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Reaction of Phosphites with the Electrophilic Allenyl Complex $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2\text{-}(H)C_\alpha{=}C_\beta{=}C_\gamma H_2\}]$: Stepwise Transformation of a $\mu\text{-}\eta^1{:}\eta^2$-Allenyl into a $\mu\text{-}\eta^1{:}\eta^2$-Acetylide *vs* Phosphite Activation

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Summary: Nucleophilic addition of $P(OR)_3$ *(R = Me, Et) to the electrophilic allenyl ligand in* $[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1{:}\eta^2\text{-}(H)C_\alpha{=}C_\beta{=}C_\gamma H_2\}]$ ***(1)*** *affords the* β,γ-*unsaturated phosphonate-bridged complexes* $[Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1{:}\eta^2\text{-}(CH_3)C{=}CH\{PO(OR)_2\})]$*, which we suggest result either from an Arbuzov-type dealkylation or a direct nucleophilic attack of water on the phosphorus atom of a zwitterionic phosphonium intermediate. In contrast, in the presence of PhC≡CLi, which acts to remove extraneous water from the reaction mixture,* $P{-}C_\alpha$ *bond formation followed by a 1,3-hydrogen migration gives* $[Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1{:}\eta^1\text{-}(CH_3)C{=}C\{P(OR)_3\})]$ *as the dominant product.*

As interest in the synthetic applications of transition metal allenyl ($-C(H){=}C{=}CH_2$) complexes intensifies, so reports of new and exciting reactivity patterns and transformations have begun to emerge.[1] In particular, the last decade has witnessed several noteworthy transformations which include the generation of central-carbon-substituted allyls *via* regiospecific nucleophilic addition to η^1-allenyl and η^3-allenyl/propargyl complexes,[2] reversible formation of an acylallenyl complex *via* migratory insertion/elimination of CO into a $\mu\text{-}\eta^1{:}\eta^2$-allenyl ligand,[3] precoordination of amine nucleophiles prior to formation of *N*-arylated η^3-azatrimethylenemethane complexes,[4] cycloaddition reactions,[5] regiospecific addition of phosphorus-based nucleophiles at C_α in $\mu\text{-}\eta^1{:}\eta^2$-allenyl complexes,[6] and novel coupling sequences, as well as new ligand bonding modes and isomerization pathways and reactivities of both mononuclear and binuclear complexes.[7] These examples suggest that, either σ- or σ-η-coordinated, the allenyl fragment offers immense potential as a building block for the synthesis of a wide range of unsaturated organic molecules. In this regard, we have recently shown that 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 organolithium reagents to give the β,γ-unsaturated ketones $[Fe_2(CO)_5(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1(O)\eta^1(C){:}\eta^2(C){-}\{RC(O)CH_2\}C{=}CH_2\}]$ *via* an unusual nucleophile−carbonyl−allenyl coupling sequence.[8] As part of our ongoing investigation into the reactivity of **1**, we reasoned that a similar coupling sequence involving alkynyllithium reagents would lead to useful organic intermediates, such as cyclopentenones. We now report that PhC≡CLi does not react directly with **1** but instead prevents facile hydrolysis of a zwitterionic phosphonium intermediate by removing extraneous water from the reaction mixture.

Herein, we wish to report some unprecedented reactivity of electrophilic σ-η-coordinated hydrocarbyls, including: (i) the transformation of a $\mu\text{-}\eta^1{:}\eta^2$-allenyl ligand ($-C(H){=}C{=}CH_2$) into a bridging acetylide ($-C{\equiv}CCH_3$) *via* stepwise $P{-}C_\alpha$ bond formation, 1-3-hydrogen migration, and $P{-}C_\alpha$ bond cleavage and (ii) the formation of an unusual α,β-unsaturated phosphonate *via* the addition of $P(OR)_3$ to an electrophilic $\mu\text{-}\eta^1{:}\eta^2$-allenyl ligand and an Arbuzov-type dealkylation. Hydrogen migration at a coordinated allenyl ligand has no literature precedent, although there have been reports of 1,3-metallotropic shifts[9] and a pseudorotation pathway,[7a] both of which interconvert η^1-allenyl complexes with their η^1-propargyl counterparts, the latter *via* a five-coordinate η^3-allenyl/propargyl intermediate. Additionally, the activation of trialkyl phosphites by an electrophilic σ-η-hydrocarbyl ligand also has no literature precedent, although trimethyl phosphite has been reported to react with $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_5H_5)$ to give the phosphonate-substituted complex $(\eta^5\text{-}C_5H_5)Fe(CO)_2\{PO(OMe)_2\}$.[10]

Addition of $P(OR)_3$ (R = Me, Et) to an etheral solution 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**) containing PhC≡CLi results in the isolation of $[Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1{:}\eta^1\text{-}(CH_3)C{=}C\{P(OR)_3\})]$ (**2a**, R = Me; **2b**, R = Et) as the major product after chromatographic work-up and crystallization. In contrast, in the absence of PhC≡CLi, **1** reacts with $P(OR)_3$ to give $[Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1{:}\eta^2\text{-}(CH_3)C{=}CH\{PO(OR)_2\})]$ (**3a**, R = Me; **3b**, R = Et) in yields of up to 65%. Notably, only minor

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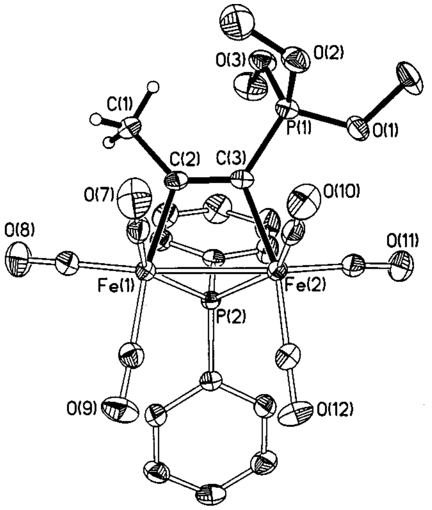

Figure 1. Molecular structure of $[Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1\text{:}\eta^1\text{-}(CH_3)C{=}C\{P(OMe)_3\})]$ (**2a**) with atom labels and 50% probability ellipsoids. Phenyl and OMe hydrogen atoms and the minor disorder component of $P(OMe)_3$ are omitted for clarity. Carbonyl C atoms have the same numbers as the O atoms.

quantities of **3a** and **3b** (<5%) have been isolated when $PhC{\equiv}CLi$ is present in the reaction mixture. The $^{31}P\{^1H\}$ NMR spectra of **2a**,**b** and **3a**,**b** each contain two sets of resonances, one at low field in the region characteristic of a phosphido ligand bridging a metal−metal bond, the other at much higher field. The high-field shift of this latter resonance strongly suggests that both products contain a carbon-coordinated phosphite.[11,12]

The molecular structure of **2a**, shown in Figure 1, revealed that the two iron atoms are bridged by a zwitterionic phosphite-substituted alkyne,[13] with a short C(2)−C(3) bond (1.342(4) Å) and appreciable multiple bond character. The P(1)−C(3) bond length (1.723(3) Å) is considerably shorter than expected for a zwitterionic phosphonium complex and, together with a short Fe(1)−C(2) (2.004(3) Å) bond, indicates a substantial contribution from a carbene−phosphorus ylide resonance form. The assignment of a low-field resonance in the $^{13}C\{^1H\}$ NMR spectra of **1a** and **1b** (δ 222.7, **1a**; 218.3, **1b**) to C_β of the bridging alkyne further supports the carbenoid nature of this carbon. The conversion of a $\mu\text{-}\eta^1\text{:}\eta^2$-allenyl fragment into a $\mu\text{-}\eta^1\text{:}\eta^2$-acetylide is unprecedented and most likely involves a 1,3-hydrogen migration *via* the unstable intermediate phosphite-substituted zwitterionic allene (**A**) (Scheme 1). The addition of phosphorus-based nucleophiles to electrophilic $\sigma\text{-}\eta$-hydrocarbyl fragments is now commonplace, and numerous zwitterionic phosphonium complexes have been crystallographically characterized.[14,15]

The molecular structure shown in Figure 2 identifies **3a** as $[Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}(CH_3)C{=}CH\{PO(OMe)_2\})]$, which contains a $\mu\text{-}\eta^1\text{:}\eta^2$-alkenyl ligand formally derived from **1** *via* an apparent Arbuzov-type dealkylation.[16] The principal feature of interest in **3a**,**b** is the bridging alkenyl−phosphonate which contains two methoxy substituents, a P=O double bond (P(1)−O(1) 1.465(2) Å) and an α,β-alkenyl functionality. The conversion of a trialkyl phosphite into a phosphonate by reaction with an electrophilic $\sigma\text{-}\eta$-coordinated hydrocarbyl fragment is unprecedented in polynuclear chemistry, although similar transformations have recently been reported for metal-coordinated phosphites.[17]

Isotopic labeling experiments have been conducted using $[^2H_1]\text{-}[Fe_2(CO)_6(\mu\text{-}PPh_2)\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}(D)C_\alpha{=}C_\beta{=}C_\gamma H_2\}]$, prepared from $BrCH_2C{\equiv}CD$[18] and $Na[Fe_2(CO)_7(\mu\text{-}PPh_2)]\cdot$thf, as previously described.[6b] The reaction of $[^2H_1]$-**1** with $P(OMe)_3$, in the presence of $PhC{\equiv}CLi$, results in deuterium incorporation solely at the methyl substituent. In contrast, in the absence of $PhC{\equiv}CLi$ but in the presence of water, $[^2H_1]$-**1** reacts with trimethyl phosphite to give $[^2H_1]\text{-}[Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1\text{:}\eta^2\text{-}(CH_3)C{=}CD\{PO(OMe)_2\})]$ ($^2H_1$-**3a**) as the sole deuterium-containing product. The isotopic composition of $^2H_1$-**2a** supports the 1,3-hydrogen migration suggested to explain the transformation of the $\mu\text{-}\eta^1\text{:}\eta^2$-allenyl ligand into the acetylide. Moreover, the isotopic composition of $^2H_1$-**3a** suggests that **2a** is unlikely to be an intermediate in its formation.

At this stage, we propose that the formation of **3a** involves initial nucleophilic attack of the trialkyl phosphite at C_α to afford $[Fe_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1\text{:}\eta^1\text{-}\{P(OMe)_3\}\text{-}HC{=}C{=}CH_2)]$ (*vide infra*), containing an unstable zwit-

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(11) Spectroscopic data for **2a** and **2b** are as follows. Compound **2a**: $^{31}P\{^1H\}$ NMR (202.0 MHz, $CDCl_3$, δ): 194.2 (s, μ-PPh_2), 17.0 (s, $P(OMe)_3$). ^1H NMR (200.13 MHz, $CDCl_3$, δ): 7.87−7.10 (m, C_6H_5, 10H), 3.24 (d, $^3J_{PH}$ = 11.4 Hz, 9H, $P(OCH_3)_3$), 2.22 (d, $^4J_{PH}$ = 1.4 Hz, 3H, $C{\equiv}CCH_3$). Anal. Calcd for $C_{24}H_{22}O_9P_2Fe_2$: C, 45.90; H, 3.53. Found: C, 46.08; H, 3.29. Compound **2b**: $^{31}P\{^1H\}$ NMR (202.0 MHz, $CDCl_3$, δ): 193.5 (d, $^3J_{PP}$ = 2.6 Hz, μ-PPh_2), 13.1 (d, $^3J_{PP}$ = 2.6 Hz, $P(OEt)_3$). ^1H NMR (500.0 MHz, $CDCl_3$, δ): 7.83−7.81 (m, C_6H_5, 2H), 7.61−7.57 (m, C_6H_5, 2H), 7.19−7.09 (m, C_6H_5, 6H), 3.48 (qAB, $^2J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, $P(OCH_2CH_3)_3$), 3.40 (qAB, $^2J_{HH}$ = 10.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, $P(OCH_2CH_3)_3$), 2.19 (d, $^4J_{PH}$ = 4.8 Hz, 3H, $C{\equiv}CCH_3$), 1.14 (dt, $^3J_{HH}$ = 7.0 Hz, $^4J_{PH}$ = 0.9 Hz, 9H, $P(OCH_2CH_3)_3$). Anal. Calcd for $C_{27}H_{28}O_9P_2Fe_2$: C, 48.39; H, 4.21. Found: C, 48.33; H, 4.04.

(12) Spectroscopic data for **3a** and **3b** are as follows. Compound **3a**: $^{31}P\{^1H\}$ NMR (202.0 MHz, $CDCl_3$, δ): 171.4 (d, $^3J_{PP}$ = 28.3 Hz, μ-PPh_2), 24.1 (d, $^3J_{PP}$ = 28.3 Hz, $PO(OMe)_2$). ^1H NMR (200.13 MHz, $CDCl_3$, δ): 7.51−7.19 (m, C_6H_5, 10H), 3.40 (d, $^3J_{PH}$ = 10.8 Hz, 6H, $O{=}P(OCH_3)_2$), 3.21 (s, 3H, $CH_3C{=}CH$), 2.14 (dd, $^2J_{PH}$ = 7.4 Hz, $^3J_{PH}$ = 9.7 Hz, 1H, $CH_3C{=}CH$). Anal. Calcd for $C_{23}H_{20}O_9P_2Fe_2$: C, 45.82; H, 3.68. Found: C, 45.39; H, 3.16. Compound **3b**: $^{31}P\{^1H\}$ NMR (202.0 MHz, $CDCl_3$, δ): 171.1 (d, $^3J_{PP}$ = 28.9 Hz, μ-PPh_2), 20.6 (d, $^3J_{PP}$ = 28.9 Hz, $P(OEt)_3$). ^1H NMR (500 MHz, $CDCl_3$, δ): 7.52−7.19 (m, C_6H_5, 10H), 3.83−3.48 (m, 4H, OCH_2CH_3), 3.15 (s, 3H, $CH_3C{=}C$), 2.18 (dd, $^2J_{PH}$ = 9.8 Hz, $^3J_{PH}$ = 7.0 Hz, $CH{=}C$), 1.01 (t, $^3J_{HH}$ = 7.0 Hz, 6H, OCH_2CH_3). Anal. Calcd for $C_{25}H_{26}O_9P_2Fe_2$: C, 46.76; H, 3.77. Found: C, 47.08; H, 3.39.

(13) Crystal data for **2a**: $C_{24}H_{22}Fe_2O_9P_2$, M = 628.1; monoclinic, space group $P2_1/c$; a = 10.0143(8) Å, b = 16.3022(13) Å, c = 16.5641(13) Å, β = 100.709(2)°, V = 2657.1(4) Å^3, Z = 4, T = 160 K, D_c = 1.570 g cm^{-3}, $F(000)$ = 1280, λ = 0.710 73 Å (Mo Kα), μ = 1.26 mm^{-1}. Intensity data were collected on a crystal of dimensions 0.14 × 0.19 × 0.34 mm mounted on a Siemens SMART CCD area detector diffractometer. Of 18 990 reflections measured (θ_{max} = 28.4°), 6079 were unique (R_{int} = 0.0321). Semi-empirical absorption corrections were applied (transmission 0.762−0.862). The structure was solved by direct methods and refined on F^2 with a statistical weighting scheme, anisotropic displacement parameters, constrained isotropic H atoms, and two-fold disorder of orientation of the $P(OMe)_3$ group. Final wR2 $= \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.0795$ for all data, conventional R = 0.0384 on F values of 5145 reflections having $F_o^2 > 2\sigma(F_o^2)$, S = 1.069 on F^2 for all data, and 364 refined parameters.

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(16) Crystal data for **3a**: $C_{23}H_{20}Fe_2O_9P_2$, M = 614.0; monoclinic, space group $P2_1/n$; a = 11.859(4) Å, b = 11.105(4) Å, c = 19.825(6) Å, β = 104.74(4)°, V = 2524.9(15) Å^3, Z = 4, T = 160 K, D_c = 1.615 g cm^{-3}, $F(000)$ = 1248, λ = 0.710 73 Å (Mo Kα), μ = 1.33 mm^{-1}. Intensity data were collected on a crystal of dimensions 0.14 × 0.19 × 0.34 mm mounted on a Siemens SMART CCD area detector diffractometer. Of 6974 reflections measured (θ_{max} = 25.0°), 4433 were unique (R_{int} = 0.0316). Corrections, structure solution, and refinement were as for **2a**: transmission 0.744−0.905, no disorder, wR2 = 0.0947, conventional R = 0.0362 (3549 reflections), S = 1.056, and 331 refined parameters. Programs used were standard control software, SHELXTL (Siemens Analytical X-ray Instrumentation Inc., Madison, Wi., version 5, 1994) and local programs.

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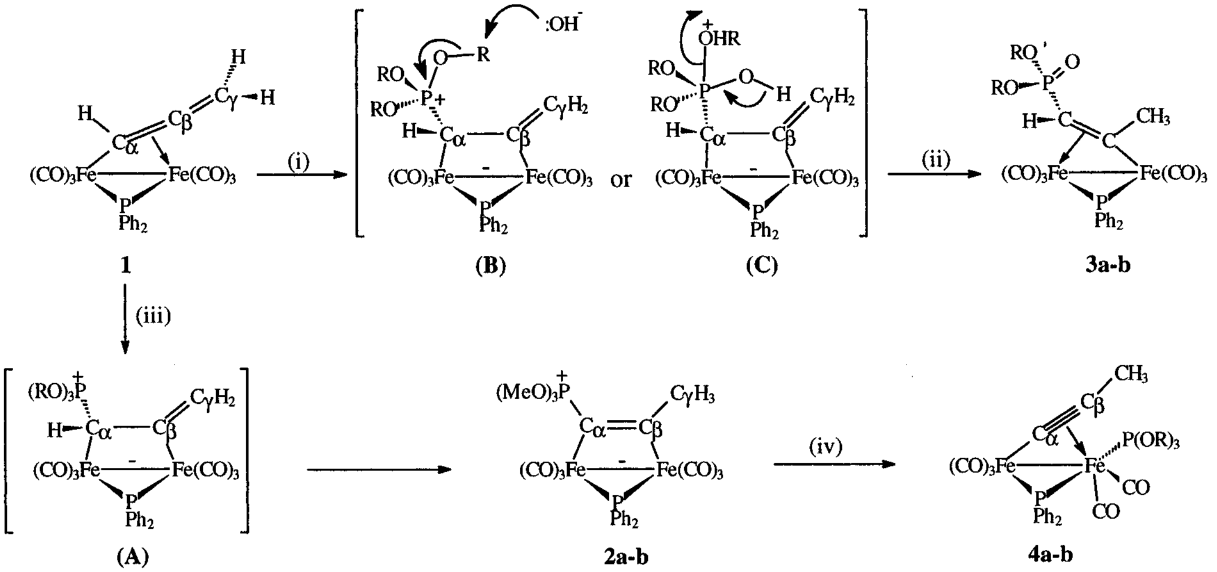
Scheme 1[a]



[a] (i) P−C$_\alpha$ bond formation to give the zwitterionic allene complex [Fe$_2$(CO)$_6$(μ-PPh$_2$){μ-η^1:η^1-{P(OR)$_3$}HC=C=CH$_2$}], (ii) formation of **3a**,**b** *via* an Arbuzov-type dealkylation (**B**) or a direct hydrolysis of the phosphonium center (**C**), (iii) formation of **2a**,**b** *via* the intermeidate zwitterionic allene (**C**) and a 1,3-hydrogen migration, (iv) decarbonylation and phosphite migration.

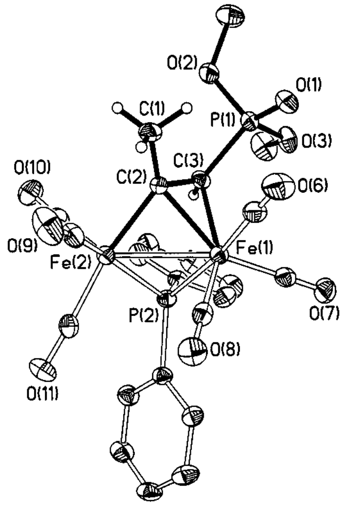


Figure 2. Molecular structure of [Fe$_2$(CO)$_6$(μ-PPh$_2$)(μ-η^1:η^2-(CH$_3$)C=CH{PO(OMe)$_2$})] (**3a**) with key atom labels and 50% probability ellipsoids. Phenyl hydrogen atoms are omitted for clarity.

terionic allene which readily undergoes an Arbuzov-type rearrangement in the presence of extraneous water (Scheme 1, **B**). As yet, though, we have not eliminated the possibility of direct nucleophilic attack of water at the phosphonium center of the proposed intermediate allene (Scheme 1, **C**), and studies are currently underway to distinguish between these two pathways. Irrespective of the mechanism, the formation of **3a**,**b** appears to require the participation of water when PhC≡CLi is omitted from the reaction mixture. In the presence of PhC≡CLi, the yields of **3a**,**b** are substantially reduced and 1,3-hydrogen migration becomes the dominant pathway. Interestingly, the sulfido-bridged allenyl complex [Fe$_2$(CO)$_6$(μ-SCy){μ-η^1:η^2-(H)-C$_\alpha$=C$_\beta$=C$_\gamma$H$_2$}][19] reacts with trimethyl phosphite to give [Fe$_2$(CO)$_6$(μ-SCy)(μ-η^1:η^1-{PO(OMe)$_2$}HC=C=CH$_2$)], bridged by a zwitterionic phosphite-substituted allene similar to intermediate **A** proposed in Scheme 1. The reactivity of this unusual bridging hydrocarbyl fragment toward various nucleophilic reagents is currently under investigation.

Upon standing, room temperature solutions of **2a**,**b** readily lose CO over several days to afford [Fe$_2$(CO)$_5$-{P(OR)$_3$}(μ-PPh$_2$)(μ-η^1:η^2-C≡CCH$_3$)] (**4a**,**b**), a transformation which occurs within several hours in refluxing *n*-hexane (Scheme 1).[20] The molecular structure of **4b** has been determined and will be reported in full in a later paper. Overall, the transformation of **1** into **4** converts a μ-η^1:η^2-allenyl ligand into a μ-η^1:η^2-acetylide and requires a 1,3-hydrogen migration and a phosphite migration.

In summary, the reaction of **1** with phosphites contrasts sharply with that previously reported for [Ru$_2$-(CO)$_6$(μ-PPh$_2$){μ-η^1:$\eta^2{}_{\beta,\gamma}$-(Ph)C$_\alpha$=C$_\beta$=C$_\gamma$H$_2$}], in which nucleophilic addition to C$_\beta$ is the dominant reaction pathway.[15a] Clearly, both the mode of allenyl coordination, μ-η^1:$\eta^2{}_{\alpha,\beta}$ vs μ-η^1:$\eta^2{}_{\beta,\gamma}$, and the substituents on C$_\alpha$ and C$_\gamma$ are likely to influence the reactivity, and in this regard we are currently investigating the reactivity of [Fe$_2$(CO)$_6$(μ-PPh$_2$){μ-η^1:η^2-(Ph)C$_\alpha$=C$_\beta$=C$_\gamma$H$_2$}] toward phosphites to compare with [Ru$_2$(CO)$_6$(μ-PPh$_2$){μ-η^1:η^2-(Ph)C$_\alpha$=C$_\beta$=C$_\gamma$H$_2$}] and determine if the reactivity of **1** is in fact determined by the kinetic accessibility of C$_\alpha$.

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Supporting Information Available: Tables of spectroscopic and analytical data for compounds **2a**,**b**, **3a**,**b**, and **4a**,**b** and tables giving full details of the crystal structure analyses of **2a** and **3a** (14 pages). Ordering information is given on any current masthead page.

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