

visible absorption band at  $16,700\text{ cm}^{-1}$  (shoulder on the  $23,800\text{-cm}^{-1}$  band) can be attributed to a penta-coordinate complex. An analogous color change was observed for solutions of  $[\text{Ni}(\text{TEP})\text{Cl}_2]$  containing a large excess (200:1 mole ratio) of the monodentate phosphine. The cream-colored  $[\text{Ni}(\text{TEP})_2][\text{B}(\text{C}_6\text{H}_5)_4]_2$  is insoluble in dichloromethane ( $26,000\text{ cm}^{-1}$ ,  $\epsilon$  940 in  $\text{CH}_3\text{CN}$ ) but forms a yellow solution with a large excess of  $\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2$  (101:1 molar ratio) that shows a symmetrical visible band at  $24,100\text{ cm}^{-1}$  ( $\epsilon$  930). Spectral comparison with other  $[\text{Ni}(\text{bidentate})_2\text{X}]^+$  species, where bidentate = AsP, SP, and SeP (ligands II–IV), indicates that the lowest electronic absorption band of the planar  $[\text{Ni}(\text{bidentate})_2]^{2+}$  cation generally shifts a few thousand reciprocal centimeters to lower energy when the five-coordinate complex is formed.<sup>3</sup> Also, since the trigonal-bipyramidal species  $[\text{Ni}(\text{phosphite})_5]^{2+}$ , where phosphite =  $\text{P}(\text{OCH}_3)_3(\text{CH}_2)_3$  and  $\text{P}(\text{OCH}_3)_3$ , absorb near  $20,000\text{ cm}^{-1}$ ,<sup>31</sup> it is reasonable to assign the  $24,100\text{-cm}^{-1}$  band to the square-pyramidal  $[\text{Ni}(\text{TEP})_2\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2]^{2+}$  cation, where the monodentate phosphine is loosely held in the apical position. To test the ease of replacing a halide from the  $[\text{Ni}(\text{TEP})_2\text{X}]^+$  cations in the presence of excess  $\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2$ , the visible absorption spectrum of  $[\text{Ni}(\text{TEP})_2\text{Br}]^+$

(31) J. M. Jenkins, T. J. Huttemann, and J. G. Verkade, *Advan. Chem. Ser.*, **No. 62**, 604 (1967); E. F. Riedel and R. A. Jacobson, Abstracts, Meeting of the American Crystallographic Association, Minneapolis, Minn., No. P-10.

$[\text{B}(\text{C}_6\text{H}_5)_4]$  is unchanged in the presence of a 48:1 molar ratio excess of  $\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2$ ; thus the bromide was not replaced by  $\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2$ .

The tendency of the  $[\text{Ni}(\text{TEP})\text{X}_2]$  complexes to become pentacoordinate depends upon the anion and appears to follow the order of polarizability of the anions rather than their relative positions in the spectrochemical series; evidence to support this general conclusion has been reported previously<sup>4,11,18,32</sup> particularly for the series  $[\text{Ni}(\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2)_2\text{X}_2]$ .<sup>18</sup>

The failure to obtain a palladium complex containing two chelating diphosphine groups has been reported by Wymore and Bailar.<sup>19</sup> In this work, the reaction of  $\text{PdI}_2$  with TEP in a 1:2 mole ratio yielded only the yellow, square-planar  $[\text{Pd}(\text{TEP})\text{I}_2]$  complex. Dichloromethane solutions of this complex remained yellow in the presence of a large excess of  $\text{C}_6\text{H}_5\text{P}(\text{CH}_3)_2$ . Attempts to isolate complexes of the type  $[\text{Pd}(\text{TEP})_2\text{X}]^+$  gave only the previously discussed square-planar complexes.

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(32) R. G. Hayter, *Inorg. Chem.*, **2**, 932 (1963).

CONTRIBUTION FROM THE ISTITUTO DI CHIMICA ANALITICA ED ELETTOCHIMICA DELL'UNIVERSITÀ, PISA, ITALY

## Kinetics of the Reaction of the Bis(oxalato)platinate(II) Ion with Thiocyanate

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Rate data for the reaction of  $\text{Pt}(\text{C}_2\text{O}_4)_2^{2-}$  with  $\text{SCN}^-$  in the presence of various cations and at several temperatures are reported. The reaction gives  $\text{Pt}(\text{SCN})_4^{2-}$  and occurs in at least two steps, as shown by the change of optical density with time. An intermediate product was isolated and identified as *trans*- $\text{K}_4[\text{Pt}(\text{C}_2\text{O}_4)_2(\text{SCN})_2] \cdot 3\text{H}_2\text{O}$ . An examination of this product has shown that the overall reaction is more complicated than shown by the optical density–time curve. The rate and the equilibrium constant of an intermediate or possibly parallel reaction were measured at  $25^\circ$ , as well as the activation parameters of the main reactions. The results are interpreted in terms of a ring-opening mechanism, involving intermediates containing unidentate oxalato ligands.

### Introduction

Many substitution reactions of square-planar platinum(II) complexes, mostly involving unidentate ligands, have been studied kinetically. In general these reactions have been found to exhibit a two-term rate law<sup>1</sup>

$$\text{rate} = k_{\text{H}_2\text{O}}[\text{complex}] + k_1[\text{complex}][\text{L}] \quad (\text{L} = \text{entering ligand})$$

However substitution reactions on Pt(II) complexes with chelating ligands have been infrequently studied, possibly because such reactions are generally very slow. For instance,  $k_{\text{H}_2\text{O}}$  and  $k_1$  for the  $\text{C}_2\text{O}_4^{2-}$  exchange with  $\text{Pt}(\text{C}_2\text{O}_4)_2^{2-}$  are smaller by about 4 orders of magnitude than the values for comparable unidentate complexes.<sup>2</sup>

For this reaction, as well as for the racemization and exchange reactions of tris(oxalato) octahedral complexes,<sup>3</sup> an intramolecular mechanism has been proposed, which involves the opening of the chelate ring and the existence of unidentate oxalato complexes as intermediates. To the best of our knowledge, such intermediates have not been isolated, and for Pt(II) only very few complexes containing acid oxalato groups<sup>4</sup> or amino acids with a free carboxyl group<sup>5</sup> are known.

In an attempt to clarify the mechanism of such reactions we have measured the rate of the reaction of  $\text{Pt}(\text{C}_2\text{O}_4)_2^{2-}$  with  $\text{SCN}^-$ , considering also the salt effects, which are already known for many reactions

(1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1967, Chapter 4, pp 300–328.

(2) J. E. Tegginis and R. M. Milburn, *Inorg. Chem.*, **3**, 364 (1964).

(3) V. I. Goremykin and K. A. Gladyshevskaya, *Dokl. Akad. Nauk SSSR*, **28**, 625 (1940).

(4) J. A. Kieft and K. Nakamoto, *J. Inorg. Nucl. Chem.*, **29**, 2561 (1967).

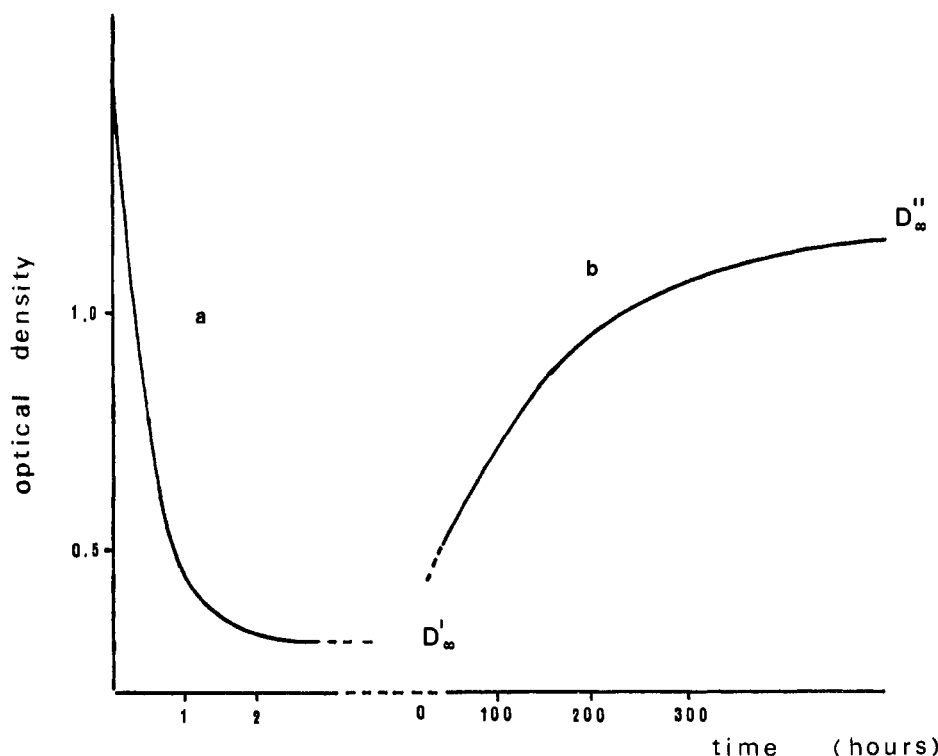


Figure 1.—Optical density of a solution of  $2 \times 10^{-4} M$   $K_2Pt(C_2O_4)_2 + 0.1 M$   $KSCN$  at 287 nm, against time; temperature  $24.8^\circ$ .

involving simple and complex anions<sup>6</sup> and for racemization reactions.<sup>7</sup>

### Experimental Section

**Materials.**—The salt  $K_2Pt(C_2O_4)_2 \cdot 2H_2O$  was prepared following the methods of the literature.<sup>8</sup> All other chemicals were Erba RP reagents, recrystallized three times from conductivity water, obtained by double distillation.

**Reaction Products.**—Figure 1 reports a plot of the optical density (OD) at 287 nm against time for a mixture of  $2 \times 10^{-4} M$   $K_2Pt(C_2O_4)_2$  and  $0.1 M$   $KSCN$ . Two steps of substitution are clearly indicated. When the minimum of OD was reached, a solution of  $Pt(NH_3)_4Cl_2$ , in a molar ratio of 2:1 with respect to the reacting complex, was added. A microcrystalline precipitate formed in a few minutes and was collected by filtration. The filtered solution did not contain either Pt or oxalate. In analogous experiments performed with higher concentrations of  $Pt(C_2O_4)_2^{2-}$  and lower concentrations of  $SCN^-$  accurate titrations showed that  $SCN^-$  had disappeared by reaction with the complex in a ratio 2:1.

The analysis of the precipitate gave the following results. *Anal.* Calcd for  $[Pt(NH_3)_4][Pt(C_2O_4)_2(SCN)_2] \cdot 2H_2O$ : Pt, 55.77; N, 13.34; H, 2.70; C, 6.90; S, 6.1. Found: Pt, 55.80; N, 13.10; H, 2.80; C, 7.10; S, 6.1.

A mixture of  $0.02 M$   $K_2Pt(C_2O_4)_2$  and  $0.1 M$   $KSCN$  was allowed to react at  $55^\circ$  and the OD was measured at frequent intervals. When it reached a minimum, 3 vol. of acetone was added and the mixture was cooled at  $0^\circ$ . A crystalline precipitate was obtained whose analysis gave the following results. *Anal.* Calcd for  $K_4[Pt(C_2O_4)_2(SCN)_2] \cdot 3H_2O$ : Pt, 27.97; N, 4.0; H, 0.86; C, 10.33; S, 9.19; K, 22.41. Found: Pt, 28.0; N, 3.6; H, 0.88; C, 10.3; S, 8.4; K, 22.5. All attempts to obtain this salt in the anhydrous state led to its decomposition, and its water content has not been determined with certainty. The  $[Pt(NH_3)_4]_2-$

$[Pt(C_2O_4)_2(SCN)_2] \cdot 2H_2O$ , precipitated from  $K_4[Pt(C_2O_4)_2(SCN)_2]$ , was identical with the sample directly precipitated from the reaction mixture, as proved by the identity of the X-ray patterns obtained by the Debye powder method. The molecular weight of the potassium salt was measured by cryoscopy in  $KNO_3-H_2O$  eutectic<sup>9</sup> and agreed with the above formula (calcd, 697.5; found, 700).

The  $K_4[Pt(C_2O_4)_2(SCN)_2] \cdot 3H_2O$  was examined by ir spectrophotometry by the Nujol mull and the KBr disk methods, and the peaks observed are reported in Table I.<sup>5,10-12</sup>

TABLE I  
OBSERVED FREQUENCIES ( $CM^{-1}$ ) OF  
 $K_4[Pt(SCN)_2(C_2O_4)_2] \cdot 3H_2O$

Freq, $cm^{-1}$	Assignments	Ref
3590 s	$\nu(H_2O)$	10
3485 s		
3375 s		
3250 s		
2130 s	$\nu(CN)$	11
2080 w		
1665 s	$\nu(OCO)$ antisym and $\delta(H_2O)$	10, 12
1620 s		
1600 s		
1412 s	$\nu(OCO)$ sym	10, 12
1275 s	$\nu(C-O)$ sym and $\delta(O-C=O)$	12
896 w	$\nu(C-O)$ sym and $\delta(O-C=O)$ or $\nu(C-C)$	12 5
855 s		5, 11
785 s	$\delta(O-C=O) + \nu(Pt-O)$	10, 12
710-690 s, b	$\delta(O-C=O)$ and $\nu(C-S)$	5, 11
580 s, b	$\nu(Pt-O)$	12
470 m	Ring def + $\delta(O-C=O)$	5, 12
428 m	$\delta(SCN)$	11

The pH of a solution of  $K_2Pt(C_2O_4)_2$  is slightly lower than that of the water and the pH of a solution of  $K_4[Pt(C_2O_4)_2(SCN)_2]$

(6) A. Indelli, V. Bartocci, F. Ferranti, and M. G. Lucarelli, *J. Chem. Phys.*, **44**, 2069 (1966); A. Indelli and P. L. Bonora, *J. Amer. Chem. Soc.*, **88**, 924 (1966); J. C. Sheppard and A. C. Wahl, *ibid.*, **79**, 1020 (1957); A. Indelli and E. S. Amis, *ibid.*, **82**, 332 (1960); M. Shporer, G. Ron, A. Lowenstein, and G. Navon, *Inorg. Chem.*, **4**, 361 (1965); B. Perlmutter-Hayman and Y. Weissmann, *J. Phys. Chem.*, **71**, 1409 (1967); M. R. Kershaw and J. E. Prue, *Trans. Faraday Soc.*, **63**, 1198 (1967).

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(8) P. Pascal, "Traité de Chimie Minérale," Masson et Cie, Paris, 1928, p 672.

(9) C. Sinistri, P. Franzosini, and G. Ajroldi, *Ric. Sci.*, **30**, 1584 (1960).

(10) M. J. Schmelz, I. Nakagawa, S. Mizushima, and J. V. Quagliano, *J. Amer. Chem. Soc.*, **81**, 287 (1959).

(11) A. Turco and C. Pecile, *Nature (London)*, **191**, 66 (1961); A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 959 (1965).

(12) J. Fujita, A. E. Martell, and K. Nakamoto, *J. Chem. Phys.*, **36**, 324, 331, 339 (1962).

is slightly higher. This and titration curves show that the former complex is slightly less basic and the latter is slightly more basic than water.

The final product of the reaction was precipitated by treating the reacting solution with  $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$  when the OD had reached the plateau ( $D'_\infty$ ) shown in Figure 1. The analysis of the precipitate gave the following results. *Anal.* Calcd for  $[\text{Pt}(\text{NH}_3)_4][\text{Pt}(\text{SCN})_4]$ : N, 16.2; S, 18.6; C, 7.0; H, 1.75. Found: N, 16.0; S, 18.1; C, 7.2; H, 1.84. The filtrate contained two  $\text{C}_2\text{O}_4^{2-}$  ions for every initial  $\text{Pt}(\text{C}_2\text{O}_4)_2^{2-}$ . These results were considered to prove that the complete reaction yields  $\text{Pt}(\text{SCN})_4^{2-}$ .

**Kinetics.**—The reaction of  $\text{Pt}(\text{C}_2\text{O}_4)_2^{2-}$  with  $\text{SCN}^-$  was followed spectrophotometrically at 287 nm with a Hilger-Watts Uvispek H 700 spectrophotometer equipped with a thermostated cell compartment. Most of the runs were performed keeping the mixture in 2-cm optical cells, sealed with Parafilm. When the progress of the reaction was very slow, the reaction mixtures were kept in a thermostat and samples were rapidly cooled and transferred to the optical cells at suitable intervals.

When  $\text{K}_4[\text{Pt}(\text{C}_2\text{O}_4)_2(\text{SCN})_2]$  is dissolved in water the OD at 250 nm decreases with time and reaches a limiting value  $D_\infty$  within about 1 hr. The addition of KSCN to a completely reacted solution reverses the change in OD. This addition was made directly in the cell by means of a microsyringe and readings could be taken after about 20 sec. Within about 20 min another limiting value ( $D_e$ ) is reached which however is not equal to the OD of the initial solution ( $D_0$ ). A plot somewhat similar to Figure 1 is therefore obtained. From the changes in OD the rates of the direct and inverse reactions could be obtained and from the values of  $D_0$ ,  $D_\infty$ , and  $D_e$  and the added  $\text{SCN}^-$  the equilibrium constants could be calculated, although with not great accuracy.

### Results

Figure 1 shows that the total reaction  $\text{Pt}(\text{C}_2\text{O}_4)_2^{2-} + 4\text{SCN}^- \rightarrow \text{Pt}(\text{SCN})_4^{2-} + 2\text{C}_2\text{O}_4^{2-}$  takes place in at least two steps, at markedly different rates.<sup>13,14</sup> The part corresponding to an increase in OD can therefore be neglected during the first part of the reaction, and the part corresponding to a decrease can be neglected during the last part. The value of the OD at the minimum ( $D'_\infty$  in Figure 1) is almost unchanged when the KSCN concentration changes from 0.1 to 0.025 M and is much smaller than either the initial or final value. Therefore it can be considered that  $D'_\infty$  is the OD at the end of the first part. By plotting  $\log(D - D'_\infty)$  against time, straight lines are obtained for at least 85% of the reaction when  $[\text{SCN}^-] = 0.1$  M and for about 80% when  $[\text{SCN}^-] \geq 0.025$  M. For lower  $[\text{SCN}^-]$  deviations are observed at about 40–50% reaction. It should be noticed that the same value  $D'_\infty$  was used throughout to make the first-order plots. The slopes, which give the first-order rate constants,  $k'_{\text{obsd}}$ , are reported in Table II for different  $\text{SCN}^-$  concentrations. Their reproducibility, as judged by many duplicated runs, is within 2%. If the usual analysis in terms of the equation<sup>1</sup>

$$\text{rate} = k'_{\text{obsd}}[\text{complex}]$$

where

$$k'_{\text{obsd}} = k_{\text{H}_2\text{O}} + k_1[\text{SCN}^-] \quad (1)$$

is applied, a small, negative, meaningless value is obtained for  $k_{\text{H}_2\text{O}}$ , because the  $k'_{\text{obsd}}$  values for the lowest concentrations are appreciably below a straight line passing through the origin (Figure 2, dots). The reasons for this will be examined later, but it can be safely assumed that  $k_{\text{H}_2\text{O}}$  is quite small.

(13) The ambiguity, which, according to Alcock, Benton, and Moore,<sup>14</sup> is always possible when two consecutive reactions are followed by spectrophotometry, does not arise in this case. In fact only if the first reaction is faster than the second, does the extinction coefficient of the intermediate product have a positive, meaningful value.

(14) N. W. Alcock, D. J. Benton, and P. Moore, *Trans. Faraday Soc.*, **66**, 2210 (1970).

TABLE II

VALUES OF  $k_{\text{obsd}}$  ( $\text{SEC}^{-1}$ ) FOR THE TWO STEPS OF THE EXAMINED REACTION IN WATER AT  $24.8 \pm 0.05^\circ$ ,  $[\text{K}_2\text{Pt}(\text{C}_2\text{O}_4)_2] = 2 \times 10^{-4}$  M, and  $I = 0.1$  M<sup>a</sup>

$[\text{K}^+], \text{M}$	$[\text{SCN}^-], \text{M}$	$10^4 k'_{\text{obsd}}, \text{sec}^{-1}$	$10^6 k''_{\text{obsd}}, \text{sec}$
0.1	0.005	0.28	1.0
0.1	0.01	0.59	1.01
0.1	0.025	1.60	1.11
0.1	0.05	3.15	1.23
0.1	0.10	6.40	1.47
0.1 (Na <sup>+</sup> )	0.10	6.00	1.53
0.1 (Li <sup>+</sup> )	0.10	5.64	1.53
0.033 (Mg <sup>2+</sup> )	0.066	8.65	5.28
0.01 (H <sup>+</sup> ) <sup>b</sup>	0.10	7.9	...
0.001 (H <sup>+</sup> ) <sup>b</sup>	0.10	7.1	...

<sup>a</sup>  $k'_{\text{obsd}} = k_{\text{H}_2\text{O}} + k_1[\text{KSCN}]$  for the first step;  $k''_{\text{obsd}} = k_3 + k_4[\text{KSCN}]$  for the second step;  $k_{\text{H}_2\text{O}} = 0$ ;  $k_1 = 6.35 \times 10^{-3} \text{M}^{-1} \text{sec}^{-1}$ ;  $k_3 = 9.8 \times 10^{-7} \text{sec}^{-1}$ ;  $k_4 = 5.0 \times 10^{-6} \text{M}^{-1} \text{sec}^{-1}$ .

<sup>b</sup> In the presence of 0.1 M K<sup>+</sup>.

Runs were also performed at 35, 44.8, and 53.8°, and the rate constants  $k_1$  were respectively  $1.40 \times 10^{-2}$ ,  $2.76 \times 10^{-2}$ , and  $4.85 \times 10^{-2} \text{sec}^{-1} \text{M}^{-1}$ . A value of  $13.3 \pm 0.4$  kcal/mol is calculated for  $\Delta H^\ddagger$ , and a value of  $-24 \pm 2$  eu, for  $\Delta S^\ddagger$ .

For the second step, a plot of  $\log(D'_\infty - D)$  against time gives the values of  $k''_{\text{obsd}}$ , which are also reported in Table II and in Figure 2 (squares). The reproducibility in this case is somewhat lower, about  $\pm 4\%$ . Using the equation  $k''_{\text{obsd}} = k_3 + k_4[\text{SCN}^-]$ , the values of  $k_3 = 9.8 \times 10^{-7} \text{sec}^{-1}$  and  $k_4 = 5.2 \times 10^{-6} \text{sec}^{-1} \text{M}^{-1}$  are found at 24.8°. At 44.8 and 53.8° the values of  $k_3$  are respectively  $1.6 \times 10^{-5}$  and  $4.8 \times 10^{-5} \text{sec}^{-1}$ , and the values of  $k_4$  are  $9.4 \times 10^{-5}$  and  $2.9 \times 10^{-4} \text{sec}^{-1} \text{M}^{-1}$ . Values of  $25.4 \pm 0.3$  and  $26.2 \pm 0.4$  kcal/mol are found for  $\Delta H^\ddagger$ , and values of  $0 \pm 1$  and  $5 \pm 2$  eu are found for  $\Delta S^\ddagger$ , for  $k_3$  and  $k_4$ , respectively.

The OD of a very dilute solution of the intermediate, identified as  $\text{K}_4[\text{Pt}(\text{C}_2\text{O}_4)_2(\text{SCN})_2]$ , changes rapidly with time. However, working at 287 nm, reproducible results could not be obtained because the OD is very small, so that we preferred to do the measurements at 250 nm, at a temperature of 24.8°. It may be assumed that the reaction proceeds to completion, since the final  $\text{SCN}^-$  concentration is very low. The rate constants  $k_{-2}$  were measured, for different concentrations, from plots of  $\log(D - D_\infty)$ .

After addition of  $\text{SCN}^-$  the OD increases and reaches a limiting value  $D_e$  which depends upon the concentration of added  $\text{SCN}^-$ . This indicates that the reaction reaches an equilibrium. The  $\text{SCN}^-$  is always in great excess over the complex, so that the two opposite reactions are both pseudo first order. From plots of  $\log(D_e - D)$  against time the values of  $k_{\text{obsd}} = k_{-2} + k_2[\text{SCN}^-]$  can be measured. The values of molar absorptivities  $\epsilon_0$  and  $\epsilon_\infty$  obtained by dividing the corresponding OD by the concentrations and by optical path length are virtually constant and equal to  $15,900 \pm 400$  and  $4900 \pm 300 \text{M}^{-1} \text{cm}^{-1}$ . Table III reports the values of  $k_{-2}$ ,  $k_{\text{obsd}}$ , and the equilibrium constant  $K$ . From Figure 3, where  $k_{\text{obsd}}$  is plotted against  $[\text{SCN}^-]$ , the values of  $k_2$  and  $k_{-2}$  can be calculated and are  $0.48 \text{sec}^{-1} \text{M}^{-1}$  and  $2.47 \times 10^{-3} \text{sec}^{-1}$ , respectively. The ionic strength in all these experiments was very low, in the range between  $1 \times 10^{-3}$  and  $5 \times 10^{-3} \text{M}^{-1}$ , so that we did not consider it necessary to keep it constant. A value of  $K = k_{-2}/k_2$  of  $5.2 \times 10^{-3} \text{M}$  can be calculated from the above data and can be com-

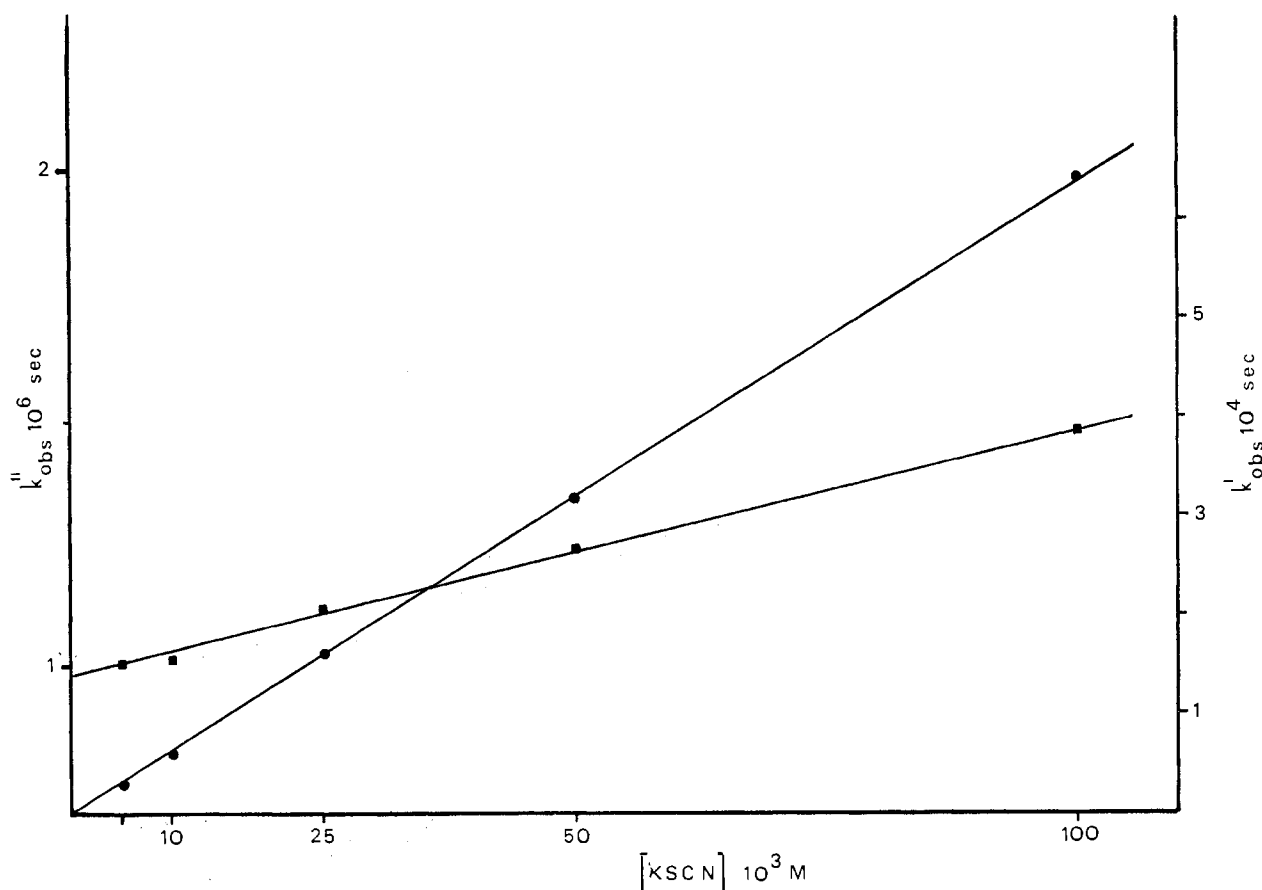


Figure 2.—Plots of  $k_{\text{obs}}'$  (dots) and  $k_{\text{obs}}''$  (squares) for the first and second stage of the reaction against the concentration of thiocyanate ion.

TABLE III  
RATE CONSTANTS OF FORWARD AND REVERSE REACTIONS  
AT 24.8° FOR THE EQUILIBRIUM INTERMEDIATE  
 $\text{III} \rightleftharpoons \text{INTERMEDIATE II} + \text{SCN}^-$  AT 24.8°

$10^3$ [intermed III], M	$10^3 k_{-2}$ , $\text{sec}^{-1}$	$10^3$ [intermed II], M	$10^3$ [KSCN], M	$10^3 k_{\text{obs}}^a$ , $\text{sec}^{-1}$	$10^3 K$ , M
1	2.37	4.98	4.98	4.78	4.3
2.5	2.36	4.55	0.91	2.48	2.6
5	2.39	2.38	4.67	4.77	3.1
10	2.45	2.38	4.67	4.62	3.3
		2.45	2.00	3.31	2.8
		0.99	4.76	4.75	3.2
		0.98	2.44	3.80	5.3
		0.91	0.91	3.00	3.8

<sup>a</sup>  $k_{\text{obs}} = k_{-2} + k_2[\text{SCN}^-]$ ;  $k_{-2} = 2.47 \times 10^{-3} \text{ sec}^{-1}$ ;  $k_2 = 0.48 \text{ sec}^{-1} \text{ M}^{-1}$ .

pared with the values reported in Table III and calculated from  $D_0$ ,  $\epsilon_0$ ,  $\epsilon_\infty$ , and  $[\text{SCN}^-]$ . Since  $D_0$  can be measured with difficulty, we think that the value  $5.2 \times 10^{-3} \text{ M}$  is more accurate than the values of Table III. A further confirmation of the reliability of these results was obtained by preparing a  $10^{-3} \text{ M}$  solution of  $\text{K}_4[\text{Pt}(\text{C}_2\text{O}_4)_2(\text{SCN})_2]$  and measuring, in a 1-mm cell, the OD as a function of time. A value of  $D_\infty$  is reached which is considerably greater than the one which can be calculated from  $\epsilon_\infty$ , due to the fact that the reaction in this case does not proceed to completion. From a plot of  $\log(D - D_\infty)$  against time a value of  $3.3 \times 10^{-3} \text{ sec}^{-1}$  is obtained for the apparent first-order rate constant, which is greater than  $k_{-2}$  because the inverse reaction is also involved. From the value of  $D_\infty$  as well as the values of  $\epsilon_0$ ,  $\epsilon_\infty$ , and the initial intermediate concentration, a value of  $4.8 \times 10^{-3} \text{ M}$  for the equi-

librium constant is calculated, in excellent agreement with  $k_{-2}/k_2$ .

The reaction of the intermediate in water can be either the reverse of a step of the substitution reaction or a side reaction which reaches an equilibrium (see below, eq 2 and 3).

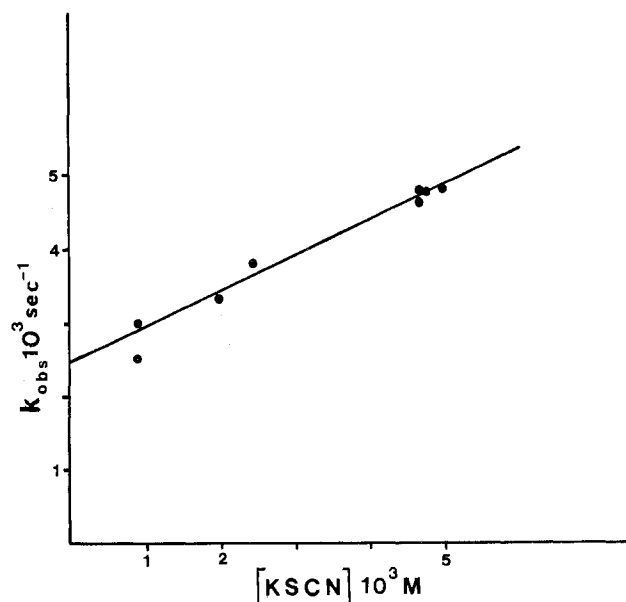
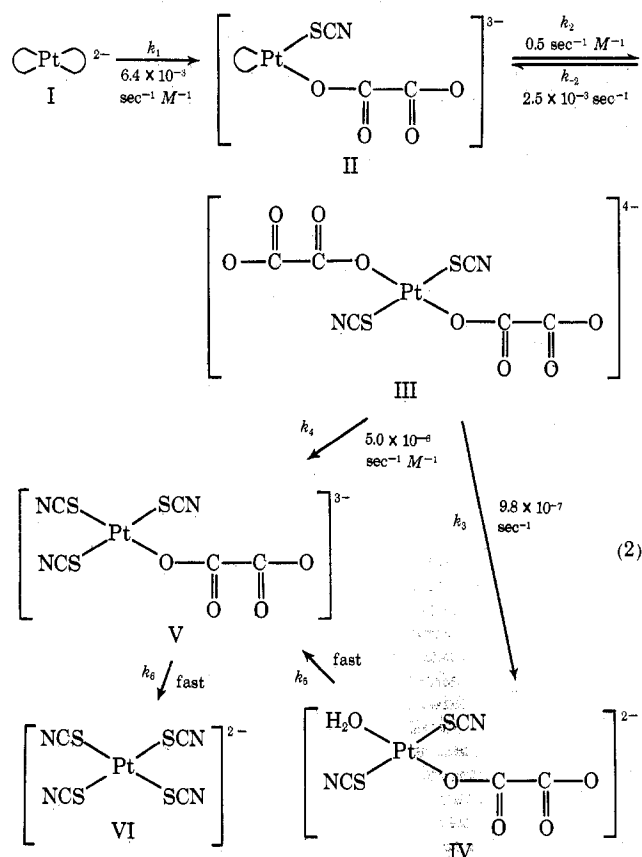


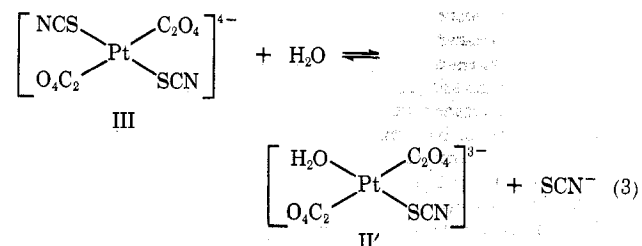
Figure 3.—Plot of the rate constant for the reaction of the completely reacted intermediate against the concentration of thiocyanate ion.

## Discussion

The total reaction between  $\text{Pt}(\text{C}_2\text{O}_4)_2^{2-}$  and  $\text{SCN}^-$  takes place according to the approximate scheme



Another possibility is that, according to reaction 3,



intermediate III is in a side equilibrium with the product II', in which case the passage from II to III is also very fast, probably even more than indicated in eq 2. We could not devise any method capable of distinguishing with certainty between these possibilities. Even attempts of statistical analyses, made using a 70/90 IBM computer, did not give significant differences between the two schemes.

An examination of the constants  $k_1$  and  $k_2$  shows that III is the only intermediate which can be isolated and that the rate constant measured when mixing  $\text{Pt}(\text{C}_2\text{O}_4)_2^{2-}$  with  $\text{SCN}^-$  (part a of the curve of Figure 1) is essentially  $k_1$ . Only at very low  $\text{SCN}^-$  concentrations will the influence of the return reaction III  $\rightarrow$  II be felt, and therefore the measured rate constant will be appreciably lower than  $k_1$ .

The fact that the I  $\rightarrow$  II reaction is essentially second order, without the usual first-order contribution due to a path involving a solvent molecule, is probably due to the fact that  $\text{H}_2\text{O}$  is not a nucleophile strong enough to displace one end of the chelating oxalate. This is in agreement with what has been found in the exchange

reaction of  $\text{Pt}(\text{C}_2\text{O}_4)_2^{2-}$  with  $\text{C}_2\text{O}_4^{2-}$ ,<sup>2</sup> where the first-order path has a constant of about  $10^{-9} \text{ sec}^{-1}$ . It is also possible that the free end of the nonchelated oxalate competes very efficiently with the  $\text{SCN}^-$  (or with another  $\text{C}_2\text{O}_4^{2-}$ ) in displacing the water molecule, so that no first-order path can be observed.

On the contrary the reaction III  $\rightarrow$  V takes place through clearly discernible first- and second-order paths, and this is to be expected, because at this point there are no more chelating ligands.

Although it is difficult to ascertain the contemporaneous presence of uncoordinated and Pt-bonded COO groups, the ir spectrum of the  $\text{K}_4[\text{Pt}(\text{C}_2\text{O}_4)_2(\text{SCN})_2]$  can give the following information. (1) The presence of COOH groups is ruled out, because the typical peaks<sup>5,16</sup> near 1750 and 1000  $\text{cm}^{-1}$  are lacking. This is in agreement with the titration curves and with the potassium content. (2) The two peaks assigned to symmetric stretching (1410  $\text{cm}^{-1}$ ) and to antisymmetric stretching (1620–1600  $\text{cm}^{-1}$ ) of  $-\text{COO}$  have frequencies almost equal to the ones of  $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$  (1408 and 1600  $\text{cm}^{-1}$ )<sup>16</sup> and markedly different from the ones of  $\text{K}_2\text{Pt}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$  (1388 and 1674–1700  $\text{cm}^{-1}$ )<sup>12</sup> and of dimethyl oxalate (1325 and 1770  $\text{cm}^{-1}$ ).<sup>16</sup> These differences are in agreement with the presence of uncomplexed  $-\text{COO}^-$  groups in  $\text{K}_4[\text{Pt}(\text{C}_2\text{O}_4)_2(\text{SCN})_2]$ .<sup>10</sup> (3) The single peak at 2130  $\text{cm}^{-1}$  indicates that the two SCN groups are in a trans position.<sup>11</sup> (4) The peak at 855  $\text{cm}^{-1}$  is typical for the isothiocyanate complexes but is found also in many oxalato complexes<sup>12,16</sup> and in *trans*- $\text{Pt}(\text{NH}_3)_2(\text{NH}_2\text{CH}_2\text{COO})_2$ .<sup>5</sup> (5) In the region 3250–3600  $\text{cm}^{-1}$  four peaks are observed which can be attributed to the OH stretching of the water. In  $\text{K}_2\text{Pt}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$  only two peaks are visible.

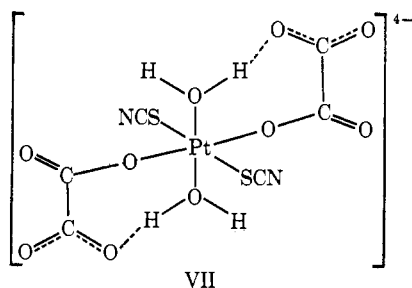
Attempts to substitute  $\text{H}_2\text{O}$  with  $\text{D}_2\text{O}$  were only partially successful. Long exposure of  $\text{K}_4[\text{Pt}(\text{C}_2\text{O}_4)_2(\text{SCN})_2] \cdot 3\text{H}_2\text{O}$  in an atmosphere of  $\text{D}_2\text{O}$  vapor or recrystallization from  $\text{D}_2\text{O}$  has reduced the  $\text{H}_2\text{O}$  peaks by about 50% only. Further attempts have produced decomposition of the intermediate. This fact and the failure in obtaining the complex in an anhydrous state suggest that the water is strongly bound to the complex, probably above and below the coordination plane.

Teggins and Milburn<sup>2</sup> also suggested that the axial positions about the platinum are occupied by water molecules, but, alternatively, they considered it possible that they are occupied by the "free" ends of the oxalato groups. In this way the oxalate maintains a partial chelating character and confers greater stability to the intermediate, forming a relatively stable ring. The values of ir frequencies of the  $-\text{COO}$  groups, however, do not support the assumption of chelating oxalate. We suggest instead that the "free" ends of the oxalato groups are hydrogen bridged to the water groups in axial positions; see structure VII. A similar hypothesis has been suggested to explain the low exchange velocity between  $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})(\text{CO}_3)]^+$  and  $\text{HCO}_3^-$ .<sup>17</sup> This structure is consistent with the fact that III is a very weak base. Although we are not able to explain all details of the ir spectrum, the fact

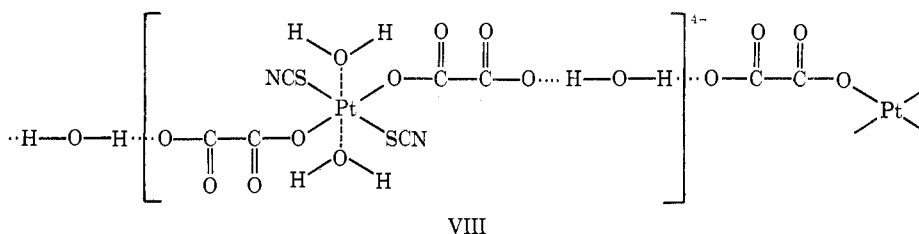
(15) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, p 206.

(16) M. J. Schmelz, T. Miyazawa, S. Mizushima, T. J. Lane, and J. V. Quagliano, *Spectrochim. Acta*, **9**, 51 (1957).

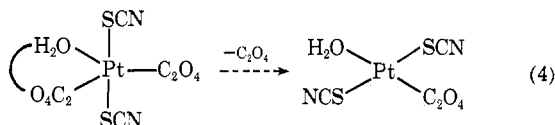
(17) G. M. Harris and D. R. Stranks, *Trans. Faraday Soc.*, **48**, 137 (1952).



that there are four stretching peaks of OH suggests that there must be protons in hydrogen bridges as well as free protons. Formula VII could therefore be an explanation for the ir spectrum. An alternative one, in the solid state, could be VIII for instance.



In the reaction III  $\rightarrow$  V the first-order contribution is very important and greater than the second-order contribution even at the highest  $\text{SCN}^-$  concentration, despite the fact that usually  $\text{SCN}^-$  is much more reactive than  $\text{H}_2\text{O}$ . This also is in agreement with the assumption of two  $\text{H}_2\text{O}$  molecules loosely coordinated and hydrogen bonded. In fact the entrance of a water molecule into a trigonal-bipyramidal activated complex will be favored and the complex itself will be stabilized

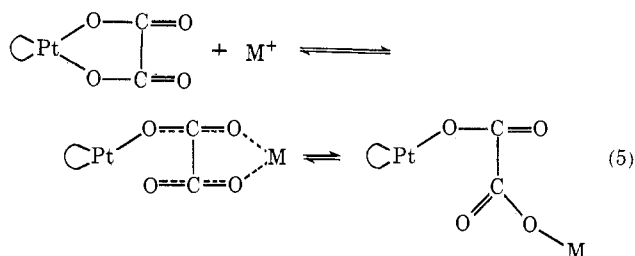


Moreover the presence of the two coordinated water groups sterically hinders the entering  $\text{SCN}^-$ . Another cause of the slowness of the second-order path is probably the high negative charge of the anion III which prevents the approach of  $\text{SCN}^-$  but not of  $\text{H}_2\text{O}$ . It is known<sup>18</sup> that the rate constants for the reaction of Pt(II) complexes with the solvent are remarkably insensitive to the charge of the complex. An examination of the activation parameters is in agreement with this picture. In fact the entropy of activation of  $-24$  eu is what we expect for a reaction between two anions of charge 1 and 2. But the activation entropy for  $k_4$ , on the same basis, should be of the order of  $-40$  eu. The fact that instead it is of the order of  $+5$  eu is related with the large amount of disorder brought by the destruction of two rings produced by the entering  $\text{SCN}^-$ .

The salt effects on  $k_1$ , reported on Table II, are in agreement with the ones found for the nucleophilic attack of  $\text{SCN}^-$  on  $\text{Pt}(\text{NO}_2)_4^{2-}$ .<sup>19</sup> They confirm the

limited validity of the Brønsted-Debye equation, which could not predict so large specific differences, and are in agreement with the results obtained in other reactions between anions.<sup>6,20</sup> The efficiency of the alkali metal decreases in the order  $\text{K}^+ > \text{Na}^+ > \text{Li}^+$ . This suggests that the action of these cations is of the external sphere type,<sup>20</sup> *i.e.*, that it takes place through their hydration sphere. In fact, whichever is the mechanism of the specific salt effect, it is clear that the cations which can approach closer the reacting anions or the activated complex will be more efficient. In analogy with the assumptions which we have made in other instances of specific salt effects,<sup>21</sup> we suggest that the cation interacts with the filled, nonbonding, originally  $5d_{z^2}$  orbital of the platinum. In this way the

resulting decreased electron density on the central metal reduces the repulsion between the said orbital and the entering nucleophile  $\text{SCN}^-$ , facilitating the formation of the five-coordinated activated complex. A similar mechanism has been proposed for the isotopic exchange reaction of  $\text{trans-Pt}[\text{P}(\text{C}_2\text{H}_5)_3]_2\text{HCl} + \text{D}^+$ <sup>22</sup> and for the cleavage by acids of the metal-carbon bond in Pt(II) complexes.<sup>23</sup> The accelerating effect of the hydrogen ion which is comparable with the one of  $\text{Mg}^{2+}$  supports this assumption. In fact the  $\text{H}^+$  ion interacts through an internal sphere type mechanism with the axial water molecule and because of its small size is more efficient than the alkali metal cations. Other explanations can also be given, and one which may explain the strong accelerating action of the cations and mostly of  $\text{H}^+$  is that the cations interact with the coordinated oxalate



This favors the opening of the chelate ring.<sup>7</sup> It must be understood however that in all cases the interactions are very weak, but they are sufficient to produce an appreciable increase in the rate. It is well known in fact that strong specific salt effects can be observed even when no appreciable amounts of ion pairs can be detected.<sup>21</sup>

The  $\text{Mg}^{2+}$  ion has an accelerating effect on the second

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step which becomes 4 times faster than in the presence of the alkali metal cations. This is in agreement with the fact that the reaction of the second step involves a  $4^-$  ion, so that both the electrostatic and the nonelectrostatic effects are magnified.

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## Conformational Studies of Bridging Carboxylate Complexes of Palladium(II) and Platinum(II)

BY JOHN POWELL\* AND THOMAS JACK

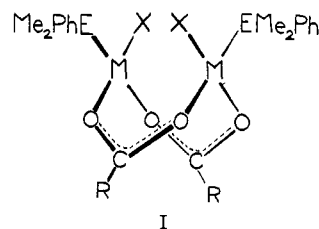
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A series of bridging *cis*-di- $\mu$ -carboxylate complexes of palladium(II) and platinum(II) of the general types  $[X(\text{Me}_2\text{PhE})\text{M}(\text{O}_2\text{CR})_2]$  and  $[X_2(\text{Me}_2\text{PhE})_2\text{M}_2[\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2]]$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ;  $\text{E} = \text{P}, \text{As}$ ;  $\text{M} = \text{Pd}, \text{Pt}$ ;  $\text{R} = \text{CH}_3, \text{CH}_2\text{Cl}, \text{CH}_2\text{Br}, \text{CF}_3, \text{CCl}_3, \text{CMe}_3, \text{CPh}_3$ ;  $n = 3-8$ ) have been synthesized and structurally characterized. The dynamic stereochemistry of these complexes has been investigated using variable-temperature nmr techniques. The  $\Delta G^\ddagger$  of the process whereby the stereochemically nonequivalent methyl groups of the coordinated  $\text{Me}_2\text{PhE}$  ligand become magnetically equivalent is dependent on metal substituents, carboxylate substituents, and the solvent. The exchange process has low activation energies (3–6 kcal/mol) and large negative entropies of activation (–20 to –40 eu). The results obtained indicate that the exchange mechanism involves the rapid solvolysis of a metal–carboxylate bond to give a mono- $\mu$ -carboxylate intermediate rather than a simple inversion of the  $\text{Pd}_2\text{C}_2\text{O}_4$  ring. The structurally analogous *cis*-di- $\mu$ -1,3-diphenyltriazene complex  $[\text{Cl}(\text{Me}_2\text{PhP})\text{Pd}(\text{Ph}_2\text{N}_3)]_2$  did not undergo such exchange reactions. The exchange processes occurring in  $\pi$ -allylic palladium carboxylates have been reinvestigated and the rates found to be markedly affected by the solvent.

### Introduction

Recently,  $\pi$ -allylic palladium acetate dimers have been shown by  $^1\text{H}$  nmr spectroscopy to exist as a mixture of two conformational isomers in chloroform solution.<sup>1,2</sup> The temperature dependence of their  $^1\text{H}$  nmr spectra has been interpreted in terms of a rapid intramolecular process which leads to nmr equivalence of nonequivalent  $\pi$ -allylic groups in the nonsymmetrical isomer together with a rapid bimolecular process which is operative at higher temperatures and which leads to nmr equivalence of the conformational isomers. It has been suggested that the intramolecular process be ascribed to a rapid boat  $\rightarrow$  chair  $\rightarrow$  boat conformational isomerism of the  $\text{Pd}_2\text{O}_4\text{C}_2$  ring. The geometrically similar  $\pi$ -allylic palladium 1,3 diphenyltriazene dimers have also been shown to exist in solution as two conformational isomers.<sup>3</sup> In contrast to the carboxylate complexes, no evidence for rapid intramolecular or intermolecular exchange processes was observed for these complexes, their nmr spectra being temperature independent from  $-60$  to  $+30^\circ$  in  $\text{CDCl}_3$  and from  $+50$  to  $+110^\circ$  in  $\text{CHBr}_3$ .

In an effort to clarify the nature of the apparent intramolecular process observed in the  $\pi$ -allylic palladium carboxylate systems we have succeeded in synthesizing a series of di- $\mu$ -carboxylate complexes of general formulas  $[(\text{Me}_2\text{PhE})\text{XM}(\text{OOCR})_2]$  and structure I ( $\text{E} = \text{P}, \text{As}$ ;  $\text{M} = \text{Pd}, \text{Pt}$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ;  $\text{R} = \text{CH}_3, \text{CH}_2\text{Cl}, \text{CH}_2\text{Br}, \text{CCl}_3, \text{CF}_3, \text{CMe}_3, \text{CPh}_3$ ) from the reaction of the appropriate bridged halide



dimer with 2 mol of a silver carboxylate salt in chloroform:  $[(\text{Me}_2\text{PhE})\text{MX}_2]_2 + 2\text{AgOOCR} \rightarrow \text{I} + 2\text{AgX}\downarrow$ .

In the absence of any exchange, a molecule of structure I should give two methyl proton resonances of equal intensities in the  $^1\text{H}$  nmr spectrum assignable to nonequivalent methyl groups on the  $\text{Me}_2\text{PhE}$  ligand (there is no plane of symmetry passing through the E–M axis). However any rapid process which effectively inverts the boat conformation of the  $\text{Pd}_2\text{O}_4\text{C}_2$  ring of I will also interchange the nonequivalent methyl groups of the  $\text{Me}_2\text{PhE}$  ligands and as such will be amenable to variable-temperature nmr studies. In this paper we report the synthesis and structural characterization of complexes of type I and some related complexes, and discuss the mechanistic implications of the temperature dependence of their  $^1\text{H}$  nmr spectra.

### Experimental Section

**Preparation of Compounds.**—Bridging halide complexes of the type  $[(\text{Me}_2\text{PhE})\text{MX}_2]_2$  were prepared by the method of Jenkins and Shaw.<sup>4</sup> Dimethylphenylphosphine and dimethylphenylarsine were synthesized in the general manner described elsewhere.<sup>5</sup>

**Di- $\mu$ -acetato-dichlorobis(dimethylphenylphosphine)dipalladium(II).**—A solution of di- $\mu$ -chloro-dichlorobis(dimethylphenylphos-

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