Stereospecific Functionalization of (π-Allyl)molybdenum Complexes Derived from Cyclopentenone. Toward the Stereocontrolled Construction of Substituted 2-Cyclopentenones

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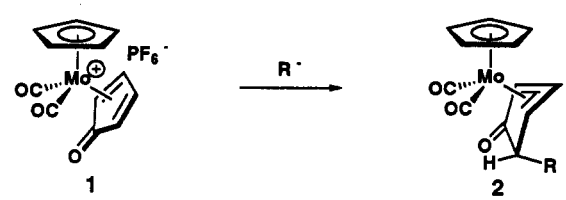
(η^5-Cyclopentadienyl)[(2,3,4-η)-1-oxo-2-cyclopenten-4-yl]dicarbonylmolybdenum on treatment with $NOPF_6$ in 1,2-dimethoxyethane at 0 °C evolves CO and formed carbonyl(η^5-cyclopentadienyl)[(2,3,4-η)-1-oxo-2-cyclopenten-4-yl]nitrosylmolybdenum hexafluorophosphate in a highly diastereoselective manner. This electrophilic species reacted with nucleophiles (higher-order cuprates, malonates, enolates, and cyanoborodeuteride) to form (η^2-alkene)carbonyl(η^5-cyclopentadienyl)nitrosylmolybdenum complexes of 4-substituted 2-cyclopentenones in good to excellent yields and with high regioselectivity. High yield oxidative demetallation with ceric ammonium nitrate provided the 4-substituted cyclopentenones. The product resulting from reaction of carbonyl(η^5-cyclopentadienyl)[(2,3,4-η)-1-oxo-2-cyclopenten-4-yl]nitrosylmolybdenum hexafluorophosphate with $Me_2Cu(CN)Li_2$ was characterized by X-ray diffraction, proving that the methyl group was delivered *anti* to the molybdenum atom and to the 4-position of the cyclopentenone ligand. In the crystal structure, the metal carbonyl (Mo–CO) moiety is situated parallel to the metal olefin unit while the metal nitrosyl (Mo–NO) bisects the olefin. The stereochemistry at molybdenum relative to the 4-methylcyclopentenone ligand (2*S*,3*R*,4*S*,-Mo*R*/2*R*,3*S*,4*R*,Mo*S*) demonstrates that either the nucleophilic attack has occurred *trans* to NO in the *exo* conformer of the η^3-allyl or *cis* to the NO in the *endo* conformer. This stands in direct contrast to earlier studies of unbiased cationic (π-allyl)molybdenum nitrosyl complexes where nucleophilic addition occurred *trans* to the NO in the *endo* conformer and *cis* to the NO in the *exo* conformer. A parallel series of reactions (CO → NO^+ conversion then nucleophilic addition) was conducted on (η^5-cyclopentadienyl)dicarbonyl[(2,3,4-η)-1-oxo-5-methyl-2-cyclopenten-4-yl)]molybdenum. Small, sterically unbiased nucleophiles ($NaCH(COOMe)_2$ and deuteride) reacted with high selectivity to produce *cis*-4,5-disubstituted cyclopentenones η^2-coordinated to molybdenum, while larger nucleophiles [$Me_2Cu(CN)Li_2$ and $NaC(Me)(COOEt)_2$] gave predominantly the 2,5-disubstituted cyclopentenone η^2-complex.

Introduction

The development of methods for the stereocontrolled construction of substituted cyclopentenones remains an important goal of organic synthesis research.[2-5] The use of cyclopentenyl-based metal π-complex intermediates to control both the regiochemistry and stereochemistry of the introduction of substituents has been explored in recent years.[6-14] In one example, the stable cationic cyclopentadienone complex (η^4-cyclopentadienone)(η^5-cyclopentadienyl)dicarbonylmolybdenum hexafluorophosphate, **1**, was shown to be a useful scaffold for the stereospecific construction of certain *cis*-4,5-disubstituted 2-cyclopentenones.[15] In this chemistry, a wide variety of carbon nucleophiles (alkyllithium reagents, Grignard reagents, sodium malonate, ketone enolates, and enamines) underwent reaction at the terminus of the η^4-cyclopentadienone α to the ketone moiety and *anti* to the bound molybdenum to provide (η^5-cyclopentadienyl)[(2,3,4-η)-1-oxo-2-cyclopenten-4-yl]dicarbonylmolybdenum complexes **2** (eq 1).



1 2 (1)

These underwent oxidative demetalation and gave 4,5-disubstituted cyclopentenones in good yields. Following a protocol well-established with simple (π-allyl)molybdenum complexes, the 5-substituted (1-oxocyclopentenyl)-molybdenum species should undergo reactivation via CO → NO^+ exchange, allowing the addition of a second

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(2) Ellison, R. A. *Synthesis* **1973**, 397.

(3) Piancatelli, G. *Heterocycles* **1982**, *19*, 1735.

(4) Santelli Rouvier, C.; Santelli, M. *Synthesis* **1983**, 429.

(5) Pauson, P. L. *Tetrahedron* **1985**, *41*, 5855.

(6) Trost, B. M.; Vanvranken, D. L. *J. Am. Chem. Soc.* **1993**, *115*, 444.

(7) Trost, B. M.; Ito, N.; Greenspan, P. D. *Tetrahedron Lett.* **1993**, *34*, 1421.

(8) Trost, B. M.; Li, L. P.; Guile, S. D. *J. Am. Chem. Soc.* **1992**, *114*, 8745.

(9) Falckpedersen, M. L.; Benneche, T.; Undheim, K. *Acta Chim. Scand.* **1993**, *47*, 72.

(10) Gundersen, L. L.; Benneche, T.; Rise, F.; Gogoll, A.; Undheim, K. *Acta Chim. Scand.* **1992**, *46*, 761.

(11) Mori, M.; Nukui, S.; Shibasaki, M. *Chem. Lett.* **1991**, 1797.

(12) Savillestones, E. A.; Lindell, S. D.; Jennings, N. S.; Head, J. C.; Ford, M. J. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2603.

(13) Tolstikov, G. A.; Miftakhov, M. S.; Danilova, N. A.; Vel'der, Y. L.; Spirkhin, L. V. *Synthesis* **1989**, 625.

(14) Deardorff, D.; Shambayati, S.; II, R.; Dunn, M. *J. Org. Chem.* **1988**, *53*, 189.

(15) Liebeskind, L. S.; Bombrun, A. *J. Am. Chem. Soc.* **1991**, *113*, 8736.

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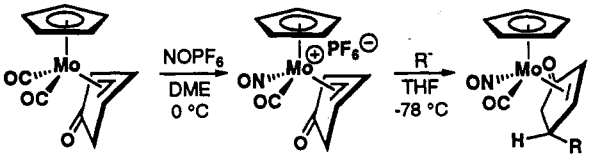
Table 1. Nucleophilic Additions to Cationic Nitrosyl Allyl Complex 3

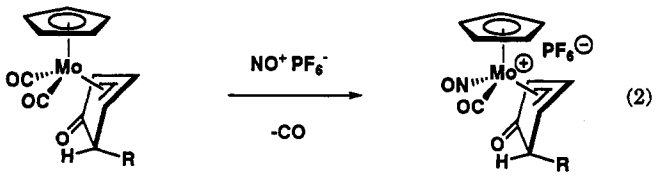


2a 3a 4 a-l

entry	nucleophile	cmpd	product	yield (%)
1	$Me_2Cu(CN)Li_2$	**4a**	R = Me	89
2	$n\text{-}Bu_2Cu(CN)Li_2$	**4b**	R = *n*-Bu	91
3	$s\text{-}Bu_2Cu(CN)Li_2$	**4c**	R = *s*-Bu	65
4	$Ph_2Cu(CN)Li_2$	**4d**	R = phenyl	43
5	$(2\text{-propenyl})_2Cu(CN)Li_2$	**4e**	R = 2-propenyl	45
6	$(PhC{\equiv}C)_2Cu(CN)Li_2$	**4f**	R = 2-phenylethynyl	35
7	$NaCNBD_3$[a]	**4g**	R = D	97
8	$NaCNBH_3$[a]	**4h**	R = H	92
9	$NaCH(CO_2Et)_2$	**4i**	R = $CH(CO_2Et)_2$	80
10	$NaC(CH_3)(CO_2Et)_2$	**4j**	R = $C(CH_3)(CO_2Et)_2$	80
11	$LiCH_2COC_6H_5$	**4k**	R = CH_2COPh	66
12	((*E*)-1-hexenyl)(2-thienyl)Cu(CN)Li_2	**4l**	R = (*E*)-1-hexenyl	31

[a] Nucleophile added to **3a** in THF at 0 °C.

nucleophile to the cyclopentenyl moiety (eq 2).[16-22] Re-



2 a, R = H; b, R = Me; c, R = D 3 (2)

activation of **2a** (R = H) by CO → NO^+ replacement was attempted, but the relatively electron deficient allylmolybdenum moiety did not react cleanly with NO^+ sources under conditions known to provide nitrosylmolybdenum cations from allylmolybdenum complexes lacking a conjugating ketone group.

Subsequent to the study depicted above, an improved process for the preparation of cationic (η^3-allyl)carbonyl(η^5-cyclopentadienyl)nitrosylmolybdenum complexes from the corresponding (η^3-allyl)(η^5-cyclopentadienyl)dicarbonylmolybdenum was discovered.[23] The simple expedient of conducting the CO → NO^+ exchange in dimethoxyethane (DME), a solvent that appears to moderate the reactivity of $NOPF_6$, provided analytically pure [(η^3-allyl)carbonyl(η^5-cyclopentadienyl)nitrosylmolybdenum][PF_6] complexes in most cases investigated. This discovery has allowed a high-yield synthesis of **3** (**a**, R = H; **b**, R = Me; **c**, R = D). The results of a study of the diastereoselective formation of **3a–c** followed by the addition of nucleophiles as a means of constructing substituted cyclopentenones are described within.

Results and Discussion

Slow addition of solid $NOPF_6$ to a 0 °C solution of (η^5-cyclopentadienyl)[(2,3,4-η)-1-oxo-2-cyclopenten-4-yl]dicarbonylmolybdenum, **2a**,[15] in DME led to evolution of CO and formation of a yellow-green solution which produced a bright yellow precipitate on addition to excess diethyl ether at −78 °C. Isolation by decantation of the ether provided the yellow cationic nitrosyl complex carbonyl(η^5-cyclopentadienyl)[(2,3,4-η)-1-oxo-2-cyclopenten-4-yl]nitrosylmolybdenum hexafluorophosphate, **3a**, in 80% yield. The solid, once isolated, was stable in air for an extended period of time; however, decomposition in solution (CH_3CN, DMSO, and acetone) was observed. The highly reactive nature of the cationic species with NMR solvents in which it was soluble limited the availability of usable spectroscopic data and precluded direct characterization of the complex.

Indirect evidence for the highly diastereoselective nature of the CO → NO^+ exchange was achieved by characterization of products **4**, formed by reaction of nitrosyl complex **3a** with nucleophiles. Organolithium and Grignard reagents did not react cleanly with **3a**; however, higher order cuprates ($R_2Cu(CN)Li_2$),[24] deuteride (and hydride), malonates, and acetophenone enolate reacted with in situ generated **3a** to provide good to excellent yields of (η^2-alkene)carbonyl(η^5-cyclopentadienyl)nitrosylmolybdenum complexes of 4-substituted 2-cyclopentenones with very high diastereocontrol, as judged by ^1H NMR[25] (Table 1). The products **4** were stable to flash SiO_2 chromatography; recrystallization from CH_2Cl_2 and hexanes was accomplished under an inert atmosphere. Prolonged exposure of solutions to air resulted in decomposition. Infrared spectra showed a typical NO stretch (~1645 cm^{-1}), CO stretch (~1990 cm^{-1}), and the η^2-cyclopentenone CO stretch (~1690 cm^{-1}) indicative of an α,β-unsaturated system.

As indicated below, the structure of the product from addition of $Me_2Cu(CN)Li_2$ to **3a** was determined by an X-ray diffraction study. In all other cases of nucleophilic

(16) Faller, J. W.; Lambert, C. *Tetrahedron* **1985**, *41*, 5755.
(17) VanArsdale, W. E.; Winter, R. E. K.; Kochi, J. K. *Organometallics* **1986**, *5*, 645.
(18) Faller, J. W.; Chao, K. H.; Murray, H. H. *Organometallics* **1984**, *3*, 1231.
(19) Faller, J. W.; Chao, K.-H. *Organometallics* **1984**, *3*, 927.
(20) Faller, J. W.; Chao, K.-H. *J. Am. Chem. Soc.* **1983**, *105*, 3893.
(21) Faller, J. W.; Murray, H. H.; White, D. L.; Chao, K. H. *Organometallics* **1983**, *2*, 400.
(22) Adams, R. D.; Chodosh, D. F.; Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1979**, *101*, 2570.
(23) Cosford, N. D. P.; Liebeskind, L. S. *Organometallics* **1994**, *13*, 1498.
(24) Lipshutz, B. H. *Synth. Lett.* **1990**, 119.
(25) ^1H NMR spectra of the *crude* products showed the presence of one diastereomer, predominantly; although additional very small resonances were noticeable prior to purification. These extra absorptions might be due to the presence of small amounts of complexes epimeric at molybdenum or derived from nucleophilic attack at C-2 of the 1-oxocyclopentenyl ligand. Because the compounds responsible for the appearance of these extra ^1H NMR peaks were not identifiable, the CO → NO^+ conversion and subsequent nucleophilic addition are claimed to be highly diastereoselective, rather than diastereospecific. Isolated yields of purified materials give an indication of the selectivity of the processes.

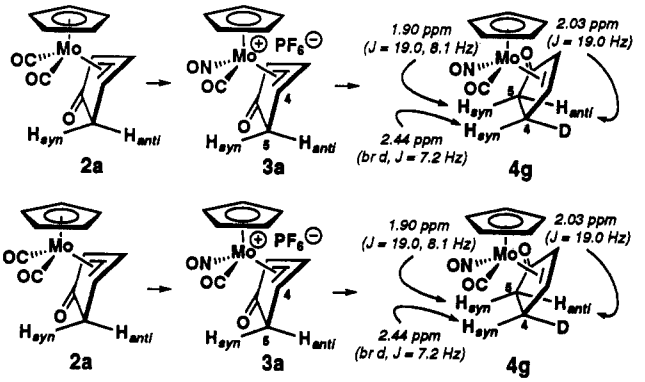


Figure 1. ^{1}H NMR assignments in 4 through deuteride addition.

addition, the regio- and stereospecificity were supported by ^{1}H NMR and infrared spectroscopic data and by comparison to the data of the methyl adduct. In the olefin complexes, the protons were unambiguously assigned by strategically labeling with deuterium accomplished by treatment of the cationic complexes **3a** and **3c** with $NaCNBD_3$. The ^{1}H NMR chemical shifts of the geminal methylene protons of **2a** were previously assigned by nOe studies.[15] In that study, the methylene protons of compound **2a** appeared at 2.28 and 3.13 ppm in the ^{1}H NMR in $CDCl_3$ solvent. Irradiation of the cyclopentadienyl singlet produced a 7% enhancement of the 2.28 ppm singlet and only a 1% enhancement of the 3.13 ppm singlet, allowing assignment of the 2.28 ppm absorption to the hydrogen *syn* to the molybdenum. Deuteride addition to 1 produced a product (**2c**) that retained a 2.26 ppm absorption but lost the 3.13 ppm absorption, indicating that addition occurred at C-5 and was stereoselective *anti* to the molybdenum.

In the present study depicted in Figure 1, deuteride addition to **3a** produced the 4-deuterio-η^2-alkene complex **4g**, showing absorptions at 1.90 ppm (dd, J = 19.0, 8.1 Hz), 2.03 ppm (d, J = 19.0 Hz), and 2.44 ppm (br d, J = 7.2 Hz). An analogous deuteride addition to **3c**, the cationic nitrosyl complex produced from **2c**, gave the alkene complex 4-deuterio-**4g** showing resonances at 1.91 ppm (br d, J = 8.0 Hz) and 2.45 ppm (br d, J = 8.0 Hz). Since the 2.03 ppm absorption disappears on going from the monodeuterated **4g** to the dideuterated compound 4-deuterio-**4g**, it can securely be assigned to C(5)–$\mathbf{H}_{anti}$. Since *trans* C(4)–C(5) vicinal coupling constants in cyclopentenones are near zero and *cis* vicinal coupling constants are 5–7 Hz,[26] comparison of the remaining resonances and their coupling constants allows assignment of the absorption near 1.9 ppm in both products to C(5)–H_{syn} and that near 2.4 ppm in both products to C(4)–H_{syn}.

To determine conclusively the stereoselectivity of the CO → NO^+ exchange (**2a** → **3a**) and the regio- and stereochemistry of the subsequent reaction with nucleophiles, a translucent yellow crystal of the methyl adduct **4a** was grown from methylene chloride and hexane under an argon atmosphere. An X-ray crystallographic analysis established the molecular structure of **4a** as that depicted by the ORTEP representation shown in Figure 2, confirming that the methyl group was delivered *anti* to the molybdenum atom and to the 4-position of the cyclopentenone ligand. The metal carbonyl moiety (Mo–CO) is

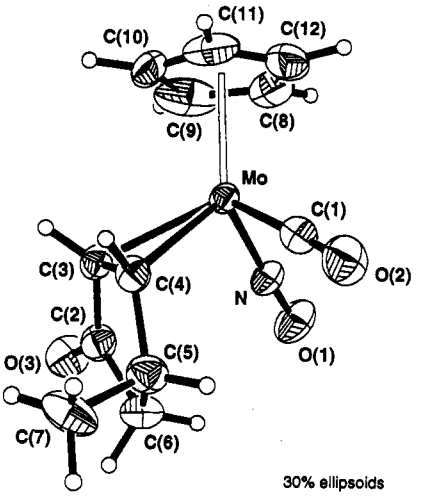


Figure 2. ORTEP of **4a**.

situated parallel to the metal olefin unit while the metal nitrosyl (Mo–NO) bisects the olefin. Refinement of trial structures where NO and CO were exchanged resulted in unreasonably small thermal ellipsoids for the nitrogen and high R values verifying the indicated placement of these ligands. A listing of crystal data, crystallography experimental details, bond lengths and bond angles are given in Tables 3–5 in the Experimental Section. Typical bond lengths and angles were exhibited by this complex in comparison with other nitrosyl olefin complexes. The Mo–N length was determined to be 1.770 Å.

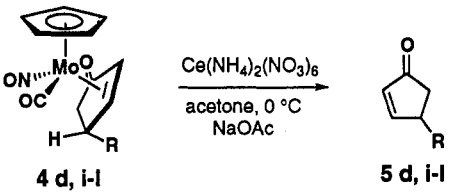
The molecular structure of **4a** can arise by one of the two processes. Either the nucleophilic attack has occurred *trans* to NO in the *exo* conformer or *cis* to the NO in the *endo* conformer. This stands in direct contrast to earlier studies of unbiased cationic π-allyl nitrosyl complexes where nucleophilic addition occurred *trans* to the NO in the *endo* conformer and *cis* to the NO in the *exo* conformer.[18,22,27] Clearly, there is a significant electronic bias imposed by the 1-oxo substituent on the η^3-cyclopentenyl that overrides the previously described directing effect of the NO ligand.

It was deduced recently on the basis of ^{1}H and ^{13}C NMR data that [carbonyl(η^3-cyclohexenyl)(η^5-cyclopentadienyl)-nitrosylmolybdenum][PF_6] and [carbonyl(η^5-cyclopentadienyl)(η^3-cyclopentenyl)nitrosylmolybdenum][PF_6] are isolated exclusively in their *exo* conformations when the corresponding dicarbonylmolybdenum complexes are treated with $NOPF_6$ in 1,2-dimethoxyethane.[23] In the present system, if the 1-oxocyclopentenyl complex similarly produces the *exo* conformer directly on CO → NO^+ conversion, then nucleophilic addition has occurred *trans* to the NO to produce the structure depicted in Figure 2. *Why is the usual directing effect of the NO ligand overridden in this system*? Perhaps the reaction selectivity is controlled by product stability, the nucleophile adding so as to produce the α,β-unsaturated ketone π-complex which is presumed to be more stable than the isomeric β,γ-unsaturated isomer (better back-bonding). However, given the very high reactivity of carbonyl(η^5-cyclopentadienyl)[(2,3,4-η)-1-oxo-2-cyclopenten-4-yl]nitrosylmolybdenum hexafluorophosphate, it is unlikely that the reaction proceeds through a productlike transition structure. Alternatively, kinetic factors might determine the product selectivity, either a

(26) Cocu, F. G.; Wolczunowicz, G.; Bors, L.; Posternak, T. *Helv. Chim. Acta* **1970**, *53*, 739.

(27) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592.

Table 2. Decomplexation of Nitrosyl Allyl Complexes 4



4 d, i-l 5 d, i-l

entry	R	η²-Alkene	product	yield (%)
1	C_6H_5	**4d**	**5d**	76
2	$(EtO_2C)_2CH$	**4i**	**5i**	78
3	$(EtO_2C)_2C(CH_3)$	**4j**	**5j**	74
4	$C_6H_5COCH_2$	**4k**	**5k**	81
5	*E*-1-hexenyl	**4l**	**5l**	73

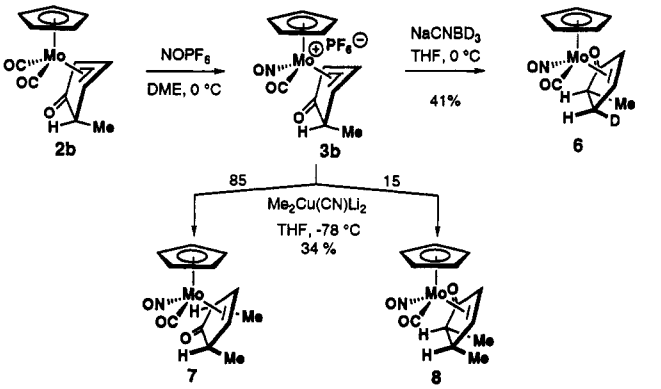
charge-controlled process or distortion of the η³-allyl frontier orbitals by the ketone functionality to favor attack of a nucleophile at the 4-position, as observed. Elaboration of these conjectures will require additional studies.

Having determined the relative stereochemistry of the methyl addition product of nitrosyl cation **3**, the question remains: why does (η⁵-cyclopentadienyl)[(2,3,4-η)-1-oxo-2-cyclopenten-4-yl]dicarbonylmolybdenum **2** react with $NOPF_6$ with such high diastereoselectivity? *This is only the second example of a highly diastereoselective CO → NO⁺ conversion in the (η³-allyl)(η⁵-cyclopentadienyl)-dicarbonylmolybdenum series.*[28] Although various scenarious can be envisaged that are based on selective η³–η¹-allyl slippage prior to loss of CO in the CO → NO⁺ conversion,[29] meaningful mechanistic speculation must await additional examples of highly diastereoselective CO → NO⁺ conversion using unsymmetrically substituted (η³-allyl)(η⁵-cyclopentadienyl)dicarbonylmolybdenum complexes.[30]

Decomplexation of the olefin complex was performed efficiently at 0 °C with ceric ammonium nitrate ($Ce(NH_4)_2(NO_3)_6$)(CAN) in acetone with NOAc as the buffer.[31] Liberation of the cyclopentenone ligands from the metal occurred in very good yields and no isomerization of the cyclopentenone double bond was noted under these conditions (Table 2).

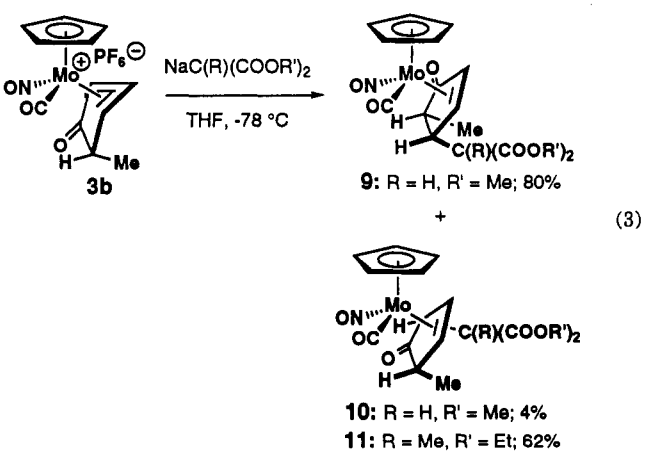
Given the high yield reaction of the η⁴-cyclopentadienone complex **1** with nucleophiles to produce 1-oxo-η³-cyclopentenylmolybdenum complexes **2** (eq 1),[15] subsequent CO → NO⁺ exchange and nucleophilic addition could establish a useful synthesis of 4,5-disubstituted 2-cyclopentenones. To probe this idea, (η⁵-cyclopentadienyl)-dicarbonyl[(2,3,4-η)-1-oxo-5-methyl-2-cyclopenten-4-yl]-molybdenum, **2b**, was treated with $NOPF_6$ in DME at 0 °C to generate the corresponding cationic nitrosyl complex, **3b**. Addition of deuteride gave carbonyl(η⁵-cyclopentadienyl)[(2,3-η)-4-*anti*-deuterio-5-*anti*-methyl-2-cyclopenten-1-one]nitrosylmolybdenum, **6**, in 41% yield (Scheme 1). Although the pure product was isolated in only modest yield, a ^1H NMR spectrum of the crude product prior to purification did not indicate the presence of any other diastereomer in significant quantity,[25] suggesting that a highly diastereoselective CO → NO⁺ exchange had occurred. It is presumed that the cationic nitrosyl(π-allyl)-molybdenum complex **3b** bears the same stereochemistry

Scheme 1



at molybdenum relative to the oxocyclopentenyl ligand as **3a**. Addition of $(Me_2Cu(CN)Li_2)$ at −78 °C via cannula, workup, and purification provided in 34% yield an 85:15 ratio of products resulting from addition to both termini of the π-allyl system, respectively the less polar carbonyl-(η⁵-cyclopentadienyl)[(3,4-η)-2,5-dimethyl-2-cyclopenten-1-one]nitrosylmolybdenum, **7**, and the more polar carbonyl-(η⁵-cyclopentadienyl)[(2,3-η)-4,5-dimethyl-2-cyclopenten-1-one]nitrosylmolybdenum, **8**. The two compounds can be readily distinguished by infrared spectroscopy, the 2,5-dimethyl isomer showing a reasonable ketone stretch at 1738 cm^{-1} (CH_2Cl_2), while the 4,5-dimethyl product had a lower absorption at 1695 cm^{-1} indicative of significant delocalization.

Since it was shown above that nucleophilic addition to the 5-*unsubstituted* carbonyl(η⁵-cyclopentadienyl)[(2,3,4-η)-1-oxo-2-cyclopenten-4-yl]nitrosylmolybdenum hexafluorophosphate, **3a**, occurred exclusively at the 4-position, apparently the result of electronic perturbation by the 1-oxo functional group, it is presumed that the steric effect of the 5-methyl group in **3b** has perturbed the product selectivity away from addition to the 4-position because of nonbonded interactions between the 5-methyl substituent and the incoming nucleophile. To probe the steric effect of the 5-methyl substituent, malonate nucleophiles of different steric demand were used (eq 3). (η⁵-Cyclo-



(3)

pentadienyl)dicarbonyl[(2,3,4-η)-1-oxo-5-methyl-2-cyclopenten-4-yl]molybdenum, **2b**, was treated with $NOPF_6$ in DME at 0 °C to generate the corresponding cationic nitrosyl complex, and this was treated with sodium dimethyl malonate in THF at −78 °C. Workup and isolation provided the 4,5-disubstituted product, **9**, in 80% isolated yield along with a trace (4%) of the 2,5-disubstituted product, **10** (95:5 ratio). Interestingly, the more

(28) Faller, J. W.; Lambert, C.; Mazzieri, M. R. *J. Organomet. Chem.* **1990**, *383*, 161.
(29) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1976**, *98*, 3388.
(30) Additional highly diastereoselective CO → NO⁺ conversions of unsymmetrically substituted π-allylmolybdenum complexes are currently under study and will be reported in due course.
(31) Shvo, Y.; Hazum, E. *J. Chem. Soc., Chem. Commun.* **1974**, 336.

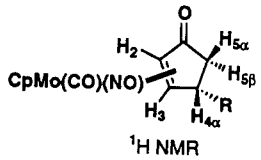
hindered nucleophile, sodium diethyl methylmalonate provided exclusively the 2,5-disubstituted cyclopentenone product **11** in 62% yield.

Conclusions

Carbonyl(η^5-cyclopentadienyl)[(2,3,4-η)-1-oxo-2-cyclopenten-4-yl]nitrosylmolybdenum hexafluorophosphate can be generated as a single diastereomer in good yield from (η^5-cyclopentadienyl)[(2,3,4-η)-1-oxo-2-cyclopenten-4-yl]-dicarbonylmolybdenum on treatment with $NOPF_6$ in 1,2-dimethoxyethane at 0 °C. Stereo- and regiospecific nucleophilic addition (higher-order cuprates, malonates, enolates, and borodeuteride) generates single diastereomers of (η^2-alkene)carbonyl(η^5-cyclopentadienyl)nitrosylmolybdenum complexes which undergo oxidative demetalation in high yield with ceric ammonium nitrate to provide 4-substituted cyclopentenones. Ultimately, efficient synthetic access to the separate enantiomers of (η^5-cyclopentadienyl)[(2,3,4-η)-1-oxo-2-cyclopenten-4-yl]dicarbonylmolybdenum could allow these stable metal π-complexes to be used as scaffolds for the enantiocontrolled construction of various substituted cyclopentenone-derived materials.

Experimental Section

Materials and Methods. Unless otherwise indicated, all reactions were carried out in flame-dried glassware under dry argon with standard inert atmosphere techniques. All solvents were dried before use. THF and diethyl ether were distilled from sodium and benzophenone. Dichloromethane and hexanes were distilled from calcium hydride. 1,2-Dimethoxyethane (DME) was purchased from Aldrich Chemical Co. in a Sure Seal bottle. Nitrosyl hexafluorophosphate was purchased from Pfaltz & Bauer, Inc., stored under inert atmosphere, and was used as received. Cuprous cyanide was purchased from Fluka Chemika, stored under an inert atmosphere, and gently flamed-dried under vacuum before generation of cuprate reagents. Lithium (2-thienyl)cyanocuprate and lithium phenylacetylide were purchased from Aldrich and were used as received. Thin-layer chromatography (TLC) was performed with E. Merck silica gel 60F-254 glass plates of 0.25-mm thickness, with UV light, phosphomolybdic acid (10% in ethanol), and vanillin (1 g in 200 mL of methanol and 50 mL of 50% H_2SO_4) 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. (η^5-Cyclopentadienyl)dicarbonyl[(2,3,4-η)-1-oxo-2-cyclopenten-4-yl]-molybdenum, **2**, was prepared according to the literature method.[15] Compounds are numbered as follows for NMR data:



^{1}H NMR

Generation of 3a by CO → NO$^+$ Exchange. Carbonyl(η^5-cyclopentadienyl)[(2,3,4-η)-1-oxo-2-cyclopenten-4-yl]nitrosylmolybdenum Hexafluorophosphate, 3a. Into a 100-mL Schlenk flask equipped with a magnetic stir bar was placed (η^5-cyclopentadienyl)[(2,3,4-η)-1-oxo-2-cyclopenten-4-yl]dicarbonylmolybdenum, **2a** (0.200 mg, 0.671 mmol), and 8 mL of 1,2-dimethoxyethane (DME), and the solution was cooled to 0 °C. Nitrosonium hexafluorophosphate (0.120 g, 0.671 mmol) was added gradually as a solid, by gently tapping a Schlenk tube containing the $NOPF_6$ which was fitted to the Schlenk flask holding the reaction mixture. Evolution of CO was observed, and by completion of the addition, the solution had obtained a yellow-green color. TLC showed consumption of starting material (R_f = 0.55, EtOAc) and a new spot (R_f = 0.40, EtOAc) that easily stained with 5% phosphomolybdic acid in ethanol (PMA). The high reactivity of **3a** suggests that the TLC spot at R_f = 0.40 is the result of reaction of **3a** at the silica gel surface (possibly hydration to an alcohol or elimination to a diene). The nucleophilic addition reactions, described below, were carried on from this point without isolation of the nitrosyl complex.

To isolate the product **3a**, the following procedure was followed. After generation of the nitrosyl complex, the solution was allowed to stir for 5 min. Into another 100-mL Schlenk flask equipped with a magnetic stir bar was placed diethyl ether, and the vessel was cooled to −78 °C with stirring. The solution of nitrosyl complex **3a** was transferred into the ether in a dropwise manner via cannula, producing a bright yellow precipitate. Stirring was stopped, and after the precipitate had settled, the ether was decanted via cannula. The precipitate was washed with cold diethyl ether, and the excess ether was removed under vacuum to provide 239 mg (80%) of **3a**. The solid, once isolated, is stable in air for an extended period of time. It dissolves in CH_3CN, DMSO, and acetone; however, decomposition in solution was observed. Mp = 145 °C (dec. R_f = 0.40 (EtOAc). IR (KBr pellet): 3118, 2116, 2046, 1800, 1754, 1688, 1550 cm^{-1}. Anal. Calcd for $C_{11}H_{10}F_6MoNPO_3$: C, 29.68; H, 2.26; N, 3.15. Found: C, 29.17; H, 2.63; N, 3.30.

Synthesis of η^2-Cyclopentenone Complexes 4. Carbonyl(η^5-Cyclopentadienyl)nitrosyl(2,3-η)-4-methyl-2-cyclopenten-1-one]molybdenum, 4a. In a 100-mL Schlenk flask equipped with magnetic stirring bar was generated carbonyl(η^5-cyclopentadienyl)[(2,3,4-η)-1-oxo-2-cyclopenten-4-yl]nitrosylmolybdenum hexafluorophosphate, **3a** (1.39 mmol) in 16 mL of DME from (η^5-cyclopentadienyl)[(2,3,4-η)-1-oxo-2-cyclopenten-4-yl]-dicarbonylmolybdenum, **2a** (0.414 mg, 1.39 mmol), and $NOPF_6$ (243 mg, 1.39 mmol) following the procedure above. This solution was then cooled to −78 °C. Into a 50-mL Schlenk flask equipped with a magnetic stirring bar was placed dried CuCN (188 mg, 2.10 mmol, 1.5 equiv). THF (20 mL) was added, and the reaction mixture was cooled to −40 °C. To this mixture was added methyllithium (2.98 mL of 1.4 M in diethyl ether, 4.20 mmol). Upon completion of addition, a bright yellow color was noted. The mixture was allowed to stir at −40 °C for 45 min by which time all CuCN should have dissolved producing a cloudy solution. The solution was then allowed to warm to 0 °C. The cuprate was then added dropwise via cannula to the nitrosyl complex at −78 °C. Upon addition, the solution acquired to a deep red color. The solution was allowed to stir for 1 h at −78 °C; then the reaction was quenched with 20 mL of degassed saturated aqueous NH_4Cl solution. The reaction mixture was extracted with Et_2O and dried over Na_2SO_4. Filtration and removal of solvent gave a yellow solid that was purified by air-free column chromatography (silica gel, 230–400 mesh/degassed ethyl acetate as eluant, R_f = 0.78, UV, PMA stain) and gave 390 mg (89%) of **3a** as a yellow solid. Further purification by recrystallization from CH_2Cl_2 and hexanes gave yellow needles. The product is soluble in most solvents and decomposes upon exposure to air while in solution. It is stable in degassed and distilled solvents if kept free from air. Mp = 120–124 °C. IR (CH_2Cl_2): 2925, 2819, 1993, 1894, 1737, 1694, 1638 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 5.65 (s, Cp, 5H), 3.82 (d, H_3, J = 6.0 Hz, 1H), 3.75 (d, H_2, J = 6.0 Hz, 1H), 2.77 (m, H_4, J = 6.6, 7.2 Hz, 1H), 2.06 (dd, $H_{5\alpha}$, J = 7.5, 18.6 Hz, 1H), 1.54 (d, $H_{5\beta}$, J = 18.6 Hz, 1H), 1.30 (d, CH_3, J = 6.9 Hz, 3H). ^{13}C NMR (CH_2Cl_2, 75.48 MHz): δ 227.4, 210.5, 96.7, 75.1, 51.5, 41.5, 37.1, 25.4; Anal. Calcd for $C_{12}H_{13}NO_3Mo$: C, 45.73; H, 4.16; N, 4.44. Found: C, 45.80; H, 4.18; N, 4.43.

[(2,3-η)-4-*n*-Butyl-2-cyclopenten-1-one]carbonyl(η-^{5}-cyclopentadienyl)nitrosylmolybdenum, 4b. In a 100-mL Schlenk flask equipped with a magnetic stirring bar was generated carbonyl(η^5-cyclopentadienyl)[(2,3,4-η)-1-oxo-2-cyclopenten-4-yl]nitrosylmolybdenum hexafluorophosphate, **3a** (0.260 mmol) from **2a** (77.5 mg, 0.260 mmol), and $NOPF_6$ (45.5 mg, 0.260 mmol) in 4 mL of DME following the procedure above for **4a**. The

solution was cooled to −78 °C. In a fashion similar to that of **4a**, the cuprate was generated from dried CuCN (35 mg, 1.5 equiv, 0.390 mmol) in THF (4 mL) at −40 °C by adding *n*-butyllithium (0.488 mL, 1.6 M in hexanes, 0.780 mmol). After 90 min at −40 °C the solution was allowed to warm to 0 °C and the cuprate, thus generated, was added via cannula to the nitrosyl complex at −78 °C. The reaction was processed as for **4a**, above, to give a yellow solid that was purified by air-free column chromatography (silica gel, 230–400 mesh/degassed mixture 1:1 of ethyl acetate/hexanes as eluant, UV, PMA stain) which gave 84 mg (91%) of a yellow solid. MP = 96–98 °C (CH_2Cl_2/hexanes under argon). R_f = 0.90 (EtOAc) IR ($CHCl_3$): 3011, 2925, 1993, 1694, 1637 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.65 (s, Cp, 5H), 3.85 (d, H_3, J = 6.0 Hz, 1H), 3.81 (d, H_2, J = 6.0 Hz, 1H), 2.66 (dt, H_4, J = 7.2, 6.6 Hz, 1H), 2.14 (dd, $H_{5\alpha}$, J = 20.1, 7.2 Hz, 1H), 1.71 (d, $H_{5\beta}$, J = 20.1 Hz, 1H), 1.7–1.2 (m, butyl methylenes, 6H), 0.90 (t, butyl CH_3, 3H). ^{13}C NMR ($CDCl_3$, 75.48 MHz): δ 227.6, 210.6, 96.7, 73.6, 52.0, 42.6, 40.2, 39.9, 29.3, 22.6, 13.7. Anal. Calcd for $C_{15}H_{19}NO_3Mo$: C, 50.43; H, 5.36; N, 3.92. Found: C, 50.93; H, 5.63; N, 3.33.

Carbonyl(η⁵-cyclopentadienyl)nitrosyl[(2,3-η)-4-*sec*-butyl-2-cyclopenten-1-one]molybdenum, 4c. In a 100-mL Schlenk flask equipped with a magnetic stirring bar was generated carbonyl(η⁵-cyclopentadienyl)[(2,3,4-η)-1-oxo-2-cyclopenten-4-yl]nitrosylmolybdenum hexafluorophosphate, **3a** (0.671 mmol) from **2a** (200 mg, 0.671 mmol), and $NOPF_6$ (120 mg, 0.671 mmol) in 8 mL of DME following the procedure above for **4a**. The solution was cooled to −78 °C. In a fashion similar to that of **4a**, the cuprate was generated from dried CuCN (72 mg, 0.810 mmol, 1.2 equiv) in THF (2 mL) at −40 °C by adding *sec*-butyllithium (1.25 mL, 1.3 M in cyclohexane, 1.62 mmol). After 90 min at −40 °C the solution was allowed to warm to 0 °C and the cuprate, thus generated was added via cannula to the nitrosyl complex at −78 °C. The reaction was processed as for **4a**, above, to give a yellow solid that was purified by air-free column chromatography (silica gel, 230–400 mesh/degassed mixture 1:1 of ethyl acetate/hexanes as eluant, UV, PMA stain) yielding 155 mg (65%) of a yellow solid. Mp = 108–110 °C (CH_2Cl_2/hexanes under argon). R_f = 0.90 (EtOAc). IR (CH_2Cl_2): 3056, 2966, 2933, 2878, 1993, 1701, 1640, 1418, 1270 cm^{-1}. ^1H NMR (CD_2Cl_2, 300 MHz) (^1H NMR shows diastereomers): δ 5.65 (s, Cp, 5H), 3.86 (d, H_3, J = 6.0 Hz, 1H), 3.84 (d, H_2, J = 6.0 Hz, 1H), 2.72 (m, H_4, 1H), 2.11, 2.02 (2 overlapping dd, $H_{5\alpha}$, J = 18.9, 7.8 Hz, 1H), 1.84, 1.77 (2 overlapping dd, $H_{5\beta}$, J = 18.9, 7.8 Hz, 1H), 1.64–1.40 (m, *sec*-butyl methylenes, 2H), 1.30–1.17 (m, 1H), 0.934 (d, CH_3, J = 6.6, 3H), 0.93 (t, CH_3, J = 7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75.48 MHz) (^{13}C NMR shows diastereomers): δ 227.49, 227.54, 211.43, 211.52, 96.66, 96.80, 72.36, 71.11, 53.37, 53.06, 47.55, 47.45, 41.84, 41.73, 38.15, 36.40, 26.72, 26.54, 15.14, 15.05, 11.94, 11.90; Anal. Calcd for $C_{15}H_{19}NO_3Mo$: C, 50.43; H, 5.36; N, 3.92. Found: C, 50.52; H, 5.41; N, 3.88.

Carbonyl(η⁵-cyclopentadienyl)nitrosyl[(2,3-η)-4-phenyl-2-cyclopenten-1-one]molybdenum, 4d. In a 100-mL Schlenk flask equipped with a magnetic stirring bar was generated carbonyl(η⁵-cyclopentadienyl)[(2,3,4-η)-1-oxo-2-cyclopenten-4-yl]nitrosylmolybdenum hexafluorophosphate, **3a** (0.671 mmol) from **2a** (200 mg, 0.671 mmol), and $NOPF_6$ (120 mg, 0.671 mmol) in 8 mL of DME following the procedure above for **4a**. The solution was cooled to −78 °C. In a fashion similar to that of **4a**, the cuprate was generated from dried CuCN (72 mg, 0.805 mmol, 1.2 equiv) in THF (1 mL) −78 °C by adding phenyllithium (0.89 mL of 1.8 M in cyclohexane/diethyl ether, 1.62 mmol) and the mixture was allowed to stir at −78 °C for 3 h. The cuprate thus generated was added via cannula to the nitrosyl complex at −78 °C. The reaction was processed as for **4a**, above, to give a viscous red liquid. Purification by air-free column chromatography (silica gel, 230–400 mesh/degassed mixture 1:1 of ethyl acetate/hexanes as eluant, R_f = 0.60, UV, PMA stain) gave 109 mg (43%) of a yellow oil. IR ($CHCl_3$): 2953, 1998, 1693, 1644 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.40–7.20 (m, phenyl, 5H), 5.26 (s, Cp, 5H), 4.00 (d, H_2, J = 5.7 Hz, 1H), 3.87 (m, H_4, 1H), 3.86 (d, H_2, J = 5.4 Hz, 1H), 2.48 (dd, $H_{5\alpha}$, J = 19.2, 8.1 Hz, 1H), 2.13 (d, $H_{5\beta}$, J = 19.2 Hz, 1H). ^{13}C NMR (CH_2Cl_2, 75.48 MHz): δ 226.7, 210.1, 147.4, 128.8, 126.5, 126.4, 96.9, 73.1, 51.4, 41.9, 47.9. Anal. Calcd for $C_{17}H_{15}NO_3Mo$: C, 54.13; H, 4.01; N, 3.71. Found: C, 53.90; H, 4.37; N, 3.65.

Carbonyl(η⁵-cyclopentadienyl)nitrosyl[(2,3-η)-4-(2-propenyl)-2-cyclopenten-1-one]molybdenum, 4e. In a 100-mL Schlenk flask equipped with a magnetic stirring bar was generated carbonyl(η⁵-cyclopentadienyl)[(2,3,4-η)-1-oxo-2-cyclopenten-4-yl]nitrosylmolybdenum hexafluorophosphate, **3a** (0.450 mmol) from **2a** (134 mg, 0.450 mmol), and $NOPF_6$ (79 mg, 0.45 mmol) in 5 mL of DME following the procedure above for **4a**. The solution was cooled to −78 °C. Into a 50-mL Schlenk flask equipped with a magnetic stirring bar was placed 2-bromopropene (0.545 g, 4.50 mmol), THF (4 mL) was added, and the solution was cooled to −78 °C. In a dropwise manner, *tert*-butyllithium (5.82 mL of 1.7 M in pentane, 9.90 mmol, 2 equiv) was added and the mixture was allowed to stir for 30 min; then dried CuCN (200 mg, 2.25 mmol, 5 equiv) was added and the reaction mixture was stirred at −78 °C for additional 1.5 h. The cuprate, thus generated, was added via cannula to the nitrosyl complex at −78 °C. The reaction was processed as for **4a**, above, to give a red oil that was purified by air-free column chromatography (silica gel, 230–400 mesh/degassed mixture 1:1 of ethyl acetate/hexanes as eluant, R_f = 0.68, UV, PMA stain) to give 69 mg (45%) of a yellow solid. Mp = 164–165 °C (CH_2Cl_2/hexanes under argon). IR ($CHCl_3$): 3018, 1993, 1694, 1645 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.65 (s, Cp, 5H), 4.89 (s, vinyl H, 1H), 4.78 (s, vinyl H, 1H), 3.91 (d, H_3, J = 6.0 Hz, 1H), 3.76 (d, H_2, J = 6.0 Hz, 1H), 3.35 (d, H_4, J = 7.2 Hz, 1H), 2.19 (dd, $H_{5\alpha}$, J = 19.2, 7.8 Hz, 1H), 1.88 (d, $H_{5\beta}$, J = 19.2 Hz, 1H), 1.78 (s, propenyl CH_3, 3H). ^{13}C NMR ($CDCl_3$, 75.48 MHz): δ 226.4, 210.8, 149.3, 110.8, 96.7, 71.4, 51.9, 49.4, 38.6, 19.1. Anal. Calcd for $C_{14}H_{15}NO_3Mo$: C, 49.28; H, 4.43; N, 4.11. Found: C, 49.36; H, 4.47; N, 4.02.

Carbonyl(η⁵-cyclopentadienyl)nitrosyl[(2,3-η)-4-(2-phenylethynyl)-2-cyclopenten-1-one]molybdenum, 4f. In a 100-mL Schlenk flask equipped with a magnetic stirring bar was generated carbonyl(η⁵-cyclopentadienyl)[2,3,4-η)-1-oxo-2-cyclopenten-4-yl]nitrosylmolybdenum hexafluorophosphate, **3a** (0.671 mmol) from **2a** (200 mg, 0.671 mmol), and $NOPF_6$ (120 mg, 0.671 mmol) in 8 mL of DME following the procedure above for **4a**. The solution was cooled to −78 °C. In a similar fashion to **4a**, the cuprate was generated from dried CuCN (93 mg, 1.01 mmol, 1.5 equiv) in THF (3 mL) at −78 °C by adding lithium phenylacetylide (2.22 mL of 1.0 M in THF, 1.11 mmol), producing a red solution that turned yellow on further stirring at −78 °C for 1 h. The cuprate, thus generated, was added via cannula to the nitrosyl complex at −78 °C. The reaction was processed as for **4a**, above, to give a yellow solid that was purified by air-free column chromatography (silica gel, 230–400 mesh/degassed mixture 1:1 of ethyl acetate/hexanes as eluant, R_f = 0.64, UV, PMA stain) to yield 94 mg (35%) of a yellow solid that was soluble in most solvents and stable to air while in solution. Mp = 115–120 °C (CH_2Cl_2/hexanes under argon). IR ($CHCl_3$): 3011, 2200, 2002, 1703, 1645 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.5–7.2 (m, phenyl, 5H), 5.65 (s, Cp, 5H), 4.01 (d, H_3, J = 6.0 Hz, 1H), 3.89 (d, H_2, J = 6.0 Hz, 1H), 3.66 (dd, H_4, J = 7.5, 2.4 Hz, 1H), 2.35 (dd, $H_{5\alpha}$, J = 18.5, 7.5 Hz, 1H), 2.24 (dd, $H_{5\beta}$, J = 18.5, 2.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75.48 MHz): δ 225.4, 209.2, 131.6, 128.3, 128.1, 123.1, 97.0, 93.6, 82.0, 69.1, 50.6, 40.8, 33.7. Anal. Calcd for $C_{19}H_{15}NO_3Mo$: C, 56.87; H, 3.77; N, 3.49. Found: C, 56.79; H, 3.82; N, 3.43.

Carbonyl(η⁵-cyclopentadienyl)[(2,3-η)-4-*anti*-deuterio-2-cyclopenten-1-one]nitrosylmolybdenum, 4g. In a 100-mL Schlenk flask equipped with a magnetic stirring bar was generated carbonyl(η⁵-cyclopentadienyl)[(2,3,4-η)-1-oxo-2-cyclopenten-4-yl]nitrosylmolybdenum hexafluorophosphate, **3a** (0.340 mmol) from **2a** (100 mg, 0.340 mmol), and $NOPF_6$ (60 mg, 0.340 mmol) in 8 mL of DME following the procedure above for **4a**. *It is important that nitrosyl 3a be diluted as indicated.* This solution was maintained at 0 °C. Into a Schlenk flask was added $NaCNBD_3$ (0.022 g, 0.340 mmol, 1.0 equiv) dissolved in 10 mL of THF and the $NaCNBD_3$/THF solution was added slowly to

the nitrosyl complex via cannula, resulting in a color change to light yellow-green. The solvent was evaporated, and the greenish oil was purified by air-free column chromatography (silica gel, 230–400 mesh/degassed ethyl acetate as eluant, R_f = 0.68, UV, PMA stain) to give 101 mg (98%) of a yellow solid that was soluble in most solvents and stable to air while in solution. Mp = 117–119 °C (CH_2Cl_2/hexanes under argon). IR (CH_2Cl_2): 3054, 1993, 1699, 1640 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.62 (s, Cp, 5H), 3.96 (d, H_3, J = 6.0 Hz, 1H), 3.82 (d, H_2, J = 6.0 Hz, 1H), 2.44 (br d, H_4, J = 7.2 Hz, 1H), 2.03 (d, $H_{5\beta}$, J = 19.0 Hz, 1H), 1.89 (dd, $H_{5\alpha}$, J = 19.0, 8.1 Hz, 1H), ^{13}C NMR ($CDCl_3$, 75.48 MHz): δ 227.3, 211.9, 96.6, 68.3, 53.3, 32.5, 29.1 (t, J = 19.5 Hz). HRMS Calcd for $C_{10}H_{10}DO_2NMo$ ($C_{11}H_{10}DO_3NMo$ – CO): 275.990674. Found: 275.9906605 (error 4.7 × 10^{-6}%).

Carbonyl(η^5-cyclopentadienyl)[(2,3-η)-4,5-*anti*-dideuterio-2-cyclopenten-1-one]nitrosylmolybdenum, 4-deuterio-4g. In a 100-mL Schlenk flask equipped with a magnetic stirring bar was generated carbonyl(η^5-cyclopentadienyl)[(2,3,4-η)-1-oxo-5-*anti*-deuterio-2-cyclopenten-4-yl]nitrosylmolybdenum hexafluorophosphate, **3c** from **2c**[15] (157 mg, 0.525 mmol), and $NOPF_6$ (94 mg, 0.525 mmol) in 13 mL of DME following the procedure above for **4a**. The solution was cooled to 0 °C and treated dropwise via cannula with $NaCNBD_3$ (35 mg, 0.525 mmol) dissolved in 10 mL of THF. The resulting solution was allowed to stir at 0 °C for 2 h; then the solvent was evaporated. The resulting dark green oil showed a new spot by TLC assay (R_f = 0.68, EtOAc). Purification by air-free column chromatography (SiO_2, 230–400 mesh, degassed EtOAc) gave 137 mg (87%) of 4-deuterio-**4g** as a yellow solid. Mp = 115–117 °C (CH_2Cl_2/hexanes under argon). IR (CH_2Cl_2): 3054, 2960, 1991, 1697, 1641 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 5.56 (s, Cp, 5H), 4.00 (d, H_3, J = 5.7 Hz, 1H), 3.86 (d, H_2, J = 5.7 Hz, 1H), 2.47 (br d, H_4, J = 8.4 Hz, 1H), 1.92 (br d, $H_{5\alpha}$, J = 7.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75.48 MHz): δ 227.4, 211.9, 96.7, 68.4, 53.4, 32.5, 29.4. Anal. Calcd for $C_{11}H_{13}NO_3Mo$ (for $C_{11}H_9D_2NO_3Mo$): C, 43.58; H, 4.32; N, 4.62. Found: C, 43.42; H, 3.72; N, 4.62.

Carbonyl(η^5-cyclopentadienyl)[(2,3-η)-2-cyclopenten-1-one]nitrosylmolybdenum, 4h. In a 100-mL Schlenk flask equipped with a magnetic stirring bar was generated carbonyl(η^5-cyclopentadienyl)[(2,3,4-η)-1-oxo-2-cyclopenten-4-yl]nitrosylmolybdenum hexafluorophosphate, **3a** (0.340 mmol) from **2a** (100 mg, 0.340 mmol), and $NOPF_6$ (60 mg, 0.340 mmol) in 8 mL of DME following the procedure above for **4a**. *It is important that nitrosyl **3a** is diluted as indicated.* This solution was cooled to 0 °C. Into a 50-mL Schlenk flask was added $NaCNBH_3$ (0.022 g, 0.340 mmol, 1.0 equiv) dissolved in 10 mL of THF and the $NaCNBH_3$/THF solution was added slowly to the nitrosyl complex via cannula, resulting in a change to a light yellow-green color upon completion of addition. The solvent was evaporated, and the resulting greenish oil was purified by air-free column chromatography (silica gel, 230–400 mesh/degassed ethyl acetate as eluant, R_f = 0.62, UV, PMA stain) to give 94 mg (92%) of a yellow solid that was soluble in most solvents and stable to air while in solution. Mp = 118–120 °C (CH_2Cl_2/hexanes under argon). IR (CH_2Cl_2): 3054, 1995, 1698, 1639 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.64 (s, Cp, 5H), 4.00 (dd, H_3, J = 5.7, 5.4 Hz, 1H), 3.85 (d, H_2, J = 6.0 Hz, 1H), 3.10 (m, $H_{4\beta}$, 1H), 2.50 (ddd, $H_{4\alpha}$, J = 15.3, 8.1, 1.8 Hz, 1H), 2.11–2.02 (m, $H_{5\beta}$, 1H), 1.98–1.87 (m, $H_{5\alpha}$, 1H). ^{13}C NMR ($CDCl_3$, 75.48 MHz): 227.3, 211.9, 96.6, 68.4, 53.3, 32.6, 29.5. Anal. Calcd for $C_{11}H_{11}NO_3Mo$: C, 43.87; H, 3.68; N, 4.65. Found: C, 43.77; H, 3.73; N, 4.60.

Carbonyl(η^5-cyclopentadienyl)nitrosyl(2,3-η)-4-(1,3-diethoxy-1,3-dioxo-2-propyl)-2-cyclopenten-1-one]molybdenum, 4i. In a 100-mL Schlenk flask equipped with a magnetic stirring bar was generated carbonyl(η^5-cyclopentadienyl)[(2,3,4-η)-1-oxo-2-cyclopenten-4-yl]nitrosylmolybdenum hexafluorophosphate, **3** (0.671 mmol) from **2a** (200 mg, 0.671 mmol), and $NOPF_6$ (120 mg, 0.671 mmol) in 8 mL of DME following the procedure above for **4a**. This solution was cooled to –78 °C and treated with $NaCH(CO_2Et)_2$ prepared at 0 °C from NaH (16.0 mg, 0.671 mmol) and diethyl malonate (0.110 mL, 0.671 mmol) in 10 mL of THF. The nucleophile was transferred via cannula, and the resulting solution was allowed to stir at 0 °C for 1 h. The solvent was evaporated, and the resulting dark red oil was purified by air-free column chromatography (silica gel, 230–400 mesh/degassed mixture 1:1 of ethyl acetate/hexanes as eluant, R_f = 0.35, UV, PMA stain) to give 243 mg (79%) of a yellow solid. Mp = 115–117 °C (CH_2Cl_2/hexanes under argon). IR (CH_2Cl_2): 3058, 2986, 2002, 1905, 1936, 1727, 1704, 1643 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 5.67 (s, Cp, 5H), 4.23 (m, propyl methylenes, 4H), 3.90 (d, H_3, J = 6.0 Hz, 1H), 3.81 (d, H_2, J = 6.0 Hz, 1H), 3.53 (d, propyl methyne, J = 8.1 Hz, 1H), 3.37 (ddd, H_4, J = 2.1, 2.4, 8.1 Hz, 1H), 2.25 (dd, $H_{5\alpha}$, J = 18.9, 7.8 Hz, 1H), 1.97 (d, $H_{5\beta}$, J = 18.9 Hz, 1H) 1.28, 1.27 (overlapping t, propyl methyls, J = 7.2 Hz, 6 H). ^{13}C NMR ($CDCl_3$, 75.48 MHz): δ 224.7, 209.2, 168.0, 168.0, 96.9, 67.5, 61.8, 61.7, 59.6, 51.8, 42.0, 37.8, 14.1. Anal. Calcd for $C_{18}H_{21}NO_7Mo$: C, 47.07; H, 4.61; N, 3.05. Found: C, 47.04; H, 4.59; N, 2.97.

Carbonyl(η^5-cyclopentadienyl)[(2,3-η)-4-(1,3-diethoxy-1,3-dioxo-2-methyl-2-propyl)-2-cyclopenten-1-one]nitrosylmolybdenum, 4j. In a 100-mL Schlenk flask equipped with a magnetic stirring bar was generated carbonyl(η^5-cyclopentadienyl)[(2,3,4-η)-1-oxo-2-cyclopenten-4-yl]nitrosylmolybdenum hexafluorophosphate, **3** (0.671 mmol) from **2a** (200 mg, 0.671 mmol), and $NOPF_6$ (120 mg, 0.671 mmol) in 8 mL of DME following the procedure above for **4a**. This solution was cooled to –78 °C and treated with $NaC(CH_3)(CO_2Et)_2$ prepared at 0 °C from NaH (16.0 mg, 0.671 mmol) and methyl diethyl malonate (0.115 mL, 0.671 mmol) in 10 mL of THF. The nucleophile was transferred via cannula, and the resulting solution was allowed to stir at 0 °C for 1 h. At the end of this period, the solvent was evaporated and the resulting dark red oil was purified by air-free column chromatography (silica gel, 230–400 mesh/degassed mixture 1:1 of ethyl acetate/hexanes as eluant, R_f = 0.35, UV, PMA stain) to give 292 mg (92%) of a yellow solid. Mp = 102–103 °C (CH_2Cl_2/hexanes under argon). IR (CH_2Cl_2): 3063, 2985, 2936, 2002, 1725, 1702, 1640, 1277, 1104, 816 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 5.68 (s, Cp, 5H), 4.17 (overlapping q, propyl methylenes, J = 7.2 Hz, 4H), 3.83 (d, H_3, J = 6.0 Hz, 1H), 3.77 (d, H_2, J = 6.0 Hz, 1H), 3.39 (dd, H_4, J = 8.1, 1.8 Hz, 1H), 2.06 (dd, $H_{5\alpha}$, J = 19.1, 7.8 Hz, 1H), 1.88 (d, $H_{5\beta}$, J = 19.2 Hz, 1H), 1.46 (s, propyl methyl, 3H), 1.24 (t, propyl methyls, J = 7.2 Hz, 3H), 1.23 (t, propyl methyls, J = 7.2 Hz, 3H). ^{13}C NMR (CD_2Cl_2, 75.48 MHz): δ 225.7, 208.8, 171.2, 170.8, 97.0, 67.2, 61.5, 59.1, 46.9, 36.5, 29.3, 16.8, 14.1. Anal. Calcd for $C_{19}H_{23}NO_7Mo$: C, 48.21; H, 4.90; N, 2.96. Found: C, 48.46; H, 4.74; N, 2.55.

Carbonyl(η^5-cyclopentadienyl)nitrosyl-(2,3-η)-4-(2-oxo-2-phenylethyl)-2-cyclopenten-1-one]molybdenum, 4k. In a 100-mL Schlenk flask equipped with a magnetic stirring bar was generated carbonyl(η^5-cyclopentadienyl)[(2,3,4-η)-1-oxo-2-cyclopenten-4-yl]nitrosylmolybdenum hexafluorophosphate, **3a** (1.33 mmol) from **2a** (400 mg, 1.33 mmol), and $NOPF_6$ (240 mg, 1.33 mmol) in 16 mL of DME following the procedure above for **4a**. This solution was then cooled to –78 °C. Into a 50-mL Schlenk flask equipped with a magnetic stirring bar was placed acetophenone (0.78 mL, 6.65 mmol) in 10 mL of THF and the solution was treated dropwise at 0 °C with *n*-BuLi (0.67 mL of 10 M in hexanes, 6.65 mmol). After stirring for 30 min, the solution was cooled to –78 °C and transferred to the nitrosyl complex via cannula. The reaction was processed as for **4a**, above, to give a yellow solid that was purified by air-free column chromatography (silica gel, 230–400 mesh/degassed mixture 1:1 of ethyl acetate and hexanes as eluant, UV, PMA stain), yielding 368 mg (66%) of a yellow solid. Further purification for elemental analysis was performed by recrystallization from CH_2Cl_2 and hexanes. Mp = 108–110 °C. R_f = 0.90 (EtOAc). IR (CH_2Cl_2): 3054, 2988, 1999, 1700, 1641 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.98 (d, phenyl *o*-H's, J = 7.2 Hz, 2H), 7.58 (t, phenyl *p*-H, J = 7.2 H, 1H), 7.46 (t, phenyl *m*-H's, J = 7.2 Hz, 2H), 5.66 (s, Cp, 5H), 3.93 (d, H_3, J = 6.0 Hz, 1H), 3.83 (d, H_2, J = 6.0 Hz, 1H), 3.30 (m, H_4 and acetophenone methylenes, 3H), 2.35 (dd, $H_{5\alpha}$, J = 18.0, 7.5 Hz, 1H), 1.79 (d, $H_{5\beta}$, J = 18.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75.48 MHz): δ 225.3, 210.6, 198.4, 136.7, 133.4, 128.7, 128.0, 96.8, 71.1,

51.3, 49.0, 40.0, 38.4. Anal. Calcd for $C_{19}H_{17}NO_4Mo$: C, 54.43; H, 4.09; N, 3.34. Found: C, 54.34; H, 4.11; N, 3.27.

Carbonyl(η^5-cyclopentadienyl)[(2,3-η)-4-((*E*)-1-hexenyl)-2-cyclopenten-1-one]nitrosylmolybdenum, 4l. In a 100-mL Schlenk flask equipped with a magnetic stirring bar was generated carbonyl(η^5-cyclopentadienyl)[(2,3,4-η)-1-oxo-2-cyclopenten-4-yl]nitrosylmolybdenum hexafluorophosphate, **3a** (0.671 mmol) from **2a** (200 mg, 0.671 mmol), and $NOPF_6$ (120 mg, 0.671 mmol) in 8 mL of DME following the procedure above for **4a**. This solution was then cooled to −78 °C. In a 50-mL Schlenk flask equipped with a magnetic stirring bar was placed (*E*)-1-iodo-1-hexene (0.317 g, 1.51 mmol) prepared by a literature procedure.[32] THF (4 mL) was added, the mixture was cooled to −78 °C, and in a dropwise manner *tert*-butyllithium (1.78 mL of 1.7 M in pentane, 3.02 mmol, 2 equiv) was added. After stirring for 30 min, a white precipitate (LiI) was formed. It was separated from the vinyl anion by filtering through an inverted syringe packed with Celite into another Schlenk flask cooled to −78 °C. A few milliliters of THF was used to rinse the flask and to help transfer the anion. After cooling to −78 °C, lithium (2-thienyl)cyanocuprate (6.04 mL of 0.25 M in THF, 1.51 mmol) was added, producing a yellow solution. The solution was warmed to −40 °C for 1 h and 0 °C for 15 min. Upon recooling to −78 °C, the cuprate was added to the nitrosyl complex via cannula, producing a deep red color. The reaction was processed as for **4a**, above, to give a red oil that was purified by air-free column chromatography (silica gel, 230–400 mesh/degassed mixture 1:9 of diethyl ether/hexanes as eluant, R_f = 0.10, UV, PMA stain) to give 79.5 mg (31%) of a yellow solid. Mp = 96–98 °C (CH_2Cl_2/hexanes under argon). R_f = 0.65 (1:1 EtOAc/hexane). IR (CH_2Cl_2): 2983, 2961, 2926, 1996, 1701, 1641, 1607, 970 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.66 (s, Cp, 5H), 5.73–5.40 (m, hexenyl olefin H's, 2H), 3.86 (d, H_3, J = 6.0 Hz, 1H), 3.75 (d, H_2, J = 6.0 Hz, 1H), 3.28 (t, H_4, J = 7.5 Hz, 1H), 2.23 (dd, $H_{5\alpha}$, J = 18.9, 7.5 Hz, 1H), 2.03 (apparent q, –CH=CH—CH_2—CH_2–, J = 6.6 Hz, 2H), 1.83 (d, $H_{5\beta}$, J = 18.6 Hz, 1H), 1.31 (br m, hexenyl methylenes, 4H), 0.89 (t, hexenyl methyl, J = 6.9 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75.48 MHz): δ 226.7, 210.97, 135.5, 130.5, 96.6, 72.6, 51.7, 45.5, 40.1, 31.9, 31.4, 22.1, 13.8. Anal. Calcd for $C_{17}H_{21}O_3NMo$: C, 53.27; H, 5.52; N, 3.65. Found: C, 53.20; H, 5.57; N, 3.62.

Nucleophilic Additions to carbonyl(η^5-cyclopentadienyl)[(2,3,4-η)-1-oxo-5-methyl-2-cyclopenten-4-yl]nitrosylmolybdenum Hexafluorophosphate, 3b. Carbonyl(η^5-cyclopentadienyl)[(2,3-η)-4-*anti*-deuterio-5-*anti*-methyl-2-cyclopenten-1-one]nitrosylmolybdenum, 6. In a 100-mL Schlenk flask equipped with a magnetic stirring bar was placed (η^5-cyclopentadienyl)dicarbonyl[(2,3,4-η)-1-oxo-5-methyl-2-cyclopenten-4-yl]-molybdenum, **2b** (195 mg, 0.624 mmol), and 8 mL of DME. The solution was cooled to −40 °C. Nitrosonium hexafluorophosphate (110 mg, 0.624 mmol) was added gradually as a solid, by gently tapping a Schlenk tube containing the $NOPF_6$ which was fitted to the Schlenk flask holding the reaction mixture. Evolution of CO was observed and by completion of the addition, a bright yellow precipitate of **3b** had formed. The mixture was cooled to 0 °C and treated with a 0 °C THF (3-mL) solution of $NaCNBD_3$ (41 mg, 0.624 mmol). The nucleophile was transferred via cannula, and the resulting solution was allowed to stir at 0 °C for 2 h. The solvent was evaporated, leaving a dark green oil that showed a new product by TLC assay (silica gel, R_f = 0.78, EtOAc). Purification by air-free column chromatography (SiO_2, 230–400 mesh/degassed 1:1 diethyl ether/hexanes, UV and PMA stain) gave 80 mg (41%) of **6** as a yellow solid. Unexpectedly, a significant proportion of protio compound was formed in this reaction. The compound is unstable and decomposes over time. Mp = 148–150 °C (CH_2Cl_2/hexanes under argon). IR (CH_2Cl_2): 3054, 2987, 1992, 1697, 1639, 1422, 1086 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 300 MHz, a 7:3 mixture of deuterio and protio compounds): δ 5.65 (s, Cp, 5H), 3.90 (dd, H_3, J = 6.0, 5.4 Hz, 0.3H), 3.90 (d, H_3, J = 7.5 Hz, 0.7 H), 3.86 (d, H_2, J = 6.0 Hz, 1H), 2.81 (dd, H_4, J = 15.3, 7.8 Hz, 0.3 H), 2.79 (d, H_4, J = 7.5 Hz, 0.7 H), 2.67 (ddd, $H_{4\beta}$, J = 15.3, 5.1 Hz, 0.3 H), 1.94 (m, H_5, 1H), 1.10 (d, CH_3, J = 7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75.48 MHz): δ 227.5, 214.4, 96.7, 66.4, 66.3, 52.2, 38.8, 38.4 (t, J = 19.6 Hz), 36.7, 36.6, 16.3, 16.2. Anal. Calcd for $C_{12}H_{12}DO_3NMo$: C, 45.58; H, 4.46; N, 4.16. Found: C, 45.47; H, 4.19; N, 4.39.

Carbonyl(η^5-cyclopentadienyl)[(3,4-η)-2,5-dimethyl-2-cyclopenten-1-one]nitrosylmolybdenum, 7, and carbonyl(η^5-cyclopentadienyl)[(2,3-η)-4,5-dimethyl-2-cyclopenten-1-one]-nitrosylmolybdenum, 8. In a 100-mL Schlenk flask equipped with a magnetic stirring bar was generated carbonyl(η^5-cyclopentadienyl)[(2,3,4-η)-1-oxo-5-methyl-2-cyclopenten-4-yl]nitrosylmolybdenum hexafluorophosphate, **3b** (1.49 mmol) from **2b** (465 mg, 1.49 mmol), and $NOPF_6$ (261 mg, 1.49 mmol) in 14 mL of DME following the procedure above. This mixture was then diluted with 30 mL of THF and cooled to −78 °C. In a fashion similar to that of **4a**, the cuprate was generated from dried CuCN (60 mg, 1.79 mmol, 1.5 equiv) in 13 mL of THF at −40 °C by adding methyllithium (2.56 mL of 1.6 M in diethyl ether, 3.58 mmol), and the cuprate thus generated was added via cannula to the nitrosyl complex at −78 °C. Upon addition, the solution changed to a deep red color. After stirring for 1 h, 20 mL of degassed saturated NH_4Cl solution was added. TLC analysis of the resulting reaction mixture showed two distinct spots (UV, PMA stain) separated by an R_f of 0.12 (50:50 hexanes/EtOAc). Extraction with Et_2O, drying over Na_2SO_4, and evaporation of solvent gave a yellow solid that was purified by air-free column chromatography (silica gel, 230–400 mesh/degassed mixture 1:1 of ethyl acetate and hexanes as eluant) to give two fractions in an overall yield of 34% yield. Fraction one yielded 144 mg of carbonyl(η^5-cyclopentadienyl)[(3,4-η)-2,5-dimethyl-3-cyclopenten-1-one]nitrosylmolybdenum, **7** as a yellow solid (R_f = 0.89, UV, PMA stain). Mp = 110 °C dec (CH_2Cl_2/hexanes under argon). IR (CH_2Cl_2): 2926, 1972, 1738, 1624 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.55 (s, Cp, 5H), 3.70 (d, H_3 or H_4 J = 7.8 Hz, 1H), 3.33 (d, H_3 or H_4, J = 7.8 Hz, 1H), 3.21 (q, $H_{5\alpha}$ or H_2, J = 7.6 Hz, 1H), 3.08 (q, $H_{5\alpha}$ or H_2, J = 7.6 Hz, 1H), 1.42 (d, CH_3, J = 7.8 Hz, 3H), 1.35 (d, CH_3, J = 7.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75.48 MHz): δ 229.5, 223.0, 104.1, 103.8, 95.3, 50.4, 49.8, 21.7, 21.4. Anal. Calcd for $C_{13}H_{15}O_3NMo$: C, 47.43; H, 4.59; N, 4.25. Found: C, 47.55; H, 4.63; N, 4.32. Fraction two yielded 25 mg of the anticipated product **8** as a yellow solid (R_f = 0.77, UV, PMA stain). Mp = 150 °C dec (CH_2Cl_2/hexanes under argon). IR (CH_2Cl_2): 2926, 1987, 1695, 1638 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.65 (s, Cp, 5H), 3.86 (d, H_3, J = 6.3 Hz, 1H), 3.68 (d, H_2, J = 6.3 Hz, 1H), 2.93 (pent, H_4, J = 7.2 Hz, 1H), 2.09 (pent, $H_{5\alpha}$, J = 7.2 Hz, 1H), 1.21 (d, C-5 CH_3, J = 7.2 Hz, 3H), 0.95 (d, C-4 CH_3, J = 7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75.48 MHz): δ 227.3, 214.7, 96.8, 73.8, 49.9, 40.0, 39.9, 21.7, 10.4. Anal. Calcd for $C_{13}H_{15}O_3NMo$: C, 47.43; H, 4.59; N, 4.25. Found: C, 47.51; H, 4.60; N, 4.21.

Carbonyl(η^5-cyclopentadienyl)[(2,3-η)-4-(1,3-dimethoxy-1,3-dioxo-2-propyl)-5-methyl-2-cyclopenten-1-one]nitrosylmolybdenum, 9. In a 100-mL Schlenk flask equipped with a magnetic stirring bar was generated carbonyl(η^5-cyclopentadienyl)[(2,3,4-η)-1-oxo-5-methyl-2-cyclopenten-4-yl]nitrosylmolybdenum hexafluorophosphate, **3b** (0.580 mmol) from **2b** (181 mg, 0.580 mmol), and $NOPF_6$ (102 mg, 0.580 mmol) in 8 mL of DME following the procedure above. This solution was cooled to 0 °C and treated with $NaCH(CO_2CH_3)_2$ prepared at 0 °C from NaH (14.0 mg, 0.580 mmol) and dimethyl malonate (0.065 mL, 0.568 mmol) in 10 mL of THF. The nucleophile was transferred via cannula and the resulting solution was followed to stir for 1 h. The solvent was evaporated, leaving a dark red oil that showed two new spots (R_f = 0.92 and 0.82; EtOAc) by TLC assay. Purification by air-free column chromatography gave two fractions in a 4:96 ratio (silica gel, 230–400 mesh/degassed mixture of 1:1 Et_2O/hexanes as eluant, R_f = 0.33, UV, PMA stain). Fraction 1 gave 11 mg of the 2,5 adduct, carbonyl(η^5-cyclopentadienyl)[(3,4-η)-2-(1,3-dimethoxy-1,3-dioxo-2-propyl)-5-methyl-2-cyclopenten-1-one]nitrosylmolybdenum, **10**, as a yellow oil. IR (CH_2Cl_2): 2955, 1982, 1742, 1626 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 5.62 (s, Cp, 5H), 3.92 (d, H_2, J = 6.0 Hz, 1H), 3.83 (s, propyl CH_3, 3H), 3.77 (s, propyl CH_3, 3H), 3.86–3.69 (m, propyl

(32) Stille, J. K.; Simpson, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 2138.

methyne, H_3 and H_4, 3H), 3.05 (q, H_5, J = 7.8 Hz, 1H), 1.42 (d, CH_3, J = 7.8, 3H). ^{13}C NMR ($CDCl_3$, 75.48 MHz): δ 229.3, 219.7, 168.7, 168.1, 135.9, 127.9, 96.3, 54.8, 54.6, 52.8, 52.7, 50.6, 19.5. The instability of this compound precluded obtaining satisfactory combustion analysis and mass spectral data. Fraction 2 gave 257 mg (80%) of a **9** as a yellow oil. IR (CH_2Cl_2): 2957, 2001, 1750, 1734, 1704, 1642 cm^{-1}. ^1H NMR (CD_2Cl_2, 300 MHz): δ 5.66 (s, Cp, 5H), 3.80 (s, propyl CH_3, 3H), 3.74 (s, propyl CH_3, 3H), 3.84–3.78 (m, H_2 and H_3, 2H), 3.70 (d, propyl methyne, J = 5.4 Hz, 1H), 3.53 (dd, H_4, J = 7.8, 5.4 Hz, 1H), 2.28 (m, $H_{5\alpha}$, 1H), 1.06 (d, CH_3, J = 7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75.48 MHz): δ 225.3, 212.5, 169.4, 168.7, 97.0, 65.5, 54.4, 52.7, 52.5, 50.3, 45.1, 39.0, 10.7. The instability of this compound precluded obtaining satisfactory combustion analysis and mass spectral data.

Carbonyl(η^5-cyclopentadienyl)[(3,4-η)-2-(1,3-diethoxy-1,3-dioxo-2-methyl-2-propyl)-5-methylcyclopenten-1-one]nitrosylmolybdenum, 11. In a 100-mL Schlenk flask equipped with a magnetic stirring bar was generated carbonyl(η^5-cyclopentadienyl)[(2,3,4-η)-1-oxo-5-methyl-2-cyclopenten-4-yl]nitrosylmolybdenum hexafluorophosphate, **3b** (0.320 mmol) from **2b** (99 mg, 0.320 mmol), and $NOPF_6$ (56 mg, 0.320 mmol) in 4 mL of DME following the procedure above. This solution was then cooled to 0 °C and treated with $NaC(CH_3)(CO_2Et)_2$ prepared at 0 °C from NaH (8.0 mg, 0.320 mmol) and methyl diethyl malonate (55 mg, 0.671 mmol) in 10 mL of THF. The nucleophile was transferred via cannula and the resulting solution was allowed to stir for 1 h. The solvent was evaporated, leaving a dark red oil that was purified by air-free column chromatography (silica gel, 230–400 mesh/degassed mixture 1:1 of ethyl acetate/hexanes as eluant, R_f = 0.35, UV, PMA stain) and gave 96 mg (62%) of 11 as a yellow oil. The compound is unstable and decomposes over time regardless of conditions. IR (CH_2Cl_2): 2984, 2938, 1981, 1730, 1626, 1426 cm^{-1}. ^1H NMR (CD_2Cl_2, 300 MHz): δ 5.64 (s, Cp, 5H), 4.25 (q, propyl methylene, J = 7.5 Hz, 2H), 4.24 (q, propyl methylene, J = 7.5 Hz, 2H), 3.99 (br s, H_2, 1H), 3.71 (d, H_3 or H_4, J = 8.1 Hz, 1H), 3.37 (d, H_3 or H_4, J = 8.1 Hz, 1H), 3.00 (q, H_5, J = 7.8 Hz, 1H), 1.56 (s, propyl CH_3, 3H), 1.36 (d, C-5 CH_3, J = 7.8 Hz, 3H), 1.284 (t, propyl methyls, J = 7.5 Hz, 3H), 1.28 (t, propyl methyls, J = 7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75.48 MHz): δ 229.8, 220.2, 171.3, 170.1, 135.8, 128.5, 96.2, 61.6, 61.7, 59.3, 57.9, 50.9, 18.8, 17.8, 14.0. The instability of this compound precluded obtaining satisfactory combustion analysis and mass spectral data.

Decomplexation of η^2-Cyclopentenone Complexes. 4-(1,3-Diethoxy-1,3-dioxo-2-propyl)-2-cyclopenten-1-one, 5a. In a 100-mL round-bottom flask was placed carbonyl(η^5-cyclopentadienyl)[(2,3-η)-4-(1,3-diethoxy-1,3-dioxo-2-propyl)-2-cyclopenten-1-one]nitrosylmolybdenum (245 mg, 0.533 mmol) and $NaOAc{\cdot}3H_2O$ (0.4 g) in acetone (10 mL) at 0 °C. After stirring for 10 min, ceric ammonium nitrate (440 mg, 1.5 equiv) dissolved in acetone (5 mL) was added and the mixture was stirred at 0 °C for 30 min. Upon completion of the addition the mixture changed from an orange to a brown color. Diethyl ether (25 mL) and H_2O (10 mL) were added, the mixture was stirred for 10 min and then filtered through a pad of Celite, and the phases separated. The aqueous phase was extracted with diethyl ether (2 × 20 mL), the combined organic phases were dried over Na_2SO_4 and filtered, and the solvent was evaporated. Purification by flash column chromatography (silica gel, 230–400 mesh/mixture 10:90 of ethyl acetate and hexanes as eluant, R_f = 0.78, vanillin) gave 100.5 mg (78%) of **5a** as a clear oil. IR (CH_2Cl_2): 3059, 2986, 2941, 1747, 1729, 1717, 1372, 1188, 1155, 1026 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.68 (dd, H_3, J = 5.7, 2.4 Hz, 1H), 6.25 (dd, H_2, J = 6.0, 2.1 Hz, 1H), 4.22 (m, propyl methylenes, 4H), 3.64 (m, H_4, 1H), 3.45 (d, propyl methyne, J = 8.1 Hz, 1H), 2.63 (dd, $H_{5\alpha}$, J = 19.1, 6.6 Hz, 1H), 2.27 (dd, $H_{5\beta}$, J = 19.1, 2.4 Hz, 1H), 1.27 (m, propyl methyls, 6H). ^{13}C NMR ($CDCl_3$ 75.48 MHz): δ 207.75, 167.63, 167.51, 164.06, 135.45, 61.89, 54.91, 40.39, 38.82, 14.05. Anal. Calcd for $C_{12}H_{16}O_5$: C, 59.99; H, 6.71. Found: C, 59.83; H, 6.70.

4-(1,3-Diethoxy-1,3-dione-2-methyl-2-propyl)-2-cyclopenten-1-one, 5b. In a 100-mL round-bottom flask was placed carbonyl(η^5-cyclopentadienyl)[(2,3-η)-4-(1,3-diethoxy-1,3-dioxo-2-propyl)-2-cyclopenten-1-one]nitrosylmolybdenum (107.4 mg, 0.227 mmol) and $NaOAc{\cdot}3H_2O$ (0.2 g) in acetone (30 mL) at 0 °C. After stirring for 10 min, ceric ammonium nitrate (200 mg, 1.5 equiv) dissolved in acetone (5 mL) was added and the mixture was stirred at 0 °C for 30 min. Workup as for **5a** and purification by flash column chromatography (silica gel, 230–400 mesh/mixture 1:1 of ethyl acetate and hexanes as eluant, R_f = 0.78, vanillin) gave 68 mg (74%) of **5b** as a clear oil. IR (CH_2Cl_2): 3057, 2987, 2942, 1740, 1729, 1716, 1675, 1231, 1097, 1020 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.66 (dd, H_3, J = 5.7, 2.1 Hz, 1H), 6.21 (dd, H_2, J = 6.0, 2.1 Hz, 1H), 4.17 (overlapping q, propyl methylenes, J = 6.9, 4H), 3.66 (m, H_4, 1H), 2.47 (dd, $H_{5\alpha}$, J = 18.9, 6.6 Hz, 1H), 2.16 (dd, $H_{5\beta}$, J = 18.9, 2.7 Hz, 1H), 1.32 (s, propyl methyl, 3H), 1.22 (t, propyl methyls, J = 6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75.48 MHz): δ 207.9, 170.5, 170.6, 164.1, 135.4, 61.61, 61.63, 55.5, 45.5, 37.2, 17.4, 13.9.

HRMS Calcd for $C_{13}H_{18}O_5$: 254.115423866. Found: 254.1154239 (error 1.0 × 10^{-6}%).

4-Phenyl-2-cyclopenten-1-one, 5c.[33-35] In a 100-mL round-bottom flask was placed carbonyl(η^5-cyclopentadienyl)[(2,3-η)-4-(1,3-diethoxy-1,3-dioxo-2-propyl)-2-cyclopenten-1-one]nitrosylmolybdenum (115 mg, 0.305 mmol) and $NaOAc{\cdot}3H_2O$ (0.4 g) in acetone (10 mL) at 0 °C. After stirring for 10 min, ceric ammonium nitrate (495 mg, 1.5 equiv) dissolved in acetone (5 mL) was added and the mixture was stirred at 0 °C for 30 min. Workup as for **5a** and purification by flash column chromatography (silica gel, 230–400 mesh/degassed mixture 10:90 of ethyl acetate and hexanes as eluant, R_f = 0.78, UV, vanillin) gave 36.6 mg (76%) of **5c** as a clear oil. IR ($CHCl_3$): 3025, 2925, 1710, 1669, 1601, 1589, 1182 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.68 (dd, H_3, J = 5.4, 2.4 Hz, 1H), 7.24–7.14 (m, phenyl, 5H), 6.33 (dd, H_2, J = 5.4, 2.1 Hz, 1H), 4.17 (m, H_4, 1H), 2.90 (dd, $H_{5\alpha}$, J = 18.9, 6.9 Hz, 1H), 2.33 (dd, $H_{5\beta}$, J = 19.1, 2.1 Hz, 1H). ^{13}C NMR ($CDCl_3$ 75.48 MHz): δ 209.8, 166.6, 131.4, 134.0, 129.0, 127.2, 127.1, 46.7, 44.0. HRMS Calcd for $C_{11}H_{10}O$: 158.0731650. Found: 158.07316501 (error 2.7 × 10^{-6}%).

4-(2-Oxo-2-phenylethyl)-2-cyclopenten-1-one, 5d. In a 100-mL round-bottom flask was placed carbonyl(η^5-cyclopentadienyl)[(2,3-η)-4-(1,3-diethoxy-1,3-dioxo-2-propyl)-2-cyclopenten-1-one]nitrosylmolybdenum (50 mg, 0.121 mmol) and $NaOAc{\cdot}3H_2O$ (250 mg) in acetone (10 mL) at 0 °C. After stirring for 10 min, ceric ammonium nitrate (200 mg, 1.5 equiv) dissolved in acetone (5 mL) was added and the mixture was stirred at 0 °C for 30 min. Workup as for **5a** and purification by flash column chromatography (silica gel, 230–400 mesh/degassed mixture 10:90 of ethyl acetate and hexanes as eluant, R_f = 0.76, UV, vanillin) gave 19.7 mg (81%) of **5d** as a white solid. Mp = 99–100 °C (CH_2Cl_2/hexanes). IR (CH_2Cl_2): 3054, 2983, 1713, 1687, 1183 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 7.96 (dd, H-*o*-phenyl, J = 0.9, 6.8 Hz, 2H), 7.76 (dd, H_3, J = 5.4, 2.5 Hz, 1H), 7.61 (t, H-*p*-phenyl, J = 6.0 Hz, 1H), 7.50 (t, H-*m*-phenyls, J = 6.0 Hz, 2H), 6.23 (dd, H_2, J = 5.9, 1.8 Hz, 1H), 3.62 (m, H_4, 1H), 3.21 (m, H-methylenes, 2H), 2.77 (dd, $H_{5\alpha}$, J = 19.1, 6.5 Hz, 1H), 2.06 (dd, $H_{5\beta}$, J = 19.1, 2.2 Hz, 1H). ^{13}C NMR ($CDCl_3$ 75.48 MHz): δ 209.0, 197.6, 167.2, 136.4, 134.4, 133.5, 128.8, 128.0, 43.1, 41.3, 36.9. HRMS Calcd for $C_{13}H_{12}O_3$: 200.0837234. Found: 200.0837298 (error 3.1 × 10^{-6}%).

4-((*E*)-1-Hexenyl)-2-cyclopenten-1-one, 5e. In a 100-mL round-bottom flask was placed carbonyl(η^5-cyclopentadienyl)-[(2,3-η)-4-(1,3-diethoxy-1,3-dioxo-2-propyl)-2-cyclopenten-1-one]-nitrosylmolybdenum (76.4 mg, 0.1995 mmol) and $NaOAc{\cdot}3H_2O$ (~200 mg) in acetone (10 mL) at 0 °C. After stirring for 10 min, ceric ammonium nitrate (~180 mg, 1.5 equiv) dissolved in acetone (5 mL) was added and the mixture was stirred at 0 °C for 30 min. Workup as for **5a** and purification by flash column chromatog-

(33) Rizzo, J. C.; Dunlap, N. K.; Smith, A. B. *J. Org. Chem.* **1987**, *52*, 5280.

(34) Kjeldsen, G.; Knudsen, J. S.; Ravn-Petersen, L. S.; Torssel, K. B. G. *Tetrahedron* **1983**, *39*, 2237.

(35) Jones, T. K.; Denmark, S. E. *Helv. Chim. Acta* **1983**, *66*, 2377.

Table 3. Summary of Crystal Data, Intensity Collection, and Structure Refinement for (η^5-C_5H_5)(η^2-C_6H_8O)(CO)(NO)Mo, 4a

formula	$C_{12}H_{13}MoNO_3$
mol wt	315.2
a,[a] Å	6.545(2)
b, Å	11.789(2)
c, Å	16.494(3)
β, deg	94.38(3)
vol, Å^3	1268.9(6)
cryst syst	monoclinic
space group	$P2_1/n$
d_{calcd}, g/cm^3	1.650
Z	4
temp, °C	23
diffractometer	Siemens P4/RA
radiation (λ, Å)	Cu Kᾱ (1.541 78)
abs coeff (μ), mm^{-1}	8.439
cryst size, mm	0.10 × 0.19 × 0.45
scan speed, deg/min in ω	variable; 10.00–60.00
scan range, deg	0.40 + ($\omega K\alpha_2 - \omega K\alpha_1$)
scan/bckgd ratio	0.6
scan technique	ω
data collected	$-1 \le h \le 6, -12 \le k \le 12, -17 \le l \le 17, (2° \le 2\theta \le 110°)$
structure solution and refinement	Siemens SHELXTL IRIS
abs corr	semiempirical
min, max transm coeff	0.2773, 0.7124
no. of reflns collcd	3735
total no. of data	1572 (2.23)
no. of unique data ($I > 4\sigma(I)$)	1519
F(000)	632
R_{merge} (R_σ), %	2.97 (2.79)
no. of variables	154
goodness of fit[c]	1.45
R (R_w (wR)), %[c]	3.87 (4.29 (5.49))
R (R_w), % (all data)[c]	4.08 (5.80)
weighting scheme	$w^{-1} = \sigma^2(E) + 0.0010F^2$
max and min diff peaks, e/Å^3	0.33, −1.13
largest and mean Δ/σ	0.001, 0.000

[a] Least squares treatment of 31 centered reflections between 28 and 56° in 2θ. [b] Goodness of fit = $[w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$, where n_o and n_v denote the number of data and variables, respectively. [c] For *syn* trial structure: R (R_w (wR)), % = 4.31 (4.85 (6.36)); R (R_w, % (all data) = 4.51 (6.61).

Table 4. Bond Lengths (Å) of Carbonyl(η^5-cyclopentadienyl)nitrosyl-[(2,3-η)-4-methyl-2-cyclopenten-1-one]molybdenum, 4a

Mo–N	1.781(4)	C(2)–C(3)	1.460(6)
Mo–C(1)	1.996(5)	C(2)–C(6)	1.510(6)
Mo–C(3)	2.237(4)	C(3)–C(4)	1.400(5)
Mo–C(4)	2.305(4)	C(4)–C(5)	1.514(6)
Mo–C(8)	2.333(6)	C(5)–C(6)	1.522(7)
Mo–C(9)	2.341(6)	C(5)–C(7)	1.535(7)
Mo–C(10)	2.376(6)	C(8)–C(9)	1.445(12)
Mo–C(11)	2.358(8)	C(8)–C(12)	1.324(11)
Mo–C(12)	2.343(7)	C(9)–C(10)	1.447(12)
O(1)–N	1.185(5)	C(10)–C(11)	1.322(11)
O(2)–C(1)	1.141(6)	C(11)–C(12)	1.367(10)
O(3)–C(2)	1.231(5)		

raphy (silica gel, 230–400 mesh/degassed mixture 1:2 of ethyl acetate and hexanes as eluant, R_f = 0.65, UV, vanillin) gave 23.7 mg (73%) of **5e** as a clear oil. IR (CH_2Cl_2): 2961, 2930, 2875, 2859, 1710, 1074, 971, 908 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.51 (dd, H_3, J = 5.4, 2.4 Hz, 1H), 6.14 (dd, H_2, J = 5.4, 1.5 Hz, 1H), 5.53 (dd, R—CH=C*H*—CH_2–, J = 15.0, 6.6 Hz, 1H), 5.28 (dd, R—C*H*=CH—CH_2–, J = 15.3, 7.8 Hz, 1H), 3.50 (br s, H_4, 1H), 2.61 (dd, $H_{5\alpha}$, J = 18.9, 6.6 Hz, 1H), 2.09 (dd, $H_{5\beta}$, J = 18.9, 2.1 Hz, 1H), 2.01 (br m, –CH=CH—C*H*$_2$—CH_2–, 2H), 1.30 (br m, hexenyl methylenes, 4H), 0.87 (br t, hexenyl methyl, J = 6.6 Hz, 3H). ^{13}C NMR ($CDCl_3$ 75.48 MHz): δ 209.8, 167.2, 133.6, 132.6, 129.5, 44.2, 41.6, 32.1, 31.4, 22.2, 13.9. HRMS Calcd for $C_{11}H_{16}O$: 164.120115232. Found: 164.1201153 (error −4.5 × 10^{-6}%).

Table 5. Bond Angles (deg) of Carbonyl(η^5-cyclopentadienyl)nitrosyl-[(2,3-η)-4-methyl-2-cyclopenten-1-one]molybdenum, 4a

N–Mo–C(1)	91.3(2)	C(9)–Mo–C(12)	57.5(3)
N–Mo–C(3)	94.8(2)	C(10)–Mo–C(12)	55.7(2)
C(1)–Mo–C(3)	106.7(2)	C(11)–Mo–C(12)	33.8(3)
N–Mo–C(4)	103.7(2)	Mo–N–O(1)	172.8(3)
C(1)–Mo–C(4)	71.9(2)	Mo–C(1)–O(2)	177.8(5)
C(3)–Mo–C(4)	35.9(1)	O(3)–C(2)–C(3)	127.2(4)
N–Mo–C(8)	96.6(2)	O(3)–C(2)–C(6)	123.9(4)
C(1)–Mo–C(8)	116.9(2)	C(3)–C(2)–C(6)	108.8(4)
C(3)–Mo–C(8)	134.4(2)	Mo–C(3)–C(2)	111.6(3)
C(4)–Mo–C(8)	157.8(2)	Mo–C(3)–C(4)	74.7(2)
N–Mo–C(9)	105.5(2)	C(2)–C(3)–C(4)	108.3(4)
C(1)–Mo–C(9)	148.4(3)	Mo–C(4)–C(3)	69.4(2)
C(3)–Mo–C(9)	98.4(3)	Mo–C(4)–C(5)	121.1(3)
C(4)–Mo–C(9)	127.1(3)	C(3)–C(4)–C(5)	110.7(4)
C(8)–Mo–C(9)	36.0(3)	C(4)–C(5)–C(6)	103.9(3)
N–Mo–C(10)	140.4(2)	C(4)–C(5)–C(7)	108.0(4)
C(1)–Mo–C(10)	126.0(3)	C(6)–C(5)–C(7)	111.9(4)
C(3)–Mo–C(10)	86.9(2)	C(2)–C(6)–C(5)	104.8(4)
C(4)–Mo–C(10)	100.5(2)	Mo–C(8)–C(9)	72.3(4)
C(8)–Mo–C(10)	57.5(2)	Mo–C(8)–C(12)	74.0(4)
C(9)–Mo–C(10)	35.7(3)	C(9)–C(8)–C(12)	108.7(6)
N–Mo–C(11)	151.8(2)	Mo–C(9)–C(8)	71.7(4)
C(1)–Mo–C(11)	96.0(2)	Mo–C(9)–C(10)	73.4(3)
C(3)–Mo–C(11)	108.9(2)	C(8)–C(9)–C(10)	103.1(7)
C(4)–Mo–C(11)	104.5(2)	Mo–C(10)–C(9)	70.8(4)
C(8)–Mo–C(11)	55.9(3)	Mo–C(10)–C(11)	73.1(4)
C(9)–Mo–C(11)	57.1(3)	C(9)–C(10)–C(11)	108.4(6)
C(10)–Mo–C(11)	32.4(3)	Mo–C(11)–C(10)	74.5(5)
N–Mo–C(12)	119.2(2)	Mo–C(11)–C(12)	72.5(5)
C(1)–Mo–C(12)	91.0(2)	C(10)–C(11)–C(12)	110.1(7)
C(3)–Mo–C(12)	141.5(2)	Mo–C(12)–C(8)	73.1(4)
C(4)–Mo–C(12)	134.3(2)	Mo–C(12)–C(11)	73.7(4)
C(8)–Mo–C(12)	32.9(3)	C(8)–C(12)–C(11)	109.6(7)

X-ray Crystal Structure Determination of Carbonyl(η^5-cyclopentadienyl)[(2,3-η)-4-methyl-2-cyclopenten-1-one]-nitrosylmolybdenum, 4a. Crystals suitable for X-ray structure determination were grown under an argon atmosphere at 25 °C. The compound was dissolved in a minimum amount of CH_2Cl_2, the solution was filtered through a plug of Celite, and hexanes was added until the solution turned slightly cloudy. A few drops of CH_2Cl_2 were then added to clarify the solution which was allowed to stand for 5 h, providing translucent yellow crystals. A fragment of dimensions 0.10 × 0.19 × 0.45 mm was cut from a large rhombic yellow crystal and mounted on a quartz fiber with cyanoacrylate glue, covered with glue, and placed on a Siemens P4-RA diffractometer for data collection. Crystal data, reflection intensity collection parameters, and structure refinement data are provided in Table 3. The intensities of three check reflections (30$\bar{7}$, 0$\bar{7}$1, $\bar{1}$0$\bar{8}$ measured every 100 reflections at approximately 1-h intervals) exhibited little decay. A semiempirical correction for absorption was applied, and the data were corrected for *Lp* effects.

The structure was solved by the Patterson method and refined by full matrix least squares using the program SHELXTL IRIS (SHELXTL: Simens Analytical X-ray Instruments, Inc. (previously Nicolet Instrument Corp.), Madison, WI). The hydrogen atoms were included, but not refined, in calculated positions (C–H = 0.96 Å) with isotropic thermal parameters set at 0.05. All non-hydrogen atoms were refined with anisotropic thermal parameters. The maximum shift/ESD for the final cycle was 0.001 and the maximum and minimum peaks in the difference electron density map were 0.32 and −1.33 e/Å^3. The scattering factors for all atoms, the anomalous dispersion corrections, as well as the linear absorption coefficients are from the *International Tables for X-ray Crystallography* (Mathematical, Physical and Chemical Tables; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C).

The nitrosyl nitrogen and the metal-bound carbonyl carbon were distinguished by comparing thermal parameters obtained after refinement of trial structures for both possible geometries (nitrosyl *anti* to the methyl group and nitrosyl *syn* to the methyl group). *R* factors and relevant thermal parameters obtained by refinement of the *syn* trial structure appear as footnotes to Table 3 and Table S-II (supplementary material), respectively. A disproportional difference between the thermal parameters was obtained for the *syn* trial structure, which led to assignment of the *anti* geometry.

The analysis yielded the structure shown in Figure 2 in the body of the paper. Bond distances and bond angles are shown in Tables 4 and 5, respectively. Tables of atom coordinates, thermal parameters, and hydrogen atom coordinates and temperature factors can be found in the supplementary material.

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Supplementary Material Available: Tables of atom coordinates, thermal parameters, and hydrogen atom coordinates and temperature factors for $(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_6H_8O)(CO)(NO)Mo$, **4a** (3 pages). Ordering information is given on any current masthead page.

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