The Difficulty of Coordinating Mutually *trans* Phosphine and Aryl Ligands in Palladium Complexes and Its Relation to Important Coupling Processes. Syntheses and Crystal Structures of a Family of Palladium Phosphino, Triflato, Perchlorato, and Aquo-2-(arylazo)aryl Complexes

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The reaction between [Pd(C_6H_3N=NR-2, X-5)Cl]$_2$ and phosphines gives [Pd(C_6H_3N=NTo-2,Me-5)Cl(L)] [To = C_6H_4Me-4, L = PEt_3 (**1a**), PPh_2Me (**1b**)] or *trans*-[Pd($C_6H_3N_2$To-2,Me-5)ClL$_2$] (L = PEt_3 (**2a**), PPh_2Me (**2b**), L$_2$ = bis(diphenylphosphino)methane = dppm (**2c**)) or *trans*-[Pd($C_6H_3N_2$X-2, R-5)Cl(μ-dppm)]$_2$ (X = Me, R = To (**3a**); X = H, R = Ph (**3b**)), depending on the molar ratio of the reagents. Tl(OTf) (OTf = O_3SCF_3), $AgClO_4$, or $AgSbF_6$ react with **1a**,**b**, **2a**, **2c**, or **3a** to give, variously, [Pd(C_6H_3N=NTo-2,Me-5)(Y)(L)] (L = PEt_3, Y = TfO (**4a**); L = PPh_2Me, Y = TfO (**4b**), ClO_4 (**4b′**)), *trans*-[Pd($C_6H_3N_2$To-2,Me-5)(OTf)(PEt_3)$_2$] (**5**), [Pd($C_6H_3N_2$To-2,Me-5)(η^1-dppm)(η^2-dppm)]TfO (**6**), or [Pd(C_6H_3N=NR-2,X-5)(η^2-dppm)]Y (X = Me, R = To, Y = TfO (**7a**)). Complexes [Pd(C_6H_3N=NR-2,X-5)(η^2-dppm)]SbF_6 (X = Me, R = To (**7a′**); X = H, R = Ph (**7b**)) can be prepared by reacting [Pd(C_6H_3N=NR-2,X-5)Cl]$_2$ with $AgSbF_6$ and dppm. Complex **4b′** reacts with PPh_2Me to give [Pd($C_6H_3N_2$To-2,Me-5)(PPh_2-Me)$_3$]ClO_4 (**8**). Attempts to obtain single crystals of **4a**, [Pd(C_6H_3N=NR-2,X-5)(PPh_3)(Me_2-CO)]ClO_4, or **7b** lead to different products. From **4**, an insertion into the Pd−OTf bond of one molecule of water gives [Pd(C_6H_3N=NTo-2,Me-5(OH_2···OTf)(PEt_3)] (**9**) while substitution of the acetone molecule by two water molecules occurs in the second case to give [Pd(C_6H_3N=NTo-2,Me-5){(μ_3-OH_2)(···$OClO_3$)(···OH_2)}(PPh_3)] (**10**). Finally, ready oxidation in the air of **7b** gives [Pd(C_6H_4N=NPh-2)(η^2-dppmO)]SbF_6 (**11**) [dppmO = bis(diphenylphosphino)methane monoxide]. [Pt(PPh_3)$_3$] reacts with [Hg($C_6H_3N_2$To-2, Me-5)Cl] to give *trans*-[Pt($C_6H_3N_2$To-2,Me-5)Cl(PPh_3)$_2$] (**12**), which in turn reacts with Tl(OTf) to give [Pt(C_6H_3N=NTo-2,Me-5)(PPh_3)$_2$]TfO (**13**). Crystal structures of **2c·$^1/_2$$CH_2Cl_2$**, **4b′**, **5**, **6**, **7a**, **9**, **10**, and **11·2MeOH** have been determined.

Introduction

Arylpalladium complexes with phosphines are intermediates in useful catalytic organic reactions. Thus, *trans*-[Pd(Ar)X(PR_3)$_2$] (Ar = aryl) complexes (obtained, for example, by oxidative addition of ArX to [Pd(PR_3)$_n$]) react with organometallic derivatives of main group elements R−[M] (R = alkyl, aryl, alkenyl, allyl, benzyl and M = Li, Mg, Cu, Zn, B, Al, Sn) to give the coupling product Ar−R (Scheme 1).[1] We have extended the observation to gold(III) systems. Thus, the complexes *cis*-[Au(C_6H_3N=NR-2,X-5)(R′)Cl] (X = Me, H; R = To, Ph; R′ = C_6F_5, $C_6H_4NO_2$-2, $C_6H_4N_2Ph$, $CH_2C(O)Me$) react with PPh_3 to give the corresponding coupling products and [AuCl(PPh_3)] (Scheme 1).[2]

We have recently observed that all attempts to prepare [Pd(C_6H_3N=NR-2,X-5)(PPh_3)$_2$]$^+$ (X = Me, H; R = To, Ph) were unsuccessful (Scheme 2).[3] Thus, by

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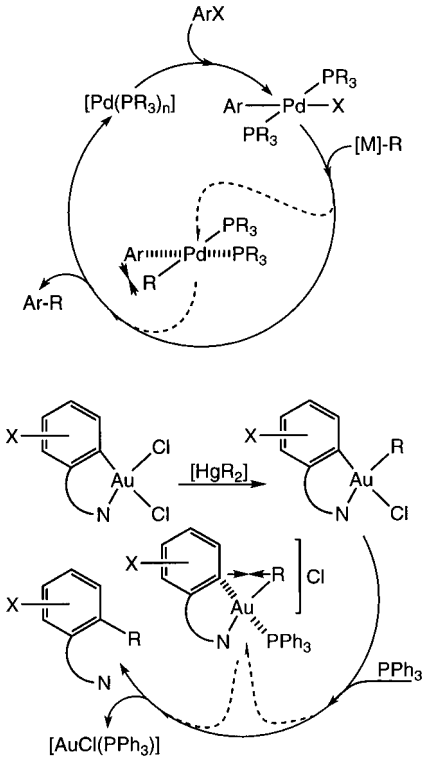
Scheme 1. Examples of C−C Coupling[a]



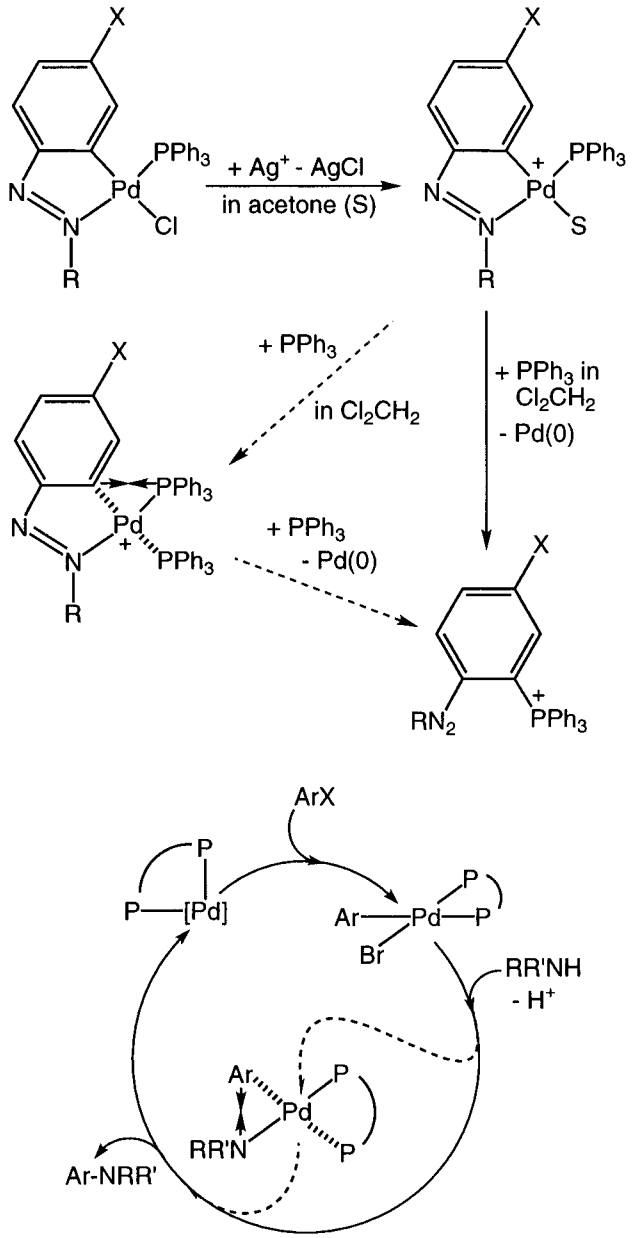
[a] The dashed arrows indicate postulated processes. The mutually *trans* aryl and phosphine ligands are indicated by |||||| and the coupling processes by →←.

reacting [Pd(C$_6$H$_3$N=NR-2,X-5)(acac)] (acac = acetylacetonate) with aqueous $HClO_4$ and PPh_3 in acetone, the complex [Pd(C$_6$H$_3$N=NR-2,X-5)(PPh_3)(acetone)]ClO_4 was isolated, even using a Ph_3P to Pd ratio of 2:1. If the reaction is attempted in dichloromethane, the C−P coupling product, phosphonium salt [Ph_3P(C$_6$H$_3$N$_2$R-2,X-5)]$^+$, was obtained instead.

There are many other examples of coupling reactions when a phosphine is forced to be coordinated *trans* to an organic group. Thus, C−P coupling products allyltriphenylphosphonium salts form when complexes [Pd(η^3-allyl)(PPh_3)$_2$]$^+$ react with excess of PPh_3.[4a] Similarly, C−N coupling products are obtained when excess of PPh_3 is added to [Pd(η^3-allyl)(μ-Cl)]$_2$, where the allyl group has a pyridyl substituent.[4b] Addition of PPh_3 to C,N-palladacyclic complexes leads to C−N coupling products.[5] Improved catalytic systems for the synthesis of secondary amines from aryl halides and primary amines have recently been developed using palladium complexes with some special phosphines (Scheme 2).[6]

In the course of this work, we have also found that, in contrast to phosphorus donor ligands, coordination of weak O-donor ligands, such as triflato, perchlorato, or aquo, *trans* to an aryl ligand is relatively easy. There

Scheme 2. Examples of C−P and C−N Couplings[a]



[a] The dashed arrows indicate postulated processes. The mutually *trans* aryl and phosphine ligands are indicated by |||||| and the coupling processes by →←.

is considerable interest in this type of palladium complexes, mainly associated with the high activity and selectivity that they show in several important reactions, such as the dimerization of methyl acrylates[7] and CO−olefin copolymerization.[8]

Experimental Section

C, H, N, and S analyses, melting point measurements, infrared and NMR spectra, and purification of solvents were carried out as described previously.[9] Pt(PPh_3)$_3$,[10] [Hg(C$_6$H$_3$N$_2$-To-2, Me-5)Cl],[11] and [Pd(C$_6$H$_3$N=NR-2, X-5)Cl]$_2$ (R = H, Me;

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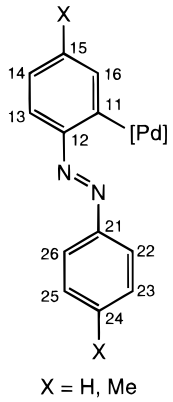
Chart 1



X = H, Me

X = Ph, To)[12] were prepared following reported procedures. Reactions were carried without precautions to exclude atmospheric moisture (except for **1a**, **2a**) and at room temperature unless otherwise stated. Chart 1 shows the atom numbering of the azoaryl groups used in the assignment of NMR resonances.

Synthesis of [Pd(C$_6$H$_3$N=NTo-2,Me-5)Cl(L)] (L = PEt$_3$ (1a), PPh$_2$Me (1b)), *trans*-[Pd(C$_6$H$_3$N$_2$To-2,Me-5)Cl(L)$_2$] (L = PEt$_3$ (2a), PPh$_2$Me (2b), L$_2$ = Bis(diphenylphosphino)-methane = dppm (2c)) and *trans*-[Pd(C$_6$H$_3$N$_2$X-2,R-5)Cl-(μ-dppm)]$_2$ (X = Me, R = To (3a); X = H, R = Ph (3b)). To a suspension of [Pd(C$_6$H$_3$N=NTo-2,Me-5)Cl]$_2$ (To = C$_6$H$_4$Me-4) or [Pd(C$_6$H$_4$N=NPh-2)Cl]$_2$ in dichloromethane (**1a**, **2a**,**c**, **3a**,**b**) or acetone (**1b**, **2b**), the corresponding ligand (L:Pd = 0.9 (**1a**), 1 (**1b**, **3a**,**b**), 2 (**2a**,**b**,**c**)) was added. The solution was stirred for 5 (**1a**), 10 (**2b**, **3a**), and 15 (**2a**) min or 2 (**1b**, **3b**) or 3 (**2c**) h. Complex **1b** was obtained by filtration of the resulting suspension. Complexes **1a**, **2c**, and **3a** were isolated by concentration of the resulting solution (2−3 mL) and addition of *n*-hexane (15−20 mL), and complexes **2a**,**b**, and **3b** were obtained by evaporation of the solvent and washing the solid with *n*-hexane. Color: yellow (**1a**,**b**), orange (**2a**), orange-red (**3a**), orange-yellow (**3b**), purple (**2b**,**c**).

1a. Yield: 197 mg, 70%. Mp: 107 °C. IR: ν(Pd−Cl) 290 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 7.90 (d, 1 H, H$_{13}$, $^3J_{HH}$ = 7.8 Hz), 7.78 (d, 2 H, H$_{22}$, H$_{26}$, $^3J_{HH}$ = 8.1 Hz), 7.24 (d, 2 H, H$_{23}$, H$_{25}$, $^3J_{HH}$ = 9.3 Hz), 7.08 (d, 1 H, H$_{14}$, $^3J_{HH}$ = 6.3 Hz), 7.06 (d, 1 H, H$_{16}$, $^4J_{PH}$ = 4.5 Hz), 2.40 (s, 6 H, Me (azotolyl)), 2.10 (dq, 8 H, CH$_2$, $^3J_{HH}$ = 7.5 Hz, $^2J_{HP}$ = 8.1 Hz), 1.22 (dt, 9 H, Me (PEt$_3$), $^3J_{HP}$ = 17.4 Hz). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$, δ, ppm): 31.34 (s). Anal. Calcd for C$_{20}$H$_{28}$N$_2$ClPPd: C, 51.18; H, 6.026; N, 5.97. Found: C, 51.35; H, 6.11; N, 5.77.

1b. Yield: 558 mg, 81%. Mp: 197 °C (dec). IR: ν(Pd−Cl) 288 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 7.83 (d, 2 H, H$_{22}$, H$_{26}$, $^3J_{HH}$ = 8.4 Hz), 7.82 (d, 1 H, H$_{13}$, $^3J_{HH}$ = 7.8 Hz), 7.8−7.4 (m, aromatic protons of PPh$_2$Me), 7.25 (d, 2 H, H$_{23}$, H$_{25}$, $^3J_{HH}$ = 8.4 Hz), 6.87 (dd, 1 H, H$_{14}$, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 0.9 Hz), 6.06 (dd, 1 H, H$_{16}$, $^4J_{HP}$ = 8.1 Hz, $^4J_{HH}$ = 0.9 Hz), 2.41 (s, 3 H, Me (azotolyl)), 2.29 (d, 3 H, Me (PPh$_2$Me), $^2J_{HP}$ = 10.8 Hz), 1.81 (s, 3 H, Me (azotolyl)). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$, δ, ppm): 25.01 (s). Anal. Calcd for C$_{27}$H$_{26}$N$_2$ClPPd: C, 58.81; H, 4.76; N, 5.08. Found: C, 58.78; H, 4.65; N, 5.18.

2a. Yield: 607 mg, 84%. Mp: 130 °C. IR: ν(Pd−Cl) 304 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 7.96 (d, 2 H, H$_{22}$, H$_{26}$, $^3J_{HH}$ = 8.4 Hz), 7.5 (d, 1 H, H$_{13}$, $^3J_{HH}$ = 8.1 Hz), 7.39 (s, 1 H, H$_{16}$), 7.27 (d, 2 H, H$_{23}$, H$_{25}$, $^3J_{HH}$ = 8.1 Hz), 6.83 (d, 1 H, H$_{14}$, $^3J_{HH}$ = 7.5 Hz), 2.41 (s, 3 H, Me (azotolyl)), 2.32 (s, 3H, Me (azotolyl)), 1.48 (m, 12 H, CH$_2$), 0.98 (apparent quintuplet, 18 H, Me (PEt$_3$)). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$, δ, ppm): 12.00 (s). Anal. Calcd for C$_{26}$H$_{43}$N$_2$ClP$_2$Pd: C, 53.15; H, 7.39; N, 4.77. Found: C, 52.76; H, 7.43; N, 4.66.

2b. Yield: 1260 mg, 87%. Mp: 146 °C. ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 7.95 (d, 2 H, H$_{22}$, H$_{26}$, $^3J_{HH}$ = 8.4 Hz), 7.6−7 (m, aromatic protons), 6.79 (s, 1 H, H$_{16}$), 6.52 (d, 1 H, H$_{14}$, $^3J_{HH}$ = 8.1 Hz), 2.47 (s, 3 H, Me (azotolyl)), 1.89 (s, 3 H, Me (azotolyl)), 1.63 (s, br, Me of PPh$_2$Me). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$, δ, ppm): 6.67 (s). Anal. Calcd for C$_{40}$H$_{39}$N$_2$ClP$_2$-Pd: C, 63.92; H, 5.24; N, 3.77. Found: C, 64.00; H, 5.26; N, 3.60.

2c. Yield: 620 mg, 95%. Mp: 144 °C. ^{1}H NMR (300 MHz, CDCl$_3$, −60 °C, δ, ppm): 7.84−6.43 (m, aromatic protons), 4.5−2.7 and 2.4−2.1 (m, CH$_2$ (dppm)), 2.516, 1.591 (Me (azotolyl), **2c**), 2.525, 2.002 (Me, [Pd(C$_6$H$_3$N$_2$To-2, Me-5)(η^1-dppm)(η^2-dppm)]Cl), 2.495, 1.838 (Me (azotolyl), **3a**). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$, −60 °C, δ, ppm) (Chart 2). **2c**: 13.53 and −29.36 ("t" of an AA′XX′ system, $|^2J_{AX} + {}^4J_{AX'}|$ = 39 Hz). [Pd(C$_6$H$_3$N$_2$-To-2, Me-5)(η^1-dppm)(η^2-dppm)]Cl: 11.16 (ddd, P$_A$, $^2J_{AM}$ = 351.6 Hz, $^2J_{AQ}$ = 51.2 Hz, $^2J_{AX}$ = 26.6 Hz), −25.44 (dd, P$_M$, $^2J_{MX}$ = 69.2 Hz), −32.62 (d, P$_Q$), −33.79 (dd, P$_X$). **3a**: 6.63 (s). dppm: −25.90. Anal. Calcd for C$_{64}$H$_{57}$N$_2$P$_4$Pd: C, 68.51; H, 5.15; N, 2.53. Found: C, 68.63; H, 5.14; N, 2.50. Single crystals of **2c** were obtained by slow diffusion of *n*-hexane into a solution of **2c** in dichloromethane.

3a. Yield: 564 mg, 87%. Mp: 157 °C. ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 7.54−6.58 (m, aromatic protons), 4.11−3.60 (dm, 2 H, CH$_2$ (dppm)), 2.48 (s, 3 H, Me (azotolyl)), 1.95 (s, 3 H, Me (azotolyl)), 1.27 (m, CH$_2$ *n*-hexane), 0.88 (t, Me *n*-hexane, $^3J_{HH}$ = 7.2 Hz). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$, δ, ppm): 6.68. Anal. Calcd for C$_{78}$H$_{70}$Cl$_2$N$_4$P$_4$Pd$_2$·0.17*n*-hexane: C, 63.87; H, 4.91; N, 3.77. Found: C, 64.04; H, 4.81; N, 3.81.

3b. Yield: 366 mg, 95%. Mp: 188 °C. ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 7.64−6.75 (m, aromatic protons), 3.99−3.91 (m, 2H, CH$_2$ of dppm). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$, δ, ppm): 5.88. Anal. Calcd for C$_{74}$H$_{62}$Cl$_2$N$_4$P$_4$Pd$_2$: C, 62.81; H, 4.42; N, 3.96. Found: C, 62.57; H, 4.64; N, 4.33.

Synthesis of [Pd(C$_6$H$_3$N=NTo-2,Me-5)(X)(L)] (X = OTf (OTf = CF$_3$SO$_3$), L = PEt$_3$ (4a), PPh$_2$Me (4b); X = ClO$_4$, L = PPh$_2$Me (4b′)), *trans*-[Pd(C$_6$H$_3$N$_2$To-2,Me-5)(OTf)(PEt$_3$)$_2$] (5), [Pd(C$_6$H$_3$N$_2$To-2,Me-5)(η^1-dppm)(η^2-dppm)]TfO (6), [Pd(C$_6$H$_3$N=NTo-2,Me-5)(η^2-dppm)]OTf (7a). To a solution of the corresponding chloro complex in acetone (10−15 mL), Tl(OTf) or AgClO$_4$ was added (molar ratio X:Pd = 1). The resulting suspension was stirred for 30 (**4a**, **5**) min or 1 (**4b′**, **7a**) or 2 (**4b**, **6**) h. The solvent was evaporated, and the residue was extracted with dichloromethane (10 mL) and then filtered through Celite. The resulting solution was concentrated (2 mL), and addition of *n*-hexane (10−15 mL, **4a**,**b**) or diethyl ether (25 mL, **7a**) precipitated the complexes. Alternatively, the solution was concentrated to dryness and the solid washed with diethyl ether to give **4b′, 5, 6**. Color: yellow (**4a**,**b**,**b′**, **7a**), red (**5**), orange (**6**).

4a. Yield: 210.0 mg, 87%. Mp: 149 °C. ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 7.86 (d, 1 H, H$_{13}$, $^3J_{HH}$ = 7.8 Hz), 7.70 (d, 2 H, H$_{22}$, H$_{26}$, $^3J_{HH}$ = 8.4 Hz), 7.23 (d, 2 H, H$_{23}$, H$_{25}$, $^3J_{HH}$ = 8.4 Hz), 7.10 (d, 1 H, H$_{14}$, $^3J_{HH}$ = 7.5 Hz), 6.91 (d, 1 H, H$_{16}$, $^4J_{PH}$ = 6.0 Hz), 2.40 (s, 3 H, Me (azotolyl)), 2.37 (s, 3 H, Me (azotolyl)), 2.08 (dq, 6 H, CH$_2$ (PEt$_3$), $^2J_{PH}$ = 7.5 Hz, $^3J_{HH}$ = 7.5 Hz), 1.24 (dt, 9 H, Me (PEt$_3$), $^3J_{HH}$ = 7.8 Hz, $^3J_{PH}$ = 17.4 Hz). ^{31}P{^{1}H} NMR (121 CDCl$_3$, δ, ppm): 32.09 (s). Anal. Calcd for C$_{21}$H$_{28}$F$_3$N$_2$O$_3$PPdS: C, 43.26; H, 4.85; N, 4.81; S, 5.50. Found: C, 43.77; H, 4.95; N, 4.91; S, 5.56.

4b. Yield: 91 mg, 74%. Mp: 144 °C. ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 7.83−7.26 (m, 15 H, aromatic protons), 6.92 (d, 1 H, H$_{14}$, $^3J_{HH}$ = 7.2 Hz), 6.21 (d, 1 H, H$_{16}$, $^4J_{HP}$ = 9.3 Hz), 2.42 (s, 3 H, Me (azotolyl)), 2.21 (d, 3 H, Me of PPh$_2$Me, $^2J_{HP}$ = 11.1 Hz), 1.87 (s, 3 H, Me (azotolyl)). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$, δ, ppm): 25.30 (s). Anal. Calcd for C$_{28}$H$_{26}$-F$_3$N$_2$O$_3$PPdS: C, 50.57; H, 3.95; N, 4.22; S, 4.82. Found: C, 50.70; H, 4.03; N, 4.18; S, 4.58.

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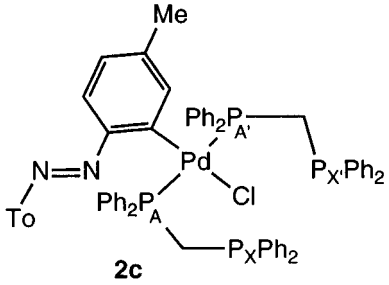
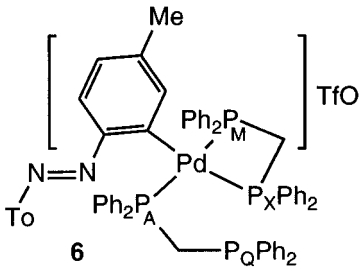
Chart 2



2c



6

4b′. Yield: 288 mg, 85%. Mp: 173 °C. IR: ν_{sym}(Cl−O) 1168, 1148, 1128, 1104 cm^{-1}; ν_{asym}(Cl−O) 618, 608 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.1−7.30 (m, 15 H, aromatic protons), 6.94 (d, 1 H, H_{14}, $^3J_{HH}$ = 7.8 Hz), 6.20 (d, 1 H, H_{16}, $^4J_{HP}$ = 7.8 Hz), 2.42 (s, 3 H, Me (azotolyl)), 2.21 (d, 3 H, Me of PPh_2Me, $^2J_{PH}$ = 11.1 Hz), 1.86 (s, 3 H, Me (azotolyl)). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, δ): 25.91 (s). Anal. Calcd for $C_{27}H_{26}ClN_2O_4PPd$: C, 52.69; H, 4.27; N, 4.55. Found: C, 52.64; H,4.24; N, 4.36. Single crystals of **4b′** were obtained by slow diffusion of diethyl ether into a solution of **4b′** in dichloromethane.

5. Yield: 228 mg, 73%. Mp: 108 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.01 (d, 2 H, H_{22}, H_{26}, $^3J_{HH}$ = 8.4 Hz), 7.57 (d, 1 H, H_{13}, $^3J_{HH}$ = 8.1 Hz), 7.33 (d, 2 H, H_{23}, H_{25}, $^3J_{HH}$ = 8.1 Hz), 7.31 (s, 1 H, H_{16}), 6.90 (d, 1 H, H_{14}, $^3J_{HH}$ = 8.1 Hz), 2.43 (s, 3 H, Me (azotolyl)), 2.34 (s, 3 H, Me (azotolyl)), 1.43 (m, 12 H, CH_2 (PEt_3)), 0.98 (apparent quintuplet, 18 H, Me (PEt_3)). ^{31}P-{^{1}H} NMR (121 MHz, $CDCl_3$, δ, ppm): 10.91 (s). Anal. Calcd for $C_{27}H_{43}F_3N_2O_3P_2PdS$: C, 46.23; H, 6.19; N, 4.03; S, 4.57. Found: C, 46.08; H, 6.48; N, 4.10; S, 4.48. Single crystals of **5** were obtained by slow diffusion of n-hexane into a solution of **5** in diethyl ether.

6. Yield: 265 mg, 85%. Mp: 133 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.68−6.90 (m, aromatic protons), 4.37 (m, br, 1 H, CH_2 (dppm)), 4.1 (m, br, 1 H, CH_2 (dppm)), 2.53 (s, 3 H, Me (azotolyl)), 2.33 (m, br, 2 H, CH_2 (dppm)), 2.00 (s, 3 H, Me (azotolyl)). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, δ, ppm, −60 °C) (Chart 2): 11.68 (ddd, P_A, $^2J_{AM}$ = 353.4 Hz, $^2J_{AQ}$ = 50.7 Hz, $^2J_{AX}$ = 26.1 Hz), −24.85 (dd, P_M, $^2J_{MX}$ = 61.9 Hz), −32.52 (d, P_Q), −33.32 (dd, P_X). Anal. Calcd for $C_{65}H_{57}F_3N_2O_3P_4PdS$: C, 63.28; H, 4.67; N, 2.27; S, 2.60. Found: C, 63.21; H, 4.73; N, 2.26; S, 2.89. Single crystals of **6** were obtained by slow diffusion of *n*-hexane into a solution of **6** in dichloromethane.

7a. Yield: 178 mg, 76%. Mp: 206 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.96−6.44 (m, aromatic protons), 4.47 (dd, CH_2 of dppm, $^2J_{PH}$ = 11.8 and 8.3 Hz), 2.29 (s, 3 H, Me (azotolyl)), 2.01 (s, 3 H, Me (azotolyl)). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, δ, ppm): −5.35 (d, $P_{trans\ to\ N}$, $^2J_{PP}$ = 67.7 Hz), −30.60 (d, $P_{trans\ to\ C}$). Anal. Calcd for $C_{40}H_{35}F_3N_2O_3P_2PdS$: C, 56.57; H, 4.16; N, 3.30; S, 3.77. Found: C, 56.92; H, 4.23; N, 3.23; S, 3.60.

Synthesis of [Pd(C_6H_3N=NTo-2,Me-5)(η^2-dppm)]SbF_6 (7a′) and [Pd(C_6H_4N=NPh-2)(η^2-dppm)]SbF_6 (7b). To a solution of [Pd(C_6H_3N=NTo-2,Me-5)Cl]$_2$ or [Pd(C_6H_4N=NPh-2)Cl]$_2$ in acetone (20 mL) was added $AgSbF_6$ (molar ratio Pd:Ag = 1). The resulting suspension was refluxed for 30 min. The AgCl formed was removed by filtration thorough Celite, and dppm (molar ratio Pd:dppm = 1) was added to the resulting solution. The solution was stirred at room temperature for 1 h, evaporated almost to dryness, and diethyl ether (20 mL) was added to give **7a′** or **7b** as an orange solid.

7a′. Yield: 230 mg, 60%. Mp: 223 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.94 (dd, H_{13}, $^3J_{HH}$ = 7.5 Hz, $^5J_{PH}$ = 3.60 Hz), 7.79−7.72 (m, aromatic protons), 7.59−7.31 (m, aromatic protons), 7.09 (d, H_{14}, $^3J_{HH}$ = 7.8 Hz), 6.93 (d, H_{23}, H_{25}, $^3J_{HH}$ = 8.4 Hz), 6.46 (t, H_{16}, $^4J_{PH}$ = 9 Hz), 4.35 (dd, CH_2 of dppm, $^2J_{PH}$ = 11.4 and 8.1 Hz), 2.30 (s, 3 H, Me(azotolyl)), 2.01 (s, 3 H, Me(dmpap)). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, δ, ppm): −4.76 (d, $^2J_{PP}$ = 67.27 Hz), −30.06 (d, $^2J_{PP}$ = 67.39 Hz). Anal. Calcd for $C_{39}H_{35}F_6N_2P_2PdSb$: C, 50.05; H, 3.78; N, 2.99. Found: C, 50.14; H, 3.75; N, 2.94.

7b. Yield: 250 mg, 69%. Mp: 226 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.12−6.75 (m, aromatic protons), 4.34 (dd, CH_2 of dppm, $^2J_{PH}$ = 11.4 and 8.7 Hz). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, δ, ppm): −6.72 (d, $^2J_{PP}$ = 69.57 Hz), −32.43 (d, $^2J_{PP}$ = 68.24 Hz). Anal. Calcd for $C_{37}H_{31}F_6N_2P_2PdSb$: C, 48.96; H, 3.44; N, 3.09. Found: C, 49.04; H, 3.29; N, 3.03.

Synthesis of [Pd($C_6H_3N_2$To-2,Me-5)(PPh_2Me)$_3$]ClO_4 (8). To a solution of **4b′** (209 mg, 0.34 mmol) in chloroform (6 mL) was added PPh_2Me (128 μL, 0.68 mmol). The solution was stirred for 2 h and then concentrated to dryness. Addition of diethyl ether (10 mL) and vigorous stirring for 20 min gave **8** as an orange solid. Yield: 300 mg, 87%. Mp: 116 °C. IR: ν(Cl−O) 1093 cm^{-1}; ν(Cl−O) 623 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.90 (d, 2 H, H_{22}, H_{26}, $^3J_{HH}$ = 8.1 Hz), 7.53 (d, 2 H, H_{23}, H_{25}, $^3J_{HH}$ = 7.8 Hz), 7.46−6.80 (m, aromatic protons), 6.65 (d, 1 H, H_{13}, $^3J_{HH}$ = 6.9 Hz), 6.46 (s, 1 H, H_{14}, $^3J_{HH}$ = 8.1 Hz), 2.61 (s, 3 H, Me (azotolyl)), 1.79 (s, 3 H, Me (azotolyl)), 1.62 (d, 3 H, Me (PPh_2Me), $^2J_{PH}$ = 6.9 Hz), 1.37 (s, br, 6H, 2 Me of PPh_2Me). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, δ, ppm): 6.24 (d, $^2J_{PP}$ = 36 Hz), −2.63 (t). Anal. Calcd for $C_{53}H_{52}ClN_2O_4P_3Pd$: C, 62.66; H, 5.17; N, 2.76. Found: C, 61.67; H, 5.07; N, 2.71.

Synthesis of [Pd(C_6H_3N=NTo-2,Me-5)(OH_2···OTf)(PEt_3)] (9). Single crystals of **9** were obtained by slow diffusion of n-pentane into a solution of **4a** in dichloromethane. Mp: 171 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.87 (d, 1 H, H_{13}, $^3J_{HH}$ = 7.8 Hz), 7.67 (d, 2 H, H_{22}, H_{26}, $^3J_{HH}$ = 8.4 Hz), 7.28 (d, 2 H, H_{23}, H_{25}, $^3J_{HH}$ = 8.4 Hz), 7.11 (d, 1 H, H_{14}, $^3J_{HH}$ = 7.8 Hz), 6.87 (d, 1 H, H_{16}, $^4J_{PH}$ = 6.1 Hz), 2.76 (s, H_2O), 2.41 (s, 3 H, Me (azotolyl)), 2.40 (s, 3 H, Me (azotolyl)), 2.05 (dq, 6 H, CH_2 (PEt_3), $^2J_{PH}$ = 9.9 Hz, $^3J_{HH}$ = 7.5 Hz), 1.25 (dt, 9 H, Me (PEt_3), $^3J_{HH}$ = 7.5 Hz, $^3J_{PH}$ = 17.7 Hz). ^{31}P{^{1}H} NMR (121 $CDCl_3$, δ, ppm): 21.65 (s). Anal. Calcd for $C_{21}H_{30}F_3N_2O_4PPdS$: C, 41.95; H, 5.04; N, 4.70; S, 5.33. Found: C, 41.85; H, 5.05; N, 4.69; S, 5.37.

Synthesis of [Pd(C_6H_3N=NTo-2,Me-5){(μ_3-OH_2)(···OCl-O_3)(···OH_2)}(PPh_3)] (10). Single crystals of this compound were obtained by slow diffusion of *n*-hexane into a solution of [Pd($C_6H_3N_2$To-2,Me-5)(PPh_3)(acetone)]ClO_4 in dichloromethane.[3] ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.75−7.26 (m, aromatic protons), 6.93 (d, H_{14}, $^3J_{HH}$ = 7.8 Hz), 6.16 (d, H_{16}, $^3J_{HP}$ = 7.8 Hz), 2.405 (s, 3 H, Me(azotolyl)), 1.78 (s, 4 H, H_2O), 1.76 (s, 3 H, Me(dmpap)). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, δ, ppm): 41.47. Anal. Calcd for $C_{32}H_{32}ClN_2O_6PPd$: C, 53.87; H, 4.53; N, 3.93. Found: C, 53.81; H, 4.35; N, 3.84.

Synthesis of [Pd(C_6H_4N=NPh-2)(η^2-dppmO)]SbF_6 (11). To a suspension of [Pd(C_6H_4N=NPh-2)(μ-Cl)]$_2$ (73 mg, 0.113 mmol) in acetone (10 mL) was added $AgSbF_6$ (78 mg, 0.227 mmol). The resulting suspension was refluxed for 1 h and then concentrated to dryness; dichloromethane (20 mL) was added, and the suspension was filtered thorough Celite. The ligand dppmO was added to the resulting solution, the mixture stirred

for 1 h, and then was concentrated to 2 mL. Addition of diethyl ether (25 mL) gave **11** as a yellow solid. Yield: 100 mg, 96%. Mp: 230 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.37−6.45 (m, aromatic protons), 3.86 (dd, CH_2, $^2J_{PH}$ = 12.00 and 9.9 Hz). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, δ, ppm): 55.56 (d, $^2J_{PP}$ = 16.0 Hz), 32.30 (d). Anal. Calcd for $C_{37}H_{31}F_6N_2OP_2PdSb$: C, 48.10; H, 3.39; N, 3.03. Found: C, 48.14; H, 3.35; N, 2.64. Single crystals of **11** were obtained from MeOH.

Synthesis of *trans*-[Pt(C$_6$H$_3$N$_2$To-2,Me-5)Cl(PPh$_3$)$_2$] (12). To a suspension of [Pt(PPh$_3$)$_3$] (277 mg, 0.282 mmol) in toluene (20 mL) was added [Hg(C$_6$H$_3$N$_2$To-2,Me-5)Cl] (126 mg, 0.283 mmol). The resulting suspension was refluxed for 15 min and then concentrated to dryness; the residue was extracted with dichloromethane (30 mL) and filtered thorough Celite to remove Hg. The solution was concentrated to 1 mL. Addition of diethyl ether (8 mL) gave a solid that was a mixture. The mother liquor was concentrated to dryness; addition of diethyl ether (4 mL) and *n*-pentane (8 mL) gave **12** as an orange solid. Yield: 180 mg, 66%. Mp: 168 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.67−6.4 (m, aromatic protons), 2.46 (s, 3 H, Me (azotolyl)), 1.71 (s, 3 H, Me (azotolyl)). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, δ, ppm): 25 °C, 23.54 (br); −60 °C, 23.30 (s, $^1J_{Pt,P}$ = 1554.5 Hz). Anal. Calcd for $C_{50}H_{43}ClN_2P_2Pt$: C, 62.26; H, 4.50; N, 2.90. Found: C, 62.15; H, 4.46; N, 2.75.

Synthesis of [Pt(C$_6$H$_3$N=NTo-2,Me-5)(PPh$_3$)$_2$]TfO (13). To a solution of **12** (125 mg, 0.130 mmol) in acetone (10 mL) was added Tl(OTf) (47 mg, 0.133 mmol). The resulting suspension was stirred for 30 min. The suspension was concentrated to dryness, and the residue was extracted with dichloromethane (20 mL); the extract was filtered through Celite and concentrated to 1 mL. Addition of diethyl ether (8 mL) gave **13** as an orange solid. Yield: 100 mg, 72%. Mp: 203 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.94−6.42 (m, aromatic protons), 2.18 (s, 3 H, Me (azotolyl)), 1.82 (s, 3 H, Me (azotolyl)). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, δ, ppm): 19.46 (d, $^2J_{PP}$ = 16.5 Hz, $^1J_{PPt}$ = 2067 Hz), 15.03 (d, $^2J_{PP}$ = 16.9 Hz, $^1J_{PPt}$ = 3817 Hz). Anal. Calcd for $C_{51}H_{43}F_3N_2O_3P_2PtS$: C, 56.82; H, 4.03; N, 2.60; S, 2.97. Found: C, 56.86; H, 3.99; N, 2.560; S, 2.74.

X-ray Structure Determinations. Crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of the diffractometer (Stoe STADI-4 for **4b′**, **5**, and **6**, otherwise Siemens P4, both with a Siemens LT-2 low-temperature attachment). Data were collected using monochromated Mo Kα radiation in ω/θ (**4b′**, **5**, **6**), otherwise ω, mode. Cell constants were refined from $\pm\omega$ angles (**4b′**, **5**, **6**) or setting angles of ca. 50 reflections up to 2θ = 23°. Absorption corrections were applied for **2c** and **10** with SHELXA (G. M. Sheldrick, unpublished report) and for **5** and **9** on the basis of ψ-scans. Structures were solved by direct methods (**4b′**), otherwise by the heavy atom method, and refined anisotropically on F^2 (program SHELXL-93, G. M. Sheldrick, University of Göttingen). Restraints to local aromatic ring symmetry or light atom displacement factor components were applied in some cases. Hydrogen atoms were included using rigid methyl groups or a riding model. Full details are given in Table 1. *Particular features*: **2c** contains a dichloromethane molecule badly disordered over an inversion center. One terminal ethyl carbon (C32) of **5** is disordered over two positions. For **4b′**, the absolute structure was determined by an *x* refinement, with $x = -0.06(2)$. In **6**, the uncoordinated PPh_2 group shows significant residual electron density and may be slightly disordered. The phenyl group C31−36 of compound **7** is disordered over two positions, and the triflate anion is badly resolved. The water H of compounds **9** and **10** were located in difference syntheses and refined using distance restraints (command SADI). Compound **11** crystallizes with two molecules of methanol, which are badly resolved and do not enter into H bonding interactions.

Results

Scheme 3 presents our reaction sequences. In some cases, salts with different anions were prepared in order to obtain crystals suitable for X-ray structure analysis. Our interest in obtaining useful intermediates for preparing complexes with a phosphine ligand *trans* to the aryl group prompted us to isolate interesting complexes with weak donor ligands, such as triflato and perchlorato, and new types of aquo complexes of palladium. Thus, the reaction of [Pd(C$_6$H$_3$N=NR-2,X-5)Cl]$_2$, orthometalation products of azobenzene or azotoluene, with phosphines gives [Pd(C$_6$H$_3$N=NTo-2,Me-5)Cl(L)] (To = C$_6$H$_4$Me-4, L = PEt$_3$ (**1a**), PPh$_2$Me (**1b**)) when the reaction is carried out with a 1:2 molar ratio or *trans*-[Pd(C$_6$H$_3$N$_2$To-2,Me-5)ClL$_2$] (L = PEt$_3$ (**2a**), PPh$_2$Me (**2b**), bis(diphenylphosphino)methane = dppm (**2c**)) with a 1:4 molar ratio. Complexes of both types have been previously reported.[13] The reaction with dppm in a 1:1 molar ratio gives *trans*-[Pd(C$_6$H$_3$N$_2$X-2,R-5)Cl(μ_2-dppm)]$_2$ (X = Me, R = To (**3a**); X = H, R = Ph (**3b**)). Complex **3b** crystallizes with *n*-hexane, which could not be removed. It is known that some dppm complexes tend to occlude solvent molecules.[14] The reaction of **1a** or **1b** with Tl(OTf) (OTf = O$_3$SCF$_3$) or **1b** with AgClO$_4$ gives [Pd(C$_6$H$_3$N=NTo-2,Me-5)(Y)(L)] (L = PEt$_3$, Y = TfO (**4a**); L = PPh$_2$Me, Y = TfO (**4b**), ClO$_4$ (**4b′**)). Tl(OTf) reacts with **2a** to give *trans*-[Pd(C$_6$H$_3$N$_2$-To-2, Me-5)(OTf)(PEt$_3$)] (**5**), in which the weak donor triflate anion is coordinated to palladium *trans* to the aryl group, while it reacts with **2c** or **3a** to give [Pd(C$_6$H$_3$N$_2$To-2,Me-5)(η^1-dppm)(η^2-dppm)]TfO (**6**) or [Pd(C$_6$H$_3$N=NTo-2,Me-5)(η^2-dppm)]TfO (**7a**), respectively. The SbF_6 salt analogous to **7a** was prepared directly starting from [Pd(C$_6$H$_3$N=NTo-2,Me-5)Cl]$_2$; reaction with $AgSbF_6$ (1:2) in acetone, removal of AgCl and addition of dppm (Pd:dppm = 1:1) gives [Pd(C$_6$H$_3$N=NTo-2,Me-5)(η^2-dppm)]SbF_6 (**7a′**). The complex [Pd(C$_6$H$_4$N=NPh-2)(η^2-dppm)]SbF_6 (**7b**) was obtained similarly. The synthesis of complex [Pd(C$_6$H$_4$N=NPh-2)(η^2-dppm)]ClO_4 in a similar manner was already known.[13c] Complex **2b** reacts with $AgClO_4$ to give a mixture of [Pd(C$_6$H$_3$N$_2$To-2,Me-5)(PPh$_2$Me)$_3$]ClO_4 (**8**, see below) and **4b**. However, $AgSbF_6$ reacts with **2c** to give a 1:1 mixture of **3a** and [Ag(dppm)]$_2$(SbF_6)$_2$.

From **4b′**, the perchlorato ligand is displaced by PPh$_2$Me and the aryl chelate ring is opened to give [Pd(C$_6$H$_3$N$_2$To-2, Me-5)(PPh$_2$Me)$_3$]ClO_4 (**8**), which also contains *trans* aryl and phosphine ligands. Attempts to prepare the phosphonium salt [MePh$_2$P(C$_6$H$_3$N$_2$Me-2,-To-5)]$^+$ via C−P coupling[3] by refluxing **8** in chloroform (7 h) or [Et$_3$P(C$_6$H$_3$N$_2$Me-2,To-5)]$^+$ by refluxing complex **5** with Et$_3$P (1:1, 4 h) in chloroform failed because

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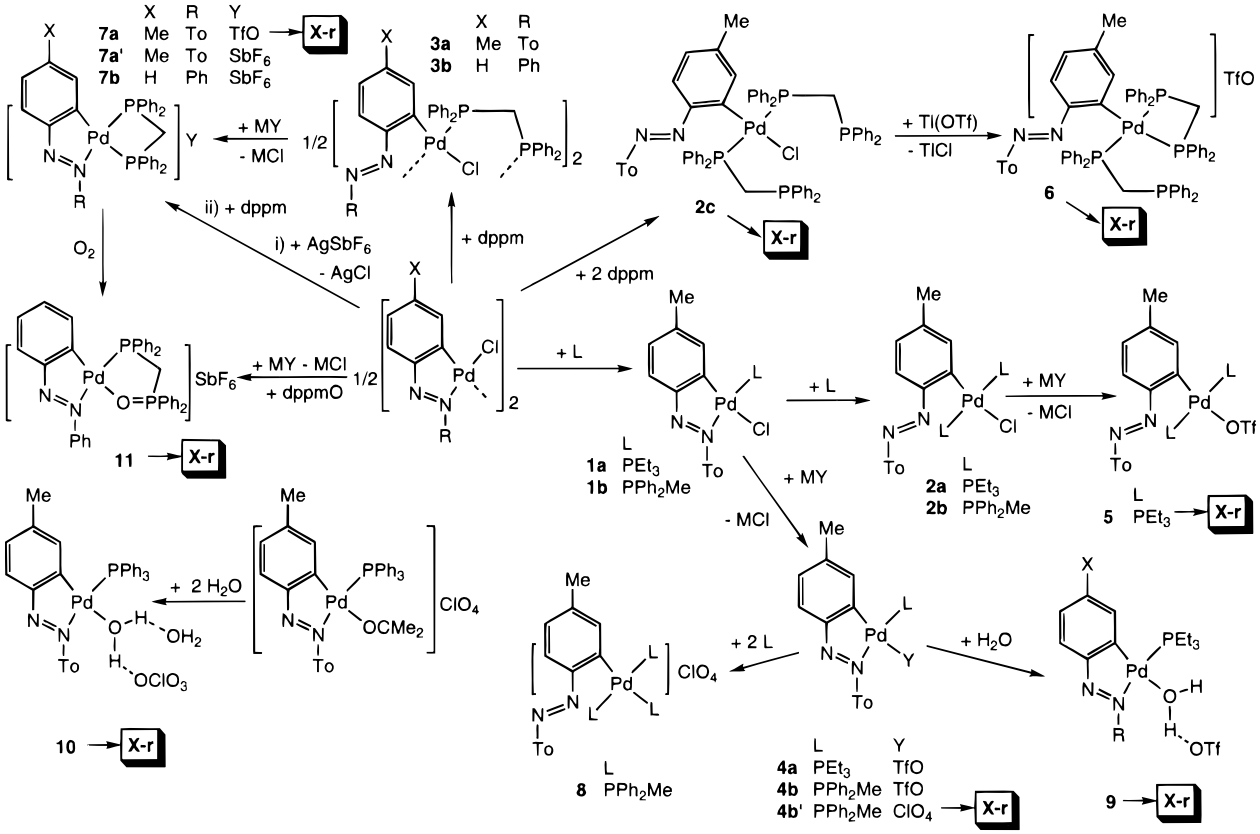
Table 1. Crystal Data and Structure Refinement

	2c·$^1/_2$CH$_2$Cl$_2$	**4b′**	**5**	**6**	**7a**	**9**	**10**	**11·2CH$_3$OH**
formula	$C_{64.5}H_2H_{58}Cl_2N_2P_4Pd$	$C_{27}H_{26}ClN_2O_4PPd$	$C_{27}H_{43}F_3N_2O_3P_2PdS$	$C_{65}H_{57}F_3N_2O_3P_4PdS$	$C_{40}H_{35}F_3N_2O_3P_2PdS$	$C_{21}H_{30}F_3N_2O_4PPdS$	$C_{32}H_{32}ClN_2O_6PPd$	$C_{39}H_{39}F_6N_2O_3P_2PdSb$
M_r	1162.31	615.32	701.03	1233.47	849.10	600.90	713.42	987.81
cryst habit	red plate	orange tablet	red prism	orange plate	yellow tablet	yellow tablet	yellow plate	yellow tablet
cryst size (mm)	1.0 × 0.4 × 0.1	0.8 × 0.55 × 0.35	0.38 × 0.38 × 0.3	0.5 × 0.4 × 0.15	0.6 × 0.25 × 0.1	0.5 × 0.4 × 0.25	0.7 × 0.3 × 0.08	0.4 × 0.2 × 0.06
cryst syst	triclinic	orthorhombic	orthorhombic	triclinic	triclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$	$P2_12_12_1$	$Pbca$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
cell constants								
a (Å)	10.399(2)	10.565(2)	15.116(3)	12.378(3)	12.006(3)	11.3002(12)	9.188(2)	12.478(3)
b (Å)	12.353(2)	13.261(3)	20.455(4)	13.777(4)	12.894(3)	10.420(2)	13.274(3)	12.751(3)
c (Å)	23.665(3)	18.70042	21.316(4)	18.945(5)	14.865(4)	22.002(3)	14.866(3)	12.796(3)
α (deg)	88.771(10)	90	90	83.18(2)	69.28(2)	90	111.28(2)	82.20(2)
β (deg)	79.829(10)	90	90	76.11(2)	67.92(2)	96.285(11)	92.92(2)	77.72(2)
γ (deg)	75.468(12)	90	90	70.36(2)	65.84(2)	90	109.35(2)	84.47(2)
V (Å^3)	2895.6	2619.8	6591	2951.3	1890.3	2575.1	1563.5	1.9661
Z	2	4	8	2	2	4	2	2
D_x (Mg m^{-3})	1.333	1.560	1.413	1.388	1.492	1.550	1.515	1.669
μ (mm^{-1})	0.57	0.91	0.77	0.52	0.69	0.91	0.78	1.29
F(000)	1198	1248	2896	1268	864	1224	728	984
T (°C)	−100	−130	−130	−130	−100	−110	−100	−100
$2\theta_{max}$	50	55	50	50	45	50	50	45
no. of rflns								
measd	10 711	7153	9465	14 456	5099	4803	11 042	5122
unique	10 129	6005	5813	10 400	4821	4528	5318	5087
transmissions	0.72−0.96	no abs corr	0.73−0.78	no abs corr	no abs corr	0.72-0.75	0.63−0.94	no abs corr
R_{int}	0.067	0.021	0.042	0.124	0.042	0.029	0.048	0.033
no. of parameters	667	328	357	714	441	309	402	467
no. of restraints	529	0	280	636	390	199	316	366
$R_w(F^2$, all reflns)	0.091	0.064	0.130	0.139	0.225	0.103	0.069	0.122
$R(F, >4\sigma(F))$	0.036	0.027	0.050	0.057	0.081	0.044	0.034	0.050
S	1.01	1.05	1.09	1.03	1.05	1.06	0.90	0.90
max Δ/σ	0.3	0.004	0.001	0.001	0.01	0.004	<0.001	0.007
max $\Delta\rho$ (e Å^{-3})	0.76	0.50	0.76	1.7	3.0	0.61	0.47	1.4

Scheme 3

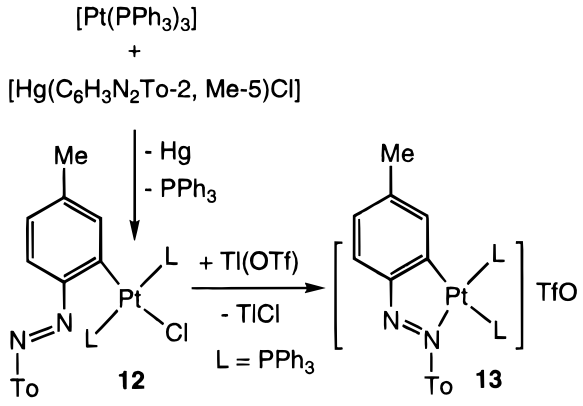


metallic palladium was not observed. Instead, a mixture that could not be separated or an intractable oil was obtained.

Attempts to grow single crystals of **4a** or [Pd(C$_6$H$_3$N=NTo-2,Me-5)(PPh$_3$)(Me$_2$CO)]ClO$_4$ (Scheme 2) or **7b** in air led to various complexes. In the first case, an insertion of one molecule of water into the Pd−OTf bond occurs to give the complex [Pd(C$_6$H$_3$N=NTo-2,Me-5)(OH$_2$···OTf)(PEt$_3$)] (**9**). In the second case, the acetone ligand is replaced by two molecules of water; one is coordinated to palladium and, via hydrogen bonding, bridges the other water molecule and the perchlorate anion to give [Pd(C$_6$H$_3$N=NTo-2,Me-5){(μ_3-OH$_2$)(···OClO$_3$)(···OH$_2$)}(PPh$_3$)] (**10**). Finally, aerial oxidation of **7b** takes place to give **11** containing dppm monoxide (dppmO). This complex can also be obtained by reacting [Pd(C$_6$H$_3$N=NR-2,X-5)Cl]$_2$ with AgSbF$_6$ and dppmO.

The orthoplatination of azobenzene has been achieved by reacting azobenzene with K$_2$[PtCl$_4$][12] or with PtCl$_2$,[13a] but in very low yields. The reaction between [Pt(PPh$_3$)$_3$] and [Hg(C$_6$H$_4$N$_2$Ph-2)Cl] was reported to give [Pt(C$_6$H$_4$N=NPh-2)Cl(PPh$_3$)].[15] However, by reacting [Pt(PPh$_3$)$_3$] and [Hg(C$_6$H$_3$N$_2$To-2,Me-5)Cl], we obtain a different type of product, *trans*-[Pt(C$_6$H$_3$N$_2$To-2,Me-5)Cl(PPh$_3$)$_2$] (**12**) (Scheme 4). The synthesis of [Pt(C$_6$H$_4$N$_2$Ph-2)Cl(PEt$_3$)$_2$] has been reported by treating [Hg(C$_6$H$_4$N$_2$Ph-2)$_2$] with *cis*-[PtCl$_2$(PEt$_3$)$_2$], but in low yield.[13a] By treating **12** with Tl(OTf), the complex [Pt(C$_6$H$_3$N=NTo-2,Me-5)(PPh$_3$)$_2$]TfO (**13**) can be isolated. We have previously reported that the related palladium complex could not be isolated, and instead, the phosphonium salt [Ph$_3$P(C$_6$H$_3$N$_2$R-2,X-5)]$^+$ was obtained.[3] This phosphonium salt was not observed when **13** was reacted with PPh$_3$ (in the NMR tube). The observed mixture of compounds gave **13** after removing the solvent.

Scheme 4



(15) This product was reported in a review (Sokolov, V. I.; Reutov, O. A. *Coord. Chem. Rev.* **1978**, *27*, 89), however, it was not obtained in pure form and, consequently, was never published. Private communication of V. I. Sokolov.

Discussion

Structures of Complexes. The crystal structures of complexes **2c**, **4b′**, **5**, **6**, **7a**, **9**, **10**, and **11** have been solved. Complex **2c** (Figure 1 and Table 2) shows both dppm ligands acting as monocoordinate and in *trans* positions. A short contact between N(2) and Pd (2.634(2) Å) is observed, which however does not significantly

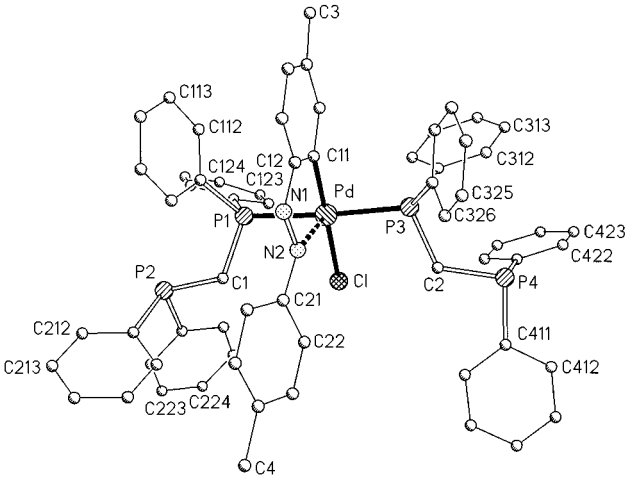


Figure 1. Crystal structure of complex **2c**.

distort the planar coordination around the metal atom (mean deviation of five atoms from best plane 0.03Å). A similar situation occurs in complex **5** (Figure 2 and Table 2); however, the Pd−N(2) bond is shorter (2.576(4) Å) and, correspondingly, the square planar coordination of palladium is distorted to give two planes about the axis C11,O1,Pd with an interplanar angle of 21° (cf. P1−Pd−P2 163.66(6)°). Such weak interactions have been observed in a few other palladium complexes; the range of observed Pd···N distances is 2.523(8)−2.805(5) Å.[16] A genuinely trigonal bipyramidal Pd(II) complex shows an axial Pd−N bond distance of 2.23(2) Å.[17]

As far as we are aware, only two crystal structures of palladium(II) triflato complexes have been reported.[18,19] The Pd−O(1) bond distance in **5** (2.184(4) Å) is intermediate between that in the only similar reported complex [Pd{C(=O)$(CH_2)_2$$NEt_2$}(OTf)($NEt_2$H)] (2.271(7) Å)[19] and that in [Pd(OTf···HOH···OTf){1,3-bis(diphenylphosphino)propane}] (2.159(3) Å), where the triflato ligand is hydrogen bonded to a coordinated water molecule.[18] This trend in bond lengths can be attributed to the decrease in the *trans* influence in the series (diethylamino)propionyl, azophenyl, and phosphine ligands. As in reference 19, there are C−H···O contacts that may be described as hydrogen bonds: C43−H43A···O2 (0.5 + *x*, 1.5 − *y*, 1 − *z*), with C···O 3.38 Å, H···O 2.51 Å and C-H···O 146°, and C33−H33B···O3 (−0.5 + *x*, 1.5 − *y*, 1 − *z*; 3.41, 2.44 Å, 168°). The S−O(1) bond distance, 1.453(4) Å, is significantly longer than the other two bond lengths between the sulfur atom and the noncoordinated oxygen atoms [1.419(4), 1.428(4) Å], whereas in [Pd{C(=O)$(CH_2)_2$$NEt_2$}(OTf)($NEt_2$H)], the three S−O bond distances are not significantly different.[19]

In complex **4b′** (Figure 3 and Table 2), the expected coordination of PPh_2Me *cis* to the carbon atom is observed, as is the monocoordination of the perchlorato ligand. As far as we are aware, only two X-ray crystal structures of perchlorato palladium(II) complexes have been previously reported.[20,21] Although both are neutral aryl complexes and show the perchlorato ligand *trans* to the aryl group, the Pd−O bonds (2.202(3)[20] 2.222(3)[21] Å) are significantly longer than in **4b′** (2.186(2) Å). The expected lengthening of the Cl−O bond involving the coordinated oxygen atom (1.484(2) Å) with respect to the other three ClO bonds (1.397(3)−1.420(3) Å) is observed. The same feature is observed in one of the reported structures (Cl-O(Pd) = 1.474(3) and 1.471(3) Å for the two independent molecules and Cl−O = 1.411(4)−1.430(4) Å).[20] In the other structure, the perchlorato ligand is disordered.[21]

Complex **6** (Figure 4 and Table 2) shows one chelating and one monocoordinate dppm ligand, whereas complex **7a** (Figure 5 and Table 3) shows both the azophenyl and dppm ligands chelating. The strong *trans* influence of the aryl ligand is shown by the longer Pd−$P_{trans\ to\ aryl}$ distances (2.359(2) (**6**), 2.413(3) Å (**7a**)) than Pd−$P_{cis\ to\ aryl}$ (2.324(2) (**6**), 2.318(2) (**6**), 2.259(3) Å (**7a**)). Crystal structures of arylpalladium complexes containing chelating diphosphines, and therefore with aryl and phosphine ligands in *trans* positions, have been reported.[22] However, those of **6** and **7a** are the first with dppm. Most crystal structures of palladium(II) complexes containing phosphines *trans* to a carbon donor ligand are aryl complexes and also show Pd−$P_{trans\ to\ aryl}$ distances (2.340(2)−2.403(2) Å) longer than Pd−$P_{cis\text{-}to\ aryl}$ (2.223(2)−2.325(3) Å).[16a,22a−f,23a−d] In those complexes with two or three phosphorus donor atoms, the difference Δ = (Pd−$P_{trans\ to\ aryl}$) − (Pd−$P_{cis\ to\ aryl}$) depends on the nature of the complex. Thus, in those complexes of the form $[Pd(aryl)P_3]^+$ (including **6**), Δ is in the range 0.035−0.06 Å[16a,23d] while in those of the type *cis*-$[Pd(aryl)P_2(L)]^+$, where P_2 is a chelating diphosphine ligand and L = Cl, I, or a nitrogen donor ligand (like **7a**),[22a−f,23c] Δ is in the range 0.097−0.154 Å because of smaller *trans* influence of L than phosphorus ligands. The only exception to all the above observations is found in the structure of [Pd(C_6F_5)(PPh_3){(PPh_2)$_2$$CPPh_2$}], in which the Pd−$P_{trans\ to\ aryl}$ bond (2.329(3)Å) is shorter than one of the two Pd−$P_{cis\ to\ aryl}$ bonds (2.366(3) Å).[22g] In addition, this last distance is longer than any other Pd−$P_{cis\ to\ aryl}$ bond length. Complex **6**, similar to **5**,

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Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes 2c, 4b′, 5, and 6

2c		4b′		5		6	
Pd−C(11)	1.987(3)	Pd−C(11)	1.979(3)	Pd−C(11)	1.975(5)	Pd−C(91)	2.040(5)
Pd−P(3)	2.3217(8)	Pd−N(2)	2.121(2)	Pd−O(1)	2.184(4)	Pd−P(2)	2.3181(15)
Pd−P(1)	2.3298(8)	Pd−O(1)	2.186(2)	Pd−P(2)	2.331(2)	Pd−P(3)	2.3243(15)
Pd−Cl	2.4119(8)	Pd−P	2.2742(7)	Pd−P(1)	2.339(2)	Pd−P(1)	2.3592(15)
Pd−N(2)	2.634(2)	N(1)−N(2)	1.267(3)	Pd−N(2)	2.576(4)	P(1)−C(1)	1.842(5)
N(1)−N(2)	1.259(3)	ClO(4)	1.397(3)	N(1)−N(2)	1.263(6)	P(2)−C(1)	1.833(5)
P(1)−C(1)	1.830(3)	Cl−O(3)	1.416(3)	S(1)−O(2)	1.419(4)	P(3)−C(2)	1.837(5)
P(2)−C(1)	1.851(3)	Cl−O(2)	1.420(3)	S(1)−O(3)	1.428(4)	P(4)−C(2)	1.828(6)
P(3)−C(2)	1.825(3)	Cl−O(1)	1.484(2)	S(1)−O(1)	1.453(4)	N(1)−N(2)	1.250(6)
P(4)−C(2)	1.840(3)						
C(11)−Pd−P(3)	87.92(8)	C(11)−Pd−N(2)	79.06(10)	C(11)−Pd−P(2)	88.2(2)	C(91)−Pd−P(2)	96.20(14)
C(11)−Pd−P(1)	89.43(8)	N(2)−Pd−O(1)	97.61(8)	O(1)−Pd−P(2)	92.16(11)	C(91)−Pd−P(3)	90.69(14)
P(3)−Pd−Cl	93.04(3)	C(11)−Pd−P	93.86(8)	C(11)−Pd−P(1)	90.6(2)	P(2)−Pd−P(1)	70.38(5)
P(1)−Pd−Cl	89.58(3)	O(1)−Pd−P	90.01(6)	O(1)−Pd−P(1)	91.19(11)	P(3)−Pd−P(1)	102.61(5)
C(11)−Pd−N(2)	71.89(10)			C(11)−Pd−N(2)	73.7(2)	P(2)−C(1)−P(1)	94.4(2)
P(3)−Pd−N(2)	96.46(6)			O(1)−Pd−N(2)	98.54(14)	P(4)−C(2)−P(3)	120.8(3)
P(1)−Pd−N(2)	86.45(6)			P(2)−Pd−N(2)	93.80(11)		
Cl−Pd−N(2)	108.57(5)			P(1)−Pd−N(2)	101.51(11)		

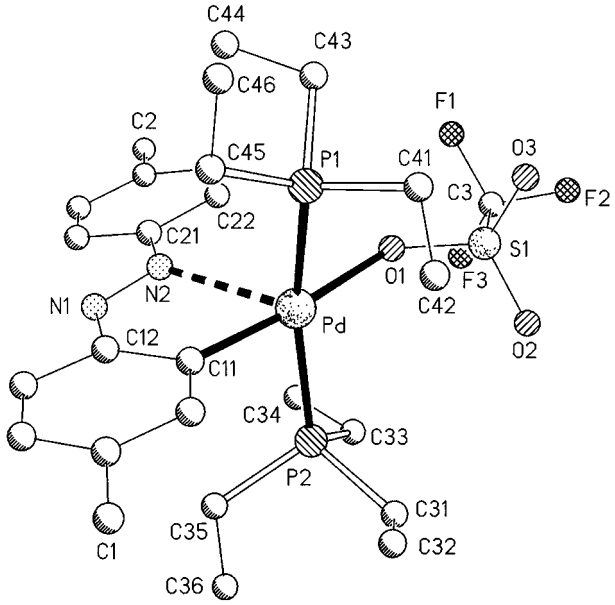


Figure 2. Crystal structure of complex **5**.

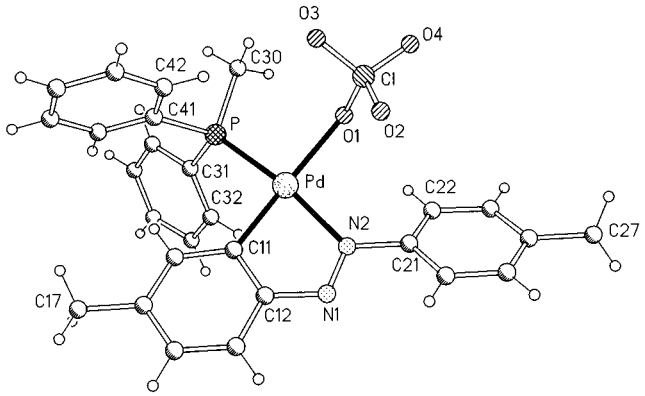


Figure 3. Crystal structure of complex **4b′**.

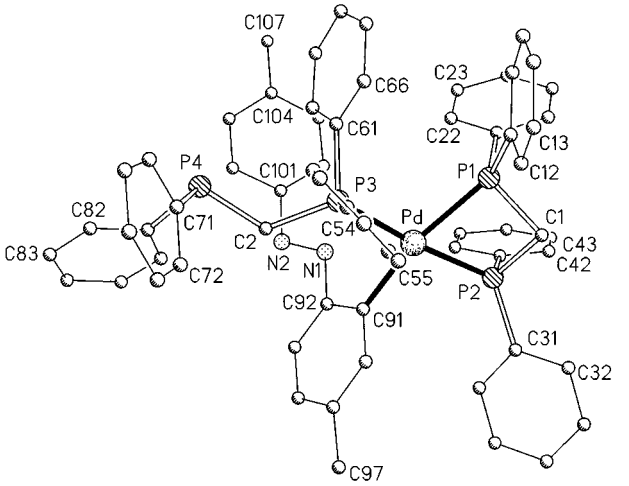


Figure 4. Crystal structure of the cation of complex **6**.

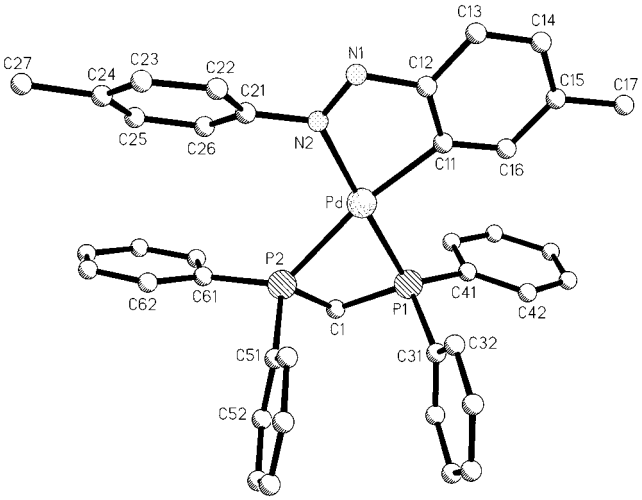


Figure 5. Crystal structure of the cation of complex **7a**.

displays possible C−H···O hydrogen bonds: C1−H1B··· O1 ($1 - x$, $-y$, $1 - z$; 3.25, 2.47 Å, 136°); C14−H14··· O2 (x, y, $1 + z$; 3.41, 2.48 Å, 163°); and C26−H26··· O3 ($1 + x$, y, $1 + z$; 3.31, 2.48 Å, 137°).

The crystal structures of the aquo complexes **9** and **10** (Figures 6 and 7 and Table 3) show the azophenyl ligand acting as a chelating ligand, the phosphine ligand bonded *trans* to the N(2) atom and one coordinated molecule of water. In **10**, a second water molecule is hydrogen bonded to the aquo ligand. The resulting cationic units are connected by the anion through hydrogen bonds, leading to an isotactic (**9**) or syndiotactic (**10**) polymer (Scheme 5 and Figures 7 and 8). Hydrogen bonding parameters for **9** are O1−H1···O2 2.721, 1.96 Å, 159°; O1−H2···O3 ($1 - x$, $-0.5 + y$,$1.5 - z$) 2.618, 1.83 Å, 176° and for **10** are O1···H1−O6 2.673, 1.87 Å, 174°; O1−H2···O3 2.855, 2.11 Å, 154°; O6−H3···O3 ($1 - x$, $1 - y$, $1 - z$) 2.987, 2.18 Å, 177°; and

Table 3. Selected Bond Distances (Å) and Angles (deg) for Complexes 7a, 9, 10, and 11

7a		9		10		11	
Pd−C(11)	2.056(10)	Pd−C(11)	1.987(5)	Pd−C(11)	1.991(3)	Pd−C(11)	1.993(8)
Pd−N(2)	2.096(8)	Pd−N(2)	2.115(4)	Pd−N(2)	2.093(3)	Pd−N(2)	2.117(7)
Pd−P(1)	2.259(3)	Pd−O(1)	2.139(4)	Pd−O(1)	2.141(3)	Pd−O(1)	2.134(5)
Pd−P(2)	2.413(3)	Pd−P	2.2673(13)	Pd−P	2.2753(12)	Pd−P(1)	2.261(2)
P(1)−C(1)	1.829(10)	N(1)−N(2)	1.264(5)	N(1)−N(2)	1.266(4)	P1C1	1.850(8)
P(2)−C(1)	1.858(10)	S−O(4)	1.405(4)	Cl−O(5)	1.426(3)	P2C1	1.806(9)
N(1)−N(2)	1.258(11)	S−O(2)	1.405(5)	Cl−O(2)	1.433(3)	P(2)−O(1)	1.519(6)
		S−O(3)	1.436(5)	Cl−O(4)	1.433(3)	N(1)−N(2)	1.267(9)
				Cl−O(3)	1.453(3)		
C(11)−Pd−N(2)	77.3(4)	C(11)−Pd−N(2)	79.5(2)	C(11)−Pd−N(2)	79.55(13)	C(11)−Pd−N(2)	79.7(3)
C(11)−Pd−P(1)	101.1(3)	N(2)−Pd−O(1)	91.89(15)	N(2)−Pd−O(1)	90.26(11)	N(2)−Pd−O(1)	97.5(2)
N(2)−Pd−P(2)	111.1(2)	C(11)−Pd−P	94.80(15)	C(11)−Pd−P	95.55(11)	C(11)−Pd−P(1)	94.8(2)
P(1)−Pd−P(2)	70.36(9)	O(1)−Pd−P	94.21(11)	O(1)−Pd−P	94.69(8)	O(1)−Pd−P(1)	87.8(2)
P(1)−C(1) P(2)	93.9(4)					P(2)−C(1)−P(1)	107.0(4)
						P(2)−O(1)−Pd	116.8(3)

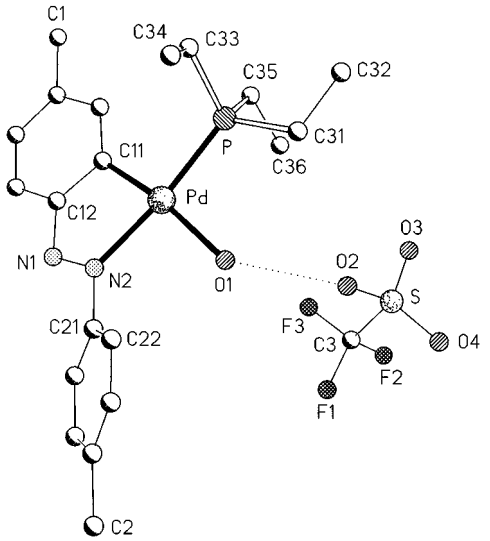


Figure 6. Crystal structure of complex **9**.

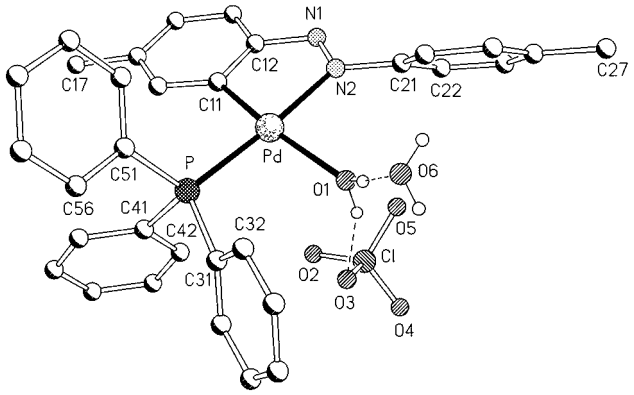
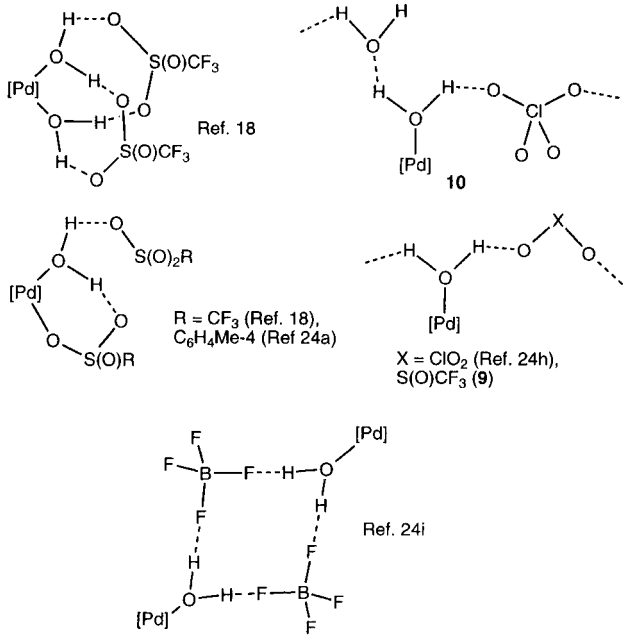


Figure 7. Crystal structure of complex **10**.

O6−H4···O2 (1 + *x*, *y*, *z*) 2.898, 2.10 Å, 172°. Among the few reported crystal structures of aquopalladium(II) complexes,[18,24] five are reported to show interactions between the anion and the water molecule.[18,24a,h,i] Although this interaction is always through hydrogen bonds, these structures and those of **9** and **10** display five different structural motifs, as shown in Scheme 5.

Scheme 5



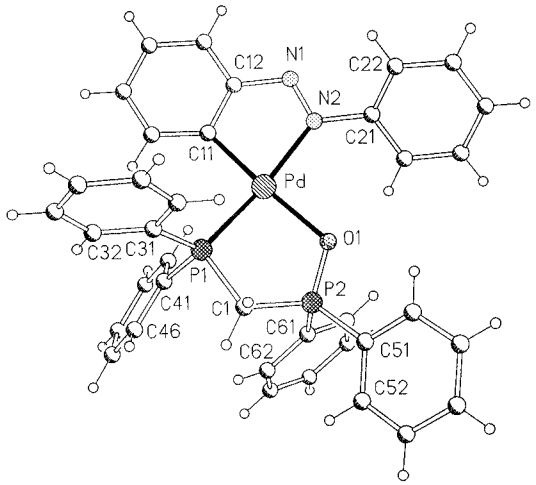


Figure 8. Crystal structure of the cation of complex **11**.

Most aquopalladium(II) complexes exhibit very similar Pd−O bond distances (range 2.106(4)−2.141(3) Å for

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those with reasonable precision)[18,24a,d,f] regardless of the nature of the *trans* ligand (aryl or alkyl phosphine) or the presence or absence of hydrogen bonds between the aquo ligand and the anion. The Pd−O bond distances in **9** (2.139(4) Å) and **10** (2.141(3) Å) are thus among the longest. Out of this range are the metallaheteroborane [2-(H_2O)-2-(PPh_3)-*closo*-2,1-$PdTeB_{10}H_9(PPh_3)$]BF_4 (2.208(4) Å),[24b] the metalated phosphine [Pd{PBu^t_2-$(CH_2)_2CH(CH_2)_2PBu^t_2$}($H_2O$)]$BPh_4$ (2.301(6) Å),[24c] and *trans*-[$PdH(PCy_3)_2(H_2O)$]BF_4 (2.206(5) Å),[24i] in which very bulky *cis* ligands prevent optimal binding of the water molecule. In complex **9**, the S−O(3) distance (1.435(5) Å) is significantly longer that the other two S−O distances (1.405(4) and 1.405(5) Å) and the same occurs in **10**, with Cl−O(3) (1.453(3) Å) longer than the other three (1.426(3), 1.433(3), and 1.433(3) Å). There is no obvious explanation in terms of H-bonding interactions, since the H bond acceptors in **9** are O2 and O3 and in **10** are O2 and O3 (the latter accepting two H bonds).

The crystal structure of **11** (see Figure 8) shows that the oxidation of dppm in complex **7b** has occurred at the phosphorus atom *trans* to the aryl group. As far as we are aware, the crystal structure of **11** is the first of a palladium complex with dppmO. The P−O (1.519(6) Å) bond distance is normal.[25]

Spectroscopic Properties of Complexes. The NMR data of complexes **1**−**13** are in agreement with the proposed structures. In the ^{31}P NMR spectra of complexes containing chelating dppm (**6**, **7**), the chemical shift of the phosphorus *trans* to the aryl ligand (P_X; Chart 2) appears at high field (−33.32 and −30.60 ppm), near the value of the chemical shift of the nonbonded phosphorus in **6** ($\delta(P_Q) = -32.52$ ppm).

Equilibria among different species in solutions of *trans*-[$Pd(C_6H_3N_2$To-2, Me-5)$Cl(\eta^1$-dppm$)_2$] (**2c**) and a fluxional behavior in the case of [$Pd(C_6H_3N_2$To-2, Me-5)(η^1-dppm)(η^2-dppm)]TfO (**6**) are observed. Thus, at room temperature, the ^1H NMR spectrum of **2c** shows broad resonances around 4 and 3.2 ppm and several singlets in the region 1.5−2.6 ppm corresponding, respectively, to CH_2 and Me groups of different dppm and azotolyl ligands. At −60 °C, six singlets corresponding to three different azotolyl ligands (see assignment in the Experimental section) and several multiplets (difficult to assign) are observed. The ^{31}P NMR spectrum at −60 °C shows the following subspectra: a first-order spectrum corresponding to four different nuclei, corresponding to the complex [$Pd(C_6H_3N_2$To-2,-Me-5)(η^1-dppm)(η^2-dppm)]Cl (by comparison with **6**); two singlets corresponding to the dimer **3a** and free dppm; two deceptively simple triplets of an AA′XX′ system, corresponding to the static structure of complex **2c**. These data can be explained if the following equilibria are assumed: [$Pd(C_6H_3N_2$To-2,Me-5)$Cl(\eta^1$-dppm$)_2$] ⇌ [$Pd(C_6H_3N_2$To-2,Me-5)(η^1-dppm)(η^2-dppm)]Cl and [Pd-$(C_6H_3N_2$To-2,Me-5)$Cl(\eta^1$-dppm$)_2$] ⇌ $^1/_2$*trans*-[$Pd(C_6H_3N_2$-Me-2,To-5)$Cl(\mu$-dppm$)]_2$ + dppm. According to the ^1H NMR spectrum, the ratios of [$Pd(C_6H_3N_2$To-2,Me-5)(η^1-dppm)(η^2-dppm)]Cl:[$Pd(C_6H_3N_2$To-2,Me-5)$Cl(\eta^1$-dppm$)_2$]: *trans*-[$Pd(C_6H_3N_2$Me-2,To-5)$Cl(\mu$-dppm$)]_2$ are 4:2:1 at −60 °C.

The ^{31}P NMR spectrum of **6** at room temperature shows broad resonances in the region from −20 to −32 ppm. At −60 °C a first-order spectrum is observed corresponding to four different nuclei of the static structure of complex **6**.

Mutually *trans* Phosphine and Aryl Ligands. The difficulty in preparing *cis*-[Pd(Ar)X$(PPh_3)_2$] complexes was first observed by Pfeffer[26] and was related to the antisymbiotic effect. According to this effect, *two soft ligands in mutually trans positions will have a destabilizing effect on each other when attached to class b metal atoms*.[27] This effect has been used to explain the geometries of metal complexes[2b,3,28] and also to discuss linkage isomerism of some ligands.[29] We believe that this effect is also responsible for all the above-mentioned coupling reactions. In particular, the decomposition reaction of [Pd(Ar)(Ar′)$(PPh_3)_2$] complexes to give biaryls (Scheme 1) is a consequence of the *phobia* of all pairs of ligands Ar/Ar′, Ar/PPh_3, and Ar′/PPh_3 against being *trans*. However, it seems that such a destabilizing effect between the pair Ar/Ar′ is greater than that for Ar/PPh_3, and this is the reason for obtaining *cis*-[Pd(Ar)(Ar′)$(PPh_3)_2$]. The geometry of the resulting complex and the destabilizing effect of both Ar/PPh_3 and Ar′/PPh_3 pairs of ligands in *trans* positions explains the coupling of the aryl groups to give Ar−Ar′.

A search of the Cambridge Structural Database reveals only one crystal structure of a *trans*-diarylpalladium(II) complex, [$Pd(C_6F_5)_2${$PPh_2CH_2Ph_2PAu(C_6$-F_5)}$_2$],[30] and only one of a diarylpalladium(II) complex containing a *trans* phosphine ligand, *cis*-[$Pd(C_6F_5)_2$-$(PPh_3)_2$].[23a] Probably, the first complex adopts a *trans* geometry because of the steric hindrance of the large phosphine ligands and the second one, which has the expected *cis* geometry, does not give the corresponding biaryl because of the two very strong C−Pd bonds. Most reported structures of monoarylpalladium complexes do not have a phosphine *trans* to the aryl group. In the few that do, the *trans* coordination of phosphine and carbon donor ligands is forced by the nature of the phosphine,[22,23c,d] the complex,[16a] or the aryl group.[23b] In addition, there are no reported crystal structures of monoarylpalladium complexes containing the aryl and

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PPh_3 ligands in *trans* positions. However, an interesting and rare familly of palladacycles containing PPh_3 and other phosphines *trans* to an aryl ligand has recently been reported. As the authors point out, the stability of these complexes is due to the high energy of the expected C−C coupling products.[23e]

The aforementioned facts, the synthesis of complexes **6**, **7a**−**c**, and **8**, and our unsuccessful attempts to prepare $[Pd(C_6H_3N{=}NR\text{-}2,X\text{-}5)(PPh_3)_2]^+$ (X = Me, H; R = To, Ph) (Scheme 2),[3] as well as Pfeffer's failure to prepare similar cyclometalated complexes,[23b,26] suggests that the antisymbiotic effect is greater for PPh_3 than for $P(alkyl)_3$. In addition, the successful synthesis of $[Pt(C_6H_3N{=}NTo\text{-}2,Me\text{-}5)(PPh_3)_2]OTf$ (**13**) means that the destabilizing effect between the pair of ligands Ar/PPh_3 is greater for palladium than that for platinum. Furthermore, the facile oxidation of **7b** can be related to the weak $Pd-P_{trans\ to\ aryl}$ bond. We are aware of examples of such oxidations when the oxidized phosphorus atom is a noncoordinated atom of a bi- or tridentate phosphorus ligand[22g,31] but, as far as we are aware, never when the phosphine is acting as a chelating ligand. It can be concluded that this destabilizing effect affects both ligands in *trans* positions and that not only can it induce coupling processes but also other transformations that avoid the Ar/PPh_3 *trans* geometry.

A different view of this destabilizing effect is that it increases with the *trans* influence of the ligands. Thus, the order of decreasing *trans* influence Ar > PR_3 requires the following order Ar/Ar > Ar/PR_3 > PR_3/PR_3 for the *phobia* of ligands to be *trans* to each other.

A clear example of application of these ideas is furnished by the very recent and simultaneous reports of Buchwald and Hartwig about a second generation of palladium catalysts for cross-coupling of aryl halides with amines.[6] Both have found that a Pd(0)/PP catalyst, where PP is a strongly chelating diphosphine, improves the result, allowing it to work with primary amines or aryl iodides and also leading to better yields in some cases for which poor results were previously obtained. According to the authors' data, the product from the oxidative addition reaction reacts with $R'R''N^-$ to give *cis*-[Pd(Ar)(NR′R″)(PP)] (Scheme 2). In our opinion, the coupling to give ArNR′R″ occurs because of the destabilizing effect of the aryl and phosphine ligands in the *trans* positions. Such couplings do not occur when PPh_3 and similar monodentate phosphines are used because the intermediate complex, $[Pd(Ar)(NR'R'')(PR_3)_2]$, is the most stable *trans* isomer (no Ar/PPh_3 in trans). It is so stable that no coupling process occurs. The use of potentially chelating diphosphines, such as 1,2-bis(diphenylphosphino)ethane (dppe), also fails to give the desired anilines because they can easily bond as monocoordinate ligands (*e.g.*, *trans*-[Pd(Ar)(NR′R″)(dppe)$_2$] similar to **2c**) or in a bridging mode (*e.g.*, *trans*-[Pd(Ar)(NR′R″)(μ-dppe)]$_2$ similar to **3a**,**b**) that in any case would give the desired *trans* Ar/PR_3 coordination.

Conclusions

A family of palladium 2-(arylazo)aryl complexes with phosphines has been isolated, and the crystal structures of eight of them have been determined. Most of these structures correspond to complexes with weak donor ligands (such as triflato, perchlorato, or aquo) or with phosphines coordinated *trans* to the aryl ligand. For the first group, there are very few precedents. We report new types of aquo complexes of palladium. The crystal structures of two complexes containing chelating dppm show a large value of $\Delta = (Pd-P_{trans\ to\ aryl}) - (Pd-P_{cis\ to\ aryl})$. The weakening of the $Pd-P_{trans\ to\ aryl}$ bond is responsible for the fluxional behavior of $[Pd(C_6H_3N_2\text{-}To\text{-}2,Me\text{-}5)(\eta^1\text{-}dppm)(\eta^2\text{-}dppm)]TfO$ (**6**) and the facile oxidation of $[Pd(C_6H_4N{=}NPh\text{-}2)(\eta^2\text{-}dppm)]SbF_6$ (**7b**). We also report the structure of two complexes with weak Pd···N interactions (**2c**, **5**), one of which posseses a coodination plane which is markedly folded about a L−Pd−L axis, with interesting C−H···O contacts that may be described as hydrogen bonds (**5**, **6**) and the best way to prepare 2-(arylazo)aryl platinum complexes. The data we present in this paper, together with observations we and others have previously made, shows the difficulty of coordinating a phosphine *trans* to an aryl ligand in palladium complexes. We propose to name this destabilizing effect as *transphobia*.

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Supporting Information Available: Tables of all crystal data and structure refinement details, refined and calculated atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for compounds **2c·$^1/_2CH_2Cl_2$**, **4b′**, **5**, **6**, **7a**, **9**, **10**, and **11·2MeOH** (61 pages). Ordering information is given on any any current masthead page.

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