

Preliminary communication

NUCLEOPHILIC ADDITION TO THE TRICARBONYL(η -CYCLOHEPTADIENYL)IRON CATION BY ALKOXIDE IONS. FORMATION OF CARBOALKOXY INTERMEDIATES

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Summary

Nucleophilic addition to the title compound by alkoxide ions (OR^-) at $0^\circ C$ proceeds via a red intermediate probably involving metal—nucleophile interaction, and subsequent formation of the carboalkoxy compound $C_7H_9Fe(CO)_2(CO_2R)$. On raising the temperature, the latter compound rearranges spontaneously by a dissociative mechanism to give the corresponding 5-*exo*-ring compound $C_7H_9ORFe(CO)_3$.

Nucleophilic addition to the title compound by alkoxide ions (OR^-) at (polyene) [1] the metal [2] and the carbonyl carbon atom [3]. Ring addition normally yields the *exo*-product [1] and so it is generally concluded that the incoming nucleophile approaches the polyene ring on the opposite side from the metal tricarbonyl group, without involvement of the latter in addition.

We have shown recently that nucleophilic addition to $[C_7H_9Fe(CO)_3]BF_4$ (I) by, for example, azide and alkoxide ions may involve metal attack or metal association (e.g. ion-pair formation) although the *exo*-ring product is still obtained as final product [4]. This result is in accord with the large partial valence-inactive population (P_{metal}^{LUMO}) of the frontier orbital in I [5]. A similar mechanism involving the formation of an intermediate with a M—I bond has been proposed from stopped-flow Fourier transformation NMR kinetic studies of the substitution of $[C_7H_7M(CO)_3]^+$ ($M = Mo; W$), by iodide ions [6]. However, our suggestion [4] of involvement of the $M(CO)_3$ group in the nucleophilic addition to $[C_7H_9Fe(CO)_3]^+$ has been queried recently [7] and so we report further evidence for such involvement in this note.

Reaction of $[C_7H_9Fe(CO)_3]BF_4$ (I) with NaOEt in EtOH at room temperature gave the *exo*-product $C_7H_9OEtFe(CO)_3$ (V) as reported previously [1,4]. Careful monitoring of the infrared spectrum during this reaction showed initially a band

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at 1650 cm^{-1} , which decreased in intensity as the *exo*-product formed, thus suggesting the presence of a carboethoxy derivative. However, on lowering the temperature to 0°C and adding I (3.31 mmol) in small portions over 5 minutes to a well stirred slight excess of sodium ethoxide (3.52×10^{-3} g-atom of sodium in 20 ml of ethanol), the initial red colour ($\lambda_{\text{max}} 470\text{ nm}$) was again observed to develop during and slightly after the addition of I. After a further 10 minutes, the pale orange solution was evaporated to dryness in an ice-bath. After extraction with $3 \times 20\text{ ml}$ petroleum ether, washing with degassed cold water, drying with MgSO_4 and evaporation of solvent, recrystallization from pentane on an ice-salt bath gave yellow crystals of the carboethoxy complex, $\text{C}_7\text{H}_9\text{Fe}(\text{CO})_2(\text{CO}_2\text{Et})$ (II, m.p. 56°C (dec.)). The IR spectrum of II (in *n*-hexane) showed $\nu(\text{CO})$ peaks at 2032 and 1988 cm^{-1} and another carbonyl band at 1650 cm^{-1} . The ^1H NMR spectrum (CDCl_3) showed multiplets (τ values) centred at 3.67 (H(3)), 4.94 (H(2,4)), 5.79 (H(1,5)), 6.10 (OCH₂), 7.62 (H(6',7')), 8.47 (H(6,7)), 8.89 (CH₃) with respect to TMS ($\tau = 10$).

These spectral features are similar to those previously reported for the analogous carbomethoxy compound $\text{C}_6\text{H}_7\text{Os}(\text{CO})_2(\text{CO}_2\text{Me})$ prepared from tricarbonyl(η -cyclohexadienyl)osmium [8]. Reaction of I with OMe^-/MeOH and $\text{O-}i\text{-Pr}^-/i\text{-PrOH}$ under similar conditions again gave transient red colours and analogous carbomethoxy (III) and carboisopropoxy complexes (IV). The IR of III showed metal-carbonyl peaks at 2038 and 1991 cm^{-1} , with carbonyl peak at 1656 cm^{-1} (in *n*-hexane). The ^1H NMR spectrum (CDCl_3) showed, apart from the OMe singlet at 6.59, multiplets at 3.65 (H(3)), 4.94 (H(2,4)), 5.78 (H(1,5)), 7.62 (H(6',7')), 8.48 (H(6,7)).

IV displayed metal carbonyl bands at 2032 and 1986 cm^{-1} , with the other carbonyl group at 1649 cm^{-1} (in *n*-hexane). The ^1H NMR spectrum (C_6D_{12}) had multiplets at 3.90 (H(3)), 5.15 (H(2,4)), 5.96 (H(1,5)), 7.72 (H(6',7')), 8.66 (H(6,7)), with OCH and CH₃ multiplets at 5.24 and 9.05, respectively.

On raising the temperature, the above carboalkoxy complexes (II, III and IV) undergo spontaneous rearrangement both in the solid state and in solution with formation of the corresponding 5-*exo*-ring product. The stereochemistry of the 5-*exo*-ethoxy compound (V) was confirmed from spectral data; thus the mass spectrum showed a strong peak corresponding to the fragment ion $[\text{M} - \text{CO} - \text{H}_2]^+$ and only a very weak one at $[\text{M} - \text{CO}]^+$, a pattern typical of *exo* isomers [9]. Similarly, the IR spectrum (CCl_4 , KBr) in the C-H stretching region showed no peak in the $2700\text{--}2800\text{ cm}^{-1}$ range [10]. Finally the ^1H NMR spectrum already reported also supports the *exo*-structure [1,4]. The rearrangements of both II and III (in CDCl_3) to give the corresponding *exo*-products (V and VI) were followed by ^1H NMR and obeyed first order kinetics suggesting a dissociative mechanism with loss of OR^- and subsequent ring addition giving the *exo*-product. This was confirmed by rearranging III (in CDCl_3) in the presence of EtOH (five-fold excess) and II (in CDCl_3) in the presence of MeOH (five-fold excess). In both cases, product isolation and in situ following of the reaction by ^1H NMR (2 fold excess) confirmed the formation of a mixture of V and VI with the major product being derived from the added nucleophile (i.e. II \rightarrow mainly VI and III \rightarrow mainly V). Independent experiments proved that neither V or VI could be interconverted by treatment with the appropriate alcohol. (For example, the ethoxy derivative suffered no change after 64 h in methanol at

20°C.) It has been reported [11] that the corresponding cyclohexa-1,3-diene derivatives can undergo interconversion.

These results show that nucleophilic addition to the tricarbonyl(η -cycloheptadienylium)iron cation by alkoxide ions under these conditions involves an initial red intermediate which by analogy with the observed absorption band in $C_7H_9Fe(CO)_2I$ (λ_{max} 485 nm), we ascribe again to association of the attacking nucleophile with the iron atom, followed by formation of the carboalkoxy compound due to attack at a carbonyl carbon atom. The product is stable only at low temperatures and rearranges by a dissociative mechanism to give the corresponding 5-*exo*-ring-product. It appears that the energy barriers between the different routes of nucleophilic attack of this particular polyene- $M(CO)_3$ complex are small. Whether this conclusion is valid for a range of nucleophiles and complexes is not clear, and further studies are in progress to clarify this point.

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