Palladium(II) Complexes of Pyridine- and Pyrazine-Based Ligands with Trans Bis(carbon–metal) Bonds.[1] Ligand Synthesis, Complexation, and Crystal Structure

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A new series of trans bis(carbon–palladium) complexes has been prepared. The initial ligands, prepared from 2-(chloromethyl)pyridines or -pyrazines, were treated with dimethyl malonate in anhydrous *N,N*-dimethylformamide in presence of potassium carbonate. Except for the 6-methyl-substituted ligands, the bis C-palladated complexes have isolated and characterized. A single-crystal X-ray structure analysis was conducted on bis{2-[2,2-bis(carbomethoxy)ethyl]pyridine}palladium(II), $PdC_{22}H_{24}N_2O_8$, which revealed it to possess nearly C_2 symmetry. The two heteroaromatic rings are exactly trans but are not coplanar; the dihedral angle is 63.0°, and the palladium coordination is distorted somewhat from ideal square-planar geometry. It crystallizes in the triclinic space group $P\bar{1}$ with cell constants of a = 11.308 (2) Å, b = 13.765 (2) Å, c = 8.412 (2) Å, α = 107.78 (1)°, β = 111.81 (1)°, γ = 91.65 (1)°, and Z = 2. Bond lengths involving palladium average 2.041 (3) Å for Pd–N and 2.149 (2) Å for Pd–C bonds.

Introduction

Even though palladium(II) complexes with N ligands such as pyridine are well-known,[3] there are very few stable organometallic complexes which possess one or more palladium(II)–aliphatic (sp^3) carbon σ bond(s). Earlier, we reported the preparation of a new class of palladium(II) complexes containing two Pd(II)–C σ bonds and two pyridine ligands[4]. The potential catalytic properties[5] of these C_2N_2-type organometallic compounds have prompted our interest in evaluating structural changes in this series. We herein report the synthesis and single crystal X-ray analysis of the square-planar palladium(II) complex of 2-[2,2-bis(carbomethoxy)ethyl]pyridine, **1a** ($R_1 = R_2 = R_3$ = H; X = CH) and then the extension to substituted pyridines and pyrazines (X = N). The "obstacle effect" exhibited by a 6-methyl group[6] during complex generation will be considered.

Experimental Section

General Comments. All melting points were taken in capillary tubes with a Thomas-Hoover Uni-Melt apparatus and are uncorrected. ^{1}H NMR spectra were determined on a Bruker WP-200 NMR spectrometer using $CDCl_3$ as solvent with tetramethylsilane as the internal standard. IR spectra were recorded on a Perkin-Elmer 621 grating infrared spectrophotometer. Mass spectral (MS) data (70 eV) were determined by Mr. D. Patterson on a Hewlett-Packard HP 5985 GC mass spectrometer (assignment, relative intensity). X-ray diffraction data were collected with graphite-monochromatized CuKα radiation on an Enraf-Nonius CAD-4 diffractometer. Reported R_f values were ascertained by a standardized thin-layer chromatographic (TLC) procedure: Baker-flex silica gel IR2-F plates eluting with the stipulated solvent system. For preparative thick-layer chromatography (ThLC), 2-mm silica gel PF-254-366 plates were used. Elemental analyses were performed by Mr. R. Seab in these laboratories.

Ligand Synthesis. General Procedure. A. Halogenation of the methyl group(s) of electron-deficient heterocycles was accomplished via free-radical substitution using *N*-chlorosuccinimide with benzoyl peroxide initiator. A detailed comparative study of this reaction will be published elsewhere.[7] The major product was generally the mono-α-chloromethyl product under the reaction conditions; the yield data cited for the bis esters were based on the unpurified halogenation product.

B. Bis Ester Formation. A mixture of 2-(chloromethyl)-pyridine hydrochloride (1.64 g, 10 mmol), dimethyl malonate (3.3 g, 25 mmol), anhydrous potassium carbonate (5.5 g, 40 mmol) in anhydrous *N,N*-dimethylformamide (DMF, 30 mL)[8] was stirred at 25 °C for 20 h. The solid was filtered and washed with methylene chloride; the organic mixture was concentrated in vacuo and chromatographed (ThLC) on silica, eluting with ethyl acetate/cyclohexane (1:3) to afford **2-[2,2-bis(carbomethoxy)-ethyl]pyridine (1a)**, as an oil: 2 g (90%); R_f 0.14; ^{1}H NMR δ 3.39 (d, CH_2, J = 7.3 Hz, 2 H), 3.67 (s, OCH_3, 6 H), 4.18 (t, CH, J = 7.3 Hz, 1 H), 7.09 (dd, 5-pyH, $J_{4,5}$ = 7.9 Hz, $J_{5,6}$ = 4.3 Hz, 1 H), 7.19 (d, 3-pyH, J = 7.9 Hz, 1 H), 7.57 (dd, 4-pyH, $J_{4,3} = J_{4,5}$ = 7.9 Hz, 1 H), 8.46 (d, 6-pyH, J = 4.3 Hz, 1 H); IR (neat) 1765 (C=O), 1590, 1565, 1475, 1435 cm^{-1}; MS, m/e 223 (M^+, 3), 192 (M^+ – OMe, 15), 164 ($M^+ - C_2H_3O_2$, 94), 132 ($M^+ - C_3H_7O_3$, *100*). Anal. Calcd for $C_{11}H_{13}NO_4$: C, 59.19; H, 5.87; N, 6.27. Found: C, 58.97; H, 6.02; N, 6.14.

4-Methyl-2-[2,2-bis(carbomethoxy)ethyl]pyridine (1b) was prepared from 2-(chloromethyl)-4-methylpyridine:[7] oil; 2 g (84%); R_f 0.13; ^{1}H NMR δ 2.29 (s, 4-pyCH_3, 3H), 3.34 (d, CH_2, J = 7.3 Hz, 2 H), 3.70 (s, OCH_3, 6H), 4.15 (t, CH, J = 7.3 Hz, 1 H), 6.93 (d, 5-pyH, J = 5.5 Hz, 1 H), 7.01 (s, 3-pyH, 1 H), 8.33 (d, 6-pyH, J = 5.5 Hz, 1 H); IR (neat) 1740 (C=O), 1605, 1560, 1435, 1030 cm^{-1}; MS, m/e 237 (M^+, 6), 206 (M^+ – OMe, 18), 178 ($M^+ - C_2H_3O_2$, 80), 146 ($M^+ - C_3H_7O_3$, *100*). Anal. Calcd for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37; N, 5.90. Found: C, 60.39; H, 6.28; N, 5.67.

5-Methyl-2-[2,2-bis(carbomethoxy)ethyl]pyridine (1c) was prepared from 2-(chloromethyl)-5-methylpyridine:[7] oil; 1.9 g (80%); R_f 0.15; ^{1}H NMR δ 2.27 (s, 5-pyCH_3, 3H), 3.35 (d, CH_2, J = 7.3 Hz, 2 H), 3.70 (s, OCH_3, 6H), 4.11 (t, CH, J = 7.3 Hz, 1 H), 7.08 (d, 3-pyH, J = 7.9 Hz, 1 H), 7.38 (dd, 4-pyH, $J_{3,4}$ = 7.9 Hz, $J_{4,6}$ = 1.8 Hz, 1 H), 8.32 (d, 6-PyH, $J_{4,6}$ = 1.8 Hz, 1 H); IR (neat) 1730 (C=O), 1600, 1485, 1430, 1025 cm^{-1}; MS, m/e 237 (M^+, 3), 206 (M^+ – OMe, 16), 178 ($M^+ - C_2H_3O_2$, *100*). Anal. Calcd for $C_{12}H_{15}O_4$: C, 60.75; H, 6.37; N, 5.90. Found: C, 60.42; H, 6.58; N, 5.73.

6-Methyl-2-[2,2-bis(carbomethoxy)ethyl]pyridine (1d) was prepared from 2-(chloromethyl)-6-methylpyridine:[7] oil; 2.2 g (93%); R_f 0.18; ^{1}H NMR δ 2.46 (s, 6-pyCH_3, 3H), 3.35 (d, CH_2, J = 7.3 Hz, 2H), 3.70 (s, OCH_3, 6 H), 4.09 (t, CH, J = 7.3 Hz, 1

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(8) DMF in light slowly releases HCN; therefore care must be taken to prevent decomposition. [Newkome, G. R.; Robinson, J. M. *Tetrahedron Lett.* **1974**, 691; Trisler, J. C.; Freasier, B. F.; Wu, S.-M. *Ibid.* **1974**, 687.]

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H), 6.96 (d, 3,5-pyH, J = 7.9 Hz, 2 H), 7.45 (dd, 4-pyH, J = 7.9 Hz, 1 H); IR (neat) 1740 (C=O), 1590, 1575, 1455 cm^{-1}; MS, m/e 237 (M^+, 6), 206 (M^+ - OMe, 16), 178 ($M^+ - C_2H_3O_2$, 87), 146 ($M^+ - C_3H_7O_3$, *100*). Anal. Calcd for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37; N, 5.90. Found: C, 60.68; H, 6.41; N, 5.89.

2-[2,2-Bis(carbomethoxy)ethyl]pyrazine (1e) was prepared from 2-(chloromethyl)pyrazine:[7] microcrystals; mp 51–52 °C; 2 g (89%); R_f 0.12; ^1H NMR δ 3.43 (d, CH_2, J = 7.3 Hz, 2 H), 3.74 (s, OCH_3, 6 H), 4.11 (t, CH, J = 7.3 Hz, 1 H), 8.44 (2 d, 5,6-pyra-H, J = 7.3 Hz, 2 H), 8.52 (bs, 3-pyra-H, 1 H); IR (CsI) 1715 (C=O), 1575, 1520, 1470, 1430 cm^{-1}; MS, m/e 224 (M^+, 2), 193 (M^+ - OMe, 12), 165 ($M^+ - C_2H_3O_2$, 77), 133 ($M^+ - C_3H_7O_3$, *100*). Anal. Calcd for $C_{10}H_{12}N_2O_4$: C, 53.57; H, 5.39; N, 12.49. Found: C, 53.39; H, 5.31; N, 12.38.

3-Methyl-2-[2,2-bis(carbomethoxy)ethyl]pyrazine (1f) was prepared from 2-(chloromethyl)-3-methylpyrazine:[7] oil; 1.67 g (70%); R_f 0.1; ^1H NMR δ 2.59 (s, pyra-CH_3, 3H), 3.42 (d, CH_2, J = 7.3 Hz, 2H), 3.75 (s, OCH_3, 6 H), 4.26 (t, CH, J = 7.3 Hz, 1 H), 8.26, 8.28 (2 d, 5,6-pyra-H, J = 5.5 Hz, 2 H); IR (neat) 1730 (C=O), 1525, 1430 cm^{-1}; MS, m/e 238 (M^+, 6), 207 (M^+ - OMe, 11), 179 ($M^+ - C_2H_3O_2$, 43), 147 ($M^+ - C_3H_7O_3$, *100*). Anal. Calcd for $C_{11}H_{14}N_2O_4$: C, 55.46; H, 5.92; N, 11.76. Found: C, 55.21; H, 6.14; N, 11.58.

5-Methyl-2-[2,2-bis(carbomethoxy)ethyl]pyrazine (1g) was prepared from 2-(chloromethyl)-5-methylpyrazine:[7] needles; 1.74 g (73%); mp 128–129 °C; R_f 0.08; ^1H NMR δ 2.53 (s, pyra-CH_3, 3H), 3.39 (d, CH_2, J = 7.3 Hz, 2 H), 3.77 (s, OCH_3, 6 H), 4.08 (t, CH, J = 7.3 Hz, 1 H), 8.36, 8.39 (2 s, 3- and 6-pyra-H, 2 H); IR (CsI) 1730 (C=O), 1485, 1435 cm^{-1}; MS, m/e 238 (M^+, 4), 207 (M^+ - OMe, 8), 179 ($M^+ - C_2H_3O_2$, 48), 147 ($M^+ - C_3H_7O_3$, *100*). Anal. Calcd for $C_{11}H_{14}N_2O_4$: C, 55.46; H, 5.92; N, 11.76. Found: C, 55.31; H, 5.89; N, 11.67.

6-Methyl-2-[2,2-bis(carbomethoxy)ethyl]pyrazine was prepared from 2-(chloromethyl)-6-methylpyrazine:[7] oil; 1.81 g (76%); R_f 0.1; ^1H NMR δ 2.48 (s, 6-pyra-CH_3, 3H), 3.38 (d, CH_2, J = 7.3 Hz, 2 H), 3.72 (s, OCH_3, 6 H), 4.09 (t, CH, J = 7.3 Hz, 1 H), 8.30, 8.32 (2 s, 3- and 5-pyra-H, 2 H); IR (neat) 1725 (C=O), 1525, 1430 cm^{-1}; MS m/e 238 (M^+, 6), 207 (M^+ - OMe, 9) 179 ($M^+ - C_2H_3O_2$, 59), 147 ($M^+ - C_3H_7O_3$, *100*). Anal. Calcd for $C_{11}H_{14}N_2O_4$: C, 55.46; H, 5.92 N, 11.76. Found: C, 55.40; H, 5.86; N, 11.71.

General Preparation of the Complexes. A mixture of the 2-[2,2-bis(carbomethoxy)ethyl]pyridine or -pyrazine (1 mmol) and anhydrous potassium carbonate (500 mg) in acetonitrile (20 mL) was stirred at 25 °C for 30 min. Then palladium(II) chloride (0.5 mmol) in warm acetonitrile (30 mL) was added, followed by stirring at 25 °C under a nitrogen atmosphere for 20 h. The heterogeneous mixture was filtered and then concentrated in vacuo to give the crude complex, which was recrystallized from chloroform/methanol to afford the yellow crystalline product. Ligands **1d** and **1h** did *not* form complexes under these conditions.

***trans*-Bis{2-[2,2-bis(carbomethoxy)ethyl]pyridine}palladium(II) (4a)** was prepared from pyridine **1a**: yellow rhomboid-shaped crystals; 250 mg (91%); mp 189–191 °C dec; ^1H NMR δ 3.40 (s, CH_3, 12 H), 3.75 (s, CH_2, 4 H), 7.17 (dd, 5-pyH, $J_{4,5}$ = 7.9 Hz, $J_{5,6}$ = 5.7 Hz, 2 H), 7.33 (d, 3-pyH, J = 7.9 Hz, 2 H), 7.70 (dd, 4-pyH, $J_{3,4} = J_{4,5}$ = 7.9 Hz, 2 H), 9.06 (d, 6-pyH, J = 5.7 Hz, 2 H); IR (CsI) 1670 (C=O), 1560, 1480, 1430 cm^{-1}; MS, m/e 328 ($M^+ - C_{11}H_{12}NO_4$, 25), 190 ($M^+ - C_{12}H_{16}NO_5Pd$, 84), 132 ($M^+ - C_{14}H_{18}NO_7Pd$, *100*). Anal. Calcd for $C_{22}H_{24}N_2O_8Pd$: C, 47.97; H, 4.39; N, 5.09. Found: C, 47.87; H, 4.42; N, 5.06.

***trans*-Bis{4-methyl-2-[2,2-bis(carbomethoxy)ethyl]pyridine}palladium(II) (4b)** was prepared from pyridine **1b**: yellow crystals; 173 mg (60%); mp 158–161 °C dec; ^1H NMR δ 2.36 (s, 4-pyCH_3, 6 H), 3.42 (s, OCH_3, 12 H), 3.67 (s, CH_2, 4 H), 6.96 (dd, 5-pyH, $J_{5,6}$ = 6.1 Hz, $J_{3,5}$ = 1.8 Hz, 2 H), 7.15 (d, 3-pyH, $J_{3,5}$ = 1.8 Hz, 2 H), 8.84 (d, 6-pyH, J = 6.1 Hz, 2 H); IR (CsI) 1680 (b, C=O), 1428, 1062 cm^{-1}. Anal. Calcd for $C_{24}H_{28}N_2O_8Pd$: C, 49.80; H, 4.88; N, 4.84. Found: C, 49.71; H, 5.08; N, 4.63.

***trans*-Bis{5-methyl-2-[2,2-bis(carbomethoxy)ethyl]pyridine}palladium(II) (4c)** was prepared from pyridine **1c**: yellow microcrystals; 179 mg (62%); mp 89–91 °C dec; ^1H NMR δ 2.35 (s, 5-pyCH_3, 6H), 3.40 (s, OCH_3, 12 H), 3.77 (s, CH_2, 4 H), 7.20 (d, 3-pyH, J = 7.9 Hz, 2 H), 7.49 (dd, 4-pyH, $J_{3,4}$ = 7.9 Hz, $J_{4,6}$ = 1.8 Hz, 2 H), 8.88 (d, 6-pyH, $J_{4,6}$ = 1.8 Hz, 2 H); IR (CsI) 1730–1670 (b, C=O), 1495, 1430, 1065 cm^{-1}. Anal. Calcd for $C_{24}H_{28}N_2O_8Pd$: C, 49.80; H, 4.88; N, 4.84. Found: C, 49.52; H, 4.98; N, 4.76.

***trans*-Bis{2-[2,2-bis(carbomethoxy)ethyl]pyrazine}palladium(II) (4e)** was prepared from pyrazine **1e**: yellow crystals; 220 mg (80%); 89–91 °C dec; ^1H NMR δ 3.46 (s, OCH_3, 12 H), 3.74 (s, CH_2, 4 H), 8.55 (d, 5-pyra-H, J = 3.1 Hz, 2 H), 8.74 (s, 3-pyra-H, 2 H), 9.16 (d, 6-pyra-H, $J_{5,6}$ = 3.1 Hz, 2 H); IR (CsI) 1700–1645 (C=O), 1520, 1425, 1050 cm^{-1}. Anal. Calcd for $C_{20}H_{22}N_4O_8Pd$: C, 43.45; H, 4.01; N, 10.13. Found: C, 43.36; H, 4.18; N, 10.02.

***trans*-Bis{3-methyl-2-[2,2-bis(carbomethoxy)ethyl]pyrazine}palladium(II) (4f)** was prepared from pyrazine **1f**: yellow crystals; 203 mg (70%); mp 51–52 °C; ^1H NMR δ 2.68 (s, 3-pyra-CH_3, 6 H), 3.46 (s, OCH_3, 12 H), 3.70 (s, CH_2, 4 H), 8.41 (d, 5-pyra-H, J = 3.0 Hz, 2 H), 8.96 (d, 6-pyra-H, J = 3.0 Hz, 2 H); IR (CsI) 1710–1680 (C=O), 1425, 1060 cm^{-1}. Anal. Calcd for $C_{22}H_{26}N_4O_8Pd$: C, 45.49; H, 4.51; N, 9.65. Found: C, 45.22, H, 4.79, N, 9.56.

***trans*-Bis{5-methyl-2-[2,2-bis(carbomethoxy)ethyl]pyrazine}palladium(II) (4g)** was prepared from pyrazine **1g**: yellow microcrystals; 255 mg (88%); mp 85–86 °C; ^1H NMR δ 2.64 (s, 5-pyra-CH_3, 6 H), 3.45 (s, OCH_3, 12 H), 3.77 (s, CH_2, 4H), 8.60 (s, 3-pyra-H, 2 H), 9.02 (s, 6-pyra-H, 2 H); IR (CsI) 1710–1670 (C=O), 1485, 1430, 1060 cm^{-1}. Anal. Calcd. for $C_{22}H_{26}N_4O_8Pd$: C, 45.49; H, 4.51; N, 9.65. Found: C, 45.26; H, 4.64; N, 9.58.

X-ray Experimental Data. Intensity data were collected from a yellow crystal of dimensions 0.12 × 0.32 × 0.44 mm at T = 24 ± 2 °C. Cell dimensions and crystal orientation were determined from diffractometer coordinates of 25 accurately centered reflections having 33° ≤ θ ≤ 44°.

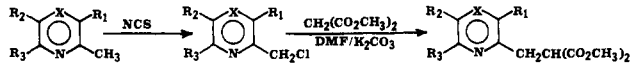
Crystal Data: $PdC_{22}H_{24}N_2O_8$ mol wt 550.9; triclinic space group $P\bar{1}$; a = 11.308 (2) Å, b = 13.765 (2) Å, c = 8.412 (2) Å, α = 107.78 (1)°, β = 111.81 (1)°, γ = 91.65 (1)°, Z = 2, d_{calcd} = 1.601 g cm^{-3}, λ = 1.541 84 Å, μ(Cu K_α) = 72.2 cm^{-1}. Intensity data were collected by the θ–2θ scan technique at variable rates designed to yield $I \simeq 50\sigma(I)$ for all significant data. The scan rate was determined during a 20° min^{-1} prescan, reflections failing to have $I > \sigma(I)$ during the prescan were flagged as unobserved, and the maximum time spent on a single scan was 120 s. All data in one hemisphere having 2° ≤ θ ≤ 75° were thus measured. Three periodically remeasured standard reflections were used to correct for crystal decay, which amounted to 18% of the original intensities. Background, Lorentz, and polarization corrections were applied to the data. Absorption corrections were applied by using an empirical method based upon ψ scans of reflections near χ = 90°. The minimum relative transmission coefficient was 75.7%. Of the 4709 unique data measured, 3642 had $F > 3\sigma(F)$ and were used in the refinement.

Results and Discussion

A. Ligand Synthesis. Lutidines, methylpyrazine, or dimethylpyrazines (**2**) on chlorination with *N*-chlorosuccinimide (NCS) in carbon tetrachloride gave a mixture of diverse halomethyl products. The reaction conditions were varied in order to obtain the desired 2-(chloromethyl)pyridine or -pyrazine derivatives (**3**), as the major product. Numerous polyhalogenated compounds were also obtained and characterized and will be reported in detail elsewhere.[7] The product distribution can, in most cases, be analyzed by NMR spectrometry through the appearance of a singlet (ca. δ 4.7) for the CH_2Cl group and the diminished spike (ca. δ 2.55) for the methyl substituent.

Treatment of these halomethyl reagents with dimethyl malonate and anhydrous potassium carbonate in dry N,N-dimethylformamide[8] gave the desired ligands **1** in excellent yields. In view of the precautions necessary in handling these halomethyl compounds and their instability as the free base, it was advantageous to analyze (NMR) the crude mixtures, calculate the conversion yield, and use the mixture directly in the ligand synthesis. This technique circumvented the isolation of the obnoxious α-chloromethyl intermediates; *care must be exercised in handling all of these halomethyl derivatives since they*

are extremely irritating to the skin and mucous membranes. [Other detrimental properties of these compounds have been recently demonstrated (NCI): 3-chloromethylpyridine is a carcinogen, in rats, whereas the 2 isomer is not (personal communication of Dr. T. D. Bailey, Reily Tar and Chemical Corp.). Thus *EXTREME CARE* must be taken in view of the potential alkylating properties—common with all of these α-halomethyl starting materials.] Other byproducts from the halogenation procedure (e.g., starting materials and dihalo- and trihalomethyl compounds) do not react under these alkylating conditions.

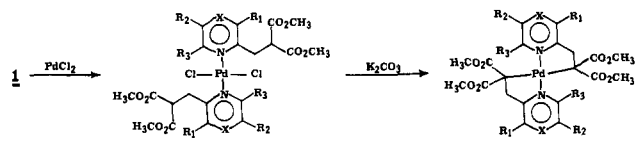


2 3 1

a, X = CH, $R_1 = R_2 = R_3 = H$; b, X = CMe, $R_1 = R_2 = R_3 = H$; c, X = CH, $R_1 = R_3 = H$, $R_2 = Me$; d, X = CH, $R_1 = R_2 = H$, $R_3 = Me$; e, X = N, $R_1 = R_2 = R_3 = H$; f, X = N, $R_1 = Me$, $R_2 = R_3 = H$; g, X = N, $R_1 = R_3 = H$, $R_2 = Me$; h, X = N, $R_1 = R_2 = H$, $R_3 = Me$

The NMR spectral data for 1 showed a characteristic doublet (J = 7.3 Hz) at δ 3.34–3.43 for the heteroaryl methylene and a triplet at δ 4.08–4.26 for the adjacent methine proton. The carbomethoxy moiety showed a spike at δ 3.67–3.77, and interestingly none of these malonate ligands exhibited any detectable enolization at 30 °C in deuteriochloroform. The carbonyl absorption of the free ligands was observed at 1765–1715 cm^{-1}.

B. Complex Formation. An acetonitrile solution of 1 was treated with 0.5 equiv of $PdCl_2$ and anhydrous potassium carbonate. After 20 h of stirring at ambient temperature, the desired complexes were isolated as yellow crystals. The initial trans bis N-bonded complex **5** was slowly transformed into **4** via stepwise, intramolecular Pd–C bond formation. The intermediate complex **5** can be isolated as a stable crystalline compound.



5 4

a, X = CH, $R_1 = R_2 = R_3 = H$; b, X = CMe, $R_1 = R_2 = R_3 = H$; c, X = CH, $R_1 = R_3 = H$, $R_2 = Me$; d, X = CH, $R_1 = R_2 = H$, $R_3 = Me$; e, X = N, $R_1 = R_2 = R_3 = H$; f, X = N, $R_1 = Me$, $R_2 = R_3 = H$; g, X = N, $R_1 = R_3 = H$, $R_2 = Me$

The 200-MHz ^1H NMR spectra of **4** show a spike at δ 3.74–3.77 for the pyridine (or pyrazine) α-methylenic hydrogens indicative of a symmetry plane through the N–Pd–N axis. The singlet at δ 3.40–3.46 for the methyl ester suggests that all methyl groups are in a magnetically equivalent environment. As a result of complexation, the H_3, H_4, and/or H_5 pyridine hydrogens or the H_3 and/or H_5 pyrazine hydrogens are shifted downfield by 0.1–0.2 ppm, whereas H_6 experiences a much more dramatic downfield shift (0.5–0.7ppm). The IR spectra of **4** exhibit a very strong carbonyl absorption at 1730–1645 cm^{-1}; the 50–70-cm^{-1} shift upon complexation is further supportive of the palladium–carbon σ bonds. From CPK models, it was anticipated that the complex should have a trans geometry with the H_6 hydrogen being forced into the immediate vicinity of the ester groups. The cis structure has been disregarded on the basis of steric effects caused by the interaction of the heteroaromatic 6-positions and the juxtaposition of the two malonate moieties.

Table I. Bond Distances (Å) in Complex 4a

Pd-N(1)	2.040 (3)	Pd-N(2)	2.042 (3)
Pd-C(7)	2.156 (2)	Pd-C(18)	2.142 (2)
N(1)-C(1)	1.344 (4)	N(2)-C(12)	1.341 (3)
N(1)-C(5)	1.338 (4)	N(2)-C(16)	1.346 (4)
C(1)-C(2)	1.377 (4)	C(12)-C(13)	1.382 (4)
C(2)-C(3)	1.371 (6)	C(13)-C(14)	1.425 (6)
C(3)-C(4)	1.354 (5)	C(14)-C(15)	1.376 (5)
C(4)-C(5)	1.385 (4)	C(15)-C(16)	1.379 (4)
C(5)-C(6)	1.498 (4)	C(16)-C(17)	1.494 (4)
C(6)-C(7)	1.522 (4)	C(17)-C(18)	1.545 (3)
C(7)-C(8)	1.481 (3)	C(18)-C(19)	1.500 (3)
C(7)-C(9)	1.490 (3)	C(18)-C(20)	1.460 (3)
O(1)-C(8)	1.209 (3)	O(5)-C(19)	1.200 (3)
O(2)-C(8)	1.348 (3)	O(6)-C(19)	1.341 (3)
O(2)-C(10)	1.435 (3)	O(6)-C(21)	1.439 (3)
O(3)-C(9)	1.204 (3)	O(7)-C(20)	1.211 (3)
O(4)-C(9)	1.341 (3)	O(8)-C(20)	1.348 (3)
O(4)-C(11)	1.424 (3)	O(8)-C(22)	1.435 (3)

The substitution of H_6 with methyl groups sterically retards complex formation (for example, with **1d** and **1h**). For establishment of a better picture of the juxtaposed substituent interactions and conformation of the regiochemistry of these complexes, a single-crystal X-ray analysis of **4a** was undertaken.

C. Structure Solution and Refinement. The structure of **4a** was solved by routine heavy-atom methods. Refinement was carried out by weighted full-matrix least-squares methods based upon F, where the weights were $\sigma^{-2}(F_o)$. The variances were based on counting statistics and included a term $(0.05I)^2$. Calculations were performed on a PDP 11/34 computer using the Enraf-Nonius SDP system of programs. Non-hydrogen atoms were treated anisotropically. Hydrogen atoms were located from difference maps and included as fixed contributions. Secondary extinction was a problem and an extinction coefficient refined to a value of 4.39 (2) × 10^{-5}. Convergence was achieved with R = 0.043, R_w = 0.068, and GOF = 2.502 based on observed data. The maximum residual in a final ΔF map was 0.55 e $Å^{-3}$ associated with palladium.

The central Pd atom in **4a** is σ bonded with two carbon atoms and coordinated by two pyridine nitrogen atoms corroborating the net overall square-planar trans configuration having nearly C_2 symmetry (Figure 1). The pyridine rings are not coplanar with each other; the dihedral angle is 63.0°. Palladium and the coordinating atoms N(1), C(7), N(2), and C(18) approximate a plane, but the carbon atoms C(7) and C(18) are bent away from the molecular C_2 axis, forming a C–Pd–C angle of 168.63 (9)° (Table II). Displacements from the mean coordination plane are 0.129 (3) Å for C(7) and 0.130 (3) Å for C(18). The Pd–N bond lengths (average 2.041 Å) are experimentally equal and are comparable to those in similar palladium(II)–pyridine complexes[9] whereas, the Pd(II)–C(sp^3) bonds differ but are typical.[9b,10] The heteroaromatic rings exhibit normal geometries; the C–C distances average 1.381 Å and C–N distances average 1.342 Å. Distances and angles within the four carbomethoxy groups show excellent internal agreement as well as agreement with accepted values. No unusual intermole-

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Table II. Selected Bond Angles (Deg) in Complex 4a

N(1)-Pd-N(2)	179.70 (6)	N(1)-C(5)-C(4)	120.5 (3)	C(13)-C(14)-C(15)	119.0 (3)
N(1)-Pd-C(7)	79.6 (1)	N(1)-C(5)-C(6)	114.2 (2)	C(14)-C(15)-C(16)	119.6 (3)
N(1)-Pd-C(18)	99.9 (1)	C(4)-C(5)-C(6)	125.4 (3)	N(2)-C(16)-C(15)	121.2 (3)
N(2)-Pd-C(7)	100.2 (1)	C(5)-C(6)-C(7)	110.7 (2)	N(2)-C(16)-C(17)	114.9 (2)
N(2)-Pd-C(18)	80.3 (1)	C(6)-C(7)-C(8)	111.5 (2)	C(15)-C(16)-C(17)	123.9 (3)
C(7)-Pd-C(18)	168.63 (9)	C(6)-C(7)-C(9)	111.1 (2)	C(16)-C(17)-C(18)	110.1 (2)
C(8)-O(2)-C(10)	116.3 (3)	C(8)-C(7)-C9)	118.3 (2)	C(17)-C(18)-C(19)	110.0 (2)
C(9)-O(4)-C(11)	116.4 (3)	O(1)-C(8)-O(2)	121.1 (2)	C(17)-C(18)-C(20)	110.2 (2)
C(19)-O(6)-C(21)	116.4 (3)	O(1)-C(8)-C(7)	123.8 (2)	C(19)-C(18)-C(20)	118.5 (2)
C(20)-O(8)-C(22)	117.3 (3)	O(2)-C(8)-C(7)	114.9 (2)	O(5)-C(19)-O(6)	121.8 (2)
C(1)-N(1)-C(5)	119.2 (3)	O(3)-C(9)-O(4)	121.6 (3)	O(5)-C(19)-C(18)	124.5 (3)
C(12)-N(2)-C(16)	120.2 (3)	O(3)-C(9)-C(7)	124.1 (3)	O(6)-C(19)-C(18)	113.4 (2)
N(1)-C(1)-C(2)	121.8 (3)	O(4)-C(9)-C(7)	114.3 (2)	O(7)-C(20)-O(8)	120.8 (3)
C(1)-C(2)-C(3)	118.8 (3)	N(2)-C(12)-C(13)	121.5 (3)	O(7)-C(20)-C(18)	124.5 (3)
C(2)-C(3)-C(4)	119.3 (3)	C(12)-C(13)-C(14)	117.8 (3)	O(8)-C(20)-C(18)	114.7 (2)
C(3)-C(4)-C(5)	120.2 (3)				

Table III. Table of Coordinates for 4a

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Pd	0.24998 (2)	0.25001 (1)	−0.00283 (2)	C(7)	0.3746 (3)	0.1354 (2)	−0.0232 (4)
O(1)	0.3346 (3)	0.0102 (2)	0.1002 (3)	C(8)	0.3857 (3)	0.0950 (2)	0.1251 (4)
O(2)	0.4505 (3)	0.1630 (2)	0.2947 (3)	C(9)	0.4950 (3)	0.1822 (2)	−0.0235 (4)
O(3)	0.4999 (3)	0.2058 (2)	−0.1478 (3)	C(10)	0.4571 (5)	0.1281 (4)	0.4416 (5)
O(4)	0.6012 (2)	0.1944 (2)	0.1269 (3)	C(11)	0.7190 (4)	0.2380 (3)	0.1323 (6)
O(5)	0.1649 (3)	0.4903 (2)	0.2554 (3)	C(12)	0.5000 (3)	0.3922 (3)	0.2635 (4)
O(6)	0.0500 (2)	0.3377 (2)	0.1818 (3)	C(13)	0.5851 (4)	0.4843 (3)	0.3480 (5)
O(7)	0.0018 (3)	0.2945 (2)	−0.3521 (3)	C(14)	0.5465 (4)	0.5688 (3)	0.2873 (6)
O(8)	−0.1007 (2)	0.3067 (2)	−0.1682 (3)	C(15)	0.4255 (4)	0.5566 (3)	0.1536 (5)
N(1)	0.1168 (3)	0.1182 (2)	−0.1350 (3)	C(16)	0.3444 (3)	0.4632 (3)	0.0805 (4)
N(2)	0.3837 (2)	0.3817 (2)	0.1306 (3)	C(17)	0.2089 (3)	0.4437 (2)	−0.0575 (4)
C(1)	0.0003 (3)	0.1064 (3)	−0.1291 (4)	C(18)	0.1249 (3)	0.3630 (2)	−0.0340 (4)
C(2)	−0.0829 (4)	0.0138 (3)	−0.2213 (5)	C(19)	0.1137 (3)	0.4061 (2)	0.1456 (4)
C(3)	−0.0471 (5)	−0.0671 (3)	−0.3266 (6)	C(20)	0.0067 (3)	0.3195 (2)	−0.1985 (4)
C(4)	0.0721 (4)	−0.0563 (3)	−0.3271 (5)	C(21)	0.0420 (4)	0.3720 (4)	0.3566 (5)
C(5)	0.1550 (3)	0.0369 (2)	−0.2275 (4)	C(22)	−0.2198 (4)	0.2636 (4)	−0.3245 (6)
C(6)	0.2911 (3)	0.0571 (3)	−0.2093 (4)				

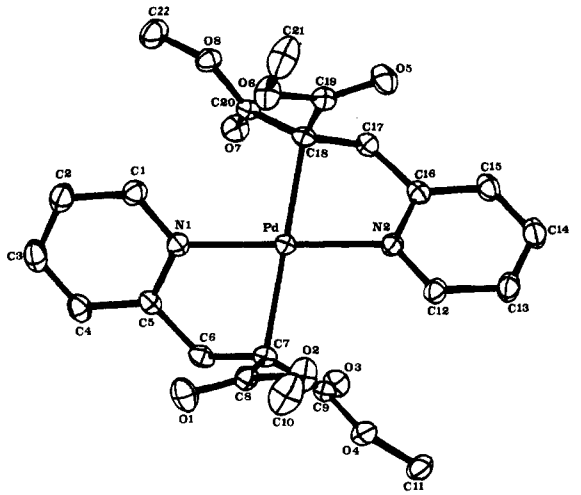

Figure 1. ORTEP drawing of trans bis[2-[2,2-bis(carbomethoxy)ethyl]pyridine]palladium(II). Hydrogen atoms have been omitted for clarity.

cular contacts are noted. Bond distances and angles are listed in Tables I and II; coordinates of nonhydrogen atoms are given in Table III.

D. Obstacle Effects. The nature of substituents on C(1) or C(12) (Figure 1; e.g., R_3 in **4**) is critical with respect to complex formation. The enhanced downfield shift shown for H_6 is indicative of a strong proximal interaction between H_6 and the adjacent carbomethoxy group(s). When R_3 = Me (e.g., **1d** and **1h**), no C-metalated products were detected; this is suggestive of a strong steric repulsion caused by C(1) and/or C(12) substituents and is supportive of the so-called "obstacle effect".[6] Such an interaction between the methyl group(s) and carbomethoxy functionality inhibits the approach of the anion sites at C(7) or C(18) to the palladium core. Methyl substituents present elsewhere on the heteroaromatic rings (i.e., **4b**, **4c**, **4f**, and **4g**) had little or no effect on the formation of the Pd–C bonds.

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Registry No. 1a, 13470-57-0; **1b**, 81831-60-9; 1c, 81831-61-0; **1d**, 81831-62-1; **1e**, 81831-63-2; **1f**, 81831-64-3; **1g**, 81831-65-4; **1h**, 81831-66-5; **3a** HCl, 6959-47-3; **3b**, 38198-16-2; **3c**, 767-01-1; **3d**, 3099-29-4; **3e**, 39204-47-2; **3f**, 81831-67-6; **3g**, 81831-68-7; **3h**, 81831-69-8; **4a**, 81831-06-3; **4b**, 81831-07-4; **4c**, 81831-08-5; **4e**, 81831-09-6; **4f**, 81831-10-9; **4g**, 81846-74-7.

Supplementary Material Available: Tables of the coordinates of hydrogen atoms and anisotropic thermal parameters and a listing of observed and calculated structure factors for complex **4a** (19 pages). Ordering information is given on any current masthead page.