

the determination of which features these may be, can best be clarified by further structural studies on other useful anticonvulsants and by comparisons to the drugs already structurally determined. Such studies are in progress in these laboratories.

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## Communications to the Editor

### On the Completely Stereospecific Exchange of Carbon Monoxide in Bis(trichlorosilyl)tetracarbonylruthenium

Sir:

Exchange or displacement reactions of  $^{13}\text{CO}$  or  $\text{C}^{18}\text{O}$  with metal carbonyls and their derivatives provide a powerful tool in mechanistic studies, since the site of the labeled ligand in the coordination sphere can be determined by a suitable vibrational analysis. In most reported cases (e.g.,  $\text{XMn}(\text{CO})_5$ ,<sup>1,2</sup>  $\text{I}_2\text{Fe}(\text{CO})_4$ )<sup>3</sup> the labeled carbon monoxide is distributed statistically among the nonequivalent sites of the product molecule.

In order to observe preferential enrichment in specific sites, not only must the introduction at a specific site be kinetically favored, but, as pointed out by Brown,<sup>4</sup> nondissociative exchange between sites must be slow; that is, the molecule in question must be stereochemically rigid under the conditions of the experiment. Two systems have recently been reported which appear to meet these criteria: *o*-phenanthroline-tetracarbonylchromium<sup>5</sup> and piperidine-pentacarbonylmolybdenum.<sup>6</sup> In both compounds, carbonyl groups trans to the nitrogen ligands exchanged more slowly by a factor of 3 or 4.

We now report our discovery of the novel properties of *cis*- $\text{Ru}(\text{CO})_4(\text{SiCl}_3)_2$  (**1**), which exchanges *two* equatorial carbonyl ligands while the axial carbonyls do not exchange at all.<sup>7</sup> We believe that this behavior has important implications for the understanding of the five-coordinate intermediate in dissociative metal carbonyl reactions.

Bis(trichlorosilyl)tetracarbonylruthenium has been prepared<sup>8</sup> as an equilibrium mixture of *cis* and *trans* isomers which may be separated by fractional sublimation; the isomers are not interconverted at an observable rate at room temperature in solution or in the solid state.<sup>9</sup> A solution of **1** in *n*-heptane at room

temperature was placed under *ca.* 1 atm of  $^{13}\text{CO}$  (95.5% enriched) and the ir spectrum was examined at intervals over an 18-hr period. The spectrum of the final enriched product showed no change over an additional 24 hr. The initial and final spectra are shown in Figure 1. By means of the usual energy-factored vibrational analysis, the major bands in the final spectrum were shown to correspond to those calculated for the equatorially disubstituted form of **1**.<sup>10</sup> At intermediate stages of the exchange, bands predicted for equatorially monosubstituted **1** were observed, but these became weak as the exchange neared completion. At no stage were any of the predicted bands uniquely characteristic of mono- or diaxially substituted **1** observed. In fact, even a qualitative consideration of Figure 1 indicates that the exchange is stereospecific. The asymmetric stretching vibration of the axial set of carbonyls<sup>7</sup> ( $B_1$  in all- $^{12}\text{CO}$  molecule of  $C_{2v}$  symmetry,  $A''$  in the  $C_s$  molecule **5**, and  $B_1$  in the equatorially di- $^{13}\text{CO}$  molecule) cannot couple to other vibrations of the molecule. Hence its position and intensity will remain unchanged if the axial set is not substituted, and this is observed for the 2084- $\text{cm}^{-1}$  band.

The rate constant for the exchange of **1** with 95.5% enriched  $^{13}\text{CO}$  (26.6°, *n*-heptane, 750 mm) was  $1.04 \times 10^{-4} \text{ sec}^{-1}$ . The value was unchanged within experimental error when 95.5%  $^{13}\text{CO}$  was diluted with nitrogen to  $^{13}\text{CO}$  contents of 60, 40, and 20%, thereby establishing that the reaction follows overall first-order kinetics. From runs at 20.2 and 34.8°, we estimate  $\Delta H^\ddagger = 26.7 \pm 1.0 \text{ kcal}$  and  $\Delta S^\ddagger = 3.0 \pm 3.0 \text{ eu}$ .

Under similar conditions, *trans*- $\text{Ru}(\text{CO})_4(\text{SiCl}_3)_2$  (**2**) undergoes no exchange with  $^{13}\text{CO}$ , but ultraviolet irradiation under  $^{13}\text{CO}$  rapidly brings about its conversion to the *cis* isomer which is stereospecifically enriched exclusively in the equatorial positions.<sup>11</sup>

The foregoing results can be rationalized in terms of a common five-coordinate intermediate having the geometry designated in **3**, with both trichlorosilyl groups in equatorial positions of the trigonal bipyramid, as indicated in Scheme I.

The favored intermediate **3** might appear to be capable of reaction with  $^{13}\text{CO}$  to form the enriched

(1) H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, *J. Amer. Chem. Soc.*, **89**, 2844 (1967).

(2) B. F. G. Johnson, J. Lewis, J. R. Miller, B. H. Robinson, P. W. Robinson, and A. Wojcicki, *J. Chem. Soc. A*, 522 (1968).

(3) I. S. Butler and H. K. Spindjian, *J. Organometal. Chem.*, **18**, 145 (1969); B. F. G. Johnson, J. Lewis, P. W. Robinson, and J. R. Miller, *J. Chem. Soc. A*, 1043 (1968).

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

(5) M. Dokiya, R. D. Johnston, and F. Basolo, *ibid.*, **9**, 996 (1970).

(6) D. J. Darensbourg, M. Y. Darensbourg, and R. J. Dennenberg, *J. Amer. Chem. Soc.*, **93**, 2807 (1971).

(7) In accord with normal practice in these *cis* octahedral carbonyl systems, we take the trichlorosilyl ligands to lie in the equatorial plane, as the drawings suggest. We take the  $C_2$  axis as *z* and the equatorial plane as the *yz* plane.

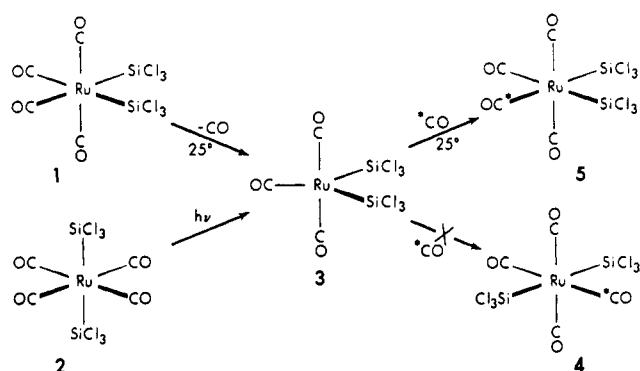
(8) Details of the synthesis from  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{Cl}_3\text{SiH}$  will shortly be submitted for publication.

(9) See, however, R. K. Pomeroy and W. A. G. Graham, *J. Amer. Chem. Soc.*, **94**, 274 (1972).

(10) Force constants used were  $k_{\text{ax}} = 17.96$ ,  $k_{\text{eq}} = 17.91$ ,  $k_{\text{ax,ax}} = 0.42$ ,  $k_{\text{eq,eq}} = 0.19$ , and  $k_{\text{ax,eq}} = 0.22 \text{ mdyn } \text{\AA}^{-1}$ . Calculated frequencies ( $\text{cm}^{-1}$ ) for various species are as follows: all- $^{12}\text{CO}$ , 2149.6, 2102.8, 2084.2, 2093.3; axial mono- $^{13}\text{CO}$ , 2139.9, 2099.2, 2050.4, 2093.3; equatorial mono- $^{13}\text{CO}$ , 2145.0, 2099.4, 2054.2, 2084.2; equatorial di- $^{13}\text{CO}$ , 2140.5, 2064.6, 2084.2, 2046.6. Observed band positions are listed in the caption to Figure 1.

(11) During the isomerization of unenriched **2** under  $^{13}\text{CO}$ , the first new bands to appear were those of equatorially monosubstituted **1**. Therefore **2** goes *directly* to enriched **1** and is not converted to unenriched **1** with subsequent  $^{13}\text{CO}$  exchange.

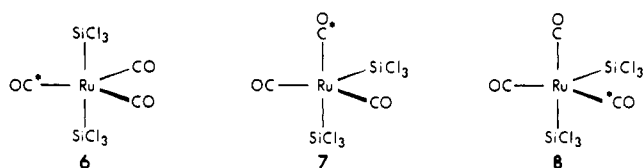
Scheme I



*trans* isomer 4 (with loss of stereospecificity in subsequent reactions), but microscopic reversibility implies that since the barrier for 2 → 3 is much greater than that for 1 → 3, the barrier for 3 → 4 is much greater than that for 3 → 5.

In general, a five-coordinate intermediate may be stereochemically nonrigid in ways which exchange the initially axial and equatorial carbonyls and yet still react with labeled carbon monoxide to give a stereospecifically *singly labeled* product; this consequence of microscopic reversibility was first pointed out in this context by Brown.<sup>4</sup> However, in the present case, stereospecificity persists as a *second* <sup>13</sup>CO is introduced. This establishes that the initially axial and equatorial sets of carbonyl groups are at all times differentiated in the five-coordinate intermediate.

Accordingly, there must be restrictions on the non-rigid processes which the intermediate can undergo. Of the other isomeric five-coordinate structures to which singly labeled 3 might be converted by the Berry mechanism,<sup>12,13</sup> 6 can be excluded since all carbonyls are equivalent. Isomer 7 cannot be rigorously excluded



but we consider that it is probably not involved since its conversion to forms such as 8, with scrambling of carbonyls from the two initial sites, would be expected to be facile. In summary, we suggest that there are significant energy differences among the isomeric five-coordinate intermediates, with 3 the most stable and the others essentially inaccessible.

Arguments of the sort advanced by Muetterties<sup>13</sup> for other types of five-coordinate intermediates may be applicable here as well. For example, the fact that *trans*-Ru(CO)<sub>4</sub>(SiCl<sub>3</sub>)<sub>2</sub> goes to the *cis* form under ultraviolet irradiation, even though this is not favored thermodynamically,<sup>9</sup> could be explained in terms of the relative stabilities of the five-coordinate intermediates. On the other hand, a rationale for the formation of *trans*-Fe(CO)<sub>4</sub>I<sub>2</sub> on irradiation of solutions of *cis*-Fe(CO)<sub>4</sub>I<sub>2</sub><sup>14</sup> lies in the assumption that

(12) R. S. Berry, *J. Chem. Phys.*, **32**, 933 (1960).

(13) E. L. Muetterties, *Accounts Chem. Res.*, **3**, 266 (1970).

(14) M. Pankowski and M. Bigorgne, *J. Organometal. Chem.*, **19**, 393 (1969).

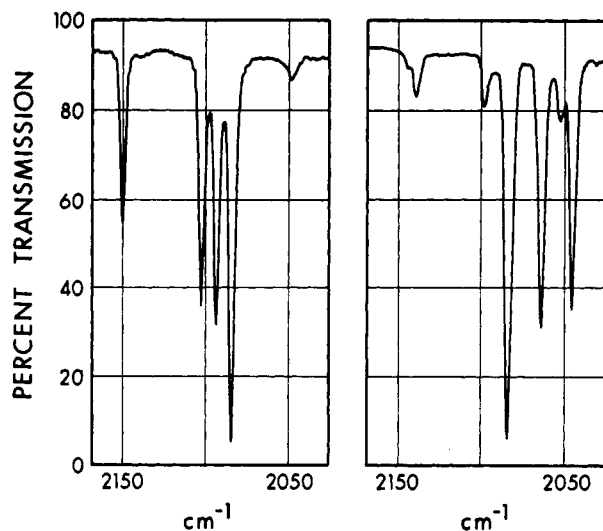


Figure 1. Infrared spectra (*n*-heptane solution) of *cis*-Ru(CO)<sub>4</sub>(SiCl<sub>3</sub>)<sub>2</sub>. At left, before exchange, showing major bands assigned to the all-<sup>12</sup>CO species at 2150, 2103, 2084, and 2094 cm<sup>-1</sup>; weaker bands at 2140, 2054, and 2051 cm<sup>-1</sup> assigned to mono-<sup>13</sup>CO species in natural abundance. At right, after exchange with 95.5% <sup>13</sup>CO for 18 hr at room temperature; bands at 2140, 2084, 2064, and 2046 cm<sup>-1</sup> assigned to equatorially di-<sup>13</sup>CO-substituted molecule; bands at 2145, 2100, and 2054 cm<sup>-1</sup> assigned to equatorially mono-<sup>13</sup>CO-substituted molecule. Calculated band positions are listed in ref 10.

the preferred five-coordinate intermediate in this case has iodine ligands in axial positions.

There is perhaps a common explanation for the nonexchange of fluorines in R<sub>2</sub>PF<sub>3</sub><sup>13</sup> and the nonexchange of carbonyls in [Ru(CO)<sub>3</sub>(SiCl<sub>3</sub>)<sub>2</sub>]; one might expect that stereospecific double exchange in a molecule of LMn(CO)<sub>5</sub> type would not be possible, since the intermediate [LMn(CO)<sub>4</sub>] would resemble RPF<sub>4</sub> in its ability to exchange axial and equatorial ligands without traversing high-energy isomeric forms. Among the phosphoranes, it is established that equatorial positions are preferred by the more electropositive substituents. It is not clear in the present case whether the same principle can be applied, *i.e.*, that a trichlorosilyl group is more electropositive than a carbonyl.<sup>15</sup>

Further study has revealed that *cis*-Ru(CO)<sub>4</sub>(GeCl<sub>3</sub>)<sub>2</sub> undergoes a similar double stereospecific exchange, although extremely slowly at room temperature; the exchange proceeds rapidly with the same stereospecificity under ultraviolet light. On the other hand, we find that the known<sup>18</sup> iron analog, *cis*-Fe(CO)<sub>4</sub>-

(15) On the other hand, it may be more appropriate to discuss stereochemical preferences in five-coordinate metal carbonyl derivatives in terms of the  $\pi$ -bonding properties of the ligands. It has been suggested, for example, that axial sites in Fe(O) compounds are favored by poorer  $\pi$ -bonding ligands.<sup>16</sup> If this principle is valid and can be extended to coordinatively unsaturated intermediates such as 3, then it would be necessary to regard the carbonyl group as a poorer  $\pi$  acceptor than a trichlorosilyl group.<sup>17</sup> However, as a referee has correctly pointed out, our understanding of axial *vs.* equatorial preferences in terms of the electronic properties of the substituent is in a primitive state.

(16) C. A. Udovitch, R. J. Clark, and H. Haas, *Inorg. Chem.*, **8**, 1066 (1969).

(17) While this would be an unorthodox position, there is other evidence that Cl<sub>3</sub>Si may be at least as good a  $\pi$  acceptor at CO. For example, stretching force constants in 1 are almost the same for both sets of carbonyls.<sup>10</sup> Also, the *trans* effect of the trichlorosilyl group in 1 is much greater than that of a carbonyl group, although this is no doubt due to several factors.

(18) W. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, **89**, 2773 (1967).

(SiCl<sub>3</sub>)<sub>2</sub>, 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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### Stereochemical Nonrigidity and Cis-Trans Isomerization in Silylruthenium and Silylosmium Carbonyls

Sir:

Although stereochemical nonrigidity is a common feature of five-coordinate complexes,<sup>1</sup> its occurrence in nonchelate octahedral compounds has been established only in a special group of dihydrido complexes, H<sub>2</sub>ML<sub>4</sub> (M = Fe, Ru; L = phosphine or phosphite).<sup>2</sup> 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.

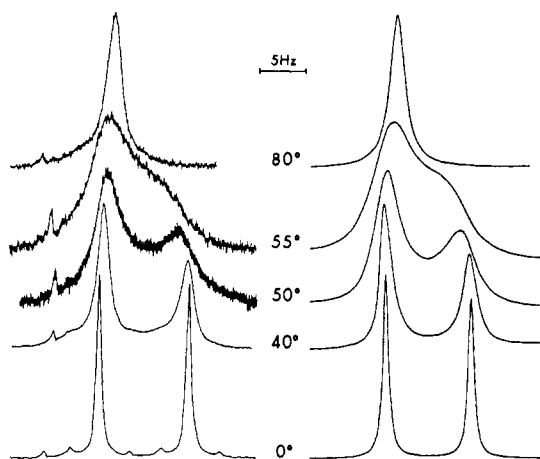
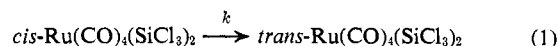


Figure 1. Observed (left) and calculated (right) proton nmr spectra (100 MHz) of *cis*- and *trans*-Os(CO)<sub>4</sub>(SiMe<sub>3</sub>)<sub>2</sub> in dibromomethane at various temperatures. The small peak at low field in the observed spectra is due to an impurity. Spectra are completely reversible as the solution is cooled. The low-field peak is due to the *trans* isomer.

The stereospecific exchange of <sup>13</sup>CO observed in certain *cis*-tetracarbonylruthenium derivatives<sup>3</sup> led us to investigate the kinetics of the following reaction



Although reaction 1 does not proceed at an appreciable rate at room temperature,<sup>3</sup> 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<sup>4</sup> and the derived activation parameters were  $\Delta H^\ddagger = 24.9 \pm 1.0$  kcal mol<sup>-1</sup> and  $\Delta S^\ddagger = -6.9 \pm 3.0$  eu. The negative activation entropy would suggest that the isomerization proceeds by a nondissociative process.<sup>5</sup>

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)<sub>4</sub>(SiMe<sub>3</sub>)<sub>2</sub><sup>6</sup> proved ideally suited. The proton nmr spectrum at 100 MHz in dibromomethane consists of peaks at  $\tau$  9.37 and 9.46, in good agreement with reported values.<sup>6</sup> 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<sup>-1</sup> and  $\Delta S^\ddagger = 1.6 \pm 1.7$  eu.<sup>7</sup>

The coalescence temperature was independent of concentration. Moreover, when a sample of Os(CO)<sub>4</sub>(SiMe<sub>3</sub>)<sub>2</sub> was kept under <sup>13</sup>CO at 55° for 165 min, no significant <sup>13</sup>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<sub>3</sub> 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.<sup>8</sup>

As Muetterties has pointed out, the barrier to intramolecular (non-bond-breaking) rearrangement in most octahedral complexes is very high.<sup>1,9</sup> As noted, the only nonchelated complexes previously shown to undergo such a rearrangement are a special class of the type H<sub>2</sub>ML<sub>4</sub>. It was suggested<sup>1,2</sup> 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

(4) For Ru(CO)<sub>4</sub>(SiCl<sub>3</sub>)<sub>2</sub>, the equilibrium constant for *cis* ⇌ *trans* is ca. 1.9 (73.8°, decalin) and varies little with temperature.

(5) The dissociative process by which <sup>13</sup>CO is stereospecifically introduced<sup>3</sup> 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)<sub>4</sub>(SiMe<sub>3</sub>)<sub>2</sub> ⇌ *trans*-Os(CO)<sub>4</sub>(SiMe<sub>3</sub>)<sub>2</sub> equilibrium:  $\Delta H^\circ = 0.8$  kcal mol<sup>-1</sup>,  $\Delta S^\circ = 3.1$  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).

(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).