

Perhalophenyl complexes of palladium(II) containing keto-stabilized phosphorus ylides of the type $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\text{CHC}(\text{O})\text{R}$

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Abstract

From suitable perhalophenyl derivatives of palladium(II), viz.: $\text{Pd}(\text{C}_6\text{F}_5)_2\text{-(SC}_4\text{H}_8)_2$, $[\text{Pd}(\mu\text{-X})(\text{C}_6\text{X}_5)_2]_2(\text{NBu}_4)_2$, $[\text{Pd}(\mu\text{-Cl})(\text{C}_6\text{X}_5)(\text{SC}_4\text{H}_8)]_2$ ($\text{X} = \text{F, Cl, X}' = \text{Cl, Br}$), new complexes of various types have been prepared, viz.: *trans*- $\text{Pd}(\text{C}_6\text{F}_5)_2(\text{Y})_2$, $\text{Pd}(\text{C}_6\text{X}_5)_2(\text{Y})$, $\text{PdCl}(\text{C}_6\text{X}_5)(\text{Y})$ ($\text{X} = \text{F, Cl}$). The neutral ligand Y is a keto-stabilized phosphorus ylide of the type $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\text{CHC}(\text{O})\text{R}$ ($n = 1$, $\text{R} = \text{CH}_3$, C_6H_5 ; $n = 2$, $\text{R} = \text{C}_6\text{H}_5$) acting in a terminal monodentate P-donor or a bidentate chelate P,C-donor mode. The reaction of $\text{PdCl}(\text{C}_6\text{F}_5)(\text{Y})$ complexes with HCl leads to the corresponding $\text{PdCl}_2(\text{C}_6\text{F}_5)(\text{YH})$ complexes in which the phosphonium cation $[\text{YH}]^+$ behaves as monodentate P-donor at its phosphinic end.

IR and ^{31}P NMR spectroscopy were used to decide the coordination mode of the ligands and, in some cases, to reveal the presence of two isomers.

Introduction

The conversion of one of the two phosphine moieties in bis(diphenylphosphino)methane or 1,2-bis(diphenylphosphino)ethane into keto-stabilized ylides gives air-stable, asymmetric mixed ketoylide-phosphine compounds, $\text{PPh}_2(\text{CH}_2)_n\text{-PPh}_2\text{CHC}(\text{O})\text{R}$ ($n = 1, 2$; $\text{R} = \text{CH}_3$, C_6H_5), which have several potential sites for coordination to a metal center [1].

The coordination of palladium(II) with this type of ylide ligands has received little attention [1–5]. We described below a series of neutral perhalophenyl derivatives with the $\text{PPh}_2(\text{CH}_2)_n\text{PPh}_2\text{CHC}(\text{O})\text{R}$ (Y) ligand * in the terminal monoden-

* bdmp: benzoylmethylenediphenyldiphenylphosphinomethylphosphorane $\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{CHC}(\text{O})\text{Ph}$.
 admp: acetylmethylenediphenyldiphenylphosphinomethylphosphorane $\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{CHC}(\text{O})\text{CH}_3$.
 bdep: benzoylmethylenediphenyl-2-diphenylphosphinoethylphosphorane $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\text{-CHC}(\text{O})\text{Ph}$.

tate P-donor or the bidentate chelate P,C-donor mode. Two pentafluorophenyl derivatives of palladium(II) in which a phosphonium cation $[YH]^+$ acts as P(phosphinic)-donor ligand are also described. IR and ^{31}P NMR has been used to study the coordination mode of the ligands, and in some cases has revealed the presence of two isomers.

We previously described the synthesis of some cationic palladium(II) complexes with a monodentate keto-stabilized phosphoylide ligand involving previously undescribed O-coordination of acetylmethylenetriphenylphosphorane [6].

Results and discussion

Analytical and melting point data are listed in Table 1. Relevant IR absorptions are shown in Table 2. ^{31}P NMR parameters are summarized in Table 3.

Table 1

Analyses (found (calcd.) (%)), and melting points of the complexes

Complex	C	H	N	m.p. °
I <i>trans</i> -Pd(C ₆ F ₅) ₂ (bdmp) ₂	63.96 (64.81)	3.71 (3.91)		218(d)
II <i>trans</i> -Pd(C ₆ F ₅) ₂ (admp) ₂	62.21 (61.82)	4.03 (3.97)		185(d)
III Pd(C ₆ F ₅) ₂ (bdmp)	57.45 (57.31)	3.18 (2.97)		253(d)
IV Pd(C ₆ F ₅) ₂ (admp)	54.08 (54.54)	3.05 (2.98)		220(d)
V Pd(C ₆ F ₅) ₂ (bdep)	57.06 (57.73)	3.34 (3.16)		217(d)
VI Pd(C ₆ Cl ₅) ₂ (bdmp)	48.58 (48.80)	2.58 (2.53)		256(d)
VII Pd(C ₆ Cl ₅) ₂ (admp)	45.95 (45.96)	3.03 (2.51)		215(d)
VIII PdCl(C ₆ F ₅)(bdmp)	57.20 (57.73)	3.52 (3.45)		226(d)
IX PdCl(C ₆ F ₅)(admp)	54.20 (54.49)	3.44 (3.50)		271(d)
X PdCl(C ₆ Cl ₅)(bdmp)	51.98 (52.42)	2.97 (3.16)		257(d)
XI PdCl(C ₆ Cl ₅)(admp)	48.70 (49.11)	3.32 (3.15)		277(d)
XII PdCl(C ₆ Cl ₅)(bdep)	52.28 (52.93)	3.16 (3.33)		210(d)
XIII Pd(SCN)(C ₆ F ₅)(bdmp)	57.13 (57.60)	3.29 (3.36)	1.65 (1.68)	235(d)
XIV PdI(C ₆ F ₅)(bdmp)	51.70 (51.88)	3.23 (3.10)		261(d)
XV Pd(SCN)(C ₆ Cl ₅)(bdmp)	51.51 (52.43)	3.21 (3.08)	1.52 (1.53)	248(d)
XVI PdI(C ₆ Cl ₅)(bdmp)	46.98 (46.55)	2.88 (2.86)		209(d)
XVII PdCl ₂ (C ₆ F ₅)(bdmpH)	55.30 (55.25)	3.59 (3.45)		210(d)
XVIII PdCl ₂ (C ₆ F ₅)(admpH)	49.85 (50.24)	3.13 (3.22)		232(d)

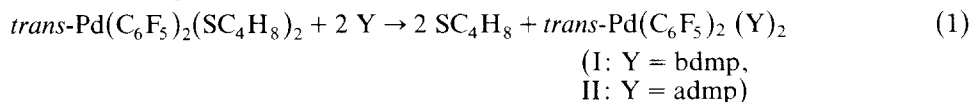
^a d = decomposition.

Table 2. Infrared spectral data

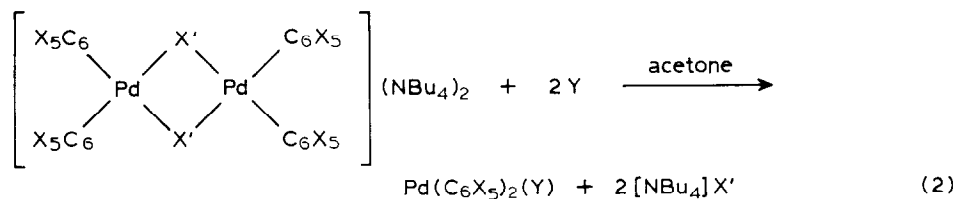
	$\nu(\text{C=O})$ (cm^{-1})	$\Delta\nu(\text{C=O})$ (cm^{-1})
bdmp	1525	
admp	1532	
bdep	1525	
[bdmpH]Br	1670	
[admpH]Cl	1715	
[bdepH]Br	1673	
I	1525	0
II	1541	9
III	1609	84
IV	1640	108
V	1617	92
VI	1625	100
VII	1635	103
VIII	1610	85
IX	1632	100
X	1610	85
XI	1618	93
XII	1611	86
XIII	1615	90
XIV	1610	85
XV	1615	90
XVI	1610	85
XVII	1679	9
XVIII	1712	-3

Synthesis of the complexes

Addition of Y (bdmp, admp) to dichloromethane solutions of bis(pentafluorophenyl)bis(tetrahydrothiophene)palladium(II) results in displacement of the S-ligand, as shown in eq. 1.



The reaction of anionic binuclear palladium(II) complexes of the type $[\text{Pd}(\mu\text{-X}')(\text{C}_6\text{X}_5)_2]_2(\text{NBu}_4)_2$ ($\text{X}' = \text{Cl}, \text{Br}; \text{X} = \text{F}, \text{Cl}$) with a stoichiometric amount of Y (molar ratio 1/2) gives the corresponding mononuclear palladium(II) complexes, $\text{Pd}(\text{C}_6\text{X}_5)_2(\text{Y})$, according to eq. 2.



(III : $\text{X}' = \text{Cl}$, $\text{X} = \text{F}$, $\text{Y} = \text{bdmp}$;

IV : $\text{X}' = \text{Cl}$, $\text{X} = \text{F}$, $\text{Y} = \text{admp}$;

V : $\text{X}' = \text{Cl}$, $\text{X} = \text{F}$, $\text{Y} = \text{bdep}$;

VI : $\text{X}' = \text{Br}$, $\text{X} = \text{Cl}$, $\text{Y} = \text{bdmp}$;

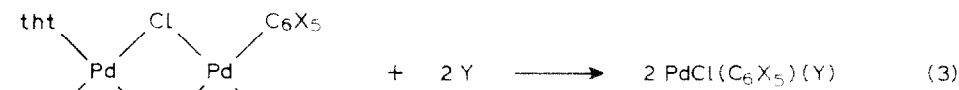
VII : $\text{X}' = \text{Br}$, $\text{X} = \text{Cl}$, $\text{Y} = \text{admp}$)

Table 3. $^{31}\text{P}\{^1\text{H}\}$ NMR data (δ , ppm; J , Hz). Shifts are related to external 85% H_3PO_4 , with positive values to high field

		Phosphonium or ylide P	Phosphine P	$^2J(\text{PP})$	$^3J(\text{PP})$	N^a
bdmp		13.8	-27.4	63		
[bdmpH]Br		23.4	-27.1	63		
admp		11.5	-27.5	62		
[admpH]Br		21.2	-27.2	68		
bdep		17.1	-12.2		42	
[bdepH]Br		26.4	-12.4		38	
<i>trans</i> -Pd(C ₆ F ₅) ₂ (bdmp) ₂	I	10.1	15.6			21
<i>trans</i> -Pd(C ₆ F ₅) ₂ (admp) ₂	II	7.5	15.2			20
Pd(C ₆ F ₅) ₂ (bdmp)	III	40.3	17.9	69		
Pd(C ₆ F ₅) ₂ (admp)	IV	38.3	17.9	68		
Pd(C ₆ F ₅) ₂ (bdep)	V	28.4	10.7		27	
Pd(C ₆ Cl ₅) ₂ (bdmp)	VI	39.9	18.7	68		
Pd(C ₆ Cl ₅) ₂ (admp)	VII	37.8	19.1	70		
PdCl(C ₆ F ₅)(bdmp)	VIII	A 32.5	28.7	40		
		B 44.6	12.3	81		
PdCl(C ₆ F ₅)(admp)	IX	A 30.8	25.8	41		
		B 42.1	11.9	85		
PdCl(C ₆ Cl ₅)(bdmp)	X	A 29.4	24.5	42		
		B 47.1	9.8	82		
PdCl(C ₆ Cl ₅)(admp)	XI	A 30.0	22.0	43		
		B 44.5	11.2	83		
PdCl(C ₆ Cl ₅)(bdep)	XII	A 25.7	20.4		16	
		B 27.8	6.2		40	
Pd(SCN)(C ₆ F ₅)(bdmp)	XIII	A 35.3	26.2	45		
		B 42.6	17.5	75		
PdI(C ₆ F ₅)(bdmp)	XIV	A 39.4	24.4	50		
		B 41.6	12.5	78		
Pd(SCN)(C ₆ Cl ₅)(bdmp)	XV	A 33.3	22.6	48		
		B 44.5	15.0	78		
PdI(C ₆ Cl ₅)(bdmp)	XVI	A 36.6	19.4	52		
		B 43.9	10.1	81		
PdCl ₂ (C ₆ F ₅)(bdmpH)	XVII	<i>cis</i> 32.5	28.7	40		
		<i>trans</i> 37.4	25.8	45		
PdCl ₂ (C ₆ F ₅)(admpH)	XVIII	<i>cis</i> 30.8	25.9	37		
		<i>trans</i> 35.0	23.4	47		

^a $N = |^2J(\text{P}_\text{A}-\text{P}_\text{B}) + ^4J(\text{P}_\text{A}-\text{P}_\text{B})|$.

Complexes of the type $\text{PdCl}(\text{C}_6\text{X}_5)(\text{Y})$ were obtained by the addition of neutral ligands Y to benzene solutions of neutral dinuclear palladium(II) complexes: $[\text{Pd}(\mu\text{-Cl})(\text{C}_6\text{X}_5)(\text{tht})]_2$, according to eq. 3.



(VIII : X = F, Y = bdmp ;

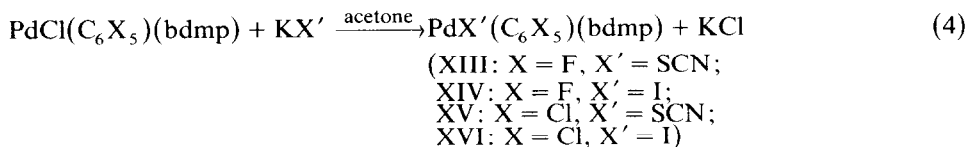
IX : X = F, Y = admp ;

X : X = Cl, Y = bdmp ;

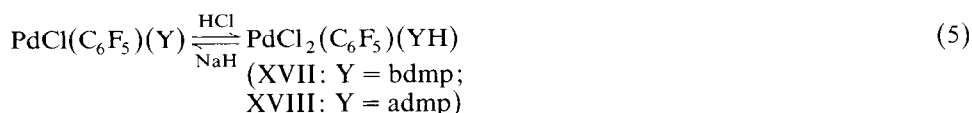
XI : X = Cl, Y = admp ;

XII : X = Cl, Y = bdep)

The Cl group in the complexes $\text{PdCl}(\text{C}_6\text{X}_5)(\text{Y})$ can be replaced by other halogen (I^-) or pseudohalogen groups (SCN^-) by treatment of $\text{PdCl}(\text{C}_6\text{X}_5)(\text{Y})$ with the corresponding KX' salt in acetone solution, as shown in eq. 4.



Treatment of VIII or IX with a stoichiometric amount of HCl leads to the protonation of the Y ligand and formation of the corresponding $\text{PdCl}_2(\text{C}_6\text{F}_5)(\text{YH})$ complexes, as shown in eq. 5; on the other hand, when the $\text{PdCl}_2(\text{C}_6\text{F}_5)(\text{YH})$ complexes are treated with NaH in THF solution, the corresponding $\text{PdCl}(\text{C}_6\text{F}_5)(\text{Y})$ complexes are obtained (eq. 5).



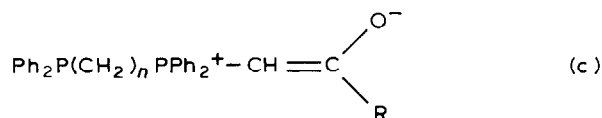
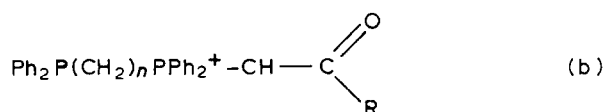
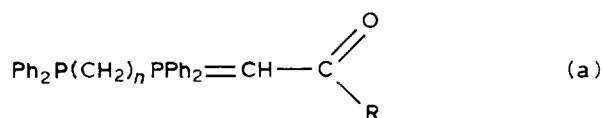
Acetone solutions of complexes I–XVIII ($c \ 5 \times 10^{-4} \text{ M}$) are non-conducting.

Structural studies: IR and ^{31}P NMR spectra

The structures of the complexes were assigned on the basis of their IR (Table 2) and ^{31}P NMR (Table 3) data.

The carbonyl stretching frequency of keto-stabilized ylides and ylide complexes is a convenient indicator of the mode of coordination of the ylide to the metal. In Table 2 are shown the $\nu(\text{C}=\text{O})$ absorptions due to the free ylide ligands, the phosphonium salts, and the palladium(II) derivatives.

The structures of the ylides used here can be represented in terms of the canonical forms (a), (b), (c)



The ylides (bdmp, admp, bdep) have three potential donor atoms (phosphine P, enol O, and ylide C). Shifts of $\nu(\text{CO})$ to higher frequencies upon complex formation of this type of the ylide ligands are considered to indicate the coordination of the

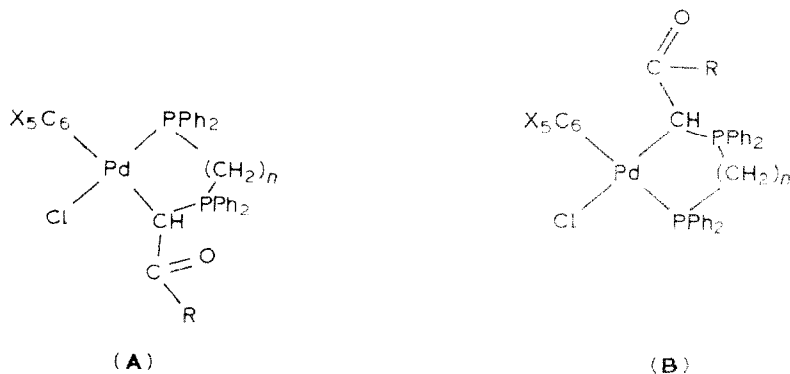
ylide carbon to the metal center [7,8]. On the contrary, a negative value of $\Delta\nu$ ($\Delta\nu = \nu(\text{CO})(\text{complex}) - \nu(\text{CO})(\text{ylide})$) suggests that the ylide ligand is attached via the oxygen atom [6,9,10], and P-coordination of the ylide (acting as monodentate ligand) does not alter the $\nu(\text{C}=\text{O})$ value significantly.

In the case of complexes I and II, the value of $\nu(\text{CO})$ for $\text{Pd}(\text{C}_6\text{F}_5)_2(\text{Y})_2$ is very close to that for the free ylide, indicating that the two Y ligands coordinate to palladium only through phosphine phosphorus atoms. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of these complexes shows two signals; one of them is a deceptive triplet, corresponding to the ylide P; the other, corresponding to phosphine P coordinated to a Pd center, does not appear as a triplet owing to broadening of the signal produced by unresolved P–F couplings; this pattern corresponds to an AA'BB' system with a large value of $^2J(\text{P}–\text{Pd}–\text{P})$ arising from the *trans* geometry of complexes I and II.

The IR spectra of complexes of the types $\text{PdR}_2(\text{Y})$ ($\text{R} = \text{C}_6\text{F}_5$, C_6Cl_5) (III–VII), $\text{PdCl}(\text{R})(\text{Y})$ ($\text{R} = \text{C}_6\text{F}_5$, C_6Cl_5) (VIII–XII) and $\text{PdXC}_6\text{F}_5(\text{Y})$ ($\text{X} = \text{SCN}^-$, I^-) (XIII–XVI) show a single $\nu(\text{CO})$ band at $1625\text{--}1609\text{ cm}^{-1}$. The positive value of $\Delta\nu$ points clearly to C-coordination of the ylide ligand, which must act as a P,C-chelate ligand.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the bis(perhalophenyl) derivatives, $\text{PdR}_2(\text{Y})$ ($\text{R} = \text{C}_6\text{F}_5$, C_6Cl_5) (III–VII) shows the typical pattern for an AB system, in agreement with the assumed structure.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the chloroperhalophenyl derivatives shows two pairs of doublets, corresponding to two AB systems due to the presence of two isomers, **A** and **B**.



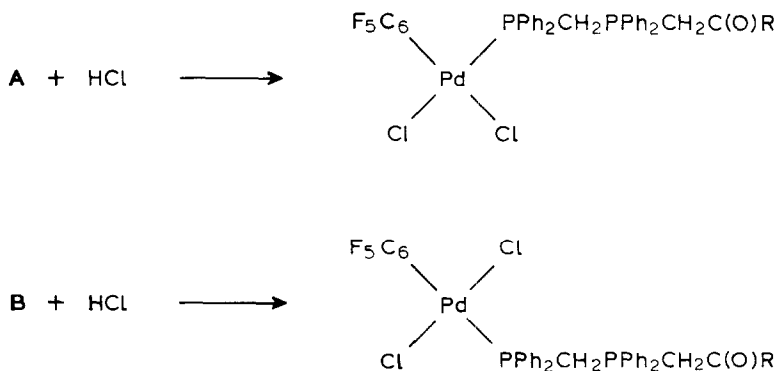
Assignment of the various ^{31}P NMR signals was unambiguous (in the case of the perfluorophenyl derivatives) because of the presence of a very broad doublet, which can be assigned to the phosphine P of the isomer **B**, this phosphine P being *trans* to a C_6F_5 group. The relative intensity of the signals can be used to evaluate the **A** to **B** isomer ratios, and these were found to be complex VIII, 10/1; IX, 4/1; X, 2/1; XI, 10/1; XII, 7/1.

The ^{31}P NMR spectra in CDCl_3 solutions of complexes XIII–XVI also show the presence of the two types of isomers (**A**, **B**); the **A**/**B** molecular ratios are: 4/1 (XIII–XIV); 8/1 (XV); or 3/1 (XVI). The **A**/**B** ratio for complexes $\text{PdX}'(\text{C}_6\text{X}_5)(\text{bdmp})$ ($\text{X}' = \text{SCN}^-$, I^- ; $\text{X} = \text{F}$, Cl) (XIII–XVI) is different from that for the corresponding starting complexes $\text{PdCl}(\text{C}_6\text{X}_5)(\text{bdmp})$ ($\text{X} = \text{F}$, Cl) (VIII, X) (see eq. 4). Either substitution process (eq. 4) does not take place with stereoretention, or

the $A \rightleftharpoons B$ equilibrium is different for each halide or pseudohalide derivative (VIII–XVI).

The free phosphonium salts $[PPh_2CH_2PPh_2CH_2C(O)R]^+ X^-$ give a $\nu(CO)$ absorption at 1670 cm^{-1} ([bdmpH]Br) or 1715 ([admpH]Cl), corresponding to a ketonic-carbonyl group. The C-ylidic protonation of a chelate coordinated ylide (bdmp, admp) leads to the corresponding complexes (see eq. 5) having a $[YH]^+$ cation coordinated to the palladium(II) center. The $\nu(CO)$ frequency of the complexes $PdCl_2(C_6F_5)(YH)$ (XVII–XVIII) is consistent with P(phosphinic) coordination of the phosphonium group; this type of coordination does not alter the $\nu(CO)$ value significantly.

The $^{31}P\{^1H\}$ NMR of the complexes XVII and XVIII also show a pattern corresponding to two AB systems, in keeping with the presence of *cis* and *trans* isomers of the $PdCl_2(C_6F_5)(YH)$ complexes (XVII–XVIII). The *cis*/*trans* ratio is similar to the *A*/*B* ratio in the starting materials. The protonation of the *A* isomers leads to the *cis* complexes, and protonation of the *B* isomers to the *trans* species.



All the pentafluorophenyl complexes exhibit IR absorptions at ca. 1500s and 950s cm^{-1} characteristic of the C_6F_5 group [11,12]. The pentachlorophenyl derivatives show characteristic absorptions of the C_6Cl_5 group ($1290\text{--}1230\text{ cm}^{-1}$ region and ca. 620 cm^{-1}) [13,15]. The complexes XIII and XV exhibit a bond at ca. 2100 cm^{-1} assignable to the $\nu(C\equiv N)$ of the SCN group [14]. All the chloro derivatives show IR absorptions in the $350\text{--}250$ region due to $\nu(Pd\text{--}Cl)$ stretching. In acetone solutions the complexes are non-conducting.

Experimental

C and H analyses were carried out with a Perkin–Elmer 240 microanalyzer. Melting points were determined with a Buchi apparatus and are uncorrected. Conductivities were measured in ca. $5 \times 10^{-4}\text{ M}$ solutions with a Philips PW 9501/01 conductimeter. The IR spectra were recorded (in the $4000\text{--}200\text{ cm}^{-1}$ range) on a Perkin–Elmer spectrophotometer using Nujol mulls between polyethylene sheets. ^{31}P NMR spectra were recorded on a Varian XL 200.

The compounds $Ph_2PCH_2PPh_2CHC(O)Ph(bdmp)$ [1], $Ph_2PCH_2PPh_2CHC(O)Me(admp)$ [1], $Ph_2PCH_2CH_2PPh_2CHC(O)Ph(bdep)$ [1], $t\text{-}Pd(C_6F_5)_2(tht)_2$ [15], $(NBu_4)_2[Pd(\mu\text{-}Cl)(C_6F_5)_2]_2$ [16], $(NBu_4)_2[Pd(\mu\text{-}Br)(C_6Cl_5)_2]_2$ [17], $[Pd(\mu\text{-}Cl)(C_6F_5)(tht)]_2$ [15], $[Pd(\mu\text{-}Cl)(C_6Cl_5)(tht)]_2$ [15] were prepared as described elsewhere.

trans-Pd(C₆F₅)₂(Y)₂ (I: Y = *bdmp*; II: Y = *admp*)

To a solution of *trans*-Pd(C₆F₅)₂(tht)₂ (0.306 g, 0.496 mmol) in 40 ml of dichloromethane was added *bdmp* (0.499 g, 0.993 mmol). The mixture was stirred for 1 h at room temperature and then evaporated to ca. 3 ml. Addition of ~ 20 ml of Et₂O produced a white precipitate, which was filtered off and air dried, 78% yield (complex I).

Complex II was obtained similarly from *admp*. Yield: 76%.

Pd(C₆X₅)₂(Y) (III: X = F; Y = *bdpm*; IV: X = F; Y = *admp*; V: X = F; Y = *bdep*; VI: X = Cl; Y = *bdmp*; VII: X = Cl; Y = *admp*)

To a solution of (NBu₄)₂[Pd(μ-Cl)(C₆F₅)₂]₂ (0.300 g, 0.209 mmol) in 30 ml of acetone was added *bdmp* (0.209 g, 0.418 mmol). The mixture was stirred for 30 min at room temperature, and then evaporated to dryness. Addition of 30 ml of EtOH gave a white solid, which was filtered off, washed with EtOH (2 × 5 ml), and air dried, 67% yield (complex III).

Complexes IV and V were obtained similarly from *admp* and *bdep*. Yields 70% (IV) and 57% (V).

Complexes VI and VII were obtained similarly from (NBu₄)₂[Pd(μ-Br)(C₆Cl₅)₂]₂ as the starting palladium(II) complex and *bdmp* (for complex VI) or *admp* (for complex VII) as the ylide. Yields 69% (VI) and 65% (VII).

PdCl(C₆X₅)(Y) (VIII: X = F, Y = *bdmp*; IX: X = F, Y = *admp*; X: X = Cl, Y = *bdpm*; XI: X = Cl, Y = *admp*; XII: X = Cl, Y = *bdep*)

(a) From [Pd(μ-Cl)(C₆X₅)(tht)]₂. To a solution of [Pd(μ-Cl)(C₆F₅)(tht)]₂ (0.302 g, 0.381 mmol) in 40 ml of benzene was added *bdmp* (0.382 g, 0.762 mmol). The mixture was stirred for 30 min at room temperature, and the white precipitate formed was then filtered off, washed with Et₂O (2 × 10 ml), and air-dried, to give VIII (78%).

Complex IX was obtained similarly from *admp*. Yield 76%.

Complexes X, XI and XII were obtained similarly from [Pd(μ-Cl)(C₆Cl₅)(tht)]₂ and *bdmp* (for complex X), *admp* (for XI) or *bdep* (for XII). Yields 81% (X), 72% (XI), and 69% (XII).

(b) From complex XVII. To a suspension of HNa (0.180 g) in 30 ml of dried THF under N₂ was added PdCl₂(C₆F₅)(*bdmpH*) (0.183 g, 0.217 mmol). The mixture was stirred for 4 h at room temperature, then filtered and the filtrate concentrated to ca. 5 ml. Addition of Et₂O (~ 5 ml) gave a white precipitate, which was filtered off, air-dried, and identified as complex VIII. Yield: 69%.

PdX'(C₆X₅)(*bdmp*) (XIII: X = F, X' = SCN; XIV: X = F, X' = I; XV: X = Cl, X' = SCN; XVI: X = Cl; X' = I)

To a solution of PdCl(C₆F₅)(*bdmp*) (VIII) (0.253 g, 0.312 mmol) in 60 ml of acetone was added KSCN (0.033 g, 0.343 mmol). The mixture was stirred for 4 h at reflux, then filtered, and the filtrate evaporated to dryness. The solid residue was recrystallized from Cl₃CH/EtOH, to give XIII (73%).

Complexes XIV, XV and XVI were obtained analogously, using KI as KX' salts to obtain XIV and using complex X and KSCN or KI to obtain XV or XVI, respectively. Yields 62% (XIV), 71% (XV), and 62% (XVI).

$\text{PdCl}_2(\text{C}_6\text{F}_5)(\text{YH})$ (XVII: $\text{Y} = \text{bdmp}$; XVIII: $\text{Y} = \text{admp}$)

To a solution of $\text{PdCl}(\text{C}_6\text{F}_5)(\text{bdmp})$ (VIII) (0.203 g, 0.255 mmol) in 40 ml of Cl_2CH_2 was added 0.5 ml of an 0.464 M solution of HCl in MeOH (0.278 mmol). The mixture was stirred for 4 h at room temperature, then evaporated to ca. 5 ml. Addition of Et_2O (ca. 50 ml) gave a yellow precipitate, which was filtered off and air-dried to give complex XVII. Yield 86%.

Complex XVIII was obtained similarly from $\text{PdCl}(\text{C}_6\text{F}_5)(\text{admp})$ (IX). Yield 70%.

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