Journal of Organometallic Chemistry, 161 (1978) 61—73
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STUDIES ON THE REACTIONS OF BIS(ACETYLACETONATO)PLATINUM(II) WITH LEWIS BASES

IV. PREPARATIONS AND CHARACTERIZATION OF NOVEL ACETYLACETONATO COMPLEXES [Pt($C_5H_6O_2$)L_2]

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(Received June 7th, 1978)

Summary

Novel complexes [Pt($C_5H_6O_2$)L_2] (IVa, L = PPh_3; IVb, L = $PMePh_2$, IVc, L = PMe_2Ph) were prepared by the reactions of [Pt(acac)$_2$] with tertiary phosphines either at elevated temperature (when L = PPh_3) or at room temperature (L = $PMePh_2$ and PMe_2Ph), whereas $AsPh_3$ yielded [Pt(acac)(γ-acac)$AsPh_3$] (Id) by the reaction with [Pt(acac)$_2$] even under rigorous conditions. Complexes IV were characterized on the basis of their IR and NMR spectra, elemental analyses and chemical reactions, and a structure which possesses a chelate type "acetylacetonato" ligand involving π-oxoallyl bonding is proposed.

In previous papers of this series we have reported that acetylacetonato (acac) ligands in [Pt(acac)$_2$] which are bonded to platinum as chelate ligands via two oxygen atoms rearrange on reaction with Lewis bases to give complexes with unidentate central C-bonded or O-bonded acetylacetonato ligand(s) [1—3]. It was found that the mode of coordination of the resulting complex depended on the Lewis base employed, i.e., triphenylphosphine and tricyclohexylphosphine afforded complex I [Pt(acac)(γ-acac)L] * (L = PPh_3 (Ia) and P(cyclo-C_6H_{11})$_3$ (Ib)), in which one acac ligand rearranged to the C-bonded form [1], whereas pyridine (py) gave two types of complexes, Ic (L = py) and II [Pt(γ-

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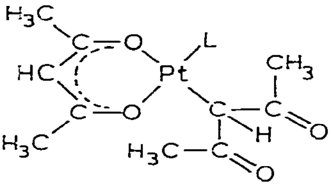
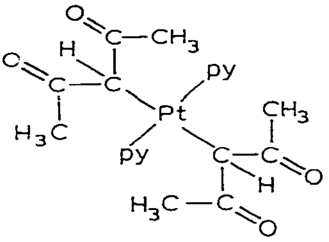
* Throughout this paper abbreviations for the acetylacetonato ligands in various modes of coordination are used as follows: acac, acetylacetonato ligand coordinated to the central metal in an enol bidentate form through two oxygen atoms; γ-acac, the diketo form of acetylacetonato ligand coordinated to the metal in a unidentate way through the central (γ-) carbon atom; O-acac, acetylacetonato ligand coordinated in a unidentate mode through an enolic oxygen atom; and "acetylacetonato" denotes the ligand of the type $C_5H_6O_2{}^{2-}$ in which two protons are removed from acetylacetone (Hacac).

acac)$_2$(py)$_2$], depending on the reaction temperature [2]. Furthermore, the unidentate, O-bonded acetylacetonato complex of the type III [Pt(O-acac)$_2$(PEt$_3$)$_2$], in which the acetylacetonato ligand is coordinated to Pt through one of two O atoms was obtained by the reaction of [Pt(acac)$_2$] with triethylphosphine [3].



(Ia) L = PPh_3
(Ib) L = $P(cyclo\text{-}C_6H_{11})_3$
(Ic) L = py



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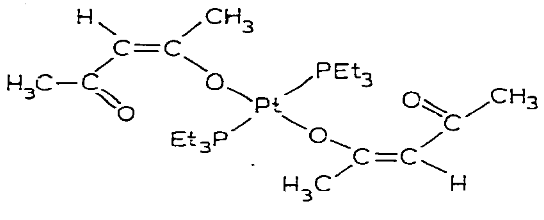
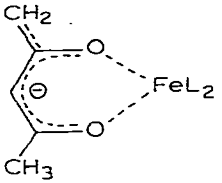


(III)

Continuation of this line of study resulted in the isolation of new complexes of the type [Pt($C_5H_6O_2$)L_2] (IVa, L = PPh_3, IVb, L = $PMePh_2$; IVc, L = PMe_2Ph) from the reaction of [Pt(acac)$_2$] with tertiary phosphines under more rigorous conditions, when L = PPh_3, than those used for the synthesis of complex Ia. Complexes IV appear to contain a chelated "acetylacetonato" ligand ($C_5H_6O_2^{2-}$) presumably having an π-oxoallyl group. Although the iron complex with a chelated "acetylacetonato" ($C_5H_6O_2^{2-}$) ligand such as:



has been postulated as one of the possible products in the reductive decyanation of organic nitriles promoted by Fe(acac)$_3$ [4], there has been no precedent for the isolation of such a new type of "acetylacetonato" complex.

Results and discussion

Preparation of the complex

As we have reported previously, [Pt(acac)$_2$] reacts with an equimolar amount of triphenylphosphine in toluene or diethyl ether at room temperature to yield [Pt(acac)(γ-acac)PPh$_3$] (Ia) [1]. Employment of more rigorous conditions, i.e., reflux in tetrahydrofuran (THF) for several hours, using more than 2 molar equivalents of PPh$_3$, resulted in the formation of a colorless crystalline solid whose analysis corresponded to the composition [Pt($C_5H_6O_2$)(PPh$_3$)$_2$] (IVa). Release of one mol of acetylacetone (Hacac) per mol of the complex in the reaction was confirmed by GLC. The reaction can be carried out similarly at elevated temperatures (100—150° C) using a hydrocarbon solvent such as toluene, decalin or 1,5 cyclooctadiene (eq. 1). In contrast with this reaction, a similar reaction with [Pd(acac)$_2$] has been reported to give a palladium(0) complex [Pd(PPh$_3$)$_4$] [5].

$$[\mathrm{Pt(acac)_2}] + 2\,\mathrm{PPh_3} \xrightarrow{\text{solvent}} \underset{\text{(IVa)}}{[\mathrm{Pt(C_5H_6O_2)(PPh_3)_2}]} + \mathrm{Hacac} \qquad (1)$$

Complex IVa can be obtained also by the reaction of either [Pt(acac)(γ-acac)-PPh$_3$] (Ia) with an equimolar amount of PPh$_3$ in boiling THF or of [Pt(γ-acac)$_2$-(py)$_2$] (II) with 2 molar equivalents of PPh$_3$ in refluxing benzene. These facts, together with the observation that [PtEt(γ-acac)(PPh$_3$)$_2$] (V) rearranges to IVa with evolution of ethane on treatment with THF [1], suggest that the reaction represented in eq. 1 proceeds in a stepwise fashion, passing through the γ-acac mode of coordination.

The diamagnetic, colorless complex IVa is highly soluble in chlorinated solvents such as CHCl$_3$ and CH$_2$Cl$_2$, and moderately soluble in pyridine and hot THF. The complex can be recrystallized from these solvents to give crystals containing each solvent (except CHCl$_3$) which was difficult to remove even by prolonged pumping. Analytical results for these solvated and unsolvated compounds are listed in Table 1. The complexes are stable to air in the solid state, but they are slowly decomposed by air in solution.

TABLE 1

MICROANALYSES AND IR ABSORPTIONS (KBr) OF [Pt($C_5H_6O_2$)L_2], S (IV)

Complex		Microanalyses (Found (calcd.) (%))			IR bands (cm^{-1})
L	S	C	H	Others	
PPh$_3$ (IVa)		60.0 (60.2)	4.5 (4.4)		1650s, 1600vs, 1590(sh), 1570(sh)
PPh$_3$ (IVa)	THF	60.2 (60.7)	4.8 (5.0)		1670s, 1655s, 1625(sh), 1610vs
PPh$_3$ (IVa)	CH$_2$Cl$_2$	55.9 (55.9)	4.5 (4.2)	Cl: 7.7 (7.9)	1655s, 1642(sh), 1593vs, 1582vs
PPh$_3$ (IVa)	$\frac{1}{2}$ py	60.4 (60.9)	4.6 (4.5)	N: 1.0 (0.8)	1650s, 1600vs, 1580(sh)
PPh$_2$Me (IVb)		54.1 (53.7)	4.7 (4.7)		1640s, 1595vs, 1580(sh)
PPhMe$_2$ (IVc)		43.5 (44.3)	4.8 (5.0)		1570s, 1535s

TABLE 2

^{1}H NMR DATA FOR [Pt($C_5H_6O_2$)L_2] (IV) [a]

Assignment		[Pt($C_5H_6O_2$)(PPh_3)$_2$] (IVa)			[Pt($C_5H_6O_2$)($PMePh_2$)$_2$] (IVb)		[Pt($C_5H_6O_2$)(PMe_2Ph)$_2$] (IVc)	
		δ (ppm)	J(Pt—H) (Hz)	Other J's (Hz)	δ (ppm)	J(Pt—H) (Hz)	δ (ppm)	J(Pt—H) (Hz)
$C_5H_6O_2$	CH_3	1.28 (s 3)	~0	H_a—H_b 6.5	1.57 (s 3)	~0	2.13 (s 3)	6
	H_a	2.66 (m 1)	~0	H_a—H_c 3	2.53 (m 1)	*b*	2.66 (m 1)	*b*
	H_b	3.12 (dds 1)	67	H_b—H_c ~0	2.90 (ms 1)	~50	2.97 (ms 1)	~45
	H_c	4.36 (dds 1)	36	P—H_b 11	4.10 (ms 1)	48	4.10 (ms 1)	56
L	Ph	~7.2 (m 30)	*b*		~7.3 (m 20)	*b*	~7.35 (m 10)	*b*
	Me				1.71 (ds 3) J(P—H) 9 1.86 (ds 3) J(P—H) 9	28 36	~1.65 (m 12)	*b*

[a] In $CDCl_3$, 100 MHz, at 25°C. Chemical shifts are in δ values (ppm) with respect to Me_2Si as internal standard. In parentheses are multiplicity and number of protons. Multiplicity symbols: s, singlet; m, multiplet; ds, doublet with satellites due to ^{195}Pt; dds, doublet of doublets with satellites due to ^{195}Pt, ms, multiplet with satellites due to ^{195}Pt. [b] Uncertain.

The use of $PMePh_2$ and PMe_2Ph in place of PPh_3 yielded analogous complexes, $[Pt(C_5H_6O_2)(PMePh_2)_2]$ (IVb) and $[Pt(C_5H_6O_2)(PMe_2Ph)_2]$ (IVc), under milder conditions than those adopted for the synthesis of IVa (see Experimental section). The analytical results for these complexes are included also in Table 1. It is interesting that PEt_3, a more electron-donating tertiary phosphine, affords the unidentate O-acac type complex III on reaction with $[Pt(acac)_2]$ [3].

In contrast to the tertiary phosphine ligands, triphenylarsine afforded only the mono-γ-acac complex, $[Pt(acac)(\gamma\text{-acac})AsPh_3]$ (Id), on reaction with $[Pt(acac)_2]$ even under rigorous conditions. In view of the fact that type I complexes, $[Pt(acac)(\gamma\text{-acac})L]$, were converted to "acetylacetonato" complexes of type IV (when L = PPh_3) or to bis-γ-acac complex of type II (when L = py) on further reaction with respective Lewis bases, the exceptional inertness of Id toward further attack of $AsPh_3$ is noteworthy.

$$[Pt(acac)_2] + AsPh_3 \xrightarrow[\text{reflux}]{\text{toluene}} \underset{\text{(Id)}}{[Pt(acac)(\gamma\text{-acac})AsPh_3]} \tag{2}$$

Attempts to obtain complex IV by the reaction of *cis*-$[PtCl_2L_2]$ (L = PPh_3 and $PMePh_2$) with acetylacetone in the presence of pyridine or triethylamine at 120° C failed and the reactants were recovered. Furthermore, neither $[Pt(PPh_3)_4]$ nor $[Pt(PPh_3)_3]$ reacted with acetylacetone even on heating at 110° C for 16 h in toluene, in spite of a brief report on the isolation of a complex with a platinacyclopropane ring from essentially the same system [6].

IR and ^1H NMR spectra

The IR spectra of complexes of type IV show strong absorptions around 1600 cm^{-1} in addition to bands due to coordinated phosphine ligands. There was no band assignable to $\nu(OH)$. As is shown in Table 1, the characteristic bands in the 1500—1700 cm^{-1} region are sensitive to the nature of ligand L and the attached solvent S, but they are definitely different from those of the complexes of type $[Pt(acac)(\gamma\text{-acac})L]$ (I) as there is no band below 1550 cm^{-1} in the spectra of the former. The absorptions of IV also differ distinctly from those of bis-γ-acac complex II whose carbonyl absorptions appear above 1600 cm^{-1}.

The ^1H NMR spectra (Table 2) of IVa in $CDCl_3$ consisted of signals at $\delta \sim$ 7.2 (30H) and 1.29 ppm (3H) together with three groups of multiplets each centered at 4.36, 3.12, and 2.66 ppm (total intensities corresponded to 3H). The complicated pattern of the last three blocks of signals (Fig. 1A) was simplified considerably by irradiating the ^{31}P nucleus to remove its coupling. As illustrated in Fig. 1B, the $^1H\{^{31}P\}$ NMR spectrum suggests that there exist three protons H_a, H_b, H_c, where H_a couples with both H_b and H_c, whereas no coupling exists between H_b and H_c, and that H_b and H_c signals accompany the satellite bands due to coupling with ^{195}Pt. Although the higher counterpart of the H_b satellite bands is not discernible in the 100 MHz spectrum owing to overlapping with the H_a signal, the 220 MHz spectrum of the same sample clearly resolved them, suggesting the validity of the assignments made on the 100 MHz spectrum. There was no appreciable change in the ^1H NMR signals

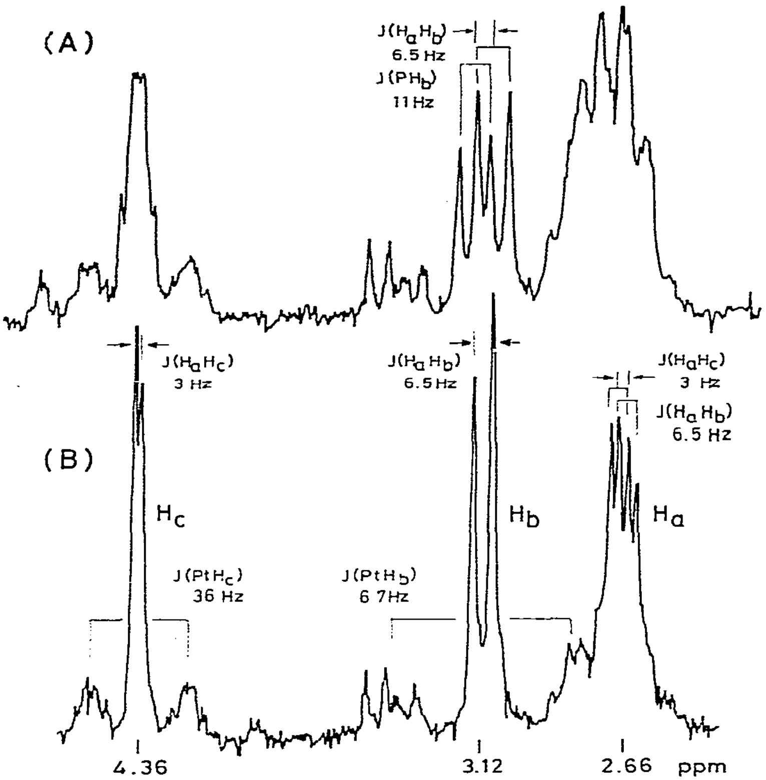


Fig. 1. ^{1}H NMR spectrum (A) and ^{1}H $\{^{31}P\}$ NMR spectrum (B) of $[Pt(C_5H_6O_2)(PPh_3)_2]$ (IVa) (2—5 ppm region).

when the temperature was changed from —40 to 60° C. As is shown in Table 2, the ^{1}H NMR spectra of IVb and IVc possess the characteristic signals essentially similar to those of IVa except that there exist some complicated phosphine-methyl signals in the former. The fact that the methyl groups of $PMePh_2$ in complex IVb appeared as two sets of doublets suggests that the complex has a square planar *cis*-configuration with respect to two phosphine ligands.

The *cis*-configuration of IV was further supported by the ^{31}P NMR spectral data of the PPh_3 complex IVa. $^{31}P\{^{1}H\}$ NMR spectrum of IVa in $CDCl_3$ at 25° C shows a pair of singlets at δ 25.5 and 25.9 ppm (with respect to external PPh_3 reference, downfield positive) each accompanied by the satellite bands due to ^{195}Pt (^{1}J(Pt—P) 2880 and 3195 Hz, respectively). This means that the two phosphine ligands in IVa are in different electronic environments due to the different *trans* substituents. The values for ^{1}J(Pt—P) are somewhat smaller than the reported value of 3875 Hz for *cis*-$[PtCl_2(PPh_3)_2]$ [7]. In $^{13}C\{^{1}H\}$ NMR spectrum (in $CDCl_3$ at 25° C) there are three sets of fairly weak signals in addition to the strong multiplet at δ 127.7—134.0 ppm (downfield from internal $SiMe_4$) due to carbon atoms in the coordinated PPh_3. The singlet at 31.0 ppm may be assigned to the methyl group as it changes to quartet by a "gated" decoupling experiment. Two doublets at a low magnetic field (δ 178.0 and 202.9 ppm, *J*(P—C) 4.9 Hz) remained doublet on a "gated" decoupling experiment, hence they were assigned to the carbon atoms attached to oxygen in the "acetylacetonato" ligand. The signals of the remaining two carbon atoms could not be discerned in the $^{13}C\{^1H\}$ NMR spectrum but might be either included in the multiplet signals of PPh_3 or split into the multiplet due to the coupling with phosphorus nuclei.

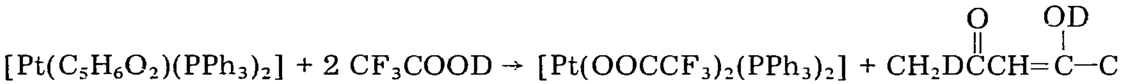
Some reactions of [Pt($C_5H_6O_2$)(PPh_3)$_2$] (IVa)

Complex IVa reacted with acetyl or benzoyl chloride at room temperature to give the known dichloro complex, *cis*-[$PtCl_2(PPh_3)_2$]. This is in contrast to the behavior of [Pt(acac)(γ-acac)PPh_3] (Ia), which undergoes mono-chlorination on a similar reaction with benzoylchloride to give [PtCl(acac)PPh_3] [1]. It is noteworthy that even dichloromethane, which was used as a solvent for recrystallization of IVa, can readily chlorinate IVa in the presence of gaseous CO or CO_2 to give the *cis*-dichloro complex.

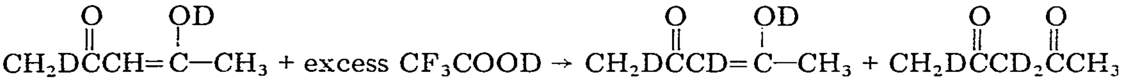
The reaction of IVa with an excess of trifluoroacetic acid at room temperature afforded [$Pt(OOCCF_3)_2(PPh_3)_2$] [8] and acetylacetone (eq. 3). The stoichiometry of the reaction was confirmed on the basis of the ^1H NMR spectrum.

$$[Pt(C_5H_6O_2)(PPh_3)_2] + 2\ CF_3COOH \rightarrow [Pt(OOCCF_3)_2(PPh_3)_2] + C_5H_8O_2(\mathrm{Hacac}) \qquad (3)$$

That is, the ^1H NMR signals of the samples prepared by dissolving [$Pt(C_5H_6O_2)$-$(PPh_3)_2$]CH_2Cl_2 in CF_3COOH consisted of those ascribable to the coordinated PPh_3 at δ 7.5 ppm (multiplet, 30H), CH_2Cl_2 at δ 5.28 ppm (singlet, 2H), and free acetylacetone (enol/keto 1/1; enol-CH_3 at δ 2.27 ppm and keto-CH_3 at δ 2.54 ppm, total 6H; enol-CH at δ 5.82 ppm and keto-CH_2 at δ 4.03 ppm, total 1.5H; each singlet). The contents of each component in the reaction mixture was determined as 2.05 mol/mol of the initial complex for PPh_3, 0.88 mol for CH_2Cl_2 and 0.93 mol for acetylacetone using 1,1,1′,1′-tetrachloroethane as an internal standard. When deuteriated trifluoroacetic acid, CF_3COOD, was used in place of CF_3COOH, signals due to the keto-CH_2 and the enol-CH of acetylacetone disappeared completely and the signal intensity of its methyl protons decreased by about 26%. These results indicate that the "acetylacetonato" ligand of IVa may be such that one of the two methyl groups of acetylacetone is participating in bonding to the platinum atom (eq. 4, 5).



$$[Pt(C_5H_6O_2)(PPh_3)_2] + 2\ CF_3COOD \rightarrow [Pt(OOCCF_3)_2(PPh_3)_2] + CH_2D\overset{O}{\overset{\|}{C}}CH{=}\overset{OD}{\overset{|}{C}}{-}C \qquad (4)$$



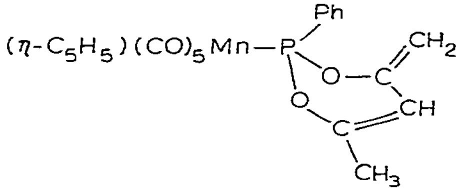
$$CH_2D\overset{O}{\overset{\|}{C}}CH{=}\overset{OD}{\overset{|}{C}}{-}CH_3 + \text{excess } CF_3COOD \rightarrow CH_2D\overset{O}{\overset{\|}{C}}CD{=}\overset{OD}{\overset{|}{C}}{-}CH_3 + CH_2D\overset{O}{\overset{\|}{C}}CD_2\overset{O}{\overset{\|}{C}}CH_3 \qquad (5)$$

Furthermore, no change was observed in the shape of the ^1H NMR signals due to the PPh_3 ligand between two systems: IVa/CF_3COOH and IVa/CF_3COOD. This fact suggests that there is no orthometallation involved in the bonding of PPh_3 with platinum in complex IVa.

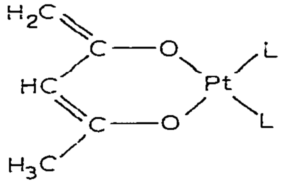
Possible structure for complex IV

The spectral, chemical and elementary analytical results described above all agree with the formula [Pt($C_5H_6O_2$)L_2] for complexes IVa—IVc. Especially the results of the chemical reactions strongly suggest that IV contains an "acetylacetonato" ligand in which one of the two methyl groups of the acetylacetone participate in the bonding to the central metal. There are several possible structures to meet these requirements as follows.

The first example of a compound which possesses a *cis*-diene diolate type acetylacetonato group, such as VI, has recently been reported and its molecular structure was determined by X-ray analysis [9]. Although ^{1}H NMR data for the present complex IV (Table 2) are somewhat similar to those reported for the "acetylacetonato" ligand in VI [9] (δ 3.75 and 4.32 ppm (=CH_2), δ 4.58 ppm ($\geqslant$CH), and δ 1.25 ppm (—CH_3); no data were given on the coupling constants of the signals) assignment of complex IV to structure I seems to be less probable since the strong IR absorptions observed around 1600 cm^{-1} for complex IV cannot be explained by structure A with an exocyclic methylene group.

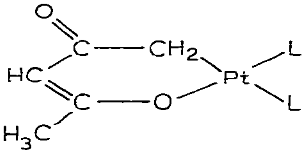


(VI)



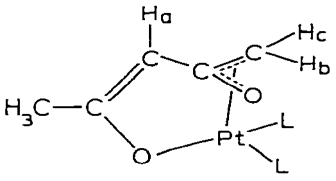
(A)

Participation of the terminal methyl group(s) of the β-diketonato ligand in the form of a methylene group in the bonding to the metal has been reported for tellurium [10] and palladium [11]. However, there is no precedent for the chelating β-diketonato complex possessing both terminal CH_2—metal and enol O—metal σ-bonds similar to structure B. Structure B is not consistent with the ^{1}H NMR parameters of IV (Fig. 1 and Table 2). For example the CH_2 group should be equivalent and have a large coupling with ^{195}Pt.



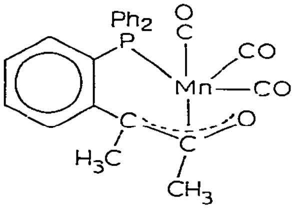
(B)

Structure C which involves π-oxoallyl mode of coordination can be regarded as a delocalized intermediate between two structural extremes, A and B.



(C)

Although some π-oxoallyl complexes of Co [12,13], Ru [14], Fe [13,15], and Ni [13] have been postulated as active intermediates in reactions involving organic carbonyl compounds, few examples of the unambiguous isolation of such π-oxoallyl complex have been reported. Except the manganese complex of VII [16], whose structure has been confirmed through X-ray structural analysis [17], other π-oxoallyl derivatives of Pd [18—20] and Fe [21] of type VIII so far reported have all been assumed on the basis of IR and ^{1}H NMR,



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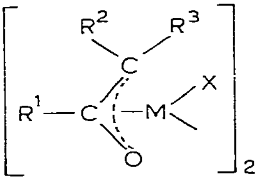
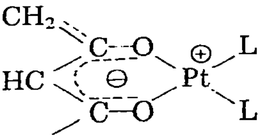


(VIII)

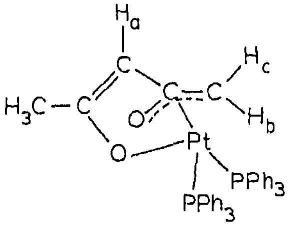
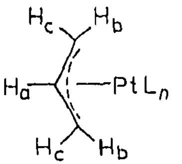
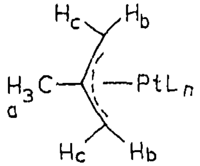
and/or mass spectrometry. A contradictory observation has been reported on their IR absorption, i.e., complexes VII [16] and VIII (M = Pd, R^1 = Me and Ph, R^2 = H, R^3 = X = Cl) [18] lack the ν(C=O) band, whereas the rest of the complexes [19—21] are claimed to show strong bands assignable to ν(C=O) in the 1500—1580 cm^{-1} region. If one assumes that the very strong bands around 1600 cm^{-1}, the region which is too high for structure A and too low for B, observed in the present complexes IV is due to the ν(C=O) of π-oxoallyl group, its ^{1}H NMR spectral data (Table 2) can be explained reasonably well by considering structure C, where H_a, H_b and H_c in Table 2 correspond to, respectively, the proton attached to vinylic carbon, *anti*, and *syn* pseudo-allylic protons. Since there have been no ^{1}H NMR data reported which are relevant to structure C, the comparison was made between ^{1}H NMR data of IV and some reported π-(meth)allylplatinum complexes, such as $(\pi\text{-}C_5H_5)(\pi\text{-allyl})Pt$ [22], $[(\pi\text{-(meth)allyl})Pt(PPh_3)_2]^+$ [23,24] and $(\pi\text{-(meth)allyl})Pt(C_6Cl_4H)(PPh_3)$ [25] (Table 3). The only difficulty in assigning complexes IV to structure C is that there exists considerable coupling between H_a and H_b/H_c, since such coupling is usually minimal when a carbon—carbon single bond intervenes. Alternatively, structure D which is similar to that postulated by van Tamelen et al. for iron [4], may also meet the requirement of these observed H—H coupling constants as well as other ^{1}H NMR parameters.



(D)

TABLE 3

COMPARISON OF THE ^{1}H NMR PARAMETERS BETWEEN IVa AND SOME π-ALLYL COMPLEXES OF PLATINUM

	Chemical shifts δ (ppm)			Coupling constants, J (Hz)						
	H_a	H_b	H_c	H_a—H_b	H_a—H_c	H_b—H_c	Pt—H_a	Pt—H_b	Pt—H_c	P—H_b
$[Pt(C_5H_6O_2)(PPh_3)_2]$ (IVa)	2.66	3.12	4.36	6.5	3	c	c	67	36	11
$[Pt(\pi\text{-}C_3H_5)(\pi\text{-}C_5H_5)]$ [a]	~3.6	2.03	3.57	8	4	~0	c	54	29	
$[Pt(\pi\text{-}C_3H_5)(PPh_3)_2]^+BPh_4^-$ [b]	4.8	2.60	3.55	13	7	~0	c	40	c	8
$[Pt(\pi\text{-}CH_3\text{-}C_3H_4)(PPh_3)_2]^+BPh_4^-$ [b]	1.82	2.67	3.28	~0	~0	~0	63	40	c	8

[a] Ref. 24. In C_6H_6, 40 MHz, room temperature. [b] Ref. 26. In $CDCl_3$, 100 MHz, room temperature. [c] Not observable.

The lack of success in preparing a single crystal suitable for X-ray studies * so far prevents us from presenting a definite structure for complexes IV. However, structure C or D seem to be most appropriate for the structure of IV on the basis of spectral, chemical, and analytical results.

Experimental

All manipulation were carried out under an atmosphere of nitrogen or argon. $[Pt(acac)_2]$ was prepared according to the reported method [26]. Triphenylphosphine was kindly donated by Ihara Chemical Industry Co. Ltd., to which we are indebted. Methyldiphenylphosphine [27] and dimethylphenylphosphine [28] were prepared as described in the literature. Triphenylarsine (Strem) was used as purchased.

Infrared spectra were recorded on a Hitachi 295 spectrometer as KBr discs. ^1H NMR (100 MHz) and $^{31}P\{^1H\}$ NMR (40.5 MHz) spectra were measured by Mr. Y. Nakamura on JEOL PS-100 spectrometer which was operated in the Fourier transform mode for the latter nucleus. ^{13}C NMR spectra (15.1 MHz) was recorded on JEOL FX-60 by Mr. K. Kosaka of Japan Electron Optics Laboratory, Ltd., to whom the authors are indebted. The 220 MHz ^1H NMR spectra were measured on Varian HR-220 spectrometer by T. Hattori of Kyoto University. Elemental analyses of carbon, hydrogen, nitrogen and chlorine were performed by Mr. T. Saito of our research Laboratory.

Preparation of $[Pt(C_5H_6O_2)(PPh_3)_2]$ *(IVa).* A mixture of $[Pt(acac)_2]$ (0.43 g, 1.09 mmol), PPh_3 (0.60 g, 2.29 mmol) and THF (10 ml) was heated under reflux for 5 h to give a yellow solution. GLC analysis (SDC-550, 50° C, H_2 as carrier gas, and di-n-propylketone as an internal standard) of the solution revealed that 0.82 mol of acetylacetone per mol of the starting $[Pt(acac)_2]$ was liberated in the solution. On cooling the yellow solution to room temperature, a white precipitate was deposited. In order to complete the precipitation, 10 ml of hexane was added to the system with stirring. The white precipitate was filtered, washed with hexane, and dried in vacuo to give 0.83 g (93%) of unpurified $[Pt(C_5H_6O_2)(PPh_3)_2]$THF. Recrystallization of the white powder from a 1/2 mixture of CH_2Cl_2 and hexane afforded white prisms of $[Pt(C_5H_6O_2)(PPh_3)_2]$-CH_2Cl_2 (m.p., 210—220° C, with decomposition). Similarly, recrystallization of the crude product from either hot THF or pyridine/hexane gave crystals containing each solvent. A solvent-free complex was obtained by the analogous reaction in refluxing toluene or heptane or in decalin at 160° C or 1,5-cyclooctadiene at 130° C. Analytical results of the solvated and unsolvated products are listed in Table 1.

Preparation of $[Pt(C_5H_6O_2)(PMePh_2)_2]$ *(IVb).* Stirring a diethyl ether (10 ml) solution of $[Pt(acac)_2]$ (0.35 g, 0.90 mmol) and $PMePh_2$ (0.50 ml, 2.66 mmol) at room temperature overnight afforded a pale yellow precipitate. The precipitate was filtered, washed with Et_2O and hexane and dried in vacuo. The crude product (0.41 g, 66%) was recrystallized from CH_2Cl_2/toluene to give pale-orange crystals of $[Pt(C_5H_6O_2)(PMePh_2)_2]$.

Preparation of $[Pt(C_5H_6O_2)(PMe_2Ph)_2]$ *(IVa).* A similar reaction as above

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* Good crystals of IVa we obtained from the $CHCl_3$/hexane system were found to be twins.

was applied for the synthesis of IVc. The powdery, deep-yellow crude product was recrystallized from a 1/3 mixture of CH_2Cl_2 and Et_2O to give pale-orange crystals. The product was characterized by elemental analysis, IR (Table 1) and ^{1}H NMR (Table 2) spectroscopy.

Reaction of [Pt(acac)₂] with AsPh₃. The pale-yellow suspension of [Pt(acac)$_2$] (0.23 g, 0.59 mmol) and $AsPh_3$ (0.50 g, 1.6 mmol) in 5 ml of toluene was heated under reflux for 11 h, affording a pale-yellow solution. The solution was concentrated to ca. 0.5 ml in vacuo to yield a cream precipitate. Hexane (5 ml) was added to the system to complete the precipitation. The cream powder (0.35 g) was filtered, washed with hexane and dried in vacuo. The crude product was reprecipitated from CH_2Cl_2/hexane to give, again, the cream powder (0.22 g), the ^{1}H NMR spectrum of which in $CDCl_3$ indicated that it consists of [Pt(acac)(γ-acac)$AsPh_3$] (Id) (ca. 75%) and the starting [Pt(acac)$_2$] (25%). Characteristic IR absorptions of Id: 1686s, 1675s, 1570s, 1550s, 1522s cm^{-1}. ^{1}H NMR data of Id ($CDCl_3$, 25°C): δ 1.63 (3H,s,acac-CH_3 *trans* to γ-acac ligand), 2.01 (3H,s,acac-CH_3 *trans* to $AsPh_3$), 2.21 (6H,s,γ-acac-CH_3), 4.40 (1H,ss, γ-acac-CH,J(PtH) 15 Hz) and 5.48 ppm (1H,s,acac-CH).

Reactions of [Pt($C_5H_6O_2$)(PPh_3)$_2$] (IVa). Reaction with acetyl chloride and benzoyl chloride. On stirring the mixture of complex IVa (0.19 g, 0.23 mmol) and 7 ml of CH_3COCl (98.5 mmol) at room temperature for 5 h, the initial cream suspension changed to a heterogeneous, pink mixture. The pink precipitate was filtered, washed with hexane and dried in vacuo. The pale-pink powder thus obtained was identified as [$PtCl_2(PPh_3)_2$] on the basis of its IR spectrum (0.145 g, 90%). The product was further purified by recrystallization from CH_2Cl_2/toluene. The reaction of IVa with benzoyl chloride, which gave the same dichloro complex, was carried out similarly.

Reaction with methylene chloride in the presence of carbon dioxide and carbon monoxide. Carbon dioxide was passed through the CH_2Cl_2 (10 ml) solution of IVa (0.17 g) at room temperature. The initial yellow solution gradually changed to green. After 4 h of reaction, the resulting deep green solution was concentrated to ca. 5 ml. Addition of hexane to the solution yielded a greenish white precipitate, which was filtered, washed with hexane and dried in vacuo. It was purified by recrystallization from CH_2Cl_2 to give off-white crystals, which were identified as [$PtCl_2(PPh_3)_2$] (the yield was almost quantitative) on the basis of its IR spectrum and elemental analysis.

When the same reaction was carried out in the presence of 2 molar equivalents of added PPh_3, a similar reaction proceeded, although a color change to deep green was not observed in this case.

The use of carbon monoxide in place of carbon dioxide resulted in the formation of the same dichloro complex as above without appreciable color change.

Reaction with CF₃COOH. To the white suspension of IVa (0.10 g, 0.12 mmol) in THF (2 ml), trifluoroacetic acid (0.5 ml, 6.7 mmol) was added to produce a yellow solution. The solution was stirred at room temperature for 17 h, during which period the system became heterogeneous with formation of a white precipitate. Six ml of hexane was added to complete the precipitation. The white precipitate was filtered, washed with hexane and dried in vacuo. The white powder thus obtained was characterized as [$Pt(CF_3COO)_2(PPh_3)_2$] (yield was almost quantitative) on the basis of its IR spectrum ($\nu_{asym}(CO_2)$, 1730vs and 1700s; $\nu_{sym}(CO_2)$, 1400s cm^{-1}) and elemental analysis (Found: C, 50.5; H, 3.3. $C_{40}F_6H_{30}O_4P_2Pt$ calcd.: C, 50.8; H, 3.2%). The release of acetylacetone in this reaction was confirmed qualitatively by GLC analysis (SCD-550, 50° C) of the colorless filtrate.

Acknowledgement

The authors express appreciation to Mr. T. Kiriyama for his experimental assistance. We are indebted to Professors N. Kasai and N. Yasuoka and their colleagues at Osaka University for helpful advice on the crystallization of the sample of compound IVa and for attempting its preliminary X-ray analysis.

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