

THE TERMINAL-CARBON-BONDED PALLADIUM(II) COMPLEXES OF ACETYLACETONE

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Dichlorobis(benzonitrile)palladium(II) reacts with acetylacetone in acetone at room temperature to afford an insoluble product $\text{PdCl}(\text{C}_5\text{H}_7\text{O}_2)$ [1]. The reactions of 1 with a base L such as triphenylphosphine and triphenylarsine, or lithium chloride yield $\text{PdCl}(\text{C}_5\text{H}_7\text{O}_2)\text{L}$ or $\text{PdCl}_2(\text{C}_5\text{H}_7\text{O}_2)^-$, respectively. The σ, η -coordination of the acetylacetonate ligand in these complexes was deduced by the IR and NMR studies. The compound 1 reacts with 2,2'-bipyridine to produce $\text{PdCl}(\text{C}_5\text{H}_7\text{O}_2)(\text{bipy})$, in which the terminal-carbon-bonded acetylacetonate ligand attains the keto-enol equilibrium in solution.

Acetylacetone is a very versatile ligand taking various modes of coordination to a metal atom.¹⁾ The central-carbon bonding of the acetylacetonate anion to a several kinds of metals²⁾ including palladium(II)³⁾ has been well established. The present communication reports a novel σ, η -bonding and the terminal-carbon linkage of this ligand to palladium(II).

Dichlorobis(benzonitrile)palladium(II) (1g) was dissolved in a 1:1 (by volume) mixture (25ml) of acetylacetone and acetone, and allowed to react overnight at room temperature. A yellow precipitate [1] of the composition $\text{PdCl}(\text{C}_5\text{H}_7\text{O}_2)$ was obtained in a 40% yield. The insolubility of 1 prevents the full characterization, but its IR spectrum shows a close resemblance to that of the η -allylic palladium(II) complexes of acetoacetic acid⁴⁾ and its esters.⁵⁾

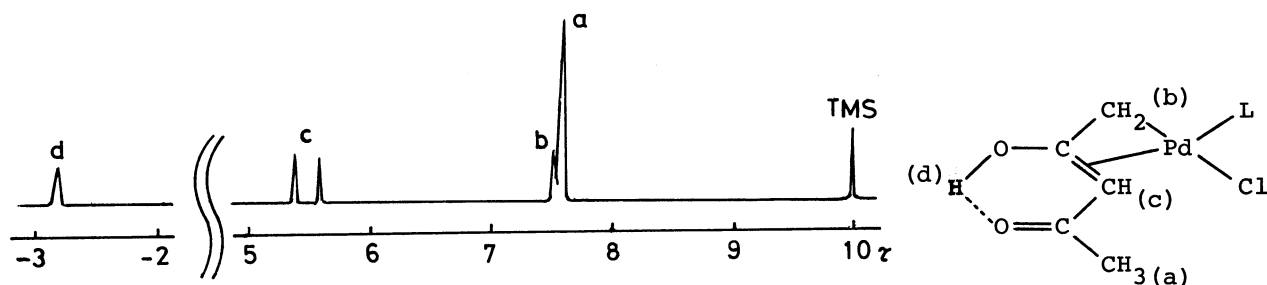
The compound 1 reacted with triphenylphosphine or triphenylarsine in benzene to give $\text{PdCl}(\text{C}_5\text{H}_7\text{O}_2)(\text{PPh}_3)$ [2] and $\text{PdCl}(\text{C}_5\text{H}_7\text{O}_2)(\text{AsPh}_3)$ [3] in 85 and 80% yields respectively. The reaction of 1 with lithium chloride in acetone followed by treatment with tetraphenylphosphonium chloride resulted in $\text{Ph}_4\text{P}[\text{PdCl}_2(\text{C}_5\text{H}_7\text{O}_2)]$ [4] in a 70% yield. The characteristic IR and NMR data of these compounds are summarized in Table 1, and the NMR spectrum of 2 is displayed in Fig. 1.

Rather low frequency of the $\nu(\text{C}=\text{O})$ vibrations and the down field shift of the OH proton signals in NMR indicate the existence of the intramolecular hydrogen bonding in these compounds. The end methylene protons resonate at around $\tau 7.5$ and do not show any appreciable change in shape at lower temperatures down to -60°C . On the basis of this evidence we prefer the σ, η -bonded unsymmetric structure rather than the symmetric η -allylic bonding. If the latter were the case two signals separated by ca. 1 ppm are expected for the end methylene protons.⁴⁾ Although a coupling of the $\text{CH}_2(\text{b})$ signal with ^{31}P can not be detected, the methine signal of 2 appears as a doublet, and the value of $J_{\text{P-H}}=8\text{Hz}$ seems to suggest the trans configuration of CH with respect to PPh_3 . The OH signal is completely lost upon deuteration.

The reaction of 1 with equimolar 2,2'-bipyridine in chloroform produced $\text{PdCl}(\text{C}_5\text{H}_7\text{O}_2)(\text{bipy})$ [5] in a 90% yield, whose IR spectrum shows the $\nu(\text{C}=\text{O})$ bands both at 1720 and 1629 cm^{-1} . The NMR spectrum reveals the coexistence of keto and enol tautomers of the terminal-carbon-bonded acetylacetonate ligand. The equilibrium quotient $K=[\text{enol}]/[\text{keto}]$ is estimated to be 0.7 in CDCl_3 at room temperature. The K value of free acetylacetone was reported to be 6.7 in chloroform at 33°C ,⁶⁾ and it is well established that the introduction of an electron-releasing group into acetylacetone diminishes the K value, while an electron-attracting group increases K .⁷⁾ The effect of metalation at the terminal carbon upon K is quite striking, disclosing the remarkable electron donation of the palladium atom.

Table 1. The Characteristic IR and NMR(100MHz) Data

	L			Assignment
	PPh_3	AsPh_3	Cl^-	
IR (cm^{-1})	1630	1633	1631	$\nu(\text{C}=\text{O})$
	1523	1524	1529	$\nu(\text{C}=\text{C})$
	510	505	505	$\nu(\text{Pd}-\text{C})$
	290	291	287, 270	$\nu_t(\text{Pd}-\text{Cl})$
NMR (τ)	7.56	7.60	7.70	CH_3 (a)
	7.52	7.46	7.70	CH_2 (b)
	5.51($J_{\text{P}-\text{H}}=8$)	5.63	6.22	CH (c)
	-2.80	-2.36	-1.30	OH (d)

Fig. 1. The NMR spectrum of $\text{PdCl}(\text{C}_5\text{H}_7\text{O}_2)(\text{PPh}_3)$ [2] in CDCl_3 at 100MHz.

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