Reactions of *trans*-Chloro(cyanomethyl)bis(triphenylphosphine)- and Chloro-(cyanomethyl){1,2-bis(diphenylphosphino)ethane}palladium(II) Complexes with Various Thallium(I) β-Diketonates††

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Reactions of *trans*-chloro(cyanomethyl)bis(triphenylphosphine)palladium(II), *trans*-[PdCl(CH_2CN)(PPh_3)$_2$] (**1**), with an equimolecular amount of Tl(β-dik) (β-dik=etac, acac, tfac, bzac, and dbm) in dichloromethane afforded the *O,O'*-chelated β-dik complexes [Pd(CH_2CN)(β-dik)(PPh_3)] (**3**). Hydrogen peroxide oxidation and chloride abstraction by $AgClO_4$ or $AgBF_4$ of **1** gave the neutral [PdCl(CH_2CN)PPh_3]$_n$ and the cationic [Pd(CH_2CN)(PPh_3)$_2$]$_m$X$_m$ (X=ClO_4 or BF_4), respectively, from either of which complexes **3** were also obtained by the reactions with the β-dik anions. No pure product corresponding to **3** was isolated by a similar treatment of **1** with Tl(hfac). On the other hand, chloro(cyanomethyl){1,2-bis(diphenylphosphino)ethane}palladium(II), [PdCl(CH_2CN)(dppe)] (**2**), reacted only with Tl(hfac) in refluxing acetone to give the cationic [Pd(CH_2CN)(dppe)]$_2$-(hfac)$_2$, which was also derived from **2** *via* [Pd(CH_2CN)(dppe)]$_2$X$_2$ (X=ClO_4 or BF_4).

In recent years many cyanoalkyl complexes of the type [MX(RCN)L_2] (M=Pd^{II}, Pt^{II}; X=halides or other monoanions; R=$(CH_2)_n$ (n=1,2,3), $CH_2C_6H_4$; L_2=2PPh_3, diphosphines) have been prepared[1-7] and their structures and various kinds of reactions have been studied extensively.[5-14] Among the cyanoalkyls examined, the complexes of *o*-cyanobenzyl, [MX(*o*-$CH_2C_6H_4CN$)L_2], underwent the widest range of reactions: (1) displacement of L by bidentate phosphorus ligands, (2) insertion of CO in the σ M–C bond, (3) formation of the cationic *cis*-[M($CH_2C_6H_4CN$)L_2]$_2$-(BF_4)$_2$ by abstraction of X,[6,7] and (4) nucleophilic attack by alcohols, thiols, and other nucleophiles on the coordinated CN group.[6,10-12] Moreover, the thermodynamically unstable *cis*-[PtX($CH_2C_6H_4CN$)-(PPh_3)$_2$] (X=Cl, Br) isomerized to the trans isomers, the reaction being catalyzed by free PPh_3.[6]

Although the cyanomethyl complexes of platinum-(II), [PtX(CH_2CN)L_2], have been also known to undergo the similar reactions to (1) and (3), and cis-trans isomerization,[3,5] only few studies have been performed on reactions of the palladium(II) analogue[2,14] which was found to decompose on irradiation in the solid state or in solution.[9] In this paper, we report the reactions of *trans*-[PdCl(CH_2CN)(PPh_3)$_2$] (**1**) and [PdCl(CH_2CN)-(dppe)] (**2**) with various Tl(β-dik) to know what kind of bonding mode is found for the β-dik ligands in the product complexes since β-dik anions are well-known as versatile ligands to coordinate to metal ions in various kinds of bonding modes.[15]

Results and Discussion

Thallium(I) β-diketonates employed, except 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate, readily react with **1** in dichloromethane at room temperature to yield the *O,O'*-chelated β-dik complexes [Pd(CH_2CN)(β-dik)PPh_3] (**3**). Hydrogen peroxide oxidation of **1** in a dichloromethane–acetone mixture causes precipitation of the rather insoluble neutral species [PdCl(CH_2CN)PPh_3]$_n$ (**4**), from which complexes 3 are also produced by the reactions with Tl(β-dik). Abstraction of chloride from **1** by $AgClO_4$ or $AgBF_4$ in a dichloromethane–methanol mixture gives the less soluble cationic species [Pd(CH_2CN)(PPh_3)$_2$]$_m$X$_m$ (**5**) (X=ClO_4 (**5a**) or BF_4 (**5b**)), which reacts with K(β-dik) in the same solvent mixture to afford **3**. Thus, complexes **3** can be derived from **1** by the three routes.

In the case of the reaction with the hfac anion which is the least basic β-dik ligand employed, the complex of type **3** can not be obtained by any route mentioned above. This is presumably because of incapable displacement of the coordinated PPh_3 by the hfac anion (see Experimental section). Instead, the cationic *trans*-[Pd(CH_2CN)(S)(PPh_3)$_2$](hfac) (**6**) is isolated, after some make-up, from the reaction mixture of **5** and K(hfac). The complex contains an acetone molecule (S) in the coordination sphere.

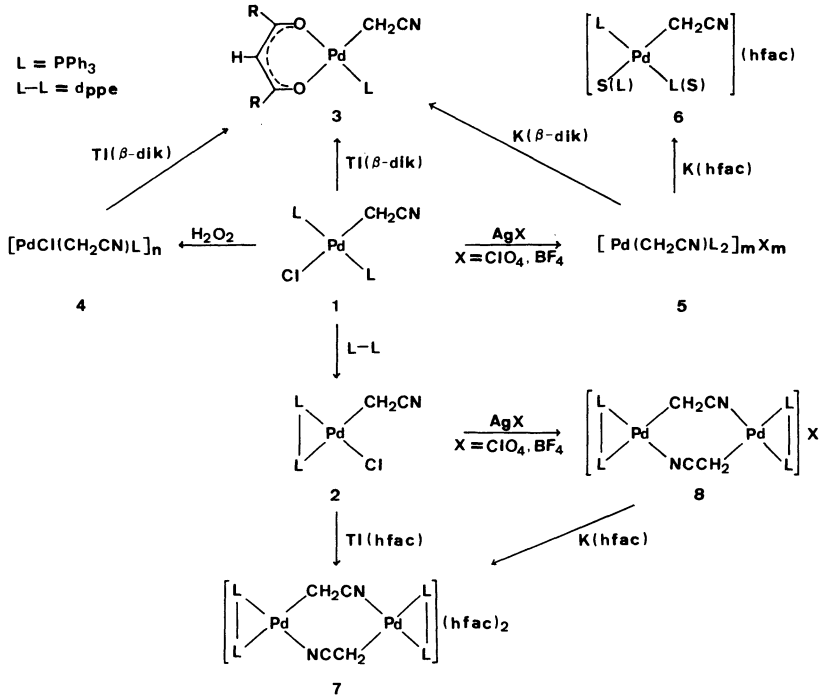
In the reactions of **2**, which bears the chelating diphosphine ligand, with the more basic β-dik anions, the formation of the complexes containing the centralcarbon-bonded or *O*-unidentate β-dik ligand is expected. Nevertheless, such a product can not be isolated as a pure solid in these reactions. On the contrary, Tl(hfac) reacts with **2** in refluxing acetone to give the cationic [Pd(CH_2CN)(dppe)]$_2$(hfac)$_2$ (**7**) with the *N*-bonded CN groups. When the chloride ion is abstracted from **2** by $AgClO_4$ or $AgBF_4$ to yield [Pd(CH_2CN)(dppe)]$_2$X$_2$ (**8**) (X=ClO_4 (**8a**) or BF_4 (**8b**)) and then **8** is allowed to react with K(hfac), complex **7** is also produced by the anion exchange.

All the reactions are summarized in Scheme 1. The analytical and molecular weight data for the newly prepared complexes are listed in Table 1.

Characterization of the O,O'-Chelated β-dik Complexes 3. As is seen in Table 2, the IR spectra of complexes **3a—3e** exhibit a sharp band at the 2200—2212 cm^{-1} region, which is assigned to the ν(C≡N) vibration of the free CN group.[16] The bands of strong to medium intensities at the 1620—1500 cm^{-1} region are assigned to the ν(C···O) + ν(C···C) vibrations of the *O,O'*-chelated β-dik ligands.[17]

††In this paper β-dik represents a monoanion of ethyl 3-oxobutanoate (etacH) or that of β-diketones such as 2,4-pentanedione (acacH), 1,1,1-trifluoro-2,4-pentanedione (tfacH), 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfacH), 1-phenyl-1,3-butanedione (bzacH), and 1,3-diphenyl-1,3-propanedione (dbmH).

Table 3 lists the ^1H NMR data for the *O,O'*-chelated β-dik complexes **3** in $CDCl_3$. The spectrum of **3b** is very simple and exhibits three singlets at 1.63, 1.98, and 5.23 ppm and a doublet at 1.35 ppm with relative intensities of 3:3:1:2 in addition to other signals assignnable to the phenyl protons. The doublet is due to the cyanomethyl protons which couples to cis ^{31}P, the coupling constant being 3.0 Hz appropriate for cis coupling.[2] The 5.23-ppm signal is due to the methine proton of the acac ligand and others due to the methyl protons, of which the higher-field signal at 1.63 ppm is assigned to the methyl cis to P and the lower one at 1.98 ppm to trans to P by reference to the data for the analogous complexes [PdCl(acac)PPh_3], [Pd(acac)(acac-



Scheme 1.

TABLE 1. ANALYTICAL DATA FOR THE NEWLY PREPARED COMPLEXES

No.	Complex	Found(Calcd)			
		C(%)	H(%)	N(%)	Mol wt[a]
3a	[Pd(CH_2CN) (etac)PPh_3]	58.43(58.06)	4.95(4.87)	2.60(2.60)	540(538)
3b	[Pd(CH_2CN) (acac)PPh_3]	59.11(59.13)	4.79(4.76)	2.80(2.76)	493(508)
3c	[Pd(CH_2CN) (tfac)PPh_3]	53.73(53.45)	3.76(3.77)	2.32(2.49)	527(562)
3d	[Pd(CH_2CN) (bzac)PPh_3]	62.93(63.22)	4.58(4.60)	2.41(2.46)	558(570)
3e	[Pd(CH_2CN) (dbm)PPh_3]	66.46(66.52)	4.45(4.47)	2.25(2.21)	646(632)
4	[PdCl(CH_2CN)PPh_3]$_n$	53.66(54.03)	3.86(3.85)	3.07(3.15)	
5a	[Pd(CH_2CN) (PPh_3)$_2$]$_m$(ClO_4)$_m$	58.13(59.24)	4.17(4.19)	1.78(1.82)	385[b] (771)[c]
5b	[Pd(CH_2CN) (PPh_3)$_2$]$_m$(BF_4)$_m$	58.67(60.23)	4.30(4.26)	1.84(1.85)	376[b] (758)[c]
6	[Pd(CH_2CN) (C_3H_6O) (PPh_3)$_2$] (hfac)	59.08(59.00)	4.24(4.20)	1.54(1.50)	
7	[Pd(CH_2CN) (dppe)]$_2$(hfac)$_2$	52.17(52.71)	3.62(3.62)	1.84(1.86)	504(1504)
8a	[Pd(CH_2CN) (dppe)]$_2$(ClO_4)$_2$	52.25(52.20)	4.15(4.08)	2.19(2.17)	452[b] (1289)
8b	[Pd(CH_2CN) (dppe)]$_2$(BF_4)$_2$	53.39(53.26)	4.20(4.15)	2.22(2.22)	424[b] (1263)

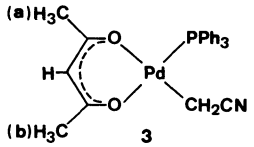
a) In CH_2Cl_2 at 28 °C unless otherwise stated. b) In CH_3CN at 39 °C. c) The formula weight was calculated as m=1.

TABLE 2. CHARACTERISTIC IR BANDS (cm^{-1}) IN NUJOL

No.	ν(C≡N)	ν(C=O)+ν(C=C)	No.	ν(C≡N)	Anion (X)
3a	2205m	1605vs, 1567w, 1509s	**5a**	2247s	1090vs, br, 925w, 620s (ClO_4)
3b	2200s	1583s, 1564s, 1510s	**5b**	2245s	1058s, br, 750m, 560s (BF_4)
3c	2212s	1618vs, 1580m, 1570sh 1518m, 1510sh	**6**	2200m 2200s, 2250w[b]	1673s, 1548s, 1520w (hfac)[c]
3d	2207s	1592s, 1585sh, 1570sh 1560s, 1510s	**7**	2234s	1670s, 1588w, 1552s (hfac)[c]
3e	2210m	1590s, 1545vs, 1515vs	**8a**	2240m	1100vs, br, 940w, 630s (ClO_4)
4	2250s, 2260sh	315w, 280w[a]	**8b**	2240s	1058s, br, 750w, 520s (BF_4)

a) ν(Pd–Cl). b) In $CHCl_3$. c) ν(C=O)+ν(C=C).

Table 3. ^{1}H NMR Data for the *O,O'*-chelated β-dik complexes **3** in $CDCl_3$[a]



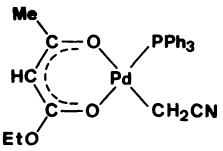
3

No.	cis / trans	Isomer[b]	β-dik CH3(a)	β-dik CH3(b)	β-dik CH	β-dik CH2CN
3a[c]	1 / 2	cis	1.62	OEt	4.73	1.49d (3.0)
		trans	OEt	1.97		
3b			1.63	1.98	5.23	1.35d (3.0)
3c	1 / 2	cis	1.78		5.46	1.45d (3.0)
		trans		2.10		
3d	2 / 3	cis	1.80	Ph	5.96	1.44d (3.5)
		trans	Ph	2.16	5.99	1.41d (3.5)
3e			Ph	Ph	6.63	1.55d (3.0)

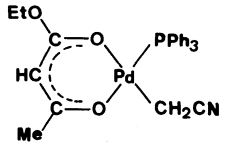
a) Chemical shift (δ) in ppm from internal Me_4Si at 33 °C. Figures in parentheses are $^3J(^{31}P\text{-}H)$ in Hz. d: Doublet. b) Cis and trans abbreviate cis(Me, P) and trans(Me, P), respectively. See text. c) CH_3-CH_2 signals for the ester appear at 1.28 (triplet), 4.20 (quartet) ppm (cis isomer) and at 0.77 (triplet), 3.21 (quartet) ppm (trans isomer), respectively.

C^3)PPh_3],[18] and [Pd(acac)(etac-C^3)PPh_3].[19] Complex **3e** exhibits a methine singlet at 6.63 ppm and a cyanomethyl doublet at 1.55 ppm with ^2J(P-H)=3.0 Hz.

On the other hand, the spectrum of **3a** in $CDCl_3$ is rather complex and shows two methyl signals at 1.62 and 1.97 ppm in the intensity ratio of *ca.* 1:2. Owing to the unsymmetrical nature of etac, two geometrical isomers, cis(Me,P) and trans(Me,P), coexist in the case of **3a**. By reference to the data of **3b**, these two signals at



cis (Me, P)



trans (Me, P)

higher and lower fields are readily attributed to the methyl protons of the cis and trans isomers, respectively. A similar situation is present in either case of **3c** and **3d**, the isomer ratios of cis to trans being *ca.* 1:2 and *ca.* 2:3, respectively. In the case of **3d**, splitting of the cyanomethyl proton signal is observed, discriminating a slightly different magnetic environment based on the different trans ligands.

Table 4. $^{31}P\{^1H\}$ NMR Data for the starting complexes and some products in $CDCl_3$[a]

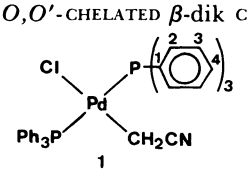
No.	P (PPh_3) or P^1, P^2 (dppe)	$J(P^1\text{-}P^2)$
1	27.0	
3a-*cis*[b]	64.4	
3a-*trans*[b]	33.5	
3b	33.3	
5a[c]	25.2[d]	
2	44.1d 60.3d	23
7	50.4d, br 62.5d[e]	20
8a[c]	55.2d 65.0d	17

a) Chemical shift (δ) in ppm downfield from external H_3PO_4 and coupling constant (J) in Hz. d: Doublet, br: broad. b) The major component in equilibrium was assigned to trans. c) In CD_3CN. d) The half width slightly increased with increasing temperature as follows: 2 (−30 °C), 4 (−10 °C), and 10 (30 °C) Hz. e) Minor signals appear at the higher-field side (52.1 and 68.8 ppm) of each doublet. See Fig. 1.

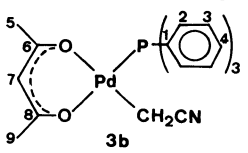
The $^{31}P\{^1H\}$ NMR data for the starting complexes and some products in $CDCl_3$ or CD_3CN are listed in Table 4. The spectrum of **3b** in $CDCl_3$ exhibits a single signal at 33.3 ppm downfield from external H_3PO_4, while **3a** shows two signals at 33.5 and 64.4 ppm in the same solvent, disclosing the presence of cis and trans isomers in the solution. On the basis of their relative intensities, the more intense higher-field signal is assigned to the PPh_3 ligand of the trans(Me,P) isomer and the lower-field one to that of cis(Me,P) isomer.

The $^{13}C\{^1H\}$ NMR spectra of **3a**, **3b**, and *trans*-[$PdCl(CH_2CN)(PPh_3)_2$] (**1**) were measured in $CDCl_3$ using Me_4Si as internal standard at room temperature. These data are collected in Table 5. As is seen in the Table, the cyanomethyl-CH_2 signal of **1** appears at −5.0 ppm as a triplet indicating the trans configuration of two PPh_3, while that of **3b** is observed at −9.1 ppm as a doublet owing to cis coupling to one phosphorus atom. For the acac ligand in **3b**, either signal of the methyl and carbonyl carbons is splitting indicating

Table 5. $^{13}C\{^1H\}$ NMR Data for the starting complex **1** and the *O,O'*-chelated β-dik complexes **3a** and **3b** in $CDCl_3$[a]



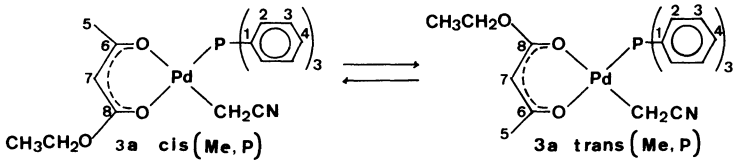
1



3b

No.	CH_2CN CH_2	CH_2CN CN	PPh_3 C^1	PPh_3 C^2	PPh_3 C^3	PPh_3 C^4	acac C^5, C^9	acac C^6, C^8	acac C^7
1	−5.0t (3)	124.0	129.9vt ((24))	134.7vt ((6))	128.4vt ((5))	130.5vt ((1))			
3b	−9.1d (10)	125.5	128.8d (53)	134.2d (11)	128.4d (11)	130.9d (3)	27.4 27.6d (9)	186.4 186.4d (2)	99.6

TABLE 5. (Continue)

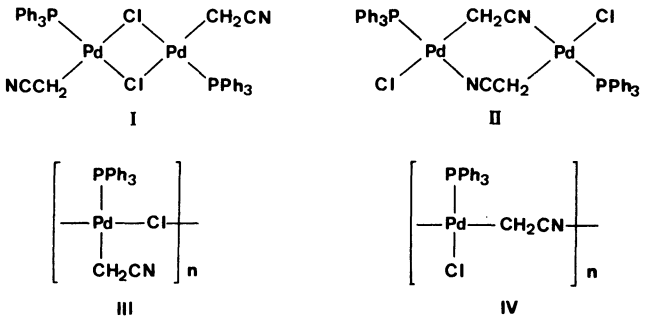


No.	CH_2CN		PPh_3				etac				
	CH_2	CN	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	CH_3-CH_2
3a-*cis*[b]	−9.5d (9)	125.2	128.6d (54)	134.3d (12)	128.5d (11)	131.1d[c] (3)	27.2	186.7	84.2	171.3d (2)	14.6 60.4
3a-*trans*[b]	−8.7d (9)	124.8	128.8d (52)	134.2d (12)	128.7d (11)	131.1d[c] (3)	27.3d (9)	187.2d (2)	84.3	171.0	14.2 59.5

a) Chemical shift (δ) in ppm from internal Me_4Si. Figures in parentheses and double parentheses give $J(^{31}P\text{-}C)$ and $1/2|^nJ(P\text{-}C)+^{n+2}J(P\text{-}C)|$ (n=1—4) in Hz, respectively. d: Doublet, t: triplet, vt: virtual triplet. b) Except for C^5, C^6, and C^8, the major component in equilibrium was assigned to trans. c) No splitting of signals for the cis and trans isomers was observed.

that two acetyl groups have a slightly different magnetic environment. Two singlets appearing at 27.4 and 186.4 ppm are assigned to the methyl (C^5) and carbonyl (C^6) carbons cis to P, respectively, whereas two doublets resonating at 27.6 and 186.4 ppm are attributed to those (C^9, C^8) trans to P. The $^{13}C\{^1H\}$ NMR spectrum of **3a** also discloses the presence of cis(Me,P) and trans(Me,P) isomers in solution. The ethoxycarbonyl carbon (C^8) of the cis isomer and the methyl (C^5) and acetyl carbonyl (C^6) carbons of the trans isomer couple to the trans phosphorus atom, each appearing as a doublet and hence, two sets of these signals are readily assigned as shown in Table 5. The cis and trans isomer ratio based on the ^1H NMR data is referred to assign other signals.

*Neutral Species [PdCl(CH_2CN)PPh_3]$_n$ (**4**).* The yellow precipitate obtained by hydrogen peroxide oxidation of **1** in a dichloromethane–acetone mixture gives satisfactory analysis as [PdCl(CH_2CN)PPh_3]$_n$. Four possible structures are conceivable:

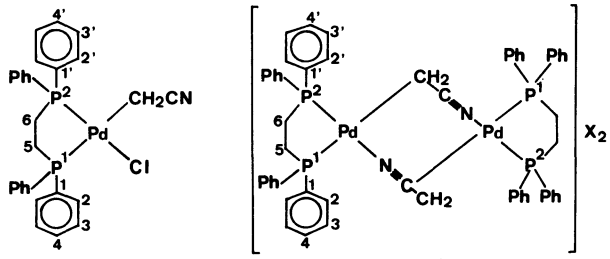


The NMR data for this species are not available because of its insolubility in any solvent appropriate to measurement. As is seen in Table 2, the IR spectrum of **4** shows two ν(Pd-Cl) bands at 315 and 280 cm^{-1}, frequencies of which are comparable to 288 cm^{-1} for **1**, indicating that the chloride-bridging structures I and III are eliminated. In contrast with **3**, species **4** exhibits two $\nu(C\equiv N)$ bands at 2250 and 2260 cm^{-1}, the former one as a strong band and the latter as a shoulder. These frequencies are 40—60 cm^{-1} higher than those for **3a—e**, revealing that the CN group coordinates to another palladium atom.[16,20] Thus, it seems likely that the *N*-bonded CN-bridging structures II and IV coexist in the solid state of **4**. This is not the case of the dimers [PdCl($CH_2C_6H_4Y$)PPh_3]$_2$ (Y=H or CN), in which the chloride-bridging structure of type I was proposed.[7]

Cationic Diphosphine Complexes. All the cationic complexes except **6** have the *N*-bonded CN-bridging structure on the basis of the $\nu(C\equiv N)$ frequencies in their IR spectra (Table 2). The cationic diphosphine complexes **8** derived from **2** are soluble only in coordinating solvents and the cations are dimeric in CH_3CN as is revealed by their molecular weight measurements (Table 1). As described earlier, this type of complex has been prepared by Ros *et al.* for the cyanomethyl complexes with platinum(II)[5] and for the *o*-cyanobenzyl complexes with platinum(II)[6] and palladium(II).[7] Addition reactions of a variety of nucleophiles to the *N*-bonded CN groups of the *o*-cyanobenzyl complexes[10—12] have been also studied. However, the present cyanomethyl complexes of palladium(II) fails to add these nucleophiles so long as we have tried briefly. The X-ray analysis for [Pt(*o*-$CH_2C_6H_4CN$)(dpe)]$_2$(BF_4)$_2$ (dpe=*cis*-1,2-bis(diphenylphosphino)ethylene) established the *N*-bonded CN-bridging structure of the dimeric cation.[21]

As is seen in Table 4, the $^{31}P\{^1H\}$ NMR spectrum of the starting PPh_3 complex **1** in $CDCl_3$ shows a singlet at 27.0 ppm, while that of the diphosphine complex **2** in the same solvent exhibits two doublets at 44.1 and 60.3 ppm with $J(P^1\text{-}P^2)$=23 Hz, reflecting a different magnetic environment of two phosphorus atoms P^1 and P^2. The higher-field signal at 44.1 ppm is assigned to P^1 trans to the CH_2CN ligand, which has the greater trans influence than chloride, while the 60.3-ppm signal is due to P^2 trans to the chloride. The spectrum of the ClO_4 salt **8a** in CD_3CN is similar to that of **2** in $CDCl_3$ and two doublets appear at 55.2 (P^1) and 65.0 (P^2) ppm with $J(P^1\text{-}P^2)$=17 Hz. The downfield shift of the P^1 and P^2 signals for **8a** compared with those of **2** can be generally understood as the coordination effect of the free CN group of **2** to another metal atom and as the replacement effect of chloride by the second CN group, although the solvent effect can not be ignored, too (see data for **7** in $CDCl_3$). The ^1H NMR spectrum of **8a** in CD_3CN shows a cyanomethyl signal at 1.34 ppm as a

Table 6. $^{13}C\{^1H\}$ NMR Data for the diphosphine complexes **2**, **7**, and **8a**[a)]



2 **7** (X = hfac); **8a** (X = ClO_4)

No.	CH_2CN		dppe						hfac		
	CH_2	CN	C^1, $C^{1'}$	C^2, $C^{2'}$	C^3, $C^{3'}$	C^4, $C^{4'}$	C^5	C^6	CF_3	CO	CH
2[b)]	−0.7dd	125.5	129.5d	132.7d	129.0d	131.3d	24.3dd	30.9dd			
	(105)		{32}	{12}	{11}	{3}	(29)	(21)			
	((3))				129.3d	132.2d	((12))	((34))			
					{11}	{3}					
7[b)]	−2.1dd	125.7d	d)	132.9d	129.4d	131.8	24.0dd	30.7dd	118.1q	173.5q	85.2
	(92)			{12}	{10}		(31)	(18)	[291]	[31]	
	((4))	((40))		133.0d	129.7d	131.9	((9))	((36))			
				{12}	{12}						
8a[c)]	d)	126.2d	131.9d	134.1d	129.3d	133.9d	24.6dd	31.4dd			
		((43))	{41}	{12}	{13}	{3}	(33)	(18)			
				133.8d	129.2d		((9))	((37))			
				{12}	{11}						

a) Chemical shift (δ) in ppm from internal Me_4Si. Figures in parentheses, double parentheses, braces, and brackets give $J(^{31}P^1\text{-}C)$, $J(^{31}P^2\text{-}C)$, $J(^{31}P\text{-}C)$, and $J(^{19}F\text{-}C)$ in Hz, respectively. $J(^{31}P\text{-}C)$ describes $J(^{31}P^1\text{-}C^n)$ and/or $J(^{31}P^2\text{-}C^n)$. b) In $CDCl_3$. c) In CD_3CN. d) Indiscernible because of overlapping with other signals.

doublet of doublets with $^3J(P^1\text{-}H)=9.0$ and $^3J(P^2\text{-}H)=3.0$ Hz in accordance with the diphosphine-chelating structure.

Table 6 lists the $^{13}C\{^1H\}$ NMR data for the diphosphine complexes **2**, **7**, and **8a**. The starting complex **2** shows the cyanomethyl-CH_2 and -CN signals at −0.7 and 125.5 ppm, respectively. The CH_2 signal appears as a doublet of doublets by coupling to trans P^1 and cis P^2 with $^2J(P^1\text{-}C)=105$ and $^2J(P^2\text{-}C)=3$ Hz, respectively. The coupling constant of 105 Hz for $^2J(P^1\text{-}C)$ is surprisingly large, but it is not impossible because the appreciably large trans coupling constants are observed: $^2J(P\text{-}C)=75$ Hz for $[Pt(CH_3)\{P(CH_3)_2(C_6H_5)\}_3]^+$,[22] 72 Hz for $[Pt(tfac(2\text{-})\text{-}C,O)(PPh_3)_2]$,[23] and 70 Hz for $[Pd(tfac(2\text{-})\text{-}C,O)(PPh_3)_2]$[24] and *cis*-$[Pt(acac\text{-}C^1)(py)\{P(p\text{-}ClC_6H_4)_3\}_2]^+$.[25] When the cationic dimer (**8a**) with the *N*-bonded CN group is prepared, it is interesting to see that the cyanomethyl-CN signal observed at 126.2 ppm couples to a phosphorus atom, although three-bond coupling of the CN carbon in **2** to trans P^1 is not appreciated. This fact suggests that the CN carbon signal of **8a** couples to trans P^2 through C-N-Pd-P^2 bond. The large coupling constant of 43 Hz for $^3J(P^2\text{-}C)$ may be allowed when it is compared with 105 Hz for the two-bond trans coupling ($^2J(P^1\text{-}C)$) of the cyanomethyl-CH_2 signal in **2**.

In contrast to **8**, the hfac salt **7** is appreciably soluble even in noncoordinating solvents and the cation is found to be dimeric in dichloromethane by the molecular weight measurement. Figure 1 displays the temperature-dependent $^{31}P\{^1H\}$ NMR spectra of **7** in $CDCl_3$. The spectrum at 32°C is of the basically AB quartet type, exhibiting two doublets at 50.4 (P^1) and

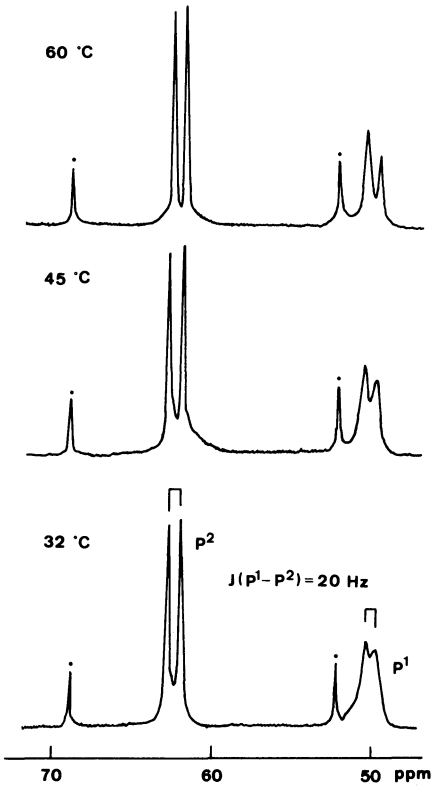
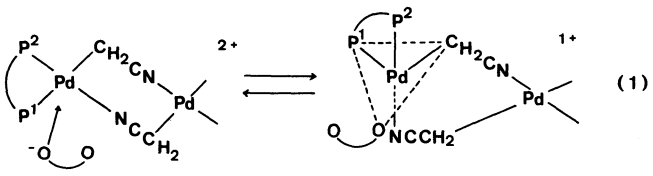


Fig. 1. Temperature-dependent $^{31}P\{^1H\}$ (24.2 MHz) NMR spectra of $[Pd(CH_2CN)(dppe)]_2(hfac)_2$ (**7**) in $CDCl_3$ with external H_3PO_4. Two minor signals denoted by asterisks are due to some decomposed species.

62.5 (P^2) ppm with J(P^1-P^2)=20 Hz, although the broadening is taking place in the higher field signal. In contrast to the ClO_4 anion, the hfac anion in **7** has the potentially coordinating power to form the five-coordinate complex. If the oxygen donor of the anion approaches from the P^1 side to the central palladium atom, the resulting complex **A** should have the trigonal-bipyramidal structure in which only the P^1 atom is appreciably sterically distorted, as exemplified below.



(1)

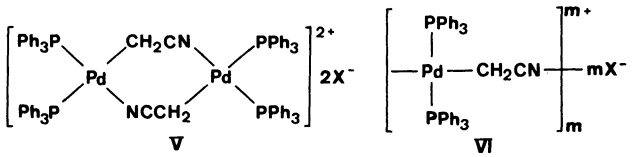
7 A

When the addition-elimination rate of the hfac anion in equilibrium (1) is slow on the NMR time scale, the broadening of only the P^1 signal can be observed with retention of the P^1-P^2 coupling. As the rate becomes more rapid, the normal AB quartet pattern will be restored. In fact, the broad P^1 signal sharpen gradually with increasing temperature, giving the well-resolved doublet at 60 °C. Minor signals observed at each lower-field side of the two doublets increase in their intensities with time, and hence these signals can be regarded as those of some decomposed species.

In spite of the existence of equilibrium (1) in solution, the cyanomethyl-proton signal of **7** in $CDCl_3$ appears at 1.32 ppm as a doublet of doublets, the coupling constants being the same degree (^3J(P^1-H)=10.5; ^3J(P^2-H)=3.5 Hz) as those for **8a**. The methine proton of the hfac anion in **7** resonates at higher field (5.38 ppm in $CDCl_3$) than that in [Pd(hfac)$_2$] (6.42 ppm in the same solvent). Such a upfield shift is generally recognized as is due to the higher charge density on the noncoordinating anion.[26]

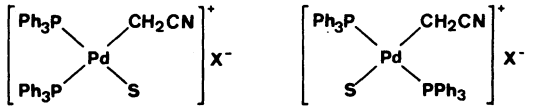
As is seen in Table 6, the $^{13}C\{^1H\}$ NMR spectrum of **7** in $CDCl_3$ shows three signals originated from the hfac anion in addition to the spectrum of **8a**. The CF_3-, CH-, and CO-carbon signals appear at 118.1, 85.2, and 173.5 ppm as a quartet with ^1J(C-F)=291 Hz, a singlet, and a quartet with ^2J(C-F)=31 Hz, respectively. These chemical shifts and coupling constants are very similar to those for the outer-sphere complexes [Pd(PMe$_2$Ph)$_4$](hfac)$_2$ and [Pd(dppe)$_2$](hfac)$_2$ in $CDCl_3$ and CD_3OD, respectively,[26b] indicating that the hfac ligand in **7** is present as a counter anion. The cyanomethyl-CN signal appears at 125.7 ppm as a doublet with ^3J(P^2-C)=40 Hz, also supporting the N-bonded CN-bridging structure of the cation.

Cationic Triphenylphosphine Complexes. The IR spectra of the cationic PPh$_3$ complexes **5** in the solid state exhibit only one sharp ν(C≡N) band at around 2250 cm^{-1} and either one of two possible structures of the cationic dimer V and polimer VI is conceivable as

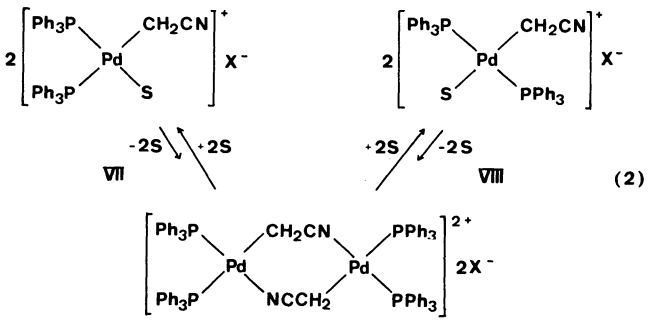


V VI

the solid state structure of **5**. Because of the less soluble nature in noncoordinating solvents, the molecular weight and NMR measurements of **5** were performed in CH_3CN and CD_3CN, respectively. As is seen in Table 1, each molecular weight of **5a** and **5b** has a half value of the formula weight in CH_3CN, and hence the Pd-N bonds in structure V or VI are brorken to give the following *cis*- or *trans*-PPh$_3$ complex in which a solvent molecule S occupies the vacant coordination site. The



^{1}H NMR spectrum of **5a** at 33 °C shows a broad signal assignable to the cyanomethyl proton at 1.26 ppm from internal Me_4Si. However, when the temperature is decreased, the signal further broadens until it begin to split into three peaks at −5 °C, and then gives a sharp triplet with ^3J(P-H)=6.8 Hz at −30 °C. These results imply that two molecules of PPh$_3$ have the mutually trans configuration like structure VIII at −30 °C, although the complex is stereochemically nonrigid at the higher temperature. For such a spectral change in ^{1}H NMR, two explanations are possible: (1) dissociation and coordination of a PPh$_3$ molecule in structure VIII are taking place rapidly on the NMR time scale, (2) cis-trans isomerization (Eq. 2) is taking place between structures VII and VIII *via* the cationic dimer similar to **8**, both at the higher temperatures. In



(2)

the case of (2), the isomerization can be promoted by the coordination of the free CN group in structure VII or VIII to another molecule. The choice of either one of the two mechanisms mentioned above is not possible at the present stage of investigation.

These dynamic behaviors of the species in solution are also consistent with the temperature-dependent $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR data for **5a** in CD_3CN. The $^{31}P\{^1H\}$ NMR spectrum of **5a** at −30 °C shows a single signal at 25.2 ppm with the half width of *ca.* 2 Hz, indicating the existence of the environmentally equivalent two phosphorus atoms at this temperature, although the half width slightly increases with increasing temperature owing to the occurrence of the stereochemical nonrigidity. In the case of the $^{13}C\{^1H\}$ NMR spectrum of **5a**, the signal intensities for the cyanomethyl-CH$_2$ and -CN carbons are too weak to perceive their temperature-dependent spectral changes, while the phenyl-ring carbon signals of the PPh$_3$ ligands are useful to examine the structural

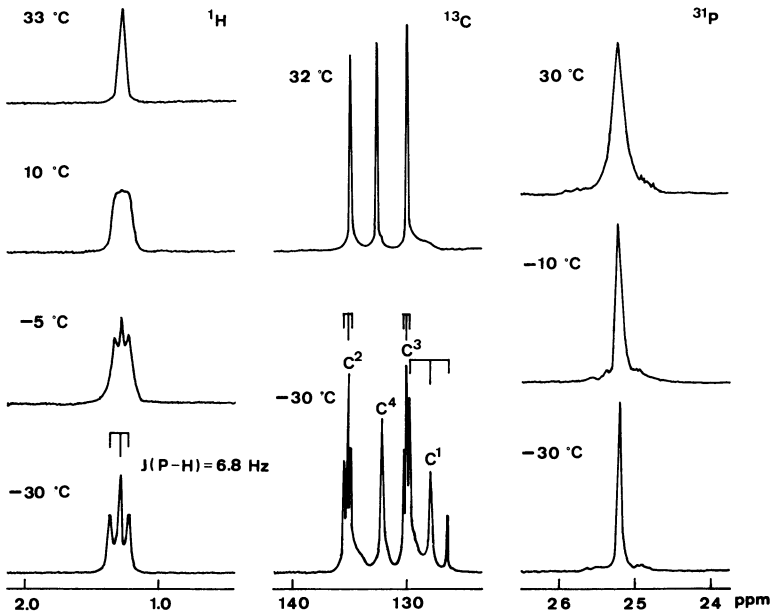


Fig. 2. Temperature-dependent ^{1}H (100 MHz), ^{13}C{^{1}H} (15.0 MHz), and ^{31}P{^{1}H} (24.2 MHz) NMR spectra of $[Pd(CH_2CN)(PPh_3)_2]_m(ClO_4)_m$ (**5a**) in CD_3CN with internal Me_4Si, external Me_4Si, and external H_3PO_4, respectively.

change of the complex in solution. At −30 °C, each signal appears at 127.8 (C^1), 134.8 (C^2), 129.8 (C^3), and 132.4 (C^4) ppm from external Me_4Si (see Table 5 for the numbering system). Except for C^4, which is most distant from P, all other carbon signals resonate as triplets by virtual coupling to the mutually trans 2P atoms, the coupling constants being 24.2 (C^1), 6.5 (C^2), and 5.1 (C^3) Hz. On the other hand, these couplings are lost at 32 °C and each signal appears as a singlet, again indicating the dynamic behavior of **5a** at this temperatures. These spectral change are summarized in Fig. 2.

Although no attempt is made to isolate the cationic species $[Pd(CH_2CN)(CH_3CN)(PPh_3)_2]X$ (X=ClO_4 or BF_4) which is thought to exist in the acetonitrile solution of **5**, a similar complex [Pd(CH_2CN)(acetone)-(PPh_3)$_2$](hfac) (**6**) can be isolated. The IR spectrum of **6** in the solid state shows a strong ν(C≡N) band at 2200 cm^{-1} and three strong to medium bands assignable to the ν(C⋯O) and ν(C⋯C) at 1673, 1548, and 1520 cm^{-1}. These frequencies are consistent with the formulation as [Pd(CH_2CN)(acetone)(PPh_3)$_2$](hfac). When the complex is dissolved in $CHCl_3$, however, another weak band appears at the higher-frequency side of the strong ν(C≡N) band, suggesting the formation of the cationic species with the *N*-bonded CN group in the solution. The ^{1}H NMR spectrum of **6** in $CDCl_3$ at 33 °C exhibits a sharp signal at 1.43 ppm and a broad one at 5.37 ppm, which are assigned to the cyanomethyl and the hfac-CH protons, respectively. As the temperature is decreased, the CH signal moved gradually to the higher-field side and newly two signal appeared, giving three methine proton signals at 6.34, 5.72, and 4.68 ppm at −45 °C. Although such a complex behavior in the IR and ^{1}H NMR spectra of **6** predicts the formation of the *O,O'*-chelated and *O*-unidentate species of the hfac ligand in solution in addition to the existence of equilibrium (2) (X=hfac), this ambiguity is not pursued further in view of their insufficient data.

Experimental

The starting complexes *trans*-[PdCl(CH_2CN)(PPh_3)$_2$] (**1**) and [PdCl(CH_2CN)(dppe)] (**2**) were prepared according to the literature.[2]

Preparation of [Pd(CH_2CN)(β-dik)(PPh_3)] (3) by the Reactions of 1 with Tl(β-dik). General Procedure: Equimolecular amounts of an appropriate Tl(β-dik)[27] were allowed to react with **1** in dichloromethane at room temperature. Thallium(I) chloride began to precipitate immediately and the mixture was stirred for the time noted below before filtration. The filtrate was concentrated under reduced pressure and petroleum ether was added to the concentrate to obtain a crude precipitate. The color and appearance, the reaction time, the solvent of crystallization, and the yield were as follows. **3a**: White needles, 1 h, dichloromethane-petroleum ether, 62%; **3b**: yellow plates, 3 h, acetone, 89%; **3c**: yellow needles, 3 h, dichloromethane-petroleum ether, 63%; **3d**: white needles, 12 h, dichloromethane-petroleum ether, 93%; **3e**: yellow needles, 5 h, dichloromethane-petroleum ether, 98%.

In a similar reaction of **1** with Tl(hfac), only oily substance was obtained, from which a pure solid could not be isolated. The crude substance shows two ν(C≡N) bands at 2210 and 2240 cm^{-1} and their relative intensity varies with repeated preparations. The ν(C⋯O)+ν(C⋯C) bands appear at 1668s, 1638sh, and 1525s cm^{-1}, indicating that the main product contains the hfac ligand as a counter anion.[28] The signal intensity of the ^{1}H NMR spectrum reveals that the molar ratio of PPh_3 to CH_2CN in the specimen is always 1:1≪PPh_3:CH_2CN<2:1.

Preparation of the Neutral [PdCl(CH_2CN)(PPh_3)]$_n$ (4) by Hydrogen Peroxide Oxidation of 1. Acetone (20 cm^3) and a 30% aqueous solution (5 cm^3) of H_2O_2 were added successively to a dichloromethane (10 cm^3) solution of **1** (616 mg, 0.814 mmol) and the mixture was stirred for 40 h during which a small amount of white precipitate was formed. The total volume of the mixture was reduced before filtration to obtain **4** in a satisfactory yield. The yield was 326 mg (84%).

*Preparation of the Cationic [Pd(CH_2CN)(PPh_3)$_2$]$_m$X$_m$ (X= ClO_4 (**5a**) or BF_4 (**5b**)) by Chloride Abstraction of **1**.* A methanol (10 cm^3) solution of $AgClO_4$ (260 mg, 1.25 mmol) was added to a solution of **1** (935 mg, 1.24 mmol) in dichloromethane (40 cm^3). Silver chloride began to precipitate immediately and the mixture was stirred for 24 h at room temperature before filtration. The filtrate was concentrated under reduced pressure to obtain a pale yellow powder of **5a**. The yield was 840 mg (88%). Similarly, **1** (304 mg, 0.402 mmol) in dichlomethane (20 cm^3) was allowed to react with $AgBF_4$ (78.4 mg, 0.402 mmol) in methanol (10 cm^3) for 22 h. After the same procedure as described above, addition of petroleum ether to the concentrate gave a white precipitate (214 mg) of **5b** in a 70% yield.

*Reactions of **4** with Tl(acac) and Tl(tfac).* A methanol (10 cm^3) solution of Tl(acac) (74 mg, 0.243 mmol) was added to a suspension of **4** (104 mg, 0.234 mmol for n=1) in acetone (20 cm^3) at room temperature. After being stirred for 10 h, the precipitated TlCl was filtered off and the filtrate was evaporated to dryness under reduced pressure. The residue was redissolved in acetone and the solution was concentrated to separate out yellow plates of **3b**. The yield was 85 mg (71%). Similarly, Tl(tfac) (127 mg, 0.356 mmol) in methanol (10 cm^3) was allowed to react with a acetone (30 cm^3) suspension of **4** (120 mg, 0.271 mmol for n=1) overnight. Filtration, concentration to dryness, and then redissolution of the residue in dichloromethane (5 cm^3) afforded a yellowish green solution, from which **3c** was deposited on addition of petroleum ether. Recrystallization from acetone–petroleum ether gave yellow crystals in a 63% yield (96%).

*Reaction of **5a** with K(acac).* To a solution of **5a** (224 mg, 0.296 mmol for n=1) in dichloromethane (20 cm^3) was added dropwise a methanol (10 cm^3) solution of K(acac) (57 mg, 0.412 mmol). After being stirred for 2 h, the solvent was evaporated to dryness under reduced pressure. Dichloromethane (10 cm^3) was added to the residue and the undissolved $KClO_4$ was filtered off. Addition of petroleum ether to the filtrate gave a yellow plates (126 mg) of **3b** in an 84% yield.

*Preparation of the Cationic [Pd(CH_2CN)(acetone)(PPh_3)$_2$](hfac) (**6**) by the Reaction of **5a** with K(hfac).* A solution of K(hfac) (70 mg, 0.282 mmol) in methanol (3 cm^3) was added slowly to a dichloromethane (20 cm^3) solution of **5a** (218 mg, 0.282 mmol for m=1). After being stirred for 10 min, the solvent was evaporated to dryness, the residue was redissolved in a small amount of acetone, and then the undissolved $KClO_4$ was filtered off. Petroleum ether was added to the filtrate and the solution was allowed to stand to separate yellow needles of **6** in a 26% yield (65 mg).

*Preparation of the Cationic [Pd(CH_2CN)(dppe)]$_2$(hfac)$_2$ (**7**) by the Reaction of **2** with Tl(hfac).* Complex **2** (232 mg, 0.400 mmol) was allowed to react with Tl(hfac) (165 mg, 0.400 mmol) in refluxing acetone over 20 h. After the solvent was evaporated to dryness, dichloromethane was added to the residue, the undissolved TlCl was filtered off, and again the solvent was evaporated to dryness. The residue was redissolved in a small amount of acetone and diethyl ether was added to precipitate acetone solvate of **7**. The product was collected, washed with diethyl ether, and then dried *in vacuo* at 50 °C for 3 h. The yield of a yellow powder of **7** was 109 mg (36%).

*Preparation of the Cationic [Pd(CH_2CN)(dppe)]$_2$X$_2$ (X= ClO_4(**8a**) or BF_4 (**8b**)) by Chloride Abstraction of **2**.* To a solution of **2** (160 mg, 0.275 mmol) in dichloromethane (13 cm^3) was added dropwise a solution of $AgClO_4$ (57 mg, 0.275 mmol) in methanol (15 cm^3). After being stirred for 19 h, the precipitated AgCl was filtered off and the filtrate was concentrated under reduced pressure to deposit a white powder of **8a**, which was gathered and washed with acetone and dried *in vacuo*. The yield was 136 mg (77%). In the case of the reaction of **2** with $AgBF_4$, after removal of the precipitated AgCl, the solvent was evaporated to dryness. The residue was redissolved in dichloromethane and diethyl ether was added to obtain a white precipitate of **8b**. Recrystallization twice from dichloromethane–diethyl ether gave a white powder in a 79% yield.

*Reaction of **8a** with K(hfac).* A solution of K(hfac) (74 mg, 0.300 mmol) in methanol (10 cm^3) was added to a suspension of **8a** (120 mg, 0.132 mmol) in dichloromethane (10 cm^3). After being stirred for 2 h at room temperature, the solvent was evaporated to dryness under reduced pressure to leave **7** and $KClO_4$. The residue was redissolved in methanol and the undissolved $KClO_4$ was removed by filtration. The solvent was again evaporated to dryness and the crude product was recrystallized twice from acetone-diethyl ether to give a white powder of **7**. The yield was 119 mg (56%).

Measurements. Infrared spectra were obtained in Nujol mull or in a chloroform solution with a JASCO DS 701G (4000—200 cm^{-1}) infrared spectrophotometer. NMR spectra in $CDCl_3$ or CD_3CN were recorded on JEOL JNM MH-100 (for ^{1}H), FX-60Q (for ^{13}C and ^{31}P) instruments. Molecular weight was determined in CH_2Cl_2 (at 28 °C) or CH_3CN (at 39 °C) with a vapor pressure osmometer manufactured by Knauer, West Berlin, West Germany.

References

1) W. J. Blend, R. D. W. Kemmitt, and R. D. Moore, *J. Chem. Soc., Dalton Trans.*, **1973**, 1292.
2) K. Suzuki and H. Yamamoto, *J. Organomet. Chem.*, **54**, 385 (1973).
3) K. Suzuki, H. Yamamoto, and S. Kanie, *J. Organomet. Chem.*, **73**, 131 (1974).
4) K. Suzuki, J. Ooyama, and M. Sakurai, *Bull. Chem. Soc. Jpn.*, **49**, 464 (1976).
5) R. Ros, J. Renaud, and R. Roulet, *Helv. Chim. Acta*, **58**, 133 (1975).
6) R. Ros, J. Renaud, and R. Roulet, *J. Organomet. Chem.*, **87**, 379 (1975).
7) R. Ros, M. Lenarda, T. Boschi, R. Roulet, *Inorg. Chim. Acta*, **25**, 61 (1977).
8) A. D. Pra, G. Zanotti, G. Bombieri, and R. Ros, *Inorg. Chim. Acta*, **36**, 121 (1979).
9) R. McCrindle, G. Ferguson, A. J. McAlees, M. Parvez, and P. J. Roberts, *J. Chem. Soc., Dalton Trans.*, **1982**, 1699.
10) R. Ros, J. Renaud, and R. Roulet, *J. Organomet. Chem.*, **104**, 271 (1976).
11) R. Ros, J. Renaud, and R. Roulet, *J. Organomet. Chem.*, **104**, 393 (1976).
12) R. Ros, R. A. Michelin, T. Boschi, and R. Roulet, *Inorg. Chim. Acta*, **35**, 43 (1979).
13) K. Suzuki and M. Sakurai, *Inorg. Chim. Acta*, **20**, L13 (1976).
14) K. Suzuki and K. Hanaki, *Inorg. Chim. Acta*, **20**, L15 (1976).
15) R. C. Mehrotra, R. Bohra, and D. P. Gaur, "Metal β-Diketonates and Allied Derivatives," Academic Press, New York (1978).
16) B. N. Storhoff and H. C. Lewis, Jr., *Coord. Chem. Rev.*, **23**, 1 (1977).
17) S. Okeya, S. Ooi, K. Matsumoto, Y. Nakamura, and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **54**, 1085 (1981).
18) S. Baba, T. Ogura, and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **47**, 665 (1974).
19) K. Yamada, S. Baba, Y. Nakamura, and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **56**, 1393 (1983).
20) G. Oehme, K.-C. Roeber, and H. Praceijus, *J. Organomet. Chem.*, **105**, 127 (1976).

21) D. Schwarzenbach, A. Pinkerton, G. Chapuis, J. Wenger, R. Ros, and R. Roulet, *Inorg. Chim. Acta*, **25**, 255 (1977).
22) M. H. Chisholm, H. C. Clark, L. E. Manzer, J. B. Stothers, and J. E. H. Ward, *J. Am. Chem. Soc.*, **95**, 8574 (1973).
23) S. Okeya, Y. Nakamura, S. Kawaguchi, and T. Hinomoto, *Inorg. Chem.*, **20**, 1576 (1981).
24) S. Okeya, Y. Kawakita, S. Matsumoto, Y. Nakamura, S. Kawaguchi, N. Kanehisa, K. Miki, and N. Kasai, *Bull. Chem. Soc. Jpn.*, **55**, 2134 (1982).
25) S. Okeya, Y. Nakamura, S. Kawaguchi, and T. Hinomoto, *Bull. Chem. Soc. Jpn.*, **55**, 477 (1982).
26) a) 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); b) S. Okeya, Y. Nakamura, and S. Kawaguchi, *ibid.*, **54**, 3396 (1981).
27) Various Tl(β-dik) complexes were prepared according to the preparative method for Tl(bzac): W. H. Nelson, W. J. Randall, and D. F. Martin, Inorg. Synth., Vol. IX, 53 (1967).
28) See text and Ref. 26.