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Stable Palladium(II) Complexes with *Trans*-Bis-γ-acetylacetonato Ligands

GEORGE R. NEWKOME* and TOSHIO KAWATO

Department of Chemistry, Louisiana State University, Baton Rouge, La. 70803, U.S.A.

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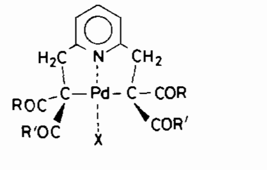
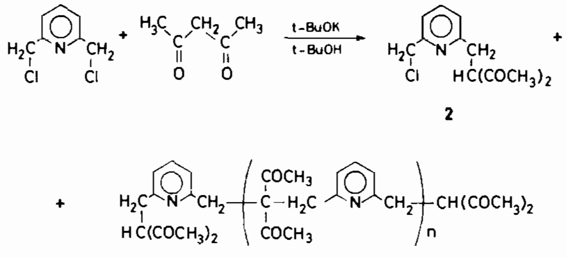
Recently, the first palladium(II) bis(central-carbon-bonded ethyl acetoacetate) complex was reported [1]. Synthesis of a Pd(II) complex with two C-3 bonded acetylacetone ligands has been attempted; however, due to the favored stability of the O,O′-chelate, the desired bis-C-3 Pd(II) complex was not isolated [2]. Reaction of bis(acetylacetonato)platinium with pyridine generated the Pt(γ-acac)$_2$(py)$_2$ complex, which probably possesses the favored *trans* configuration [2]. These neutral complexes as well as Pt(II) complex dianions, which possess two γ-acac ligands, are unstable in solution and easily rearrange to the isomeric oxygen-coordinated complexes [3].

In order to generate a new series of chelating reagents, which incorporate a noble metal ion *via* anionic carbon σ bonds, we melded two molecules of a β-dicarbonyl compound with a 2,6-pyridine bis methylene moiety. From inspection of molecular models, the resultant ligand would afford a chelate structure with suitable bond lengths and angles for stabilizing *trans* carbon–metal–carbon complexation. To the best of our knowledge, the resultant palladium complex (*1*) with two central-carbon-bonded acetylacetonato ligands is the first stable member of this class.



1 ($R = R' = CH_3$, X = Pyridine)

When a mixture of 2,6-di(chloromethyl)pyridine [4], acetylacetone, potassium tert-butoxide, and potassium iodide was heated in tert-butanol, the desired ligand (*3*) (53%) along with *2* (3%), *4* (30%), and other oligomers were obtained. Preparative thick-layer chromatography on silica gel of this mixture afforded an analytical sample of *3*, as a pale yellow oil: IR: 1725 (s, C=O), 1695 (s, C=O), 1590 (s, C$\overset{\cdots}{-}$C$\overset{\cdots}{-}$O), 1575 (s, C$\overset{\cdots}{-}$C) cm^{-1}; MS (70 eV): 303 (M$^+$, 8.6%), 260 (M$^+$–C$_2$H$_3$O, 74.8), 218-(C$_{13}$H$_{16}$NO$_2$, 100), 176(C$_{11}$H$_{14}$NO, 63.6), 109-(C$_7$H$_{11}$N, 83), 43 (C$_2$H$_3$O, 60.8); *Anal.* Found: C, 66.94; H, 6.94; N, 4.41. Calcd for C$_{17}$H$_{21}$NO$_4$: C, 67.31; H, 6.98; N, 4.62.



2

3 (n = 0)
4 (n = 1)

The NMR spectrum of *3* is shown in Fig. 1, in which the peak assignments are depicted. From the pattern intensity ratios of methylene peaks, the ratio of tautomers *3a*, *3b*, and *3c* was found to be approximately 43, 48, and 9%, respectively in CDCl$_3$. For ligands *2* and *4*, reasonable spectral and analytical data were obtained to support the structures. The diketo–enol tautomeric ratio for the acac moieties of *2* in CDCl$_3$ was ascertained to be 72:78 *via* the NMR spectral data.

An aqueous mixture of *3*, potassium hydroxide, K$_2$[PdCl$_4$], and excess pyridine was agitated for several hours, then extracted with CH$_2$Cl$_2$ to afford the organic soluble Pd complex *1*, which was recrystallized from CH$_2$Cl$_2$-diethyl ether as yellow needles: mp *ca.* 195 °C (dec); 62%); IR (KBr): 1635 (s, C=O), 1605 (vs, C=O); *Anal.* Found: C, 52.68; H, 5.03; N, 5.51. Calcd. for C$_{22}$H$_{24}$N$_2$O$_4$Pd·1/4CH$_2$Cl$_2$: C, 52.59; H, 4.86; N, 5.51. Inclusion of (or part of) a solvent molecule (CH$_2$Cl$_2$) during crystallization has been demonstrated by the spike at δ 5.33 in the NMR spectrum and is well documented in related complexes [5]. Complex *1* is very soluble in CHCl$_3$, CH$_2$Cl$_2$, and pyridine, as well as soluble in benzene. The NMR spectrum and peak assignments are shown in Fig. 1. The 2,6-pyridine hydrogens appear as a doublet of doublets at δ 8.30, thus shifted up-field from those of the free ligand and nearly identical to the chemical shift of the 2,6-hydrogens in pyridine N-oxide [6] and close to those of Pt(γ-acac)$_2$(py)$_2$ complex [2]. Equivalence of the methyl groups, demonstrated by the sharp singlet at δ 1.90, presence of coordination-free carbonyl bonds in the IR, and the high solubility in even non polar organic solvents are in accord with the *trans* bis-γ-acetylacetonato palladium structure *1*.

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*Author to whom correspondence should be addressed.

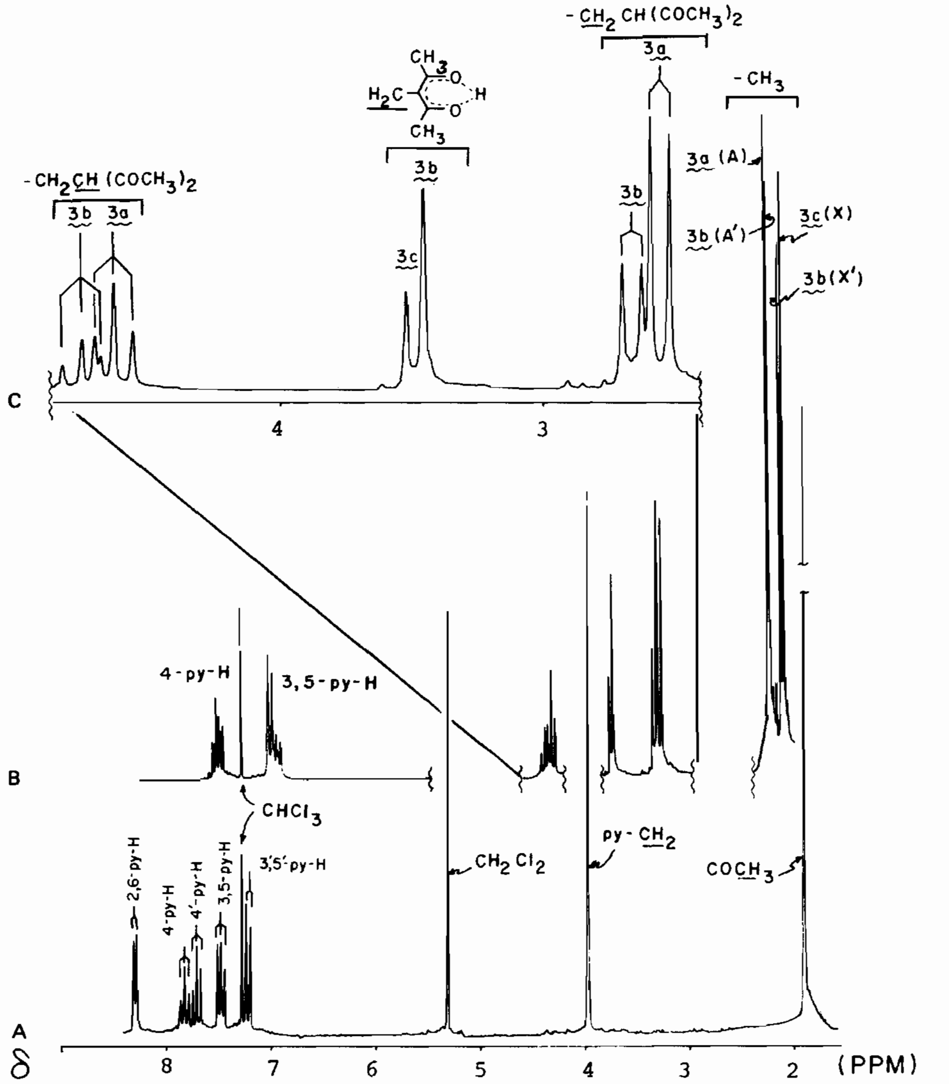
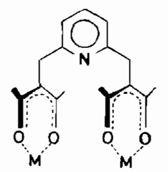


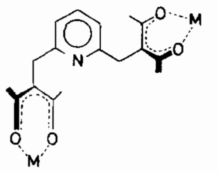
Fig. 1. 200 MHz NMR spectrum in $DCCl_3$ (1% TMS): A, Palladium complex *1*; B, Ligand *3*; C, Expand spectrum of ligand *3*.

The metal complex *1* has one readily exchangeable coordination site; substitution of pyridine (X) and the effect on the orientation of the carbonyl groups is in progress.

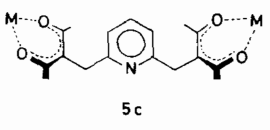
Ligand *3* can afford another type of complex *5*, in which O,O′-chelation predominates. Metal–metal spin interactions can be easily evaluated in *5a* (monomeric with other ligands, *e.g.* acetate, or dimeric); however, polymeric structures *5b* or *5c* can also be envisioned. Therefore for comparative purposes, the copper complex of *3* was synthesized by treatment of *3* with methanolic Cu(II) acetate at ambient temperature for 12 hours. The resultant precipitate was collected, washed with cold methanol, and dried *in vacuo* to give (95%) *5*, as a dull green crystalline powder: IR (KBr): 1565 (vs, C⩵C⩵O) cm^{-1}; *Anal.* Found: C, 53,35; H, 5.03; N, 3.63. Calcd. for $C_{17}H_{19}NO_4Cu \cdot H_2O$: C, 53.32; H, 5.53; N, 3.66. Excess copper acetate was recovered from the filtrate and the copper complex was shown to be insoluble in most common organic solvents, except for acetic acid (yellow solution).



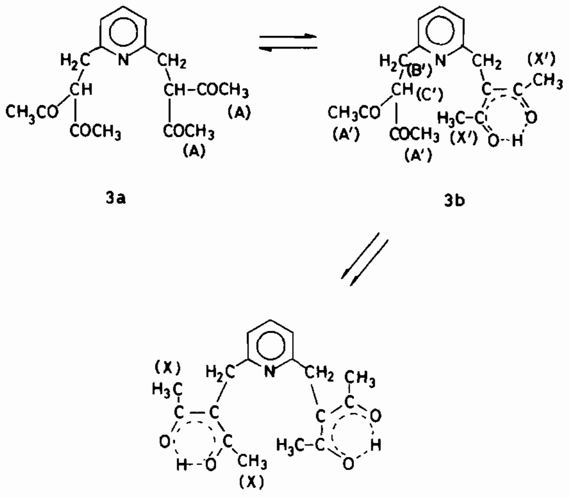
5a



5b



5c



3a 3b 3c

The use of diethyl malonate and ethyl acetoacetate instead of acetylacetone afforded similar ligands. The synthesis and structure of these ligands and corresponding bis-central metal bonded complexes will be reported in detail elsewhere.

Acknowledgement

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