Formation of Cyclohexenones by Oxidative Cyclization of Alkene-Functionalized Carbyne Complexes

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Deprotonation of the complexes $(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}Mo{\equiv}CR$ (R = Me or c-C_3H_5) with *n*-BuLi followed by reaction with allyl bromide generates the carbynes $(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}Mo{\equiv}CR$ (**1a**, R = $CH_2CH_2CH{=}CH_2$; **1b**, R = $C(CH_2CH{=}CH_2)CH_2CH_2$). Photooxidation of **1a** in $CDCl_3$ yields 2-cyclohexenone (**2a**). Protonation of **1a** with HCl also affords **2a** in addition to the η^2-acyl complex $(\eta^5\text{-}C_5H_5)\{P(OMe)_3\}Cl_2Mo[CO(CH_2)_3CH{=}CH_2]$ (**3**), while thermal decomposition in $CDCl_3$ yields **2a** and 1,4-pentadiene (**4a**). Deuterium-labeling studies suggest that **2a** forms by a mechanism involving initial formation of a cationic carbene complex followed by cyclization *via* an intramolecular ene reaction. Carbyne **1b** forms 2-cyclohexenone-5-spirocyclopropane (**2b**) upon decomposition in chloroform, but the principal product is the metallacycle $(\eta^5\text{-}C_5H_5)Cl\{P(OMe)_3\}Mo\{CH_2CH{=}C(C_3H_5)CH(CHO)\}$ (**5**). Derivatives of **1a** with substituents on the tethered olefin do not form cyclohexenones upon thermal decomposition, yielding instead substituted pentadienes.

Introduction

The photochemistry of carbyne complexes is a subject that has recently attracted significant interest due to the number of modes of reactivity exhibited by the carbyne ligand.[1] In the course of our investigations into the behavior of the metal carbynes $(\eta^5\text{-}C_5H_5)L_2M{\equiv}CR$ (M = Mo, W; L = CO, $P(OMe)_3$; R = alkyl or aryl) under both photochemical and thermal conditions, we have demonstrated that it is possible for the carbyne ligand to undergo rearrangement and decoordination from the metal to yield organic molecules such as cyclopentenones,[2] olefins,[2c] and dienes.[2d] The reaction pathways and thus final products are sensitive to the carbyne substituents and reaction conditions. However, it appears that these reactions share a common first step: conversion of the metal carbyne into a cationic carbene complex. This transformation can be accomplished by protonation of the starting carbyne or, more interestingly, by photochemical oxidation to a paramagnetic carbyne followed by hydrogen abstraction from the reaction medium.[2d] The high reactivity of the oxidized carbyne complexes in these systems provides an interesting contrast to the stable paramagnetic carbynes that have recently been reported.[3] Our mechanistic investigations of these reactions suggest that further transformations of the resulting cationic carbene complex depend on the functionality of the substituent and the identity of the ancillary ligands. Here we report the conversion of the carbyne ligand of $(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}Mo{\equiv}CCH_2CH_2CH{=}CH_2$ to cyclohexenone upon oxidation. The results of deuterium labeling studies are consistent with cyclization by a formal ene reaction involving a metal–carbon double bond which is, to our knowledge, unprecedented. Substitution of the carbyne moiety at various positions results in alternative organic and organometallic products and demonstrates a delicate balance of reactivity depending on the nature of the carbyne ligand.

Results and Discussion

Synthesis and Photooxidation of 1a. The complex $(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}Mo{\equiv}CCH_2CH_2CH{=}CH_2$ (**1a**) was generated from $(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}Mo{\equiv}CMe$[2c] by deprotonation with *n*-butyllithium followed by addition of allyl bromide (Scheme I). Similar elaborations of carbyne ligands by deprotonation and alkylation have been reported previously by Green and Templeton and provide a powerful synthetic route to functionalized carbyne complexes.[1f,4] Irradiation of **1a** in $CDCl_3$ resulted in rapid decomposition and the formation of 2-cyclohexenone (**2a**) in 40% yield (eq 1). The 6-position of **2a** was 20%

1a 2a (Eq. 1)

deuterated, demonstrating that the hydrogen is derived mainly from the starting material, although some attack

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(1) (a) Mayr, A.; Kjelsberg, M. A.; Lee, K. S.; Asaro, M. F.; Hsieh, T.-C. *Organometallics* **1987**, *6*, 2610–2612. (b) Sheridan, J. B.; Pourreau, D. B.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1988**, *7*, 289–294. (c) Sheridan, J. B.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1986**, *5*, 1514–1515. (d) Vogler, A.; Kisslinger, J.; Roper, W. R. *Z. Naturforsch.* **1983**, *38b*, 1506–1509. (e) Green, M. *J. Organomet. Chem.* **1986**, *300*, 93–109. (f) Beevor, R. G.; Freeman, M. J.; Green, M.; Morton, C. E.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1991**, 3021–3030.

(2) (a) Kingsbury, K. B.; Carter, J. D.; McElwee-White, L. *J. Chem. Soc., Chem. Commun.* **1990**, 624–625. (b) Carter, J. D.; Kingsbury, K. B.; Wilde, A.; Schoch, T. K.; Leep, C. J.; Pham, E. K.; McElwee-White, L. *J. Am. Chem. Soc.* **1991**, *113*, 2947–2954. (c) Carter, J. D.; Schoch, T. K.; McElwee-White, L. *Organometallics* **1992**, *11*, 3571–3578. (d) Kingsbury, K. B.; Carter, J. D.; Wilde, A.; Park, H.; Takusagawa, F.; McElwee-White, L.; *J. Am. Chem. Soc.*, in press.

(3) (a) Felixberger, J. K.; Kiprof, P.; Herdtweck, E.; Herrmann, W. A.; Jakobi, R.; Gütlich, P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 334–337. (b) Herrmann, W. A.; Felixberger, J. K.; Anwander, R.; Herdtweck, E.; Kiprof, P.; Riede, J. *Organometallics* **1990**, *9*, 1434–1443. (c) Manna, J.; Gilbert, T. M.; Dallinger, R. F.; Geib, S. J.; Hopkins, M. D. *J. Am. Chem. Soc.* **1992**, *114*, 5870–5873. (d) Lemos, M. A. N. D. A.; Pombeiro, A. J. L.; Hughes, D. L.; Richards, R. L. *J. Organomet. Chem.* **1992**, *434*, C6–C9.

(4) Brower, D. C.; Stoll, M.; Templeton, J. L. *Organometallics* **1989**, *8*, 2786–2792.

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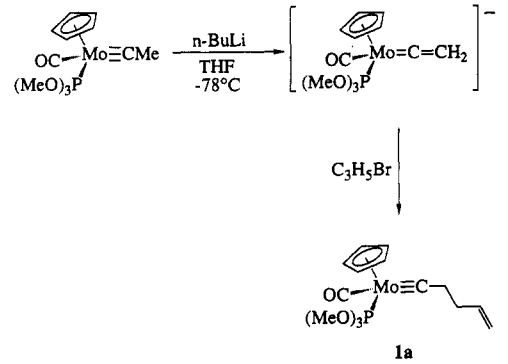
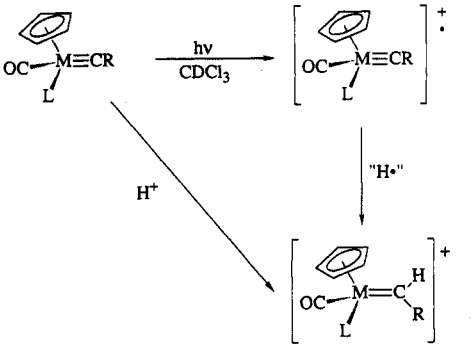
Scheme I



Scheme II



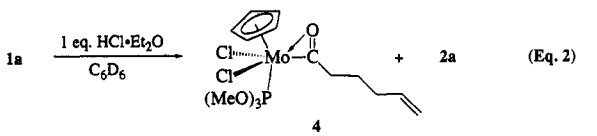
on the solvent does occur. No inorganic products could be isolated from the reaction mixture, and according to ^{1}H NMR spectra of the solutions, the remaining material is composed of a complex mixture of minor products.

Transformation of **1a** into **2a** also occurred slowly in room light in $CDCl_3$. These milder conditions gave significantly higher yields of **2a** (55%), and as a byproduct 1,4-pentadiene (**3a**) was observed in 7% yield. It is possible that **3a** is formed during photolysis of **1a**, although it is not observed in the reaction mixtures. In control experiments where **1a** was photolyzed in the presence of added **3a**, no pentadiene remained at the end of the reaction, demonstrating that it does not survive the experimental conditions.

Previous studies on the photooxidation of related carbynes[2c] have shown that reaction takes place through excitation of the low-energy d-π^* (or MLCT) band, followed by electron transfer to $CDCl_3$. The UV spectrum of **1a** shows the presence of such a band at 440 nm, and irradiation of **1a** through a 430-nm long pass filter in $CDCl_3$ resulted in complete disappearance of **1a**. No cyclohexenone was formed upon irradiation in C_6D_6, implying that an electron acceptor is required in the system. Cyclohexenone was formed upon photolysis in CD_2Cl_2, though with this less strongly oxidizing acceptor, a lower yield of 18% was obtained. Cyclic voltammetry studies on the butenylcarbyne **1a** showed an irreversible oxidation wave at 0.0 V relative to the ferrocene/ferricinium couple in CH_2Cl_2, consistent with rapid decomposition of the radical cation following oxidation.

In order to confirm that formation of **2a** was in fact due to photooxidation of the carbyne complex and not to protonation by acid formed within the chloroform during photolysis,[5] experiments were performed in which **1a** was photolyzed in the presence of base. Generation of organic radical cations in the presence of 2,6-di-*tert*-butylpyridine has been used to distinguish radical cation chemistry from acid-catalyzed reactions.[6] Similar experiments using either 2,6-di-*tert*-butylpyridine or proton sponge resulted in no change in the rate of reaction or yield of **2a**.

Reaction of 1a with Acid. However, since prior studies[2d] have shown that upon occasion the photooxidation reaction manifold can be accessed *via* protonation of the carbyne complexes, the reaction of **1a** with HCl was examined. Protonation of **1a** with a small excess of ethereal HCl in C_6D_6 resulted in relatively rapid formation of (η^5-C_5H_5)Cl_2{P(OMe)$_3$}Mo{η^2-C(O)$CH_2CH_2CH_2CH{=}CH_2$} (**4**) (eq 2) as the result of the addition of 2 equiv of HCl per



(Eq. 2)

complex. Unreacted **1a** was also initially present in the reaction mixture, but over the course of 24 h all **1a** was consumed and **2a** was generated in a yield of *ca.* 20% by NMR. Solutions of **1a** in C_6D_6 without acid showed no tendency to form **2a** after the same period of time. Kreissl has demonstrated that η^2-acyl complexes similar to **4** are formed *via* carbene intermediates upon protonation of carbynes with HCl.[7] Preferential formation of η^2-acyl complexes over the photooxidation products upon addition of HCl to metal carbynes was also observed for cyclopropylcarbyne complexes.[2d] The differing rates of formation of **2a** and **4** imply that while concentration of chloride is high in the reaction mixture the acyl complex is the preferred product, but as the chloride concentration drops intramolecular rearrangement becomes the dominant pathway.

These results suggest that the first mechanistic steps in the formation of cyclohexenone match those of our proposed mechanism for the decomposition of cyclopropylcarbynes in $CDCl_3$[2d] in which a cationic carbene species is an early intermediate. This intermediate can be accessed either by photochemical electron transfer to the solvent and abstraction of a hydrogen atom from the reaction medium or, under certain conditions, directly by protonation of the carbyne (Scheme II). Reactions where H^+ is added by a 1 e^- oxidation/H abstraction pathway have been reported for other organometallic complexes.[8,9] In conjunction with the observation that photooxidation and protonation do not always yield the same products,[2] it should be noted that the carbyne carbon is not necessarily the expected site of protonation in carbyne complexes of this type. Depending on the exact nature of the ancillary

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

(6) (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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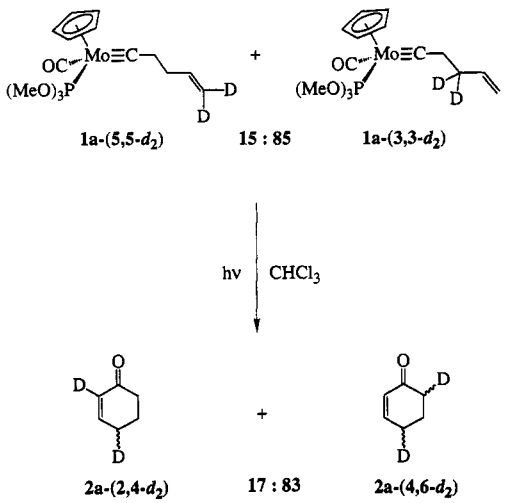
(8) (a) Armstead, J. A.; Cox, D. J.; Davis, R. *J. Organomet. Chem.* **1982**, *236*, 213–219. (b) Waterman, P. S.; Giering, W. P. *J. Organomet. Chem.* **1978**, *155*, C47–C50.

(9) The related pathway in which net H^- addition occurs by electron transfer/H-abstraction is also known in organometallic systems. Representative examples include the following: (a) Astruc, D. *Acc. Chem. Res.* **1991**, *24*, 36–42. (b) Nlate, S.; Guerchais, V.; Lapinte, C. *J. Organomet. Chem.* **1992**, *434*, 89–96. (c) Narayanan, B. A.; Amatore, C.; Kochi, J. K. *Organometallics* **1987**, *6*, 129–139. (d) Kuchynka, D. J.; Amatore, C.; Kochi, J. K. *Inorg. Chem.* **1986**, *25*, 4087–4097.

Scheme III

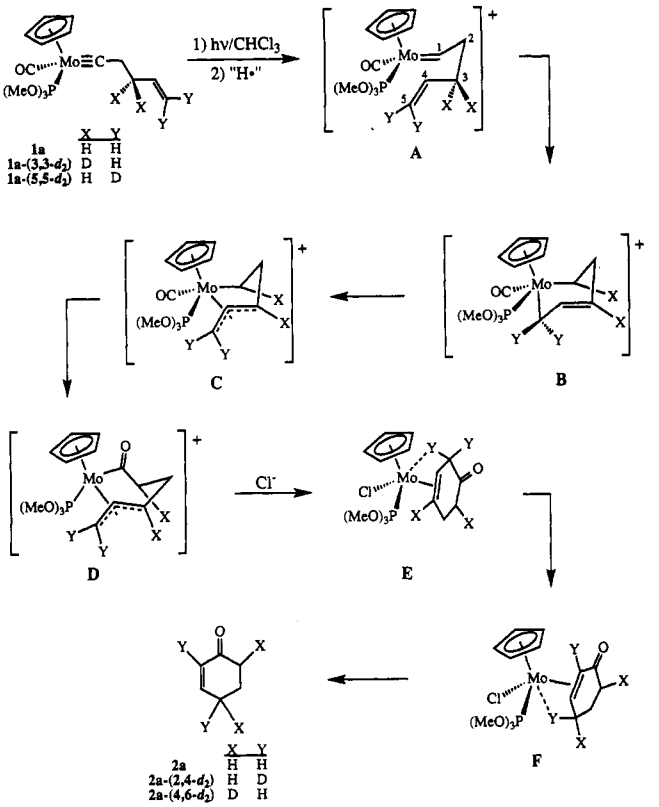


ligands, it is possible to find the proton either adding to the carbyne carbon to form a carbene, as postulated in this case, or adding to the metal center to form a metal hydride carbyne complex.[10] Intermediate complexes in which there is an agostic interaction between the carbene hydrogen and the metal have also been observed.[11] It has been suggested that the proton always adds to the carbyne carbon and subsequently may transfer to the metal;[10] if so, such a shift is not competitive with the intraligand transformation discussed herein.

Photooxidation of 1a-*d*$_2$. To gain information about the cyclization step, deuterium-labeled **1a** was prepared from a 79:21 mixture of CH_2=$CHCD_2Br$ and CD_2=$CHCH_2Br$, yielding **1a-(*3,3-d*$_2$)** and **1a-(*5,5-d*$_2$)** as an 85:15 mixture. Mass spectral analysis of the 2-cyclohexenone obtained by photolysis of the mixture in $CHCl_3$ confirmed that it was 100% d_2. Integration of its ^{1}H NMR spectrum was consistent with a mixture of **2a-(*4,6-d*$_2$)** and **2a-(*2,4-d*$_2$)** in 83:17 ratio, the same within experimental error as the isomer ratio of the starting material **1a** (Scheme III).

Mechanism of Cyclization. This distribution of deuterium label in **2a-*d*$_2$** strongly suggests the mechanism of cyclization shown in Scheme IV. After formation of the cationic carbene complex **A** as previously discussed, either by protonation of **1a** or by photooxidation followed by abstraction of hydrogen from the reaction mixture, conversion of **A** to **B** is formally an intramolecular ene reaction, in which hydrogen shifts from C3 to the carbene carbon and a C5–Mo bond is formed. To our knowledge, ene reactions involving a metal–carbon double bond as enophile are unknown, but pericyclic processes involving M=C bonds have been proposed for the rearrangement of chromium vinylcyclopropylcarbenes into cyclopentenones,[12] and intramolecular ene reactions in organic systems are well documented.[13] Conversion of the σ-allyl complex **B** into the π-allyl complex **C** is followed by carbonyl insertion into the Mo–C bond to give **D** and reductive

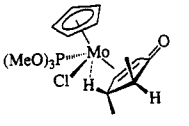
Scheme IV



elimination to yield the 3-cyclohexenone complex **E**. Isomerization of the coordinated olefin would yield **F** as precursor to **2a**. These further steps in the mechanism are precedented in the literature. The organic ligands of **C** and **D** have been observed previously in the iron carbonyl complexes $(CO)_3Fe(\sigma,\eta^3\text{-}C_5H_9)$ (**6**) and $(CO)_3Fe\{\sigma,\eta^3\text{-}C(O)\text{-}C_5H_9\}$ (**7**) and were reported as yielding 2-cyclohexenone

6 7

upon air oxidation.[14] Complexes **E** and **F** provide a facile pathway for the isomerization from nonconjugated to conjugated enone *via* an agostic hydride interaction between the ligand and the metal. Complex **8**, containing a dimethylcyclopentenone moiety ligated to molybdenum in a similar fashion to **F**, has been structurally characterized,[2d] and chromium-mediated isomerizations of cyclic alkenes have been observed and are believed to proceed through metal hydride intermediates.[15]



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Substituent Effects on Carbyne Cyclization. To investigate effects of olefin substituents on the reaction,

(10) Bottrill, M.; Green, M.; Orpen, A. G.; Saunders, D. R.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1989**, 511–518.

(11) (a) Wengrovius, J. H.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1982**, *104*, 1739–1740. (b) Mayr, A.; Asaro, M. F.; Kjelsberg, M. A.; Lee, K. S.; van Engen, D. *Organometallics* **1987**, *6*, 432–434.

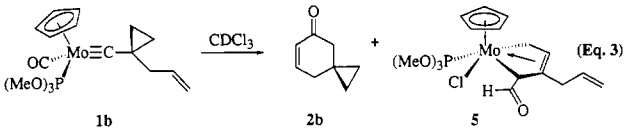
(12) Herndon, J. W.; McMullen, L. A. *J. Am. Chem. Soc.* **1989**, *111*, 6854–6856.

(13) Snider, B. B. In *Comprehensive Organic Synthesis Vol.* 5; Trost, B. M., Fleming, I. Eds.; Pergamon Press: Oxford, 1991; pp 9–20.

(14) (a) Aumann, R. *J. Am. Chem. Soc.* **1974**, *96*, 2631–2632. (b) McDaniel, K. F.; Kracker, L. R.; Thamburaj, P. K. *Tetrahedron Lett.* **1990**, *31*, 2373–2376.

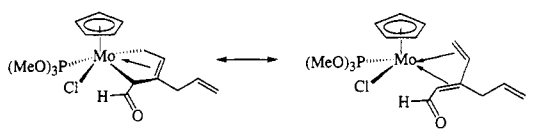
(15) (a) Barton, D. H. R.; Davies, S. G.; Motherwell, W. B. *Synthesis* **1979**, 265–266. (b) Herndon, J. W.; Tumer, S. U.; Schnatter, W. F. K. *J. Am. Chem. Soc.* **1988**, *110*, 3334–3335.

carbynes **1b–g** were prepared and their decomposition in chloroform was monitored. The cyclopropyl(allyl) carbyne **1b** was synthesized in a similar manner to **1a** by deprotonating the cyclopropyl carbyne $(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}Mo{\equiv}C(c\text{-}C_3H_5)$[2a] with *n*-butyllithium followed by reaction with allyl bromide. Thermal decomposition of **1b** in $CDCl_3$ afforded the expected cyclohexenone derivative 2-cyclohexenone-5-spirocyclopropane (**2b**) in *ca.* 5% yield, but the principal product was characterized as $(\eta^5\text{-}C_5H_5)Cl\{P(OMe)_3\}Mo\{CH_2CH{=}C(C_3H_5)CH(CHO)\}$ (**5**) which was isolated in 43% yield (eq 3).



1b 2b 5

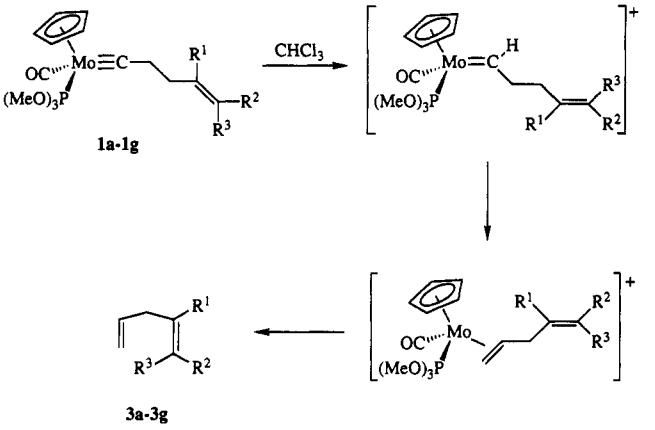
In complex **5** the presence of the aldehyde group is confirmed by a doublet resonance in the ^1H NMR spectrum at 10.22 ppm and by C=O and CH stretches in the IR spectrum at 1644 and 2849 cm^{-1}, respectively. For the methylene group directly attached to the metal, decoupling experiments demonstrate ^{31}P coupling to both protons with values of 3 and 8 Hz, and the methyne group bonded to the metal shows broadening which we also attribute to unresolved ^{31}P coupling. In the ^{13}C NMR spectrum the metal-bonded methylene carbon resonates at 38.5 ppm with a typical aliphatic ^1H coupling of 126 Hz. However, the relatively strong (7 Hz) ^{31}P coupling of the methyne hydrogen adjacent to this methylene group suggests that a resonance structure in which the organic ligand is a coordinated dienal moiety may contribute to the bonding in this molecule. This and other reactions of α-substituted cyclopropylcarbynes leading to metallacycles are currently under further investigation.



The formation of a cyclohexenone product from **1b** demonstrates the tolerance of the cyclization to α,α-substitution on the carbyne ligand, but the competing ring-opening pathway leading to **5** makes it difficult to quantify the intrinsic effect on the yield. Attempts to prepare the α-methyl- and α,α-dimethylsubstituted butenylcarbynes which would not be susceptible to ring-opening reactions were unsuccessful, instead giving complex mixtures of products.

A number of butenylcarbynes, **1c–g**, with various substituents on the olefin were prepared according to the deprotonation/electrophilic addition methodology. Upon photolysis, these complexes failed to give identifiable products. However, when allowed to decompose in $CDCl_3$ in the dark or under room light, the known dienes **3c–g**[16] were identified by comparison of the ^1H NMR spectra of the reaction mixtures with authentic samples or published spectra. No cyclohexenone derivatives were detected following decomposition of **1c–g**, and diene yields from decomposition reactions of the substituted carbynes were

Scheme V



1a-1g 3a-3g

	R^1	R^2	R^3
1a	H	H	H
1c	Me	H	H
1d	CO_2Et	H	H
1e	H	Me	Me
1f, 1g	H	Me	H
	H	H	Me

	R^1	R^2	R^3	Yield (%)
3a	H	H	H	7
3c	Me	H	H	52
3d	CO_2Et	H	H	32
3e	H	Me	Me	30
3f, 3g	H	Me	H	50
	H	H	Me	

observed to be considerably higher than from the parent complex **1a**. Diene formation in this reaction is easily rationalized by a [1,2] H-shift within the cationic carbene intermediate, giving an olefin complex which ejects the observed organic product (Scheme V). There is ample precedent for formation of olefins upon decomposition of alkylcarbene complexes.[17] Cyclization reactions requiring approach of a tethered olefin to the metal center have been observed to be sensitive to steric congestion,[18] and it appears that when substituents are present on the double bond, formation of the metallacylic intermediate leading to cyclohexenone products is sufficiently slowed that the hydride shift mechanism predominates.

Conclusion

Our previous studies on the photooxidation of metal carbynes have demonstrated that formation of organic products via rearrangement of the carbyne ligands is general for carbyne complexes with alkyl substituents. The studies reported here extend the range of available processes by establishing that cyclization of carbyne ligands bearing pendant olefins can be triggered by photooxidation and, in some cases, by reaching a common intermediate through protonation of the starting material. Deuterium-labeling studies have allowed the course of the reaction to be followed, providing evidence for an ene-type reaction, the first such in which a metal–carbon multiple bond functions as an enophile. The sensitivity of the reaction to substitution at the tethered alkene is consistent with the proposed cyclization mechanism. Further studies on generation of organic products from metal carbynes are underway.

Experimental Section

General Methods. Standard inert atmosphere techniques were used throughout. Diethyl ether and THF were distilled from Na/Ph_2CO. Hexane, chloroform (ethanol free), and methylene chloride were distilled from CaH_2. All NMR solvents

(16) The dienes **4a, 4c, 4f,** and **4g** are commercially available (Aldrich). For **4d**: Sheffy, F. K.; Godschalx, J. P.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 4833–4840. For **4e**: Barluenga, J.; Yus, M.; Concellon, J. M.; Bernad, P. *J. Chem. Res., Miniprint* **1980**, 0677–0692.

(17) (a) Casey, C. P.; Albin, L. D.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 2533–2539. (b) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258–264. (c) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411–432.

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were degassed by three freeze–pump–thaw cycles. Benzene-d_6 was vacuum transferred from Na/Ph_2CO. $CDCl_3$ and CD_2Cl_2 were stored over 3-Å molecular sieves. Ethyl α-(bromomethyl)-acrylate was prepared by esterification of α-(bromomethyl)acrylic acid, which was synthesized according to published methods.[19] All other starting materials were purchased in reagent grade and used without further purification. Column chromatography separations were performed at low temperature (−40 °C) on neutral alumina (Brockmann Activity I).

^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian XL-400 NMR spectrometer. ^{31}P NMR shifts are referenced to 85% H_3PO_4. IR spectra were recorded on a Perkin-Elmer 1600 spectrometer. UV–vis spectra were recorded on a Hewlett-Packard 8425A diode array spectrophotometer. 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 Mass Spectrometry Facility, University of California, San Francisco. Microanalyses were carried out by Robertson Microlit Laboratories, Inc., Madison, NJ. Complexes **1a–g** were obtained as oils which were unsuitable for microanalysis due to solvent contamination that could not be removed upon extended exposure to vacuum. Complexes **1b** and **1d** were also found to contain small amounts of the complex *cis*-Mo(CO)$_4${P(OMe)$_3$}$_2$[20] which could not be removed by chromatography. Copies of the ^1H NMR spectra of **1a–g** are available in the supplementary material.

Synthesis of (η^5-C_5H_5)(CO){P(OMe)$_3$}Mo≡CCH$_2$CH$_2$CH=CH$_2$ (1a). The methylcarbyne (η^5-C_5H_5)(CO){P(OMe)$_3$}Mo≡CMe[2c] (214 mg, 0.63 mmol) in 15 mL of THF was reacted with a 2.5 M hexane solution of *n*-butyllithium (500 μL, 1.25 mmol) at −78 °C. After 30 min, allyl bromide (130 μL, 1.50 mmol) was added and the solution warmed to room temperature. Solvent was removed *in vacuo* and the residue extracted with hexane and then chromatographed on neutral alumina using 3:1 hexane/Et_2O as eluent to afford **1a** as a yellow oil (149 mg, 62%) after removal of solvent. For **1a**: ^1H NMR (C_6D_6) 5.85 (m, 1 H, =CH), 5.26 (d, 5 H, C_5H_5, J_{PH} = 1 Hz), 4.98 (m, 2 H, =CH_2), 3.37 (d, 9 H, OMe, J_{PH} = 12 Hz), 2.33 (m, 4 H, CH_2) ppm; $^{13}C\{^1H\}$ NMR (C_6D_6) 314.3 (d, Mo≡C, J_{PC} = 27 Hz), 241.9 (d, CO, J_{PC} = 18 Hz), 137.8 (=CH), 115.0 (=CH_2), 91.0 (C_5H_5), 51.2 (OMe), 49.4 (CCH_2), 32.8 (CH_2) ppm; $^{31}P\{^1H\}$ NMR (C_6D_6) 203.8 ppm; IR (CH_2Cl_2) 1901 cm^{-1} (ν_{CO}); UV (*n*-hexane) 230 (ϵ = 20 000), 250 (sh), 328 (sh), 440 (ϵ = 90) nm; HRMS (FAB) *m/z* calcd for M$^+$ ($C_{14}H_{21}O_4$PMo) 382.0232, found 382.0237.

Synthesis of (η^5-C_5H_5)(CO){P(OMe$_3$}Mo≡CC(CH$_2$CH=CH$_2$)CH$_2$CH$_2$ (1b). The cyclopropylcarbyne (η^5-C_5H_5)(CO){P(OMe)$_3$}Mo≡C(c-C_3H_5)[2a] (270 mg, 0.74 mmol) in 10 mL of THF was reacted with a 2.5 M hexane solution of *n*-butyllithium (440 μL, 1.11 mmol) at −78 °C. After 30 min, allyl bromide (130 μL, 1.50 mmol) was added and the solution warmed to room temperature. Solvent was removed *in vacuo* and the residue extracted with hexane and then chromatographed on neutral alumina using 3:1 hexane/Et_2O as eluent to afford **1b** as a yellow oil (296 mg, 98%) after removal of solvent. For **1b**: ^1H NMR ($CDCl_3$) 5.93 (m, 1 H, =CH), 5.35 (s, 5 H, C_5H_5), 5.02 (m, 2 H, =CH_2), 3.55 (d, 9 H, OMe, J_{PH} = 12 Hz), 2.10–2.22 (m, 2 H, CH_2), 1.05 (m, 2 H, c-C_3H_4), 0.50 (m, 2 H, c-C_3H_4) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) 318.4 (d, Mo≡C, J_{PC} = 26 Hz), 241.5 (d, CO, J_{PC} = 18 Hz), 136.2 (=CH), 115.9 (=CH_2), 90.6 (C_5H_5), 51.4 (OMe), 40.0 (CH_2), 39.4 (Mo≡CC), 16.2, 16.0 (CH_2CH_2) ppm; $^{31}P\{^1H\}$ NMR (C_6D_6) 204.7 ppm; IR (CH_2Cl_2) 1895 cm^{-1} (ν_{CO}); HRMS (FAB) *m/z* calcd for M$^+$ ($C_{16}H_{23}O_4$PMo) 408.0388, found 408.0392.

Synthesis of (η^5-C_5H_5)(CO){P(OMe)$_3$}Mo≡CCH$_2$CH$_2$C(Me)=CH$_2$ (1c). As described for the preparation of **1a**, deprotonation of (η^5-C_5H_5)(CO){P(OMe)$_3$}Mo≡CMe (87 mg, 0.26 mmol) in 10 mL of THF with 2.5 M *n*-butyllithium (200 μL, 0.51 mmol) followed by reaction with H_2C=C(Me)CH_2Br (70 μL, 0.67 mmol) afforded **1c** as a yellow oil (66 mg, 64%). For **1c**: ^1H NMR ($CDCl_3$) 5.36 (s, 5 H, C_5H_5), 4.67, 4.62 (br s, 1 H, =CH_2), 3.57 (d, 9 H, OMe, J_{PH} = 12 Hz), 2.28–2.43 (m, 4 H, CH_2), 1.66 (s, 3 H, Me) ppm; $^{13}C\{^1H\}$ NMR (C_6D_6) 314.2 (d, Mo≡C, J_{PC} = 28 Hz), 241.8 (d, CO, J_{PC} = 19 Hz), 144.5 (=CMe), 110.6 (=CH_2), 91.0 (C_5H_5), 51.2 (OMe), 48.4 (Mo≡CC), 36.4 (CH_2), 22.4 (Me) ppm; $^{31}P\{^1H\}$ NMR (C_6D_6) 203.8 ppm; IR (CH_2Cl_2) 1900 cm^{-1} (ν_{CO}); HRMS (FAB) *m/z* calcd for M$^+$ ($C_{15}H_{23}O_4$PMo) 396.0388, found 396.0399.

Synthesis of (η^5-C_5H_5)(CO){P(OMe)$_3$}Mo≡CCH$_2$CH$_2$C(CO$_2$Et)=CH$_2$ (1d). As described for the preparation of **1a**, deprotonation of (η^5-C_5H_5)(CO){P(OMe)$_3$}Mo≡CMe (104 mg, 0.31 mmol) in 10 mL of THF with 2.5 M *n*-butyllithium (270 μL, 0.67 mmol) followed by reaction with H_2C=C(CH_2Br)CO_2Et (100 μL, *ca.* 3 equiv) afforded **1d** as a yellow oil (66 mg, 47%). For **1d**: ^1H NMR ($CDCl_3$) 6.14, 5.57 (s, 1 H, =CH_2), 5.35 (s, 5 H, C_5H_5), 4.17 (q, 2 H, OCH_2, J_{HH} = 7 Hz), 3.56 (d, 9 H, OMe, J_{PH} = 12 Hz), 2.42–2.55 (m, 4 H, CH_2), 1.27 (t, 3 H, Me, J_{HH} = 7 Hz) ppm; $^{13}C\{^1H\}$ NMR (C_6D_6) 312.9 (d, Mo≡C, J_{PC} = 27 Hz), 241.9 (d, CO, J_{PC} = 20 Hz), 166.5 (C=O), 139.8 (*C*=CH_2), 125.1 (C=*C*H$_2$), 91.0 (C_5H_5), 60.5 (OCH_2), 51.2 (OMe), 48.6 (Mo≡CC), 31.0 (CH_2), 14.1 (Me) ppm; $^{31}P\{^1H\}$ NMR (C_6D_6) 203.5 ppm; IR (CH_2Cl_2) 1906 (ν_{MoCO}), 1712 cm^{-1} ($\nu_{C=O}$); HRMS (FAB) *m/z* calcd for M$^+$ ($C_{17}H_{25}O_6$PMo) 454.0443, found 454.0425.

Synthesis of (η^5-C_5H_5)(CO){P(OMe)$_3$}Mo≡CCH$_2$CH$_2$CH=CMe$_2$ (1e). As described for the preparation of **1a**, deprotonation of (η^5-C_5H_5)(CO){P(OMe)$_3$}Mo≡CMe (88 mg, 0.26 mmol) in 10 mL of THF with 2.5 M *n*-butyllithium (210 μL, 0.52 mmol) followed by reaction with H_2C=CHC(Cl)$(Me)_2$ (70 μL, 0.62 mmol) afforded **1e** as a yellow oil (65 mg, 61%). For **1e**: ^1H NMR ($CDCl_3$) 5.36 (d, 5 H, C_5H_5, J_{PH} = 1 Hz), 5.10 (t, 1 H, CH, J_{HH} = 13 Hz), 3.57 (d, 9 H, OMe, J_{PH} = 12 Hz), 2.17–2.31 (m, 4 H, CH_2), 1.65, 1.58 (s, 3 H, Me) ppm; $^{13}C\{^1H\}$ NMR (C_6D_6) 315.6 (d, Mo≡C, J_{PC} = 28 Hz), 241.9 (d, CO J_{PC} = 19 Hz), 131.7 (=CH), 124.1 (=CMe_2), 91.0 (C_5H_5), 51.2 (OMe), 50.3 (Mo≡CC), 27.5 (CH_2), 25.8, 17.7 (Me) ppm; $^{31}P\{^1H\}$ NMR (C_6D_6) 203.9 ppm; IR (CH_2Cl_2) 1901 cm^{-1} (ν_{CO}); HRMS (FAB) *m/z* calcd for M$^+$ ($C_{16}H_{25}O_4$PMo) 410.0545, found 410.0535.

Synthesis of (η^5-C_5H_5)(CO){P(OMe)$_3$}Mo≡CCH$_2$CH$_2$CH=CHMe (1f + 1g). As described for the preparation of **1a**, deprotonation of (η^5-C_5H_5)(CO){P(OMe)$_3$}Mo≡CMe (97 mg, 0.29 mmol) in 10 mL of THF with 2.5 M *n*-butyllithium (120 μL, 0.29 mmol) followed by reaction with a mixture of *cis*- and *trans*-$BrCH_2CH$=$CHCH_3$ (80 μL, 0.79 mmol; Aldrich crotyl bromide, 85%) afforded a mixture of **1f** and **1g** in approximately 3:2 proportions as a yellow oil (37 mg, 32%). It is not possible to unambiguously state which is the major isomer. For a mixture of **1f** and **1g** [an asterisk (*) denotes the minor isomer]: ^1H NMR ($CDCl_3$) 5.42 (m, 2 H, HC=CH), 5.37 (s, 5 H, C_5H_5), 5.36* (s, 5 H, C_5H_5), 3.56 (d, 9 H, OMe, J_{PH} = 12 Hz), 3.56* (d, 9 H, OMe, J_{PH} = 12 Hz), 2.26 (m, 4 H, CH_2), 1.61 (d, 3 H, Me, J_{HH} = 4 Hz), 1.58* (d, 3 H, Me, J_{HH} = 6 Hz) ppm; $^{13}C\{^1H\}$ NMR (C_6D_6) 315.5 (d, Mo≡C, J_{PC} = 31 Hz), 242.1 (d, CO, J_{PC} = 16 Hz), 130.8, 130.0* (*C*=CHMe), 125.8, 124.6* (C=*C*HMe), 91.2 (C_5H_5), 51.2 (OMe), 50.4, 50.1* (Mo≡CC), 32.1*, 32.0 (CH_2), 23.2*, 18.3 (Me) ppm; $^{31}P\{^1H\}$ NMR (C_6D_6) 203.9, 203.9* ppm; IR (CH_2Cl_2) 1900 cm^{-1} (ν_{CO}); HRMS (FAB) *m/z* calcd for M$^+$ ($C_{15}H_{23}O_4$PMo) 396.0388, found 396.0382.

Synthesis of (η^5-C_5H_5)Cl$_2${P(OMe)$_3$}Mo{η^2-C(O)(CH$_2$)$_3$CH=CH$_2$} (4). The butenylcarbyne (η^5-C_5H_5)(CO){P(OMe)$_3$}Mo≡CCH_2CH_2CH=CH_2 (88 mg, 0.23 mmol) in 10 mL of Et_2O was treated with a 1 M solution of HCl·Et_2O (460 μL, 0.46 mmol) to afford a brown oil after removal of solvent. Recrystallization from CH_2Cl_2/Et_2O yielded orange crystals of **4** (74 mg, 77%). For **3**: ^1H NMR ($CDCl_3$) 5.78 (ddt, 1 H, =CH, J_{HH} = 17, 10, 7 Hz), 5.43 (d, 5 H, C_5H_5, J_{PH} = 4 Hz), 5.07 (br d, 1H, =CH_2, J_{HH} = 17 Hz), 5.04 (br d, 1H, =CH_2, J_{HH} = 10 Hz), 3.87 (d, 9 H, OMe, J_{PH} = 10 Hz), 3.17 (t, 2 H, $C(O)CH_2$, J_{HH} = 7 Hz), 2.19 (dt, 2 H, CH_2CH, J_{HH} = 7, 6 Hz), 1.90 (m, 2 H, CH_2) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) 279.0 (d, C=O, J_{PC} = 13 Hz), 137.1 (=CH), 115.9 (=CH_2),

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96.9 (C_5H_5), 55.1 (OMe), 41.2 [C(O)CH_2], 32.8 (CH_2CH), 24.5 (CH_2) ppm; $^{31}P\{^1H\}$ NMR (C_6D_6) 175.9 ppm; IR (CH_2Cl_2) 1544 cm^{-1} ($\nu_{C=O}$). Anal. Calcd for $C_{14}H_{23}Cl_2O_4PMo$: C, 37.1; H, 5.1; Cl, 15.6. Found C, 37.0; H, 4.9; Cl, 15.7.

Synthesis of (η^5-C_5H_5)Cl{P(OMe)$_3$}Mo{CH_2CH=C-(C_3H_5)CH(CHO)} (5). The cyclopropyl(allyl)carbyne **1b** (152 mg, 0.37 mmol) was dissolved in 1 mL of $CDCl_3$ and left under a N_2 atmosphere in room light for 15 days until no further change was seen in the ^1H NMR. The volatile components including 2-cyclohexenone-5-spirocyclopropane (**2b**) were removed by vacuum transfer, and the residue was taken up in Et_2O (*ca.* 2 mL). The solution was chromatographed on alumina and a purple band eluted using a 9:1 Et_2O/MeOH mixture. Solvent was removed and the resulting oil recrystallized from hexane/Et_2O (4:1) to afford purple microcrystals of **5** (71 mg, 43%). For **5**: ^1H NMR (C_6D_6) 10.22 (d, 1 H, CHO, J_{HH} = 8 Hz), 6.22 (dt, 1 H, =C*H*CH_2Mo, J_{HH} = 7, J_{PH} = 7 Hz), 6.12 (m, 1 H, =CH), 5.23 (br d, 1 H, =CH_2, J_{HH} = 17 Hz), 5.08 (br d, 1 H, =CH_2, J_{HH} = 10 Hz), 4.52 (d, 5 H, C_5H_5, J_{PH} = 2 Hz), 4.06 (d, 1 H, CH_2, J_{HH} = 7 Hz), 4.02 (d, 1 H, CH_2, J_{HH} = 7 Hz), 3.19 (d, 9 H, OMe, J_{PH} = 10 Hz), 2.04 (dd, 1 H, CH_2Mo, J_{HH} = 7, J_{PH} = 3 Hz), 1.86 (br d, 1 H, CHMo, J_{HH} = 8 Hz), 0.28 (dd, 1 H, CH_2Mo, J_{HH} = 7, J_{PH} = 8 Hz), ppm; ^{13}C NMR (C_6D_6) 201.0 (d, CHO, J_{HC} = 173 Hz), 138.1 (d, *C*H=CH_2, J_{HC} = 153 Hz), 130.0 (s, *C*=CH), 116.8 (t, CH=*C*H_2, J_{HC} = 156 Hz), 104.5 (d, C=*C*H, J_{HC} = 163 Hz), 92.8 (dd, C_5H_5, J_{HC} = 176, 8 Hz), 65.1 (dd, CHMo, J_{HC} = 154, 19 Hz), 53.3 (dd, OMe, J_{HC} = 146, J_{PC} = 10 Hz), 44.4 (t, CH_2, J_{HC} = 157 Hz), 38.5 (t, CH_2Mo J_{HC} = 126 Hz) ppm; $^{31}P\{^1H\}$ NMR (C_6D_6) 164.4 ppm; IR (CH_2Cl_2) 1644 cm^{-1} ($\nu_{C=O}$), 2849 cm^{-1} ($\nu_{CH,aldehyde}$); HRMS (EI) *m/z* calcd for M^+ ($C_{16}H_{24}ClO_4PMo$) 444.0155, found 444.0290. Anal. Calcd for $C_{16}H_{24}ClO_4PMo$: C, 43.4; H, 5.5; Cl, 8.0. Found: C, 43.4; H, 5.6; Cl, 7.9.

Photolysis of Carbynes. A typical procedure follows: A 5-mm NMR tube was charged with a solution of **1a** (15 mg, 0.39 mmol) in $CDCl_3$ containing 0.5% TMS (0.8 mL). The solution was irradiated in a Pyrex immersion well with a Hanovia medium-pressure mercury vapor lamp for 3 h. Volatile components of the reaction mixture were removed by vacuum transfer, yielding **2a** in 40% yield as determined by integration against the TMS peak in the ^1H NMR spectrum. Wavelength-dependence studies on **1a** were carried out using a 430-nm Corning 3-73 sharp cut filter.

Photolysis of 1a in the Presence of Base. A solution of **1a** (20 mg, 0.53 mmol) in $CDCl_3$ containing 0.5% TMS (1.2 mL) was prepared and split into two parts, each sample being placed in a 5-mm NMR tube. Excess 2,6-di-*tert*-butylpyridine (2 equiv) was added to one tube. The two samples were photolyzed for a total of 4 h with monitoring by ^1H NMR at hourly intervals. No change in rate of reaction or final yield was observed between the two samples. A similar procedure was followed using proton sponge as a base.

Thermal Decomposition of Carbynes. A typical procedure follows: A 5-mm NMR tube was charged with a solution of **1a** (20 mg, 0.53 mmol) in $CDCl_3$ containing 0.5% TMS (0.8 mL). The solution was left under an oxygen-free atmosphere for 48 h. Volatile components of the reaction mixture were removed by vacuum transfer, yielding **2a** in 55% yield and **3a** in 7% yield as determined by integration against the TMS peak in the ^1H NMR spectrum.

Formation of 2-Cyclohexenone-5-spirocyclopropane (2b). A solution of **1b** in $CDCl_3$ was allowed to decompose in room light for 4 days until no starting material could be detected by ^1H NMR, and then the organic fraction containing **2b** was vacuum transferred. For **2b**: ^1H NMR (C_6D_6) 6.99 (dt, 1 H, =CH, J_{HH} = 10, 4 Hz), 6.09 (dt, 1 H, =CH, J_{HH} = 10, 2 Hz), 2.26 (s, 2 H, CH_2CO), 2.22 (d, 1 H, =CHCH_2, J_{HH} = 10, 2 Hz), 0.63, 0.41 (m, 2 H, CH_2CH_2); GC/MS *m/z* 122 (M^+), 123 [$(M + 1)^+$].

Deuterium-Labeling Experiments. Allyl alcohol-1-d_2 was prepared by treatment of acryloyl chloride with $LiAlD_4$[21] and converted to a 79:21 mixture of CH_2=$CHCD_2Br$ and CD_2=$CHCH_2Br$ by the method described for unlabeled material.[22] Synthesis of **1a**-d_2 as described above for **1a** afforded an 85:15 mixture of **1a**-(**3,3**-d_2) and **1a**-(***5,5***-d_2). For the mixture: ^1H NMR (C_6D_6) 5.85 (m, 1.00 H, =CH), 4.98 (m, 1.70 H, =CH_2), 2.33 (m, 2.30 H, CH_2CH_2) ppm. Photolysis in $CHCl_3$ yielded an 83:17 mixture of **2a**-(***4,6***-d_2) and **2a**-(***2,4***-d_2). For the mixture: ^1H NMR (C_6D_6) 6.15 (1.00 H, H3), 5.92 (0.83 H, H2), 2.04 (1.16 H, H6), 1.48 (0.98 H, H4), 1.22 (2.03 H, H5) ppm; GC/MS *m/z* [rel intensity] 98 [M^+, 5195], 99 [$(M + 1)^+$, 376]. For **2a**-d_2, the calculated intensity for $(M + 1)^+$ is 6.6% of M^+.

Cyclic Voltammetry of 1a. Cyclic voltammetry experiments were carried out in CH_2Cl_2 using a Princeton Applied Research Model 273A potentiostat in conjunction with a three-electrode cell. The working electrode was a platinum bead, the auxiliary electrode a platinum wire, and the reference an Ag/Ag^+ electrode in CH_2Cl_2 separated from the test solution by a fine porosity frit. Solutions were 0.5×10^{-3} M in **1a** and 0.1 M in [^{n}Bu$_4$N]Cl as supporting electrolyte.

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Supplementary Material Available: ^1H NMR spectra for the complexes **1a–g** (18 pages). Ordering information is given on any current masthead page.

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