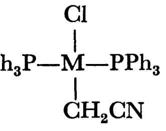
Cyanoalkyl Complexes of Transition Metals. IV. Geometry and Spectroscopic Properties of Cyanomethyl Complexes of Palladium(II) and Platinum(II)

Keinosuke Suzuki, Junichi Ooyama, and Masami Sakurai
Inorganic Chemistry Laboratory, Faculty of Science, Nagoya University, Chikusa, Nagoya 464

(Received August 11, 1975)

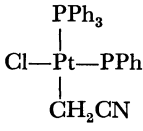
A number of cyanomethyl complexes of palladium(II) and platinum(II) were prepared and characterized by proton nuclear magnetic resonance and infrared spectroscopy. It was shown that the methylene resonance, phenyl resonance, and a strong band at 550±5 cm^{-1} are acceptable criteria for deducing the geometry of the complexes $MX(CH_2CN)(PPh_3)_2$ (M=Pd, Pt). The criteria allow us to assign the *cis* geometry to the bromo and iodo complexes of platinum(II) both of which showed an unusual methylene resonance. An approximately linear relationship holds between ^2J(Pt-H) of *trans*-$PtX(CH_2CN)(PPh_3)_2$ and that of *trans*-$PtX(CH_3)(PPh_3)_2$ (X=Cl, Br, I, N_3, NO_2, NO_3).

It has been well established that the stereochemistry of square-planar bis(phosphine)-transition metal complexes can be determined by ^1H NMR if the phosphines contain methyl or methylene groups attached to the phosphorus atom.[1-8] However, this method is inadequate when the phosphine is triphenylphosphine. Recently we reported the synthesis and spectroscopic properties of $PdCl(CH_2CN)(PPh_3)_2$[9] (**1a**), *trans*- and *cis*-$PtCl(CH_2CN)(PPh_3)_2$[10] (**1b**, **2**) and demonstrated that the gross geometry of these complexes could be determined by the ^1H NMR spectrum of the cyanomethyl protons. The methylene resonance of **1a** and **1b** appeared as a triplet due to spin-spin coupling with two equivalent phosphorus atoms. On the other hand the same resonance of **2** occurred as a 1 : 1 : 1 : 1 doublet of doublets because of the two non-equivalent phosphorus atoms. The cyanomethyl protons of $PtCl(CH_2CN)(diphos)$ (**3**, diphos=$Ph_2PCH_2CH_2PPh_2$) also gave a doublet of doublets in accordance with *cis* geometry. The methylene resonance seems to be useful as a criterion for determining the stereochemistry of the complexes $MX(CH_2CN)(PPh_3)_2$. However, we found in the course of studies on cyanomethyl complexes that care should be taken in making deductions about the geometry of $MX(CH_2CN)(PPh_3)_2$ solely from the methylene resonance. In this paper we describe the preparation of several cyanomethyl complexes of palladium(II) and platinum(II) and discuss the method of establishing their geometry on the basis of IR and ^1H NMR spectral data.



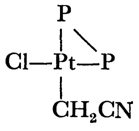
$$\begin{array}{c} Cl \\ | \\ Ph_3P{-}M{-}PPh_3 \\ | \\ CH_2CN \end{array}$$

1a, M=Pd
1b, M=Pt



$$\begin{array}{c} PPh_3 \\ | \\ Cl{-}Pt{-}PPh_3 \\ | \\ CH_2CN \end{array}$$

2



$$\begin{array}{c} P \\ |\diagdown \\ Cl{-}Pt{-}P \\ | \\ CH_2CN \end{array}$$

3, P-P=diphos

Experimental

High frequency infrared spectra (4000—700 cm^{-1}) were recorded on a JASCO-DS-402G spectrometer with samples prepared as Nujol or hexachlorobutadiene mulls. Low frequency spectra (700—200 cm^{-1}) were recorded on a HITACHI EPI-L2 spectrometer with samples as Nujol mulls. The ^1H NMR spectra were recorded on a JEOL-C6OH spectrometer with TMS as an internal standard.

Starting Materials. Chlorocyanomethylbis(triphenylphosphine)-palladium (II) **1a**, *trans*- and *cis*-chlorocyanomethylbis(triphenylphosphine)platinum(II) **1b** and **2**, were prepared as reported previously.[9,10] Commercial reagents and solvents were used without purification. Microanalyses were performed by Wako Pure Chemical Industries, Ltd.

Preparation of $PdX(CH_2CN)(PPh_3)_2$ *(X=NCO,* N_3*, I,* NO_2*,* $N(CO)_2C_6H_4$*, CN).* Potassium cyanate (0.07 g, 0.86 mmol) was added to a solution of **1a** (0.50 g, 0.71 mmol) dissolved in 150 ml of acetone and stirred for 3 hr at room temperature. The yellow color of the solution disappeared and a small amount of white solid was obtained. It was filtered off and the filtrate was concentrated to give a white precipitate of $Pd(NCO)(CH_2CN)(PPh_3)_2$. The precipitate was filtered, washed with acetone and dried *in vacuo.* The azido, iodo, nitro, and phthalimido complexes were prepared similarly in acetone (sodium azide, potassium iodide) or methanol (sodium nitrite, potassium phthalimide).

A suspension of potassium cyanide (0.046 g, 0.73 mmol) and **1a** (0.50 g, 0.71 mmol) in 150 ml of methanol was heated at 55—60 °C for 2 hr. The resulting yellow solution was allowed to stand at room temperature to afford pale yellow crystals of $Pd(CN)(CH_2CN)(PPh_3)_2$ containing two molecules of methanol.

Preparation of trans-$PtX(CH_2CN)(PPh_3)_2$ *(X=NCO,* N_3*,* NO_2*,* $N(CO)_2C_6H_4$*,* NO_3*,* CH_3COO*),* Potassium cyanate (0.045 g, 0.55 mmol) and **1b** (0.35 g, 0.44 mmol) were suspended in a mixed solvent of benzene (100 ml) and ethanol (50 ml) and refluxed for 5 hr. The resulting yellow solid was filtered and recrystallized from chloroform-diethyl ether to give *trans*-$Pt(NCO)(CH_2CN)(PPh_3)_2$. Similarly *trans*-$Pt[N(CO)_2C_6H_4](CH_2CN)(PPh_3)_2$ was prepared by the reaction of **1b** with potassium phthalimide in a mixed solvent of acetone and ethanol (1 : 1). *trans*-$Pt(N_3)(CH_2CN)(PPh_3)_2$ was synthesized by the reaction of **1b** with sodium azide in ethanol at room temperature.

A suspension of **1b** (0.50 g, 0.63 mmol) and silver nitrate (0.107 g, 0.63 mmol) in 150 ml of acetone was stirred for 12 hr at room temperature in the dark. The silver chloride formed was removed by filtration and the filtrate was concentrated to dryness *in vacuo.* The white residue was recrystallized from dichloromethane-diethyl ether to give white crystals of *trans*-$Pt(NO_3)(CH_2CN)(PPh_3)_2$. It contained one molecule of dichloromethane. *trans*-$Pt(CH_3COO)(CH_2CN)(PPh_3)_2$ was prepared in the same way with the use of silver acetate. *trans*-$Pt(NO_2)(CH_2CN)(PPh_3)_2$ was prepared by the reaction of *trans*-$Pt(NO_3)(CH_2CN)(PPh_3)_2$ with potassium nitrite in acetone.

Preparation of cis-$PtX(CH_2CN)(PPh_3)_2$*(X=NCO,* N_3*,* NO_2*, Br, I).* Lithium bromide (0.04 g, 0.46 mmol) and **2**

TABLE 1. PHYSICAL PROPERTIES AND ANALYTICAL DATA OF $MX(CH_2CN)(PPh_3)_2$

Complex		Color	Mp,[a] °C	Yield %	Analyses, % found (calcd)		
M	X				C	H	N
Pt (*trans*)	N_3	pale yellow	211—215	70	56.40 (56.90)	4.05 (4.03)	6.77 (6.99)
	NCO	pale yellow	230—235	80	58.11 (58.40)	4.16 (4.03)	3.53 (3.49)
	NO_2	white	223—226	50	56.13 (56.62)	3.89 (4.01)	3.23 (3.48)
	$N(CO)_2C_6H_4$	white	260—272	70	60.52 (60.83)	3.98 (4.23)	2.80 (3.09)
	$NO_3 \cdot CH_2Cl_2$[b]	white	185—200	50	51.55 (51.64)	3.64 (3.79)	3.05 (3.09)
	CH_3CO_2	white	205—217	50	57.92 (58.65)	4.41 (4.32)	1.37 (1.71)
Pt (*cis*)	N_3	white	190—220	60	56.60 (56.90)	3.91 (4.03)	7.13 (6.99)
	NCO	white	240—260	80	57.86 (58.40)	4.01 (4.03)	3.22 (3.49)
	NO_2	white	220—234	75	55.95 (56.62)	3.96 (4.01)	3.14 (3.48)
	$Br \cdot CH_2Cl_2$[b]	pale yellow	240—250	60	49.99 (50.67)	3.61 (3.71)	1.47 (1.51)
	I	yellow	235—241	75	51.10 (51.45)	3.71 (3.65)	1.65 (1.58)
Pd	$N_3 \cdot CH_2Cl_2$[b]	yellow	155—161	65	58.73 (58.69)	4.26 (4.26)	7.03 (7.02)
	$NCO \cdot (CH_3)_2CO$[b]	pale yellow	183—188	80	65.00 (65.42)	4.72 (4.93)	3.55 (3.64)
	NO_2	white	178—185	50	63.26 (63.65)	3.62 (3.91)	4.25 (4.50)
	$N(CO)_2C_6H_4$	white	192—198	60	66.86 (67.63)	4.34 (4.43)	3.28 (3.43)
	$I \cdot (CH_3)_2CO$[b]	yellow	172—178	55	54.83 (54.55)	3.95 (4.35)	1.31 (1.56)
	$CN \cdot 2CH_3OH$[b]	pale yellow	140—150	50	64.71 (64.97)	5.29 (4.98)	3.68 (3.52)

a) All complexes melted with decomposition. b) The existence of one mole of dichloromethane and acetone and two moles of methanol was confirmed by ^1H NMR.

(0.20 g, 0.25 mmol) were dissolved in a mixed solvent of methanol (30 ml) and bromoform (15 ml). The solution was refluxed for 0.5 hr and then concentrated *in vacuo*. Addition of diethyl ether to the solution caused the precipitation of a pale yellow solid, which was recrystallized from dichloromethane-petroleum ether to afford pale yellow crystals of *cis*-$PtBr(CH_2CN)(PPh_3)_2$. It contained one molecule of dichloromethane.

A suspension of **2** (0.50 g, 0.63 mmol) and lithium iodide trihydrate (0.15 g, 0.80 mmol) in methanol (20 ml) was stirred for 5 hr at room temperature. The white suspension turned into a yellow solid. It was filtered and recrystallized from dichloromethane-diethyl ether to give yellow crystals of *cis*-$PtI(CH_2CN)(PPh_3)_2$. *cis*-$Pt(NCO)(CH_2CN)(PPh_3)_2$ and *cis*-$Pt(NO_2)(CH_2CN)(PPh_3)_2$ were synthesized by the reaction of **2** with potassium cyanate or potassium nitrite in a similar manner, after being stirred for 24 hr at room temperature. *cis*-$Pt(N_3)(CH_2CN)(PPh_3)_2$ was similarly prepared by the reaction of **2** with sodium azide. Heating under reflux for 5 hr was necessary.

Physical properties and analytical data of new cyanomethyl complexes are given in Table 1.

Results and Discussion

Most of the cyanomethyl complexes were prepared by simple metathesis according to

$$MCl(CH_2CN)(PPh_3)_2 + X^- \rightarrow MX(CH_2CN)(PPh_3)_2 + Cl^-$$

For the nitrato and acetato complexes of platinum(II), it was necessary to utilize silver nitrate or silver acetate in order to abstract the chloride ion. However, application of this method to **1a** and **2** was unsuccessful.

An interesting property of the palladium complexes is photochromism. In the solid state, all palladium complexes except the cyano derivative change color (B) when exposed to light, but revert to the original color (A) in the dark. This color change is reversible but not observed in solution. The observed color changes are summarized in Table 2. In contrast to the palladium complexes, neither *cis*- nor *trans*-$PtX(CH_2CN)(PPh_3)_2$ showed similar color changes. Thus the phenomenon seems to be characteristic of the cyanomethyl complexes of palladium(II), but the cause has not been clarified.

TABLE 2. PHOTOCHROMISM OF $PdX(CH_2CN)(PPh_3)_2$

X	N_3	NCO	NO_2	$N(CO)_2C_6H_4$	I
A	yellow	pale yellow	white	white	yellow
B	orange	pale orange	pale orange	red	brown

All the complexes are stable in the air both in the solid state and in solution. They are soluble in chloroform and dichloromethane but sparingly soluble in diethyl ether.

Spectroscopic Features of $MX(CH_2CN)(PPh_3)_2$. ^1H NMR spectral data are given in Table 3. They show that the methylene resonance of complexes prepared from **1a** and **1b** consists of a 1 : 2 : 1 triplet without exception while the same resonance of azido, cyanato, and nitro complexes derived from **2** occurs as a 1 : 1 : 1 : 1 doublet of doublets. For the platinum complexes of the same composition, the triplet always appeared at much higher field relative to the doublet of doublets (*ca.* 0.6 ppm). The coupling constants, ^2J(Pt–H) of the triplets (90.0—109.5 Hz) are much larger than those for the doublet of doublets (76.5—79.5 Hz). The methylene resonance of two azide complexes of platinum (II) illustrates these spectroscopic features (Fig. 1). The results confirm the previous observation based on the spectral data of the chloro complexes and suggest that the methylene resonance, if it satisfies the conditions mentioned above, will provide a method to distinguish *cis*-$MX(CH_2CN)(PPh_3)_2$ from the corresponding *trans* isomer. The difference of the chemical shift of the methylene protons (0.6 ppm) is larger than

Table 3. ^{1}H NMR Data for the cyanomethyl complexes $MX(CH_2CN)(PPh_3)_2$[a]

M	X	$\tau(CH_2CN)$ ppm	^2J(Pt-H) Hz	^3J(P-H) Hz	τ(Ph)[b] ppm
Pt (*trans*)	N_3	9.09 t	102.0	7.5	2.5m, 2.3m
	NCO	9.12 t	103.5	8.0	2.5m, 2.3m
	NO_2	9.03 t	90.0	8.0	2.5m, 2.3m
	$N(CO)_2C_6H_4$	8.89 t	97.0	7.5	2.7m,[e] 2.3m
	NO_3	8.68 t	109.5	7.5	2.5m, 2.3m
	CH_3CO_2[c]	8.95 t	105.5	7.5	2.6m, 2.3m
Pt (*cis*)	N_3	8.50 dd	76.5	9.0, 5.0	2.6m
	NCO	8.52 dd	78.0	9.5, 6.0	2.7m
	NO_2	8.38 dd	78.0	8.5, 5.5	2.7m
	Br	8.19	78.0	[d]	2.6m
	I	7.91	79.5	[d]	2.7m
Pd	N_3	9.21 t		7.5	2.5m, 2.3m
	NCO	9.27 t		7.5	2.5m, 2.3m
	NO_2	9.27 t		7.5	2.5m, 2.3m
	$N(CO)_2C_6H_4$	9.10 t		7.5	2.7m,[e] 2.3m
	I	8.86 t		7.5	2.6m, 2.3m
	CN	9.48 t		7.5	2.5m, 2.3m

a) Spectra were recorded in $CDCl_3$ at 21 °C. Key: m, multiplet; dd, doublet of doublets; t, triplet. b) The approximate center of each multiplet is listed. c) $\tau(CH_3)=9.21$, $^4J(Pt-H)=\sim 3$ Hz. d) See text. e) An apparent doublet also appeared at τ 2.90.

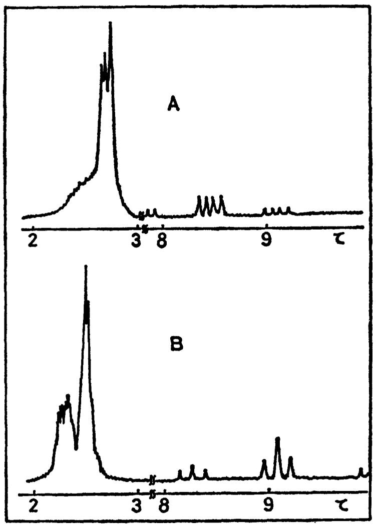


Fig. 1. ^{1}H NMR spectra of (A) *cis*- and (B) *trans*-$Pt(N_3)(CH_2CN)(PPh_3)_2$.

that of the methyl protons for *cis*- and *trans*-$PtX(CH_3)(PEt_3)_2$[11] (*ca.* 0.2 ppm). The larger difference found in the cyanomethyl complexes might be due to the ring current of the coordinated triphenylphosphine.

Nelson *et al.*[12] showed that when two phenylphosphines, in square-planar complexes, are *trans* to one another the phenyl resonance occurs as two broad multiplets, whereas if they are *cis*, only one broad multiplet is usually observed. Figure 1 indicates this is true for the complexes we studied. The phenyl resonance of the cymplexes which exhibited a triplet occurred as two broad multiplets centered at τ 2.3 and 2.5—2.7 while only one multiplet was found for the complexes accompanied by a doublet of doublets. Thus the phenyl resonance of $MX(CH_2CN)(PPh_3)_2$ also provides identification of the stereochemistry of the cyanomethyl complexes.

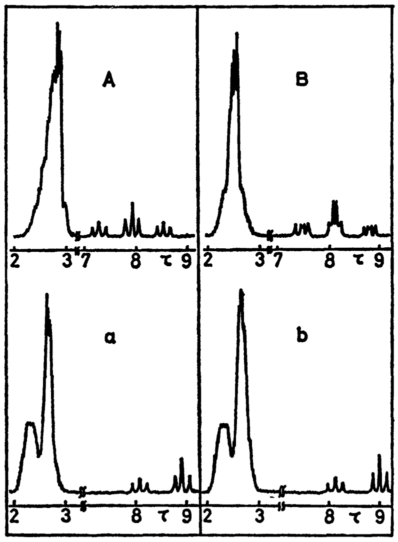


Fig. 2. ^{1}H NMR spectra of the bromo and iodo complexes of platinum(II). (A) *cis*-$PtI(CH_2CN)(PPh_3)_2$, (a) *trans*-$PtI(CH_2CN)(PPh_3)_2$, (B) *cis*-$PtBr(CH_2CN)(PPh_3)_2$, (b) *trans*-$PtBr(CH_2CN)(PPh_3)_2$.

Recently, Mastin[13] gave a convenient method for directly determining the stereochemistry of the complexes $PtXY(PPh_3)_2$ and proposed the use of the intensity of a band at 550±5 cm^{-1} as a simple criterion for assignment of their stereochemistry. The complexes which showed a doublet of doublets and one multiplet gave a strong absorption at 550±5 cm^{-1} without exception (Table 4). On the other hand, none of the complexes to which the *trans* geometry was assigned on the basis of the methylene and phenyl resonance showed any strong absorption in this region. Thus Mastin's proposal is a useful tool for determining the geometry of $MX(CH_2CN)(PPh_3)_2$.

For the cyanomethyl complexes discussed so far, one of the three criteria was consistent with the other two, suggesting each of them is normally a reliable criterion in determining the stereochemistry of the complexes $MX(CH_2CN)(PPh_3)_2$.

Geometry of $PtX(CH_2CN)(PPh_3)_2$*(X=Br, I).* ^1H NMR spectra of the bromo and iodo complexes of platinum(II) prepared from **2** are shown in Fig. 2, which includes the spectra of the corresponding *trans* isomers for the sake of comparison. The splitting pattern of the methylene resonance differs from that expected for the *cis* geometry. In particular the NMR spectrum of the iodo complex is of interest in that the methylene resonance appeared as a 1 : 2 : 1 triplet which is typical of *trans*-$PtX(CH_2CN)(PPh_3)_2$ (Figs. 1 and 2). However, this triplet is not due to the formation of *trans*-$PtI(CH_2CN)(PPh_3)_2$ since its chemical shift (τ 7.91) and the coupling constant ^2J(Pt-H) (79.5 Hz) are quite different from those of the *trans* isomer[10] (τ 8.88, ^2J(Pt–H)=102.0 Hz). Thus, in order to deduce their geometry, the other criteria were considered. First, the methylene resonance of the bromo (τ 8.19) and iodo (τ 7.91) complexes in question appear at much lower fields than those of the *trans* isomers (τ 8.98 (Br), τ 8.81(I)) and rather close to those of the diphosphine complexes (τ 8.27 (Br), τ 8.03(I)).[10] Furthermore, the coupling constant ^2J(Pt–H) of both complexes (Br=78.0, I=79.5 Hz) is also comparable with the values found for the other *cis* isomers (Table 3) but smaller than those obtained for the *trans* isomers. Second, the phenyl resonance exhibits only one broad multiplet centered at τ 2.6 (Br) and 2.7 (I), while *trans* isomers gave two broad multiplets (Fig. 2). A strong absorption was observed at 545 cm^{-1} for both bromo and iodo complexes but not for the corresponding *trans* isomers. These spectroscopic data led us to assign the *cis* geometry to the bromo and iodo complexes, although their methylene resonance showed no expected nultiplets. This demonstrates that the spectral pattern of the methylene protons alone is insufficient for deducing the geometry of $MX(CH_2CN)(PPh_3)_2$.

The methylene resonance of *cis*-$PtBr(CH_2CN)(PPh_3)_2$ shows different multiplet structures in the side bands and in the center band (Fig. 2). Similar unusual spectra have been reported for some hydride complexes of platinum(II)[14] and interpreted on the basis of the relative magnitude of the chemical shift difference of two phosphorus atoms and the coupling constant J(Pt–P). Although we could not analyze the spectrum, the observed anomaly might be explained in a similar manner.

Recently, Ros *et al.*[15] have measured the proton decoupled ^{31}P NMR spectrum of *cis*-$PtCl(CH_2CN)(PPh_3)_2$ and observed two sets of doublet with equal intensity. Therefore we assumed an AMX_2 spin system (A=M=P, X=H) for the *cis* complexes which showed a doublet of doublets. The coupling constants ^3J(P–H) for these complexes are listed in Table 3. The unusual methylene resonance of the bromo and iodo complexes cannot be explained in terms of the same spin system. Instead of the ^3J(P–H) we tentatively report a separation between the two inside strong peaks (*ca.* 2.5 Hz) and one between the two outside peaks (*ca.* 14.5 Hz) for the bromo complex, and a separation between the central peak and one of the two outside peaks (*ca.* 7.5 Hz) for the iodo complex.

The methylene resonance of *cis*-$PtX(CH_2CN)(PPh_3)_2$ changes from a doublet of doublets (X=Cl)[10] to a triplet (X=I) through an intermediate pattern (X=Br), but no similar variations have been observed for $PtX(CH_2CN)(P\text{–}P)$ (X=Cl, Br, I). X-Ray structural analysis of $[Rh(P\text{–}P)_2]^+$ [16] and $[Ir(PMePh_2)_4]^+$ [17] indicates that the steric crowding around the central metal atom is larger for the latter. Since triphenylphosphine is more bulky than methyldiphenylphosphine, it is likely that greater distortion from the planar configuration is found in $PtX(CH_2CN)(PPh_3)_2$ than $PtX(CH_2CN)(P\text{–}P)$ and enhanced with increase in the size of a halogen atom. Thus, the observed variation in the methylene resonance might be partially due to this distortion.

^2J(Pt–H). The coupling constant, ^2J(Pt–H) of *trans*-$PtX(CH_2CN)(PPh_3)_2$ is larger than that of *trans*-$PtX(CH_3)(PPh_3)_2$.[18] These two coupling constants are related to one another by a reasonably linear relationship (Fig. 3). The dependence of ^2J(Pt–H) on the substituent R in the $Pt\text{–}CH_2R$ moiety is not clear at present, but it is evident that the nitrile group increases the absolute value of ^2J(Pt–H) as is found for the coupling constant ^2J(H–H).[19]

The coupling constant ^2J(Pt–H) of *trans*-$PtX(CH_2CN)(PPh_3)_2$ increases in the order

$$NO_2 < N(CO)'_2C_6H_4 < N_3,\ I$$
$$< NCO,\ Br < Cl < CH_3CO_2 < NO_3^-$$

This is in line with the NMR *trans*-influence order given by Appleton, Clark, and Manzer.[20]

Infrared Spectra. All the complexes studied showed a sharp strong band due to ν(CN) at *ca.* 2200 cm^{-1}. The band is useful in identifying the presence of the CH_2CN group but gives little information on the geometry of the cyanomethyl complexes.

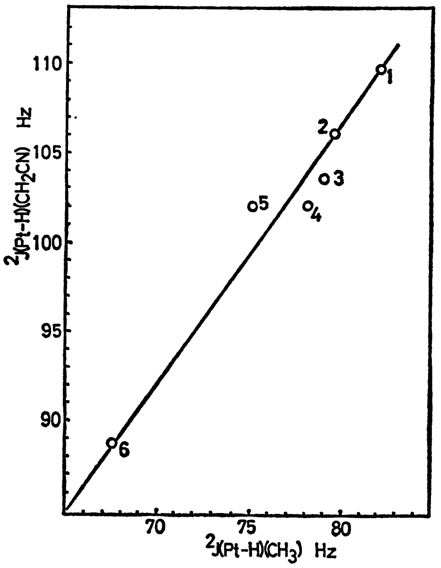


Fig. 3. A plot of ^2J(Pt–H) of *trans*-$PtX(CH_2CN)(PPh_3)_2$ *vs.* ^2J(Pt–H) of *trans*-$PtX(CH_3)(PPh_3)_2$. X=NO_3 (1), Cl (2), Br (3), I (4), N_3 (5), NO_2 (6).

Table 4. Characteristic infrared frequencies (cm^{-1}) in $MX(CH_2CN)(PPh_3)_2$

M	X	ν(CN)	ν(MX)	Band at *ca.* 550 cm^{-1} a)
Pt	N_3	2215 s	375m	
(*trans*)	NCO	2210 s	335w	
	NO_2	2220 s	286m	543w
	$N(CO)_2C_6H_4$	2215 s	353m	
	NO_3	2210 s	292m	546w
	CH_3CO_2	2210 s		544w
Pt	N_3	2210 s	378m	548 s
(*cis*)	NCO	2200 s	360m	550 s
	NO_2	2210 s	289m	545 s
	Br	2200 s		545 s
	I	2200 s		545 s
Pd	N_3	2210 s	355w	
	NCO	2220 s	330w	
	NO_2	2220 s	280m	
	$N(CO)_2C_6H_4$	2220 s	350m	
	I	2200 s		
	CN	2210 s		

a) See text.

A comparison between ν(Pt–X) of *cis*- and *trans*-$PtX(CH_2CN)(PPh_3)_2$ ($X=N_3$, NCO, NO_2) indicates that the *trans*-influence of the CH_2CN group is slightly higher than that of triphenylphosphine.

We could not prepare *cis*-$PdX(CH_2CN)(PPh_3)_2$ and examine the presence or absence of a strong band at 550±5 cm^{-1}. Thus, for the palladium complexes, the validity of Mastin's criterion is uncertain, although none of the *trans*-$PdX(CH_2CN)(PPh_3)_2$ complexes showed a strong absorption in this region.

References

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

2) D. G. Cooper and J. Powell, *J. Amer. Chem. Soc.*, **95**, 1102 (1973).

3) D. A. Redfield and J. H. Nelson, *Inorg. Chem.*, **12**, 15 (1973).

4) B. E. Mann, B. L. Shaw, and, R. C. Stainbank, *Chem. Commun.*, **1972**, 151.

5) D. G. Cooper and J. Powell, *Can. J. Chem.*, **51**, 1634 (1973).

6) M. H. Chisholm and H. C. Clark, *Inorg. Chem.*, **12**, 991 (1973).

7) D. A. Redfield, J. H. Nelson, R. A. Henry, D. W. Moore, and H. B. Jonassen, *J. Amer. Chem. Soc.*, **96**, 6298 (1974).

8) D. A. Redfield, L. W. Carry, and J. H. Nelson, *Inorg. Chem.*, **14**, 50 (1975).

9) K. Suzuki and H. Yamamoto, *J. Organometal. Chem.*, **54**, 385 (1973).

10) K. Suzuki, H. Yamamoto, and S. Kanie, *J. Organometal. Chem.*, **73**, 131 (1974).

11) F. H. Allen and A. Pidcock, *J. Chem. Soc., A*, **1968**, 2700.

12) J. H. Nelson, A. W. Verstuyft, J. D. Kelly, and H. B. Jonassen, *Inorg. Chem.*, **13**, 27 (1974).

13) S. H. Mastin, *ibid.*, **13**, 1003 (1974).

14) T. W. Dingle and K. R. Dixon, *ibid.*, **13**, 846 (1974).

15) R. Ros, J. Renaud, and R. Roulet, *Helv. Chim. Acta*, **58**, 133 (1975).

16) M. C. Hall(nee Barrett), B. T. Kilbourn, and K. A. Taylor, *J. Chem. Soc., A*, **1970**, 2539.

17) G. R. Clark, B. W. Skelton, and T. N. Waters, *J. Organometal. Chem.*, **85**, 375 (1975).

18) C. D. Cook and K. Y. Wan, *ibid.*, **92**, 2595 (1970).

19) M. Barfield and D. M. Grant, *ibid.*, **85**, 1899 (1963).

20) T. G. Appleton, H. C. Clark, and L. E. Manzer, *Coord. Chem. Rev.*, **10**, 335 (1973).