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First Alkyl Radical Additions to (η^6-Arene)tricarbonylmanganese Complexes

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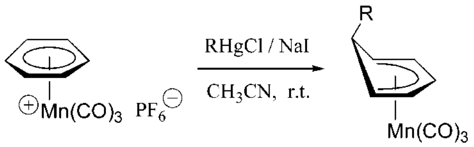
ABSTRACT

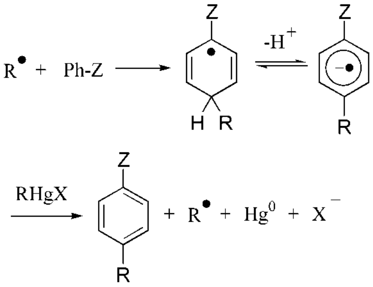


Reactions of alkylmercury chlorides with arene manganese tricarbonyl complexes in the presence of NaI led to the formation of the addition–reduction products. The mechanism was postulated to be the alkyl radical addition to $ArMn(CO)_3^+$ cation to form the corresponding 17 valence electron intermediate, which was then reduced by alkylmercury chloride via a singlet electron transfer process to afford the product and regenerate an alkyl radical.

Nucleophilic additions to arene metal complexes are one of the unique characteristics of organometallic chemistry and have attracted considerable interest in organic synthesis.[1] However, free radical additions to arene metal complexes are rarely seen and the chemistry is much less understood.[2] Moreover, no example has been published on alkyl radical additon to arene manganese complexes. We report here that alkyl radical addition to arene manganese complexes can be efficiently achieved by reaction of alkylmercury halides with arenetricarbonylmanganese hexafluorophosphates.

Alkylmercury halides have been demonstrated to be excellent alkyl radical precursors.[3] Base-promoted reactions of alkylmercury halides with electronegatively substituted benzene derivatives afforded the corresponding aromatic alkylation products (Scheme 1).[4] On the other hand, electron-rich benzene derivatives failed to react with alkylmercury halides, implying strong polar effect in these reactions.

Scheme 1



We envisioned that, with $Mn(CO)_3^+$ or $Cr(CO)_3$ as a powerful electron-withdrawing group, arenetricarbonylman-

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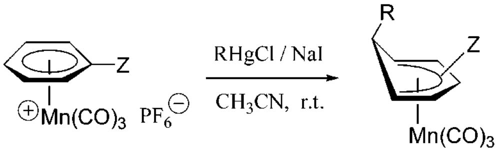
ganese or -chromium complexes might also undergo similar homolytic alkylation reactions. Thus, we treated benzenetricarbonylmanganese hexafluorophosphate (**1a**)[5] with *tert*-butylmercury chloride[6] in acetonitrile with NaI as the catalyst and DABCO as base. The reaction was complete within 2 h at room temperature, and only one product was detected by TLC (Scheme 2). After purification by column chromatography on silica gel with hexane as the eluent, the product was characterized to be the manganese complex **2a** rather than the expected homolytic alkylation product. X-ray diffractional analysis of **2a** showed that the addition occurred in the exo mode. On the basis of this result, it seemed that DABCO is unnecessary in the reaction. We then carried out the above reaction without DABCO and **2a** was isolated in 96% yield. The reaction was inhibited by 10 mol % of di-(*tert*-butyl)nitroxide for weeks and the kinetic chain length was thus measured to be around 19 000, indicating that the reaction is an excellent radical chain process. Use of excess NaI is necessary for the reaction because the yield of **2a** was significantly lowered with only 1 equiv of NaI while no **2a** could be detected without NaI. The requirement of NaI is likely to be attributed to the easy decomposition of the ate complexes ^{t}BuHgI$_2^-$ formed in situ as extensively demonstrated by Russell.[3] ^{i}PrHgCl reacted with benzenetricarbonylmanganese hexafluorophosphate to give **2b** in 76% yield. However, ^{i}BuHgI gave only a trace amount of the corresponding product. Among the solvents screened, acetonitrile gave the best yield of product. For example, **2b** was produced in 76% yield in acetonitrile, while lower yields were observed in acetone (29%), THF (20%), and DMSO (59%). Other (η^6-arene)tricarbonylmanganese complexes underwent similar reactions, and the results are summarized in Table 1. On the other hand, benzenetricarbonylchromium failed to react with *tert*-butylmercury halides.

Scheme 2



1 **2**

As shown in Table 1, ^{t}BuHgCl gave higher yields of **2** than ^{i}PrHgCl. The toluene complex afforded the corresponding products in lower yields than the benzene complex (e.g., entries a and c, Table 1), and the yields of **2** were further lowered in the cases of 1,2- or 1,4-dimethylbenzene complexes (entries e−h). Moreover, when ^{t}BuHgCl/NaI was treated with anisolemanganesetricarbonyl hexafluorophosphate under similar conditions, the corresponding product **2** was generated in about 10% yield determined by ^{1}H NMR and its isolation in pure form was unsuccessful. This trend seems to imply the sensitivities of the addition reactions toward the electron densities of the phenyl rings in **1**.

Table 1. Reactions of RHgCl/NaI with $ArMn(CO)_3{}^+PF_6{}^-$

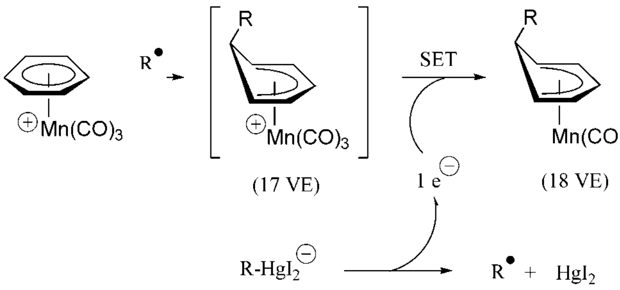
entry	Z	R	time (h)	yield (%)[a]	regioselectivity[b]
a	H	^{t}Bu	2	96	
b	H	^{i}Pr	7	76	
c	Me	^{t}Bu	5	74	5:76:19 (o:m:p)
d	Me	^{i}Pr	7	76	29:57:14 (o:m:p)
e	1,2-di-Me	^{t}Bu	20	64	16:84 (o:m)
f	1,2-di-Me	^{i}Pr	20	46	48:52 (o:m)
g	1,4-di-Me	^{t}Bu	21	50	
h	1,4-di-Me	^{i}Pr	21	42	

[a] Isolated yield based on **1**. [b] Determined by HPLC.

For substituted benzene derivatives, radical addition occurred at all ortho-, meta-, and para-positions. Meta addition was favored over para addition, and the ratio was about four to one (entries c and d, Table 1). With the increase of the bulkiness of alkyl radicals, the ortho addition was significantly inhibited. This regioselectivity was different from that of nucleophilic additions by alkyl anions in which para addition was preferred.[7]

On the basis of the above results, a plausible mechanism could be drawn as depicted in Scheme 3. The alkyl radical added to the arenetricarbonylmanganese complex **1**, forming the 17 valence electron intermediate, which was then reduced by RHgI$_2^-$ via singlet electron transfer process to afford the stable 18-VE product **2** and regenerate an alkyl radical. Therefore, alkylmercury halides serve as both radical precursors and reducing agents.[8] Higher yields of **2** were obtained with ^{t}BuHgCl than with ^{i}PrHgCl while ^{i}BuHgCl gave only a trace amount of the reductive alkylation products. This reactivity sequence is likely to result from the efficiencies of the steps in which R$^\bullet$ is formed.[9] The failure of RHgCl to react with benzenetricarbonylchromium might be ascribed

Scheme 3



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to the weaker electron-withdrawing effect of $Cr(CO)_3$ than $Mn(CO)_3^+$, which might result in the higher reductive potential of the 17-VE chromium intermediate than the corresponding manganese intermediate.

In conclusion, we find that alkylmercury halides can undergo free radical reductive alkylation reactions with arenetricarbonylmanganese complexes. More detailed research on the behaviors of alkyl radical addition toward $ArMn(CO)_3^+$ and the substitution for alkylmercury halides by other radical initiation systems to avoid the high toxicity of organomercurials are currently under investigation in our group.

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Supporting Information Available: Preparations of **1**, typical experimental procedure for the synthesis of **2**, characterization of **2a**−**h**, X-ray crystal data of **2a** and **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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