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Formation of Olefins Upon Oxidation of Molybdenum Alkyl Carbynes. Organic Radical Reactivity in an Organometallic Radical Cation

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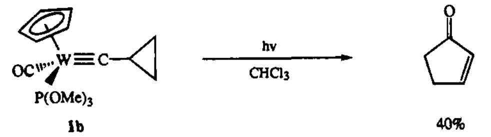
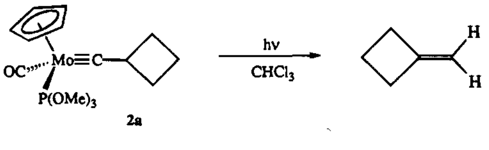
Abstract: Decomposition of the complexes $(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}Mo{\equiv}CR$ [R = c-C_4H_9, $(CH_2)_3CH_3$, and $CH(CH_2CH_2CH_3)_2$] in $CHCl_3$ results in conversion of the carbyne ligand to a terminal olefin. The reaction is initiated by oxidation and occurs during photolysis in $CHCl_3$ or upon slow diffusion of O_2 into the reaction mixtures. Corroborating evidence for initiation of the reaction by electron transfer has been obtained by conversion of the butyl carbyne ligand of $(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}Mo{\equiv}C(CH_2)_3CH_3$ to 1-pentene upon electrochemical oxidation. Mechanistic studies were consistent with H-abstraction by the carbyne radical cation to yield a cationic carbene complex which forms the olefin in a H-shift process. INDO calculations on the carbyne radical cation $[(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}Mo{\equiv}CCH_2CH_3]^{\bullet+}$ indicate stabilization upon bending the Mo≡C−C angle from 180° to 120°. This change in geometry places spin density on the carbyne carbon in the radical cation although the initial oxidation occurs from an orbital that is primarily nonbonding metal d in character. The oxidized carbyne is thus able to function as a carbon-centered radical and abstract a hydrogen atom at the carbyne carbon. Although the olefin-forming reaction is general for alkyl carbynes with a hydrogen on C2, the *tert*-butyl carbyne $(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}Mo{\equiv}CC(CH_3)_3$ (**2e**) did not form an olefin upon oxidation. Instead, photolysis of **2e** in $CHCl_3$ yielded the dichloromolybdenum carbyne $(\eta^5\text{-}C_5H_5)Cl_2\{P(OMe)_3\}Mo{\equiv}CC(CH_3)_3$ (**5e**) via a Cl-abstraction pathway.

Introduction

Several years ago it was observed that the cyclopropyl carbynes $(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}M{\equiv}C(c\text{-}C_3H_5)$ [M = Mo (**1a**), W (**1b**)] form cyclopentenone upon photolysis in $CHCl_3$ or under other oxidative conditions (eq 1).[2] Although four-membered rings are known to undergo ring-expansion processes to yield a variety of organic products,[3] ring opening is less facile than for their three-membered counterparts.[4] Thus, the related cyclobutyl carbynes $(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}M{\equiv}C(c\text{-}C_4H_7)$ [M = Mo (**2a**), W] do not undergo reactions analogous to eq 1 that yield six-membered rings. Instead, oxidation of **2a** produces methylenecyclobutane (eq 2).[5]



(1)



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This paper discusses the formation of olefins upon oxidative decomposition of the complexes $(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}Mo{\equiv}CR$ where R = cyclobutyl (**2a**), *n*-butyl (**2b**), and 4-heptyl (**2c**). The reaction is general for alkyl carbynes with hydrogens on C2, as shown by these results with **2a−c** and the previously reported formation of 1,4-pentadienes from the substituted butenyl carbyne complexes $(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}Mo{\equiv}CCH_2CH_2CR{=}CR'R''$.[6] Mechanistic studies are consistent with oxidation of the metal carbyne to its radical cation, H-abstraction at the carbyne carbon to yield a cationic carbene complex, and formation of the olefin in a H-shift process.

The H-abstraction process is a highly unusual one.[7] Chemistry at an organic ligand is known to occur in metal radicals, although it is much less common than reactions at the metal atom.[5] Radical processes have been observed for complexes containing conjugated π ligands such as cyclopentadienyl rings, vinylidene ligands, or acetylide ligands, but these almost always involve formation of dimeric complexes through coupling at the π-ligand.[5,8] The H-abstraction behavior observed in these $(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}Mo{\equiv}CR$ systems is consistent with the results of INDO calculations on the carbyne radical cation

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[1] (a) University of Florida. (b) Aarhus University.

[2] (a) Kingsbury, K. B.; Carter, J. D.; Wilde, A.; Park, H.; Takusagawa, F.; McElwee-White, L. *J. Am. Chem. Soc.* **1993**, *115*, 10056−10065. (b) Kingsbury, K. B.; Carter, J. D.; McElwee-White, L. *J. Chem. Soc., Chem. Commun.* **1990**, 624−625.

[3] Wong, H. N. C.; Lau, K.-L.; Tam, K.-T. *Top. Curr. Chem.* **1986**, *133*, 83−157.

[4] March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 133.

[5] McElwee-White, L.; Kingsbury, K. B.; Carter, J. D. In *Photosensitive Metal−Organic Systems. Mechanistic Principles and Applications*; Kutal, C., Serpone, N., Eds.; ACS Advances in Chemistry Series No. 238; American Chemical Society: Washington, DC, 1993; pp 335−349.

[6] Mortimer, M. D.; Carter, J. D.; McElwee-White, L. *Organometallics* **1993**, *12*, 4493−4498.

[7] H-abstraction at the carbene carbon has been observed upon reduction of $Cp^*(CO)_2Fe{=}C(OMe)Me$ to its radical anion in THF. Nlate, S.; Guerchais, V.; Lapinte, C. *J. Organomet. Chem.* **1992**, *434*, 89−96.

[8] For representative examples, see: (a) Connelly, N. G. *Chem. Soc. Rev.* **1989**, *18*, 153−185. (b) Geiger, W. E.; Gennett, T.; Lane, G. A.; Salzer, A.; Rheingold, A. L. *Organometallics* **1986**, *5*, 1352−1359. (c) Cron, S.; Morvan, V.; Lapinte, C. *J. Chem. Soc., Chem. Commun.* **1993**, 1611−1612. (d) Iyer, R. S.; Selegue, J. P. *J. Am. Chem. Soc.* **1987**, *109*, 910−911. (e) Seitz, F.; Fischer, H.; Riede, J.; Schöttle, T.; Kaim, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 744−746 and references therein.

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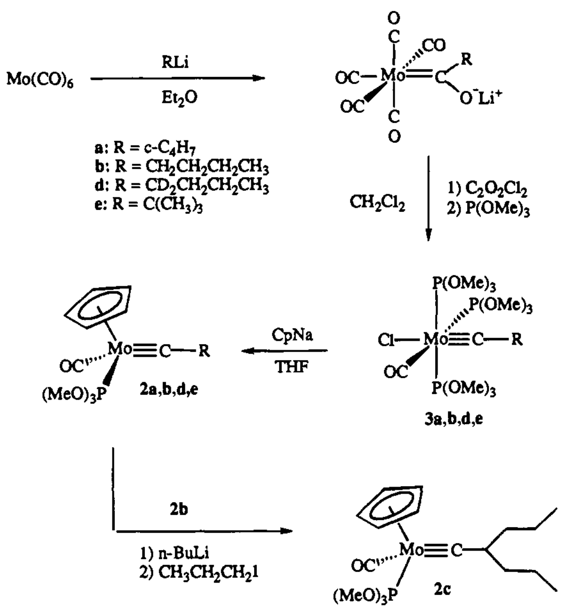
Scheme 1

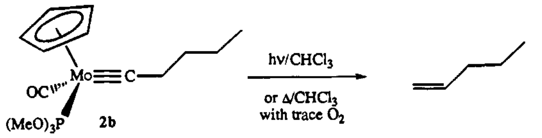


$[(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}Mo{\equiv}CCH_2CH_3]^{\bullet +}$ for which distortion from the original linear geometry to a bent carbyne with spin density on the carbyne carbon is a favorable process.

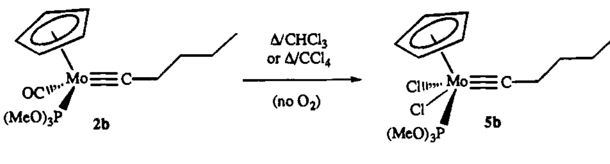
Results and Discussion

Synthesis of Complexes 2a–e. Carbyne complexes **2a–e** were synthesized as shown in Scheme 1. The tris(phosphite) complexes $Cl(CO)[P(OMe)_3]_3Mo{\equiv}CR$ (**3a**,**b**,**d**,**e**) were prepared from $Mo(CO)_6$ using a modification of the methods of Mayr.[9] Conversion to **2a**,**b**,**d**,**e** was accomplished by addition of CpNa to the corresponding tris(phosphite) complex **3a**,**b**,**d**,**e**. Compound **2c** was prepared from **2b** via a deprotonation/alkylation sequence according to the method of Green.[10] Compounds **2a–e** were isolated as yellow oils which required storage at −40 °C to avoid decomposition.

Formation of Olefins. Photolysis of cyclobutyl carbyne **2a** in $CHCl_3$ results in formation of methylenecyclobutane (eq 2). Under the same conditions, *n*-butyl carbyne **2b** is converted to 1-pentene in 35% yield (eq 3). In the absence of light, the reaction proceeds slowly, but with an increased yield of 45% provided that a small amount of O_2 is present. If O_2 is meticulously excluded from the reaction mixtures, the product of thermal decomposition in chlorinated solvents is the dichloromolybdenum carbyne **5b** (eq 4). In a sealed NMR tube, this reaction required 3 weeks to go to completion, and **5b** was formed in only 20% yield. In CCl_4, formation of **5b** proceeds much faster and with an improved yield of 60–70%. Carbyne **5b** was also formed during photooxidation and during thermal decomposition in the presence of O_2, but in much smaller amounts (*ca.* 5% yield). As noted during photooxidation experiments with the cyclopropyl carbynes $(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}M{\equiv}C(c\text{-}C_3H_5)$ [M = Mo, W],[2] methyl chloride is also formed but no other products could be identified in the reaction mixtures.

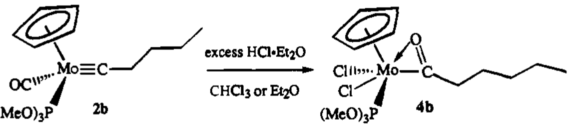


(3)



(4)

Since the 1-pentene formed in the reaction contains one more hydrogen atom than the butyl carbyne ligand, either protonation or hydrogen abstraction must be taking place during the reaction. Acid-induced chemistry was a possibility since $CHCl_3$ often contains small amounts of HCl, especially during photolysis.[11] In addition, protonation of metal carbynes is well-known although the site can be either the metal center or the carbyne carbon.[12] To explore the possible role of protonation in the formation of olefins, $HCl{\bullet}Et_2O$ was added to $CHCl_3$ and Et_2O solutions of **2b**. Addition of excess HCl yielded an orange solid which was found to be nearly pure $CpCl_2[P(OMe)_3]Mo\{\eta^2\text{-}C(O)(CH_2)_4CH_3\}$ (**4b**) (eq 5). This η^2-acyl complex results from addition of 2 equiv of HCl and carbonyl insertion into the Mo–C bond. Formation of η^2-acyl complexes upon treatment of metal carbynes with protic acids has been previously reported by Kreissl,[13] and also is seen in the reaction of cyclopropyl carbynes **1a**,**b** with HCl.[2a] Just as for **1a**,**b**, adding less than 1 equiv of HCl to **2b** resulted in a mixture of the η^2-acyl complex **4b** and starting material.



(5)

Other control experiments involved adding base to the solutions to scavenge any HCl that formed from solvent decomposition during the reaction. The addition of di-*tert*-butylpyridine to solutions in which radical cations are generated has previously been used to distinguish electron transfer chemistry from acid chemistry.[14] In reaction mixtures where **2b** was oxidized in the presence of di-*tert*-butylpyridine or proton sponge, the samples with added base showed the same yield and reaction time as the control samples. These experiments demonstrate that protonation cannot be the main pathway to olefins in this reaction.

Under the oxidative conditions of the reaction, the other possible source is H• abstraction in a radical process. Addition of 1,4-cyclohexadiene (a good H• abstraction substrate) in large excess to the reaction mixtures containing **2b** improved the yield

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(9) (a) McDermott, G. A.; Dorries, A. M.; Mayr, A. *Organometallics* **1987**, *6*, 925–931. (b) Mayr, A.; Dorries, A. M.; McDermott, G. A.; Van Engen, D. *Organometallics* **1986**, *5*, 1504–1506.

(10) (a) Mortimer, M. D.; Carter, J. D.; Kingsbury, K. B.; Abboud, K. A.; McElwee-White, L. *J. Am. Chem. Soc.* **1994**, *116*, 8629–8637. (b) Beevor, R. G.; Freeman, M. J.; Green, M.; Morton, C. E.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1991**, 3021–3030. (c) Beevor, R. G.; Freeman, M. J.; Green, M.; Morton, C. E.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1985**, 68–70.

(11) Bühler, R. E. In *The Chemistry of the Carbon–Halogen Bond*; Patai, S., Ed.; Wiley: London, 1973; p 852.

(12) (a) Howard, J. A. K.; Jeffery, J. C.; Li, S.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1992**, 627–634. (b) Bottrill, M.; Green, M.; Orpen, A. G.; Saunders, D. R.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1989**, 511–518. (c) Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schrock, R. R.; Schubert, U.; Weiss, K. *Carbyne Complexes*; VCH: Weinheim, 1988; pp 128–131. (d) Green, M.; Orpen, A. G.; Williams, I. G. *J. Chem. Soc., Chem. Commun.* **1982**, 493–495.

(13) (a) Kreissl, F. R.; Sieber, W. J.; Wolfgruber, M.; Riede, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 640. (b) Kreissl, F. R.; Sieber, W. J.; Keller, H.; Riede, J.; Wolfgruber, M. *J. Organomet. Chem.* **1987**, *320*, 83–90. (c) Kreissl, F. R.; Keller, H.; Schütt, W. *J. Organomet. Chem.* **1992**, *441*, 75–80.

(14) (a) Mirafzal, G. A.; Bauld, N. L. *Organometallics* **1991**, *10*, 2506–2508. (b) Gassmann, P. G.; Singleton, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 7993–7994.

Table 1. Isotopic Composition of 1-Pentene from Decomposition of **2b** and **2d** in $\mathrm{CHCl_3}$ or $\mathrm{CDCl_3}$

%	**2b** in $\mathrm{CDCl_3}$	**2d** in $\mathrm{CDCl_3}$	**2d** in $\mathrm{CHCl_3}$
d_0	84.3	3.2	3.7
d_1	15.7	19.7	22.0
d_2	0.0	62.8	68.8
d_3	0.0	14.3	5.5

of olefin (66% vs 41%) yet did not accelerate the disappearance of starting material. Also, experiments conducted in $\mathrm{CDCl_3}$ with 70 equiv of 1,4-cyclohexadiene yielded less deuterium incorporation in the 1-pentene product than a control reaction (3% vs 20% by GC/MS), indicating that hydrogen abstraction from the diene occurred in preference to D-abstraction from the solvent. These results are consistent with a radical process involving H-abstraction by the initially formed radical cation.

Electrochemical Oxidation. Corroborating evidence for initiation of olefin formation by electron transfer was obtained from electrochemical experiments on carbyne **2b**. The cyclic voltammogram of **2b** shows a single irreversible oxidation wave in $\mathrm{CH_2Cl_2}$ at 0.63 V (100 mV/s), consistent with rapid chemical reaction of the initially formed radical cation. In DME this wave is shifted to 0.68 V (100 mV/s). Potentiostatically controlled electrolysis at an overpotential of 0.80 V, in DME under nitrogen, caused the solution to turn from yellow to green. After isolation of the volatile components from the electrolysis solution, GC analysis was performed on the clear solution. The presence of 1-pentene was established by comparison to authentic samples of 1-pentene in DME. The identification of 1-pentene in the product mixture was confirmed by GC/MS analysis of the isolated volatile components, in which the molecular ion peak for 1-pentene was observed at the retention time assigned by comparison with the standard solution. These results are consistent with those obtained from photooxidation of the carbyne, in which electron transfer is postulated to be the first step in olefin formation.

Deuterium-Labeling Experiments. Although the above experiments were consistent with $\mathrm{H^\bullet}$ abstraction, there were several possible sources of $\mathrm{H^\bullet/D^\bullet}$ in the reaction mixtures. Decomposition of **2b** in $\mathrm{CDCl_3}$ yielded olefin that was only 16−25% 1-pentene-d_1, showing that most of the abstraction did not occur from the solvent. Deuteration levels of 15−30% were also observed for olefins obtained from the cyclobutyl (**2a**) and 4-heptyl (**2c**) carbynes in $\mathrm{CDCl_3}$. Given that abstraction of a hydrogen from C2 of the carbyne substituent would give rise to a stabilized radical, it seemed possible that those hydrogens served as $\mathrm{H^\bullet}$ donors in a process that sacrificed a portion of the carbyne complexes. The low yields of olefins and observation of intractable material in the reaction mixtures were also consistent with this hypothesis. In order to investigate this possibility, the deuterium-labeled carbyne $\mathrm{Cp(CO)[P(OMe)_3]Mo{\equiv}CCD_2(CH_2)_2CH_3}$ (**2d**) was prepared. From analysis of HRMS data, **2d** was determined to be 79% d_2 and 21% d_1 for an overall 89.5% deuteration at C2 of the carbyne ligand.

Decomposition of **2b** and **2d** was studied using a combination of GC/MS, ^{1}H, and ^{2}H NMR spectroscopy. Table 1 summarizes the results of the deuterium-labeling experiments. Three series of experiments were conducted: decomposition of **2b** in $\mathrm{CDCl_3}$, **2d** in $\mathrm{CHCl_3}$, and **2d** in $\mathrm{CDCl_3}$. From the first of these, it was determined that the 1-pentene formed from **2b** in $\mathrm{CDCl_3}$ was 16% deuterated. Since the only source of deuterium in this reaction is $\mathrm{CDCl_3}$, this shows that most of the "$\mathrm{H^\bullet}$" in the olefin-forming reaction is coming from a source other than the solvent. If other metal carbyne molecules are suitable $\mathrm{H^\bullet}$ donors, this is not unexpected since the isotope effect on abstraction from $\mathrm{CDCl_3}$ will disfavor this process. Chloroform generally exhibits a k_H/k_D in the range of 2−5 for hydrogen/deuterium abstraction by radicals,[15] but given that these values are dependent on the identity of the abstracting species,[16] k_H/k_D for abstraction from $\mathrm{CHCl_3}$ by the carbyne radical cation could conceivably be higher.[17]

If the metal carbynes themselves are the primary source of $\mathrm{H^\bullet}$, then based on statistics and anticipated C−H bond strengths, there are two likely abstraction sites: the C2 hydrogens of the carbyne ligand and the methyl groups of the phosphite ligand. The cyclopentadienyl and C3−C5 hydrogens of the carbyne ligand are viewed as less likely donors since their C−H bond strengths should be high in comparison. The low incorporation of deuterium (16%) during decomposition of **2b** in $\mathrm{CDCl_3}$ shows that the radical prefers to abstract the hydrogens of the phosphite and/or carbyne ligands to the deuteriums of chloroform. Abstraction from the carbyne ligand must be occurring because when **2d** is decomposed in $\mathrm{CHCl_3}$, 5.5% of the molecules formed have incorporated a deuterium from another carbyne complex. Note that although this process transfers D atoms from one carbyne to another, the total amount of D label in the olefin pool is virtually unchanged when **2d** is decomposed in $\mathrm{CHCl_3}$. The phosphite ligand is likely to be a donor based on the experiment with **2d** in $\mathrm{CDCl_3}$, in which it must be the source of hydrogen unless the C3−C5 (or Cp) hydrogens serve as donors or k_H/k_D for abstraction of the residual H's on C2 of the carbyne ligand is >200. The magnitudes of primary isotope effects for atom abstraction depend on the nature of the donor as well as the abstracting radical so exact values are difficult to estimate, but based on k_H/k_D values for abstraction by resonance stabilized carbon radicals they would be expected to be in the range 2−12.[18]

Obtaining an olefin from the carbyne complexes also requires an H-shift from C2 to C1 of the carbyne ligand. The deuterium-labeling experiments also provided information on the H-shift step of the reaction. The decomposition of **2d** in $\mathrm{CHCl_3}$ was monitored by ^{2}H NMR spectroscopy which showed the single peak of **2d** at 2.3 ppm decreasing and the peaks of 1-pentene at 5.9 and 5.0 ppm growing in. The integrals of the olefin peaks were roughly equal, indicating that half the deuterium label had shifted to the former carbyne carbon during olefin formation. This result is consistent with the shift of one of the two C2 hydrogens during the reaction and is similar to that obtained by Gladysz for formation of the deuterium-labeled olefin complex upon rearrangement of $[(\eta^5\text{-}\mathrm{C_5H_5})(\mathrm{NO})\{\mathrm{PPh_3}\}\mathrm{Re{=}C\text{-}HCD_2CH_3}]^+[\mathrm{PF_6}]^-$.[19a]

Alkyl Substitution at C2. As discussed above, carbyne complexes whose substituents are the secondary alkyls cyclobutyl (**2a**) and 4-heptyl (**2c**) also form olefins upon photolysis

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[15] (a) Foon, R.; Reid, G. P.; Tait, K. B. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 1311−1138. (b) Carmichael, H.; Johnston, H. S. *J. Chem. Phys.* **1964**, *41*, 1975−1982.

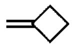
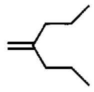
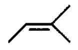
[16] (a) Nicovich, J. M.; van Dijk, C. A.; Kreutter, K. D.; Wine, P. H. *J. Phys. Chem.* **1991**, *95*, 9890−9896. (b) Bockrath, B.; Bittner, E.; McGrew, J. *J. Am. Chem. Soc.* **1984**, *106*, 135−138.

[17] (a) Skell, P. S. *J. Am. Chem. Soc.* **1984**, *106*, 1838−1840. (b) Skell, P. S.; Tlumak, R. L.; Seshadri, S. *J. Am. Chem. Soc.* **1983**, *105*, 5125−5131.

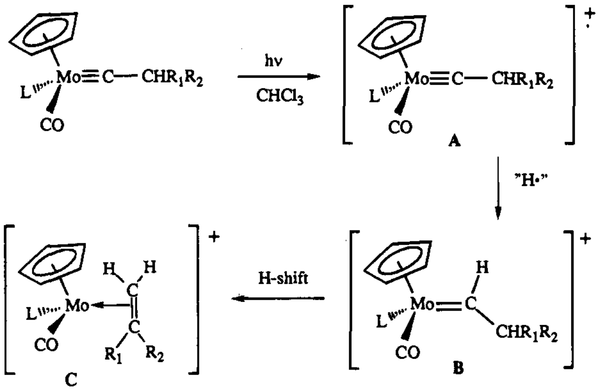
[18] (a) Lewis, E. S. *Top. Curr. Chem.* **1978**, *74*, 31−44. (b) Bochrath, B. C.; Bittner, E. W.; Marecic, T. C. *J. Org. Chem.* **1986**, *51*, 15−19. (c) Franz, J. A.; Suleman, N. K.; Alnajjar, M. S. *J. Org. Chem.* **1986**, *51*, 19−25. (d) Franz, J. A.; Alnajjar, M. S.; Barrows, R. D.; Kaisaki, D. L.; Camaioni, D. M.; Suleman, N. K. *J. Org. Chem.* **1986**, *51*, 1446−1456.

[19] (a) Roger, C.; Bodner, G. S.; Hatton, W. G.; Gladysz, J. A. *Organometallics* **1991**, *10*, 3266−3274. (b) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258−264. (c) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282−7292. (d) Casey, C. P.; Albin, L. D.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2533−2539.

Table 2. Olefin Products from Oxidative Decomposition of **2a**–**c** and **2e**

carbyne	olefin product	% yield of olefin		% d_1 in $CDCl_3$
		$h\nu/CDCl_3$	O_2/dark	
2a		44	61	20
2b		35	45	16
3c		37	62	10
2e		0	0	0

Scheme 2



or oxidation by O_2 in $CHCl_3$. These results are summarized in Table 2. Olefins formed from carbynes **2a** and **2c** show approximately the same amount of deuterium incorporation but are formed more rapidly and in slightly improved yields with respect to **2b**. Again, photooxidation conditions resulted in a lower yield and more formation of CH_3Cl and other unidentified products. The *tert*-butyl carbyne **2e** decomposes faster than **2a** or **2c**, forming the dichloromolybdenum carbyne **5e** in 50–60% yield. No olefins could be detected during this reaction, or upon air oxidation of the reaction mixture. This result contrasts with the oxidation of *n*-butyl carbyne **2b**, in which 1-pentene dominates the reaction products under these conditions and dichloromolybdenum carbyne **5b** is formed only very slowly and upon careful exclusion of light and O_2. As in the case of **2b** → **5b**, the yield of **5e** from **2e** can be improved to 80% by changing the solvent from $CHCl_3$ to CCl_4. Traces of analogues of **5e** could be detected in the decomposition of **2a** and **2c**, but they were not isolated.

Mechanistic Considerations. In previous work, we have postulated mechanisms for formation of various organic products upon oxidation of related carbynes of the type $(\eta^5\text{-}C_5H_5)(CO)[P(OMe)_3]M{\equiv}CR$ [M = Mo, W].[2,5,10a] In these reactions, the first two steps are electron transfer and hydrogen abstraction. We now propose that the first two steps in the olefin-forming reaction are identical. Oxidation of the carbyne complex results in generation of the 17-electron radical cation **A** which abstracts $H^\bullet$ from the reaction medium to form the cationic carbene complex **B** (Scheme 2).

At this point, the olefin-forming reaction deviates from previously observed chemistry. In the route to olefins, **B** undergoes a hydride shift to form the olefin complex **C**, which releases the olefin ligand. Precedent for the conversion of **B** to olefins can be found in several systems involving electrophilic alkyl carbene complexes.[19] The tendency of cationic species to undergo such rearrangements has led to comparison with Wagner–Meerwein shifts in organic carbocations.[19a]

As discussed above, the source of $H^\bullet$ in the conversion of **A** to **B** can be the solvent, the C2 hydrogens of the carbyne ligand, or a phosphite methyl group. Although **B** could in principle be accessed by protonation of the neutral carbyne, efforts to enter the reaction manifold by adding small amounts of HCl led to formation of η^2-acyl complexes, and experiments in which base was added showed no change from the control samples. Exclusive formation of η^2-acyl species generally dominates the reactions of $(\eta^5\text{-}C_5H_5)(CO)[P(OMe)_3]M{\equiv}CR$ [M = Mo, W] with HCl.[2a,10a,20] Interestingly, there are a few examples such as $(\eta^5\text{-}C_5H_5)(CO)[P(OMe)_3]Mo{\equiv}C(c\text{-}C_3H_5)$ and its 1-alkylcyclopropyl derivatives where the formation of η^2-acyl complexes is accompanied by smaller amounts of products common to the photooxidation manifold. This suggests that in these particular examples, a type **B** intermediate is formed by direct protonation and leads to the same products as photooxidation, although that is not usually the case.

The faster reaction rates for **2a** and **2c** are consistent with stabilization of radical cation **A** by the additional alkyl group. Complexes **2a** and **2c** also exhibit improved yields of olefin in their decomposition. This effect could be due to the decreased availability of C2 hydrogens in the carbyne ligand (compared to **2b**), since abstraction of hydrogen from a carbyne ligand is likely to lead to nonproductive decomposition pathways in the carbyne that serves as donor.

Note that *tert*-butyl carbyne **2e** does not yield olefins, but instead produces dichloromolybdenum carbyne **5e** in which the carbyne ligand is intact. There are two points in the pathway to olefins where the chemistry of **2e** could deviate. The first possibility is that radical cation $\mathbf{2e}^{\bullet+}$ is too sterically crowded for H-abstraction at the carbyne carbon. Formation of dichlorometal carbynes similar to **5e** has also been observed in other oxidation reactions of $(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}M{\equiv}CR$ [M = Mo, W] complexes.[10a] These carbynes are the product of ligand substitution at the metal, and have been postulated to arise from substitution of Cl^- for CO in the $17e^-$ radical cation **A** followed by $Cl^\bullet$ abstraction from the $CHCl_3$ solvent. In the absence of a sterically viable H-abstraction pathway for $\mathbf{2e}^{\bullet+}$, this chemistry could dominate. A second possibility is that the *tert*-butyl cationic carbene **B** forms but is unable to undergo an alkyl shift from the 3° center in analogy to the H-shifts to yield 2-methyl-2-butene. Deprotonation of **B** would regenerate the carbyne ligand.

Electronic Structure and Geometry of the Carbyne Radical Cation $\mathbf{2f}^{\bullet+}$. One of the most intriguing aspects of this chemistry is the unanticipated reactivity of the carbyne radical cations as carbon-centered radicals. In order to explore this issue, the electronic structure of the cation radical $[(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}Mo{\equiv}C{-}CH_2CH_3]^{\bullet+}$ ($\mathbf{2f}^{\bullet+}$) has been studied using the INDO model Hamiltonian[21] in the program ZINDO[22] (for computational and structural details see the Experimental Section). The calculations have been performed using an ethyl substituent at the carbyne atom as a model for the more elaborate complexes $(\eta^5\text{-}C_5H_5)(CO)[P(OMe)_3]Mo{\equiv}C{-}R$ (R = $c\text{-}C_4H_9$ (**2a**), $(CH_2)_3CH_3$ (**2b**), $CH(CH_2CH_2CH_3)_2$ (**2e**)].

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(20) Kingsbury, K. B.; Carter, J. D.; McElwee-White, L.; Ostrander, R. L.; Rheingold, A. L. *Organometallics* **1994**, *13*, 1635–1640.

(21) (a) Pople, J. A.; Beveridge, D. L.; Debosh, P. A. *J. Chem. Phys.* **1967**, *47*, 2026–2033. (b) Ridley, J. S.; Zerner, M. C. *Theor. Chem. Acta (Berlin)* **1973**, *32*, 111–134. (c) Zerner, M. C.; Loew, G. H.; Kirscher, R. F.; Mueller-Westerhoff, U. T. *J. Am. Chem. Soc.* **1980**, *102*, 589–599. (d) Anderson, W. P.; Cundari, T. R.; Drago, R. S.; Zerner, M. C. *Inorg. Chem.* **1990**, *29*, 1–3.

(22) Zerner, M. C., *et al.*, Department of Chemistry, University of Florida.

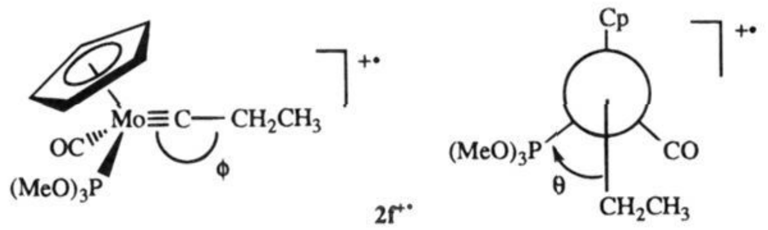


Figure 1. Definition of the bond angle (ϕ) and the dihedral angle (θ) for calculations on the carbyne radical cation **2f**$^{\bullet+}$.

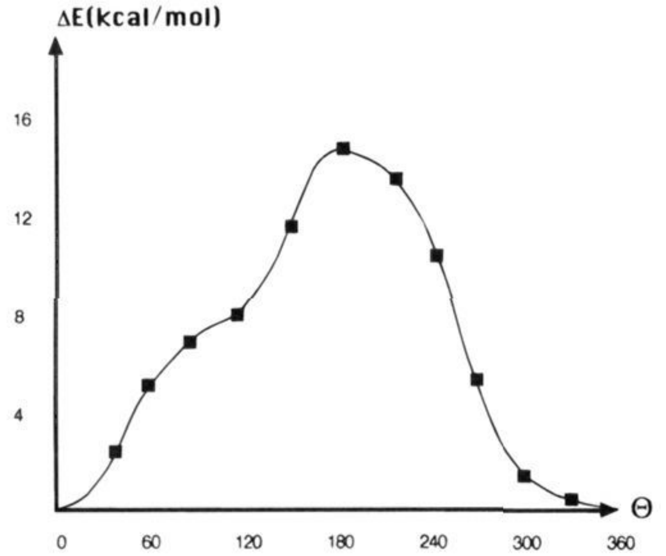


Figure 2. Change in calculated relative total energy of **2f**$^{\bullet+}$ upon variation of the dihedral angle θ from 0° to 360°. The bond angle ϕ was fixed at 120° for these calculations.

The geometry of the cation radical **2f**$^{\bullet+}$ has been studied keeping all the bond lengths, bond angles, and dihedral angles fixed, except the bond and dihedral angles ϕ and θ, respectively (see Figure 1). The total energy of **2f**$^{\bullet+}$ has been determined for ϕ in the range 180−120°. Bending ϕ from 180° to 120° causes a decrease in energy from −3395.395 to −3396.113 eV, *i.e.*, **2f**$^{\bullet+}$ is stabilized by 17 kcal/mol (0.718 eV) upon this distortion. The stabilization of **2f**$^{\bullet+}$ with $\phi = 120°$ relative to $\phi = 180°$ cannot be traced to a single orbital but is mainly due to obtaining slightly more σ bond character between the molybdenum and carbon atoms at the expense of π bond character between those two atoms.

The changes in total energy for **2f**$^{\bullet+}$ with $\phi = 120°$ during variation of θ from 0° to 360° (where $\theta = 0°$ corresponds to the orientation of the substituent in Figure 1) were also determined. The relative change in total energy of **2f**$^{\bullet+}$ for variation of θ from 0° to 360° is shown in Figure 2. It appears from Figure 2 that **2f**$^{\bullet+}$ is most stable with $\theta = 0°$, *i.e.* the ethyl substituent of the carbyne ligand located between the phosphine and carbonyl. The highest energy conformation of **2f**$^{\bullet+}$ is with the ethyl substituent *syn* to the Cp ring ($\theta = 180°$). This conformation is destabilized by 15 kcal/mol (0.65 eV) relative to the orientation of the ethyl substituent with $\theta = 0°$.

The change in frontier orbitals of **2f**$^{\bullet+}$ has also been studied at the two extrema of ϕ, 180° and 120°, respectively, with $\theta = 0°$. The frontier orbitals of **2f**$^{\bullet+}$ at these two angles are outlined in Figure 3 (only the orbitals at the molybdenum and carbon atoms are shown). Figure 3 also illustrates the correlation of the frontier orbitals of the bent form of **2f**$^{\bullet+}$ to those in the linear geometry. It should be noted that bending the Mo≡C−R angle *in* **2f**$^{\bullet+}$ *facilitates a great deal of orbital mixing and only* the main contributions from the linear form of **2f**$^{\bullet+}$ to the more stable form of **2f**$^{\bullet+}$ will be considered.

The singly occupied molecular orbital (SOMO) in the bent form of **2f**$^{\bullet+}$ is located at −12.0 eV and is a combination of p_y and p_z orbitals at the carbon atom mixed with mainly the molybdenum d_{yz} orbital with a minor contribution from the d_{z^2} and $d_{x^2-y^2}$ orbitals. This orbital is formed mainly from the SOMO and the HOMO−1 of linear **2f**$^{\bullet+}$ as depicted by the connection lines in Figure 3. The SOMO and HOMO−1 of linear **2f**$^{\bullet+}$ are located at −12.6 and −13.3 eV, respectively, and are of molybdenum $d_{x^2-y^2}$ orbital character for the former and molybdenum d_{yz} and carbon p_z character for the latter. It is notable that there is *no contribution* from orbitals at the carbon atom to the SOMO of linear **2f**$^{\bullet+}$, a consequence of near threefold symmetry. The HOMO−1 of the bent form of **2f**$^{\bullet+}$, located at −12.8 eV, is composed of a mixture of d_{xy} and d_{xz} orbitals on the molybdenum atom with a carbon p_x orbital, and this orbital is in principle a $\pi_{\mathrm{Mo-C}}$ orbital. The HOMO of the bent form, located at −12.6 eV, consists of a mixture of the $d_{x^2-y^2}$ and d_{yz} orbitals on the molybdenum atom, a consequence of reduced symmetry. Note that the SOMO and the HOMO of the bent form are composed of the same orbitals that comprise the SOMO and HOMO−1 of the linear form, but the reduced symmetry of the bent form allows mixing. The LUMO of the bent form of **2f**$^{\bullet+}$ at −4.7 eV is the antibonding partner to the SOMO. In the linear form, this orbital is located several electron volts higher in energy. The LUMO+1 of the bent form is mainly the s orbital at the molybdenum atom. The energy of this orbital is not affected by bending the Mo≡C−R angle and its counterpart is the LUMO of linear **2f**$^{\bullet+}$.

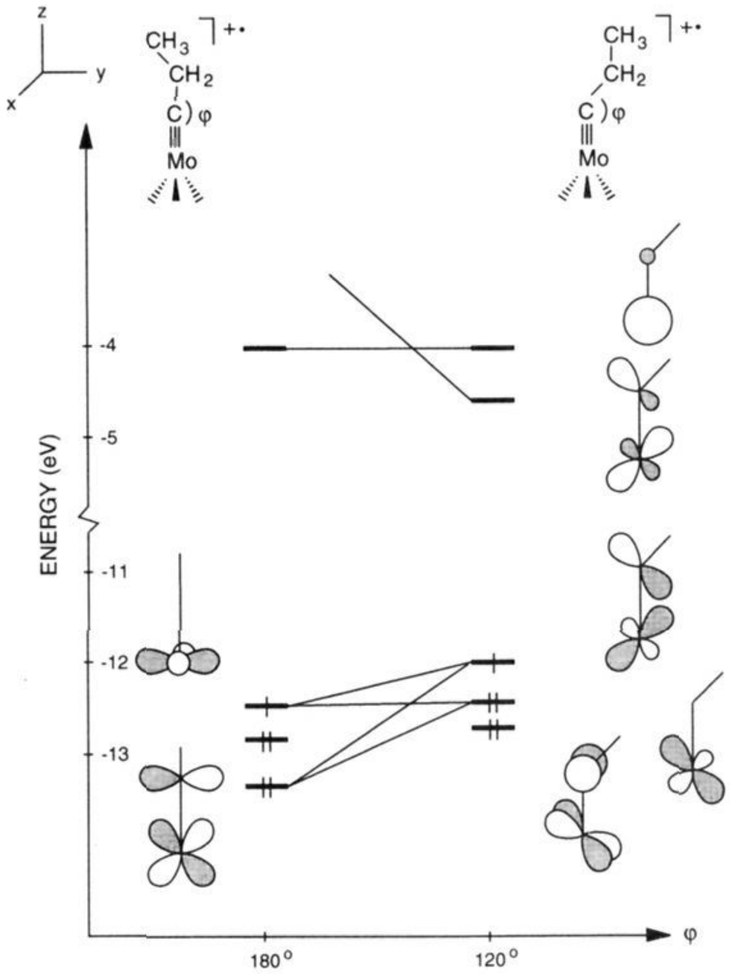
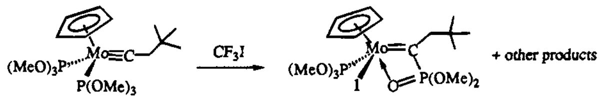


Figure 3. Frontier orbitals of **2f**$^{\bullet+}$ with the bond angle $\phi = 180°$ (left) or 120° (right). The dihedral angle θ was fixed at 0° for these calculations.

The most striking change when moving from the linear form to the bent form of **2f**$^{\bullet+}$ is the change in the shape and energy of the SOMO. Upon bending the Mo≡C−R angle in **2f**$^{\bullet+}$ from $\phi = 180°$ to 120° the energy of the SOMO is increased by 0.6 eV. However, the most important change in relation to the *present investigation is that orbitals at the carbon atom mix in* when bending the Mo≡C−R angle in **2f**$^{\bullet+}$ from $\phi = 180°$ to 120° to give a new SOMO which has a significant contribution from the carbon atom to the new MO. The spin density in the SOMO is distributed more or less equally at the molybdenum and carbon atoms and thus opens up the possibility of radical reactivity at the "carbyne" carbon in accordance with the present experimental results.[23] If the system were not allowed to bend, radical reactivity would be expected to occur only at the molybdenum atom, as the SOMO in the linear form of **2f**$^{\bullet+}$ is located exclusively on molybdenum.

The presence of spin density at the carbyne carbon in **2f**$^{\bullet+}$ not only is consistent with the H-abstraction reactions described in this paper but also provides an alternative mechanistic explanation for a reaction reported by Green.[24] Upon one-electron oxidation of $(\eta^5\text{-}C_5H_5)\{P(OMe)_3\}_2Mo{\equiv}CCH_2{}^tBu$ (**6**) by CF_3I, the products included the unusual chelated carbene complex **7** (eq 6). The authors postulated abstraction of methyl radical from the phosphite ligand of radical cation **6**$^{\bullet+}$ by $CF_3^\bullet$ followed by iodide-induced migration of $P(O)(OMe)_2$. However, the results are equally well explained by radical-induced Arbuzov reaction[25] initiated by intramolecular attack of the carbyne carbon of bent **6**$^{\bullet+}$ on the phosphite. Addition of iodide would then generate **7**.



6 **7** (6)

Conclusions

We have shown that alkyl carbynes of the type $(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}M{\equiv}CCHR_2$ [M = Mo, W] are subject to an oxidation reaction which converts the carbyne ligand to an olefin. The reaction can be initiated by photolysis in $CHCl_3$ or oxidation by trace amounts of O_2. Corroborating evidence for initiation of the reaction by electron transfer has been obtained by conversion of the butyl carbyne ligand of **2b** to 1-pentene upon electrochemical oxidation in DME. The generality of the reaction for carbynes with a primary or secondary substituent is shown by the production of olefins from alkyl carbynes **2a–d**. The first two mechanistic steps are postulated to be electron transfer and H$^\bullet$ abstraction, identical to those proposed for the production of organic products upon photooxidation of other complexes of the type $(\eta^5\text{-}C_5H_5)(CO)[P(OMe)_3]M{\equiv}CR$. The observation of radical reactivity at the carbyne carbon of the radical cations is consistent with the results of INDO calculations which predict considerable spin density on carbon following bending of the carbyne ligand. After generation of the cationic carbene intermediate by oxidation and H-abstraction, a hydride shift produces the olefin complex. In the *tert*-butyl carbyne complex **2e**, the reactivity of the carbyne ligand is effectively blocked and the only product observed results from chlorination of the metal.

Experimental Section

General Methods. Standard inert atmosphere techniques were used throughout. Hexane, petroleum ether, chloroform, and methylene chloride were distilled from CaH_2. Diethyl ether, THF, and toluene were distilled from Na/Ph_2CO. All NMR solvents were degassed by 3 freeze–pump–thaw cycles. Benzene-d_6 was vacuum transferred from Na/Ph_2CO. $CDCl_3$ was stored over 3Å molecular sieves. 1-Chlorobutane-*1,1*-d_2 was prepared by a literature procedure.[26] All other starting materials were purchased in reagent grade and used without further purification.

^1H, ^2H, ^{31}P, and ^{13}C NMR spectra were recorded on Varian XL-400 and VXR-300 NMR spectrometers. IR spectra were recorded on a Perkin-Elmer 1600 spectrometer. GC/MS was performed on a HP5890A chromatograph (containing a 5 m × 0.25 mm column of SE-54 on fused silica) equipped with a HP5970 series mass selective detector. High-resolution mass spectra were obtained at the University of California, San Francisco and at the University of Florida.

Electrochemical experiments were performed under nitrogen using a PAR Model 273 potentiostat/galvanostat or an IBM EC225 voltammetric analyzer. Cyclic voltammograms were recorded in a standard three-electrode cell with a glassy carbon working electrode. All potentials are reported vs NHE and were determined in CH_2Cl_2 or dimethoxyethane (DME) using 0.5 or 0.1 M TBAH, respectively. Decamethylferrocene ($E_{1/2}$ = 0.04 V) was used in situ as a calibration standard. Bulk electrolyses were performed using 2.0 × 3.5 cm stainless steel plates for the working and auxiliary electrodes in a standard three-electrode cell. The stirred solutions were electrolyzed at the appropriate potential until a color change was observed.

Unless otherwise stated, all photolyses were performed at room temperature in 5-mm NMR tubes by irradiation with a Hanovia medium-pressure mercury-vapor lamp in a Pyrex immersion well.

Synthesis of $Cl(CO)[P(OMe)_3]_3Mo{\equiv}C\overline{CHCH_2CH_2CH_2}$ (3a). Cyclobutyl bromide (1.0 g, 7.4 mmol) was dissolved in Et_2O and added to lithium metal in Et_2O (100 mg, 15 mmol) and the solution was stirred for 3.5 h. The resulting solution of cyclobutyllithium was added to an Et_2O solution of $Mo(CO)_6$ (1.88 g, 7.4 mmol) at 0 °C which was then stirred for 30 min. After removal of the Et_2O and addition of 50 mL of CH_2Cl_2, the procedure for **3b** was followed (*vide infra*), resulting in the isolation of yellow oil **3a** (0.8 g, 20% yield). ^1H NMR ($CDCl_3$) δ 3.70 (m, 27H, $P[OMe]_3$), 2.77 (m, 1H, CH), 2.47 (m, 2H, CH_2), 1.90 (m, 2H, CH_2), 1.6–1.7 (m, 4H, CH_2).

Synthesis of $(\eta^5\text{-}C_5H_5)(CO)[P(OMe)_3]Mo{\equiv}C\overline{CHCH_2CH_2CH_2}$ (2a). Carbyne **3a** (0.62 g, 1.0 mmol) was dissolved in 25 mL of THF and CpNa solution was added (1.0 mL, 2 mmol). The mixture was stirred for 24 h at room temperature after which the solvent was removed. The residue was dissolved in Et_2O and run through a short alumina column with Et_2O as the eluent. Upon removal of the solvent, **2a** was isolated as a yellow oil in 70% yield.[27] ^1H NMR ($CDCl_3$) δ 5.34 (s, 5H, Cp), 3.50 (d, 9H, $P[OMe]_3$, J_{HP} = 12 Hz), 2.92 (d quintet, 1H, ${\equiv}CCH$, J_{HP} = 5 Hz, J_{HH} = 7 Hz), 2.09 (m, 4H, CH_2), 1.72 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$) δ 317.9 (d, J_{CP} = 26 Hz, Mo≡C), 242.0 (CO), 90.7 (Cp), 51.1 (d, J_{CP} = 25 Hz, $P[OMe]_3$), 53.3, 29.2, 28.9, 18.4. ^{31}P NMR ($CDCl_3$) δ 204.5. IR (CH_2Cl_2) 1906 cm^{-1} (ν_{MoCO}) HRMS (FAB), *m/z* calcd for M$^+$ ($C_{14}H_{21}O_4{}^{98}MoP$) 382.0231, found 382.0225.

Synthesis of $Cl(CO)[P(OMe)_3]_3Mo{\equiv}CCH_2CH_2CH_2CH_3$ (3b). $Mo(CO)_6$ (8.0 g, 30 mmol) was dissolved in 100 mL of Et_2O. A solution of *n*-butyllithium (2.0 M in pentane, 18 mL, 36 mmol) was added and the mixture was stirred for 30 min. The Et_2O was removed by vacuum, CH_2Cl_2 (80 mL) was added, and the solution was cooled to −98 °C. Oxalyl chloride (2.5 mL, 28 mmol) was added and the solution warmed to −10 °C. During this time effervescence was observed. After returning the solution to the low-temperature bath, excess $P(OMe)_3$ was added (30 mL, 240 mmol). After the solution was stirred at room temperature for 24 h, the CH_2Cl_2 was removed under vacuum, leaving a black-brown solid which was extracted with Et_2O and run through a fritted funnel containing alumina to remove $P(OMe)_3$. Upon removal of Et_2O, **3b** was obtained as a yellow oil in 55% yield. ^1H NMR ($CDCl_3$) δ 3.72 (m, 27H, $P[OMe]_3$), 2.1 (dt, 2H, ${\equiv}CCH_2$), 1.45 (quintet, 2H, ${\equiv}CCH_2CH_2CH_2{-}$), 1.23 (sextet, 2H, ${\equiv}CCH_2CH_2CH_2CH_3$), 0.80 (t, 3H, CH_3).

Synthesis of $(\eta^5\text{-}C_5H_5)(CO)[P(OMe)_3]Mo{\equiv}CCH_2CH_2CH_2CH_3$ (2b). Carbyne **3b** (10.0 g, 16.7 mmol) was dissolved in 40 mL of THF. A 2.0 M solution of CpNa in THF (15.0 mL, 30 mmol) was

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[23] (23) Observation of radical reactivity in the ligand does not require that the spin density be predominantly on carbon. See: (a) Zou, C.; Ahmed, K. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1989**, *111*, 1133–1135. (b) Hamon, J.-R.; Astruc, D.; Michaud, P. *J. Am. Chem. Soc.* **1981**, *103*, 758–766.

[24] (24) Baker, P. K.; Barker, G. K.; Gill, D. S.; Green, M.; Orpen, A. G.; Williams, I. D.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1989**, 1321–1331.

[25] (25) (a) Bakkas, S.; Julliard, M.; Chanon, M. *Tetrahedron* **1987**, *43*, 501–512. (b) For a review of Arbuzov-type reactions in metal phosphite complexes, see: Brill, T. B.; Landon, S. J. *Chem. Rev.* **1984**, *84*, 577–585.

[26] (26) Westaway, K. C.; Lai, Z. *Can. J. Chem.* **1988**, *66*, 1263–1267.

[27] (27) Carbyne complexes prepared by this procedure sometimes contain small amounts of a mixture of $Mo(CO)_2[P(OMe)_3]_4$ and $Mo(CO)_3[P(OMe)_3]_3$ that cannot be removed by chromatography. This impurity can be seen in the ^1H NMR spectra of **2a** and **2b** (supplementary material). We have prepared $Mo(CO)_2[P(OMe)_3]_4$ and $Mo(CO)_3[P(OMe)_3]_3$ independently for identification purposes. Control experiments demonstrate that they do not affect the chemistry of the carbyne complexes.

added and the mixture was stirred at room temperature for 24 h. The solvent was removed in vacuo, hexane/Et_2O (3:1) was added, and the solution was filtered to remove excess CpNa. Following removal of the solvent, the product was chromatographed on neutral alumina (8 cm × 1.5 cm) with hexane as eluent to give **2b** in 60% yield: ^{1}H NMR ($CDCl_3$) δ 5.37 (s, 5H, Cp), 3.58 (d, 9H, P[OMe]$_3$, J = 12 Hz), 2.26 (dt, 2H, $\equiv CCH_2-$, J_{HP} = 4 Hz, J_{HH} = 7 Hz), 1.50 (m, 2H, $\equiv CCH_2C\mathit{H}_2CH_2-$), 1.35 (m, 2H, $\equiv CCH_2CH_2C\mathit{H}_2CH_3$), 0.85 (t, 3H, CH_3, J = 7 Hz). ^{13}C NMR ($CDCl_3$) δ 317.5 ($Mo\equiv C$), 241.3 (MoCO), 90.7 (Cp), 51.4 (P[OMe]$_3$), 49.7, 30.3, 22.1, 13.7. ^{31}P NMR ($CDCl_3$) δ 204.0. IR (CH_2Cl_2) 1897 cm^{-1} (ν_{MoCO}). HRMS (FAB), *m/z* calcd for M$^+$ ($C_{14}H_{23}O_4{}^{98}MoP$) 384.0388, found 384.0373.

Synthesis of $(\eta^5\text{-}C_5H_5)(CO)[P(OMe)_3]Mo{\equiv}CCH(CH_2CH_2CH_3)_2$ (2c). Carbyne **2b** (0.2 g, 0.5 mmol) was dissolved in 40 mL of THF and cooled to −78 °C. *n*-BuLi was added (1.8 M solution in pentane, 1.1 equiv, 0.3 mL, 0.55 mmol) and the color of the solution changed from yellow to orange. After addition of 1-iodopropane (170 mg, 1.0 mmol), a slight lightening of the solution was observed when the mixture was allowed to warm to 25 °C. After the mixture was stirred at room temperature for 1 h, the THF was removed under vacuum and the residue chromatographed on alumina using hexane as the eluent to give **2c** in 72% yield. ^{1}H NMR (C_6D_6) δ 5.37 (s, 5H, Cp), 3.49 (d, 9H, P[OMe]$_3$, J = 12 Hz), 2.40 (m, 1H, $\equiv CCH$), 1.7−1.8 (m, 4H, $\equiv CCHC\mathit{H}_2CH_2-$), 1.43 (m, 4H, $\equiv CCHCH_2C\mathit{H}_2CH_3$), 1.05 (dt, 6H, CH_3, J = 7 Hz). ^{13}C NMR (C_6D_6) δ 324.6 (d, $Mo\equiv C$, J_{CP} = 29 Hz), 242.1 (MoCO), 90.8 (Cp), 51.1 (P[OMe]$_3$), 58.3, 36.7, 21.0, 14.5. ^{31}P NMR (C_6D_6) δ 204.4. IR (CH_2Cl_2) 1902 cm^{-1} (ν_{MoCO}). HRMS (FAB), *m/z* calcd for M$^+$ ($C_{17}H_{29}O_4{}^{98}MoP$) 426.0858, found 426.0870.

Synthesis of $Cl(CO)[P(OMe)_3]_3Mo{\equiv}CCD_2CH_2CH_2CH_3$ (3d) and $(\eta^5\text{-}C_5H_5)(CO)[P(OMe)_3]Mo{\equiv}CCD_2CH_2CH_2CH_3$ (2d). 1-Chlorobutane-*1,1-d*$_2$ (2.15 g, 23 mmol) in pentane was added dropwise to lithium wire (0.32 g, 46 mmol) in pentane and refluxed for 2.5 h, whereupon the solution turned purple. This solution was filtered under N_2 into an Et_2O solution of $Mo(CO)_6$ (10 g, 38 mmol) and the rest of the synthesis proceeded as for **3b** and **2b**. For **3d**: ^{1}H NMR ($CDCl_3$) δ 3.70 (m, 27H, P[OMe]$_3$), 1.45 (t, 2H, $\equiv CCD_2C\mathit{H}_2CH_2-$), 1.20 (m, 2H, $\equiv CCD_2CH_2C\mathit{H}_2CH_3$), 0.80 (t, 3H, CH_3). For **2d**: ^{1}H NMR ($CDCl_3$) δ 5.37 (s, 5H, Cp), 3.58 (d, 9H, P[OMe]$_3$, J = 12 Hz), 1.50 (t, 2H, $\equiv CCD_2C\mathit{H}_2CH_2-$), 1.35 (sextet 2H, $\equiv CCD_2CH_2C\mathit{H}_2CH_3$), 0.85 (t, 3H, CH_3). HRMS (FAB), *m/z* calcd for M$^+$ ($C_{14}H_{21}D_2O_4{}^{98}MoP$) 386.0513, found 386.0508.

Synthesis of $(\eta^5\text{-}C_5H_5)Cl_2[P(OMe)_3]Mo(\eta^2\text{-}C(O)CH_2CH_2CH_2CH_3)$ (4b). Complex **2b** (200 mg, 5.2 mmol) was dissolved in 20 mL of Et_2O and excess HCl was added (1.0 M solution in Et_2O, 26 mmol). An orange precipitate formed immediately. The solution was stirred for 1 h, after which the solvent was decanted and the orange powder placed under vacuum for 2 h to yield pure **4b** (220 mg, 93%). ^{1}H NMR ($CDCl_3$) δ 5.43 (d, 5H, Cp, J_{HP} = 4 Hz), 3.86 (d, 9H, P[OMe]$_3$, J = 10 Hz), 3.17 (m, 2H, $C(O)C\mathit{H}_2-$), 1.8 (m, 2H, $C(O)CH_2C\mathit{H}_2CH_2-$), 1.37 (m, 4H, $C(O)CH_2CH_2C\mathit{H}_2C\mathit{H}_2CH_3$), 0.91 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$) δ 278.8 (d, C=O, J_{CP} = 15 Hz), 96.8 (Cp), 55.0 (d, J_{CP} = 8 Hz, P[OMe]$_3$), 42.0, 31.2, 25.0, 22.1, 13.7. ^{31}P NMR ($CDCl_3$) δ 137.4. IR (KBr pellet) 1522 cm^{-1} (ν_{MoCO}). HRMS (FAB), *m/z* calcd for M$^+$ ($C_{14}H_{25}O_4MoPCl_2$) 455.9923, found 455.9944.

Synthesis of $Cl(CO)[P(OMe)_3]Mo{\equiv}CC(CH_3)_3$ (3e). $Mo(CO)_6$ (8.0 g, 30 mmol) and tetramethylethylenediamine (4.5 g, 39 mmol) were dissolved in 100 mL of Et_2O. A solution of *tert*-butyllithium was added (1.7 M in pentane, 21 mL, 36 mmol) and the mixture was refluxed for 5 h. The Et_2O was removed by vacuum, 80 mL of CH_2Cl_2 was added, and the solution was cooled to −98 °C. Oxalyl chloride (1.85 mL, 21 mmol) was added and the solution warmed to −10 °C. During this time effervescence was observed. After returning the solution to the low-temperature bath, excess $P(OMe)_3$ was added (15 mL, 120 mmol). After the solution was stirred at room temperature for 24 h, the CH_2Cl_2 was removed under vacuum, leaving a black-brown solid which was extracted with 5:1 hexane/Et_2O and run through a fritted funnel containing alumina to remove $P(OMe)_3$. The solvent mixture was removed, leaving a purple-red oil which was redissolved in hexane and placed in a −40 °C freezer for 20 h. The purple solution was decanted and the hexane removed under vacuum to obtain **3e** as a purple-red oil in 15% yield. ^{1}H NMR ($CDCl_3$) δ 3.65 (m, 27H, P[OMe]$_3$), 1.22 (s, 9H, CH_3).

Synthesis of $(\eta^5\text{-}C_5H_5)(CO)[P(OMe)_3]Mo{\equiv}CC(CH_3)_3$ (2e). Carbyne **1e** (2.3 g, 3.8 mmol) was dissolved in 40 mL of THF. A 2.0 M solution of CpNa in THF (4.0 mL, 8 mmol) was added and the mixture was stirred at room temperature for 24 h. The solvent was removed in vacuo and extracted with hexane (50 mL). The hexane solution was allowed to stand for 12 h at −40 °C, after which the liquid fraction was decanted and the solvent removed. The orange oil obtained was chromatographed on neutral alumina (8 cm × 1.5 cm) with hexane as eluent to give **2e** in 70% yield: ^{1}H NMR ($CDCl_3$) δ 5.37 (s, 5H, Cp), 3.56 (d, 9H, P[OMe]$_3$, J = 12 Hz), 1.05 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$) δ 328.0 ($Mo\equiv C$, J_{CP} = 27 Hz), 241.4 (CO), 90.4 (Cp), 51.6 (P[OMe]$_3$), 51.1, 28.4. ^{31}P NMR ($CDCl_3$) δ 205.5. IR (CH_2Cl_2) 1899 cm^{-1} (ν_{MoCO}). HRMS (FAB), *m/z* calcd for M$^+$ ($C_{14}H_{23}O_4{}^{98}MoP$) 384.0388, found 384.0410.

Synthesis of $(\eta^5\text{-}C_5H_5)Cl_2[P(OMe)_3]Mo{\equiv}CCH_2CH_2CH_2CH_3$ (5b). Carbyne **2b** (200 mg, 5 mmol) was dissolved in 15 mL of CCl_4 and the solution was stirred at room temperature for 30 h. The yellow solution slowly turned orange, accompanied by effervescence. The carbon tetrachloride was removed under vacuum and the resulting solid washed with diethyl ether. ^{1}H NMR ($CDCl_3$) δ 5.95 (d, 5H, Cp, J_{HP} = 3 Hz), 3.91 (d, 9H, P[OMe]$_3$, J_{HP} = 11 Hz), 3.16 (m, 2H, $\equiv CCH_2-$), 1.65 (m, 2H, $\equiv CCH_2C\mathit{H}_2CH_2-$), 1.44 (m, 2H, $\equiv CCH_2CH_2C\mathit{H}_2CH_3$), 0.91 (t, 3H, CH_3, J = 7 Hz). ^{13}C NMR ($CDCl_3$) δ 373.5 (d, $Mo\equiv C$, J_{CP} = 54 Hz), 105.5 (Cp), 55.0 (d, J_{CP} = 7 Hz, P[OMe]$_3$), 51.7 (d, J_{CP} = 5 Hz, $\equiv C-\mathit{C}$), 13.1 (CH_3). ^{31}P NMR ($CDCl_3$) δ 144.7.

Synthesis of $(\eta^5\text{-}C_5H_5)Cl_2[P(OMe)_3]Mo{\equiv}CC(CH_3)_3$ (5e). Carbyne **2e** (100 mg, 3 mmol) was dissolved in 15 mL of CCl_4 and the mixture was stirred for 2 days. The solvent was then removed under vacuum and the remaining material recrystallized from 1:1 CH_2Cl_2/Et_2O, giving an orange-yellow powder in 75% yield. ^{1}H NMR ($CDCl_3$) δ 5.98 (d, 5H, Cp, J_{HP} = 4 Hz), 3.95 (d, 9H, P[OMe]$_3$, J_{HP} = 11 Hz), 1.22 (s, 9H, CH_3). ^{13}C NMR ($CDCl_3$) δ 382.2 (d, $Mo\equiv C$, J_{CP} = 60 Hz), 103.8 (Cp), 55.8 (d, P[OMe]$_3$, J_{CP} = 7 Hz), 55.4, 27.4. ^{31}P NMR ($CDCl_3$) δ 142.4. HRMS (FAB), *m/z* calcd for (M$^+$ − Cl) ($C_{13}H_{23}O_3Cl{}^{98}MoP$) 391.0128, found 391.0113 (no M$^+$ peak observed).

Bulk Electrolysis of 2b. Carbyne **2b** (0.10 g, 0.3 mmol) was dissolved in 50 mL of 0.1 M TBAH in DME. The yellow solution was cannula transferred to the electrochemical cell and, under a blanket of nitrogen, electrolyzed with stirring at 0.80 V until the solution was deep green (20 min). The solution was transferred to a Schlenk flask and the volatile components vacuum transferred to a separate Schlenk. Samples were removed by syringe for analysis of the product 1-pentene by GC and GC/MS.

Deuterium-Labeling Experiments: Oxidation of 2b and 2d by O_2 in $CHCl_3$ or $CDCl_3$. A typical procedure follows: Carbyne **2d** (40 mg, 0.10 mmol) was dissolved in 1.0 mL of $CDCl_3$ and placed in an NMR tube capped with a rubber septum to allow slow O_2 diffusion into the sample. The solution was monitored by ^{1}H NMR for 13 days until the starting material had disappeared. Samples were removed by syringe for analysis of the product 1-pentene by GC/MS. Isotopic distribution of the 1-pentene: d_0 3.2%, d_1 19.7%, d_2 62.8%, d_3 14.3%.

Reaction of 2b with HCl. Carbyne **2b** (25 mg, 0.065 mmol) was dissolved in 1 mL $CDCl_3$ and an initial NMR spectrum was obtained. An Et_2O solution of HCl was added (1.0 M, 33 μL, 0.033 mmol) and the solution immediately changed color from yellow to orange. A subsequent NMR spectrum showed a 5:4 ratio of η^2-acyl complex **4b** to **2b**.

Reaction of 2b with Di-*tert*-butylpyridine, Proton Sponge. Carbyne **2b** (45 mg, 0.12 mmol) was dissolved in 3 mL of $CDCl_3$. The solution was split into three NMR tubes, and to the first was added di-*tert*-butylpyridine (6 mg, 0.03 mmol). To the second tube was added proton sponge (1,8-bis(dimethylamino)naphthalene, 8 mg, 0.04 mmol). The third tube was retained as a control. All the tubes were wrapped in foil to exclude light, and ^{1}H NMR spectra were taken at intervals over 4 days. By integration, the yields of 1-pentene after 4 days were 33% for tube 1, 32% for tube 2, and 32% for the control tube.

Reaction of 2b with 1,4-Cyclohexadiene. Carbyne **2b** (40 mg, 0.1 mmol) and 1 drop of cyclopentane were dissolved in 0.5 mL of $CHCl_3$ and the solution split into two vials. To one vial was added degassed 1,4-cyclohexadiene (0.35 mL, 3.7 mmol) and to the control vial 0.35 mL of $CHCl_3$. The vials were wrapped in foil to exclude light, and the reactions were monitored by GC, using the cyclopentane peak as an internal standard. After 15 days, the 1-pentene peaks were integrated vs the internal standard, showing a yield of 66% for the reaction mixture containing 1,4-cyclohexadiene vs 41% in the control reaction. The volatile components of the vials were removed via a vacuum transfer and GC/MS was run on each, showing the 1-pentene from the 1,4-cyclohexadiene tube to be 3% deuterated, while the control tube showed 25% deuteration.

Computational Methods. The calculations were performed using the INDO/1 procedure included in the ZINDO program.[22] The following geometry was used for the radical cation $[(\eta^5\text{-}C_5H_5)(CO)[P(OMe)_3]Mo{\equiv}C{-}CH_2CH_3]^{\bullet+}$ (**2f**$^{\bullet+}$). Bond lengths: Mo≡C = 1.80 Å; Mo−C(Cp) = 2.51 Å; Mo−C(CO) = 1.94 Å; Mo−P = 2.33 Å; C(carbyne)−C = 1.53 Å; C−C(ethyl) = 1.53 Å; the remaining bond lengths used were standard bond lengths. Bond angles: C(CO)−Mo−P = 90°; Cp(centroid)−Mo−C(carbyne) = 135°; P−Mo−C(carbyne) = 90°; the remaining bond and dihedral angles used were standard bond and dihedral angles. In the geometrical analysis, only the bond and dihedral angles, ϕ and θ, were varied. All other geometrical parameters were fixed.

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Supplementary Material Available: Cyclic voltammogram for **2b** and ^1H NMR spectra for **2a**−**e**, **4b**, and **5b**,**e** (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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