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THE CENTRAL-CARBON-BONDED PALLADIUM(II) COMPLEXES OF ETHYL ACETOACETATE

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The reaction of sodium tetrachloropalladate(II) with ethyl acetoacetate in aqueous alkaline solution afforded a key intermediate Pd-$(C_6H_9O_3)_2\cdot\frac{1}{2}H_2O$ [1]. The compound 1 reacts with a base L such as pyridine, 2-methylpyridine, n-butylamine, benzylamine, or 2,2'-bipyridine, resulting in Pd(1-ethoxycarbonylacetonato-$C^1)_2L_2$ [2]. The central-carbon-bonding of ethyl acetoacetate to palladium has been deduced from the IR and NMR spectra, and finally ascertained by the X-ray analysis of a compound with 2-methylpyridine as L.

The reaction of bis(acetylacetonato)palladium(II) with a base such as triphenylphosphine, pyridine or diethylamine converted one of the chelating ligands to the central-carbon-bonded state.[1] On the other hand the reaction of the π-allylic Pd-(II) complexes of acetoacetate esters with pyridine or its derivatives afforded the terminal-carbon-bonded complexes, $PdCl(CH_2COCH_2COOR)L_2$.[2] Now we report some Pd(II) complexes containing the central-carbon-bonded ethyl acetoacetate.

Preparations. To an aqueous 0.5 M solution of Na_2PdCl_4 containing a few times as many moles of ethyl acetoacetate was added an aqueous solution of KOH(twice moles) under vigorous stirring. A resinous product was washed and triturated with water to transform into a tractable yellow powder [1]. Yield 53%. The compound 1 has the composition $Pd(C_6H_9O_3)_2\cdot\frac{1}{2}H_2O$ and exhibits strong ν(C=O) bands at 1710 and 1560 cm^{-1} in Nujol. The nature of 1 is not yet clear, but it is a very interesting intermediate, and turns to bis(1-ethoxycarbonylacetonato-O,O')palladium(II) by recrystallization from methylene chloride-petroleum ether.

On the other hand, when 1 was dissolved in pyridine and ethyl ether was added to the solution, yellow crystals of $Pd(C_6H_9O_3)_2(C_5H_5N)_2\cdot\frac{1}{2}H_2O$ [2a] were produced in a 27% yield on the basis of Pd. IR: ν(C=O) 1696vs, 1654s; ν(OH) 3470w, 3320w; ν(Pd-C) 560 cm^{-1}. The analogous complexes Pd(1-ethoxycarbonylacetonato-$C^1)_2L_2$ were prepared in a similar or slightly modified fashion, where L is 2-methylpyridine [2b],

n-butylamine, benzylamine, or $\frac{1}{2}$(2,2'-bipyridine). The IR spectra of these compounds show the ν(C=O) and the ν(Pd-C) bands in the 1700-1630 and 570-555 cm^{-1} regions, respectively, revealing that the ester ligands are linked to the palladium atom through the central carbon atom.[1,2]

NMR Spectra. As is seen in Fig. 1 the NMR spectrum of bis(1-ethoxycarbonylacetonato-C^1)bis(pyridine)palladium(II) [2a] in pyridine exhibits two sets of signals: CH_2CH_3, τ8.76t and 8.71t (J=7Hz); CH_2CH_3, τ5.92q and 5.73q; $COCH_3$, τ7.80s and 7.52s. The intensity ratio is 1:1 in either case. The CH proton resonates at τ5.59 as a single peak, probably denying the coexistence of geometrical isomers. The spectral behavior can not be attributed to the hindered rotation of the σ-bonded ester ligands, since no remarkable change in the spectrum was observed up to 90°C. The relative configurations of the two ester ligands around the asymmetric carbon atoms (R-R or S-S vs R-S) might be responsible for the spectral pattern.

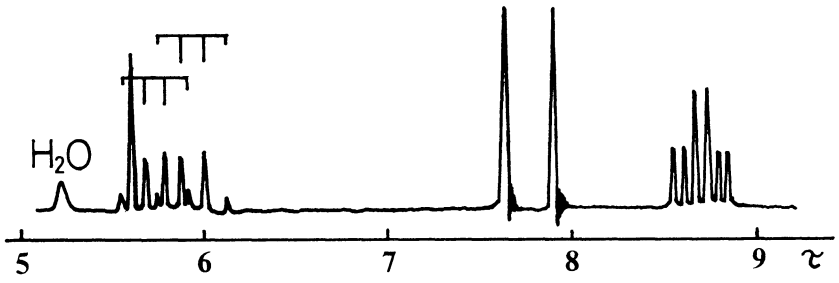

Fig. 1. The NMR spectrum of bis(1-ethoxycarbonylacetonato-C^1)-bis(pyridine)palladium(II) in pyridine immediately after dissolution with TMS as an internal reference.

X-Ray Analysis. Bis(1-ethoxycarbonylacetonato-C^1)bis(2-methylpyridine)-palladium(II) [2b] afforded the best crystals among similar compounds. Crystals are pale yellow plates elongated along the b-axis. The shape and size of crystals were not so suitable to be used for the X-ray work, but no attempt of recrystallization has been successful.

Crystal Data: $C_{24}H_{32}N_2O_6Pd$, F.W. = 551.0, monoclinic, a = 23.811(5), b = 9.222(2), c = 24.013(5) Å, β = 104.51(2)°, U = 5105(2) $Å^3$, D_c = 1.43 $g \cdot cm^{-3}$ for Z = 8, space group C2/c, μ(Mo Kα) = 7.6 cm^{-1}.

The crystal used in the intensity measurement had approximate dimensions of 0.02 x 0.20 x 0.30 mm. The unit-cell dimensions were determined by the least-squares fit of 2θ values of 24 reflections carefully centered on a diffractometer (λ(Mo Kα) = 0.71069 Å). The intensity data were collected on a Rigaku automated four-circle diffractometer using graphite-monochromatized Mo Kα radiation. The diffracted intensity had rapidly fallen with an increase of 2θ value, and therefore the data collection was terminated out to 2θ value of 40°. The θ-2θ scan technique was employed. A total of 2392 reflections was measured, and of these 496 reflections were less than σ(F) and were recorded as zero. Lorentz and polarization corrections were made, but no absorption correction was applied to the intensity data, which might limit the accuracy of the present structure determination.

The structure was solved by the conventional heavy-atom method. A three-dimensional Patterson function was computed and interpreted to give the coordinates of the palladium atom. The remaining non-hydrogen atoms were easily located on the successive Fourier maps. Structure refinement was carried out by the method of block-diagonal least-squares with HBLS V program.[3] A few cycles of isotropic refinement followed by anisotropic cycles converged the R value to 0.066 for 1896 non-zero reflections (0.104 for all 2392 reflections). Hydrogen atoms other than methyl hydrogens, whose coordinates were calculated from stereochemical considerations, were included in the structure factor calculation.

The molecular structure projected onto the coordination plane is shown in Fig. 2 together with the numbering scheme of atoms. An ORTEP drawing of the molecule and a drawing of the inner coordination plane around the palladium atom are shown in Figs. 3 and 4 respectively. As is shown in these figures, the coordination is square-planar. Five atoms, Pd, N(10), N(20), C(33) and C(43), form a plane with the maximum deviation of 0.07 Å. Two 2-methylpyridine ligands occupy the trans positions and are locked in the syn configuration, two methyl groups locating under the coordination plane. The non-bonded distance from C(16) to C(26) is 3.953(22) Å. A similar configuration is observed in dichlorobis(2-methylpyridine)copper(II) and its dibromo analogue, which are essentially square-planar complexes.[4,5] The Pd-N bond distances are normal.[6] Both the pyridine rings are approximately perpendicular to the coordination plane, the dihedral angles being 96.5° and 85.0°. Each ester ligand is bonded to the palladium atom via its central carbon atom. The Pd-C bond distance of 2.193 Å is on the longer limit for the expected Pd(II)-C(sp^3) single bond length.[7] The configurations of these

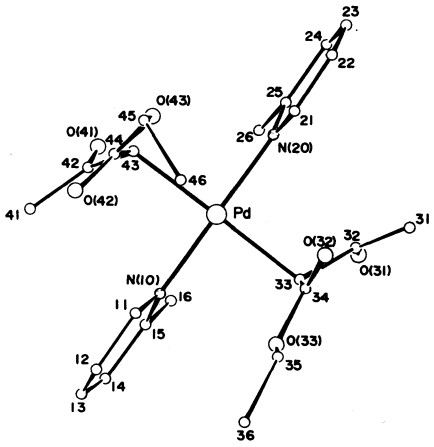

Fig. 2. The molecular structure projected onto the coordination plane together with the numbering scheme of atoms. Only numbers are indicated for carbon atoms.

asymmetric carbon atoms, C(33) and C(43), are similar, both being in either R- or S-form in a given molecule. Since there are glide planes in the unit cell, there is equal number of two optical antipodes in the crystal. The corresponding bond lengths and bond angles in two ester ligands agree well to each other, whereas the torsional angles are different. The largest difference is observed along the $-O-CH_2-$ bond: the torsional angle along the O(33)-C(35) bond is 171.6°, whereas the one along O(43)-C(45) is 67.0°. No unusual intermolecular contacts are observed, the shortest contact between non-hydrogen atoms being 3.411(20) Å for C(23)(x,y,z)-O(42)(-x,-y,-z).

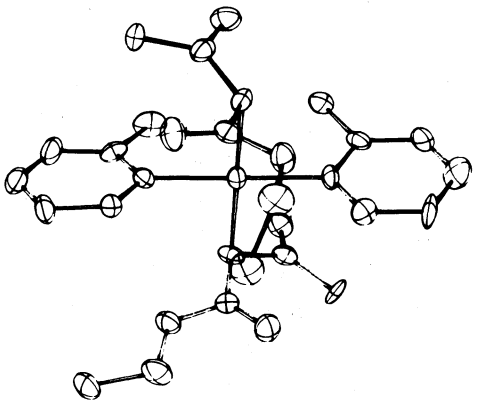

Fig. 3. The ORTEP drawing of the molecule.

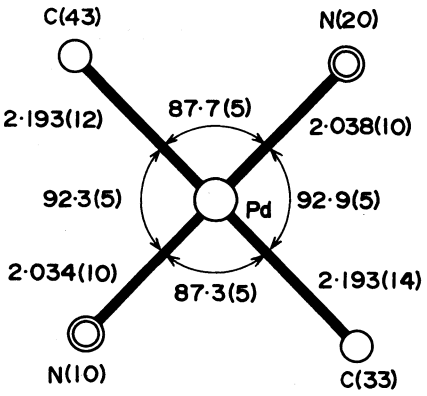

Fig. 4. Inner coordination geometry around the palladium atom.

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