

Oxidation of Metal Carbynes in the Presence of Alkynes. Alkyne Addition vs H-Shift in the Carbene Intermediate

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One-electron oxidation of the carbyne complex $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\{\text{P}(\text{OPh})_3\}\text{Mo}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (**1a**) in the presence of phenylacetylene results in H-abstraction and addition of the alkyne to the resulting metal carbene. The final product of the addition is the $\eta^1\eta^2$ -allyl complex $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\{\text{P}(\text{OPh})_3\}\text{Mo}[\eta^1:\eta^2\text{-CH}\{\text{P}(\text{OPh})_3\}\text{C}(\text{Ph})=\text{CH}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)]$ (**2a**), the structure of which was confirmed by X-ray crystallography.

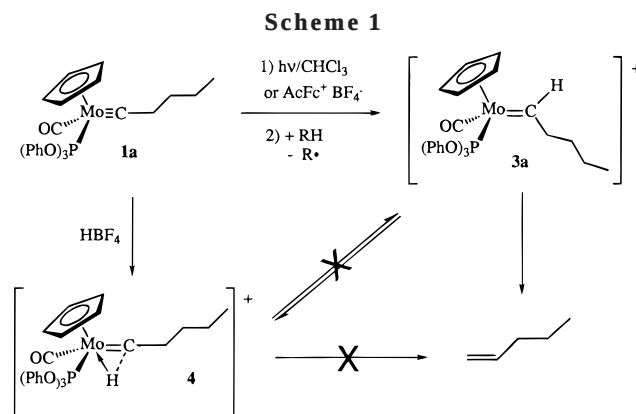
Introduction

We have previously reported that oxidation of the carbyne complexes $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\{\text{P}(\text{OR}')_3\}\text{M}\equiv\text{CR}$ [$\text{M} = \text{Mo}, \text{W}$; $\text{R} = \text{alkyl}$; $\text{R}' = \text{Me}, \text{Ph}$]¹ results in formation of 17-electron complexes that abstract hydrogen at the carbyne carbon to form cationic metal carbenes.^{2,3} When R is a primary alkyl group, hydride shift in the carbene complex yields an alkene as the final organic product. We now report that when $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\{\text{P}(\text{OPh})_3\}\text{Mo}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (**1a**) undergoes one-electron chemical oxidation in the presence of phenylacetylene, the H-shift pathway of the metal carbene intermediate is suppressed. Instead, addition of the alkyne and nucleophilic trapping with phosphite yield the $\eta^1\eta^2$ -allyl complex $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\{\text{P}(\text{OPh})_3\}\text{Mo}[\eta^1:\eta^2\text{-CH}\{\text{P}(\text{OPh})_3\}\text{C}(\text{Ph})=\text{CH}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)]$ (**2a**).

Results and Discussion

In prior studies, the oxidations were carried out by photochemical electron transfer from the carbyne complexes to CHCl_3 . However, there are aspects of this method that make it difficult to obtain products in high yield. Upon reduction, CHCl_3 fragments to Cl^- and $\cdot\text{CHCl}_2$.⁴ Evidence for side reactions involving the $\cdot\text{CHCl}_2$ radical can be found in the formation of CH_3Cl ⁵ by Arbuzov reaction of $\text{P}(\text{OMe})_3$ ligands.⁶ The use of outer sphere chemical oxidants⁷ at low temperatures provides an alternative approach in which side reactions from $\cdot\text{CHCl}_2$ can be avoided.

To confirm that chemical oxidation generates the same intermediates as photooxidation, butyl carbyne **1a** was reacted with acetylferrocenium tetrafluoroborate ($\text{AcFc}^+\text{BF}_4^-$). Photolysis of **1a** in the presence of CDCl_3



is known to result in the formation of 1-pentene (Scheme 1) in a process involving H-abstraction by the oxidized carbyne followed by a facile 1,2-hydride shift in the resulting carbene complex (**3a**).³ Observation of 1-pentene after oxidation of **1a** is thus a marker for the H-abstraction/H-shift sequence that is typical of these 17-electron alkyl carbynes. In the test reaction, a solution of **1a** in CD_2Cl_2 at -95°C was slowly mixed with a dilute solution of $\text{AcFc}^+\text{BF}_4^-$ in CD_2Cl_2 to yield a dark purple reaction mixture. Warming to ambient temperature produced an orange-brown solution whose color is characteristic of acetylferrocene. Analysis of the volatile components by ^1H NMR spectroscopy revealed the presence of 1-pentene, as also seen following photooxidation.

Once it had been established that oxidation of **1a** with $\text{AcFc}^+\text{BF}_4^-$ yields the same product as photooxidation, the reaction was carried out in the presence of phenylacetylene. A mixture of butyl carbyne **1a** plus 10 equiv of phenylacetylene was dissolved in CD_2Cl_2 . A dilute solution of acetylferrocenium tetrafluoroborate was then added at -95°C to yield a dark purple solution. Upon slow warming to ambient temperature, the reaction mixture became an orange-brown color similar to that observed in the absence of alkyne. Examination of the volatile components by ^1H NMR confirmed that no 1-pentene had been formed and thus, in the presence of the alkyne, the expected H-abstraction/H-shift sequence had been suppressed. Instead, compound **2a** was isolated in 25% yield (Scheme 2). In subsequent

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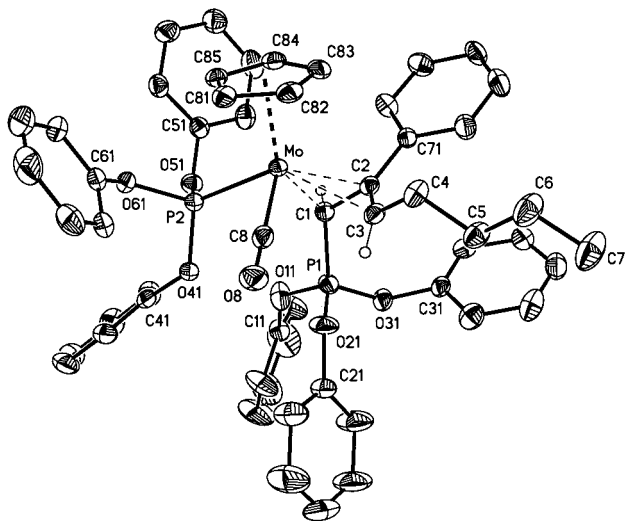
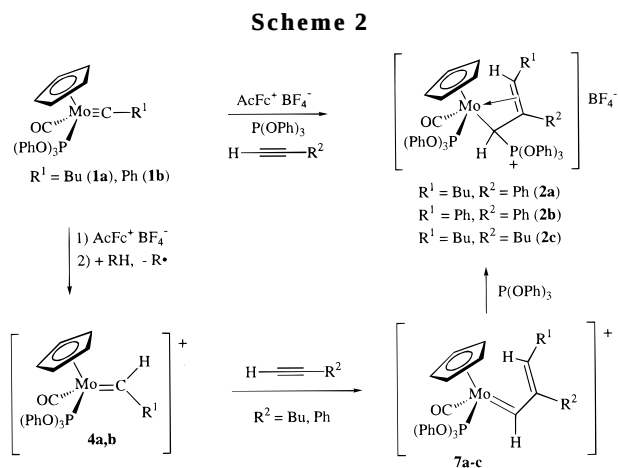


Figure 1. Thermal ellipsoid diagram of **2a** showing the crystallographic numbering scheme. Thermal ellipsoids are drawn at the 40% probability level. The majority of the hydrogens are removed for clarity.



experiments where 1 equiv of P(OPh)₃ was added to the reaction mixtures, the isolated yield of **2a** rose to 51%.

Slow recrystallization of **2a** in CH₂Cl₂/toluene (1:2) resulted in golden-orange crystals that were suitable for X-ray crystallography.⁸ A thermal ellipsoid diagram appears in Figure 1. The crystal structure shows clearly that the C2–C3 bond of the allyl ligand resulted from carbon–carbon bond formation between the carbyne carbon and phenylacetylene. The allyl ligand also bears a P(OPh)₃ moiety derived from addition of a second phosphite to C1. Because the C1–C2 [1.476(5) Å] and C2–C3 [1.427(5) Å] bond lengths differ as do the Mo–C1 [2.297(3) Å] and Mo–C3 [2.363(4) Å] distances, the coordination of the allyl ligand is best described as η¹:η². In solution, complex **2a** exists as a mixture of exo and endo isomers in an 87:13 ratio, as determined by ¹H NMR spectroscopy. NOE enhancement between the protons on the C2 phenyl substituent and the Cp ring allows assignment of the major isomer as exo.

A similar reaction occurred between the phenyl carbyne **1b** and phenylacetylene in the presence of 1 equiv

(8) Crystal data for **2a**: Orthorhombic, space group $P2_12_12_1$, golden-orange, $a = 13.4673(1)$ Å, $b = 19.1788(2)$ Å, $c = 20.3437(2)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, volume = 5254.51(8) Å³, $Z = 4$. A total of 695 parameters were refined in the final cycle of refinement using 11 064 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 4.07% and 9.60%, respectively. GOF on F^2 = 1.108.

of free P(OPh)_3 to produce **2b** in 39% isolated yield (Scheme 2). In addition, **1a** reacted with 1-hexyne under similar conditions to furnish **2c** in 28% yield. The structures of these compounds were assigned by comparison of their spectral data to that of **2a**.

Since control experiments have established that the carbynes **1a,b** do not react with alkynes in the absence of an oxidant, the first step in formation of **2a–c** must be generation of the 17-electron carbyne. The structures of the adducts require hydrogen abstraction, addition of the alkyne, and addition of the phosphite. Given the previously observed chemistry, it is reasonable to postulate initial H-abstraction, then subsequent chemistry derived from the 16-electron cationic carbenes **3a,b**. Insertion of the alkyne into the Mo=C double bond⁹ would produce vinylcarbene complexes **5a–c**, which could undergo nucleophilic attack by the phosphite¹⁰ to yield **2a–c**.

An adduct similar to **2a** was previously observed by Geoffroy following protonation of $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{W}\equiv\text{CTol}$ with HBF_4 in the presence of diphenylacetylene and PBu_3 .¹¹ Although the intermediate derived from the initial protonation could not be directly observed, it was postulated to be the cationic carbene $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{W}=\text{CHTol}]^+$ (**6**). Given the analogy between intermediates **6** and **3a,b**, we attempted to independently generate **3a** by protonation of **1a** with HBF_4 . However, this control experiment did not produce 1-pentene, as expected if cationic carbene **3a** were formed (Scheme 1). As a result of this discrepancy, the product of the protonation was characterized by low-temperature ^1H NMR. This experiment revealed that protonation of **1a** results in the face-protonated carbyne complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\{\text{P}(\text{OPh})_3\}(\text{H})\text{Mo}\equiv\text{CBu}]^+$ (**4**) as evidenced by the proton signal at -2.96 ppm and a C–H coupling constant of 73 Hz at the carbyne carbon.¹² At no time during the warming of the sample from -85 °C to room temperature could signals corresponding to **3a** be detected. Interestingly, reaction of the carbyne **1a** with HBF_4 in the presence of phenylacetylene at low temperature does result in formation of **2a**. However, since protonation of **1a** yields the face-protonated complex instead of **3a**,^{13,14} it is not yet clear what relationship this pathway bears to either the oxidation chemistry of **1a** or the Geoffroy results.¹⁵

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In previous cases where we have generated intermediates of the type $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\{\text{P}(\text{OR})_3\}\text{M}=\text{CHR}^+$ via oxidation of carbyne complexes, intramolecular rearrangement of the carbene ligand has been the dominant process.¹ These examples are the first where the carbene could be intercepted in a bimolecular reaction. Competition between H-shift and intermolecular trapping has also been observed for the related electrophilic carbenes $\text{Cp}(\text{CO})\text{LFe}=\text{CHCH}_2\text{CH}_3^+$, in which cyclopropanation of olefins is slower than the H-shift to yield propene,¹⁶ but insertion into Si–H bonds is faster than the H-shift.¹⁷ Such competition between H-shift and bimolecular reactivity is rare in highly electrophilic carbenes with alkyl groups larger than methyl because the H-shift is accelerated by increasing electron density at the migration origin.^{16–18}

Summary. We have demonstrated that one-electron oxidation of molybdenum carbynes in the presence of terminal alkynes results in H-abstraction and addition of the alkyne to produce $\eta^1\eta^2$ -allyl complexes as the final products. Under these conditions, the expected H-shift in the cationic carbene intermediate is not observed.

Experimental Section

General. Standard inert atmosphere techniques were used throughout. Hexane, petroleum ether, chloroform, and methylene chloride were distilled from CaH_2 . Diethyl ether and THF were distilled from $\text{Na}/\text{Ph}_2\text{CO}$. All NMR solvents were degassed by three freeze–pump–thaw cycles. Benzene- d_6 was vacuum transferred from $\text{Na}/\text{Ph}_2\text{CO}$. CDCl_3 was stored over 3 Å molecular sieves. $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\{\text{P}(\text{O}i\text{Pr})_3\}\text{Mo}\equiv\text{CCH}_2\text{CH}_2\text{CH}_3$ (**1a**) and $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\{\text{P}(\text{O}i\text{Pr})_3\}\text{Mo}\equiv\text{CC}_6\text{H}_5$ (**1b**) were synthesized by adaptations of previously reported methods.⁵ Phenyl acetylene and 1-hexyne were vacuum distilled from NaBH_4 . Triphenyl phosphite was purified by rinsing an ethereal solution with 10% KOH and then brine. After drying over Na_2SO_4 and removal of solvent, pure triphenyl phosphite was obtained by vacuum distillation. All other starting materials were purchased in reagent grade and used without further purification.

¹H, ³¹P, and ¹H NMR spectra were recorded on Gemini-300, VXR-300, and UNITY 500 NMR spectrometers. IR spectra were recorded on a Perkin-Elmer 1600 spectrometer. High-resolution mass spectrometry was performed by the University of Florida analytical service.

$(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\{\text{P}(\text{O}i\text{Pr})_3\}\text{Mo}[\eta^1\eta^2\text{-CH}\{\text{P}(\text{O}i\text{Pr})_3\}\text{C}(\text{Ph})=\text{CH}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)](\text{BF}_4)$ (**2a**). Butyl carbyne **1a** (140 mg, 0.245 mmol) was mixed with phenylacetylene (270 μL , 2.45 mmol) in 20 mL of CH_2Cl_2 . The solution was cooled to -95°C . A solution of acetylferrocenium tetrafluoroborate (73.4 mg, 0.233 mmol) in 25 mL of CH_2Cl_2 was slowly cannulated into

the carbyne solution keeping the temperature below -90°C . A dark violet-purple solution resulted. After 10 min triphenyl phosphite (64.3 μL , 0.245 mmol) was added. After 15 min, the solution was warmed to -78°C for 35 min. The bath was removed and the solution was allowed to warm to ambient temperature, upon which the solution changed color to orange-brown. Following removal of solvent in vacuo, acetylferrocene was extracted with ether ($3 \times 8\text{ mL}$). Addition of 2 mL of CH_2Cl_2 followed by 10 mL of ether resulted in the formation of a brown powder. Removal of the filtrate afforded crude product (193 mg, 73.7%). Analytically pure product could be obtained after three successive recrystallizations from CH_2Cl_2 /ether (134 mg, 51.0%). For **2a** (*exo:endo* 87:13): ¹H NMR (CDCl_3) δ 6.59–7.02 (m, 35H, Ph), 5.12 (s, 5H, C_5H_5 , *endo*), 4.32 (s, 5H, C_5H_5 , *exo*), 3.72 (dd, 1H, $\text{CHP}(\text{OPh})_3$, $J_{\text{PH}} = 3, 7.5\text{ Hz}$), 2.83 (m, 1H, $\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.21 (m, 1H, $\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.69 (m, 1H, $\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$) 1.58 (m, 2H, CH_2), 1.39 (m, 2H, CH_2), 0.95 (t, 3H, CH_3) ppm; ¹³C{¹H} NMR (CD_2Cl_2) δ 237.1 (d, CO, $J_{\text{PC}} = 30\text{ Hz}$), 151.2 (d, Ph, $J_{\text{PC}} = 9\text{ Hz}$), 149.6 (d, Ph, $J_{\text{PC}} = 12\text{ Hz}$), 140.7 (d, Ph, $J_{\text{PC}} = 8\text{ Hz}$), 131.3, 131.0, 130.5, 129.8, 128.7, 128.2, 128.1, 127.7, 126.5, 126.2, 125.2, 121.4 (d, Ph, $J_{\text{PC}} = 4\text{ Hz}$), 120.7, 120.0 (d, Ph, $J_{\text{PC}} = 4\text{ Hz}$), 95.5 (C_5H_5 , *exo*), 91.4 (C_5H_5 , *endo*), 84.0 (d, CPh, $J_{\text{PC}} = 6\text{ Hz}$), 62.3 (d, $\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, $J_{\text{PC}} = 6\text{ Hz}$), 34.4 ($\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 34.2 (dd, $\text{CHP}(\text{OPh})_3$, $J_{\text{PC}} = 161, 20\text{ Hz}$), 33.1, 22.9, 14.0 ppm; ³¹P{¹H} NMR (CDCl_3) δ 178.4 (d, $J_{\text{PP}} = 13\text{ Hz}$, *exo*), 162.5 (d, $J_{\text{PP}} = 22\text{ Hz}$, *endo*), 52.5 (d, $J_{\text{PP}} = 21\text{ Hz}$, *endo*), 49.8 (d, $J_{\text{PP}} = 13\text{ Hz}$, *exo*) ppm; IR (CH_2Cl_2) 1881 cm^{-1} (ν_{CO}); HRMS (FAB) m/z calcd for M^+ ($\text{C}_{55}\text{H}_{51}^{98}\text{MoO}_7\text{P}_2$) 983.2179, found 983.2163.

$(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\{\text{P}(\text{O}i\text{Pr})_3\}\text{Mo}[\eta^1\eta^2\text{-CH}\{\text{P}(\text{O}i\text{Pr})_3\}\text{C}(\text{C}_6\text{H}_5)=\text{CH}(\text{C}_6\text{H}_5)](\text{BF}_4)$ (**2b**). Phenyl carbyne **1b** (122 mg, 0.207 mmol) was mixed with phenyl acetylene (228 μL , 2.07 mmol) in 30 mL of CH_2Cl_2 . The solution was cooled to -95°C . A solution of acetylferrocenium tetrafluoroborate (62.0 mg, 0.197 mmol) in 20 mL of CH_2Cl_2 was slowly cannulated into the carbyne solution keeping the temperature below -90°C . A dark brown violet-purple solution resulted. After 10 min triphenyl phosphite (54.3 μL , 0.207 mmol) was added. After reacting for 10 min, the solution was warmed to -78°C for 2 h. The bath was removed and the solution was allowed to warm to ambient temperature, upon which the solution changed color to orange-brown. Following removal of solvent in vacuo, acetylferrocene was extracted with ether ($3 \times 8\text{ mL}$). Addition of 2 mL of CH_2Cl_2 followed by 10 mL of hexane resulted in the formation of a brown powder of the crude product (165 mg, 73.2%). Analytically pure product could be obtained after two successive recrystallizations from CH_2Cl_2 /ether (88.0 mg, 39.0%). For **2b** (*exo:endo* 90:10): ¹H NMR (CD_2Cl_2) δ 6.59–7.47 (m, 40H, Ph), 5.03 (s, 5H, C_5H_5 , *endo*), 4.45 (s, 5H, C_5H_5 , *exo*), 3.61 (s, 1H, CHPh), 3.45 (dd, 1H, $\text{CHP}(\text{OPh})_3$, $J_{\text{PH}} = 4, 9\text{ Hz}$) ppm; ¹³C{¹H} NMR (CD_2Cl_2) δ 237.7 (d, CO, $J_{\text{PC}} = 31\text{ Hz}$), 151.1 (d, Ph, $J_{\text{PC}} = 9\text{ Hz}$), 149.6 (d, Ph, $J_{\text{PC}} = 12\text{ Hz}$), 140.3 (d, Ph, $J_{\text{PC}} = 6\text{ Hz}$), 137.9, 131.1, 130.6, 130.5, 130.2, 130.0, 128.9, 128.4, 127.9, 127.7, 126.3, 121.5 (d, Ph, $J_{\text{PC}} = 5\text{ Hz}$), 119.7 (d, Ph, $J_{\text{PC}} = 5\text{ Hz}$), 96.9 (C_5H_5 , *exo*), 92.0 (C_5H_5 , *endo*), 82.1 (CC_6H_5), 59.4 (CHC_6H_5), 35.0 (dd, $\text{CHP}(\text{OPh})_3$, $J_{\text{PC}} = 159, 20\text{ Hz}$) ppm; ³¹P{¹H} NMR (CDCl_3) δ 177.1 (d, $J_{\text{PP}} = 23\text{ Hz}$), 49.9 (d, $J_{\text{PP}} = 23\text{ Hz}$) ppm; IR (CH_2Cl_2) 1885 cm^{-1} (ν_{CO}); HRMS (FAB) m/z calcd for M^+ ($\text{C}_{57}\text{H}_{47}^{98}\text{MoO}_7\text{P}_2$) 1003.187, found 1003.195.

$(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\{\text{P}(\text{O}i\text{Pr})_3\}\text{Mo}[\eta^1\eta^2\text{-CH}\{\text{P}(\text{O}i\text{Pr})_3\}\text{C}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)=\text{CH}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3)](\text{BF}_4)$ (**2c**). Butyl carbyne **1a** (101 mg, 0.177 mmol) was mixed with 1-hexyne (204 μL , 1.77 mmol) in 20 mL of CH_2Cl_2 . The solution was cooled to -95°C . A solution of acetylferrocenium tetrafluoroborate (53.0 mg, 0.168 mmol) in 25 mL of CH_2Cl_2 was slowly cannulated into the carbyne solution keeping the temperature below -90°C . A dark violet-purple solution resulted. After 20 min triphenyl phosphite (46.5 μL , 0.177 mmol) was added. The solution was warmed to -78°C for 20 min. The bath was removed and the solution was allowed to warm to ambient

(13) Protonation experiments using the related carbyne complex $(\eta^5\text{-C}_5\text{H}_5)\{\text{P}(\text{O}i\text{Pr})_3\}_2\text{Mo}\equiv\text{C}-\text{CH}_2^t\text{Bu}$ have been interpreted in terms of initial protonation at the carbyne carbon followed by irreversible conversion to the metal hydride.¹⁴ If **1a** were to initially protonate at the carbyne carbon to yield **3a**, rearrangement of **3a** to **4** would have to be faster than formation of 1-pentene from **3a** under these conditions. This is highly unlikely since **4** has never been observed following generation of **3a** under oxidative conditions.

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temperature, upon which the solution changed color to orange-brown. Following removal of solvent in vacuo, acetylferrocene was extracted with ether (3×8 mL). Addition of 2 mL of CH_2Cl_2 followed by 10 mL of hexane resulted in the formation of a brown powder. Dissolving the solid in 2 mL of CH_2Cl_2 followed by 15 mL of ether yielded the crude product (117 mg, 62.8%). Analytically pure product could be obtained after two successive recrystallizations from CH_2Cl_2 /hexanes (52.3 mg, 28.1%). For **2c** (*exo:endo* 60:40): ^1H NMR (CD_2Cl_2) δ 6.98–7.52 (m, 30H, Ph), 5.08 (s, 5H, C_5H_5 , *endo*), 4.62 (d, 5H, C_5H_5 , $J_{\text{PH}} = 1.5$ Hz, *exo*), 4.22 (m, 1H, $\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, *endo*), 3.26 (dd, 1H, $\text{CHP}(\text{OPh})_3$, $J_{\text{PH}} = 4$, 14 Hz, *exo*), 3.17 (m, 1H, $\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, *exo*), 2.73 (d, 1H, $\text{CHP}(\text{OPh})_3$, $J_{\text{PH}} = 12$ Hz, *endo*) 2.21–2.51 (m), 2.10 (m), 1.94 (m), 1.77 (m), 1.60 (m), 1.34–1.49 (m), 0.98 (m), 0.63 (t, 3H) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 245.0 (d, CO, $J_{\text{PC}} = 33$ Hz, *endo*), 238.9 (d, CO, $J_{\text{PC}} = 33$ Hz, *exo*), 152.1 (d, Ph, $J_{\text{PC}} = 14$ Hz, *endo*), 151.6 (d, Ph, $J_{\text{PC}} = 9$ Hz, *exo*), 150.4 (d, Ph, $J_{\text{PC}} = 12$ Hz, *exo*), 149.8 (d, Ph, $J_{\text{PC}} = 11$ Hz, *endo*), 131.8, 131.3, 130.7, 130.5, 128.6, 127.9, 126.2, 125.9, 121.6 (d, Ph, $J_{\text{PC}} = 4$ Hz), 121.4, 120.1 (d, Ph, $J_{\text{PC}} = 5$ Hz), 103.2 ($\text{CH}\{\text{P}(\text{OPh})_3\}\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, *endo*), 93.8 (C_5H_5 , *exo*), 91.3 (C_5H_5 , *endo*), 89.4 ($\text{CH}\{\text{P}(\text{OPh})_3\}\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, *exo*), 66.1 ($\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 38.4, 34.6, 34.3, 33.7, 32.6, 31.7, 31.1, 28.1 (dd, $\text{CHP}(\text{OPh})_3$, $J_{\text{PC}} = 166$, 18 Hz, *exo*), 23.2, 23.0, 21.4 (d, $\text{CHP}(\text{OPh})_3$, $J_{\text{PC}} = 145$ Hz, *endo*), 14.0, 13.7 ppm; $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 181.1 (s, *exo*), 168.3 (d, $J_{\text{PP}} = 18$ Hz, *endo*), 49.4 (d, $J_{\text{PP}} = 18$ Hz, *endo*), 46.2 (s, *exo*) ppm; IR (CH_2Cl_2) 1876 cm^{-1} (ν_{CO}); HRMS (FAB) m/z calcd for M^+ ($\text{C}_{53}\text{H}_{55}^{98}\text{MoO}_7\text{P}_2$) 963.2492, found 963.2503.

$[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\{\text{P}(\text{OPh})_3\}(\text{H})\text{Mo}\equiv\text{CBu}](\text{BF}_4)$ (4**).** Butyl carbyne **1a** (201 mg, 0.353 mmol) was mixed with a 54% solution of HBF_4 in ether (48.7 μL , 0.353 mmol) in 10 mL of CH_2Cl_2 at -95°C . After 10 min, 30 mL of hexane at -95°C was added and an orange oil precipitated from solution. The oil was rinsed with hexanes at -78°C , and some of the remaining solvent was removed in vacuo at -78°C . Keeping the temperature below -78°C , 1 mL of CD_2Cl_2 was added. The resulting solution was cannulated into an NMR tube for spectral characterization at -40°C . For **4**: ^1H NMR (CD_2Cl_2) δ 7.20–7.50 (m, 15H, Ph), 5.40 (s, 5H, C_5H_5), 2.33 (m, 1H), 2.07 (m, 1H), 1.52 (m, 1H), 1.44 (m, 1H), 1.21 (m, 2H), 0.79 (m, 3H), -2.82 (d, 1H, $J_{\text{PH}} = 10$ Hz) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2) δ 276.8 (d, $J_{\text{PC}} = 12$ Hz, MoC, $J_{\text{CH}} = 73$ Hz), 226.8 (d, $J_{\text{PC}} = 22$ Hz, CO), 149.9 (d, $J_{\text{PC}} = 6$ Hz), 130.8, 126.7, 121.2 (d, $J_{\text{PC}} = 4$ Hz), 96.9 (Cp), 47.2, 30.4, 22.0, 13.5 ppm

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Supporting Information Available: Tables of bond distances, bond angles, positional parameters, and anisotropic displacement parameters for **2a** (16 pages). See any current masthead page for ordering information and Web access instructions.

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