Reactions of the [PtCl$_2$L$_2$] Complexes (L=Sulfide or Tertiary Phosphine) with β-Diketonate Anions

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cis- and *trans*-[PtCl$_2$(Et$_2$S)$_2$] as well as [PtCl$_2$(EtSCH$_2$CH$_2$SEt)] reacted with thallium(I) β-diketonates, Tl(β-dik), to give complexes containing a central-carbon-bonded β-dik ligand. The reaction of *cis*-[PtCl$_2$(PEt$_3$)$_2$] with Tl(acac) (acac=acetylacetonato) did not give an acetylacetonato complex, but resulted in [Pt(CO$_3$)(PEt$_3$)$_2$], while *trans*-[PtCl$_2$(PEt$_3$)$_2$] yielded [PtCl(acac)(PEt$_3$)]. [Pt(PPh$_3$)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ derived from *cis*-[PtCl$_2$(PPh$_3$)$_2$] reacted with K(acac) and K(tfac) (tfac=trifluoroacetylacetonato) to afford [Pt(acac)(PPh$_3$)$_2$]ClO$_4$ and [Pt(tfac)(PPh$_3$)$_2$]-ClO$_4$, respectively. Bases such as Et$_3$N, K(acac), and K(tfac) removed a proton from the latter complex to give [Pt(tfac(2−)-*C,O*)(PPh$_3$)$_2$] containing a *C,O*-chelated tfac dianion.

Bis(acetylacetonato)platinum(II) was first prepared by Werner by the reaction of the tetrachloroplatinate(II) with acetylacetone in basic aqueous solution,[1] and the yield reported by Grinberg and Chapurskii[2] was only 35%.[3] The low yield was caused partly by formation of [Pt(acac)(acac-C^3)Cl]$^-$ as a by-product which contains the central-carbon-bonded acetylacetonate anion (acac-C^3) as a ligand.[4] This complex seems to be produced by the ligand substitution reaction of [Pt(acac)Cl$_2$]$^-$ with an acac anion and it is worth noting that the [Pt-(acac)Cl] moiety prefers the central carbon bonding to the oxygen bonding when it accepts the acac anion as a unidentate ligand.

Recently the reaction between [Pd(acac)$_2$] and diethylamine to afford [Pd(acac)(acac-C^3)(Et$_2$NH)][5] was found by kinetic and equilibrium studies to proceed not directly but *via* [Pd(acac)(Et$_2$NH)$_2$](acac).[6] When the diethylamine ligand is replaced by an acac anion, the [Pd(acac)(Et$_2$NH)]$^+$ moiety also favors the central carbon bonding over the oxygen bonding. On the other hand, *trans*-[PdCl(C$_5$H$_3$(6-Cl)N-C^2)(PEt$_3$)$_2$], which contains the 6-chloro-2-pyridyl group as a carbon-bonded ligand, reacts with thallium(I) β-diketonate such as acetylacetonate, trifluoroacetylacetonate, and hexafluoroacetylacetonate to afford *trans*-[Pd(β-dik-O)(C$_5$H$_3$(6-Cl)N-C^2)(PEt$_3$)$_2$].[7] In this case the [Pd(C$_5$H$_3$-(6-Cl)N-C^2)(PEt$_3$)$_2$]$^+$ group prefers oxygen bonding to central carbon bonding of the unidentate β-diketonate ligand.

In recent years very extensive studies have been performed on the reactions of bis(β-diketonato) palladium-(II) and -platinum(II) complexes with various nitrogen bases,[8] tertiary phosphines,[9] and arsines[9b] to convert the O,O'-chelated β-diketonate anion to other several types of coordination modes. Factors which favor each of these coordination modes were also investigated. As an extention of these studies, reactions of the [PtCl$_2$L$_2$]-type complexes containing dialkyl sulfides and tertiary phosphines as L with thallium(I) β-diketonates have been examined, and the results are reported in this paper.[10]

Experimental

Preparation of Complexes. Thallium(I) β-diketonates were prepared by the method analogous to that reported for thallium(I) benzoylacetonate.[11] Potassium acetylacetonate and trifluoroacetylacetonate were obtained by adding acetylacetone or trifluoroacetylacetone to a methanol solution of potassium hydroxide and concentrating the reaction product. Starting complexes, *cis*- and *trans*-[PtCl$_2$(SEt$_2$)$_2$],[12] *cis*- and *trans*-[PtCl$_2$(PEt$_3$)$_2$],[13] *cis*-[PtCl$_2$(PPh$_3$)$_2$],[14] and *trans*-[PtHCl-(PEt$_3$)$_2$][15] were also prepared according to literatures. 1,2-Bis(ethylthio)ethane, C$_2$H$_5$SCH$_2$CH$_2$SC$_2$H$_5$ (S-S), was prepared in the following way similar to that used for 1,2-bis-(methylthio)ethane.[16] Sodium (0.5 g) was dissolved in ethanol and the solution was concentrated to get nearly saturated solution of sodium ethoxide. Ethanethiol (1.5 cm^3) was added to the solution and the mixture was stirred at room temperature for 15 h, when the colorless solution turned to light yellow. 1,2-Dibromoethane (0.83 cm^3) was then added to the solution in small portions. The mixture was heated under reflux for 10 h. After separation of sodium bromide by filtration the solution was refluxed for an additional hour. Water was added to the reaction mixture and the heavy oil layer was separated. The water layer was extracted with diethyl ether. The organic solutions were combined, passed through a column of anhydrous sodium sulfate, and distilled under reduced pressure (bp 37 °C/3 Torr, 1 Torr=133.322 Pa) to obtain colorless liquid (0.7 g).

The following procedures including evaporation of solvents in a rotary evaporator were carried out at room temperature unless otherwise stated.

(Acetylacetonato)(acetylacetonato-C^3)(diethyl sulfide)platinum-(II), [Pt(acac)(acac-C^3)(Et$_2$S)] (1a): A methanol solution (15 cm^3) of Tl(acac) (0.681 g, 2.25 mmol) was added drop by drop to a methanol solution (15 cm^3) of *cis*-[PtCl$_2$(Et$_2$S)$_2$] (0.500 g, 1.12 mmol) with stirring. Color of the solution changed from yellow to colorless and thallium(I) chloride precipitated. After being stirred for 3 h, the precipitate was filtered off and the filtrate was evaporated to dryness. The residue was treated with dichloromethane and remaining Tl(acac) was separated by filtration. After concentration of the solution, diethyl ether was added to the concentrate to obtain a white precipitate of **1a**. The yield was 0.201 g (37%).

[Pt(tfac)(tfac-C^3)(Et$_2$S)] (1b): A mixture of *cis*-[PtCl$_2$(Et$_2$S)$_2$] (0.400 g, 0.90 mmol) and Tl(tfac) (0.640 g, 1.84 mmol) in methanol (30 cm^3) was stirred for 3 h. After separation of TlCl and evaporation of the solvent, the residue was dissolved in dichloromethane and Tl(acac) was filtered off. The yield was 0.186 g (35%).

[Pt(hfac)(hfac-C^3)(Et$_2$S)] (1c): The reaction of *cis*-[PtCl$_2$(Et$_2$S)$_2$] with Tl(hfac) in a similar way as above gave **1c** in a 30%

yield. Complexes **1b** and **1c** are readily soluble in diethyl ether, while **1a** is sparingly soluble in the same solvent.

Dichloro[1,2-bis(ethylthio)ethane]platinum(II), $[PtCl_2(S-S)]$, was prepared by a method analogous to that exemplified by Cross *et al.*[17] Aqueous solution of an equimolar mixture of $K_2[PtCl_4]$ and the disulfide was stirred for 4 h and then heated under reflux for 1 h. A yellow precipitate was filtered, dried, and recrystallized from hot dichloromethane. The yield was 79%.

[PtCl(acac-C³)(S-S)] (2): A methanol solution ($15\,cm^3$) of Tl(acac) (0.240 g, 0.79 mmol) was added to a suspension of $[PtCl_2(S-S)]$ (0.330 g, 0.79 mmol) in methanol ($15\,cm^3$) and the mixture was stirred for 5 h. After separation of TlCl, the solvent was evaporated to dryness. The residue was treated with dichloromethane ($10\,cm^3$) and Tl(acac) was filtered off. The filtrate was again concentrated to dryness and the residue was treated with diethyl ether. A light yellow solid of **2** was purified by reprecipitation from dichloromethane–diethyl ether. The yield was 0.216 g (48%).

$[Pt(CO_3)(PEt_3)_2]$ (3): A methanol solution ($15\,cm^3$) of Tl(acac) (0.600 g, 2.00 mmol) was added dropwise to a solution of *cis*-$[PtCl_2(PEt_3)_2]$ (0.500 g, 1.00 mmol) in methanol ($15\,cm^3$) through which carbon dioxide was being passed. The mixture was stirred for 5 h under CO_2 bubbling. After separation of TlCl the solvent was evaporated to dryness. The residue was dissolved in a small amount of dichloromethane containing a very small portion of pyridine. Diethyl ether was carefully added until the solution became turbid and the mixture was allowed to stand overnight. White crystals (0.087 g) were obtained in an 18% yield.

$[Pt(PPh_3)_2(H_2O)_2](ClO_4)_2$ (4): A methanol solution ($10\,cm^3$) of silver perchlorate (0.250 g, 1.19 mmol) was added to a suspension of *cis*-$[PtCl_2(PPh_3)_2]$ (0.470 g, 0.60 mmol) in chloroform ($10\,cm^3$). Both solutions were cooled with ice in advance and the mixture was stirred at 0 °C for 5 min. After separation of silver chloride, the filtrate was evaporated to dryness under cooling. A white solid of **4** (0.280 g) was obtained in a 49% yield after purification by reprecipitation from dichloromethane–diethyl ether at room temperature.

$[Pt(acac)(PPh_3)_2]ClO_4$ (5a): A methanol solution ($15\,cm^3$) of K(acac) (0.020 g, 0.13 mmol) was added drop by drop to a suspension of complex **4** (0.100 g, 0.11 mmol) in the same solvent ($15\,cm^3$). After stirring for 24 h, a precipitate of potassium perchlorate was filtered off and the filtrate was evaporated to dryness. The residue was purified by reprecipitation from dichloromethane–diethyl ether and the yield was 0.049 g (49% yield).

$[Pt(tfac)(PPh_3)_2]ClO_4$ (5b): A methanol solution ($5\,cm^3$) of K(tfac) (0.080 g, 0.43 mmol) was added to a dichloromethane solution ($30\,cm^3$) of **4** (0.400 g, 0.43 mmol) and the mixture was stirred for 16 h. After separation of potassium perchlorate, the yellow filtrate was concentrated to dryness. The residue was dissolved in dichloromethane and precipitated K(tfac) was separated by filtration. The filtrate was concentrated to 2—3 cm^3. On addition of diethyl ether to the concentrate a light yellow precipitate appeared, which was purified by reprecipitation from chloroform–hexane. The yield was 0.208 g (50%).

$[Pt(acac)(PEt_3)_2]PF_6$ (6): Acetylacetone ($1\,cm^3$) was added to a methanol solution ($15\,cm^3$) of *trans*-$[PtHCl(PEt_3)_2]$ (0.500 g, 1.10 mmol) and to this solution was added dropwise a methanol solution ($15\,cm^3$) of silver hexafluorophosphate (0.270 g, 1.10 mmol). After stirring of the mixture for 24 h, silver chloride was filtered off and the filtrate was concentrated to about one-half volume. Scratching of the flask stimulated crystallization. A white precipitate was recrystallized from dichloromethane–diethyl ether. The yield was 0.236 g (32%).

$[Pt(tfac(2-)$-C,O$)(PPh_3)_2]$ (7): A methanol solution ($30\,cm^3$) containing complex **4** (0.340 g, 0.35 mmol) and K(tfac) (0.140 g, 0.73 mmol) was stirred for 24 h. After separation of potassium perchlorate, the yellow filtrate was evaporated to dryness. The residue was dissolved in a small amount of dichloromethane. Diethyl ether was added carefully to the solution until the upper portion of the solution became turbid and the mixture was allowed to stand overnight. A white crystalline product (0.077 g) was obtained in a 25% yield.

Complex **7** was also derived from **5b** by treating with bases. *(i)* Triethylamine (0.036 g, 0.36 mmol) was added drop by drop to a methanol solution ($20\,cm^3$) of complex **5b** (0.222 g, 0.23 mmol) and the mixture was stirred for 19 h. The solution was then evaporated under reduced pressure to leave an oily substance, which was dissolved in a tiny amount of dichloromethane. Diethyl ether was added dropwise to the solution to deposite a white precipitate, which was recrystallized from dichloromethane–diethyl ether. The yield was 0.040 g (20%). When a ten times molar amount of triethylamine was employed the yield of **7** was improved to 36%.

(ii) A methanol solution ($15\,cm^3$) of K(acac) (0.043 g, 0.31 mmol) was added to a solution of **5b** (0.301 g, 0.31 mmol) in the same solvent ($15\,cm^3$) and the mixture was stirred for 24 h. Work-up similar to that starting with **4** gave **7** (0.103 g) in a 38% yield. Employment of an equimolar amount of K(tfac) instead of K(acac) gave a similar yield of **7**.

$[PtCl(acac)(PEt_3)]$ (8): A methanol solution ($30\,cm^3$) containing *trans*-$[PtCl_2(PEt_3)_2]$[13] (0.300 g, 0.60 mmol) and Tl(acac) (0.630 g, 2.1 mmol) was stirred for one week. After separation of thallium(I) chloride by filtration, the filtrate was evaporated under reduced pressure to leave an oily substance, which was dissolved in a mixture ($15\,cm^3$) of diethyl ether and petroleum ether (1:2 by volume). Scratching of the flask stimmulated crystallization of the product, which was dissolved in the smallest amount of dichloromethane and passed through a column ($40\,cm\times\phi 1.3\,cm$) of silica gel. A mixture ($60\,cm^3$) of benzene and petroleum ether (1:2 by volume) was used as the eluant. A light yellow solid (0.18 g) was obtained by evaporation of the eluate. Purity of the product was not good, giving unsatisfactory analysis. The IR and ^1H NMR data in comparison with those for $[PtCl(acac)(PMe_2Ph)]$[18] showed that the product is **8** contaminated with the starting complex.

Measurements. Infrared spectra were measured in Nujol mulls with JASCO IR-E (4000—650 cm^{-1}), Hitachi EPI-L (700—200 cm^{-1}), and JASCO DS 701 G (4000—200 cm^{-1}) spectrophotometers. Electronic spectra were taken on a Hitachi EPS-3T recording spectrophotometer and ^1H NMR spectra on a JNM MH-100 instrument with tetramethylsilane as an internal reference. Molecular weight was determined with a vapor pressure osmometer manufactured by Knauer in West Berlin, West Germany.

Results and Discussion

Characterization of Complexes. Results of elemental analysis and molecular weight determination for

TABLE 1. ANALYTICAL DATA FOR THE NEWLY PREPARED COMPLEXES

Complex		Found (Calcd) C(%)	Found (Calcd) H(%)	Found (Calcd) Mol wt[a)]
[Pt(acac)(acac-C^3)(Et_2S)]	(**1a**)	34.43(34.78)	4.97(5.00)	482(484)
[Pt(tfac)(tfac-C^3)(Et_2S)]	(**1b**)	28.46(28.43)	3.02(3.07)	574(591)
[Pt(hfac)(hfac-C^3)(Et_2S)]	(**1c**)	24.04(24.04)	1.76(1.73)	
[PtCl(acac-C^3)(S-S)]·CH_2Cl_2	(**2**)	25.16(25.52)	4.17(4.10)	532(565)
[$Pt(CO_3)(PEt_3)_2$]	(**3**)	31.89(31.77)	6.21(6.15)	486(491)
[$Pt(PPh_3)_2(H_2O)_2$]$(ClO_4)_2$	(**4**)	45.05(45.30)	3.64(3.59)	
[$Pt(acac)(PPh_3)_2$]ClO_4	(**5a**)	54.36(54.05)	4.15(4.09)	830(911)
[$Pt(tfac)(PPh_3)_2$]ClO_4	(**5b**)	50.03(50.65)	3.50(3.53)	929(972)
[$Pt(acac)(PEt_3)_2$]PF_6	(**6**)	30.03(30.23)	5.37(5.52)	604(676)
[Pt(tfac(2−)-*C*,*O*)$(PPh_3)_2$]	(**7**)	55.64(56.49)	3.93(3.82)	

a) Determined in dichloromethane (0.01—0.03 mol dm^{-3}) at 27 °C.

TABLE 2. CHARACTERISTIC IR BANDS (cm^{-1})[a)]

Complex	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})+\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{C})$ of chelated β-dik	ν(C=O) of C^3-bonded β-dik	Others
1a	1560 vs, 1525 vs	1690 vs	
1b	1660 s, 1590 vs	1720 vs	
1c	1608 vs	1750 vs	
2		1650 vs	ν(Pt–Cl) 310 m
3			ν(C=O) 1660 vs, 1630 s, 1610 s ν(C–O) 1195 vs, 990 s
5a	1560 vs, 1530 vs		$\nu(ClO_4)$ 1100 vs
5b	1600 vs, 1530 m		$\nu(ClO_4)$ 1100 vs
6	1570 vs, 1535 vs		$\nu(PF_6)$ 840 vs
7	1620 vs, 1597 s		
8[b)]	1560 vs, 1540 s		ν(Pt–Cl) 305 m

a) vs=very strong, s=strong, m=medium. b) [$PtCl(acac)(PEt_3)$].

TABLE 3. ^1H NMR SIGNALS IN $CDCl_3$[a)]

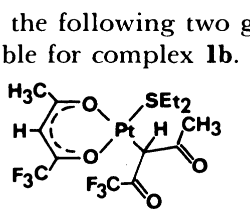
Complex	Chelated β-dik		*C*-Bonded β-dik		Neutral ligand		
	CH_3	CH	CH_3	CH	CH_3	CH_2	Ph
1a	1.85 1.92	5.35(4)	2.18	4.78(128)	1.32	2.57	
1b	2.08 2.10	6.00(6)	2.32 2.36	5.30(124)	1.35 1.28	2.63	
1c		6.38(4)		5.80(b)	1.30	2.60	
2			2.11	4.98(112)	1.42	2.78, 3.02	
3					1.20	1.89	
5a	1.50	5.58(4)					7.32
5b	1.66	5.97(5)					7.29
6	1.87	5.19(4)			1.07	1.71	
7	2.80[c)] (58)	5.10					7.29
8	2.00	5.58(5)			1.20	2.00	

a) Chemical shifts in ppm from internal Me_4Si. Figures in parentheses give the *J*(Pt–H) values. b) Indiscernible. c) CH_2 bound to platinum in the tfac(2−)-*C*,*O* ligand, appearing as a doublet of doublets with ^3J(*cis*-P-H)=6.0 Hz and ^3J(*trans*-P-H)=12 Hz flanked by the ^{195}Pt satellites.

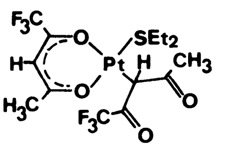
the newly prepared complexes are collected in Table 1, and their characteristic IR bands are shown in Table 2. These data are consistent with the proposed structures of these complexes, the IR data for complexes **1a**, **1b**, and **1c** supporting coexistence of chelated and central-carbon-bonded β-diketonate ligands.

The ^1H NMR signals listed in Table 3 are readily assigned based on the proposed structures. For example, complex **1a** exhibits four methyl signals at 1.32, 1.85, 1.92, and 2.18 ppm. The triplet signal at 1.32 ppm is assigned to the methyl protons of diethyl sulfide. The relative intensity of the δ 2.18 signal corresponds to six protons and it is ascribed to methyl protons of the carbon-bonded acac ligand. The remaining two signals of equal intensity come from two methyl groups of the chelated acac anion. By reference to the case of [Pd(acac)(acac-C^3)L] (L=PPh_3, py, and Et_2NH),[5)] the higher-field signal (δ 1.85) is assigined to the methyl group positioned trans to the carbon-bonded acac ligand and the δ 1.92 signal to that cis to the acac-C^3 ligand. Both of two methine signals are flanked by ^{195}Pt satellites and the δ 4.78 signal showing a very strong coupling to Pt is unequivocally assigned to the methine group bound to the metal.

Since the tfac anion forms an unsymmetric chelate ring, the following two geometrical isomers are conceivable for complex **1b**. Three signals at 1.35, 2.08, and 2.32 ppm are assigned similarly to the case of **1a** to methyl protons of Et_2S, chelated tfac, and carbon-bonded tfac, respectively. Each of these signals is accompanied by a minor signal at 1.28, 2.10 or 2.36 ppm indicating contamination with a geometrical isomer as expected. Unfortunately, the corresponding pair of signals are so close to each other as to preclude measurement of the area ratio. Unequivocal assignment of the two sets of signals to these isomers is difficult, but minor signals are tentatively assigned to the *trans*-(Me, L) isomer, since of the two methyl signals at 2.08 and 2.10 ppm from the chelated tfac anion, the minor lower-field one is assigned to the methyl protons positioned cis to the carbon-bonded tfac ligand by reference to the case of **1a**.



cis-(Me, L)-1b



trans-(Me, L)-1b

It is worth noting that the product from the reaction between *trans*-$[PtCl_2(Et_2S)_2]$ and Tl(tfac) gives the same ^1H NMR spectrum as above. During the preparative reactions the platinum(II) complexes seem to undergo geometrical isomerization to yield a thermodynamically favored mixture of isomers. Recently Cattalini and his collaborators studied kinetically the reactions of *cis*- and *trans*-$[PtCl_2(Me_2S)_2]$ with pyridine and other nitrogen bases (L) to afford *cis*- and *trans*-$[PtCl_2(Me_2S)L]$ and found that the reactions of the cis complex were complicated by its tendency to isomerize to the more stable trans isomer.[19)]

Complex **4** was prepared by the reaction of *cis*-$[PtCl_2(PPh_3)_2]$ with silver perchlorate in a mixture of chloroform and methanol at 0 °C. Two molecules of water retained per one platinum atom seem to have come from the organic solvents and be coordinated with the metal, perchlorate anions lying in the outer sphere. Hartley and his coworkers[20)] prepared the $[Pt(PPh_3)_2L_2](ClO_4)_2$-type complexes containing various solvent molecule as L and found that anhydrous perchlorate complexes are explosive (**Caution!**). Fortunately complexes **4**, **5a**, and **5b** containing perchlorate in the outer sphere could be handled safely.

The ^1H NMR spectra of complexes **5a**, **5b**, and **6** are simple. Methyl protons of the acac and tfac ligands in **5a** and **5b**, respectively, resonate at much higher field than those in **1a** and **1b** owing to the anisotropic shielding effect of the phenyl rings in the ancillary triphenylphosphine ligands.[5)] Thus the chemical shift of methyl protons of acac in **6**, which contains PEt_3 in place of PPh_3 in **5a**, coincides with that for **1a**. The PEt_3 ligands in **3** and **6** exhibit the 2:2:3:2:1 quintet signal in the methyl proton region and another symmetric quintet signal of methylene protons in accordance with the cis arrangement.[21)] The IR and ^1H NMR data for complex **7** nearly coincide with those reported by Okeya *et al*,[9b)] certifying that the same tfac (2−)-*C*,*O* chelate was obtained from the present reactions.

Synthetic Reactions. The reactions of *cis*-$[PtCl_2(Et_2S)_2]$ with twice molar amounts of Tl (β-dik) gave $[Pt(\beta\text{-dik})(\beta\text{-dik-}C^3)(Et_2S)]$.

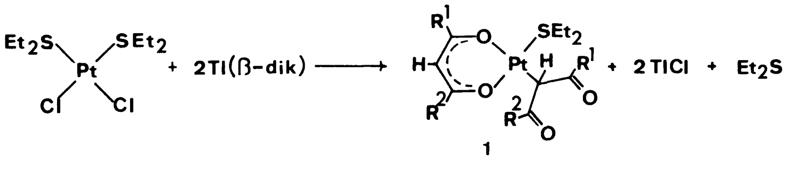
The reaction was almost complete by one hour and a half in either case as evidenced by the quantitative yield of TlCl and absence of the starting complex on the thin layer chromatogram(TLC) of the reaction mixture on silica gel. Although stirring was continued for three hours (Experimental), yields of complexes **1** were not high (30—37%), but products other than **1** could not be detected.

The reactions of *trans*-$[PtCl_2(Et_2S)_2]$ with Tl(β-dik) (β-dik=acac, tfac, and hfac) were solwer than those of the cis complex, giving the same products **1a**—**1c**. Thus, the TLC assay showed that the starting complex remained in the reaction mixture even after being stirred for four hours and was exhausted after seven hours. The yield of TlCl also increased slowly with time for several hours.

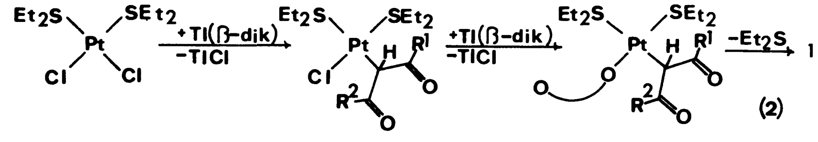
The difference in reactivities of *cis*- and *trans*-$[PtCl_2(Et_2S)_2]$ with Tl(β-dik) to give complexes **1** seems to accord with the stronger trans effect of the sulfide than that of chloride, and to suggest that the rate controlling step is displacement of the chloride ligand. (The above-mentioned substitution of Me_2S in $[PtCl_2(Me_2S)_2]$ with a neutral ligand proceeds more slowly for the cis isomer than for the trans complex due to the stronger trans effect of the sulfide.[18)])

Bis(β-diketonato)platinum(II) complexes react with a number of nitrogen bases[8d)] and tertiary phosphines[9b—d)] to give various types of complexes, but $[Pt(acac)_2]$ does not react with excess Et_2S under various conditions. Converesely the reaction between $[PtCl_2(Et_2S)_2]$ and Tl(acac) did not yield $[Pt(acac)_2]$ beyond **1a**. Even when $[PtCl_2(Et_2S)_2]$ was first treated with silver perchlorate to remove chloride ligands and then forced to react with K(acac), only complex **1a** was produced.

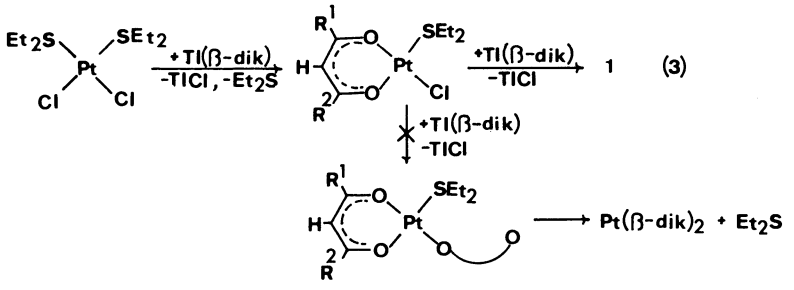
On the other hand, lowering of reaction temperature



(1)



(2)



(3)

or decreasing of the amount of Tl(acac) depressed the rate and yield of **1a** but gave no intermediary product. Thus no clue was obtained to find either of the chelated and carbon-bonded β-diketonate ligands of **1** entered first into the coordination sphere.

In the case of [PtCl$_2$(S–S)], complex **2** was formed exclusively. No other product was obtained even when excess Tl(acac) up to ten times moles was employed. These results indicate that the [PtCl(S–S)]$^+$ moiety prefers the central carbon bonding to the oxygen bonding of acac, and that [PtCl(acac-C^3)(S–S)] (**2**) is thermodynamically more stable than other conceivable complexes such as [Pt(acac)(S–S)]X (X=Cl or acac), [Pt(acac-C^3)$_2$(S–S)], and [Pt(acac-C^3)(acac-O)(S–S)].

Production of **2** might suggest that in reaction 1 the β-diketonate carbanion first substitutes a chloride ligand and the second β-diketonate anion replaces the other chloride anion to form an O-unidentate linkage and then a sulfide ligand is expelled to close the chelate ring (Eq. 2).

Another alternative mechanism also looks reasonable: A β-dik chelate is first formed and the [Pt(β-dik)-(SEt$_2$)]$^+$ moiety favors the carbon bonding of the second β-dik anion over the oxygen bonding which should be stabilized by intramolecular substitution to close the chelate ring (Eq. 3).

It is rather surprizing that complexes **1** and **2** containing a carbon-bonded β-dik ligand were obtained in methanol, since in the following palladium(II) case the carbon bonding of acac is completely disfavored in methanol.⁶⁾

$$[\mathrm{Pd(acac)_2}] + 2\,\mathrm{Et_2NH} \overset{K_1}{\rightleftharpoons} [\mathrm{Pd(acac)(Et_2NH)_2}](\mathrm{acac})$$

$$[\mathrm{Pd(acac)(acac\text{-}C^3)(Et_2NH)}] + \mathrm{Et_2NH} \overset{K_2}{\rightleftharpoons} [\mathrm{Pd(acac)(Et_2NH)_2}](\mathrm{acac})$$

Thus K_1=32.9±1.1 dm^6 mol^{-2} and K_2=0.224±0.007 dm^3 mol^{-1} in dichloromethane at 25 °C, but in methanol at 25 °C K_1=(3.93±0.04)×10^6 dm^6 mol^{-2} and K_2 was immeasurablly large, no trace of the carbon-bonded acac complex being detected in the equilibrium mixture.⁶⁾

If the latter mechanism (Eq. 3) is the case for the present sulfide complex, the tendency of the [Pt(acac)-(Et$_2$S)]$^+$ moiety to favor the carbon bonding of acac may be very much greater than that of [Pd(acac)(Et$_2$NH)]$^+$. At the present stage of investigation, it is difficult to conclude which of the two mechanisms is operative.

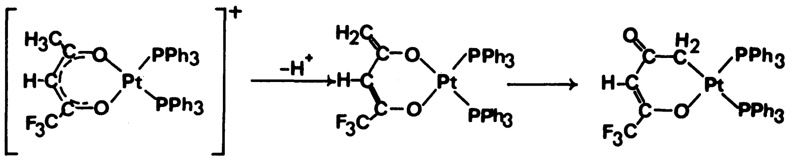
In contrast with the case of *cis*-[PtCl$_2$(Et$_2$S)$_2$] (Eq. 1), the reaction of *cis*-[PtCl$_2$(PEt$_3$)$_2$] with Tl(acac) did not give any acetylacetonato complex, but resulted in [Pt(CO$_3$)(PEt$_3$)$_2$] (**3**). The observed IR bands included in Table 2 accord with the bidentate coordination of the carbonate ion.²²⁾ When the reaction was carried out under the atmospheric condition, the yield of **3** was as low as a few percent. Addition of water and bubbling of carbon dioxide through the methanol solution improved the yield of **3** to 18%. Conversely the same reaction under nitrogen gave no trace of **3**.

In either case the reaction of Tl(acac) with *cis*-[PtCl$_2$-(PEt$_2$)$_2$] to remove the chloride ligands was complete, since the yield of TlCl was almost quantitative and the UV spectrophotometric assay of the filtrate confirmed acetylacetone molecules in a satisfactory yield. Concentration of the solution by evaporation under reduced pressure resulted in a viscous substance, which showed broad IR bands in the 3600—3200 cm^{-1} region and at 1600 cm^{-1} indicative of the aqua or hydroxo ligand.

Thus the reaction sequence to form **3** might be shown by Eq. 4, although the aqua and hydroxo complexes presumed as intermediates have not been isolated.

$$\begin{gathered} cis\text{-}[\mathrm{PtCl_2(PEt_3)_2}] \xrightarrow[-2\mathrm{TlCl}]{+2\mathrm{Tl(acac)}+2\mathrm{H_2O}} \\ cis\text{-}[\mathrm{Pt(H_2O)_2(PEt_3)_2}](\mathrm{acac})_2 \xrightarrow[-2\mathrm{acacH}]{} \\ cis\text{-}[\mathrm{Pt(OH)_2(PEt_3)_2}] \xrightarrow[-\mathrm{H_2O}]{+\mathrm{CO_2}} \underset{\mathbf{3}}{[\mathrm{Pt(CO_3)(PEt_3)_2}]} \end{gathered} \tag{4}$$

On the other hand, the reaction of *trans*-[PtCl$_2$-(PEt$_3$)$_2$] with Tl(acac) was much slower than that of the cis isomer and gave [PtCl(acac)(PEt$_3$)] instead of the carbonato complex **3**. Such a difference between the two isomers in reactivities and products may be



rationalized based on the strong trans effect of triethylphosphine.

The chloride ligand in *cis*-$[PtCl_2(PEt_3)_2]$ is readily substituted by a carbonyl end of acac anion, which may fail in displacing a PEt_3 ligand to close the chelate ring and be in turn replaced by a water molecule. On the contrary, the chloride ligand in *trans*-$[PtCl_2(PEt_3)_2]$ is less readily substituted by an acac anion, but the dangling carbonyl group of the *O*-unidentate acac ligand may release more easily a PEt_3 ligand which is labilized by the other PEt_3 molecule positioned trans to each other. The bond between the metal and the remaining chloride is strengthened in $[PtCl(acac)(PEt_3)]$ and is not readily cleaved by attack of another acac anion.

When the chloride ligand in *trans*-$[PtHCl(PEt_3)_2]$ was removed by silver hexafluorophosphate in methanol containing acetylacetone, $[Pt(acac)(PEt_3)_2]PF_6$ (**6**) was resulted. Geometrical isomerization probably followed by dihydrogen evolution rather than displacement of a PEt_3 ligand seems to have been induced by acetylacetone.

cis-Dichlorobis(triphenylphosphine)platinum(II) is less reactive than the corresponding triethylphosphine complex and hardly reacts with Tl(β-dik). When the chloride ligands were removed by silver perchlorate, $[Pt(PPh_3)_2(H_2O)_2](ClO_4)_2$ (**4**) was obtained, which is slightly soluble only in haloalkanes such as chloroform and dichloromethane and was characterized by elemental analysis and IR spectra. A very broad and strong band at $1100\,cm^{-1}$ and a band of medium intensity at $625\,cm^{-1}$ suggest that the perchlorate ions lie in the outer sphere.[23] The aqua ligands in **4** can be readily substituted by other ligands. Thus **4** reacted with K(acac) in methanol at room temperature to give $[Pt(acac)(PPh_3)_2]ClO_4$ (**5a**). Similarly the reaction of **4** with an equimolar amount of K(tfac) in a mixture (1:6 by volume) of methanol and dichloromethane gave $[Pt(tfac)(PPh_3)_2]ClO_4$ (**5b**). On the other hand, the reaction of **4** with a twice molar amount of K(tfac) in methanol gave rise to $[Pt(tfac(2-)\text{-}C,O)(PPh_3)_2]$ (**7**).

Complex **7** was previously obtained by Okeya *et al* by the reaction of $[Pt(tfac)_2]$ with PPh_3 and shown to contain a *C,O*-chelated trifluoroacetylacetonate dianion.[9b] More recently similar palladium(II) complexes $[Pd(tfac(2-)\text{-}C,O)LL']$ containing triphenylphospine, pyridine and their derivatives as L and L′ were prepared, and the molecular structure of the complex containing triphenylphosphine and 2,6-dimethylpyridine as neutral ligands was confirmed by X-ray analysis.[9e] Complex **7** was inferred to be produced through deprotonation of the chelated tfac ligand by the outer-sphere tfac anion in the presumed intermediate $[Pt(tfac)(PPh_3)_2](tfac)$.[9c] Now the cationic complex was isolated as **5b**, of which reactions with various bases were examined.

Potassium acetylacetonate and trifluoroacetylacetonate as well as triethylamine were successful in abstracting a proton from **5b** to give **7**. On the other hand, pyridine derivatives such as 4-amino-, 4-dimethylamino- and 2,6-dimethylpyridines were proved to be unsuccessful in giving **7**, although they were effective in deprotonating $[Pd(tfac)(PPh_3)_2]^+$ to afford $[Pd(tfac(2-)\text{-}C,O)(PPh_3)L]$.[9e] The tfac ligand in **5b** was displaced by pyridines and complexes $[Pt(PPh_3)_2L_2](ClO_4)_2$ containig 4-amino- and 4-dimethylaminopyridines as L were isolated and characterized, the yields being 10 and 29%, respectively. These results suggest that the Pt(II) tfac chelate is more labile than the corresponding Pd(II) chelate against the nucleophilic attack of nitrogen bases. Deprotonation of the chelating tfac monoanion by a base may produce a dienediolate intermediate as was postulated in the case of the Pd(II) complexes.[9e]

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References

1) A. Werner, *Chem. Ber.*, **34**, 2584 (1901).

2) A. A. Grinberg and I. N. Chapurskii, Russ. *J. Inorg. Chem.*, **4**, 137 (1959).

3) Recently a revised procedure of preparation was proposed to attain a higher yield (75%). S. Okeya and S. Kawaguchi, *Inorg. Synth.*, **20**, 65 (1980).

4) X-Ray molecular structure: R. Mason, G. B. Robertson, and P. J. Pauling, *J. Chem. Soc. (A)*, **1969**, 485.

5) S. Baba, T. Ogura, and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **47**, 665 (1974).

6) S. Matsumoto and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **53**, 1577 (1980).

7) H. Tanaka, K. Isobe, S. Kawaguchi, and S. Okeya, *Bull. Chem. Soc. Jpn.*, **57**, 1850 (1984).

8) a) S. Okeya and S. Kawaguchi, *Inorg. Chem.*, **16**, 1730 (1977); b) S. Okeya, H. Sazaki, M. Ogita, T. Takemoto, Y. Onuki, Y. Nakamura, B. K. Mohapatra, and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **54**, 1978 (1981); c) S. Okeya, H. Yoshimatsu, Y. Nakamura, and S. Kawaguchi, *ibid.*, **55**, 483 (1982); d) S. Okeya, Y. Nakamura, and S. Kawaguchi, *ibid.*, **55**, 1460 (1982).

9) a) S. Okeya, T. Miyamoto, S. Ooi, Y. Nakamura, and S. Kawaguchi, *Inorg. Chim. Acta*, **45**, L135 (1980); b) S. Okeya, Y. Nakamura, S. Kawaguchi, and T. Hinomoto, *Inorg. Chem.*, **20**, 1576 (1981); c) S. Okeya, Y. Nakamura, and S. Kawaguchi, *Bull. Chem. Soc. Jpn*,. **54**, 3396 (1981); d) S. Okeya, Y. Nakamura, S. Kawaguchi, and T. Hinomoto, *ibid.*,

55, 477 (1982); e) S. Okeya, Y. Kawakita, S. Matsumoto, Y. Nakamura, S. Kawaguchi, N. Kanehisa, K. Miki, and N. Kasai, *ibid.*, **55**, 2134 (1982); f) S. Ooi, T. Matsushita, K. Nishimoto, Y. Nakamura, S. Kawaguchi, and S. Okeya, *Inorg. Chim. Acta*, **76**, L55 (1983).

10) In this paper the *O,O′*-chelated monoanions of β-diketones such as acetylacetone, trifluoroacetylacetone, and hexafluoroacetylacetone are abbreviated by β-dik, acac, tfac, and hfac, respectively, and β-dik-C^3 and β-dik-*O* represent the central-carbon-bonded and *O*-unidentate β-diketonate monoanions, respectively. The *C,O*-chelated dianion of trifluoroacetylacetone is shown by tfac(2−)-*C,O*.

11) W. H. Nelson, W. J. Randall, and D. F. Martin, *Inorg. Synth.*, **9**, 52 (1967).

12) G. B. Kauffman and D. O. Cowan, *Inorg. Synth.*, **6**, 211 (1953).

13) J. Chatt and R. G. wilkins, *J. Chem. Soc.*, **1952**, 273.

14) R. D. Gillard and M. F. Pilbrow, *J. Chem. Soc., Dalton Trans.*, **1974**, 2320.

15) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, **1962**, 5075.

16) G. T. Morgan and W. Ledburg, *J. Chem. Soc.*, **1922**, 2882.

17) R. J. Cross, I. G. Dalgleish, G. J. Smith, and R. Wardle, *J. Chem. Soc., Dalton Trans.*, **1972**, 992.

18) J. M. Jenkins and B. L. Shaw, *J. Chem. Soc. (A)*, **1966**, 770.

19) L. Canovese, L. Cattalini, G. Marangoni, G. Michelon, and M. L. Tobe, *Inorg. Chem.*, **20**, 4166 (1981).

20) J. A. Davies, F. R. Hartley, and S. G. Murray, *J. Chem. Soc., Dalton Trans.*, **1980**, 2246.

21) W. J. Louw, *Inorg. Chem.*, **16**, 2147 (1977).

22) K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," 3rd ed., Wiley-Interscience, New York (1978), p. 243.

23) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, **1961**, 3091.