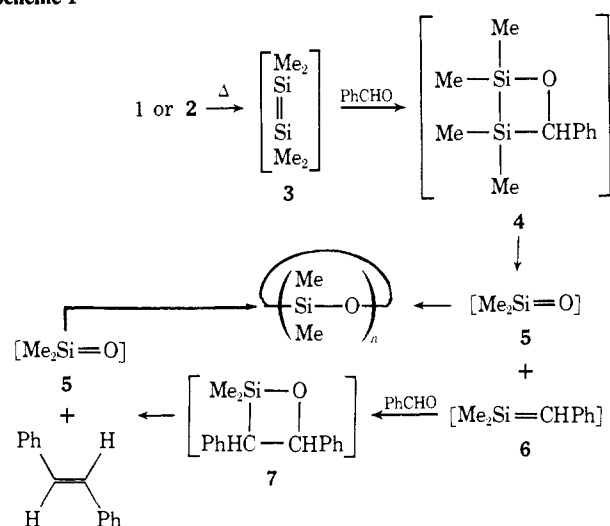


Scheme I



through silanone (5) intermediacy. However, the absence of the normal gas-phase isomerization products of 8 from our reaction mixtures is sufficient for tentative exclusion of such a mechanism.⁶⁻⁸

The dramatic reaction reported here emphasizes the necessity of invoking (p-p) π bonded silicon in a variety of reactions. We are continuing our efforts to prepare a stable molecule containing a (p-p) π bonded silicon so that the exact nature of the bonding can be determined.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Research Corporation for support of this research.

(6) Pyrolysis of the sodium salt of benzaldehyde tosylhydrazone (250°, 40 Torr, N₂ flow) is reported to afford 15% stilbenes and 30% heptafulvalene.⁷ It has been concluded that, in the gas phase, phenylcarbene (8) undergoes ring expansion to cycloheptatrienylidene at temperatures $\leq 600^\circ$ and ring contraction to fulvenallene above 600°.⁸ Our product mixture (trapped at -196°) was only slightly yellow, both before and after warming under nitrogen, thus indicating an absence of heptafulvalene which was confirmed by nmr. Pyrolysis of 2, PhCHO and cyclohexene (1:4:10) did not afford any detectable 7-phenylnorcaradiene.

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Temperature and Axial Ligand Dependence of the Dynamic Character of Allylcobaloximes

Sir:

Organocobaloximes have been widely studied because of the many similarities between their chemistry and that of vitamin B₁₂ coenzyme and analogous cobalamins.¹ Though there is excellent evidence for the formation of transient olefinic π -complexes in solution,²

(1) (a) D. Dodd and M. D. Johnson, *J. Organometal. Chem.*, **52**, 1 (1973); (b) J. M. Pratt, "The Inorganic Chemistry of Vitamin B₁₂," Academic Press, New York, N. Y., 1972.

(2) (a) B. T. Golding, H. L. Holland, U. Horn, and S. Sakrikar, *Angew. Chem., Int. Ed. Engl.*, **9**, 959 (1970); (b) B. T. Golding and S. Sakrikar, *J. Chem. Soc., Chem. Commun.*, 1183 (1972); (c) E. A. Parfenov, T. G. Chervyakova, and A. M. Yurkevich, *Zh. Obshch. Khim.*, **42**, 2584 (1972); (d) R. B. Silverman, D. Dolphin, and B. M. Babior, *J.*

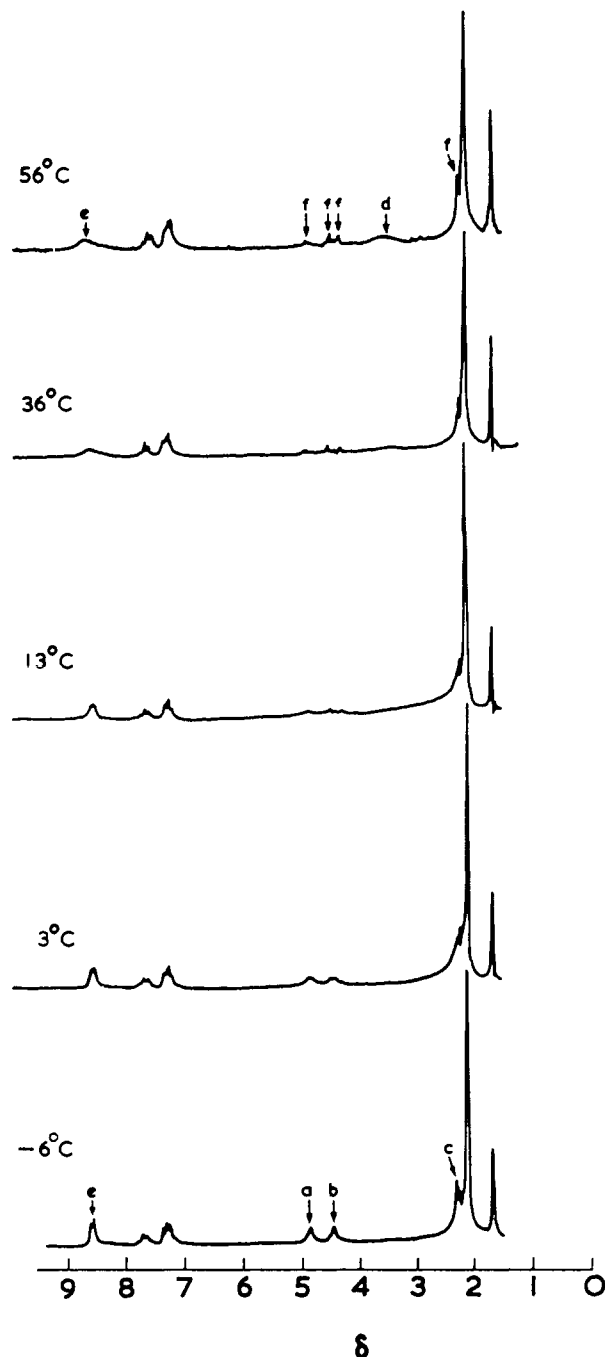


Figure 1. Temperature dependence of the 100-MHz ¹H nmr spectrum of I (CDCl₃). Impurities⁷ (marked f) are evident in the region of δ 4-5 above 10°.

only σ -bonded organocobaloximes and -cobalamins have been isolated,³ and it has been generally assumed that the similar character of the carbon-cobalt bonds in these complexes is largely a result of the steric and electronic effect of the relatively inflexible equatorial ligand and, to a lesser extent, of the other axial ligand.

We now report that the character of allylcobaloximes is dependent upon the nature of the other axial ligand and that, in some cases, dynamic σ -allylcobaloximes are formed. Thus, at -6° and below, the 100-MHz ¹H nmr spectrum (CDCl₃; Figure 1) of 2-methylallylbis-

Amer. Chem. Soc., **94**, 4028 (1972); (e) R. B. Silverman and D. Dolphin, *ibid.*, **95**, 1686 (1973).

(3) Reference 1a Table I, gives a comprehensive list of such compounds.

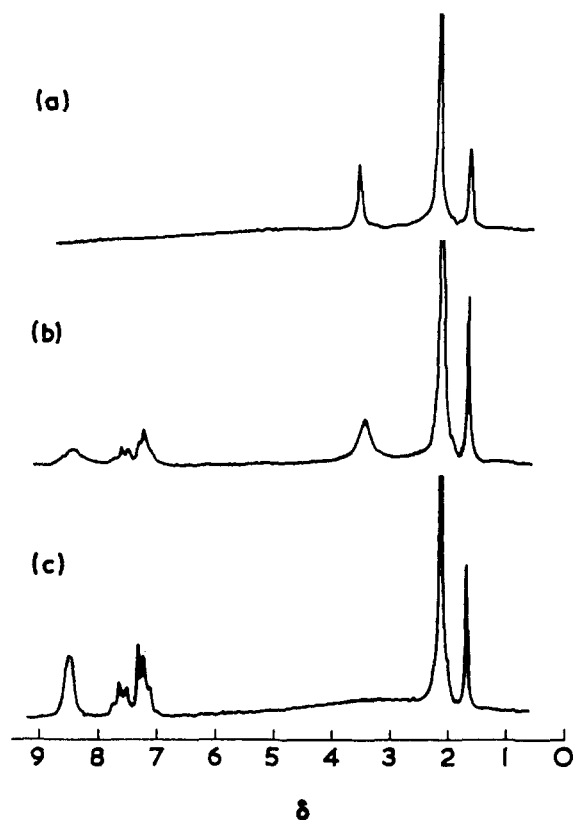


Figure 2. 60-MHz ^1H nmr spectra of (a) II (CDCl_3 - CD_3OD , 10:1 by volume); (b) I (CDCl_3); (c) I + 3 mol of pyridine (CDCl_3).

(dimethylglyoximato)pyridinecobalt(III) (I)⁴ shows the characteristic spectrum expected for a σ -2-methylallyl complex, with a well-resolved set of resonances of the axial pyridine ligand. On increasing the temperature⁵ the methylene proton resonances at δ 4.90, 4.45, and 2.33 (a, b, and c on Figure 1) collapse but even at 56° do not fully coalesce (d; Figure 1) to the four-proton singlet expected for a dynamic 2-methylallylcobaloxime.^{6,7}

The four-proton singlet resonance at *ca.* δ 3.5 is, however, fairly well resolved in the corresponding 60-MHz spectrum (CDCl_3) of I (Figure 2; spectrum b) but collapses on the addition of an excess of pyridine (Figure 2; spectrum c). The best resolution of the four-proton resonance was achieved in the case of the aquo complex 2-methylallylbis(dimethylglyoximato)-aquocobalt(III) (II) in CDCl_3 : CD_3OD 10/1 by volume (Figure 2; spectrum a).

Though the methyl singlet resonances of I and of II *ca.* δ 1.75 are virtually unchanged under all the conditions described above, the collapse of the methylene resonances of I is accompanied by appreciable broadening of the resonances of the pyridine α -protons at δ 8.6 (Figure 1; e), *i.e.*, of those pyridine protons most influenced by coordination. Such broadening of the pyridine α -protons does not occur in the variable

(4) All complexes described in this communication have been characterized by elemental analysis.

(5) Unless otherwise indicated, all the changes described here are reversible.

(6) The exact temperature dependences of all of the allylic spectra are influenced by the composition of the solvent.

(7) At temperatures $>0^\circ$ the rate of decomposition of I is appreciable, and resonances of decomposition products (f; Figure 1) are also evident in the spectra.

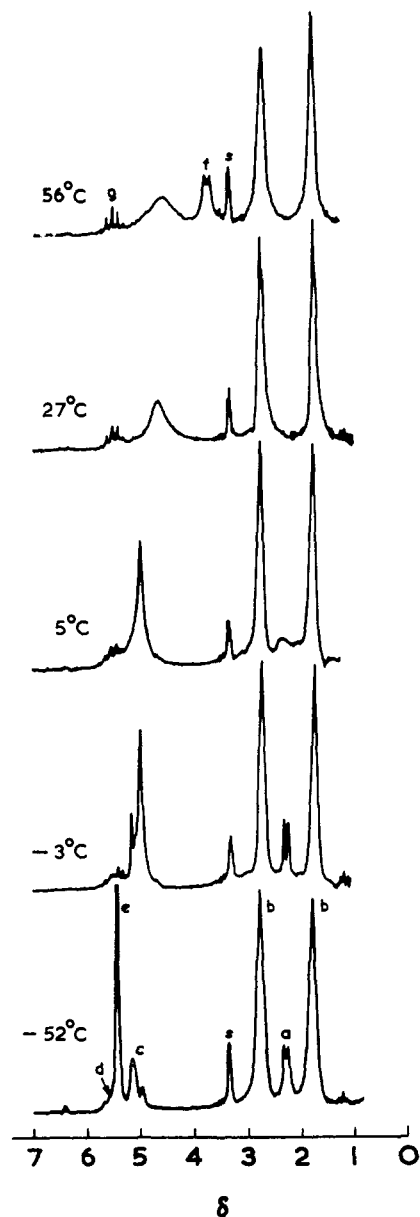


Figure 3. Temperature dependence of the 100-MHz ^1H nmr spectrum of III (CDCl_3 - CD_3OD , 1:1 by volume). The sharp resonance (s) at δ 3.3 is due to solvent.

temperature spectra of alkylbis(dimethylglyoximato)-pyridinecobalt(III) complexes.

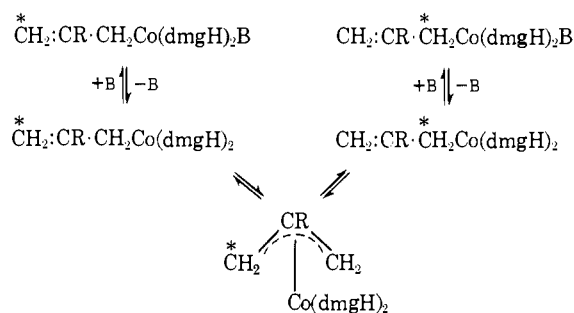
Similar temperature-dependent changes are observed in the 100-MHz ^1H nmr spectrum (CDCl_3 : CD_3OD 1:1 by volume) of allylbis(cyclohexanedionedioximato)-aquocobalt(III) (III). At -52° the spectrum is that of a typical σ -allyl complex with a doublet methylene resonance at δ 2.29 (a in Figure 3) between the two broad cyclohexanedionedioximato resonances (b in Figure 3), a multiplet methylene resonance at *ca.* δ 5.1 (c in Figure 3), and a multiplet methine resonance at *ca.* δ 5.5 (d in Figure 3) obscured by the residual hydroxyl resonance (e of Figure 3) of the largely deuterated solvent.

On increasing the temperature the spectrum collapses until at 56° it shows the characteristic AX_1 spectrum of a dynamic allyl complex, with the four proton doublet methylene resonance at δ 3.76 (f; Figure 3) and the well-resolved methine proton quintuplet resonance no longer obscured at δ 5.54 (g; Figure 3). These changes

are accompanied by an upfield shift and marked broadening of the residual solvent hydroxyl resonance and by a broadening and disappearance of the bridging hydroxyl resonance of the equatorial dioximato ligands at δ 18.6 (not shown in the figure).

The reversible changes in the character of the axial ligand resonances which accompany the reversible changes in the character of the allyl and 2-methylallyl proton resonances clearly indicate that the dynamic character of the allyl group is closely associated with axial ligand exchange. Five-coordinate organocobaloximes are believed to be transient intermediates in such ligand exchanges,⁸ but attempts to obtain stable five-coordinate species have shown that, even in non-coordinating solvents in the absence of suitable axial ligands, an oxygen of an equatorial dioximato ligand of one molecule prefers to act as an axial ligand of a second molecule thus maintaining six-coordination.⁹ We therefore ascribe the formation of the dynamic σ -allylcobaloximes to the fact that transient intermediate five-coordinate allyl complexes can adopt the π -allyl configuration, even though the relatively inflexible dioximato equatorial ligands ensure that six-coordinate σ -allyl complexes predominate in solution, the rate of the dynamic exchange being dependent upon the rate of formation of the five-coordinate species. (See Scheme I.)

Scheme I



(dmgH)₂ = conjugate base of dimethylglyoxime;

B = axial ligand

Thus, with a weakly coordinating axial ligand such as water,¹⁰ the rate of formation and the proportion of the five-coordinate species are large. With a more strongly bound axial ligand, such as pyridine, the rates of formation and proportion of the five-coordinate species are appreciably smaller and may be reduced still further by the addition of an excess of that ligand.

These observations contrast with those for the more flexible allyl-¹¹ and 3-methylallyltetracyanocobaltate(III)^{12,13} ions, which clearly demonstrate that the latter complexes have π -allyl character in D₂O and revert to six-coordinate σ -allyl complexes on addition of an excess of cyanide ion.

(8) (a) Reference 1a, pp 42–51; (b) T. Sakurai, J. P. Fox, and L. L. Ingraham, *Inorg. Chem.*, **10**, 1105 (1971); (c) A. L. Crumbliss and W. K. Wilmarth, *J. Amer. Chem. Soc.*, **92**, 2593 (1970); (d) J. Halpern and D. N. Hague, *Inorg. Chem.*, **6**, 2059 (1967); (e) K. L. Brown and R. G. Kallen, *J. Amer. Chem. Soc.*, **94**, 1894 (1972).

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(13) 3-Methylallylcobaloxime and other unsymmetrical substituted allylcobaloximes show characteristic σ -allyl spectra under all the conditions described above.

Though the exact configuration of the five-coordinate allyl complexes is not known, these results demonstrate the relative ease with which the dioximato ligands may allow attack of a reagent cis to the organic ligand. In particular, it is interesting that oxygen insertion reactions of allylcobaloximes are very rapid under conditions in which the five-coordinate allyl complex is formed and may be suppressed by the addition of ligands which induce formation of the six-coordinate complex.¹⁴ The 2-methylallylcobaloximes, which have not previously been described and which show the most pronounced dynamic character, are also especially prone to thermal reaction with oxygen.

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An Unusual Case of Selectivity in a Photochemical Reaction. Photoisomerization of Unsymmetrical 1,3-Dienes

Sir:

Two major questions concerning photochemical reactions where multiple pathways exist are those of selectivity and the factors governing selectivity where observed. A case where these questions apply is photoisomerization phenomena of dienes and polyenes. Studies to date have been limited mostly to relatively simple alkyl-substituted systems.^{1–5} For these systems relatively little selectivity is observed; most isomerization phenomena for dienes can be accounted for in terms of equilibrating allyl methylene intermediates for triplet states^{1–3} and nonequilibrating allyl methylene intermediates for singlets.⁵ Intersystem crossing is unimportant in most systems investigated.^{1–3,5} For the few trienes and polyenes studied,^{2,4} little preference has been found as to the site—central or terminal bond—of isomerization.^{2a} The present paper reports a study of isomerization phenomena of an unsymmetrical diene, 1-(4-pyridyl)-4-phenylbutadiene. Rather surprisingly this diene exhibits high selectivity in photoisomerization which can best be explained in terms of rapid or selective radiationless decay from one of several equilibrating species.

1-(4-Pyridyl)-4-phenyl-*trans*-1, *trans*-3-butadiene (1) and 1-(4-pyridyl)-4-phenyl-*trans*-1, *cis*-3-butadiene (2) were prepared by a Wittig condensation of benzyltriphenylphosphonium bromide with 3-(4-pyridyl)acrolein.^{6,7} The product mixture (~60% 2) was separated

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(2) (a) R. S. H. Liu and Y. Butt, *J. Amer. Chem. Soc.*, **93**, 1532 (1971); (b) R. S. H. Liu, *Pure Appl. Chem., Suppl.*, **1**, 335 (1971).

(3) (a) J. Saltiel, D. E. Townsend, and A. Sykes, *J. Amer. Chem. Soc.*, **95**, 5968 (1973); (b) J. Saltiel, A. D. Rousseau, and A. Sykes, *ibid.*, **94**, 5903 (1972); (c) J. Saltiel, L. Metts, and M. Wrighton, *ibid.*, **91**, 5684 (1969).

(4) K. J. Crowley, *J. Org. Chem.*, **33**, 3679 (1968).

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