Ylidyl-substituted Phosphonio-benzophospholides as Chelating Ligands

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Dedicated to Professor Michael Veith on the Occasion of his 60^th^ Birthday

Abstract. Phosphonio-benzo[c]phospholides with an additional phosphonium ylide substituent in 3-position were synthesized by deprotonation of appropriately substituted 1,3-bis-phosphonio benzophospholide cations and characterized by spectroscopic and analytical data. The ability of these molecules to act as bidentate *P,C*-chelating ligands to transition metal atoms was demonstrated in the reactions with [W(CO)$_4$(norbornadiene)] and [MCl$_2$(cyclooctadiene)] (M = Pd, Pt). The Pd^{II} and Pt^{II} complexes are distinguished by a strong inclination towards addition of H_2O to the 10π-electron system of the ligand. The molecular structures of a W^0 complex with a P,C-chelating ylidyl-phosphonio-benzophospholide ligand and of the product resulting from H_2O-addition to a corresponding Pt^{II} complex were determined. The structural parameters of the W^0 complex provide evidence for the presence of substantial steric strain around the metal atom.

Keywords: Phosphorus heterocycles; Benzophospholides; Ylides; P ligands

Ylidyl-substituierte Phosphonio-benzophospholide als Chelatliganden

Inhaltsübersicht. Phosphonio-benzo[c]phospholide mit einem zusätzlichen Phosphoniumylid-Substituenten in 3-Position wurden durch Deprotonierung geeignet substituierter 1,3-Bis-phosphonio-benzophospholid-Kationen dargestellt und durch spektroskopische und analytische Daten charakterisiert. Die Fähigkeit dieser Moleküle als zweizähnige *P,C*-Chelatliganden zu agieren wurde in Reaktionen mit [W(CO)$_4$(norbornadien)] und [MCl$_2$(cyclooctadien)] (M = Pd, Pt) demonstriert. Die Pd^{II} und Pt^{II} Komplexe zeichnen sich durch eine starke Neigung zur Addition von H_2O an das 10π-Elektronensystem des Liganden aus. Die Molekülstrukturen eines W^0-Komplexes mit einem *P,C*-chelatisierenden Ylidyl-Phosphonio-benzophospholid-Liganden und eines aus der H_2O-Addition an den entsprechenden Pt^{II}-Komplex resultierenden Produktes wurden bestimmt. Die strukturellen Parameter des W^0-Komplexes geben Hinweise auf das Vorhandensein einer beträchtlichen sterischen Spannung um das Metallatom.

Introduction

In the course of our investigations of the chemistry of zwitterionic phosphonio- benzophospholides we have shown that the derivatives **1** and **4** (Scheme 1) can act as bidentate chelating ligands via the ring phosphorus atom and the sulfur atom or a BH-σ-bond of the pendant thioxophosphoranyl or phosphine-borane substituents, respectively [1]. Regarding that thioxophosphoranes and phosphine-boranes form a row of valence-isoelectronic compounds together with monophosphazenes and phosphonium ylides and that the ligand properties of the latter are well documented [2], one can expect that the ylide- and phosphazene-substituted phosphonio-benzophospholides **2a, 3** (Scheme 1) display a similar ligand behavior as **1, 4**. Some recent reports on the coordination properties and catalytic application of bifunctional phosphino-phosphonium ylide ligands [3, 4] stimulated us to perform a study of the synthesis and coordination chemistry of **2a** whose results will be reported here.

Results and Discussion

Preparation and characterization of ylidyl-substituted phosphonio-benzophospholides

The target compounds were readily prepared from the phosphinyl-substituted zwitterion **5** [5] by a standard two-step procedure (Scheme 2). Reaction of **5** with appropriate alkyl halides afforded first the 1,3-bis-phosphonio-benzophospholide salts **6a-d** which were isolated in good yield as air and moisture stable solids. These salts were then reacted with BuLi or metal amides such as LiN(SiMe$_3$)$_2$, NaN(SiMe$_3$)$_2$, or NaNH$_2$, respectively. ^{31}P NMR studies showed that the deprotonation of **6b** proceeded unselectively to give an inseparable mixture, but that the ylides **2a,c,d** were formed in near quantitative yield. The choice of the base had practically no influence on the outcome of the deprotonation, but the use of NaN(SiMe$_3$)$_2$ facilitated the separation of the ylides from the salts formed as by-products.

The stabilized ylides **2c,d** were readily isolated as light yellow solids. Isolation of **2a** in pure form was prevented by

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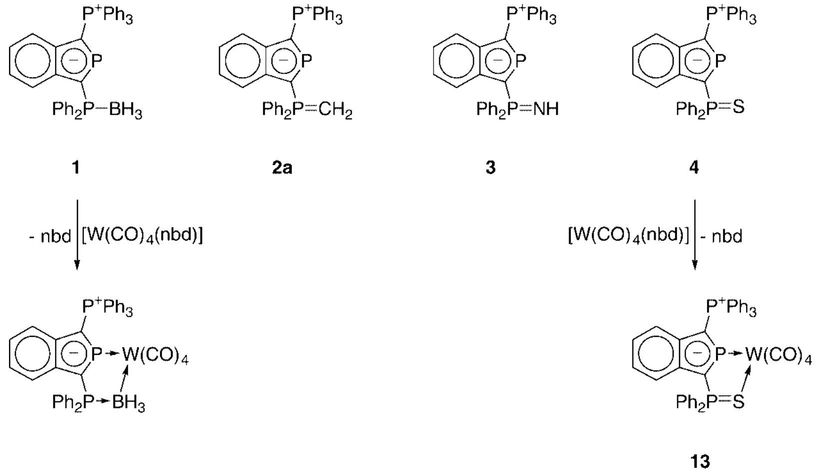
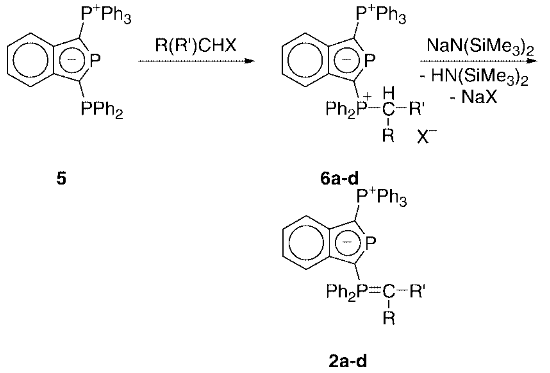
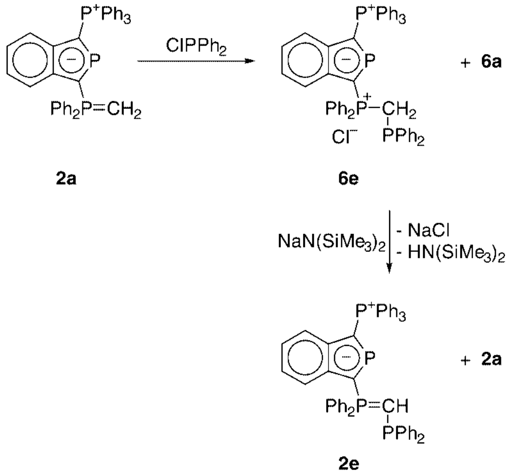


Scheme 1 (nbd = norbornadiene)



Scheme 2 (**6a:** R = R′ = H; X = I; **6b:** R = H, R′ = Ph, X = Br; **6c:** R = H, R′ = CN, X = Cl; **6d:** RR′ = 9-fluorenylidene, X = Br)

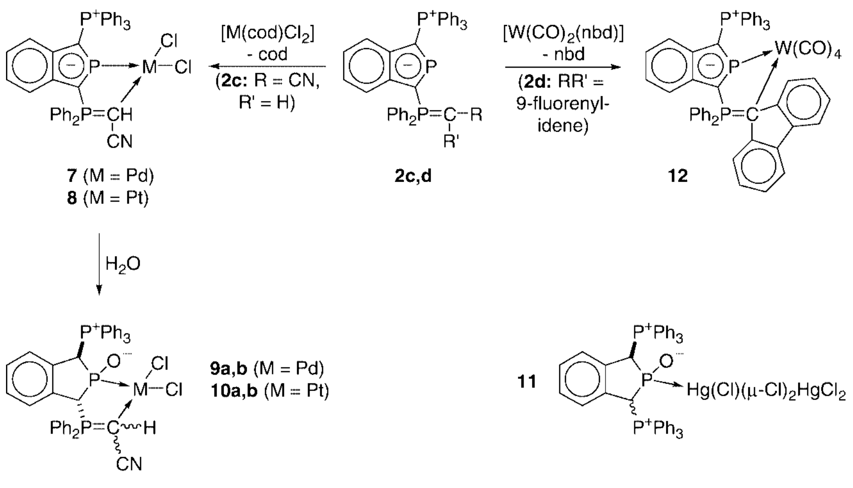


Scheme 3

partial decomposition (mainly re-protonation and reductive cleavage of a carbene fragment to produce **5**) during work-up, but the product was unambiguously identified by means of NMR spectroscopy. Treatment of a freshly prepared solution of crude **2a** with $ClPPh_2$ gave a mixture of two compounds which were identified as the cations **6a** and **6e** (cf. Scheme 3) by their characteristic patterns in $^{31}P\{^1H\}$ and $^1H,^{31}P$ HMQC NMR spectra. Subsequent deprotonation by $NaN(SiMe_3)_2$ afforded the ylides **2a** and **2e**. The latter precipitated together with the NaCl formed and was characterized by NMR and mass spectrometry. Attempts to purify **2e** by fractional crystallization failed, and the product could thus not be obtained in pure form. The reaction pattern leading to **2e** is well established for phosphonium ylides [6] and can be considered as independent validation of the identity of **2a**.

The ylides **2a** (as a mixture of the crude product and NaI) and **2c,d** are yellow solids which are stable in dry air. The stabilization of the formal carbanion by an electron withdrawing CN substituent or the incorporation into an aromatic π-electron system in **2c,d** induce a marked decrease in basicity and an increased chemical stability. Thus, **2a** decomposes rapidly in almost any solvent other than toluene, whereas **2c** can be handled in anhydrous THF or DME, and **2d** is soluble in most polar organic solvents, including alcohols, and tolerates even the presence of water without detectable decomposition. Interestingly, **2c** undergoes a quantitative reaction to give the phosphine **5** besides unidentified by-products upon the attempted dissolution in anhydrous CH_2Cl_2.

The identity of the ylides **2a,c,d** was unambiguously established by analytical and spectroscopic data. The most characteristic NMR spectral changes as compared to the conjugated acids, **6a,c,d**, involve an increase by some 70 Hz of the $^1J_{PC}$ coupling to the ylide carbon atom and a larger shielding of the directly attached protons ($\Delta\delta = -1.9$ (**2a**), -3.6 (**2c**)). The variation of $\delta^{13}C$ and $\delta^{31}P$ of the atoms in the ylide moiety upon deprotonation displays no common trend, but the chemical shifts of the P-2 atoms in **2a,c,d** show a small, although hardly significant, additional shielding by some 5 ppm.



Scheme 4 (nbd = norbornadiene; cod = 1,5-cyclooctadiene)

Complex formation reactions of ylidyl-substituted phosphonio-benzophospholides

In consideration of the recent report on a phosphino-phosphonium ylide complex of Pd^{II} [4], we attempted the synthesis of Pd and Pt complexes of the potential *P,C*-bidentate ylide **2c**. Treatment of the ligand with one equivalent of [$PtCl_2$(COD)] (COD = 1,5-cyclooctadiene) or [$PdCl_2(MeCN)_2$] resulted according to the results of ^{31}P NMR studies in clean formation of products which were, in regard of the similarity of their spectral data with those of previously reported Pt and Pd complexes with bis-phosphonio-benzophospholide cations [7], assigned as the expected complexes **7, 8** (Scheme 4). Attempted isolation of the products was under all conditions prevented by the onset of hydrolytic decomposition[1] to give a mixture of two species assigned (see below) as the diastereomers **9a,b** and **10a,b**. The quantitative hydrolysis of **7** occurred upon prolonged exposition of the reaction mixture to moist air, and a mixture containing nearly equal amounts of **9a** and **9b** was isolated after precipitation with hexanes. The hydrolysis of the Pt complex **8** proceeded less selectively; here, the addition products **10a,b** were merely detectable as intermediates which decayed further under complete cleavage of the five membered heterocyclic ring.

The constitution of **9a,b** and **10a,b** was established by one and two-dimensional NMR studies (see Experimental section for data) and an X-ray diffraction study of a sample of **10a** which was serendipitously isolated during attempts directed at the crystallization of **8**. The structure of **10a** (space group $R\bar{3}$) is composed of isolated molecular complexes (Figure 1) and contains three solvent molecules (THF) in the asymmetric unit. The metal atom adopts a square-planar coordination with bond angles (from 87.2(2)° to 93.4(2)°) deviating only slightly from the ideal value. The intra-ligand bond distances and angles display no peculiarities and match closely the corresponding data in **11** [8] (cf. Scheme 4). The Pt(1)-C(40) distance of 2.071(7) Å fits well into the range of known bond distances in Pt-complexes of phosphonium ylides (2.04 − 2.16 Å[2]).

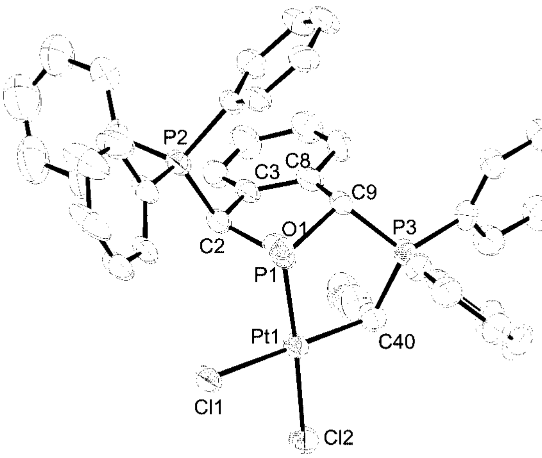


Fig. 1 Molecular structure of **10a**. Thermal ellipsoids are drawn at 50 % probability level, and H atoms have been omitted for clarity. Selected bond lengths/Å: Pt(1)-C(40) 2.071(7), Pt(1)-P(1) 2.1970(19), Pt(1)-Cl(1) 2.3510(18), Pt(1)-Cl(2) 2.3922(19), P(1)-O(1) 1.493(5), P(1)-C(2) 1.850(8), P(1)-C(9) 1.907(7), C(2)-C(3) 1.532(10), C(2)-P(2) 1.836(7), C(3)-C(8) 1.409(10), C(8)-C(9) 1.506(11), C(9)-P(3) 1.811(7).

The envelope conformation of the dihydrophosphole ring in the ligand of **10a** is similar as in **11**, but the phosphonio-substituents reside in *trans*- rather than *cis*-positions, and the metal rather than the oxygen atom occupies the “flagpole” position at the P1 atom. This arrangement causes a

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[1] As **9a,b** and **10a,b** formed also slowly when the whole reaction was conducted in carefully dried solvents and under complete exclusion of oxygen and moisture in a glove box, it cannot be excluded that the source of H_2O is provided by a wall reaction with the material of the reaction flask.

[2] Result of a query in the CSD database for complexes with the structural fragment $X_3Pt-CX_2-PR_3$ (X = any group; R = alkyl or aryl)

strong folding between the dihydrophosphole and the adjacent PtPCPC-chelate rings and is presumably a consequence of the geometrical constraints imposed by the conformational rigidity of the heterocyclic rings and steric congestion by peripheral substituents. The nitrile moiety at C(40) resides in an *endo*-position with respect to the dihydrophosphole ring, leading to a *cis*-arrangement the two CH-bonds in the chelate ring. Keeping in mind that the same conformational constraints as in **10a** (which fix the relative configurations at three of the four stereo-centres present) should also apply for the second diastereomer, both isomers are most likely distinguished by an inverted configuration at the ylide carbon atom. This suggests for **10b** an arrangement where the nitrile occupies the *exo*-position with respect to the dihydrophosphole ring, and the CH-bonds in the chelate ring are *trans* to each other. An attempt to verify the relative stereochemistry of the diastereomeric Pd-complexes **9a,b** from ^{1}H NOESY NMR spectra failed, owing to the absence of any correlations interconnecting the three ring hydrogen atoms.

The formation of the complexes **9, 10** resembles the known activation of bis- phosphonio-benzophospholide cations to undergo hydrolysis upon protonation [9] or transition metal coordination [8−10], and the spectroscopic and structural data of **9a,b** and **10a,b** display indeed close similarity to those of the products formed by hydrolysis of Hg^{II} or Au^{I} complexes with cationic bis-phosphonio-benzophospholide ligands [8−10].

Considering that complexes of zerovalent metal fragments with bis-phosphonio-benzophospholides are more stable towards hydrolysis than those with divalent metals [7], we explored the reactions of **2c** with [W(CO)$_4$(COD)] and [Pt(PPh$_3$)$_2$(C$_2$H$_4$)]. Whereas the Pt^0 complex did not react at all, the reaction of **2c** with the W^0 complex gave, according to ^{31}P NMR studies, a mixture of three phosphorus containing species. Whereas IR spectra showed νCO bands indicating the presence of a *cis*-W(CO)$_4$-fragment in the major product, the absence of ^{183}W satellites on any of the signals attributable to the ring phosphorus atoms excluded that a chelate complex with a κ^2-*P,C*-coordinated ligand had formed[3]. As all attempts towards isolation of pure products, or unequivocal spectroscopic identification of the species in the reaction mixture remained unsuccessful, the reaction was not pursued further. Similar results were also obtained for the reaction of **2c** with [Cr(CO)$_4$(nbd)].

The successful synthesis of a complex with a *P,C*-chelating phosphonio-benzophospholide-ylide ligand was finally achieved by reacting [W(CO)$_4$(COD)] with **2d** to give **12** (Scheme 4) as the only detectable product. The complex was isolated after layering the reaction mixture with hexanes, and characterized by analytical and spectroscopic data and a single-crystal X-ray diffraction study. Exclusive formation of **12** was also observed during the reaction of **2d** with a slight excess of [W(CO)$_3$(toluene)]. The absence of any species with η^5-coordinated cyclopentadienyl rings [11] in this reaction owes presumably to the high degree of benzannelation, as coordination of a metal atom to the five-membered ring would result in a very unfavorable loss of local aromaticity in the adjacent six-membered rings.

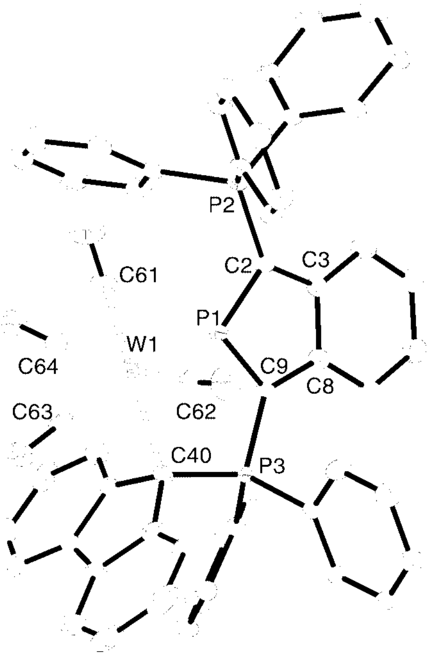

Fig. 2 Molecular structure of **12**. Thermal ellipsoids are drawn at 50 % probability level, and H atoms have been omitted for clarity. Selected bond lengths/Å: W1 C61 1.957(6), W1 C62 2.039(5), W1 C63 1.983(5), W1 C64 2.038(5), W1 C40 2.454(6), W1 P1 2.4130(11), P1 C9 1.710(4), P1 C2 1.722(4), P3 C9 1.754(4), P2 C2 1.752(4), C8 C9 1.431(5), C8 C3 1.436(6), C2 C3 1.457(5).

The ^{31}P NMR data of **12** reveal as most characteristic features a deshielding of the resonance of the ylide phosphorus atom by some 15 ppm, and the presence of ^{183}W satellites with substantially different couplings between the metal and the ring phosphorus ($^1J_{WP}$ = 240 Hz) and the ylide phosphorus atoms ($^2J_{WP}$ = 3 Hz), respectively. The ^{13}C NMR spectrum displays a characteristic set of three signals with relative intensities of 1:2:1 for the *cis*-W(CO)$_4$ unit, and the signal of the ylide carbon atom displays a moderate negative coordination shift ($\Delta\delta = -16$) and a reduction of the magnitude of $^1J_{PC}$ from 127 to 42 Hz as compared to **2d**.

The molecular structure of **12** (Figure 2) bears close similarities to that of the complex **13** [1] (cf. Scheme 1) with a *P,S*-chelating phosphonio-benzophospholide ligand.

Common features in the structures of both complexes include the bidentate coordination of a *cis*-W(CO)$_4$ unit by a *P,E*-chelating ligand whose small bite angle (**12**: E = C; P1-W1-C40 77.6(1)°; **13**: E = S; P1-W1-S1 79.9(1)° [1]) induces a "bent" coordination of the phosphorus atom (as illus-

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[3] As one of the products was also formed as the major product of the reaction of **2c** with [W(CO)$_5$(cyclooctene)] and the IR data gave evidence for the formation of a pentacarbonyl complex as side product, the constitution of this species was tentatively assigned as the ylide complex [W(CO)$_5$(κ^1-*C*-**2c**)].

trated by the large difference in C9-P1-W1 (120.0(2)°) and C2-P1-W1 (145.7(2)°) angles) and a marked deviation from a regular octahedral coordination polyhedron at the metal atom. The five-membered chelate rings adopt flat twist-conformations whose planarization (which might help to reduce the distortion in the metal coordination sphere) is presumably prevented by steric interference between the ancillary CO ligands and the bulky Ph_3P-group. The "intra-ligand" bonds P1-C9 (**12**: 1.710(4) Å; **13** [1]: 1.722(6) Å) and C9-P3 (**12**: 1.754(4) Å; **13**: 1.760(6) Å) in the chelate rings are similar in both complexes whereas the W1-P bond in **12** (2.4130(11) Å) is measurably shorter than in **13** (2.4605(15) Å). The W1-E (**12**: 2.454(6) Å; **13**: 2.602(3) Å) and P3-E bond distances (**12**: 1.824(5) Å; **13**: 2.015(2) Å) reflect the larger covalent radius of a sulfur as compared to a carbon atom and are thus longer in **13**. Further unique structural features of **12** include a marked non-linearity in the *trans*-$W(CO)_2$-unit (C62-W1-C64 168.0(2)°) and the presence of close non-bonding contacts involving these carbonyls and the fluorenylidene moiety (C64-C42 3.08 Å, C62-C52 3.31 Å). These interactions are considerably shorter than the sum of van-der-Waals radii (3.50 Å) and suggest that the non-linear distortion of the *trans*-$W(CO)_2$-unit is a consequence of a significant repulsive interference between the carbonyls and the fluorenylidene moiety. Comparison of the structural data of **12** with further literature data reveals that the W1-C40 and P3-C40 distances in **12** are much longer than average bond lengths in known tungsten complexes with phosphonium ylide ligands (W-C 2.30 ± 0.06 Å; C-P 1.78 ± 0.02 Å[4]).

On the whole, the observed structural features of **12** suggest rather weak bonding between the tungsten atom and both donor atoms of the chelate ligand whose origin may be related to two major sources, viz. (i) the mismatch of the bite angle and the alignment of the coordinating lone-pairs in the chelate ligand with respect to the steric requirements of the metal atom, and (ii) additional steric strain resulting from interference between the ancillary carbonyl ligands with the bulky triphenylphosphonio- and fluorenylidene-moieties in the chelate ligand. Comparison of the structural parameters of the closely related complexes **12** and **13** indicates that the importance of steric strain may be somewhat more pronounced for the former.

Conclusions

The synthesis and coordination abilities of phosphonio-benzophospholide zwitterions with an additional ylide substituent in 3-position have been demonstrated. The stability of these species depends crucially on the electronic stabilization of the ylide moiety by electron withdrawing substituents or incorporation into a delocalized π-electron system. The compounds may coordinate as bidentate chelating ligands to a transition metal atom, even though the structural features of a W^0 complex suggest that the bonding is hampered by a geometrical mismatch between the ligand and the metal, and substantial steric crowding.Complexes of Pt^{II} and Pd^{II} formed display further a high liability to undergo reactions under addition to the benzophospholide π-electron system which could limit their use in catalytic applications.

Experimental Section

General Remarks: All manipulations were carried out under dry argon. Solvents were dried by standard procedures. NMR spectra: Bruker DPX 400 (^1H: 400.13 MHz, ^{31}P 161.9 MHz, ^{13}C: 100.3 MHz) or AC 250 (^1H: 250 MHz, ^{31}P 101.2 MHz) in thf-D_8 at 30 °C; chemical shifts referenced to ext. TMS (^1H, ^{13}C), 85 % H_3PO_4 (Ξ = 40.480747 MHz, ^{31}P); 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 C-4, 5-H, etc. The assignment of ^1H, ^{13}C and ^{31}P resonances was verified from two-dimensional $^1H,^1H$ COSY, $^1H,^{31}P$ and $^1H,^{13}C$ HMQC, and $^1H,^{13}C$ HMBC NMR spectra where necessary. MS: Kratos Concept 1H, Xe-FAB, m-NBA matrix. IR spectra: Perkin-Elmer Paragon FT-IR spectrometer. Elemental analysis: Perkin-Elmer 2400 CHSN/O Analyser. Melting points were determined in sealed capillaries.

General procedure for the preparation of the phosphonium salts 6a-d.

One equivalent of the appropriate alkyl halide was added to a stirred solution of **5** (0.20 to 2.00 g) in toluene (15 to 50 ml). The solution was gently warmed (**6a**) or refluxed (**6b-d**), and stirring was continued until a pale yellow to white precipitate separated. The product was collected by filtration, washed with hexane (20 ml) and ether (20 ml), and dried in vacuum.

The spectroscopic data of **6a,b** were described previously [1].

[3-(Cyanomethyl-diphenyl-phosphonio)-1-triphenylphosphonio-benzo[c]phospholide] chloride (6c). Colorless solid, yield 87 %, mp 234 °C. −

Anal. for $C_{40}H_{30}ClNP_3$ (653.7): calcd. C 73.46 H 4.67 N 2.62 %; found: C 67.37 H 4.78 N 2.14 %.

^{31}P NMR: δ = 237.9 (dd, $^2J_{PP}$ = 90.2, 92.9 Hz, P-2), 11.9 (dd, $^2J_{PP}$ = 92.2 Hz, $^4J_{PP}$ = 8.3 Hz, PPh_2), 10.0 (dd, $^2J_{PP}$ = 90.9 Hz, $^4J_{PP}$ = 8.3 Hz, PPh_3). − **^{1}H NMR** (CD_2Cl_2): δ = 8.07 (m, 4 H, o-H(PPh_2)), 7.76−7.52 (m, 15 H, H(PPh_3)), 7.25 (m, 2 H, p-H(PPh_2)), 7.15 (m, 4 H, m-H(PPh_2)), 7.12−6.88 (m, 4 H, 4-H − 7-H), 5.41 (d, 2 H, J_{PH} = 14.2 Hz, PCH_2CN). − **^{13}C{^{1}H} NMR** (CD_2Cl_2): δ = 144.2 (ddd, J_{PC} = 16.9, 8.8, 2.2 Hz, C-7a/3a), 144.0 (ddd, J_{PC} = 16.2, 9.3, 1.5 Hz, C-7a/3a), 134.5 (d, $^4J_{PC}$ = 3.2 Hz, p-C(PPh_2)), 134.2 (d, $^4J_{PC}$ = 3.2 Hz, p-C(PPh_3)), 133.9 (dd, $^2J_{PC}$ = 10.5 Hz, $^4J_{PC}$ = 1.1 Hz, o-C(PPh_3)), 133.6 (d, $^2J_{PC}$ = 11.0 Hz, o-C(PPh_2)), 129.8 (d, $^3J_{PC}$ = 12.8 Hz, m-C(PPh_3)), 129.7 (d, $^3J_{PC}$ = 13.1 Hz, m-C(PPh_2)), 122.7 (dd, $^1J_{PC}$ = 90.8 Hz, $^3J_{PC}$ = 2.9 Hz, I-C(PPh_3)), 121.7 (s, C-4 -C-7), 121.6 (s, C-4−C-7), 121.2 (d,J_{PC} = 2.6 Hz, C-4−C-7), 121.0 (dd, $^1J_{PC}$ = 90.0 Hz, $^3J_{PC}$ = 2.6 Hz, i-C(PPh_2)), 120.5 (m, C-4−C-7), 112.8 (d, $^2J_{PC}$ = 8.9 Hz, CN), 110.9 (ddd, $^1J_{PC}$ = 55.5 Hz, 96.0 Hz, $^3J_{PC}$ = 15.0 Hz, C-1/3), 106.7 (ddd, $^1J_{PC}$ = 57.2, 94.3 Hz, $^3J_{PC}$ = 14.8 Hz, C-1/3), 19.1 (dd, $^1J_{PC}$ = 56.8 Hz, $^3J_{PC}$ = 7.4 Hz, PCH_2). − **MS** ((+)-Xe-FAB, mNBA): m/z = 618 (100 %, $C_{40}H_{30}P_3N^+$). −

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[4] Average and standard deviation as result of a query in the CSD database for complexes with the structural fragment R_3P-CX_2-W (X = any group; R = alkyl or aryl)

[3-{(9-Fluorenyl)-diphenylphosphonio}-1-triphenylphosphonio-benzo[c]phospholide] bromide (6d). Light yellow solid, yield 83 %, mp 234 °C. −
Anal. for $C_{51}H_{38}BrP_3$ (823.1): calcd. C 72.84 H 4.65 %, found: C 74.37 H 5.18 %.

^{31}P{^{1}H} NMR: δ = 237.2 (dd, $^{2}J_{PP}$ = 92.5, 75.3 Hz, P-2), 22.3 (dd, $^{2}J_{PP}$ = 75.3 Hz, $^{4}J_{PP}$ = 8.0 Hz, PPh_2P), 16.4 (dd, $^{2}J_{PP}$ = 92.5 Hz, $^{4}J_{PP}$ = 8.0 Hz, PPh_3). − **^{1}H NMR** (CD_2Cl_2): δ = 7.70 (m, 3 H, p-H(PPh_3)), 7.57 (m, 6 H, o-H(PPh_3)), 7.58 (m, 6 H, m-H(PPh_3)), 7.54 (m, 4 H, o-H(PPh_2)), 7.53 (m, 2 H, p-H(PPh_2)), 7.50 (m, 2 H, Fl-H), 7.38 (m, 4 H, m-H(PPh_2)), 7.22 (m, 2 H, Fl-H), 6.94 (m, 2 H, 4-H−7-H), 6.90 (m, 4 H, Fl-H), 6.65 (m, 2 H, 4-H −7-H), 6.16 (dd, 1 H, J_{PH} = 16.7, 1.2 Hz, Fl-H). − **^{13}C{^{1}H} NMR** (CD_2Cl_2): δ = 144.9 (ddd, J_{PC} = 16.3, 7.9, 2.1 Hz, C-7a/3a), 144.1 (ddd, J_{PC} = 16.5, 8.5, 1.8 Hz, C-7a/3a), 142.8 (dd, J_{PC} = 4.9, 1.1 Hz, Fl-C), 137.2 (d, J_{PC} = 4.6 Hz, Fl-C), 134.5 (d, $^{4}J_{PC}$ = 3.1 Hz, p-C(PPh_3)), 134.3 (dd, $^{2}J_{PC}$ = 10.5 Hz, $^{4}J_{PC}$ = 1.1 Hz, o-C(PPh_3)), 134.2 (d, $^{4}J_{PC}$ = 3.1 Hz, p-C(PPh_2)), 133.8 (d, $^{2}J_{PC}$ = 9.6 Hz, o-C(PPh_2)), 130.0 (d, $^{3}J_{PC}$ = 12.6 Hz, m-C(PPh_3)), 129.6 (d, $^{3}J_{PC}$ = 12.4 Hz, m-C(PPh_2)), 129.3 (d, J_{PC} = 2.5 Hz, Fl-C), 127.4 (d, J_{PC} = 2.7 Hz, Fl-C), 127.0 (dd, J_{PC} = 3.9 Hz, Fl-C), 122.7 (dd, $^{1}J_{PC}$ = 90.6 Hz, $^{3}J_{PC}$ = 3.1 Hz, i-C(PPh_3)), 121.4 (m, C-4−C-7), 121.3 (dd, $^{1}J_{PC}$ = 85.2 Hz, $^{3}J_{PC}$ = 2.6 Hz, i-C(PPh_2)), 120.6 (d, $^{3}J_{PC}$ = 1.3 Hz, Fl-C), 120.5 (s, C-4−C-7), 110.3 (ddd, $^{1}J_{PC}$ = 95.8, 54.8 Hz, $^{3}J_{PC}$ = 13.1 Hz, C-1/3), 108.0 (ddd, $^{1}J_{PC}$ = 87.9, 58.7 Hz, $^{3}J_{PC}$ = 15.7 Hz, C-1/3), 45.8 (dd, $^{1}J_{PC}$ = 49.4 Hz, $^{3}J_{PC}$ = 6.8 Hz, Fl-C). − **MS** ((+)-Xe-FAB, mNBA): m/z = 743 (100 %, $C_{51}H_{38}P_3^{+}$). −

1-Methylenediphenylphosphonio-3-triphenylphosphonio-benzo[c]-phospholide (2a). A solution of sodium trimethylsilyl amide (0.24 g, 1.31 mmol) in 15 ml of toluene was added via syringe to a cooled (−78 °C) and stirred suspension of **6a** (0.70 g, 1.18 mmol) in 40 ml of toluene. The mixture was allowed to warm to room-temperature, and stirring was continued for 24 hours. The precipitated solids were filtered off, and the crude product identified by means of NMR spectroscopy in the filtrate.

^{31}P NMR: δ = 229.0 (dd, $^{2}J_{PP}$ = 87.7, 82.0 Hz, P-2), 16.6 (dd, $^{2}J_{PP}$ = 82.0 Hz, $^{4}J_{PP}$ = 6.7 Hz, PPh_2), 13.7 (dd, $^{2}J_{PP}$ = 87.7 Hz, $^{4}J_{PP}$ = 6.7 Hz, PPh_3). − **^{1}H NMR** (C_6D_6): 7.94 (m, 4 H o-H(PPh_2)), 7.79 (m, 2 H, p-H(PPh_2)), 7.47−7.41 (m, 12 H, m/o-H(PPh_3)), 7.07 (m, 4 H, m-H(PPh_2)), 6.87 (m, 3 H, p-H(PPh_3)), 6.87−6.78 (m, 4 H, 4-H − 7-H), 0.81 (br d, 2 H, $^{2}J_{PH}$ = 7 Hz, PCH_2).

3-{(1-Cyanomethylene)-diphenyl-phosphonio}-1-triphenylphosphonio-benzo[c]phospholide (2c). A solution of sodium trimethylsilyl amide (0.14 g, 0.77 mmol) in 20 ml of toluene was added via syringe to a cooled (−78 °C) and stirred suspension of **6c** (0.50 g, 0.77 mmol) in 20 ml of toluene. The mixture was allowed to warm to room-temperature, and stirring was continued for 24 hours. The precipitated solids were filtered off and washed with 10 ml of THF. The filtrate was evaporated to dryness to give 0.43 g (91 %) of a brown solid of mp 156 °C (dec). −
Anal. for $C_{40}H_{30}P_3N_1$ (617.2): calcd. C 77.79 H 4.90 N 2.27 %; found C 76.46 H 5.20 N 2.36 %.

^{31}P{^{1}H} NMR: δ = 232.9 (dd, $^{2}J_{PP}$ =178.9, 89.5 Hz, P-2), 16.1 (dd, $^{2}J_{PP}$ = 178.9 Hz, $^{4}J_{PP}$ = 7.6 Hz, PPh_3), 14.6 (dd, $^{2}J_{PP}$ = 89.5 Hz, $^{4}J_{PP}$ = 7.6 Hz, PPh_2). − **^{1}H NMR** (THF-d_8): δ = 8.14−7.91 (m, 12 H, m/o-H(PPh_3)), 7.91−7.77 (m, 7 H, o-H(PPh_2)/p-H(PPh_3)), 7.76−7.61 (m, 6 H, m/p-H(PPh_2)), 7.61 (m, 1 H, 4-H − 7-H), 7.25 − 7.05 (m, 2 H, 4-H − 7-H), 7.00 (m, 1 H, 4-H − 7-H), 1.77 (dd, 1 H, $^{2}J_{PH}$ = 9.0 Hz, $^{4}J_{PH}$ = 0.8 Hz,, PCHCN). − **^{13}C{^{1}H} NMR** (THFd_8): δ = 145.9 (ddd, J_{PC} = 13.2, 8.4, 4.7 Hz, C-3a/7a), 145.4 (dd, J_{PC} = 14.7, 8.9 Hz, C-3a/7a), 135.1 (dd, $^{2}J_{PC}$ = 10.5 Hz, $^{4}J_{PC}$ = 1.6 Hz, o-C(PPh_3)), 134.4 (d, $^{4}J_{PC}$= 3.6 Hz, p-C(PPh_3)), 133.9 (dd, $^{1}J_{PC}$ = 89.4 Hz, $^{3}J_{PC}$ = 2.6 Hz, i-C(PPh_2)), 133.6 (dd, $^{2}J_{PC}$ = 10.0 Hz, $^{4}J_{PC}$ = 1.6 Hz, o-C(PPh_2)), 131.8 (d, $^{4}J_{PC}$ = 2.6 Hz, p-C(PPh_2)), 130.3 (d, $^{3}J_{PC}$ = 12.1 Hz, m-C(PPh_3)), 128.9 (d, $^{3}J_{PC}$ = 12.1 Hz, m-C(PPh_2)), 127.5 (ddd, $^{1}J_{PC}$ = 98.7, 52.9 Hz, $^{3}J_{PC}$ = 13.8 Hz, C-3); 127.0 (d, $^{2}J_{PC}$ = 8.0 Hz, CN), 125.3 (dd, $^{1}J_{PC}$ = 89.9 Hz, $^{3}J_{PC}$ = 2.6 Hz, i-C(PPh_3)), 123.2 (dd, J_{PC} = 4.5, 4.5 Hz, C-4−C-7), 121.2 (d, J_{PC} = 4.2 Hz, C-4−C-7), 120.8 (d, J_{PC} = 2.1 Hz, C-4−C-7), 120.4 (s, C-4−C-7), 102.3 (ddd, $^{1}J_{PC}$ = 97.9, 57.5 Hz, $^{3}J_{PC}$ = 14.2 Hz, C-1), 0.12(dd, $^{1}J_{PC}$ = 136.5 Hz, $^{3}J_{PC}$= 6.6 Hz, PCH). − **MS** ((+)-Xe-FAB, mNBA): m/z = 618 (100 %, $[M+H]^{+}$). −

3-(9-Fluorenylidene)-diphenylphosphonio-1-triphenylphosphonio-benzo[c]phospholide (2d). A solution of sodium trimethylsilyl amide (0.14 g, 0.77 mmol) in 20 ml of toluene was added via syringe to a stirred suspension of **6d** (0.60 g, 0.73 mmol) in 20 ml of toluene. The mixture was gently warmed to 80 °C, and stirring was continued until a white-brown precipitate separated and the solution become yellow. The precipitate was filtered off and washed with toluene. The combined yellow filtrates were refluxed for 12 h, allowed to cool to room temperature, and filtered again. The filtrate was concentrated in vacuum and crystallised at −22 °C. The precipitated yellow crystals were collected by filtration, washed with 20ml of cold n-hexane, and dried in vacuum to give 0.34 g (63 %) of 4d of mp 217 °C (dec). −
Anal. for $C_{51}H_{37}P_3$ (743.0): calcd. C 82.47 H 5.02 %, found C 80.18 H 5.56 %.

^{31}P{^{1}H} NMR: δ = 233.2 (dd, $^{2}J_{PP}$ = 88.5, 87.7 Hz, P-2), 16.3 (dd, $^{2}J_{PP}$ = 88.5 Hz, $^{4}J_{PP}$ = 8.0 Hz, PPh_3), 0.8 (dd, $^{2}J_{PP}$ = 88.5 Hz, $^{4}J_{PP}$ = 8.0 Hz, PPh_2). − **^{1}H NMR** (CD_2Cl_2): δ = 8.06 (m, 2 H, Fl-H), 7.77 (m, 4 H, o-H(PPh_2)), 7.61 (m, 3 H, p-H(PPh_3)), 7.58 (m, 6 H, o-H(PPh_3)), 7.46 (m, 6 H, m-H(PPh_3)), 7.42 (m, 2 H, p-H(PPh_2)), 7.31 (m, 4 H, m-H(PPh_2)), 7.22 (m, 1 H, 4/7-H), 6.94 (m, 1 H, 4/7-H), 6.85 (m, 2 H, Fl-H), 6.76 − 6.74 (m, 3 H, 5/6-H + Fl-H), 6.70 (m, 1 H, 5/6-H), 6.47 (m, 2 H, Fl-H). − **^{13}C{^{1}H} NMR** (CD_2Cl_2): δ = 146.0 (ddd, J_{PC} = 16.8, 8.7, 4.4 Hz, C-3a/7a), 144.8 (dd, $^{2}J_{PC}$ = 14.8, 9.1 Hz, C-3a/7a), 141.9 (d, J_{PC} = 15.1 Hz, Fl-C), 134.7 (dd, $^{2}J_{PC}$ = 10.3 Hz, $^{4}J_{PC}$ = 2.1 Hz, o-C(PPh_2)), 134.0 (d, $^{4}J_{PC}$ = 2.9 Hz, p-C(PPh_3)), 133.4 (dd, $^{2}J_{PC}$ = 10.3 Hz, $^{4}J_{PC}$ = 1.3 Hz, o-C(PPh_3)), 131.9 (d, $^{4}J_{PC}$ = 2.9 Hz, p-C(PPh_2)), 130.1 (d, J_{PC} = 13.8 Hz, Fl-C), 130.0 (dd, $^{1}J_{PC}$ = 89.0 Hz, $^{3}J_{PC}$ = 3.0 Hz, i-C(PPh_2)), 129.8 (d, $^{3}J_{PC}$ = 12.4 Hz, m-C(PPh_3)), 128.8 (d, $^{3}J_{PC}$ = 12.0 Hz, m-C(PPh_2)), 124.1 (dd, $^{1}J_{PC}$ = 90.1 Hz, $^{3}J_{PC}$ = 2.5 Hz, i-C(PPh_3)), 123.3 (ddd, $^{1}J_{PC}$ = 93.9, 52.6 Hz, $^{3}J_{PC}$ = 13.8 Hz, C-3), 122.5 (s, Fl-C), 122.4 (m, C-4/7), 120.7 (d, J_{PC} = 1.9 Hz, C-5/6), 120.4 (s, C-5/6), 119.5 (dd, J_{PC} = 5.2, 1.3 Hz, C-4/7), 119.3 (d, J_{PC} = 1.3 Hz, Fl-C), 117.3 (s, Fl-C), 115.1 (s, Fl-C), 102.9 (ddd, $^{1}J_{PC}$ = 97.4, 56.6 Hz, $^{3}J_{PC}$ = 13.6 Hz, C-1), 59.6 (dd, $^{1}J_{PC}$ = 126.8 Hz, $^{3}J_{PC}$ = 3.5 Hz, C-9(Fl)). − **MS** ((+)-Xe-FAB, mNBA): m/z = 743 (100 %, M^{+}). −

Reaction of 2a with Chlorodiphenylphosphine

Chlorodiphenylphosphine (0.22 g, 1.05 mmol) dissolved in 15 ml of toluene was added to a solution of **2a** (0.50 g, 0.85 mmol) in 20 ml of toluene and the reaction mixture was stirredfor 24 h at room temperature. The white precipitate formed was filtered off and washed with 10 ml of cold toluene. A sample of the product was dissolved in CH_2Cl_2 and shown by ^{31}P{^{1}H} and ^{1}H,^{31}P HMQC NMR spectroscopy to consist of a mixture of the phosphonium salts **6a** and **6e**, respectively. The product mixture was then again suspended in 30 ml of toluene, 0.20 g (1.1 mmol) of $NaN(SiMe_3)_2$ dissolved in 10 ml of toluene were added, and the mixture was stirred for 48 hours. The brown precipitate formed was filtered off, washed with 10 ml of cold toluene, and dried in vacuum. The ylide **2e** was identified in the crude product by ^{31}P NMR and mass spectroscopy. −

6e: **^{31}P{^{1}H} NMR**: δ = 237.8 (ddd, $^{2}J_{PP}$ = 92.5, 82.0 Hz, $^{4}J_{PP}$ = 41.9 Hz, P-2), 17.2 (dd, $^{2}J_{PP}$ = 92.5 Hz, $^{4}J_{PP}$ =7.6 Hz, PPh_3), 16.1 (ddd, $^{2}J_{PP}$ = 82.0, 69.6 Hz, $^{4}J_{PP}$ = 7.6 Hz, PPh_2), -26.6 (dd, $^{2}J_{PP}$ = 69.6 Hz, $^{4}J_{PP}$ = 41.9 Hz, P(Phosphanyl)). −

2e: **^{31}P{^{1}H}NMR**: δ = 237.8 (ddd, $^{2}J_{PP}$ = 90.1, 81.5 Hz, $^{4}J_{PP}$ = 10.0 Hz, P-2), 21.0 (dd, $^{2}J_{PP}$ = 90.1 Hz, $^{4}J_{PP}$ = 8.6 Hz, PPh_3), 20.9 (ddd, $^{2}J_{PP}$ = 81.5, 151.6 Hz, $^{4}J_{PP}$ = 8.6 Hz, PPh_2), −11.5 (dd, $^{2}J_{PP}$ = 151.6 Hz, $^{4}J_{PP}$ = 10.0 Hz, P(Phosphanyl)); MS: ((+)-Xe-FAB, mNBA): m/z(%) = 777 (100 %, $(M+H)^{+}$).

Reaction of 2c with [$PdCl_2$(COD)]

To a toluene solution (20 ml) of **2c** (0.50 g, 0.81 mmol) was added [$PdCl_2$(cod)] (0.23 g, 0.84 mmol). The resulting solution was stirred for 3 d at room temperature. Reaction control by ^{31}P NMR allowed to monitor the formation of the complex **7** and the hydrolysis products **9a,b**. The formation of the latter was complete after 3 d. The mixture was then layered with 10 ml of hexane and stored until a light yellow precipitate formed. This product was collected by filtration, washed with 20 ml of hexane, and dried in vacuum to give 0.58 g (yield 88 %) ofa mixture of the diastereomers **9a,b**.

7: **^{31}P{^{1}H} NMR**: $\delta = 191.9$ (dd, $^{2}J_{PP} = 110.6$, 55.9 Hz), 23.3 (dd, $^{2}J_{PP} = 55.9$ Hz, $^{4}J_{PP} = 4.5$ Hz, PPh_3), 14.7 (dd, $^{2}J_{PP} = 110.6$ Hz, $^{4}J_{PP} = 4.5$ Hz, PPh_2). − **^{1}H NMR** (CD_2Cl_2): $\delta = 8.11$-7.60 (m, 25H, Ph), 7.7 (m, 1H, 4-H − 7-H), 7.34-6.94 (m, 3H, 4-H − 7-H), 4.21 (m, 1H, CHCN). −

9a,b: isomer 1: ^{31}P{^{1}H} NMR: $\delta = 91.8$ (dd, $^{2}J_{PP} = 16.5$ Hz, 42.0 Hz, P-2), 40.6 (dd, $^{2}J_{PP} = 42.0$ Hz, $^{4}J_{PP} = 2.5$ Hz, PPh_2), 23.8 (dd, $^{2}J_{PP} = 16.5$ Hz, $^{4}J_{PP} = 2.5$ Hz, PPh_3); − **^{1}H NMR** (CD_2Cl_2): $\delta = 7.93$-7.74 (m, 12H o,m-H(PPh_3)), 7.81-7.68 (m, 10H, H(PPh_2)), 7.68-7.56 (m, 3H, p-H(PPh_3)), 7.01-7.15 (m, 3H, 4-H − 7-H), 6.91 (m, 1H, 4-H − 7-H), 6.29 (m, 1H, 1-H), 3.62 (m, 1H, CHCN), 3.04 (m, 1H, 3-H); **isomer 2**: **^{31}P{^{1}H} NMR**: $\delta = 86.2$ (dd, $^{2}J_{PP} = 18.4$, 42.6 Hz, P-2), 36.2 (dd, $^{2}J_{PP} = 42.6$ Hz, $^{4}J_{PP} = 2.5$ Hz, PPh_2), 23.0 (dd, $^{2}J_{PP} = 18.4$ Hz, $^{4}J_{PP} = 2.5$ Hz, PPh_3); − **^{1}H NMR** (CD_2Cl_2): $\delta =$ 8.04-7.92 (m, 4H, o-H(PPh_2)), 7.93-7.68 (m, 18H, m,p-H(PPh_3/PPh_2)), 7.68-7.56 (m, 3H, p-H(PPh_3)), 7.15-7.01 (m, 3H, 4-H − 7-H), 6.91 (m, 1H, 4-H − 7-H), 6.68 (m, 1H, 1-H), 3.40 (m, 1H, CHCN), 3.14 (m, 1H, 3-H); − **MS**: ((+)-Xe-FAB, mNBA): m/z(%) = 776 (64 %, $M^{+}-Cl$).

Reaction of 2c with [$PtCl_2$(COD)]

The reaction of **2c** (0.50 g, 0.81 mmol) and [$PtCl_2$(cod)] (0.31 g, 0.83 mmol) was carried out as described above. Stirring the solution for 12 h produced a small amount of a crystalline light yellow precipitate which was collected and identified as the hydrolysis product **10a** by single-crystal X-ray diffraction. Reaction control by ^{31}P NMR allowed to monitor the formation of the complex **8** and the hydrolysis products **10a,b**. Prolonged stirring resulted in the formation of a larger amount of a colorless precipitate that was insoluble in polar and unpolar organic solvents and water and was not further characterized.

8: **^{31}P{^{1}H} NMR**: $\delta = 184.7$ (dd, $^{2}J_{PP} = 50.2$, 101.1 Hz, $^{1}J_{PtP} = 4658$ Hz, P-2), 23.3 (dd, $^{2}J_{PP} = 101.1$ Hz, $^{4}J_{PP} = 3.8$ Hz, PPh_2), 14.9 (dd, $^{2}J_{PP} = 50.2$ Hz, $^{4}J_{PP} = 3.8$ Hz, PPh_3). −

10a,b: **isomer 1**: **^{31}P{^{1}H} NMR**: $\delta = 60.7$ (dd, $^{2}J_{PP} = 34.9$, 12.1 Hz, $^{1}J_{PtP} = 3616$ Hz, P-2), 41.8 (dd, $^{2}J_{PP} = 34.9$ Hz, $^{4}J_{PP} = 6.4$ Hz, PPh_2), 23.4 (dd, $^{2}J_{PP} = 12.1$ Hz, $^{4}J_{PP} = 6.4$ Hz, PPh_3); **isomer 2**: **^{31}P{^{1}H} NMR**: $\delta = 55.2$ (dd, $^{2}J_{PP} = 36.2$, 13.4 Hz, $^{1}J_{PtP} = 2118$ Hz, P-2), 39.5 (dd, $^{2}J_{PP} = 36.2$ Hz, $^{4}J_{PP} = 6.7$ Hz, PPh_2), 22.6 (dd, $^{2}J_{PP} = 13.4$ Hz, $^{4}J_{PP} = 6.7$ Hz, PPh_3).

[Tetracarbonyl-κ^{2}-*P,C*-{1-Triphenylphosphonio-3-Fluorenylidenediphenylphosphonio-benzo[c]phospholide}tungsten(0)] (12). A solution of [$W(CO)_4$(nbd)] (0.50 g, 1.35 mmol) and **2d** (1.00 g, 1.35 mmol) in 40 ml of THF was stirred for 72 h at room temperature and then layered with 10 ml of hexane. The brown precipitate formed after diffusion of the solvents was collected by filtration, washed with 20 ml of hexane, and dried in vacuum. Recrystallization from CH_2Cl_2 gave 1.00 g (yield 72 %) of **12**, m.p. 228 °C (dec.). −

^{31}P{^{1}H} NMR: $\delta = 238.3$ (dd, $^{2}J_{PP} = 103.8$, 63.7 Hz, $^{1}J_{WP} = 243.6$ Hz, P-2), 21.7 (dd, $^{2}J_{PP} = 63.7$ Hz, $^{4}J_{PP} = 6.1$ Hz, PPh_3), 15.1 (dd, $^{2}J_{PP} = 103.8$ Hz, $^{4}J_{PP} = 6.1$ Hz, $^{2}J_{WP} = 5.7$ Hz, PPh_2). **^{183}W NMR**: $\delta = 2541$ ($^{1}J_{WP} = 240$ Hz). − **^{1}H NMR** (CD_2Cl_2): $\delta = 7.92$ (m, 6 H, o-H(PPh_3)), 7.77 (m, 2 H, Fl-H), 7.54 (m, 6 H, m-H(PPh_3)), 7.62 (m, 3 H, p-H(PPh_3)), 7.29 (m, 2 H, p-H(PPh_2)), 7.16 (m, 4 H, o-H(PPh_2)), 7.11 (m, 4 H, m-H(PPh_2)), 6.92 (m, 2 H, 4-H − 7-H), 6.88 (m, 2 H, Fl-H), 6.80 (m, 1 H, 4-H − 7-H), 6.77 (m, 4 H, Fl-H), 6.75−6.64 (m, 2 H, 4-H − 7-H). − ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 210.2$ (dd, $^{2}J_{PC} = 43.1$ Hz, $^{3}J_{PC} = 0.7$ Hz, CO), 207.2 (dd, $^{2}J_{PC} = 5.5$ Hz, $^{3}J_{PC} = 0.9$ Hz, CO), 204.7 (d, CO, $^{2}J_{PC} = 10.1$ Hz), 154.9 (dd, $^{2}J_{PC} = 2.9$ Hz, $^{4}J_{PC} = 1.3$ Hz, Fl-C), 145.8 (ddd, $J_{PC} = 14.4$, 8.6, 3.8 Hz, C-3a/7a), 143.1 (ddd, $J_{PC} = 14.9$, 6.8, 2.4 Hz, C-3a/7a), 135.0 (d, $^{3}J_{PC} = 8.2$ Hz, Fl-C), 134.6 (d, $^{2}J_{PC} = 10.1$ Hz, o-C(PPh_3)), 134.1 (d, $^{4}J_{PC} = 3.1$ Hz, p-C(PPh_3)), 133.8 (d, $^{2}J_{PC} = 8.8$ Hz, o-C(PPh_2)), 132.2 (d, $^{4}J_{PC} = 2.9$ Hz, p-C(PPh_2)), 130.1 (d, $^{3}J_{PC} = 12.6$ Hz, m-C(PPh_3)), 128.6 (d, $^{3}J_{PC} = 11.7$ Hz, m-C(PPh_2)), 127.5 (ddd, $^{1}J_{PC} = 98.3$, 59.3 Hz, $^{3}J_{PC} = 11.2$ Hz, C-3), 126.4 (dd, $^{1}J_{PC} = 79.5$ Hz, $^{3}J_{PC} = 5.2$ Hz, i-C(PPh_2)), 125.0 (dd, $J_{PC} = 2.6$ Hz, 1.4 Hz, Fl-C), 124.7 (d, $J_{PC} = 2.3$ Hz, Fl-C), 122.5 (dd, $^{1}J_{PC} = 90.8$ Hz, $^{3}J_{PC} = 2.5$ Hz, i-C(PPh_3)), 121.7 (d, $J_{PC} = 2.7$ Hz, Fl-C), 120.9 (m, C-5/6), 120.5 (d, $J_{PC} = 8.4$ Hz, C-5/6), 120.0 (d, $J_{PC} = 1.1$ Hz, C-4/7), 119.8 (s, Fl-C), 119.5 (ddd, $J_{PC} = 6.40$, 3.3, 0.7 Hz, C-4/7), 96.6 (ddd, $^{1}J_{PC} = 103.7$, 56.6 Hz, $^{3}J_{PC} = 9.1$ Hz, C-1), 43.6 (dd, $^{1}J_{PC} = 42.3$ Hz, $^{3}J_{PC} = 2.6$ Hz, Fl-C9), **IR**: (CH_2Cl_2, NaCl): ν(CO) 2003, 1901, 1882, 1839 cm^{-1}. − **MS** ((+)-Xe-FAB, mNBA): m/z = 1038 (18 %, M^{+}), 1011 (22 %, $M^{+} - CO$), 982 (100 %, $M^{+} - 2\,CO$).

Crystal structure determinations:

10a: colorless crystals, $C_{40}H_{32}Cl_2NOP_3Pt - 3\,C_4H_8O$, $M = 1117.9$, crystal size 0.15 x 0.10 x 0.05 mm, rhombohedral, space group R$\bar{3}$ (No. 148): $a = 20.8201(3)$ Å, $\alpha = 107.773(1)°$, $V = 7351.9(2)$ Å^{3}, $Z = 6$, ρ(calcd) = 1.515 Mg m^{-3}, $F(000) = 3384$, $\mu = 3.11$ mm^{-1}, 70566 reflexes ($2\,\theta_{max} = 50.0°$) measured on a Nonius Kappa-CCD diffractometer at 123(2) K using MoK_{α} radiation ($\lambda = 0.71073$ Å), 8631 unique [$R_{int} = 0.105$] used for structure solution (Direct Methods, SHELXS-97 [12]) and refinement (full-matrix least-squares on F^2, SHELXL-97 [12]) with 524 parameters and 96 restraints, empirical absorption correction from multiple reflections, H-atoms with a riding model, $R1$ ($I > 2\sigma(I)$) = 0.046, $wR2 = 0.125$, largest diff. peak and hole 1.316 and −0.788 e Å^{-3}.

12: colorless crystals, $C_{55}H_{37}O_4P_3W$, $M = 1038.6$, monoclinic, space group Cc (No. 9): $a = 23.0640(3)$ Å, $b = 10.5804(1)$ Å, $c = 20.5278(2)$ Å, $\beta = 118.861(1)°$, $V = 4387.13(8)$ Å^{3}, $Z = 4$, ρ(calcd) = 1.572 Mg m^{-3}, $F(000) = 2072$, $\mu = 2.79$ mm^{-1}, Flack x = −0.0167(43), 55573 reflexes ($2\,\theta_{max} = 54.9°$) measured on a Nonius Kappa-CCD diffractometer at 100(2) K using MoK_{α} radiation ($\lambda = 0.71073$ Å), 9859 unique [$R_{int} = 0.095$] used for structure solution (Direct Methods, SHELXS-97 [12]) and refinement (full-matrix least-squares on F^2, SHELXL-97 [12]) with 569 parameters and 2 restraints, numerical absorption correction [13], H-atoms with a riding model, $R1$ ($F_0 > 4\sigma(F_0)$) = 0.030, $wR2 = 0.071$, largest diff. peak and hole 1.348 and −1.191 e Å^{-3}.

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-239656 (**11a**) and CCDC-240286 (**13**). 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+(1223)336-033; e-mail:teched@chemcrys.cam.ac.uk).

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