Synthesis and Double C–H Activation of Palladium(II) Complexes with the Cationic Ligand $[To_3PCH_2(Py\text{-}2)]^+$ (To = C_6H_4Me-4, Py = Pyridine). Some Evidence of the Formation of a Palladium(IV) Complex. Crystal and Molecular Structures of *trans*-$[PdCl_2\{Py\{CH_2PTo_3\}\text{-}2\}_2](ClO_4)_2\cdot 4Cl_2CH_2$, $[PdCl\{\mu^2\text{-}\kappa^3\text{-}C_6H_3\{PTo_2CH(Py\text{-}2')\text{-}2\}Me\text{-}4\}]_2\cdot 2Cl_2CH_2$, and *cis*-$[PdI_2\{\kappa^2\text{-}C_6H_3\{PTo_2CHCl(Py\text{-}2')\text{-}2\}Me\text{-}4\}]\cdot Cl_2CH_2$

José Vicente,* María-Teresa Chicote,* and María-Cristina Lagunas

Grupo de Química Organometálica, Departamento de Química Inorgánica, Facultad de Química, Universidad de Murcia, Apartado 4021, Murcia, 30071 Spain

Peter G. Jones* and Eberhard Bembenek

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, 38023 Braunschweig, Germany

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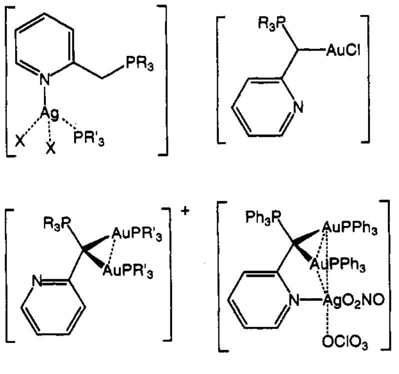
$[PdCl_2(NCPh)_2]$ reacts with $[To_3PCH_2(Py\text{-}2)]ClO_4$ (1:2) (To = C_6H_4Me-4, Py = pyridine) or with $[To_3PCH_2(Py\text{-}2)]Cl$ (1:1) to give, respectively, *trans*-$[PdCl_2\{Py\{CH_2PTo_3\}\text{-}2\}_2](ClO_4)_2$ (**1**) or $[PdCl_3\{Py\{CH_2PTo_3\}\text{-}2\}]$ (**2**). By reacting **1** with 1,8-bis(dimethylamino)naphthalene (1:2 or 1:4) or $[To_3PCH_2(Py\text{-}2)]Cl$ with $[PdCl_2(NCPh)_2]$ and Na_2CO_3 (1:1:1), the complex $[PdCl\{\mu^2\text{-}\kappa^3\text{-}C_6H_3\{PTo_2CH(Py\text{-}2')\text{-}2\}Me\text{-}4\}]_2\cdot{}^1/_2H_2O$ (**3**) is obtained. This complex reacts (i) with PEt_3 (1:2) to give (*SP*-4-3)$[PdCl\{\kappa^2\text{-}C_6H_3\{PTo_2CH(Py\text{-}2')\text{-}2\}Me\text{-}4\}(PEt_3)]$ (**4**), (ii) with $AgClO_4$ and PEt_3 (1:2:2) to give $[Pd\{\kappa^3\text{-}C_6H_3\{PTo_2CH(Py\text{-}2')\text{-}2\}Me\text{-}4\}(PEt_3)]_2(ClO_4)_2$ (**5**), (iii) with an excess of Cl_2 to give $[PdCl_2\{\kappa^2\text{-}C_6H_3\{PTo_2CHCl(Py\text{-}2')\text{-}2\}Me\text{-}4\}]$ (**6**), and (iv) with NaI (1:2) to give $[PdI\{\mu^2\text{-}\kappa^3\text{-}C_6H_3\{PTo_2CH(Py\text{-}2')\text{-}2\}Me\text{-}4\}]_2$ (**7**). Complex **6** reacts with excess of NaI to give *cis*-$[PdI_2\{\kappa^2\text{-}C_6H_3\{PTo_2CHCl(Py\text{-}2')\text{-}2\}Me\text{-}4\}]$ (**8**). The crystal structures of $\mathbf{1}\cdot 4Cl_2CH_2$, $\mathbf{3}\cdot 2Cl_2CH_2$, and $\mathbf{8}\cdot Cl_2CH_2$ were determined. [**1**: space group $P\bar{1}$, a = 12.227(4) Å, b = 12.565(4) Å, c = 12.720(4) Å, α = 61.95(2)°, β = 87.44(3)°, γ = 71.89(3)°, V = 1627.2(9) Å^3, Z = 1, R_{int} = 0.024, $R(F, >4\sigma(F))$ = 0.036. **3**: space group $C2/c$, a = 23.597(6) Å, b = 8.385(2) Å, c = 27.320(6) Å, β = 99.93(2)°, V = 5325(2) Å^3, Z = 4, R_{int} = 0.029, $R(F, >4\sigma(F))$ = 0.028. **7**: space group $P\bar{1}$, a = 10.379(3) Å, b = 11.961(4) Å, c = 14.289(4) Å, α = 105.03(3)°, β = 97.87(3)°, γ = 113.87(3)°, V = 1506.8(8) Å^3, Z = 2, R_{int} = 0.026, $R(F, >4\sigma(F))$ = 0.027.] Complex **1** adopts a *trans* geometry with short Pd–Cl and Pd–N bond distances [2.2886(11) and 2.035(3) Å, respectively]. The strong *trans* influence of the Pd–C(methine) and Pd–aryl bonds in complex **3** promotes the lengthening of both the Pd–Cl [2.3725(10) Å] and the Pd–N [2.135(3) Å] bonds. In complex **8** the coordination around the palladium atom is not exactly planar; the N atom lies 0.38 Å out of the plane of the other four atoms.

We have recently reported the synthesis and structure of mono-, di-, and tri-, homo- and heteronuclear Au(I), Ag(I), and Cu(I) complexes derived from phosphonium salts $[R_3PCH_2(Py\text{-}2)]X$ [R = Ph, C_6H_4Me-4 (To), Py = pyridine, X = ClO_4, CF_3SO_3].[1] These cationic ligands can coordinate through the nitrogen and also, after single or double deprotonation, through the methylene carbon atom. Both donor atoms can bridge up to three metal centers, allowing metal–metal interactions (see Chart 1). The strong tendency of palladium to give orthometalated complexes and the possibility of preparing Pd(I) and -(IV) complexes move us to extend the study of the coordination ability of these cationic ligands to palladium. In this paper, we show that a third coordination mode is also possible after orthometalation of one of the aryl groups. In Chart 2 we represent all modes of coordination found in the palladium complexes reported here, along with the notation used. This notation gives the general symbol R to the skeleton of the phosphonium salt, or RCl to the

Chart 1



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(1) Vicente, J.; Chicote, M. T.; Lagunas, M. C. *Inorg. Chem.* **1993**, *32*, 3748.

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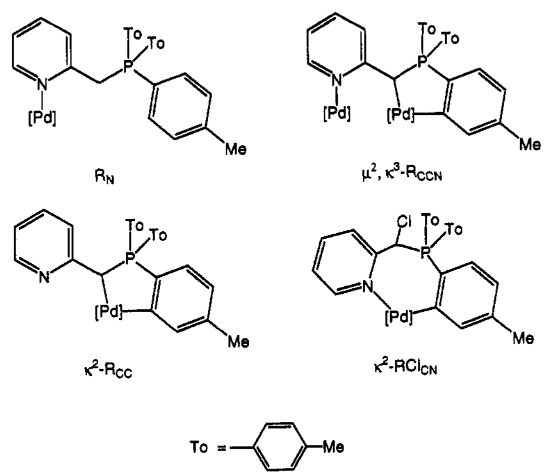
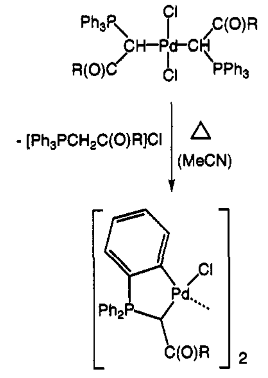
Chart 2



Scheme 1



chlorinated salt, and the donor atoms appear as subscripts. The κ notation is used to indicate the number of coordinated atoms.

Complexes containing the CC-five-membered ring shown in the ligand κ^2-R_{CC} (see Chart 2) have been obtained by thermal orthometalation of carbonyl-stabilized ylide palladium(II) complexes (see Scheme 1).[2] In our case, starting from complexes containing the N-bonded R_N ligand, it is possible to form the ylide– and aryl–palladium bonds using deprotonating agents at room temperature, which involves a rare double C–H bond activation.[3]

Experimental Section

The IR and C, H, and N analyses, conductance measurements, and melting point determinations were carried out as described elsewhere.[1] Unless otherwise stated, NMR spectra were recorded in $CDCl_3$ in a Varian Unity 300 and conductivity measurements in acetone. Chemical shifts are referred to TMS [^1H and $^{13}C\{^1H\}$] or H_3PO_4[$^{31}P\{^1H\}$].

[$PdCl_2(R_N)_2$](ClO_4)$_2$ (1). To a solution of [To_3PCH_2(Py-2)]ClO_4 (531.0 mg, 1.071 mmol) in dichloromethane (10 mL) was added [$PdCl_2(NCPh)_2$] (205.3 mg, 0.535 mmol). The resulting yellow solution changed into a suspension which, after 14.5 h of stirring, was filtered. The yellow solid was washed with dichloromethane (2 × 1 mL) and diethyl ether (2 mL) and air-dried. Yield: 544 mg, 87%. Mp: 178 °C. Λ_M: 270 Ω^{-1} cm^2 mol^{-1}. IR [ν(PdCl)]: 350 cm^{-1}. NMR [$(CD_3)_2SO$, δ]: ^1H (200 MHz), 2.40 [s, 9 H, Me (To)], 5.28 (d, 2 H, CH_2, $^2J_{PH}$ = 15.6 Hz), 7.2–7.7 (m, 15 H, To + Py), 8.33 [m, 1 H, Py (H6)]. $^{31}P\{^1H\}$ (80 MHz), 22.7 (s). Anal. Calcd for $C_{54}H_{54}Cl_4N_2O_8P_2Pd$: C, 55.47; H, 4.65; N, 2.39. Found: C, 55.96; H, 4.84; N, 2.15.

[$PdCl_3(R_N)$] (2). To a suspension of [To_3PCH_2(Py-2)]Cl (161.0 mg, 0.373 mmol) in acetone (40 mL) was added [$PdCl_2(NCPh)_2$] (142.9 mg, 0.373 mmol). After a few minutes the resulting orange solution became a suspension which was stirred for 14 h. The suspension was filtered, and the solid was washed with acetone (2 mL) and diethyl ether (1 mL), recrystallized twice from dichloromethane/diethyl ether, and dried in an oven (80 °C, 2 h). Yield: 173 mg, 76%. Mp: 246 °C. Λ_M: 5 Ω^{-1} cm^2 mol^{-1}. IR [ν(PdCl)]: 335, 316 cm^{-1}. NMR [Cl_2CD_2, δ]: ^1H, 2.48 [s, 9 H, Me (To)], 6.05 (d, 2 H, CH_2, $^2J_{PH}$ = 14 Hz), 6.85 [m, 1 H, Py (H3)], 7.22 [m, 1 H, Py (H5)], 7.4–7.7 (m, 13 H, To + Py), 9.06 [m, 1 H, Py (H6)]. $^{31}P\{^1H\}$, 21.55 (s). Anal. Calcd for $C_{27}H_{27}Cl_3NPPd$: C, 53.23; H, 4.47; N, 2.30. Found: C, 52.80; H, 4.44; N, 2.34.

[$PdCl(\mu^2$-κ^3-$R_{CCN})]_2\cdot{}^1/_2H_2O$ (3). To a suspension of [To_3PCH_2(Py-2)]Cl (671.0 mg, 1.553 mmol) in acetone (80 mL) were added [$PdCl_2(NCPh)_2$] (397.2 mg, 1.036 mmol) and Na_2CO_3 (219.6 mg, 2.072 mmol) to give an orange suspension which was stirred for 17 h. The resulting pale yellow suspension was filtered off and the solid recrystallized from dichloromethane/*n*-hexane to give **3** as a pale yellow solid which was first dried in air and then in an oven (80 °C, 1 h). Yield: 500 mg, 90%. Mp: 296 °C dec. Λ_M: 0 Ω^{-1} cm^2 mol^{-1}. IR [ν(PdCl)]: 290 cm^{-1}. NMR (δ): ^1H, 1.58 (s, 1 H, H_2O), 2.25 [s, 3 H, Me (To)], 2.33 [s, 3 H, Me (To)], 2.39 [s, 3 H, Me (To)], 5.86 [m, 1 H, Py (H3)], 6.29 [m, 1 H, Py (H5)], 6.55 [m, 1 H, Py (H4)], 6.70 (d, 1 H, CH, $^2J_{PH}$ = 10 Hz), 6.77 (m, 1 H, C_6H_3Me), 6.89 (dd, 1 H, C_6H_3Me, $^3J_{PH}$ = 9.6 Hz, $^3J_{HH}$ = 7.8 Hz), 7.26 (dd, 2 H, To, $^4J_{PH}$ = 2.5 Hz, $^3J_{HH}$ = 8 Hz), 7.42 (dd, 2 H, To, $^4J_{PH}$ = 2.1 Hz, $^3J_{HH}$ = 8 Hz), 7.81 (dd, 2 H, To, $^3J_{PH}$ = 12 Hz, $^3J_{HH}$ = 8 Hz), 7.98 [m, 1 H, Py (H6)], 8.03 (dd, 2 H, To, $^3J_{PH}$ = 11.2 Hz, $^3J_{HH}$ = 8 Hz), 8.29 (s, 1 H, C_6H_3Me). $^{31}P\{^1H\}$, 28.99 (s). Anal. Calcd for $C_{54}H_{51}Cl_2N_2O_{1/2}P_2Pd_2$: C, 59.96; H, 4.75; N, 2.59. Found: C, 60.21; H, 4.71; N, 2.51.

(*SP*-4-3)[$PdCl(\kappa^2$-$R_{CC})(PEt_3)$] (4). To a solution of **3** (210.5 mg, 0.194 mmol) in degassed dichloromethane (20 mL) was added PEt_3 (60 μL, 0.407 mmol). The solution was stirred under N_2 for 3 h and concentrated (2 mL). Addition of *n*-hexane (20 mL) and cooling (0 °C) precipitates a solid (a mixture of isomers *SP*-4-3 and *SP*-4-4) which was filtered off, dissolved in acetone, and stirred for 24 h. The solution was concentrated (1 mL), *n*-hexane at 0 °C added, the resulting suspension filtered, and the solid dried in the air and then in an oven (80 °C, 24 h) to give **4** as an off-white solid. Yield: 150 mg, 59%. Mp: 130 °C. Λ_M: 0 Ω^{-1} cm^2 mol^{-1}. NMR: ^1H (200 MHz, δ), 0.77 [dt, 9 H, Me (Et), $^3J_{PH}$ = 15 Hz, $^3J_{HH}$ = 7.5 Hz], 1.65 [m, 6 H, CH_2 (Et)], 2.28 [s, 3 H, Me (To)], 2.34 [s, 3 H, Me (To)], 2.38 [s, 3 H, Me (To)], 4.51 (dd, 1 H, CH, $^2J_{PH}$ = 10 Hz, $^3J_{PH}$ = 2.5 Hz), 6.66 [m, 1 H, Py (H4)], 6.89 [m, 1 H, Py (H5)], 7.1–7.8 [m, 12 H, To + Py], 7.94 [m, 1 H, Py (H6)]. $^{31}P\{^1H\}$, 16.88 (d, J_{PP} = 23.8 Hz), 17.79 (d). Anal. Calcd for $C_{33}H_{40}ClNP_2Pd$: C, 60.56; H, 6.16; N, 2.14. Found: C, 60.58; H, 6.22; N, 2.06.

[$Pd\{\mu^2$-κ^3-$R_{CCN}\}(PEt_3)]_2(ClO_4)_2$ (5). Method a. To a suspension of **3** (153 mg, 0.141 mmol) in acetone (20 mL) was added $AgClO_4$ (59.1 mg, 0.285 mmol). The resulting suspension was stirred in the dark for 0.5 h and then filtered through $MgSO_4$. The resulting solution was purged with N_2, and then molecular sieves and PEt_3 (45 μL, 0.305 mmol) were added. After 2 h of stirring under a N_2 atmosphere, it was concentrated (1 mL), and diethyl ether (20 mL) was added to precipitate **5** as a white solid.

Method b. To a solution of **4** (110.2 mg, 0.168 mmol) in acetone (10 mL) was added $AgClO_4$ (35 mg, 0.168 mmol), and the resulting suspension was stirred for 1.5 h and then filtered through $MgSO_4$. The solution was concentrated (1 mL) and diethyl ether (10 mL) added to give **5**. Yields: 165 mg, 81%, or 96 mg, 80%, respectively. Mp: 232 °C dec. Λ_M: 253 Ω^{-1} cm^2 mol^{-1}. NMR (δ): ^1H, 0.62 [dt,

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Table 1. Crystal Data and Refinement Details for Compounds 1, 3, and 8

compound	**1**·4CH_2Cl_2	**3**·2CH_2Cl_2	**8**·CH_2Cl_2
formula	$C_{58}H_{62}Cl_{12}$-$N_2O_8P_2Pd$	$C_{56}H_{54}Cl_6$-$N_2P_2Pd_2$	$C_{28}H_{27}Cl_3$-I_2NPPd
M_r	1508.84	1242.45	875.03
crystal habit	yellow tablet	yellow tablet	yellow tablet
crystal size (mm)	0.8 × 0.3 × 0.15	0.4 × 0.3 × 0.1	0.5 × 0.3 × 0.1
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$
temperature (°C)	–95	–95	–100
cell constants:			
a (Å)	12.227(4)	23.597(6)	10.379(3)
b (Å)	12.565(4)	8.385(2)	11.961(4)
c (Å)	12.720(4)	27.320(6)	14.289(4)
α (deg)	61.95(2)		105.03(3)
β (deg)	87.44(3)	99.93(2)	97.87(3)
γ (deg)	71.89(3)		113.87(3)
V (Å^3)	1627.2(9)	5325(2)	1506.8(8)
Z	1	4	2
D_x (mg m^{-3})	1.540	1.550	1.929
F(000)	768	2512	840
μ (mm^{-1})	0.88	1.08	3.00
transmissions	0.92–0.96	0.76–0.80	0.76–1.00
no. of reflections:			
measured	5741	9370	7934
independent	5729	4698	5331
R_{int}	0.024	0.029	0.026
R_w (F^2, all refl.)[a]	0.104	0.078	0.071
R (F, $F > 4\sigma(F)$)[b]	0.036	0.028	0.027
no. of parameters	379	310	328
no. of restraints	252	228	254
S[c]	1.04	1.11	1.06
max Δ/σ	0.9	0.09	0.001
max $\Delta\rho$ (e Å^{-3})	0.56	0.86	0.87

[a] $R_w(F^2) = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants adjusted by the program. [b] $R(F) = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$. [c] $S = [\Sigma\{w(F_o^2 - F_c^2)^2\}/(n - p)]^{0.5}$, where n is the number of data and p the number of parameters.

9 H, Me (Et), $^3J_{PH}$ = 16 Hz, $^3J_{HH(A)}$ = $^3J_{HH(B)}$ = 8 Hz], 1.25 [septuplet (see text), 3 H, H(A) of CH_2, $^2J_{AB}$ = 16 Hz], 1.44 [septuplet (see text), 3 H, H(B) of CH_2], 2.34 [s, 3 H, Me (To)], 2.38 [s, 3 H, Me (To)], 2.50 [s, 3 H, Me (To)], 4.84 (t, 1 H, CH, J_{PH} = 8.6 Hz), 6.76 [m, 2 H, To + Py], 6.97 [m, 1 H, C_6H_3Me], 7.1–7.3 [m, 8 H, To + Py], 7.53 (m, 2 H, To), 7.98 [m, 2 H, To]. $^{31}P\{^1H\}$: 12.56 (s), 14.69 (s). Anal. Calcd for $C_{33}H_{40}ClNO_4P_2Pd$: C, 55.16; H, 5.61; N, 1.95. Found: C, 55.39; H, 5.54; N, 1.90.

[PdCl$_2$(κ^2-RCl$_{CN}$)] (6). To a solution of **3** (200.5 mg, 0.185 mmol) in dichloromethane (5 mL) was added Cl_2IPh (102.0 mg, 0.374 mmol). The resulting orange solution turns to yellow in a few minutes. After 0.5 h *n*-hexane (20 mL) was added to precipitate **6** as a pale yellow solid. Yield: 195 mg, 87%. Mp: 230 °C dec. Λ_M: 0 Ω^{-1} cm^2 mol^{-1}. IR [ν(PdCl)]: 325, 260 cm^{-1}. NMR (δ): ^{1}H, 2.27 [s, 3 H, Me (To)], 2.46 [s, 3 H, Me (To)], 2.51 [s, 3 H, Me (To)], 6.44 (m, 1 H, C_6H_3Me), 6.62 (m, 1 H, C_6H_3Me), 7.21–7.97 (m, 12 H, To + Py), 8.91 (s br, 1 H, CH), 9.02 [m, 1 H, Py (H6)]. $^{31}P\{^1H\}$, 24.84 (s). Anal. Calcd for $C_{54}H_{50}Cl_6N_2P_2Pd_2$: C, 53.40; H, 4.15; N, 2.31; Cl, 17.51. Found: C, 53.03; H, 4.17; N, 2.28; Cl, 17.28.

[PdI{μ^2-κ^3-R$_{CCN}$}]$_2$ (7). To a suspension of **3** (104.4 mg, 0.096 mmol) in acetone (20 mL) was added NaI·2H_2O (36.2 mg, 0.195 mmol) The resulting yellow suspension was stirred for 0.5 h and concentrated to dryness, and the residue was extracted with dichloromethane (20 mL) and filtered through anhydrous $MgSO_4$. The solution was concentrated (1 mL), and 30 mL of diethyl ether was added to precipitate **7** as a yellow solid. Yield: 106 mg, 88%. Decomposition point: 284 °C. Λ_M: 0 Ω^{-1} cm^2 mol^{-1}. NMR (δ): ^{1}H, 2.26 [s, 3 H, Me (To)], 2.43 [s, 3 H, Me (To)], 2.48 [s, 3 H, Me (To)], 6.33 [m, 3 H, Py (H3 + H5) + CH], 6.73 [m, 1 H, Py (H4)], 6.83 (m, 1 H, C_6H_3-Me), 6.97 (m, 1 H, C_6H_3-Me), 7.45 (m, 4 H, To), 7.73 [m, 1 H, Py (H6)], 8.02 (dd, 2 H, To, $^3J_{PH}$ = 11 Hz, $^3J_{HH}$ = 8 Hz), 8.40 (dd, 2 H, To, $^3J_{PH}$ = 12 Hz, $^3J_{HH}$ = 8 Hz), 8.51 (s, 1 H, C_6H_3-Me). $^{31}P\{^1H\}$, 21.72 (s). Anal. Calcd for $C_{54}H_{50}I_2N_2P_2Pd_2$: C, 51.65; H, 4.01; N, 2.23. Found: C, 51.74; H, 4.23; N, 2.14.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for 1[a]

	x	y	z	U(eq)
Pd	5000	5000	5000	21.1(1)
Cl	4046.5(7)	5295.3(9)	3326.6(7)	33.9(2)
P	7473.6(6)	6344.3(7)	2800.8(7)	21.6(2)
C(1)	7659(3)	5153(3)	4393(3)	24.4(6)
N	6441(2)	3782(2)	4809(2)	23.1(5)
C(12)	7506(3)	3919(3)	4649(3)	23.3(6)
C(13)	8452(3)	2926(3)	4697(3)	32.0(7)
C(14)	8319(3)	1800(3)	4900(3)	38.1(8)
C(15)	7231(3)	1684(3)	5014(3)	37.0(8)
C(16)	6316(3)	2691(3)	4962(3)	31.2(7)
C(21)	7458(3)	5709(3)	1803(3)	24.0(6)
C(22)	8235(3)	5849(3)	948(3)	29.1(7)
C(23)	8125(3)	5521(3)	69(3)	32.3(7)
C(24)	7258(3)	5041(3)	20(3)	30.6(7)
C(25)	6509(3)	4873(3)	904(3)	30.9(7)
C(26)	6597(3)	5206(3)	1777(3)	29.1(7)
C(27)	7111(3)	4741(4)	–967(3)	40.2(8)
C(31)	8666(3)	6952(3)	2559(3)	23.8(6)
C(32)	8466(3)	8263(3)	1919(3)	27.4(7)
C(33)	9391(3)	8722(3)	1681(3)	30.4(7)
C(34)	10532(3)	7889(3)	2067(3)	28.3(7)
C(35)	10716(3)	6578(3)	2701(3)	28.0(7)
C(36)	9800(3)	6108(3)	2949(3)	25.4(6)
C(37)	11536(3)	8394(4)	1799(3)	40.1(8)
C(41)	6145(3)	7626(3)	2486(3)	25.5(6)
C(42)	5960(3)	8180(3)	3235(3)	29.5(7)
C(43)	4975(3)	9209(3)	2995(3)	34.2(7)
C(44)	4156(3)	9704(3)	2015(3)	35.0(8)
C(45)	4349(3)	9140(3)	1287(3)	38.6(8)
C(46)	5336(3)	8115(3)	1503(3)	31.6(7)
C(47)	3085(3)	10830(4)	1765(4)	53.6(11)
C(100)	3554(4)	8572(5)	7502(4)	56.9(11)
Cl(2)	4914.0(10)	7883.5(13)	7186.3(14)	73.2(4)
Cl(3)	3582.1(13)	8324.5(13)	8983.0(12)	75.0(4)
C(101)	284(4)	7907(4)	8040(4)	48.5(10)
Cl(4)	116.7(9)	7760.5(11)	9479.7(9)	53.2(3)
Cl(5)	540.8(10)	9326.4(10)	7069.9(9)	51.3(3)
Cl(6)	8186.1(7)	7794.1(8)	5742.2(7)	34.5(2)
O(1)	8417(4)	7014(4)	6994(3)	98.9(14)
O(2)	8836(3)	8651(3)	5423(3)	73.6(10)
O(3)	6995(3)	8566(4)	5365(4)	89.1(13)
O(4)	8545(3)	7041(3)	5154(3)	64.2(9)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

***cis*-[PdI$_2$(κ^2-RCl$_{CN}$)] (8).** To a suspension of **6** (132.3 mg, 0.109 mmol) in acetone (40 mL) was added NaI·2H_2O (81.1 mg, 0.436 mmol), and then the mixture was stirred for 1 h. The resulting suspension was concentrated to dryness, and the residue was extracted with dichloromethane (20 mL) and filtered through anhydrous $MgSO_4$. The solution was concentrated (1 mL), and addition of diethyl ether (30 mL) precipitated **8** as a yellow solid. Yield: 130 mg, 75%. Decomposition point: 189 °C. Λ_M: 0 Ω^{-1} cm^2 mol^{-1}. NMR [Cl_2CD_2, δ]: ^{1}H, 2.27 [s, 3 H, Me (To)], 2.51 [s, 3 H, Me (To)], 2.52 [s, 3 H, Me (To)], 6.66–8.04 [m, 14 H, Py + To], 8.98 [m, 1 H, Py (H6)], 9.02 (d, 1 H, CH, $^2J_{PH}$ = 9 Hz). $^{31}P\{^1H\}$: 27.63 (s). Anal. Calcd for $C_{54}H_{50}Cl_2I_4N_2P_2Pd_2$: C, 41.04; H, 3.19; N, 1.77. Found: C, 40.86; H, 3.31; N, 1.63.

X-ray Structure Determination of Complexes 1, 3, and 8. Crystal data are given in Table 1. Data collection and reduction: Crystals were mounted in inert oil (type RS3000, donated by Fa. Riedel de Haën) on glass fibers and transferred to the cold gas stream of the diffractometer (Siemens R3 system with LT-2 low-temperature attachment). Intensities were measured with ω-scans using monochromated Mo Kα radiation (λ = 71.073 pm) to $2\theta_{max}$ 50°. Cell constants were refined from diffractometer angles of *ca.* 50 reflections in the 2θ range 20–23°. Absorption corrections were based on ψ-scans. Structure solution and refinement: The structures were solved by direct methods and refined anisotropically on F^2 using the program SHELXL-93 (G. M. Sheldrick, University of Göttingen). Hydrogen atoms were included with a riding model. Final atomic coordinates are given in Tables 2–4, with derived bond lengths and angles in Tables 5–7.

Table 3. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for 3[a]

	x	*y*	*z*	*U*(eq)
Pd	5874.8(1)	5591.3(3)	2382.3(1)	19.0(1)
P	6001.3(3)	5070.1(10)	3517.3(3)	19.7(2)
Cl(1)	6331.8(3)	5444.7(11)	1675.1(3)	31.0(2)
C(1)	5491.0(12)	5821(4)	3014.5(11)	19.4(7)
C(11)	6295.9(12)	3715(4)	2718.8(11)	19.1(6)
C(12)	6324.6(12)	3496(4)	3233.3(11)	20.5(7)
C(13)	6616.1(14)	2215(4)	3491.6(13)	26.1(7)
C(14)	6880.7(14)	1120(4)	3236.9(13)	27.4(7)
C(15)	6855.2(13)	1256(4)	2725.3(12)	23.3(7)
C(16)	6567.8(13)	2532(4)	2476.5(12)	22.5(7)
C(17)	7155.8(15)	23(4)	2458.7(13)	30.9(8)
C(21)	5670.1(13)	4347(4)	4019.5(12)	24.0(7)
C(22)	5997.3(14)	3805(5)	4463.0(13)	30.7(8)
C(23)	5737(2)	3144(5)	4829.0(13)	35.7(9)
C(24)	5138(2)	2992(4)	4767.3(14)	33.1(8)
C(25)	4815.4(14)	3551(5)	4330.9(14)	33.4(8)
C(26)	5072.0(14)	4220(4)	3957.5(13)	27.3(7)
C(27)	4854(2)	2280(5)	5168.8(15)	43.0(10)
C(31)	6572.8(13)	6408(4)	3780.7(12)	21.6(7)
C(32)	7049.5(13)	6566(4)	3541.0(12)	23.0(7)
C(33)	7514.5(13)	7475(4)	3755.4(12)	25.9(7)
C(34)	7525.0(14)	8248(4)	4203.0(12)	25.6(7)
C(35)	7040.4(14)	8146(4)	4425.7(12)	29.5(8)
C(36)	6567.0(14)	7240(4)	4219.7(12)	30.4(8)
C(37)	8050(2)	9153(5)	4441.2(14)	37.2(9)
C(41)	5223.3(13)	7405(4)	3087.3(11)	21.9(7)
N(42)	4641.2(11)	7496(3)	2970.1(10)	23.1(6)
C(43)	4387.1(15)	8895(4)	3025.9(14)	33.3(8)
C(44)	4680(2)	10261(4)	3194(2)	39.9(10)
C(45)	5269(2)	10186(4)	3305(2)	40.7(10)
C(46)	5541.9(14)	8765(4)	3244.8(14)	31.2(8)
C(50)	6885(2)	8619(5)	995.8(15)	45.2(10)
Cl(2)	6303.4(5)	9943(2)	913.5(5)	64.4(3)
Cl(3)	7221.4(5)	8543.9(15)	469.2(4)	51.3(3)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Results and Discussion

Synthesis and Reactivity of Complexes. The cation of the phosphonium salt [To_3PCH_2(Py-2)]ClO_4 (To = C_6H_4Me-4, Py = pyridine) is able to replace the labile benzonitrile ligand when it is reacted with [$PdCl_2(NCPh)_2$] in the molar ratio 1:2. The reaction product, [$PdCl_2(R_N)_2$]-$(ClO_4)_2$ (1) (see Chart 2 and Scheme 2), precipitates in the reaction medium (acetone). When the phosphonium salt [To_3PCH_2(Py-2)]Cl is reacted with the same palladium complex in molar ratios ≥1, both anion and cation coordinate to the metal to give [$PdCl_3(R_N)$] (2) (see Scheme 2). Even when the ratio is 1:1, 2 is still obtained but contaminated with insoluble compounds that could not be identified. We have previously shown[3] that phosphonium salts [To_3PCH_2(Py-2)]X (X = Cl, ClO_4, CF_3SO_3) react with some silver salts of weakly coordinating anions, such as ClO_4 or CF_3SO_3, to give complexes of the types [$AgX_2(R_N)$] and [$AgX_3(R_N)_2$], whereas $AgNO_3$ or Ag(AcO) do not react.

When 1 is reacted with Proton Sponge [1,8-bis(dimethylamino)naphthalene = bdan; see Scheme 2] in molar ratios 1:2 or 1:4 the complex [PdCl{μ^2-κ^3-R_{CCN}}]$_2$·$^1/_2H_2O$ (3) is obtained. This complex results from 1 through a double deprotonation of one of the phosphonium ligands along with substitution of one chloro and the other phosphonium ligand. The anionic ligand resulting from the double C–H activation acts as a C,C chelating ligand while also bridging the other palladium atom, through the pyridine group (see below). It crystallizes with $^1/_4$ mol of water per palladium atom which cannot be removed by heating it in an oven at 80 °C for 1 h.

Table 4. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for 8[a]

	x	*y*	*z*	*U*(eq)
Pd	1917.3(3)	437.3(3)	6904.1(2)	22.7(1)
I(1)	13.5(3)	34.2(3)	7926.1(2)	33.2(1)
I(2)	1757.8(3)	−1956.3(3)	6503.6(3)	40.1(1)
P	5114.0(11)	2975.0(10)	8285.3(7)	22.4(2)
Cl(1)	7129.5(11)	1891.4(10)	7650.6(8)	29.8(2)
N	3241(4)	868(3)	5946(2)	24.9(7)
C(12)	4708(4)	1452(4)	6268(3)	23.1(8)
C(13)	5572(5)	1823(4)	5644(3)	28.5(9)
C(14)	4901(5)	1585(4)	4652(3)	33.2(10)
C(15)	3395(5)	982(4)	4325(3)	34.4(10)
C(16)	2606(5)	639(4)	4987(3)	30.6(9)
C(17)	5282(4)	1647(4)	7355(3)	23.7(8)
C(21)	2272(4)	2277(4)	7236(3)	24.9(8)
C(22)	3699(4)	3304(4)	7753(3)	23.1(8)
C(23)	4013(5)	4610(4)	7913(3)	27.3(9)
C(24)	2920(5)	4891(4)	7561(3)	30.7(9)
C(25)	1498(5)	3911(4)	7060(3)	28.4(9)
C(26)	1201(4)	2617(4)	6906(3)	27.3(9)
C(27)	291(5)	4213(5)	6684(4)	39.6(11)
C(31)	4771(4)	2426(4)	9319(3)	25.2(8)
C(32)	3607(4)	2424(4)	9698(3)	27.1(9)
C(33)	3385(4)	2032(4)	10514(3)	27.9(9)
C(34)	4317(4)	1639(4)	10975(3)	26.1(8)
C(35)	5466(5)	1636(5)	10585(3)	33.5(10)
C(36)	5700(5)	2031(5)	9775(3)	37.1(10)
C(37)	4078(5)	1220(5)	11869(3)	35.3(10)
C(41)	6834(4)	4425(4)	8693(3)	25.5(8)
C(42)	7386(5)	4937(4)	7979(3)	30.5(9)
C(43)	8677(5)	6086(4)	8282(3)	31.4(9)
C(44)	9441(4)	6749(4)	9301(3)	31.3(9)
C(45)	8898(5)	6215(4)	10004(3)	33.7(10)
C(46)	7609(4)	5060(4)	9705(3)	29.6(9)
C(47)	10794(5)	8042(5)	9628(4)	45.6(12)
C(99)	2577(6)	3741(5)	4528(5)	51.8(14)
Cl(2)	2276.8(15)	5119.6(13)	4834.7(12)	56.3(4)
Cl(3)	3823(2)	3871.0(14)	3784.3(10)	54.8(3)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for 1[a]

Pd–N	2.035(3)	Pd–Cl	2.2886(11)
P–C(21)	1.793(3)	P–C(41)	1.793(3)
P–C(31)	1.798(3)	P–C(1)	1.836(3)
C(1)–C(12)	1.498(4)	N–C(16)	1.348(4)
N–C(12)	1.360(4)		
N′–Pd–N	180.0	N′–Pd–Cl	89.84(8)
N–Pd–Cl	90.16(8)	Cl–Pd–Cl′	180.0
C(21)–P–C(41)	109.4(2)	C(21)–P–C(31)	108.73(14)
C(41)–P–C(31)	109.0(2)	C(21)–P–C(1)	113.43(14)
C(41)–P–C(1)	108.7(2)	C(31)–P–C(1)	107.41(14)
C(12)–C(1)–P	115.8(2)	C(16)–N–C(12)	118.6(3)
C(16)–N–Pd	114.4(2)	C(12)–N–Pd	126.7(2)

[a] Symmetry transformation (indicated by a prime) used to generate equivalent atoms: $-x + 1, -y + 1, -z + 1$.

Complex 3 can also be obtained in a one-pot synthesis by reacting [To_3PCH_2(Py-2)]Cl with [$PdCl_2(NCPh)_2$] and Na_2CO_3 (1:1:1). The reaction gives first an orange suspension that slowly changes to pale yellow (complex 3). This reaction is not only easier but also yields a purer product because the byproducts (H_2O, CO_2, and NaCl) are easily separated. The best yield (90%) was attained using excess of [To_3PCH_2(Py-2)]Cl (50%) and Na_2CO_3 (100%). This reaction is, however, slower than that using Proton Sponge. The orange suspension first obtained is probably complex 2, which indeed reacts with Na_2CO_3 to give 3.

Both reactions leading to 3 can be assumed to occur through one of the two pathways depicted in Scheme 3. It is reasonable to postulate that the first process is formation of the ylide A because the most acidic protons

Table 6. Selected Bond Lengths (Å) and Angles (deg) for 3[a]

Pd–C(11)	1.998(3)	Pd–C(1)	2.093(3)
Pd–N(42)′	2.135(3)	Pd–Cl(1)	2.3725(10)
P–C(12)	1.770(3)	P–C(1)	1.779(3)
P–C(21)	1.797(3)	P–C(31)	1.806(3)
C(1)–C(41)	1.499(4)	C(11)–C(16)	1.407(4)
C(11)–C(12)	1.408(4)	C(12)–C(13)	1.399(4)
C(41)–N(42)	1.358(4)	C(41)–C(46)	1.393(5)
N(42)–C(43)	1.338(4)		
C(11)–Pd–C(1)	86.81(12)	C(11)–Pd–N(42)′	175.15(11)
C(1)–Pd–N(42)′	90.53(11)	C(11)–Pd–Cl(1)	94.24(9)
C(1)–Pd–Cl(1)	177.36(9)	N(42)′–Pd–Cl(1)	88.60(7)
C(12)–P–C(1)	102.17(14)	C(12)–P–C(21)	111.1(2)
C(1)–P–C(21)	112.5(2)	C(12)–P–C(31)	106.82(14)
C(1)–P–C(31)	116.6(2)	C(21)–P–C(31)	107.4(2)
C(41)–C(1)–P	117.1(2)	C(41)–C(1)–Pd	116.3(2)
P–C(1)–Pd	105.86(14)	C(16)–C(11)–C(12)	115.5(3)
C(16)–C(11)–Pd	124.7(2)	C(12)–C(11)–Pd	119.8(2)
C(13)–C(12)–C(11)	122.6(3)	C(13)–C(12)–P	124.3(2)
C(11)–C(12)–P	113.0(2)	N(42)–C(41)–C(46)	119.8(3)
N(42)–C(41)–C(1)	116.8(3)	C(46)–C(41)–C(1)	123.3(3)
C(43)–N(42)–C(41)	118.5(3)	C(43)–N(42)–Pd′	118.4(2)
C(41)–N(42)–Pd′	122.6(2)		

[a] Symmetry transformation (indicated by a prime) used to generate equivalent atoms: $-x + 1, y, -z + 1/2$.

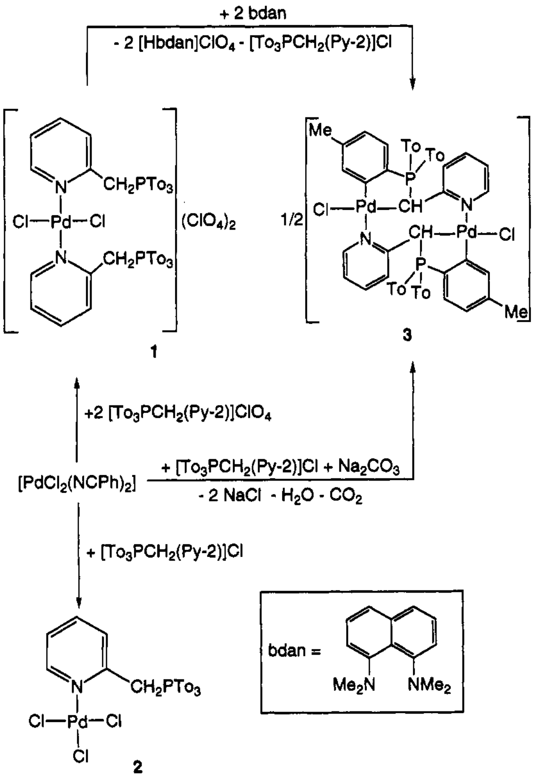
Table 7. Selected Bond Lengths (Å) and Angles (deg) for 8

Pd–C(21)	1.990(4)	Pd–N	2.082(3)
Pd–I(1)	2.5795(9)	Pd–I(2)	2.7004(11)
P–C(31)	1.788(4)	P–C(22)	1.790(4)
P–C(41)	1.794(4)	P–C(17)	1.875(4)
Cl(1)–C(17)	1.789(4)	N–C(12)	1.340(5)
N–C(16)	1.342(5)	C(12)–C(13)	1.378(6)
C(12)–C(17)	1.506(5)	C(21)–C(26)	1.394(6)
C(21)–C(22)	1.416(6)	C(22)–C(23)	1.408(6)
C(21)–Pd–N	84.6(2)	C(21)–Pd–I(1)	89.81(12)
N–Pd–I(1)	170.30(9)	C(21)–Pd–I(2)	173.73(12)
N–Pd–I(2)	91.59(9)	I(1)–Pd–I(2)	94.60(3)
C(31)–P–C(22)	112.2(2)	C(31)–P–C(41)	109.8(2)
C(22)–P–C(41)	109.1(2)	C(31)–P–C(17)	105.3(2)
C(22)–P–C(17)	112.2(2)	C(41)–P–C(17)	108.1(2)
C(12)–N–C(16)	118.6(4)	C(12)–N–Pd	122.6(3)
C(16)–N–Pd	118.6(3)	N–C(12)–C(13)	121.9(4)
N–C(12)–C(17)	113.4(3)	C(13)–C(12)–C(17)	124.7(4)
C(12)–C(17)–Cl(1)	112.5(3)	C(12)–C(17)–P	114.5(3)
Cl(1)–C(17)–P	109.8(2)	C(26)–C(21)–C(22)	117.3(4)
C(26)–C(21)–Pd	122.9(3)	C(22)–C(21)–Pd	119.5(3)
C(23)–C(22)–C(21)	120.8(4)	C(23)–C(22)–P	118.5(3)
C(21)–C(22)–P	120.6(3)		

are those on the methylene carbon atom. From **A** it is possible to imagine first an intramolecular C–Pd bond formation to give **B** followed by a C–H activation process to give **C**, which dimerizes to give **3**. The second route assumes an intermolecular C–Pd bond formation to give **B′** followed by an intramolecular cyclization to give **C′**. From this intermediate, C–H activation of the ortho C–H bonds would give **3**.

NMR data and the X-ray diffraction study (see below) prove that only the (*RR*)- + (*SS*)-**3** mixture is obtained. The result can be explained using both pathways in Scheme 3. Through the first route, an equilibrium between C and **3** would give the insoluble (*RR*)- + (*SS*)-**3** mixture if the (*RS*)-**3** isomer were soluble in acetone. If the reaction occurred through the second route, the chirality of the methine carbon atom in **B′** could induce the chirality of the second methine carbon atom in **C′**. Because we find this last explanation more reasonable and formation of the four-membered ring in **B** seems unlikely, we suggest the route **A** → **B′** → **C′** → **3** as the more probable pathway.

Scheme 2

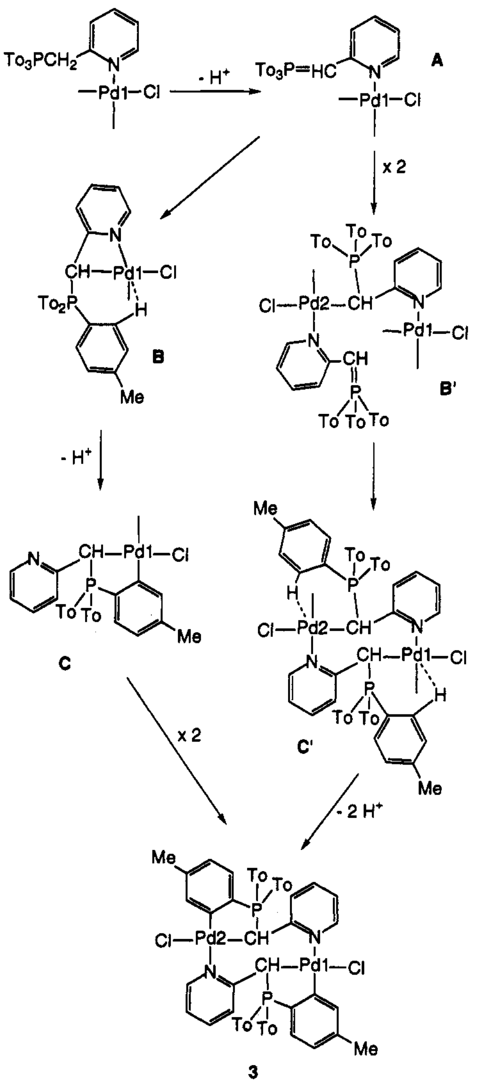


Complex **3** reacts with PEt_3 (1:2) to give a 3:1 mixture of isomers (*SP*-4-3)- and (*SP*-4-4)-[PdCl{κ^2-C_6H_3{PTo_2-CH(Py-2′)-2}Me-4}(PEt_3)] (**4**) (see Scheme 4). When this mixture is left in acetone solution for 24 h, the isomer (*SP*-4-4)-**4** is transformed into (*SP*-4-3)-**4**.

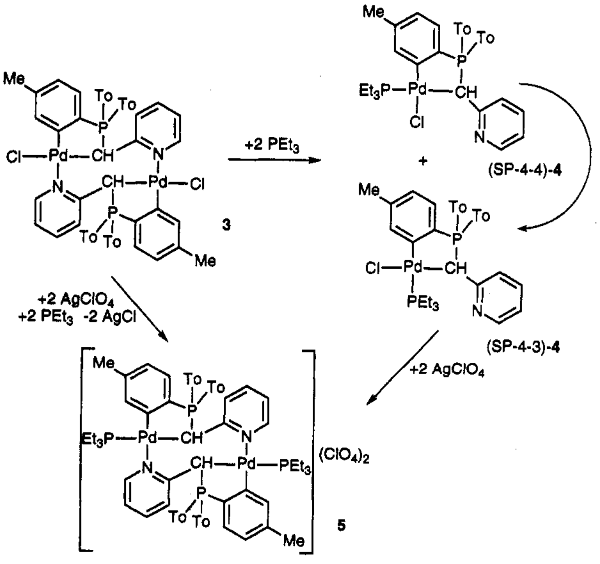
We attempted to prepare Pd(I), Pd(III), and Pd(IV) complexes from complex **3**. Thus, we reacted **3** with $AgClO_4$ and NaH (1:2:2), giving a very complex mixture that we could not separate, or with $Pd_2(dba)_3{\cdot}Cl_3CH$ (1:1) or NaH (1:2), giving the starting materials. Oxidation reactions with chlorine (excess) or Cl_2IPh (1:2) gave red solutions that become yellow after a few minutes and from which a complex of stoichiometry "$PdCl_3R_{CCN}$" was then obtained. When a 1:1 molar ratio Cl_2IPh:**3** was used a mixture of "$PdCl_3R_{CCN}$" and **3** was obtained. Two possible formulations were assumed for "$PdCl_3R_{CCN}$": a Pd(IV) complex such as **A** (see Scheme 5) resulting from an oxidative addition reaction or a Pd(II) complex resulting from the cleavage and chlorination of the Pd–C_{ylidic} bond, i.e., complex **6**. In an attempt to solve this problem we decided to react "$PdCl_3R_{CCN}$" with excess of NaI. From **A** we would expect to obtain complex **B** or complex **7**, which we prepared directly from **3**, plus NaI. If "$PdCl_3R_{CCN}$" were **6**, the diiodo derivative **8** should be obtained. Although a small amount of iodine was obtained, the main product of this reaction was **8**, as proved by an X-ray crystal structure (see below).

We have followed the chlorination reaction of **3** at low temperatures in $CDCl_3$ by ^{31}P NMR spectroscopy. These experiments show that this reaction takes place above −40 °C. At −30 °C the chlorination is immediately observed, because an intermediate (**X**) is formed giving a resonance at 33.3 ppm. After 7 min, **X** starts decomposing to complex **6**. After 1 h, **X** is much more abundant than the other two components of the mixture, **3** and **6**. The ^1H NMR spectrum of this mixture shows two doublets at 8.9 and 8.6 ppm, one of which must be assigned to the methine proton and the other to the H6 of the pyridine group of **X**. The increase of δ(CH) with respect to that in **3** (6.70 ppm) is that expected for a change of a Pd(II) to a Pd(IV)

Scheme 3

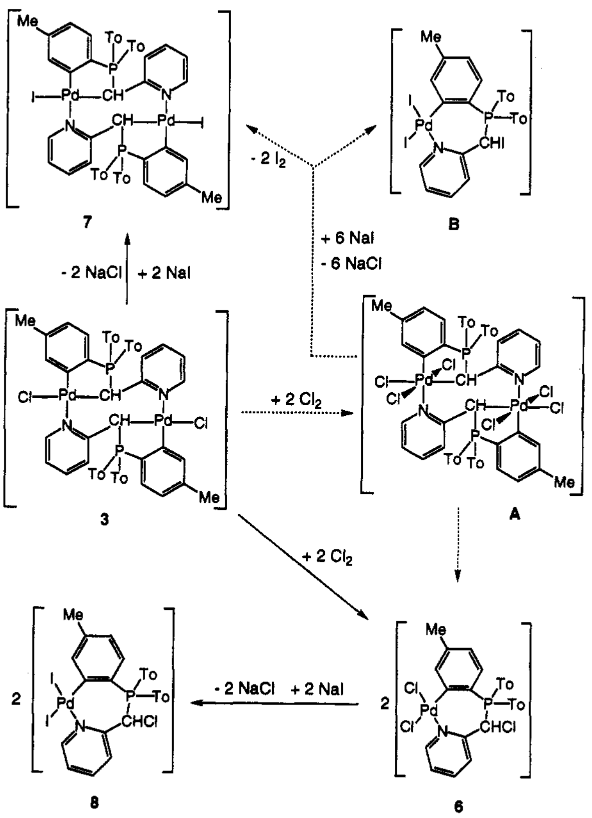


Scheme 4

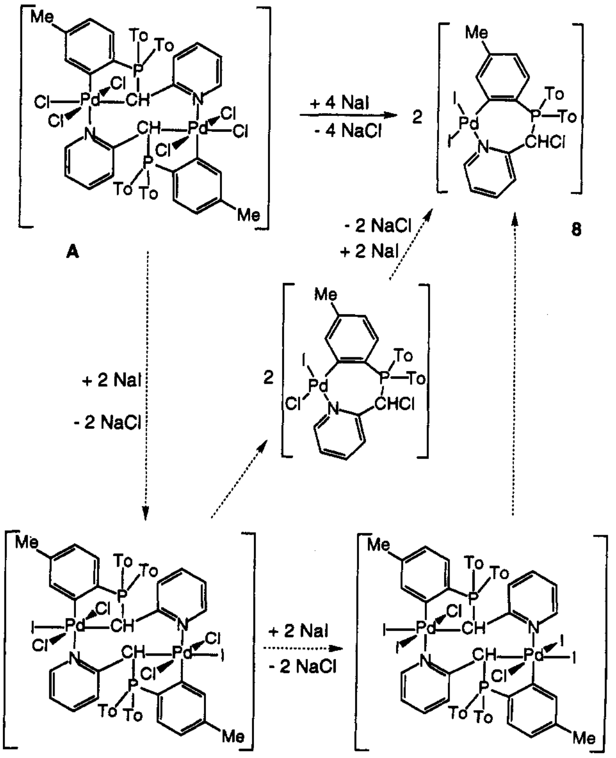


complex. Therefore, X could be complex A in Scheme 5. At −25 °C, the chlorination of complex 3 is completed after 50 min. If NaI is then added (I:Pd = 3:1), the resulting mixture contains at least six complexes (by ^{31}P NMR spectroscopy). The most abundant one is complex 8 that

Scheme 5



Scheme 6



can arise from the reaction of 6 or A with NaI, as shown in Schemes 5 and 6, respectively.

Recently, van Koten has reported that chlorination of the orthometalated complex [PdCl{C_6H_4{$CH_2N(Me)(CH_2)_2$-NMe_2}-2}] gives the Pd(IV) complex that arises from oxidative addition of Cl_2 (see Scheme 7).[4] This Pd(IV)

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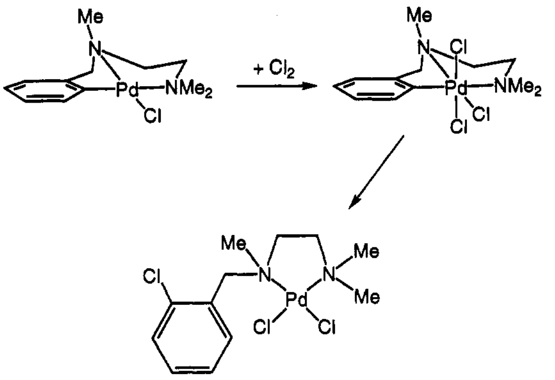
[4] Alsters, P. L.; Engel, P. F.; Hogerheide, M. P.; Copijn, M.; Speck, A. L.; van Koten, G. *Organometallics* **1993**, *12*, 1831.

Scheme 7



complex, which was not isolated, decomposes into the product of the chlorination of the Pd–C bond in a similar way to that we propose for the process **A** → **6** (see Scheme 7).

Like **3**, the dinuclear complexes **5** and **7** (see Schemes 4 and 5) consist also of mixtures of one pair of enantiomers. Because the reactions leading to these complexes from **3** do not require the cleavage of the C–Pd bond, it is reasonable to assume that both are mixtures of the *RR*- + *SS*-stereoisomers.

Structure of Complexes. The asymmetric unit of compound **1** (Table 5, Figure 1) consists of half a complex cation, one perchlorate anion, and two molecules of dichloromethane. The Pd atom lies on a crystallographic inversion center, and its coordination geometry is thus exactly planar and *trans*. The bond lengths Pd–N 2.035(3) and Pd–Cl 2.2886(11) Å are significantly shorter than the mean values found for pyridine– and chloro–palladium(II) complexes,[5] which may be due to the double positive charge of **1**.

The asymmetric unit of compound **3** (Table 6, Figure 2) consists of half a molecule of the complex and one molecule of dichloromethane. The complete molecule of **3** possesses crystallographic 2-fold symmetry; the 2-fold axis passes through the center of the bridging eight-membered ring, which displays a boat configuration. C(41), N(42), and their symmetry equivalents are approximately coplanar. The molecule is chiral; Figure 2 shows the *RR* molecule, but the overall composition is a racemate. The coordination at Pd is planar (mean deviation of five atoms 0.05 Å). The chelating (C,C′) five-membered ring has a bite angle of 86.81(12)°. The Pd–Cl and Pd–N bonds, 2.3725(10) and 2.135(3) Å, are appreciably longer than in **1**, associated with the absence of overall positive charge and with the high *trans* influence of the carbon ligands. The Pd–C bonds, Pd–C(1) 2.093(3) and Pd–C(11) 1.998(3) Å, are slightly longer than mean values for Pd–alkyl and Pd–aryl bonds (2.027 and 1.981 Å, respectively).[5]

Complex **8** (Table 7, Figure 3) crystallizes with one molecule of dichloromethane; it displays no crystallographic symmetry. The iodine ligands are *cis* to each other. The molecule is chiral; in Figure 3 the configuration at C(17) is *R*, but the compound is a racemate. The coordination at the metal atom is nonplanar, with the nitrogen atom lying 0.38 Å out of the plane of the other four atoms. Possible causes for this distortion include steric effects from the large iodine ligands or an agostic interaction [Pd···C(17) 3.09 Å, Pd···H(17) 2.67 Å, calculated for the idealized hydrogen position]. In complex **1**, this interaction, if it exists, is weaker [Pd···C(1) 3.35 Å, Pd···H 2.82 Å] than in **8**. The *trans* influence of the carbon ligand is reflected in the Pd–I bond lengths: Pd–I(1) 2.5795(9) and Pd–I(2) 2.7004(11) Å.

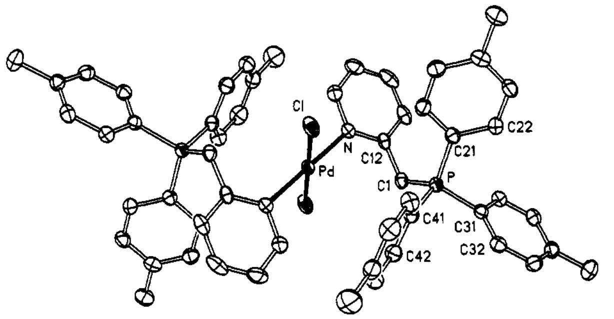


Figure 1. The cation of compound **1** in the crystal (H atoms omitted). Ellipsoids represent 50% probability levels. Only the asymmetric unit is numbered.

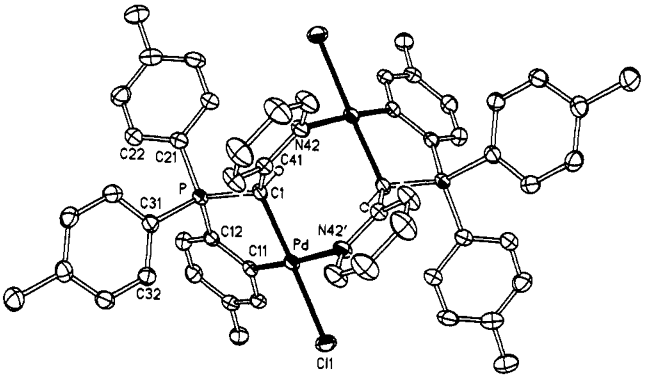


Figure 2. The molecule of compound **3** in the crystal (H atoms except H1 omitted). Ellipsoids represent 50% probability levels. Only the asymmetric unit is numbered.

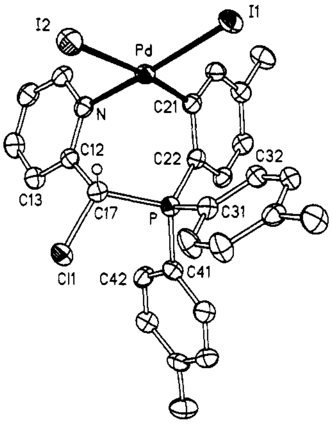


Figure 3. The molecule of compound **8** in the crystal (H atoms except H17 omitted). Ellipsoids represent 50% probability levels.

The only difference between the infrared spectra of complexes **3** and **7** is the band assignable in complex **3** (290 cm^{-1}) to the mode ν(PdCl). Therefore, both probably have the same structure. The corresponding ν(PdI) in **7** must lie below the limit of our spectrophotometer. The shorter Pd–Cl bond distance in **1** with respect to that in **3** (see above) is also shown by the higher energy of the ν(PdCl) mode in **1** (350 cm^{-1}) than in **3** (290 cm^{-1}). In **2** (see Scheme 2) the two observed bands assignable to the three IR-active ν(PdCl) modes appear at lower wavelengths

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[5] Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

(316 and 335 cm^{-1}) than that in complex 1, as expected when the positive charge of a complex is reduced.[6]

The methine proton resonances of the mixture obtained by reacting 3 with PEt_3 (see Scheme 4) appear as two doublets of doublets at *ca.* 4.5 and 3.8 ppm. The coupling constants are 10 and 2.5 Hz for the first one and ≈8 Hz for both doublets of the second one. Therefore, the high-frequency doublet of doublets is assigned to the isomer in which PEt_3 is *cis* to the methine proton which is the species to which the other isomer reverts in solution. Because the methine proton resonance in complex 5 shows, like the (*SP*-4-4)-4 isomer, an apparent triplet with $^2J_{PH} = {}^3J_{PH} = 9$ Hz, it is reasonable to assign to 5 the structure shown in Scheme 4, *viz.*, that resulting by replacement of the chloro ligand in 3 by PEt_3.

The spectrum of 5 in the Et proton region can be interpreted assuming that in the ABM_3X system ($A = B = M = {}^1H$; $X = {}^{31}P$) $^3J_{MX} = {}^2J_{AB} = 2{}^2J_{XA} = 2{}^2J_{XB} = 2{}^3J_{MA} = 2{}^3J_{MB} = 16$ Hz. In this way, the methyl protons appear as a doublet of triplets and methylene protons as two septuplets of approximate intensities 1:3:6:8:8:5:2. In the spectrum of 4 the Me protons also appear as a doublet of triplets, but the AB part is a nonresolved multiplet.

Conclusions. Unusual dicationic $[PdCl_2L_2]^{2+}$ and neutral $[PdCl_3L]$ complexes containing as ligand L the phosphonium cation $[To_3PCH_2(Py\text{-}2)]^+$ undergo an easy double C–H activation process. Reaction of the corresponding orthometalated complex with chlorine gives, possibly through a Pd(IV) complex, a Pd(II) complex resulting from the cleavage and chlorination of a Pd–C bond.

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Supplementary Material Available: Tables of crystal data, positional and thermal parameters, and bond distances and angles of 1, 3, and 8 (13 pages). Ordering information is given on any current masthead page.

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[6] See, for example: Vicente, J.; Arcas, A.; Borrachero, M. V.; Tiripicchio, A.; Tiripicchio-Camellini, M. *Organometallics* **1991**, *10*, 3873.