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Metal Complexes of Trindane: Possible Precursors of Sumanene

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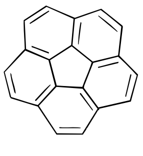
Trindane (the condensation trimer of cyclopentanone) yields complexes of the type (η^6-trindane)ML$_n$, where ML$_n$ = Cr(CO)$_3$ (**6**), Mo(CO)$_3$ (**8**), Mn(CO)$_3^+$ (**9**), or (C$_5$H$_5$)Fe$^+$ (**10a**,**10b**). X-ray crystallographic data are reported for (η^6-trindane)Cr(CO)$_3$ (**6**) and show that the three five-membered rings adopt envelope conformations in which the central methylene groups are bent toward the metal. When the chromium complex **6** is stirred with DMSO-d_6 in the presence of *t*-BuOK, up to 12 benzyl protons can be exchanged for deuterons, giving a mixture of partially deuterated products. In contrast, the iron complex **10b** undergoes complete H/D exchange at all 12 benzylic sites. The possibility of preparing *all-cis* hexamethyltrindane as a precursor to sumanene is discussed.

Introduction

While the burgeoning chemistry of C$_{60}$ continues to attract almost frantic world-wide attention,[1] rational attempts to synthesize fragments of the fullerene skeleton proceed at a more measured pace. Corannulene (C$_{20}$H$_{10}$; **1**), which represents the 5-fold-symmetric polar cap of C$_{60}$, was first obtained by Lawton and Barth in a now classic 18-step synthesis.[2] Since that time, shorter routes have been developed by Scott,[3] Siegel,[4] and Zimmermann;[5] nevertheless, since the final cyclization step requires flash vacuum pyrolysis (FVP), corannulene is still not available in quantities sufficient for the investigation of its organometallic chemistry.[6]



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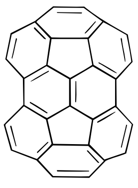
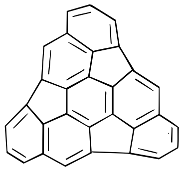


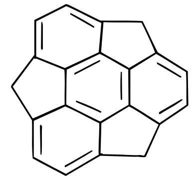
2a



2b

Very recently, Rabideau has reported elegant routes to the semi-buckminsterfullerenes (C$_{30}$H$_{12}$) **2a** and **2b**. Once again, however, the final cyclization involves FVP and the products are available only in minimal quantities.[7]

Any route to C$_{60}$ necessitates the introduction of some degree of strain, and a number of approaches have been analyzed by Jemmis, Mehta, and their colleagues.[8] They concluded that a viable concave intermediate would be the 3-fold-symmetric molecule C$_{21}$H$_{12}$ (**3**), for which the name *sumanene* was proposed.[9] Figure 1 depicts a sumanene fragment within C$_{60}$. At present, no synthesis of **3** has been reported, but the potential precursor **4** has been obtained in low yield by FVP and characterized by X-ray crystallography.[10]



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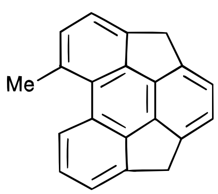

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Here we describe the preliminary steps that we have made toward developing an organometallic route to sumanene which does not require a low-yield FVP step. This approach introduces the three cyclopentene moieties early in the synthesis rather than trying to make a five-membered ring in the final cyclization, and a retrosynthetic analysis is presented in Scheme 1.

Results and Discussion

Synthetic and Structural Aspects. Tris(cyclopenteno)benzene (*trindane*; **5**) is readily prepared by acid-catalyzed condensation of three molecules of cyclopen-

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[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1997.

[1] (a) Kroto, H. W.; Allaf, A. W.; Balm, S. P. *Chem. Rev.* **1991**, *91*, 1213. (b) *Acc. Chem. Res.* **1992**, *25* (Special issue on Buckminsterfullerenes). (c) *Buckminsterfullerenes*; Billups, W. E., Ciufolini, M. A., Eds.; VCH Publishers: New York, 1993. (d) *The Fullerenes*; Kroto, H. W., Fischer, J. E., Cox, D. E., Eds.; Pergamon: Oxford, 1993. (e) Hirsch, A. *The Chemistry of the Fullerenes*; Thieme: New York, 1994.

[2] (a) Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 380. (b) Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 1730.

[3] (a) Scott, L. T.; Hashemi, M. M.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 7082. (b) Scott, L. T.; Bratcher, M. S.; Hagen, S. *J. Am. Chem. Soc.* **1996**, *118*, 8743.

[4] Borchardt, A.; Fuchicello, A.; Kilway, K. V.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 1921.

[5] Zimmermann, G.; Nuechter, U.; Hagen, S.; Nuechter, M. *Tetrahedron Lett.* **1994**, *35*, 4747.

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[7] (a) Rabideau, P. W.; Sygula, A. *Acc. Chem. Res.* **1996**, *29*, 235. (b) Rabideau, P. W.; Abdourazak, A. H.; Folsom, H. E.; Marcinow, Z.; Sygula, A.; Sygula, R. *J. Am. Chem. Soc.* **1994**, *116*, 7891. (c) Abdourazak, A. H.; Marcinow, Z.; Sygula, A.; Sygula, R.; Rabideau, P. W. *J. Am. Chem. Soc.* **1995**, *117*, 6410.

[8] Sastry, G. N.; Jemmis, E. D.; Mehta, G.; Shah, S. R. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1867.

[9] Sumanene is derived from the Sanskrit word *suman* which translates as "flower". The ring edges are considered to resemble petals; hence, the trivial name "sumanene" has been proposed for this molecule (see ref 10).

[10] Mehta, G.; Shah, S. R.; Ravikumar, K. *J. Chem. Soc., Chem. Commun.* **1993**, 1006.

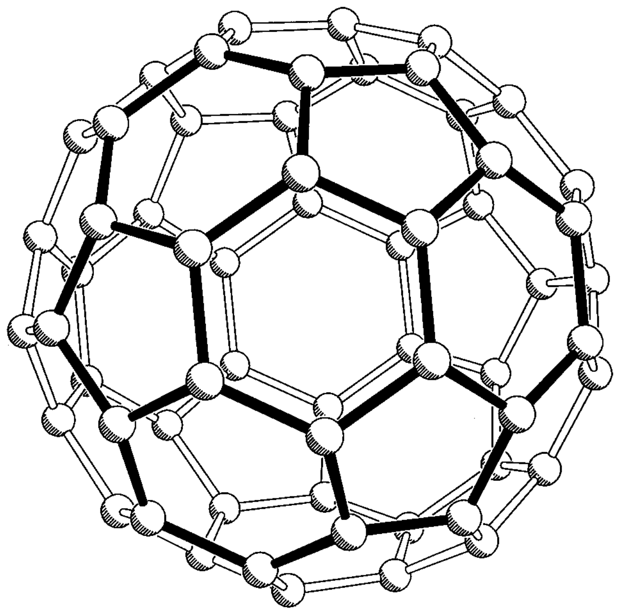
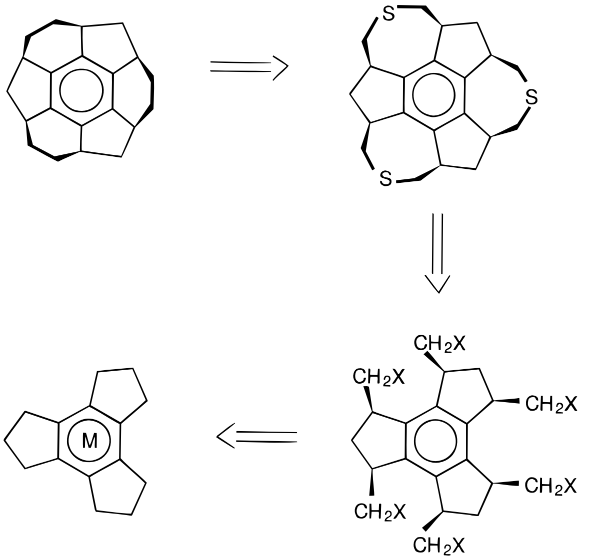
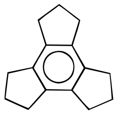


Figure 1. The sumanene motif is shown as a fragment of C_{60}.

Scheme 1. Proposed Route to Sumanene Skeleton



tanone.[11] It was reported some years ago by Katz and



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Slusarek that photochemical hexabromination of trindane and subsequent debromination yields dihydro-1*H*-trindene, the trianion of which can be complexed by a variety of organometallic fragments.[12,13] More recently, the tribenzo analogue of trindene, *viz.* truxene,[14] has been investigated by Lynch and the migration of Mn(CO)$_3$ or Re(CO)$_3$ units across this polycyclic surface has been unequivocally demonstrated.[15]

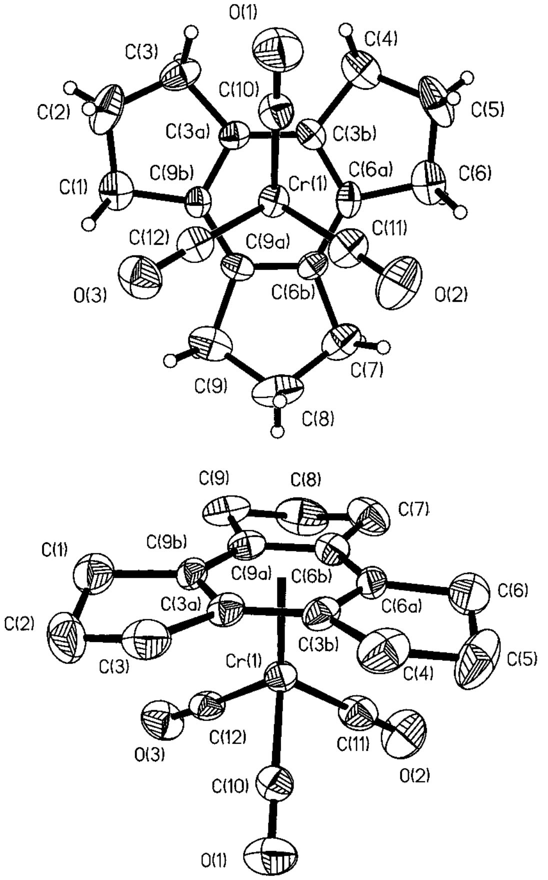

Figure 2. Molecular structure of $[(C_{15}H_{18})Cr(CO)_3]$ (**6**) showing (a) the staggered orientation of the tripodal Cr(CO)$_3$ moiety and (b) the envelope conformation of the peripheral rings. Thermal ellipsoids are shown at the 30% probability level. In (a) the hydrogen atoms are drawn arbitrarily small, and in (b) the hydrogen atoms are removed for clarity.

We are aware of only one reference to an organometallic derivative of trindane.[16] In that case, a series of cationic complexes of the type $^{99m}Tc(arene)_2^+$ was prepared where the arene was C_6H_6, C_6Me_6, C_6Et_6, indane, trindane, *etc.* These materials were injected into rats to study the biodistribution of radioactive technetium to test their viability as myocardial imaging agents. These studies were, of necessity, carried out on trace quantities of material, and no analytical nor spectroscopic data were reported for $[(trindane)_2Tc]^+PF_6^-$.

Trindane reacts with Cr(CO)$_6$ under standard conditions (dibutyl ether/THF/130 °C) to give yellow crystals of (η^6-trindane)Cr(CO)$_3$ (**6**), which was characterized by X-ray crystallography. As shown in Figure 2a, the tripodal moiety is oriented such that the three carbonyl ligands are staggered with respect to the cyclopentenyl rings. The observed bond lengths within the aromatic ring range from 1.376(6) to 1.401(6) Å; it is evident that

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[11] (a) Mayer, R. *Chem. Ber.* **1956**, *89*, 1443. (b) Petru, F.; Galik, V. *Chem. Listy* **1957**, *51*, 2371. (c) Wallach, O. *Chem. Ber.* **1897**, *30*, 1094.

[12] (a) Katz, T. J.; Slusarek, W. *J. Am. Chem. Soc.* **1980**, *102*, 1058.

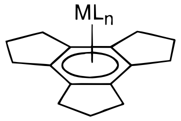
[13] (a) Helvenston, M. C.; Lynch, T. J. *J. Organomet. Chem.* **1989**, *359*, C50. (b) Lynch, T. J.; Helvenston, M. C.; Rheingold, A. L.; Staley, D. L. *Organometallics* **1989**, *8*, 1959. (c) Bang, H.; Lynch, T. J.; Basolo, F. *Organometallics* **1992**, *11*, 40. (d) Winter, R.; Pierce, D. T.; Geiger, W. E.; Lynch, T. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1949.

[14] (a) Seka, R.; Kellerman, W. *Chem. Ber.* **1942**, *75*, 1730. (b) Bergman, J.; Egestad, B. *Chem. Scr.* **1986**, *26*, 287. (c) Drake, J. A. G.; Jones, D. W. *Org. Magn. Reson.* **1980**, *14*, 276.

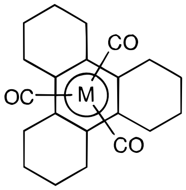
[15] Tisch, T. L.; Lynch, T. J.; Dominguez, R. *J. Organomet. Chem.* **1989**, *377*, 265.

[16] Wester, D. W.; Coveney, J. R.; Nosco, D. L.; Robbins, M. S.; Dean, R. T. *J. Med. Chem.* **1991**, *34*, 3284.

there is no marked bond fixation, indicating that Mills–Nixon effects are not significant in this system.[17] It is, however, noticeable that the five-membered rings adopt envelope conformations such that the three central methylene "wingtips" (C(2), C(5), C(8)) are directed in an *endo* fashion with respect to the metal (Figure 2b). An early X-ray study of free ligand **5** was based on film data and indicated some disorder in these regions of the molecule.[18] The structure of **6** may be profitably compared with that of the known molecules [tris(cyclohexeno)benzene]M(CO)$_3$, M = Cr(CO)$_3$ (**7a**), or Mn(CO)$_3^+$ (**7b**), which also crystallize in a staggered orientation; in those cases, the peripheral six-membered rings exhibit conventional half-chair conformations.[19]



ML$_n$ = Cr(CO)$_3$ 6
ML$_n$ = Mo(CO)$_3$ 8
ML$_n$ = [Mn(CO)$_3$]$^+$ 9
ML$_n$ = [Fe(C$_5$H$_5$)]$^+$ 10a, 10b



M = Cr 7a
M = Mn$^+$ 7b

In an analogous fashion, trindane reacts with Mo(CO)$_6$, BrMn(CO)$_5$/AgBF$_4$, (η^5-C$_5$H$_5$)Fe(CO)$_2$I / AlCl$_3$, or ferrocene/AlCl$_3$ to yield (η^6-trindane)Mo(CO)$_3$ (**8**), [(η^6-trindane)Mn(CO)$_3$]$^+$[BF$_4$]$^-$ (**9**), [(η^6-trindane)Fe(η^5-C$_5$H$_5$)]$^+$[BF$_4$]$^-$ (**10a**), or [(η^6-trindane)Fe(η^5-C$_5$H$_5$)]$^+$ [PF$_6$]$^-$ (**10b**), respectively. These complexes were readily identified by the usual mass spectrometric and infrared spectroscopic techniques, as well as by their ^{1}H and ^{13}C NMR spectra.

Trindane itself exhibits a very simple ^{1}H NMR spectrum, *i.e.*, a triplet (12H) for the benzylic protons and a quintet (6H) for the central methylene groups. The incorporation of a π-complexed organometallic fragment renders the faces of the trindane ligand inequivalent, thus giving rise to four ^{1}H NMR environments in molecules **6** and **8**–**10b**. The benzylic proton environments (each 6H) are easily distinguished from the two resonances for the central methylenes (each 3H) by their relative intensities, but the assignment to *exo* or *endo* positions is less trivial. One is tempted to assign the peaks on the basis of the different anisotropies of the ML$_n$ fragments,[20] but such an approach is not always unequivocal. Fortunately, the X-ray data for the chromium complex **6** provide a rational means of assigning these resonances. Figure 3 illustrates the dihedral angles between a pair of benzylic protons and those of the neighboring central methylene group in a five-membered ring. The ring conformations are not identical, but the dihedral angles differ only slightly, and in all cases the *endo*-benzylic proton and its adjacent *exo*-wingtip methylene hydrogen make a dihedral angle of approximately 90°. The Karplus relationship suggests that the corresponding $^3J_{\mathrm{H-H}}$ value between these particular protons should be rather small.[21] This is particularly evident in a series of ruthenium complexes of trindane, which are discussed in an accompanying paper.[22] These complexes show that, where coupling constants are clearly resolvable in the ^{1}H spectrum, one can assign the *exo* and *endo* positions definitively. For example, the 500 MHz ^{1}H NMR spectrum of (trindane)Mo(CO)$_3$ (**8**), exhibits three multiplets in the intensity ratio 12:3:3. Although the *exo* and *endo* benzylic environments are severely overlapped for this particular complex, the wingtip protons can be differentiated. The $^3J_{\mathrm{H-H}}$ value for the *exo*-benzylic/*endo*-wingtip protons (a diaxial interaction) is 12.2 Hz, while the coupling constant between the *endo*-benzylic/*exo*-wingtip protons (which are diequatorially disposed) is too small to be resolved. The other two coupling constants of 4.4 (*exo*-benzylic/*exo*-wingtip) and 9.6 Hz (*endo*-benzylic/*endo*-wingtip) are typical for axial–equatorial interactions. It is a reasonable assumption that the Cr (**6**) and Mo (**8**) complexes will have similar structures in the solution and solid states and justifies the assignment of the NMR spectrum of **8** on the basis of the solid state structure of **6**. The ^{1}H NMR spectral data for molecules **6** and **8**–**10b** are collected in the Experimental Section, and their overall similarities suggest that all of these trindane complexes adopt analogous conformations.

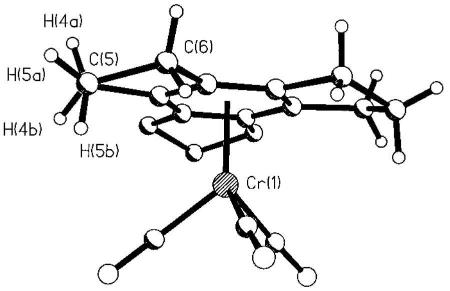


Figure 3. View of [(C$_{15}$H$_{18}$)Cr(CO)$_3$] (**6**) showing the dihedral angle between H5a (wingtip *exo*) and H4b (benzylic *endo*) to be approximately 90°. Some hydrogen atoms are removed for clarity.

In the course of the mass spectrometric characterization of the neutral complexes (trindane)M(CO)$_3$ (**6**, M = Cr; **8**, M = Mo), a series of peaks at *m*/*z* values much higher than that of the parent peak for **6** or **8** were consistently observed in the routine electron impact spectra. These peaks corresponded to [(trindane)$_2$M$_2$(CO)$_3$]$^+$ and subsequent fragmentation; this ion was also clearly detected in the chemical ionization spectra. One can speculate about the structure of such a species, and one viable candidate is the triple-decker system (η^6-trindane)M(μ-CO)$_3$M(η^6-trindane), **11**, entirely analo-

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(17) For a comprehensive summary of recent thinking on the Mills–Nixon effect, see: (a) Frank, N. L.; Baldridge, K. K.; Gantzel, P.; Siegel, J. S. *Tetrahedron Lett.* **1995**, *36*, 4389. (b) Bürgi, H.-B.; Baldridge, K. K.; Hardcastle, K.; Frank, N. L.; Gantzel, P.; Siegel, J. S.; Ziller, J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1454.

(18) Boyko, E. R.; Vaughan, P. A. *Acta Crystallogr.* **1964**, *17*, 152.

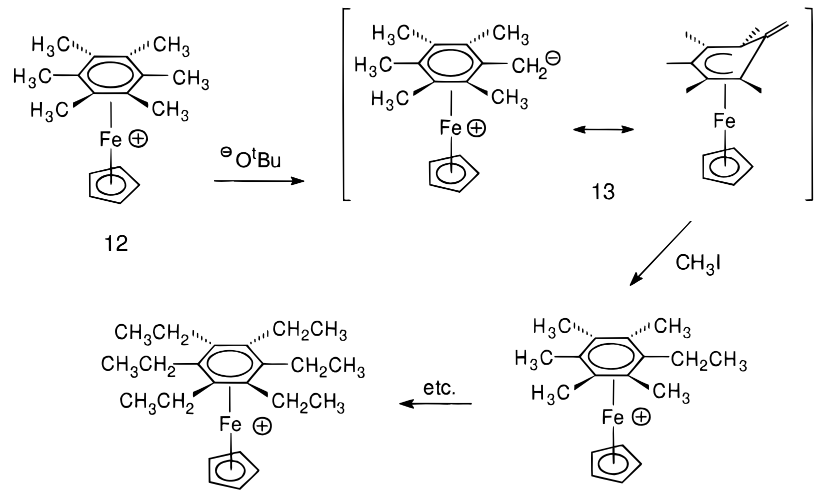
(19) Gommans, L. H. P.; Main, L.; Nicholson, B. K. *J. Organomet. Chem.* **1988**, *346*, 385.

(20) (a) McGlinchey, M. J.; Burns, R. C.; Hofer, R.; Top, S.; Jaouen, G. *Organometallics* **1986**, *5*, 104. (b) Top, S.; Jaouen, G.; Vessières, A.; Abjean, J.; Davoust, D.; Rodger, C. A.; Sayer, B. G.; McGlinchey, M. J. *Organometallics* **1985**, *4*, 2143. (c) Mailvaganam, B.; Perrier, R. E.; Sayer, B. G.; McCarry, B. E.; Bell, R. A.; McGlinchey, M. J. *J. Organomet. Chem.* **1988**, *354*, 325. (d) Moriarty, R. M.; Ku, Y.-Y.; Gill, U. S.; Gilardi, R.; Perrier, R. E.; McGlinchey, M. J. *Organometallics* **1989**, *8*, 960.

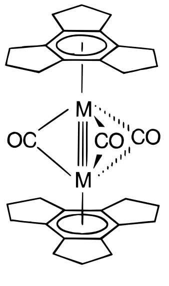
(21) (a) Karplus, M. *J. Am. Chem. Soc.* **1963**, *85*, 2870. (b) Bothner-By, A. A. *Adv. Magn. Reson.* **1965**, *1*, 195.

(22) Gupta, H. K.; Lock, P. E.; Hughes, D. W.; McGlinchey, M. J. *Organometallics*, accepted for publication.

Scheme 2. Metal-Promoted Conversion of a C_6Me_6 into a C_6Et_6 Ligand



gous to the known 30-electron complexes $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\mu\text{-CO})_3\text{Re}(\eta^5\text{-C}_5\text{Me}_5)$,[23] $[(\eta^5\text{-C}_5\text{Me}_5)_3\text{Ru}_2]^+$,[24] or $(\eta^6\text{-mesitylene})_3\text{Cr}_2$,[25] whereby the large surface area of the trindane ligands could provide steric protection at the outer layers of the sandwich. Since a number of triple-decker complexes first observed mass spectrometrically have been subsequently been isolated on a macroscale, as in the case of $[\text{Cp}_3\text{Ni}_2]^+$,[26] we are currently exploring rational routes to molecules of the type $[(\text{trindane})_2\text{M}_2(\text{CO})_3]$.

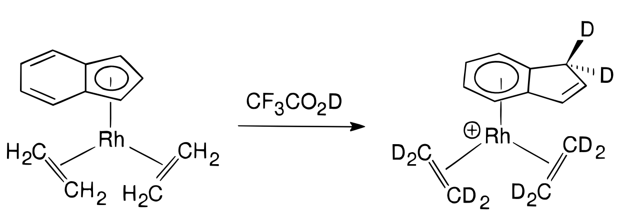


11 M = Cr, Mo

Deuterium Exchange Studies. It has been reported that base-catalyzed hydrogen/deuterium exchange occurs upon treatment of $(\text{indane})\text{Cr}(\text{CO})_3$ with DMSO-d_6 and sodium methoxide.[27] Moreover, it has been conclusively demonstrated that alkylation of (3-*O*-benzyl-17β-*O*-(*tert*-butyldimethylsilyl)estradiol)Cr$(\text{CO})_3$ occurs on the face anti to the π-bonded metal atom.[28] It was hoped that one could introduce deuterium atoms (or other substituents) only at the six *exo*-benzylic sites in $(\text{trindane})\text{Cr}(\text{CO})_3$, **6**. However, when **6** was allowed to react with *t*-BuOK in DMSO-d_6, multiple (0−12) deuterium incorporation at the benzylic H sites was observed, as confirmed by mass spectrometry evidence.

In recent years, many examples of arene activation by the $(\text{C}_5\text{H}_5)\text{M}^+$ moiety, where M = Fe or Ru, have been reported.[29,30] Typically, as shown in Scheme 2, Astruc has shown that treatment of $[(\text{C}_6\text{Me}_6)\text{Fe}(\text{C}_5\text{H}_5)]^+$ (**12**) with *t*-BuOK and excess methyl iodide leads to ready formation of the cation $[(\text{C}_6\text{Et}_6)\text{Fe}(\text{C}_5\text{H}_5)]^+$,[31] presumably *via* successive reactions of zwitterionic intermediates such as **13**.[32,33]

To test the viability of functionalizing all of the *exo*-benzylic sites in a $(\text{trindane})\text{ML}_n$ system, the iron cation **10b** was stirred with *t*-BuOK in DMSO-d_6. To our initial surprise, the product isolated was not the anticipated hexadeuterated product; instead, the ^{13}C NMR spectrum indicated that all 12 benzylic protons in $(\text{trindane})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]^+[\text{PF}_6]^-$ (**10b**) had been replaced by deuterons. This result was confirmed by mass spectrometry, which revealed the exclusive formation of **10b**-d_{12}. Such an observation is reminiscent of the reaction of $(\eta^5\text{-indenyl})\text{Rh}(\text{C}_2\text{H}_4)_2$ (**14**) with $\text{CF}_3\text{CO}_2\text{D}$, which shows not merely that Rh has undergone a haptotropic shift but also reveals incorporation of deuterium into the ethene ligands to give $[(\eta^6\text{-indene-}d_3)\text{Rh}(\text{C}_2\text{D}_4)_2]^+$ (**15**). This presumably occurs through



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[23] Hoyano, J. K.; Graham, W. A. G. *J. Chem. Soc., Chem. Commun.* **1982**, 27.

[24] Kudinov, A. R.; Rybinskaya, M. I.; Struchkov, Y.-T.; Yanovskii, A. I.; Petrovskii, P. V. *J. Organomet. Chem.* **1987**, *336*, 187.

[25] Lamanna, W. M.; Gleason, W. B.; Britton, D. *Organometallics* **1987**, *6*, 1583.

[26] (a) Schumacher, E.; Taubenest, R. *Helv. Chim. Acta* **1964**, *47*, 1525. (b) Werner, H.; Salzer, A. *Synth. Inorg. Met.—Org. Chem.* **1972**, *2*, 239.

[27] Trahanovsky, W. S.; Card, R. J. *J. Am. Chem. Soc.* **1972**, *94*, 2897.

[28] (a) Jaouen, G.; Top, S.; Laconi, A.; Couturier, D.; Brocard, J. *J. Am. Chem. Soc.* **1984**, *106*, 2207. (b) CH_2O has also been used to trap a chromium-stabilized benzylic anion, See: Brocard, J.; Goetgheluck, S.; Pelinski, L. *J. Organomet. Chem.* **1994**, *476*, C12.

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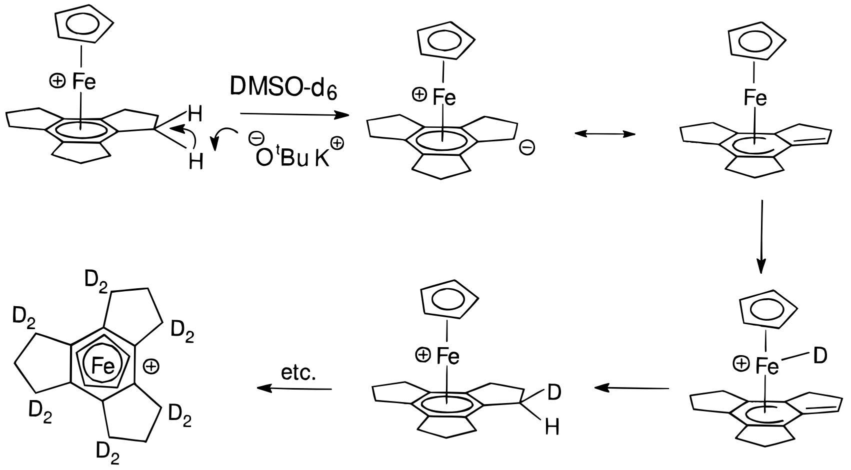
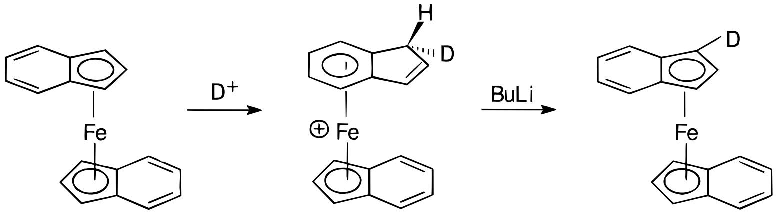
[32] For structural data on **13**, see: Hamon, J.-R.; Astruc, D; Roman, E. *J. Am. Chem. Soc.* **1981**, *103*, 2431.

[33] For kinetic data on related systems, see: Terrier, F.; Vichard, D.; Chatrousse, A.-P.; Top, S.; McGlinchey, M. J. *Organometallics* **1994**, *13*, 690.

Scheme 3. Proposed Mechanism for Deuteration of CpFe(trindane)$^+$



Scheme 4. Proposed Deuteration Mechanism in (indenyl)$_2$Fe



D$^+$ attack at the rhodium center with subsequent scrambling via an ethyl intermediate.[34]

One is led to the conclusion that, although deprotonation of (trindane)Fe(η^5-C_5H_5)]$^+$ presumably occurs on the *exo* face, the incoming deuteron can attack at the metal center and then migrate to an *endo* position, as indicated in Scheme 3. A similar mechanism has previously been invoked by Treichel to account for the sites of deuteration in the (indenyl)$_2$Fe system (Scheme 4).[35]

It may be the case that larger electrophiles will attack only at the *exo* positions, thus providing a straightforward route to [(*all-cis*-hexamethyltrindane)Fe(C_5H_5)]$^+$, and experiments toward the realization of this goal are in progress. In principle, enhanced activation of an aromatic ring can be achieved by complexation of a dicationic fragment, as in [(trindane)$_2$Ru]$^{2+}$2BF$_4^-$, and the syntheses, structures, and NMR spectra of this and several related molecules are the subject of an accompanying paper.[22]

Experimental Section

All manipulations were carried out using standard techniques under nitrogen. Acetone was dried over molecular sieves, and all other solvents were dried and distilled by standard procedures.[36] Cyclopentanone, [CpFe(CO)$_2$]$_2$, Mn$_2$(CO)$_{10}$, Cr(CO)$_6$, Mo(CO)$_6$, AgBF$_4$, and NH$_4$PF$_6$ were purchased from Aldrich Chemicals Co., Inc., and used as received. AlCl$_3$ was sublimed before use. Trindane was prepared as described in the literature.[11] Mass spectra (direct electron impact (DEI) and direct chemical ionization (DCI)) were obtained on a VG Analytical ZAB-E spectrometer with an accelerating potential of 8 kV and a resoultion of 1000. Electrospray (ESI) spectra were acquired on a Fisons Platform quadrupole mass spectrometer. NMR spectra were recorded on a Bruker DRX 500 or AC 200 spectrometer. ^{1}H and ^{13}C NMR chemical shifts are given relative to TMS. Infrared spectra were recorded on a Bio-Rad FTS-40 spectrometer, using NaCl windows.

Preparation of [(η^6-Trindane)Cr(CO)$_3$] (6). A mixture of trindane (0.891 g, 4.5 mmol) and Cr(CO)$_6$ (0.99 g, 4.5 mmol) in dry di-*n*-butyl ether (30 mL) and dry THF (20 mL) was heated under reflux in the dark for 72 h. The resulting yellow solution was then cooled and filtered, the solvent was removed under reduced pressure, and the residue was chromatographed on a silica gel column (eluent CH$_2$Cl$_2$/hexane 20/80). A yellow band was collected, the solvents were removed under reduced pressure, and the residue was crystallized from a CH$_2$Cl$_2$/hexane solution to give **6** (1.07 g, 3.20 mmol; 71%), mp 202 °C. ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ 2.71 (m, 12H), 2.10 (m, 3H), 1.99 (m, 3H). ^{13}C NMR (50.288 MHz, CDCl$_3$): δ 227.4 (Cr$-$*C*O), 110.6 (aromatic *C*), 30.2 (benzylic *C*H$_2$), 24.0 (wingtip *C*H$_2$). IR (CDCl$_3$): υ_{CO} 1869 (s), 1947 (s) cm^{-1}. MS *m*/*z* (DEI): 585 (100, [($C_{15}H_{18}$)$_2$Cr$_2$(CO)$_3$H]$^+$), 557 (30, [($C_{15}H_{18}$)$_2$Cr$_2$(CO)$_2$H]$^+$), 448 (15, [($C_{15}H_{18}$)$_2$Cr]$^+$), 334 (79, [M$^+$, ($C_{15}H_{18}$)Cr(CO)$_3^+$]), 278 (13, [M $-$ 2CO]$^+$), 250 (58, [M $-$ 3CO]$^+$), 197 (17, [$C_{15}H_{17}$]$^+$). MS *m*/*z* (DCI): 584 (16, [($C_{15}H_{18}$)$_2$Cr$_2$(CO)$_3$]$^+$), 335 (100, [M + H]$^+$), 197 (5, [$C_{15}H_{17}$]$^+$). Anal. Calcd for $C_{18}H_{18}O_3Cr$: C, 64.67; H, 5.39. Found: C, 64.49; H, 5.35.

Deuteration of [(η^6-Trindane)Cr(CO)$_3$] (6). In a typical experiment, [(η^6-trindane)Cr(CO)$_3$] (33.0 mg, 0.10 mmol) was dissolved in 2 mL of DMSO-*d*$_6$ containing 0.112 g of KO^{t}Bu and left under N$_2$ at room temperature for 1.5 h. Distilled water (5 mL) was added, and the mixture was filtered. The residue was extracted with diethyl ether, the ether layer was dried over anhydrous MgSO$_4$, and the solvent was removed under pressure, leaving 22 mg (0.065 mmol) of product. ^{1}H NMR (200 MHz, CDCl$_3$): δ 2.68 (m, br, 5H, benzylic C*H*$_2$), 2.02 (m, br, 6H, wingtip C*H*$_2$). ^{13}C NMR (50.288 MHz, CDCl$_3$): δ 227.5 (Cr-*C*O), 110.7 (aromatic *C*), 30.2 (benzylic *C*H$_2$), 24.1 (wingtip *C*H$_2$). MS *m*/*z* (DCI): 363 (8, [$C_{15}H_6D_{12}$Cr(CO)$_3$NH$_3$]$^+$), 361 (58, [$C_{15}H_8D_{10}$Cr(CO)$_3$NH$_3$]$^+$), 359 (100, [$C_{15}H_{10}D_8$Cr(CO)$_3$NH$_3$]$^+$), 358 (94, [$C_{15}H_{11}D_7$Cr(CO)$_3$NH$_3$]$^+$), 357 (60, [$C_{15}H_{12}D_6$Cr(CO)$_3$NH$_3$]$^+$), 356 (62, [$C_{15}H_{13}D_5$Cr(CO)$_3$NH$_3$]$^+$), 355 (53, [$C_{15}H_{14}D_4$Cr(CO)$_3$NH$_3$]$^+$), 354 (60, [$C_{15}H_{15}D_3$Cr-

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[35] Treichel, P. M.; Johnson, J. W. *J. Organomet. Chem.* **1975**, *88*, 207.

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Table 1. Crystal Data and Structure Refinement for 6

Crystal Data	
formula	$C_{18}H_{18}CrO_3$
fw	334.32
color, habit	yellow, multifaceted block
cryst size, mm	0.31 × 0.25 × 0.20
cryst syst	orthorhombic
space group	*Pbca* (No. 61)
a, Å	14.376(3)
b, Å	14.600(4)
c, Å	14.973(4)
V, Å^3	3145(1)
Z	8
D(calcd), Mg/m^3	1.413
μ, mm^{-1}	0.389
F(000)	1392
Data Collection	
diffractometer	Siemens P3
radiation	Ag Kα ($\lambda = 0.560\ 86$ Å)
T, K	292(2)
monochromator	graphite
θ range, deg	1.90−17.55
scan type	$\omega/2\theta$
std refln	3 std/97 reflns; no decay; 1.1% variation
index ranges	$-1 \le h \le 15$, $-1 \le k \le 15$, $-1 \le l \le 16$
no of reflns collected	2645
no of independent reflns used	2041 (R(int) = 0.0295)
abs corr	ψ scan
Solution and Refinement	
solution method	direct methods
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	2041/0/199
data:parameter	10.3:1
goodness-of-fit on F^2	0.745
R indices (all data)	R1 = 0.1090, wR2 = 0.0550
$\Delta\sigma$ max, e/Å^3	0.220
$\Delta\sigma$ min, e/Å^3	-0.162
weighting scheme	$[\sigma^2(F_o)^2 + (0.0094P)^2 + 0.00P]^{-1}$ $(P = (\max(F_o{}^2,0) + 2F_c{}^2)/3)$

Table 2. Selected Bond Distances and Bond Angles for 6

Cr(1)−C(3a)	2.214(4)	C(1)−C(2)	1.511(6)
Cr(1)−C(3b)	2.221(5)	C(2)−C(3)	1.504(6)
Cr(1)−C(6a)	2.199(5)	C(4)−C(5)	1.511(6)
Cr(1)−C(6b)	2.205(5)	C(5)−C(6)	1.500(5)
Cr(1)−C(9a)	2.200(5)	C(7)−C(8)	1.502(6)
Cr(1)−C(9b)	2.203(5)	C(8)−C(9)	1.528(5)
C(3a)−C(3b)	1.401(6)	C(9b)−C(1)	1.501(5)
C(3b)−C(6a)	1.388(6)	C(3)−C(3a)	1.491(5)
C(6a)−C(6b)	1.376(6)	C(3b)−C(4)	1.501(5)
C(6b)−C(9a)	1.378(6)	C(6)−C(6a)	1.494(6)
C(9a)−C(9b)	1.391(5)	C(6b)−C(7)	1.501(6)
C(9b)−C(3a)	1.392(6)	C(9)−C(9a)	1.494(6)
C(9b)−C(1)−C(2)	102.6(4)	C(3b)−C(4)−C(5)	102.7(4)
C(1)−C(2)−C(3)	106.9(4)	C(4)−C(5)−C(6)	106.2(4)
C(2)−C(3)−C(3a)	103.7(4)	C(5)−C(6)−C(6a)	105.1(4)
C(3)−C(3a)−C(9b)	109.7(5)	C(6)−C(6a)−C(3b)	108.3(5)
C(3a)−C(9b)−C(1)	110.5(4)	C(6a)−C(3b)−C(4)	111.5(5)
C(6b)−C(7)−C(8)	104.1(4)	C(3a)−C(3b)−C(6a)	119.6(5)
C(7)−C(8)−C(9)	105.3(4)	C(3b)−C(6a)−C(6b)	120.8(5)
C(8)−C(9)−C(9a)	103.7(5)	C(6a)−C(6b)−C(9a)	119.8(5)
C(9)−C(9a)−C(6b)	110.2(5)	C(6b)−C(9a)−C(9b)	120.5(5)
C(9a)−C(6b)−C(7)	110.1(5)	C(9a)−C(9b)−C(3a)	120.0(5)
		C(9b)−C(3a)−C(3b)	119.2(4)

$(CO)_3NH_3]^+)$, 353 (52, $[C_{15}H_{16}D_2Cr(CO)_3NH_3]^+$), 352 (12, $[C_{15}H_{17}D_1Cr(CO)_3NH_3]^+$), 351 (7, $[C_{15}H_{18}Cr(CO)_3NH_3]^+$), 346 (4, $[C_{15}H_6D_{12}Cr(CO)_3]^+$), 345 (10, $[C_{15}H_7D_{11}Cr(CO)_3]^+$), 344 (22, $[C_{15}H_8D_{10}Cr(CO)_3]^+$), 343 (19, $[C_{15}H_9D_9Cr(CO)_3]^+$), 342 (19, $[C_{15}H_{10}D_8Cr(CO)_3]^+$), 341 (21, $[C_{15}H_{11}D_7Cr(CO)_3]^+$), 340 (13, $[C_{15}H_{12}D_6Cr(CO)_3]^+$), 339 (5, $[C_{15}H_{13}D_5Cr(CO)_3]^+$), 338 (3, $[C_{15}H_{14}D_4Cr(CO)_3]^+$). MS *m/z* (DEI): 210 (5, $[C_{15}H_6D_{12}]^+$), 209 (16, $[C_{15}H_7D_{11}]^+$), 208 (13, $[C_{15}H_8D_{10}]^+$), 207 (20, $[C_{15}H_9D_9]^+$), 206 (70, $[C_{15}H_{10}D_8]^+$), 205 (65, $[C_{15}H_{11}D_7]^+$), 204 (50, $[C_{15}H_{12}D_6]^+$), 203 (39, $[C_{15}H_{13}D_5]^+$), 202 (45, $[C_{15}H_{14}D_4]^+$), 201 (37, $[C_{15}H_{15}D_3]^+$), 200 (47, $[C_{15}H_{16}D_2]^+$), 199 (15, $[C_{15}H_{17}D]^+$), 198 (9, $[C_{15}H_{18}]^+$).

Preparation of [(η^6-Trindane)Mo(CO)$_3$] (8). A mixture of trindane (1.98 g, 10 mmol) and $Mo(CO)_6$ (2.64 g, 10 mmol) in dry THF (50 mL) was heated under reflux for 66 h under nitrogen. The reaction mixture was cooled, concentrated to a volume of 20 mL under reduced pressure, and treated with excess hexane (approximately 50 mL). The resulting yellow powdery precipitate was filtered, dried, and recrystallized from chloroform/hexane (60/40) to give **8** as a yellow microcrystalline solid (2.34 g, 6.19 mmol; 62%), mp 145 °C (dec). ^1H NMR (500 MHz, CD_2Cl_2): δ 2.77 (m, 12H), 2.17 (d (J =12.4 Hz) of t (J = 4.4 Hz), 3H), 2.06 (d (12.4 J = Hz) of t (J = 12.2 Hz) of t (J = 9.6 Hz), 3H); ^2J(*exo*-wingtip/*endo*-wingtip) = 12.4 Hz; ^3J(*endo*-wingtip/*exo*-benzylic) = 12.2 Hz; ^3J(*endo*-wingtip/*endo*-benzylic) = 9.6 Hz; ^3J(*exo*-wingtip/*exo*-benzylic) = 4.4 Hz. ^{13}C NMR (50.288 MHz, $CDCl_3$): δ 224.6 (Mo−CO), 115.3 (aromatic *C*), 30.8 (benzylic *C*H_2), 24.6 (wingtip *C*H_2). IR ($CDCl_3$): υ_{CO} 1866 (s), 1947 (s) cm^{-1}. MS *m/z* (DEI): 676 (10, $[(C_{15}H_{18})_2Mo_2(CO)_3]^+$), 492 (5, $[(C_{15}H_{18})_2Mo]^+$), 380 (100, [M$^+$, $(C_{15}H_{18})Mo(CO)_3{}^+$]), 352 (15, $[M - CO]^+$), 324 (15, $[M - 2CO]^+$), 296 (5, $[M - 3CO]^+$), 198 (30, $[C_{15}H_{18}]^+$). MS *m/z* (DCI): 381 (100, $[M + H]^+$), 198 (22, $[C_{15}H_{18}]^+$). Mass spectral data quoted for ^{98}Mo; appropriate isotopic abundance patterns for Mo were observed. Anal. Calcd for $C_{18}H_{18}O_3Mo$: C, 57.14; H, 4.76. Found: C, 57.09; H, 4.66.

Preparation of [(η^6-Trindane)Mn(CO)$_3$][BF$_4$] (9). A mixture of $Mn(CO)_5Br$ (2.75 g, 10 mmol) and $AgBF_4$ (1.95 g, 10 mmol) in dry CH_2Cl_2 (50 mL) was heated under reflux for 3 h under nitrogen and then cooled to room temperature. To this reaction mixture a solution of trindane (1.98 g, 10 mmol) in dry CH_2Cl_2 (10 mL) was added, and the reaction mixture was refluxed overnight. After cooling and filtration, the filtrate was passed through Celite and concentrated to about one-third of its volume under reduced pressure, and excess hexane (50 mL) was added. The resulting orange-yellow solid precipitate was filtered and dried *in vacuo* to give **9** (2.37 g, 5.59 mmol; 56%), mp 227 °C. ^1H NMR (200 MHz, CD_2Cl_2): δ 3.03 (m, 6H), 2.75 (m, 6H), 2.33 (m, 3H), 1.85 (m, 3H). ^{13}C NMR (50.288 MHz, $CDCl_3$): δ 215.7 (Mn−*C*O), 117.2 (aromatic *C*), 29.4 (benzylic *C*H_2), 23.3 (wingtip *C*H_2). IR ($CDCl_3$): υ_{CO} 1996 (s), 2050 (s) cm^{-1}. MS spectrum *m/z* (positive ion electrospray): 337 (100, $[M]^+$), 281 (15, $[M - 2CO]^+$), 253 (35, $[M - 3CO]^+$. Anal. Calcd for $C_{18}H_{18}O_3BF_4Mn$: C, 50.94; H, 4.25. Found: C, 51.15; H, 4.05.

Preparation of [(η^6-Trindane)Fe(η^5-C$_5$H$_5$)][BF$_4$] (10a). A mixture of (η^5-C_5H_5)$Fe(CO)_2I$ (3.04 g, 10 mmol), $AlCl_3$ (1.34 g, 10 mmol), and trindane (1.98 g, 10 mmol) in dry $CHCl_3$ (50 mL) was refluxed under nitrogen for 17 h. The reaction mixture was cooled, 50 mL of water was added, and the resulting aqueous solution was filtered and washed several times with ether. Upon slow addition of an aqueous solution of $AgBF_4$ (1.76 g, 10 mmol) in water (10 mL), **10a** precipitated out as a beige solid. The precipitate was filtered, washed with water and then with ether, and dried *in vacuo*. Yield: 2.80 g, (6.90 mmol; 69%), mp 145 °C (dec). ^1H NMR (200 MHz, CD_3OD): δ 4.64 (s, 5H, C_5H_5), 3.05 (m, 6H), 2.79 (m, 6H), 2.30 (m, 6H). ^{13}C NMR (50.288 MHz, CD_3OD): δ 103.8 (aromatic *C*), 78.8 (Cp ring), 30.8 (benzylic *C*H_2), 24.1 (wingtip *C*H_2). MS *m/z* (positive ion electrospray): 319 (100, [M$^+$]).

Preparation of [(η^6-Trindane)Fe(η^5-C$_5$H$_5$)][PF$_6$] (10b). A mixture of ferrocene (1.81 g, 10 mmol), trindane (1.98 g, 10 mmol), $AlCl_3$ (2.68 g, 20 mmol), and Al powder (0.27 g, 10 mmol) was heated at 150−200 °C to melt together under nitrogen for 20 h. The melt was cooled and extracted with water (150 mL). The aqueous solution was filtered and washed several times with excess light petroleum ether, until all unreacted ferrocene was washed away. The salt **10b** was precipitated by adding an aqueous solution of NH_4PF_6 (1.63 g, 10 mmol) in water (10 mL). The precipitate was filtered, washed with water and ether, and dried *in vacuo* to give **10b** (3.99 g, 8.60 mmol; 86%), mp 230 °C (dec). ^{1}H NMR (200 MHz, acetone-d_6): δ 4.86 (m, 5H, Cp ring), 3.27 (m, 6H), 2.95 (m, 6H), 2.74 (m, 3H), 2.49 (m, 3H). ^{13}C NMR (50.288 MHz, acetone-d_6): δ 102.70 (aromatic *C*), 79.14 (Cp ring), 31.31 (benzylic *C*H$_2$), 23.94 (wingtip *C*H$_2$). MS *m/z* (positive ion electrospray): 319 (100, [M$^+$]).

Deuteration of [(η^6-Trindane)Fe(η^5-C$_5$H$_5$)][PF$_6$] (10b). [(η^6-Trindane)Fe(η^5-C$_5$H$_5$)][PF$_6$] (46.4 mg, 0.10 mmol) was dissolved in 2 mL of DMSO-d_6 containing 0.112 g KO^{t}Bu and left at room temperature overnight. Distilled water (5 mL) was added, and the mixture was filtered. The residue was extracted from 10 mL of ethanol, and the solvent was removed under pressure, leaving 30 mg (0.063 mmol) of product. ^{1}H NMR (200 MHz, acetone-d_6): δ 2.98 (s, br, integration not resolvable, benzylic C*H*$_2$), 2.50 (s, br, 3H, wingtip C*H*$_2$), 2.40 (s, br, 3H, wingtip C*H*$_2$). ^{13}C NMR (50.288 MHz, acetone-d_6): δ 78.4 (Cp ring), 30.1 (1:2:3:2:1 quintet, $^1J(^2\mathrm{D}-^{13}\mathrm{C}) = 19.3$ Hz, benzylic *C*D$_2$), 24.0 (wingtip *C*H$_2$). MS *m/z* (positive ion electrospray): 331 (100, [M$^+$-d_{12}, C$_{20}$H$_{11}$D$_{12}$Fe$^+$]), 319 (10, [M$^+$, C$_{20}$H$_{23}$Fe$^+$]). MS *m/z* (DEI): 210 (48, [C$_{15}$H$_6$D$_{12}$]$^+$), 198 (50, [C$_{15}$H$_{18}$]$^+$), 66 (100, [C$_5$H$_6$]$^+$).

X-ray Crystallographic Analysis. X-ray intensity data were collected at 292 K with the use of graphite-monochromated Ag Kα ($\lambda = 0.560\,86$ Å) radiation on a Siemens P3 diffractometer. Data were corrected for Lorentz and polarization factors. Crystal stability was monitored by measuring three standard reflections every 97 measurements. An empirical absorption correction was based on 360 data (transmission factors 0.313 (max) and 0.290 (min)). Calculations were performed with the use of the SHELXTL PC[37] program library. Crystal data, data collection and reduction, and structure details for C$_{15}$H$_{18}$O$_3$Cr (**6**) are listed in Table 1. Selected bond lengths and bond angles are listed in Table 2.

X-ray Analysis for C$_{15}$H$_{18}$O$_3$Cr (6). Crystals of compound **6** were grown from a solution of CH$_2$Cl$_2$/hexane by slow evaporation of the solvent. A yellow crystal measuring approximately 0.31 × 0.25 × 0.20 mm was mounted on a glass pin and aligned on the diffractometer. Unit cell parameters were determined by a least-squares fit of the angular settings of 38 reflections with $15.45° \leq 2\theta \leq 27.98°$. The structure was successfully solved in *Pbca* (No. 61) with $a = 14.376(3)$ Å, $b = 14.600(4)$ Å, $c = 14.973(4)$ Å, $V = 3145(1)$ Å^3, and $Z = 8$. The positions of the non-hydrogen atoms were determined by direct methods and refined anisotropically with the use of full-matrix least-squares methods. All H atoms were included with the use of a riding model; isotropic thermal parameters were set at 0.05 Å^2. The refinement on 2041 unique reflections (R(int) = 2.95%) from 3.80 to 35.10 in 2θ converged to R1 = 0.1090, wR2 = 0.0550, and GOF = 0.745 for 199 parameters.

Acknowledgment. Financial support from the Natural Sciences and Engineering Research Council of Canada and also from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. P.E.L thanks the Province of Ontario for a graduate scholarship. Mass spectra were obtained courtesy of Dr. Richard Smith of the McMaster Regional Centre for Mass Spectrometry.

Supporting Information Available: Tables of atomic parameters, including fractional atomic coordinates and equivalent isotropic displacement parameters, bond distances and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters and cell and packing diagrams for the crystal structure of **6** (8 pages). Ordering information is given on any current masthead page.

OM961077S

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[37] Sheldrick, G. M. *SHELXTL PC*, Release 4.1; Siemens Crystallographic Research Systems; Madison, WI, 1990.