Reactions of Acyl-Substituted Molybdenum Carbyne Complexes under Photooxidative and Thermal Conditions. Formation of Cyclopentenones and Oxymetallacycles

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Deprotonation of the complexes $Cp(CO)\{P(OMe)_3\}Mo{\equiv}CR$ (R = c-C_3H_5, Me) with *n*-BuLi generates anionic vinylidene species that undergo electrophilic attack at the β-carbon. Quenching of the cyclopropylidene complexes with acid chlorides and chloroformates affords the acylcyclopropyl carbyne complexes $Cp(CO)\{P(OMe)_3\}Mo{\equiv}C\{C(COR)CH_2CH_2\}$ (**3a–f**). Complexes **3a–f** undergo nucleophilic opening of the cyclopropyl ring by Cl^- to yield the oxymetallacycles $[Cp(CO)\{P(OMe)_3\}Mo\{CH{=}C(CH_2CH_2Cl)C(O)R\}]$ (**4a–f**). Similar oxymetallacycles of the type $[Cp(CO)\{P(OMe)_3\}Mo\{CH{=}C(R')C(O)R\}]$ (R′ = H, COR) are obtained upon treatment of the parent vinylidene species with acid chlorides and chloroformates. Upon photooxidation of the cyclopropyl carbynes **3a–f** in $CHCl_3$, the carbyne ligands undergo ring expansion and carbonylation to yield 3-acylcyclopentenones. A competing pathway involves formation of oxymetallacycles **4a–f**. Under thermal conditions, formation of **4a–f** predominates. Ring opening of **3a** (R = Me) and **3d** (R = OMe) with other nucleophiles ($PhNH_2$, PhSH, Br^-, H_2O) under thermal conditions also generates oxymetallacycles, but no cyclopentenones are formed in these reactions. Complex **4a** (R = Me) was characterized by X-ray crystallography: $P2_1/c$; a = 9.9718 (23) Å, b = 19.0260 (53) Å, c = 9.8171 (29) Å, β = 92.765 (22)°, V = 1860.4 (9) Å^3, Z = 4, $R(F)$ = 7.3%, $R(wF)$ = 8.8% for 2280 reflections, $F_o > 3\sigma(F_o)$.

Introduction

We recently reported that the cyclopropyl carbynes $Cp(CO)\{P(OMe)_3\}M{\equiv}C(c\text{-}C_3H_5)$ (M = Mo, W) afford cyclopentenone upon irradiation in chlorinated solvents.[1] Given that the photooxidation of metal carbynes produces species that exhibit metal radical chemistry[2] and that odd-electron organometallics have a strong tendency to undergo reaction at the metal atom instead of within an organic ligand,[3,4] these results were most unusual. As part of our investigation into this reaction, we required substituted cyclopropyl carbyne complexes. Upon substitution with acyl groups at C_β, the chemistry of the system changed dramatically to yield oxymetallacycles as well as the expected 3-substituted cyclopentenones. The synthesis and reactions of the acyl-substituted carbyne complexes are the subject of this paper.

The interconversion of carbyne and vinylidene ligands[5] has proven to be a fruitful strategy for the synthesis of metal–carbon multiply bonded complexes. For example, hydride addition to the aromatic ring of the tolyl ligand in $[(CO)_2(PPh_3)_2Os{\equiv}C(p\text{-}Tol)]^+$ generates an unusual vinylidene complex.[6] Similarly, a vinylidene species was postulated as an intermediate in the desilylation of $Ind\{P(OMe)_3\}_2Mo{\equiv}CCH(R)SiMe_3$ (Ind = η^5-C_9H_7; R = H, Ph) with NaF in aqueous acetonitrile (eq 1).[7]

$$Ind L_2Mo{\equiv}CCH(R)SiMe_3 \xrightarrow[(2)\ MeCN/H_2O]{(1)\ NaF} Ind L_2Mo{\equiv}CCH_2R \quad (1)$$

More recently, Green has elaborated the carbyne ligand of the molybdenum complexes $Cp\{P(OMe)_3\}_2Mo{\equiv}CCH_2R$ (R = Ph, ^{t}Bu) via deprotonation of the relatively acidic β-hydrogens and electrophilic quenching of the resulting anionic vinylidene species $[Cp\{P(OMe)_3\}_2Mo{=}C{=}C(H)R]^-$ (eq 2).[8] An analogous deprotonation–alkylation sequence

$$Cp L_2Mo{\equiv}CCH_2R \xrightarrow[(2)\ R'X]{(1)\ n\text{-BuLi}} Cp L_2Mo{\equiv}CCHRR' \quad (2)$$

was reported by Templeton for the Tp′ complexes $Tp'(CO)_2Mo{\equiv}CCH_2R$ (Tp′ = hydrotris(3,5-dimethylpyrazolyl)borate; R = H, Me).[9] With very few exceptions electrophilic addition takes place exclusively at the β-carbon of the vinylidene ligand to generate a new carbyne complex. Unlike the original methods used to prepare the carbyne complexes $L_nM{\equiv}CR$ in which the substituent R is derived from a lithium reagent RLi,[10] this methodology allows the introduction of a wide variety of functional groups into the carbyne moiety.

Application of this deprotonation/electrophilic attack methodology to the molybdenum carbyne complex $Cp(CO)\{P(OMe)_3\}Mo{\equiv}C(c\text{-}C_3H_5)$ has allowed the synthesis

(1) Kingsbury, K. B.; Carter, J. D.; McElwee-White, L. *J. Chem. Soc., Chem. Commun.* **1990**, 624–626.

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

(3) Recent reviews on metal radical chemistry include: (a) Trogler, W. C., Ed. *Organometallic Radical Processes*; Elsevier: Amsterdam, 1990. (b) Astruc, D. *Acc. Chem. Res.* **1991**, *24*, 36–42. (c) Baird, M. *Chem. Rev.* **1988**, *88*, 1217–1227.

(4) For examples of radical reactions within ligands see: (a) Geiger, W. E.; Gennett, T.; Lane, G. A.; Salzer, A.; Rheingold, A. L. *Organometallics* **1986**, *5*, 1352–1359. (b) Iyer, R. S.; Selegue, J. P. *J. Am. Chem. Soc.* **1987**, *109*, 910–911. (c) Freeman, M. J.; Orpen, A. G.; Connelly, N. G.; Manners, I.; Raven, S. J. *J. Chem. Soc., Dalton Trans.* **1985**, 2283–2289. (d) Zou, C.; Ahmed, K. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1989**, *111*, 1133–1135. (e) Seitz, F.; Fischer, H.; Riede, J.; Schottle, T.; Kaim, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 744–746.

(5) (a) Werner, H.; Höhn, A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 737–738. (b) Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 4474–4483. (c) Birdwhistell, K. R.; Burgmayer, S. J. N.; Templeton, J. L. *J. Am. Chem. Soc.* **1983**, *107*, 7789–7790. (d) Beevor, R. G.; Green, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Chem. Commun.* **1983**, 673–675. (e) Carvalho, M. F. N. N.; Henderson, R. A.; Pombeiro, A. J. L.; Richards, R. L. *J. Chem. Soc., Chem. Commun.* **1989**, 1796–1797. (f) Pombeiro, A. J. L.; Hills, A.; Hughes, D. L.; Richards, R. L. *J. Organomet. Chem.* **1988**, *352*, C5–C7.

(6) Roper, W. R.; Waters, J. M.; Wright, L. J. *J. Organomet. Chem.* **1980**, *201*, C27–C30.

(7) Allen, S. R.; Beevor, R. G.; Green, M.; Orpen, A. G.; Paddick, K. E.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1987**, 591–604.

(8) (a) Beevor, R. G.; Freeman, M. J.; Green, M.; Morton, C. E.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1991**, 3021–3030. (b) Beevor, R. G.; Freeman, M. J.; Green, M.; Morton, C. E.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1985**, 68–70.

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

(10) Fischer, E. O.; Massböl, A. *Chem. Ber.* **1967**, *100*, 2445–2456.

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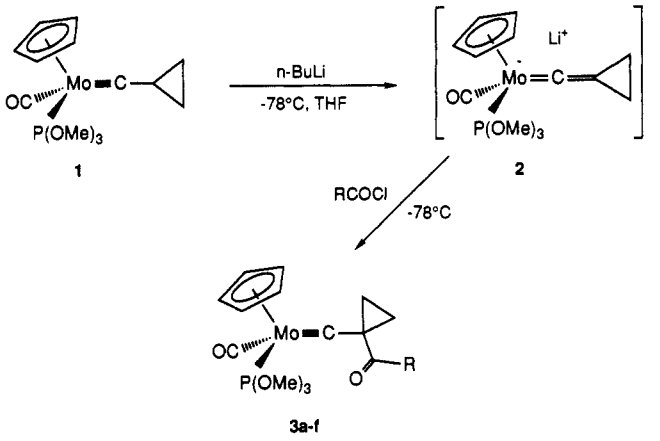
Scheme I



of a variety of acyl-substituted carbyne complexes. In this paper, we discuss their preparation and the competition between cyclopentenone formation and nucleophilic attack on the cyclopropyl ring to form oxymetallacycles. In addition, related oxymetallacycle formation from deprotonation and acylation of the methyl carbyne $Cp(CO)\{P(OMe)_3\}Mo{\equiv}CCH_3$ is discussed.

Results and Discussion

Synthesis of Acyl-Substituted Carbynes. Formation of Oxymetallacycle Complexes. Addition of 1 equiv of *n*-BuLi to a cold (−78 °C) tetrahydrofuran solution of $Cp(CO)\{P(OMe)_3\}Mo{\equiv}C(c\text{-}C_3H_5)$ (**1**) led to deprotonation of the cyclopropyl group and formation of a deep orange solution. Low-temperature ^1H NMR showed only one set of cyclopentadienyl and phosphite signals, indicating clean conversion to the cyclopropylidene anion $[Cp(CO)\{P(OMe)_3\}Mo{=}C{=}\overline{CCH_2CH_2}]^-$ (**2**). Quenching at −78 °C with acid chlorides (RCOCl; R = Me, $c\text{-}C_3H_5$, Ph) resulted in an immediate return to yellow, whereupon the solvent was removed in vacuo. The residues were extracted with hexane and filtered to remove lithium chloride, but the resultant yellow oils could not be purified by chromatography. The low-field signals of 303.2–307.8 ppm in the ^{13}C NMR spectra and characteristic carbonyl IR stretches confirmed formation of the acyl-substituted cyclopropyl carbynes $Cp(CO)\{P(OMe)_3\}Mo{\equiv}C\{\overline{C(COR)CH_2CH_2}\}$ (**3a–c**), in 69–92% yield (Scheme I). **3a** could also be prepared in high yield by the addition of acetic anhydride to **2**. Similarly, electrophilic quenching at the β-carbon of **2** with chloroformates (ROCOCl; R = Me, Et, Ph) gave the ester-substituted cyclopropyl carbynes $Cp(CO)\{P(OMe)_3\}Mo{\equiv}C\{\overline{C(CO_2R)CH_2CH_2}\}$ (**3d–f**) in 68–76% yield after chromatography on neutral alumina.

If the crude reaction mixtures containing **3a–c** and excess acyl halide were allowed to warm to room temperature and stirred for several hours, the solutions turned orange. Spectroscopic analysis indicated a mixture of the acyl carbyne and a new organometallic product in which the cyclopropyl ring was no longer intact. The analogous ester carbynes **3d–f** yielded no additional product by ^1H NMR upon warming to room temperature. Identification of the product arising from **3a** as the five-membered oxymetallacycle $Cp(CO)\{P(OMe)_3\}\overline{Mo\{CH{=}C(CH_2CH_2Cl)C(O)Me\}}$ (**4a**) was confirmed by an X-ray structure determination on the isolated dark red crystals. The ORTEP drawing is provided in Figure 1 together with pertinent bond distances and angles. Complex **4a** exhibits ring bond lengths similar to previously characterized group VI oxymetallacycles in which the ring geometry is taken as evidence for extensive π-delocalization (eq 3).[11] The vinyl proton appears at 11.71 ppm in the ^1H NMR and shows no phosphorus coupling, while C_α resonates at 253.9 ppm in the ^{13}C NMR. Such low-field resonances suggest that C_α has substantial carbenoid character and are characteristic of alkenyl carbonyl metallacycles.[11,12] Interestingly, the acetyl carbonyl carbon does show a small coupling to phosphorus ($^3J_{CP}$ = 8.1 Hz).

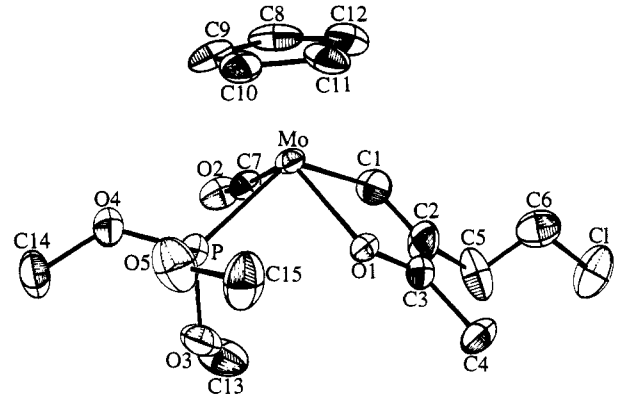
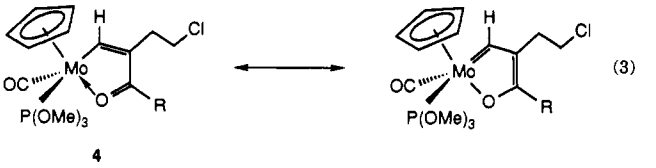


Figure 1. ORTEP drawing of **4a**. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg) are as follows: Mo–P, 2.411 (3); Mo–O1, 2.135 (6); Mo–C1, 2.11 (1); Mo–C7, 1.92 (1); C7–O2, 1.17 (1); C1–C2, 1.38 (2); C2–C3, 1.41 (2); C3–O1, 1.27 (1); P–Mo–C7, 84.3 (4); O1–Mo–C1, 72.9 (4); Mo–C1–C2, 119 (1); C1–C2–C3, 112 (1); C2–C3–O1, 118 (1); Mo–O1–C3, 118.6 (7).



To probe formation of oxymetallacycles **4a–c**, the ring cleavage by chloride anion was examined in the presence of a proton source. Addition of 1 equiv of ethereal HCl to **3a–c** in THF results in formation of **4a–c** at a substantially faster rate, possibly due to increased electrophilicity of the cyclopropyl group upon protonation of the carbonyl oxygen and rapid intramolecular proton transfer.[13] Isolated yields were limited to less than 50% due to a competing reaction in which addition of 2 equiv of HCl results in formation of the η^2-acyl complexes **5a–c** (eq 4).[14]

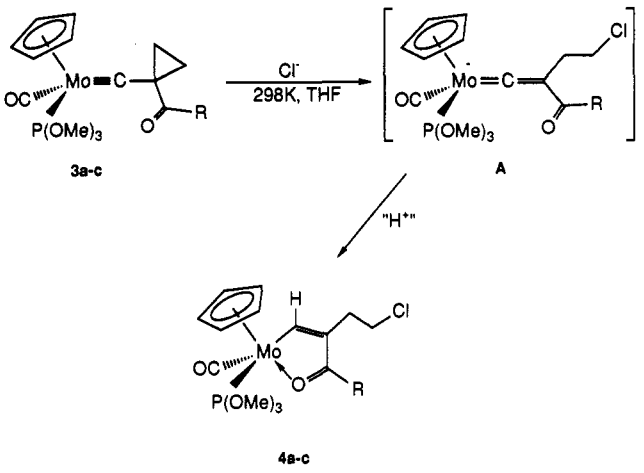
(11) (a) Chaona, S.; Lalor, F. J.; Ferguson, G.; Hunt, M. M. *J. Chem. Soc., Chem. Commun.* **1988**, 1606–1608 and references therein. (b) Alt, H. G.; Engelhardt, H. E.; Thewalt, U.; Riede, J. *J. Organomet. Chem.* **1985**, *288*, 165–177. (c) Allen, S. R.; Green, M.; Norman, N. C.; Paddick, K. E.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1983**, 1625–1633. (d) DeShong, P.; Sidler, D. R.; Rybczynski, P. J.; Slough, G. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 2575–2585.

(12) (a) Rusik, C. A.; Collins, M. A.; Gamble, A. S.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 2550–2560. (b) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *96*, 1–100. (c) Alt, H. G.; Hayen, H. I. *J. Organomet. Chem.* **1986**, *315*, 337–352. (d) Ito, T.; Tosaka, H.; Yoshida, S.; Mita, K.; Yamamoto, A. *Organometallics* **1986**, *5*, 735–739. (e) Alt, H. G.; Engelhardt, H. E. *J. Organomet. Chem.* **1985**, *288*, 149–163. (f) Charrier, C.; Collin, J.; Merour, J. Y.; Roustan, J. L. *J. Organomet. Chem.* **1978**, *162*, 57–66. (g) Watson, P. L.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 2055–2062.

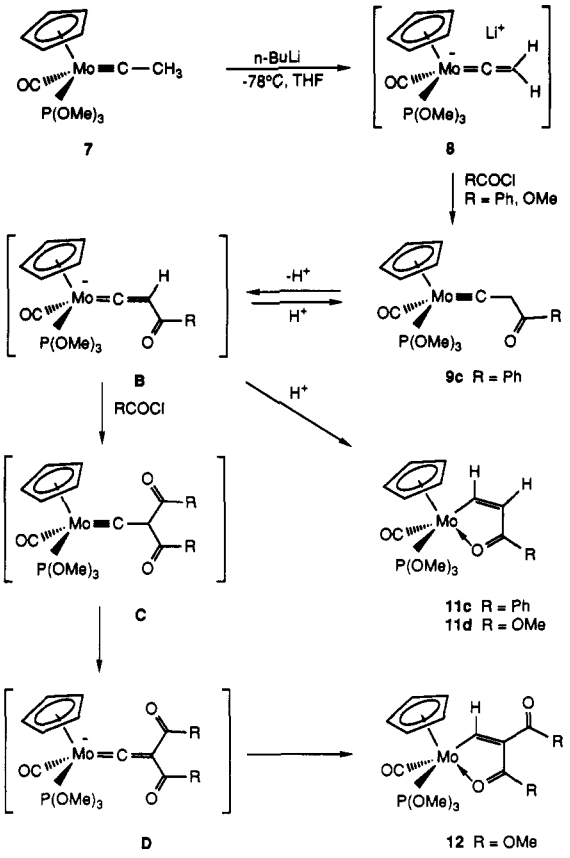
(13) Electrophilic cyclopropanes are known to undergo ring opening reactions with protic acids such as HBr; see, for example: (a) Townsend, C. A.; Christensen, S. B.; Davis, S. G. *J. Am. Chem. Soc.* **1982**, *104*, 6152–6153. (b) Bacchetti, T.; Fiecchi, A. *Gazz. Chim. Ital.* **1953**, *83*, 1037–1042.

(14) Formation of η^2-acyl complexes via protonation of group VI carbyne complexes of the type $CpL(CO)M{\equiv}CR$ (R = aryl, alkyl) is well established. For example see: Kreissl, F. R.; Sieber, W. J.; Keller, H.; Riede, J.; Wolfgruber, M. *J. Organomet. Chem.* **1987**, *320*, 83–90.

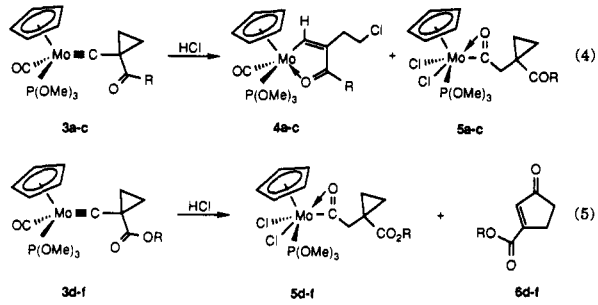
Scheme II



Scheme III



The latter reaction dominates in the addition of HCl to the esters **3d–f** in THF with only trace quantities of the metallacycles **4d–f** formed. Small amounts of the 3-oxo-1-cyclopentene-1-carboxylates **6d–f** are also formed (eq 5).



In the absence of added HCl, formation of **4a–c** can be understood in terms of initial nucleophilic attack by chloride anion on the cyclopropyl group of the acyl carbyne and addition of a proton from the reaction medium to C_α of the resulting vinylidene anion A (Scheme II). This result is somewhat surprising considering the propensity of the anionic cyclopropylidene and vinylidene complexes to undergo electrophilic addition at C_β to form metal carbynes. However, formation of **4a–c** could also occur via a multistep proton-transfer pathway in which protonation occurs initially at the metal center to generate a vinylidene hydride followed by migration to C_α with concomitant coordination of the carbonyl oxygen to the metal atom. Under acidic conditions a further mechanistic possibility involves initial protonation of the carbyne carbon followed by chloride attack on the resulting carbene cation.

In light of these observations, we examined the deprotonation and acylation of the methyl carbyne complex $Cp(CO)\{P(OMe)_3\}Mo{\equiv}CCH_3$ (**7**). As with the related Tp′ compound $Tp'(CO)_2Mo{\equiv}CCH_3$, deprotonation of **7** (−78 °C) requires approximately 2 equiv of *n*-BuLi. Addition of benzoyl chloride at −78 °C to the resultant anionic vinylidene $[Cp(CO)\{P(OMe)_3\}Mo{=}C{=}CH_2]^-$ (**8**) resulted in an immediate deepening of the orange color. Upon warming, the color of the reaction mixture intensified until after 3 h it was deep red-brown. Workup afforded $Cp(CO)\{P(OMe)_3\}Mo{\equiv}CCH_2C(O)Ph$ (**9c**), $Cp(CO)\{P(OMe)_3\}Mo{\equiv}CCH_2C(OH)(Bu)Ph$ (**10**), and the oxymetallacycle $Cp(CO)\{P(OMe)_3\}\overline{Mo\{CH{=}CHC(O)Ph\}}$ (**11c**) as a mixture (Scheme III). In the ^1H NMR spectrum, the α and β ring protons of **11c** resonate as doublets ($^3J_{\alpha\beta}$ = 8.1 Hz) at 12.06 and 7.70 ppm, respectively. The former signal also shows a fine coupling of 1.5 Hz to phosphorus. Under the same conditions quenching of **8** with methyl chloroformate yielded a mixture of the mono and diester metallacycles $Cp(CO)\{P(OMe)_3\}\overline{Mo\{CH{=}CHC(O)OMe\}}$ (**11d**) and $Cp(CO)\{P(OMe)_3\}\overline{Mo\{CH{=}C(CO_2Me)C(O)OMe\}}$ (**12**). Confirmation of the second ester group is seen in the IR stretch of 1693 cm^{-1}, while the alkenyl proton of **12** is shifted upfield to 13.35 ppm. No carbyne compounds were detected.

A likely mechanistic pathway for formation of these oxymetallacycles is shown in Scheme III. Carbyne **9** would originally arise from reaction of **8** with the acid chloride and then deprotonate to B. Formation of vinylidene anion B and its conversion to **11** have precedent in protonation of the anionic molybdenum vinylidene complexes $[Tp(CO)_2Mo{=}C{=}CXY]^-$ (X, Y = CN, CO_2Et) to form oxymetallacycle species.[11a] Note that the corresponding carbyne complexes $Tp(CO)_2Mo{\equiv}CCHXY$ were postulated as intermediates in the formation of these vinylidene compounds from attack of secondary carbanions on the chlorocarbyne ligand of $Tp(CO)_2Mo{\equiv}CCl$ but no spectroscopic evidence for their intervention could be detected. β-addition to B by a second equivalent of the acyl electrophile would yield C. In the case of benzoyl chloride the formation of **9** dominates, while for methyl chloroformate formation of **12** is competitive.

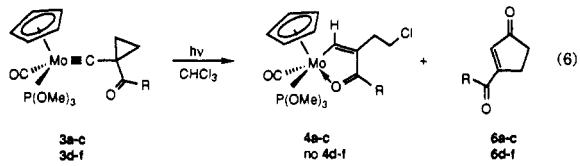
Reactions of $Cp(CO)\{P(OMe)_3\}Mo{\equiv}C\{\overline{C(COR)CH_2CH_2}\}$ with Chloroform. Irradiation of **3a** (Pyrex filtered) in $CHCl_3$ at −50 °C results in decomposition that is slow relative to that of the unsubstituted cyclopropyl complex **1** and gives lower yields of the cyclopentenone product. ^1H NMR shows the only identifiable organic products to be 3-acetyl-2-cyclopenten-1-one (**6a**, 15%), CH_3Cl (45%), and trimethyl phosphate. While the majority of the metal-containing material is intractable, **4a** is formed in about 10% yield. Further photolysis results

Table I. Product Ratios from Decomposition of 3a–f

	R	4:6 (% yield)[a] $h\nu$[b]	4:6 (% yield)[a] Δ[c]
3a	Me	10:15	50:3
3b	c-C_3H_5	6:13	54:3
3c	Ph	10:21[d]	81:0
3d	OMe	0:42	27:23
3e	OEt	0:38	38:26
3f	OPh	5:12	44:17[e]

[a] Yields were determined by integration of ^{1}H NMR spectra of reaction mixtures. [b] Temperature of photolysis: **3a–c** 223 K, **3d–f** 298 K. [c] Product ratio depends on initial concentration of carbyne. [d] Includes 13% yield of cyclopentenone. [e] Includes 4% yield of **11d**.

in the disappearance of **4a**. Similar observations are made with **3b** and **3c** (eq 6 and Table I). Photolysis of **3d** in



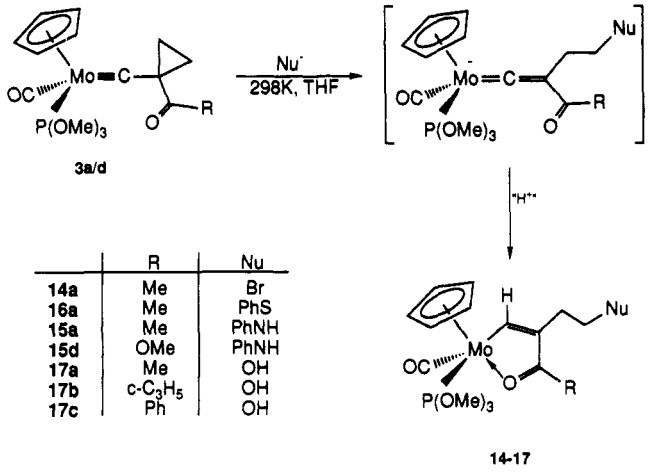
(6)

$CHCl_3$ at 0 °C gives methyl 3-oxo-1-cyclopentene-1-carboxylate, **6d**, in 42% yield by ^{1}H NMR, together with trimethyl phosphate, CH_3Cl, and small amounts of several phosphite-containing products, but no oxymetallacycle is observed. Ester carbynes **3e** and **3f** behave in similar fashion (eq 6). When the photolysis of **3d–f** is performed in $CDCl_3$, integration of ^{1}H NMR spectra shows the vinyl position of **6d–f** to be approximately 20% $^2H_1$. The poor mass balance and low percentage of ^{2}H label suggest that H abstraction is occurring from the starting materials and/or products in preference to attack on the $CDCl_3$.

In contrast to the photochemical result, allowing sealed samples of **3a–c** in $CHCl_3$ to stand at 298 K without photolysis results in clean conversion to the oxymetallacycle **4a–c**, with only traces of **6a–c** and CH_3Cl observed. Allowing sealed samples of **3d–f** to decompose under thermal conditions (room temperature, $CHCl_3$) also results in a much different product distribution. The yield of cyclopentenone **6d–f** decreases while the oxymetallacycle, **4d** is now formed in isolable quantities. The spectroscopic data for oxymetallacycles **4d–f** are very similar to those for **4a–c**. A summary of the photochemical and thermal reactivity of **3a–f** in $CHCl_3$ is shown in Table I.

Under thermal conditions the homoconjugate addition pathway dominates. Consistent with the observations upon addition of HCl, formation of **4a–f** probably proceeds via reaction with the small amounts of HCl generated from $CHCl_3$. Since η^2-acyl species are formed only when HCl is added, the concentration of acid must be critical in determining the product distribution. Under photochemical conditions the acyl–cyclopropyl complexes have two distinct modes of reactivity. The 17-e$^-$ radical species formed upon photochemical electron transfer to chloroform[15] can undergo either nucleophilic ring opening by the released chloride or a complex rearrangement and loss of the carbyne ligand to yield substituted cyclopentenones. Competition between the two pathways is clearly strongly dependent on the nature of the electron-withdrawing substituents. For esters **3d–f**, photooxidation leads only to cyclopentenones while ketones **3a–c** also give small amounts of oxymetallacycles photochemically. However,

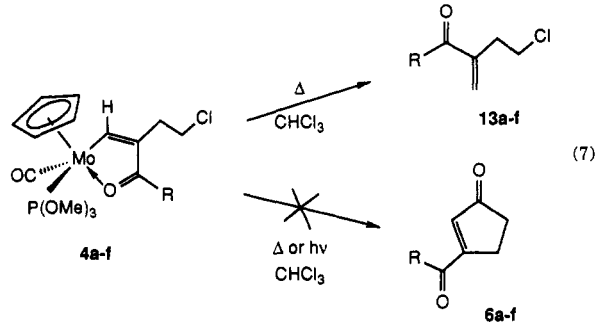
Scheme IV



	R	Nu
14a	Me	Br
16a	Me	PhS
15a	Me	PhNH
15d	OMe	PhNH
17a	Me	OH
17b	c-C_3H_5	OH
17c	Ph	OH

the observation of secondary photolysis of **4a–f** in chloroform suggests the ring-opening step may be more competitive than the overall yields indicate.

Control experiments involving both thermal and photolytic decomposition of pure **4a–f** in $CHCl_3$ were performed. These experiments do not yield cyclopentenones **6a–f** (eq 7), thus ruling out ring cleavage by chloride anion



(7)

as the initial step in the mechanism of cyclopentenone formation. Instead, solutions of oxymetallacycles **4a–f** in $CHCl_3$ undergo slow thermal degradation and the alkenyl ligand is partially recovered as the α,β-unsaturated ketone [RCOC(=CH_2)CH_2CH_2Cl] (**13a–f**), in 68–73% yield. Photolysis of **4a–f** results in decomposition but no identifiable products. Surprisingly, mass spectral analysis indicates minimal deuteration in **13a–f** (<10% $^2H_1$) when the thermolysis is carried out in $CDCl_3$. Since cleavage of the hydrido-σ-alkenyl complexes, RuH(CH=C(CH_3)-CO_2R)(PPh_3)$_3$ by DCl is known to result in stereospecific incorporation of the statistically expected 0.5 D per complex,[16] this result would seem to preclude formation of **13a–f** as a result of generation of DCl from the $CDCl_3$. However, prior exchange of any DCl with trace amounts of water in the solvent would produce the same result and also account for the relatively low deuterium incorporation in **6d–f**.

Reactions of Cp(CO){P(OMe)$_3$}Mo≡C{C(COR)-CH_2CH_2} with Nucleophiles. Electron-deficient cyclopropanes are known to undergo nucleophilic ring opening.[17] This similarity between activated organic cyclopropyl compounds and **3a–f** was explored further by reaction with

(15) One-electron reduction of $CHCl_3$ is known to give the fragmentation products Cl$^-$ and $^\bullet CHCl_2$. Buehler, R. E. In *The Chemistry of the Carbon–Halogen Bond*; Patai, S., Ed.; Wiley: London, 1973; pp 795–864.

(16) Komiya, S.; Ito, T.; Cowie, M.; Yamamoto, A.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 3874–3884.

(17) (a) Rappoport, Z., Ed. *The Chemistry Of The Cyclopropyl Group*, 1987; Chapter 9, 517–564. (b) Danishefsky, S. *Acc. Chem. Res.* **1979**, *12*, 66–72 and references therein.

a variety of nucleophilic reagents (Scheme IV). Addition of acetyl bromide to **2** at −78 °C followed by stirring at room temperature yields the bromo analogue of **4a**, Cp(CO){P(OMe)$_3$}Mo{CH=C(CH$_2$CH$_2$Br)C(O)Me} (**14a**) in 85% yield. Consistent with the increased nucleophilicity of bromide relative to chloride anion the rate of ring opening was significantly accelerated. Ring opening by nucleophiles other than halides was also observed. The reaction of **3a** with aniline led to formation of the expected oxymetallacycle, **15a**. Although the reaction time was appreciably longer, **3d** also underwent ring opening with aniline to afford **15d**. Interestingly, addition of 3-Å molecular sieves significantly accelerated the rate of formation of **15d**. Column chromatography on neutral alumina with excess aniline also facilitated clean conversion to the metallacycle. In the absence of acid or base, **3a** undergoes ring cleavage with thiophenol to give oxymetallacycle **16a** as well as several unidentified products. Isolation of pure **16a** was not possible. No oxymetallacycle was seen upon reaction of **3d** with thiophenol, although a complex mixture of products was detected. Neither **3a** nor **3d** was observed to undergo any ring opening with acetate or hydroxide anions even after prolonged exposure. However, the hydroxy metallacycles **17a–c** were slowly formed upon contact of **3a–c** with neutral alumina contaminated with water.

Summary. We have shown that the deprotonation–alkylation sequence described by Green may be applied to carbyne complexes of the type Cp(CO){P(OMe)$_3$}Mo≡CR (R = c-C$_3$H$_5$, Me). The cyclopropylidene species generated upon deprotonation is susceptible to attack at the β-carbon by acid halides and chloroformates to form the acylcyclopropyl carbyne complexes **3a–f**. Nucleophilic ring opening of the cyclopropyl group of **3a–f** by Cl$^-$ produces oxymetallacycles instead of rearranged carbyne complexes. Similarly, quenching of the anionic vinylidene species with acid chlorides and chloroformates also leads to oxymetallacycle complexes. Ring opening by Cl$^-$ is a minor pathway in the photooxidation of the acylcyclopropyl carbyne complexes in CHCl$_3$, the major pathway leading to the expected 3-acylcyclopentenones. Higher yields of the chloride-substituted metallacycles result from nucleophilic attack under thermal conditions. Treatment of **3a** and **3c** with other nucleophiles also leads to oxymetallacycles, but no cyclopentenones are formed.

Experimental Section

General Methods. Standard inert-atmosphere techniques were used throughout. Diethyl ether and THF were distilled from Na/Ph$_2$CO. Hexane, chloroform (ethanol free), and methylene chloride were distilled from CaH$_2$. All NMR solvents were degassed by three freeze–pump–thaw cycles. Benzene-d_6 and THF-d_8 were vacuum transferred from Na/Ph$_2$CO. CDCl$_3$ and CD$_2$Cl$_2$ were stored over 3-Å molecular sieves. All other starting materials were purchased in reagent grade and used without further purification.

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian XL-400 NMR spectrometer. ^{31}P NMR signals are referred to 85% H$_3$PO$_4$ and are proton decoupled. IR spectra were recorded on a Perkin-Elmer 1600 spectrometer. A Hewlett-Packard 8450A diode array spectrophotometer was used to obtain UV–vis spectra. GC/MS was performed on a HP5890A chromatograph (containing a 5 m × 0.25 mm column of SE-54 on fused silica) equipped with a HP5970 series mass-selective detector. Elemental analyses were performed by Robertson Laboratories, Madison, NJ. High-resolution mass spectra were obtained at the University of California, San Francisco.

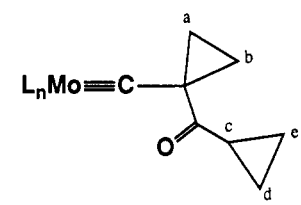
All photolyses were performed in 5-mm NMR tubes by irradiation with a Hanovia medium-pressure mercury vapor lamp in a Pyrex immersion well. Column chromatography separations were performed at low temperature (−40 °C) unless otherwise stated.

Cp(CO){P(OMe)$_3$}Mo≡CR [R = c-C$_3$H$_5$ (1), R = Me (7)] were prepared using the method described previously for their tungsten congeners.[2a]

Deprotonation of Cp(CO){P(OMe)$_3$}Mo≡C(c-C$_3$H$_5$) (1). A yellow solution of 1 (0.1–0.4 mmol) in THF (10–15 mL) was cooled to −78 °C, and 1 equiv of 2.5 M *n*-BuLi in hexane slowly added. Stirring for 30–45 min at −78 °C resulted in an orange solution due to the formation of Li[Cp(CO){P(OMe)$_3$}Mo=C=CCH$_2$CH$_2$] (**2**). Attempts at isolation of the cyclopropylidene anion failed. ^{1}H NMR (THF-d_8) δ 5.17 (s, 5 H, Cp), 3.43 (d, 9 H, P(OMe)$_3$, J = 11.9 Hz). Cyclopropyl signals were masked by hexane.

Cp(CO){P(OMe)$_3$}Mo≡C{C(COMe)CH$_2$CH$_2$} (3a). Complex 1 (111.7 mg, 0.305 mmol) was dissolved in 10 mL of THF, and the solution cooled to −78 °C. One equiv of 2.5 M *n*-BuLi (122 μL) in hexane was slowly added and the solution stirred for 45 min, during which time the reaction mixture turned from yellow to orange. To the cold solution was added excess acetic anhydride (60 μL, 0.636 mmol), and the orange color of the cyclopropylidene anion **2** was immediately discharged. Stirring of the yellow solution was continued for a further 10 min, whereupon the solvent was removed. The residue was extracted and filtered with cold hexane (−40 °C), and the crude product was obtained as a yellow oil after solvent evaporation (115.0 mg, 92%). Purification via chromatography on alumina was not possible. ^{1}H NMR (CDCl$_3$) δ 5.40 (s, 5 H, Cp), 3.57 (d, 9 H, P(OMe)$_3$, J = 12.1 Hz), 2.61 (s, 3 H, CH$_3$), 1.32–1.47 (m, 4 H, CH$_2$CH$_2$); ^{13}C NMR (C$_6$D$_6$) δ 307.0 (d, $^2J_{CP}$ = 28.8 Hz, Mo≡C), 242.0 (d, $^2J_{CP}$ = 17.9 Hz, MoCO), 203.4 (s, C=O), 91.2 (Cp), 50.9 [P(OMe)$_3$], 34.9 (Mo≡C—*C*), 30.6 (CH$_3$), 24.6, 23.9 (CH$_2$CH$_2$); ^{31}P NMR (C$_6$D$_6$) δ 202.7; IR (CH$_2$Cl$_2$) 1912 (ν_{MoCO}), 1692 cm^{-1} ($\nu_{C=O}$); HRMS (FAB), m/z calc for M$^+$ (C$_{15}$H$_{21}$O$_5$P^{98}Mo) 410.0169, found 410.0181.

Cp(CO){P(OMe)$_3$}Mo≡C[C{CO(c-C$_3$H$_5$)}CH$_2$CH$_2$] (3b). **3b** was prepared as a yellow oil in 84% yield from **1**, *n*-BuLi, and cyclopropane carbonyl chloride using the same procedure described for **3a**:



^{1}H NMR (C$_6$D$_6$) δ 5.23 (s, 5 H, Cp), 3.70 (m, 1 H, H$_c$), 3.30 (d, 9 H, P(OMe)$_3$, J = 12.2 Hz), 1.46–1.65 (m, 4 H, H$_a$ + H$_b$), 1.16 (m, 2 H, H$_d$ + H$_e$), 0.72–0.84 (m, 2 H, H$_{d'}$ + H$_{e'}$); ^{13}C NMR (C$_6$D$_6$) δ 307.6 (d, $^2J_{CP}$ = 27.4 Hz, Mo≡C), 242.3 (d, $^2J_{CP}$ = 18.9 Hz, MoCO), 205.4 (s, C=O), 91.2 (Cp), 51.2 [P(OMe)$_3$], 51.0 (Mo≡C—*C*), 24.8, 24.0 (C$_{a,b}$), 19.8 (C$_c$), 12.1, 11.8 (C$_{d,e}$); ^{31}P NMR (C$_6$D$_6$) δ 202.8; IR (CH$_2$Cl$_2$) 1905 cm^{-1} (ν_{MoCO}), 1672 cm^{-1} ($\nu_{C=O}$); HRMS (FAB), m/z calc for M$^+$ (C$_{17}$H$_{23}$O$_5$P^{92}Mo) 436.0337, found 436.0340.

Cp(CO){P(OMe)$_3$}Mo≡C{C(COPh)CH$_2$CH$_2$} (3c). **3c** was prepared as a dark yellow oil in 69% yield from **1**, *n*-BuLi, and benzoyl chloride using the same procedure described for **3a**, except only 1 equiv of the acid chloride was used: ^{1}H NMR (CDCl$_3$) δ 8.17 (d, 2 H, Ph), 7.53 (t, 1 H, Ph), 7.44 (t, 2 H, Ph), 5.19 (d, 5 H, Cp, $^2J_{HP}$ = 0.8 Hz), 3.40 (d, 9 H, P(OMe)$_3$, J = 12.2 Hz), 1.48–1.58 (m, 4 H, CH$_2$CH$_2$); ^{13}C NMR (THF-d_8) δ 303.4 (d, $^2J_{CP}$ = 27.4 Hz, Mo≡C), 241.9 (d, $^2J_{CP}$ = 19.2 Hz, MoCO), 194.9 (s, C=O), 138.1 (C$_{ipso}$), 130.9, 129.3, 128.5 (Ph), 92.0 (Cp), 51.5 [P(OMe)$_3$], 49.9 (Mo≡C—*C*), 21.2, 18.5 (CH$_2$CH$_2$); ^{31}P NMR (C$_6$D$_6$) δ 202.1; IR (CH$_2$Cl$_2$) 1911 cm^{-1} (ν_{MoCO}), 1672 cm^{-1} ($\nu_{C=O}$); HRMS (FAB), m/z calc for M$^+$ (C$_{20}$H$_{23}$O$_5$P^{98}Mo) 472.0337, found 472.0340.

Cp(CO){P(OMe)$_3$}Mo≡C{C(CO$_2$Me)CH$_2$CH$_2$} (3d). A THF solution of **1** (73.5 mg, 0.201 mmol) was deprotonated as previously described. After quenching of the vinylidene anion with methyl chloroformate the crude reaction mixture was warmed to room temperature, whereupon the solvent was removed. The residue was extracted with cold 4:1 hexane/Et$_2$O and chromatographed on neutral alumina. Elution of a pale orange band with

cold 1:3 hexane/Et_2O afforded a yellow solution. Removal of solvent gave **3d** (60.3 mg, 71%) as a dark yellow oil: ^1H NMR ($CDCl_3$) δ 5.39 (s, 5 H, Cp), 3.69 (s, 3 H, OMe), 3.56 (d, 9 H, $P(OMe)_3$, J = 12.2 Hz), 1.34–1.50 (m, 4 H, CH_2CH_2); ^{13}C NMR (C_6D_6) δ 302.3 (d, $^2J_{CP}$ = 29.5 Hz, Mo≡C), 241.9 (d, $^2J_{CP}$ = 18.7 Hz, MoCO), 171.5 (s, C=O), 91.3 (Cp), 51.8 (OMe), 51.2 [$P(OMe)_3$], 41.8 (Mo≡C—*C*), 22.4, 21.6 (CH_2CH_2); ^{31}P NMR (C_6D_6) δ 203.7; IR (THF) 1906 cm^{-1} (ν_{MoCO}), 1724 cm^{-1} ($\nu_{C=O}$); HRMS (FAB), m/z calc for M^+ ($C_{15}H_{21}O_6P^{98}Mo$) 426.0130, found 426.0142.

Cp(CO){P(OMe)$_3$}Mo≡C{C(CO$_2$Et)CH$_2$CH$_2$} (3e). **3e** was prepared from **1**, *n*-BuLi, and ethyl chloroformate as a yellow oil in 68% yield using the same method described for **3d**: ^1H NMR ($CDCl_3$) δ 5.39 (s, 5 H, Cp), 4.13 (q, 2 H, OCH_2), 3.56 (d, 9 H, $P(OMe)_3$, J = 12.2 Hz), 1.34–1.45 (m, 4 H, CH_2CH_2), 1.28 (t, 3 H, CH_3); ^{13}C NMR (C_6D_6) δ 303.0 (d, $^2J_{CP}$ = 29.8 Hz, Mo≡C), 242.1 (d, $^2J_{CP}$ = 19.3 Hz, MoCO), 171.0 (s, C=O), 91.2 (Cp), 61.1 (OCH_2), 51.3 [$P(OMe)_3$], 41.9 (Mo≡C—*C*), 22.3, 21.5 (CH_2CH_2), 14.2 (CH_3); ^{31}P NMR (C_6D_6) δ 203.8; IR (THF) 1903 cm^{-1} (ν_{MoCO}), 1712 cm^{-1} ($\nu_{C=O}$); HRMS (FAB), m/z calc for M^+ ($C_{16}H_{23}O_6P^{98}Mo$) 440.0286, found 440.0268.

Cp(CO){P(OMe)$_3$}Mo≡C{C(CO$_2$Ph)CH$_2$CH$_2$} (3f). **3f** was prepared from **1**, *n*-BuLi, and phenyl chloroformate as a yellow oil in 76% yield using the same method described for **3d**: ^1H NMR ($CDCl_3$) δ 7.35 (t, 2 H, Ph), 7.20 (t, 1 H, Ph), 7.08 (d, 2 H, Ph), 5.41 (s, 5 H, Cp), 3.57 (d, 9 H, $P(OMe)_3$, J = 12.2 Hz), 1.50–1.64 (m, 4 H, CH_2CH_2); ^{13}C NMR (C_6D_6) δ 299.9 (d, $^2J_{CP}$ = 29.0 Hz, Mo≡C), 241.4 (d, $^2J_{CP}$ = 17.1 Hz, MoCO), 170.1 (s, C=O), 150.9, 129.3, 125.7, 121.4 (Ph), 91.1 (Cp), 51.5 [$P(OMe_3)$], 41.4 (Mo≡C—*C*), 22.3, 21.5 (CH_2CH_2); ^{31}P NMR (C_6D_6) δ 203.8; IR (CH_2Cl_2) 1902 cm^{-1} (ν_{MoCO}), 1737 cm^{-1} ($\nu_{C=O}$); HRMS (FAB); m/z calc for M^+ ($C_{20}H_{23}O_6P^{98}Mo$) 488.0286, found 482.0272.

Cp(CO){P(OMe)$_3$}Mo{CH=C(CH$_2$CH$_2$Cl)C(O)Me} (4a). Acetyl chloride was added to a solution of **2** (0.204 mmol), prepared as previously described, and stirred for 30 min at −78 °C. The yellow reaction mixture was warmed to room temperature. Ethereal 1.0 M HCl (80 μL, 0.08 mmol) was carefully added over 1 h, resulting in a gradual color change to deep orange-red. Stirring was continued for a further 3 h whereupon the solvent was removed. The residue was extracted with Et_2O, and chromatographed on neutral alumina. Elution with 3:1 Et_2O/hexane afforded an orange-red band, which was collected. A yellow band due to unreacted **3a** remained on the column. Recrystallization (−30 °C) for 1:4 Et_2O/hexane gave dark red crystals of **4a** (41.5 mg, 46%): ^1H NMR ($CDCl_3$) δ 11.71 (s, 1 H, CH), 5.17 (d, 5 H, Cp, $^2J_{HP}$ = 0.9 Hz), 3.47–3.62 (m, 2 H, CH_2Cl), 3.41 (d, 9 H, $P(OMe)_3$, J = 11.2 Hz), 2.80–2.92 (m, 2 H, =CCH_2), 2.38 (s, 3 H, CH_3); ^{13}C NMR (CD_2Cl_2) δ 253.9 (s, *C*H=C), 252.5 (d, $^2J_{CP}$ = 29.4 Hz, MoCO), 191.4 (d, $^3J_{CP}$ = 8.1 Hz, C=O), 133.5 (s, CH=*C*), 91.7 (Cp), 52.2 [$P(OMe)_3$], 46.1 (CH_2Cl), 36.3 (=*C*CH_2), 22.7 (CH_3); ^{31}P NMR (C_6D_6) δ 194.7; IR ($CDCl_3$) 1850 cm^{-1} (ν_{MoCO}); HRMS (FAB), m/z calc for M^+ ($C_{15}H_{22}{}^{37}ClO_5P^{98}Mo$) 447.9918, found 447.9882. Anal. Calc for $C_{15}H_{22}ClO_5PMo$: C, 40.51; H, 4.99; Cl, 7.97. Found: C, 40.67; H, 4.88; Cl, 7.51.

Cp(CO){P(OMe)$_3$}Mo{CH=C(CH$_2$CH$_2$Cl)C(O)c-C$_3$H$_5$} (4b). Cyclopropane carbonyl chloride was added to **2** (0.200 mmol) prepared as previously described and the solution warmed to room temperature. Ethereal 1.0 M HCl (180 μL, 0.180 mmol) was slowly added over 1 h, during which time the solution turned orange-red. Stirring was continued for a further 4 h, whereupon the solvent was removed in vacuo. Workup using the identical procedure described for **4a** gave dark red crystals of **4b** (43.7 mg, 46%): ^1H NMR (C_6D_6) δ 11.79 (s, 1 H, CH), 4.86 (s, 5 H, Cp), 3.35–3.48 (m, 2 H, CH_2Cl), 3.21 (d, 9 H, $P(OMe)_3$, J = 11.2 Hz), 2.87–3.01 (m, 2 H, =CCH_2), 1.73 (m, 1 H, c-C_3H_5), 1.01 (m, 2 H, c-C_3H_5), 0.53 (m, 2 H, c-C_3H_5); ^{13}C NMR (C_6D_6) δ 253.2 (s, *C*H=C), 251.5 (d, $^2J_{CP}$ = 30.2 Hz, MoCO), 192.4 (d, $^3J_{CP}$ = 6.7 Hz, C=O), 133.2 (s, CH=*C*), 91.3 (Cp), 51.4 [$P(OMe)_3$], 45.8 (CH_2Cl), 36.4 (=*C*CH_2), 16.1, 9.2, 8.6 (c-C_3H_5); ^{31}P NMR (C_6D_6) δ 196.3; IR (CH_2Cl_2) 1848 cm^{-1} (ν_{MoCO}). Anal. Calc for $C_{17}H_{24}ClO_5PMo$: C, 43.38, H, 5.14, Cl, 7.53. Found: C, 43.05, H, 5.01, Cl, 7.42.

Cp(CO){P(OMe)$_3$}Mo{CH=C(CH$_2$CH$_2$Cl)C(O)Ph} (4c). Benzoyl chloride was added to **2** (0.306 mmol) as previously described and the solution warmed to room temperature. Ethereal 1.0 M HCl (180 μL, 0.180 mmol) was slowly added over 1 h, during which time the solution turned dark orange-red. Stirring was continued for a further 6 h, whereupon the solvent was removed in vacuo. Workup using the identical procedure described for **4a** gave dark red crystals of **4c** (68.5 mg, 44%): ^1H NMR (C_6D_6) δ 12.03 (s, 1 H, CH), 7.69 (d, 2 H, Ph), 7.18 (t, 1 H, Ph), 7.07 (t, 2 H, Ph), 4.94 (d, 5 H, Cp, $^2J_{HP}$ = 0.9 Hz), 3.42–3.52 (m, 2 H, CH_2Cl), 3.26 (d, 9 H, $P(OMe)_3$, J = 11.4 Hz), 3.07–3.27 (m, 2 H, =CCH_2); ^{13}C NMR (THF-d_8) δ 256.0 (d, *C*H=C, $^2J_{CP}$ = 9.4 Hz), 250.3 (d, $^2J_{CP}$ = 29.8 Hz, MoCO), 185.0 (d, $^3J_{CP}$ = 5.2 Hz, C=O), 139.7 (C_{ipso}, Ph), 133.7 (s, CH=*C*), 129.0, 128.8, 128.2 (Ph), 92.3 (Cp), 52.2 [$P(OMe)_3$], 45.7 (CH_2Cl), 37.2 (=*C*CH_2); ^{31}P NMR (C_6D_6) δ 191.7; IR (CH_2Cl_2) 1863 cm^{-1} (ν_{MoCO}). Anal. Calc for $C_{20}H_{24}ClO_5PMo$: C, 47.40, H, 4.77, Cl, 7.00. Found: C, 47.40; H, 4.96, Cl, 7.00.

Cp(CO){P(OMe)$_3$}Mo{CH=C(CH$_2$CH$_2$Cl)C(O)OMe} (4d). Complex **3d** (131.1 mg, 0.309 mmol) was dissolved in approximately 40 mL of $CHCl_3$ and stirred at room temperature until there was no starting material by IR. The volatile material was removed from the resultant dark orange-brown suspension. The residue was extracted with 2:1 hexane/Et_2O and chromatographed on neutral alumina. Phosphite impurities were removed by flushing the column with cold 4:1 hexane/Et_2O, and the residual orange band eluted with neat Et_2O. Recrystallization (−40 °C) from 4:1 hexane/Et_2O gave orange-red crystals of **4d** (31.3 mg, 22%): ^1H NMR (C_6D_6) δ 11.48 (s, 1 H, CH), 4.92 (d, 5 H, Cp, $^2J_{HP}$ = 0.9 Hz), 3.43 (t, 2 H, J = 7.4 Hz, CH_2Cl), 3.39 (s, 3 H, OCH_3), 3.29 (d, 9 H, $P(OMe)_3$, J = 11.5 Hz), 2.83 (t, 2 H, J = 7.4 Hz, =CCH_2); ^{13}C NMR (C_6D_6) δ 252.8 (br s, MoCO), 242.5 (s, *C*H=C), 173.7 (d, $^3J_{CP}$ = 4.7 Hz, C=O), 118.6 (s, CH=*C*), 91.2 (Cp), 51.4 [$P(OMe)_3$], 53.2 (OCH_3), 44.5 (CH_2Cl), 35.9 (=*C*CH_2); ^{31}P NMR (C_6D_6) δ 204.0; IR (CH_2Cl_2) 1826 cm^{-1} (ν_{MoCO}). Anal. Calc for $C_{15}H_{22}ClO_6PMo$: C, 39.11, H, 4.81, Cl, 7.70. Found: C, 39.17, H, 4.66, Cl, 7.48.

Cp(CO){P(OMe)$_3$}Mo{CH=C(CH$_2$CH$_2$Cl)C(O)OEt} (4e). **4e** was prepared as orange-red crystals (38%) from **3e** and $CHCl_3$ using the same procedure described for **4d**: ^1H NMR (C_6D_6) δ 11.47 (s, 1 H, CH), 4.93 (s, 5 H, Cp), 3.97 (m, 2 H, OCH_2), 3.46 (t, 2 H, J = 7.5 Hz, CH_2Cl), 3.31 (d, 9 H, $P(OMe)_3$, J = 11.5 Hz), 2.85 (t, 2 H, J = 7.5 Hz, =CCH_2), 0.93 (t, 3 H, J = 7.2 Hz, CH_3); ^{13}C NMR (C_6D_6) δ 252.7 (br s, MoCO), 241.7 (s, *C*H=C), 173.8 (d, $^3J_{CP}$ = 5.1 Hz, C=O), 119.0 (s, CH=*C*), 91.2 (Cp), 61.8 (OCH_2), 51.0 [$P(OMe)_3$], 44.6 (CH_2Cl), 35.9 (=*C*CH_2), 14.8 (CH_3); ^{31}P NMR (C_6D_6) δ 204.5; IR (CH_2Cl_2) 1828 cm^{-1} (ν_{MoCO}). Anal. Calc for $C_{16}H_{24}ClO_6PMo$: C, 40.48, H, 5.10, Cl, 7.47. Found: C, 40.40, H, 4.87, Cl, 7.25.

Cp(CO){P(OMe)$_3$}Mo{CH=C(CH$_2$CH$_2$Cl)C(O)OPh} (4f). **4f** was prepared as orange-red crystals (27%) from **3f** and $CHCl_3$ using the same procedure described for **4d**: ^1H NMR ($CDCl_3$) δ 11.55 (s, 1 H, CH), 7.33 (t, 2 H, Ph), 7.17 (t, 1 H, Ph), 7.04 (d, 2 H, Ph), 5.07 (s, 5 H, Cp), 3.64 (dt, 2 H, CH_2Cl), 3.26 (d, 9 H, $P(OMe)_3$, J = 11.4 Hz), 2.88 (dt, 2 H, =CCH_2); ^{13}C NMR (CD_2Cl_2) δ 253.6 (d, $^2J_{CP}$ = 31.7 Hz, MoCO), 246.6 (s, *C*H=C), 170.7 (d, $^3J_{CP}$ = 7.5 Hz, C=O), 152.4, 129.6, 125.7, 121.9 (Ph), 118.4 (s, CH=*C*), 91.5 (Cp), 51.3 [$P(OMe)_3$], 45.1 (CH_2Cl), 35.6 (=*C*CH_2); ^{31}P NMR (C_6D_6) δ 201.4; IR (CH_2Cl_2) 1837 cm^{-1} (ν_{MoCO}).

Deprotonation of Cp(CO){P(OMe)$_3$}Mo≡CCH$_3$ (8). Yellow solutions of **5** (0.1–0.4 mmol) in THF (10–15 mL) were cooled to −78 °C, and approximately 2 equiv of 2.5 M *n*-BuLi in hexane was slowly added. Stirring for 25–35 min at −78 °C resulted in a pale orange solution due to the formation of Li[Cp(CO){P(OMe)$_3$}Mo=C=CH_2] (**8**). Attempts at isolation and spectroscopic characterization of the vinylidene anion failed.

Cp(CO){P(OMe)$_3$}Mo{CH=CHC(O)Ph} (11c). To a chilled (−78 °C) THF solution of **20e** (0.34 mmol) was added excess PhCOCl (120 μL, 1.03 mmol). The orange solution immediately deepened in color and intensified upon warming to room temperature. After stirring for 2 h, solvent and excess acyl chloride were removed. The dark residue was extracted with cold 3:1 hexane/Et_2O (−40 °C) and chromatographed on neutral alumina. The column was flushed with the same solvent mixture and a dark orange band eluted with 1:1 THF/Et_2O. Solvent removal gave

a red-brown solid containing three products by ^{1}H NMR: Cp(CO){P(OMe)$_3$}Mo≡CCH$_2$C(O)Ph (**9c**), Cp(CO){P(OMe)$_3$}Mo≡CCH$_2$C(OH)(Bu)Ph (**10**), and Cp(CO){P(OMe)$_3$}Mo{CH=CHC(O)Ph} (**11c**). Leaving the mixture on alumina for 1–2 days resulted in slow conversion of **9c** into **11c**. **11c**: ^{1}H NMR ($CDCl_3$) δ 12.06 (dd, 1 H, H$_\alpha$, $J_{\alpha\beta}$ = 8.1 Hz, $^3J_{\alpha P}$ = 1.5 Hz), 7.80 (d, 2 H, Ph), 7.70 (d, 1 H, H$_\beta$), 7.36 (t, 2 H, Ph), 7.26 (t, 1 H, Ph), 5.21 (s, 5 H, Cp), 3.45 (d, 9 H, P(OMe)$_3$, J = 11.4 Hz); ^{13}C NMR (C_6D_6) δ 252.6 (br s, MoCO), 246.2 (s, MoC=C), 176.1 (d, $^3J_{CP}$ = 4.4 Hz, C=O), 111.3 (s, MoC=C), 91.2 (Cp), 52.5 (OMe), 51.4 [P(OMe)$_3$]; ^{31}P NMR (C_6D_6) δ 203.5; IR (CH_2Cl_2) 1861 cm^{-1} (ν_{MoCO}); m/z calc for M$^+$ ($C_{18}H_{21}O_5P^{98}Mo$) 446.0181, found 446.0171.

Cp(CO){P(OMe)$_3$}Mo{CH=C(R)C(O)OMe} [R = H (11d), CO$_2$Me (12)]. Similarly, excess ClCO$_2$Me (100 μL, 1.29 mmol) was added to a THF solution of **20e** (138.3 mg, 0.41 mmol) at −78 °C. The quenched reaction mixture was warmed to room temperature and stirred for 3 h, during which time the color changed from pale orange to deep orange brown. The solvent was removed, the residue extracted with cold 1:4 Et$_2$O/hexane and chromatographed on alumina. After the column was flushed with the same solvent mixture, an orange band was eluted with 3:1 Et$_2$O/hexane. Recrystallization from hexane afforded dark orange crystals of **11d** (35 mg, 21%): ^{1}H NMR (C_6D_6) δ 11.97 (d, 1 H, H$_\alpha$, $J_{\alpha\beta}$ = 8.5 Hz), 6.59 (d, 1 H, H$_\beta$), 4.91 (s, 5 H, Cp), 3.45 (s, 3 H, OMe), 3.32 (d, 9 H, P(OMe)$_3$, J = 11.3 Hz); ^{13}C NMR (C_6D_6) δ 252.6 (br s, MoCO), 246.2 (s, MoC=C), 176.1 (d, $^3J_{CP}$ = 4.4 Hz, C=O), 111.3 (s, MoC=C), 91.2 (Cp), 52.5 (OMe), 51.4 [(P(OMe)$_3$)]; ^{31}P NMR (C_6D_6) δ 203.5; IR (CH_2Cl_2) 1830 cm^{-1} (ν_{MoCO}). Elution of a second red brown band with 2:1 Et$_2$O/THF gave red crystals of **12** (47.6 mg, 26%) after recrystallization: ^{1}H NMR (C_6D_6) δ 13.35 (s, 1 H, CH), 4.82 (s, 5 H, Cp), 3.64 (s, 3 H, OMe), 3.54 (s, 3 H, OMe), 3.17 (d, 9 H, P(OMe)$_3$, J = 11.5 Hz); ^{13}C NMR (C_6D_6) δ 263.0 (s, MoC=C), 249.9 (s, MoCO), 175.6 (d, $^3J_{CP}$ = 4.6 Hz, C=O$_{ring}$), 160.8 (s, C=O), 113.8 (s, MoC=C), 91.7 (Cp), 53.0 (OMe), 51.4 [P(OMe)$_3$], 50.6 (OMe); ^{31}P NMR (C_6D_6) δ 197.1; IR (CH_2Cl_2) 1854 cm^{-1} (ν_{MoCO}), 1693 cm^{-1} ($\nu_{C=O}$); HRMS (FAB), m/z calc for M$^+$ ($C_{14}H_{21}O_8P^{98}Mo$) 458.0028, found 458.0029.

3-Acetyl-2-cyclopenten-1-one (6a). An NMR tube was charged with 10–15 mg of **3a** and $CHCl_3$ and photolyzed at −50 °C for 6–12 h. The crude reaction mixture was vacuum transferred and the organic fraction containing **6a** and trimethyl phosphate concentrated by evaporation. Chromatography on silica gel with 5:1 Et$_2$O/hexane afforded clean **6a** by NMR upon removal of solvent: ^{1}H NMR ($CDCl_3$) δ 6.62 (t, 1 H, CH, J = 2.1 Hz), 2.79 (m, 2 H, CH$_2$), 2.51 (m, 2 H, CH$_2$), 2.47 (s, 3 H, CH$_3$); IR ($CDCl_3$) $\nu_{C=O}$ 1719, 1685 cm^{-1}; HRMS (FAB), m/z calc for M$^+$ ($C_7H_8O_2$) 124.0524, found 124.0527.

3-(Cyclopropylcarbonyl)-2-cyclopenten-1-one (6b). An NMR tube was charged with 10–15 mg of **3b** and $CHCl_3$ and photolyzed at −50 °C for 6–9 h. The crude reaction mixture was completely oxidized by exposure to air and the solvent removed by evaporation. The organic material was extracted from the residue with hexane and chromatographed on silica gel. Elution with Et$_2$O afforded clean **6b** upon removal of solvent: ^{1}H NMR ($CDCl_3$) δ 6.74 (t, 1 H, CH, J = 2.1 Hz), 2.82 (m, 2 H, CH$_2$), 2.51 (m, 2 H, CH$_2$), 2.41 (s, 1 H, CH), 0.98 (m, 2 H, CH$_2$), 0.69 (m, 2 H, CH$_2$); IR ($CDCl_3$) 1713, 1669 cm^{-1} ($\nu_{C=O}$); GC/MS m/z (rel intensity) 150 (M$^+$, 27), 69 (100).

3-Benzoyl-2-cyclopenten-1-one (6c). Irradiation of **3c** in $CHCl_3$ gave a mixture of 2-cyclopenten-1-one and **6c** upon workup using the same method described for **6b**. Decomposition of **6c** was minimized by oxidizing the crude reaction mixture in hexane: ^{1}H NMR (C_6D_6) δ 7.10–7.70 (m, 5 H), 5.97 (t, 1 H), 2.32 (m, 2 H), 1.87 (m, 2 H).

Methyl 3-Oxo-1-cyclopentene-1-carboxylate (6d). Prepared in pure form from **3d** by the same method described for **6a**: ^{1}H NMR ($CDCl_3$) δ 6.74 (t, 1 H), 3.86 (s, 3 H), 2.84 (m, 2 H), 2.53 (m, 2 H). Literature values are in agreement.[18]

Ethyl 3-Oxo-1-cyclopentene-1-carboxylate (6e). Prepared in pure form from **3e** by the same method described for **6a**: ^{1}H NMR ($CDCl_3$) δ 6.73 (t, 1 H), 4.31 (q, 2 H), 2.84 (m, 2 H), 2.52 (m, 2 H), 1.33 (t, 3 H). Literature values are in agreement.[18]

Phenyl 3-Oxo-1-cyclopentene-1-carboxylate (6f). Prepared from **3f** using the same method described for **6b**. A significant amount of **6d** was also isolated: ^{1}H NMR (CD_2Cl_2) δ 7.45 (t, 2 H), 7.31 (t, 1 H), 7.18 (d, 2 H), 6.93 (t, 1 H), 2.96 (m, 2 H), 2.58 (m, 2 H); IR (CH_2Cl_2) 1735, 1719 cm^{-1} ($\nu_{C=O}$); GC/MS m/z (rel intensity) 202 (M$^+$, 38), 109 (100).

RCOC(=CH$_2$)CH$_2$CH$_2$Cl [R = Me (13a), c-C$_3$H$_5$ (13b), Ph (13c)]. The procedure described is for **13a** which is typical of the series. A Schlenk flask was charged with **4a** and $CHCl_3$ and stirred at room temperature until the red color was dissipated. The crude reaction mixture was vacuum transferred, and the organic fraction containing **13a** and trimethyl phosphate concentrated by evaporation. Chromatography on silica gel with Et$_2$O afforded clean **13a** by NMR upon removal of solvent. Alternatively, a solution of **3a** in $CHCl_3$ was stirred at room temperature until no further color changes took place and worked up in identical fashion. **13a**: ^{1}H NMR ($CDCl_3$) δ 6.15 (s, 1 H), 5.93 (s, 1 H), 3.61 (t, 2 H), 2.71 (t, 2 H), 2.34 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 199.1 (s, C=O), 144.7 (C=CH$_2$), 128.3 (C=CH$_2$), 43.1 (CH$_2$Cl), 34.2 (=CCH$_2$), 25.7 (CH$_3$); IR ($CDCl_3$) 1676 cm^{-1} ($\nu_{C=O}$); GC/MS m/z (rel intensity) 134/132 (M$^+$, 4), 53 (100). **13b**: ^{1}H NMR ($CDCl_3$) δ 6.28 (s, 1 H), 5.91 (s, 1 H), 3.60 (t, 2 H), 2.73 (t, 2 H), 2.41 (m, 1 H), 1.06 (m, 2 H), 0.91 (m, 2 H); IR ($CDCl_3$) 1662 cm^{-1} ($\nu_{C=O}$) GC/MS m/z (rel intensity) 160/158 (M$^+$, 10/34), 109 (100). A slight modified procedure was used for **13c**. Instead of vacuum transfer, the crude reaction mixture was completely oxidized by exposure to air and chromatographed with 5:1 Et$_2$O/hexane as the eluent: ^{1}H NMR ($CDCl_3$) δ 7.75 (d, 1 H), 7.54 (t, 2 H), 7.43 (t, 2 H), 6.00 (s, 1 H), 5.78 (s, 1 H), 3.61 (t, 2 H), 2.92 (t, 2 H); IR ($CDCl_3$) 1654 cm^{-1} ($\nu_{C=O}$); GC/MS m/z (rel intensity) 196/194 (M$^+$, 2/5), 105 (100).

ROCOC(=CH$_2$)CH$_2$CH$_2$Cl [R = Me (13d), Et (13e), Ph (13f)]. Clean **13d** and **13e** were prepared from **4d** and **4e**, respectively, using the same method described for **13a**. Ester **13f** was prepared in analogous fashion to **13c**. For **13d**: ^{1}H NMR ($CDCl_3$) δ 6.29 (s, 1 H), 5.69 (s, 1 H), 3.75 (s, 3 H), 3.65 (t, 2 H), 2.75 (t, 2 H); IR ($CDCl_3$) 1720 cm^{-1} ($\nu_{C=O}$); GC/MS m/z ($CDCl_3$) 119/117 (M$^+$ − OMe, 11/35), 53 (100). **13e**: ^{1}H NMR ($CDCl_3$) δ 6.27 (d, 1 H), 5.66 (q, 1 H), 4.19 (q, 2 H), 3.60 (t, 2 H), 2.73 (t, 2 H), 1.28 (t, 3 H); IR ($CDCl_3$) 1712 cm^{-1} ($\nu_{C=O}$); GC/MS m/z ($CDCl_3$) 127 (M$^+$ − Cl, 46), 98 (100). **13f**: ^{1}H NMR ($CDCl_3$) δ 7.38 (t, 2 H), 7.23 (t, 1 H), 7.10 (d, 2 H), 6.55 (s, 1 H), 5.89 (s, 1 H), 3.74 (t, 2 H), 2.86 (t, 2 H); IR ($CDCl_3$) 1727 cm^{-1} ($\nu_{C=O}$); GC/MS m/z ($CDCl_3$) 212/210 (M$^+$, 2/6), 119/117 (31/100).

Cp{P(OMe)$_3$}(CO)Mo{CH=C(CH$_2$CH$_2$R)C(O)Me} [R = Br (14a), NHPh (15a), SPh (16a)]. Excess acetyl bromide was added to a chilled solution of **2** (0.383 mmol) and stirred for 30 min at −78 °C. The yellow reaction mixture was warmed to room temperature and stirred for a further 3 h whereupon the solvent was removed. The orange red residue was extracted with Et$_2$O and purified via chromatography on neutral alumina with neat Et$_2$O as eluent. Recrystallization (−30 °C) of the resultant oil (159.0 mg, 85%) from hexane gave **14a** as dark red crystals: ^{1}H NMR (C_6D_6) δ 11.84 (s, CH), 4.94 (d, Cp, $^2J_{HP}$ = 0.9 Hz), 3.75 (t, 2 H, CH$_2$Br, J = 6.3 Hz), 3.27 (d, 9 H, P(OMe)$_3$, J = 11.2 Hz), 2.80 (m, 2 H, =CCH$_2$), 2.12 (s, 3 H, CH$_3$); ^{31}P NMR (C_6D_6) δ 194.6; IR (CH_2Cl_2) 1850 cm^{-1} (ν_{MoCO}). Anal. Calc for $C_{15}H_{22}BrO_5PMo$: C, 36.82, H, 4.50, Cl, 16.34. Found: C, 36.51, H, 4.34, Cl, 15.87.

To a solution of **3d** (52.1 mg, 0.128 mmol) in Et$_2$O (15 mL) was added excess PhNH$_2$ (0.30 mL, 3.29 mmol), and the mixture stirred for 8 h at room temperature. Solvent was removed and the crude reaction mixture worked up in similar fashion to **14a** to give **15a** as an orange red solid (33.6 mg, 52%): ^{1}H NMR ($CDCl_3$) δ 11.67 (s, 1 H, CH), 7.13 (t, 2 H, Ph), 6.65 (t, 1 H, Ph), 6.56 (d, 2 H, Ph), 5.15 (s, 5 H, Cp), 3.37 (d, 9 H, P(OMe)$_3$, J = 11.2 Hz), 3.03–3.27 (m, 2 H, CH$_2$NHPh), 2.62–2.82 (m, 2 H, =CCH$_2$), 2.34 (s, 3 H, CH$_3$); ^{31}P NMR (C_6D_6) δ 194.6; IR (C_6D_6) 1875 cm^{-1} (ν_{MoCO}).

Using the same method as described for **14a** quenching of **2** with phenyl thioacetate yielded **16a** and a number of unidentified products upon workup. Attempts at purification of **16a** failed: ^{1}H NMR (C_6D_6) δ 11.96 (s, 1 H, CH), 7.33 (d, 2 H, Ph), 7.03 (t, 2 H, Ph), 6.91 (t, 2 H, Ph), 4.96 (s, 5 H, Cp), 3.31 (d, 9 H, P(OMe)$_3$,

(18) Spectral data are in agreement with literature: Lange, G. L.; Decicco, C. P.; Willson, J.; Strickland, L. A. *J. Org. Chem.* **1989**, *54*, 1805–1810. For **11e** see: Mori, K. *Tetrahedron* **1978**, 915–920.

J = 11.3 Hz), 2.98 (t, 2 H, CH_2SPh), 2.77 (t, 2 H, $=CCH_2$), 2.16 (s, 3 H, CH_3).

Cp(CO){P(OMe)$_3$}Mo{CH=C(CH$_2$CH$_2$NHPh)C(O)OMe} (15d). A mixture of **3a** (52.1 mg, 0.124 mmol) and $PhNH_2$ (0.20 mL, 2.19 mmol) in Et_2O was applied to a column of alumina and left to stand at 298 K. After approximately 9 h the column was flushed with 4:1 Et_2O/CH_3CN and a pale orange solution collected. Removal of the solvent and excess $PhNH_2$ afforded **15d** as an orange solid in 33% yield: ^1H NMR ($CDCl_3$) δ 11.18 (s, 1 H, CH), 7.13 (t, 2 H, Ph), 6.64 (t, 1 H, Ph), 6.57 (d, 2 H, Ph), 5.10 (d, Cp, $^2J_{HP}$ = 0.9 Hz), 3.82 (s, 3 H, OMe), 3.45 (d, 9 H, $P(OMe)_3$, J = 11.4 Hz), 3.02-3.21 (m, 2 H, CH_2NHPh), 2.52-2.67 (m, 2 H, $=CCH_2$), 2.12 (s, 3 H, CH_3); ^{31}P NMR (C_6D_6) δ 203.6; IR (THF) 1843 cm^{-1} (ν_{MoCO}); HRMS (FAB), m/z calc for M^+ ($C_{17}H_{25}NO_6P^{98}Mo$) 519.0708, found 519.0696.

Cp(CO){P(OMe)$_3$}Mo{CH=C(CH$_2$CH$_2$OH)C(O)R} [R = Me (17a), c-C$_3$H$_5$ (17b), Ph (17c)]. A yellow solution of **3a** (57.2 mg, 0.14 mmol) in Et_2O was applied to a column of alumina to which approximately 1.3% H_2O had been added. The resultant orange band was eluted at regular intervals for 72 h with 20:1 THF/EtOH and **17a** obtained as a red solid (30.7 mg, 51%) upon removal of solvent. The cyclopropyl and phenyl complexes were prepared in similar fashion from **3b** and **3c** in 74% and 46% yield, respectively. **17a**: ^1H NMR ($CDCl_3$) δ 11.67 (s, 1 H, CH), 5.15 (s, 5 H, Cp), 3.60-3.65 (m, 2 H, CH_2OH), 3.38 (d, 9 H, $P(OMe)_3$, J = 11.1 Hz), 2.62-2.74 (m, 2 H, $=CCH_2$), 2.35 (s, 3 H, CH_3); ^{13}C NMR (C_6D_6) δ 253.5 (d, $CH=C$, $^2J_{CP}$ = 4.3 Hz), 251.5 (d, $^2J_{CP}$ = 29.4 Hz, MoCO), 191.1 (s, $C=O$), 133.6 (s, $CH=C$), 91.4 (Cp), 63.7 (CH_2OH), 51.7 [$P(OMe)_3$], 36.7 ($=CCH_2$), 22.7 (CH_3); ^{31}P NMR (C_6D_6) δ 195.2; IR (CH_2Cl_2) 1845 cm^{-1} (ν_{MoCO}); HRMS (FAB), m/z calc for M^+ ($C_{15}H_{23}O_6P^{98}Mo$) 428.0286, found 428.0261. **17b**: ^1H NMR (C_6D_6) δ 11.88 (s, 1 H, CH), 4.87 (s, 5 H, Cp), 3.65 (m, 2 H, CH_2OH), 3.22 (d, 9 H, $P(OMe)_3$, J = 11.6 Hz), 2.76-2.89 (m, 2 H, $=CCH_2$), 1.91 (m, 1 H, c-C_3H_5), 1.05 (m, 2 H, c-C_3H_5), 0.57 (m, 2 H, c-C_3H_5); ^{31}P NMR (C_6D_6) δ 196.7; IR (CH_2Cl_2) 1844 cm^{-1} (ν_{MoCO}); HRMS (FAB), m/z calc for M^+ ($C_{17}H_{25}O_6P^{98}Mo$) 490.0433, found 490.0440. **17c**: ^1H NMR (C_6D_6) δ 12.13 (d, 1 H, CH, $^3J_{HP}$ = 1.4 Hz), 7.82 (d, 2 H, Ph), 7.21 (t, 2 H, Ph), 7.10 (t, 1 H, Ph), 4.95 (s, 5 H, Cp), 3.70 (m, 2 H, CH_2OH), 3.27 (d, 9 H, $P(OMe)_3$, J = 11.2 Hz), 2.94-3.10 (m, 2 H, $=CCH_2$); ^{31}P NMR (C_6D_6) δ 192.1; IR (CH_2Cl_2) 1862 cm^{-1} (ν_{MoCO}); HRMS (FAB), m/z calc for M^+ ($C_{20}H_{25}O_6P^{98}Mo$) 490.0443, found 490.0417.

Crystal Structure of 4a. X-ray data collection was performed on a crystal sealed in a 0.5 mm capillary under nitrogen. The diffractometer used was a Siemens $P2_1$ equipped with Mo radiation. Data reduction was done on a DEC micro VAX computer running the SDP programs.[19] The observed data were corrected for decay, Lorentz, and polarization factors, and for absorption. The structure was solved using the Patterson heavy atom method and refined with full-matrix least squares. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were not refined due to an error in the data which resulted from a fluctuation in the power supply while collecting.

Crystal Data for 4a: empirical formula $C_{15}H_{22}ClO_5PMo$; color, habit, dark red blocks; crystal size, 0.20 × 0.35 × 0.20 mm^3; crystal system, $P2_1/c$; a (Å), 9.9718 (23); b (Å), 19.0260 (53); c (Å), 9.8171 (29); β (deg), 92.765 (22); V (Å^3), 1860.4 (9); Z, 4; FW, 444.707; D_{calc} (g/cm^3), 1.588; abs coeff, 9.360; diffractometer, Syntex $P2_1$; radiation, graphite-monochromated Mo Kα (0.710 73 Å); 2θ range (deg), 3-50; scan type, θ-2θ; scan speed, variable 4-29; std reflections, 3 std/47 refl; refl collected, 5068; independent refl, 4356; obsd refl $F_o > 3\sigma(F_o)$, 2280; data/parameter, 10.9; final $R(F)$, $R(wF)$, 7.3%, 8.8%; weighting scheme, $1/w = \sigma^2(I)/4F^2 + 0.000225F^2$; final GOF, 3.22; D/s (mean), 0.000; highest peak in diff map, 2.686 (peaks over 1.3 were Mo ghosts).

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Supplementary Material Available: Tables of bond distances, bond angles, positional parameters, and anisotropic displacement parameters (6 pages). Ordering information is given on any current masthead page.

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(19) Frenz, B. A.; Okaya, Y. *Enraf-Nonius Structure Determination Package*; Enraf-Nonius: Delft, The Netherlands, 1981.

Hydroxylation of Aromatics with Hydrogen Peroxide Catalyzed by Cationic Complexes of Platinum(II). Evidence for the Intermolecular Oxidation of Platinum Aryls

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The catalytic hydroxylation of a variety of aromatic substrates is reported using 70% hydrogen peroxide as primary oxidant and a series of (P-P)Pt(CF$_3$)X complexes (P-P = different tetraaryldiphosphines; X = CH_2Cl_2, -OH, -OPh) as catalysts. The reactivity observed increases with the presence of electron-releasing substituents at the aromatic ring, selectively producing ortho and para products. Good amounts of products are obtained with the most activated substrates phenol, anisole, *m*-cresol, and 1,3-dimethoxybenzene, and in all cases an interesting ortho selectivity (up to 95%) is observed. A mechanistic study carried out on the last substrate suggests the involvement of an electrophilic metalation of the aromatic ring to produce platinum-aryl intermediates followed by oxygen transfer from a platinum-hydroperoxy species. This seems to represent a rare example in which a soluble transition-metal complex catalyzes the *direct* hydroxylation of an aromatic ring via *electrophilic metalation* under mild conditions.

Introduction

The hydroxylation of aromatics to produce phenols is a very important industrial reaction that finds applications in a variety of sectors ranging from plastics to agrochemicals to pharmaceuticals and is generally accomplished in the industrial practice in multistage processes.[1] For this

(1) (a) *Kirk-Othmer Encyclopedia of Chemical Technology*, 3rd ed.; Wiley-Interscience: New York, 1980-1984; Vol 13, pp 46-64. *Ibid.*, Vol. 17, pp 373-382. (b) Weissermel, K.; Arpe, H. J. *Industrial Organic Chemistry*; Verlag Chemie: Weinheim, Germany, 1978; pp 303-320.

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