

Formation of α, ω -dienes upon photooxidation of alkenyl carbyne complexes

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Abstract

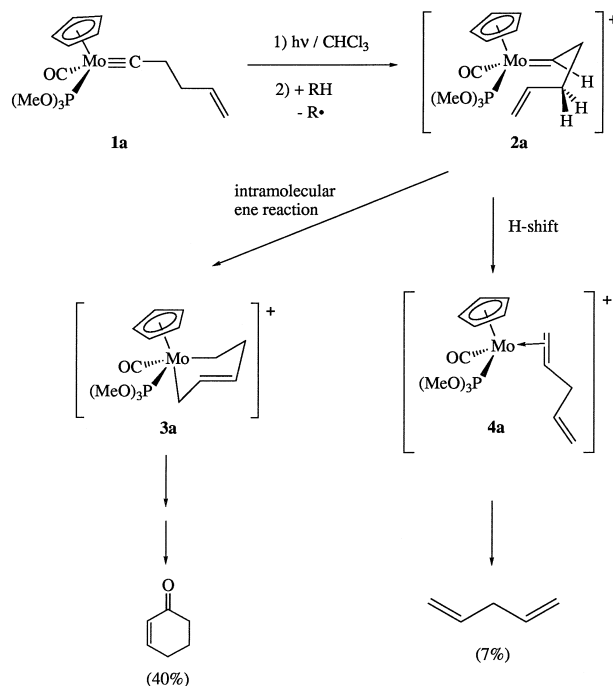
Photolysis of the alkenyl carbyne complexes $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\{\text{P}(\text{OMe})_3\}\text{Mo} \equiv \text{CCH}_2(\text{CH}_2)_n\text{CH}=\text{CH}_2$ ($n = 2$ (**1b**), 3 (**1c**) and 4 (**1d**)) in CHCl_3 results in the formation of the corresponding α, ω -dienes $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{CH}=\text{CH}_2$. Also produced are the dichloromolybdenum carbynes $(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2\{\text{P}(\text{OMe})_3\}\text{Mo} \equiv \text{C-CH}_2(\text{CH}_2)_n\text{CH}=\text{CH}_2$ ($n = 2$ (**8b**), 3 (**8c**), and 4 (**8d**)). Both sets of products arise following the generation of highly reactive 17-electron complexes via photochemical electron transfer from **1b–d** to the solvent. These radical cations either undergo H-abstraction at the carbyne carbon followed by H-shift to form the dienes or they undergo exchange of Cl^- for the CO ligand and Cl-abstraction at the metal to yield **8b–d**. The product ratios reflect partitioning of the 17-electron species between reactivity at the metal center vs. the carbyne carbon. © 1998 Elsevier Science S.A.

Keywords: Metal carbyne; Photooxidation; Metal radical; 17-Electron complex

1. Introduction

We previously reported that photolysis of the butenyl carbyne complex $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\{\text{P}(\text{OMe})_3\}\text{Mo} \equiv \text{C-CH}_2\text{CH}_2\text{CH}=\text{CH}_2$ (**1a**) in CHCl_3 resulted in the formation of cyclohexenone (Scheme 1) [1]. Mechanistic studies on cyclohexenone formation were consistent with a pathway initiated by electron transfer from the carbyne complex to yield a radical cation. Hydrogen abstraction at the carbyne carbon then generates a cationic carbene (**2a**) that undergoes an intramolecular ene reaction to form the metallacycle **3a** [1]. Next, CO insertion into the metallacycle ring of **3a**, reductive elimination and hydride shift yield cyclohexenone.

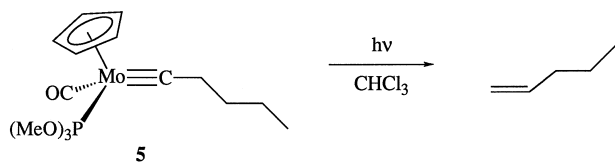
The minor organic product of this reaction is 1,4-pentadiene (Scheme 1). The diene undoubtedly arises from an alternative pathway for carbene **2a**. Hydride shift from C2 to C1 of the carbene ligand would yield the η^2 -diene complex **4a**, which would be prone to diene loss under oxidative conditions. A related process has



Scheme 1.

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been observed in complexes such as butyl carbyne **5** (Scheme 2) [2].



Scheme 2.

Formation of cyclohexenone from the butenyl carbyne **1a** suggested that other alkenyl carbynes might also form cyclic products via the mechanism in Scheme 1. For example, if the homologous series ($\eta^5\text{-C}_5\text{H}_5$)(CO){P(OMe)₃}Mo $\equiv$ CCH₂(CH₂)_nCH=CH₂ ($n = 2$ (**1b**), 3 (**1c**), and 4 (**1d**)) were to undergo the same sequence of reactions as **1a**, the products would be cycloheptenone, cyclooctenone and cyclononenone, respectively.

The crucial step in the Scheme 1 mechanism is the intramolecular ene reaction **2a** $\rightarrow$ **3a**, in which the carbene moiety functions as the enophile. This is an extremely unusual mode of metal participation in the ene reaction. In the extensively studied ‘metallo-ene reaction,’ the metal either serves as the migrating group [3] or catalyzes the ene reaction in an organic substrate [4].

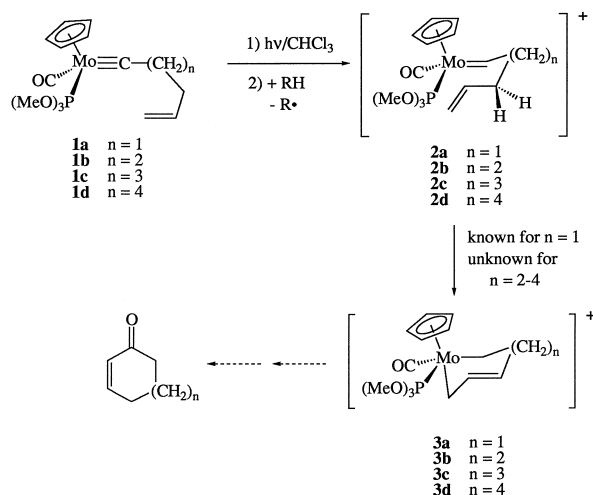
Three types of intramolecular ene reaction have been classified according to the pattern of connectivity between ene and enophile [5]. The conversion of **2a** to **3a** is an example of the type III ene reaction (Scheme 3), in which the enophile is attached to the allylic terminus of the ene.

Type III intramolecular ene reactions are unusual, but known examples in purely organic systems include ring closure of α,ω -dienes to yield 7-, 8-, and 9-membered rings [5,6]. If the ring size dependence of the organometallic system were similar, the homologous alkenyl carbynes **1b–d** could access the 7-, 8-, and 9-membered metallacycles **3b–d**, respectively. Completion of the Scheme 1 pathway would then yield larger cycloalkenones (Scheme 4).

This work is an examination of the photooxidation of the alkenyl carbynes **1b–d**. Although the chemistry of these complexes exhibits significant differences from that of **1a**, the results lead to significant insight into the radical cations arising from one-electron oxidation of metal carbynes.



Scheme 3.



Scheme 4.

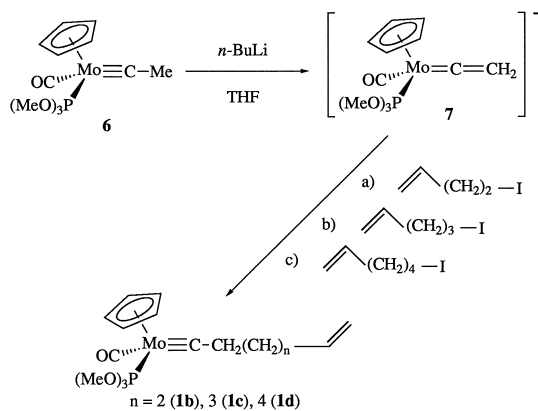
2. Results and discussion

2.1. Synthesis of **1b–d**

The alkenyl carbynes ($\eta^5\text{-C}_5\text{H}_5$)(CO){P(OMe)₃}Mo $\equiv$ CCH₂(CH₂)_nCH=CH₂ ($n = 2$ (**1b**), 3 (**1c**) and 4 (**1d**)) were synthesized by a deprotonation/alkylation strategy first reported by Green and Templeton [7]. Deprotonation of methyl carbyne **6** with ⁿBuLi and subsequent alkylation of the resulting vinylidene anion with the alkenyl iodides I(CH₂)_nCH=CH₂ ($n = 2-4$) yielded the carbyne complexes **1b–d** (Scheme 5). In order to obtain good yields of pure products, care must be taken to ensure that the alkenyl iodides are free of protic impurities. In the presence of proton sources, reprotonation of the vinylidene anion **7** results in regeneration of methyl carbyne **6** which is virtually inseparable from the alkylated products. If the amount of **6** in the reaction mixtures is minimal, **1b–d** can be purified by chromatography on neutral alumina. The pure carbyne complexes **1b–d** are yellow oils at room temperature and are thermally sensitive, thus requiring storage in dry ether at -40°C to avoid decomposition.

2.2. Photooxidation of **1b–d**

Photolysis of **1b–d** resulted in the production of both organic and organometallic products. In order to identify the organic products, GC and ¹H-NMR data for the photolysis mixtures were compared with those from corresponding authentic samples of the anticipated enone and diene products. However, the GC and ¹H-NMR data for the products from **1b–d** were not consistent with the presence of enones. Instead, the dienes CH₂=CH(CH₂)_nCH=CH₂ were the only identifiable organic products that were derived from the original



Scheme 5.

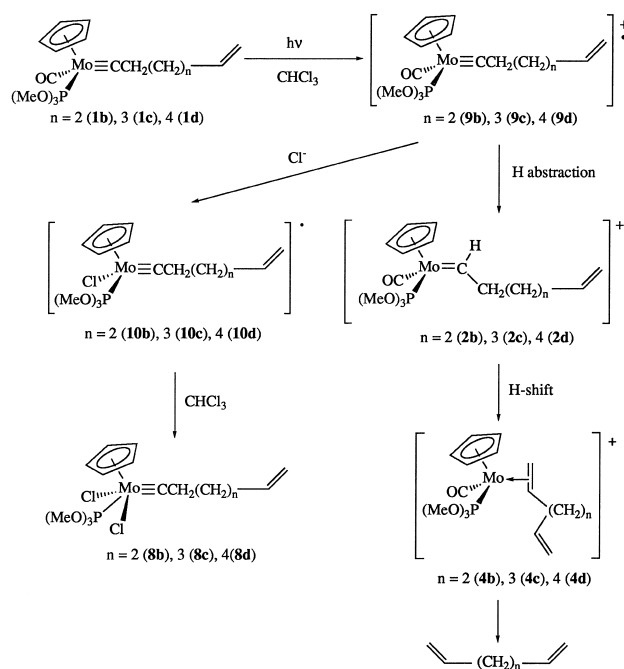
carbyne substituents. They were accompanied by the dichloromolybdenum carbynes **8b–d** (Scheme 6). Carbynes **8b–d** were identified by comparison to ^1H -NMR and ^{31}P -NMR spectra of authentic samples generated by reaction of the alkenyl carbynes **1b–d** with PCl_5 . Owing to the lability of **8b–d**, pure samples could not be isolated. However, the spectral data were in strong agreement with the data from other $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\{\text{P}(\text{OMe})_3\}\text{Mo}\equiv\text{C-R}$ complexes [2], including the 1-methylcyclopropyl derivative, for which a crystal structure was obtained [8].

The photooxidation of $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\{\text{P}(\text{OMe})_3\}\text{Mo}\equiv\text{C-CH}_2(\text{CH}_2)_2\text{CH=CH}_2$ (**1b**) was carried out by irradiation in CDCl_3 at 0°C . During the photolysis, the extent of starting material loss was monitored by ^1H -NMR. At about half conversion of **1b**, 1,5-hexadiene had been formed in 72% yield as determined by GC analysis. Integration of the ^1H -NMR spectrum of the reaction mixture indicated a diene yield of 73%, in excellent agreement with the GC value. The corresponding dichloromolybdenum carbyne complex **8b** was formed in 17% yield as determined by integration of the ^1H -NMR spectrum. The yields are reported at half-conversion of the carbyne because both the dichloromolybdenum carbyne **8b** and 1,5-hexadiene are sensitive to the photolysis reaction conditions. For example, at 33% conversion, the carbyne **1b** had produced the dichloromolybdenum carbyne **8b** in 25% overall yield. By the time 47% conversion of **1b** had been reached, the yield of **8b** had dropped to 17%. The carbyne **1c** was oxidized under the same conditions to form 1,6-heptadiene in 72% yield and the dichloromolybdenum carbyne **8c** in 21% yield as determined by integration of the ^1H -NMR spectrum of the reaction mixture. Likewise, **1d** formed 1,7-octadiene in 67% yield and **8d** in 17% yield. The presence of methyl chloride was also observed in all of the reaction mixtures by ^1H -NMR. Methyl chloride has been detected in previous reactions of related complexes and is a product of Arbusov reaction of the $\text{P}(\text{OMe})_3$ ligands [9].

2.3. Mechanistic considerations

Formation of the diene products upon photooxidation of the alkenyl carbynes **1b–d** has precedent in the formation of 1,4-pentadiene as a minor product from the photolysis of the butenyl carbyne **1a** in CHCl_3 (Scheme 1 and Scheme 2). Prior mechanistic studies on the formation of organic products upon photooxidation of metal carbynes are consistent with single electron transfer from the carbyne excited state to the solvent as the first step on the pathway (Scheme 6) [10]. Next, the 17-electron radical cation **9** abstracts hydrogen from the reaction medium to form the cationic carbene complex **2** [2]. Diene formation results from [1,2]-H-shift in the intermediate **2** to produce the η^2 -diene complex **4**, in a process related to Wagner–Meerwein shifts in organic carbocations. Such rearrangements have previously been observed in electrophilic carbene complexes [11]. Under the oxidative conditions of the photolysis, the η^2 -diene complex **4** would be prone to loss of diene to yield the free organic product.

In the chemistry of butenyl carbyne **1a** (Scheme 1), the fate of cationic carbene complex **2a** determines the partitioning between diene and cycloalkenone products. Although enone formation predominates from butenyl carbyne **1a**, the reaction fails for the longer alkenyl chains derived from **1b–d**. Formation of cycloalkenones from **1b–d** would require intramolecular ene reactions from **2b–d**. Although this process is favorable for **2a**, which produces the 6-membered metallacycle **3a**, the



Scheme 6.

ene reaction is slower for systems which would form larger rings. In these cases, the ene reaction cannot compete with the fast [1,2]-H shift that leads to diene products.

Formation of the dichloromolybdenum carbynes **8b–d** also has precedent. Dichloromolybdenum carbynes are minor products of most photolyses of similar carbynes in CHCl_3 and result from reactivity of the initial 17-electron radical cation species **9** at the metal center (Scheme 6). Rapid ligand exchange and halogen atom abstraction are characteristic reactions of metal-centered radicals [12–15]. If **9** undergoes these processes instead of H-abstraction at the carbyne carbon, dichloromolybdenum carbyne **8** is the final product. It arises from chloride exchange at the metal center of **9** to yield the radical compound **10** which undergoes halogen abstraction to form **8**. Although reversing the order of the ligand exchange and halogen abstraction steps would yield the same product, consideration of the relative rates of these processes in other metal radical systems [13] suggests the sequence shown in Scheme 6.

The formation of both the dienes and the dichloromolybdenum carbynes stems from partitioning of the 17-electron radical cation species **9b–d** between ‘metal radical’ and ‘organic radical’ behavior. Which product is produced from this common intermediate depends on the reactivity of the metal toward ligand exchange with Cl^- vs. the tendency of the carbyne carbon to abstract hydrogen. Because at least 85% of the starting material can be accounted for in the form of organic dienes or the dichloromolybdenum carbynes, these product ratios allow an estimate of the preference for **9b–d** to undergo reaction at the metal vs. the carbyne carbon. Under these reaction conditions, the dienes are produced preferentially over the dichloromolybdenum carbynes by a factor of about 4 to 1. Thus, hydrogen abstraction at the carbyne carbon is faster than ligand exchange at the metal center for the radical cations **9b–d**, which have sterically unhindered 1° alkyl substituents on the carbyne ligands. These results can be contrasted with carbynes bearing 3° substituents, for which H-abstraction is significantly slowed by steric hindrance and Cl^- exchange to yield dichloromolybdenum carbynes dominates the reactivity [2,8].

2.4. Conclusion

Although the photooxidation of the alkenyl carbynes **1b–d** did not produce cycloalkenones, this chemistry provides an interesting opportunity to assess the reactivity of the 17-electron radical cation species that are produced upon photooxidation of metal carbynes. The organic dienes and the dichloromolybdenum carbynes produced in these photooxidations result from reactivity of those radicals at the carbyne carbon and the metal respectively. The organic product is favored over the

organometallic one by about 4:1 under these reaction conditions. The fact that both products are produced provides a rare example in which both metal and carbon radical reaction manifolds can be accessed from the same species.

3. Experimental section

Standard inert atmosphere techniques were used throughout. Hexane, petroleum ether, chloroform, and methylene chloride were distilled from CaH_2 . Diethyl ether and THF were distilled from $\text{Na}/\text{Ph}_2\text{CO}$. All NMR solvents were degassed by three freeze–pump–thaw cycles. Benzene- d_6 was vacuum transferred from $\text{Na}/\text{Ph}_2\text{CO}$. CDCl_3 was stored over 3-Å molecular sieves. 4-Iodo-1-butene, 5-iodo-1-pentene and 6-iodo-1-hexene were prepared from the corresponding tosylates using the Finkelstein reaction [16]. Authentic samples of 1,5-hexadiene, 1,6-heptadiene, 1,7-octadiene, and 2-cyclohepten-1-one were purchased from Aldrich. $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\{\text{P}(\text{OMe})_3\}\text{Mo} \equiv \text{CCH}_3$ (**6**) was synthesized as reported previously [1,17]. 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 Gemini-300 and VXR-300 NMR spectrometers. IR spectra were recorded on a Perkin–Elmer 1600 spectrometer. GC was performed on an HP5890 chromatograph containing a 30 m $\times$ 0.75 mm column of SPB-20 on fused silica. High resolution mass spectrometry was performed by the University of Florida analytical service.

Column chromatography was performed at 0°C on neutral alumina (Brockmann Activity 1). All photolyses were performed at 0°C and analyzed by ^1H -NMR spectroscopy using decane as an internal standard. Irradiation was done with a Hanovia medium pressure mercury vapor lamp in a Pyrex immersion well.

3.1. Synthesis of alkenyl carbyne complexes

3.1.1. $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\{\text{P}(\text{OMe})_3\}\text{Mo} \equiv \text{CCH}_2(\text{CH}_2)_2\text{CH}=\text{CH}_2$ (**1b**)

Methyl carbyne **6** (175 mg, 0.514 mmol) was dissolved in 15 ml of THF and allowed to react with a 2.3 M hexane solution of *n*-butyllithium (335 μl , 0.771 mmol) at -78°C . After 25 min, 4-iodo-1-butene (374 mg, 2.05 mmol) was added. The solution was allowed to react for 15 min at -78°C and then warmed to room temperature. Following removal of solvent in vacuo, the residue was extracted with ether and chromatographed on neutral alumina using 4:1 hexane/ether as eluent followed by 1:1 hexane/ether after the 4-iodo-1-butene was eluted. The product **1b** was obtained as a yellow oil (145 mg, 71.5%) after removal of solvent. For **1b**:

$^1\text{H-NMR}$ (C_6D_6) δ 5.71 (m, 1H, =CH), 5.26 (d, 5H, C_5H_5 , $J_{\text{PH}} = 1$ Hz), 4.99 (m, 2H, =CH₂), 3.38 (d, 9H, OMe, $J_{\text{PH}} = 12$ Hz), 2.27 (m, 2H, CH₂), 2.10 (q, 2H, CH₂), 1.63 (p, 2H, CH₂) ppm; $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (C_6D_6) δ 315.9 (d, Mo $\equiv$ C, $J_{\text{PC}} = 28$ Hz), 241.8 (d, CO, $J_{\text{PC}} = 18$ Hz), 138.5 (=CH), 115.1 (=CH₂), 91.0 (C_5H_5), 51.2 (OMe), 49.4 (Mo $\equiv$ CC), 33.3, 27.9 ppm; $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$ (CDCl_3) δ 203.8 ppm; IR (CH_2Cl_2) 1901 cm^{-1} (ν_{CO}); HRMS (FAB) m/z calcd. for M^+ ($\text{C}_{15}\text{H}_{23}^{98}\text{MoO}_4\text{P}$) 396.0392, found 396.0387.

3.1.2. $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\{\text{P}(\text{OMe})_3\}\text{Mo} \equiv \text{C-CH}_2(\text{CH}_2)_3\text{CH=CH}_2$ (**1c**)

Methyl carbyne **6** (232 mg, 0.682 mmol) was dissolved in 15 ml of THF and allowed to react with a 2.3 M hexane solution of *n*-butyllithium (445 μl , 1.02 mmol) at -78°C . After 25 min, 5-iodo-1-pentene (535 mg, 2.73 mmol) was added. The solution was allowed to react for 15 min at -78°C and then warmed to room temperature. Following removal of solvent in vacuo, the residue was extracted with ether and then chromatographed on neutral alumina using 4:1 hexane/ether as eluent followed by 1:1 hexane/ether after the 5-iodo-1-pentene was eluted. The product **1c** was obtained as a yellow oil (198 mg, 71.1%) after removal of solvent. For **1c**: $^1\text{H-NMR}$ (C_6D_6) δ 5.76 (m, 1H, =CH), 5.27 (d, 5H, C_5H_5 , $J_{\text{PH}} = 1$ Hz), 4.99 (m, 2H, =CH₂), 3.39 (d, 9H, OMe, $J_{\text{PH}} = 12$ Hz), 2.27 (m, 2H, CH₂), 1.94 (q, 2H, CH₂), 1.56 (p, 2H, CH₂), 1.43 (p, 2H, CH₂) ppm; $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (C_6D_6) δ 316.2 (d, Mo $\equiv$ C, $J_{\text{PC}} = 28$ Hz), 241.7 (d, CO, $J_{\text{PC}} = 19$ Hz), 138.9 (=CH), 114.6 (=CH₂), 91.0 (C_5H_5), 51.2 (OMe), 49.9 (Mo $\equiv$ CC), 33.8, 28.5, and 28.1 ppm; $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$ (CDCl_3) δ 203.8 ppm; IR (CH_2Cl_2) 1900 cm^{-1} (ν_{CO}); HRMS (FAB) m/z calcd. for M^+ ($\text{C}_{16}\text{H}_{25}^{98}\text{MoO}_4\text{P}$) 410.0549, found 410.0557.

3.1.3. $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\{\text{P}(\text{OMe})_3\}\text{Mo} \equiv \text{C-CH}_2(\text{CH}_2)_4\text{CH=CH}_2$ (**1d**)

Methyl carbyne **6** (180 mg, 0.529 mmol) was dissolved in 15 ml of THF and allowed to react with a 2.3 M hexane solution of *n*-butyllithium (346 μl , 0.795 mmol) at -78°C . After 25 min, 6-iodo-1-hexene (446 mg, 2.12 mmol) was added. The solution was allowed to react for 15 min at -78°C and then warmed to room temperature. Following removal of solvent in vacuo, the residue was extracted with ether and then chromatographed on neutral alumina using 4:1 hexane/ether as eluent followed by 1:1 hexane/ether after the 6-iodo-1-hexene had eluted. The product **1d** was obtained as a yellow oil (169 mg, 75.6%) after removal of solvent. For **1d**: $^1\text{H-NMR}$ (C_6D_6) δ 5.76 (m, 1H, =CH), 5.28 (d, 5H, C_5H_5 , $J_{\text{PH}} = 1$ Hz), 5.00 (m, 2H, =CH₂), 3.40 (d, 9H, OMe, $J_{\text{PH}} = 12$ Hz), 2.27 (m, 2H, CH₂), 1.97 (q, 2H, CH₂), 1.57 (p, 2H, CH₂), 1.30 (m, 4H, CH₂) ppm; $^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (C_6D_6) δ 316.4 (d, Mo $\equiv$ C, J_{PC}

= 27 Hz), 241.7 (d, CO, $J_{\text{PC}} = 20$ Hz), 139.1 (=CH), 114.5 (=CH₂), 91.0 (C_5H_5), 51.2 (OMe), 50.0 (Mo $\equiv$ CC), 34.0, 31.9, 29.0, 28.5 ppm; $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$ (CDCl_3) δ 203.9 ppm; IR (CH_2Cl_2) 1900 cm^{-1} (ν_{CO}); HRMS (FAB) m/z calcd. for $(\text{M} + \text{H})^+$ ($\text{C}_{17}\text{H}_{28}^{98}\text{MoO}_4\text{P}$) 425.0784, found 425.0799.

3.2. Synthesis of dichloromolybdenum carbynes

3.2.1. $(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2\{\text{P}(\text{OMe})_3\}\text{Mo} \equiv \text{CCH}_2(\text{CH}_2)_2\text{CH=CH}_2$ (**8b**)

Alkenyl carbyne **1b** (38.5 mg, 0.0976 mmol) was dissolved in 0.5 ml CDCl_3 and allowed to react with PCl_5 (20.0 mg, 0.0976 mmol) at 0°C . The solution reacted for 1 min producing effervescence and was characterized by NMR spectroscopy without further purification. The resulting $^1\text{H-NMR}$ spectrum indicated a mixture of compounds containing the dichloromolybdenum carbyne as the major component. Owing to the lability of **8b**, it could not be purified further. The NMR signals of **8b** were identified by comparison to the spectral data of related compounds [2,8]. For **8b**: $^1\text{H-NMR}$ (CDCl_3) δ 5.95 (d, 5H, C_5H_5 , $J_{\text{PH}} = 3$ Hz), 5.78 (m, 1H, =CH), 5.01 (m, 2H, =CH₂), 3.92 (d, 9H, OMe, $J_{\text{PH}} = 11$ Hz), 3.18 (m, 2H, CH₂) ppm; $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$ (CDCl_3) δ 144.2 ppm.

3.2.2. $(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2\{\text{P}(\text{OMe})_3\}\text{Mo} \equiv \text{C-CH}_2(\text{CH}_2)_3\text{CH=CH}_2$ (**8c**)

Alkenyl carbyne **1c** (11.5 mg, 0.0281 mmol) was dissolved in 0.5 ml CDCl_3 and allowed to react with PCl_5 (20 mg, 0.0281 mmol) at 0°C . The solution reacted for 1 min producing effervescence and was characterized by NMR spectroscopy without further purification. The resulting $^1\text{H-NMR}$ spectrum indicated a mixture of compounds containing the dichloromolybdenum carbyne as the major component. Owing to the lability of **8c**, it could not be purified further. The NMR signals of **8c** were identified by comparison to the spectral data of related compounds [2,8]. For **8c**: $^1\text{H-NMR}$ (CDCl_3) δ 5.95 (d, 5H, C_5H_5 , $J_{\text{PH}} = 3$ Hz), 5.79 (m, 1H, =CH), 4.97 (m, 2H, =CH₂), 3.91 (d, 9H, OMe, $J_{\text{PH}} = 11$ Hz), 3.17 (m, 2H, CH₂) ppm; $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$ (CDCl_3) δ 144.3 ppm.

3.2.3. $(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2\{\text{P}(\text{OMe})_3\}\text{Mo} \equiv \text{C-CH}_2(\text{CH}_2)_4\text{CH=CH}_2$ (**8d**)

Alkenyl carbyne **1d** (33.5 mg, 0.0793 mmol) was dissolved in 0.5 ml CDCl_3 and allowed to react with PCl_5 (16.5 mg, 0.0793 mmol) at 0°C . The solution reacted for 1 min producing effervescence and was characterized by NMR spectroscopy without further purification. The resulting $^1\text{H-NMR}$ spectrum indicated a mixture of compounds containing the dichloromolybdenum carbyne as the major component. Owing to the lability of **8d**, it could not be purified further. The NMR

signals of **8d** were identified by comparison to the spectral data of related compounds [2,8]. For **8d**: $^1\text{H-NMR}$ (CDCl_3) δ 5.94 (d, 5H, C_5H_5 , $J_{\text{PH}} = 3$ Hz), 5.79 (m, 1H, $=\text{CH}$), 4.95 (m, 2H, $=\text{CH}_2$), 3.91 (d, 9H, OMe, $J_{\text{PH}} = 11$ Hz), 3.16 (m, 2H, CH_2) ppm; $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3) δ 144.3 ppm.

3.3. Photooxidation of alkenyl carbynes

3.3.1. Photooxidation of $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\{\text{P}(\text{OMe})_3\}\text{Mo} \equiv \text{CCH}_2(\text{CH}_2)_2\text{CH}=\text{CH}_2$ (**1b**)

Carbyne **1b** (60 mg) was dissolved in 1 ml of CDCl_3 , and 1.6 μl of decane was added as the internal standard for GC analysis. An NMR tube was charged with this mixture. The reaction mixture was photolyzed at 0°C while the progress of the reaction was monitored by $^1\text{H-NMR}$. The photolysis was stopped at approximately half conversion of **1b**. 1,5-hexadiene was formed in 72% yield as determined by GC analysis. Integration of the $^1\text{H-NMR}$ spectrum led to a value of 73% yield. The corresponding dichloromolybdenum carbyne complex $(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2\{\text{P}(\text{OMe})_3\}\text{Mo} \equiv \text{CCH}_2(\text{CH}_2)_2\text{CH}=\text{CH}_2$ (**8b**) was formed in 17% yield as determined by integration of the $^1\text{H-NMR}$ spectrum.

3.3.2. Photooxidation of $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\{\text{P}(\text{OMe})_3\}\text{Mo} \equiv \text{C-CH}_2(\text{CH}_2)_3\text{CH}=\text{CH}_2$ (**1c**)

When photolyzed as described for **1b**, carbyne **1c** formed 1,6-heptadiene in 72% yield and the dichloromolybdenum carbyne complex $(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2\{\text{P}(\text{OMe})_3\}\text{Mo} \equiv \text{CCH}_2(\text{CH}_2)_3\text{CH}=\text{CH}_2$ (**8c**) in 21% yield as determined by integration of the $^1\text{H-NMR}$ spectrum.

3.3.3. Photooxidation of $(\eta^5\text{-C}_5\text{H}_5)(\text{CO})\{\text{P}(\text{OMe})_3\}\text{Mo} \equiv \text{C-CH}_2(\text{CH}_2)_4\text{CH}=\text{CH}_2$ (**1d**)

When photolyzed as described for **1b**, carbyne **1d** formed 1,7-octadiene in 67% yield and the dichloromolybdenum carbyne complex $(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2\{\text{P}(\text{OMe})_3\}\text{Mo} \equiv \text{C-CH}_2(\text{CH}_2)_4\text{CH}=\text{CH}_2$ (**8d**) in 17% yield as determined by integration of the $^1\text{H-NMR}$ spectrum.

3.4. GC analysis of reaction products from **1b**

A standard calibration curve was prepared for obtaining the concentration of the diene product from the area obtained from the GC integration. The reaction mixture was prepared as described above. Before starting the photolysis, GC was performed on the reaction mixture. As indicated by the GC, the diene product is detectable before the photolysis takes place. This, coupled with the absence of diene peaks in the starting $^1\text{H-NMR}$ indicates that the diene product is formed from **1b** in the injection port of the GC. Hence, **1b** had to be removed from the reaction mixture to obtain accurate yields of

diene product at half conversion. In order to remove the starting alkenyl carbyne **1b**, the final reaction mixture was cannulated onto a pipette column of alumina under N_2 . The organics were rinsed off the column with pentane into a 5-ml volumetric flask. The flask was filled to the line with pentane and mixed well. The yield of the diene was calculated from the integration of the GC trace of the resulting mixture.

The yield of the dienes was determined by integration of the $^1\text{H-NMR}$ spectrum and compared to the GC analysis. Given the close agreement of the GC and NMR values for diene yield from **1b** and the difficulty of quantitatively separating the carbyne complexes from the organic products, only the yields based on the $^1\text{H-NMR}$ integration are reported for the photooxidation of the alkenyl carbynes **1c–d**.

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