Mercurated and Palladated Iminophosphoranes. Synthesis and Reactivity

José Vicente,*,† José-Antonio Abad,*,† Rafael Clemente, and Joaquín López-Serrano

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

M. Carmen Ramírez de Arellano*,‡

Departamento de Química Orgánica, Facultad de Farmacia, Universidad de Valencia, 46100 Valencia, Spain

Peter G. Jones§

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

Delia Bautista||

SACE, Universidad de Murcia, Apartado 4021, E-30071 Murcia, Spain

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Reaction of the iminophosphorane $Ph_3P{=}NC_6H_4Me$-4 (**1a**) with $Hg(OAc)_2$ and LiCl gives the mercurated iminophosphorane [Hg{C_6H_3(N═PPh_3)-2-Me-5}Cl] (**2**). The latter reacts with NaBr to give [Hg{C_6H_3(N═PPh_3)-2-Me-5}Br] (**3**). **2** reacts with MeC_6H_4NCO-4 or CX_2 (X = O, S) to give [Hg{C_6H_3(N═C═NC_6H_4Me-4′)-2-Me-5}Cl] (**4**) or [Hg{C_6H_3\{N═C═NC_6H_3(HgCl)-1′-Me-5′\}-2-Me-5}Cl] (**5**), respectively. Iminophosphoranes $Ph_3P{=}NC_6H_4R$-4 (**1b**) react with $Pd(OAc)_2$ to give the complexes [Pd{κ^2-*C*,*N*-C_6H_4($PPh_2{=}NC_6H_4$R-4′)-2}(μ-OAc)]$_2$ (R = Me (**6a**), MeO (**6b**)), in which the palladation takes place at one of the phenyl substituents of the PPh_3 group. Complex **6b** reacts with NaBr or ^{t}BuNC to give [Pd{κ^2-*C*,*N*-C_6H_4($PPh_2{=}NC_6H_4$-OMe-4′)-2}(μ-Br)]$_2$ (**7**) or [Pd{κ^2-*C*,*N*-C_6H_4($PPh_2{=}NC_6H_4$OMe-4′)-2}(OAc)(CN^{t}Bu)] (**8**), respectively. Complexes **6a**,**b** react with $NaClO_4$ and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda), yielding [Pd{κ^2-*C*,*N*-C_6H_4($PPh_2{=}NC_6H_4$R-4′)-2}(tmeda)]ClO_4 (R = Me (**9a**), MeO (**9b**)). The compound $Ph_3P{=}NC_6H_4$I-2 (**1c**) adds oxidatively to $[Pd_2(dba)_3]$·dba (dba = dibenzylideneacetone) in the presence of tmeda, resulting in the formation of complex [Pd{C_6H_4(N═PPh_3)-2}I(tmeda)] (**10**). The complex **10** reacts (i) with PPh_3 and TlOTf (TfO = CF_3SO_3) to give [Pd{C_6H_4(N═PPh_3)-2}(tmeda)(PPh_3)]TfO (**11**·TfO), (ii) with XyNC (Xy = C_6H_3Me-2,6) (1:3 molar ratio) to give [Pd{κ^2-*C*,*N*-C(═NXy)C_6H_4(N═PPh_3)-2}I(CNXy)] (**12**), and (iii) with XyNC and TlOTf (1:3:1) to give [Pd{κ^2-*C*,*N*-C(═NXy)C_6H_4(N═PPh_3)-2}(CNXy)$_2$]-TfO (**13**). An excess of the alkyne $MeO_2CC{\equiv}CCO_2Me$ reacts with **10** and $AgClO_4$ (4:1:1) to give the inserted compound [Pd{κ^2-*C*,*N*-C(CO_2Me)═C(CO_2Me)C_6H_4(N═PPh_3)-2}(tmeda)]ClO_4 (**14**·ClO_4). The crystal structures of **2**, **6a**·CH_2Cl_2, **9a**, **11**·TfO, and **14**·ClO_4 have been determined by X-ray diffraction studies.

Introduction

Iminophosphoranes $R_3P{=}NR'$ are very important compounds, in view of their numerous applications in organic chemistry,[1] as well as in coordination and organometallic chemistry. N-bonded complexes are known for many metals of the periodic table (class I in Chart 1).[2−5] In addition, organometallic complexes have been prepared through metalation of some of the R groups. This family consists mainly of a numerous group of alkyl complexes containing an N,C-chelating ligand prepared from iminophosphoranes $R(Ar)_2P{=}NR'$ (R = alkyl, Ar = aryl, R′ = Me_3Si, aryl) after the deprotonation of the α-methylene of the R group (class IIa)[3,6] and a few aryl derivatives prepared by metalation or transmetalation reactions (class IIb). Thus, lithiation of $Ph_3P{=}NPh$ with PhLi was long ago reported to give [$LiC_6H_4(Ph_2P{=}NPh)$-2],[7] and more recently Stalke reported the lithiation of $Ph_3P{=}NSiMe_3$ with MeLi, affording [$LiC_6H_4(Ph_2P{=}NSiMe_3)$-2],[8] which in reactions with halides of Zn, Cu(I), In(III), Fe(II), Sn(II), and Pb(II) or with Ph_3GeCl gives the corresponding aryl

† E-mail: J.V., jvs@um.es; J.-A.A., jaab@um.es. Web: http://www.um.es/gqo/.
‡ E-mail: mcra@uv.es.
§ E-mail: p.jones@tu-bs.de.
|| E-mail: dbc@um.es.

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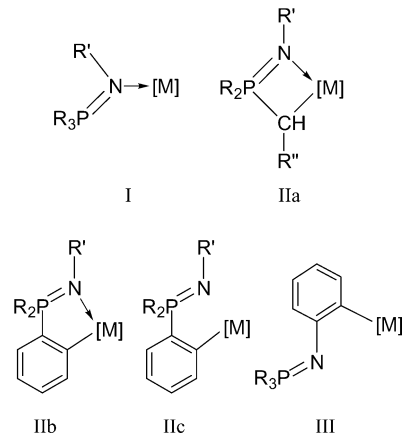
Chart 1



complexes.[9] In a few of the above-mentioned organo complexes, the N is not coordinated (class IIc).[10] Finally, reactions of $Ar_3P{=}NR$ with $[M(CH_2Ph)(CO)_5]$, $Na_2[PdCl_4]$, or $AlPh_3$ have been reported to give the C,N-cyclometalated complexes $[M\{\kappa^2\text{-}C,N\text{-}C_6H_4\{P(Ph)_2{=}NPh\text{-}2\}\}(CO)_5]$ (M = Mn, Re),[11] $[Pd\{\kappa^2\text{-}C,N\text{-}(C_6H_3R^1\text{-}5)\{P(C_6H_4R^1\text{-}4)_2{=}NC_6H_4R^2\text{-}n\}(\mu\text{-}Cl)\}_2$ (R^1 = H, R^2 = Me (n = 3, 4), OMe (n = 4); R^1 = Me, R^2 = OMe (n = 4)),[12] and $[Al\{\kappa^2\text{-}C,N\text{-}C_6H_4\{P(Ph)_2{=}NSiMe_3\}\text{-}2\}Ph_2]$.[13] The main features of the organo derivatives of iminophosphoranes are that the metal is always attached to substituents at phosphorus and that, in most cases, it is coordinated to the nitrogen atom. In this paper we study the palladation and mercuration of iminophosphoranes $Ph_3P{=}NAr$ and report the synthesis of the first organometallics of class III, in which the metal is bonded to the substituent at nitrogen, as well as some palladium complexes of class IIb and the first organomercurated iminophosphoranes. From the latter complexes we have prepared the first aryl complexes of any metal containing a carbodiimide group.

Experimental Section

The IR (solid state) and NMR spectra, elemental analyses, and melting point determinations were performed as described earlier.[14] Conductivity measurements were made in acetone, unless otherwise stated. When needed, NMR signals were assigned with the help of DEPT, COSY, and HETCOR techniques. The mass spectra were recorded in a Fisons VG-Autospec apparatus using 3-nitrobenzyl alcohol as a matrix. "Pd(dba)$_2$" ([$Pd_2(dba)_3$]·dba, dba = dibenzylideneacetone) was prepared as described previously.[15] The iminophosphoranes $Ph_3P{=}NC_6H_4$Me-4 (**1a**) and $Ph_3P{=}NC_6H_4$(OMe)-4 (**1b**) were prepared following the Kirsanov method[1] from the corresponding amine and Ph_3PBr_2.[16] 2-Iodoaniline was purchased from Aldrich. The synthesis of the compounds was carried out without precautions against light and moisture, unless otherwise stated. The products were filtered in air and dried under a current of air. The preparative thin-layer chromatographic separations were performed using silica gel 60 ACC (70−200 μm). In the case of colorless substances fluorescent silica gel (GF_{254}) was added (approximately 5%).

Synthesis of $Ph_3P{=}NC_6H_4$I-2 (1c). The reaction was carried out under nitrogen using freshly distilled benzene. To a stirred solution of triphenylphosphine (4.58 g, 17.4 mmol) in benzene (10 mL) was added dropwise a solution of bromine (2.78 g, 17.4 mmol) in the same solvent (10 mL) using an addition funnel while keeping the temperature below 10 °C. After the addition was completed, the resulting yellowish suspension was stirred for a further 30 min, allowing it to reach room temperature. 2-Iodoaniline (3.87 g, 17.4 mmol) and dry triethylamine (5 mL) were then added, and the volume of the reaction mixture was made up to 60 mL with benzene. The mixture was refluxed under nitrogen for 4 h, the resulting suspension was filtered through anhydrous magnesium sulfate, and the filtrate was evaporated to dryness. The crude product was redissolved in warm Et_2O (100 mL) and cooled to room temperature. Colorless, well-shaped crystals were collected by filtration, washed with Et_2O, and air-dried. Yield: 6.40 mg, 77%. Mp: 124−126 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87−7.79 (m, 6 H, PPh_3), 7.77 (dt, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 2.5 Hz, $J_{H,P}$ = 2.5 Hz, 1 H, H3 or H6 C_6H_4), 7.64−7.40 (m, 9 H, PPh_3), 6.84 (td, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 2.5 Hz, 1 H, H4 or H5 C_6H_4), 6.46 (dt, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 2.5 Hz, $J_{H,P}$ = 2.5 Hz, 1

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H, H3 or H6), 6.35 (td, $^3J_{H,H}$ = 8 Hz, $^4J_{H,H}$ = 2.5 Hz, 1H, H5 or H4). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 151.58 (d, J_{CP} = 2 Hz, C, C1 C_6H_4), 138.77 (d, $^1J_{P,C}$ = 2 Hz, CH C_6H_4), 132.72 (d, $^2J_{P,C}$ = 10 Hz, *m*-CH PPh_3), 131.72 (d, $J_{P,C}$ = 2.5 Hz, *p*-CH PPh_3), 129.75 (s, quaternary C, probably one of the signals of the doublet corresponding to *i*-C-PPh_3, whereby the other one may be obscured by other signals), 128.60 (d, $J_{P,C}$ = 13 Hz, *o*-CH PPh_3), 128.16 (s, CH), 119.87 (d, $J_{P,C}$ = 9.5 Hz, CH), 118.73 (d, $J_{P,C}$ = 1 Hz, CH), 99.9 (d, $J_{P,C}$ = 27.5 Hz, quaternary C). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 2.55 (s). Anal. Calcd for $C_{24}H_{19}INP$: C, 60.14; H, 4.00; N, 2.92. Found: C, 60.19; H, 3.84; N, 2.96.

Synthesis of [Hg{C_6H_3(N=PPh_3)-2-Me-5}Cl] (2). Hg(OAc)$_2$ (4.00 gr, 12.55 mmol) and **1a** (4.61 gr, 12.55 mmol) were mixed in THF (100 mL) under nitrogen and the resulting mixture refluxed for 9 h and then cooled to room temperature, and a 100% excess of LiCl was added. The suspension was stirred for a further 12 h at room temperature and filtered. The resulting solution was evaporated to dryness. The residue was extracted with CH_2Cl_2 (5 cm^3) and filtered through Celite. Addition of Et_2O (10 mL) precipitated complex **2** as an ivory-colored solid. Yield: 5.86 gr, 74%. Mp: 186 °C. IR (Nujol, cm^{-1}): ν 1420 (P=N), 330 (Hg−Cl). ^1H NMR (200 MHz, $CDCl_3$): δ 7.66−7.77 (m, 6 H, PPh_3), 7.41−7.59 (m, 9 H, PPh_3), 6.91 (s, 1 H, H6), 6.65 (d, $^3J_{H,H}$ = 7.9 Hz, 1 H, H4 or H3), 6.41 (d, $^3J_{H,H}$ = 7.9 Hz, 1 H, H3 or H4), 2.17 (s, 3 H, Me). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 151.87 (C, C1), 149.2 (d, $^2J_{P,C}$ = 4.5 Hz, C2), 136.22 (d, $^4J_{P,C}$ = 4.7 Hz, C6), 132.47 (d, $^2J_{P,C}$ = 9.7 Hz, *o*-C PPh_3), 131.89 (d, $^4J_{P,C}$ = 2.8 Hz, *p*-C PPh_3), 129.98 (d, $^1J_{P,C}$ = 99 Hz, *i*-C PPh_3), 129.68 (CH, C4 or C3), 128.68 (d, $^3J_{P,C}$ = 12 Hz, *m*-C PPh_3), 127.47(C, C5), 119.82 (d, $^3J_{P,C}$ = 8.4 Hz, C3 or C4), 20.51 (Me). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 3.16 (s). FAB MS: *m*/*z*, 603 (M$^+$, 58%), 366 (M$^+$ − HgCl, 100%), 262 (PPh_3, 26%). Anal. Calcd for $C_{25}H_{21}NClHgP$: C, 49.84; H, 3.51; N, 2.32. Found: C, 49.65; H, 3.48; N, 2.36. Single crystals of **2** were grown by slow diffusion of methanol into solutions of **2** in CH_2Cl_2.

Synthesis of [Hg{C_6H_3(N=PPh_3)-2-Me-5}Br] (3). NaBr (456 mg, 4.43 mmol) was added to a solution of **2** (445 mg, 0.74 mmol) in acetone (20 mL). The resulting suspension was stirred for 16 h and then filtered. The filtrate was evaporated to dryness, and CH_2Cl_2 (10 mL) was added to the residue. The solution was concentrated to ca. 3 mL, and *n*-hexane (20 mL) was added to give **3** as a pale brown solid. Yield: 371 mg, 78%. Mp: 193 °C. IR (Nujol, cm^{-1}): ν 1316 (P=N). ^1H NMR (200 MHz, $CDCl_3$): δ 7.66−7.77 (m 6 H, PPh_3), 7.40−7.57 (m, 9 H, PPh_3), 6.92 (s, 1 H, H6), 6.65 (d, $^3J_{H,H}$ = 8 Hz, 1 H, H4 or H3), 6.42 (d, $^3J_{H,H}$ = 8 Hz, 1 H, H3 or H4), 2.16 (s, 3 H, Me). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 3.11 (s). FAB MS: *m*/*z*, 647 (M$^+$, 76%), 366 (M$^+$ − HgBr, 54%), 262 (PPh_3, 18%). Anal. Calcd for $C_{25}H_{21}BrHgNP$: C, 46.42; H, 3.27; N, 2.17. Found: C, 46.21; H, 3.01; N, 2.15.

Synthesis of [Hg{C_6H_3(N=C=NC_6H_4Me-4′)-2-Me-5}Cl] (4). *p*-Tolyl isocyanate (200 mg, 1.34 mmol) was added to a THF (50 mL) solution of **2** (603 mg, 1.00 mmol). The resulting mixture was stirred for 15 h at room temperature. Then it was evaporated to dryness. The residue was treated with ethanol, giving a white precipitate, which was collected by filtration and air-dried to yield white **4**. Yield: 234 mg, 51%. Mp: 155 °C. IR (Nujol, cm^{-1}): ν 2128, 2109 (N=C=N), 329 (Hg−Cl). ^1H NMR (300 MHz, $CDCl_3$): δ 7.24−7.05 (m, 7 H, arom), 2.34 (s, 3 H, Me), 2.31 (s, 3 H, Me). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 145.63 (s, C), 140.63 (s, C), 138.05 (s, C), 136.91 (s, CH), 135.97 (s, C), 135.91 (s, C), 134.61 (s, C), 131.08 (s, CH), 130.12 (s, CH, C11), 124.22 (s, CH, C10), 21.02 (s, 2 Me). FAB MS: *m*/*z*, 458 (RHgCl, 65%), 221 (R, 100%). Anal. Calcd for $C_{15}H_{13}ClHgN_2$: C, 39.40; H, 2.87; N, 6.13. Found: C, 39.40; H, 2.64; N, 5.96.

Synthesis of [Hg{C_6H_3{N=C=NC_6H_3(HgCl)-1′-Me-5′}-2-Me-5}Cl] (5). Method A. A dichloromethane (40 mL) solution of **2** (441 mg, 0.73 mmol) was cooled in an acetone/CO_2 bath at −78 °C. Then, a large excess of solid CO_2 was added. The mixture was stirred at room temperature for 24 h, allowing it to reach room temperature. After this time the white precipitate thus formed was filtered off, washed with CH_2Cl_2, and dried in vacuo to give **5**. Yield: 176 mg, 70%.

Method B. An excess of CS_2 (160 μL, 2.64 mmol) was added to a solution of **2** (400 mg, 0.66 mmol) in CH_2Cl_2 (15 mL), and the resulting mixture was stirred at room temperature for 24 h. The white precipitate that formed was collected by filtration and worked up as above. Yield: 114 mg, 50%. Mp: 133−135 °C. IR (Nujol, cm^{-1}): ν 2132, 2100, 2026 (N=C=N), 320 (Hg−Cl). NMR: not sufficiently soluble. EI MS: *m*/*z* 692 (M$^+$ 1.2%), 420 (M$^+$ − $HgCl_2$, 44%) 221 (M$^+$ − 2HgCl, 52%). Anal. Calcd for $C_{15}H_{12}N_2Cl_2Hg_2$: C, 26,02; H, 1.75; N, 4.05. Found: C, 26,-08; H, 1.83; N, 3.95.

Synthesis of [Pd{κ^2-*C*,*N*-C_6H_4(PPh_2=NC_6H_4Me-4′)-2}(μ-OAc)]$_2$ (6a). Pd(OAc)$_2$ (610 mg, 2.72 mmol) and **1a** (1 g, 2.72 mmol) were mixed in THF (40 mL) under nitrogen. The deep red solution was stirred for 24 h. The solvent was removed under reduced pressure, CH_2Cl_2 was added to the residue, and the mixture was filtered through Celite. The solution was concentrated to ca. 5 mL and Et_2O (50 mL) added, precipitating **6a** as a yellow solid. Yield: 1.11 g, 77%. Dec pt: 200 °C. IR (Nujol, cm^{-1}): ν 1584, 1556 (C=O), 1186 (P=N). ^1H NMR (200 MHz, $CDCl_3$): δ 7.52−6.67 (several m, 18H, aryl), 2.13 (d, $^7J_{P,H}$ = 2 Hz, 3 H, *Me*CO_2), 1.13 (s, 3 H, Me). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 179.63 (C=O), 150.83 (d, $^2J_{P,C}$ = 23 Hz, CPd), 143.13 (d, $^2J_{P,C}$ = 5 Hz, C1 C_6H_4Me-4), 139.11 (d, $^1J_{P,C}$ = 140 Hz, C2 C_6H_4Pd), 135.54 (d, $^2J_{P,C}$ = 15 Hz, C3 C_6H_4Pd), 132.21 (s, C4 C_6H_4Me-4), 131.65−133.10 (m, CH), 130.67 (d, $J_{P,C}$ = 6 Hz, CH), 129.93 (d, $^2J_{P,C}$ = 3 Hz, CH), 129.51 (s, *i*-C PPh_2, the other component of the doublet may be obscured by other signals), 128.37 (d, $J_{P,C}$ = 12 Hz, CH), 128.16 (d, $J_{P,C}$ = 3 Hz, CH), 128.11 (d, $^1J_{P,C}$ = 84 Hz, C1 *i*-C PPh_2), 128.01 (s, *p*-CH PPh_2), 123.85 (d, $^3J_{P,C}$ = 14 Hz, C2 C_6H_4Me-4), 23.03 (s, *Me*CO_2), 20.91 (s, C_6H_4*Me-4*). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 53.69 (s). FAB MS: *m*/*z* 1062 ([M$^+$]$_2$, 2%), 531 (M$^+$, 12%), 366 (M$^+$ − PdOAc, 100%). Anal. Calcd for $C_{27}H_{24}NO_2PPd$: C, 60.97; H, 4.55; N, 2.63. Found: C, 60.80; H, 4.59; N, 2.65. Single crystals of **6a**·CH_2Cl_2 were grown by slow diffusion of *n*-hexane into solutions of **6a** in CH_2Cl_2.

Synthesis of [Pd{κ^2-*C*,*N*-C_6H_4(PPh_2=NC_6H_4OMe-4′)-2}-(μ-OAc)]$_2$ (6b). Pd(OAc)$_2$ (293 mg, 1.30 mmol) and Ph_3P=N-C_6H_4OMe-4 (**1b;** 500 mg, 1.30 mmol) were mixed in THF (25 mL) under nitrogen. The deep red solution was stirred for 20 h. The solvent was removed under reduced pressure, CH_2Cl_2 was added to the residue, and the mixture was filtered through Celite. The solution was concentrated to ca. 4 mL and Et_2O (50 mL) was added, precipitating **6b** as a yellow solid. Yield: 587 mg, 82%. Dec pt: 242 °C. IR (Nujol, cm^{-1}): ν 1585, 1577, 1557 (AcO), 1497, 1175 (P=N). ^1H NMR (200 MHz, $CDCl_3$): δ 7.52−6.71 (several m, 16H, aryl), 6.49 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, C_6H_4Me-4), 3.67 (s, 3 H, OMe), 1.37 (s, 3 H, Me). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 179.58 (C=O), 155.53 (d, $^5J_{P,C}$ = 3 Hz, C4 C_6H_4OMe-4), 150.92 (d, $^2J_{P,C}$ = 23 Hz, C2 C_6H_4Pd), 138.84 (d, $^1J_{P,C}$ = 140 Hz, CPd), 138.70 (d, $^2J_{P,C}$ = 5 Hz, C1 C_6H_4OMe-4), 135.44 (d, $^2J_{P,C}$ = 15 Hz, C3 C_6H_4Pd), 133.01−127.91 (m, several CH), 129.9 (d, $^1J_{P,C}$ = 88 Hz, *i*-C PPh_2), 127.85 (d, $^1J_{P,C}$ = 83 Hz, *i*-C PPh_2), 123.8 (d, $^3J_{P,C}$ = 14 Hz, C2 C_6H_4OMe-4), 112.82 (d, $^4J_{P,C}$ = 3 Hz, C3 C_6H_4OMe-4), 55.38 (s, OMe), 22.99 (s, Me). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 55.41 (s). FAB MS: *m*/*z*, 1036 ([M$^+$]$_2$ − AcO, 17%), 547 (M$^+$, 35%), 382 (M$^+$ − PdOAc, 100%). Anal. Calcd for $C_{27}H_{24}NO_3PPd$: C, 59.19; H, 4.42; N, 2.56. Found: C, 58.80; H, 4.33; N, 2.57.

Synthesis of [Pd{κ^2-*C*,*N*-C_6H_4(PPh_2=NC_6H_4OMe-4′)-2}-(μ-Br)]$_2$ (7). NaBr (75 mg, 0.73 mmol) was added to a THF suspension of **6b** (200 mg, 0.18), and the mixture was stirred at reflux temperature for 6 h. The resulting orange suspension was evaporated to dryness, the residue was treated with CH_2Cl_2, and the suspension was filtered through Celite. The filtrate was concentrated to ca. 2 mL, and Et_2O (20 mL) was

added, precipitating a solid that was collected and dried in vacuo to give pale orange **7**. Yield: 93 mg, 50%. Dec pt: 243 °C. IR (Nujol, cm^{-1}): ν 1174 (P═N). ^1H NMR (200 MHz, $CDCl_3$): δ 7.83−6.93 (several m, 16 H, arom), 6,49 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H), 3.65 (s, 3 H, OMe). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 46.68 (s). FAB MS: *m*/*z* 1137 (M^+_2, 3%), 569 (M^+, 3%), 382 ($C_6H_4[PPh_2{=}NC_6H_4(OMe)$-4]-2, 100%). Anal. Calcd for $C_{25}H_{21}BrNOPPd$: C, 52.80; H, 3.72; N, 2.46. Found: C, 52.41; H, 3.79; N, 2.58.

Synthesis of [Pd{κ^2-*C*,*N*-$C_6H_4(PPh_2{=}NC_6H_4OMe$-4′)-2}(OAc)(CN^{t}Bu)] (8). ^{t}BuNC (62 μL, 0.55 mmol) was added to a solution of **6b** (100 mg, 0.09 mmol) in THF (20 mL) under nitrogen. The yellow solution turned pale green and was stirred at room temperature for 24 h. After this time the protective nitrogen atmosphere was no longer needed. The solvent was evaporated to dryness, CH_2Cl_2 (15 mL) was added, and the mixture was filtered through Celite. The filtrate was evaporated to dryness, and *n*-hexane (30 mL) was added to the residue, precipitating a grayish solid. Yield: 91 mg, 79%. Mp: 180 °C. IR (Nujol, cm^{-1}): ν 2194 (C≡N), 1598, 1576 (OAc), 1196 (N═P). ^1H NMR (200 MHz, $CDCl_3$): δ 7.83−6.96 (several m, 14 H, arom), 6.68 (AB system (δA = 6.84, δB = 6.53), 4 H, C_6H_4, $^2J_{H,H}$ = 8 Hz), 3.65 (s, 3 H, OMe), 1.56 (s, 9 H, ^{t}Bu), 1.47 (s, 3 H, $MeCO_2$). $^{13}C\{^1H\}$ NMR: the compound decomposes during the experiment. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 48.48 (s). Anal. Calcd for $C_{32}H_{33}N_2O_3PPd$: C, 60.91; H, 5.27; N, 4,44. Found: C, 60.80; H, 5.51; N, 4.51.

Synthesis of [Pd{κ^2-*C*,*N*-$C_6H_4(PPh_2{=}NC_6H_4Me$-4′)-2}(tmeda)]ClO_4 (9a). $NaClO_4$ (21 mg, 0.17 mmol), was added to a suspension of **6a** (60 mg, 0.055 mmol) in acetone (30 mL). An excess of tmeda (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine, 26 μL, 0.17 mmol), was added to the stirring suspension and the resulting yellow solution was stirred for a further 4h. The solvent was evaporated, the residue treated with CH_2Cl_2 (10 mL) and the solution filtered through Celite. The filtrate was concentrated to ca. 2 mL. The compound **9a** precipitated as a yellow solid after addition of Et_2O (20 mL). Yield: 77 mg, 99%. Mp: 206 °C. Λ_M = 150 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): ν 1189 (P═N), 1081, 621 (ClO_4). ^1H NMR (200 MHz, $CDCl_3$): δ 7.71−6.75 (several m, 18 H, arom), 2.78 (s, 6 H, 2Me tmeda), 2.58−2.55 (m, 4 H, $2CH_2$), 2.16 (d, $^7J_{H,P}$ = 2 Hz, 3 H, Me C_6H_4Me), 2.08 (s, 6 H, 2Me tmeda). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 159.13 (d, $^2J_{P,C}$ = 19 Hz, C−Pd), 143.14 (d, $^2J_{P,C}$ = 5 Hz, C1 C_6H_4Me-4), 143.10 (d, $^1J_{P,C}$ = 126 Hz, C2), 133.65−124.88 (m, CH), 132.32 (d, $^5J_{P,C}$ = 3 Hz, C4 C_6H_4Me-4), 126.70 (d, $^1J_{P,C}$ = 94 Hz, *i*-C PPh_3), 124.83 (d, $^3J_{P,C}$ = 14 Hz, C2 and C6 C_6H_4-Me-4), 63.88 (CH_2), 58.83 (CH_2), 51.18 (Me, tmeda), 49.25 (Me, tmeda), 20.66 (Me). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 41.72 (s). FAB MS: *m*/*z* 588 (M^+, 100%), 437 (M^+ − tmeda, 7%), 366 (M^+ − Pd(tmeda), 35%). Anal. Calcd for $C_{31}H_{37}ClN_3O_4PPd$: C, 54.08; H, 5.42; N, 6.10. Found: C, 53.77; H, 5.17; N, 6.52. Single crystals of **9a** were grown by slow diffusion of *n*-hexane into solutions of **9a** in CH_2Cl_2.

Synthesis of [Pd{κ^2-*C*,*N*-$C_6H_4(PPh_2{=}NC_6H_4OMe$-4′)-2}(tmeda)]$ClO_4$ (9b). $NaClO_4$ (50 mg, 0.41 mmol), was added to a suspension of **6b** (150 mg, 0.14 mmol) in acetone (30 mL). An excess of tmeda (62 μL, 0.41 mmol), was added to the stirred suspension, and the resulting orange solution was stirred for a further 4 h. The solvent was removed, the residue was treated with CH_2Cl_2 (10 mL), and the solution was filtered through Celite. The filtrate was concentrated to ca. 2 mL, and Et_2O (20 mL) was added, precipitating **9b** as a pink solid. Yield: 177 mg, 92%. Mp: 196 °C. Λ_M = 151 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): ν 1178 (P═N), 1089, 622 (ClO_4). ^1H NMR (200 MHz, $CDCl_3$): δ 7.70−7.30 (several m, 12 H, arom), 7.11 (m, 1 H, arom), 6.89 (d, $^3J_{H,H}$ = 9 Hz 2 H, C_6H_4OMe-4), 6.82 (m, 1 H, arom), 6.57 (d, $^3J_{H,H}$ = 9 Hz, 2 H, C_6H_4OMe-4), 3.68 (s, 3 H, OMe), 2.77 (s, 6 H, 2Me), 2.74−2.54 (m, 4 H, $2CH_2$), 2.11 (s, 6 H, 2Me). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 159.03 (d, $^2J_{P,C}$ = 19 Hz, C−Pd), 155.54 (d, $^5J_{P,C}$ = 3 Hz, C4 C_6H_4OMe-4), 142.96 (d, $^1J_{P,C}$ = 124.4 Hz, C2), 138.74 (d, $^2J_{P,C}$ = 5 Hz, C1 C_6H_4OMe-4), 133.70−133.38 (m, CH), 130.76 (d, $J_{P,C}$ = 3 Hz, CH), 129.65 (d, $J_{P,C}$ = 18.5 Hz, CH), 129.06 (d, $J_{P,C}$ = 12 Hz, CH), 128.11 (d, $J_{P,C}$ = 7 Hz, CH), 126.7 (d, $^1J_{P,C}$ = 94.5 Hz, ipso C PPh_3), 124.82 (d, $^3J_{P,C}$ = 13.5 Hz, C2, C6 C_6H_4OMe-4), 114.02 (d, $^4J_{P,C}$ = 2.5 Hz, C3, C5 C_6H_4OMe-4), 63.84 (CH_2), 58.75 (CH_2), 55.31 (Me), 51.10 (Me, tmeda), 49.18 (Me, tmeda). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 42.42 (s). FAB MS: *m*/*z* 604 (M^+, 100%), 489 (M^+ − tmeda, 7%), 382 (M^+ − Pd(tmeda), 29%). Anal. Calcd for $C_{31}H_{37}ClN_3O_5PPd$: C, 52.85; H, 5.29; N, 5.96. Found: C, 52.62; H, 5.23; N, 5.96.

Synthesis of [Pd{$C_6H_4(N{=}PPh_3)$-2}I(tmeda)] (10). "Pd(dba)$_2$" (401 mg, 0.70 mmol) and tmeda (105 μL, 0.70 mmol) were mixed in toluene (30 mL) under nitrogen, the mixture was stirred for 15 min, and then **1c** (500 mg, 1.04 mmol) was added. The resulting suspension was stirred at room temperature for 3 h. After this time the nitrogen atmosphere was no longer needed. The solvent was evaporated in vacuo, the greenish residue was treated with CH_2Cl_2 (20 mL), and the suspension was filtered through Celite. The orange solution was then evaporated to dryness and the residue triturated with Et_2O, filtered, washed with Et_2O, and air-dried to give **10** as a pale orange solid. Yield: 337 mg, 70%. Dec pt: 160−169 °C. IR (Nujol, cm^{-1}): ν 1336 (P═N). ^1H NMR (300 MHz, $CDCl_3$): δ 8.03−7.96 (m, 6 H, PPh_3), 7.48−7.36 (m, 9 H, PPh_3), 7.01 (dt, $^3J_{H,H}$ = 7 Hz, $^4J_{H,H}$ = 2 Hz, $J_{P,H}$ = 2 Hz, 1 H, H3 or H6 C_6H_4), 6.41−6.36 (m, 2 H, C_6H_4), 5.99 (b d, $^3J_{H,H}$ = 7 Hz, 1 H, C_6H_4), 2.78 (s, 3 H, Me), 2.72 (s, 3 H, Me), 2.64−2.49 (m, 4 H, $2CH_2$), 2.46 (s, 3 H, Me), 2.38 (s, 3 H, Me). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 138.34 (s, quaternary C), 137.95 (s, quaternary C), 137.26 (d, $J_{P,C}$ = 5 Hz, CH), 132.80 (d, $J_{P,C}$ = 9 Hz, meta CH, PPh_3), 131.56 (s, quaternary C), 130.97 (s, para CH, PPh_3), 128.21 (d, $J_{P,C}$ = 12 Hz, ortho CH, PPh_3), 122.619 (s, CH), 118.64 (d, $J_{P,C}$ = 10 Hz, CH), 116.55 (s, CH), 61.95 (s, CH_2), 58.31 (s, CH_2), 50.30 (s, Me), 50.10 (s, Me), 49.61 (s, Me), 48.87 (s, Me). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ −5.26 (s). Anal. Calcd for $C_{30}H_{35}IN_3PPd$: C, 51.33; H, 5.03; N, 5.99. Found: C, 51.42; H, 5.13; N, 5.93.

Synthesis of [Pd{$C_6H_4(N{=}PPh_3)$-2}(tmeda)(PPh_3)]TfO (11·TfO). TlOTf (60 mg, 0.17 mmol) was added to a solution of **10** (120 mg, 0.17 mmol) in acetone (10 mL). PPh_3 (52 mg, 0.2 mmol) was then added to the suspension. The reaction mixture was stirred for a further 30 min and was filtered through Celite. The resulting yellow solution was evaporated to dryness and the residue triturated with Et_2O (15 mL). The solid was collected by filtration, washed with Et_2O, and dried in vacuo to yield **11**·TfO as a pale yellow solid. Yield: 160 mg, 95%. Mp: 148−150 °C. Λ_M = 144 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): ν 1272, 1030 (triflate). ^1H NMR (300 MHz, $CDCl_3$): δ 7.63−7.51 (m, 9 H, PPh_3), 7.45−7.34 (m, 15 H, PPh_3), 7.19−7.12 (m, 6 H, PPh_3), 7.08−7.03 (m, 1 H, H3 or H6 C_6H_4), 6.44 (td, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1 Hz, 1 H, H4 or H5 C_6H_4), 6.31 (td, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1 Hz, 1 H, H4 or H5 C_6H_4), 5.96 (dd, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1, 1 H, H3 or H6 C_6H_4), 3.35−3.28 (m, 1 H, CH_2), 3.08−2.99 (m, 1 H, CH_2), 2.73 (s, 3 H, Me), 2.70−2.64 (m, 1 H, CH_2), 2.53−2.48 (m, 1 H, CH_2), 2.17 (s, 3 H, Me), 2.00 (s, 3 H, Me), 1.94 (s, 3 H, Me). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 153.4 (s, C2), 144.20 (d, $J_{C,P}$ = 9.5 Hz, CPd), 135.30 (t, ^4J = 5.3 Hz, CH6), 134.50 (d, $J_{C,P}$ = 11.7 Hz, ortho CH's PPh_3), 132.43 (d, $^2J_{C,P}$ = 9.5 Hz, ortho CH's PPh_3), 131.85 (s, para CH's PPh_3), 130.85 (d, $^1J_{C,P}$ = 97.0 Hz, *i* C's PPh_3), 130.55 (s, para CH's PPh_3), 130.54 (d, $^1J_{C,P}$ = 47.3 Hz, *i* C's PPh_3), 128.58 (d, $J_{C,P}$ = 11.6 Hz, *meta* CH's PPh_3), 128.29 (d, $^3J_{C,P}$ = 9.9 Hz, meta CH's PPh_3), 124.66 (s, CH4), 121.53 (d, $^3J_{C,P}$ = 10.9 Hz, CH3), 117.37 (s, CH5), 61.20 (s, CH_2), 60.90 (s, CH_2), 51.20 (s, Me), 50.80 (s, Me), 47.90 (s, Me), 47.00 (s, Me). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 27.55 (s, Pd−PPh_3), 2.55 (s, N═PPh_3). Anal. Calcd for $C_{49}H_{50}F_3N_3O_3P_2PdS$: C, 59.67; H, 5.11; N, 4.26; S, 3.25. Found: C, 59.39; H, 5.23; N, 4.15; S, 3.12. Single crystals of **11**·TfO were grown by slow diffusion of Et_2O into solutions of **11**·TfO in $CDCl_3$.

Synthesis of [Pd{κ^2-*C,N*-C(=NXy)C_6H_4(N=PPh_3)-2}I(CNXy)] (12). To a solution of **10** (100 mg, 0.14 mmol) in CH_2Cl_2 (15 mL) was added XyNC (Xy = 2,6-dimethylphenyl; 57 mg, 0.44 mmol), and the mixture was stirred for 10 min. Then the solution was filtered through Celite and the solvent removed in vacuo. The orange crude product was stirred in Et_2O (10 mL), and the solid obtained was filtered, washed with Et_2O, and air-dried to yield **12** as a yellow solid. Yield: 110 mg, 91%. Mp: 188−190 °C. IR (Nujol, cm^{-1}): ν 2156 (C≡N), 1666 (C=N). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10−8.00 (m, 6 H, ortho or meta H's PPh_3), 7.78 (dt, $^3J_{H,H}$ = 7.5 Hz, $^4J_{H,H}$ = 1.5 Hz, $J_{P,H}$ = 1.5 Hz, 1 H, H3 or H6 C_6H_4), 7.64−7.59 (m, 3 H, para H's PPh_3), 7.56−7.51 (m, 6 H, ortho or meta H's PPh_3), 7.03 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H4, Xy), 6.88 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, Xy), 6.76−6.69 (m, 3 H, Xy and H4 or H5 C_6H_4), 6.65 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, H4 or H5), 6.40 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H4, Xy), 6.16 (d, $^3J_{H,H}$ = 7.5 Hz, 1H, H3 or H6 C_6H_4), 2.38 (s, 6 H, 2 Me), 2.11 (s, 6 H, 2Me). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 180.55 (quaternary C), 154.79 (d, $J_{P,C}$ = 2.5 Hz, quaternary C), 151.24 (quaternary C), 142.93 (quaternary C), 142.76 (quaternary C), 134.22 (d, $J_{P,C}$ = 9.6 Hz, ortho or meta CH's PPh_3), 134.02 (quaternary C), 132.97 (d, $^4J_{P,C}$ = 2 Hz, *p* CH's PPh_3), 130.00 (CH, Xy), 128.70 (d, $J_{P,C}$ = 9.7 Hz, ortho or meta CH's PPh_3), 128.21 (CH, Xy), 127.43 (CH, Xy), 127.22 (quaternary C), 127.14 (CH, Xy), 126.40 (d, $^2J_{P,C}$ = 100 Hz, ipso C's PPh_3), 125.43 (CH, C3 or C6 C_6H_4), 122.99 (CH, Xy), 120.38 (CH, C4 or C5 C_6H_4), 119.86 (d, $J_{P,C}$ = 7.5 Hz, CH, C3 or C6 C_6H_4), 19.29 (s, Me), 18.59 (s, Me). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 26.45 (s). Anal. Calcd for $C_{42}H_{37}IN_3PPd$: C, 59.48; H, 4.40; N, 4.95. Found: C, 59.31; H, 4.44; N, 5.07.

Synthesis of [Pd{κ^2-*C,N*-C(=NXy)C_6H_4(N=PPh_3)-2}-(CNXy)$_2$]TfO (13). XyNC (53 mg, 0.41 mmol) and TlOTf (51 mg, 0.14 mmol) were added to a solution of **10** (100 mg, 0.14 mmol) in acetone (5 mL). The resulting suspension was stirred for 5 min and then filtered through Celite. The yellow solution was evaporated to dryness, the residue was treated with Et_2O (10 mL), and the solid was filtered, washed with Et_2O, and dried in an air stream, giving **13** as a yellow solid. Yield: 120 mg, 90% with respect to isonitrile. Dec pt: 173−5 °C. Λ_M = 140 Ω^{-1} cm^2 mol^{-1}. IR (Nujol, cm^{-1}): ν 2180 (C≡N), 2168 (C≡N), 1634 (C=N). ^{1}H NMR (300 MHz, $CDCl_3$, 40 °C): δ 8.02−7.95 (m, 6 H, ortho or meta H's PPh_3), 7.88 (d, $^3J_{H,H}$ = 7.5 Hz, 1 H, H3 or H6 C_6H_4), 7.72−7.69 (m, 3 H, para H's PPh_3), 7.60−7.59 (m, 6 H, ortho or meta H's PPh_3), 7.17 (t, $^3J_{H,H}$ = 7.5 Hz, 2 H, 2 × H4 coord XyNC), 6.98 (d, $^3J_{H,H}$ = 7.5 Hz, 4 H, 2 × H3 and H5 coord XyNC), 6.81−6.72 (m, 4 H, H3 and H5 insert XyNC and H4 and H5 C_6H_4), 6.49 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, H4 insert XyNC), 6.26 (d, $^3J_{H,H}$ = 7.5 Hz, 1 H, H3 or H6 C_6H_4), 2.38 (s, 6 H, 2Me), 1.97 (b s, 12 H, 4Me). ^{1}H NMR (300 MHz, $CDCl_3$, −60 °C): δ 8.09−8.02 (m, 6 H, ortho or meta H's PPh_3), 7.88 (d, $^3J_{H,H}$ = 7.5 Hz, 1 H, H3 or H6 C_6H_4), 7.83−7.78 (m, 3 H, para H's PPh_3), 7.68−7.65 (m, 6 H, ortho or meta H's PPh_3), 7.24−7.17 (m, 2 H, 2 × H4 coord XyNC), 7.03 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, H3 and H5 coord XyNC), 6.97 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, H3 and H5 coord. XyNC), 6.91−6.84 (m, 3 H, H3 and H5 insert XyNC and H4 or H5 C_6H_4), 6.80 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, H4 or H5 C_6H_4), 6.55 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, H4 insert XyNC), 6.27 (d, $^3J_{H,H}$ = 7.5 Hz, 1 H, H3 or H6 C_6H_4), 2.47 (s, 6 H, 2Me), 2.11 (s, 6 H, 2Me), 1.63 (s, 6 H, 2Me). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 28.6 (s). Anal. Calcd for $C_{52}H_{46}F_3N_4O_3PPdS$: C, 62.37; H, 4.63; N, 5.59; S, 3.20. Found: C, 62.07; H, 4.67; N, 5.71; S, 2.90.

Synthesis of [Pd{κ^2-*C,N*-C(CO_2Me)=C(CO_2Me)C_6H_4(N=PPh_3)-2}(tmeda)]ClO_4·CH_2Cl_2 (14·ClO_4). $MeO_2CC{\equiv}CCO_2Me$ (70 μL, 0.57 mmol) and $AgClO_4$ (30 mg, 0.145 mmol) were added to a stirred suspension of **10** (100 mg, 0.14 mmol) in acetone (15 mL). The mixture was stirred for 30 min and then filtered through Celite. The resulting solution was evaporated to dryness, Et_2O (10 mL) was added to the residue, and the solid obtained was filtered, washed with Et_2O, and air-dried to give **14**·ClO_4 as a pale yellow powder. The crude sample was recrystallized from CH_2Cl_2/Et_2O. Yield: 105 mg, 92% for the crude sample; 85 mg, 74% after recrystallization. Dec pt: 138−140 °C. Λ_M = 171 Ω^{-1} cm^2 mol^{-1}. IR (KBr pellet, cm^{-1}): ν 1694 (C=O), 1094, 624 (ClO_4). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79 (d, $^3J_{H,H}$ = 7.5 Hz, 1 H, C_6H_4), 7.73−7.70 (m, 9 H ortho and para H's PPh_3), 7.60−7.57 (m, 6 H meta H's PPh_3), 7.1−7.05 (m, 1 H, C_6H_4), 7.00−6.98 (m, 2 H, C_6H_4), 5.31 (s, 2 H, CH_2Cl_2), 3.69 (s, 3 H, CO_2Me), 3.39 (s, 3 H, CO_2Me), 2.8−2.6 (m, 2 H, CH_2, tmeda), 2.68 (s, 3 H, Me tmeda), 2.59 (s, 3 H, Me tmeda), 2.55 (s, 3 H, Me, tmeda), 2.4−2.3 (m, 2 H, CH_2 tmeda), 1.69 (s, 3 H, Me, tmeda). ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ 172.18 (CO), 162.89 (CO), 149.24 (d, $J_{P,C}$ = 5 Hz, quaternary C), 142.11 (d, $J_{P,C}$ = 6 Hz, quaternary C), 141.12 (d, $J_{P,C}$ = 5.5 Hz, quaternary C), 134.48 (d, $^2J_{P,C}$ = 10 Hz, ortho CH, PPh_3), 134.01 (d, $^4J_{P,C}$ = 2.5 Hz, para CH, PPh_3), 132.01 (d, $J_{P,C}$ = 1.5 Hz, quaternary C), 130.09 (d, $J_{P,C}$ = 3 Hz, CH), 129.27 (d, $^3J_{P,C}$ = 12 Hz, meta CH, PPh_3), 126.06 (d, $J_{P,C}$ = 3.5 Hz, CH), 125.13 (d, $^1J_{P,C}$ = 100 Hz, ipso C PPh_3), 124.33 (d, $J_{P,C}$ = 3.5 Hz, CH), 63.74 (s, CH_2), 58.77 (CH_2), 53.02 (Me), 51.65 (Me), 51.60 (Me), 49.14 (Me), 48.34 (Me), 47.38 (Me). ^{31}P-{^{1}H} NMR (121 MHz, $CDCl_3$): δ 35.3 (s). Anal. Calcd for $C_{37}H_{43}Cl_3N_3O_8PPd$: C, 49.30; H, 4.81; N, 4.66. Found: C, 49.03; H, 4.73; N, 4.82. Single crystals of **14**·ClO_4·$CDCl_3$ were grown by slow diffusion of Et_2O into solutions of **14**·ClO_4 in $CDCl_3$.

Crystal Structure Determinations. Crystal data and numerical details of data collection and structure refinement are given in Table 1. For the compounds **11**·TfO and **14**·ClO_4·$CDCl_3$, data were collected on a Bruker SMART 1000 CCD diffractometer and those for the compounds **2**, **6a**·CH_2Cl_2, and **9a** on a Siemens P4 diffractometer. Special features of refinement: **9a**, the perchlorate anion is disordered over two sites, which were refined with 50% occupancy; **11**·TfO, the poor crystal quality is reflected in the lack of precision; **14**·ClO_4·$CDCl_3$, the solvent molecule is disordered over two positions with a common carbon site. The structures were refined anisotropically using the program SHELXL-97 (G. M. Sheldrick, University of Göttingen, Göttingen, Germany). Hydrogen atoms were included using rigid methyl groups or a riding model.

Results and Discussion

Objectives and Methods. One of the main objectives of our research has been the synthesis of ortho-functionalized arylpalladium(II) complexes, because we have found that they undergo insertion of unsaturated reagents, e.g. isocyanides, alkynes, and CO, to give interesting complexes or organic compounds.[17−20] At the beginning of this work we were interested in preparing palladated complexes containing the ortho iminic aryl group of type III (Chart 1) (i) because we assumed they would be more reactive toward the above-mentioned unsaturated reagents than those containing a chelating ligand of type IIb, (ii) because no organometallic compound of any metal with such group was known, and (iii) because of the interesting chemistry that the iminophosphorane group could offer if the N atom were not coordinated to Pd(II). Four different synthetic routes

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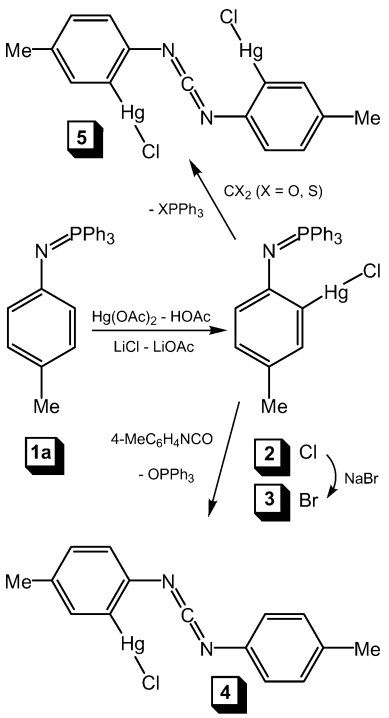
Table 1. Crystal Data for Compounds 2, 6a·CH_2Cl_2, 9a, 11·TfO, and 14·ClO_4

	2	**6a**·CH_2Cl_2	**9a**	**11**·TfO	**14**·ClO_4·$CDCl_3$
formula	$C_{25}H_{21}ClHgNP$	$C_{55}H_{50}Cl_2N_2O_4P_2Pd_2$	$C_{31}H_{37}ClN_3O_4PPd$	$C_{49}H_{50}F_3N_3O_3P_2PdS$	$C_{37}H_{42}Cl_4N_3O_8PPd$
cryst color, habit	colorless, block	yellow, block	yellow, prism	pale yellow, plate	pale yellow, prism
cryst size (mm)	0.56 × 0.26 × 0.24	0.50 × 0.34 × 0.18	0.28 × 0.23 × 0.14	0.31 × 0.20 × 0.05	0.40 × 0.15 × 0.10
cryst syst	triclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	8.978(2)	10.802(2)	11.1979(8)	10.966(7)	13.6861(8)
b (Å)	10.714(3)	11.848(2)	9.0604(6)	30.880(18)	14.6217(11)
c (Å)	12.053(3)	21.500(4)	30.930(2)	13.527(8)	21.1817(12)
α (deg)	86.500(18)	97.91(3)	90	90	90
β (deg)	72.212(14)	91.32(3)	97.071(6)	100.00(4)	104.121(3)
γ (deg)	85.46(2)	111.29(3)	90	90	90
V (Å^3)	1099.6(5)	2531.7(9)	3114.2(4)	4511(5)	4110.7(5)
Z	2	2	4	4	4
ρ_{calcd} (Mg m^{-3})	1.819	1.507	1.468	1.452	1.512
M_r	602.44	1148.61	688.46	986.32	935.91
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
T (K)	173	173	298	133	133
F(000)	580	1164	1416	2032	1912
μ(Mo Kα) (mm^{-1})	7.204	0.93	0.773	0.59	0.80
θ range (deg)	3.0−25.0	3.2−25.0	3.0−25.0	1.3−26.4	1.6−30.0
abs cor	ψ scans	ψ scans	ψ scans	face indexed	face indexed
no. of rflns coll	4163	10 204	5888	40 136	81 456
no. of indep rflns	3844	8849	5469	9245	12 038
R_{int}	0.0246	0.023	0.0278	0.294	0.046
transmissn	0.0874−0.2767	0.756−0.912	0.8127−0.8995	0.867−0.978	0.785−0.927
no. of data/restraints/ params	3844/27/263	8849/32/608	5469/178/412	9245/147/559	12 038/339/521
R1 ($I > 2\sigma(I)$)	0.0273	0.0271	0.0374	0.107	0.032
wR2 (all rflns)	0.0674	0.073	0.0771	0.250	0.085
max $\Delta\rho$ (e Å^{-3})	1.4	0.6	0.28	1.7	0.9
$S(F^2)$	1.03	1.03	1.034	1.12	1.03

were envisaged. (i) Iminophosphoranes could be mercurated, followed by transmetalation to palladium. This was the first attempted method, in view of our wide experience in the synthesis of organomercurials and their use to prepare organo complexes of different metals, including Pd(II),[20−23] and because mercuration of the related benzylidenanilines occurs at the ortho iminic aryl group.[24] (ii) Iminophosphoranes could be palladated using reaction conditions different from those previously reported that led to complexes of type IIb.[12] (iii) A Kirsanov reaction could be used, starting from some *o*-aminoaryl complexes that we had previously reported.[17] (iv) An iminophosphorane could be synthesized containing an *o*-iodo substituent at the iminic aryl group followed by an oxidative addition reaction using a Pd(0) complex.

Mercuration of Iminophosphoranes. Synthesis of Aryl Complexes Containing a Carbodiimide Group. The reaction of the iminophosphorane **1a** with

Scheme 1



$Hg(OAc)_2$ in refluxing THF followed by the addition of LiCl resulted in the formation of the mercurated species [Hg{C_6H_3(N=PPh_3)-2-Me-5}Cl] (**2**) (Scheme 1), in which the metalation had taken place at the imine aryl group, giving the first example of a class III metalated iminophosphorane (Chart 1) and also the first organomercurated iminophosphorane. The metathetical reaction of **2** with NaBr gave the complex [Hg{C_6H_3(N=PPh_3)-2-Me-5}Br] (**3**).

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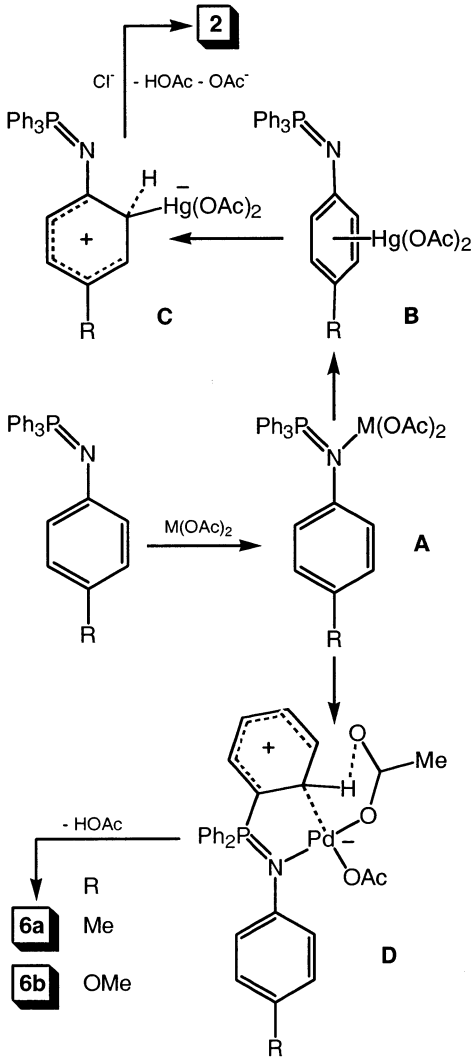
Zimmer reported that the room-temperature reactions of HgX_2 (X = Cl, Br, I) with **1a** and similar iminophosphoranes lead to the adducts $[HgX_2\{N(=PPh_3)Ar\}]$; the crystal structure of one such compound shows it to be the dimer $[HgCl(\mu\text{-}Cl)\{N(=PPh_3)Ph\}]_2$.[4] When these room-temperature reactions were carried out with iminophosphoranes substituted at the meta position or with the electron-withdrawing *p*-NO_2 group, no reaction took place, and if elevated temperatures (80 °C) and extended reaction times were used, $OPPh_3$ and $[Ph_3PNHAr]X$ were isolated. Therefore, our use of the appropriate Ar group and of $Hg(OAc)_2$ instead of mercury halides and the heating of the reaction mixture seem to be the factors responsible for the different reaction products obtained from mercury salts and iminophosphoranes.

The formation of **2** contrasts with that observed in all the other metalation reactions of iminophosphoranes, which take place at one of the aryl groups bonded to the phosphorus atom (see Introduction). However, the result is not unexpected, since mercuration occurs through electrophilic aromatic substitution and the imine nitrogen activates its aryl ring toward such substitution.[25] In addition, Wu et al. have reported that mercuration of a large number of benzylidenanilines also occurs at the ortho position of the *N*-phenyl ring[24] and corrected a previous suggestion that such mercuration occurred at the C-aryl group.[26] Wu suggested a four-step mechanism for the mercuration of benzylidenanilines that could also operate in the case of **1a**: (i) formation of the adduct **A** (Scheme 2) such as those reported by Zimmer (see above, X = OAc);[4] (ii) formation of the π-complex **B** with an *N*-phenyl ring, as proposed for some γ-(arylpropyl)mercury compounds;[27] (iii) conversion of the π-complex into the Wheland or σ-complex intermediate **C**; (iv) loss of HOAc and formation of an acetato complex that would react with LiCl to give **2**.

The presence of the iminophosphorane group at the ortho position of these aryl mercurials encouraged us to exploit its well-known reactivity. Thus, the compound **2** reacts with *p*-tolyl isothiocyanate, resulting in its transformation into the mercurated carbodiimide $[Hg\{C_6H_3(N{=}C{=}NC_6H_4Me\text{-}4')\text{-}2\text{-}Me\text{-}5\}Cl]$ (**4**) (Scheme 1). The reaction of **2** with CO_2 or CS_2 permits the isolation of the dimetalated carbodiimide $[Hg\{C_6H_3\{N{=}C{=}NC_6H_3(HgCl)\text{-}1'\text{-}Me\text{-}5'\}\text{-}2\text{-}Me\text{-}5\}Cl]$ (**5**). **4** and **5** are the first aryl complexes of any metal containing a carbodiimide group.

Attempts to Transmetalate the Triphenylphosphoraneiminoaryl Group. We have reported the synthetic utility of organomercurials in the synthesis of organo derivatives of Au(I),[28,29] Au(III),[29,30] Pd(II),[20−23] Pt(II),[21,31] Rh(III),[32] Sn(IV),[33] and Tl(III).[34] However, attempted analogous reactions of **2** and **3** with $Me_4N[AuCl_4]$, $(Me_4N)_2[Pd_2Cl_6]$, $[PdCl_2(PPh_3)_2]$, $[Pd(PPh_3)_3]$,

Scheme 2



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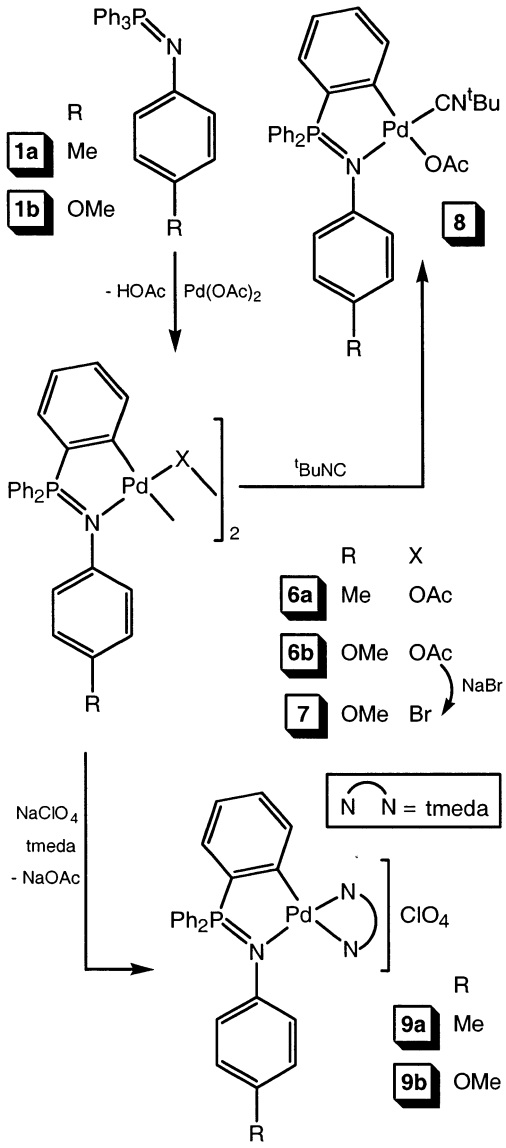
and $[PtCl_2(bpy)]$ have proved unsuccessful. Because diarylmercurials are generally better transmetalating agents, we also attempted to prepare $[Hg\{C_6H_3(N{=}PPh_3)\text{-}2\text{-}Me\text{-}5\}_2]$. However, **2** does not symmetrize with ammonia[35] and gives mixtures when reacted with Me_4NCl[22] or PPh_3.[36]

Palladation of Iminophosphoranes. The only paper on the palladation of iminophosphoranes reported the synthesis of the complexes $[Pd\{\kappa^2\text{-}C,N\text{-}(C_6H_3R^1\text{-}5)\text{-}\{P(C_6H_4R^1\text{-}4)_2{=}NC_6H_4R^2\text{-}n\}(\mu\text{-}Cl)]_2$ (R^1 = H, R^2 = Me (n = 3, 4), OMe (n = 4); R^1 = Me, R^2 = OMe (n = 4)) by addition of the ligand to a methanol solution of $Na_2[PdCl_4]$.[5] We decided to try a similar reaction, but using $Pd(OAc)_2$ and THF, to compare the results with those obtained in the mercuration and to see if the change of the reaction conditions could lead to a triphenylphosphoraneiminoaryl complex. However, not unexpectedly, the room-temperature reaction of the iminophosphorane **1a** or **1b** with $Pd(OAc)_2$ results in the formation of the cyclopalladated complex $[Pd\{\kappa^2\text{-}C,N\text{-}C_6H_4(PPh_2{=}NC_6H_4R\text{-}4')\text{-}2\}(\mu\text{-}OAc)]_2$ (R = Me (**6a**), MeO (**6b**)) (Scheme 3), similar to those previously reported in which the palladation has taken place at the ortho position of one of the phenyl rings bonded to the phosphorus atom, permitting the formation of a five-membered ring through the coordination of the nitrogen atom; in addition, the acetato ligand acts as bridge forming a dimer, as confirmed by the X-ray diffraction study for **6a**·CH_2Cl_2 (see below).

Although formation of an adduct is, as in mercuration reactions, the proposed first step in palladation reactions involving N-donor aryl ligands (intermediate **A** in Scheme 2**)**,[37] the formation of the five-membered-ring σ-complex intermediate **D** seems to be preferred to the postulated formation of a π-complex with the *N*-phenyl ring in mercuration reactions. In fact, it is quite general that formation of a five-membered ring including a double bond (endo isomer), as in complexes **6a**,**b**, is preferred to other alternatives in cyclopalladation reactions.[38]

Complex **6b** reacted with NaBr to give the bromo derivative $[Pd\{\kappa^2\text{-}C,N\text{-}C_6H_4(PPh_2{=}NC_6H_4OMe\text{-}4')\text{-}2\}(\mu\text{-}Br)]_2$ (**7**) and with an excess of the isonitrile ^{t}BuNC to give the complex $[Pd\{\kappa^2\text{-}C,N\text{-}C_6H_4(PPh_2{=}NC_6H_4OMe\text{-}4')\text{-}2\}(OAc)(CN^tBu)]$ (**8**). However, the reactions of **6a** with ^{t}BuNC (1:3) or XyNC (Xy = 2,6-dimethylphenyl; 1:3) and of **6b** with XyNC (1:2 and 1:3 molar ratios) gave intractable mixtures. CO did not react with complex **6a** but with **6b** gave Pd metal, unreacted **6b**, and an intractable mixture. When a mixture of **6a** or **6b** was refluxed with PhC≡CPh in $CHCl_3$ or toluene, most starting materials were recovered. Although **6a** reacted with $MeO_2CC{\equiv}CCO_2Me$, and ^{1}H NMR and IR spectra were in agreement with the formation of a monoinserted complex (such as **14**·ClO_4; see below), the product of the reaction could not be isolated analytically pure. Complexes **6a**,**b** reacted with $NaClO_4$ and tmeda (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine), affording the cationic complexes $[Pd\{\kappa^2\text{-}C,N\text{-}C_6H_4(PPh_2{=}NC_6H_4R\text{-}4')\text{-}2\}(tmeda)]ClO_4$ (R = Me (**9a**), MeO (**9b**)) (Scheme 3).

Scheme 3



Synthesis of Triphenylphosphoraneiminoaryl Palladium(II) Complexes. After the above fruitless attempts to prepare triphenylphosphoraneiminoaryl palladium(II) complexes, we attempted reactions based on the Kirsanov reaction, i.e., $ArNH_2 + PPh_3Br_2 \rightarrow ArN{=}PPh_3 + 2BrH$. The first attempt consisted of the synthesis, through oxidative addition reactions, of some *o*-aminoaryl complexes ($ArNH_2 = [Pd(C_6H_4Y\text{-}5\text{-}NH_2\text{-}2)X(L_2)]$, Y = H, X = I, L_2 = bpy (2,2′-bipyridine); Y = NO_2, X = Br, L_2 = tmeda) that we had previously prepared.[17] However, ^{31}P NMR spectra of the mixture resulting from the reactions of these complexes with PPh_3Br_2 in

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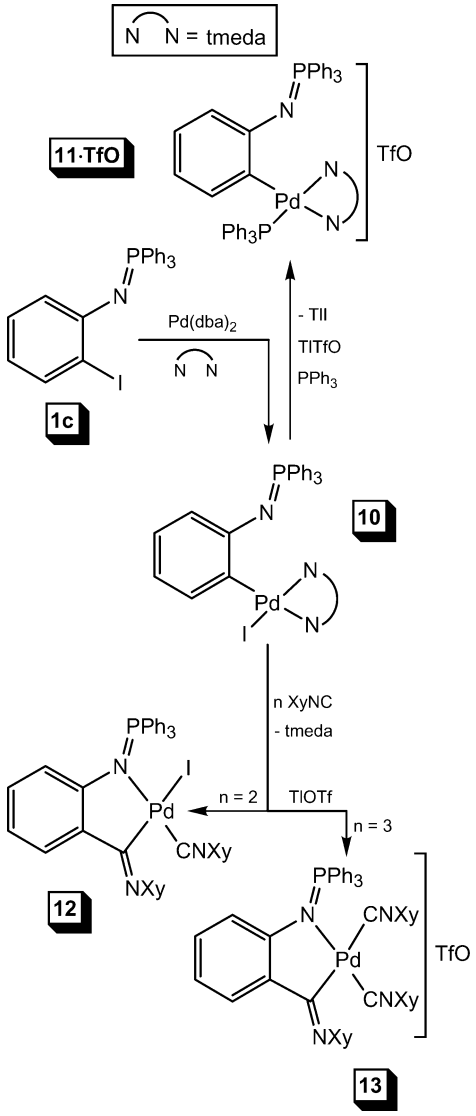
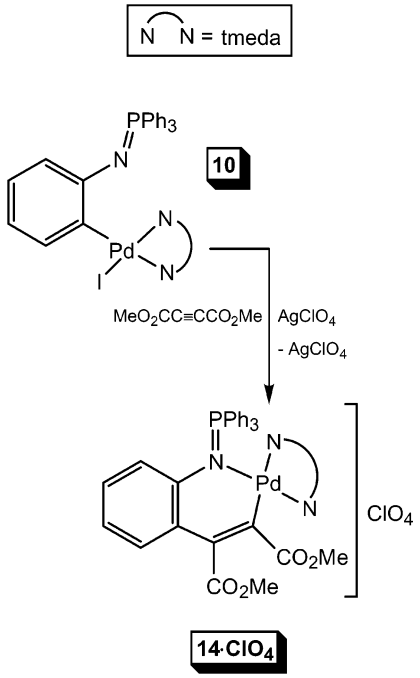
Scheme 4



refluxing benzene show a complex mixture that we could not separate. Finally, we succeeded by reacting $Ph_3P{=}NC_6H_4I$-2 (**1c**), prepared by the Kirsanov method[1] from 2-iodoaniline and Ph_3PBr_2,[16] with a mixture of "Pd(dba)$_2$" ([Pd$_2$(dba)$_3$]·dba, dba = dibenzylideneacetone) and tmeda to give [Pd{C_6H_4(N=PPh_3)-2}I(tmeda)] (**10**) (Scheme 4). Reaction of **10** with PPh_3 and TlOTf (TfO = CF_3SO_3) resulted in the formation of the cationic [Pd{C_6H_4(N=PPh_3)-2}(tmeda)(PPh_3)]TfO (**11**·TfO). When in this reaction $AgClO_4$ was used instead of TlOTf, the NMR spectra of the product **11**·ClO_4 were similar to those of **11**·TfO but it did not give the correct analysis.

As mentioned above, we planned to study the reactions of some of these new complexes with unsaturated molecules. Thus, complex **10** reacted with XyNC (Xy = 2,6-dimethylphenyl; 1:3.1 molar ratio; Scheme 4) to give [Pd{κ^2-*C*,*N*-C(=NXy)C_6H_4(N=PPh_3)-2}I(CNXy)] (**12**). Surprisingly, when the reaction was carried out in a 1:1 molar ratio, **12** and the starting material **10** were isolated. We have reported that when similar complexes containing the ortho substituent C(O)Me or CN were reacted with XyNC, the first isolable compound was the product of the insertion of the isocyanide.[18] It is then reasonable to assume that formation of the inserted complex [Pd{C(=NXy)C_6H_4(N=PPh_3)-2}I(tmeda)] would

Scheme 5



be followed by coordination of the imine nitrogen, forming a chelate and displacing the tmeda ligand to give the intermediate [Pd{κ^2-*C*,*N*-C(=NXy)C_6H_4(N=PPh_3)-2}I]$_2$. This would be the slower step of the process. The dinuclear intermediate would rapidly react with unreacted XyNC to give **12**, even when using an 1:1 molar ratio. Complex **10** reacted with ^{t}BuNC in a 1:1 or 1:3 molar ratio or using an excess of isocyanide giving complex mixtures. The cis geometry of the carbon donor ligands in **12** is in accord with the high *transphobia*[18,21,39] between such ligands. The reaction of **10** with TlOTf and 2 equiv of XyNC gave the cationic complex [Pd{κ^2-*C*,*N*-C(=NXy)C_6H_4(N=PPh_3)-2}(CNXy)$_2$]TfO (**13**).

Reactions of **10** with CO led to complex mixtures. The same reaction followed by addition of TlOTf gave a product whose ^{31}P NMR and IR spectra are compatible with monoinsertion of CO and coordination of the nitrogen atom to give a five-membered ring, in addition to some minor impurities that could not be removed.

Insertion reactions of alkynes into the Pd−C bond are also of current interest.[20,40] Complex **10** reacts with $MeO_2CC{\equiv}CCO_2Me$ (dmad) and $AgClO_4$ to give the alkenyl derivative [Pd{κ^2-*C*,*N*-C(CO_2Me)=C(CO_2Me)-C_6H_4(N=PPh_3)-2}(tmeda)]ClO_4 (**14**·ClO_4), the result of insertion of the alkyne into the Pd−C bond and coordination of the nitrogen atom, creating a six-membered chelate ring (Scheme 5), as confirmed by X-ray diffraction studies. Several attempts to prepare similar complexes were unfruitful. Thus, using PhC≡CPh, 3-hexyne, or PhC≡CCO_2Me instead of dmad gave intractable mixtures of products. When in the reaction of **10**, TlOTf was used instead of $AgClO_4$, the NMR spectra of the product **14**·OTf showed the presence of the pure monoinserted complex but a low (by 1.5%) elemental analysis of carbon was found.

Complex **10** reacts with 4-MeC_6H_4NCO to give the corresponding carbodiimide complex. However, it was obtained impure in low yield.

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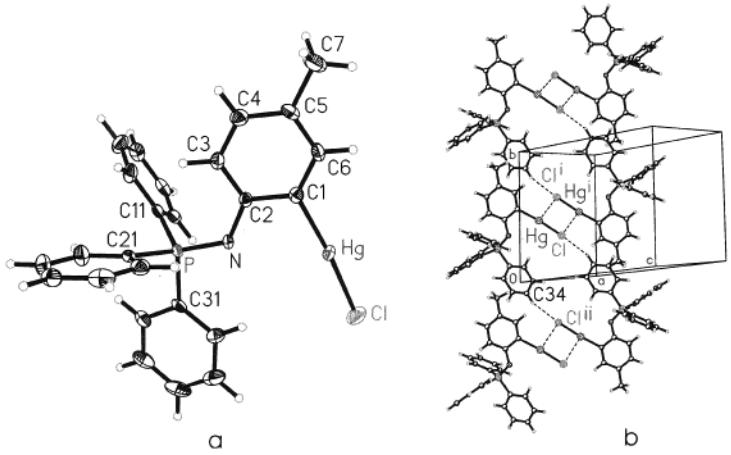

Figure 1. (a) Thermal ellipsoid plot (50% probability) of **2** with the labeling scheme. Selected bond lengths (Å) and angles (deg): Hg−C(1) = 2.042(5), Hg−Cl = 2.3184(14), P−N = 1.576(4), N−C(2) = 1.393(6); C(1)−Hg−Cl = 173.02(13), C(2)−N−P = 127.1(3). (b) Ladders parallel to the *b* axis formed through Hg···Cl^{i} contacts ((i) $1-x$, $1-y$, $-z$, Hg···Cl^{i} = 3.4125(17) Å) and C(34)−H(34)···Cl^{ii} hydrogen bonds ((ii) $-x+1$, $-y$, $-z$, C(34)···Cl^{ii} = 3.663(6) Å, H(34)···Cl^{ii} = 2.77 Å, C(34)−H(34)···Cl^{ii} = 156.8°).

Spectroscopic Data. The spectroscopic data of the reported compounds are in accordance with the proposed structures. The insolubility of **5** has prevented us from studying it by NMR, but its EI MS spectrum shows a signal of low intensity (1.2%) corresponding to the molecular ion.

The dimeric complexes **6a**,**b** show in their ^{13}C NMR spectra that the two phenyl rings of the PPh_2 group are inequivalent, since their respective ipso carbons resonate at different frequencies. This is in accordance with the X-ray structural determination of **6a**·CH_2Cl_2 (see below).

The tmeda complexes **10**, **11**·TfO, and **14**·ClO_4 show four Me signals in their ^{1}H and ^{13}C NMR spectra. This suggests, in the cases of **10** and **11**·TfO, that the aryl ring has restricted rotation around the C−Pd bond and, in the case of **14**·ClO_4, that the six-membered chelate ring is not planar, as is observed in the solid state according to the X-ray diffraction studies of **14**·ClO_4·$CDCl_3$ (see below). Because the complex **11**·TfO slowly decomposes in solution, the ^{13}C NMR spectrum shows minor peaks due to impurities. To distinguish the signals belonging to **11**·TfO, a long-range C−H correlation (HMBC) was done. C2 and CPd assignments (153.4 and 144.20 ppm, respectively) were tentative and were based upon experimental data from organic aryl iminophosphoranes (chemical shifts for C1 in **1** and **2** are 151.58 and 151.87 ppm, respectively). After the ^{13}C NMR spectra were acquired and HMBC experiments (3.5 h) carried out, the ^{31}P NMR spectrum showed two additional signals at 22.03 and 12.08 ppm and a very weak signal at 29.9 ppm.

A recent ^{1}H, ^{19}F, ^{31}P, and ^{35}Cl PGSE diffusion study on the complexes **11**·TfO, **11**·ClO_4, **14**·TfO, and **14**·ClO_4 shows that the diffusion coefficients of cation and anion in acetone are quite different. The cation seems to move independently and move much slower than the anion. However, in chloroform, the diffusion coefficients for cation and anion in the triflates are almost identical, indicating complete ion pairing, while in the perchlorates they are slightly different, suggesting that the ion pairing is not as strong.[41]

The compound **13** is fluxional. Its ^{1}H NMR spectrum shows a signal at 2.38 ppm corresponding to the two methyls of a Xy group and another signal at 1.97 ppm integrated to 12 H, corresponding to two Xy groups. When the temperature is lowered to −60 °C, the expected three signals (at 2.47, 2.11, and 1.63 ppm) were observed. The signal at about 2.4 ppm should be assigned to the inserted isonitrile if a fast exchange of the coordinated cis isocyanides at room temperature is assumed. We have reported a similar behavior in the complex [Pd{{κ^2-*C*,*N*-C(=NXy)$C_6H_4NH_2$-2}(CNXy)$_2$]TfO.[17]

X-ray Structure Determinations. The crystal and molecular structures of the compounds **2**, **6a**·CH_2Cl_2, 9a, **11**·TfO, and **14**·ClO_4·$CDCl_3$ have been determined by X-ray diffraction studies (Table 1). The mercurial **2** (Figure 1a) shows a distorted linear structure (C(1)−Hg−Cl = 173.03(13) Å). The P−N distance (1.576(4) Å) corresponds to a double bond,[42] and it is similar to that observed in related iminophosphoranes.[43] In the crystal the mercury atom forms dimers through Hg···Cl contacts shorter than the sum of the van der Waals radii (Figure 1b). Similar interactions have been reported.[44]

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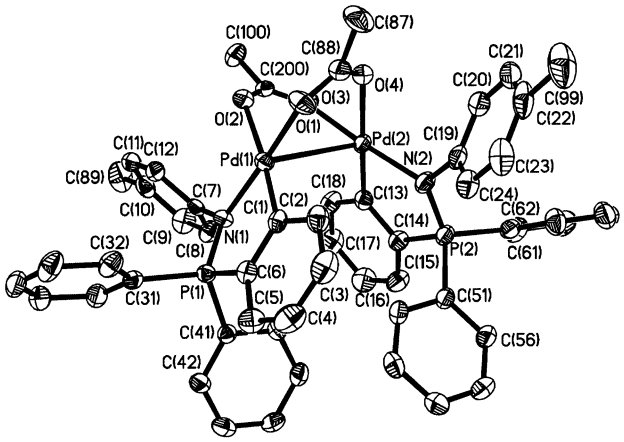

Figure 2. Ellipsoid representation of **6a** with 50% probability ellipsoids and the labeling scheme. The solvent has been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)−C(1) = 1.959(3), Pd(1)−O(3) = 2.041(2), Pd(1)−N(1) = 2.050(2), Pd(1)−O(2) = 2.1153(19), Pd(1)−Pd(2) = 3.0113(8), Pd(2)−C(13) = 1.964(3), Pd(2)−N(2) = 2.051(2), Pd(2)−O(1) = 2.0601(19), Pd(2)−O(4) = 2.143(2), P(1)−N(1) = 1.605(2), P(2)−N(2) = 1.610(2); C(1)−Pd(1)−O(3) = 90.34(10), C(1)−Pd(1)−N(1) = 86.74(10), O(3)−Pd(1)−N(1) = 174.39(8), C(1)−Pd(1)−O(2) = 173.95(9), C(13)−Pd(2)−N(2) = 85.79(10), C(13)−Pd(2)−O(1) = 91.80(10), N(2)−Pd(2)−O(1) = 173.23(8), C(13)−Pd(2)−O(4) = 177.48(9).

A C−H···Cl−Hg hydrogen bond, within the strong angularly dependent C−H···Cl interaction range, connects the mercury dimers, forming a ladder (Figure 1b).[45] It has been shown that metal-bound chlorine is a good hydrogen bond acceptor.[46]

The palladated complex **6a**·CH_2Cl_2 shows a dimeric structure with two bridging acetato ligands (Figure 2). Each palladium has a square-planar geometry, but the molecule is not planar. The iminophosphorane has been metalated at one of the ortho carbons of one of the Ph groups, and the iminic nitrogen coordinates to the palladium, forming a five-membered chelate ring. The P−N distances (P(1)−N(1) = 1.607(2) Å; P(2)−N(2) = 1.611(2) Å) are somewhat longer than that found in **2**, and they are quite similar to the P−N distances found in an ortho-manganated iminophosphorane (1.603(3), 1.597(4), 1.594(4) Å).[11] Therefore, the P−N lengthening could be due to the N coordination. The different Pd−O distances found (Pd(1)−O(1) = 2.0429(19) Å (trans to N); Pd(1)−O(3) = 2.1148(18) Å (trans to C); Pd(2)−O(2) = 2.1433(19) Å (trans to C); Pd(2)−O(4) = 2.0599(18) Å (trans to N)) reflect the greater trans influence exerted by the carbon donor ligand with respect to the iminic nitrogen. The bridging acetates hold both Pd atoms at a distance of 3.0113(8) Å. Similar complexes show equal or even shorter distances.[47] The molecular packing involves two C−H···O contacts. One of them (C(11)−H(11)···O(2) ($-x + 2$, $-y + 1$, $-z + 1$)) links the molecules into dimers.

The structure of **9a** (Figure 3) reveals a distorted-square-planar coordination around the palladium atom. The dihedral angle between the planes defined by Pd−N(2)−N(3) and Pd−C(11)−N(1) is 12.8°. The P−N(1) distance (1.611(4) Å) is virtually identical with that shown by the complex **6a**·CH_2Cl_2. The different Pd−N(2) (2.204(4) Å) and Pd−N(3) (2.116(3) Å) distances indicate again the greater trans influence of the carbon donor ligand.

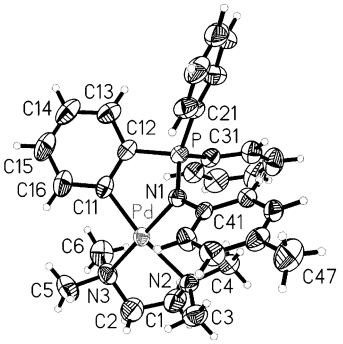

Figure 3. Thermal ellipsoid representation (50% probability) of **9a** with the labeling scheme. Selected bond lengths (Å) and angles (deg): Pd−C(11) = 2.019(3), Pd−N(1) = 2.055(2), Pd−N(3) = 2.117(3), Pd−N(2) = 2.201(3), P−N(1) = 1.607(3); C(11)−Pd−N(1) = 82.78(12), C(11)−Pd−N(3) = 97.38(13), N(1)−Pd−N(2) = 95.34(10), N(3)−Pd−N(2) = 84.17(11).

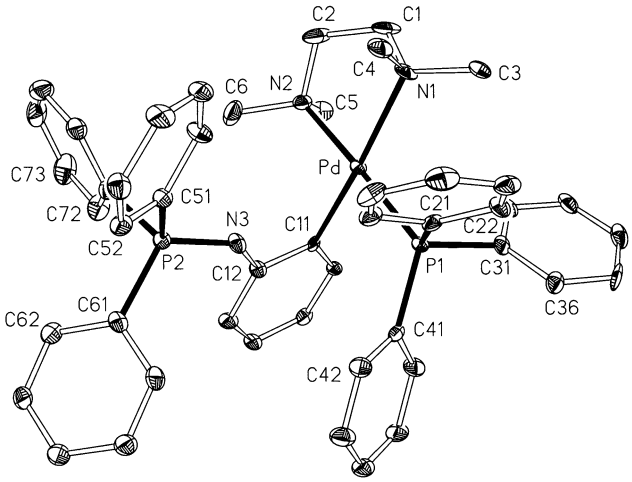

Figure 4. Ellipsoid representation of **11**·TfO with 50% probability ellipsoids and the labeling scheme. The anion has been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd−C(11) = 1.997(7), Pd−N(2) = 2.177(7), Pd−N(1) = 2.239(6), Pd−P(1) = 2.252(3), P(2)−N(3) = 1.570(7), N(3)−C(12) = 1.373(10); C(11)−Pd−N(2) = 92.2(3), N(2)−Pd−N(1) = 82.1(3), C(11)−Pd−P(1) = 84.4(2), N(1)−Pd−P(1) = 101.2(2), C(12)−N(3)−P(2) = 127.8(5).

The structure of **11**·TfO confirms the palladation at the N-aryl substituent (Figure 4). In agreement with

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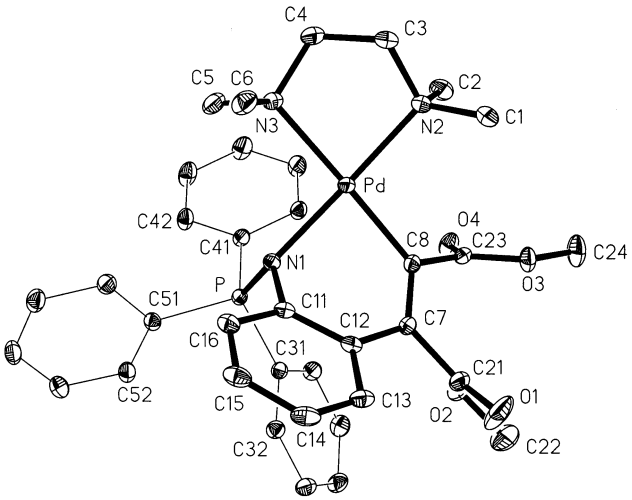

Figure 5. Ellipsoid representation of **14**·ClO_4 with 50% probability ellipsoids and the labeling scheme. The anion has been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd−C(8) = 2.0068(18), Pd−N(1) = 2.0519(15), Pd−N(2) = 2.1114(16), Pd−N(3) = 2.1692(16), P−N(1) = 1.6317(16), C(7)−C(8) = 1.341(2); C(8)−Pd−N(1) = 85.24(7), C(8)−Pd−N(2) = 97.08(7), N(1)−Pd−N(3) = 93.36(6), N(2)−Pd−N(3) = 84.04(6), C(11)−N(1)−P = 115.18(12), C(11)−N(1)−Pd = 109.83(11), P−N(1)−Pd = 124.64(8), C(8)−C(7)−C(12) = 123.54(17), C(8)−C(7)−C(21) = 119.56(17), C(12)−C(7)−C(21) = 116.89(16), C(7)−C(8)−C(23) = 118.69(16), C(7)−C(8)−Pd = 122.45(14), C(23)−C(8)−Pd = 118.70(12).

the above conclusion on the influence of coordination on the P−N distance, the P(2)−N(3) length (1.570(7) Å) is very similar to that of the mercurial **2** and shorter than those in the complexes **6a**·CH_2Cl_2 and **9a**. The greater trans influence of the aryl as compared to the PPh_3 ligand is shown by the longer Pd−N(1) distance (2.239(6) Å) as compared to Pd−N(2) (2.177(7) Å). The molecular packing involves four very short C−H···O contacts that link the molecules into thick layers parallel to the *xz* plane.

The complex **14**·ClO_4·$CDCl_3$ exhibits a square-planar coordination around the palladium, which confirms the insertion of the alkyne into the Pd−C bond, giving a six-membered chelate ring (Figure 5). The iminic P−N(1) distance is 1.6317(16) Å, somewhat longer than those in the complexes **6a**·CH_2Cl_2 and **9a**. The C(7)−C(8) bond distance (1.341(2) Å) corresponds to a C=C double bond. The N−Pd bond distances of the tmeda ligands (Pd−N(2) = 2.1114(16) Å; Pd−N(3) = 2.1692(16) Å) are in accordance with the smaller trans influence of the iminic nitrogen ligand as compared to the alkenyl ligand. When the Pd−N(3) distance is compared with the Pd−N(2) length in the cationic complex **9a**, the scale of trans influence C-aryl > C-alkenyl > N-donor ligand can be established. The molecular packing involves four short C−H···O contacts, three of which link the molecules into layers parallel to the *xy* plane.

Conclusions

We have studied transmetalation, metalation, and oxidative addition reactions to prepare iminophosphoranes metalated in the substituent at N. Mercuration leads to the desired complexes, which are the first organomercurated iminophosphoranes. From one of them we have prepared the first aryl complexes of any metal containing a carbodiimide group. Palladation of iminophosphoranes occurs at one aryl group attached at P. However, the desired palladium complexes can be prepared through oxidative addition reactions. These complexes insert an isocyanide or an alkyne to give iminoacyl or vinyl derivatives. The products of the oxidative addition reactions, their derivatives, and their related mercuric compounds are the first iminophosphoranes metalated at the substituent at N of any metal.

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Supporting Information Available: Listings of all refined and calculated atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for **2**, **6a**·CH_2Cl_2, **9a**, **11**·TfO, and **14**·ClO_4·$CDCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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