

A BICYCLOBUTANE-BRIDGED DIENE IRONTRICARBONYL COMPLEX. SYNTHESIS,  $\text{Ag}^{\oplus}$ -CATALYZED  
VALENCE ISOMERISATION AND FLUXIONAL BEHAVIOUR.

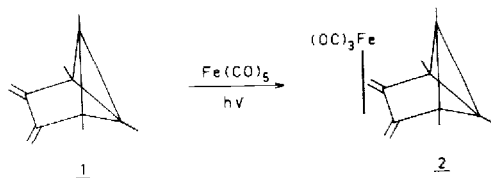
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(Received in UK 12 May 1976; accepted for publication 27 May 1976)

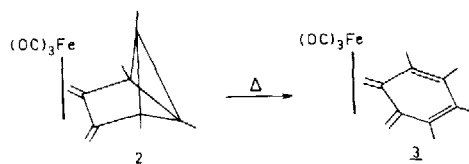
A simple one-pot synthesis<sup>1</sup> makes available from hexamethyl (Dewar benzene) 1,2,5,6-tetramethyl-3,4-dimethylene tricyclo[3.1.0.0<sup>2,6</sup>]hexane (1). This highly strained compound possesses the interesting feature of two interacting functionalities, *viz.* the butadiene and the bicyclobutane moieties. In a number of reactions compound 1 has been shown to react at the butadiene part of the molecule with, in some cases,<sup>2</sup> concomitant isomerisation of the bicyclobutane fragment. The  $\text{Ag}^{\oplus}$ -catalyzed reaction of 1 leads to a complex reaction mixture, possibly via the intermediacy of tetramethyl-*o*-xylylene.<sup>2</sup>

We intended to stabilize the diene fragment of 1 in order to open up the possibility of exclusive reaction at the bicyclobutane fragment. An obvious means to this end is to synthesize the corresponding irontricarbonyl complex 2.

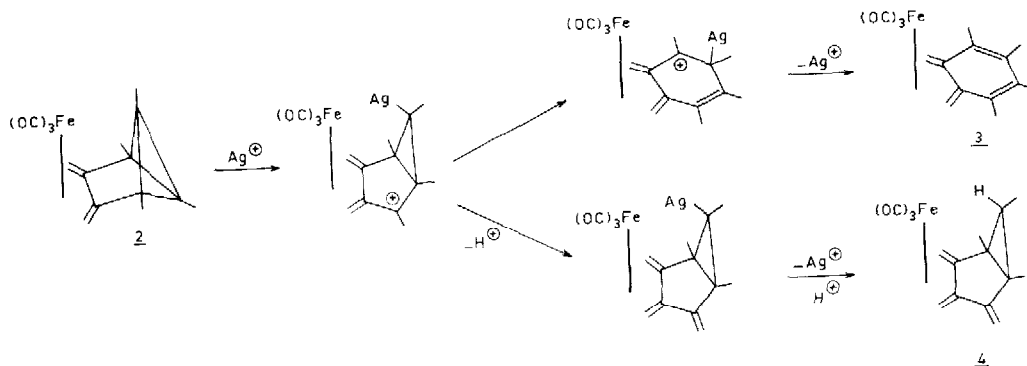


Compound 1 (5.0 gr, 31 mmoles) was irradiated in 800 mls benzene with a 2:1 excess  $\text{Fe}(\text{CO})_5$  during three days (nitrogen atmosphere, Q-700 Hanau high-pressure Hg arc), yielding the irontricarbonyl complex 2 in 40% yield (3.7 gr, 12 mmoles) as an orange oil b.p.  $50^{\circ}\text{C}/0.01$  mm Hg pressure. Structural assignment to 2 is based on the following data: correct elemental analysis (H,C,Fe); IR absorptions at  $2060$  and  $1980\text{ cm}^{-1}$  ( $\text{Fe}(\text{CO})_3$ ), MS  $m/e$   $300$  ( $\text{M}^{\oplus}$ ),  $272$ ,  $244$ ,  $216$  (successive loss of CO ligands);

PMR ( $\text{CCl}_4$ )  $\delta$  2.10 (d,  $J = 2.5$  Hz, 2H), 1.58 (s, 3H), 1.48 (s, 3H), 1.20 (s, 6H), 0.40 ppm (d,  $J = 2.5$  Hz, 2H); CMR ( $\text{CD}_2\text{Cl}_2/\text{CS}_2$  1:1,  $-89^\circ\text{C}$ )  $\delta$  216.5 (apical CO), 210.9 (basal CO's), 116.7, 66.8, 47.9, 44.7, 37.2, 7.9, 7.1, 2.5 ppm (relative to TMS). During distillation of 2 yellow crystals of a new complex 3<sup>3</sup> with m.p. 164.5-165.5°C sublimed in the top of the column. The same compound was obtained in 60% yield - in addition to 40% hexamethylbenzene - on refluxing 2 in ethylbenzene for two hours. Structural assignment to 3 is based on the following data: correct elemental analysis (H,C,Fe); IR absorptions at 2050 and 1980  $\text{cm}^{-1}$  ( $\text{Fe}(\text{CO})_3$ ); MS  $m/e$  300 ( $\text{M}^+$ ), 272, 244, 216 (successive loss of CO ligands); PMR ( $\text{C}_6\text{D}_6$ )  $\delta$  2.40 (d,  $J = 3.5$  Hz, 2H), 2.03 (s, 6H); 1.86 (s, 6H); -0.16 ppm (d,  $J = 3.5$  Hz, 2H). Compound 3 is formed from 2 by a thermal ring opening of the bicyclobutane moiety; the precise mechanism of this valence isomerisation and the possible role of the Fe-atom are unknown.



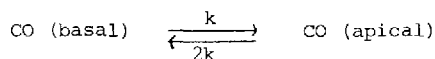
Treatment of complex 2 in  $\text{CCl}_4$  solution with a catalytic amount (5 mol %) of  $\text{AgClO}_4$  during three days at room temperature afforded a reaction mixture containing 3 (9%), 4 (85%) and hexamethylbenzene (6%).<sup>4</sup> Bulb to bulb distillation in vacuum afforded 4 as a yellow oil in 70% yield. The following reaction mechanism accounts for the formation of 4 (and 3).<sup>5</sup>



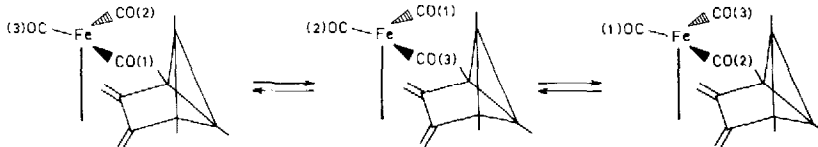
It should be pointed out that there is no compelling evidence that the cyclopropyl ring and the  $\text{Fe}(\text{CO})_3$  group in 4 are cis as indicated rather than trans. The remaining structural characteristics of 4 are based on the following data: correct elemental analysis (H,C,Fe); IR absorptions at 2080,

1990 ( $\text{Fe}(\text{CO})_3$ ) and  $1640 \text{ cm}^{-1}$  ( $\text{C}=\text{C}$ ); MS  $m/e$  300 ( $\text{M}^{\oplus}$ ), 272, 244, 216 (successive loss of CO ligands); PMR ( $\text{CCl}_4$ )  $\delta$  5.03 (s, 1H), 4.80 (s, 1H), 2.06 (d,  $J = 3.0 \text{ Hz}$ , 1H), 1.88 (d,  $J = 3.0 \text{ Hz}$ , 1H), 1.26 (s, 3H), 1.17 (s, 3H), 1.10 (severely distorted d and q, 4H), 0.30 (d,  $J = 3.0 \text{ Hz}$ , 1H), 0.08 ppm (d,  $J = 3.0 \text{ Hz}$ , 1H); CMR ( $\text{CDCl}_3$ ,  $35^\circ$ )  $\delta$  211.0, 157.0, 122.2, 100.8, 99.8, 39.4, 34.8, 34.0, 31.9, 31.1, 10.3, 9.8, 7.8 ppm.

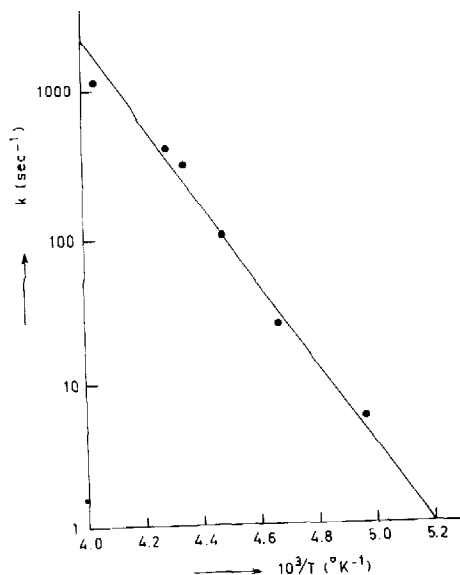
In view of the recent interest in the fluxional behaviour of diene-irontricarbonyl complexes,<sup>6</sup> we investigated this process in complex 2 by CMR line-broadening. At about  $-90^\circ\text{C}$  two sharp signals (ratio 1:2) at  $\delta$  216.5 (1 apical CO) and 210.9 ppm (2 basal CO's) are observed, which start to line-broaden at higher temperatures and coalesce at about  $-20^\circ\text{C}$  into one sharp signal at  $\delta$  212.8 ppm. The experimental spectra at various temperatures were compared with computer-generated spectra<sup>7</sup> for various values of the rate constant  $k$  of the interconversion process



which is associated with rotation<sup>8</sup> of the irontricarbonyl group in 2.



By a least-squares fit of the Arrhenius-plot (Figure) the activation parameters were calculated to



be  $E_a = 12.8 \pm 0.3$  kcal/mole and  $\log A = 14.4 \pm 0.3$ . The energy of activation is about 3 kcal/mole higher than that for butadiene irontricarboxyl, <sup>6a</sup> which may be due to an increased steric hindrance to rotation. We intend to extend these measurements to other bi- and polycyclic diene irontricarboxyl complexes in order to check this suggestion.

The authors wish to thank Drs. J.H. Wieringa and W. Mellink for recording the CMR spectra (XL-100) and Dr. J. Runsink for assistance in obtaining the computer-simulated spectra.

#### References and Notes.

1. H. Hogeveen and P.W. Kwant, *Tetrahedron Lett.*, 1973, 3747; *J. Org. Chem.*, 39, 2624 (1974).
2. H. Hogeveen and W.F.J. Hurdeman, *Tetrahedron Lett.*, 1974, 1255; H. Hogeveen, W.F.J. Hurdeman and E.P. Schudde, *ibid.*, 1974, 4211; R.F. Heldeweg and H. Hogeveen, *ibid.*, 1975, 1517; *J. Am. Chem. Soc.*, 98, 0000 (1976); R.F. Heldeweg and W.F.J. Hurdeman, unpublished results.
3. The corresponding complex of the parent  $\alpha$ -xylylene has been prepared previously in a different manner by W.R. Roth and J.D. Meier, *Tetrahedron Lett.*, 1967, 2053.
4. With different transition metal complexes ( $(\text{OCN})_2\text{PdCl}_2$ ,  $\text{Rh}_2(\text{norbornadiene})_2\text{Cl}_2$ ) different products ratios are obtained.
5. Compare e.g. L.A. Paquette, R.P. Henzel and S.E. Wilson, *J. Am. Chem. Soc.*, 94, 7780 (1972).
6. a. L. Kruczynski and J. Takats, *J. Am. Chem. Soc.*, 96, 932 (1974);  
b. C.G. Kreiter, S. Stüber and L. Wackerle, *J. Organomet. Chem.*, 66, C49 (1974).
7. Computer-generated spectra were obtained on basis of the NMREX-III programme by Dr. S. van der Werf, adapted by Dr. J. Runsink.
8. It has been pointed out that actually the fluxional process in diene irontricarboxyl complexes is likely to be more complicated (ref. 6).