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Electron transfer versus nucleophilic pathways in the ion-pair annihilation of organoborate anions by carbonylmanganese(I) cations

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Abstract

Substituted carbonylmanganese cations $[Mn(CO)_5L]^+$, where L = py, PPh_3 and PPh_2Me, readily react with various organoborate anions (tetramethylborate, methyltriphenylborate and tetraphenylborate) in THF solution to afford a mixture of dimanganese carbonyls, hydridomanganese carbonyls and alkylmanganese carbonyls. The formation of the dimanganese carbonyl dimers as well as the hydridomanganese carbonyls suggests the involvement of 19-electron carbonylmanganese radicals that stem from an initial electron transfer. On the other hand, the acetonitrile-substituted analogue $[Mn(CO)_5(CH_3CN)]^+$ reacts with the same borate anions to afford the alkylated $RMn(CO)_5$, where R = CH_3 and C_6H_5, as the sole carbonylmanganese product. As such, this alkylative annihilation is best formulated as a direct attack on the carbonyl carbon by the borate nucleophile. The two different pathways can be understood in terms of the balance between the electrophilicity of the carbonyl ligand and the electron affinity of the carbonylmanganese cation.

Keywords: Electron transfer; Nucleophilic attack; Ion-pair annihilation; Carbonylmanganese cations; Organoborate anions; Tetramethylborate

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1. Introduction

Nucleophilic addition to the coordinated ligands of transition metal carbonyls is a useful strategy in the organometallic synthesis and considered to be the key step in a variety of metal carbonyl-catalyzed reactions [1]. Thus various alkyllithium and Grignard reagents, borohydrides or amines add to the carbonylmanganese cation, $[Mn(CO)_5L]^+$, to yield the corresponding acyl, alkyl, formyl or carbamoyl derivatives via nucleophilic attack on the carbonyl carbon atom [2–4]. However, the same carbonylmanganese cations are also readily convertible to the neutral 19-electron radicals by chemical or electrochemical reduction [5], and there is a recent report that the alkylation of carbonylrhenium(I) cation $[(bpy)Re(CO)_3(py)]^+$ can be effected by photo-induced electron transfer from alkylborate anions [6]. Can this photochemical process have a thermal counterpart? In order to answer this question, we follow the mechanistic dichotomy previously established between nucleophilic attack and single electron transfer with metal carbonyl anions as nucleophiles [7], and now inquire whether the thermal nucleophilic alkylation of metal carbonyls such as $[Mn(CO)_5L]^+$ by alkylborate anions is actually preceded by an electron-transfer step in Eq. (1), i.e.

$$[Mn(CO)_5L]^+ + BR_4^- \rightarrow BR_4^{\bullet} + [Mn(CO)_5L]^{\bullet} \rightarrow RMn(CO)_5, \text{ etc.} \quad (1)$$

To probe this question, we chose the anionic organoborates: tetramethylborate, methyltriphenylborate, and tetraphenylborate, as mild alkylating reagents with varied nucleophilic properties [8]. For example, tetraalkylborates is known to react with acyl chlorides such as benzoyl chloride to selectively give ketones, and

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the reaction is considered to proceed via an S_N2 mechanism. Furthermore, these organoborates are also electron donors in photoinduced electron transfer to the cationic cyanine dye, *N*-(*p*-benzoylbenzyl)-*N*,*N*,*N*-tri-*n*-butylammonium ion [9], as well as in the thermal nucleophilic alkylation of pyridinium cations [10]. For these studies, we analyzed the carbonylmanganese products to provide the mechanistic basis for the intermediacy of the 19-electron carbonylmanganese radical via an initial transfer of a single electron from the borate anion (electron donor) to the manganese carbonyl cation (electron acceptor), as presented in Eq. (1). We hope that further time-resolved spectroscopic and electrochemical studies of reactive intermediates [11] will establish the mechanistic validity of the product studies.

2. Results

The manganese cations, $[Mn(CO)_5(L)]^+$ where L = CH_3CN, py, PPh_3 and PPh_2Me, readily reacted with tetramethylborate, methyltriphenylborate, and tetraphenylborate in tetrahydrofuran (in the dark) to give a mixture of alkylmanganese carbonyls and/or dimanganese decacarbonyls and hydridomanganese carbonyls. In more polar solvents such as acetonitrile, no thermal reaction was observed; and the large solvent effect on reactivity suggested that ion pairing was important [12].

The reactivity of different borates decreased in the order: $BMe_4^- > BMePh_3^- > BPh_4^-$. Thus tetramethylborate readily reacted with the carbonylmanganese cations at − 20°C, whereas methyltriphenylborate was less reactive, and yielded a similar mixture in a few hours at room temperature. Tetraphenylborate was the least reactive, and the completion of the reaction required 20 h at room temperature (or more rapidly at elevated temperatures). Such a reactivity pattern follows the general order of the oxidation potentials of these tetraalkylborates [13]. By the same token, the cationic manganesecarbonyls $[Mn(CO)_5(CH_3CN)]^+$ and $[Mn(CO)_5(Py)]^+$ were more reactive than the phosphine-substituted analogues $[Mn(CO)_5(PPh_3)]^+$ and $[Mn(CO)_5(PPh_2Me)]^+$ in accord with the relative values of their reduction potentials [14].

The redox products (and their distribution) were dependent on the ligand L of the substituted carbonylmanganese cations as well as on the organoborates. Since the nature of the carbonylmanganese products is more informative, particular attention was paid on their identification and analysis as follows.

2.1. *Tetramethylborate*

Typically, a THF solution of tetra-*n*-butylammonium tetramethylborate was mixed with the acetonitrile-substituted carbonylmanganese cation $[Mn(CO)_5(CH_3CN)]^+PF_6^-$ at − 78°C, and the mixture was allowed to slowly warm to 0°C. Periodic IR analysis indicated that the reaction occurred mainly at − 20°C to give methylmanganese pentacarbonyl $CH_3Mn(CO)_5$ as the sole product (Table 1). When the reaction was carried out in THF-d_8, the solvate $(CH_3)_3B(OC_4D_8)$ was observed by ^{1}H-NMR (Eq. (2)) [15].

$$[Mn(CO)_5(CH_3CN)]^+ + B(CH_3)_4^- \xrightarrow{THF} CH_3Mn(CO)_5 + (CH_3)_3B(OC_4H_8) \qquad (2)$$

Interestingly, when the same reaction was carried out at 23°C, a mixture of carbonylmanganese products was obtained—with pentacarbonylmanganate $Mn(CO)_5^-$ as the major component [16].

When two equivalents of tetramethylborate was treated with one equivalent of $[Mn(CO)_5(CH_3CN)]^+$ at − 20°C, $CH_3Mn(CO)_5$ was observed initially. However, as the mixture was allowed to warm to room temperature, $CH_3Mn(CO)_5$ was rapidly converted to $[Mn(CO)_5]^-$ as monitored by infrared spectroscopy. In a control experiment, $CH_3Mn(CO)_5$ was found to rapidly react with tetramethylborate in THF at room temperature to generate pentacarbonylmanganate $[Mn(CO)_5]^-$ in quantitative yield [17]. As such, we consider the interaction of tetramethylborate with $[Mn(CO)_5(CH_3CN)]^+$ at room temperature to proceed in two steps, viz. Eq. (2) followed by Eq. (3).

$$CH_3Mn(CO)_5 + B(CH_3)_4^- \xrightarrow{THF} [Mn(CO)_5]^- + C_2H_6 + Me_3B(THF) \qquad (3)$$

Table 1
Annihilation of carbonylmanganese cations $[Mn(CO)_5L]^+$ with tetramethylborate anion in tetrahydrofuran[a]

Entry	L	Product (yield %)[b]
1	CH_3CN	$CH_3Mn(CO)_5$ (88)
2	CH_3CN[c]	$[Mn(CO)_5]^-$ [d]
3	CH_3CN[e]	$[Mn(CO)_5]^-$ (85)
4	—[c,g]	$[Mn(CO)_5]^-$ (100)
5	Pyridine	$CH_3Mn(CO)_5$ (54), $Mn_2(CO)_{10}$ (10)
6	PPh_3	$CH_3Mn(CO)_4L$ (15)[f], $HMn(CO)_4L$ (12)[f], $Mn_2(CO)_8L_2$ (58)[f]
7	PPh_2Me	$CH_3Mn(CO)_4L$ (5)[f], $HMn(CO)_4L$ (11)[f], $Mn_2(CO)_8L_2$ (61)[f]

[a] Reaction carried out from − 78 to 0°C in the period of 2 h unless indicated otherwise.

[b] Products quantified by IR analysis unless indicated otherwise.

[c] At 23°C.

[d] Not quantified.

[e] Two equivalents of $TBA^+BMe_4^-$ used.

[f] Isolated yield.

[g] $CH_3Mn(CO)_5$ used instead of $[Mn(CO)L]^+$.

Table 2
Annihilation of carbonylmanganese cations $[Mn(CO)_5L]^+$ with methyltriphenylborate anion in tetrahydrofuran[a]

	L	Product (yield %)[b]
1	CH_3CN	$CH_3Mn(CO)_5$ (82)[c]
2	Pyridine	$Mn_2(CO)_{10}$ (33)[c]
3	PPh_3	$CH_3Mn(CO)_4L$ (24), $HMn(CO)_4L$ (37), $Mn_2(CO)_8L_2$ (28)
4	PPh_2Me	$CH_3Mn(CO)_4L$ (10), $HMn(CO)_4L$ (65), $Mn_2(CO)_8L_2$ (5)

[a] Reaction carried out at 23°C for 6 h.

[b] Isolated yield unless indicated otherwise.

[c] Products quantified by IR analysis.

When tetramethylborate was treated with the pyridine derivative $[Mn(CO)_5(Py)]^+$ under the same conditions, it afforded methylmanganese pentacarbonyl as the major carbonyl product. In addition, a small amount of $Mn_2(CO)_{10}$ was detected by TLC. On the other hand, when tetramethylborate was treated with the phosphine-substituted carbonylmanganese cation $[Mn(CO)_5(PPh_3)]^+$ in THF solution, dimanganese carbonyl $Mn_2(CO)_8(PPh_3)_2$ was generated as the major carbonyl product, together with the alkylated product $CH_3Mn(CO)_4(PPh_3)$ and the substituted hydridomanganese complex $HMn(CO)_4(PPh_3)$ in small amounts. Essentially the same results were obtained with tetramethylborate and $[Mn(CO)_5(PPh_2Me)]^+$ in THF solution, as shown in Table 1. In the latter, the characterization of the boron-containing products indicated the presence of trimethylborane [as the pyridine adduct $Me_3B(NC_5H_5)$] in 60% yield.

2.2. *Methyltriphenylborate*

Methyltriphenylborate reacted with the acetonitrile-substituted manganese cation to give methylmanganese pentacarbonyl cleanly as the sole carbonyl product. However, the reaction of methyltriphenylborate with the pyridine-substituted manganese cation was complicated, and afforded a mixture of dimanganese decacarbonyl and other unidentified carbonyl products in low yields. In contrast to the reaction with $[Mn(CO)_5(CH_3CN)]^+$, no methylmanganese pentacarbonyl was detected. Methyltriphenylborate behaved similarly to tetramethylborate, and reacted with the phosphine-substituted carbonylmanganese cations $[Mn(CO)_5(PPh_3)]^+$ and $[Mn(CO)_5(PPh_2Me)]^+$ in THF at room temperature to afford a mixture of $CH_3Mn(CO)_4(L)$, $Mn_2(CO)_8(L)_2$ and $HMn(CO)_4(L)$ where L = PPh_3 and PPh_2Me, respectively (Table 2).

2.3. *Tetraphenylborate*

The annihilation of tetraphenylborate by the acetonitrile-substituted manganese cation cleanly afforded phenylmanganese pentacarbonyl in high yield, as quantified by infrared spectroscopy. When the volatile components of the reaction mixture were condensed in vacuo at −196°C, a small amount of benzene and 98% yield of acetonitrile were found by GC analysis. However, the pyridine derivative $[Mn(CO)_5(py)]^+$ reacted with tetraphenylborate to afford dimanganese decacarbonyl. The volatile component of the reaction mixture was benzene (81%), but no pyridine was detected by GC analysis [The pyridine is presumed to form the adduct $Ph_3B(NC_5H_5)$ with triphenylborane [18].] Tetraphenylborate reacted with phosphine-substituted $[Mn(CO)_5(PPh_3)]^+$ and $[Mn(CO)_5(PPh_2Me)]^+$ at room temperature at such a slow rate that almost no reaction was observed after 24 h. The reactions were subsequently effected by heating the mixture to 60°C for 24 h; and the carbonylmanganese products were characterized as a mixture of $C_6H_5Mn(CO)_4(L)$, $Mn_2(CO)_8(L)_2$ and $HMn(CO)_4(L)$, where L = PPh_3 and PPh_2Me as summarized in Table 3.

3. Discussion

In order to account for the various carbonylmanganese products obtained from the treatment of various $[Mn(CO)_5(L)]^+$ cations with BMe_4^-, $BMePh_3^-$, BPh_4^- in Tables 1–3, let us first summarize the characteristic behavior of the corresponding 19- and 17-electron carbonylmanganese radicals as follows.

3.1. *Fate of 19- and 17-electron carbonylmanganese radicals*

Cathodic reduction of the substituted carbonylmanganese cations $[Mn(CO)_5(L)]^+$ (L = CO, CH_3CN, py, PPh_3, PPh_2Me, etc.) produces transient carbonylmanganese radicals $[Mn(CO)_5(L)]^\bullet$ [5a,b]. As supersaturated 19-electron species, $[Mn(CO)_5(L)]^\bullet$ is known to undergo

Table 3
Annihilation of carbonylmanganese cations $[Mn(CO)_5L]^+$ with tetraphenylborate anion in tetrahydrofuran[a]

	L	Product (yield %)[b]
1	CH_3CN	$C_6H_5Mn(CO)_5$ (86)[c]
2	Pyridine	$Mn_2(CO)_{10}$ (65)[c]
3	PPh_3[d]	$C_6H_5Mn(CO)_4L$ (35), $HMn(CO)_4L$ (21), $Mn_2(CO)_8L_2$ (32)
4	PPh_2Me[d]	$C_6H_5Mn(CO)_4L$ (23), $HMn(CO)_4L$ (41), $Mn_2(CO)_8L_2$ (22)

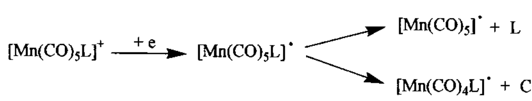
[a] Reaction carried out at 23°C for 18 h.

[b] Isolated yield unless indicated otherwise.

[c] Products quantified by IR analysis.

[d] At 60°C for 24 h.

two basic transformations, namely, (a) ligand dissociation to afford the corresponding 17-electron radicals $[\mathrm{Mn(CO)_5}]^\bullet$ and/or $[\mathrm{Mn(CO)_4(L)}]^\bullet$ (Eqs. (4) and (5)) [5],



(4,5)

and (b) hydrogen abstraction to produce the hydridomanganese complexes $\mathrm{HMn(CO)_4(L)}$ (Eq. (6)) [5],

$$[\mathrm{Mn(CO)_5L}]^+ \xrightarrow{+e} [\mathrm{Mn(CO)_5L}]^\bullet \xrightarrow{\mathrm{HS}} \mathrm{HMn(CO)_4L + CO} \qquad (6)$$

where HS is the hydrogen-donor solvent. The competition between these two pathways is highly dependent on the nature of ligand L in the following way. In the case of $\mathrm{L = CH_3CN}$ and py, acetonitrile or pyridine dissociation is much faster than either hydrogen abstraction or CO dissociation [5], and the 17-e carbonylmanganese radical $[\mathrm{Mn(CO)_5}]^\bullet$ then formed is subject to ready dimerization to afford dimanganese decacarbonyl (Eq. (7)) [5c], i.e.

$$2[\mathrm{Mn(CO)_5L}]^\bullet \xrightarrow{-2\mathrm{L}} 2[\mathrm{Mn(CO)_5}]^\bullet \rightarrow \mathrm{Mn_2(CO)_{10}} \qquad (7)$$

where $\mathrm{L = CH_3CN}$ and pyridine. When L is a phosphine ligand such as $\mathrm{PPh_3}$ and $\mathrm{PPh_2Me}$, the loss of CO is preferred over the dissociation of phosphine. As a result, dimanganese decacarbonyl is not an important reduction product of phosphine-substituted carbonylmanganese cations. However, the rate of hydrogen abstraction from the solvent HS is comparable to that of the ligand dissociation (i.e. loss of carbon monoxide) [5]. Hydrogen abstraction of 19-electron carbonylmanganese radicals from the solvent forms the formylmanganese intermediate $\mathrm{HCOMn(CO)_4(L)}$, which is readily converted to hydridomanganese carbonyl $\mathrm{HMn(CO)_4(L)}$ via the rapid extrusion of carbon monoxide [19]. Loss of CO from the 19-e carbonylmanganese radicals $[\mathrm{Mn(CO)_5(L)}]^\bullet$ produces 17-e radicals; and the $[\mathrm{Mn(CO)_4(L)}]^\bullet$ readily dimerize to yield $\mathrm{Mn_2(CO)_8(L)_2}$ where L = phosphines (Eqs. (8) and (9)) [5].

$$[\mathrm{Mn(CO)_5L}]^\bullet \xrightarrow{-\mathrm{CO}} [\mathrm{Mn(CO)_4L}]^\bullet \xrightarrow{\mathrm{fast}} 1/2\ \mathrm{Mn_2(CO)_8L_2} \qquad (8)$$

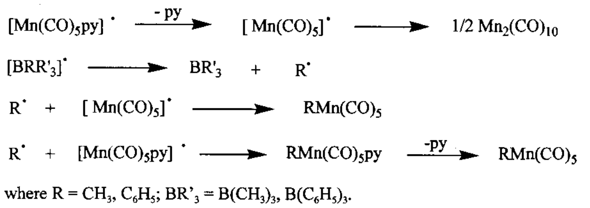
$$[\mathrm{Mn(CO)_5L}]^\bullet \xrightarrow{\mathrm{HS}} \mathrm{HCOMn(CO)_4L} \xrightarrow[\mathrm{fast}]{-\mathrm{CO}} \mathrm{HMn(CO)_4L} \qquad (9)$$

3.2. *Comments on the electron-transfer mechanism*

The comparison of the carbonylmanganese products in Tables 1–3 with the known behavior of the 19-e carbonylmanganese radicals supports their intermediacy in the nucleophilic interaction of $[\mathrm{Mn(CO)_5(L)}]^+$ ($\mathrm{L = py, PPh_3}$ and $\mathrm{PPh_2Me}$) with tetramethylborate, methyltriphenylborate or tetraphenylborate via an initial electron transfer (Eq. (10)) [5,7,11], i.e.

$$[\mathrm{Mn(CO)_5L}]^+ + \mathrm{BRR'_3}^- \xrightarrow{\mathrm{ET}} [\mathrm{Mn(CO)_5L}]^\bullet + \mathrm{BRR'_3}^\bullet \qquad (10)$$

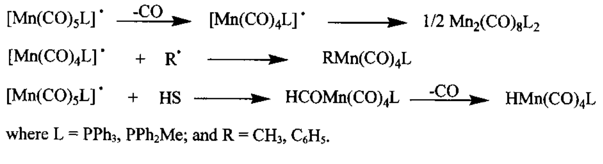
where the ligand L is either py, $\mathrm{PPh_3}$ or $\mathrm{PPh_2Me}$ and the alkylborate $\mathrm{BRR'_3}^-$ is either $\mathrm{B(CH_3)_4^-}$, $\mathrm{B(CH_3)(C_6H_5)_3^-}$ or $\mathrm{B(C_6H_5)_4^-}$.



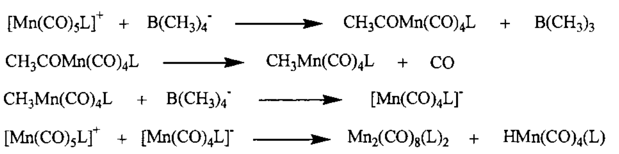
Scheme 1.

For L = pyridine, the 19-electron carbonylmanganese radicals $[\mathrm{Mn(CO)_5(py)}]^\bullet$ rapidly lose pyridine to yield 17-electron radical $[\mathrm{Mn(CO)_5}]^\bullet$, the coupling of which leads to dimanganese decacarbonyl $\mathrm{Mn_2(CO)_{10}}$ [5]. The tetramethylboranyl, methyltriphenylboranyl and tetraphenylboranyl radicals are also labile and subject to boron–carbon bond cleavage to yield (a) methyl radical and trimethylborane, (b) methyl radical and triphenylborane, or (c) phenyl radical and triphenylborane [6,9,10], respectively. Methylmanganese pentacarbonyl $\mathrm{CH_3Mn(CO)_5}$ can derive from either the coupling of methyl radical and the 17-e carbonylmanganese radical $[\mathrm{Mn(CO)_5}]^\bullet$ or the coupling of methyl radical and the 19-e radical $[\mathrm{Mn(CO)_5(py)}]^\bullet$ followed by the expulsion of pyridine (Scheme 1).

When L is either $\mathrm{PPh_3}$ or $\mathrm{PPh_2Me}$, the dissociation of CO from the 19-e radicals $[\mathrm{Mn(CO)_5(PPh_3)}]^\bullet$ or $[\mathrm{Mn(CO)_5(PPh_2Me)}]^\bullet$ competes with hydrogen abstraction [5,19]. Dissociation of CO produces 17-e carbonylmanganese radicals $[\mathrm{Mn(CO)_4(PPh_3)}]^\bullet$ or $[\mathrm{Mn(CO)_4(PPh_2Me)}]^\bullet$, which subsequently undergo (a) dimerization to afford $\mathrm{Mn_2(CO)_8(L)_2}$ with L = phosphines, or (b) coupling with methyl radical or phenyl radical to form $\mathrm{CH_3Mn(CO)_4(L)}$ or $\mathrm{C_6H_5Mn(CO)_4(L)}$ where $\mathrm{L = PPh_3}$ and $\mathrm{PPh_2Me}$. The 19-e radicals $[\mathrm{Mn(CO)_5(PPh_3)}]^\bullet$ and $[\mathrm{Mn(CO)_5(PPh_2Me)}]^\bullet$ can also abstract hydrogen atom from the solvent (HS) to generate formylmanganese complexes $\mathrm{HCOMn(CO)_4(PPh_3)}$ and $\mathrm{HCOMn(CO)_4(PPh_2Me)}$, respectively, which subsequently yield the hydridomanganese complexes $\mathrm{HMn(CO)_4(PPh_3)}$ and $\mathrm{HMn(CO)_4(PPh_2Me)}$ by ready extrusion of carbon monoxide [5,19] (Scheme 2).



Scheme 2.



Scheme 3.

Another route to $CH_3Mn(CO)_4(L)$ or $C_6H_5Mn(CO)_4(L)$ for $L = PPh_3$ and PPh_2Me involves the coupling of the 19-e radicals $[Mn(CO)_5(PPh_3)]^\bullet$ and $[Mn(CO)_5(PPh_2Me)]^\bullet$ with methyl radical (or phenyl radical), followed by decarbonylation of CH_3CO-$Mn(CO)_4(L)$ or $C_6H_5COMn(CO)_4(L)$ [20] (Eq. (11)), i.e.

$$[\mathrm{Mn(CO)_5L}]^\bullet + \mathrm{R}^\bullet \rightarrow \mathrm{RCOMn(CO)_4L} \xrightarrow{-\mathrm{CO}} \mathrm{RMn(CO)_4L} \qquad (11)$$

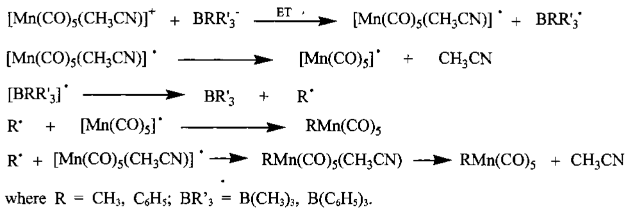
where $L = PPh_3$, PPh_2Me and $R = CH_3$, C_6H_5.

$CH_3Mn(CO)_5$ reacts rapidly with tetramethylborate to afford pentacarbonylmanganate $Mn(CO)_5^-$ as described in Eq. (3). Since $[Mn(CO)_5(PPh_3)]^+$ has been reported to react with $[Mn(CO)_4(PPh_3)]^-$ to generate $Mn_2(CO)_8(PPh_3)_2$ and $HMn(CO)_4(PPh_3)$ (Eq. (12)) [5c], i.e.

$$[\mathrm{Mn(CO)_5(PPh_3)}]^+ + [\mathrm{Mn(CO)_4(PPh_3)}]^- \rightarrow \mathrm{Mn_2(CO)_8(PPh_3)_2} + \mathrm{HMn(CO)_4(PPh_3)} \qquad (12)$$

There is an alternative possibility for the formation of $Mn_2(CO)_8(L)_2$ and $HMn(CO)_4(L)$ (where $L = PPh_3$ and PPh_2Me) in the reaction of $[Mn(CO)_5(L)]^+$ with tetramethylborate. Thus $[Mn(CO)_5(L)]^+$ may react with tetramethylborate via nucleophilic attack of tetramethylborate on the carbonyl ligand followed by decarbonylation to give $CH_3Mn(CO)_4(L)$, which then reacts with the unreacted tetramethylborate to afford $[Mn(CO)_4(L)]^-$. The $[Mn(CO)_4(L)]^-$ subsequently reacts with $[Mn(CO)_5(L)]^+$ to produce $Mn_2(CO)_8(L)_2$ and $HMn(CO)_4(L)$ (where $L = PPh_3$ and PPh_2Me) as described in Scheme 3.

In order to test this possibility, we carried out a control experiment of the reaction of $CH_3Mn(CO)_4$-(PPh_3) with tetramethylborate, and found that $CH_3Mn(CO)_4(PPh_3)$ does not react with tetramethylborate under identical reaction conditions. Another pathway to form $[Mn(CO)_4(PPh_3)]^-$ via the interaction of $CH_3COMn(CO)_4(PPh_3)$ with tetramethylborate [21] is also unlikely, as indicated by the control experiment. We conclude therefore that $Mn_2(CO)_8(L)_2$ and $HMn(CO)_4(L)$ where $L = PPh_3$ and PPh_2Me is unlikely to be derived from the direct ion-pair annihilation of manganate(-I) anion and manganese(I) cation.



Scheme 4.

3.3. Comments on the nucleophilic mechanism

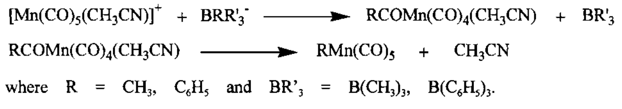
The acetonitrile-substituted carbonylmanganese cation reacts with tetramethylborate, methyltriphenylborate and tetraphenylborate to produce either $CH_3Mn(CO)_5$ or $C_6H_5Mn(CO)_5$ as the only carbonylmanganese product. There are two pathways possible for the formation of $CH_3Mn(CO)_5$ and $C_6H_5Mn(CO)_5$. One is the electron-transfer mechanism as discussed above for $L = Py$, PPh_3 and PPh_2Me, which simultaneously generates the 19-e carbonyl radical $[Mn(CO)_5(CH_3CN)]^\bullet$ and the boranyl radicals in Scheme 4.

The subsequent cleavage of the carbon–boron bond leads to methyl or phenyl radical. The 19-e radical $[Mn(CO)_5(CH_3CN)]^\bullet$ then couples with either methyl or phenyl radical to yield $CH_3COMn(CO)_4(CH_3CN)$ or $C_6H_5COMn(CO)_4(CH_3CN)$, which immediately form $CH_3Mn(CO)_5$ or $C_6H_5Mn(CO)_5$ by expulsion of acetonitrile [22,23].

An alternative, direct pathway involves tetramethylborate, methyltriphenylborate and tetraphenylborate acting as nucleophiles by their direct attack on the carbonyl group of $[Mn(CO)_5(CH_3CN)]^+$ as outlined in Scheme 5 [2–4].

The alkylated $CH_3COMn(CO)_4(CH_3CN)$ or $C_6H_5COMn(CO)_4(CH_3CN)$ is then converted to $CH_3Mn(CO)_5$ or $C_6H_5Mn(CO)_5$ by rapid expulsion of CH_3CN [22]. The singular absence of dimanganese decacarbonyl in the carbonylmanganese product suggests that the electron-transfer pathway is unlikely [5,7,24,25]. As a result, we believe the more reasonable pathway involves the direct nucleophilic attack of tetraalkylborates on the acetonitrile-substituted carbonylmanganese cation $[Mn(CO)_5(CH_3CN)]^+$.

A question is then raised as to why the behavior of the acetonitrile-substituted carbonylmanganese cation $[Mn(CO)_5(CH_3CN)]^+$ is so different from that of the pyridine- and phosphine-substituted analogues in the reaction with tetraalkylborates. The interaction of car-



Scheme 5.

Table 4
Infrared CO stretching frequencies and CO stretching force constants of $Mn(CO)_5(L)^+$

L	ν_{CO} (cm^{-1})	Force constant (mdyn/Å)[a]
CH_3CN	2161(w), 2074(s), 2047m	17.05, 17.83
py	2154(w), 2063(s), 2042m	16.97, 17.67
PPh_3	2142(w), 2063(sh), 2052s	17.37, 17.46
PPh_2Me	2144(w), 2062(sh), 2051s	17.36, 17.45

[a] From Drew et al. in Ref. [2b].

bonylmanganese cations with tetraalkylborates may result in either single electron transfer from tetraalkylborates to the carbonylmanganese cations or nucleophilic attack of tetraalkylborates on the carbonyl ligand of the carbonylmanganese cations. These two processes can compete and the predominant pathway will be dependent on the electrophilicity of the carbonyl groups as well as the electron affinity of the carbonylmanganese cations [5,26]. Since acetonitrile is a poor σ-donor and relatively good π-acceptor [27], the electron density on the carbonyl group in $[Mn(CO)_5(CH_3CN)]^+$ is withdrawn onto the CH_3CN ligand. Thus the electrophilicity of the carbonyl ligand is enhanced to an extent that the nucleophilic attack of tetraalkylborates on the carbonyl ligand should predominate over electron transfer. By contrast, pyridine, triphenylphosphine and diphenylmethylphosphine are relatively good σ-donors and relatively poor π-acceptors [27]. As a result, the electron density on the pyridine or phosphine ligand is partially transferred to the carbonyl groups, and the carbonyl ligands in carbonylmanganese cations $[Mn(CO)_5(L)]^+$ (L = py, PPh_3 and PPh_2Me) are not sufficiently electrophilic to encourage nucleophilic attack of borates. Indeed, the electron density residing on the carbonyl group of these carbonylmanganese cations is reflected in the CO stretching frequencies [28] in Table 4, which lists the CO stretching frequencies of $[Mn(CO)_5(L)]^+PF_6^-$ (L = CH_3CN, py, PPh_3 and PPh_2Me) and their calculated force constants derived from the spectroscopic data [2b]. It can be seen that $[Mn(CO)_5(CH_3CN)]^+$ has the highest CO stretching frequencies and force constants, suggesting that the carbonyl carbon atoms in $[Mn(CO)_5(CH_3CN)]^+$ are more positively charged and thus more electrophilic. As a result, nucleophilic attack of BR_4^- on the carbonyl ligand of $[Mn(CO)_5(CH_3CN)]^+$ is preferred over the electron-transfer process [29].

4. Conclusion

The annihilation of carbonylmanganese cations $[Mn(CO)_5(L)]^+$ by organoborate anions proceeds via either an electron-transfer or a nucleophilic pathway, depending on the electrophilicity of the carbonyl ligands and the electron affinity of the carbonylmanganese cations (which in turn can be readily modulated by varying the ligand L). The organoborate anions can thus be used to probe the electrophilicity of the carbonyl carbons and the overall electron affinities of the carbonylmanganese cations.

5. Experimental

5.1. Materials and instrumentation

Dimanganese decacarbonyl from Strem was sublimed, and triphenylphosphine was recrystallized from ethanol prior to use. Diphenylmethylphosphine and pyridine were redistilled. The carbonylmanganese cations $[Mn(CO)_5(L)]^+PF_6^-$ (L = CH_3CN, py, PPh_3 and PPh_2Me) [2,5], the tetrabutylammonium salts of tetramethylborate, methyltriphenylborate and *n*-butyltrimethylborate [30,31], and the authentic samples of $CH_3Mn(CO)_5$ [32], $C_6H_5Mn(CO)_5$ [33] $CH_3Mn(CO)_4(PPh_3)$ [20b], $CH_3Mn(CO)_4(PPh_2Me)$ [20b], $C_6H_5Mn(CO)_4(PPh_3)$ [20a], $C_6H_5Mn(CO)_4(PPh_2Me)$ [20a] and $HMn(CO)_4(PPh_3)$ [34] were prepared according to the previously reported methods. Sodium tetraphenylborate from Aldrich was used as received. Tetrahydrofuran was distilled from sodium benzophenone and stored in a Schlenk flask under argon. Acetonitrile was refluxed over 0.1% $KMnO_4$ for 1 h and distilled into another flask. The purified solvent was then redistilled serially from P_2O_5 and CaH_2 and stored in a Schlenk flask under argon. Chloroform-*d*, anhydrous THF-d_8 and benzene-d_6 from Aldrich (in small ampoules) were used as received. All the reactions were carried out under an atmosphere of argon using standard Schlenk techniques or in a drybox. ^1H- and ^{13}C-NMR spectra were recorded on a General Electric QE-300 spectrometer. IR spectra were obtained with NaCl cells (0.1 mm) using a Nicolet 10 DX FT spectrometer with 4 cm^{-1} resolution.

5.2. Reaction of $[Mn(CO)_5L]^+PF_6^-$ with the borates

5.2.1. $Bu_4N^+BMe_4^-$

Typically 5 ml of 0.01 M solution of Bu_4NBMe_4 in THF was added to 5 ml of 0.01 M solution of $[Mn(CO)_5L]^+PF_6^-$ in THF at −78°C. The resulting mixture was slowly warmed to 0°C over the course of 2 h. The reaction was monitored (by periodically extracting a sample for IR analysis) until the starting material was completely consumed. The products were identified by spectral comparisons with those of the authentic samples or those reported in the literature. $CH_3Mn(CO)_5$ and $Mn_2(CO)_{10}$ were quantified by comparison with calibration curves constructed from the IR absorbance of the unique carbonyl stretching band versus the concentration of the solution. For L = CH_3CN, $CH_3Mn(CO)_5$ was observed as the only manganese carbonyl product by the IR analysis of the reaction mixture. The carbonyl stretching bands with $\nu_{CO} = 2114$ (vw), 2045 (vw), 2008 (s), 1984 (m) cm^{-1} were in good agreement with an authentic sample of $CH_3Mn(CO)_5$. $CH_3Mn(CO)_5$ was quantified by the principal carbonyl band at 2008 cm^{-1}. In a NMR scale experiment of this reaction in THF-d_8, $Me_3B(THF)$ was observed ($\delta = 0.20$ ppm [10], not quantified). In the case of $[Mn(CO)_5(Py)]^+PF_6^-$, in addition to $CH_3Mn(CO)_5$, a small amount of $Mn_2(CO)_{10}$ was detected by TLC using a 4:1 mixture of hexane and THF as the eluent. A yellow band on TLC had the same R_f value as the authentic $Mn_2(CO)_{10}$ sample. The yield of $Mn_2(CO)_{10}$ was estimated by the IR band at 2045 cm^{-1}. For L = PPh_3 and PPh_3Me, the carbonyl stretching bands of the products were severely overlapped, and quantitative IR analysis could not be performed. Therefore, a larger scale of reaction was carried out for L = PPh_3 and PPh_3Me with 0.2 mmol of $[Mn(CO)_5L]^+PF_6^-$ and Bu_4NBMe_4. After the reactions were completed (as monitored by IR analysis), the volatile was removed in vacuo and the residue was chromatographed on a deactivated alumina column (hexane as eluent) to give the following products: For L = PPh_2Me, $Mn_2(CO)_8(PPh_2Me)_2$ [5]: 45 mg, 61% yield, ν_{CO}, 1981 (vw), 1952 (s) cm^{-1}; $HMn(CO)_4(PPh_2Me)$ [5,34]: 8 mg, 11% yield. ν_{CO} 2062 (m), 1971 (sh), 1965 (s), 1949 (m) cm^{-1}. ^{1}H-NMR (C_6D_6), δ -7.34 ppm ($J_{PH} = 39.0$ Hz); Only a trace of $CH_3Mn(CO)_4(PPh_2Me)$ [20a] was detected by TLC using a 4:1 mixture of hexane and THF as the eluent and IR comparison with an authentic sample. In this experiment, the volatile was condensed into another flask at -196°C. After a drop of pyridine was added, the solvent was removed at -30°C to give a liquid, which was identified by NMR as a mixture of $Me_3B(NC_5H_5)$ [35] and THF (30 mg). The ratio of $Me_3B(NC_5H_5)$ to THF was determined to be 3:2 by ^{1}H-NMR, and the yield of $Me_3B(NC_5H_5)$ was calculated to be 60%. ^{1}H-NMR (C_6D_6), δ ppm 0.434 (s, 9H, BMe_3), 6.45 (m, 2H, py), 6.77 (m, 1H, py), 8.32 (m, 2H, py). For L = PPh_3, $Mn_2(CO)_8(PPh_3)_2$ [5]: 49 mg, 58% yield. ν_{CO}, 1983 (vw), 1954 (s) cm^{-1}; $HMn(CO)_4(PPh_3)$ [5]: 10 mg, 12% yield. ν_{CO}, 2062 (m), 1970 (sh), 1965 (s), 1952 (m) cm^{-1}. ^{1}H-NMR (C_6D_6), δ -6.90 ppm ($J_{PH} = 34.4$ Hz); $CH_3Mn(CO)_4(PPh_3)$ [20a]: 13 mg, 15% yield. ν_{CO}, 2055 (w), 1970 (sh), 1965 (s), 1934 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$), δ -0.50 ppm ($J_{PH} = 7.6$ Hz).

5.2.2. $Bu_4N^+BMePh_3^-$

Typically 5 ml of 0.01 M solution of $Bu_4N^+BMePh_3^-$ in THF and 5 ml of 0.01 M solution of $[Mn(CO)_5L]^+PF_6^-$ in THF were mixed at room temperature and the resulting mixture was stirred at this temperature for a few hours. The products were identified and quantified as described above, and the results are summarized in Table 2.

5.2.3. $NaBPh_4$

Typically 5 ml of 0.01 M solution of $NaBPh_4$ in THF and 5 ml of 0.01 M solution of $[Mn(CO)_5L]^+PF_6^-$ in THF were mixed at room temperature. For L = CH_3CN and C_5H_5N, the resulting mixture was stirred at this temperature for 20 h. For L = PPh_3 and PPh_3Me, the resulting mixture was heated to 60°C and kept at this temperature for a day. The products were identified and quantified as described above, and the results are summarized in Table 3.

5.2.4. $Bu_4N^+B(Bu^n)Me_3^-$

A volume of 10 ml of 0.01 M solution of $Bu_4N^+B(Bu^n)Me_3^-$ in THF was added to 10 ml of 0.01 M solution of $[Mn(CO)_5L]^+PF_6^-$ in THF at -78°C. When the solution was warmed to -60°C, IR analysis indicated that the starting material was completely consumed. Only four carbonyl stretching bands with $\nu_{CO} = 2114$ (vw), 2045 (vw), 2008 (s), 1984 (m) cm^{-1} appeared and were in good agreement with those reported for $CH_3Mn(CO)_5$ in the literature [36]. Furthermore, when the solution was kept at room temperature for 2 days, no change in shape and intensity of the carbonyl stretching bands was observed. Since n-$C_4H_9Mn(CO)_5$ has been reported to be very thermally unstable [36], this suggested that the product was $CH_3Mn(CO)_5$ and no n-$C_4H_9Mn(CO)_5$ was observable (if any n-$C_4H_9Mn(CO)_5$, only very small amount of it existed). In another run of this reaction, when IR analysis indicated that the starting material was completely consumed at -60°C, an equivalent of PPh_2Me was added. The mixture was then warmed to 0°C. IR analysis indicated that $RMn(CO)_5$ was converted to $RCOMn(CO)_4(PPh_2Me)$ [20], which was isolated by filtration through a layer of deactivated alumina and identified as $CH_3COMn(CO)_4(PPh_2Me)$ [20]: 28.0 mg, 71% yield. ν_{CO} 2066 (w), 1989 (m), 1963 (s), 1952 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$), δ ppm 2.13 (s, 3H, PMe), 2.40 (s, 3H, MeCO), 7.5 (s, 10H, Ph).

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[23] Alternatively, the 19-e radical [Mn(CO)$_5$(CH$_3$CN)]$^\bullet$ first loses acetonitrile to form 17-electron radical [Mn(CO)$_5$]$^\bullet$, which then couples with methyl or phenyl radical to yield CH$_3$Mn(CO)$_5$ or C$_6$H$_5$Mn(CO)$_5$, respectively.

[24] Furthermore, if the reaction proceeded via an electron-transfer mechanism, *n*-butyltrimethylborate is expected to generate butyltrimethylboranyl radical, which would preferentially rupture the boron–butyl bond to give butyl radical and trimethylborane (Note the boron–butyl bond is weaker than the boron–methyl bond [9,10], and butyl radical is more stable than methyl [25]). Butylmanganese pentacarbonyl C$_4$H$_9$Mn(CO)$_5$ should thus be the major alkylmanganese product. However, the reaction of *n*-butyltrimethylborate with [Mn(CO)$_5$(CH$_3$CN)]$^+$ produces methylmanganese pentacarbonyl, and no butylmanganese pentacarbonyl is observed.

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