The Synthesis of New Phosphonium Cyclopentadienylides and Fluorenylides and Several Derived Metal Complexes

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In a search for ambidentate chelating phosphane/ylide ligands two [(diphenylphosphino)alkyl]-diphenylphosphonium fluorenylides **2a,b** and 1,3-propanediylbis(diphenylphosphonium fluorenylide) (**5**) were synthesized from α,ω-bis(diphenylphosphino)alkanes $(C_6H_5)_2P[CH_2]_nP(C_6H_5)_2$, n = 1 – 3, and 9-bromofluorene, via the parent phosphonium salts. [2-(Diphenylphosphino)-ethyl]diphenylphosphonium cyclopentadienylide (**1b**) could only be obtained in low yield. – Ylide **2a** forms tetracarbonylmetal complexes with $(CO)_3W(NCCH_3)_3$ and $Cr(CO)_6$, which are assigned a chelating five-membered ring structure, the cyclopentadienyl ring being in an unusual monohapto state of bonding (**6a,b**). A by-product of the $Cr(CO)_6$ reaction is identified as the $Cr(CO)_3$ complex **7** with the metal attached to one benzene ring of the fluorene system. 1 : 1 complexes of $PdCl_2$ and $PtCl_2$ with **2a** are again assigned a chelate monohapto-fluorene mode of complexation (**10a,b**), but with **2b** an ionic product **13** is encountered. $HgCl_2$ forms 2 : 1 and 3 : 2 complexes with **2a**, for which only tentative formulae can be proposed (e. g. **14**). AuCl forms an ionic 1 : 1 complex **15** with the bis-fluorenylide **5**.

Synthese neuer Phosphonium-cyclopentadienylide und -fluorenylide und davon abgeleiteter Metallkomplexe

Im Rahmen einer Suche nach ambidenten, chelatisierenden Phosphan/Ylid-Liganden wurden die beiden [(Diphenylphosphino)alkyl]diphenylphosphonium-fluorenylide **2a,b** und 1,3-Propandiyl-bis(diphenylphosphonium-fluorenylid) (**5**) aus α,ω-Bis(diphenylphosphino)alkanen $(C_6H_5)_2$-$P[CH_2]_nP(C_6H_5)_2$, n = 1 – 3, und 9-Bromfluoren auf dem Weg über die korrespondierenden Phosphoniumsalze hergestellt. [(2-Diphenylphosphino)ethyl]diphenylphosphonium-cyclopenta-dienylid (**1b**) konnte nur in geringen Ausbeuten erhalten werden. – Ylid **2a** bildet mit $(CO)_3$-$W(NCCH_3)_3$ oder $Cr(CO)_6$ die Tetracarbonylmetall-Komplexe **6a,b**, denen eine Chelatstruktur mit fünfgliedrigem Ring zugeschrieben wird, in der der Cyclopentadienylring in der seltenen Mo-nohaptoform auftritt. Ein Nebenprodukt der $Cr(CO)_6$-Reaktion wurde als $Cr(CO)_3$-Komplex identifiziert, in dem das Metall an einen Benzolring des Fluorens koordiniert ist (**7**). Den 1 : 1-Komplexen von **2a** mit $PdCl_2$ und $PtCl_2$ wird ebenfalls eine Struktur mit Monohaptofluoren-Che-latring zugeordnet (**10a, b**); mit **2b** wird aber ein ionischer Pd-Komplex gefunden (**13**). $HgCl_2$ bil-det mit **2a** sowohl einen 2 : 1- als auch einen 3 : 2-Komplex, nur für den ersteren kann jedoch eine vorläufige Formel angegeben werden (z. B. **14**). Das Doppel-Ylid **5** ergibt mit AuCl eine ionische 1 : 1-Verbindung **15**.

The formation of phosphonium and sulfonium cyclopentadienylide metal complexes is a relatively new area and one of considerable activity[1–5]. One of the particularly interesting features of this chemistry is the rich variety of bonding exhibited by the

cyclopentadienylide group: Metal complexes in which cyclopentadienyl formally serves as a 2-electron-[1], 3-electron-[2], 4-electron-[3], and 5-electron-donor are reported[4]. This variety of bonding suggested to us that it would be interesting to introduce another potential donor site into the ylide molecule, thereby transforming it into a chelating ligand. Through this additional functionality it might be possible to form metal complexes in which the bonding exhibited by the cyclopentadienyl moiety varied, for example, as a function of the chain length bridging the two binding sites. For this additional ligand we have chosen the phosphane group.
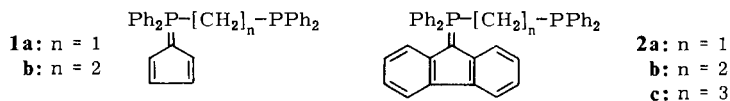

Our efforts have been directed towards the preparation of several new phosphonium cyclopentadienylides and fluorenylides in which the length of the alkyl chain linking the two functional groups was varied, and to the synthesis of a few exploratory metal derivatives of these ylides.

I. Synthesis of Phosphonium Cyclopentadienylides and Fluorenylides

Phosphonium cyclopentadienylides are generally prepared by the method of *Ramirez*[5] which involves bromination of cyclopentadiene at low temperature, treatment with a nucleophile such as triphenylphosphane, resulting in a bis-phosphonium salt, and generation of the ylide with base.
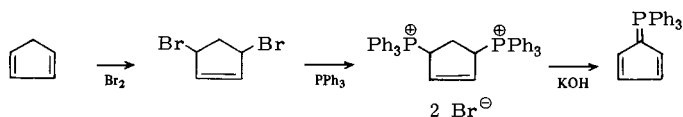
This approach was attempted for the synthesis of the bifunctional ylides. After bromination of cyclopentadiene, addition of bis(diphenylphosphino)methane, and treatment with aqueous potassium hydroxide, a red oil was isolated, which, from ^{13}C- and ^{1}H NMR spectra, clearly contained the desired **1a**, albeit in low yield. The spectra suggested, however, that the major product was most likely the tautomer of the desired compound.
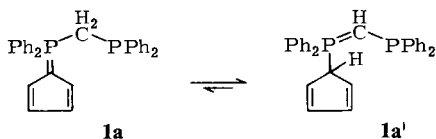

This red oil was unstable at room temperature and gradually polymerized, probably by a Diels-Alder process. Because of the instability of this mixture, the synthesis of the methylene-bridged ligand was not continued. Instead, assuming the methylene hydrogens on the ethyl-bridged analog would be less acidic, we turned our attentions to

the synthesis of **1b**, again employing the *Ramirez* approach. In this case our efforts were successful, and the compound has been fully characterized. The yield, however, was a disappointing 14%. A thorough investigation into the causes of the low yield was not made, but two sources of difficulty are known. In the step in which the phosphonium salt is treated with aqueous hydroxide, it is important that the temperature be maintained under 10°C, or the major product becomes the half-phosphane oxide of 1,2-bis(diphenylphosphino)ethane. Another difficulty is intermolecular bis-phosphonium salt formation (see below).

To hopefully avoid the problems inherent in the unsubstitued cyclopentadienyl system we turned our attentions to the synthesis of the corresponding fluorenyl analogues.

Synthesis of the fluorenyl ylide with the methylene bridge, **2a**, proceeds in overall 95% yield[6]. We wish to report here the successful synthesis of the ethylene-bridged ylide (**2b**). The best procedure was to warm for a short time an excess of 1,2-bis(diphenylphosphino)ethane with 9-bromofluorene in dimethylformamide to obtain first the phosphonium salt **3b** in 73% yield. Quantitative conversion of this salt to the ylide was accomplished by addition of an equimolar amount of $Ph_3P=CH_2$ in almost quantitative yield. Hydroxide should not be used both to avoid formation of phosphane oxides and to prevent trapping of water in the product which could subsequently interfere in reactions with metal complexes. The ylide is air-stable, and fairly soluble in toluene and tetrahydrofuran.
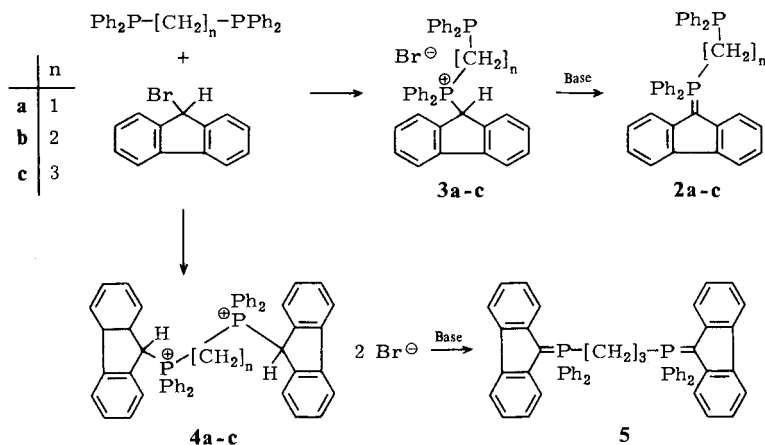
The salt **3b** was not the only product obtained. Also formed is the bis-salt **4b**. With an excess of the bisphosphane and a short reaction time in dimethylformamide, the bis-salt amounted to only 20% of the reaction products. In refluxing toluene, however, and after long reaction times, **4b** becomes the major product. It is to be noted that formation of the bis-salt was not observed when the starting phosphane was bis(diphenylphosphino)*methane*. Formation of the bis-salt **4a** was achieved but required severe conditions. Partial explanation for the greater favorability of the bis-salt **4b** with the ethylene bridge lies in electronic effects. Formation of the mono-salt creates an

electron-withdrawing phosphonium center, which reduces the nucleophilicity of the remaining phosphane. The reduction in nucleophilicity of the second phosphane should decrease as the length of the chain increases.
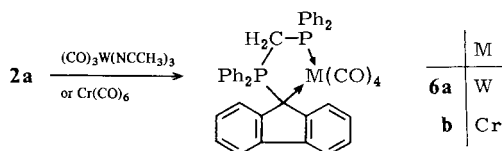
Treating the bis-salt **4b** with base does not lead to a bis-ylide. Rather, a yellow precipitate, highly insoluble in several solvents, was obtained. Apparently deprotonation occurred at the bridge instead of at both 9-positions of fluorene, generating, through elimination, a vinylphosphane, which then polymerized. Bridge deprotonation is consistent with the behavior of the bis-salt of the methylene analog (**4a**), which deprotonates at one 9-position and at the methylene bridge[6].

Treatment of 9-bromofluorene with 1,3-bis(diphenylphosphino)propane leads to an even greater percentage of the bis-salt, **4c**. A variety of solvents, stoichiometries, temperatures, and reaction times have been explored in an attempt to increase the percentage of the mono-salt, evident by the AB pattern in the ^{31}P NMR spectrum of the product, but in every case it remained the minor product. Isolation of the pure mono-salt **3c** from the mixture has not been accomplished. Efforts to isolate it by fractional crystallization or chromatography have failed. The bis-salt **4c**, however, has been isolated. Double-deprotonation of **4c** leads to the bis-ylide **5** in essentially quantitative yield. Ylide **5** is air-stable, and remarkably soluble in both THF and toluene.

II. Synthesis of Complexes from Fluorenyl Ylides

The synthesis of metal complexes from the new ylides was probed in order to determine their characteristics as ligands. We have initially studied reactions with metal carbonyls because the most substantial literature is on metal carbonyl complexes with cyclopentadiene, cyclopentadienyl, fluorene, and fluorenyl ligands, thereby making it possible to assess the characteristics of the novel chelating ylides.

The reaction of the ylide **2a** with $W(CO)_3(CH_3CN)_3$ is complete in a few hours at room temperature in THF. This ylide is considerably more reactive than $CpPPh_3$, which, with the same metal carbonyl, requires reflux for 1 hour at $160\,^\circ C$[7a] (Cp = C_5H_4).

$$
\mathbf{2a} \xrightarrow[\text{or } Cr(CO)_6]{(CO)_3W(NCCH_3)_3}
$$

$$
\begin{array}{c|c}
 & M \\
\hline
\mathbf{6a} & W \\
\mathbf{b} & Cr \\
\end{array}
$$

The product, **6a**, is a tetracarbonyl complex, clearly indicated by the infrared spectrum, which shows four bands very similar to those of $(Phen)W(CO)_4$[7b]. The ^{31}P NMR spectrum reveals a significant downfield shift for both phosphorus atoms, an observation consistent with bonding at both the phosphane and ylidic functions[8]. The mass spectrum fragmentation pattern of **6a** has no peaks above $M^+ - 2\,CO$. The major fragmentation modes proceed through stepwise loss of CO or through cleavage of the fluorenyl $C(9) - P$ bond to form [bis(diphenylphosphino)methane]tungsten carbonyls.

Complex **6a** appears to be the first example of a cyclopentadienyl tungsten carbonyl derivative in which the Cp is monohapto. The most obvious explanation for this

unusual bonding pattern is that the chain of the pendant phosphane ligand is not long enough to permit the tungsten to move to a center position over the ring[9].

The results of the reaction between **2a** and $Cr(CO)_6$ are somewhat different than those obtained with the tungsten carbonyl. Refluxing the ylide and $Cr(CO)_6$ in dibutyl ether, followed by chromatography, resulted in two products. One of these has an IR spectrum virtually identical with that of **6a** except that the bands were shifted a few wavenumbers to lower energy. Both phosphorus resonances are again shifted downfield in the ^{31}P NMR spectrum. These observations are consistent with structure **6b**. Furthermore, the mass spectrum displays a peak at 712, corresponding to that of the molecular ion. The fragmentation proceeds by loss of CO, M – CO: $m/e = 684$ (92), and then loss of $Cr(CO)_3$ to leave the ylide $m/e = 548$ (100).

The second product proved to be a tricarbonyl derivative. The IR spectrum has three carbonyl bands. Particularly interesting was the ^{31}P NMR spectrum, in which neither phosphorus resonance was significantly downfield-shifted. From the ^{31}P NMR data it is concluded that the metal cannot be coordinated over the 5-membered fluorenyl ring. They are consistent, however, with bonding over one of the fluorenyl benzene rings. Structure **7** is supported further by the mass spectrum in that the major fragmentation mode proceeds through cleavage of the bisphosphane to yield carbonyl(fluorene)-chromium species. The mass spectrum is inconsistent with the bonding of the metal to one of the phenyl rings at phosphorus.
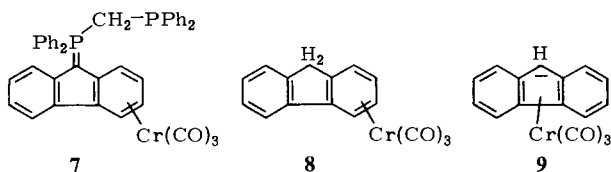

The position of the metal in the ylide complex is like that in the fluorene derivative **8**, which, of course, lacks an "aromatic" central ring[10]. But it is well-established that when **8** is deprotonated at the 9-position, the metal carbonyl migrates to an h^5-position (**9**)[11].

The reaction of **2a** with $(Ph_3P)_2PdCl_2$ is particularly interesting because there are three conceivable reaction courses. The ligand could serve simply as a phosphane, with the ylide function not coordinating to the metal. A second possibility is that both the phosphane and ylidic centers could coordinate. Finally, palladium could insert into a C – H bond, the most likely position being the C-1 position of fluorene[12]. Stirring the ylide **2a** in THF at room temperature with an equimolar amount of $(Ph_3P)_2PdCl_2$ produces a light-yellow precipitate within a few minutes. This product is air-stable, insoluble in non-polar solvents, and has but modest solubility in polar solvents such as dimethylformamide or dimethylsulfoxide.

The elemental analysis was inconsistent with products expected from C – H bond insertion, but consistent with either formula **10** or **11**. Structure **11** is excluded for two reasons. For **11** three Pd – Cl bands should be present in the IR spectrum, independent whether the structure is *cis* or *trans*[13]. Only two Pd – Cl bands are present. Little shift of the signal of the phosphonium phosphorus would be expected in the ^{31}P NMR

spectrum. In reality the downfield shift is 44.9 ppm, even greater than that observed for the phosphonium phosphorus in **12**, as compared to the uncomplexed ylide[14].
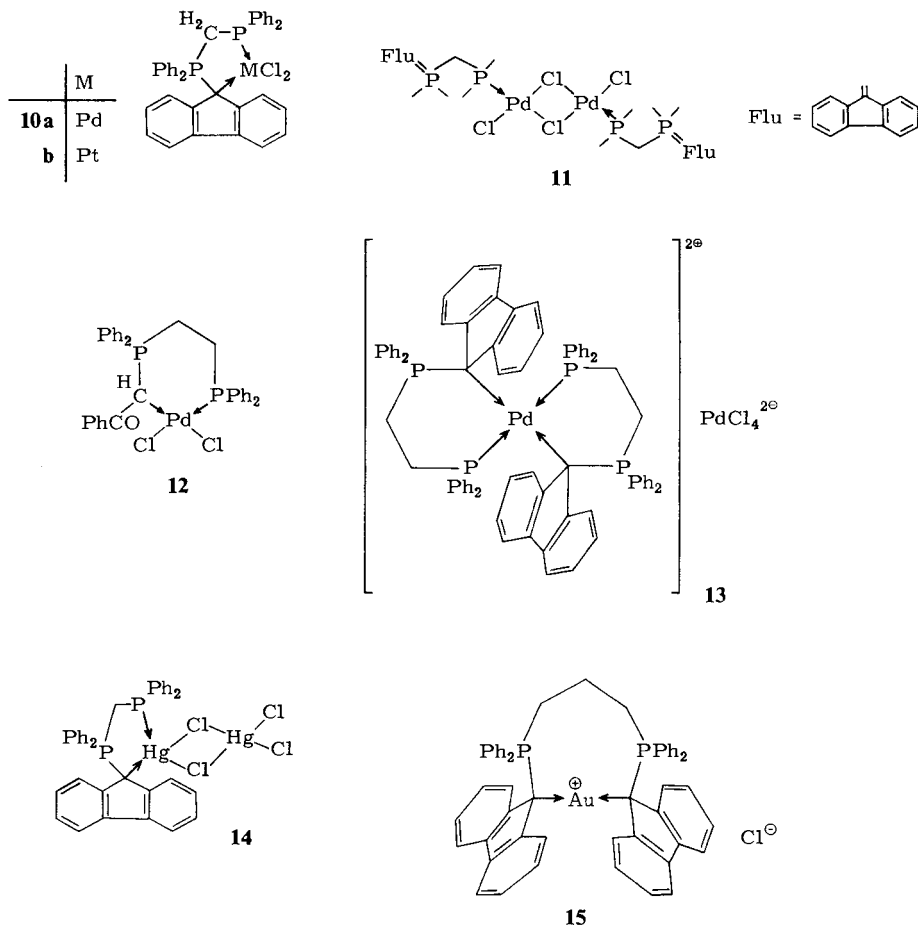
The IR spectrum, with broad bands at 368 and 292 cm^{-1}, is typical for *cis*-PdCl$_2$ units. The ^{31}P NMR shifts, similar to those observed in the metal carbonyl derivatives, are also consistent with **10a**.

Since platinum inserts in C – H bonds more readily than does palladium, we were curious to determine whether the course of the reaction was metal-dependent. Refluxing **2a** with PtCl$_2$ in THF, however, led to **10b**. Heating **10b** in dimethylformamide at 110°C for 15 hours did not cause C – H bond insertion either, and **10b** was recovered.

In the reaction of (Ph$_3$P)$_2$PdCl$_2$ with the fluorene ylide having an ethylene bridge (**2b**), the effects of the longer bridge were immediately apparent. The IR spectrum showed only one Pd – Cl absorption and the red complex, highly soluble in THF, had a ^{31}P NMR spectrum showing a pair of triplets. "Magnus" structure **13** is therefore

proposed. The single Pd – Cl absorption is at 352 cm^{-1} and is virtually at the same value as that observed for K_2PdCl_4. Note: For **13** an AA'BB' ^{31}P-spin system would be anticipated.

Because of our fairly long interest in mercury complexes[15] and in mercury toxicology[16], the reaction of **2a** with HgCl$_2$ was also investigated. In THF, with a 2:1 stoichiometric ratio of HgCl$_2$ to ylide, two derivatives were obtained. One of these precipitated during the reaction, the other upon addition of pentane. Both complexes were air-stable. Elemental analysis revealed that the ylide : HgCl$_2$ relationship was 1:1.5 for the THF-insoluble product, and 1:2.0 for the soluble product **(14)**. We have not been able to determine the structures of these complexes with certainty. In the 1:2.0 complex it is clear from the large downfield shifts of both phosphorus atoms in the ylide that mercury is coordinated at both the phosphane and ylidic functions. The compound has very low conductivity and is clearly non-ionic. According to cryoscopic molecular weight determination the complex is monomeric and structure **14** is suggested.

For the 1:1.5 complex the phosphane phosphorus is substantially upfield from its position in the 1:2.0 complex in the ^{31}P spectrum. This compound also has a conductivity too low to be ionic, and is not sufficiently soluble to determine the molecular weight. No structural proposal is appropriate at this time.

AuCl forms a 1:1 complex with the bis-ylide **5**, which shows only a singlet ^{31}P resonance. The symmetrical formula **15** is therefore assigned, supported by analytical and conductivity data.

Experimental Part

All experiments were carried out under an atmosphere of purified nitrogen. Glassware and solvents were dried and free of oxygen.

NMR instruments: Jeol C 60 HL, FX 60; Bruker WH 90. – IR spectrometer: Perkin Elmer 577. The syntheses of **2a** and **3a** are already described[6].

Cyclopentadienylidene[2-(diphenylphosphino)ethyl]diphenylphosphoran **(1b)**: To a solution of freshly distilled cyclopentadiene (2.48 g, 37.5 mmol) in 20 ml of chloroform at – 40 °C was slowly added a solution of bromine (6.00 g, 37.5 mmol) in 30 ml of chloroform. After stirring for 1 h, a solution of 1,2-bis(diphenylphosphino)ethane (29.9 g, 75.1 mmol) was added. The solution was permitted to warm to room temperature, stand for 22 h, and treated with cold 1.3 N aqueous KOH. After removal of the solvent, the ylide (mp. 150 °C) was isolated in 14% yield by crystallization from ethanol (2.43 g). – ^{1}H-NMR (CDCl$_3$): δ = 2.3, m, CH$_2$; 7.4, m, C$_5$H$_4$ and C$_6$H$_5$. – ^{31}P-NMR (CDCl$_3$): δ = 11.72 and – 13.11, d, ^3J(PP) = 47.2 Hz. – ^{13}C-NMR (CDCl$_3$): δ = 20.3, dd, CH$_2$, ^1J(PC) = 55.7, ^2J(PC) = 12.7 Hz; 22.7, dd, CH$_2$, ^1J(PC) = 19.5, ^2J(PC) = 4.9 Hz; 76.2, d, P=C, ^1J(PC) = 110.4 Hz; 114.0 and 115.3, d, C$_5$H$_4$, ^2J(PC) = 17.6, ^3J(PC) = 15.6 Hz; C$_6$H$_5$ was not assigned.

C$_{31}$H$_{28}$P$_2$ (462.5) Calcd. C 79.54 H 5.97 Found C 80.50 H 6.10

[2-(Diphenylphosphino)ethyl](9-fluorenyl)diphenylphosphonium bromide (**3b**): 1,2-Bis(diphe-nylphosphino)ethane (8.22 g, 20.7 mmol) and 9-bromofluorene (2.52 g, 10.3 mmol) were heated in dimethylformamide for 1 h at 110 °C. DMF was then removed in vacuo, the residue trated with toluene, and the insoluble product collected and recrystallized from methanol/diethyl ether. Colorless salt, m.p. 264 °C, 4.84 g (73%) yield. − ^{1}H-NMR (CF_3CO_2H): δ = 1.8, m, CH_2; 3.8, m, CH_2; 7.2, m, arom. H. − ^{31}P-NMR (CF_3CO_2H): δ = 12.7, d; 33.8, d; $^2J(PP)$ = 41.2 Hz.

$C_{39}H_{33}BrP_2$ (643.55)   Calcd. C 72.79 H 5.17   Found C 72.59 H 5.33

1,2-Ethanediylbis[(9-fluorenyl)diphenylphosphonium] dibromide (**4b**): 1,2-Bis(diphenylphos-phino)ethane (6.00 g, 15.1 mmol) and 9-bromofluorene (3.70 g, 15.1 mmol) were refluxed in toluene for 15 h. After cooling, the crystals were collected and recrystallized from methanol/diethyl ether. Colorless crystals, m.p. 308 °C, 7.51 g (56%) yield. − ^{31}P-NMR (CF_3CO_2H): δ = 31.33, s. − ^{13}C-NMR (CF_3CO_2H): δ = 26.8, "t", N = 21; 45.7, "t", CH, N = 21; olefinic and aromatic carbon atoms not assigned.

$C_{52}H_{42}Br_2P_2$ (888.7)   Calcd. C 70.28 H 4.76   Found C 70.39 H 4.96

[2-(Diphenylphosphino)ethyl](9-fluorenyliden)diphenylphosphoran (**2b**): Treatment of **3b** (4.44 g, 5.0 mmol) with 1 equivalent of methylenetriphenylphosphorane in tetrahydrofuran at room temperature gives a precipitate of methyltriphenylphosphonium bromide which is filtered. From the yellow filtrate, 2.62 g yellow crystals are isolated, 93% yield, m.p. 200 °C. − ^{1}H-NMR (CDCl$_3$): δ = 0.9 − 1.9 and 2.0 − 3.2, m, CH_2; 6.8 − 8.2, m, aromatic H. − ^{31}P-NMR (CDCl$_3$): δ = 9.76 and − 11.02, d, $^3J(PP)$ = 51.8 Hz. − ^{13}C-NMR (CDCl$_3$): δ = 20.15, dd, $^1J(PC)$ = 21.5, $^2J(PC)$ = 16.6 Hz; 23.29, dd, $^1J(PC)$ = 55.7, $^2J(PC)$ = 3.9 Hz; 61.24, d, P=C, $^1J(PC)$ = 122.1 Hz; aromatic carbon atoms not assigned.

$C_{39}H_{32}P_2$ (562.6)   Calcd. C 83.26 H 5.73   Found C 82.98 H 5.78

1,3-Propanediylbis[(9-fluorenyl)diphenylphosphonium] dibromide (**4c**): 1,3-Bis(diphenylphos-phino)propane (4.12 g, 10.0 mmol) and 9-bromofluorene (2.45 g, 10.0 mmol) were combined in a 1:1 stoichiometry and heated at 70 °C for 1 d in Toluene. The precipitate was collected and recrystallized from methanol/diethyl ether, m.p. 215 °C (3.4 g, 70%). (The analytical sample contains two mol of crystal methanol.) − ^{1}H-NMR (CF_3CO_2H): δ = 0.9 − 1.3 and 3.8 − 4.4, m, CH_2; 6.6, d, CH, $^2J(PH)$ = 10.0 Hz; 7.0 − 7.8, m, aromatic H. − ^{31}P-NMR (CF_3CO_2H): δ = 31.0, s.

$C_{53}H_{44}Br_2P_2 \cdot 2\ CH_3OH$ (966.8)   Calcd. C 68.33 H 5.42   Found C 67.94 H 5.72

1,3-Propanediylbis[9-fluorenylidenediphenylphosphorane] (**5**): The solution of **4c** (5.00 g, 5.17 mmol) in dimethylformamide was treated with cold aqueous Na_2CO_3. A yellow precipitate formed and was isolated by filtration. The crude product was dissolved in chloroform and the solution dried with Na_2SO_4. After evaporation of $CHCl_3$ the residue was recrystallized from tetrahydrofuran/pentane mixture, m.p. 166 °C, 3.6 g (85%). − ^{1}H-NMR (CDCl$_3$): δ = 2.4 − 2.8, m, CH_2; 6.8 − 8.5, m, aromatic H. − ^{31}P-NMR (CDCl$_3$): δ = 6.20, s. − ^{13}C-NMR (CDCl$_3$): δ = 16.76, s, br, CH_2; 25.5, dd, $^1J(PC)$ = 56.7, $^3J(PC)$ = 10.2 Hz; 50.50, C-9 (flu), $^1J(PC)$ = 122.0 Hz; 115.9, 116.4, 119.6, 122.9, s; 131.0, d, $^2J(PC)$ = 13 Hz; 142.0, d, $^3J(PC)$ = 15 Hz (fluorene carbon atoms); phenyl carbon atoms not assigned.

$C_{53}H_{42}P_2 \cdot C_4H_8O$ (813.0)   Calcd. C 84.21 H 6.20   Found C 84.17 H 6.37

Tetracarbonyl[[(diphenylphosphino)methyl](9-fluorenylidene)diphenylphosphorane-P',C-9]-tungsten (**6a**): Equimolar amounts of **2a** (0.17 g, 0.31 mmol) and tricarbonyltris(acetonitrile)-tungsten (0.12 g, 0.31 mmol) were stirred at room temperature in tetrahydrofuran for 15 h. After addition of pentane to the resulting solution a yellow precipitate formed, which was recrystallized

several times from tetrahydrofuran/pentane, m.p. 195 °C, 0.26 g (75%). − IR (KBr): 1830 s, 1878 s, 1905 s, 2005 s cm^{-1}. − ^{1}H-NMR (CDCl$_3$): δ = 1.2, d, CH$_2$, ^2J(PH) = 17 Hz; 6.8 − 7.4, m, aromatic H. − ^{31}P-NMR (CDCl$_3$): δ = 23.0 and 36.7, d, ^2J(PP) = 61.0 Hz.

C$_{42}$H$_{30}$O$_4$P$_2$W (844.5) Calcd. C 59.74 H 3.58 W 21.77 Found C 58.43 H 3.79 W 21.79

Tetracarbonyl[[[(diphenylphosphino)methyl](9-fluorenylidene)diphenylphosphorane-P',C-9]-chromium (**6b**): 1.3 g **2a** (2.4 mmol) were dissolved in 25 ml of di-*n*-butyl ether and added to 0.75 g Cr(CO)$_6$ (3.40 mmol, excess). The mixture was heated to 140 °C for 1 d in an apparatus, which recycled sublimed metal carbonyl back into the solution. An orange precipitate was formed. The solvent was removed in vacuo and replaced by tetrahydrofuran. ^{31}P-NMR spectroscopy showed the solution to contain two products (2:1), which could be separated by column chromatography (SiO$_2$, tetrahydrofuran/toluene, 1:1).

6b: m.p. 197 °C, dec. (ca. 50% yield). − ^{1}H-NMR (CDCl$_3$, 80 °C): δ = 5.0, br., 2H; 7.8 − 8.7, m, 28 aromatic H. − ^{31}P-NMR (C$_6$D$_6$/THF): δ = 34.01 and 56.55, d, ^2J(PP) = 73.2 Hz. − IR (Nujol or KBr): 1832, 1868, 1898, 1986 cm^{-1}, s. − MS (FD): *m/e* = 712, M$^+$ (8.7%); 684, M$^+$ − CO (90.6); 548, **2a**$^+$ (100).

C$_{42}$H$_{30}$CrO$_4$P$_2$ (712.65) Calcd. C 70.79 H 4.24 Found C 73.87 H 4.94

Tricarbonyl[[[(diphenylphosphino)methyl](1 − 4a,9a-η^6-fluorenylidene)diphenylphosphorane]-chromium (**7**) is the second product of the above reaction, m.p. 93 °C, orange crystals, soluble in toluene and tetrahydrofuran (ca. 25% yield). **7** is also formed on heating **6b** in toluene. − ^{1}H-NMR (C$_6$D$_6$): δ = 3.55, d, CH$_2$, ^2J(PH) = 13.5 Hz; 6.2 − 8.2, m, aromatic H. − ^{31}P-NMR (C$_6$D$_6$): δ = 4.73 and −29.03, d, ^2J(PP) = 58.0 Hz. − IR (Nujol or KBr): 1825, 1920, 1950 cm^{-1}, s. − MS (EI): *m/e* = 683, M$^+$ − 1 (0.02%); 600, M$^+$ − 3 CO (0.16); 548, **2a**$^+$ (2.7).

C$_{41}$H$_{30}$CrO$_3$P$_2$ (684.7) Calcd. C 71.93 H 4.42 Found C 69.52 H 4.42

[[(Diphenylphosphino)methyl](9-fluorenylidene)diphenylphosphorane-P',C-9]palladium dichloride (**10a**): Equimolar amounts of **2a** (0.23 g, 0.42 mmol) and [(C$_6$H$_5$)$_3$P]$_2$PdCl$_2$ (0.18 g, 0.41 mmol) were stirred in 10 ml tetrahydrofuran. After 5 min a yellow precipitate began to form. After 10 h the solid was collected by filtration and purified by recrystallization from tetrahydrofuran/pentane, m.p. 308 °C, 0.16 g (56%). − ^{1}H-NMR (DMSO): δ = 5.4, br. m, CH$_2$; 7.1 − 8.5, m, aromatic H. − ^{31}P-NMR (DMSO): δ = 17.2 and 48.7, d, ^2J(PP) = 59.0 Hz. − IR (KBr): 292, 368 cm^{-1}, v(*cis*-PdCl$_2$).

C$_{38}$H$_{30}$Cl$_2$P$_2$Pd (725.9 Calcd. C 62.87 H 4.16 Cl 9.77 Pd 14.66
Found C 62.58 H 4.23 Cl 9.83 Pd 14.51

[[(Diphenylphosphino)methyl](9-fluorenylidene)diphenylphosphorane-P',C-9]platinum dichloride (**10b**): Equimolar amounts of **2a** (0.55 g, 1.0 mmol) and PtCl$_2$ (0.26 g, 1.0 mmol) were refluxed in 25 ml THF for 3 h. The mixture was cooled and filtered to yield 0.76 g (93%) **10b**, m.p. >310 °C. The product was recrystallized from dioxane. − IR (KBr): 295 and 375 cm^{-1}, v(PtCl$_2$ *cis*). − ^{31}P-NMR (DMF): δ = 55.04 and −0.08, dd, ^2J(PP) = 45.78 Hz.

C$_{38}$H$_{30}$Cl$_2$P$_2$Pt (816.8) Calcd. C 55.88 H 3.97 Found C 54.95 H 3.95

Bis[[2-(diphenylphosphino)ethyl](9-fluorenylidene)diphenylphosphorane-P',C-9]palladium(II) tetrachloropalladate(II) (**13**): Equimolar amounts of **2b** (0.15 g, 0.27 mmol) and [(C$_6$H$_5$)$_3$P]$_2$PdCl$_2$ (0.12 g, 0.27 mmol) were stirred in 10 ml tetrahydrofuran at room temperature for 24 h. Upon addition of pentane a red precipitate formed, m.p. 235 °C, 0.18 g (90%). − ^{1}H-NMR (CDCl$_3$): δ = 2.3 − 4.0, m, CH$_2$; 6.3 − 8.3 m, aromatic H. − ^{31}P-NMR (CDCl$_3$): δ = 14.3 and 23.6, d, ^2J(PP) = 26 Hz. − IR (KBr): 352 cm^{-1}, v(Pd − Cl).

C$_{78}$H$_{64}$Cl$_4$P$_4$Pd$_2$ (1479.9) Calcd. C 63.31 H 4.36 Found C 63.84 H 4.91

Mercuric chloride complexes **14** *and unknown of [(diphenylphosphino)methyl](9-fluorenyl-idene)diphenylphosphorane:* A solution of $HgCl_2$ (0.96 g, 3.54 mmol) in 5 ml of tetrahydrofuran was added dropwise to a solution of 1.10 g **2a** (2.01 mmol) in 10 ml THF. After 2 h a white precipitate was collected, recrystallized from dimethylsulfoxide/water, and dried at $20\,°C/0.1$ Torr. m.p. $248\,°C$, 0.53 g (27%). – ^{31}P-NMR (DMSO, [D_6]acetone): δ = 35.4 and – 12.9, d, $^2J(PP)$ = 51.8 Hz. – Λ_M (DMSO): 20.8 Ω^{-1} cm^{-2} (20°C).

Unknown: $C_{76}H_{72}Cl_6Hg_3P_4$ (1923.8)   Calcd. C 47.45   H 3.77   Found C 48.12   H 3.63

A second product precipitated by adding pentane to the filtrate of the above complex. The light grey compound was recrystallized from tetrahydrofuran/pentane, m.p. 145°C, 0.73 g (38%). – ^{31}P-NMR (DMSO): δ = 28.5 and 33.0, d, $^2J(PP)$ = 6 Hz. – Λ_M (DMSO): 14.6 Ω^{-1} cm^{-2} (20°C).

14: $C_{38}H_{36}Cl_4Hg_2P_2$ (1097.65)   Calcd. C 41.58   H 3.31   Found C 41.70   H 3.05

1,3-Propanediylbis[(9-fluorenylidene)diphenylphosphorane]gold chloride (**15**): Equimolar amounts of **5** (0.13 g, 0.16 mmol) and Me_3PAuCl (0.050 g, 0.16 mmol) were refluxed in 25 ml THF for 20 h, then the THF was evaporated in vacuo. Pumping at 0.1 torr and 30°C was continued for 1 h to remove Me_3P. The residue was heated in dioxane and the insoluble material removed by filtration. Upon cooling a 0.050 g (30%) yield of **15** was formed, m.p. 150°C. – IR (KBr): No absorption in the $250 - 400$ cm^{-1} region. – ^{31}P-NMR (CDCl$_3$): δ = 32.59 s.

$C_{53}H_{42}AuClP_2$ (973.3)   Calcd. C 65.41   H 4.35   Found C 65.86   H 5.30

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