Organometallics **1998,** *17,* 4413−4416

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

Karen E. Torraca, Khalil A. Abboud, and Lisa McElwee-White*

Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200

Received June 24, 1998

One-electron oxidation of the carbyne complex (η^5-C_5H_5)(CO){P(OPh)$_3$}Mo≡$CCH_2CH_2CH_2$-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 (η^5-C_5H_5)(CO){P(OPh)$_3$}Mo[η^1:η^2-CH{P(OPh)$_3$}C(Ph)=CH($CH_2CH_2CH_2CH_3$)] (**2a**), the structure of which was confirmed by X-ray crystallography.

Introduction

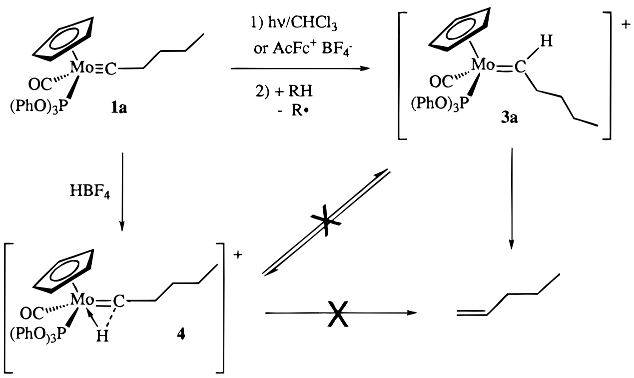
We have previously reported that oxidation of the carbyne complexes (η^5-C_5H_5)(CO){P(OR′)$_3$}M≡CR [M = Mo, W; R = alkyl; R′ = Me, Ph][1] results in formation of 17-electron complexes that abstract hydrogen at the carbyne carbon to form cationic metal carbenes.[2,3] When R is a primary alkyl group, hydride shift in the carbene complex yields an alkene as the final organic product. We now report that when (η^5-C_5H_5)(CO){P(OPh)$_3$}Mo≡$CCH_2CH_2CH_2CH_3$ (**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 (η^5-C_5H_5)(CO){P(OPh)$_3$}Mo[η^1:η^2-CH{P(OPh)$_3$}C(Ph)=CH($CH_2CH_2CH_2CH_3$)] (**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 $^\bullet CHCl_2$.[4] Evidence for side reactions involving the $^\bullet CHCl_2$ radical can be found in the formation of CH_3Cl[5] by Arbuzov reaction of P(OMe)$_3$ ligands.[6] The use of outer sphere chemical oxidants[7] at low temperatures provides an alternative approach in which side reactions from $^\bullet CHCl_2$ can be avoided.

To confirm that chemical oxidation generates the same intermediates as photooxidation, butyl carbyne **1a** was reacted with acetylferrocenium tetrafluoroborate ($AcFc^+BF_4^-$). 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 $AcFc^+BF_4^-$ 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 ^{1}H NMR spectroscopy revealed the presence of 1-pentene, as also seen following photooxidation.

Scheme 1



Once it had been established that oxidation of **1a** with $AcFc^+BF_4^-$ 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 ^{1}H 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

---

(1) McElwee-White, L. *Synlett* **1996**, 806−814.

(2) Main, A. D.; McElwee-White, L. *J. Am. Chem. Soc.* **1997**, *119*, 4551−4552.

(3) (a) Schoch, T. K.; Orth, S. D.; Zerner, M. C.; Jørgensen, K. A.; McElwee-White, L. *J. Am. Chem. Soc.* **1995**, *117*, 6475−6482. (b) Torraca, K. E.; Storhoff, D. A.; McElwee-White, L. *J. Organomet. Chem.* **1998**, *554*, 13−18.

(4) Buehler, R. E. In *The Chemistry of the Carbon−Halogen Bond*; Patai, S., Ed.; Wiley: London, 1973; pp 795−864.

(5) Kingsbury, K. B.; Carter, J. D.; Wilde, A.; Park, H.; Takusagawa, F.; McElwee-White, L. *J. Am. Chem. Soc.* **1993**, *115*, 10056−10065.

(6) Brill, T. B.; Landon, S. J. *Chem. Rev.* **1984**, *84*, 577−85.

(7) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877−910.

S0276-7333(98)00534-2 CCC: $15.00
Publication on Web 09/04/1998

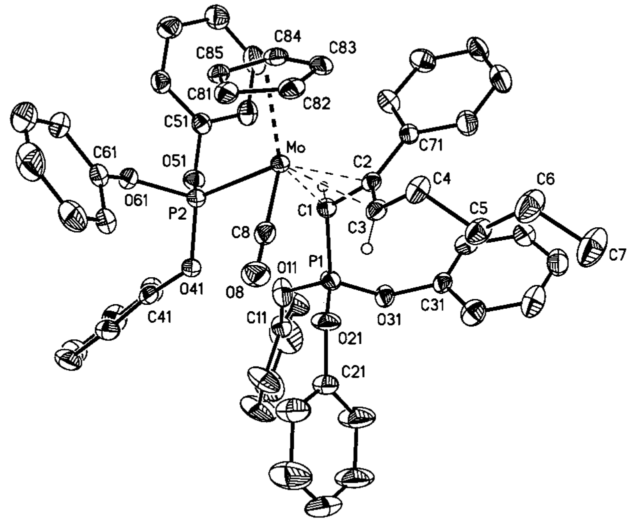
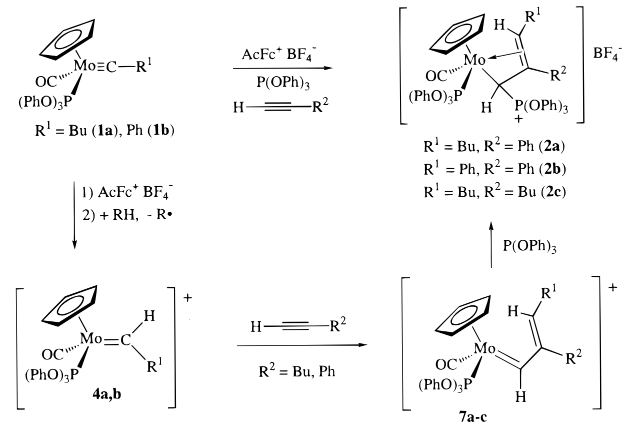


Figure 1. Thermal ellipsoid diagram of **2a** showing the crystallographic numbering scheme. Thermal ellipsoids are drawn at the 40% probability level. The majority of the hydrogens are removed for clarity.

Scheme 2



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 CH_2Cl_2/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 η^1:η^2. In solution, complex **2a** exists as a mixture of exo and endo isomers in an 87:13 ratio, as determined by ^{1}H 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 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 bond[9] would produce vinylcarbene complexes **5a**−**c**, which could undergo nucleophilic attack by the phosphite[10] to yield **2a**−**c**.

An adduct similar to **2a** was previously observed by Geoffroy following protonation of $(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}CTol$ 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 $[(\eta^5\text{-}C_5H_5)(CO)_2W{=}CHTol]^+$ (**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 ^{1}H NMR. This experiment revealed that protonation of **1a** results in the face-protonated carbyne complex $[(\eta^5\text{-}C_5H_5)(CO)\{P(OPh)_3\}(H)Mo{\equiv}CBu]^+$ (**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]

---

[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, α = 90°, $\beta = 90°$, $\gamma = 90°$, volume = 5254.51(8) Å^3, $Z = 4$. 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 $F^2 = 1.108$.

[9] (a) Barluenga, J.; Aznar, F.; Martín, A.; García-Granda, S.; Pérez-Carreño, E. *J. Am. Chem. Soc.* **1994**, *116*, 11191−11192. (b) Fischer, H.; Hofmann, J.; Mauz, E. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 998−999. (c) Schneider, K. J.; Neubrand, A.; van Eldik, R.; Fischer, H. *Organometallics* **1992**, *11*, 267−269. (d) Fischer, H.; Dötz, K. H. *Chem. Ber.* **1980**, *113*, 193−202. (e) Dötz, K. H. *Chem. Ber.* **1977**, *110*, 78−85. (f) Dötz, K. H.; Pruskil, I. *J. Organomet. Chem.* **1977**, *213*, 115−120. (g) Dötz, K. H.; Kreiter, C. G. *J. Organomet. Chem.* **1975**, *99*, 309−314.

[10] (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, 1983; pp 156−159. (b) Casey, C. P.; Polichnowski, S. W. *J. Am. Chem. Soc.* **1977**, *99*, 6097−6098. (c) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282−7292. (d) Bodnar, T.; Cutler, A. *J. Organomet. Chem.* **1981**, *213*, C31−C36. (e) Fischer, H.; Reindl, D. *J. Organomet. Chem.* **1990**, *385*, 351−361.

[11] Garrett, K. E.; Sheridan, J. B.; Pourreau, D. B.; Feng, W. C.; Geoffroy, G. L.; Staley, D. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 8383−8391.

[12] (a) Holmes, S. J.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *Organometallics* **1984**, *3*, 476−84. (b) Wengrovius, J. H.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1982**, *104*, 1739−40. (c) Holmes, S. J.; Clark, D. N.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 6322−6329. (d) Jeffrey, J. C.; Weller, A. S. *J. Organomet. Chem.* **1997**, *548*, 195−203.

In previous cases where we have generated intermediates of the type (η^5-C_5H_5)(CO){P(OR)$_3$}M═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 Cp(CO)LFe═CHCH$_2$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 Na/Ph$_2$CO. All NMR solvents were degassed by three freeze−pump−thaw cycles. Benzene-d_6 was vacuum transferred from Na/Ph$_2$CO. CDCl$_3$ was stored over 3 Å molecular sieves. (η^5-C_5H_5)(CO){P(OPh)$_3$}Mo≡CCH$_2$CH$_2$CH$_2$CH$_3$ (**1a**) and (η^5-C_5H_5)(CO){P(OPh)$_3$}Mo≡CC$_6$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$_2$SO$_4$ 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.

^{1}H, ^{31}P, and ^{1}H 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.

[(η^5-C_5H_5)(CO){P(OPh)$_3$}Mo[η^1:η^2-CH{P(OPh)$_3$}C(Ph)═CH(CH$_2$CH$_2$CH$_2$CH$_3$)](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$_2$Cl$_2$. The solution was cooled to −95 °C. A solution of acetylferrocenium tetrafluoroborate (73.4 mg, 0.233 mmol) in 25 mL of CH$_2$Cl$_2$ 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 × 8 mL). Addition of 2 mL of CH$_2$Cl$_2$ 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$_2$Cl$_2$/ether (134 mg, 51.0%). For **2a** (*exo*:*endo* 87:13): ^{1}H NMR (CDCl$_3$) δ 6.59−7.02 (m, 35H, Ph), 5.12 (s, 5H, C$_5$H$_5$, *endo*), 4.32 (s, 5H, C$_5$H$_5$, *exo*), 3.72 (dd, 1H, CHP(OPh)$_3$, J_{PH} = 3, 7.5 Hz), 2.83 (m, 1H, C*H*CH$_2$CH$_2$CH$_2$CH$_3$), 2.21 (m, 1H, CHC*H*$_2$CH$_2$CH$_2$CH$_3$), 1.69 (m, 1H, CHC*H*$_2$CH$_2$CH$_2$CH$_3$) 1.58 (m, 2H, CH$_2$), 1.39 (m, 2H, CH$_2$), 0.95 (t, 3H, CH$_3$) ppm; ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 237.1 (d, CO, J_{PC} = 30 Hz), 151.2 (d, Ph, J_{PC} = 9 Hz), 149.6 (d, Ph, J_{PC} = 12 Hz), 140.7 (d, Ph, J_{PC} = 8 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_{PC} = 4 Hz), 120.7, 120.0 (d, Ph, J_{PC} = 4 Hz), 95.5 (C$_5$H$_5$, *exo*), 91.4 (C$_5$H$_5$, *endo*), 84.0 (d, CPh, J_{PC} = 6 Hz), 62.3 (d, *C*HCH$_2$CH$_2$CH$_2$CH$_3$, J_{PC} = 6 Hz), 34.4 (CH*C*H$_2$CH$_2$CH$_2$CH$_3$), 34.2 (dd, *C*HP(OPh)$_3$, J_{PC} = 161, 20 Hz), 33.1, 22.9, 14.0 ppm; ^{31}P{^{1}H} NMR (CDCl$_3$) δ 178.4 (d, J_{PP} = 13 Hz, *exo*), 162.5 (d, J_{PP} = 22 Hz, *endo*), 52.5 (d, J_{PP} = 21 Hz, *endo*), 49.8 (d, J_{PP} = 13 Hz, *exo*) ppm; IR (CH$_2$Cl$_2$) 1881 cm^{-1} (ν_{CO}); HRMS (FAB) *m/z* calcd for M$^+$ (C$_{55}$H$_{51}$^{98}MoO$_7$P$_2$) 983.2179, found 983.2163.

[(η^5-C_5H_5)(CO){P(OPh)$_3$}Mo[η^1:η^2-CH{P(OPh)$_3$}C(C$_6$H$_5$)═CH(C$_6$H$_5$)](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$_2$Cl$_2$. The solution was cooled to −95 °C. A solution of acetylferrocenium tetrafluoroborate (62.0 mg, 0.197 mmol) in 20 mL of CH$_2$Cl$_2$ 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 × 8 mL). Addition of 2 mL of CH$_2$Cl$_2$ 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$_2$Cl$_2$/ether (88.0 mg, 39.0%). For **2b** (*exo*:*endo* 90:10): ^{1}H NMR (CD$_2$Cl$_2$) δ 6.59−7.47 (m, 40H, Ph), 5.03 (s, 5H, C$_5$H$_5$, *endo*), 4.45 (s, 5H, C$_5$H$_5$, *exo*), 3.61 (s, 1H, CHPh), 3.45 (dd, 1H, CHP(OPh)$_3$, J_{PH} = 4, 9 Hz) ppm; ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 237.7 (d, CO, J_{PC} = 31 Hz), 151.1 (d, Ph, J_{PC} = 9 Hz), 149.6 (d, Ph, J_{PC} = 12 Hz), 140.3 (d, Ph, J_{PC} = 6 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_{PC} = 5 Hz), 119.7 (d, Ph, J_{PC} = 5 Hz), 96.9 (C$_5$H$_5$, *exo*), 92.0 (C$_5$H$_5$, *endo*), 82.1 (*C*C$_6$H$_5$), 59.4 (*C*HC$_6$H$_5$), 35.0 (dd, *C*HP(OPh)$_3$, J_{PC} = 159, 20 Hz) ppm; ^{31}P{^{1}H} NMR (CDCl$_3$) δ 177.1 (d, J_{PP} = 23 Hz), 49.9 (d, J_{PP} = 23 Hz) ppm; IR (CH$_2$Cl$_2$) 1885 cm^{-1} (ν_{CO}); HRMS (FAB) *m/z* calcd for M$^+$ (C$_{57}$H$_{47}$^{98}MoO$_7$P$_2$) 1003.187, found 1003.195.

[(η^5-C_5H_5)(CO){P(OPh)$_3$}Mo[η^1:η^2-CH{P(OPh)$_3$}C(CH$_2$CH$_2$CH$_2$CH$_3$)═CH(CH$_2$CH$_2$CH$_2$CH$_3$)](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$_2$Cl$_2$. The solution was cooled to −95 °C. A solution of acetylferrocenium tetrafluoroborate (53.0 mg, 0.168 mmol) in 25 mL of CH$_2$Cl$_2$ 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 (η^5-C$_5$H$_5$){P(OPh)$_3$}$_2$Mo≡C−CH$_2$^{t}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**, rearrangment 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.

[14] Bottrill, M.; Green, M.; Orpen, A. G.; Saunders: D. R.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1989**, 511−518.

[15] Protonations of metal complexes with unsaturated ligands can involve highly complex scenarios. See: Henderson, R. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 946−967.

[16] Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258−264.

[17] Scharrer, E.; Brookhart, M. *J. Organomet. Chem.* **1995**, *497*, 61−71.

[18] Roger, C.; Bodner, G. S.; Hatton, W. G.; Gladysz, J. A. *Organometallics* **1991**, *10*, 3266−3274.

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, $J_{PH} = 1.5$ Hz, *exo*), 4.22 (m, 1H, $C\mathit{H}CH_2CH_2CH_2CH_3$, *endo*), 3.26 (dd, 1H, $CHP(OPh)_3$, $J_{PH} = 4, 14$ Hz, *exo*), 3.17 (m, 1H, $CHC\mathit{H}_2CH_2CH_2CH_3$, *exo*), 2.73 (d, 1H, $CHP(OPh)_3$, $J_{PH} = 12$ 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; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 245.0 (d, CO, $J_{PC} = 33$ Hz, *endo*), 238.9 (d, CO, $J_{PC} = 33$ Hz, *exo*), 152.1 (d, Ph, $J_{PC} = 14$ Hz, *endo*), 151.6 (d, Ph, $J_{PC} = 9$ Hz, *exo*), 150.4 (d, Ph, $J_{PC} = 12$ Hz, *exo*), 149.8 (d, Ph, $J_{PC} = 11$ Hz, *endo*), 131.8, 131.3, 130.7, 130.5, 128.6, 127.9, 126.2, 125.9, 121.6 (d, Ph, $J_{PC} = 4$ Hz), 121.4, 120.1 (d, Ph, $J_{PC} = 5$ Hz), 103.2 ($CH\{P(OPh)_3\}\mathit{C}CH_2CH_2CH_2CH_3$, *endo*), 93.8 ($C_5H_5$, *exo*), 91.3 ($C_5H_5$, *endo*), 89.4 ($CH\{P(OPh)_3\}\mathit{C}CH_2CH_2CH_2CH_3$, *exo*), 66.1 ($\mathit{C}HCH_2CH_2CH_2CH_3$), 38.4, 34.6, 34.3, 33.7, 32.6, 31.7, 31.1, 28.1 (dd, $\mathit{C}HP(OPh)_3$, $J_{PC} = 166, 18$ Hz, *exo*), 23.2, 23.0, 21.4 (d, $\mathit{C}HP(OPh)_3$, $J_{PC} = 145$ Hz, *endo*), 14.0, 13.7 ppm; $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 181.1 (s, *exo*), 168.3 (d, $J_{PP} = 18$ Hz, *endo*), 49.4 (d, $J_{PP} = 18$ Hz, *endo*), 46.2 (s, *exo*) ppm; IR (CH_2Cl_2) 1876 cm^{-1} (ν_{CO}); HRMS (FAB) *m*/*z* calcd for M^+ ($C_{53}H_{55}{}^{98}MoO_7P_2$) 963.2492, found 963.2503.

$[(\eta^5\text{-}C_5H_5)(CO)\{P(OPh)_3\}(H)Mo{\equiv}CBu](BF_4)$ (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, $J_{PH} = 10$ Hz) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 276.8 (d, $J_{PC} = 12$ Hz, Mo*C*, $J_{CH} = 73$ Hz), 226.8 (d, $J_{PC} = 22$ Hz, CO), 149.9 (d, $J_{PC} = 6$ Hz), 130.8, 126.7, 121.2 (d, $J_{PC} = 4$ Hz), 96.9 (Cp), 47.2, 30.4, 22.0, 13.5 ppm

Acknowledgment. We thank the National Science Foundation (Grant CHE-9424134) for support of this work. K.A.A. wishes to acknowledge the National Science Foundation and the University of Florida for funding the purchase of the X-ray equipment.

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.

OM980534X