A New Example of a Palladium-Assisted Aryl Rearrangement. Synthesis and Reactivity of (2,3,4-Trimethoxy-6-X-phenyl)palladium [X = CHO, CH=N(*n*-$C_{10}H_{21}$), CH=N$C_6H_4(NH_2)$-2, C(O)Me] and (3,4,5-Trimethoxy-2-X-phenyl)palladium [X = CHO, CH=N$C_6H_4(NH_2)$-2] Complexes. Crystal and Molecular Structure of [Pd(κ^3-C_6H{CH=N$C_6H_4(NH_2)$-2}-6-$(OMe)_3$-2,3,4)(PPh_3)]CF_3SO_3, [Pd(κ^3-C_6H{CH=N$C_6H_4(NH_2)$-2}-2-$(OMe)_3$-3,4,5)(PPh_3)]CF_3SO_3, and [Pd(κ^2-C_6H{C(O)Me}-6-$(OMe)_3$-2,3,4)(2,9-dimethyl-1,10-phenanthroline)]CF_3SO_3

José Vicente, José-Antonio Abad,* and Juan Gil-Rubio

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

Received May 4, 1993®

The reaction of [Pd(R)Cl(bpy)] [R = C_6H(CHO)-6-$(OMe)_3$-2,3,4; bpy = 2,2′-bipyridine] (1) with $AgClO_4$ results in the O-coordination of the formyl group and the isomerization of the aryl ring to give [Pd(κ^2-R′)(bpy)]ClO_4 (2) [R′ = C_6H(CHO)-2-$(OMe)_3$-3,4,5]. [HgR_2] or [Hg(R)Cl] reacts with *n*-decylamine or *o*-phenylenediamine to give respectively [$Hg(RN)_2$] (3) [RN = C_6H{CH=N(*n*-$C_{10}H_{21}$)}-6-$(OMe)_3$-2,3,4] or [Hg(RNN)Cl] (4) [RNN = C_6H{CH=N{$C_6H_4(NH_2)$-2}-6-$(OMe)_3$-2,3,4]. [$PdCl_2(MeCN)_2$] reacts with 3 to give [Pd(κ^2-RN)(μ-Cl)]$_2$ (5) and with 4, PPh_3, and K(CF_3SO_3) giving [Pd(κ^3-RNN)(PPh_3)]CF_3SO_3 (6). The reaction of 5 with $AgClO_4$ and, after removal of AgCl, with 2,2′-bipyridine (bpy) gives [Pd(κ^2-RN)(bpy)]ClO_4 (7). [Pd(κ^2-R′)(μ-Cl)]$_2$ (8) reacts with *o*-phenylenediamine to give [Pd(κ^3-R′NN)Cl] (9) [R′NN = C_6H-{CH=N$C_6H_4(NH_2)$-2}-2-$(OMe)_3$-3,4,5] which reacts with PPh_3 in the presence of K(CF_3SO_3), yielding [Pd(κ^3-R′NN)(PPh_3)]CF_3SO_3 (6′). [Hg(RMe)Cl] (10) [RMe = C_6H{C(O)Me}-6-$(OMe)_3$-2,3,4] can be obtained by direct mercuriation of 3,4,5-trimethoxyacetophenone with $Hg(MeCO_2)_2$ and subsequent treatment with KCl. [$Hg(RMe)_2$] (11), obtained by symmetrization of 10 with Me_4NCl, reacts with [$PdCl_2(MeCN)_2$] or aqueous $[PdCl_4]^{2-}$ to give the cyclometalated [Pd(κ^2-RMe)(μ-Cl)]$_2$ (12) which reacts with bpy or 2,9-dimethyl-1,10-phenanthroline (dmphen), giving the neutral complexes [Pd(RMe)Cl(N-N)] [N-N = bpy (13), dmphen (14)]. 13 and 14 react with $Ag(CF_3SO_3)$, giving the cationic cyclometalated compounds [Pd(κ^2-RMe)(N-N)]CF_3SO_3 [N-N = bpy (15), dmphen (16)]. The structures of 6·CH_2Cl_2, 6′·Et_2O, and 16·CH_2Cl_2 have been determined by X-ray crystallography at −95 °C. Crystal data for 6·CH_2Cl_2: space group $P\bar{1}$, a = 12.452(3) Å, b = 12.754(3) Å, c = 13.275(3) Å, α = 111.34(2)°, β = 104.21(2)°, γ = 95.32(2)°, V = 1846.5 Å^3, Z = 2, R_{int} = 0.033; $R(F, >4\sigma(F))$ = 0.040. Crystal data for 6′·1.5Et_2O: space group $P2_1/c$, a = 11.228(6) Å, b = 16.818(6) Å, c = 22.650(9) Å, β = 101.61(4)°, V = 4190 Å^3, Z = 4, R_{int} = 0.033, $R(F, >4\sigma(F))$ = 0.050. Crystal data for 16·CH_2Cl_2: space group $P2_1/n$, a = 12.199(4) Å, b = 7.801(3) Å, c = 30.910(11) Å, β = 95.80(3)°, V = 2927 Å^3, Z = 4, R_{int} = 0.061, $R(F, >4\sigma(F))$ = 0.050. The three complexes show distorted square planar geometries.

Introduction

We are currently interested in illustrating the synthetic utility of organomercury derivatives in the preparation of new types of functionalized aryl complexes not easily accessible through the "standard" methods (see Scheme I).[1] For example, we have recently used this method to prepare the first 2-formylaryl complexes of palladium(II) containing the aryl group R = C_6H(CHO)-6-$(OMe)_3$-2,3,4.[2] This transmetalation reaction takes place in water, but extraction of the product with dichloromethane gave a palladium(II) derivative containing the rearranged aryl

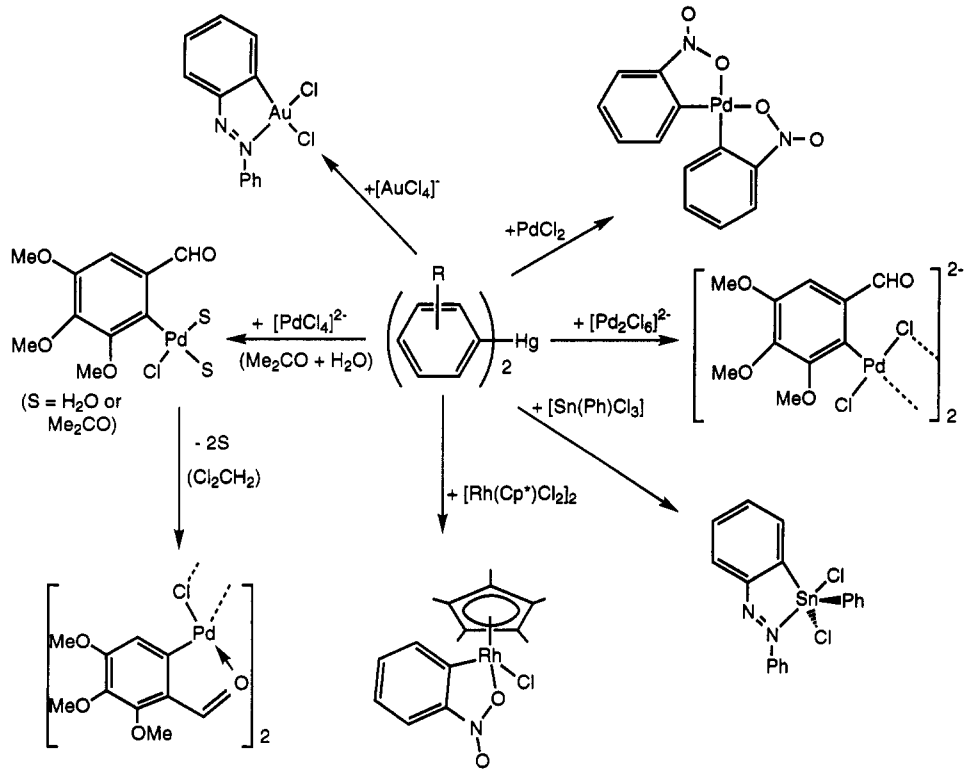
(1) See for example: Vicente, J.; Chicote, M. T.; Ramírez-de-Arellano, M. C.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1992**, 1839 and references therein.

(2) Vicente, J.; Abad, J. A.; Stiakaki, M. A.; Jones, P. G. *J. Chem. Soc., Chem. Commun.* **1991**, 137. (b) Vicente, J.; Abad, J. A.; Jones, P. G. *Organometallics* **1992**, *11*, 3512.

* Abstract published in *Advance ACS Abstracts*, September 15, 1993.

0276-7333/93/2312-4151$04.00/0

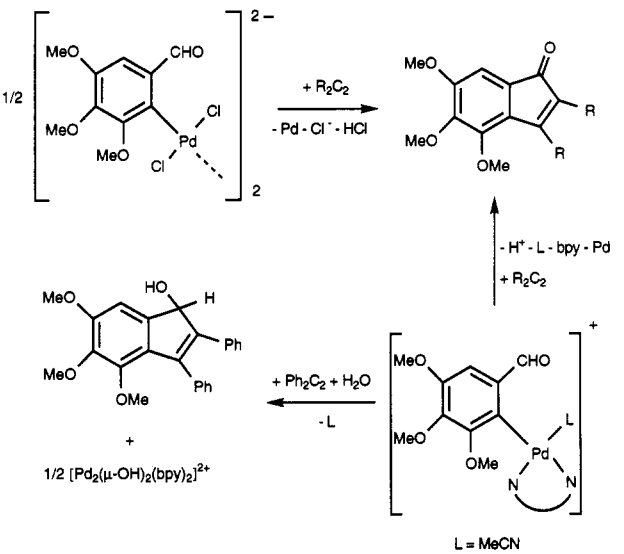
Scheme I. Some Examples of the Synthetic Utility of Organomercury Derivatives



group R′ = $C_6H(CHO)$-2,$(OMe)_3$-3,4,5 (see Scheme I). In this paper we report investigations of the scope of this rearrangement reaction, using similar palladium complexes in which the formyl substituent is replaced by others also able to coordinate to the metal atom. The presence of three methoxy substituents in the aryl ring was decided upon because these electron releasing groups could confer special properties to the formyl group, e.g. facilitating its coordination to palladium to give cyclometalated species. In addition, this aryl moiety is present in organic molecules of pharmaceutical interest, for example the antileukemic lactones steganacin and steganangin,[3] the antibacterial agent trimethoprim,[4] or the cytotoxic colchicine.[5] We plan to use these aryl complexes in organic synthesis, and we have already reported preliminary results concerning the synthesis of indenones and indenols obtained from these (formyltrimethoxyaryl)palladium(II) derivatives (see Scheme II).[6]

Ortho-manganated acetophenones have been prepared by reacting these ketones with $PhCH_2Mn(CO)_5$.[7] Some of these compounds have been used as transmetalating reagents in the synthesis of the corresponding chloromercury derivatives.[7i] The method was implemented on the assumption that, because direct mercuriation of acetophenone occurs at the Me group rather than at the aryl ring,[8] all acetophenones would behave similarly.[7h,i] In this paper we report the synthesis of [Hg{C_6H{C(O)Me}-6-$(OMe)_3$-2,3,4}Cl] by direct mercuriation of the corresponding acetophenone. These arylmanganese derivatives

Scheme II. Synthesis of Indenones and Indenols Obtained from (Formyltrimethoxyaryl)palladium(II) Derivatives



have also been used, directly[7l] or indirectly, through palladium(II) complexes,[7h] in organic synthesis. These latter reactions should occur *via* the mediation of an

(3) Ziegler, F. E.; Chliwner, I.; Fowler, K. W.; Kanfer, S. J.; Kuo, S. J.; Sinha, N. D. *J. Am. Chem. Soc.* **1980**, *102*, 790. Tomioka, K.; Ishiguro, T.; Mizuguchi, H.; Komeshima, N.; Koga, K.; Tsukogoshi, S.; Tsuruo, T.; Tashiro, T.; Tanida, S.; Kishi, T. *J. Med. Chem.* **1991**, *34*, 54 and references therein.

(4) Chan, J. H.; Roth, B. *J. Med. Chem.* **1991**, *34*, 550 and references therein.

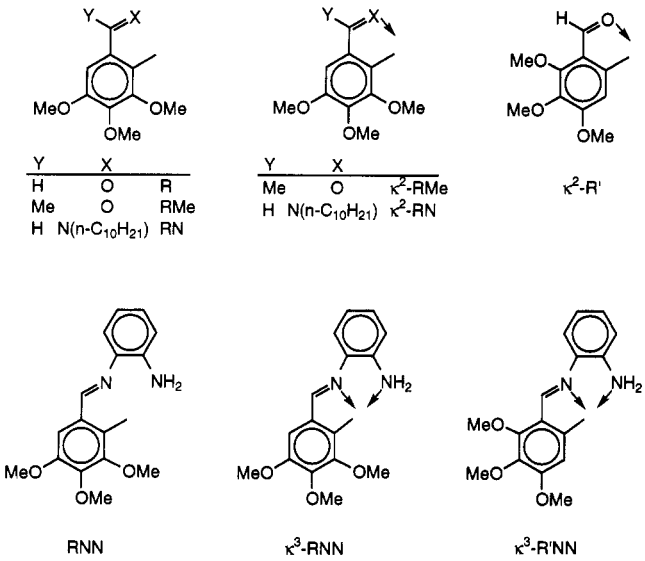
(5) Ringel, I.; Jaffe, D.; Alerhand, S.; Boye, O.; Mazafar, A.; Brossi, A. *J. Med. Chem.* **1991**, *34*, 3334.

(6) Vicente, J.; Abad, J. A.; Gil-Rubio, J. *J. Organomet. Chem.* **1992**, *436*, C9.

(7) (a) McKinney, R. J.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3065. (b) McKinney, R. J.; Firestein, G.; Kaesz, H. D. *Inorg. Chem.* **1975**, *14*, 2057. (c) Knobler, C. B.; Crawford, S. S.; Kaesz, H. D. *Inorg. Chem.* **1975**, *14*, 2062. (d) Huie, B. T.; Knobler, C. B.; Firestein, G.; McKinney, R. J.; Kaesz, H. D. *J. Am. Chem. Soc.* **1977**, *99*, 7852. (e) Huie, B. T.; Knobler, C. B.; McKinney, R. J.; Kaesz, H. D. *J. Am. Chem. Soc.* **1977**, *99*, 7862. (f) Crawford, S. S.; Kaesz, H. D. *Inorg. Chem.* **1977**, *16*, 3193. (g) McGuiggan, M. F.; Pignolet, L. H. *Inorg. Chem.* **1982**, *21*, 2523. (h) Gommans, L. H. P.; Main, L.; Nicholson, B. K. *J. Chem. Soc., Chem. Commun.* **1987**, 761. (i) Cooney, J. M.; Gommans, L. H. P.; Main, L.; Nicholson, B. K. *J. Organomet. Chem.* **1987**, *336*, 293. (j) *Ibid.* **1988**, *349*, 197. (k) Robinson, N. P.; Main, L.; Nicholson, B. K. *J. Organomet. Chem.* **1988**, *349*, 209. (l) Liebeskind, L. S.; Gasdaska, J. R.; McCallum, J. S.; Tremont, S. J. *J. Org. Chem.* **1989**, *54*, 669.

(8) O. Dimroth (1902) quoted in: Larock, R. C. *Organomercury Compounds in Organic Synthesis*; Springer-Verlag: Berlin, 1985; p 28.

Chart I



arylpalladium complex. In this work we report the synthesis of an *ortho*-palladated acetophenone, which cannot be obtained by a direct metalation reaction, using the corresponding mercurial.

Experimental Section

C, H, and N analyses, melting point determinations, and recording of the IR and NMR spectra were performed as described elsewhere.[9] The group $C_6H(CHO)$-6-$(OMe)_3$-2,3,4 has been symbolized as R, the rearranged group $C_6H(CHO)$-2-$(OMe)_3$-3,4,5 as R', the ketone $C_6H\{C(O)Me\}$-6-$(OMe)_3$-2,3,4 as RMe, and the Schiff bases $C_6H(CH{=}N(n\text{-}C_{10}H_{21})(OMe)_3$-3,4,5, $C_6H\{CH{=}NC_6H_4(NH_2)$-2$\}$-6-$(OMe)_3$-2,3,4, and $C_6H\{CH{=}NC_6H_4(NH_2)$-2$\}$-2-$(OMe)_3$-3,4,5 as RN, RNN, and R'NN (see Chart I). When some of these ligands are bonded to palladium through two or three donor atoms we use the κ notations κ^2 or κ^3, respectively, while only the abbreviation of the ligand if it is bonded through one donor atom (see Chart I). The ligands 2,2'-bipyridine and 2,9-dimethyl-1,10-phenanthroline have been symbolized as bpy and dmphen, respectively. Complexes **1**, **8**,[2] $[HgR_2]$, and [Hg(R)Cl][9,10] were prepared following previously described procedures.

[Pd(κ^2-R')(bpy)]ClO_4 (2). Complex **1** (181 mg, 0.37 mmol) and $AgClO_4$ (76 mg, 0.37 mmol) were mixed in dichloromethane (15 cm³), and the mixture was stirred for 2.5 h. The precipitated solid was filtered and extracted with 5-cm³ portions of dichloromethane, until the extract was colorless. The combined extracts were evaporated to *ca.* 5 cm³ and diethyl ether was added, precipitating **2**. Yield: 95 mg, 46%. Complex **2** has spectroscopic properties the same as those obtained previously.[2b]

[Hg(RN)$_2$] (3). $[HgR_2]$ (257 mg, 0.43 mmol) and *n*-decylamine (141 mg, 0.87 mmol) were reacted in boiling toluene for 6 h. The mixture was evaporated to dryness under vacuum and the residue extracted with *n*-hexane. The extract was filtered over anhydrous $MgSO_4$ and the solvent evaporated to give an oil which was washed with methanol and dried under vacuum to afford liquid **3**. Yield: 231 mg, 62%. IR: ν(CN) 1640 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 8.42 (s, CH=N, 1 H), 6.96 (s, C_6H, 1 H), 4.04, 4.02, and 4.01 (s, MeO, 3 H), 3.56 (m, CH_2N, 2 H), 1.5–1.0 (m, br, $(CH_2)_8$, 16 H), 0.87 (t, *Me*—$(CH_2)_9$, 3 H, $^3J_{HH}$ = 6 Hz).

[Hg(RNN)Cl] (4). [Hg(R)Cl] (1.56 g, 3.6 mmol) and *o*-phenylenediamine (0.39 g, 3.6 mmol) were mixed in toluene (40 cm³), and the mixture boiled for 5 h. The solvent was evaporated and the residue recrystallized from dichloromethane/hexane giving yellow **4**. Yield: 0.99 g, 53%. Mp: 138 °C. IR: ν(NH) 3470 and 3380, ν(Hg—Cl) 330 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 8.47 (s, CH=N, 1 H), 7.3–7.2, 7.15–7.0, 6.95–6.8, and 6.75–6.6 (m, C_6H, C_6H_4, and NH_2, 7 H), 3.95, 3.94, and 3.93 (s, MeO, 3 H). Anal. Calcd for $C_{16}H_{17}N_2ClHgO_3$: C, 36.86; H, 3.29; N, 5.37. Found: C, 36.66; H, 3.72; N, 5.43.

[Pd(κ^2-RN)(μ-Cl)]$_2$ (5). The mercurial **3** (194 mg, 0.22 mmol) and $[PdCl_2(MeCN)_2]$ (58 mg, 0.22 mmol) were reacted in dichloromethane (10 cm³) for 3 h. The mixture was filtered over anhydrous $MgSO_4$ and the solution concentrated (3 cm³). By addition of diethyl ether yellow **5** precipitated. Yield: 93 mg, 89%. Mp: 150 °C. IR: ν(CN) 1615 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 7.69 (s, CH=N, 1 H), 6.67 (s, C_6H, 1 H), 3.82 (s, MeO, 3 H), 3.80 (s, MeO, 6 H), 3.45 (m, CH_2N, 2 H), 1.79 and 1.25 (m, br, $(CH_2)_8$, 16 H), 0.87 (t, *Me*—$(CH_2)_9$, 3 H, $^3J_{HH}$ = 6 Hz). Anal. Calcd for $C_{20}H_{32}NClO_3Pd$: C, 50.35; H, 6.53; N, 2.71. Found: C, 50.43; H, 6.77; N, 2.94.

[Pd(κ^3-RNN)(PPh$_3$)]CF_3SO_3 (6). The mercurial **4** (33 mg, 0.06 mmol) and $[PdCl_2(MeCN)_2]$ (16 mg, 0.06 mmol) were reacted in dichloromethane (10 cm³) overnight. The solvent was evaporated, acetone (10 cm³), $K(CF_3SO_3)$ (12 mg, 0.06 mmol), and PPh_3 (16 mg, 0.06 mmol) were added, and the mixture was stirred for 2 h. The mixture was filtered over Celite, and the solvent was evaporated, the residue being recrystallized from dichloromethane/diethyl ether to give yellow **6**. Yield: 33 mg, 66%. Mp: 165 °C dec. Λ_M (acetone): 90 Ω^{-1} cm^2 mol^{-1}. IR: ν(NH) 3220, 3190, and 3150 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 8.64 (d, CH=N, 1 H, J_{PH} = 9 Hz), 8.0–7.6, 7.5–7.3, 7.2–7.0, 7.0–6.8, and 6.8–6.6 (m, Ph, C_6H_4, C_6H, 20 H), 4.34 (s, NH_2, 2 H), 3.90, 3.51, and 2.62 (s, MeO, 3 H). ^{31}P NMR ($CDCl_3$, δ): 34.0. Anal. Calcd for $C_{35}H_{32}N_2F_3O_6SPPd$: C, 52.35; H, 4.02; N, 3.49. Found: C, 51.82; H, 4.36; N, 3.79.

[Pd(κ^2-RN)(bpy)]ClO_4 (7). $AgClO_4$ (18 mg, 0.085 mmol) and **5** (40 mg, 0.085 mmol) were reacted in acetone (10 cm³) for 30 min. The mixture was filtered, bpy (13 mg, 0.085 mmol) was added to the solution which was concentrated, and diethyl ether was added to precipitate **7** as a yellow solid. Yield: 43 mg, 73%. Mp: 128 °C. Λ_M (acetone): 123 Ω^{-1} cm^2 mol^{-1}. IR: ν(CN) 1598, 1610 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 8.85, 8.6, 8.5, 8.2, 7.7, and 7.4 (m, br, bpy) 8.04 (s, CH=N, 1 H), 6.91 (s, C_6H, 1 H), 3.89, 3.82, and 3.60 (s, MeO, 3 H), 3.73 (t, CH_2N, 2 H, $^3J_{HH}$ = 7 Hz) 1.73, 1.35, and 1.2 (m, br, $(CH_2)_8$, 16 H), 0.77 (t, *Me*—$(CH_2)_9$, 3 H, $^3J_{HH}$ = 7 Hz). Anal. Calcd for $C_{30}H_{40}N_3ClO_7Pd$: C, 51.73; H, 5.79; N, 6.03. Found: C, 51.56; H, 5.83; N, 6.02.

[Pd(κ^3-R'NN)Cl] (9). *o*-Phenylenediamine (20 mg, 0.18 mmol) was added to a solution of **8** (61 mg, 0.09 mmol) in dichloromethane (10 cm³) and reacted for 30 min. The yellow precipitate of **9** was collected by filtration and washed with dichloromethane (2 × 3 cm³) and diethyl ether (2 × 3 cm³). Yield: 40 mg, 52%. Mp: 261 °C dec. IR: ν(NH) 3210, 3170, 3130, and 3090 cm^{-1}. Anal. Calcd for $C_{16}H_{17}N_2ClO_3Pd$: C, 44.99: H, 4.01; N, 6.56. Found: C, 45.09; H, 4.21; N, 6.85.

[Pd(κ^3-R'NN)(PPh$_3$)]CF_3SO_3 (6'). Complex **9** (37 mg, 0.09 mmol) was reacted with PPh_3 (23 mg, 0.09 mmol) and $K(CF_3SO_3)$ (16 mg, 0.09 mmol) in acetone (10 cm³) for 30 min. The solvent was exaporated and the residue recrystallized from dichloromethane/diethyl ether giving yellow **6'**. Yield: 45 mg, 64%. Mp: 207 °C dec. Λ_M (acetone): 131 Ω^{-1} cm^2 mol^{-1}. IR: ν(NH) 3210 (br) cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 8.74 (d, CH=N, 1 H, J_{PH} = 9 Hz), 7.8–7.6, 7.54, and 7.4–7.1 (m, Ph, C_6H_4, 19H), 5.68 (d, C_6H, 1 H, J_{PH} = 5 Hz), 4.75 (s, NH_2, 2 H), 4.05, 3.75, and 2.94 (s, MeO, 3 H). ^{31}P NMR ($CDCl_3$, δ): 36.7. Anal. Calcd for $C_{35}H_{32}N_2F_3O_6SPPd$: C, 52.35; H, 4.02; N, 3.49. Found: C, 52.07; H, 4.39; N, 3.63.

[Hg(RMe)Cl] (10). 3,4,5-Trimethoxyacetophenone (5.0 g, 24 mmol), $Hg(MeCO_2)_2$ (7.6 g, 24 mmol), and acetic acid (2.5 cm³) in ethanol were refluxed for 4 h. The mixture was poured into aqueous KCl. The precipitate was filtered off, washed with water and air dried to give **10**. Yield: 8.0 g, 75%. Mp: 224 °C. IR: ν(CO) 1645 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 7.38 (s, C_6H, 1 H), 3.96, 3.95, and 3.89 (s, MeO, 3H), 2.67 (s, MeCO, 3 H). Mass spectrum: *m/z* (% abundance) 446 (M^+, 42), 431 (M^+ – Cl, 25), 202 (Hg^+, 54), 179 ([M + H]$^+$ – HgCl – OMe, 62), 151 (57), 123 (60), 93 (100). Anal. Calcd for $C_{11}H_{13}ClHgO_4$: C, 29.67; H, 2.94. Found: C, 29.22; H, 3.15.

(9) Vicente, J.; Abad, J. A.; Sandoval, A. *J. Organomet. Chem.* **1992**, *434*, 1.

(10) Sharp, T. M. *J. Chem. Soc.* **1937**, 852.

Table I. Crystal Data for Compounds 6, 6′, and 16 at −95 °C

compd	**6**·CH_2Cl_2	**6′**·1.5$C_4H_{10}O$	**16**·CH_2Cl_2
formula	$C_{36}H_{34}Cl_2F_3N_2O_6PPdS$	$C_{41}H_{47}F_3N_2O_{7.5}PPdS$	$C_{27}H_{27}Cl_2F_3N_2O_7PdS$
M_r	888.0	914.2	757.9
cryst habit	yellow tablet	yellow prism	yellow plate
cryst size (mm)	0.3 × 0.25 × 0.1	0.6 × 0.2 × 0.15	0.9 × 0.1 × 0.03
space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$
cell constants			
a (Å)	12.452(3)	11.228(6)	12.199(4)
b (Å)	12.754(3)	16.818(6)	7.801(3)
c (Å)	13.275(3)	22.650(9)	30.910(11)
α (deg)	111.34(2)		
β (deg)	104.21(2)	101.61(4)	95.80(3)
γ (deg)	95.32(2)		
V (Å^3)	1864.5	4190	2927
Z	2	4	4
D_x (Mg m^{-3})	1.582	1.449	1.720
F(000)	900	1884	1528
μ (mm^{-1})	0.80	0.60	0.96
transmissions (min/max)	0.85–0.97	0.89–0.93	no abs corr
$2\theta_{max}$ (deg)	50	50	50
no. of reflns			
measd	8081	13156	7127
ind	6583	7368	5192
R_{int}	0.033	0.033	0.061
R_w (F^2, all reflns)	0.109	0.151	0.148
R (F, $>4\sigma(F)$)	0.040	0.050	0.050
no. of params	472	475	394
S	1.05	1.02	1.04
max Δ/σ	<0.001	0.002	0.007
max $\Delta\rho$ (e Å^{-3})	1.6	0.97	1.46

[Hg(RMe)$_2$] (11). **10** (0.96 g, 2.2 mmol) and Me_4NCl (0.33 g, 3 mmol) were refluxed in acetone for 8 h. The solvent was evaporated, the residue was extracted with dichloromethane, and the suspension was filtered over anhydrous $MgSO_4$. The solution was concentrated (4 cm^3) and diethyl ether added to precipitate **11**. Yield: 0.39 g, 60%. Mp: 178–179 °C. IR: ν(CO) 1654 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 7.42 (s, C_6H, 1 H), 3.98, 3.95, and 3.92 (s, MeO, 3 H), 2.64 (s, MeCO, 3 H). Mass spectrum: m/z (% abundance) 620 (M^+, 5), 209 (R^+, 49), 195 (R^+ − Me, 66), 179 (100), 166 (23), 151 (59), 123 (59), 119 (50), 93 (67). Anal. Calcd for $C_{22}H_{26}HgO_8$: C, 42.69; H, 4.23. Found: C, 42.71; H, 4.26.

[Pd(κ^2-RMe)(μ-Cl)]$_2$ (12). Method A. **11** (960 mg, 1.57 mmol) and [$PdCl_2(MeCN)_2$] (406 mg, 1.57 mmol) in dichloromethane (25 cm^3) were reacted for 6 h. The yellow precipitated solid was filtered, washed with dichloromethane (4 × 15 cm^3) and dried in an oven at 60 °C. Yield: 456 mg, 83%.

Method B. $PdCl_2$ (430 mg, 2.42 mmol) and KCl (361 mg, 4.84 mmol) were dissolved in water (10 cm^3). **11** (1500 mg, 2.42 mmol) and acetone (30 cm^3) were added, and the mixture was stirred for 1 h. The yellow solid was filtered, washed with acetone/water 3/1 (3 × 15 cm^3) and acetone (3 × 15 cm^3), and dried as indicated above. Yield: 598 mg, 70%. Mp: 192 °C dec. IR: ν(CO) 1515 cm^{-1}. Anal. Calcd for $C_{11}H_{13}ClO_4Pd$: C, 37.63; H, 3.73. Found: C, 37.59; H, 3.75.

[Pd(RMe)Cl(bpy)] (13). 2,2′-Bipyridine (71 mg, 0.46 mmol) was added to complex **12** (160 mg, 0.23 mmol) in dichloromethane (15 cm^3). After 35 min of stirring, the resulting solution was passed through Celite and evaporated to *ca.* 4 cm^3. The yellow compound **13** precipitated by addition of diethyl ether. Yield: 215 mg, 92%. Mp: 183 °C. IR: ν(CO) 1664 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 9.28 (d, bpy, 1 H, J = 5 Hz) 8.2–7.9 (m, bpy, 4 H), 7.75 (d, bpy, 1 H, J = 5 Hz) 7.56 (t, bpy, 1 H, J = 6 Hz), 7.3–7.2 (m, bpy, 1 H), 7.19 (s, C_6H, 1 H), 4.07, 3.98, and 3.90 (s, MeO, 3 H), 3.02 (s, MeCO, 3 H). Anal. Calcd for $C_{21}H_{21}N_2ClO_4Pd$: C, 49.73; H, 4.17; N, 5.52. Found: C, 49.50; H, 4.27; N, 5.68.

[Pd(RMe)Cl(dmphen)] (14). 2,9-Dimethyl-1,10-phenanthroline (71 mg, 0.34 mmol) was added to a suspension of **12** (120 mg, 0.17 mmol). After 40 min of stirring, **14** was obtained as a yellow solid after filtration; by concentration of the mother liquor and addition of diethyl ether more **14** was obtained. Total yield: 166 mg, 87%. Mp: 216 °C. IR: ν(CO) 1652 cm^{-1}. Anal. Calcd for $C_{25}H_{25}N_2ClO_4Pd$: C, 53.70; H, 4.47; N, 5.01. Found: C, 53.76; H, 5.01; N, 5.02.

[Pd(κ^2-RMe)(N-N)]CF_3SO_3 [N-N = bpy (15), dmphen (16)]. Compound **13** (200 mg, 0.39 mmol) or **14** (112 mg, 0.20 mmol) was mixed with equimolar amounts of Ag(CF_3SO_3)·0.5PhMe in dichloromethane (20 cm^3) and reacted for 3 h. The corresponding mixtures were filtered and the solids extracted with dichloromethane until the extracts were colorless. The combined extracts were evaporated until *ca.* 5 cm^3, and the deep yellow complexes **15** and **16** precipitated by addition of diethyl ether. **15**: yield 212 mg, 86%; mp 164 °C dec; Λ_M (acetone) 129 Ω^{-1} cm^2 mol^{-1}; IR ν(CO) 1509 cm^{-1}. Anal. Calcd for $C_{22}H_{21}N_2F_3O_7SPd$: C, 42.56; H, 3.41; N, 4.51. Found: C, 41.64; H, 3.30; N, 4.56. **16**: yield 124 mg, 92%; mp 142 °C dec; Λ_M (acetone) 134 Ω^{-1} cm^2 mol^{-1}; IR ν(CO) 1506 cm^{-1}. ^{1}H NMR ($CDCl_3$, δ, −80 °C, see Discussion): 8.59 [d, H(4,7) dmphen, 2 H, $^3J_{HH}$ = 8 Hz) 8.03 [s, H(5,6) dmphen, 2 H], 7.81 [d, H(3,8) dmphen, 1 H], 7.78 [d, H(3,8) dmphen, 1 H], 7.01 (s, C_6H, 1 H), 3.96 (s, MeO, 3 H), 3.93 (s, MeO, 3 H), 3.12 (s, Me dmphen, 3 H), 3.01 (s, Me dmphen + MeO, 6 H), 2.82 (s, MeCO, 3 H). Anal. Calcd for $C_{26}H_{25}N_2F_3O_7SPd$: C, 46.41; H, 3.74; H, 4.76; S, 4.76. Found: C, 46.10; H, 4.08; N, 4.23; S, 5.10.

Crystal Structure Determination of Complexes 6, 6′, and 16. Table I gives crystallographic data for the three complexes. For data collection and reduction crystals were mounted on glass fibers in inert oil and transferred to the cold gas stream of the diffractometer (Siemens R3 with LT-2 low temperature attachment. Orientation matrices were refined from setting angles of *ca.* 50 reflections in the 2θ range 20–23° with monochromated Mo Kα radiation). Absorption corrections for **6** and **6′** were based on ψ scans; an attempted absorption correction for **16** led to no improvement of R_{int}. For structure solution and refinement the structures were solved by the heavy-atom method and refined anisotropically on F^2 (program system: SHELXL-92, G. M. Sheldrick, unpublished). H atoms were included by using a riding model. Weighting schemes of the form $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$ were employed, with $P = (F_o^2 + 2F_c^2)/3$. Special features of refinement for compound **6′** are as follows. **6′** crystallizes with two poorly resolved molecules of diethyl ether, one of which is disordered over an inversion center. These atoms were refined isotropically; the solvent H atoms were not identified. The atoms C8a and C8b represent alternative sites of a disordered methoxy group. Tables II–VII give final atomic coordinates and selected bond lengths and angles for complexes **6**, **6′**, and **16**. Figures 1–3 show the structures of the cations of **6**, **6′**, and **16**, respectively.

Table II. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for 6

	x	y	z	U(eq)[a]
Pd	5780.9(3)	2413.8(3)	4581.7(3)	23.1(1)
P	7154.9(9)	3772.2(9)	4665.7(9)	24.0(2)
C(1)	4818(3)	1883(3)	2959(3)	24.0(8)
C(2)	5042(3)	1919(3)	1996(3)	23.6(8)
C(3)	4188(3)	1506(3)	956(3)	25.6(9)
C(4)	3106(3)	962(4)	836(3)	26.9(9)
C(5)	2874(3)	833(3)	1751(3)	26.3(9)
C(6)	3722(3)	1300(3)	2797(3)	25.4(9)
C(7)	3571(3)	1064(3)	3748(3)	25.5(9)
C(8)	6669(4)	1527(4)	1452(4)	31.1(10)
C(9)	4056(5)	2609(4)	-117(4)	45.9(12)
C(10)	1220(4)	103(5)	-354(4)	44.7(12)
O(1)	6112(2)	2384(2)	2052(2)	26.0(6)
O(2)	4423(2)	1633(2)	43(2)	30.1(7)
O(3)	2348(2)	591(3)	-225(2)	35.2(7)
C(11)	4548(3)	1232(3)	5628(3)	23.2(8)
C(12)	5575(4)	1786(3)	6486(3)	26.5(9)
C(13)	5786(4)	1651(4)	7500(4)	31.4(10)
C(14)	4960(4)	973(4)	7664(4)	35.7(11)
C(15)	3939(4)	441(4)	6824(4)	33.5(10)
C(16)	3724(4)	558(3)	5800(4)	29.8(9)
N(1)	4445(3)	1399(3)	4619(3)	22.5(7)
N(2)	6403(3)	2527(3)	6290(3)	28.1(8)
C(21)	7801(3)	4663(3)	6182(3)	26.5(9)
C(22)	7351(4)	5595(4)	6713(4)	36.7(11)
C(23)	7744(5)	6197(4)	7886(4)	48.1(13)
C(24)	8573(5)	5866(5)	8535(4)	50.9(14)
C(25)	9022(4)	4932(4)	8021(4)	44.9(12)
C(26)	8642(4)	4341(4)	6853(4)	34.7(10)
C(31)	6796(3)	4838(3)	4097(4)	27.1(9)
C(32)	5731(4)	4708(4)	3381(4)	31.9(10)
C(33)	5496(4)	5497(4)	2901(4)	39.5(11)
C(34)	6319(5)	6425(4)	3147(4)	41.6(12)
C(35)	7368(4)	6590(4)	3898(4)	40.1(11)
C(36)	7611(4)	5812(4)	4375(4)	33.6(10)
C(41)	8292(3)	3196(3)	4146(3)	24.9(9)
C(42)	8877(4)	3645(4)	3580(4)	32.8(10)
C(43)	9700(4)	3136(4)	3179(4)	36.6(11)
C(44)	9966(4)	2167(4)	3342(4)	38.2(11)
C(45)	9398(4)	1712(4)	3906(4)	38.9(11)
C(46)	8563(4)	2221(4)	4310(4)	32.0(10)
S	813.4(10)	8601.7(11)	2529.0(11)	40.0(3)
O(4)	1605(3)	8462(4)	3419(4)	63.9(12)
O(5)	725(5)	7777(5)	1422(4)	107(2)
O(6)	841(3)	9741(3)	2618(4)	60.6(11)
C(50)	-538(4)	8171(5)	2680(6)	54.5(15)
F(1)	-1378(3)	8327(5)	2004(5)	122(2)
F(2)	-596(4)	8825(4)	3720(4)	94.1(14)
F(3)	-709(3)	7106(3)	2615(4)	88.4(13)
C(100)	7331(6)	4244(6)	1029(6)	75(2)
Cl(1)	6452(2)	4824(2)	144(2)	90.6(6)
Cl(2)	8129.7(13)	3424.4(15)	319.4(14)	69.3(4)

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

Table III. Selected Bond Lengths (Å) and Angles (deg) for 6

Pd–C(1)	2.014(4)	Pd–N(1)	2.032(3)
Pd–N(2)	2.154(3)	Pd–P	2.2710(12)
P–C(31)	1.820(4)	P–C(41)	1.823(4)
P–C(21)	1.833(4)	C(1)–C(2)	1.388(6)
C(1)–C(6)	1.419(6)	C(2)–O(1)	1.381(5)
C(2)–C(3)	1.401(6)	C(3)–O(2)	1.374(5)
C(3)–C(4)	1.401(6)	C(4)–O(3)	1.370(5)
C(4)–C(5)	1.377(6)	C(5)–C(6)	1.400(6)
C(6)–C(7)	1.449(6)	C(7)–N(1)	1.281(5)
C(8)–O(1)	1.445(5)	C(9)–O(2)	1.433(5)
C(10)–O(3)	1.426(5)	C(11)–N(1)	1.409(5)
C(12)–N(2)	1.467(5)		
C(1)–Pd–N(1)	80.90(14)	C(1)–Pd–N(2)	160.81(14)
N(1)–Pd–N(2)	80.35(13)	C(1)–Pd–P	100.59(12)
N(1)–Pd–P	171.37(10)	N(2)–Pd–P	98.56(10)
C(31)–P–C(41)	107.4(2)	C(31)–P–C(21)	102.2(2)
C(41)–P–C(21)	105.9(2)	C(31)–P–Pd	120.74(14)
C(41)–P–Pd	113.89(13)	C(21)–P–Pd	105.01(13)
C(2)–C(1)–C(6)	116.3(4)	C(2)–C(1)–Pd	132.9(3)
C(6)–C(1)–Pd	110.7(3)	O(1)–C(2)–C(1)	120.4(3)
O(1)–C(2)–C(3)	118.6(3)	C(1)–C(2)–C(3)	121.0(4)
O(2)–C(3)–C(4)	119.9(4)	O(2)–C(3)–C(2)	119.2(4)
C(4)–C(3)–C(2)	120.9(4)	O(3)–C(4)–C(5)	125.0(4)
O(3)–C(4)–C(3)	115.2(4)	C(5)–C(4)–C(3)	119.8(4)
C(4)–C(5)–C(6)	118.5(4)	C(5)–C(6)–C(1)	123.3(4)
C(5)–C(6)–C(7)	120.5(4)	C(1)–C(6)–C(7)	115.6(4)
N(1)–C(7)–C(6)	115.9(4)	C(2)–O(1)–C(8)	112.5(3)
C(3)–O(2)–C(9)	112.0(3)	C(4)–O(3)–C(10)	116.5(3)
C(7)–N(1)–C(11)	127.6(3)	C(7)–N(1)–Pd	115.3(3)
C(11)–N(1)–Pd	116.8(3)	C(12)–N(2)–Pd	109.0(2)

Discussion

Synthesis and Rearrangement of the Arylpalladium(II) Complexes. The reaction of [**Pd**(R)Cl(bpy)] (**1**) (see Chart I) with $AgClO_4$ in dichloromethane gives rise to the complex $[Pd(\kappa^2\text{-}R')(bpy)]ClO_4$ (**2**). This is a new example of a process involving the coordination of the formyl group and a rearrangement of aryl substituents, with C–C and C–Pd bond breaking/re-forming (see Scheme III). When this reaction was carried out in a 1:10 (v:v) acetonitrile/dichloromethane mixture as solvent, the compound $[Pd(R)(MeCN)(bpy)]ClO_4$ was instead obtained.[2b] These two reactions confirm our previous proposal that formation of the chelate ring, facilitated in the first case by the labile character of the perchlorato ligand, is the driving force for the observed rearrangement in order to avoid the repulsion between the 2-MeO group and the ligand *trans* to the coordinated oxygen atom (see A in Scheme IV).[2] In the second reaction, the rearrangement does not occur, probably because the presence of acetonitrile prevents the intramolecular coordination of the aryl ligand. In the other two cases in which the rearrangement has been observed (extraction of $[Pd(R)Cl(S)_2]$, where S = H_2O or acetone, with dichloromethane or reaction between $[HgR_2]$ and $[PdCl_2(PhCN)_2]$) labile ligands were also involved (see Scheme I).[2] In addition, no complex containing the R group as a chelating ligand has been obtained.

The yield of the reaction leading to **2** is relatively low (46%) compared to our previous yield of 73% starting from [Pd(R')Cl(bpy)] and $Ag(ClO_4)$ (see Scheme III).[2] We have investigated the precipitate formed in the first reaction and found that, in addition to the expected AgCl, the complex $[Pd(\mu\text{-}OH)(bpy)]_2(ClO_4)_2$[6] was present (by IR) (see Scheme III). Moreover, the arene RH was isolated from the mother liquor. We suggest that, from the possible intermediate $[Pd(\kappa^2\text{-}R)(bpy)]^+$, a hydrolytic side reaction competes with the rearrangement process (see Schemes III and IV).

Once the intramolecular coordination is known to be crucial in the rearrangement process, we have tried to investigate how it could be influenced by substitutions at the formyl group. Several attempts to condense aromatic or aliphatic amines [e.g. *o*-phenylenediamine, $H_2NC_6H(OMe)_3$-3,4,5, Bu^tNH_2, or $n\text{-}C_{10}H_{21}NH_2$] onto $(PhCH_2PPh_3)_2[Pd(R)Cl(\mu\text{-}Cl)]_2$ (see Scheme I)[2] were unsuccessful. The Schiff base $C_6H(CH{=}N(n\text{-}C_{10}H_{21})(OMe)_3$-3,4,5 gives a mixture (by NMR) when reacted with $PdCl_2$/ClLi. The mercurial route was, however, successful. Thus, $[HgR_2]$ reacts with *n*-decylamine to give $[Hg(RN)_2]$ (**3**), and [Hg(R)Cl], with *o*-phenylenediamine to give [Hg(RNN)Cl] (**4**) (see Chart I). Complex **3** reacts with $[PdCl_2(MeCN)_2]$ to give $[Pd(\kappa^2\text{-}RN)(\mu\text{-}Cl)]_2$ (**5**), which reacts with $AgClO_4$ and, after removal of AgCl, with 2,2′-bipyridine to give $[Pd(\kappa^2\text{-}RN)(bpy)]ClO_4$ (**7**) (see Scheme V). However, **4** reacts with $[PdCl_2(MeCN)_2]$ giving an ill-defined material of stoichiometry [PdHg(RNN)Cl_3] (by elemental analyses), which it has not been possible to characterize; however

Table IV. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for 6′

	x	y	z	U(eq)[a]
Pd	3208.1(3)	5377.9(2)	1465.6(2)	33.5(1)
P	2402.2(11)	6219.5(7)	2058.6(5)	33.5(3)
C(1)	1897(4)	4535(3)	1399(2)	37.4(11)
C(2)	2175(5)	3891(3)	1042(2)	38.1(11)
C(3)	1414(5)	3213(3)	933(2)	45.2(13)
C(4)	389(5)	3166(3)	1182(2)	46.6(13)
C(5)	118(5)	3797(3)	1531(2)	43.0(12)
C(6)	842(5)	4479(3)	1625(2)	40.3(12)
C(7)	3276(5)	3944(3)	816(2)	40.2(12)
C(8a)	2262(10)	1962(7)	794(5)	63(2)
C(8b)	1247(14)	1858(9)	509(7)	63(2)
C(9)	−1478(6)	2568(4)	710(4)	79(2)
C(10)	−1263(6)	4317(4)	2109(3)	66(2)
O(1)	1749(4)	2641(2)	570(2)	69.3(12)
O(2)	−309(3)	2483(2)	1119(2)	60.1(11)
O(3)	−896(3)	3685(2)	1770(2)	57.9(10)
C(11)	5049(5)	4765(3)	832(2)	37.9(11)
C(12)	5523(4)	5504(3)	1036(2)	38.2(11)
C(13)	6643(5)	5750(3)	923(2)	46.7(13)
C(14)	7283(5)	5245(4)	618(3)	51.9(14)
C(15)	6820(5)	4511(3)	418(2)	49.6(14)
C(16)	5718(5)	4264(3)	526(2)	45.9(13)
N(1)	3919(4)	4578(2)	966(2)	34.2(9)
N(2)	4795(4)	6019(2)	1350(2)	38.9(10)
C(21)	2046(4)	5727(3)	2717(2)	36.4(11)
C(22)	1175(5)	6014(3)	3019(2)	50.2(14)
C(23)	990(6)	5632(4)	3543(3)	63(2)
C(24)	1654(6)	4968(4)	3753(3)	62(2)
C(25)	2515(6)	4667(3)	3451(2)	54.0(15)
C(26)	2699(5)	5045(3)	2932(2)	41.6(12)
C(31)	3390(4)	7036(3)	2369(2)	35.0(11)
C(32)	3760(5)	7170(3)	2983(2)	46.2(13)
C(33)	4482(6)	7825(4)	3189(3)	59(2)
C(34)	4838(6)	8344(4)	2787(3)	65(2)
C(35)	4484(6)	8216(3)	2175(3)	55.0(15)
C(36)	3762(5)	7565(3)	1965(2)	42.7(12)
C(41)	1055(5)	6745(3)	1675(2)	45.2(13)
C(42)	675(6)	7444(4)	1911(3)	64(2)
C(43)	−335(7)	7845(5)	1587(5)	91(3)
C(44)	−962(7)	7576(6)	1053(5)	101(3)
C(45)	−591(7)	6899(5)	818(4)	87(3)
C(46)	425(5)	6481(4)	1116(3)	57(2)
S	5188.9(13)	7780.5(8)	379.9(6)	45.4(3)
O(4)	6006(5)	7939(4)	920(3)	111(2)
O(5)	4104(4)	7379(2)	456(2)	56.1(10)
O(6)	5769(7)	7468(3)	−70(3)	137(3)
C(50)	4720(6)	8744(4)	99(4)	74(2)
F(1)	3919(6)	8752(4)	−371(3)	198(4)
F(2)	4267(6)	9148(3)	523(4)	151(3)
F(3)	5645(4)	9180(2)	5(2)	91.1(13)
O(7)	6649(7)	6170(5)	2519(3)	137(2)
C(51)	7572(11)	7444(8)	2458(5)	141(4)
C(52)	7743(13)	6678(9)	2529(6)	161(5)
C(53)	6282(13)	5404(8)	2850(7)	159(5)
C(54)	5939(18)	5436(11)	3360(10)	224(8)
O(8)	0	10000	0	111(3)
C(55)	1263(13)	9789(9)	465(7)	74(3)
C(56)	1414(11)	9069(8)	670(6)	146(4)
C(55′)	234(13)	9361(9)	147(6)	74(3)

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

this compound reacts with PPh_3 and $K(CF_3SO_3)$ giving $[Pd(\kappa^3\text{-RNN})(PPh_3)]CF_3SO_3$ (**6**), which can be also obtained in a one-pot synthesis. In complexes **5–7** the aryl group remains unchanged after coordination of palladium as shown by the reaction with aqueous HCl giving RH. Heating dichloromethane or acetone solutions of **6** at 90 °C (in a closed Schlenk tube) results in some decomposition, and unchanged complex **6** is recovered. To compare **6** with its isomer **6′**, containing the (κ^3-R′NN) group, we have reacted $[Pd(\kappa^2\text{-R}')(\mu\text{-Cl})]_2$ with *o*-phenylenediamine to give $[Pd(\kappa^3\text{-R}'NN)Cl]$ (**9**) and then with PPh_3 in the presence of $K(CF_3SO_3)$ to give **6′** (see Scheme V).

Table V. Selected Bond Lengths (Å) and Angles (deg) for 6′

Pd–N(1)	2.023(4)	Pd–C(1)	2.027(5)
Pd–N(2)	2.144(4)	Pd–P	2.2617(14)
P–C(41)	1.816(5)	P–C(31)	1.816(5)
P–C(21)	1.819(5)	C(1)–C(6)	1.385(7)
C(1)–C(2)	1.424(7)	C(2)–C(3)	1.415(7)
C(2)–C(7)	1.433(7)	C(3)–O(1)	1.368(6)
C(3)–C(4)	1.382(8)	C(4)–O(2)	1.381(6)
C(4)–C(5)	1.393(7)	C(5)–O(3)	1.369(6)
C(5)–C(6)	1.397(7)	C(7)–N(1)	1.294(6)
C(9)–O(2)	1.453(7)	C(10)–O(3)	1.420(7)
C(11)–N(1)	1.397(6)	C(12)–N(2)	1.470(6)
N(1)–Pd–C(1)	81.7(2)	N(1)–Pd–N(2)	80.5(2)
C(1)–Pd–N(2)	162.1(2)	N(1)–Pd–P	176.96(11)
C(1)–Pd–P	96.3(2)	N(2)–Pd–P	101.50(11)
C(41)–P–C(31)	101.7(2)	C(41)–P–C(21)	108.3(2)
C(31)–P)–C(21)	104.2(2)	C(41)–P–Pd	114.5(2)
C(31)–P–Pd	114.7(2)	C(21)–P–Pd	112.5(2)
C(6)–C(1)–C(2)	117.4(4)	C(6)–C(1)–Pd	133.0(4)
C(2)–C(1)–Pd	109.6(4)	C(3)–C(2)–C(1)	121.2(5)
C(3)–C(2)–C(7)	121.5(5)	C(1)–C(2)–C(7)	117.3(4)
O(1)–C(3)–C(4)	123.8(5)	O(1)–C(3)–C(2)	116.2(5)
C(4)–C(3)–C(2)	119.9(5)	O(2)–C(4)–C(3)	120.5(5)
O(2)–C(4)–C(5)	120.5(5)	C(3)–C(4)–C(5)	118.8(5)
O(3)–C(5)–C(4)	114.4(5)	O(3)–C(5)–C(6)	123.9(5)
C(4)–C(5)–C(6)	121.7(5)	C(1)–C(6)–C(5)	120.9(5)
N(1)–C(7)–C(2)	115.7(4)	C(8a)–O(1)–C(3)	121.6(6)
C(3)–O(1)–C(8b)	123.9(7)	C(4)–O(2)–C(9)	113.9(4)
C(5)–O(3)–C(10)	117.7(4)	C(7)–N(1)–C(11)	127.7(4)
C(7)–N(1)–Pd	115.6(3)	C(11)–N(1)–Pd	116.7(3)
C(12)–N(2)–Pd	108.6(3)		

Direct mercuriation of acetophenone has been reported to occur at the Me group rather than at the aryl ring.[8] On the basis of the assumption that this behavior could be extended to other aryl-substituted acetophenones, an indirect method has been proposed that consists of the following sequence of reactions: $[Mn_2(CO)_{10}] \rightarrow [Mn(CO)_5]^- \rightarrow PhCH_2Mn(CO)_5 \rightarrow$ *ortho*-manganated acetophenone → 2-(chloromercurio)acetophenone.[7h,i] The reaction of $[Hg(MeCO_2)_2]$ with 3,4,5-trimethoxyacetophenone and KCl gives the first 2-(chloromercurio)acetophenone obtained by mercuriation, [Hg(RMe)Cl] (**10**) (see Chart I). This compound is easily symmetrized to give $[Hg(RMe)_2]$ (**11**) (see Scheme VI).

The reaction of **11** with $[PdCl_2(MeCN)_2]$ (1:1) or $K_2[PdCl_4]$ (1:1 in acetone/water) affords the cyclometalated $[Pd(\kappa^2\text{-RMe})(\mu\text{-Cl})]_2$ (**12**) (see Scheme VI). This compound cannot be prepared by direct metalation. Treatment of **12** with aqueous HCl gives the arene 3,4,5-trimethoxyacetophenone, which indicates that isomerization has not taken place. Compound **12** reacts with 2,2′-bipyridine or 2,9-dimethyl-1,10-phenanthroline to give the corresponding complexes [Pd(RMe)Cl(N-N)] [N-N = bpy (**13**), dmphen (**14**)]. Both of them react with $Ag(CF_3SO_3)$ giving the cyclometalated complexes $[Pd(\kappa^2\text{-RMe})(N\text{-}N)]CF_3SO_3$ [N-N = bpy (**15**), dmphen (**16**)]. When these complexes are reacted with aqueous HCl, 3,4,5-trimethoxyacetophenone is again obtained, indicating no isomerization. No isomerization is observed even when **12**, **15**, or **16** is heated in various solvents at temperatures in the range 40–130 °C.

The above results seem to indicate that, as previously suggested,[2b] electronic effects, in addition to steric effects, could also be responsible for the rearrangement process, since the 2-MeO group in complexes **5–7**, **12**, **15**, and **16** suffers considerable steric hindrance from the *cis* ligand, particularly in the case of **16** where the effects are enhanced by the methyl substituents of the 2,9-dimethyl-1,10-phenanthroline ligand. We have suggested a pathway for this process that involves the cleavage of the C–Pd bond and an electronic rearrangement induced by the *p*-methoxy

Table VI. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for 16

	x	y	z	U(eq)[a]
Pd	3453.0(4)	1619.9(7)	5753.2(2)	25.4(2)
N(1)	4225(4)	1873(7)	5160(2)	26.4(12)
C(2)	3816(5)	1889(9)	4745(2)	31(2)
C(2a)	2700(6)	1146(10)	4624(2)	37(2)
C(3)	4420(5)	2657(9)	4425(2)	32(2)
C(4)	5424(2)	3328(10)	4535(2)	37(2)
C(4a)	5896(5)	3306(9)	4972(2)	27.8(14)
C(5)	6963(5)	3968(9)	5119(2)	33(2)
C(6)	7381(5)	3801(9)	5540(2)	32(2)
C(6a)	6780(5)	2922(8)	5846(2)	27.0(14)
C(7)	7223(5)	2483(9)	6272(2)	31.8(15)
C(8)	6629(5)	1439(10)	6519(2)	35(2)
C(9)	5541(5)	970(9)	6374(2)	28.3(14)
C(9a)	4937(5)	-277(9)	6632(2)	31.4(15)
N(10)	5065(4)	1540(7)	5994.7(15)	22.3(10)
C(10a)	5707(5)	2373(8)	5718(2)	24.0(13)
C(10b)	5253(5)	2540(8)	5273(2)	24.1(13)
C(11)	2730(5)	2086(8)	6295(2)	28.4(15)
C(12)	3151(5)	2796(9)	6690(2)	28.1(14)
C(13)	2466(5)	3053(9)	7029(2)	29.5(15)
C(14)	1343(5)	2610(10)	6967(2)	32(2)
C(15)	901(5)	1967(9)	6573(2)	32(2)
C(16)	1590(5)	1759(9)	6235(2)	28.6(14)
O(1)	1838(3)	1439(6)	5506.7(13)	32.4(11)
C(17)	1169(5)	1368(9)	5796(2)	29.4(15)
C(18)	-1(5)	972(10)	5650(2)	37(2)
O(2)	4252(3)	3188(6)	6776.4(14)	31.6(10)
C(19)	4528(6)	4940(10)	6720(3)	46(2)
O(3)	2941(4)	3846(6)	7394.8(14)	36.5(12)
C(20)	2866(6)	3059(10)	7807(2)	43(2)
O(4)	748(4)	2909(6)	7311.5(14)	35.1(11)
C(21)	-373(6)	2343(11)	7265(2)	43(2)
S	1626.4(14)	2814(3)	3423.3(6)	36.9(4)
O(5)	1120(5)	4386(7)	3547(2)	51.3(14)
O(6)	2802(4)	2770(9)	3509(2)	63(2)
O(7)	1050(5)	1292(7)	3532(2)	54.2(15)
C(1)	1429(7)	2861(11)	2835(2)	47(2)
F(1)	1819(5)	1474(8)	2662(2)	83(2)
F(2)	378(5)	2992(9)	2691(2)	90(2)
F(3)	1935(5)	4191(7)	2677(2)	76(2)
C(10)	981(7)	6328(13)	6045(3)	59(2)
Cl(1)	2220(2)	7406(3)	6023.0(7)	58.1(6)
Cl(2)	354(2)	5849(4)	5512.9(8)	71.0(7)

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

group, both giving rise to the cleavage of the aryl–carbon bond.[2] Scheme IV tries to adapt that pathway to the new results. The previous proposal assumed the route 1 → A → C → **2**, with a slight difference with respect to the first step 1 → A, in which now we do not assume three-coordination for palladium because it is clear that tetra-coordination is possible. The main difference is that we now assume an additional species (B) between A and C. The step A → B involves the cleavage of both C–Pd and Pd–O bonds and coordination of the aryl ligand to palladium as a C–C–O π-allylic system. The driving force for this change of bonding should be the above-mentioned steric hindrance. The intermediate (B) could be the species responsible for the hydrolytic process leading to $[Pd(\mu\text{-}OH)(bpy)]_2(ClO_4)_2$ (see Scheme IV).

We suggest that the rearrangement does not occur in the case of the RMe ligand because the Me group should decrease the electron-releasing character of the *p*-MeO group and increase the strength of the Pd–O bond. The same effects are expected for those complexes containing the κ^3-RNN and RN groups, although in these two cases the cleavage of the N–Pd bond must be even more difficult. Moreover, it could be considered that the high stability of these complexes, with strong O→Pd or N→Pd bonds, would prevent isomerization.

Table VII. Selected Bond Lengths (Å) and Angles (deg) for 16

Pd–C(11)	2.002(6)	Pd–N(10)	2.032(5)
Pd–O(1)	2.044(4)	Pd–N(1)	2.153(5)
N(1)–C(2)	1.330(8)	N(1)–C(10b)	1.370(8)
C(2)–C(3)	1.423(9)	C(2)–C(2a)	1.491(9)
C(3)–C(4)	1.344(10)	C(4)–C(4a)	1.413(9)
C(4a)–C(10b)	1.411(9)	C(4a)–C(5)	1.430(9)
C(5)–C(6)	1.357(9)	C(6)–C(6a)	1.428(9)
C(6a)–C(10a)	1.396(8)	C(6a)–C(7)	1.413(9)
C(7)–C(8)	1.372(10)	C(8)–C(9)	1.405(9)
C(9)–N(10)	1.331(8)	C(9)–C(9a)	1.499(9)
N(10)–C(10a)	1.379(8)	C(10a)–C(10b)	1.436(8)
C(11)–C(12)	1.391(9)	C(11)–C(16)	1.408(8)
C(12)–O(2)	1.377(7)	C(12)–C(13)	1.420(9)
C(13)–O(3)	1.365(8)	C(13)–C(14)	1.407(9)
C(14)–O(4)	1.368(7)	C(14)–C(15)	1.377(9)
C(15)–C(16)	1.415(9)	C(16)–C(17)	1.432(8)
O(1)–C(17)	1.272(7)	C(17)–C(18)	1.486(9)
O(2)–C(19)	1.422(9)	O(3)–C(20)	1.427(8)
O(4)–C(21)	1.430(8)		
C(11)–Pd–N(10)	100.9(2)	C(11)–Pd–O(1)	80.5(2)
N(10)–Pd–O(1)	174.3(2)	C(11)–Pd–N(1)	164.3(2)
N(10)–Pd–N(1)	79.9(2)	O(1)–Pd–N(1)	100.2(2)
C(2)–N(1)–C(10b)	119.2(5)	C(2)–N(1)–Pd	132.0(4)
C(10b)–N(1)–Pd	106.6(4)	N(1)–C(2)–C(3)	120.3(6)
N(1)–C(2)–C(2a)	118.8(6)	C(3)–C(2)–C(2a)	120.8(6)
C(4)–C(3)–C(2)	120.7(6)	C(3)–C(4)–C(4a)	120.7(6)
C(10b)–C(4a)–C(4)	115.8(6)	C(10b)–C(4a)–C(5)	119.5(6)
C(4)–C(4a)–C(5)	124.7(6)	C(6)–C(5)–C(4a)	120.8(6)
C(5)–C(6)–C(6a)	120.9(6)	C(10a)–C(6a)–C(7)	116.6(6)
C(10a)–C(6a)–C(6)	119.3(6)	C(7)–C(6a)–C(6)	124.0(6)
C(8)–C(7)–C(6a)	119.2(6)	C(7)–C(8)–C(9)	120.9(6)
N(10)–C(9)–C(8)	120.5(6)	N(10)–C(9)–C(9a)	119.4(6)
C(8)–C(9)–C(9a)	119.9(6)	C(9)–N(10)–C(10a)	118.6(5)
C(9)–N(10)–Pd	130.8(4)	C(10a)–N(10)–Pd	110.3(4)
N(10)–C(10a)–C(6a)	123.0(5)	N(10)–C(10a)–C(10b)	116.6(5)
C(6a)–C(10a)–C(10b)	120.2(6)	N(1)–C(10b)–C(4a)	123.2(5)
N(1)–C(10b)–C(10a)	117.7(5)	C(4a)–C(10b)–C(10a)	119.0(5)
C(12)–C(11)–C(16)	117.4(6)	C(12)–C(11)–Pd	130.7(5)
C(16)–C(11)–Pd	111.7(4)	O(2)–C(12)–C(11)	121.7(6)
O(2)–C(12)–C(13)	117.4(5)	C(11)–C(12)–C(13)	120.8(6)
O(3)–C(13)–C(14)	123.4(6)	O(3)–C(13)–C(12)	116.3(6)
C(14)–C(13)–C(12)	120.2(6)	O(4)–C(14)–C(15)	124.1(6)
O(4)–C(14)–C(13)	116.0(6)	C(15)–C(14)–C(13)	119.9(6)
C(14)–C(15)–C(16)	119.2(6)	C(11)–C(16)–C(15)	122.3(6)
C(11)–C(16)–C(17)	114.7(5)	C(15)–C(16)–C(17)	122.7(5)
C(17)–O(1)–Pd	113.8(4)	O(1)–C(17)–C(16)	117.6(5)
O(1)–C(17)–C(18)	117.3(5)	C(16)–C(17)–C(18)	125.1(6)
C(12)–O(2)–C(19)	115.3(5)	C(13)–O(3)–C(20)	119.0(5)
C(14)–O(4)–C(21)	116.5(5)		

Spectroscopic Properties and Structure of the Complexes. The coordination of the oxygen atom of the carbonyl group in complexes **12**, **15**, and **16** is substantiated by the presence of a band around 1510 cm^{-1}, assignable to ν(CO), which is shifted to lower frequency by around 130–150 cm^{-1} with respect to the mercurials **10** and **11** and complexes **13** and **14**.

An additional structural feature arises from the study of complex **16**. Its ^1H NMR spectrum at room temperature indicates that the two halves of the ligand 2,9-dimethyl-1,10-phenanthroline are equivalent. Unusual pentacoordinated complexes of gold(III),[11] palladium(II),[12] and platinum(II)[13] with the dmphen ligand are known; their formation seems to be favored by the potentially great steric hindrance if this ligand were in a square planar disposition. In our case such steric hindrance should be even greater because of the 2-OMe substituent. However,

(11) Robinson, W. T.; Sinn, E. *J. Chem. Soc., Dalton Trans.* **1975**, 726.
(12) Albano, V. G.; Castellari, C.; Cucciolito, M. E.; Panunzi, A.; Vitaliano, A. *Organometallics* **1990**, *9*, 1269.
(13) Fanizzi, F. P.; Intini, F. P.; Maresca, L.; Natile, G.; Lanfranchi, M.; Tiripichio, A. *J. Chem. Soc., Dalton Trans.* **1991**, 1007. Albano, V. G.; Castellari, C.; Monari, M.; De Felice, V.; Panunzi, A.; Ruffo, F. *Organometallics* **1992**, *11*, 3665.

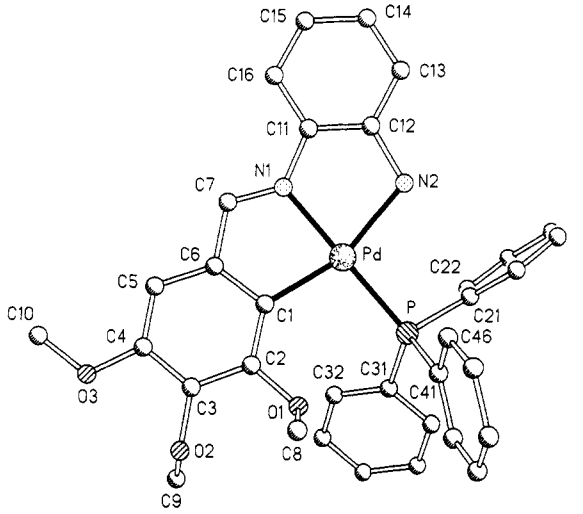


Figure 1. Structure of the cation of complex **6**.

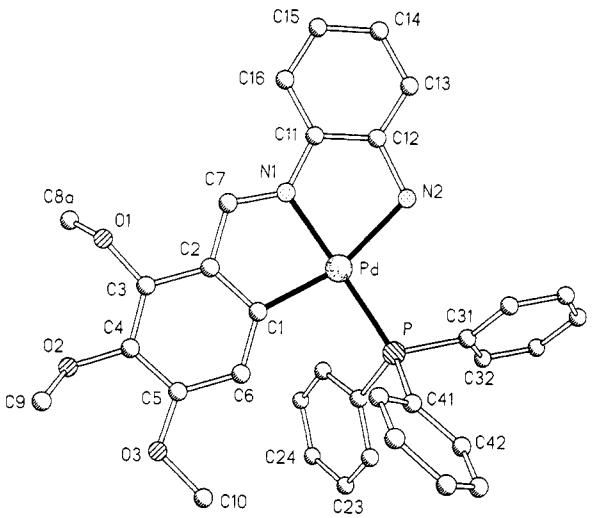


Figure 2. Structure of the cation of complex **6′**.

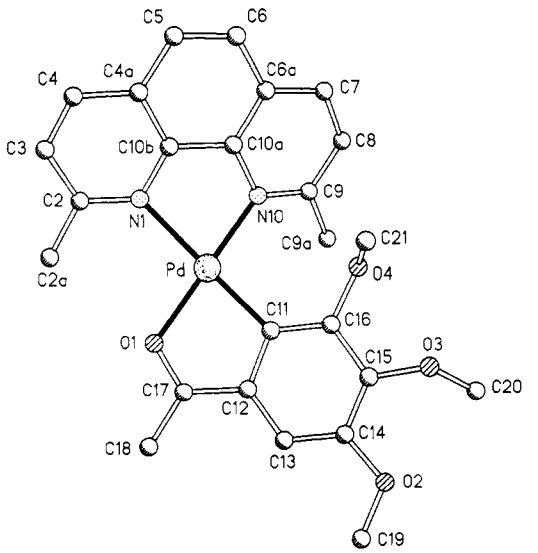
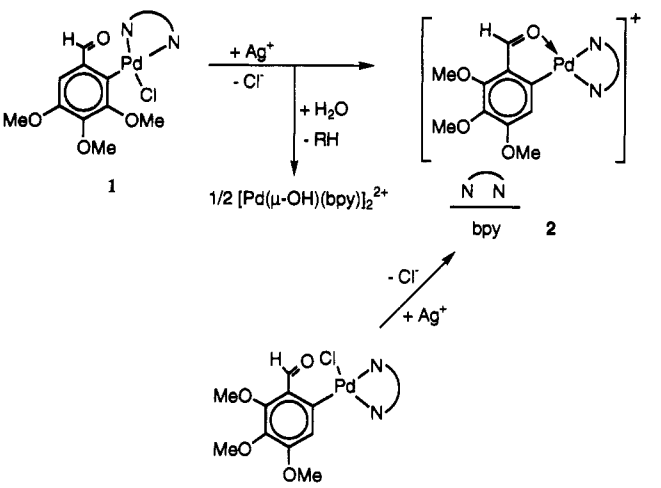


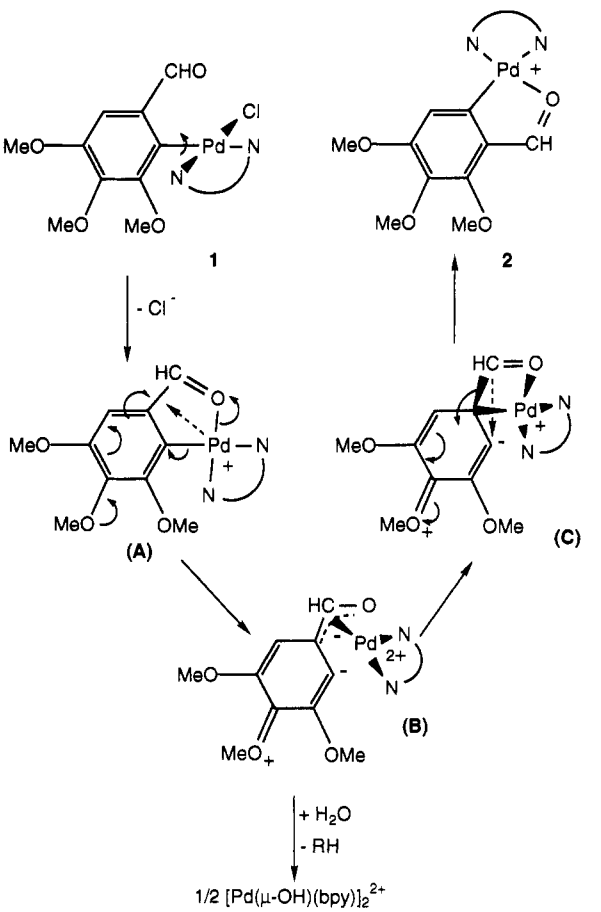
Figure 3. Structure of the cation of complex **16**.

the crystal structure and the low temperature ^{1}H NMR spectra of **16** (see Figures 4 and 5) demonstrate that it is a four-coordinated complex. From room temperature to −30 °C five singlets can be seen (Figure 4) corresponding to the three methoxy groups (3.96, 3.91, and 3.02 ppm), the two equivalent methyl groups of dmphen (3.05 ppm), and the ketone methyl group (2.77 ppm). At −40 °C the

Scheme III



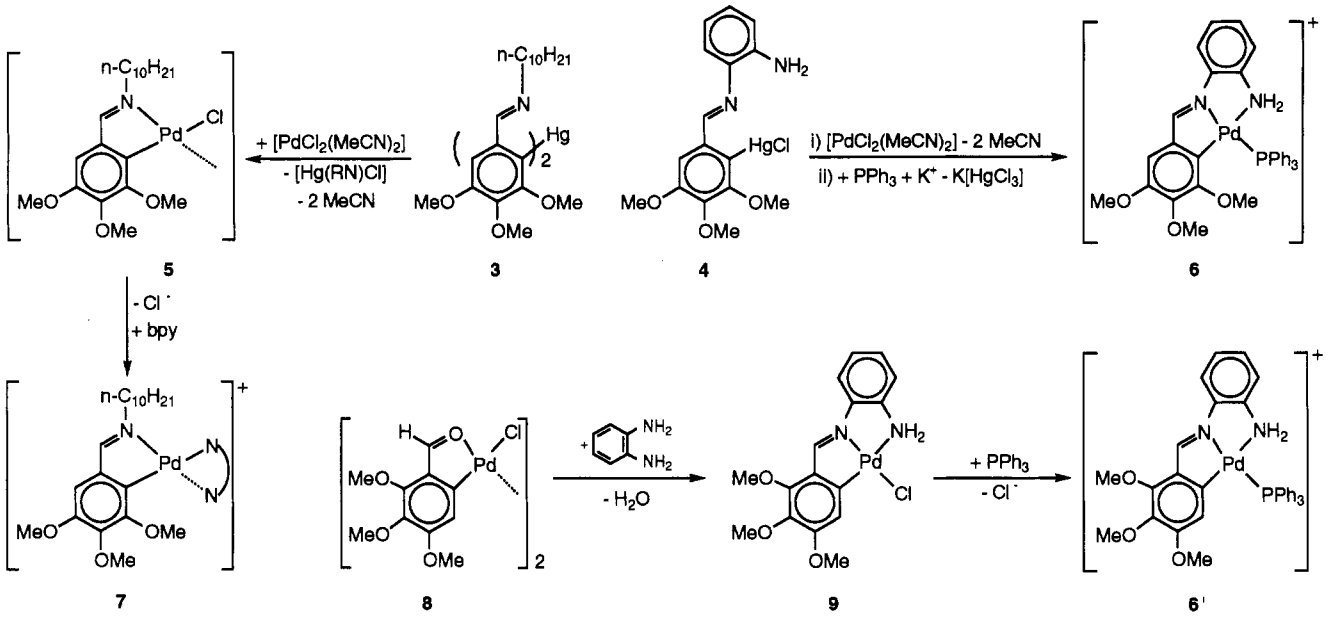
Scheme IV



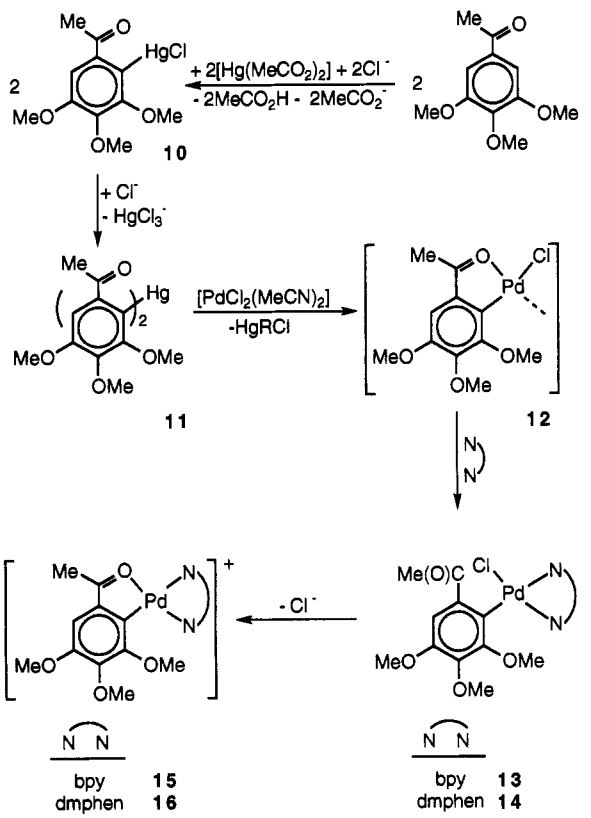
dmphen methyl singlet starts to widen and between −60 and −80 °C becomes a doublet whose right-hand component coincides with the higher field methoxy resonance. In the 8.8–6.8 ppm region (Figure 5) the cooling only has the effect of making the H(3) and H(8) protons inequivalent, whereas the other dmphen protons remain fortuitously equivalent. We assume that the observed behavior in solution at room temperature occurs because a pentacoordinate triflate complex allows rotation of dmphen (see Scheme VII).

Crystal Structure of Complexes 6, 6′, and 16. Figures 1–3 show the structures and Tables III, V, and VII give selected bond lengths and angles of the cations of **6**, **6′**,

Scheme V



Scheme VI



T (° C)

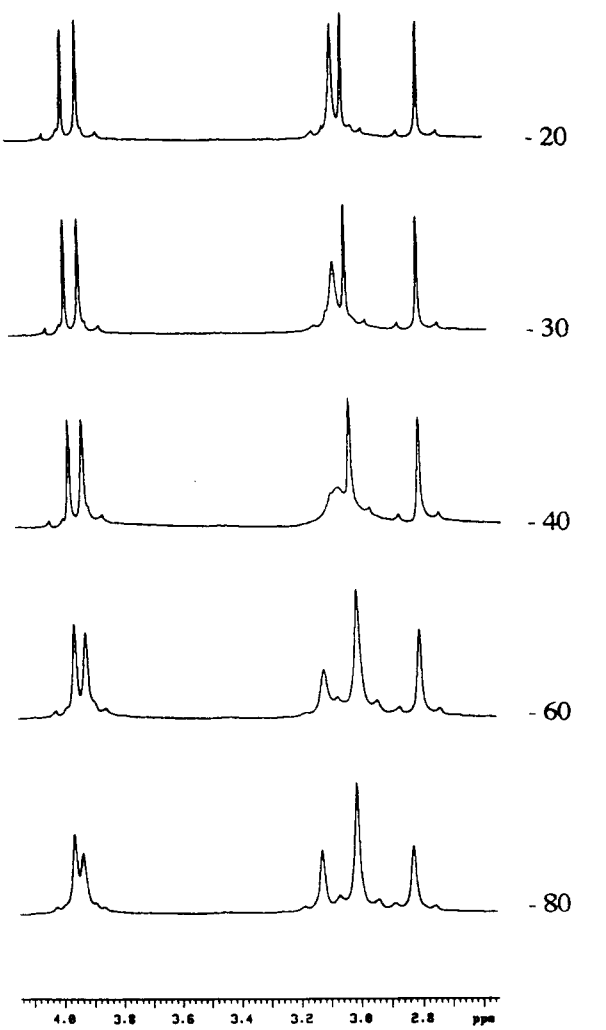


Figure 4. High field ^1H NMR spectra of **16** at low temperatures.

and **16**, respectively. All complexes show distorted square planar geometries because of the restricted bite angles (80–82 °C) of the five-membered chelate rings. The coordination at the metal center of **6'** can be described as planar, since there is only a slight distortion; N(1) lies 0.10 Å out of the plane of Pd,P,C(1),N(2), and the dihedral angle between the aromatic rings is only 6°. In the other two derivatives, there are considerable distortions from the ideal geometry. In **6**, N(1) lies 0.33 Å out of the plane of Pd,P,C(1),N(2), and the angle between the rings increases to 14°. This may be due to steric pressure between the P atom and the methoxy group at O(1) (in **6**, the corresponding position of the aromatic ring is unsubstituted); the chelating ligand twists to reduce this, with O(1) and N(1) being forced to opposite sides of the ligand plane. The distance P···O(1) is 3.12 Å.

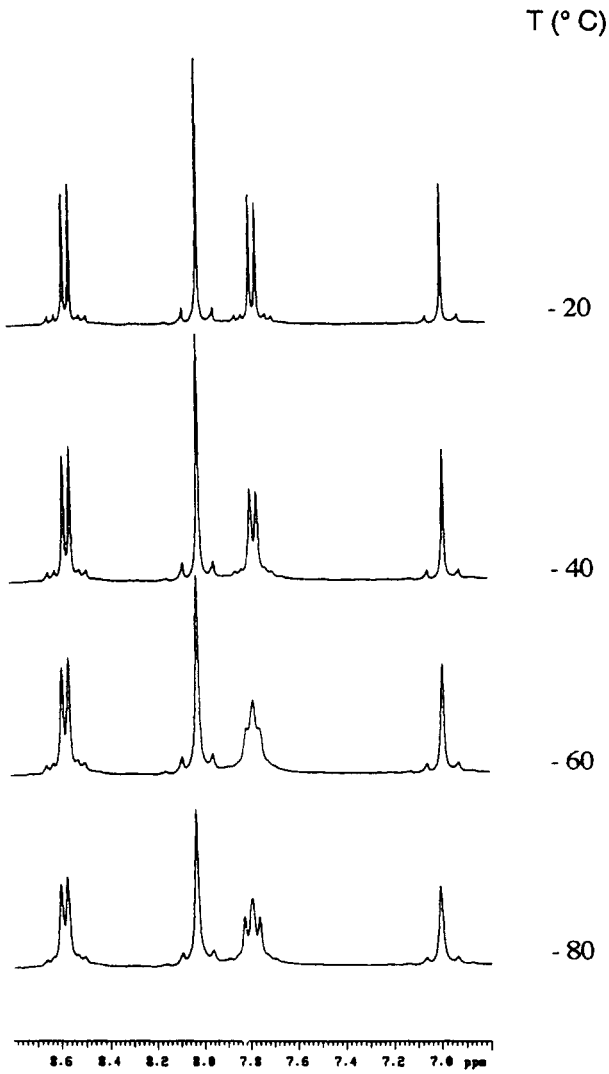
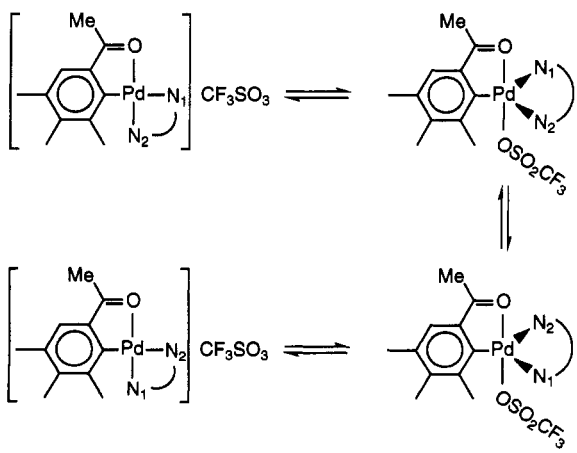


Figure 5. Low field ^1H NMR spectra of **16** at low temperatures.

Scheme VII



Compound **16** displays a major degree of distortion, presumably arising from steric compression between the phenanthroline methyl groups. The coordination at Pd is twisted by 18° [the dihedral angle between the planes Pd,N(1),N(10) and Pd,O(1),C(11)]; C(11) lies 0.67 Å out of the best plane through the other four atoms. The phenanthroline ligand can be described as consisting of two planes; the ring at N(1) together with the central ring makes an angle of 12° with the ring at N(10). The Pd atom is forced out of the former ligand plane by no less than 0.70 Å.

A further factor that may influence the conformation of **6** and **6′** is the presence of hydrogen bonds from the NH_2 group. Compound **6** shows one H bond to an anion oxygen, N(2)···O(4) (1 − *x*, 1 − *y*, 1 − *z*) 2.89 Å, whereas compound **6′** has two rather longer contacts, N(2)···O(5) (anion) 3.05 Å and N(2)···O(7) (ether) 3.03 Å.

The aryl–O–Me bond angles (112–119°) lie between values expected for sp^3 and sp^2 hybridization and the MeO–aryl bond lengths (range: 1.37–1.38 Å) are shorter than those found in dialkyl ethers (*cf.* standard value: 1.416 Å[14]) while they are as expected for aryl alkyl ethers [*cf.* standard value: 1.370(11) Å[14]]. Although this could indicate some electron releasing from methoxy groups to the aryl rings, the ring C–C bond distances (range: 1.38–1.42 Å) are normal [*cf.* standard value: 1.384(13) Å[14]]. Coordination to palladium of the carbonyl oxygen atom in **16** might be responsible for the lengthening of the C–O bond distances [1.272(7) Å] with respect to that in aryl alkyl ketones [*cf.* standard value: 1.221(14) Å[14]].

Bond distances at palladium in **6** [Pd—C, 2.014(4); Pd—P, 2.271(1); Pd—NH_2, 2.154(3); Pd—N(=C), 2.032(3) Å] are similar to those in **6′** [Pd—C, 2.027(5); Pd—P, 2.262(1); Pd—NH_2, 2.144(4); Pd—N(=C)l 2.023(4) Å]. Pd—N(=C) bond lengths are similar to those found in other aryl—palladium complexes with Schiff bases [*cf.* standard value: 2.037(40) Å[15]]. The Pd—NH_2 [2.154 (3), 2.144 (4) Å] bond distances are longer than those found in $[Pd\{\kappa^2\text{-}C_6H_4\{CH(Me)NH_2\}\text{-}3\}(COD)]ClO_4$ [2.082(6) Å] and $[Pd\{\kappa^2\text{-}C_6H_4\{CH(Me)NH_2\}\text{-}2\}Br(PPh_3)]$ [2.092(3) Å][16] because the olefin or PPh_3 ligands in these complexes have a weaker *trans* influence than the aryl ligand in **6** and **6′**. The mutually *trans* Pd—C [2.002(6) Å] and Pd—N [2.153(5) Å] bond lengths in **16** are similar to those in complexes $[Pd(R)(PPh_3)(bpy)]CF_3SO_3$ [2.010(5) and 2.143(4) Å] and $[Pd(R')(PPh_3)(bpy)]CF_3SO_3$ [1.986(3) and 2.137(3) Å].[2a] The weak mutual *trans* influence of the oxygen and nitrogen donor atoms in **16** explains why the Pd—O [2.044(4) Å] and Pd—N [2.032(5) Å] bond lengths are shorter than those found in the complex *cis*-$[Pd(\kappa^2\text{-}C_6H_4NO_2)(C_6H_4NO_2)(pyridine)]$ [2.138(3) and 2.143(4) Å, respectively[17]] because in this case both oxygen and nitrogen donor atoms have a *trans* aryl ligand. The same argument explains the different Pd—N bond distances in **16**.

Acknowledgment. We thank the Fonds der Chemischen Industrie and Dirección General de Investigación Científica y Técnica (PB92-0982-C) for financial support.

Supplementary Material Available: Complete listings of crystal data, atomic parameters, and bond lengths and angles for **6**, **6′**, and **16** (23 pages). Ordering information is given on any current masthead page.

OM9302958

(14) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1987**, S1.
(15) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.
(16) Vicente, J.; Saura-Llamas, I.; Jones, P. G. Unpublished results.
(17) Vicente, J.; Chicote, M. T.; Martin, J.; Artigao, M.; Solans, X.; Font-Altaba, M.; Aguiló, M. *J. Chem. Soc., Dalton Trans.* **1988**, 141.