

Reactivity of [Pd(C[^]N)(C₆F₅)(NCMe)] (C[^]N = ((Dimethylamino)methyl)phenyl-C²,N, 8-Quinolylmethyl-C,N) toward 2,2'-Bipyridine or 1,10-Phenanthroline. Synthesis and Structures of [[Pd(8-mq)(C₆F₅)₂(μ-bpy)] and [(C₆F₅)(8-mq)Pd(μ-8-mq)Pd(C₆F₅)(phen)], Dinuclear Complexes Containing Unusual 2,2'-Bipyridine or Unprecedented 8-Quinolylmethyl-C,N Acting as Bridging Ligands

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[Pd(dmba)(C₆F₅)(NCMe)] (**A**) (dmba = ((dimethylamino)methyl)phenyl-C²,N) reacts with bpy or phen (N-N), yielding the corresponding mononuclear derivatives [Pd(dmba)(C₆F₅)(N-N)] (N-N = bpy (**1**), phen (**2**)) irrespective of the molar ratio used (1:1 or 2:1). [Pd(8-mq)(C₆F₅)(NCMe)] (**B**) (8-mq = 8-quinolylmethyl-C,N) reacts with bpy (molar ratio 1:1 or 2:1), yielding [Pd(8-mq)(C₆F₅)₂(μ-bpy)] (**4**), a dinuclear compound containing 2,2'-bipyridine acting as a bridging ligand. The reactions of **B** with phen (molar ratio 1:1) renders the mononuclear four-coordinated derivative [Pd(8-mq)(C₆F₅)(phen)] (**3**) while the reaction in a 2:1 molar ratio renders [(C₆F₅)(8-mq)Pd(μ-8-mq)Pd(C₆F₅)(phen)] (**5**), a dinuclear compound containing one 8-mq group coordinated as a chelate ligand and the other acting as an unprecedented bridging one. The structural behaviors of these complexes have been established on the bases of ¹H and ¹⁹F NMR spectra and the X-ray structure of compounds **2**, **4**, and **5**. Crystal data for complex **2**: monoclinic P2₁/c, *a* = 12.651(3) Å, *b* = 9.982(2) Å, *c* = 19.351(4) Å, β = 91.27(3)°, *Z* = 4, *R* = 0.056. Crystal data for complex **4**: monoclinic C2/c, *a* = 9.8801(4) Å, *b* = 24.8399(12) Å, *c* = 34.1826(16) Å, β = 95.352(8)°, *Z* = 8, *R* = 0.058. Crystal data for complex **5**: monoclinic P2₁/c, *a* = 12.3935(5) Å, *b* = 12.9381(6) Å, *c* = 24.1387(12) Å, β = 102.72(4)°, *Z* = 4, *R* = 0.034.

Introduction

Dimethylbenzylamine and 8-methylquinoline have been used as precursors of cyclometalating ligands, for the synthesis of five-membered-ring complexes containing the ((dimethylamino)methyl)phenyl-C²,N (dmba) or the 8-quinolylmethyl-C,N (8-mq) groups acting as C,N chelating ligands (C[^]N).¹ As far as we are aware, no complexes containing one of these C[^]N groups (dmba or 8-mq) acting as bridging ligands have been described.

Recently we reported the synthesis of [Pd(C[^]N)(C₆F₅)(NCMe)] complexes and studied their reactivity toward neutral (phosphines) or anionic (halides) monodentate ligands.² In all cases, displacement of acetonitrile takes place, but it is interesting to notice that because of the high lability of acetonitrile, dinuclear complexes containing single bridging halide ligands [(NBu₄)-[Pd(C[^]N)(C₆F₅)₂(μ-X)]] can be obtained by adequate choice of the molar ratio of the reactants.²

In this paper, we study the reactions between the above mentioned (acetonitrile)palladium substrates [Pd(C[^]N)(C₆F₅)(NCMe)] (C[^]N = dmba (**A**), 8-mq (**B**)) and 2,2'-bipyridine or 1,10-phenanthroline (N-N) in different molar ratios (1:1 or 2:1). The purpose of the 1:1 reactions was to establish whether square-planar mononuclear complexes (with one of the typical bidentate chelate C[^]N or N-N ligands acting as monodentate) or five-coordinated species were formed. On the other hand, the 2:1 reactions were carried out with the aim of forcing the formation of dinuclear complexes containing either C[^]N or N-N acting as bridging ligands, since such structural behavior would be most unusual for either the anionic C[^]N or the neutral N-N ligands which usually behave as chelating ligands.

The resulting products of these reactions are dependent on the C[^]N and on the N-N ligands. Preliminary results have been reported earlier.³

Experimental Section

General Information. C, H, and N analyses, infrared spectroscopy, and ¹H and ¹⁹F NMR spectroscopy were performed as described elsewhere.⁴ The starting materials [Pd(dmba)(C₆F₅)(NCMe)] (**A**) and [Pd(8-mq)(C₆F₅)(NCMe)] (**B**) were prepared as described previously.²

Synthesis of Complexes. [Pd(dmba)(C₆F₅)(N-N)] (N-N = bpy (**1**), phen (**2**)). **Compound 1.** To a solution of 0.178 g (0.397 mmol) of **A** in 10 mL of CH₂Cl₂ was added 0.062 g (0.397 mmol) of bpy, and the mixture was stirred at room temperature for 15 min. The resulting yellow solution was evaporated to ca. 5 mL, and the addition of *n*-hexane (10 mL) rendered **1** (88% yield). Anal. Calcd for C₂₃F₅H₂₀N₃Pd: C, 53.25; H, 3.57; N, 7.45. Found: C, 53.64; H, 3.53; N, 7.50. Relevant IR absorptions (cm⁻¹): C₆F₅⁵ 1495 (vs), 1051 (vs), 948 (s), 776 (s); bpy⁶ 1596 (s), 760 (vs), 411 (vs); dmba 851 (m), 738 (vs). ¹H NMR^{7a} in CDCl₃ at 20 °C (δ): bpy 8.25 (d, H(6), H(6')), *J*₆₋₅ = 8.2 Hz), 8.17 (d, H(3), H(3')), *J*₃₋₄ = 4.5 Hz), 7.97 (m, H(5), H(5')), 7.38 (m, H(4), H(4')); dmba 7.38 (H(A)), 7.19 (d, H(D), *J*_{D-C} = 6.7 Hz), 6.93 (m, H(B), H(C)), 3.90 (s, CH₂), 2.12 (s, NMe₂). ¹H NMR⁷ in CD₂Cl₂ at -90 °C (δ): bpy 8.16 (m, H(6), H(6')), 8.01 (m, H(5), H(5')), 7.80 (d, H(3), *J*₃₋₄ = 4.72 Hz), 7.56 (d, H(3')), *J*_{3'-4'} = 4.72 Hz), 7.39 (m, H(4)),

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- (2) Forniés, J.; Navarro, R.; Sicilia, V.; Martínez, F.; Welch, A. J. *J. Organomet. Chem.* 1991, 408, 425.

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- (5) Maslowsky, E., Jr. *Vibrational Spectra of Organometallic Compounds*; Wiley: New York, 1977; p 437 and references therein.
- (6) Uson, R.; Forniés, J.; Gimeno, J.; Espinet, P.; Navarro, R. *J. Organomet. Chem.* 1974, 81, 115.
- (7) (a) Proton signals due to phen or bpy have been assigned by taking into account that *J*₃₋₄ > *J*₂₋₃ (phen) or that *J*₃₋₄ > *J*_{3-4'} (bpy).^{8,9} An NOE experiment on **2** confirms this assignment. Proton labeling is shown in Figure 1. (b) The assignment of these signals has been carried out by using a Varian Unity (300 MHz) and selective homodecoupling.
- (8) Dixon, K. R. *Inorg. Chem.* 1977, 16, 2618.
- (9) Kramer, F. A., Jr.; West, R. *J. Phys. Chem.* 1965, 69, 673.

7.27 (m, H(4')); dmba 7.50 (d, H(A)) $J_{A-B} = 7.4$ Hz), 7.18 (d, H(D)), $J_{D-C} = 7.4$ Hz), 6.92 (t), 6.81 (t) (H(B), H(C)), $J_{B-C} = 7.4$ Hz), 3.76 (d), 4.00 (d) (CH_2 , $^2J_{H-H} = 12$ Hz), 2.07 (s, NMe_2). ^{19}F NMR in CDCl_3 at 20 °C (δ): -115.7 (Fo), -164.8 (Fm), -163.4 (Fp).

Compound 2 was obtained similarly from 0.228 g (0.509 mmol) of A and 0.100 g (0.509 mmol) of phen- H_2O in 20 mL of CH_2Cl_2 . The resulting yellow solution was evaporated to dryness and the residue washed with 20 mL of diethyl ether (65% yield). Anal. Calcd for $\text{C}_{27}\text{F}_5\text{H}_{20}\text{N}_3\text{Pd}$: C, 55.16; H, 3.43; N, 7.14. Found: C, 54.73; H, 3.54; N, 6.98. Relevant IR absorptions (cm^{-1}): C_6F_5^5 1496 (vs), 1054 (vs), 948 (s), 781 (s); phen⁶ 845 (vs); dmba 867 (m), 745 (vs). ^1H NMR^{7a} in CDCl_3 at 20 °C (δ): phen 8.47 (d, H(4)), H(7), $J_{4-3} = J_{7-8} = 8.1$ Hz), 8.17 (d, H(2), H(9)), $J_{2-3} = J_{9-8} = 4.0$ Hz), 7.97 (s, H(5), H(6)), 7.68 (m, H(3), H(8)); dmba 7.78 (d, H(A)), $J_{A-B} = 6.9$ Hz), 7.35 (d, H(D)), $J_{D-C} = 6.7$ Hz), 7.02 (m, H(B), H(C)), 4.03 (s, CH_2), 2.17 (s, NMe_2). ^1H NMR⁷ in CD_2Cl_2 at -90 °C (δ): phen 7.75 (d, H(2), $J_{2-3} = 4.4$ Hz), 7.52 (dd, H(3), $J_{3-4} = 8.0$ Hz), 8.50 (d, H(4)), 7.80 (ν_A), 7.87 (ν_B) (AB system, H(5), H(6)), 8.43 (d, H(7), $J_{7-8} = 8.0$ Hz), 7.69 (m, H(8), overlapped with H(A) of dmba), 8.1 (d, $J_{9-8} = 4.4$ Hz); dmba 7.69 (H(A)), 7.24 (d, H(D)), $J_{D-C} = 7.1$ Hz), 6.92 (t), 6.98 (t) (H(B), H(C)), $J_{C-B} = J_{B-A} = 7.1$), 4.00 (d), 3.74 (d) (CH_2 , $^2J_{H-H} = 12$ Hz), 2.04 (s, NMe_2). ^{19}F NMR in CDCl_3 at 20 °C (δ): -115.6 (Fo), -164.8 (Fm), -163.2 (Fp).

[Pd(8-mq)(C₆F₅)(phen)] (3). A 0.040-g (0.201-mmol) sample of phen- H_2O was added to a solution of B (0.092 g, 0.201 mmol) in acetone (15 mL). After the solution had been stirred for 5 min, it was evaporated to ca. 5 mL and 3 precipitated. An additional amount of 3 was obtained by evaporating the mother liquors to dryness and washing the residue with diethyl ether. Total yield: 68%. Anal. Calcd for $\text{C}_{28}\text{F}_5\text{H}_{16}\text{N}_3\text{Pd}$: C, 56.44; H, 2.71; N, 7.05. Found: C, 56.24; H, 2.85; N, 7.06. Relevant IR absorptions (cm^{-1}): C_6F_5^5 1495 (vs), 1055 (vs), 945 (vs); phen⁶ 844 (vs); 8-mq 825 (s), 772 (m). ^1H NMR in HDA at 20 °C (δ): phen 8.8 (dd, H(4), H(7), $J_{4-3} = J_{7-8} = 8.2$ Hz, $J_{4-2} = J_{7-9} = 1.4$ Hz), 8.17 (s, H(5), H(6)), 8.1 (m, H(2), H(9), H(3), H(8)); 8-mq 8.70 (dd, H(A), $J_{A-B} = 4.0$ Hz, $J_{A-C} = 1.7$ Hz), 8.16 (H(F)), 7.42 (dd, H(C), $J_{B-C} = 8.0$ Hz), 7.27 (dd, H(B)), 7.09 (m, H(E)), 6.96 (m, H(D)), 3.74 (s, CH_2). ^{19}F NMR in CDCl_3 at 20 °C (δ): -113.6 (Fo), -163.7 (Fm, Fp).

[Pd(8-mq)(C₆F₅)₂(μ -bpy)] (4). To a solution of B (0.174 g, 0.382 mmol), in 20 mL of acetone, was added 0.030 g (0.191 mmol) of bpy, and the mixture was stirred at room temperature for 10 min. The resulting solution was evaporated to dryness, and the residue was washed with *n*-hexane (20 mL), yielding a pale-yellow solid (4) in 69% yield. Anal. Calcd for $\text{C}_{42}\text{F}_{10}\text{H}_{24}\text{N}_4\text{Pd}_2$: C, 51.08; H, 2.45; N, 5.67. Found: C, 51.07; H, 2.70; N, 5.44. Relevant IR absorptions (cm^{-1}): C_6F_5^5 1491 (vs), 1056 (vs), 946 (vs); bpy⁶ 1596 (s, br), 764 (vs); 8-mq 820 (s), 752 (s). ^1H NMR in CDCl_3 at 20 °C (δ): 9.31 (m, 4H), 7.65 (m, 4H), 7.31 (m, 4H), 7.19 (m, 2H), 7.07 (m, 2H), 6.70 (m, 2H), 6.51 (d, 2H) ($\text{N}_2\text{C}_{10}\text{H}_8$, C_9H_6), 2.82 (A), 2.74 (B) (4H, CH_2 , AB system, $J_{A-B} = 16.4$ Hz). ^{19}F NMR in CDCl_3 at 20 °C (δ): -115.3 (Fo), -116.6 (Fo), -165.1 (Fm), -165.9 (Fm), -164.3 (Fp).

[(C₆F₅)(8-mq)Pd(μ -8-mq)Pd(C₆F₅)(phen)] (5). A 0.223-g (0.489-mmol) sample of B in CH_2Cl_2 /acetone (30/10 mL) was treated with 0.048 g (0.244 mmol) of phen- H_2O at room temperature for 10 min. The evaporation of the solution to ca. 5 mL resulted in the crystallization of a yellow solid (5) in 66% yield.

Complex 5 could also be prepared by reacting 3 (0.058 g, 0.098 mmol) and B (0.045 g, 0.098 mmol) in 30 mL of acetone (30-min stirring at room temperature). The evaporation of the solution to dryness yielded 5, which was washed with diethyl ether (30 mL); 73% yield. Anal. Calcd for $\text{C}_{44}\text{F}_{10}\text{H}_{24}\text{N}_4\text{Pd}_2$: C, 52.25; H, 2.39; N, 5.54. Found: C, 52.03; H, 2.57; N, 5.77. Relevant IR absorptions (cm^{-1}): C_6F_5^5 1490 (vs), 1051 (vs), 946 (vs); phen⁶ 843 (vs); 8-mq 820 (s), 762 (m), 756 (m).

Single-Crystal X-ray Diffraction. Single-crystal structural analyses were carried out on three samples: [Pd(dmba)(C₆F₅)(phen)] (2), [[Pd(8-mq)(C₆F₅)₂(μ -bpy)] (4), and [(C₆F₅)(8-mq)Pd(μ -8-mq)Pd(C₆F₅)(phen)] (5). Suitable crystals of these complexes for X-ray studies were obtained by slow diffusion of *n*-hexane into dichloromethane solutions of the corresponding complexes at 0 °C. Crystal sizes (mm): 2, 0.2 × 0.12 × 0.3; 4, 0.4 × 0.7 × 0.1; 5, 0.23 × 0.4 × 0.23.

Diffraction data were collected on a Siemens/STOE AED2 diffractometer with graphite-monochromated Mo K α radiation and were corrected for Lorentz and polarization effects. The refined cell constants and the most relevant data for these complexes can be found in Table I. The SHELX-76¹⁰ (for 5) and the SHELXTL PLUS¹¹ (for 4 and 2) crystallographic software packages were used.

[Pd(dmba)(C₆F₅)(phen)] (2). A total of 7330 reflections were collected in the range of 4° < 2 θ < 45° (*hkl*: 0 to 13, 0 to 10, -20 to 20) using

Table I. Summary of Crystallographic Data for 2, 4, and 5

	2	4	5
formula	$\text{PdC}_{27}\text{N}_3\text{F}_5\text{H}_{20}$	$\text{Pd}_2\text{C}_{42}\text{N}_4\text{F}_{10}\text{H}_{24} \cdot 1.5 \text{CH}_2\text{Cl}_2$	$\text{Pd}_2\text{C}_{44}\text{N}_4\text{F}_{10}\text{H}_{24}$
<i>a</i> (Å)	12.651(3)	9.8801(4)	12.3935(5)
<i>b</i> (Å)	9.982(2)	24.8399(12)	12.9381(6)
<i>c</i> (Å)	19.351(4)	34.1826(16)	24.1387(12)
β (deg)	91.27(3)	95.352(8)	102.721(4)
<i>V</i> (Å ³)	2443.1(9)	8352.5(7)	3775.6(3)
<i>Z</i>	4	8	4
<i>fw</i>	587.9	1114.6	1011.49
space group (No.)	$P2_1/c$ (14)	$C2/c$ (15)	$P2_1/c$ (14)
<i>T</i> (K)	243	291	291
λ (Å)	0.710 67	0.710 67	0.710 67
ρ (g/cm ³)	1.598	1.78	1.78
μ (cm ⁻¹)	8.2	11.2	9.79
<i>R</i> (<i>F</i>) ^a	0.056	0.058	0.034
<i>R</i> _w (<i>F</i>) (g) ^a	0.055	0.096	0.036
	(0.0004)	(0.0043)	(0.000 72)

$$^a R(F) = \sum |F_o| - |F_c| / \sum |F_o| \quad R_w(F) = [(\sum w(|F_o| - |F_c|)^2) / \sum w(F_o^2)]^{1/2} \\ w^{-1} = \sigma^2(F) + gF.$$

ω -2 θ scans. Empirical correction for absorption was applied (maximum and minimum transmission factors: 0.44 and 0.39, respectively). The structure was solved by direct methods and refined to *R* = 0.056 and *R*_w = 0.055 (1889 reflections with $F_o^2 > 2\sigma(F_o^2)$). Hydrogen atoms were added at calculated positions except for those of the methyl groups where one of the hydrogen atoms was located from the difference Fourier map and then used for calculating the positions of the two remaining hydrogen atoms. The common isotropic displacement parameter for the hydrogen atoms refined to *U* = 0.062 Å². All non-hydrogen atoms were refined with anisotropic displacement parameters. The highest peak on the final difference Fourier map was 0.79 e Å⁻³. Final atom coordinates are given in Table VI, and selected bond lengths and angles, in Table VII.

[[Pd(8-mq)(C₆F₅)₂(μ -bpy)] (4). A total of 8010 reflections were collected in the range 4.0° < 2 θ < 50° (*hkl*: 0 to 11, 0 to 29, -40 to 40) by a learned profile procedure¹² using ω scans. Correction for a 9% linear decay was applied. The structure was solved by the Patterson method. The centrosymmetric space group $C2/c$ was selected and shown to be correct by the smooth and chemically reasonable refinement of the structure. Two sites in the crystallographic asymmetric unit were found to be occupied by disordered CH_2Cl_2 moieties. At one site, a CH_2Cl_2 molecule is disordered about a 2-fold axis, with one chlorine atom sitting on the symmetry element. At the other site, two disordered congeners of CH_2Cl_2 share common, fully occupied sites for the carbon atom and one of the chlorine atoms. The remaining chlorine atom was found to be disordered over two atomic sites, with occupancies (established by constrained population refinement) of 0.70(1) and 0.30(1). In the final, full-matrix refinement of the structure, loose geometrical restraints were applied to the C-Cl and Cl...Cl distances of the solvent molecules. No hydrogen atoms were located. All the atoms, except those of the solvent molecules were refined with anisotropic displacement parameters. The final cycle of least-squares refinement was based on 5461 unique reflections ($F_o^2 > 3\sigma(F_o^2)$) and 549 variables; *R* = 0.058 and *R*_w = 0.096. The highest peak on the final difference Fourier map corresponds to 1.09 e Å⁻³, and it is located close to one of the two disordered CH_2Cl_2 molecules. Final atom coordinates are given in Table II, and selected bond lengths and angles, in Table III.

[(C₆F₅)(8-mq)Pd(μ -8-mq)Pd(C₆F₅)(phen)] (5). A total of 7330 reflections were collected in the range 4.0° < 2 θ < 50° (*hkl*: 0 to 15, 0 to 15, -29 to 29) using ω -2 θ scans. The structure was solved by the Patterson method and refined to *R* = 0.034 and *R*_w = 0.036 (3791 reflections with $F_o^2 > 3\sigma(F_o^2)$ and 541 variables). The hydrogen atoms were not located. All atoms were refined with anisotropic temperature factors. The highest peak on the final difference Fourier map was 0.57 e Å⁻³. Final atom coordinates are given in Table IV, and selected bond lengths and angles, in Table V.

(10) SHELX-76: Program of Crystal Structure Determination; University of Cambridge: Cambridge, England, 1976.

(11) SHELX-PLUS Software Package for the Determination of Crystal Structures, Release 4.0; Analytical X-ray Instruments, Inc.: Madison, WI, 1990.

(12) Clegg, W. *Acta Crystallogr.* 1981, A37, 22.

Table II. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$) for Complex 4

	x	y	z	U(eq)
Pd(1)	4223(1)	902(1)	744(1)	44(1)
Pd(2)	4290(1)	1587(1)	1810(1)	50(1)
N(1)	3602(5)	1742(2)	800(2)	46(2)
N(2)	5915(6)	1766(2)	1434(2)	48(2)
C(13)	2413(7)	1841(3)	609(2)	55(2)
C(14)	1934(9)	2363(3)	515(3)	66(3)
C(15)	2759(9)	2788(3)	615(3)	70(3)
C(16)	4025(9)	2696(3)	817(2)	62(3)
C(17)	4436(7)	2174(3)	905(2)	45(2)
C(18)	7186(8)	1684(3)	1617(2)	58(2)
C(19)	8346(8)	1894(4)	1489(2)	66(3)
C(20)	8199(8)	2222(3)	1156(3)	69(3)
C(21)	6921(7)	2315(3)	964(2)	57(2)
C(22)	5791(7)	2066(3)	1113(2)	46(2)
F(2)	7513(4)	725(2)	906(1)	70(2)
F(3)	9530(5)	1161(3)	561(2)	107(3)
F(4)	9042(6)	1801(3)	-86(2)	107(3)
F(5)	6411(6)	2022(2)	-361(2)	88(2)
F(6)	4375(4)	1574(2)	-34(1)	74(2)
C(1)	5826(6)	1127(3)	461(2)	45(2)
C(2)	7170(8)	1036(3)	587(2)	55(2)
C(3)	8248(7)	1254(3)	416(3)	67(3)
C(4)	7988(9)	1585(3)	88(3)	68(3)
C(5)	6671(8)	1683(3)	-48(2)	58(3)
C(6)	5662(7)	1452(3)	120(2)	55(2)
N(3)	2635(6)	562(2)	1029(2)	52(2)
C(23)	4629(8)	129(3)	613(3)	67(3)
C(24)	3688(8)	-233(3)	831(2)	59(3)
C(25)	3782(12)	-788(3)	833(3)	83(4)
C(26)	2884(12)	-1104(4)	1037(4)	95(4)
C(27)	1856(13)	-855(4)	1221(3)	92(4)
C(28)	1729(9)	-285(3)	1223(2)	62(3)
C(29)	2643(7)	21(3)	1028(2)	53(2)
C(30)	745(8)	1(4)	1431(3)	71(3)
C(31)	748(8)	549(3)	1421(2)	64(3)
C(32)	1709(7)	825(3)	1230(2)	55(2)
F(8)	5947(5)	2618(2)	2115(2)	83(2)
F(9)	5363(9)	3670(3)	2075(2)	125(3)
F(10)	2982(11)	4019(3)	1765(3)	150(4)
F(11)	1020(8)	3269(4)	1474(2)	145(4)
F(12)	1565(5)	2226(3)	1498(2)	98(2)
C(7)	3756(8)	2379(3)	1810(2)	59(3)
C(8)	4690(9)	2768(3)	1947(2)	65(3)
C(9)	4426(12)	3314(4)	1926(3)	83(4)
C(10)	3138(16)	3475(5)	1787(3)	98(5)
C(11)	2223(11)	3122(5)	1646(3)	87(4)
C(12)	2572(9)	2578(4)	1662(3)	77(3)
N(4)	4656(7)	767(3)	1848(2)	62(2)
C(33)	3002(10)	1434(4)	2214(3)	79(3)
C(34)	2875(10)	837(4)	2265(2)	76(3)
C(35)	1865(12)	616(5)	2498(3)	106(5)
C(36)	1870(17)	38(7)	2507(4)	142(8)
C(37)	2733(17)	-304(7)	2330(4)	130(7)
C(38)	3663(13)	-68(5)	2109(3)	97(4)
C(39)	3723(9)	512(3)	2086(2)	67(3)
C(40)	5464(9)	461(3)	1658(3)	72(3)
C(41)	5493(13)	-94(4)	1674(3)	95(4)
C(42)	4637(13)	-357(5)	1901(4)	103(5)
C(43)	945(23)	2788(9)	2611(7)	92(6)
Cl(1)	0	2265(4)	2500	201(3)
Cl(2)	499(11)	3361(4)	2543(4)	184(4)
C(44)	4045(14)	4624(6)	530(3)	232(11)
Cl(3)	3054(7)	4252(2)	837(2)	185(2)
Cl(4)	3237(14)	4614(6)	50(2)	271(5)
Cl(4')	4399(32)	4218(10)	131(6)	271(5)

Results and Discussion

(a) Reactions between $[\text{Pd}(\text{C}^{\wedge}\text{N})(\text{C}_6\text{F}_5)(\text{NCMe})]$ and N-N (bpy or phen). The reactions between $[\text{Pd}(\text{dmba})(\text{C}_6\text{F}_5)(\text{NCMe})]$ (A) and L-L (L-L = bpy or phen) in CH_2Cl_2 result in the formation of the corresponding mononuclear derivatives $[\text{Pd}(\text{dmba})(\text{C}_6\text{F}_5)(\text{L-L})]$ (L-L = bpy (1), phen (2)) not only for a Pd:N-N molar ratio of 1:1 (Scheme Ia) but also for a molar ratio of 2:1. In this case, unreacted starting material can also be recovered (Scheme Ib).

Table III. Selected Bond Distances and Bond Angles for Complex 4

Bond Distances (\AA)			
Pd(1)-N(1)	2.188(5)	Pd(2)-N(2)	2.196(6)
Pd(1)-C(1)	2.010(7)	Pd(2)-C(7)	2.037(8)
Pd(1)-N(3)	2.101(6)	Pd(2)-N(4)	2.071(7)
Pd(1)-C(23)	2.018(7)	Pd(2)-C(33)	2.000(10)
Bond Angles (deg)			
C(1)-Pd(1)-N(1)	91.0(2)	C(7)-Pd(2)-N(2)	90.4(3)
N(1)-Pd(1)-N(3)	96.6(2)	N(2)-Pd(2)-N(4)	95.9(2)
C(1)-Pd(1)-C(23)	88.7(3)	C(7)-Pd(2)-C(33)	90.2(4)
N(3)-Pd(1)-C(23)	83.8(3)	N(4)-Pd(2)-C(33)	83.6(3)

Table IV. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{\AA}^2 \times 10^3$) for Complex 5

	x	y	z	B
Pd(1)	797(1)	2217(1)	272(1)	3.29(2)
Pd(2)	4194(1)	2739(1)	759(1)	3.17(2)
C(35)	2968(5)	2962(4)	1201(3)	3.43(31)
C(36)	2779(5)	2138(4)	1597(2)	3.19(30)
C(37)	3201(5)	2247(5)	2179(3)	4.37(35)
C(38)	3160(7)	1431(7)	2564(3)	5.56(47)
C(39)	2725(6)	488(6)	2386(3)	5.19(45)
C(40)	2242(5)	348(5)	1802(3)	4.18(37)
C(41)	2237(5)	1179(4)	1406(2)	3.02(30)
C(42)	1807(7)	-610(5)	1593(4)	5.40(47)
C(43)	1386(6)	-737(5)	1030(4)	5.33(46)
C(44)	1334(5)	113(5)	660(3)	4.12(36)
N(4)	1719(4)	1051(3)	842(2)	3.29(26)
C(23)	6138(6)	1909(6)	252(3)	4.87(40)
C(24)	6793(7)	1861(6)	-163(3)	5.91(49)
C(25)	6578(7)	2529(6)	-622(3)	5.61(47)
C(26)	5701(6)	3250(6)	-664(3)	4.50(38)
C(27)	5450(7)	4015(6)	-1115(3)	5.17(44)
C(28)	4603(7)	4678(6)	-1141(3)	5.18(44)
C(29)	3893(6)	4630(5)	-734(3)	4.18(36)
C(30)	2982(7)	5272(5)	-762(3)	5.09(42)
C(31)	2362(7)	5185(5)	-361(3)	5.36(44)
C(32)	2660(6)	4454(5)	79(3)	4.34(37)
C(33)	4145(5)	3913(4)	-282(2)	3.42(31)
C(34)	5064(5)	3227(5)	-244(2)	3.58(32)
N(2)	5306(4)	2574(4)	209(2)	3.84(28)
N(3)	3542(4)	3829(3)	113(2)	3.39(26)
C(7)	4974(5)	1801(5)	1383(3)	3.38(31)
C(8)	5609(5)	2172(5)	1888(3)	3.88(34)
C(9)	6107(5)	1579(6)	2331(3)	4.19(37)
C(10)	5989(6)	517(6)	2283(3)	4.75(42)
C(11)	5374(6)	92(5)	1805(3)	4.56(41)
C(12)	4910(5)	739(5)	1360(3)	3.98(36)
F(8)	5720(3)	3209(3)	1962(2)	5.44(23)
F(9)	6703(4)	1986(3)	2816(2)	6.37(27)
F(10)	6474(4)	-93(3)	2722(2)	7.85(32)
F(11)	5253(4)	-943(3)	1757(2)	6.96(31)
F(12)	4315(4)	269(3)	882(2)	5.56(25)
C(1)	-122(5)	2479(4)	851(3)	3.61(33)
C(2)	-829(5)	1765(5)	994(3)	4.08(36)
C(3)	-1386(5)	1859(6)	1417(3)	4.29(37)
C(4)	-1248(6)	2738(6)	1734(3)	4.68(38)
C(5)	-571(6)	3496(6)	1620(3)	4.85(41)
C(6)	-28(5)	3361(5)	1188(3)	4.25(37)
F(2)	-997(3)	841(3)	696(2)	5.61(24)
F(3)	-2060(4)	1109(3)	1536(2)	6.85(30)
F(4)	-1804(4)	2874(4)	2155(2)	6.89(29)
F(5)	-434(4)	4370(3)	1933(2)	8.13(36)
F(6)	625(4)	4152(3)	1084(2)	6.29(28)
C(13)	2534(6)	1421(5)	-368(3)	4.80(41)
C(14)	2972(7)	1268(6)	-860(4)	6.01(52)
C(15)	2431(7)	1680(6)	-1365(4)	6.13(54)
C(16)	1458(7)	2293(6)	-1394(3)	5.43(44)
C(17)	796(8)	2753(7)	-1900(3)	6.52(53)
C(18)	-135(8)	3330(7)	-1873(3)	6.56(55)
C(19)	-457(6)	3499(5)	-1357(3)	5.21(43)
C(20)	143(6)	3070(5)	-857(3)	4.06(35)
C(21)	1065(6)	2452(4)	-880(3)	4.02(36)
C(22)	-138(6)	3225(5)	-283(3)	4.26(36)
N(1)	1615(4)	1988(4)	-382(2)	3.82(28)

On the other hand $[\text{Pd}(\text{8-mq})(\text{C}_6\text{F}_5)(\text{NCMe})]$ (B) reacts differently with bpy than with phen. The reaction with phen in

Scheme I

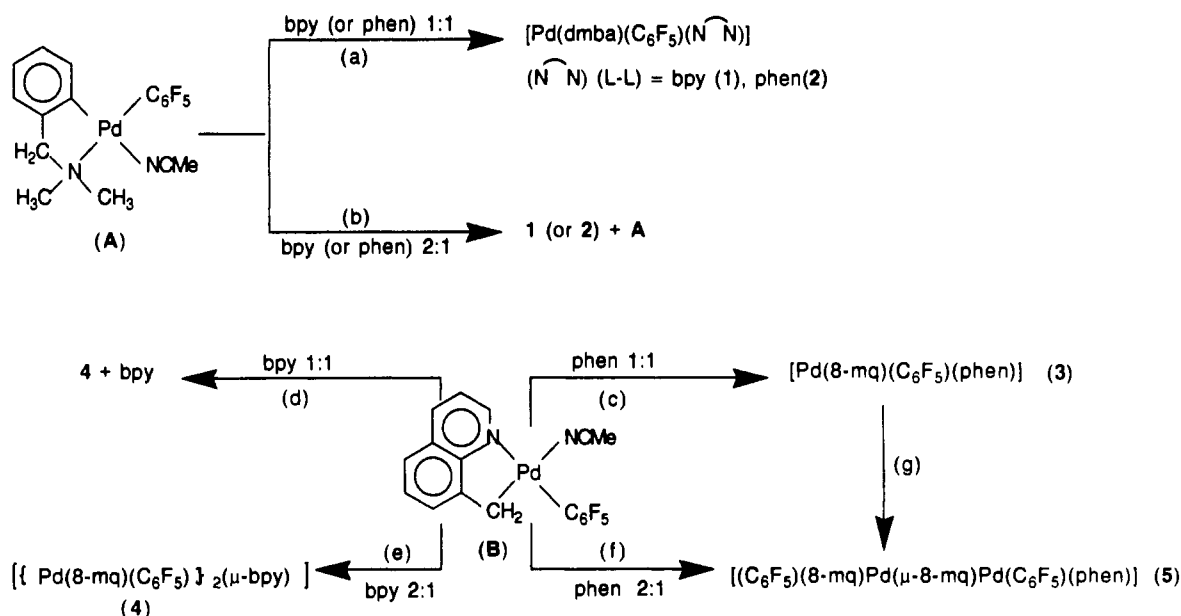


Table V. Selected Bond Distances and Bond Angles for Complex 5

Bond Distances (Å)			
Pd(1)–C(1)	2.016(7)	Pd(2)–C(7)	2.009(6)
Pd(1)–C(22)	2.038(6)	Pd(2)–C(35)	2.061(7)
Pd(1)–N(1)	2.078(6)	Pd(2)–N(2)	2.124(6)
Pd(1)–N(4)	2.188(4)	Pd(2)–N(3)	2.124(4)
Bond Angles (deg)			
C(22)–Pd(1)–N(1)	83.9(2)	N(3)–Pd(2)–N(2)	78.6(2)
N(1)–Pd(1)–N(4)	96.0(2)	N(2)–Pd(2)–C(7)	97.8(2)
N(4)–Pd(1)–C(1)	88.6(2)	C(7)–Pd(2)–C(35)	89.1(2)
C(1)–Pd(1)–C(22)	91.3(3)	C(35)–Pd(2)–N(3)	94.7(2)

CH_2Cl_2 (molar ratio 1:1) (Scheme Ic) renders the expected mononuclear derivative $[\text{Pd}(8\text{-mq})(\text{C}_6\text{F}_5)(\text{phen})]$ (3) while a similar reaction with bpy (molar ratio 1:1) (Scheme Id) yields the dinuclear compound $[\{\text{Pd}(8\text{-mq})(\text{C}_6\text{F}_5)\}_2(\mu\text{-bpy})]$ (4), containing 2,2'-bipyridine acting as a bridging ligand, and unreacted starting material. Needless to say, the use of the adequate molar ratio (B:bpy = 2:1) for the formation of 4 results in a better yield (Scheme Ie). Finally, B reacts with 1,10-phenanthroline (molar ratio 2:1) (Scheme If) in acetone/dichloromethane, yielding the dinuclear compound $[(\text{C}_6\text{F}_5)(8\text{-mq})\text{Pd}(\mu\text{-8-mq})\text{Pd}(\text{C}_6\text{F}_5)(\text{phen})]$ (5), which contains the 8-quinolylmethyl group, a typical didentate chelate ligand, acting as a bridging ligand. Moreover, the mononuclear compound 3 reacts, as expected, with B (1:1 molar ratio), yielding the dinuclear derivative 5 (Scheme Ig).

Experimental details, analytical results and spectroscopic data for all complexes are given in the Experimental Section. The protons, for NMR assignments, are labeled as shown in Figure 1. The structural assignments were carried out on the bases of these spectroscopic data, and the structures of complexes 2, 4, and 5 were established by X-ray diffraction studies.

(b) **Structural Study.** (1) **Dinuclear Complexes 4 and 5.** $[\{\text{Pd}(8\text{-mq})(\text{C}_6\text{F}_5)\}_2(\mu\text{-bpy})]$ (4). The structure of 4 is shown in Figure 2. Selected bond distances (Å) and angles (deg) are given in Table III.

As can be seen, complex 4 is dinuclear and comprises two "Pd(8-mq)(C₆F₅)" fragments connected by a 2,2'-bipyridine molecule which is acting as a bridging ligand. Each palladium atom is located in a slightly distorted square-planar environment formed by the C₆F₅ group, the 8-mq chelate ligand, and one of the N atoms of 2,2'-bipyridine. The C atoms of the C₆F₅ and 8-mq ligands are in cis positions. Bond distances related to the palladium environment are similar to those found in other palladium complexes containing these kinds of ligands.¹³⁻¹⁶

Table VI. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($\text{Å}^2 \times 10^3$) for Complex 2

	x	y	z	U(eq)
Pd	2808(1)	3236(1)	5879(1)	38(1)
C(1)	3298(9)	3751(11)	6832(5)	37(4)
C(2)	4062(9)	3101(13)	7215(5)	44(4)
C(3)	4416(10)	3473(13)	7862(6)	52(5)
C(4)	3993(12)	4577(14)	8175(6)	61(6)
C(5)	3220(11)	5297(13)	7822(7)	55(5)
C(6)	2904(10)	4879(13)	7169(6)	47(5)
F(2)	4536(5)	2009(7)	6952(3)	53(3)
F(3)	5161(6)	2765(8)	8206(3)	75(3)
F(4)	4284(6)	4906(8)	8826(3)	82(3)
F(5)	2774(7)	6367(7)	8126(4)	87(4)
F(6)	2147(6)	5657(7)	6855(4)	71(3)
N(1)	3431(7)	4895(9)	5333(4)	35(3)
N(2)	2367(7)	2740(9)	4860(4)	38(3)
C(7)	1813(9)	1700(14)	4650(6)	54(5)
C(8)	1539(9)	1499(12)	3948(6)	55(5)
C(9)	1894(11)	2384(13)	3473(6)	53(5)
C(10)	2491(9)	3496(11)	3679(5)	40(4)
C(11)	2705(8)	3642(10)	4389(5)	33(4)
C(12)	3273(8)	4781(11)	4633(5)	34(4)
C(13)	3639(9)	5763(12)	4172(6)	42(4)
C(14)	3432(10)	5555(14)	3454(6)	57(5)
C(15)	2899(11)	4484(14)	3225(6)	55(5)
C(16)	4160(9)	6877(13)	4457(6)	52(5)
C(17)	4311(10)	6964(14)	5152(6)	61(5)
C(18)	3944(9)	5951(13)	5574(6)	51(5)
C(19)	2183(9)	1571(12)	6281(5)	39(4)
C(20)	1207(11)	1557(14)	6559(5)	50(5)
C(21)	752(11)	359(15)	6816(6)	60(5)
C(22)	1319(14)	-803(16)	6759(7)	72(7)
C(23)	2296(13)	-838(15)	6470(7)	71(6)
C(24)	2750(10)	360(12)	6247(5)	51(5)
C(25)	539(11)	2798(14)	6592(6)	66(6)
N(3)	186(9)	3285(16)	5909(6)	82(5)
C(26)	-605(13)	2383(19)	5598(9)	118(9)
C(27)	-299(13)	4620(18)	5959(9)	121(9)

The dihedral angle formed by the best least-squares planes defined by each palladium environment (Pd(1), N(1), C(1),

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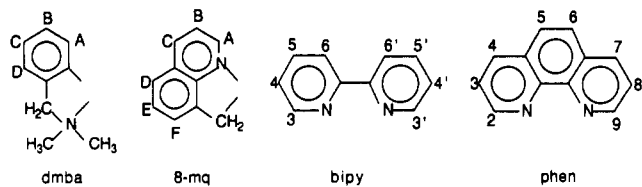


Figure 1. Proton labeling for NMR spectra.

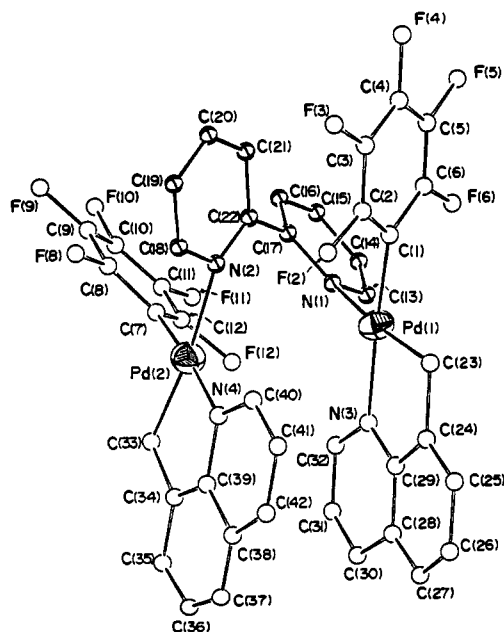
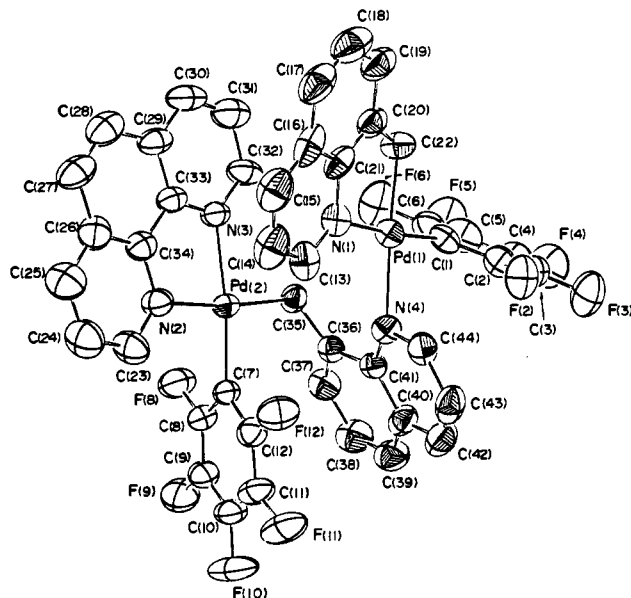
Figure 2. Molecular structure of $[(\text{Pd}(8\text{-mq})(\text{C}_6\text{F}_5)_2)(\mu\text{-bpy})]$ (4).

Table VII. Selected Bond Distances and Bond Angles for Complex 2

Bond Distances (Å)			
Pd–C(1)	2.000(10)	Pd–N(2)	2.096(8)
Pd–N(1)	2.125(9)	Pd–C(19)	2.005(11)
Bond Angles (deg)			
C(1)–Pd–N(1)	98.5(4)	C(1)–Pd–C(19)	88.4(4)
N(1)–Pd–N(2)	79.1(3)	N(2)–Pd–C(19)	94.0(4)

C(23), N(3) and Pd(2), N(2), C(7), C(33), N(4)) is $9.81(14)^\circ$.¹⁷ The pentafluorophenyl rings form dihedral angles with their respective palladium coordination planes of $59.43(19)^\circ$ and $61.96(24)^\circ$.¹⁷ These C_6F_5 groups are in a cisoidal arrangement, the torsion angle C(1)–Pd(1)–Pd(2)–C(7) being $75.4(4)^\circ$.

2,2'-Bipyridine acts as a bridging nonplanar ligand. Because of this special mode of coordination, both pyridine rings are rotated around the C(17)–C(22) bond, the dihedral angle formed by the best least-squares pyridinic planes being $51.4(3)^\circ$.¹⁷ The nitrogen atoms are in cis positions, and the torsion angle N(1)–C(17)–C(22)–N(2) is $52.8(9)^\circ$. This is a very uncommon mode of coordination for 2,2'-bipyridine, which, as is well-known, usually acts as a chelate ligand.¹⁸ In fact, only a few complexes containing bpy, or a derivative, as bridging ligand have been described^{19,20} although, as far as we are aware, such structural situations have been unequivocally established by X-ray studies in only two cases: $(\text{PPN})_2[\{\text{Pt}(\text{C}_6\text{F}_5)_3\}_2(\mu\text{-bpy})]$ ¹⁹ and $[\{\text{Cr}(\text{CO})_5\}_2(\mu\text{-4,4'-Me}_2\text{-2,2'-bipyridine})]$.²⁰ It is noteworthy that the structural dispositions of the bpy ligands are different in each of them.

(17) Nardelli, M. *Comput. Chem.* 1983, 7, 95.(18) Reedijk, J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: London, 1987; Vol. 2, p 73.(19) Usón, R.; Forníes, J.; Tomás, M.; Casas, J. M.; Fortuño, C. *Polyhedron* 1989, 8, 2209 and references therein.(20) Creaven, B. S.; Long, C.; Howie, R. A.; McQuillan, G. P.; Low, J. *Inorg. Chim. Acta* 1989, 157, 151.Figure 3. Molecular structure of $[(\text{C}_6\text{F}_5)(8\text{-mq})\text{Pd}(\mu\text{-8-mq})\text{Pd}(\text{C}_6\text{F}_5)(\text{phen})]$ (5).

While the pyridinic rings form a dihedral angle of 42° and the nitrogen atoms are in trans position in the platinum derivative,¹⁹ these rings are almost perpendicular in the chromium compound²⁰ and the N atoms are in cis positions in the palladium derivative described here.

NMR Spectra. Both ^1H and ^{19}F NMR spectra of this compound indicate that in solution there is free rotation around the C(22)–C(17) bond, so that the halves of the molecule are equivalent. The ^{19}F NMR spectrum shows five signals indicating chemical nonequivalence of all fluorine atoms. The equivalence of both C_6F_5 groups is clearly established by the presence of only one signal at δ 164.3, due to the *p*-F atom of each C_6F_5 group. In the ^1H NMR spectrum, the CH_2 group of 8-mq appears as an AB system (δ 2.74, 2.82), indicating that both H atoms are diastereotopic. The aryl groups of bpy and 8-mq cannot be analyzed separately.

$[(\text{C}_6\text{F}_5)(8\text{-mq})\text{Pd}(\mu\text{-8-mq})\text{Pd}(\text{C}_6\text{F}_5)(\text{phen})]$ (5). The molecular structure of 5 has been determined by single-crystal X-ray diffraction.³ The structure of 5 is shown in Figure 3, and selected bond distances (Å) and bond angles (deg) are given in Table V.

As can be seen, 5 is a dinuclear palladium complex and the two palladium centers are bridged by an 8-mq group. Each palladium atom is located in a distorted square-planar environment, both environments being different. Pd(2) is bonded to a C_6F_5 group, phenanthroline, and the C(sp³) atom of the bridging 8-mq ligand, while Pd(1) is bonded to a C_6F_5 group, the 8-mq chelate ligand, and the N atom of the bridging 8-mq. The coordination planes of both metal centers are almost parallel, the dihedral angle formed by the best least-squares planes defined by Pd(1), N(1), N(4), C(1), C(22) and Pd(2), N(2), N(3), C(7), C(35) is $9.40(13)^\circ$.¹⁷ In both palladium environments the Pd–C bonds are cis to each other. The pentafluorophenyl rings form with their respective palladium coordination planes dihedral angles of $70.62(18)^\circ$ (Pd(1)) and $78.84(19)^\circ$ (Pd(2)), and both C_6F_5 groups are located in a cisoidal arrangement, the torsion angle C(1)–Pd(1)–Pd(2)–C(7) being $64.07(27)^\circ$. The most remarkable structural feature in complex 5 is the presence of two very different 8-mq groups, one of them acting as a typical chelate ligand and the other acting as an unusual bridging group. The structural parameters related to the chelate ligand are similar to those found in other palladium complexes containing 8-mq,^{14,15} while the unprecedented bridging one displays some special structural features: (i) The whole ligand (8-mq) is almost perpendicular to the Pd(1) and Pd(2) coordination planes, the dihedral angles formed by the best least-squares

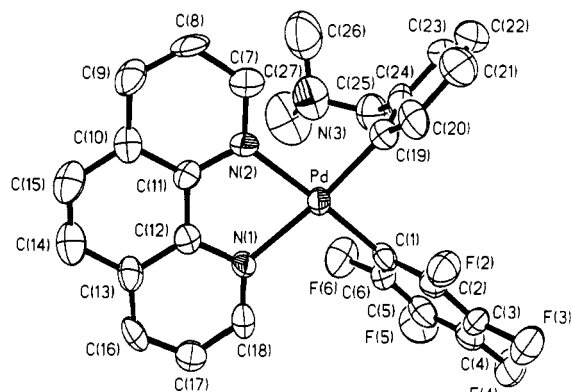


Figure 4. Molecular structure of $[\text{Pd}(\text{dmba})(\text{C}_6\text{F}_5)(\text{phen})]$ (**2**).

planes through the atoms of the aromatic rings (N(4), C(36), C(37), C(38), C(39), C(40), C(41), C(42), C(43), C(44)) and the coordination planes around Pd(1) and Pd(2) being $85.68(12)$ and $83.18(12)^\circ$, respectively. (ii) The bridging 8-quinolymethyl-*C,N* ligand is not planar, the dihedral angle formed by the two aromatic rings being $4.24(20)^\circ$. (iii) It is also remarkable that C(35) and Pd(1) are $0.323(6)$ and $1.094(5)$ Å, respectively, from the best least-squares plane defined by the atoms of the aromatic rings of the 8-mq, and it should be expected to be approximately in the same plane since such atoms are connected to the 8-mq moiety through C(36) and N(4), respectively, which use sp^2 planar orbitals for bonding to the other atoms. This effect is stronger for the N(4)–Pd(1) bond, which forms an angle of $61.93(14)^\circ$ with the perpendicular to the aromatic ring. As expected in such a case of misdirected valence, the bond N(4)–Pd(1) is significantly longer ($2.188(4)$ Å) than that formed with Pd(1) by the atom N(1) ($2.078(6)$ Å) of the chelate 8-mq. All these structural data suggest that, as expected, the unusual μ -8-mq bridging group is more strained than the chelate 8-mq ligand.

Complex **5** is not sufficiently soluble in any usual organic solvents for significative NMR studies.

(2) Mononuclear Complexes $[\text{Pd}(\text{CN})(\text{C}_6\text{F}_5)(\text{N-N})]$ (1–3**).** According to their stoichiometries, if all possible donor atoms of the ligands are bonded to the palladium center, complexes **1–3** should present a five-coordinated structure. However, it has been reported that some Pd or Pt complexes of this type show, in the solid state, a four-coordinated square-planar structure with bpy or phen acting as a monodentate ligand, although in solution they display a dynamic behavior involving five-coordinated intermediates with chelating bpy or phen.⁸ In our complexes (**1–3**) there are two potentially didentate ligands ($\text{C}\equiv\text{N}$ and N–N) and hence two structural questions: (a) Are they five- or four-coordinated and (b) in the latter case which ligand is acting as monodentate? The molecular structure of **2** established by an X-ray crystal structure determination, and the ^1H NMR studies are presented in the following.

Structure of $[\text{Pd}(\text{dmba})(\text{C}_6\text{F}_5)(\text{phen})]$ (2**).** General crystallographic information is presented in Table I, and positional and equivalent isotropic parameters are listed in Table VI. The molecule is illustrated in Figure 4, together with the atomic numbering scheme. Selected bond distances (Å) and bond angles (deg) are listed in Table VII. The palladium atom is in a distorted square-planar environment formed by a C_6F_5 group, a chelating 1,10-phenanthroline, and the C atom (C(19)) of dmba, which is acting as monodentate. The Pd–N(3) distance is 3.32 Å, which excludes a bonding interaction between both atoms. Similar structural situations have been found in $[\text{PdCl}(\text{C}_6\text{H}_4\text{N}=\text{NC}_6\text{H}_5)(\text{PEt}_3)_2]$ ²¹ and $[\text{PdBr}\{\text{C}_6\text{H}_4\text{CH}_2\text{N}=\text{CH}(2,6\text{-Cl}_2\text{C}_6\text{H}_3)\}(\text{PEt}_3)_2]$ ²² which contain the $\text{C}\equiv\text{N}$ ligand acting as monodentate, although

in other cases palladium five-coordinated species with didentate ligands and Pd–N distances around 2.7 Å have been described.^{23–25}

The pentafluorophenyl ring forms with the best least-squares coordination plane of palladium a dihedral angle of 67.3° , and the phenyl ring of dmba is almost perpendicular to this coordination plane (81.3°). Finally, the Pd–N (of dmba) vector forms with the perpendicular to the palladium coordination plane an angle of 29.1° .

The structure of complex **2** indicates that the reaction of **A** with 1,10-phenanthroline results in the coordination of phen as a chelate ligand through the displacement of NCMe and the breaking of the Pd–N bond of the dmba ligand, which acts as a monodentate ligand. It seems sensible to assume a similar structure in the solid state for complex **1**. Finally, we think that although **3** contains a different cyclometalating ligand (8-mq), it should have a structure similar to that of **2**, with 8-mq acting as a monodentate ligand and 1,10-phenanthroline as a chelate ligand. The formation of **5** by reacting **3** and $[\text{Pd}(8\text{-mq})(\text{C}_6\text{F}_5)(\text{NCMe})]$ (**B**) (Scheme I) is in keeping with this assumption.

NMR Spectra. The ^1H NMR spectra of **1** and **2** at room temperature in CDCl_3 (see Experimental Section) show equivalence of (a) both halves of bpy or phen and (b) both H atoms of the CH_2 group and both CH_3 groups of dmba. However, the ^1H NMR spectra of **1** and **2** at -90°C in CD_2Cl_2 show (a) nonequivalence of the H atoms of the CH_2 groups (**1** δ 4.00 (d) and 3.76 (d), $^2J_{\text{H-H}} = 12$ Hz; **2** δ 4.00 (d) and 3.74 (d), $^2J_{\text{H-H}} = 12$ Hz), (b) equivalence of both CH_3 groups of dmba, and (c) nonequivalence of both halves of the corresponding bpy (**1**) or phen (**2**) (see Experimental Section).

These spectroscopic data indicate that at low temperature both complexes show a four-coordinated structure with bpy or phen acting as a chelate ligand and dmba as a monodentate ligand. The X-ray study shows a similar structure for **2** in the solid state (Figure 4).

The NMR spectra at room temperature can be explained by assuming the existence of dynamic processes, including five-coordinated intermediates which facilitate the interchange between four-coordinated species with either bpy (or phen) or dmba acting as a monodentate ligand.⁸

The ^1H NMR spectrum of **3** at room temperature (HDA) shows the signals due to phen and 8-mq partially overlapped; however, it is clear that the halves of the phenanthroline ligand behave equivalently; on the other hand, the H atoms of the CH_2 group of 8-mq appear as equivalent. Both facts indicate that similar dynamic processes must also be operating at this temperature. The low solubility of **3** in the usual organic solvents precludes the NMR study at low temperature.

Concluding Remarks

All the reactions presented in this paper are summarized in Scheme I, and there are several facts concerning these processes which are worth commenting on.

In spite of the similarity of both **A** and **B**; only **A** renders mononuclear complexes when reacted with both bpy and phen even if a 2:1 molar ratio is used. **B** renders both mono- and dinuclear compounds when reacted with phen in adequate molar ratio, but surprisingly, only the dinuclear derivative is obtained when it is reacted with bpy irrespective of the molar ratio used.

The formation of **5**, a dinuclear compound containing the bridging 8-mq ligand, is especially surprising if it is considered that a similar derivative containing bridging dmba cannot be obtained, in spite of the apparently higher flexibility of dmba to

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act as a bridging ligand. We cannot give a satisfactory explanation to these differing facts.

Finally, while the flexibility of the bpy ligand permits the formation of **4**, with bpy as a bridging ligand, the inflexibility of phen prohibits the formation of the analogous phen-bridged dinuclear compound; and we observe instead the formation of **5**, in which the 8-quinolylmethyl ligand has adopted a very unusual bridging conformation.

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Supplementary Material Available: Tables of bond distances, bond angles, and anisotropic thermal parameters for **2**, **4**, and **5** and H atom coordinates and isotropic thermal parameters for **2** (10 pages). Ordering information is given on any current masthead page.