Notes

An Improved Method for the Synthesis of Cationic (η^5-Cyclopentadienyl)(η^3-allyl)Mo(CO)(NO) Complexes: The Benefit of 1,2-Dimethoxyethane as a Solvent

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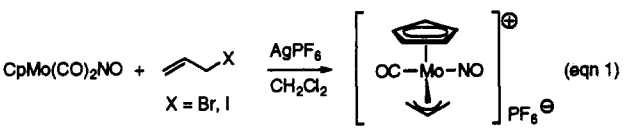
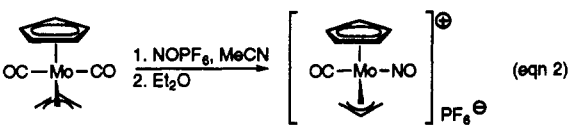
Summary: In contrast to suggestions in the literature that ether solvents are incompatible with nitrosonium salts, treatment of (η^3-allyl)(η^5-cyclopentadienyl)dicarbonylmolybdenum complexes with solid $NOPF_6$ in 1,2-dimethoxyethane at −10 °C produces analytically pure [(η^3-allyl)carbonyl(η^5-cyclopentadienyl)nitrosylmolybdenum][PF_6] as yellow solids.

Introduction

Cationic (η^5-cyclopentadienyl)(η^4-diene)dicarbonylmolybdenum complexes undergo stereo- and regiospecific addition of a wide variety of nucleophiles in a synthetically useful fashion.[1–13] The resulting neutral (η^3-allyl)(η^5-cyclopentadienyl)dicarbonylmolybdenum complexes can be reactivated for a second nucleophilic addition by conversion to cationic (η^3-allyl)carbonyl(η^5-cyclopentadienyl)nitrosylmolybdenum complexes.[10,12,14–19] Studies published to date describe the addition of only a restricted range of nucleophiles.[10,14–17,19–23]

The original preparation of cationic (η^3-allyl)carbonyl(η^5-cyclopentadienyl)nitrosylmolybdenum complexes was investigated independently by Faller and McCleverty.[19,23–26] McCleverty treated $CpMo(CO)_2NO$ with an allylic bromide in the presence of a silver salt to give the cationic nitrosyl complex directly (eq 1). In a procedure that has subsequently found widespread use, Faller treated a dicarbonylmolybdenum π-allyl dissolved in acetonitrile at 0 °C with a solution of either $NOBF_4$ or $NOPF_6$; under these conditions, CO is evolved and the nitrosyl cation remains in solution until workup (eq 2).[10,15–17] If desired, isolation





can be accomplished by cannulation of the reaction mixture into a stirred excess of diethyl ether, precipitating the product as a powder.[10,15] In order to isolate the kinetically formed conformational isomer (either *exo* or *endo*, see *Endo–Exo* Isomerism) and to prevent the formation of brown oils, Faller indicated the necessity of performing this procedure as quickly as possible, since *endo* ⇔ *exo* equilibration occurs within a matter of hours in solution for most cationic nitrosyl complexes. Furthermore, some nucleophiles catalyze the conversion to the thermodynamically favored isomer.[15] For these reasons, some past workers have formed the nitrosyl cation *in situ* in acetonitrile solution and then immediately treated it with a nucleophile, a practice restricted to nucleophiles compatible with acetonitrile.[14,22]

Results and Discussion

Synthesis. During an examination of the addition of carbon nucleophiles to cationic (η^3-allyl)carbonyl(η^5-cyclopentadienyl)nitrosylmolybdenum complexes, a useful modification of the current method for conversion of (η^3-

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(1) Rubio, A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 891.
(2) Liebeskind, L. S.; Bombrun, A. *J. Am. Chem. Soc.* **1991**, *113*, 8736.
(3) Hansson, S.; Miller, J. F.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1990**, *112*, 9660.
(4) Pearson, A. J.; Mallik, S.; Pinkerton, A. A.; Adams, J. P.; Zheng, S. *J. Org. Chem.* **1992**, *57*, 2910.
(5) Pearson, A. J.; Khetani, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6778.
(6) Pearson, A. J.; Blystone, S. L.; Nar, H.; Pinkerton, A. A.; Roden, B. A.; Yoon, J. *J. Am. Chem. Soc.* **1989**, *111*, 134.
(7) Pearson, A. J. *Recent Developments in the Synthetic Applications of Organoiron and Organomolybdenum Chemistry.* In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, CT, 1989; Vol. I, p 1.
(8) Pearson, A. J. *Phil. Trans. R. Soc. Lond. A* **1988**, *326*, 525.
(9) Pearson, A. J.; Kole, S. L.; Yoon, J. *Organometallics* **1986**, *5*, 2075.
(10) Faller, J. W.; Lambert, C. *Tetrahedron* **1985**, *41*, 5755.
(11) Pearson, A. J.; Khan, M. N. I.; Clardy, J. C.; He, C.-H. *J. Am. Chem. Soc.* **1985**, *107*, 2748.
(12) Faller, J. W.; Murray, H. H.; White, D. L.; Chao, K. H. *Organometallics* **1983**, *2*, 400. Pearson, A. J.; Khan, M. N. I. *J. Org. Chem.* **1985**, *50*, 5276.
(13) Pearson, A. J.; Khan, M. N. I. *J. Org. Chem.* **1985**, *50*, 5276.
(14) VanArsdale, W. E.; Winter, R. E. K.; Kochi, J. K. *Organometallics* **1986**, *5*, 645.
(15) Faller, J. W.; Chao, K. H.; Murray, H. H. *Organometallics* **1984**, *3*, 1231.
(16) Faller, J. W.; Chao, K.-H. *Organometallics* **1984**, *3*, 927.
(17) Faller, J. W.; Chao, K.-H. *J. Am. Chem. Soc.* **1983**, *105*, 3893.
(18) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592.
(19) Adams, R. D.; Chodosh, D. F.; Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1979**, *101*, 2570.
(20) Faller, J. W.; Lambert, C.; Mazzieri, M. R. *J. Organomet. Chem.* **1990**, *383*, 161.
(21) VanArsdale, W. E.; Kochi, J. K. *J. Organomet. Chem.* **1986**, *317*, 215.
(22) VanArsdale, W. E.; Winter, R. E. K.; Kochi, J. K. *J. Organomet. Chem.* **1985**, *296*, 31.
(23) McCleverty, J. A.; Murray, A. J. *Trans. Met. Chem.* **1979**, *4*, 273.
(24) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1976**, *98*, 3388.
(25) Bailey, N. A.; Kita, W. G.; McCleverty, J. A.; Murray, A. J.; Mann, B. E.; Walker, N. W. J. *J. Chem. Soc., Chem. Commun.* **1974**, 592.
(26) McCleverty, J. A.; Murray, A. J. *J. Chem. Soc., Dalton Trans.* **1979**, 1424.

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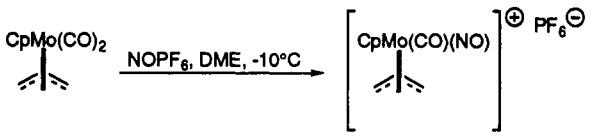
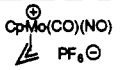
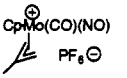
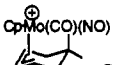
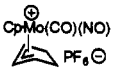
Table 1. Generation of Cationic π-Allylmolybdenum Nitrosyl Complexes in DME



starting material	compd	product	compd	yield (%)
	1		2	81
	3		4	84
	5		6	80
	7		8	83
	9		10	87

allyl)(η^5-cyclopentadienyl)dicarbonylmolybdenum to [(η^3-allyl)carbonyl(η^5-cyclopentadienyl)nitrosylmolybdenum][PF_6] was uncovered. A solvent system was required for the CO ⇒ NO^+ exchange which (a) allowed generation of the requisite nitrosyl cation in sufficiently pure form for further reaction and (b) would be inert to commonly encountered nucleophiles and basic reaction conditions. Acetonitrile does not fit the latter requirement since it contains labile protons and a potentially electrophilic CN triple bond. Ethereal solvents, which are clearly ideal for reactions of many carbanioic nucleophiles, are claimed to be reactive toward nitrosonium salts even when carefully purified.[27,28] Nevertheless, a qualitative survey of the solubility of $NOPF_6$ in a range of ethereal solvents was carried out. As expected, $NOPF_6$ in THF quickly formed a dark brown polymeric mass, while $NOPF_6$ in diethyl ether formed an insoluble yellow oil. *However, it was found that $NOPF_6$ dissolves in 1,2-dimethoxyethane (DME) to give a yellow solution which is stable for several hours at low temperature* (<0 °C). 1,2-Dimethoxyethane proved to be an excellent solvent for the generation and isolation of cationic (η^3-allyl)carbonyl(η^5-cyclopentadienylnitrosylmolybdenum complexes. When a stirring solution of an (η^3-allyl)(η^5-cyclopentadienyl)dicarbonylmolybdenum complex in DME at −10 °C was treated with solid $NOPF_6$, added gradually in small portions, CO was evolved and a yellow solution formed. With continued stirring a bright yellow precipitate of the product nitrosyl cation was deposited. Removal of the supernatant followed by washing the yellow solid twice with diethyl ether and drying *in vacuo* allowed isolation of *analytically pure* product (see the Experimental Section). Cannulation of the supernatant into excess diethyl ether provided a second crop in some cases. No further purification was necessary or desirable since manipulation of the solid invariably resulted in the formation of a brown oil. To illustrate the generality of the reaction, a number of (η^3-allyl)(η^5-cyclopentadienyl)dicarbonylmolybdenum complexes were subjected to the new conditions, and the results are displayed in Table 1. In the present study, only complexes

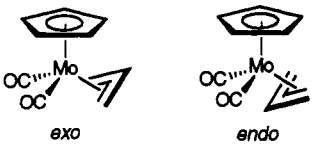
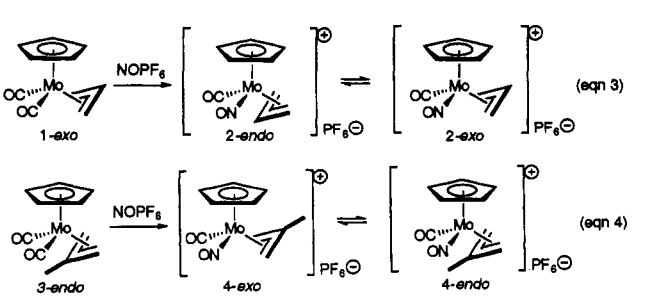


Figure 1.

with symmetrical π-allyl ligands were investigated in order to prevent the formation of diastereomers and hence simplify the spectral information. All of the nitrosyl cations were isolated as analytically pure yellow solids, and full spectral data were recorded on the previously unknown compounds. Although the parent π-allyl **2** and the 2-methylpropenyl analog **4** have been previously reported, this is the first time that all their spectral data are presented, including complete high-field ^1H and ^{13}C NMR data.[14,22-24] The nitrosyl cation of the cyclohexyl π-allyl **6** was previously reported as a red-brown powder using the acetonitrile method (see below).[12]

Spectroscopy. *Exo–Endo* Isomerism. In their original studies Davison and Faller independently showed that (η^3-allyl)carbonyl(η^5-cyclopentadienyl)(L)molybdenum complexes exist in two conformations in dynamic equilibrium.[29,30] These are depicted in Figure 1 and have been designated *exo* and *endo*. In subsequent extensive studies of both the dicarbonyl and carbonyl nitrosyl π-allyls, Faller demonstrated that the preferred conformation for a particular complex is largely dependent upon steric factors, *i.e.*, the extent and type of substitution about the π-allyl.[31,32] This property may be observed in the spectra of the complexes, particularly temperature-dependent NMR spectra. Faller showed that for the unsubstituted dicarbonyl π-allyl **1** the thermodynamically preferred orientation is *exo*.[30,31,33] According to Faller the mechanism by which the *exo* and *endo* forms interconvert is either a π–σ–π rearrangement, which is possible for open chain π-allyls, or by rotation of the η^3-ligand.[24,32] For the π-cycloalkenyl nitrosyl cations, the geometric constraints of the ring prevent the π–σ–π rearrangement, and therefore the only possible path is *via* rotation.

Upon reaction of **1** with $NOPF_6$ to give the nitrosyl cation **2**, the kinetically formed product is **2-*endo***, and in solution this gradually converts to the thermodynamically favored conformation **2-*exo*** (eqn 3).[24] The (2-methylpropenyl)-dicarbonylmolybdenum π-allyl **3**, on the other hand, exists as the *endo* isomer at room temperature, due to steric interference between the methyl group and the cyclopentadienyl ring, and this initially forms the kinetic product **4-*exo*** as the major isomer on treatment with $NOPF_6$ (eq 4). Again, in solution this slowly converts to the thermodynamically favored conformer **4-*endo*** as the predominant species.

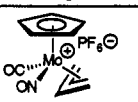
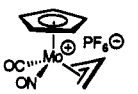
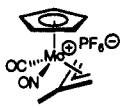
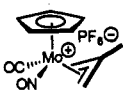
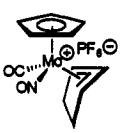


(27) Mocella, M. T.; Okamoto, M. S.; Barefield, E. K. *Synth. React. Inorg. Metal-Org. Chem.* **1974**, *4*, 69.
(28) Caulton, K. G. *Coord. Chem. Rev.* **1975**, *14*, 317.
(29) Davison, A.; Rode, W. C. *Inorg. Chem.* **1967**, *6*, 2124.
(30) Faller, J. W.; Incorvia, M. J. *Inorg. Chem.* **1968**, *7*, 840.

Complete ^1H and ^{13}C NMR spectroscopic characterization of both the *exo* and *endo* conformers of the parent nitrosyl π-allyl **2** is not available in the literature.[23,24] Thus, the unsubstituted nitrosyl π-allyl **2** was prepared as indicated in the Experimental Section and the first crop, which precipitated from the DME solution without addition to diethyl ether, was collected and fully analyzed. According to the ^1H NMR spectrum, this was predominantly the *endo* isomer **2-*endo*** (ca. 30:1 *endo*:*exo*) as indicated by the integral ratios of the Cp resonances at δ_H 6.51 (s, *endo*) and 6.36 (s, *exo*). The ^{13}C NMR spectrum of **2-*endo*** exhibited a resonance due to the C2 at δ_C 114.3 (d). The deuterioacetone solution of this compound was allowed to stand at ambient temperature for several days, and spectra were recorded periodically. In addition to the changes in the resonances of the ^1H NMR spectrum, the ^{13}C NMR spectrum showed corresponding changes in the intensity of signals. Most interestingly, the resonance due to C2 for **2-*exo*** which grew in appeared considerably upfield at δ_C 101.1 compared to the *endo* signal (δ_C 114.3); it appears that the upfield shift of δ_C C2 in the exo conformer may be used diagnostically to distinguish the *exo* and *endo* conformers. Similar trends were observed for the 2-methylpropenyl derivative **4** (*exo*, δ_C 125.4; *endo*, δ_C 134.5). Two crops were isolated in the preparation of this compound, both of which consisted of *endo*–*exo* mixtures which were predominantly *exo* initially. The equilibration to predominantly the *endo* isomer in deuterioacetone solution was followed by ^1H NMR. Once again all of the ^1H NMR spectral data were recorded for compound **4**, including the Me signals which were erroneously reported previously.[23] As in the unsubstituted complex, the ^{13}C NMR spectrum was instructive since an upfield trend in the chemical shift of the "diagnostic" C2 resonance of the *exo* conformer (δ_C 125.4) compared to the *endo* conformer (δ_C 134.5) was observed.

Since (η^3-cyclohexenyl)(η^5-cyclopentadienyl)dicarbonylmolybdenum **5** exists in the *exo* conformation,[11,12] the kinetically formed carbonyl(η^3-cyclohexenyl)(η^5-cyclopentadienyl)nitrosylmolybdenum cation should be the *endo* conformer. Faller had already shown that this was the case for the analogous cyclooctenyl complexes.[15] The cyclooctenyl *endo* isomer was converted to the thermodynamically favored *exo* isomer either by allowing the complex to stand in solution at room temperature for several hours or by the addition of catalytic sodium iodide to an acetone solution of the complex. In an earlier paper Faller had reported the preparation of cyclohexenyl nitrosyl cation **6** as a red-brown powder and listed some of the ^1H NMR peaks.[12] The partially reported data indicated the presence of two isomers in the ratio of 5:2. Preparation of cyclohexenyl nitrosyl cation **6** using the DME method led to a yellow powder that showed only one set of resonances. Only after the compound was allowed to stand in solution for several days were "minor" peaks observed (at δ_H 6.7, 6.1, and 5.0), but they remained small. Furthermore, treatment of the pure major isomer with catalytic NaI in acetone at room temperature for 12 h did not result in conversion to another isomer; analysis of the reaction mixture by ^1H NMR showed only peaks due to the major isomer and minor impurity peaks. The analogous isomerization of the *endo* cyclooctenyl complex occurs in 3 h in solution and in 0.5 h with NaI catalysis, 100% *exo*, 90% yield.[15]

Table 2. Selected NMR Resonances of [(η^3-Allyl)(CO)(η^5-Cp)(NO)Mo][PF_6]

complex	δ_H Cp	δ_H C2-H	δ_C C2
	6.51	5.68	114.3
	6.36	5.38	101.1
	6.50		134.5
	6.33		125.4
	6.29	5.31	87.8
	6.33	5.45	95.7
	6.31	5.50	93.6
cyclooctenyl *endo*	6.44	5.59	
cyclooctenyl *exo*	6.34	5.02	

One of three situations is operative in the cyclohexenyl case. The observed π-allyl nitrosyl cation from the DME system might be the *endo* conformer because it is produced kinetically and the barrier to conversion to the *exo* conformer is very high. Or, the observed π-allyl nitrosyl cation from the DME system might be the *exo* conformer because (1) the *endo* conformer is produced kinetically and the barrier to conversion to the *exo* is very low or (2) the cyclohexenyl system behaves differently from other (η^3-ally)(η^5-cyclopentadienyl)dicarbonylmolybdenum complexes and forms the *exo* conformer directly on CO ⇒ NO conversion. Comparison of the spectral data of complexes in Table 2 support assignment of [carbonyl(η^3-cyclohexenyl)(η^5-cyclopentadienyl)nitrosylmolybdenum][PF_6] **6** as the *exo* conformer. First, Faller has already suggested that the proton chemical shift of the Cp resonance is diagnostic of an *endo* or an *exo* orientation of the π-allyl moiety. On comparing the data for the cationic complexes **2** and **4** and the cycloalkenyl derivatives, it is apparent that the complexes known to be *exo* exhibit Cp resonances at about δ_H 6.3, *as do the cyclic complexes*, while the Cp resonances of the *endo* isomers appear at approximately δ_H 6.5. Furthermore, the carbon resonances of C2 in the unsubstituted and 2-methyl complexes **2** and **4** appear at considerably different chemical shifts, there being an upfield shift of about 13 and 9 ppm, respectively, in going from *endo* to *exo*. Since only one isomer was isolated in the case of each cyclic complex, it is impossible to make direct comparisons; however, the C2 values (assigned with

(31) Faller, J. W.; Chen, C.-C.; Mattina, M. J.; Jakubowski, A. *J. Organomet. Chem.* **1973**, *52*, 361.
(32) Faller, J. W.; Shvo, Y.; Chao, K.; Murray, H. H. *J. Organomet. Chem.* **1982**, *226*, 251.
(33) Faller, J. W.; Jakubowski, A. *J. Organomet. Chem.* **1971**, *31*, C75.

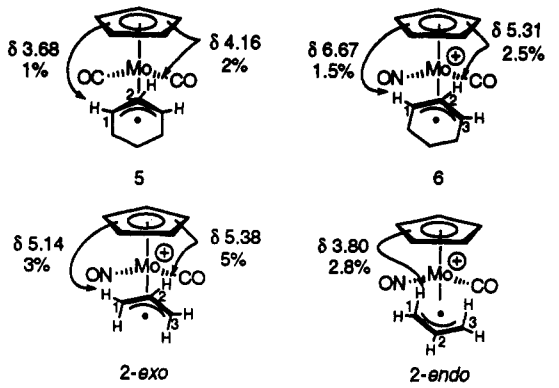


Figure 2.

C-H correlation experiments) lie within 8 ppm of each other and are all less than 100 ppm, suggesting an *exo* orientation.

The final piece of evidence is provided by NOE data. Complexes in the *exo* conformation possess a C2 proton which is relatively close in space to the Cp ligand. The *exo* complexes which have a C2-H should therefore exhibit an NOE of this proton resonance upon irradiation of the Cp signal and also possibly to one or both of the *syn* proton resonances. Thus NOE experiments were performed on three compounds, the cyclohexenyl dicarbonyl **5**, the cyclohexenyl nitrosyl cation **6**, and the *endo* and *exo* isomers of the unsubstituted nitrosyl cation **2** (Figure 2). Consistent with an *exo* conformation, irradiation of the Cp signal of dicarbonyl cyclohexenyl complex **5** led to NOE's of the C2-H resonance (2%) and the C1 and C3 proton resonances (1%). A similar experiment performed on the cyclohexenyl nitrosyl cation gave a 2.5% enhancement of the C2-H signal (δ_H 5.31) and a 1.5% NOE of the C1-H resonance (δ_H 6.67) consistent with an *exo* orientation.

In order to prove that these findings were self-consistent, the unsubstituted nitrosyl cation **2** was examined at −80 °C as a mixture of *endo* and *exo* isomers. For this complex, a low temperature was required in order to slow the rate of exchange between the conformers. As expected, irradiation of the *exo* Cp signal led to a 5% NOE of the C2-H *exo* signal (δ_H 5.38) and an enhancement of 3% of the *syn* C1-H *exo* resonance (δ_H 5.14). On the other hand a 2.8% NOE was observed for the *anti* C1-H *endo* resonance (δ_H 3.80) upon irradiation of the *endo* Cp signal; no enhancement was seen for any of the other signals. In each case, the most downfield of the two η^3-allyl *syn*-H resonances and *anti*-H resonances in the ^{1}H NMR spectra of the nitrosyl cations was assigned to the η^3-allyl hydrogen adjacent to the nitrosyl ligand (C1-H). These assignments are in accord with earlier studies by Faller who showed that the electronic dissymmetry of the CpMo(CO)(NO) moiety distorts the allyl group to bring one end of the allyl closer to the NO ligand as depicted in Figure 2.[15]

Finally, the ^{1}H NMR spectrum of the nitrosyl cyclohexenyl cation was intriguing in view of the coupling constants of the C5-H resonances. It has already been established that the Mo dicarbonyl cyclohexenyl π-allyl complex exists in a pseudochair conformation in the solid state.[11,12] In the solution ^{1}H NMR spectrum, the vicinal

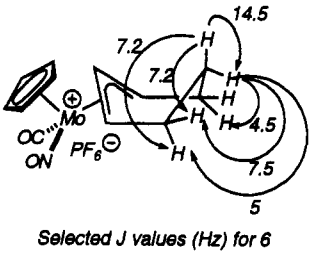


Figure 3. Selected J values (Hz) for **6**.

^{1}H coupling constants J_{5-6} and J_{4-5} are large (11.5 Hz), suggesting a diaxial relationship and indicating that the chair-like conformation predominates in solution. This contrasts with the ^{1}H NMR spectrum of the nitrosyl cyclohexenyl π-allyl **6** in which the largest vicinal coupling constants between the C4, C5, and C6 proton resonances are 7.5 and 7.2 Hz (Figure 3). This data is suggestive of a solution conformation for this molecule which on a time average is *boat*-like. Earlier papers have documented boat conformations for certain cyclohexenylpalladium systems.[34-36]

Conclusions

Dimethoxyethane has been shown to be an excellent solvent for the generation of analytically pure [(η^3-allyl)carbonyl(η^5-cyclopentadienyl)nitrosylmolybdenum]-[PF_6] from (η^3-allyl)(η^5-cyclopentadienyl)dicarbonylmolybdenum complexes and solid $NOPF_6$.

Experimental Section

Materials and Methods. General. All reactions and manipulations were performed under an atmosphere of dry argon using standard Schlenk techniques. Glassware was dried under vacuum just prior to use. The dicarbonylmolybdenum π-allyls **1**, **3**, **5**, **7**, and **9** were prepared using the recently described allylic diphenylphosphinic ester method.[37] Diethyl ether was distilled from sodium benzophenone ketyl. Anhydrous 1,2-dimethoxyethane (DME) packaged under nitrogen was purchased from the Aldrich Chemical Co. and degassed by sparging with argon for 15 min. Nitrosonium hexafluorophosphate ($NOPF_6$) was obtained from Pfaltz and Bauer and used without further purification. It is a stable colorless solid which is somewhat hygroscopic.[27,28] The compound was stored in a screw-top container under argon and was weighed in air when required. If prolonged exposure to air is minimized, the $NOPF_6$ may be stored at 4 °C for months without appreciable decomposition. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm downfield from TMS and are referenced to the residual proton peaks of the deuterated solvents. ^{13}C NMR spectra were resonances were assigned from DEPT, single-frequency DEPT, and C–H correlation experiments. The solvent used for all NMR experiments was acetone-d_6 obtained from Cambridge Isotope Laboratories which was dried over $CaSO_4$, freeze–pump–thaw–degassed, and stored under argon.

General Procedure for the Preparation of [(η^3-Allyl)(CO)(η^5-cyclopentadienyl)(NO)Mo][PF_6] Complexes. The dicarbonylmolybdenum π-allylic complex was dissolved in dry, degassed 1,2-dimethoxyethane (DME) (1 mmol of complex:5–10 mL of DME) and stirred under an argon atmosphere at −10 °C (ice/MeOH cooling bath). Nitrosonium hexafluorophosphate (1.1 equiv) 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 during the addition. When the last of the $NOPF_6$ was added, the

(34) Hall, S. S.; Åkermark, B. *Organometallics* **1984**, *3*, 1745.
(35) Söderberg, B. C.; 'Akermark, B.; Hall, S. S. *J. Org. Chem.* **1988**, *53*, 2925.
(36) Grennberg, H.; Langer, V.; Bäckvall, J.-E. *J. Chem. Soc., Chem. Commun.* **1991**, 1190.
(37) McCallum, J. S.; Sterbenz, J. T.; Liebeskind, L. S. *Organometallics* **1993**, *12*, 927.

mixture was stirred at −10 °C for 1 h, by which time the product had precipitated as a bright yellow solid. In most cases the supernatant was cannulated into an excess of diethyl ether to produce a second crop of product, while the first crop was washed twice with diethyl ether and dried under vacuum. The second crop was collected by filtration, washed with diethyl ether, and similarly dried under vacuum.

[(CO)(η^5-C_5H_5)(NO)(η^3-C_3H_5)Mo][PF_6], 2. (η^5-Cyclopentadienyldicarbonyl(η^3-propenyl)molybdenum (**1**) (903 mg, 3.5 mmol) in DME (35 mL) was stirred at −10 °C under Ar. $NOPF_6$ (674 mg, 3.85 mmol) was added in portions and after 1 h the supernant separated from the yellow precipitate by cannulation into stirred, ice cold diethyl ether (20 mL) to give a second crop of product. The first crop was washed with diethyl ether (2 × 10 mL) and dried *in vacuo* (1.02 g, 72%). The supernatant was removed from the second crop which was then washed with diethyl ether (2 × 5 mL) and dried (100 mg, 7%). The combined yield of carbonyl(η^5-cyclopentadienyl)nitrosyl(η^3-propenyl)molybdenum hexafluorophosphate (**2**) for the reaction was 79%. In other runs of this reaction the yields were in the range 79–81%. The data collected were identical to those previously recorded:[23,24] mp of precipitate 195–203 °C dec; IR (KBr) 2099 (ν CO), 1721 (ν NO) 853 (ν PF) cm^{-1}; *endo* ^1H NMR (360 MHz, $(CD_3)_2CO$) δ 6.51 (s, 5H, C_5H_5), 5.68 (overlapping dddd, $^3J_{2\text{-}3anti}$ = 14, $^3J_{2\text{-}1anti}$ = 12.5, $^3J_{2\text{-}1syn}$ = 7.5, $^3J_{2\text{-}3syn}$ = 7.2 Hz, 1 H, C2-H), 5.08 (ddd, $^3J_{2\text{-}1syn}$ = 7.5, $^4J_{1syn\text{-}3syn}$ = 3.5, $^2J_{1syn\text{-}1anti}$ = 1 Hz, 1 H, Cl-H_{syn}), 4.30 (dd, $^3J_{2\text{-}3syn}$ = 7.2, $^4J_{1syn\text{-}3syn}$ = 3.5 Hz, 1 H, C3-H_{syn}), 3.80 (dd, $^3J_{2\text{-}1anti}$ = 12.5, $^2J_{1syn\text{-}1anti}$ = 1 Hz, 1 H, C1-H_{anti}), 3.27 (d $^3J_{2\text{-}3anti}$), 3.27 (d, $^3J_{2\text{-}3anti}$ = 14 Hz, 1 H, C3-H_{anti} = 14 Hz, 1 H, C3-H_{anti} = 14 Hz, 1 H, C3-H_{anti}); ^{13}C NMR (75.5 MHz, $(CD_3)_2CO$) δ 207.9 (s, MoCO), 114.3 (d, C2), 101.9 (d, C_5H_5), 68.3 (t, C1), 60.1 (t, C3); *exo* ^1H NMR (360 MHz, $(CD_3)_2CO$) δ 6.36 (s, 5 H, C_5H_5), 5.38 (overlapping dddd, $^3J_{2\text{-}3anti}$ = 14, $^3J_{2\text{-}1anti}$ = 13.5, $^3J_{2\text{-}1syn}$ = 7.6, $^3J_{2\text{-}3syn}$ = 8 Hz, 1 H, C2-H), 5.14 (dd, $^3J_{2\text{-}1syn}$ = 7.6, $^4J_{1syn\text{-}3syn}$ = 3.2 Hz, 1 H, C1-H_{syn}), 4.89 (dd, $^3J_{2\text{-}3syn}$ = 8, $^4J_{1syn\text{-}3syn}$ = 3.2 Hz, 1 H, C3-H_{syn}), 3.56 (d, $^3J_{2\text{-}1anti}$ = 13.5 Hz, 1 H, C1-H_{anti}), 3.41 (d, $^3J_{2\text{-}3anti}$), 3.41 (d, $^3J_{2\text{-}3anti}$ = 14 Hz, 1 H, C3-H_{anti}); ^{13}C NMR (75.5 MHz, $(CD_3)_2CO$) δ 211.1 (s, MoCO), 101.1 (d, C2), 100.9 (d, C_5H_5), 68.1 (t, C1), 64.6 (t, C3); ^1H NOE, **8-*endo***, presaturation of the Cp singlet (δ 6.51) resulted in enhancement of the C1-H_{anti} multiplet (δ 3.80, 2.8%); ^1H NOE, **8-*exo***, presaturation of the Cp singlet (δ 6.36) resulted in enhancement of the C2-H multiplet (δ 5.38, 5%) and of the C1-H_{syn} multiplet (δ 5.14, 3%).

[(η^5-C_5H_5)Mo(CO)(NO)(η^3-2-MeC_3H_4)] [PF_6], 4. (η^5-Cyclopentadienyl)dicarbonyl(η^3-2-methylpropenyl)molybdenum (**3**) (408 mg, 1.5 mmol) in DME (15 mL) was stirred at −10 °C under Ar. $NOPF_6$ (289 mg, 1.65 mmol) was added in portions, and after 1 h the supernatant was separated from the yellow precipitate by cannulation into stirred, ice-cold diethyl ether (10 mL) to give a second crop of product. The first crop was washed with diethyl ether (2 × 5 mL) and dried *in vacuo* (228 mg, 36.3%). The supernatant was removed from the second crop which was then washed with diethyl ether (2 × 5 mL) and dried (300 mg, 47.7%). The combined yield of carbonyl(η^5-cyclopentadienyl)-(η^3-2-methylpropenyl)nitrosylmolybdenum hexafluorophosphate (**4**) for the reaction was 84%. The data collected were identical to those previously recorded:[23,24] mp of precipitate 165–175 °C dec; IR (KBr) 2092 (ν CO), 1744(ν NO) 828 (ν PF) cm^{-1}; *endo* ^1H NMR (360 MHz, $(CD_3)_2CO$) δ 6.50 (s, 5 H, C_5H_5), 4.98 (dd, $^4J_{1syn\text{-}3syn}$ = 4.5, $^2J_{1syn\text{-}1anti}$ = 1 Hz, 1 H, C1-H_{syn}), 4.22 (dd, $^4J_{1syn\text{-}3syn}$ = 4.5, $^2J_{1syn\text{-}1anti}$ = 1.5 Hz, 1 H, C3-H_{syn}), 3.73 (br s, 1 H, C1-H_{anti}), 3.08 (br s, 1 H, C3-H_{anti}), 2.12 (s, 3 H, CH_3); ^{13}C NMR (75.5 MHz, $(CD_3)_2CO$) δ 208.0 (s, MoCO), 134.5 (s, C2), 102.3 (d, C_5H_5), 66.9 (t, C1), 61.7 (t, C3), 22.1 (q, CH_3); *exo* ^1H NMR (360 MHz, $(CD_3)_2$-CO) δ 6.33 (s, 5 H, C_5H_5), 5.04 (br d, $^4J_{1syn\text{-}3syn}$ = 3.9 Hz, 1 H, C1-H_{syn}), 4.94 (br d, $^4J_{1syn\text{-}3syn}$ = 3.9 Hz, 1 H, C3-H_{syn}), 3.61 (br s, 1 H, C1-H_{anti}), 3.46 (br s, 1 H, C3-H_{anti}), 2.04 (s, 3 H, CH_3); ^{13}C NMR (75.5 MHz, $(CD_3)_2CO$) δ 210.5 (s, MoCO), 125.4 (s, C2), 101.8 (d, C_5H_5), 69.3 (t, C1), 63.4 (t, C3), 24.9 (q, CH_3).

[(η^5-C_5H_5)Mo(CO)(NO)(η^3-C_6H_9)][PF_6], 6. (η^5 -Cyclopentadienyl)(η^3-cyclohexenyl)dicarbonylmolybdenum (**5**) (2.09 g, 7 mmol) in DME (30 mL) was stirred at −10 °C under Ar. $NOPF_6$ (1.35 g, 7.7 mmol) was added in small portions, and the mixture was stirred at −10 °C for 1 h. Diethyl ether (30 mL) was added, and the supernatant was removed by cannulation. The resulting bright yellow precipitate carbonyl(η^3-cyclohexenyl)(η^5-cyclopentadienyl)nitrosylmolybdenum hexafluorophosphate (**6**) was washed with diethyl ether (2 × 10 mL) and dried *in vacuo* (2.5 g, 80%). In other runs of this reaction the yields were in the range 80–82%. (This compound was originally isolated as a red-brown powder and limited IR and ^1H NMR data reported.[12]) **6**: mp of precipitate 148–156 °C dec; IR (KBr) 2061 (ν CO), 1711 (ν NO) 834 (ν PF) cm^{-1}; ^1H NMR (500 MHz, $(CD_3)_2CO$) δ 6.67 (overlapping dddd, $^3J_{2\text{-}1}$ = 7.5, $^3J_{1\text{-}6eq}$ = 5, $^4J_{1\text{-}3}$ = 4.5, $^3J_{1\text{-}6ax}$ = 3 Hz, 1 H, C1-H), 6.29 (s, 5 H, C_5H_5), 5.87 (overlapping dddd, $^3J_{2\text{-}3}$ = 7.5, $^3J_{3\text{-}4eq}$ = 4.5, $^4J_{1\text{-}3}$ = 4.5, $^3J_{3\text{-}4ax}$ = 3 Hz, 1 H, C3-H), 5.31 (dd, $^3J_{1\text{-}2}$ = $^3J_{2\text{-}3}$ = 7.5 Hz, 1 H, C2-H), 2.82 (dddd, $^2J_{6eq\text{-}6ax}$ = 17, $^3J_{5eq\text{-}6eq}$ = 7.5, $^3J_{5ax\text{-}6eq}$ = 7.2, $^3J_{1\text{-}6eq}$ = 5 Hz, 1 H, C6-H_{eq}), 2.72 (ddddd, $^2J_{4eq\text{-}4ax}$ = 19, $^3J_{5eq\text{-}4eq}$ = 7.5, $^3J_{5ax\text{-}4eq}$ = 7.2, $^3J_{3\text{-}4eq}$ = 4.5, J = 1.5 Hz, 1 H, C4-H_{eq}), 2.27 (dddd, $^2J_{4eq\text{-}4ax}$ = 19, $^3J_{5ax\text{-}4ax}$ = 7.2, $^3J_{5eq\text{-}4ax}$ = 4.5, $^3J_{3\text{-}4ax}$ = 3 Hz, 1 H, C4-H_{ax}), 2.20 (dddd, $^2J_{6eq\text{-}6ax}$ = 17, $^3J_{5ax\text{-}6ax}$ = 7.2, $^3J_{5eq\text{-}6ax}$ 5, $^3J_{1\text{-}6ax}$ = 3 Hz, 1H, C6-H_{ax}), 1.43 (ddddd, $^2J_{5eq\text{-}5ax}$ = 14.5, $^3J_{5eq\text{-}6eq}$ = 7.5, $^3J_{5eq\text{-}4eq}$ = 7.5, $^3J_{5eq\text{-}6ax}$ = 5, $^3J_{5eq\text{-}4ax}$ = 4.5 Hz, 1 H, C5-H_{eq}), 0.95 (ddddd, $^2J_{5eq\text{-}5ax}$ = 14.5, $^3J_{5ax\text{-}4eq}$ = 7.2, $^3J_{5ax\text{-}6eq}$ = 7.2, $^3J_{5ax\text{-}4ax}$ = 7.2, $^3J_{5ax\text{-}6ax}$ = 7.2 Hz, 1 H, C5-H_{ax}); ^{13}C NMR (75.5 MHz, $(CD_3)_2CO$) δ 214.9 (s, MoCO), 101.6 (d, C_5H_5), 96.3 (d, C1), 87.8 (d, C2), 86.8 (d, C3), 25.0 (t, C6), 23.9 (t, C4), 17.8 (t, C5). Anal. Calcd for $C_{12}H_{14}F_6NO_2PMo$: C, 32.38; H, 3.17; N, 3.15. Found: C, 32.48; H, 3.16; N, 2.96. ^1H NOE, **5**, presaturation of the Cp singlet (δ 5.29) resulted in enhancement of the C2-H multiplet (δ 4.16, 2%) and of the C1-H multiplet (δ 3.68, 1%); ^1H NOE, **6**, presaturation of the Cp singlet (δ 6.29) resulted in enhancement of the C2-H multiplet (δ 5.31, 2.5%) and of the C1-H multiplet (δ 6.67, 1.5%).

[(η^5-C_5H_5)Mo(CO)(NO)(η^3-(5-Me_2)C_6H_7)] [PF_6], 8. (η^5-Cyclopentadienyl)dicarbonyl(η^3-5,5-dimethylcyclohexenyl)molybdenum (**7**) (652 mg, 2 mmol) in DME (10 mL) was stirred at −10 °C under Ar. $NOPF_6$ (385 mg, 2.2 mmol) was added in small portions, and the mixture was stirred at −10 °C for 1 h. Diethyl ether (20 mL) was added, and the supernatant was removed by cannulation. The resulting bright yellow precipitate of carbonyl-(η^5-cyclopentadienyl)(η^3-5,5-dimethylcyclohexenyl)nitrosylmolybdenum hexafluorophosphate (**8**) was washed with diethyl ether (2 × 10 mL) and dried *in vacuo* (790 mg, 83%): mp of precipitate 121–126 °C dec; IR (KBr) 2081 (ν CO), 1713 (ν NO) 834 (ν PF) cm^{-1}; ^1H NMR (360 MHz, $(CD_3)_2CO$) δ 6.69 (overlapping dd, $^3J_{2\text{-}1}$ = 7, $^3J_{1\text{-}6eq}$ = 7 Hz, 1 H, C1-H), 6.45 (overlapping dd, $^3J_{2\text{-}3}$ = 7, $^3J_{3\text{-}4eq}$ = 7.8 Hz, 1 H, C3-H), 6.33 (s, 5 H, C_5H_5), 5.45 (dd, $^3J_{1\text{-}2}$ = $^3J_{2\text{-}3}$ = 7 Hz, 1 H, C2-H), 2.54 (ddd, $^2J_{6eq\text{-}6ax}$ = 19, $^3J_{1\text{-}6eq}$ = 7, $^4J_{4eq\text{-}6eq}$ = 1.5 Hz, 1 H, C6-H_{eq}), 2.49 (ddd, $^2J_{4eq\text{-}4ax}$ = 18, $^3J_{3\text{-}4eq}$ = 7.8, $^4J_{4eq\text{-}6eq}$ = 1.5 Hz, 1 H, C4-H_{eq}), 2.24 (d, $^2J_{6eq\text{-}6ax}$ = 19 Hz, 1 H, C6-H_{ax}), 2.04 (d, $^2J_{4eq\text{-}4ax}$ = 18 Hz, 1 H, C4-H_{ax}), 1.13 (s, 3 H, CH_3), 0.80 (s, 3 H, CH_3); ^{13}C NMR (75.5 MHz, $(CD_3)_2$-CO) δ 213.5 (s, MoCO), 101.5 (d, C_5H_5), 95.7 (d, C2), 91.0 (d, C3), 88.6 (d, C1), 41.1 (t, C6), 38.4 (t, C4), 28.7 (q, CH_3), 28.6 (s, C5), 28.1 (q, CH_3). Anal. Calcd for $C_{14}H_{18}F_6NO_2PMo$: C, 35.54; H, 3.83; N, 2.96. Found: C, 35.59; H, 3.78; N, 2.95.

[(η^5-C_5H_5)Mo(CO)(NO)(η^3-C_5H_7)][PF_6], 10. (η^5-Cyclopentadienyl)(η^3-cyclopentenyl)dicarbonylmolybdenum (**9**) (284 mg, 1 mmol) in DME (10 mL) was stirred at −10 °C under Ar. $NOPF_6$ (193 mg, 1.1 mmol) was added in small portions, and the mixture was stirred at −10 °C for 1 h. Diethyl ether (20 mL) was added, and the supernatant was removed by cannulation. The resulting bright yellow precipitate of carbonyl(η^5-cyclopentadienyl)(η^3-cyclopentenyl)nitrosylmolybdenum hexafluorophosphate (**10**) was washed with diethyl ether (2 × 10 mL) and dried *in vacuo* (375 mg, 87%): mp of precipitate 146–152 °C dec; IR (KBr) 2051 (ν CO), 1694 (ν NO), 837 (ν PF) cm^{-1}; ^1H NMR (360 MHz, $(CD_3)_2$-CO) δ 6.79 (complex dd, 1 H, $^3J_{1\text{-}5}$ = 5, C1-H), 6.49 (complex dd, 1 H, $^3J_{3\text{-}4}$ = 5, C3-H), 6.31 (s, 5 H, C_5H_5), 5.50 (dd, $^3J_{1\text{-}2}$ = $^3J_{2\text{-}3}$ = 3.5 Hz, 1 H, C2-H), 2.75–2.85 (m, 2 H, C4-H, C5-H), 2.29–2.40 (m, 2 H, C4-H, C5-H); ^{13}C NMR (75.5 MHz, $(CD_3)_2CO$) δ 214.6 (s, MoCO), 100.9 (d, C_5H_5), 99.8 (d, C1), 97.1 (d, C3), 93.6 (d, C2),

31.8 (t, C4), 30.1 (t, C5). Anal. Calcd for $C_{11}H_{12}F_6NO_2PMo$: C, 30.65; H, 2.81; N, 3.25. Found: C, 30.69; H, 2.84; N, 3.25.

NOE Experiments. NOE difference spectra were recorded at 360 MHz and were performed on 5 mg of sample in 0.5 mL of benzene-d_6 (11) or acetone-d_6 (12, 8-*endo-exo*) which had been freeze–pump–thaw–degassed and sealed under vacuum. The parameters employed are as follows: preirradiation times were 10 (11), 10 (12), and 15 s (8-*endo-exo*); delay times of 20 μs for all samples; data acquisition times of 8.66 (11, 8-*endo-exo*) and 2.5 μs (12); predelay of 2 (11, 8-*endo-exo*) and 1 s (12). The resulting FIDs were subjected to exponential multiplication to provide line broadening of 1 Hz and then transformed and subtracted. The observed enhancements are reported in the text.

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