Unexpected Reaction of (trindane)$Mn(CO)_3^+BF_4^-$ with Potassium *tert*-Butoxide: Three C−H Insertions and a Haptotropic Shift

Nada Reginato and Michael J. McGlinchey*

Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada

Received August 8, 2001

Summary: *(η^6-trindane)$Mn(CO)_3^+BF_4^-$ (**1**) reacts with Bu^tOK in THF in the presence of alkyl halides (CH_3I, $CH_2{=}CHCH_2Br$, CH_2Cl_2) to yield the corresponding (η^6-$C_{15}H_{18}$)$Mn(CO)_2X$, where X = I, Br, Cl. In contrast, **1** and Bu^tOK react, in the presence of a donor ligand, to generate (η^5-$C_{15}H_{15}$)$Mn(CO)_2L$, where L = CO, $P(OMe)_3$, PPh_3, in which the metal has migrated from the central ring onto a peripheral ring that has lost three hydrogens; (η^6-indane)$Mn(CO)_3^+BF_4^-$ behaves similarly. A mechanism is proposed in which the initially formed (η^6-trindane)$Mn(CO)_2CO_2Bu^t$ suffers loss of CO_2 and isobutene to yield the hydride (η^6-trindane)$Mn(CO)_2H$, which in turn undergoes three successive C−H insertions with concomitant loss of 2 mol of dihydrogen.*

In a continuation of our studies on metal complexes of tricyclopentanobenzene (trindane),[1,2] we chose to attempt the alkylation of the exo-benzylic positions of the ligand using the now classic Astruc methodology.[3] Eyman has already shown that [(hexamethylbenzene)-$Mn(CO)_3$]$^+$ readily undergoes abstraction of a benzylic proton to yield a corresponding cyclohexadienyl system that reacts with electrophiles to functionalize the benzylic site.[4] We here describe the reaction of [(trindane)-$Mn(CO)_3$]$^+BF_4^-$ (**1**) with potassium *tert*-butoxide and subsequent addition of alkyl halides or phosphines that led to unexpected rearrangement products.

When [(trindane)$Mn(CO)_3$]$^+BF_4^-$ (**1**) and Bu^tOK were mixed as dry solids and then treated with allyl bromide (or methyl iodide) in THF, the major product, after chromatographic separation, was a deep red crystalline material whose NMR, mass, and infrared spectra indicated it to be (trindane)$Mn(CO)_2Br$ (**2**) (or the corresponding iodide, **3**). The X-ray crystal structure[5] of **2** appears as shown in Figure 1 and is reminiscent of the geometry previously reported for (C_6Me_6)$Mn(CO)_2Cl$,

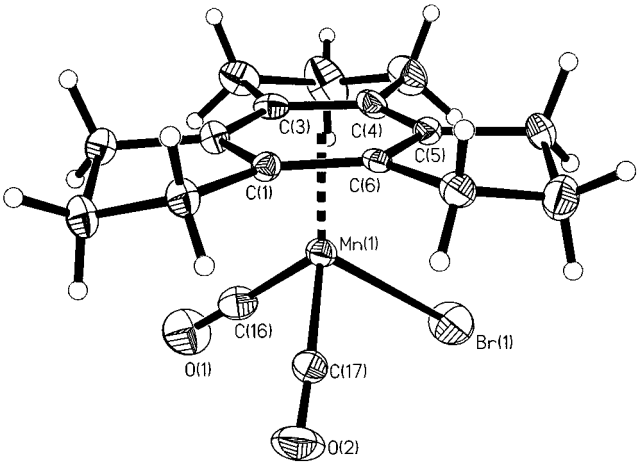


Figure 1. X-ray structure of (η^6-trindane)$Mn(CO)_2Br$ (**2**) (30% ellipsoids).

whereby the tripod is staggered relative to the alkyl substituents.[6] Moreover, the cyclopentene rings in **2** (and **3**) adopt envelope conformations such that the "wingtip" methylene groups are folded endo with respect to the plane of the central six-membered ring, as was previously found in both (trindane)$Cr(CO)_3$ and (trindane)$RuCl_2[P(OMe)_3]$.[1,2]

Replacement of a carbonyl by a phosphine or a halide in [(C_6Me_6)$Mn(CO)_3$]$^+$ requires either photolysis or use of Me_3NO;[6−8] therefore, it was somewhat surprising that the formation of the (trindane)$Mn(CO)_2X$ species **2** and **3** should have occurred so readily. Since (C_6Me_6)Mn-$(CO)_2H$ is known to yield (C_6Me_6)$Mn(CO)_2Cl$ in the presence of CCl_4 or $CHCl_3$ (but not CH_2Cl_2),[6] one is tempted to invoke the intermediacy of (trindane)Mn-$(CO)_2H$ (**4**). Eyman has shown that (C_6Me_6)$Mn(CO)_2I$ reacts with *tert*-butyllithium to yield thermally stable (C_6Me_6)$Mn(CO)_2H$, apparently via loss of isobutene from the presumed *tert*-butyl intermediate.[9] Since the cationic complexes [(arene)$Mn(CO)_3$]$^+$ (arene = C_6H_6, C_6Me_6) react with methoxide in methanol to yield the rather unstable esters (arene)$Mn(CO)_2CO_2Me$,[10] one might

* To whom correspondence should be addressed. Phone: (905) 525-9140, ext. 27318. Fax: (905) 522-2509. E-mail: mcglinc@mcmaster.ca.

(1) Gupta, H. K.; Lock, P. E.; McGlinchey, M. J. *Organometallics* **1997**, *16*, 3628.

(2) Gupta, H. K.; Lock, P. E.; Hughes, D. W.; McGlinchey, M. J. *Organometallics* **1997**, *16*, 4355.

(3) (a) Hamon, J.-R.; Saillard, J.-Y.; Le Beuze, A.; McGlinchey, M. J.; Astruc, D. *J. Am. Chem. Soc.* **1982**, *104*, 7549. (b) Valério, C.; Alonso, E.; Ruiz, J.; Blais, J.-C.; Astruc, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 1747 and references therein.

(4) (a) LaBrush, D. M.; Eyman, D. P.; Baenziger, N. C.; Mallis, L. M. *Organometallics* **1991**, *10*, 1026. (b) Moler, J. L.; Eyman, D. P.; Neilson, J. M.; Morken, A. M.; Schauer, S. J.; Snyder, D. B. *Organometallics* **1993**, *12*, 3304.

(5) Crystal data for **2**: $C_{17}H_{18}MnBrO_2$, $T = 299 \pm 2$ K, space group $P2_1/c$, $a = 9.8049(13)$ Å, $b = 8.8852(13)$ Å, $c = 18.682(3)$ Å, $\beta = 94.825(3)°$, $V = 1621.8(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.594$ g cm^{-3}, $\mu = 3.278$ mm^{-1}; R1 = 0.0550 and wR2 = 0.1313 (based on F^2) for 245 variables and 10 041 reflections (2318 unique and $R_{int} = 0.0907$) with $I > 2\sigma(I)$, $2.08 < \theta < 23.25°$, GOF = 1.075.

(6) Bernhardt, R. J.; Wilmoth, M. A.; Weers, J. J.; LaBrush, D. M.; Eyman, D. P.; Huffman, J. C. *Organometallics* **1986**, *5*, 883.

(7) (a) Kane-Maguire, L. A. P.; Sweigart, D. A. *Inorg. Chem.* **1979**, *18*, 700. (b) Sun, S.; Dullaghan, C. A.; Sweigart, D. A. *J. Chem. Soc., Dalton Trans.* **1996**, 4493. (c) Pike, R. D.; Sweigart, D. A. *Coord. Chem. Rev.* **1999**, *187*, 183.

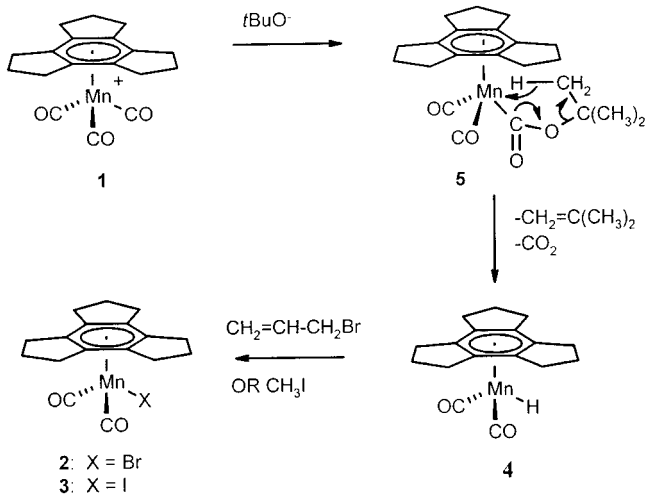
(8) Bernhardt, R. J.; Eyman, D. P. *Organometallics* **1984**, *3*, 1445.

(9) Schlom, P. J.; Morken, A. M.; Eyman, D. P.; Baenziger, N. C.; Schauer, S. J. *Organometallics* **1993**, *12*, 3461.

(10) (a) Walker, P. J. C.; Mawby, R. J. *Inorg. Chim. Acta* **1973**, *7*, 621. (b) There is an early report of $Bu^t{-}OCO{-}Co(CO)_4$: Heck, R. F. *J. Organomet. Chem.* **1964**, *2*, 195.

10.1021/om010722e CCC: $20.00
Publication on Web 09/07/2001

Scheme 1



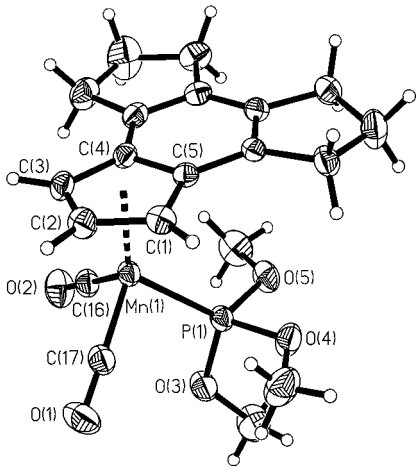


Figure 2. X-ray structure of (η^5-$C_{15}H_{15}$)$Mn(CO)_2[P(OMe)_3]$ (**7**) (30% ellipsoids).

propose that a reaction between **1** and Bu^{t}OK could generate the *tert*-butyl ester **5**, which readily eliminates both isobutene and carbon dioxide via a very favorable six-membered transition state to produce **4**, as depicted in Scheme 1. Treatment of **1** with Bu^{t}OK in CH_2Cl_2 gave (trindane)$Mn(CO)_2Cl$, suggesting that **4** is more reactive than (C_6Me_6)$Mn(CO)_2H$ toward alkyl halides.

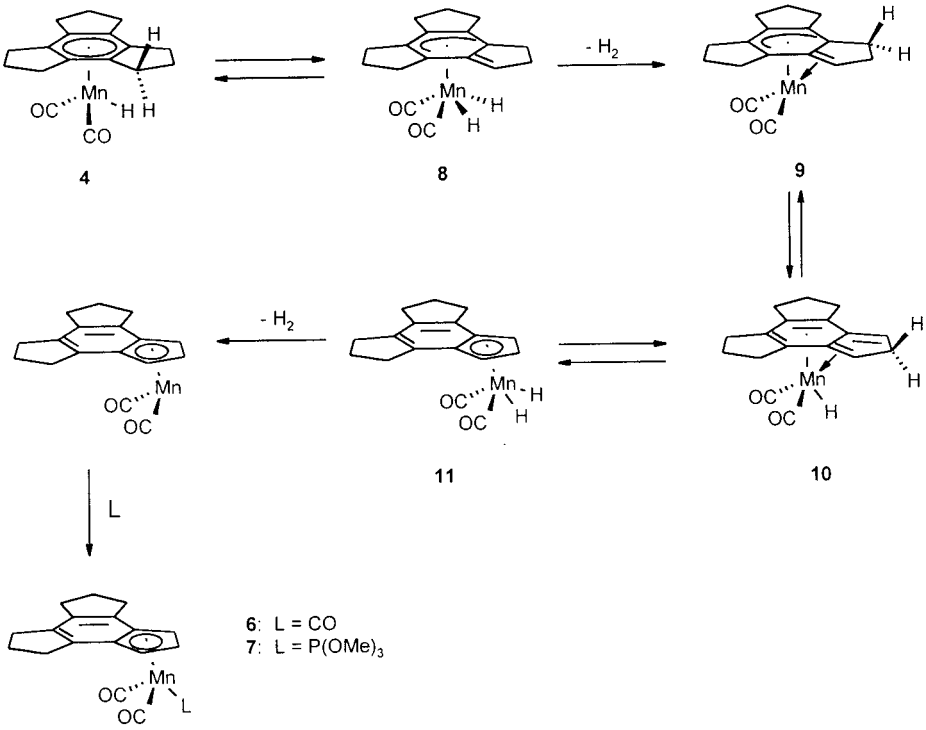
Numerous attempts to synthesize **4** by treatment of (trindane)$Mn(CO)_2Br$ (**2**) with $Bu_4N^+BH_4^-$ or to detect the hydride signal by NMR at low temperature were unsuccessful. Consequently, we chose to try to intercept the purported hydride **4** either as (trindane)Mn(CO)-(PR_3)H or as the formyl complex (trindane)Mn(CO)-(CHO)(PR_3).

When the cation **1** and Bu^{t}OK were treated with trimethyl phosphite in THF and stirred at 40 °C for 20 h, to our surprise, the two products, after chromatographic separation, were the yellow crystalline materials **6** and **7**, whose ^{1}H and ^{13}C NMR spectra indicated that the 3-fold symmetry of the trindane ligand had been broken. The mass spectra of **6** and **7** exhibited parent peaks at *m*/*z* 334 and 430, respectively, indicating a molecular formula of ($C_{15}H_{15}$)$Mn(CO)_2L$, where L = CO for **6** and L = $P(OMe)_3$ for **7**. The latter product was definitively characterized by X-ray crystallography[11] (Figure 2) as an η^5-indenyl complex in which the manganese has migrated from the central arene onto a five-membered ring that has evidently lost three hydrogens.

The analogous complex where L = PPh_3 is also preparable in this manner. Likewise, the corresponding reactions of (η^6-indane)$Mn(CO)_3^+$ and Bu^{t}OK yield the known complexes (η^5-indenyl)$Mn(CO)_2L$, where L = $P(OMe)_3$, PPh_3.[12]

We suggest that, in the absence of an alkyl halide, the initially generated (trindane)$Mn(CO)_2H$ (**4**) under-

Scheme 2



goes a hydrogen migration from an endo-benzyl site onto the metal, thus producing the cyclohexadienyl complex **8**, which in turn loses dihydrogen to give **9**. A second endo-benzyl hydrogen migration to yield the isoindene framework **10** is followed by the final hydrogen migration, producing **11**. Loss of dihydrogen and incorporation of either a carbonyl or a phosphite ligand would give the observed products **6** and **7**, respectively, as depicted in Scheme 2.

In seeking a precedent for the proposal outlined above, we note the report by Ustynyuk[13] whereby (η^5-indenyl)$Cr(CO)_3Me$ undergoes a "ricochet reaction" in which the methyl is delivered onto the five-membered ring and the tricarbonylchromium fragment migrates to the six-membered ring. DFT calculations by these workers indicate that the reaction proceeds through an isoindene structure in which the chromium is bonded to the diene portion of the six-membered ring and one double bond of the cyclopentadiene ring and provide some justification for the structures **9** and **10** proposed in Scheme 2. Similar intermediates are also invoked in the η^6 to η^5 haptotropic shifts observed for (fluorenyl)-ML_n or (cyclopenta[*def*]phenanthrenyl)ML_n systems, where $ML_n = [Cr(CO)_3]^-$, $Mn(CO)_3$.[14]

Other experiments to probe the detailed mechanism and generality of this novel rearrangement are in progress and will be the subject of a future report.

Acknowledgment. Financial support from the NSERC of Canada is gratefully acknowledged. Mass spectra were acquired courtesy of Dr. Kirk Green of the McMaster Regional Mass Spectrometry Facility. We also thank Dr. James F. Britten for X-ray crystallographic advice.

Supporting Information Available: Tables giving X-ray crystallographic data for **2** and **7** and text giving synthetic details and characterization data for all new compounds prepared in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

OM010722E

(11) Crystal data for **7**: $C_{20}H_{24}MnO_5P$, $T = 299 \pm 2$ K, space group $P2_1/c$, $a = 9.7266(8)$ Å, $b = 22.349(2)$ Å, $c = 9.6034(8)$ Å, $\beta = 106.4810(10)°$, $V = 2001.8(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.428$ g cm^{-3}, $\mu = 0.767$ mm^{-1}; R1 = 0.0348 and wR2 = 0.0867 (based on F^2) for 244 variables and 17 829 reflections (4584 unique and $R_{int} = 0.0305$) with $I > 2\sigma(I)$, $1.82 < \theta < 27.50°$, GOF = 1.029.

(12) King, R. B. *J. Organomet. Chem.* **1970**, *23*, 527.

(13) Trifonova, O. I.; Ochertyanova, E. A.; Akhmedov, N. G.; Roznyatovsky, V. A.; Laikov, D. N.; Ustynyuk, N. A.; Ustynyuk, Y. A. *Inorg. Chim. Acta* **1998**, *280*, 328.

(14) (a) Nicholas, L. M.; Kerber, R. C.; Steifel, E. I. *Inorg. Chem.* **1971**, *10*, 1519. (b) Treichel, P. M.; Johnson, J. W. *J. Am. Chem. Soc.* **1977**, *99*, 427. (c) Decken, A.; Britten, J. F.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1993**, *115*, 7275. (d) Decken, A.; Rigby, S. S.; Girard, L.; Bain, A. D.; McGlinchey, M. J. *Organometallics* **1997**, *16*, 1308. (e) Veiros, L. F. *Organometallics* **2000**, *19*, 3127.