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

We observe that $RCo[DH]_2OH_2$ reacts with SCN^- or N_3^- in the following relative order for various alkyl groups: $-CH_3 < -C_2H_5 < -CH(CH_3)_2$. 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 $R = -CH_3$ to $R = -CH(CH_3)_2$, 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, $Co(DH)_2(NO_2)(OH_2)$ undergoes anation by N_3^- with a second-order rate constant 10^5 times lower than that of the analogous reaction reported here.[8] Our results are in accord with the qualitative observation that the pK_a of the aquo complex is a measure of the lability of the H_2O ligand. The following order found for the pK_a of the coordinated aquo group, $Co(DH)_2(NO_2)(OH_2)$[10] < $[Co(DH)_2(SO_3)OH_2]^-$ [11] < $CH_3Co(DH)_2OH_2$,[12] is also the order for the second-order rate constants for replacement of the bound H_2O by N_3^-.[8,11,12]

Formation quotients for reaction 1 with $L = Cl^-$ or I^- and $R = -CH_3$ are diagnostic of the hard or soft, or class a or b behavior of the cobalt center in this particular ligand environment.[13] 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.[14]

Schrauzer has pointed out that the complexes studied here are reasonable models for the biologically important cobalamins.[4] 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 SCN^- in aquocobalamin has a rate constant of 7.1×10^3 at 25°.[15] 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 complete details of our results will be reported at a later date.

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(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 $CH_3Co(DH)_2L$ (L = dimethyl sulfoxide, 1,4- thioxane) in nonaqueous media (see ref 2).

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Insertion Reactions of SiH_2

Sir:

The suggestion that SiH_2 might be an intermediate in silane pyrolyses was first made by Stokland,[1] 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[2] concluded that the reaction played a predominant role in monosilane pyrolysis and, simultaneously, Gaspar, Pate, and Eckelman[3] invoked the reaction in their account of neutron irradiation of $^{31}PH_3$ in the presence of SiH_4. The work of Skell and Goldstein[4] had, somewhat earlier, indicated the occurrence of insertion of the analogous entity, $Si(CH_3)_2$, into Si–H bonds, while, more recently, Strausz, Obi, and Duholke[5] have presented evidence of CH_3SiH insertion into Si–H bonds. There is thus strong background evidence indicating the generality of SiX_2 insertion into Si–H bonds. Results of a recent study of disilane pyrolysis[6] have been rationalized in terms of a mechanism, formally identical with that of Purnell and Walsh,[2] for monosilane, a view supported by our own very detailed studies of disilane pyrolysis[7] and further evidence cited here.

The products of disilane pyrolysis[7] (283–339°) 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

$$\left.\begin{array}{l} Si_2H_6 \longrightarrow SiH_4 + SiH_2 \\ SiH_2 + Si_2H_6 \longrightarrow Si_3H_8 \end{array}\right\} \text{initial reactions}$$

$$SiH_2 + Si_3H_8 \longrightarrow n\text{- or } i\text{-}Si_4H_{10} \quad \text{early secondary process}$$

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

(7) M. Bowrey and J. H. Purnell, manuscript in preparation.

for the early stages of reaction. Later, hydrogen, polymeric silicon hydride, and, ultimately, silicon, are formed. Absolute gas chromatographic calibration of the tetrasilanes was precluded by the small amounts which were available only as reaction product. However, an empirical relationship connecting silane molecular weight and chromatographic thermal conductivity response (in hydrogen carrier) was found to be valid for the lower silanes and its use for the tetrasilanes seems well justified. The yield ratio, *n*-tetrasilane/isotetrasilane, which is difficult to measure accurately because of the small amounts produced, was found to lie between the limits 4.4 and 5.2, significantly above the statistical value of 3. This result suggests that some insertion into the Si–Si bond, which can only give *n*-tetrasilane, may occur, but this proposal can only be taken as speculative pending more detailed and extended study.

To establish further the validity of the proposed pyrolysis mechanism we have studied the copyrolyses at 320° of mixtures of varying proportions of disilane and, respectively, each of the four methylated silanes. In the conditions quoted the alkyl silanes are all thermally stable with respect to disilane. The qualitative findings of the experiments are given in Table I.

Table I. Products, Other Than Those of Disilane Pyrolysis, Formed in the Copyrolysis of Disilane and Indicated Reactant at 320°

Reactant	No. of new products	Identity
CH_3SiH_3	1	$CH_3Si_2H_5$
$(CH_3)_2SiH_2$	1	$(CH_3)_2SiHSiH_3$
$(CH_3)_3SiH$	1	$(CH_3)_3SiSiH_3$
$(CH_3)_4Si$	0	
C_2H_6	0	
C_3H_8	0	

The identifications of the above products, and the proof that no others were formed, are based on comprehensive gas chromatographic retention volume studies involving use of a range of column types. Mass spectrometry and occasionally nmr analyses were also conducted.

Careful measurement showed that the monosilane yields were unaffected by the presence of the coreactant and that the amount of new product formed balanced reductions in tri- and tetrasilane yields exactly. Replacement of Si_2H_6 by Si_2D_6 in the reaction with methylsilane yielded a monosilane which proved on mass spectroscopic examination to be virtually exclusively SiD_4. These combined findings establish unambiguously for the first time the correctness of the mechanism proposed earlier for disilane pyrolysis.

The new product formed in the Si_2D_6–methylsilane reaction was also examined mass spectrometrically and this procedure indicated that, while $CH_3SiH_2SiD_2H$ predominated, some $CH_3SiD_2SiH_3$ was present. If true, this would indicate SiD_2 insertion into the C–Si bond. However, the observation of the quoted unique product in the reaction of Si_2H_6 with both dimethyl- and trimethylsilane (the alternatives, 1,2-dimethyldisilane and 1,1,2-trimethyldisilane would have been chromatographically resolved) and the failure to induce any reaction with tetramethylsilane are clear evidence that insertion into C–Si bonds does not occur in our conditions and that the observations on methyldisilane-d_2 are mass spectrometric artifacts. Further, the tetramethylsilane experiments establish that SiH_2 insertion into primary C–H bonds does not occur, a result confirmed by experiments with ethane, while the failure to observe reaction with propane indicates that secondary C–H bonds are also inert. An energy barrier to silene insertion is thus clearly established from this work.

The ability of SiH_2 to insert into SiH bonds cannot now be questioned and there is some possibility that insertion into Si–Si bonds occurs. Work with disilyl compounds to establish the truth or otherwise of the latter proposition is proceeding. There is evidently every possibility of both insertion of SiH_2 into bonds of lower bond dissociation energy than Si–H and of ring closure reactions by silene to yield a wide range of interesting new molecules. Obviously, any one of the silanes can act as an appropriate thermal source of SiH_2. Provided the coreactant is thermally stable at *ca.* 400°, monosilane offers the best source since its synthesis is simple and the most economical, and the conversion of Si is, potentially, 100%. However, the coreactant is usually likely to be thermally unstable with respect to monosilane and so disilane, which is more readily synthesized than is trisilane, would appear to be the preferred reagent in future thermal synthetic work of the type discussed.

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Carbon Orbital Hybridization in Some Organoplatinum Compounds

Sir:

The use of ^{13}C isotopic labeling for nuclear magnetic resonance studies of transition metal derivatives has, thus far, received scant attention.[1] The sporadic activity in this area is in marked contrast to the situation in organic chemistry where, in the last decade, considerable information has accumulated concerning ^{13}C chemical shifts[2] and ^{13}C–H coupling constants[3] for numerous simple and complex molecules. The essentially linear variation of $J_{^{13}C-H}$ values with the fractional s character (ρ) of the ^{13}C–H bond is now accepted for simple hydrocarbons and has been occasionally employed for the determination of molecular param-

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