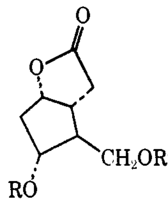
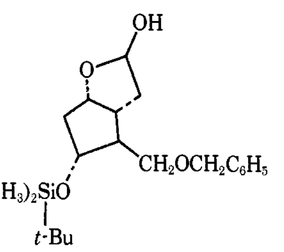
Exposure of **2** to tetra-*n*-butylammonium fluoride[13] (2 equiv) in tetrahydrofuran (10.6 ml/g of **2**) at 0° for 5 min and 25° for 40 min regenerated **1** which was isolated in pure condition in 92% yield. Reaction of **2** with diisobutylaluminum hydride (2 equiv) in toluene (26 ml/g of **2**) under nitrogen at $-78°$ for 10 min, quenching in the cold with methanol, and extractive isolation afforded the chromatographically pure, crystalline lactol **3**[12a] in 94% yield. Treatment of **3** under nitrogen with 2.8 equiv of the Wittig ylide derived from 5-triphenylphosphoniovaleric acid[10] in dry dimethyl sulfoxide (7.8 ml/g of **3**) at 25° for 3.5 hr afforded the acid **4**,[12a] $[\alpha]^{25}\mathrm{D}$ +24.75° (*c* 0.8, tetrahydrofuran), in 54% yield after chromatographic purification as a colorless, viscous oil. Removal of the silyl protecting group in **4** was accomplished using 3 equiv of tetra-*n*-butylammonium fluoride in tetrahydrofuran (11 ml/g of **4**) at 25° for 40 min to give the dihydroxy acid **5**[12a] in >99% yield. Oxidation of **4** with Jones reagent in acetone solution at $-15°$ for 25 min produced the oily keto acid **6**,[12a] $[\alpha]^{25}\mathrm{D}$ $-20.3°$ (*c* 1.7, tetrahydrofuran), in 87% yield.



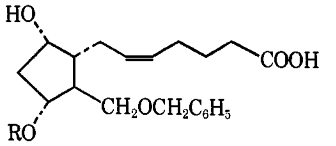
1, $R = H; R' = C_6H_5CH_2$

2, $R = Si(CH_3)_2\text{-}t\text{-}Bu; R' = C_6H_5CH_2$

7, $R = Si(CH_3)_2\text{-}t\text{-}Bu; R' = H$

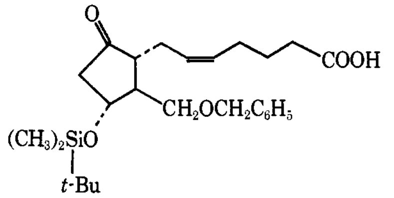


3

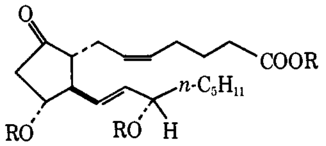


4, $R = Si(CH_3)_2\text{-}t\text{-}Bu$

5, $R = H$



6



8, $R = H$

9, $R = Si(CH_3)_2\text{-}t\text{-}Bu$

Selective removal of the benzyl protecting group from **2** was easily accomplished by hydrogenation at 25° and 1 atm over 10% Pd/C (200 mg/g of **2**) in tetrahydrofuran for 1 hr to give **7**,[12] mp 37°, in 96% yield.

To demonstrate the applicability of the dimethyl-*tert*-butylsilyl blocking group to substances which are sensitive to both acid and base, we have examined the silylation and desilylation of prostaglandin E_2 (**8**). Treatment of **8** with dimethyl-*tert*-butylsilyl chloride (5 equiv) and imidazole (10 equiv) in dimethylformamide (3.5 ml/g of **8**) at 25° for 48 hr afforded (88% yield) the disilyl ether–silyl ester **9**[12] as a chromatographically homogeneous colorless oil which was sufficiently stable thermally to yield a very satisfactory mass spectrum[14] (parent peak at *m/e* 694). The derivative **9** was reconverted to prostaglandin E_2 by exposure to acetic acid–water–tetrahydrofuran (3:1:1) at 25° for 20 hr. It is important to note that an attempted desilylation of **9** to form **8** using tetra-*n*-butylammonium fluoride under the usual conditions was unsuccessful due to the fact that fluoride ion in THF is a sufficiently strong base[15] to affect the highly sensitive β-ketol system in **8** or **9**.

The results of this study lead us to the view that the dimethyl-*tert*-butylsilyl group will find widespread application in the protection of hydroxylic groups.[16,17]

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(13) D. L. Fowler, W. V. Loebenstein, D. B. Pall, and C. A. Kraus, *J. Amer. Chem. Soc.*, **62**, 1140 (1940). The reagent employed in this work was prepared by neutralization of a 10% aqueous solution of tetra-*n*-butylammonium hydroxide with 48% hydrofluoric acid, concentration under reduced pressure, drying by azeotropic distillation under reduced pressure using several portions of benzene–acetonitrile (1:1), and final drying at 30° and 0.5 mm for 20 hr.

(14) In contrast to the corresponding tris-THP derivative.

(15) See J. Hayami, N. Ono, and A. Kaji, *Tetrahedron Lett.*, 1385 (1968).

(16) See E. J. Corey and T. Ravindranathan, *J. Amer. Chem. Soc.*, **94**, 4013 (1972).

(17) This work was assisted financially by the National Institutes of Health and the Agency for International Development.

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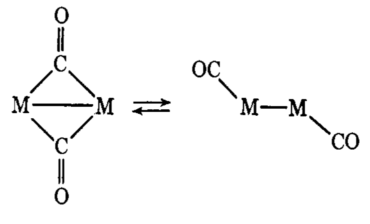
Direct Evidence from Carbon-13 Nuclear Magnetic Resonance for Intramolecular Scrambling of Carbonyl Groups in a Metal Atom Cluster Carbonyl, Tetrarhodium Dodecacarbonyl

Sir:

Several years ago it was shown by Bullitt, Cotton, and Marks[1] that bridge–nonbridge interchange (eq 1)



(1)

occurs rapidly in $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$. In the reports of this work it was explicitly proposed that processes of this general type (not necessarily in the specific mode of two bridges exchanging with two terminals) should be the basis for a large but generally unrecognized genre of fluxional molecules. Actually, the same essen-

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(1) J. G. Bullitt, F. A. Cotton, and T. J. Marks, *J. Amer. Chem. Soc.*, **92**, 2155 (1970). Recently a more extended account of the work has appeared: J. G. Bullitt, F. A. Cotton, and T. J. Marks, *Inorg. Chem.*, **11**, 671 (1972). A recent study of the same molecule using carbon-13 nmr has verified the occurrence of the postulated bridge–terminal exchanges and also supplied a more detailed picture of how they occur in that system.[2]

(2) O. A. Gansow, A. R. Burke, and W. D. Vernon, *J. Amer. Chem. Soc.*, **94**, 2550 (1972).

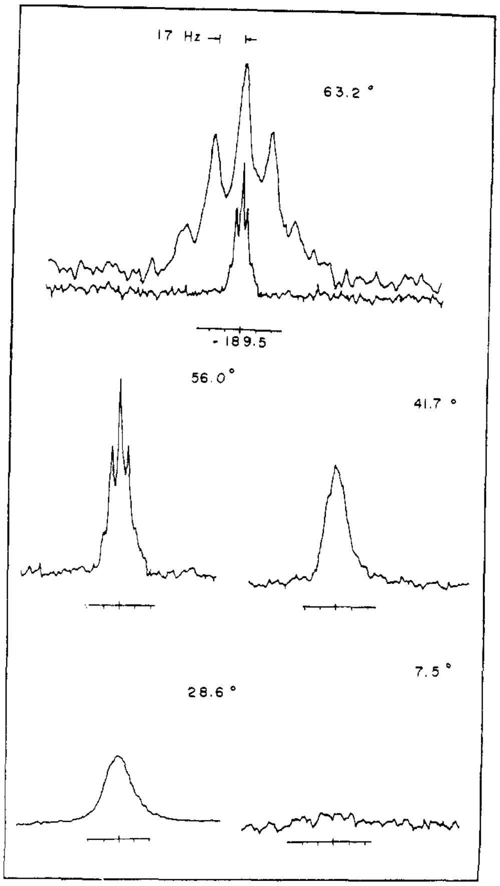


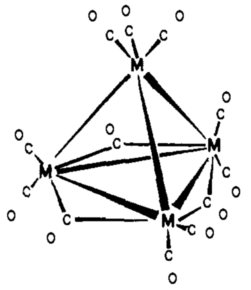
Figure 1. ^{13}C nmr spectra of $Rh_4(CO)_{12}$ at various temperatures. For conditions of recording, see text. δ_c (parts per million downfield from TMS) = 190.3, essentially invariant over the temperature range shown. The upper portion shows the fast-exchange limit spectrum blown up to show the quintet structure more clearly.

tial idea had been proposed with reference to $Co_4(CO)_{12}$ by one of us in 1966,[3] as will be detailed below.

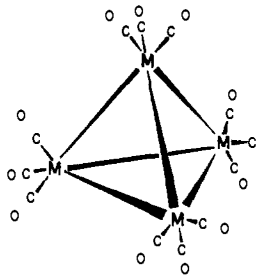
We present here our preliminary observations on scrambling of carbonyl groups in $Rh_4(CO)_{12}$. These observations are important in demonstrating the generality of rapid permutational isomerization reactions (fluxionality) through the agency of bridge–terminal interconversions of CO groups. The particular results also emphasize the enormous power of ^{13}C nmr spectroscopy in exploring this new field.

After prolonged uncertainty and controversy[4] the structure of $Co_4(CO)_{12}$ was finally shown unambiguously to be **1a**, both in the crystal[5] and in solution.[6,7] Soon after, Dahl and coworkers reported that $Ir_4(CO)_{12}$ has the nonbridged structure **2c** and that $Rh_4(CO)_{12}$ has the same type of bridged structure as $Co_4(CO)_{12}$, namely **1b**.[8]

Before any of these structures had been established with certainty, either in the solid or solution phases, Cotton[3] proposed that any or all of the $M_4(CO)_{12}$ molecules might be fluxional, by means of a sequence of rapid **1** $\rightleftharpoons$ **2** isomerizations or possibly in still other ways. For a structure of type **1** there are 159, 667, 720 permutational isomers,[9] each of which is accessible by a **2** → **1** rearrangement. We report here a ^{13}C nmr study of $Rh_4(CO)_{12}$ (**1b**) which shows that rapid scrambling of the CO groups does occur.



1. a: M = Co
b: M = Rh



2. a: M = Co
b: M = Rh
c: M = Ir

Tetrarhodium dodecacarbonyl is ideally suited to the study of its dynamical behavior by ^{13}C nmr. ^{103}Rh is 100% abundant and has a nuclear spin of $^1/_2$. The carbonyl can be prepared readily[10] and enriched in $^{13}C-^{16}O$ by direct exchange with enriched CO.

In the work reported here, a 27-mg sample of the carbonyl enriched to ~16% ^{13}CO and dissolved in 0.8 ml of deuteriochloroform contained in an 8-mm o.d. sample tube was used. Spectra were recorded in the Fourier transform mode on a Varian Associates XL-100-15 spectrometer operating at 25.16 MHz (the solvent deuteriochloroform provided the internal deuterium heteronuclear lock). Trisacetylacetonatochromium(III) (15 mg) was added to reduce T_1 for the ^{13}C nuclei.[2]

Structure **1b** has four different sites for ^{13}C, populated in 3:3:3:3 ratio.[11] At room temperature, however, the ^{13}C spectrum shows only a single broad resonance (full width at half-height ~65 Hz)[12] (Figure 1). As the temperature is raised this resonance narrows and begins to show fine structure. The spectrum characteristic of the fast-exchange limit is reached at around 50°. It consists of a 1:4:6:4:1 quintet with a splitting of 17.1 Hz. We have measured $^1J_{Rh-C}$ = ±68.8 Hz in $[Rh(CO)_2Cl]_2$. If it is assumed that the coupling of ^{13}C to a rhodium atom other than one to which it is bonded is relatively small, a splitting of the order of ($^1/_4$) × 67.5 = 17.2 Hz is to be expected, in good agreement with our observation.

This limiting spectrum shows unequivocally that the carbonyl groups are rapidly scrambled over the four types of site provided by structure **1** by an intramolecular mechanism. Intermolecular exchange would abolish the $^{103}Rh-^{13}C$ coupling and is therefore ruled out. We consider it reasonable to believe that the

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(3) F. A. Cotton, *Inorg. Chem.*, **5**, 1083 (1966).

(4) See ref 3 for citations of early literature.

(5) C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, **88**, 1821 (1966).

(6) H. Haas and R. K. Sheline, *J. Inorg. Nucl. Chem.*, **29**, 693 (1967).

(7) E. A. C. Lucken, K. Noack, and D. F. Williams, *J. Chem. Soc. A*, 148 (1967).

(8) C. H. Wei, G. R. Wilkes, and L. F. Dahl, *J. Amer. Chem. Soc.*, **89**, 4792 (1967).

(9) This number is given by 12! divided by the order (3) of the pure rotational symmetry group (C_3) of the molecular point group (C_{3v}), *i.e.*, by 12!/3.

(10) P. Chini and S. Martinengo, *Inorg. Chim. Acta*, **3**, 315 (1969); P. E. Cattermole and A. G. Osborne, *J. Organometal. Chem.*, **37**, C17 (1972).

(11) It has previously been reported that the infrared spectrum of $Rh_4(CO)_{12}$ is very similar to that of $Co_4(CO)_{12}$ [W. Beck and K. Lottes, *Chem. Ber.*, **94**, 2578 (1961)]. We have examined the infrared spectrum of $Rh_4(CO)_{12}$ at both the natural abundance level of ^{13}C and using samples enriched to 30%. These data fully substantiate structure **1b** in hydrocarbon solvents at 25°.

(12) Samples which have been heated in $CDCl_3$ show weak peaks due to $[Rh(CO)_2Cl]_2$.

mechanism is a sequence of **1b** ⇄ **2b** interconversions. Studies at lower temperatures, now in progress, may give further insight into mechanistic details.[13]

(13) This work was supported by research grants from the Robert A. Welch Foundation to F. A. C. (A-494) and B. L. S. (A-410).

(14) Postdoctoral Fellow of the National Research Council of Canada, 1970–1972.

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New Evidence for Carbonyl- and Isonitrile-Bridged Transition States for Intramolecular Carbonyl Scrambling

Sir:

Evidence has been presented for $[(h^5\text{-}C_5H_5)Fe(CO)_2]_2$ that the cis and trans isomers interconvert rapidly and this has been attributed to the ready rearrangement of each of the bridged molecules to the nonbridged tautomer.[1] It was also stressed that this observation implied that bridge–terminal CO exchanges probably afford a basis for widespread stereochemically nonrigid behavior in polynuclear metal carbonyls. We present here a preliminary account of recent observations which substantiate this proposal.

The $[(h^5\text{-}C_5H_5)M(CO)_3]_2$ molecules, M = Cr, Mo, and W, have structures without bridging CO groups, but bridge–terminal exchange which scrambles the carbonyl groups between the two metal atoms could still be occurring. Efforts to detect a minute quantity of the bridged tautomer of the Cr compound in solution have been negative. We have now prepared the compound $[(h^5\text{-}C_5H_5)Mo(CO)_3\text{-}Mo(CO)_2(CNCH_3)(h^5\text{-}C_5H_5)]$ (I) by two routes: (1) in low yield by uv irradiation of a toluene solution of $[(h^5\text{-}C_5H_5)Mo(CO)_3]_2$ in the presence of isonitrile; (2) by coupling of the appropriate halves (in 13% yield). The relatively stable red-violet compound was isolated by chromatography on alumina. The infrared spectrum in cyclohexane shows a single broad absorption (terminal isonitrile ligand) at 2125 cm^{-1} and five strong sharp absorptions at 1975, 1960, 1935, 1920, and 1900 cm^{-1} (terminal carbonyl groups). The mass spectrum[2] shows a parent ion at *m/e* 503 with ions corresponding to the successive loss of five carbonyl groups. At +60° the pmr spectrum of I shows single sharp absorptions for C_5H_5 and CH_3 protons. Upon cooling each signal broadens and reaches a coalescence point at about +2°. On further cooling, the C_5H_5 resonance is resolved into two sharp pairs of lines with relative intensities 6.5:1 at −43°. At the same temperature the methyl resonance appears as two lines with relative intensities of 6.5:1. These changes were independent of sample concentration over a factor of 4. Some representative spectra are shown in Figure 1.

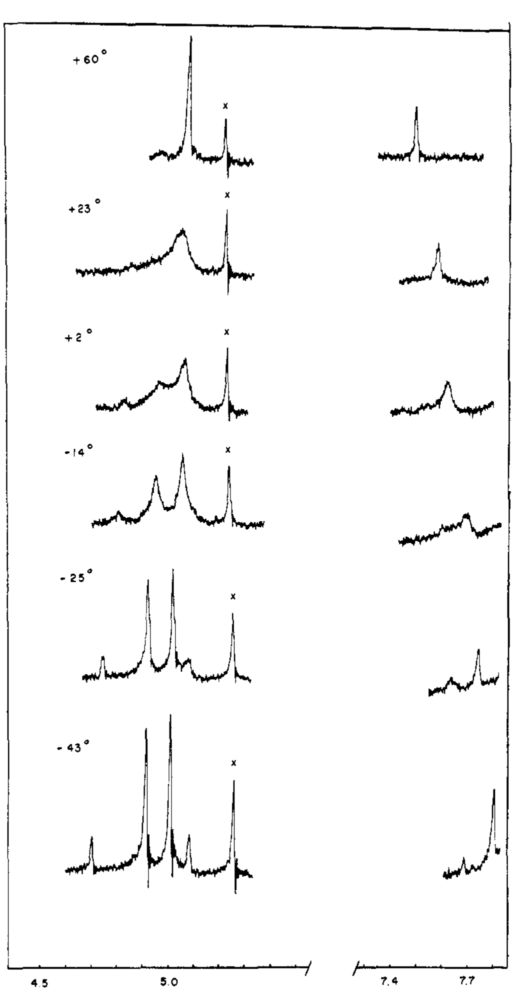

Figure 1. The pmr spectra of I at 100 MHz and various temperatures in toluene-d_8 solvent. The chemical shift of the methyl resonance is temperature dependent in toluene-d_8 but not in other solvents. × is $[C_5H_5Mo(CO)_3]_2$ impurity.

We postulate the presence of two isomers, A and B (Scheme I), having the isonitrile ligand trans and cis to the metal–metal bond.[2a] Isomerizations exchanging isonitrile between the cis and trans positions *via* either or both of rearrangements 1, or 2 and 3, and also between the metal atoms *via* either or both of mechanisms 4 apparently have similar rates. Rearrangements 2 and 3 combined lead to isomerization through a bis carbonyl bridged intermediate C. Rearrangement 1 could occur through a trigonal-bipyramidal type of intermediate.[3] These rearrangements coalesce C_5H_5 resonances a and c, and b and d. Changes in the methyl resonance are dependent only on this cis–trans isomerization. Transposition of the isonitrile between metal atoms *via* rearrangements 4 can occur only through intermediate D, simultaneously exchanging the isonitrile and one carbonyl. This coalesces C_5H_5 resonances a and b.

The molecule $[(h^5\text{-}C_5H_5)Fe(CO)_2\text{-}Fe(CO)(CN\text{-}t\text{-}C_4H_9)(h^5\text{-}C_5H_5)]$ (II) is reported[4] to have a terminal isonitrile and spectroscopically equivalent cyclopentadienyl rings. The C_5H_5 resonance, a sharp singlet at +26° in CS_2,

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(1) J. G. Bullitt, F. A. Cotton, and T. J. Marks, *J. Amer. Chem. Soc.*, **92**, 2155 (1970); *Inorg. Chem.*, **11**, 671 (1972).

(2) Kindly provided by Mr. Carl Renner at the Massachusetts Institute of Technology; acceptable elemental analyses were obtained.

(2a) Note Added in Proof. Present evidence does not permit us to rule out the possibility that the two isomers are rotamers, but cis and trans isomers seem more probable. Our evidence for end-to-end exchange of CO and $CNCH_3$ ligands is valid in either case.

(3) J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, **92**, 5852 (1970).

(4) W. J. Jetz and R. J. Angelici, *J. Organometal. Chem.*, **35**, C37 (1972).