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Dinuclear platinum(II) complex bridged by an acetylacetonate(3−) anion [1]

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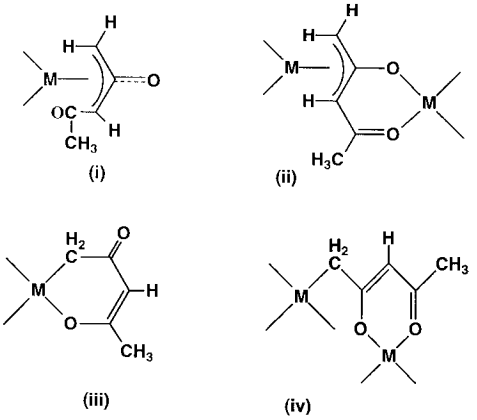
Abstract

$[Pt(acac)_2]$ reacted with twice the molar amount of PPh_3 in hot MeOH to afford the first metal complex with an acetylacetonate trianion, $[Pt_2(\mu\text{-acac}(3-))(PPh_3)_4](acac)$, as a major product via $[Pt(acac)(PPh_3)_2](acac)$. The η^3:*C*, *O*-bridging structure of the trianion was deduced by ^1H, ^{13}C, ^{31}P and ^{195}Pt NMR spectra. This reaction system also afforded a minor product of an acetylacetonate dianion complex, $[Pt(\eta^3\text{-acac}(2-))(PPh_3)_2]$; while $[Pd(acac)_2]$ gave only $[Pd(\eta^3\text{-acac}(2-))(PPh_3)_2]$ in the same reaction conditions. © 1998 Elsevier Science S.A.

Keywords: Dinuclear platinum(II); acetylacetonate trianion; metal complex

1. Introduction

Acetylacetone (abbr. acacH) and its derivatives have been used as useful chelating reagents, forming *O*,*O*′-chelate as the monoanion with almost all metal ions. Besides this normal chelating mode, they exhibit many other bonding modes to metal ions as the neutral molecule, the monoanion and the dianion [1–3]. The chemistry of Pd(II) and Pt(II) complexes with these ligands has been especially studied extensively. We have reported the following four bonding modes for the dianion of acac(2−) or its derivatives.



(i) $\eta^3(C^1\text{–}C^3)$-coordination: $[Pt(\eta^3\text{-acac}(2-))\{P(p\text{-}ClC_6H_4)_3\}_2]$ was prepared by the reaction of $[Pt(acac)_2]$

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[1] Dedicated to Professor Peter M. Maitlis on the occasion of his 65th birthday.
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with tris(*p*-chlorophenyl)phosphine in chloroform at room temperature [4]. A similar Pd(II) complex, [Pd(η^3-acac(2 −))(bpy)] was derived from the reaction of [Pd(μ-Cl)(η^3-acac(1 −))]$_2$ with bipyridine, forming [PdCl(η^1-$CH_2COCHCOCH_3$)(bpy)], followed by the reaction with T1(acac) [5]. Bipyridine ligand in this complex was easily displaced by diphosphine ligands such as bis(diphenylphosphino)ethane (dppe) and *cis*-bis(diphenylphosphino)ethylene [6]. The X-ray structure determination of this type of η^3-allylic complex was performed by Kemmitt et al. on [Pt{CH(COR)COCH(COR)}(PPh_3)$_2$] (R = OMe [7]; Me [8]) and [Pd{CH(COOMe)COCH(COOMe)}L_2] (L = PPh_3, $AsPh_3$, 1/2 bpy) [9]. These crystal structures suggest that the bonding mode of the triketonate(2 −) ligands is rather close to an η^2-metallacycrobutane-3-one type.

(ii) η^3:*O*,*O*′-bridging: the η^3-acac(2 −) ligand in [Pd(η^3-acac(2 −))(PP)] (PP = dppe, etc.) reacted with another metal compound such as [Pd(dppe)(H_2O)$_2$](ClO_4)$_2$ to give [(PP)Pd(C^1–C^3-η^3-acac(2 −)-*O*,*O*′)Pd(PP)](ClO_4)$_2$ [7].

(iii) *C*, *O*-chelation: bis(trifluoroacetylacetonato)-platinum(II), [Pt(tfac)$_2$], reacted with two equivalents of PPh_3, P(*p*-ClC_6H_4)$_3$ and $AsPh_3$ in diethyl ether or chloroform at room temperature to afford [Pt(tfac(2 −)-*C*, *O*)L_2] [10]. [Pd(tfac(2-)-*C*, *O*)LL′] (L,L′ = 2PPh_3, bpy; L = PPh_3, L′ = py etc.) was also prepared, and the structure of [Pd(tfac(2 −)-*C*, *O*)(PPh_3)(2,6-dimethylpyridine)] was determined by X-ray diffraction [11]. The existence of the acac(2 −) analogue with Pt(II) was reported [4].

(iv) η^1(C^1):*O*,*O*′-bridging: the above-mentioned [PdCl(η^1-acac(1 −))(bpy)] (abbr. YH) still has an enol proton and reacts with the other metal compounds such as Pd(acac)$_2$ to afford the complex with η^1(C^1):*O*,*O*′-bridging acac(2 −) ligand, [PdY$_2$] and [Pd(acac)Y] [12]. Thus, we have seen several kinds of complexes with the dianion of acac or its derivatives. However, the complex with their trianion has not been reported to the best of our knowledge. We report here the preparation and spectroscopic characterization of the first acac(3 −) trianion complex.

2. Experimental

2.1. Starting materials

The starting bischelate complexes, [Pt(acac)$_2$] and [Pd(acac)$_2$], were prepared according to the previously reported method [13,14]. Commercially supplied triphenylphosphine, methyldiphenylphosphine, potassium hexafluorophosphate and sodium perchlorate were used without further purification.

2.2. Measurements

Infrared spectra were obtained with a Perkin Elmer 1725-X infrared spectrophotometer. NMR spectra were recorded on JEOL EX-90, GX-400, LA-400 and GX-500 spectrometers. Chemical shifts are described in ppm (downfield positive) to the internal reference of TMS (for ^{1}H and ^{13}C) and external ones of 85% H_3PO_4 (for ^{31}P) and aqueous solution of K_2PtCl_4 (for ^{195}Pt). A vapour-pressure osmometer (Knauer; Berlin, Germany) was used for molecular weight determination.

2.3. Preparation of [Pt(acac)(PPh_3)$_2$](acac) **1a**, [Pt(acac)(PPh_3)$_2$](PF_6) **1b**, [Pd(acac)(PPh_3)$_2$](acac) **1c** and [Pd(acac)(PPh_3)$_2$](ClO_4) **1d**

A suspension of [Pt(acac)$_2$] (198 mg, 0.503 mmol) and twice molar quantity of PPh_3 (269 mg) in a small quantity of MeOH (1 ml) was stirred vigorously with a spatula at 60°C for several minutes to afford a clear pale yellow solution of [Pt(acac)(PPh_3)$_2$](acac) **1a**. Any attempts to isolate the complex as solid have been unsuccessful, but its yield in solution checked by NMR was quantitative. δ_H (CD_3OH): 7.49, 7.31 (complex, ≈ 30H, Ph); 5.67 (s, 1H, chelating acac; CH); 5.16 (s, 1H, $acac^-$; CH); 2.05 (br, 6H, $acac^-$; CH_3), 1.51 (s, 6H, chelating acac; CH_3). δ_c (CD_3OH): 193.7 (br, $acac^-$; CO); 186.8 (virtual triplet (abbr. vt), chelating acac; CO, $|^3J(cis\ \text{P–C}) + {}^3J(trans\ \text{P-C})| = 2$ Hz, ^2J(Pt–C) = 20 Hz); 135.7 (vt, PPh_3; *o*-C, $|^2J(\text{P–C}) + {}^4J(\text{P–C})| = 10$ Hz, ^3J(Pt–C) = 17 Hz); 133.1 (vt, PPh_3; *p*-C, $|^4J(\text{P–C}) + {}^6J(\text{P–C})| = 2$ Hz); 129.7 (vt, PPh_3; *m*-C, $|^3J(\text{P–C}) + {}^5J(\text{P–C})| = 12$ Hz); 127.3 (m, PPh_3; *ipso*-C, ^2J(Pt–C) = 29 Hz); 102.9 (s, chelating acac; CH, ^3J(Pt–C) = 66 Hz); 102.4 (s, $acac^-$; CH); 28.2 (br, $acac^-$; CH_3); 26.4 (vt, chelating acac; CH_3, $|^4J(cis\ \text{P–C}) + {}^4J(trans\ \text{P–C})| = 8$ Hz, ^3J(Pt–C) = 28 Hz). δ_p (CD_3OH): 7.6 (s, ^1J(Pt–P) = 3867 Hz). CD_3OH was used as a solvent to prevent the complication caused by H–D scrambling between CD_3OD and the complexes.

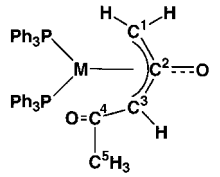
On addition of an equimolar amount of KPF_6 (97 mg), $NaClO_4$ or *p*-toluenesulfonic acid to the hot MeOH solution containing **1a** white precipitates of [Pt(acac)(PPh_3)$_2$]X (X = PF_6 (**1b**), ClO_4, OTs) were formed immediately. Precipitates were filtered and recrystallized from the mixture of CH_2Cl_2 and *n*-C_5H_{12} to deposit colourless plates, which were filtered and air-dried. The yield of **1b** was 355 mg, 72% (Pt-base). A quarter molecule of CH_2Cl_2 per complex molecule was involved in the crystal. Anal. Found: C, 50.38; H, 3.85. Calcd. as $C_{41.25}H_{27.5}O_2P_3F_6Cl_{0.5}Pt$: C, 50.30; H, 3.84%. Molecular weight in CH_2Cl_2: 883 (calcd. 902). ν_{max} (KBr); 3059w, 1563vs, 1529vs, 1482m, 1437vs, 1368s, 1313vw, 1281w, 1188w, 1163vw, 1101s, 1028w,

1000w, 941w, 840vs (PF_6), 748s, 711s, 693vs, 620w, 558vs, 531vs, 521s, 514s, 501s cm^{-1}. δ_H ($CDCl_3$): 7.3–7.4 (br, ≈30H, Ph); 5.58 (s, 1H, acac; CH, ^4J(Pt–H) = 5 Hz); 1.50 (s, 6H, acac; CH_3, ^4J(Pt–H) = 3 Hz). δ_C($CDCl_3$): 185.1 (vt, acac; CO, $|^3J(cis\ P–C) + {}^3J(trans\ P–C)| = 2$ Hz, ^2J(Pt–C) = 22 Hz); 134.2 (vt, PPh_3; *o*–C, $|^2J(P–C) + {}^4J(P–C)| = 11$ Hz, ^3J(Pt–C) = 22 Hz, 132.0 (s, PPh_3; *p*-C), 128.6 (vt, PPh_3; *m*-C, $|^3J(P–C) + {}^5J(P–C)| = 11$ Hz), 125.7 (m, PPh_3; *ipso*–C), 102.4 (s, acac; CH), 26.3 (vt, acac; CH_3, $|^4J(cis\ P–C) + {}^4J(trans\ P–C)| = 8$ Hz, ^3J(Pt–C) = 27 Hz). ^1J(P–C) and ^3J(P–C) for the *ipso*-carbon, and ^2J(P–P) values in complexes **1a** and **1b** are calculated as 66, < 5, and around 30 Hz, respectively [15]. δ_P ($CDCl_3$): 8.2 (s, PPh_3 ^1J(Pt–P) = 3851 Hz); −143.9 (heptet, PF_6, ^1J(F–P) = 712 Hz).

A suspension of [Pd(acac)$_2$] (75 mg, 0.25 mmol) and two equivalents of PPh_3 (134 mg) in a small quantity of MeOH (1 ml) was stirred vigorously with a spatula to afford a yellow solution of [Pd(acac)(PPh_3)$_2$](acac) **1c** quantitatively. Complex **1c** could not be isolated as solid. δ_H (CD_3OH): 7.4 (br, ≈30H, Ph); 2.08, (br, 1H, $acac^-$; CH_3); 1.53 (s, 6H, chelating acac; CH_3). δ_C(CD_3OH): 193.2 (br, $acac^-$; CO); 187.5 (s, chelating acac; CO); 135.4 (br, PPh_3; *o*-C); 132.9 (s, PPh_3; *p*-C); 129.8 (br, PPh_3; *m*-C); 102.1 (s, chelating acac; CH); 101.0 (s, $acac^-$; CH); 27.8 (br, $acac^-$; CH_3); 26,3 (br, chelating acac; CH_3). δ_p(CD_3OH): 34.5 br. The broadening of the NMR signals (^{1}H, ^{13}C, ^{31}P) is caused by the fractional motion of the acac interconversion between the inner and outer spheres through the five-coordinated complex [16]. On addition of an equimolar amount of $NaClO_4$ (32 mg), KPF_6 or *p*-toluenesulfonic acid to the hot MeOH solution containing **1c** yellow precipitates of [Pd(acac)(PPh_3)$_2$]X (X = ClO_4 (**1d**), PF_6, OTs) were formed immediately. The crude products were recrystallized from the mixture of CH_2Cl_2 and *n*-C_5H_{12}. The yield of **1d** was 158 mg, 75% (Pd-base). One-third of CH_2Cl_2 molecule per complex molecule was involved in the crystal. Anal. Found: C, 57.85; H, 4.53. Calcd. as $C_{41.33}H_{37.66}O_6P_2Cl_{1.66}Pd$: C, 57.87; H, 4.43%. ν_{max} (in nujol); 1560vs, 1530vs, 1440vs, 1315w, 1294m, 1189w, 1160w, 1095vs (ClO_4), 1024m, 1000m, 940w, 850w, 810w, 760m, 745s, 712s, 697vs, 629s, 560s, 534vs, 520s, 516s, 500m, 465w cm^{-1}. δ_H ($CDCl_3$): 7.4 (br, ≈30H, PPh_3); 5.45 (s, 1H, acac; CH); 1.53 (s, 6H, acac; CH_3). δ_C ($CDCl_3$): 186.2 (vt, acac; CO, $|^3J(cis\ P–C) + {}^3J(trans\ P–C)| = 4$ Hz); 134.2 (vt, PPh_3; *o*-C, $|^2J(P–C) + {}^4J(P–C)| = 11$ Hz); 132.1 (vt, PPh_3; *p*-C, $|^4J(P–C) + {}^6J(P–C)| = 3$ Hz); 128.9 (vt, PPh_3; *m*-C, $|^3J(P–C) + {}^5J(P–C)| = 11$ Hz); 126.0 (m, PPh_3; *ipso*-C); 100.7 (s, acac; CH); 26.3 (vt, acac; CH_3, $|^4J(cis\ P–C) + {}^4J(trans\ P–C)| = 10$ Hz). ^1J(P–C) and ^3J(P–C) for *ipso*-C (PPh_3), and ^2J(P–P) values in this complex are calculated as 57, < 5, and around 30 Hz [15]. δ_P ($CDCl_3$): 35.2, s.

2.4. Preparation of [Pt(η^3-acac(2 −))(PPh_3)$_2$]**3a** and [Pd (η^3-acac(2 −))(PPh_3)$_2$]**3b**

Complex **3a** was isolated by the method reported previously [4] in a 55% yield and characterized. δ_C (CD_2Cl_2): 203.0 (d, C^4, J(P–C) = 4 Hz, J(Pt–C) = 45 Hz); 178.8 (t, C^2),



3a (M = Pt)
3b (M = Pd)

J(P–C) = 5 Hz, J(Pt–P) = 163 Hz); 134.4 (d, PPh_3; *o*-C, J(P–C) = 10 Hz, J(Pt–C) = 22 Hz); 130.7 and 130.6 (s, PPh_3; *p*-C); 128.4 (d, PPh_3; *m*-C, J(P–C) = 10 Hz); 73.3 (dd, C^3, J(P–C) = 6 and 53 Hz, J(Pt–C) = 246 Hz); 47.2 (dd, C^1, J(P–C) = 6 and 57 Hz, J(Pt–C) = 233 Hz); 31.0 (s, C^5). δ_p(CD_2Cl_2): 20.1 (AB, ^2J(P–P) = 9 Hz, ^1J(Pt–P) = 3210 Hz); 19.4 (AB, ^1J(Pt–P) = 2896 Hz). ^{31}P NMR revealed that a small quantity of [Pt(acac(2 −)-*C*,*O*)(PPh_3)$_2$] **4** was contaminated. δ_P(CD_2Cl_2): 33.6 (d, ^2J(P–P) = 14 Hz, ^1J(Pt–P) = 2043 Hz); 13.6 (d, ^1J(Pt–P) = 4081 Hz). Other spectral data were essentially the same as reported values [17]. The MeOH solution (2 ml) containing **1c** (0.35 mmol) was kept at room temperature. This solution was allowed to evaporate spontaneously for 3 days and it gave yellow plates of **3b**, which were filtered and washed with Et_2O. The crude products were recrystallized from the mixture of CH_2Cl_2 and *n*-C_5H_{12}. The yield was 105 mg, 37% (Pd-base). One molecule of CH_2Cl_2 per complex molecule were involved. Anal. Found: C, 61.97; H, 4.71. Calcd. as $C_{42}H_{38}O_2P_2Cl_2Pd$: C, 61.97;H, 4.71%. M.p.: 105– 110°C (dec.). IR: ν_{max} (in Nujol); 1600m, 1540vs, 1483s, 1435vs, 1357s, 1334s, 1158s, 1102s, 1098s, 1030m, 1019m, 1000m, 756s, 740vs, 702vs, 697vs, 535s, 520vs, 511s cm^{-1}. δ_H ($CDCl_3$): 8–7.2 (≈30H, complex, Ph); 4.46 (1H, t, br, acac; CH, J(P–H) = 4 Hz); 3.04 (2H, t, br, acac; CH_2, J(P–H) = 6 Hz); 1.25 (3H, s, sl. br, acac; CH_3). δ_C ($CDCl_3$): 201.2 (d, C^4, J(P–C) = 4 Hz); 173.8 (t, C^2, J(P–C) = 4 Hz); 133.9 and 133.8 (d, PPh_3; *o*-C, J(P–C) = 13 Hz); 130.3 and 130.1 (s, PPh_3; *p*-C); 128.3 (d, PPh_3; *m*-C, J(P–C) = 11 Hz); 79.5 (dd, C^3, J(P–C) = 4 and 40 Hz, ^1J(H–C) = 151 Hz); 55.0 (d, C^1, J(P–C) = 46 Hz, ^1J(H–C) = 152 Hz); 31.0 (s, C^5, ^1J(H–C) = 127 Hz). δ_P($CDCl_3$): 31.8 (d. ^2J(P–P) = 29 Hz); 23.6 (d).

2.5. Preparation of [Pt_2(μ-acac(3 −))(PPh_3)$_4$](acac) (**5a**) and [Pt_2(μ-acac(3 −)) (PPh_3)$_4$](PF_6) (**5b**)

Pt(acac)$_2$ (744 mg, 1.89 mmol) and twice molar amounts of PPh_3 (1000 mg) were dissolved in hot MeOH (5 ml) and sealed in a glass tube. After heating at 60°C for 6 h, the glass tube was maintained at room

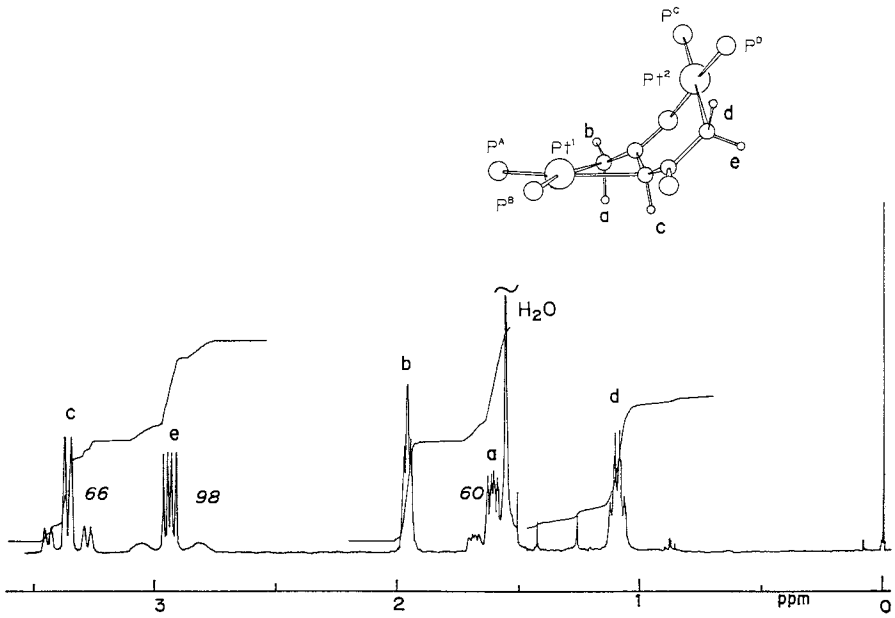
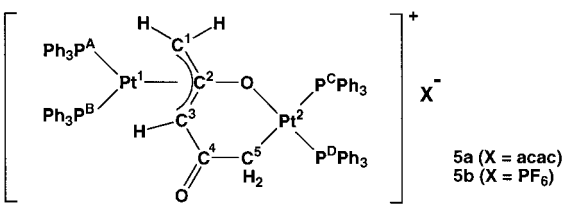


Fig. 1. ^{1}H NMR spectrum (400 Hz, CD_2Cl_2) except for Ph signals and a proposed conformation of complex **5b**.

temperature overnight. To the resulting pale yellow solution was added Et_2O (15 ml) and the mixture was kept at −5°C in a refrigerator. The obtained white precipitates were filtered and washed with Et_2O (yield 676 mg). Et_2O and *n*-C_5H_{12} were added to the filtrate, then the solution was kept in the refrigerator to deposit white precipitates, which were filtered and washed with Et_2O (yield 459 mg). These crude products were recrystallized twice from the mixture of CH_2Cl_2 and *n*-C_5H_{12} to give white-maple micro-crystals of **5a**. They were filtered, washed with Et_2O and dried in vacuo. The yield was 759 mg, 44% (Pt-base). Two molecules of CH_2Cl_2 per complex molecule are involved. Anal. Found: C, 55.91; H, 4.24. Calcd. as $C_{84}H_{76}O_4P_4Cl_4Pt_2$: C, 55.90; H, 4.24%. M.p.: 150–160°C (dec.). IR: ν_{max} (KBr); 3052w, 1636s, 1587m, 1573m, 1479vs, 1435vs, 1412s, 1312w, 1251w, 1186w, 1160w, 1120w, 1097s, 1073w, 1027w, 999m, 946w, 881w, 861w, 745s, 694vs, 551s, 541s, 526vs, 514vs, 500s cm^{-1}. ^{1}H and ^{31}P NMR spectra were almost the same as those of **5b** except for the signals assigned to acac$^-$; CH_3 (δ_H: 2.54 br) and CH (δ_H: 5.2 very br). δ_{Pt} ($CDCl_3$): −2600 (dd, Pt^2, J(P–Pt) = 2216 and 4181 Hz); −3450 (ddd, Pt^1, J(P–Pt) = 24,3384 and 3470 Hz).



Addition of KPF_6 (150 mg) to the MeOH solution (4 ml) of **5a** (1.49 mmol) led to form white precipitates, and they were filtered and washed with Et_2O. Recrystallization from the mixture of CH_2Cl_2 and *n*-C_5H_{12} was repeated twice to afford white fine needles of **5b**, which were filtered and dried in vacuo. The yield was 703 mg, 56% (Pt-base). Anal. Found: C, 54.34; H, 3.99. Calcd. as $C_{77}H_{65}O_2P_5F_6Pt_2$: C, 55.00; H, 3.90%. M.p.: 221–228°C (dec.). Molecular weight in CH_2Cl_2: 1310 (calcd. 1681). IR spectrum (KBr disc) was essentially similar to that of complex **5a** except for the additional absorption band at 840vs (PF_6^-) and lack of 1573 (acac$^-$) cm^{-1}. Following assigned ^{1}H nuclei has an alphabetical scheme as shown in Fig. 1. δ_H (CD_2Cl_2): 7.0–7.3 (complex, 60H, Ph); 3.28 (d, 1H, H^c, ^3J(P–H) = 11 Hz, ^2J(Pt–H) = 66 Hz); 2.86 (dd, 1H, H^e, $^2J_{gem}$ = 8 Hz, ^3J(P–H) = 13 Hz, ^2J(Pt–H) = 98 Hz); 1.88 (dt, 1H, H^b), J_{gem} = 6 Hz, ^3J(P–H) = 2 and 6 Hz); 1.53 (dd, 1H, H^a, J_{gem} = 6 Hz, ^3J(P–H) = 11 Hz, ^2J(Pt–H) = 60 Hz); 1.01 (complex, 1H, H^d, J_{gem} = 8 Hz). δ_C (CD_2Cl_2): 207.1 (d, C^4, ^3J(P–C) = 5 Hz, ^2J(Pt–C) = 56 Hz); 176.7 (dd, C^2, ^2J(P–C) = 2 and 5 Hz, ^1J(Pt–C) = 9 and 95 Hz); 137–125 (complex, Ph); 68.4 (dd, C^3, ^2J(P–C) = 6 and 45 Hz, ^1J(Pt–C) = 172 Hz, ^3J(Pt–C) = 14 Hz); 52.4 (complex, C^1, ^1J(Pt–C) = 159 Hz); 38.0 (dd, C^5, ^2J(P–C) = 3 and 67 Hz, ^1J(Pt–C) = 414 Hz). δ_P (CD_2Cl_2): 32.3 (dd, P^C, J(P–P) = 1 and 16 Hz, J(Pt–P) = 26 and 2214 Hz); 17.6 (AB, P^A, J(P–P) = 1 and 11 Hz, J(Pt–P) = 7 and 3468 Hz); 17.1 (AB, P^B, J(P–C) = 11 Hz, J(Pt–P) = 3379 Hz); 8.7 (d, P^D, J(P–P) = 16 Hz, J(Pt–P) = 9 and 4180 Hz); −144.1 (heptet, PF6, J(F–P) = 711 Hz).

2.6. Reaction of [Pt(acac)$_2$] with two equivalents of PMePh$_2$

The mixture of [Pt(acac)$_2$] (143 mg, 0.364 mmol) and two equivalents of $PMePh_2$ (146 mg) in a small

quantity of CD_3OD (2 ml) was kept at 60°C for 6 h. The ^{31}P NMR spectrum showed the formation of $[Pt(\eta^3\text{-acac}(2-))(PMePh_2)_2]$ {δ_P (CH_3OH, locked by ext. D_2O):0.2 (AB, $^2J(P-P) = 11$ Hz, $J(Pt-P) = 2986$ Hz; −0.8 (AB, $J(Pt-P) = 3370$ Hz)} and a small quantity of $[Pt_2(\mu\text{-acac}(3-))(PMePh_2)_4](acac)$, which could not be isolated as solid. δ_P: 15.9 (dd, P^C, $J(P-P) = 2$ and 16 Hz, $J(Pt-P) = 31$ and 2288 Hz; −0.8 (dd, P^A, $J(P-P) = 3$ and 12 Hz, $J(Pt-P) = 3471$ Hz); −3.3 (d, P^B, $J(P-P) = 12$ Hz, $J(Pt-P) = 3244$ Hz); −8.3 (d, P^D, $J(P-P) = 16$ Hz, $J(Pt-P) = 8$ and 3963 Hz).

3. Results and discussion

The novel acac trianion bridging dinuclear complex, $[Pt_2(\mu\text{-acac}(3-))(PPh_3)_4](acac)$ **5a**, is formed by the reaction of $[Pt(acac)_2]$ with PPh_3 in hot MeOH through the intermediates of the acac *O,O′*-chelate monoanion complex, $[Pt(acac)(PPh_3)_2](acac)$ **1a**, and the acac diendienolate dianion complex, $[Pt(acac(2-)\text{-}O,O')(PPh_3)_2]$ **2**. Complex **5a** was isolated from the reaction system and was recrystallized repeatedly to get pure micro-crystals. The acac anion in the outer sphere of **5a** was easily exchanged with PF_6^- by treating with KPF_6 to give $[Pt_2(\mu\text{-acac}(3-))(PPh_3)_4](PF_6)$ **5b**. The ^1H NMR spectrum (δ 1.0 ~ 3.5) in CD_2Cl_2 and a proposed structure of **5b** are shown in Fig. 1, in which five kinds of ^1H signals of acac(3−) are clearly separated. Signal assignments are mainly based on the coupling correlation analyzed by $^1H-^1H$ decoupling and $^1H\{^{31}P\}$ NMR measurements. The six-membered chelate ring including Pt^2 is not planar, and only one conformational isomer seems to exist exclusively (see Fig. 1). The ^{13}C, ^{31}P and ^{195}Pt NMR spectra strongly suggest the η^3:*C*, *O*-bridging structure of the acac(3−) ligand. The main signal part of the ^{31}P NMR spectrum of **5b**

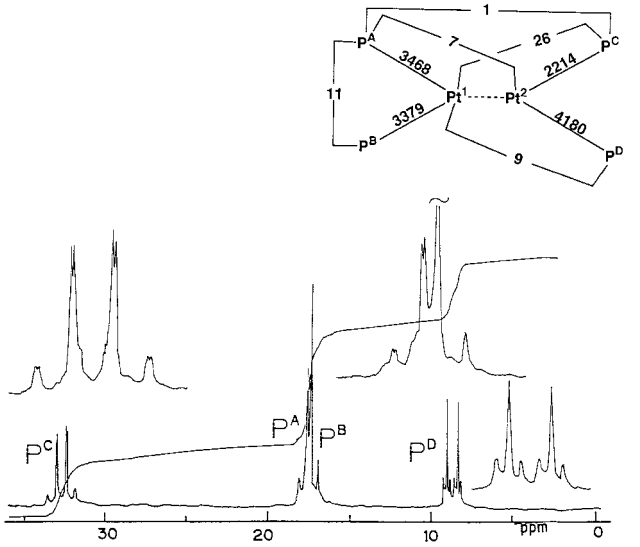
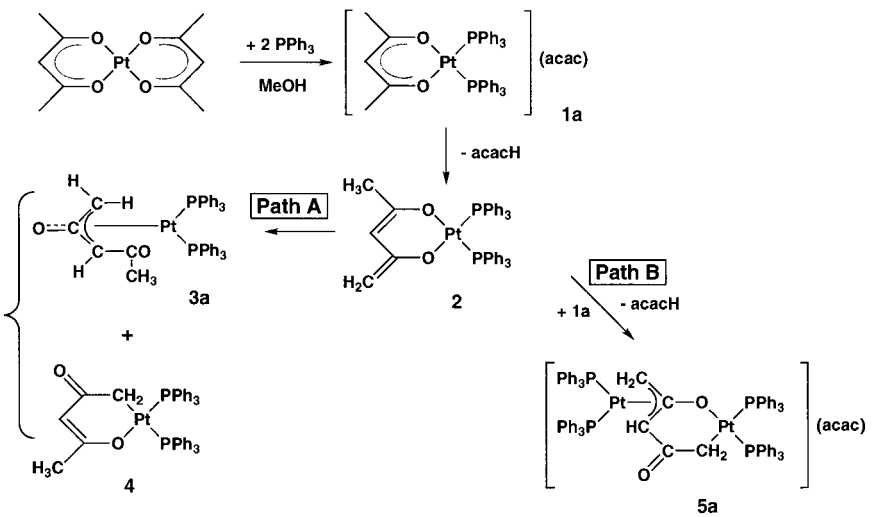


Fig. 2. Main signals of the ^{31}P NMR spectrum (24 MHz, CD_2Cl_2) of complex **5b** and a network of the $^{31}P-^{31}P$ and $^{195}Pt-^{31}P$ coupling constants.

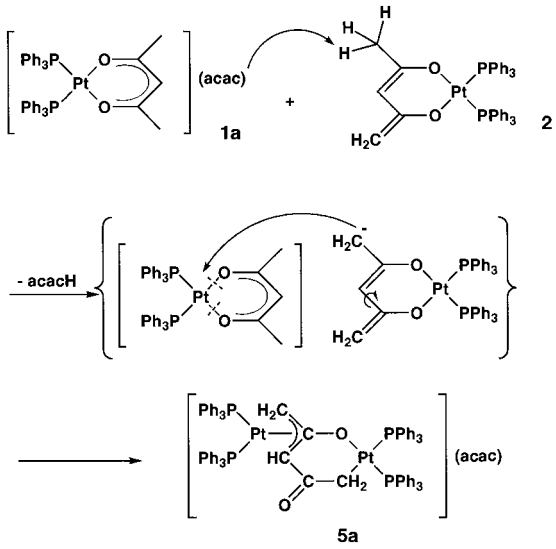
and a network of $^{31}P-^{31}P$ and $^{195}Pt-^{31}P$ coupling constants are shown in Fig. 2. The chemical shifts and coupling constants of the signals assigned to C^1, C^2 and C^3 for ^{13}C NMR, P^A and P^B for ^{31}P NMR and Pt^1 for ^{195}Pt NMR are similar to those of η^3-acac(2−) complexes [4,17], and those of the other signals assigned to C^4 and C^5 for ^{13}C NMR, P^C and P^D for ^{31}P NMR and Pt^2 for ^{195}Pt NMR are similar to those of *C*, *O*-chelated tfac(2−) complex [10]. The $^1J(H-C)$ values of C^1 and C^3 are 154 and 152 Hz, showing the sp^2 character of them. On the other hand, that of C^5 is 136 Hz, showing its sp^3 character. Unfortunately, suitable crystals of **5** for X-ray experiment could not be obtained yet.

We have elucidated the formation of **5a** as shown in Scheme 1 based on isolation of the intermediates and



Scheme 1.

the monitoring of the reaction steps by ^{1}H, ^{13}C and ^{31}P NMR spectroscopies. The reaction of $[Pt(acac)_2]$ with two equivalents of PPh_3 gave an intermediate of **1a** with the acac *O*,*O*′-chelate monoanion at the beginning. Although complex **1a** could not be isolated as a solid, when the reaction mixture was treated with KPF_6, the crystals of **1b** were isolated in a good yield. The isolated complex **1b** was subjected to further reaction under the same reaction conditions: in hot MeOH at 60°C. It did not give the acac trianion complex. This means that the acac anion in the outer sphere of **1a** plays an important role to form the trianion of acac by a proton abstraction from the coordinated acac ligand. This is supported by the fact that the acac anion in the outer sphere acts as a good proton acceptor because of its strong basicity (pK_a of acacH is 8.80), and that the acac anions in $[Pd(acac)L_2](acac)$ and $[PdL_4](acac)_2$ (L = amines) abstract even the proton from chloroform [18,19]. To form the trianion of acac in **5a**, two protons of the chelating monoanion of acac in **1a** must be abstracted, but complex **1a** has only one acac counter-anion as a proton abstractor. Therefore, a stepwise proton abstraction from **1a** to **5a** probably takes place, and another intermediate that has a dianion of acac might exist in the reaction. Although the intermediate was not detected in the reaction in MeOH, it was found with a diendienolate dianion of acac, **2**, by means of the ^{31}P NMR spectroscopy in the sample prepared as follows: after quick evaporation of a fresh MeOH solution of complex **1a** in vacuo, the resulting pale yellow oil was redissolved in C_6D_6. Within 6 min after dissolution, the sample showed an AB quartet {δ_P: 10.3 (J(P–P) = 27 Hz, J(Pt–P) = 3848 Hz); 5.9 (J(Pt–P) = 3859 Hz)}. This signal diminished and the signals due to **5a** appeared, by addition of MeOH to the sample. Without addition of MeOH, complex **2** changed gradually to **3a** contaminated with **4** that was isolated and characterized. The solvent is an important factor to select the reaction path A or B, and the MeOH solvent lead to form the cationic complex **5a**. Although further experiments are needed to establish the formation mechanism of **2** and **5a**, we propose a possible mechanism in Scheme 2, that is, an acetylacetonate(1 −) counter anion in complex **1a** abstracts a methyl proton from the chelating acac ligand to afford the intermediate **2**; in the next stage the counter acac anion in another **1a** abstracts a methyl proton from the acac(2 −) ligand in complex **2**. The resulting -CH_2^- attacks $[Pt(acac)(PPh_3)_2]^+$, expelling the chelating acac ligand to the outer sphere, to form an η^3-bond. Simultaneously –C(=CH_2)O− group rearranges to form a *C*, *O*-chelate. In this study the diendienolate intermediate **2** could not be isolated but Imran et al. [8] reported the X-ray structural analysis of this complex type, $[Pt\{OC(CHCOPh)CHC(Ph)O\}(PPh_3)_2]$. Another factor controlling the reaction course is the kind of tertiary phosphine. When $PMePh_2$ was used in



Scheme 2.

place of PPh_3, the ^{31}P signals of $[Pt(\eta^3\text{-acac}(2-))(PMePh_2)_2]$ and $[Pt_2(\mu\text{-acac}(3-))(PMePh_2)_4](acac)$ were also observed. In this case, the η^3-acac(3 −) bridged dimer complex **5** is a minor product.

The reaction of $[Pd(acac)_2]$ with two equivalents of PPh_3 in MeOH gave $[Pd(\eta^3\text{-acac}(2-))(PPh_3)_2]$ **3b** exclusively via $[Pd(acac)(PPh_3)_2](acac)$ **1c**. It was formed through the corresponding path A in Scheme 1. The Pd(II) analogue with acac(3 −) could not be detected by NMR even for the reaction using refluxing condition in MeOH.

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