Manganese-Mediated Reductions of Arenes to Cyclohexa-1,3-dienes via Mn–H–C Bridged Cyclohexenylmanganese Tricarbonyl Complexes

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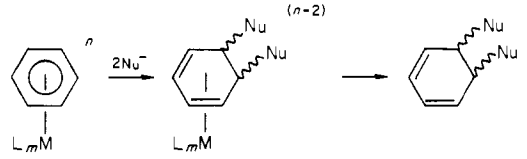
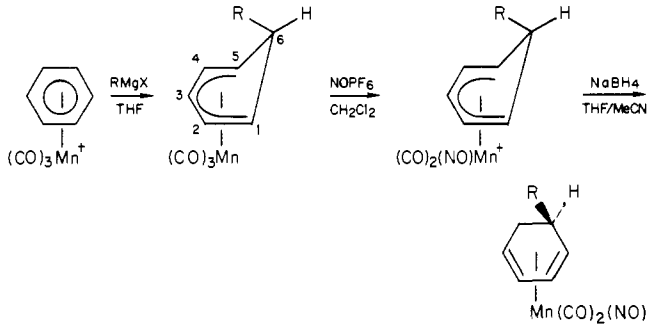
Abstract: Conversions of cationic manganese tricarbonyl complexes of toluene, **1a**, *o*-xylene, **1b**, biphenyl, **1c**, and anisole, **1d**, to free cyclohexa-1,3-dienes are reported. The reaction sequence involves double hydride reduction of **1a–d** and protonation to give the M–H–C bridged (cyclohexenyl)$Mn(CO)_3$ complexes **4a–d**. These species are converted by KH to the substituted anionic (cyclohexadiene)$Mn(CO)_3$ complexes, **3a–d**, which upon oxidative cleavage give the free substituted cyclohexa-1,3-dienes in good yield. For anisole, the reduction sequence is highly regiospecific and gives 2-methoxycyclohexa-1,3-diene as the sole isomer; for the other three arenes, isomeric mixtures of the conjugated dienes are obtained. Using spin saturation transfer experiments, analyses of the equilibrium mixtures of the fluxional M–H–C bridged cyclohexenyl compounds isolated from the double hydride reduction/protonation of (biphenyl)- and (anisole)manganese tricarbonyl cations are also described.

Double nucleophilic addition to transition-metal arene complexes followed by disengagement of the resulting diene ligand represents a potentially useful method for the transition-metal-mediated reduction of arenes to functionalized cyclohexa-1,3-dienes:[1]

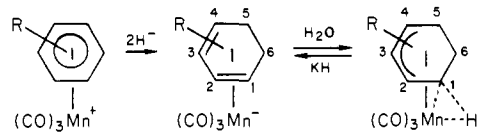


To date, however, few arene complexes have been demonstrated to undergo such double additions. Those which do include the dicationic salts of $(C_6H_6)_2Ru^{2+}$,[2] $\{C_6(CH_3)_3\}(C_6H_6)Ru^{2+}$,[3] and $(C_6H_6)(C_5H_5)Co^{2+}$,[4] as well as the monocationic arene complexes $(C_6H_6)\{C_5(CH_3)_5\}M^+$ of iridium and rhodium.[3] Recently, Sweigart[5] prepared neutral methyl- and phenyl-substituted (cyclohexa-1,3-diene)$Mn(CO)_2(NO)$ complexes via the addition of a single equivalent of methyl or phenyl Grignard to (benzene)-manganese tricarbonyl cation, followed by reactivation of the ring using $NOPF_6$ and subsequent reduction by $NaBH_4$:



In none of the above-mentioned cases, however, have disengagement reactions yielding free cyclohexa-1,3-dienes been reported.[6]

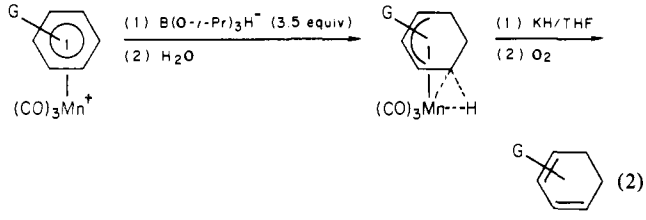
(Benzene)manganese tricarbonyl cation and its alkyl-substituted derivatives have also been shown to undergo double hydride reduction to give cyclohexa-1,3-diene anions. Upon protonation these species yield fluxional cyclohexenyl complexes containing a two-electron, three-center Mn–H–C bond:[7,8]



(1)

(several rapidly equilibrating isomers)

(The 5-*endo*-methyl derivative of this system has been recently characterized by neutron diffraction.[9]) We have noted that the most efficient route to clean generation of the cyclohexa-1,3-diene anions involves isolation and purification of the bridged species followed by deprotonation with potassium hydride. Exposure of the unsubstituted anion to oxygen results in oxidative degradation of the complex and isolation of cyclohexa-1,3-diene in 79% yield.[7c] Thus, a feasible general route for the conversion of (arene)-manganese tricarbonyl complexes to cyclohexa-1,3-dienes is represented by the two-step procedure below:



(2)

(1) The preparation of substituted cyclohexa-1,3-dienes has also been accomplished via nucleophilic addition to cationic cyclohexadienyliron tricarbonyl species and oxidative cleavage of the resulting neutral (cyclohexadiene)iron tricarbonyl complexes. For these systems, however, cationic cyclohexadienyl precursors are prepared via hydride abstraction from a neutral cyclohexa-1,3-diene complex which is generated via complexation of the free diene. In contrast to the present systems, diene complexes are not prepared via reductions of metal arene complexes. See the following reference for a summary of this chemistry: Pearson, A. J. *Acc. Chem. Res.* **1980**, *13*, 463.

(2) Jones, D.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1962**, 4458.

(3) Grundy, S. L.; Maitlis; P. M. *J. Chem. Soc., Chem. Commun.* **1982**, 379.

(4) Lai, Y.-H.; Tam, W.; Vollhardt, K. P. C. *J. Organomet. Chem.* **1981**, *216*, 97.

(5) Chung, Y. K.; Choi, H. S.; Sweigart, D. A. *J. Am. Chem. Soc.* **1982**, *104*, 4245.

(6) By way of comparison, useful conversions of arenes directly to cyclohexa-1,3-dienes have been achieved by Semmelhack via the addition of a single equivalent of nucleophile to (arene)$Cr(CO)_3$ complexes followed by protonation and ring disengagement in strong acid. See the following reference for a review of these reactions: Semmelhack, M. F.; Clark, G. R.; Garcia, J. L.; Harrison, J. J.; Thebtaranonth, Y.; Wulfe, W.; Yamashita, A. *Tetrahedron* **1981**, *37*, 3957.

(7) (a) Lamanna, W.; Brookhart, M. *J. Am. Chem. Soc.* **1981**, *103*, 989. (b) Brookhart, M.; Lamanna, W.; Humphrey, M. B. *J. Am. Chem. Soc.* **1982**, *104*, 2117. (c) Brookhart, M.; Lamanna, W.; Pinhas, A. R. *Organometallics* **1983**, *2*, 638. (d) Brookhart, M.; Lukacs, A. *Organometallics* **1983**, *2*, 649.

(8) (a) Bladon, P.; Munro, G. A. M.; Pauson, P. L.; Mahaffy, C. A. L. *J. Organomet. Chem.* **1981**, *221*, 79. (b) The phenylcyclohexenyl system has also been prepared by Pauson (ref 8a) via an alternate route—the lithium aluminum hydride reduction of 6-*exo*-phenylcyclohexadienylmanganese tricarbonyl. No detailed analysis of exact isomer ratios was reported.

(9) Schultz, A. J.; Teller, R. G.; Beno, M. A.; Williams, J. M.; Brookhart, M.; Lamanna, W.; Humphrey, M. B. *Science* **1983**, *220*, 197.

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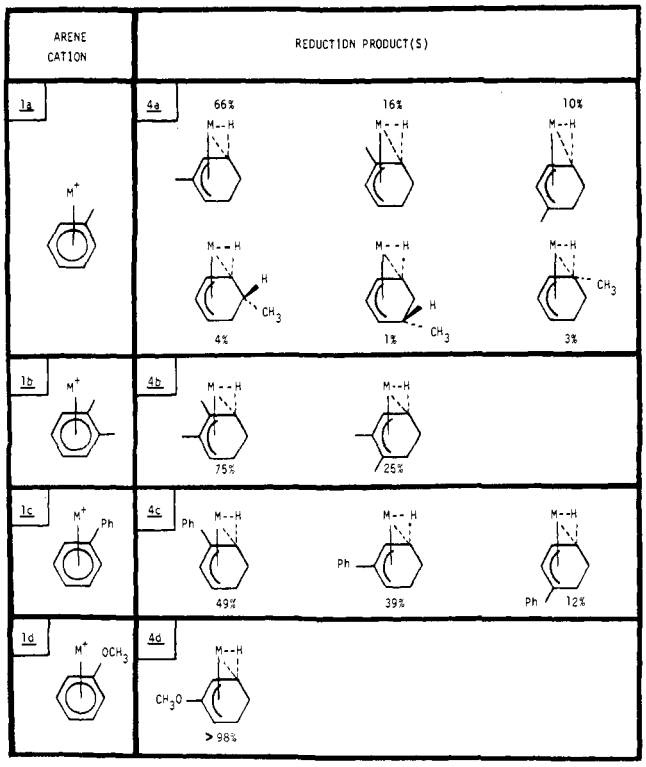
Table I. Isomeric Ratios of the (cyclohexenyl)$Mn(CO)_3$ Complexes (**4a–d**) Obtained in the Reduction of the Four (Arene)manganese Tricarbonyl Cations (**1a–d**)[a]



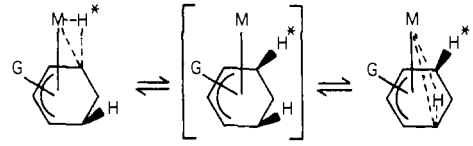
[a] Ratios are given as percentages of the room temperature equilibrium mixture of interconverting isomers. M = $Mn(CO)_3$.

We report here a study of these reactions for the cationic manganese tricarbonyl complexes of toluene, *o*-xylene, biphenyl, and anisole. This work includes an analysis of the isomeric ratios of the fluxional phenyl- and methoxy-substituted cyclohexenyl complexes and determination of the regioselectivities obtained in the formation of substituted cyclohexadienes for each of the four systems. Results obtained for the methoxy-substituted derivative indicate that high regioselectivity may be achieved for strongly electron donating substituents.

Results and Discussion

A. Reduction of (arene)$Mn(CO)_3$ Cations and Generation of Bridged (cyclohexenyl)$Mn(CO)_3$ Species. The bridged complexes **4a–d** depicted in Table I were each prepared by double hydride reduction of the corresponding arene tricarbonyl cation **1a–d**. Stepwise addition of 2 equiv of hydride was achieved by treating a tetrahydrofuran suspension of each salt with excess potassium triisopropoxyborohydride (3.5 equiv). Infrared monitoring of the carbonyl region of the spectrum in each case indicated a rapid addition of the first equivalent of hydride (ca. 20 min) to generate neutral cyclohexadienyl complexes **2a–d**. Subsequent addition of the second equivalent occurred more slowly (ca. 15 h). Addition could be monitored by noting the disappearance of those bands due to the cyclohexadienyl product (ν_{CO} (THF) ca. 2005, 1935 cm^{-1}) and the appearance of new bands characteristic of the substituted cyclohexa-1,3-diene anions **3a–d** (ν_{CO} (THF) ca. 1930, 1830, 1790 cm^{-1}). Under an inert atmosphere near quantitative conversion to isomeric mixtures of the oxgyen-sensitive cyclohexa-1,3-diene anions could be achieved. Protonation of the anions with degassed NaCl brine, standard workup, and subsequent column chromatography (except for **4d** which was observed to undergo loss of methanol on an alumina column) resulted in isolation of the equilibrium mixtures of the bridged compounds **4a–d** shown in Table I.

As reported previously for the parent compound,[7a,b] each of these substituted derivatives undergoes two modes of isomerization at room temperature, together accounting for the equilibrium mixtures of isomers indicated. The first of these processes ($\Delta G^{\ddagger}$ = ca. 8.5 kcal/mol) proceeds via the 16-electron cyclohexenyl complex as shown below:

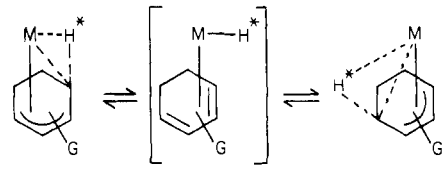


M ≡ $Mn(CO)_3$

For isomers in which the substituent G is symmetrically disposed with respect to this process the isomerization is degenerate.

An unsymmetrical substitution pattern leads to a nondegenerate isomerization in which a distinct isomeric preference is often observed (see below).[7d]

The second dynamic process ($\Delta G^{\ddagger}$ = ca. 16.0 kcal/mol) proceeds via an 18-electron diene hydride intermediate as outlined below:



M ≡ $Mn(CO)_3$

For each reduction studied hydride addition at only unsubstituted ring carbons has been observed. As a result, the bridged isomers reported here contain substituents relegated to one of six ring sites, namely, the three allylic positions and the three "*exo*"-methylene sites. A more detailed description of the dynamic processes outlined above as well as the NMR techniques used to fully characterize isomeric mixtures of bridged isomers has been described.[7b,c,d] Brief summaries outlining the preparation of bridged systems **4a–d** are presented below.

Methylcyclohexenylmanganese Tricarbonyl (4a) and Dimethylcyclohexenylmanganese Tricarbonyl (3b). The preparation and characterization of these species was reported previously.[7d] Results of isomer ratios observed are summarized in Table I.

Phenylcyclohexenylmanganese Tricarbonyl (4c). The addition of 1 equiv of $KB(O\text{-}i\text{-}Pr)_3H$ to the (biphenyl)manganese tricarbonyl cation **1c** (as prepared via the reaction of $Mn(CO)_5Br$ with biphenyl and $AlCl_3$) led to the isolation (73%) of three neutral cyclohexadienyl complexes **2c** in ratios of 45:41:14 (Scheme I). Addition, instead, of 3.5 equiv of hydride to **1c** to generate the 1-phenyl- and 2-phenylcyclohexa-1,3-diene anions **3c** followed by protonation with water resulted in isolation of the three isomeric cyclohexenyl bridged structures **4c** as their equilibrium mixture in ratios of 49:39:12 (81% yield based on the cation).[8b]

The method of assignment of the isomer ratios is briefly described below and is based on previously established procedures.[7d] Most informative is the 25 °C ^1H NMR spectrum in which the low-temperature averaging process is rapid on the NMR time scale, but no line broadening due to the high-temperature process has occurred. The spectrum above δ – 1.0 is shown in Figure 1. The resonance at δ −5.81 can be assigned to a 2 H signal of a bridged species undergoing a degenerate averaging process (i.e., either a 3- or 6-phenyl-substituted isomer). In these cases, the shift of the averaging endo hydrogens (H_{1n}, H_{5n}) would be expected at approximately δ −6.0, the average value of the chemical shift observed for the static bridged interaction (H_{1n}) δ −13.0, and that expected for a proton populating the nonbridged *endo*-methylene site (H_{5n}) δ 1.0. The lack of a signal for an H_3 proton immediately establishes this species as the 3-phenyl isomer. All other ^1H and ^{13}C NMR data are consistent with this assignment (see Experimental Section).

The two equal-intensity signals symmetrically disposed about δ −6.0 can be assigned to a pair of nondegenerate equilibrating isomers. From the chemical shift difference, the isomer ratio can

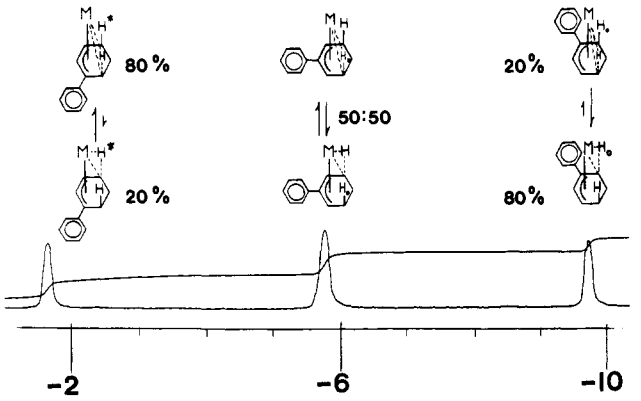
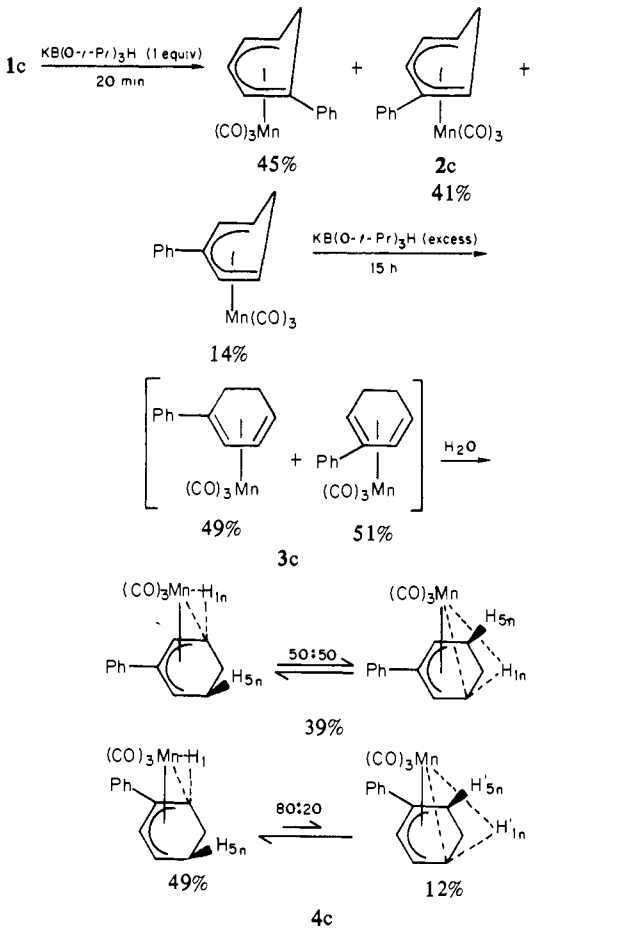


Figure 1. Room temperature, 250-MHz ^1H NMR spectrum (C_6D_6) of phenylcyclohexenylmanganese tricarbonyl (**4c**). Only that portion of the spectrum from −1 to −10 ppm is shown. The single two-proton signal at −5.8 ppm represents the degenerate isomer, while the remaining pair of signals arise from the interconverting nondegenerate pair as indicated. M = $Mn(CO)_3$.

Scheme I



be estimated as ca. 4:1.[7d] The bridging hydrogen (H_{1n}) of the major isomer (80%) averages with H_{5n} of the minor isomer (20%) to give the band at δ −9.83, while the bridging hydrogen (H_{1n}) of the minor isomer (20%) averages with H_{5n} of the major isomer (80%) to give the signal at δ −1.63. The appearance of the H_3 resonance as a doublet (δ 5.19, $J \approx 8$ Hz) establishes this equilibrating pair as the 2- and 4-phenyl system shown.

Although the isomer *pair* can be assigned and the ratio estimated, assignment of the specific structural identities to the major and minor isomer relies on spin saturation transfer (SST). The experiment takes advantage of the fact that at higher temperatures (40 °C) interconversion between the symmetrically substituted

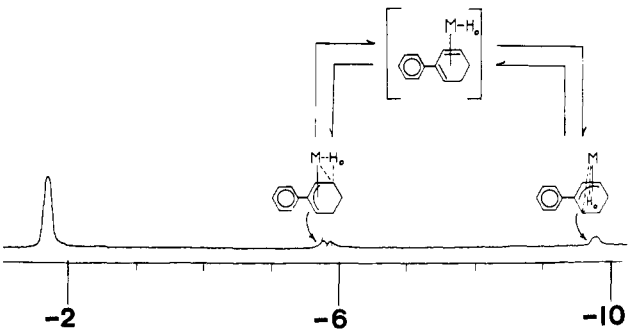
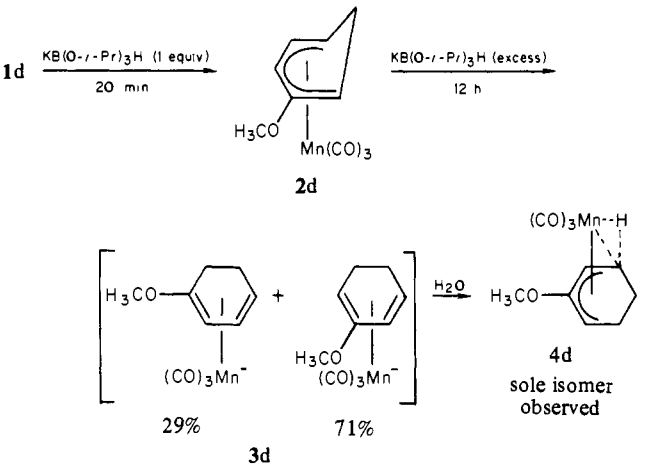
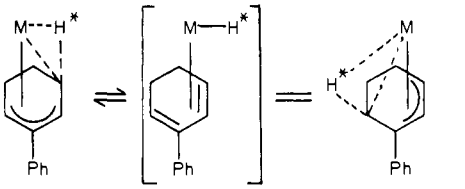


Figure 2. ^1H NMR spin saturation transfer experiment (40 °C) in C_6D_6 for phenylcyclohexenylmanganese tricarbonyl (**4c**). Since H_o populates the bridged site in the 2-phenyl- and 3-phenyl-substituted isomers only (which interconvert via the diene hydride), irradiation at either band provides the necessary crossover to assign these structures. Only that portion of the spectrum from −1 to −10 ppm is shown. M = $Mn(CO)_3$.

Scheme II



isomer and the 2-phenyl-substituted isomer occurs via the high-energy process and can be detected by SST:



As indicated by the H* label, signal saturation at δ −5.81 would be expected to result in a substantial decrease in intensity (via SST) of that band representing the bridging hydrogen in the 2-substituted isomer *only*. The result of irradiation at δ −5.81 is shown in Figure 2. A substantial decrease in band intensity for the signal situated at δ −9.83 allowed assignment of this resonance to the bridging hydrogen of the 2-phenyl-substituted isomer which averages (80:20) with the H_{5n} site of the 4-phenyl system. The 2-phenyl structure thus represents the major isomer (80%), while the 4-phenyl isomer represents only 20% of the equilibrium mixture. ^{13}C NMR data obtained at −95 °C (at which temperature both dynamic processes are "slow" on the NMR time scale) bear out these assignments, confirming vinylic substitution for all three isomers (see Experimental Section).

Methoxycyclohexenylmanganese Tricarbonyl (4d). The preparation of the 3-methoxy-substituted bridged complex **4d** proceeded along similar lines. The addition of a single equivalent of KB(O-*i*-Pr)$_3$H to (anisole)manganese tricarbonyl hexafluorophosphate (**1d**) (as prepared from reaction of (chlorobenzene)-$Mn(CO)_3PF_6$ with sodium methoxide) resulted in isolation of the single 2-substituted cyclohexadienyl complex **2d** in 68% yield

Table II. Ratios of the Isomeric Cyclohexa-1,3-dienes Obtained from the Deprotonation/Cleavage of the Four Fluxional Substituted (cyclohexenyl)$Mn(CO)_3$ Systems (**4a–d**)[a]

BRIDGED ISOMERS[1]	CYCLOHEXADIENE PRODUCT(S)	YIELD
4a	5a OBSERVED RATIOS (PREDICTED)[3] 25% (13%) 67% (82%) 8% (5%)	55%[2]
4b	5b OBSERVED RATIOS (PREDICTED)[3] 42% (25%) 58% (75%)	81%
4c	5c OBSERVED RATIOS (PREDICTED)[3] 37% (12%) 63% (88%)	89%
4d	5d OBSERVED RATIOS: (PREDICTED)[3] >98% (>98%)	83%

[a] 1: See Table I for distributions. 2: Isolated as their TCNE Diels–Alder adducts. 3: Those values in parentheses represent the ratios that are expected from a rapid deprotonation of the equilibrium mixture of bridged isomers at room temperature (see text).

(Scheme II). The addition of 3.5 equiv of hydride to **1d** to generate the isomeric 1-methoxy- and 2-methoxycyclohexa-1,3-diene anions **3d** proceeds to completion in 12 h (as determined by IR monitoring). Subsequent protonation of the mixture resulted in isolation of the single 3-methoxy-substituted bridged isomer **4d** (70% yield based on the anisole cation), characterized by means of ^1H and ^{13}C NMR spectroscopy.

The symmetric nature of the isomer is borne out by the single two-proton signal observed for the product at δ −5.94, while vinylic substitution is again confirmed by ^1H and low-temperature ^{13}C NMR data (see Experimental Section). No other isomers are present in concentrations greater than 2%.

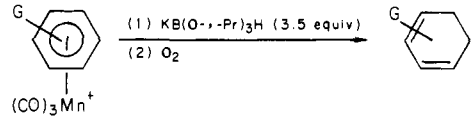
B. Generation of (cyclohexa-1,3-diene)$Mn(CO)_3$ Anions and Oxidative Cleavage to Free Cyclohexa-1,3-dienes. Via (cyclohexenyl)$Mn(CO)_3$ Intermediates. The observation that electron-donating groups prefer substitution at the vinylic carbons of the bridged manganese complexes dscribed suggested that a certain degree of regioselectivity might be achieved upon oxidative degradation of the cyclohexa-1,3-diene anions derived from these systems. The equilibrium mixture of the bridged complexes can be used to accurately predict the isomeric mixtures of diene anions formed upon deprotonation under two conditions: (a) if all bridged isomers have equal kinetic acidities and/or (b) deprotonation is very rapid relative to isomer interconversions. If kinetic acidities are not equivalent and deprotonation is slow relative to isomer interconversion, then isomer ratios of diene anions formed could vary markedly from those predicted on the basis of conditions a and/or b.

The deprotonation of the bridged systems **4a–d** was accomplished by adding each to a stirred suspension of potassium hydride in tetrahydrofuran. In each case the yellow color characteristic of the bridged compounds immediately faded to give a clear, colorless solution. Quantitative conversion to the corresponding cyclohexa-1,3-diene anions **3a–d** was confirmed at this point by the infrared spectra of the solutions {$\nu_{CO(\text{diene anions}}$ = ca. 1930, 1830, 1790 cm^{-1}}. Oxidative cleavage of the diene ligands was effected by vigorous stirring under an oxygen atmosphere for 5 min. Subsequent filtering through Celite gave clear, colorless solutions which, after solvent removal, yielded the free dienes.[10]

The results of these experiments are summarized in Table II. The "predicted" ratios of cyclohexadiene isomers are those based on conditions a/b stated above. As is clear, although the predicted values are not strictly obtained, they serve as an approximate guide to the observed ratios of diene isomers. In cases **4a–c** the minor bridged isomers appear to have enhanced kinetic acidities relative to the major isomers. For example, the 5-methylcyclohexadiene isomer (8%) is formed only from isomers **4a** which bear methyl substituents at C_5 or C_6. These account for only 5% of the bridged isomers. Similarly, the 4-phenyl isomer of mixture **4c** is present in only 12% abundance and is the only source of the 1-phenylcyclohexadiene which is formed in 37% abundance.

The case of the methoxy-substituted system is the most interesting as regards regioselectivity imposed by the isomer preferences displayed in the bridged systems. The 3-methoxy-substituted complex is the sole bridged isomer observed (>98%), and deprotonation/cleavage results in formation of 2-methoxycyclohexadiene as the sole detectable isomer (>98%). We see no evidence for product formation from preferential deprotonation of any of the minor isomers (<2% abundance).

Via Direct Reduction of (arene)$Mn(CO)_3$ Cations. Preliminary experiments were carried out on the oxidative cleavage of the anionic diene complexes derived directly from addition of 2 equiv of hydride to the (arene)$Mn(CO)_3$ cations **1a–d** via the following procedure (see Experimental Section for details):



Although cyclohexadienes can be obtained by using this "one-pot" procedure, several disadvantages were noted relative to the procedures described above using the bridged complexes: (a) in general, isolated yields of the dienes were lower, (b) substantial contamination of the dienes with corresponding arenes resulting from over oxidation of the incipient diene product was noted, and (c) purification of the diene products in the presence of the boron-containing byproducts was difficult. A summary of diene isomer ratios and yields obtained from **1a** is 1-methyl- and 2-methylcyclohexa-1,3-diene (64:36, 12% yield); from **1b**, 1,2-dimethyl- and 2,3-dimethylcyclohexa-1,3-diene (80:20, 10% yield); from **1c**, 1-phenyl- and 2-phenylcyclohexa-1,3-diene (49:51, 56% yield); and from **1d**, 1-methoxy- and 2-methoxycyclohexa-1,3-diene (29:71, 10% yield).

The ratios of dienes observed were assumed to correspond to the approximate ratios of diene anions formed. In each case using this method a higher proportion of the 1-substituted diene was obtained relative to that noted for dienes formed via the bridged species.

Summary

The results obtained indicate that the reduction sequence described in eq 2 (see the introduction) via the bridged cyclohexenyl complexes is a viable one for the conversion of substituted benzenes to the corresponding substituted cyclohexa-1,3-dienes. The ratio of diene isomers observed can be roughly estimated from the equilibrium ratios of the isomeric bridged cyclohexenyl complexes. In all cases studied substituents in the diene products occupy vinylic sites. For the alkyl and phenyl substitutents there is no strong regioselectivity for either the 1- or 2-position (see Table III). Interesting from a synthetic viewpoint is the fact that reduction and cleavage of the anisole complex leads solely to 2-methoxycyclohexa-1,3-diene. Clearly, this complete regiospecificity results from the preference of the methoxyl substituent to exclusively occupy the 3-position in the cyclohexenyl complex **4a**. This method represents the first reported reduction of anisole to the 2-methoxycyclohexa-1,3-diene isomer. Only one other method for the preparation of this compound has been reported.[11] The synthesis proceeds from cyclohexanone and results in the production of both 1- and 2-methoxycyclohexa-1,3-diene in a 1:10 ratio. Dissolving metal reductions of anisole generally lead to 2,5-dihydroanisole or to a mixture of the 2,5-dihydro compound and 1-methoxycyclohexa-1,3-diene.[12]

(10) For the monomethyl derivative product dienes were isolated via Diels–Alder trapping using tetracyanoethylene. See Experimental Section for details.

(11) (a) de Waard, E. R.; Kattenberg, J.; Huisman, H. O. *Tetrahedron Lett.* **1970**, *50*, 4427. (b) A related compound, 2-(trimethylsiloxy)cyclohexadiene, is readily available from silyation of the enolate of 2-cyclohexenone.

The reduction of anisole to 2-methoxycyclohexadiene in itself is of limited synthetic interest.[11b] However, as a model system it suggests that for other arenes containing strongly electron-donating substituents high regioselectivity for conversion to 2-substituted isomers should be observed, and thus this reduction procedure may be of synthetic utility for more highly functionalized arenes where alternate routes are not viable.

Experimental Section

General. All reactions were performed under a dry, oxygen-free nitrogen atmosphere. Tetrahydrofuran solvent was freshly distilled from lithium aluminum hydride under a nitrogen atmosphere; other solvents were simply degassed unless otherwise noted. Dimanganese decacarbonyl was obtained from Strem or Pressure Chemical. Compounds prepared by previously described procedures include manganese pentacarbonyl bromide,[13] (toluene)manganese tricarbonyl hexafluorophosphate (**1a**),[13] (o-xylene)manganese tricarbonyl perchlorate (**1b**),[7d,14] (anisole)manganese tricarbonyl hexafluorophosphate (**1d**),[7d,15] 1- and 2-methylcyclohexadienylmanganese tricarbonyl (**2a**),[7d,14] 1,2- and 2,3-dimethylcyclohexadienylmanganese tricarbonyl (**2b**),[7d] methylcyclohexenylmanganese tricarbonyl (**4a**),[7d,8] and dimethylcyclohexenylmanganese tricarbonyl (**4b**).[7d]

^{1}H NMR spectra were recorded at 100 MHz on a Varian XL-100 FT NMR spectrometer or at 250 MHz on a Bruker WM250 FT NMR spectrometer. ^{13}C NMR spectra were recorded at 62.9 MHz on the Bruker instrument. In all cases residual solvent resonances were used as internal standards for determining chemical shifts [^{1}H NMR C_6D_5H, δ 7.15; $C_6D_5CD_2H$, δ 2.09; $CHCl_3$, δ 7.24; $CHDCl_2$, δ 5.32]. The format used to report NMR data is as follows: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = unresolved multiplet), coupling constants (Hz) listed so as to correspond with multiplicity, format, integration, and assignment where possible. NMR probe temperatures were calibrated by measurement of peak separations in standard methanol or ethylene glycol samples. NMR samples were degassed by several freeze–pump–thaw cycles and NMR sample tubes were sealed under vacuum (0.01 mm). Deuterated NMR solvents were dried over molecular sieves (4 Å) and stored under nitrogen in ampules equipped with Teflon stopcocks.

Infrared spectra were recorded on a Beckman spectrophotometer (IR 4250) and frequencies (cm^{-1}) were assigned relative to a polystyrene standard. Only bands in the carbonyl stretching region (ca. 1500–2300 cm^{-1}) are reported.

Gas chromatography was done with a Varian Aerograph A-90P gas chromatograph. Columns consisted of 25% OV-210 on Chromasorb W.

Column packings for liquid column chromatography consisted of neutral or basic Alumina (Al_2O_3: 70/90 mesh).

(Biphenyl)manganese Tricarbonyl Hexafluorophosphate (1c). The hexafluorophosphate salt of (biphenyl)manganese tricarbonyl was prepared by using a modification of procedures used to prepare the toluene cation. Manganese pentacarbonyl bromide (6.0 g, 0.0218 moles) and anhydrous, technical grade aluminum chloride (15.0 g, 0.1125 mol) were heated at 100 °C with biphenyl (5.06 g, 0.0328 mol) in 100 mL of octane for 16 h. During the course of the reaction the solution gradually darkened, with the formation of a brown residue. After cooling to 0 °C, 150 mL of ice water were added dropwise with constant stirring. The resulting yellow aqueous layer was separated, washed with 200 mL of isopentane, and then treated dropwise with 20 mL of an aqueous NH_4PF_6 solution while the mixture was stirred vigorously at 0 °C. The product was taken up into 100 mL of acetone and filtered through a medium frit and the solvent removed. The pale yellow solid was dried in vacuo (0.01 mm) to yield 3.89 g (40.7% based on $Mn(CO)_5Br$) of (biphenyl)manganese tricarbonyl hexafluorophosphate: IR (ν_{CO}, $(CH_3)_2CO$) 2059, 2002 cm^{-1}; ^{1}H NMR ($(CD_2)_2CO$) δ 6.80 (t, t, 1), 7.14 (t, 2), 7.28 (d, d, 2), 7.64 (m, 3), 8.02 (dd, 2). Anal. Calcd for $C_{13}H_{10}F_6MnO_3P$: C, 41.11; H, 2.30; Mn, 12.54. Found: C, 41.31; H, 2.19; Mn, 12.24.

1-, 2-, and 3-Phenylcyclohexadienylmanganese Tricarbonyl (2c). A stirred suspension of (biphenyl)manganese tricarbonyl hexafluorophosphate (0.65 g, 0.0015 mol) in tetrahydrofuran (30 mL, freshly distilled) was treated with a 1 M solution of potassium triisopropoxyborohydride in tetrahydrofuran (1.65 mL, 0.00165 mol) at room temperature. After 20 min, 30 mL of NaCl brine were added dropwise at 0 °C. The organic layer was dried with anhydrous sodium sulfate and the solvent removed. The crude product was taken up into 60 mL of isopentane and dried further with anhydrous sodium sulfate. The material was purified by chromatography on neutral alumina (activity II) using isopentane as the eluent. The yellow band eluting first was collected and the solvent removed to give a yellow solid. Recrystallization of this material from a minimum amount of isopentane at −78 °C yielded yellow crystals (0.33 g, 74.8% based on $C_6H_5(Ph)Mn(CO)_3PF_6$) of the isomeric products: IR (ν_{CO}, THF) 2019, 1936 cm^{-1}; ^{1}H NMR for the 1-phenyl isomer (C_6D_6, δ 3.0 to 6.0 region) δ 3.98 (m, 1), 4.70 (d, 1, J = 6), 5.16 (t d, 1, J = 6, 1.5); ^{1}H NMR for the 2-phenyl isomer (C_6D_6, δ 3.0 to 6.0 region) δ 3.98 (m, 1), 5.69 (d, 1, J = 6); ^{1}H NMR for the 3-phenyl isomer (C_6D_6, δ 3.0 to 6.0 region) δ 4.88 (d, 2, J = 6.8). Signals in the δ 6.0 to 7.5 region along with those in the δ 0 to 3.0 region overlapped significantly and could not be assigned to individual isomers.

2-Methoxycyclohexadienylmanganese Tricarbonyl (2d). This compound was prepared in identical fashion to the isomers of phenylcyclohexadienylmanganese tricarbonyl with the following exceptions: 1.0 g of (anisole)manganese tricarbonyl hexafluorophosphate was used in place of the biphenyl cation and all reagents were adjusted accordingly. The product was a yellow solid (0.43 g, 65.3% based on $C_6H_5(CH_3O)Mn(CO)_3PF_6$), the structure of which was confirmed by ^{1}H NMR: IR (ν_{CO}, THF) 2016, 1924 cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.67 (d, 1, J = 9), 2.26 (m, 1), 2.33 (m, 1), 4.16 (apparent t, 1, J = 6.5), 5.24 (d, 1, J = 6.5). This compound has also been prepared by a different method.[16] The reported ^{1}H NMR spectrum in CS_2 is similar to that reported here.

Reduction of (Biphenyl)manganese Tricarbonyl Hexafluorophosphate to Phenylcyclohexenylmanganese Tricarbonyl (4c). In a method similar to that used to prepare the methyl derivatives, (biphenyl)manganese tricarbonyl hexafluorophosphate (2.0 g, 0.0046 mol) was suspended in 100 mL of tetrahydrofuran and 16.1 mL of potassium triisopropoxyborohydride (1 M in THF) were added dropwise with stirring. After 15 h at reflux, infrared analysis of the reaction solution indicated complete conversion to the isomeric diene anions, **3c** (ν_{CO} (THF) 1934, 1845, 1795 cm^{-1}). [IR monitoring during the course of the reaction indicated stepwise reduction to the anions through the neutral phenylcyclohexadienyl complexes **2c**]. The solution was then cooled to 0 °C and 100 mL of degassed NaCl brine were added slowly with constant stirring. The organic layer was dried over anhydrous sodium sulfate and filtered and the solvent removed to yield a red oil. This oil was extracted into 75 mL of isopentane, dried again over sodium sulfate, and filtered and the solvent removed. The resulting yellow oil was chromatographed on basic alumina (activity II) using isopentane as the eluent. The first band eluting (yellow) was collected and stripped of solvent to yield a yellow oil. The product was further dried in vacuo (0.01 mm) to give 1.1 g (80.7% based on $C_6H_5(Ph)Mn(CO)_3PF_6$) of the isomeric bridged complexes **4c** as a yellow oil: IR (ν_{CO}, isopentane) 2026, 1943 cm^{-1}; ^{1}H NMR for the 3-phenyl isomer (C_6D_6) δ −5.81 (br s, 2), 0.08 (complex, 1), 0.42 (complex, 1), 0.95 (d, 2), 4.54 (br t, 2), 7.0–7.5 (Ph); ^{1}H NMR for the 2-phenyl and 4-phenyl isomers (C_6D_6) δ −9.83 (br t, 1, proton bridging in the 2-phenyl isomer), −1.63 (br m, 1, proton bridging in the 4-phenyl isomer), 0.08 (complex, 1), 0.42 (complex, 1), 0.95 (d, 2), 3.73 (m, 1), 5.19 (d, 1, J = 8), 7.0–7.5 (Ph); ^{13}C NMR for the 3-phenyl isomer (CD_2Cl_2, −95 °C, δ 60–110 region) δ 66.0 (d, J = 164), 71.7 (d, J = 179), 107.9 (s); ^{13}C NMR for the 2-phenyl isomer (CD_2Cl_2, −95 °C, δ 60–110 region) δ 63.4 (d, J = 159), 89.6 (d, J = 167), 89.9 (s); exact mass calcd for $C_{15}H_{13}MnO_3$ 296.0245, found 296.0247.

Reduction of (Anisole)manganese Tricarbonyl Hexafluorophosphate to Methoxycyclohexenylmanganese Tricarbonyl (4d). Methoxycyclohexenylmanganese tricarbonyl was prepared from (anisole)manganese tricarbonyl hexafluorophosphate by the identical method used for the preparation of the phenyl-substituted complex with the following exceptions: 2.0 g of (anisole)manganese tricarbonyl hexafluorophosphate were substituted for the biphenyl cation and all other reagents were adjusted accordingly. Conversion to the isomeric anions **3d** was observed after 12 h at reflux (ν_{CO} (THF) 1928, 1819, 1778 cm^{-1}). Workup was identical with that described for the phenyl system with the exception that the product was not chromatographed. (All attempts to purify the material on alumina columns resulted in loss of methanol from the complex to yield (cyclohexadienyl)manganese tricarbonyl). Recrystallization of the material from a minimum amount of isopentane at −78 °C yielded 1.01 g (79.1% based on $C_6H_5(CH_3O)Mn(CO)_3PF_6$) of the bridged complex **4d** as a yellow oil at 25 °C: IR (ν_{CO}, isopentane) 2020, 1945 cm^{-1}; ^{1}H NMR (C_6D_6) δ −5.94 (br s, 2), −0.06 (complex, 1), 0.22 (complex, 1) 0.94 (d, 2), 3.06 (s, 3), 3.94 (br s, 2); ^{13}C NMR (CD_2Cl_2, −95 °C) δ 7.3 (d d, J = 84, 146), 16.6 (t, J = 133), 24.5 (q, J = 131), 26.5 (t, J = 130), 80.0 (d, J = 176), 97.5 (d, J = 167), 139.9 (s). Anal. Calcd for

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$C_{10}H_{11}MnO_4$: C, 48.02; H, 4.43; Mn, 21.96. Found: C, 47.98; H, 4.23; Mn, 21.72.

1-, 2-, and 5-Methylcyclohexa-1,3-diene (5a) (Diels–Alder Adducts). Method A: Via Deprotonation of Methylcyclohexenylmanganese Tricarbonyl Isomers 4a. A solution of methylcyclohexenylmanganese tricarbonyl (1.0 g, 0.0043 mol) in tetrahydrofuran 5 mL, freshly distilled) was added to a stirred suspension of potassium hydride (0.19 g, 0.0047 mol) in tetrahydrofuran (70 mL, freshly distilled) at room temperature. The yellow color characteristic of THF solutions of the bridged species immediately disappeared, giving rise to an almost colorless solution of the diene anions **3a** [as confirmed by IR analysis of the solution (ν_{CO} (THF) 1925, 1831, 1782 cm^{-1})]. After 15 min the anion solution was filtered through oven-dried Celite to remove excess KH. The solution was then flushed briefly with dry oxygen (5 min), during which time a dark brown precipitate formed. The resulting solution was filtered through Celite and added dropwise to a stirred solution of tetracyanoethylene (1.05 g, 0.0080 mol) in tetrahydrofuran (10 mL, freshly distilled). After 16 h at 25 °C the solvent was evaporated (20 mm, 25 °C). The brown precipitate was extracted with 100 mL of benzene, filtered, and stripped of solvent. The resulting white powder was taken up into a minimum amount of benzene and precipitated by adding isopentane to yield 0.52 g (55% based on methylcyclohexenylmanganese tricarbonyl) of a white powder which proved to be the Diels–Alder adducts of isomers **5a** as confirmed by ^1H NMR: ^1H NMR for TCNE adduct of 1-methylcyclohexa-1,3-diene ($(CD_3)_2CO$, δ 3.0 to 7.0 region) δ 3.81 (complex d, 1), 6.46 (d, 1), 6.75 (apparent t, 1); ^1H NMR for TCNE adduct of 2-methylcyclohexa-1,3-diene ($(CD_3)_2CO$, δ 3.0 to 7.0 region) δ 3.66 (complex, 1), 3.77 (complex d, 1), 6.33 (d, 1); ^1H NMR for TCNE adduct of 5-methylcyclohexa-1,3-diene ($(CD_3)_2CO$, δ 3.0 to 7.0 region) δ 3.70 (broad, 1), 3.95 (broad, 1), 6.70 (d, 2); exact mass calcd for $C_{13}H_{10}N_4$ 222.0905, found 222.0908. Anal. Calcd for $C_{13}H_{10}N_4$: C, 70.26; H, 4.54; N, 25.20. Found: C, 70.10; H, 4.62; N, 25.03.

Method B: Via Direct Reduction of (Toluene)manganese Tricarbonyl Hexafluorophosphate (1a). A stirred suspension of (toluene)manganese tricarbonyl hexafluorophosphate (1.5 g, 0.0040 mol) in tetrahydrofuran (50 mL, freshly distilled) was treated at room temperature with a 1 M solution of potassium triisopropoxyborohydride in tetrahydrofuran (14.0 mL, 0.0140 mol). The solution was heated at reflux for 27 h, at which time quantitative conversion to the isomeric diene anions **3a** was observed (ν_{CO} (THF) 1925, 1831, 1782, cm^{-1}). The solution was flushed briefly with dry oxygen (5 min), during which time a dark brown precipitate formed. Subsequent workup and trapping with tetracyanoethylene was identical with that used for the dienes prepared from the bridged isomers **4a**. The reaction yielded 0.11 g (12% based on $C_6H_5(CH_3)Mn(CO)_3PF_6$) of the Diels–Alder adducts of 1-methyl- and 2-methylcyclohexa-1,3-diene as confirmed by ^1H NMR. See Method A above for spectroscopic details.

1,2- and 2,3-Dimethylcyclohexa-1,3-diene (5b). Method A: Via Deprotonation of Dimethylcyclohexenylmanganese Tricarbonyl Isomers (4b). 1,2- and 2,3-dimethylcyclohexa-1,3-diene were prepared from dimethylcyclohexenylmanganese tricarbonyl by the method (A) used to generate the isomeric cyclohexadienes **5a** with the following exceptions: 1.0 g of dimethylcyclohexenylmanganese tricarbonyl was used and the proportions of all reagents were adjusted accordingly. After treatment of the anions (ν_{CO} (THF) 1925, 1830, 1780 cm^{-1}) with dry oxygen, the solution was filtered through Celite and the solvent evaporated (20 mm, 25 °C) to give a pale yellow oil. Gas chromatographic analysis of this liquid against an internal cyclohexanone standard indicated an 81% recovery (based on **4b**) of the isomeric dimethylcyclohexa-1,3-dienes (**5b**); ^1H NMR for 1,2-dimethylcyclohexa-1,3-diene (CD_2Cl_2) δ 1.70 (s, 3), 1.74 (s, 3), 2.01 (br s, 2) 2.08 (br s, 2), 5.63 (d, m, 1), 5.79 (d, 1, J = 8.4); ^1H NMR for 2,3-dimethylcyclohexa-1,3-diene (CD_2Cl_2) δ 1.77 (s, 6), 2.01 (br s, 4), 5.51 (br s, 2). These values agree with those reported in the literature;[17] exact mass calcd for C_8H_{12} 108.0938, found 108.0937.

Method B: Via Direct Reduction of (*o*-Xylene)manganese Tricarbonyl Perchlorate (1b). 1,2- and 2,3-dimethylcyclohexa-1,3-diene were prepared from **1b** by the method (B) used to generate the isomeric cyclohexadienes **5a** with the following exceptions: 1.5 g of (*o*-xylene)manganese tricarbonyl perchlorate was used and all reagents were adjusted accordingly. After treatment of the anions (ν_{CO} (THF) 1925, 1830, 1786 cm^{-1}) with dry oxygen, the solution was filtered through Celite and the solvent evaporated (20 mm, 25 °C) to give 0.39 g of a yellow oil. ^1H NMR analysis of this oil indicated an approximate 10% overall yield of isomers **5b** based on (*o*-xylene)manganese tricarbonyl perchlorate. See Method A above for spectroscopic details.

1- and 2-Phenylcyclohexa-1,3-diene (5c). Method A: Via Deprotonation of Phenylcyclohexenylmanganese Tricarbonyl Isomers (4c). 1- and 2-phenylcyclohexa-1,3-diene were prepared from phenylcyclohexenylmanganese tricarbonyl by the method (A) used to generate the isomeric cyclohexadienes **5a** with the following exceptions: 1.0 g of phenylcyclohexenylmanganese tricarbonyl was used and the proportions of all reagents were adjusted accordingly. After treatment of the anions (ν_{CO} (THF) 1934, 1845, 1795 cm^{-1}) with dry oxygen, the solution was filtered through Celite and the solvent evaporated (20 mm, 25 °C) to give a yellow oil. Residual solvent was removed in vacuo (0.01 mm) for 10 min to give 0.47 g (89% based on phenylcyclohexenylmanganese tricarbonyl) of the desired product as a pale yellow oil: ^1H NMR for 1-phenylcyclohexa-1,3-diene (C_6D_6) δ 2.01 (m, 2), 2.08 (m, 2), 5.74 (m, 1), 6.02 (m, 1), 6.25 (d, 1, J = 6.6), 7.0–7.5 (Ph); ^1H NMR for 2-phenylcyclohexa-1,3-diene (C_6D_6) δ 2.01 (m, 2), 2.08 (m, 2), 5.85 (d t, 1, J = 8.4, 3.8), 5.94 (t, 1, J = 3.8), 6.33 (d d, 1, J = 8.4, 1.9), 7.0–7.5 (Ph). These values compare favorably to those reported in the literature;[18] exact mass calcd for $C_{12}H_{12}$ 156.0938, found 156.0940.

Method B: Via Direct Reduction of (Biphenyl)manganese Tricarbonyl Hexafluorophosphate (1c). 1- and 2-phenylcyclohexa-1,3-diene were prepared from **1c** by the method (B) used to generate the isomeric cyclohexadienes **5a** with the following exceptions: 1.5 g of (biphenyl)-manganese tricarbonyl hexafluorophosphate was used and all reagents were adjusted accordingly. After treatment of the anions (ν_{CO} (THF) 1934, 1845, 1795 cm^{-1}) with dry oxygen, the solution was filtered through Celite and the solvent evaporated (20 mm, 25 °C) to give 0.32 g of a pale yellow oil. Residual solvent was removed in vacuo (0.01 mm) for 10 min. ^1H NMR analysis indicated a sample of >90% purity representing a 56% overall recovery of dienes **5c** based on (biphenyl)manganese tricarbonyl hexafluorophosphate. See Method A above for spectroscopic details.

2-Methoxycyclohexa-1,3-diene (5d). Method A: Via Deprotonation of 3-Methoxycyclohexenylmanganese Tricarbonyl (4d). 2-Methoxycyclohexa-1,3-diene was prepared from 3-methoxycyclohexenylmanganese tricarbonyl by the method (A) used to generate the isomeric cyclohexadienes **5a** with the following exceptions: 1.0 g of 3-methoxycyclohexenylmanganese tricarbonyl was used and the proportions of all reagents were adjusted accordingly. After treatment of the anions (ν_{CO} (THF) 1928, 1819, 1778 cm^{-1}) with dry oxygen, the solution was filtered through Celite and the solvent evaporated (20 mm, 25 °C) to give a pale yellow oil. Gas chromatographic analysis of this oil against an internal cyclohexanone standard indicated an 83% recovery (based on 3-methoxycyclohexenylmanganese tricarbonyl) of 2-methoxycyclohexa-1,3-diene: ^1H NMR for 2-methoxycyclohexa-1,3-diene (CD_2Cl_2) δ 2.15 (m, 2), 2.25 (m, 2), 3.51 (s, 3), 4.67 (br s, 1), 5.75 (d, 1, J = 11.5), 5.91 (d t, 1, J = 11.5 2.4). These values agree with those reported previously;[11] exact mass calcd for $C_7H_{10}O$ 110.0731, found 110.0732.

Method B: Via Direct Reduction of (Anisole)manganese Tricarbonyl Hexafluorophosphate (1d). 1- and 2-methoxycyclohexa-1,3-diene were prepared from **1d** by the method (B) used to generate the isomeric cyclohexadienes **5a** with the following exceptions: 1.5 g of (anisole)manganese tricarbonyl hexafluorophosphate was used and all reagents were adjusted accordingly. After treatment of the anions (ν_{CO} (THF) 1928, 1819, 1778 cm^{-1}) with dry oxygen the solution was filtered through Celite and the solvent evaporated (20 mm, 25 °C) to give 0.26 g of a pale yellow oil. ^1H NMR analysis of this oil indicated on approximate 10% overall yield of dienes **5d** based on (anisole)manganese tricarbonyl hexafluorophosphate. A substantial fraction of the product mixture consisted of anisole: ^1H NMR for 1-methoxycyclohexa-1,3-diene (CD_2Cl_2) δ 2.15 (m, 2), 2.25 (m, 2), 3.58 (s, 3), 4.94 (d, 1, J = 12), 5.41 (m, 1), 5.90 (m, 1) [verified by means of comparison to a ^1H NMR spectrum (CD_2Cl_2) of an authentic sample]; see Method A for ^1H NMR spectrum of 2-methoxycyclohexa-1,3-diene.

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