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SOME PALLADIUM(II) AND PLATINUM(II) AMINE COMPLEXES CONTAINING β-DIKETONATE ANIONS IN THE OUTER SPHERE

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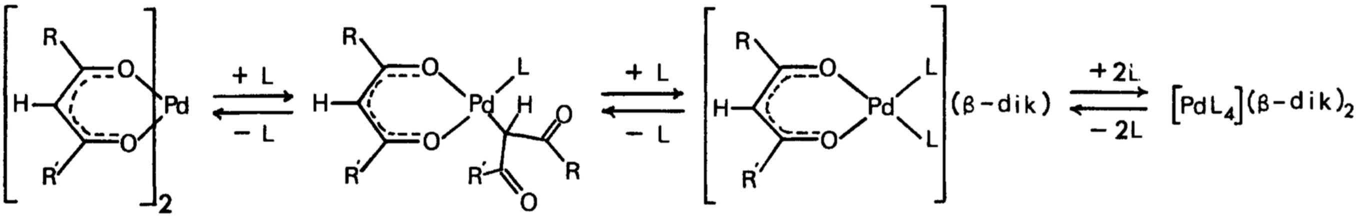
Bis(β-diketonato)palladium(II) reacts with excess amines(L) to afford $[Pd(\beta\text{-dik})L_2](\beta\text{-dik})$ or $[PdL_4](\beta\text{-dik})_2$ depending upon whether L is a secondary or a primary amine, respectively. These reactions are reversible and the relative stability in solution of the complexes containing the β-diketonate anion in the outer sphere is in the order: acac $<$ tfac $<$ hfac.

It has been reported that bis(acetylacetonato)palladium(II)[1)] and bis(ethyl acetoacetato)palladium(II)[2)] react with an equimolar amount of various bases to transform one of the chelating ligands into the central-carbon-bonded state(2). The present communication reports that in the reaction of $Pd(\beta\text{-dik})_2$ with excess amines(L) the β-diketonate ligand is expelled from the coordination sphere, resulting in $[Pd(\beta\text{-dik})L_2](\beta\text{-dik})$ (3) or $[PdL_4](\beta\text{-dik})_2$ (4) depending upon whether L is a secondary or a primary amine, respectively. Pyridine also gives compounds 4.



1 2 3 4

When $Pd(acac)_2$ was dissolved in diethylamine and the mixture was kept in a refrigerator, $[Pd(acac)(Et_2NH)_2](acac)$ (3a) precipitated as yellow crystals in a 40% yield. The following compounds 3 of the type $[Pd(\beta\text{-dik})L_2](\beta\text{-dik})$ were prepared in this way.[3)]

β-dik = acetylacetonate(acac); L = Me_2NH, Et_2NH(3a), piperidine(pip)
β-dik = trifluoroacetylacetonate(tfac); L = Me_2NH, Et_2NH(3b), pip, $\frac{1}{2}$bpy
β-dik = hexafluoroacetylacetonate(hfac); L = $\frac{1}{2}$bpy

Similarly $Pd(\beta\text{-dik})_2$ was stirred in a primary amine such as listed below to afford a white powder of the tetrakis(primary amine)palladium(II) β-diketonate(4) in a quantitative yield.3) The ammine complexes were readily obtained by the reaction of Pd(β-dik)$_2$ with gaseous ammonia in dichloromethane solution.3)

β-dik = acac; L = NH_3, $MeNH_2$, $EtNH_2$, n-$PrNH_2$(4a), $\frac{1}{2}$en
β-dik = tfac; L = NH_3(4b), $MeNH_2$, $EtNH_2$, n-$PrNH_2$(4c), py(4d), $\frac{1}{2}$en
β-dik = hfac; L = NH_3, $MeNH_2$, $EtNH_2$, n-$PrNH_2$(4e), py(4f), $\frac{1}{2}$en

The IR and PMR data for the representative compounds are shown in Table 1. The IR bands in the carbonyl stretching region for compounds 4 nearly coincide with those for the corresponding potassium β-diketonates. Compounds 3 exhibit extra carbonyl bands attributable to the chelated β-diketonate anions. The PMR spectra indicate that the two β-diketonate anions in each 4 exist in the same environment, while those in 3 exist in different environments.(The amine protons in these compounds resonate at appreciably lower fields as compared with those of free amines and the ligated amines in neutral complexes 2 in accordance with that complexes 3 and 4 are cationic.) The chemical shifts of the methyl and methine protons for 4b in D_2O exactly agree with those of potassium trifluoroacetylacetonate, indicating that 4b dissociates into ions in aqueous solution. Similarly compound 4d reacts with a twice molar amount of silver nitrate in pyridine to afford $[Pd(py)_4](NO_3)_2$ in an 83% yield. These results support that one and both of the two β-diketonate anions in 3 and 4, respectively, exist as the counter ion in the outer sphere.

Bis(hexafluoroacetylacetonato)platinum(II)(5) dissolves in neat pyridine with heat evolution. Addition of n-hexane to the solution precipitates $[Pt(py)_4](hfac)_2$ (6) in an 80% yield.3) The methine proton in 5 resonates at 6.44ppm(from internal TMS) in $CDCl_3$ accompanied by the satellite bands with $^4J_{Pt-H}$= 10.5Hz. The ^{19}F signal at 4.74ppm(from external CF_3COOH) in CH_2Cl_2 also shows coupling to ^{195}Pt($^4J_{Pt-F}$= 72Hz). On the other hand neither of the methine ^1H(5.90ppm) and ^{19}F(1.90ppm) signals of 6 couples to ^{195}Pt certifying non-coordination of the hfac anion.

A copper(II) compound analogous to 4, $[Cu(en)_2](acac)_2 \cdot 2H_2O$, was prepared by the reaction of $Cu(acac)_2$ with ethylenediamine in moist dichloromethane. The acac anions were shown by the X-ray analysis to occupy the axial positions 2.79Å apart from the copper atom.4) The molecular weights of 3b and 4f were determined to be 534 and 811 in dichloromethane and are very close to the calculated values 559 and 837, respectively, indicating that these compounds exist as tight ion pairs in dichloromethane. On the contrary, compounds 4c and 4e gave the values 1330 and 1522 in the same solvent which are nearly twice the calculated values 649 and 757, respectively. The dimeric structure of tetrakisaminepalladium(II) complexes such as 4c and 4e is quite fantastic and the X-ray analysis is keenly desired.

The reaction of 1 with a primary amine to yield 4 is tentatively assumed to proceed via 2 and 3, although no compound of the type 3 has been isolated. The thermodynamic stability of 4 seems to be much higher than that of 3. On the other hand the secondary amine dose not give a tetrakis(amine) complex 4 presumably because of the steric requirement of the bulky ligand.

The compounds such as 3a and 4a, which have the acac anion in the outer sphere, are very unstable in solution as compared with the tfac and hfac compounds, and liberate the amine ligand to revert to 2.5) Compound 4d is less stable than 4f and performs a similar reaction. Thus the relative stability in solution of compounds containing

Table 1. Characteristic IR and PMR Data for the $[Pd(\beta\text{-dik})L_2](\beta\text{-dik})$ (3) and $[PdL_4](\beta\text{-dik})_2$ (4) Complexes

Compound	IR spectra in Nujol ν(C═O) and ν(C═C═C) (cm^{-1})	PMR spectra in C_6D_6 δ(ppm from TMS) β-dik[*1] CH_3	 CH	 amine[*2] NH or NH_2
3a	1604, 1517, 1573,[*3] 1543[*3]	1.59, 2.09[*3]	4.93, 5.41[*3]	8.0
3b[*4]	1658, 1646, 1613,[*3] 1535[*3]	1.99, 2.13[*3]	5.40, 5.78[*3]	7.0
4a	1602, 1506	1.89	5.47	6.0
4b	1640, 1510	2.22[*5]	5.38[*5]	——
4c	1638, 1505	1.77	5.75	5.5
4d[*6]	1635, 1555, 1505	2.47[*7]	5.97[*7]	——
4e	1662, 1630, 1524	——	5.89[*8]	4.9[*8]
4f	1675, 1530	——	5.97[*8]	——
6[*9]	1676, 1530	——	5.90[*8]	——

*1 The methyl and methine proton signals are all singlet.

*2 The amine proton signals are all broad.

*3 Assignable to the chelated β-diketonate anion.

*4 Two sets of ethyl proton signals are observed due to the unsymmetric tfac ligand.

*5 In D_2O (ppm from DSS).

*6 Trihydrate.

*7 In pyridine(ppm from TMS).

*8 In $CDCl_3$ (ppm from TMS).

*9 $[Pt(py)_4](hfac)_2$.

the β-diketonate anion in the outer sphere is in the order: acac $<$ tfac $<$ hfac.6) This is in accordance with the relative acid strength of β-diketones.7) The fact deserves to be noticed that in the reaction of 3a to 2 the Pd-C bond is formed by a mere ligand substitution. The Pd(acac-O,O')(amine) moiety prefers the Pd-C bonding with the acac anion to the Pd-O linkage.

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References and Notes

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5) The reaction of 1 to 2 is also reversible. The kinetic study of the reaction

Pd(acac-O,O')(acac-C^3)(py) $\longrightarrow$ Pd(acac-O,O')$_2$ + py is now under investigation.

6) Metal complexes containing a tfac or a hfac anion in the outer sphere have sometimes been obtained (e.g. see S. Komiya and J. K. Kochi, J. Am. Chem. Soc., 99, 3695 (1977)), but an acetylacetonate has not yet been reported except ref. 4.

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