

shifts at  $-145^\circ$ . They agree that the spectrum at  $-145^\circ$  is that of I, but propose that the valency tautomerism  $Ia \rightleftharpoons Ib$  is still very rapid at  $-145^\circ$ . By using plausible chemical shifts (see Ia), they predict that the low-temperature spectrum should consist of two bands at  $\tau$  4.1 and 5.5, roughly as observed.<sup>13</sup>

KSP<sup>4</sup> claim support for their theory from the fact that the nmr spectrum of methylcyclooctatetraeneiron tricarbonyl ( $MeCOTFe(CO)_3$ ) consists of three bands ( $\tau$  4.33, 4.92, and 5.50; intensity ratios of 3:2.3:1.8) at room temperature and of two bands ( $\tau$  4.05 and 5.62, reported as of "approximately equal areas") at  $-120^\circ$ . They argue that the room-temperature band at  $\tau$  5.50 must be the average between two bands, one of which is of the normal olefinic type and at low field; therefore, the other band must be at much higher field than  $\tau$  5.5 for the average to be at  $\tau$  5.5. It is quite clear that this argument is fallacious as is shown below. Thus the nmr spectrum of  $MeCOTFe(CO)_3$  does not support the ideas of KSP.<sup>14</sup>

We now show that the data of KSP on  $MeCOTFe(CO)_3$  are actually in excellent agreement with our interpretation.<sup>2</sup> The evidence indicates that the  $Fe(CO)_3$  group prefers to be attached to certain carbon atoms of the ring of MeCOT, a possibility ignored by KSP. These carbons are 8123 and 7812 in IIa and IIb, respectively. In our view, the spectrum at low temperatures is that of frozen IIa and IIb, whereas at room temperature the chemical shifts are the average of those in IIa and IIb. On this basis, and using<sup>15</sup> the value  $\tau$  4.1 for any of the protons of noncomplexed olefinic groups and  $\tau$  5.4 for any of the iron-bonded olefinic protons, the chemical shifts shown in Table I

Table I. Predicted Chemical Shifts for IIa and IIb

Positions	Chemical shifts at $-145^\circ$ , $\tau$		Av of IIa and IIb (intensity) at room temp
	IIa	IIb	
2 and 8	5.4, 5.4	5.4, 5.4	5.4 (2)
3 and 7	5.4, 4.1	4.1, 5.4	4.75 (2)
4 and 6	4.1, 4.1	4.1, 4.1	4.1 } (3)
5	4.1	4.1	4.1 }

are predicted for  $MeCOTFe(CO)_3$  at  $-145^\circ$  and at room temperature. The predicted low-temperature spectrum ( $\tau$  4.1 and 5.4, relative intensities 4:3) and the high-temperature spectrum ( $\tau$  4.1, 4.75, and 5.4, relative intensities 3:2:2) are in substantial agreement with those reported by KSP.<sup>4</sup> Valency tautomers with the  $Fe(CO)_3$  at positions different from those in IIa or IIb give calculated spectra in gross disagreement with the experimental data and thus cannot be present in significant amounts.

(13) The high-field band<sup>2</sup> of  $COTFe(CO)_3$  is actually much too broad and complex to be due to four protons all having the same chemical shift, as is required by KSP's theory.

(14) These authors do not attempt to explain the spectra of  $MeCOTFe(CO)_3$ . We find that it is impossible to explain both the room- and low-temperature spectra of  $MeCOTFe(CO)_3$  with KSP's theory.

(15) For this calculation we have used rounded values of the chemical shifts given by KSP.<sup>4</sup>

The spectra of a deuterated derivative of  $MeCOTFe(CO)_3$ , described in the accompanying communication,<sup>16</sup> confirm our conclusions.

(16) F. A. L. Anet, *J. Am. Chem. Soc.*, **89**, 2491 (1967).

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## Valency Tautomerism in Methylcyclooctatetraeneiron Tricarbonyl<sup>1</sup>

Sir:

We have shown<sup>2</sup> that the nmr data of Keller, Shoulders, and Pettit on methylcyclooctatetraeneiron tricarbonyl (I) can best be explained on the basis that the  $Fe(CO)_3$  group exhibits a preference for bonding with carbon atoms 1, 2, 7, and 8 (Ia) or 1, 2, 3, and 8 (Ib) of the ligand, and that valency tautomerism,  $Ia \rightleftharpoons Ib$ , is fast (on the nmr time scale) at room temperature, but slow at  $-145^\circ$ . An examination of the nmr spectrum of methyl-*d*-cyclooctatetraene-2,3,4,5,6,7-*d*<sub>6</sub>-iron tricarbonyl (II), presented in this communication, confirms our deductions and clearly shows that the terminal and internal protons in the iron-bonded diene moiety of II have only slightly different chemical shifts.

Lithium aluminum hydride reduction of cyclooctatetraenyl-2,3,4,5,6,7-*d*<sub>6</sub>-methyl-*d* bromide<sup>3</sup> in diethyl ether gave methyl-*d*-cyclooctatetraene-2,3,4,5,6,7-*d*<sub>6</sub> (III)<sup>4</sup> as a yellow oil, isolated by glpc. Reaction of III with an equimolecular amount of  $Fe(CO)_5$  in boiling hexane for a few minutes gave, after removal of the solvent, the dark red complex<sup>5</sup> II, which was purified by evaporative distillation *in vacuo*.

The nmr spectrum of II in deuterated chloroform showed only two bands: the  $CH_2D$  protons at  $\tau$  8.15 and the ring proton at  $\tau$  5.44. The high-field chemical shift of the ring proton is only consistent with IIa and IIb being the dominant species at room temperature.<sup>6</sup>

In  $CHCl_2F$  solution, the ring proton in II changed from a sharp line at room temperature to two sharp lines at  $-145^\circ$  (Figure 1). No change was observed in the  $CH_2D$  band, apart from some broadening at very low temperatures.<sup>7</sup> At the coalescence temper-

(1) Work supported by National Science Foundation Grant No. G.P. 3780.

(2) F. A. L. Anet, H. D. Kaesz, A. Maasbol, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 2489 (1967).

(3) F. A. L. Anet, A. J. R. Bourn, and Y. S. Lin, unpublished results; cf. F. A. L. Anet, A. J. R. Bourn, and Y. S. Lin, *J. Am. Chem. Soc.*, **86**, 3576 (1964). The undeuterated compounds have been prepared previously: A. C. Cope and H. C. Campbell, *ibid.*, **74**, 179 (1952); A. C. Cope, R. M. Pike and D. F. Rugen, *ibid.*, **76**, 4945 (1954).

(4) The rate of bond shift in III has been determined from the temperature dependence of the nmr spectrum, which also confirms the structure and isotopic labeling of the compound (to be published).

(5) The same procedure applied to cyclooctatetraene was found to give a good yield of pure iron tricarbonyl complex. Mass spectra of II showed a ratio of I-*d*<sub>7</sub>:I-*d*<sub>6</sub>:I-*d*<sub>5</sub> of 30:5:1 and a cracking pattern consistent with its structure.

(6) Other tautomers would have the ring proton at least half of the time in the unbonded diene portion of the molecule and would therefore exhibit a low chemical shift ( $\tau < 5$ ). The presence of appreciable amounts of these tautomers would lower the average chemical shift of the ring proton of II, as compared with the high-field band (*ca.*  $\tau$  5.5) in the spectrum of  $COTFe(CO)_3$  at  $-145^\circ$ .

(7) The greater broadening of the  $CH_2D$  protons relative to the ring proton is consistent with the closeness of the two protons in the  $CH_2D$

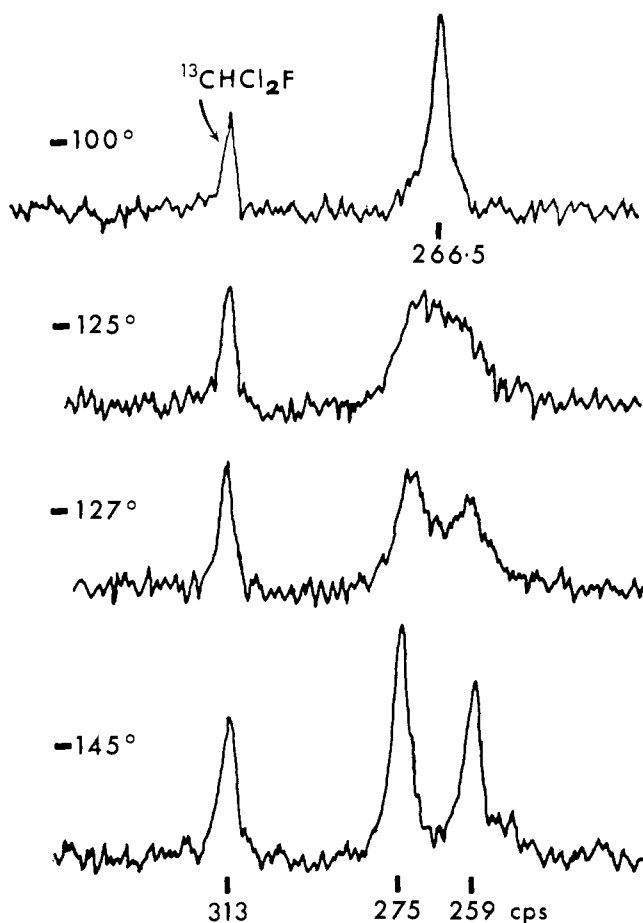
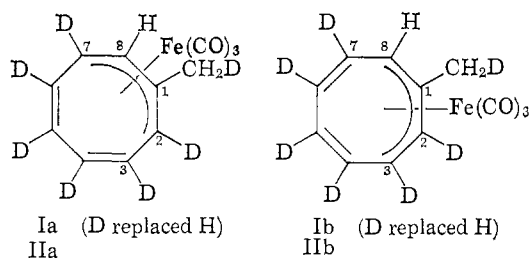


Figure 1. Proton spectrum (60 Mc/sec, deuterons decoupled) of II in  $\text{CHCl}_2\text{F}$  at various temperatures. Only the olefinic region is shown. The scale is cps downfield from internal tetramethylsilane.

ature ( $-125^\circ$ ) for the ring-proton bands, the rate constant for the valency tautomerism,  $\text{IIa} \rightleftharpoons \text{IIb}$ , is  $35 \text{ sec}^{-1}$ , and the free energy of activation ( $\Delta F^*$ ) is  $7.5 \text{ kcal/mole}$ , a value close to the  $7.2 \text{ kcal/mole}$  observed<sup>8</sup> for the parent compound.



The average of the chemical shifts of the two ring-proton bands at  $-150^\circ$  is very close to the chemical shift of the coalesced bands (*e.g.*, at  $-100^\circ$  or higher). This is in agreement with the conclusion based on the chemical shift of the ring proton that tautomers other than IIa or IIb must be present in very small amounts.

Tautomers other than IIa or IIb should show a ring-proton band at low field (*ca.*  $\tau$  4) at  $-145^\circ$ , but unfortunately this region is partly obscured by a  $^{13}\text{C}$  satellite of the solvent as well as being very close to an

group and relaxation by the direct spin-spin interactions modulated by molecular rotation.

(8) C. G. Kreiter, A. Maasbol, F. A. L. Anet, H. D. Kaesz, and S. Winstein, *J. Am. Chem. Soc.*, **88**, 3444 (1966).

intense solvent peak. We plan to examine the spectrum further in a deuterated solvent, which should allow the detection of small peaks in this region. On the basis of the present evidence, it appears that more than 90% of II is in the form of IIa and IIb.

The present work does not allow an unambiguous assignment to be made to the ring-proton bands in the low-temperature spectrum of II. Since the ring proton in IIb would be expected to be upfield from that in IIa,<sup>9</sup> the bands at  $\tau$  5.42 and 5.68 can be assigned tentatively to IIa and IIb, respectively.

The origin of the low energy of IIa and IIb is of interest. In IIa or IIb the methyl group is attached to a ring carbon atom which in cyclooctatetraeneiron tricarbonyl<sup>10</sup> has an internal angle of  $124.6^\circ$ . In other tautomers of II the methyl group would be attached to carbon atoms having internal angles greater than  $130^\circ$ . From previous work<sup>3,11</sup> on the rates of ring inversion and bond shift in derivatives of cyclooctatetraene (COT), it is known that large groups, and even methyl groups,<sup>12</sup> destabilize the planar form of COT (bond angles of  $135^\circ$ ) relative to the tub form (bond angles of about  $125^\circ$ ). This effect was ascribed to the greater steric repulsions existing between a substituent and adjacent hydrogen atoms in the planar form relative to the tub form. Although II is nonplanar, these steric effects should operate to make IIa and IIb more stable than other tautomers. Steric repulsions between the  $\text{Fe}(\text{CO})_3$  and the methyl group would destabilize IIa and IIb and therefore do not appear to be important. Inductive and hyperconjugative effects of the methyl group may be significant in stabilizing IIa and IIb; experimental investigations of this possibility are planned.

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(12) The rate constant for bond shift<sup>4</sup> in III at  $-10^\circ$  is not more than one-tenth of that<sup>11</sup> in cyclooctatetraene.

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## Mass Spectrometric Evidence for the Gaseous $\text{Si}_2\text{N}$ Molecule

Sir:

Optical spectroscopic studies<sup>1</sup> and ionic-model calculations<sup>2</sup> have indicated that the binding energies of gaseous nitrides should be of the order of  $100 \text{ kcal mole}^{-1}$ , and thus one expects that gaseous nitrides should be relatively stable. Most of the refractory nitrides have been reported, however, to dissociate when heated under vacuum.<sup>3-7</sup> Only gaseous gallium

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