Regioselectivity in the Reaction of Borohydrides with $[(\eta^6\text{-}C_6(CH_3)_nH_{6-n})Mn(CO)_3]^+$ (n = 0, 6): Metal Formyls as Intermediates[1]

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A solvent-dependent regioselective hydride addition is observed for the reaction of borohydrides with $[(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_3]X$ (X = PF_6, I, OTf, hydrolysate[2] (Cl or Br)) to produce endo and exo isomers of $(\eta^5\text{-}C_6(CH_3)_6H)Mn(CO)_3$ (*endo*-**2** and *exo*-**2**). Hydride deposition directly on the exo side of the ring affords the endo isomer, while attack at the carbonyl followed by hydride migration to the endo side of the ring results in the exo isomer. In aprotic solvents such as THF, CH_2Cl_2, and DMF, attack by smaller borohydrides gives *endo*-**2** exclusively, while bulkier borohydrides favor the formation of *exo*-**2**. In protic solvents, such as alkyl alcohols or *N*-methylacetamide, a mixture of *endo*- and *exo*-**2** results. When $[(\eta^6\text{-}C_6H_6)Mn(CO)_3]PF_6$ (**5**) is treated with $NaBD_4$ in THF, the only product formed is *exo*-$(\eta^5\text{-}C_6H_6D)Mn(CO)_3$, while the same reaction in CH_3OH leads to a mixture of 15–18% *endo*-$(\eta^5\text{-}C_6H_6D)Mn(CO)_3$ (*endo*-**4**) and 82–85% *exo*-$(\eta^5\text{-}C_6H_6D)Mn(CO)_3$. *exo*-**2** and *endo*-**4** are proposed to arise from direct migration of H^- or D^- from a metal formyl to the underside of the arene ring. The intermediacy of a metal formyl is supported by the detection of downfield ^2H and ^1H NMR signals in a study of the reactions of $NaBD_4$ (–83 °C) with **1** (X = PF_6) in CH_3OD and $NaBH_4$ (–50 °C) with **5** in CH_3OH.

Introduction

The activation of arenes toward nucleophilic attack by coordination to transition metals is a well-developed and -documented synthetic strategy.[3] The nucleophilic attack, as observed with most π-carbocyclic ligands, displays steric preference for the site that is exo to the coordinated metal.[4] Sweigert[5] has demonstrated that an upper limit of 50% prevails for endo nucleophilic attack on π-carbocyclic metal "piano stool" complexes having three carbonyls. Replacement of a carbonyl with an electron-withdrawing ligand such as NO increases the electrophilicity at the metal and at the remaining carbonyl carbon.[6] Thus, nucleophilic attack at the metal or at any carbonyl carbon is enhanced, often giving products that rearrange or decompose to position the nucleophile on the endo side of the π-carbocyclic ligand.[7]

The role of solvent in imparting directive influence in the reactions of metal-coordinated π-carbocyclic ligands has been the subject of numerous investigations. The addition of tertiary phosphines to $(\eta^5\text{-}C_7H_9)Fe(CO)_3$ in CH_2Cl_2 is reported to result in the formation of the exo isomer, while in the solvent CH_3CN the endo isomer is formed via a metal-assisted substitution.[8] Astruc[9] observed a strong solvent dependence on the extent to which borohydride transfers hydride to the carbonyl carbon of $[(C_5(CH_3)_5)Fe(CO)_3]^+$. In CH_2Cl_2 $(C_5(CH_3)_5)Fe(CO)_2CH_2OH$ was observed, whereas in THF two products are formed, $(C_5(CH_3)_5)Fe(CO)_2H$ (20%) and $(C_5(CH_3)_5)Fe(CO)_2CH_3$ (80%) (the latter resulting from $(C_5(CH_3)_5)Fe(CO)_2CH_2OH$). In THF/H_2O or H_2O the isolated product was $(C_5(CH_3)_5)Fe(CO)_2H$. In the latter case a formyl intermediate was detected at 0 °C.

While Astruc's results suggest that borohydride reaction with $[(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_3]^+$ (**1**) may lead to a more convenient synthesis of $(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_2H$ (**3**), via an intermediate metal formyl complex, only the endo and exo isomers of $(\eta^5\text{-}C_6(CH_3)_6H)Mn(CO)_3$ (*endo*-**2** and *exo*-**2**) are formed. *exo*-**2** has previously been synthesized in significant yield only by the reaction of CH_3Li with $[(\eta^6\text{-}C_6(CH_3)_5H)Mn(CO)_3]^+$.[4a] We have reported that the reaction of KH with **1** in THF produces *exo*-**2** as the major product with $(\eta^5\text{-}C_6(CH_3)_5CH_2)Mn(CO)_3$ also identified as a second product.[10]

This paper reports the effect of solvent as well as the nature of the borohydride on the regioselectivity of hydride addition to **1** to form *exo*-**2** and *endo*-**2** and on $(\eta^6\text{-}C_6H_6)Mn(CO)_3^+$ (**5**) to form $(\eta^5\text{-}C_6H_6D)Mn(CO)_3$ (*endo*-**4** and *exo*-**4**). In the reaction of **1** with borohydrides, the endo isomer presumably results from direct hydride attack on the exo side of the ring. Spectroscopic evidence indicates that the exo isomer is formed by initial attack of hydride on the carbonyl followed by migration to the endo side of the ring (Scheme I).

(1) In a portion of this work previously reported (Wilmoth, M. A.; Bernhardt, R. J.; Eyman, D. P.; Huffman, J. C. *Organometallics* **1986**, *5*, 2559), it was erroneously stated that the possible role of a metal formyl as an intermediate in the formation of exo-**2** is eliminated by the results of that paper. The sentence should read *endo*-**2**.

(2) The counterion could be Cl or Br.

(3) Kane-Maguire, L. A. P.; Honig, E. D.; Sweigart, D. A. *Chem. Rev.* **1984**, *84*, 525 and references therein.

(4) (a) Munro, G. A. M.; Pauson, P. L. *Isr. J. Chem.* **1976/77**, *15*, 258. (b) Pauson, P. L.; Segal, J. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1683. (c) Pauson, P. L.; Segal, J. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1677. (d) Winkhaus, G.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961**, 3807. (e) Winkhaus, G.; Wilkinson, G. *Proc. Chem. Soc., London* **1960**, 311.

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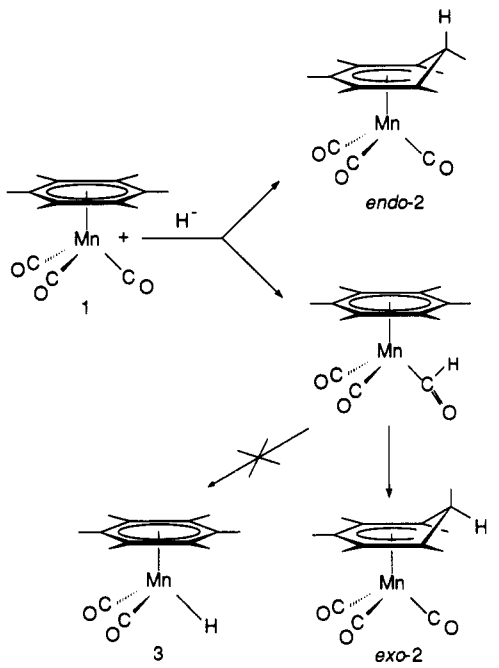
Scheme I



Results and Discussion

Solvent- and Borohydride-Dependent Regioselective Formation of *endo*-2 and *exo*-2. It is well-established that arene rings can be activated toward nucleophilic attack by coordination to transition metals.[11] It has previously been shown that $NaBH_4$ attacks the ring of **1** to form *endo*-**2**.[4d] Our investigations have been designed to address the factors which influence the conversion of **1** to *exo*-**2** and *endo*-**2**. The reaction parameters varied included solvent (THF, CH_2Cl_2, DMF, *N*-methylacetamide (NMA), CH_3OH, CH_3CH_2OH, H_2O, H_2O/THF, H_2O/CH_2Cl_2), type of borohydride (BH_4^-, BEt_3H^-, $B(i\text{-}OPr)_3H^-$, $B[CH(CH_3)C_2H_5]_3H^-$), borohydride counterion (Li^+, Na^+, K^+, $N(n\text{-}Bu)_4^+$), and the counterion of **1** (PF_6^-, I^-, OTf^-, hydrolysate (Cl^- or Br^-)). Although **5** has been reported to undergo double addition of hydride to produce $[(\eta^4\text{-}C_6H_8)Mn(CO)_3]^-$ when treated with 2 equiv of BEt_3H^- or $B(i\text{-}OPr)_3H^-$,[12] a second hydride addition has not been observed in our studies of **1**, even when a large excess of any borohydride has been employed.

When $NaBH_4$ is used as the hydride source in dry THF, CH_2Cl_2, or DMF, *endo*-**2** is formed exclusively. However, when the reaction is performed in protic solvents, a mixture of *exo*-**2** and *endo*-**2** results with the endo isomer being favored (Table I).

The consistent formation of *exo*-**2** in the reaction of **1** with BH_4^- in protic solvents led to a systematic study of this reaction involving a variation of solvent and reactant parameters, including counterions of **1** and the borohydride. Initially, reaction of THF and CH_3OH solutions of **1** (X = PF_6, I) were studied with hydride sources differing only in the counterion of the borohydride. The ratios *exo*-**2**:*endo*-**2** were found to be fairly consistent in each case; reaction in THF afforded 100% *endo*-**2**, while reaction in CH_3OH resulted in 80–90% *exo*-**2** (Table II). From this we conclude that the size of the borohydride counterion has little effect on the product ratio.

Variation of the R group in the borohydride led to an interesting result. Treatment of **1** with $KB(i\text{-}PrO)_3H$ in THF gave a mixture of *endo*-**2** and *exo*-**2** (30:70). This was the first observation of the production of *exo*-**2** in an aprotic solvent. These results suggest that the steric bulk of the borohydride may be influencing the site of reactivity. In order to test this hypothesis, a series of reactions were studied in an aprotic solvent, THF, with hydride sources of increasing steric bulk (Table III). With a small borohydride such as BH_4^-, *endo*-**2** is formed exclusively. As the steric bulk of the borohydride is increased, as with $LiBEt_3H$ and $KBEt_3H$, the product ratio *exo*-**2**:*endo*-**2** changes to 33:67 and 40:60, respectively. The very bulky borohydrides $B[CH(CH_3)C_2H_5]_3H^-$, as the Li or K salts, form approximately 90% *exo*-**2**. This suggests that bulkier borohydrides react preferentially at the less sterically demanding endo side of the ring, proceeding through an intermediate metal formyl.

It should be noted that, in the previous reactions utilizing the bulkier borohydrides, $[(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_2]_2$ (Mr'_2)[13,14] was occasionally observed as a minor product. This may be due to adventitious water in the hydride source, which would produce hydroxides. Hydride from new Sure/Seal bottles, which are expected to contain less water, did not produce significant amounts of Mr'_2, while

Table I. Product Distribution of *endo*-2 and *exo*-2 from the Reaction of 1(X) with $NaBH_4$

X	solvent	hydride source	amt of endo (%)	amt of exo (%)	isolated yield (%)
PF_6	CH_2Cl_2	$(n\text{-}Bu)_4NBH_4$	100		73
PF_6	DMF	$NaBH_4$	100		64
OTf	H_2O	$NaBH_4$	90	10	59
Cl or Br	H_2O	$NaBH_4$	80	20	*a*
PF_6	NMA[b]	$NaBH_4$	75	25	*a*

[a] Total yields were not calculated. [b] NMA = *N*-methylacetamide.

Table II. Product Distribution of *endo*-2 and *exo*-2 from the Reaction of 1(X) with Various Hydride Sources

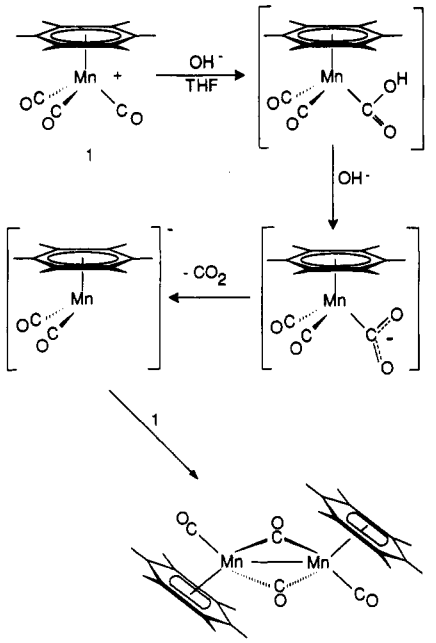
X	solvent	hydride source	amt of endo (%)	amt of exo (%)	isolated yield (%)
PF_6	THF	$NaBH_4$	100		90
PF_6	CH_3OH	$NaBH_4$	11	89	86
PF_6	THF	$NaBD_4$	100		90
PF_6	CH_3OD	$NaBD_4$	11	89	85
PF_6	THF	KBH_4	100		69
PF_6	CH_3OH	KBH_4	20	80	78
PF_6	THF	$(n\text{-}Bu)_4NBH_4$	100		85
PF_6	CH_3OH	$(n\text{-}Bu)_4NBH_4$	15	85	58
I	THF	$(n\text{-}Bu)_4NBH_4$	100		79
I	CH_3OH	$(n\text{-}Bu)_4NBH_4$	20	80	84
PF_6	THF	$LiBH_4$	100		67
PF_6	CH_3OH	$LiBH_4$	12	88	87

Table III. Product Distribution of *endo*-2 and *exo*-2 from the Reaction of 1 (X = PF_6) in THF with Hydride Sources Varying in Steric Bulk

hydride source	amt of endo (%)	amt of exo (%)	isolated yield (%)
KBH_4	100		69
$LiBEt_3H$	67	33	71
$KBEt_3H$	60	40	69
$KB(i\text{-}PrO)_3H$	30	70	85
$LiB[CH(CH_3)C_2H_5]_3H$	10	90	63
$KB[CH(CH_3)C_2H_5]_3H$	8	92	49

(11) Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* 1978, *34*, 3047.
(12) (a) Brookhart, M.; Lukacs, A. *Organometallics* 1983, *2*, 649. (b) Brookhart, M.; Lamanna, W.; Pinhas, A. R. *Organometallics* 1983, *2*, 638. (c) Lamanna, W.; Brookhart, M. *J. Am. Chem. Soc.* 1981, *103*, 989.
(13) Schauer, S. J. Ph.D. Thesis, University of Iowa, 1990.
(14) Schlom, P. J. Ph.D. Thesis, University of Iowa, 1990.

Scheme II



aged bottles produced larger amounts of this species. Even in small amounts, hydroxides can react with 1 (X = PF_6) to form Mr'$_2$. Test reactions in THF with varying amounts of water resulted in the formation of increasing amounts of Mr'$_2$ when more water was present. Formation of Mr'$_2$ is proposed to result from initial attack of OH^- on a carbonyl to form an unstable metallo carboxylic acid (Scheme II).[13] Such complexes usually are not very stable, and when deprotonated by another OH^-, they can deinsert CO_2.[15] The resulting anion can then react with 1 to afford Mr'$_2$. This reaction has been verified by an independent study.[14]

The observed influence of the borohydride bulk on the site of reactivity in aprotic solvents suggests that the same effect would be possible in any solvent. The persistent formation of *exo*-2 in protic solvents suggests that hydrogen bonding of the solvent to BH_4^-, resulting in the formation of a bulky borohydride solvate entity, may influence the regioselectivity of hydride addition. The treatment of 1 (X = OTf, hydrolysate (Cl or Br)) with $NaBH_4$ in water results in an *exo*-2:*endo*-2 ratio of 90:10 for X = OTf and 80:20 for X = hydrolysate (Cl or Br). In addition, the reaction of 1 (X = PF_6) with $NaBH_4$ in *N*-methylacetamide (NMA) produced a similar result (*exo*-2:*endo*-2 = 75:25) (Table IV). While the counterion of the borohydrides or the manganese complex in homogeneous systems has little effect on the product selectivity, it greatly affects the solubility of the reactants and can indirectly influence selectivity (Table IV). For compound 1 (X = OTf, hydrolysate (Cl or Br)), which is very soluble in water, hydride attack occurs predominantly at the exo side of the arene ring, producing *endo*-2:*exo*-2 ratios of 90:10 for X = OTf and 80:20 for X = hydrolysate (Cl or Br). With the less soluble 1 (X), eg. X = I^- and PF_6^-, the preferred site of attack is the carbonyls. This results in *endo*-2:*exo*-2 ratios of 20:80 for X = I and 10:90 for X = PF_6. This regioselectivity may originate with the reaction of undissolved cation at the solvent–crystal interface. The carbonyl sites would be anticipated to be more hydrophilic than the arene portion, so that endo attack would be favored over attack at the exo side of the ring.

(15) Sweet, J. R.; Graham, W. A. G. *Organometallics* **1982**, *1*, 982.

Table IV. Product Distribution of *endo*-2 and *exo*-2 from the Reaction of 1(X) with $NaBH_4$ in Protic Solvents

X	solvent	amt of endo (%)	amt of exo (%)	isolated yield (%)
OTf	H_2O	90	10	59
Cl or Br	H_2O	80	20	*d*
I	H_2O[a]	20	80	58
PF_6	H_2O[a]	10	90	75
PF_6	NMA	75	25	*d*
PF_6	isopropyl alcohol[a]	70	30	72
PF_6	ethyl alcohol[a]	37	63	61
PF_6	CH_3OH[a]	11	89	86
PF_6	H_2O/THF[b]	40	60	85
PF_6	H_2O/CH_2Cl_2[c]	60	40	70

[a] Heterogeneous suspension. [b] Borohydride soluble in water, 1 (X = PF_6) insoluble in THF and H_2O. [c] Borohydride soluble in water, 1 soluble in CH_2Cl_2. [d] Total yields were not calculated.

These observations are consistent with the fact that solubility is a determining factor in the reaction of 1 (X) with BH_4^-. When the (arene)$Mn(CO)_3^+$ cation is completely soluble, attack occurs at the ring. When 1 is not soluble, the amount of *exo*-2 is increased. This is illustrated by the two-phase reaction of 1 (X = PF_6) with $NaBH_4$ in water/CH_2Cl_2. In this case 1 (X = PF_6) is soluble in CH_2Cl_2 exclusively, while the borohydride prefers dissolution in water. Significant amounts of *exo*-2 are produced in this reaction (*endo*-2:*exo*-2 = 60:40) while exclusively *endo*-2 was detected in pure CH_2Cl_2. These results suggest that reaction at the solvent interface can proceed by attack at the carbonyl, leading to *exo*-2. The reaction of 1 (X = PF_6) with $NaBH_4$ in CH_2Cl_2 is limited by the solubility of the borohydride in the solvent, but the only product detected is *endo*-2 in low yield, along with unreacted 1. Reaction of 1 (X = PF_6) in a water/THF mixture results in a 40:60 *endo*-2:*exo*-2 ratio. In this case, 1 is more soluble in the mixture than in H_2O, and less soluble than in THF; the intermediate amount of *exo*-2 is consistent with these observations.

It would be expected that other hydrogen-bonding solvents would give similar results. The reaction of 1 with $NaBH_4$ in *N*-methylacetamide, a homogeneous system, shows an *endo*-2:*exo*-2 product ratio of 75:25. The presence of *exo*-2 is consistent with the anticipated presence of a borohydride solvate complex resulting from hydrogen bonding. Because of the limited solubility of 1(X = PF_6) in isopropyl alcohol, ethyl alcohol, and methanol, larger amounts of *exo*-2 are produced. The observed decrease in endo attack with increasing size of the R group in these alcohols suggests that hydrogen-bonding ability, rather than R group size, is the determining factor in the bulkiness of a borohydride solvate complex.

It appears from the results discussed here that the extent of hydride attack at the carbonyl to afford the exo product is controlled by steric factors on the borohydride and solubility of 1(X). In order to test the steric bulk argument, reactions were carried out on the non-methylated derivative 5. Treatment of 5 in THF with $NaBD_4$ gave exclusively *exo*-4, resulting from direct attack at the exo side of the ring. With the reaction in CH_3OH at 23 °C or in an acetone slurry at −95 °C, both homogeneous solutions, the predominant product was *exo*-4 but some *endo*-4 (15–18%) was produced (Table V). These observations support the premise that steric factors are imparting some regiocontrol in the reactions of (arene)$Mn(CO)_3^+$ systems with

Table V. Product Distribution of *exo*-4 and *endo*-4 from the Reaction of 5 in THF with $NaBD_4$

solvent	amt of exo (%)	amt of endo (%)	isolated yield (%)
THF	100	0	72
CH_3OH (23 °C)	82	18	85
CH_3OH (−95 °C)	85	15	80

borohydrides. This is consistent with the fact that (benzene)$Mn(CO)_3^+$ cations react with far less endo attack. Consideration must also be given to electronic effects which arise upon methylation of the arene ring. The $C_6(CH_3)_6$ ring would be expected to donate more electron density to the metal than C_6H_6, causing an increase in π backbonding in the carbonyls and a decrease in electrophilicity at the carbonyl carbons. This would be expected to lead to more attack at the carbonyl in the benzene case, which is opposite to the effect observed in these studies. This analysis is supportive of the suggestions that the regioselectivity is primarily due to steric factors.

Mechanism of Exo Isomer Formation. Increasing the degree of alkyl group substitution on the arene in π-carbocyclic transition-metal carbonyl compounds results in increased steric hindrance to addition to the ring, making the carbonyl carbons more attractive to nucleophiles.[4a] For example, addition of OH^- to **5** results in addition to the ring, rather than attack at the carbonyl, as reported here with the permethylated species.[16] Also, small amounts of (η^6-$C_6(CH_3)_6$)$Mn(CO)_2CH_3$ were detected when **1** (X = PF_6) was reduced by $LiAlH_4$ in THF.[17] These results support the idea that the carbonyl carbon is also a potential site for nucleophilic attack by H^-, which would produce in the first step of the reaction a metal formyl, (η^6-$C_6(CH_3)_6$)$Mn(CO)_2C(O)H$ (**6**).

The first successful synthesis of a metal formyl compound, $[Fe(CO)_4(C(O)H)]^-$, by the addition of $[Fe(CO)_4]^{2-}$ to acetic formic anhydride was reported by Collman[18] in 1973. Casey[19] reported that this synthetic method could not be successfully extended using the anions $[C_5H_5Fe(CO)_2]^-$, $[Cr(CO)_5]^{2-}$, $[[(C_6H_5)_3P]Mn(CO)_4]^-$, and $[[(C_6H_5)_3P]_2Mn(CO)_3]^-$. However, sodium trimethoxyborohydride when reacted with $Cr(CO)_6$, $W(CO)_6$, $(CO)_5CrPPh_3$, $(CO)_5WPPh_3$, and $(CO)_4FePPh_3$ resulted in the formation of metal formyl compounds, as determined by NMR spectroscopy.[19] Fiato[20] reported that the reaction of $CH_3C(O)O^{13}C(O)H$ with $[Mn(CO)_5]^-$ produces $(CO)_4(^{13}CO)MnH$. This reaction is proposed to proceed via the initial formation of $(CO)_5Mn^{13}C(O)H$, an intermediate that is too unstable to detect directly, with subsequent in situ decomposition to the product. The thermal instability of formyls in general[21] lends credence to the intermediacy of **6** in the intramolecular formation of *exo*-**2** by hydride attack on **1**(X). The formyl $[(i\text{-}PrO)_3P]_2Mn(CO)_3C(O)H$, prepared by the reaction of $[(i\text{-}PrO)_3P]_2Mn(CO)_4]^+$ with $NaBH_4$ in methanol, is reported to decompose by carbonyl deinsertion to form the metal hydrides $[(i\text{-}PrO)_3P]_2Mn(CO)_3H$ and $[(i\text{-}PrO)_3P]_3Mn(CO)_2H$.[22]

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(19) Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1976**, *98*, 5395.
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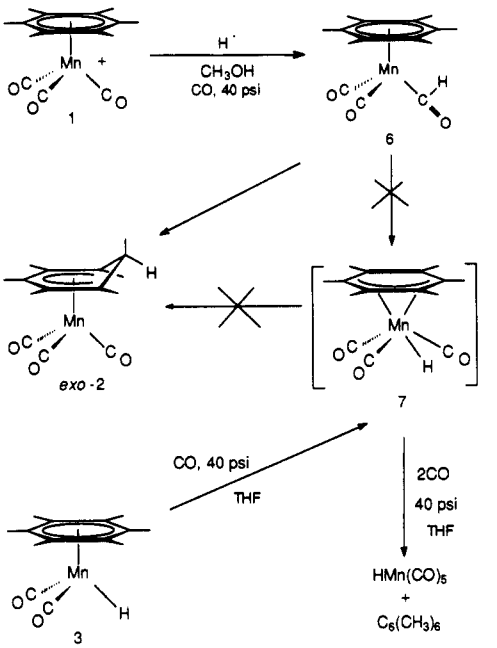
(21) Gladysz, J. A. *Adv. Organomet. Chem.* **1982**, *20*, 1.
(22) Weiler, G.; Huttner, G.; Zsolnai, L.; Berke, H. *Z. Naturforsch.* **1987**, *42B*, 203.

Scheme III



The formation and the reaction modes of the formyl species (η^6-$C_6(CH_3)_6$)$Mn(CO)_2C(O)H$ are of interest in the studies reported here. The formyl is the first product expected in the endo attack of hydride on **1**. Earlier work in our laboratory has established that this formyl can also be formed by reaction of the anion of Li[(η^6-$C_6(CH_3)_6$)-$Mn(CO)_2$] with $HC(O)OC(O)CH_3$.[1] We want to establish here the intermediacy of **6** from the reaction of **1** with borohydrides and offer evidence establishing a mechanism for its subsequent reaction to give *exo*-**2**.

Low-temperature NMR studies have confirmed the existence of **6**. In the reaction of **1** (X = PF_6) with $NaBD_4$ in CH_3OH at −63 °C, a ^2H NMR spectrum displayed a resonance at 12.5 ppm, consistent with a metal formyl. A similar experiment involving reaction of **5** with $NaBH_4$ in CH_3OH at −50 °C produced a resonance at 15.0 ppm in the ^1H NMR spectrum. Unlike the other manganese carbonyl formyls reported, **6** has two possible products which could arise from its decomposition (Scheme I). Formation of **3** could result from loss of CO followed by deinsertion of the formyl,[22] whereas migration of H^- from the formyl to the endo position of the arene could produce *exo*-**2**. Of these two, only *exo*-**2** has been detected (^1H NMR) after thermal decomposition of the formyl at room temperature.

The thermal decomposition of **6** to produce *exo*-**2** proceeds quantitatively. Two possible mechanistic pathways for this process are presented in Scheme III. We have reported previously that the pressurization of **3** with CO at 40 psi does not produce *exo*-**2** but rather produces *endo*-**2**.[1] The intermediate $HMn(CO)_5$ in this reaction, detected by FTIR, is presumably formed by a stepwise carbonylation induced displacement of $C_6(CH_3)_6$ to give $HMn(CO)_5$. This process would involve addition of CO to the manganese with associated decrease in hapticity of the arene ring. The mechanism involved in this reaction will be the subject of a subsequent publication.[23] It has been observed that the reaction of **1** with H^- in CH_3OH under 40 psi of CO pressure results in the formation of **6**.

(23) Manuscript in preparation.

These observations support the premise that formyl deinsertion of **6** to give the intermediate $(\eta^4\text{-}C_6(CH_3)_6)Mn(CO)_3H$ (**7**) does not occur, because **7** would immediately be converted to $HMn(CO)_5$ and $C_6(CH_3)_6$. It is concluded that the mechanism of formation of *exo*-**2** involves migration of the hydride from the formyl carbon directly to the endo side of the ring, rather than deinsertion of the formyl, followed by migration.

While the majority of **6** is observed to react to form the exo isomer, a small amount of endo isomer is always detected. This product may arise from direct attack of H^- on the exo side of the ring or by an alternate pathway such as intermolecular hydride transfer from the formyl to the exo side of the η^6-arene ring of **1**. It has been observed (^{1}H NMR) that during the reaction of **1** (X = PF_6) with $NaBH_4$ at low temperature (−50 °C), a small amount of **1** is insoluble and presumably does not react to form **6**. When the reaction mixture is warmed to −10 °C, the formation of *exo*- and *endo*-**2** is initiated. At this temperature, complete reaction of **6** is evidenced by loss of the singlet at 12.5 ppm, attributed to the hydrogen of the formyl. The resulting homogeneous solution displayed a 40:60 *exo*-**2**:*endo*-**2** product ratio. The endo isomer is believed to have formed via an intermolecular pathway involving hydride transfer of the formyl hydride to **1**. As noted previously, the ratio of *exo*-**2**:*endo*-**2** at room temperature is 89:11. Apparently at lower temperatures, *endo*-**2** is formed by intermolecular hydride transfer from **6** to **1** at a rate which is competitive with the rate of intramolecular transfer to form *exo*-**2**. The insolubility of **1** in CH_3OH at low temperatures has precluded experiments to determine the deuterium kinetic isotope effect.

Conclusions

The regioselective addition of hydride from borohydrides to **1** is influenced by both the size of the borohydride, or its solvate, and the solubilities of the (arene)$Mn(CO)_3^+$ reactants. In aprotic solvents, the addition of hydride from sterically nondemanding borohydrides results in preferential attack on the exo side of the ring to produce *endo*-**2**. As the steric bulk of the borohydride increases, attack occurs at the more sterically accessible carbonyl, increasing the amount of *exo*-**2**. In protic solvents, hydrogen bonding of the solvent to the borohydride increases its effective size, leading to preferential attack at carbonyls. The polarity of the carbonyls makes them more susceptible to hydride attack in cases where there is limited solubility of the (arene)$Mn(CO)_3^+$ cation. The studies reported here have established that the proper choice of solvent can lead to selective synthesis of *exo*-**2** and *endo*-**2**.

Experimental Section

General Procedures. **1**(X) (X = PF_6, hydrolysate (Cl or Br)), **1**(X), (X = I), and **5**, were prepared by published methods.[4c,d,24] Synthesis of the previously reported *endo*- and *exo*-**2**[4c,d,24] was modified to accommodate the use of various solvents and hydride sources and is described below in detail. Solvents were dried, distilled, and degassed thoroughly with nitrogen or argon prior to use.[25] All reactions were carried out under an atmosphere of nitrogen or argon using standard Schlenk or glovebox techniques. IR spectra were recorded on a Perkin-Elmer 421 grating spectrometer, an IBM/Bruker IR98 interferometer, or a Mattson Cygnus 25 FTIR spectrometer. The ^{1}H NMR spectra were recorded on a JEOL FX90Q, Bruker AC300, or Bruker WM360 spectrometer. ^{1}H NMR chemical shifts are reported (in ppm) as positive downfield from tetramethylsilane. The reactions were monitored by FTIR spectra of samples removed from the reaction mixture and assumed to be complete when the CO bands of the reactants and products ceased to change. Chromatographic separations were performed on untreated silica gel (60–200 mesh), using hexane and acetone. Ratios of products were calculated by integration of the methyl doublet of *endo*-**2** versus that of *exo*-**2** in the ^{1}H NMR. The identities of the products were confirmed by comparison to authentic samples using ^{1}H NMR.

Formation of $(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_2C(O)H$. A solution of $[(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_2]Li$ was prepared from the reaction of **3** and CH_3Li in THF.[26] To this solution was added formic acetic anhydride, and the progress of the reaction was followed by IR. Disappearance of the CO band for $Li[(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_2]$ and the appearance of two bands corresponding to either *endo*- or *exo*-**2** were detected. The THF was removed by vacuum evaporation. The ^{1}H NMR spectrum indicated the formation of *exo*-**2**.

NMR Detection of $(\eta^6\text{-}C_6(CH_3)_6)Mn(CO)_2C(O)D$ and $(\eta^6\text{-}C_6H_6)Mn(CO)_2C(O)H$. In an NMR tube the sample of **1** (X = PF_6) or **5** was dissolved in 1 mL of CH_3OH and cooled to −63 °C (−50 °C for **5**) using a $CHCl_3/N_2$(l) slush bath. The NMR probe was cooled to −83 °C (−50 °C for **5**). Prior to insertion of the tube into the instrument, a sample of $NaBD_4$ ($NaBH_4$ for **5**) was added. Gas was observed evolving from the solution immediately after addition of the reagent. The sample was placed in the instrument, and ^{2}H (^{1}H for **5**) NMR spectra were collected periodically over 30 min. The deuterium resonance of the formyl species **6** occurs at 12.5 ppm (the formyl proton resonance occurs at 15.0 ppm for $(\eta^6\text{-}C_6H_6)Mn(CO)_2C(O)H$).

Reaction of 1 (X = PF_6) with $NaBH_4$ in H_2O/THF. A solution of $NaBH_4$ (0.0821 g, 2.16 mmol) in 10 mL of deionized H_2O was added to a suspension of **1** (X = PF_6) (0.482 g, 1.08 mmol) in 10 mL of THF at −10 °C. The resulting yellow mixture was stirred for 10 min after the addition was complete. After the mixture was allowed to come to room temperature, it was then extracted with two 10-mL portions of CH_2Cl_2. The extracts were combined, and the solvent was removed by rotary evaporation. The residue was extracted with hexane, and the solvent was removed from the filtered solution by rotary evaporation. The yellow product was sublimed at room temperature and 1×10^{-3} Torr, affording *endo*-**2** (0.272 g, 85% yield).

Reaction of 1 (X = PF_6) with $NaBH_4$ in CH_2Cl_2/H_2O. A solution of $NaBH_4$ (0.0252 g, 0.661 mmol) in H_2O was added to a solution of **1** (X = PF_6) (0.150 g, 0.336 mmol) in CH_2Cl_2. This two-layer system was allowed to react for 1 h. The product, primarily soluble in the CH_2Cl_2 layer, was isolated by removal of the solvent. The solids were dissolved in hexane and filtered. The solvent was removed, yielding 60:40 *endo*-**2**:*exo*-**2** (0.011 g, 65% yield).

Reaction of 1 (X = PF_6, I, Hydrolysate (Cl or Br), OTf) with $NaBH_4$ in H_2O. Compound **1** (X = PF_6, I, OTf) (0.206 g, 0.462 mmol) was added to 20 mL of deionized water. Compound **1** (X = OTf), prepared by metathesis of **1** (X = I) with AgOTf in CH_2Cl_2, is soluble in water while **1** (X = PF_6, I) forms a suspension. Compound **1** (X = hydrolysate (Cl or Br)) was prepared by the hydrolysis of the Fischer–Haffner reaction of $Mn(CO)_5Br$, hexamethylbenzene, and $AlCl_3$ and was used directly. To this was added a solution of $NaBH_4$ (0.0513 g, 1.32 mmol) in 10 mL of water. The product was extracted with CH_2Cl_2, and the solvent was removed by rotary evaporation. The product was redissolved in hexane and the solution filtered. Rotary evaporation resulted in *endo*-**2** and *exo*-**2**. See Table IV for ratios and yields.

(24) Winkhaus, G.; Singer, H. *Z. Naturforsch.* **1963**, *18B*, 418.
(25) Shriver, D. F.; Drezdon, M. A. In *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.
(26) Bernhardt, R. J.; Wilmoth, M. A.; Weers, J. J.; LaBrush, D. M.; Eyman, D. P. *Organometallics* **1986**, *5*, 883.

Reaction of 1 (X = PF_6) with $(n\text{-Bu})_4NBH_4$ in CH_2Cl_2. $(n\text{-Bu})_4NBH_4$ (0.0400 g, 0.155 mmol) and 1 (X = PF_6) (0.158 g, 0.354 mmol) were combined as solids. A 25-mL portion of dry CH_2Cl_2 was added, and the solution was stirred for 15 min. The solvent was removed, the resulting solid was dissolved in hexane, and the solution was filtered. The hexane was removed, yielding a yellow solid, *endo*-2 (0.078 g, 73% yield).

Reaction of 1 (X = PF_6) with $NaBH_4$ in NMA. Compound 1 (X = PF_6) (0.0754 g, 0.168 mmol) was dissolved in 7.5 mL of NMA. The reaction mixture was warmed to 32 °C to keep the NMA liquid. To this solution was added $NaBH_4$ (0.0142 g, 0.370 mmol). The solvent was removed under vacuum, and the solids were purified by column chromatography. Elution with acetone yielded 75:25 *endo*-2:*exo*-2. No yield was calculated.

Reaction of 1 (X = PF_6) with $NaBH_4$ in Isopropyl or Ethyl Alcohol. Compound 1 (X = PF_6) (0.100 g, 0.224 mmol) was dissolved in 25 mL of isopropyl or ethyl alcohol. To this solution was added $NaBH_4$ (0.0221 g, 0.582 mmol) in 5 mL of isopropyl or ethyl alcohol. The solvent was removed under vacuum, and the solids were purified by column chromatography. Elution with acetone yielded *endo*-2 and *exo*-2. See Table IV for ratios and yields.

Reaction of 1 (X = PF_6) with $NaBH_4$ in DMF. Compound 1 (X = PF_6) (0.300 g, 0.672 mmol) was dissolved in 30 mL of DMF. After addition of $NaBH_4$ (0.0561 g, 1.34 mmol), the solvent was removed under vacuum. The solids were purified by column chromatography to afford *endo*-2 (0.135 g, 66% yield).

General Procedure for Reaction of 1 (X = PF_6, I) with Various Hydride Sources in THF. Two general methods were used with the same results. A suspension of borohydride was added to a suspension of 1 (X = PF_6, I). An alternate method involved combining 1 (X = PF_6, I) and the hydride source as solids in a 100-mL Schlenk flask. After addition of 50 mL of THF the solution was stirred for 15 min to 1.5 h. Unless otherwise specified, the solvent was removed and the solids were sublimed at 100 °C and 1×10^{-3} Torr.

(a) Reaction of 1 (X = PF_6) with $NaBH_4$. A suspension of $NaBH_4$ (0.0824 g, 2.16 mmol) in 10 mL of THF was added to a suspension of 1 (X = PF_6) (0.482 g, 1.08 mmol) in 25 mL of THF. Concentration by vacuum solvent removal and cooling of the extract resulted in the formation of yellow crystals of *endo*-2 (0.294 g, 90% yield).

(b) Reaction of 1 (X = PF_6) with KBH_4. A suspension of KBH_4 (0.0231 g, 0.417 mmol) in 10 mL of THF was added to a suspension of 1 (X = PF_6) (0.0933 g, 0.208 mmol). Subsequent purification yielded *endo*-2 (0.031 g, 69% yield).

(c) Reaction of 1 (X = PF_6) with $NaBD_4$. A suspension of $NaBD_4$ (0.187 g, 4.48 mmol) in 10 mL of THF was added to a suspension of 1 (X = PF_6) (1.00 g, 2.24 mmol) Subsequent purification yielded *endo*-2 (0.650 g, 96% yield).

(d) Reaction of 1 (X = PF_6) with $(n\text{-Bu})_4NBH_4$. Compound 1 (X = PF_6) (0.103 g, 0.230 mmol) and $(n\text{-Bu})_4NBH_4$ (0.204 g, 0.792 mmol) were combined as solids. Sublimation yielded *endo*-2 (0.059 g, 85% yield).

(e) Reaction of 1 (X = I) with $(n\text{-Bu})_4NBH_4$. Compound 1 (X = I) (0.0935 g, 0.217 mmol) and $(n\text{-Bu})_4NBH_4$ (0.156 g, 0.605 mmol) were combined as solids. Sublimation yielded *endo*-2 (0.050 g, 79% yield).

(f) Reaction of 1 (X = PF_6) with $LiBH_4$. Compound 1 (X = PF_6) (0.0991 g, 0.221 mmol) and $LiBH_4$ (0.0153 g, 0.703 mmol) were combined as solids. Sublimation yielded *endo*-2 (0.046 g, 67% yield).

(g) Reaction of 5 with $NaBD_4$. Compound 5 (0.0871 g, 0.241 mmol) and $NaBD_4$ (0.0252 g, 0.588 mmol) were combined as solids. Sublimation yielded *exo*-4 (0.038 g, 72% yield).

General Procedure for Reaction of 1 (X = PF_6, I) with Various Hydride Sources in CH_3OH. Compound 1 (X = PF_6, I) and the hydride source were combined as solids in a 100-mL Schlenk flask. After addition of 50 mL of CH_3OH the solution was stirred for 15 min to 1.5 h. The extent of reaction was monitored using IR spectra in a CaF_2 cell. The solvent was removed, and the solids were sublimed at 100 °C. In each case, the ^1H NMR spectrum revealed the presence of a mixture of *endo*-2 and *exo*-2.

(a) Reaction of 1 (X = PF_6) with $NaBH_4$. Compound 1 (X = PF_6) (0.482 g, 1.08 mmol) was suspended in 30 mL of CH_3OH. $NaBH_4$ (0.0823 g, 2.16 mmol) was dissolved in 10 mL of methanol and was added to the suspension. Subsequent purification yielded 89:11 *exo*-2:*endo*-2 (0.280 g, 86% yield).

(b) Reaction of 1 (X = PF_6) with KBH_4 in CH_3OH. Compound 1 (X = PF_6) (0.0931 g, 0.208 mmol) and KBH_4 (0.0237 g, 0.417 mmol) were combined in CH_3OH at room temperature. Subsequent purification yielded 80:20 *exo*-2:*endo*-2 (0.035 g, 78% yield).

(c) Reaction of 1 (X = PF_6) with $NaBD_4$ in CH_3OD. Compound 1 (X = PF_6) (2.00 g, 4.48 mmol) and $NaBD_4$ (0.375 g, 8.96 mmol) were combined in CH_3OD at room temperature. Subsequent purification yielded 89:11 *exo*-2:*endo*-2 (1.00 g, 74% yield).

(d) Reaction of 1 (X = PF_6) with $(n\text{-Bu})_4NBH_4$. Compound 1 (X = PF_6) (0.0997 g, 0.223 mmol) and $(n\text{-Bu})_4NBH_4$ (0.118 g, 0.460 mmol) were combined as solids, and subsequent purification yielded 85:15 *exo*-2:*endo*-2 (0.039 g, 58% yield).

(e) Reaction of 1 (X = I) with $(n\text{-Bu})_4NBH_4$. Compound 1 (X = I) (0.0951 g, 0.223 mmol) and $(n\text{-Bu})_4NBH_4$ (0.136 g, 0.529 mmol) were combined as solids, and subsequent purification yielded 80:20 *exo*-2:*endo*-2 (0.054 g, 84% yield).

(f) Reaction of 1 (X = PF_6) with $LiBH_4$. Compound 1 (X = PF_6) (0.0992 g, 0.221 mmol) and $LiBH_4$ (0.0133 g, 0.574 mmol) were combined as solids, and subsequent purification yielded 88:12 *exo*-2:*endo*-2 (0.061 g, 87% yield).

(g) Reaction of 5 with $NaBD_4$ (Room Temperature). To a solution of 5 (0.0906 g, 0.276 mmol) in 30 mL of CH_3OH was added $NaBD_4$ (0.0542 g, 0.129 mmol) at 23 °C. Subsequent purification yielded 82:18 *exo*-4:*endo*-4 (0.0513 g, 85% yield).

(h) Reaction of 5 with $NaBD_4$ (Low Temperature). A solution of 5 (0.0872 g, 0.240 mmol) in 30 mL of CH_3OH was cooled in an acetone slurry (−95 °C) until equilibrated. To this was added $NaBD_4$ (0.0378 g, 0.981 mmol), and the reaction mixture warmed up as it reacted. Subsequent purification yielded 85:15 *exo*-4:*endo*-4 (0.042 g, 80% yield).

Reaction of 1 (X = PF_6) with Borohydrides Varying in Steric Bulk. Compound 1 (X = PF_6) (0.700 g, 1.57 mmol) was suspended in 30 mL of THF. In separate experiments, one of the following borohydrides (0.75 mL, 0.75 mmol) was added to the suspension via syringe: KEt_3BH (1.0 M solution in THF), $K(i\text{-PrO})_3BH$, $LiB[CH(CH_3)C_2H_5]_3H$ (1.0 M solution in THF), or $KB[CH(CH_3)C_2H_5]_3H$ (1.0 M solution in THF). Each mixture was stirred for 15–30 min. In some cases the mixture turned green, indicating Mr'_2 formation. The solvent was removed by vacuum evaporation, and the residue was extracted with hexane. The hexane was removed from the yellow solution by rotary evaporation, yielding *exo*-2 and *endo*-2. When Mr'_2 was present, an additional step involving dissolving the solids in acetone and filtering off Mr'_2 was necessary.

Reaction of 1 (X = PF_6) with OH^- To Form Mr'_2. To a suspension of 1 (X = PF_6) (0.100 g, 0.224 mmol) in 30 mL of acetone or THF was added $(n\text{-Bu})_4NOH$ (2 equiv). An immediate color change from yellow to green was observed. IR analysis revealed complete conversion to Mr'_2.

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