tion of Ce(IV) leads to stepwise oxidation of coordinated oxalate without evidence for change in oxidation state of the rhodium center.[3a] The greater accessibility of higher oxidation states in the case of third-row transition elements is clearly illustrated by the rapid and quantitative Ce(IV) oxidation of $Ir(C_2O_4)_3{}^{3-}$.

Acknowledgment. We wish to thank Dr. D. H. Fortnam, who made some initial observations on the $Ir(C_2O_4)_3{}^{3-}$-Ce(IV) system. We are also indebted to Matthey Bishop, Inc., Malvern, Pa., for the generous loan of some potassium hexachloroiridate(IV).

Registry No. $Ir(C_2O_4)_3{}^{2-}$, 42401-85-4; $Ir(C_2O_4)_3{}^{3-}$, 18307-27-2; Ce^{4+}, 16065-90-0.

Contribution from the Institute of Physical and Chemical Research,
Wako-shi, Saitama, Japan

Studies on Interactions of Isocyanides with Transition Metal Complexes. IX.[1] Single and Multiple Insertion of Isocyanide into Palladium-to-Carbon σ Bonds[2]

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Reactions of trans square-planar complexes of palladium alkyls with isocyanides have led to the preparation of four classes of new complexes: *trans*-$PdL_2X[C(R)=NR']$ (type I) ($R = CH_3$, Ph, *o*-$C_6H_4CH_3$; $R' = C_6H_{11}$, $(CH_3)_3C$, $PhCH_2$, Ph; X = Br, I; L = PPh_3, $PPh(CH_3)_2$, $P(CH_3)_3$, $P(n\text{-}C_4H_9)_3$, $PPh_2(C_6H_{11})$), $[Pd\{PPh_2(CH_3)\}I\{C(CH_3)=NR'\}]_2$ (type II) ($R' = C_6H_{11}$, $(CH_3)_3C$), *trans*-$PdL_2I[(C=NC_6H_{11})_2(CH_3)]$ (type III) (L = PPh_3, $PPh_2(CH_3)$, $PPh(CH_3)_2$, $P(CH_3)_3$), and $Pd[PPh_2(CH_3)]I$-$[(C=NC_6H_{11})_3(CH_3)]$ (type IV). The type I complex ($R = CH_3$; $R' = C_6H_{11}$; X = I; L = $PPh(CH_3)_2$, $P(CH_3)_3$, $P(n\text{-}C_4H_9)_3$) and the type II complex ($R' = C_6H_{11}$, in the presence of $PPh_2(CH_3)$) were converted to the corresponding type III complex; the type III complex (L = $PPh_2(CH_3)$) was converted to the corresponding type IV complex, when treated with cyclohexyl isocyanide. The steric effects of ligands and the incoming isocyanide were observed in these insertion reactions. The possible insertion pathways of isocyanide into palladium-to-carbon bonds were discussed.

Introduction

Many examples of the insertion reactions of small molecules such as carbon monoxide, olefins, acetylenes, and sulfur dioxide into carbon-transition metal σ bonds are well-known.[3] This type of reaction is one of the most essential reactions in organometallic chemistry and is thought to be an important intermediate step in catalytic processes. There have also been several insertion reactions of isocyanides which are isoelectronic with carbon monoxide.[4]

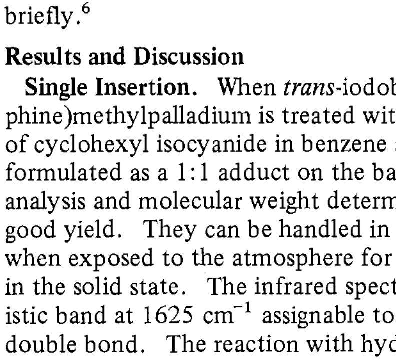
Otsuka, *et al.*, reported that tetrakis(*tert*-butyl isocyanide)-nickel undergoes multiple successive insertion of isocyanide molecules, when allowed to react with methyl iodide or benzoyl chloride.[5] Such a multiple insertion occurs in the reactions with trans square-planar palladium alkyls.[6] Recently, we found that dicarbonyl-π-cyclopentadienylbenzyliron leads to a successive insertion of three isocyanide molecules to produce $\pi\text{-}C_5H_5Fe(CO)[(C=NC_6H_{11})_3(CH_2Ph)]$, when treated with cyclohexyl isocyanide.[7] These multiple insertions are considered as an intermediate process of the coordinated polymerization of isocyanides catalyzed by transition metal complexes.[8,9]

In this paper, we wish to report more fully on the single and multiple insertion of isocyanides into the palladium-carbon σ bond, on which we have already communicated briefly.[6]

Results and Discussion

Single Insertion. When *trans*-iodobis(dimethylphenylphosphine)methylpalladium is treated with an equimolar amount of cyclohexyl isocyanide in benzene at 5°, yellow crystals, formulated as a 1:1 adduct on the basis of the elemental analysis and molecular weight determination, are obtained in good yield. They can be handled in air, but decompose when exposed to the atmosphere for longer periods of time in the solid state. The infrared spectrum shows a characteristic band at 1625 cm^{-1} assignable to a carbon-nitrogen double bond. The reaction with hydrogen peroxide gives *N*-cyclohexylacetamide.

These results suggest *trans*-iodobis(dimethylphenylphosphine)(1-cyclohexyliminoethyl)palladium for the complex in question (eq 1). The stereochemistry is provided by the proton nmr spectrum. The spectrum in $CDCl_3$ shows a triplet at τ 7.76 ($C\text{-}CH_3$, $J_{P\text{-}H}$ = 1.5 Hz) and a well-defined



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[9] Y. Yamamoto, Ph.D. Thesis, Osaka University, 1968.

Table I. Analytical Data and Physical Properties of Mono(imino) Complexes *trans*-$PdL_2X[C(R)=NR']$ (Type I)

						Analysis, %							
						C		H		N		I	
L	X	R	R′	Yield, %	Mp (dec), °C	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
PPh_3[a]	I	CH_3	C_6H_{11}	53	98–102	61.28	61.35	5.14	5.33	1.52	1.69	13.78	13.97
$PPh(CH_3)_2$	I	CH_3	C_6H_{11}	73	166–169	45.48	45.32	5.73	5.88	2.21	2.23	20.02	20.48
$P(n\text{-}C_4H_9)_3$	I	CH_3	C_6H_{11}	40	66–69	50.44	50.18	8.77	8.99	1.84	1.76	16.65	17.00
$PPh_2(C_6H_{11})$	I	CH_3	C_6H_{11}	33	129–133	59.10	59.01	6.31	6.27	1.57	1.55	14.19	13.88
$PPh(CH_3)_2$	I	C_6H_5	C_6H_{11}	77	162–164	50.05	50.48	5.50	5.38	2.01	2.17	18.24	18.57
$PPh_2(CH_3)$	I	$o\text{-}C_6H_4CH_3$	C_6H_{11}	70	110–114	57.60	57.36	5.32	5.18	1.68	1.60	15.22	14.93
$PPh_2(CH_3)$	I	CH_3	C_6H_5	89	95–112	54.31	54.19	4.56	4.43	1.86	1.79	16.88	16.99
$PPh(CH_3)_2$	I	CH_3	C_6H_5	81	143–145	45.92	46.13	4.82	4.88	2.23	2.19	20.22	19.89
$PPh(CH_3)_2$	I	CH_3	$(CH_3)_3C$	67	112–115	43.48	43.45	5.64	5.79	2.30	2.40	20.88	20.38
$PPh(CH_3)_2$	I	CH_3	$PhCH_2$	62	153–157	46.79	46.68	5.03	5.12	2.18	2.20	19.77	20.01
$P(CH_3)_3$	I	CH_3	$(CH_3)_3C$	51	156–160	29.80	30.20	6.24	6.39	2.90	3.00	26.24	26.56
$PPh(CH_3)_2$	Br	CH_3	C_6H_{11}	61	131–134	49.12	49.08	6.18	6.17	2.39	2.45		

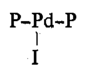
[a] One-half of benzene is included in crystallization.

Table II. Infrared and Proton Magnetic Resonance of Mono(imino) Complexes *trans*-$PdL_2X[C(R)=NR']$ (Type I)

						Nmr			
						τ,[b] ppm			
								L	
L	X	R	R′	Ir,[a] $\nu_{C=N}$, cm^{-1}	Solvent	R′	R	P-CH_3	P-Ph
PPh_3	I	CH_3	C_6H_{11}	1628	$CDCl_3$	8.1–9.3 (b),[c] 6.2–6.5 (b)[d]	7.77 (t)[e]		2.45–2.8 (b),[g] 2.0–2.4 (b)[h]
$PPh(CH_3)_2$	I	CH_3	C_6H_{11}	1625	$CDCl_3$	8.1–9.3 (b),[c] 6.1–6.6 (b)[d]	7.75 (t)[e]	8.19 (t),[f] 8.14 (t)[f]	2.45–2.75 (b),[g] 1.8–2.35 (b)[h]
$P(n\text{-}C_4H_9)_3$	I	CH_3	C_6H_{11}	1623	$CDCl_3$	7.7–9.3 (c),[i] 6.0–6.6 (b)[d]	7.73 (t)[e]		
$PPh_2(C_6H_{11})$	I	CH_3	C_6H_{11}	1620	$CDCl_3$	7.6–9.5 (c),[j] 6.5–7.5 (b)[d]	7.78 (t)		2.5–2.8 (b),[g] 2.1–2.45 (b)[h]
$PPh(CH_3)_2$	I	C_6H_5	C_6H_{11}	1606	C_6D_6	8.1–9.2 (b),[c] 5.6–6.0 (b)[d]	2.85 (s)	8.72 (t),[f] 8.32 (t)[f]	1.3–3.0 (b)
$PPh_2(CH_3)$	I	$o\text{-}C_6H_5CH_3$	C_6H_{11}	1603	$CDCl_3$	8.1–9.2 (b),[c] 5.6–6.0 (b)[d]	7.86 (s)	8.20 (t)[f]	2.15–3.3 (b)
$PPh_2(CH_3)$	I	CH_3	C_6H_{11}	1609	C_6D_6	2.8–3.1 (b)	7.82 (t)[e]	8.09 (t)[f]	1.8–2.15 (b)
$PPh(CH_3)_2$	I	CH_3	C_6H_{11}	1614	$CDCl_3$	2.65 (s)	7.76 (t)[e]	8.37 (t),[j] 8.18 (t)[j]	2.1–3.0 (b)
$PPh(CH_3)_2$	I	CH_3	$(CH_3)_3C$	1626	$CDCl_3$	8.58 (s)	7.76 (t)[e]	8.31 (t),[f] 8.06 (t)[f]	2.45–2.75 (b),[g] 1.9–2.4 (b)[h]
$PPh(CH_3)_2$	I	CH_3	$PhCH_2$	1611	C_6D_6	5.05 (bs)[k]	7.88 (t)[e]	8.60 (t),[j] 8.40 (t)[j]	2.15–3.2 (b)
$P(CH_3)_3$	I	CH_3	$(CH_3)_3C$	1631	$CDCl_3$	8.55 (s)	7.75 (t)[e]	8.45 (t)[j]	
$PPh(CH_3)_2$	Br	CH_3	C_6H_{11}	1628	$CDCl_3$	8.1–9.2 (b),[c] 6.0–6.5 (b)[d]	7.75 (t)[e]	8.55 (t),[f] 8.43 (t)[f]	2.1–2.8 (b)

[a] KBr pellets. [b] Abbreviations: b, broad; s, singlet; bs, broad singlet; t, triplet; c, complex. [c] C_6H_{10} protons. [d] α proton of the cyclohexyl group. [e] $J_{P-H} = 1.5$ Hz. [f] $|^2J_{P-H} + {}^4J_{P-H}| = 6.5$ Hz. [g] Meta and para protons of the phenyl group. [h] Ortho protons of the phenyl group. [i] $P(n\text{-}C_4H_9)_3$ and C_6H_{10} protons. [j] $|^2J_{P-H} + {}^4J_{P-H}| = 7.0$ Hz. [k] Benzylic methylene protons. Other protons are contained in the P-Ph.

1:3:3:1 pattern centered at τ 8.17 (P-CH_3). The triplet due to the C-CH_3 group indicates that two phosphorus nuclei are equivalent. The P-CH_3 resonance is interpreted to arise from two overlapping virtually coupled 1:2:1 triplet patterns at τ 8.14 and 8.20. When the complex was dissolved in C_6D_6, the P-CH_3 protons appear as a well-defined 1:2:2:2:1 pattern, implying also two overlapping 1:2:1 triplets separated by 7.2 Hz. The triplet resulting from the virtually coupled system shows that the two phosphorus ligands are coordinated to the palladium in mutual trans positions.[10,11] The presence of two triplets due to the P-CH_3 groups suggests that the two methyl groups on the same phosphorus atom are magnetically nonequivalent.[12] If the complex had simply a trans square-planar structure accompanied by free rotation around the Pd-C bond, the magnetic nonequivalence of the P-CH_3 groups would not be observed. It seems likely that the complex has the structure in which the imino nitrogen group stays on either side of the plane[13]


$$\begin{array}{c}\text{P-Pd-P}\\ | \\ \text{I}\end{array}$$

Similar mono(imino) complexes (type I) *trans*-$PdL_2X[C(R)=NR']$ are prepared from *trans*-$PdL_2X(R)$ and isocyanides. Analytical data and physical properties of the mono(imino) compound are provided in Tables I and II.

2,6-Dimethylphenyl isocyanide failed to react with *trans*-

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[10] R. K. Harris, *Can. J. Chem.*, 42, 2275 (1964).

[11] J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc., London*, 291 (1963).

[12] Another possibility is that the methyl groups on the different phosphorus atoms are magnetically nonequivalent. However, the P-CH_3 proton resonance of *trans*-$Pd[PPh_2(CH_3)]_2I[C(CH_3)=NC_6H_{11}]$ appears as only one triplet. We could rule out the aforementioned possibility.

[13] In a previous paper [Y. Yamamoto and H. Yamazaki, *Bull. Chem. Soc. Jap.*, 43, 3634 (1970)], we stressed that the coordination of the nitrogen atom to palladium would cause the P-CH_3 proton resonances to be magnetically nonequivalent. However, the behavior in the magnetic nonequivalence does not necessarily arise from the N-coordination. It seems more likely to result from the hindered rotation of the Pd-C bond rather than from the N-coordination, although we cannot completely rule out the latter. We appreciate to suggestion of Dr. R. D. Adams (MIT), who pointed out our incomplete conclusion.

Table III. Analytical Data and Physical Properties of Iodo-Bridged Complexes $[Pd\{PPh_2(CH_3)\}I\{C(CH_3)=NR'\}]_2$ (Type II)

			Analysis, %									
			C		H		N		I		Mol wt[a]	
R'	Yield, %	Mp (dec), °C	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
C_6H_{11}	49	134–137	45.22	45.53	4.88	4.93	2.45	2.45	22.75	23.03	1115	1053
$(CH_3)_3C$	53	156–159	42.92	43.12	4.74	4.76	2.63	2.61	23.87	23.54	1063	1042

[a] Measured in $CHCl_3$.

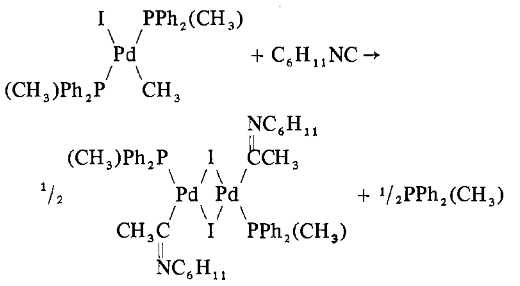
Table IV. Infrared and Proton Magnetic Resonance of Iodo-Bridged Complexes $[Pd\{PPh_2(CH_3)\}I\{C(CH_3)=NR'\}]_2$ (Type II)

		Nmr, τ,[b,c] ppm			
R'	Ir,[a] $\nu_{C=N}$, cm^{-1}	R'	CH_3	P-CH_3	P-Ph
C_6H_{11}	1572	8.0–9.3 (b)	9.04 (d, $J_{P-H} = 5.5$ Hz), 8.33 (d, $J_{P-H} = 4.2$ Hz)	7.25 (d, $J_{P-H} = 10$ Hz)	1.8–2.9 (b)
$(CH_3)_3C$	1569	8.44 (s)	8.08 (d, $J_{P-H} = 4.5$ Hz)	7.46 (d, $J_{P-H} = 10$ Hz)	1.8–2.85 (b)

[a] KBr pellets. [b] Measured in $CDCl_3$. [c] For abbreviations see Table II.

$Pd[PPh(CH_3)_2]_2I(CH_3)$, an observation explicable in terms of steric hindrance of isocyanide. The operation of a steric effect for the σ-bonded alkyl group is also indicated by the finding that the reaction of *trans*-$Pd[PPh_2(CH_3)]_2I(o\text{-}C_6H_4CH_3)$ with *tert*-butyl isocyanide did not occur. A similar steric effect has been observed in the reactions of triphenylphosphine-π-cyclopentadienylalkylnickel[14] or tricarbonyl-π-cyclopentadienylalkylmolybdenum[15] with isocyanides.

When the diphenylmethylphosphine complex is used, the reaction gives the iodo-bridged complex. The reaction of *trans*-$Pd[PPh_2(CH_3)]_2I(CH_3)$ with cyclohexyl isocyanide produces bis[μ-iodo-(diphenylmethylphosphine)(1-cyclohexyliminoethyl)palladium] (type II) (eq 2). The orange


(2)

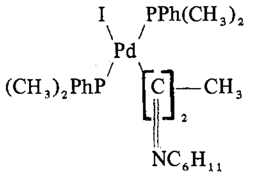
complex is stable in the solid state but decomposes when exposed to air in solution. The dimeric structure is confirmed by the osmometric molecular weight determination. The proton nmr spectrum shows the P-CH_3 groups at τ 7.25 split into the symmetrical 1:1 doublet, indicating that there is no long-range coupling between the two far phosphorus atoms. The two C-CH_3 proton resonances appear at τ 8.33 ($J_{P-H} = 4.2$ Hz) and 9.04 ($J_{P-H} = 5.5$ Hz) as doublets, respectively, implying that the product exists as a mixture of two isomers in a ratio of 7:3. Numerous possible structures for two isomers may be considered. No further attempts to confirm the structure of isomers were made in this paper. No isomers are observed in the iodo-bridged complex $[Pd\{PPh_2(CH_3)\}I\{C(CH_3)=NC(CH_3)_3\}]_2$, obtained from the reaction with *tert*-butyl isocyanide, probably because of the steric effect of a bulky *tert*-butyl group. A complex of a similar type $[Pd(PPh_3)Cl\{C(OCH_3)=NC_6H_5\}]_2$ has been obtained in the reaction of *cis*-$Pd(PPh_3)Cl_2[C(OCH_3)NHPh]$ with alcoholic KOH.[16] Analytical data and physical properties of bridged complexes prepared here are summarized in Tables III and IV.

In addition, treatment of *trans*-$PdL_2I(CH_3)$ (L = $P(OPh)_3$, $P(OC_2H_5)_3$) with cyclohexyl isocyanide at 25° leads to recovery of the starting material.

These results demonstrate the delicate balance of steric and electronic controls of ligands (phosphine, phosphite, alkyls) and the incoming isocyanide.

Double and Triple Insertion. Reaction of *trans*-$Pd[PPh(CH_3)_2]_2I(CH_3)$ with cyclohexyl isocyanide in a 1:2 molar ratio gives a yellow 1:2 adduct *trans*-$Pd[PPh(CH_3)_2]_2I[(C=NC_6H_{11})_2(CH_3)]$ (type III), characterized by the presence of two infrared peaks assignable to two carbon–nitrogen double bonds at 1632 and 1582 cm^{-1} (eq 3). The C-CH_3 proton

trans-$Pd[PPh(CH_3)_2]_2I(CH_3) + 2C_6H_{11}NC \rightarrow$


(3)

resonance appears at τ 7.96 as a sharp singlet in the proton nmr spectrum of this compound. Furthermore, two P-CH_3 proton resonances which arise from magnetic nonequivalence appear at τ 8.45 ($|^2J_{P-H} + {}^4J_{P-H}| = 6.5$ Hz) and 8.22 ($|^2J_{P-H} + {}^4J_{P-H}| = 6.5$ Hz) as triplets, respectively. The structure is interpreted to be analogous to that of the mono(imino) complex. The similar bis(imino) complexes *trans*-$PdL_2I[(C=NC_6H_{11})_2(CH_3)]$ are readily prepared under similar conditions. They show no signs of decomposition even when exposed to the atmosphere for longer periods of time in the solid state and are more stable than mono(imino) complexes. Analytical data and physical properties are provided in Tables V and VI.

Treatment of *trans*-$Pd[PPh_2(C_6H_{11})]_2I(CH_3)$ having the bulky phosphorus ligands with cyclohexyl isocyanide in a 1:2 molar ratio gives the corresponding mono(imino) complex without producing the expected bis(imino) complex. The reaction of *trans*-$PdL_2I(CH_3)$ (L = PPh_3, $PPh_2(CH_3)$, $P(CH_3)_3$) with bulky *tert*-butyl isocyanide gives also only the mono(imino) complex. Reaction of *trans*-$Pd[PPh_2(CH_3)]_2I(o\text{-}C_6H_4CH_3)$ with $C_6H_{11}NC$ failed to give the bis(imino) complex, suggesting that the steric effect of the σ-bonded alkyl group is also operative. Thus, the steric effect of bulky phosphine, isocyanide, and/or alkyl group seems to be an important factor to control reactivity in the double insertion reactions as well as in the single insertion ones.

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(14) Y. Yamamoto, H. Yamazaki, and N. Hagihara, *Bull. Chem. Soc. Jap.*, 41, 532 (1968); *J. Organometal. Chem.*, 18, 189 (1969).

(15) Y. Yamamoto and H. Yamazaki, *J. Organometal. Chem.*, 24, 717 (1970).

(16) B. Crociani and T. Boshi, *J. Organometal. Chem.*, 24, C1 (1970).

Table V. Analytical Data and Physical Properties of Bis(imino) and Tris(imino) Complexes: *trans*-$PdL_2I[(C{=}NC_6H_{11})_2(CH_3)]$ (Type III) and $Pd[PPh_2(CH_3)]I[(C{=}NC_6H_{11})_3(CH_3)]$ (Type IV)

			Analysis, %									
			C		H		N		I		Mol wt[a]	
L	Yield, %	Mp (dec), °C	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
Type III												
PPh_3	51	117–119	61.80	61.81	5.59	5.51	2.83	2.47	15.18		991	985
$PPh_2(CH_3)$	57	126–130	58.90	59.17	6.15	6.25	3.35	3.05	17.08	14.73	866	844
$PPh(CH_3)_2$	56	223–227	50.11	50.37	6.38	6.35	3.77	3.56	20.57	17.53	634	641
$P(CH_3)_3$	43	176–181	40.88	40.52	7.02	6.72	4.54	4.41	14.63	20.65	484	488
$P(n\text{-}C_4H_9)_3$	42	80–84	54.01	54.31	8.72	8.81	3.23	3.20		14.92		
Type IV	67	149–152	54.14	54.17	6.36	6.24	5.41	5.09	16.35	16.50	775	772

[a] Measured in $CHCl_3$.

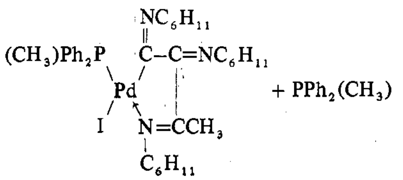
Table VI. Infrared and Proton Magnetic Resonance of Bis(imino) and Tris(imino) Complexes: *trans*-$PdL_2I[(C{=}NC_6H_{11})_2(CH_3)]$ (Type III) and $Pd[PPh_2(CH_3)]I[(C{=}NC_6H_{11})_3(CH_3)]$ (Type IV)

		Nmr				
			τ,[b] ppm			
L	Ir,[a] $\nu_{C=N}$, cm^{-1}	Solvent	NC_6H_{11}	C-CH_3	P-CH_3	P-Ph
Type III						
PPh_3	1626, 1576	CS_2	8.2–9.3 (b),[c] 7.1–7.7 (b),[d] 5.3–5.9 (b)[d]	8.81 (s)		2.0–3.1 (b)
$PPh_2(CH_3)$	1626, 1587	$CDCl_3$	7.8–9.3 (b),[c] 6.3–7.0 (b),[d] 5.7–6.3 (b)[d]	8.43 (s)	8.07 (t)[f]	1.8–2.8 (b)
$PPh(CH_3)_2$	1632, 1582	$CDCl_3$	7.9–9.2 (b),[c] 6.2–6.7 (b),[d] 5.8–6.1 (b)[d]	7.96 (s)	8.45 (t),[f] 8.22 (t)[f]	1.9–2.8 (b)
$P(CH_3)_3$	1630, 1585	$CDCl_3$	7.9–9.1 (b),[c] 6.7–7.3 (b),[d] 6.0–6.5 (b)[d]	7.66 (s)	8.56 (t)[f]	
Type IV	1636, 1598	$CDCl_3$	7.9–9.6 (b),[c] 6.9–7.7 (b),[d] 6.0–6.8 (b)[d]	7.68 (s)	7.80 (d)[e]	2.1–3.0 (b)

[a] KBr pellets. [b] For abbreviations see Table II. [c] C_6H_{10} protons. [d] α proton of N-cyclohexylimino group. [e] $J_{P-H} = 9.0$ Hz. [f] $|{}^2J_{P-H} + {}^4J_{P-H}| = 6.5$ Hz.

Reaction of *trans*-$Pd[PPh_2(CH_3)]_2I(CH_3)$ with cyclohexyl isocyanide in a 1:3 molar ratio was also carried out. The reaction gives orange-yellow crystals (type IV) (eq 4). The complex is postulated to be a five-membered chelate structure coordinated through the lone-pair electrons of the terminal imino nitrogen atom, based on the molecular weight measurement, electronic configuration of palladium atom, and spectroscopic studies. The infrared spectrum shows carbon-nitrogen double bonds at 1636 and 1598 cm^{-1}. The nmr spectrum shows a sharp singlet at τ 7.68 due to the C-CH_3 group and a doublet at τ 7.80 ($J_{P-H} = 9.0$ Hz) assignable to the P-CH_3 group. The similar five-membered chelate structure has been noted in the nickel[5] and iron[7] complexes.

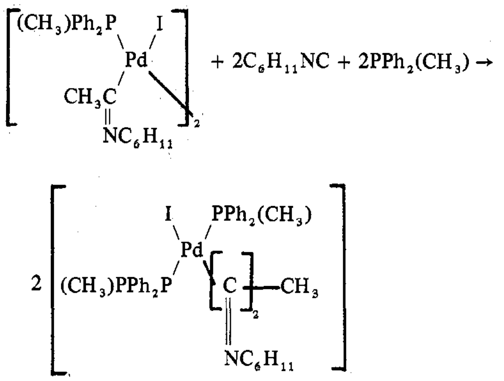
trans-$Pd[PPh_2(CH_3)]_2I(CH_3) + 3C_6H_{11}NC \rightarrow$



(4)

All attempts to prepare other tris(imino) complexes were unsuccessful.

Possible Pathways of Insertion Reactions. When *trans*-$PdL_2I[C(CH_3){=}NC_6H_{11}]$ ($L = PPh(CH_3)_2, P(CH_3)_3$) is treated with an equimolar amount of cyclohexyl isocyanide, an insertion takes place and the corresponding bis(imino) complex is obtained. This shows that the insertion of isocyanide molecule proceeds stepwise as follows: methylpalladium complex → mono(imino) complex (type I) → bis(imino) complex (type III). Treatment of the iodo-bridged complex with cyclohexyl isocyanide in a 1:2 molar ratio in the presence of diphenylmethylphosphine produces the bis(imino) complex *trans*-$Pd[PPh_2(CH_3)]_2I[(C{=}NC_6H_{11})_2(CH_3)]$ (eq 5). Addition of an equimolar amount of cyclohexyl isocyanide to this compound gives the tris(imino) complex (type IV). No further insertion of tris(imino) complex with cyclohexyl isocyanide takes place, suggesting higher stability of the five-membered chelate structure.

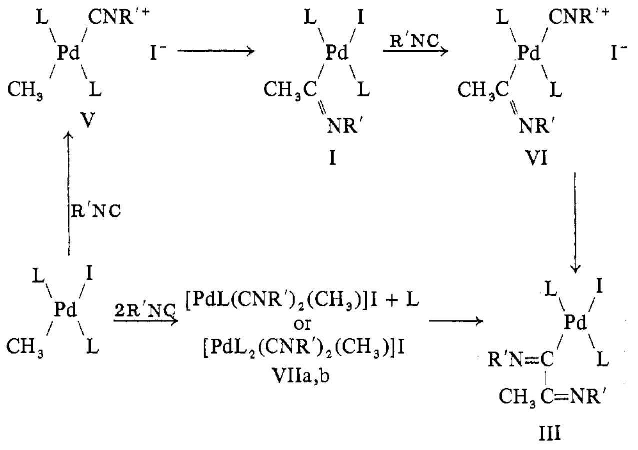


(5)

Although no reaction of *trans*-$Pd(PPh_3)_2I[C(CH_3){=}NC_6H_{11}]$ with cyclohexyl isocyanide in benzene at room temperature is observed, in the reaction at 70°, the complex ultimately undergoes an insertion of isocyanide, affording the corresponding bis(imino) complex. However, as mentioned in the previous section, reaction of *trans*-$Pd(PPh_3)_2I(CH_3)$ with cyclohexyl isocyanide in a 1:2 molar ratio occurs readily even at 5° to furnish the bis(imino) compound. Differences in these reactivities indicate the presence of another insertion pathway besides the stepwise insertion reaction. This double insertion may be considered to be sterically and energetically more favorable than the stepwise insertion.

The possible pathways for the single and multiple insertion of isocyanide may be sketched as in Scheme I. The complex

Scheme I. Possible Routes of Single and Double Insertion Reactions of Isocyanide



of type V is not isolable in the present reactions, but analogous platinum complexes *trans*-$[PtL_2(CNR')(CH_3)]X$ were isolated from the reaction of *trans*-halobis(tertiary phosphine)alkylplatinum with isocyanide.[17-19] These cationic platinum complexes undergo an insertion of isocyanide to give the mono(imino) complexes, when heated in benzene and toluene. Failure to isolate type V complexes would arise from the rapid migration of the methyl group to the isocyanide ligand through the nucleophilic attack of iodine anion, giving the mono(imino) compound (type I). The results may be correlated with the lower lability of the Pd-C bond than that of the Pt-C bond. The bis(imino) complex (type III) is formed *via* a type VI complex, arising from approach of an incoming isocyanide from the reverse side where the imino group stays.

The other route leading to the bis(imino) compound, which is considered to be sterically and energetically preferable, may proceed *via* the intermediate type VIIa or VIIb which is coordinated to the palladium atom by two isocyanide molecules. The intermediate VIIa or VIIb is postulated by analogy to the platinum complex $[PtL(CNR')_2(CH_3)]PF_6$[19] or the five-coordinate ionic complex $[PdL_2I(CNR')_2]I$ ($L = PPh_3, PPh_2(CH_3)$), respectively.

Experimental Section

General Procedures. The preparation and all handling of organometallic compounds were carried out under an atmosphere of nitrogen. Melting points were taken on a Yanagimoto Model MP-S2 apparatus and were uncorrected.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer Model 521 spectrometer. Proton nmr spectra were measured on JEOL C-60 and Varian HA-100B instruments, using tetramethylsilane as a reference. Molecular weights were measured in $CHCl_3$ by means of a Mechrolab 301A vapor pressure osmometer.

Materials. Isocyanides were prepared in the same manner as already described.[20] The organopalladium compounds *trans*-PdL_2X_2 were prepared by treatment of a suspension of palladium dihalide in methylene chloride with the corresponding tertiary phosphine and phosphite.

Preparation of *trans*-$PdL_2I(R)$. *trans*-Iodobis(tertiary phosphine)alkylpalladium and tertiary phosphite analogs were prepared by the modification of the method of Chatt and Shaw.[21]

(a) To a slurry of *trans*-$Pd[PPh(CH_3)_2]_2I_2$ (0.8 g, 1.25 mmol) in benzene (30 ml) was added phenylmagnesium bromide (5 mmol) in ether (5 ml) at 0°. After being stirred for 30 min, the reaction mixture was treated with water. The yellow-orange layer was separated and the aqueous layer was extracted twice with 5-ml portions of benzene. The yellow-orange solution and the extracts were combined and washed with water. After being dried over anhydrous sodium sulfate, the solvent was evaporated to dryness under reduced pressure. Recrystallization of the residue from benzene–hexane gave *trans*-$Pd[PPh(CH_3)_2]_2I(C_6H_5)$ (0.59 g, 80%; mp 130–132° dec).

Anal. Calcd for $C_{22}H_{27}IP_2Pd$: C, 45.04; H, 4.64; I, 21.63. Found: C, 45.10; H, 4.63; I, 21.39. The proton nmr spectrum in $CDCl_3$ has the following resonances (τ): multiplet at 2.60 (10 H), singlet at 3.20 (5 H), and triplet at 8.48 (12 H, $|^2J_{P-H} + {}^4J_{P-H}| =$ 7 Hz).

(b) Very pale yellow crystals of *trans*-$Pd[PPh_2(CH_3)]_2I(o\text{-}C_6H_4CH_3)$ (0.28 g, 50%; mp 191–192.5° dec) were obtained from the reaction of *trans*-$Pd[PPh_2(CH_3)]_2I_2$ (0.6 g, 0.78 mmol) with *o*-tolylmagnesium bromide (3 mmol) in a same manner.

Anal. Calcd for $C_{33}H_{33}IP_2Pd$: C, 54.68; H, 4.59; I, 17.51. Found: C, 54.68; H, 4.63; I, 17.78.

The elemental analyses, melting points, and proton nmr spectra of methylpalladium complexes prepared herein are summarized in Table VII.

Formation of Imino Complexes. (a) Reaction of *trans*-Iodobis(dimethylphenylphosphine)methylpalladium with Cyclohexyl Isocyanide in a 1:1 Molar Ratio. To a solution of *trans*-$Pd[PPh(CH_3)_2]_2I(CH_3)$ (0.28 g, 0.55 mmol) in benzene (20 ml) was added cyclohexyl isocyanide (0.065 g, 0.55 mmol) at 5°. After 2 hr, the solvent was removed to dryness under reduced pressure. Recrystallization of the residue from a benzene–hexane mixture gave yellow crystals of *trans*-$Pd[PPh(CH_3)_2]_2I[C(CH_3)=NC_6H_{11}]$ (0.25 g, 73%).

Analytical data and physical properties of this compound and other new compounds analogously prepared are provided in Tables I and II.

(b) Reaction of *trans*-Iodobis(diphenylmethylphosphine)methylpalladium with Cyclohexyl Isocyanide in a 1:1 Molar Ratio. A solution of *trans*-$Pd[PPh_2(CH_3)]_2I(CH_3)$ (0.54 g, 0.83 mmol) in benzene (20 ml) was treated with cyclohexyl isocyanide (0.09 g, 0.8 mmol) at 5° and then stirred for 1 hr. The solvent was removed under reduced pressure and the residue was crystallized from benzene–hexane. The resulting orange solid was identified as $[Pd\{PPh_2(CH_3)\}I\{C(CH_3)=NC_6H_{11}\}]_2$ (0.23 g, 49%).

(c) Reaction of *trans*-Iodobis(diphenylmethylphosphine)methylpalladium with Cyclohexyl Isocyanide in a 1:2 Molar Ratio. By using procedures analogous to those described above, *trans*-$Pd[PPh_2(CH_3)]_2I[(C=NC_6H_{11})_2(CH_3)]$ (0.49 g, 57%) was obtained from *trans*-$Pd[PPh_2(CH_3)]_2I(CH_3)$ (0.3 g, 0.46 mmol) and cyclohexyl isocyanide (0.11 g, 1.0 mmol).

(d) Reaction of *trans*-Iodobis(diphenylmethylphosphine)methylpalladium with Cyclohexyl Isocyanide in a 1:3 Molar Ratio. To a solution of *trans*-$Pd[PPh_2(CH_3)]_2I(CH_3)$ (0.39 g, 0.56 mmol) in benzene (25 ml) was added cyclohexyl isocyanide (0.21 g, 2.0 mmol) at 5°; the mixture was kept for 3 hr. The solvent was removed under vacuum and the residue was crystallized from benzene–hexane at 25°, giving yellow crystals of $Pd[PPh_2(CH_3)]I[(C=NC_6H_{11})_3(CH_3)]$ (0.37 g, 69%).

(e) Reaction of *trans*-Iodobis(dimethylphenylphosphine)(1-cyclohexyliminomethyl)palladium with Cyclohexyl Isocyanide. *trans*-$Pd[PPh(CH_3)_2]_2I[C(CH_3)=NC_6H_{11}]$ (0.25 g, 0.33 mmol), dissolved in methylene chloride (20 ml), was treated with cyclohexyl isocyanide (0.036 g, 0.33 mmol) in benzene at 5°; the mixture was kept for 2 hr. The solvent was evaporated to dryness under reduced pressure. Crystallization of the residue from benzene–hexane gave *trans*-$Pd[PPh(CH_3)_2]_2I[(C=NC_6H_{11})_2(CH_3)]$ (0.2 g, 70%).

(f) Reaction of Bis[μ-iodo-(diphenylmethylphosphine)(1-cyclohexyliminomethyl)palladium] with Cyclohexyl Isocyanide in the Presence of Diphenylmethylphosphine. $[Pd\{PPh_2(CH_3)\}I\{C(CH_3)=NC_6H_{11}\}]_2$ (0.175 g, 0.16 mmol) and diphenylmethylphosphine (0.07 g, 0.35 mmol), dissolved in benzene (25 ml), were treated with cyclohexyl isocyanide (0.038 g, 0.35 mmol) in benzene (3.5 ml) at 25°; the mixture was then kept for 1 hr. The reaction mixture was evaporated almost to dryness under reduced pressure. Crystallization from a benzene–hexane mixture gave *trans*-$Pd[PPh_2(CH_3)]_2I[(C=NC_6H_{11})_2(CH_3)]$ (0.15 g, 57%).

(g) Reaction of *trans*-Iodobis(diphenylmethylphosphine)(1,2-dicyclohexyliminopropyl)palladium with Cyclohexyl Isocyanide. By using procedures strictly analogous to those described above, $Pd[PPh_2(CH_3)]I[(C=NC_6H_{11})_3(CH_3)]$ (0.27 g, 58%) was obtained from *trans*-$Pd[PPh_2(CH_3)]_2I[(C=NC_6H_{11})_2(CH_3)]$ (0.53 g, 0.61 mmol) and cyclohexyl isocyanide (0.09 g, 0.82 mmol).

Preparation of *trans*-$[PdL_2I(CNR')_2]I$. (a) To a suspension of

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Table VII. Analytical Data and Proton Magnetic Resonance of Methylpalladium Complexes *trans*-PdL$_2$X(CH$_3$)

			Analysis, %						
			C		H		X		
L	X	Mp (dec), °C	Calcd	Found	Calcd	Found	Calcd	Found	Chem shift (τ, ppm)[b] of *Pd*-CH$_3$ in CDCl$_3$
PPh$_3$	I	147–154	57.50	57.65	4.30	4.41	16.42	17.01	9.92 (t, J_{P-H} = 6 Hz)
PPh$_2$(CH$_3$)	I	140–142	49.99	50.04	4.51	4.73	19.56	19.36	9.90 (t, J_{P-H} = 6 Hz)
PPh(CH$_3$)$_2$	I	126–128	38.92	39.19	4.80	4.97	24.19	24.02	9.77 (t, J_{P-H} = 6.5 Hz)
P(CH$_3$)$_3$	I	138	20.99	21.25	5.29	5.34	31.68	31.08	9.46 (t, J_{P-H} = 6.5 Hz)
P(*n*-C$_4$H$_9$)$_3$[a]	I								9.60 (t, J_{P-H} = 6 Hz)
PPh$_2$(C$_6$H$_{11}$)	I	155–160	56.61	56.35	5.78	6.01	16.17	15.92	9.67 (t, J_{P-H} = 5.5 Hz)
PPh(CH$_3$)$_2$	Br	130–132	42.75	42.39	5.28	5.11	16.73	17.27	9.86 (t, J_{P-H} = 6 Hz)
P(OPh)$_3$	I	104–107	51.15	51.38	3.83	3.79	14.60	14.92	9.33 (t, J_{P-H} = 4.5 Hz)
P(OC$_2$H$_5$)$_3$	I	64–65	26.89	26.99	5.73	5.78	21.86	21.60	9.13 (t, J_{P-H} = 5 Hz)

[a] Oily product. [b] Abbreviation: t, triplet.

trans-Pd[PPh$_2$(CH$_3$)]$_2$I$_2$ (1.0 g, 1.3 mmol) in methylene chloride (10 ml) was added cyclohexyl isocyanide (0.44 g, 4 mmol) in benzene (4 ml) at 25°; the mixture was then stirred for 20 min. Evaporation of the solvent and crystallization of the residue from methylene chloride–hexane gave [Pd{PPh$_2$(CH$_3$)}$_2$(CNC$_6$H$_{11}$)$_2$I]I (1.16 g, 92%).

Anal. Calcd for C$_{40}$H$_{48}$N$_2$I$_2$P$_2$Pd: C, 49.07; H, 4.98; N, 2.86. Found: C, 49.07; H, 5.07; N, 2.52. The infrared spectrum (KBr) shows a strong band at 2195 cm^{-1} due to the terminal isocyanide group. The proton nmr spectrum in CDCl$_3$ consists of three broad peaks at τ 8.2–9.2 (20 H), 6.3–6.8 (2 H), and 2.0–2.6 (30 H) and a singlet at τ 7.24 (6 H). The molar conductivity in nitrobenzene is 15.2 ohm^{-1} cm^{-1} at 25°. This is in agreement with those of the uni-univalent electrolyte of palladium.[22]

(b) By using analogous procedures, [Pd(PPh$_3$)$_2$I(CNC$_6$H$_{11}$)$_2$]I (1.8 g, 91%; mp 119–122° dec) was obtained from treatment of Pd(PPh$_3$)$_2$I$_2$ (1.6 g, 1.8 mmol) with cyclohexyl isocyanide (0.45 g, 4.1 mmol) in methylene chloride (30 ml).

Anal. Calcd for C$_{50}$H$_{52}$N$_2$I$_2$P$_2$Pd: C, 54.44; H, 4.76; N, 2.54; I, 23.01. Found: C, 54.06; H, 4.77; N, 2.31; I, 23.84. The infrared spectrum (KBr) shows a strong band 2195 cm^{-1} ($\nu_{N\equiv C}$). The proton nmr spectrum in CDCl$_3$ consists of three peaks at τ 8.3–9.2 (20 H), 6.3–6.7 (2 H), and 2.1–2.7 (30 H).

Oxidative Reaction of *trans*-Iodobis(diphenylmethylphosphine)-(1-cyclohexyliminomethyl)palladium with Hydrogen Peroxide. To a solution of *trans*-Pd[PPh$_2$(CH$_3$)]$_2$I[C(CH$_3$)=NC$_6$H$_{11}$] (1.0 g, 1.30 mmol) in benzene (20 ml) was added H$_2$O$_2$ (0.5%, 10 ml). After 1 hr, the brown organic layer was separated and dried over anhydrous sodium sulfate. The solution was chromatographed on silica gel, eluting with benzene–acetone (20:1). The first layer gave *N*-cyclohexylacetamide (0.12 g, 65%) and the second one gave diphenylmethylphosphine oxide (0.65 g, 89%).

Registry No. *trans*-Pd(PPh$_3$)$_2$I[C(CH$_3$)=NC$_6$H$_{11}$], 42582-33-2; *trans*-Pd[PPh(CH$_3$)$_2$]I[C(CH$_3$)=NC$_6$H$_{11}$], 42582-34-3; *trans*-Pd[P(*n*-C$_4$H$_9$)$_3$]$_2$I[C(CH$_3$)=NC$_6$H$_{11}$], 42582-35-4; *trans*-Pd[PPh$_2$(C$_6$H$_{11}$)]$_2$I[C(CH$_3$)=NC$_6$H$_{11}$], 42582-36-5; *trans*-Pd[PPh(CH$_3$)$_2$]$_2$I[C(C$_6$H$_5$)=NC$_6$H$_{11}$], 42582-37-6; *trans*-Pd[PPh$_2$(CH$_3$)]$_2$I[C(*o*-C$_6$H$_4$CH$_3$)=NC$_6$H$_{11}$], 42582-52-5; *trans*-Pd[PPh$_2$(CH$_3$)]$_2$I[C(CH$_3$)=NC$_6$H$_5$], 42582-51-4; *trans*-Pd[PPh(CH$_3$)$_2$]$_2$I[C(CH$_3$)=NC$_6$H$_5$], 42582-50-3; *trans*-Pd[PPh(CH$_3$)$_2$]$_2$I[C(CH$_3$)=NC(CH$_3$)$_3$], 42582-49-0; *trans*-Pd[PPh(CH$_3$)$_2$]$_2$I[C(CH$_3$)=NCH$_2$Ph], 42582-47-8; *trans*-Pd[P(CH$_3$)$_3$]$_2$I[C(CH$_3$)=NC(CH$_3$)$_3$], 42582-46-7; *trans*-Pd[PPh(CH$_3$)$_2$]$_2$Br[C(CH$_3$)=NC$_6$H$_{11}$], 42582-45-6; [Pd{PPh$_2$(CH$_3$)}I{C(CH$_3$)=NC$_6$H$_{11}$}]$_2$, 29186-97-8; [Pd{PPh$_2$(CH$_3$)}I{C(CH$_3$)=NC(CH$_3$)$_3$}]$_2$, 42735-36-4; *trans*-Pd(PPh$_3$)$_2$I[(C=NC$_6$H$_{11}$)$_2$(CH$_3$)], 29190-51-0; *trans*-Pd[PPh$_2$(CH$_3$)]$_2$I[(C=NC$_6$H$_{11}$)$_2$(CH$_3$)], 29186-98-9; *trans*-Pd[PPh(CH$_3$)$_2$]$_2$I[(C=NC$_6$H$_{11}$)$_2$(CH$_3$)], 42582-43-4; *trans*-Pd[P(CH$_3$)$_3$]$_2$I[(C=NC$_6$H$_{11}$)$_2$(CH$_3$)], 42582-42-3; *trans*-Pd[P(*n*-C$_4$H$_9$)$_3$]$_2$I[(C=NC$_6$H$_{11}$)$_2$(CH$_3$)], 42582-41-2; Pd[PPh$_2$(CH$_3$)]I[(C=NC$_6$H$_{11}$)$_3$(CH$_3$)], 42735-35-3; *trans*-Pd(PPh$_3$)$_2$I(CH$_3$), 18115-58-7; *trans*-Pd[PPh$_2$(CH$_3$)]$_2$I(CH$_3$), 42582-53-6; *trans*-Pd[PPh(CH$_3$)$_2$]$_2$I(CH$_3$), 42582-38-7; *trans*-Pd[P(CH$_3$)$_3$]$_2$I(CH$_3$), 42582-39-8; *trans*-Pd[P(*n*-C$_4$H$_9$)$_3$]$_2$I(CH$_3$), 42582-40-1; *trans*-Pd[PPh$_2$(C$_6$H$_{11}$)]$_2$I(CH$_3$), 42744-99-0; *trans*-Pd[PPh(CH$_3$)$_2$]$_2$Br(CH$_3$), 42745-00-6; *trans*-Pd[P(OPh)$_3$]$_2$I(CH$_3$), 42745-01-7; *trans*-Pd[P(OC$_2$H$_5$)$_3$]$_2$I(CH$_3$), 42719-81-3; *trans*-Pd[PPh(CH$_3$)$_2$]$_2$I(C$_6$H$_5$), 42745-02-8; *trans*-Pd[PPh$_2$(CH$_3$)]$_2$I(*o*-C$_6$H$_4$CH$_3$), 42745-03-9; [Pd{PPh$_2$(CH$_3$)}$_2$(CNC$_6$H$_{11}$)$_2$I]I, 42745-04-0; [Pd(PPh$_3$)$_2$I(CNC$_6$H$_{11}$)$_2$]I, 42745-05-1; cyclohexyl isocyanide, 931-53-3; *trans*-Pd[PPh$_2$(CH$_3$)]$_2$I$_2$, 25332-94-9; H$_2$O$_2$, 7722-84-1.

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The Ylide-Metal Complex. Preparations and Structures of Palladium(II) and Platinum(II) Halide Complexes with a Stable Sulfur Ylide

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Platinum(II) and palladium(II) halide complexes with a stable sulfur ylide, PtX$_2$(R$_2$S)(Sy) and PdX$_2$(Sy)$_2$ [X = Cl, Br, I; R = CH$_3$, C$_2$H$_5$; Sy = CH$_3$(C$_6$H$_5$)SCHC(O)C$_6$H$_4$Cl-*p*], have been prepared. The ν(C=O) band of the complexes occurs at higher frequencies than the original one of the ylide, and spin-spin coupling between the ylide methine proton and the ^{195}Pt nucleus is observed. These facts indicate the formation of the ylide carbon-metal bond in the complexes. The configurations of the complexes are elucidated on the basis of ir and pmr spectra. The trans influence of this ylide is concluded to be more or less larger than that of dimethyl or diethyl sulfide on the basis of measurements of ν(Pt–Cl) and the spin-spin coupling constants between the methyl protons of the coordinating dimethyl sulfide and the ^{195}Pt nucleus.

Introduction

Generally, ylides which have an electronic structure $>C^--X^+$ (X = heteroatoms)[1] are expected to interact with various Lewis acids through the nucleophilic carbon atom having lone-pair electrons. Recently many studies have been reported concerning the reactions of various ylides with boron,[2-4]

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