

### Evidence for Direct Metal Attack in Nucleophilic Substitution of the Tricarbonylcycloheptadienyl Iron Cation

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Metal complexes  $\eta\text{-C}_n\text{H}_n\text{M}(\text{CO})_3$ , where M is a transition metal,  $n = 4\text{--}7$ , undergo ligand substitution reactions with a nucleophile L, by four possible paths; *a* addition to the organic moiety  $\text{C}_n\text{H}_n$ , *b* ring displacement, *c* carbonyl displacement and *d* attack at the carbonyl carbon atom. In the case of pathway *c*, semi-empirical M.O. calculations predict a relatively low reactivity for complexes with  $n = 5$  and  $6$ ,<sup>1</sup> whilst for cationic arene complexes such as  $[\text{C}_6\text{H}_6\text{Mn}(\text{CO})_3]\text{BF}_4$ , nucleophilic addition occurs by pathway *a* to give  $[\text{C}_6\text{H}_6\text{LM}(\text{CO})_3]\text{BF}_4$ .<sup>2</sup> Similarly, for  $n = 7$ , although  $\text{M}(\text{CO})_3\text{L}_3$  (pathway *b*) and  $\text{C}_7\text{H}_7\text{M}(\text{CO})_2\text{L}$  (pathway *c*) are formed,<sup>3</sup> initial ring addition has recently been confirmed.<sup>4</sup> In both cases, it is not yet clear whether ring addition compounds are genuine precursors of the other pathways.<sup>2,4</sup>

Similar pathways apply to analogous cyclic diene complexes, for example  $[\text{cyclooctadienylFe}(\text{CO})_3]\text{-BF}_4$  suffers nucleophilic attack by pathway *a* and in some cases also by pathway *d*.<sup>5</sup> Thus, the azide ion gives both ring azide addition complexes and also isocyanate complexes formed by Curtius rearrangement after initial attack at carbonyl carbon atom as first observed in  $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_3]\text{BF}_4$ .<sup>6</sup> We would like to report that for the analogous seven-membered cyclic-diene complex cation  $[\text{C}_7\text{H}_9\text{Fe}(\text{CO})_3]\text{BF}_4$ , nucleophilic attack occurs initially at the metal atom followed by ring addition, pathway *a*, e.g.  $\text{N}_3^-$ ,  $\text{OEt}^-$ ,  $\text{PR}_3$  ( $\text{R} = n\text{Bu}$  and  $\text{Et}$ ). To the best knowledge of the authors, this is the first example where attack at the metal centre clearly precedes ring addition (Fig. 1).

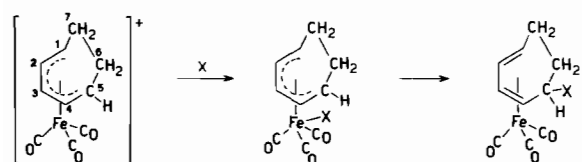


Fig. 1. Reaction scheme.  $\text{X} = \text{N}_3^-$ ,  $\text{OEt}^-$  and  $\text{PR}_3$  ( $\text{R} = n\text{Bu}$ ,  $\text{Et}$ ).

Reaction of  $[\text{C}_7\text{H}_9\text{Fe}(\text{CO})_3]\text{BF}_4$  (I) with  $\text{NaN}_3$  in  $\text{CH}_2\text{Cl}_2$  gave instantaneously a red solution ( $\lambda_{\text{max}} = 470$  nm), which was accompanied by the rapid growth of a shoulder in the i.r. spectrum at  $2033$   $\text{cm}^{-1}$ , and by the slower growth of a band at  $2085$

$\text{cm}^{-1}$  which developed at the expense of the band at  $2033$   $\text{cm}^{-1}$ . On complete reaction (30 minutes) and purification, a yellow oil was obtained  $[\text{C}_7\text{H}_9\text{N}_3\text{Fe}(\text{CO})_3]$  (II;  $\nu_{\text{CO}}$  in  $\text{CHCl}_3$ :  $2049$ ,  $1975$   $\text{cm}^{-1}$ ;  $\nu_{\text{ring-N}_3}$ :  $2085$   $\text{cm}^{-1}$ ). Both during and at completion of the preparation of  $\text{C}_7\text{H}_9\text{Fe}(\text{CO})_2\text{I}$ , a band is observed having  $\lambda_{\text{max}}$  at  $485$  nm; in this complex, the iodide is unambiguously attached to the metal. The band at  $2033$   $\text{cm}^{-1}$  is attributed to the asymmetric stretching frequency of an azide group bonded directly to the iron atom by analogy with the closely related cyclopentadienyl complex,  $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{N}_3$  ( $2064$ ,  $2024$ ,  $2010$   $\text{cm}^{-1}$ ).<sup>6</sup> In II, the band at  $2085$   $\text{cm}^{-1}$  is assigned to  $\nu_{\text{asymmetric}}$  of an azide group bonded to the ring;<sup>7</sup> other bands lie close to the carbonyl modes in products III and IV obtained by ring addition to I by the ethoxide ion and  $\text{PnBu}_3$  respectively. The  $^1\text{H}$  n.m.r. data support this conclusion, and the spectrum of II obtained on a JEOL PS 100 instrument in  $\text{CDCl}_3$  gave peaks of relative intensities 2:1:2:4 at  $\tau = 4.7$  (multiplet H at  $\text{C}_2$  and  $\text{C}_3$ ), 6.4 (multiplet H at  $\text{C}_5$ ), 7.1 (multiplet H at  $\text{C}_1$  and  $\text{C}_4$ ), 7.8 to 9.3 (multiplet H at  $\text{C}_6$  and  $\text{C}_7$ ). In the azide complex the splitting of all the band patterns as compared with the ethoxy case indicates possible fluxional behaviour. Low temperature studies are now in progress on these compounds. Initial reaction of I with  $\text{OEt}^-$  in ethanol also proceeded via the initial red colour ( $\lambda_{\text{max}} = 470$  nm) to the formation of the known tricarbonyl-5 ethoxy cyclohepta-1-3 diene iron,  $\text{C}_7\text{H}_9\text{OEtFe}(\text{CO})_3$ .<sup>8</sup>

Finally, reaction of I with  $\text{PnBu}_3$  in  $\text{CH}_2\text{Cl}_2$  at room temperature again gave an initial red colour ( $\lambda_{\text{max}} = 475$  nm) and on completion (30 minutes) a yellow oil (IV;  $\nu_{\text{CO}}$  in  $\text{CH}_2\text{Cl}_2$ :  $2053$  and  $1984$   $\text{cm}^{-1}$ ) and  $^1\text{H}$  n.m.r. of approximate relative intensities 2:1:2:2:19:10,  $\tau = 4.6$ ,  $6.8$ ,  $7.2$ ,  $7.8$ ,  $8.5$  and  $9.0$ . The lines were very broad in this spectrum, and no fine structure was observed; however, a similar assignment of the compound is indicated. A corresponding product was obtained on reaction of I with  $\text{PEt}_3$ .

We suggest, therefore, that in the above 7-membered cyclic diene metal carbonyl complexes initial attack by a nucleophile at the metal atom precedes ring addition in contrast with analogous arene and tropylium complexes where ring addition competes with metal attack and may possibly precede it. This implies that there is greater localization of positive charge in the ring of these latter complexes which is consistent with simple M.O. considerations.<sup>9</sup> Observation of direct attack at the metal centre prior to ring addition is novel, and further work is in progress on related complexes to test whether this mode of attack is more general.

## References

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