

the Hückel charge density of the corresponding carbon atom in which the excess charge density is restricted to the periphery of the molecule. Such a plot produces a reasonably straight line as shown even without correcting for differential ring current effects. Most surprising is the fact that the points for dilithium dibenzopentalenide (II) fall almost exactly on this line. Table I

Table I. Charge Distribution

Position	$\delta$	Experimental	HMO	SCF
1	5.340	1.34	1.33	1.29
2	6.245	1.16	1.16	1.18
3	6.670	1.06	1.04	1.06

compares the charge densities obtained from this plot with the Hückel and SCF calculated values. Excellent agreement is observed. Such agreement provides strong evidence that all the excess negative charge resides on the periphery of the molecule with effectively little, if any, charge delocalized over the central double bond. This charge distribution strongly supports the peripheral electronic model description of the dibenzopentalene system.

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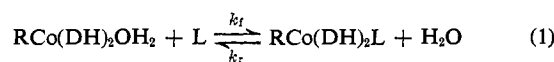
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### Substitution Kinetics of Alkylbis(dimethylglyoximate)aquocobalt(III) in Aqueous Solution<sup>1</sup>

Sir:

In view of recent interest concerning the kinetics of some alkyl-cobalt (III)<sup>2,3</sup> complexes and the similarity between certain dimethylglyoxime complexes of cobalt and vitamin B<sub>12</sub>,<sup>4</sup> we wish to present a preliminary report of our investigation into the substitution reactions of various alkylbis(dimethylglyoximate)aquocobalt(III) complexes. The overall reaction studied is



where [DH] represents the dimethylglyoximate monoanion,  $[\text{ON}=\text{C}(\text{CH}_3)\text{C}(\text{CH}_3)=\text{NOH}]^-$ , R = methyl, ethyl or isopropyl, L = SCN<sup>-</sup>, N<sub>3</sub><sup>-</sup>, py, CN<sup>-</sup>, or NH<sub>3</sub>, and  $k_f$  is the second-order ligation rate constant expressed in M<sup>-1</sup> sec<sup>-1</sup>.

The rate data were collected in aqueous solution at 10° and unit ionic strength by means of stopped-flow spectrophotometry.<sup>5</sup> Formation quotient data were

(1) A brief comment on the lability of these compounds was included in a paper presented at the 158th National Meeting of the American Chemical Society, New York, N. Y., 1969.

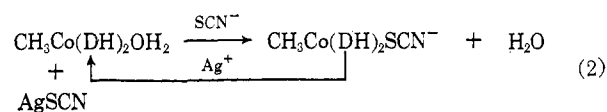
(2) L. M. Ludwick and T. L. Brown, *J. Amer. Chem. Soc.*, **91**, 5188 (1969).

(3) G. Costa, G. Mestroni, G. Tauzher, D. M. Goodall, M. Green, and H. A. O. Hill, *Chem. Commun.*, **34** (1970).

(4) G. N. Schrauzer, *Accounts Chem. Res.*, **1**, 97 (1968); G. Costa, G. Mestroni, and L. Stefani, *J. Organometal. Chem.*, **7**, 493 (1967).

collected under the same conditions by use of a Cary 14 spectrophotometer. Direct exposure to room lights was avoided during these measurements. The method of preparation of these complexes is that described by Schrauzer.<sup>6</sup>

In agreement with previous observations made by Schrauzer,<sup>4</sup> we find the cobalt-carbon bond to be stable under the conditions employed in this study.<sup>7</sup> Cyclic reactions such as the following were carried out to show that the observed rapid reaction 1 is indeed substitution of the aquo group by L, leaving the cobalt-carbon bond intact.



The regeneration of the aquo starting material was demonstrated spectrophotometrically. Retention of the planar bis(dimethylglyoximate) configuration has been demonstrated by previous authors in other dimethylglyoxime complexes.<sup>8</sup>

Table I is a summary of thermodynamic and kinetic data for reaction 1 when R = -CH<sub>3</sub>. The pH of these reaction solutions was such that hydrolysis of the nucleophile was negligible and deprotonation of the complex did not occur. For a wide range of charged and un-

Table I. Rate and Formation Quotient Data for Ligation Reactions of CH<sub>3</sub>Co(DH)<sub>2</sub>OH<sub>2</sub><sup>a</sup>

L	$k_f$ , M <sup>-1</sup> sec <sup>-1</sup>	$K$ , M <sup>-1</sup>
SCN <sup>-</sup>	49.6	9.6 × 10
N <sub>3</sub> <sup>-</sup>	34.7	2.04 × 10 <sup>2</sup>
Py	29.9	4.81 × 10 <sup>3</sup>
CN <sup>-</sup>	14.0	10 <sup>5</sup>
NH <sub>3</sub>	3.1	3.64 × 10 <sup>3</sup>
OH <sup>-</sup>		2.7 × 10

<sup>a</sup> Data collected at 10° and unit ionic strength (NaClO<sub>4</sub>).

charged nucleophiles, L, the second-order ligation constants only vary by approximately a factor of 10. However, the cobalt center demonstrates a great deal of thermodynamic discrimination between nucleophiles, as is shown in the 10<sup>5</sup> variation in formation quotients.

This narrow range of rate constants for the methyl complex on reaction with various nucleophiles is an indication that the detailed nature of the ligand substitution process is that of a dissociative interchange mechanism.<sup>9</sup> That is to say that L group participation in the transition state is not as significant as rupture of the cobalt-aquo bond. However, our data do not strictly preclude the possibility of an extreme dissociative mechanism in which H<sub>2</sub>O behaves as a more efficient nucleophile than L. Plots of pseudo-first-order rate constants as a function of nucleophile concentration show no sign of curvature in the range of concentrations

(5) P. H. Tewari, R. H. Gaver, H. K. Wilcox, and W. K. Wilmarth, *Inorg. Chem.*, **6**, 611 (1967).

(6) G. N. Schrauzer and R. J. Windgassen, *J. Amer. Chem. Soc.*, **88**, 3738 (1966).

(7) Cobalt-carbon bond cleavage was not observed even on warming a 10<sup>-4</sup> M solution of CH<sub>3</sub>Co(DH)<sub>2</sub>OH<sub>2</sub> in 1 M NaCN for 1 hr at ca. 65°.

(8) D. N. Hague and J. Halpern, *Inorg. Chem.*, **6**, 2059 (1967).

(9) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1967; C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin and Co., New York, N. Y., 1965.

studied [0.01–0.5 M].<sup>5</sup> This is in contrast to that observed by Costa and coworkers in a similar alkyl-substituted cobalt complex in a mixed solvent.<sup>3</sup>

We observe that  $\text{RCo}(\text{DH})_2\text{OH}_2$  reacts with  $\text{SCN}^-$  or  $\text{N}_3^-$  in the following relative order for various alkyl groups:  $-\text{CH}_3 < -\text{C}_2\text{H}_5 < -\text{CH}(\text{CH}_3)_2$ . This is also the order of increasing electron density on the carbon atom bonded to the cobalt. Hence these relative rates can be interpreted as an increased labilization of the aquo group as the *trans* ligand increases the electron density on the cobalt. We also note that while there is a large change in rate on going from  $\text{R} = -\text{CH}_3$  to  $\text{R} = -\text{CH}(\text{CH}_3)_2$ , there is little change in formation quotients. This gross change in free energy of activation with little change in relative ground state free energies may be an indication that the rate enhancement is partially due to steric effects. The larger isopropyl group will cause a greater distortion of the tetragonal transition state, thus making rupture of the cobalt–aquo bond a more facile process. We postulate that the relative reactivities of these alkyl complexes may be due to inductive or steric effects, or a combination of both.

Of further interest is the extreme lability of all of the alkyl–cobalt species in this study, which demonstrates the strong *trans* effect of the alkyl group in these octahedral complexes. For example,  $\text{Co}(\text{DH})_2(\text{NO}_2)(\text{OH}_2)$  undergoes anation by  $\text{N}_3^-$  with a second-order rate constant  $10^5$  times lower than that of the analogous reaction reported here.<sup>8</sup> Our results are in accord with the qualitative observation that the  $\text{p}K_a$  of the aquo complex is a measure of the lability of the  $\text{H}_2\text{O}$  ligand. The following order found for the  $\text{p}K_a$  of the coordinated aquo group,  $\text{Co}(\text{DH})_2(\text{NO}_2)(\text{OH}_2)^{10} < [\text{Co}(\text{DH})_2(\text{SO}_3)\text{OH}_2]^-^{11} < \text{CH}_3\text{Co}(\text{DH})_2\text{OH}_2$ ,<sup>12</sup> is also the order for the second-order rate constants for replacement of the bound  $\text{H}_2\text{O}$  by  $\text{N}_3^-$ .<sup>8, 11, 12</sup>

Formation quotients for reaction 1 with  $\text{L} = \text{Cl}^-$  or  $\text{I}^-$  and  $\text{R} = -\text{CH}_3$  are diagnostic of the hard or soft, or class a or b behavior of the cobalt center in this particular ligand environment.<sup>13</sup> While these quotients in aqueous solution are too small to be accurately determined, we can say that the iodide complex is more stable than the chloride. This indicates that the cobalt center behaves as a soft or class b Lewis acid in these complexes.<sup>14</sup>

Schrauzer has pointed out that the complexes studied here are reasonable models for the biologically important cobalamins.<sup>4</sup> Our observation that the cobalt center in this particular ligand environment is very labile is in accord with this view. Randall and Alberty report that substitution of water by  $\text{SCN}^-$  in aquo-cobalamin has a rate constant of  $7.1 \times 10^3$  at  $25^\circ$ .<sup>15</sup> We are continuing our studies of these alkyl–cobalt complexes in an effort to understand the reactivity patterns of the cobalt ion in this particular ligand environment and its similarity to the cobalamins. More

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(11) H. G. Tsiang and W. K. Wilmarth, *Inorg. Chem.*, **7**, 2535 (1968).

(12) See Table I.

(13) For a general discussion of these classifications, see ref 9, Chapter 1.

(14) Ludwick and Brown have also commented on the soft nature of cobalt in  $\text{CH}_3\text{Co}(\text{DH})_2\text{L}$  ( $\text{L} =$  dimethyl sulfoxide, 1,4-thioxane) in nonaqueous media (see ref 2).

(15) W. C. Randall and R. A. Alberty, *Biochemistry*, **5**, 3189 (1966); **6**, 1520 (1967).

complete details of our results will be reported at a later date.

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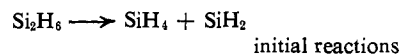
## Insertion Reactions of $\text{SiH}_2$

Sir:

The suggestion that  $\text{SiH}_2$  might be an intermediate in silane pyrolyses was first made by Stokland,<sup>1</sup> but an explicit proposal, based on comprehensive evidence, that silene readily undergoes insertion into Si–H bonds, was not made until quite recently when Purnell and Walsh<sup>2</sup> concluded that the reaction played a predominant role in monosilane pyrolysis and, simultaneously, Gaspar, Pate, and Eckelman<sup>3</sup> invoked the reaction in their account of neutron irradiation of  $^{31}\text{PH}_3$  in the presence of  $\text{SiH}_4$ . The work of Skell and Goldstein<sup>4</sup> had, somewhat earlier, indicated the occurrence of insertion of the analogous entity,  $\text{Si}(\text{CH}_3)_2$ , into Si–H bonds, while, more recently, Strausz, Obi, and Duholke<sup>5</sup> have presented evidence of  $\text{CH}_3\text{SiH}$  insertion into Si–H bonds. There is thus strong background evidence indicating the generality of  $\text{SiX}_2$  insertion into Si–H bonds. Results of a recent study of disilane pyrolysis<sup>6</sup> have been rationalized in terms of a mechanism, formally identical with that of Purnell and Walsh,<sup>2</sup> for monosilane, a view supported by our own very detailed studies of disilane pyrolysis<sup>7</sup> and further evidence cited here.

The products of disilane pyrolysis<sup>7</sup> ( $283\text{--}339^\circ$ ) in the early stages ( $< ca. 5\%$ ) are monosilane, trisilane, and both tetrasilanes. At measurable extents of reaction monosilane yields slightly exceed those of trisilane and the discrepancy increases slowly with increasing extent of reaction. At all times, at these low extents of reaction, the yields of tetrasilane balance the trisilane yield deficits. The detailed form of the results suggests that at true zero reaction time, monosilane and trisilane are in balance. The tetrasilane-forming reactions are thus secondary but occur so readily that, because of experimental limitations, they appear superficially to be primary.

Detailed study of the kinetics of the reaction has allowed us to establish the mechanism



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(3) P. P. Gaspar, B. D. Pate, and W. Eckelman, *J. Amer. Chem. Soc.*, **88**, 3878 (1966).

(4) P. S. Skell and E. J. Goldstein, *ibid.*, **86**, 1442 (1964).

(5) O. P. Strausz, K. Obi, and W. K. Duholke, *ibid.*, **90**, 1359 (1968).

(6) E. M. Tebben and M. A. Ring, *Inorg. Chem.*, **8**, 1787 (1969).

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