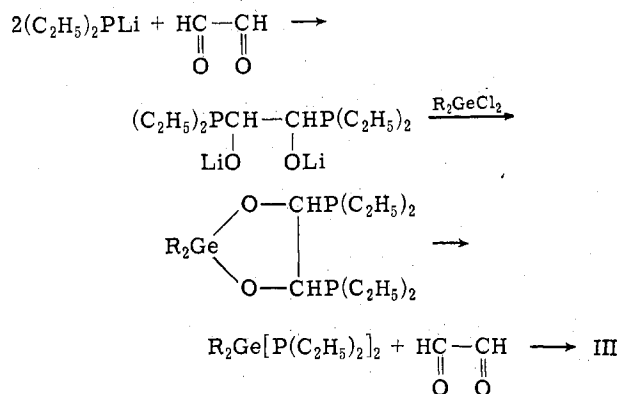
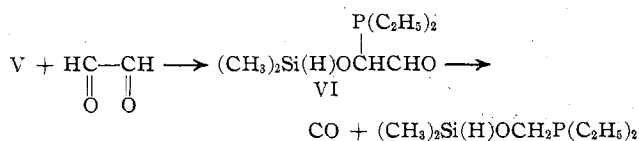


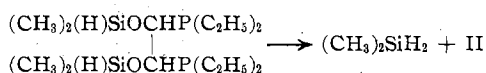
However, 2-germa-1,3-dioxolane must form transiently in the course of this reversible addition reaction as in the direct action of a dichlorodialkylgermane on the glyoxal diphospholithium derivative. In this latter reaction also, only III is isolated



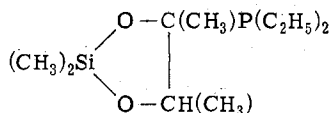
The condensation of diethyl(hydrodimethylsilyl)-phosphine,  $(\text{CH}_3)_2\text{Si}(\text{H})\text{P}(\text{C}_2\text{H}_5)_2$  (V), leads to the monoinsertion derivative which decarbonylates quickly



and to the diinsertion derivative which undergoes redistribution into dimethylsilane and the *trans-threo*-2-sila-1,3-dioxolane II already isolated



The instability of the monoinsertion derivative VI has not allowed the intramolecular cyclization by Si-H to carbonyl addition which is observed in the case of diacetyl<sup>2</sup> with formation of the dioxolane



The same reaction studied from the hydrogermylphosphine  $(\text{C}_2\text{H}_5)_2\text{Ge}(\text{H})\text{P}(\text{C}_2\text{H}_5)_2$  (VII) has not allowed isolation of the corresponding unstable germanium derivatives. This reaction leads exclusively to the diethylgermane and bis(diethylphosphinomethoxy)diethylgermane, probably according to Scheme I.

The higher thermodynamic stability of the silicon derivatives in comparison with the germanium derivatives can be attributed to stronger silicon-oxygen bond energy than germanium-oxygen<sup>9</sup> and to strong stabilization of the Si-O bond by  $p\pi-d\pi$  effects.<sup>10</sup>

(9) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed, Butterworths, London, 1958.

(10) E. A. V. Ebsworth, "Organometallic Compounds of the Group IV Elements," Vol. 1, Part 1, A. G. MacDiarmid, Ed., Marcel Dekker, Inc., New York, N. Y., 1968, Chapter 1.

## Reaction of *trans*-Diazidobis(ethylenediamine)iridium(III) Cation with Acid. Synthesis of *trans*-Bis(chloramine)bis(ethylenediamine)-iridium(III) and *trans*-Diamminebis(ethylenediamine)iridium(III) Salts

By THOMAS RAY WEAVER, BRUCE C. LANE, AND FRED BASOLO\*

Received January 24, 1972

The initial report<sup>1</sup> that *trans*- $[\text{Ir}(\text{en})_2(\text{N}_3)_2]^+$  reacts with concentrated hydrochloric acid to yield 2 mol of nitrogen indicated the discovery of a new type of reaction. However, the fate of the iridium in this reaction was not determined. As a result of other studies<sup>2,3</sup> on such reactions, it has now been possible to return to the original system and establish that the iridium complex formed is *trans*- $[\text{Ir}(\text{en})_2(\text{NH}_2\text{Cl})_2]^{3+}$ . This paper also reports the synthesis of salts of the new complex *trans*- $[\text{Ir}(\text{en})_2(\text{NH}_3)_2]^{3+}$ .

### Experimental Section

**Materials.**—Iridium trichloride was a loan from the Matthey Bishop Co. Other chemicals were readily available commercially and were used without further purification.

**Potassium Hexachloroiridate(IV),  $\text{K}_2\text{IrCl}_6$ .**—This starting material was prepared from commercial iridium trichloride by boiling it in aqua regia for several hours, reducing the volume to near dryness, repeating this procedure several times with concentrated hydrochloric acid to remove all oxides of nitrogen, and finally precipitating from hydrochloric acid solution with potassium chloride. The black microcrystals were washed with water and methanol and air-dried. Yields are 60–80%.

***trans*-Dichlorobis(ethylenediamine)iridium(III) Perchlorate,  $[\text{Ir}(\text{en})_2\text{Cl}_2]\text{ClO}_4$ .**—This complex was prepared by a modification of the literature method.<sup>1</sup> Potassium hexachloroiridate(IV) (12.8 g) was suspended in 75 ml of water at 80° and reduced by the slow addition of 2.85 g (slight excess) of  $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ . The solution was boiled for 10 min to remove all  $\text{CO}_2$  and filtered to remove any unreacted solid.<sup>4</sup> The filtrate was boiled for 20 min with 13 g of ethylenediamine dihydrochloride and 0.1 g of sodium hypophosphite ( $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ ). Concentrated hydrochloric acid (15 ml) was added and the solution was allowed to stand at room temperature for a few hours. The resulting green-brown precipitate was collected by suction filtration. This precipitate was then suspended in 60 ml of hot water and 5 ml of neat ethylenediamine was added to dissolve the solid. The solution was boiled for 10 min, 5 ml of ethylenediamine was added, and the solution was boiled for 1 hr more, the volume being reduced to 30 ml. Enough 12 M HCl was added to neutralize the solution (to alkacid test paper) and 1 ml of excess acid was added, lowering the pH to below 2. This solution was boiled for 30 min, the volume being reduced to 30 ml once again. The solution was cooled at 0° for 3 hr and the ethylenediamine dihydrochloride formed was removed by filtration. The resulting filtrate was treated with 7 ml of concentrated  $\text{HClO}_4$ . After 20 min the yellow crystals formed were collected by filtration, washed with methanol and ether, and air dried. Yields varied from 20 to 30%. The product was identified by its reported ultraviolet spectrum.<sup>1</sup> Yields can be increased somewhat by allowing the filtrate from the green-brown precipitate formed in the first step to stand for several days at room temperature and treating the resulting precipitate in the same way.

(1) R. A. Bauer and F. Basolo, *Inorg. Chem.*, **8**, 2231 (1969).

(2) L. A. P. Kane-McGuire, P. S. Sheridan, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **92**, 5865 (1970).

(3) B. C. Lane, J. W. McDonald, F. Basolo, and R. G. Pearson, *ibid.*, **94**, 3786 (1972).

(4) All filtrations up to this point were made using filter paper, as fine black precipitates formed in these steps will ruin glass frits.

**trans-Diazidobis(ethylenediamine)iridium(III) Chloride**,  $[\text{Ir}(\text{en})_2(\text{N}_3)_2]\text{Cl}$ .—The salt *trans*- $[\text{Ir}(\text{en})_2(\text{N}_3)_2]\text{PF}_6$  was prepared and recrystallized by the literature method.<sup>4,5</sup> This complex was dissolved in a minimum amount of water and passed through a Dowex 1-X8 anion-exchange column in the chloride form. The eluent was evaporated to near dryness on a rotary evaporator, and the resulting slurry was washed onto a glass frit with a little cold, anhydrous methanol, washed with diethyl ether, and air-dried. This salt is very soluble in water and slightly soluble in methanol. Yields were 40–50%.

**trans-Bis(chloramine)bis(ethylenediamine)iridium(III) Chloride**,  $[\text{Ir}(\text{en})_2(\text{NH}_2\text{Cl})_2]\text{Cl}$ .—Concentrated hydrochloric acid (40 ml) was added to  $[\text{Ir}(\text{en})_2(\text{N}_3)_2]\text{Cl}$  (0.2 g) and the mixture was heated at 50–60° for 45 min. This solution was evaporated to near dryness on the rotary evaporator. The resulting solid was washed onto a glass frit with anhydrous methanol and washed with methanol until the filtrate was colorless and all of the unreacted diazido complex had been removed. The white powder was washed with diethyl ether and dried *in vacuo* overnight. Yields were 70–80%. *Anal.* Calcd for  $[\text{Ir}(\text{en})_2(\text{NH}_2\text{Cl})_2]\text{Cl}$ : N, 16.11; H, 3.86; C, 9.21; Cl, 33.98. Found: N, 15.95; H, 3.88; C, 9.01; Cl, 34.0.

**trans-Diamminebis(ethylenediamine)iridium(III) Perchlorate**,  $[\text{Ir}(\text{en})_2(\text{NH}_3)_2](\text{ClO}_4)_3$ .—The complex  $[\text{Ir}(\text{en})_2(\text{NH}_2\text{Cl})_2]\text{Cl}$  (0.2 g) was treated at room temperature with 10 ml of 57% HI solution. The reaction mixture was stirred well and then cooled at 0° for a few minutes. A yellow-brown solid, a mixture of the  $\text{I}^-$  and  $\text{I}_3^-$  salts of the desired product, was collected by filtration. This solid was dissolved in a minimum amount of hot water and an equal amount of methanol was added, followed by 10 ml of concentrated  $\text{HClO}_4$ . The resulting mixture was cooled at 0° overnight and the white crystals formed were collected, washed with methanol and ether, and dried *in vacuo* overnight. The yield was 70%. *Anal.* Calcd for  $[\text{Ir}(\text{en})_2(\text{NH}_3)_2](\text{ClO}_4)_3$ : N, 13.04; H, 3.14; C, 7.45;  $\text{ClO}_4^-$ , 46.28. Found: N, 12.73; H, 3.50; C, 7.39;  $\text{ClO}_4^-$ , 46.0.

**Quantitative Measurement of Released Gas.**—The gas released from the reaction of *trans*- $[\text{Ir}(\text{en})_2(\text{N}_3)_2]^+$  with concentrated hydrochloric acid was measured quantitatively by the use of a Toepler pump. The gas was shown to be nitrogen by mass spectral analysis on a consolidated Electroynamics Corp. 21–104 mass spectrograph. The reaction was carried out in an all-glass cell which could be connected to a vacuum line *via* an O-ring joint. The cell had two arms that could be separately evacuated. In a typical run, 5 ml of 12 *M* HCl was degassed in one arm of the cell and that arm was evacuated. The solid complex was placed in the other arm and that side was evacuated. The reactants were then mixed and the amount of liberated gas was measured after several hours.

**Quantitative Measurement of Liberated Iodine.**—Iodine liberated by the reaction of  $[\text{Ir}(\text{en})_2(\text{NH}_2\text{Cl})_2]^{3+}$  with  $\text{I}^-$  in acidic solution was determined volumetrically using freshly standardized  $\text{Na}_2\text{S}_2\text{O}_3$  solution. Samples of the complex were stirred for 10 min with a freshly prepared solution of KI in 1.2 *M* HCl and then titrated immediately. Blank runs with no complex added gave negligible amounts of iodine.

**Physical Measurements.**—Infrared spectra were recorded on a Perkin-Elmer 337 grating spectrophotometer calibrated against polystyrene. Ultraviolet and visible spectra were measured on a Cary 14 spectrophotometer using 1-cm matched silica cells. Magnetic susceptibilities of solids were measured at room temperature on a Faraday balance.

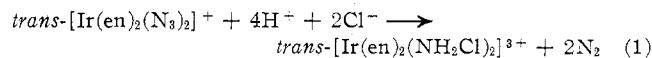
**Analyses.**—Carbon, hydrogen, and nitrogen analyses were carried out by Miss H. Beck of this department. Perchlorate ion was determined gravimetrically as  $(\text{C}_6\text{H}_5)_4\text{AsClO}_4$  by a method previously described.<sup>6</sup> Chloride ion was determined by titration with standardized  $\text{AgNO}_3$  solution using a  $\text{Ag}-\text{AgCl}$  standard electrode on an automatic titrator, the Radiometer Titrator 11 Titrigraph.

### Results and Discussion

Previous studies<sup>3</sup> show that the reaction of  $[\text{Ir}(\text{NH}_3)_5\text{N}_3]^{2+}$  with concentrated hydrochloric acid yields  $[\text{Ir}(\text{NH}_3)_5\text{NH}_2\text{Cl}]^{3+}$  and 1 mol of nitrogen. The same type of reaction takes place with *trans*- $[\text{Ir}(\text{en})_2(\text{N}_3)_2]^+$ , as illustrated by eq 1. The stoichiometry of this reac-

(5) This complex was stored in the dark as the more stable  $\text{PF}_6^-$  salt. The chloride salt is quite light sensitive.

(6) T. S. Gould and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1321 (1964).

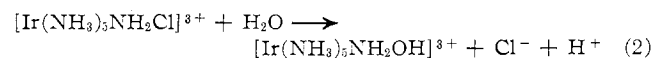


tion was established by the characterization of the *trans*- $[\text{Ir}(\text{en})_2(\text{NH}_2\text{Cl})_2]\text{Cl}_3$  product and by determining that the reaction evolves 2 mol of nitrogen gas per mole of complex. In order to obtain the pure bis(chloramine) product, it is necessary to use 12 *M* HCl. Lower hydrochloric acid concentrations lead to products that do not give consistent elemental analyses. This is probably due to the hydrolysis of the coordinated chloramine. This also makes it unprofitable to attempt to recrystallize the product. In the solid state, however, this complex is reasonably stable.

The ultraviolet spectrum of  $[\text{Ir}(\text{en})_2(\text{NH}_2\text{Cl})_2]^{3+}$  can be measured in 1 *M* HCl, but the spectrum shows slow decomposition of the complex even at this acid concentration, making it impossible to measure exact extinction coefficients. Two peaks are observable. A prominent shoulder appears at 320 nm with an extinction coefficient at 210 l. mol<sup>-1</sup> cm<sup>-1</sup> which does not change upon standing. Most of the complexes of the type  $[\text{Ir}(\text{en})_2\text{X}_2]^{n+}$  exhibit similar bands in this region.<sup>1</sup> A strong band appears at 253 nm with an extinction coefficient of approximately 1300. This band slowly decreases in intensity. This band is much stronger than any found in most other  $[\text{Ir}(\text{en})_2\text{X}_2]^{n+}$  complexes<sup>1</sup> and is consistent with the band observed for  $[\text{Ir}(\text{NH}_3)_5\text{NH}_2\text{Cl}]^{3+}$  at 258 nm ( $\epsilon$  870)<sup>3</sup> and for free  $\text{NH}_2\text{Cl}$  at 243 nm ( $\epsilon$  458).<sup>7</sup>

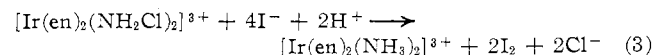
The salt  $[\text{Ir}(\text{en})_2(\text{NH}_2\text{Cl})_2]\text{Cl}_3$  definitely contains two kinds of chlorine. If it is titrated with standard silver nitrate in 3 *M*  $\text{HNO}_3$ , only three chloride ions are titrated, plus a small excess due to the hydrolysis of coordinated chloramine. If the complex is dissolved in dilute base, reacidified, and titrated with  $\text{AgNO}_3$ , the complex is completely hydrolyzed and the chloride ion:metal ratio was found to be 5:1.

Chloraminepentaammineiridium(III) hydrolyzes readily in neutral or weakly acidic solution to form the corresponding hydroxylamine complex (eq 2).<sup>3</sup> The



complex  $[\text{Ir}(\text{en})_2(\text{NH}_2\text{Cl})_2]^{3+}$  also hydrolyzes in aqueous solution, but its tendency to hydrolyze is considerably greater, slow decomposition occurring even in strong acid solutions. This makes it impractical to measure  $\text{pK}_a$  values. Attempts to isolate the hydrolysis products also lead to difficulty, probably due to the aquation of the hydroxylamine product. The products formed gave variable analyses, with carbon:nitrogen ratios varying between 4:4 and 4:6.

Another reaction of the coordinated chloramine is its reduction to ammonia by iodide ion.<sup>3</sup> In strong acid solution,  $[\text{Ir}(\text{en})_2(\text{NH}_2\text{Cl})_2]^{3+}$  reacts rapidly with iodide ion to give 2 mol (average of three trials 1.97) of iodine per mole of complex (eq 3). The pure white,



diamagnetic perchlorate salt of this product has been isolated and identified. It is shown to be the *trans* complex by the appearance of only one band in the ir spectrum in both the  $\text{NH}_2$  asymmetric deformation

(7) J. Kleinberg, M. Tecotzky, and L. F. Audrieth, *Anal. Chem.*, **26**, 1388 (1954).

(1600  $\text{cm}^{-1}$ ) and  $\text{CH}_2$  rocking (800  $\text{cm}^{-1}$ ) regions.<sup>8,9</sup> This was expected since Bauer<sup>1</sup> did not observe cis-trans isomerism of similar  $[\text{Ir}(\text{en})_2\text{X}_2]^{2+}$  complexes under any conditions and since the ligand transformation is believed to take place without Ir-N bond rupture. The ultraviolet spectrum exhibits a broad shoulder at 325 nm ( $\epsilon$  35) and a band at 225 nm ( $\epsilon$  390).

**Acknowledgment.**—This research was supported by a grant from the National Science Foundation. We wish to thank Dr. J. W. McDonald for helpful discussions. The iridium used was loaned to us by the Matthey Bishop Co.

(8) M. T. Baldwin, *J. Chem. Soc.*, 4369 (1960).

(9) C. S. Chan and F. Leh, *J. Chem. Soc. A*, 760 (1966).

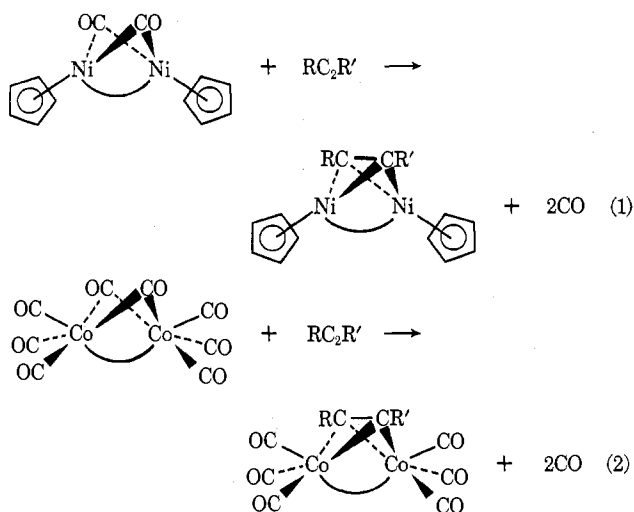
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
UNIVERSITY OF CALIFORNIA, RIVERSIDE, CALIFORNIA 92502

### Kinetics and Mechanism of the Reaction of Di- $\mu$ -carbonyl-bis(cyclopentadienyl)nickel with Alkynes

BY PAUL C. ELLGEN

Received February 8, 1972

At least in the solid state, the complexes  $\text{Co}_2(\text{CO})_8$  and  $\text{Ni}_2(\text{CO})_2(\text{C}_5\text{H}_5)_2$  are structurally analogous,<sup>1,2</sup> each having a metal-metal bond and two bridging carbon monoxide ligands. Moreover, each reacts with alkynes<sup>3,4</sup> to displace the bridging carbon monoxid-groups and give products whose structural similarity parallels that of the original metal carbonyls.<sup>2,5</sup> Equations 1 and 2 attempt to display these parallels.



On the basis of an elegant analysis of rate data for (2), Tirpak and coworkers<sup>6</sup> originally proposed the mechanism shown as eq 3 for this reaction.

(1) G. G. Sumner, H. P. Klug, and L. E. Alexander, *Acta Crystallogr.*, **17**, 732 (1964).

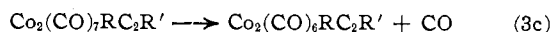
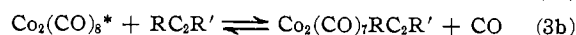
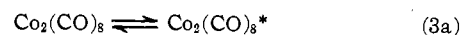
(2) O. S. Mills and B. W. Shaw, *J. Organometal. Chem.*, **11**, 595 (1968).

(3) H. W. Sternberg, et al., *J. Amer. Chem. Soc.*, **76**, 1457 (1954); H. Greenfield, et al., *ibid.*, **78**, 120 (1956).

(4) J. F. Tilney-Bassett and O. S. Mills, *ibid.*, **81**, 4757 (1959); J. F. Tilney-Bassett, *J. Chem. Soc.*, 577 (1961).

(5) W. G. Sly, *J. Amer. Chem. Soc.*, **81**, 18 (1959).

(6) M. R. Tirpak, J. H. Wotiz, and C. A. Hollingsworth, *ibid.*, **80**, 4265 (1958).

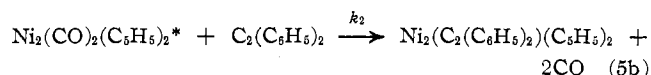
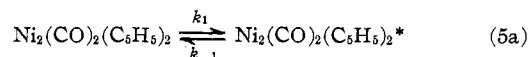


Recently, Cetini and coworkers<sup>7</sup> have reported that reaction 1 follows rate law 4 (for  $\text{R} = \text{R}' = \text{C}_6\text{H}_5$ ).

$$-d[\text{Ni}_2(\text{CO})_2(\text{C}_5\text{H}_5)_2]/dt = k_{\text{obsd}}[\text{Ni}_2(\text{CO})_2(\text{C}_5\text{H}_5)_2] \quad (4a)$$

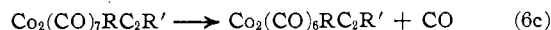
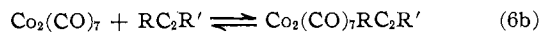
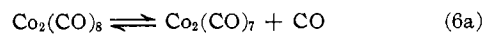
$$k_{\text{obsd}} = \frac{k_1 k_2 [\text{C}_2(\text{C}_6\text{H}_5)_2]}{k_{-1} + k_2 [\text{C}_2(\text{C}_6\text{H}_5)_2]} \quad (4b)$$

From this rate law, the mechanism shown as eq 5 was



inferred. In these proposed mechanisms, the symbols " $\text{Ni}_2(\text{CO})_2(\text{C}_5\text{H}_5)_2^*$ " and " $\text{Co}_2(\text{CO})_8^*$ " represent reactive isomers present at concentrations sufficiently low to be well approximated by a steady-state treatment.

Both of these reactions have been intensively studied in this laboratory. Reinvestigation of reaction 2 has established that the mechanism of eq 3 is incorrect. Instead, the stoichiometric mechanism depicted by eq 6 now appears to be securely established.<sup>8</sup> It should be noted that the original kinetic study of (2) was carried out at constant carbon monoxide pressure.<sup>6</sup> Under these conditions, the mechanisms of eq 6 and eq 3 are



kinetically equivalent.

It is the purpose of this paper to point out that rate law 4 proposed for reaction 1 is incorrect. Cetini and coworkers monitored the disappearance of the 1855- $\text{cm}^{-1}$  ir band of  $\text{Ni}_2(\text{CO})_2(\text{C}_5\text{H}_5)_2$  in the presence of large excesses of diphenylacetylene and calculated pseudo-first-order rate constants for this decay. Figure 1 presents their reported values for the pseudo-first-order rate constants plotted against the diphenylacetylene concentration for experiments done at 80° in heptane solution. The dashed line in this plot is the best fit to these data afforded by rate law 4. The salient feature of this rate law is the prediction that the pseudo-first-order rate constant becomes essentially independent of the diphenylacetylene concentration when the latter exceeds  $5.0 \times 10^{-2} M$ . Since this contradicts unreported observations previously made in these laboratories, a brief reinvestigation of (1) under the conditions used by Cetini has been undertaken.

Pseudo-first-order rate constants calculated for the disappearance of  $\text{Ni}_2(\text{CO})_2(\text{C}_5\text{H}_5)_2$  do not approach a constant value at high concentrations of diphenylacetylene. (See Table I.) At  $[\text{C}_2(\text{C}_6\text{H}_5)_2] = 0.50 M$  and 80°, the pseudo-first-order rate constant observed is almost 6 times that expected from (4) and the data of ref 7. It is concluded that rate law 4 is incorrect and that the fit afforded by the dashed line in Figure 1 is accidental.

(7) P. L. Stanghellini, R. Rossetti, O. Gambino, and G. Cetini, *Inorg. Chem.*, **10**, 2672 (1971).

(8) P. C. Ellgen, *ibid.*, **11**, 691 (1972).