Formation of Pentadienal Complexes upon Protonation of Molybdenum (1-Alkylcyclopropyl)carbynes. Electronic Effects on Reductive Elimination versus β-Hydrogen Elimination in Metallacyclohexenones

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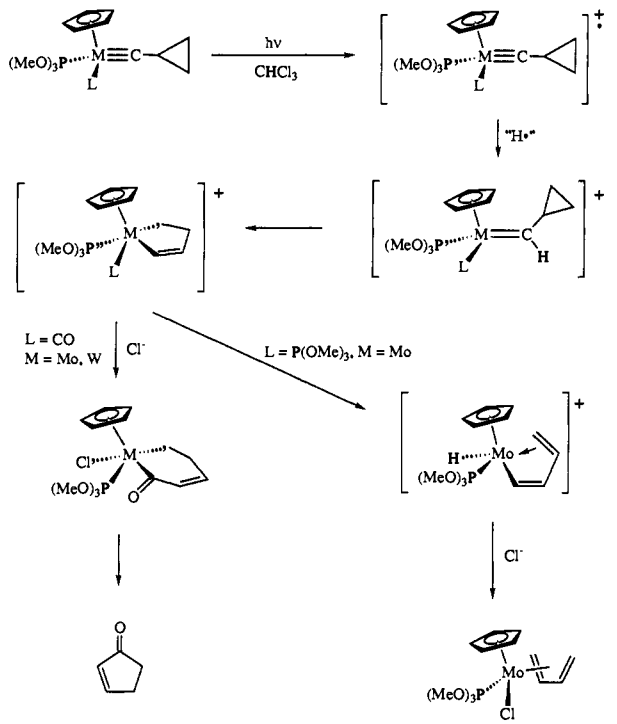
Abstract: The (1-alkylcyclopropyl)carbynes $(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}Mo{\equiv}CC(R)CH_2CH_2$ [R = $CH_2CH{=}CH_2$ (**3a**), CH_3 (**3b**), SCH_3 (**3c**), $CH_2C_6H_5$ (**3d**)] have been prepared and characterized. Reaction of **3a–d** with $HCl{\cdot}Et_2O$ yields mixtures of the η^4-2,4-pentadien-1-al complexes $(\eta^5\text{-}C_5H_5)Cl\{P(OMe)_3\}Mo\{CH_2{=}CHC(R){=}CH(CHO)\}$ (**4a–d**) and the η^2-acyl complexes $(\eta^5\text{-}C_5H_5)Cl_2\{P(OMe)_3\}Mo\{\eta^2\text{-}C(O)CH_2C(R)CH_2CH_2\}$ [R = CH_3 (**5a**), SCH_3 (**5b**)]. Only one isomer of **4a–d** forms initially, but over a period of days, there is interconversion of a series of isomers. Formation of dienal complexes **4a–d** when R is an electron-donating group contrasts with the previously observed formation of cyclopentenones from derivatives of **3** where R = H, COR′, and CO_2R'. These results are consistent with an electronic effect on the partitioning between reductive elimination and β-hydrogen elimination in a metallacyclohexenone intermediate. Complexes **3b** and **3c** oxidize slowly in $CHCl_3$ to give the dichloro derivatives $(\eta^5\text{-}C_5H_5)Cl_2\{P(OMe)_3\}Mo{\equiv}CC(R)CH_2CH_2$ [R = CH_3 (**6a**), SCH_3 (**6b**)]. The structures of **4b** and **6a** have been determined by X-ray diffraction: (**4b**) monoclinic, $P2_1/n$, a = 10.188(1) Å, b = 11.666(1) Å, c = 14.128(2) Å, β = 90.73(1)°, V = 1679.0(8) Å^3, Z = 4, R = 4.33, R_w = 5.09% for 2826 reflections $I > 3\sigma(I)$; (**6a**) orthorhombic, $P2_12_12_1$, a = 9.480(1) Å, b = 13.383(1) Å, c = 13.585(1) Å, V = 1723.5(3) Å^3, Z = 4, R = 4.41, R_w = 4.96% for 2024 reflections $I > 2\sigma(I)$.

Introduction

We recently reported that photolysis of the cyclopropylcarbynes $(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}M{\equiv}C(c\text{-}C_3H_5)$ [M = Mo (**1a**), W (**1b**)] in chlorinated solvents results in ring expansion and carbonyl insertion to yield cyclopentenone (Scheme 1).[2a] The unusual nature of this reaction has led us to investigate its generality under differing conditions and with a wide range of substituents.[2b,c] We have demonstrated that cyclopentenones are not only produced from cyclopropylcarbynes upon irradiation, but in certain cases can also be obtained upon protonation with HCl, or when the carbynes are allowed to decompose thermally in $CHCl_3$. These alternative methods of generation do, however, tend to give different product mixes.[2b,4] When protonation affords cationic carbene species by electrophilic attack on the carbyne carbon, it gives an independent means of generating a common intermediate with the photooxidation pathway. Formation of cyclopentenone upon thermal decomposition may arise either as a result of protonation as HCl is generated in the chloroform[5] or by thermal electron transfer and hydrogen abstraction in a manner analogous to the photochemical reaction.

The effect of substitution at different positions of the cyclopropyl ring has also been investigated. The photolytic preparation of cyclopentenones is tolerant of alkyl and aryl substituents at the 2- and/or 3-positions of the cyclopropyl ring. However, substitution at C1 can cause the chemistry to follow different pathways. Carbynes with electron-withdrawing acyl substituents at the 1-position of the cyclopropyl ring (**2a–f**) also yield the expected 3-substituted cyclopentenones. In this case, however, a competing

Scheme 1



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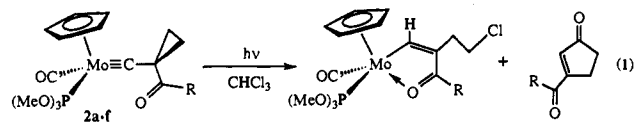
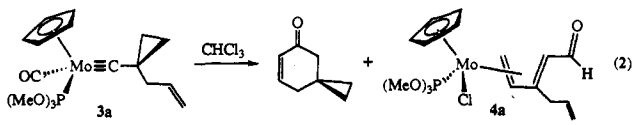
reaction is observed whereby the electron-deficient cyclopropyl ring is opened by nucleophilic attack of chloride, and the acyl oxygen coordinates to the metal to yield an oxametallacycle (eq 1).[2c]



R = Me (2a) OMe (2d)
c-C_3H_5 (2b) OEt (2e)
Ph (2c) OPh (2f)

The possibility that electron-donating substituents at the 1-position of the cyclopropyl ring might also lead to different products was first suggested by recent work on the (1-allylcyclopropyl)carbyne **3a**, which contains both butenyl and cyclopropyl groups. Upon thermal decomposition of **3a** in chloroform, a small amount of 2-cyclohexenonespiro-5′-cyclopropane was observed, arising from cyclization of the butenyl moiety,[4] but the major product was the 3-allyl-2,4-pentadien-1-al complex **4a** (eq 2). No 3-allylcyclopentenone was observed.



Compound **4a** is the result of ring opening of the cyclopropyl group as for the cyclopentenone-forming reactions mentioned above. However, although the carbonyl insertion takes place, the ring closure leading to cyclopentenone does not. Protonation of the bis(phosphite) carbyne (η^5-C_5H_5){$P(OMe)_3$}$_2$Mo≡C-(c-C_3H_5), which has no carbonyls, initiates a similar process that yields the butadiene complex (η^5-C_5H_5)Cl{$P(OMe)_3$}Mo(η^4-CH_2=CHCH=CH_2)[6] as shown in Scheme 1.

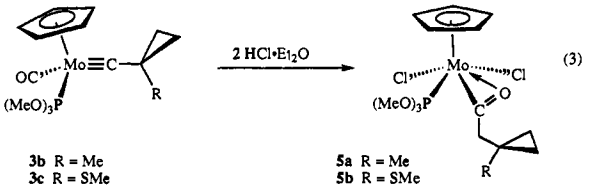
In this paper, we have examined in more detail the effects of electron-donating substituents at the 1-position of the cyclopropyl group. We conclude that the effect of electron donation into the cyclopropyl moiety favors a β-hydride shift in the metallacyclohexenone intermediate at the expense of the reductive elimination step which would form cyclopentenones. The dominant pathway thus leads to pentadienal complexes analogous to **4a**. We also observe that the presence of a substituent at the 1-position of the cyclopropyl ring apparently hinders hydrogen abstraction from the reaction medium by the radical cations produced upon carbyne oxidation. Instead, the radical intermediates are attacked by chloride to yield the dichloro carbynes (η^5-C_5H_5)Cl_2{$P(OMe)_3$}Mo≡CC(R)CH_2CH_2 [R = Me (**6a**), SMe (**6b**)]. Thus, the effect of Cl substituents depends on their electron demand. This effect can be seen in two places. For reaction of the metallacyclohexenone intermediate, electron-withdrawing substituents give rise to reductive elimination while donor-substituted complexes undergo β-hydride elimination. In the case of chloride attack on the oxidized carbynes, if the Cl substituents are electron withdrawing, the cyclopropyl ring is the site of chloride attack (eq 1),[2c] but with electron-donating groups, chloride substitution at the metal results (see Scheme 4, below).

Results and Discussion

Synthesis of 3a–d. The alkyl-substituted cyclopropylcarbynes (η^5-C_5H_5)(CO){$P(OMe)_3$}Mo≡CC(R)CH_2CH_2 [R = CH_2-CH=CH_2 (**3a**) CH_3 (**3b**), SCH_3 (**3c**), $CH_2C_6H_5$ (**3d**)] were prepared by deprotonation of (η^5-C_5H_5)(CO){$P(OMe)_3$}Mo≡C-(c-C_3H_5)[2a] using *n*-BuLi to generate an anionic vinylidene complex, followed by reaction *in situ* with a suitable electrophile [allyl bromide (**3a**), methyl iodide (**3b**), dimethyl disulfide (**3c**), or benzyl bromide (**3d**)] according to the method of Green.[7] Complex **3a** has been previously described.[4] These complexes are yellow oils at room temperature and like most alkylcarbynes are somewhat thermally sensitive, requiring storage at −40 °C to avoid slow decomposition.

Photooxidation of 3a–d. Under photooxidative conditions, complete decomposition of **3a–d** occurred, but no pentadienal complexes similar to **4a** could be observed. Photolysis of **3a–d** in chloroform produced identifiable free organic products only from **3a** and **3b**. For **3a**, 2-cyclohexenonespiro-5′-cyclopropane was identified in the reaction mixture in *ca.* 5% yield.[4] For **3b**, a trace of 3-methyl-2-cyclopentenone was generated and identified by comparison with an authentic sample.[8] Vacuum transfer of the reaction mixtures of **3a–d** followed by examination of the ^{1}H NMR spectra revealed the presence of small amounts of organic products, each characterized by a doublet resonance around 9.90–10.20 ppm with a coupling constant of about 8 Hz. It seems likely that these signals are due to free pentadienals arising from decomposition of pentadienal complexes under photolysis conditions, but the yields were too low for full characterization.

Reaction of 3a–d with HCl. Our failure to obtain substantial amounts of organic products by photolysis led us to explore alternative methods. Preparation of **4a** had been previously achieved by allowing a sample of **3a** to decompose in chloroform over a period of 15 days, but the formal requirement for a proton and a chloride suggested the quicker and more direct method of protonating the carbynes with hydrochloric acid. Slow addition of 1 equiv of HCl·Et_2O to **3a–d** in Et_2O resulted in a color change from yellow to red and was accompanied by deposition of an orange-brown precipitate. The precipitates were primarily composed of η^2-acyl complexes,[2b,4,9] which arise from addition of 2 equiv of HCl to the carbynes (eq 3). For purposes of positive



identification, carbynes **3b** and **3c** were treated with a large excess of acid to yield the η^2-acyl complexes (η^5-C_5H_5)Cl_2{$P(OMe)_3$}-Mo{η^2-C(O)CH_2C(R)CH_2CH_2} [R = CH_3 (**5a**), R = SCH_3 (**5b**)] and full data were obtained on these products. In addition to the expected signals for cyclopentadienyl, phosphite, and cyclopropyl groups, these complexes exhibit characteristic low-field resonances in the ^{13}C NMR spectrum at 278.6 and 277.1 ppm arising from the acyl carbon, and methylene signals at 52.5 and 50.9 ppm from the adjacent (formerly carbyne) carbon for **5a** and **5b**, respectively.

The red solutions were purified by chromatography on alumina, with mixtures of THF and methanol eluting purple bands which afforded red-brown solids on removal of solvent. Yields were somewhat variable, and appeared to depend on factors such as the rate of addition of acid and the concentration of the solution. Rapid addition of acid and concentrated solutions tended to favor η^2-acyl complexes, whereas slow addition of dilute acid solutions gave improved yields of the pentadienal complexes **4a–d**.

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Table 1. ^{1}H NMR Assignments for η^4-Pentadienal Complexes[a]

compd	R	H^1 (d)	H^2 (ddd)	H^4 (ddd)	H^{5syn} (dd)	H^{5anti} (dd)	J_{12}	$J_{4,5syn}$	$J_{4,5anti}$	$J_{5anti,5syn}$	J_{24}	J_{2P}
4a-I	n-C_3H_5	8.27	3.47	5.45	2.89	2.46	8	9	9	2	2	5
4b-I	Me	8.23	3.40	5.33	2.85	2.46	8	9	9	2	2	4
4d-I	CH_2Ph	8.06	3.62	5.60	2.88	2.37	8	9	9	2	2	5
compd	R	H^1 (d)	H^2 (d)	H^4 (ddd)	H^{5syn} (dd/br d)	H^{5anti} (dd)	J_{12}	$J_{4,5syn}$	$J_{4,5anti}$	J_{4P}	$J_{5anti,P}$	$J_{5syn,P}$
4a-II	n-C_3H_5	8.71	3.95	6.38	2.23	1.92	6	8	7	7	11	3
4b-II	Me	8.67	3.90	6.23	2.21	1.90	6	7	9	8	11	unresolved
compd	R	H^1 (d)	H^2 (dd)	H^4 (dd)	H^{5syn} (d)	H^{5anti} (d)	J_{12}	$J_{4,5syn}$	$J_{4,5anti}$	J_{2P}		
4a-III	n-C_3H_5	9.61	1.41	obscured	2.90	1.17	8	7	8	4		
4b-III	Me	9.53	1.43	5.08	2.86	1.15	8	8	8	5		
4c-III	SMe	9.87	1.61	5.30	2.93	1.16	8	8	8	6		
4d-III	CH_2Ph	9.80	1.34	5.34	2.90	1.11	8	7	9	5		
compd	R	H^1 (d)	H^2 (d)	H^4 (ddd)	H^{5syn} (dd)	H^{5anti} (dd)	J_{12}	$J_{4,5syn}$	$J_{4,5anti}$	J_{4P}	$J_{5anti,P}$	$J_{5syn,P}$
4a-IV	n-C_3H_5	10.22	1.86	6.22	2.04	0.28	8	7	7	7	8	3
4b-IV	Me	10.19	1.82	6.04	2.02	0.24	8	7	7	7	9	3
4c-IV	SMe	10.35	2.12	6.06	2.23	0.33	7	7	7	7	10	3
4d-IV	CH_2Ph	10.38	1.82	6.34	2.04	0.27	8	7	8	8	8	2

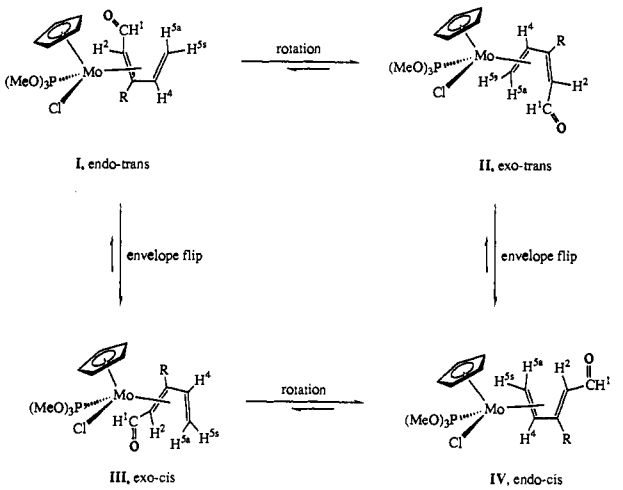
[a] Chemical shift values in parts per million (δ), coupling constants in hertz.

The ^{1}H NMR spectra of these products (**4a–d**) exhibited signals corresponding to cyclopentadienyl and phosphite groups and to the Cl substituent from the starting material. In addition, five discrete multiplets each integrating to one proton demonstrated the presence of an organic group. Coupling constants within this group were deduced from decoupling and COSY experiments. The products **4a**, **4b**, and **4d** showed similar chemical shifts in their ^{1}H NMR spectra, but those of **4c** were somewhat different and will be discussed later. Upon standing, all isomerized via the pathways in Scheme 2 (*vide infra*), but the similarities in their ^{1}H NMR spectra suggested that the initially formed isomers of **4a**, **4b**, and **4d** were structurally analogous. This isomer is assigned as **I** in Scheme 2.

For **4a-I**, **4b-I**, and **4d-I**, the presence of a distinctive doublet in the ^{1}H NMR spectrum in the region 8.0–8.3 ppm (H^1) with a coupling constant of 8 Hz and signals in the IR spectra around 1635 and 2850 cm^{-1} clearly indicated the presence of a conjugated aldehyde group (Scheme 2). A multiplet appearing at 5.3–5.6 ppm (H^4) showed strong coupling (*ca.* 9 Hz) to two of the other signals, one falling in the region 2.8–2.9 (H^{5syn}), and the other around 2.4–2.5 (H^{5anti}). These were ascribed to a coordinated vinyl moiety. The final multiplet in each spectrum fell in the range 3.4–3.6 (H^2) and was coupled strongly to the aldehyde proton (8 Hz) and weakly (2 Hz) to the vinyl signal at 5.3–5.6. This signal also showed a significant (4–5 Hz) coupling to phosphorus. The data are entirely consistent with formation of a 3-substituted 2,4-pentadien-1-al ligand η^4-coordinated to molybdenum, although in the ensuing discussion it will be occasionally useful to regard the ligand as a 1,2-substituted diene. It should be noted that the ^{1}H NMR data obtained from the protonation of **3a**, though similar, did not match those previously observed for the product arising from slow decomposition in chloroform. Clearly the altered reaction conditions had led to detection of a different isomer.

Over the course of 7 days, monitoring of the initial product (**4a-I**) formed by protonation of **3a** by ^{1}H NMR in C_6D_6 revealed slow disappearance of the original peaks and their replacement by signals corresponding to three more isomers (**4a-II**, **4a-III**, **4a-IV**). Isomers **II** and **III** appeared to arise simultaneously and independently, although **III** was present in consistently higher concentration than **II**. Isomer **IV** arose from **II** and/or **III**, but could not arise directly from **I**, since at one stage of the isomerization all of isomer **I** had been consumed, but the concentration of **IV** continued to increase as **II** and **III** decreased. Eventually, the isomerization terminated in an equilibrium mixture of *ca.* 1:1:6 (**4a-II**:**4a-III**:**4a-IV**). For all four isomers, the phosphite and cyclopentadienyl signals showed very little variation in chemical shift, indicating similar electronic characteristics. However, the five multiplets were notably shifted from isomer to isomer, and considerable variation in the couplings between them was seen. These data are summarized in Table 1. The peaks for isomer **4a-IV** corresponded to those previously reported for **4a**.[4] Similar isomerization processes took place for **4b** and **4d**, with minor differences. The final equilibrium mix for **4b** after 5 days was *ca.* 1:13 (**4b-III**:**4b-IV**). Peaks corresponding to isomer **4d-II** were not observed at any point during isomerization of **4d**, and isomer **4d-IV** was the only observable product remaining after 7 days.

Scheme 2



The product mixture arising from protonation of **3c** differed from the others in that no type **I** or type **II** isomers were seen. ^{1}H NMR spectra taken less than 1 h after reaction showed a predominance of isomer **4c-III** and some **4c-IV**, which over 5 days achieved a final product ratio of *ca.* 1:6 (**4c-III**:**4c-IV**). This observation could imply a separate mechanism for the formation of **4c** leading directly to **4c-III**. However, it seems more likely that the initial isomerization process from **4c-I** is simply much more facile with this substituent.

We were interested in understanding the mechanism of isomerization for the dienal complexes **4a–d**. Within the pentadienal ligand, two geometric isomers can exist, with the aldehyde group either *cis* or *trans* to the R-group. In addition, the orientation of the backbone of the pentadienal ligand with respect to the cyclopentadienyl ring may be either *endo* or *exo*. Finally, the side of the diene moiety bearing the aldehyde and R-group substituents may be *cisoid* either to the phosphite or to the chloride group. This gives rise to a total of eight possible

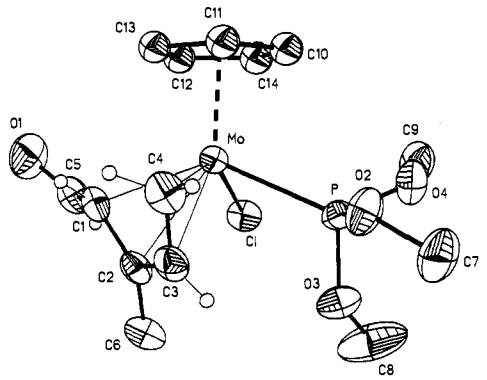


Figure 1. ORTEP drawing of compound **4b** showing the crystallographic numbering scheme. Thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (deg) are as follows: Mo–Cl, 2.5239(13); Mo—P, 2.4370(13); Mo—C1, 2.303(5); Mo—C2, 2.378(5); Mo—C3, 2.332(6); Mo—C4, 2.256(6); Cl—C2, 1.423(8); C2—C3, 1.404(8); C3—C4, 1.400(8); C1—C5, 1.452(8); C2—C6, 1.496(9); C5—O1, 1.207(8); C1—Mo—C4, 73.6(2); C4—Mo—P, 88.2(2); P—Mo—C1, 81.39(5); C1—Mo—C1, 86.67(14); C2—C3—C4, 120.8(5); C1—C2—C3, 115.4(5); C1—C2—C6, 123.9(5); C3—C2—C6, 120.7(5); C2—C1—C5, 124.1(5); C1—C5—O1, 124.7(6).

isomers. Interconversion between *endo* or *exo* may be achieved either by rotation of the pentadienal ligand around an axis perpendicular to the plane of the carbon backbone or *via* an "envelope flip" mechanism having a transition state resembling a planar five-membered metallacycle. This latter process also serves to interchange the *syn* and *anti* substituents of the diene moiety and has been reported under both thermal and photochemical conditions.[10]

The concurrent appearance of isomers **II** and **III** followed by their convergence upon **IV** suggests that both processes occur simultaneously. However, the observation of only four of the possible eight isomers implies that initial formation of the pentadienal ligand is regiospecific with respect to the metal center (Scheme 2). Regiospecific conversion of a molybdenum (1-deuteriocyclopropyl)carbyne to a 2-deuteriobutadiene complex has been previously observed for the related complex (η^5-C_5H_5){$P(OMe_3)_2$}Mo≡CC(D)CH_2CH_2 (rearrangement of the unlabeled compound is depicted in Scheme 1).[6]

Crystal Structure of 4b-IV. To unambiguously determine the stereochemistry of one isomer, a structural study was carried out on crystals obtained from a solution of **4b** which had been allowed to reach final equilibrium and was thus essentially all isomer **4b-IV**. The results are illustrated in Figure 1, which shows the crystallographic numbering scheme used in discussion of the structure. The molecule is well described as having square-pyramidal geometry, with the cyclopentadienyl ligand occupying the apical position and the atoms P, Cl, C1, and C4 defining a mean square plane with an estimated standard deviation of 0.04 Å. None of these atoms deviates from this plane by more than 0.04 Å. The substituted double bond of the diene moiety lies *cisoid* to the chloride, and the diene is in the *endo* configuration. The methyl and aldehyde groups are mutually *cis*. It should be noted that in this configuration unfavorable steric interactions are minimized, as the substituents on the diene moiety are directed away from the relatively bulky phosphite ligand. This is to be expected for the thermodynamically most favored isomer.

Within the diene fragment, the bond lengths C2—C3 [1.404(8) Å] and C3—C4 [1.400(8) Å] are essentially equal, revealing a strong conjugation effect, although the substituted double bond C1—C2 is somewhat longer at 1.423(8) Å, presumably due to a certain amount of additional conjugation to the aldehyde group. The Mo—C1 and Mo—C4 bond lengths are markedly shorter than Mo—C2 and Mo—C3 [C1—Mo, 2.303(5), and C4—Mo, 2.256(6) Å, as compared with C2—Mo, 2.378(5), and C3—Mo 2.332(6) Å]. The crystal structure implies that there is a significant amount of metallacycle character to the molecule, but that neither a 3-metallacyclopentene nor a coordinated diene description is fully satisfactory and the molecule bears some of the character of both resonance forms. Previous work has shown that groups 4 and 5 transition-metal "diene complexes" tend to favor a metallacyclic formulation,[11] whereas a true diene description fits late-transition-metal complexes better.[10b,12] The substituted side of the diene lies at a somewhat greater distance from the metal center than the unsubstituted side, which further relieves steric stress. This structural feature can be observed in the related molybdenum diene complex Cp(I){$P(OMe)_3$}Mo(η^4-CH_2=CHCH=$CHCH_2$^{t}Bu).[7]

Conformation of Isomers I–IV. By definitively assigning a conformation to **4b-IV**, it is possible to deduce the stereochemistry of the remaining isomers. Either mechanism of isomerization, envelope flip or rotation of the diene, changes the *exo/endo* conformation of the ligand. Therefore, **II** and **III** must have the diene in the *exo* conformation. Clearly, a further isomerization of either **II** or **III** by the alternative mechanism affords **I** as the *endo* isomer. It is not possible to distinguish the conformations of **II** and **III** purely by deduction from the structure of **IV**, since it is not known which mechanism affords which isomer, but we can assign their stereochemistry on the basis of ^{1}H NMR spectroscopy. In isomer **IV**, the unsubstituted end of the diene moiety is found to be *cisoid* to the phosphite group, and all three protons (H^4, H^{5syn}, and H^{5anti}) of this vinyl group exhibit coupling to phosphorus. Similar couplings are seen for isomer **II**, and it may therefore be deduced that **II** and **IV** are related by an envelope flip mechanism rather than by rotation of the diene. Isomers **I** and **III**, having the substituted end of the diene moiety *cisoid* to the phosphite group, similarly show coupling between phosphorus and H^2. The envelope flip mechanism apparently has a lower energy barrier than rotation of the diene ligand in this system, since greater concentrations of isomer **III** than **II** are observed. Previous comparisons of these processes in mid-to-late transition metal diene complexes have concluded that the energy barrier to rotation is lower. However, these studies were carried out on complexes with very little metallacycle character, and mostly small or no substituents.[10] Significant metallacycle character lowers the energy barrier for envelope flip, and on purely steric grounds it seems likely that large or multiple substituents would have less effect on the barrier to envelope flip than that of rotation.

Mechanistic Considerations. Since rearrangements of cyclopropylcarbyne complexes of the type (η^5-C_5H_5)(CO){$P(OMe)_3$}-Mo≡CC(R)CH_2CH_2 can give rise to either cyclopentenones or pentadienals, a primary question arising from these studies is where the two reaction manifolds bifurcate.[13,14] A mechanism leading to pentadienal complexes is outlined in Scheme 3, and in the early steps resembles that given in Scheme 1. There seems little doubt that the initial step is protonation of the carbyne carbon to yield the 16-electron cationic carbene **A**. Intermediate **A** can also be accessed by the Scheme 1 photooxidation/H-abstraction sequence as occurs in the conversion of **1a,b** and **2a–f** to cyclopentenones (eq 1).[2b,c] This is followed by ring expansion to form metallacyclopentene **B**, and CO insertion which yields

(10) (a) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 4858–4859. (b) Eaton, B.; King, J. A., Jr.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 1359–1360.

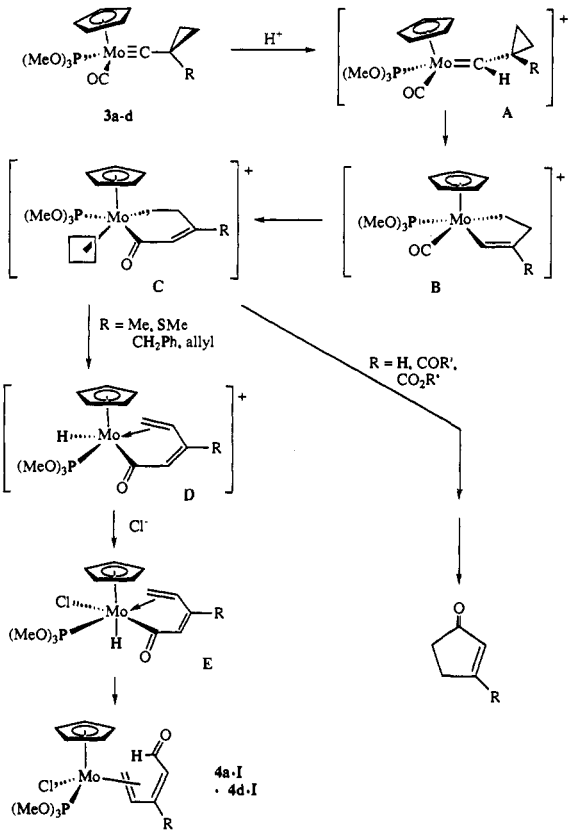
(11) Erker, G.; Krüger, C.; Müller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1–39.

(12) (a) Erker, G.; Engel, K.; Krüger, C.; Chiang, A.-P. *Chem. Ber.* **1982**, *115*, 3311–3323. (b) Benn, R.; Schroth, G. *J. Organomet. Chem.* **1982**, *228*, 71–85.

(13) Reactions of enynes with Fischer carbenes also yield product mixtures containing cyclopentenones and dienals.[14] However, that process is mechanistically unrelated to the carbyne reactions described here. This issue is discussed more fully in ref 2b.

(14) Harvey, D. F.; Lund, K. P.; Neil, D. A. *J. Am. Chem. Soc.* **1992**, *114*, 8424–8434.

Scheme 3



metallacyclohexenone **C** and generates a vacant site at the metal. The **B** → **C** step is certainly well precedented. Carbonyl insertion is known for metallacyclopentanes,[15] metallacyclopentenes,[16] and metallaindans.[17] However, in metallacyclopentenes and metallaindans, insertion into the metal—alkyl bond is generally preferred over insertion into the metal—vinyl or metal—aryl bond.[17] In order to obtain dienal products from **B**, insertion of CO must occur into the metal—vinyl bond of the metallacyclopentene. This implies that the ring opening in **A** → **B** is regiospecific such that **B** forms as the isomer in which CO is *cis* to the vinyl moiety. It is not clear for what reason the regiospecificity arises, but it seems unlikely to be a purely steric effect since the 1-alkylcyclopropyl group of the carbene moiety is required to be on the same side of the molecule as the relatively bulky phosphite group.

At this stage, reductive elimination of the alkyl and acyl groups of **C** (or its chloride adduct as in Scheme 1) would give a cyclopentenone, and this is observed when R = acyl or H. However, the major pathway when R is an electron-donating substituent involves a β-hydride shift to yield intermediate **D**. This requires that the vacant coordination site be *cis* to the alkyl substituent of the metal. The proper geometry may be achieved by a square pyramid–trigonal bypyramid–square pyramid pseudorotation serving to exchange the phosphite group with the vacant site, which would be expected to be facile in such a system.[18] Chloride coordination at this stage would give the pseudooctahedral intermediate **E** in which the acyl group and the hydride are mutually *cis*. Reductive elimination of these ligands would yield the pentadienal complexes **4a–d** as type **I** isomers.

The difference in products from metallacycle **C** when R = alkyl and acyl is unexpected. Although β-hydride shift is in general faster than reductive elimination,[19] the rates of β-hydride shift in five- and six-membered metallacycles are slowed by the difficulty in achieving the optimal M—C—C—H dihedral angle of 0°. Thus, other processes become competitive.[15,20] The tendency of acyl substituents to accelerate formation of ketones by reductive elimination[21] makes the formation of cyclopentenones the most likely alternative to β-hydride shift in **C**. In fact, for reactions that generate metallacyclohexanones and metallacyclohexenones,[15-17,22] reductive elimination to form the cyclic ketone is ordinarily favored and β-hydride shift products are not observed.

The product dependence on the substituent R is difficult to ascribe to a steric effect, since there is not a correlation between the steric bulk of the substituents[23] and the identities of the final products. In addition, the R group of **C** is distant from the sterically demanding metal center. The determining factor between reductive elimination and β-hydride shift in **C** must therefore be electronic in origin. Given that the formation of cyclopentenones would be the expectation from metallacyclohexenones (*vide supra*), the implication is that electron-donating substituents R in some way favor the β-hydride shift pathway that leads ultimately to dienals. This conclusion is in accord with studies of substituent effects on β-hydride elimination[24] and its microscopic reverse, the insertion of olefins into metal hydride bonds.[25] β-Hydride elimination from $Cp^*_2ScCH_2CH_2$-*p*-C_6H_4X derivatives was shown to have a Hammett ρ-value of −1.87, indicative of positive charge development at the β-carbon in the transition state. Olefin insertion studies supported the same conclusion about charge distribution. The effects seen in the product distribution from metallacycle **C** are consistent. For R-groups where $\sigma^+ \geq 0$ (R = COR′, CO_2R', H), reductive elimination to the cyclopentenone is the dominant pathway. For R-groups where $\sigma^+ < 0$ (R = Me, CH_2Ph, SMe, allyl), β-hydride elimination eventually leads to the dienal complex. Although the preferred geometry for β-hydride elimination still cannot be achieved in **C**, the additional capability for stabilization of positive charge at the β-carbon appears to make dienal formation competitive for complexes with electron-donating substituents.

Formation of High-Valent Carbyne Complexes. When **3b** and **3c** were allowed to decompose in $CHCl_3$ or CCl_4 over a period of days, the predominant products were not pentadienal complexes, although these were formed in small quantities (10–20%). Upon removal of chloroform from the reaction mixture, washing the residue with Et_2O to remove the pentadienal complexes, and recrystallizing from CH_2Cl_2/Et_2O, previously unobserved products could be isolated. The new complexes, **6a** and **6b**, still had intact cyclopropyl groups, and in the ^1H NMR spectra the peaks for the cyclopentadienyl and phosphite groups were shifted somewhat downfield from the starting materials (*ca.* 5.9 and 3.9 ppm, respectively, as compared with 5.4 and 3.6 ppm in **3b** and

(15) (a) McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529–6536. (b) McDermott, J. X.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 947–948. (c) Grubbs, R. H., Miyashita, A. *J. Chem. Soc., Chem. Commun.* **1977**, 864–865.

(16) Negishi, E.-i.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2568–2569.

(17) (a) Carmona, E.; Gutiérrez-Puebla, E.; Marín, J. M.; Monge, A.; Paneque, M.; Poveda, M. L.; Ruiz, C. *J. Am. Chem. Soc.* **1989**, *111*, 2883–2891. (b) Erker, G. *Acc. Chem. Res.* **1994**, *17*, 103–109.

(18) (a) Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852–5860. (b) Kalck, P.; Pince, R.; Poilblanc, R.; Roussel, J. *J. Organomet. Chem.* **1970**, *24*, 445–452.

(19) Stille, J. K. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: Chichester, 1985; Vol. 2, pp 625–787.

(20) (a) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521–6528. (b) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 4451–4452.

(21) Brown, J. M.; Cooley, N. A. *Chem. Rev.* **1988**, *88*, 1031–1046.

(22) James, B. R.; Young, C. G. *J. Organomet. Chem.* **1985**, *285*, 321–332.

(23) For this analysis, the steric bulk of the substituent was evaluated by its $\Delta G°_x$ (or *A*-value), the difference in free energy corresponding to the equilibrium between axial and equatorial substituents on a cyclohexane ring. See: (a) Hirsch, J. A. *Top. Stereochem.* **1967**, *1*, 199–222. (b) Jensen, F. R.; Bushweller, C. H. *Adv. Alicyclic Chem.* **1971**, *3*, 139–194.

(24) Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566–1577.

(25) (a) Burger, B. J.; Santarsiero, B. D.; Trimmer, M. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 3134–3146. (b) Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670–2682.

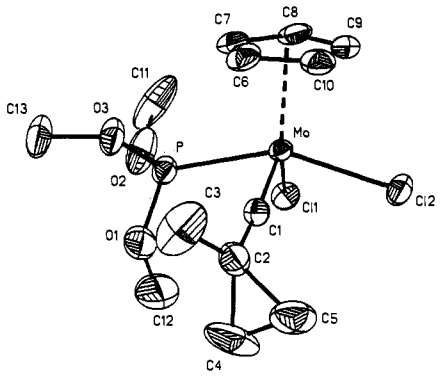
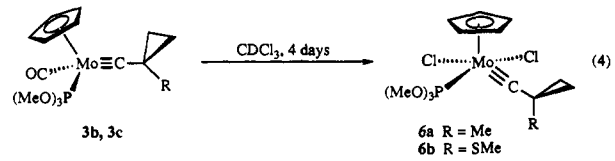


Figure 2. ORTEP drawing of compound **6a** showing the crystallographic numbering scheme. Thermal ellipsoids are drawn at the 40% probability level. Selected bond lengths (Å) and angles (deg) are as follows: Mo—C1, 1.781(8); Mo—C11, 2.479(2); Mo—C12, 2.493(2); Mo—P, 2.459(2); C1—C2, 1.437(12); C2—C3, 1.469(15); C2—C4, 1.53(2); C2—C5, 1.525(15); C4—C5, 1.41(2); C1—Mo—P, 79.4(2); P—Mo—C11, 75.79(7); C11—Mo—C12, 80.53(7); C12—Mo—C1, 91.3(2); Mo—C1—C2, 172.3(7); C1—C2—C3, 117.8(8); C1—C2—C4, 115.4(8); C1—C2—C5, 115.1(8); C4—C2—C5, 62.4(8).

3c). Most significantly though, the ^{13}C NMR spectra of these products contained unusually low field signals [375.5 (**6a**), 367.2 (**6b**) ppm], diagnostic of high oxidation state carbyne complexes. The ^{13}C NMR and IR spectra contained no signals ascribable to a carbonyl group. Determination of the molecular weights by HRMS allowed unambiguous assignment of the complexes as the high-valent carbynes $(\eta^5\text{-}C_5H_5)Cl_2\{P(OMe)_3\}Mo{\equiv}C\overline{C(R)\text{-}CH_2CH_2}$ [R = CH_3 (**6a**), SCH_3 (**6b**)] (eq 4). The formation of



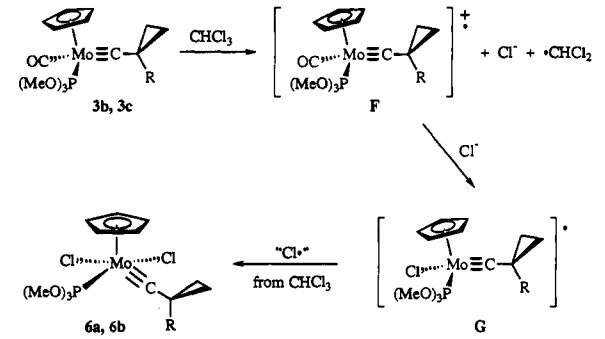
(4)

these complexes represents an unusual transformation between low oxidation state "Fischer-type" carbynes and high oxidation state "Schrock-type" carbynes. Only a few examples of such oxidations which leave the carbyne group intact have been reported.[26] The formulation of **6a** was confirmed by the growth of crystals suitable for an X-ray diffraction study, and the results are illustrated in Figure 2.

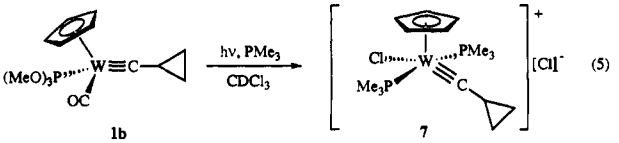
Crystal Structure of 6a. The carbyne **6a** is a distorted square pyramid with the cyclopentadienyl group occupying the apical position. The carbyne and phosphite groups are *cisoid* in the solid state as was predicted for the similar aminocarbynes $(\eta^5\text{-}C_5H_5)X_2(CO)Mo{\equiv}CNEt_2$ (X = Br, I) prepared by Filippou,[26b] and there was no evidence in the solution spectra for any other isomer. The Mo—C1 bond length is 1.781 Å, and the M—C1—C2 angle is 172.3(7)°. These values are characteristic of a high oxidation state Mo—C triple bond.[27]

Mechanistic Considerations. The formation of **6a** and **6b** represents an interesting departure from the organic rearrangements which are characteristic of oxidation of cyclopropylcarbynes by electron-accepting solvents. However, they closely parallel previous observations we have made on the photooxidation of carbynes in the presence of phosphines. When the carbyne $(\eta^5\text{-}C_5H_5)(CO)[P(OMe)_3]W{\equiv}C(c\text{-}C_3H_5)]$ (**1b**) is photolyzed in

Scheme 4



chloroform containing an excess of PMe_3, electron transfer to the solvent is followed by ligand exchange and chloride abstraction to yield the cationic carbyne $[(\eta^5\text{-}C_5H_5)Cl(PMe_3)_2W{\equiv}C\text{-}(c\text{-}C_3H_5)]Cl$ (**7**) (eq 5). This reaction is general for a range of carbynes of the general formula $(\eta^5\text{-}C_5H_5)L_2M{\equiv}CR$ (M = W, Mo; L = CO, $P(OMe)_3$; R = alkyl, aryl).[28]



(5)

The mechanism of formation of **6a** and **6b** is clearly related to that for **7**, and a reasonable pathway is outlined in Scheme 4. Formation of the 17-electron carbyne **F** by electron transfer to chloroform (whether promoted by ambient light or a thermal process) is followed by ligand loss and attack of the chloride, yielding the neutral paramagnetic carbyne **G**. This then abstracts a chlorine radical from the solvent to give the product. The reaction differs from the formation of the cationic carbyne **7** in that chloride, rather than a phosphine, is now acting as the donor ligand. This implies a fine balance for carbyne radical cations of type **F** between abstraction of a hydrogen radical, leading ultimately to organic products as exemplified in Scheme 1, and attack of chloride and metal-centered chemistry. The pathway taken appears to depend on the exact ligand set. It is interesting to note that when cyclopropylcarbynes with no substituent at the 1-position are allowed to decompose in $CDCl_3$, the resultant cyclopentenones are typically only about 48% deuterated although a hydrogen must be abstracted to form the product.[2b] Much of the hydrogen must therefore be scavenged from other carbyne molecules. Blocking the 1-position of the cyclopropyl ring by substitution as in **3b** and **3c** makes one viable hydrogen source unavailable, and thus tips the balance toward reaction with chloride.

Conclusions

We have demonstrated that protonation of (1-alkylcyclopropyl)carbynes leads to the production of pentadienal complexes by a mechanism related to that previously elucidated for cyclopentenone formation. There is evidence that the partitioning of the metallacyclohexenone intermediate between reductive elimination to yield cyclopentenones and β-hydride shift to give dienal complexes is controlled by the electron-withdrawing or donating capability of the C1 substituent on the cyclopropyl ring. We have also discovered new dichlorometal carbyne products arising from metal-centered reactivity of the intermediate paramagnetic species formed upon oxidation. We postulate that the carbyne α-hydrogen is one of the sites where carbyne radical cations can abstract hydrogen to form reactive cationic carbenes

(26) (a) Mayr, A.; McDermott, G. A. *J. Am. Chem. Soc.* **1986**, *108*, 548–549. (b) Filippou, A. C.; Fischer, E. O.; Grünleitner, W. *J. Organomet. Chem.* **1990**, *386*, 333–347.

(27) Structural data for metal–carbon triple bonds are summarized in the following: (a) Kim, H. P.; Angelici, R. J. *Adv. Organomet. Chem.* **1987**, *27*, 51–111. (b) Mayr, A.; Hoffmeister, H. *Adv. Organomet. Chem.* **1991**, *32*, 227–324.

(28) (a) Leep, C. J.; Kingsbury, K. B.; McElwee-White, L. *J. Am. Chem. Soc.* **1988**, *110*, 7535–7536. (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.

in the oxidation reactions. Since it is the cationic carbenes which undergo organic rearrangements, slowing abstraction by blocking this site opens the way for competition by chloride attack on the intermediate. Once again the mode of reactivity is determined by the electron demand of the substituent. If the Cl group is an acyl substituent, chloride attack on the electron-deficient cyclopropyl ring is observed, whereas alkyl substituents direct chloride attack to the metal.

Experimental Section

General Methods. Standard inert atmosphere techniques were used throughout. Diethyl ether and THF were distilled from Na/Ph_2CO. Hexane, chloroform, and methylene chloride were distilled from CaH_2. All NMR solvents were degassed by three freeze–pump–thaw cycles. Benzene-d_6 was vacuum transferred from Na/Ph_2CO. $CDCl_3$ and CD_2Cl_2 were stored over a mixture of 3 and 4 Å molecular sieves. 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 Varian XL-400 and VXR-300 NMR spectrometers. ^1H and ^{13}C shifts are referenced to TMS. ^{31}P NMR shifts are referenced to 85% H_3PO_4. IR spectra were recorded on a Perkin-Elmer 1600 spectrometer. High-resolution mass spectra were obtained at the Mass Spectrometry Facility, Univeristy of California, San Francisco, and at the Department of Chemistry, University of Florida. Microanalyses were carried out by Robertson Microlit Laboratories, Inc., Madison, NJ, and at the Department of Chemistry, University of Florida.

Synthesis of $(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}Mo{\equiv}C\overline{C(CH_3)CH_2CH_2}$ (3b). The cyclopropylcarbyne **1a** (110 mg, 0.30 mmol) in 10 mL of THF was reacted with a 2.5 M hexane solution of *n*-butyllithium (180 μL, 0.45 mmol) at –78 °C. During the following 30 min a deep orange color developed due to formation of the cyclopropylidene anion $Li[(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}Mo{=}C{=}\overline{CCH_2CH_2}]$. Excess methyl iodide (100 μL, 1.61 mmol) was added, resulting in a rapid color change to yellow, and the solution was 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 **3b** as a yellow oil (91 mg, 81%) after removal of solvent: ^1H NMR ($CDCl_3$) 5.35 (d, 5H, C_5H_5, J_{PH} = 1 Hz), 3.57 (d, 9H, OMe, J_{PH} = 12 Hz), 1.20 (s, 3H, CH_3), 1.06, 0.47 (m, 2H, c-C_3H_4) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) 318.8 (d, Mo≡C, J_{PC} = 29 Hz), 241.2 (d, CO, J_{PC} = 20 Hz), 90.6 (C_5H_5), 51.4 (OMe), 35.3 (Mo≡*C*C), 21.5 (CH_3) 18.2, 17.8 (CH_2) ppm; $^{31}P\{^1H\}$ NMR (C_6D_6) 205.0 ppm; IR (CH_2Cl_2) 1894 cm^{-1} (ν_{CO}); HRMS (FAB) for $C_{14}H_{21}O_4PMo$ (m/z), calcd 382.0232, found 382.0231 (M^+).

Synthesis of $(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}Mo{\equiv}C\overline{C(SCH_3)CH_2CH_2}$ (3c). In a manner similar to the formation of **3b**, the cyclopropylcarbyne **1a** (99 mg, 0.27 mmol) in 10 mL of THF was reacted with a 2.5 M hexane solution of *n*-butyllithium (170 μL, 0.41 mmol) at –78 °C. After 30 min, excess dimethyl disulfide (75 μL, 0.83 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 **3c** as a yellow oil (95 mg, 85%) after removal of solvent: ^1H NMR ($CDCl_3$) 5.38 (s, 5H, C_5H_5), 3.57 (d, 9H, OMe, J_{PH} = 12 Hz), 2.30 (s, 3H, CH_3), 1.37, 0.95 (m, 2H, c-C_3H_4) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) 307.5 (d, Mo≡C, J_{PC} = 26 Hz), 241.5 (d, CO, J_{PC} = 17 Hz), 90.9 (C_5H_5), 51.5 (OMe), 41.2 (Mo≡*C*C), 21.0, 20.4 (CH_2), 15.8 (CH_3) ppm; $^{31}P\{^1H\}$ NMR (C_6D_6) 203.6 ppm; IR (CH_2Cl_2) 1900 cm^{-1} (ν_{CO}); HRMS (FAB) for $C_{14}H_{21}O_4PMoS$ (m/z), calcd 413.9952, found 413.9934 (M^+).

Synthesis of $(\eta^5\text{-}C_5H_5)(CO)\{P(OMe)_3\}Mo{\equiv}C\overline{C(CH_2C_6H_5)CH_2CH_2}$ (3d). In a manner similar to the formation of **3b**, the cyclopropylcarbyne **1a** (158 mg, 0.43 mmol) in 10 mL of THF was reacted with a 2.5 M hexane solution of *n*-butyllithium (260 μL, 0.65 mmol) at –78 °C. After 30 min, excess benzyl bromide (100 μL, 0.84 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 **3d** as a yellow oil (181 mg, 92%) after removal of solvent: ^1H NMR ($CDCl_3$) 7.17–7.32 (m, 5H, C_6H_5), 5.20 (s, 5H, C_5H_5), 3.48 (d, 9H, OMe, J_{PH} = 12 Hz), 2.83, 2.71 (d, 1H, CH, J_{HH} = 15 Hz), 1.13, 0.61 (m, 2H, c-C_3H_4) ppm; $^{13}C\{^1H\}$ NMR (C_6D_6) 317.8 (d, Mo≡C, J_{PC} = 26 Hz), 241.5 (d, CO, J_{PC} = 19 Hz), 139.8, 129.4, 127.8, 126.0 (C_6H_5), 90.8 (C_5H_5), 51.3 (OMe), 41.4 (CH_2), 40.0 (Mo≡*C*C), 16.5, 16.3 (CH_2) ppm; $^{31}P\{^1H\}$ NMR (C_6D_6) 204.6 ppm; IR (CH_2Cl_2) 1895 cm^{-1} (ν_{CO}); HRMS (FAB) for $C_{20}H_{25}O_4PMo$ (m/z) 458.0545, found 458.0567 (M^+).

Synthesis of $(\eta^5\text{-}C_5H_5)Cl\{P(OMe)_3\}Mo\{\eta^4\text{-}CH_2{=}CHC(C_3H_5){=}CH(CHO)\}$ (4a). The (1-allylcyclopropyl)carbyne **3a** (210 mg, 0.52 mmol) was dissolved in 40 mL of Et_2O and a solution of 1 M $HCl{\cdot}Et_2O$ (520 μL, 0.52 mmol) slowly added while stirring vigorously. After 10 min, the solution was filtered through a glass frit to remove precipitate. The solvent was removed *in vacuo* and the residue taken up in Et_2O (*ca.* 2 mL). The solution was chromatographed on alumina and flushed with Et_2O and a purple band eluted using a 5:1 Et_2O/MeOH mixture. The solvent was removed and the resulting oil dissolved in C_6D_6. Isomerization of the product was monitored by ^1H NMR over a period of 7 days until no further change was observed. Recrystallization from hexane/Et_2O (4:1) afforded purple microcrystals of **4a** (99 mg, 43%). Isomer **4a-IV** has previously been synthesized by another route:[3] ^1H NMR (C_6D_6) (**4a-I**) 8.27 (d, 1H, H^1, J_{HH} = 8 Hz), 6.12 (dddd, 1H, =CH, J_{HH} = 17, 9, 8, 7 Hz), 5.45 (ddd, 1H, H^4, J_{HH} = 9, 9, 2 Hz), 5.23 (br d, 1H, $=CH_2$, J_{HH} = 17 Hz), 5.05 (br d, 1H, $=CH_2$, J_{HH} = 9 Hz), 4.61 (d, 5H, C_5H_5, J_{PH} = 2 Hz), 3.67 (br d, 1H, CH_2, J_{HH} = 7 Hz), 3.63 (br d, 1H, CH_2, J_{HH} = 8 Hz), 3.47 (ddd, 1H, H^2, J_{HH} = 8,2 Hz, J_{PH} = 5 Hz), 3.15 (d, 9H, OMe, J_{PH} = 10 Hz), 2.89 (dd, 1H, H^{5syn}, J_{HH} = 9,2 Hz), 2.46 (dd, 1H, H^{5anti}, J_{HH} = 9,2 Hz); (**4a-II**) 8.71 (d, 1H, H^1, J_{HH} = 6 Hz), 6.38 (ddd, 1H, H^4, J_{HH} = 8, 7 Hz, J_{PH} = 7 Hz), 5.31 (br d, 1H, $=CH_2$, J_{HH} = 18 Hz), 5.12 (br d, 1H, $=CH_2$, J_{HH} = 9 Hz), 4.61 (d, 5H, C_5H_5, J_{PH} = 2 Hz), 3.95 (d, 1H, H^2, J_{HH} = 6 Hz), 3.19 (d, 9H, OMe, J_{PH} = 10 Hz), 2.23 (dd, 1H, H^{5syn}, J_{HH} = 8 Hz, J_{PH} = 3 Hz), 1.92 (dd, 1H, H^{5anti}, J_{HH} = 7 Hz, J_{PH} = 11 Hz), remaining allyl group signals obscured by other isomers; (**4a-III**) 9.61 (d, 1H, H^1, J_{HH} = 8 Hz), 5.19 (br d, 1H, $=CH_2$, J_{HH} = 17 Hz), 5.05 (br d, 1H, $=CH_2$, J_{HH} = 9 Hz), 4.58 (d, 5H, C_5H_5, J_{PH} = 1 Hz), 4.10 (d, 1H, CH_2, J_{HH} = 7 Hz), 4.06 (d, 1H, CH_2, J_{HH} = 7 Hz), 3.22 (d, 9H, OMe, J_{PH} = 10 Hz), 2.90 (d, 1H, H^{5syn}, J_{HH} = 7 Hz), 1.41 (dd, 1H, H^2, J_{HH} = 8 Hz, J_{PH} = 4 Hz), 1.17 (d, 1H, H^{5anti}, J_{HH} = 8 Hz), H^4 signal and remaining allyl group signal obscured by other isomers; (**4a-IV**) 10.22 (d, 1H, H^1, J_{HH} = 8 Hz), 6.22 (ddd, 1H, H^4, J_{HH} = 7, 7 Hz, J_{PH} = 7 Hz), 6.12 (m, 1H, =CH), 5.23 (br d, 1H, $=CH_2$, J_{HH} = 17 Hz), 5.08 (br d, 1H, $=CH_2$, J_{HH} = 10 Hz), 4.52 (d, 5H, C_5H_5, J_{PH} = 2 Hz), 4.06 (d, 1H, CH_2, J_{HH} = 7 Hz), 4.02 (d, 1H, CH_2, J_{HH} = 7 Hz), 3.19 (d, 9H, OMe, J_{PH} = 10 Hz), 2.04 (dd, 1H, H^{5syn}, J_{HH} = 7, J_{PH} = 3 Hz), 1.86 (d, 1H, H^2, J_{HH} = 8 Hz), 0.28 (dd, 1H, H^{5anti}, J_{HH} = 7 Hz, J_{PH} = 8 Hz) ppm; $^{13}C\{^1H\}$ NMR (C_6D_6) (**4a-IV**) 201.0 (CHO), 138.1 (*C*H=CH_2), 130.0 (*C*=CH), 116.8 (CH=*C*H_2), 104.5 (C=*C*H), 92.8 (C_5H_5), 65.1 (CHMo), 53.3 (OMe), 44.4 (CH_2), 38.5 (CH_2Mo) ppm; $^{31}P\{^1H\}$ NMR (C_6D_6) (**4a-I**) 160.8; (**4a-II**) 162.1; (**4a-III**) 163.2; (**4a-IV**) 164.4 ppm; IR (CH_2Cl_2) (**4a-I**) 1637 ($\nu_{C=O}$), 2849 ($\nu_{CH\ aldehyde}$); (**4a-IV**) 1644 ($\nu_{C=O}$), 2849 ($\nu_{CH\ aldehyde}$) cm^{-1}; HRMS (EI) for $C_{16}H_{24}ClO_4PMo$ (m/z), calcd 444.0155, found 444.0290 (M^+). Anal. Calcd for $C_{16}H_{24}ClMoO_4P$: C, 43.4; H, 5.5; Cl, 8.0. Found: C, 43.4; H, 5.6; Cl, 7.9.

Synthesis of $(\eta^5\text{-}C_5H_5)Cl\{P(OMe)_3\}Mo\{\eta^4\text{-}CH_2{=}CHC(CH_3){=}CH(CHO)\}$ (4b). In a manner similar to the preparation of **4a**, the (1-methylcyclopropyl)carbyne **3b** (149 mg, 0.39 mmol) was dissolved in 40 mL of Et_2O and a solution of 1 M $HCl{\cdot}Et_2O$ (390 μL, 0.39 mmol) added. After filtration, the solution was concentrated *in vacuo* and chromatographed on alumina. The column was flushed with Et_2O and a purple band eluted using a 9:1 Et_2O/MeOH mixture. The solvent was removed and the resulting oil dissolved in C_6D_6. Isomerization of the product was monitored by ^1H NMR over a period of 5 days until no further change was observed. Recrystallization from hexane/Et_2O (4:1) afforded purple microcrystals of **4b** (29 mg, 18%). Slow evaporation of C_6D_6 from the sample over a period of several weeks at 0 °C yielded crystals suitable for an X-ray study: ^1H NMR (C_6D_6) (**4b-I**) 8.23 (d, 1H, H^1, J_{HH} = 8 Hz), 5.33 (ddd, 1H, H^4, J_{HH} = 10,9,2 Hz), 4.63 (d, 5H, C_5H_5, J_{PH} = 1 Hz), 3.40 (ddd, 1H, H^2, J_{HH} = 8, 2 Hz, J_{PH} = 4 Hz), 3.18 (d, 9H, OMe, J_{PH} = 10 Hz), 2.85 (dd, 1H, H^{5syn}, J_{HH} = 9, 2 Hz), 2.46 (dd, 1H, H^{5anti}, J_{HH} = 10,2 Hz), 2.42 (d, 3H, CH_3, J_{PH} = 3 Hz); (**4b-II**) 8.67 (d, 1H, H^1, J_{HH} = 6 Hz), 6.23 (ddd, 1H, H^4, J_{HH} = 9, 7 Hz, J_{PH} = 8 Hz), 5.73 (d, 5H, C_5H_5, J_{PH} = 1 Hz), 3.90 (d, 1H, H^2, J_{HH} = 6 Hz), 2.21 (br d, 1H, H^{5syn}, J_{HH} = 7 Hz), 2.19 (s, 3H, CH_3), 1.90 (dd, 1H, H^{5anti}, J_{HH} = 9 Hz, J_{PH} = 11 Hz), phosphite signal hidden beneath other isomers; (**4b-III**) 9.53 (d, 1H, H^1, J_{HH} = 8 Hz), 5.08 (dd, 1H, H^4, J_{HH} = 8, 8 Hz), 4.59 (d, 5H, C_5H_5, J_{PH} = 2 Hz), 3.23 (d, 9H, OMe, J_{PH} = 10 Hz), 2.86 (d, 1H, H^{5syn}, J_{HH} = 8 Hz), 2.56 (d, 3H, CH_3, J_{PH} = 3 Hz), 1.43 (dd, 1H, H^2, J_{HH} = 8 Hz, J_{PH} = 5 Hz), 1.15 (d, 1H, H^{5anti}, J_{HH} = 8 Hz);

(**4b-IV**) 10.19 (d, 1H, H^1, J_{HH} = 8 Hz), 6.04 (ddd, 1H, H^4, J_{HH} = 7, 7 Hz, J_{PH} = 7 Hz), 4.52 (d, 5H, C_5H_5, J_{PH} = 2 Hz), 3.21 (d, 9H, OMe, J_{PH} = 10 Hz), 2.38 (s, 3H, CH_3), 2.02 (dd, 1H, H^{5syn}, J_{HH} = 7 Hz, J_{PH} = 3 Hz), 1.82 (d, 1H, H^2, J_{HH} = 8 Hz), 0.24 (dd, 1H, H^{5anti}, J_{HH} = 7 Hz, J_{PH} = 9 Hz) ppm; $^{13}C\{^1H\}$ NMR (C_6D_6) (**4b-IV**) 201.4 (CHO), 115.4 (*C*=CH), 104.2 (C=*C*H), 92.7 (C_5H_5), 65.9 (CHMo), 53.2 (OMe), 43.7 (CH_2Mo), 19.3 (CH_3) ppm; $^{31}P\{^1H\}$ NMR (C_6D_6) (**4b-I**) 161.1; (**4b-II**) 166.6; (**4b-III**) 164.9; (**4b-IV**) 168.3 ppm; IR (C_6D_6) (**4b-I**) 1635 ($\nu_{C=O}$), 2846 ($\nu_{CH\ aldehyde}$); (**4b-IV**) 1656 ($\nu_{C=O}$), 2846 ($\nu_{CH\ aldehyde}$) cm^{-1}; HRMS (FAB) for $C_{14}H_{23}ClMoO_4P$ (*m/z*), calcd 419.0078, found 419.0047 $(M + H)^+$. Anal. Calcd for $C_{14}H_{22}ClMoO_4P$: C, 40.35; H, 5.33. Found: C, 40.59; H, 5.33.

Synthesis of $(\eta^5\text{-}C_5H_5)Cl\{P(OMe)_3\}Mo\{\eta^4\text{-}CH_2{=}CHC(SCH_3){=}CH(CHO)\}$ (4c). In a manner similar to the preparation of **4a**, the [1-(methylthio)cyclopropyl]carbyne **3c** (150 mg, 0.36 mmol) was dissolved in 40 mL of Et_2O and a solution of 1 M HCl·Et_2O (360 μL, 0.36 mmol) added. The solution was filtered through a glass frit to remove precipitate. The filtrate was concentrated *in vacuo* and chromatographed on alumina. After flushing with Et_2O, a purple band was eluted using a 5:1 Et_2O/MeOH mixture. Solvent was removed and the resulting oil recrystallized from hexane/Et_2O (4:1) to afford purple microcrystals of **4c** (45 mg, 28%). Isomerization of this product reached equilibrium after 5 days in C_6D_6: ^1H NMR (C_6D_6) (**4c-III**) 9.87 (d, 1H, H^1, J_{HH} = 8 Hz), 5.30 (dd, 1H, H^4, J_{HH} = 8, 8 Hz), 4.57 (d, 5H, C_5H_5, J_{PH} = 2 Hz), 3.28 (d, 9H, OMe, J_{PH} = 10 Hz), 2.93 (d, 1H, H^{5syn}, J_{HH} = 8 Hz), 2.15 (s, 3H, CH_3), 1.61 (dd, 1H, H^2, J_{HH} = 8 Hz, J_{PH} = 6 Hz), 1.16 (d, 1H, H^{5anti}, J_{HH} = 8 Hz); (**4c-IV**) 10.35 (d, 1H, H^1, J_{HH} = 7 Hz), 6.06 (ddd, 1H, H^4, J_{HH} = 7, 7 Hz, J_{PH} = 7 Hz), 4.48 (d, 5H, C_5H_5, J_{PH} = 2 Hz), 3.20 (d, 9H, OMe, J_{PH} = 10 Hz), 2.23 (dd, 1H, H^5, H^{5syn}, J_{HH} = 7 Hz, J_{PH} = 3 Hz), 2.19 (s, 3H, CH_3), 2.12 (d, 1H, H^2, J_{HH} = 7 Hz), 0.33 (dd, 1H, H^{5anti}, J_{HH} = 7 Hz, J_{PH} = 10 Hz) ppm; $^{13}C\{^1H\}$ NMR (C_6D_6) (**4c-III**) 193.0 (CHO), 100.9 (*C*H=C) 93.3 (C_5H_5), 61.2 (CHMo), 53.9 (OMe), 53.0 (CH_2Mo), 17.0 (CH_3), *C*=CH obscured; (**4c-IV**) 200.6 (CHO), 112.7 (*C*=CH), 98.0 (*C*H=C) 92.7 (C_5H_5), 68.4 (CHMo), 53.5 (OMe), 42.3 (CH_2Mo), 15.4 (CH_3) ppm; $^{31}P\{^1H\}$ NMR (C_6D_6) (**4c-III**) 159.1; (**4c-IV**) 163.4 ppm; IR (CH_2Cl_2) (**4c-III**) 1643 ($\nu_{C=O}$), 2849 ($\nu_{CH\ aldehyde}$); (**4c-IV**) 1643 ($\nu_{C=O}$), 2850 ($\nu_{CH\ aldehyde}$) cm^{-1}; HRMS (FAB) for $C_{14}H_{22}ClMoO_4PS$ (*m/z*), calcd 449.9720, found 449.9781 (M^+). Anal. Calcd for $C_{14}H_{22}ClMoO_4PS$: C, 37.47; H, 4.95. Found: C, 37.50; H, 4.88.

Synthesis of $(\eta^5\text{-}C_5H_5)Cl\{P(OMe)_3\}Mo\{\eta^4\text{-}CH_2{=}CHC(CH_2C_6H_5){=}CH(CHO)\}$ (4d). In a manner similar to the preparation of **4a**, the (1-benzylcyclopropyl)carbyne **3d** (180 mg, 0.39 mmol) was dissolved in 40 mL of Et_2O and a solution of 1 M HCl·Et_2O (390 μL, 0.39 mmol) added. The solution was filtered to remove precipitate. The filtrate was concentrated *in vacuo* and chromatographed on alumina. After flushing with Et_2O, a purple band was eluted using a 5:1 Et_2O/MeOH mixture. Solvent was removed to yield **4d** as a purple oil (46 mg, 24%). Isomerization of this product reached equilibrium after 7 days in C_6D_6: ^1H NMR (C_6D_6) (**4d-I**) 8.06 (d, 1H, H^1, J_{HH} = 8 Hz), 7.00–7.20 (m, 5H, C_6H_5), 5.60 (ddd, 1H, H^4, J_{HH} = 9, 9, 2 Hz), 4.52 (d, 5H, C_5H_5, J_{PH} = 2 Hz), 4.23 (d, 1H, CH_2, J_{HH} = 13 Hz), 3.92 (d, 1H, CH_2, J_{HH} = 13 Hz), 3.62 (ddd, 1H, H^2, J_{HH} = 8, 2 Hz, J_{PH} = 5 Hz), 3.22 (d, 9H, OMe, J_{PH} = 10 Hz), 2.88 (dd, 1H, H^{5syn}, J_{HH} = 9, 2 Hz), 2.37 (dd, 1H, H^{5anti}, J_{HH} = 9, 2 Hz); (**4d-III**) 9.80 (d, 1H, H^1, J_{HH} = 8 Hz), 7.00–7.20 (m, 5H, C_6H_5), 5.34 (dd, 1H, H^4, J_{HH} = 9, 7 Hz), 4.57 (d, 5H, C_5H_5, J_{PH} = 2 Hz), 4.55 (d, 1H, CH_2, J_{HH} = 14 Hz), 4.15 (d, 1H, CH_2, J_{HH} = 14 Hz), 3.27 (d, 9H, OMe, J_{PH} = 10 Hz), 2.90 (d, 1H, H^{5syn}, J_{HH} = 7 Hz), 1.34 (dd, 1H, H^2, J_{HH} = 8 Hz, J_{PH} = 5 Hz), 1.11 (d, 1H, H^{5anti}, J_{HH} = 9 Hz); (**4d-IV**) 10.38 (d, 1H, H^1, J_{HH} = 8 Hz), 7.00–7.20 (m, 5H, C_6H_5), 6.34 (ddd, 1H, H^4, J_{HH} = 7, 7 Hz, J_{PH} = 8 Hz), 4.66 (d, 1H, CH_2, J_{HH} = 14 Hz), 4.52 (d, 5H, C_5H_5, J_{PH} = 2 Hz), 3.85 (d, 1H, CH_2, J_{HH} = 14 Hz), 3.21 (d, 9H, OMe, J_{PH} = 10 Hz), 2.04 (dd, 1H, H^{5syn}, J_{HH} = 7 Hz, J_{PH} = 2 Hz), 1.82 (d, 1H, H^2, J_{HH} = 8 Hz), 0.27 (dd, 1H, H^{5anti}, J_{HH} = 7 Hz, J_{PH} = 8 Hz) ppm; $^{13}C\{^1H\}$ NMR (C_6D_6) (**4d-IV**) 200.3 (CHO), 141.1, 129.1, 128.5, 126.2 (C_6H_5), 105.0 (*C*=CH), 104.7 (C=*C*H), 92.6 (C_5H_5), 65.0 (CHMo), 53.1 (d, OMe, J_{PC} = 7 Hz), 44.3 (d, CH_2Mo, J_{PC} = 5 Hz), 40.2 (CH_2) ppm; $^{31}P\{^1H\}$ NMR (C_6D_6) (**4d-I**) 161.4; (**4d-III**) 164.7; (**4d-IV**) 167.1 ppm; IR (CH_2Cl_2) (**4d-I**) 1636 ($\nu_{C=O}$), 2849 ($\nu_{CH\ aldehyde}$); (**4d-IV**) 1645 ($\nu_{C=O}$), 2852 ($\nu_{CH\ aldehyde}$) cm^{-1}; HRMS (FAB) for $C_{20}H_{26}ClMoO_4P$ (*m/z*), calcd 494.0312, found 494.0413 (M^+).

Synthesis of $(\eta^5\text{-}C_5H_5)Cl_2\{P(OMe)_3\}Mo\{\eta^2\text{-}C(O)CH_2\overline{C(CH_3)CH_2CH_2}\}$ (5a). The (1-methylcyclopropyl)carbyne **3b** (64 mg, 0.17 mmol) in 10 mL of Et_2O was treated with a solution of 1 M HCl·Et_2O (850 μL, 0.85 mmol). The resulting orange precipitate was filtered, washed with Et_2O (3 × 10 mL portions), and recrystallized from CH_2Cl_2 to yield orange microcrystals of **5a** (39 mg, 51%): ^1H NMR ($CDCl_3$) 5.40 (d, 5H, C_5H_5, J_{PH} = 3 Hz), 3.37 (d, 9H, OMe, J_{PH} = 9 Hz), 3.10, 2.89 (d, 1H, C(O)-CH_2, J_{HH} = 18 Hz), 1.21 (s, 3H, CH_3), 0.38–0.61 (m, 4H, CH_2) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) 278.6 (d, C=O, J_{PC} = 15 Hz), 97.3 (C_5H_5), 55.7 (d, OMe, J_{PC} = 10 Hz), 52.5 [C(O)*C*H_2], 23.6 (CH_3), 14.5 (*C*CH_3) 13.6, 13.4 (CH_2) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$) 138.0 ppm; IR (CH_2Cl_2) 1549 cm^{-1} ($\nu_{C=O}$). Due to decomposition of solid samples, elemental analysis could not be obtained.

Synthesis of $(\eta^5\text{-}C_5H_5)Cl_2\{P(OMe)_3\}Mo\{\eta^2\text{-}C(O)CH_2\overline{C(SCH_3)CH_2CH_2}\}$ (5b). The [1-(methylthio)cyclopropyl]carbyne **3c** (90 mg, 0.22 mmol) in 10 mL of Et_2O was treated with a solution of 1 M HCl·Et_2O (1.10 mL, 1.10 mmol). The resulting orange precipitate was filtered, washed with Et_2O (3 × 10 mL portions), and recrystallized from CH_2Cl_2 to yield orange microcrystals of **5b** (62 mg, 58%): ^1H NMR ($CDCl_3$) 5.43 (d, 5H, C_5H_5, J_{PH} = 4 Hz), 3.87 (d, 9H, OMe, J_{PH} = 10 Hz), 3.23 (d, 2H, $C(O)CH_2$, J_{HH} = 18 Hz), 2.18 (s, 3H, CH_3), 0.88–1.10 (m, 4H, CH_2) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) 277.1 (d, C=O, J_{PC} = 15 Hz), 96.8 (C_5H_5), 54.8 (d, OMe, J_{PC} = 7 Hz), 50.9 [C(O)*C*H_2], 22.8 (*C*SCH_3), 16.2, 15.7 (CH_2), 14.2 (SCH_3) ppm; $^{31}P\{^1H\}$ NMR (C_6D_6) 136.6 ppm; IR (CH_2Cl_2) 1549 cm^{-1} ($\nu_{C=O}$). Anal. Calcd for $C_{14}H_{23}Cl_2MoO_4PS$: C, 34.66; H, 4.78. Found: C, 33.89; H, 4.58.

Synthesis of $(\eta^5\text{-}C_5H_5)Cl_2\{P(OMe)_3\}Mo{\equiv}C\overline{C(CH_3)CH_2CH_2}$ (6a). A solution of the (1-methylcyclopropyl)carbyne **3b** (105 mg, 0.27 mmol) in 1.0 mL of CCl_4 in a 5 mm NMR tube was left under N_2 in room light for 4 days until no further change was observed by NMR. Solvent was removed *in vacuo* and the residue washed with Et_2O (3 × 10 mL). Recrystallization of the solid remainder from CH_2Cl_2/Et_2O yielded brown-orange microcrystals of **6a** (53 mg, 45%). Orange crystals suitable for a structure determination were grown by slow diffusion of a CH_2Cl_2 solution layered with Et_2O at –40 °C: ^1H NMR ($CDCl_3$) 5.91 (d, 5H, C_5H_5, J_{PH} = 3 Hz), 3.97 (d, 9H, OMe, J_{PH} = 11 Hz), 1.50 (m, 1H, CH_2), 1.30 (s, 3H, CH_3), 1.30 (m, 1H, CH_2), 0.74 (m, 2H, CH_2) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) 375.5 (d, Mo≡C, J_{PC} = 51 Hz), 103.5 (C_5H_5), 55.4 (OMe), 38.9 (*C*CH_3), 20.9, 18.7 (CH_2), 17.9 (CH_3) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$) 145.3 ppm; HRMS (EI) for $C_{13}H_{21}ClMoO_3P$ (*m/z*), calcd 388.9972, found 388.9982 $(M - Cl)^+$. Anal. Calcd for $C_{13}H_{21}Cl_2MoO_3P$: C, 36.90; H, 5.01. Found: C, 36.53; H, 4.95.

Synthesis of $(\eta^5\text{-}C_5H_5)Cl_2\{P(OMe)_3\}Mo{\equiv}C\overline{C(SCH_3)CH_2CH_2}$ (6b). A solution of the [1-(methylthio)cyclopropyl]carbyne **3c** (80 mg, 0.19 mmol) in 1.0 mL of $CDCl_3$ in a 5 mm NMR tube was left under N_2 in room light for 4 days until no further change was observed by NMR. Solvent was removed *in vacuo* and the residue washed with Et_2O (3 × 10 mL). Recrystallization of the solid remainder from CH_2Cl_2/Et_2O yielded brown microcrystals of **6b** (26 mg, 30%): ^1H NMR ($CDCl_3$) 5.92 (d, 5H, C_5H_5, J_{PH} = 2 Hz), 3.86 (d, 9H, OMe, J_{PH} = 12 Hz), 2.37 (s, 3H, SCH_3), 1.71, 1.53 (m, 1H, CH_2), 1.22 (m, 2H, CH_2) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$) 367.2 (d, Mo≡C, J_{PC} = 51 Hz), 103.8 (C_5H_5), 55.3 (OMe), 44.1 (*C*SCH_3), 21.6, 21.0 (CH_2), 16.6 (CH_3) ppm; $^{31}P\{^1H\}$ NMR ($CDCl_3$) 136.9 ppm; HRMS (FAB) for $C_{13}H_{21}Cl_2MoO_3PS$ (*m/z*) calcd 455.9381, found 455.9391 (M^+). Anal. Calcd for $C_{13}H_{21}Cl_2MoO_3PS$: C, 34.30; H, 4.66. Found: C, 34.08; H, 4.58.

Structure Determinations of 4b and 6a. Data were collected for both compounds at room temperature on a Siemens P3m/v diffractometer equipped with a graphite monochromator utilizing MoKα radiation (λ = 0.710 73 Å). Thirty-two reflections with 20.00° ≤ 2θ ≤ 22.00° were used to refine the cell parameters for each compound. For **4b** and **6a** 4274 and 2277 reflections, respectively, were collected using the ω-scan method. For each datum, 4 reflections were measured every 96 reflections to monitor instrument and crystal stability (maximum corrections on *I* were <1%). Absorption corrections were applied on the basis of measured crystal faces using SHELXTL plus;[29] the absorption coefficients μ = 1.05 and 1.17 mm^{-1} for **4b** and **6a**, respectively.

The structures were solved by the heavy-atom method in SHELXTL plus, from which the locations of the Mo atoms were obtained. The rest of the non-hydrogen atoms were obtained from subsequent difference Fourier maps. The structures were refined in SHELXTL plus using full-matrix least squares. For **4b**, all of the non-H atoms, except the Cp C atoms, were treated anisotropically. The Cp ring was found to be disordered around the 5-fold rotation axis of the ring. Two partial Cp rings, with idealized H atoms, were refined with isotropic thermal parameters for the C atoms; their site-occupation factors were refined to 0.69(1) and 0.31(1), respectively. Positions of the methyl H atoms

(29) Sheldrick, G. M. *SHELXTL plus*; Nicolet XRD Corp.: Madison, WI, 1990.

Table 2. Crystallographic Data

	4b	6a
	A. Crystal Data (298 K)	
a, Å	10.188(1)	9.480(1)
b, Å	11.666(1)	13.383(1)
c, Å	14.128(2)	13.585(1)
β, deg	90.73(1)	
V, Å^3	1679.0(8)	1723.5(3)
d_{calc}, g cm^{-3} (298 K)	1.648	1.631
empirical formula	$C_{14}H_{22}O_4PClMo$	$C_{13}H_{21}O_3PCl_2Mo$
formula wt, g	416.68	423.11
crystal system	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_12_12_1$
Z	4	4
F(000), e	848	856
crystal size (mm^3)	0.57 × 0.19 × 0.09	0.36 × 0.30 × 0.20
	B. Data Collection (298 K)	
radiation, λ (Å)	Mo Kα, 0.710 73	
mode	ω-scan	
scan range	symmetrically over 1.2° about Kα$_{1,2}$ max	
background	offset +1.0 and −1.0 in ω from Kα$_{1,2}$ max	
scan rate, deg min^{-1}	3–6	3–6
2θ range, deg	3–55	3–55
range of hkl	$0 \le h \le 13$	$0 \le h \le 12$
	$0 \le k \le 15$	$0 \le k \le 17$
	$-18 \le l \le 18$	$0 \le l \le 17$
total reflections measured	4274	2277
unique reflections	3859	2254
absorption coeff μ (Mo Kα), mm^{-1}	1.05	1.17
min and max transmission	0.767 and 0.933	0.762 and 0.816
	C. Structure Refinement	
S, goodness of fit	1.60	1.48
reflections used	2826, $I > 3\sigma(I)$	2024, $I > 2\sigma(I)$
no. of variables	218	181
R, wR^a (%)	4.33, 5.09	4.41, 4.96
R_{int} (%)	0.013	0.00
max shift/esd	0.007	0.0004
min peak in diff Fourier map (e Å^{-3})	−0.61	−0.54
max peak in diff Fourier map (e Å^{-3})	1.11	0.65

[a] Relevant expressions are as follows, where F_o and F_c represent, respectively, the observed and calculated structure-factor amplitudes. The function minimized was $w(|F_o| - |F_c|)^2$, where $w = (\sigma(F))^{-2}$. $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. $wR = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$. $S = [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

on C7, C8, and C9 were idealized and their thermal parameters fixed. The rest of the H atoms were obtained from a difference Fourier map and refined without constraints. For **6a**, the positions of the H atoms were calculated in ideal positions and their isotropic thermal parameters were fixed. For **4b** and **6a**, 218 and 181 parameters were refined and $\sum w(|F_o| - |F_c|)^2$ was minimized; $w = 1/(\sigma|F_o|)^2$, $\sigma(F_o) = 0.5kI^{-1/2}\{[\sigma(I)]^2 + (0.02I)^2\}^{1/2}$, I(intensity) = $(I_{peak} - I_{background})$(scan rate), $\sigma(I) = (I_{peak} + I_{background})^{1/2}$(scan rate), k is the correction due to decay and Lp effects, and 0.02 is a factor used to down weight intense reflections and to account for instrument instability. The linear absorption coefficient was calculated from values from the *International Tables for X-ray Crystallography*.[30] Scattering factors for non-hydrogen atoms were taken from Cromer and Mann[31] with anomalous-dispersion corrections from Cromer and Liberman,[32] while those of hydrogen atoms were from Stewart, Davidson and Simpson.[33]

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Supplementary Material Available: Tables of bond distances, bond angles, positional parameters, and anisotropic displacement parameters for **4b** and **6a** (10 pages); listing of observed and calculated structure factors for **4b** and **6a** (23 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(30) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV, p 55 (present distributor: D. Reidel, Dordrecht).

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