Synthetic Routes to Butadienyl Complexes. Double Addition of Methylene to an Acetylide and Hydrometallation of an Ene–Yne. X-Ray Crystal Structure of $[Fe_2(CO)_5\{\mu\text{-}\eta^2,\eta^3\text{-}H_2C{=}C(Me)C{=}CH_2\}(\mu\text{-}PPh_2)]$

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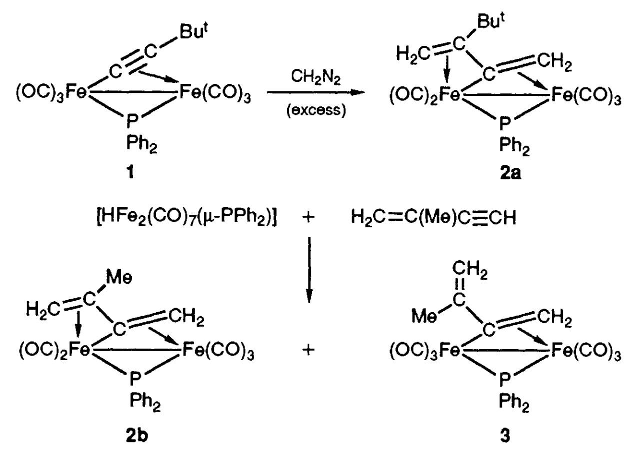
Binuclear butadienyl complexes $[Fe_2(CO)_5\{\mu\text{-}\eta^2,\eta^3\text{-}H_2C{=}C(R)C{=}CH_2\}(\mu\text{-}PPh_2)]$ (R = Bu^t, Me) have been synthesized *via* double addition of CH_2 fragments to an acetylide in $[Fe_2(CO)_6(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}CBu^t)(\mu\text{-}PPh_2)]$ or hydrometallation of the ene–yne $CH_2{=}C(Me)C{\equiv}CH$ with $[HFe_2(CO)_7(\mu\text{-}PPh_2)]$.

Although the chemistry of unsaturated organic ligands at bi-and poly-nuclear centres has been a major focus of activity in organometallic chemistry for many years, only recently has attention turned to more complex polyunsaturated fragments such as allenylidenes[1] and allenyls.[2] Polyunsaturated four-carbon groups, including butadiynyl ($-C{\equiv}C{-}C{\equiv}CH$), butatrienylidene ($C{=}C{=}C{=}CH_2$) and isomeric 1- or 2-butadienyl ($HC{=}CH{-}CH{=}CH_2$ or $H_2C{=}CH{-}C{=}CH_2$) fragments are rare in organometallic chemistry[3] and their chemical behaviour remains largely undeveloped. We are exploring synthetic routes to binuclear complexes bearing four-carbon atom polyunsaturated ligands and in this communication we describe the generation of $\mu\text{-}\eta^2,\eta^3$-butadienyl ligands at a binuclear centre *via* double methylene addition to a $\mu\text{-}\eta^1,\eta^2$-acetylide and *via* hydrometallation of the ene–yne $CH_2{=}C(Me)C{\equiv}CH$ by $[HFe_2(CO)_7(\mu\text{-}PPh_2)]$.

Treatment of $[Fe_2(CO)_6(\mu\text{-}\eta^1,\eta^2\text{-}C{\equiv}CBu^t)(\mu\text{-}PPh_2)]$ **1** (0.40 g, 0.73 mmol) in CH_2Cl_2 (5 ml) with an excess of freshly generated diazomethane in diethyl ether (0.2 mol dm^{-3}), added dropwise in 2 ml portions every 20 min until all starting



Scheme 1

material has been consumed, gave a red solution, which after column chromatography on Florisil (hexane eluent) and crystallisation at −5 °C afforded **2a** in 67% yield.† ^{1}H and ^{13}C NMR data for **2a** were suggestive of the presence of an alkenyl [–C(R)=CH$_2$] moiety, a second =CH$_2$ group and a carbon-13 resonance with no nuclear Overhauser enhancement. Recognising that diynes and ene–ynes represented a potential source of μ-η-coordinated four-carbon fragments we treated the hydride [HFe$_2$(CO)$_7$(μ-PPh$_2$)] (0.33 g, 0.68 ml) generated from Na[Fe$_2$(CO)$_7$(μ-PPh$_2$)]·1.5thf^4 (thf = tetrahydrofuran) *via* reaction with 85% HBF$_4$·Et$_2$O, with HC≡CC(Me)=CH$_2$ (0.05 g, 0.68 mmol). After 12 h, the mixture was chromatographed on alumina, yielding two bands, the major product being [Fe$_2$(CO)$_5${μ-η^2,η^3-H$_2$C=C(Me)C=CH$_2$}(μ-PPh$_2$)] **2b** (55%) and the minor [Fe$_2$(CO)$_6${μ-η^1,η^2-H$_2$C=C(Me)C=CH$_2$}(μ-PPh$_2$)] **3**. Spectroscopic data for **2b**‡ indicated an analogous structure to **2a**, a result confirmed by X-ray diffraction (*vide infra*). Both synthetic routes (Scheme 1) provide **2** in good yields. The diazomethane–acetylide coupling strategy should be applicable to other diazoalkanes and μ-η^1,η^2-acetylides. Double methylene additions to coordinated unsaturated ligands are unusual.^{5} Hydrodimetallation of ene–ynes by the reagent [HFe$_2$(CO)$_7$(μ-PPh$_2$)] is a potentially powerful method of accessing 2-butadienyl complexes since the [Fe]$_2$–H addition across the triple bond of alkynes is predominantly Markovnikov and *cis*.^{6} Thus, the generation of butadienyldiiron complexes *via* this route may be limited only by the availability of ene-ynes.

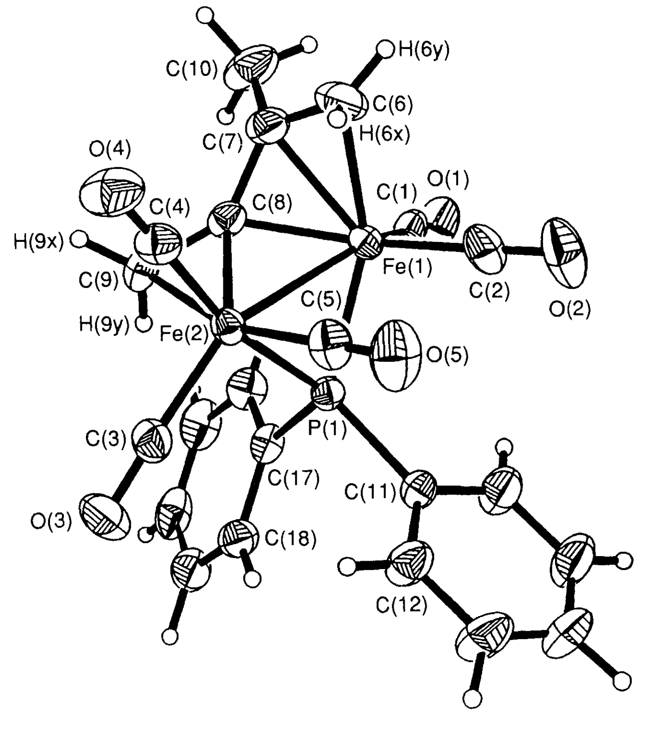


Fig. 1 The molecular structure of [Fe$_2$(CO)$_5${μ-η^2,η^3-H$_2$C=C(Me)-C=CH$_2$}(μ-PPh$_2$)] **2b** showing the atomic numbering. Selected bond lengths (Å) and angles (°) are as follows: Fe(1)–Fe(2) 2.635(1); Fe(1)–P 2.157(1); Fe(2)–P 2.272(1); Fe(1)–C(6) 2.148(3); Fe(1)–C(7) 2.103(2); Fe(1)–C(8) 1.929(2); Fe(2)–C(8) 2.063(2); Fe(2)–C(9) 2.174(2); C(6)–C(7) 1.399(4); C(7)–C(8) 1.421(3); C(8)–C(9) 1.386(3); Fe(1)–P–Fe(2) 73.0(1); C(6)–C(7)–C(8) 116.7(2); C(7)–C(8)–C(9) 143.4(1).

In order to confirm the nature of **2a** and **2b** an X-ray analysis of **2b** was carried out§ (Fig. 1). The hydrocarbyl interacts with the binuclear framework through all four carbon atoms C(6)–C(9) with Fe(1) attached *via* an alkenic η^2-bond to C(7)–C(8) and a σ-bond to C(8) while Fe(2) is attached to the second double bond between C(8) and C(9). The C(6)–C(7) [1.399(4) Å] and C(8)–C(9) [1.386(3) Å] distances are longer than the C=C double bond lengths (1.337 Å) in buta-1,3-diene,^{7} but within the range observed for η^2-alkene and μ-η^1,η^2-alkenyl complexes of iron.^{6g,8} The central C(7)–C(8) bond [1.421(3) Å] is slightly shorter than in butadiene (1.483 Å). The 2-butadienyl ligand can be viewed as an alkenyl ligand substituted with a 2-propenyl group at the α-carbon and is a net five-electron donor to the binuclear framework. Other four-carbon butadienyl chains in bi- or poly-nuclear complexes of which we are aware include the cations [Cp$_2$(CO)$_2$Fe$_2$(μ-CO){μ-η^1,η^2-*E*-CH=CHCH=CRR^1}]$^+$ (R = R^1 = Me; R = H, R^1 = Ph) and [Cp$_2$(CO)$_2$Fe$_2$(μ-CO){μ-η^1,η^2-*E*-CH=CHCH=C(CH$_2$)$_4$CH$_2$]$^+$,^{3b} the cluster [Ru$_3$(CO)$_6$(μ-CO)(PPh$_3$){μ$_3$-η^1,η^2,η^2-CH$_2$=C(Pr^i)C=CH$_2$}(μ-PPh$_2$)] (Cp = η^5-cyclopentadienyl)^{9a} and several butadienyl

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† *Selected spectroscopic data* for **2a**: IR(C$_6$H$_{14}$) ν(CO)/cm^{-1}: 2047m, 2005s, 1987m, 1972w, 1940m. ^{31}P{^{1}H} NMR (81.0 MHz; C$_6$D$_6$; 298 K): δ 178.2 (s). ^{13}C{^{1}H} NMR (50.3 MHz; CDCl$_3$; 298 K): δ 216.8 (d, CO, $^2J_{PC}$ 8.4 Hz), 216.4 (d, CO, $^2J_{PC}$ 16.7 Hz), 175.4 (d, *C*=CH$_2$, $^2J_{PC}$ 26.2 Hz), 140.8–127.9 (m, Ph*C*), 107.4 (s, *C*Bu^t=CH$_2$), 45.0 (s, CBu^t=*C*H$_2$), 39.1 (d, C=*C*H$_2$, $^2J_{PC}$ 9.1 Hz), 35.1 (s, *C*Me$_3$) 29.1 (s, C*Me*$_3$). ^{1}H NMR (250.1 MHz; CDCl$_3$; 298 K): δ 7.71–7.24 (m, Ph-*H*), 3.60 (s, CBu^t=C*H*H′), 2.91 (dd, $^2J_{HH}$ 4.9 Hz, $^3J_{PH}$ 11.2 Hz, C=C*H*H′), 2.04 (≈t, $^2J_{HH}$ 4.9 Hz, $^3J_{PH}$ ≈ 4.9 Hz, C=CH*H*′), 1.81 (s, CBu^t=CH*H*′), 1.34 (s, CMe$_3$). Satisfactory elemental analyses were obtained.

‡ *Selected spectroscopic data* for **2b**: IR(C$_6$H$_{14}$) ν(CO)/cm^{-1}: 2047m, 2006s, 1988m, 1972w, 1945m. ^{31}P{^{1}H} NMR (81.0 MHz; CDCl$_3$; 298 K): δ 174.7 (s). ^{13}C{^{1}H} NMR (50.3 MHz; CDCl$_3$; 298 K): δ 216.6 (d, CO, $^2J_{PC}$ 7.0 Hz), 215.0 (d, CO, $^2J_{PC}$ 15.5 Hz), 175.5 (d, *C*=CH$_2$, $^2J_{PC}$ 27.4 Hz), 140.3–126.3 (m, Ph-*C*), 92.7 (s, *C*Me=CH$_2$), 51.9 (s, CMe=*C*H$_2$), 38.6 (d, C=*C*H$_2$, $^2J_{PC}$ 9.1 Hz), 27.1 (s, Me). ^{1}H NMR (200.1 MHz; CDCl$_3$; 298 K): δ 7.49–7.03 (m, Ph-*H*); 3.34 (s, CMe=C*H*H′), 2.70 (dd, $^2J_{HH}$ 5.0 Hz, $^3J_{PH}$ 10.8 Hz, C=C*H*H′), 2.12 (d, $^4J_{PH}$ 1.7 Hz, Me), 1.92 (s, CMe=CH*H*′), 1.83 (≈t, $^2J_{HH}$ 5.0 Hz, $^3J_{PH}$ ≈ 5.0 Hz, C=CH*H*′). Satisfactory elemental analyses were obtained.

§ *Crystal data*: C$_{22}$H$_{17}$Fe$_2$O$_5$P, M = 504.0, triclinic, space group $P\bar{1}$, a = 8.928(2), b = 10.363(1), c = 12.844(2) Å, α = 89.35(1), β = 84.25(1), γ = 68.37(1)°, U = 1098.7(3) Å^3, Z = 2, D_c = 1.524 g cm^{-3}, μ(Mo-Kα) = 0.71073 Å, F(000) = 512. Diffraction data were collected with a Siemens R3m/V diffractometer (ω scans; 200 ± 1 K). The structure solution (Patterson, Fourier methods) and refinement (full-matrix least-squares) was performed using the Siemens SHELXTL PLUS software and was based on 4415 observed intensities [$F > 6.0\sigma(F)$] from 5083 measured data (2θ ≤ 55°). Final R and R_w values were 0.025 and 0.043. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

binuclear species.[9b–e] Unlike **2a**, **b**, however, the cations[3b] are substituted μ-η^1,η^2-alkenyl species with an alkenic substituent uncoordinated. Despite the greater number of interacting metal atoms in the triruthenium cluster, the carbon–carbon bond lengths and the *trans* stereochemistry of the hydrocarbyl chain are remarkably similar. The three-carbon fragment C(8)–C(7)–C(6) may also be compared with allenyl ligands at binuclear centres.[2] Recent work has shown that these are of two types: type (*a*) with μ-η^1,η^2-coordination and a free double bond; type (*b*) with μ-η^2,η^3-bonding. Complex **2b** is related to type (*b*) by the addition of a coordinated $=CH_2$ group. A significant and distinctive chemistry is emerging for these compounds, including their use in the synthesis of dimetallacyclopentane and dimetallacyclopentene derivatives[2b] and mixed-metal clusters.[2b,10] Thus, the butadienyl ligands in **2a**,**b** should also prove useful as a source of four-carbon units in organometallic or cluster synthesis. We are currently examining the broader scope of the synthetic routes to butadienyl systems shown in Scheme 1 and the patterns of reactivity of these four-carbon hydrocarbyls.

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