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A NOVEL TYPE OF BRIDGING OF THE β-DIKETONATE DIANIONS BETWEEN TWO PALLADIUM(II) ATOMS: η^3-COORDINATION AND O,O'-CHELATION

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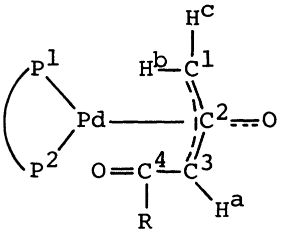
Complexes of a novel type, [(PP)Pd(O,O'-β-dik(2-)-C^1-C^3)Pd(PP)]-$(ClO_4)_2$ containing dianions of acetylacetone and ethyl acetoacetate as a bridging ligand and diphosphines (PP) were prepared and characterized mainly by IR and ^1H, ^{13}C, and ^{31}P NMR spectroscopy.

Dianions of β-dicarbonyl compounds are very useful for organic syntheses,$^{1)}$ but their transition metal complexes are scanty.$^{2)}$ Some palladium(II) complexes containing dianions of acetylacetone and ethyl acetoacetate as a trihapto ligand were reported in a previous paper,$^{3)}$ where a novel type of compound [(bpy)Pd(O,O'-acac(2-)-C^1-C^3)Pd(bpy)]$(hfac)_2$ was mentioned briefly. The present communication is concerned with this kind of dinuclear palladium(II) complexes of bridging β-dicarbonyl dianions containing phosphine ligands in place of 2,2'-bipyridine (bpy) to increase solubility in organic solvents.

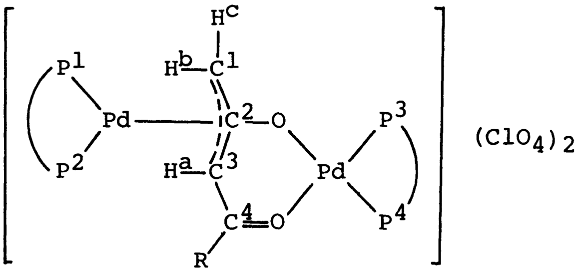
Preparation. The nitrogen base in [Pd(β-dik(2-)-C^1-C^3)(bpy)] was readily substituted by tertiary phosphines in dichloromethane at room temperature to afford the [Pd(β-dik(2-)-C^1-C^3)(PP)] complexes (A) in 87-94% yields. Here β-dik(2-) represents a dianion of acetylacetone (acac(2-)) or ethyl acetoacetate (etac(2-)) and PP a bidentate phosphine such as 1,2-bis(diphenylphosphino)ethane (dppe) and cis-1,2-bis(diphenylphosphino)ethylene (dpe) or two molecules of triphenylphosphine.

Dichloro(diphosphine)palladium(II) was prepared according to the literature method,$^{4)}$ and the chloride ligands were displaced by the reaction with silver(I) perchlorate in acetone. Diphosphinepalladium(II) perchlorate was then treated with complexes A in methanol at 0°C to obtain yellow precipitates of [(PP)Pd(β-dik(2-))-

Pd(PP)]$(ClO_4)_2$ (B) in 55-83% yields. Complexes A (1-5) and B (6-10) gave satisfactory analyses and molecular-weight data in conformity with the following structures. The ν(C=O) bands observed for complexes A in the 1630-1660 cm^{-1} region are lost in the IR spectra of compounds B and only bands in the 1540-1590 cm^{-1} region are observed, indicating coordination of the carbonyl oxygens in B.



A



B

P^1P^2 = dpe; R = CH_3(1), OC_2H_5(2)
P^1P^2 = dppe; R = CH_3(3), OC_2H_5(4)
P^1P^2 = 2PPh_3; R = OC_2H_5(5)

P^1P^2 = P^3P^4 = dpe; R = CH_3(6), OC_2H_5(7)
P^1P^2 = P^3P^4 = dppe; R = CH_3(8), OC_2H_5(9)
P^1P^2 = 2PPh_3; P^3P^4 = dppe; R = OC_2H_5(10)

NMR Spectra. ^1H NMR spectra for these complexes are not conclusive for the structure assignment, since the signals ascribable to H^b and H^c overlap with each other and with other signals. However, the signal from H^a is useful. Thus, H^a of compound 2 resonates at 4.28 ppm from internal Me_4Si in $CDCl_3$ as a doublet of doublets due to coupling to P^1 (J = 8 Hz) in the trans position and to H^c (J = 2 Hz) according to the "W rule."[5] On the other hand, the signal from H^a of compound 7 appears as a doublet at 4.78 ppm with $J(P^1-H^a)$ = 9 Hz. The downfield shift seems to be caused by coordination to the second palladium atom via the oxygen atoms and loss of coupling to H^c by violence of the W rule due to transposition from syn in 2 to anti in 7.

^{31}P and ^{13}C NMR spectra are very helpful. The $^{31}P\{^1H\}$ spectrum of compound 1 in $CDCl_3$ shows two signals at 52.7_9 and 60.2_2 ppm downfield from external H_3PO_4 both as doublets with J(P-P) = 11 Hz, reflecting unsymmetric coordination of the acac(2-) anion to Pd(II), although individual assignment of the signals to P^1 and P^2 is not possible at the present stage of investigation. As is seen in Fig. 1, compound 6 shows two broader signals at 66.1_7 and 68.2_0 ppm besides two doublets at 60.8_5 and 66.6_4 ppm with J(P-P) = 18 Hz in $(CD_3)_2CO$ at 27°C. The latter doublets are assigned to P^1 and P^2 by reference to the spectrum of 1. The former signals, which are probably assigned to P^3 and P^4, become broader with increasing temperature and coalesce at about 50°C, indicating occurrence of the coordination site exchange of the chelating oxygen atoms.

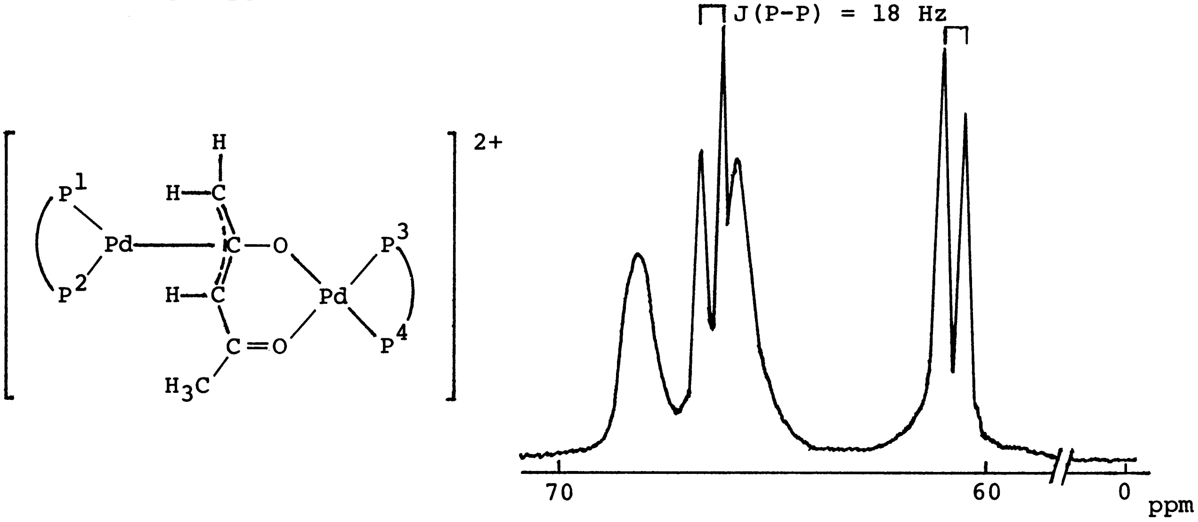
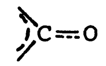
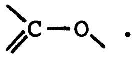


Fig. 1. $^{31}P\{^1H\}$ NMR spectrum of [(dpe)Pd(acac(2-))Pd(dpe)](ClO$_4$)$_2$ (6) in (CD$_3$)$_2$CO at 27°C.

Table 1. ^{13}C NMR chemical shifts δ (ppm from internal Me$_4$Si) and coupling constants J (Hz) in CDCl$_3$ (for 1 and 2) and (CD$_3$)$_2$CO (for 6 and 7)

	δ	J(P^1-C)	J(P^2-C)	J(C-H)	δ	J(P^1-C)	J(P^2-C)	J(C-H)
	[Pd(acac(2-)-C^1-C^3)(dpe)] (1)				[Pd(etac(2-)-C^1-C^3)(dpe)] (2)			
C^1	48.4d	~0	52.$_7$	149	48.3d	~0	52.$_0$	150
C^2	177.0t	5.$_5$	5.$_5$		176.4dd	5.$_5$ and 6.$_2$		
C^3	75.9d	40	~0	145	62.5dd	46.$_5$	1.$_8$	152
C^4	203.7dd	~5	~2		171.1dd	5.$_9$	1.$_2$	
	[(dpe)Pd(acac(2-))Pd(dpe)](ClO$_4$)$_2$ (6)				[(dpe)Pd(etac(2-))Pd(dpe)](ClO$_4$)$_2$ (7)			
C^1	53.4d,br	~0	43	153	53.5d,br	~0	43	154
C^2	166.7t	6	6		170.1t	6	6	
C^3	76.9d	28	~0	158	63.7d	33	0	157
C^4	208.4s	~0	~0		180.5s,br	~0	~0	

Table 1 lists the ^{13}C NMR data for the C^1-C^4 carbons of compounds 1 and 2 in $CDCl_3$ and of 6 and 7 in $(CD_3)_2CO$. The dpe complexes are more stable than the corresponding dppe and PPh_3 complexes, exhibiting very good ^{13}C NMR spectra. The C^1 and C^3 carbons of 1 and 2 resonate at about 10 ppm downfield compared with those of [Pd(acac(2-)-C^1-C^3)(bpy)] and [Pd(etac(2-)-C^1-C^3)(Me_2bpy)],$^{3)}$ indicating larger back donation of palladium to the phosphine than to bipyridines. The C^1 and C^3 nuclei couple much more strongly to the phosphorus atoms situated at the trans position than to those at cis. It is worth noting that C^2 in 2 discriminates P^1 and P^2, giving different coupling constants. The spectra of 6 and 7 are quite similar to those of 1 and 2, approving that the β-dicarbonyl dianions retain the trihapto bonding to palladium. Signals from C^1, C^3, and C^4 are shifted downfield more or less on chelation to another metal atom. Only C^2 shows substantial upfield shift. It might be caused by the change in the bonding mode around C^2 from  to  . Preparation and characterization of analogous dinuclear platinum(II) complexes are now in progress.

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