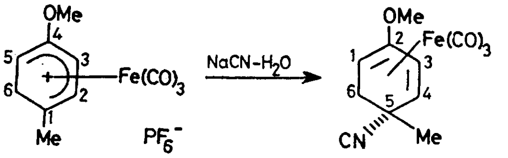
New Approach to the Introduction of Functionalised Angular Substituents *via* Tricarbonyldieneiron Complex Intermediates

By Anthony J. Pearson

(*Research School of Chemistry, Australian National University, P.O. Box* 4, *Canberra, A.C.T.* 2600, *Australia*)

Summary The reaction of tricarbonyl(4-methoxy-1-methylcyclohexadienyl)iron hexafluorophosphate (**1**), or tricarbonyl(2—8a-η-3-methoxyhexahydronaphthyl)iron tetrafluoroborate (**5**) with cyanide anion results in addition of the nucleophile to the more electron-deficient terminus of the dienyl system, forming quaternary centres and angularly substituted compounds (**2**) and (**6**), respectively.

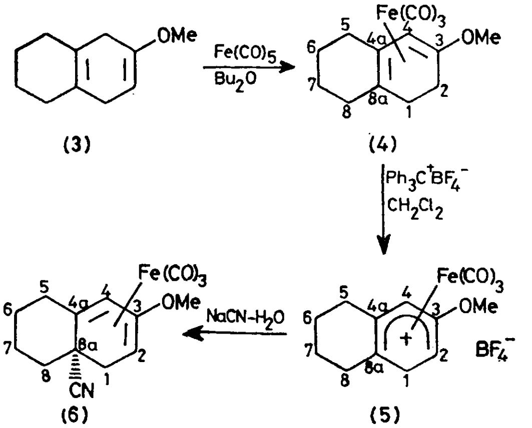
Some observations in the literature[1] that morpholine and hydroxide ion add to the cation (**1**) at the methylated terminus C-1 of the diene system in preference to the electronically deactivated terminus C-5 suggest that this behaviour might be extended to reactions with carbon nucleophiles which would allow further elaboration and thereby give synthetically useful intermediates. The most obvious candidate for achieving this is the cyanide anion, since it is known[2] that this will add to simple dienyl complexes to produce a nitrile which can then undergo further conversions, such as acidic methanolysis, and subsequent reduction of the ester.[3] Furthermore, comparison of (**1**) with the hitherto unreported dienyl complex (**5**) suggests that, should (**5**) behave in an analogous manner towards nucleophiles then addition to the angular carbon atom 8a would occur, thereby providing a new method of introducing a functionalised angular substituent, a reaction of potential value in steroid conversions.



(**1**) (**2**)

The hexafluorophosphate (**1**) was stirred with an excess of NaCN in aqueous solution under nitrogen, and extraction with ethyl acetate afforded a 52% yield of the crude compound shown to be 90—95% (**2**) by ^{1}H n.m.r. spectroscopy. Recrystallisation from light petroleum gave pure (**2**), m.p. 89—90 °C, easily identified from its ^{1}H n.m.r. spectrum; ν_{max} (CCl_4): 2230 (CN), 2055, and 1970 [$Fe(CO)_3$] cm^{-1}; ^{1}H n.m.r. δ ($CDCl_3$) 1·32 (3H, s, 5-Me), 1·68 and 2·38 (each 1H, dd, J_{gem} 16, $J_{1,6}$ 3 Hz, 6-H_2), 2·55 (1H, d, $J_{3,4}$ 6·5 Hz, 4-H), 3·4 (1H, m, 1-H), 3·64 (3H, s, MeO), and 5·12 (1H, dd, $J_{3,4}$ 6·5, $J_{1,3}$ 2 Hz); *M* 289. Comparison with literature data[1,4,5] for similarly substituted analogues allows the structure (**2**) to be unambiguously assigned to the product. In particular the position of the methoxy signal, the occurrence of the 5-methyl group as a singlet, and the observation of a single proton at δ 5·12, the region in which are found 2-H and 3-H of complexed 1,3-dienes, are particularly diagnostic.

Compound (**4**) was prepared by refluxing the diene (**3**) with an excess of pentacarbonyliron in Bu_2O. Removal of unchanged (**3**) (50%) at 100 °C and 0·05 mmHg, followed by chromatography of the product complex on silica yielded pure (**4**), which reacted with triphenylmethyl tetrafluoroborate to yield the dienyl complex (**5**) [overall yield 43%, based on recovered (**3**)]. These compounds were readily identified from their ^{1}H n.m.r. spectra,† by comparison with the monocyclic analogues. Reaction of (**5**) with NaCN in the above manner yielded a single yellow crystalline compound in 80% yield, which could be recrystallised from light petroleum to give (**6**), m.p. 91—93 °C; ν_{max} 2230 (CN), 2045, and 1970 [$Fe(CO)_3$] cm^{-1}; ^{1}H n.m.r.: δ 1·3—2·3 (10H, 5 × CH_2), 3·32 (1H, m, 2-H), 3·60 (3H, s, MeO), and 4·91 (1H, d, $J_{2,4}$ 2 Hz, 4-H); *M* 329. The spectral data are in complete agreement with this structure, in particular the position of the methoxy resonance compared to that given by (**4**) (δ 3·4) and (**2**), and the observation of the typical long-range coupling[1,5] between 2-H and 4-H leading to the close doublet for 4-H. This is not given by (**4**), the spectrum of which shows 4-H as a sharp singlet at δ 5·4, similar to monocyclic analogues. Lastly, the typical multiplet for 2-H is absent in the spectrum of (**4**); the overall similarity between the spectra of (**6**) and (**2**), and the relationship of these with well known cyclohexadiene complexes is compelling evidence for the structures shown. It is assumed that the cyanide anion adds to the face of the dienyl system opposite to that occupied by $Fe(CO)_3$ from the known behaviour of such complexes,[4,6] and consequently the reaction may be considered as stereospecific.



The factors controlling the position of addition of nucleophiles to these systems have not yet been fully elucidated, but it has been observed that a methoxy substituent causes the α-carbon atom to become more electron rich, and therefore deactivated towards addition.[7]

(*Received*, 18*th February* 1977; *Com.* 142.)

---

† Full details of the syntheses and spectral properties of these precursor complexes will be given in a later publication. All compounds gave satisfactory microanalytical data.

[1] A. J. Birch, K. B. Chamberlain, M. A. Haas, and D. J. Thompson, *J.C.S. Perkin I*, 1973, 1882.

[2] M. A. Hashmi, J. D. Munro, P. L. Pauson, and J. M. Williamson, *J. Chem. Soc.* (*A*), 1967, 240; A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *ibid.*, 1968, 332.

[3] A. J. Birch and D. H. Williamson, *J.C.S. Perkin I*, 1973, 1892.

[4] R. E. Ireland, G. G. Brown, Jr., R. H. Stanford, Jr., and T. C. McKenzie, *J. Org. Chem.*, 1974, **39**, 51.

[5] R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1961, 594; A. J. Pearson, *Austral. J. Chem.*, 1977, **30**, 407.

[6] A. J. Pearson, *Austral. J. Chem.*, 1976, **29**, 1101.

[7] A. J. Birch, P. W. Westerman, and A. J. Pearson, *Austral. J. Chem.*, 1976, **29**, 1671.