Preparation of Cationic Cyclopentadienyl Diene Molybdenum Complexes through Hydride Abstraction Effected by Di- or Triarylmethyl Halides in the Presence of Hexafluoro-2-propanol

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Hydride abstraction from the model system (η^5-cyclopentadienyl)dicarbonyl[(1−3-η)-1-cyclohexen-3-yl]molybdenum (**1**) was effected using halides such as Ph_3CCl (**3b**), Ph_3CBr (**3a**), and $(4\text{-}MeOC_6H_4)_2CHBr$ (**5**), or their polymer-bound analogues, as carbocation precursors. The presence of hexafluoro-2-propanol (HFiP) as a cosolvent was critical for hydride abstraction to proceed. Good yields of (η^5-cyclopentadienyl)dicarbonyl[(1−4-η)-cyclohexadiene]-molybdenum halides **2a**,**b** were obtained from soluble as well as polymer-supported hydride abstractors. The influence of HFiP concentration and carbocation precursor on reaction efficiency was investigated.

Introduction

Cationic diene molybdenum complexes of the type (η^5-L)(diene)$Mo(CO)_2X$ constitute a valuable class of electrophiles for organic synthesis.[1] In particular, the temporary complexation of carbo- or heterocyclic dienes to molybdenum has been elegantly utilized for stereoselective syntheses of cis-disubstituted targets (Figure 1), as well as for the construction of quaternary centers.[2] The stabilizing effect of the η^5 ligand in these molybdenum π-complexes conveys enough chemical robustness to allow sequential metal-assisted reactions and convenient isolation and purification of the organometallic intermediates. Recent development of mild and selective decomplexation protocols[3] should further enhance the value of these molybdenum-mediated synthetic strategies.

Two routes of preparative significance are available for the preparation of the requisite cationic diene complexes: direct complexation and oxidation of an allylic precursor. Stable dienes may be attached to cationic templates such as $[(\eta^5\text{-L})Mo(CO)_2(MeCN)_2]^+$ (η^5-L = indenyl, pentamethylcyclopentadienyl) via an exchange reaction. Typically, (η^5-L)$MoMe(CO)_3$ in MeCN is acidified at low temperature to afford the cationic template and the diene introduced at room temperature.[4] A similar route involving replacement of an allylic ligand under acidic conditions has also been described.[4a,5] Alternatively, oxidation of the precursor $[(\eta^5\text{-L})Mo(CO)_3]_2$ with silver ion in CH_2Cl_2 or MeCN can be used to generate the cationic species.[3c,4,6]

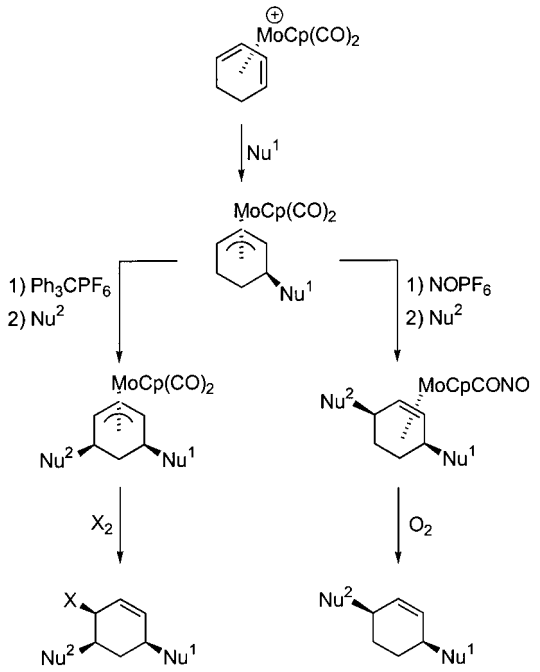

Figure 1. Hydride abstraction/nucleophilic addition sequences involving organomolybdenum complexes.

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(1) Review: Pearson, A. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, E. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 12, Chapter 6.3.

(2) For recent accounts, see: (a) Liu, R.-S. *Adv. Met.-Org. Chem.* **1998**, *6*, 145. (b) Li, C.-L.; Liu. R.-S. *Chem. Rev.* **2000**, *100*, 3127−3161.

(3) (a) Yin, J.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1999**, *121*, 5811. (b) Bjurling, E.; Johansson, M. H.; Andersson, C.-M. *Organometallics* **1999**, *18*, 5606. (c) Pearson, A. J.; Khetani, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6778. (d) Knölker, H.-J.; Goesmann, H.; Hofmann, C. *Synlett* **1996**, 737. (e) Pearson, A. J.; Khan, M. N. I. *J. Am. Chem. Soc.* **1984**, *106*, 1872.

(4) (a) Green, M.; Greenfield, S.; Kersting, M. *J. Chem. Soc., Chem. Commun.* **1985**, *18*. (b) Bottrill, M.; Green, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2365.

(5) (a) Giulieri, F.; Benaim, J. *J. Organomet. Chem.* **1984**, *276*, 367. (b) Gusev, O. V.; Krivykh, V. V.; Petrovskii, P. V.; Rybinskaya, M. I. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1987**, 1532.

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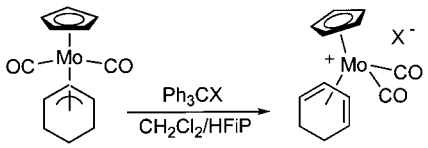
Transformation of allylic precursors of the type (η^3-allyl)$MoCp(CO)_2$ into (η^4-diene)$MoCp(CO)_2$ cations almost exclusively involves abstraction of a hydride ion. This methodology offers the most general entry into cationic diene complexes, since the precursors are usually obtained in high yields via oxidative addition of readily available allylic halides or acetates. Reactive Mo(0) species such as $(MeCN)_3Mo(CO)_3$ are conveniently formed in situ upon refluxing molybdenum hexacarbonyl in acetonitrile. Importantly, this two-step procedure allows the preparation of synthetically useful complexes also with labile dienes, such as cyclopentadienone[7] and 2*H*-pyran.[8]

The standard protocol for hydride abstraction from (π-allyl)molybdenum complexes involves treatment with a trityl salt (Ph_3CPF_6 or Ph_3CBF_4) in dichloromethane, followed by precipitaion.[9] These reactions proceed uneventfully with most simple substrates. However, application to more highly substituted allylic substrates is problematic, probably as a consequence of the steric bulkiness of the trityl ion in combination with the stereoelectronic requirement[1,9b] for removal of a hydride anti to molybdenum.[10] Unfortunately, traditional trityl ion mediated hydride abstraction has remained the only general source of diene complexes from allylic precursors. An alternative oxidation procedure, entailing treatment of the allylmolybdenum precursor with DDQ in the presence of $HBF_4 \cdot Et_2O$ at low temperature, has been reported but not generally adapted. In special cases, where the η^3-organomolybdenum substrate carries a suitably positioned leaving group, such as alkoxy[3c,4,6,8a,b] or indolyl,[3b] elimination forming diene complexes has been observed.

We recently communicated on an alternative procedure for hydride abstraction, in which trityl cation was generated in situ from Ph_3CBr. Key to this protocol was the utilization of 1,1,1,3,3,3-hexafluoro-2-propanol[11] (HFiP) as a cosolvent. HFiP is a weakly acidic (pK_a = 9.4)[12] and strongly hydrogen bonding[13] solvent, which has previously been used in studies of carbocation behavior[14] and also as a convenient and efficient reagent for the cleavage of synthetic peptides from 2-chlorotrityl resin.[15] We anticipated that generating trityl ion in situ in this fashion might provide a convenient alternative to the traditional methodology, which requires handling of moisture-sensitive and expensive trityl salts as well as operating under strictly anhydrous conditions. We also speculated that in situ generation of carbocations might allow the use of additional carbocation precursors, especially those presenting less sterical requirements, which do not form isolable cation salts. Herein, we report full details of extended studies on the use of tri- and diarylmethane derivatives as hydride abstraction reagents.



1 **2a;** X = Br **2b;** X = Cl

Figure 2. Reactions of model substrate **1** with trityl halides in the presence of HFiP.

Results and Discussion

We recently reported[16] that hydride abstraction from the allylic complex **1** proceeds smoothly in 80−86% yield using Ph_3CBr as a trityl cation precursor in 20% (v/v) of HFiP in dichloromethane. The procedure involved stirring at 0 °C for 1 h and simple isolation of the cationic product by addition of degassed diethyl ether followed by decantation. The objective of the work reported herein was to explore the influence of variables such as the concentration of HFiP, solvent, and carbocation precursor on the efficiency of the hydride abstraction process.

Solvent Mixture Composition. In dichloromethane containing 20% (v/v) HFiP, Ph_3CBr presumably dissociates into free trityl cation, which, in turn, mediates hydride abstraction from a suitable donor (Figure 2). Evaluation of the minimum concentration of HFiP required for the reaction was undertaken by NMR experiments. In solutions of Ph_3CBr in CD_2Cl_2 containing 0, 2, 5, 10, 15, or 20% (v/v) HFiP, the ^1H NMR signals from the aromatic protons changed dramatically with increasing concentration of HFiP. The original multiplet from Ph_3CBr observed at low HFiP concentrations (0, 2, and 5%) was disrupted into two triplets and a doublet moving downfield with increasing concentrations (10, 15, and 20%). In comparison, the resonances recorded from the ionic Ph_3CPF_6 in the same solvent mixtures[17] were unaffected by the HFiP concentration. In the presence of about 15% (v/v) of HFiP, the appearance of the spectrum resulting from trityl bromide was observed to approach that of Ph_3CPF_6. Our interpretation was that significant dissociation to form trityl cation occurred at 10, 15, and 20% HFiP and that the equilibrium between trityl bromide and trityl cation was in favor of the latter at the highest HFiP concentrations. At low HFiP content, the situation was further complicated by apparent hydrolysis forming trityl alcohol.

Upon introduction of the hydride donor **1** into the NMR samples, rapid hydride abstraction was observed at concentrations of HFiP from 10% (v/v) and above.

(6) Pearson, A. J.; Khetani, V. D. *J. Org. Chem.* **1988**, *53*, 3395.
(7) (a) Liebeskind, L. S.; Bombrun, A. *J. Am. Chem. Soc.* **1991**, *113*, 8736. (b) Slugovc, C.; Mauthner, K.; Mereiter, K.; Schmid, R.; Kirchner, K. *Organometallics* **1996**, *15*, 2954.
(8) (a) Rubio, A.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1993**, *115*, 891. (b) Hansson, S.; Miller, J. F.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1990**, *112*, 9660.
(9) (a) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 4858. (b) Faller, J. W.; Murray, H. H.; White, D. L.; Chao, K. H. *Organometallics* **1983**, *2*, 400. (c) Pearson, A. J.; Khan, M. N. I. *J. Org. Chem.* **1985**, *50*, 5276. (d) Pearson, A. J.; Khan, M. N. I.; Clardy, J. C.; Cunheng, H. *J. Am. Chem. Soc.* **1985**, *107*, 2748.
(10) The same factors preclude sequential 1,2-difunctionalisation in the analogous cyclohexadienyl iron series; e.g., see ref 1.
(11) HFiP is a sensory irritant, see: Nielsen, G. D.; Abraham, M. H.; Hansen, L. F.; Hammer, M.; Cooksey, C. J.; Andonian-Haftvan, J.; Alarie, Y. *Arch. Toxicol.* **1996**, *70*, 319.
(12) Arrowsmith, C. H.; Kresge, A. J.; Tang, Y. C. *J. Am. Chem. Soc.* **1991**, *113*, 179.
(13) Abraham, M. H.; Duce, P. P.; Prior, D. V.; Barratt, D. G.; Morris, J. J.; Taylor, P. J. *J. Chem. Soc., Perkin Trans. 2* **1989**, 1355.
(14) (a) McClelland, R. A.; Mathivanan, N.; Steenken, S. *J. Am. Chem. Soc.* **1990**, *112*, 4857. (b) Cozens, F.; Li, J.; McClelland, R. A.; Steenken, S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 743.
(15) Bollhagen, R.; Schmiedberger, M.; Barlos, K.; Grell, E. *J. Chem. Soc., Chem. Commun.* **1994**, 2559.
(16) Bjurling, E.; Andersson, C.-M. *Tetrahedron Lett.* **1999**, *40*, 1981.
(17) Resonances were as follows: δ 8.29 (tt, J = 7.5, 1.2 Hz), 7.90 (t, J = 7.5 Hz), 7.68 (dd, J = 1.2, 8.4 Hz).

Table 1. Influence of HFiP Concentration on Hydride Abstraction[a] from Substrate 1 with Ph_3CBr (Figure 2)

entry	solvent CH_2Cl_2/HFiP	product (yield, %)[b]	color
1	98/2	**2a** (35)	blue-green
2	95/5	**2a** (66)	green
3	90/10	**2a** (82)	yellow-green
4	80/20	**2a** (86)	yellow

[a] Reactions employed **1** (100−200 mg) and 1.2 equiv of Ph_3CBr in 10 mL of the solvent mixture. After reaction at 0 °C for 1 h, the product was isolated through precipitation with diethyl ether. [b] Isolated yield.

Reaction progress was readily monitored via observation of the replacement of the Cp resonance associated with **1** (5.3 ppm) with that of cationic complex **2** (5.8 ppm), as well as the occurrence of a singlet originating from Ph_3CH (5.6 ppm). At HFiP concentrations under 10%, only traces of product appeared.

The results of preparative reactions employing different concentrations of HFiP are presented in Table 1. These reactions were run under oxygen-free conditions using ordinary solvent grades. The color of the product was useful as a measure of the performance of the reaction and the purity of the product, which, when pure, should be bright yellow. In the absence of HFiP, no hydride abstraction took place. With only 2 or 5% of HFiP present in the reaction, the isolated yields of **2a** were 35 and 66% of blue and green solids, respectively (entries 1 and 2). We interpreted these reaction outcomes in terms of competing hydrolysis of trityl bromide at low HFiP content, leading to partial protolytic decomposition of **1** or possibly **2**. Although the material isolated from these reactions gave clean NMR spectra, the observed discoloration was indicative of the presence of inorganic, molybdenum-containing decomposition products. However, when the reaction mixture was made up with 10 or 20% of HFiP (entries 3 and 4, Table 1), the isolated yields of **2a** were much better, 82 and 86%, respectively, and were accompanied by improvement of product purity, returning yellow-green or yellow solids. In conclusion, the most reliable results from the procedure are obtained using HFiP concentrations of at least 10%. Surprisingly, replacing dichloromethane with chloroform and using 20% HFiP, the product **2a** could be isolated in only 30% yield. Similarly, experiments evaluating a variety of other solvents, including acetonitrile, were uniformly unsuccessful.

Carbocation Precursors. An extension of the HFiP-supported hydride abstraction protocol to additional, readily available carbocation precursors would enhance its applicability. In particular, our incentive for initiating the studies summarized here was a need for a less sterically demanding alternative to trityl ion. We first examined whether the bromine of Ph_3CBr could be exchanged for other nucleofuges. This would possibly be interesting in order to extend availability of diene complexes beyond the currently known hexafluorophosphates and tetrafluoroborates.[18] The preparative results using a few different trityl derivatives (**3a**−**e**) are summarized in Figure 3 and Table 2 (entries 1−5).

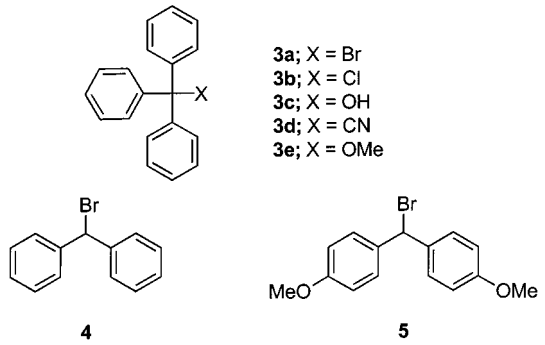


Figure 3. Carbocation precursors evaluated in the hydride abstraction reaction.

Table 2. Hydride Abstractions[a] Using Various Carbocation Precursors

entry	hydride abstractor	solvent CH_2Cl_2/HFiP	product (yield, %)[b]
1	Ph_3CBr, **3a**	80/20	**2a** (80−86)
2	Ph_3CCl, **3b**	80:20	**2b** (62)
3	Ph_3COH, **3c**	75/25	no reacn[c]
4	Ph_3CCN, **3d**	80/20	no reacn
5	Ph_3COCH_3, **3e**	95/5	no reacn
6	Ph_2CHBr, **4**	80/20	**2a** (25)
7	$(p\text{-}MeOC_6H_4)_2CHBr$, **5**	80/20	**2a** (84)

[a] Reactions employed **1** (100−200 mg) and 1.2 equiv of hydride abstractor in 10 mL of solvent mixture. After reaction at 0 °C for 1−2 h, the product was isolated through precipitation with diethyl ether. The substrate used in all cases was **1**. [b] Isolated yield. [c] Addition of 1.5 equiv of HPF_6 returned an 80% yield of (η^5-cyclopentadienyl)dicarbonyl[(1−4-η)cyclohexadiene]molybdenum hexafluorophosphate.

Trityl chloride (**3b**) gave chloride **2b** as yellow crystals in a yield of 62%. Possibly, the lower yield returned in this experiment, compared to analogous synthesis of the bromide **2a**, was a consequence of a more troublesome isolation, since the precipitate did not settle very well. As shown in entries 3−5 of Table 2, attempted use of trityl alcohol (**3c**), trityl cyanide (**3d**), and methyl trityl ether (**3e**) as precursors met with failure. Still, the addition of 1.5 equiv of HPF_6 to the reaction employing trityl alcohol gave an 80% yield of (η^5-cyclopentadienyl)-dicarbonyl [(1−4-η)-cyclohexadiene]molybdenum hexafluorophosphate.

We were especially intrigued by the opportunity to identify less sterically compromised hydride abstractors, since that would potentially allow a much wider range of organomolybdenum substrates to take part in synthetically useful sequences, such as those depicted in Figure 1. Entry 6 of Table 2 represents our first success in this direction, employing commercially available bromodiphenylmethane (**4**). Although the desired **2a** was only isolated in modest yield, this result encouraged us to study alternative diarylhalomethanes. Further stabilization of the presumed intermediate benzhydryl cation by introduction of electron-donating substituents in the phenyl rings turned out to be very productive. Bromobis(4-methoxyphenyl)methane (**5**), readily available from 4,4′-dimethoxybenzhydrol,[19] returned an excellent yield (84%) of **2b** under the standard conditions developed for trityl bromide. We regard this result—to our knowledge the first example of the use of a non-trityl-derived carbocation precursor for hydride abstrac-

(18) Complex fluorine-containing counterions display reactivity, for example, toward silyl ethers: (a) Baxter, J. S.; Green, M.; Lee, T. V. *J. Chem. Soc., Chem. Commun.* **1989**, 1595. (b) Butters, C.; Carr, N.; Deeth, R. J.; Green, M.; Green, S. M.; Mahon, M. F. *J. Chem. Soc., Dalton Trans.* **1996**, 2299.

(19) Henneuse, C.; Boxus, T.; Tesolin, L.; Pantano, G.; Marchand-Brynaert, J. *Synthesis* **1996**, 495.

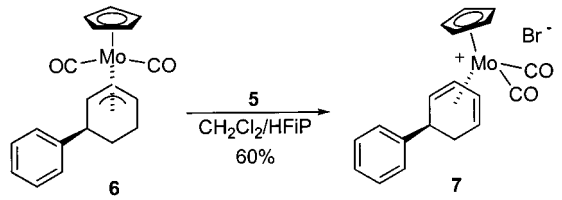


Figure 4. Abstraction of the severely hindered hydride of **6** effected by halide **5**.

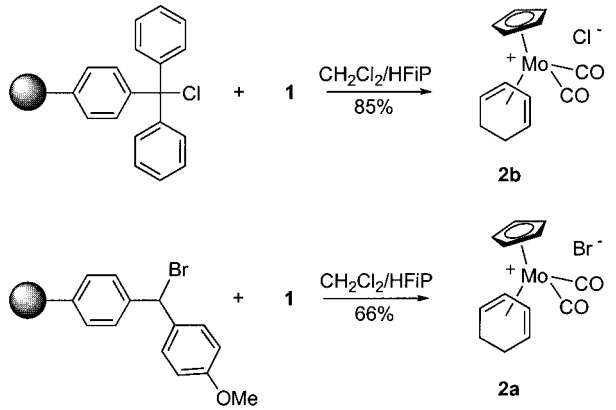


Figure 5. Heterogeneous hydride abstractions.

tion—to be the most significant in the series. To compare the utility of bromide **5** with **3a**, we performed hydride abstractions employing the sterically demanding substrate (η^5-cyclopentadienyl)dicarbonyl[(2−4-η)-1-phenyl-2-cyclohexen-4-yl]molybdenum (**6**). Experiments in the NMR tube, utilizing 2 equiv of the carbocation precursors, indicated a more rapid reaction with **5**. Similarly, in a preparative run performed under our standard conditions, carbocation precursor **5** delivered a modest yield of **7**,[20] whereas **3a** provided only traces of the product (Figure 4).[21]

Heterogeneous Reactions using Polystyrene Resins. The advent of high-throughput synthesis has recently popularised the utilization of polymer-supported reagents, which facilitate product isolation by simple filtration. A report[15] describing the use of HFiP for cleaving peptides from a trityl resin invited the application of trityl chloride resin (**8**) in our hydride abstraction procedure. This commercially available reagent was found to effectively replace trityl chloride in the preparation of **2b**, which could be isolated in 85% yield (Figure 5). The resin was carefully washed with CH_2Cl_2 before the reaction solvent and allylic substrate **1** were added. Introduction of HFiP to the mixture resulted in a sharp color change, turning the resin dark red. Simple filtration and addition of diethyl ether to the filtrate returned pure **2b**. Similarly, when bromo(4-methoxyphenyl)methyl polystyrene resin **9** was employed, cationic diene complex **2a** was isolated in 66% yield. The lower yield as compared to the corresponding homogeneous reaction involving **5** might reflect less efficient stabilization of a cation derived from **9**. Further studies regarding the use of substituted homogeneous as well as heterogeneous diarylmethyl halides for hydride abstraction from sterically hindered allylic molybdenum complexes and in enantioselective hydride abstractions are underway in our laboratories.

Conclusion

We have developed an alternative method for the preparation of cationic diene molybdenum complexes, using either trityl halides or hitherto unexplored diarylmethyl halides as carbocation precursors. The presence of hexafluoro-2-propanol as a cosolvent is critical for the hydride abstraction to proceed. Yields obtained by the convenient homogeneous or heterogeneous procedures described herein compare favorably with those reported for the traditional conditions. The results observed with bromobis(*p*-methoxyphenyl)methane hold promise that the methods might find further application, especially with more highly substituted allylic molybdenum complexes as substrates.

Experimental Section

General Considerations. All reactions were performed under an argon atmosphere. Solvents and reagents were used as received from commercial sources, unless otherwise indicated. HFiP was purchased from Lancaster Synthesis. Trityl chloride resin and bromo(4-methoxyphenyl)methyl polystyrene resin were from Advanced ChemTech and NovaBiochem, respectively. Degassing of solvents was accomplished through ultrasound irradiation for approximately 1 h. NMR spectra were recorded on a Bruker ARX400 instrument at 400.132 MHz (^{1}H) or 100.6 MHz (^{13}C) or on a Bruker ARX300 instrument at 300.135 MHz (^{1}H) or 75.5 MHz (^{13}C). The chemical shifts are given relative to CD_2Cl_2 (δ 5.32, residual ^{1}H; δ 54.0, ^{13}C) and CD_3CN (δ 1.94, residual ^{1}H; δ 118.7, ^{13}C). IR spectra were recorded on an FT-IR Nicolet Impact 410. Melting points were uncorrected. Elemental analyses were obtained from H. Kolbe Mikroanalytisches Laboratorium, Mülheim a. d. Ruhr, Germany. (η^5-Cyclopentadienyl)dicarbonyl[(1−3-η)-1-cyclohexen-3-yl]molybdenum (**1**),[9b] bromobis(4-methoxyphenyl)methane (**5**),[19] trityl cyanide (**3d**),[22] and methyl trityl ether (**3e**)[23] were prepared according to the literature.

Representative Procedure for Homogeneous Hydride Abstractions. (η^5-Cyclopentadienyl)dicarbonyl[(1−4-η)-cyclohexadiene]molybdenum Bromide (2a). In a Schlenk flask were placed degassed 1,1,1,3,3,3-hexafluoro-2-propanol (2.0 mL), degassed dichloromethane (6.0 mL), and (η^5-cyclopentadienyl)dicarbonyl[(1−3-η)-1-cyclohexen-3-yl]molybdenum (**1**; 0.21 g, 0.71 mmol). The flask was sequentially flushed with argon and evacuated several times. The flask was cooled to 0 °C, whereupon bromobis(4-methoxyphenyl)methane (**5**; 0.28 g, 0.92 mmol, 1.3 equiv), dissolved in degassed dichloromethane (2 mL), was added, and the reaction mixture was stirred at 0 °C for 1 h. Degassed diethyl ether (40 mL) was added, and the solid was allowed to settle before the supernatant was removed. The product precipitate was triturated with 2 × 10 mL of diethyl ether, leaving, after drying under vacuum, 0.32 g (85%) of (η^5-cyclopentadienyl)dicarbonyl[(1−4-η)-cyclohexadiene]molybdenum bromide (**2a**). Mp: ∼140 °C dec. Anal. Calcd for $C_{13}H_{13}BrMoO_2$: C, 41.41; H, 3.48. Found: C, 41.22; H, 3.62. ^{1}H NMR (CD_2Cl_2): δ 6.50 (br s, 2H), 6.00 (s, 5H), 5.00 (br s, 2H), 2.25 (br d, J = 13.0 Hz, 2H), 2.02 (br d, J = 13.0 Hz, 2H). ^{13}C NMR (CD_2Cl_2): δ 225.1, 94.9, 89.4, 84.8, 24.6. IR (KBr): 2000, 1934 cm^{-1}. HRMS (FAB+): *m/z* calcd for $C_{13}H_{13}MoO_2$, 298.9969; found M^+, 298.9963.

(20) Product isolation was compromised by incomplete precipitation of the diene complex. However, addition of diethyl ether to the crude reaction mixture returned a 26% isolated yield of pure **7**.

(21) The corresponding tetrafluoroborate has been discussed earlier, but no experimental data were provided; see: Wang, S.-H.; Cheng, Y.-C.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *Organometallics* **1993**, *12*, 3282.

(22) Zieger, H. E.; Wo, S. *J. Org. Chem*. **1994**, *59*, 3838.

(23) Stoochnoff, B. A.; Benoiton, N. L. *Tetrahedron Lett*. **1973**, 21.

Heterogeneous Reactions using Trityl Chloride Polystyrene Resin. (η^5-Cyclopentadienyl)dicarbonyl[(1−4-η)-cyclohexadiene]molybdenum Chloride (2b). Trityl chloride polystyrene resin (0.94 mmol, 1.4 equiv) was placed in a Schlenk flask and washed with 3 × 10 mL of degassed dichloromethane before 1,1,1,3,3,3-hexafluoro-2-propanol (degassed, 2 mL) and dichloromethane (degassed, 8 mL) were added. The polymer became dark red. The flask was cooled to 0 °C, whereupon **1** (0.20 g, 0.68 mmol) was added, and the reaction mixture was stirred at 0 °C for 2 h.

(a) Isolation by Precipitation. The reaction mixture was filtered under an inert atmosphere, and the resin was rinsed with 2 × 10 mL of dichloromethane. Diethyl ether (200 mL) was then added to the combined organic solutions, and the yellow solid was allowed to settle before the supernatant was removed. The product was triturated with 2 × 15 mL of diethyl ether, giving, after drying under vacuum, 0.19 g (85%) of (η^5-cyclopentadienyl)dicarbonyl[(1−4-η)cyclohexadiene]molybdenum chloride (**2b**). Mp: ∼ 140 °C dec. Anal. Calcd for $C_{13}H_{13}ClMoO_2$: C, 46.94; H, 3.94. Found: C, 47.11; H, 4.06. ^{1}H NMR (CD_2Cl_2): δ 6.38 (br t, J = 4.0 Hz, 2H), 5.95 (s, 5H), 4.82 (br s, 2H), 2.26 (br d, J = 13.3 Hz, 2H), 2.03 (br d, J = 13.3 Hz, 2H). ^{13}C NMR (CD_2Cl_2): δ 224.8, 94.8, 88.9, 84.4, 24.5. IR (KBr): 1996, 1934 cm^{-1}.

(b) Isolation by Concentration. Trityl chloride polystyrene resin (0.48 mmol, 1.4 equiv) was placed in a Schlenk flask and washed with 3 × 10 mL of degassed dichloromethane before dichloromethane (degassed, 8 mL) and **1** (0.10 g, 0.34 mmol) were added. The flask was cooled to 0 °C, whereupon 1,1,1,3,3,3-hexafluoro-2-propanol (degassed, 2 mL) was added. The polymer became dark red. The reaction mixture was kept at 0 °C (ice bath) overnight without stirring and then filtered under an inert atmosphere. The resin was rinsed with 2 × 10 mL of dichloromethane. Evaporation of the combined filtrates gave, after drying under vacuum, 0.1 g (83%) of **2b**.

Heterogeneous Reactions using Bromo(4-methoxyphenyl)methyl Polystyrene Resin. Bromo(4-methoxyphenyl)-methyl polystyrene resin (1.0 mmol, 1.5 equiv) was placed in a Schlenk flask and washed with 2 × 10 mL of degassed dichloromethane. Degassed dichloromethane (8 mL) and **1** (0.20 g, 0.68 mmol) were added. The flask was cooled to 0 °C, whereupon degassed 1,1,1,3,3,3-hexafluoro-2-propanol (2 mL) was added dropwise. The reaction mixture was stirred at 0 °C for 2 h and then filtered under an inert atmosphere into diethyl ether (250 mL). The resin was rinsed with additional of dichloromethane (2 × 10 mL). The solid was allowed to settle before the supernatant was removed. The product was finally triturated with 2 × 15 mL of diethyl ether, giving, after drying under vacuum, 0.17 g (66%) of (η^5-cyclopentadienyl)dicarbonyl-[(1−4-η)-cyclohexadiene]molybdenum bromide (**2a**).

(η^5-Cyclopentadienyl)dicarbonyl[(2−4-η)-1-phenyl-2-cyclohexen-4-yl]molybdenum (6). In a dry, two-necked flask were placed (η^5-cyclopentadienyl)dicarbonyl[(1−4-η)-cyclohexadiene]molybdenum hexafluorophosphate[9b,24] (0.30 g, 0.67 mmol) and dry THF (20 mL). The suspension was cooled to 0 °C, whereupon a 1 M solution of PhMgBr in THF (5 mL, 5 mmol, 7.5 equiv) was added. The reaction mixture was stirred for 2 h at 0 °C. Saturated aqueous NH_4Cl (30 mL) was added, and the reaction mixture was extracted with 2 × 30 mL of dichloromethane. The combined organic phases were dried over Na_2SO_4, filtered, and evaporated, and the crude product was subjected to flash chromatography (heptane/CH_2Cl_2, 4:1, R_f = 0.15) to give 0.19 g (78%) of a yellow solid. ^{1}H NMR (CD_3CN, 300 MHz): δ 7.44−7.48 (m, 2H), 7.30−7.36 (m, 2H), 7.21 (tt, J = 7.3 and 1.5 Hz, 1H), 5.41 (s, 5H), 4.59 (t, J = 7.0 Hz, 1H), 3.87−3.91 (m, 1H), 3.62 (dm, J = 7.0 Hz, 1H), 3.01 (dm, J = 7.0 Hz, 1H), 2.02−2.12 (m, 1H), 1.57−1.66 (m, 1H), 0.88−0.95 (m, 1H) and 0.69−0.82 (m, 1H). ^{13}C NMR (CD_3CN): δ 238.7, 227.8, 149.4, 129.9, 128.8, 127.5, 94.0, 59.5, 58.3, 57.2, 40.1, 27.2, 20.2. HRMS (FAB+): m/z calcd for $C_{19}H_{18}MoO_2$, 376.0361; found M$^+$, 376.0356.

(η^5-Cyclopentadienyl)dicarbonyl[(1−4-η)-5-phenylcyclohexadiene]molybdenum Bromide (7). In a Schlenk flask were placed degassed 1,1,1,3,3,3-hexafluoro-2-propanol (2.0 mL), degassed dichloromethane (6.0 mL), and **6** (0.10 g, 0.27 mmol). The flask was sequentially flushed with argon and evacuated several times. The flask was cooled to 0 °C, whereupon bromobis(4-methoxyphenyl)methane (**5**; 0.17 g, 0.55 mmol, 2.0 equiv), dissolved in degassed dichloromethane (2 mL), was added, and the reaction mixture was stirred at 0 °C. After 1 h, an additional portion of **5** (70 mg, 0.23 mmol, 0.8 equiv) was added, and stirring was continued for 45 min. The yield of (η^5-cyclopentadienyl)dicarbonyl[(1−4-η)-5-phenylcyclohexadiene]molybdenum bromide (**7**) was determined by NMR integration, using 1,3,5-trimethoxybenzene as the internal standard. After addition of the standard (22.5 mg), the crude reaction mixture was concentrated under reduced pressure, affording an oil. Integration of relevant peaks (CD_3CN) indicated an approximately 60% yield of the desired **7**. Subsequent addition of degassed diethyl ether (100 mL) to the crude material gave partial precipitation of the product (NMR analysis confirmed the presence of additional **7** in the filtrate), and inert filtration then returned 0.032 g (26%) of pure **7**. ^{1}H NMR (CD_3CN, 300 MHz): δ 7.30−7.35 (m, 2H), 7.19−7.25 (m, 3H), 6.18 (br s, 1H), 6.00 (br s, 1H), 5.83 (s, 5H), 4.69−4.72 (m, 1H), 4.56 (br d, J = 4.5 Hz, 1H), 3.57 (dm, J = 10.5 Hz, 1H), 2.62−2.72 (m, 1H), 2.3 (1H, obscured by the water signal). ^{13}C NMR (CD_3CN): δ 222.7, 222.5, 146.1, 130.4, 128.64, 128.61, 95.7, 88.2, 86.8 (br, weak), 84.4 (br, weak), 84.1, 45.3, and 34.5 (partial decomposition complicated recording the ^{13}C NMR). HRMS (FAB+): m/z calcd for $C_{19}H_{17}MoO_2$, 375.0283; found M$^+$, 375.0287.

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(24) Compound **6** may be similarly prepared from **2a** or **2b**.