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Preliminary communication

Cationic 1,2,3-trimethoxybenzene manganese tricarbonyl complexes: structure and reactivity

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Abstract

1,2,3-Trimethoxybenzene reacts with $BF_4Mn(CO)_5$ in CH_2Cl_2 or $ClMn(CO)_5$ in CF_3CO_2H then with HPF_6 to afford 1,2,3-trimethoxybenzene manganese tricarbonyl tetrafluoroborate 2a or hexafluorophosphate 2b, the X-ray structure of which indicates an arene nonplanarity and an eclipsed conformation of C1, C3 and C5 carbons; $LiEt_3BH$, $EtMgBr$, and $SiR_3CHLiCN$ (R = Me, i-Pr) additions occur mainly on the C5 eclipsed carbon of complex 2a.

Keywords: η^6-Arene; η^5-Cyclohexadienyl-tricarbonylmanganese complexes; Regioselectivity; Nucleophilic addition

1. Introduction

(η^6-Arene) tricarbonylmanganese complexes have significant applications in organic synthesis [1]. Their reactivity toward a variety of carbon nucleophiles and toward hydrides is well-documented and gives rise to neutral η^5-cyclohexadienyl-Mn(CO)$_3$ complexes **1a** [2]. These η^5-Mn complexes are usually air stable which is contrary to the corresponding anionic η^5-cyclohexadienylchromiumtricarbonyl complexes **1b** [3a] which give well-characterized bimetallic neutral complexes **1c** in reaction with ClSnPh$_3$ [3b,c]. We are currently studying the regioselectivity of the addition of hydride and carbon nucleophiles to arene metal complexes particu-

larly to 1,2,3-trimethoxybenzene complex **2**. Indeed, functionalization of the C5 carbon could give rise to the precursors of natural products (for example, mescaline which is substituted with a CH_2–CH_2–NH_2 chain) as well as compounds having interesting pharmaceutical properties. In this communication we report the first results of this study.

Results and discussion

1,2,3-Trimethoxybenzene reacts with $BF_4Mn(CO)_5$ [4a], (made in situ from $BrMn(CO)_5$ and $AgBF_4$) in CH_2Cl_2 yielding complex **2a** [1] (95% yield). If

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[1] Satisfactory spectral and analytical data have been obtained for all new compounds. **2a**: ^{1}H NMR (Me$_2$CO, d$_6$) δ 4.08 (s, OMe, C2), 4.27 (s, OMe C1,3), 6.25 (d, *J* 7 Hz, H4,6), 7.00 (t, *J* 7 Hz, H5); **3a** ^{1}H NMR (C$_6$D$_6$) δ 1.65 (d, *J* 13 Hz, H5$_{exo}$), 2.10 (d, *J* 9 Hz, H4,6), 2.20 (dd, *J* 9 and 13 Hz, H5$_{endo}$), 2.85 (s, OMe C1,3), 3.86 (s, OMe C2); **3c** ^{1}H NMR (CDCl$_3$) δ 1.09 (d, *J* 6 Hz, (C*H*$_3$)$_2$CH)$_3$Si), 1.22 (m, Si(C*H*-Me$_2$)$_3$), 1.44 (d, *J* 6 Hz, C*H*CNSi-iPr$_3$), 2.83 (dd, *J* 6 and 1.9 Hz, H4or6), 2.93 (quad, *J* 6 Hz, H5$_{endo}$), 3.14 (dd, *J* 6 and 1.9 Hz, H6or4), 3.43 (s, OMe C1or3), 3.58 (s, OMe C3or1), 4.02 (s, OMe C2); **3d** ^{1}H NMR (CDCl$_3$) δ 1.67 (d, *J* 6Hz, C*H*$_2$CN), 2.90 (m, H4,5$_{endo}$6), 3.48 (s, OMe C1,3), 4.06 (s, OMe C2); **3e** [1]H NMR (CDCl$_3$) δ 0.19 (s, (C*H*$_3$)$_3$Si), 1.28 (d, *J* 6.3 Hz, C*H*CNSiMe$_3$), 2.77 (quad, *J* 6.3 Hz, H5$_{endo}$), 2.84 (dd, *J* 6.3 and 1.9 Hz, H4or6), 3.09 (dd, *J* 6.3 and 1.9 Hz, H6or4), 3.47 (s, OMe, C1or3), 3.58 (s, OMe, C3or1), 4.06 (s, OMe C2); **4** [1]H NMR (CDCl$_3$) δ 0.99 (t, *J* 6.1 Hz, C*H*CN), 2.52 (quad, *J* 6.1 Hz, H5$_{endo}$), 2.66 (dd, *J* 6.1 and 1.4 Hz, H4or6) 2.76 (dd, *J* 6.1 and 1.4 Hz, H6or4) 3.50 (s, OMe, C1or3), 3.59 (s, OMe C3or1), 3.99 (s, OMe, C2); **6a** [1]H NMR (CDCl$_3$) δ 0.16 (s, (C*H*$_3$)$_3$Si), 1.29 (d, *J* 6 Hz, C*H*CNSiMe$_3$), 2.81 (quad, *J* 6 Hz, H6$_{endo}$), 3.13 (tdd, *J* 6, 2.3 and 1.4 Hz, H1or5), 3.37 (tdd, *J* 6, 2.3 and 1.4 Hz, H5or1), 4.94 (m, H2,4), 5.84 (tt, *J* 6 and 1.4 Hz, H3); **7a** [1]H NMR (Me$_2$CO, d$_6$) δ 0.26 (s, (C*H*$_3$)$_3$Si), 3.03 (t, *J* 5.5 Hz, H6$_{endo}$), 3.37 (tdd, *J* 5.5, 2.7 and 1.3 Hz, H1or5), 3.67 (tdd, *J* 5.5, 2.7 and 1.3 Hz, H5or1), 5.21 (td, *J* 5.5 and 1.3 Hz, H2or4), 5.31 (td, *J* 5.5 and 1.3 Hz, H2or4), 6.03 (tt, *J* 5.5 and 1.3 Hz, H3).
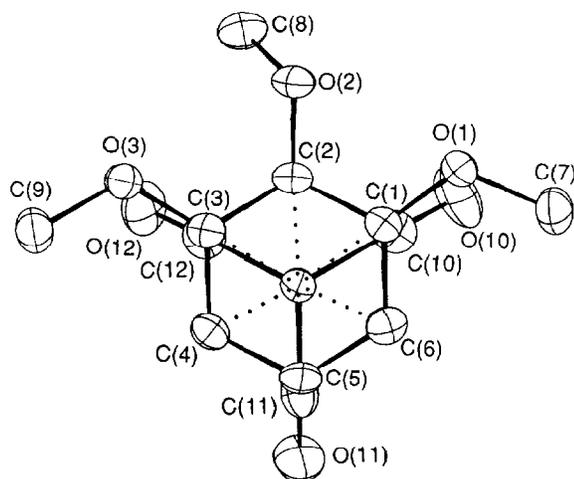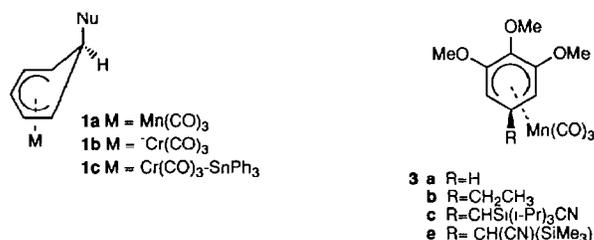
Fig. 1. X-ray structure of complex 2b C_6H_3 $(1,2,3-(OMe)_3)Mn(CO)_3$, PF_6. Selected bond lengths (Å): Mn–C(1), 2.283(5); Mn–C(2), 2.248(5); Mn–C(3), 2.287(5); Mn–C(4), 2.190(5); Mn–C(5), 2.146(5); Mn–C(6), 2.190(5); Mn–C(10), 1.807(6); O(10)–C(10), 1.151(6); Mn–C(11), 1.834(6); O(11)–C(11), 1.128(7); Mn–C(12), 1.817(6); O(12)–C(12), 1.135(6).

ClMn(CO)$_5$, CF$_3$CO$_2$H and 1,2,3-trimethoxybenzene are heated for 2 h, after evaporation under reduced pressure and extraction of the residue with ether and aqueous hexafluorophosphoric acid [4b], complex 2b is obtained in only 8% yield. Recrystallisation of the powder 2b in a mixture of acetone and ether affords yellow single crystals which are suitable for X-ray spectroscopy [2]: indeed cationic arene–metal complexes are usually described as amorphous powders [5]. The structure indicates an eclipsed conformation of C1, C3, and C5 carbons by the manganese carbonyl bonds (Fig. 1). It can be related to the structure of the chromium analogue complex [6]. In both cases, the longest metal–$C_{aromatic}$ bonds are metal to C1 and C3 distances and the shortest metal–$C_{aromatic}$ bond is metal to C5 distance. External methoxy groups attached to C1 and C3 carbons lie

almost in the plane of the arene ring. This is not the case of the central methoxy group (C2 carbon): indeed the C-2 methoxy group unexpectedly points out toward the Mn(CO)$_3$ entity in good agreement with theoretical conformational study of trimethoxybenzene [7a] and X-ray structures of trimethoxybenzene derivatives [7a] and 1-trimethylsilyl 2,3-dimethoxybenzenetricarbonyl chromium complex [7b]. The angle: C(8), O(2), C(2) is 118.3(4)°. The η^6-aromatic cycle presents an unusual structure, the deformation ($-9.2°$) of C-2 from the plane of carbons 3, 4, 5, 6. 1 is unprecedented and can be compared with those described in the case of tricarbonylchromium complexes of diethylaniline [6], anisole [8a], and acetophenone [8b] ($+5.89°$, $+1.90°$ and $-1.04°$ respectively). It is also worthy to note that the longest Mn–C11 bond is associated with the shortest C11–O11 bond in agreement with the slight triple bond character of the C11–O11 bond which could stabilize the electrophilic eclipsed C-5 carbon.

Treatment of (η^6-1,2,3-trimethoxybenzene)manganesetricarbonyl tetrafluroborate 2a with L-Selectride (1 equiv.) in THF ($-78°$C, 1 mn; 25°C, 5 mn) affords the neutral complex 3a, R=H (40% yield) [9]. Treatment of complex 2a with EtMgBr in THF (1.5 equiv., $-78°$C, 1 mn) or Si(i-Pr)$_3$CHLiCN (1.2 equiv.) in THF ($-78°$C, 1 mn) yields the neutral η^5-cyclohexadienyl complexes 3b (R = Et, 24% yield) or 3c (R = CHSi(i-Pr)$_3$CN, 38% yield). If SiMe$_3$CHLiCN is used as nucleophile under the same experimental conditions, desilylated complex 3d is obtained as the major product (38% yield) [10] as well as a dinuclear complex 4 (12% yield, Eq. (1))
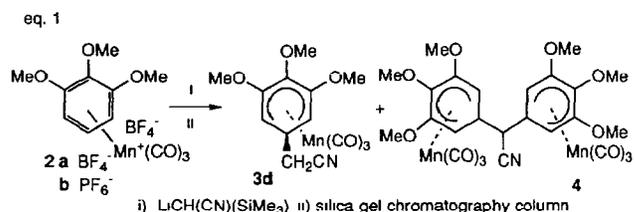
[2] (a) The Mn is bound to the six carbons of the phenyl ring. The Mn atom is shifted away from the 2-OMe group as shown by the longer Mn to C2 vs. C5 distances (2.248(5), 2.146(5) Å, respectively) but is centered laterally as shown by the distances from Mn to C1 and C3 (2.283(5), 2.287(5) Å, respectively) and to C4 and C6 (2.190(5), 2.190(5) Å,); (b) crystallographic data were collected using a Enraf Nonius CAD4F diffractometer. Monoclinic $P2_1/n$, $a = 9.189(1)$ Å, $b = 23.034(6)$ Å, $c = 7.993(1)$ Å, $V = 1668.2$ Å^3, $Z = 4$. Structure was solved by interpretation of the Patterson maps which clearly indicated Mn atom position. All remaining non-hydrogen atoms were found by successive electron density map calculations. Their atomic coordinates were refined together with anisotropic temperature factors. At this stage, hydrogen atoms were located on a difference electron map; their coordinates were refined with an overall isotropic temperature factor. Refinement to convergence of the 235 parameters on 2917 unique data gave $R = 3.9\%$, $R_w = 4.0\%$. Supplementary material: listing of complete crystallographic data of compound 2b (17 pages).

Form 1.

eq. 1

i) LiCH(CN)(SiMe$_3$) ii) silica gel chromatography column

after silica gel chromatography column. In order to prove that the counter anion BF_4^- or PF_6^- is not responsible of the desilylation reaction, we treated benzenetricarbonylmanganese tetrafluoroborate 5a [4b], hexaflu-

orophosphate **5b** [4c] or tetraphenylborate **5c** with SiMe$_3$CHLiCN and obtained a mixture of the desilylated complex **6b** and the dinuclear complex **7b**, a minor product, after column chromatography (Eq. (2)). If the chromatography is performed very rapidly [10], the silylated complexes **6a**, **7a** (and **3e** in the case of the reaction starting from complex **2a**) can be obtained.

eq. 2
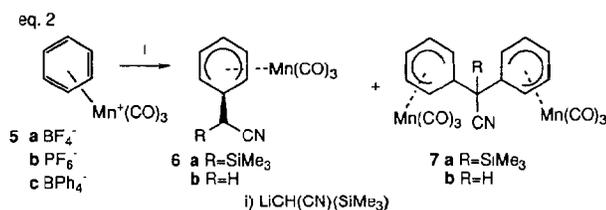
In the case of chromium complexes, the conformation of the Cr(CO)$_3$ tripod has been used to explain the regioselectivity of the addition, under kinetic control, of stabilized carbanions on carbons eclipsed by a Cr–CO bond [11]. In the case of Mn complexes, this work shows that addition of H$^\ominus$, Et$^\ominus$ or $^\ominus$CH(SiR$_3$)CN to the cationic complex **2a** regioselectively occurs at the C5 carbon, which is eclipsed by a carbon–manganese bond. During the course of this study we have also described unexpected C–Si cleavages [12] which have never been described, to the best of our knowledge, as being the result of chromatography column. Further work will be directed at using the conformational study of the tricarbonylmanganese tripod with respect to the arene complex in order to explain the regioselectivity of the addition of a nucleophile on such complexes [13].

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