Synthesis and Structure of [(C_6F_5)(8-mq)Pd(μ-8-mq)Pd((C_6F_5)(phen)], a Binuclear Derivative Containing an Unprecedented 8-Quinolylmethyl-*C*,*N* Bridging Ligand

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Summary: When [Pd(8-mq)(C_6F_5)(NCMe)] (**1**; 8-mq = 8-quinolylmethyl-*C*,*N*) is reacted with 1,10-phen, the binuclear complex [(C_6F_5)(8-mq)Pd(μ-8-mq)Pd(C_6F_5)(phen)] (**2**), containing one 8-mq group coordinated as a chelate ligand and the other acting as an unprecedented bridging one, is obtained.

8-Methylquinoline and its derivatives have been extensively used as cyclometalating ligands,[1] for the preparation of five-membered-ring complexes containing these groups acting as C,N-chelate ligands (Figure 1A). No complexes containing 8-quinolylmethyl-*C*,*N* (8-mq) acting as a bridging ligand (Figure 1B) have been synthesized, probably because the structure of the ligand forces the chelate coordination. We herein report the synthesis and structural characterization of [(C_6F_5)(8-mq)Pd(μ-8-mq)Pd(C_6F_5)(phen)], a binuclear derivative that contains two 8-mq groups in very different structural situations, one acting as a chelate ligand and the other as a bridging one.

Recently, we reported on the chemistry of C,N-cyclopalladated derivatives,[2] and now we present the reactions between [Pd(8-mq)$(NCMe)_2$]ClO_4[3] and $(NBu_4)_2$[M$(C_6F_5)_4$] (M = Pd, Pt),[4] which give [Pd(8-mq)(C_6F_5)(NCMe)] (1) according to eq 1, through an arylation process in which $(NBu_4)_2$[M$(C_6F_5)_4$] is the arylating agent.[4,5a]

$$[\mathrm{Pd(8\text{-}mq)(NCMe)_2]ClO_4} + \mathrm{(NBu_4)_2[M(C_6F_5)_4]} \xrightarrow{\mathrm{CH_2Cl_2}} [\mathrm{Pd(8\text{-}mq)(C_6F_5)(NCMe)}] + \mathrm{(NBu_4)[M(C_6F_5)_3(NCMe)]} + \mathrm{(NBu_4)ClO_4} \quad (1)$$

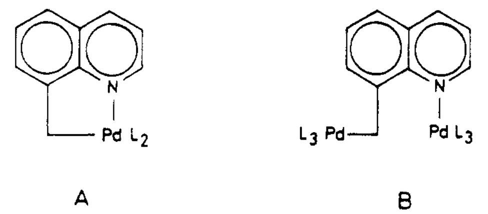
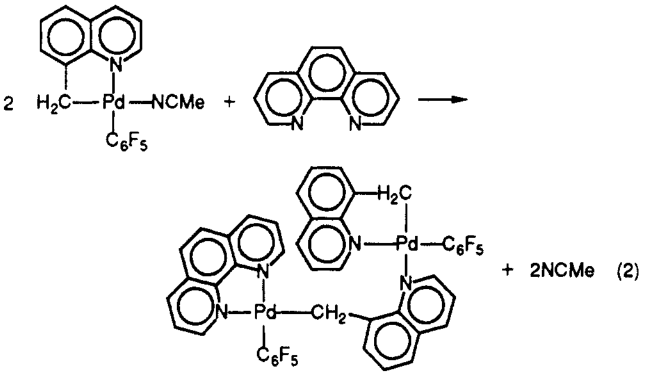


Figure 1.

1 reacts with 1,10-phen·H_2O (molar ratio 2:1) in CH_2Cl_2/acetone, yielding the binuclear derivative [(C_6F_5)(8-mq)Pd(μ-8-mq)Pd(C_6F_5)(phen)] (**2**), which shows an unprecedented bridging 8-mq group (eq 2).[5b]



Other syntheses with 1 as the starting material are presently under study in our laboratory.

The molecular structure of **2** has been determined by single-crystal X-ray crystallography (Figure 2).[6] The main distances and angles are given in the caption to Figure 2. As can be seen from this figure, two palladium centers are bridged by an 8-mq group. Each palladium atom is located in a distorted-square-planar environment. Pd(1) is bonded to a C_6F_5 group, a 8-mq chelate ligand, and the N atom of the 8-mq bridging ligand, while Pd(2) is bonded to a C_6F_5 group, the phenanthroline, and the C(sp^3) atom of the bridging 8-mq ligand. The dihedral angle formed by the best least-squares planes through Pd(1), N(1), N(4), C(1), C(22) (plane 1) and through Pd(2), N(2), N(3), C(7), C(35) (plane 2) is 9.40 (13)°;[7] i.e., both coordination planes are almost parallel. The pentafluorophenyl groups are in a cisoidal arrangement, the torsion angle C(1)–Pd(1)–Pd(2)–C(7) being 64.07 (27)°.

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(5) (a) Preparation of 1: To a CH_2Cl_2 (20 mL) solution of $(NBu_4)_2$[Pd$(C_6F_5)_4$] (0.585 g, 0.465 mmol) was added [Pd(8-mq)$(CNMe)_2$]ClO_4[3] (0.200 g, 0.465 mmol) in CH_2Cl_2 (25 mL), and the mixture was stirred at room temperature for 20 min, so that a white solid precipitated. The suspension was evaporated to ~15 mL, and the white solid 1 (0.148 g, 70% yield) was separated by filtration. When the mother liquor was evaporated to dryness and the residue was washed with Et_2O (20 mL), a mixture of $(NBu_4)ClO_4$ and (NBu_4)[Pd$(C_6F_5)_3$(NCMe)] was obtained. The separation was carried out by washing with isopropyl alcohol, in which the palladium derivative is insoluble. 1 was recrystallized from CH_2Cl_2. A similar reaction takes place when $(NBu_4)_2$[Pt$(C_6F_5)_4$] is used as the arylating agent, although the required reaction time is longer (5 h). Anal. Calcd (found) for $PdC_{18}F_5H_{11}N_2$: C, 47.27 (47.34); H, 2.75 (2.43); N, 6.04 (6.13). IR (Nujol, cm^{-1}): C_6F_5, 1492 vs, 1051 vs, 1042 vs, 946 vs; 8-mq 1590 m, 816 m, 751 s; NCMe, 2314 m, 2284 m. ^{1}H NMR (room temperature, acetone-d_6, 200 MHz; δ, ppm): 7.7 (m, 5 H), 8.6 (d, 1 H) (aryl); 3.19 (s, 2 H, $-CH_2-$); 2.15 (s, 6 H, $-CH_3$). ^{19}F NMR ($CFCl_3$ reference, 188 MHz, δ): −112.6 (*o*-F), −164.3 (*m*-F), −163.2 (*p*-F). (b) Preparation of **2**: To a solution of [Pd(C_6F_5)(8-mq)(NCMe)] (1; 0.223 g, 0.489 mmol) in CH_2Cl_2/acetone (30 mL/10 mL) was added 1,10-phen·H_2O (0.048 g, 0.244 mmol), and the mixture was stirred at room temperature for 10 min. The evaporation of the solution to ~5 mL gives the yellow solid **2** (0.162 g, 66% yield). Anal. Calcd (found) for $Pd_2C_{44}F_{10}H_{24}N_2$: C, 52.03 (52.25); H, 2.57 (2.39); N, 5.77 (5.54). IR (Nujol, cm^{-1}): C_6F_5, 1490 vs, 1051 s, 1041 s, 946 vs; 8-mq, 829 s, 822 s; phen, 1511 m, 843 vs. Complex **2** is not soluble enough in any donor solvents for significative NMR studies.

(6) Suitable crystals for X-ray study were obtained by slow diffusion at 0 °C of *n*-hexane into a solution of **2** in CH_2Cl_2. Crystal data: monoclinic, space group $P2_1/c$; a = 12.3935 (5) Å, b = 12.9381 (6) Å, c = 24.1387 (12) Å, β = 102.721 (4)°, Z = 4, V = 3775.6 Å^3; d(calcd) = 1.78 g cm^{-3}, μ(Mo Kα) = 9.79 cm^{-1}; F(000) = 1992; four-circle diffractometer, Siemens/Stoe AED2; crystal size (mm) 0.23 × 0.4 × 0.23; scan mode $\omega/2\theta$, T = 296 K; 7330 measured reflections; range of *hkl* 0–15, 0–15, −29 to +29 ($2\theta_{max}$ = 50°); 5986 unique reflections (R_{merge} = 0.0162); 3791 reflections used in analysis ($F_o^2 > 3\sigma(F_o^2)$; structure solved by heavy-atom method and refined to R = 0.034 and R_w = 0.036.[9] All atoms were refined with anisotropic temperature factors. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.00072F^2$: 541 variables; $\Delta/\mathrm{esd}_{max}$ 0.136; highest peak 0.57 e Å^{-3}.

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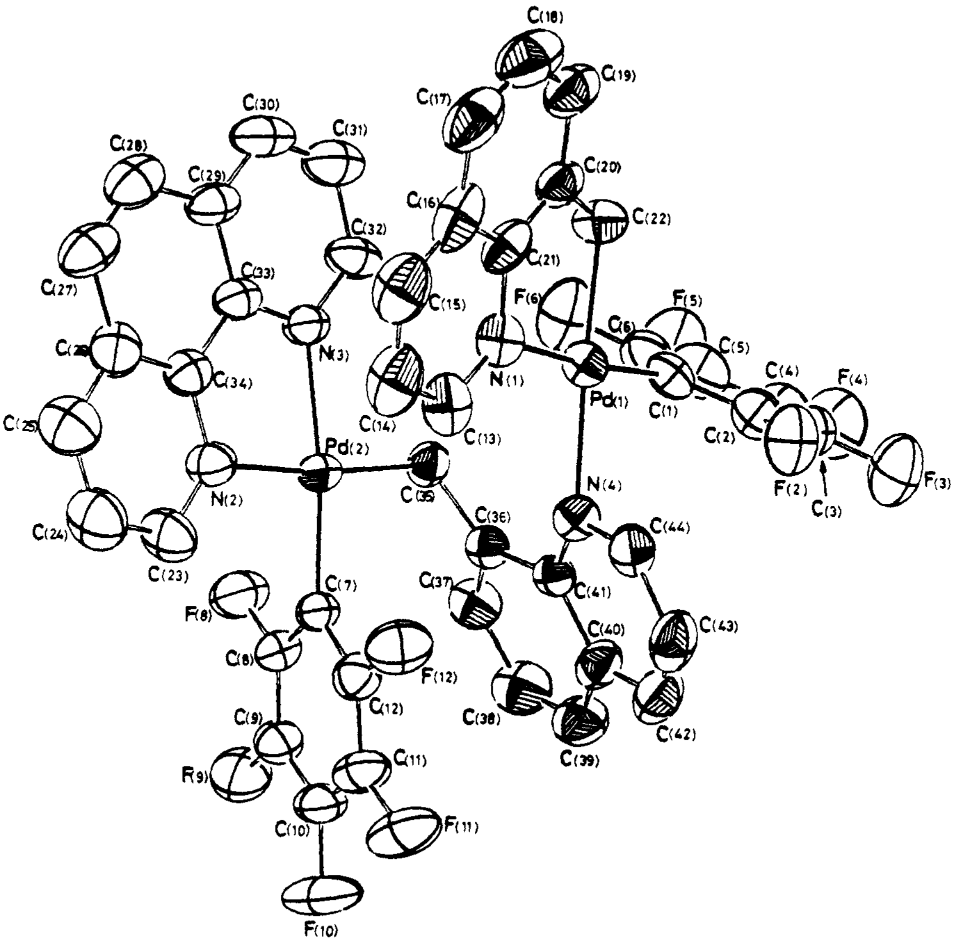

Figure 2. Molecular structure of complex **2**. Selected bond lengths (Å) and bond angles (deg): Pd(1)–C(1) = 2.016 (7), Pd(1)–C(22) = 2.038 (6), Pd(1)–N(1) = 2.078 (6), Pd(1)–N(4) = 2.188 (4), Pd(2)–C(7) = 2.009 (6), Pd(2)–C(35) = 2.061 (7), Pd(2)–N(2) = 2.124 (6), Pd(2)–N(3) = 2.124 (4); C(22)–Pd(1)–N(1) = 83.9 (2), N(1)–Pd(1)–N(4) = 96.0 (2), N(4)–Pd(1)–C(1) = 88.6 (2), C(1)–Pd(1)–C(22) = 91.3 (2), N(3)–Pd(2)–N(2) = 78.6 (2), N(2)–Pd(2)–C(7) = 97.8 (2), C(7)–Pd(2)–C(35) = 89.1 (2) C(35)–Pd(2)–N(3) = 94.7 (2).

The most remarkable structural feature in complex **2** is the presence of two very different 8-mq groups. One of them displays the usual C,N-cyclometalated chelate coordination mode on Pd(1); the structural parameters related to this ligand are similar to those in other palladium complexes containing 8-mq.[8] The other 8-mq group is acting as a bridging ligand between the palladium centers. Several points concerning this unprecedented μ-8-mq ligand are as follows. (a) The μ-8-mq ligand is almost perpendicular to the Pd(1) and Pd(2) coordination planes (plane 1 and plane 2, respectively), the dihedral angles formed by the best least-squares plane through the atoms of the aromatic rings (plane 3) and the coordination planes around Pd(1) and Pd(2) being 85.68 (12) and 83.18 (12)°, respectively.[7] (b) The quinoline moiety of the bridging ligand is not planar, the dihedral angle formed by the two aromatic rings being 4.24 (20)°.[7] (c) Another interesting structural feature is that Pd(1) is 1.094 (5) Å from plane 3, and this is very surprising since N(4) is bonded to metal center Pd(1) and to the carbon atoms of the aromatic ring C(41) and C(44) through sp^2 planar orbitals. (d) Finally the Pd(1)–N(1) (terminal chelate 8-mq ligand) and Pd(1)–N(4) (bridging 8-mq) distances are rather different (2.078 (6) and 2.188 (4) Å, respectively), indicating a stronger Pd(1)–N(1) bond. All these structural data suggest that, as expected, the μ-8-mq group is more strained than the usual terminal 8-mq ligand.

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Supplementary Material Available: Listings of bond distances and angles, atomic positional parameters, and thermal parameters (4 pages); a listing of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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