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β-DIKETONATE DIANION AS A BRIDGING OR C,O-CHELATING LIGAND

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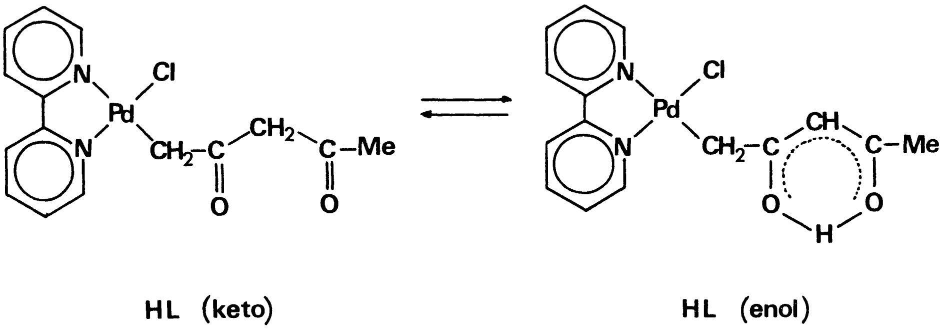
The 2,4-pentanedionate dianion acts as a bridging ligand in [Be(acac)L] and [Pd(acac)L] which were prepared by the reactions of (2,2'-bipyridine)chloro(2,4-pentanedionato-C^1)palladium(II) (HL) with [Be(acac)$_2$] and [Pd(acac)$_2$]. On the other hand the 1,1,1-trifluoro-2,4-pentanedionate dianion is chelating to the metal atom in [Pt($C_5H_3O_2F_3$)L'_2] (L'= PPh_3 and $AsPh_3$).

β-Dicarbonyl compounds such as acetylacetone (acacH) and ethyl acetoacetate are very important ligands, their univalent anions exhibiting various modes of bonding to palladium(II)$^{1,2)}$ and other metal ions.$^{3)}$ On the other hand the complexes containing bivalent anions of β-dicarbonyl compounds have scarcely been reported thus far. On the basis of IR and NMR data, the selenium compound [Se_2($C_5H_6O_2$)$_2$] was concluded to be tetraacetyldiselenacyclobutane, while the tellurium compounds [Te($C_5H_6O_2$)] and [$TeCl_2$($C_5H_6O_2$)] to have the telluracyclohexane-3,5-dione structure.$^{4)}$ Chelation of an acetylacetonate dianion through the terminal carbon atoms in these tellurium compounds$^{5)}$ and a related one$^{6)}$ has been confirmed by X-ray analysis. Recently Ito et al.$^{7)}$ obtained complexes with the composition of [Pt($C_5H_6O_2$)L'_2] by the reactions of [Pt(acac)$_2$] with more than two mole equivalents of tertiary phosphines (L') such as PPh_3, PPh_2Me and $PPhMe_2$ in refluxing THF or toluene. The acetylacetonate dianion in these compounds was presumed to have an η-oxoallylic coordination to platinum. The present communication is concerned with some binuclear metal complexes containing an acetylacetonate dianion as a bridging ligand and also with platinum(II) complexes in which a trifluoroacetylacetonate dianion is chelated to the metal atom through carbon and oxygen atoms.

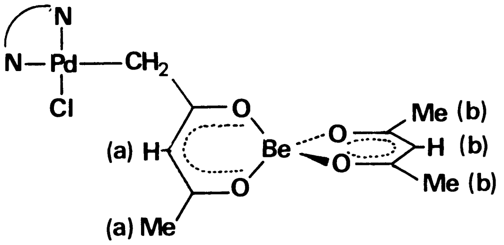
(2,2'-Bipyridine)chloro(2,4-pentanedionato-C^1)palladium(II), [PdCl(acac-C^1)-(bpy)] (HL), which was prepared recently,$^{1)}$ still retains an acidic proton and can



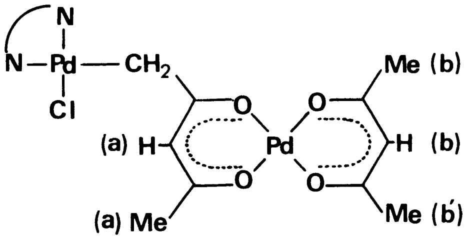
act as a ligand to afford a binuclear complex. The reaction of HL (0.10 mmol) with a large excess of [Be(acac)$_2$] (2.78 mmol) in refluxing benzene (20 ml) for 10 h gave a yellow product [Be(acac)L] in a 78% yield. Similarly the reaction of HL (0.506 mmol) with [Pd(acac)$_2$] (4.92 mmol) in refluxing CH_2ClCH_2Cl (75 ml) for 3 h gave [Pd(acac)L] in a 65% yield.

The ν(CO) bands of HL at 1723 and 1630 cm^{-1} which are attributed to the keto and enol tautomers, respectively, were lost on ligation to Be(II) and Pd(II). Instead two strong bands are observed for [Be(acac)L] and [Pd(acac)L] in the 1550 – 1500 cm^{-1} region which are characteristic of the O,O'-chelated β-diketonate ligand. Proton NMR spectrum of [Be(acac)L] in $CDCl_3$ exhibits two methyl signals at 2.03 and 1.98 ppm from TMS in the area ratio of 1 : 2. These are assigned to CH_3(a) in L and two equivalent methyls(b) in acac, respectively, in accordance with the tetrahedral structure around Be(II). Of the two methine signals observed, the lower-field one at 6.21 ppm may be assigned to CH(a) in L and the other one at 5.59 ppm to CH(b) in acac. On the other hand three methyl signals are found in the spectrum of [Pd(acac)L]. The lowest signal at 2.07 ppm may be assigned to CH_3(a) in L and those at 2.05 and 2.04 ppm to the two methyls(b and b') in acac which are not equivalent because of the square-planar structure around Pd(II). Two methine signals at 6.15 and 5.37 ppm are attributed similarly to CH(a) in L and CH(b) in acac, respectively.

These IR and NMR data together with the satisfactory analyses support the following binuclear structures of these complexes in which the 2,4-pentanedionate dianion acts as a bridging ligand between two metal atoms via the O,O' and C^1 atoms.



[Be(acac)L]



[Pd(acac)L]

The reaction of cis-bis(trifluoroacetylacetonato)platinum(II), [Pt(tfac)$_2$]8) (0.457 mmol) with PPh_3 (1.01 mmol) in dry diethyl ether (10 ml) at room temperature for 0.5 h gave rise to a Naples yellow precipitate. Recrystallization from dichloromethane-petroleum ether afforded tiny crystals with the composition of [Pt($C_5H_3O_2F_3$)-(PPh_3)$_2$]$\cdot\frac{1}{4}CH_2Cl_2$ [1] in a 55% yield, while white plates with no solvent of crystallization were obtained from an acetone solution. trans-[Pt(tfac)$_2$]8) also gave the same product in a 58% yield. A similar reaction of [Pt(tfac)$_2$] with more than twice moles of $AsPh_3$ resulted in pale yellow needles of [Pt($C_5H_3O_2F_3$)($AsPh_3$)$_2$]$\cdot\frac{1}{4}CH_2Cl_2$ [2] in a 71% yield. Both of compounds 1 and 2 gave satisfactory analyses and molecular weights in dichloromethane.

As is seen in Fig. 1, ^{1}H NMR spectrum of compound 1 shows three signals at ca. 7.2, 5.08 and 2.78 ppm from TMS. The area ratio is ca. 30 : 1 : 2 and the signal at

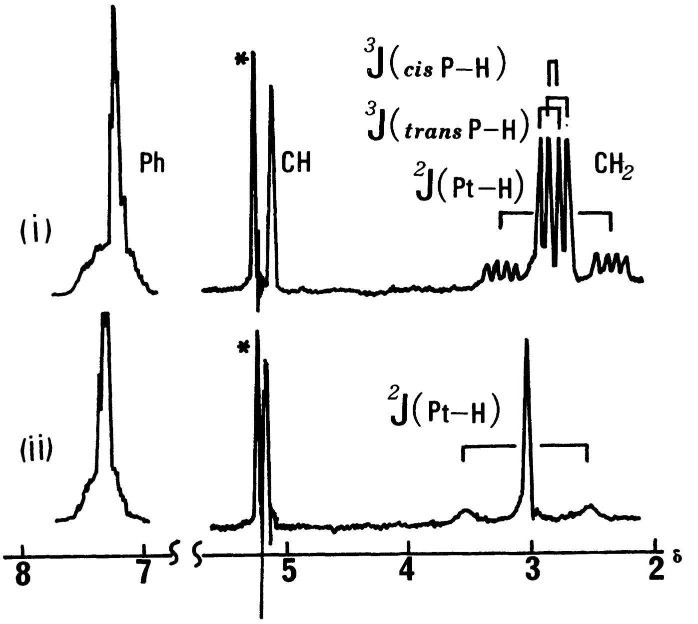
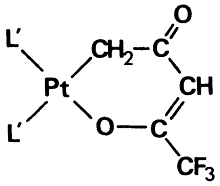


Fig. 1. ^1H NMR spectra of $[Pt(C_5H_3O_2F_3)(PPh_3)_2]\cdot\frac{1}{4}CH_2Cl_2$ (i) and $[Pt(C_5H_3O_2F_3)(AsPh_3)_2]\cdot\frac{1}{4}CH_2Cl_2$ (ii) in $CDCl_3$ at 60 MHz with internal TMS. The peak marked with an asterisk is due to CH_2Cl_2 and the peak for the phenyl protons is reduced to one tenth in area.

the highest field is composed of four lines of equal intensity carrying ^{195}Pt satellites ($^2J_{PtCH_2}$ = 53.5 Hz). The spectrum is in accordance with the following structure, since the four-line pattern of the methylene protons is caused by



1, L' = PPh_3
2, L' = $AsPh_3$

coupling to ^{31}P nuclei at the cis ($^3J_{PPtCH_2}$ = 5.5 Hz) and trans ($^3J_{PPtCH_2}$ = 10 Hz) positions. Invariance of the coupling constants at 60 and 100 MHz and the singlet appearance of the methylene signals ($^2J_{PtCH_2}$ = ca. 60 Hz) for compound **2** (Fig. 1. (ii)) support the proposed structure.

The coupling constants $^2J_{PtCH_2}$ for the present complexes are somewhat lower than those for K[PtCl(acac-O,O')(acac-C^3)] (120 Hz)[9] and [Pt(acac-O,O')(acac-C^3)-PPh_3] (110 Hz)[10] in conformity to the stronger trans influence of the phosphine and arsine ligands as compared with the oxygen donors. In fact they are close to $^{2}J_{PtCH_3}$ values for cis-$[PtX(CH_3)(PEt_3)_2]$ (52.2 – 59.4 Hz)[11] and $[PtX(CH_3)(Ph_2PCH_2CH_2PPh_2)]$ (48.5 – 64.0 Hz)[12] containing various anions as X. IR bands in the ν(C=O) region are observed at 1620vs and 1597s cm^{-1} for **1** and at 1624s and 1600vs cm^{-1} for **2**. The frequencies are remarkably low and may be caused by the electron-donating character of the bis(triphenylphosphine)platinum(II) moiety. The ν(C=O) band was also found at 1630 cm^{-1}, and 1642 and 1627 cm^{-1} for $[PtX(CH_3)(Ph_2PCH_2CH_2PPh_2)]$ complexes with CH_2COCH_3 and $CH(COCH_3)_2$ as X, respectively.[12]

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