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A new approach to organomanganese compounds: the tellurium/manganese exchange reaction

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ABSTRACT

Diorganomanganese compounds react with aryl, vinyl, and alkynyl tellurides in a tellurium/manganese exchange reaction. The new mixed organomanganese reagents react selectively with electrophiles.

The use of organomanganese compounds for synthetic purposes is attractive because this element is readily available, cheap, and more environmentally benign in comparison with some other metals commonly used in synthesis. The intensive study of organomanganese compounds started only in 1976 when Professor J. F. Normant and G. Cahiez initiated a systematic study on their preparation and reactivity. Currently there are many studies that describe the preparation and the reactivity of this class of organometallic compounds.[1]

On the other hand, organotellurides have been efficiently transformed into a number of organometallics by tellurium/metal exchange. This methodology focused mainly on the Te/Li exchange, because it is fast and clean, leading to useful organolithiums[2] and other organometallics derived from them by transmetallation[3], or even to other organoelemental compounds not easily obtained by other methods, such as the preparation of *Z*-vinyl stananes from *Z*-vinyl-lithiums, derived from *Z*-vinyl-tellurides.[4] However, the direct Te/metal exchange is also well documented for Te/Zn,[5] Te/Cu,[6] Te/Na,[7] Te/Mg[7], and Te/Ca[7] exchanges. This easy access to a range of organometallics from organotellurides allowed the use of these organochalcogenides in the synthesis of biologically active compounds.[8] In addition, there are many efficient and well-established methodologies to prepare organotellurides from elemental tellurium.[2,3]

Having in mind these features and the feasible Te/metal exchange reaction presented before, we can consider organotellurides as one of the most versatile precursors of reactive organometallics.

Two general methods are available for the preparation of organomanganese species, namely, the transmetallation of organolithium or organomagnesium reagents with manganese salts and the oxidative addition of organic halides to manganese.[8] A third method, involving a heteroatom/manganese exchange is restricted to organic halides and even so, the method is scarcely studied.[1,9] In view of the easy Te/metal exchange reactions commented above and the availability of several classes of organic tellurides,[2] we decided to investigate the Te/Mn exchange reaction as a straightforward method to access structurally more complex representatives of this interesting but still little-explored class of organometallics.

In this work we introduce the unprecedented tellurium/manganese exchange and the capture of the new organometallics with aldehydes and ketones.

This study was initiated by reacting telluride **5a** with different organomanganese reagents **4** in order to determine the reagent of choice to perform the tellurium/manganese exchange reaction. The formed organomanganese **6** was captured with benzaldehyde (**7a**) or acetophenone (**7b**). The vinyl telluride **5a** was prepared in 85% yield by hydrotelluration of phenyl acetylene, starting from elemental tellurium and *n*-butyllithium as depicted in the scheme of Table 1.[13–16] All other organotellurides used in this study were prepared according to the references indicated in Table 2.

The exchange reaction could be visualized by the change in the color of the solution of **4** after the addition of **5a**, from limpid brownish to limpid purple. This change in the reaction mixture appearance was almost instantaneous and identical for all the species **4** shown in Table 1, except for the reaction with compound **4a**,

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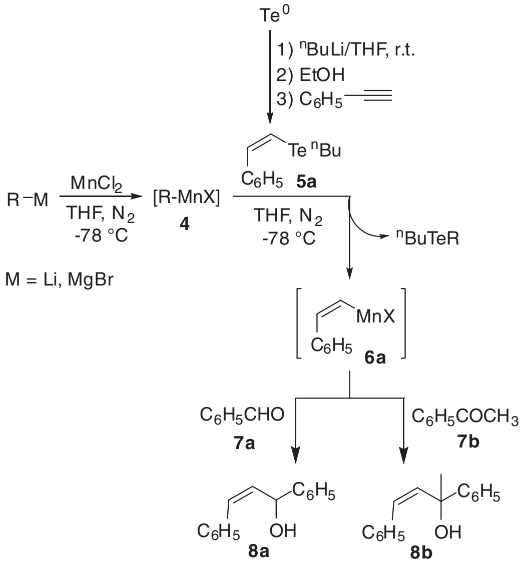
Table 1
Tellurium/manganese exchange reaction[10]



Entry	RMnX[a]	Electrophile	Product/time (h)/yield[b] (%)
1	^{n}BuMnCl[c] **4a**	C_6H_5CHO **7a**	—
2	^{n}BuMn^{n}Bu **4b**	**7a**	**8a**/0.5/82
3	**4b**	$C_6H_5COCH_3$ **7b**	**8b**/1.0/70
4	^{n}Bu$_3$MnLi **4c**	**7a**	**8a**/0.5/48
5	**4c**	**7b**	**8b**/1.0/30
6	^{n}Bu$_3$MnMgBr **4d**	**7a**	**8a**/0.5/58
7	**4d**	**7b**	**8b**/1.0/36
8	MeMnMe **4e**	**7a**	**8a**/0.5/77
9	**4e**	**7b**	**8b**/1.0/52

[a] The organomanganese reagents were prepared by reacting organolithium or Grignard reagents with $MnCl_2$.
[b] Isolated yields.
[c] The tellurium/manganese exchange reaction failed.

in which case no color change was observed. After the formation of the vinyl manganese species **6**, it was captured with benzaldehyde (**7a**), leading to **8a**. In the case of compound **4a**, no addition product was observed, the telluride **5a** being recovered unchanged (Table 1, entry 1).

As it is shown in Table 1, the species **4b**–e, all undergo the Te/Mn exchange reaction and react with **7a** and **7b** leading to products in variable yields. Typically, the exchange reaction took place within 30 minutes at −78 °C.

As a rule, benzaldehyde (**7a**) behaved as a better electrophile, allowing the isolation of the corresponding allylic secondary alcohol **8a** in higher yields and lower reaction times than the tertiary alcohol **8b** (entries 2–9). By comparing the performance of the organometallics, the superiority of the di-alkylmanganese over all the others (Table 1) becomes evident. Dimethyl (**4e**) and dibutylmanganese (**4b**) had similar reactivity toward benzaldehyde (**7a**) (Table 1, entries 2 and 8), but in the reaction with acetophenone (**7b**), compound **4b** gave a better product yield than **4e** (Table 1, entries 3 and 9). Magnesium manganate **4d** presented slightly better results than the corresponding lithium analog **4c** (Table 1, entries 4–7). It is worthy of note that in no instance was *n*-butyl transfer observed.

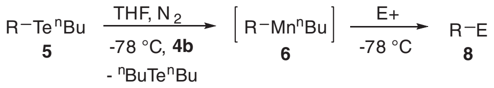
The chemoselectivity of the mixed organomanganese reagent **6a** was also investigated toward a mixture of an aldehyde and a ketone. An equimolar solution of benzaldehyde (**7a**) and acetophenone (**7b**) in THF was added to a solution of the preformed butyl-vinylmanganese reagent **6a** at -78 °C. While compound **8b**, resulting from the addition of **6a** to **7b**, was isolated in 10% yield, the secondary alcohol **8a** resulting from the reaction of **6a** with **7a** was isolated in 65% yield after flash chromatography purification (Scheme 1).

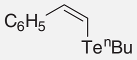
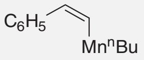
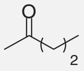
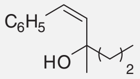
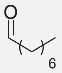
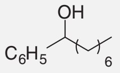
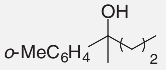
Such selectivity is similar to the one observed for organomanganese halides.[11]

In view of these results, di-butylmanganese was chosen as the ideal partner in the preparation of other mixed organomanganese reagents by Te/Mn exchange reaction. In Table 2 the results of the reaction of some aldehydes and ketones with vinyl-, aryl-, heteroaryl-, and alkynyl-manganese reagents derived from the corresponding organotellurides are summarized. It is worthy of note that all tellurides used in this study are not pungent compounds, and can be manipulated in the presence of light and air.

As can be observed, vinyl, aryl, heteroaryl, and alkynyltellurides undergo the tellurium/manganese exchange reaction within 30 min under the reaction with di-butylmanganese **4b** at −78 °C,

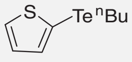
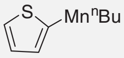
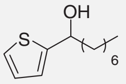
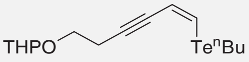
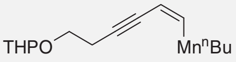
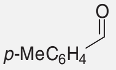
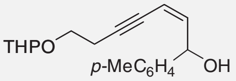
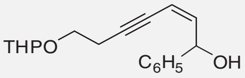
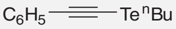
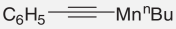
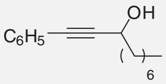
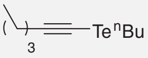
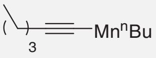
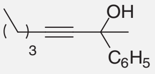
Table 2
Preparation of organomanganese reagents by tellurium/manganese exchange and their reaction with aldehydes and ketones



Entry	Organotelluride **5**	^{n}Butyl organomanganese **6**	Electrophile E$^+$	Product **8**	Time (h)/yield[a] (%)
1	 **5a**[13]	 **6a**	 **7c**	 **8c**	1.0 h/75%
2	$C_6H_5Te^nBu$ **5b**[14]	$C_6H_5Mn^nBu$ **6b**	 **7d**	 **8d**	0.5 h/88%
3	*o*-$MeC_6H_4Te^nBu$ **5c**[14]	*o*-$MeC_6H_4Mn^nBu$ **6c**	**7c**	 **8e**	1.0 h/72%

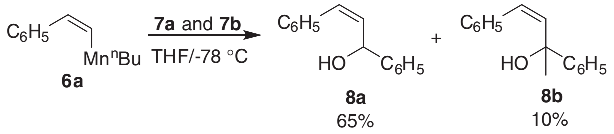
(*continued on next page*)

Table 2 (*continued*)

Entry	Organotelluride **5**	^{n}Butyl organomanganese **6**	Electrophile E$^+$	Product **8**	Time (h)/yield[a] (%)
4	 **5d**[15]	 **6d**	**7d**	 **8f**	0.5 h/80%
5	 **5e**[13]	 **6e**	 **7e**	 **8g**	0.5 h/75%
6	**5e**	**6e**	**7a**	 **8h**	0.5 h/68%
7	 **5f**[16]	 **6f**	**7d**	 **8i**	0.5 h/56%[b]
8	 **5g**[16]	 **6g**	**7b**	 **8j**	1.0 h/48%[b]

[a] Isolated yields after column chromatography.

[b] The low yield is a consequence of the competitive *n*-butyl transfer to the electrophile.



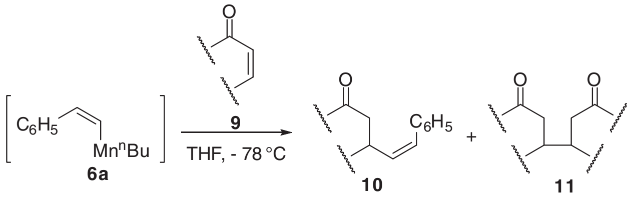
Scheme 1. Chemoselectivity of the mixed organomanganese reagent (**6a**) toward benzaldehyde (**7a**) and acetophenone (**7b**).

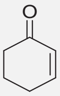
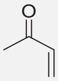
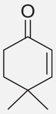
yielding the new mixed di-organomanganese **6**, along with the inert di-butyltelluride (Table 2). As commented before, for the reaction of **6a** with benzaldehyde (**7a**) and acetophenone (**7b**), the organomanganese reagents **6a–g** prepared from tellurides **5a–g** reacted faster, leading to products in better yields, in the use of aldehydes as compared to ketones. Contrary to vinyl, aryl, and heteroaryl organomanganese reagents **6a–e**, the alkynylbutylmanganese **6f** and **6g** presented lower yield on reaction with both an aldehyde and a ketone, due to the competitive butyl transfer (Table 2, entries 7 and 8). In all these reactions, di-butyltelluride was produced as the only by-product in the exchange reaction step.

When *Z*-vinylic tellurides **5a** and **5e** were used, the retention of the olefin configuration was observed. An interesting experimental feature of the exchange step is that the addition of the tellurides **5b** through **5g** to a solution of **4b** did not cause any change in the color of the reaction mixture, as did the addition of telluride **5a**. However, TLC analysis showed the immediate disappearance of the starting telluride, indicating that the exchange reaction in these cases is also fast.

Another interesting experiment was performed by capturing the butyl-vinylmanganese compound **6a** with enones **9**. In this case, besides the 1,4-addition product **10**, the formation of **11**, the product of the oxidative dimerization of the enone was observed, as the result of a long time known reaction of organomanganese compounds with enones.[12] The results are shown in Table 3

Table 3
Reactivity of (*Z*)-butyl-vinylmanganese compound **6b** with enones



Entry	Enone	Time (h)	Yield[a] (%)
1		0.5	55:25 **10a 11a**
2		0.5	42:28 **10b 11b**
3		1.0	5:74 **10c 11c**

[a] Isolated yield.

In conclusion, the Te/Mn exchange reaction is easily performed leading to mixed diorganomanganese reagents, which react with organic substrates in the expected way. The present study and all other previously reported Te/metal exchange reactions show that the organotellurides constitute one of the best options to access structurally complex reactive organometallics by element/metal exchange reactions.

Acknowledgments

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Betzer, F. In *Handbook of Functionalized Organometallics*; Knochel, P., Ed.; Wiley VCH: Weinheim, Germany, 2005; pp 541–567.

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10. *General procedure for the reaction of organotellurides **5** with dibutylmanganese **4b** followed by the addition of an electrophile* (**7a** or **7b**): butyllithium (1.43 mL of a 1.40 mol L^{-1} solution in hexane, 2.0 mmol) was added dropwise to a suspension of dry $MnCl_2$ (0.126 g, 1 mmol) in THF (9 mL) under nitrogen atmosphere at −78 °C and the reaction mixture was stirred for 10 min. A brownish homogeneous solution was formed. To this solution was added organotelluride **5a** (1.0 mmol) in THF (1 mL). The reaction mixture was stirred for additional 30 min. After this time, it was added a solution of the electrophile **7a** or **7b** (1.1 mmol) in THF (1 mL). The reaction progress was monitored by TLC. When the electrophile was consumed, the reaction mixture was quenched with saturated NH_4Cl aqueous solution (15 mL), and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using hexane with gradual increase of the polarity of the eluent to hexane/ethyl acetate (80:20), affording the desired products.

    Compound **8a**: (*Z*)-1,3-diphenylprop-2-en-1-ol (Table 1, entry 2). Yield: 0.17 g (82%). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.42–7.44 (m, 2H), 7.26–7.38 (m, 8H), 6.68 (d, *J* = 6.9 Hz, 1H), 5.92 (dd, *J* = 6.9 Hz and *J* = 5.7 Hz, 1H), 5.62 (d, *J* = 5.4 Hz, 1H), 2.06 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 143.19, 136.38, 133.23, 131.35, 128.81, 128.68, 128.36, 127.76, 127.48, 126.30, 70.04. CAS N°: 1003558-27-7.

    Compound **8b**: (*Z*)-2,4-diphenylbut-3-en-2-ol (Table 1, entry 3). Yield: 0.15 g (70%). Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.46–7.49 (m, 2H), 7.28–7.32 (m, 2H), 7.11–7.23 (m, 6H), 6.56 (d, *J* = 12.3 Hz, 1H), 6.12 (d, *J* = 12.3 Hz, 1H), 2.23 (br s, 1H), 1.61 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 148.56, 138.49, 136.91, 129.09, 128.80, 128.26, 128.10, 127.17, 126.78, 125.04, 75.10, 32.85. CAS No. 71832-03-6.

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