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Addition of Organolithium Nucleophiles to the Diiron Allenyl Complex $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2_{\alpha,\beta}\text{-}(H)C_\alpha{=}C_\beta{=}C_\gamma H_2\}]$: Synthesis and Characterization of Organodiiron-Coordinated β,γ-Unsaturated Ketones

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The binuclear allenyl complex $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2_{\alpha,\beta}\text{-}(H)C_\alpha{=}C_\beta{=}C_\gamma H_2\}]$ (**1**) has been prepared, and its reactivity with organolithium nucleophiles is described. Prop-2-yne bromide reacts with $[Fe_2(CO)_7(\mu\text{-}PPh_2)]^-Na^+$, *via* an S_N2 mechanism, to give $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2_{\alpha,\beta}\text{-}(H)C_\alpha{=}C_\beta{=}C_\gamma H_2\}]$, the first example of a phosphido-bridged allenyl complex. The molecular structure of $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2\text{-}(H)C_\alpha{=}C_\beta{=}C_\gamma H_2\}]$ (**1**) was determined by single-crystal X-ray diffraction and shows that the allenyl ligand is coordinated through $C_\alpha{-}C_\beta$. Variable-temperature ^1H and ^{13}C NMR studies reveal a high-energy exchange process that equilibrates the diastereotopic allenyl protons, presumably *via* a zwitterionic intermediate, as well as two independent trigonal rotations that act to exchange the carbonyl ligands on each unique $Fe(CO)_3$ group. Complex **1** reacts with organolithium reagents (RLi; R = Me, ^{n}Bu, Ph, C_4H_3S), *via* allenyl−carbonyl−nucleophile coupling, to afford the binuclear β,γ-unsaturated ketones $[Fe_2(CO)_5\{P(OMe)_3\}(\mu\text{-}PPh_2)(\mu\text{-}\eta^1{:}\eta^2\text{-}\{RC(O)CH_2\}C{=}CH_2)]$ (R = Me, **3a**; ^{n}Bu, **3b**; Ph, **3c**; C_4H_3S, **3d**), and a single-crystal X-ray structure determination of **3a** was undertaken to confirm the connectivity of the hydrocarbyl ligand. The most likely mechanism for the formation of **3a**−**d** involves nucleophilic attack of R^- at CO to give an acylate intermediate followed by migration of RCO to C_α of the allenyl and protonation of the resulting enolate to give the unstable alkenyl complexes $[Fe_2(CO)_5(\mu\text{-}PPh_2)(\mu\text{-}\eta^1(C){:}\eta^1\text{-}(C){:}\eta^2(C)\text{-}\{RC(O)CH_2\}C{=}CH_2)]$ (R = Me, **2a**; Bu, **2b**; Ph, **2c**; C_4H_3S, **2d**). Finally, substitution of the metal-coordinated ester carbonyl in **2a**−**d** with trimethylphosphite affords **3a**−**d** as stable crystalline products.

Introduction

Nucleophilic addition of organolithium reagents to transition metal carbonyl complexes is a common strategy for generating practical organometallic reagents and intermediates for the synthesis of a wide range of organic products.[1] For instance, organolithium reagents react with homoleptic metal carbonyls to give acylates, which react with electrophiles either at the metal center, leading ultimately to coupled products, or at oxygen to give carbene complexes.[2] In the case of transition metal complexes containing both carbon monoxide and an unsaturated hydrocarbyl ligand, additional reaction pathways are possible, including carbon−carbon coupling between an acylate intermediate and the unsaturated hydrocarbon[3] and direct nucleophilic attack at the coordinated hydrocarbon to afford functionalized organic products.[4] Since their discovery, both of these reaction types have been applied to the synthesis of numerous unsaturated carbonyl compounds. For instance, tricarbonyliron(0) complexes of α,β-unsaturated ketones react with alkylithium reagents under an atmosphere of nitrogen to afford 1,4-diketones,[5] while under an atmosphere of carbon monoxide, tricarbonyl(η^4-vinylketene)iron(0) complexes are generated in good yield.[6] Thomas and co-workers have used these iron(0)vinylketene complexes to synthesise a number of important organic products, including phenols, cyclopentadienones,[7] cyclopropanes,[8] β,γ-unsaturated carbonyl compounds,[9] and vinylketeneimines.[10]

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In contrast, the reactivity of organolithium nucleophiles with binuclear complexes bearing σ-η-coordinated unsaturated hydrocarbyl ligands is relatively undeveloped. In fact, the reactivity of these complexes has largely been confined to neutral protic and aprotic nucleophiles, such as amines,[11] isonitriles,[12] phosphines,[13] azoalkanes,[14] and alkynes.[15] In this regard, we have been investigating the reactivity of the newly prepared diiron allenyl complex $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2{}_{\alpha,\beta}\text{-}(H)C_\alpha{=}C_\beta{=}C_\gamma H_2\}]$ (**1**) and found that primary and secondary phosphines react via regiospecific nucleophilic attack at C_α to afford phosphino-substituted μ-η^1:η^2-alkenyl complexes[16] while amines react at CO or C_β to give amido-functionalized alkenyl complexes and dimetallacyclopentanes, respectively.[17] As part of our ongoing investigations into the general reactivity of **1** with nucleophiles, we have examined its reaction with organolithium reagents.

To the best of our knowledge, the reactions of binuclear complexes of σ-η-unsaturated hydrocarbyl ligands with organolithium reagents has not been reported. Herein, we report details of the synthesis and characterization of **1**, including its single-crystal X-ray structure and solution NMR properties. Complex **1** reacts with a range of organolithium reagents to give the binuclear β,γ-unsaturated ketones $[Fe_2(CO)_5\{P(OMe)_3\}(\mu\text{-}PPh_2)(\mu\text{-}\eta^1{:}\eta^2\text{-}\{RC(O)CH_2\}C{=}CH_2)]$ (R = Me, **3a**; ^{n}Bu, **3b**; Ph, **3c**; C_4H_3S, **3d**), *via* an unusual nucleophile–carbonyl–allenyl coupling sequence. The selectivity of this reaction is quite remarkable and suggests that μ-η^1:η^2-allenyl complexes may yet find a role as three carbon transfer reagents in the synthesis of complex unsaturated carbonyl compounds. Indeed, such a strategy, if applied to other C2-, C3-, and C4-binuclear μ-σ-η-hydrocarbyl complexes of group VIII, lends itself to the synthesis of an even broader range of unsaturated products.[18] In addition, this strategy, if extended to include more elaborate organolithium reagents, also holds promise for preparing highly functionalized carbonyl compounds.

Experimental Section

General Procedures. Unless otherwise stated, all manipulations were carried out in an inert atmosphere glovebox or using standard Schlenk line techniques. Diethyl ether and hexane were distilled from potassium/sodium alloy, tetrahydrofuran from potassium, and dichloromethane from calcium hydride. Deuteriochloroform was predried with calcium hydride, then vacuum transferred and stored over 4 Å molecular sieves. Solution infrared spectra were recorded on a Mattson Genesis FTIR spectrometer operating WINFIRST software. Prop-2-yne bromide was purchased from Aldrich Chemical Co. and used without further purification. Reactions were monitored by thin layer chromatography (Baker flex, silica gel, 1B-F). Reagent grade methanol and propan-2-ol were used without further purification. Column chromatography was carried out with alumina purchased from Aldrich Chemical Co. and deactivated with 6% w/w water. The diiron complex $[Fe_2(CO)_7(\mu\text{-}PPh_2)]^-Na^+$ was prepared as previously described.[19]

Preparation of $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2{}_{\alpha,\beta}\text{-}(H)C_\alpha{=}C_\beta{=}C_\gamma H_2\}]$ (1). A slight excess of propargyl bromide (0.51 mL, 4.30 mmol) was added to a solution of $[Fe_2(CO)_6(\mu\text{-}PPh_2)]^-Na^+$ (2.10 g, 4.30 mmol) in diethyl ether (50 mL). The solution was left to stir overnight, during which time the color changed from deep red to intense golden yellow with the appearance of a precipitate. The solution was filtered using a cannula and the solvent removed to leave a sticky amber oil. This residue was dissolved in a minimum volume of dichloromethane (1–2 mL), and the solution was absorbed onto deactivated alumina, desolvated, placed on a 330 × 30 mm column, and eluted with hexane. The first major yellow band to elute was collected and crystallized from acetonitrile to give **1** as deep orange red crystals in 55% yield (1.30 g). IR (ν(CO), cm^{-1}, C_6H_{14}): 2063 m, 2031 s, 2000 m, 1990 w, 1980 m 1974 w. $^{31}P\{^1H\}$ NMR (81.0 MHz, $CDCl_3$, 298 K): δ 173.9 (s). ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 4.5 (s, br $HC{=}C{=}CH_2$, 2H), 7.0–7.4 (m, C_6H_5, 10H), 8.7 (ddd, $^4J_{HH} = {}^4J_{HH} = 4.15$ Hz, $^3J_{PH} = 9.52$ Hz, $HC{=}C{=}CH_2$, ^1H). $^{13}C\{^1H\}$ NMR (125.7 MHz, $CDCl_3$, 230 K): δ 212.1 (s, br CO), 212.0 (d, $^2J_{PC} = 12.6$ Hz, CO), 209.1 (d, $^2J_{PC} = 33.0$ Hz, CO), 207.0 (d, $^2J_{PC} = 21.4$ Hz, CO), 180.0 (s, $HC{=}C{=}CH_2$), 139.0 (d, ipso, $^1J_{PC} = 40.0$ Hz), 133.0 (m, C_6H_5), 130.1 (s, para), 129.7 (s, para), 128.3 (d, $^3J_{PC} = 10.0$ Hz, ortho), 127.3 (d, $^2J_{PC} = 11.2$ Hz, ortho), 118.3 (d, $^2J_{PC} = 23.8$ Hz, $CH{=}C{=}CH_2$), 96.2 (s, $CH{=}C{=}CH_2$). Anal. Calcd for $C_{21}H_{13}Fe_2O_6P$: C, 50.05; H, 2.60. Found: C, 50.71; H, 2.58.

Preparation of $[Fe_2(CO)_5\{P(OMe)_3\}(\mu\text{-}PPh_2)(\mu\text{-}\eta^1{:}\eta^2\text{-}\{MeC(O)CH_2\}C{=}CH_2)]$ (3a). Methyllithium (0.4 mmol) was added to complex **1** (0.200 g, 0.4 mmol) in diethyl ether (30 mL) at −78 °C, and the mixture was stirred for 0.5 h. The resulting dark solution was allowed to warm to −20 °C, treated with tetrafluoroboric acid dimethyl ether complex (0.048 mL, 0.4 mmol), and allowed to warm to room temperature, during which time a deep red coloration appeared. The resulting

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[18] For example: C2, $-C{\equiv}CR^1$ (acetylide), $CR^1{=}CR^2R^3$ (vinyl), $C{=}CR^1R^2$ (alkylidene); C3, $-CR^1{=}CR^2{=}CR^3R^4$ (allyl), $-CR^1{=}C{=}CR^2R^3$ (allenyl), $-CR^1R^2{=}C(R^3)C{=}CR^4R^5$ (butadienylidene), $-C{\equiv}CC{\equiv}CR^1$ (butadiynyl).

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mixture was filtered, the solvent removed under reduced pressure, and the oily residue dissolved in fresh diethyl ether. Trimethyl phosphite (0.061 mL, 0.5 mmol) was added, and the solution was left to stir overnight. The solvent was removed, the product extracted into dichloromethane, and the resultant solution absorbed onto deactivated alumina. After removal of excess solvent, the sample was placed on a 300 × 30 mm alumina column and eluted with *n*-hexane/dichloromethane (70:30 v/v) to afford a single major band corresponding to **2a**. The collected fraction was crystallized from dichloromethane/*n*-hexane at room temperature to afford deep red X-ray quality crystals of **3a** (40%, 0.100 g). IR (ν(CO), cm^{-1}, $\mathrm{C_6H_{14}}$): 2038 s, 1976 s, 1958 s, 1925 w, 1603 w. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ (200.5 MHz, $\mathrm{CDCl_3}$, δ): 177.0 (d, $^2J_{\mathrm{PP}} = 89.1$ Hz, $\mathrm{P(OMe)_3}$), 168.9 (d, $^2J_{\mathrm{PP}} = 89.1$ Hz, μ-$\mathrm{PPh_2}$). ^{1}H NMR (500.1 MHz, $\mathrm{CDCl_3}$, δ): 7.17–7.58 (m, 10H, $\mathrm{C_6}\mathit{H}_5$), 4.41 (d, $^2J_{\mathrm{HH}} = 12.8$ Hz, ^{1}H, $\mathrm{C}\mathit{H}_\mathrm{c}\mathrm{H_dC(O)Me}$), 3.62 (d, $^3J_{\mathrm{PH}} = 11.0$ Hz, 9H, $\mathrm{P(OC}\mathit{H}_3)_3$), 3.16 (d, $^2J_{\mathrm{HH}} = 12.8$ Hz, ^{1}H, $\mathrm{CH_c}\mathit{H}_\mathrm{d}\mathrm{C(O)Me}$), 2.69 (ddd, $^3J_{\mathrm{PH}} = 12.3$ Hz, $^3J_{\mathrm{PH}} = 7.0$ Hz, $^2J_{\mathrm{HH}} = 2.8$ Hz, ^{1}H, $\mathrm{C}\mathit{H}_\mathrm{a}\mathrm{H_b{=}C}$), 2.21 (ddd, $^3J_{\mathrm{PH}} = 11.2$ Hz, $^3J_{\mathrm{PH}} = 10.8$ Hz, $^2J_{\mathrm{HH}} = 2.8$ Hz, ^{1}H, $\mathrm{CH_a}\mathit{H}_\mathrm{b}\mathrm{{=}C}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (125.7 MHz, $\mathrm{CDCl_3}$, δ): 216.7 (dd, $^2J_{\mathrm{PC}} = 23.7$ Hz, $^2J_{\mathrm{PC}} = 20.3$ Hz, CO), 215.3 (dd, $^2J_{\mathrm{PC}} = 37.7$ Hz, $^2J_{\mathrm{PC}} = 5.5$ Hz, CO), 212.0 (br, s, $\mathit{C}\mathrm{O}$), 207.0 (s, $\mathit{C}\mathrm{(O)Me}$), 179.4 (d, $^2J_{\mathrm{PC}} = 22.6$ Hz, $\mathit{C}\mathrm{{=}CH_2}$), 128.0–140.0 (m, $\mathit{C}_6\mathrm{H_5}$), 72.2 (s, $\mathit{C}\mathrm{H_2C(O)Me}$), 71.1 (dd, $^2J_{\mathrm{PC}} = 14.4$ Hz, $^2J_{\mathrm{PC}} = 5.4$ Hz, $\mathrm{C{=}}\mathit{C}\mathrm{H_2}$), 52.5 (d, $^2J_{\mathrm{PC}} = 6.3$ Hz, $\mathrm{P(O}\mathit{C}\mathrm{H_3)_3}$), 28.9 (s, $\mathrm{C(O)}\mathit{C}\mathrm{H_3}$). Anal. Calcd for $\mathrm{C_{25}H_{26}Fe_2O_9P_2}$: C, 46.62; H, 4.07. Found: C, 46.53; H, 4.04.

Compounds **3b**–**d** were prepared using a procedure similar to that described above for **3a**. Selected spectroscopic and analytical data are listed for all compounds.

Preparation of [$\mathbf{Fe_2(CO)_5\{P(OMe)_3\}(\mu\text{-}PPh_2)(\mu\text{-}\eta^1{:}\eta^2\text{-}\{BuC(O)CH_2\}C{=}CH_2)}$] (3b). Obtained as deep orange crystals in 54% yield from dichloromethane/*n*-hexane at room temperature. IR (ν(CO), cm^{-1}, $\mathrm{C_6H_{14}}$): 2041 s, 1984 s, 1975 s, 1965 m, 1927 w, 1605 w. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ (200.5 MHz, $\mathrm{CDCl_3}$, δ): 177.5 (d, $^2J_{\mathrm{PP}} = 85.0$ Hz, $\mathrm{P(OMe)_3}$), 167.7 (d, $^2J_{\mathrm{PP}} = 85.0$ Hz, μ-$\mathrm{PPh_2}$). ^{1}H NMR (500.1 MHz, $\mathrm{CDCl_3}$, δ): 7.16–7.61 (m, 10H, $\mathrm{C_6}\mathit{H}_5$), 4.42 (d, $^2J_{\mathrm{HH}} = 12.8$ Hz, ^{1}H, $\mathrm{C}\mathit{H}_\mathrm{c}\mathrm{H_dC(O)^nBu}$), 3.61 (d, $^3J_{\mathrm{PH}} = 11.1$ Hz, 9H, $\mathrm{P(OC}\mathit{H}_3)_3$), 3.14 (d, $^2J_{\mathrm{HH}} = 12.8$ Hz, 1H, $\mathrm{CH_c}\mathit{H}_\mathrm{d}\mathrm{C(O)Bu}$), 2.75 (ddd, $^3J_{\mathrm{PH}} = 15.2$ Hz, $^3J_{\mathrm{PH}} = 10.2$ Hz, $^2J_{\mathrm{HH}} = 3.0$ Hz, 1H, $\mathrm{C}\mathit{H}_\mathrm{a}\mathrm{H_bC}$), 2.67 (m, 2H, C(O)Bu), 2.20 (ddd, $^3J_{\mathrm{PH}} = 11.4$ Hz, $^3J_{\mathrm{PH}} = 8.8$ Hz, $^2J_{\mathrm{HH}} = 3.0$ Hz, 1H, $\mathrm{CH_a}\mathit{H}_\mathrm{b}\mathrm{C}$), 1.50 (m, 2H, C(O)*Bu*), 1.30 (m, 2H, C(O)*Bu*), 0.86 (t, $^3J_{\mathrm{HH}} = 7.4$ Hz, 3H, C(O)*Bu*). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (125.7 MHz, $\mathrm{CDCl_3}$, δ): 216.9 (dd, $^2J_{\mathrm{PC}} = 24.3$ Hz, CO), 215.2 (dd, $^2J_{\mathrm{PC}} = 35.7$ Hz, $^2J_{\mathrm{PC}} = 5.6$ Hz, CO), 212.0 (br, s, $\mathit{C}\mathrm{O}$), 209.0 (s, $\mathit{C}\mathrm{(O)Bu}$), 180.0 (d, $^2J_{\mathrm{PC}} = 22.1$ Hz, $\mathit{C}\mathrm{{=}CH_2}$), 128.0–140.0 (m, $\mathit{C}_6\mathrm{H_5}$), 71.2 (s, $\mathit{C}\mathrm{H_2CO}$), 71.2 (dd, $^2J_{\mathrm{PC}} = 14.7$ Hz, $^2J_{\mathrm{PC}} = 5.4$ Hz, $\mathrm{C{=}}\mathit{C}\mathrm{H_2}$), 52.6 (d, $^2J_{\mathrm{PC}} = 7.0$ Hz, $\mathrm{P(O}\mathit{C}\mathrm{H_3)_3}$), 41.6 (s, C(O)*Bu*), 25.8 (s, C(O)*Bu*), 22.4 (s, C(O)*Bu*), 14.0 (s, C(O)*Bu*). Anal. Calcd for $\mathrm{C_{28}H_{32}Fe_2O_9P_2}$: C, 48.98; H, 4.70. Found: C, 49.03; H, 4.56.

Preparation of [$\mathbf{Fe_2(CO)_5\{P(OMe)_3\}(\mu\text{-}PPh_2)(\mu\text{-}\eta^1{:}\eta^2\text{-}\{PhC(O)CH_2\}C{=}CH_2)}$] (3c). Obtained as deep orange crystals from dichloromethane/*n*-hexane at room temperature; overall yield 44%. IR (ν(CO), cm^{-1}, $\mathrm{C_6H_{14}}$): 2037 s, 1977 s, 1962 s, 1926 w, 1603 w. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ (200.5 MHz, $\mathrm{CDCl_3}$, δ): 178.5 (d, $^2J_{\mathrm{PP}} = 83.0$ Hz, $\mathrm{P(OMe)_3}$), 167.7 (d, $^2J_{\mathrm{PP}} = 83.0$ Hz, μ-$\mathrm{PPh_2}$). ^{1}H NMR (500.1 MHz, $\mathrm{CDCl_3}$, δ): 7.12–8.00 (m, 15H, $\mathrm{C_6}\mathit{H}_5$), 5.14 (d, $^2J_{\mathrm{HH}} = 15.2$ Hz, 1H, $\mathrm{C}\mathit{H}_\mathrm{c}\mathrm{H_dC(O)Ph}$), 3.69 (d, $^2J_{\mathrm{HH}} = 15.2$ Hz, 1H, $\mathrm{CH_c}\mathit{H}_\mathrm{d}\mathrm{C(O)Ph}$), 3.65 (d, $^3J_{\mathrm{PH}} = 11.0$ Hz, 9H, $\mathrm{P(OC}\mathit{H}_3)_3$), 2.67 (ddd, $^3J_{\mathrm{PH}} = 15.8$ Hz, $^3J_{\mathrm{PH}} = 10.4$ Hz, $^2J_{\mathrm{HH}} = 3.5$ Hz, 1H, $\mathrm{C}\mathit{H}_\mathrm{a}\mathrm{H_b{=}C}$), 2.30 (ddd, $^3J_{\mathrm{PH}} = 11.8$ Hz, $^3J_{\mathrm{PH}} = 9.0$ Hz, $^2J_{\mathrm{HH}} = 3.5$ Hz, 1H, $\mathrm{CH_a}\mathit{H}_\mathrm{b}\mathrm{{=}C}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (125.7 MHz, $\mathrm{CDCl_3}$, δ): 216.9 (dd, $^2J_{\mathrm{PC}} = 23.3$ Hz, CO), 215.2 (dd, $^2J_{\mathrm{PC}} = 35.7$ Hz, $^2J_{\mathrm{PC}} = 5.6$ Hz, CO), 212.0 (br, s, $\mathit{C}\mathrm{O}$), 198.9 (s, $\mathit{C}\mathrm{(O)Ph}$), 179.9 (d, $^2J_{\mathrm{PC}} = 21.8$ Hz, $\mathit{C}\mathrm{{=}CH_2}$), 127.0–141.0 (m, $\mathit{C}_6\mathrm{H_5}$), 71.6 (dd, $^2J_{\mathrm{PC}} = 14.6$ Hz, $^2J_{\mathrm{PC}} = 5.4$ Hz, $\mathrm{C{=}}\mathit{C}\mathrm{H_2}$), 65.7 (s, $\mathit{C}\mathrm{H_2C(O)Ph}$), 52.5 (d, $^2J_{\mathrm{PC}} = 5.3$ Hz, $\mathrm{P(O}\mathit{C}\mathrm{H_3)_3}$). Anal. Calcd for $\mathrm{C_{30}H_{29}Fe_2O_9P_2}$: C, 50.93; H, 4.13. Found: C, 50.03; H, 4.56.

Preparation of [$\mathbf{Fe_2(CO)_5\{P(OMe)_3\}(\mu\text{-}PPh_2)(\mu\text{-}\eta^1{:}\eta^2\text{-}\{C_4H_3SC(O)CH_2\}C{=}CH_2)}$] (3d). Obtained as deep orange crystals in 46% yield from dichloromethane/*n*-hexane at room temperature. IR (ν(CO), cm^{-1}, $\mathrm{C_6H_{14}}$): 2037 s, 1977 s, 1963 s, 1925 w, 1604 w. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ (200.5 MHz, $\mathrm{CDCl_3}$, δ): 177.9 (d, $^2J_{\mathrm{PP}} = 85.0$ Hz, $\mathrm{P(OMe)_3}$), 168.4 (d, $^2J_{\mathrm{PP}} = 85.0$ Hz, μ-$\mathrm{PPh_2}$). ^{1}H NMR (500.1 MHz, $\mathrm{CDCl_3}$, δ): 7.88 (dd, $^2J_{\mathrm{HH}} = 3.8$ Hz, $^2J_{\mathrm{HH}} = 1.1$ Hz, 1H, $\mathrm{C_4H_3S}$), 7.69 (dd, $^2J_{\mathrm{HH}} = 3.9$ Hz, $^2J_{\mathrm{HH}} = 1.1$ Hz, 1H, $\mathrm{C_4}\mathit{H}_3\mathrm{S}$), 7.63 (m, 2H, $\mathrm{C_6}\mathit{H}_5$), 7.00–7.40 (m, $\mathrm{C_6}\mathit{H}_5$, 8H, $\mathrm{C_4H_3S}$, 1H), 5.09 (d, $^2J_{\mathrm{HH}} = 14.3$ Hz, 1H, $\mathrm{C}\mathit{H}_\mathrm{c}\mathrm{H_dCO}$), 3.71 (d, $^3J_{\mathrm{PH}} = 11.1$ Hz, 9H, $\mathrm{P(OC}\mathit{H}_3)_3$), 3.70 (d, $^2J_{\mathrm{HH}} = 14.3$ Hz, 1H, $\mathrm{CH_c}\mathit{H}_\mathrm{d}\mathrm{CO}$), 2.82 (ddd, $^3J_{\mathrm{PH}} = 15.7$ Hz, $^3J_{\mathrm{PH}} = 7.0$ Hz, $^2J_{\mathrm{HH}} = 3.2$ Hz, 1H, $\mathrm{C}\mathit{H}_\mathrm{a}\mathrm{H_b{=}C}$), 2.37 (ddd, $^3J_{\mathrm{PH}} = 11.8$ Hz, $^3J_{\mathrm{PH}} = 9.0$ Hz, $^2J_{\mathrm{HH}} = 3.2$ Hz, 1H, $\mathrm{CH_a}\mathit{H}_\mathrm{b}\mathrm{{=}C}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (125.7 MHz, $\mathrm{CDCl_3}$, δ): 217.0 (dd, $^2J_{\mathrm{PC}} = 22.5$ Hz, $^2J_{\mathrm{PC}} = 21.3$ Hz, CO), 215.4 (dd, $^2J_{\mathrm{PC}} = 35.0$ Hz, $^2J_{\mathrm{PC}} = 5.5$ Hz, CO), 212.0 (br, s, $\mathit{C}\mathrm{O}$), 207.1 (s, $\mathit{C}\mathrm{(O)C_4H_3S}$), 178.9 (d, $^2J_{\mathrm{PC}} = 21.4$ Hz, $\mathit{C}\mathrm{{=}CH_2}$), 127–144 (m, $\mathit{C}_6\mathrm{H_5}$ and $\mathrm{C(O)}\mathit{C}_4\mathrm{H_3S}$), 72.3 (s, $\mathit{C}\mathrm{H_2CO}$), 71.2 (dd, $^2J_{\mathrm{PC}} = 14.3$ Hz, $^2J_{\mathrm{PC}} = 5.2$ Hz, $\mathrm{C{=}}\mathit{C}\mathrm{H_2}$), 66.3 (s, $\mathit{C}\mathrm{H_2CO}$), 52.6 (d, $^2J_{\mathrm{PC}} = 6.3$ Hz, $\mathrm{P(O}\mathit{C}\mathrm{H_3)_3}$). Anal. Calcd for $\mathrm{C_{28}H_{26}Fe_2O_9P_2S}$: C, 47.20; H, 3.68. Found: C, 46.81; H, 3.34.

Crystal Structure Determination of 1 and 3a. Single crystals of both compounds were obtained by recrystallization from dichloromethane/*n*-hexane solutions at room temperature. Intensity data were collected on a Siemens SMART CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) and narrow frames (0.3° steps in ω). Cell parameters were refined from the observed setting angles of all strong reflections in each complete data set. Data were corrected for Lorentz and polarization effects and for absorption by a semi-empirical method based on analysis of symmetry-equivalent and repeated data. This analysis additionally indicated no significant intensity decay. The structures were solved by direct methods and refined on F^2 values by full-matrix least-squares for all unique data, Table 1. All non-H atoms were refined anisotropically. Phenyl and methyl H atoms were constrained with U_{iso} set at 1.2 (1.5 for methyl groups) times U_{eq} for the parent atom. Coordinates were freely refined for H-atoms on C(1) and C(3) for **1** and on C(1) for **3a**, with U_{iso} set as described above. Programs used were SHELXTL[20a] for structure solution, refinement, and molecular graphics, Siemens SMART (control) and SAINT[20b] (integration), and local programs on Silicon Graphics Indy workstations and personal computer systems.

Results and Discussion

Synthesis. The binuclear phosphido-bridged allenyl complexes [$\mathrm{M_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2\text{-}(Ph)C{=}C{=}CR_2\}}$] (M = Ru, Os; R = H, Me, Ph) are readily prepared *via* the carbon–carbon coupling reaction between $\mathrm{R_2CN_2}$ and $\mathrm{C_\alpha}$ of the acetylide in [$\mathrm{M_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CPh)}$].[21] In contrast, [$\mathrm{Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}C^tBu)}$] reacts with diazomethane to afford the butadienylidene complex [$\mathrm{Fe_2(CO)_5(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2{:}\eta^2\text{-}CH_2C(^tBu)C{=}CH_2\}}$],[22] presumably via the desired but kinetically reactive allenyl complex [$\mathrm{Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2\text{-}(^tBu)C{=}C{=}CH_2\}}$]. Thus, in order to conduct a comparative study between ruthenium and iron phosphido-bridged allenyl complexes, it became important to develop an alternative synthesis. Several years ago, Seyferth and co-workers developed a convenient high-yield synthesis of the sulfido-bridged complexes [$\mathrm{Fe_2(CO)_6(\mu\text{-}SR)\{\mu\text{-}\eta^1{:}\eta^2_{\alpha,\beta}\text{-}(H)C{=}C{=}CH_2\}}$] by reacting [$\mathrm{Fe_2(CO)_7(\mu\text{-}SR)}$]$^-$ with

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[20] (a) Sheldrick, G. M. *SHELXTL*, version 5; Siemens Analytical X-ray Instruments, Inc.: Madison, WI. (b) *SMART and SAINT software for CCD diffractometers*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI.

[21] (a) Nucciarone, D.; Taylor, N. J.; Carty, A. J. *Organometallics* **1986**, *5*, 1179. (b) Cherkas, A. A.; Randall, S. M.; MacLaughlin, S. A.; Mott, G. N.; Taylor, N. J.; Carty, A. J. *Organometallics* **1988**, *7*, 969.

[22] Breckenridge, S. M.; MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1991**, 1718.

Table 1. Summary of Crystal Data and Structure Determination for Compounds 1 and 3a

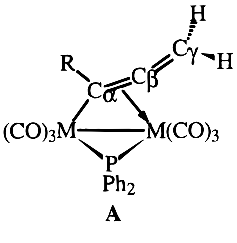
	1	**3a**
mol form	$C_{21}H_{13}Fe_2O_6P$	$C_{25}H_{26}Fe_2O_9P_2$
fw	503.98	644.10
temperature, K	160(2)	160(2)
cryst size, mm	0.50 × 0.40 × 0.38	0.64 × 0.26 × 0.21
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a, Å	16.6824(9)	9.9361(6)
b, Å	9.0201(5)	21.8451(13)
c, Å	15.1966(8)	12.6218(7)
β, deg	109.546(2)	91.847(2)
V, Å^3	2155.0(2)	2738.2(3)
Z	4	4
D_{calcd}, g cm^{-3}	1.553	1.562
μ, mm^{-1}	1.454	1.227
F(000)	1016	1320
no. of reflns for cell refinement (θ range, deg)	12 144 (2.59−28.56)	19 160 (1.61−28.37)
θ range, deg	1.30−28.70	1.86−28.38
max indices: *hkl*	−21 to 18, −11 to 11, −18 to 20	−12 to 13, −27 to 25, −15 to 11
no. of reflns measured	15 410	16 653
no. of unique reflns	5064	6225
no. of reflns with $F^2 > 2\sigma(F^2)$	4545	5376
transmission coefficient range	0.545−0.638	0.582−0.762
R_{int} (on F^2)	0.0183	0.0197
weighting parameters[a] a, b	0.0282, 0.8885	0.0267, 1.1747
extinction coefficient x[b]	0.0012(2)	0.00139(13)
R1 $[F^2 > 2\sigma(F^2)]$[c]	0.0278	0.0249
wR2 [all data][d]	0.0670	0.0610
no. of params	281	354
GOF[e] on F^2	1.099	1.039
max, min in diff map, e Å^{-3}	0.360, −0.313	0.318, −0.284

[a] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = (F_o^2 + 2F_c^2)/3$. [b] $F'_c = F_c(1 + 0.001xF_c^2\lambda^3/\sin 2\theta)^{-1/4}$. [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [d] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. [e] $\text{GOF} = [\Sigma w(F_o^2 - F_c^2)^2/(\text{no. of unique reflns} - \text{no. of params})]^{1/2}$.

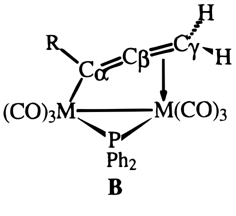
$RC{\equiv}CCH_2X$ (X = Cl, Br).[23] This suggested to us that, if accessible, $[Fe_2(CO)_7(\mu\text{-}PPh_2)]^-$ should provide a practical route to the desired allenyl complex $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2{}_{\alpha,\beta}\text{-}(H)C{=}C{=}CH_2\}]$, thus avoiding use of the carcinogenic explosive CH_2N_2.

A solution of $[Fe_2(CO)_7(\mu\text{-}PPh_2)]^-Na^+$ in diethyl ether was treated with prop-2-ynyl bromide, stirred overnight, filtered, and then purified by column chromatography. This led to the isolation of $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2{}_{\alpha,\beta}\text{-}(H)C_\alpha{=}C_\beta{=}C_\gamma H_2\}]$ (**1**) as a yellow oil, which, because of its reluctance to crystallize, was initially characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy.[16] We have now found that concentrated acetonitrile solutions of **1** (2.0 g in 3−4 mL) deposit large orange-red crystals suitable for X-ray diffraction, further spectroscopic characterization, and use in stoichiometric reactions. The ^1H NMR spectrum of **1** contains an exchange-broadened resonance associated with $C_\gamma H_2$ (*vide infra*) and a single high-field signal corresponding to the proton attached to C_α. ^{13}C NMR spectroscopy is a particularly reliable probe of structure and bonding in binuclear allenyl complexes,[24] and the chemical shifts of $\delta(C_\beta)$ 180.0, $\delta(C_\alpha)$ 118.3, and $\delta(C_\gamma)$ 79.0 are close to those previously reported for $[Fe_2(CO)_6(\mu\text{-}SR)\{\mu\text{-}\eta^1{:}\eta^2{}_{\alpha,\beta}\text{-}(H)C{=}C{=}CH_2\}]$, which contains an allenyl ligand coordinated through the $C_\alpha{-}C_\beta$ double bond to a second iron atom.[23] The protons attached to C_γ resonate close to the region commonly associated with olefinic protons ($\delta(C_\gamma H_aH_b)$ = 4.90, 4.12), again suggesting $\mu\text{-}\eta^1{:}\eta^2{}_{\alpha,\beta}$ coordination of the allenyl ligand. Indeed, the respective chemical shifts for the allenyl ligand in $[M_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2{}_{\beta,\gamma}\text{-}(Ph)C{=}C{=}CH_2\}]$ ($\delta(C_\gamma)$ = 1.0, Ru; −3.3, Os; $\delta(C_\gamma H_aH_b)$ = 2.11, 1.46, Ru; 2.54, 1.71, Os) are vastly different from those of **1** and in both cases reflect a uniquely different $\mu\text{-}\eta^1{:}\eta^2{}_{\beta,\gamma}$ bonding arrangement for the allenyl ligand.[25]

X-ray Structure of $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2{}_{\alpha,\beta}\text{-}(H)C_\alpha{=}C_\beta{=}C_\gamma H_2\}]$. A number of bonding modes have now been established for allenyl ligands in binuclear complexes.[26] For homometallic complexes, $\mu\text{-}\eta^1{:}\eta^2{}_{\alpha,\beta}$-bonding, with the metal π-bound through the $C_\alpha{-}C_\beta$ double bond,[21a] is well established while both $\mu\text{-}\eta^1{:}\eta^2{}_{\alpha,\beta}$- and $\mu\text{-}\eta^2{:}\eta^3$-bonding are commonplace in heterometallic complexes.[27] Recently, Carty and co-workers demonstrated the existence of the bond coordination isomers $\mu\text{-}\eta^1{:}\eta^2{}_{\alpha,\beta}$ (**A**) and $\mu\text{-}\eta^1{:}\eta^2{}_{\beta,\gamma}$ (**B**), in which the π-coordinated allenyl ligand is attached *via* the $C_\alpha{-}C_\beta$ and $C_\beta{-}C_\gamma$ double bonds, respectively.[25] Although we were confident of our formulation of **1** as $\mu\text{-}\eta^1{:}\eta^2{}_{\alpha,\beta}$-coordi-



A



B

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[23] (a) Seyferth, D.; Womack, G. B.; Archer, C. M.; Dewan, J. C. *Organometallics* **1989**, *8*, 430. (b) Seyferth, D.; Archer, C. M.; Ruschke, D. P.; Cowie, M.; Hilts, R. W. *Organometallics* **1991**, *10*, 3363.

[24] Cherkas, A. A.; Breckenridge, S. M.; Carty, A. J. *Polyhedron* **1991**, *11*, 1075.

[25] Carleton, N.; Corrigan, J. F.; Doherty, S.; Pixneur, R.; Sun, Y.; Taylor, N. J.; Carty, A. J. *Organometallics* **1994**, *13*, 4179.

[26] For recent comprehensive reviews on allenyl chemistry, see: (a) Doherty, S.; Corrigan, J. F.; Carty, A. J.; Sappa, E. *Adv. Organomet. Chem.* **1995**, *37*, 39. (b) Wojcicki, A. *New J. Chem.* **1994**, *18*, 61. (c) Wojcicki, A.; Shuchart, C. E. *Coord. Chem. Rev.* **1990**, *105*, 35.

[27] Young, G. H.; Raphael, M. V.; Wojcicki, A.; Calligaris, M.; Nardin, G.; Bresciani-Pahor, N. *Organometallics* **1991**, *10*, 1934.

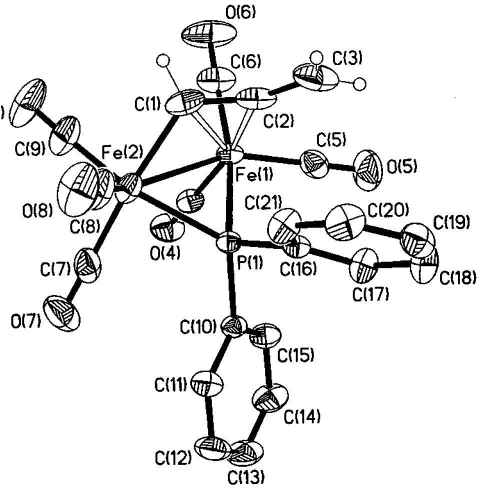


Figure 1. Molecular structure of $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1\text{:}\eta^2_{\alpha,\beta}\text{-}(H)C_\alpha{=}C_\beta{=}C_\gamma H_2\}]$ (**1**) illustrating the $\mu\text{-}\eta^1\text{:}\eta^2_{\alpha,\beta}$ coordination of the allenyl ligand to Fe(1). Phenyl hydrogen atoms have been omitted. Carbonyl carbons have the same numbers as oxygen atoms. Ellipsoids are at the 50% probability level.

nated, a single-crystal X-ray structure analysis was undertaken in order to provide precise structural details.

A perspective view of the molecular structure together with the atomic numbering scheme is shown in Figure 1, and selected bond distances and angles are given in Table 2. The molecular structure clearly shows that the allenyl ligand is σ-bonded via C(1) to Fe(2) (Fe(2)−C(1) 1.969(2) Å) and π-bonded to Fe(1) through C(1)−C(2) (Fe(1)−C(1) 2.0948(17) Å, Fe(1)−C(2) 2.0908(17) Å). The bond lengths C(1)−C(2) (1.365(3) Å) and C(2)−(3) (1.316(3) Å) are substantially different and reflect this bonding arrangement. The allenyl ligand in $[Fe_2(CO)_6(\mu\text{-}S^tBu)\{\mu\text{-}\eta^1\text{:}\eta^2_{\alpha,\beta}\text{-}(H)C{=}C{=}CH_2\}]$ is coordinated in a similar $\mu\text{-}\eta^1\text{:}\eta^2_{\alpha,\beta}$-manner, and a comparable elongation of the π-coordinated C−C double bond was noted.[23] The angle C(1)−C(2)−C(3) (153.1(2) °) in **1** is noticeably smaller than that in $[Ru_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1\text{:}\eta^2_{\beta,\gamma}\text{-}(Ph)C{=}C{=}CH_2\}]$ (172.3(3)°) in which the allenyl is coordinated through the $C_\beta-C_\gamma$ double bond.[27] The preferential coordination through $C_\alpha-C_\beta$ in **1** is somewhat surprising, since this bonding arrangement requires a substantial distortion from pure metalloallenic character compared with the alternative of $C_\beta-C_\gamma$ coordination for which the filled π-orbital is orientated favorably for η^2-interaction with a second metal atom. This distortion is most evident in the dihedral angle of 106.1° between the planes defined by H(1)−C(1)−Fe(2) and H(3a)−C(3)−H(3b). At this stage, we tentatively speculate that the preferred bonding arrangement in **1** is the result of shorter M−M bonding interactions for first row transition metals compared with their heavier counterparts. The remaining structural characteristics associated with the bridging hydrocarbyl ligand, the metal atom framework, and ancillary ligands are similar to those in $[Fe_2(CO)_6(\mu\text{-}S^tBu)\{\mu\text{-}\eta^1\text{:}\eta^2_{\alpha,\beta}\text{-}(H)C{=}C{=}CH_2\}]$.[23]

^{1}H and ^{13}C NMR Studies. Carty[14a] and Seyferth[23] have both described a dynamic exchange in binuclear allenyl complexes of group VIII, concluding that the exchange mechanism is similar to the "windshield-wiper" motion of μ-σ-π-bound alkenyl and acetylide ligands. In order to further investigate the ligand exchange process in σ-π-allenyl complexes, variable-temperature ^{1}H and ^{13}C NMR studies were performed, the results of which are shown in Figures 2 and 3, respectively.

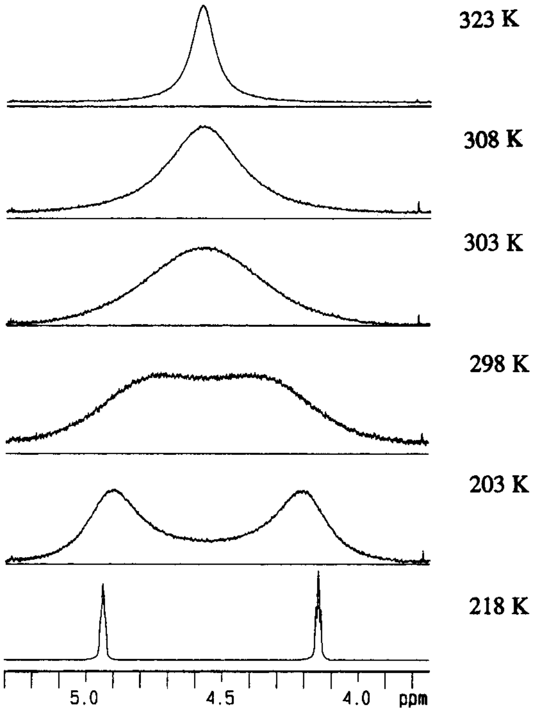


Figure 2. Variable-temperature ^{1}H NMR spectra of $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1\text{:}\eta^2_{\alpha,\beta}\text{-}(H)C_\alpha{=}C_\beta{=}C_\gamma H_2\}]$ (**1**).

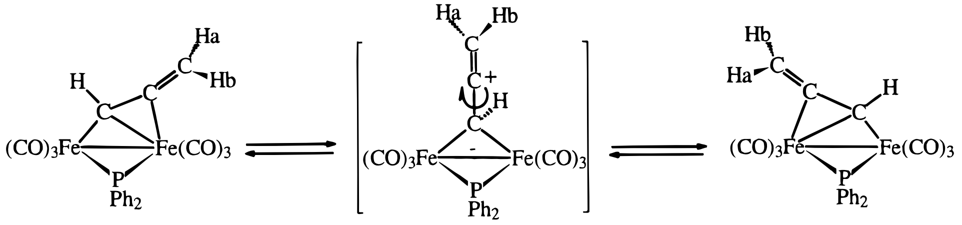
Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound 1

Fe(1)−Fe(2)	2.5907(3)	Fe(1)−C(1)	2.0948(17)
Fe(1)−C(2)	2.0908(17)	Fe(2)−C(1)	1.969(2)
C(1)−C(2)	1.365(3)	C(2)−C(3)	1.317(3)
Fe(2)−P(1)	2.2072(4)	Fe(1)−P(1)	2.2504(4)
Fe(1)−C(5)	1.7753(19)	Fe(1)−C(4)	1.7976(17)
Fe(2)−C(7)	1.799(2)	Fe(1)−C(6)	1.8102(18)
Fe(2)−C(8)	1.780(2)	Fe(2)−C(9)	1.814(2)
C(1)−C(2)−C(3)	153.1(2)	Fe(1)−P(1)−Fe(2)	71.060(14)
Fe(2)−C(1)−C(2)	126.64(13)		

The room-temperature ^{1}H NMR spectrum of **1** contains a single exchange-broadened resonance at δ 4.51 associated with $C_\gamma H_aH_b$, while the proton attached to C_α appears as a sharp multiplet to low-field of the aromatic region. As the temperature is lowered, the former resonance sharpens into two distinct signals at δ 4.89 and 4.12, and at 218 K, they eventually appear as an ABX doublet of doublets. Using a coalescence temperature of 298 K, the free energy of activation for exchange of H_a and H_b was calculated to be $\Delta G^\ddagger = 13.4$ kcal mol^{-1}. This value is close to that calculated for the exchange of Me_a and Me_b in $[Fe_2(CO)_6(\mu\text{-}S^tBu)\{\mu\text{-}\eta^1\text{:}\eta^2_{\alpha,\beta}\text{-}(H)C{=}C{=}CMe_aMe_b\}]$, strongly suggesting that similar exchange mechanisms operate in both complexes.

Variable-temperature $^{13}C\{^1H\}$ NMR spectra of **1** are shown in Figure 3. The low-temperature spectrum of **1** (223 K) contains three distinct carbonyl resonances, each with different J_{PC} coupling constants, together with a single exchange-broadened signal, which presumably corresponds to coalescence of a similar set of three resonances. Raising the temperature results in a sharpening of the exchange-broadened resonance and collapse of the remaining set of three carbonyl reso-

Scheme 1. Exchange of the σ- and π-Allenyl Bonding Interactions in 1[a]



[a] One possible mechanism responsible for the interchange of H_a and H_b.

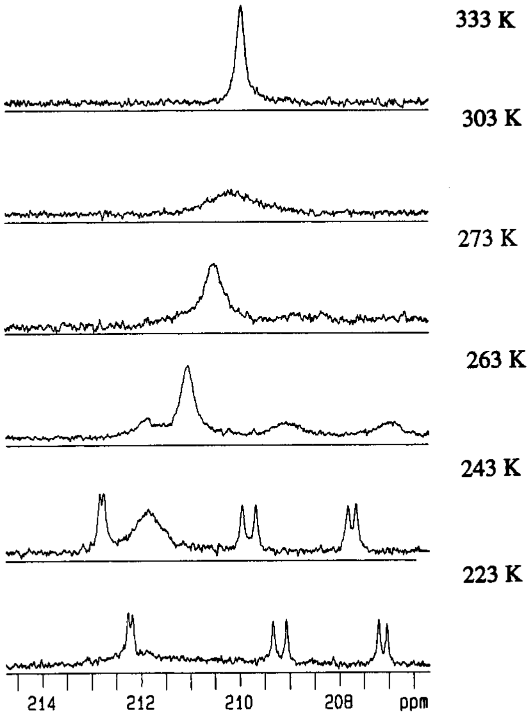


Figure 3. Variable-temperature $^{13}C\{^1H\}$ NMR spectra of $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2{}_{\alpha,\beta}\text{-}(H)C_\alpha{=}C_\beta{=}C_\gamma H_2\}]$ (**1**) in the carbonyl region.

nances. Above room temperature (303−333 K), the ^{13}C NMR spectrum contains a single resonance at δ 210.5, corresponding to rapid exchange of all six carbonyl ligands. Qualitatively these line broadening characteristics define three fluxional processes, a low-energy trigonal rotation (turnstile mechanism) that equilibrates one set of three carbonyls, a similar higher energy process that occurs between 243 and 273 K, and an additional process responsible for exchanging the two independent iron sites. In contrast, even at room temperature the $^{13}C\{^1H\}$ NMR spectrum of $[Ru_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2{}_{\alpha,\beta}\text{-}(Ph)C{=}C{=}CPh_2\}]$ contains six unique resonances consistent with its solid state structure, although a single nondegenerate trigonal rotation was observed between 303 and 363 K. This is the most striking difference between the $^{13}C\{^1H\}$ NMR spectra of $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2{}_{\alpha,\beta}\text{-}(H)C{=}C{=}CH_2\}]$ and $[Ru_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2{}_{\alpha,\beta}\text{-}(Ph)C{=}C{=}CPh_2\}]$, namely that within similar temperature limits we observe vastly disparate exchange regimes, the fast exchange limit in the former and a static structure in the latter.

The spectroscopic studies described above are consistent with the dynamic process shown in Scheme 1, which involves interchange of the σ and π bonding interactions via a windshield-wiper type motion that involves rotation about a carbon−carbon single bond in a zwitterionic transition state.[28] Firstly, this mechanism accounts for the exchange of H_a and H_b, which necessitates free rotation about a C−C single bond. The same process is also responsible for equilibrating all six carbonyl ligands in the high-temperature limiting $^{13}C\{^1H\}$ spectrum of **1** (see Figure 3). Two low-energy nondegenerate turnstile mechanisms act to exchange the carbonyl ligands at each unique $Fe(CO)_3$ unit and only when both operate do all six carbonyls ligands begin to exchange. Nondegenerate trigonal rotations in $\mu\text{-}\sigma\text{-}\eta^2$-coordinated hydrocarbyl complexes are commonplace,[29] the lowest energy process usually being associated with the π-coordinated $Fe(CO)_3$ fragment. The process described by Scheme 1 is closely related to the σ-π-fluxionality of binuclear alkenyl,[29,30] acetylide,[31] and acyl[32] complexes. In the vast majority of cases, σ-π-allenyl fluxionality in binuclear complexes of group VIII involves exchange of the diastereotopic substituents (H or Me) attached to C_γ,[21a] although, in the case of $[\{Mo(C_5H_4Me)(CO)_2\}_2\{\mu\text{-}\eta^2{:}\eta^3\text{-}C(H){=}C{=}CH_aH_b\}]^+$, Curtis and co-workers reported that the three ^1H NMR signals associated with the bridging allenyl ligand were temperature independent, even though the proposed mechanism of exchange should have equilibrated H_a and H_b.[33] In contrast, σ-π-alkenyl fluxionality has only rarely been reported to exchange the diastereotopic C_β protons.[34]

Reaction of 1 with Organolithium Reagents. A solution of **1** in diethyl ether was cooled to −78 °C and treated with 1.1 equiv of organolithium reagent RLi (R = Me, *n*-butyl, Ph, C_4H_3S). After 30 min of stirring, the solution was allowed to warm to −20 °C and then quenched with a tetrafluoroboric acid−dimethyl ether complex to afford a deep cherry red solution of $[Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1(O){:}\eta^1(C){:}\eta^2(C)\text{-}\{RC(O)CH_2\}C{=}CH_2)]$ (R = Me, **2a**; ^{n}Bu, **2b**, Ph, **2c**; C_4H_3S, **2d**). Unfortunately, our attempts to purify **2a**−**d** using column chromatography (alumina deactivated with 6% water) proved unsuccessful, although the IR spectra of these compounds are similar to those of the closely related amido-functionalized alkenyl complexes $[Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1(O){:}\eta^1(\mathbf{C}){:}\eta^2(\mathbf{C})\{RHNC(O)CH_2\}C{=}CH_2)]$ prepared

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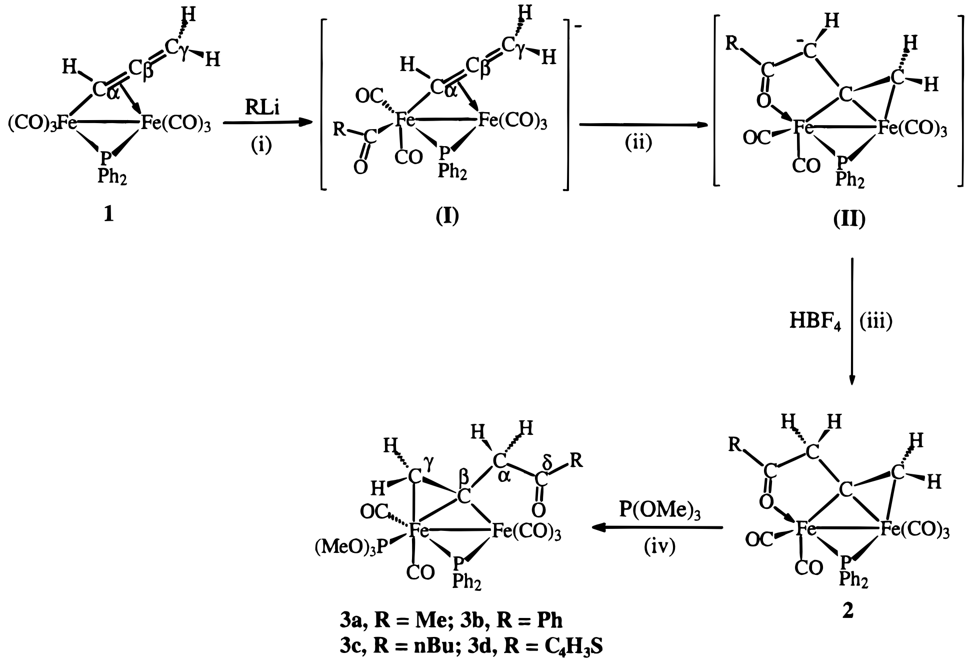
Scheme 2[a]



[a] (i) Reaction of **1** with RLi to give acylate (**I**), (ii) migration of RCO to C$_\alpha$ of the allenyl, (iii) protonation of enolate (**II**), and (iv) substitution of the metal-coordinated ester carbonyl by trimethyl phosphite.

earlier in our laboratory.[17] However, stable derivatives of **2a**–**d** were prepared by adding trimethyl phosphite to the reaction mixture prior to work-up, which resulted in the appearance of a golden yellow coloration and the high-yield formation of [Fe$_2$(CO)$_5${P(OMe)$_3$}(μ-PPh$_2$)(μ-η^1:η^2-{RC(O)CH$_2$}C=CH$_2$)] (**3a**–**d**) (Scheme 2). The ^{1}H NMR spectra of **3a**–**d** each contain four distinct sets of resonances corresponding to the diastereotopic protons of the β,γ-unsaturated carbonyl ligand. For each compound **3a**–**d**, two of these signals, the vinylic resonances, appear as complex multiplets with a small geminal coupling constant ($^2J_{HH}$ = 2.80–3.0 Hz) and additional couplings to both the phosphido bridge and the trimethyl phosphite ligand, while the remaining two signals appear as doublets with considerably larger geminal couplings ($^2J_{HH}$ = 12.0–13.0 Hz). For each compound **3a**–**d** the ^{13}C{^{1}H} NMR spectrum contains three distinctive resonances, two at low field, one in the region commonly associated with C$_\alpha$ of a μ-η^1:η^2-alkenyl bridging ligand,[23] the other a ketonic carbonyl (δ 175–210), and one at high field (δ 65–75), coupled to the phosphido bridge (J_{PC} = 14.7 Hz) which corresponds to C$_\beta$ of the bridging alkenyl ligand.

A single-crystal X-ray study of **3a** was undertaken in order to provide precise structural details. The molecular structure, shown in Figure 4, identifies **3a** as [Fe$_2$(CO)$_5${P(OMe)$_3$}(μ-PPh$_2$)(μ-η^1:η^2-{MeC(O)CH$_2$}C=CH$_2$)], formally derived from allenyl **1** via methyl–carbonyl–allenyl coupling and protonation at C$_\alpha$ of the allenyl ligand. The most notable feature of this structure is the β,γ-unsaturated ketone, σ-coordinated to Fe(2) (Fe(2)–C(2) = 1.9969(16) Å) and η^2-coordinated to Fe(1) (Fe(1)–C(1) = 2.1605(16); Fe(1)–C(2) = 2.0959(15) Å). The C(1)–C(2) bond length (1.398(2) Å) is comparable to previously reported values in alkenyl-bridged complexes[29,30] and shows the expected elongation upon coordination to a metal center. The alkenyl ligand adopts the familiar endo conformation with respect to the phosphido ligand, presumably to avoid unfavorable steric interactions between the substitutents on C$_\alpha$ and the phenyl substituent on the bridging phosphido group. A comparison of the structure of **3a** with [Fe$_2$(CO)$_5$(μ-PPh$_2$)(μ-η^1(C):η^1:(C):η^2(C)-{^{i}PrOC(O)CH$_2$}C=CH$_2$)],[35] which also contains a functionalized alkenyl bridging ligand, reveals that substitution of the metal-coordinated ester carbonyl with trimethyl phosphite results in a significant reduction of the Fe–C π-bond length (Table 4). The preference for trimethyl phosphite to coordinate to the η^2-bound iron is likely to be electronic in origin, reflecting enhanced back-donation and stronger metal–carbon and weaker carbon–

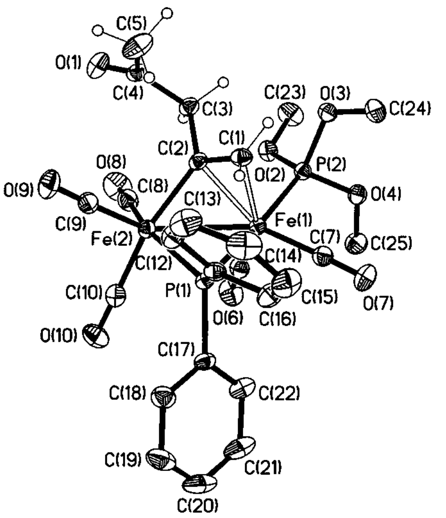


Figure 4. Molecular structure of [Fe$_2$(CO)$_5${P(OMe)$_3$}(μ-PPh$_2$)(μ-η^1:η^2-{MeC(O)CH$_2$}C=CH$_2$)] (**3a**) highlighting the σ-η^2-coordinated β,γ-unsaturated ketone. Phenyl and phosphite methyl hydrogen atoms have been omitted. Carbonyl carbons have the same numbers as oxygen atoms. Ellipsoids are at the 50% probability level.

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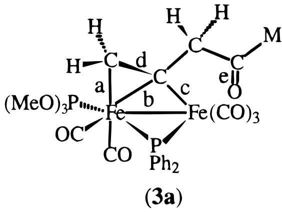
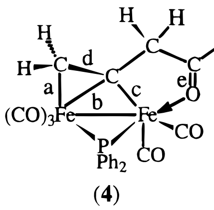
Table 3. Selected Bond Distances (Å) and Angles (deg) for Compound 3a

Fe(1)−Fe(2)	2.5930(3)	Fe(1)−C(1)	2.1605(16)
Fe(1)−C(2)	2.0959(15)	Fe(1)−P(2)	2.1666(4)
Fe(1)−P(1)	2.2457(5)	Fe(1)−C(7)	1.7669(17)
Fe(1)−C(6)	1.7719(17)	Fe(2)−C(2)	1.9969(16)
Fe(2)−P(1)	2.2191(5)	Fe(2)−C(8)	1.8218(17)
Fe(2)−C(9)	1.7758(18)	Fe(2)−C(10)	1.8105(18)
C(1)−C(2)	1.398(2)	C(2)−C(3)	1.532(2)
C(3)−C(4)	1.519(2)	C(4)−O(1)	1.210(2)
C(4)−C(5)	1.504(3)		
P(1)−Fe(1)−P(2)	174.953(18)	C(1)−C(2)−C(3)	115.26(14)
C(2)−C(3)−C(4)	110.62(13)	C(3)−C(4)−C(5)	117.32(15)
Fe(1)−P(1)−Fe(2)	71.007(14)		

Table 4. Comparison of the Fe−C, C−C, and C═O Bond Lengths in $[Fe_2(CO)_5\{P(OMe)_3\}(\mu\text{-}PPh_2)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}\{MeC(O)CH_2\}C{=}CH_2)]$ and $[Fe_2(CO)_5(\mu\text{-}PPh_2)(\mu\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{-}\{{}^iPrCO(O)CH_2\}C{=}CH_2)]$



(**3a**)



(**4**)

bond type	bond distance (Å) for **3a**	bond distance (Å) for **4**
a	2.1605(16)	2.179(3)
b	2.0959(15)	2.135(3)
c	1.9969(16)	1.956(3)
d	1.398(2)	1.398(4)
e	1.210(2)	1.229(3)

carbon bonding, although this latter effect does not manifest itself in elongation of the carbon−carbon bond length.

The formation of **3a,b** from the reaction of organolithium nucleophiles with complex **1** is consistent with the formation of a metal acyl intermediate. Thomas and co-workers have suggested that iron tricarbonyl complexes of vinyl ketones react with nucleophiles via an acyl intermediate prior to transfer to the vinyl ketone and subsequent protonation.[4] At this stage, we tentatively suggest that **1** reacts with RLi to give the acylate intermediate (**I**). Migration of the RCO group to C_α of the allenyl, to give the enolate (**II**), followed by protonation at C_α and substitution of the metal-coordinated ester carbonyl with trimethyl phosphite leads to **3a**−**d** (Scheme 2). Further reactivity studies are currently underway to identify the intermediate enolate complexes and further exploit their reactivity.

Conclusions. Binuclear allenyl complexes of group VIII have previously been synthesized via carbon−carbon bond formation between CH_2 and C_α of the acetylide in $[M_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{\equiv}CPh)]$ (M= Ru, Os).[21] However, a similar reaction involving $[Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{\equiv}C^tBu)]$ and CH_2N_2 led, not to the desired allenyl complex $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}(^tBu)\text{-}C_\alpha{=}C_\beta{=}C_\gamma H_2\}]$, but to the butadienylidene complex $[Fe_2(CO)_5(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-}CH_2C(^tBu)C{=}CH_2\}]$,[22] presumably via addition of CH_2 to C_α of a highly reactive allenyl intermediate. The binuclear phosphido-bridged allenyl complex $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1\text{:}\eta^2{}_{\alpha,\beta}\text{-}(H)\text{-}C_\alpha{=}C_\beta{=}C_\gamma H_2\}]$ (**1**) has been isolated from the reaction between $[Fe_2(CO)_7(\mu\text{-}PPh_2)]^-Na^+$ and propargyl bromide. This synthesis, based on a strategy developed by Seyferth in the late 1980's for preparing the sulfido-bridged allenyl complexes $[Fe_2(CO)_6(\mu\text{-}SR)\{\mu\text{-}\eta^1\text{:}\eta^2{}_{\alpha,\beta}\text{-}(R)\text{-}C_\alpha{=}C_\beta{=}C_\gamma H_2\}]$,[23] has now enabled us to explore fully the reactivity of previously inaccessible phosphido-bridged iron allenyl complexes.

Our reactivity studies have shown $[Fe_2(CO)_6(\mu\text{-}PPh_2)\text{-}\{\mu\text{-}\eta^1\text{:}\eta^2{}_{\alpha,\beta}\text{-}(H)C_\alpha{=}C_\beta{=}C_\gamma H_2\}]$ (**1**) to be highly reactive toward protic and aprotic nucleophiles; primary, secondary, and tertiary phosphines all react regiospecifically at C_α while primary amines react at CO and/or C_β of the allenyl ligand.[16,17] We have now found that alkyllithium reagents react with **1**, via a highly selective nucleophile−carbonyl−allenyl coupling sequence, to give the β,γ-unsaturated carbonyl compounds $[Fe_2(CO)_5\text{-}\{P(OMe)_3\}(\mu\text{-}PPh_2)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}\{RC(O)CH_2\}C{=}CH_2)]$ (R = Me, Et, ^{n}Bu, C_4H_3S). Until now, β,γ-unsaturated carbonyl compounds have typically been synthesized using mononuclear iron complexes of unsaturated hydrocarbyl ligands,[36] for example, direct nucleophilic attack of R^- on a coordinated vinylketone,[9] bis(diphenylphosphino)-methane-induced migration of CO into an η^3-allyl ligand,[37] and reaction of organic electrophiles with the anionic allyl complex $[(\eta^3\text{-allyl})Fe(CO)_3]^-$.[38] Although unexpected, the synthesis of β,γ-unsaturated carbonyl compounds at a binuclear center and the selectivity of the coupling sequence suggest that it should be possible to access an even broader range of unsaturated carbonyl compounds simply by extending this strategy to include other C_2, C_3, and C_4 σ-η-hydrocarbyl complexes or by reacting **1** with more elaborate organolithium reagents.

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Supporting Information Available: Text giving the experimental and computational procedures and tables of the details of structure determination, non-hydrogen atomic positional parameters, full listings of bond distances and angles, anisotropic displacement parameters, and hydrogen atomic coordinates for **1** and **3a** (12 pages). Ordering information is given on any current masthead page. Observed and calculated structure factor tables are available from the authors upon request.

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