Effect of Ligand Variation on the Site of Protonation in the Metal Carbynes $CpL_2Mo{\equiv}CBu$ and $TpL_2Mo{\equiv}CBu$ [L = CO, $P(OR)_3$]

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The site of thermodynamic protonation of the Fischer carbynes $CpL_2Mo{\equiv}CBu$ and $TpL_2Mo{\equiv}CBu$ [L = CO, $P(OR)_3$] with HBF_4 depends on the number of π-acid CO ligands. As the number of carbonyls increases from zero to two and the electron density at the metal center is decreased by back-bonding, the protonation site shifts from the metal to the carbyne carbon. Parallel behavior in the Tp and Cp series of complexes allows the change in protonation site to be attributed to electronic effects in the ancillary ligands.

Introduction

Protonation of carbyne (alkylidyne) complexes has been a topic of long-standing interest due to the variety of observed products and the difficulty of predicting which will be obtained.[1,2] In addition, complications arise in discerning kinetic vs thermodynamic protonation sites.[3] On the basis of computational studies that assigned a net negative charge to the carbyne carbon, kinetic protonation has been assumed to involve charge-controlled addition of the proton at that site.[4] However, the final thermodynamic outcome is variable. The protonation product is dependent on the metal, the ancillary ligands, and the counterion of the acid. Products obtained from simple protonation of alkylidyne complexes include metal carbenes (alkylidenes) from protonation at the carbyne carbon,[5] metal hydrides from addition to the metal center,[6] and "face-protonated" alkylidynes in which the product is an alkylidene whose C−H bond is engaged in agostic interaction with the metal.[1,7] In the presence of coordinating anions, carbyne protonation can induce further reaction to produce η^2-acyl complexes[8] and compounds in which the original alkylidyne ligand has been lost via protonolysis.[6c,d]

In alkylidyne complexes that bear no π-acid ligands, thermodynamic protonation occurs either on the alkylidyne face or at the metal. Steric considerations have been invoked to explain the preference.[1,6a,b,9] However, in the presence of π-acid ligands, electronic effects appear to be the overriding factor in determining the ultimate site of protonation. It has been suggested that alkylidene (face-protonated) complexes that bear π-acid ligands do not rearrange into the corresponding alkylidyne hydride species because the resulting oxidation of the metal center would interfere with back-bonding.[1] A noted absence in the discussion is a closely related series of compounds where all three protonation outcomes (alkylidene, face-protonated alkylidyne, and alkylidyne hydride) are available.

We now report that protonation of the Fischer carbynes $CpL_2Mo{\equiv}CBu$ and $TpL_2Mo{\equiv}CBu$ [L = CO, $P(OR)_3$] with HBF_4 results in a systematic shift of the thermodynamic protonation product from the alkylidyne hydride to the face-protonated alkylidyne to the nonagostic alkylidene as the number of carbonyl groups increases from zero to two. These results are consistent with determination of the final protonation site by the electron density at the metal. As π-back-bonding to the carbonyl ligands decreases the electron density at the metal, the protonation site shifts from the metal toward the carbyne carbon, consistent with earlier calculations

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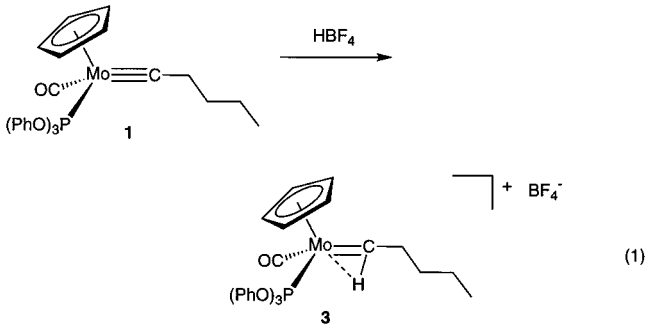
which assign negative charge to the alkylidyne carbon in cationic complexes.[4]

Results and Discussion

We previously reported that oxidation of the butyl carbyne Cp{P(OPh)$_3$}(CO)Mo≡CBu (**1**) with acetyl ferrocenium results in the formation of 1-pentene.[10] In the proposed mechanism, electron transfer generates a 17-electron complex that undergoes H atom abstraction to yield the electrophilic carbene [Cp{P(OPh)$_3$}(CO)Mo=CHBu]$^+$ (**2**). Carbene **2** then undergoes a facile 1,2-hydride shift followed by decomplexation to yield the free alkene.[8e] Although carbene **2** has never been directly observed in these studies, its presence is implied by the formation of 1-pentene. Subsequent observation that the formation of 1-pentene is suppressed upon oxidation of **1** in the presence of alkynes[10] raised the question of whether the alkyne had reacted with carbene **2** or with the 17-electron cationic carbyne prior to hydrogen abstraction. In conjunction with mechanistic studies on oxidation of **1** in the presence of alkynes, we began to explore ways to generate carbene **2** independently.

In a formal sense, carbene **2** results from addition of H$^+$ to carbyne **1**. Although the protonation chemistry of metal carbynes is complex, it seemed possible that employing an acid with a noncoordinating anion could provide an independent generation of **2**. However, protonation of butyl carbyne **1** with HBF_4 at low temperature resulted in an unstable species whose ^{1}H NMR spectra were not consistent with the expected carbene. While the protons on electrophilic carbenes are known to exhibit ^{1}H NMR signals between 10 and 18 ppm,[11] the newly generated species showed a new resonance at −2.96, with J_{PH} = 10 Hz.

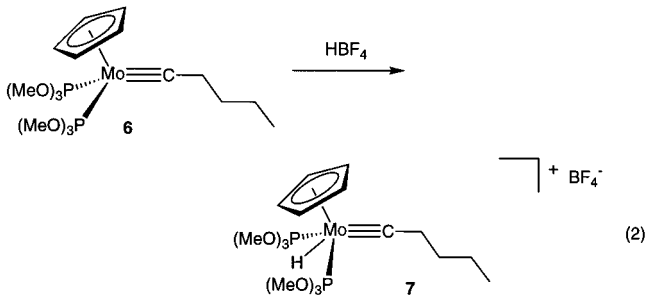
Although the ^{1}H NMR spectrum appeared to rule out a carbene product, the ^{13}C NMR spectrum of the product contained two deshielded carbons at 276.8 and 226.8 ppm, consistent with carbene and carbonyl carbons. Elucidation of the structure was carried out by 2D NMR. Of the two deshielded carbons at 226.8 and 276.8 ppm, the latter is C_α of the original alkylidyne ligand, as indicated by its long-range coupling to the protons on C_β and C_γ (1.44, 1.52, 2.07, and 2.33 ppm) observed in the HMBC[12] spectrum. The carbon at 276.8 ppm is coupled to the proton at −2.96 ppm, as indicated by the HMQC[13] spectrum. The value of the coupling constant was then measured more accurately in a 1D HMQC spectrum optimized for the *J* value observed in the 2D HMQC. The value $^1J_{CH}$ = 73.4 ± 0.7 Hz indicates that the proton is centered neither on the metal nor on the carbon. Instead, the complex is face-protonated carbyne **3**, in which the hydrogen participates in an agostic interaction with the metal center (eq 1). Similar J_{CH} values in the range of 45−84 Hz have been reported for other face-protonated alkylidynes.[7,9]



(1)

Generation of the agostic alkylidene species **3** upon protonation of **1** was intriguing. Complex **3** was clearly not the species generated in the previously reported oxidative chemistry of **1** because it did not produce 1-pentene upon decomposition. Face-protonation was also a different outcome from what we had obtained by protonation of the related complex Cp{P(OMe)$_3$}$_2$Mo≡C(c-C_3H_5) (**4**) with HBF_4.[6e] The protonation of **4** occurred at the metal center to yield the hydrido carbyne species [Cp{P(OMe)$_3$}$_2$(H)Mo≡C(c-C_3H_5)]$^+$[BF_4]$^-$ (**5**). The ^{1}H NMR spectrum of complex **5** had also exhibited an upfield resonance at −2.42 ppm, but the much larger J_{PH} = 64.7 Hz clearly identified the complex as a metal hydride. In addition, the carbyne carbon of **5** was shifted downfield to 344 ppm, as compared to 299.5 ppm for the neutral carbyne **4** and 276.8 ppm for the face-protonated alkylidyne **3**.

Cyclopropyl carbyne **4** and butyl carbyne **1** differ both in the alkyl substituent and the ancillary ligand set (two phosphites for **4** vs one phosphite and one carbonyl for **1**). To differentiate the effects on the site of protonation, the bis(phosphite) butyl carbyne complex Cp{P(OMe)$_3$}$_2$-Mo≡CBu (**6**) was synthesized. Reaction of **6** with HBF_4 at −78 °C (eq 2) results in protonation at the metal center to yield the hydrido carbyne species [Cp{P(OMe)$_3$}$_2$(H)Mo≡CBu]$^+$[BF_4]$^-$ (**7**), as characterized by the ^{1}H NMR resonance at −2.6 ppm with J_{PH} = 64 Hz. Carbyne **7** exhibits a downfield shift of the



(2)

carbyne carbon to 347 ppm in the ^{13}C NMR, similar to what is observed for the related hydrido carbyne complex **4**. As further evidence that the proton resides at the metal center, J_{CH} between the carbyne carbon and the added proton was determined to be less than 6 Hz.

As discussed above, kinetic protonation of alkylidyne complexes has been postulated to be charge-controlled, which should result in protonation at the carbyne carbon. Consistent with this interpretation, a different species was observed upon reaction of carbyne **6** with HBF_4 at low temperature. ^{1}H NMR spectra recorded at −50 °C exhibited a resonance at −5 ppm, with the small

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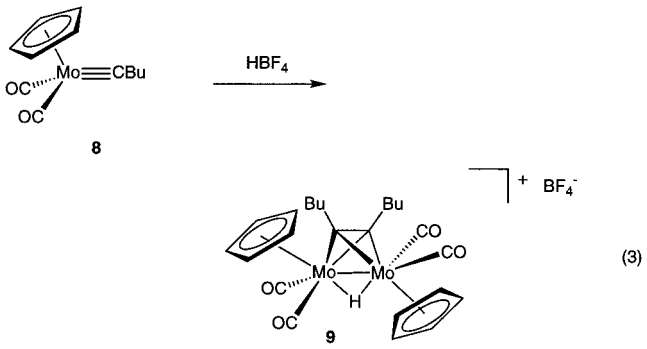
J_{PH} indicative of a face-protonated carbyne. Upon warming, this species converted irreversibly to hydrido carbyne **7**.

The difference in protonation behavior between butyl carbynes **1** and **6** can be attributed to the change in ancillary ligands. The carbyne with two phosphite ligands (**6**) was protonated at the metal. In the related complex with one carbonyl and one phosphite (**1**), the site of thermodynamic protonation was shifted toward the carbyne carbon to yield the face-protonated alkylidyne. This change is consistent with withdrawal of electron density from the metal by the π-acid carbonyl, rendering the metal less basic with respect to the carbyne carbon. If this were the case, a second carbonyl ligand might be expected to decrease the electron density at the metal to the point where the protonation site would shift completely to the carbon. As a test of this hypothesis, we prepared the dicarbonyl carbyne Cp-$(CO)_2$Mo≡CBu (**8**) by reaction of the bis(pyridine) complex $Cl(C_5H_5N)_2(CO)_2$Mo≡CBu with NaCp.

Reaction of carbyne **8** with HBF_4 at low temperature resulted in the dinuclear species $[Mo_2(\mu\text{-H})\{\mu\text{-}C_2(Bu)_2\}(CO)_4Cp_2][BF_4]$ (**9**) (eq 3). Complex **9** is structurally

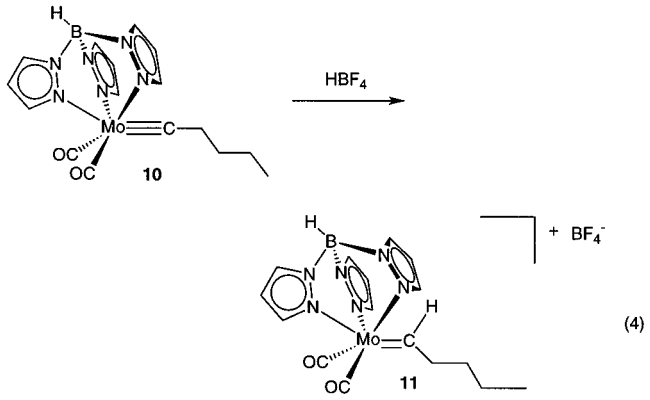


(3)

equivalent to a product previously prepared by protonation of $Cp(CO)_2$W≡CTol with HBF_4[5a] and could be identified by the characteristic ^{1}H NMR resonance at −15.7 ppm for the bridging hydride. In the original report on the tungsten analogue of **9**, Stone proposed that protonation of the carbyne carbon produced the corresponding cationic carbene. Reaction of the carbene with starting material then yielded the binuclear alkyne complex. However, the carbene intermediate was not directly observed. To verify that the dicarbonyl complexes did indeed undergo protonation at the carbon, we prepared the analogous but more sterically encumbered complex $Tp(CO)_2$Mo≡CBu (**10**) in which dimerization would be inhibited.

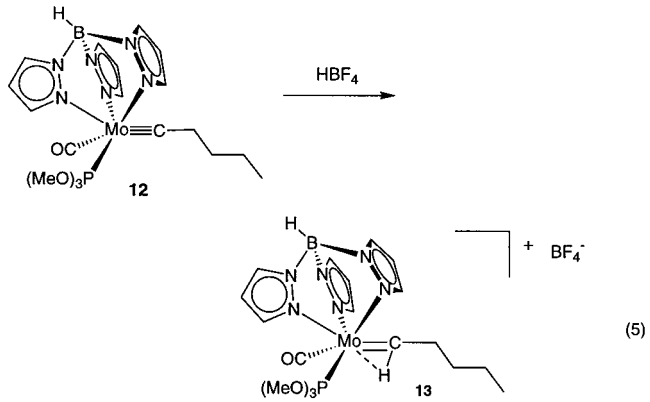
Protonation of **10** with HBF_4 at −78 °C resulted in a species that was difficult to characterize spectroscopically due to poor solubility at low temperatures. However, the structure could be assigned as carbene **11** (eq 4) on the basis of certain resonances in its ^{1}H and ^{13}C spectra. A proton signal at 12.6 ppm and a carbon resonance at 260 ppm are in agreement with similar Tp carbene complexes, one of which was characterized by X-ray crystallography.[5b]

Although protonation of the Tp carbyne **10** at the carbon was as expected on the basis of its two carbonyl ligands, concerns about the electronic differences between the Tp and Cp ligands led us to prepare Tp-{$P(OMe)_3$}(CO)Mo≡CBu (**12**) in order to confirm that



(4)

the same protonation trend held for the Tp carbynes as for the Cp derivatives. As predicted, protonation of the Tp carbyne **12** results in face-protonation to yield complex **13** (eq 5) just as protonation of its Cp analogue **1** yields **3** (eq 1). Assignment of **13** as the face-



(5)

protonated species was possible via its ^{1}H and ^{13}C NMR spectra, which exhibited a proton resonance at 0.45 ppm that is coupled to the carbon at 253 ppm with J_{CH} = 91.0 ± 0.4 Hz. Hence, despite the electronic difference between Tp and Cp ligands, the protonation site once again shifted from the carbon to the alkylidyne face upon replacement of a strong π-acid carbonyl with a phosphite.

Summary. We have demonstrated that the site of protonation in metal carbynes can be shifted from the carbon to the metal by manipulation of the ancillary ligand set. In the absence of π-acid ligands, the metal is sufficiently basic for the thermodynamic protonation product to be the alkylidyne hydride complex. Replacing one phosphite with a π-acid carbonyl results in a loss of electron density at the metal and a shift to face-protonation of the carbyne. Carbynes bearing two carbonyl ligands selectively react with HBF_4 at the carbyne carbon to produce cationic carbenes. These carbenes undergo secondary reactions unless the remaining ligands are sufficiently sterically encumbered to prevent dimerization.

Experimental Section

General Procedures. 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_2CO. All NMR solvents were degassed by three freeze−pump−thaw

cycles. Benzene-d_6 was vacuum transferred from Na/Ph_2CO. $CDCl_3$ and CD_2Cl_2 were stored over 3 Å molecular sieves. 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. Cl{P(OMe)$_3$}$_3$(CO)Mo≡CBu (**14**)[8e] and [Cp(CO){P(OPh)$_3$}HMo≡CBu](BF$_4$) (**3**)[10] were synthesized as reported previously.

^{1}H, ^{31}P, and ^{13}C 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.

Cl{P(OPh)$_3$}$_2$(CO)$_2$Mo≡CBu (15). Mo(CO)$_6$ (2.408 g, 9.122 mmol) was dissolved in 30 mL of Et_2O and cooled to 0 °C. A solution of *n*-butyllithium (2.0 M in hexane, 4.56 mL, 9.12 mmol) was added dropwise. After 1 h, the solution volume was reduced to 5 mL in vacuo. The solution was filtered through Celite and the solvent removed in vacuo to leave a golden-tan powdery solid. This solid was dissolved in 30 mL of CH_2Cl_2. After cooling to −95 °C, oxalyl chloride (0.637 mL, 7.30 mmol) was added dropwise, ensuring the temperature remained below −90 °C. After the addition was complete, the bath was removed and the solution warmed to −30 °C. During this time effervescence was observed. After cooling the solution below −50 °C, excess P(OPh)$_3$ (9.56 mL, 36.5 mmol) was added. The solution was allowed to stir at room temperature for 2 h. The solvent was removed in vacuo to leave a golden-brown oil, and excess P(OPh)$_3$ was extracted with pentane (4 × 10 mL). The resulting residue was dissolved in Et_2O and filtered through Celite. The remaining solvent was removed in vacuo to leave a golden-brown oil (6.010 g, 75.1% yield) which was a mixture of **15**, the tris(triphenyl phosphite) carbyne Cl{P(OPh)$_3$}$_3$(CO)Mo≡CBu (**16**), and free P(OPh)$_3$ (50% by ^{31}P NMR). The crude solid was used in the preparation of **1** without further purification. For **15**: ^{31}P{^{1}H} NMR ($CDCl_3$) δ 148.4. For **16**: ^{31}P{^{1}H} NMR ($CDCl_3$) δ 146.6 (d, J_{PP} = 56 Hz), 140.2 (t, J_{PP} = 56 Hz) ppm. For the mixture: IR (CH_2Cl_2) 1997 (s), 1924 (w) cm^{-1} (ν_{CO}).

Cp{P(OPh)$_3$}(CO)Mo≡CBu (1). The golden-brown oil from above was dissolved in 40 mL of THF, and solid CpNa (1.206 g, 13.70 mmol) was added. The mixture was stirred at ambient temperature for 3 h. The solvent was removed in vacuo to leave a dark brown oil, which was chromatographed on alumina using Et_2O as eluent at −78 °C. A bright orange-yellow fraction was collected, and the solvent was removed in vacuo to leave a bright orange oil. After three successive columns eluting with hexane/Et_2O (4:1) at −78 °C, **1** was obtained as a bright yellow powder (0.964 g, 18.6% yield overall from Mo(CO)$_6$): ^{1}H NMR (C_6D_6) δ 7.36 (d, J_{CH} = 7.8 Hz, 6H), 7.06 (t, J_{CH} = 7.8 Hz, 6H), 6.87 (t, J_{CH} = 7.2 Hz, 3H), 4.81 (s, 5H, Cp), 2.12 (m, 2H), 1.52 (pentet, 2H), 1.32 (sextet, 2H), 0.81 (t, 3H) ppm; ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 323.8 (d, J_{PC} = 31 Hz, Mo≡*C*), 238.9 (d, J_{PC} = 19 Hz, CO), 152.7 (d, J_{PC} = 4 Hz), 130.0, 125.1, 122.9 (d, J_{PC} = 4 Hz), 91.3 (Cp), 50.0, 30.4, 22.43, 13.8 ppm; ^{31}P{^{1}H} NMR ($CDCl_3$) δ 192.3 ppm; IR (CH_2Cl_2) 1917 cm^{-1} (ν_{CO}); HRMS (FAB) *m*/*z* calcd for M$^+$ ($C_{29}H_{29}{}^{98}MoPO_4$) 570.0865, found 570.0863.

Cl{P(OMe)$_3$}$_4$Mo≡CBu (18). Cl{P(OMe)$_3$}$_3$(CO)Mo≡CBu (2.897 g, 4.824 mmol) was dissolved in trimethyl phosphite (5.69 mL, 48.2 mmol). The mixture was refluxed 12 h and some of the excess phosphite removed in vacuo. Impurities were extracted into a minimal amount of hexanes (3 × 5 mL), and the remaining solvent was removed to yield **18** as a gray-tan oil (2.135 g, 63.5% yield), which was used in the preparation of **6** without further purification: ^{1}H NMR (C_6D_6) δ 3.79 (virtual t, 36H), 2.28 (m, 2H), 1.65 (pentet, 2H), 1.22 (sextet, 2H), 0.87 (t, 3H) ppm.

Cp{P(OMe)$_3$}$_2$Mo≡CBu (6). Cl{P(OMe)$_3$}$_4$(CO)Mo≡CBu (2.135 g, 3.065 mmol) was dissolved in 25 mL of THF. After addition of solid NaCp (0.404 g, 4.60 mmol), the mixture was heated to 55 °C for 15 h. The solvent was removed in vacuo, and the resulting residue was filtered through alumina eluting with Et_2O at −78 °C. After removal of the solvent, the golden-brown oil was chromatographed on alumina at −78 °C with hexane as the eluent. Increasing amounts of Et_2O were added to obtain a bright yellow fraction. Removal of the solvent in vacuo yielded **6** as a bright yellow oil (619 mg, 42.2% yield): ^{1}H NMR (C_6D_6) δ 5.29 (s, 5H), 3.52 (virtual t, 18 H), 2.30 (m, 2H), 1.60 (pentet, 2H), 1.41 (sextet, 2H), 0.89 (t, 3H) ppm; ^{13}C{^{1}H} NMR (C_6D_6) δ 310.4 (t, J_{PC} = 29 Hz, Mo≡*C*), 89.0 (Cp), 50.8 (P(OMe)$_3$), 49.1, 31.6, 22.6, 14.1 ppm; ^{31}P{^{1}H} NMR ($CDCl_3$) δ 214.3 ppm; HRMS (FAB) *m*/*z* calcd for M$^+$ ($C_{16}H_{32}{}^{98}MoP_2O_6$) 480.0733, found 480.0725.

[Cp{P(OMe)$_3$}$_2$HMo≡CBu][BF$_4$] (7). Butyl carbyne **6** (245 mg, 0.512 mmol) was dissolved in 8 mL of CH_2Cl_2 at −78 °C and mixed with a 54% solution of HBF_4 in ether (70.6 μL, 0.512 mmol). After 25 min, 30 mL of pentane at −78 °C was added and a red-orange oil formed. The solution was removed by filter cannulation to yield a solid, which was rinsed with pentane at −78 °C. 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 −50 °C. For **7**: ^{1}H NMR (CD_2Cl_2) δ 5.67 (s, 5H), 3.67 (d, J_{PH} = 12 Hz, 18 H), 2.47 (m, 2H), 1.47 (pentet, 2H), 1.27 (sextet, 2H), 0.82 (t, 3H), −2.60 (t, J_{PH} = 64 Hz, 1H) ppm; ^{13}C{^{1}H} NMR (CD_2Cl_2) δ 347.0 (t, J_{PC} = 33 Hz, Mo≡*C*), 96.2 (Cp), 53.5 (P(OMe)$_3$), 51.4, 29.5, 22.2, 13.5 ppm.

Cl(C$_5$H$_5$N)$_2$(CO)$_2$Mo≡CBu (17). Mo(CO)$_6$ (2.248 g, 8.515 mmol) was dissolved in 30 mL of Et_2O and cooled to 0 °C. A solution of *n*-butyllithium (2.3 M in hexane, 3.70 mL, 8.51 mmol) was added dropwise. After 1.5 h, the solution volume was reduced to 5 mL in vacuo. The solution was filtered through Celite and the solvent removed in vacuo to leave a golden-tan powdery solid. This solid was dissolved in 30 mL of CH_2Cl_2. After cooling to −95 °C, oxalyl chloride (0.669 mL, 7.66 mmol) was added dropwise, ensuring the temperature remained below −90 °C. After the addition was complete, the bath was removed and the solution was allowed to warm to −30 °C. During this time effervescence was observed. After cooling the solution to −78 °C, excess pyridine (2.15 mL, 25.5 mmol) was added. After 5 min the bath was removed and the solution was allowed to stir 25 min before the solvent was removed in vacuo. The residue was dissolved in 5 mL of CH_2Cl_2 and filtered through Celite. The solvent was removed in vacuo to leave a sticky brown solid which was dissolved in 5 mL of CH_2Cl_2. After addition of 5 mL of Et_2O and 10 mL of hexanes, the solution was concentrated until a golden precipitate formed. The solid was isolated by filtration and rinsed with hexanes (2 × 15 mL). Evaporation of the remaining solvent in vacuo yielded **17** as a golden brown powder (3.200 g, 90.6% yield). This crude solid was used in the preparation of **8** and **10** without further purification. For **17**: ^{1}H NMR (C_6D_6) δ 9.05 (d, J_{HH} = 4.8 Hz, 4H), 6.68 (t, J_{HH} = 6.6 Hz, 2H), 6.35 (t, J_{HH} = 6.6 Hz, 4H), 2.39 (t, 2H), 1.54 (pentet, 2H), 1.27 (sextet, 2H), 0.78 (t, 3H) ppm; IR (CH_2Cl_2) 1998 (s), 1912 (s) cm^{-1} (ν_{CO}).

Cp(CO)$_2$Mo≡CBu (8). Cl(C$_5$H$_5$N)$_2$(CO)$_2$Mo≡CBu (**17**) (417 mg, 1.00 mmol) was dissolved in 20 mL of THF. After addition of solid NaCp (133 mg, 1.51 mmol) the mixture was stirred for 1.5 h at ambient temperature. The solvent was removed in vacuo, and the resulting residue was filtered through alumina eluting with Et_2O at −78 °C. After removal of solvent, the golden oil was chromatographed on alumina at −78 °C with hexane as the eluent. A bright yellow fraction was collected. Removal of solvent in vacuo yielded **8** as a bright yellow oil (170 mg, 59.0% yield): ^{1}H NMR (C_6D_6) δ 5.05 (s, 5H), 2.19 (t, 2H), 1.42 (pentet, 2H), 1.25 (sextet, 2H), 0.75 (t,

3H) ppm; $^{13}C\{^1H\}$ NMR (C_6D_6) δ 332.7 (Mo≡*C*), 229.9 (CO), 92.1 (Cp), 50.5, 29.7, 21.9, 13.3 ppm; IR (CH_2Cl_2) 1992 (s), 1913 (s) cm^{-1} (ν_{CO}); HRMS (FAB) *m/z* calcd for M^+ ($C_{12}H_{14}{}^{98}MoO_2$) 288.0051, found 288.0074.

[Mo$_2$(μ-H){μ-C$_2$(Bu)$_2$}(CO)$_4$Cp$_2$][BF$_4$] (9). Butyl carbyne **8** (210 mg, 0.735 mmol) was dissolved in 8 mL of CH_2Cl_2 at −78 °C and mixed with a 54% solution of HBF_4 in ether (101 μL, 0.735 mmol). After 25 min, 30 mL of pentane at −78 °C was added, and a red crystalline solid precipitated from solution. The solution was removed by filter cannulation to yield a solid, which was rinsed with pentane at −78 °C. Some of the remaining solvent was removed in vacuo at −78 °C. Keeping the temperature below −60 °C, 2 mL of $CDCl_3$ was added. The resulting solution was cannulated into an NMR tube for spectral characterization at −50 °C. For **9**: ^1H NMR ($CDCl_3$) δ 5.54 (s, 10H, C_5H_5), 2.92 (m, 2H), 2.70 (m, 2H), 1.40 (m, 8H), 0.83 (m, 6H), −15.67 (s, 1H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 220.6, 219.6, 91.4 (Cp), 77.2, 69.8, 37.9, 22.4, 13.2 ppm.

Tp(CO)$_2$Mo≡CBu (10). Cl(C_5H_5N)$_2$(CO)$_2$Mo≡CBu (**17**) (823 mg, 1.98 mmol) was dissolved in 25 mL of THF. After addition of solid KTp (750 mg, 2.97 mmol) the mixture was stirred for 30 min at ambient temperature. The solvent was removed in vacuo, and the resulting residue was filtered through alumina eluting with Et_2O at −78 °C. After removal of solvent, the golden-brown oil was chromatographed on alumina at −78 °C with hexane as the eluent. Increasing amounts of Et_2O were added to elute a bright yellow fraction. Removal of solvent in vacuo yielded **10** as a yellow powder (566 mg, 65.8% yield): ^1H NMR (C_6D_6) δ 7.75 (d, J_{HH} = 1.2 Hz, 2H), 7.30 (m, 4H), 5.80 (t, J_{HH} = 1.8 Hz, 2H), 5.68 (t, J_{HH} = 1.8 Hz, 1H), 2.43 (t, 2H), 1.58 (pentet, 2H), 1.33 (sextet, 2H), 0.78 (t, 3H) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 315.9 (Mo≡*C*), 225.9 (CO), 144.6, 143.3, 135.9, 105.6, 50.2, 29.6, 22.9, 13.9 ppm; IR (CH_2Cl_2) 1992 (s), 1902 (s) cm^{-1} (ν_{CO}); HRMS (FAB) *m/z* calcd for M^+ ($C_{16}H_{19}B^{98}MoN_6O_2$) 436.0723, found 436.0717.

[Tp(CO)$_2$Mo≡C(H)Bu][BF$_4$] (11). Butyl carbyne **10** (201 mg, 0.463 mmol) was dissolved in 10 mL of CH_2Cl_2 at −78 °C and mixed with a 54% solution of HBF_4 in ether (63.9 μL, 0.463 mmol). After 15 min, 30 mL of pentane at −78 °C was added and an orange solid formed. The solution was removed by filter cannulation to yield an orange solid, which was rinsed with pentane at −78 °C. 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 −50 °C. For **11**: ^1H NMR (CD_2Cl_2) δ 12.56 (s, 1H) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 260.0 (Mo═C), 212.9 (CO) ppm.

Tp{P(OMe)$_3$}(CO)Mo≡CBu (12). Cl{P(OMe)$_3$}$_3$(CO)Mo≡CBu (2.732 g, 4.549 mmol) was dissolved in 30 mL of THF. After addition of solid KTp (1.720 g, 6.824 mmol) the mixture was stirred for 12 h at ambient temperature. The solvent was removed in vacuo, and the resulting residue was filtered through alumina eluting with Et_2O at −78 °C. After removal of solvent, the golden oil was chromatographed on alumina at −78 °C with hexane/Et_2O (1:1) as the eluent. A bright yellow-orange fraction was collected. Removal of solvent in vacuo yielded **12** as a yellow-orange powder (1.803 g, 74.7% yield): ^1H NMR (C_6D_6) δ 8.24 (s, 1H), 8.05 (s, 1H), 7.70 (s, 1H), 7.42 (m, 3H), 5.90 (m, 3H), 3.27 (d, J_{PH} = 11 Hz, 9H), 2.62 (m, 2H), 1.73 (pentet, 2H), 1.43 (sextet, 2H), 0.85 (t, 3H) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 304.2 (d, J_{PC} = 31 Hz, Mo≡*C*), 240.7 (d, J_{PC} = 15 Hz, CO), 144.8, 143.6, 135.9, 135.5, 135.3, 105.3, 105.1 (d, J_{PC} = 3 Hz), 50.9 (d, J_{PC} = 4 Hz, P(OMe)$_3$), 49.5 (d, J_{PC} = 3 Hz), 30.2 (d, J_{PC} = 4 Hz), 22.9, 14.0 ppm; $^{31}P\{^1H\}$ NMR (C_6D_6) δ 185.9 ppm; IR (CH_2Cl_2) 1889 cm^{-1} (ν_{CO}); HRMS (FAB) *m/z* calcd for M^+ ($C_{18}H_{28}B^{98}MoN_6O_4P$) 532.1065, found 532.1061.

[Tp(CO){P(OMe)$_3$}HMo≡CBu][BF$_4$] (13). Butyl carbyne 12 (218 mg, 0.411 mmol) was dissolved in 8 mL of CH_2Cl_2 at −78 °C and mixed with a 54% solution of HBF_4 in ether (56.7 μL, 0.411 mmol). After 30 min, 40 mL of pentane at −78 °C was added and a red-orange oil formed. The solution was removed by filter cannulation to yield a red-orange oil, which was rinsed with pentane at −78 °C. 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 −50 °C. For **13**: ^1H NMR (CD_2Cl_2) δ 8.01 (m, 1H), 7.88 (m, 1H), 7.83 (m, 3H), 7.63 (m, 1H), 6.40 (m, 3H), 3.31 (d, J_{PH} = 11 Hz, 9H), 2.96 (m, 2H), 1.71 (pentet, 2H), 1.43 (sextet, 2H), 0.93 (t, 3H), 0.45 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 253.6 (d, J_{PC} = 45 Hz, Mo≡C), 225.1 (d, J_{PC} = 14 Hz, CO), 145.7 (d, J_{PC} = 2 Hz), 144.4, 143.7, 138.1, 137.8, 137.1 (d, J_{PC} = 2 Hz), 107.5, 106.9, 106.8, 52.6 (d, J_{PC} = 6 Hz, P(OMe)$_3$), 44.9 (d, J_{PC} = 5 Hz), 30.0 (d, J_{PC} = 3 Hz), 22.1, 13.5 ppm; $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 152.4 ppm; IR (CH_2Cl_2) 1997 cm^{-1} (ν_{CO}).

HMQC and HMBC Spectra. HMQC and HMBC spectra were recorded at −50 °C on a Varian UNITY 500 spectrometer equipped with a 5 mm indirect detection probe. The HMQC spectra were optimized for a $^1J_{CH}$ = 71 Hz (measured in a scouting run) and run in phase-sensitive mode. BIRD nulling (null = 0.5 s), a relaxation delay of 0.2 s, and no ^{13}C decoupling during acquisition were used. For the 2D spectrum, the full proton region (6525 Hz covering the region from −4.2 to 8.6 ppm) was taken in *f 2* and a spectral width of 12583 Hz, covering the region from 200 to 300 ppm, in *f 1*. The 2D FID had 2K points in *f 2* and 64 increments in *f 1* and were acquired with 64 scans per increment. A Gaussian function with a time constant of 0.09 s was used for weighting in *f 2*. Zero-filling to 256 points followed by a shifted Gaussian with a time constant of 0.001 s and a shift of 0.001 s was applied in *f 1* prior to the Fourier transform. The 1D HMQC spectrum was recorded with 256 points over a spectral width of 363 Hz centered about the signal at −2.98 ppm, in 1024 transients. Zero-filling twice and a shifted Gaussian window function with a time constant of 0.126 s and a shift of 0.084 s were applied prior to the Fourier transform, affording a precision of 0.7 Hz for the coupling constant. The HMBC spectrum was optimized for a $^nJ_{CH}$ of 8 Hz. The spectral width, number of points, relaxation delay, and apodization in *f 2* were the same as for the 2D HMQC experiment. In *f 1*, 64 increments (128 transients each) were collected for a spectral width of 39 024 Hz, covering the region −20−300 ppm. Zero-filling twice and multiplication with a Gaussian with a time constant of 0.001 s were applied prior to the Fourier transform.

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Supporting Information Available: ^1H NMR spectra of compounds **1** and **6**−**13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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