

**Figure 1.** The 9.5-gHz spectra of (a) trans isomer **10** and (b) cis isomer **11** ( $1 \times 10^{-4}$  M) in egg lecithin vesicles (60 mg/ml in 10 mM Tris buffer, pH 7.4) at 25 °C, scaled to the same total double integral.

converted into the mesylates **5**<sup>6</sup> and thence into iodides<sup>7</sup> **6** (74%, *m/e* 450.221) and **7** (16%, *m/e* 450.223) which were separable by silica gel chromatography (elution with  $\text{CHCl}_3$ ). Following the procedure of Meyers,<sup>8</sup> **6** and **7** separately were converted into oxazolines **8** and **9** and thence by quaternization and base hydrolysis<sup>8</sup> into azethoxyl acids **10** (60%, *m/e* 382.332) and **11** (35%, *m/e* 382.332).

Evidence for the smaller steric size of an azethoxyl nitroxide as compared with a doxyl<sup>9</sup> or proxyl nitroxide<sup>3</sup> of similar chain length was obtained by trapping **10** in the cavity of a thiourea inclusion crystal.<sup>10</sup> Neither the doxyl nor the proxyl nitroxides could be included in the thiourea crystals under similar conditions, presumably because they are sterically too large to fit into the cavity.

While the solution ESR spectra of **10**<sup>11</sup> and **11** were virtually identical, significant differences (over a temperature range of 25–45 °C) were observed in the spectra of the two isomers when diffused into egg lecithin vesicles (Figure 1). Computer simulation<sup>12</sup> of the ESR spectra led to an estimate of  $50 \pm 3^\circ$  and  $57 \pm 3^\circ$  for the angle between the nitroxide *Z* axis and the long axis of rotation of **10** and **11**, respectively. Simulations also revealed that the rotational motion experienced by cis isomer **11** was less than that of the trans isomer **10**.

A preliminary study of the relative rates of reduction of 12-doxylstearic acid, 14-proxylstearic acid<sup>13</sup> and azethoxyl acid **10** indicate that the azethoxyl nitroxide is the most resistant toward reduction. In one series of experiments the nitroxides ( $1.1 \times 10^{-4}$  M) were dissolved in 0.1 M phosphate buffer, pH 7.5, containing sucrose (0.25 M), EDTA ( $10^{-3}$  M), and sodium ascorbate (0.011 M).<sup>14</sup> After 20 min only 3% of the original signal intensity remained for the doxyl nitroxide, whereas 90% remained for the proxyl nitroxide and 94% remained for the azethoxyl nitroxide.

**Acknowledgments.** This work was supported by Public Health Service Research Grants CA-17338 and CA-10337 from the National Cancer Institute.

## References and Notes

- (1) For a review see "Spin Labeling: Theory and Applications", L. J. Berliner, Ed., Academic Press, New York, N.Y., 1976.
- (2) It is convenient to name spin-labeled molecules as derivatives of their parent molecules. Thus, nitroxide **10** can be named as a *trans*-10-aza-9,11-ethano-*N*-oxyleicosanoic acid which is shortened to *trans*-10-azethoxyleicosanoic acid. This system has the advantage that it immediately locates the position of the label.
- (3) J. F. W. Keana, T. D. Lee, and E. M. Bernard, *J. Am. Chem. Soc.*, **98**, 3052 (1976).

- (4) J. F. Elsworth and M. Lamchen, *J. S. Afr. Chem. Inst.*, **24**, 196 (1971); *Chem. Abstr.*, **75**, 151083d (1971).
- (5) R. Bonnett, R. F. C. Brown, V. M. Clark, I. O. Sutherland, and A. Todd, *J. Chem. Soc.*, 2094 (1959).
- (6) R. K. Crossland and K. L. Servis, *J. Org. Chem.*, **35**, 3195 (1970).
- (7) The method used to establish the identity of the isomers is covered in the full paper to be published later.
- (8) A. I. Meyers, D. L. Temple, R. L. Nolen, and E. D. Mihelich, *J. Org. Chem.*, **39**, 2778 (1974).
- (9) J. F. W. Keana, S. B. Keana, and D. Beetham, *J. Am. Chem. Soc.*, **89**, 3055 (1967).
- (10) T. B. Marriott, G. B. Birrell, and O. H. Griffith, *J. Am. Chem. Soc.*, **97**, 627 (1975). The diameter of the thiourea cavity is  $\sim 7$  Å. To a lesser extent, isomer **11** can also be trapped in the cavity of thiourea inclusion crystals. Molecular models indicate that an approximately linear structure can be achieved by imposing a gauche conformation on each side of the pyrrolidine ring.
- (11) Isotropic *A* and *g* values for  $2 \times 10^{-4}$  M solutions of **10** are *A* = 14.1 G, *g* = 2.0062 in hexane and *A* = 16.3 G, *g* = 2.0054 in 0.1 M phosphate buffer (pH 7.5). The corresponding values for 14-proxylstearic acid are *A* = 14.5 G, *g* = 2.0058 (hexane) and *A* = 16.3 G, *g* = 2.0055 ( $\text{H}_2\text{O}$ ); and for 12-doxylstearic acid *A* = 14.4 G, *g* = 2.0062 (hexane) and *A* = 16.0 G, *g* = 2.0056 ( $\text{H}_2\text{O}$ ). Experimental errors are estimated to be  $\pm 0.1$  G for *A* and  $\pm 0.0002$  for *g*.
- (12) L. J. Libertini, C. A. Burke, P. C. Jost, and O. H. Griffith, *J. Magn. Reson.*, **15**, 460 (1974).
- (13) J. F. W. Keana, R. Roman, E. M. Bernard, manuscript in preparation.
- (14) C. M. Paleos and P. Dias, *J. Chem. Soc., Chem. Commun.*, 345 (1977).
- (15) Alfred P. Sloan Foundation Fellow; NIH Research Career Development Award Recipient.

Terry D. Lee, G. Bruce Birrell, John F. W. Keana\*<sup>15</sup>

Department of Chemistry, University of Oregon,  
Eugene, Oregon 97403

Received October 13, 1977

## Detection and Measurement of the Rate of 1,3 Iron Shift in Cycloheptatrieneiron Tricarbonyl

Sir:

Many fluxional organometallic systems are known in which a transition metal is bound to a fragment of a totally conjugated cyclic polyenyl or polyene system.<sup>1</sup> Examples include complexes containing the  $(\eta^3\text{-C}_7\text{H}_7)\text{M}$ ,<sup>2</sup>  $(\eta^5\text{-C}_7\text{H}_7)\text{M}$ ,<sup>3</sup>  $(\eta^4\text{-C}_8\text{H}_8)\text{M}$ ,<sup>4</sup>  $(\eta^6\text{-C}_8\text{H}_8)\text{M}$ ,<sup>5</sup> and  $(\eta^4\text{-C}_6\text{R}_6)\text{M}$ <sup>6</sup> moieties. In almost every case where the fluxional mechanism has been determined, the metal migrates around the ring via a series of 1,2 shifts with concomitant  $\pi$ -bond migration.<sup>1–8</sup>

In similar cyclic polyene complexes, such as cycloheptatrieneiron tricarbonyl (I), cyclooctatrieneiron tricarbonyl (II), and cyclononatetraeneiron tricarbonyl (III) where the cyclic conjugation of the polyene system has been interrupted by a  $(\text{-CH}_2\text{-})_n$  group, the facile 1,2 metal migration is precluded and the complex displays no fluxional behavior at moderate temperatures. For example, the <sup>1</sup>H NMR spectrum of I shows no line broadening up to temperatures of  $\sim 100$  °C, where initial decomposition begins.<sup>9</sup>

Although 1,2 metal shifts are ruled out for complexes such as I, II, and III, degenerate isomerization by net 1,3 metal shifts is possible. Such formal 1,3 iron shifts have been observed by Takats and Li Shing Man for  $(7\text{-exo-MMe}_3\text{C}_7\text{H}_7)\text{Fe}(\text{CO})_3$  (*M* = Si or Ge).<sup>10</sup> In an effort to determine the activation energy for the 1,3 metal shift in the simplest unsubstituted non-conjugated polyene system and to contrast this with the energetics of 1,2 metal shifts, we have examined cycloheptatrieneiron tricarbonyl using the Forsén and Hoffman technique of spin saturation transfer.<sup>11</sup>

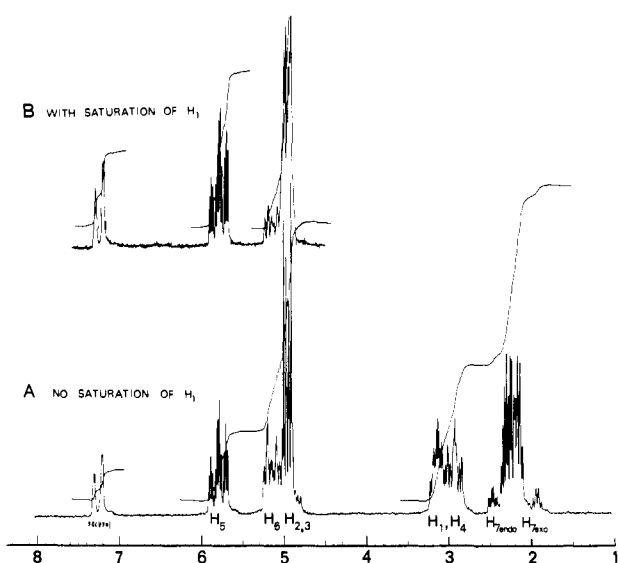
In the spin saturation transfer (SST) experiment, the rate constant for exchange, *k*, in a two-site, equal-population system,  $\text{A} \rightleftharpoons \text{B}$ , is given by<sup>12</sup>

$$k = \frac{1}{T_{1A}} \left[ \frac{M(0)}{M(\infty)} - 1 \right] \quad (1)$$

**Table I.** Spin Saturation Transfer Data, Rate Constants, and Free Energies of Activation

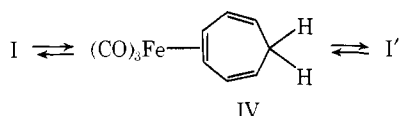
Complex	$T, ^\circ\text{C}$	$M(0)/M(\infty)$	$T_1$ of $\text{H}_6^a$	$k \times 10^2 \text{ s}^{-1}$	$\Delta G^\ddagger, \text{kcal mol}^{-1}$
I	61	1.27	14.5	1.90	22.2
	75	1.80	17.5	4.55	22.4
	86	2.52	10.7	14.2	22.5
	90	4.50	10.7	32.7	22.1
VI	80	1.12	7.7	1.56	23.6
	80	1.13	7.6	1.71	23.5
	95	1.20	7.9	2.53	24.3
	95	1.10	3.4	2.94	24.2
	105	1.36	4.1	8.77	24.0

<sup>a</sup> Measured by the fast inversion recovery method: D. Canet and G. C. Levy, *J. Magn. Reson.*, **18**, 199 (1975).

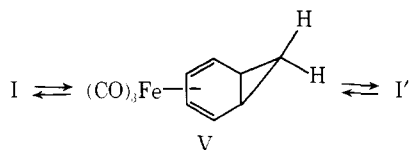


**Figure 1.**  $^1\text{H}$  NMR spectra of cycloheptatrieneiron tricarbonyl at  $90^\circ\text{C}$  in toluene- $d_8$ : A, no saturation of  $\text{H}_1$ ; B, with saturation of  $\text{H}_1$ .

#### Scheme I

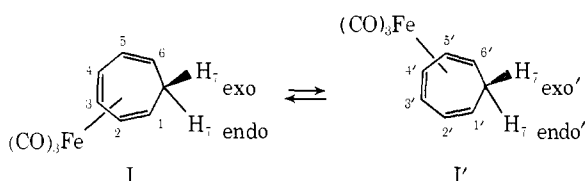


#### Scheme II



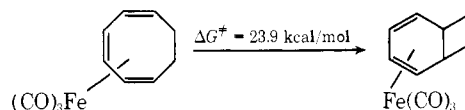
where  $T_{1A}$  is the spin-lattice relaxation time of the proton at site A,  $M(0)$  is the normal equilibrium magnetization of the proton at A and  $M(\infty)$  is the equilibrium magnetization of the proton at A after saturating the proton at site B.<sup>11</sup> Experimentally  $M(0)/M(\infty)$  is determined by comparing the signal areas of proton A with and without saturation of proton B.

Through extensive decoupling experiments the  $^1\text{H}$  resonances for complex I have been assigned as follows:  $\delta$  1.89 ( $\text{H}_{7\text{-exo}}$ ), 2.12 ( $\text{H}_{7\text{-endo}}$ ), 2.72 ( $\text{H}_4$ ), 2.89 ( $\text{H}_1$ ), 4.59–4.74 ( $\text{H}_{2,3}$ ), 5.03 ( $\text{H}_6$ ), and 5.68 ( $\text{H}_5$ ).<sup>13</sup> Degenerate 1,3 iron shifts interconvert  $\text{H}_1$  with  $\text{H}_6$ ,  $\text{H}_2$  with  $\text{H}_5$ , and  $\text{H}_3$  with  $\text{H}_4$ . To test for



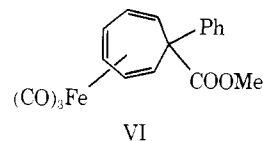
spin saturation transfer, it was experimentally most desirable to saturate  $\text{H}_1$  and examine the  $\text{H}_6$  signal since the resonances were well separated and irradiation of  $\text{H}_1$  resulted in no nuclear Overhauser enhancement of the  $\text{H}_6$  signal. Indeed, a reduction in intensity of the  $\text{H}_6$  signal was observed upon saturation of  $\text{H}_1$  at temperatures between  $60$  and  $90^\circ\text{C}$ . A typical set of spectra (taken at  $90^\circ\text{C}$ ) is shown in Figure 1, in which the area of the  $\text{H}_6$  resonance decreased by 78% upon saturation of  $\text{H}_1$ . Data for  $M(0)/M(\infty)$  are summarized in Table I along with  $T_1$  values measured for  $\text{H}_6$ . Also included are the rate constants calculated from eq 1 and the corresponding  $\Delta G^\ddagger$  values for the 1,3 iron migration in I. The SST experiments clearly rule out any other averaging process such as hydrogen migration through a metal hydride intermediate since saturation of  $\text{H}_1$  results only in reduction of intensity for  $\text{H}_6$ ; similarly, saturation of  $\text{H}_6$  results in reduction of intensity of  $\text{H}_1$ .

Although the averaging process corresponds to a *net* 1,3 iron shift, two mechanisms for iron migration seem feasible: (1) a direct 1,3 shift involving dechelation of the 1,2 double bond to form the symmetrical  $\eta^2$ -cycloheptatrieneiron tricarbonyl intermediate, IV, which can collapse to I', as shown in Scheme I; (2) two sequential 1,2 iron shifts involving a norcaradieneiron tricarbonyl intermediate, V, as shown in Scheme II. A norcaradiene intermediate is attractive in that only 1,2 metal shifts are involved, and also an analogous transformation of cyclooctatrieneiron tricarbonyl (II), to bicyclo[4.2.0]octa-2,4-dieneiron tricarbonyl has been observed.<sup>14</sup>



The substantially higher free energy of activation for the unsubstituted system ( $\Delta G^\ddagger = 22.3 \text{ kcal/mol}$ ) as compared to the  $\text{GeMe}_3$  substituted system of Takats ( $\Delta G^\ddagger \approx 17.0 \text{ kcal/mol}$ )<sup>10</sup> is compatible with the norcaradiene intermediate in that a  $\text{C}_7$  substituent would likely have a larger effect on the stability of the norcaradiene intermediate than on the transition state for a direct 1,3 iron shift.<sup>15</sup>

To gain additional information regarding the effect of  $\text{C}_7$  substitution on the rate of degenerate isomerization, we examined 7-phenyl-7-carbomethoxycycloheptatrieneiron tricarbonyl (VI). The free ligand<sup>17</sup> is known to exist as an  $\sim 2:1$



ratio of norcaradiene to cycloheptatriene at  $25^\circ\text{C}$ .<sup>18</sup> Even though the norcaradiene isomer predominates in the uncomplexed ligand, reaction with either  $\text{Fe}(\text{CO})_5$  photolytically or benzylideneacetoneiron tricarbonyl thermally gave no norcaradiene complex, and only a single isomer of the triene

complex, VI, of unknown stereochemistry was isolated.<sup>19</sup> Application of the SST technique to the measurement of the 1,3 iron shift in VI gave the results summarized in Table I. Surprisingly,  $\Delta G^\ddagger$  (23.9 kcal/mol) for iron migration is slightly greater for this compound than for I. Although significant lowering of the  $\Delta G^\ddagger$  might have been anticipated for VI relative to I if the norcaradiene mechanism obtains (Scheme II), we feel that these results do not necessarily rule out a possible norcaradiene intermediate for this fluxional process. If, for example, the phenyl group is exo to iron in VI, then steric interactions of the phenyl group with the cyclohexadiene unit in the norcaradiene-like transition state may offset any electronic stabilization of the transition state owing to the C<sub>7</sub> substituents.<sup>18</sup>

Although the detailed mechanism of the 1,3 iron shift cannot be precisely specified for I, it is clear from these results that activation energies for 1,3 iron shifts are higher than those for 1,2 iron shifts in cyclic polyene and polyenyl complexes. ( $\Delta G^\ddagger$ s range from  $\sim 7$  kcal for C<sub>8</sub>H<sub>8</sub>Fe(CO)<sub>3</sub><sup>20</sup> to  $\sim 15$  kcal for ( $\eta^3$ -C<sub>7</sub>H<sub>7</sub>)Fe(CO)( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>).<sup>2</sup>) The results obtained in this study and those reported by Mann<sup>7c</sup> demonstrate that spin saturation transfer is a very useful technique for studying relatively "slow" fluxional organometallic systems where thermal sensitivity of the complex precludes the use of standard line-broadening techniques at higher temperatures. Indeed, for these cycloheptatrieneiron tricarbonyl complexes, line broadening would have been observable by <sup>1</sup>H NMR only above 140 °C where decomposition is quite rapid.

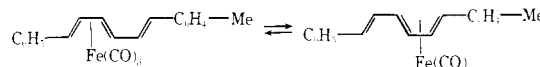
We are currently applying the spin saturation technique to other organometallic systems which are expected to exhibit fluxional processes with high activation energies.<sup>21</sup>

**Acknowledgment** is made to the National Science Foundation (Grant MPS75-01239) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

## References and Notes

- (1) F. A. Cotton, "Dynamic Nuclear Magnetic Resonance Spectroscopy", L. M. Jackman and F. A. Cotton, Eds., Academic Press, New York, N.Y., 1975, Chapter 10.
- (2) (a) M. A. Bennett, R. Bramley, and R. Watt, *J. Am. Chem. Soc.*, **91**, 3089 (1969); (b) J. W. Faller, *Inorg. Chem.*, **8**, 767 (1969); (c) D. Ciappenelli and M. Rosenblum, *J. Am. Chem. Soc.*, **91**, 6876 (1969).
- (3) (a) T. H. Whitesides and R. A. Budnik, *Chem. Commun.*, 1514 (1971); (b) J. E. Mahler, D. A. K. Jones, and R. Pettit, *J. Am. Chem. Soc.*, **86**, 3589 (1969).
- (4) (a) W. K. Bratton, F. A. Cotton, A. Davison, A. Musco, and J. W. Faller, *Proc. Natl. Acad. Sci. U.S.A.*, **58**, 1324 (1967); (b) F. A. Cotton, A. Davison, T. J. Marks, and A. Musco, *J. Am. Chem. Soc.*, **91**, 6598 (1969).
- (5) (a) R. B. King, *J. Organomet. Chem.*, **8**, 129 (1967); (b) F. A. Cotton, J. W. Faller, and A. Musco, *J. Am. Chem. Soc.*, **90**, 1438 (1968).
- (6) (a) J. W. Kang, R. F. Childs, and P. M. Maitlis, *J. Am. Chem. Soc.*, **92**, 721 (1970); (b) R. S. Dickson and G. Wilkinson, *J. Chem. Soc.*, 2699 (1964).
- (7) An exception appears to be the C<sub>8</sub>H<sub>8</sub>M(CO)<sub>3</sub> systems (M = Cr, Mo, W). Cotton<sup>7b</sup> has reported that the <sup>13</sup>C resonances of the ring carbons in this compound broaden and collapse at the same rate—a result consistent only with 1,3 shifts or a random process. More recently, using spin saturation transfer Mann has shown that, for C<sub>8</sub>H<sub>8</sub>Cr(CO)<sub>3</sub>, the migration of Cr occurs predominantly by 1,3 shifts, with a possible minor 1,3 component.<sup>7c</sup> (b) F. A. Cotton, D. L. Hunter, and P. Lahuerta, *J. Am. Chem. Soc.*, **96**, 4723, 7926 (1974). (c) B. E. Mann, *J. Chem. Soc., Chem. Commun.*, 626 (1977).
- (8) Mann has recently reported that  $\eta^3$ -C<sub>7</sub>H<sub>9</sub>PdL<sub>2</sub><sup>+</sup> systems are fluxional and exhibit facile 1,3 Pd shifts; see B. E. Mann and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1058 (1976).
- (9) M. Brookhart, E. R. Davis, and D. L. Harris, *J. Am. Chem. Soc.*, **94**, 7853 (1972), footnote 25.
- (10) (a) L. K. K. Li Shing Man and J. Takats, *J. Organomet. Chem.*, **117**, C104 (1976). (b) The stereochemistry of (7-*exo*-GeMe<sub>3</sub>C<sub>7</sub>H<sub>7</sub>)Fe(CO)<sub>3</sub> was determined by x-ray crystallography and reported at the Second Joint Meeting of the Chemical Institute of Canada—The American Chemical Society, Montreal, May 29–June 2, 1977 (Inorganic, Section C, No. 90). (c) The activation energy cited in this paper,  $\Delta G^\ddagger = 17$  kcal/mol, is a personal communication from J. Takats.
- (11) (a) R. A. Hoffman and S. Forsén, "Progress in NMR-Spectroscopy," Vol. 1, Pergamon Press, Oxford, England, 1966, p 15; (b) J. W. Faller, "Determination of Organic Structure by Physical Methods", F. C. Nachod and J. J. Zuckerman, Eds., Vol. V, Academic Press, New York, N.Y., 1973, Chapter 2.

- (12) B. E. Mann, *J. Magn. Reson.*, **21**, 17 (1976).
- (13) M. Brookhart, K. J. Karel and L. E. Nance, *J. Organomet. Chem.*, **140**, 203 (1977).
- (14) M. Brookhart, N. M. Lippman, and E. J. Reardon, *J. Organomet. Chem.*, **54**, 247 (1973).
- (15) Whitlock has determined that  $E_a \approx 33$  kcal/mol for a 1,3 iron shift in the acyclic system.<sup>16</sup> This shift must occur by dechelation, and, if  $E_a$  in this system is a reasonable model for  $E_a$  for dechelation in I, this further suggests a norcaradiene mechanism. The accuracy of this model is complicated by differing substitution at the  $\pi$  bond which dechelates and by possible strain effects in I.<sup>14</sup>



- (16) (a) H. W. Whitlock and Y. N. Chuah, *J. Am. Chem. Soc.*, **87**, 3606 (1965); (b) H. W. Whitlock, C. Reich, and W. D. Woessner, *ibid.*, **93**, 2483 (1971).
- (17) E. Ciganek, *J. Am. Chem. Soc.*, **93**, 2207 (1971).
- (18) G. E. Hall and J. D. Roberts, *J. Am. Chem. Soc.*, **93**, 2203 (1971).
- (19) <sup>1</sup>H NMR of VI in toluene-*d*<sub>6</sub>:  $\delta$  3.08 (H<sub>1</sub>,  $J_{1,2} = 7.9$ ,  $J_{1,3} = 1.5$ ,  $J_{1,6} = 2.2$  Hz), 4.67–4.85 (H<sub>2</sub>,  $J_{2,3} = 4.7$ ,  $J_{2,4} = 1.5$  Hz), 4.85–5.01 (H<sub>3</sub>,  $J_{3,4} = 7.3$  Hz), 2.77 (H<sub>4</sub>,  $J_{4,5} = 7.4$ ,  $J_{4,6} = 1.6$  Hz), 6.07 (H<sub>5</sub>,  $J_{5,6} = 11$  Hz), 5.89 (H<sub>6</sub>), 3.59 (COOMe), 7.17–7.47 (Ph).
- (20) C. G. Kreiter, A. Maasbol, F. A. L. Anet, H. O. Kaesz, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 3444 (1966).
- (21) NOTE ADDED IN PROOF. Using a <sup>13</sup>C spin saturation experiment, the 1,3 iron shift in I has also been detected by B. Mann, *J. Organomet. Chem.*, **141**, C33 (1977).

Karin J. Karel, Maurice Brookhart\*

Department of Chemistry, University of North Carolina  
Chapel Hill, North Carolina 27514

Received October, 17, 1977.

## Design of an Ion-Molecule Reaction Specific for Neutral Nitriles

Sir:

Only a few ion-molecule reactions have been observed which are so characteristic of a neutral functional group that the reaction may be used to identify the group. The classical examples of these are the reactions of ionized butadiene with olefins;<sup>1</sup> the metathesis of substituents between ionized and neutral olefins,<sup>2</sup> which may be used to locate double bonds;<sup>3</sup> and the reactions of trihalomethyl cations with neutral carbonyl compounds.<sup>4</sup> Reactions which distinguish between epimers because of their specificity for less hindered isomers<sup>5</sup> are related to this category.

A reaction specific for nitriles was designed as follows. Transfer, not simple addition, pathways are more effective ion-molecule reactions at low pressures. Proton transfers are the best understood transfers. The proton affinity of acetonitrile is 5 kcal/mol greater than that of methanol,<sup>6,7</sup> and, for reasons paralleling those adduced for series of nitrogen-containing<sup>8</sup> and triply-bonded<sup>9</sup> compounds, the proton affinities of nitriles with larger alkyl substituents are greater.<sup>6,7</sup> Thus proton transfer from methanol to all nitriles should be observed, but of course proton transfer is not specific. Since methyl cation affinities have similar trends as proton affinities, with clear exceptions which bound the analogy,<sup>10</sup> we examined other alkyl cations. While a positively charged atom is the primary reaction site in ion-molecule reactions, to create specific reactivity for a functional group, it is necessary to introduce another reaction site into the alkyl group. We chose a radical site. A radical site has little influence on electronic effects of alkyl groups, for the electronic effects of C<sub>2</sub>H<sub>5</sub> and C<sub>3</sub>H<sub>7</sub> are very similar to those of the analogous radicals from which a hydrogen atom has been removed,  $\cdot$ C<sub>2</sub>H<sub>4</sub>– and  $\cdot$ C<sub>3</sub>H<sub>5</sub>–, in at least one series of compounds.<sup>11</sup> The most desirable location of the radical site is adjacent to carbenium carbon, for this will permit four-center reactions with the nitrile group; rapid four-center reactions are common; and there is precedent for involvement of triply bonded atoms in a four-center reac-