July, 1971] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1873—1875 (1971) 1873

Studies on the Interaction of Isocyanides with Transition-metal Complexes. VII.[1] Insertion Reactions of Isocyanide into Alkyl-platinum Sigma Bonds[2]

Yasuhiro YAMAMOTO and Hiroshi YAMAZAKI
The Institute of Physical and Chemical Research, Wako-shi, Saitama

(Received October 29, 1970)

The reactions of *trans*-iodobis(phosphine)aklylplatinum(II) compounds with isocyanide were carried out. The reactions of isocyanide with the methyl and benzyl derivatives of platinum(II) with triphenylphosphine or dimethylphenylphosphine gave salt-like complexes [*trans*-Pt$(PR_3)_2(CNR')CH_3$]I (**1**) (PR_3=PPh_3, $PPhMe_2$; R'=C_6H_{11}, $C(CH_3)_3$). When **1** was refluxed in benzene or toluene, an insertion of isocyanide took place, affording *trans*-iodobis(phosphine)(1-cyclohexylimino)alkylplatinum(II). Two P-CH_3 proton resonances were observed in the NMR spectrum of *trans*-Pt$(PPhMe_2)_2I[C(CH_3)=NC_6H_{11}]$, indicating that the two methyl groups on the same phosphorus atom are magnetically nonequivalent. It was deduced from this NMR behavior that all the iminoacyl complexes prepared have a five-coordinate structure.

We have reported that the reactions of cyclohexyl isocyanide with the metal alkyls, such as triphenylphosphine-π-cyclopentadienylnickel and tricarbonyl-π-cyclopentadienylbenzylmolybdenum, inserted isocyanide into a carbon-to-metal bond to give π-cyclopentadienyl(cyclohexyl isocyanide)(1-cyclohexylimino)ethylnickel[3] and tricarbonyl-π-cyclopentadienyl(1-cyclohexylimino)(2-phenyl)ethylmolybdenum.[4] Recently we also found that the reaction of isocyanide with *trans*-iodobis(phosphine)alkylpalladium(II) took place with successive insertions of isocyanide molecules, thus affording the iminoacyl complexes of palladium(II) with five-coordinate structures.[5,6]

In our extensive studies of the alkyl complexes of platinum(II), we found that isocyanides react with methyl and benzyl complexes of platinum(II) to produce five-coordinate iminoacyl complexes.

A recent note[7] on the reaction of methyl isocyanide with *trans*-halobis(triphenylphosphine)alkylplatinum(II) to give the iminoacyl complexes of platinum(II) has prompted us to report on other iminoacyl complexes obtained from isocyanides and alkyl complexes of platinum(II). We found that this type of iminoacyl complexes has a five-coordinate structure with a platinum atom bound to imino-nitrogen.

Results and Discussion

The treatment of cyclohexyl isocyanide with *trans*-iodobis(phosphine)methylplatinum(II) in a 1 : 1 molar ratio in benzene at room temperature gave colorless crystals formulated as a 1 : 1 adduct $Pt(PR_3)_2(CNC_6H_{11})(CH_3)I$ (**1**), based on its elemental analysis. The compounds (**1**) are soluble in methyl alcohol, methylene chloride, and chloroform, and are insoluble in nonpolar solvents such as benzene and hexane.

The IR spectrum of each compound showed a characteristic band in the range from 2178 to 2210 cm^{-1}, this spectrum was attributable to the coordinated isocyanide group. The value of the $\nu_{N\equiv C}$ bond of the coordinated isocyanide group was approximately 70 cm^{-1} higher than the corresponding value of the uncoordinated one. The formation of $[Pt(PPh_3)_2(CNC_6H_{11})(CH_3)]BPh_4$ from the reaction of **1a** with sodium tetraphenylborate in ethanol suggests an ionic nature for the (**1**) complexes.

In the NMR spectrum of **1a** measured in $CDCl_3$, the methyl resonance centered at 9.95 τ appears as a set of three triplets; it is interpreted to give $J_{P,H}$= 7.5 Hz and $J_{^{195}Pt,H}$=60 Hz, the central one with an intensity approximately four times that of the outer triplets. The triplet resonance implies that the two phosphorus ligands are in mutually *trans*-positions.

It may be deduced from these results that the (**1**) complexes have an ionic square-planar structure.

When the **1a** complex in benzene was kept at 80°C for 2 hr, the migration of the methyl group to the isocyanide ligand took place, affording *trans*-iodobis(triphenylphosphine)(1-cyclohexylimino)ethylplatinum(II) (**2a**), *trans*-Pt$(PPh_3)_2I[C(CH_3)=NC_6H_{11}]$, characterized by the presence of an infrared band due to carbon-nitrogen double bond at 1604 cm^{-1}, as is seen in the IR spectrum. This structure was supported by the formation of *N*-cyclohexylacetoamide from the degradation of 2a with moist air.

$$2a \longrightarrow CH_3CONHC_6H_{11}$$

An analogous complex, *trans*-Pt$(PPh_3)_2Cl[C(CH_2Ph)=NC_6H_{11}]$ (**2d**), was obtained from the reaction of *trans*-chlorobis(triphenylphosphine)benzylplatinum(II) with cyclohexyl isocyanide in a 1:1 molar ratio at 80°C. In this case, no attempts were made to isolate an intermediate ionic complex.

We had already reported that the insertion reaction of cyclohexyl isocyanide into the corresponding pal-

---

[1] Part VI: Y. Yamamoto and H. Yamazaki, *J. Organometal. Chem.*, **24**, 717 (1970).

[2] A part of this paper was presented at the Symposium of Organometallic Chemistry, Osaka, October 7, 1969. Preprints p. 172; The 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April 3, 1970. Preprints III, p. 1195.

[3] Y. Yamamoto, H. Yamazaki, and N. Hagihara, This Bulletin, **41**, 532 (1968); *J. Organometal. Chem.*, 18, 189 (1969).

[4] T. Yamamoto and H. Yamazaki, *ibid.*, **24**, 717 (1970).

[5] Y. Yamamoto and H. Yamazaki, This Bulletin, **43**, 2653 (1970).

[6] Y. Yamamoto and H. Yamazaki, *ibid.*, **43**, 3634 (1970).

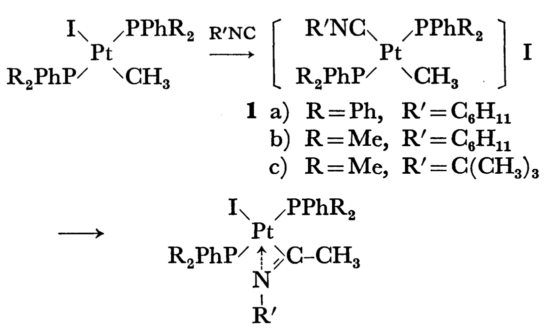
[7] P. M. Treichel and R. W. Hess, *J. Amer. Chem. Soc.*, **92**, 4731 (1970)

ladium(II) complex occurred at 0°C.[5,6] In the present reactions, the initial formation of a salt-like complex, accompanied by the insertion of isocyanide into a platinum-carbon sigma bond at an elevated to temperature, suggests that the reactivity of the Pt–CH_3 bond is lower than that of the Pd–CH_3 one.

When **1b** was handled in a way similar to that in the above-mentioned reaction (**1a**→**2a**), the unconverted starting materials were recovered without undergoing an insertion. On the refluxing of **1b** in toluene for 5 hr, the insertion of isocyanide proceeded, ultimately affording the iminoacyl complex (**2b**), *trans*-Pt$(PPhMe_2)_2I[C(CH_3){=}NC_6H_{11}]$.

It was presumably the electronic effect of the phosphine ligands that the migration of the methyl group to the isocyanide ligand in the **1a** complex containing triphenylphosphine occurred more easily than that in **1b** containing dimethylphenylphosphine.

In the NMR spectrum of **2b** in $CDCl_3$, the C–CH_3 proton resonance showed a well-defined 1:4:1 triplet at 7.73 τ, arising from the coupling of ^{195}Pt–H ($^3J_{^{195}\mathrm{Pt,H}}$ =33 Hz). The long-range coupling of $^4J_{\mathrm{P,H}}$ was not observed, although it was noted in the analogous complexes of Pd(II).[5,6] The P–CH_3 proton resonances



2a, b

Scheme 1

TABLE 1. PRODUCTS OF REACTIONS OF *trans*-Pt $(PR_3)_2$ X(R) WITH ISOCYANIDES

Compound	Yield(%)	mp(°C)[a]	Analyses Found(Calcd)				IR(cm^{-1})[b]	
			C	H	N	X	N≡C	C=N
[*trans*-Pt$(PPh_3)_2$ $(CNC_6H_{11})CH_3]I$	73	140—150	57.09	4.92	1.32	12.53	2203	
C_6H_6 (**1a**)			(57.26)	(4.81)	(1.34)	(12.10)		
[*trans*-Pt$(PPhMe_2)_2$ $(CNC_6H_{11})CH_3]I$	93	55— 60	42.27	5.17	1.85	16.90	2183	
$1/2C_6H_6$ (**1b**)			(42.58)	(5.16)	(1.84)	(16.66)		
[*trans*-Pt$(PPhMe_2)_2$ $(CNC(CH_3)_3)$ $CH_3]I$	89	97— 99	40.56	5.04	1.90	17.59	2178	
$1/2C_6H_6$ (**1c**)			(40.83)	(5.07)	(1.90)	(17.25)		
[*trans*-Pt$(PPh_3)_2$ $(CNC_6H_{11})CH_3]BPh_4$	100	170—180	71.65	5.89	1.12		2182	
C_6H_6			(71.61)	(5.68)	(1.13)			
trans-Pt$(PPh_3)_2$ $I[C(CH_3){=}NC_6H_{11}]$	89	163—167	54.01	4.54	1.41	13.41		1604
(**2a**)			(54.44)	(4.57)	(1.44)	(13.07)		
trans-Pt$(PPhMe_2)_2$ $I[C(CH_3){=}NC_6H_{11}]$	88	188—189	40.02	5.15	1.95	17.23		1611
(**2b**)			(39.95)	(5.03)	(1.91)	(17.59)		
trans-Pt$(PPh_3)_2Cl[C(CH_2Ph){=}NC_6H_{11}]$	44	169—173	62.88	4.98	1.33	3.82		1590
(**2d**)			(62.86)	(5.06)	(1.47)	(3.71)		

a) All complexes decomposed with melting. b) KBr method.

TABLE 2. NMR SPECTRA OF THE ISOCYANIDE COMPLEXES IN $CDCl_3$

Compound	τ
[*trans*-Pt$(PPh_3)_2(CNC_6H_{11})CH_3]I$ C_6H_6 (**1a**)	9.95(t,[b] $J_{\mathrm{P,H}}$=7.5Hz, $J_{^{195}\mathrm{Pt,H}}$=60*Hz*, Pt–CH_3), 8.5–9.5(b, C_6H_{10}), 6.7–7.1 (b, C_6H[c]), 2.45(b, P-C_6H_5), 2.70(s, C_6H_6[d]))
[*trans*-Pt$(PPhMe_2)_2(CNC_6H_{11})CH_3]I$ $1/2C_6H_6$ (**1b**)	9.75(t,[b] $J_{\mathrm{P,H}}$=7.5Hz, $J_{^{195}\mathrm{Pt,H}}$=60Hz, Pt–CH_3), 8.2–8.8(b, C_6H_{10}), 8.00(t,[b] $\lvert{}^2J_{\mathrm{P,H}}+{}^4J_{\mathrm{P,H}}\rvert$=7.5Hz, $J_{^{195}\mathrm{Pt,H}}$=30Hz, P–CH_3) 5.85–6.4(b, C_6H[c]), 2.0–2.6(b, P–C_6H_5), 2.65(s, C_6H_6)
[*trans*-Pt$(PPhMe_2)_2$ $(CNC(CH_3)_3)$ $CH_3]I$ $1/2C_6H_6$ (**1c**)	9.70(t,[b] $J_{\mathrm{P,H}}$= 7.5 Hz, $J_{^{195}\mathrm{Pt,H}}$=60Hz, Pt–CH_3), 8.75(s,$C(CH_3)_3$), 7.98(t,[b] $\lvert{}^2J_{\mathrm{P,H}}+{}^4J_{\mathrm{P,H}}\rvert$=8Hz, $J_{^{195}\mathrm{Pt,H}}$=60Hz, P-CH_3), 2.1–2.7(b, P–C_6H_5), 2.65 (s, C_6H_6) [d]
trans-Pt$(PPh_3)_2I[C(CH_3){=}NC_6H_{11}]$ (**2a**)	9.05(t, $J_{^{195}\mathrm{Pt,H}}$=33Hz, C–CH_3), 8.0–9.5 (b, C_6H_{10}), 5.25–5.60(b, C_6H[c]), 2.0–3.15(b, P-C_6H_5)
trans-Pt$(PPhMe_2)_2I[C(CH_3){=}C_6H_{11}]$[a] (**2b**)	8.2–9.3(b,C_6H_{10}), 8.01 and 8.07 (t,[b] $\lvert{}^2J_{\mathrm{P,H}}+{}^4J_{\mathrm{P,H}}\rvert$=8Hz, $J_{^{195}\mathrm{Pt,H}}$=38Hz, P–CH_3), 7.73 (s, $J_{^{195}\mathrm{Pt,H}}$=33Hz, C–CH_3) 5.95–6.3(b, C_6H[c]), 1.9–2.7(b, P–C_6H_5)
trans-Pt$(PPh_3)_2Cl[C(CH_2Ph){=}NC_6H_{11}]$ (**2d**)	8.4–9.3(b, C_6H_{10}), 6.77(t, $J_{^{195}\mathrm{Pt,H}}$=27Hz, C–CH), 6.0–6.4(b, C_6H[c]), 3.10(s, C–C_6H_5), 2.2–2.9(b, P–C_6H_5)

a) Recorded by Varian HA-100B. Other samples were measured by JEOL C-60.
b) a set of three triplets.
c) α-proton of cyclohexyl group.
d) Benzene contained in the complexes.

appeared as two sets of three triplets centered at 8.01 and 8.07 τ respectively. The two P–CH_3 resonances are interpreted to arise from $J_{P,H}$[8] $=7$ Hz and $J_{^{195}Pt,H}$ $=38$ Hz. The triplet resonance indicated that the two phosphorus ligands were coordinated to a metal in mutual *trans*-positions.[9] The presence of the two triplets also indicated that the two methyl groups on the same phosphorus atom were magnetically nonequivalent. If the **2b** complex has a square-planar structure, the magnetic nonequivalence will not be observed. Therefore, it seems reasonable to assume that the origin of nonequivalence is the absence of a plane of symmetry resulting from the coordination of lone-pair electrons of imino nitrogen to the platinum atom, thus giving the five-coordinate structure.

It may be concluded from the NMR spectrum of **2b** that these types of iminoacyl complexes of platinum (II), including those prepared in another recent paper,[5] have the five-coordinate structure.

Experimental

All the reactions were carried out under a nitrogen atmosphere. All the melting points are uncorrected; they were measured by a micro-melting-point apparatus, Yanagimoto Model MP-S2. The IR spectra were obtained by a Perkin-Elmer 521 spectrometer. The NMR spectra were recorded in $CDCl_3$ by means of JEOL C-60 and Varian HA-100B instruments, using tetramethylsilane as the internal standard. Isocyanides were prepared according to the procedures described in the literature.[10] *Trans*-iodobis(triphenylphosphine)methylplatinum(II) was prepared by Chatt and Shaw's method.[11] The elemental analyses, melting points, yields, and IR and NMR spectra of all the complexes prepared here are summarized in Tables 1 and 2.

Preparation of trans-*$Pt(PPhMe_2)_2(CH_3)$*. *Trans*-iodobis(dimethylphenylphosphine)methylplatinum was obtained by the reaction of *trans*-diiodobis(dimethylphenylphosphine)-platinum(II) with methylmagnesiumiodide.

Found: C, 33.17; H, 3.95; I, 20.12%. Calcd for $C_{17}H_{25}IP_2Pt$: C, 33.29; H, 4.11; I, 20.69%. Mp 146—150°C (decomp).

Preparation of trans-*$Pt(PPh_3)_2Cl(CH_2Ph)$*. A mixture of tetrakis (triphenylphosphine)platinum(II) (1 g, 0.98 mmol) and benzylchloride (10 ml) was kept at 75°C. After 5 hr, white crystals were observed. The evaporation of benzylchloride and recrystallization from benzene-hexane gave *trans*-chlorobis(triphenylphosphine)benzylplatinum(II) (0.6 g, 73%; mp 208—211°C (decomp.).)

Found: C, 61.03; H, 4.41; Cl, 4.18%. Calcd for $C_{43}H_{37}ClP_2Pt$: C, 61.41; H, 4.64; Cl, 14.29%. NMR ($CDCl_3$,τ): 7.69 (a set of three triplets, $J_{^{195}Pt,H}=99$Hz, $J_{P,H}=7.5$ Hz, CH_2), 2.1—3.5 (broad, P-Ph and Ph).

Preparation of [trans-*$Pt(PPhMe_2)_2(CNC_6H_{11})CH_3]I$*. Cyclohexyl isocyanide (0.065 g, 0.6 mmol) in benzene (0.6 m*l*) was added, drop by drop to a solution of *trans*-$Pt(PPhMe_2)_2I(CH_3)$ (0.36 g 0.59 mmol) in benzene (15 m*l*) at room temperature, and the solution was kept overnight. Colorless crystals (0.39 g, 93%) were filtered, washed by benzene-hexane, and identified as [*trans*-Pt-$(PPhMe_2)_2(CNC_6H_{11})CH_3]I$.

The other ionic complexes were obtained by the procedures described above.

Preparation of trans-*$Pt(PPh_3)_2[C(CH_3)=NC_6H_{11}]$*. [*trans*-Pt-$(PPh_3)_2(CNC_6H_{11})CH_3]I$ (0.2 g, 0.21 mmol) in benzene (25 m*l*) was kept at 80°C. After 2 hr, the reaction mixture was evaporated almost to dryness under a reduced pressure. Recrystallization from a benzene-hexane mixture gave colorless crystals, *trans*-iodobis(triphenylphosphine)(1-cyclohexylimino)ethylplatinum(II) (0.18 g, 90%).

Preparation of trans-*$Pt(PPh_3)_2Cl[C(CH_2Ph)=NC_6H_{11}]$*. Cyclohexyl isocyanide (0.05 g, 0.45 mmol) in benzene (0.45 m*l*) was added to a soluton of *trans*-chlorobis(triphenylphosphine)benzylplatinum(II) (0.38 g, 0.49 mmol). After the evaporation of the solvent almost to dryness, the viscous residue was kept at 80°C for 4 hr. Colorless crystals obtained were washed with benzene and identified as *trans*-chlorobis (triphenylphosphine) (1-cyclohexylimino) (2-phenyl)ethyl-platinum (II).

Preparation of trans-*$Pt(PPhMe_2)_2I[C(CH_3)=NC_6H_{11}]$*. [*trans*-$Pt(PPhMe_2)_2(CNC_6H_{11})CH_3]I$ (0.22 g, 0.31 mmol) in toluene (3 m*l*) was refluxed for 5 hr. The reaction mixture was evaporated almost to dryness. Recrystallization from benzene-hexane gave colorless crystals, *trans*-iodobis(dimethylphenylphosphine)(1-cyclohexylimino)ethylplatinum(II) (0.19 g, 88%).

Preparation of trans-*$Pt(PPhMe_2)_2I(CN)$*. [*trans*-$Pt(PPhMe_2)_2(CNC(CH_3)_3[CH_3]I$ (0.16 g, 0.24 mmol) in toluene (3 m*l*) was refluxed for 4 hr. The reaction mixture was evaporated almost to dryness. Recrystallization from benzene-hexane gave colorless crystals, iodo-cyanobis(dimethylphenylphosphine)platinum(II) (0.12 g, 82%; mp(decomp.) 150—153°C).

Found: C, 34.38; H, 3.68; N, 2.77; I, 21.89%. Calcd for $C_{17}G_{22}NP_2IPt$; C, 34.41; H, 3.74; N, 2.36; I, 21.39%. IR(KBr): 2122 cm^{-1} (N≡C). NMR($CDCl_3$, τ): 7.84 (a set of three triplets, $J_{^{195}Pt,H}=30$ Hz, $|^2J_{P,H}+^4J_{P,H}|=7.5$ Hz, P-CH_3), 2.1—2.7 (broad, C_6H_5).

---

[8] Apparent coupling constant, $|^2J_{P,H}+^4J_{P,H}|$

[9] J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, **1963**, 291.

[10] I. Ugi and R. Meyer, *Chem. Ber.*, **93**, 239 (1960).

[11] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, **1959**, 705.