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).

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F. A. Cotton,* L. Kruczynski,[14] B. L. Shapiro
Department of Chemistry, Texas A & M University
College Station, Texas 77843

L. F. Johnson
Varian Associates, Palo Alto, California 94303

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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.

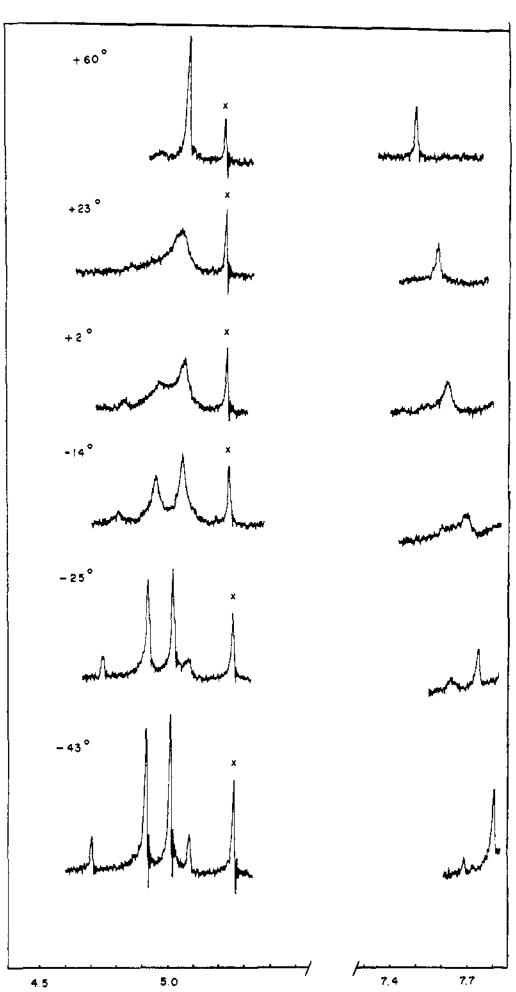

Figure 1. The pmr spectra of I at 100 MHz and various temperatures in toluene-d_8 solvent. The chemical shift of the methyl resonance is temperature dependent in toluene-d_8 but not in other solvents. X is $[C_5H_5Mo(CO)_3]_2$ impurity.

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).

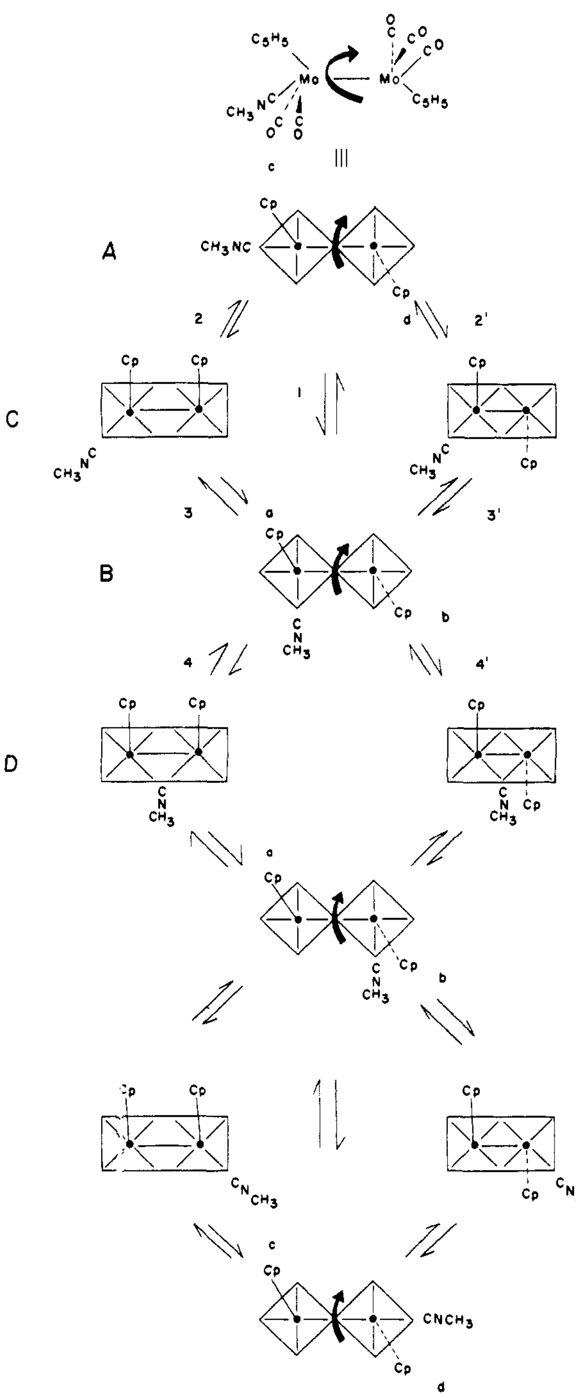
(2) Kindly provided by Mr. Carl Renner at the Massachusetts Institute of Technology; acceptable elemental analyses were obtained.

(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).

Scheme I

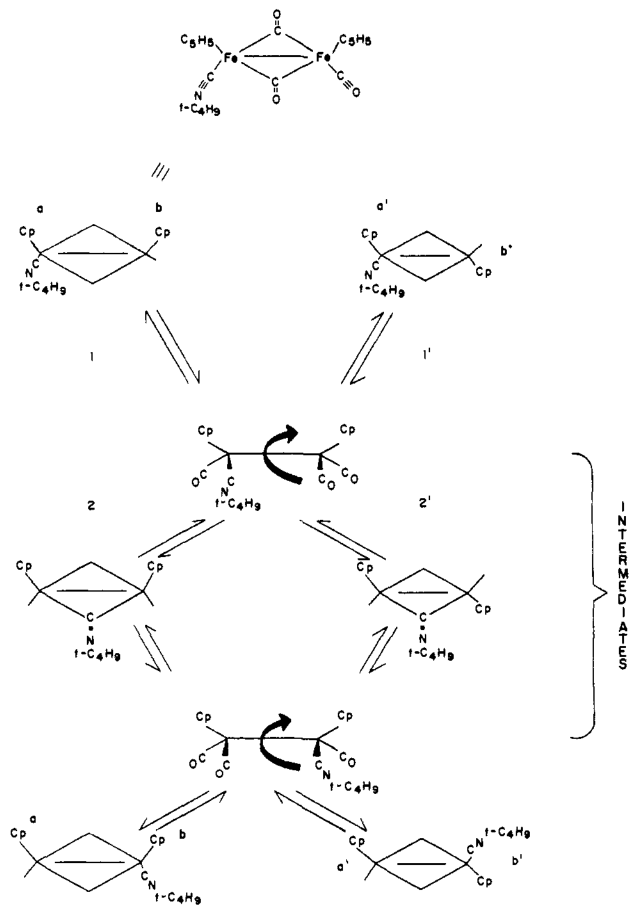


collapses on cooling and re-forms as two sharp singlets of equal intensity at −44°. The *tert*-butyl resonance is single at all temperatures but noticeably broadened at −129°.

This clearly demonstrates a dynamic rearrangement which exchanges the isonitrile ligand between the iron atoms. Scheme II shows the most plausible pathways for this exchange. Rearrangements 1 and 2 together are necessary for transposition of the isonitrile. We resolved two broad terminal isonitrile ir absorptions at 2060 and 2100 cm^{-1}. These can be attributed to two isomers which can interconvert by rearrangements 1. Broadening of the *tert*-butyl resonance at −129° may result from slowing this interconversion.

The observation that isonitrile ligands exhibit the same bifunctional bridge–terminal behavior of carbonyls is significant, since changes in the nitrogen substituent may allow deliberate and useful changes in the bridge–terminal tendency.[5,7,8]

Scheme II



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[5] In the solid state $[(h^5\text{-}C_5H_5)Fe(CO)_2\text{–}Fe(CO)(CN\text{-}t\text{-}C_4H_9)(h^5\text{-}C_5H_5)]$ has a terminal isonitrile, but in $[(h^5\text{-}C_5H_5)Fe(CO)_2\text{–}Fe(CO)(CNC_6H_5)(h^5\text{-}C_5H_5)]$ the isonitrile is bridging.[6]

[6] K. K. Joshi, O. S. Mills, P. L. Pauson, B. W. Shaw, and W. H. Stubbs, *Chem. Commun.*, 181 (1965).

[7] Much of this work was done in the Department of Chemistry, MIT, Cambridge, Mass.

[8] This work was supported in part by the National Science Foundation.

R. D. Adams, F. A. Cotton*
Department of Chemistry, Texas A & M University
College Station, Texas 77843

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Structural Isomerization and Rapid Interconversion of Two Five-Coordinate Cobalt(II) Complexes Containing Chelating Diphosphine Ligands

Sir:

Several new complexes of empirical composition $Co(dpe)_2SnX_4$ (dpe = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$; X = Cl, Br, and I) have been isolated from nonaqueous solutions containing a mixture of a cobalt(II) halide, the corresponding stannous halide, and the diphosphine ligand.[1] For the bromide and chloride cases, either a deep red or a deep green crystalline material of identical composition can be isolated depending on the solvent, temperature, and isolation procedures.

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[1] J. K. Stalick, G. Dyer, C. A. McAuliffe, and D. W. Meek, unpublished results.