

is not as great. It should be noted that the delocalization energy is 30% greater for  $h = 0.2$  to  $0.4$  and  $k = 1.6$  than for the parameters used by West and Powell ( $h = 1.0, k = 0.8$ ).<sup>5</sup> The delocalization energy increases almost linearly with  $k$ . For smaller values of  $h$ , the slope decreases, indicating a decreased dependence on  $k$ .

The value of  $h$  that gives the prescribed electron densities (in the HMO and OAOMO calculations) is between  $0.2$  and  $0.4$ . The increased delocalization energy as  $h$  decreases also lends weight to the choice of this range for  $h$ . This range for  $h$  is close to the value  $0.15$  which was determined by Brown and Hefferman<sup>22</sup> by reproducing with HMO calculations the electron densities predicted by "self-consistent electronegativity" MO calculations.

The value of  $k$  that gives the observed bond orders is between  $1.4$  and  $1.6$ ; these values can be used in either the HMO or OAOMO calculations. The choice of the value of  $k$  in this range is made more plausible by the increased delocalization energy calculated for the higher values of  $k$ . The range above includes the value ( $1.56$ ) used by Vincow and Fraenkel to give

(22) R. D. Brown and M. L. Hefferman, *Trans. Faraday Soc.*, **54**, 757 (1958).

the spin density distribution observed in the e.s.r. spectra of semiquinone ions.<sup>23</sup>

Table IV shows the difference between the calculated quantities using the HMO and OAOMO methods. In all cases the differences between the bond orders and electron densities are small. These differences are not large enough to make the extra calculations necessary in the OAOMO method worthwhile. Calculations using  $S_{CO}$  values of  $0.1, 0.2, 0.3,$  and  $0.4$  resulted in little change for the bond orders and electron densities.

As a result, the most appropriate parameters for use in HMO and OAOMO calculations of the oxocarbons are  $h = 0.2$  to  $0.4$  and  $k = 1.4$  to  $1.6$ . The appropriateness of these parameters in the MO calculations of the squarate ( $C_4O_4^{-2}$ ) and rhodizonate ( $C_6O_6^{-2}$ ) ions will be known when the molecular geometry of these ions has been determined.

**Acknowledgment.**—Part of this work was supported by Grant No. DA-ARO(D)-31-124-G26 from the Army Research Office, Durham. The authors wish to acknowledge Mr. Jerry Farlow for adapting Given's method to the IBM-7070, and Mr. Tom Hegenbarth for the independent intensity estimations.

(23) G. Vincow and G. K. Fraenkel, *J. Chem. Phys.*, **34**, 1333 (1961).

[CONTRIBUTION FROM THE ISTITUTO CHIMICA GENERALE, UNIVERSITA DI PADOVA, PADOVA, ITALY]

## Rates of Substitution Reactions of Square-Planar Platinum(II) Complexes. II.<sup>1</sup> Reactions of *trans*-Dichlorobis(piperidine)platinum(II)

BY UMBERTO BELLUCO, LUCIO CATTALINI, AND ALDO TURCO

RECEIVED DECEMBER 9, 1963

The rates of the reactions of *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>Cl<sub>2</sub>] with <sup>36</sup>Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and N<sub>3</sub><sup>-</sup> and of *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>NO<sub>2</sub>Cl] (C<sub>5</sub>H<sub>11</sub>N = piperidine) with NO<sub>2</sub><sup>-</sup> are reported. These are compared with the rates obtained previously for similar reactions of *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]. The relative increase in reactivity of NO<sub>2</sub><sup>-</sup> in the reaction with [Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>Cl<sub>2</sub>] is discussed. It is observed that the ligands in the *cis* position influence the *trans* effect of the *trans* ligand.

The first paper of this series reports<sup>1</sup> the nucleophilic substitution reactions of <sup>36</sup>Cl<sup>-</sup> and NO<sub>2</sub><sup>-</sup> with *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] in methanol. In this system nitrite ion is a poorer reagent than chloride ion. This is believed to result from the  $\pi$ -bonding of phosphine with platinum(II) which in turn makes less important the electrophilic contribution of the entering reagent, e.g., NO<sub>2</sub><sup>-</sup>.

This paper reports investigations of the reactions of *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>NO<sub>2</sub>Cl] with NO<sub>2</sub><sup>-</sup> and of *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>Cl<sub>2</sub>] (C<sub>5</sub>H<sub>11</sub>N = piperidine) with <sup>36</sup>Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, and N<sub>3</sub><sup>-</sup> in methanol. This complex was chosen because Stuart models show that the steric hindrance caused by piperidine is approximately the same as that of triethylphosphine in the previously studied *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]. Moreover *cis-trans* isomerization is known not to occur<sup>2</sup> for the piperidine compound under the conditions of these experiments. Hence replacement of triethylphosphine with piperidine is expected to affect the kinetic process solely through changes of the electronic features caused by

the different bonding properties of the two ligands. In the course of this investigation it was also felt necessary to study the reaction of *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] with N<sub>3</sub><sup>-</sup>.

### Experimental

**Preparation of Materials.**—*trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>Cl<sub>2</sub>] was prepared from [Pt(SMe<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>] and piperidine in *n*-butyl ether.<sup>2</sup> The compound was recrystallized from ethanol, m.p. 252–253°. *Anal.* Calcd. for C<sub>10</sub>H<sub>22</sub>N<sub>2</sub>Cl<sub>2</sub>Pt: N, 6.4. Cl, 16.5. Found: N, 6.3; Cl, 16.7. The compound is a nonelectrolyte in methanol ( $\Lambda_M < 1$  ohm<sup>-1</sup> cm.<sup>-2</sup> mole<sup>-1</sup>). [Pt(SMe<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>] was prepared by the reaction of K<sub>2</sub>PtCl<sub>4</sub> with S(CH<sub>3</sub>)<sub>2</sub> in water solution.<sup>3</sup> The S(CH<sub>3</sub>)<sub>2</sub> used was obtained from the reaction between CH<sub>3</sub>I and Na<sub>2</sub>S in a water-ethanol mixture.<sup>4</sup>

*trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>] was obtained by the reaction of *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>Cl<sub>2</sub>] ( $10^{-3}$  M) with NaNO<sub>2</sub> ( $10^{-1}$  M) at 30° in methanol, containing  $10^{-2}$  M toluenesulfonic acid, for 4 days. The compound was recrystallized from methanol, m.p. 258–260°. *Anal.* Calcd. for C<sub>15</sub>H<sub>22</sub>N<sub>4</sub>O<sub>4</sub>Pt: N, 12.25. Found: N, 12.1.

*trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>] was obtained by the reaction of *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>Cl<sub>2</sub>] ( $10^{-3}$  M) with NaN<sub>3</sub> ( $5 \times 10^{-2}$  M) in methanol at 30° for 4 days. The product was recrystallized from methanol, m.p. 172–173°. *Anal.* Calcd. for C<sub>10</sub>H<sub>22</sub>N<sub>8</sub>Pt: N, 24.9. Found: N, 24.4.

(1) Part I: U. Belluco, L. Cattalini, and A. Turco, *J. Am. Chem. Soc.*, **86**, 226 (1964).

(2) J. Chatt, L. A. Ducanson, and L. M. Venanzi, *J. Chem. Soc.*, 4461 (1955).

(3) C. Enebuske, *J. prakt. Chem.*, **38**, 358 (1888).

(4) D. S. Tarbell and C. Weaver, *J. Am. Chem. Soc.*, **63**, 2941 (1941).

*trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>ClNO<sub>2</sub>] was obtained by the reaction of *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>Cl<sub>2</sub>] (10<sup>-3</sup> M) with NaNO<sub>2</sub> (10<sup>-3</sup> M) in methanol in the presence of toluenesulfonic acid (10<sup>-4</sup> M) at 30° for 1 week. The product was recrystallized from methanol, m.p. 241–243°, λ<sub>max</sub> 2930 Å. (ε<sub>max</sub> 1420). Anal. Calcd. for C<sub>10</sub>H<sub>22</sub>N<sub>3</sub>O<sub>2</sub>ClPt: N, 9.4; Cl, 7.9. Found: N, 9.6; Cl, 8.0.

*trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] was prepared by the method of Jensen<sup>5</sup> as described earlier.<sup>1</sup>

*trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>] was prepared by the reaction of *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (10<sup>-3</sup> M) with excess of NaN<sub>3</sub> (5 × 10<sup>-2</sup> M) in methanol for 2 days. The product was recrystallized from methanol, m.p. 141–142°. Anal. Calcd. for C<sub>12</sub>H<sub>30</sub>N<sub>6</sub>P<sub>2</sub>Pt: N, 16.3. Found: N, 16.2.

Anhydrous CH<sub>3</sub>OH was prepared by distillation over (CH<sub>3</sub>O)<sub>2</sub>Mg. The Li<sup>36</sup>Cl was obtained from LiCl and H<sup>36</sup>Cl by isotopic exchange. It was recrystallized from acetone.

**Kinetics. *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>Cl<sub>2</sub>]-NO<sub>2</sub><sup>-</sup> Reactions.**—The reaction between *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>Cl<sub>2</sub>] and NO<sub>2</sub><sup>-</sup> was studied spectrophotometrically in methanol at 30° at a constant ionic strength (LiNO<sub>3</sub>). Preliminary spectrophotometric tests had shown that the nitrate ion does not react with *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>Cl<sub>2</sub>]. The initial complex concentration was held constant and that of NaNO<sub>2</sub> varied. It was also found that *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>Cl<sub>2</sub>] and *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>] obey Beer's law in methanol in the 3600–2400 Å. region for the range of concentration used. All spectrophotometric measurements were made on a Beckman DK2A recording spectrophotometer, with a thermostated cell compartment. The absorption spectra of the piperidine complexes are shown in Fig. 1. In order to investigate the effect of

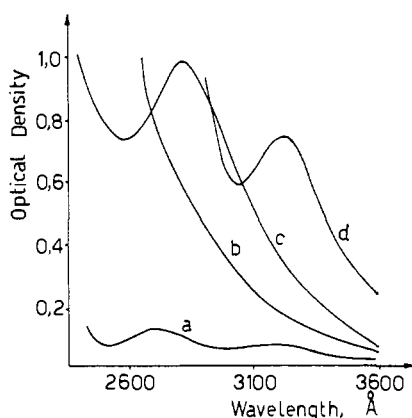


Fig. 1.—The absorption spectra of the piperidine complexes: a, *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>Cl<sub>2</sub>] 7 × 10<sup>-4</sup> M; b, *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>] 7 × 10<sup>-4</sup> M; c, *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>ClNO<sub>2</sub>] 7 × 10<sup>-4</sup> M; d, *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>] 10<sup>-3</sup> M.

CH<sub>3</sub>O<sup>-</sup>, some runs were made in the presence of sodium methoxide. It was found that addition of CH<sub>3</sub>ONa (10<sup>-3</sup> M) has no effect on the reaction rate. In other experiments *p*-toluenesulfonic acid was added to the reaction mixture. With the addition of small amounts (3.35 × 10<sup>-4</sup> M) of *p*-toluenesulfonic acid, the results changed dramatically. The rate increased and the spectral changes accompanying the reaction were quite different from that of a reaction containing no added acid. The effect of acid on this reaction is being studied and the results of this investigation will be reported later. Applying these observations to the preparative scale it was possible to isolate the intermediate *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>ClNO<sub>2</sub>] by the method described above. The spectrum of this compound is given in Fig. 1. The consumption of *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>Cl<sub>2</sub>] to give *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>ClNO<sub>2</sub>] was followed by measuring the rate of change of optical density at the wave length of the isosbestic point at 2665 Å. (Fig. 1). The simple relation

$$A_{2665} = \epsilon_1(a - x) + \epsilon_2x$$

was used to calculate the concentration of *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>Cl<sub>2</sub>] during the course of the reaction, where  $\epsilon_1$  = molar extinction coefficient of the dichloro compound,  $\epsilon_2$  = molar extinction

coefficient of the nitro complexes,  $x$  = total concentration of nitro complexes, and  $a$  = initial concentration of dichloro complex.

The second step of the reaction with NO<sub>2</sub><sup>-</sup> was followed at 2800 Å. by using solutions of *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>ClNO<sub>2</sub>].

**Isotopic Exchange.**—The isotopic exchange experiments with <sup>36</sup>Cl<sup>-</sup> were made following procedures described in part I.<sup>1</sup>

***trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>Cl<sub>2</sub>]-N<sub>3</sub><sup>-</sup> Reactions.**—Rates of reaction between *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>Cl<sub>2</sub>] and N<sub>3</sub><sup>-</sup> have been studied in the presence of added LiNO<sub>3</sub> to maintain a constant ionic strength. The complex concentration was not varied while that of NaN<sub>3</sub> covered a 15-fold range. Some runs were made in the presence of various amounts of *p*-toluenesulfonic acid. In every case there was no change in the observed rate constant. The absorption spectrum of *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>] in methanol is given in Fig. 1.

The reaction was followed by measuring the optical density at 2800, 3040, and 3220 Å., where the absorption of the product is considerably larger than that of the starting complex. The absorption was measured against a blank of NaN<sub>3</sub> (and *p*-toluenesulfonic acid when necessary) in the same concentrations as in the solution under investigation. The reaction product is *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>]; however, the rate-determining step must be the substitution of the first chlorine atom, leading to the formation of the more reactive *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>ClN<sub>3</sub>].

***trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]-N<sub>3</sub><sup>-</sup> Reactions.**—The rates of these reactions were studied at 55° in methanol. The procedure followed was the same as that described above.

## Results and Discussion

The values of  $k_{\text{obsd}}$  for all the reactions studied are given in Table I. The observed rate constants  $k_{\text{obsd}}$  were obtained by treating the kinetics as a pseudo-

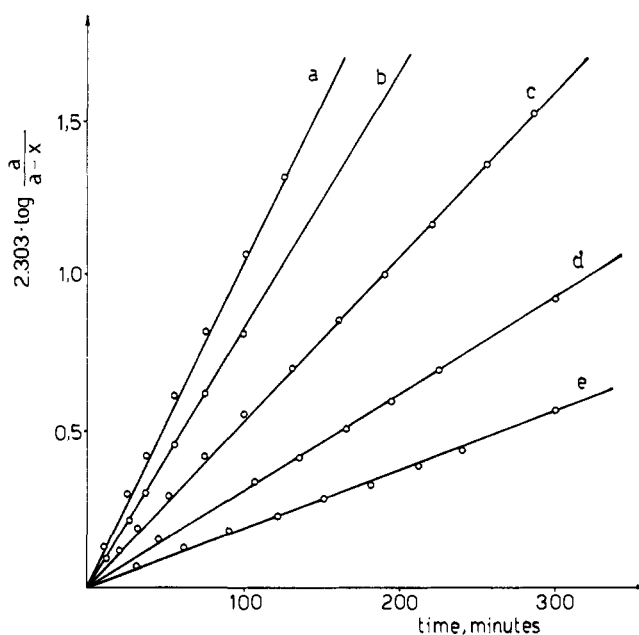


Fig. 2.—Typical first-order plots for the experimental data for *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>]-N<sub>3</sub><sup>-</sup> reactions with [complex] = 1.58 × 10<sup>-4</sup> M, solvent = CH<sub>3</sub>OH, temperature = 30°. a, 0.10 M NaN<sub>3</sub>; b, 0.075 M NaN<sub>3</sub>; c, 0.05 M NaN<sub>3</sub>; d, 0.025 M NaN<sub>3</sub>; e, 0.0125 M NaN<sub>3</sub>.

first-order process. The  $k_{\text{obsd}}$  values of Table I were obtained graphically according to the first-order rate law (Fig. 2)

$$\log \frac{a}{a-x} = \frac{kt}{2.303}$$

The variation of the pseudo-first-order rate constants,  $k_{\text{obsd}}$ , with initial concentration of reagent was con-

(5) K. A. Jensen, *Z. anorg. allgem. Chem.*, **229**, 225 (1936).

TABLE I

RATES FOR REACTIONS OF PLATINUM(II) COMPLEXES WITH  $^{36}\text{Cl}^-$ ,  $\text{NO}_2^-$ , AND  $\text{N}_3^-$  IN  $\text{CH}_3\text{OH}$  AT  $30^\circ$

Complex concn., $M$	Reactant concn., $M$	Added $\text{LiNO}_3$ concn., $M$	$k_{\text{obsd}} \times 10^4$ , $\text{sec.}^{-1}$	
<i>trans</i> -[Pt(C <sub>5</sub> H <sub>11</sub> N) <sub>2</sub> Cl <sub>2</sub> ]	$^{36}\text{Cl}^-$ (LiCl)	0.010	0.265	
		0.033	0.242	
		0.050	0.225	
		0.075	0.200	
		0.152	0.123	
	$\text{NO}_2^-$ (NaNO <sub>2</sub> )	0.01	0.045	
		0.02	0.035	
		0.03	0.025	
		0.05	0.005	
		0.0175	0.0925	
$\text{N}_3^-$ (NaN <sub>3</sub> )	0.0175	0.0725		
	0.050	0.060		
	0.050	0.060		
	0.050	0.060		
	0.050	0.060		
	0.075	0.035		
	0.10	0.01		
	<i>trans</i> -[Pt(C <sub>5</sub> H <sub>11</sub> N) <sub>2</sub> ClNO <sub>2</sub> ]	$\text{NO}_2^-$ (NaNO <sub>2</sub> )	0.005	0.05
			0.010	0.045
			0.02	0.035
0.015			0.040	
0.035			0.020	
0.050			0.005	
<i>trans</i> -[Pt(PEt <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> ] <sup>b</sup>	$\text{N}_3^-$ (NaN <sub>3</sub> )	0.0125	0.0975	
		0.025	0.085	
		0.050	0.060	
		0.075	0.035	
		0.10	0.01	

<sup>a</sup>  $k_{\text{obsd}} = R/[\text{complex}]$

$$R = \frac{2[\text{Cl}^-][\text{Pt}(\text{C}_5\text{H}_{11}\text{N})_2\text{Cl}_2]}{2[\text{Pt}(\text{C}_5\text{H}_{11}\text{N})_2\text{Cl}_2] + [\text{Cl}^-]} \ln \frac{C_\infty - C_0}{C_\infty - C_t}$$

<sup>b</sup> Reaction in  $\text{CH}_3\text{OH}$  at  $55^\circ$ .

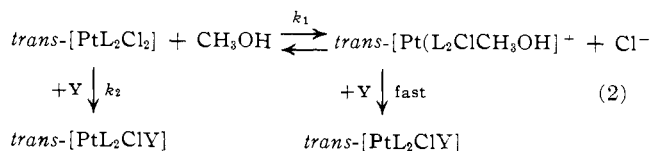
sistent with the expression

$$k_{\text{obsd}} = k_1 + k_2[\text{Y}] \quad (1)$$

since the plots of  $k_{\text{obsd}}$  vs.  $[\text{Y}]$  give straight lines with nonzero intercepts, as in Fig. 3.

Equation 1, where  $k_1$  is a first-order rate constant for solvent-controlled reaction, conforms to the general law found for the substitution reactions of platinum(II) square-planar complexes.<sup>6</sup>

The over-all reaction for the kinetics discussed here can be summarized as



The calculated rate constants  $k_1$  and  $k_2$  are presented in Table II. It was necessary to study the kinetics of the two complexes, *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>X<sub>2</sub>] and *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>X<sub>2</sub>], at different temperatures; however, this fact does not complicate the discussion. The data in Table II show that all the reactions of *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>Cl<sub>2</sub>] proceed at a higher rate than those of *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>].

(6) F. Basolo and R. G. Pearson, "Progress in Inorganic Chemistry," Vol. 4, F. A. Cotton, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, p. 392.

TABLE II

RATE CONSTANTS FOR THE REACTIONS OF PLATINUM(II) COMPLEXES WITH  $^{36}\text{Cl}^-$ ,  $\text{NO}_2^-$ , AND  $\text{N}_3^-$  IN  $\text{CH}_3\text{OH}$

Complex	Reactant	Temp., $^\circ\text{C}$ .	$k_1 \times 10^5$ , $\text{sec.}^{-1}$	$k_2 \times 10^4$ , $M^{-1}\text{sec.}^{-1}$
<i>trans</i> -[Pt(C <sub>5</sub> H <sub>11</sub> N) <sub>2</sub> Cl <sub>2</sub> ]	$\text{NO}_2^-$	30	1.5	20.4
	$^{36}\text{Cl}^-$ <sup>a</sup>	30	1.5	9.25
	$\text{N}_3^-$	30	1.5	53
<i>trans</i> -[Pt(C <sub>5</sub> H <sub>11</sub> N) <sub>2</sub> ClNO <sub>2</sub> ]	$\text{NO}_2^-$	30	7	57.3
	$^{36}\text{Cl}^-$ <sup>a</sup>	30	7.4	2.52
<i>trans</i> -[Pt(PEt <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> ]	$\text{NO}_2^-$ <sup>b</sup>	55	4.47	0.97
	$^{36}\text{Cl}^-$ <sup>b</sup>	55	4.5	4.2
	$\text{N}_3^-$	55	1.0	16.3

<sup>a</sup> U. Belluco, L. Cattalini, and A. Orio, *Gazz. chim. ital.*, in press. <sup>b</sup> Data taken from ref. 1.

The anomalous value for  $k_1$  in the reaction between *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] and  $\text{N}_3^-$  is possibly outside the limits of experimental error. There is no apparent reason for this discrepancy and a careful investigation at very low azide concentration will be necessary before any theoretical significance can be attached to the observation.

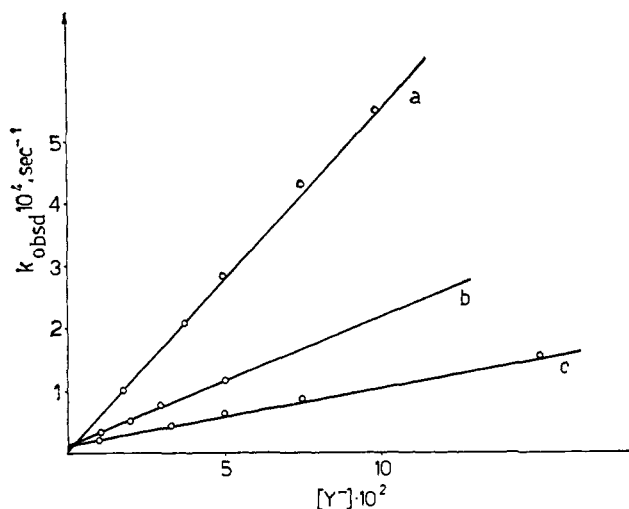


Fig. 3.—The variation of  $k_{\text{obsd}}$  with reagent concentration for *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>Cl<sub>2</sub>] + X<sup>-</sup> reactions: a, X<sup>-</sup> =  $\text{N}_3^-$ ; b, X<sup>-</sup> =  $\text{NO}_2^-$ ; c, X<sup>-</sup> =  $^{36}\text{Cl}^-$ .

In the case of the reaction with *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>],  $\text{Cl}^-$  should act as a better nucleophile than in the reaction with *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>Cl<sub>2</sub>] since the acceptor properties of platinum are expected to be enhanced by the presence of the phosphine molecule in the complex. The fact that the opposite occurs tells us that rearrangement of the square configuration to give the assumed trigonal bipyramidal transition state apparently involves a larger free energy change in the case of the phosphine complex, and the most obvious explanation is that bond making is more developed in this case.

Additional reasoning is necessary in order to explain the larger increase of the reaction rate with  $\text{NO}_2^-$  in going from *trans*-[Pt(PEt<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] to *trans*-[Pt(C<sub>5</sub>H<sub>11</sub>N)<sub>2</sub>Cl<sub>2</sub>]. The most important effect caused by the replacement of the two phosphine molecules by two piperidine molecules is probably the enhancement of

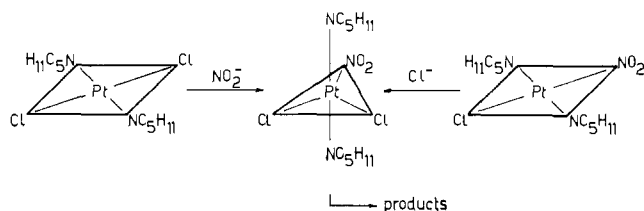


Fig. 4.—The transition state for  $[\text{Pt}(\text{C}_5\text{H}_{11}\text{N})_2\text{Cl}_2\text{NO}_2]$ .

the ability of platinum to donate its  $\pi$ -electrons to the incoming reagent, thus favoring the electrophilic attack of the nitrite ion. In other words  $\text{NO}_2^-$  can make relatively stronger bonds in the activated complex of the reaction with the piperidine compound. It has already been shown that  $\text{NO}_2^-$  reacts rapidly with negatively charged platinum(II) complexes but slowly with positively charged complexes.<sup>7</sup> Thus its effectiveness is apparently due mainly to its electrophilic ability. The previous paper<sup>1</sup> in this series gives a short explanation of the biphilic nature of this reagent. It is interesting to note that the results reported here were obtained with a neutral complex, where the formal charge on the central atom has been changed by varying the nature of two neutral ligands. Nevertheless the effect on the reaction rates is of the same type as that obtained by Gray<sup>7</sup> by replacing neutral ligands with charged ligands, for example, going from *trans*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$  to  $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$ . It is tempting to conclude that on the one hand our results are in agreement with the biphilic character of  $\text{NO}_2^-$  and on the other hand they are in agreement with the general picture which looks at the phosphine molecule as a  $\sigma$ -donating- $\pi$ -accepting ligand.

The results of the reactions of *trans*- $[\text{Pt}(\text{C}_5\text{H}_{11}\text{N})_2\text{ClNO}_2]$  with  $\text{Cl}^-$  show that the replacement of one chloride by nitrite as a ligand in *trans*- $[\text{Pt}(\text{C}_5\text{H}_{11}\text{N})_2\text{Cl}_2]$  causes a significant decrease of the reaction rate with  $\text{Cl}^-$ . However, the opposite is true for the reaction with  $\text{NO}_2^-$ ; the chloronitro complex reacts faster than the dichloro. The presence of  $\text{NO}_2^-$  in the position *trans* to the leaving chloride ion might have been expected to increase the reaction rate in both cases, owing to the larger *trans* effect of nitrite groups as compared to chloride.

The composition of the transition state for the reaction between *trans*- $[\text{Pt}(\text{C}_5\text{H}_{11}\text{N})_2\text{Cl}_2]$  and  $\text{NO}_2^-$  is the same as that of the reaction between *trans*- $[\text{Pt}(\text{C}_5\text{H}_{11}\text{N})_2\text{ClNO}_2]$  and  $\text{Cl}^-$ . In both cases, there are two chlorines and a nitro group in the trigonal plane and, if all bonds were well developed, the transition state would be identical (Fig. 4).

Thus the slower reaction in the second case is in agreement with the observation that the nitro group stabilizes the square-planar complex more effectively than does  $\text{Cl}^-$ .<sup>8</sup> Since  $\text{Cl}^-$  reacts faster with *trans*- $[\text{Pt}(\text{C}_5\text{H}_{11}\text{N})_2\text{Cl}_2]$  than with *trans*- $[\text{Pt}(\text{C}_5\text{H}_{11}\text{N})_2\text{ClNO}_2]$ , the nitrite could not have stabilized the transition state as much as it did the ground state. The reactivity order toward  $\text{NO}_2^-$ , *trans*- $[\text{Pt}(\text{C}_5\text{H}_{11}\text{N})_2\text{ClNO}_2] > \text{trans-}[\text{Pt}(\text{C}_5\text{H}_{11}\text{N})_2\text{Cl}_2]$ , also suggests that the introduction of a second nitrite in the transition state has a greater effect than introduction of the first nitrite group in the substrate. In other words, the substitution of a chloride by a nitrite group in the penta-

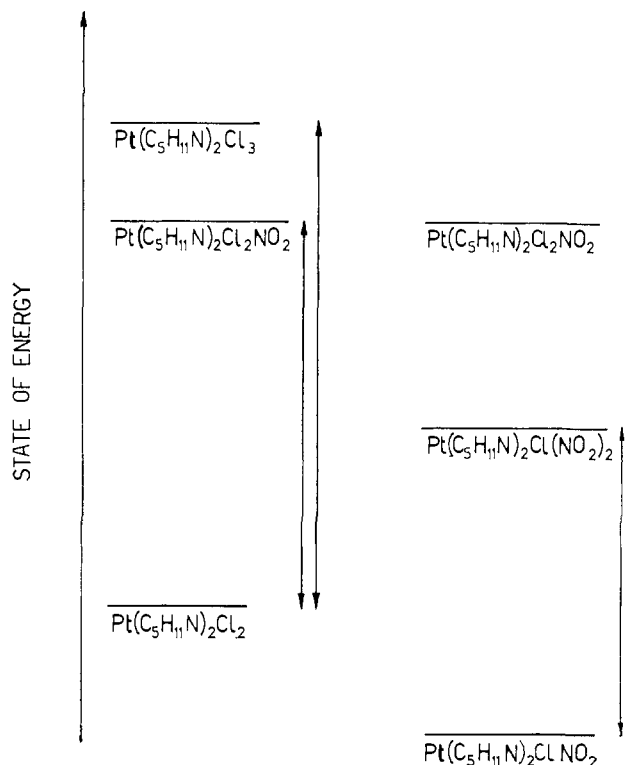


Fig. 5.—Scheme of the relative energy states.

coordinated species, already containing one nitrite, leads to a greater decrease in energy than does the change of a chloride to a nitrite in the square-planar complex containing no other nitrite as a ligand. As a consequence the larger amount of energy required to form the transition state from a chloronitro complex compared to a dichloro complex is more than compensated by the addition of an entering  $\text{NO}_2^-$  but not by the addition of an entering  $\text{Cl}^-$ . The relative energy states discussed above are illustrated in Fig. 5.

Returning to the phosphine complex *trans*- $[\text{Pt}(\text{PEt}_3)_2\text{Cl}_2]$ , the reactivity order is  $\text{Cl}^- > \text{NO}_2^-$ , showing that nitrite destabilizes the pentacoordinate transition state relative to chloride. This behavior is opposite to that observed for the case of the piperidine complex *trans*- $[\text{Pt}(\text{C}_5\text{H}_{11}\text{N})_2\text{Cl}_2]$  and perhaps indicates that relevant platinum orbitals are no longer available to  $\text{NO}_2^-$  in the bipyramid when phosphine molecules are bound in the complex.

The reactions with  $\text{N}_3^-$  indicate that this ion behaves as a nucleophilic reagent. The azide ion has an empty  $\pi$ -antibonding orbital which could confer electrophilic properties to this reagent by receiving electrons from the metal. However, this  $\pi$ -orbital is mainly localized on the central nitrogen,<sup>9</sup> and, when the attack occurs through one of the terminal nitrogens, it will shift toward the opposite end of the triatomic group,<sup>10</sup> thus causing the potential electrophilic character to decrease further. The observed rate constants for the substitution by  $\text{N}_3^-$  show that this ion behaves similarly to  $\text{Cl}^-$ . The increase of the reactivity of these ions on going from the reactions with *trans*- $[\text{Pt}(\text{PEt}_3)_2\text{Cl}_2]$  to those with *trans*- $[\text{Pt}(\text{C}_5\text{H}_{11}\text{N})_2\text{Cl}_2]$  is approximately the same. The ratio  $k_2^{\text{N}_3^-}/k_2^{\text{Cl}^-}$  for the reactions of the two ions with the single

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complexes is slightly in favor of the azide ion, showing that  $N_3^-$  is a better nucleophilic reagent than is  $Cl^-$ .

**Acknowledgments.**—We are grateful for financial support from the North Atlantic Treaty Organization

(N.A.T.O.) and the Italian "Consiglio Nazionale delle Ricerche." We thank Professors F. Basolo and R. G. Pearson and Dr. M. L. Tobe for helpful correspondence and stimulating discussions.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, THE STANDARD OIL COMPANY (OHIO), CLEVELAND, OHIO]

## Novel Acetylene Tungsten Carbonyl Complexes

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RECEIVED MARCH 30, 1964

Disubstituted alkynes such as 3-hexyne, diphenylacetylene, and methylphenylacetylene react with tris(acetonitrile)tungsten tricarbonyl or mono(acetonitrile)tungsten pentacarbonyl to give  $(RC\equiv CR)_3W(CO)$ . The structure and a qualitative molecular orbital picture are discussed. Similar reactions with the trisacetonitrile complexes of chromium and molybdenum cause cyclization to give hexaalkylbenzene or tetraphenylcyclopentadienone. Monosubstituted acetylenes do not give identifiable products under comparable reaction conditions. The reaction of stilbene with mono(acetonitrile)tungsten pentacarbonyl gives a normal olefin complex, mono(stilbene)tungsten pentacarbonyl.

### Introduction

Metal carbonyls can react with alkynes to give one of three general types of complexes: (1) the alkynes might cyclize with formation of a homocyclic ring system such as cyclobutadiene derivatives,<sup>1-4</sup> benzene derivatives,<sup>5-7</sup> cyclic ketones such as cyclopentadienones, quinones, and tropones,<sup>2,3,8-14</sup> or with formation of heterocyclic rings<sup>13,15-17</sup>; (2) the alkyne acts as a dinuclear bridging ligand<sup>2,3,18-22</sup>; and (3) the alkyne is bonded to a single transition metal atom without ring formation. Only a very few compounds of the latter type are reported in the literature.<sup>23-30</sup>

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We recently reported the preparation of a new acetylenic complex of tungsten that appears to be of the latter type.<sup>31</sup> This study has now been extended to other alkynes and the other subgroup VIB metals.

### Experimental

$(CH_3CH_2C\equiv CCH_2CH_3)_3W(CO)$  (I) was prepared as described in an earlier publication.<sup>31</sup>

$(C_6H_5C\equiv CC_6H_5)_3W(CO)$  (II).—Diphenylacetylene (4.5 g.) and  $(CH_3CN)_3W(CO)_3$  (3.3 g.) in 55 ml. of ethanol were refluxed under nitrogen for 18 hr. Carbon monoxide was evolved (about 380 cc.) (calcd. for 2 equiv., 422). The pale yellow crystals (5.2 g.) were collected, taken up in benzene, and precipitated with ethanol giving  $(C_6H_5C\equiv CC_6H_5)_3W(CO)$ , m.p. 193°, color change around 175°.

*Anal.* Calcd. for  $C_{28}H_{30}OW$ : C, 69.25; H, 4.03; W, 24.67; mol. wt., 746. Found: C, 69.77, 69.96; H, 4.34, 4.21; W, 24.55; mol. wt., 754 (osmometer, benzene).

This compound may be made similarly starting with diphenylacetylene and  $(CH_3CN)_3W(CO)_3$ . It can also be prepared by simply heating the reactants to 70° under vacuum without solvent for a few hours.

$(CH_3C\equiv CC_6H_5)_3W(CO)$  (III).—Methylphenylacetylene (10 ml.) and  $(CH_3CN)_3W(CO)_3$  (3.9 g.) were heated to 90° with stirring under reduced pressure (195 mm.). Gas evolution ceased within 1 hr. The pressure was then lowered to 5 mm. and the excess methylphenylacetylene distilled off at 90°. The brown viscous residue was taken up in 8 ml. of ether and filtered. This solution was added to 80 ml. of methanol. Dropwise addition of water precipitated light yellow crystals which on crystallization from benzene gave  $(CH_3C\equiv CC_6H_5)_3W(CO)$ , m.p. 96–98°.

*Anal.* Calcd. for  $C_{28}H_{24}OW$ : C, 60.02; H, 4.32; W, 32.81; mol. wt., 560. Found: C, 60.3; H, 4.3; W, 33.4; mol. wt., 564 (osmometer, benzene).

Oxidation with excess  $I_2$  in refluxing ethanol evolved 0.97 equiv. of CO based on a molecular weight of 560. Methylphenylacetylene could be recovered from a Dry Ice trap after pyrolyzing this compound under vacuum.

$(C_6H_5CH=CHC_6H_5)_3W(CO)_3$ .—A mixture of *trans*-stilbene (0.6 g.) and  $(CH_3CN)_3W(CO)_3$  (1.0 g.) was heated to 130° under good vacuum until gas evolution ceased. The black residue was extracted with benzene and the benzene solution evaporated to dryness. The orange-red solid was crystallized from hexane-benzene to give (stilbene) $W(CO)_3$ , m.p. 135°.

*Anal.* Calcd. for  $C_{19}H_{12}O_3W$ : C, 45.25; H, 2.38. Found: C, 45.27, 45.24; H, 2.82, 2.68.

**Nuclear Magnetic Resonance Spectra.**—Proton magnetic resonances were observed with a fully equipped Varian DP-60

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