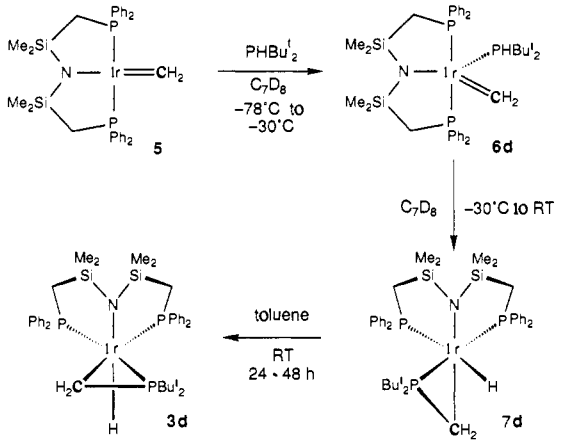
Scheme VIII



However, addition of di-*tert*-butylphosphine ($HPBu^t_2$) to methylidene complex **5** at −78 °C affords phosphine adduct $Ir(=CH_2)(PHBu^t_2)[N(SiMe_2CH_2PPh_2)_2]$ (**6d**), which, above −30 °C, rearranges to cyclometalated derivative **7d**. The stereochemistry was shown to be that analogous to the kinetic stereoisomer found for the diphenylphosphine series in which the hydride is trans to one of the phosphine donors of the ancillary ligand; further rearrangement occurs in solution to generate stereoisomer **3d** having the hydride trans to the amide donor. This is summarized in Scheme VIII.

Conclusions

A series of alkyl phosphide complexes of iridium(III) have been shown to rearrange both thermally and photochemically to ultimately generate iridium(I) phosphine complexes. For phenylphosphide derivative **1c** this process occurs with no detectable isotope effect (k_H/k_D = 1.0 (1)), thus indicating that breaking the C–H bond of the methyl ligand is probably not involved in the rate-determining step. It is proposed that the mechanism involves the direct reductive transfer of the methyl to the phosphide to generate iridium(I) phosphine complex $Ir(PHPhMe)[N(SiMe_2CH_2PPh_2)_2]$ (**4c**) via a three-centered transition state (cf. **F**).

With diphenyl- and dimethylphosphide derivatives **1a** and **1b**, the thermal rearrangement has been shown to involve the formation of cyclometalated hydride complexes *fac*-$Ir(\eta^2\text{-}CH_2PR_2)H[N(SiMe_2CH_2PPh_2)_2]$ as the kinetic products on the way to the formation of iridium(I) phosphine derivatives. Mechanistic studies on this transformation revealed that the rearrangement to the cyclometalated complexes is solvent dependent and involves a modest isotope effect (k_H/k_D = 1.6 (1)). Modelling studies using methylidene complex **5** provided strong evidence that the phosphide abstracts a C–H bond from the coordinated methyl via a highly solvated four-centered transition state (cf. **C**).

The formation of a cyclometalated hydride complex as a kinetic product on the way to the formation of a phosphine derivative is in complete contrast to literature precedent. Previous work[9] has shown that coordinatively unsaturated phosphine complexes can rearrange to cyclometalated derivatives via intramolecular C–H bond activation. In our system this is certainly not occurring. Presumably, the stability of square-planar iridium(I) phosphine complexes **4** is such that there is no tendency to undergo intramolecular C–H activation. Yet not all square-planar iridium(I) derivatives exhibit such stability,[39] and this therefore underscores the importance of ancillary ligands in determining the outcome of reactions within the coordination sphere of a particular metal complex.

Acknowledgment. We gratefully acknowledge NSERC of Canada for financial support in the form of operating grants and an E. W. R. Steacie Fellowship to M. D. F. Johnson-Matthey is also acknowledged for the generous loan of $IrCl_3$.

Supplementary Material Available: Tables of final atomic coordinates and thermal parameters for $Ir(CH_3)PPh_2[N(SiMe_2CH_2PPh_2)_2]$ (**1a**) and *fac*-$Ir(\eta^2\text{-}CH_2PPh_2)H[N(SiMe_2CH_2PPh_2)_2]$ (**3a**) (4 pages). Ordering information is given on any current masthead page.

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Synthesis and Structural Characterization of (η^4-Cyclopentadienone)(η^5-cyclopentadienyl)dicarbonylmolybdenum Hexafluorophosphate. A Template for the Stereospecific Construction of *cis*-4,5-Disubstituted-2-cyclopentenones

Lanny S. Liebeskind* and Agnès Bombrun

Contribution from the Department of Chemistry, Emory University, Atlanta, Georgia 30322.
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Abstract: A stable, cationic metal π-complex of cyclopentadienone, (η^4-cyclopentadienone)(η^5-cyclopentadienyl)dicarbonylmolybdenum hexafluorophosphate, has been prepared in good yield. A variety of nucleophiles (RLi, RMgX, $NaCH(CO_2Et)_2$, $RCOCH_2Li$, enamine) add α to the cyclopentadienone C=O moiety and anti to the $CpMo(CO)_2$ group to give good yields of stable π-cyclopentenoyl products. These compounds have been demetalated by (1) protonation with CF_3COOH to give 5-substituted-2-cyclopentenones and (2) oxidation with $IOCOCF_3$ to give *cis*-5-substituted-4-(trifluoroacetoxy)-2-cyclopentenones. The cyclopentenoyl complexes derived from ketone enolate addition to the cyclopentadienone undergo intramolecular nucleophilic attack by the carbonyl oxygen giving the 2-oxabicyclo[3.3.0]-3,7-octadien-6-one ring system.

Introduction

The development of stereocontrolled methods for the construction of cyclopentanone-based ring systems remains an important goal in synthetic organic methodology.[1-4] Within this context, substituents are often attached at the 2- and 3-position on the cyclopent*anone* ring in a trans relative relationship via a

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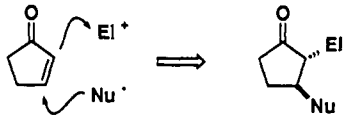
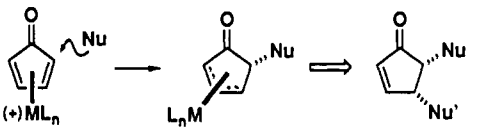
two-step sequence performed on a cyclopen*tenone*; i.e., nucleophilic addition β to the carbonyl group via conjugate addition followed by electrophilic addition α to the carbonyl group with enolate technology (eq 1). Construction of 4,5-disubstituted-2-cyclo-



(1)

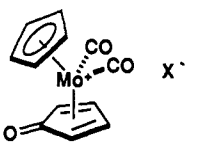
pent*enones* via such reactions is thwarted by the instability of the necessary precursor, cyclopentadienone, although strategies to various substituted cyclopentanones and cyclopentenones proceeding through functionally equivalent compounds have been developed.[5-12] Stabilization of cyclopentadienone by coordination to an appropriate metal–ligand set provides a potentially significant alternative to the traditional means of attaching substituents to a cyclopentenone core. Numerous metal complexes of cyclopentadienones have been prepared, and the vast majority are neutral species bearing an $Fe(CO)_3$ or $Co(\eta^5\text{-}C_5H_5)$ moiety for stabilization of the organic ligand.[13-32] The cobalt complexes have been utilized for the synthesis of some cyclopentenones, but conversion to cationic cobaltacene derivatives (by electrophilic addition at the carbonyl oxygen) is required prior to reaction with nucleophiles.[15,20]

While a conventional organic analysis of the uncomplexed cyclopentadienone ligand would suggest addition of nucleophiles either at, or β to, the carbonyl functionality,[33] coordination to a metal–ligand set provides the additional possibility of nucleophilic addition at the terminus of the coordinated diene chromophore.[34] This corresponds to nucleophilic addition α to the carbonyl group (eq 2), a reaction regiochemistry reminiscent of nucleophilic



(2)

addition to cycloheptatrienone.[35-37] Utilization of the resultant cyclopentenoyl metal complex for a second nucleophilic addition could provide *cis*-4,5-disubstituted-2-cyclopentenones[38-42] with the metal–ligand set biasing all entering nucleophiles to the same face of the cyclopentenone ring. Precedented nucleophilic functionalization reactions of η^3-allyl and η^4-1,3-diene units coordinated to an $(\eta^5\text{-}C_5H_5)Mo(CO)L(+)$ metal–ligand set (allyl, L = NO; diene, L = CO)[43-46] lead to the choice of cationic cyclopentadienone complex **1** as a target for synthesis and reactivity studies. Presented within are details of the synthesis, X-ray structure determination, and preliminary reaction studies of the complex **1**, X = PF_6.



1

Results and Discussion

Since the instability of the parent cyclopentadienone renders direct complexation to a cationic molybdenum species impractical,[47] elaboration of the unstable ligand from a suitable precursor precoordinated to the metal was investigated. Following procedures established with simple allylic halides, treatment of 4-bromo-2-cyclopentenone[48] with $Mo(CH_3CN)_3(CO)_3$[43] in acetonitrile gave an orange precipitate of bis(acetonitrile)bromodicarbonyl(η-(2,3,4)-2-cyclopentenon-4-yl)molybdenum (**2**) in 91%

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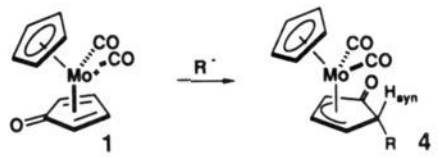
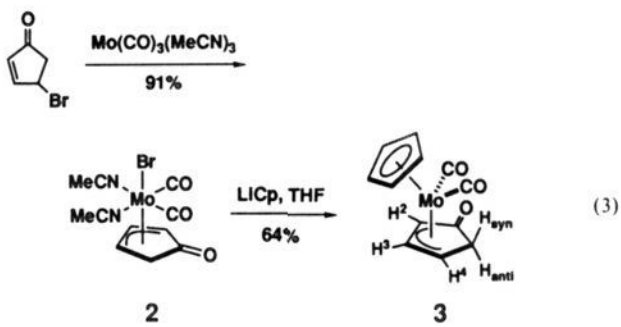
Table I. Nucleophilic Additions to Cyclopentadienone Complex **1**



entry	nucleophile	product		yield (%)
1	$NaBD_3CN^a$	**4a**	R = D	97
2	$NaCH(COOEt)_2^b$	**4b**	R = $CH(COOEt)_2$	69
3	CH_3Li^b	**4c**	R = Me	51
4	CH_3MgCl^b	**4c**	R = Me	92
5	n-$BuMgCl^b$	**4d**	R = n-Bu	92
6	$PhCOCH_2Li^c$	**4e**	R = CH_2COPh	85
7	$H_2C{=}CHMgBr^b$	**4f**	R = $CH{=}CH_2$	86
8	p-$CH_3C_6H_5MgBr^b$	**4g**	R = p-$C_6H_5CH_3$	79
9	$PhC{\equiv}CMgBr^b$	**4h**	R = $C{\equiv}CPh$	68
10	1-pyrrolidino-1-cyclohexene^d	**4i**	R = 2-oxocyclohexyl^e	73

^{a} Nucleophile added to **1** in THF at 0 °C. ^{b} Nucleophile added to **1** in THF, −78 °C. ^{c} Complex **1** added at −78 °C to enolate prepared in THF. ^{d} CH_2Cl_2, −78 °C 5 h, then H_3O^+. ^{e} Isolated as a 1:1 mixture of diastereomers.

yield (eq 3). Conversion to the cyclopentadienyl analogue **3** was accomplished in 64% yield under standard conditions by treatment of **2** with LiC_5H_5 in THF.



(3)

Cyclopentenoyl complex **3** showed a ketonic ν_{CO} at 1670 cm^{-1}. The observation of two pairs of CO ligand stretches in the infrared spectrum taken in CH_2Cl_2 (ca. 4:1 ratio) suggested the presence of exo and endo conformers of **3**. This was confirmed by temperature-dependent ^1H and ^{13}C NMR spectroscopy, which also showed the position of the conformer equilibrium to be solvent dependent. In the 360-MHz ^1H NMR spectrum in CD_2Cl_2 at room temperature, only one set of slightly broadened resonances (the Cp resonance was sharp) for **3** was apparent. On lowering the temperature of the NMR probe to −70 °C, exchange between the two conformations was slowed, and the spectrum showed a 82:18 ratio of two components. Spectra in acetone-d_6 showed similar temperature-dependent phenomena; however, the exo–endo equilibrium was shifted to favor only one of the isomers, predominantly. ^{13}C NMR spectra taken in acetone-d_6 displayed sharp resonances only at low temperature (−40 °C). Nuclear Overhauser enhancement experiments at low temperature in acetone-d_6 showed a strong interaction between the cyclopentadienyl protons and H^3 of the allyl ligand (12%) suggesting that the exo conformation (**3** as drawn) is the predominant conformer in solution, at least at low temperature. The exo conformation is also observed in the crystal structure of analogous cyclohexenyl-$Mo(CO)_2Cp$ complexes.[49,50] The solvent dependence of the exo–endo ratio has been observed previously.[51]

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Table II. Crystallographic Data for $(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_4O)(CO)_2MoPF_6$

(A) Crystal Parameters for $MoC_{12}O_3H_9PF_6$	
molecular wt	443.92
crystal system	monoclinic
space group	$P2_1/c$
a, Å	11.202 (5)
b, Å	10.520 (4)
c, Å	12.107 (4)
β, °	91.66 (3)
Z	4
V, Å^3	1426.15
μ, cm^{-1}	10.85
ρ_{calcd}, g × cm^{-3}	2.067
color	yellow
size, mm	0.6 × 0.3 × 0.42
R(merge), $R(\sigma)$	0.0182, 0.0112
$F(000)$	863.76
(B) Intensity Measurements and Refinement	
diffractometer	syntex $P2_1$ (Nicolet P3/F)
monochromator	graphite
radiation	λ (Mo Kα) = 0.71073 Å
temp of data collection	20 °C
scan method	θ–2θ
scan limits, deg	3–55
scan speed, deg min^{-1}	5–30
no. of read reflcns	2858
no. of reflcns used in the final refinement, $F_o^2 > 3\sigma(F_o^2)$	2551
data collected	$h,k,\pm l$
R (F_o)	0.0311
R_w (F_o)	0.0391
GOOF	1.543
convergence, mean shift/error	0.003

Table III. Bond Lengths (Å) of $(\eta^4$-Cyclopentadienone$)(\eta^5$-cyclopentadienyl)dicarbonylmolybdenum Hexafluorophosphate **1**

bond	length (Å)	bond	length (Å)	bond	length (Å)
Mo–C(2)	2.292 (3)	Mo–C(8)	2.321 (3)	C(6)–C(9)	1.413 (5)
Mo–C(3)	2.264 (3)	Mo–C(5)	2.356 (3)	C(6)–C(10)	1.413 (5)
Mo–C(4)	2.313 (3)	Mo–C(7)	2.319 (3)	C(7)–C(8)	1.388 (6)
Mo–C(6)	2.278 (4)	C(1)–C(2)	1.476 (4)	C(7)–C(10)	1.408 (5)
Mo–C(9)	2.310 (4)	C(1)–C(5)	1.480 (5)	C(8)–C(9)	1.391 (5)
Mo–C(10)	2.288 (3)	C(2)–C(3)	1.414 (5)	C(11)–O(2)	1.124 (4)
Mo–C(11)	2.029 (3)	C(3)–C(4)	1.427 (5)	C(12)–O(3)	1.130 (4)
Mo–C(12)	2.036 (3)	C(4)–C(5)	1.387 (5)	C(1)–O(1)	1.212 (4)

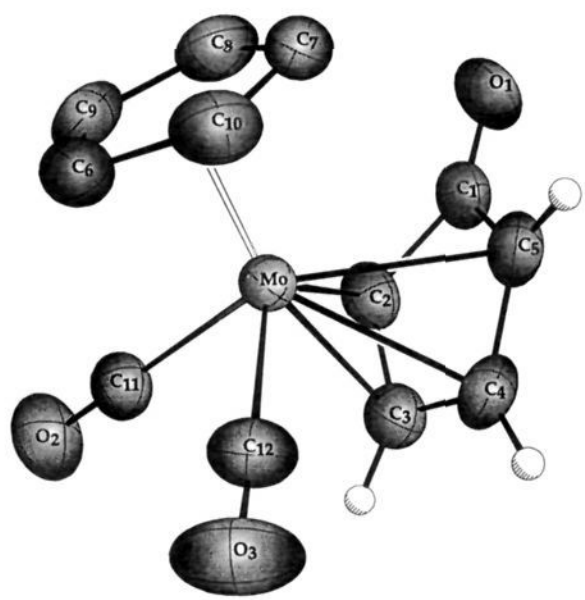
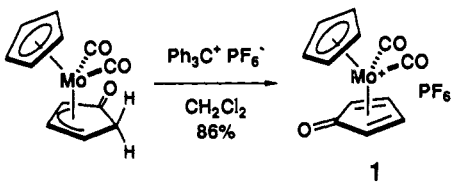


Figure 1. ORTEP of $(\eta^4$-cyclopentadienone$)(\eta^5$-cyclopentadienyl)dicarbonylmolybdenum hexafluorophosphate, **1** (PF_6^- omitted for clarity).

Treatment of **3** with $Ph_3C^+PF_6^-$ in methylene chloride solution at 0 °C led to facile hydride abstraction and formation of the

desired cationic cyclopentadienone complex **1** in 86% yield (eq 4). The mustard yellow **1**, although stable as a solid, decomposed to give an olive green colored solution when exposed to air. Complex **1** showed a strong ν_{CO} in the infrared at 1660 cm^{-1} for the ketonic carbonyl, a value consistent with that seen for other known cyclopentadienone complexes. The solution IR showed two pairs of Mo–CO stretches, indicating the presence of both exo and endo conformers. The ^1H NMR spectrum in acetone-d_6 showed one set of well-resolved time-averaged resonances (η^5-Cp, 6.18; η^4-cyclopentadienone, two apparent triplets at 6.73 and 4.93 expected for an AA'XX' spin system). The η^4-cyclopentadienone ligand in the ^{13}C NMR spectrum in CD_3CN showed resonances at 175.1 (C=O), 92.3, and 76.6 (C_α and C_β).



(4)

1

Since **1** appeared to be the first cationic metal π-complex of a cyclopentadienone, its molecular structure was determined by X-ray crystallographic analysis of a suitable translucent yellow single crystal grown by slow vapor diffusion of benzene into a solution of **1** in acetonitrile. A representation of the molecular structure of **1** is depicted in Figure 1 (PF_6^- omitted for clarity), and listings of bond lengths and bond angles are given in Tables III and IV in the Experimental Section. The cyclopentadienone ligand crystallized in the endo conformation. The cyclopentadienyl and cyclopentadienone rings are staggered with respect to one another, when the complex is viewed along the axis passing through the middle of the two C_5 rings. The cyclopentadienone ring is not planar; the torsional angle between the plane defined by the atoms C(2), C(3), C(4), and C(5) and the carbonyl functionality C(1)–O(1) is 18° with the ketone functional group leaning away from the molybdenum atom. The length of the C(1)–O(1) bond of the cyclopentadienone (1.212 (4) Å) agrees with the value expected for a normal Csp^2–O double bond. Exceptionally, the bond distances between Mo and C(2), C(3), C(4), and C(5) are all different. The longer bonds are between Mo and C(4) and C(5) {2.313 (3) and 2.356 (3) Å, respectively}. The shorter bonds between Mo and C(2) and C(3) are 2.292 (3) and 2.264 (3) Å, respectively. The lengths of the C(2)–C(3), C(3)–C(4), and C(4)–C(5) bonds are all significantly different suggesting a small π-electron delocalization over the four atoms of the cyclopentadienone ring. The length of the C(4)–C(5) bond is shortest at 1.387 (5) Å, consistent with decreased backbonding due to the longer bond to Mo.

The electrophilicity of cyclopentadienone complex **1** was surveyed by reaction with a variety of nucleophiles. It is noteworthy that the molybdenum complex proved exceptionally reactive to a broad series of nucleophiles ranging from enamines to organolithium reagents (Table I). All nucleophiles attacked the cyclopentadienone anti to the coordinated molybdenum and exclusively α to the ketone functional group. Stable, neutral η^3-cyclopentenoyl products, **4**, were isolated in high yield. Confirmation of the regioselectivity of the nucleophilic addition was readily apparent from the spectroscopic characterization of the products. Proof of the stereospecific anti addition was obtained through NOE experiments as follows. The geminal methylene protons of compound **3** appear at 2.28 and 3.13 ppm in the ^1H NMR in $CDCl_3$ solvent. Irradiation of the cyclopentadienyl ligand singlet led to a 7% enhancement of the 2.28 ppm singlet and only a 1% enhancement of the 3.13 singlet, allowing assignment of the 2.28 ppm absorption to the hydrogen syn to the molybdenum. Compound **4a**, prepared by deuteride addition to the cyclopentadienone complex, showed only one absorption at 2.26 ppm, demonstrating that deuteride addition had occurred anti to the molybdenum. Both the malonate adduct, **4b**, and the methyl adduct, **4c**, showed methine absorbances near that seen for H_{syn} in **4a** (2.91 ppm for **4b** and 2.30 ppm for **4c**), and an NOE experiment on **4b** showed a 5% enhancement of the methine under consideration when the cyclopentadienyl singlet was irradiated. The substituents introduced in **4e–4i** perturb the chemical shift of the remaining hydrogen to lower field and make assignment of stereochemistry from chemical shift alone ambiguous. However, taken together, the NOE experiments and general trends noted above strongly suggest that all nucleophilic additions occurred anti to the molybdenum.

Having established the ability of molybdenum complex **1** to function as the synthetic equivalent of an α electrophilic cyclopentadienone, liberation of a free substituted cyclopentenone from the molybdenum with a concomitant second functionalization was briefly explored. Reactivation of cyclopentenoylmolybdenum complexes **3** and **4c** by CO → NO^+ replacement[52-57] was attempted, but the relatively electron-deficient allylmolybdenum moiety did not react cleanly with NO^+ sources under conditions

Table IV. Bond Angles (deg) of (η^4-Cyclopentadienone)(η^5-cyclopentadienyl)dicarbonylmolybdenum Hexafluorophosphate **1**

bond	angle (deg)	bond	angle (deg)
C(2)–Mo–C(3)	36.1 (1)	C(7)–Mo–C(8)	34.8 (1)
C(2)–Mo–C(4)	59.6 (1)	Mo–C(4)–C(5)	74.4 (2)
C(2)–Mo–C(6)	145.8 (1)	C(5)–Mo–C(9)	128.4 (1)
C(2)–Mo–C(9)	109.9 (1)	C(3)–C(4)–C(5)	108.7 (3)
C(2)–Mo–C(10)	145.3 (1)	C(7)–Mo–C(9)	58.3 (1)
C(2)–Mo–C(11)	125.7 (1)	C(1)–C(5)–C(4)	109.3 (3)
C(2)–Mo–C(12)	81.1 (1)	C(8)–Mo–C(10)	59.0 (1)
C(3)–Mo–C(4)	36.3 (1)	C(8)–Mo–C(11)	141.4 (1)
C(3)–Mo–C(6)	165.9 (1)	C(5)–Mo–C(12)	135.5 (1)
C(3)–Mo–C(9)	141.9 (1)	Mo–C(6)–C(9)	73.3 (2)
C(3)–Mo–C(10)	156.0 (1)	Mo–C(6)–C(10)	72.4 (2)
C(3)–Mo–C(11)	89.6 (1)	C(7)–Mo–C(12)	137.3 (1)
C(3)–Mo–C(12)	78.4 (1)	Mo–C(5)–C(4)	71.0 (2)
C(4)–Mo–C(6)	152.6 (1)	C(9)–C(6)–C(10)	107.2 (3)
C(4)–Mo–C(9)	162.2 (1)	Mo–C(7)–C(10)	71.0 (2)
C(4)–Mo–C(10)	119.7 (1)	Mo–C(8)–C(7)	72.5 (2)
C(4)–Mo–C(11)	77.5 (1)	C(8)–C(7)–C(10)	108.5 (3)
C(4)–Mo–C(12)	111.3 (1)	C(2)–Mo–C(5)	59.2 (1)
C(6)–Mo–C(9)	35.9 (1)	C(7)–C(8)–C(9)	108.4 (3)
C(6)–Mo–C(10)	36.1 (1)	C(4)–Mo–C(5)	34.5 (1)
C(6)–Mo–C(11)	85.3 (1)	Mo–C(9)–C(6)	70.8 (2)
C(6)–Mo–C(12)	88.1 (1)	Mo–C(9)–C(8)	73.0 (2)
C(9)–Mo–C(10)	59.3 (1)	C(5)–Mo–C(6)	134.7 (1)
C(9)–Mo–C(11)	118.7 (1)	C(6)–C(9)–C(8)	108.4 (3)
C(9)–Mo–C(12)	79.1 (1)	C(3)–Mo–C(7)	134.4 (1)
C(10)–Mo–C(11)	83.7 (1)	C(5)–Mo–C(7)	77.6 (1)
C(10)–Mo–C(12)	123.7 (1)	Mo–C(10)–C(6)	71.6 (2)
C(11)–Mo–C(12)	85.5 (1)	Mo–C(10)–C(7)	73.4 (2)
C(2)–C(1)–C(5)	101.9 (3)	C(2)–Mo–C(8)	92.7 (1)
C(2)–C(1)–O(1)	129.5 (3)	C(6)–C(10)–C(7)	107.5 (3)
C(5)–C(1)–O(1)	128.5 (3)	C(4)–Mo–C(8)	127.5 (1)
Mo–C(2)–C(1)	85.1 (2)	C(6)–Mo–C(8)	59.3 (1)
C(3)–Mo–C(5)	59.3 (1)	Mo–C(11)–O(2)	177.4 (3)
Mo–C(2)–C(3)	70.9 (2)	Mo–C(12)–O(3)	178.1 (3)
C(2)–Mo–C(7)	109.7 (1)	Mo–C(8)–C(9)	72.1 (2)
C(1)–C(2)–C(3)	109.0 (3)	C(8)–Mo–C(9)	35.0 (1)
C(4)–Mo–C(7)	109.5 (1)	C(5)–Mo–C(10)	99.8 (1)
Mo–C(3)–C(2)	73.0 (2)	C(7)–Mo–C(10)	35.6 (1)
C(6)–Mo–C(7)	59.3 (1)	C(5)–Mo–C(11)	102.8 (1)
Mo–C(3)–C(4)	73.7 (2)	C(7)–Mo–C(11)	115.4 (1)
C(3)–Mo–C(8)	128.4 (1)	C(8)–Mo–C(12)	106.3 (1)
C(2)–C(3)–C(4)	107.4 (3)	Mo–C(5)–C(1)	82.6 (2)
C(5)–Mo–C(8)	93.5 (1)	Mo–C(7)–C(8)	72.7 (2)
Mo–C(4)–C(3)	70.0 (2)		

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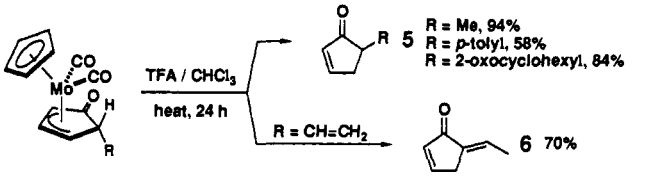
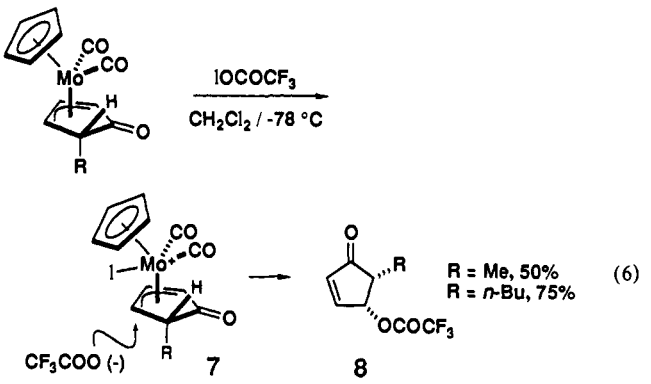
known to provide nitrosylmolybdenum cations from allylmolybdenum complexes lacking a conjugating ketone group. Simple decomplexation was achieved by protonation of the cyclopentenoylmolybdenum complexes **4c,f,g,i** with trifluoroacetic acid in $CHCl_3$ at reflux (eq 5). 5-Substituted-2-cyclopentenones **5** were isolated, exclusively, without evidence of isomerization of the internal double bond to give the more stable 2-substituted isomers. The 5-vinyl-substituted molybdenum complex, **4f**, however, did give the more stable (*E*)-5-ethylidene-2-cyclopentenone, **6**, on decomplexation with trifluoroacetic acid. An attempt to assess the stereochemistry of the protonation reaction was made by treatment of **4c** with trifluoroacetic acid-d_1 in $CHCl_3$ at reflux. However, the stereochemical analysis was compromised by rapid epimerization (and deuteration) at the 5-position of the cyclopentenone under the reaction conditions.



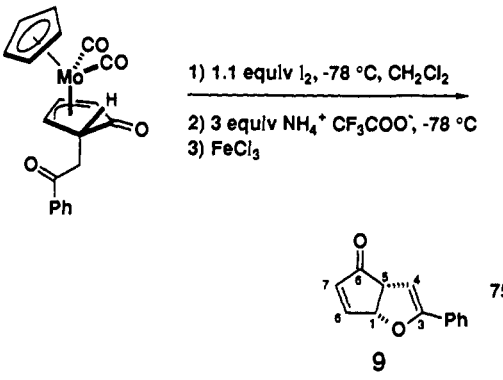
(5)

Successful, stereospecific oxidative decomplexation reactions of the cyclopentenoylmolybdenum complexes were accomplished in a variety of ways. Reaction of cyclopentenoyl complexes **4c** and **4d** with $IOCOCF_3$ in CH_2Cl_2 at −78 °C gave *cis*-5-methyl-4-(trifluoroacetoxy)-2-cyclopentenone, **8** (R = Me, 50%), and *cis*-5-*n*-butyl-4-trifluoroacetoxy-2-cyclopentenone, **8** (R = *n*-Bu, 75%), respectively. Only cis products were isolated from the reaction mixture, a result rationalized to proceed by attack of I^+ at molybdenum to form the species **7** which undergoes nucleophilic attack of CF_3COO^- anti to the 18-electron molybdenum. The stereochemistry of 4,5-disubstituted-2-cyclopentenones has been previously analyzed, cis hydrogens showing larger vicinal couplings (ca. 6–7 Hz) than trans hydrogens (ca. 2–3 Hz).[58,59]

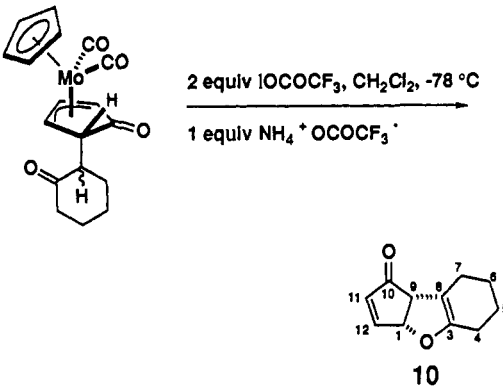


(6)

Complex **4e** and **4i** provide an internal nucleophile to attack the presumed cationic π-allylmolybdenum intermediate. Although treatment with $IOCOCF_3$ did not give a clean reaction mixture, oxidation of **4e** with 1.1 equiv of I_2 followed by addition of 3 equiv of $NH_4^+CF_3COO^-$ as base led to a reaction product still containing molybdenum. Direct oxidation of the reaction product with $FeCl_3$ delivered the bicyclic product **9** in 77% yield (eq 7). The corresponding ring closure product from **4i** was also prepared; however, different reaction conditions were necessary to obtain a good yield of product, **10** (eq 8). Further studies are required to sort out the response of the substrates to the different reaction conditions used.



(7)



(8)

Summary

The first cationic cyclopentadienone metal π-complex, (η^4-cyclopentadienone)(η^5-cyclopentadienyl)dicarbonylmolybdenum hexafluorophosphate, has been prepared and fully characterized. It reacts with a wide variety of nucleophiles within minutes at −78 °C to yield 5-anti-substituted cyclopentenoylmolybdenum complexes in very good yield. The cyclopentenoylmolybdenum complexes have been demetalated in a variety of ways. Protonolysis with CF_3COOH in $CHCl_3$ delivers 5-functionalized cyclopentenones, while oxidation with $IOCOCF_3$ in CH_2Cl_2 gives *cis*-5-substituted-4-(trifluoroacetoxy)-2-cyclopentenones which should be suitable for further elaboration.[60] The cyclopentenoyl complexes derived from the addition of ketone enolates to the cyclopentadienone undergo intramolecular nucleophilic attack of the carbonyl oxygen giving the 2-oxabicyclo[3.3.0]-3,7-octadien-6-one ring system. Further development of the chemistry described in this manuscript could provide a practical method for the synthesis of *cis*-4,5-disubstituted-2-cyclopentenones.

Experimental Section

Materials and Methods. All reactions were carried out in flame-dried glassware under dry argon with standard inert atmosphere techniques. All solvents were dried before use. THF was distilled from sodium and benzophenone, and acetonitrile and dichloromethane were distilled from calcium hydride. Thin-layer chromatography was performed with E. Merck silica gel 60F-245 glass plates of 0.25-mm thickness, with UV light and phosphomolybdic acid (10% in ethanol) for visualization. Flash grade silica gel was obtained from EM Science (230–400 mesh). The NMR chemical shifts are expressed in parts per million (δ) relative to the protio form of the solvent used. NOE difference spectroscopy, performed at 360 MHz and used to assign the major conformation of (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4)-2-cyclopenten-1-on-4-yl)molybdenum and of (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4)-5-substituted-2-cyclopenten-1-on-4-yl)molybdenum complexes with the observed enhancements described in the following text, was performed with 3 mg of sample in 0.5 mL in C_2D_6CO, 99.5% D atom, which was freeze–pump–thaw degassed and sealed. Preirradiation times of 10–15 s, resulting in 70–90% reduction of intensity, were used to transfer polarization; data acquisition commenced after a delay of 10 ms for (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4)-5-substituted-2-cyclopenten-1-on-

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4-yl)molybdenum and 2 μs for (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4)-2-cyclopenten-1-on-4-yl)molybdenum. Data acquisition was followed by a delay of 2 s for (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4)-5-substituted-2-cyclopenten-1-on-4-yl)molybdenum and 100 ms for (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4)-2-cyclopenten-1-on-4-yl)-molybdenum for return to equilibrium before repetition of the experiment. The resulting free-induction decays were subjected to exponential multiplication to provide a line broadening of 1 Hz, then transformed, and subtracted.

Synthesis of (η^4-Cyclopentadienone)(η^5-cyclopentadienyl)dicarbonylmolybdenum Hexafluorophosphate, 1. Bis(acetonitrile)bromodicarbonyl(η-(2,3,4)-2-cyclopenten-1-on-4-yl)molybdenum, 2. A 200-mL Schlenk flask equipped with a magnetic stirring bar, a reflux condenser, and an argon inlet was charged with 13.52 g (51.17 mmol) of $Mo(CO)_6$ and 54 mL of acetonitrile, and the resulting suspension was heated to reflux for 5 h under a dry argon atmosphere. The resulting yellow solution was treated at 40 °C with 8.24 g (51.17 mmol) of 4-bromo-2-cyclopentenone[48] in 14 mL of THF. The reaction mixture was cooled to 0 °C, and an orange solid precipitated. The supernatant was decanted, and the solid was washed with two 10-mL portions of acetonitrile. The residual solvent was removed in vacuo at 25 °C to yield 18.30 g (46.33 mmol, 90.5%) of bis(acetonitrile)bromodicarbonyl(η-(2,3,4)-2-cyclopenten-1-on-4-yl)molybdenum as orange crystals: no decomposition observed before 260 °C; IR (CH_2Cl_2) 3000, 2960, 2920, 2320, 2290, 1970, 1820, 1700, 1640, 1420, 1360, 1280, 1170 cm^{-1}; ^1H NMR (CD_3CN, 300 MHz) δ 5.23 (br s, 1 H), 4.17 (m, 1 H), 3.93 (br s, 1 H), 2.90 (dd, J = 2.0 and 16.7 Hz, 1 H), 2.26 (br s, CH_3, 6 H), 1.98 (d, J = 16.7 Hz, 1 H). Well-resolved ^{13}C NMR data could not be obtained at room temperature. Anal. Calcd for $C_{11}H_{11}O_3N_2MoBr$: C, 33.34; H, 2.80; N, 7.07; Br, 19.93. Found: C, 33.33; H, 2.76; N, 6.99; Br, 20.11. The product could be stored under argon in the dark.

(η^5-Cyclopentadienyl)dicarbonyl(η-(2,3,4)-2-cyclopenten-1-on-4-yl)-molybdenum, 3. At −23 °C, under a dry argon atmosphere, 10.25 mL (1.15 equiv) of n-BuLi (2.6 M in hexane) was added to a solution of 2.5 mL (1.3 equiv) of freshly distilled cyclopentadiene in 50 mL of dry THF. The resulting suspension was allowed to warm to 0 °C and stir for 20 min. The mixture was then recooled to −23 °C and transferred via cannula to a suspension of 9.15 g (23.16 mmol) of bis(acetonitrile)-bromodicarbonyl(η-(2,3,4)-2-cyclopenten-1-on-4-yl)molybdenum in 60 mL of dry THF contained in a 200-mL Schlenk flask under a dry argon atmosphere. The mixture was stirred for 1 h at −23 °C and 4 h at room temperature. TLC monitoring (SiO_2—10:90 of MeOH/EtOAc) showed the presence of a UV active compound of R_f 0.4 and some byproducts (UV, R_f 0 and 0.8). The solvent was evaporated, and the red residue was flash chromatographed on silica gel with a degassed mixture of 10% methanol and 90% ethyl acetate as eluant. Removal of solvent left a yellow crystalline product that was recrystallized from hexane to yield 4.45 g (14.83 mmol, 64%) of the desired (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4)-2-cyclopenten-1-on-4-yl)molybdenum. Purification by sublimation was also possible. The product is air stable, very polar, soluble in chloroform, methylene chloride, and acetone, but sensitive to decomposition in such media when exposed to air: mp 160–162 °C (recrystallized from hexane); UV $\lambda_{(THF)}$ = 256 nm, ε = 31; IR (CH_2Cl_2) 3040, 2900, 1995, 1975, 1930, 1900, 1680 cm^{-1}; IR (KBr pellet) 3100, 2980, 1960 (br), 1880 (br), 1670 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.27 (s, Cp, 5 H), 5.20 (br s, H(3), 1 H), 3.90 (s, H(4), 1 H), 3.85 (s, H(2), 1 H), 3.13 (d, J = 17.5 Hz, H_{anti}, 1 H), 2.28 (d, J = 17.5 Hz, H_{syn}, 1 H). Variable-temperature NMR experiments were necessary for the determination of the coupling constants: ^1H NMR (40 °C, C_2D_6CO, 360 MHz) δ 5.61 (s, H(3), 1 H), 5.54 (s, Cp, 5 H), 4.07–4.05 (quintuplet, H(4), 1 H), 3.62 (t, J = 2.7 Hz, H(2), 1 H), 2.85–2.79 (dd, J = 2.5 and 17.34 Hz, H_{anti}, 1 H), 2.15–2.10 (d, J = 17.34 Hz, H_{syn}, 1 H); ^1H NMR (−54 °C, C_2D_6CO, 360 MHz) δ 5.80 (br t, H(3), 1 H), 5.66 (s, Cp, 5 H), 4.12–4.10 (quintuplet, J = 2.4 Hz, H(4), 1 H), 3.59–3.57 (t, J = 2.7 Hz, H(2), 1 H), 2.81–2.75 (dd, J = 2.7 and 17.46 Hz, H_{anti}, 1 H), and H_{syn} might be underneath the acetone peaks. An NOE difference experiment at 40 °C in acetone-d_6 showed, after irradiation of the Cp singlet, H(4), H(2), H_{syn} and H_{anti} with, respectively, 7, 10, 4, and 2% NOE. At room temperature, the protons H(2), H(4), H_{syn}, and H_{anti} showed, respectively, 4, 4, 7, and 1% NOE. At −56 °C, the protons H(2), H(3), H(4), H_{syn}, and H_{anti} showed, respectively, 6.4, 12, 1.5, 3, and 0% NOE. A VT ^{13}C experiment was necessary to detect the signals of the cyclopentenone ligand: ^{13}C NMR (40 °C, C_2D_6CO, 360 MHz) δ 236.85, 233.47, 200.55, 93.50, 53.61, 43.62; ^{13}C NMR (22 °C, C_2D_6CO, 360 MHz) δ 232.30, 199.25, 92.20, 52.14, 42.30; ^{13}C NMR (−20 °C, C_2D_6CO, 360 MHz) δ 237.40, 233.79, 200.23, 93.18, 74.93, 59.04, 52.66, 43.15; ^{13}C NMR (−40 °C, C_2D_6CO, 360 MHz) δ 237.52, 233.93, 200.23, 93.15, 74.96, 59.09, 52.56, 43.12; MS (high-resolution EI), m/e (rel intensity) 300 (M^+, 14), 272 (14), 246 (22), 244 (51), 242 (40), 241 (38), 240 (20), 238 (30), 218 (36), 216 (100), 215 (44), 214 (96), 213 (70), 212 (63), 211 (58), 210 (60), 208 (48), 188 (43), 187 (21), 186 (35), 185 (32), 182 (26), 163 (19); calcd for $C_{12}H_{10}MoO_3$ 299.9689683, found 299.9683993 (error 0.00018%). Anal. Calcd for $C_{12}H_{10}MoO_3$: C, 48.0; H, 3.36. Found: C, 48.25; H, 3.36.

(η^5-Cyclopentadienyl)dicarbonyl(η-(2,3,4,5)-cyclopentadienone)molybdenum(+) Hexafluorophosphate, 1. In a 100-mL Schlenk flask under a dry argon atmosphere, 0.71 g (2.36 mmol) of the yellow (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4)-2-cyclopenten-1-on-4-yl)molybdenum complex was dissolved in 7 mL of dry methylene chloride. To this solution at 0 °C was added 0.90 g (0.98 equiv) of triphenylcarbenium hexafluorophosphate. The resulting brown suspension was stirred for 1 h at 0 °C and overnight at room temperature. The solution was transferred with a cannula into 70 mL of dry diethyl ether being agitated with gaseous nitrogen, and an olive green solid immediately precipitated. The solvent was decanted, and the solid was washed with two 20-mL portions of dry diethyl ether. A further purification was effected by dissolving the complex in the minimum amount of acetone and filtering through a filter paper. The salt was then precipitated by adding 10 mL of dry diethyl ether. After decantation and vacuum removal of the solvent, 0.90 g (2.02 mmol, 86%) of a mustard yellow sandy solid was isolated. It is air-sensitive in solution and turns olive green upon decomposition: mp 190 °C decomposition (recrystallized from benzene); IR (CH_2Cl_2) 3040, 2960, 1980, 1955, 1910, 1880, 1660, 1600 cm^{-1}; IR (KBr pellet) 3050, 3030, 2900, 2040, 2020, 1970 (w), 1925 (w), 1660 cm^{-1}; ^1H NMR (C_2D_6CO, 300 MHz) δ 6.73 (t, J = 2.56 and 2.89 Hz, 2 H), 6.18 (s, Cp, 5 H), 4.93 (t, J = 2.71 and 2.75 Hz, 2 H); ^{13}C NMR (CD_3CN, 300 MHz) δ 211.29 (2C), 175.18, 97.06 (5C), 92.31 (2C), 76.60 (2C). Anal. Calcd for $MoC_{12}O_3H_9PF_6$: C, 32.44; H, 2.04. Found: C, 32.68; H, 2.11.

X-ray Crystal Structure Determination of (η^4-Cyclopentadienone)(η^5-cyclopentadienyl)dicarbonylmolybdenum Hexafluorophosphate, 1. Crystals suitable for X-ray structure determination were grown in a nitrogen atmosphere at 23.5 °C. The compound was dissolved in CH_3CN, the solution was filtered, and the vial containing the mother liquor was placed into a larger one containing benzene. Slow vapor evaporation for 5 days provided translucent yellow crystals. All crystallographic data were collected at 20 °C on a Nicolet P 3/F diffractometer from a crystal fragment of the dimensions 0.6 × 0.3 × 0.42 mm^3 that had been cut from a larger piece. A graphite-monochromated Mo Kα radiation was used. Measurements were carried out by the θ–2θ scanning method with $3 \le 2\theta \le 55°$. Reflections with Miller indices $0 \le h \le 15$, $0 \le k \le 14$, $-16 \le l \le 16$ were collected; of these 2551 were observed with $F_o^2 > 3\sigma(F_o^2)$. Calculations were performed with SHELXS86 and SHELXTL programs. The space group is $P2_1/c$ from the systematic extinctions. No systematic absences were observed in the hkl; in the $h0l$, $l = 2n + 1$ and in the $0k0$, $k = 2n + 1$. The structure was solved by conventional Patterson and Fourier methods to a final R value of 0.0311 and a goodness of fit (GOOF) of 1.543. An absorption correction was made ($\mu \times r$ = 0.540). The data/parameter ratio was 11 (2551 independent reflections/226 variables). The hexafluorophosphate anion was found to be disordered. The disorder was interpreted as due to two anion orientations of about 0.7884 and 0.2116 occupancies around the axial direction F(1)–P–F(2). The weighting scheme was $w = 1/(\sigma^2(F) + \text{abs}(g)F^2)$ where g = 0.0009. A free variable of 3 was used for refining an empirical (and physically dubious) isotropic extinction parameter x, where the calculated structure becomes: $F^* = F_c/[1.0 + 0.002xF_c^2/\sin 2\theta]^{0.25}$. Data were collected as summarized in Table II. The analysis yielded the structure shown in Figure 1. Bond distances and bond angles are shown in Tables III and IV, respectively. Tables of thermal parameters and observed and calculated structure factors can be found in the supplementary material.

Nucleophilic Additions to Cyclopentadienone Complex 1 Giving Cyclopentenoyl Complexes 4. (η^5-Cyclopentadienyl)dicarbonyl(η-(2,3,4)-5-deuterio-2-cyclopenten-1-on-4-yl)molybdenum, 4a. In a 25-mL Schlenk flask under a dry argon atmosphere, 0.18 g (0.40 mmol) of (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4,5)-cyclopentadienone)molybdenum(+) hexafluorophosphate was dissolved in 7 mL of dry THF. The solution was cooled to 0 °C, and 0.027 g (1 equiv) of sodium cyanoborodeuteride was added as a solid. The mixture became lighter. The reaction mixture was stirred for 2 h at 0 °C and for 2 h at room temperature, then solvent was removed in vacuo, and the crude product was dissolved in CH_2Cl_2 and purified via flash chromatography (30 g of silica gel, 230–400 mesh/degassed mixture 10:90 of methanol and ethyl acetate as eluant/1.5 × 30 cm^2 column). Removal of the solvent gave (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4)-5-deuterio-2-cyclopenten-1-on-4-yl)-molybdenum as a yellow solid. Recrystallization from hexane gave 0.12 g (0.39 mmol, 97%) of the product which was stored under argon: mp 166 °C; IR (CH_2Cl_2) 3060, 2995, 1995, 1970, 1930, 1900, 1680 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.27 (s, Cp, 5 H), 5.20 (s, H(3), 1 H), 3.89 (s, H(4), 1 H), 3.79 (s, H(2), 1 H), 2.26 (s, H_{syn}, 1 H). H_{syn} lost its geminal coupling constant. H_{anti} was totally missing. Anal. Calcd

for $C_{12}H_9O_3DMo$: C, 47.84; H, 3.68. Found C, 48.08; H, 3.39. Deuterium was analyzed as though it were hydrogen. MS (high resolution EI), *m/e* (rel intensity) 301 (M^+, 7), 245 (21), 217 (43), 215 (34), 214 (30), 213 (22), 212 (20); calcd for $C_{12}H_9O_3DMo$ 300.9767929, found 300.9746761 (error 0.0007%).

(η^5-Cyclopentadienyl)dicarbonyl(η-(2,3,4)-5-(diethyl malonyl)-2-cyclopenten-1-on-4-yl)molybdenum, 4b. Following the general protocol above, 0.22 g (0.48 mmol) of (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4,5)-cyclopentadienone)molybdenum(+) hexafluorophosphate in 10 mL of dry THF was treated with $NaCH(CO_2Et)_2$ prepared at 0 °C from 73 μL (1 equiv) of diethyl malonate and 0.013 g (1.1 equiv) of NaH in 7 mL of dry THF. The nucleophile was transferred via cannula into the −78 °C solution of (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4,5)-cyclopentadienone)molybdenum(+) hexafluorophosphate. After 1 h at −78 °C and 45 min at room temperature, TLC monitoring (SiO_2, 10:90 of methanol/ethyl acetate) showed the formation of a new product (UV, R_f 0.78). Flash chromatography (30 g of silica gel, 230–400 mesh/degassed mixture 10:90 of methanol and ethyl acetate as eluant/1.5 × 30 cm^2 column) and then recrystallization from hexane provided 0.15 g (0.33 mmol, 69%) of (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4)-5-(diethyl malonyl)-2-cyclopenten-1-on-4-yl)molybdenum as a pale yellow solid: mp 99 °C; IR (CH_2Cl_2) 2980, 2910, 2880, 1990, 1970, 1930, 1900, 1720, 1660 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.21 (s, Cp, 5 H), 5.02 (br s, H(3), 1 H), 4.18–4.09 (two overlapping quartets, J = 7.15 Hz, diastereotopic CH_2, 4 H), 3.83 (br s, H(4), 1 H), 3.69 (br s, H(2), 1 H), 3.35 (d, J = 6.20 Hz, $CH(CO_2Et)_2$, 1 H), 2.91 (dd, J = 6.20 and 1.25 Hz, H_{syn}, 1 H), 1.25–1.16 (two triplets, J = 7.15 Hz, diastereotopic CH_3, 6 H). MS (high resolution EI), *m/e* (rel intensity) 458 (M^+, 0.63), 402 (8), 256 (10), 254 (8); calcd for $MoC_{19}O_7H_{20}$ 458.0268707, found 458.0263083 (error 0.00012%). Anal. Calcd for $MoC_{19}O_7H_{20}$: C, 49.78; H, 4.4. Found C, 50.04; H, 4.43.

An NOE difference experiment on a sample in C_2D_6CO suggested an anti substitution of (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4,5)-cyclopentadienone)molybdenum(+) hexafluorophosphate: ^1H NMR (C_2D_6CO, 360 MHz) δ 5.6 (s, Cp, 5 H), 4.08–4.19 (two overlapping quartets, J = 7.0 Hz, diastereotopic CH_2, 4 H), 4.05 (br s, H(3), 1 H), 3.61 (t, J = 0.9 Hz, H(4), 1 H), 3.26 (d, J = 7.0 Hz, $CH(CO_2Et)_2$, 1 H), 2.87 (d, J = 7.0 Hz, H_{syn}, 1 H), 2.80 (s, H(2), 1 H), 1.18–1.26 (two overlapping triplets, J = 7.0 Hz, diastereotopic CH_3, 6 H). After irradiation of the cyclopentadienyl ligand at 20 °C, H(4) showed 15% NOE, H(3) 11%, H(2) 2%, and H_{syn} 5%. $CH(CO_2Et)_2$ and the protons of CH_2 and CH_3 of the ester functionality showed no NOE.

(η^5-Cyclopentadienyl)dicarbonyl(η-(2,3,4)-5-methyl-2-cyclopenten-1-on-4-yl)molybdenum, 4c. Following the protocol above, 0.20 g (0.45 mmol) of (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4,5)-cyclopentadienone)molybdenum(+) hexafluorophosphate in 10 mL of dry THF was treated at −78 °C with 0.20 mL (1.3 equiv) of MeMgCl (3.0 M in THF). After 2 h at −78 °C and 1 h at room temperature, TLC monitoring (SiO_2, 10:90 of methanol/ethyl acetate) showed the formation of a new product (UV, R_f 0.67) and some decomposition (UV, R_f 0.01). Flash chromatography (30 g of silica gel, 230–400 mesh/degassed mixture 10:90 of methanol and ethyl acetate as eluant/1.5 × 30 cm^2 column) and then recrystallization from hexane provided 0.13 g (0.41 mmol, 92%) of (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4)-5-methyl-2-cyclopenten-1-on-4-yl)molybdenum as a crystalline yellow solid: mp 137–138 °C; IR (CH_2Cl_2) 3020, 2960, 2920, 1995, 1975, 1930, 1900, 1675 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.24 (s, Cp, 5 H), 5.16 (s, H(3), 1 H), 3.77 (s, H(4), 1 H), 3.71 (s, H(2), 1 H), 2.30 (quartet, J = 6.8 Hz, H_{syn}, 1 H), 1.06 (d, J = 6.8 Hz, CH_3, 3 H). MS (high resolution EI), *m/e* (rel intensity) 314 (M^+, 10), 260 (11), 258 (33), 256 (31), 230 (44), 228 (100), 227 (48), 226 (72), 225 (64), 224 (38), 222 (56); calcd for $MoC_{13}H_{12}O_3$ 313.9846175, found 313.9840494 (error 0.00018%). Anal. Calcd for $MoC_{13}H_{12}O_3$: C, 49.68; H, 3.85. Found C, 49.90; H, 3.94.

(η^5-Cyclopentadienyl)dicarbonyl(η-(2,3,4)-5-butyl-2-cyclopenten-1-on-4-yl)molybdenum, 4d. Following the protocol above, 0.18 g (0.40 mmol) of (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4,5)-cyclopentadienone)molybdenum(+) hexafluorophosphate in 15 mL of dry THF was treated at −78 °C with 0.26 mL (1.3 equiv) of BuMgCl (2.0 M in THF). After 2 h at −78 °C and 45 min at room temperature, TLC monitoring (SiO_2, 30:70 of hexanes/ethyl acetate) showed the formation of a new product (UV, R_f 0.64) and some decomposition (UV, R_f 0.1). Flash chromatography (30 g of silica gel, 230–400 mesh/degassed mixture of 30:70 of hexanes and ethyl acetate as eluant/1.5 × 30 cm^2 column) and then recrystallization from hexane provided 0.13 g (0.37 mmol, 92%) of (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4)-5-butyl-2-cyclopenten-1-on-4-yl)molybdenum as a crystalline yellow solid: mp 104 °C; IR (CH_2Cl_2) 3054, 2982, 2933, 2854, 1972, 1933, 1928, 1899, 1669 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.23 (s, Cp, 5 H), 5.16 (s, H(3), 1 H), 3.83 (s, H(4), 1 H), 3.72 (s, H(2), 1 H), 2.25–2.21 (apparent t, J = 5.6, 6.2 Hz, 1 H, H_{syn}), 1.60–1.50 (m, 1 H), 1.12–1.36 (m, 5 H), 0.83–0.88 (t, J = 7.1 Hz, 3 H, CH_3). Anal. Calcd for $MoC_{16}H_{18}O_3$: C, 54.25; H, 5.12. Found C, 54.10; H, 5.20.

(η^5-Cyclopentadienyl)dicarbonyl(η-(2,3,4)-5-(2-oxo-2-phenylethyl)-2-cyclopenten-1-on-4-yl)molybdenum, 4e. Acetophenone (0.06 mL, 0.56 mmol) in 10 mL of dry THF was treated dropwise at 0 °C with 0.23 mL (0.56 mmol) of *n*-BuLi (2.4 M in hexane). After stirring for 30 min, the reaction mixture was cooled to −78 °C, and 0.05 g (0.11 mmol) of (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4,5)-cyclopentadienone)molybdenum(+) hexafluorophosphate was added as a solid. The resulting mixture was stirred at −78 °C for 3 h, when TLC monitoring (SiO_2, 30:70 of hexane/ethyl acetate as eluant) showed two new products (UV, R_f 0.39 and R_f 0.14). At −78 °C, 0.5 mL of glacial acetic acid was added, and after 15 min of stirring the mixture was allowed to warm to room temperature. The mixture was washed with two 15-mL portions of water. The aqueous layers were washed with two 15-mL portions of ether, and the combined organic layers were dried over Na_2SO_4. After removal of solvent in vacuo, the crude product was dissolved in methylene chloride and purified via flash chromatography (30 g of silica gel, 230–400 mesh/degassed mixture 30:70 of hexane and ethyl acetate as eluant/1.5 × 30 cm^2 column). Removal of the solvent from the fraction of R_f 0.39 and recrystallization from hexane provided 0.04 g (0.094 mmol, 85%) of (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4)-5-(2-oxo-2-phenylethyl)-2-cyclopenten-1-on-4-yl)molybdenum as a crystalline yellow solid. The minor fraction of R_f 0.14, formed in 5% yield, was identified as 1-bis{(η^5-cyclopentadienyl)dicarbonyl(η-(3,4,5)-3-cyclopenten-2-on-5-yl)molybdenum}2-oxo-2-phenylethyl complex. The major product **4e**: mp 115–116 °C; IR (CH_2Cl_2) 3040, 1990, 1970, 1930, 1900, 1670 (br), 1420 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.89 (d, J = 7.5 Hz, aromatic H, 2 H), 7.55 (t, J = 7.2 Hz, aromatic H, 1 H), 7.45 (t, J = 7.6 Hz, aromatic H, 2 H), 5.26 (s, Cp, 5 H), 5.10 (s, H(3), 1 H), 3.92 (s, H(4), 1 H), 3.81 (s, H(2), 1 H), 3.43 (dd, J = 16.8 and 2.6 Hz, H_{syn}, 1 H), 2.86 (d, J = 10.7 Hz, CH_2, 1 H), 2.71 (dd, J = 16.7 and 10.7 Hz, CH_2, 1 H). Anal. Calcd for $MoC_{20}H_{16}O_4$: C, 57.41; H, 3.86. Found C, 57.69; H, 3.96.

(η^5-Cyclopentadienyl)dicarbonyl(η^3-(2,3,4)-5-ethenyl-2-cyclopenten-1-on-4-yl)molybdenum, 4f. (η^5-Cyclopentadienyl)dicarbonyl(η-(2,3,4,5)-cyclopentadienone)molybdenum(+) hexafluorophosphate (0.23 g, 0.52 mmol) in 15 mL of dry THF was treated dropwise at −78 °C with 0.68 mL (1.3 equiv) of vinyl magnesium bromide (1.0 M in THF). After stirring for 2 h at −78 °C and for 1 h at room temperature, TLC monitoring (SiO_2, 10:90 of methanol/ethyl acetate) showed the formation of a new product (UV, R_f 0.73). Flash chromatography (30 g of silica gel, 230–400 mesh/degassed mixture 10:90 of methanol/ethyl acetate as eluant/1.5 × 30 cm^2 column) and then recrystallization from hexane provided 0.15 g (0.45 mmol, 86%) of (η^5-cyclopentadienyl)dicarbonyl(η^3-(2,3,4)-5-ethenyl-2-cyclopenten-1-on-4-yl)molybdenum as a crystalline yellow solid: mp 118–119 °C; IR (CH_2Cl_2) 3080, 3050, 2980, 2930, 2000, 1980, 1935, 1905, 1670, 1630, 1420 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.5–5.6 (m, $CH{=}CH_2$, 1 H), 5.25 (s, Cp, 5 H), 5.17 (s, H(3), 1 H), 5.07–5.13 (d, J = 17.11 Hz, $CHCH_2$ trans, 1 H), 4.97–5.00 (d, J = 10.13 Hz, $CHCH_2$ cis, 1 H), 3.72 (br s, H(4) and H(2), 2 H), 2.88–2.90 (d, J = 7.15 Hz, H_{syn}, 1 H). Anal. Calcd for $MoC_{14}H_{12}O_3$: C, 51.54; H, 3.71. Found C, 51.78; H, 3.76.

(η^5-Cyclopentadienyl)dicarbonyl(η-(2,3,4)-5-*p*-tolyl-2-cyclopenten-1-on-4-yl)molybdenum, 4g. (η^5-Cyclopentadienyl)dicarbonyl(η-(2,3,4,5)-cyclopentadienone)molybdenum hexafluorophosphate (0.20 g, 0.45 mmol) in 10 mL of dry THF was treated at −78 °C with 0.59 mL (1.3 equiv) of *p*-tolyl magnesium chloride (1.0 M in diethyl ether). After stirring for 1 h at −78 °C and for 2 h at room temperature; TLC monitoring (SiO_2, 10:90 of methanol/ethyl acetate) showed the formation of a new product (UV sensitive, R_f 0.69) and some decomposition (UV sensitive, R_f 0.01). Flash chromatography (30 g of silica gel, 230–400 mesh/degassed mixture 10:90 of methanol and ethyl acetate as eluant/1.5 × 30 cm^2 column) and then recrystallization from hexane provided 0.14 g (0.36 mmol, 79%) of a crystalline yellow solid: mp 185 °C; IR (CH_2Cl_2) 3050, 2980, 2920, 1995, 1970, 1920, 1900, 1665 cm^{-1}; ^1H NMR (C_2D_6CO, 300 MHz) δ 7.13–7.16 (d, J = 8.0 Hz, H aromatic, 2 H), 7.05–7.08 (d, J = 8.0 Hz, H aromatic, 2 H), 5.81 (s, H(3), 1 H), 5.6 (s, Cp, 5 H), 4.0 (s, H(4), 1 H), 3.65–3.67 (t, J = 2.4, 2.2 Hz, H(2), 1 H), 3.34 (s, $H(5)_{syn}$, 1 H), 2.24 (s, CH_3, 3 H). Anal. Calcd for $MoC_{19}H_{16}O_3$: C, 58.46; H, 4.13. Found C, 58.71; H, 4.18.

(η^5-Cyclopentadienyl)dicarbonyl(η-(2,3,4)-5-(2-phenylethynyl)-2-cyclopenten-1-on-4-yl)molybdenum, 4h. (η^5-Cyclopentadienyl)dicarbonyl(η-(2,3,4,5)-cyclopentadienone)molybdenum(+) hexafluorophosphate (0.20 g, 0.45 mmol) in 10 mL of dry THF was treated with PhC≡CMgBr prepared from 0.45 mL (1 equiv) of EtMgBr (2.0 M in THF) and 0.1 mL (1 equiv) of phenyl acetylene in 7 mL of dry THF. After 60 min of stirring at 0 °C, the nucleophile was transferred via cannula into the solution of (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4,5)-cyclopentadienone)molybdenum(+) hexafluorophosphate that

was cooled to −78 °C. After stirring for 7 h at −78 °C, TLC monitoring (SiO_2, 10:90 of methanol/ethyl acetate) showed the formation of a new product (UV, R_f 0.89). The mixture was allowed to warm to room temperature, and then flash chromatography (30 g of silica gel, 230–400 mesh/degassed mixture 10:90 of methanol and ethyl acetate as eluant/1.5 × 30 cm^2 column) and recrystallization from hexane provided 0.12 g (0.30 mmol, 68%) of (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4)-5-(2-phenylethynyl)-2-cyclopenten-1-on-4-yl)molybdenum as a crystalline yellow solid: mp 186 °C; IR (CH_2Cl_2) 3020, 2960, 2340, 2000, 1980, 1935, 1905, 1690, 1660, 1600, 1450 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.36–7.39 (multiplet, H aromatic, 2 H), 7.24–7.26 (multiplet, H aromatic, 3 H), 5.27 (s, Cp, 5 H), 5.18 (s, H(3), 1 H), 3.90 (s, H(4), 1 H), 3.83 (s, H(2), 1 H), 3.27 (s, H_{syn}, 1 H). Anal. Calcd for $MoC_{20}H_{14}O_3$: C, 60.32; H, 3.54. Found C, 60.45; H, 3.59.

(η^5-Cyclopentadienyl)dicarbonyl(η-(2,3,4)-5-(2-oxocyclohexyl-2-cyclopenten-1-on-4-yl)molybdenum, 4i. (η^5-Cyclopentadienyl)dicarbonyl(η-(2,3,4,5)-cyclopentadienone)molybdenum(+) hexafluorophosphate (0.16 g, 0.35 mmol) in 10 mL of dry methylene chloride was treated at −78 °C with 114 μL (2 equiv of 1-pyrrolidino-1-cyclohexene. After 5 h at −78 °C and 30 h at room temperature, TLC monitoring (SiO_2, 10:90 of methanol/ethyl acetate) showed the formation of a new product (UV, R_f 0.61) and some byproducts (UV, R_f 0.4 and R_f 0.9). The reaction was hydrolyzed with 0.5 mL (75 equiv) of water. The crude red product was purified via flash chromatography (30 g of silica gel, 230–400 mesh/degassed mixture 10:90 of methanol and ethyl acetate as eluant/1.5 × 30 cm^2 column) and recrystallized from hexane to provide 0.10 g (0.26 mmol, 73%) of (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4)-5-(2-oxocyclohexyl-2-cyclopenten-1-on-4-yl)molybdenum as a crystalline yellow solid: mp 191–192 °C; IR (CH_2Cl_2) 3040, 2940, 2860, 1990, 1970, 1930, 1900, 1700, 1665 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.23 (s, Cp, 5 H), 5.06 (s, H(3), 1 H), 3.81 (s, H(4), 1 H), 3.69 (s, H(2), 1 H), 2.94 (t, H_{syn}, 1 H), 2.64 (m, H of cyclohexanone, 1 H), 2.20–2.48 (overlapping multiplets, H of cyclohexanone, 2 H), 1.99–2.05 (m, H of cyclohexanone, 1 H), 1.78–1.90 (overlapping multiplets, H of cyclohexanone, 2 H), 1.55–1.64 (overlapping multiplets, H of cyclohexanone, 3 H); MS (high resolution EI), *m/e* (rel intensity) 396 (M^+, 5), 343 (39), 340 (100), 336 (37), 335 (56), 322 (17), 320 (17), 292 (24), 242 (20), 241 (18), 240 (20), 239 (16), 180 (16), 145 (15); calcd for $MoC_{18}H_{18}O$ 396.0259143, found 396.0264792 (error 0.00014%). Anal. Calcd for $MoC_{18}H_{18}O_4$: C, 54.54; H, 4.58. Found C, 54.60; H, 4.56.

Protonation–Demetalation of Cyclopentenoyl Complexes 4. 5-Methyl-2-cyclopenten-1-one, 5, R = Me. In a 25-mL round-bottomed flask 0.1 g (0.32 mmol) of (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4)-5-methyl-2-cyclopenten-1-on-4-yl)molybdenum, **4c**, was dissolved in 8 mL of dry chloroform under a dry argon atmosphere. At room temperature 0.25 mL (10 equiv) of trifluoroacetic acid was added dropwise. The resulting orange solution was refluxed for 15 h, resulting in a black mixture. Monitoring by TLC (SiO_2, 40:60 of hexane/ethyl acetate) showed the formation of four different compounds: a green byproduct, R_f 0.9, an orange byproduct, R_f 0.7, the desired faint yellow product, R_f 0.6, and another yellow byproduct, R_f 0.3. The mixture was washed with two 10-mL portions of a saturated solution of $NaHCO_3$, and the aqueous layers were extracted with two 7-mL portions of diethyl ether. The combined organic layers were washed with 15 mL of a saturated solution of NaCl and dried over Na_2SO_4. The solvent was evaporated, and the product was purified via flash chromatography (10 g of silica gel 230–400 mesh/28 × 1.3 cm^2 column/mixture 40:60 of hexane/ethyl acetate). Careful removal of solvent left 5-methyl-2-cyclopenten-1-one as a yellow oil (29 mg, 0.30 mmol, 94%). The product could be stored in the refrigerator under argon for a few days. The spectroscopic data were consistent with the assigned structure: IR (CH_2Cl_2) 3050, 3000, 2960, 2920, 1715, 1415, 1370 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.64–7.67 (m, H(3), 1 H), 6.15–6.18 (m, H(2), 1 H), 2.89–2.97 (m, H(4), 1 H), 2.30–2.37 (m, H(5), 1 H), 2.22–2.30 (m, H(4), 1 H), 1.16–1.19 (d, J = 7.4 Hz, CH_3, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 16.18, 37.78, 39.38, 133.31, 163.11, 213.00.

5-*p*-Tolyl-2-cyclopenten-1-one, 5, R = *p*-Tolyl. Following the procedure above, 0.26 g (0.66 mmol) of (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4)-5-*p*-tolyl-2-cyclopenten-1-on-4-yl)molybdenum, **4g**, in 15 mL of dry chloroform was treated at room temperature with 0.51 mL (10 equiv) of trifluoroacetic acid. After refluxing for 30 h, TLC (SiO_2, 40:60 of hexane/ethyl acetate) showed the formation of four different compounds: a green byproduct, R_f 0.9, an orange byproduct, R_f 0.8, the desired faint yellow product, R_f 0.7, and another yellow byproduct, R_f 0.34. Workup as above followed by flash chromatography (25 g of silica gel 230–400 mesh/28 × 2.2 cm^2 column/mixture 40:60 of hexane/ethyl acetate as eluant) gave 5-*p*-tolyl-2-cyclopenten-1-one as a yellow oil (65 mg, 0.38 mmol, 58%): IR (CH_2Cl_2) 3020, 2910, 2850, 1715, 1580, 1510 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.85–7.82 (m, H(3), 1 H), 7.13–7.11 (d, aromatic protons, J = 8.0 Hz, 2 H), 7.03–7.01 (d, aromatic protons, J = 8.0 Hz, 2 H), 6.26–6.29 (m, H(2), 1 H), 3.52–3.49 (dd, J = 2.5, 6.9 Hz, H(5), 1 H), 3.28–3.18 (ddt, J = 20, 6.9, 2.4 Hz, H(4), 1 H), 2.83–2.74 (dq, J = 20, 2.3 Hz, H(4), 1 H), 2.29 (s, CH_3, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 209.70, 163.88, 136.59, 136.21, 133.54, 129.51, 127.46, 50.51, 38.78, 21.02; MS (high resolution EI) *m/e* (rel intensity) 172 (M^+, 100), 143 (12), 129 (29), 128 (19), 119 (11), 117 (11), 115 (13), 105 (15), 91 (15); calcd for $C_{12}H_{12}O$ 172.0888093, found 172.0888151 (error 3.37 × 10^{-6}%).

5-(2-Oxocyclohexyl)-2-cyclopenten-1-one, 5, R = 2-Oxocyclohexyl. Following the procedure above, 0.14 g (0.43 mmol) of (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4)-5-(2-oxocyclohexyl)-2-cyclopenten-1-on-4-yl)molybdenum, **4i**, in 25 mL of dry chloroform was treated with 0.26 mL (10 equiv) of trifluoroacetic acid. After 16 h at reflux, TLC (SiO_2, 40:60 of hexane/ethyl acetate) showed the formation of three different compounds: a green byproduct, R_f 0.9, and the desired product as two faint yellow spots, R_f 0.77 and R_f 0.69. After workup as above, the product was purified via preparative chromatography (silica gel 60 F_{254} precoated plate, 20 × 20 cm^2/mixture 40:60 of hexane/ethyl acetate as eluant). The two diastereoisomers were isolated in a ratio of 1:1 (64 mg, 0.36 mmol, 84%) as orange oils.

(a) Analysis of the less polar diastereomer: IR (CH_2Cl_2) 2980, 2950, 2890, 1745, 1700, 1610 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.73–7.70 (m, H(3), 1 H), 6.21–6.18 (m, H(2), 1 H), 3.00–2.82 (overlapping multiplets, 3 H), 2.44–2.30 (overlapping multiplets, 2 H), 2.11–2.04 (m, 1 H), 1.87–1.40 (overlapping multiplets, 6 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 211.23, 193.05, 164.62, 134.57, 51.06, 44.26, 42.00, 32.94, 27.80, 27.28, 24.83; MS (high resolution EI) *m/e* (rel intensity) 178 (M^+, 2), 131 (9), 91 (21), 82 (11), 79 (12), 69 (13), 67 (14), 60 (10), 57 (20), 56 (10), 55 (26); calcd for $C_{11}H_{14}O_2$ 178.0993726, found 178.0993798 (error 4.04 × 10^{-6}%).

(b) Analysis of the more polar diastereomer: IR (CH_2Cl_2) 3060, 2950, 2880, 1745, 1710, 1590 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.66–7.62 (m, H(3), 1 H), 6.28–6.26 (m, H(2), 1 H), 3.10–3.00 (m, 1 H), 2.80–2.76 (m, 1 H), 2.73–2.70 (m, 1 H), 2.53–1.90 (overlapping multiplets, 6 H), 1.75–1.57 (overlapping multiplets, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 210.17, 192.25, 162.02, 133.90, 50.98, 46.30, 41.98, 33.36, 32.02, 27.26, 25.18. MS (high resolution EI) *m/e* (rel intensity) 178 (M^+, 37), 121 (21), 108 (27), 107 (23), 97 (49), 82 (11), 96 (22), 95 (22), 91 (24), 82 (100), 79 (37), 77 (26), 68 (18), 67 (16), 55 (23), 53 (22); calcd for $C_{11}H_{14}O_2$ 178.0993726, found 178.0993798 (error 4.04 × 10^{-6}%).

(*E*)-5-Ethylidene-2-cyclopenten-1-one, 6.[61–63] Following the procedure above, 0.09 g (0.29 mmol) of (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4)-5-ethenyl-2-cyclopenten-1-on-4-yl)molybdenum, **4f**, in 10 mL of dry chloroform was treated with 0.22 mL (10 equiv) of trifluoroacetic acid. After 24 h at reflux, TLC (SiO_2, 40:60 of hexane/ethyl acetate) showed the formation of four different compounds: a green byproduct, R_f 0.9, an orange byproduct, R_f 0.7, the desired faint yellow product, R_f 0.6, and another yellow byproduct, R_f 0.4. Workup as above followed by flash chromatography (10 g of silica gel 230–400 mesh/28 × 1.3 cm^2 column/mixture 40:60 of hexane/ethyl acetate) gave (*E*)-5-ethylidene-2-cyclopenten-1-one as a yellow oil (21 mg, 0.19 mmol, 70%). The spectroscopic data were consistent with the assigned structure and with literature data:[61–63] IR (CH_2Cl_2) 2920, 2860, 1700, 1660, 1610 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.54–7.57 (m, H(3), 1 H), 6.63–6.71 (dq, J = 7.2 and 1.1 Hz, C*H*CH_3, 1 H), 6.34–6.38 (dt, J = 6.0 and 2.0 Hz, H(2), 1 H), 3.19 (br s, H(4), 2 H), 1.86 (d, J = 7.2 Hz, CH_3, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 196.29, 156.64, 136.23, 135.21, 130.78, 31.98, 15.16.

Oxidative Demetalations. 4-(Trifluoroacetoxy)-5-methyl-2-cyclopenten-1-one, 8, R = Me. In a 50-mL, round-bottomed flask which was protected from light with aluminum foil, 0.37 g of iodine (2.0 equiv) was added to a suspension of 0.35 g (2.2 equiv) of silver trifluoroacetate in 20 mL of dry methylene chloride under a dry argon atmosphere. After 30 min of stirring at room temperature, the reaction mixture was cooled to −78 °C, and a solution of 0.22 g (0.72 mmol) of (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4)-5-methyl-2-cyclopenten-1-on-4-yl)molybdenum, **4c**, in 4 mL of dry methylene chloride was added dropwise. The pink mixture became orange. After 1 h of stirring at −78 °C, the reaction mixture was allowed to warm slowly to room temperature and stir for an additional 45 min. TLC monitoring (SiO_2, CH_2Cl_2) of the brown reaction mixture showed the formation of a new compound (R_f 0.64, UV) along with a pink spot (UV, R_f 0.9) and an orange byproduct (UV, R_f 0.52). The reaction mixture was washed with 0.1 N sodium thiosulfate until disappearance of the iodine color. The combined organic

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(62) Smith, R. A. J.; Spencer, T. A. *J. Org. Chem.* **1970**, *35*, 3220.
(63) DuBois, J. E.; Dubois, M. *Compt. Rend. Hebd. Seances Acad. Sci. Ser. C* **1963**, *256*, 715.

layers were dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified via flash chromatography (30 g of silica gel, 230–400 mesh/methylene chloride as eluant 1.5 × 30 cm^2 column) giving 0.073 g (0.35 mmol, 50%) of a compound of R_f 0.64 which was analyzed to be the cis diastereomer of 4-(trifluoroacetoxy)-5-methyl-2-cyclopenten-1-one. It is an orange oil: IR (CH_2Cl_2) 2960, 2920, 2850, 1785 (CO of trifluoroacetate), 1725 (CO of cyclopentenone), 1340 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.52 (dd, J = 2.2 and 5.7 Hz, H(3), 1 H), 6.44 (d, J = 5.7 Hz, H(2), 1 H), 6.07 (d, J = 5.5 Hz, H(4), 1 H), 2.70–2.80 (quintuplet, H(5), 1 H), 1.12–1.15 (d, J = 7.6 Hz, CH_3, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 206.58, 162.30, 154.96, 137.43, 109.22, 61.28, 42.62, 10.34; MS (high resolution EI) m/e (rel intensity) 208 (M^+, 3), 149 (13), 112 (23), 111 (50), 97 (13), 96 (100), 83 (15); calcd for $C_8H_7O_3F_3$ 208.0347211, found 208.0347289 (error 3.75 × 10^{-6}%). The coupling constant J = 5.5 Hz between H(4) and H_{syn} suggested a cis relationship between the two substituents in the 4 and 5 positions of the 2-cyclopenten-1-one.[58,59]

4-(Trifluoroacetoxy)-5-butyl-2-cyclopenten-1-one, 8, R = *n*-Bu. Following the procedure above, $IOCOCF_3$ generated from 0.17 g of iodine (1.5 equiv) and 0.16 g (1.6 equiv) of silver trifluoroacetate in 15 mL of dry methylene chloride was added at −78 °C to a solution of 0.15 g (0.44 mmol) of (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4)-5-butyl-2-cyclopenten-1-on-4-yl)molybdenum, **4d**, in 4 mL of dry methylene chloride. TLC monitoring (SiO_2, CH_2Cl_2) showed the formation of a new compound (R_f 0.68, UV) along with a pink spot (UV, R_f 0.9) and an orange byproduct (UV, R_f 0.52). Workup as above and flash chromatography (30 g of silica gel, 230–400 mesh/methylene chloride as eluant/1.5 × 30 cm^2 column) gave 0.083 g (0.33 mmol, 75%) of a compound of R_f 0.68 which was analyzed to be the cis diastereoisomer of 4-(trifluoroacetoxy)-5-butyl-2-cyclopenten-1-one. It is an orange oil: IR (CH_2Cl_2) 2962, 2875, 1787 (CO of trifluoroacetate), 1725 (CO of cyclopentenone), 1422, 1382, 1346, 1225, 1177, 1154, 1003 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.53 (dd, J = 2.5, 5.8 Hz, H(3), 1 H), 6.44 (d, J = 5.8 Hz, H(2), 1 H), 6.11 (dd, J = 1.8, 6.4 Hz, H(4), 1 H), 2.66–2.59 (dt, J = 6.0, 8.2 Hz, H(5), 1 H), 1.72–1.63 (m, 1 H), 1.60–1.50 (m, 1 H), 1.44–1.24 (m, 4 H), 0.90–0.85 (t, J = 7 Hz, CH_3, 3 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 206.07, 157.30, 154.81, 137.88, 112.46, 49.87, 47.70, 29.45, 25.60, 22.59, 13.67; MS (high resolution EI) m/e (rel intensity): 250 (M^+, 3), 194 (43), 136 (12), 98 (25), 97 (18), 94 (10), 80 (94), 55 (12); calcd for $C_{11}H_{13}O_3F_3$ 250.0816687, found 250.0816791 (error 4.15 × 10^{-6}%).

2-Oxabicyclo[3.3.0]-3-phenyl-3,7-octadien-6-one, 9. In a 50-mL, round-bottomed flask under a dry argon atmosphere, 0.08 g (0.19 mmol) of (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4)-5-(2-oxo-2-phenylethyl)-2-cyclopenten-1-on-4-yl)molybdenum, **4e**, was dissolved in 12 mL of dry methylene chloride. At −78 °C, 0.054 g (1.1 equiv) of iodine was added. The yellow solution gradually became pink. After 1.5 h of stirring (−78 °C to −40 °C), no more starting material was detected by TLC. At −78 °C, 0.078 g (3 equiv) of ammonium trifluoroacetate was added to the mixture. The reaction mixture was stirred for 1 h at −78 °C and for 30 min at room temperature. Then at −40 °C, 0.033 g (1.1 equiv) of $FeCl_3$ was added, and the reaction mixture was allowed to warm to room temperature and was stirred for 30 min. TLC monitoring (silica gel which was pretreated with 10% of triethylamine in methylene chloride, CH_2Cl_2 as eluant) showed formation of a new compound (R_f 0.64, UV). The mixture was washed with five 15-mL portions of 0.5 N sodium thiosulfate. The combined organic layers were dried over Na_2SO_4. The crude product was purified via preparative chromatography (silica gel 60 F_{254} precoated plate which was pretreated with 10% of triethylamine in CH_2Cl_2, 20 × 20 cm^2/CH_2Cl_2 as eluant) giving 29 mg (0.15 mmol, 77%) of an orange oil analyzed as 2-oxabicyclo[3.3.0]3-phenyl-3,7-octadien-6-one, **9**, with a cis junction between the two rings: IR (CH_2Cl_2) 3056, 2987, 2962, 2929, 1721, 1603, 1495, 1449, 1345 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, see numbering scheme for **9** in eq 7) δ 7.57 (dd, J = 5.6, 2.1 Hz, H(8), 1 H), 7.52 (m, aromatic protons, 2 H), 7.32 (m, aromatic protons, 3 H), 6.34 (d, J = 5.6 Hz, H(7), 1 H), 5.70 (dd, J = 2.1, 6.95 Hz, H(1), 1 H), 5.33 (d, J = 2.8 Hz, H(4), 1 H), 3.75 (dd, J = 2.8, 7.0 Hz, H(5), 1 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 206.35, 157.93, 156.57, 135.42, 130.01, 129.08, 128.35 (2C), 125.31 (2C), 94.08, 82.64, 53.73; MS (high resolution EI) m/e (rel intensity) 198 (M^+, 38), 144 (29), 141 (10), 115 (24), 105 (100), 77 (44), 65 (14); calcd for $C_{13}H_{10}O_2$ 198.0680742, found 198.0680797 (error 2.78 × 10^{-6}%).

2-Oxatricyclo[4.3.1.$0^{8,9}$]-3(8),11-dodecadien-10-one, 10. In a 50-mL, round-bottomed flask which was protected from light with aluminum foil, 0.11 g (2.0 equiv) of iodine was added to a suspension of 0.11 g (2.2 equiv) of silver trifluoroacetate in 20 mL of dry methylene chloride under a dry argon atmosphere. The reaction mixture was allowed to stir for 30 min at room temperature. It was then transferred via cannula into a solution of 0.09 g (0.22 mmol) of (η^5-cyclopentadienyl)dicarbonyl(η-(2,3,4)-5-(2-oxocyclohexyl)-2-cyclopenten-1-on-4-yl)molybdenum, **4i**, premixed with 0.03 g (1 equiv) of ammonium trifluoroacetate in 5 mL of dry methylene chloride which was cooled to −78 °C. The reaction mixture was orange. It was allowed to stir for 1 h at −78 °C and for 1 h at room temperature. TLC monitoring (SiO_2, CH_2Cl_2) showed formation of a new compound (R_f 0.42, UV). The reaction mixture was washed with three 20-mL portions of 0.5 N sodium thiosulfate. The combined organic layers were dried over Na_2SO_4. The crude product was purified via flash chromatography (30 g of silica gel, 230–400 mesh/methylene chloride as eluant/1.5 × 30 cm^2 column) giving 0.032 g (0.18 mmol, 82%) of 2-oxatricyclo[4.3.1.$0^{8,9}$]-3(8),11-dodecadien-10-one which was isolated as an orange oil: IR (CH_2Cl_2) 3056, 2987, 2944, 2848, 1715 (ν of CO), 1607, 1341, 1200 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz, see numbering scheme for **10** in eq 8) δ 7.45 (dd, J = 5.8, 2.3 Hz, H(12), 1 H), 6.24 (d, J = 5.8 Hz, H(11), 1 H), 5.42 (dd, J = 6.85, 2.3 Hz, H(1), 1 H), 3.34 (m, H(9), 1 H), 1.90–2.1 (m, H of cyclohexene ring, 4 H), 1.49–1.68 (m, H of cyclohexene ring, 4 H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 205.87, 157.63, 152.25, 134.85, 104.68, 81.81, 55.03, 23.23, 22.61 (2C), 21.59; MS (high resolution EI) m/e (rel intensity) 176 (M^+, 33), 149 (33), 120 (45), 107 (25), 94 (19), 91 (33), 83 (10), 81 (13), 79 (27), 77 (23), 73 (12), 71 (14), 70 (13), 69 (21), 67 (17), 65 (13), 62 (12), 60 (19), 58 (13), 57 (33); calcd for $C_{11}H_{12}O_2$ 176.0837234, found 176.0837296 (error 3.52 × 10^{-6}%).

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Supplementary Material Available: Listings of thermal parameters and atomic coordinates (2 pages); table of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.