An unprecedented regiospecific attack of phosphorus nucleophiles at C_α of the allenyl ligand in $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1:\eta^2_{\alpha,\beta}\text{-}(H)C_\alpha{=}C_\beta{=}C_\gamma H_2\}]$

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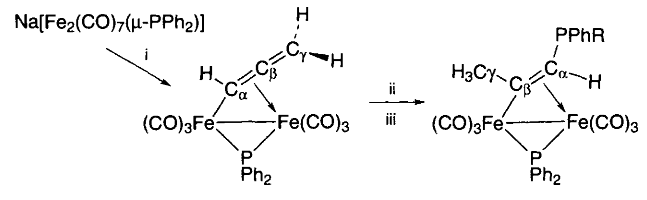
The binuclear allenyl complex $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1:\eta^2\text{-}(H)C_\alpha{=}C_\beta{=}C_\gamma H_2\}]$ 1 reacts with PPh_2H and $PPhH_2$ to afford $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1:\eta^2\text{-}(Me)C{=}CH(PPh_2)\}]$ 2 and $[\{Fe_2(CO)_6(\mu\text{-}PPh_2)\text{-}(\mu\text{-}\eta^1:\eta^2\text{-}(Me)C{=}CH)\}_2PPh]$ 3 respectively both of which contain $\mu\text{-}\eta^1:\eta^2$-coordinated phosphino-substituted alkenyl ligands formed *via* an unprecedented regiospecific attack of phosphorus nucleophiles at C_α of the $\mu\text{-}\eta^1:\eta^2$-coordinated allenyl followed by a facile 1,4-hydrogen migration.

While the first transition-metal allenyl complexes were prepared over two decades ago the potential utility of these complexes, as three-carbon reagents, in organic synthesis has only recently been realised.[1] As a result, interest in the synthesis and reactivity of transition-metal allenyl complexes has intensified with the past few years witnessing several noteworthy developments including, new η^3- and $\mu\text{-}\eta^1:\eta^2_{\beta,\gamma}$-allenyl coordination modes[2] and an unusual ligand coupling/insertion reaction.[3] Considering the wealth of coordination chemistry associated with this C_3 hydrocarbon,[4] we were somewhat surprised to learn that its reactivity has, until recently, been dominated by the electrophilic nature of C_β, generating β-heterosubstituted allyl ligands from mononuclear η^3-allenyl complexes[5] and dimetallocyclopentanes and pentenes from their $\mu\text{-}\eta^1:\eta^2$ binuclear counterparts.[6] Unfortunately, the synthetic utility of this ligand will be severely limited unless its reactivity can be tailored to access a broader range of organic products. With this in mind we became interested in developing synthetic routes to diiron allenyl complexes because of the intrinsic interest in iron as a readily available and inexpensive transition metal for mediating organic transformations. However, in contrast to the extensive chemistry documented for $[Ru_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1:\eta^2_{\beta\gamma}\text{-}(Ph)C{=}C{=}CH_2\}]$, the chemistry of its diiron counterpart remains unexplored because of the difficulties associated with synthesis.[7] Herein we report our synthesis of $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1:\eta^2_{\alpha\beta}\text{-}(H)C{=}C{=}CH_2\}]$ 1, some initial comments on its unprecedented and highly regiospecific reactivity with phosphorus nucleophiles and labelling studies that support a formal 1,3-addition of PPhHR (R = Ph, H) across the cumulated C_3-hydrocarbyl fragment.

The preparative route to 1 involved treatment of a diethyl ether solution of $Na[Fe_2(CO)_7(\mu\text{-}PPh_2)]\cdot$thf (0.250 g, 0.43 mmol) with prop-2-ynyl bromide (0.038 ml, 0.43 mmol) at 298 K. Unfortunately we have been unable to obtain X-ray quality crystals of 1 but combined evidence from ^1H (variable temperature), $^1H\{^{31}P\}$, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ and $^{13}C\{^1H\}$–^1H correlated NMR spectroscopy support our formulation of 1 as $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1:\eta^2_{\alpha\beta}\text{-}(H)C{=}C{=}CH_2\}]$ (Scheme 1).‡ The ^{13}C NMR chemical shifts of the allenyl ligand in 1 [$\delta(C_\beta)$ 180.0, $\delta(C_\alpha)$ 118.3, $\delta(C_\gamma)$ 79.0] are similar to those of $[Fe_2(CO)_6(\mu\text{-}SBu^t)\{\mu\text{-}\eta^1:\eta^2_{\alpha\beta}\text{-}(H)C{=}C{=}CH_2\}]$[8] which suggests a $\mu\text{-}\eta^1:\eta^2_{\alpha\beta}$ coordination of this hydrocarbyl fragment, in contrast to the recently discovered alternative $\mu\text{-}\eta^1:\eta^2_{\beta\gamma}$ bonding mode[2,4a] (Scheme 1). We have examined the reactivity of 1 with phosphorus-based nucleophiles to compare with the behaviour of $[Ru_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1:\eta^2_{\beta\gamma}\text{-}(Ph)C{=}C{=}CH_2\}]$, which is dominated by nucleophilic attack at C_β.

Treatment of 1 (0.120 g, 0.24 mmol) in diethyl ether with 1 equiv. of PPh_2H (0.044 ml, 0.24 mmol) afforded $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1\text{-}\eta^2\text{-}(Me)C{=}CH(PPh_2)\}]$ 2 as deep orange crystals in 80–85% yield, after crystallisation from dichloromethane–acetonitrile. The $^{31}P\{^1H\}$ NMR spectrum of 2 consists of two mutually coupled resonances, one at low field (δ 173.1, $^3J_{PP}$ 4.1 Hz) characteristic of a $\mu\text{-}PR_2$ ligand bridging a metal–metal bond, the other at high field in the region commonly associated with tertiary phosphines (δ −6.6, $^3J_{PP}$ 4.1 Hz). In addition, ^{13}C resonances at δ 194.3 and 85.6 have remarkably similar values to those reported for a series of $\mu\text{-}\eta^1:\eta^2$-alkenyl bridged diiron complexes prepared by hydrodimetallating alkynes with $[HFe_2(CO)_7(\mu\text{-}PPh_2)]$.[9] The precise nature of this bridging hydrocarbyl ligand was of particular interest and prompted a single-crystal X-ray determination of 2.§ The molecular structure, shown in Fig. 1, identifies 2 as $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1:\eta^2\text{-}(Me)C{=}CH(PPh_2)\}]$, formally derived from allenyl 1 *via* the 1,3-addition of PPh_2H across the cumulated C_3-hydrocarbyl fragment. The most notable feature of 2 is the phosphino substituted hydrocarbyl bridging ligand, an alkenylphosphine whose P–C bond length [P(1)–C(1) 1.835(2) Å] is similar to the previously reported value of 1.87(2) Å for the σ–π-co-ordinated



Scheme 1 *Reagents and conditions*: i, $BrCH_2C{\equiv}CH$, Et_2O; ii, $PPh_2H\cdot Et_2O$ (R = Ph); iii, $PPhH_2\cdot Et_2O$ [R = $Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1:\eta^2\text{-}(Me)C{=}CH\}$]

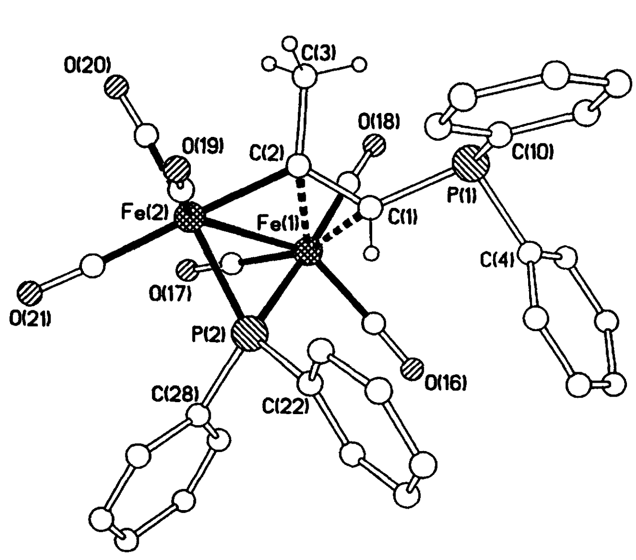


Fig. 1 Molecular structure of 2 showing the phosphino-substituted hydrocarbyl bridge. Phenyl hydrogens have been omitted for clarity. Carbonyl carbon atoms have the same numbers as oxygen atoms.

diphenyl(vinyl)phosphine in $[Ru_3(\mu\text{-}H)(CO)_8(PPh_2PCH{=}CH_2)(\mu_3\text{-}PPh_2CH{=}CH_2)]$. The P–C bond formation at C_α is associated with the formation of a new C_γ–H bond to generate a 1,3-addition product, most aptly described as a diphenyl(alkenyl)phosphine.

An isotopic labelling experiment using PPh_2D and **1** resulted in the exclusive formation of the single isotopomer $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1:\eta^2\text{-}(CH_2D)C{=}CH(PPh_2)\}]$, $[^2H_1]$**2**. The incorporation of deuterium solely at the alkenyl methyl substituent was confirmed by the appearance of a separate resonance for $[^2H_1]$**2** (20 ppb lower frequency, 10 Hz at 500 MHz) due to the deuterium isotope shift of the methyl resonance together with a single broad resonance in the ^2H NMR spectrum at δ 3.10. The isotopic composition of $[^2H_1]$**2** lends support to the generation of the $\mu\text{-}\eta^1:\eta^2$-alkenyl ligand *via* initial nucleophilic attack at C_α followed by a rapid 1,4-hydrogen migration.

Reaction of **1** and $PPhH_2$ results in the rapid and high yield formation of $[\{Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1:\eta^2\text{-}(Me)C{=}CH)\}_2PPh]$ **3** *via* the facile 1,3-addition of both P–H bonds across 2 equiv. of the allenyl fragment. The molecular structure (Fig. 2) confirms that the $\mu\text{-}\eta^1:\eta^2_{\alpha\beta}$-allenyl ligand in **3**, and presumably **2**, is functionalised by the incoming phosphorus nucleophile and not *via* a novel coupling sequence involving the bridging phosphido ligand.§ A principal structural feature of **3** is the hydrocarbyl bridging ligand, a novel bis(alkenyl) substituted phosphine, σ bonded to Fe(1) and Fe(4) and π bonded to Fe(2) and Fe(3). These two alkenyl ligands adopt an *exo* stereochemistry with respect to the phosphido bridges and both carbon–carbon bonds [C(1)–C(2) 1.402(8), C(4)–C(5) 1.427(9) Å] are of similar length to that in **2**.

Our preliminary reactivity studies of **1** with bis(diphenylphosphino)methane and 1,2-bis(diphenylphosphino)ethane reinforce this C_α directed regiospecific attack of phosphorus nucleophiles; however, in the absence of a labile P–H bond, P–C_α bond formation affords the zwitterionic products $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\eta^1(P):\eta^2(C)\text{–}Ph_2P(CH_2)_nPPh_2\text{-}CH{=}C{=}CH_2\}]$ (n = 1, 2).

In summary, the unprecedented regiospecific addition of phosphorus nucelophiles to C_α in $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1:\eta^2_{\alpha\beta}\text{-}(H)C_\alpha{=}C_\beta{=}C_\gamma H_2\}]$ **1** contrasts sharply with the formation of dimetallacyclopentanes and β-substituted allyl ligands from binuclear $\mu\text{-}\eta^1:\eta^2_{\alpha\beta}$- and mononuclear η^3-allenyl complexes respectively. This new reactivity pattern for transition-metal allenyl complexes will open alternative avenues for hydrocarbyl elaboration and broaden the horizons of this C_3 hydrocarbon in metal-mediated synthesis.

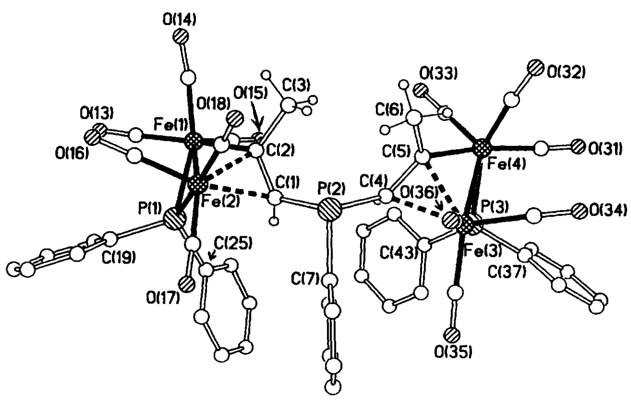


Fig. 2 Molecular structure of **3** highlighting the bridging bis(alkenyl)phosphine ligand in $[\{Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1:\eta^2\text{-}(Me)C{=}C(H)\}_2PPh]$. Phenyl hydrogens have been omitted for clarity. Carbonyl carbon atoms have the same numbers as oxygen atoms.

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Footnotes

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‡ Satisfactory analytical and spectroscopic data were obtained for **1–3**.

§ *Crystal data*: for **2**; $C_{33}H_{24}Fe_2O_6P_2$, M = 690.16, monoclinic, space group $C2/c$, a = 27.915(2), b = 9.4860(7), c = 23.090(2) Å, β = 102.780(2)°, U = 5962.9(8) Å^3, Z = 8, D_c = 1.538 g cm^{-3}, λ(Mo-Kα) = 0.71073 Å, μ = 1.126 mm^{-1}, F(000) = 2816, T = 160 K. Of 18838 reflections measured on a Siemens SMART CCD area-detector diffractometer to $2\theta_{max}$ = 57° and corrected semiempirically for absorption (crystal size: 0.41 × 0.26 × 0.10 mm, transmission: 0.696–0.828), 6811 were unique (R_{int} = 0.0354). The structure was solved by direct methods and refined by full-matrix least squares on F^2 to give $wR2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma[w(F_o^2)^2\}]^{\frac{1}{2}}$ = 0.0726 for all data, conventional R = 0.0305 for 5646 data with $F^2 > 2\sigma(F^2)$, goodness of fit = 1.112 on F^2 with 393 parameters. The final difference map features lay within ±0.360 Å^{-3}.

For **3**; $C_{48}H_{33}Fe_4O_{12}P_3$, M = 1118.5, orthorhombic, space group $Pbcn$, a = 44.046(4), b = 11.7624(10), c = 18.661(2) Å, U = 9668.1(14) Å^3, Z = 8, D_c = 1.536 g cm^{-3}, μ = 1.337 mm^{-1}, F(000) = 4528, T = 160 K. Of 47753 reflections ($2\theta_{max}$ = 50°, crystal size 0.59 × 0.15 × 0.10 mm, transmission 0.575–0.904), 8511 were unique (R_{int} = 0.1121). Final $wR2$ = 0.1411 for all data, conventional R = 0.0818 for 6753 data with $F^2 > 2\sigma(F^2)$, goodness of fit = 1.345 on F^2 with 607 parameters; final difference map features within ±0.550 e Å^{-3}. Programs: Siemens SHELXTL, SMART and SAINT software for data collection and reduction and local programs. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/121.

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