



Preparation of Allyl-, Alkenyl- and of Functionalized Arylmanganese Reagents by Oxidative Insertion of Manganese-Graphite into Organic Halides

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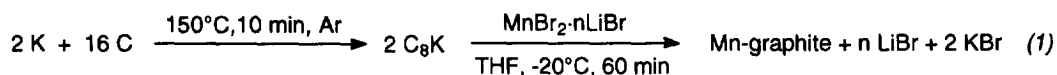
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Abstract: Reduction of $\text{MnBr}_2 \cdot n\text{LiBr}$ ($n = 1,2$) with 2 C_8K in THF affords highly active Mn-graphite, which readily inserts into allyl-, alkenyl-, (substituted) aryl- and heteroaryl halides. The functionalized organomanganese compounds thus obtained may be efficiently trapped with different electrophiles such as aldehydes, anhydrides and acid chlorides, or can be cross-coupled with alkenyl halides in the presence of catalytic amounts of $\text{Fe}(\text{acac})_3$.

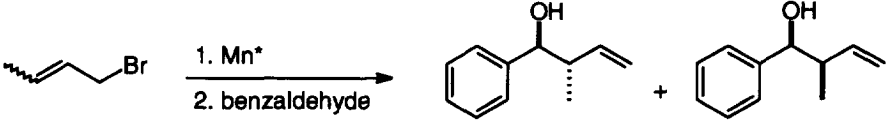
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Organomanganese reagents are usually prepared by transmetalation of *e. g.* organolithium- or organomagnesium compounds with $\text{Mn}(2+)$ -salts and turned out to be valuable nucleophiles for selective C-C-bond formations.^{1,2} However, the need for reactive RLi (RMgX) precursors largely precludes the formation of *functionalized* organomanganese species by such a metathetic route. As they are perfectly feasible in view of the tolerance of the C-Mn bond towards an array of functional groups, the preparation of RMnX by oxidative insertion of $\text{Mn}(0)$ into substituted organic halides is tempting. Metallic manganese exhibits an appropriate reduction potential but its reactivity is corrupted by the resistant oxide coating of its surface.^{3,4} Thus, commercial Mn powder, when activated with iodine or by Lewis acids such as ZnCl_2 , inserts only into the most reactive substrates such as allylic halides or α -bromoesters at elevated temperatures,^{5,6} while ultrasonication results in exclusive Wurtz coupling of such compounds.⁷ Reports on the use of more appropriately activated Mn^* samples are scarce: an ill-defined species was obtained upon reduction of MnCl_2 with LiAlH_4 , which affords homoallylic alcohols from allylic halides and carbonyl compounds;⁸ only recently, Rieke-Mn has been described which holds the promise of a broader scope, although only reactions with simple alkyl bromides and with 3-bromothiophene have been disclosed so far.⁹



In the following we report some preliminary results on the preparation and use of highly activated Mn-graphite which properly adds to a wide range of allyl-, alkenyl-, and differently substituted aryl halides at ambient temperature. This reagent is obtained upon reduction of the well soluble *ate*-complex $\text{MnBr}_2 \cdot n\text{LiBr}$ ($n = 1,2$)¹⁰ with the potassium-graphite intercalation compound C_8K in THF at -20°C (Eq. 1).¹¹⁻¹³ Other manganese salts gave inferior results, mainly due to their low solubility and/or to concomitant cleavage of the ethereal solvent used.

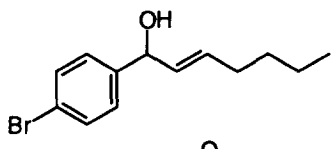
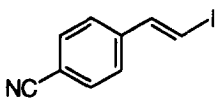
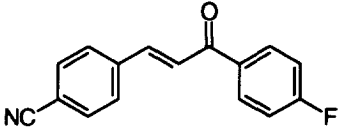
Mn-graphite promotes stereodivergent reactions of crotyl bromide with aldehydes as shown in Table 1 (entries 1,2). Although this outcome reflects the behavior of many other crotyl metal species,¹⁴ it is surprising in the light of the results of *Hiyama* who reported just the reversed selectivity in a reaction of (*E*)-crotyl bromide promoted by Mn^* obtained from MnCl_2 and LiAlH_4 (Table 1, entry 3).⁸

Table 1. Mn⁺-induced reactions of (*Z*)- and (*E*)-crotyl bromide with benzaldehyde.


Entry	Substrate	Reagent	Yield (%)	<i>threo:erythro</i>
1	(<i>Z</i>)-crotyl bromide	Mn-graphite	65%	41 : 59
2	(<i>E</i>)-crotyl bromide	Mn-graphite	72%	64 : 36
3	(<i>E</i>)-crotyl bromide	MnCl ₂ + LiAlH ₄	78%	35 : 65 ⁸

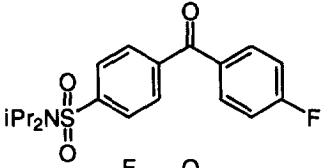
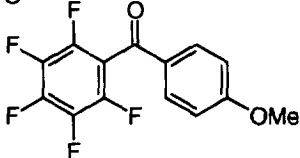
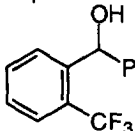
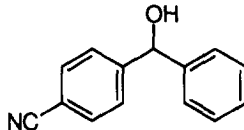
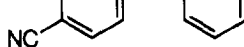
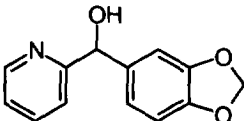
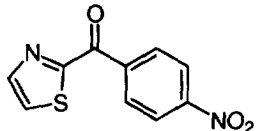
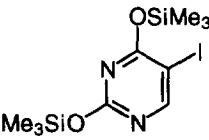
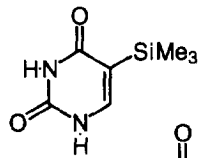
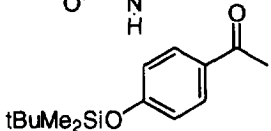
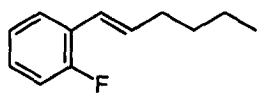
Mn-graphite (1.5-3 eq.) also reacts smoothly with different alkenyl-, aryl- and heteroaryl halides tolerating several functional groups in the starting materials. Even 4-chlorobenzonitrile is metallated (Table 3, entry 5), although a slightly higher amount of the reagent (5 eq.) is necessary in this case in order to achieve complete conversion. Our results are summarized in Tables 2 and 3. The nucleophiles obtained show the regular reactivity pattern of RMnX species and can be trapped *i.a.* with differently substituted aldehydes, acid chlorides or anhydrides. Of interest is the efficient O→C silatropic rearrangement observed upon metallation of 2,4-bis-(trimethylsilyloxy)-5-iodopyrimidine which leads to 5-trimethylsilyluracil¹⁵ in 75% isolated yield (Table 3, entry 8). Finally it should be noted that the cross-coupling of *o*-FC₆H₄MnBr with (*E*)-1-iodo-1-hexene catalyzed by Fe(acac)₃ (3 mol%) worked nicely (Table 3, entry 10). This methodology which was recently pioneered by Cahiez *et al.*^{2a} may well evolve into an attractive alternative to the established Pd- or Ni-catalyzed C-C-bond formations between C(sp²)-centers. Further work on this and related projects is currently in progress.

Table 2. Mn-graphite induced reactions of alkenyl iodides.

Entry	RX	Electrophile	Product	Yield (%)
1	(<i>E</i>)-1-iodo-1-hexene	<i>p</i> -BrC ₆ H ₄ CHO		62
2		<i>p</i> -FC ₆ H ₄ COCl		61

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Table 3. Mn-graphite induced reactions of aryl halides¹⁶

Entry	RX	Electrophile	Product	Yield (%)
1	4-BrC ₆ H ₄ SO ₂ N-iPr ₂	p-FC ₆ H ₄ COCl		64
2	F ₅ C ₆ Br	p-MeOC ₆ H ₄ COCl		69
3	2-(CF ₃)C ₆ H ₄ Br	PhCHO		75
4	4-NC-C ₆ H ₄ Br	PhCHO		65
5	4-NC-C ₆ H ₄ Cl	PhCHO		68 [a]
6	2-bromopyridine	2,3-(methylenedioxy)-benzaldehyde		70
7	2-bromothiazole	p-NO ₂ C ₆ H ₄ COCl		60
8				75
9	4-(tBuMe ₂ SiO)C ₆ H ₄ Br	Ac ₂ O		66
10	2-F-C ₆ H ₄ Br	(E)-1-iodo-1-hexene		67 [b]

[a] with 5 equiv. of Mn-graphite; [b] in the presence of Fe(acac)₃ (3 mol%) as catalyst using THF rather than THF/NMP as the solvent as described in ref. 2a.

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