Stereocontrolled Functionalization of 1,5-Cyclooctadiene Using Organomolybdenum Chemistry

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The preparation and reactions of several new functionalized η^3-cyclooctenyl-$Mo(CO)_2Cp$ complexes are described. Dicarbonyl(η^5-cyclopentadienyl)(1–3-η-cycloocta-1,5-dienyl)molybdenum (**6a**) undergoes regio- and stereoselective hydroboration to give dicarbonyl(η^5-cyclopentadienyl)(1–3-η-6-*endo*-hydroxycyclooctenyl)molybdenum (**7**) as the major product. Swern oxidation of **7** proceeds cleanly to give dicarbonyl(η^5-cyclopentadienyl)(1–3-η-6-oxocyclooctenyl)molybdenum (**9**). Reactions of **9** with nucleophiles proceed with excellent stereoselectivity (anti to the $Mo(CO)_2Cp$ moiety). Conversion of **9** to enol silanes and thence to enolates is readily accomplished, and reaction of the enol silanes and enolates with electrophiles proceeds with complete stereoselectivity to give substituted ketones. Further regio- and stereoselective conversion of these substituted ketones to enolates and thence to disubstituted ketones is described. The stereochemical outcome of these reactions is discussed in terms of the preferred conformations for the enolates. Demetalation of dicarbonyl(η^5-cyclopentadienyl)(1–3-η-6-*endo*-hydroxy-5,7-*endo*-dimethylcyclooctenyl)molybdenum (**23**) to give a stereodefined tetrasubstituted cyclooctene **27** is described.

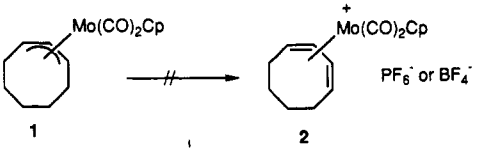
Introduction

We have previously reported methods for stereocontrolled alkylation of six- and seven-membered carbocyclic rings via multiple nucleophilic addition to cationic dienyliron[2] and dienemolybdenum[3] complexes, which leads to the construction of building blocks for the synthesis of macrolide antibiotics.[4] More recently, we have expanded on this concept by showing that alkylation of enolates[5] and functionalization of carbon–carbon double bonds[6] also proceed stereoselectively. However, unlike nucleophile addition to the complexed diene or dienyl ligand, which almost always proceeds anti to the metal,[7] these reactions are sensitive to both conformational (ligand) and steric (metal) effects, particularly with seven-membered ring systems.

The eight-membered ring presents special challenges and potential opportunities. While Still and co-workers have shown that cyclooctane derivatives can be functionalized stereoselectively and have rationalized this behavior on the basis of conformational analysis using molecular mechanics calculations,[8] very little work has been done using organometallic systems that might lead to useful conformational, steric, and stereoelectronic effects.[9] This paper reports our studies on the chemistry and conformational analysis of cyclooctenyl–molybdenum complexes in which we show that uncomplexed double bonds and ketone and derived enolates can be functionalized with high degrees of stereocontrol.

Results and Discussion

Faller and co-workers have previously shown that η^3-cyclooctenyl-$Mo(CO)_2Cp$ complexes (**1**) can be prepared and that functionalization via ligand exchange (CO replaced by NO^+) and subsequent nucleophile additions can be accomplished, giving substituted cyclooctenes.[9b] In our laboratory[10] we have found that hydride abstraction to give the diene complex **2** does not proceed. Consequently, if extensive functionalization of the cyclooctene ring is required, an alternative approach must be sought.



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(1) (a) Case Western Reserve University. (b) University of Toledo.

(2) Pearson, A. J.; Kole, S. L.; Ray, T. *J. Am. Chem. Soc.* **1984**, *106*, 6060. Pearson, A. J.; Ong, C. W. *J. Org. Chem.* **1982**, *47*, 3780.

(3) Pearson, A. J.; Khan, M. N. I.; Clardy, J. C.; Cun-heng, H. *J. Am. Chem. Soc.* **1985**, *107*, 2748. Pearson, A. J.; Khan, M. N. I. *J. Org. Chem.* **1985**, *50*, 2587.

(4) Pearson, A. J.; Lai, Y. S.; Lu, W.; Pinkerton, A. A. *J. Org. Chem.* **1989**, *54*, 3882 and references cited therein. Pearson, A. J. *Synlett* **1990**, 10.

(5) Pearson, A. J.; Mallik, S.; Mortezaei, R.; Perry, M. W. D.; Shively, R. J., Jr.; Youngs, W. J. *J. Am. Chem. Soc.* **1990**, *112*, 8034. Pearson, A. J.; Chang, K. *J. Chem. Soc., Chem. Commun.* **1991**, 394.

(6) Pearson, A. J.; Srinivasan, K. *J. Chem. Soc., Chem. Commun.* **1991**, 392. See also: Rosenblum, M.; Watkins, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 6316. Franck-Neumann, M.; Martina, D. *Tetrahedron Lett.* **1975**, 1759. Rigby, J. H.; Ogbu, C. O. *Tetrahedron Lett.* **1990**, *31*, 3385.

(7) Exceptions of which we are aware are: (1) the addition of methoxide or methanol to cyclohexadienyl–$Os(CO)_3$, and (2) the borohydride reduction of cyclohexadienyl–$Mn(CO)_2NO$ cations, and certain sterically hindered cyclohexadienyl–$Fe(CO)_3$ complexes, all of which appear to involve prior attack on a CO ligand: (a) Bryan, E. G.; Burrows, A. L.; Johnson, B. F. G.; Lewis, J.; Schiavon, G. M. *J. Organomet. Chem.* **1977**, *129*, C19. Hine, K. E.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1975**, 81. Cowles, R. J. H.; Johnson, B. F. G.; Josty, P. L.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1969**, 392. (b) Ittel, S. D.; Whitney, J. F.; Chung, Y. K.; Williard, P. G.; Sweigart, D. A. *Organometallics* **1988**, 7, 1324, and references cited therein. Birch, A. J.; Chamberlain, K.; Haas, M. A.; Thompson, D. J.; *J. Chem. Soc., Perkin Trans. 1* **1973**, 1882. Birch, A. J.; Bandara, B. M. R.; Chamberlain, K.; Chauncy, B.; Dahler, P.; Day, A. I.; Jenkins, I. D.; Kelly, L. F.; Khor, T.-C.; Kretschmer, G.; Liepa, A. J.; Narula, A. S.; Raverty, W. D.; Rizzardo, E.; Sell, C.; Stephenson, G. R.; Thompson, D. J.; Williamson, D. H. *Tetrahedron, Supplement 1* **1981**, *37*, 289. Birch, A. J.; Stephenson, G. R. *J. Organomet. Chem.* **1981**, *218*, 91.

(8) Still, W. C.; Galynker, I. *Tetrahedron* **1981**, *37*, 3981. Still, W. C. *J. Am. Chem. Soc.* **1979**, *101*, 2493.

(9) (a) For previous work on cyclooctadieneiron complexes, see: Fleckner, H.; Grevels, F. W.; Hess, D. *J. Am. Chem.* **1984**, *106*, 2027. Ioset, J.; Helm, L.; Merbach, A.; Roulet, R.; Grepioni, F.; Braga, D. *Helv. Chim. Acta* **1988**, *71*, 1458. Koerner von Gustorf, E.; Hogan, J. C.; *Tetrahedron Lett.* **1968**, 3191. King, R. B.; Manuel, T. A.; Stone, F. G. A. *J. Inorg. Nucl. Chem.* **1961**, *16*, 233. Deeming, A. J.; Ullah, S. S.; Domingos, A. J. P.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1974**, 2093. Arnett, J. E.; Pettit, R. *J. Am. Chem. Soc.* **1968**, *83*, 2954. McFarlane, W.; Pratt, L. Wilkinson, G. *J. Chem. Soc.* **1963**, 2162. Cotton, F. A.; Deeming, A. J.; Josty, P. L.; Ullah, S. S.; Domingos, A. J. P.; Johnson, B. F. G.; Lewis, J. *J. Am. Chem. Soc.* **1971**, *93*, 4624. Edwards, R.; Howell, J. A. S.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1974**, 2105. Shiavon, G.; Paradisi, C.; Boanini, C. *Inorg. Chim. Acta* **1975**, *14*, L5. Shiavon, G.; Paradisi, C. *J. Organomet. Chem.* **1981**, *210*, 247. Hine, K. E.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1975**, 81. (b) For studies on cyclooctenyl–Mo(CO)(NO)Cp cation, see: Faller, J. W.; Chao, K. H.; Murray, H. H. *Organometallics* **1984**, *3*, 1231.

(10) Blystone, S. L. Ph.D. Dissertation, Case Western Reserve University, 1988. In a personal communication, Professor J. W. Faller reported the same difficulty.

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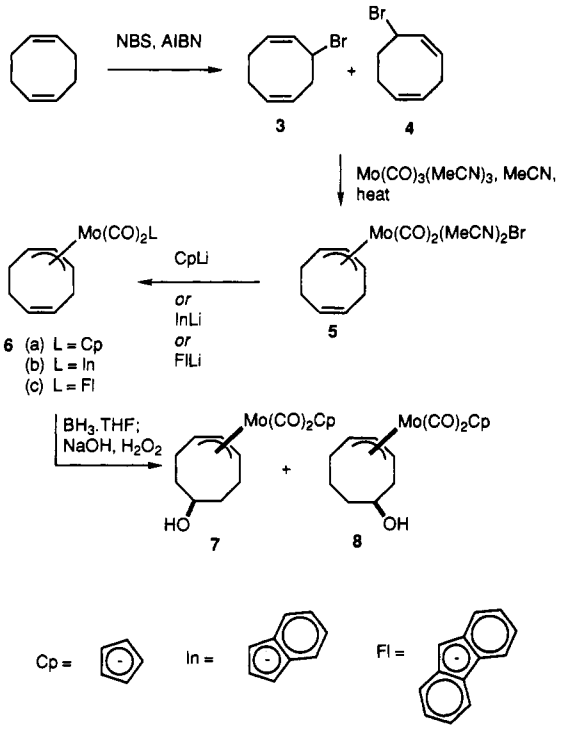
Scheme I



Allylic bromination of 1,5-cyclooctadiene, using the literature procedure,[11] gave a mixture of allylic bromides **3** and **4**, which was treated directly with $Mo(CO)_3(CH_3CN)_3$ to give a single π-complex **5**. Treatment of **5** with cyclopentadienyllithium afforded the complex **6a** in good overall yield (Scheme I). Reactions of **5** with indenyllithium and fluorenyllithium also proceeded in high yield to give complexes **6b** and **6c**, respectively, but, since these behaved almost identically to **6a** in subsequent reactions, they are not described in detail in this paper.

Hydroboration of **6a** gave a mixture of isomeric alcohols **7** and **8** in 95% yield which were readily separated chromatographically. Each regioisomer was stereochemically pure, and a reasonable degree of regioselectivity was observed (3.4:1) in favor of the symmetrical complex **7**. The use of more sterically demanding boranes did not improve the regioselectivity, and an equimolar mixture was produced using catecholborane in the presence of Wilkinson's catalyst.[12] The stereochemistry of **7** was confirmed by X-ray crystallography (Figure 1). Interestingly, three conformations were found in the unit cell, two of which have a boat–boat arrangement of the cyclooctenyl ligand, differing only in the rotational arrangement of cyclopentadienyl ring, while the remaining conformation is a boat chair. All conformations maintain an antiperiplanar arrangement of ring C–C bonds (C7–C8 and C3–C2 in Figure 1) and C–Mo bonds, as was observed for analogous cycloheptenyl–$Mo(CO)_2Cp$ complexes,[5] apparently minimizing nonbonded repulsions. This observation may be useful as a guiding principle in assigning conformations to organometallic complexes of medium ring olefinic ligands.

The cis relationship between hydroxyl and $Mo(CO)_2Cp$ groups in **7** was unexpected, based on our previous experience with analogous six- and seven-membered ring systems,[5,6] but is readily explained on the basis of the preferred conformation for the alkene **6**, which was determined by X-ray crystallography (Figure 2). It is seen that the cyclooctenyl ring again adopts a boat conformation. Reagent approach to the double bond is preferred at the

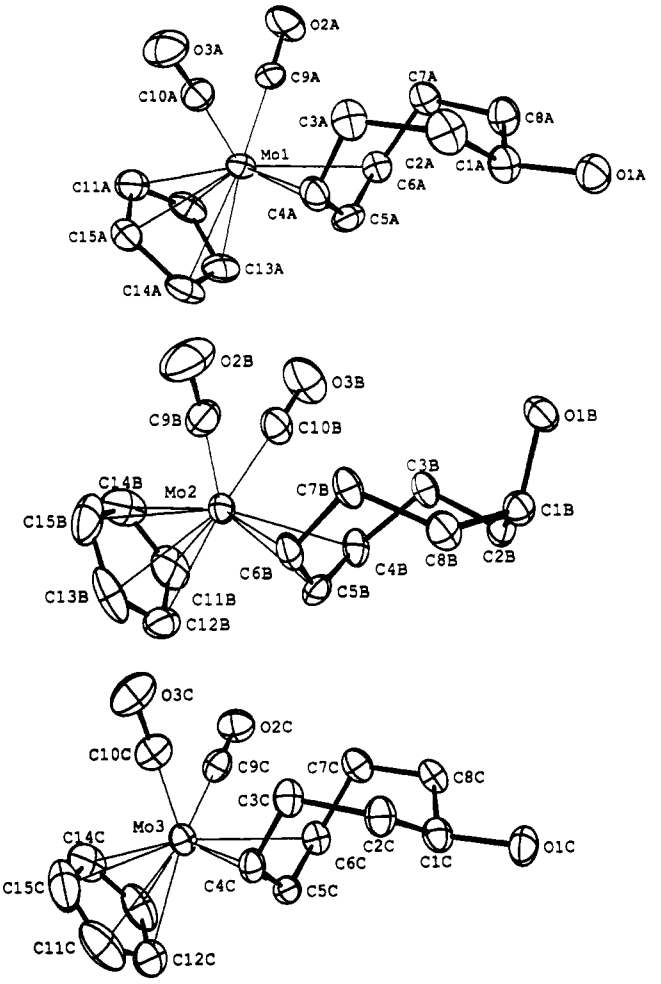


Figure 1. X-ray crystal structure of complex **7** showing three conformations (numbering is arbitrary). Selected bond lengths and bond angles with standard deviations for conformation A are as follows: Bond lengths (Å): Mo–C4A = 2.394 (7); C4A–C5A = 1.397 (9); C3A–C4A = 1.52 (1); C2A–C3A = 1.55 (1); C1A–C2A = 1.52 (1); C1A–O1A = 1.443 (8). Bond angles (deg): C4A–Mo–C5A = 35.1 (2); C4A–C5A–C6A = 123.7 (6); C3A–C4A–C5A = 123.1 (6); C1A–C2A–C3A = 117.8 (6); C2A–C1A–C8A = 117.2 (6); O1A–C1A–C2A = 107.7 (5). Complete details are given in the supplementary material.

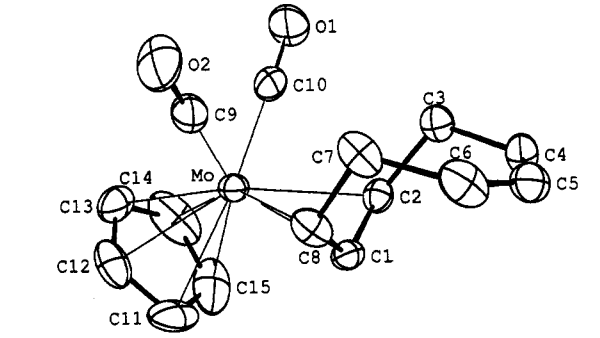
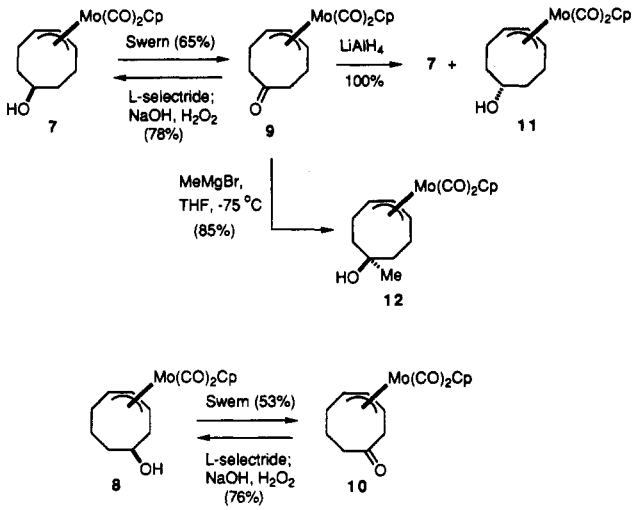


Figure 2. X-ray crystal structure of complex **6a** (numbering is arbitrary; C=C double is C5–C6). Selected bond lengths and bond angles with standard deviations are as follows: Bond lengths (Å): Mo–C1 = 2.207 (2); C1–C2 = 1.407 (3); C1–C8 = 1.430 (3); C2–C3 = 1.517 (3); C7–C8 = 1.509 (4); C6–C7 = 1.507 (4); C5–C6 = 1.371 (4); C4–C5 = 1.437 (5); C3–C4 = 1.521 (4). Bond angles (deg): C1–Mo–C2 = 35.75 (9); C2–C1–C8 = 121.2 (2); C1–C2–C3 = 123.7 (2); C2–C3–C4 = 111.2 (2); C3–C4–C5 = 120.7 (2); C4–C5–C6 = 131.9 (3); C5–C6–C7 = 124.7 (3).

(11) Moon, S.; Ganz, C. R. *J. Org. Chem.* **1970**, *35*, 1241. Presumably, the facilitation of this deprotonation is due to prior coordination of the carbony oxygen with silicon.

(12) Zhang, J.; Lou, B.; Guo, G.; Dai, L. *J. Org. Chem.* **1991**, *56*, 1670.

Scheme II

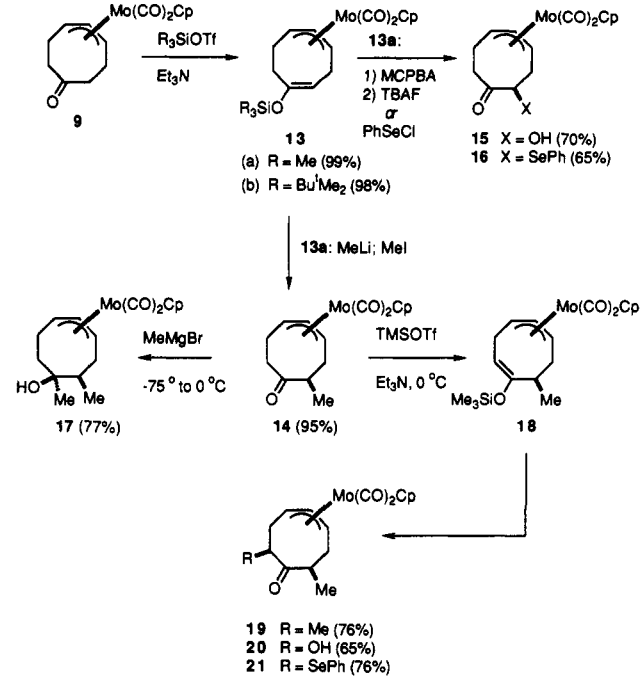


more open convex face of the molecule (syn to the metal). This is different from the six- and seven-membered rings because in these the exposed double bond is immediately adjacent to, and therefore co-planar with the π-allyl–Mo system, so that reagent approach is sterically controlled and therefore anti to the metal. Based on the stereochemistry observed for **7** and the conformation of **6**, we have assigned syn stereochemistry for the complex **8**. At this time we do not have a reasonable explanation for the regioselectivity observed during hydroboration. The conformation and associated stereodirecting effects for the alkene **6** also allow some predictive capability for the enolate chemistry to be described later.

Swern oxidation[13] of the alcohols **7** and **8** gave the ketones **9** and **10**, respectively. Reduction of **9** with $LiAlH_4$ in tetrahydrofuran at −75 °C gave a 5:1 mixture of stereoisomeric alcohols **7** and **11**. The use of a bulkier reducing agent, L-Selectride (Aldrich), gave exclusively **7**. This stereocontrol most likely results from conformational effects rather than the steric bulk of the metal (see later discussion). Reaction of **9** with MeMgBr at −25 °C also gave a single product **12**, the stereochemistry of which was assigned by analogy with the reduction. Treatment of ketone **10** with L-Selectride gave exclusively the alcohol **8** (Scheme II).

The ketone **9** was quite resistant to deprotonation. Treatment with LDA (up to 10 equiv) from −75 to 0 °C, followed by either MeI treatment or D_2O quench, gave no product of methylation or deuterium incorporation. Several other bases were tried but were also unsuccessful. This may be due to stereoelectronic effects, since there are no α-C–H bonds parallel to the carbonyl π-system in the preferred conformations which are presumed to resemble those for the alcohol **7** shown in Figure 1. This problem was readily overcome by converting **9** to the enol silanes **13** via treatment with a trialkylsilyl triflate in the presence of triethylamine (Scheme III).[14] The enol trimethylsilane could be functionalized either by conversion to the enolate, followed by alkylation with MeI, or by direct conversion to ketol following the Rubottom protocol,[15] or by direct treatment with phenylselenenyl chloride.[16] Thus were obtained good yields of complexes **14**, **15**, and **16** as single

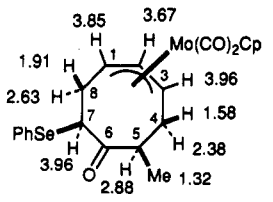
Scheme III



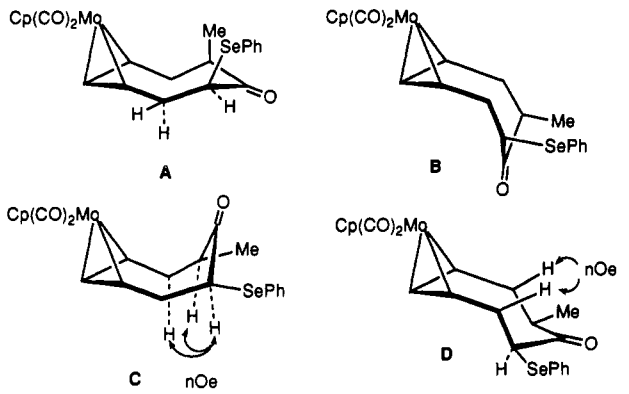
stereoisomers. By analogy with the hydroboration reaction discussed above, the stereochemistry was assigned as shown in the structures. Attempts to convert **16** to the α,β-unsaturated ketone via selenoxide syn elimination[16] failed.

Further reactions of the methylated compound **14** are also shown in Scheme III. Reaction with MeMgBr gave a single tertiary alcohol in 77% yield, which was assigned the structure **17** by analogy with the reactions of **9** (Scheme II). Treatment of **14** with Me_3SiOTf gave *exclusively* the enol silane **18**, which was converted to stereochemically homogeneous complexes **19**, **20**, and **21** in the manner described for complex **13a**. The symmetry observed in the ^1H NMR spectrum of **19** demonstrates that the methyl groups are cis to each other. The stereochemistry shown in the structures is supported by 2D NMR experiments on **21**. The connectivity and complete assignments for the ^1H NMR spectrum were made via a 300-MHz COSY experiment, and conformation/stereochemistry was assigned via a 300 MHz NOESY experiment. Inspection of ^1H NMR spectra for cyclohexenyl–[3,17] cycloheptenyl-[3] and cyclooctenyl– $Mo(CO)_2Cp$[9b] complexes reveals the following general trend. The hydrogens syn to the $Mo(CO)_2Cp$ moiety on the carbons adjacent to the π-allyl typically appear approximately 1 ppm upfield from the anti hydrogens. On the basis of this observation and the COSY spectrum, the assignments were made for **21** as shown in Figure 3, which also shows four possible conformations of **21**. Conformations A and B are unlikely because they involve severe nonbonded 1,3-interaction between CH_3 and SePh, and were ruled out by the observation of strong NOE between H(5) and H(7), which is more consistent with conformation C or D. The NOESY experiment was consistent with the presence of both conformations C and D at room temperature, since cross peaks were also observed between H(7) and anti- H(4) (conformational C) and between syn-H(4) and syn-H(8) (conformation D; anti

(13) Mancuso, A. J.; Huang, S. L.; Swern, D. *J. Org. Chem.* **1978**, *43*, 2480.
(14) Emde, H.; Domsch, D.; Feger, H.; Frick, U.; Gotz, A.; Hergot, H. H.; Hofmann, K.; Kober, W.; Krageloh, K.; Oesterle, T.; Steppan, W.; West, W.; Simchen, G. *Synthesis* **1982**, 1.
(15) Rubottom, G. M.; Gruber, J. M. *J. Org. Chem.* **1978**, *43*, 1599.
(16) Murai, S.; Kuroki, Y.; Hasegawa, K.; Tsutsumi, S. *J. Chem. Soc., Chem. Commun.* **1972**, 946. Sharpless, K. B.; Lauer, R. F.; Teranishi, A. Y. *J. Am. Chem. Soc.* **1973**, *95*, 6137.
(17) Faller, J. W.; Murray, H. H.; White, D. L.; Chao, K. H. *Organometallics* **1983**, *2*, 400.



^{1}H NMR Chemical Shift Assignments for **21** (δ ppm)



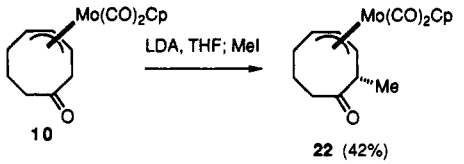
Possible Conformations for Complex **21**

Figure 3. ^{1}H NMR experimental assignments and conformational analysis of complex **21**.

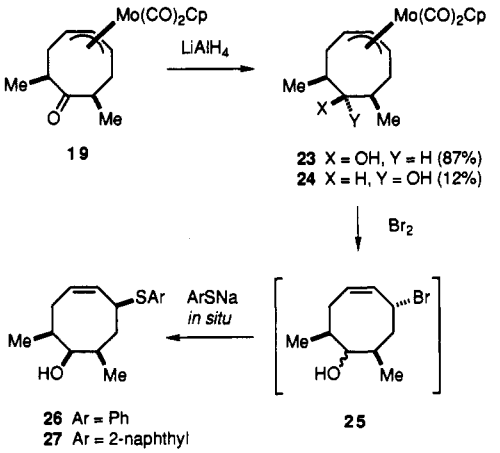
and syn refer to stereochemistry relative to the metal). The observation of a cross peak between H(7) and anti-H(4) also supports the stereochemical assignment, since these protons would be anti in a complex having Me and SePh anti to the metal. It may be noted that conformation D is essentially the same as one of the conformations observed crystallographically for the alcohol **7**, but the other conformation (B) which corresponds to **7** is not observed because of the 1,3-diaxial interactions present. It appears that conformations analogous to C and D are also major contributors for the unsubstituted ketone **9**, and addition of nucleophiles (hydride and RMgX) occurs with steric approach control along the equatorial vector.

The α-methylene groups in complex **10** are nonequivalent, so enolization may proceed in two different directions. We have previously demonstrated that deprotonation of a similar unsymmetrical ketone in the seven-membered ring complex occurs at the methylene α to the π-allyl moiety, due to partial stabilization of the developing negative charge by the neighboring organometallic group,[5,18] a phenomenon not uncommon in organometallic chemistry.[19] Treatment of **10** with LDA proceeded without problem, in contrast with complex **9**, to give a red solution of enolate, thereby attesting to the enhanced stabilization of charge. Subsequent treatment with methyl iodide afforded a single product, which was assigned the structure **22** by ^{1}H NMR spectroscopy. While the regiochemical assignment is unambiguous, the stereochemistry is unconfirmed and was assigned by analogy with the related cycloheptenyl–$Mo(CO)_2Cp$ systems.[5]

Decomplexation of π-allylmolybdenum systems is still a challenging problem,[20] since it must be accompanied by



the introduction of new functionality. For unsymmetrically substituted complexes, regiocontrol is difficult. For symmetrical compounds, decomplexation has fewer problems. Accordingly, the dimethyl-substituted compound **19** was treated with $LiAlH_4$ to give an epimeric 7:1 mixture of alcohols **23** and **24**, the major product being assigned as **23** by analogy with the unsubstituted derivatives. The



use of L-Selectride did not improve the ratio. Since the epimers could not be separated chromatographically, the mixture was treated with bromine, followed by in situ reaction of the so-produced allylic bromide **25** with NaSPh to give the sulfide **26**. This procedure has been shown to give overall retention of stereochemistry in the six-membered ring,[5] as depicted in the structures **23** through **26**, and the stereochemistry of the products is assigned by analogy. The phenyl thioether **26** was unstable on silica gel and could not be fully purified. Using 2-naphthalenethiolate in the decomplexation afforded **27** which was stable to chromatographic purification.

Conclusions

Stereo- and regiocontrolled functionalization of the eight-membered ring proceeds extremely well using the π-allylmolybdenum system as a functional conformational anchor that may be removed selectively. The formation of ketone enolates and their reactions with electrophiles are well-behaved and does not lead to decomposition of the organometallic moiety. This methodology allows the preparation of stereochemically defined tetrasubstituted cyclooctenes, although improved procedures for demetalation are still desirable.

Experimental Section

General procedures and analyses were carried out as described previously.[5] The stereochemical outcome of each reaction was determined by NMR spectroscopy on crude reaction products; unless otherwise stated, each compound was stereochemically homogeneous.

Bis(acetonitrile)dicarbonyl(1-3-η-cycloocta-1,5-dienyl)-molybdenum Bromide (5). Freshly distilled acetonitrile (80 mL, 1.5 mol) and $Mo(CO)_6$ (21.8 g, 82.8 mmol) were refluxed for 4 h to give a clear deep yellow solution. To this solution was added 15.5 g of the bromide mixture (82.8 mmol) in 10 mL of THF. The reaction mixture was cooled to room temperature when an orange solid separated slowly. The reaction was cooled at −10 °C for 1 h, and the solid was filtered, washed with cold acetonitrile, and

(18) Pearson, A. J.; Khetani, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6778.
(19) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books; Mill Valley, CA, 1987; p 931.
(20) Hansson, S.; Miller, J. F.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1990**, *112*, 9660.

kept under vacuo. The orange solid thus obtained (22.7 g, 65%) was taken directly to the next step without purification (the complex **5** is unstable in $CDCl_3$ solution, and NMR spectroscopic characterization was not possible).

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-cycloocta-1,5-dienyl)molybdenum (6). Freshly cracked cyclopentadiene (1.1 mL, 13.2 mmol) was taken up in 50 mL of THF, and the solution was cooled to −15 °C. To this was added 8.0 mL of BuLi (1.6 M in hexanes, 12.8 mmol), and the reaction mixture was stirred at room temperature for 45 min. To this clear solution was added 5.0 g of the complex **5** (11.9 mmol), stirring was continued for 5 h, and the solvent was removed under vacuum. The brown oil was taken up in CH_2Cl_2, filtered through a plug of alumina (Neutral, Fisher Adsorption Grade), and evaporated to give the pure product **6** (3.6 g, 95%) as a yellow solid: mp 129–130 °C; IR ($CDCl_3$) 1973, 1852 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.82–5.73 (dddt, 1 H, H-5, J = 11.3, 8.0, 7.4, 2.2 Hz), 5.40–5.35 (m, 1 H, H-6), 5.21 (s, 5 H, Cp), 4.24–4.17 (qd, 1 H, H-3, J = 8.0, 2.0 Hz), 4.00–3.93 (qd, 1 H, H-3, J = 8.0, 2.0 Hz), 3.81 (t, 1 H, H-2, J = 8.0 Hz), 2.47–2.40 (dt, 1 H, H-4 anti, J = 15.2, 8.0 Hz), 2.37–2.29 (ddt, 1 H, H-8 anti, J = 15.0, 8.0, 3.9 Hz), 2.28–2.19 (m, 2 H, H-7), 2.07–1.99 (dt, br, 1 H, H-4 syn, J = 15.2, 7.4 Hz), 1.70–1.60 (m, 1 H, H-8 syn); HRMS calcd for $C_{15}H_{16}MoO_2$ 326.0210, found 326.0209. Anal. Calcd: C, 55.57; H, 4.97. Found: C, 55.62; H, 4.97.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-6-*endo*-hydroxycyclooctenyl)molybdenum (7). To a stirred solution of the complex **6** (1.5 g, 4.6 mmol) in 30 mL of THF at 0 °C was added 10 mL of BH_3–THF (1.0 M in THF, 10.0 mmol). The cooling bath was removed, the reaction mixture was stirred at room temperature for 40 min, and excess borane was *carefully* destroyed by dropwise addition of water while cooling in an ice bath. Aqueous NaOH (12.0 mL, 15% solution) and aqueous H_2O_2 (30%, 12.0 mL) were added in succession, and the mixture was stirred at room temperature for 1 h. Ether was added, the layers were separated, and the organic phase was washed with water and brine and was dried ($MgSO_4$). Evaporation followed by purification by flash chromatography (10% hexane in ether) gave the title compound (1.17 g, 73%) as a yellow solid along with **8** (351 mg, 22%): R_f 0.2 (ether); mp 84–86 °C; IR ($CDCl_3$) 3608, 1939, 1854 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.20 (s, 5 H, Cp), 4.57–4.48 (m, 1 H, H-6), 3.93–3.79 (m, 3 H, H-1, H-2 and H-3), 2.29–2.15 (m, 2 H, anti H-8 and anti H-4), 1.98–1.81 (m, 2 H, anti H-7 and anti H-5), 1.58–1.35 (m, 4 H, syn H-4, H-5, H-7, H-8); HRMS [M − CO]$^+$ calcd for $C_{15}H_{18}MoO_3$ 316.0366, found 316.0366. Anal. Calcd: C, 52.64; H, 5.30. Found: C, 52.25; H, 5.42.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-5-*endo*-hydroxycycloocteny)molybdenum (8) gave the following analytical data: R_f 0.4 (ether); mp 160–161 °C; IR ($CDCl_3$) 3610, 1941, 1856 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.21 (s, 5 H, Cp), 4.06 (t, 1 H, H-2, J = 8.0 Hz), 4.00–3.91 (m, 1 H, H-5), 3.88–3.65 (2 dq, partially superposed, 2 H, H-1 and H-3, J = 8.0, 2.0 Hz), 2.57–2.25 (m, 3 H), 1.78–1.41 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 238.3, 237.7, 91.5, 72.2, 67.6, 58.1, 52.6, 40.9, 31.7, 31.4, 23.4; HRMS calcd for $C_{15}H_{18}MoO_3$ 316.0366, found 316.0353.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-6-oxocyclooctenyl)molybdenum (9). To a stirred solution of oxalyl chloride (0.6 mL, 6.9 mmol) in 10 mL of CH_2Cl_2 at −100 °C was added dropwise a solution of 980 μL of DMSO (13.8 mmol) in 8 mL of CH_2Cl_2. The resulting solution was stirred for 2 min, and a solution of the alcohol **7** (1.18 g, 3.45 mmol) in 20 mL of CH_2Cl_2 was added dropwise over 5 min. The reaction mixture was stirred for 5 min, and 5 mL of Et_3N (excess) was added. It was allowed to warm to −20 °C over 2.5 h, and then the cooling bath was removed. At room temperature, the reaction mixture was filtered through a plug of silica gel, the solvent was evaporated in vacuo, and the product was purified by flash chromatography (30% AcOEt in hexane) to give **9** as a yellow solid (761 mg, 61%): R_f 0.3 (40% AcOEt in hexane); mp 188–189 °C; IR ($CDCl_3$) 1944, 1860, 1686 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.21 (s, 5 H, Cp), 3.97 (q with fine splitting, 2 H, H-1 and H-3, J = 8.2 Hz). 3.67 (t, 1 H, H-2, J = 8.2 Hz), 2.60–2.49 (m, 4 H), 2.40–2.30 (m, 2 H), 1.90–1.79 (m, 2 H); HRMS calcd for $C_{15}H_{16}MoO_2$ 342.0159, found 342.0160. Anal. Calcd: C, 52.95; H, 4.74. Found: C, 52.86; H, 4.77.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-5-oxocyclooctenyl)molybdenum (10). This compound was prepared via the same procedure as **9** but starting from the alcohol **8**. The quantities of reagents employed were: oxalyl chloride, 230 μL (2.6 mmol); DMSO, 370 μL (5.2 mmol); alcohol **8**, 300 mg (0.88 mmol); Et_3N, 1.2 mL (8.6 mmol). The crude product was purified by flash chromatography (40% AcOEt in hexane) to give the ketone **10** as a yellow solid (155 mg, 53%): R_f 0.4 (40% AcOEt in hexane); mp 143–145 °C dec; IR (CH_2Cl_2) 1939, 1856, 1682 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.25 (s, 5 H, Cp), 4.12 (t, 1 H, H-2, J = 8.4 Hz), 4.04–3.91 (qd, 1 H, J = 8.4, 2.0 Hz), 3.89–3.75 (qd, 1 H, J = 8.4, 2.0 Hz), 3.23–2.97 (dt and dd, partially superimposed, 2 H, J = 12.7, 8.0 Hz for dt, J = 17.1, 8.9 Hz for dd), 2.57–2.41 (m, 1 H), 2.21–2.08 (m, 2 H), 1.80–1.60 (m, 2 H), 1.23–0.99 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 237.7, 237.6, 213.2, 92.2, 66.7, 59.7, 51.1, 47.5, 40.4, 31.6, 27.6; HRMS [M − 2CO] calcd for $C_{15}H_{16}MoO_3$ 286.0256, found 286.0240.

Reduction of 9 with L-Selectride. A solution of 40 mg of the ketone **9** (0.12 mmol) in 2 mL of THF was stirred at −75 °C while 0.5 mL of L-Selectride (1.0 M in THF, 0.5 mmol) was added. After 1 h, the reaction was quenched with water and the cooling bath was removed. NaOH (1 mL, 15% aqueous) and H_2O_2 (1 mL, 30% aqueous) were added, and the mixture was stirred at room temperature for 1 h. Ether was added, and the product was isolated in the usual way. ^1H NMR indicated exclusive formation of the alcohol **7**. This was further purified by preparative TLC (40% AcOEt in hexane) to give 32 mg (78%) of pure **7**.

Reduction of the Ketone 10 with L-Selectride. Following the same procedure and using the same quantities of reagents afforded 32 mg of a solid. ^1H NMR indicated this to be a mixture (6:1) of the alcohol **8** and starting ketone **10**. For the alcohol **8** only one epimer was detected.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-6-*endo*-hydroxy-6-*exo*-methylcycloocteny)molybdenum (12). To a stirred solution of the ketone **9** (50 mg, 0.15 mmol) in 5 mL of THF at −75 °C was added MeMgBr (0.5 mL of a 3.0 M solution in ether, 1.5 mmol). After 5 h, TLC (ether) indicated complete consumption of the starting ketone. The reaction was brought to room temperature and quenched with saturated NH_4Cl solution. Ether was added, and the product was extracted into ether in the usual way. The crude product was purified by preparative TLC (10% hexane in ether) to give the pure tertiary alcohol as a yellow solid (44 mg, 85%): R_f 0.6 (10% hexane in ether); mp 136–138 °C; IR ($CDCl_3$) 3603, 1938, 1854 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.18 (s, 5 H, Cp), 4.13 (q with fine splitting, 2 H, H-1 and H-3, J = 8.5 Hz), 3.71 (t, 1 H, H-2, J = 8.5 Hz), 2.24–2.07 (dt, 2 H, H-8 anti and H-4 anti, J = 16.0, 8.5 Hz), 1.88–1.76 (dd, 2 H, one of H-7 and one of H-5, J = 14.5, 9.5 Hz), 1.65–1.53 (dd, 2 H, one of H-7 and one of H-5, J = 14.5, 9.5 Hz), 1.41–1.24 (dt, 2 H, H-4 syn and H-8 syn, J = 16.0, 9.2 Hz), 1.13 (s, 3 H, CH_3), 0.88 (s, br, 1 H, O*H*); ^{13}C NMR ($CDCl_3$) δ 238.0, 91.9, 69.8, 64.1, 62.9, 45.2, 33.3, 25.9; HRMS calcd for $C_{16}H_{20}MoO_3$ 358.0472, found 358.0470.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-6-((*tert*-butyldimethylsilyl)oxy)cycloocta-1,5-dienyl)molybdenum (13b). To a suspension of the ketone **9** (40 mg, 0.12 mmol) in 3 mL of ether at room temperature was added 80 μL of TBS–OTf (0.35 mmol) followed by 70 μL of Et_3N (0.50 mmol). The reaction mixture was stirred for 1 h and then filtered through a plus of silica gel (pretreated with Et_3N) with 50% Et_3N in ether as the eluant, and solvent was removed under vacuum to give the silyl enol ether **13b** as a yellow solid (53 mg, 98%): R_f 0.4 (10% AcOEt in hexane); mp 143–145 °C; IR ($CDCl_3$) 1938, 1853 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.20 (s, 5 H, Cp), 5.14 (t, br, 1 H, J = 6.6 Hz), 4.34–4.20 (qd with fine splitting, 1 H, H-3, J = 8.0, 2.0 Hz), 4.02–3.89 (qd with fine splitting, 1 H, H-1, J = 8.0, 2.0 Hz), 3.73 (t, 1 H, H-2, J = 8.0 Hz), 2.38–2.14 (m, 4 H, H-4 anti, H-8 anti, H-7), 2.11–1.88 (m, 1 H, H-4 syn), 1.75–1.55 (m, 1 H, H-8 syn), 0.89 (s, 9 H, C_4H_9), 0.12 (s, 3 H, $SiCH_3$), 0.08 (s, 3 H, $SiCH_3$); ^{13}C NMR ($CDCl_3$) δ 238.4, 238.0, 153.2, 111.5, 91.9, 63.9, 63.1, 60.9, 37.9, 29.2, 27.8, 25.7, 18.0, −4.3, −4.4; HRMS [M − CO]$^+$ calcd for $C_{21}H_{30}MoO_3Si$ 428.1070, found 428.1079.

Dicarbonyl(η^5-cyclopentadienyl)(1-3-η-6-((trimethylsilyl)oxy)cycloocta-1,5-dienyl)molybdenum (13a). To a stirred suspension of the ketone **9** (830 mg, 2.44 mmol) in 25 mL of ether at room temperature was added dropwise 1.1 mL of Et_3N (7.9 mmol) and 1.2 mL of TMS–OTf (6.2 mmol). After stirring for 1.5 h the clear yellow solution was filtered through a plug of silica gel (pretreated with Et_3N) with 1:1 Et_3N in ether as the eluant.

Evaporation of the solvent afforded 980 mg (98%) of the silyl enol ether **13a** as yellow solid: R_f 0.7 (ether); mp 143–144 °C; IR ($CDCl_3$) 1938, 1853 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.20 (s, 5 H, Cp), 5.15 (t, 1 H, H-5, J = 8.0 Hz), 4.32–4.20 (qd with fine splitting, 1 H, H-3, J = 8.0, 2.0 Hz), 3.99–3.89 (qd with fine splitting, 1 H, H-3, J = 8.0, 2.0 Hz), 3.72 (t, 1 H, H-2, J = 8.0 Hz), 2.39–2.13 (m, 4 H, H-4 anti, H-8 anti, H-7), 1.75–1.57 (m, 1 H, H-8 syn), 2.04–1.88 (m, 1 H, H-4 syn), 0.15 (s, 9 H, $Si(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 238.4, 237.9, 152.9, 111.8, 91.9, 63.9, 62.9, 61.0, 37.9, 29.3, 27.8, −0.4; HRMS calcd for $C_{18}H_{24}MoO_3Si$ 386.0601, found 386.0592.

Dicarbonyl(η^5-cyclopentadienyl)(1–3-η-5-*endo*-methyl-6-oxocyclooctenyl)molybdenum (14). To a stirred solution of the silyl enol ether **13a** (380 mg, 0.92 mmol) in 10 mL of ether in a Schlenk flask at room temperature was added 920 μL of MeLi (1.2 M in ether, 1.1 mmol). Slowly a yellow precipitate appeared, and after 2 h TLC (40% AcOEt in hexane) indicated complete consumption of the starting material. Ether was removed in a vacuum pump, the solid was dissolved in 20 mL of THF and cooled to −80 °C, and 0.5 mL of MeI (8.0 mmol) was added. The reaction mixture was allowed to warm to −15 °C over 4 h, quenched with water, and brought to room temperature. Ether was added, and the product was isolated in the usual way as a yellow solid (310 mg, 95%) which was pure by ^1H NMR. This was recrystallized from CH_2Cl_2/pentane to give an analytically pure sample of **14**: R_f 0.4 (40% AcOEt in hexane); mp 139–141 °C; IR ($CDCl_3$) 1943, 1859, 1684 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.20 (s, 5 H, Cp), 3.95 (q with fine splitting, 2 H, H-1 and H-3, J = 8.0 Hz), 3.69 (t, 1 H, H-2, J = 8.0 Hz), 2.75–2.63 (m, 2 H, H-5 and one of H-7), 2.49–2.25 (m, 3 H, H-4 anti, H-8 anti, one of H-7), 1.85–1.62 (m, 1 H, H-8 syn), 1.60–1.39 (ddd, 1 H, H-4 syn, J = 15.3, 13.1, 10.1 Hz); HRMS [M − 2CO] calcd for $C_{16}H_{18}MoO_3$ 300.0417, found 300.0421. Anal. Calcd: C, 54.24; H, 5.12. Found: C, 54.20; H, 5.05.

Dicarbonyl(η^5-cyclopentadienyl)(1–3-η-5-*endo*-hydroxy-6-oxocyclooctenyl)molybdenum (15). To a stirred solution of the silyl enol ether **13a** (160 mg, 0.4 mmol) in 5 mL of CH_2Cl_2 at 0 °C was added 120 mg of mCPBA (0.7 mmol) dissolved in 5 mL of CH_2Cl_2. After stirring for 1.5 h at 0 °C the cooling bath was removed and 0.8 mL of TBAF solution (1.0 M in THF, 0.8 mmol) was added. The mixture was stirred for 30 min, ether was added, and the organic solution was washed with dilute aqueous $NaHCO_3$ solution and brine, dried ($MgSO_4$), and concentrated. The crude product was purified by column chromatography (ether) to give **15** (97 mg, 70%) as a yellow solid: R_f 0.4 (40% AcOEt in hexane); mp 141–143 °C; IR ($CDCl_3$) 3607, 1948, 1865, 1695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.23 (s, 5 H, Cp), 4.26–3.91 (m, 3 H, H-1, H-3, H-5), 3.05 (d, 1 H, O*H*, J = 4.5 Hz), 2.92–2.80 (ddd, 1 H, one of H-7, J = 14.2, 6.8, 3.5 Hz), 2.69–2.37 (m, 3 H, H-4 anti, H-8 anti, and one of H-7), 1.63–1.45 (m, 2 H, H-4 syn and H-8 syn); ^{13}C NMR ($CDCl_3$) δ 237.1, 212.6, 92.3, 80.0, 63.4, 59.9, 54.9, 43.7, 39.3, 28.8; HRMS [M − 2CO] calcd for $C_{15}H_{16}MoO_4$ 302.0210, found 302.0211.

Dicarbonyl(η^5-cyclopentadienyl)(1–3-η-5-*endo*-(phenylselenyl)-6-oxocyclooctenyl)molybdenum (16). To a stirred solution of the silyl enol ether **13a** (50 mg, 0.12 mmol) in 3 mL of THF at −75 °C was added dropwise a solution of 30 mg of PhSeCl (0.16 mmol) in 3 mL of THF. After 30 min of stirring, the cooling bath was removed and the reaction mixture was warmed to room temperature. Solvent was removed under vacuum, and the crude product was directly purified by flash chromatography (20% AcOEt in hexane) to give **16** (39 mg, 65%) as a yellow solid: R_f 0.4 (20% AcOEt in hexane); mp 158–160 °C; IR ($CDCl_3$) 1947, 1864, 1678 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.49–7.22 (m, 5 H, Ph), 5.23 (s, 5 H, Cp), 4.01–3.86 (m, 3 H, H-1, H-3 and H-5), 3.70 (t, 1 H, H-2, J = 8.0 Hz), 3.33–3.20 (m, 1 H, one of H-7), 2.78–2.64 (dt, 1 H, H-4 anti, J = 14.5, 6.8 Hz), 2.53–2.04 (m, 2 H, H-8 anti and one of H-7), 1.89–1.69 (dt, 1 H, H-4 syn, J = 14.5, 10.2 Hz), 1.73–1.60 (m, 1 H, H-8 syn); HRMS calcd for $C_{21}H_{20}MoO_3Se$ 497.9637, found 497.9619. Anal. Calcd: C, 50.93; H, 4.07. Found: C, 50.62; H, 4.06.

Dicarbonyl(η^5-cyclopentadienyl)(1–3-η-5-*endo*,6-*exo*-dimethyl-6-*endo*-hydroxycyclooctenyl)molybdenum (17). A solution of the ketone **14** (50 mg, 0.14 mmol) in 4 mL THF was added dropwise to a cooled (−75 °C) solution of MeMgBr (250 μL, 3.0 M in ether, 0.75 mmol) in 1 mL of THF. The reaction was allowed to warm to 10 °C over a 2-h period and quenched with saturated aqueous NH_4Cl solution. Ether was added, and a standard extractive workup afforded the crude product as an yellow oil. This was purified by preparative TLC (15% AcOEt in hexane) to give the tertiary alcohol **17** as a foamy solid (34 mg, 65%) along with 8 mg of the starting ketone **14**: R_f 0.6 (20% hexane in ether); IR ($CDCl_3$) 3610, 1938, 1853 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.18 (s, 5 H, Cp), 4.21–4.04 (m, 2 H, H-1 and H-3), 3.74 (t, 1 H, H-2, J = 8.2 Hz), 2.23–2.11 (dt, 1 H, J = 16.0, 8.3 Hz), 1.90–1.42 (m, 6 H), 1.10 (s, 3 H, CH_3), 0.99 (d, 3 H, CH_3, J = 7.2 Hz), 0.90 (s, br, 1 H, O*H*); ^{13}C NMR ($CDCl_3$) δ 238.6, 238.3, 92.3, 71.8, 64.7, 63.0, 62.5, 47.9, 47.7, 35.9, 30.9, 26.4, 19.5. HRMS [M − CO]$^+$ calcd for $C_{17}H_{22}MoO_3$ 316.0730, found 316.0731.

Dicarbonyl(η^5-cyclopentadienyl)(1–3-η-7-*endo*-methyl-6-((trimethylsilyl)oxy)cycloocta-1,5-dienyl)molybdenum (18). To a stirred suspension of the ketone **14** (323 mg 0.91 mmol) in 15 mL of ether at 0 °C was added successively 0.9 mL of Et_3N (6.4 mmol) and 0.9 mL of TMS–OTf (4.6 mmol). After stirring for 3 h at room temperature the reaction mixture was filtered through a plug of silica gel (pretreated with Et_3N) with 1:1 ether in Et_3N as the eluant. Solvent was removed under vacuum to give the silyl enol ether **18** as a yellow oil which slowly solidified (383 mg, 99%): ^1H NMR ($CDCl_3$) δ 5.20 (s, 5 H, Cp), 5.13 (t, 1 H, J = 9.0 Hz), 4.24–4.19 (qd, 1 H, J = 8.0, 2.0 Hz), 3.97–3.89 (qd with fine splitting, 1 H, J = 8.0, 2.0 Hz), 3.76 (t, 1 H, H-2, J = 8.0 Hz), 2.27–2.14 (m, 3 H), 2.12–1.92 (m, 1 H), 1.60–1.40 (m, 1 H), 0.99 (d, 3 H, CH_3, J = 6.8 Hz). This was taken to the next stages without further characterization.

Dicarbonyl(η^5-cyclopentadienyl)(1–3-η-7-*endo*-hydroxy-5-*endo*-methyl-6-oxocyclooctenyl)molybdenum (20). To a stirred solution of the silyl enol ether **18** (144 mg, 0.34 mmol) in 5 mL of CH_2Cl_2 at −15 °C was added a solution of 100 mg of mCPBA (0.58 mmol) in 5 mL of CH_2Cl_2. The mixture was stirred for 1.5 h, the cooling bath was removed, and 1 mL of TBAF solution (1.0 M in THF, 1.0 mmol) was added. Stirring was continued at room temperature for 30 min, ether was added, and the organic phase was washed with dilute aqueous $NaHCO_3$ solution and brine and was dried ($MgSO_4$). After evaporation of the solvent, the crude product was purified by flash chromatography (35% AcOEt in hexane) followed by recrystallization from CH_2Cl_2/pentane to give **20** product as yellow crystals (82 mg, 65%): R_f 0.2 (40% AcOEt in hexane); mp 143–145 °C; IR ($CDCl_3$) 3597, 1948, 1865, 1696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.24 (s, 5 H, Cp), 4.35–4.07 (m, 3 H, H-1, H-3 and H-7), 3.81 (t, 1 H, H-2, J = 8.2 Hz), 3.68 (d, 1 H, O*H*, J = 5.0 Hz), 2.86 (q, with fine splitting, 1 H, H-5, J = 7.5 Hz), 2.62–2.49 (ddd, 1 H, H-8 anti, J = 15.6, 8.7, 1.4 Hz), 2.19–2.07 (dd, 1 H, H-4 anti, J = 16.0, 8.3 Hz), 1.62–1.26 (m, 2 H, H-8 syn and H-4 syn), 1.10 (d, 3 H, CH_3, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 237.0, 213.8, 92.2, 79.8, 62.9, 60.2, 56.4, 49.8, 40.1, 37.9, 17.8; HRMS [M − 2CO] calcd for $C_{16}H_{18}MoO_4$ 316.0366, found 316.0356.

Dicarbonyl(η^5-cyclopentadienyl)(1–3-η-5-*endo*-methyl-7-*endo*-(phenylselenyl)-6-oxocyclooctenyl)molybdenum (21). To a solution of the silyl enol ether **18** (154 mg, 0.36 mmol) in 4 mL of THF at −75 °C was added dropwise a solution of PhSeCl (88 mg, 0.46 mmol) in 4 mL of THF. The reaction was allowed to warm up to room temperature over 2 h, the solvent was removed under vacuum, and the crude product was directly purified by flash chromatography (25% AcOEt in hexane) to give **21** as yellow foamy solid (140 mg, 76%): R_f 0.4 (25% AcOEt in hexane); mp 62–64 °C; IR ($CDCl_3$) 1942, 1861, 1669 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.54–7.46 and 7.30–7.20 (m, 5 H, Ph), 5.21 (s, 5 H, Cp), 4.00–3.94 (m, 2 H, H-3 and H-7), 3.88–3.82 (qd, 1 H, H-1, J = 8.0, 1.8 Hz), 3.67 (t, 1 H, H-2, J = 8.0 Hz), 2.86–2.80 (m, 1 H, H-5), 2.67–2.60 (ddd, 1 H, H-8 anti, J = 15.1, 7.0, 5.4 Hz), 2.31–2.25 (ddd, 1 H, H-4 anti, J = 15.4, 7.4, 5.0 Hz), 1.96–1.87 (dt, 1 H, H-8 syn, J = 14.8, 10.0 Hz), 1.62–1.53 (ddd, 1 H, H-4 syn, J = 15.3, 13.6, 10.7 Hz), 1.32 (d, 3 H, CH_3, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 236.7, 136.5, 211.8, 129.2, 133.7, 128.7, 127.6, 91.8, 61.9, 59.2, 56.8, 54.5, 54.3, 38.1, 36.5, 21.2; HRMS calcd for $C_{22}H_{22}MoO_3Se$ 511.9788, found 511.9789.

Dicarbonyl(η^5-cyclopentadienyl)(1–3-η-5,7-*endo*-dimethyl-6-oxocyclooctenyl)molybdenum (19). To a solution of the silyl enol ether **18** (100 mg, 0.23 mmol) in 5 mL of ether was added 380 μL of MeLi (1.2 M in ether, 0.48 mmol). After 4 h, the resulting precipitate was dissolved by the addition of 5

mL of THF, the reaction mixture was cooled to −75 °C, and 200 μL of MeI (3.2 mmol) was added. The reaction was allowed to warm to room temperature over 3 h and was quenched with water. Standard extractive workup with ether afforded the crude product as a yellow solid which was purified by recrystallization from CH_2Cl_2/pentane to give **19** (65 mg, 76%): R_f 0.7 (40% AcOEt in hexane); mp 186–187 °C; IR ($CDCl_3$) 1943, 1859, 1678 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.21 (s, 5 H, Cp), 4.03–3.89 (m, 2 H, H-1 and H-3), 3.66 (t, 1 H, H-2, J = 8.0 Hz), 2.86–2.39 (m, 2 H, H-5 and H-7), 2.31–2.15 (ddd, 1 H, H-4 anti and H-8 anti, J = 15.3, 7.1, 4.7 Hz), 1.69–1.49 (ddd, 2 H, H-4 syn and H-8 syn, J = 15.3, 13.3, 10.2 Hz), 1.08 (d, 6 H, CH_3, J = 7.5 Hz); HRMS [M − 2CO] calcd for $C_{17}H_{20}MoO_3$ 314.0574, found, 314.0565. Anal. Calcd: C, 55.44, H, 5.47. Found: C, 55.01; H, 5.44.

Reduction of the Ketone 19. To a stirred suspension of $LiAlH_4$ (50 mg, 1.3 mmol) in 10 mL of THF at −75 °C was added dropwise a solution of the ketone **19** (94 mg, 0.25 mmol) in 5 mL of THF. After stirring for 1 h, TLC (40% AcOEt in hexane) indicated complete consumption of the starting ketone. The reaction was brought to room temperature and quenched with saturated aqueous NH_4Cl solution and ether was added. The standard workup afforded the two epimeric alcohols **23** and **24** in the ratio 7:1 as a yellow oil (93 mg, 99%) which was taken to the next step without purification: R_f 0.6 (CH_2Cl_2); IR ($CDCl_3$) 3615, 1936, 1849 cm^{-1}; ^1H NMR ($CDCl_3$, for the major isomer) δ 5.17 (s, 5 H, Cp), 4.22–4.08 (2 quartets, partially overlapping, 2 H, H-1 and H-2, J = 8.3 Hz), 3.77–3.69 (triplet superposed on multiplet, 2 H, H-2 and H-6, J = 8.3 Hz), 3.35 (s, 1 H, OH), 1.82–1.62 (m, 3 H), 1.48–1.32 (m, 2 H), 1.08–1.02 (m, 1 H), 0.99 (d, 6 H, CH_3, J = 7.3 Hz); HRMS [M − 2CO] calcd for $C_{17}H_{22}MoO_3$ 316.0726, found 316.0732.

Dicarbonyl(η⁵-cyclopentadienyl)(1-3-η-4-*exo*-methyl-5-oxocyclooctenyl)molybdenum (22). Diisopropylamine (35 μL, 0.25 mmol) was taken up in 5 mL of THF and was cooled to −75 °C. To this cooled, stirred solution was added 130 μL of BuLi (1.6 M in hexanes, 0.21 mmol), the mixture was stirred for 5 min, and the cooling bath was removed. After the reaction reached room temperature, it was again cooled to −90 °C and a solution of 55 mg of the ketone **10** (0.16 mmol) in 3 mL of THF was added. The reaction mixture was allowed to warm slowly. A red color was noticed from −10 °C; it was stirred for 15 min at room temperature and recooled to −70 °C, and 200 μL of MeI (1.5 mmol) was added. After warming up to room temperature over 2 h, water and ether were added and the standard extractive workup procedure was followed. The crude product was purified by column chromatography (30% AcOEt in hexane) to give **22** as yellow solid (24 mg, 42%): R_f 0.4 (30% AcOEt in hexane); mp 166–167 °C; IR ($CDCl_3$) 1944, 1860, 1696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.23 (s, 5 H, Cp), 4.21–4.08 (qd with fine splitting, 1 H, H-1, J = 8.0, 2.0 Hz), 3.90 (t, 1 H, H-2, J = 8.0 Hz), 3.41–3.32 (td, 1 H, H-3, J = 8.0, 2.0 Hz), 2.79–2.66 (ddd, 1 H, one of H-6, J = 12.5, 7.3, 5.2 Hz), 2.64–2.47 (dddd, 1 H, H-8 anti, J = 15.6, 7.4, 6.2, 3.0 Hz), 2.32 (q, 1 H, H-4, J = 7.5 Hz), 2.20–2.07 (ddd, 1 H, one of H-6, J = 12.5, 8.6, 5.5 Hz), 2.02–1.63 (m, 2 H, H-7), 1.25 (d, 3 H, CH_3, J = 7.5 Hz), 1.27–1.11 (m, 1 H, H-8 syn); ^{13}C NMR ($CDCl_3$) δ 238.1, 236.7, 215.9, 91.8, 65.3, 63.7, 58.6, 48.0, 41.9, 31.8, 27.6, 16.7; HRMS [M − 2CO] calcd for $C_{16}H_{18}MoO_3$ 300.0413, found 300.0414.

3-(2′-Naphthylthio)-5,7-dimethyl-6-hydroxycyclooct-1-ene (27). The mixture of the alcohols **23** and **24** (46 mg, 0.12 mmol) was dissolved in 3 mL of THF and was cooled to −75 °C. To this cooled solution was added 105 μL of a solution of bromine (1.3 M in CH_2Cl_2, 0.14 mmol), and the reaction mixture was stirred for 5 h. In a separate flask, 2-naphthalenethiol (60 mg, 0.37 mmol) was dissolved in 3 mL of THF and cooled to −50 °C, 220 μL of BuLi (1.6 M in hexanes, 0.35 mmol) was added, and the mixture was stirred at room temperature for 5 min. This solution was transferred via cannula to the reaction mixture at −75 °C. The cooling bath was removed, the reaction mixture was stirred under oxygen atmosphere for 14 h, water and ether were added, and the standard extractive workup procedure was followed. The crude product was purified by flash chromatography (20% AcOEt in hexane) to give the major product **27** as pale brown oil (17 mg, 45%): R_f 0.4 (20% AcOEt in hexane); IR ($CDCl_3$) 3559, 3051–2865 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.80–7.67 and 7.52–7.36 (m, 7 H, Naph), 6.06–5.92 (m, 1 H, H-1), 5.74–5.65 (dd, 1 H, H-2, J = 10.9, 7.0 Hz), 4.28–4.17 (m, 1 H, H-6), 3.48 (s, br, 1 H, H-3), 2.49–2.35 (m, 1 H), 2.27–1.85 (m, 4 H), 1.82–1.72 (dt, 1 H, J = 13.8, 2.5 Hz), 1.56 (s, br, 1 H, OH), 1.08 (d, 3 H, CH_3, J = 7.0 Hz), 1.06 (d, 3 H, CH_3, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 135.4, 134.0, 133.0, 132.7, 130.1, 129.3, 128.7, 128.1, 127.7, 126.9, 126.3, 80.5, 46.3, 41.2, 39.1, 38.8, 29.5, 24.9, 19.1; HRMS calcd for $C_{20}H_{24}OS$ 312.1548, found 312.1546.

X-ray Structure Determination for Complex 7. Unit cell parameters: $C_{15}H_{18}MoO_3$: M_r = 342.25; monoclinic, $P2_1/c$; a = 27.0.14 (2) Å, b = 12.653 (2) Å, c = 12.740 (4) Å, β = 93.03 (1)°; V = 4349 (2) Å^3; Z = 12; D_x = 1.57 g cm^{-3}; λ(Mo Kα) 0.710 73 Å; μ = 8.8 cm^{-1}; $F(000)$ = 2088; T = 294 ± 1 K; R = 0.048 for 6099 unique observed reflections of 9337 total data.

Light yellow, elongated plate, 0.21 × 0.23 × 0.18 mm, mounted on a glass fiber, Enraf-Nonius CAD4 diffractometer, graphite monochromator, ω–2θ scan technique, backgrounds obtained from analysis of the scan profile,[21] unit cell constants from the setting angles of 24 reflections in the range 12 < θ < 14°, empirical absorption correction (from 0.957 to 0.998 on I), maximum 2θ = 52.0°, 0 < h, < 15; 0 < k < 15; −33 < l < 33; anisotropic decay (from 0.968 to 1.057 on I), reflection averaging R(int) = 1.7%, 9337 total reflections measured, 8922 unique, 6099 reflections with $F_o^2 > 3.0\sigma(F_o^2)$, solution by direct methods (MULTAN),[22] refinement by full-matrix least-squares, function minimized was $\Sigma w(|F_o| - |F_c|)^2$, weight w is defined as $4F_o^2/\sigma^2(F_o^2)$, hydrogen atoms riding in ideal positions, 514 refined parameters, R = 0.048, R_w = 0.067, S = 2.55, largest shift = 0.99σ, high peak in final difference map 0.86 (12) e/Å^3, low peak −0.25 (12) e/Å^3. Scattering factors for neutral atoms and the values for Δf and $\Delta f''$ were taken from ref 23; computer programs MolEN (Fair, 1990).[24] Final atomic coordinates are reported in Table 1 and bond lengths and angles in Table 2 of the supplementary material. Figures were prepared by ORTEP.[25]

X-ray Structure Determination for Complex 6a. Unit cell parameters: $C_{15}H_{17}MoO_2$; M_r = 325.24; monoclinic; $P2_1/c$; a = 10.941 (1) Å, b = 10.260 (3) Å, c = 12.432 (2) Å, β = 108.21 (1)°; V = 1326 (1) Å^3; Z = 4; D_c = 1.63 g cm^{-3}; λ(Mo Kα) 0.710 73 Å; μ = 9.6 cm^{-1}; $F(000)$ = 660; T = 294 ± 1 K; R = 0.027 for 2323 unique observed reflections of 2912 total data.

Yellow, rectangular block, 0.50 × 0.43 × 0.38 mm, mounted on a glass fiber, Enraf-Nonius CAD4 diffractometer, graphite monochromator, ω–2θ scan technique, backgrounds obtained from analysis of the scan profile,[21] unit cell constants from the setting angles of 25 reflections in the range 12 < θ < 14°, empirical absorption correction (from 0.929 to 0.999 on I), maximum 2θ = 52.0°, 0 < h < 13; 0 < k < 12; −15 < l < 14; anisotropic decay (from 0.987 to 1.042 on I), reflection averaging R(int) = 1.8%, 2912 total reflections measured, 2765 unique, 2323 reflections with $F_o^2 > 3.0\sigma(F_o^2)$, solution by Patterson and Fourier methods, refinement by full-matrix least-squares, function minimized was $\Sigma w(|F_o| - |F_c|)^2$, weight w is defined as $4F_o^2/\sigma^2(F_o^2)$, hydrogen atoms refined with U_{iso} = 1.3U bonding atom, 217 refined parameters, R = 0.027, R_w = 0.042, S = 1.61, largest shift = 0.02σ, high peak in final difference map 0.34 (7) e/Å^3, low peak −0.57 (7) e/Å^3. Scattering factors for neutral atoms and the values for Δf and $\Delta f''$ were taken from ref 23; computer programs MolEN (Fair, 1990).[24] Final atomic coordinates are reported in Table 1 and bond lengths and angles in Table 2 of the supplementary material. Figures were prepared by ORTEP.[25]

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(21) Blessing, R. H.; Coppens, P.; Becker, P. *J. Appl. Crystallogr.* **1974**, *7*, 488–492.

(22) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; DeClerq, J. P.; Woolfson, M. M. *MULTAN80*; University of York: England, 1980.

(23) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham (Present distributor Klewer Academic Publishers, Dordrecht), 1974; Vol. IV.

(24) Fair, C. K. *MolEN, An Interactive Intelligent System for Crystal Structure Analysis, User Manual*; Enraf-Nonius: Delft, The Netherlands, 1990.

(25) Johnson, C. K. *ORTEP, Report ORNL -5138*; Oak Ridge National Laboratory: Oak Ridge: TN, 1976.

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Supplementary Material Available: Tables of crystal data, data collection, data reduction, refinement details, positional and thermal parameters, bond distances and angles, and thermal ellipsoid plots for the crystal structures of $C_{15}H_{17}MoO_2$ (**6a**) and $C_{15}H_{18}MoO_3$ (**7**), ^1H NMR spectra for compounds **10**, **12**, **13a**, **13b**, **15**, **17**, **20**, **21**, **22**, and **27**, and a NOESY spectrum for complex **21** (36 pages). Ordering information is given on any current masthead page.

A Convenient Synthesis of 9,9-Dialkyl-9,10-dihydroanthracenes and 10,10-Dialkylanthrones: Silicon-Mediated Regioselective Dialkylation of 9,10-Dihydroanthracene

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Described is a short and convenient approach to the synthesis of 9,9-dialkyl-9,10-dihydroanthracenes, 9,9,10-trialkyl-9,10-dihydroanthracenes, and 10,10-dialkylanthrones, some of which are otherwise unknown or inaccessible by conventional methods. Deprotonation of 9-(trimethylsilyl)-9,10-dihydroanthracene (**2**; 9-(trimethylsilyl)-9,10-DHA) followed by reaction with alkyl halides (RX) produces 9-alkyl-9-(trimethylsilyl)-9,10-DHAs **3-7** in 80-90% yields. Treatment of **3-7** with *n*-BuLi produces the 10-lithio derivatives that rearrange to 9-alkyl-9-lithio-10-(trimethylsilyl) intermediates; subsequent alkylation with RX generates 9,9-dialkyl-10-(trimethylsilyl)-9,10-DHAs **8-19**. Formation of single stereoisomers **13-19** was suggested by NMR and confirmed in two cases, **15** and **16**, by X-ray structure determination. The trimethylsilyl group is removed by tetrabutylammonium fluoride (TBAF) to provide 9,9-dialkyl-9,10-DHAs **20-29** with impressive yields. Oxidation of either the 9,9-dialkyl-9,10-DHAs or 9,9-dialkyl-10-(trimethylsilyl)-9,10-DHAs with Cr(VI) oxidant furnished 10,10-dialkylanthrones **36-41** in 80-90% yields.

Introduction

9,10-Dihydroanthracenes (9,10-DHAs) substituted in the central ring have received considerable attention due to questions about the possible stereochemical consequences.[1] These compounds have been studied experimentally by X-ray crystallography[2] and dynamic NMR spectroscopy,[3] as well as by theoretical methods[4] in an attempt to understand their structure and dynamic processes such as ring inversion. Our own investigations required several 9,9-dialkyl-9,10-DHAs that are either only available in low yields by long routes[5] or are unknown and inaccessible by conventional methods. Several applications of silicon-modified, regioselective reduction and reductive alkylation have been recently demonstrated for polynuclear aromatics,[6] and, having reported a preliminary account,[7] we now describe in detail the synthesis, scope, and mechanism of silicon-mediated, dialkylation of 9,10-dihydroanthracene.

Results and Discussion

Preparation of 9-(Trimethylsilyl)-9,10-DHA. 9-(Trimethylsilyl)-9,10-DHA (**2**) was prepared in >95% yield by deprotonation and silylation[8] of 9,10-dihydroanthracene (**1**). An alternative route, metal-ammonia reduction[9] of 9-(trimethylsilyl)anthracene, produced lower yields (70%), and so the former method is recommended.

Preparation of 9-Alkyl-9-(trimethylsilyl)-9,10-DHAs. A variety of 9-(trimethylsilyl)-9-alkyl-9,10-DHAs, **3-7**, have been prepared by some modification of the method of Daney and co-workers.[10] Although deprotonation of **2** by *n*-BuLi in THF at -78 or at -35 °C was not successful (Table I), the reaction did proceed at 0 °C and alkylation with 1.5-2.0 equiv of alkyl halide produced

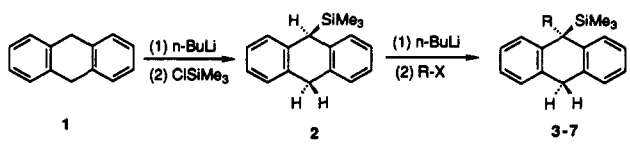

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Table I. Alkylation of 9-TMS-9,10-DHA with Various Alkyl Halides

entry	*n*-BuLi (equiv)	deprotntn (°C)	time[a] (h)	alkyl iodide (equiv)	product	yield[b] (%)
1	1.0	-78[c]	3.0	MeI (1.1)	**3**	traces
2	1.0	-35[c]	3.0	MeI (1.1)	**3**	traces
3	1.0	0	1.0	MeI (1.1)	**3**	>55
4	1.25	0	1.0	MeI (1.1)	**3**	70
5	1.25	0	1.3	MeI (1.1)	**3**	82
6	1.25	0	1.3	MeI (2.0)	**3**	96
7	1.25	0	1.3	MeI (1.5)	**3**	90
8	1.25	0	1.3	EtI (2.0)	**4**	84
9	1.25	0	2.0	*i*-PrI (2.0)	**5**	70-80
10	1.25	0	1.3	allylI (1.5)	**6**	82
11	1.10	0	1.3	BnI (2.0)	**7**	75

[a] Deprotonation time. [b] Based on GC analysis for runs 1-6, isolated yield for runs 7-11. [c] Warmed to 0 °C after addition of MeI.

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(1) (a) Rabideau, P. W. In *The Conformational Analysis of Cyclohexenes, Cyclohexadienes and Related Hydroaromatic Compounds*; Rabideau, P. W., Ed.; VCH: New York, 1989; Chapter 4. (b) Rabideau, P. W. *Acc. Chem. Res.* **1978**, *11*, 141.

(2) (a) Ahmad, N.; Goddard, R. J.; Hatton, I. K.; Lewis, H. N. J.; MacMillan, J. *J. Chem. Soc., Perkin Trans. 1* **1985**, 1859. (b) Toda, F.; Tanaka, K.; Mak, T. C. W. *Tetrahedron Lett.* **1984**, *13*, 1359. (c) Bartoli, G.; Bosco, M.; Pozzo, R. D.; Sgarabotto, P. *J. Chem. Soc., Perkin Trans. 2* **1982**, 929.

(3) (a) Rabideau, P. W.; Smith, W. K. *Magn. Reson. Chem.* **1989**, 191. (b) Cho, H.; Harvey, R. G.; Rabideau, P. W. *J. Am. Chem. Soc.* **1975**, *97*, 1140. (c) Leung, P. T.; Curtin, D. Y. *J. Am. Chem. Soc.* **1975**, *97*, 6790.

(4) (a) Rabideau, P. W.; Govindarajan, U. *J. Org. Chem.* **1989**, *54*, 988. (b) Sygula, A.; Rabideau, P. W. *J. Org. Chem.* **1987**, *52*, 3521. (c) Rabideau, P. W.; Mooney, J. L.; Lipkowitz, K. B. *J. Am. Chem. Soc.* **1986**, *108*, 8130. (d) Rabideau, P. W.; Maxwell, A. J.; Sygula, A. *J. Org. Chem.* **1986**, *51*, 3181.

(5) Leung, P. T.; Curtin, D. Y. *J. Am. Chem. Soc.* **1975**, *97*, 6790.

(6) (a) Rabideau, P. W. *Tetrahedron* **1989**, *45*, 1579. (b) Marcinow, Z.; Clawson, D. K.; Rabideau, P. W. *Tetrahedron* **1989**, 5441.

(7) Rabideau, P. W.; Dhar, R. K.; Clawson, D. K.; Zhan, Z. *Tetrahedron Lett.* **1991**, *32*, 3969.

(8) Cho, H.; Harvey, R. G. *J. Org. Chem.* **1975**, *40*, 3097.

0022-3263/92/1957-2917$03.00/0