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Intramolecular Hydrogen Bonding within Cyclometalated Palladium(II) Complex Containing L(-)-1-Phenylethylamine Ligand

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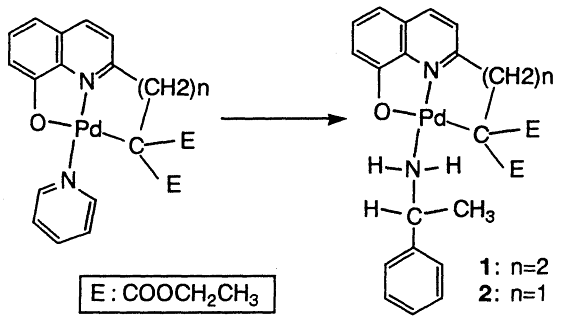
Tow novel *C*-metalated Pd(II) complexes containing diethylmalonate pendants have been prepared. A single crystal X-ray structure analysis of $C_{26}H_{30}N_2O_5Pd$ reveals that two molecules are adjoined and exactly oriented face to face due to intra- and inter-molecular hydrogen bonds. The structural evidence was also observed in solution from the ^1H NMR spectroscopy.

Recently we reported1) the synthesis of novel cyclometalated palladium complexes by incorporation of a 2-substituted 8-quinolinol containing C, N, O-donor sites and a pyridine, thereby taking advantage of added stabilization through fused 5,5- or 5,6-bicyclic chelate-ring system. The ligand exchange reaction2) of pyridine with L(-)-1-phenylethylamine in benzene readily afforded yellow crystalline complex **1**, which also sustained Pd(II)-C(sp^3) σ bond. H-bonded interactions by L-alanine3) and L-phenylethylamine4) have recently attracted much attention, as a key component to molecular self-assembly.5,6) This paper reports on X-ray crystal structure and the ^1H NMR spectroscopy of **1**, together with data on the analogous palladium complex **2**.

Figure 1 illustrates the crystal structure of **1**.7) Table 1 and 2 show the important bond distances and angles, respectively. The coordination sphere about Pd(II) is planar and the Pd-C bond length, 2.11(3) Å, is typical of Pd(II)-C(sp^3) bond2). A fixed keto form allows hydrogen-bond acceptance [O(2B)-H(2B)= 1.7(3) Å] by the amine proton.4) The surprising structural aspect of **1** is the relative orientations indicating as a self-assembly molecule by face to face contact between two complexes with a Pd··Pd distance of 5.100(2) Å which is far longer than related complexes containig a Pd···Pd bond (3.0960 Å).8) This shows a fairly strong intermolecular hydrogen



1: n=2
2: n=1

bond, with [N(2A)-]H(2A)···O(1B) distance 2.1(3) Å.

Table 1. Selected bond length (Å)

Pd(B)···Pd(A)	5.100(2)	Pd(B)-O(1B)	2.08(2)
Pd(B)-N(1B)	2.05(2)	Pd(B)-N(2B)	2.09(2)
Pd(B)-C(18B)	2.11(3)	O(1B)···N(2A)	3.05(3)
O(2B)···N(2B)	2.89(3)	O(1B)-H(2A)	2.1(3)
O(2B)-H(2B)	1.7(3)		

Table 2. Selected bond angle (°)

N(1B)-Pd(B)-N(2B)	169.1(8)
N(1B)-Pd(B)-O(1B)	81.2(7)
N(1B)-Pd(B)-C(18B)	97.0(9)
C(18B)-Pd(B)-O(1B)	171.9(8)
N(2B)-Pd(B)-O(1B)	90.2(7)
N(2B)-Pd(B)-C(18B)	92.5(9)
Pd(B)-O(1B)-C(8B)	112(1)
C(18B)-C(25B)-C(26B)	115(2)
C(1B)-C(26B)-C(25B)	115(2)
O(1B)-H(2A)-N(2A)	147(21)
O(2B)··H(2B)-N(2B)	143(21)
C(19B)-O(2B)-H(2B)	103(9)

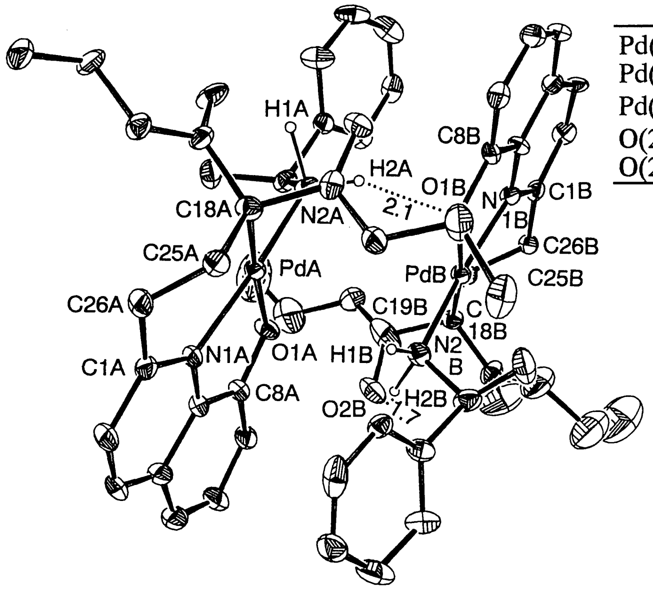


Fig. 1. ORTEP drawing of **1**.

The NMR spectrum of **1** in $CDCl_3$ shows two distinct triplets at δ 1.15 (J = 7.1 Hz, 3H) and δ 1.31 (J = 7.1 Hz, 3H) for the ester methyl hydrogen. The separation for these hydrogens, when compared to the external pyridine ligand (δ 1.10, t, J = 7.3 Hz, 6H), suggests that the two ester groups of ethyl malonate moiety are nonequivalent due to their different chemical environments, since one of the ester groups must be fixed due to an intramolecular 6-membered H-bond with the N-bonded phenylethylamine ligand. Similar shifts appeared at 1.13 (J = 7.3 Hz, 3H) and 1.27 (J = 7.3 Hz, 3H) for the related complex **2**. The two hydrogen signals for the NH_2 appeared at δ 3.16 (d) and δ 3.82 (d,d) supporting this conjecture. The downfield shift of the latter signal was caused by the magnetic anisotropy due to the adjacent ester C=O group as the results of the intramolecular H-bonding with NH proton. These two NH_2 hydrogens of **2** did not undergo facile deuterium exchange in $CHCl_3$ at 25 ° C with D_2O. The doublets (J = 6.9 Hz) at δ 4.05 and 4.08 for the quinolinol α-CH_2 are due to the justaposition of the adjacent enantiotopic center. These results are supporting an intramolecular H-bonding in $CDCl_3$ between the amine and ester carbonyl. The ^1H NMR spectrum of **1** shows similar shifts, namely two peaks at δ 3.32 and 4.49 for the amine protons.

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7) Crystallographic data for **1**; $C_{26}H_{30}N_2O_5Pd$, Fw=556.94, orthorhombic, $P2_12_12_1$, a=19.50(1), b=21.70 (1), c=11.40(1) Å, V=4824 $Å^3$, Z=8, Dc=1.534 gm^{-3}, T=295 K, R=0.072 for 4346 reflections with monochromated Mo-Kα radiation. Two independent molecules are present in an asymmetric unit of this crystal.
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