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η-ALLYLIC COORDINATION OF β-DIKETONATE DIANIONS TO PALLADIUM(II)

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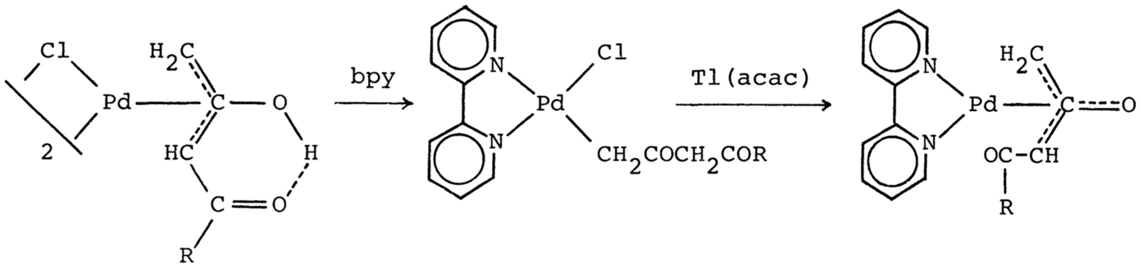
The terminal-carbon-bonded monoanions of 2,4-pentanedione and ethyl acetoacetate in the [PdCl(β-dik-C^1)(bpy)] complexes were deprotonated and converted into the trihapto dianions in the reactions with thallium(I) 2,4-pentanedionate in benzene and in dichloromethane, respectively.

The terminal-carbon-bonded complexes of β-diketonate anions, (2,2'-bipyridine)chloro(2,4-pentanedionato-C^1)palladium(II) (2a)[1)] and (2,2'-bipyridine)-chloro(4-ethoxy-2,4-butanedionato-C^1)palladium(II) (2b)[2)] were derived from di-μ-chlorobis(η^3-1-acetyl-2-hydroxyallyl)dipalladium(II) (1a)[1)] and di-μ-chlorobis-(η^3-1-ethoxycarbonyl-2-hydroxyallyl)dipalladium(II) (1b),[3)] respectively. Complexes 2a and 2b are the β-dicarbonyl compounds of which one methyl proton was substituted by the (2,2'-bipyridine)chloropalladium(II) moiety and still preserve an acidic proton. In fact compound 2a coordinates with another metal ion to produce di- and trinuclear complexes.[4)]

Thallium(I) 2,4-pentanedionate was allowed to react with 2a in benzene and with 2b in dichloromethane at room temperature. Contrary to expectation, the 2,4-pentanedionate anion was not coordinated to palladium(II) in place of the chloride ion, but acted as a base to accept a proton from 2a and 2b, producing a novel type of palladium(II) complexes, 3a and 3b, in more than 90% yields, which contain dianions of 2,4-pentanedione and ethyl acetoacetate, respectively. Found for 3a: C, 49.32; H, 3.83; N, 7.69%; mol wt 392 in dichloromethane. Calculated for $C_{15}H_{14}N_2O_2Pd$: C, 49.95; H, 3.91; N, 7.77%; mol wt 361. Found for the hemi hydrate of 3b: C, 47.41; H, 4.19; N, 6.86%; mol wt 415 in dichloromethane. Calculated for $C_{16}H_{17}N_2O_{3.5}Pd$: C, 47.13; H, 4.20; N, 6.87%; mol wt 391.



1a: R = CH_3 2a: R = CH_3 3a: R = CH_3

1b: R = OC_2H_5 2b: R = OC_2H_5 3b: R = OC_2H_5

Compound 3b was also derived from 1b via another route. After treatment of 1b with silver perchlorate in acetone, the product was reacted with 2,2'-bipyridine in chloroform to afford $[Pd(\eta^3\text{-etac})(bpy)]ClO_4$ (4b) in a 97% yield. Several kinds of bases have been examined and potassium 2,4-pentanedionate was found to be the best reagent to produce 3b almost quantitatively by the reaction with 4b in methanol at -15°C.

Proton NMR spectra of 1b and 3b displayed in Figs. 1 and 2, respectively, are quite similar to each other, indicating that the coordination mode of the dianion of ethyl acetoacetate in complex 3b is essentially the same as that of the monoanion in 1b. Although the syn structure of 1b is stabilized by the intramolecular hydrogen bonding, the enolic proton H_d is lost in 3b and the anti structure is preferred to minimize the repulsive interaction between the anion oxygen and the carbonyl group. Coupling of H_a to H_c in 3b conforms to this structure.

The chemical shifts of H_a and H_c in 3b are strikingly smaller than those observed for syn protons in usual η-allylic complexes.[5)] The up-field shift may be caused by delocalization of the negative charge on the oxygen atom through the allylic carbons. This assumption is also supported by the ^{13}C NMR data. The chemical shift (180.0 ppm) of C^2, the central carbon of allyl group in 3b is 28 ppm larger than that of C^2 in 1b, while the chemical shift (36.5 ppm) of C^3, the end methylene carbon in 3b is 10 ppm smaller than that of C^3 in 1b.

As is seen in Fig. 1, the methylene protons of the ethyl group in 1b resonate at 4.29 ppm as a multiplet. The ethyl group is diastereotopic in this case and the methylene protons are environmentally nonequivalent, exhibiting the 16-lines pattern. In the spectrum of 3b (Fig. 2), on the other hand, the signal for the methylene protons is observed as a simple quartet. The reason for the discrepancy between these two spectra is not apparent, but the difference in the chemical

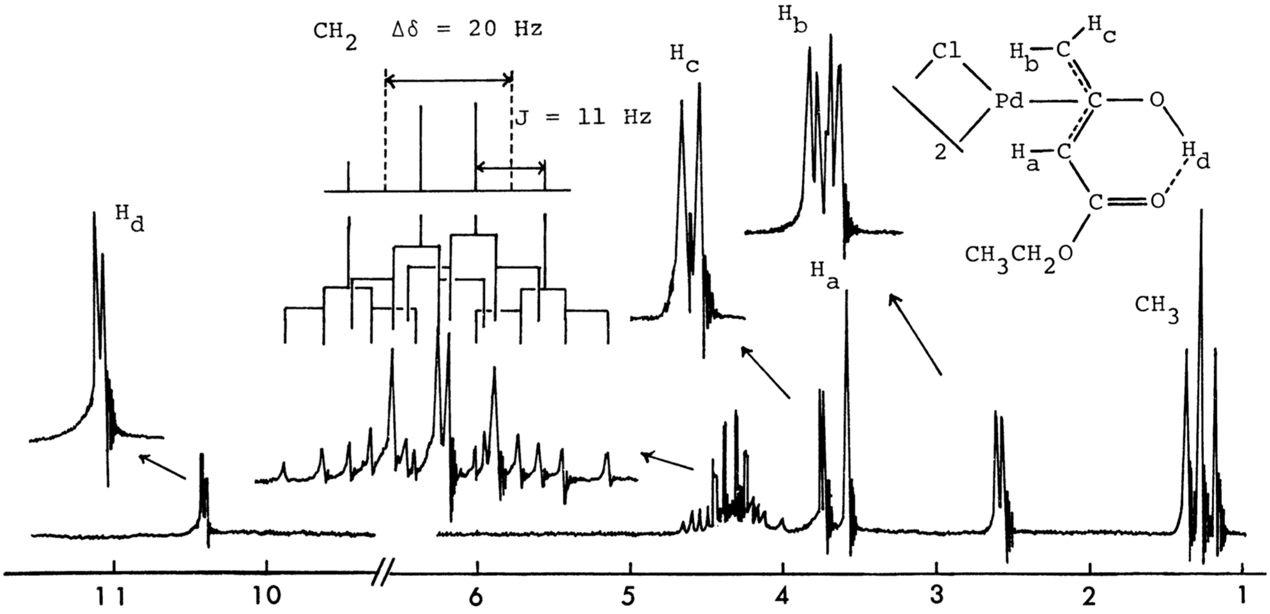


Fig. 1. Proton NMR spectrum of $[PdCl(\eta^3\text{-etac})]_2$ (<u>1b</u>) in $CDCl_3$ with internal TMS, the chemical shifts (in ppm) and coupling constants being CH_3 1.31, CH_2 4.29, $J(CH_3\text{-}CH_2)$ = 7.2 Hz; H_a 3.59, H_b 2.59, H_c 3.74, H_d 10.46, $J(H_b\text{-}H_c)$ = 3.4 Hz, $J(H_b\text{-}H_d)$ = 1.2 Hz.

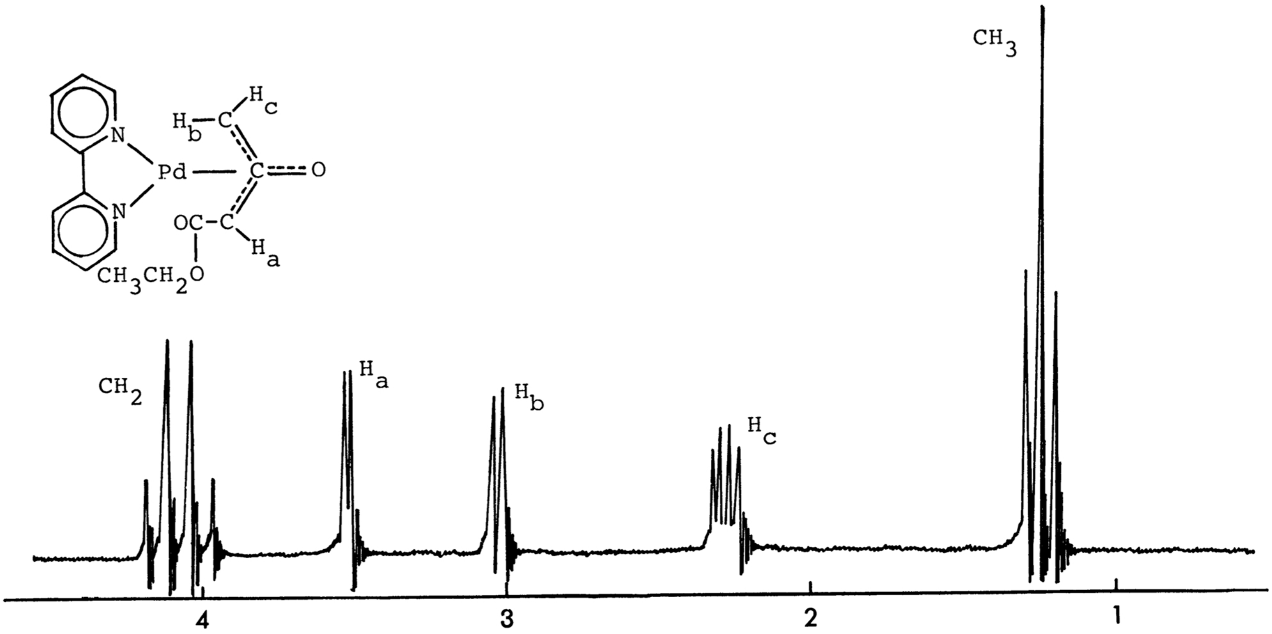


Fig. 2. Proton NMR spectrum of $[Pd(bpy)(\eta^3\text{-etac-H})]$ (<u>3b</u>) in CD_2Cl_2 with internal TMS, the chemical shifts (in ppm) and coupling constants of the ester ligand being CH_3 1.23, CH_2 4.07, $J(CH_3\text{-}CH_2)$ = 7.2 Hz; H_a 3.53, H_b 3.02, H_c 2.27, $J(H_b\text{-}H_c)$ = 4.4 Hz, $J(H_a\text{-}H_c)$ = 2.3 Hz.

shifts of the two protons might be negligibly small by chance in this environment.

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References and Note

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