$(SiCl_3)_2$, which requires ultraviolet irradiation for exchange, does not undergo the same type of absolutely stereospecific exchange as its ruthenium analog; however, our present experimental method would not detect small preferences of one site over the other. We are continuing the investigation of exchange in these and related systems.

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R. K. Pomeroy, R. S. Gay, G. O. Evans, W. A. G. Graham*
Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada

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Stereochemical Nonrigidity and Cis–Trans Isomerization in Silylruthenium and Silylosmium Carbonyls

Sir:

Although stereochemical nonrigidity is a common feature of five-coordinate complexes,[1] its occurrence in nonchelate octahedral compounds has been established only in a special group of dihydrido complexes, H_2ML_4 (M = Fe, Ru; L = phosphine or phosphite).[2] In view of widespread interest in phenomena of this type, we now report our discovery of stereochemical nonrigidity in another, quite different class of octahedral complexes.

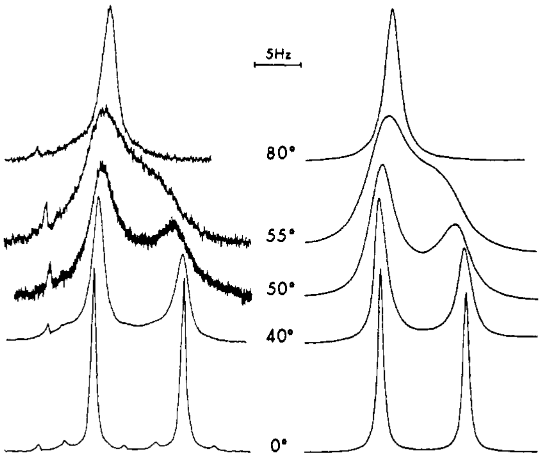

Figure 1. Observed (left) and calculated (right) proton nmr spectra (100 MHz) of *cis*- and *trans*-$Os(CO)_4(SiMe_3)_2$ in dibromomethane at various temperatures. The small peak at low field in the observed spectra is due to an impurity. Spectra are completely reversible as the solution is cooled. The low-field peak is due to the trans isomer.

The stereospecific exchange of ^{13}CO observed in certain *cis*-tetracarbonylruthenium derivatives[3] led us to investigate the kinetics of the following reaction

$$cis\text{-}Ru(CO)_4(SiCl_3)_2 \xrightarrow{k} trans\text{-}Ru(CO)_4(SiCl_3)_2 \qquad (1)$$

Although reaction 1 does not proceed at an appreciable rate at room temperature,[3] the kinetics of isomerization could be followed between 70 and 100° by infrared spectroscopy (*n*-octane solution, 1 atm of carbon monoxide to stabilize the labile cis isomer). Good first-order plots were obtained in the early stages of the reaction[4] and the derived activation parameters were $\Delta H^\ddagger = 24.9 \pm 1.0$ kcal mol^{-1} and $\Delta S^\ddagger = -6.9 \pm 3.0$ eu. The negative activation entropy would suggest that the isomerization proceeds by a nondissociative process.[5]

To provide more direct evidence for an intramolecular isomerization process, a compound of similar type was sought to which the nmr technique could be applied; the recently reported compound $Os(CO)_4(SiMe_3)_2$[6] proved ideally suited. The proton nmr spectrum at 100 MHz in dibromomethane consists of peaks at τ 9.37 and 9.46, in good agreement with reported values.[6] We have confirmed the previous assignment of these bands as the trans and cis isomers, respectively. We now find that as the dibromomethane solution is warmed (Figure 1), the two peaks broaden and coalesce. Comparison of observed line shapes with those calculated for various lifetimes over the range 30–80° led to the activation parameters $\Delta H^\ddagger = 17.9 \pm 0.6$ kcal mol^{-1} and $\Delta S^\ddagger = 1.6 \pm 1.7$ eu.[7]

The coalescence temperature was independent of concentration. Moreover, when a sample of $Os(CO)_4(SiMe_3)_2$ was kept under ^{13}CO at 55° for 165 min, *no significant ^{13}CO enrichment of the compound was observed in the infrared.* The averaging process is thus first order and does not involve dissociation of carbon monoxide ligands. The possibility that a five-coordinate intermediate is formed by dissociation at the $Os–SiMe_3$ bond seems unlikely because of the long-term stability of solutions of the compound and because of the small value of the entropy of activation.[8]

As Muetterties has pointed out, the barrier to intramolecular (non-bond-breaking) rearrangement in most octahedral complexes is very high.[1,9] As noted, the only nonchelated complexes previously shown to undergo such a rearrangement are a special class of the type H_2ML_4. It was suggested[1,2] that the lower barrier in this particular case resulted from a sterically imposed distortion of the heavy ligands toward tetrahedral positions in the ground state; isomerization could then occur by "tetrahedral tunneling" (not necessarily

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[1] E. L. Muetterties, *Accounts Chem. Res.*, **3**, 266 (1970).

[2] (a) F. N. Tebbe, P. Meakin, J. P. Jesson, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **92**, 1068 (1970); (b) P. Meakin, L. J. Guggenberger, J. P. Jesson, D. H. Gerlach, F. N. Tebbe, W. G. Peet, and E. L. Muetterties, *ibid.*, **92**, 3842 (1970); (c) P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *ibid.*, **93**, 4701 (1971).

[3] R. K. Pomeroy, R. S. Gay, G. O. Evans, and W. A. G. Graham, *ibid.*, **94**, 272 (1972).

[4] For $Ru(CO)_4(SiCl_3)_2$, the equilibrium constant for cis $\rightleftharpoons$ trans is *ca.* 1.9 (73.8°, decalin) and varies little with temperature.

[5] The dissociative process by which ^{13}CO is stereospecifically introduced[3] proceeds rapidly even at room temperature and thus is entirely distinct from the isomerization.

[6] S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc. A*, 3147 (1970).

[7] Allowance was made in these calculations for changes in the equilibrium ratio of cis–trans isomers. Relative intensities of the two proton nmr peaks between −40 and +30° led to the following thermodynamic values for the *cis*-$Os(CO)_4(SiMe_3)_2 \rightleftharpoons$ *trans*-$Os(CO)_4(SiMe_3)_2$ equilibrium: $\Delta H° = 0.8$ kcal mol^{-1}, $\Delta S° = 3.1$ eu.
Error limits on activation parameters are standard deviations calculated from a least-squares fit of the Eyring equation. Nine data points were used in the 30–80° temperature range.

[8] In this system, direct evidence for nondissociation of the trimethylsilyl ligands in terms of the preservation of coupling to the central metal atom or to the other ligands could not be obtained. Substitution of a phosphine for carbon monoxide might make this possible and we are investigating this approach.

[9] E. L. Muetterties, *J. Amer. Chem. Soc.*, **90**, 5097 (1968).

quantum mechanical) of hydrogen ligands from one face to another. In $Os(CO)_4(SiMe_3)_2$, a large distortion from regular octahedral geometry is not expected in view of the known structures of *cis*- and *trans*-$Ru(CO)_4(GeCl_3)_2$.[10] While a different mechanism seems indicated, we can at present only speculate on what it may be.

A trigonal twist mechanism, traversing a trigonal prismatic intermediate, is one possibility, although it is not generally thought to be an attractive one energetically.[1,9,11] Another possibility is that the trimethylsilyl group might migrate across a carbonyl carbon, *via* a kind of pseudo-five-coordinate, acyl-type intermediate. Such a possibility for ligand interchange in $XMn(CO)_5$ systems has in fact been suggested.[12] Since ^{13}CO does not exchange with $Os(CO)_4(SiMe_3)_2$ during isomerization as it would be expected to do in a normal five-coordinate intermediate, the species postulated must be transitory in character, or not "fully" five coordinate. A shift of the trimethylsilyl group to carbon would be related to the nonrigid behavior of cyclopentadienyltrimethylsilane and related compounds.[13] A discussion of other possible mechanisms, including turnstile rotations,[14] does not seem justified at the present time.

We have investigated the effect of replacing the methyl groups on silicon by chlorine atoms.[15] For $Os(CO)_4(SiMe_2Cl)_2$, the coalescence temperature is raised to between 120 and 140°; the barrier to isomerization in $Os(CO)_4(SiMeCl_2)_2$ is sufficiently high that the isomers are separable at room temperature; a cis form of $Os(CO)_4(SiCl_3)_2$ was not detected.[16] We have also reexamined the reported[6] cis and trans isomers of the tin derivative, $Os(CO)_4(SnMe_3)_2$, and find them to be nonrigid, with a coalescence temperature approximately the same as that of $Os(CO)_4(SiMe_3)_2$.

A search for other examples of nonrigidity in octahedral systems is in progress, and it is anticipated that variable temperature ^{13}C nmr spectroscopy will play a key role in these investigations.

Acknowledgment. We thank the National Research Council of Canada for financial support and Professor D. L. Rabenstein for assistance in nmr line-shape calculations.

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(10) R. Ball and M. J. Bennett, *Inorg. Chem.*, in press.

(11) Recent studies have demonstrated that this mechanism obtains in certain six-coordinate chelate complexes which exhibit significant distortion toward a trigonal prismatic configuration in the ground state: L. H. Pignolet, R. A. Lewis, and R. H. Holm, *J. Amer. Chem. Soc.*, **93**, 360 (1971); S. S. Eaton and R. H. Holm, *ibid.*, **93**, 4913 (1971).

(12) T. L. Brown, *Inorg. Chem.*, **7**, 2673 (1968).

(13) A. Davison and P. E. Rakita, *ibid.*, **9**, 289 (1970).

(14) I. Ugi, D. Marquarding, H. Klusacek, and P. Gillespie, *Accounts Chem. Res.*, **4**, 288 (1971).

(15) Details of the synthesis of these new compounds, which have been fully characterized, will be submitted shortly.

(16) It is of interest to note the trend in relative stabilities of cis and trans isomers in this group: $Fe(CO)_4(SiCl_3)_2$ is exclusively cis;[17] the trans form of $Ru(CO)_4(SiCl_3)_2$ is slightly more stable in decalin; while $Os(CO)_4(SiCl_3)_2$ appears to consist only of the trans form.

(17) W. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, **89**, 2773 (1967); *Inorg. Chem.*, **10**, 4 (1971).

R. K. Pomeroy, W. A. G. Graham*
Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada

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The Detection of Intermediates During the Conversion of Propane-1,2-diol to Propionaldehyde by Glyceroldehydrase, a Coenzyme B_{12} Dependent Reaction

Sir:

Recently there has been[1,2] renewed discussion of the mechanism of dioldehydrase,[3] an enzyme which requires as coenzyme, 5′-deoxyadenosylcobalamin, and catalyzes the conversion of L- or D-propane-1,2-diol to propionaldehyde, and ethylene glycol to acetaldehyde. Elegant experiments[4] have traced the fate of the hydrogen which migrates in these conversions: the C-1 hydrogen of the substrate is transferred to C-5′ of the coenzyme, where it becomes one of three equivalent hydrogens from which a C-2 hydrogen of product is ultimately derived.

We have isolated and purified[5] an enzyme closely related to dioldehydrase, *viz.*, a glyceroldehydrase[6] from *Aerobacter aerogenes* (No. 572 PZH), which, in addition to those reactions catalyzed by dioldehydrase, converts glycerol to β-hydroxypropionaldehyde.

The electronic absorption spectrum of a solution containing propane-1,2-diol and the glyceroldehydrase holoenzyme is similar to that reported[7,8] for propanedioldehydrase and by a detailed examination of the spectrum at wavelengths longer than 600 nm, we have identified[9] the species present (accounting for at least 80% of the enzyme-bound coenzyme present initially), as "base-on" B_{12r} *i.e.*, Co(II)cobalamin which has the 5,6-dimethylbenzimidazole coordinated. We have measured the absorption spectrum as a function of time, simultaneously monitoring the formation of propionaldehyde from propane-1,2-diol (Figure 1). The apoenzyme was incubated anaerobically with substrate, and a solution of 5′-deoxyadenosylcobalamin was added.[10] The pronounced lag[11] between the addition of coenzyme and both the attainment of the maximum rate of formation of product and the generation of the maximum concentration of Co(II)cobalamin is presumably connected with the slow binding of coenzyme to form the holoenzyme. Using the absorption bands at 611 and 655 nm diagnostically,[9] the concentration of Co(II)cobalamin increases to a steady-state value, concomitant with the formation of propionaldehyde. When all the substrate had been consumed, the concentration of Co(II)cobalamin decreased, and the coenzyme reformed, although not completely. When more substrate was added, Co(II)cobalamin was again formed.

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(3) H. A. Lee, Jr., and R. H. Abeles, *J. Biol. Chem.*, **238**, 2367 (1963).

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(10) All manipulations involving the coenzyme were carried out in the dark.

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