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Preliminary communication

Trimethylenemethane *vs.* diene coordination in the reaction of 2,2-dimethylallylidenecyclopropane with $Fe_2(CO)_9$

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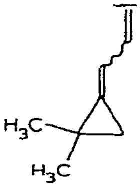
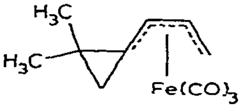
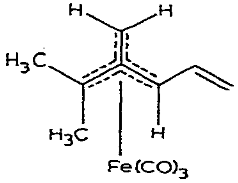
There is considerable interest in transition metal promoted cleavage of strained carbon–carbon σ bonds and stabilization of the resulting ligand by coordination with the metal*. The present communication reports on the stable iron complexes II, III and IV derived from 2,2-dimethylallylidenecyclopropane (I) and $Fe_2(CO)_9$.



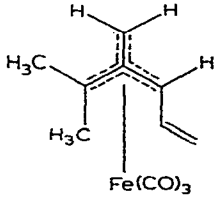
(I)



(II)



(III)



(IV)

Reaction of 50 mmol of I[2] (mixture of stereoisomers) with 50 mmol of $Fe_2(CO)_9$ in refluxing benzene (70 ml) for 50 min followed by bulb-to-bulb distillation gives a mixture (3.96 g, 32%) of $C_8H_{12}Fe(CO)_3$ complexes. Gas chromatography (10 ft. x 0.25 in. 10% UCON W-98 on Chromosorb P operated at 130°) showed two major products in a 41/59 ratio**. Final purification was accomplished by adsorption chromatography (silica gel–CCl_4). Compound II was found in early fractions and identified by its spectral properties: the mass spectrum showed a parent molecular ion, *m/e* 248, *M*-CO, *m/e* 220, *M*-2CO, *m/e* 192. *M*-3CO, *m/e* 164; the infrared spectrum showed C≡O absorptions at 2045 and 1975 cm^{-1}; the ^1H NMR spectral parameters are shown in Table 1. Pure III (NMR) was isolated from later fractions: mass spectrum (parent molecular ion *m/e* 248); IR absorptions at 2045 and 1975 (C≡O) and 1610 cm^{-1} (C=C). The ^1H NMR spectrum (Table 1) provides convincing evidence for the proposed stereochemistry. (The ^1H NMR

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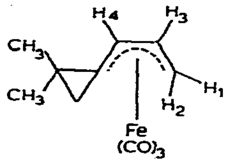
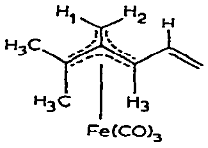
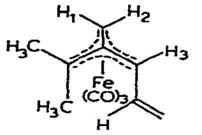
*For references relevant to the present study see ref. 1a–1h.

**The reaction occurs at lower temperatures but the extended reaction time and the resulting decomposition gives lower yields of products.

TABLE 1

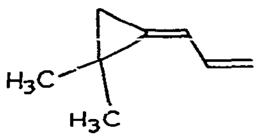
^{1}H NMR DATA (60 MHz) FOR COMPOUNDS II, III AND IV^a

Compound	*δ (ppm)*	*J (Hz)*
	cyclo- 0.27 (AB_q) propyl 0.68 H-1 0.92 (m) methyls 1.15 (s); 1.22 (s) H-2 1.92 (m) H-3,4 5.00–5.70 (m)	J_{AB} 4.66
	methyls 1.53 (s); 1.60 (s) H-1 2.46 (d) H-2 2.53 (s) H-3 4.11 (d,d) vinyl 4.75–6.00 (m)	$J_{1,3}$ 2.43 $\{J_{1,3}$ 2.43, $J_{3,4}$ 9.43$\}$
	methyls 1.46 (s); 1.48 (s) H-1 2.20 (s) H-2 2.24 (s) H-3 3.47 (d) vinyl 4.55–5.80 (m)	$J_{3,4}$ 9.43

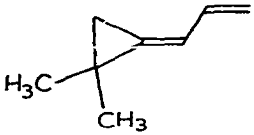
^{a}TMS = 0.

spectrum of trimethylenemethaneiron tricarbonyl appears as a sharp singlet[3], whereas substitution causes all the ligand protons to become nonequivalent[4]. Further, only *trans* coupling (W coupling)[5] of the ligand protons are observed. Thus, for compound III (Table 1) the proton, H_1, couples with H_3 by long range *trans* or W coupling, whereas H_2 appears as a singlet since it is located over a W configuration from the methyl substituent.) It was not possible to purify IV, although it was obtained in sufficient purity from intermediate cuts (mixed with II) for characterization by NMR (Table 1). We have no indication that these products interconvert during purification. In fact, attempts to thermally interconvert the isomers by heating II or III in refluxing benzene or CCl_4 resulted in decomposition but not isomerization. In addition, when the pure isomers were passed through the silica gel column no isomerization was observed.

It was of interest to determine whether the *syn* (Ia) and *anti* (Ib) stereoisomers



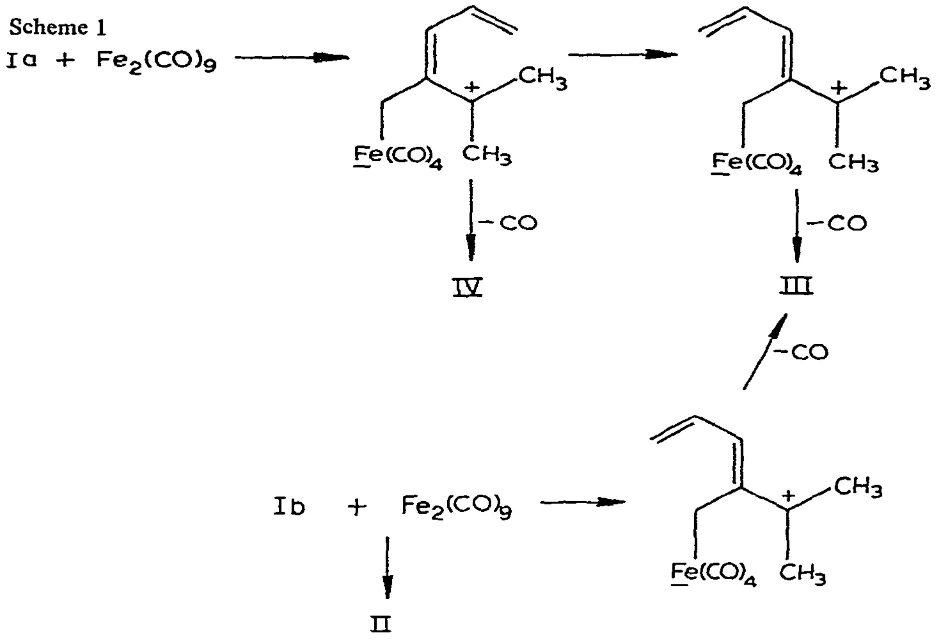
(Ia)



(Ib)

of I behave differently in their reactions with $Fe_2(CO)_9$. The pure isomers are readily available by preparative GLPC (15 ft. x 0.25 in. 15% β,β′-oxydipropionitrile on neutral Chromosorb P operated at 45°), but stereochemical assignments have not been made[2,10]. Isomer A, which had the shorter retention time and showed NMR signals at δ 0.94(2H), 1.19(6H), 4.64–5.40(2H) and 6.04–6.74(2H) (the remaining isomer (isomer B) showed signals at δ 1.01 (2H), 1.23(6H), 4.68–5.43(2H) and 6.00–6.75(2H)), gave 67% II and 33% III (46% yield) upon reaction with $Fe_2(CO)_9$, whereas the remaining isomer,(isomer B) gave III (21% yield) and traces of IV.

Scheme 1



The reaction sequence shown in Scheme 1 accounts for the observed products and allows a tentative assignment of stereochemistry to A and B. Formation of II from Ia would be difficult since the *gem*-dimethyl group imposes severe steric restraints for diene coordination. These steric impositions are not present in Ib. On this basis isomer A can be identified with Ib and isomer B with Ia.

Finally, reaction of I (mixture of isomers) with $PdCl_2(PhCN)_2$ in benzene gave an insoluble yellow powder. A strong IR band at 1500 cm^{-1} and lack of absorbance between 1550–1700 cm^{-1} indicated both double bonds were coordinated to palladium[7]. The mass spectrum showed a highest mass of 493 (calc. mol. wt. 570 for the dimer). It seems probable[7] that this material is polymeric, although its extreme insolubility in most solvents prevented further structure elucidation.

ACKNOWLEDGEMENT

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