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Indium-Mediated Alkyl Radical Addition to (η^6-Arene)tricarbonylmanganese Complexes in Aqueous Media

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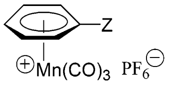
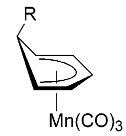
Alkyl radical addition to (η^6-arene)tricarbonylmangenese complexes was investigated with SmI_2, zinc, or indium as the radical initiator. Among them, the indium-mediated reactions of (η^6-arene)tricarbonylmangenese cations with various alkyl iodides in aqueous media afforded the corresponding radical addition−reduction products in moderate to excellent yields.

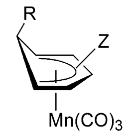
Complexation of an arene ring with a $Cr(CO)_3$ or $Mn(CO)_3^+$ moiety significantly reduces the electron density of the arene ring, thus allowing nucleophilic addition to occur.[1] The reduction of the electron density of the phenyl ring also encourages the addition of nucleophilic radicals.[2] For example, Merlic and co-workers demonstrated that ketyl radical addition to $Cr(CO)_3$-complexed benzene is at least 100 000 times faster than attack on free benzene.[3] However, only a few examples were reported on radical addition to arene-metal complexes, most of which dealt with ketyl radical addition to (η^6-arene)$Cr(CO)_3$ complexes.[3−5] Recently, we reported the first examples of radical addition to (η^6-arene)tricarbonylmangenese cations (**1**) by reaction with alkylmercury halides.[5c] The alkyl radical added to the phenyl ring in **1** to generate the corresponding 17-valence electron intermediate, which was presumably further reduced by alkylmercury halide, leading to the formation of the stable 18-valence-electron product **2** and to the regeneration of an alkyl radical.[6] In this reaction the alkylmercury halide served not only as the radical precursor but also as the reducing agent. This radical chain process worked well for *tert*-butylmercury halide, and an excellent yield of the product **2a** was achieved. However, with isopropylmercury halide the chain process was less efficient, while almost no reaction could be observed for isobutyl- or *n*-butyl-mercury halide. Moreover, the high toxicity of alkylmercury halides also limited the application of the above method in organic synthesis. To develop general and convenient methods to conduct the radical reactions, we carried out the following investigation. We report here that alkyl radical addition to (η^6-arene)$Mn(CO)_3^+$ complexes can be successfully carried out in aqueous media by reaction with indium(0) and alkyl iodides.



1a (Z = H)
1b (Z =Me)
1c (Z = *i*-Pr)
1d (Z = OMe)



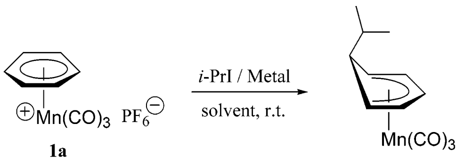
2a (R = *t*-Bu), **2b** (R = *i*-Pr)
2c (R = *c*-hexyl), **2d** (R = *s*-Bu)
2e (R = *n*-Bu), **3** (R = H)



4 (Z = Me)
5 (Z = *i*-Pr)
6 (Z = OMe)

Results and Discussion

As discussed above and also in the literature,[2,5c] successful radical addition to arene-$Mn(CO)_3^+$ complexes would require both a radical precursor and a reducing agent. A metal reductant and an alkyl halide would be an ideal combination to meet this requirement. Thus, we chose manganese complex **1a** as the model substrate and isopropyl iodide as the radical source to explore this possibility (eq 1). The results are presented in Table 1.



(Eq 1)

1a **2b**

Treatment of an alkyl iodide with SmI_2 to generate an alkyl radical is well documented.[7] Thus, we first tested the SmI_2/*i*-PrI system. The reaction of **1a** with

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[1] For reviews, see: (a) Kane-Maguire, L. A. P.; Honig, E. P.; Sweigart, D. A. *Chem. Rev.* **1984**, *84*, 525. (b) Semmelhack, M. F. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: New York, 1991; Vol. 4, p 517. (c) Semmelhack, M. F. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: New York, 1995; Vol. 12, p 979. (d) Sun, S.; Dullaghan, C. A.; Sweigart, D. A. *J. Chem. Soc., Dalton Trans.* **1996**, 4493. (e) Pape, A. R.; Kaliappan, K. P.; Kundig, E. P. *Chem. Rev.* **2000**, *100*, 2917. (f) Rose-Munch, F.; Rose, E. *Curr. Org. Chem.* **1999**, *3*, 445. (g) Rose-Munch, F.; Rose, E. *Eur. J. Inorg. Chem.* **2002**, 1269.

[2] For a review article, see: Lin, H.; Shen, M.; Yang, L.; Li, C. *Chin. J. Org. Chem.* **2003**, *23*, 944.

[3] Merlic, C. A.; Miller, M. M.; Hietbrink, B. N.; Houk, K. N. *J. Am. Chem. Soc.* **2001**, *123*, 4904.

[4] (a) Schmalz, H.-G.; Siegel, S.; Bats, J. W. *Angew. Chem., Int. Ed.* **1995**, *34*, 2383. (b) Schmalz, H.-G.; Siegel, S.; Schwarz, A. *Tetrahedron Lett.* **1996**, *37*, 2947. (c) Hoffmann, O.; Schmalz, H.-G. *Synlett* **1998**, 1426. (d) Schwarz, O.; Brun, R.; Bats, J. W.; Schmalz, H.-G. *Tetrahedron Lett.* **2002**, *43*, 1009. (e) Schmalz, H.-G.; Kiehl, O.; Gotov, B. *Synlett* **2002**, 1253.

[5] (a) Lin, H.; Yang, L.; Li, C. *Organometallics* **2002**, *21*, 3848. (b) Lin, H.; Yang, L.; Li, C. *Chin. J. Chem.* **2003**, *21*, 797. (c) Lin, H.; Zhang, H.; Yang, L.; Li, C. *Org. Lett.* **2002**, *4*, 823.

10.1021/om050721c CCC: \$30.25

Table 1. Synthesis of 2b via the Reaction of 1a at 20 °C

entry	metal (equiv)	solvent	time (h)	yield (%)[a]
1	SmI_2 (4)[b]	THF	2	15
2	SmI_2 (4)[b]	CH_3CN	2	38
3	SmI_2 (4)[b]	CH_3CN/HMPA (12:1)	2	12
4	Zn (2)[c]	sat. NH_4Cl	10	10
5	Zn (2)[c]	sat. NH_4Cl/CH_3CN (2:1)	10	31
6	Zn (2)[c]	sat. NH_4Cl/CH_3CN (1:2)	10	25
7	Zn (3)[c]	sat. NH_4Cl/CH_3CN (2:1)	10	17
8	Zn (5)/CuI (0.5)[d]	H_2O/CH_3CN (3:1)	10	88
9	In (3)[e]	H_2O	10	85

[a] Isolated yield based on **1a**. [b] Two equivalents of *i*-PrI was employed. [c] Four equivalents of *i*-PrI was employed. [d] Ultrasonic irradiation was used. [e] Six equivalents of *i*-PrI was employed.

Table 2. Synthesis of 2a via Reaction of 1a with In(0)/*t*-BuI

entry	$H_2O:CH_3CN$	temp (°C)	time (h)	yield (%)[a]
1	1:3	20	2	trace
2	1:3	20	24	46
3	3:1	20	24	49
4	1:2	40	10	47
5	2:1	70	10	46
6	1:2	70	10	62
7	CH_3CN	70	10	trace
8	H_2O	70	10	50

[a] Isolated yield based on **1a**.

i-PrI (2 equiv) and SmI_2 (4 equiv) in THF at room temperature for 2 h afforded the expected product **2b** in only 15% yield (entry 1, Table 1). When the reaction was carried out in acetonitrile, the yield of **2b** was improved to 38% (entry 2, Table 1). Introduction of HMPA resulted in a decrease of yield (12%), while the direct reduction product of **1a**, (η^5-cyclohexadienyl)-tricarbonylmanganese complex **3**, was obtained in about 50% yield (entry 3, Table 1).[8] Varying the amount of *i*-PrI or SmI_2 or changing the reaction temperature did not result in any improvement. Under the above optimized condition (CH_3CN, rt), **2a** was achieved in 59% yield by reaction of **1a** with *t*-BuI, while no **2e** could be obtained in the reaction of **1a** with *n*-BuI. This difference might be rationalized by the relative efficiencies of generation of the alkyl radicals (*t*-Bu > *i*-Pr > *n*-Bu). In all the above cases, the direct reduction of **1a** was, more or less, always observed.

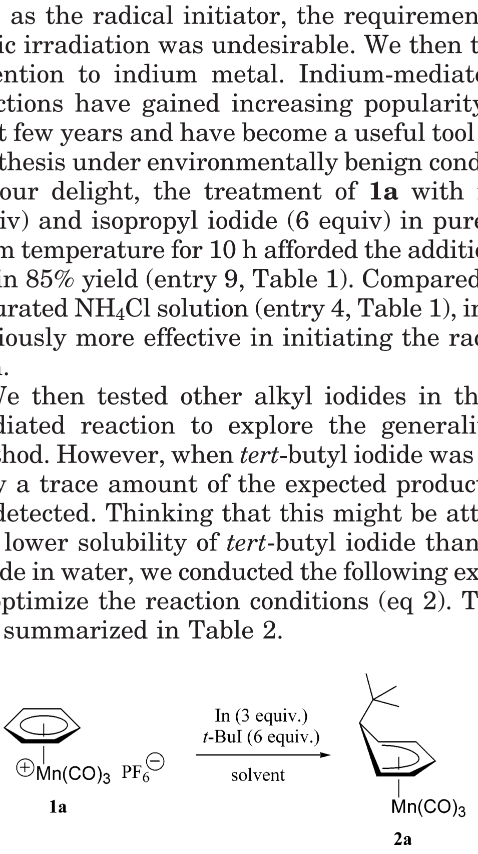
It should be mentioned that we also tested the possibility of ketyl radical addition to (η^6-arene)Mn-$(CO)_3^+$ by reaction with SmI_2 and a carbonyl compound. However, in sharp contrast to the success in ketyl radical addition to (η^6-arene)$Cr(CO)_3$ complexes,[3–5] under various experimental conditions screened, only the direct reduction product **3** was observed. The easy reduction of **1a** should be attributed to the much stronger electron-withdrawing effect of $Mn(CO)_3^+$ than $Cr(CO)_3$.

We next selected zinc as the radical initiator. Zinc-mediated radical reactions in aqueous media have received considerable attention from both economical and environmental points of view.[9,10] The reaction of **1a** with zinc (2 equiv) and *i*-PrI (4 equiv) in saturated ammonium chloride solution at rt for 10 h afforded the product **2b** in 10% yield (entry 4, Table 1). Since the radical addition showed a better performance in acetonitrile,[5c] we used acetonitrile as the cosolvent to enhance the solubility of *i*-PrI, and a higher yield (31%) was achieved when the ratio of saturated NH_4Cl solution to CH_3CN was 2:1 (entry 5, Table 1). Increasing the amount of zinc did not show much difference in the product yield (entry 7, Table 1). Since the presence of CuI as the catalyst significantly enhanced the zinc-mediated radical reactions in aqueous media,[10b] we carried out the reaction of **1a** with Zn/CuI under ultrasonic irradiation, and the product **2b** was thus obtained in 88% yield (entry 8, Table 1).

It should be noted that the above zinc-mediated radical addition showed a different reactivity pattern from the nucleophilic addition of alkylzinc reagents such as $IZn(CH_2)_3OAc$ in THF, in which alkylation of the manganese cation at the C-2 position of THF was observed.[11]

Although a satisfactory yield was achieved with Zn/CuI as the radical initiator, the requirement of ultrasonic irradiation was undesirable. We then turned our attention to indium metal. Indium-mediated radical reactions have gained increasing popularity over the past few years and have become a useful tool in organic synthesis under environmentally benign conditions.[12,13] To our delight, the treatment of **1a** with indium (3 equiv) and isopropyl iodide (6 equiv) in pure water at room temperature for 10 h afforded the addition product **2b** in 85% yield (entry 9, Table 1). Compared to zinc in saturated NH_4Cl solution (entry 4, Table 1), indium was obviously more effective in initiating the radical reaction.

We then tested other alkyl iodides in the indium-mediated reaction to explore the generality of this method. However, when *tert*-butyl iodide was employed, only a trace amount of the expected product **2a** could be detected. Thinking that this might be attributed to the lower solubility of *tert*-butyl iodide than isopropyl iodide in water, we conducted the following experiments to optimize the reaction conditions (eq 2). The results are summarized in Table 2.



(Eq 2)

To increase the solubility of *tert*-butyl iodide, acetonitrile was again used as the cosolvent. The reaction in water/acetonitrile solution at room temperature was very slow. After 24 h, the expected product **2a** was

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(6) Zaworotko et al. reported that the reactions of arene-$Mn(CO)_3^+$ cations with trialkylaluminum could involve an electron-transfer process. However, the proposed mechanism was single-electron transfer to arene-$Mn(CO)_3^+$ to form the neutral 19-electron complex rather than alkyl radical addition to arene-$Mn(CO)_3^+$ to form the 17-electron intermediates. See: Gaudet, M. V.; Hanson, A. W.; White, P. S.; Zaworotko, M. J. *Organometallics* **1989**, *8*, 286.

(7) For reviews on SmI_2-mediated radical reactions, see: (a) Molander, G. A. In *Radicals in Organic Synthesis*; Renaud, P., Sibi, M. P., Eds.; Wiley-VCH: New York, 2001; Vol. 1, p 153. (b) Molander, G. A.; Harris, C. R. *Chem. Rev.* **1996**, *96*, 307.

(8) Direct reduction of arenetricarbonylmanganese cations with $NaBH_4$ or $LiAlH_4$ was reported in the literature. See: Winkhaus, G.; Pratt, L.; Wilkinson, G. *J. Chem. Soc.* **1961**, 3807.

(9) For reviews, see: (a) Li, C.-J. *Chem. Rev.* **1993**, *93*, 2023. (b) Lubineau, R.; Ange, J.; Queneau, Y. *Synthesis* **1994**, 741. (c) Li, C.-J. *Tetrahedron* **1996**, *52*, 5643. (d) Podlech, J.; Maier, T. C. *Synthesis* **2003**, 633. (e) Li, C.-J.; Wang, D. *Chemtracts* **2003**, *16*, 59.

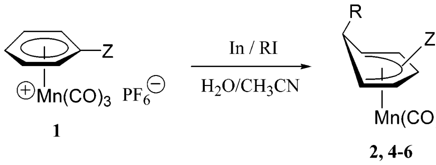
Table 3. In(0)-Mediated Alkyl Radical Addition to Manganese Complexes 1 in Aqueous Media

entry	Z	R	temp (°C)	product	yield (%)[a]	*o*:*m*:*p*[b]
1	H	*t*-Bu	70	**2a**	62	
2	H	*i*-Pr	40	**2b**	96	
3	H	*c*-hexyl	40	**2c**	83	
4	H	*s*-Bu	40	**2d**	91	
5	H	*n*-Bu	70	**2e**	35	
6	Me	*t*-Bu	70	**4a**	36	0:93:7
7	Me	*i*-Pr	40	**4b**	66	21:67:12
8	Me	*c*-hexyl	40	**4c**	72	8:80:12
9	Me	*s*-Bu	40	**4d**	50	15:75:10
10	*i*-Pr	*i*-Pr	50	**5b**	86	2:67:31
11	*i*-Pr	*c*-hexyl	50	**5c**	71	1:70:29
12	*i*-Pr	*s*-Bu	50	**5d**	60	2:67:31
13	OMe	*i*-Pr	50	**6b**	45	0:100:0
14	OMe	*c*-hexyl	50	**6c**	42	0:100:0
15	OMe	*s*-Bu	50	**6d**	40	0:100:0

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

isolated in 46% yield (entries 1 and 2, Table 2). Changing the ratio of water to acetonitrile showed little difference (entry 3, Table 2). Increasing the reaction temperature to 40 °C resulted in a faster reaction, and **2a** was obtained in 47% yield within 10 h (entry 4, Table 2). When the reaction was carried out at 70 °C with H_2O/CH_3CN in a 1:2 ratio as the solvent, the yield of **2a** jumped to 62% (entry 6, Table 2). The advantage of the mixed solvent was further evidenced by running the reaction in H_2O or CH_3CN alone, which gave **2a** in lower yields (entries 7 and 8, Table 2).

Thus, we used H_2O/CH_3CN (1:2, v/v) as the solvent and conducted the reactions of manganese complexes **1a**−**d** with a number of alkyl iodides of typical structure (eq 3). The results are summarized in Table 3.



(Eq 3)

As can be seen in Table 3, radical addition to cations **1** proceeded smoothly for all the primary, secondary, and tertiary carbon radicals, and the corresponding addition products were achieved in moderate to excellent yields. The secondary alkyl radicals gave the best results, and the corresponding addition products **2b**−**d** were achieved in excellent yields (entries 2−4, Table 3). The tertiary butyl radical gave the higher yield of addition product than the primary butyl radical (entries 1 and 5, Table 3). These phenomena are in line with the observations in many other indium-mediated radical reactions.[13] This trend (2° > 3° > 1° radicals) is different from that in the reactions of **1** with alkylmercury halides (3° > 2° > 1° radicals).[5c] The benzene complex **1a** gave higher yields of reductive alkylation products than the toluene complex **1b** or the isopropylbenzene complex **1c**, which in turn showed better performance than the anisole complex **1d**. These results indicate the sensitivity of the radical addition toward the electron densities of the arene ring in **1**. With regard to the regioselectivity in the reactions of **1b**−**d**, *meta*-addition was preferred for **1b**,**c**, while exclusively *meta*-addition was achieved for methoxy-substituted complex **1d** (entries 13−15, Table 3). The increase of the bulkiness of alkyl radicals inhibited the *ortho*-addition, and thus only *meta*- and *para*-addition products could be detected in the reaction of *tert*-butyl radical (entry 6, Table 3). The above regioselectivity pattern is similar to that in the nucleophilic addition reactions with Grignard reagents[14−23] or organolithium reagents[16,19−21,24−25] but slightly better than that in the reactions of **1b** with alkylmercury halides.[5c]

To further demonstrate the advantage of the above methodology, we prepared alkyl iodides **7a**−**e** bearing various functional groups and carried out their reactions with complex **1a** (Table 4). As can be seen in Table 4, the corresponding radical addition products **8a**−**e** were achieved in satisfactory yields. The *trans*-substituted substrate **7d** gave the product **8d** as the mixture of two stereoisomers in 6:1 ratio determined by HPLC. Surprisingly, the reaction of *trans*-2-iodocyclohexanol **7e** with **1a** produced exclusively the *trans* isomer **8e**, whose structure was unambiguously determined by its X-ray diffraction experiment (Figure 1). Although the reason for the different behaviors between **7d** and **7e** is still unclear, the excellent stereoselectivity in the case of **7e** might be attributed to the possible coordination of In(I) to the hydroxyl group, which could impose a significant steric effect on the radical addition.

The results in Table 4 clearly demonstrated the advantage of the above radical methodology over the conventional ionic processes.[1,11,14−31] Although the addition of functionalized nucleophiles to arene-$Mn(CO)_3^+$ complexes gave the corresponding products in reasonable to high yields, stabilized carbanions such as ketone enolates or α-ester carbanions were usually em-

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(10) For recent examples, see: (a) Liu, X.; Zhu, S.; Wang, S. *Synthesis* **2004**, 683. (b) Suarez, R. M.; Sestelo, J. P.; Sarandeses, L. A. *Chem. Eur. J.* **2003**, *9*, 4179. (c) Ueda, M.; Miyabe, H.; Nishimura, A.; Sugino, H.; Naito, T. *Tetrahedron: Asymmetry* **2003**, *14*, 2857. (d) Sugi, M.; Sakuma, D.; Togo, H. *J. Org. Chem.* **2003**, *68*, 7629. (e) Suarez, R. M.; Sestelo, J. P.; Sarandeses, L. A. *Synlett* **2002**, 1435.

(11) Yeh, M.-C. P.; Hwu, C.-C.; Lee, A.-T.; Tsai, M.-S. *Organometallics* **2001**, *20*, 4965.

(12) For a review article, see: Li, C.-J.; Chan, T.-H. *Tetrahedron* **1999**, *55*, 11149.

(13) For recent examples, see: (a) Yanada, R.; Koh, Y.; Nishimori, N.; Matsumura, A.; Obika, S.; Mitsuya, H.; Fujii, N.; Takemoto, Y. *J. Org. Chem.* **2004**, *69*, 2417. (b) Yanada, R.; Obika, S.; Nishimori, N.; Yamauchi, M.; Takemoto, Y. *Tetrahedron Lett.* **2004**, *45,* 2331. (c) Miyabe, H.; Ueda, M.; Nishimura, A.; Naito, T. *Tetrahedron* **2004**, *60*, 4227. (d) Sugi, M.; Sakuma, D.; Togo, H. *J. Org. Chem.* **2003**, *68*, 7629. (e) Ueda, M.; Miyaba, H.; Nishimura, A.; Miyata, O.; Takemoto, Y.; Naito, T. *Org. Lett.* **2003**, *5*, 3835. (f) Yanada, R.; Nishimori, N.; Matsumura, A.; Fujii, N.; Takemoto, Y. *Tetrahedron Lett.* **2002**, *43*, 4585. (g) Jang, D. O.; Cho, D. H. *Synlett* **2002**, 631. (h) Miyabe, H.; Nishimura, A.; Ueda, M.; Naito, T. *Chem. Commun.* **2002**, 1454. (i) Miyabe, H.; Ueda, M.; Nishimura, A.; Naito, T. *Org. Lett.* **2002**, *4*, 131.

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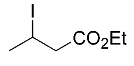
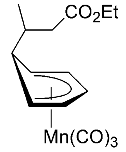
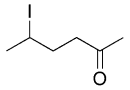
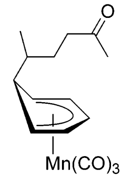
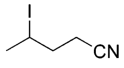
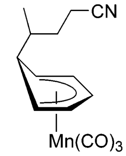
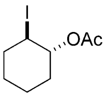
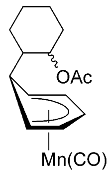
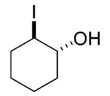
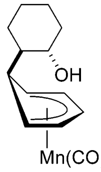
Table 4. Reactions of Functionalized Alkyl Iodides 7a–e with Complex 1a

entry	iodide	product[a]	yield (%)[b]
1	 **7a**	 **8a**	72
2	 **7b**	 **8b**	71
3	 **7c**	 **8c**	70
4	 **7d**	 **8d**[c]	82
5	 **7e**	 **8e**	85

[a] Reaction conditions: **1a** (1 equiv), **7** (6 equiv), In (3 equiv), 50 °C, 10 h. [b] Isolated yield based on **7**. [c] *Trans*:*cis* = 6:1 determined by HPLC.

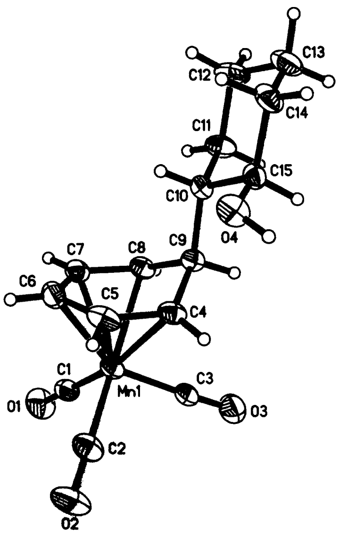
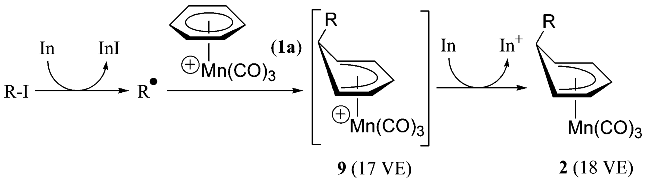


Figure 1. ORTEP drawing of compound **8e**.

Scheme 1. Proposed Mechanism for In(0)-Mediated Alkyl Radical Addition to 1



ployed.[14,21,26–30] On the other hand, the nucleophilic addition of the functionalized zinc reagent $IZn(CH_2)_2CO_2Et$ or $IZn(CH_2)_2CN$ to complex **1a** afforded the α-alkylated product rather than the expected β-alkylated product because of deprotonation of the acidic proton α to the ester or cyano group as reported by Yeh and co-workers.[11] A Grignard reagent equivalent to **7a** or **7b** would be impossible.[14–23] A nucleophilic anionic reagent equivalent to **7d** would result in β-elimination to give cyclohexene.[32,33] Moreover, the ionic processes require strict anhydrous conditions, while the radical reactions proceed readily in aqueous media, although excess amounts of In(0) and alkyl iodides are used.

On the basis of the above results, a plausible mechanism could be drawn for In(0)-mediated radical addition reactions, as shown in Scheme 1. The interaction of an alkyl iodide with indium generates an alkyl radical, which adds to (η^6-benzene)$Mn(CO)_3^+$ cation to give the corresponding 17-valence-electron intermediate **9**. The intermediate **9** is then further reduced presumably by another molecule of indium metal via a single electron-transfer process to give the stable 18-valence-electron product **2**. The reactivity pattern of alkyl iodides observed above strongly implies that the generation of an alkyl radical is the rate-determining step for the reaction.

Conclusion

In summary, we have demonstrated that alkyl radical addition to (η^6-arene)$Mn(CO)_3^+$ complexes can be successfully carried out in aqueous media with indium as the radical initiator. The reactions exhibit different reactivity pattern from those of organomercurials. Moreover, the reactions also show excellent tolerance to various functional groups, thus broadening the scope of the radical addition, and should be of application in organic synthesis.

Experimental Section

Typical Procedure for SmI_2-Mediated Radical Reactions of 1a. A THF solution of SmI_2 (8 mL, 0.8 mmol) was concentrated in vacuo to give a blue solid, which was diluted with anhydrous acetonitrile (8 mL). A CH_3CN solution of SmI_2 was then added to the mixture of (η^6-benzene)$Mn(CO)_3^+PF_6^-$

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(**1a**, 72.4 mg, 0.2 mmol)[34] and *tert*-butyl iodide (74 mg, 0.4 mmol) in acetonitrile (4 mL) at room temperature under nitrogen atmosphere. The mixture was stirred at rt for 2 h. A saturated $NaHSO_3$ solution (10 mL) was then added to quench the reaction. The resulting mixture was extracted with ether (3 × 20 mL). The combined organic phase was washed with brine (10 mL) and then dried over anhydrous $MgSO_4$. After removal of solvent under reduced pressure, the crude product was purified by column chromatography on silica gel with hexane as the eluent to afford the pure **2a** as a yellowish solid. Yield: 32.4 mg (59%). Mp: 73−75 °C.[5c]

Typical Procedure for Zn(Cu)-Mediated Radical Reactions of 1a. The mixture of manganese complex **1a** (72.4 mg, 0.2 mmol), zinc (65 mg, 1 mmol), CuI (19 mg, 0.1 mmol), *i*-PrI (0.12 mL, 1.2 mmol), CH_3CN (0.5 mL), and H_2O (1.5 mL) in a 10 mL tube was stirred at rt under ultrasonic irradiation for 10 h. The resulting mixture was extracted with EtOAc (3 × 10 mL). The combined organic phase was washed with brine and then dried over anhydrous $MgSO_4$. After removal of solvent under reduced pressure, the crude product was purified by column chromatography on silical gel with hexane as the eluent to give pure **2b** as a yellowish solid. Yield: 45.7 mg (88%). Mp: 36 °C.[5c]

Typical Procedure for Indium-Mediated Alkyl Radical Addition to 1 in Aqueous Media. The mixture of manganese complex **1a** (72.4 mg, 0.2 mmol), indium (68.8 mg, 0.6 mmol), cyclohexyl iodide (0.155 mL, 1.2 mmol), CH_3CN (1.4 mL), and H_2O (0.7 mL) in a 10 mL tube was stirred at 40 °C for 10 h. Water (5 mL) was added, and the resulting mixture was extracted with EtOAc (3 × 10 mL). The combined organic phase was washed with saturated brine and then dried over anhydrous $MgSO_4$. After removal of solvent under reduced pressure, the crude product was purified by column chromatography on silical gel with hexane as the eluent to give pure **2c** as a yellowish solid. Yield: 50 mg (83%). IR (KBr): ν (cm^{-1}) 1926, 2002, 2021. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.37−0.45 (1H, m), 0.49−0.56 (2H, m), 0.92−1.07 (4H, m), 1.57−1.65 (4H, m), 2.12−2.19 (1H, m), 3.23 (2H, t, J = 6.0 Hz), 4.80 (2H, t, J = 6.6 Hz), 5.73 (1H, t, J = 5.4 Hz). EIMS: *m/z* (rel intensity) 300 (M$^+$, 7), 216 (100), 189 (20), 161 (20), 133 (20), 91 (9), 83 (5), 55 (47). Anal. Calcd for $C_{15}H_{17}MnO_3$: C, 60.01; H, 5.71. Found: C, 60.10; H, 5.78.

Complex 2d: yellowish solid. IR (KBr): ν (cm^{-1}) 1914, 2010. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.58 (3H, d, J = 6.3 Hz), 0.72−0.77 (5H, m), 1.32−1.37 (1H, m), 2.11−2.17 (1H, m), 3.23−3.28 (2H, m), 4.80 (2H, t, J = 6.3 Hz), 5.72 (1H, t, J = 5.4 Hz). EIMS: *m/z* (rel intensity) 274 (M$^+$, 0.6), 217 (69), 190 (100), 161 (32), 133 (40), 105 (11), 91 (10), 55 (75). Anal. Calcd for $C_{13}H_{15}MnO_3$: C, 56.94; H, 5.51. Found: C, 56.98; H, 5.59.

Complex 4c: yellowish oil. IR (KBr): ν (cm^{-1}) 1920, 2013. ^{1}H NMR (300 MHz, $CDCl_3$) *meta* isomer: δ 0.30−0.42 (1H, m), 0.48−0.60 (2H, m), 0.96−1.06 (4H, m), 1.53−1.63 (4H, m), 1.87 (3H, s), 2.17−2.23 (1H, m), 3.15−3.20 (2H, m), 4.79 (1H, dd, J = 5.4, 7.2 Hz), 5.62 (1H, d, J = 5.1 Hz); *para* isomer: δ 0.30−0.42 (1H, m), 0.48−0.60 (2H, m), 0.96−1.06 (4H, m), 1.53−1.63 (4H, m), 2.04−2.10 (1H, m), 2.46 (3H, s), 3.06−3.12 (2H, m), 4.85 (2H, d, J = 6.9 Hz); *ortho* isomer: δ 0.30−0.42 (1H, m), 0.48−0.60 (2H, m), 0.96−1.06 (4H, m), 1.53−1.63 (4H, m), 1.70 (3H, s), 2.36−2.39 (1H, m), 3.21−3.22 (1H, m), 4.61 (1H, d, J = 5.4 Hz), 4.73−4.78 (1H, m), 5.55 (1H, t, J = 5.4 Hz). EIMS: *m/z* (rel intensity) 314 (M$^+$, 0.5), 273 (0.8), 230 (100), 203 (15), 175 (22), 147 (21), 91 (7), 55 (26). Anal. Calcd for $C_{16}H_{19}MnO_3$: C, 61.15; H, 6.09. Found: C, 61.54; H, 6.48.

Complex 4d: yellowish oil. IR (KBr): ν (cm^{-1}) 1928, 2016. ^{1}H NMR (300 MHz, $CDCl_3$) *meta* isomer: δ 0.56 (3H, d, J = 6.3 Hz), 0.74−0.78 (5H, m), 1.25−1.31 (1H, m), 1.86 (3H, s), 2.15−2.23 (1H, m), 3.17−3.25 (2H, m), 4.78 (1H, t, J = 5.4 Hz), 5.61 (1H, d, J = 4.8 Hz); *para* isomer: δ 0.56 (3H, d, J = 6.3 Hz), 0.74−0.78 (5H, m), 1.25−1.31 (1H, m), 2.02−2.09 (1H, m), 2.45 (3H, s), 3.48 (2H, dd, J = 7.2, 13.8 Hz), 4.85 (2H, d, J = 7.5 Hz); *ortho* isomer: δ 0.56 (3H, d, J = 6.3 Hz), 0.74−0.78 (5H, m), 1.25−1.31 (1H, m), 1.70 (3H, s), 2.36−2.40 (1H, m), 3.03−3.09 (1H, m), 4.62 (1H, d, J = 5.1 Hz), 4.75−4.78 (1H, m), 5.50 (1H, t, J = 5.4 Hz). EIMS: *m/z* (rel intensity) 288 (M$^+$, 1), 231 (70), 204 (100), 175 (39), 147 (50), 119 (8), 91 (14), 55 (49). Anal. Calcd for $C_{14}H_{17}MnO_3$: C, 58.32; H, 6.24. Found: C, 58.32; H, 6.30.

Complex 5b: yellowish oil. IR (KBr): ν (cm^{-1}) 1921, 2011. ^{1}H NMR (300 MHz, $CDCl_3$) *meta* isomer: 0.60 (7H, br), 1.26 (3H, d, J = 6.9 Hz), 1.40 (3H, d, J = 6.6 Hz), 2.02−2.10 (1H, m), 2.14−2.22 (1H, m), 3.23 (1H, dd, J = 6.0, 13.8 Hz), 3.23 (1H, d, J = 7.2 Hz), 4.81 (1H, t, J = 7.5 Hz), 5.63 (1H, d, J = 4.8 Hz); *para* isomer: δ 0.60 (7H, br), 1.04 (3H, d, J = 6.9 Hz), 1.26 (3H, d, J = 6.9 Hz), 2.02−2.10 (1H, m), 2.79−2.89 (1H, m), 3.16 (2H, t, J = 6.0 Hz), 4.80 (2H, d, J = 7.8 Hz). EIMS: *m/z* (rel intensity) 302 (M$^+$, 1.96), 301 (12), 274 (M$^+$ − CO, 0.27), 218 (25), 260 (31), 217 (33), 203 (8), 175 (10), 105 (7), 55 (100). HRMS: calcd for $C_{12}H_{19}Mn$ (M$^+$ − 3CO) 218.0870, found 218.0867.

Complex 5c: yellowish oil. IR (KBr): ν (cm^{-1}) 1920, 2010. ^{1}H NMR (300 MHz, $CDCl_3$) *meta* isomer: δ 0.31−0.38 (1H, m), 0.49−0.60 (2H, m), 0.95−1.05 (4H, m), 1.26 (3H, d, J = 6.6 Hz), 1.41 (3H, d, J = 6.6 Hz), 1.56−1.63 (4H, m), 2.13−2.22 (2H, m), 3.20 (1H, dd, J = 5.7, 12.9 Hz), 3.20 (1H, d, J = 7.2 Hz), 4.80 (1H, t, J = 7.8 Hz), 5.63 (1H, d, J = 4.5 Hz); *para* isomer: δ 0.31−0.38 (1H, m), 0.49−0.60 (2H, m), 0.95−1.05 (4H, m), 1.03 (3H, d, J = 6.3 Hz), 1.26 (3H, d, J = 6.6 Hz), 1.56−1.63 (4H, m), 2.13−2.22 (1H, m), 2.83−2.87 (1H, m), 3.12 (2H, t, J = 6.3 Hz), 4.79 (2H, d, J = 7.8 Hz). EIMS: *m/z* (rel intensity) 342 (M$^+$, 0.3), 300 (42), 301 (35), 259 (21), 258 (33), 245 (16), 217 (33), 175 (11), 55 (100). Anal. Calcd for $C_{18}H_{23}MnO_3$: C, 63.12; H, 6.77. Found: C, 63.09; H, 6.82.

Complex 5d: yellowish oil. IR (KBr): ν (cm^{-1}) 1920, 2012. ^{1}H NMR (300 MHz, $CDCl_3$) *meta* isomer: δ 0.34−0.45 (1H, m), 0.56 (3H, d, J = 6.3 Hz), 0.74−0.80 (5H, m), 1.27 (3H, d, J = 6.6 Hz), 1.40 (3H, d, J = 6.6 Hz), 2.11−2.22 (2H, m), 3.19−3.29 (2H, m), 4.82 (1H, t, J = 6.3 Hz), 5.63 (1H, m); *para* isomer: δ 0.34−0.45 (1H, m), 0.56 (3H, d, J = 6.3 Hz), 0.74−0.80 (5H, m), 1.06 (3H, d, J = 6.6 Hz), 1.27 (3H, d, J = 6.6 Hz), 2.11−2.22 (1H, m), 2.79−2.88 (1H, m), 3.12−3.19 (2H, m), 4.81 (2H, d, J = 6.3 Hz). EIMS: *m/z* (rel intensity) 316 (M$^+$, 0.2), 288 (M$^+$ − CO, 2), 259 (32), 232 (44), 203 (18), 175 (33), 55 (100). HRMS: calcd for $C_{13}H_{21}Mn$ (M$^+$ − 3CO) 232.1014, found 232.1024.

Complex 6b: yellowish oil. IR (KBr): ν (cm^{-1}) 1921, 2014. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.53 (7H, br), 2.12−2.25 (1H, m), 3.12−3.23 (2H, m), 3.49 (3H, s), 4.84 (1H, dd, J = 6.6, 12.6 Hz), 5.67 (1H, d, J = 5.4 Hz). EIMS: *m/z* (rel intensity) 247 (M$^+$ − C_3H_7, 2), 232 (11), 206 (M$^+$ − 3CO, 2), 203 (5), 175 (8), 85 (34), 69 (39), 55 (100). HRMS: calcd for $C_{10}H_{15}MnO$ (M$^+$ − 3CO) 206.0492, found 206.0503.

Complex 6c: yellowish oil. IR (KBr): ν (cm^{-1}) 1918, 2013. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.35−0.42 (1H, m), 0.49−0.60 (2H, m), 0.96−1.03 (4H, m), 1.50−1.63 (4H, m), 2.25−2.32 (1H, m), 3.12−3.16 (1H, m), 3.15 (1H, d, J = 6.0 Hz), 3.48 (3H, s), 4.82 (1H, t, J = 6.0 Hz), 5.66 (1H, d, J = 5.1 Hz). EIMS: *m/z* (rel intensity) 330 (M$^+$, 0.1), 302 (M$^+$ − CO, 1), 247 (41), 246 (43), 219 (8), 191 (18), 163 (17), 109 (34), 55 (100). HRMS: cald for $C_{13}H_{19}MnO$ (M$^+$ − 3CO) 246.0797, found 246.0816.

Complex 6d: yellowish oil. IR (KBr): ν (cm^{-1}) 1919, 2014. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.41−0.52 (1H, m), 0.58 (3H, m), 0.71−0.82 (5H, m), 2.25−2.32 (1H, m), 3.17−3.23 (2H, m), 3.48 (3H, s), 4.84 (1H, t, J = 6.6 Hz), 5.66 (1H, d, J = 4.8 Hz). EIMS: *m/z* (rel intensity) 304 (M$^+$, 0.1), 276 (M$^+$ − CO, 1), 247 (38), 220 (34) 191 (19), 163 (21), 109 (48), 55 (100). HRMS: cald for $C_{11}H_{17}MnO$ (M$^+$ − 3CO) 220.0668, found 220.0660.

Complex 8a: yellowish oil. IR (KBr): ν (cm^{-1}) 1730, 1920, 2015. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.68 (3H, d, J = 6.9 Hz), 1.06−1.12 (1H, m), 1.25 (3H, t, J = 7.2 Hz), 1.72−1.80 (1H,

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m), 2.19−2.25 (2H, m), 3.21 (1H, dd, J = 7.2, 13.5 Hz), 3.23 (1H, dd, J = 6.3, 13.8 Hz), 4.10 (2H, q, J = 7.2 Hz), 4.85 (2H, t, J = 5.7 Hz), 5.75 (1H, t, J = 5.4 Hz). EIMS: *m/z* (rel intensity) 248 ($M^+ - 3CO$, 11), 231 (4), 217 (22), 189 (6), 174 (17), 133 (10), 105 (27), 55 (100). Anal. Calcd for $C_{15}H_{17}MnO_5$: C, 54.23; H, 5.16. Found: C, 54.46; H, 5.39.

Complex 8b: yellowish oil. IR (KBr): ν (cm^{-1}) 1718, 1919, 2013. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.59 (3H, d, J = 5.4 Hz), 0.89−1.02 (1H, m), 1.56−1.70 (2H, m), 2.11 (3H, s), 2.14−2.25 (2H, m) 2.32−2.43 (1H, m), 3.26 (2H, m), 4.83 (2H, dd, J = 5.1, 11.0 Hz), 5.73 (1H, t, J = 5.4 Hz). EIMS: *m/z* (rel intensity) 316 (M^+, 2), 219 (7), 217 (1), 191 (3), 169 (5), 85 (18), 55 (100). Anal. Calcd for $C_{15}H_{17}MnO_4$: C, 56.97; H, 5.42. Found: C, 57.33; H, 5.44.

Complex 8c: yellowish oil. IR (KBr): ν (cm^{-1}) 1937, 2021, 2247. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.65 (3H,. d, J = 5.4 Hz), 0.96−1.10 (1H, m), 1.65−1.79 (2H, m), 2.13−2.22 (2H, m), 2.26−2.37 (1H, m), 3.22 (2H, m), 4.87 (2H, m), 5.76 (1H, t, J = 5.1 Hz). EIMS: *m/z* (rel intensity) 299 (M^+, 0.7), 165 (41), 149 (23), 132 (35), 91 (25), 55 (79). Anal. Calcd for $C_{14}H_{14}MnNO_3$: C, 56.20; H, 4.72; N, 4.68. Found: C, 56.22; H, 4.93; N, 4.59.

Complex 8d: yellowish oil. IR (KBr): ν (cm^{-1}) 1718, 1737, 1937, 2021. ^{1}H NMR (300 MHz, $CDCl_3$) *trans* isomer: δ 0.68−0.90 (2H, m), 0.96−1.18 (2H, m), 1.50−1.69 (4H, m), 1.82−1.86 (1H, m), 2.05 (3H, s), 2.66 (1H, q, J = 6.0 Hz), 3.07 (1H, t, J = 6.6 Hz), 3.14 (1H, t, J = 6.6 Hz), 4.45 (1H, dt, J = 4.8, 9.6 Hz), 4.84 (2H, dd, J = 7.8, 13.6 Hz), 5.71 (1H, t, J = 5.4 Hz); *cis* isomer: δ 0.68−0.90 (2H, m), 0.96−1.18 (2H, m), 1.50−1.69 (4H, m), 1.82−1.86 (1H, m), 2.07 (3H, s), 2.24−2.31 (1H, m), 3.19 (2H, t, J = 6.6 Hz), 4.96−5.01 (1H, m), 5.75 (1H, t, J = 5.4 Hz). EIMS: *m/z* (rel intensity) 274 ($M^+ - 3CO$, 0.4), 248 (5), 230 (10), 217 (28), 189 (7), 174 (9), 91 (53), 55 (100). HRMS: calcd for $C_{14}H_{19}MnO_2$ ($M^+ - 3CO$) 274.0766, found 274.0776.

Complex 8e: yellowish solid. IR (KBr): ν (cm^{-1}) 1919, 2013, 3363. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.55−0.64 (2H, m), 1.09−1.19 (2H, m), 1.56−1.66 (4H, m), 1.76−1.87 (1H, m), 2.79−2.87 (1H, m), 3.11 (1H, t, J = 6.6 Hz), 3.16−3.27 (1H, m), 3.43 (1H, t, J = 6.6 Hz), 4.80 (1H, t, J = 6.3 Hz), 4.86 (1H, t, J = 6.3 Hz), 5.72 (1H, t, J = 5.1 Hz). ^{13}C NMR ($CDCl_3$): δ 223.2, 96.5, 96.1, 79.6, 73.0, 60.1, 54.6, 37.9, 36.1, 29.7, 25.6, 24.8, 24.4. EIMS: *m/z* (rel intensity) 316 (M^+, 0.1), 232 ($M^+ - 3CO$, 3), 230 (14), 217 (20), 176 (12), 91 (100), 55 (56). Anal. Calcd for $C_{15}H_{17}MnO_4$: C, 56.97; H, 5.42. Found: C, 57.07; H, 5.66.

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Supporting Information Available: X-ray crystal data of **8e** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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