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Reactions of *trans*- and *cis*-Dichlorobis(benzonitrile)platinum(II) with Acetylacetonate and Benzoylacetonate Carbanions. Formation of *N*-Acetyl β-Ketoamine Complexes by the Acetyl Group Migration†

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trans-Dichlorobis(benzonitrile)platinum(II) reacted with twice the molar amount of thallium(I) acetylacetonate and benzoylacetonate in dichloromethane at room temperature to afford mainly *N*-acetyl β-ketoamine chelates, *trans*-[Pt{N(COMe)=C(Ph)CH=COMe(and Ph)}$_2$] (**1a** and **3a**). This *N,O*-chelate structure of **1a** was determined by X-ray analysis. Reactions of *cis*-[PtCl$_2$(PhCN)$_2$] gave *C*-acetyl and *C*-benzoyl β-ketoamine chelates, *cis*-[Pt{NH=C(Ph)C(COMe(and Ph))=COMe}$_2$], together with other minor products. Formation of these β-ketoamine chelates is explained by the nucleophilic reactions of the β-diketonate carbanions at the coordinated cyanide carbon atom, followed by migration of the acetyl group or the methine proton of the nucleophiles onto the imino nitrogen atom formed during these reactions. In the presence of free β-diketones, migration of the acyl group was generally suppressed; this led to high yields of *C*-acyl complexes especially in reactions of *cis*-[PtCl$_2$(PhCN)$_2$]. In each case, the reaction proceeded with retention of the geometrical configuration around the central metal atom. The structures of other products, including a compound obtained by acid hydrolysis of **1a**, were explored and discussed, based on IR and ^{1}H NMR data.

It is well known that nitriles in the coordination sphere of metal ions are very susceptible to nucleophilic attack and readily react with water, alcohols, and amines to yield the corresponding amides, imidic esters, and amidines, respectively.[1] Stephenson[2] examined the X-ray structure of the reaction product between [PtCl$_2$(MeCN)$_2$] and aqueous ammonia. The product originally formulated as [Pt(NH$_3$)$_4$(MeCN)$_2$]Cl$_2$·H$_2$O was shown to be an amidine complex of the stoichiometry [Pt(NH$_3$)$_2${NHC(NH$_2$)Me}$_2$]$^{2+}$ in which the imine nitrogens are bound to the platinum. Recently, Braunstein *et al.*[3] demonstrated that cyanide carbons in the benzonitrile analogue [PtCl$_2$(PhCN)$_2$] undergo the nucleophilic attack of carbanions Ph$_2$P$\bar{C}$HY (Y= CO$_2$Et and CN) in tetrahydrofuran at 0 °C to afford *trans*-[Pt{P(Ph)$_2$C(Y)=C(Ph)NH}$_2$]. Similar reactions of metal complexes with β-diketonate ions have not been examined, although the nucleophiles are known to add to the coordinated unsaturated hydrocarbon[4–6] and imine[7] ligands. We have briefly reported[8] the reaction of [PtCl$_2$(PhCN)$_2$] with an acetylacetonate ion in dichloromethane at room temperature to give an *N*-acetyl β-ketoamine chelate, *trans*-[Pt{N(COMe)=C(Ph)CH=COMe}$_2$] (**1a**). It is noteworthy that the nucleophilic reaction occurred for [PtCl$_2$(PhCN)$_2$], which has been widely used as a starting material for the preparation of organoplatinum(II) complexes.[9] In our previous study,[10] the complex [PtCl$_2$(PhCN)$_2$] prepared by Kharasch's procedure[11] was found to exist as a mixture of *cis* and *trans* isomers, and both isomers were successfully isolated by column chromatography on silica gel. Details of reactions of *trans*- and *cis*-[PtCl$_2$(PhCN)$_2$] with thallium(I) acetylacetonate, Tl(acac), and benzoylacetonate, Tl(bzac), in dichloromethane at room temperature are presented here, together with the full account of the X-ray structure of **1a** as an example of products in these reactions.

Experimental

Materials. The *trans*- and *cis*-[PtCl$_2$(PhCN)$_2$] complexes were prepared as described in the previous paper.[10] Thallium (I) salts of acetylacetone and benzoylacetone were synthesized according to the literature.[12] Dichloromethane over Molecular Sieve Type 3A was decanted, further dried over calcium hydride, and then distilled. For column chromatographic separation of reaction products, silica gel 60 F$_{254}$ (Merck, 70-230 mesh) or aluminium oxide 60 (Merck, active, basic) was used as a packing. A technique of preparative layer chromatography (PLC) was applied in order to collect samples in the preparative scale, using the chromatoplate of silica gel 60PF$_{254}$ containing CaSO$_4$ (Merck) or aluminium oxide 60PF$_{254}$ (Merck, Type E). For the preparation of a PLC plate, one (25 g) of these adsorbents was suspended in deionized water (60 cm^3) and the mixture was applied on a glass plate (20×20 cm) and activated before use at 130—140 °C for 4 h.

Reaction of trans-*[PtCl$_2$(PhCN)$_2$] with Thallium (I) Acetylacetonate.* When Tl (acac) (376 mg, 1.24 mmol) was added to a yellow solution of *trans*-[PtCl$_2$(PhCN)$_2$] (293 mg, 0.62 mmol) in dichloromethane (20 cm^3) and the mixture was stirred for 1 h at room temperature, a white precipitate of thallium (I) chloride was formed and the solution turned brown-yellow. The mixture was passed through a short column (5×2 cm d) of silica gel, leaving thallium (I) chloride and a brown residue at the top of the column. The yellow eluent was concentrated and put on the PLC plate of silica gel. Development with benzene split the original band into two. The first band component with a large R_f value was extracted with benzene and the solvent was evaporated to dryness, leaving the yellow compound **1a** (26 mg, 7% yield). A dichloromethane-extract of the second band was concentrated and developed, once again, on the PLC plate in diethyl ether, resulting in two bands. Yellow compound **1b** (16 mg, 5% yield based on the platinum atom used) precipitated on addition of hexane to a diethyl ether-extract of the smaller R_f component. A trace amount of substance was obtained from

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† In this paper, the term "β-ketoamine" means an α,β-unsaturated β-amino ketone.

the larger R_f component; this was not characterized.

Reaction of cis-*[PtCl$_2$(PhCN)$_2$] with Thallium (I) Acetylacetonate.* Tl (acac) (413 mg, 1.36 mmol) was suspended in a dichloromethane solution (20 cm^3) of *cis*-[PtCl$_2$(PhCN)$_2$] (320 mg, 0.68 mmol), and the mixture was stirred for 5 h at room temperature. After the volume of the solution was reduced by vacuum evaporation, the concentrate was mounted on the PLC plate of aluminium oxide without removal of thallium (I) chloride. Two bands appeared upon development with a benzene–acetone (20 : 1 by volume) mixture. The components with small and large R_f values were extracted separately with dichloromethane and the extracts were concentrated to obtain a yellow powder of **2a** (72 mg, 18% yield) and red crystals of **2b** (34 mg, 8% yield) on addition of diethyl ether, respectively. Reprecipitation of **2a** from acetone by adding diethyl ether gave yellow needles.

Reaction of trans-*[PtCl$_2$(PhCN)$_2$] with Thallium (I) Benzoylacetonate.* A mixture of *trans*-[PtCl$_2$(PhCN)$_2$](297 mg, 0.63 mmol) and Tl(bzac) (461 mg, 1.26 mmol) in dichloromethane (25 cm^3) was stirred for 5 h at room temperature. After filtration of the precipitated thallium (I) chloride, the filtrate was concentrated to a small volume and placed on a PLC plate of silica gel. Development with benzene–hexane (3 : 2 by volume) resulted in three bands; each component was extracted with dichloromethane and isolated on addition of diethyl ether to the concentrated extract. Orange (**3a**) and yellow (**3a′**) powders were isolated from bands with middle and small R_f values, respectively, and another orange powder (**3b**) from that with a large R_f. The yields of **3a**, **3a′**, and **3b** were 48 mg (11%), 28 mg (6%), and 27 mg (6%), respectively.

Reaction of cis-*[PtCl$_2$(PhCN)$_2$] with Thallium (I) Benzoylacetonate.* *cis*-[PtCl$_2$(PhCN)$_2$] (282 mg, 0.60 mmol) was allowed to react with Tl(bzac) (439 mg, 1.20 mmol) in the same way as described above. After filtration of thallium (I) chloride, the concentrated orange-yellow solution was placed on the top of the column (40×2 cm d) of silica gel and developed with dichloromethane. The first fraction contained benzoylacetone (5 mg, 3% yield based on the Tl(I) salt used). After evaporation of the last and middle fractions to dryness, the resulting powders were recrystallized from acetone–petroleum ether and diethyl ether to give yellow needles of **4a** (19 mg, 4% yield) and red crystals of **4b** (14 mg, 3% yield), respectively.

Reactions of trans- *and* cis-*[PtCl$_2$(PhCN)$_2$] with Thallium (I) Acetylacetonate and Benzoylacetonate in the Presence of the Corresponding Free β-Diketones in Large Excess.* For example, in the case of reactions with Tl(acac), a mixed solvent of dichloromethane–acetylacetone (1 : 1 by volume) was used. Molar ratios of Tl(acac) and free acetylacetone to [PtCl$_2$(PhCN)$_2$] were 2 : 1 and *ca.* 350 : 1, respectively. After reactions for 5 h, adequate treatments were performed to isolate products. In the case of reaction with *trans*-[PtCl$_2$(PhCN)$_2$], yellow powders of **5a** and **5b** were obtained in 3 and 8% yields, respectively, while in the case of *cis*-[PtCl$_2$(PhCN)$_2$], compound **2a** was isolated in a 75% yield.

In the reactions with Tl(bzac), 2.5 g (*ca.* 15 mmol) of solid benzoylacetone was added to [PtCl$_2$(PhCN)$_2$] in dichloromethane prior to the reaction. Molar ratios of Tl(bzac) and free benzoylacetone to [PtCl$_2$(PhCN)$_2$] were 2 : 1 and *ca.* 24 : 1, respectively. Isolation of the reaction products without any contamination with benzoylacetone was somewhat difficult. After reactions for 7 h, compounds **3a** and **3a′** and yellow powder **6** were isolated from the reaction mixture with *trans*-[PtCl$_2$(PhCN)$_2$] in 15, 4, and 5% yields, respectively, while compound **4a** was obtained from the reaction mixture with *cis*-[PtCl$_2$(PhCN)$_2$] in a 57% yield.

Reaction of cis-*[PtCl$_2$(PhCN)$_2$] with Thallium (I) Acetylacetonate in the Presence of Excess* o-*Nitrophenol.* To examine the effect of protonic acids on the yield of **2a**, *o*-nitrophenol was used as a proton donor instead of acetylacetone. Ten times the molar amount of *o*-nitrophenol was added to *cis*-[PtCl$_2$(PhCN)$_2$] in dichloromethane and the mixture was allowed to react with twice the molar amount of Tl(acac) for 4 d, giving **2a** only in a 14% yield.

*Acid Hydrolysis of **1a** with Perchloric Acid.* Compound **1a** (88 mg, 0.15 mmol) was dissolved in a dichloromethane–acetone (1 : 1 by volume) mixture (160 cm^3) and 60% HClO$_4$ (6 cm^3) was added to the solution. After being stirred for 2.5 h, the solution was concentrated to 30 cm^3 at room temperature under reduced pressure and allowed to stand overnight to deposit **7**. After addition of methanol to the mother liquor, the mixture was concentrated to a small volume and allowed to stand overnight again, depositing another crop of **7**. The total yield of golden crystals **7** was 58 mg, 76%. Attempts to detect acetic acid, which was thought to be produced in this reaction, were unsuccessful.

*An Attempt to Synthesize Complex **1a** by the Reaction of Bis(acetylacetonato)platinum(II) with Benzonitrile.* Although a mixture of bis(acetylacetonato)platinum (II) (92 mg, 0.23 mmol) and benzonitrile (2 cm^3) in dichloromethane (7 cm^3) was stirred at room temperature for **3d**, no reaction occurred and 40% of the starting platinum (II) complex was recovered. Even in benzonitrile at 100 °C for 5 h, 26% of the starting material was recovered with some decomposed black residue.

*An Attempt to Synthesize 4-Acetylamino-4-phenyl-3-buten-2-one (the Ligand in **1a**) by a Schiff Base Condensation.* Benzoylacetone (3.55 g, 22.0 mmol) was allowed to react with acetamide (1.30 g, 22.0 mmol) in refluxing ethanol (2.5 cm^3) for 5 h, but no condensation occurred. Seventy-six per cent of the benzoylacetone used was recovered.

*Crystal Data for **1a**.* Crystals of **1a** suitable for X-ray crystallography were obtained by slow evaporation of a dichloromethane solution. They are monoclinic with $a=8.426(2)$, $b=9.347(3)$, $c=15.293(9)$ Å, $\beta=111.62(4)°$, $U=1119.8(9)$ Å^3, $Z=2$, $D_c=1.77$, $D_m=1.76\ \mathrm{g\cdot cm^{-3}}$, $\mu(\mathrm{Mo}\ K\alpha)=66.2\ \mathrm{cm^{-1}}$, and space group $P2_1/c$. The Laue symmetries, space group, and approximate unit-cell dimensions were determined from oscillation and Weissenberg photographs taken with Cu $K\alpha$ radiation. The unit-cell dimensions were refined by the least-squares analysis of 30θ values measured on a Philips PW 1100 four circle diffractometer with Mo $K\alpha$ radiation.

X-Ray Data Collection. The intensity data with $2\theta \leq 55°$ were collected by the ω-scan mode with graphite-monochromated Mo $K\alpha$ radiation. The specimen size was 0.23× on a Philips PW 1100 four circle diffractometer with Mo $K\alpha$ 0.13×0.11 mm. A scan speed of 1°/min and a scan range of $(1.3+0.2\tan\theta)°$ were chosen. The background was counted for 20 s on each side of the scan range. Three standard reflections ($\bar{3}02$, 060, 002), measured every 4 h, showed no appreciable decay throughout the data collection. A total of 1433 independent reflections with $I>3\sigma(I)$ were classified as observed. The Lorenz-polarization corrections were applied and relative structure factors were derived.[13]

Structure Determination and Refinement. The structure of **1a** was solved by the heavy-atom technique. The positional and thermal parameters were initially refined isotropically by the block-diagonal least-squares method. Further refinement with an anisotropic temperature factor for the Pt atom gave an R value of 5.1%. At this stage, the absorption correction was applied.[14] The maximum and minimum transmission coefficients were 2.48 and 1.82, respectively. The convergence was attained with $R=3.9\%$. The function

Table 1. Positional and thermal parameters ($\times 10^4$)

Atom	*x*	*y*	*z*	U/Å^2
Pt	0	0	0	276(3)[a]
O(1)	757(10)	1746(8)	−470(5)	415(16)
O(2)	−112(11)	−3528(10)	−959(6)	532(20)
N	1171(11)	−1308(10)	−612(6)	376(18)
C(1)	2061(17)	3238(16)	−1244(9)	565(31)
C(2)	1674(13)	1746(12)	−986(7)	593(22)
C(3)	2302(15)	564(13)	−1284(8)	435(24)
C(4)	2114(13)	−903(11)	−1072(7)	341(20)
C(5)	1040(14)	−2872(12)	−442(7)	399(22)
C(6)	2400(17)	−3436(15)	427(9)	555(30)
C(7)	3045(14)	−1947(12)	−1457(7)	383(21)
C(8)	2170(15)	−3018(13)	−2093(8)	456(25)
C(9)	3113(17)	−3973(15)	−2433(9)	509(27)
C(10)	4864(17)	−3843(15)	−2119(9)	524(28)
C(11)	5713(19)	−2783(16)	−1516(10)	590(32)
C(12)	4810(16)	−1777(14)	−1164(8)	474(26)

a) Equivalent isotropic thermal parameter.

minimized was $\sum w(F_o-|F_c|)^2$, with $w=(54.0/F_o)^2$ for $F_o>54.0$, $w=1.0$ for $54.0\geq F_o\geq 17.3$, $w=0.6$ for $F_o>17.3$. The scattering factors for the neutral Pt, O, N, and C atoms were taken from Ref. 15. No attempt was made to locate hydrogen atoms. In the final cycle of the refinement all parameter shifts were less than 0.2σ. A final difference map showed no significant features. The atomic coordinates are presented in Table 1, along with their temperature factors. The observed and calculated structure factors are preserved by the Chemical Society of Japan (Document No. 8118). All the calculations were performed on a FACOM 230-60 computer at Osaka City University by the use of a local version of the UNICS.[16)]

Measurements. IR spectra (4000—200 cm^{-1}) were measured in Nujol mull with a JASCO DS 701G spectrophotometer. ^{1}H NMR spectra were recorded at 100 M Hz on a JEOL JNM-MH 100 spectrometer. Molecular weights were determined with a vapor pressure osmometer manufactured by Knauer, West Berlin, West Germany.

Results and Discussion

In recent studies, we have found that $[PdCl_2(PhCN)_2]$ reacts with acetylacetone in acetone at room temperature to produce di-μ-chloro-bis(η^3-1-acetyl-2-hydroxyallyl)dipalladium(II), liberating benzonitrile molecules.[17)] On the contrary, no reaction occurred between $[PtCl_2(PhCN)_2]$ and acetylacetone even in refluxing acetone, but the complex reacted with the acetylacetonate anion in dichloromethane at room temperature, giving rise to a nucleophilic attack on the cyanide carbons. A similar reaction occurred with the benzoylacetonate anion. Analytical data for all products isolated in this study are listed in Table 2, where compounds **1** and **2** represent products obtained by reactions of Tl(acac) with *trans*- and *cis*-$[PtCl_2(PhCN)_2]$, respectively, and **3** and **4** represent the corresponding reaction products of Tl(bzac). In each of these reactions, two or three compounds were isolated by PLC. Figure 1 depicts the structures proposed on the basis of spectroscopic data. Although compounds **3b** and **4b** were not obtained in amounts sufficient for measurements, the molecular weight data of all other compounds indicate that these are mononuclear in each solvent used.

Table 2. Analytical data for products of nucleophilic attack of β-diketonate carbanions on benzonitrile–Pt (II) complexes

No.	Appearance	Yield %	Found (Calcd) C%	H%	N%	Mol wt[a)]
1a	Yellow powder	7	48.8 (48.1)	4.04 (4.04)	4.65 (4.67)	580[b)] (600)
1b	Yellow powder	5	41.8 (42.6)	3.21 (3.21)	5.10 (5.23)	508 (536)
2a	Yellow needles	18	48.0 (48.1)	4.04 (4.04)	4.67 (4.67)	619[c)] (600)
2b	Red crystals	8	48.1 (48.1)	4.06 (4.04)	4.62 (4.67)	614 (600)
3a	Orange powder	11	56.0 (56.4)	4.02 (3.91)	3.73 (3.87)	757 (724)
3a′	Yellow powder	6	55.4 (56.4)	3.98 (3.91)	3.72 (3.87)	783 (724)
3b	Orange powder	6	56.4 (56.4)	3.90 (3.85)	4.07 (4.11)	
4a	Yellow needles	4	55.4 (56.4)	3.92 (3.91)	3.88 (3.87)	722[c)] (724)
4b	Red crystals	3	55.5 (56.4)	3.90 (3.91)	3.60 (3.87)	
5a	Yellow powder	3	48.3 (48.1)	4.16 (4.04)	4.60 (4.67)	593 (600)
5b	Yellow powder	8	43.0 (42.6)	3.31 (3.21)	5.13 (5.23)	
6	Yellow powder	5	55.9 (56.4)	3.94 (3.91)	3.80 (3.87)	
7[d)]	Golden crystals	76	46.7 (46.6)	3.89 (3.92)	5.43 (5.44)	488 (516)

a) In CH_2Cl_2 at 28 °C. b) At 37 °C. c) In $(CH_3)_2CO$ at 41 °C. d) Acid hydrolysis product of **1a**.

X-Ray Structure of Compound **1a**. Two yellow compounds, **1a** and **1b**, were isolated from the reaction mixture of *trans*-$[PtCl_2(PhCN)_2]$ with Tl(acac) in dichloromethane at room temperature. Although compound **1a** was analyzed to have the composition of $Pt(acac)_2(PhCN)_2$, its X-ray structure analysis disclosed that the compound is the bis(N-acetyl β-ketoamine)-chelate of platinum(II), $[\overline{\mathrm{Pt}\{\mathrm{N(COMe)=C(Ph)CH=CO}}\text{-}\mathrm{Me}\}_2]$, as shown in Fig. 2. The Pt atom has a *trans* planar coordination by 2N and 2O atoms. The molecule has a crystallographically imposed center of symmetry. The six-membered chelate ring, phenyl group, and N-acetyl moiety are planar within ±0.03, ±0.01, and ±0.02 Å, respectively. The N-acetyl plane is perpendicular to the chelate ring plane (interplanar angle =89.7°). The C(6) and O(2) are in contact with the O′(1) atom, the C(6)···O′(1) and O(2)···O′(1) distances being 3.12(2) and 2.96(1) Å, respectively. Such a disposition of the acetyl group relative to the chelate ring imposes some restriction on the rotational orientation of the phenyl group about C(4)–C(7) axis: the short contact between the O(2) and the C(8) atoms makes the phenyl ring slant (59.2°) against the chelate ring plane. Much smaller angles (16° and 41°) between the phenyl and chelate rings are found in *cis*-bis(benzoylacetonato)palladium(II),[18)] but in this case the disposition of the phenyl group relative to the chelate ring results from the intermolecular interaction. Bond

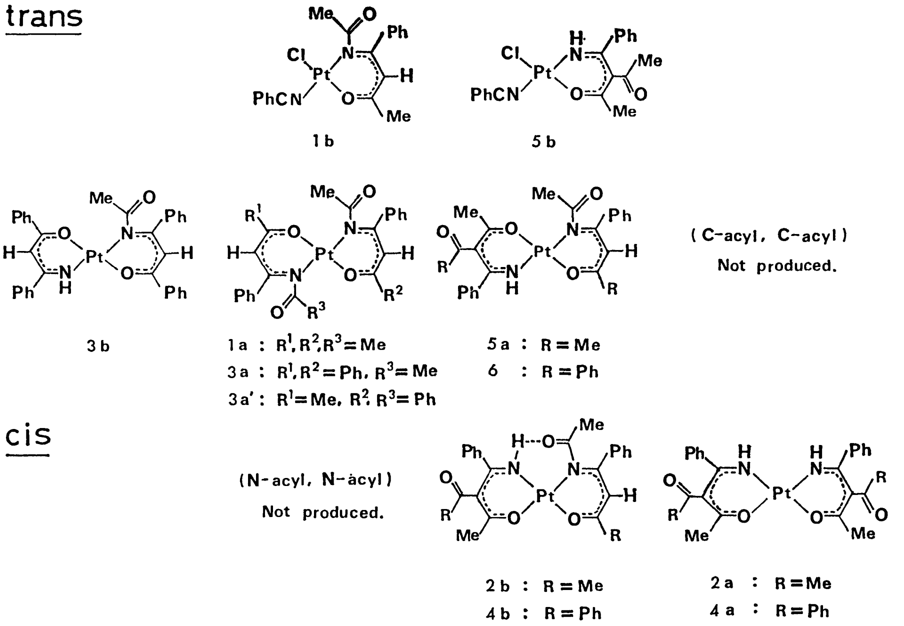


Fig. 1. Schematic drawings of the structure of reaction products between $[PtCl_2(PhCN)_2]$ and Thallium(I) β-diketonates. Numbering indicates products from the following reactions; **1**, *trans*-$[PtCl_2(PhCN)_2]+Tl(acac)$; **2**, *cis*-$[PtCl_2(PhCN)_2]+Tl(acac)$; **3**, *trans*-$[PtCl_2(PhCN)_2]+Tl(bzac)$; **4**, *cis*-$[PtCl_2(PhCN)_2]+Tl(bzac)$. **5** and **6** denote reaction products between *trans*-$[PtCl_2(PhCN)_2]$ and Tl(acac) or Tl(bzac), respectively, in the presence of the corresponding free β-diketones in large excess.

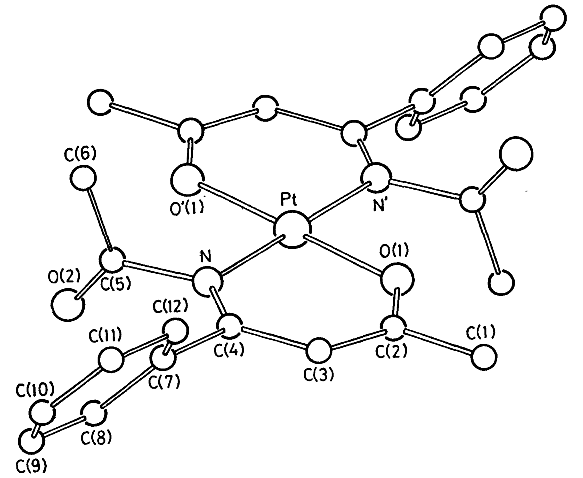


Fig. 2. A perspective view of **1a** with the atom numbering scheme.

distances and angles are summarized in Table 3.

Characterization of the Isolated Compounds by IR and ^1H NMR. Two compounds (**1a** and **1b**) were obtained by the reaction of *trans*-$[PtCl_2(PhCN)_2]$ with Tl(acac); the IR spectrum of **1a** showed no absorption due to the cyano group at around 2200 cm^{-1}, but instead a strong band at 1748 cm^{-1} and three medium to strong bands at 1580—1500 cm^{-1}, as shown in Table 4. Based on the molecular structure of **1a** given in the previous section, we can unequivocally assign the former band to the C=O stretching vibration of the *N*-acetyl group, although the frequency is a little higher than that of the amide I band of gaseous *N*-methylacetamide.[19] On the other hand, the latter three bands may be ascribed to the skeletal vibrations (ν(C=O), ν(C=N), and ν(C=C)) of the β-ketoamine chelate[20] and phenyl rings, but cannot be identified separately.

The ^1H NMR spectrum of **1a** in $CDCl_3$ showed one methine signal at 5.10 ppm and two methyl signals at 2.00 and 1.81 ppm, together with phenyl resonances as shown in Table 5. Of these, the methine signal and one of the methyl signals at 1.81 ppm are accompanied by ^{195}Pt satellites, the coupling constants, $^4J_{Pt-H}$ being 4 and 5 Hz, respectively; these two signals are assigned to the ring-proton and the methyl group attached to the β-ketoamine chelate ring, respectively. Similar couplings of methine and methyl protons to ^{195}Pt are observed to be 11 and 5 Hz, respectively, in the case of bis(acetylacetonato)platinum(II).[21] The other methyl signal at 2.00 ppm, with no coupling to ^{195}Pt was attributed to the *N*-acetyl protons. Compound **1b**, whose composition was $PtCl(acac)(PhCN)_2$, was easily identified to be the 1 : 1 reaction product, since it showed the same IR and ^1H NMR spectral patterns as those for **1a**, except the presence of ν(C≡N) and ν(Pt–Cl) bands in the IR spectrum.

If a similar nucleophilic reaction occurs between *cis*-$[PtCl_2(PhCN)_2]$ and Tl(acac), at least one of the products should show the same spectral patterns in IR and ^1H NMR as those of **1a**. Contrary to our expectation, both of the two products (**2a** and **2b**) isolated exhibited different IR and ^1H NMR patterns. Compound **2a** showed a single ν(C=O) band at 1675 cm^{-1}, much lower than 1748 cm^{-1} for **1a**, with an additional band of ν(NH) at 3270 cm^{-1}, indicating the absence of *N*-acetyl substituents. We can suppose the structure of **2a** to be that shown in Fig. 1 by ascribing

Table 3. Interatomic distances (l) and bond angles (ϕ)

Bond length			
Bond	l/Å	Bond	l/Å
Pt–O(1)	1.98(1)	N–C(5)	1.50(1)
Pt–N	2.01(1)	O(2)–C(5)	1.18(1)
C(2)–O(1)	1.29(2)	C(5)–C(6)	1.50(2)
C(4)–N	1.30(2)	C(7)–C(8)	1.40(2)
C(2)–C(3)	1.37(2)	C(8)–C(9)	1.42(2)
C(3)–C(4)	1.43(2)	C(9)–C(10)	1.38(2)
C(1)–C(2)	1.52(2)	C(10)–C(11)	1.36(2)
C(4)–C(7)	1.50(2)	C(11)–C(12)	1.43(2)
		C(12)–C(7)	1.40(2)
Short contact			
Contact	l/Å	Contact	l/Å
C(6)···O′(1)	3.12(2)	C(2)···C(8)$^{\rm I}$	3.49
C(7)···O(2)	3.37(2)	C(9)···C(1)$^{\rm II}$	3.48
C(8)···O(2)	3.06(2)	O(2)···C(11)$^{\rm III}$	3.37
O(2)···O′(1)	2.95(1)		

Roman numeral superscripts refer to the following equivalent positions: I $-x$, $1/2+y$, $-1/2-z$; II $x, y-1, z$; III $x-1, y, z$

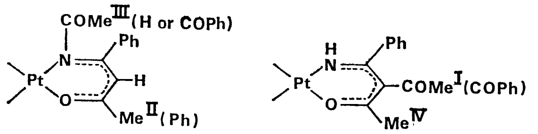
Bond angle			
Angle	ϕ/°	Angle	ϕ/°
N–Pt–O(1)	93.1(4)	C(4)–N–C(5)	119(1)
Pt–O(1)–C(2)	124.5(7)	N–C(5)–O(2)	119(1)
Pt–N–C(4)	125.5(7)	N–C(5)–C(6)	115(1)
O(1)–C(2)–C(3)	126(1)	O(2)–C(5)–C(6)	126(1)
N–C(4)–C(3)	123(1)	C(7)–C(8)–C(9)	119(1)
C(2)–C(3)–C(4)	127(1)	C(8)–C(9)–C(10)	119(1)
O(1)–C(2)–C(1)	113(1)	C(9)–C(10)–C(11)	122(1)
C(1)–C(2)–C(3)	121(1)	C(10)–C(11)–C(12)	121(1)
N–C(4)–C(7)	122(1)	C(11)–C(12)–C(7)	117(1)
C(3)–C(4)–C(7)	115(1)	C(12)–C(7)–C(8)	122(1)
Pt–N–C(5)	116(1)	C(4)–C(7)–C(8)	121(1)
		C(4)–C(7)–C(12)	117(1)

Table 4. Characteristic IR bands a)

No.	ν(N–H)	ν(C≡N)	ν(C=O)				ν(C=O, C=N, C=C)	ν(Pt–Cl)
			N-COMe	*N*-COPh	*C*-COMe	*C*-COPh		
1a			1748s				1578m, 1548s, 1502s	
1b		2285w	1752s				1595w, 1550s, 1503s	346w
2a	3270s				1675s		1581m, 1547s	
2b	3270m		1680sh b)		1667s		1580m, 1540s, 1518s	
3a			1748s				1600w, 1586m, 1550s 1502s	
3a′			1750s	1698s			1600w, 1580m, 1548s 1502s	
3b	3350m		1750s				1600w, 1587m, 1552s 1516s, 1500s	
4a	3310w 3300m 3250m					1655s	1590w, 1580m, 1540sh 1535s	
4b	3290m		1700s b)			1650s	1580m, 1540s, 1520s	
5a	3320w		1743s		1658s		1580m, 1548s, 1503s	
5b	3340m	2280w			1688s		1590w, 1580m, 1553s	350w
6	3260m		1750s			1658s	1598m, 1582m, 1552s 1502s	
7	3360m						1588s, 1567s, 1513s	

a) Wave numbers in cm^{-1}. s: strong, m: medium, w: weak, sh: shoulder. b) Bands due to ν(C=O) of hydrogen-bonded N–C(Me)=O···H–N.

Table 5. ^{1}H NMR data$^{a)}$: Chemical shifts (δ) in ppm from internal TMS and coupling constants (J) in Hz.



No.	CH$_3$$^{b)}$ I	CH$_3$$^{b)}$ II	CH$_3$$^{b)}$ III	CH$_3$$^{b)}$ IV	CH	NH
1a		1.81s	2.00s		5.10s	
		$^4J_{\text{Pt-H}}=5$			$^4J_{\text{Pt-H}}=4$	
1b		1.95s	2.00s		5.16s	
		$^4J_{\text{Pt-H}}=2$			$^4J_{\text{Pt-H}}=2$	
2a	1.60s			2.07s		c)
2b	1.64s	1.71s	2.10s	2.17s	5.42s	8.80br
3a			2.03s		5.84s	
3a′		1.86s	2.04s		5.19, 5.45s	
3b			2.06s		6.05d, 5.74s	c)
					$^4J_{\text{H-H}}=3$	
4a				2.02s		7.89br
5a	1.63s	1.83s	1.92s	1.96s	5.01s	7.76br
5b	1.65s			2.02s		c)
6			1.92s	2.12s	5.88s	c)
7		1.88s			5.34d	7.86br
					$^4J_{\text{H-H}}=4$	

a) In $CDCl_3$, except for **1b**, **3a**, **5b**, and **6**, whose spectra were recorded in CD_2Cl_2. Phenyl resonances are omitted for brevity. b) As shown above, I, II, III, and IV represent the following methyl resonances: I, *C*-acetyl; II, methyl on the *C*-unsubstituted chelate ring; III, *N*-acetyl; IV, methyl on the *C*-acetylated or -benzoylated chelate ring. c) Not detectable or overlapped with phenylsignals.

the band at 1675 cm^{-1} to vibration of the uncoordinated *C*-acetyl carbonyl. The uncoodinated acetyl carbonyls in the central-carbon-bonded acetylacetonate complex, $Na_2[PtCl_2(acac)_2]\cdot 2H_2O$,[22] absorb at 1652 and 1626 cm^{-1}, and those in the cobalt(III) tris-chelate of 3-acetyl-acetylacetone[23] at 1680 cm^{-1}.

In conformity with the proposed structure, no ring-methine signal appeared in the ^{1}H NMR spectrum of **2a**, although no signal assignable to the NH proton was detected, probably due to the H–D exchange with $CDCl_3$ used as the solvent.[24] Difficulty arose in finding any coupling to ^{195}Pt of the methyl signals at 2.07 and 1.66 ppm; this made it impossible to determine which signal is due to the methyl groups on the chelate rings. Collman *et al.*[23] examined ^{1}H NMR spectra of cobalt(III) tris-chelates of acetylacetone and 3-acetyl-acetylacetone in benzene and assigned peaks at 1.90 and 2.02 ppm to their corresponding ring-methyls. Such a downfield shift of the ring-methyl signal on acetylation at the central carbon atom of the chelate rings was also recognized in the case of rhodium(III) acetylacetonate in chloroform, and seems to be reasonable because of the electron-attracting nature of the acetyl substituent. If this relative resonance position of these two signals is valid in the case of the present β-ketoamine chelates, the methyl signal at 2.07 ppm, lower than 1.81 ppm found for **1a**, can be assigned to the methyl groups on the *C*-acetylated chelate rings of **2a**, while the signals at 1.66 ppm can be assigned to the uncoordinated *C*-acetyl groups.

These four methyl signals, including two for **1a**, resonate at their characteristic fields and can be classified into four types: I, II, III, and IV, as described in Table 5. This classification can facilitate structural assignments for other products. Thus compound **2b**, which exhibits four methyl signals at all these fields and a methine signal at 5.42 ppm in the intensity ratios of 3 : 3 : 3 : 3 : 1, was supposed to have the mixed-ligand chelate structure which comprises both chelate rings of *N*-acetyl and *C*-acetyl β-ketoamines, as shown in Fig. 1. The somewhat lower frequency in *N*-acetyl carbonyl stretching for **2b** may be caused by its hydrogen-bonded structure, indicating *cis* configuration around the platinum atom.

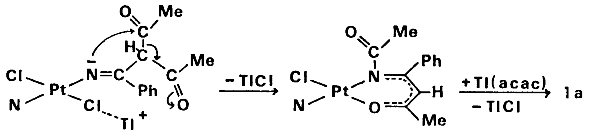
Compounds **4a** and **4b**, produced by the reaction between *cis*-$[PtCl_2(PhCN)_2]$ and Tl(bzac), exactly correspound to **2a** and **2b** in their structures, although the uncoordinated *C*-acyl groups are benzoyl instead of the acetyl groups in the former compounds. Unfortunately, the amount of **4b** obtained was not enough to allow recording of the ^{1}H NMR spectrum. However, the similarities in color and IR data of **4b** and **2b** support the structures depicted in Fig. 1.

Three compounds were produced by the reaction between *trans*-$[PtCl_2(PhCN)_2]$ and Tl(bzac). **3a** exhibits a single ν(C=O) band at 1748 cm^{-1} in its IR spectrum and one methine and one methyl signal at 5.84 and 2.03 ppm, respectively, in the intensity ratio of 1 : 3 in its ^{1}H NMR spectrum. These features are quite similar to those for **1a** except for the loss of a ring-methyl resonance, and hence a *trans*-bis-(*N*-acetyl β-ketoamine)chelate structure like **1a** was assigned for **3a**. On the contrary, **3a′** shows two ν(C=O) bands at 1750 and 1698 cm^{-1}, and two methine and two methyl signals at 5.45 and 5.19 ppm and at 2.04 and 1.86 ppm, respectively, in the intensity ratios of 1 : 1 : 3 : 3. Especially, the presence of two methine signals and a ring-methyl signal suggests that the structure of **3a′** has different chelate rings of *N*-acetyl and *N*-benzoyl *β*-ketoamines (see Fig. 1).

The presence of *N*-acetyl carbonyl and NH bands in the IR spectrum of **3b** allowed us to presume that this compound was the *trans* counterpart of **4b**. No band appeared, however, in the region of *C*-benzoyl carbonyl stretching. A similar disparity also arose in the ^{1}H NMR spectrum of **3b**. No ring-methyl signal of type II is present, but a methyl signal of type III was observed along with two methine signals, in the intensity ratios of 3 : 1 : 1, indicating the presence of the *N*-acetyl group and the two central ring-methines of a different magnetic environment. Thus the structure shown in Fig. 1 was assigned for **3b**; this structure is in good agreement with its analytical data. Of the two methine signals resonating at 6.05 and 5.74 ppm, the downfield signal appeared as a doublet with $J=3$ Hz and was ascribed to the methine proton on the *N*-unsubstituted chelate ring based on the W-rule.[25]

Nucleophilic Reactions of β-Diketonate Carbanions at Coordinated Cyanide Carbons in trans- *and* cis-*[PtCl$_2$(PhCN)$_2$].* Based on the confirmed structures of products, we suggest the following reaction course: 1) the initial step of these reactions involves the nucleophilic attack by a *β*-diketonate carbanion on the coordinated cyanide carbon atom; 2) the acetyl group or the central methine proton of the nuclephile migrates to the coordinated nitrogen atom in order to stabilize the imino anion formed in the initial step; 3) the carbonyl group in the residue coordinates to the metal to form the *N*,*O*-chelate ring, in cooperation with metal-assisted abstraction of the chloride ion. Thus the reaction path to produce **1a** can be formulated as below.

trans-[PtCl$_2$(PhCN)$_2$]+TI(acac) ⟶



(1)

As was ascertained by X-ray analysis, *trans* configuration around the metal atom in the starting complex is kept in the reaction product **1a**. Although IR and ^{1}H NMR spectra were not helpful in deciding geometrical configurations for other reaction products, it was possible to confirm that neither of the products (**1** and **3**) from *trans*-[PtCl$_2$(PhCN)$_2$] is the same as either of those (**2** and **4**) from *cis*-[PtCl$_2$(PhCN)$_2$]. Moreover, the *cis*(*N*,*N*)-configuration was the most probable for the two products (**2b** and **4b**) from *cis*-[PtCl$_2$(PhCN)$_2$], on the basis of the IR data showing the presence of the hydrogen bond. Formation of the hydrogen bond will induce the *N*-acetyl group and the *N*-acetyl chelate ring to be coplanar. The red color of **2b** and **4b** might be brought about by the increased delocalization of *π*-electrons through these two planes. All these facts suport the above-mentioned reaction scheme, which proceeds with retention of the original configuration without breaking of the metal-nitrogen bond. No reaction to produce **1a** occurred between bis(acetylacetonato)platinum(II) and free benzonitrile even at 100 °C, although hexafluoro-2-butyne underwent 1,4-addition across palladium(II)–acetylacetonato rings on treating C$_4$F$_6$ with bis(acetylacetonato)-palladium(II).[26]

When *trans*-[PtCl$_2$(PhCN)$_2$] was reacted with *β*-diketonate anions, all products (**1** and **3**) were the *N*–acyl *β*-ketoamine chelates. In the case of reaction with a benzoylacetonate anion, only the former two complexes (**3a** and **3a′**) of all the possible (*N*-acetyl, *N*-acetyl)-, (*N*-acetyl, *N*-benzoyl)-, and (*N*-benzoyl, *N*-benzoyl)-complexes were isolated in 11 and 6% yields, respectively, indicating greater electrophilicity of the acetyl carbonyl carbon atom. On the contrary, the main products from *cis*-[PtCl$_2$(PhCN)$_2$] were (*C*-acyl, *C*-acyl)-(**2a** and **4a**) or (*C*-acyl, *N*-acyl)-(**2b** and **4b**)-complexes, and no (*N*-acyl, *N*-acyl)-complexes were obtained. These results may be due to steric hindrance at the *cis*-*N*,*N* positions to prevent an (*N*-acyl, *N*-acyl)-complex. Among these isolated compounds, **1a**, **2a**, and **2b** are isomers, and **3a**, **4a**, and **4b**, which are products from a benzoylacetonate anion, also are the corresponding isomers. These isomers which comprise the different combinations of *N*-acyl and *C*-acyl chelate rings are classified to summation isomerism.

The series of *N*-acetyl *β*-ketoamine chelates produced by the nucleophilic attack of *β*-diketonate carbanions on the cyanide carbons in *trans*- and *cis*-[PtCl$_2$(PhCN)$_2$] are a kind of Schiff base complexes having the acid amide moiety in the ligand. However, such an *N*-acetyl Schiff base has never been prepared by condensation of benzoylacetone and acetamide since the amide protons are generally protected against reactions by the acetyl group. This fact and the acid-lability of the *N*–acetyl bond (see later), together with the difficulty in separation of analogous complexes by PLC, cause the lowering in yields of the reaction products.

Table 6. Reaction products in the presence of excess free *β*-diketones or *o*-nitrophenol[a)]

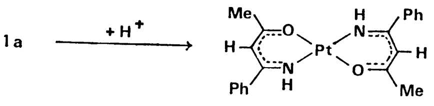
	Tl-(RCOCHCOMe)	Products (Yields/%)
trans-[PtCl$_2$(PhCN)$_2$]	R=Me	**5a** (3),**5b**(8)
	Ph	**3a** (15),**3a′**(4),**6**(5)
cis-[PtCl$_2$(PhCN)$_2$]	R=Me	**2a** (75)
	Me*	**2a** (14)
	Ph	**4a** (57)

a) The asterisk mark denotes the reaction in the presence of excess *o*-nitrophenol.

Reactions of trans- *and* cis-*[PtCl$_2$(PhCN)$_2$] with Thallium(I) β-Diketonate in the Presence of the Corresponding Excess Free β-Diketone or* o-*Nitrophenol.* With the exceptions of **5a**, **5b**, and **6**, each of the other compounds produced in these reactions is also found in the reaction products in the absence of free *β*-diketones. These products are summarized in Table 6 with their yields. **5a** and **5b** are compounds in which one *N*-acetyl chelate ring in **1a** and **1b** was formally replaced by a *C*-acetyl chelate ring, respectively, and hence **5a** corresponds to the *trans* isomer of **2b**. Similarly, **6** and **4b** make another isomeric pair of *trans* and *cis*. From Table 6, we can see that the *C*-acyl compounds are main products in these cases; their amounts are increased especially in the reactions with *cis*-$[PtCl_2(PhCN)_2]$. The following process can produce such high yields of *C*-acyl products: protons from free *β*-diketone are used to stabilize imino nitrogens produced during the reaction; hence, migration of *C*-acyl groups onto the nitrogen atoms are suppressed; and then CH protons are accepted by the *β*-diketonate anions present in solution.

To examine the effect of other proton donors, *o*-nitrophenol instead of free *β*-diketone was used in the reaction of *cis*-$[PtCl_2(PhCN)_2]$ with Tl(acac), as an example. However, no increase in yield of *C*-acetyl product **2a** was found (see Table 6). The reason why the reagent has no effect has not yet been elucidated, but the rather strong acidity ($pK_a=7.2$) of *o*-nitrophenol compared with that of acetylacetone ($pK_a=9.0$) might be the reason for its inefficancy as catalyst.

Acid Hydrolysis of trans-N-*Acetyl Compound* **1a.** In the previous section, we showed that the presence of free *β*-diketone suppresses migration of the *C*-acyl group onto the imino nitrogen atom, affording *C*-acyl compounds, namely, *N*-unsubstituted *β*-ketoamine chelates in high yields. Next we examined the acid stability of the *N*-acetyl bonds in **1a**. This bond is readily hydrolyzed by aqueous perchloric acid to yield golden crystals of **7**. The compound did not show any IR band in the carbonyl region higher than 1600 cm^{-1}, indicating the absence of uncoordinated acetyl carbonyl. The ^1H NMR spectrum exhibited only one methine and one ring-methyl signal at 5.34 and 1.88 ppm, respectively, together with one broad NH signal at 7.86 ppm in the intensity ratios of 1 : 3 : 1; this shows that the *N*-acetyl bonds in **1a** are hydrolyzed to the N–H. In fact, coupling ($^4J_{H-H}=4.0$ Hz) based on the W-rule[25] is again observed between the ring methine and the NH protons. Such an acid lability of the *N*-acetyl bonds might also play a part in the original reactions of $[PtCl_2(PhCN)_2]$ with *β*-diketonate anions. The compound **3b**, which is one of the reaction products between *trans*-$[PtCl_2(PhCN)_2]$ and Tl(bzac), might have been produced by the effect of a little amount of acid present accidentally in solution.



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(2)

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