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Nucleophilic Attack on Neutral Tricarbonyl(η^5-cyclohexadienyl)manganese Complexes: Preparation of Substituted 1,3-Cyclohexadienes

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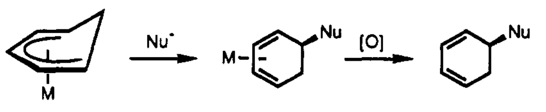
Received August 4, 1992

The reaction of nucleophiles with tricarbonyl(η^5-cyclohexadienyl)manganese (**13**) takes place at the terminus of the π-system, generating tricarbonyl(5-substituted-η^4-cyclohexadiene)-manganese anions **14**. Oxidation of these anions produces 5-substituted-1,3-cyclohexadienes (**15**) in 65–91% yields. No products resulting from attack at the C2/C4 position of the π-system or at the carbonyl ligands were produced. Reaction of nucleophiles with tricarbonyl(6-methyl-η^5-cyclohexadienyl)manganese (**18**) followed by oxidation provides *cis*-5-substituted-6-methyl-1,3-cyclohexadienes (**20**) in 43–73% yields, confirming that nucleophilic attack takes place on the exo face of the (η^5-cyclohexadienyl)manganese complex.

Introduction

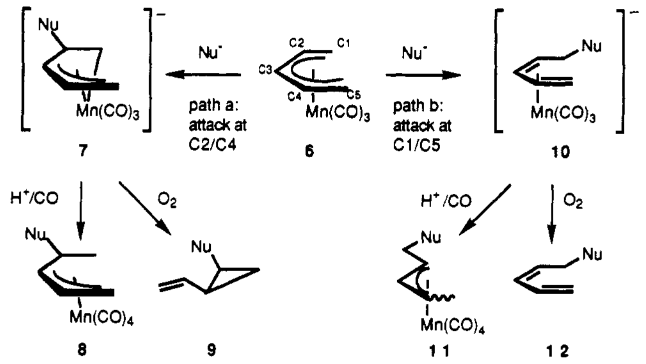
The reaction of nucleophiles with transition metal π-complexes is a valuable tool in organic synthesis.[1] One area of intense investigation for the past twenty years has been the reaction of cationic η^5-dienyl transition metal complexes with nucleophiles. It has been demonstrated, for example, that the reaction of a variety of nucleophiles with cationic tricarbonyl(η^5-cyclohexadienyl)iron (**1**) produces (η^4-diene)iron complexes (**2**), which can be oxidized readily to provide the substituted cyclohexadienes **3** (eq 1).[2] The reaction of cationic dicarbonylnitroso(η^5-cyclohexadienyl)manganese (**4**) with nucleophiles has also been demonstrated, generating (η^4-diene)manganese complexes **5** by attack at the terminus of the π-system (eq 1).[3] Investigation of the reactivity of related cationic (η^5-pentadienyl)iron complexes has demonstrated that reaction at either the C1/C5 position or the C2/C4 position of the π-system is possible, leading to η^4-diene complexes[4] or σ,η^3-enediyl complexes,[5] respectively. In addition, nucleophilic attack on neutral (η^5-pentadienyl)manganese complexes has been examined. In these laboratories it has been demonstrated that tricarbonyl(η^5-pentadienyl)-manganese (**6**) reacts with certain nucleophiles specifically at the C2/C4 position of the π-system to produce (σ,η^3-enediyl)manganese complex **7** (Scheme I, path a). Reaction of complex **7** with acid under 1 atm of carbon monoxide generates (π-allyl)manganese complex **8**.[6] Oxidation of σ,η^3-enediyl complex **7** provides vinylcyclopropane **9**, most likely via an oxidatively-induced reductive coupling.[7,8] Recent studies indicate, however, that other nucleophiles attack at the C1/C5 position of the η^5-pentadienyl π-system of complex **6** to generate η^4-diene complex **10**. Reaction of **10** under acidic conditions provides π-allyl complex **11**, whereas oxidation of **10** generates diene **12**.[7] Sheridan and co-workers recently have reported that neutral tricarbonyl(η^5-cyclohexadien-



(1)

1 M = $^+$Fe(CO)$_3$
4 M = $^+$Mn(CO)$_2$NO
2 M = Fe(CO)$_3$
5 M = Mn(CO)$_2$NO
3

Scheme I



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[1] See for example: (a) 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. (b) Harrington, P. J. *Transition Metals in Total Synthesis*; John Wiley & Sons: New York, 1990.

[2] (a) Birch, A. J.; Kelly, L. F. *J. Organomet. Chem.* **1985**, *285*, 267. (b) Pearson, A. J.; Kole, S. J.; Yoon, J. *Organometallics* **1985**, *5*, 2075. (c) Pearson, A. J.; Ray, T. *Tetrahedron* **1985**, *41*, 5765. (d) Ghazy, T.; Kane-Maguire, L. A. P. *J. Organomet. Chem.* **1988**, *338*, 47. (e) Howard, P. W.; Stephenson, G. R.; Taylor, S. C. *J. Organomet. Chem.* **1988**, *339*, C5. (f) Howell, J. A. S.; Tirvengadum, M.-C.; Walton, G. *J. Organomet. Chem.* **1988**, *338*, 217.

[3] (a) Chung, Y. K.; Choi, H. S.; Sweigart, D. A.; Connelly, N. G. *J. Am. Chem. Soc.* **1982**, *104*, 4245. (b) Chung, Y. K.; Ephralm, D. H.; Robinson, W. T.; Sweigart, D. A.; Connelly, N. G.; Ittel, S. D. *Organometallics* **1983**, *2*, 1479. (c) Chung, Y. K.; Sweigart, D. A.; Connelly, N. G.; Sheridan, J. B. *J. Am. Chem. Soc.* **1985**, *107*, 2388. (d) Chung, Y. K.; Sweigart, D. A. *J. Organomet. Chem.* **1986**, *308*, 223. (e) Ittel, S. D.; Whiney, J. F.; Chung, Y. K.; Williard, P. G.; Sweigart, D. A. *Organometallics* **1988**, *7*, 1323.

[4] (a) Mahler, J. E.; Gibson, D. H.; Pettit, R. *J. Am. Chem. Soc.* **1963**, *85*, 3959. (b) Mahler, J. E.; Pettit, R. *J. Am. Chem. Soc.* **1963**, *85*, 3955. (c) Whitesides, T. H.; Neilan, J. P. *J. Am. Chem. Soc.* **1975**, *97*, 907. (d) Birch, A. J.; Pearson, A. J. *J. Chem. Soc., Perkin Trans. 1* **1976**, 954. (e) Bayoud, R. S.; Biehl, E. R.; Reeves, P. C. *J. Organomet. Chem.* **1978**, *150*, 75. (f) Bayoud, R. S.; Biehl, E. R.; Reeves, P. C. *J. Organomet. Chem.* **1979**, *174*, 297. (g) Donaldson, W. A.; Ramaswamy, M. *Tetrahedron Lett.* **1988**, *29*, 1343. (h) Donaldson, W. A.; Ramaswamy, M. *Tetrahedron Lett.* **1989**, *30*, 1339.

[5] (a) McDaniel, K. F.; Kracker, L. R.; Thamburaj, P. K. *Tetrahedron Lett.* **1990**, *31*, 2373. (b) Bleeke, J. R.; Hays, M. K. *Organometallics* **1987**, *6*, 1367. (c) Bleeke, J. R.; Rauscher, J. J. *J. Am. Chem. Soc.* **1989**, *111*, 8972. (d) Donaldson, W. A.; Ramaswamy, M. *Tetrahedron Lett.* **1989**, *30*, 1343. (e) Bleeke, J. R.; Wittenbrink, R. J.; Clayton, T. W.; Chiang, M. Y. *J. Am. Chem. Soc.* **1990**, *112*, 6539.

[6] Roell, B. C.; McDaniel, K. F. *J. Am. Chem. Soc.* **1990**, *112*, 9004.

[7] McDaniel, K. F.; Roell, B. C. Manuscript in preparation.

[8] Oxidation of a (σ,η^3-pentenediyl)iron complex to generate a vinylcyclopropane has been reported. See ref 5d.

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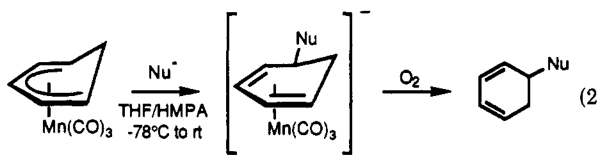
yl)manganese[9] and tricarbonyl(η^5-cycloheptadienyl)manganese[10] complexes react with phenyllithium or methyllithium at 25 °C in diethyl ether to generate acylmetalates by reaction of the carbanions at a carbonyl ligand rather than at the carbon π-system. In light of these results, an investigation of the reactivity of tricarbonyl(η^5-cyclohexadienyl)manganese (**13**) under the conditions utilized for the reaction of tricarbonyl(η^5-pentadienyl)manganese (**6**) with nucleophiles was undertaken. The results of this investigation are presented below.

Results and Discussion

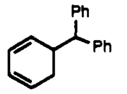
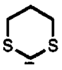
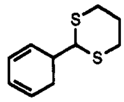
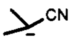
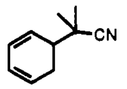
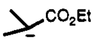
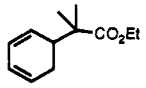
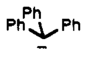
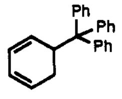
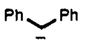
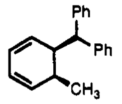
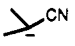
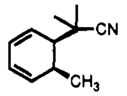
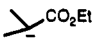
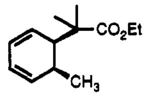
The reaction of (η^5-cyclohexadienyl)manganese complex **13**[11] with (diphenylmethyl)lithium, 2-lithio-1,3-dithiane, α-lithioisobutyronitrile, α-lithiopropionitrile, (triphenylmethyl)lithium, and ethyl α-lithioisobutyrate in tetrahydrofuran was examined. Complex **13** was added to a solution of the nucleophile in tetrahydrofuran and HMPA at −78 °C, and the reaction mixture was stirred at −78 °C for 20 min followed by stirring at room temperature for 1.5 h. During the course of the reaction the mixture remained light yellow. At this point oxygen was bubbled through the solution for 15 min at 0 °C followed by stirring in air overnight at room temperature. After purification by silica gel chromatography, cyclohexadienes **15** were isolated in 65–91% yield (eq 2; Table I). Reactions run under the same conditions using diethyl ether instead of tetrahydrofuran gave cyclohexadienes **15** in comparable yields. These products apparently arise by the reaction of the nucleophiles at the terminus of the π-system, followed by decomplexation of the manganese from intermediate η^4-cyclohexadiene manganese complex **14**. This decomplexation is extremely rapid, with immediate deposition of an oxidized manganese species evident upon contact with oxygen.[12] Under acidic workup conditions, yields of the cyclohexadiene **15** were poor and significant amounts of unreacted starting material often were isolated.[13] Attempts to carry out this reaction with less powerful nucleophiles, such as diethyl lithiomalonate or ketone enolates, failed to provide cyclohexadiene **15**, instead returning only starting η^5-cyclohexadienyl complex **13**. This limitation parallels the reactivity of tricarbonyl(arene)chromium[14] and tricarbonyl(η^4-diene)iron[15] complexes, which also require the use of powerful nucleophiles.



(2)

13 **14** **15**

Table I. Synthesis of 1,3-Cyclohexadienes According to Eqs 2 and 3

η^5-complex	nucleophile	product	yield	compd no.
13			77%	15a
13			65%	15b
13			88%	15c
13			91%	15d
13			90%	15e
18			73%	20a
18			58%	20b
18			43%	20c

Although the extremely oxygen sensitive anionic η^4-diene complex **14** was not isolated, spectroscopic examination of the reaction mixture confirmed its presence. Infrared spectra of the reaction mixture formed by the reaction of (diphenylmethyl)lithium with (η^5-cyclohexadienyl)manganese complex **13** in tetrahydrofuran, for example, contained carbonyl stretching vibrations at 1929, 1853, 1834, 1813, and 1762 cm^{-1}.[16] No acyl stretching vibrations were observed, indicating that nucleophilic attack occurs at the η^5-cyclohexadienyl π-system and not the carbonyl ligand.[17] An NMR spectrum of the reaction of (diphenylmethyl)lithium with complex **13** in d_8-tetrahydrofuran contained a multiplet at δ 4.4–4.7, characteristic of the internal protons on anionic tricarbonyl(η^4-cyclohexadiene)-

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[9] (a) Sheridan, J. B.; Padda, R. S.; Chaffee, K.; Wang, C.; Huang, Y.; Lalancette, R. *J. Chem. Soc., Dalton Trans.* **1992**, 1539. (b) Padda, R. S.; Sheridan, J. B.; Chaffee, K. *J. Chem. Soc., Chem. Commun.* **1990**, 1226.

[10] Wang, C.; Lang, M. G.; Sheridan, J. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 3236.

[11] Brookhart, M.; Lamanna, W.; Pinhas, A. R. *Organometallics* **1983**, *2*, 638.

[12] Formation of free 1,3-cyclohexadienes by oxidative decomplexation of the tricarbonyl(η^4-1,3-cyclohexadiene)manganese anions has been reported. See: Brookhart, M.; Lukacs, A. *J. Am. Chem. Soc.* **1984**, *106*, 4161.

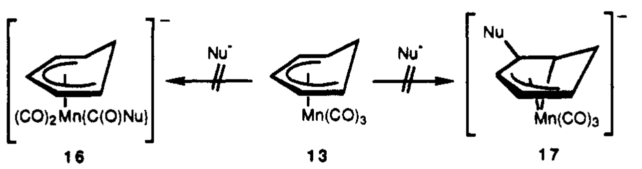
[13] When an acid workup was involved, trace amounts (<5%) of what appeared to be 3-substituted-cyclohexenes were also produced in some cases.

[14] (a) Semmelhack, M. F.; Hall, H. T. *J. Am. Chem. Soc.* **1974**, *96*, 7091, 7092. (b) Semmelhack, M. F.; Hall, H. T.; Farina, R.; Yoshifuji, M.; Clark, G.; Bargar, T.; Hirotsu, K.; Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 3535. (c) Semmelhack, M. F.; Hall, H. T.; Yoshifuji, M.; Clark, G. *J. Am. Chem. Soc.* **1975**, *97*, 1247.

[15] (a) Semmelhack, M. F.; Herndon, J. W.; Springer, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 2497. (b) Semmelhack, M. F.; Herndon, J. W. *Organometallics* **1983**, *2*, 363. (c) Semmelhack, M. F.; Le, H. T. M. *J. Am. Chem. Soc.* **1984**, *106*, 2715.

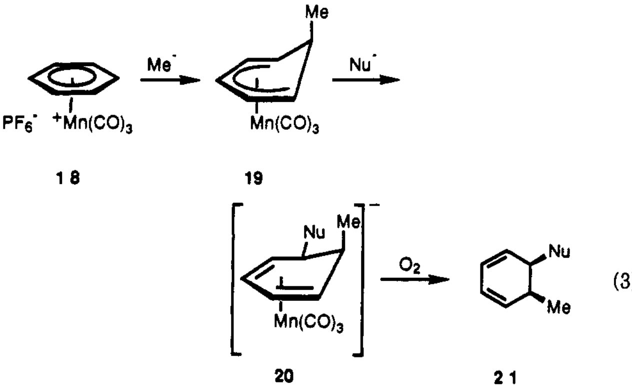
[16] The infrared spectrum of the unsubstituted tricarbonyl(η^4-1,3-cyclohexadiene)manganese anion in tetrahydrofuran reported by Brookhart and co-workers contained carbonyl stretching vibrations at 1929, 1853, 1831, 1811, and 1758 cm^{-1}. See ref 11.

[17] Sheridan et al. observed acyl stretching vibrations at approximately 1400 cm^{-1} upon attack of methyl- or phenyllithium on a carbonyl ligand of tricarbonyl(η^5-cyclohexadienyl)manganese (**13**). See ref 9.



manganese complexes.[18] No signals corresponding to H_3 of the acylmetalate complex **16**,[9] typically found in the region δ 5.0–5.5, were observed. In addition, no peaks corresponding to the σ,η^3-cyclohexendiyl intermediate **17**,[19] which would be produced by nucleophilic attack at the C2/C4 position of the π-system, were observed.

In order to confirm that nucleophilic attack had taken place on the exo face of the η^5-cyclohexadienyl π-system, as opposed to at a carbonyl ligand, reaction of the methyl-substituted complex **19** with nucleophiles was examined. It has been demonstrated that reaction of methyllithium or methylmagnesium chloride with (arene)manganese complex **18** generates complex **19**, with the methyl group added exo to the manganese.[20] Reaction of complex **18** with (diphenylmethyl)lithium, lithioisobutyronitrile, or ethyl lithioisobutyrate followed by oxidation generated only the *cis*-cyclohexadienes **21** (eq 3; Table I). The cis relationship between the nucleophile and the methyl group was confirmed by NOE studies.[21] Since both substituents are added stereoselectively exo to the metal, this procedure offers a straightforward approach to *cis*-5,6-disubstituted-1,3-cyclohexadienes.[22] Although sequential cis addition of two carbon nucleophiles to manganese-complexed arenes has been demonstrated, activation of the (η^5-cyclohexadienyl)manganese complex **19**, by substitution of a carbon monoxide ligand by a nitrosyl ligand to generate a cationic η^5-cyclohexadienyl complex, was required prior to addition of the second nucleophile.[3c] Experiments currently are underway to determine if trapping of anionic complex **20** with electrophiles[23] will allow for the formation of three contiguous stereocenters with relative stereocontrol.



(3)

Conclusions

The regiochemistry of the nucleophilic attack on neutral (η^5-cyclohexadienyl)manganese complexes stands in marked contrast to the reactions of the analogous neutral (η^5-pentadienyl)manganese complex but does follow the selectivity found for nucleophilic attack on cationic (η^5-cyclohexadienyl)manganese complexes. In no case was there any evidence of attack at the internal C2/C4 position of the π-system, as has been demonstrated with η^5-pentadienyl complex **6**. This pattern mimics the trend followed in the isoelectronic cationic iron series, where nucleophilic attack on cationic (η^5-cyclohexadienyl)iron complexes has been demonstrated only at the terminus of the π-system,[2] whereas reaction at both the pentadienyl terminus and the internal C2/C4 positions of cationic (η^5-pentadienyl)iron complexes has been observed.[6] In fact, the literature apparently contains only two references to nucleophilic attack at the C2/C4 position of η^5-cyclohexadienyl transition metal complexes to generate (σ,η^3-cyclohexendiyl)metal complexes.[19,24] Several examples of nucleophilic attack at the internal position of η^5-cycloheptadienyl transition metal complexes have also been reported.[25] It appears, therefore, that although the majority of the literature in this area centers on reactions of nucleophiles with η^5-cyclohexadienyl complexes, the regioselectivity shown in this reaction does not represent the trend followed by other η^5-dienyl complexes. Efforts currently are underway in these laboratories to determine the cause of these differences in regioselectivity.

In addition, it is clear that the course of the reaction of nucleophiles with neutral tricarbonyl(cyclohexadienyl)-manganese complexes is strongly dependent upon the nature of the nucleophile utilized. Sheridan's work indicates that extremely reactive nucleophiles such as methyllithium and phenyllithium react initially at a carbonyl ligand and transfer to the endo face of the π-complex upon acidification.[9] This tendency of unstabilized alkyl- and aryllithium reagents to react with transition metal complexed carbonyl ligands to form "ate" complexes is well-known and has been utilized extensively

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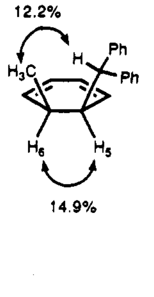
[18] The ^{1}H NMR spectrum of the tricarbonyl(η^4-1,3-cyclohexadiene)-manganese anion has been reported. See ref 11.

[19] Protons located on the carbon which is σ-bonded to the metal in (σ,η^3-enediyl)metal complexes typically are shifted to between 0 and −3 ppm in the ^{1}H NMR spectrum. See for example: Pike, R. D.; Ryan, W. J.; Lennhoff, N. S.; Van Epp, J.; Sweigart, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 4798.

[20] (a) Munro, G. A. M.; Pauson, P. L. *Z. Anorg. Allg.* **1979**, *458*, 211. (b) Chung, Y. K.; Williard, P. G.; Sweigart, D. A. *Organometallics* **1982**, *1*, 1053.

[21] For example, the stereochemical integrity of 5-(diphenylmethyl)-6-methyl-1,3-cyclohexadiene was determined by the following NOE data: 12.2% Enhancement was observed between the methyl group and the diphenylmethyl methine hydrogen; 14.9% enhancement was observed between H_5 and H_6. Negligible enhancements of −0.2% and −3.81% were observed between the methyl group and the H_5 hydrogen and diphenylmethyl methine hydrogen and the H_6 hydrogen, respectively.



[22] For an excellent discussion of the sequential addition of a nucleophile and an electrophile to tricarbonyl(η^6-benzene)chromium complexes, generating trans-disubstituted-1,3-cyclohexadienes, see: Kündig, E. P.; Cunningham, A. F.; Paglia, P.; Simmons, D. P. *Helv. Chim. Acta* **1990**, *73*, 386.

[23] Brookhart's group has demonstrated that the reaction of tricarbonyl(η^4-cyclohexadiene)manganese anions with electrophiles generates (π-allyl)manganese complexes with the electrophile adding to the endo face of the π-system. See ref 11.

[24] Burrows, A. L.; Johnson, B. F. G.; Lewis, J.; Parker, D. G. *J. Organomet. Chem.* **1980**, *194*, C11.

[25] (a) Pearson, A. J.; Burello, M. P. *Organometallics* **1992**, *11*, 448. (b) Pearson, A. J.; Kole, S. L.; Ray, T. *J. Am. Chem. Soc.* **1984**, *106*, 6060. (c) Edwards, R.; Howell, J. A. S.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1974**, 2105. (d) Domingos, A. J. P.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1975**, 2288. (e) Sosinsky, B. A.; Knox, S. A. R.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1633.

for the preparation of Fischer carbene complexes.[26] Nucleophilic attack by moderately stabilized lithium reagents such as those reported here, on the other hand, occurs solely at the cyclohexadienyl π-system, exo to the metal. It should be noted that the reaction of neutral tricarbonyl(η^4-cyclohexadiene)iron complexes with unstabilized organolithium and organomagnesium reagents also shows a tendency to occur at a carbonyl ligand, whereas attack by more stabilized anions takes place at the η^4-diene moiety.[15b] Utilization of these two modes of reactivity with tricarbonyl(η^5-cyclohexadienyl)manganese complexes represents complementary approaches to *cis*- and *trans*-5,6-disubstituted-1,3-cyclohexadienes.

Experimental Section

General Procedures. All reactions were carried out under an argon atmosphere using standard Schlenck techniques unless otherwise indicated. THF was distilled under argon from Na/benzophenone or lithium aluminum hydride. Tricarbonyl(η^5-cyclohexadienyl)manganese (**13**) was prepared according to the method of Brookhart, Lamanna, and Pinhas.[11] Tricarbonyl(6-*exo*-methyl-η^5-cyclohexadienyl)manganese (**19**) was prepared according to the method of Munro and Pauson.[20a] Ethyl isobutyrate and isobutyronitrile were purchased from Aldrich Chemical Co. and distilled from calcium hydride prior to use. Diphenylmethane was purchased from Eastman Chemical Co. and distilled from calcium hydride prior to use. 1,3-Dithane and triphenylmethane were purchased from Aldrich Chemical Co. and used as received. *n*-Butyllithium was purchased from Aldrich Chemical Co. as a 2.5 M solution in hexane. ^1H NMR spectra were obtained on a JEOL FX-90Q spectrometer (90 MHz) or a Varian VXR-400S spectrometer (400 MHz) with tetramethylsilane (0.00 ppm) as the reference. ^{13}C NMR spectra were obtained on a JEOL FX-90Q spectrometer (22.5 MHz) or a Varian VXR-400S spectrometer (100 MHz) with tetramethylsilane (0.00 ppm) as the reference. Infrared spectra were obtained on a Perkin-Elmer 1600 spectrometer, and low-resolution mass spectral data were obtained on a Hewlett-Packard 5988 spectrometer. High-resolution mass spectral data were obtained at the Midwest Center for Mass Spectrometry at the University of Nebraska—Lincoln, Lincoln, NE. Purification of products was accomplished using radical chromatography on a Harrison Research chromatotron using silica gel with pentane/ethyl ether as the eluant.

General Procedure for Reaction of Cyclohexadienyl Complexes with Nucleophiles. (1) Preparation of Ethyl Lithioisobutyrate and α-Lithioisobutyronitrile. To a solution of 0.120 g (1.19 mmol) of diisopropylamine in 7 mL of THF stirring at −78 °C was added 0.48 mL of 2.5 M *n*-butyllithium (1.19 mmol). After the mixture was stirred at −78 °C for 20 min, 1.19 mmol of ethyl isobutyrate, isobutyronitrile, or propionitrile was added followed by 1.5 mL of HMPA. The mixture was stirred at −78 °C for 20 min and then used immediately in the reaction with the manganese complexes.

(2) Preparation of 2-Lithio-1,3-dithiane, (Diphenylmethyl)lithium, and (Triphenylmethyl)lithium. To a solution of 1.19 mmol of 1,3-dithiane, diphenylmethane, or triphenylmethane in 7 mL of THF stirring at −78 °C was added 0.48 mL of 2.5 M *n*-butyllithium (1.19 mmol) followed by 1.5 mL of HMPA. The mixture was stirred for 1.5 h at 0 °C and then cooled to −78 °C immediately prior to reaction with the manganese complexes.

General Procedure for the Reaction of (η^5-Cyclohexadienyl)manganese Complexes 13 or 19 with Nucleophiles. To a solution of 1.19 mmol (1.3 equiv) of the nucleophile in THF/HMPA stirring at −78 °C was added, via cannula, a solution of 0.917 mmol of complex **13** (0.200 g) or complex **19** (0.213 g) in 2 mL of THF. The reaction mixture was stirred at −78 °C for 20 min and then at room temperature for 1.5 h. Oxidation of the reaction mixture was carried out by bubbling oxygen through the solution for 15 min followed by stirring in air overnight. After addition of 50 mL of diethyl ether the reaction mixture was filtered through Celite, washed with 50 mL of saturated aqueous ammonium chloride solution, and washed with 50 mL of saturated aqueous sodium chloride solution. The organic layer was dried over anhydrous magnesium sulfate and filtered, and the solvent was evaporated under reduced pressure. The crude material was purified on silica gel by radial chromatography.

5-(Diphenylmethyl)-1,3-cyclohexadiene (15a). Radial chromatography eluting with pentane gave 0.173 g (77%) of **15a** as a white solid. ^1H NMR ($CDCl_3$ at 400 MHz): δ 1.95 (m, 1 H, H_6), 2.13 (m, 1 H, H_6) 3.14 (m, 1 H, H_5), 3.88 (d, J = 11.6 Hz, 1 H, Ph_2CH-), 5.55 (m, 1 H, H_4), 5.71 (m, 1 H, H_1), 5.87 (m, 1 H, H_3), 5.93 (m, 1 H, H_2), 7.12–7.32 (m, 10 H, ArH). ^{13}C NMR ($CDCl_3$ at 22.5 MHz): δ 27.5, 36.5, 55.2, 124.4, 124.5, 125.7, 126.3, 128.0, 128.5, 128.6, 129.8, 143.5, 144.0. IR (CH_2Cl_2): 3081 (w), 3025 (w), 1596 (m), 1497 (m), 1450 (m), 749 (m), 683 (s) cm^{-1}. MS (*m/z*): 246 (M^+), 244 (M − 2H), 167 (M − C_6H_7), 79 (M − $CHPh_2$). HRMS: calcd for $C_{19}H_{16}$ $(M - 2H)^+$, *m/z* 244.1248; found, *m/z* 244.1250.

2-(2,4-Cyclohexadien-1-yl)-1,3-dithiane (15b).[27] Radial chromatography eluting with 10% ethyl ether/pentane gave 0.118 g (65%) of **15b** as a slightly yellow oil. ^1H NMR ($CDCl_3$ at 400 MHz): δ 1.82 (m, 1 H, $-CH_2CH_2CH_20$), 2.08 (m, 1 H, $CH_2CH_2CH_2$), 2.27 (m, 2 H, H_6), 2.44 (m, 1 H, H_1), 2.84 (m, 4 H, $-CH_2CH_2CH_2-$), 4.16 (d, J = 5.6 Hz, 1 H, −SCHS−), 5.80 (m, 2 H, $H_{2,4}$), 5.89 (m, 1 H, H_5), 5.95 (m, 1 H, H_3). ^{13}C NMR ($CDCl_3$): δ 25.9, 26.1, 30.6, 38.2, 52.4, 124.1, 125.1, 126.1, 126.6. IR (neat): 3034 (s), 2935 (s), 2894 (s), 2821 (s), 1677 (m), 1582 (w), 1420 (s), 1276 (s), 1183 (m), 908 (m), 773 (m), 717 (m), 670 (s). MS (*m/z*): 198 (M^+), 119 (M − $C_4H_7S_2$).

2-(2,4-Cyclohexadien-1-yl)-2-methylpropanenitrile (15c). Radial chromatography eluting with 5% ethyl ether/pentane gave 0.118 g (87.5% yield) of **15c** as a colorless oil. ^1H NMR ($CDCl_3$ at 400 MHz): δ 1.33 (s, 3 H, $-C(CH_3)_2$), 1.35 (s, 3 H, $-C(CH_3)_2$), 2.249 (m, 1 H, H_6), 2.377 (m, 1 H, H_6), 2.48 (m, 1 H, H_1), 5.69 (dd, J = 9.6, 3.2 Hz, 1 H, H_2), 5.81 (m, 1 H, H_5), 5.88 (m, 1 H, H_4), 6.03 (m, 1 H, H_3). ^{13}C NMR ($CDCl_3$ at 22.5 MHz): δ 23.6, 23.9, 24.4, 35.9, 41.0, 123.9, 124.0, 124.8, 125.9, 126.9. IR (neat): 3041 (s), 3000 (s), 2940 (m), 2876 (m), 2827 (m), 2232 (m), 1583 (w), 1462 (s), 1370 (s), 1207 (m), 965 (m), 704 (s), 672 (s) cm^{-1}. MS (*m/z*): 147 (M^+), 79 (M − C_4H_6N). HRMS: calcd for $C_{10}H_{13}N$, *m/z* 147.1045; found, *m/z* 147.1049.

Ethyl 2-(2,4-Cyclohexadien-1-yl)-2-methylpropanoate (15d). Radial chromatography eluting with 5% ethyl ether/pentane gave 0.162 g (91.0%) of **15d** as a colorless oil. ^1H NMR ($CDCl_3$ at 400 MHz): δ 1.13 (s, 3 H, $-C(CH_3)_2$), 1.15 (s, 3 H, $-C(CH_3)_2$), 1.23 (t, J = 7.2 Hz, 3 H, $-CH_2CH_3$), 1.99–2.18 (m, 2 H, H_6), 2.73 (m, 1 H, H_1), 4.12 (q, J = 7.2 Hz, 2 H, $-CH_2CH_3$), 5.58 (dd, J = 12.0, 3.2 Hz, 1 H, H_2), 5.75 (m, 1 H, H_5), 5.83 (m, 1 H, H_4), 5.91 (m, 1 H, H_3). ^{13}C NMR ($CDCl_3$): δ 14.2, 21.9, 22.4, 24.1, 40.5, 47.3, 60.4, 123.7, 125.2, 126.2, 126.7, 177.5. IR (neat): 3038 (m), 2978 (m), 2939 (m), 2874 (m), 1728 (s), 1680 (w), 1580 (w), 1468 (m), 1387 (m), 1252 (s), 1125 (s), 1029 (m), 688 (m) cm^{-1}. MS (*m/z*): 194 (M^+), 116 (M − C_6H_7). HRMS: calcd for $C_{12}H_{18}O_2$, *m/z* 194.1302; found, *m/z* 194.1309.

5-(Triphenylmethyl)-1,3-cyclohexadiene (15e). Radial chromatography eluting with 10% ethyl ether/pentane gave 0.264 g (90.0%) of **15e** as a white solid. ^1H NMR ($CDCl_3$ at 400 MHz): δ 1.76 (t, J = 16.8 Hz, 1 H, H_6), 2.32 (m, 1 H, H_6) 4.26 (m, 1 H, H_5), 5.66–5.81 (m, 4 H, $H_{1,2,3,4}$), 7.07–7.32 (m, 15 H, ArH). ^{13}C NMR ($CDCl_3$ at 90 MHz): δ 26.3, 39.2, 60.3, 123.5, 125.2, 125.8, 126.3, 127.1, 127.2, 127.7, 128.3, 130.1, 143.9. IR (CH_2Cl_2): 3050 (m), 3038 (m), 2953 (w), 2882 (w), 1644 (w), 1596 (m), 1493 (s), 1446 (s), 699 (s). MS (*m/z*): 320 $(M - 2H)^+$, 243 (M − C_6H_7), 165 (M − $C_{12}H_{13}$). HRMS: calcd for $C_{25}H_{20}$ $(M - 2H)^+$, *m/z* 320.1560; found, *m/z* 320.1550.

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(26) See, for example, ref 1a, Chapter 7.

(27) Astruc, D.; Michaud, P.; Madonik, A. M.; Saillard, J.-Y.; Hoffmann, R. *Nouv. J. Chim.* **1985**, *9*, 41.

***cis*-5-(Diphenylmethyl)-6-methyl-1,3-cyclohexadiene (21a).** Radial chromatography eluting with pentane gave 0.162 g (72.3%) of **21a** as a white solid. ^{1}H NMR ($CDCl_3$ at 400 MHz): δ 0.77 (d, J = 6.8 Hz, 3 H, $-CH_3$), 2.09 (m, 1 H, H_6), 3.48 (m, 1 H, H_5), 3.94 (d, J = 12.8 Hz, 1 H, Ph_2CH-), 5.30 (dd, J = 9.2, 1.6 Hz, 1 H, H_4), 5.87 (m, 3 H, $H_{1,2,3}$), 7.11–7.38 (m, 10 H, ArH). ^{13}C NMR ($CDCl_3$ at 22.5 MHz): δ 9.7, 28.7, 41.3, 52.4, 122.9, 124.5, 126.3, 127.7, 127.9, 128.4, 128.7, 133.8, 143.7, 144.0. IR (CH_2Cl_2): 3026 (w), 2960 (m), 2822 (w), 1595 (w), 1581 (w), 1491 (m), 1449 (m), 1408 (w), 1370 (2), 744 (m), 691 (s) cm^{-1}. MS (*m/z*): 260 (M^+), 258 (M – 2H) 167 ($M - C_7H_9$), 93 ($M - C_{13}H_{11}$). HRMS: calcd for $C_{20}H_{18}$ $(M - 2H)^+$, *m/z* 258.1404; found, *m/z* 258.1414.

***cis*-2-(6-Methyl-2,4-cyclohexadien-1-yl)-2-methylpropanenitrile (21b).** Radial chromatography eluting with 10% ethyl ether/pentane gave 0.080 g (58%) of **21b** as a colorless liquid. ^{1}H NMR ($CDCl_3$ at 400 MHz): δ 1.01 (d, J = 6.8 Hz, 3 H, $-CH_3$), 1.42 (s, 3 H, $-C(CH_3)_2$), 1.44 (s, 3 H, $-C(CH_3)_2$), 2.40–2.49 (m, 2 H, $H_{1,6}$), 5.67 (m, 1 H, H_2), 5.83–5.91 (m, 2 H, $H_{4,5}$), 6.024 (m, 1 H, H_3). ^{13}C NMR ($CDCl_3$): δ 10.99, 25.0, 27.0, 29.9, 32.7, 46.9, 122.8, 124.5, 125.0, 125.9, 133.7. IR (neat): 3035 (m), 2974 (s), 2934 (m), 2878 (m), 2817 (w), 2230 (m), 1684 (w), 1455 (m), 1390 (m), 1053 (w), 996 (w), 684 (m) cm^{-1}. MS (*m/z*): 161 (M^+), 93 ($M - C_4H_6N$). HRMS: calcd for $C_{11}H_{15}N$, *m/z* 161.1201; found, *m/z* 161.1197.

Ethyl *cis*-2-(6-Methyl-2,4-cyclohexadien-1-yl)-2-methylpropanoate (21c). Radical chromatography eluting with 10% ethyl ether/pentane gave 0.082 g (43%) of **21c** as a colorless liquid. ^{1}H NMR ($CDCl_3$ at 400 MHz): δ 0.83 (d, J = 7.2 Hz, 3 H, $-CHCH_3$), 1.23 (s, 3 H, $-C(CH_3)_2$), 1.25 (s, 3 H, $-C(CH_3)_2$), 1.25 (t, J = 8.4 Hz, $-OCH_2CH_3$), 2.47 (sextet, J = 7.2 Hz, 1 H, H_6), 2.74 (m, 1 H, H_5), 4.11 (q, J = 7.2 Hz, 1 H, $-OCH_2CH_3$), 4.12 (q, J = 7.2 Hz, 1 H, $-OCH_2CH_3$), 5.72 (dd, J = 5.6, 9.6 Hz, 1 H, H_1), 5.83 (m, 2 H, $H_{2,4}$), 5.93 (m, 1 H, H_3). ^{13}C NMR ($CDCl_3$): δ 12.5, 14.0, 23.28, 24.8, 30.5, 44.0, 45.9, 60.4, 122.4, 124.2, 127.2, 133.8, 178.1. IR (neat): 2982 (m), 2942 (w), 1728 (bs), 1470 (m), 1391 (m), 1250 (m), 1142 (m). HRMS: calcd for $C_{13}H_{18}O_2$ $(M - 2H)^+$, *m/z* 206.1302; found, *m/z* 206.1310.

Acknowledgment. High-resolution mass spectral determinations were made at the Midwest Center for Mass Spectrometry with partial support by the National Science Foundation, Biology Division (Grant No. DIR90107262). Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Ohio University Baker Fund for support of this research. We thank Dr. Cathy Sultany for help obtaining 400-MHz NMR data and Elaine Saulinskas for help obtaining low-resolution mass spectral data.

OM920477M