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Synthesis, Reactivity, and X-ray Crystallographic Characterization of Mono-, Di-, and Tetranuclear Palladium(II)-Metalated Species

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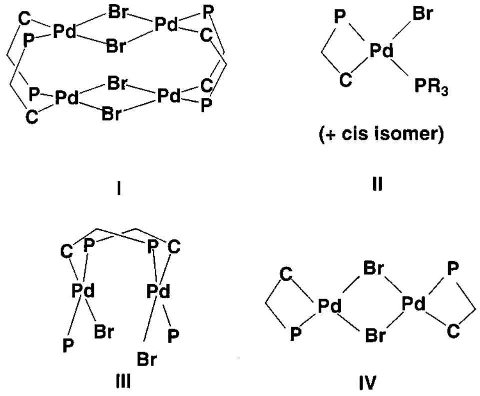
The reactivity of the tetranuclear metallated palladium compound $\{Pd[\mu_2\text{-}(C_6H_4)PPh_2]Br\}_4$ (**1**) with different ligands has been investigated with the aim of evaluating the influence of the entering ligand on the nature of the reaction products. The results confirmed the ability of the ligand $[(C_6H_4)PPh_2]^-$ to expand a bridging [μ_2-] or a chelating [η^2-] coordination mode, depending on the auxiliary ligands present in the complex. Bulky phosphines stabilize mononuclear species of formula $\{Pd[\eta_2\text{-}(C_6H_4)PPh_2]Br[P]\}$, with a four-atom metallocycle, while small phosphines give dinuclear compounds. The molecular structures of three different metalated palladium compounds have been determined by single-crystal X-ray crystallography; the tetranuclear $\{Pd[\mu_2\text{-}(C_6H_4)PPh_2]Cl\}_4$ (**2**), the dinuclear-$\{Pd[\mu_2\text{-}(C_6H_4)PPh_2]Br[PMe_3]\}_2$ (**3**), and the mononuclear $\{Pd[\eta_2\text{-}(C_6H_4)PPh_2]Br[PCBr]\}$, (PCBr = $P(o\text{-}BrC_6H_4)Ph_2$) (**9**) were obtained, the first one by halogen exchange reaction and the others by frame degradation of **1**.

Introduction

Cyclometalated palladium compounds have received great attention in past years. By far the most common metalated palladium compounds are those including one metal atom in a five-atom metallocycle.[1] We have recently reported the characterization of one interesting metalated palladium compound, $\{Pd[\mu_2\text{-}(C_6H_4)PPh_2]Br\}_4$ (**1**), having $[(C_6H_4)PPh_2]^-$, $(PC)^-$, anions bridging two palladium atoms in a tetranuclear structure of type **I** [2] (Scheme 1). This tetranuclear frame was cleaved when **1** was reacted with phosphines like PPh_3 or PCy_3 to form mononuclear compounds with structure type **II**. Surprisingly, when the phosphine was $P(o\text{-}BrC_6H_4)Ph_2$ (PCBr), the cleavage was not complete and compound **1** was in equilibrium with species of type **II**. Intermediate products of the frame degradation with structures of type **III** or **IV** (Scheme 1), relatively common for palladium(II) compounds, were not detected in our preliminary studies.[2]

To pursue this type of chemistry, we have further examined the reactivity of **1** with different ligands with the aim of evaluating the influence of the steric factors on the nature of the products of this particular reaction. We report in this paper the characterization of different palladium compounds, with structures of type **I**−**III**, resulting from halogen exchange or frame degradation of **1**. These results also confirm the ability of the ligand PC to adopt a bridging or a chelating coordination mode, depending on the auxiliary ligand present in the complex. In some particular cases equilibrium between mononuclear (**II**) and dinuclear (**III**) species was observed.

Scheme 1



Experimental Section

All reactions were carried out under argon atmosphere, using standard Schlenk techniques. Compounds **1**, $\{Pd[\eta_2\text{-}(C_6H_4)PPh_2]Br[P]\}$ (P = PPh_3, **5**, P = PCBr, **9**, and P = PCy_3, **11**), were prepared according to literature procedures.[2] The phosphine $P(o\text{-}ClC_6H_4)Ph_2$ (PCCl) was prepared according to a literature procedure.[3] The other phosphines are commercially available (PMe_3 as a 1 M THF solution) (Strem Chemicals) and were used as received. All solvents were of analytical grade (Aldrich) and were degassed and used without further purification. Elemental analyses were performed by Servicio de Microanálisis Elemental, Universidad de Madrid. NMR spectra were recorded in Bruker AC-200 and Varian Unity-300 spectrometers. Chemical shifts (δ) are given in ppm relative to TMS (^1H,^{13}C), 85% H_3PO_4 aqueous solution (^{31}P) or $CFCl_3$ (^{19}F). Coupling constants (J) are given in hertz.

Synthesis of $\{Pd[\mu_2\text{-}(C_6H_4)PPh_2]Cl\}_4$ (2). A suspension of 0.060 g (0.034 mmol) of **1** and 0.540 mmol of Bu_4NCl in 20 mL of 1,2-dichloroethane was refluxed for 1 h. The yellow solution obtained was evaporated to dryness. Crystallization of the residue from acetone gave 0.036 g (65% yield) of $\{Pd[\mu_2\text{-} (C_6H_4)PPh_2]Cl\}_4$ (**2**) as a yellow solid. Anal. Calcd for $C_{72}H_{56}Cl_4P_4Pd_4$: C, 53.63; H, 3.50. Found: C, 53.13; H, 3.47. ^1H NMR ($CDCl_3$): δ 6.4 (12H, m, aromatics), 6.8−7.2 (32H, m, aromatics), 7.2−7.4 (12H, m, aromatics). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 124.1 (s, aromatic), 129.2 (s, aromatic), 129.6 (s, aromatic), 130.9 (d, J = 12, aromatic), 131.4 (s, aromatic), 162.0 (metalated). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 28.4.

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Synthesis of Dinuclear $\{Pd[\mu_2\text{-}(C_6H_4)PPh_2]Br[P]\}_2$ (3 and 4). To a yellow suspension of 0.050 g of **1** (0.028 mmol) in 20 mL of CH_2Cl_2 0.112 mmol of *P* (*P* = PMe_3 or PMe_2Ph) was added. The yellow solution was stirred for 30 min at room temperature and was evaporated to dryness. Crystallization of the residue from a CH_2Cl_2−hexane mixture gave $\{Pd[(C_6H_4)PPh_2]Br[P]\}_2$, (*P* = PMe_3, **3**; *P* = PMe_2Ph, **4**) as yellow crystalline solids.

1. *P* = PMe_3 (3). Yield, 0.046 g (79%). Anal. Calcd for $C_{42}H_{46}Br_2P_4Pd_2$: C, 48.17; H, 4.43. Found: C, 48.28; H, 4.18. ^{1}H NMR ($CDCl_3$): δ 1.2 (18H, dd, $^2J_{H-P}$ = 10, $^4J_{H-P}$ = 2, CH_3), 6.6 (2H, t, *J* = 7, aromatic), 6.7 (2H, t, *J* = 7, aromatic), 6.9 (4H, t, *J* = 9, aromatic), 7.0 (8H, t, *J* = 6, aromatic), 7.1 (2H, t, *J* = 7, aromatic), 7.4 (6H, m, aromatic), 7.9 (4H, m, aromatic). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 15.7 (d, $^1J_{C-P}$ = 29, CH_3), 121.8 (d, *J* = 4, aromatic), 126.7 (d, *J* = 9, aromatic), 127.3 (d, *J* = 4, aromatic), 127.8 (s, aromatic), 129.4 (s, aromatic), 129.6 (s, aromatic), 132.0 (d, *J* = 8, aromatic), 134.1 (m, aromatic), 134.6 (m, aromatic), 135.7 (d, *J* = 10, aromatic), 136.3 (s, aromatic), 167.8 (metalated, m). ^{31}P{^{1}H} NMR ($CDCl_3$), (AA′BB′ system): δ 21.5, −14.0, $^4J_{AA'}$ = 21, $^2J_{AB}$ = 438, $^4J_{AB'}$ = 10, $^6J_{BB'}$ = 0. (Values of *J* are from simulated spectrum).

2. *P* = PMe_2Ph (4). Yield, 0.049 g (79%). Anal. Calcd for $C_{52}H_{50}Br_2P_4Pd_2$: C, 53.31; H, 4.30. Found: C, 52.99; H, 3.94.^{1}H: NMR ($CDCl_3$): δ 0.6 (6H, d, *J* = 9, CH_3), 1.9 (6H, d, *J* = 10, CH_3), 6.0−8.5 (38H, m, aromatics). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 11.0 (d, *J* = 29, CH_3), 17.9 (d, *J* = 30, CH_3), 122.7 (s, aromatic), 127.8 (s, aromatic), 128.0 (s, aromatic), 128.9 (d, *J* = 9, aromatic), 129.8 (d, *J* = 13, aromatic), 130.5 (s, aromatic), 132.6 (d, *J* = 9 Hz), 133.1 (s, aromatic), 135.8 (s, aromatic), 137.2 (s, aromatic), 139.5 (d, *J* = 10, aromatic), 165.9 (d, *J* = 28, metalated). ^{31}P{^{1}H} NMR ($CDCl_3$), (AA′BB′ system): δ 21.02, −4.9, $^4J_{AA'}$ = 21, $^2J_{AB}$ = 439, $^4J_{AB'}$ = 12, $^6J_{BB'}$ = 0. (Values of *J* are from simulated spectrum).

Synthesis of Mononuclear $\{Pd[\eta^2\text{-}(C_6H_4)PPh_2]Br[P]\}$ (6−8, 10). To a suspension of 0.050 g (0.028 mmol) of **1** in 20 mL of degassed CH_2Cl_2, 0.112 mmol of *P* was added. The mixture was stirred at room temperature for a variable period of time, and the resulting pale-yellow solution was evaporated to dryness. Crystallization of the residue from a CH_2Cl_2−hexane mixture gave yellow crystalline solids of $\{Pd[\eta^2\text{-}(C_6H_4)PPh_2]Br[P]\}$ as a mixture of cis and trans isomers.

1. *P* = $P(p\text{-}MeC_6H_4)_3$ (6). The mixture was stirred for 1 h. Yield, 0.063 g (75%). Anal. Calcd for $C_{39}H_{35}BrP_2Pd$: C, 62.30; H, 4.66. Found: C, 61.20; H, 4.70.^{1}H NMR ($CDCl_3$): δ 2.3 (s, CH_3, cis isomer), 2.4 (s, CH_3, trans isomer), 6.0−8.0 (m, aromatics). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 21.6 (s, CH_3, trans isomer), 22.8 (s, CH_3, cis isomer), 125−145 (aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 12.9, −81.0 ($^2J_{P-P}$ = 14) (cis isomer), 28.6, −86.7 ($^2J_{P-P}$ = 460) (trans isomer). Cis/trans ratio = 0.20.

2. *P* = $P(m\text{-}MeC_6H_4)_3$ (7). The mixture was stirred for 1 h. Yield, 0.055 g (65%). Anal. Calcd for $C_{39}H_{35}BrP_2Pd$: C, 62.30; H, 4.66. Found: C, 62.64; H, 4.31.^{1}H NMR ($CDCl_3$): δ 2.1 (s, CH_3, cis isomer), 2.3 (s, CH_3, trans isomer), 6.0−8.0 (m, aromatics). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 21.3 (s, CH_3, cis isomer), 21.5 (s, CH_3, trans isomer), 126.2 (d, *J* = 9, aromatic), 128.6 (s, aromatic), 128.7 (s, aromatic), 128.8 (s, aromatic), 129.3 (s, aromatic), 129.4 (s, aromatic), 129.6 (s, aromatic), 130.0 (s, aromatic), 131.3 (s, aromatic), 131.4 (s, aromatic), 131.9 (s, aromatic), 132.2 (d, *J* = 11, aromatic), 133.1 (d, *J* = 13, aromatic), 133.9 (d, *J* = 12, aromatic), 134.4 (d, *J* = 11, aromatic), 135.7, 136.5 (d, *J* = 13, aromatic), 138.3 (d, *J* = 10, aromatic), 138.4 (d, *J* = 10, aromatic). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 8.2, −80.4 ($^2J_{P-P}$ = 15) (cis isomer), 30.9, −86.3 ($^2J_{P-P}$ = 459), (trans isomer). Cis/trans ratio = 0.45.

3. *P* = $P(o\text{-}ClC_6H_4)Ph_2$ (8). The mixture was stirred for 15 days. Yield, 0.050 g (60%). Anal. Calcd for $C_{36}H_{28}ClBrP_2Pd$: C, 58.09; H, 3.79. Found: C, 57.60; H, 3.49. ^{1}H NMR ($CDCl_3$): δ 6.2−8.2 (m, aromatics). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 124−148 (aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 15.7, −81.0 ($^2J_{P-P}$ = 14) (cis isomer), 23.7, −87.4 ($^2J_{P-P}$ = 473) (trans isomer). Cis/trans ratio = 0.93.

4. *P* = $P(o\text{-}MeOC_6H_4)Ph_2$ (10). The mixture was stirred for 48 h. Yield, 0.071 g (86% yield). Anal. Calcd for $C_{37}H_{31}BrOP_2Pd$: C, 60.06; H, 4.22. Found: C, 59.30; H, 4.02. ^{1}H NMR ($CDCl_3$): δ 3.4 (s, CH_3O, cis isomer), 3.5 (s, CH_3O, trans isomer), 6.2−8.2 (m, aromatics). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 55.6 (s, CH_3O), 55.7 (s, CH_3O), 111.4 (d, *J* = 4, aromatic), 111.6 (s, aromatic), 120.6 (t, *J* = 8, aromatic), 125.5 (d, *J* = 9, aromatic), 126.3 (d, *J* = 8, aromatic), 127.7 (d, *J* = 8, aromatic), 128.0 (s, aromatic), 128.6 (s, aromatic), 128.8 (s, aromatic), 129.2 (s, aromatic), 129.7 (s, aromatic), 130.1 (s, aromatic), 130.6 (d, *J* = 5, aromatic), 132.0 (s, aromatic), 132.6 (s, aromatic), 133.3 (s, aromatic), 133.7 (d, *J* = 5, aromatic), 134.8 (d, *J* = 13, aromatic), 135.4 (d, *J* = 12, aromatic). ^{31}P{^{1}H} NMR: δ 9.7, −81.0 ($^2J_{P-P}$ = 14) (cis isomer), 20.9, −86.6 ($^2J_{P-P}$ = 473) (trans isomer). Cis/trans ratio = 0.64.

Synthesis of $\{Pd[\mu_2\text{-}(OOCCR_3)][\mu_2\text{-}(C_6H_4)PPh_2]\}_2$ (12 and 13). To a suspension of 0.050 g (0.028 mmol) of **1** in 20 mL of degassed CH_2Cl_2, 0.113 mmol of AgO_2CCR_3 was added. After 5 h of stirring at room temperature, the suspension was filtered and the resulting solution was evaporated to dryness. The yellow solid obtained in each case was recrystallized from a CH_2Cl_2−hexane mixture.

1. R = F (12). Yield, 0.049 g (91%). Anal. Calcd for $C_{40}H_{28}O_4F_6P_2Pd_2$: C, 49.97; H, 2.94. Found: C, 49.10; H, 2.98. ^{1}H NMR ($CDCl_3$): δ 6.63 (4H, q, *J* = 11, *J* = 7, aromatics), 6.77 (2H, d, *J* = 5, aromatics), 6.90 (4H, m, aromatics), 7.07 (4H, t, *J* = 7, aromatics), 7.28 (5H, m, aromatics), 7.42 (6H, m, aromatics), 7.55 (3H, q, *J* = 12, *J* = 7, aromatics). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 115 (q, $^1J_{C-F}$ = 288, CF_3), 123.7 (s, aromatic), 128.0 (m, aromatic), 128.3 (m, aromatic), 129.8 (s, aromatic), 131.0(s, aromatic), 132.0 (s, aromatic), 132.2 (s, aromatic), 133.7 (m, aromatic), 134.7 8 (s, aromatic), 139.4 (t, *J* = 13, aromatic), 156.9 (t, $^2J_{C-P}$ = 12, metalated), 165.2 ppm (q, $^2J_{C-F}$ = 38, OCO). ^{31}P{^{1}H} NMR($CDCl_3$): δ 20.1. ^{19}F NMR ($CDCl_3$): δ −75.37.

2. R = H (13). Yield, 0.040 g (84%). Anal. Calcd for $C_{40}H_{34}O_4P_2Pd_2$: C, 56.29; H, 4.02. Found: C, 56.40; H, 3.95. ^{1}H NMR ($CDCl_3$): δ 1.10 (6H, s, CH_3), 6.5−8 (28H, m, aromatics). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 23.1 (s, CH_3), 123−140 (m, aromatics), 160 (t, metalated), 181.55 (s, OCO). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 18.9.

Synthesis of Cationic Compounds 14−18. To a suspension of 0.050 g (0.028 mmol) of **1** in 15 mL of degassed CH_2Cl_2 were added 22 mg (0.113 mmol) of $AgBF_4$ and 3 mL of degassed THF. The yellow suspension was stirred for 5 h at room temperature, protected from the light. The solution was filtered off, and 0.225 mmol of the phosphine or 0.112 mmol of diphosphine was added. After being stirred for 15 min at room temperature the resulting suspension was evaporated to dryness. The residue was extracted with CH_2Cl_2; addition of hexane and slow evaporation gave in each case a yellow crystalline solid.

1. $\{Pd[\mu_2\text{-}(C_6H_4)PPh_2][PMe_3]_2\}_2\{BF_4\}_2$ (14). Yield, 0.040 g (60%). Anal. Calcd for $C_{48}H_{64}B_2F_8P_6Pd_2$: C, 47.50; H, 5.28. Found: C, 47.15; H, 5.61.^{1}H NMR (CD_2Cl_2): δ 0.9 (18H, d, $^2J_{H-P}$ = 8, CH_3), 1.0 (18H, dd, $^2J_{H-P}$ = 19, $^4J_{H-P}$ = 2, CH_3), 6.4 (2H, t, *J* = 8, aromatics), 6.5 (2H, t, *J* = 7, aromatics), 6.7 (2H, t, *J* = 7, aromatics), 7.3 (2H, d, *J* = 3, aromatic), 7.7 (8H, m, aromatics), 7.8 (8H, m, aromatics), 8.5 (4H, broad band, aromatics). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 15.4 (d, $^1J_{C-P}$ = 29, CH_3), 16.5 (d, $^1J_{C-P}$ = 24, CH_3), 125−140 (m, aromatics), 166.1 (d, $^2J_{C-P}$ = 116, metalated). ^{31}P{^{1}H} NMR(CD_2Cl_2), AA′BB′CC′ system: δ_A = 26.4, δ_B = −18.3, δ_C = −31.7, $^4J_{AA'}$ = 3, $^2J_{AB}$ = 371, $^4J_{AB'}$ = 5, $^2J_{AC}$ = −37, $^4J_{AC'}$ = 15, $^6J_{BB'}$ = 0, $^4J_{BC}$ = −37, $^6J_{BC'}$ = 0, $^6J_{CC'}$ = 0. (*J* values are from the simulated spectra).

2. $\{Pd[\eta^2\text{-}(C_6H_4)PPh_2][PPh_3]_2\}\{BF_4\}$ (15). Yield, 0.093 g (86%). Anal. Calcd for $C_{54}H_{44}BF_4P_3Pd$: C, 66.28; H, 4.50. Found: C, 65.55; H, 4.79. ^{1}H NMR (CD_2Cl_2): δ 6.4 (1H, dd, *J* = 14, *J* = 8, aromatics), 6.8 (1H, m, aromatics), 6.9−7.7 (42H, m, aromatics). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 127.4 (d, *J* = 5, aromatic), 128.3 (d, *J* = 5, aromatic), 128.9 (d, *J* = 9, aromatic), 129.7 (s, aromatic), 129.9 (s, aromatic), 130.0 (s, aromatic), 130.2 (s, aromatic), 130. 5 (s, aromatic), 130.7 (s, aromatic), 131.0 (m, aromatic), 131.6 (s, aromatic), 132.0 (m, aromatic), 132.4 (s, aromatic), 132.6 (m, aromatic), 132.9 (m, aromatic), 134.4 (s, aromatic), 134.6 (s, aromatic), 134.9 (s, aromatic), 136.2 (s, aromatic), 136.5 (s, aromatic). ^{31}P{^{1}H} NMR(CD_2Cl_2): δ 32.4, (dd, $^2J_{P-P'}$ = 376, $^2J_{P-P''}$ = 29), 20.9, (t, $^2J_{P-P'}$ = 29), −82.3 (dd, $^2J_{P-P'}$ = 376, $^2J_{P-P''}$ = 29).

3. $\{Pd[\eta^2\text{-}(C_6H_4)PPh_2][P(p\text{-}MeC_6H_4)_3]_2\}\{BF_4\}$ (16). Yield, 0.111 g (93%). ^{1}H NMR ($CDCl_3$): δ 2.28 (9H, s, CH_3), 2.31 (9H, s, CH_3), 6.3−7.5 (38H, m, aromatics). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 21.3 (s, CH_3), 21.4 (s, CH_3), 127.7 (s, aromatic), 128.8 (m, aromatic), 129.0 (m, aromatic), 129.4 (m, aromatic), 131.6 (s, aromatic), 132.0 (d, *J* = 10, aromatic), 133.3 (m, aromatic), 133.4 (m, aromatic), 134.9 (d, *J* = 13, aromatic), 141.4 (d, *J* = 2, aromatic), 141.8 (d, *J* = 2, aromatic). ^{31}P-

Table 1. Crystallographic Data for Compounds **2**, **3**·$2CH_2Cl_2$, and *trans*-**9**·$2CDCl_3$

	2	**3**	*trans*-**9**
empirical formula	$C_{72}H_{56}Cl_4P_4Pd_4$	$C_{44}H_{50}Br_2Cl_4P_4Pd_2$	$C_{38}H_{30}Br_2Cl_6P_2Pd$
fw	1612.45	1217.14	1027.48
radiation (λ, nm)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
temp, K	298	173(2)	173(2)
space group	*Fddd*	*C*2/*c*	*P*$\bar{1}$
a, Å	18.096(4)	16.146(1)	10.058(2)
b, Å	20.990(4)	14.763(1)	12.287(2)
c, Å	34.171(7)	21.229(2)	18.029(4)
α, deg	90.00	90.00	72.86(1)
β, deg	90.00	111.09(1)	86.61(1)
γ, deg	90.00	90.00	70.99(1)
V, Å^3	12980(5)	4721(1)	2011(1)
Z	8	4	2
R^a	0.0249	0.0316	0.0739
$R_w{}^b$	0.0521	0.0680	0.1762

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = \sum||F_o| - |F_c||w^{1/2}/\sum|F_o|w^{1/2}$.

{^{1}H} NMR ($CDCl_3$): δ 31.1 (dd, $^2J_{P-P} = 381$, $^2J_{P-P} = 29$), 19.5 (t, $^2J_{P-P} = 29$), −81.3 (dd, $^2J_{P-P'} = 381$, $^2J_{P-P''} = 29$).

4. {Pd[*μ*$_2$-(C_6H_4)PPh_2][*μ*$_2$-$Ph_2PCH_2PPh_2$]}$_2${BF_4}$_2$ (17). Yield, 0.090 g (94%). ^{1}H NMR (CD_2Cl_2): δ 2.94 (2H, dd, $^2J_{H-P} = 25$, $^2J_{H-P} = 11$, CH_2), 3.89 (2H, dd, $^2J_{H-P} = 14$, $^2J_{H-P} = 9$, CH_2), 6.02 (4H, dd, $J = 12$, $J = 7$, aromatics), 6.5−7.0 (64H, m, aromatics). ^{13}C{^{1}H} NMR (CD_2Cl4_2): δ 32.8 (m, CH_2), 122−138 (aromatics), 154.5 (d, $^2J_{C-P} = 105$, metalated). ^{31}P{^{1}H} NMR(CD_2Cl_2), AA′BB′CC′ system: $\delta_A = 17.8$, $\delta_B = -19.3$, $\delta_C = -33.1$, $^4J_{AA'} = 4$, $^2J_{AB} = 376$, $^4J_{AB'} = -8$, $^2J_{AC} = -16$, $^4J_{AC'} = -9$, $^4J_{BB'} = 13$, $^2J_{BC} = -37$, $^4J_{BC'} = 0$, $^4J_{CC'} = 0$. (Values of *J* are from simulated spectrum).

5. {Pd[*η*^{2}-(C_6H_4)PPh_2][*η*^{2}-$Ph_2PCH_2CH_2PPh_2$]}{BF_4} (18). Yield, 0.87 g (91%). Anal. Calcd for $C_{44}H_{38}BF_4P_3Pd$: C, 61.96; H, 4.49. Found: C, 61.29; H, 4.29.^{1}H NMR (CD_2Cl_2): δ 2.4−3.0 (4H, m, CH_2), 6.8−7.9 (34H, m, aromatics). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 26.5 (dd, $^1J_{P-C} = 29$, $^2J_{P-C} = 12$, CH_2), 29.1 (dd, $^1J_{P-C} = 32$, $^2J_{P-C} = 17$, CH_2), 125−135 (aromatics), 149.4 ppm (d, $^1J_{P-C} = 49$, aromatic). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 55.8, (dd, $^2J_{P-P'} = 378$, $^2J_{P-P''} = 24$), 44.1, (t, $^2J_{P-P'} = 24$), −74.6, (dd, $^2J_{P-P'} = 378$, $^2J_{P-P''} = 24$).

Crystallographic Data Collection and Refinement of the Structures. A Siemens SMART CCD diffractometer was used for data collection on crystals of compound **2**, and a Siemens P4 diffractometer was used for crystals of compounds **3** and *trans*-**9**. The crystal structure determination was done by direct methods, using SHELXTL, version 5.05;[4] the refinement on F^2 was done using all reflections. The positions of all non-hydrogen atoms were deduced from difference Fourier maps and were refined anisotropically. Hydrogen atoms were placed in their geometrically generated positions and were refined riding on the carbon atom to which they are attached, except for rigid methyl groups.

Results and Discussion

Ligand Exchange Reactions. Compound **1** undergoes exchange of bromides by chloride ligands, without significant cleavage of the tetranuclear unit, when it was reacted with excess of NBu_4Cl in refluxing 1,2-dichloroethane for 1 h. The resulting chloride derivative {Pd[*μ*$_2$-(C_6H_4)PPh_2]Cl}$_4$, **2**, was characterized by elemental analysis and ^{1}H, ^{13}C, and ^{31}P{^{1}H} NMR spectroscopy. In particular the ^{13}C NMR spectrum shows the characteristic low-field signal ($\delta = 162$, t, $J = 16$ Hz) due to the carbon atom bonded to palladium.

Table 2. Selected Bond Distances (Å) and Angles (deg) for {Pd[*μ*$_2$-(C_6H_4)PPh_2]Cl}$_4$, **2**

Pd−ClB	2.4007(7)	Pd−Cl	2.4576(8)
Pd−P	2.2258(8)	Pd−C1	2.019(3)
ClB−Pd−Cl	84.57(3)	ClB−Pd−P	177.71(3)
ClB−Pd−C1	92.51(8)	Cl−Pd−P	95.91(3)
Cl−Pd−C1	171.74(8)	P−Pd−C1	86.71(8)

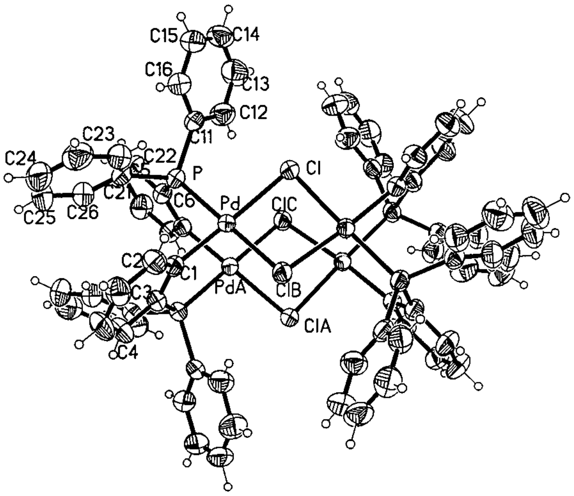

Figure 1. Molecular view of {Pd[*μ*$_2$-(C_6H_4)PPh_2]Cl}$_4$, **2**.

Compound **2** has also been characterized by X-ray diffraction. Details of the data collection and structure solution are summarized in Table 1. Relevant bond distances and angles are given in Table 2. The molecular structure of **2** (Figure 1) consists of a parallelogram of four palladium atoms with alternate sides bridged either by two orthometalated phosphines or by two chlorides. The metalated phosphines are in a head-to-tail arrangement. Each palladium has a slightly distorted square planar coordination, bound to one carbon, one phosphorus, and two chlorides that are bridging two palladium atoms. The chloride bridges are not symmetric; Pd−Cl = 2.4576(8) Å, and Pd−ClB = 2.4007(7) Å The distances between nonbonded palladium atoms across the metalated ligands are considerably closer (Pd−PdA 3.07 Å) than across the Pd_2Cl_2 bridge (3.58 Å). Compounds **1** and **2** are structurally very similar. The values of the bond distances and angles for these two compounds are within the standard error, with the only logical exception of the palladium−halide bond distances (ca. 0.12 Å shorter in **2**).

Frame Degradation Reaction. Reaction with PR_3. The reaction of **1** with monodentate phosphines readily produces cleavage of the tetranuclear frame, yielding mononuclear species, dinuclear species, or a mixture of both, depending on the size (conic angle *θ*) of the phosphine used (Scheme 2).

The less bulky phosphine PMe_3 ($\theta = 118°$)[5] reacted with **1**, forming a yellow crystalline product that was formulated as {Pd[*μ*$_2$-(C_6H_4)PPh_2]Br[PMe_3]}$_2$ (**3**). The second-order ^{31}P NMR spectrum observed for this compound, of the type AA′BB′, was quite informative and showed two different signals due to the phosphorus of the metalated phosphines ($\delta_A = 21.5$) and of the PMe_3 ligands ($\delta_B = -14.0$). The chemical shift for the first resonance is in the normal range for bridging metalated phosphine ligands.[2] The high value of the $^2J_{PP}$ coupling constant, 438 Hz, indicates that these two phosphorus atoms are in a relative trans disposition (Table 3). These spectroscopic values suggest a dinuclear structure for compound **3**.

This structural assignment was confirmed by an X-ray structure determination of compound **3**. Table 1 summarizes the pertinent information, and Table 4 contains the important bond distances and angles. The structure of **3** (Figure 2) consists of a dinuclear palladium(II) unit where the palladium atoms

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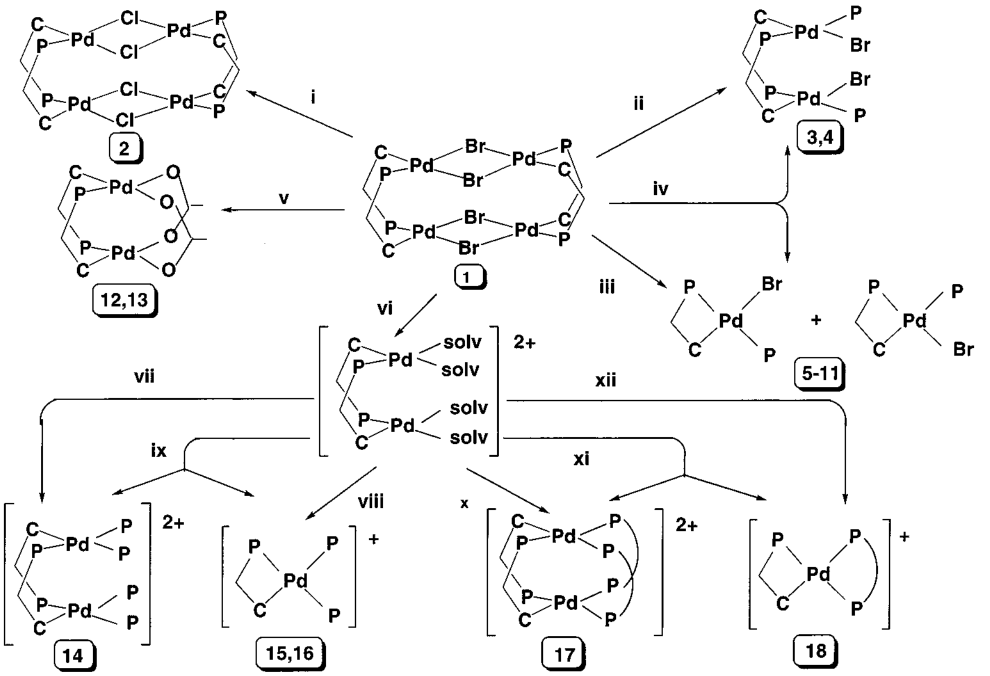
[4] *SHELXTL*, version 5.05; AXS Siemens: The Netherlands, 1996.

[5] Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

Scheme 2 [a]



[a] (i) Refluxing with a molar excess of Bu_4NCl in 1,2-dichloroethane. (ii) 4 mol of P at room temperature (P = PMe_3, **3**; P = $PMe_2(C_6H_5)$, **4**). (iii) 4 mol of P at room temperature (P = $P(C_6H_5)_3$, **5**; P = (*p*-$CH_3C_6H_4$)$(C_6H_5)_2$, **6**; P = P(*m*-$CH_3C_6H_4$)$(C_6H_5)_2$, **7**; P = (*o*-ClC_6H_4)$(C_6H_5)_2$, **8**; P = P(*o*-BrC_6H_4)$(C_6H_5)_2$, **9**; P = (*o*-$CH_3OC_6H_4$)$P(C_6H_5)_2$ **10**; P = PCy_3 **11**. (iv) 4 mol of $PMe(C_6H_4)_2$ at room temperature. (v) 4 mol of AgO_2CCX_3 (X = F, **12**; X = H, **13**). (vi) 4 mol of $AgBF_4$ in CH_2Cl_2/THF (1:1) (solv = THF). (vii) 4 mol of PMe_3, **14**. (viii) 4 mol of P (P = $P(C_6H_5)_3$, **15**; P = (*p*-$CH_3C_6H_4$)$(C_6H_5)_2$, **16**. (ix) 4 mol of $PMe_2(C_6H_5)$. (x) 2 mol of $(C_6H_5)_2PCH_2P(C_6H_5)_2$, **17**. (xi) 2 mol of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, **18**. (xii) As in (xi) after stirring 30 min.

Table 3. ^{31}P NMR Data for the Compounds (δ in ppm and J in Hz)

compound	coordinated phosphine	chemical shifts			coupling constants		
		P_A[a]	P_B[b]	P_C[b]	J_{PAPB}	J_{PAPC}	J_{PBPC}
3	PMe_3	21.5	−14.0		438		
4	PMe_2Ph	21.0	−4.9		439		
	$P(OC_6H_5)_3$	21.6	89.1		660		
cis-**5**	PPh_3	−79.8	16.0		16		
trans-**5**	PPh_3	−85.8	30.9		462		
cis-**6**	P(*p*-MeC_6H_4)$_3$	−81.0	12.9		14		
trans-**6**	P(*p*-MeC_6H_4)$_3$	−86.7	28.6		460		
cis-**7**	P(*m*-MeC_6H_4)$_3$	−80.4	8.2		15		
trans-**7**	P(*m*-MeC_6H_4)$_3$	−86.3	30.9		459		
cis-**8**	P(*o*-ClC_6H_4)Ph_2	−81.0	15.7		14		
trans-**8**	P(*o*-ClC_6H_4)Ph_2	−87.4	23.7		473		
cis-**9**	P(*o*-BrC_6H_4)Ph_2	−81.2	20.4		12		
trans-**9**	P(*o*-BrC_6H_4)Ph_2	−87.9	27.2		460		
cis-**10**	P(*o*-$CH_3OC_6H_4$)Ph_2	−81.0	9.7		14		
trans-**10**	P(*o*-$CH_3OC_6H_4$)Ph_2	−86.6	20.9		473		
cis-**11**	PCy_3	−78.1	24.5		14		
trans-**11**	PCy_3	−88.6	34.2		440		
12		20.1					
13		18.9					
14	PMe_3	26.4	−18.3	−31.7	371	−37	−37
15	PPh_3	−82.3	32.4	20.9	376	29	29
16	P(*p*-MeC_6H_4)$_3$	−81.3	31.1	19.5	381	29	29
17	$Ph_2PCH_2PPh_2$	17.8	−19.3	−33.1	376	−16	−37
18	$Ph_2PCH_2CH_2PPh_2$	−74.6	55.8	44.1	378	24	24

[a] Metalated phosphine. [b] Coordinated phosphine.

Table 4. Selected Bond Distances (Å) and Angles (deg) for $\{Pd[\mu_2\text{-}(C_6H_4)PPh_2]Br[PMe_3]\}_2$, **3**·$2CH_2Cl_2$

Pd−C1	2.023(4)	Pd−P1	2.3561(10)
Pd−P2	2.3127(10)	Pd−Br	2.5042(5)
C1−Pd−P2	86.55(11)	C1−Pd−P1	89.57(10)
P1−Pd−P2	168.09(4)	C1−Pd−Br	175.74(11)
P2−Pd−Br	89.53(3)	P1−Pd−Br	93.94(3)

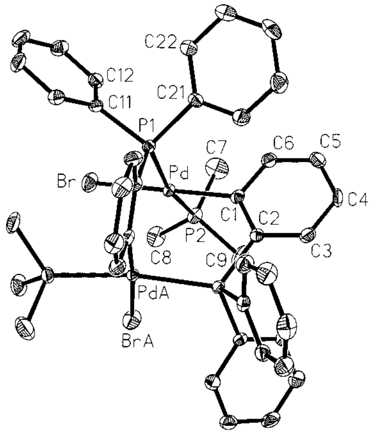


Figure 2. Molecular view of $\{Pd[\mu_2\text{-}(C_6H_4)\ PPh_2]Br[PMe_3]\}_2$, **3**.

are linked by two metalated phosphine ligands, $[P(C_6H_4)Ph_2]^-$, in a cis head-to-tail arrangement. One PMe_3 is trans to the phosphorus atom of the metalated phosphine; one bromide, trans to the carbon atom of the metalated phosphine, completes the square planar coordination for each palladium(II) atom. The distance between palladium atoms is shorter in compound **3** (2.9999(6) Å) than in compound **1** (3.09 Å),[2] and it is in the range observed for similar dinuclear palladium(II) species (2.90 Å).[6] The Pd−C distance (2.023(4) Å) is also very similar to the observed Pd−C distance in **1** (2.03(8) Å).[2] The angles around each palladium atom do not show a big distortion from the square planar arrangement: P1−Pd−Br = 93.94(3)°, C1−Pd−P1 = 89.57(10)°, C1−Pd−P2 = 86.55(11)°, and P2−Pd−Br = 89.53(3)°.

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(6) Yao, C. L.; He, L. P.; Korp, J. D.; Bear, J. L. *Inorg. Chem.* **1988**, *27*, 4389.

Table 5. Selected Bond Distances (Å) and Angles (deg) for *trans*-{Pd[η^2-(C_6H_4)PPh_2]Br[PCBr]}, *trans*-**9**·$2CDCl_3$

Pd−C1	2.042(9)	Pd−P1	2.285(3)
Pd−P2	2.340(3)	Pd−Br1	2.5818(12)
C1−Pd−P1	69.0(3)	C1−Pd−P2	96.0(3)
P1−Pd−P2	164.73(9)	C1−Pd−Br1	164.7(3)
P1−Pd−Br1	96.21(7)	P2−Pd−Br1	98.98(7)

The reaction of **1** and PMe_2Ph ($\theta = 122°$) yields a pale-yellow crystalline product of formula {Pd[μ_2-(C_6H_4)PPh_2]Br-[PMe_2Ph]}$_2$ (**4**). It is stable in the solid state and in solution at room temperature, even when additional phosphine is added. According to the spectroscopic data (Table 3), **4** has a dinuclear structure similar to that of **3**. The reaction of **1** with $P(OPh)_3$ ($\theta = 128°$) gives a species with spectroscopic data similar to **3** of limited stability, even in the solid state.

Bulkier phosphines ($\theta > 150°$) produced the cleavage of the tetranuclear unit of **1**, yielding only mononuclear species of formula {Pd[η^2-(C_6H_4)PPh_2]Br[*P*]} (*P* = P(*p*-MeC_6H_4)$_3$ (**6**), *P* = P(*m*-MeC_6H_4)$_3$, (**7**), *P* = P(*o*-ClC_6H_4)Ph_2 (**8**), and *P* = P(*o*-$CH_3OC_6H_4$)Ph_2 (**10**)). The $^{31}P\{^1H\}$ NMR spectra of the resulting products showed signals with negative values of the chemical shift (−78 to −88 ppm), characteristic of a four-atom metallocycle.[2]

It has been observed in square planar arylpalladium(II) compounds containing phosphines as auxiliary ligands that the arrangement of a phosphine trans to an aryl group is much less favorable than a cis arrangement.[7] This general tendency has been described as “transphobia”.[8] It is noticeable that all the mononuclear compounds of formula {Pd[η^2-(C_6H_4)PPh_2]Br[*P*]}, obtained by degradation of the tetranuclear **1**, exist in solution as a mixture of cis and trans isomers in equilibrium, not following the general tendency described above. The observed cis/trans ratio of isomers in solution varies with the temperature and also with the phosphine (see Experimental Section).

The only single crystals of these types of compound suitable for X-ray analysis were obtained for *trans*-**9**, {Pd[η^2-(C_6H_4)-PPh_2]Br[PCBr]}. The cis isomer was also present in solution but did not give good quality crystals. A summary of the fundamental crystal data is given in Table 1, and selected bond lengths and angles are collected in Table 5. The structure of *trans*-**9** (Figure 3) consists of a mononuclear palladium(II) species with a cyclometalated phosphine ligand $[P(C_6H_4)Ph_2]^-$ forming a four-atom Pd−P−C−C ring. One PCBr phosphine, trans to the P from the metalated phosphine, and one bromide complete the square planar coordination around the metal. The angles around the palladium atom are relatively distorted from the perfect square planar configuration. The C−Pd−P angle found in compound **9**, 69.0(3)°, is among the smallest values observed in the four-member cyclometalated phosphine palladium compound, 68.7(2)−71.2(2)°.[9]

The ^{31}P NMR data of compounds **6**−**8** and **10** show chemical shifts values similar to that of compound **9**, suggesting a mononuclear structure for all these compounds.

Few examples of compounds with a fouratom metallocycle are described in the literature for palladium(II) compounds.[1] Despite the tension associated with this metallocycle, these compounds are quite stable. This stability might be associated with the existence of geometrical rigidity around the metal center produced by a sterically congested situation due to bulky phosphine ligands. This behavior, which has been extensively documented,[10] can explain that mononuclear compounds with a four-atom metallocycle are stabilized by the presence of relatively bulky phosphines while less sterically demanding ligands only produce the dinuclear species with the more open bridging metallocycle.

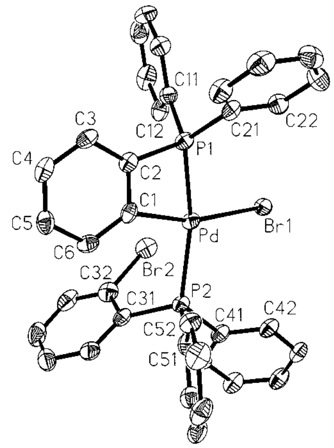

Figure 3. Molecular view of *trans*-{Pd[η^2-(C_6H_4) PPh_2]Br[PCBr]}, *trans*-**9**.

The behavior observed with the phosphine $PMePh_2$ ($\theta = 136°$) is borderline between the two situations described above because a mixture of mononuclear and dinuclear palladium compounds is detected in solution by ^{31}P NMR when **1** and $PMePh_2$ were reacted (in a 1:1 [Pd]/[P] molar ratio) at room temperature.

Synthesis of Dinuclear and Mononuclear Cationic Compounds. Compound **1** reacts at room temperature with a slight excess of silver acetate or trifluoroacetate to form dinuclear compounds of formula Pd[μ_2-(C_6H_4)PPh_2](μ_2-O_2CCX_3)$_2$, X = F (**12**) and X = H (**13**), in high yield. On the basis of the spectroscopic data, we assign to these compounds a dinuclear structure with two carboxylates and two metalated phosphines acting as bridging ligands.

The reaction of **1** and a stoichiometric amount of $AgBF_4$ in a mixture of CH_2Cl_2−THF gave solvated species in solution, which we tentatively formulate as $\{Pd[\mu_2\text{-}(C_6H_4)PPh_2](THF)_n\}_2^{2+}$. This compound was also crystallyzed in the form of acetonitrile solvate $\{Pd[\mu_2\text{-}(C_6H_4)PPh_2](CH_3CN)_n\}_2[BF_4]_2$. These two solvated species did not give reproducible elemental analysis results and gave broad resonances in the ^1H and ^{31}P NMR spectra even at −60° C, suggesting the existence in solution of a dynamic process. However, exchange of the solvent molecules by P donor ligands gave stable mononuclear and dinuclear cationic palladium compounds of general formula {Pd[η^2-(C_6H_4)PPh_2][*P*]$_2$}-{BF_4} or {Pd[μ_2-(C_6H_4) PPh_2][*P*]$_2$}$_2${BF_4}$_2$, depending on the nature of the phosphine.

Thus, the reaction of $\{Pd[\mu_2\text{-}(C_6H_4)PPh_2](THF)_n\}_2[BF_4]_2$ with PMe_3 gave a crystalline compound resulting from the replacement of the two bromides by two PMe_3 ligands in compound **3** (Scheme 2), which we formulated as {Pd[μ_2-(C_6H_4)PPh_2]-[PMe_3]$_2$}{BF_4}]$_2$ (**14**). The ^{31}P NMR spectrum is consistent with a AA′BB′CC′ spin system that supports a dinuclear structure for compound **14**.

As in the case of the neutral species previously described, the stability of the dinuclear frame in cationic solvated species

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(7) (a) Pfeffer, M.; Grandjean, D.; Le Borgne, G. *Inorg. Chem.* **1981**, *20*, 4426. (b) Pearson, R. G. *Inorg. Chem.* **1973**, *12*, 712.

(8) Vicente, J.; Arcas, A.; Bautista, D.; Jones, P. G. *Organometallics* **1997**, *16*, 2127.

(9) (a) Mullica, D. F.; Sappenfield, E. L.; Leschnitzer, D. H. *J. Crystallogr. Spectrosc. Res.* **1991**, *21*, 675. (b) Carmichael, D.; Hitchcock, P. B.; Nixon, J. F.; Mathey, F.; Ricard, L. *J. Chem. Soc., Dalton Trans.* **1993**, 1811.

(10) Zhang, L.; Zetterberg, K. *Organometallics* **1991**, *10*, 3806.

is dictated by the size of the phosphine ligand. Thus, the reaction of the cationic solvated species with PMe_2Ph ([P]/[Pd] = 2) gave the mononuclear and the dinuclear compound according to the low-temperature $^{31}P\{^1H\}$ NMR spectrum recorded for this reaction mixture. At room temperature the spectrum showed broad signals, indicating that a ligand exchange process takes place under these conditions. The reaction with bulkier phosphines gave only mononuclear cationic species $\{Pd[\eta_2\text{-}(C_6H_4)PPh_2][P_2]\}^+$ ($P = PPh_3$ (**15**); $P = P(p\text{-}MeC_6H_4)_3$ (**16**)) (Scheme 2).

Addition of 2 equiv of $Ph_2PCH_2PPh_2$ to a solution of cationic solvated species results in the formation of a yellow solution from which the complex $\{Pd[\mu_2\text{-}(C_6H_4)PPh_2][Ph_2PCH_2PPh_2]\}_2\{BF_4\}_2$ (**17**) was isolated in high yield. Analysis of the ^{31}P NMR spectrum of this compound showed an AA′BB′CC′ system consistent with the dinuclear formulation (Scheme 2). The absence of signals at high field, characteristic of a phosphorus atom in a four-atom metallocycle, suggested that in compound **17** the diphosphine is acting as a bridging ligand.

When the diphosphine $Ph_2PCH_2CH_2PPh_2$ was used in this reaction, a mixture of dinuclear and mononuclear species was formed. The evolution of the dinuclear to the mononuclear species, followed by $^{31}P\{^1H\}$ NMR spectroscopy, was completed after 30 min. The mononuclear compound $\{Pd[\eta^2\text{-}(C_6H_4)PPh_2][Ph_2PCH_2CH_2PPh_2]\}\{BF_4\}$ (**18**) was isolated in good yield as the only product of the reaction.

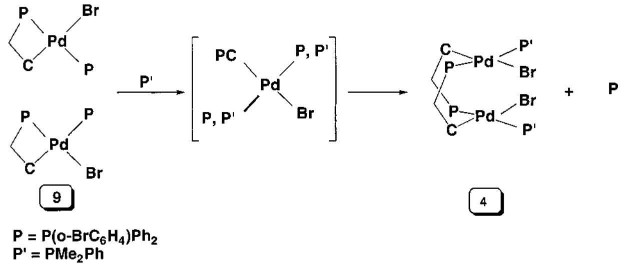
Under some particular conditions, working with the less sterically demanding phosphines, we have obtained spectroscopic evidence of a palladium species with one orthometalated phosphine coordinated only via a carbon atom $[(CC_5H_4)PPh_2]$.

Thus, we caused **1** and $PMePh_2$ to react in different [P]/[Pd] ratios and we studied the distribution of products by ^{31}P NMR spectroscopy in the range −50 to +30 °C. When [P]/[Pd] is less than 1, the new compounds detected in solution were the mononuclear $\{Pd[\eta^2\text{-}(C_6H_4)PPh_2]Br[PMePh_2]\}$ (cis and trans isomers) and the dinuclear $\{Pd[\mu_2\text{-}(C_6H_4)PPh_2]Br[PMePh_2]\}_2$ (trans isomer). The trans/cis ratio of the mononuclear species increased by decreasing the temperature. The dinuclear compound slowly transforms into the mononuclear ones, but the transformation is not complete after 6 h at room temperature.

When an additional amount of phosphine was added to this mixture until [P]/[Pd] ≈ 1.3, two signals were observed in the ^{31}P NMR spectrum: one doublet at 8.3 ppm and one triplet at 9.9 ppm ($^2J_{PP'} = 35$ Hz). These spectroscopic data are consistent with the formation of a new mononuclear species, $\{Pd[(CC_5H_4)PPh_2]Br[PMePh_2]_2\}$, having one palladium atom bonded to one bromide, two $PMePh_2$ ligands in a relative trans disposition, and one metalated phosphine coordinated only via the carbon atom. At −30 °C, sharp signals for all the species in solution, $\{Pd[\eta^2\text{-}(C_6H_4)PPh_2]Br[PMePh_2]\}$ (cis and trans isomers), the dinuclear $\{Pd[\mu_2\text{-}(C_6H_4)PPh_2]Br[PMePh_2]\}_2$ and $\{Pd\text{-}[(CC_5H_4)PPh_2]Br[PMePh_2]_2\}$, were observed in the spectrum. However at room temperature the signals due to the two mononuclear species collapsed into two broad resonances. We propose that the equilibrium represented in Scheme 3, which involves reversible coordination of one $PMePh_2$ phosphine with simultaneous opening of the four-atom metallocycle, must be responsible for the broadening of the NMR signals. The dinuclear compound did not participate in this rapid process, and its resonances were sharp in all the range of temperatures.

Spectroscopic evidence has been also obtained for the analogous species with the ligands PMe_2Ph and PMe_3. Because the reaction of **1** and PMe_3(or PMe_2Ph) only gave dinuclear species, the synthesis of the $\{Pd[\eta^2\text{-}(C_6H_4)PPh_2]Br[P]\}$ species was achieved by ligand substitution reaction. As starting material, $\{Pd[\eta^2\text{-}(C_6H_4)PPh_2]Br[PCBr]\}$ (**9**) was used, a readily available product having a bulky and easily displaced phosphine. Thus, a 1:1 mixture of **9** and PMe_2Ph gave two new signals in the ^{31}P NMR spectrum recorded at 0 °C, one doublet at −6.3 ppm and one triplet at −10.3 ppm ($^2J_{PP'} = 33$ Hz), which can be attributed to the species $\{Pd[(CC_5H_4)PPh_2]Br[PMe_2Ph]_2\}$. After 24 h at room temperature, the system rearranged to form only the dinuclear compound **4** in solution. Similar experiments with PMe_3 also gave the analogous species $\{Pd[(CC_5H_4)PPh_2]Br[PMe_3]_2\}$ characterized by two signals in the ^{31}P NMR spectrum: one doublet at −15.8 ppm and one triplet at −9.7 ppm ($^2J_{PP'} = 26$ Hz). The stability of this species with PMe_3 is considerably higher, and the evolution to the dinuclear compound **3** is slow. All the efforts to isolate this species have been unsuccessful.

Scheme 3



This ligand displacement reaction did not occur so readily with bulkier triarylphosphines. Thus, the reaction of **9** with $P(p\text{-}MeC_6H_4)_3$ (1:1 ratio) only gave broad signals in the ^{31}P NMR spectrum. At −50 °C the spectrum was consistent with the formation of several species in solution: *trans*-**9**, *trans*-$\{Pd[\eta^2\text{-}(C_6H_4)PPh_2]Br[P(p\text{-}MeC_6H_4)_3]\}$, and two cationic species resulting from bromide displacement, $\{Pd[\eta^2\text{-}(C_6H_4)PPh_2][P(p\text{-}MeC_6H_4)_3][PCBr]\}^+Br^-$, and $\{Pd[\eta^2\text{-}(C_6H_4)PPh_2][P(p\text{-}MeC_6H_4)_3]_2\}^+Br^-$. With 3 molar excess of phosphine, the last cationic species becomes dominant. The ^{31}P NMR spectrum of this species at −50 °C is almost identical to that described for **16**, the analogous cationic compound with a BF_4^- counteranion. The fluxional behavior observed for $\{Pd[\eta^2\text{-}(C_6H_4)PPh_2][P(p\text{-}MeC_6H_4)_3]_2\}^+Br^-$ must be due to the presence of a coordinating species, the bromide, that competes with the phosphine for coordination to palladium.

Conclusions

The results described above clearly confirm the ability of the ligand $[(C_6H_4)PPh_2]$ to expand a bridging $[\mu_2\text{-}(C_6H_4)PPh_2]$ or a chelating $[\eta^2\text{-}(C_6H_4)PPh_2]$ coordination mode when coordinating to palladium(II) atoms. In compounds of general formula $Pd[(C_6H_4)PPh_2]BrP$, this particular ligand is able to adopt one or the other mode of coordination depending on the size of *P*. Bulky phosphines stabilize the chelating coordination mode by producing steric congestion on the resulting four-atom metallocycle, while the less sterically demanding phosphines clearly favor the bridging mode.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structures of **2**, **3**, and *trans*-**9** complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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