Regioselective and Stereoselective Formation of Cyclopentenones upon Photooxidation of Cyclopropyl Carbyne Complexes

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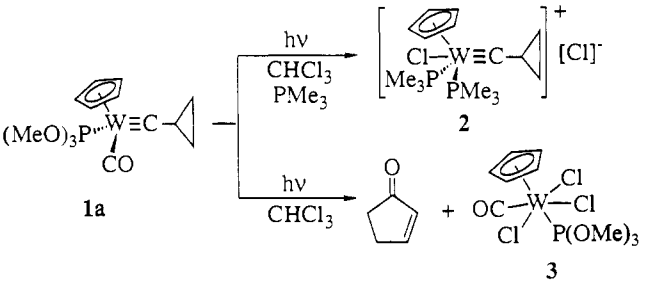
Abstract: Photolysis of the cyclopropyl carbyne complexes Cp(CO)LM≡CR [M = W, Mo; L = CO, $P(OMe)_3$, $P(OPh)_3$; R = C_3H_5, 2-ethylcyclopropyl, 2-phenylcyclopropyl, 2,2-dimethylcyclopropyl, *trans*-2,3-dimethylcyclopropyl, *cis*-2,3-dimethylcyclopropyl, bicyclo[4.1.0]heptyl (**1a–o, 6a,m, 11a,m**)] in chloroform results in photooxidation of the metal carbynes. Further reactions of the 17-electron carbyne complexes ultimately form cyclopentenones. Conversion of the 2-phenyl- and 2-ethylcyclopropyl carbyne complexes **1c,d** occurs regiospecifically to yield 4-phenyl- and 4-ethylcyclopentenone (**14c,d**), respectively. Complexes bearing 2,3-dimethylcyclopropyl substituents (**1g–n**) undergo an initial photochemical isomerization prior to oxidation and formation of the *trans*- and *cis*-4,5-dimethylcyclopentenones (**14g,i**). The intermediate cyclopentenone complex $CpCl[P(OMe)_3]MoL$ (L = *trans*-4,5-dimethylcyclopentenone) (**15m**) has been isolated and a crystal structure obtained: $P2_1/c$; a = 14.101(3) Å; b = 9.516(2) Å; c = 13.497(2) Å; β = 112.68(1)°; V = 1671.1(5) Å^3; Z = 4; R = 3.4%; R_w = 4.3% for 2187 reflections $I > 0.01\sigma(I)$.

Introduction

We recently reported the generation of 17e$^-$ carbyne complexes by photooxidation of the carbynes $CpL_2M{\equiv}CR$ [M = W, Mo; L = CO, $P(OMe)_3$; R = Ph, Me, (c-C_3H_5)].[1] If the cations are generated in the presence of the strong donor ligand PMe_3, they undergo rapid ligand exchange followed by abstraction of chloride to give the cationic carbyne complexes $[Cp(Cl)(PMe_3)_2M{\equiv}CR]^+Cl^-$. These facile ligand exchange and atom abstraction reactions are typical of the chemistry of metal radicals.[2] However, when photooxidation of the alkyl carbyne complexes $CpL_2M{\equiv}CR$ is carried out in the absence of added ligands, the site of reactivity is switched from the metal atom to the carbyne moiety. As an example, we have recently shown that photolysis of the carbyne complex $Cp(CO)[P(OMe)_3]W{\equiv}C(c\text{-}C_3H_5)$ (**1a**) in $CHCl_3$ results in conversion of the carbyne ligand to cyclopentenone (Scheme **I**).[3] This result is highly unusual not only because the reactivity of the oxidized species occurs at the ligand but because the reactivity can be switched from metal-centered to ligand-centered by a change in the reaction conditions.

Formation of cyclopentenone from carbyne **1a** poses interesting mechanistic questions. The experiments described below address the fate of the 17e$^-$ cationic complex initially produced in this reaction. Regiochemical and stereochemical outcomes of photooxidation of C2- and C3-substituted cyclopropyl carbynes are discussed as well as the isolation of an intermediate in the reaction pathway. The results of these experiments have led us to propose a mechanism involving conversion of the metal carbynes to metallacyclic intermediates followed by formation of cyclopentenone complexes which release the enones upon further oxidation.

Scheme I



Results and Discussion

Synthesis of Carbynes. The carbyne complexes $CpL_2M{\equiv}CR$ were synthesized as shown in Scheme II. The tris(phosphite) complexes $Cl(CO)[P(OMe)_3]_3M{\equiv}CR$ (**7a–p**) were prepared from the acyl complexes **4a–p** by the method of Mayr[4a] as were the tetracarbonyl complexes $Cl(CO)_4M{\equiv}CR$ (**5a–p**). The tetrakis(phosphite) complex $Cl[P(OMe)_3]_4Mo{\equiv}C(c\text{-}C_3H_5)$ (**8b**) was synthesized by heating the tris(phosphite) complex **7b** in neat trimethyl phosphite.[4b] The bis(phosphite) complexes $Cl(CO)_2[(P(OPh)_3]_2M{\equiv}CR$ [M = W, R = (c-C_3H_5); M = Mo, R = *trans*-2,3-dimethylcyclopropyl] (**10a,m**) were prepared by the method of Fischer.[4c]

Reactions of carbynes **7a–p** with CpNa led to displacement of the chloride anion and two of the phosphite ligands to yield the desired Cp-substituted carbynes **1a–p**. The dicarbonyl compounds **6a,m** were prepared by reaction of **5a,m** with CpNa at low temperature. Higher temperatures and longer reaction times were required to react tetrakis(phosphite) complex **8b** with CpNa in THF to yield **9b**. Reaction of CpNa with the bis(phosphite) compounds **10a,m** resulted in substitution of the chloride anion, one carbonyl, and one phosphite to produce the compounds **11a,m.**

Photooxidation of Cyclopropyl Carbyne 1a. As we recently reported, photolysis of $Cp(CO)[P(OMe)_3]W{\equiv}C(c\text{-}C_3H_5)$ (**1a**)

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(2) (a) Trogler, W. C., Ed. *Organometallic Radical Processes*; Elsevier: Amsterdam, 1990. (b) Astruc, D. *Ac. Chem. Res.* **1991**, *24*, 36–42. (c) Baird, M. *Chem. Rev.* **1988**, *88*, 1217–1227.

(3) Kingsbury, K. B.; Carter, J. D.; McElwee-White, L. *J. Chem. Soc., Chem. Commun.* **1990**, 624–625.

(4) (a) Mayr, A.; Dorries, A. M.; McDermott, G. A.; Van Engen, D. *Organometallics* **1986**, *5*, 1504–1506. (b) McDermott, G. A.; Dorries, A. M.; Mayr, A. *Organometallics* **1987**, *6*, 925–931. (c) Fischer, E. O.; Ruhs, A.; Kriessl, F. R. *Chem. Ber.* **1977**, *110*, 805–815.

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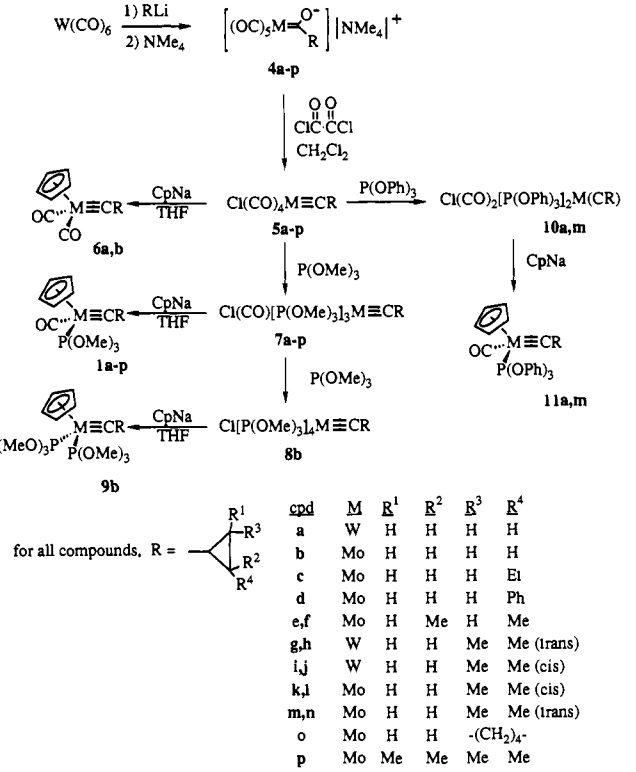
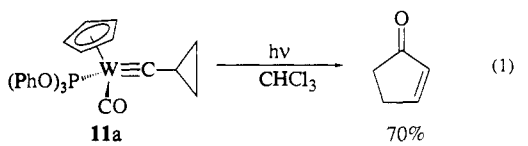
Scheme II



cpd	M	R^1	R^2	R^3	R^4
a	W	H	H	H	H
b	Mo	H	H	H	H
c	Mo	H	H	H	Et
d	Mo	H	H	H	Ph
e,f	Mo	H	Me	H	Me
g,h	W	H	H	Me	Me (trans)
i,j	W	H	H	Me	Me (cis)
k,l	Mo	H	H	Me	Me (cis)
m,n	Mo	H	H	Me	Me (trans)
o	Mo	H	H	-$(CH_2)_4$-	
p	Mo	Me	Me	Me	Me

in $CHCl_3$ results in disappearance of starting material and formation of $Cp(CO)[P(OMe)_3]WCl_3$ (**3**) in 58% yield and cyclopentenone in 38% yield (Scheme **I**).[3] Methyl chloride is the only other identifiable product and is produced in 25% yield. Under the same conditions, the molybdenum congener $Cp(CO)[P(OMe)_3]Mo{\equiv}C(c\text{-}C_3H_5)$ (**1b**) also produces cyclopentenone in 40% yield and methyl chloride in 25% yield. This reaction also produces some trimethyl phosphate, as identified by ^1H NMR and GC/MS. Its origin is unknown, but it could arise from adventitious oxygen. The analogous inorganic product $Cp(CO)[P(OMe)_3]MoCl_3$ is not observed presumably due to its instability under the reaction conditions. In both reactions, a significant amount of intractable material is produced.

The methyl chloride seen in these reactions is consistent with an Arbuzov reaction between the trimethyl phosphite ligand and chloroform. The Arbuzov reaction is known to be initiated by light or radicals,[5] both of which are present under the reaction conditions. In order to minimize the extent of Arbuzov reaction in this system, we synthesized the triphenyl phosphite complex $Cp(CO)[P(OPh)_3]W{\equiv}C(c\text{-}C_3H_5)$ (**11a**). Photolysis of **11a** in chloroform under identical conditions as for **1a** also resulted in formation of cyclopentenone, but in a significantly improved yield of 70% (eq 1).

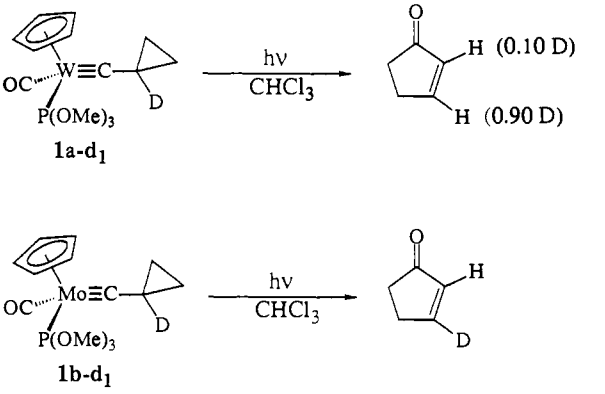


(1)

The cyclopentenone product contains one hydrogen not derived from the original cyclopropyl carbyne ligand. Mass spectroscopy and ^1H NMR analysis of the cyclopentenone produced from the photolysis of either **1a** or **1b** in $CDCl_3$ reveal 48% $^2H_1$ on C2. The hydrogen is thus supplied in part from the solvent. The source of the additional hydrogen has not been determined.

(5) (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.

Scheme III



Photooxidation of 1a-d_1 and 1b-d_1. In the mechanistically simplest transformations of starting materials **1a** and **1b** to cyclopentenone, the carbyne carbon becomes C2 of the product and C1 of the cyclopropyl group becomes C3. To confirm this assignment, **1a** and **1b** were deuterium labeled at C1 by successive treatment with *n*-BuLi and D_2O. Mass spectral and ^1H NMR analysis of cyclopentenone isolated from irradiation of **1a-d_1** in $CHCl_3$ indicate retention of all of the deuterium label, with 90% of it remaining at C3 (Scheme III). For **1b-d_1**, photolysis in $CHCl_3$ produces cyclopentenone labeled exclusively at C3.

Control Experiments: The Role of HCl. Since these reactions involved photolysis in $CHCl_3$ or $CDCl_3$, concern arose over the possible participation of HCl (or DCl) which could arise from decomposition of the solvent.[6] In order to determine whether trace amounts of HCl are necessary for the reaction to occur, several control experiments were performed. Generation of organic radical cations in the presence of di-*tert*-butylpyridine has been used to distinguish radical cation chemistry from acid-catalyzed reactions.[7] In similar experiments, photooxidation of **1a** or **1b** in the presence of Proton Sponge or di-*tert*-butylpyridine produced cyclopentenone in the same yields as obtained in the absence of base.

Also, electron transfer to acceptors other than chloroform resulted in the same chemistry. Although neither carbyne **1a** nor **1b** produces cyclopentenone upon photolysis in C_6D_6 in the absence of an electron acceptor, cyclopentenone is produced upon photolysis of **1a** or **1b** in CCl_4, which cannot form HCl. In addition, photoinduced electron transfer from **1a** to methyl viologen in nonchlorinated solvents afforded small amounts of cyclopentenone, indicating that rearrangement of the cyclopropyl group in $\mathbf{1a}^+$ is competitive with back transfer from the reduced acceptor molecule. Also, oxidation by O_2 in C_6D_6 yields cyclopentenone (Scheme IV). These experiments in which cyclopentenone is formed under conditions where HCl is not generated confirm that the reactions are not triggered by acid.

Other control experiments were performed in order to assess the effect of added HCl. Protonation of metal carbynes can occur either at the metal or at the carbyne carbon.[8] However, as shown in eq 2, treatment of **1a** with ethereal solutions of HCl resulted only in formation of the η^2-acyl complex $Cp(Cl)_2[P(OMe)_3]WCOCH_2(c\text{-}C_3H_5)$ (**12a**). Several η^2-acyl complexes have been prepared by addition of protic acids to metal carbynes

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(7) (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.

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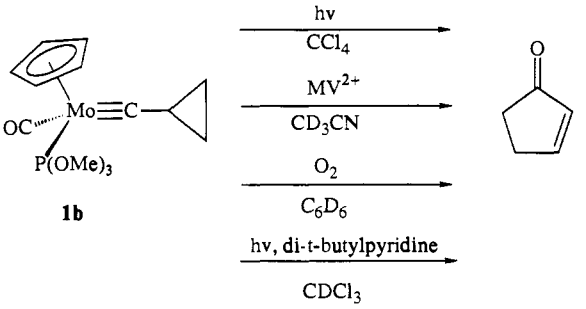
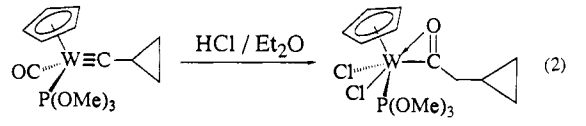
Scheme IV



1b

including the similar complex $Cp(CF_3CO_2)_2(CO)WCOCH_2(c\text{-}C_3H_5)$.[9] Formation of **12a** was quantitative with respect to HCl, even when less than 1 equiv of acid was added. Treatment of molybdenum complex **1b** with HCl resulted in formation of the analogous acyl complex $Cp(Cl)_2[P(OMe)_3]MoCOCH_2(c\text{-}C_3H_5)$ (**12b**). However, in the case of **1b**, a second product which eventually forms cyclopentenone could also be observed (vide infra).



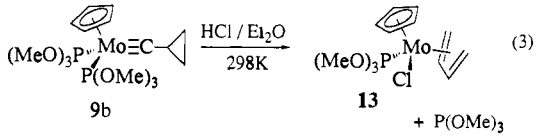
(2)

1a **12a**

Control Experiments: The Role of the CO Ligand. Carbyne complexes containing carbonyl ligands have been observed to undergo carbonyl–carbyne coupling to form ketenyl complexes under a variety of conditions.[10] Coupling products have been obtained by addition of nucleophiles or electrophiles as well as photochemically.[11] In addition, an η^2-ketenyl species was postulated as an intermediate in the photochemical *cis–trans* isomerization of *cis,cis*-$[(M{\equiv}CPh)X(CO)_2(PR_3)_2]$ complexes (M = Mo, W).[12] Thus, one mechanistic possibility for cyclopentenone formation involved initial coupling of a carbonyl to the carbyne ligand followed by rearrangement. However, efforts to observe ketenyl intermediates by following the photooxidation of **1a** and **1b** by low-temperature IR and NMR spectroscopy were unsuccessful. Attempts to trap η^1-ketenyl species by the addition of nucleophiles such as methanol and allyl alcohol failed, as did attempts to trap η^2-ketenyl species by the addition of electrophiles such as trimethylsilyl chloride and trimethyloxonium salts.[10] Thus, no evidence for ketenyl species was obtained, either by spectroscopic methods or by trapping experiments.

The role of CO was also examined by changing the ancillary ligands and by running the reaction under CO pressure. The yield of cyclopentenone was slightly improved (to 50%) upon photolysis of **1a** under 3 atm of CO, but no improvement in yield was obtained upon photooxidation of the related dicarbonyl carbynes **6a,m.**

Studies were also carried out on the bis(phosphite) carbyne complex $Cp[P(OMe)_3]_2Mo{\equiv}C(c\text{-}C_3H_5)$ (**9b**), in which carbonyl insertion is impossible. Irradiation of **9b** in $CDCl_3$ resulted in only intractable material, although careful addition of 1 equiv of ethereal HCl resulted in formation of a new purple-brown crystalline compound and free trimethyl phosphite (eq 3).

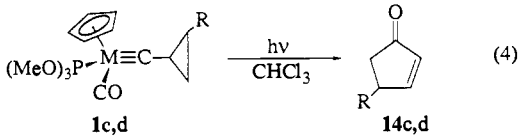


(3)

9b **13**

Formulation of this compound as the diene complex $Cp[P(OMe)_3]_2(Cl)Mo(\eta^4\text{-}CH_2{=}CHCH{=}CH_2)$ (**13**) was based on spectroscopic data and comparison to the related complexes $Cp(X)[P(OMe)_3]Mo(\eta^4\text{-}CH_2{=}CHCH{=}CHCH_2R)$ (R = Ph, ^{t}Bu; X = Br, I).[13] Air oxidation of **13** in benzene produced butadiene. Authentic samples of **13** were destroyed but did not produce any identifiable products upon photolysis in benzene or chloroform. Thus, if **13** were formed during photolysis of carbyne **9b** in chloroform, it would not survive the reaction conditions.

Photooxidation of 2-Substituted Cyclopropyl Carbynes. Rearrangement of unsymmetrically substituted cyclopropyl carbynes was explored with 2-substituted cyclopropyl complexes **1c** and **1d**. Since the formation of cyclopentenone involves a highly reactive radical species, rearrangement might be expected to give rise to mixtures of regioisomers. However, photolysis of **1c** in $CDCl_3$ resulted in formation of only 4-ethylcyclopentenone **14c** (eq 4).



(4)

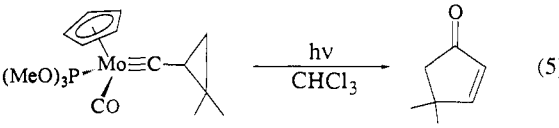
1c,d **14c,d**

1c: M = Mo, R = Et
1d: M = Mo, R = Ph

14c: R = Et
14d: R = Ph

Substitution of a phenyl ring at the 2-position of the cyclopropyl group would be expected to bias ring cleavage toward the C1–C2 bond more strongly since any ring-opened species would be stabilized through conjugation with the phenyl group.[14] Cleavage of the cyclopropyl C1–C2 bond of **1d** would then ultimately give rise to 5-phenylcyclopentenone. However, photolysis of **1d** in chloroform gives only 4-phenylcyclopentenone (**14d**). This regiochemical outcome is the same as for ethylcyclopropyl carbyne **1c**. Herndon has observed similar results[15] upon reaction of the 2-phenylcyclopropyl carbene complex $(CO)_5W{=}C(OMe)$(2-phenylcyclopropyl) with diphenylacetylene. Ring opening in that system also occurred in the less substituted C1–C3 bond, and the selectivity was attributed to steric effects.

Photooxidation of 2,2-Disubstituted Cyclopropyl Carbynes. Photolysis of the 2,2-dimethyl-substituted carbyne complexes **1e,f** in $CDCl_3$ resulted in formation of 4,4-dimethylcyclopentenone **14e** in 40% yield (eq 5). As seen for the ethyl- and phenyl-substituted carbynes **1c** and **1d**, ring opening occurs on the less substituted C1–C3 bond upon reaction of **1e,f.**



(5)

1e,f **14e**

(9) Kreissl, F. R.; Sieber, W. J.; Keller, H.; Riede, J.; Wolfgruber, M. *J. Organomet. Chem.* **1987**, *320*, 83–90.

(10) For reviews on this topic, see: (a) Geoffroy, G. L.; Bassner, S. L. *Adv. Organomet. Chem.* **1988**, *28*, 1–83. (b) Mayr, A.; Bastos, C. M. *Prog. Inorg. Chem.* **1992**, *40*, 1–98. (c) Mayr, A.; Hoffmeister, H. *Adv. Organomet. Chem.* **1991**, *22*, 227–324.

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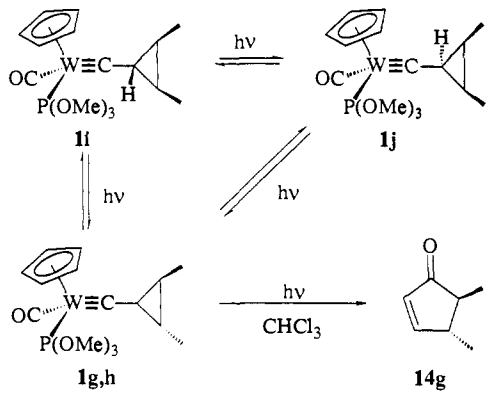
Scheme V



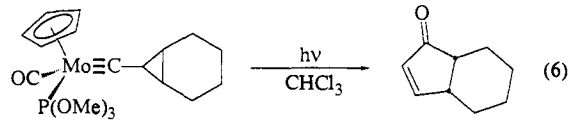
Photooxidation of 2,3-Disubstituted Cyclopropyl Carbynes. To probe the relative stereochemistry of C2 and C3 in this reaction, both the *cis*- and *trans*-2,3-dimethylcyclopropyl tungsten carbynes were prepared. Preparation of the *trans*-dimethylcyclopropyl carbyne afforded a mixture of the two diastereomers (**1g,h**). Photolysis of the mixture in $CHCl_3$ yielded *trans*-4,5-dimethylcyclopentenone (**14g**) in approximately 40% yield (Scheme V). The trichloride complex **3** was again formed, as was a 25% yield of CH_3Cl. Interestingly, one of the diastereomers reacted much more quickly than the other, thus providing a method of isolating the less reactive isomer. However, the stereochemistry of **1g** and **1h** could not be unambiguously assigned as attempts to grow crystals were unsuccessful.

Preparation of the *cis*-dimethylcyclopropyl tungsten carbyne also gave a mixture of two isomers (**1i,j**). In contrast to **1g** and **1h**, separation of **1i** and **1j** was possible by careful column chromatography. NOE experiments allowed **1i** and **1j** to be assigned as shown in Scheme V. Photolysis of either **1i** or **1j** in $CDCl_3$ resulted in formation of only *trans*-dimethylcyclopentenone. In control experiments, authentic *cis*-dimethylcyclopentenone was added to reaction mixtures before photooxidation of **1i** and **1j** and was not epimerized under the reaction conditions. Failure to observe *cis*-substituted **14i** indicates that stereochemistry is set during and not after the rearrangement. As in the photolysis of **1g** and **1h**, the rates of reaction were markedly different for the two *cis* isomers **1i** and **1j**, with **1i** being the isomer which decomposes more rapidly. However, both *trans* isomers **1g** and **1h** are converted to product more quickly than either *cis* isomer.

Photolysis of **1g,h, 1i,** or **1j** in C_6D_6 in the absence of an electron acceptor resulted in isomerization of the carbyne ligand to the equilibrium mixture of 18:60:20 for **1i:1g+1h:1j**. Also, photooxidation of any of **1g–j** in the presence of PMe_3 resulted in scrambling of the stereochemistry of the cyclopropyl group to yield photoproducts **2g–j** in the same ratio as seen for isomerization of the parent carbynes **1g–j**. However, addition of HCl to any of the compounds **1g–j** resulted in formation of the acyl complexes **12g–j** without isomerization of the cyclopropyl group. Given that one of the *trans* diastereomers undergoes conversion to the dimethylcyclopentenone much more rapidly than any of the other three isomers, it is reasonable to ascribe the stereoselectivity of the reaction to rapid photoisomerization of the starting materials followed by formation of *trans*-dimethylcyclopentenone from either **1g** or **1h**.

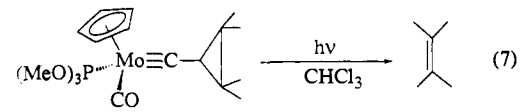
The analogous *cis*- (**1k,l**) and *trans*-dimethylcyclopropyl (**1m,n**) molybdenum carbynes were also prepared. As with tungsten complexes, the syntheses resulted in pairs of diastereomers for each but none of the four molybdenum diastereomers could be obtained in pure form. Photolysis of a mixture of the *cis*-dimethylcyclopropyl compounds **1k** and **1l** again resulted in isomerization of the starting materials, but unlike the tungsten complexes, the molybdenum carbynes **1k,l** produce a mixture of the isomeric dimethylcyclopentenones **14g** and **14i**, in a *trans:cis* ratio of 3:1 (in 40% yield). Photolysis of the *trans*-dimethylcyclopropyl carbynes **1m** and **1n**, however, only produced *trans*-dimethylcyclopentenone in 40% yield. Addition of HCl to **1k,l** led to formation of *cis*-dimethylcyclopropyl acyl complexes **12k,l** only. When left in the absence of light at room temperature over several days, **1k** and **1l** decompose to give only *cis*-dimethylcyclopentenone in 40% yield. Complexes **1m** and **1n** yield only *trans*-dimethylcyclopentenone under identical conditions. As with the tungsten complexes, it appears that photochemical scrambling of the cyclopropyl group occurs before photooxidative conversion to cyclopentenones.

Despite the preference for conversion of *trans*-dimethylcyclopropyl carbynes to cyclopentenones, the formation of *cis*-dialkylcyclopentenones can be enforced by ring fusion. Photolysis of the bicyclic carbyne **1o** results in formation of the bicyclic cyclopentenone **14o**, although in only 10% yield (eq 6).



1o 14o (6)

Photooxidation of 2,2,3,3-Tetrasubstituted Cyclopropyl Carbynes. Since steric effects appeared to be important in determining the product distribution, we prepared the tetramethylcyclopropyl carbyne **1p** in order to test the limitations placed on the system by steric crowding. Not surprisingly, photolysis of compound **1p** in chloroform did not produce the expected cyclopentenone, but instead produced tetramethylethylene in 36% yield (eq 7).

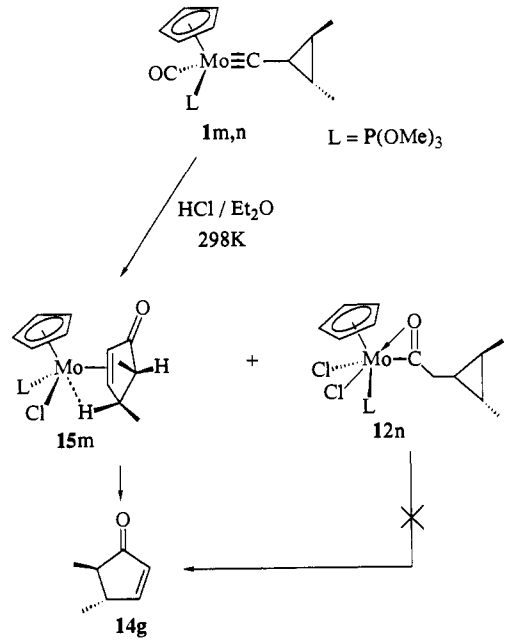


1p 36% (7)

Addition of HCl produced only the acyl complex **12p**. Tetramethylethylene is most likely produced by fragmentation of an open-chain intermediate produced by cleavage of the C1–C2 bond of the cyclopropyl ring. Formation of such intermediates followed by their ring closure also provides the simplest explanation of the stereochemical scrambling of the dimethylcyclopropyl carbynes **1g–n**. For the tetramethyl case **1p**, hindrance of the ring closure reaction would allow cleavage to be competitive.

Observation and Characterization of Intermediates. When the photolysis of **1b** in $CDCl_3$ was monitored by ^1H NMR at −50 °C, a broad cyclopentadienyl resonance centered at 5.07, a phosphite doublet at 3.70 (J = 10.4 Hz), and a complex multiplet at −8.15 ppm gradually grew in. After **1b** was completely consumed, these signals were still present and only a trace of cyclopentenone had formed. Continued photolysis resulted in disappearance of this intermediate (**15b**) and formation of cyclopentenone. Unfortunately, **15b** proved too unstable for isolation. Although an analogous intermediate could not be observed for the tungsten complex **1a**, a similar species was detected upon photolysis of the *trans*-dimethylcyclopropyl tungsten carbynes **1g,h**. Photooxidation of the *trans*-dimethylcyclopropyl molybdenum carbynes **1m,n** produced a similar set of signals in the ^1H NMR, and this intermediate (**15m**) proved stable enough for isolation. Preparation of large quantities of the intermediate **15m** was more practical by an alternate synthetic route in which 0.5 equiv of ethereal HCl was added carefully to the mixture of **1m** and **1n**. Under these conditions, **15m** was produced as a purple crystalline

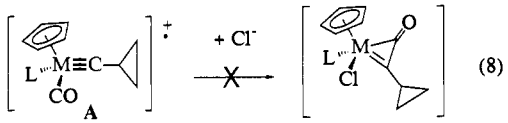
Scheme VI



solid in 50% yield[16] along with the acyl complex **12n** (Scheme VI). One of the *trans* isomers **1m,n** produces compound **15m** upon HCl addition, while the second isomer goes to the acyl compound. Acyl complex **12n** is stable to the reaction conditions and cannot be forced to produce cyclopentenone. However, intermediate **15m** decomposes in chloroform upon further photolysis or upon addition of coordinating solvents such as acetonitrile to give *trans*-2,3-dimethylcyclopentenone in quantitative yield.

Crystal Structure of 15m. A single-crystal X-ray study confirmed the structure of **15m** as the cyclopentenone complex shown in Scheme VI. As seen in the ORTEP drawing (Figure 1), the complex has pseudo-three(or four)-legged piano stool geometry. The metal is bound to the carbon–carbon double bond of the cyclopentenone, as evidenced by the distances of 2.258(4) and 2.133(5) Å for Mo–C2 and Mo–C3, respectively. The C2–C3 bond distance of 1.469(7) Å is quite long for a double bond and indicates significant metallacyclopropane character. An interesting feature of this molecule is an agostic interaction between H4 and the metal, as seen by the bond distance 1.82(4) Å for Mo–H4. This agostic interaction is also evident in the NMR spectra of **15m.** In the ^{1}H NMR, H4 gives rise to a complex multiplet shifted upfield to −8.15 ppm. The proton-coupled ^{13}C NMR signal for C4 at 24.7 ppm is a doublet with $^1J_{CH}$ = 79.7 Hz, indicative of agostic interactions.[17]

Mechanistic Considerations. Single-electron transfer from the carbyne excited state to $CHCl_3$ has previously been observed upon photolysis of alkyl and aryl carbynes similar to **1**.[1] The same primary photoprocess is most likely operating here. The resulting radical cations could undergo H-abstraction, carbonyl insertion, or ring opening as the next mechanistic step. Initial CO insertion would be coupling of the carbyne ligand to the carbonyl of radical cation **A** to yield a ketenyl complex[10] (eq 8).



(8)

However, despite efforts to detect such species by direct

(16) Yield is based on HCl addition.

(17) (a) Brookhart, M.; Green, M. L. H.; Wong, L. *Prog. Inorg. Chem.* **1988**, *36*, 1–124. (b) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395–408.

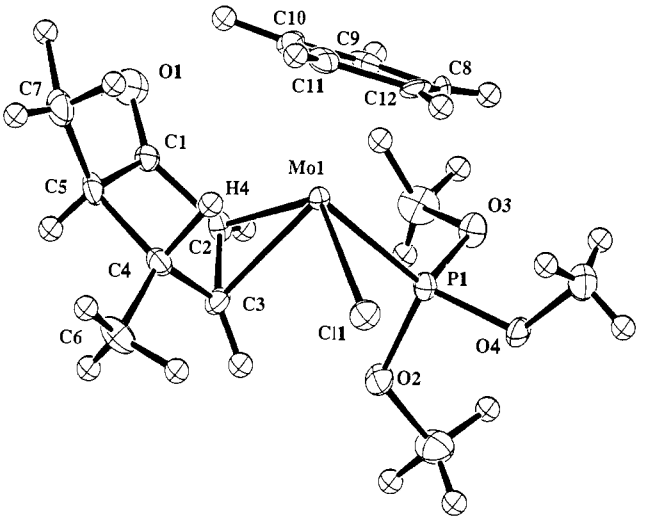
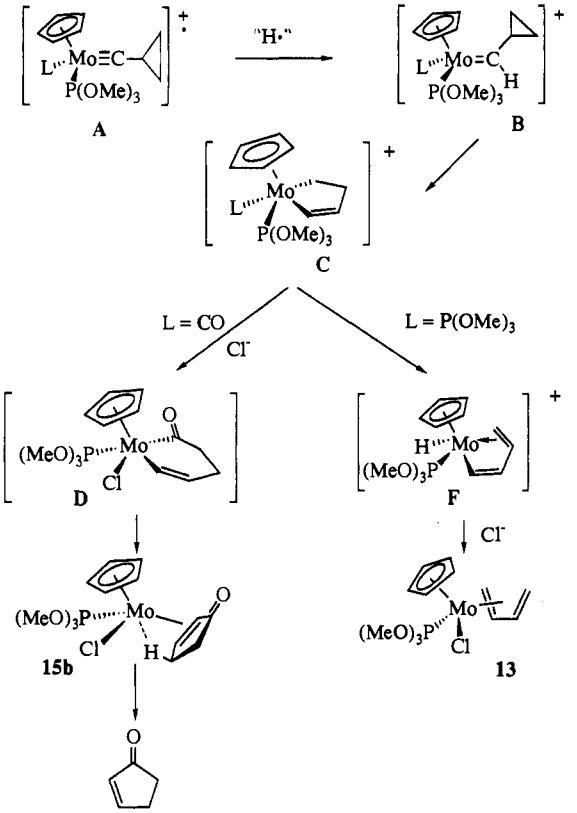


Figure 1. ORTEP drawing of **15m**. Thermal ellipsoids are drawn at the 75% probability level. Selected bond distances (Å) and angles (deg) are as follows: Mo1–C2, 2.258(4); Mo1–C3, 2.133(5); Mo1–Cl1, 2.492(1); Mo1–H4, 1.82(4); C2–C3, 1.469(7); C4–H4, 1.22(4); C2–Mo1–C3, 38.9-(2); Mo1–C2–C3, 65.9(3); Mo1–C3–C2, 75.1(3); Cl1–Mo1–P1, 84.89-(4); Cl1–Mo1–C3, 88.9(1); P1–Mo1–C2, 82.3(1).

Scheme VII



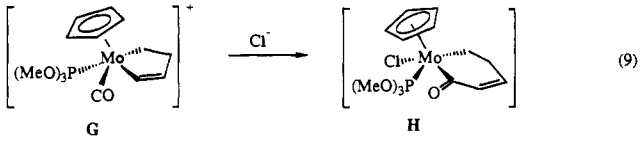
observation or trapping (vide supra), we have no evidence for formation of a ketenyl intermediate. Another possibility is ring opening in intermediate **A**. As noted earlier, photolysis of *cis*-dimethyl carbynes **1k,l** in benzene results in isomerization to a mixture of **1k,l,m,n**. This result demonstrates that ring opening can occur photochemically without electron transfer, yet is a nonproductive process (at least in the neutral complexes).

On the basis of the evidence presented above, we favor initial H-abstraction by radical cation **A** to give cationic carbene complex **B** (Scheme VII). Reactions where H^+ is added by a 1e$^-$ oxidation/H-abstraction pathway have been reported for other organome-

tallic complexes.[18,19] Although the dominant pathway for conversion of cyclopropyl carbynes to cyclopentenones does not appear to involve photogenerated HCl (vide supra), in certain cases, addition of a proton does generate some cyclopentenone. This is consistent with formation of a common intermediate, most likely carbene **B**.

Ring expansion would then occur to form metallacycle **C** from carbene **B**. This process is the organometallic analogue of the well-known vinylcyclopropane to cyclopentene rearrangement.[20] Although there is no literature precedent for conversion of a cyclopropyl metal carbene to a metallacyclopentene,[21] a related mechanistic step in which a cyclopropylvinyl carbene complex rearranges to a metallacycloheptene has been proposed for the reaction of $(CO)_5Cr{=}C(OMe)(c\text{-}C_3H_5)$ with diphenylacetylene.[15] It should also be noted that although $(CO)_5Cr{=}C(OMe)(c\text{-}C_3H_5)$ itself does not undergo ring expansion in the absence of alkynes,[15a] the cationic (and non-heteroatom stabilized) cyclopropyl carbene complex $Cp(CO)_2Fe{=}CH(C_3H_5)^+$ undergoes a rapid rearrangement below 0 °C for which the products have not been identified.[22]

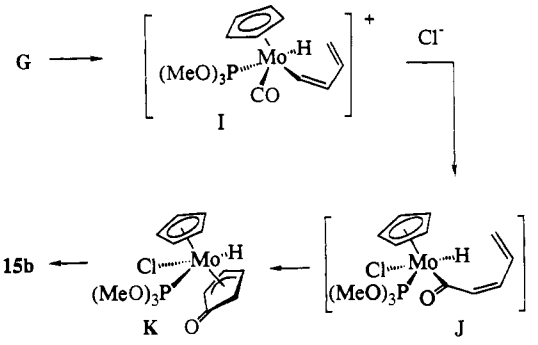
In Scheme VII, the CO insertion is depicted as occurring into the metal–alkyl bond of **C** to yield **D** instead of the isomeric alternative **G** → **H** in which CO has inserted into the metal–vinyl bond (eq 9). Since both **D** and **H** would yield the observed complex **15b** upon coordination of Cl^- and reductive elimination of the organic ligand, there is no experimental evidence for preference of **C** and **D** over **G** and **H**. Although there is evidence that insertion of CO into a metal–alkyl bond is generally preferred over metal–vinyl insertion,[15a,23] both are known. In either case, carbonyl insertion into the ligand should occur easily since carbonylation of alkyl ligands is known to be rapid in oxidized systems when entering nucleophiles are present.[24]



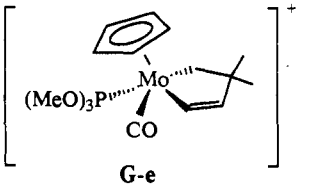
G H (9)

In the case of bis(phosphite) complex **9b**, the ultimate product is diene complex **13**. When carbonylation is not possible, metallacyclopentene **C** apparently undergoes β-hydride shift to form dienyl hydride complex **F**. Addition of a Cl^- ligand and reductive elimination of butadiene would yield **13**. Dienes are not formed from the carbonyl-containing complexes. This is consistent with rapid carbonylation to give metallacycle **D**, whose β–H shift product would be a ketene.[25]

Scheme VIII



An alternative route to **15b** involves β–H elimination in **G** followed by carbonylation and cyclization (Scheme VIII). Pathways involving intermediates similar to **J** and **K** are invoked in syntheses of cyclopentenones from group VI Fischer carbenes and alkynes.[25] The Scheme VIII route to **15** can be ruled out in the carbyne chemistry by the conversion of the 2,2-dimethylcyclopropyl carbyne **1e,f** to cyclopentenone **14e**. For the rearrangement of **1e,f**, the putative intermediate **G-e** would have no β-hydrogens and yet the product **14e** is formed in a yield comparable to that for the parent carbyne **1a**.



G-e

Summary

We have shown that the formation of cyclopentenones upon photooxidation of cyclopropyl carbyne complexes is a general reaction for complexes **1a–o**, **6a,m**, and **11a,m**. For compounds bearing a 2-aryl- or 2-alkylcyclopropyl group (**1c,d**), the 4-substituted cyclopentenones are formed regiospecifically. The selective formation of *trans*-4,5-dimethylcyclopentenones upon photolysis of the 2,3-dimethylcyclopropyl carbynes **1g–n** arises from rapid photoisomerization prior to generation of the 17e⁻ carbyne complexes by photooxidation.

Mechanistic studies are consistent with photochemical electron transfer from the carbyne complex to chloroform followed by H atom abstraction. Ring expansion then occurs to give a metallacyclopentene, which undergoes carbonyl insertion. Finally, reductive elimination yields a cyclopentenone complex that slowly releases the free enone. In the absence of a carbonyl ligand, the metallacyclopentene undergoes β-hydrogen elimination and ultimately yields a diene complex.

Control experiments demonstrate that the photooxidation reaction does not result from attack by HCl derived from the chloroform solvent. Formation of acyl complexes by addition of 2 equiv of HCl is the predominant pathway upon addition of even small amounts of HCl to the reaction mixtures. However, cyclopentenone products can, in a few special cases, be obtained upon HCl addition. Presumably, in these cases, the cationic carbenes invoked as intermediates following electron transfer and H-abstraction were independently generated by protonation of the carbyne complexes. This result provides support for the proposed mechanism.

Formation of cyclopentenones in this system provides a striking example of the activation of metal carbyne complexes by 1e⁻oxidation. While the neutral complexes are stable, the formation of radical cations is followed by a multistep process involving H-abstraction, ring expansion, and carbonylation of

(18) (a) Armstead, J. A.; Cox, D. J.; Davis, R. *J. Organomet. Chem.* **1982**, *236*, 213–219. (b) Waterman, P. S.; Giering, W. P. *J. Organomet. Chem.* **1978**, *155*, C47–C50.

(19) The related pathway in which net H^- addition occurs by electron transfer/H-abstraction is also known in organometallic systems. For representative examples, see ref 2b and the following: (a) Nlate, S.; Guerchais, V.; Lapinte, C. *J. Organomet. Chem.* **1992**, *434*, 89–96. (b) Narayanan, B. A.; Amatore, C.; Kochi, J. K. *Organometallics* **1987**, *6*, 129–136. (c) Kuchynka, D. J.; Amatore, C.; Kochi, J. K. *Inorg. Chem.* **1986**, *25*, 4087–4097.

(20) For a review of the vinylcyclopropane to cyclopentene rearrangement, see: Hudlicky, T.; Kutcham, T. M.; Naqvi, S. M. *Org. React.* **1985**, *33*, 247.

(21) Herndon, J. W.; McMullen, L. A. *J. Am. Chem. Soc.* **1989**, *111*, 6854–6856.

(22) (a) Brookhart, M.; Studabaker, W. B.; Husk, G. R. *Organometallics* **1987**, *6*, 1141–1145. (b) Brookhart, M.; Studabaker, W. B.; Husk, G. R. *Organometallics* **1985**, *4*, 943–944.

(23) Doxsee, K. M.; Mouser, J. K. *Organometallics* **1990**, *9*, 3012–3014.

(24) See: (a) Therien, M. J.; Trogler, W. C. *J. Am. Chem. Soc.* **1987**, *109*, 5127–5133. (b) Golovin, M. N.; Meirowitz, R.; Rahman, M. M.; Liu, H. Y.; Prock, A.; Giering, W. P. *Organometallics* **1987**, *6*, 2285–2289 and references therein.

(25) (a) Harvey, D. F.; Lund, K. P.; Neil, D. A. *J. Am. Chem. Soc.* **1992**, *114*, 8424–8434. (b) Challener, C. A.; Wulff, W. D.; Anderson, B. A.; Chamberlin, S.; Faron, K. L.; Kim, O. K.; Murray, C. K.; Xu, Y.-C.; Yang, D. C.; Darling, S. D. *J. Am. Chem. Soc.* **1993**, *115*, 1359–1376. We thank Professor Harvey for providing us with a copy of ref 25a prior to publication.

the ligand. Further studies on formation of organic products in related systems are in progress.

Experimental Section

General Methods. Standard inert atmosphere techniques were used throughout. Hexane, petroleum ether, chloroform, methylene chloride, and carbon tetrachloride were distilled from CaH_2. Acetonitrile was distilled from P_2O_5. Diethyl ether, THF, and toluene 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. $CDCl_3$, CCl_4, CD_2Cl_2, and CD_3CN were stored over 3-Å molecular sieves. All other starting materials were purchased in reagent grade and used without further purification.

^1H, ^{31}P, and ^{13}C NMR spectra were recorded on a Varian XL-400 NMR spectrometer. IR spectra were recorded on an IBM IR/90 FTIR spectrometer. Gas chromatography was performed on a HP5890A chromatograph containing a 5 m × 0.25 mm column of SE-54 on fused silica. High-resolution mass spectra were obtained at the University of California, San Francisco.

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.

1-Bromo-2-phenylcyclopropane was prepared by the method of Martel[26] and converted to the lithium reagent by addition of lithium wire to the bromide at −98 °C in THF. 1-Bromo-2,2,3,3-tetramethylcyclopropane was prepared in the same way[26] and converted to the lithium reagent by the method of Seyferth.[27] All other cyclopropyl bromides were produced by the method of Miyano.[28]

The acyl complexes **4a–p** were obtained by addition of the appropriate lithium reagent to the metal hexacarbonyl.[29] $Cp(CO)[P(OMe)_3]Mo{\equiv}C(c\text{-}C_3H_5)$ (**1b**) was prepared using the method described previously for its tungsten congener.[1b] $Cp(CO)_2W{\equiv}C(c\text{-}C_3H_5)$ (**6a**) was prepared using the method described previously.[30]

$Cp(CO)[P(OMe)_3]W{\equiv}C(c\text{-}\overline{CDCH_2CH_2})$ (1a-d_1). $Cp(CO)[P(OMe)_3]W{\equiv}C(c\text{-}C_3H_5)$ (**1a**) (200 mg, 0.44 mmol) was dissolved in 20 mL of THF. A solution of 1.6 M *n*-BuLi (350 μL, 0.56 mmol) was added at room temperature to afford an orange-red solution. Excess D_2O was then added, which resulted in an immediate color change to yellow. After removal of the solvent, the product was chromatographed on neutral alumina (8 cm × 1.5 cm) with 1:3 Et_2O/hexane as eluent. Final purification was achieved by recrystallization from hexane to afford **1a-d_1** as yellow crystals in 96% yield: ^1H NMR (C_6D_6) δ 5.39 (s, 5H, Cp), 3.56 (d, 9H, J = 12 Hz, $P(OMe)_3$), 0.80 (m, 2H, H_β), 0.68 (m, 2H, H_β).

$Cp(CO)[P(OMe)_3]Mo{\equiv}C(c\text{-}\overline{CDCH_2CH_2})$ (1b-d_1). $Cp(CO)[P(OMe)_3]Mo{\equiv}C(c\text{-}C_3H_5)$ (**1b**) (46 mg, 0.13 mmol) was dissolved in 5 mL of THF and cooled to −78 °C. A solution of 2.5 M *n*-BuLi (51 μL, 0.13 mmol) was slowly added, and the solution was stirred for 30 min whereupon a deep orange solution had formed. Excess D_2O (10 μL, 1.6 mmol) was added, and the orange color was discharged within 10 min. After warming to room temperature, the solvent was removed and the residue extracted with cold hexane (−40 °C) and chromatographed on neutral alumina. Elution with 4:1 hexane/Et_2O gave a yellow solution, which afforded **1b-d_1** as a yellow solid (45.5 mg, 97%) upon removal of solvent: ^1H NMR (C_6D_6) δ 5.26 (s, 5H, Cp), 3.51 (d, 9H, J = 12 Hz, $P(OMe)_3$), 0.85 (m, 2H, H_β), 0.41 (m, 2H, H_β).

$Cl(CO)[P(OMe)_3]_3Mo{\equiv}C(c\text{-}\overline{CHCH_2CHEt})$ (7c). Acyl complex **4c** (1.15 g, 2.83 mmol) was dissolved in 50 mL of CH_2Cl_2 and cooled to −98 °C. Oxalyl chloride (244 μL, 2.83 mmol) was added to the solution. Upon warming to −20 °C, effervescence began and the dark solution became yellow. The solution was returned to the low-temperature bath, and excess $P(OMe)_3$ was added (3.3 mL, 28 mmol). The bright yellow solution was allowed to warm to room temperature and stirred for 24 h. After removal of the solvent, the residue was dissolved in cold Et_2O and filtered to remove NMe_4Cl. Final purification was achieved by column chromatography on neutral alumina (3 cm × 1.5 cm) at −30 °C with 3:1 Et_2O/hexane as eluent. Removal of the solvent mixture gave **7c** in 58% yield: ^1H NMR (C_6D_6) δ 3.75 (m, 27 H, $P[OMe]_3$), 1.82 (m, 1H, H_α), 1.60 (m, 1H, H_β), 1.54 (m, 1H, H_β), 0.65 (m, 1H, H_β), 1.03 (t, 3H, CH_3).

$Cp(CO)[P(OMe)_3]Mo{\equiv}C(c\text{-}\overline{CHCH_2CHEt})$ (1c). Carbyne **7c** (1.00 g, 1.63 mmol) was dissolved in 20 mL of THF. A 2.0 M solution of CpNa in THF (1.5 mL, 3.0 mmol) was added, and the reaction mixture was stirred at room temperature for 12 h. The solvent was removed in vacuo, cold Et_2O was added, and the solution was filtered to remove excess CpNa. Following removal of Et_2O, the product was chromatographed on neutral alumina (8 cm × 1.5 cm) at −30 °C with 1:3 Et_2O/hexane as eluent to give **1c** as a mixture of two isomers in 79% yield: ^1H NMR (C_6D_6) δ 5.27 (s, 5H, Cp), 5.26 (s, 5H, Cp), 3.45 (d, 9H, J = 12 Hz, $P[OMe]_3$), 3.43 (d, 9H, J = 12 Hz, $P[OMe]_3$), 2.01–0.54 (m, 12H, $CHCH_2CHCH_2$), 1.13 (t, J = 7 Hz, CH_3), 1.05 (t, J = 7 Hz, CH_3); ^{13}C NMR (C_6D_6) δ 314.1 (d, J = 30 Hz, Mo≡C), 312.4 (d, J = 30 Hz, Mo≡C), 242.3 (d, J = 19 Hz, MoCO), 240.5 (d, J = 19 Hz, MoCO), 91.1 , 90.9 (Cp), 51.3, 50.9 ($P[OMe]_3$), 35.6, 35.4 (s, C_α), 26.1, 25.8, 23.3 (s, C_β), 17.5, 16.8 (s, CH_2), 14.5 (s, CH_3); IR (CH_2Cl_2) 1916.2 cm^{-1} (ν_{MoCO}); ^{31}P NMR (C_6D_6) δ 204.4, 204.2; HRMS (FAB), *m/z* calcd for M^+ ($C_{15}H_{23}O_4{}^{98}MoP$) 396.0388, found 396.0460.

$Cl(CO)[P(OMe)_3]_3Mo{\equiv}C(c\text{-}\overline{CHCH_2CHPh})$ (7d). Acyl complex **4d** (1.10 g, 2.43 mmol) was dissolved in 50 mL of CH_2Cl_2 and cooled to −98 °C. Oxalyl chloride (211 μL, 2.43 mmol) was added and the solution warmed to −20 °C where effervescence began and the solution lightened in color. After returning the solution to the low-temperature bath, excess $P(OMe)_3$ (3.5 mL, 30 mmol) was added. After stirring at room temperature for 24 h, **7d** was purified by the same procedure as **7c**: ^1H NMR ($CDCl_3$) δ 6.92–7.05, 7.20–7.40 (m, 5H, Ph), 3.60–3.70 (m, 27H, $P[OMe]_3$), 1.65 (m, 1H, H_α), 1.50 (m, 1H) 1.10 (m, 2H).

$Cp(CO)[P(OMe)_3]Mo{\equiv}C(c\text{-}\overline{CHCH_2CHPh})$ (1d). Carbyne **7d** (0.40 g, 0.60 mmol) was dissolved in 10 mL of THF. A 2.0 M solution of CpNa in THF (0.6 mL, 1.2 mmol) was added, and the mixture was stirred at room temperature for 12 h. The solvent was removed in vacuo, cold Et_2O was added, and the solution was filtered to remove excess CpNa. Following removal of Et_2O, the product was chromatographed on neutral alumina (8 cm × 1.5 cm) at −30 °C with 1:3 Et_2O/hexane as eluent to give **1d** as a mixture of two isomers in 75% yield: ^1H NMR ($CDCl_3$) δ 7.05–7.30 (m, 5H, Ph), 5.42 (s, 5H, Cp), 3.62 (d, 9H, J = 12 Hz, $P(OMe)_3$), 2.42–2.50 (m, 1H, H_α), 1.70–2.00 (m, 1H), 1.50–1.60 (m, 1H), 1.10–1.30 (m, 1H); ^{13}C NMR (C_6D_6) δ 309.7 (d, J = 30 Hz, Mo≡C), 309.4 (d, J = 26.1 Hz, Mo≡C), 242.4 (d, J = 17.5 Hz, MoCO), 241.8 (d, J = 19 Hz, MoCO), 129.7, 129.3, 128.6, 126.4, 126.3, 126.2, 126.0 (Ph), 91.1 (s, Cp), 51.3 (s, $P[OMe]_3$), 28.1, 27.9 (s, C_α), 15.8, 15.5 (s, C_β); ^{31}P NMR (C_6D_6) δ 204.3, 204.4; IR (CH_2Cl_2) 1896.3 cm^{-1} (ν_{MoCO});HRMS (FAB), *m/z* calcd for M^+ ($C_{19}H_{23}O_4{}^{98}MoP$) 444.0388, found 444.0386.

$Cl(CO)[P(OMe)_3]_3Mo{\equiv}C(c\text{-}\overline{CHCH_2CMe_2})$ (7e). **7e** was prepared in a manner analogous to **7c** and was isolated as a yellow solid in 70% yield: ^1H NMR (C_6D_6) δ 3.70 (m, 27H, $P[OMe]_3$), 1.55 (s, 3H, CH_3), 1.45 (m, 1H, H_α), 1.05 (m, 1H), 0.76 (s, 3H, CH_3), 0.40 (m, 1H).

$Cp(CO)[P(OMe)_3]Mo{\equiv}C(c\text{-}\overline{CHCH_2CMe_2})$ (1e,f). **1e,f** was prepared in the same manner as **1c** and was isolated as a mixture of two isomers in 70% yield. Isomer 1: ^1H NMR (C_6D_6) δ 5.26 (s, 5H, Cp), 3.46 (d, 9H, J = 12 Hz, $P(OMe)_3$), 1.51 (s, CH_3), 0.76 (s, CH_3), 1.50 (m, 1H), 0.82 (m, 1H), 0.54 (m, 1H); ^{13}C (C_6D_6) δ 312.8 (d, J = 26 Hz, Mo≡C), 242.2 (d, J = 16.6 Hz, MoCO), 90.9 (s, Cp), 51.3 (s, $P[OMe]_3$), 44.5 (s, C_α), 26.6, 21.7 (s, C_β, CH_3). Isomer 2: ^1H NMR (C_6D_6) δ 5.27 (s, 5H, Cp), 3.47 (d, 9H, J = 12 Hz, $P(OMe)_3$), 1.42 (s, CH_3), 0.75 (s, CH_3), 1.05 (m, 1H), 0.85 (m, 1H), 0.45 (m, 1H); ^{13}C NMR (C_6D_6) δ 314.1 (d, J = 29.9 Hz, Mo≡C), 242.4 (d, J = 20.4 Hz, MoCO), 91.0 (s, Cp), 51.3 (s, $P[OMe]_3$), 44.5 (s, C_α), 25.6, 21.6 (s, C_β, CH_3). For the mixture: ^{31}P NMR (C_6D_6) δ 204.3, 204.5; IR (CH_2Cl_2) 1893.0 cm^{-1} (ν_{MoCO}); HRMS (FAB), *m/z* calcd for M^+ ($C_{19}H_{23}O_4{}^{98}MoP$) 396.0388, found 396.0403.

$Cl(CO)[P(OMe)_3]_3W{\equiv}C[trans\text{-}(c\text{-}\overline{CHCHMeCHMe})]$ (7g). Acyl complex **4g** (1.14g, 2.3 mmol) was dissolved in 50 mL of CH_2Cl_2 and cooled to −98 °C. Oxalyl chloride (200 μL, 2.3 mmol) was added and the solution warmed to −20 °C, where effervescence began and the solution lightened in color. After returning the solution to the low-temperature bath, excess $P(OMe)_3$ was added (4.7 mL, 40 mmol). After stirring at room temperature for 24 h, **7g** was purified by the same procedure as **7c:** ^1H NMR ($CDCl_3$) δ 3.75 (m, 27H, $P[OMe]_3$), 1.32 (m, 1H, H_α), 1.12 (d, 3H, CH_3), 0.95 (m, 1H, H_β), 0.90 (d, 3H, CH_3), 0.45 (m, 1H, H_β).

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Cp(CO)[P(OMe)$_3$]W≡C[*trans*-(c-CHCHMeCHMe)] (1g,h). Carbyne **7g** (1.00 g, 1.45 mmol) was dissolved in 10 mL of THF. A 2.0 M solution of CpNa in THF (1.0 mL, 2.0 mmol) was added,and the mixture was stirred at room temperature for 12 h. The solvent was removed in vacuo, cold Et_2O was added, and the solution was filtered to remove excess CpNa. Following removal of Et_2O, the product was chromatographed on neutral alumina (8 cm × 1.5 cm) with 1:3 Et_2O/hexane as eluent to give **1g,h** in 60% yield: Isomer 1:^{1}H NMR ($CDCl_3$) δ 5.37 (s, 5H, Cp), 3.57 (d, 9H, P[OMe]$_3$, J = 12 Hz), 1.28 (d, 3H, J = 6 Hz, CH_3), 0.96 (d, 3H, J = 5 Hz, CH_3), 0.80–1.30 (m, 3H, CHCHCH); ^{13}C NMR (C_6D_6) δ 299.4 (d, J = 17 Hz, W≡C), 234.4 (d, J = 9 Hz, WCO), 89.3 (Cp), 52.0 (P[OMe]$_3$), 47.1 (s, C_α), 27.4, 26.3 (s, C_β), 18.4, 14.5 (s, CH_3). Isomer 2:^{1}H NMR ($CDCl_3$) δ 5.37 (s, 5H, Cp), 3.56 (d, 9H, J = 12 Hz, P[OMe]$_3$), 1.26 (d, 3H, J = 7 Hz, CH_3), 0.92 (d, 3H, J = 6 Hz, CH_3), 0.80–1.30 (m, 3H); ^{13}C NMR (C_6D_6) δ 298.4 (d, J = 16.6 Hz, W≡C), 234.7 (d, J = 10 Hz, WCO), 89.3 (Cp), 52.0 (P[OMe]$_3$), 47.1 (s, C_α), 26.0, 25.6 (s, C_β), 18.4, 14.4 (s, CH_3). For the mixture: ^{31}P NMR (C_6D_6) δ 175.5 (J_{WP} = 677 Hz), 175.6 (J_{WP} = 677 Hz); IR (CH_2Cl_2) 1880.4 cm^{-1} (ν_{WCO}); HRMS (FAB), *m/z* calcd for M$^+$ ($C_{15}H_{23}O_4WP$) 484.0878, found 484.0873.

Cl(CO)[P(OMe)$_3$]$_3$W≡C[*cis*-(c-CHCHMeCHMe)] (7i,j). **7i,j** was prepared in the same manner as **7g** and was isolated as a yellow oil in 60% yield: ^{1}H NMR ($CDCl_3$) δ 3.75 (m, 27H, P[OMe]$_3$), 1.30 (m, 1H, H_α), 1.10 (d, 3H, CH_3), 0.95 (m, 1H, H_β), 0.92 (d, 3H, CH_3), 0.45 (m, 1H, H_β).

Cp(CO)[P(OMe)$_3$]W≡C[*cis*-(c-CHCHMeCHMe)] (1i,j). **1i,j** was prepared in a manner analogous to **1g,h**,and the 1:1 mixture of **1i:1j** was isolated as a yellow oil in 70% yield. **1j** was isolated by careful column chromatography (8 cm × 1.5 cm) on neutral alumina with 1:3 Et_2O/hexane several times followed by recrystallization from hexane to yield yellow crystals. **1j**: ^{1}H NMR (C_6D_6) δ 5.18 (s, 5H, Cp), 3.50 (d, 9H, J = 10 Hz, P[OMe]$_3$), 1.40 (d, 3H, J = 6 Hz, CH_3), 1.25 (d, 3H, J = 6 Hz, CH_3), 1.10 (m, 1H, H_α), 0.90–1.00 (m, 2H, CHCH); ^{13}C NMR (C_6D_6) δ 298.9 (d, $^2J_{CP}$ = 17 Hz, W≡C), 234.0 (d, $^2J_{CP}$ = 11 Hz, WCO), 89.3 (Cp), 52.0 (P(OMe)$_3$), 40.6 (C_α), 20.5, 20.2 (CH_3), 8.8 (C_β); ^{31}P NMR (C_6D_6) δ 175.8 (J_{WP} = 680 Hz). **1i:** ^{1}H NMR (C_6D_6) δ 5.20 (s, 5H, Cp), 3.54 (d, 9H, J = 10 Hz, P[OMe]$_3$), 0.81 (d, 3H, J = 6 Hz, CH_3), 0.78 (d, 3H, J = 3 Hz, CH_3), 1.50 (m, 1H, H_α), 0.80–1.00 (m, 2H, CHCH); ^{13}C NMR (C_6D_6) δ 300.1 (d, $^2J_{CP}$ = 17.1 Hz, W≡C), 234.9 (d, $^2J_{CP}$ = 12.3 Hz, WCO), 89.3 (Cp), 50.5 (P(OMe)$_3$), 40.6 (C_α), 24.2, 23.6 (Me), 12.1 (C_β); ^{31}P NMR (C_6D_6) δ 175.9 (J_{WP} = 680 Hz). For the mixture: IR (CH_2Cl_2) 1906.6 cm^{-1} (ν_{WCO}); HRMS (FAB), *m/z* calcd for M$^+$ ($C_{15}H_{23}O_4WP$) 484.0878, found 484.0881.

Cl(CO)[P(OMe)$_3$]$_3$Mo≡C[*cis*-(c-CHCHMeCHMe)] (7k,l). **7k,l** was prepared in the same manner as **7g**, and the mixture was isolated as a yellow oil in 75% yield: ^{1}H NMR (C_6D_6) δ 3.80 (m, 27H, P[OMe]$_3$), 1.70 (m, 1H), 0.90 (m, 1H), 0.74 (m, 1H).

Cp(CO)[P(OMe)$_3$]Mo≡C[*cis*-(c-CHCHMeCHMe)] (1k,l). **1k,l** was prepared in a manner analogous to **1g,h** and isolated as a mixture of the two isomers as a yellow oil in 70% yield. Isomer 1 (less stable): ^{1}H NMR (C_6D_6) δ 5.28 (s, 5H, Cp), 3.45 (d, 9H, P[OMe]$_3$, J = 12 Hz), 1.50–1.65 (m, 1H), 1.05 (m, 1H), 0.90 (m, 1H), 0.77 (2d, 6H, 2 CH_3); ^{13}C NMR (C_6D_6) δ 313.3 (d, $^2J_{CP}$ = 25.6 Hz, Mo≡C), 241.8 (d, $^2J_{CP}$ = 17.6 Hz, WCO), 91.0 (Cp), 51.3 (P(OMe)$_3$), 47.7 (C_α), 24.1, 21.9 (C_β), 12.0, 9.0 (CH_3); ^{31}P NMR (C_6D_6) δ 204.8. Isomer 2: ^{1}H NMR (C_6D_6) δ 5.24 (s, 5H, Cp), 3.46 (d, 9H, J = 12 Hz, P[OMe]$_3$), 1.64 (m, 1H, H_α), 1.43 (d, 3H, J = 6 Hz, CH_3), 1.25 (d, 3H, CH_3), 0.80–0.93 (m, 2H, H_β); ^{13}C NMR (C_6D_6) δ 313.8 (d, $^2J_{CP}$ = 30 Hz, Mo≡C), 242.9 (d, $^2J_{CP}$ = 19 Hz, WCO), 90.9 (Cp), 51.3 (P(OMe)$_3$), 38.8 (C_α), 24.6, 21.9 (C_β), 12.0, 9.0 (CH_3); ^{31}P NMR (C_6D_6) δ 204.6. For the mixture: IR (CH_2Cl_2) 1892.2 cm^{-1} (ν_{MoCO}); HRMS (FAB), *m/z* calcd for M$^+$ ($C_{15}H_{23}O_4$-^{98}MoP) 396.0388, found 396.0358.

Cl(CO)[P(OMe)$_3$]$_3$Mo≡C[*trans*-(c-CHCHMeCHMe)] (7m). **7m** was prepared in the same manner as **7g**, and the mixture was isolated as a yellow oil in 67% yield: ^{1}H NMR ($CDCl_3$) δ 3.72 (m, 27H, P[OMe]$_3$), 1.52 (d, 3H, J = 6 Hz, CH_3), 1.20 (m, 2H), 0.78 (d, 3H, J = 6 Hz, CH_3), 0.32 (m, 1H).

Cp(CO)[P(OMe)$_3$]Mo≡C[*trans*-(c-CHCHMeCHMe)] (1m,n). **1m,n** was prepared in a manner analogous to **1g,h** and isolated as a mixture of the two isomers as a yellow oil in 65% yield. Isomer 1: ^{1}H NMR (C_6D_6) δ 5.26 (s, 5H, Cp), 3.45 (d, 9H, J = 12 Hz, P[OMe]$_3$), 1.47 (d, 3H, J = 6 Hz, CH_3), 0.77 (d, 3H, J = 6 Hz, CH_3), 1.40 (m, 1H), 1.04 (m, 1H), 0.60 (m, 1H); ^{13}C NMR (C_6D_6) δ 313.7 (d, $^2J_{CP}$ = 25 Hz, Mo≡C), 242.4 (d, $^2J_{CP}$ = 15 Hz, CO), 90.9 (Cp), 51.3 (P(OMe)$_3$), 44.8 (C_α), 27.8, 27.2 (C_β), 18.2, 14.8 (CH_3); ^{31}P NMR (C_6D_6) δ 204.4. Isomer 2: ^{1}H NMR (C_6D_6) δ 5.27 (s, 5H, Cp), 3.47 (d, 9H, P[OMe]$_3$, J = 12 Hz), 1.40 (d, 3H, J = 6 Hz, CH_3), 0.74 (d, 3H, J = 6 Hz, CH_3), 1.35 (m, 1H), 1.20 (m, 1H), 0.60 (m, 1H, CH); ^{13}C NMR (C_6D_6) δ 312.4 (d, $^2J_{CP}$ = 29 Hz, Mo≡C), 242.5 (d, $^2J_{CP}$ = 14 Hz, CO), 91.0 (Cp), 51.3 (P(OMe)$_3$), 44.8 (C_α), 26.8, 26.7 (C_β), 18.2, 14.6 (CH_3); ^{31}P NMR (C_6D_6) δ 204.6. For the mixture: IR (CH_2Cl_2) 1891.9 cm^{-1} (ν_{MoCO}); HRMS (FAB), *m/z* calcd for M$^+$ ($C_{15}H_{23}O_4$^{98}MoP) 396.0388, found 396.0389.

Cl(CO)[P(OMe)$_3$]$_3$Mo≡C[7-(*cis*-bicyclo[4.1.0]heptyl)] (7o). **7o** was prepared in the same manner as **7g** and isolated as a yellow oil in 61% yield: ^{1}H NMR (C_6D_6) δ 3.72 (m, 27H, P[OMe]$_3$), 2.27, 1.90 (2m, 1H), 1.70–0.70 (m, 10H).

Cp(CO)[P(OMe)$_3$]Mo≡C[7-(*cis*-bicyclo[4.1.0]heptyl)] (1o). **1o** was prepared in a manner analogous to **1g,h** and isolated as a mixture of the two isomers as a yellow oil in 79% yield: ^{1}H NMR (C_6D_6) δ 5.29, 5.26 (2s, 5H, Cp), 3.46 (2d, 9H, P[OMe]$_3$, J = 12 Hz), 2.36, 2.06 (2m, 1H), 1.93–0.76 (m, 10H); ^{13}C NMR (C_6D_6) δ 314.0, 312.1 (2d, $^2J_{CP}$ = 25.6, 30.0 Hz, Mo≡C), 242.8, 241.9 (2d, $^2J_{CP}$ = 21.3, 20.8 Hz, MoCO), 91.2, 90.9 (Cp), 51.3 (P(OMe)$_3$), 44.6, 39.1 (C_α) 24.9, 24.4, 23.3, 22.9, 21.6, 21.2, 20.4, 20.3; ^{31}P NMR (C_6D_6) δ 204.1, 204.8; IR (CH_2Cl_2) 1891.0 cm^{-1} (ν_{MoCO}); HRMS (FAB), *m/z* calcd for M$^+$ ($C_{17}H_{25}O_4$^{98}MoP) 422.0545, found 422.0542.

Cl(CO)[P(OMe)$_3$]$_3$Mo≡C(c-CHCMe$_2$CMe$_2$) (7p). Acyl complex **4p** (2.22 g, 5.10 mmol) was dissolved in 50 mL of CH_2Cl_2 and cooled to –98 °C. Oxalyl chloride (442 μL, 5.10 mmol) was added to the yellow solution. Upon warming to –30 °C, effervescence was observed. When the temperature reached –15 °C, the reaction was returned to the low-temperature bath and excess P(OMe)$_3$ (6.2 mL, 53 mmol) was added. The bright yellow solution was then stirred at room temperature for 16 h. After the solvent was removed, the residue was dissolved in Et_2O and filtered to remove NMe_4Cl. Final purification was achieved by column chromatography on neutral alumina (5 cm × 1.5 cm) at –30 °C with 3:1 Et_2O/hexane as eluent. Removal of solvent gave 2.58 g (76% yield) of a lemon yellow solid: ^{1}H NMR (C_6D_6) δ 3.72 (m, 27H, P[OMe]$_3$), 1.45 (s, 6H, 2CH_3), 1.25 (q, 1H, J = 5 Hz, CH) 0.89 (s, 6H, 2CH_3).

Cp(CO)[P(OMe)$_3$]Mo≡C(c-CHCMe$_2$CMe$_2$) (1p). Carbyne **7p** (2.58 g, 4.03 mmol) was dissolved in 20 mL of THF. A 2.0 M solution of CpNa in THF (3.5 mL, 7.0 mmol) was added, and the mixture was stirred at room temperature for 14 h. The solvent was removed in vacuo, cold Et_2O was added, and the solution was filtered to remove excess CpNa. Following removal of Et_2O, the product was chromatographed on neutral alumina (8 cm × 1.5 cm) at –30 °C with 1:3 Et_2O/hexane as eluent to give **1p** in 75% yield: ^{1}H NMR ($CDCl_3$) δ 5.32 (s, 5H, Cp), 3.57 (d, 9H, J = 12 Hz, P[OMe]$_3$), 1.33 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.01 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 1.21 (d, 1H, J = 5 Hz, CH); ^{13}C NMR (C_6D_6) δ 314.1 (d, $^2J_{CP}$ = 29 Hz, Mo≡C), 243.0 (d, $^2J_{CP}$ = 20.9 Hz, MCO), 90.9 (Cp), 51.3 (P(OMe)$_3$), 54.7, 32.9, 32.4, 23.0, 22.9, 18.8; ^{31}P NMR (C_6D_6) δ 204.7; IR (CH_2Cl_2) 1889.5 cm^{-1} (ν_{MoCO}); HRMS (FAB), *m/z* calcd for M$^+$ ($C_{15}H_{23}O_4$^{98}MoP) 396.0388, found 396.0389.

Cp(CO)$_2$Mo≡C[*trans*-(c-CHCHMeCHMe)] (6m). **6m** was prepared in a manner analogous to **6a** and obtained as a yellow oil in 55% yield: ^{1}H NMR ($CDCl_3$) δ 5.45 (s, 5H, Cp), 1.54 (m, 1H), 1.20 (m, 1H), 0.95 (m, 1H), 1.32 (d, 3H, J = 6 Hz, CH_3), 1.01 (d, 3H, J = 6 Hz, CH_3); ^{13}C NMR (C_6D_6) δ 328.7 (Mo≡C), 230.7, 230.6 (MoCO), 92.1 (Cp), 46.0 (C_α), 28.9, 28.7 (C_β), 18.0, 14.8 (Me); IR (CH_2Cl_2) 1984.7, 1906.2 cm^{-1} (ν_{MoCO}); HRMS (FAB), *m/z* calcd for M$^+$ ($C_{13}H_{14}O_2$^{98}Mo) 300.0048, found 300.0060.

Cl[P(OMe)$_3$]$_4$Mo≡C(c-C$_3$H$_5$) (8b). Cl(CO)[P(OMe)$_3$]$_3$Mo≡C(c-C_3H_5) was heated to 55 °C for 70 h in neat P(OMe)$_3$. **8b** was isolated by extraction with hexane and recrystallization from Et_2O/ hexane to yield pale yellow crystals in 40% yield: ^{1}H NMR ($CDCl_3$) δ 3.75 (virtual t, 36H, P(OMe)$_3$), 1.30 (m, 1H, H_α), 0.95, 0.35 (2 m, 4H, H_β).

Cp[P(OMe)$_3$]$_2$Mo≡C(c-C$_3$H$_5$) (9b). To 1.35 g (2.09 mmol) of **8b** in 10 mL of THF was added (1.5 mL, 3.0 mmol) CpNa in THF. The solution was heated to 50 °C for 12 h and isolated by column chromatography on neutral alumina (8 cm × 1.5 cm) with Et_2O as eluent. A yellow solid was obtained in 52% yield: ^{1}H NMR (C_6D_6) δ 5.26 (s, 5H, Cp), 3.51 (virtual t, 18H, P(OMe)$_3$), 1.42 (m, 1H, H_α), 0.85, 0.41 (2m, 4H, H_β) ^{13}C NMR (C_6D_6) δ 299.5 (t, J = 29.4 Hz, Mo≡C), 89.0

(Cp), 50.9 ($P(OMe)_3$), 29.3 (C_α), 10.1 (C_β); ^{31}P NMR (C_6D_6) δ 214.8; HRMS (FAB), *m/z* calcd for M^+ ($C_{15}H_{28}O_6{}^{98}MoP_2$) 464.0415, found 464.0404.

$Cl(CO)_2[P(OPh)_3]_2W{\equiv}C(c\text{-}C_3H_5)$ (10a). Acyl complex **4a** (1.34 g, 1.97 mmol) was dissolved in 50 mL of CH_2Cl_2 and cooled to −98 °C. Oxalyl chloride (294 μL, 1.97 mmol) was added to the yellow solution. Upon warming to −20 °C, effervescence began and the dark solution became yellow. The solution was returned to the low-temperature bath and excess $P(OPh)_3$ (10 mL) was added. The bright yellow solution was warmed to 50 °C for 36 h. After removal of the solvent, the residue was dissolved in cold Et_2O and filtered to remove NMe_4Cl. Final purification was achieved by column chromatography on neutral alumina (3 cm × 1.5 cm) at −30 °C with hexane followed by Et_2O as eluent. Recrystallization from Et_2O provided pure **10a** in 40% yield: ^1H NMR ($CDCl_3$) δ 7.35–7.05 (m, 30H, $P(OPh)_3$), 2.24 (m, 1H, H_α), 1.10, 0.85 (2m, 4H, H_β).

$Cp(CO)[P(OPh)_3]W{\equiv}C(c\text{-}C_3H_5)$ (11a). **11a** was prepared by the method described for **1g,h**. After recrystallization from hexane, yellow crystals were obtained in 55% yield: ^1H NMR ($CDCl_3$) δ 7.45–7.10 (m, 15H, Ph), 4.78 (s, Cp), 0.70, 0.60 (m, 4H, H_β); ^{13}C NMR (C_6D_6) δ 305.1 (d, $^2J_{CP}$ = 22.3 Hz, W≡C), 229.9 (d, $^2J_{CP}$ = 9.5 Hz, WCO), 153.0, 129.6, 124.5, 123.0 ($P(OPh)_3$), 89.8 (Cp), 33.1 (C_α), 10.5, 10.1 (C_β); ^{31}P NMR (C_6D_6) δ 163.2 (J_{WP} = 710 Hz); IR (CH_2Cl_2) 1901.8 cm^{-1} (ν_{WCO}); HRMS (FAB), *m/z* calcd for M^+ ($C_{28}H_{25}O_4WP$) 642.1034, found 642.1060.

$Cl(CO)_2[P(OPh)_3]_2Mo{\equiv}C[trans\text{-}(c\text{-}\overline{CHCHMeCHMe})]$ (10m). Acyl complex **4m** (1.4 g, 3.4 mmol) was dissolved in 50 mL of CH_2Cl_2 and cooled to −98 °C. Oxalyl chloride (300 μL, 3.4 mmol) was then added to the solution. Upon warming to −20 °C, effervescence began and the dark solution became yellow. The solution was returned to the low-temperature bath, and excess $P(OPh)_3$ (10 mL) was added. The bright yellow solution was stirred at room temperature for 18 h. After removal of the solvent, the residue was dissolved in cold Et_2O and filtered to remove NMe_4Cl. The product was used for the synthesis of **11m** without further purification: ^1H NMR ($CDCl_3$) δ 7.34–7.05 (m, 30H, $P(OPh)_3$), 2.25 (m, 1H, H_α), 1.12, 0.85 (2m, 4H, H_β).

$Cp(CO)[P(OPh)_3]Mo{\equiv}C[trans\text{-}(c\text{-}\overline{CHCHMeCHMe})]$ (11m). **11m** was prepared by the method described for **1g,h** and was isolated as a yellow oil in 40% yield after column chromatography on neutral alumina (8 cm × 1.5 cm) with hexane followed by Et_2O as eluent: ^1H NMR ($CDCl_3$) (2 isomers) δ 7.40–7.10 (m, 30H, Ph), 4.74 (s, 10H, Cp), 1.27 (d, 3H, CH_3), 1.26 (d, 3H, CH_3), 0.98, 0.97 (2d, 3H, CH_3), 1.15 (m, 2H, H_α), 1.05 (m, 4H), 1.06–0.64 (m, 4H); ^{13}C NMR (C_6D_6) δ 318.2 (d, $^2J_{CP}$ = 30.4 Hz, Mo≡C), 316.5 (d, $^2J_{CP}$ = 31.3 Hz, Mo≡C), 238.6 (d, $^2J_{CP}$ = 8.6 Hz, MoCO), 238.5 (d, $^2J_{CP}$ = 8.6 Hz, MoCO), 152.8, 152.2, 130.0, 129.6, 124.5, 124.4, 122.9, 121.2 ($P(OPh)_3$), 91.3, 91.1 (Cp), 45.0, 44.8 (C_α), 28.0, 27.8, 27.2, 27.0 (C_β), 18.4, 18.3, 14.8, 14.7 (CH_3); ^{31}P NMR (C_6D_6) δ 193.1, 191.8; IR (hexane) 1911.0 cm^{-1} (ν_{MoCO}); HRMS (FAB), *m/z* calcd for M^+ ($C_{30}H_{29}O_4{}^{98}MoP$) 582.0858, found 582.0856.

4-Ethyl-2-cyclopenten-1-one (14c). An NMR tube was charged with 10 mg of carbyne **1c** and $CDCl_3$ and photolyzed at room temperature for 4 h, affording **14c** in 40% yield. Vacuum transfer and evaporation to near dryness provided clean **14c**: ^1H NMR ($CDCl_3$) δ 7.65 (dd, 1H, H3), 6.16 (dd, 1H, H2), 2.93 (m, 1H, H4), 2.53 (dd, 1H, H5), 2.01 (dd, 1H, H5), 1.50–1.80 (m, 2H, CH_2), 0.99 (t, 3H, CH_3).

4-Phenyl-2-cyclopenten-1-one (14d). **14d** was prepared in a manner analogous to **14c** by photolyzing **1d** in $CDCl_3$ for 2 h. A 40% yield was obtained: ^1H NMR ($CDCl_3$) δ 7.71 (q, 1H, H3), 6.35 (dd, 1H, H2), 4.22 (m, 1H, H4), 2.90 (dd, 1H, H5), 2.35 (dd, 1H, H5), 7.05–7.50 (m, 5H, Ph).

4,4-Dimethyl-2-cyclopenten-1-one (14e). **14e** was prepared in a manner analogous to **14c** by photolyzing **1e,f** in $CDCl_3$ for 2 h. A 40% yield was obtained: ^1H NMR ($CDCl_3$) δ 7.46 (d, J = 5.5 Hz, 1H, H3), 6.00 (d, J = 5.5 Hz, 1H, H2), 2.25 (s, 2H), 1.24 (s, 6H). Literature data are in agreement.[31]

***trans*-4,5-Dimethyl-2-cyclopenten-1-one (14g).** **14g** was prepared by the same method as **14c** by photolyzing any of **1g–n** in $CHCl_3$. A 40% yield was obtained. Careful addition of 1 equiv of ethereal HCl to **1m,n** produced **14g** in nearly 100% yield: ^1H NMR ($CDCl_3$) δ 7.50 (m, 1H, H3), 6.08 (m, 1H, H2), 2.63 (m, 2H, H4 and H5), 1.21 (dd, 6H, CH_3). Literature data are in agreement.[32]

***cis*-4,5-Dimethyl-2-cyclopenten-1-one (14i).** An NMR tube was charged with 10 mg of **1k,l** and allowed to stand at room temperature for 12 h. **14i** was isolated by the same method as **14c** in 40% yield: ^1H NMR ($CDCl_3$) δ 7.60 (m, 1H, H3), 6.12 (m, 1H, H2), 3.05 (m, 1H, H5), 2.40–2.50 (m, 1H, H4), 1.05 (dd, 6H, CH_3). Literature data are in agreement.[32]

***cis*-3a,4,5,6,7,7a-Hexahydro-1H-inden-1-one (14o).** **14o** was prepared in the same manner as **14c** in 40% yield: ^1H NMR ($CDCl_3$) δ 7.63 (dd, 1H, J = 3, 6 Hz, H3), 6.13 (dd, J = 2, 6 Hz, H2), 3.03–2.92 (m, 1H, H3a), 2.38 (dd, 1H, H7a), 2.02–1.01 (br m, 8H, $CH_2CH_2CH_2CH_2$).

Attempts to Trap Ketene Intermediates. The following procedure is representative. An NMR tube was charged with 10 mg of **1a** and 0.5 mL of $CDCl_3$. Allyl alcohol (3 equiv) was then added and the solution photolyzed at −40 °C. The reaction was monitored by ^1H NMR for 3 h. No ketene trapping products were observed.

Photolysis with Other Electron Acceptors. An NMR tube was charged with 10 mg of **1b** and 0.5 mL of CCl_4 and was photolyzed at room temperature until the reaction was complete. Cyclopentenone was produced in 20% yield by ^1H NMR. Reaction of **1m,n** in CCl_4 was accomplished in a similar manner and also produced *trans*-4,5-cyclopentenone in 20% yield. In a similar experiment, an NMR tube was charged with 10 mg of **1a** along with 0.5 mL of CD_3CN and excess methyl viologen. Photolysis at room temperature produced cyclopentenone in 40% yield. Similarly, reaction of **1b** with methyl viologen resulted in an NMR yield of 45% of cyclopentenone. Reaction of **1b** in C_6D_6 in the presence of O_2 produced cyclopentenone in 35% yield.

Photolysis of 1b in the Presence of Base. The following procedure is representative. **1b** (10 mg) was dissolved in 0.5 mL of $CDCl_3$, and excess di-*tert*-butylpyridine (2 equiv) was added. The reaction mixture was photolyzed at room temperature for 2 h along with an identical sample containing no base. Monitoring the progress of the photolysis by ^1H NMR revealed no change in rate of formation or yield of cyclopentenone compared to the reaction with no di-*tert*-butylpyridine.

$Cp(Cl)\{P(OMe)_3\}Mo(\eta^4\text{-}CH_2{=}CHCH{=}CH_2)$ (13). A solution of 1.0 M HCl (86 μL, 0.086 mmol) was added to 40 mg (0.086 mmol) of **9b** in 10 mL of Et_2O at room temperature. Column chromatography on neutral alumina with 1:1 Et_2O/THF as eluent was followed by recrystallization from Et_2O to afford **13** as 28 mg of purple crystals (67% yield): ^1H NMR (C_6D_6) δ 6.73 (br quintet, 1H, H3, $J_{31} = J_{34}$ = 8 Hz), 5.39 (br quartet, 1H, H4), 4.60 (s, 5H, Cp), 3.42 (d, 9H, $P(OMe)_3$, J = 10 Hz), 3.01 (d, 1H, H_5, J_{54} = 8 Hz), 1.76 (d, 1H, H2, J_{23} = 7 Hz), 1.16 (d, 1H, H6, J_{64} = 9 Hz), 0.20 (br t, 1H, H1, J_{1P} = 7 Hz); ^{31}P NMR (C_6D_6) δ 165.7; HRMS (FAB), *m/z* calcd for M^+ ($C_{12}H_{20}O_3{}^{98}MoClP$) 375.9893, found 375.9897.

Observation of $Cp(Cl)\{P(OMe)_3\}Mo(\eta^2\text{-}2\text{-cyclopenten-1-one})$ (15b). An NMR tube was charged with 10 mg of $Cp(CO)[P(OMe)_3]Mo{\equiv}C\text{-}(c\text{-}C_3H_5)$ (**1b**) dissolved in $CDCl_3$. This solution was photolyzed for 2 h at −40 °C and was monitored by ^1H NMR. **15b** was persistent for several hours in solution, though attempts to isolate it were unsuccessful. **15b** could also be generated by addition of HCl to a solution of **1b** in $CDCl_3$: ^1H NMR ($CDCl_3$) δ 5.30 (m, 1H, C3-H), 4.03 (br, 1H, C2-H), 2.90–3.10 (m, 2H, C5-H), 0.24 (m, 1H, C4-H), −8.32 (m, 1H, agostic C4-H).

$Cp(Cl)\{P(OMe)_3\}Mo(\eta^2\text{-}trans\text{-}4,5\text{-dimethyl-}2\text{-cyclopenten-1-one})$ (15m). An ethereal solution of 1.0 M HCl (95 μL, 0.095 mmol) was carefully added to a solution of 73 mg (0.19 mmol) of **1m,n** in Et_2O at −40 °C. Acyl complex **12n** was immediately filtered out as an orange powder, leaving a deep blue solution. **15m** was recrystallized from diethyl ether to afford dark purple crystals in 50% yield: ^1H NMR ($CDCl_3$) δ 5.15 (ddd, 1H, J_{12} = 1 Hz, J_{23} = 6 Hz, J_{2P} = 12 Hz, H2), 5.03 (s, 5H, Cp), 3.85 (d, 1H, J_{12} = 1 Hz, H1), 3.70 (d, 9H, $P(OMe)_3$, J = 10 Hz), 2.90 (dq, 1H, J_{4Me} = 7 Hz, J_{43} = 7 Hz, H4), 1.38 (d, 3H, J_{Me3} = 4.7 Hz, CH_3), 0.67 (d, 3H, J_{Me4} = 7 Hz, CH_3), −9.06 (m, 1H, J_{3Me} = 4.7 Hz, J_{32} = 5.5 Hz, J_{34} = 7 Hz, H3); ^{13}C NMR ($CDCl_3$) δ 207.3 (MoCO), 94.8 (Cp), 84.0, 53.9 (d, J = 9 Hz, $P(OMe)_3$), 51.7, 49.8 (C4), 24.7 (C3); IR (KBr) 1659 cm^{-1} (ν_{CO}).

Crystal Structure Analysis of 15k. Approximately 200 μL of Paratron N oil was dropped on the black prism crystals of **15k** under a nitrogen gas atmosphere. A black prism crystal having approximate dimensions of 0.20 × 0.20 × 0.10 mm was scooped with a glass fiber under a microscope and was immediately frozen on an X-ray diffractometer under a cold nitrogen stream (at 113 K). All measurements were on a Rigaku AFC5R diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.5418 Å) at 113 ± 2 K and a 12-kW rotating anode generator. Cell constants and orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered

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reflections in the range of $68.5° < 2\theta < 70.0°$, corresponded to a monoclinic cell of $a = 14.101(3)$ Å, $b = 9.516(2)$ Å, $c = 13.497(2)$ Å, $\beta = 112.68(1)°$. On the basis of systematic absences of $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, and the successful solution and refinement of the structure, the space group was determined to be $P2_1/c$ (No. 14). The data were collected using the ω–2θ scan technique to a maximum 2θ value of 112.5°. ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.34° with a takeoff angle of 6.0°. Scans of $(1.73 + 0.30 \tan\theta)°$ were made at a speed of 32.0°/min (in ω). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 2 rescans) and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm, and the crystal to detector distance was 285.0 mm. Of the 2481 reflections which were collected, 2371 were unique ($R_{int} = 0.045$). The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection, indicating crystal and electronic stability (no decay correction was applied). An empirical absorption correction (0.99–1.06), based on azimuthal scans of several reflections, was applied. The data were corrected for Lorentz and polarization effects. The structure was solved by a combination of the Patterson method and direct methods. The non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 2187 observed reflections ($I > 0.01\sigma(I)$) and 295 variable parameters and converged (largest parameter shift was 0.33 times its esd) with unweighted and weighted agreement factors of $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.034$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.043$. The weighting scheme, w, was based on counting statistics and included a factor ($p = 0.10$) to down-weight the intense reflections. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.29 and –0.22 e/Å^3, respectively. Neutral-atom scattering factors were taken from the *International Tables of X-ray Crystallography* (1974).[33] Anomalous dispersion effects were included in structure factor calculation using values of $\Delta f'$ and $\Delta f''$ listed in the *International Tables of X-ray Crystallography* (1974). The final atomic coordinates are listed in the supplementary material.

(33) Cromer, D. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. 4.

Cp(Cl)$_2$[P(OMe)$_3$]W[η^2-COCH$_2$(c-C$_3$H$_5$)] 12a. Cp(CO)[P(OMe)$_3$]-W≡C(c-C$_3$H$_5$) (**1a**) (47 mg, 0.10 mmol) was dissolved in Et$_2$O and cooled to –40 °C. To this solution was added 100 μL of 1 M HCl (0.10 mmol). An orange precipitate formed immediately and was collected by filtration to afford pure **12a** in 90% yield (47 mg): ^{1}H NMR ($CDCl_3$) δ 5.40 (d, 5H, Cp), 3.82 (d, 9H, P(OMe)$_3$), 3.20 (m, 2H, CH_2), 1.15 (m, 1H, H_α), 0.62, 0.22 (m, 2H each, H_β), agrees with data for related compounds observed by Kreissl.[30] Anal. Calcd for $C_{13}H_{21}Cl_2O_4PW$: C, 29.63; H, 4.02; Cl 13.45. Found: C, 29.60; H, 3.93; Cl, 13.72.

Cp(Cl)$_2$[P(OMe)$_3$]Mo[η^2-COCH$_2$-*trans*-(c-CHCHMeCHMe)] (12n). Carbynes **1m,n** (72 mg, 0.18 mmol) were dissolved in Et$_2$O and cooled to –40 °C. HCl (1 M) was added (180 μL, 0.18 mmol) to give immediately an orange precipitate. This precipitate was quickly filtered in order to separate **12n** from **15m**, which was also formed. **12n** was isolated as an orange solid in 52% yield (44 mg): ^{1}H NMR ($CDCl_3$) δ 5.42 (d, 5H, Cp), 3.85 (d, 9H, J = 10.1 Hz, P(OMe)$_3$), 3.02–3.20 (m, 2H, CH_2), 0.95 (m, 1H, H_α), 0.62, 0.20 (m, 1H each, H_β), 1.05 (d, 6H, J = 6.1 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 278 (s, CO), 96.8 (s, Cp), 55.0, 54.9 (s, CH_2), 41.6, 41.3 (s, P(OMe)$_3$), 20.9, 20.8, 20.4, 20.2 (s, CH), 13.2, 12.9 (s, CH_3). Anal. Calcd for $C_{15}H_{25}Cl_2O_4PMo$: C, 35.65; H, 5.39; Cl 15.18. Found: C, 38.32; H, 5.29; Cl, 15.25.

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Supplementary Material Available: Tables of bond distances, bond angles, positional parameters, and anisotropic displacement parameters for **15k** (15 pages); listing of observed and calculated structure factors for **15k** (15 pages). Ordering information is given on any current masthead page.