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η^3-2,4-Pentanedionato(2-) and Terminal-carbon-bonded β-Diketonato Complexes of Platinum(II)

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A platinum(II)complex containing a 2,4-pentanedionate dianion as a trihapto ligand [Pt(acac(2−)-C^1—C^3)-{P(p-ClC_6H_4)$_3$}$_2$] was prepared by the reaction of [Pt(acac)$_2$] with tris(p-chlorophenyl)phosphine and reacted with pyridinium perchlorate to afford [Pt(acac-C^1)(py){P(p-ClC_6H_4)$_3$}$_2$](ClO_4). A similar terminal-carbon-bonded complex of 1,1,1-trifluoro-2,4-pentanedionate monoanion with platinum(II) was also derived from [Pt(tfac(2−)-C,O)($AsPh_3$)$_2$] by the reaction with pyridinium perchlorate. These novel platinum(II) complexes were characterized mainly by IR and NMR spectroscopy.

2,4-Pentanedione and other β-dicarbonyl compounds are very popular ligands,[1] and widely used as a chelating monoanion.[2] Recently coordination chemistry of their dianions has been greatly advanced and at present seven coordination modes illustrated in Fig. 1 are known. This paper reports a platinum(II) complex of type **5** containing a trihapto 2,4-pentanedionate dianion (acac-(2−)-C^1—C^3) as well as the first examples of platinum (II) complexes containing the terminal-carbon-bonded acac and 1,1,1-trifluoro-2,4-pentanedionate (tfac) monoanions.

Experimental

Preparation. The starting chelates bis(2,4-pentanedionato)platinum(II), [Pt(acac)$_2$] and bis(1,1,1-trifluoro-2,4-pentanedionato)platinum(II), [Pt(tfac)$_2$] were prepared by the method reported recently.[12] Tris(p-chlorophenyl)phosphine was purchased and used without further purification. 1,1,1-Trifluoro-2,4-pentanedionato(2-)-C,O-bis(triphenylarsine)platinum(II), [Pt(tfac(2-)-C,O)($AsPh_3$)$_2$] was prepared by the reaction of [Pt(tfac)$_2$] with triphenylarsine.[9] Pyridinium perchlorate was prepared by adding concentrated perchloric acid dropwise to a dichlotomethane solution of pyridine kept in an ice bath and a white precipitate dried *in vacuo* was recrystallized from ethanol. Found: C, 33.29; H, 3.39; N, 7.78%. Calcd for [pyH]ClO_4=$C_5H_6O_4NCl$: C, 33.45; H, 3.37; N, 7.80%. The compound is hygroscopic.

η^3-1-Acetyl-2-oxoallylbis{tris(p-chlorophenyl)phosphine}platinum(II), [Pt(acac(2-)-C^1—C^3){P(p-ClC_6H_4)$_3$}$_2$] (8): When tris(p-chlorophenyl)phosphine (1.086 g, 2.97 mmol) was added to a chloroform solution (2 cm^3) of [Pt(acac)$_2$] (584 mg, 1.48 mmol) with stirring under nitrogen, color of the solution changed from yellow to red. After being left to stand for 10 h, the solvent was removed under reduced pressure to leave a red oil, which changed to a yellow solid on prolonged pumping. The product was pulverized and treated with a mixture of dichloromethane (5 cm^3) and hexane (30 cm^3). A pale yellow powder, which remained undissolved, was filtered and dissolved in dichloromethane (10 cm^3). Hexane (30 cm^3) was added to the solution and the mixture was left to stand, depositing a white crystalline solid, which was filtered, washed with small portions of methanol and diethyl ether, and dried *in vacuo*. The yield was 769 mg (49%). Dec temp 190—210 °C. Inclusion of one molecule of water and one fourth molecule of dichloromethane per metal atom was confirmed by ^{1}H NMR spectroscopy. Found: C, 46.68; H, 3.07%. Calcd for $C_{41.25}H_{32.5}O_3P_2Cl_{6.5}Pt$: C, 46.58; H, 3.08%. Recrystallization from pyridine–diethyl ether gave a white crystalline solid which contained one molecule of water and a half molecule of pyridine per metal atom. Found: C, 48.43; H, 3.38; N, 0.53%. Calcd for $C_{43.5}H_{34.5}N_{0.5}O_3P_2Cl_6$: C, 48.29; H, 3.21; N, 0.65%. The former specimen was used for spectral measurements and reaction studies.

2, 4-Pentanedionato-C^1-(pyridine)bis{tris(p-chlorophenyl)phosphine}platinum(II). Perchlorate, [Pt(acac-C^1)(py){P(p-ClC_6H_4)$_3$}$_2$]ClO_4 (9a): An acetone solution (2 cm^3) of pyridinium perchlorate (55 mg, 0.31 mmol) was added to a dichloromethane solution (1 cm^3) of **8** (126 mg, 0.118 mmol) and the mixture was heated to 40 °C with stirring for 5 min. Undissolved portion of the pyridinium salt was filtered and the filtrate was left standing overnight at ambient temperature to make the solvent evaporate spontaneously. White needles left on the wall of vessel were recrystallized from dichloromethane–hexane to afford white needles (96 mg) in a 64%

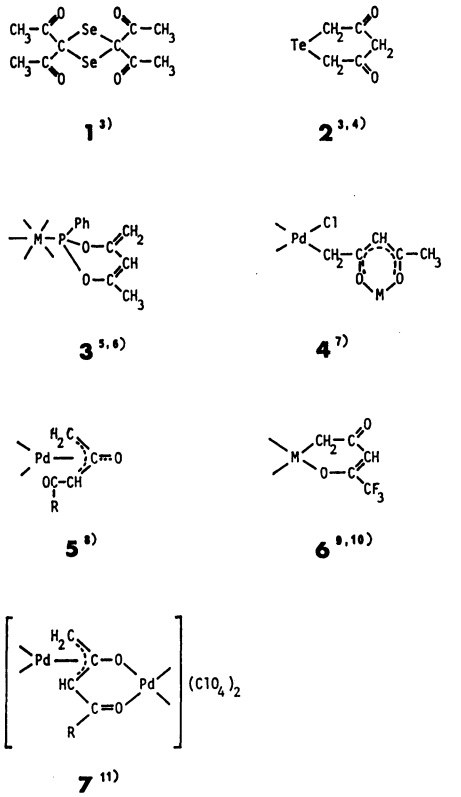


Fig. 1. Bonding modes of β-diketonate dianions in metal complexes.

yield. Dec temp 190—200 °C. Inclusion of three fourths molecule of dichloromethane as the solvent of crystallization was confirmed by ^{1}H NMR spectroscopy. Found: C, 44.31; H, 2.95; N, 1.14%. Calcd for $C_{46.75}H_{37.5}NO_6P_2Cl_{8.5}Pt$: C, 44.29; H, 2.98; N, 1.10%.

Measurements. Infrared spectra were obtained in Nujol mull with a Hitachi 295 infrared spectrophotometer. NMR spectra were recorded on JEOL FX-60Q (for ^{1}H and ^{13}C) and FX-90Q (for ^{31}P and ^{195}Pt) instruments.

Results and Discussion

Trihapto Complex of the 2,4-Pentanedionate Dianion with Platinum(II). The reaction of [Pt(acac)$_2$] with twice molar P(*p*-ClC$_6$H$_4$)$_3$ under a very mild condition gave a platinum(II) complex containing a 2,4-pentanedionate dianion as a ligand, [Pt(C$_5$H$_6$O$_2$){P(*p*-ClC$_6$H$_4$)$_3$}$_2$]·H$_2$O·S (**8**) (S=1/4CH$_2$Cl$_2$ or 1/2py depending on the solvent of recrystallization, which could not be removed by pumping). The infrared spectra in the 1700—1500 cm^{-1} region are quite similar to those of [Pd(acac(2−)-*C*^{1}—*C*^{3})(NN)] (NN=bpy (**5a**), 4,4′-Me$_2$bpy, and phen)[8] and [Pd(acac(2−)-*C*^{1}—*C*^{3})(PP)] (PP=Ph$_2$PCH$_2$CH$_2$PPh and Ph$_2$PCH=CHPPh$_2$(**5b**)),[11]

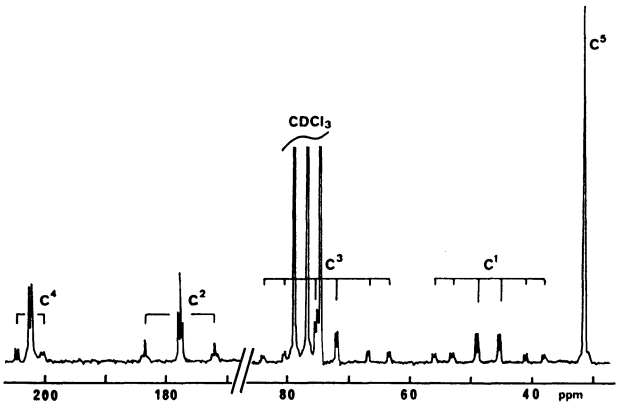


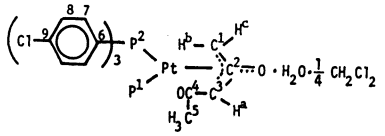
Fig. 2. ^{13}C{^{1}H}NMR spectrum at 15.0 MHz of [Pt(acac(2−)-*C*^{1}—*C*^{3}){P(*p*-ClC$_6$H$_4$)$_3$}$_2$]·H$_2$O·1/4CH$_2$Cl$_2$ (**8**) in CDCl$_3$ with Me$_4$Si as an internal reference. Signals of the phenyl carbons are omitted.

exhibiting a medium ν(C=O) band at 1650 cm^{-1} and a very strong and broad band at 1548 cm^{-1} assignable to the ν(C···O) and/or ν(C···C) vibration.

Figure 2 shows the ^{13}C{^{1}H} NMR spectrum of **8**. Assignment of the three sets of higher-field signals to the methyl, methylene, and methine carbons was made on the basis of the ^{1}H off-resonance data and listed in Table 1. Except the highest-field signal assignable to the methyl carbon, all carbons of the acac(2−) ligand couple to ^{31}P atom(s) and are flanked by the ^{195}Pt satellites. The methylene and methine carbons couple much more strongly to the ^{31}P atom situated at the *trans* position than to the *cis* ^{31}P atom, both appearing as a doublet of doublets. On the other hand, the central carbonyl carbon (C^2) resonates as a triplet, indicating that the coupling constants to both ^{31}P atoms are nearly equal in spite of their environmental nonequivalence (*vide infra*). The other carbonyl carbon (C^4) is remote from the coordination sites and weakly couples only to the *trans* ^{31}P. The fact that the J(Pt–C) values are much larger for C^1, C^2, and C^3 than for C^4 strongly supports the proposed trihapto structure, and the chemical shifts of C^1 and C^3 are well in accord with those recorded for other η-allylic systems.[13] The central carbon of the η-allyl moiety usually resonates at about 100 ppm,[13] but substitution of a proton bonded to a carbon atom with a hydroxyl group is generally known to shift the carbon resonance to 36—51 ppm lower field.[14] Now substitution with oxo anion causes downfield shift by about 80 ppm and the shielding of C^2 (177.8 ppm) nearly coincides with those of **5a** (180.5 ppm)[8] and **5b** (177.0 ppm).[11]

The ^{1}H NMR spectrum of **8** is composed of signals at 1.31 (CH$_3$), 1.97 (H$_2$O), 2.2—4.7 (CH$_2$ and CH), 5.30 (CH$_2$Cl$_2$), and 7.3 (phenyl protons) ppm with the relative intensities 3 : 2 : 3 : 0.5 : *ca.* 30 (Table 1). The signals at 1.97 and 5.30 ppm were assigned to solvents of crystallization since they increased their intensities on addition of water and dichloromethane, respectively. The signals in the 2.2—4.7-ppm region are complex because of coupling of CH$_2$ and CH protons to ^{31}P and ^{195}Pt atoms, and are divided into three groups of which two are flanked by ^{195}Pt satellites: a broad multiplet

Table 1. ^{1}H and ^{13}C{^{1}H} NMR data for complex **8** in CDCl$_3$[a]



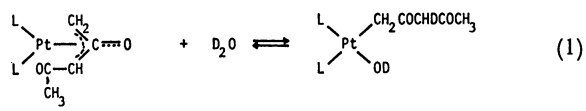
	H^a	H^b	H^c	CH_3	Ph	Other
δ_H	4.22	2.91	2.55	1.31	7.3	1.97(H_2O), 5.30(CH_2Cl_2)
J(H–H)	*ca.* 3(H^a,H^c)	*ca.* 7(H^b,H^c)				
J(Pt–H)	35	68				

	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9
δ_C	47.2	177.8	73.8	203.1	31.4	129.3	134.9	128.8	137.7
J(P^1–C)	55	5	5	0					
J(P^2–C)	5	5	52	5		65	10	10	2
J(Pt–C)	233	168	259	48			24		

a) Chemical shift (δ) in ppm from internal Me$_4$Si and coupling constant (J) in Hz.

at 2.55 ppm (H^c), a multiplet at 2.91 ppm (H^b, J(Pt–H) $=ca.$ 70 Hz), and a broad doublet at 4.22 ppm (H^a, J(Pt–H)=35 Hz). The ^{1}H NMR spectra of **5a** and related complexes are much more simpler due to lack of couplings to P and Pt atoms and were assigned unequivocally.[8] By reference to these data, the doublet at 4.22 ppm is assigned to the methine proton H^a, of which coupling to H^c demonstrates that the dangling acetyl moiety occupies the anti position of the η-allylic skeleton, making the H^a and H^c protons accord with the so-called W rule.[15]

When one drop of D_2O was added to a $CDCl_3$ solution of **8**, the signal at 1.97 ppm diminished at once and the one at 4.22 ppm decreased remarkably on stirring of the mixture overnight. The *ca.* 3 Hz coupling which had been observed for the multiplet at 2.55 ppm also disappeared on D_2O addition. These results indicate that the signal at 4.22 ppm is assigned to an exchangeable unique proton H^a. Partial decoupling of the signal at 2.55 ppm by deuteration of H^a also accords with the proposed structure. The fact that the ^{13}C signal from the methine carbon (C^3) at 73.8 ppm was remarkably diminished by the D_2O treatment also certifies that the methine proton was deuterated. As to the mechanism of methine deuteration, an intermediate containing the terminal-carbon-bonded acac ligand of keto form must be presumed.



(1)

Since the terminal-carbon-bonded acac ligand contained in the stable Pt(II) complex **9a** (*vide infra*) is composed almost of the enol tautomer, the intermediate containing the unidentate keto acac presumed in Eq. 1 may be far less stable, and this situation might be the reason why the deuteration reaction is so slow.

Assignment of the multiplet signals centered at 2.55 and 2.91 ppm to the syn (H^c) and anti (H^b) protons, respectively, was made by reference to data for **5a**. The ^{1}H{^{31}P} NMR data for [Pt($C_5H_6O_2$)(PPh_3)$_2$] reported by Ito and Yamamoto[16] were also very helpful. They obtained the complex from the reaction of [Pt(acac)$_2$] with twice molar PPh_3 in refluxing THF and tentatively presumed a π-oxoallylic coordination.

Figure 3 shows the ^{31}P{^{1}H} NMR spectrum of complex **8** in $CDCl_3$. Main signals appear as an AB quartet at 18.6_3 and 19.2_8 ppm downfield from external H_3PO_4 with ^2J(P–P)=7 Hz. Both signals are flanked by ^{195}Pt satellites, ^1J(Pt–P) being $2.88_4\times10^3$ and $3.18_6\times10^3$ Hz, respectively. The spectrum indicates that the two phosphorus atoms are not equivalent but the difference in their environments is slight, since differences in the chemical shifts and ^1J(Pt–P) values are small. Unequivocal discrimination of phosphorus atoms is not easy, but the signal at 19.2_8 ppm with larger ^1J(Pt–P) value may be assigned to P^2 situated at the site *trans* to C^3, since the dangling acetyl moiety is electron attracting and the acetonyliden group will exert slightly smaller *trans* influence than the unsubstituted methylene end (C^1).

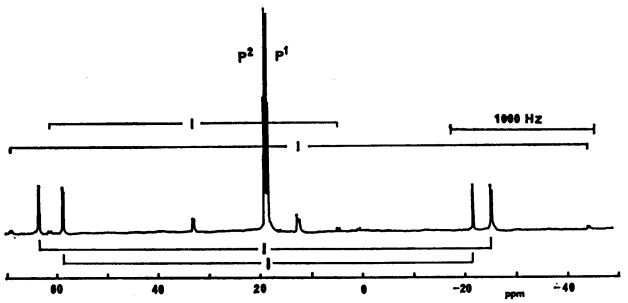


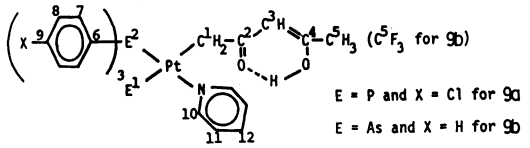
Fig. 3. ^{31}P{^{1}H}NMR spectrum at 36.3 MHz of [Pt(acac(2−)-C^1—C^3){P(*p*-ClC_6H_4)$_3$}$_2$]·H_2O·1/4CH_2Cl_2 (**8**) in $CDCl_3$ with H_3PO_4 as an external reference.

As is noticed in Fig. 3, the spectrum involves another AB quartet at 12.6_7 and 33.1_4 ppm with ^2J(P–P)=11 Hz, indicating contamination with a minor product which also contains two nonequivalent phosphine ligands. The ^1J(Pt–P) values are $4.06_0\times10^3$ and $2.03_4\times10^3$ Hz, respectively, of which the difference is large, suggesting a large difference in the environments of two phosphorus atoms situated at mutually *cis* positions. The pattern of the minor signals resembles closely to the ^{31}P{^{1}H} spectrum of [Pt(tfac(2−)-*C,O*)L_2] which contains a *C,O*-chelated 1,1,1-trifluoro-2,4-pentanedionate dianion with PPh_3 or P(*p*-ClC_6H_4)$_3$ as L (**6a**).[9] Thus the minor product is presumed to be [Pt(acac(2−)-*C,O*){P(*p*-ClC_6H_4)$_3$}$_2$] which is an isomer of **8**. Relative intensities of signals in Fig. 3 suggest that content of the minor product is less than 10% and could not be detected in ^{13}C{^{1}H} and other NMR spectra, whereas [Pd(acac(2−)-C^1—C^3)(NN)] (NN=bpy, 4,4′-Me_2bpy, and phen) contained [Pd(acac(2−)-*C,O*)-(NN)] in 20—25% proportions which were determined by ^{1}H NMR spectroscopy.[8] Isolation of the minor isomers has not been successful for either of the Pd(II) and Pt(II) complexes and it is not certain whether the isomerization equilibria are attained in solution or both isomers are inert, preserving the products ratio under the conditions of preparation.

The ^{195}Pt{^{1}H} NMR spectrum at 19.2 MHz of **8** in $CDCl_3$ was observed as a doublet of doublets at 3373.5 ppm upfield from external $K_2[PtCl_4]$. The coupling constants ^1J(Pt–P) to the two phosphorus atoms are $2.88_6\times10^3$ and $3.18_9\times10^3$ Hz, showing excellent agreement with the values obtained from the ^{31}P{^{1}H} NMR spectroscopy (*vide supra*).

It is surprising that the reaction of [Pt(acac)$_2$] with P(*p*-ClC_6H_4)$_3$ to produce **8** proceeds under a very mild condition. Comprehensive studies have been carried out on the reactions of [M(β-dik)$_2$] (M=Pd(II) and Pt(II)) with nitrogen bases[17] and tertiary phosphines.[18] The ^{1}H NMR spectroscopy revealed that the reaction of [Pt(tfac)$_2$] with twice molar PPh_3 in $CDCl_3$ produces [Pt(tfac)(PPh_3)$_2$](tfac) at first, which is then transformed into [Pt(tfac(2−)-*C,O*)(PPh_3)$_2$]. The tfac anion in the outer sphere seems to abstract a proton from the chelating tfac ligand, whereas the corresponding Pd(II) complex salt [Pd(tfac)(PPh_3)$_2$](tfac) is stable in solution and deprotonated only by added bases such as pyridine and its derivatives.[10] In the present case, changes of ^{1}H and ^{13}C NMR spectra during the reaction of

TABLE 2. ^1H AND $^{13}C\{^1H\}$ NMR DATA FOR COMPLEXES **9a** AND **9b** IN $CDCl_3$

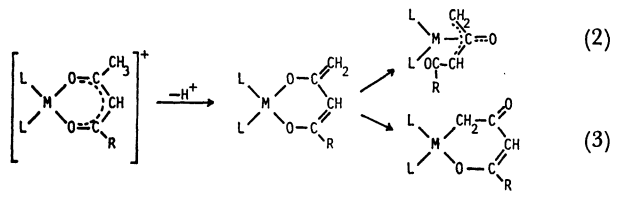


	CH_2	CH	CH_3	OH	Ring H adjacent to N	Other
9a, δ_H	2.11	4.53	1.53	15.6	8.60	7.4(ring H), 5.30(CH_2Cl_2)
$J(P^1$–H)	9					
$J(P^2$–H)	5					
J(Pt–H)	77	*ca.* 4			34	
9b, δ_H	2.71	4.91		*ca.* 15	8.67[b]	7.4(ring H), 5.30(CH_2Cl_2)
J(Pt–H)	94				40	
	C^1	C^2	C^3	C^4	C^5	Other
9a, δ_C	32.2	198.2	100.3	189.7	24.1	151.9(C^{10}), c)
$J(P^1$–C)	70	5				
J(Pt–C)	d)	40				
9b, δ_C	26.8	201.9	94.8	174.6q	d)	151.8(C^{10}), c)
J(Pt–C)	*ca.*500	*ca.*40				
J(F–C)				35		

a) Same as footnote a) for Table 1. Q=quartet. b) J(H–H)=5 Hz. c) Indistinguishable because of overlapping. d) Not recorded due to insufficient scans.

$[Pt(acac)_2]$ with twice molar PPh_3 in $CDCl_3$ were complex and could not be analyzed satisfactorily. However intermediate formation of $[Pt(acac)(PPh_3)_2]$-(acac) is evidenced by isolation in high yields of $[Pt(acac)(PPh_3)_2]X$ (X=BPh_4[19] and ClO_4[20]) on addition of NaX.

Deprotonation of the chelating β-diketonate ligand will produce a complex of type **3** primarily. Although such a dienediolate type bonding of acac(2–) was found for $[(\eta\text{-}C_5H_5)(CO)_2Mn\{PPh(C_5H_6O_2)\}]$[5] and $[(CO)_5M\{PPh(C_5H_6O_2)\}]$ (M=Cr and W),[6] analogous complex of transition metals has not been reported. In the present Pd(II) and Pt(II) cases, complexes of type **3** are not stable, but transformed either to the trihapto coordination or to *C,O*-chelation. The tfac(2–) ligand carrying the electron-attracting trifluoromethyl group prefers *C,O*-chelation in both Pd(II)[10] and Pt(II)[9]



(2)

(3)

complexes, while the dianion of ethyl acetoacetate carring the electron-releasing ethoxyl group affords the trihapto Pd(II) complexes exclusively.[8] The acac(2–) ligand exhibits an intermediate behavior, producing the trihapto complexes accompanied by a small amount of *C,O*-chelate.

Terminal-carbon-bonded Complexes of the β-Diketonate Monoanions with Platinum(II). Terminal-carbon-bonded complexes of 2,4-pentanedionate[21] and 1-ethoxy-1,3-butanedionate (etac)[22] monoanions with palladium(II) were derived from the corresponding trihapto complexes $[PdCl(\eta^3\text{-}\beta\text{-dik})]_2$, where β-dik is acac[21] and etac,[23] respectively. Trihapto complexes of β-diketonate monoanions with platinum(II) have not yet been obtained and thus the terminal-carbon-bonded β-dik complexes with platinum(II) are not known either.

Now the reaction of **8** with pyridinium perchlorate in a mixture of dichloromethane and acetone gave $[Pt(acac\text{-}C^1)(py)\{P(p\text{-}ClC_6H_4)_3\}_2]\cdot 3/4CH_2Cl_2$ (**9a**), which is the first example of the terminal-carbon-bonded acac complex with platinum(II). Figure 4 shows ^1H and ^{13}C NMR spectra of **9a** in $CDCl_3$ and results of the signal analysis are listed in Table 2. The

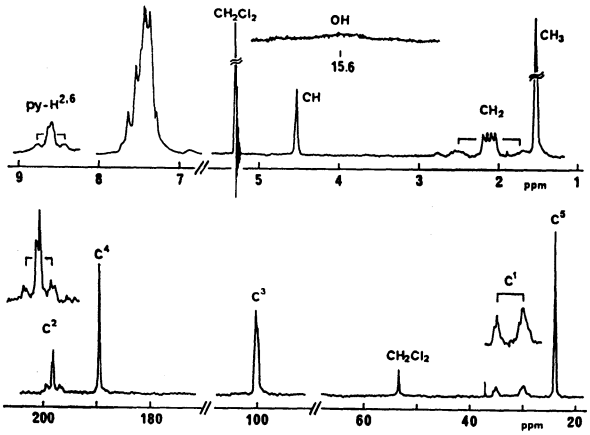


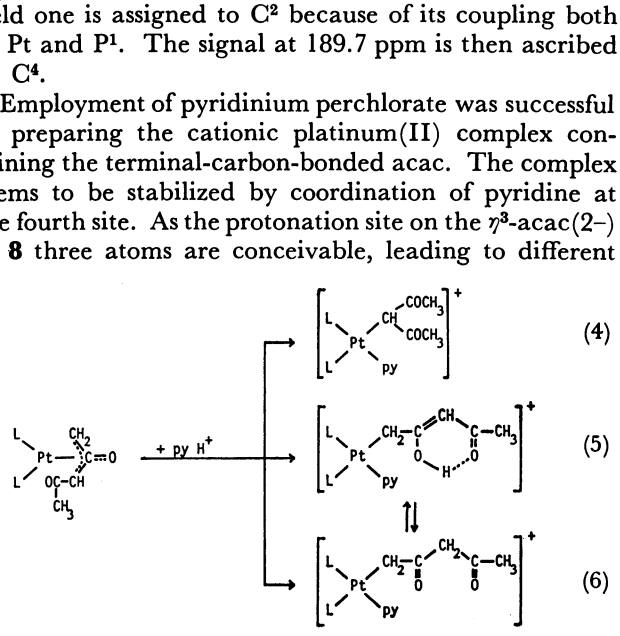
Fig. 4. ^1H and $^{13}C\{^1H\}$ NMR spectra at 100 and 15.0 MHz, respectively, of $[Pt(acac\text{-}C^1)(py)\{P(p\text{-}ClC_6H_4)_3\}_2]ClO_4\cdot 3/4CH_2Cl_2$ (**9a**) in $CDCl_3$ with Me_4Si as an internal reference. In the ^1H NMR spectrum, intensity of the ring protons except py-$H^{2,6}$ is decreased to *ca.* 1/4 and that of OH is increased about four times. In the ^{13}C NMR spectrum, signals of all ring carbons are omitted.

proton signal at 2.11 ppm appearing as a doublet of doublets flanked by ^{195}Pt satellites with a large J(Pt–H) value is assigned to the methylene group bonded to platinum(II). The signal multiplicity indicates unequivocally that **9a** has a *cis* configuration. No other methylene signal is observed, but instead a methine signal and a broad OH signal are observed, indicating that the terminal-carbon-bonded acac ligand is composed mainly of the enol tautomer. The coupling constant of the methine protons to ^{195}Pt is smaller than that in [Pt(acac)$_2$] (^4J(Pt–H) = 10.7 Hz)[24] in accordance with the unidentate state. Coordination of pyridine is demonstrated by the fact that the signal from the ring protons adjacent to nitrogen is flanked by the ^{195}Pt satellites.

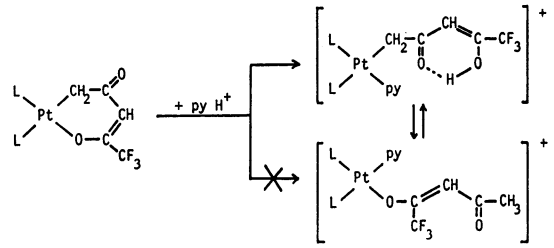
It is worth noting that keto tautomer of **9a** is not detected on the ^{1}H NMR spectrum. The equilibrium quotient Q=[enol]/[keto] for [PdCl(acac-C^1)(bpy)] was reported to be 0.7 in $CDCl_3$ at 25 °C.[21] This value is smaller than 6.7 for free acacH molecules in $CDCl_3$ at 33 °C[25] and the PdCl(bpy)$^+$ moiety was considered to be electron releasing,[21] since an electron-attracting substituent on acacH increases Q, while an electron-releasing substituent exerts the opposite effect. Thus Q is 32 for tfacH and 0.43 for 3-methyl-acacH as neat liquids at 33 °C.[26] Now the Pt(py){P(p-ClC$_6$H$_4$)$_3$}$_2^{2+}$ moiety is functioning as a powerful electron-attracting substituent comparable to the trifluoromethyl group. The remarkable discrepancy in behaviors of this and PdCl(bpy)$^+$ moieties may arise from the difference in charge densities at the central metals, since Pt is coordinated with three neutral ligands of which two are π accepting, whereas Pd is bonded to a chloride anion and 2,2′-bipyridine which is a weaker π-acceptor than phosphines.[27]

The ^{13}C{^{1}H} NMR spectrum of **9a** accords well with the proposed structure. The methylene carbon bonded to the metal appears as a broad doublet in accordance with the *cis* structure, the ^2J(P^1–C) being 70 Hz and ^2J(P^2–C) indiscernibly small. Of the two signals attributable to the carbonyl carbons, the lower field one is assigned to C^2 because of its coupling both to Pt and P^1. The signal at 189.7 ppm is then ascribed to C^4.

Employment of pyridinium perchlorate was successful in preparing the cationic platinum(II) complex containing the terminal-carbon-bonded acac. The complex seems to be stabilized by coordination of pyridine at the fourth site. As the protonation site on the η^3-acac(2−) in **8** three atoms are conceivable, leading to different products (Eqs. 4—6). If a proton adds to the terminal methylene, the central-carbon-bonded complex will be resulted (Eq. 4). On the other hand, addition of a proton to the methine carbon will give rise to a complex of the terminal-carbon-bonded keto tautomer of acac (Eq. 6). Either of these two was not the case, but reaction 5 was predominant, indicating that the proton affinity is highest at the enolate oxygen atom.



When an equimolar amount of pyridinium perchlorate was added to a solution of [Pt(tfac(2−)-C,O)(AsPh$_3$)$_2$]·1/4CH$_2$Cl$_2$[9] in $CDCl_3$, [Pt(tfac-C^1)(py)(AsPh$_3$)$_2$]ClO$_4$ (**9b**) was produced quantitatively as evidenced by ^{1}H and ^{13}C NMR spectra listed in Table 2, although its isolation was not successful. The tautomerization equilibrium of the terminal-carbon-bonded tfac in **9b** is also shifted to enol completely. Protonation did not occur at the terminal carbon, but occurred at the enolate oxygen.



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