

Structural and Synthetic Insights on Oxidative Homocouplings of Alkynes Mediated by Alkali-Metal Manganates

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Abstract: Exploiting bimetallic cooperation alkali-metal manganate (II) complexes can efficiently promote oxidative homocoupling of terminal alkynes furnishing an array of conjugated 1,3-dienes. The influence of the alkali-metal on these C–C bond forming processes has been studied by preparing and structurally characterizing the alkali-metal tetra(alkyl) manganates [(TMEDA)₂Na₂Mn(CH₂SiMe₃)₄] and [(PMDTA)₂K₂Mn(CH₂SiMe₃)₄]. Reactivity studies using phenylacetylene as a model substrate have revealed that for the homocoupling to take place initial metalation of the alkyne is required. In this regard, the lack of basicity of neutral Mn(CH₂SiMe₃)₂ precludes the formation of the diyne. Con-

trastingly, the tetra(alkyl) alkali-metal manganates behave as polybasic reagents, being able to easily deprotonate phenylacetylene yielding [(THF)₄Na₂Mn(C≡CPh)₄]_∞ and [(THF)₄Li₂Mn(C≡CPh)₄]. Controlled exposure of [(THF)₄Na₂Mn(C≡CPh)₄]_∞ and [(THF)₄Li₂Mn(C≡CPh)₄] to dry air confirmed their intermediary in formation of 1,4-diphenyl-1,3-butadiyne in excellent yields. While the Na/Mn(II) partnership proved to be the most efficient in stoichiometric transformations, under catalytic regimes, the combination of MC≡CAr (M = Li, Na) and MnCl₂ (6 mol %) only works for lithium, most likely due to the degradation of alkynylsodiums under the aerobic reaction conditions.

Introduction

Conjugated diynes are ubiquitous fragments present in a variety of natural products,^[1] pharmaceuticals,^[2] and materials,^[3] as well as finding numerous applications as versatile building blocks for the synthesis of heterocycles.^[4] Pioneering studies by Glaser over 150 years ago revealed that 1,3-dienes can be prepared via oxidative homocoupling of terminal alkynes using Cu(I) salts under stoichiometric conditions.^[5] This approach was later upgraded to catalytic regimes by Hay^[6] and nowadays it constitutes one of the most widely used and versatile synthetic

methods to access these valuable unsaturated organic molecules.^[3c,d,7] While the majority of these reports employ a copper complex as a catalyst, some other earth abundant metal complexes have also shown their potential on promoting Glaser–Hay homocoupling reactions. Thus, Hilt has reported the CoBr₂-catalysed coupling of terminal alkynes using nitrobenzene as a stoichiometric oxidant under reductive conditions,^[8] and more recently Ye has described the use of Co(salen) complexes (salen = *N,N'*-ethylenebis(salicylimine)) to catalyse these reactions employing di-*tert*-butyldiaziridine.^[9]

Within manganese chemistry, seminal work by Cahiez has shown that mixed-metal salts such as MnCl₂·2LiCl can catalyse homocoupling of Grignard reagents, including alkynyl-substituted RMgX, using oxygen as oxidant.^[10] More recently, Taillefer has also demonstrated that *in situ* generated Li-aryls and Li-acetylides can undergo homocoupling in the presence of air using catalytic amounts of MnCl₂.^[11] These reactions are proposed to occur via formation of putative Mn(II)-bis(aryl) species, however limited tangible experimental evidence is available on the constitution of these proposed organometallic intermediates which are formed in the presence of a large excess of an organometallic reagent.^[10,11] Related to these studies we have recently shown that the combination of a four-molar excess of LiCH₂SiMe₃ to MnCl₂ in the presence of Lewis donor TMEDA (TMEDA = *N,N,N',N'*-tetramethylethylenediamine) allows for the isolation and crystallisation of lithium manganate [(TMEDA)₂Li₂Mn(CH₂SiMe₃)₄] (I) which in turn can promote oxidative homocoupling of aryl iodides via sequential Mn–I exchange/C–C bond formation processes.^[12] While oxygen can be used as an oxidant, alkyl iodide ICH₂SiMe₃ generated *in situ*

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during the Mn–I exchange step can also act as an internal oxidant (Figure 1a). Mechanistic investigations allowed for the isolation of mixed Li/Mn(II) reaction intermediates and established that the synergic partnership between the two metals is key to facilitate the Mn–I exchange step of the tandem process.

Building on these studies, here we report the application of alkali-metal manganates to promote Glaser-Hay homocouplings of terminal alkynes via direct Mn–H exchange (Figure 1b). Recent advances in alkali-metal ‘ate chemistry have uncovered a markedly alkali-metal effect on the reactivity of these heterobimetallic complexes, although the vast majority of examples have focused on systems that contain main group metals.^[13] For example while [(TMEDA)₂Li₂Mg(CH₂SiMe₃)₄] fails to metalate anisole, the potassium analogue [(TMEDA)₂K₂Mg(CH₂SiMe₃)₄] promotes its *ortho*-magnesiation at room temperature in almost quantitative yields.^[14] This has also been noted in catalytic transformations such as alkene hydroamination or intramolecular alkynol hydroalkoxylation processes where potassium magnesiates offer enhanced catalytic performances than the related Li or Na analogues.^[15–17] Breaking new ground in this field, here we assess the influence of the alkali-metal on the structure and reactivity of tetra(alkyl) manganate complexes as well as evaluating their ability to promote C_{sp}–C_{sp} oxidative homocouplings.

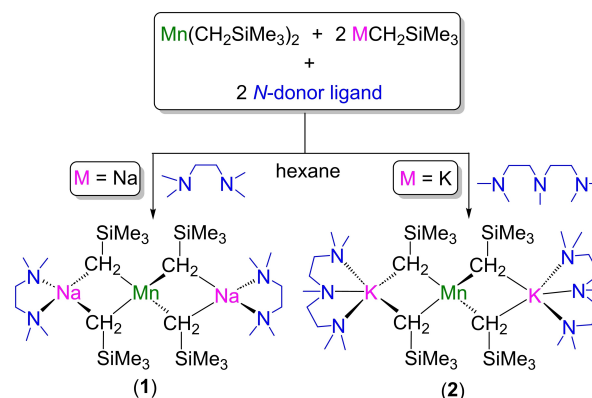
Results and Discussion

Synthesis of heavier alkali-metal manganates

We started our investigations by preparing the sodium and potassium analogues of tetraalkyllithium manganate [(TMEDA)₂Li₂Mn(CH₂SiMe₃)₄] (1). A co-complexation strategy was employed by mixing relevant heavier alkali-metal alkyl M(CH₂SiMe₃) (M=Na, K)^[18] with Mn(CH₂SiMe₃)₂^[19] in 2:1 stoichiometric ratio in hexane at room temperature. Addition of 2 molar equivalents of multidentate Lewis donors TMEDA in the case of Na or PMDETA (PMDETA = *N,N,N',N',N''*-pentamethyldiethylenetriamine) for K, afforded fine orange suspensions

which upon gentle heating produced solutions. Cooling to –30 °C yielded [(TMEDA)₂Na₂Mn(CH₂SiMe₃)₄] (1) and [(PMDETA)₂K₂Mn(CH₂SiMe₃)₄] (2) in 88 and 63 % crystalline yields, respectively (Scheme 1).

Heterobimetallic 1 and 2 exhibit discrete monomeric, contacted ion-pair structures (Figure 2). The four alkyl groups form bridges between the central Mn(II) atom and N-donor capped alkali-metals giving rise to two orthogonal {AMCMnC} four-membered rings fused by their shared Mn vertex. The central trinuclear bimetallic unit is nearly linear in 2 as



Scheme 1. Synthesis of tetra(alkyl) alkali-metal manganates 1 and 2.

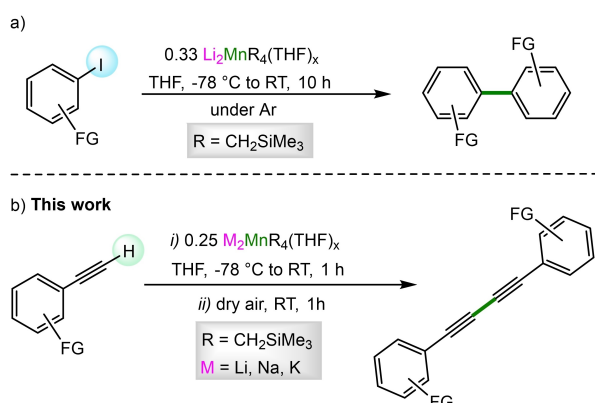


Figure 1. Examples of reactivity of alkali-metal manganates in oxidative homocoupling reactions a) via Mn–I exchange of Ar–I, and b) via Mn–H exchange of alkynes.

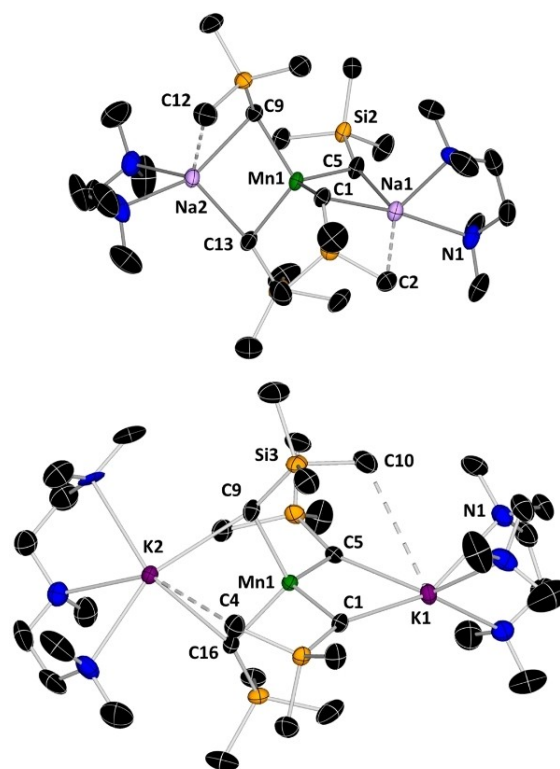


Figure 2. Molecular structure of 1 (top) and 2 (bottom) with 50 % probability displacement ellipsoids. All hydrogen atoms and minor disorder components in TMEDA (1) and PMDETA (2) ligand have been omitted for clarity.

evidenced by the K1...Mn1...K2 angle of 174.39(4)°, while **1** exhibits a more bent arrangement (Na1...Mn1...Na2 155.05(2)°).

In both structures Mn adopts marginally distorted tetrahedral geometry with a narrow range of angles [105.76(7)° to 115.05(8)° for **1** and 106.0(2)° to 115.9(2)° for **2**] and very little variation in the Mn–C bond distances (Table 1). This consistency in Mn–C bond distances (Table 1) suggests these are anchoring bonds forming the $[\{MnR_4\}^-]$ framework to which the relevant alkali-metal can be affixed by forming ancillary and more electrostatic AM–C interactions. The trinuclear core AM...Mn...AM chain arrangement found in **1** and **2** as well as observed Mn–C bond distances are closely comparable to the previously authenticated lithium congener **1**.^[12] The increase in the size and electropositivity of the alkali-metal is accompanied by the elongation of the AM–C bonds (i.e. Na–C_{av} = 2.596 Å, K–C_{av} = 3.012 Å, Table 1) and increase in the coordination number. In each case, the alkali-metal is coordinated by two bridging alkyl groups, however K requires a tridentate PMDETA ligand rather than the bidentate TMEDA which satisfies Li and Na. Additionally, unlike Li in **1**,^[12] Na (i.e., Na...Me = 2.941(2) and 3.143(2) Å) and K (i.e., K...Me = 3.611(5) and 3.896(6) Å) engage in long-distance electrostatic interaction with one methyl unit of the SiMe₃ group to achieve further coordinative stabilization (Table 1).

Reinforcing previously observed structural similarities between organomagnesium and organomanganese(II) compounds, **2** is isostructural with the potassium magnesiate derivative $[(PMDETA)_2K_2Mg(CH_2SiMe_3)_4]$.^[14] It should be noted that despite the synthetic promise shown by alkali-metal manganates containing alkyl groups, the number of compounds structurally defined is scarce. Furthermore, most of these studies have focused on lithium manganate complexes which is perhaps influenced by the widespread utility and commercial accessibility of lithium reagents. Manipulation of sodium and potassium alkyl reagents can pose a greater challenge.^[20] As mentioned before, the choice of alkali-metal can have a profound effect on the reactivity of s-block bimetallic complexes.^[13] Mulvey has also shown that alkali-metal effects can be crucial in manganate chemistry. For example, while sodium monoalkyl-bisamido manganate complex $[(TMEDA)NaMn(TMP)_2(CH_2SiMe_3)]$ (TMP = 2,2,6,6-tetramethylpiperidine) can promote the manganation of non-activated

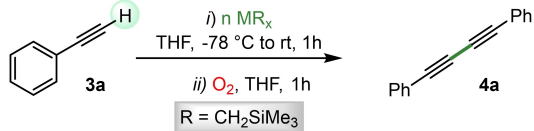
arenes like benzene, switching Na by Li suppressed the Mn–H exchange process.^[21]

As far as we can ascertain **1** and **2** represent the first examples of higher order alkali-metal manganates which contain an alkali-metal different to lithium to be structurally defined. Their structures can be compared with those previously reported by us for the lower-order analogues $[(TMEDA)_2MMn(CH_2SiMe_3)_3]$ which also exhibit contacted monomeric ion-pair structures with two of the alkyl groups bridging between the alkali-metal and the Mn(II) centre whereas the remaining alkyl group binds terminally to Mn.^[22]

Building on our previous reports that have shown that Li_2MnAr_4 species can undergo oxidative homocoupling in the presence of air (or another external oxidant such as ICH_2SiMe_3) to generate symmetrical bis(aryls) (Figure 1a),^[12] we next investigated the ability of heterobimetallic $[M_2Mn(CH_2SiMe_3)_4]$ (M = Li, Na, K) to promote homocoupling of terminal alkynes. We envisaged these couplings as a two-step process, involving first the deprotonation of terminal alkyne followed by oxygen-induced homocoupling, to furnish conjugate 1,3-diynes (Table 2).

We started by treating phenylacetylene (**3a**) with dialkylmanganese $Mn(CH_2SiMe_3)_2$ and exposing the reaction mixture to dry air for one hour which led to the isolation of 1,4-diphenyl-1,3-butadiyne (**4a**, entry 1) in a poor 16% yield. This was attributed to the poor basicity of this Mn(II) complex. Contrastingly we found that if $LiC\equiv CPh$ is reacted with 0.5 equivalents of $MnCl_2$ in THF and then exposed to air for 1 h, homocoupling product **4a** can be obtained in a 80% yield (entry 2), supporting the ability of Mn(II) acetylide species to

Table 2. Homocoupling of phenylacetylene (**3a**) using different manganese reagents containing CH_2SiMe_3 ligands.

			
Entry	n	MR _x	Yield [%] ^[a]
1	0.5	MnR ₂	16
2 ^[b]	1	LiR + 0.5 MnCl ₂	80
3 ^[c]	0.25	Li ₂ MnR ₄	88
4 ^[c]	0.25	Na ₂ MnR ₄	97
5 ^[c]	0.25	K ₂ MnR ₄	74
6 ^[c]	0.33	NaMnR ₃	63
7 ^[c]	0.25	Na ₂ MgR ₄	0
8 ^{[c][d]}	0.25	Na ₂ MnR ₄ + 4 eq 15-crown-5	0
9 ^[e]	1	NaR + MnCl ₂ (6%)	17

[a] Yields have been determined by ¹H NMR analysis of reaction mixtures after an aqueous quench using hexamethylbenzene as internal standard. [b] To hexane solution of alkyne at 0 °C LiR was added, followed by solvent exchange to THF and addition of MnCl₂. [c] All organometallic reagents were formed *in situ* by mixing relevant homoalkyls in appropriate stoichiometry in hexane at room temperature, followed by solvent exchange to THF and addition of phenylacetylene as described in Experimental section for optimized conditions. [d] 15-crown-5 added after deprotonation of phenylacetylene [e] To hexane solution of alkyne at 0 °C NaR was added, followed by solvent exchange to THF and addition of MnCl₂.

Table 1. Selected bond distances (Å) for manganates **1**, **1** and **2**.

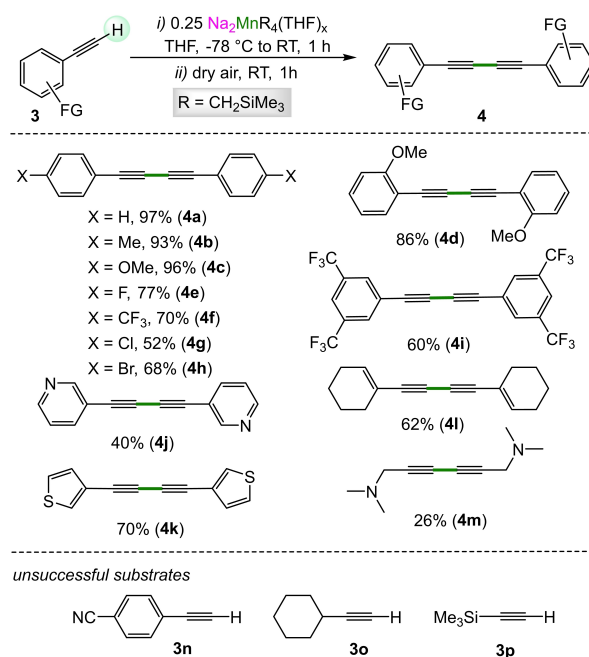
	1 (AM=Li) ^[12]	1 (AM=Na)	2 (AM=K)
Mn1–C1	2.277(5)	2.2998(18)	2.271(6)
Mn1–C5	2.272(5)	2.2332(19)	2.258(5)
Mn1–C9	– ^[a]	2.2843(19)	2.257(6)
Mn1–C13 ^[b]	– ^[a]	2.251(2)	2.241(5)
Mean Mn–CH ₂	2.275	2.267	2.257
Mean AM–CH ₂	2.230	2.596	3.012
Mean AM...Mn	2.847(8)	3.008	3.545
	–	2.941(2)	3.611(5)
AM...CH ₃	–	3.143(2)	3.896(6)

[a] **1** is a centrosymmetric structure with symmetry operator $x, y+1, -z+2$. [b] In **2** this is atom labelled C16.

undergo oxidative homocoupling. We next tested the reactivity of the kinetically more activated alkali-metal manganates $M_2Mn(CH_2SiMe_3)_4$ which were prepared in situ by co-complexation of their relevant single metal components in THF (see Table 2 for details). Considering that these systems contain four potentially basic alkyl groups the reactions were performed using 0.25 equiv. of the manganate. Remarkably, using $Li_2Mn(CH_2SiMe_3)_4$ furnished **4a** in 88% yield (entry 3) demonstrating not only the enhanced metalating power of the lithium manganate in comparison to the neutral, organomanganese precursor, but also allowing for the reaction to take place with an excellent atom economy since four of its alkyl groups are active in this deprotonative/oxidative homocoupling process. Uncovering an interesting alkali-metal effect in manganate chemistry, when $M_2Mn(CH_2SiMe_3)_4$ ($M=Na, K$) were employed under the same reaction conditions **4a** was obtained in 97 and 74% yield, respectively. These results imply that Na/Mn pairing is optimal with nearly quantitative formation of desired product. Interestingly, when **3a** is treated with the lower order sodium manganate $NaMn(CH_2SiMe_3)_3$ (0.33 eq), **4a** is obtained in a diminished 63% yield (entry 6). Entries 1, 4 and 6 of Table 2 illustrate the reactivity enhancement moving from the neutral, homometallic Mn(II) to higher order ate (2:1 Na:Mn ratio). Other control studies showed complete lack of formation of **4a** when phenylacetylene is treated with sodium magnesiate $Na_2Mg(CH_2SiMe_3)_4$ highlighting the key role of redox active Mn(II) to promote the homocoupling process. Remarkably, sodium and its coordination sphere also play a pivotal role. When **3a** was treated with $Na_2Mn(CH_2SiMe_3)_4$ in the presence of two equivalents of macrocyclic donor 15-crown-5, which can coordinate and sequester the sodium cations, complete shut-down of the formation of **4a** was noted. These findings support that Na and Mn(II) need to be in close proximity of each other, most likely forming contacted ion-pair species as those found for **1** and **2** in order to switch on bimetallic cooperation. This effect has been noticed before for other transformations which involved the use of heterobimetallic complexes such as sodium-mediated ferration^[23] and cobaltation^[24] of fluorarenes as well as for the oxidative homocoupling of ArI mediated by lithium manganate $Li_2Mn(CH_2SiMe_3)_4$.^[12]

We also assessed the possibility of employing $Na_2Mn(CH_2SiMe_3)_4$ under catalytic conditions. However, when $NaCH_2SiMe_3$ is reacted with **3a** in the presence of substoichiometric amount of $MnCl_2$ (6 mol%), **4a** is obtained in poor yields (17%, entry 9). Contrary to our findings, Taillefer combined 10% $MnCl_2$ with 2 equivalents of $tBuLi$ to access **4a** in high yield.^[11] This differing behaviour of the two systems could be attributed to the fast decomposition of excess sodium acetylide $NaC\equiv CPh$ in the presence of dry air and the donor solvent THF.

Under the optimized conditions, in order to test the scope of **1** (entry 4, Table 2), we next studied its reactivity towards an array of arylacetylenes bearing electron-donating and electron-withdrawing groups (Scheme 2). Presence of electron donating groups such as Me (**3b**) or OMe (**3c**, **3d**) at the *para*- or *ortho*-positions of the aromatic ring of the arylacetylene afforded the relevant 1,4-disubstituted-1,3-butadiyne derivatives **4b–4d** in excellent yields (86–96%). The position of substituents on



Scheme 2. One pot synthesis of symmetric 1,3-diynes from various terminal alkynes promoted by $Na_2MnR_4(THF)_x$. Yields have been determined by ¹H NMR analysis of reaction mixtures after an aqueous quench against internal standard (see Experimental section for details).

phenyl ring did not affect significantly the overall yield of the reaction as indicated by the isolation of products **4c** and **4d**, and **4f** and **4i** in very similar yields. On the other hand, the detrimental effect of electron-withdrawing groups as F or CF₃, present in **3e–i** is clearly indicated by isolation of the coupling products **4e–i** in slightly lower but still good yields (52–77%). These observations are in agreement with previous reports on Mn-promoted formation of bis(arenes).^[10,12,25] Interestingly, even halogen substituents (i.e. Cl in **3g** and Br in **3h**) are amenable to this protocol and **4g** and **4h** can be isolated in 52% and 68% yield, respectively, without obvious dehalogenation or metal-halogen exchange taking place. The methodology however does not tolerate the sensitive nitrile group in **3n** and no homocoupled product **4n** was isolated. Moderate yields of conjugated diynes were isolated when heteroaromatic alkynes such as **3j** and **3k** were subjected to established protocol and 1,4-dipyridyl-1,3-butadiyne (**4j**) and 1,4-thiophenyl-1,3-butadiyne (**4k**) were isolated in 40 and 70% yield, respectively. Reactions with non-aromatic alkynes such as 1-ethynylcyclohexene (**3l**) and 3-dimethylamino-1-propyne (**3m**) afforded corresponding 1,3-diynes **4l** and **4m** in significantly lower yields (62 and 26% yield respectively). In addition, other non-aromatic substrates such as 1-ethynylcyclohexane (**3o**) and ethynyltrimethylsilane (**3p**) were not compatible with this reaction and afforded no homocoupled products.

To gain a deeper understanding of the homocoupling process, we next set out to isolate and identify alkynyl species formed under varied conditions of optimization. To test the deprotonating power of neutral $Mn(CH_2SiMe_3)_2$, we reacted it with two equivalents of 4-methoxyphenylacetylene (**3c**) in

hexane with addition of TMEDA to aid crystallization. From the mixture only the crystals of $[\text{Mn}(\text{CH}_2\text{SiMe}_3)_2(\text{TMEDA})]^{[26]}$ were isolated (72% yield) confirming our assumption of low basicity of this homometallic precursor (Scheme 3b). We then moved to the optimized conditions of sodium-rich manganate. Co-complexation of 2:1 ratio of homometallic alkyls NaR and MnR_2 ($\text{R}=\text{CH}_2\text{SiMe}_3$) in hexanes afforded light grey suspension. Exchange of solvent to THF afforded orange solution, to which four molar equivalents of phenylacetylene was added at -78°C affording a red solution. Warming up to room temperature and layering with hexane allowed isolation of colourless $[(\text{THF})_4\text{Na}_2\text{Mn}(\text{C}\equiv\text{CPh})_4]_\infty$ (**5**) (Scheme 3a) in 44% yield.

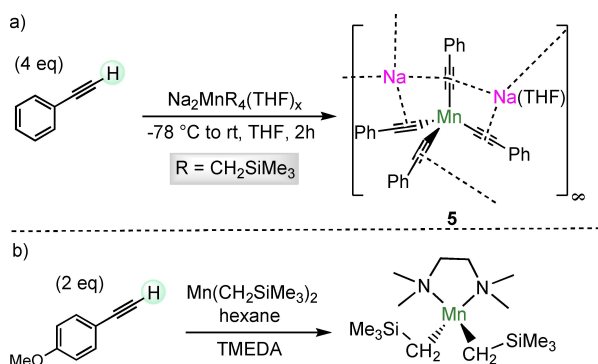
X-ray crystallographic studies unveiled an infinitely aggregated 1D-polymeric structure with the asymmetric unit comprising of two Mn-centres, each σ -bonded to four alkynyl ligands, and four Na-cations interacting with acetylide ligands through the $\text{C}\equiv\text{C}$ π -orbitals (Figure 3). The C4-tetracoordinated Mn centre exhibits a nearly ideal tetrahedral geometry (mean bond angle 109.40° , angles ranging from $102.07(6)^\circ$ to

$119.15(5)^\circ$) with an average bond length of 2.1381 \AA and is in excellent agreement with Mn–C bonds found in half-sandwich complex $[\text{Mn}(\text{C}\equiv\text{CPh})(\eta^5\text{-MeC}_5\text{H}_4)(\text{TMEDA})]$ ($2.142(2)\text{ \AA}$)^[27] or related lithium manganate $[(\text{THF})_4\text{Li}_2\text{Mn}\{2,6\text{-(Me}_3\text{Si)}_2(\text{C}_6\text{H}_3)\text{C}\equiv\text{C}\}_4]$ (average 2.1268 \AA).^[28] Unsurprisingly, Mn–C bond lengths in **5** are shorter than in Mn-complexes with bridging alkynyl ligands.^[29]

The $\text{C}\equiv\text{C}$ bond distances (ranging from $1.2163(19)\text{ \AA}$ to $1.2245(19)\text{ \AA}$) are in excellent agreement with related reported Mn-complexes,^[28,29c] indicating there is no carbene or cumulene character to the $\text{Mn}-\text{C}\equiv\text{C}-\text{Ph}$ moiety. Furthermore, despite the π -interaction between the sodium cations and the $\text{C}\equiv\text{C}$ bond, the $\text{Mn}-\text{C}\equiv\text{C}$ unit remains almost linear with bond angles ranging from $167.5(1)^\circ$ to $175.4(1)^\circ$ (average 171.7°).

Whereas the two Mn-centres show almost identical bonding parameters, the four Na-cations are found in different environments. Na1 (Figure 3) interacts with C_β -atoms of four different alkynyl ligands and coordinates one additional molecule of THF, reaching an overall coordination number of 5. The Na1– C_β distances are in range $2.6367(14) - 2.9288(15)\text{ \AA}$. The possibility of additional interactions with α -carbon atoms of the alkynyl ligands are negligible, the distances are over 3 \AA long. Na2 (Figure 3) is completely supported by the π -system as it is coordinated by four $\text{C}\equiv\text{C}$ bonds with an alternating pattern of short Na2– C_β (mean 2.5976 \AA) and long Na2– C_α (mean 2.8243 \AA) distances. Na3 is coordinated by two $\text{C}\equiv\text{C}$ bonds (mean Na3– C_β 2.6514 \AA , mean Na3– C_α 2.8022 \AA) and two terminal THF molecules. Na4, is similarly like Na1, coordinated by three different alkynyl ligands and one terminal molecule of THF. However, in this case, both short Na4– C_β (mean 2.6666 \AA) and long Na4– C_α (mean 2.9384 \AA) contacts are present. Interestingly, only Na3 is interacting with alkynyl ligands of only Mn2, while the remaining three Na-centres interact with alkynyl ligands of both Mn1 and Mn2 centre. In line with this Mn1 has only proximity to three Na centres (average distance 3.346 \AA) and Mn2 with all four Na centres (average distance 3.4204 \AA). Notably, a related Mn–C(σ) and Na–C(π) bonding preference like the one observed in **5** has been previously reported in related higher order sodium magnesiate complexes that also contain acetylide anions.^[30] These complexes can catalyse the cyclisation of alkynes with organic azides. Their special reactivity has been partially attributed to the presence of sodium centres that can act as built in Lewis acids, activating the C–C triple bonds via π -coordination.

While the number of structurally defined Mn(II) alkynyl complexes is very scarce, Berke has prepared a family of *trans*-bisalkynyl species spanning Mn in oxidation states +1 to +3 exhibiting discreet monomeric structures. Parent Mn(II) complex $[(\text{trans}-\text{C}\equiv\text{CPh})_2\text{Mn}(\text{dmpe})]$ (dmpe = 1,2-bis(dimethylphosphino)ethane) surprisingly can be oxidized in air by ferricenium hexafluorophosphate or tetrafluoroboric acid etherate to produce a stable Mn(III) intermediate $[(\text{trans}-\text{C}\equiv\text{CPh})_2\text{Mn}(\text{dmpe})][\text{OH}]$.^[31] Reduction of related *trans*-bisalkynyl Mn(II) species with Na in toluene at 100°C afforded the only structurally characterized example of mixed Na/Mn alkynyl complex $[\text{Na}][\text{Mn}(\text{dmpe})_2(\text{C}\equiv\text{CSiMe}_3)_2]$.^[32] Interestingly, anionic bisalkynyl Mn(I) species exhibits *cis*-alkynyl binding mode



Scheme 3. a) Synthesis of tetra(alkynyl)sodium manganate **5**; b) Attempted deprotonation of 4-ethynylanisole by neutral dialkylmanganese(II) reagent.

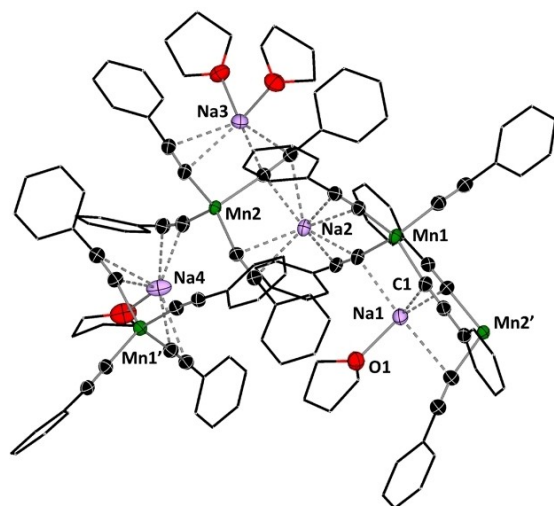


Figure 3. Portion of a polymeric structure of **5** with 50% probability displacement ellipsoids. Aromatic and THF rings shown wire frame, and minor disorder in THF omitted for clarity. Symmetry operator = $0.5-x, -0.5+y, 1.5-z$.

presumably enforced by the chelation of the Na^+ to acetylide ligands. However here, unlike in Mn(II) and Mn(III) complexes, vinylidene type resonance form has the major contribution to the electronic description.

Stability studies have shown that while **5** is stable in THF solution under Ar at room temperature for long period of time, it rapidly undergoes homocoupling in presence of dry oxygen as evidenced by the formation of insoluble brown solid which could not be characterized along with almost quantitative formation of diyne **4a**. These findings support that every alkynyl group in **5** is active towards the C–C bond forming process. Related to the formation of **5**, recent studies by Taillefer has proposed that MnCl_2 -catalysed homocoupling of *in situ* generated Li-acetylides suggests intermediacy of monomeric Mn(II) -bis(alkynyl) and η^2 -oxo manganese(IV) species.^[10,11] This made us ponder whether under these catalytic regimes, using a large excess of the lithium acetylide, formation of higher order lithium manganate species related to **5** could also be involved. In this regard we found that the reaction of $[\text{Li}_2\text{Mn}(\text{CH}_2\text{SiMe}_3)_4]$ with 4 equivalents of phenylacetylene led to the isolation of $[(\text{THF})_4\text{Li}_2\text{Mn}(\text{C}\equiv\text{CPh})_4]$ (**6**) which was structurally authenticated by X-ray crystallographic studies (Figure 4). Compound **6** could also be crystallized from the reaction of 4 equivalents of $\text{LiC}\equiv\text{CPh}$ with MnCl_2 in THF. Similarly to **5**, in **6** the acetylide ligands are σ -bonded to Mn(II) centre, with Mn–C bond distances and angles in excellent agreement, while Li cations are π -bonded to acetylide (see Table S3 in Supporting Information). However, **6** adopts a discreet monomeric structure most likely due to the harder character and smaller size of Li cations preventing polymerization through extensive π -interactions observed for Na in **5**.

We next assessed the ability of isolated crystals of **6** to undergo oxidative homocoupling under both stoichiometric and catalytic conditions. Similarly, to **5**, while **6** is stable in THF solution under inert atmosphere at room temperature, when exposed to dry air it undergoes decomposition to form **4a** in

90% yield determined by ^1H NMR spectroscopy. Remarkably when reacted with $\text{LiC}\equiv\text{CPh}$ in the presence of dry air under catalytic conditions (12 mol % of **6**), **4a** is obtained in an 87% yield (Scheme 4i), which is similar to that previously reported when MnCl_2 is used as a catalyst. Attempts to trap the possible intermediates of oxidation were unsuccessful. Nevertheless, while our studies cannot establish if the C–C bond forming process takes place with a Mn(II)/Mn(IV) redox manifold, they strongly suggest the involvement of lithium manganate(II) species rather than Mn(alkynyl)_2 complex as initially postulated.^[11] Further support to the catalytic involvement of **6** in these homocoupling processes was found when lithium p-tolylacetylide was exposed to air in the presence of 10 mol % of **6** which yielded homocoupling product **4b** in a 62% yield along with 14% of heterocoupled $\text{PhC}\equiv\text{C}(p\text{-Tol})$ (**4ab**) and small amounts of **4a** (Scheme 4ii).

Conclusion

In summary, the ability of alkali-metal manganate (II) complexes to promote homocoupling of terminal alkynes has been demonstrated. By preparing and structurally defining the alkali-metal tetra(alkyl) manganates $[(\text{TMDA})_2\text{Na}_2\text{Mn}(\text{CH}_2\text{SiMe}_3)_4]$ (**1**) and $[(\text{PMDETA})_2\text{K}_2\text{Mn}(\text{CH}_2\text{SiMe}_3)_4]$ (**2**), the influence of the choice of alkali-metal in these C–C bond forming processes has been evaluated. The Na/Mn(II) bimetallic partnership is the most efficient furnishing a wide range of 1,3-diynes using dry air as terminal oxidant. Isolation and structural characterization of organometallic intermediates revealed the inability of neutral $\text{Mn}(\text{CH}_2\text{SiMe}_3)_2$ to deprotonate terminal alkynes, whereas enhanced metalating power of **1** afforded $[(\text{THF})_4\text{Na}_2\text{Mn}(\text{C}\equiv\text{CPh})_4]$ (**5**). Isolation of **5** represent the first example of sodium manganate(II) containing alkynyl ligands, while its controlled exposure to dry air confirms its intermediary in the formation of 1,3-diynes. Attempts to upgrade this transformation to catalytic regimes using $\text{NaC}\equiv\text{CAr}$ and MnCl_2 as a catalyst were unsuccessful, probably due to the fragility of the sodium alkynyl under the reaction conditions. Assessing this reactivity with less sensitive $\text{LiC}\equiv\text{CAr}$ led to the isolation of $[(\text{THF})_4\text{Li}_2\text{Mn}(\text{C}\equiv\text{CPh})_4]$ (**6**) as possible intermediate for MnCl_2 catalysed homocoupling of lithium acetylide. Collectively this work advances the understanding of Mn mediated C–C bond forming processes and showcases the importance of alkali-metal effects in mixed-metal chemistry.

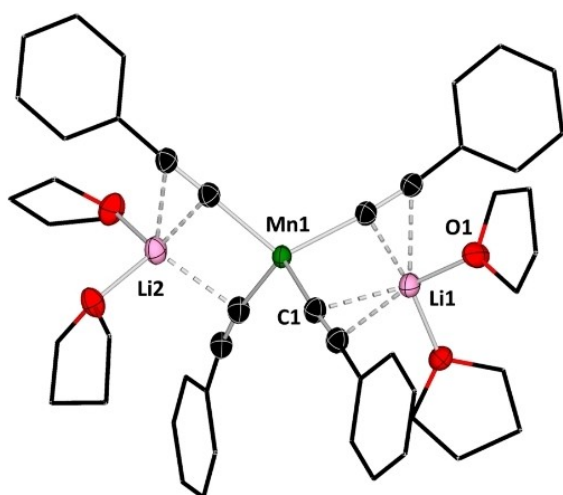
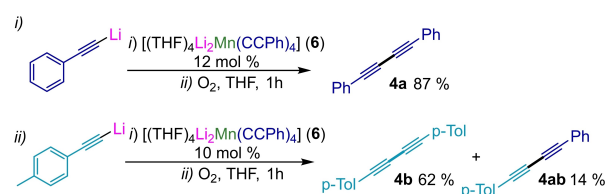


Figure 4. Molecular structure of **6** with 50% probability displacement ellipsoids. Aromatic and THF rings shown wire frame and all H atoms omitted for clarity.



Scheme 4. Reactivity studies of **6** with i) lithium phenylacetylide and ii) lithium p-tolylacetylide. Yields have been determined by ^1H NMR analysis of reaction mixtures after an aqueous quench using hexamethylbenzene as internal standard.

Experimental Section

General procedures: All experiments were carried out using standard Schlenk and glovebox techniques under an inert atmosphere of argon. Solvents (THF, toluene and hexane) were dried using a MBraun MBSPS 5 solvent purification system and stored over 4 Å molecular sieves. *N,N,N',N'*-tetramethylethylenediamine (TMEDA) and *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA) were dried by heating to reflux over calcium hydride, distilled under argon and stored over 4 Å molecular sieves. $\text{Mn}(\text{CH}_2\text{SiMe}_3)_2$, $\text{NaCH}_2\text{SiMe}_3$, and $\text{KCH}_2\text{SiMe}_3$ were prepared according to previously reported procedures.^[18,19] $\text{LiCH}_2\text{SiMe}_3$ was used as solid, obtained by removal of solvent from commercially available solutions. 15-crown-5 was sublimed under vacuum prior to use. All other reagents were used as supplied from commercially available sources. NMR spectra were recorded on Bruker Avance III HD 300 or 400 MHz spectrometers. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced internally to residual solvent peaks. CHN elemental microanalyses were performed on a Flash 2000 Organic Elemental Analyser (Thermo Scientific). Crystallographic data for compounds 1 and 2 were recorded on Oxford Diffraction Xcalibur E CCD instrument; and for compounds 5 and 6 on a Rigaku Synergy S area-detector instrument. The CrysAlisPro^[33] software package was used for data collection, cell refinement and data reduction. For all datasets the CrysAlisPro software package was used for empirical absorption corrections, which were applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. All further data processing was undertaken within the WINGX^[34] or Olex2^[35–37] software package. The molecular structures of all compounds were refined with the ShelXL^[38] refinement package using Least Squares minimisation. Non-hydrogen atoms were refined anisotropically. Disordered groups were modelled across two sites and where necessary restraints and constraints were applied to ensure that disordered groups approximated normal bond length and displacement behaviour. In detail, disorder was modelled for: two TMEDA ligands of 1; one PMDETA ligand of 2 and two THF ligands of 5. Selected crystallographic data are presented in Tables S1 and S2 and Deposition Numbers 2240970, 2240971, 2240972, 2240973 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Synthesis of $[(\text{TMEDA})_2\text{Na}_2\text{Mn}(\text{CH}_2\text{SiMe}_3)_4]$ (1): $\text{Mn}(\text{CH}_2\text{SiMe}_3)_2$ (0.23 g, 1 mmol) and $\text{NaCH}_2\text{SiMe}_3$ (0.22 g, 2 mmol) were suspended in 10 mL of hexane and stirred at room temperature for 30 min. To this suspension freshly distilled *N,N,N',N'*-tetramethylethylenediamine (TMEDA) (0.3 mL, 2 mmol) was added, affording an orange suspension that was left stirring for another 30 min at room temperature. The solvent was concentrated under vacuum to approximately 5 mL to which 2 mL of toluene was added and the obtained orange suspension was vigorously heated in order to obtain a solution. Slow cooling to room temperature afforded colorless X-ray quality crystals (598 mg, 88%). Anal. Calcd. for $\text{C}_{28}\text{H}_{76}\text{Na}_2\text{MnN}_4\text{Si}_4$: C, 49.30; H, 11.23; N, 8.21; found C, 48.55; H, 10.76; N, 8.34.

Synthesis of $[(\text{PMDETA})_2\text{K}_2\text{Mn}(\text{CH}_2\text{SiMe}_3)_4]$ (2): $\text{Mn}(\text{CH}_2\text{SiMe}_3)_2$ (0.23 g, 1 mmol) and $\text{KCH}_2\text{SiMe}_3$ (0.26 g, 2 mmol) were suspended in 10 mL of hexane and stirred at room temperature for 30 min. To this suspension freshly distilled *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA) (0.42 mL, 2 mmol) was added, affording an orange suspension that was left stirring for another 30 min at room temperature. The solvent was concentrated under vacuum to approximately 5 mL to which 2 mL of toluene was added and the obtained orange suspension was vigorously heated in order to obtain a solution. Slow cooling to room temperature afforded colorless X-ray quality crystals (518 mg, 63%). Due to the high

moisture and air sensitivity of these compounds satisfactory elemental analysis was not obtained.

Synthesis of $[(\text{THF})_4\text{Na}_2\text{Mn}(\text{CPh})_4]$ (5): $\text{NaCH}_2\text{SiMe}_3$ (0.11 g, 1 mmol) and $\text{Mn}(\text{CH}_2\text{SiMe}_3)_2$ (0.115 g, 0.5 mmol) were suspended in hexane (5 mL) and stirred at room temperature for 30 min affording a light grey suspension. The volatiles were removed under vacuum and obtained white solid was solubilized with 2 mL of THF affording an orange solution. The solution was cooled down to -78°C and phenylacetylene (0.22 mL, 2 mmol) was added dropwise, affording a red solution. The solution was then stirred at room temperature for an hour and layered with hexane (3 mL). Slow diffusion of the hexane in the solution of THF afforded colourless X-ray quality crystals (146 mg, yield: 44%). Anal. Calcd. for $\text{C}_{80}\text{H}_{72}\text{Mn}_2\text{Na}_4\text{O}_4$: C, 73.95; H, 5.59; found: C, 72.62; H 6.60.

Synthesis of $[(\text{THF})_4\text{Li}_2\text{Mn}(\text{CPh})_4]$ (6): $\text{LiCH}_2\text{SiMe}_3$ (0.095 g, 1 mmol) and $\text{Mn}(\text{CH}_2\text{SiMe}_3)_2$ (0.115 g, 0.5 mmol) were dissolved in THF (3 mL). The resulting pale orange solution was cooled down to -78°C and phenylacetylene (0.22 mL, 2 mmol) was added dropwise. The resulting red solution was allowed to stir at room temperature for 1 h. All volatiles were removed under vacuum and the resulting solid was dissolved in fresh THF (1 mL) and layered with hexane (2.5 mL). Slow diffusion of the hexane in the solution of THF afforded pink X-ray quality crystals (177 mg, yield: 47%). Due to the high moisture and air sensitivity of these compounds satisfactory elemental analysis was not obtained.

General procedure for synthesis of 1,3-dynes (4a–4m): $\text{NaCH}_2\text{SiMe}_3$ (110 mg, 1 mmol) and $\text{Mn}(\text{CH}_2\text{SiMe}_3)_2$ (115 mg, 0.5 mmol), were suspended in hexane (5 mL) and the suspension allowed to stir for 30 min at room temperature. Hexane was removed under vacuum leading to the formation of a white residue. This residue was solubilized in THF (5 mL) and cooled to -78°C . The selected alkynes (2 mmol) were added dropwise. The solution was then stirred at room temperature for 1 h. The solution was then exposed to dry air (fitted with a drying tube containing oven-dried CaCl_2) for 1 h, affording a black mixture. The reaction was quenched with brine and HCl (1 M) and extracted with ethyl acetate three times. The combined organic layers were dried over magnesium sulphate and the volatiles were removed under reduced pressure. The yield of the product was calculated by ^1H NMR against internal standard, using an aliquot of the crude reaction mixture, based on the resonances reported in the literature for the products. See Supporting Information for copies of spectra.

Homocoupling of lithium acetylide using 6 as a promoter: $\text{LiC}\equiv\text{CPh}$ (86.4 mg, 0.8 mmol) and 6 (75.8 mg, 0.1 mmol) were dissolved in THF (2 mL) and exposed to dry air (fitted with a drying tube containing oven dried CaCl_2) and stirred for 1 h producing a deep red solution. The reaction was then quenched with brine and HCl (1 M) and extracted with three times ethyl acetate. The combined organic layers were dried over magnesium sulphate and the volatiles were removed under reduced pressure. The yield of the product was calculated by ^1H NMR against hexamethylbenzene (13.5 mg, 0.083 mmol) as internal standard.

Coupling of lithium p-tolylacetylide using 6 as a promoter: $\text{Mn}(\text{CH}_2\text{SiMe}_3)_2$ (22.9 mg, 0.1 mmol) and $\text{LiCH}_2\text{SiMe}_3$ (18.8 mg, 0.2 mmol) were dissolved in 2 mL of THF. The resulting pale orange solution was cooled down to -78°C and phenylacetylene (44 μL , 0.4 mmol) was added dropwise. The resulting red solution was allowed to stir at room temperature for 1 h. $\text{LiC}\equiv\text{C}(\text{C}_6\text{H}_4\text{Me})$ (122 mg, 1 mmol) was added and the reaction mixture exposed to dry air (fitted with a drying tube containing oven dried CaCl_2) and stirred for 1 h affording a deep red solution. The reaction was then quenched with brine and HCl (1 M) and extracted three times with ethyl acetate. The combined organic layers were dried over

magnesium sulphate and the volatiles were removed under reduced pressure. The yield of the product was calculated by ^1H NMR against hexamethylbenzene (13.5 mg, 0.083 mmol) as internal standard.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: 1,3-diynes · alkali-metal effect · homocoupling · manganates · metal-metal cooperativity

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