Studies on the Reactions of Bis(acetylacetonato)platinum(II) with Lewis Bases. I. Reactions with Tertiary Phosphines Leading to a Complex Containing Carbon-Bonded Unidetate Acetylacetonato Ligand and Preparation of New Alkylplatinum Complexes

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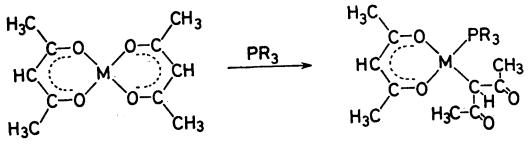
Addition of tertiary phosphines (PR_3) to [Pt(acac)$_2$] (acac=acetylacetonato-*O,O'*) causes the rearrangement of one of the O-bonded chelate acac ligands to a C-bonded form giving [Pt(acac)(γ-acac)PR_3] (γ-acac=acetylacetonato-*C*[3]) (PR_3=PPh_3, **1a**, and $P(C_6H_{11})_3$, **2a**). Complexes **1a** and **2a** were isolated and characterized by means of elemental analysis, infrared and ^{1}H- and ^{13}C-NMR spectroscopy. Some reactions involving complex **1** were investigated. The mechanism of formation of a diethylplatinum complex in the reaction of [Pt(acac)$_2$] with Al(OEt)Et_2 and PPh_3 is discussed taking into account the rearrangement of the acac ligand from the O-bonded chelate to a C-bonded form.

Various alkyl-transition metal complexes have been isolated from the systems consisted of transition metal acetylacetonates, [M(acac)$_n$],[1] alkylaluminium compounds and ligand molecules such as tertiary phosphines or amines.[2] Some of these systems also afford hydrido complexes or zero-valent complexes by decomposition of intermediate unstable alkyltransition metal complexes. The mechanism of formation of the carbon-to-metal σ bond in these systems, however, has not been studied extensively. In the course of our study on the syntheses of alkyl complexes of palladium(II) and platinum(II) from systems consisted of [M(acac)$_2$] (M=Pd and Pt), alkylaluminium compound, and Lewis bases,[3] we found that [Pt(acac)$_2$] itself reacts with a tertiary phosphine to yield the complexes **1a** and **2a** in which acetylacetonato ligand is coordinated with platinum in a unidentate form *via* central (γ-) carbon atom.

Several kinds of ionic platinum(II) complexes with a central carbon bonded acetylacetonato ligand[4–6] have been reported by Lewis *et al.* More recently, Baba *et al.* reported the preparation of palladium(II) analog of **1a** by the reaction of [Pd(acac)$_2$] with Lewis bases such as PPh_3, pyridine, and secondary amines.[7] Here we report isolation, characterization, and some reactions of complexes **1a**, **2a**, and **2b** with special reference to the alkylation reaction mentioned above.



[M(acac)$_2$][1] [M(acac)(γ-acac)PR_3][1]

{M=Pt; PR_3=PPh_3 (**1a**), $P(C_6H_{11})_3$ (**2a**)
{M=Pd; PR_3=PPh_3 (**1b**)[7], $P(C_6H_{11})_3$ (**2b**)

Results and Discussion

Reaction of [Pt(acac)$_2$] with Triphenylphosphine, PPh_3.

The reaction of [Pt(acac)$_2$] with an equimolar amount of triphenylphosphine in toluene at room temperature afforded a diamagnetic pale yellow compound, which was identified as (2,4-pentanedionato-*C*[3])(2,4-pentanedionato-*O,O'*)triphenylphosphineplatinum(II), [Pt(acac)(γ-acac)PPh_3],[1] **1a**, on the basis of its infrared and NMR spectra and elemental analysis. The product is soluble in most aromatic solvents, chlorinated organic solvents, and ethers, and can be recrystallized from these solvents. As is shown in Table 1, complex **1a** possesses intense infrared bands which are characteristic of an enol-type bidentate acac ligand (1575, 1550, and 1525 cm^{-1}) and diketo-type γ-acac ligand (1685 and 1650 cm^{-1}),[5,8,9] and are very similar to the analogous palladium complex, [Pd(acac)(γ-acac)PPh_3], **1b**. A medium band at 445 cm^{-1} was assigned to ν(Pt–C) since the band lacks in the spectra of [PtX(acac)PPh_3] (X= Cl, Br and I) and [Pt(acac)(PPh_3)$_2$]BPh_4 which are derived from complex **1a** (*vide post*).

The ^{1}H-NMR spectral data of complex **1a** are listed in Table 2 together with **1b** and **2a**. Fig. 1a shows the ^{1}H-NMR spectrum of **1a** as a typical spectrum of this type of complexes. Assignment of each signal has been achieved by comparing it with the one reported for anionic Pt(II) complexes,[5,8] Pt(IV) complexes,[9] and analogous Pd(II) complexes[7] with γ-acac ligands. Of the two singlets due to methyl protons in the chelate acac ligand, the lower field signal was assigned to that trans to the phosphorus ligand according to the assign-

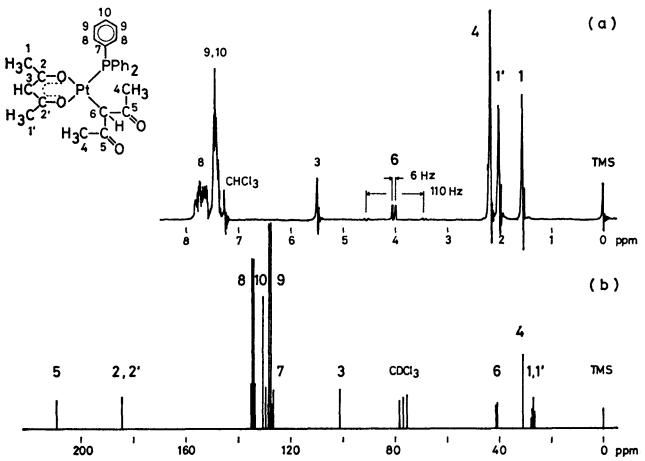


Fig. 1. ^{1}H- and ^{13}C-NMR spectra of [Pt(acac)(γ-acac)-PPh_3], **1a**, in $CDCl_3$, at room temperature.

Table 1. Relevant infrared data (in cm^{-1}) for some acetylacetonato complexes (KBr disc)

Complexes		acac Bands			γ-acac Bands	
[Pt(acac)(γ-acac)PPh_3]	**1a**	1575s	1550s	1525s	1685s	1650s
[Pd(acac)(γ-acac)PPh_3][a]	**1b**	1570s	1540m	1520s	1670s	1640s
[Pt(acac) (γ-acac)PCy_3]	**2a**	1580s	1550sh	1515vs	1645s	
[Pd(acac)(γ-acac)PCy_3]	**2b**	1585s	1540m	1515s	1675s	1665m
[PtI(acac)PPh_3]	**3a**	1565s	1560s	1524vs		
[PdI(acac)PPh_3]	**3b**	1575s	1560s	1510vs		
[Pt(acac)$(PPh_3)_2$]BPh_4	**4a**	1585sh	1565s	1530s		
[Pd(acac)$(PPh_3)_2$]BPh_4	**4b**	1580m	1565s	1520s		

a) The compound was prepared by the reported method.[7]

Table 2. ^{1}H-NMR spectral data of acetylacetonato complexes[a]

Complexes		acac ligand		γ-acac ligand				L[h]
		$\delta(CH_3)$	δ(CH)	$\delta(CH_3)$	δ(CH)	J[e]	J[f]	
[Pt(acac)(γ-acac)PPh_3]	**1a**	1.58(s, 3H) 2.04(s, 3H)	5.48(s, 1H)	2.20(s, 6H)	4.04(ds, 1H)	6	110	*o*- ~7.7(m, 6H) *m*,*p*- ~7.5(m, 9H)
[Pt(acac)(γ-acac)PPh_3]	**1a**[b]	1.52(s, 3H) 1.96(s, 3H)	5.44(s, 1H)	2.36(s, 6H)	4.28(ds, 1H)	6	109	—[i]
[Pt(acac)(γ-acac)PPh_3]	**1a**[c]	1.34(s, 3H) 1.82(s, 3H)	5.18(s, 1H)	2.52(s, 6H)	4.44(ds, 1H)	6	109	*o*- ~7.9(m, 6H) *m*,*p*- ~7.1 (m, 6H)
[Pd(acac)(γ-acac)PPh_3][d]	**1b**	1.54(s, 3H) 2.06(s, 3H)	5.30(s, 1H)	2.18(s, 6H)	3.54(d, 1H)	6	—	*o*- ~7.7(m, 6H) *m*,*p*- ~7.5(m, 9H)
[Pt(acac)(γ-acac)PCy_3]	**2a**	2.00(s, 3H) 2.08(s, 3H)	5.47(s, 1H)	2.21(s, 6H)	3.99(d, 1H)	4	—[g]	1.1—2.5(m, br)
[Pd(acac)(γ-acac)PCy_3]	**2b**	1.93(s, 3H) 2.03(s, 3H)	5.39(s, 1H)	2.35(s, 6H)	3.44(d, 1H)	4	—	1.2—2.6(m, br)

a) In $CDCl_3$ unless otherwise stated, 100 MHz, at 25 °C. Chemical shifts are in δ values (ppm) with respect to tetramethylsilane as internal standard. Coupling constants are in Hz. In the parentheses are multiplicity and number of protons. Multiplicity symbols are as follows: s, singlet; ss, singlet with satellites due to ^{195}Pt; d, doublet; ds, doublet with satellites due to ^{195}Pt; q, quintet; sex, sextet; m, multiplet; br, broad. b) In C_5H_5N. c) In C_6D_6. d) The compound was prepared by the method described in the literature.[7] e) $|^3J(PH)|$. f) $|^2J(^{195}PtH)|$. g) ^{195}Pt-Satellites were not obtained due to low S/N ratio. h) L corresponds to tertiary phosphine ligand. i) Not observable due to overlapping with solvent signals.

ment by Baba *et al.*[7] Protons in the chelate acac ligand in complex **1a** exhibit upfield shift when the solvent was changed from $CDCl_3$ through pyridine to benzene, whereas those in the C-bonded γ-acac ligand shift towards downfield. The chemical shift of the methine proton in the γ-acac ligand in **1a** is somewhat lower than in the corresponding palladium complex, **1b** (δ=3.54 ppm[7]). The phosphorus–hydrogen coupling constant for this proton ($|^3J(P–H)|$=6 Hz) is almost the same as the reported value of 6.1 Hz for *trans*-[Pt(CH_3)Cl(PEt_3)$_2$][10] and 6.3 Hz for **1b**.[7] The methine proton attached to the platinum-bonded carbon atom in γ-acac ligand is known to accompany satellite signals due to ^{195}Pt. The fairly large coupling constant of $|^2J(^{195}Pt–H)|$=110 Hz for complex **1a** is similar to the reported values for K$^+$[Pt(acac)(γ-acac)-Cl]$^-$ (120 Hz) and K$^+$[Pt(acac)(γ-acac)$_2$]$^-$ (123 Hz).[5]

The ^{31}P{^{1}H}-NMR spectrum of **1a** in $CDCl_3$ showed a singlet at 11.8 ppm (downfield from the external reference of PPh_3 in C_6D_6/C_6H_5Cl) with the satellite bands due to ^{195}Pt. The analogous Pd complex, **1b**, showed the ^{31}P resonance at 37.8 ppm. The coupling constant, $|^1J(^{195}Pt–P)|$, of 4490 Hz for **1a** does not greatly differ from reported values of 3875 Hz for *cis*-[$PtCl_2(PPh_3)_2$][11] and of 3500—3600 Hz for *cis*-[$PtCl_2$-(PR_3)$_2$],[12] and much larger than those of *ca.* 2400 Hz for *trans*-[$PtCl_2(PR_3)_2$].[12]

Table 3 summarizes the ^{13}C-NMR data of complex **1a** and its palladium analog, **1b**, together with those of [Pd(acac)$_2$], which were used to assist the assignment of the phosphine complexes. Fig. 1b compares the ^{13}C-NMR spectrum with ^{1}H-NMR spectrum for the typical complex **1a**. Although satellite bands due to ^{195}Pt could not be observed except for *ortho*-carbons (C^8) (as for the carbon numbering, refer to Fig. 1) of PPh_3 in the spectrum of complex **1a**, the assignment was made with the aid of supplementary information on the ^{13}C-NMR of [Pt(acac)(γ-acac)py] (py=pyridine)[13] which shows varying magnitudes of $|J(^{195}Pt–^{13}C)|$ values corresponding to the positions of the carbon atoms with respect to the central platinum. As is seen in Table 3, carbon signals due to the bidentate enol-acac ligand (C^1–C^3) are almost unchanged from those of [Pd(acac)$_2$] and their chemical shifts are very similar to those reported for acetylacetonato complexes of Be,[14] Al,[14] Co,[14,15] Ir,[16] and Ni.[17] Two methyl- and two keto-carbons of the bidentate acac ligand (C^1 and $C^{1'}$, and C^2 and $C^{2'}$, respectively) in **1b** are observed as non-equivalent carbons on coordination of PPh_3 as in the case for methyl protons in the ^{1}H-NMR spectrum. Resolution of the

Table 3. ^{13}C-NMR spectral data of [M(acac)(γ-acac)PPh_3] (M=Pt and Pd) and [$Pd(acac)_2$][a]

Assignment[b]			[Pt(acac)(γ-acac)PPh_3], **1a**	[Pd(acac)(γ-acac)PPh_3], **1b**	[$Pd(acac)_2$]
acac	CH_3	*1*	27.2 c	26.9 s	25.4 s
	CH_3	*1'*		28.3 d (7.6, n=4)	
	C=O	2	184.4 c	186.5 s	187.2 s
	C=O	*2'*		186.0 d (21.4, n=3)	
	H-C	*3*	101.2 s	99.6 s	101.6 s
γ-acac	CH_3	*4*	31.1 s	31.4 s	—
	>C=O	*5*	209.2 s	206.4 s	—
	-C-H	*6*	41.3 d (3.1, n=2)	51.1 d (4.6, n=2)	—
PPh_3	P-C	*7*	128.2 d (62.6, n=1)	128.7 d (51.9, n=1)	—
	o-C	*8*	134.6 ds (10.7, n=2)	134.1 d (10.7, n=2)	—
	m-C	*9*	128.2 d (10.7, n=3)	128.4 d (10.7, n=3)	—
	p-C	*10*	139.0 s	131.0 s	—

a) In $CDCl_3$ at room temperature. 25.2 MHz, Chemical shifts are in ppm, downfield positive, from tetramethylsilane as an internal reference. Coupling constants $|^nJ(^{31}P-^{13}C)|$ in Hz are in parentheses. Multiplicity abbreviations are: s, singlet; d, doublet; ds, doublet with satellite bands due to ^{195}Pt; c, complex pattern. b) See Fig. 1 for numbering of the carbon atoms. c) $|^3J(^{195}Pt-^{13}C)|$=35.1 Hz.

fine structure of the NMR spectrum for these carbons in complex **1a** was not sufficient and a complicated pattern due to the coupling with ^{195}Pt resulted. A large upfield shift is observed for the methine carbon in the γ-acac ligand (C^6) compared to that in the bidentate enol-acac ligand (C^3), and the C^6 carbon in the Pt complex resonates at a higher field than in its Pd analog. All these features parallel with those of the ^{1}H-NMR spectra. Appearance of a single C^5 signal at a lower field than for C^2 indicates that C^5 carbons belong to intact keto groups which are free from coordination to the central metal. Cheney *et al.* reported that $^{31}P-^{13}C$ coupling constants of the Pt-bonded methyl carbon in *cis*-[$PtMe_2(PMe_2Ph)_2$] are 104 and 9 Hz for mutually trans and cis ^{31}P and ^{13}C nuclei, respectively.[18] The small $|^2J(^{31}P-^{13}C)|$ values (5—9 Hz) of the methyl carbon cis to the phosphorus ligands were also reported for the cationic *trans*-monomethylbis(tertiaryl phosphine)-platinum(II) complexes.[19] A small value of the $^{31}P-^{13}C$ coupling constants for C^6 methine carbon suggests that γ-acac ligand occupies the cis position with respect to PPh_3 in complexes **1a** and **1b**. Furthermore, fairly large values of $|J(^{31}P-^{13}C)|$ observed for $C^{1'}$ and $C^{2'}$-carbons in **1b** indicate the presence of a large trans effect of PPh_3, the fact in accord with the observation in dimethylplatinum complex mentioned above. Chemical shifts and $^{31}P-^{13}C$ coupling constants of the *ortho*-, *meta*-, and *para*-carbons (C^8, C^9, and C^{10}) of the coordinated PPh_3 are similar to those of free PPh_3.[20] On the other hand, the carbon atom (C^7) attached to phosphorus moves upfield considerably (*ca.* 10 ppm) upon coordination accompanying an increase in the magnitude of the $^{31}P-^{13}C$ coupling constant (from 21 Hz for free PPh_3[20] to 62.6 Hz for **1a**). These facts may reflect an increase in M→P back donation in complexes **1a** and **1b**.

When more than one mole equivalent of PPh_3 was allowed to react with [$Pt(acac)_2$] at an elevated temperature in tetrahydrofuran, a creamy white compound was isolated, whose infrared spectrum shows ν(C=O) bands at 1653 and 1600 cm^{-1}. The ^{1}H-NMR spectrum and elemental analysis of this diamagnetic compound suggest the composition of [$Pt(CH_2COCHCOCH_3)(PPh_3)_2$]. The detailed study of this unusual complex will be reported elsewhere.

Reaction of [Pt(acac)$_2$] and [Pd(acac)$_2$] with Tricyclohexylphosphine, PCy_3. Tricyclohexylphosphine reacted with an equimolar amount of [$Pt(acac)_2$] in diethyl ether at room temperature to yield a white compound which was identified as (2,4-pentanedionato-C^3)(2,-4-pentanedionato-O,O')tricyclohexylphosphineplatinum-(II), [Pt(acac)(γ-acac)PCy_3], **2a**, on the basis of its infrared and ^{1}H-NMR spectra. Similarly obtained was its Pd-analog, [Pd(acac)(γ-acac)PCy_3], **2b**, by the reaction in benzene. Both complexes **2a** and **2b** are quite soluble in most common organic solvents to render the purification by recrystallization somewhat difficult. The infrared absorptions of **2a** and **2b** in the region of 1500 1700 cm^{-1}, listed in Table 1, indicate the presence of both acac and γ-acac ligands. Detection of the metal–carbon stretching bands for these complexes failed due to the complicated absorptions in the low frequency region.

The ^{1}H-NMR spectral data for complexes **2a** and **2b** are listed in Table 2. Signals due to the acac and γ-acac ligands are essentially the same as those of the analogous PPh_3 complexes **1a** and **1b**. Differences of the chemical shifts between two acac-CH_3 protons are less in PCy_3 complexes (0.08 ppm in **2a** and 0.10 ppm in **2b**) than in the PPh_3 complexes (0.46 ppm in **1a** and 0.50 ppm[7] in **1b**) indicating a weaker trans effect of PCy_3 as compared with PPh_3. The chemical shift of the γ-acac methine proton is lower by 0.55 ppm in Pt complex, **2a**, than in the corresponding Pd complex, **2b**, as was the case in the PPh_3 complexes, **1a** and **1b**. Unlike the Pt–PPh_3 complex, **1a**, no satellite bands due to ^{195}Pt were observed for the methine proton of γ-acac ligand in the PCy_3 complex **2a**. This may be attributable to a low S/N ratio encountered in the spectrum of **2a**.

The reaction of [$Pt(acac)_2$] with an excess amount of PCy_3 also yielded complex **2a** and the complex

analogous to [Pt($CH_2COCHCOCH_3$)(PPh_3)$_2$] was not obtained.

*Some Reactions of the Complexes [M(acac)(γ-acac)PPh$_3$] (M=Pt, **1a** and Pd, **1b**).* In order to get some information on chemical properties of the C-bonded acetylacetonato ligand, several reactions were carried out on complexes **1a** and **1b**. The reaction of **1a** with an excess amount of acetyl or benzoyl chloride afforded the known complex [PtCl(acac)(PPh_3)];[21] the similar reaction has been reported for the Pd analog, **1b**.[7] Methyl iodide reacted with **1a** and **1b** at ambient temperature to give [MI(acac)(PPh_3)] (M=Pt, **3a**; Pd, **3b**) whose characteristic infrared absorptions are included in Table 1. Similarly was obtained [PtBr(acac)(PPh_3)] by the reaction between **1a** and ethyl bromide. A cationic complex of the type [M(acac)(PPh_3)$_2$]$^+BPh_4^-$ (M=Pt, **4a**; Pd, **4b**) was obtained upon treatment of **1a** or **1b** with $NaBPh_4$ in the presence of an equimolar amount of PPh_3 in tetrahydrofuran at room temperature. These reactions accompany formation of sodium salt of acetylacetonate which was isolated and identified by means of its infrared spectrum and elemental analysis.

$$[M(acac)(\gamma\text{-acac})(PPh_3)] + PPh_3 + NaBPh_4 \longrightarrow [M(acac)(PPh_3)_2]^+BPh_4^- + Na\text{-acac}$$

1a (M=Pt), **1b** (M=Pd); **4a** (M=Pt), **4b** (M=Pd)

Absence of bands at 1600—1700 cm^{-1} in the infrared spectra of **4a** and **4b** (Table 1) indicates that the C-bonded acac ligand in **1a** and **1b** is replaced by PPh_3. The ^{1}H-NMR spectrum of **4b** in $CDCl_3$ at room temperature shows a single methyl resonance at δ 1.51 ppm (6H) and the methine resonance at δ 5.41 ppm (singlet, 1H). Complex **4b** was also obtained by a successive reaction of [Pd(acac)$_2$] with 2 molar equivalents of PPh_3 followed by $NaBPh_4$ treatment in refluxing EtOH.

Preparation of Alkyl Complexes from the System of [Pt(acac)$_2$], Alkylaluminium Compounds, and Tertiary Phosphines. A variety of mono- or di-alkyl complexes of Pt(II) or Pd(II) have been prepared by the use of alkyllithium compounds or Grignard reagents.[22,23] However, application of alkylaluminium compounds for such synthesis has been relatively limited. Formation of hydrido complexes has been reported when [M(acac)$_2$] (M=Pd or Pt) was treated with $AlEt_3$ in the presence of $P(C_6H_{11})_3$.[24] A zero-valent ethylene complex, [Pd(C_2H_4)(PR_3)$_2$], and a σ-diethyl complex, [$PdEt_2$($R_2PCH_2CH_2PR_2$)], have been prepared by the reaction of Al(OEt)Et_2 with [Pd(acac)$_2$] in the presence of an appropriate tertiary phosphine.[25] In our attempts to obtain new alkyl complexes of Pt(II) and Pd(II) using alkylaluminium compound as an alkylating agent, we succeeded in the isolation of a series of dialkylpalladium complexes[3] and some alkylplatinum complexes.

The reaction of [Pt(acac)$_2$] with a large excess of diethylmonoethoxyaluminium in the presence of 2 mol of PPh_3 in diethyl ether at room temperature yielded a white solid whose elemental analysis was close to the value for [$PtEt_2$(PPh_3)$_2$], **5a**. The infrared spectrum of the product shows aliphatic C–H stretching bands at 2800—2940 cm^{-1} in a complicated pattern and no bands due to acetylacetonato ligand were observed. There are two relatively strong bands at 460 and 425 cm^{-1} which disappear on thermolysis of the complex. These bands are absent in the spectrum of *cis*-[$PtCl_2$(PPh_3)$_2$]. Hence either one of the two or both bands may be assignable to ν(Pt–C). The ^{1}H-NMR spectrum of **5a** in toluene-d_8 at room temperature showed a complicated multiplet at δ 0.4—1.8 ppm assignable to the ethyl group together with signals at 7—8 ppm due to the phenyl protons. Upon thermolysis *in vacuo* at 160 °C, the complex evolved quantitative amounts of ethylene and ethane in a ratio of 1:1. Although a diethyl complex of the type [$PtEt_2L_2$] has been reported for L=PMe_3 and PEt_3,[22] this is the first example of the isolation of the ethylplatinum complex with L=PPh_3.

$$[Pt(acac)_2] + 2PPh_3 \xrightarrow{10Al(OEt)Et_2} [PtEt_2(PPh_3)_2]\ \mathbf{5a}$$

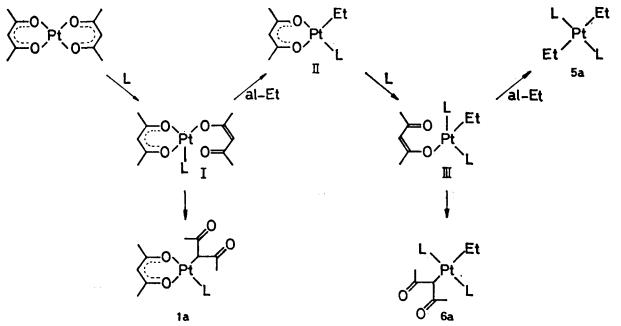
$$[Pt(acac)_2] + 2PPh_3 \xrightarrow{2Al(OEt)Et_2} [PtEt(\gamma\text{-acac})(PPh_3)_2]\ \mathbf{6a}$$

$$\mathbf{6a} \xrightarrow{-C_2H_6,\ \text{recrystallized from THF}} [Pt(CH_2COCHCOCH_3)(PPh_3)_2]$$

When a smaller amount of Al(OEt)Et_2 (2—6 mol per mol of [Pt(acac)$_2$]) was employed, a pale yellow solid of **6a** precipitated. The solid evolved ethylene and ethane (0.5:1) on thermolysis at 145 °C, the total amount of which was 105% on the basis of the formula, [$PtEt(\gamma$-acac)(PPh_3)$_2$]. Its infrared spectrum shows strong bands at 1670 and 1635 cm^{-1} indicating the acetylacetonato ligand coordinated *via* the central carbon atom. Interestingly, attempted crystallization of this monoethyl complex from tetrahydrofuran at room temperature yielded the afore-mentioned unique acetylacetonato complex, [Pt($CH_2COCHCOCH_3$)(PPh_3)$_2$], as supported by infrared and ^{1}H-NMR spectra and elemental analysis.

In alkylations of nickel(II) acetylacetonate, with alkylaluminium compounds in the presence of appropriate tertiary phosphine ligands, intermediate alkylation products having both acac and alkyl ligands have been isolated.[26,27] Therefore, it is evident that the acac ligands in the starting complexes can be replaced with alkyl ligands in a stepwise manner. In considering the replacement mechanism of the acac ligand by an alkyl group, it is natural to assume that the acac ligand in a unidentate form may be replaced more easily than the chelated acac ligand. We have observed that the methyl groups in acac ligand of [NiEt(acac)(PPh_3)],[17b] [Ni(COEt)(acac)(PPh_3)],[28] and [Pd(acac)(γ-acac)(py)][13] give rise to a singlet ^{1}H-NMR resonance in some solvents and accounted for the results by assuming an exchange process proceeding through partial dissociation of the acac ligand to give an O-bonded unidentate form. Furthermore, we have recently isolated a platinum complex, [Pt(2,4-pentanedionato-*O*)$_2$(PEt_3)$_2$], which possesses two unidentate O-bonded acetylacetonato ligands.[29]

On the basis of these results we propose the processes



Scheme.
L=PPh_3, al-Et=Al(OEt)Et_2

as represented in the Scheme as the likely alkylation mechanism of [Pt(acac)$_2$] by an alkylaluminium compound. [Pt(acac)$_2$] may be converted to a unidentate O-bonded form I in the presence of a tertiary phosphine ligand. The intermediate I may give the [Pt(acac)(γ-acac)L] type complex **1a** in the absence of an alkylating agent, but the alkylating agent such as diethylmonoethoxyaluminium may replace the unidentate O-bonded acac ligand by the ethyl group to afford II. Although the intermediate II was not isolated in the present case, the corresponding nickel analogs were isolated and fully characterized.[17,26,27,30] The intermediate complex II may further rearrange by attack of another tertiary phosphine ligand to the isolated complex, [PtEt(γ-acac)(PPh_3)$_2$] **6a** by a process as shown in the Scheme.[31] The presence of a larger amount of the alkylating agent gives rise to the dialkylplatinum complex **5a**. In view of the isolation of complexes **1a** and **6a** an alternative line of alkylation processes involving the replacement of the γ-acac ligand by an alkyl group is also conceivable, although such a mechanism seems less straightforward as compared with the one presented in the Scheme.

Experimental

All manipulations were carried out under an atmosphere of deoxygenated nitrogen or argon, or *in vacuo*. Solvents were dried in the usual manner, distilled, and stored under a nitrogen atmosphere.

Infrared spectra were recorded on Hitachi EPI-G3 and 295 spectrometers using KBr pellets prepared under an inert atmosphere. NMR spectra were measured on a JEOL PS-100 spectrometer by Mr. Y. Nakamura of our research laboratory to whom we are indebted. Measurements of ^{1}H-NMR spectra (100 MHz) were carried out in deuteriochloroform at 25 °C unless otherwise stated and ^{1}H chemical shifts are reported with tetramethylsilane as the internal standard. Proton noise decoupled ^{31}P- and ^{13}C-NMR spectra were measured on the same spectrometer operating in the Fourier transform mode at 40.5 (^{31}P) and 25.2 MHz (^{13}C), respectively. Using 10 mm sample tubes, the spectra were taken on deuteriochloroform solutions and were calibrated with triphenylphosphine (in a mixture of C_6D_6 and C_6H_5Cl) as the external reference (for ^{31}P spectra) and with tetramethylsilane as the internal reference (for ^{13}C spectra). Microanalyses were carried out by Mr. T. Saito of our research laboratory.

Bis(2,4-pentanedionato)platinum(II)[32] and -palladium (II),[33] and (2,4-pentanedionato-*C*^{3}) (2,4-pentanedionato-*O*,*O*′)triphenylphosphinepalladium(II)[7] were prepared according to the reported method. Triphenylphosphine was kindly donated by Ihara Chemical Industry Co. Ltd., and used without further purification. Tricyclohexylphosphine was prepared as described in the literature.[34] Commercially available methyl iodide, benzoyl chloride, acetyl chloride, ethyl bromide and sodium tetraphenylborate were used without further purification. Diethylmonoethoxyaluminium was prepared from triethylaluminium and ethanol by the usual method.

Analytical data of new compounds prepared in this report are listed in Table 4.

*Preparation of (2,4-Pentanedionato-*C^3*)(2,4-pentanedionato-O,O′)triphenylphosphineplatinum(II)*, **1a**. On stirring the mixture of [Pt(acac)$_2$] (0.41 g, 1.05 mmol), PPh_3 (0.29 g, 1.09 mmol) and toluene (5 cm^3) at room temperature, the initial pale yellow suspension turned to a pale yellow clear solution in 1 h. The system was stirred for another 1.5 h. Then, the solution was concentrated to 2 cm^3 to leave a yellow oily solution, from which a creamy white precipitate was yielded on digestion with hexane. The precipitate was filtered off, washed with hexane and dried *in vacuo* to give 0.61 g (89%) of crude product. Recrystallization of the creamy white powder from diethyl ether afforded 0.40 g (58%) of [Pt(acac)(γ-acac)PPh_3] as a white microcrystalline solid. The reaction could be carried out similarly in diethyl ether, but in this case much longer reaction period (*ca.* 40 h) was necessary to complete the reaction.

*Preparation of (2,4-Pentanedionato-*C^3*)(2,4-pentanedionato-O,O′)tricyclohexylphosphineplatinum(II)*, **2a**. On stirring the heterogeneous pale yellow mixture of [Pt(acac)$_2$] (0.37 g, 0.95 mmol), tricyclohexylphosphine (0.27 g, 0.95 mmol), and diethyl ether (20 cm^3) at room temperature, the amount of precipitate gradually decreased, and in 21 h of stirring, an almost clear yellow solution resulted. Then, the solvent was

Table 4. Melting points and analytical results of some new acetylacetonato complexes

Complexes		Appearance	Mp, °C[a]	Analysis[b], % C	H
[Pt(acac)(γ-acac)PPh_3]	**1a**	white crystals	148—153	51.3(51.3)	5.3(4.5)
[Pt(acac)(γ-acac)PCy_3]	**2a**	creamy white crystals	180—182	48.9(49.9)	7.1(7.0)
[Pd(acac)(γ-acac)PCy_3]	**2b**	pale yellow crystals	178—181	56.5(57.5)	8.6(8.1)
[PtI(acac)PPh_3]	**3a**	orange-yellow powder[c]	—	—	—
[PdI(acac)PPh_3]	**3b**	orange needles	184—188	47.4(46.5)	3.9(3.7)[d]
[Pt(acac)(PPh_3)$_2$]BPh_4	**4a**	white crystals	183—187	68.1(67.6)	5.6(5.2)
[Pd(acac)(PPh_3)$_2$]BPh_4	**4b**	yellow crystals	160—164	74.4(74.4)	5.9(5.5)

a) Melting points (with decomposition) were measured on a hot stage with a sample in a small capillary sealed under vacuum and are uncorrected. b) Calculated values are in parentheses. c) Not obtained pure. d) I, 20.3% (21.3%).

partially evaporated in the stream of nitrogen with stirring, which caused precipitation of a white powder. The precipitate was filtered off at about −20 °C, washed with diethyl ether at the same temperature and dried *in vacuo* at room temperature to give 0.49 g (76%) of crude product. Recrystallization of a white powder from CH_2Cl_2–hexane at low temperature yielded 0.17 g (26.5%) of pure [Pt(acac)(γ-acac)PCy_3] as a creamy white crystalline solid. The yield of recrystallization was low due to too high solubility of the product in the common organic solvents.

Similarly obtained is its Pd-analog, (2,4-pentanedionato-C^3)-(2,4-pentanedionato-*O*, *O'*) tricyclohexylphosphinepalladium-(II), **2b**, from [Pd(acac)$_2$] (0.38 g, 1.23 mmol) and PCy_3 (0.35 g, 1.25 mmol). The reaction was carried out in benzene (5 cm^3) and completed in 1 h to give, on working up, 0.42 g (58%) of the product as a pale yellow microcrystalline solid.

*Reactions of [Pt(acac)(γ-acac)PPh_3], **1a**. With Benzoyl Chloride*: Complex **1a** (0.21 g, 0.32 mmol) was allowed to react with 2.0 cm^3 (17.1 mmol) of PhCOCl in benzene (2 cm^3) at room temperature for 4 h. The initial clear yellow solution turned to heterogeneous. The amount of the precipitate was increased on addition of hexane to the system. The precipitate was filtered off, washed with hexane and dried *in vacuo*. The yellowish brown powder thus obtained was crystallized from benzene and was identified as [PtCl(acac)PPh_3] on the basis of the infrared spectrum and elemental analysis. Similarly carried out was the reaction of **1a** with neat acetyl chloride to give the same product.

With Methyl Iodide: To the flask containing 0.20 g (0.31 mmol) of complex **1a** was added 5 cm^3 of methyl iodide by means of trap-to-trap method in a vacuum. The yellow solution was stirred at room temperature for 10 days. The unreacted methyl iodide was evaporated off *in vacuo* to leave an orange solid, which was reprecipitated from toluene–hexane. The orange-yellow powder of [PtI(acac)PPh_3], **3a**, thus obtained weighed 0.11 g (58%). The reaction of **1a** with ethyl bromide was similarly carried out to give an orange-yellow powder of [PtBr(acac)PPh_3].

With Sodium Tetraphenylborate: To the yellow solution of complex **1a** (0.46 g, 0.70 mmol) and PPh_3 (0.19 g, 0.70 mmol) in tetrahydrofuran (7 cm^3), 0.24 g (0.70 mmol) of $NaBPh_4$ was added. On stirring the mixture at room temperature for a day, a white fine powder, possibly of sodium acetylacetonate, was yielded. The solvent was evaporated off *in vacuo* to leave an off-white solid, which was washed with ethanol and dried *in vacuo*. The crude white powder thus obtained was recrystallized from THF–EtOH to give white microcrystals of [Pt(acac)$(PPh_3)_2$]$^+BPh_4^-$ **4a** (0.46 g, 58%).

*Reaction of [Pd(acac)(γ-acac)PPh_3], **1b**. With Methyl Iodide*: Into the yellow suspension of **1b** (0.30 g, 0.53 mmol) in toluene (5 cm^3), 0.114 g (0.803 mmol) of methyl iodide was added by means of a microsyringe. The mixture was stirred at room temperature for 6 h to yield a pale red solution. The solvent was evaporated *in vacuo* into almost dryness. The residual orange-yellow solid was washed with hexane and dried *in vacuo*. The crude product, weighed 0.18 g (57%), was crystallized from CH_2Cl_2–hexane to afford orange needles of [PdI(acac)PPh_3], **3b**, (0.07 g, 22%).

With Sodium Tetraphenylborate: Into a clear yellow solution of **1b** (0.22 g, 0.39 mmol) and PPh_3 (0.11 g, 0.39 mmol) in tetrahydrofuran, was added 0.14 g (0.39 mmol) of $NaBPh_4$. On stirring the solution at room temperature the system became turbid in about one minute and a colorless precipitate gradually came out. After being stirred for 1.5 h, the white precipitate was removed by filtration and was identified as sodium 2,4-pentanedionate (0.04 g, 84%) on the basis of infrared spectrum and microanalysis. Found: C, 49.1; H, 6.5%. Calcd for $C_5H_7O_2Na$: C, 49.2; H, 5.8%. From the yellow filtrate, the solvent was evaporated off *in vacuo* to leave a pale yellow mass, which was washed with ethanol and hexane, and dried *in vacuo*. The crude product (0.38 g, 93%) was recrystallized from tetrahydrofuran to give a yellow crystalline solid of [Pd(acac)$(PPh_3)_2$]$^+BPh_4^-$, **4b** (0.22 g, 84%). Compound **4b** was also obtained by the direct reaction of [Pd(acac)$_2$] (0.20 g, 0.65 mmol) and PPh_3 (0.34 g, 1.31 mmol) in the presence of $NaBPh_4$ (0.23 g, 0.67 mmol) in refluxing ethanol (8 cm^3) for 2 h. The crude product of **4b** weighed 0.62 g (90%).

*Preparation of Diethylbis(triphenylphosphine)platinum(II), **5a**.* Into a cooled (−60 °C) mixture of [Pt(acac)$_2$] (1.0 g, 2.6 mmol), PPh_3 (1.35 g, 5.2 mmol) and diethyl ether (40 cm^3), 3.9 cm^3 (26 mmol) of Al(OEt)Et_2 was added by means of a syringe. The temperature of the mixture was allowed to raise gradually and the system was stirred at room temperature for 75 h, to yield a white precipitate with an accompanying evolution of ethane. The precipitate was filtered off, washed with hexane and crystallized from toluene to afford a colorless microcrystalline powder. (0.50 g, 25% based on [Pt(acac)$_2$] used.) (Found: C, 60.4; H, 5.3%. Calcd for $C_{40}H_{40}P_2Pt$: C, 61.8; H, 5.2%). A low stability of the product in solution prevented from obtaining an analytically pure compound.

Thermolysis of 0.1398 g (0.1798 mmol) of the product *in vacuo* at 160 °C evolved 0.360 mmole of gas (as measured with a Toepler pump) which consists of equimolar amounts of ethylene and ethane as analyzed by GLC.

*Preparation of Ethyl(2,4-pentanedionato-C^3)bis(triphenylphosphine)platinum(II), **6a**.* To a mixture of [Pt(acac)$_2$] (1.89 g, 4.80 mmol), PPh_3 (2.52 g, 9.63 mmol) and 50 cm^3 of diethyl ether, Al(OEt)Et_2 (3.76 g, 8.79 mmol) was added at −70 °C. The mixture was stirred at room temperature for 74 h to yield a white precipitate, which was filtered off, washed with hexane and dried *in vacuo*. The pale yellow powder thus obtained had an analytical value close to that for [PtEt(γ-acac)$(PPh_3)_2$] (0.92 g, 23%). (Found: C, 62.0; H, 5.1%. Calcd for $C_{43}H_{42}O_2P_2Pt$: C, 60.9; H, 5.0%). On thermolysis of the product (115.1 mg, 0.1358 mmol) at 145 °C, evolution of ethylene and ethane (0.5: 1), the total amount of which was 0.143 mmol (105%), was observed.

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1) Throughout this paper, abbreviation acac is used to indicate the enol type 2,4-pentanedionato (acetylacetonato) ligand which is coordinated to the central metal in a bidentate fashion through two oxygen atoms, whereas γ-acac represents the 2,4-pentanedionato ligand coordinated to the metal in a unidentate way through the central (γ-) carbon atom.

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