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STUDIES ON THE REACTIONS OF BIS(ACETYLACETONATO)PLATINUM(II) WITH LEWIS BASES. III. FORMATION OF NON-CHELATED, O-BONDED ACETYLACETONATO COMPLEX, $[Pt(ACETYLACETONATO\text{-}\underline{O})_2(PEt_3)_2]$

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Bis(acetylacetonato)platinum(II) reacted with triethylphosphine (PEt_3) in diethyl ether at low temperature to yield $[Pt(C_5H_7O_2)_2(PEt_3)_2]$, **1**, which was isolated and characterized on the basis of IR and ^1H-NMR spectroscopy and elemental analysis. Complex **1** represents the first example of the transition metal complex which possesses singly O-bonded acetylacetonato ligands.

It is known that a β-diketonato anion can coordinate to the central metal atom in a variety of ways including bidentate mode through two oxygen atoms, unidentate fashion via either γ-carbon atom or one oxygen atom, and in many other manners.$^{1,2)}$ We have recently shown that the chelated acetylacetonato ligand in the platinum(II) complex, $[Pt(acac)_2]$,$^{3)}$ can rearrange on interaction with Lewis bases$^{4,5)}$ to the γ-carbon bonded unidentate form to yield the complexes, [Pt(acac)(γ-acac)L]$^{3)}$ (L stands for triphenylphosphine,$^{4)}$ tricyclohexylphosphine,$^{4)}$ or pyridine$^{5)}$) and $[Pt(\gamma\text{-acac})_2(py)_2]$.$^{3,5)}$

Although many studies have been made on the dynamic properties of chelated β-diketonato complexes in which unidentate O-bonded enol type intermediates were postulated,$^{6,7)}$ there is few precedent of the isolation of such an intermediate. The anionic complex $[Pt(acac)(\underline{O}\text{-acac})Cl]^-$ $^{3)}$ was claimed to have been isolated at first by Werner in 1901,$^{8)}$ which later was found to be $[Pt(acac)(\gamma\text{-acac})Cl]^-$ through a crystallographic study.$^{9)}$ Bis(acetylacetonato)mercury was also reported at first as $[Hg(\underline{O}\text{-acac})_2]$.$^{10)}$ However, more rigorous examination of the ^1H-NMR spectrum of $[Hg(tmhd)_2]$ (tmhd = 2,2,6,6-tetramethyl-3,5-heptanedionato) revealed that the isolated compound in fact possesses central carbon-bonded tmhd ligands although ca. 3 % of O-bonded open enolate ligand exists in solution as an equilibrium mixture.$^{11)}$ Trimethylsilicon acetylacetonate, $(CH_3)_3Si(\underline{O}\text{-acac})$, is the only isolated compound hitherto known that contains unidentate O-bonded acetylacetonato moiety.$^{12-14)}$ Here we report the first example of isolation and characterization of a transition metal complex with singly O-bonded acetylacetonato ligands.

Triethylphosphine reduces $[Pt(acac)_2]$ to platinum metal immediately upon reaction in diethyl ether at room temperature. However, a careful control of the reaction temperature below -10°C yielded, after crystallization from CH_2Cl_2, white crystals which were identified as trans-$[Pt(\underline{O}\text{-acac})_2(PEt_3)_2]$, **1**, on the basis of the ^1H-NMR and infrared spectra and elemental analysis. (Found: C, 41.7; H, 7.60%. Calcd for

$C_{22}H_{44}O_4P_2Pt$: C, 42.0; H, 7.04%. M.p. in vacuo, 165-6°C (dec.)). The IR spectrum (KBr disc) of **1** considerably differs in the region of 1500 - 1700 cm^{-1} from that of the complex of the type [M(acac)(γ-acac)L].[4,5,15] Although there is a strong band ascribable to ν(C=O) of free ketonic groups at 1650 cm^{-1}, no absorption assignable to the bidentate chelate acac ligand was observed around 1550 cm^{-1}. Instead, a strong band, possibly due to ν(C-O), is observed at 1160 cm^{-1}. A band of medium intensity at 1605 cm^{-1} may be assigned to the stretching vibration of C-C double bond conjugated with a C=O group.[16] These lines of IR evidence suggest that complex **1** possesses acac ligands coordinated in a unidentate fashion to the central platinum atom through an enolic oxygen atoms. The ^1H-NMR spectrum in $CDCl_3$ at room temperature also strongly supports the formulation of **1**. As is shown in Figure 1(A), the methine proton (c) resonates at an exceptionally low field (δ 6.41 ppm) as a singlet accompanying ^{195}Pt satellite bands with a small coupling constant (13 Hz). This excludes the possibility that the acac ligand in **1** is attached to Pt through the central methine carbon, whose coupling constant is known to be in the region of 100 - 130 Hz.[4,5,17] Absence of delocalization of the π-electrons along the chelate ring may render the olefinic methine proton to shift downfield as compared with the conventional chelate acac complex. Of two singlets at 2.11 and 2.29 ppm, the one at the upper field is assigned to a terminal methyl group (a) and the lower one to another methyl group (b) on the basis of the following reasons. The careful examination of the spectrum revealed that the signal at 2.29 ppm accompanies the satellite bands with a coupling constant of ca. 3 Hz whereas no satellite bands were observed for the signal at 2.11 ppm. The proton (b) is more likely to couple with ^{195}Pt than proton (a) in view of the number of bonds involved between the central metal and the proton in question. Absence of a coupling between olefinic methine proton (c) and methyl protons (b) suggests that the O-bonded acac ligand is in cis configuration with respect to C=C bond as is shown in the Figure 1(A). No change in the spectrum was observed by heating the sample at 58°C as compared with that at room temperature, suggesting a rigid structure for **1**. The result is in contrast with the rapid acac methyl group exchange observed in the cis isomer of $(CH_3)_3Si(\underline{O}$-acac).[14] The methyl protons in the triethylphosphine ligands appear as a pseudo

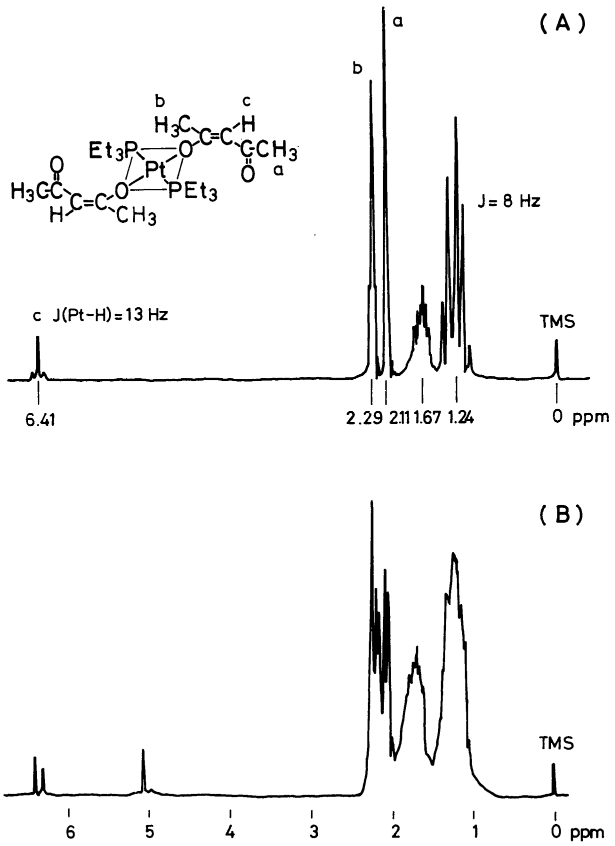


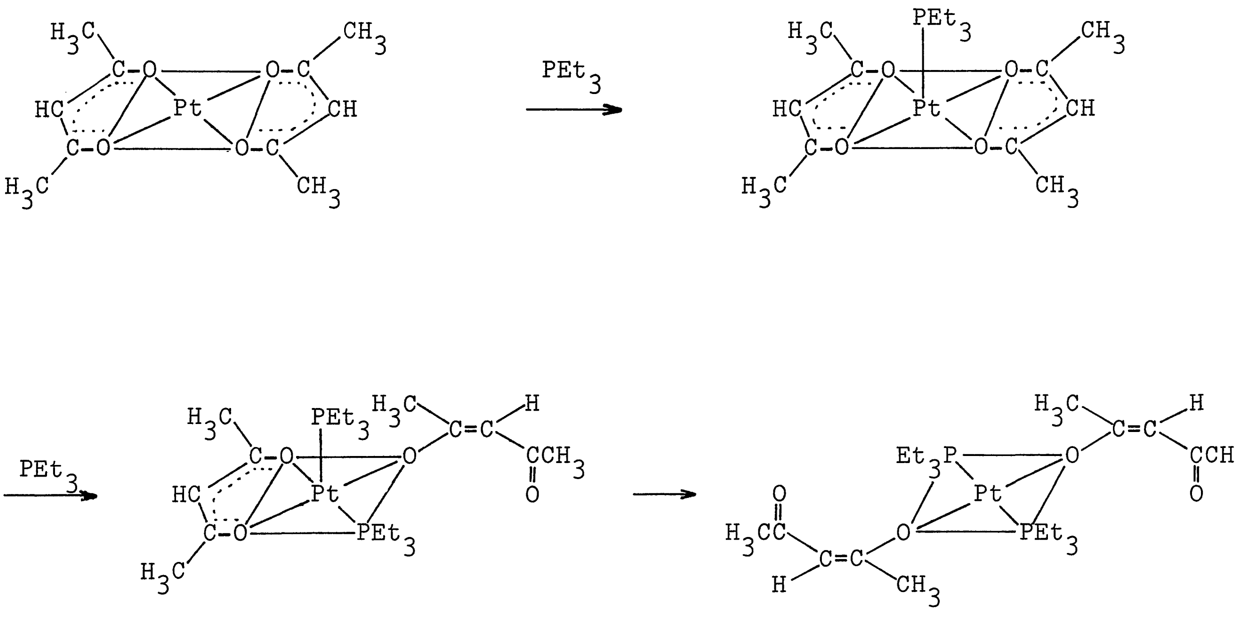
Figure 1. ^1H-NMR spectra of the reaction products between $[Pt(acac)_2]$ and PEt_3. (A) After recrystallization from CH_2Cl_2, (B) Crude product. (100 MHz, in $CDCl_3$ at 25°C)

quintet indicating that two triethylphosphines are mutually trans ($J_{H-H} \approx J_{P-H} \approx 8$ Hz).18)

The alternative octahedral structure for 1 with two chelated acac ligands in plane and the triethylphosphine ligands in axial positions would require the presence of equivalent acac-CH_3 protons and hence can be excluded from consideration.

The reaction product of $[Pt(acac)_2]$ with two moles of PEt_3 before crystallization from CH_2Cl_2 considerably differs from the complex described above. Its IR spectrum shows ν(C=O) bands at 1645m, 1603s, 1565sh, and 1545s cm^{-1} and the ^1H-NMR spectrum shows a complicated pattern as is reproduced in Figure 1(B). The presence of three signals ascribable to acac-methine protons suggests that there are at least three kinds of acetylacetonato ligands in the crude product. Although an unambiguous assignment of each signals is now impossible, it can be considered that the spectrum of the crude product may represent that of the mixture of reaction intermediates. One of the possible reaction paths of the formation of 1 may be such that shown in the following Scheme which favors the observed cis configuration of complex 1 with respect to the C-C double bond as described above.

The isolation of the singly O-bonded acetylacetonato complex may have implications related to the postulated active intermediates in the rearrangement of an acetylacetonato ligand from the bidentate enol form to the central carbon bonded unidentate diketo form5) and in the alkylation reaction of metal acetylacetonate with alkylaluminum compound.4)



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Scheme

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3) Throughout this paper, abbreviation acac is used to indicate the enol type acetylacetonato (2,4-pentanedionato) ligand which is coordinated to the central metal in a bidentate fashion through two oxygen atoms, whereas γ-acac and O-acac represent the acetylacetonato ligand coordinated to the metal in a unidentate way through the central (γ-) carbon atom and one of two oxygen atoms, respectively.

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