni(CO)$_2$ and *fac*-Fe(CO)$_3$-moieties, respectively. Comparison of the observed vibrational frequencies with those of corresponding 1,4-bis-diphenylphosphino-butane (dppb) complexes [14] (Table 2) reveals an overall shift to higher wavenumbers which is consistent with a slightly higher π-acceptor quality of **2d** as compared to dppb. A more quantitative comparison of ligand properties (e. g. by analysis of Tolman parameters [15]), or comparison of π-acceptor-abilities for the two electronically different donor centers was precluded by the unavailability of complexes featuring coordination of **2d** exclusively via the ring phosphorus atom.

Table 2 IR data (νCO, in CH_2Cl_2) of [M(**2d**)(CO)$_n$] and [M(CO)$_n$(dppb)] (dppb = 1,4-bis-diphenylphosphino-butane)

	νCO [cm^{-1}]
9	1997, 1971
[Ni(CO)$_2$(dppb)]	1995, 1937
10	2002, 1942, 1913
[Fe(CO)$_3$(dppb)]	1981, 1908, 1879

In order to obtain still some information on the properties of the two different donor centers in **2d**, we studied ligand substitution reactions of **9** and **13b** with one equivalent of Ph_3P. ^{31}P NMR spectra of the reaction mixtures revealed that in both cases quantitative displacement of the ring phosphorus atom and formation of the complexes **15a, b** occurred. The magnitude of $^2J_{\mathrm{PMP}}$ in the square planar Pt-complex **15b** suggested that the *cis*-arrangement of the two phosphine moieties was retained. Isolation of the formed complexes was not attempted. The observed behavior is consistent with earlier reports in which easy replacement of coordinated phosphaalkenes by Ph_3P had been noted [16], and suggests that the bond from the metal atom to the σ^2,λ^3-phosphorus atom is weaker than that to a phosphine (σ^3,λ^3)-center.



9[X], **13b**[X]

15a[X] (ML$_2$ = Ni(CO)$_2$)
15b[X] (ML$_2$ = PtCl$_2$)

Scheme 5 Reaction of bis-phosphonio-benzophospholide chelate complexes with PPh_3 (X = OTf, BPh_4).

Conclusions

Two different synthetic routes to bis-phosphonio-benzophospholide cations with an additional pendant donor group (CN, C=C, CO_2^-) in one of the phosphonio-moieties are described. It has been shown that this side-chain functionalization allows the use of the cations as chelating ligands and leads further to an improved steric accessibility of the ring phosphorus atom, permitting an unprecedented coordination to metal carbonyl fragments with tetrahedral and trigonal-bipyramidal coordinated metal centers. The formation of a mixture of a chelate complex **11** and a complex **12** in which two cations **2 d** bind to the metal exclusively via their phosphine-ends emphasizes the limits of the sterically releasing effect: coordination of the ring phosphorus atom to an octahedral metal center seems still possible, but the sterically induced destabilization offsets apparently the stabilization by the chelate effect, rendering alternative reaction pathways observable. The chelating coordination of the cation **2 d** to square-planar d^8-metal centers (Pd^{II}, Pt^{II}) suggests that side-chain functionalization may likewise overcome the kinetic inhibition of complexation (by destabilization of pentacoordinate transition states) which is an important finding regarding a potential use of such complexes in catalysis. Finally, the intermediates observed during the formation of the chelate complexes **9**, **13 b**, as well as their further reactions with Ph_3P, reveal that the ring phosphorus atom is more weakly bound than the phosphine moiety. The reason for this effect is consistent with different strengths of M–P bonds owing to the different hybridisation of the two donor atoms.

Experimental Section

General Remarks: All manipulations were carried out under dry argon. Solvents were dried by standard procedures. NMR spectra: Bruker AMX 300 (^{1}H: 300.1 MHz, ^{31}P 121.5 MHz, ^{13}C: 75.4 MHz, ^{195}Pt 64.2 MHz) in $CDCl_3$ at 30 °C if not stated otherwise; chemical shifts referenced to ext. TMS (^{1}H, ^{13}C), 85% H_3PO_4 (Ξ = 40.480747 MHz, ^{31}P), Ξ = 21.4 MHz (^{195}Pt); positive signs of chemical shifts denote shifts to lower frequencies, coupling constants are given as absolute values; prefixes *i*-, *o*-, *m*-, *p*- denote atoms of phenyl substituents, and atoms in the benzophospholide ring are denoted as 4-C, 5-H, etc. MS: Kratos Concept 1 H, Xe-FAB, m-NBA matrix. – FT-IR spectra: Nicolet Magma 550, CaF_2 cells, in CH_2Cl_2 solution. Elemental analyses: Heraeus CHNO-Rapid. Melting points were determined in sealed capillaries. The amount of co-crystallized solvents was verified by integration of suitable ^{1}H NMR signals. ^{31}P NMR data of cations **2 a**–**d** and complexes **8**–**14** are given in table 1.

[3-{(3-Cyanopropyl)-diphenyl-phosphonio}-1-triphenylphosphonio-benzo[c]phospholide] bromide (**2 a**[Br]): To a solution of **3** (430 mg, 0.74 mmol) in 5 ml THF was added toluene (15 ml) and 4-bromobutyronitrile (150 mg, 1.00 mmol), and the resulting mixture was stirred for 4 d at room temperature. The product separated as light yellow precipitate which was collected by filtration, washed with toluene, and dried in vacuo. Yield 460 mg (0.63 mmol, 85%), m. p. 231 °C. – Elemental Analysis for $C_{42}H_{35}BrNP_3$ (726.6): calcd. C 69.43 H 4.86 N 1.58; found C 69.36 H 5.24 N 1.65%.

^{1}H NMR: δ = 3.55 (m, 2 H, CH_2), 2.01 (m, 2 H, CH_2), 2.84 (m, 2 H, CH_2), 6.81–7.12 (m, 4 H, 4-H to 7-H), 7.46–7.96 (m, 25 H, C_6H_5). ^{13}C{^{1}H} NMR: δ = 18.2 (d, J_{PC} = 19.3 Hz, $PCCH_2$), 20.5 (s, $PCCCH_2$), 25.1 (dd, J_{PC} = 59.1, 7.4 Hz, PCH_2), 109.0 (ddd, J_{PC} = 96.6, 54.4, 13.8 Hz, C-1/3), 119,2 (s, CN), 120.7 (m, C-4/7), 121.1 (m, C-4/7), 121.4 (s, C-5/6), 121.4 (s, C-5/6), 122.1 (dd, J_{PC} = 85.6, 1.5 Hz, *i*-C(PPh_2)), 122.6 (dd, J_{PC} = 89.4, 1.9 Hz, *i*-C(PPh_3)), 129.8 (d, J_{PC} = 12.5 Hz, *m*-C(PPh_3)), 129.9 (d, J_{PC} = 12.3 Hz, *m*-C(PPh_2)), 133.3 (dd, J_{PC} = 10.1 Hz, 0.5 Hz, *o*-C(PPh_2)), 133.9 (d, J_{PC} = 3.3 Hz, *p*-C(PPh_2)), 133.9 (dd, J_{PC} = 10.3 0.9 Hz, *o*-C(PPh_3)), 134.2 (d, J_{PC} = 2,8 Hz, *p*-C(PPh_3)), 144.2 (m, C-3 a/7 a), 144.2 (m, C-3 a/7 a). – FAB-MS: m/z (%): 646(100) [**2 a**$^+$].

[3-{(3-Butenyl)-diphenylphosphonio}-1-triphenylphosphonio-benzo[c]phospholide] bromide (**2 b**[Br]): To a solution of **3** (290 mg, 0.50 mmol) in THF (5 ml) were added toluene (15 ml) and 4-bromo-butene (140 mg, 1.00 mmol), and the resulting mixture was stirred for 3 d. A light yellow precipitate formed which was collected by filtration, washed with toluene, and dried in vacuo. Yield: 300 mg (0.42 mmol, 84%), m. p. 219 °C. – Elemental analysis for $C_{42}H_{36}BrP_3$ (713.6): calcd. C 70.70 H 5.09; found C 71.7 H 5.2%.

^{1}H NMR: δ = 2.36 (m, 2 H, CH_2), 3.11 (m, 2 H, CH_2), 4.94 (m, 2 H, =CH_2), 5.74 (m, 1 H, =CH), 6.8–7.1 (m, 4 H, 4-H to 7-H), 7.5–7.8 (m, 25 H, C_6H_5). – ^{13}C{^{1}H} NMR: δ = 26.5 (ddd, J_{PC} = 57.2, 8.7, 4.0 Hz, PCH_2), 27.8 (dd, J_{PC} = 5.3, 3.0 Hz, $PCCH_2$), 109.0 (ddd, J_{PC} = 92.9, 56.3, 13.0 Hz, C-1/3), 109.6 (ddd), J_{PC} = 97.9, 54.7, 12.6 Hz, C-1/3), 117.3 (s, =CH_2), 120.9 (m, C-4/7), 121.6 (m, C-4/7), 121.8 (s, C-5/6), 121.8 (s, C-5/6), 122.3 (d, J_{PC} = 86.2 2.5 Hz, *i*-C(PPh_2)), 123.4 (dd, J_{PC} = 91.4, 2.5 Hz, *i*-C(PPh_3)), 130.3 (d, J_{PC} = 12.5 Hz, *m*-C(PPh_3)), 130.4 (d, J_{PC} = 12.3 Hz, *m*-C(PPh_2)), 133.3 (d, J_{PC} = 9.7 Hz, *o*-C(PPh_2)), 134.3 (d, J_{PC} = 10.1 Hz, *o*-C(PPh_3)), 134.5 (d, J_{PC} = 2.8 Hz, *p*-C(PPh_2)), 134.6 (d, J_{PC} = 2.8 Hz, *p*-C(PPh_3)), 135.7 (d, J_{PC} = 15.7 Hz, =CH), 144.5 (m, C-3 a/7 a), 144.5 (m, C-3 a/7 a). – FAB-MS: m/z (%): 633(80) [**2 b**$^+$], 649(100) [**2 b**$^+$ + O].

[3-{(2-Carboxylatoethyl)-diphenylphosphonio}-1-triphenyl-phosphonio-benzo[c]phospholide] **2 c**: Acrylic acid (0.1 ml, 1.5 mmol) was added to a solution of **3** (200 mg, 0.35 mmol) in 1 : 1 THF/ether (10 ml) and the mixture stirred for 12 h at room temperature. The formed colorless precipitate was filtered off, dissolved in CH_2Cl_2 (10 ml), and extracted with saturated aqueous $NaHCO_3$. The organic phase was separated and dried over Na_2SO_4. Evaporation of the solvent and vacuum-drying produced 160 mg (70%) **2 c** of m. p. 201 °C (dec). – Elemental analysis for $C_{41}H_{33}O_2P_3$ (650.6): calcd C 75.69 H 5.11; found C 75.4 H 5.6%.

^{1}H NMR: δ = 2.48 (m, 2 H, CH_2), 3.43 (m, 2 H, CH_2), 6.7–7.1 (m, 4 H, 4-H to 7-H), 7.35–7.75 (m, 25 H, C_6H_5). – ^{13}C{^{1}H} NMR: δ = 23.8 (dd, J_{PC} = 54.6, 6.9 Hz, PCH_2), 31.0 (s, $PCCH_2$), 108.0 (ddd, J_{PC} = 96.5, 55.9, 14.2 Hz, C-1/3), 111.4 (ddd, J_{PC} = 90.3, 56.1, 15.5 Hz, C-1/3), 121.0 (m, C-4/7), 121.4 (m, C-4/7), 121.4 (s, C-5/6), 121.5 (s, C-5/6), 123.0 (dd, J_{PC} = 90.2, 2.9 Hz, *i*-C(PPh_3)), 123.5 (dd, J_{PC} = 85.4, 2.4 Hz, *i*-C(PPh_2)), 129.9 (d, J_{PC} = 12.0 Hz, *i*-C(PPh2)), 130.1 (d, J_{PC} = 12.6 Hz, *m*-C(PPh_3)), 133.3 (d, J_{PC} = 9.9 Hz, *o*-C(PPh_2)), 133.8 (d, J_{PC} = 2.9 Hz, *p*-C(PPh_2)), 134.0 (d, J_{PC} = 16.8 Hz, CO_2^-), 134.2 (d, J_{PC} = 10.1 Hz, *o*-C(PPh_3)), 134.4 (d, J_{PC} = 3.1 Hz, *p*-C(PPh_3)), 144.5 (m, C-3 a/7 a), 144.5 (m, C-3 a/7 a). – FAB-MS: m/z (%): 651(100) [M^+].

[1-{(2-Diphenylphosphinoethyl)-diphenylphosphonio}-3-triphenylphosphonio-benzo[c]phospholide] tetraphenylborate (**2 d**[BPh_4]):

(a) A mixture of α,α'-dibromo *ortho*-xylene (10 g, 38 mmol), Ph_3P (9.9 g, 38 mmol), and toluene (150 ml) was stirred for 24 hrs at room temperature. The formed colorless precipitate was collected by filtration, washed twice with 20 ml of THF, and dried in vacuo to yield 12.4 g (62%) of α-bromo-α'-triphenylphosphonio-*ortho*-xylene bromide (^{31}P{^{1}H} (CH_2Cl_2): δ = 21.2) which was employed for subsequent reactions without further purification.

(b) A suspension of 2-chloroethyl-diphenylphosphine (7.5 g, 30 mmol) and α-bromo-α'-triphenylphosphonio-*ortho*-xylene bromide (12.4 g, 23.5 mmol) in CH_3CN (300 ml) was refluxed for 2 hrs and then stirred for further 24 hrs at ambient temperature. The formed colorless precipitate was collected by filtration, washed three times with CH_3CN (25 ml), and dried in vacuo to give 10.9 g (14.1 mmol, 60%) of α-(2-chloroethyl-diphenylphosphonio)-α'-triphenylphosphonio-*ortho*-xylene dibromide (**4**[Br_2]) which was used without further purification. – $^{31}P\{^1H\}$: $\delta = 26.8$ (d, $J_{PP} = 4.5$ Hz, $>PPh_2$), 22.5 (d, $J_{PP} = 4.5$ Hz, $-PPh_3$).

(c) (**4**[Br_2]) (10.4 g, 14.0 mmol) was added in four portions within one hour to a solution of Ph_2PLi (freshly prepared from Ph_2PH (8.7 g, 47 mmol) and n-BuLi (28.25 ml of 1.6 M solution in hexane) in 150 ml of THF). The formed dark red suspension was stirred for 5 hrs, ethereal HCl (ca. 70 ml of 1 M solution) was added until the color disappeared, and stirring of the mixture was continued for additional 10 hrs. After the formed solids had been allowed to settle down and the supernatant liquid carefully decanted, the residue was treated with THF (150 ml) and stirred for further 10 hrs. The formed precipitate was then filtered off, dissolved in CH_2Cl_2 (100 ml), and filtered again. The filtrate was concentrated in vacuo to a total volume of 25 ml and treated with 25 ml of warm THF. The mixture was then allowed to cool to room temperature, another 200 ml of THF were added, and the resulting suspension stirred for 12 hrs. The formed precipitate was collected by filtration and dried in vacuo to give 9.8 g (10.6 mmol, 79%) of α(2-diphenylphosphinoethyl-diphenylphosphonio)-α'-triphenylphosphonio-*ortho*-xylene dibromide **6**[Br_2] of m. p. 180 °C. – $^{31}P\{^1H\}$: $\delta = 28.3$ (dd, $J_{PP} = 3.8$, 39.4 Hz, $>PPh_2$), 22.3 (d, $J_{PP} = 3.8$ Hz, $-PPh_3$), –9.7 (d, $J_{PP} = 39.4$ Hz, $-PPh_2$).

(d) A mixture of **6**[Br_2] (45.8 g, 49.5 mmol) and $NaN(SiMe_3)_2$ (40.2 g, 219 mmol) in toluene (350 ml) was stirred for 30 min at 0 °C and then for 90 min at room temperature. The solution was cooled again to 0 °C, and a solution of Me_2SiCl_2 (7.10 g, 55 mmol) in toluene (10 ml) added dropwise. The mixture was stirred for 24 hrs at ambient temperature, filtered, and the precipitate washed three times with 20 ml of toluene. An ^{31}P NMR spectrum indicated formation of the silaheterocycle **7** ($\delta^{31}P = 9.1$ (dd, $J_{PP} = 45.1$, 8.4 Hz, $J_{PSi} = 26.2$ Hz), 7.7 (d, $J_{PP} = 8.4$ Hz, $J_{PSi} = 28.0$ Hz), –13.2 (d, $J_{PP} = 45.1$ Hz)). After cooling the combined filtrates to 0 °C and addition of triethyl amine (50 ml), a solution of PCl_3 (7.5 g, 55 mmol) in toluene (20 ml) was added dropwise with stirring. After the addition was complete, the formed brownish precipitate was allowed to settle down, the supernatant liquid was carefully decanted, and CH_2Cl_2 (100 ml) was added. After stirring the mixture for 2 hrs, all volatiles were evaporated in vacuo. The residue was divided in two portions each of which was dissolved in CH_2Cl_2 (70 ml) and rapidly extracted three times with aequeous phosphate buffer (50 ml of 0.25 M Na_2HPO_4/0.25 M KH_2PO_4, pH = 7). The combined organic phases were dried over $CaCl_2$ and concentrated in vacuo to a volume of ca. 40 ml. Addition of THF (150 ml) lead to formation of a precipitate which was collected by filtration and dried in vacuo to afford 20.5 g (24.8 mmol, 50%) **2d**[Cl] of m. p. 209 °C. An analytically pure sample of **2d**[BPh_4] was obtained after stirring **2d**[Cl] with an equimolar amount of $NaBPh_4$ for 24 hrs in CH_2Cl_2, filtration, and evaporation of the solvent. – Elemental Analysis for $C_{76}H_{63}BP_4$ (1111.0): calcd. C 82.16, H 5.72, found C 82.67 H 5.26%.

^1H NMR: $\delta = 2.17$ (m, 2 H, CH_2), 2.85 (m, 2 H, CH_2), 6.79–6.93 (m, 4 H, 4-H to 7-H), 7.07–7.69 (m, 35 H, C_6H_5). – $^{13}C\{^1H\}$ NMR: $\delta = 21.9$ (dd, $J_{PC} = 17.3$, 6.3 Hz, CH_2), 23.9 (ddd, $J_{PC} = 56.0$, 21.0 Hz, 6.8 Hz, CH_2), 107.9 (ddd, $J_{PC} = 91.6$, 56.2, 14.4 Hz, C-3), 110.1 (ddd, $J_{PC} = 96.6$, 54.4, 13.8 Hz, C-1), 120.7 (m, C-7), 121.7 (m, C-4), 121.9 (s, C-6), 122.0 (s, C-5), 122.0 (d, $J_{PC} = 85.6$ Hz, *i*-C($>PPh_2$)), 122.6 (d, $J_{PC} = 90.6$ Hz, *i*-C(PPh_3)), 129.2 (d, $2J_{PC} = 6.9$ Hz, *o*-C($-PPh_2$)), 129.8 (s, *p*-C($-PPh_2$)), 130.3 (d, $J_{PC} = 12.7$ Hz, *m*-C(PPh_3)), 130.5 (d, $J_{PC} = 12.4$ Hz, *m*-C($>PPh_2$)), 132.8 (s, *p*-C($>PPh_2$)), 133.0 (s, *p*-C(PPh_3))), 133.1 (s, *m*-C($-PPh_2$)), 134.3 (d, $J_{PC} = 10.7$ Hz, *o*-C(PPh_3)), 134.7 (d, $J_{PC} = 10.3$ Hz, *o*-C($>PPh_2$)), 136.3 (d, $J_{PC} = 19.4$ Hz, *i*-C($-PPh_2$)), 144.4 (m, C-7 a), 144.4 (m, C-3 a). – FAB-MS: m/z (%): 791(100) [**2d**$^+$].

[Dicarbonyl-κ^2P,P'-{1-((2-9Diphenylphosphinoethyl)-diphenylphosphonio)-3-triphenylphosphonio-benzo[c]phospholide}nickel(0)] triflate **9**[OTf]: A solution of **2d**[OTf] (5.0 g, 5.3 mmol) in CH_2Cl_2 (25 ml) was added dropwise at 35 °C to a solution of $Ni(CO)_4$ (1.8 g, 10.3 mmol) in CH_2Cl_2 (25 ml). After the gas evolution (CO) was complete, stirring was continued for 1 hr, and the reaction mixture was then evaporated to dryness. The residue was dissolved in THF (20 ml) and left overnight at room temperature. The separated yellow crystals of **9**[OTf] × 2 THF were filtered of, washed carefully with little cold THF, and dried in light vacuum. Yield 3.1 g (2.9 mmol, 55%), m. p. > 200 °C (dec).

^1H NMR: $\delta = 2.55$ (m, 2 H, CH_2), 3.38 (m, 2 H, CH_2), 6.55–6.83 (m, 4 H, 4-H to 7-H), 7.20–7.35 (m, 10 H, C_6H_5), 7.48–7.58 (m, 10 H, C_6H_5), 7.60 (m, 3 H, C_6H_5), 7.63 (m, 4 H, C_6H_5), 7.75 (m, 15 H, C_6H_5), 7.86 (m, 6 H, C_6H_5). – $^{13}C\{^1H\}$ NMR: 24.1 (ddd, $J_{PC} = 20.0$, 4.2, 3.8 Hz, CH_2), 25.0 (ddd, $J_{PC} = 58.0$, 16.4, 1.8 Hz), CH_2), 98.2 (dd, $J_{PC} = 103$, 56 Hz, C-1/3), 98.4 (dd, $J_{PC} = 92$, 51 Hz, C-1/3), 120.2 (q, $J_{FC} = 315.6$ Hz, CF_3), 120.3 (dd, $J_{PC} = 4.2$, 1.5 Hz, C-4/7), 120.9 (ddd, $J_{PC} = 4.6$, 1.5, 0.8 Hz, C-4/7), 121.1 (s, C-5/6), 121.2 (s, C-5/6), 122.3 (ddd, $J_{PC} = 87.3$, 3.5, 1.5 Hz, *i*-C($>PPh_2$)), 123.8 (dd, $J_{PC} = 90.4$, 2.7 Hz, *i*-C($-PPh_3$)), 129.5 (d, $J_{PC} = 9.6$ Hz, *o*-C($-PPh_2$)), 130.6 (d, $J_{PC} = 12.5$ Hz, *m*-C($-PPh_3$)), 130.7 (d, $J_{PC} = 1.9$ Hz, *p*-C($-PPh_2$)), 130.8 (d, $J_{PC} = 12.6$ Hz, *m*-C($>PPh_2$)), 132.7 (d, $J_{PC} = 13.0$ Hz, *m*-C($-PPh_2$)), 133.6 (d, $J_{PC} = 10.3$ Hz, *o*-C($>PPh_2$)), 134.6 (d, $J_{PC} = 3.0$ Hz, *p*-C($>PPh_2$)), 134.8 (d, $J_{PC} = 3.0$ Hz, *p*-C($-PPh_3$)), 135.3 (d, $J_{PC} = 10.3$ Hz, *o*-C($-PPh_3$)), 136.3 (dd, $J_{PC} = 31.6$, 6.1 Hz, *i*-C($-PPh_2$)), 143.3 (ddd, $J_{PC} = 15.9$, 7.2, 1.1 Hz, C-3 a/7 a), 144.3 (ddd, $J_{PC} = 14.9$, 8.8, 1.1 Hz, C-3 a/7 a), 197.3 (dd, $J_{PC} = 3.5$, 3.4 Hz, CO). – IR (νCO): 1997, 1971 cm^{-1}.

[Tricarbonyl-κ^2P,P'-{1-((2-diphenylphosphinoethyl)-diphenylphosphonio)-3-triphenylphosphonio-benzo[c]phospholide}-iron(0)] tetraphenyl borate (**10**[BPh_4]): **2d**[BPh_4] (220 mg, 0.20 mmol) and [$Fe(CO)_3$(cod)] (50 mg, 0.20 mmol) were dissolved in THF (10 ml). The solution was stirred for 24 hrs, reduced to 5 ml in vacuo, and 10 ml of Et_2O were added. The formed red precipitate was collected by filtration, washed with Et_2O, and dried in vacuo. Yield 200 mg (0.16 mmol, 80%), m. p. 161 °C. – Elemental analysis for $C_{79}H_{63}BFeO_3P_4 \times 2$ THF (1395.1): calcd. C 74.90 H 5.71; found C: 74.85; H: 5.75%.

^1H NMR (THF-d_8): $\delta = 3.02$ (m, 2 H, CH_2), 3.42 (m, 2 H, CH_2), 6.50–7.00 (m, 4 H, 4-H to 7-H), 7.18–8.05 (m, 55 H, C_6H_5). – $^{13}C\{^1H\}$ NMR (THF-d_8): 23.6 (d, $J_{PC} = 56.7$ Hz, PCH_2), 24.1 (d, $J_{PC} = 21.0$ Hz, PCH_2), 100.0 (dd, br, $J_{PC} = 37.5$, 103.4 Hz, C-1, C-3), 119.0 (m, C-4/7), 120.2 (s, C-5/6), 120.6 (d, $J_{PC} = 1.3$ Hz, C-4/7), 121.2 (s, C-5/6), 122.7 (dd, $J_{PC} = 90.1$, 2.0 Hz, *i*-C($>PPh_2$)), 123.2 (dd, $J_{PC} = 86.6$, 2.7 Hz, *i*-C(PPh_3)), 128.9 (d, $J_{PC} = 9.9$ Hz, *m*-C($-PPh_2$)), 130.1 (d, $J_{PC} = 12.6$ Hz, *m*-C(PPh_3)), 130.5 (d, $J_{PC} = 12.4$ Hz, *m*-C($>PPh_2$)), 131.1 (s, *p*-C($-PPh_2$)), 132.6 (d, $J_{PC} = 9.7$ Hz, *o*-C($-PPh_2$)), 133.1 (d, $J_{PC} = 10.1$ Hz, *o*-C($>PPh_2$)), 134.3 (d, $J_{PC} = 1.3$ Hz, *p*-C($>PPh_2$)), 134.5 (s, *p*-C(PPh_3)), 134.9 (d, $J_{PC} = 10.3$ Hz, *o*-C(PPh_3)), 135.4 (d, $J_{PC} = 4.2$ Hz, *i*-C($-PPh_2$)), 143.5 (m, C-3 a/C7 a), 143.5 (m, C-3 a/7 a), 216.3 (d, $J_{PC} = 14.5$ Hz, CO). – FAB-MS: m/z (%): 931(2) [**10**$^+$], 847(85) [**10**$^+$ –3 CO], 791(100) [**2d**$^+$]. – IR (νCO): 2002, 1942, 1913 cm^{-1}.

Reaction of **2d**[BPh_4] with [$Cr(CO)_4$(nbd)]:

(a) A solution of **2d**[BPh_4] (230 mg, 0.2 mmol) in THF (10 ml) was added dropwise within 45 min to a warm (60 °C) solution of [$Cr(CO)_4$(nbd)] (100 mg, 0.4 mmol) in THF (10 ml). Stirring was continued for 30 min. The mixture was then allowed to cool to room temperature and concentrated to 5 ml. Addition of Et_2O (10 ml) produced a red precipitate which was filtered off, washed with Et_2O, and dried in vacuo. An ^{31}P NMR spectrosocpic assay revealed the presence of a mixture containing approx. 56% of **11** and 44% of *cis/trans*-**12**. Attempts to chromatographic separation of the mixture allowed to recover a small amount of unreacted $[Cr(CO)_4(nbd)]$, but resulted in extensive decomposition of the phosphorus containing complexes.

(b) **2d**$[BPh_4]$ (460 mg, 0.4 mmol) and $[Cr(CO)_4(nbd)]$ (50 mg, 0.2 mmol) were dissolved in THF (10 ml). The solution was stirred for 12 hrs and concentrated in vacuo to a total of 5 ml. Et_2O (10 ml) was slowly added. An orange precipitate formed which was filtered off, washed with Et_2O and dried in vacuo. An ^{31}P NMR spectroscopic assay revealed the presence of a mixture of *cis/trans*-**12** (88% by integration of suitable resonances, data in Table 1) and **11** (10%) beside small amounts of decomposition products which were not further identified. Attempts to chromatographic separation of the mixture using different stationary and mobile phases remained unsuccessful. – IR (νCO): 2027, 1932, 1890 cm^{-1} (for **12**).

[*cis*-Dichloro-κ^2*P,P′*-{1-((2-diphenylphosphinoethyl)-diphenylphosphonio)-3-triphenylphosphonio-benzo[c]phospholide}palladium(II)] triflate (**13a**[OTf]): Addition of CH_2Cl_2 (15 ml) to a mixture of **2d**[OTf] (500 mg, 0.5 mmol) and $[PdCl_2(PhCN)_2]$ (200 mg, 0.5 mmol) immediately produced a dark red solution which was stirred for 3 hrs, then layered with 20 ml of THF, and stored at ambient temperature. An orange-red crystalline precipitate of **13a**[OTf] formed slowly which was collected by filtration, washed with THF, and dried in vacuo. Yield 370 mg (0.3 mmol, 62%), m. p. 160 °C (dec).

^1H NMR: $\delta = 2.57$ (m, 1 H, CH_2), 3.10 (m, 2 H, CH_2), 3.28 (m, 1 H, CH_2), 6.40–6.68 (m, 4 H, 4-H to 7-H), 7.00–7.52 (m, 35 H, C_6H_5). – FAB-MS: m/z (%): 987(30) [**13a**$^+$ +O], 949(80) [**13a**$^+$ +O –Cl), 913 (100) [**2d**$^+$ +O +Pd].

[*cis*-Dichloro-κ^2*P,P′*-{1-((2-diphenylphosphinoethyl)-diphenylphosphonio)-3-triphenylphosphonio-benzo[c]phospholide}platinum(II)] tetraphenyl borate (**13b**$[BPh_4]$): THF (10 ml) was added to **2d**$[BPh_4]$ (200 mg, 0.18 mmol) and $[PtCl_2(cod)]$ (70 mg, 0.20 mmol). The mixture was stirred for 2 d, then layered with 5 ml of hexane, and stored at room temperature. The formed yellow crystalline precipitate was filtered off, washed with hexane, and dried in vacuo to afford 150 mg (0.11 mmol, yield 61%) of **13b**$[BPh_4]$, m. p. 168 °C. – Elemental analysis for $C_{76}H_{63}BCl_2P_4Pt$ (1377.0): calcd. C 66.29 H 4.61; found C: 65.49; H: 4.80%.

^1H NMR: $\delta = 2.64$ (m, 2 H, CH_2), 2.85 (m, 1 H, CH_2), 3.46 (m, 1 H, CH_2), 6.60–6.87 (m, 4 H, 4-H to 7-H), 6.88–7.90 (m, 55 H, C_6H_5). – ^{195}Pt NMR: $\delta = 411$ (dd, $J_{Pt,P} = 4078$, 3281 Hz). – FAB-MS: m/z (%): 1075(100) [**13b**$^+$ +OH], 1039(80) [**13b**$^+$ +OH, –Cl], 1003(20) [**2d**$^+$ +OH +Pt].

Crystal structure determination of **2a**[Br] at 173(2) K: colourless needles, $C_{42}H_{35}BrNP_3–2\,CH_2Cl_2$, $M = 896.4$, crystal size 0.40 × 0.30 × 0.20 mm, triclinic, space group $P\overline{1}$ (No. 2): $a = 12.6362(2)$ Å, $b = 12.9799(2)$ Å, $c = 13.6969(2)$ Å, $\alpha = 97.238(1)°$, $\beta = 102.660(1)°$, $\gamma = 97.748(1)°$, $V = 2143.60(6)$ Å^3, $Z = 2$, ρ(calcd) = 1.389 Mg m^{-3}, $F(000) = 916$, $\mu = 1.35$ mm^{-1}, 63582 reflexes ($2\theta_{max} = 56.6°$) measured on a Nonius Kappa CCD diffractometer at 123(2) K using MoKα radiation ($\lambda = 0.71073$ Å), 10508 independent [$R_{int} = 0.062$] used for structure solution (Direct Methods, SHELXS-97 [17 a]) and refinement (full-matrix least-squares on F^2, SHELXL-97 [17 b]) with 495 parameters and 54 restraints, empirical absorption correction, H-atoms with a riding model, $R1$ ($I > 2\theta(I)$) = 0.062, $wR2 = 0.196$, Largest diff. peak and hole 2.261 (near solvent) and –1.240 e Å^{-3}. One of the solvent molecules was disordered. Atomic coordinates and equivalent isotropic displacement parameters are given in Table 3.

Table 3 Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **2a**[Br] (esd's in parentheses; U(eq) is defined as one third of the trace of the orthogonalized Uij tensor)

	x	y	z	U(eq)
Br(1)	6643(1)	6786(1)	1798(1)	37(1)
P(1)	3474(1)	2215(1)	2596(1)	16(1)
C(2)	2279(2)	1447(2)	2703(2)	16(1)
C(3)	1368(2)	2015(2)	2631(2)	15(1)
C(4)	288(2)	1662(2)	2709(2)	18(1)
C(5)	–464(2)	2335(2)	2643(2)	19(1)
C(6)	–171(3)	3374(2)	2498(2)	21(1)
C(7)	879(2)	3747(2)	2427(2)	19(1)
C(8)	1670(2)	3077(2)	2493(2)	15(1)
C(9)	2808(2)	3296(2)	2455(2)	16(1)
P(2)	2167(1)	130(1)	2868(1)	14(1)
C(10)	3439(2)	–343(2)	2852(2)	16(1)
C(11)	3511(3)	–1179(2)	2137(2)	22(1)
C(12)	4507(3)	–1539(3)	2188(3)	27(1)
C(13)	5426(3)	–1062(3)	2942(3)	27(1)
C(14)	5365(3)	–228(3)	3648(2)	25(1)
C(15)	4371(3)	126(2)	3614(2)	22(1)
C(16)	1072(2)	–672(2)	1882(2)	16(1)
C(17)	1146(3)	–650(2)	876(2)	20(1)
C(18)	325(3)	–1232(3)	84(2)	25(1)
C(19)	–588(3)	–1813(3)	283(3)	26(1)
C(20)	–673(3)	–1828(3)	1273(3)	27(1)
C(21)	156(3)	–1261(2)	2077(2)	22(1)
C(22)	1907(2)	–32(2)	4090(2)	19(1)
C(23)	1860(3)	844(3)	4767(2)	24(1)
C(24)	1710(3)	721(3)	5728(3)	33(1)
C(25)	1617(3)	–271(3)	6002(3)	36(1)
C(26)	1666(3)	–1147(3)	5329(3)	37(1)
C(27)	1821(3)	–1037(3)	4370(3)	27(1)
P(3)	3500(1)	4537(1)	2383(1)	14(1)
C(28)	2658(2)	5110(2)	1420(2)	16(1)
C(29)	2288(2)	4540(2)	434(2)	21(1)
C(30)	1568(3)	4922(3)	–295(3)	28(1)
C(31)	1209(3)	5865(3)	–44(3)	29(1)
C(32)	1559(3)	6420(3)	918(3)	29(1)
C(33)	2298(3)	6058(2)	1659(2)	22(1)
C(34)	3759(2)	5436(2)	3554(2)	18(1)
C(35)	4508(3)	6365(3)	3721(3)	32(1)
C(36)	4647(4)	7086(3)	4603(3)	41(1)
C(37)	4036(3)	6887(3)	5304(3)	37(1)
C(38)	3315(3)	5954(4)	5149(3)	40(1)
C(39)	3174(3)	5222(3)	4274(3)	32(1)
C(40)	4827(2)	4446(2)	2123(2)	20(1)
C(41)	4822(3)	3853(3)	1083(2)	24(1)
C(42)	6007(3)	3837(3)	980(3)	34(1)
C(43)	6649(3)	3406(4)	1811(3)	42(1)
N(44)	7116(4)	3103(5)	2488(3)	68(2)
C(1C)	–1124(5)	5910(4)	3620(4)	60(1)
Cl(1)	24(1)	6283(1)	3125(1)	54(1)
Cl(2)	–891(2)	6485(2)	4893(1)	99(1)
C(2C)	3606(5)	636(5)	–826(5)	52(1)[a]
Cl(3)	4020(2)	929(2)	489(1)	86(1)[a]
Cl(4)	2554(2)	–422(2)	–1195(1)	87(1)[a]
C(3C)	3450(20)	–641(16)	–1370(14)	52(1)[b]
Cl(5)	3647(11)	–1151(9)	–229(8)	109(3)[b]
Cl(6)	2786(11)	421(9)	–1233(8)	98(3)[b]

[a] s. o. f. = 0.81(1); [b] s. o. f. = 0.19(1)

Crystallographic data (excluding structure factors) for the structures reported in this work have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-148648. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge DB2 1EZ, UK (Fax: int.code +(12 23)3 36-0 33; e-mail:teched@chemcrys.cam.ac.uk).

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