ORGANOIRON COMPLEXES IN ORGANIC SYNTHESIS

X *. NITROMETHYLATION AND NUCLEOPHILIC FORMYLATION OF TRICARBONYLCYCLOHEXADIENYLIUMIRON COMPLEXES

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Summary

Nitromethylation of the title complexes was found to be superior in some cases to the use of cyanide anion for regioselectivily introducing a C—N substituent on a cyclohexadiene ring. As a means of nucleophilic formylation the nitromethyl group was inferior to cyanide, the latter being reduced to aldehyde in moderate yield using diisobutylaluminium hydride.

In connection with projects aimed at utilisation of diene-metal complexes in organic synthesis, we were interested in obtaining an efficient means of introducing a C—N group into tricarbonylcyclohexadieneiron complexes, and effecting carbon—carbon bond formation which would complement the growing number of methods already available for this operation. Although cyanide anion has been used successfully for a number of cases [2], we have found in the present study that its reaction with the simple 2-methyl substituted complex (Ib) gives a 1 : 1 mixture of regioisomers (IIIb) and (VIIa) (see later), consistent with our earlier conclusion that regioselectivity of nucleophilic addition to this complex is determined mainly by steric, and not electronic factors [3], CN⁻ being a sterically undemanding nucleophile. Furthermore, we have found that the product nitriles are generally unstable oils, and the present study was undertaken with a view to producing more stable complexes with a C—N grouping in the lateral chain.

Reaction of the parent complex Ia with potassionitromethanate in THF/ nitromethane occurs rapidly at 0°C, even though both reactants are only slightly soluble. Work-up afforded the product (IIa) (55%) corresponding to regiospecific reaction with the nitromethanate anion at the dienylium terminus.
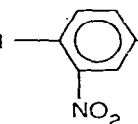
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* For part X see ref. 1.

R

Fe(CO)$_3$

PF$_6^-$

(I)

R

Fe(CO)$_3$

1 3
6 5 4

R' R"
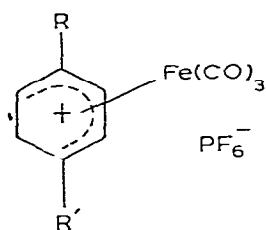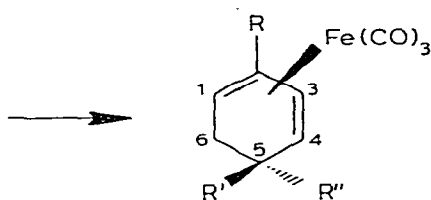
(II , R" = CH$_2$NO$_2$;

III , R" = CN   ;

IV , R" = CHO ;

V , R" = CH=N—NH—⟨ ⟩—NO$_2$;
NO$_2$

(a , R = R' = H ;

b , R = Me, R' = H ;

c , R = OMe , R' = H ;

d , R = OMe , R' = Me)

VI , R = OMe, R' = Me, R" = CH$_2$OH)

Me

R

Fe(CO)$_3$
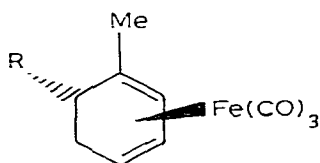
(VIIa , R = CN ;

VIIb , R = CH$_2$NO$_2$)

The structure was assigned from NMR spectral data (Experimental section). Use of tricarbonyl(1-5-η-6-*exo*-deuteriocyclohexadienylium)iron tetrafluoroborate, containing 50% label [4], gave a product which showed reduced integrated intensity of the multiplet at δ 1.42 ppm, and partial loss of the large geminal coupling (15 Hz) in the signal at δ 2.45 ppm, thereby allowing the assignment of these signals to M-*exo*-6-H and M-*endo*-6-H, respectively. Reaction of the methyl-substituted complex Ib [5], with sodionitromethanate * gave the adduct IIb in 85% yield, the NMR spectrum of which showed only a small amount (ca. 5%) of the regioisomer VIIb. Thus, this reaction occurs in better yield and with superior regioselectivity for the *para* terminus than the corresponding reaction of Ib with cyanide (1 : 1 mixture of IIIb and VIIa in only 59% yield) which is advantageous in view of the difficulty of separation of the nitrile regioisomers (see Experimental section). The 2-methoxy substituted complex (Ic) [6] similarly gave the crystalline nitromethyl derivative (IIc), regiospecifically in 71% yield (recrystallised) corresponding to the synthetically important operation of enone γ-alkylation. Unfortunately, similar reaction of the disubstituted salt Id resulted in considerable decomposition and formation of aromatic material, presumably via deprotonation of the terminal methyl

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* Reactions with both sodio- and potassionitromethanate under various conditions gave no significant differences in yield, etc.. A variety of conditions are described in the Experimental Section.

group [7] and we were able to obtain at best only 10% yield of the nitromethyl compound IId which was very unstable and could not be obtained free from aromatic material. Consequently, we have omitted this compound in the Experimental section. It may be noted that the corresponding nitrile (IIId) can be obtained in quite reasonable yield and is fairly stable [2b]. A number of attempts to convert the nitromethyl adducts thus obtained to aldehydes resulted in considerable decomposition and very low yields. In view of the instability of the aldehydes (below) we did not pursue this further. It may be noted that the nitro group in the parent complex (IIa) has been reduced to primary amine in good yield [8]. In view of the difficulty in converting the nitro-compounds to aldehydes we investigated the reduction of nitrile groups using diisobutylaluminium hydride (DIBAL-H), which we have found most useful for reduction of esters to primary alcohols in the presence of the tricarbonyliron group (lithium aluminium hydride attacks the CO ligands) [9]. The complexes used were all available by literature methods (indicated in Experimental section) except the mixture of IIIb and VIIa which have not been previously reported. The nitriles IIIa, IIIc, IIId, and the bicyclic derivative IX all reacted with DIBAL-H without

(VIII)

(IX, R = CN ;

X, R = CHO ;

XI, R = CH$_2$OH)
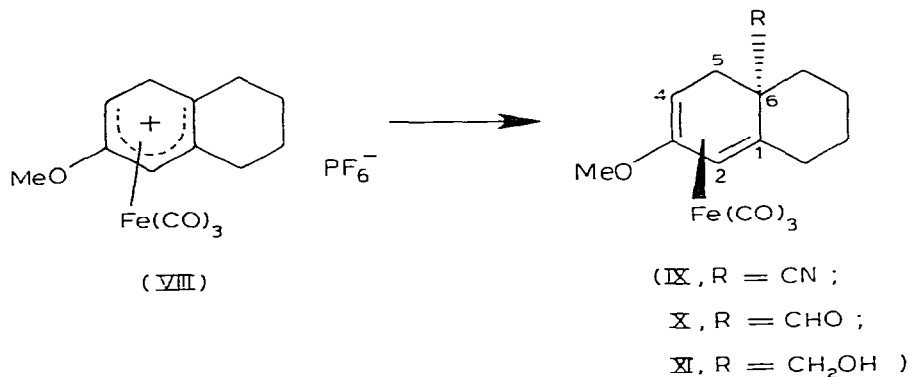
decomposition during reaction (a clean white precipitate of aluminium salts is produced on work-up) to give crude aldehyde in moderate to good yields which appeared reasonably pure upon TLC examination. Unfortunately, all of the isolated aldehydes were extremely unstable, even under high vacuum, thus precluding their complete characterisation. Consequently, they were isolated as their stable crystalline 2,4-dinitrophenylhydrazone derivatives, NMR spectral data for which, together with that for aldehydes sufficiently stable to obtain NMR spectra, are included in the Experimental section. It was also found possible to directly reduce the aldehydes to the corresponding stable crystalline primary alcohols, exemplified here by VI and XI although the yields were rather low (25% and 28% overall, respectively), and attempts to improve the reaction by one-pot procedures gave no significant change. The DIBAL-H reduction of the mixture IIIb and VIIa was not studied.

Experimental section

Melting points were recorded on a Reichert hot stage and are uncorrected. Infrared spectra were recorded on a Perkin Elmer 577, NMR spectra on

Varian HA100D, and mass spectra on AEI MS30 machines. Tetrahydrofuran was freshly distilled under nitrogen from sodium benzophenone ketyl, and nitromethane was distilled from calcium chloride. All chromatographic operations were conducted under an atmosphere of nitrogen.

Tricarbonyl(1-4-η-5-exo-nitromethylcyclohexa-1,3-diene)iron (IIa). To a stirred solution of potassium tert-butoxide (0.126 g, 1.13 mmol) in tetrahydrofuran (5 ml) at 0°C under nitrogen was added nitromethane (1 ml), giving a white precipitate of potassionitromethanate. A solution of tricarbonylcyclohexadienyliumiron hexafluorophosphate (Ia) * (0.500 g, 1.37 mmol) in nitromethane (5 ml) was added, the mixture stirred at 0°C for 15 min, poured into water (50 ml) and the product extracted with ether. The ether extracts were washed with brine, water, dried ($MgSO_4$) and evaporated under reduced pressure to give a yellow oil which was purified by preparative layer chromatography on silica gel (10% ethyl acetate in petroleum ether) to give spectroscopically pure IIa as a pale yellow oil (0.400 g, 55%). ν_{max} ($CHCl_3$) 2060, 1988, 1555 cm^{-1}; δ($CDCl_3$) 1.42 (1H, ddd, $J_{5,6exo}$ 2.5, $J_{1,6exo}$ 2.5, J_{gem} 15 Hz, *exo*-6-H), 2.45 (1H, ddd, $J_{5,6endo}$ 10.5, $J_{1,6endo}$ 4, J_{gem} 15 Hz, *endo*-6-H), 2.81 (1H, dddt, $J_{5,5'}$ 7, $J_{4,5}$ 4, $J_{5,6exo}$ 2.5, $J_{5,6endo}$ 10.5 Hz, 5-H), 2.82—3.18 (3H, m, 1-H, 4-H, 5-H), 4.23 (2H, d, $J_{5,5'}$ 7 Hz, 5'-H_2 (CH_2NO_2)), 5.40 ppm (2H, m, 2-H, 3-H); M 278.9827, $C_{10}H_{11}FeNO_5$ requires 278.9830.

Tricarbonyl(1-4-η-2-methyl-5-exo-nitromethylcyclohexa-1,3-diene) iron (IIb). Sodionitromethanate was prepared by the addition of 1.5 M ethanolic sodium ethoxide (1 ml) to nitromethane (2 ml) followed by evaporation to dryness at 0.05 mm Hg to give a white solid. To a stirred solution of this salt in nitromethane (2 ml) at 0°C under nitrogen was added a solution of tricarbonyl-(1-5-η-2-methylcyclohexadienylium)iron hexafluorophosphate (Ib) [5] (0.50 g, 1.32 mmol) in nitromethane (6 ml). 15 min work-up as above gave IIb as a yellow oil which could not be crystallised, homogeneous on TLC, and estimated to contain not more than 5% of the regioisomer VIIb from its NMR spectrum. (Yield: 0.33 g, 85%). ν_{max} ($CHCl_3$) 2050, 1980, 1555 cm^{-1}; δ ($CDCl_3$) 1.36 (1H, ddd, $J_{5,6exo}$ 3, $J_{1,6exo}$ 3, J_{gem} 15 Hz, *exo*-6-H), 1.86 (s, Me of VIIb), 1.94—2.26 (3H, s, and 1H, m, Me and *exo*-6H), 2.31 (1H, dd, $J_{4,5}$ 2.5, $J_{3,4}$ 6 Hz, 4-H), 3.01 (1H, m, 1-H), 4.05 (2H, d, $J_{5,5'}$ 6.5 Hz, 5'-H_2 (CH_2NO_2)), 5.20 ppm (1H, d, $J_{3,4}$ 6 Hz, 3-H). *m/e* 293 (M − CO), 275 (base peak, M − 2 CO). Found: M − CO 292.9972, $C_{10}H_{11}FeNO_4$ requires 292.9987.

Tricarbonyl(1-4-η-2-methoxy-5-exo-nitromethylcyclohexa-1,3-diene) iron (IIc). A 50% dispersion of sodium hydride in mineral oil (60 mg) was washed twice with dry pentane (10 ml) under nitrogen, and dry tetrahydrofuran (2 ml) followed by nitromethane (2 ml) were added. The mixture was stirred for 1 h at room temperature and then warmed to 40°C, when a violent reaction commenced, giving a white precipitate of sodionitromethanate (DANGER OF EXPLOSION). The mixture was cooled to 0°C and a solution of tricarbonyl-(1-5-η-2-methoxycyclohexadienylium)iron hexafluorophosphate [6] (Ic) (0.40 g, 1.02 mmol) in nitromethane (2 ml) was added. After 15 min, work-up and purification as above gave IIc (0.20 g, 71%) as a pale yellow crystalline

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* Prepared by treatment of the tetrafluoroborate in aqueous solution with ammonium hexafluorophosphate. The hexafluorophosphate gave better results than tetrafluoroborate. Preparation of the latter is given in ref. 10.

solid, m.p. 60—61°C (from n-pentane). ν_{max} (CHCl$_3$) 2060, 1980, 1555, 1485 cm^{-1}; δ (CDCl$_3$) 1.47 (1H, ddd, $J_{5,6exo}$ 3, $J_{1,6exo}$ 3, J_{gem} 14 Hz, *exo*-6-H), 2.12 (1H, ddd, $J_{5,6endo}$ 10, $J_{1,6endo}$ 3.5, J_{gem} 14 Hz, *endo*-6-H), 2.50 (1H, dd, $J_{4,5}$ 3, $J_{3,4}$ 6 Hz, 4-H), 2.68 (1H, dddt, $J_{5,5'}$ 7, $J_{4,5}$ 3, $J_{5,6endo}$ 10, $J_{5,6exo}$ 3 Hz, 5-H), 3.30 (1H, ddd, $J_{1,3}$ 2, $J_{1,6endo}$ 3.5, $J_{1,6exo}$ 3 Hz, 1-H), 3.63 (3H, s, OMe), 4.09 (2H, d, $J_{5,5'}$ 7 Hz, 5'-H), 5.07 ppm (1H, dd, $J_{3,4}$ 6, $J_{1,3}$ 2 Hz, 3-H). (Found: *M*, 308.9848; C, 42.82; H, 3.50; N, 4.46. Calculated for C$_{11}$H$_{11}$FeNO$_6$: *M*, 308.9891; C, 42.75; H, 3.59; N, 4.45%).

Tricarbonyl(1-4-η-6-exo-cyano-1-methyl(cyclohexa-1,3-diene)iron (VIIa) and tricarbonyl(1-4-η-5-exo-cyano-2-methylcyclohexa-1,3-diene)iron (IIIb). To a stirred solution of potassium cyanide (0.37 g, 5.5 mmol) in 20% aqueous acetone (6 ml) at 0°C under nitrogen was added the hexafluorophosphate Ib (1.0 g, 2.75 mmol) in acetone (20 ml). After 15 min the mixture was poured into ethyl acetate (100 ml) and washed successively with brine, cold 5% hydrochloric acid, aqueous sodium hydrogen carbonate, and water. The organic layer was dried (MgSO$_4$) and evaporated under reduced pressure to give the mixture of regioisomeric nitriles IIIb and VIIa as a yellow oil (ratio 1 : 1, NMR) (0.55 g, 59%). Crystallisation from pentane gave a pure sample of the isomer VIIa, m.p. 68—69°C. ν_{max} (CHCl$_3$) 2240, 2060, 1985 cm^{-1}; δ (CDCl$_3$) 1.74 (3H, s, Me), 2.05 (1H, ddd, $J_{5exo,6}$ 3, $J_{4,5exo}$ 3, J_{gem} 15 Hz, *exo*-5-H), 2.36 (1H, ddd, $J_{5endo,6}$ 11, $J_{4,5endo}$ 3, J_{gem} 15 Hz, *endo*-5-H), 2.94 (1H, dd, $J_{5endo,6}$ 11, $J_{5exo,6}$ 3 Hz, 6-H), 3.09 (1H, m, 4-H), 5.35 ppm (2H, m, 2-H, 3-H). (Found: C, 50.71; H, 3.67; N, 5.51. Calculated for C$_{11}$H$_9$FeNO$_3$: C, 51.00; H, 3.50; N, 5.41%). Comparison of the mixed NMR spectrum gave for IIIb: δ 2.09 (3H, s, Me), 3.0 (1-H and 4-H obscured by signals from VIIa), 5.3 ppm (3-H, obscured).

Tricarbonyl(1-4-η-5-exo-formylcyclohexa-1,3-diene)iron (IVa). A solution of the nitrile IIIa [2a] (0.62 g, 2.54 mmol) in dry hexane (20 ml) was treated with diisobutylaluminium hydride (DIBAL-H, Aldrich Chemical Co., 1 *M* in hexane) (2.8 ml) at 0°C under nitrogen. After 7 h the aluminium complexes were decomposed by the addition of methanol (3 ml) followed by water (3 ml). The mixture was stirred for 15 min, filtered through celite and the filter cake washed with ether. The filtrate was washed briefly with water, dried (MgSO$_4$) and the volatiles removed in vacuo to give a yellow oil (0.30 g, 63%) too unstable to permit complete characterisation, but which was a single compound on TLC, ν_{max} (CHCl$_3$) 2050, 1980, 1715 cm^{-1}. The compound was characterised as its stable 2,4-dinitrophenylhydrazone m.p. 176—177°C (d.) (from n-pentane). ν_{max} (CHCl$_3$) 2058, 1985, 1620, 1595 cm^{-1}; δ (CDCl$_3$) (primes refer to aromatic ring numbering), 1.69 (1H, m, *exo*-6-H), 2.21 (1H, ddd, $J_{5,6exo}$ 3, $J_{1,6exo}$ 3, J_{gem} 15 Hz, *endo*-6-H), 2.96—3.50 (3H, m, 5-H, 1-H, 4-H), 5.45 (2H, m, 2-H, 3-H), 7.77 (1H, d, *J* 7 Hz, CH=N), 7.84 (1H, d, $J_{5',6'}$ 10 Hz, 6'-H), 8.27 (1H, dd, $J_{3',5'}$ 2, $J_{5',6'}$ 10 Hz, 5'-H), 9.60 ppm (1H, d, $J_{3',5'}$ 2 Hz, 3'-H). *m/e* 428, 314 (base peak). (Found: C, 44.75; H, 3.01; N, 12.98. Calculated for C$_{16}$H$_{12}$FeN$_4$O$_7$: C, 44.89; H, 2.83; N, 13.09%).

Tricarbonyl(1-4-η-5-exo-formyl-2-methoxycyclohexa-1,3-diene) iron (IVc). Reaction of the nitrile IIIc [2a] (0.22 g, 0.80 mmol) with DIBAL-H (1.3 ml) as above gave the aldehyde IVc as an unstable yellow oil, homogeneous on TLC (0.197 g, 89%). ν_{max} (CHCl$_3$) 2050, 1975, 1715, 1485 cm^{-1}; δ (CDCl$_3$) 1.86—2.17 (2H, m, 6-H$_2$), 2.50—2.81 (2H, m, 4-H, 5-H), 3.35 (1H, m, 1-H), 3.63 (3H,

180

s, OMe), 5.14 (1H, m, 3-H), 9.25 (1H, d, 3 Hz, CHO). For complete characterisation, the crude aldehyde was converted directly to its 2,4-dinitrophenylhydrazone, m.p. 189—191°C (EtOAc), ν_{max} (CHCl$_3$) 2065, 1985, 1620, 1488 cm^{-1}; δ (CD$_2$Cl$_2$) 1.82 (1H, ddd, $J_{5,6exo}$ 3.5, $J_{1,6exo}$ 3.5, J_{gem} 14 Hz, exo-6-H), 2.21 (1H, ddd, $J_{5,6endo}$ 10, $J_{1,6endo}$ 3.5, J_{gem} 14 Hz, endo-6-H), 2.67 (1H, dd, $J_{4,5}$ 3.5, $J_{3,4}$ 6 Hz, 4-H), 5.78 (1H, dddd, $J_{4,5}$ 3.5, $J_{5,6exo}$ 3.5, $J_{5,6endo}$ 3.5, $J_{1,7'}$ 7 Hz, 5-H), 3.44 (1H, ddd, $J_{1,3}$ 3, $J_{1,6exo}$ 3.5, $J_{1,6endo}$ 3.5 Hz, 1-H), 3.66 (3H, s, OMe), 5.17 (1H, dd, $J_{3,4}$ 6, $J_{1,3}$ 3 Hz, 3-H), 7.12 (1H, d, $J_{5,7'}$ 7 Hz, CH=N), 7.82 (1H, d, $J_{5',6'}$ 9 Hz, 6'-H), 8.25 (1H, dd, $J_{3',5'}$ 2, $J_{5',6'}$ 9 Hz, 5'-H), 9.01 (1H, d, $J_{3',5'}$ 2 Hz, 3'-H), 10.84 (1H, s, NH). M^+ 458 (Found: C, 44.45; H, 3.20; N, 12.19. Calculated for C$_{17}$H$_{12}$FeNO$_8$: C, 44.57; H, 3.08; N, 12.23%).

Tricarbonyl(1-4-η-5-exo-formyl-2-methoxy-5-endo-methyl cyclohexa-1,3-diene)iron (IVd). The nitrile IIId [2b] (0.506 g, 1.75 mmol) was treated with DIBAL-H (1.9 ml) as above to give the unstable aldehyde IVd (0.25 g, 51%), ν_{max} (CHCl$_3$) 2050, 1980, 1715 cm^{-1}, which was converted directly to the stable crystalline 2,4-dinitrophenylhydrazone Vd, m.p. 165—166°C (EtOAc). ν_{max} (CHCl$_3$) 2058, 1984, 1620, 1590 cm^{-1}; δ (CDCl$_3$) 1.28 (3H, s, Me), 1.77 (1H, dd, $J_{1,6exo}$ 3, J_{gem} 15 Hz, exo-6-H), 2.26 (1H, dd, $J_{1,6endo}$ 3, J_{gem} 15 Hz, endo-6-H), 2.42 (1H, d, $J_{3,4}$ 6.5 Hz, 4-H), 3.46 (1H, m, 1-H), 3.68 (3H, s, OMe), 5.13 (1H, dd, $J_{3,4}$ 6.5, $J_{1,3}$ 2 Hz, 3-H), 7.14 (1H, s, CH=N), 7.82 (1H, d, $J_{5',6'}$ 9.5 Hz, 6'-H), 8.27 (1H, dd, $J_{3',5'}$ 2.5, $J_{5',6'}$ 9.5 Hz, 5'-H), 9.06 (1H, d, $J_{3',5'}$ 2.5 Hz, 3'-H), 10.86 (1H, NH). m/e 472 (M^+), 358 (base peak). (Found: C, 45.80; H, 3.46; N, 11.95. Calculated for C$_{18}$H$_{16}$FeN$_4$O$_8$: C, 45.79; H, 3.42; N, 11.87%).

Tricarbonyl(1-4-η-5-exo-hydroxymethyl-2-methoxy-5-endo-methylcyclohexa-1,3-diene)iron (VI). The crude aldehyde IVd (0.288 g), from above was dissolved directly in ethanol (5 ml) at 0°C under nitrogen, and reduced with sodium borohydride (0.038 g) for 10 min. Aqueous work-up and ether extraction followed by preparative layer chromatography afforded the stable hydroxymethyl derivative VI as a white crystalline solid, m.p. 69—70°C (from pentane) (0.072 g, 25%). ν_{max} (CHCl$_3$) 3630, 3460, 2050, 1975, 1490 cm^{-1}; δ (CDCl$_3$) 1.04 (3H, s, Me), 1.49 (1H, s, exch. D$_2$O, OH), 1.49 (1H, dd, $J_{1,6exo}$ 3, J_{gem} 15 Hz, exo-6-H), 1.79 (1H, dd, $J_{1,6endo}$ 3, J_{gem} 15 Hz, endo-6-H), 2.38 (1H, d, $J_{3,4}$ 6 Hz, 4-H), 3.18 (2H, s, CH$_2$OH), 3.32 (1H, ddd, $J_{1,3} = J_{1,6endo} = J_{1,6exo}$ = 3 Hz, 1-H), 3.66 (3H, s, OMe), 5.11 (1H, dd, $J_{1,3}$ 3, $J_{3,4}$ 6 Hz, 3-H). m/e 294 (M), 266, 238, 210 (Found: C, 48.98; H, 5.03. Calculated for C$_{12}$H$_{14}$FeO$_5$: C, 49.01; H, 4.80%).

Tricarbonyl(1-4-η-6-exo-formyl-3-methoxybicyclo[4.4.0]deca-1,3-diene)iron (X). The nitrile IX [2b] (0.364 g, 0.93 mmol) was treated as above with DIBAL-H (1.2 ml) to give the very unstable aldehyde X chromatographically pure (0.290 g, 97% crude yield, ν_{max} (CHCl$_3$) 2050, 1980, 1715 cm^{-1}) which was converted directly into its stable 2,4-dinitrophenylhydrazone (0.100 g, 24%), m.p. 180—181°C (d) (EtOAc). ν_{max} (CHCl$_3$) 2050, 1975, cm^{-1}; δ (CDCl$_3$) 1.50—2.28 (10H, m, 5 × CH$_2$), 3.33 (1H, m, 4-H), 3.72 (3H, s, OMe), 5.11 (1H, d, $J_{2,4}$ 2 Hz, 2-H), 7.20 (1H, s, CH=N), 7.84 (1H, d, $J_{2',3'}$ 10 Hz, 2'-H), 8.30 (1H, dd, $J_{2',3'}$ 10, $J_{3',5'}$ 2 Hz, 3'-H), 9.10 (1H, d, $J_{3',5'}$ 2 Hz, 5'-H), 10.93 (1H, s, NH). m/e 484 (M − CO), 428 (M − 3 CO). (Found: C, 49.12; H, 4.11; N, 11.05. Calculated for C$_{21}$H$_{18}$FeN$_4$O$_8$: C, 49.24; H, 3.94; N, 10.94%).

Tricarbonyl(1-4-η-6-exo-hydroxymethyl-3-methoxybicyclo[4.4.0]deca-1,3-diene)iron (XI). The crude aldehyde X (0.32 g) from above was dissolved in ethanol (20 ml) immediately subsequent to its isolation, and reduced at 0°C under nitrogen with sodium borohydride (0.028 g). After 15 min the reaction mixture was poured into water and extracted with ether in the usual way. The product was purified by preparative layer chromatography (10% EtOAc/petroleum ether) to give the alcohol complex XI as a white crystalline solid, m.p. 108—109°C (from pentane). ν_{max} (CHCl$_3$) 3620, 3420, 2040, 1965, 1490 cm^{-1}; δ (CDCl$_3$) 1.26—2.14 (10H, m, 5 × CH$_2$), 3.12 (1H, s, exch. D$_2$O, OH), 3.23 (1H, m, 4-H), 3.65 (2H, m, CH$_2$OH, diastereotopic), 3.68 (3H, s, OMe), 5.05 ppm (1H, d, *J* 2 Hz, 2-H). Addition of D$_2$O caused collapse of the 3.65 ppm resonance to ABq. *m/e* 250 (*M* − 3 CO), 162 (base peak). (Found: C, 54.01; H, 5.49, *M* − 3 CO, 250.0644. Calculated for C$_{12}$H$_{18}$FeO$_3$: C, 53.92; H, 5.43, *M* − 3 CO, 250.0656).

Acknowledgements

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