Notes

Synthesis, Structure, and Reactivity of the Novel Pentacoordinate Palladium Complex $[Pd(Phen)_2(CO_2CH_3)](PF_6)$

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Summary: Reaction of $[Pd(phen)(CO_2CH_3)_2]$ *(**1**) with phenanthrolinium hexafluorophosphate (**2**) gives in high yield the unprecedented pentacoordinate palladium complex* $[Pd(phen)_2(COOMe)](PF_6)$ *(**3**) in which Pd displays a strongly distorted square pyramidal coordination. The reactivity of **3** toward bases was explored too.*

Introduction

Palladium(II) and platinum(II) pentacoordinate complexes[1] are mechanistically and synthetically relevant in organometallic chemistry. Complexes of substituted phenanthrolines with pentacoordinate palladium and platinum halides[2] and cyananide[3] were studied, and the structure of $[Pt(CN)phen)_2](PF_6)$ was reported.[4] In the case of palladium, they can be synthesized either by reacting a four-coordinate complex with an olefin[5−7] or by oxidative addition of an alkyl halide to three-coordinate palladium(0) olefin complexes.[8] Steric hindrance of the N−N′ chelating ligand is a demanding requirement for the stabilization of five-coordinate palladium complexes.[9]

We have previously described the novel palladium 1,10-phenanthroline bis(carbomethoxy) complex $Pd(phen)(CO_2CH_3)_2$, **1**.[10] In the course of a study on the reactivity of **1** with acids, we found that, analogously to bis(carbomethoxy)bis(triphenylphosphine)palladium,[11] the reaction of **1** with HCl gave $Pd(phen)Cl(CO_2CH_3)$. Surprisingly, we now find that the reaction of the nonconventional acid phenanthrolinium hexafluorophosphate ($phenHPF_6$, **2**) gives the new five-coordinate complex $[Pd(phen)_2(CO_2CH_3)](PF_6)$, **3**.

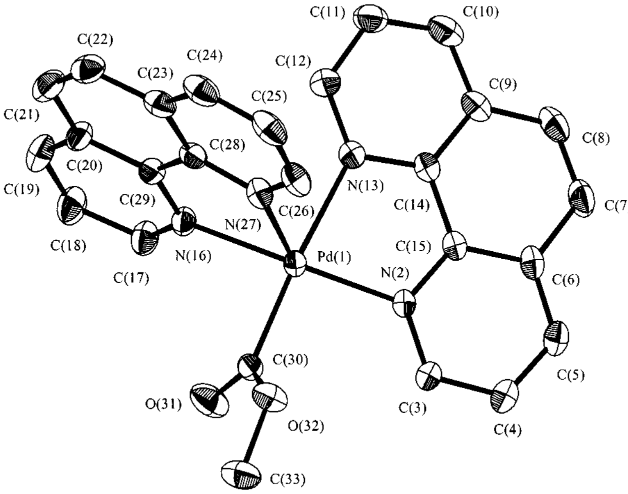

Figure 1. ORTEP[15] drawing of the structure of **3** (displacement ellipsoids are drawn at the 30% probability level). Selected bonds lengths [Å] and angles [deg]: Pd(1)−N(2) 2.044(3); Pd(1)−N(16) 0.063(3); Pd(1)−C(30) 1.957(4); Pd(1)−N(13) 2.135(4); Pd(1)−N(27) 2.637(4). N(27)−Pd(1)−C(30) 101.6(1); N(16)−Pd(1)−N(27) 70.4(1); N(13)−Pd(1)−N(27) 83.5(1); N(2)−Pd(1)−C(30) 95.0(2); N(2)−Pd(1)−N(16) 167.3(1); N(16)−Pd(1)−C(30) 87.1(1); N(16)−Pd(1)−N(13) 97.1(1); N(13)−Pd(1)−C(30) 174.3(2); N(2)−Pd(1)−N(27) 121.1(1); N(2)−Pd(1)−N(13) 80.1(2).

Results and Discussion

A light yellow solution of **1**, containing 1 equiv of **2**, suspended in methanol when stirred under inert atmosphere, undergoes a color change to orange-yellow, with concomitant CO evolution and formation of **3** (Scheme 1).

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(1) (a) Fanizzi, F. P.; Natile, G.; Lanfranchi, M.; Tiripicchio, A.; Laschi, F.; Zanello, P. *Inorg. Chem.* **1996**, *35*, 3173−3182. (b) Albano, V. G.; Castellari, C.; De Felice, V.; Panunzi, A.; Ruffo, F. *Organometallics* **1996**, *15*, 4012−4019. (c) Fanizzi, F. P.; Intini, F. P.; Maresca, L.; Natile, G.; Lanfranchi, M.; Tiripicchio, A.; Pacchioni, G. *J. Chem. Soc., Chem. Commun.* **1992**, 333−334.

(2) Plowman, R. A.; Power, L. F. *J. Aust. Chem.* **1971**, *24*, 303−308.

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(7) Fanizzi, F. P.; Intini, F. P.; Maresca, L.; Natile, G.; Lanfranchi, M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1991**, 1007−1012.

(8) Cucciolito, M. E.; Panunzi, A.; Ruffo, F.; De Felice, V. *Gazz. Chim. Ital.* **1989**, *119*, 461−462.

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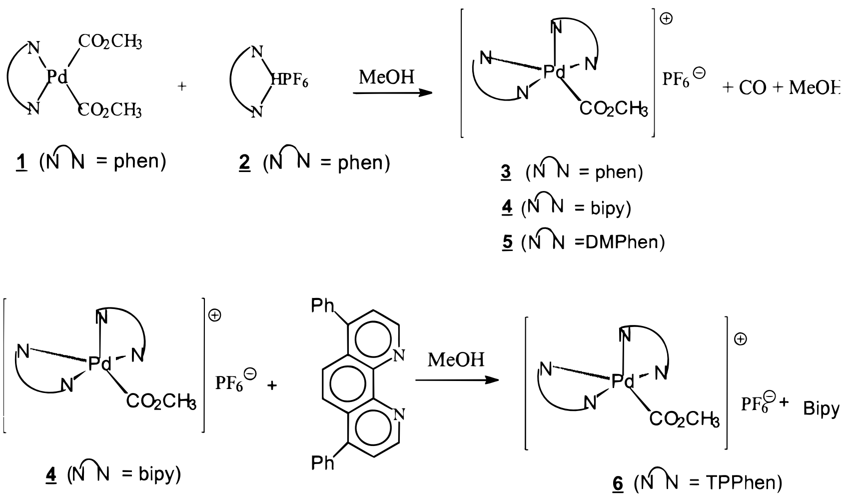
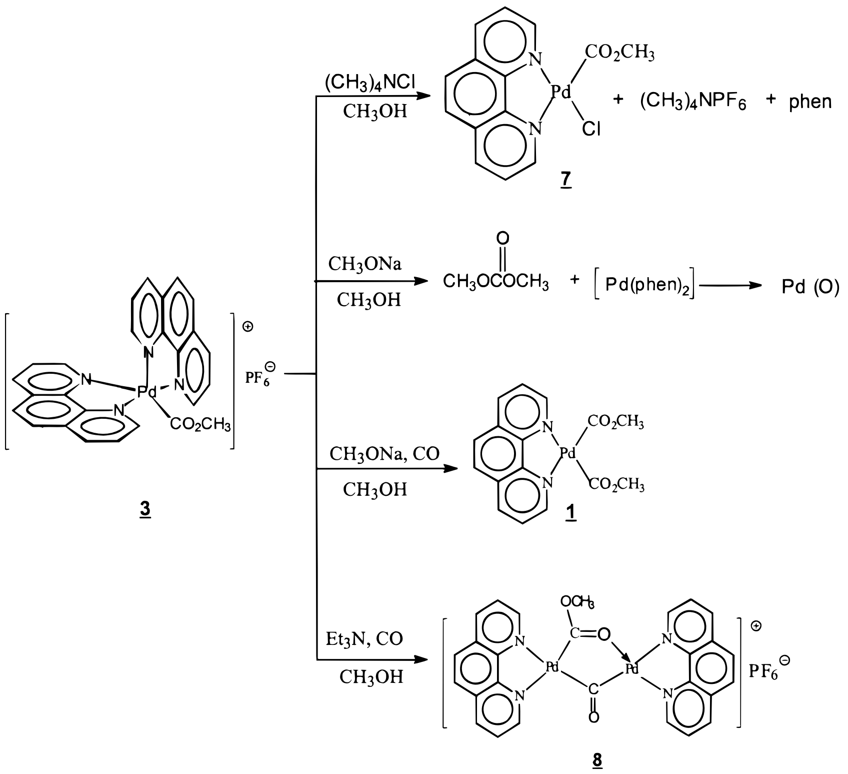
Scheme 1



Scheme 2



Large yellow-orange crystals of **3** suitable for X-rays analysis were obtained by slow diffusion of *n*-hexane into a methylene chloride solution of **3**. Single-crystal X-ray diffraction and spectroscopic analysis confirm the pentacoordinate structure of **3**, in which the Pd atom displays a strongly distorted square pyramidal coordination (Figure 1), analogously to the platinum complex [Pt(CN)phen)$_2$](PF$_6$). The square plane is formed by atoms N(2) and N(13) of the first phen molecule, the N(16) atom of the second phen ligand, and the C(30) atom of the carbomethoxy group; the apical position is occupied by atom N(27) of the second phenanthroline ligand (Figure 1). The Pd(1) atom is displaced toward atom N(27) by 0.141(5) Å from the mean plane defined by N(2), N(13), N(16), and C(30). The plane is also slightly distorted from the square symmetry, with the Pd(1)−N(13) bond (2.135(4) Å) in trans position with respect to the carbomethoxy group, longer than the other two Pd−N bonds in the plane (2.044(3) and 2.063(3) Å, for Pd(1)−N(2) and Pd(1)−N(16), respectively). The Pd(1)−C(30) distance, 1.957(4) Å, is significantly shorter than the corresponding bond observed in the square planar Pd(bipy)(CO$_2$CH$_3$)$_2$ complex (Pd−N 1.989(9) Å).[12] Finally, the N(27) atom, in apical position, is at 2.637(4) Å from Pd(1).

Complexes Pd(L−L)(CO$_2$CH$_3$)$_2$ [(L−L) = 2,2′-bipyridine (bipy) and 2,9-dimethyl-1,10-phenanthroline (DMPhen), Scheme 1] reacted with the corresponding acids (L−L)HPF$_6$ to yield [Pd(bipy)$_2$(CO$_2$CH$_3$)](PF$_6$) (**4**) and [Pd(DMPhen)$_2$(CO$_2$CH$_3$)](PF$_6$) (**5**) (89% and 90% yield, respectively). In the latter case **5** was obtained

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[12] Smith, G. D.; Hanson, B. E.; Merola, J. S.; Waller, F. J. *Organometallics* **1993**, *12*, 568−569.

in high yield as could be expected, since there was no steric crowding due to the presence of methyl groups in the 2 and 9 position, as clearly shown by X-ray diffraction of complex **3** (Figure 1). $Pd(DPPhen)_2(CO_2CH_3)](PF_6)$ (**6**) (DPPhen = 4,7-diphenyl-1,10-phenanthroline) was prepared by ligand exchange between the complex **4** and the free ligand (70% yield).

When stirred at room temperature, in methanol complex **3** reacted with tetramethylammonium chloride, affording carbomethoxy(chloro)phenanthrolinepalladium, $[Pd(phen)(CO_2CH_3)Cl]$ (**7**) (Scheme 2). ^1H NMR of the pink complex **7** showed the singlet of the carbomethoxy group shifted from 3.46 to 3.86 ppm, and the integrals indicated the presence of one phenanthroline ligand. The two protons in the 2 and 9 position gave two different signals (H_2 at 9.25 ppm and H_9 at 8.87 ppm). Moreover, the absence of the IR band at 850 cm^{-1}, attributable to the PF_6^- group, confirmed that in this case complex **3** lost a chelating ligand during the reaction, reverting to the usual tetracoordinated mode. This particular reactivity of **3** can be ascribed to the presence of the chloride anion in tetramethylammonium chloride, Me_4NCl, which could directly coordinate palladium, thus allowing the loss of one phenanthroline ligand.

Finally, **3** reacted with an excess of sodium methoxide in methanol when the reaction mixture was heated at 60 °C for 8 h, with the formation of dimethyl carbonate (DMC; Scheme 2). When the same reaction was carried out under CO pressure, no traces of DMC were detected and bis(methoxycarbonyl)phenanthrolinepalladium, $Pd(phen)(CO_2CH_3)_2$ (**1**), was formed. Even in the presence of triethylamine as a base, for 4 h at 70 °C with 40 bar of CO, the formation of DMC did not occur. From the reaction mixture we succeded in isolating a binuclear palladium complex, **8**, as a beige solid. Although the crystals did not allow X-ray analysis, unequivocal evidence of the structure was gained by mass, IR, and NMR spectroscopies. The M + 1 ion was 658. The IR spectrum showed a bridging carbonyl adsorption comparable with that found for $[Pd(phen)_2((\eta\text{-}CO)((\eta\text{-}H)](OAc)$,[13] while the carbonyl absorption of the brigded carbomethoxy group was observed at 1620 cm^{-1}, as a weak band, owing to palladium−oxygen coordination. ^{13}C NMR gave only half signals for phenanthroline as expected. ^1H NMR, which gave integrals of the methoxy group and ligand protons corresponding to a 1:2 ratio, continued to show only the enlarged signals of the ligand when free 1,10-phenanthroline was added, indicating the fluctional nature of the complex.

Apparently, the formation and structure of stable **3** are due to the presence of the noncoordinating anion, which allows pentacoordination. The structure of the stable complex **3** is unprecedented. The method used to prepare complex **3** also is unprecedented and is likely to have general character.

Experimental Section

All reactions were performed under argon atmosphere, using the Schlenk tube techniques. Solvents were dried and distilled prior to use. Nitrogen-chelating ligands, triethylammine and tretramethylammonium chloride, were obtained from Aldrich and used as received. Sodium methoxide was prepared by reacting sodium metal with anhydrous methanol. $Pd(L-L)(CO_2CH_3)_2$ and $(L-L)HPF_6$[14] were prepared according to the literature. Carbon monoxide was purchased from Rivoira.

^1H and ^{13}C NMR spectra were recorded on a 200 MHz Brucker Electrospin 200 Instrument, while IR spectra were recorded using a Perkin-Elmer 1420 Instrument. FAB MS were recorded on a Finnigan MAT M scan instrument, using *m*-nitrobenzyl alcohol as a matrix.

Synthesis of $[Pd(L-L)_2(CO_2CH_3)](PF_6)$. A light yellow suspension of 0.37 mmol of $Pd(L-L)(CO_2CH_3)_2$ in 20 cm^3 of methanol was vigorously stirred and 0.37 mmol of $(L-L)HPF_6$ was added. The mixture changed to orange-yellow, with a concomitant CO evolution (1 equiv, 9 cm^3). After 1 h, the solid was filtered and washed with diethyl ether.

$[Pd(phen)_2(CO_2CH_3)](PF_6)$, 3: 75% yield. ^1H NMR ($C_2D_2Cl_4$, ppm): 8.91 (dd, 4H); 8.60 (dd, 4H); 8.09 (s, 4H); 7.78 (m, 4 H); 3.46 (s, 3H). ^{13}C ($C_2D_2Cl_4$, ppm): 169.87, 151.36, 144.30, 138.8, 130.36, 127.82, 125.34, 53.31. ^{31}P NMR ($C_2D_2Cl_4$, ppm): −53; *J* = 711 Hz. IR (in Nujol mull): 1670, 1070, 840 cm^{-1}. MS: *m/z* 526 (M + 1). Anal. Calcd for $C_{26}H_{19}F_6N_4O_2PPd$: C, 46.56; H, 2.84; N, 8.35; P, 4.62; Pd, 15.82. Found: C, 44.98; H, 2.77; N, 8.40; P, 4.70; Pd, 15.77.

$[Pd(bipy)_2(CO_2CH_3)](PF_6)$, 4: 88% yield. ^1H NMR ($C_2D_2Cl_4$, ppm): 8.47 (dd, 4H); 8.22 (dd,4H); 8.06 (t, 4H); 7.49 (t, 4 H); 3.55 (s, 3H). ^{13}C NMR ($C_2D_2Cl_4$): 53.54; 123.98; 126.46; 139.84; 151.10; 155.24; 191.80. IR (in Nujol mull): 1690, 1090, 860 cm^{-1}. MS: *m/z* 478 (M + 1). Anal. Calcd for $C_{22}H_{15}F_6N_4O_2PPd$: C, 42.71; H, 2.42; N, 9.06; P, 5.02; Pd, 17.15. Found: C, 42.41; H, 2.39; N, 9.01; P, 4.85; Pd, 16.97.

$[Pd(DMPhen)_2(CO_2CH_3)](PF_6)$, 5: 90% yield. ^1H NMR (CD_2Cl_2, ppm): 8.46 (d, 4H); 8.00 (s, 4H); 7.70 (d, 4H); 3.06 (s, 3H); 2.67 (s, 12H). IR (in Nujol mull): 1665, 1090, 870 cm^{-1}. MS: *m/z* 554 (M + 1). Anal. Calcd for $C_{30}H_{27}F_6N_4O_2PPd$: C, 49.58; H, 3.72; N, 7.71; P, 4.27; Pd, 14.60. Found: C, 49.41; H, 3.59; N, 7.51; P, 4.65; Pd, 14.77.

Synthesis of $[Pd(DPPhen)_2(CO_2CH_3)](PF_6)$, 6. A suspension of 0.192 g of $[Pd(bipy)_2(CO_2CH_3)](PF_6)$ (**4**) (0.3 mmol) and 0.289 g of 4,7-diphenyl-1,10-phenanthroline (0.9 mmol) in 20 cm^3 of methanol was stirred for 20 h and, after this time, filtered, and the residue washed with MeOH and with diethyl ether. The solid was dried under vacuum, thus affording 0.200 g of an orange-yellow solid, in 70% yield. ^1H NMR (CD_2Cl_2, ppm): 9.06 (d, 4H); 8.11 (s, 4H); 7.75 (d, 4H); 7.60 (s, 20H); 3.55 (s, 3H). IR (in Nujol mull): 1660, 1090, 865 cm^{-1}. MS: *m/z* (M^+). Anal. Calcd for $C_{50}H_{35}F_6N_4O_2PPd$: C, 61.60; H, 3.59; N, 5.74; P, 3.18; Pd, 10.88. Found: C, 61.41; H, 3.29; N, 6.01; P, 3.25; Pd, 10.70.

Synthesis of $[Pd(phen)(CO_2CH_3)(Cl)]$, 7. A suspension of 0.2 g (0.335 mmol) of **3** and 0.044 g (0.402 mmol) of Me_4NCl was stirred at room temperature in 25 mL of MeOH; when mixed, it suddenly changed from yellow-orange to orange and, after 10 min, to pink. The solvent was then distilled and the residue washed with methylene chloride and with diethyl ether. Finally, the solid was dried under vacuum. The product weighed 100 mg (78% yield). ^1H NMR (CD_2Cl_2, ppm): 9.25 (dd, 1H); 8.87 (dd, 1H); 8.56 (m, 2H); 7.98 (s, 2H); 7.83 (m, 2H), 3.86 (s, 3H). IR (in Nujol mull): 1670, 1030 cm^{-1}. MS: *m/z* 381 (M + 1). Anal. Calcd for $C_{14}H_{11}ClN_2O_2Pd$: C, 44.21; H, 2.89; N, 7.36; Cl, 9.12; Pd, 27.89. Found: C, 44.41; H, 2.59; N, 7.01; Cl, 9.25; Pd, 28.01.

Synthesis of $Pd_2(phen)_2((\eta\text{-}CO)((\eta\text{-}COOMe)$, 8. In a 100 cm^3 stainless steel vessel were charged 0.200 g of **3** (0.3 mmol) and 0.043 mL of Et_3N (0.3 mmol) in 20 mL of methanol and pressurized with CO to 40 bar. After 4 h at 70 °C, the unreacted gas was vented off and the autoclave opened; the

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[13] Stolyarov, I. P.; Evdokimova, E. V.; Moiseev, I. I. *Koord. Khim.* **1989**, *15*, 1545−1549.z

[14] Milani, B.; Anzilutti, A.; Vicentini, L.; Sessanta o Santi, A.; Zangrando, E.; Geremia, S.; Mestroni, G. *Organometallics* **1997**, *16*, 5064.

[15] Johnson, C. K. *ORTEP II. Rep. ORNL-5138*; Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

beige solid was filtered, washed with MeOH, and dried in a vacuum. Yield: 82%. ^{1}H NMR (DMSO, ppm): 9.05 (dd, 4H); 8.50 (dd,4H); 8.27 (dd, 4H); 7.81 (s, 4 H); 3.75 (s, 3H). ^{13}C NMR (DMSO, ppm): 180.67; 167.78; 151.43; 147.51; 143.01; 139.46; 130.57; 128.96; 126.91; 125.14; 71.03; 58.00; 53.47. IR (in Nujol mull): 1880 (s), 1620 (w), 1030 (s) cm^{-1}. MS: *m*/*z* 658 (M + 1). Anal. Calcd for $C_{27}H_{19}F_6N_4O_3PPd_2$: C, 40.29; H, 2.36; N, 6.96; P, 3.85; Pd, 26.37. Found: C, 40.41; H, 2.29; N, 7.01; P, 3.65; Pd, 26.77.

Crystal Structure Data for 3. Yellow-orange crystals were grown by slow diffusion of *n*-hexane into its saturated methylene chloride solution at room temperature. **3**: formula $C_{26}H_{19}F_6N_4O_2PPd$; M_r = 670.83; crystalline system triclinic; space group $P\bar{1}$; a = 10.030(1) Å; b = 12.278(2) Å; c = 13.047(2) Å; α = 98.56(1); β = 109.87(1); γ = 111.71(1)°; V = 1332.7(4) Å^3; D_x(Mg/m^3) = 1.6717; Mo Kα radiation (λ = 0.71069 Å); μ = 8.17 cm^{-1}; crystal dimensions 0.5 × 0.5 × 0.6 mm^3; q_{max} = 35°.

The X-ray diffraction data were collected on a Siemens AED automated diffractometer at 298 K, using Mo Kα radiation (l = 0.71069 Å). A total of 11 800 reflections were measured, of which 7630 with $F > 6\sigma(F)$ observed. The structure was solved by direct methods and refined by the full-matrix least-squares method (SIR-97). The minimized function was $Sw(F_o - F_c)^2$, where $w^{-1} = s^2(F)$. The final cycles of refinement included atomic coordinates and anisotropic thermal parameters for all non-H atoms (358 parameters). The positions of the H atoms were calculated on geometrical grounds and kept fixed to the parent C atom during the refinement. The final difference Fourier map was featureless. The R and wR values were 0.062 and 0.065, respectively.

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Supporting Information Available: Tables of all bond lengths and angles, atomic coordinates, positions, and thermal parameters for **3** (7 pages). Ordering information is given on any current masthead page.

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