

0.154 mmol) in dichloromethane (20 ml) was treated with  $[(C_2H_5)_4N]Cl$  (0.028 g, 0.170 mmol) in dichloromethane (10 ml) and the reaction mixture was stirred for 2 hr. After filtering and concentrating the resulting solution, addition of excess  $NH_4PF_6$  in methanol (30 ml) gave the white crystalline  $[PtCl(CNCH_3)\{P(C_6H_5)_3\}_2]PF_6$  (0.107 g, 74% yield), which was identified by spectral properties and its melting point (231–233°).<sup>3</sup>

**Reaction of  $[Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2$  and Cyanide Ion.**—A solution of this complex (0.150 g, 0.154 mmol) in acetonitrile (30 ml) was treated with potassium cyanide (0.011 g, 0.170 mmol) in water (5 ml) and the reaction mixture was stirred for 2 hr. The system was evaporated to dryness and the residue was redissolved in chloroform. After filtering and concentrating the resulting solution, the addition of ethyl ether gave the white crystalline  $[Pt(CN)(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$  (0.128 g, 83% yield), which was identified by spectral properties and its melting point (236–239°).<sup>3</sup>

**Reaction of  $[Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2$  and Azide Ion.**—Using a similar procedure the addition of sodium azide (0.048 g, 0.738 mmol) in water (5 ml) to the acetonitrile complex (0.600 g, 0.615 mmol) in acetone (30 ml) gave the yellow crystalline  $[PtN_3(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$  (0.459 g, 84% yield). This product was recrystallized from chloroform–ethyl ether; mp 108–110°. *Anal.* Calcd for  $C_{38}H_{33}BF_4N_4P_2Pt \cdot 1.0CHCl_3$ : C, 46.3; H, 3.41; N, 5.54. Found: C, 46.3; H, 3.56; N, 5.41. Infrared spectrum ( $cm^{-1}$ ):  $\nu_{C=N}$ , 2263 (s); other bands: 3060 (w, sh), 2058 (vs), 1587 (vw), 1573 (vw), 1480 (m, sh), 1433 (s), 1330 (vw), 1310 (vw), 1278 (vw), 1180 (w), 1154 (vw), 1093 (s), 1050 (vs), 990 (w), 740 (s), 703 (m), 685 (vs), 517 (vs), 506 (vs), 496 (w, sh), 470 (vw), 440 (vw). Nmr spectrum (chloroform- $d_1$ ):  $\tau$  2.40 (multiplet),  $C_6H_5$ ; 7.45 (1:4:1 “triplet”);  $J_{Pt-H} = 19$  Hz),  $CNCH_3$ .

**Reaction of  $[Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2$  and Nitrite Ion.**—Using a similar procedure the addition of sodium nitrite (0.032 g, 0.462 mmol) in water (10 ml) to the aceto-

nitrile complex (0.300 g, 0.308 mmol) in acetonitrile (30 ml) gave pale yellow crystals of  $[Pt(NO_2)(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$  (0.218 g, 79% yield), which were purified by recrystallization from dichloromethane–ethyl ether; mp 202–204°. Infrared spectral data indicated this product was the nitro derivative.<sup>6</sup> *Anal.* Calcd for  $C_{38}H_{33}BF_4N_2O_2P_2Pt$ : C, 51.0; H, 3.73; N, 3.14. Found: C, 50.8; H, 3.75; N, 3.10. Infrared spectrum ( $cm^{-1}$ ):  $\nu_{C=N}$ : 2268 (s); other bands: 3060 (w, sh), 1587 (vw), 1577 (vw), 1486 (m, sh), 1438 (s), 1410 (s), 1340 (m), 1310 (vw), 1280 (vw), 1190 (w), 1162 (vw), 1096 (s), 1053 (vs), 996 (w), 816 (w), 746 (m), 708 (w), 690 (s), 583 (w), 520 (vs), 510 (vs), 498 (vw, sh), 450 (vw), 420 (vw). Nmr spectrum (chloroform- $d_1$ ):  $\tau$  2.36 (multiplet),  $C_6H_5$ ; 7.27 (1:4:1 “triplet”);  $J_{Pt-H} = 16$  Hz),  $CNCH_3$ .

**Reaction of  $[Pt(NCCH_3)(CNCH_3)\{P(C_6H_5)_3\}_2](BF_4)_2$  and Hydroxide Ion.**—Using a similar procedure the addition of potassium hydroxide (0.018 g, 0.324 mmol) in water (8 ml) to the acetonitrile complex (0.301 g, 0.309 mmol) in acetonitrile (20 ml) gave pale yellow microcrystals of  $[Pt(OH)(CNCH_3)\{P(C_6H_5)_3\}_2]BF_4$  (0.219 g, 82% yield), which were precipitated from acetone–water; mp 104–105°. *Anal.* Calcd for  $C_{38}H_{34}BF_4NOP_2Pt$ : C, 52.8; H, 3.97; N, 1.62. Found: C, 52.8; H, 4.06; N, 1.73. Infrared spectrum ( $cm^{-1}$ ):  $\nu_{C=N}$ : 2251 (s); other bands: 3610 (w), 3060 (w, sh), 1436 (s), 1305 (vw), 1278 (vw), 1185 (w), 1158 (vw), 1095 (s), 1055 (vs), 996 (w), 745 (m), 708 (m), 690 (s), 550 (w), 520 (s), 510 (s), 498 (vw, sh), 450 (vw), 418 (vw). Nmr spectrum (chloroform- $d_1$ ):  $\tau$  2.40 (multiplet),  $C_6H_5$ ; 7.40 (1:4:1 “triplet”);  $J_{Pt-H} = 18$  Hz),  $CNCH_3$ .

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CONTRIBUTION FROM THE CENTRO DI CHIMICA E TECNOLOGIA DEI COMPOSTI METALLORGANICI DEGLI ELEMENTI DI TRANSIZIONE DEL C.N.R. AND THE FACOLTÀ DI CHIMICA INDUSTRIALE, UNIVERSITÀ C'FOSCARI, VENICE, ITALY

## Kinetics of Nucleophilic Attacks on Palladium(II) Isocyanide Complexes

By B. CROCIANI,\* T. BOSCHI, M. NICOLINI, AND U. BELLUCO

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Kinetic data on reactions of the type  $cis-[Pd(p-YC_6H_4NC)LX] + p-ZC_6H_4NH_2 \rightarrow cis-[Pd\{C(NHC_6H_4Y)NHC_6H_4Z\}LX_2]$  ( $Y = CH_3O, CH_3, H, NO_2$ ;  $Z = CH_3O, CH_3, H, Cl, NO_2$ ;  $L = P(C_6H_5)_3, As(C_6H_5)_3$ ;  $X = Cl, Br$ ) in 1,2-dichloroethane at 30° are reported. The reactions occur according to the rate law:  $k_{obsd} = k[\text{amine}]$ . The proposed reaction mechanism implies a direct attack of the entering para-substituted amine on the carbon atom of the isocyanide linked to the central metal. For the phenyl isocyanide complex, the reactivity order of the amine is  $CH_3OC_6H_4NH_2 > CH_3C_6H_4NH_2 > C_6H_5NH_2 > ClC_6H_4NH_2 \gg O_2NC_6H_4NH_2$ . For the entering *p*-toluidine, the reactivity order of coordinated isocyanides is  $O_2NC_6H_4NC \gg C_6H_5NC > CH_3C_6H_4NC > CH_3OC_6H_4NC$ . These reactivity trends are interpreted in terms of electronic effects of para substituents Y and Z. The activation parameters for the reaction of  $cis-[Pd(C_6H_5NC)(P(C_6H_5)_3)Cl_2]$  with *p*-toluidine in 1,2-dichloroethane are  $\Delta H^* = 9.4 \pm 0.1$  kcal/mol and  $\Delta S^* = -35.1 \pm 1.7$  eu. The largely negative value of  $\Delta S^*$  suggests a transition state the formation of which involves a considerable reduction of degrees of freedom leading to a rigid activated structure.

### Introduction

Coordinated ligands containing unsaturated carbon atoms such as carbon monoxide,<sup>1–7</sup> olefins<sup>8</sup> or acety-

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lenes,<sup>9</sup> and isocyanides<sup>10–16</sup> readily undergo nucleophilic attack. In particular, the isocyanide group linked to a transition metal ion exhibits a pronounced tendency to react with amines or alcohols to give carbene complexes.<sup>10–16</sup>

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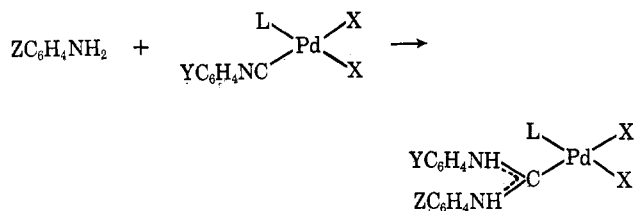
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We have already extensively studied such reactions on isocyanide derivatives of palladium(II) which lead to either neutral or cationic stable carbene complexes.<sup>11</sup>

This paper reports kinetic investigations on some reactions of palladium(II) isocyanide complexes with different entering amines. The rates of formation of neutral palladium(II) carbene complexes have been determined with the aim to elucidate the mechanistic features of these processes and to throw some light on the factors affecting the reactivity of isocyanide complexes with respect to the nature of (i) the coordinated isocyanide and (ii) the entering amine.

### Results and Discussion

The reactions studied are represented by



where Y = CH<sub>3</sub>O, CH<sub>3</sub>, H, or NO<sub>2</sub>; Z = CH<sub>3</sub>O, CH<sub>3</sub>, H, Cl, or NO<sub>2</sub>; L = P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> or As(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>; X = Cl or Br. The entering amines as well as the coordinated isocyanide groups were para substituted. The final products were isolated and identified as the carbene complexes. All the reactions occur with retention of configuration at the Pd.

All the products have a *cis* structure, as well as the starting isocyanide derivatives, as shown by the occurrence of two  $\nu(\text{Pd-X})$  bands in the far-ir spectra (see Table IV). All reactions were followed in 1,2-dichloroethane in the presence of a large excess of the entering amine in order to provide pseudo-first-order conditions and to force the reactions to completion. The pseudo-first-order rate constants,  $k_{\text{obsd}}$  (sec<sup>-1</sup>), were obtained by calculating at wavelengths where the difference in optical density between the spectra of the starting materials and of the reaction product was largest. Table I reports the rate constant values for the reac-

tions of *cis*-[Pd(L)(C<sub>6</sub>H<sub>5</sub>NC)X<sub>2</sub>] with various entering amines. Plots of  $k_{\text{obsd}}$  (sec<sup>-1</sup>) vs. the concentration of the entering amines (Figure 1) indicate a dependence of rate on the nature and concentration of the ligand,

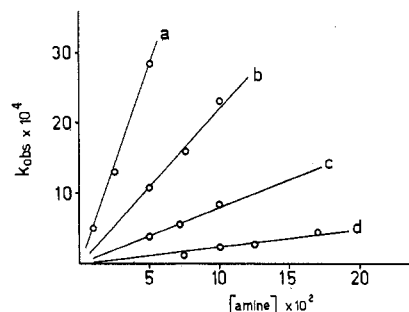
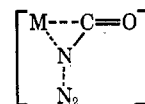


Figure 1.—Plots of the  $k_{\text{obsd}}$  (sec<sup>-1</sup>) vs. the concentration of the entering amines for the reactions of *cis*-[Pd(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>NC)<sub>2</sub>]Cl<sub>2</sub> with ZC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> at 30°: a, *p*-anisidine; b, *p*-toluidine; c, aniline; d, *p*-chloroaniline.

according to the rate law:  $k_{\text{obsd}} = k[\text{amine}]$ . This is the same kinetic law found for square-planar substitution on d<sup>8</sup> complexes, except for the missing first-order rate constant ( $k_1$ , sec<sup>-1</sup>), which is recognized to involve a solvolytic attack on the metal.<sup>17</sup> However, here the bimolecular path related to  $k$  (M<sup>-1</sup> sec<sup>-1</sup>) bears a different meaning since the site of the attack by the entering amine is the isocyanide carbon linked to palladium, aside from possible prior, fast association of the entering group with the coordinatively unsaturated complex.

There are several examples in the literature which clearly indicate nucleophilic attacks on coordinated ligands containing unsaturated carbon atoms. Thus, kinetic measurements carried out on reactions of carbonyl derivatives of the types M(CO)<sub>6</sub> (M = Cr, Mo, W) and [( $\pi$ -C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>L]<sup>+</sup> with azide ion show an S<sub>N</sub>2-type mechanism, which requires a primary, rate-determining attack of N<sub>3</sub><sup>-</sup> at the carbon atom of the CO group, with subsequent formation of a cyclic transition state and/or reaction intermediate, of the type



Accordingly, negative activation entropies have been determined for the reactions of hexacarbonyls.<sup>18,19</sup> On the other hand, the carbon atom of a coordinated CO group in M(CO)<sub>6</sub> is expected to be susceptible to nucleophilic attack, on the basis of MO calculations.<sup>20</sup>

The kinetics of the reactions carried out on four-coordinate platinum(II) carbonyl complexes of the type *trans*-[Pt(PR<sub>3</sub>)<sub>2</sub>(CO)Cl]<sup>+</sup> (R = C<sub>2</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>5</sub>) with water<sup>21</sup> and alcohols<sup>22</sup> are consistent with a mechanism which implies the nucleophilic attack on the CO group

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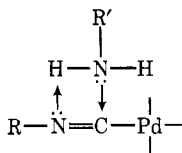
TABLE I  
RATE CONSTANTS FOR THE REACTIONS AT 30° OF  
*cis*-[PdL(C<sub>6</sub>H<sub>5</sub>NC)X<sub>2</sub>] WITH ZC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>;  
[COMPLEX]  $\approx 10^{-4}$  M

Z	L	X	[ZC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub> ], M	10 <sup>4</sup> k <sub>obsd</sub> , sec <sup>-1</sup>	10 <sup>4</sup> k, M <sup>-1</sup> sec <sup>-1</sup>
Cl	P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	Cl	0.17	4.44	2.3
			0.125	2.78	
			0.10	2.26	
			0.075	1.25	
H	P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	Cl	0.101	8.43	8.2
			0.07	5.74	
			0.05	3.99	
			0.10	23.13	
CH <sub>3</sub>	P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	Cl	0.075	16.00	22.2
			0.05	10.87	
			0.10	24.30	
			0.075	16.72	
CH <sub>3</sub>	As(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	Cl	0.05	10.70	23.0
			0.10	13.07	
			0.075	9.27	
			0.05	5.74	
CH <sub>3</sub> O	P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	Cl	0.05	28.47	55.4
			0.025	13.24	
			0.01	5.38	
			0.05	5.38	



A bimolecular attack on the coordinated isocyanide agrees with the observed reactivity order for entering amines on *cis*-[Pd(C<sub>6</sub>H<sub>5</sub>NC)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)Cl<sub>2</sub>], taken as a model substrate. This order was deduced from relative second-order rate constants  $k$  (M<sup>-1</sup> sec<sup>-1</sup>), which were obtained as the slopes of plots shown in Figure 1 and which are listed in Table I. Such a reactivity order is CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> > CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NH > C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> > ClC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> ≫ O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>. This is also the order of increasing electron-donating properties of the para substituent Z, *i.e.*, the order of increasing  $\sigma$ -donor ability of the amine nitrogen. The rate constants (log  $k$ ) for para-substituted anilines as entering groups decrease linearly with an increasing value of the Hammett  $\sigma$  parameter.<sup>23</sup> The discrimination between the various entering amines is marked: the reaction with *p*-nitroaniline does not actually proceed even under preparative conditions. It is well recognized that the entering group basicity is an important factor in nucleophilic attacks on slightly polarizable reaction sites such as the coordinated isocyanides; basicity, however, becomes negligible as compared to polarizability in attacks on polarizable centers such as d<sup>8</sup> metal ions. In agreement with the proposed bimolecular attack mechanism, the rate of entry of a given amine is practically independent of the nature of other ligands bonded to palladium (L = P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>, As(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>; X = Cl, Br). The slight influence of the halogen ( $k_{\text{Cl}}/k_{\text{Br}} \approx 2$ ) can be ascribed to the lower electronegativity of bromide relative to chloride, which makes the isocyanide carbon in the trans position less electrophilic. This is also reflected by the fact that  $\nu(\text{C}\equiv\text{N})$  in the bromo derivative is slightly lower than in the chloro derivative (2207 and 2212 cm<sup>-1</sup>, respectively, in 1,2-dichloroethane solution).

A direct attack by the amine on the isocyanide carbon probably occurs through a concerted mechanism with formation of a four-center activated complex in which the metal is not directly involved



The electrophilic character of the isocyanide carbon greatly increases upon coordination to the metal.

This mechanism is supported by the fact that the rate of attack for a given amine depends strongly on the para substituent Y on the isocyanide ring. Table II lists the rate constant values for the reactions of *p*-toluidine with a variety of isocyanide complexes. Figure 2 shows the plots of  $k_{\text{obsd}}$  vs. the *p*-toluidine concentration for the complexes examined. Second-order rate constants,  $k$  (M<sup>-1</sup> sec<sup>-1</sup>), calculated from the slopes of these plots, are listed in Table II. The observed reactivity order is O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NC ≫ C<sub>6</sub>H<sub>5</sub>NC > CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NC > CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>NC ≫ C<sub>6</sub>H<sub>11</sub>NC and parallels the order of electron-withdrawing ability of the para substituent Y. Also in these reactions there is a linear

TABLE II  
RATE CONSTANTS FOR THE REACTIONS AT 30° OF  
*cis*-[Pd(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)(YC<sub>6</sub>H<sub>4</sub>NC)Cl<sub>2</sub>] WITH *p*-TOLUIDINE;  
[COMPLEX] ≈ 10<sup>-4</sup> M

Y	[ <i>p</i> -Toluidine], M	10 <sup>4</sup> × $k_{\text{obsd}}$ , M <sup>-1</sup> sec <sup>-1</sup>	10 <sup>3</sup> $k$ , M <sup>-1</sup> sec <sup>-1</sup>	Y	[ <i>p</i> -Toluidine], M	10 <sup>4</sup> × $k_{\text{obsd}}$ , M <sup>-1</sup> sec <sup>-1</sup>	10 <sup>3</sup> $k$ , M <sup>-1</sup> sec <sup>-1</sup>
CH <sub>3</sub> O	0.125	8.65	7.3	H	0.10	23.13	22.2
	0.10	6.42			0.075	16.00	
	0.075	5.15			0.05	10.87	
CH <sub>3</sub>	0.15	17.63	11.0	O <sub>2</sub> N	0.01	88.01	804.5
	0.125	13.10			0.0075	57.21	
	0.10	10.54			0.005	37.04	
	0.075	8.24			0.002	14.84	

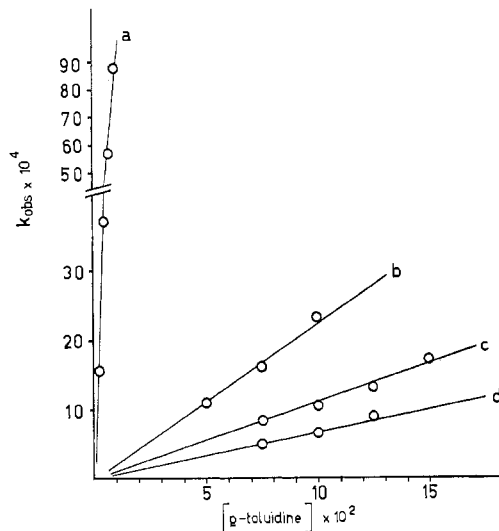


Figure 2.—Plots of the  $k_{\text{obsd}}$  (sec<sup>-1</sup>) vs. the concentration of the entering *p*-toluidine for the reactions with *cis*-[Pd(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)(YC<sub>6</sub>H<sub>4</sub>NC)Cl<sub>2</sub>], at 30°. Y: a, para NO<sub>2</sub>; b, H; c, para CH<sub>3</sub>; d, para CH<sub>3</sub>O.

relationship between the rate constants (log  $k$ ) for the various para-substituted isocyanides and the Hammett  $\sigma$  parameters. The effect of substituents is more pronounced in the case of substrates than of para-substituted attacking amines. The accelerating effect by electron-attracting substituents, which effectively increase the electrophilic character of the carbon atom linked to palladium, is also evidenced by the marked difference in reactivity between the phenyl and cyclohexyl isocyanides (which should have comparable steric hindrance). No effect due to Cl<sup>-</sup> added was observed. Kinetic runs at various temperatures have been carried out for the reaction of *cis*-[Pd(C<sub>6</sub>H<sub>5</sub>NC)(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)Cl<sub>2</sub>] with *p*-toluidine (Table III). Activa-

TABLE III  
RATE CONSTANTS AT VARIOUS TEMPERATURES FOR THE  
REACTION OF *cis*-[Pd(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>NC)Cl<sub>2</sub>] WITH  
*p*-TOLUIDINE; [COMPLEX] ≈ 10<sup>-4</sup> M

Temp, °C	[ <i>p</i> -Toluidine], M	10 <sup>4</sup> × $k_{\text{obsd}}$ , M <sup>-1</sup> sec <sup>-1</sup>	10 <sup>3</sup> $k$ , M <sup>-1</sup> sec <sup>-1</sup>	Temp, °C	[ <i>p</i> -Toluidine], M	10 <sup>4</sup> × $k_{\text{obsd}}$ , M <sup>-1</sup> sec <sup>-1</sup>	10 <sup>3</sup> $k$ , M <sup>-1</sup> sec <sup>-1</sup>
25	0.10	15.84	16.4	35	0.10	32.54	31.2
	0.075	13.24			0.075	23.24	
	0.05	7.56			0.05	14.90	
	0.025	4.32			0.025	7.30	
30	0.10	23.13	22.2	45	0.10	47.00	47.2
	0.075	16.00			0.075	36.53	
	0.05	10.87			0.05	23.24	
					0.025	11.32	

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TABLE IV  
ANALYTICAL AND PHYSICAL DATA

Complex	% C		% H		% N		% halide		Mp (dec), °C	Ir data, cm <sup>-1</sup>		ν(Pd-Cl)
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found		ν(N-H)	ν(NC)	
[Pd(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> )(p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NC)Cl <sub>2</sub> ]	56.09	56.2	3.98	3.9	2.52	2.5	12.73	12.6	214	2206 s	338 s, 296 vs	
[Pd(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> )(p-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> NC)Cl <sub>2</sub> ]	54.52	54.2	3.87	3.9	2.45	2.5	12.38	12.3	227	2216 s	325 ms, 287 s	
[Pd(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> )(C(NHC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NHC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> )Cl <sub>2</sub> ]	57.72	57.4	4.39	4.3	4.21	4.3	10.65	10.5	245	1537 s	289 m, 268 m	
[Pd(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> )(C(NHC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> )Cl <sub>2</sub> ]	58.56	57.8	4.28	4.1	4.41	4.4	11.15	11.3	245	1545 s, br	298 ms, 274 m	
[Pd(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> )(C(NHC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NHC <sub>6</sub> H <sub>4</sub> Cl)Cl <sub>2</sub> ]	55.55	55.4	3.91	3.8	4.18	4.2	15.87	16.0	260	3140 w, 3110 w	292 ms, 274 ms	
[Pd(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> )(C(NHC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NHC <sub>6</sub> H <sub>4</sub> Cl)Cl <sub>2</sub> ]	58.00	58.0	5.18	5.3	4.36	4.4	11.05	10.9	192	3170 s, br, 3120 m	292 ms, 267 ms	
[Pd(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> )(C(NHC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> N(CH <sub>3</sub> )C <sub>6</sub> H <sub>5</sub> )Cl <sub>2</sub> ]	59.14	58.8	4.50	4.6	4.31	4.3	10.91	11.0	237	3190 s, br, 3140 sh	292 ms, 267 ms	
[Pd(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> )(C(NHC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> )Br <sub>2</sub> ]	52.02	51.8	3.96	3.9	3.79	3.8	21.63	21.7	224	3315 ms, br	1536 s, br	
[Pd(As(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> )(C(NHC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> )Cl <sub>2</sub> ]	55.39	56.1	4.21	4.3	4.04	4.1	10.22	10.4	252	3190 s, br, 3120 sh	230 sh, 218 ms	
[Pd(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> )(C(NHC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> )Cl <sub>2</sub> ]	55.31	51.1	4.06	3.7	6.05	5.7	10.20	18.0	239	3170 s, br, 3120 m	302 sh, 296 ms, 274 ms	
[Pd(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> )(C(NHC <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> )Cl <sub>2</sub> ]	(50.95) <sup>b</sup>	59.70	(3.87) <sup>b</sup>	4.8	(5.66) <sup>b</sup>	4.2	(16.71) <sup>b</sup>	10.8	250	3160 s, br, 3115 m	288 m, 267 m	
[Pd(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> )(C(NHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ) <sub>2</sub> )Cl <sub>2</sub> ]	58.29	57.9	4.60	4.6	4.12	4.2	10.43	10.3	244	3190 sh, 3170 s, br, 3110 m <sup>w</sup>	287 m, 266 m	
[Pd(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> )(C(NHC <sub>6</sub> H <sub>4</sub> OCH <sub>3</sub> ) <sub>2</sub> )NHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ]	58.59	58.5	5.38	5.4	4.27	4.2	10.81	10.9	261	3190 sh, 3170 s, br, 3110 m	290 ms, 274 m	
[Pd(P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> )(C(NHC <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> NHC <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> )Cl <sub>2</sub> ]										3261 ms, 3225 m, 3185 m, 3130 w <sup>b</sup>	298 ms, 270 ms	

<sup>a</sup> The analytical data found are satisfactory with a solid product containing about 0.5 mol of chloroform. <sup>b</sup> Values calculated for the formula [Pd(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)(C(NHC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>)NHC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>]. <sup>c</sup> 0.5CHCl<sub>3</sub>. <sup>d</sup> Uncorrected melting points.

tion parameters from a least-squares computer fit are  $\Delta H^* = 9.4 \pm 0.1$  kcal/mol and  $\Delta S^* = -35.1 \pm 1.7$  eu.<sup>24</sup>

Enthalpy values for d<sup>8</sup> square-planar substitution are generally higher for a poorly nucleophilic entering group (such as an amine) and the activation entropy, although negative, does not commonly reach such extreme values. It is our view that these data support the multicenter, concerted mechanism proposed, which involves a nucleophilic attack on an "unshielded" carbon atom with formation of a tightened activated complex of rather stringent steric requirements.

The reactions with *N*-methylaniline and cyclohexylamine display an apparent kinetic order greater than one relative to the entering amine. Kinetic runs with Cl<sup>-</sup> concentrations varying in the range  $(1-5) \times 10^{-3}$  M (complex concentration  $\approx 10^{-4}$  M) have shown no appreciable effect on the reaction rate. The possibility that the central metal also is involved as reaction site at some stage through direct attack by the amine cannot be ruled out. Competition experiments in the presence of bases which are able to interact with the central metal only, such as pyridine, and the use of entering bidentate amines (ethylenediamine, *o*-phenylenediamine, etc.) will provide further clues as to the detailed mechanism of these reactions.

### Experimental Section

**Materials. Complexes of Type *cis*-[Pd(RNC)<sub>2</sub>X<sub>2</sub>].**—These were prepared by treating *cis*-[Pd(RNC)<sub>2</sub>Cl<sub>2</sub>] with a slight excess of L, according to the general method reported earlier.<sup>11</sup> All products were purified by successive reprecipitations from dichloromethane or chloroform upon addition of ethyl ether and identified by elemental analysis and ir spectra (Table IV). *cis*-[Pd(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)(C<sub>6</sub>H<sub>5</sub>NC)Br<sub>2</sub>] was prepared by metathesis from the corresponding chloro complex.

**Carbene Complexes.**—These were prepared by treating the parent isocyanide complexes with the required amines.<sup>10,11</sup> Analytical and physical data are reported in Table IV. *cis*-[Pd(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)(C(NHC<sub>6</sub>H<sub>11</sub>)NHC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>] was prepared by treating the parent cyclohexyl isocyanide complex with excess *p*-toluidine (50:1) in chloroform (reflux 24 hr).

The complex [Pd(P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>)(C(NHC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>)NHC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)Cl<sub>2</sub>] precipitates during the reaction. Its solubility is generally so low in the common organic solvents as to prevent any further purification. The analytical data (see Table IV) are in favor of the presence of chloroform in the solid product, which could not be eliminated even *in vacuo*.

**Isocyanides.**—These were prepared according to the methods described by Ugi, *et al.*<sup>25</sup>

**Amines.**—The commercial products were purified by either sublimation or fractional distillation on KOH under nitrogen atmosphere.

**Solvents.**—1,2-Dichloroethane was purified according to standard methods.<sup>26</sup>

**Kinetics.**—The reactions were followed spectrophotometrically by measuring changes in optical density in the range 330–360 mμ with time by means of a Beckman DK-2A double-beam recording instrument.

Freshly prepared solutions of the complex, stored under nitrogen in an aluminum foil wrapped flask, were used for each kinetic run. The reactions were started by mixing known volumes of standard solutions of the reagents in the thermostated ( $\pm 0.1^\circ$ ) cell compartment of the spectrophotometer. A solution containing the same concentration of the entering amine was used as a reference. Light and air were always excluded. The entering ligand was present in sufficient excess to provide pseudo-first-

(24) The error limits are standard deviations calculated by the method of R. H. Bacon, *Amer. J. Phys.*, **21**, 428 (1953).

(25) I. Ugi, U. Fetzer, U. Eholzer, H. Kuppfer, and K. Offermann, *Angew. Chem., Int. Ed. Engl.*, **4**, 472 (1965).

(26) A. Weissberger and E. S. Proskaner, "Organic Solvents" Interscience, New York, N. Y., 1955, p 415.

order conditions and to force the reactions to completion. The final spectra were generally in good agreement with those of the products prepared and characterized independently. The values of pseudo-first-order rate constants,  $k_{\text{obsd}}$  ( $\text{sec}^{-1}$ ), were obtained from the slopes of plots of  $\log(A_t - A_\infty)$  vs. time, where  $A_t$  and  $A_\infty$  are the optical densities of the reaction mixture at

time  $t$  and after 7–8 half-lives, respectively. The values of  $k_{\text{obsd}}$  were reproducible to better than 10%.

Conductivity measurements on final reaction mixtures showed the presence of cationic carbene derivatives in negligible equilibrium amounts (some per cent units), which were not sufficiently high to affect the reliability of the kinetic results.

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## Organometallic Conformational Equilibria. IX. Isomerism and Hindered Rotation about Palladium–Nitrogen Bonds in $\pi$ -Allyl Complexes<sup>1</sup>

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A study of variable-temperature behavior of the pmr spectra for some  $\pi$ -crotyl(amine)palladium(II) halide complexes from  $-100$  to  $+100^\circ$  is reported. The results are consistent with three pathways of isomerization and epimerization; the activation parameters of each route differ sufficiently to permit the observation of three distinct phases in the variable-temperature spectra of the complexes. In the lowest temperature phase the results are accounted for in terms of intramolecular hindered rotation about the palladium–amine bond. In the intermediate temperature phase intermolecular amine exchange is unequivocally established. The highest temperature phase is interpreted in terms of an equilibrium between  $\pi$ - and  $\sigma$ -bonded allylic forms. The variable-temperature studies were supplemented by double-resonance experiments.

### Introduction

Several pathways of isomerization have been proposed for palladium complexes containing  $\pi$ -bonded allylic moieties. For  $L = \text{amine}$  and  $X = \text{halide}$ , ( $\pi$ -allyl) $\text{PdXL}$  complexes have been shown to be structurally dynamic in solution by investigations of the temperature dependence of pmr spectra. Comparison of the unsymmetrical  $\pi$ -crotyl derivatives with their symmetrical  $\pi$ -allyl and  $\pi$ -2-methylallyl analogs has shown that throughout the observable temperature range the spectra may be entirely accounted for by the following mechanisms: (1) hindered rotation about the palladium–amine bond, (2) intermolecular amine exchange, and (3) an intramolecular  $\pi$ -allyl– $\sigma$ -allyl equilibrium. Other previously proposed mechanisms are inconsistent with the evidence presented.

The relative magnitudes of the activation parameters for interconversion of certain isomers are readily interpreted in terms of intramolecular steric interactions. This is also true for establishing the relative populations of isomers. These results suggest that intramolecular steric interactions play a very important role in the determination of relative thermodynamic stabilities and in the selection of rearrangement pathways.

### Results

Pertinent data from the pmr spectra of a series of ( $\pi$ -crotyl) $\text{PdXL}$  species have been summarized in Table I. Broadening and coalescence of certain resonances occurred with variations in temperature, such that three separate and distinct phases of averaging could be distinguished. Rather than attempting to relate these phases to specific rearrangements in the

entire series of complexes, the spectra of  $\pi$ -crotyl(2-picoline) halides will be discussed in detail in order to establish the general pattern of stereochemical non-rigidity in these molecules.

**Phase 1.**—At  $-80^\circ$  the spectrum of  $\pi$ -crotyl(2-picoline)palladium(II) bromide appears as recorded in Figure 1. On the basis of coupling constants and by analogy to the pmr spectra of 2-picoline and the  $[(\pi\text{-crotyl})\text{PdCl}]_2$  dimer,<sup>2</sup> the following assignments are made. In region 1 is the sextet of the central allylic hydrogen; since  $J_{\text{H}_1\text{-H}_2} \cong J_{\text{H}_1\text{-H}_6} \cong 12$  Hz (see the proton-labeling scheme accompanying Table I), the intensity ratio within the sextet is 1:1:2:2:1:1. In region 2 it is possible to detect a portion of the sextet assigned to the anti allylic proton geminal to the methyl substituent. An intensity ratio of 1:2:3:3:2:1 should derive from the coupling constants  $J_{\text{H}_1\text{-H}_2} = 12$  Hz and  $J_{\text{H}_2\text{-H}_8} = 6$  Hz. In region 3 the syn proton doublet is discernible. There are three singlets 4a, 4b, and 4c assigned to the methyl substituent in the picoline; these singlets partially obscure the methylene anti proton resonances, 6. Upfield are three doublets 8a, 8b, and 8c assigned to the methyl substituent in the allyl ligand.

As the temperature drops below  $-80^\circ$  some broadening is noted in resonance 8a; however, a more noticeable change occurs in resonance 4b which begins to broaden and collapse and at  $-100^\circ$  appears as shown in Figure 1. If the temperature is raised above  $-80^\circ$ , we observe the coalescence of resonances 8b and 8c to a single doublet at  $\tau$  8.90. Again the change in the pyridine methyl region is more dramatic than changes in the rest of the spectrum; resonances 4a and 4c broaden and coalesce to a single peak at their average value  $\tau$  7.17. Figure 1 shows the partially averaged peak at  $-60^\circ$ . Between  $-60$  and  $-30^\circ$ , no significant

(1) Part VIII: J. W. Faller and M. E. Thomsen, *J. Amer. Chem. Soc.*, **91**, 6871 (1969). The work reported in this paper (IX) was presented in part at the Middle Atlantic Regional Meeting of the American Chemical Society, April 1970.

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