Formation of 1,3-Diene Complexes upon Protonation of Cyclopropylcarbyne Complexes

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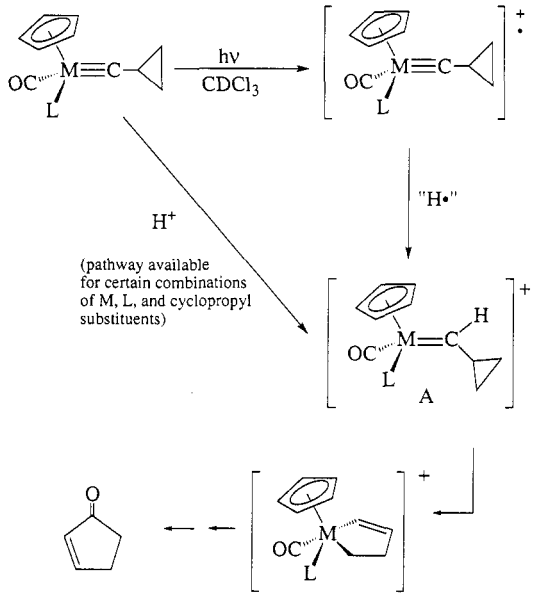
Addition of HCl to the cyclopropylcarbyne complexes $Cp[P(OMe)_3]_2Mo{\equiv}C(\overline{CRCH_2CH_2}$ [R = H, D, Me (**1**, **1-*d***, **3**)] results in formation of the diene complexes $Cp[P(OMe)_3](Cl)Mo(\eta^4\text{-}CH_2{=}CRCH{=}CH_2)$ [R = H, D, Me (**5**, **5-*d***, **6a**, **6b**)]. The metal hydride $Cp[P(OMe)_3]_2Cl_2Mo(H)$ (**4**) is the major product formed in the reaction of HCl with **1** and **1-*d***, though none is formed upon reaction with **3**. Reaction of **1** with $HBF_4{\cdot}Et_2O$ results in formation of the hydrido carbyne complex $[Cp(H)\{P(OMe)_3\}_2Mo{\equiv}C(c\text{-}C_3H_5)]^+BF_4^-$ (**7**) which eventually rearranges to the diene complex $[Cp\{P(OMe)_3\}_2Mo(\eta^4\text{-}CH_2{=}CHCH{=}CCH_2)]^+BF_4^-$ (**8**). The diene complex $Cp[P(OMe)_3](Cl)Mo(\eta^4\text{-}CH_2{=}CMeCH{=}CH_2)$ (**6b**) has been isolated and a crystal structure obtained: $P2_1/n$, a = 9.876(2) Å, b = 12.157(3) Å, c = 13.372(2) Å, β = 91.62(2)°, V = 1604.9(6) Å^3; Z = 4; R = 3.77%; R_w = 4.60% for 2162 reflections $F > 4.0\sigma(F)$.

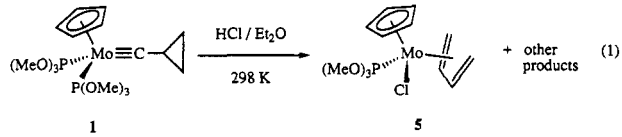
Introduction

We recently reported that photolysis of the cyclopropylcarbyne complexes $Cp(CO)[P(OMe)_3]M{\equiv}C(c\text{-}C_3H_5)$ (**9**, M = Mo; **10**, M = W) in chlorinated solvents results in formation of cyclopentenone.[1] Mechanistic studies of this reaction revealed that the photooxidation pathway did not involve acid, but in certain cases, the same products could be obtained by protonation of the starting carbyne complex.[1b] These results led us to postulate cationic carbene complexes (**A**) as common intermediates in the photooxidation and protonation pathways (Scheme 1). In the photooxidation reactions, initial electron transfer from the carbyne complex to the solvent followed by abstraction of hydrogen from the reaction medium generates cationic carbene **A**. If during thermal reaction in acidic solutions, protonation of the complex occurs at the carbyne carbon (and this is not always the case), generation of the common intermediate A would yield the same products as the photooxidation reaction.

In the related bis(phosphite) carbyne complex $Cp[P(OMe)_3]_2Mo{\equiv}C(c\text{-}C_3H_5)$ (**1**), the lack of a carbonyl makes formation of cyclopentenone impossible. Rearrangement of **1** was thus examined as a control experiment to determine the course of the reaction in the absence of CO. When **1** was treated with HCl, the majority of the inorganic material consisted of complexes in which the original carbyne ligand had been lost (vide infra). The major product in which the carbyne ligand had been retained on the metal was diene complex **5** (eq 1).[1b] Since the unexpected formation of **5** provided another entry into the well-studied class of molybdenum 1,3-diene complexes,[2] an investigation of the rearrangement was undertaken.

Scheme 1





The results implicate a mechanism related to that for the formation of cyclopentenone from **9** and **10**. The initial

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(2) (a) Pearson, A. J. *Adv. Met.-Org. Chem.* **1989**, 1–49. (b) Beevor, R. G.; Freeman, M. J.; Green, M.; Morton, C. E.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1991**, 3021–3031. (c) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 4858–4859.

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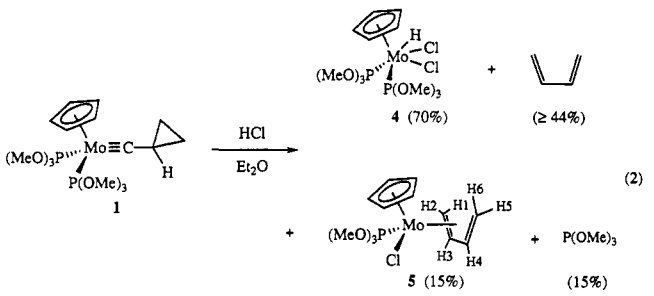
mechanistic steps for both processes are formation of a cationic cyclopropylcarbene complex and ring expansion to a metallacyclopentene.[1b] At this point the two mechanisms bifurcate and a β-H shift pathway ultimately generates the diene ligand of **5**.

Results and Discussion

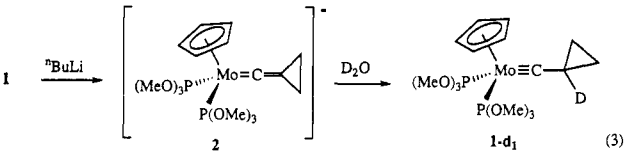
Reaction of 1 with HCl. Careful addition of 2 equiv of dilute HCl to a solution of the bis(phosphite) carbyne complex $Cp[P(OMe)_3]_2Mo{\equiv}C(c\text{-}C_3H_5)$ (**1**) in Et_2O results in formation of $Cp[P(OMe)_3]_2Cl_2MoH$ (**4**) in 70% yield (eq 2). The diene complex $Cp[P(OMe)_3](Cl)Mo(\eta^4\text{-}CH_2{=}CHCH{=}CH_2)$ (**5**) is formed in 15% yield along with an equal yield of free trimethyl phosphite (eq 2). A 44% yield of free butadiene was observed in the reaction mixtures by ^1H NMR, allowing identification of the organic fragment resulting from conversion of **1** to **4**. As no effort was made to account for the rest of the C_4 material by sampling the headspace above the solutions, the 44% represents a lower limit for the yield of butadiene. These product yields were invariant whether the reaction was performed at −40 °C or at room temperature. Also, addition of 1 equiv of HCl to **1** produced the same ratio of products [**4**:**5**:$P(OMe)_3$ = 35:8:8] while reacting with only 50% of the starting material. Control experiments in which solutions of isolated **5** were treated with HCl and $P(OMe)_3$ demonstrated that **5** is not converted to **4** under the reaction conditions.



Formulation of compound **5** as the diene complex $Cp[P(OMe)_3](Cl)Mo(\eta^4\text{-}CH_2{=}CHCH{=}CH_2)$ was based on spectroscopic data and by comparison to the related complexes $Cp[P(OMe)_3](X)Mo(\eta^4\text{-}CH_2{=}CHCH{=}CHCH_2R)$ (R = Ph, ^{t}Bu; X = Br, I).[2b] Additional evidence for the butadiene ligand was provided by air oxidation of **5** in benzene, which resulted in release of free butadiene. Complex **5** exists in solution as a single isomer with six distinct signals in the ^1H NMR, each integrating to one proton. Anisotropic shielding by the cyclopentadienyl ligand is evident in the high field signals of the anti protons H(1) (0.3 ppm) and H(6) (1.3 ppm), consistent with assignment of **5** as the endo isomer with respect to the cyclopentadienyl ligand. H(1) exhibits a 7-Hz coupling to phosphorus, as does the analogous proton in $Cp[P(OMe)_3](I)Mo(\eta^4\text{-}CH_2{=}CHCH{=}CHCH_2{}^tBu)$.[2b] Thus, the end of the diene bearing H(1) must be *cis* to the $P(OMe)_3$ ligand. The remaining ^1H NMR assignments were obtained from COSY spectra which show that H(3) is coupled to H(1) (J = 8 Hz), to H(2) (J = 7 Hz), and to H(4) (J = 8 Hz). Coupling constants among the protons in the other half of the diene ligand are similar.

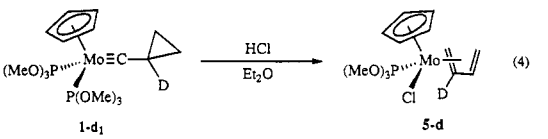
Compound **4** was identified by comparison to the related complex $Cp(PMe_3)_2I_2MoH$.[3] A weak band in the IR spectrum of **4** at 1851 cm^{-1} indicates the presence of a Mo–H bond. ^1H NMR evidence includes a triplet at 6.04 ppm (J_{PH} = 79.5 Hz) which integrates to one proton. Although the triplet is at an unusually low field for a metal hydride, its shift is comparable to that of $Cp(PMe_3)_2I_2MoH$ (a triplet at 5.21 ppm with J_{PH} = 46.6 Hz).

Reaction of 1-*d* with HCl. In order to probe the mechanism of formation of diene complexes from cyclopropylcarbyne complexes in acidic solution, we prepared the deuterated carbyne complex $Cp[P(OMe)_3]_2Mo{\equiv}C(CDCH_2CH_2)$ (**1-*d***). Deprotonation of **1** with nBuLi resulted in generation of the vinylidene anion **2** (eq 3).



Although **2** is stable at room temperature in solution, attempts at isolation were unsuccessful. Quenching of vinylidene **2** with D_2O provided **1-*d*** in 97% yield. Integration of the ^1H NMR spectra demonstrated that **1-*d*** contained less than 5% ^1H at the labeled position. Deprotonation of carbyne complexes and quenching with electrophiles has previously been utilized by Green[4,2b] and by Templeton[5] as a means of elaborating carbyne ligands. This strategy has also been used in our laboratory to prepare (1-acylcyclopropyl)carbyne complexes of the type $Cp(CO)[P(OMe)_3]Mo{\equiv}C[C(COR)CH_2CH_2]$.[6]

Addition of 2 equiv of HCl to **1-*d*** resulted in formation of the hydride complex **4** and the diene complex **5-*d*** in yields equal to those from **1**. Interestingly, the diene complex **5-*d*** was found by ^1H NMR to be 90% deuterated at H(3), cis to the trimethyl phosphite ligand (eq 4).



Reaction of 3 with HCl. In order to more firmly establish the stereochemistry assigned by ^1H NMR for **1** and **1-*d***, the methyl-substituted carbyne $Cp[P(OMe)_3]_2Mo{\equiv}C(CMeCH_2CH_2)$ (**3**) was prepared by a deprotonation/alkylation sequence similar to that employed in formation of **1-*d***. In this case, quenching of the vinylidene **2** with excess MeI at room temperature afforded **3** as a yellow solid in 90% yield.

Addition of 1 equiv of HCl to carbyne **3** in Et_2O at room temperature resulted in immediate formation of a 1:1 mixture of the two endo diene complexes **6a,b** in 70% yield (eq 5). If the reaction is carried out in toluene-d_8 at −45 °C, a 3:1 mixture of **6a**:**6b** is obtained. Interestingly, none of the hydride complex **4** was formed in this reaction. In benzene at room temperature, mixtures of **6a**:**6b** slowly convert to **6b** and after a period of 10 days, only **6b**

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(5) Brower, D. C.; Stoll, M.; Templeton, J. L. *Organometallics* **1989**, *8*, 2786–2792.
(6) Carter, J. D.; Schoch, T. K.; McElwee-White, L. *Organometallics* **1992**, *11*, 3571–3578.

Table 1. Crystallographic Data

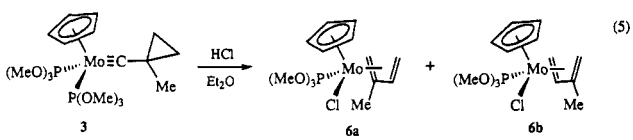
chemical formula	$C_{13}H_{22}ClMoO_3P$	T, K	295
		ρ, g cm^{-1}	1.609
fw	388.7	diffractometer	Siemens R3m/V
color, habit	dark cherry block	λ(Mo Kα), Å	0.71073
cryst size (mm)	0.20 × 0.22 × 0.30	monochromator	highly oriented graphite crystal
space group	$P2_1/n$	scan type	2θ–θ
		2θ range, deg	4.0–55.0
a, Å	9.876(2)	reflns collcd	3839
b, Å	12.157(3)	no. of ind reflns	3688 (R_{int} = 2.02%)
c, Å	13.372(2)	no. of obsd reflns	2612 ($F > 4.0\sigma(F)$)
β, deg	91.62(2)	$R(F)$, %	3.77
V, Å^3	1604.9(6)	$R_w(F)$, %	4.60
Z	4		

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)

	x	y	z	U(eq)[a]
Mo	685.2(3)	7417.9(3)	7939.5(1)	29.5(1)
Cl	1098(1)	5384.8(9)	7755(1)	47.7(4)
P	−1678(1)	6867.8(9)	7990.2(9)	34.0(3)
O(1)	−2673(3)	7826(3)	7632(3)	52(1)
O(2)	−2239(4)	6627(3)	9079(3)	51(1)
O(3)	−2285(3)	5790(3)	7467(3)	49(1)
C(1)	787(5)	7204(4)	9598(3)	48(2)
C(2)	2143(5)	7231(4)	9271(4)	53(2)
C(3)	2389(5)	8301(5)	8901(4)	53(2)
C(4)	1215(6)	8914(4)	8972(4)	55(2)
C(5)	204(5)	8256(4)	9396(4)	49(2)
C(6)	2320(5)	7599(4)	6757(4)	48(2)
C(7)	1134(5)	7340(4)	6185(3)	40(1)
C(8)	−16(5)	7973(4)	6328(3)	40(1)
C(9)	68(5)	8891(4)	6996(3)	48(2)
C(10)	1120(6)	6370(4)	5480(4)	53(2)
C(11)	−4131(5)	7682(6)	7576(6)	77(3)
C(12)	−2210(8)	5564(5)	9524(4)	80(3)
C(13)	−2123(6)	5502(5)	6459(4)	58(2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

is present. Since the conversion of **6a** to the more stable isomer **6b** is much slower than the original reaction, mixtures of **6a** and **6b** must be formed from **3** in contrast to the regiospecific rearrangement of **1**-*d*.



3 6a 6b (5)

Crystal Structure of 6b. As it was not possible to obtain single crystals of **6a**, the mixture was allowed to isomerize to **6b**. Crystals of **6b** were grown from CH_2Cl_2/hexane and were suitable for structure determination by X-ray crystallography (Table 1). An ORTEP drawing of **6b** is shown in Figure 1 and confirms the assignment of the structure as the endo isomer of the diene complex. The methyl substituent is on C(7), on the same side as the smaller chloride ligand. This relative stereochemistry of the halide and the more sterically crowded end of the diene is also found in the structure of the neopentyl-substituted diene complex Cp(I)[P(OMe)$_3$]Mo(η^4-CH_2=CHCH=$CHCH_2{}^t$Bu) (**15**).[2b]

The Mo–C bond distances in **6b** are similar to those found in other molybdenum diene complexes.[2b,7,8a] For the most closely related case, **15**, the major difference is that the neopentyl-substituted carbon is 2.388(7) Å from

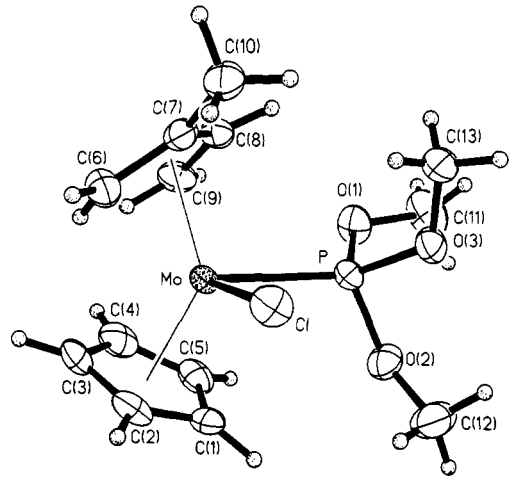


Figure 1. ORTEP drawing of **6b**. Selected bond distances (Å) and angles (deg) are as follows: Mo–Cl, 2.518(1); Mo–P, 2.430(1); Mo–C(6), 2.302(5); Mo–C(7), 2.402(5); Mo–C(8), 2.344(4); Mo–C(9), 2.264(5); C(6)–C(7), 1.416(7); C(7)–C(8), 1.390(7); C(8)–C(9), 1.430(7); Cl–Mo–P, 83.7(1); Mo–C(6)–C(7), 76.4(3); C(6)–C(7)–C(8), 118.0(4); C(7)–C(8)–C(9), 119.0(4); Mo–C(9)–C(8), 75.0(3).

the metal atom while its unsubstituted analogue in **6b** is much closer [Mo–C(6) = 2.302(5) Å]. However, asymmetry in bonding is common to both structures, with each having the substituted side of its diene fragment further from the metal than the unsubstituted side.

The internal bond of the diene ligand of **6b** [C(7)–C(8) = 1.390(7) Å] is shorter than either terminal bond [C(6)–C(7) = 1.416(7) Å; C(8)–C(9) = 1.430 Å], consistent with the metallacyclopentene resonance structures drawn for diene complexes of the electron-deficient early metals.[8c] This analysis is supported by the shorter Mo–C bonds to the terminal [Mo–C(6) = 2.302(5) Å; Mo–C(9) = 2.264(5) Å] than to the internal carbons [Mo–C(7) = 2.402(5) Å; Mo–C(8) = 2.344(4) Å].

Reaction of 1 with HBF_4. Incorporation of Cl^- into the diene complexes **5** and **6** and the regiospecific rearrangement of **1**-*d* illustrate the important role of chloride in these reactions. To investigate the function of the chloride, the reaction was performed with an acid that contains a noncoordinating anion. Reaction of the parent carbyne **1** with 1 equiv of HBF_4 in Et_2O at −40 °C resulted in formation of the hydrido carbyne complex Cp(H)[P(OMe)$_3$]$_2$Mo≡C(c-C_3H_5)]$^+BF_4^-$ (**7**) as a colorless oil in >95% yield (Scheme 2). A similar compound, [Cp(H)[P(OMe)$_3$]$_2$Mo≡$CCH_2{}^t$Bu]$^+BF_4^-$ (**11**), has been prepared by Green.[9] Unlike the neopentylcarbyne **11**, which is stable in solution, cyclopropylcarbyne **7** slowly rearranges in chloroform at room temperature to give the diene complex [Cp{P(OMe)$_3$}$_2$Mo(η^4-CH_2=CH-CH=CH_2)]$^+BF_4^-$ (**8**) in quantitative yield. Once formed, diene complex **8** does not undergo substitution by Cl^-. Addition of PPN^+Cl^- to solutions of **8** in chloroform does not result in any conversion to **5** over days at room temperature. However, addition of PPN^+Cl^- to the hydrido carbyne complex **7** in C_6D_6 does result in conversion to diene complex **5**.

(7) See, for example: (a) Cannillo, E.; Prout, K. *Acta Crystallogr.* **1977**, *B33*, 3916–3918. (b) Prout, K.; Daran, J.-C. *Acta Crystallogr.* **1977**, *B33*, 2303–2306.

(8) Diene complexes are reviewed in: (a) Kreiter, C. G. *Adv. Organomet. Chem.* **1986**, *26*, 297–375. (b) Pearson, A. J. *Adv. Met.-Org. Chem.* **1989**, *1*, 1–49. (c) Elschenbroich, Ch.; Salzer, A. *Organometallics*; VCH Publishers: New York, 1992; pp 252–272.

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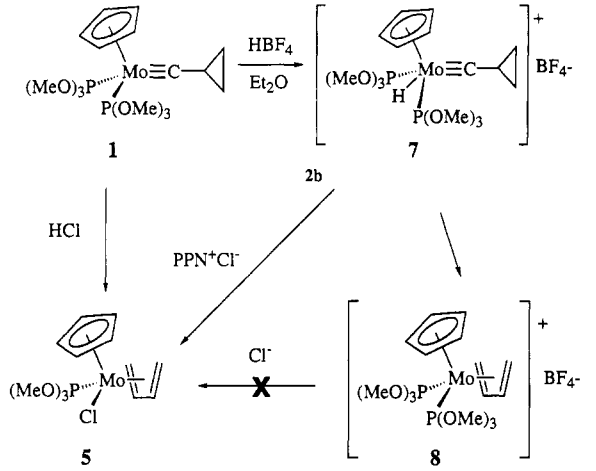
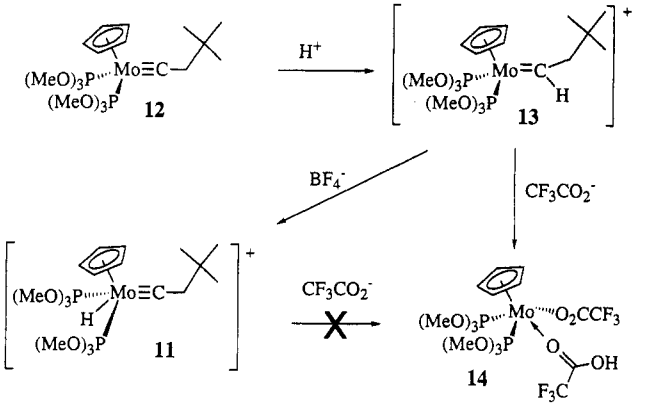
Scheme 2



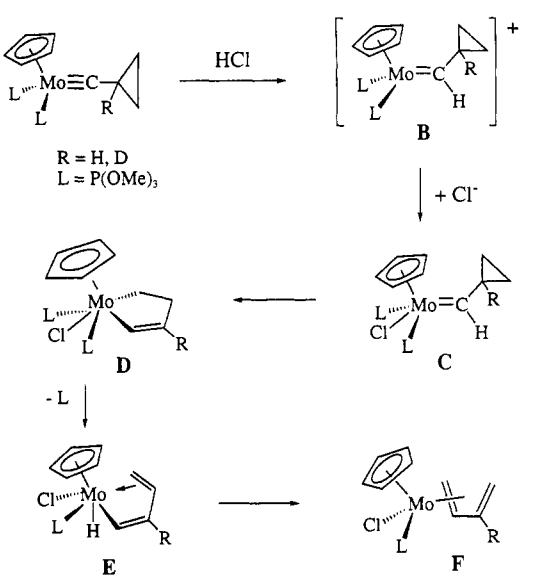
Scheme 3



These results are intriguing as protonation of carbyne complexes has been shown to yield a variety of products including metal carbenes,[10] hydrido metal carbynes,[9,12] η^2-acyl complexes,[11] and more complex binuclear species.[10b,c] If protonation proceeds via charge control, addition occurs at the carbyne carbon. Frontier control of protonation results in attack at the metal center. Previous studies by Green on protonation of the related carbyne complexes $Cp[P(OMe)_3]_2Mo{\equiv}CCH_2{}^tBu$ (**12**) have suggested that protonation is charge controlled, with addition to the carbyne carbon resulting in the 16e carbene complex **13** (Scheme 3).[9] When the counterion is the nucleophile $CF_3CO_2^-$, coordination of the anion is followed by additional protonation at the carbyne carbon, eventually leading to formation of **14** by loss of the carbyne ligand as an unidentified organic product. In the case of the BF_4^- counterion, there is no coordinating ligand and it is postulated that α-elimination of the hydride results in formation of the thermodynamically more stable hydrido carbyne complex **11**. Addition of $CF_3CO_2^-$ to solutions of **11** does not result in formation of **14**.

This behavior is similar in some regards to the protonation of **1** by HBF_4 and HCl (Scheme 2). Both **1** and **12** form hydrido carbyne complexes upon reaction with HBF_4.

Scheme 4



When the counterion is a coordinating species (Cl^- for **1**, $CF_3CO_2^-$ for **12**), the predominant inorganic product (**4** from **1**, **14** from **12**) results from protonation of the carbyne ligand and substitution by the counterion of the acid. A significant difference is that while the weakly nucleophilic $CF_3CO_2^-$ is unable to convert hydrido carbyne **11** to **14**, the stronger nucleophile Cl^- is able to react with hydrido carbyne **7** and join the mechanistic pathway to diene complex **5**.

Mechanism for Diene Complex Formation. As previously demonstrated for the photooxidative rearrangement of $Cp(CO)[P(OMe)_3]Mo{\equiv}C(c\text{-}C_3H_5)$ (**9**) to cyclopentenone,[1] much of the richness of this chemistry derives from the facile ring opening of the cyclopropyl group. The mechanism shown in Scheme 4 provides a reasonable pathway for conversion of the cyclopropyl carbyne ligands of **1** and **5** to diene ligands. The process involves a ring expansion reaction related to that invoked in the conversion of **9** to cyclopentenone. In the proposed mechanism, protonation of the carbyne carbon of **1** or **5** by HCl results in initial formation of the cationic carbene complex B. Addition of Cl^- to the metal then yields the neutral carbene complex C. Ring expansion via the organometallic version of the vinylcyclopropane-to-cyclopentene rearrangement[13] gives the metallacycle D. Phosphite loss and a β-H shift convert D to dienyl complex E. Note that a β-H shift to place the resulting olefin at the site of the departing ligand will produce a complex in which the vinyl moiety is *cis* to the remaining phosphite. This yields the proper spatial relationship between the substituent R and the phosphite ligand in the diene complexes **5**-*d* and **6a**. Reductive elimination then produces the diene complex F.

Although rearrangement of **1**-*d* regiospecifically produces **5**-*d*, as predicted by Scheme 4, the mixture of isomers **6a** and **6b** obtained from the methyl-substituted complex **3** requires that the mechanism be somewhat more complicated when substituents are present on C(1) of the cyclopropyl ring. Although it is difficult to see significant steric or electronic differences in the Scheme 4 intermediates upon methyl substitution, rearrangements in related systems are extremely sensitive to substituent effects.[1,14]

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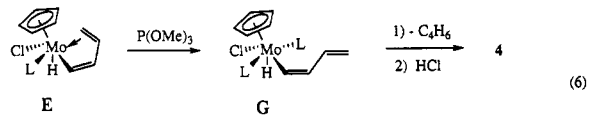
The pathway to **6b** could, for example, occur via intermediate E by decoordination of the olefin moiety of the dienyl ligand, rearrangement of the ligands, and recoordination of the dienyl fragment on the opposite face. However, at this point it is not clear where methyl substitution causes the mechanisms to diverge. The slower isomerization of **6a** to the more stable endo isomer **6b** is less mysterious, as the "envelope flip" mechanism which has been previously described[2c] would interconvert the two.

Conversion of 1 to hydride 4 and free butadiene is undoubtedly mechanistically related, but control experiments have shown that **5** does not lie on the pathway to **4**. The most reasonable point for the two pathways to diverge is at intermediate E. Decoordination of the η^2-olefin end of the diene, as suggested above as a route to **6b**, followed by addition of phosphite would yield intermediate G (eq 6). Reductive elimination of butadiene and addition of HCl would provide a pathway to **4**.



E G (6)

In the absence of the coordinating Cl^- counterion, the fate of cationic carbene complex B is somewhat different. In this case, migration of the hydrogen to the metal forms the hydrido carbyne complex **7**. Later addition of Cl^- returns **7** to the pathway to diene complexes, suggesting that the conversion of the cationic carbene B to the hydrido carbyne **7** is reversible under the reaction conditions, either by a H shift or by deprotonation/reprotonation. Interestingly, even in the absence of Cl^-, complex **7** slowly rearranges to the diene complex **8**. Reversible migration of the hydrogen from the metal to the carbyne carbon would also allow returning to a mechanistic pathway to diene complexes, although in this case, β-hydrogen elimination would not force the loss of trimethyl phosphite.

Summary

We have shown that addition of protic acids to carbynes of the type $Cp[P(OMe)_3]_2Mo{\equiv}C(\overline{CRCH_2CH_2})$ (R = H, D, Me) results in formation of the diene complexes $Cp[P(OMe)_3]ClMo(\eta^4\text{-}CH_2{=}CRCH{=}CHCH_2)$. The proposed mechanism involves initial protonation of the carbyne carbon followed by coordination of chloride. Ring expansion of the cyclopropyl group, β-hydrogen elimination, and reductive elimination yield the diene complexes. In the absence of a coordinating ligand, a hydrido carbyne complex is formed but can be converted to the diene complex upon addition of Cl^-. In the absence of Cl^-, reversible hydrogen migration provides a much slower method of joining the route to diene complexes. These mechanistic pathways are related to the route to cyclopentenones from complexes of the type $Cp(CO)[P(OMe)_3]Mo{\equiv}C(c\text{-}C_3H_5)$ but represent variants obtained when the carbonyl insertion that leads to cyclopentenones is stymied.

Experimental Section

General Methods. Standard inert atmosphere techniques were used throughout. Hexane, petroleum ether, chloroform, and methylene chloride were distilled from CaH_2. Diethyl ether, THF, and toluene were distilled from Na/Ph_2CO. All NMR solvents were degassed by three freeze–pump–thaw cycles. Benzene-d_6 was vacuum transferred from Na/Ph_2CO. $CDCl_3$ and CD_3CN were stored over 3-Å molecular sieves. All other starting materials were purchased in reagent grade and used without further purification.

^1H, ^{31}P, and ^{13}C NMR spectra were recorded on a Varian XL-400 NMR spectrometer. IR spectra were recorded on an IBM IR/90 FTIR spectrometer. High resolution mass spectra were obtained at the University of California, San Francisco.

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

$Cp[P(OMe)_3]_2Mo{\equiv}C(c\text{-}C_3H_5)$ (1). $Cp[P(OMe)_3]_2Mo{\equiv}C(c\text{-}C_3H_5)$ was prepared as described previously.[1b]

Deprotonation of $Cp[P(OMe)_3]_2Mo{\equiv}C(c\text{-}C_3H_5)$ (1). nBuLi (2.5 M, 1 equiv) in hexane was added slowly to a stirred room temperature solution of 1 (0.1–0.5 mmol) in THF (15–20 mL). Immediate formation of a deep burgundy color indicated formation of $Li[Cp[P(OMe)_3]_2Mo{=}C{=}\overline{CCH_2CH_2}]$. This compound was stable in solution at room temperature, but attempts at isolation failed. ^1H NMR (THF-d_8) = δ 5.06 (s, 5H, Cp), 3.35 (virtual t, 18H, J = 11 Hz, $P(OMe)_3$), cyclopropyl signals masked by hexane.

$Cp[P(OMe)_3]_2Mo{\equiv}C(\overline{CDCH_2CH_2})$ (1-*d*). To 154 mg (0.333 mmol) of 1 in 15 mL of THF at room temperature was added 1 equiv of 2.5 M nBuLi (133 μL) in hexane to afford an immediate color change to deep burgundy. After stirring for 5 min at room temperature, addition of excess D_2O resulted in an immediate color change back to yellow. After removal of the solvent, the residue was extracted and chromatographed on neutral alumina (3 cm × 0.5 cm) with 1:3 Et_2O/hexane as eluent. Final purification was achieved by recrystallization from hexane to afford 1-*d* as yellow crystals in 97% yield: ^1H NMR (C_6D_6) δ 5.26 (s, 5H, Cp), 3.51 (virtual t, 18H, J = 11 Hz, $P(OMe)_3$), 0.85 (dd, 2H, H_β), 0.41 (dd, 2H, H_β).

$Cp[P(OMe)_3]_2Mo{\equiv}C(\overline{CCH_3CH_2CH_2})$ (3). Compound **3** was prepared using the same procedure as described for 1-*d* and was isolated in 90% yield as a yellow solid. ^1H NMR (C_6D_6): δ 5.24 (s, 5H, Cp), 3.50 (virtual t, 18H, J = 11.6 Hz, $P(OMe)_3$), 1.24 (s, 3H, CH_3), 1.14 (m, 2H, H_β), 0.35 (m, 2H, H_β). ^{13}C NMR (C_6D_6): δ 304.4 (t, J = 28 Hz, Mo≡C), 88.8 (s, Cp), 50.8 (s, $P(OMe)_3$), 34.2 (s, C_α), 22.9 (s, C_β), 17.9 (s, CH_3). ^{31}P NMR (C_6D_6): δ 179.8. HRMS (FAB) calcd for M^+ ($C_{16}H_{30}O_6{}^{98}MoP_2$): m/z 478.0572. Found: m/z 478.0561.

$Cp[P(OMe)_3]_2Cl_2Mo(H)$ (4). To carbyne 1 (81 mg, 0.81 mmol) in 10 mL of Et_2O at −40 °C was carefully added 2 equiv (350 μL) of 1 M HCl. A red precipitate formed and was collected and washed three times with cold hexane. Recrystallization from CH_2Cl_2/hexane gave red needles in 60% yield. ^1H NMR ($CDCl_3$): δ 6.04 (t, 1H, J_{PH} = 80 Hz, Mo–H), 5.33 (t, 5H, J = 4 Hz, Cp), 3.79 (virtual t, 18H, J = 10 Hz, $P(OMe)_3$). ^{13}C NMR ($CDCl_3$): δ 98.1 (s, Cp), 53.9 (s, $P(OMe)_3$). IR (KBr): ν_{MoH} = 1851 cm^{-1} (vw). ^{31}P NMR (C_6D_6): δ 164.3. Anal. Calcd for $C_{11}H_{24}MoCl_2O_6P_2$: C, 27.46; H, 5.03; Cl, 14.74. Found: C, 27.38; H, 4.51; Cl, 14.77.

$Cp(Cl)\{P(OMe)_3\}Mo(\eta^4\text{-}CH_2{=}CHCH{=}CH_2)$ (5). A solution of 1.0 M HCl (86 μL, 0.086 mmol) was added to 1 (40 mg, 0.086 mmol) in 10 mL of Et_2O at room temperature. Column chromatography on neutral alumina with 1:1 Et_2O/THF as eluent was followed by recrystallization from Et_2O to afford **5** as purple crystals (17% yield). ^1H NMR (C_6D_6): δ 6.73 (br quintet, 1H, H(3), J_{31} = J_{34} = 8 Hz), 5.39 (br quartet, 1H, H(4)), 4.60 (s, 5H, Cp), 3.42 (d, 9H, $P(OMe)_3$, J = 10 Hz), 3.01 (d, 1H, H(5), J_{54} = 8 Hz), 1.76 (d, 1H, H(2), J_{23} = 7 Hz), 1.16 (d, 1H, H(6), J_{64} = 9 Hz), 0.20 (br t, 1H, H(1), J_{1P} = 7 Hz). ^{31}P NMR (C_6D_6): δ 165.7. HRMS (FAB) calcd for M^+ ($C_{12}H_{20}O_3{}^{98}MoClP$): m/z 375.9893. Found: m/z 375.9897.

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Cp(Cl){P(OMe)$_3$}Mo(η^4-CH$_2$=CDCH=CH$_2$) (5-*d*). 5-d was prepared in the same manner as **5** and was isolated in 15% yield. ^{1}H NMR (C_6D_6): δ 5.39 (br t, 1H, H(4), 4.60 (s, 5H, Cp), 3.42 (d, 9H, P(OMe)$_3$, J = 10 Hz), 3.01 (d, 1H, H(5), J_{54} = 8 Hz), 1.76 (s, 1H, H(2)), 1.16 (d, 1H, H(6), J_{64} = 9 Hz), 0.20 (d, 1H, H(1), J_{1P} = 7 Hz).

Cp(Cl){P(OMe)$_3$}Mo(η^4-CH$_2$=CMeCH=CH$_2$) (6a,b). A solution of 1.0 M HCl (101 μL, 0.101 mmol) was added to **1** (48 mg, 0.101 mmol) in 10 mL of Et_2O at room temperature. After stirring the violet solution for 10 min, the solvent was removed. Column chromatography on neutral alumina with 1:1 Et_2O/THF as eluent afforded **6a,b** as a 1:1 mixture in 70% yield. The mixture was entirely converted to **6b** after 10 days at room temperature in C_6D_6. **6a**: ^{1}H NMR (C_6D_6) δ 5.20 (t, 1H, H(4), J = 8 Hz), 4.56 (s, 5H, Cp), 3.40 (d, 9H, P(OMe)$_3$, J = 10 Hz), 2.95 (d, 1H, H(5), J_{54} = 8 Hz), 2.55 (s, 3H, CH$_3$), 1.61 (s, 1H, H2), 1.02 (d, 1H, H(6), J_{64} = 8 Hz), 0.31 (d, 1H, H(1), J_{1P} = 8 Hz). **6b**: ^{1}H NMR (C_6D_6) δ 6.20 (q, 1H, H(3), J_{31} = J_{32} = J_{3P} = 8 Hz), 4.58 (s, 5H, Cp), 3.35 (d, 9H, P(OMe)$_3$, J = 10 Hz), 2.60 (s, 1H, H(5)), 2.27 (s 3H, CH$_3$), 2.08 (dd, 1H, H(2), J_{2P} = 8, J_{21} = 3 Hz), 1.22 (m, 1H, H(6)), 0.25 (t, 1H, H1, J_{1P} = 8 Hz); ^{31}P NMR (C_6D_6) δ 179.8.

[Cp{P(OMe)$_3$}$_2$(H)Mo=C(c-C$_3$H$_5$)]$^+$BF$_4^-$ (7). HBF_4 (1 equiv, 39.0 mg, 0.379 mmol) in 5 mL of Et_2O was carefully added to **1** (175 mg, 0.379 mmol) in 10 mL of Et_2O at −40 °C. After stirring for 5 min, the mixture was left at −40 °C for 2 h and the solvent was then decanted, leaving 197 mg (95% yield) of **7** as a clear colorless oil. ^{1}H NMR ($CDCl_3$): δ 5.71 (s, 5H, Cp), 3.77 (virtual t, 18H, J = 11 Hz, P(OMe)$_3$), 2.00 (m, 1H, H$_\alpha$), 1.05 (m, 2H, H$_\beta$), 0.95 (m, 2H, H$_\beta$), −2.42 (t, 1H, J = 64.7 Hz, MoH). ^{13}C NMR ($CDCl_3$): δ 344 (t, J_{CP} = 25 Hz, MoC), 95.8 (s, Cp), 53.4 (s, P(OMe)$_3$), 32.1 (s, C$_\alpha$), 12.3 (s, C$_\beta$), 17.9 (s, CH$_3$). ^{31}P NMR (C_6D_6): δ 173.9.

[Cp{P(OMe)$_3$}$_2$Mo(η^4-CH$_2$=CHCH=CH$_2$)]$^+$BF$_4^-$ (8). Compound **8** is obtained from **7** in quantitative yield at room temperature in $CDCl_3$ or upon attempts to recrystallize **7**. ^{1}H NMR (C_6D_6): δ 5.60 (m, 2H, H(3)), 5.04 (s, 5H, Cp), 3.72 (virtual t, 18H, P(OMe)$_3$), 2.26 (m, 2H, H(2), 0.86 (m, 2H, H(1)). ^{13}C NMR ($CDCl_3$): δ 96.9 (s, Cp), 86.0 (s, C2), 53.8 (s, P(OMe)$_3$), 45.9 (s, C(1)). ^{31}P NMR (C_6D_6): δ 174.8. Anal. Calcd for $C_{15}H_{29}MoBF_4O_6P_2$: C, 32.75; H, 5.31; Cl, 0; F, 13.81. Found: C, 32.57; H, 5.15; Cl, 0; F, 13.43.

Crystal Structure of 6b. A dark red crystal was mounted on a glass fiber and was shown photographically to possess 2/*m* Laue symmetry. Systematic absences in the data uniquely determined the space group. No correction for absorption was required (transmission variation <10%). The structure was solved from a Patterson synthesis. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were treated as idealized isotropic contributions. All calculations used the PC version 4.2 of SHELXTL (G. Sheldrick, Siemens, Madison, WI).

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Supplementary Material Available: Figures of the ^{1}H NMR spectra for compounds **3** and **5** and tables of crystal data, bond distances and angles, hydrogen atom coordinates, and thermal parameters for **6b** (13 pages). Ordering information is given on any current masthead page.

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