C–C Bond Elimination from High-Valent Mn Aryl Complexes

Yu-Tao He,[†] Ayumu Karimata,[†] Olga Gladkovskaya,[†] Eugene Khaskin,[†] Robert R. Fayzullin,[‡] Abir Sarbajna,[†] and Julia R. Khusnutdinova*[†]

[†]Coordination Chemistry and Catalysis Unit, Okinawa Institute of Science and Technology Graduate University, 1919-1 Tancha, Onna-son, Okinawa, 904-0495 Japan.

[‡]Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center, Russian Academy of Sciences, 8 Arbuzov Street, Kazan 420088, Russian Federation.

ABSTRACT: Manganese complexes have been considered as a cheap and readily available alternative to commonly used precious metal catalysts in C–C bond coupling reactions. Although high valent Mn aryl intermediates have been proposed in such reactions, mechanistic understanding of possible organometallic intermediates in Mn-mediated C–C coupling is still lacking due to their high reactivity. We report the synthesis of stable, isolable Mn(III) aryl complexes obtained by oxidative addition of aryl bromide or aryl chloride. These complexes react with a range of organometallic alkylating or arylating reagents (alkyl and aryl Grignard reagents, MeLi, $ZnMe_2$) to undergo $C(sp^2)$–$C(sp^3)$ or $C(sp^2)$–$C(sp^2)$ bond coupling and a preliminary catalytic system could be demonstrated. The reagent scope and yield of the $C(sp^2)$–$C(sp^3)$ coupled product can further be increased by addition of TEMPO as an oxidant generating alkyl radicals.

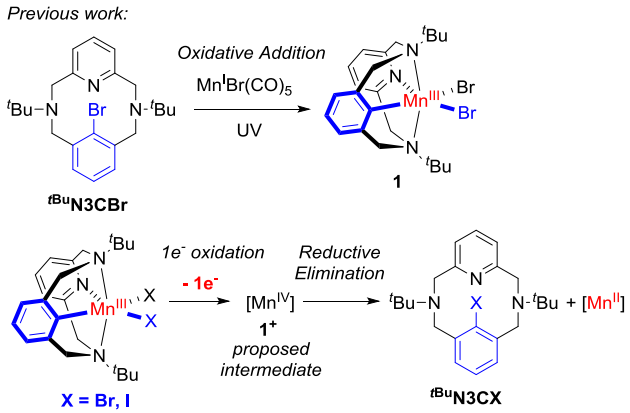
INTRODUCTION

Transition metal-catalyzed C–C bond coupling is one of the most powerful and appealing methods for the construction of C–C bonds in synthetic chemistry.[1-2] For many decades, precious metals, in particular palladium complexes, have been predominant as highly efficient homogeneous catalysts in this transformation.[3] The commonly proposed mechanism of palladium-catalyzed cross-coupling typically involves two-electron oxidative addition, transmetalation, and reductive elimination as crucial steps in the catalytic cycle.[4]

The replacement of precious metals with abundant, cheap, and less toxic first-row transition metals has recently become a perennial goal of increasing urgency in applied synthetic chemistry.[5-12] Despite this, Mn-catalyzed cross-coupling of organic halides with organometallic reagents remains relatively underdeveloped. There are notable examples of Mn-catalyzed cross-coupling and homocoupling reactions reported by Cahiez,[13-20] Madsen,[21-22] Rueping,[23] Falck,[24] and others.[25] However, mechanistic understanding of Mn-catalyzed C–C bond formation reactions is complicated by the paramagnetism of the vast majority of Mn complexes and intermediates due to the large variety of available oxidation states to this metal, and the frequently encountered low stability of organomanganese compounds that leads to a larger number of paramagnetic decomposition products.[12] In particular, the C–C bond elimination from Mn has sometimes been proposed to occur via either Mn^{III} or Mn^{IV} organometallic intermediates. For example, in the homocoupling of alkenyl lithium derivatives reported by Cahiez, Normant, et al., the C–C elimination step was proposed to occur via an initial formation of a Mn^{IV} species, followed by bond homolysis and reductive elimination from Mn^{III} organometallic intermediates.[26] Intermediacy of high-valent Mn species in $C(sp^3)$–$C(sp^2)$ bond elimination has also been proposed by Falck and co-workers as one of the steps in Mn- or $Mn/Cu(OTf)_2$-co-catalyzed Stille cross-coupling.[24] In more recent examples of homo- and cross-coupling of Grignard reagents in the presence of oxygen as an oxidant, C–C reductive elimination from Mn^{IV} bis-organyl species have been proposed based on experimental and theoretical studies. Another important class of reactions in which intermediacy of either Mn^{III} or Mn^{IV} has been implicated is the directed C–H bond functionalization that leads to C–C bond formation. Nakamura and Ilies reported Mn-catalyzed alkylation of $C(sp^2)$–H bonds using MeMgBr, in which a (cyclometalated aryl)(alkyl)Mn^{III} intermediate was proposed to undergo C–C bond reductive elimination.[27] Ackerman and co-workers proposed that a C–C bond formations step occurs from a cyclometalated aryl Mn^{III} intermediate in Mn-catalyzed C–H bond arylation or alkylation.[28-29] Interestingly, Ar-Ar elimination from Mn^{IV} has been proposed by Uzelac *et al.* in Mn-catalyzed homocoupling, and Mn^{III} species were isolated from the reaction mixtures containing Mn^{II} aryl complexes under O_2.[30] However, to the best of our knowledge, direct observation of the C–C bond coupling step from isolated Mn^{III} or Mn^{IV} aryl complexes has not been reported, although the intermediacy of Mn^{IV} diaryl complexes in C-C bond coupling has been demonstrated by Taillefer and co-workers by electrospray ionization mass spectrometry.[31]

Recently, we reported the isolation and characterization of (aryl)Mn^{III} complexes stabilized by chelation to the macrocyclic pyridinophane ^{tBu}**N3C**$^{-}$ ligand (Scheme 1).[32] These complexes enabled us to study direct Ar–Br oxidative addition to a Mn^{I} complex in the presence of light, to give stable and fully characterized (^{tBu}**N3C**)Mn^{III} monoaryl complexes. We also observed the subsequent oxidatively induced two-electron non-radical reductive elimination. Notably, Ar–X (X = Br, I, CN) bond elimination did not occur directly from Mn^{III} complexes, presumably due to the lack of a driving force to prevent the reverse Ar–X bond oxidative addition and high stability. Thus, these stable aryl Mn^{III} complexes served as convenient model compounds to study C–heteroatom bond oxidative addition and demonstrated the necessity of one-electron oxidation to induce aryl-X bond elimination.

Scheme 1. Oxidative addition and reductive elimination of Ar-X using (^{tBu}N3C)Mn aryl complexes.



In this work, we decided to study the possibility of C–C bond coupling from stable isolated Mn^{III} aryl complexes in the absence and presence of oxidants. Notably, unlike in the case of Ar-X elimination which did not occur from Mn^{III}, we observed C–C bond formation even from Mn^{III} aryl complexes in the presence of methylating or arylating reagents even in the absence of oxidants, albeit with moderate or low efficiency and limited by the alkylating reagent scope. Interestingly, we found that addition of TEMPO or other one-electron oxidants to aryl Mn^{III} complex in the presence of alkylating agents promotes more selective and efficient aryl–C(sp^3) bond elimination, presumably via an alternative pathway involving high valent Mn^{IV} intermediates. This study confirms that (aryl)Mn^{III} complexes can be considered as possible intermediates in C–C bond coupling. However, there is an alternative pathway for Ar–C(sp^3) bond coupling that is strongly affected by the presence of oxidative additives.

RESULTS AND DISCUSSION

Synthesis of (aryl)Mn^{III} complexes. We have previously reported the synthesis of complex **1** via oxidative addition of an aryl bromide **N3CBr** to $MnBr(CO)_5$ at room temperature (RT) under mercury lamp irradiation in 1,2-dichloroethane (DCE) as a solvent (Scheme 1).[32] Screening of solvents showed that comparable yields can be obtained when the reaction is performed in THF to afford **1** in 51% isolated yield (Scheme 2). We hypothesized that the role of UV light was to remove CO ligands from the Mn center, and that the oxidative addition occurs by a non-radical pathway as confirmed by the previous study.[32] Therefore, we decided to test whether the formation of **1** can be achieved under thermal conditions in the absence of UV light. Indeed, heating a mixture of ^{tBu}**N3CBr** and $MnBr(CO)_5$ in refluxing dichloroethane or toluene solution at 110 °C for 16 h also produced **1**, albeit in lower isolated yields, 32% and 16%, respectively.

We further examined the reactivity of aryl chloride derivative and reacted a chloro-substituted pyridinophane ligand ^{tBu}**N3CCl** with $MnCl(CO)_5$ in THF under UV light irradiation, as photochemical conditions gave the optimal yield of the desired product in the case of aryl bromide. Aryl chloride ^{tBu}**N3CCl** was synthesized by the reaction of 2-chloro-1,3-bis(bromomethyl)benzene with 2,6-bis(*tert*-butylaminomethyl)pyridine in THF. The expected dichloro complex **2**, was obtained in 22% isolated yield after complexation with the Mn precursor under standard conditions and recrystallization (Scheme 2). This indicates that although aryl chloride undergoes oxidative addition, it is significantly less reactive compared to bromide analog. The structure of the dichloride complex **2** was confirmed by single-crystal X-ray diffraction (Figure 1a). The octahedral complex **2** is characterized by the positional C1/N1 disordering in the crystal.

In a similar way, we attempted the synthesis of mixed chloro bromo complexes by the oxidative addition of **N3CBr** to $MnCl(CO)_5$ and the oxidative addition of **N3CCl** to $MnBr(CO)_5$. As expected, oxidative addition of aryl bromide afforded the product **3** in a good yield of 74%, while the reaction with aryl chloride afforded the analogous mixed chloro bromo complex **3** in a much lower yield of 23%. The X-ray structure of the complex obtained by the first method is shown in Figure 1b. The complex is appeared to be almost equally disordered with respect to Cl/Br and C1/N1 sites in the crystal studied. Molecule **3** shows distorted octahedral geometry at the Mn center with elongated Mn-N_{amine} distances (2.442(3)-2.465(2) Å) as compared to Mn-$N_{pyridine}$ distances (2.10(2) Å). The Mn–C_{ipso} bond distances in complexes **2** (2.02(3) Å) and **3** (1.98(3) Å) are comparable to that previously reported for complex **1** (2.027(14) Å). The analogous structure was established for complex **3** obtained by the oxidative addition of ^{tBu}**N3CCl** to $MnBr(CO)_5$ and its X-ray structure is shown in Figure S60 (see the SI). Besides single-crystal X-ray diffraction, complexes **2** and **3** were characterized by UV-vis, IR spectroscopy, high-resolution mass spectrometry (HRMS), and elemental analysis. Complex **3** shows two peaks at 440.1641 and 484.1138 (z = 1) assigned to $[M–Br]^+$ and $[M–Cl]^+$ respectively, displaying the expected isotopic patterns. Similarly, two peaks at 440.1637 and 484.1119 were also observed in complex **3** obtained by the inverted halogen precursor method.

Scheme 2. Synthesis of ($^{t\text{Bu}}$N3C)Mn^{III}(X)(Y) complexes.

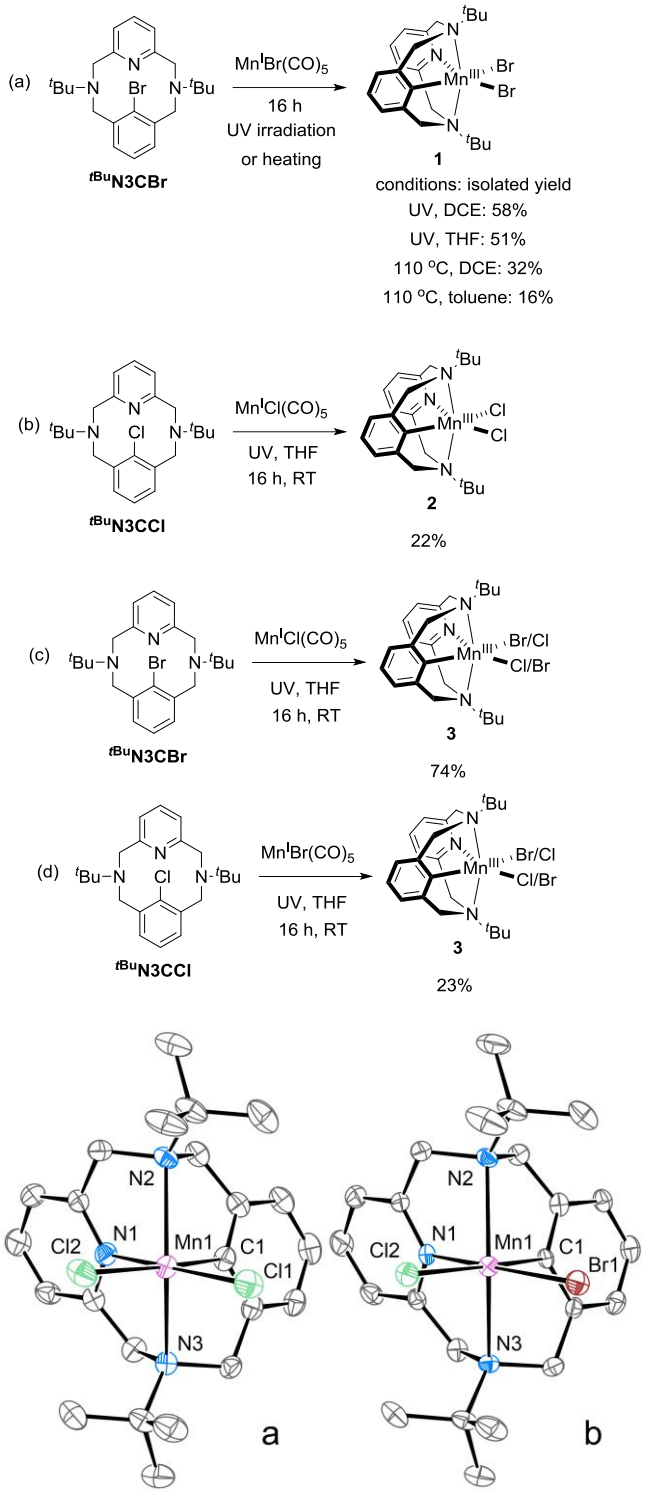
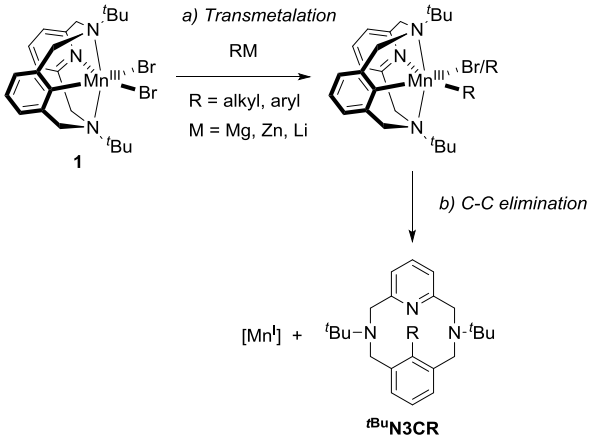


Figure 1. ORTEP of complexes **2** (a) and **3** (b) at 70 % probability level according to single-crystal X-ray diffraction data. Hydrogen atoms and minor disorder components are omitted for clarity. Selected interatomic distances [Å]: Mn1–Cl1 2.3087(8), Mn1–Cl2 2.3266(8), Mn1–C1 2.02(3), Mn1–N1 2.07(2), Mn1–N2 2.442(3), Mn1–N3 2.449(2) for **2**; Mn1–Br1 2.4576(14), Mn1–Cl2 2.321(2), Mn1–C1 1.98(3), Mn1–N1 2.10(2), Mn1–N2 2.442(3), Mn1–N3 2.465(2) for **3**.

The effective magnetic moment of new complexes **2** and **3** in solution measured by Evans method in CD_2Cl_2 solution was determined as 4.71 μ_B, and 4.78 μ_B consistent with the presence of a high spin d^4 Mn^{III} center (S = 2), similar to previously reported complex **1**. The magnetic susceptibility measurements in the solid state for **2** and **3** also have $\chi_M T$ values of 3.1-3.2 T·cm^3·mol^{-1} and 2.9-3.1 T·cm^3·mol^{-1} respectively in the temperature range from 10 to 300 K, corresponding to a high-spin d^4 center (μ_{eff} of 5.0-5.1 and 4.8-4.9 μ_B, respectively).

C–C elimination from Mn^{III} complexes without oxidants. Our previous study of Ar–X (X = Br, I or CN) reductive elimination from Mn^{III} showed that Ar–X bond formation must be preceded by oxidation with a strong one-electron oxidant.[32] As C–C bond elimination is a different type of reaction, where the metal center in the intermediate has stronger σ-donor ligands, so we set out to investigate whether Mn^{III} complexes are capable of C–C bond elimination directly, in the absence of any oxidants. We hypothesized that the reaction of complex **1** with common organometallic reagents might lead to the initial transmetalation to form Mn^{III} aryl alkyl or diaryl complexes, followed by the C–C reductive elimination (Scheme 3).

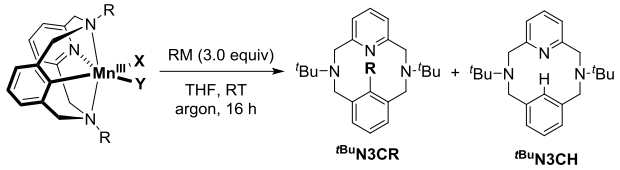
Scheme 3. Proposed C–C elimination from ($^{t\text{Bu}}$N3C)Mn^{III} complexes.

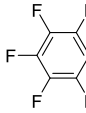


We reacted complex **1** with 3 equiv of MeMgBr in THF solution in the absence of any additives at room temperature (RT). Attempts to isolate or spectroscopically detect transmetalation intermediates either at RT or low temperature were not successful, and the reaction proceeded immediately to undergo C–C bond coupling and give the expected C–C coupling product, $^{t\text{Bu}}$**N3CMe**, which was obtained after quenching the excess MeMgBr with aqueous ammonium chloride and basic workup to remove Mn residues (58% crude NMR yield, Table 1). The C–C coupling product was further isolated and characterized by NMR and HRMS. The low yield of the desired C–C coupling product is likely due to the formation of the protonated ligand $^{t\text{Bu}}$**N3CH** as a side-product, obtained in 28% NMR yield after work-up of the reaction mixture. Reaction selectivity was decreased when only 1 equiv of

MeMgBr was used, giving $^{t\text{Bu}}$**NCMe** and $^{t\text{Bu}}$**N3CH** in 48% and 46% yields, respectively (entry 2).

Table 1. C–C coupling from complexes 1, 2, and 3 in the presence of organomagnesium, zinc, and lithium reagents without oxidants [a]



Entry	Complex	Reagent (3 equiv)	$^{t\text{Bu}}$N3CR, % yield[b]	$^{t\text{Bu}}$N3CH, %yield[b]
1	**1**	MeMgBr	**R** = Me 58	28
2[c]	**1**	MeMgBr (1 equiv)	**R** = Me 48	46
3	**2**	MeMgBr	**R** = Me 56	39
4	**3**	MeMgBr	**R** = Me 65	27
5[d]	**1**	MeMgBr (-80° to RT)	**R** = Me 75	1
6	**1**	$ZnMe_2$	**R** = Me 41	21
7[d]	**1**	$ZnMe_2$ (-80° to RT)	**R** = Me 35	22
8	**1**	MeLi	**R** = Me 22	70
9[d]	**1**	MeLi (-80° to RT)	**R** = Me 53	11
10	**1**	^{i}PrMgCl	**R** = *i*Pr n.d.[e]	88
11	**1**		**R** = CH_2=CH-CH_2- n.d.[c]	90
12	**1**		**R** = Ph 67	16
13[f]	**1**		**R** = C_6F_5 49 (isolated)	n.d.

[a]Reaction was performed in THF for 16 h at RT in the presence of 3 equiv of alkylating or arylating reagent. [b]Yields were determined after quenching excess reagent by NMR integration against 1,3,5-trimethoxybenzene as an internal standard. [c]1 equiv of MeMgBr was added at RT. [d]Methylating reagent was added at -80 °C and then the reaction mixture was slowly warmed up to RT. [e]Not detected. [f]Heated at 80 °C in benzene solution for 40 h in the presence of 6 equiv of C_6F_5MgBr.

Under analogous conditions, with 3 equiv of MeMgBr, dichloro complex **2** gave a 56% yield of $^{t\text{Bu}}$**N3CH** and a 39% yield of $^{t\text{Bu}}$**N3CH** (entry 3).

The formation of $^{t\text{Bu}}$**N3CH** likely results from quenching starting material, aryl complex **1**, with aqueous ammonia solution used to remove an excess of methylating reagent. Thus, if a typical workup procedure involving treatment with aqueous NH_4Cl solution and extraction is applied to complex **1** in the absence of methylating agents, formation of $^{t\text{Bu}}$**N3CH** is also detected. Although the alternative route to the formation of $^{t\text{Bu}}$**N3CH** could involve formation of aryl radical ($^{t\text{Bu}}$**N3CH**), the reaction with MeMgBr under typical conditions (RT, 16 h) in THF-d_8 showed that $^{t\text{Bu}}$**N3CH** by-product is formed exclusively and no deuterated product $^{t\text{Bu}}$**N3CD** was detected by GC-MS, ESI-MS or NMR.

Although the standard reaction time of 16 h was used in all experiments to ensure completion, the reaction in the case of MeMgBr occurs within several minutes at RT. Therefore, we also attempted methylation by slow addition of MeMgBr at -80° C followed by slow warming up to RT. Under these conditions, a higher yield of methylation product was obtained, while formation of $^{t\text{Bu}}$**N3CH** was significantly suppressed leading to more selective reaction (entry 5).

We have also tested the reactivity with other methylating reagents, $ZnMe_2$ and MeLi. In these cases, lower yields of the C–C coupling product $^{t\text{Bu}}$**N3CMe** were obtained under analogous conditions. In the case of MeLi, low temperature also had a beneficial effect leading to higher yield of $^{t\text{Bu}}$**N3CMe** and suppressed formation of $^{t\text{Bu}}$**N3CH** as compared to the analogous reaction at RT (entries 8 and 9), while no significant effect of temperature was observed for $ZnMe_2$ (entries 6 and 7), probably due to its lower reactivity compared to MeLi and MeMgBr. Notably, in the presence of ^{i}PrMgBr and (allyl)MgBr, no desired C–C bond coupling product was obtained, with the major product after work-up being $^{t\text{Bu}}$**N3CH** (Table 1).

We have further tested the possibility of aryl–aryl coupling and reacted complex **1** with 3 equiv of PhMgBr in THF at RT. This resulted in the formation of 67% of phenylated product, $^{t\text{Bu}}$**N3CPh**, after 16 h. The reaction with less nucleophilic pentafluorophenyl Grignard reagent, C_6F_5MgBr, gave no product at RT. However, when complex **1** was heated in the presence of 6 equiv of C_6F_5MgBr in benzene at 80 °C, the pentafluorophenyl derivative, $^{t\text{Bu}}$**N3CC$_6$F$_5$**, was obtained in 49% yield.

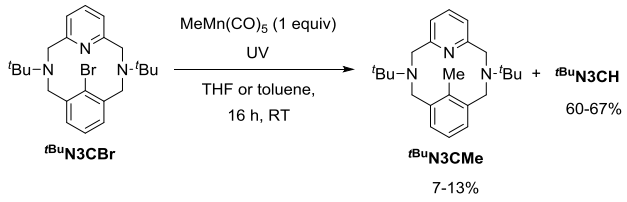
These results show that unlike Ar-X reductive elimination, aryl–C(sp^3) and aryl–C(sp^2) bond elimination in ($^{t\text{Bu}}$**N3C**)Mn^{III} complexes does not necessarily require an oxidant and likely proceeds directly via the Mn^{III} oxidation state, although the proposed methyl-aryl or bis(aryl) intermediates could not be isolated or observed, presumably due to fast C–C coupling following transmetalation (Scheme 3). We attempted a different approach to obtain such intermediates using $MeMn(CO)_5$ as a precursor and reacted it with $^{t\text{Bu}}$**N3CBr** under UV irradiation (Scheme 4). If the reactivity of $MeMn(CO)_5$ is similar to $MnBr(CO)_5$,

we could expect formation of the Ar–Br oxidative addition product where methyl group is present instead of one bromo-ligand. As anticipated, when $MeMn(CO)_5$ was reacted in the presence of 1 equiv of ^{tBu}**N3CBr** under UV light irradiation in THF or toluene solution, the reaction proceeded to form the C–C coupled product, ^{tBu}**N3CMe**, in 7-13% yield. No intermediates could be isolated suggesting that once the expected aryl methyl complex is formed, it immediately undergoes C–C elimination.

The low yield of the coupling product could be due to only one Me group being present in the oxidative addition product, while the reaction of **1** with excess MeMgBr could lead to replacement of both bromo ligands with the Me groups. However, formation of a small amount of (^{tBu}**N3C**)$Mn^{III}Me_2$ in this reaction cannot be excluded if Me group exchange between two monomethyl intermediates is involved, similar to the Schlenk equilibrium[33] present in solutions of Grignard reagents. Alternatively, the low yield in the case of the $MeMn(CO)_5$ reaction could be due to the amount of the isomer in which Ar and Me groups are present in mutual *cis*-positions.[32]

Unfortunately, the Mn^{I} product of C–C bond coupling could not be isolated due to absence of stabilizing ligands and basic work-up of the reaction mixture leading to precipitation of all Mn residues or their removal to the aqueous phase.

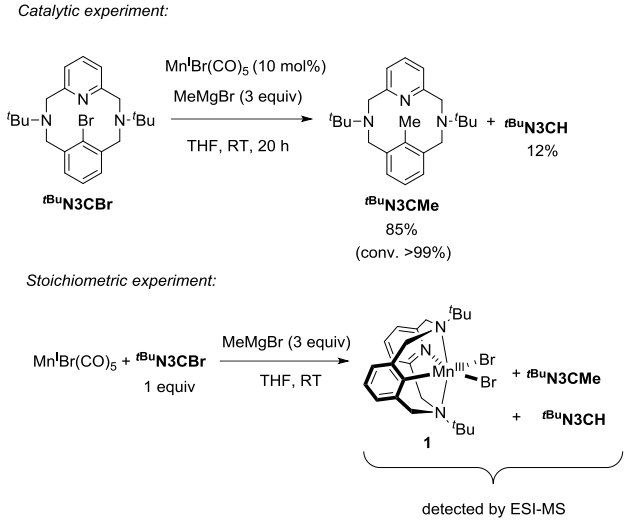
Scheme 4. Reaction of $MeMn(CO)_5$ with ^{tBu}N3CBr.



Overall, these experiments indicate that C–C coupling proceeds upon the reaction of common organometallic reagents with isolated Mn^{III} complexes in the absence of oxidative additives or chlorinated solvents that could act as oxidants, suggesting that C–C coupling step likely occurs at the Mn^{III} aryl center, although the selectivity of this reaction remains limited.

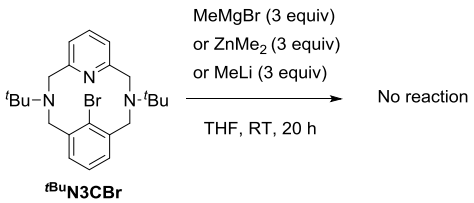
To demonstrate that the proposed sequence of oxidative addition/transmetalation/C-C elimination steps may give rise to a catalytic turnover, we performed a catalytic experiment using a mixture of only 10 mol% of $MnBr(CO)_5$, ^{tBu}**N3CBr**, and 3 equiv of Grignard reagent in THF solution (Scheme 5, top). Interestingly, we observed catalytic turnover (TON 8.5) under these conditions leading to the formation of ^{tBu}**N3CMe** in 85% yield after 20 h. This result confirms that (^{tBu}**N3C**)Mn complexes are not only suitable model compounds to study Ar–X and Ar–C bond formation, but also mimic Mn-catalyzed Ar–C bond coupling. Notably, ICP-MS analysis of the catalyst showed that no platinum group metals were present in the sample at the detectable level (see the SI).

Scheme 5. Mn-catalyzed ^{tBu}N3CBr methylation with MeMgBr.



The control experiment showed that no reaction occurs in the absence of Mn complexes when ^{tBu}**N3CBr** is treated with an excess of MeMgBr, $ZnMe_2$, or MeLi in THF under analogous conditions (Scheme 6) confirming that manganese complexes are indeed required to mediate the cross-coupling reaction. To further confirm that the C–C coupling is mediated by the formation of Mn^{III} aryl species, we performed the reaction in the presence of equivalent amounts of $Mn^{I}Br(CO)_5$, ^{tBu}**N3CBr**, and 3 equiv of MeMgBr (Scheme 5, bottom). The ESI-MS analysis of the reaction mixture confirmed the presence of the characteristic peak with m/z 486.1114 corresponding to $[M–Br]^+$ fragment of complex **1**, along with peaks of ^{tBu}**N3CMe**, ^{tBu}**N3CBr**, and ^{tBu}**N3CH** (see the SI). This experiment also shows that the reaction of $Mn^{I}Br(CO)_5$ with ^{tBu}**N3CBr** occurs prior to C-C elimination. When $Mn^{I}Br(CO)_5$ was reacted with MeMgBr in the absence of ^{tBu}**N3CBr** , no $MeMn^{I}(CO)_5$ was observed.

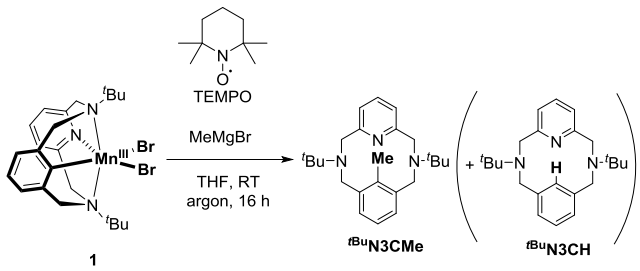
Scheme 6. Control experiment in the absence of Mn complexes.



C–C elimination in the presence of oxidants. To further test the mechanism of C–C coupling from complex **1** in the reaction with MeMgBr, we attempted to perform the reaction in the presence of TEMPO as a radical trap. Surprisingly, when C–C coupling from **1** using MeMgBr (3 equiv) as a methylating reagent was performed in the presence of 1.1 equiv of TEMPO, we observed almost clean formation of the C–C coupling product in 92% yield, while no protonation product, ^{tBu}**N3CH**, was detected under these conditions (Table 2). Notably, the yield was high even in the presence of 1.1 equiv of TEMPO and only slightly increased when the amount of TEMPO was changed to 2 and 3 equiv, showing that even 1.1 equiv was

sufficient to promote selective C–C bond formation (Table 2). A more selective C–C coupling was also observed in the reaction where only 1 equiv of MeMgBr and 1 equiv of TEMPO were used giving 60% of $^{t\text{Bu}}$**N3CMe** and 12% of protonated product $^{t\text{Bu}}$**N3CH**, as compared to the reaction with 1 equiv of MeMgBr in the absence of TEMPO, which gave only 43% of $^{t\text{Bu}}$**N3CMe** (vide supra).

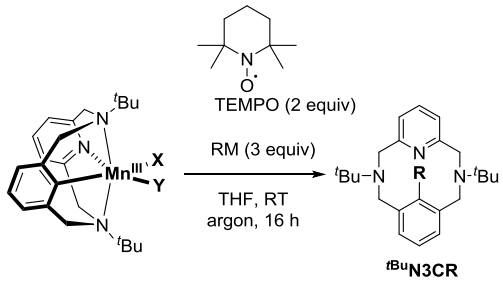
Table 2. C–C coupling from complex 1 in the presence of TEMPO.[a]

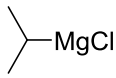
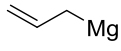
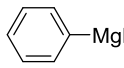


Entry	Equiv of MeMgBr	Equiv of TEMPO	$^{t\text{Bu}}$N3CMe, % yield[b]	$^{t\text{Bu}}$N3CH, %yield[b]
1	3.0	none	58	28
2	3.0	0.1	72	15
3	3.0	1.1	92	n.d.[c]
4	3.0	2.0	93	n.d.
5	3.0	3.0	97	n.d.
6	2.0	2.0	90	n.d.
7	1.0	1.0	59	13

[a]Reaction was performed in THF for 16 h at RT in the presence of indicated amounts of MeMgBr and TEMPO. [b]Yields were determined after quenching excess reagent by NMR integration against 1,3,5-trimethoxybenzene as an internal standard. [c]Not detected.

Table 3. C–C coupling from complexes 1, 2, and 3 with other alkylating and arylating reagents in the presence of TEMPO as an oxidant.



Entry	Complex	RM	$^{t\text{Bu}}$N3CR, % yield[b]
1	**1**	$ZnMe_2$	**R** = Me 95
2	**1**	MeLi	**R** = Me 40
3	**1**		R = *i*Pr 47
4	**1**		**R** = allyl 72
5	**1**		**R** = Ph 71
6	**2**	MeMgBr	**R** = Me 87
7	**3**	MeMgBr	**R** = Me 92

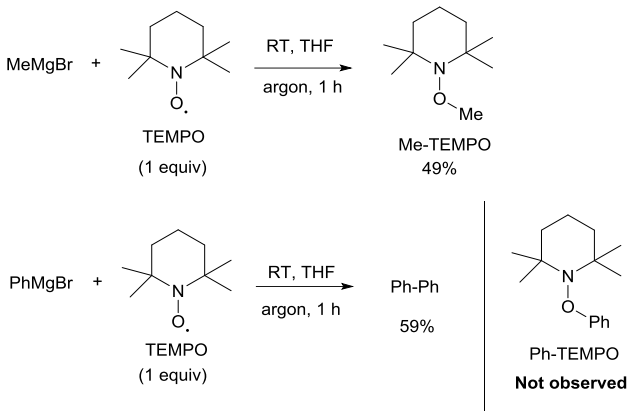
[a]Reaction was performed in THF for 16 h at RT. [b]Yields were determined after quenching excess reagent by NMR integration against 1,3,5-trimethoxybenzene as an internal standard.

Encouraged by these results, we also examined if the scope of alkylating reagents could be improved using these conditions (Table 3). Interestingly, in the presence of 2 equiv of TEMPO, the C–C coupling product was also obtained using ^{i}PrMgBr and (allyl)MgBr as coupling reagents in 47% and 72% yields, respectively. High yield of methylation product was also observed using $ZnMe_2$ (95%). The reaction with MeLi in the presence of TEMPO produced $^{t\text{Bu}}$**N3CMe** in a moderate 40% yield, as compared to only 22% obtained in the absence of additives. High yields of $^{t\text{Bu}}$**N3CMe** were also obtained using the similar dichloro and chloro bromo complexes **2** and **3** as coupling partners.

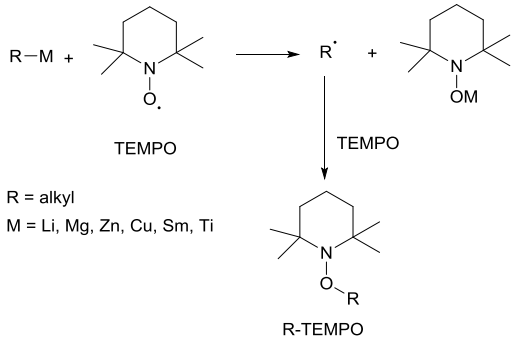
Incongruently, the presence of TEMPO did not play a significant role in the promotion of PhMgBr reaction, and $^{t\text{Bu}}$**N3CPh** was obtained in almost the same yield with and without TEMPO.

To clarify the role of TEMPO we first tested the reactivity of complex **1** with 2 equiv of TEMPO, however, no reaction was observed, and the starting material remained unchanged. When MeMgBr was allowed to react with 1 equiv of TEMPO in the absence of complex **1**, we observed the formation of MeTEMPO in 52% yield, which indicates that the Me radical is formed under these conditions trapped by TEMPO. This observation is consistent with the reported detailed studies of the reactivity of TEMPO with alkyl organometallic compounds.[34-37] TEMPO is known to react with alkyl organometallic species first via a one-electron oxidation to produce an alkyl radical, which is then trapped by another equivalent of TEMPO (Scheme 7) to produce a Me-TEMPO adduct. Independently prepared Me-TEMPO did not react with complex **1** under typical reaction conditions. Interestingly, aryl Grignard reagents react by a different pathway which does involve the formation of high energy free aryl radicals.[34] Indeed, the reaction of PhMgBr with 1 equiv of TEMPO did not produce Ph-TEMPO, but led to homocoupling to give biphenyl, as is consistent with literature precedents (Scheme 8).

Scheme 7. Reactivity of TEMPO with Grignard reagents in the absence of Mn complexes (this work).



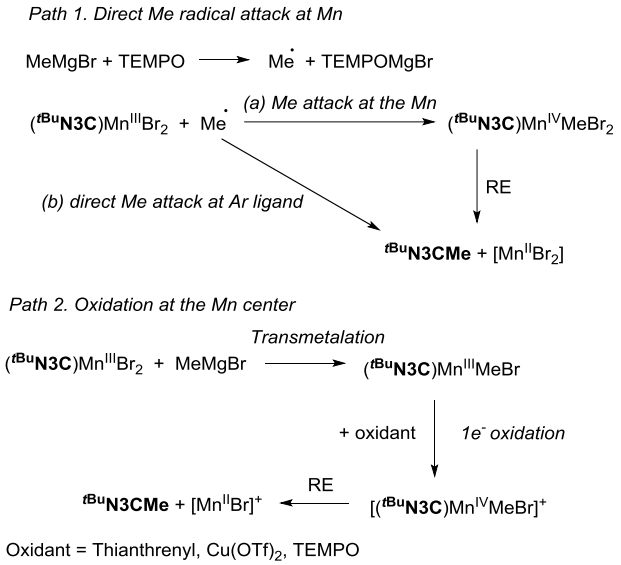
Scheme 8. Literature-reported reactivity of TEMPO with alkylmetal reagents.



Based on these observations, we propose that the increased yield of C–C coupling product from complex **1** in the presence of TEMPO could involve a different pathway via the formation of an alkyl radical, which could then react either with a Mn^{III} center to give (^{tBu}**N3C**)$Mn^{IV}(Me)X_2$ (X = halogen or Me) intermediate (Path 1a, Scheme 9), or directly attack a Mn-bound aryl ligand without changes in Mn oxidation state (Path 1b, Scheme 9). The absence of the boosting TEMPO effect in the reaction with aryl Grignard reagents could be due to absence of free radicals that would react with a Mn^{III} complex, further suggesting that the formation of alkyl radicals may be a prerequisite for the observed more efficient C(sp^2)-C(sp^3) coupling reactivity.

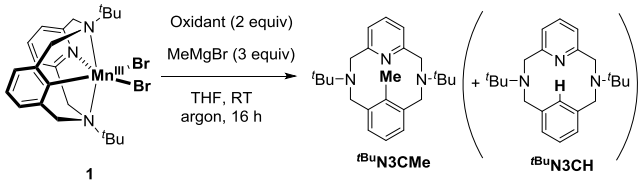
The fast reactions of Me or other alkyl radicals with transition metals leading to their formal one-electron oxidation and M-C bond formation have been studied extensively for some first-row transition metals,[38-39] and a similar mechanism was proposed for C(sp^3)–C(sp^3) bond elimination from a monomethyl Pd^{III} complex via oxidation to Pd^{IV} by a Me radical.[40] Although the Mn^{III} complex **1** is six-coordinate, with a κ⁴-bound ^{tBu}**N3C**⁻ ligand, a vacant coordination site in Path 1b could form via dissociation of a bulky *t*Bu-substituted amine group. The hemilability of *t*Bu-amine groups in structurally similar ^{tBu}**N4**-pyridinophane ligands has been studied extensively, showing facile interconversion between the κ⁴-bound and κ³-bound ligand coordination modes.[41-43]

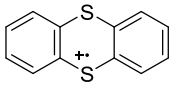
Scheme 9. Proposed mechanism of C–C coupling in the presence of TEMPO or other oxidants.



Interestingly, higher yields of C–C coupling product were also observed in the presence of some other one-electron oxidants including $Cu^{II}(OTf)_2$, ferrocenium hexafluorophosphate, and thianthrenyl hexachloroantimontate, while the yield remained unchanged or decreased in the presence of silver tetrafluoroborate and tris(4-bromophenyl)aminium hexachloroantimonate (Magic Blue), respectively, compared to the reaction in the absence of any additives (Table 4). The increased yield of ^{tBu}**N3CMe** coupling product in the presence of other one-electron oxidants could similarly be explained by the generation of a Me radical. However, we cannot exclude an alternative mechanism (Path 2, Scheme 9) via initial transmetalation followed by oxidation to a Mn^{IV} species and oxidatively-induced reductive elimination similar to the mechanism proposed by us for Ar-X (X = Br, I, CN) elimination in the presence of strong oxidants (Scheme 1).

Table 4. C–C coupling from complex 1 in the presence of MeMgBr and one-electron oxidants.[a]



Entry	Oxidant	^{tBu}N3CMe, % yield[b]	^{tBu}N3CH, %yield[b]
1	$Cu(OTf)_2$	88	n.d.[c]
2	 SbF_6^-	90	n.d.
3	$[(p\text{-}BrC_6H_4)_3N]SbCl_6$	32	n.d.
4	$AgBF_4$	68	n.d.
5	$Fc^+PF_6^-$	37	n.d.

[a]Reaction was performed in THF for 16 h at RT in the presence of 3 equiv of MeMgBr and 2 equiv of oxidant. [b]Yields were determined after quenching excess reagent by NMR integration against 1,3,5-trimethoxybenzene as an internal standard. [c]Not detected.

SUMMARY AND CONCLUSION

Mn-mediated C–C bond coupling reactions attract attention as an inexpensive alternative to the use of precious metal in C–C cross-coupling reactions. The intermediacy of Mn^{III} or Mn^{IV} species in C–C bond coupling has been a subject of debate, and such complexes have been proposed as intermediates in several examples of Mn-catalyzed C–C bond coupling reactions. In this work, we demonstrate that Mn^{III} aryl species are indeed viable intermediates in C–C bond elimination and they undergo C–C bond coupling with a range of alkylating and arylating organometallic reagents under mild conditions. Although the couplings occur in the absence of any oxidants, the presence of oxidative additives, in particular TEMPO, significantly improves the reaction selectivity and the scope of alkylating agents, presumably via oxidation to Mn^{IV} and/or alkyl radical formation. Our results suggest that two pathways, either via a Mn^{III} or a Mn^{IV} center, may be operative in C–C coupling bond elimination reactions. While we were able to develop an initial catalytic protocol via the former pathway, the latter leads to greater yield and selectivity despite requiring a sacrificial oxidant. We are currently focusing on trying to develop a more practical catalytic system via both the Mn^{III} and Mn^{IV} oxidation states for a greater variety of substrates.

EXPERIMENTAL SECTION

All manipulations, unless stated otherwise, were performed using Schlenk or glovebox techniques under dry argon atmosphere. Anhydrous solvents were dispensed from an MBRAUN solvent purification system and degassed before use. Anhydrous deuterated solvents were purchased from Eurisotop and stored over 4 Å molecular sieves. All chemicals unless noted otherwise were purchased from major commercial suppliers (TCI, Sigma-Aldrich, and NacalaiTesque) and used without purification. **$^{t\mathrm{Bu}}$N3CBr** was synthesized as described previously.[32, 44] 2-chloro-1,3-bis(bromomethyl)benzene was synthesized according to the literature procedure.[45] 2,6-Bis(*tert*-butylaminomethyl)pyridine was synthesized according to the modified literature method.[46] $MnCl(CO)_5$[47] and $MeMn(CO)_5$[48] were obtained according to literature procedures.

Instrumentation. NMR spectra were measured on JEOL ECZ600R 600 MHz, JEOL ECZ400S 400 MHz, Bruker Avance II 400 MHz, and Bruker Avance III Neo 500 MHz (CryoProbe) spectrometers. ESI-MS measurements were performed on a Thermo Scientific ETD apparatus. Elemental analyses were performed using an Exeter Analytical CE440 instrument. FT-IR spectra were measured using an Agilent Cary 630 with an ATR module in an argon-filled glovebox. The following abbreviations are used for describing FT-IR spectra: s (strong), m (medium), w (weak), br (broad). UV-vis absorbance spectra were collected using an Agilent Cary 60 instrument. The magnetic properties were measured using a 9T physical properties measurement system PPMS Dynacool from Quantum Design, equipped with the vibrating sample magnetometer (VSM) option, in a 2–300 K temperature range under a magnetic field of 10 000 Oe. For these measurements, samples were ground into powder and placed in plastic capsules. The Evans method measurements were performed in the coaxial NMR tube at 298 K; diamagnetic correction was applied.[49]

X-ray Structure Determination Details. The X-ray diffraction data were collected on a Rigaku XtaLab PRO instrument in an ω-scan mode with a PILATUS3 R 200K hybrid pixel array detector and MicroMax™-003 microfocus X-ray tubes using CuKα (1.54184 Å) or MoKα (0.71073 Å) radiation at low temperature. Images were indexed and integrated using the *CrysAlis*$^{\mathrm{Pro}}$ (version 1.171.41.93a) data reduction package. Data were corrected for systematic errors and absorption using the *ABSPACK* module: Numerical absorption correction based on Gaussian integration over a multifaceted crystal model and empirical absorption correction based on spherical harmonics according to the point group symmetry using equivalent reflections. The *GRAL* module was used for the analysis of systematic absences and space-group determination. All structures were solved by the direct methods using *SHELXT*-2018/2[50] and refined by the full-matrix least-squares on F^2 using *SHELXL*-2018/3.[51] Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were inserted at the calculated positions and refined as riding atoms. The positions of the hydrogen atoms of methyl groups were found using rotating group refinement with idealized tetrahedral angles. The disorder was resolved using free variables and reasonable restraints on geometry and anisotropic displacement parameters. The crystal structures of **3** obtained by different methods were refined as two-component inversion twins.

Crystallographic data for **2**.

$C_{23}H_{32}Cl_2MnN_3$, brown prism (0.111 × 0.061 × 0.046 mm^3), formula weight 476.35; orthorhombic, *Pbca* (No. 61), a = 14.38378(7) Å, b = 11.29423(6) Å, c = 27.85495(19) Å, V = 4525.14(5) Å^3, Z = 8, Z' = 1, T = 95(2) K, d_{calc} = 1.398 g cm^{-3}, μ(CuKα) = 7.016 mm^{-1}, F(000) = 2000; $T_{max/min}$ = 1.000/0.636; 44277 reflections were collected (4.419° ≤ θ ≤ 78.086°, index ranges: −18 ≤ h ≤ 18, −14 ≤ k ≤ 13, −27 ≤ l ≤ 34), 4819 of which were unique, R_{int} = 0.0277, R_σ = 0.0158; completeness to θ_{max} 99.4 %. The refinement of 275 parameters with 84 restraints converged to R_1 = 0.0466 and wR_2 = 0.1086 for 4789 reflections with $I > 2\sigma(I)$ and R_1 = 0.0468 and wR_2 = 0.1087 for all data with S = 1.159 and residual electron density, $\rho_{max/min}$ = 0.544 and −0.394 e Å^{-3}. The crystals were grown by diethyl ether vapor diffusion to a dichloromethane solution.

Crystallographic data for **3**.

$C_{23}H_{32}Br_{0.88}Cl_{1.12}MnN_3$, red prism (0.194 × 0.170 × 0.094 mm^3), formula weight 515.62; orthorhombic, *Pca*2$_1$ (No. 29), a = 14.6467(3) Å, b = 13.8349(3) Å, c = 11.2247(3) Å, V = 2274.53(9) Å^3, Z = 4, Z' = 1, T = 95(2) K, d_{calc} = 1.506 g cm^{-3}, μ(MoKα) = 2.278 mm^{-1}, F(000) = 1064; $T_{max/min}$ = 1.000/0.629; 26895 reflections were collected (2.719° ≤ θ ≤ 32.230°, index ranges: −19 ≤ h ≤ 21, −19 ≤ k ≤ 20, −15 ≤ l ≤ 16), 7151 of which were unique, R_{int} = 0.0339, R_σ = 0.0344; completeness to θ_{max} 93.3 %. The refinement of 296 parameters with 113 restraints converged to R_1 = 0.0321 and wR_2 = 0.0737 for 6532 reflections with $I > 2\sigma(I)$ and R_1 = 0.0366 and wR_2 = 0.0747 for all data with S = 1.055 and residual electron density, $\rho_{max/min}$ = 0.423 and −0.415 e Å^{-3}. The crystals were grown by diethyl ether vapor diffusion to a dichloromethane solution.

Crystallographic data for **3** obtained by the oxidative addition of **$^{t\mathrm{Bu}}$N3CCl** to $MnBr(CO)_5$.

$C_{23}H_{32}Br_{0.84}Cl_{1.16}MnN_3$, red prism (0.223 × 0.126 × 0.103 mm^3), formula weight 513.86; orthorhombic, *Pca*2$_1$ (No. 29), a = 14.6407(4) Å, b = 13.8107(4) Å, c = 11.2124(4) Å, V = 2267.12(12) Å^3, Z = 4, Z' = 1, T = 95(2) K, d_{calc} = 1.505 g cm^{-3}, μ(CuKα) = 7.830 mm^{-1}, F(000) = 1061; $T_{max/min}$ = 1.000/0.368; 14985 reflections were collected (3.200° ≤ θ ≤ 77.818°, index ranges: −18 ≤ h ≤ 18, −15 ≤ k ≤ 17, −13 ≤ l ≤ 13), 4393 of which were unique, R_{int} = 0.0746, R_σ = 0.0526; completeness to θ_{max} 97.6 %. The refinement of 296 pa-

rameters with 113 restraints converged to R_1 = 0.0626 and wR_2 = 0.1667 for 4193 reflections with $I > 2\sigma(I)$ and R_1 = 0.0643 and wR_2 = 0.1679 for all data with S = 1.075 and residual electron density, $\rho_{max/min}$ = 1.191 and −0.862 e Å^{-3}. The crystals were grown by diethyl ether vapor diffusion to a dichloromethane solution.

Synthesis of $^{t\text{Bu}}$N3CCl.

(a) Synthesis of 2,6-bis(*tert*-butylaminomethyl)pyridine. A 500 mL round bottom flask equipped with a magnetic stirring bar and a reflux condenser was charged with chloroform (100 mL); *tert*-butylamine (100 mL, 950 mmol, 50 equiv) was added to stirred chloroform slowly, in several portions. Solution of 2,6-bis(bromomethyl)pyridine (5 g, 19 mmol, 1 equiv) in $CHCl_3$ (150 mL) was slowly added to the stirred solution (exothermic!) at room temperature. The resulting solution was heated at 50 °C for 5 hours under N_2 atmosphere. The sample of the reaction mixture after heating for 5 hours was evaporated to dryness and redissolved in $CDCl_3$ to check the completeness of the reaction; according to ^{1}H NMR, no starting material was present after 5 hours and the diamine was the only pyridine-containing product present in solution. The reaction mixture was cooled down to RT, the chloroform solution was washed with saturated aqueous $NaHCO_3$ solution (2 × 150 mL) and water (150 mL). The organic layer was separated and dried over $MgSO_4$. The solvents were removed by rotary evaporation at RT to give a colorless or pale yellow oil, which was further dried under high vacuum for 1 hour at RT and stored under N_2 at −20 °C. Yield 4.58 g, 97%. ^{1}H NMR ($CDCl_3$, 300 MHz), δ (ppm): 7.56 (t, J = 7.5 Hz, 1H, Py CH_{para}), 7.17 (d, J = 7.5 Hz, 2H, Py CH_{meta}) 3.86 (s, 4H, CH_2), 1.67 (br s, 2H, NH), 1.19 (s, 18H, *t*Bu).

(b) Synthesis of $^{t\text{Bu}}$N3CCl. A round-bottomed flask was charged with 50 mL of toluene, 30 mL of 10 wt% Na_2CO_3 solution and 2,6-bis(*tert*-butylaminomethyl)pyridine (1.10 g, 4.4 mmol, 1 equiv). The flask was supplemented with a 2-neck extension; one neck was connected to a reflux condenser, and the other one with an addition funnel. The reaction mixture is heated up to 80 °C under nitrogen atmosphere. A solution of 2-chloro-1,3-bis(bromomethyl)benzene (1.18 g, 4.0 mmol, 0.9 equiv) in 50 mL of toluene was added dropwise through the addition funnel to the reaction mixture over 3 hours. After complete addition, the reaction mixture was heated with stirring at 90 °C for 36 h and then cooled down. The aqueous layer was discarded and the pale yellow toluene layer was washed 3 times with saturated Na_2CO_3 aqueous solution and dried over anhydrous Na_2SO_4. The solvent was removed and the solid residue was washed with a minimal amount of ethanol and filtered off. The solid product was recrystallized from warm Et_2O solution and cooled down in a freezer overnight to give a pure white crystalline product, which was filtered off and dried under vacuum. Yield 450 mg (1.17 mmol, 29%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (t, J = 7.6 Hz, 1H), 6.82 (d, J = 7.4 Hz, 2H), 6.75 (d, J = 7.6 Hz, 2H), 6.59 (t, J = 7.4 Hz, 1H), 4.15 (dd, J = 16.7, 13.3 Hz, 4H), 3.96 (d, J = 12.9 Hz, 2H), 3.52 (d, J = 13.4 Hz, 2H), 1.32 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.86, 137.26, 136.84, 135.00, 131.13, 124.99, 121.38, 56.77, 55.79, 51.38, 27.71. HRMS (ESI) (m/z): calculated for $C_{23}H_{32}ClN_3$ $[M + H]^+$ 386.2358; found 386.2335.

Synthesis of ($^{t\text{Bu}}$N3C)Mn^{III}Cl$_2$ (2). 38.5 mg of $^{t\text{Bu}}$N3CCl (0.1 mmol) and 23 mg of $MnCl(CO)_5$ (0.1 mmol) were combined in a flame-dried Schlenk flask inside a glovebox and 2 mL of THF was added to give a yellow suspension. The flask was taken outside the glovebox and stirred in a water bath in front of a mercury lamp. The reaction vessel was subjected to vacuum for 1 second every hour, then stirred under static vacuum, and after 3 h, the reaction was then stirred under a static vacuum overnight. After 13 hours, the solution color changed to wine-red and the entire solvent was evaporated under reduced pressure. The solid obtained was redissolved in a minimal amount of dichloromethane and filtered through celite. The filtrate was evaporated under reduced pressure to yield a red solid which was washed three times with copious amounts of ether (ca. 3 mL) and then dried under vacuum. Deep red crystals were grown from by vapor diffusion of ether into a dichloromethane solution of the complex (about 2 mL of DCM); yield of isolated product **($^{t\text{Bu}}$N3C)Mn^{III}Cl$_2$ (2)** 10.4 mg, 22% yield. Evans method (CD_2Cl_2, 298 K): μ_{eff} = 4.71 μ_B. ESI-HRMS of $C_{23}H_{32}Cl_2N_3Mn$ in MeOH (m/z): calculated for $[C_{23}H_{32}ClN_3Mn]^+$, ($[M–Cl]^+$) 440.1660; found 440.1632 (z = 1). Anal. Calcd. for $MnC_{23}H_{32}Cl_2N_3$: C, 57.99; H, 6.77; N, 8.82. Found: C, 57.74; H, 6.65; N, 8.73. UV-vis, λ, nm (ε, M^{-1} cm^{-1}), CH_2Cl_2: 534 (328), 301 (3412), 235 (8934). FT-IR (ATR, solid, cm^{-1}): ν 2966 (w), 2893 (w), 1601 (w), 1576 (w),1428 (w), 1376 (s), 1189 (s), 909 (w), 849 (w), 772 (s).

Synthesis of ($^{t\text{Bu}}$N3C)Mn^{III}BrCl (3) by oxidative addition of $^{t\text{Bu}}$N3CBr. 42.9 mg of $^{t\text{Bu}}$N3CBr (0.1 mmol) and 23 mg of $MnCl(CO)_5$ (0.1 mmol) were combined in a flame-dried Schlenk flask inside a glovebox and 2 mL of THF was added to give a yellow suspension. The flask was taken outside the glovebox and stirred in a water bath in front of a mercury lamp. The reaction vessel was subjected to vacuum for 1 second every hour, then stirred under static vacuum, and after 3 h, the reaction was then stirred under a static vacuum overnight. After 13 hours, the solution appeared wine-red and the entire solvent was evaporated under reduced pressure. The solid obtained was redissolved in a minimal amount of dichloromethane and filtered through celite. The filtrate was evaporated under reduced pressure to yield a red solid which was washed three times with copious amounts of ether (ca. 3 mL) and then dried under vacuum. Deep red crystals were grown from by vapor diffusion of ether into a dichloromethane solution of the complex (about 2 mL of DCM); yield of isolated product **($^{t\text{Bu}}$N3C)Mn^{III}BrCl (3)** 38.2 mg, 74% yield. HRMS (ESI) in MeOH for $C_{23}H_{32}BrClN_3Mn$ (m/z): calculated for $[C_{23}H_{32}ClN_3Mn]^+$ ($[M–Br]^+$) 440.1660; found 440.1641 (z = 1) and calculated for $[C_{23}H_{32}BrN_3Mn]^+$ ($[M–Cl]^+$): 484.1155; found: 484.1138 (z = 1), both peaks showing expected isotopic patterns. Evans method (CD_2Cl_2, 298 K): μ_{eff} = 4.78 μ_B. Anal. Calcd. for $Mn_1C_{23}H_{32}BrClN_3$: C, 53.04; H, 6.19; N, 8.07. Found: C, 53.45; H, 6.05; N, 8.07. UV-vis, λ, nm (ε, M^{-1} cm^{-1}), CH_2Cl_2: 539 (854), 304 (6637), 260 (10817). FT-IR (ATR, solid, cm^{-1}): ν 2968 (w), 2898 (w), 1601 (w), 1462 (w), 1429 (w), 1376 (s), 1188 (s), 910 (w), 849 (w), 770 (s).

Synthesis of ($^{t\text{Bu}}$N3C)Mn^{III}BrCl (3) by oxidative addition of $^{t\text{Bu}}$N3CCl. 19.3 mg of $^{t\text{Bu}}$N3CCl (0.05 mmol) and 13.7 mg of $MnBr(CO)_5$ (0.05 mmol) were combined in a flame dried Schlenk flask inside a glovebox and 2 mL of THF was added to give a yellow suspension. The flask was taken outside the glovebox and stirred in a water bath in front of a mercury lamp. The reaction vessel was subjected to vacuum for 1 second every hour, then stirred under static vacuum, and after 3 h, the reaction was then stirred under a static vacuum overnight. After 13 hours, the solution turned wine-red and the entire solvent was evaporated under reduced pressure. The solid obtained was redissolved in a minimal amount of dichloromethane and filtered through celite. The filtrate obtained was evaporated under reduced pressure to yield a red solid which was washed three times with copious amounts of ether (ca. 3 mL) and then dried under vacuum. Deep red crystals were grown from by vapor diffusion of ether into a dichloromethane solution of the complex (about 2 mL of DCM); yield of isolated product **($^{t\text{Bu}}$N3C)Mn^{III}BrCl (3)** 6.0 mg, 23% yield. HRMS (ESI) in MeOH for $C_{23}H_{32}BrClN_3Mn$ (m/z): calculated for $[C_{23}H_{32}ClN_3Mn]^+$ ($[M–Br]^+$) 440.1660; found: 440.1637 (z = 1) and calculated for $[C_{23}H_{32}BrN_3Mn]^+$ ($[M–Cl]^+$): 484.1155; found: 484.1119 (z = 1), both peaks showing expected isotopic patterns.

General Procedure for C–C coupling without oxidant. 0.05 mmol of a manganese complex (**1**, **2** or **3**) was dissolved in 2 mL of THF. Then, 3.0 equivalents of an organometal reagent

were added and the reaction mixture was stirred at RT in a glovebox for 16 h. The vial was then taken out of the glovebox and quenched by addition of a saturated aqueous solution of ammonium chloride (0.2 mL), then a 2 mL saturated solution of K_2CO_3 was added to it and vigorously stirred for 30 minutes. Workup using basic aqueous solutions was needed to remove all unreacted Mn residues after reaction and avoid the presence of unreacted paramagnetic species in solution that can potentially lead to broadening of NMR spectra. The mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed with saturated brine (15 mL) and dried over Na_2SO_4. The solvent was removed by rotary evaporation, 1,3,5-trimethoxybenzene (0.05 mmol, 1.0 equiv) was then added to this mixture as an internal standard, and NMR yields of the products were determined in C_6D_6 (see the SI). Then the above crude product was purified by flash-column chromatography on a silica gel (CH_2Cl_2/MeOH = 20/1 ~ 15/1) give the desired product.

For low temperature experiments, the solution of **1** (0.05 mmol) in THF (8 mL) was placed in a Schlenk tube, cooled down to -80 °C using methanol-dry ice cooling bath. The solution of MeMgBr (3.0 M in diethyl ether) (0.05 mL, 0.150 mmol, 3 equiv) was added slowly to the reaction mixture under argon gas flow. The reaction mixture was warmed up to RT slowly over the course of 4 h, then stirred at RT for another 16 h. The workup procedure was carried out as described above. The same procedure was followed for the reactions with MeLi and $ZnMe_2$.

General Procedure for C-C coupling with oxidant. 0.05 mmol of a manganese complex (**1**, **2** or **3**) was dissolved in 2 mL of THF. Then, 15.6 mg of TEMPO (2 equivalents), and 3.0 equivalents of an organometal reagent were added and stirred at room temperature in a glovebox for 16 h. The vial was then taken out of the glovebox and quenched by addition of a saturated aqueous solution of ammonium chloride (0.2 mL), then a 2 mL saturated solution of K_2CO_3 was added to it and vigorously stirred for 30 minutes. The mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed with saturated brine (15 mL) and dried over Na_2SO_4. The solvent was removed by rotary evaporation, 1,3,5-trimethoxybenzene (0.05 mmol, 1.0 equiv) was then added to this mixture as an internal standard, and NMR yields of the products were determined in C_6D_6 (see the SI). Then the above crude product was purified by flash-column chromatography on a silica gel (CH_2Cl_2/MeOH = 20/1 ~ 15/1) to give the desired product.

Isolation and characterization of C-C coupling products. **$^{t\mathrm{Bu}}$N3CMe.** Following the general procedure for C-C coupling with oxidant, the crude product of the reaction was collected and purified by flash-column chromatography on silica gel (CH_2Cl_2/MeOH, 20:1) to provide **$^{t\mathrm{Bu}}$N3CMe** as a white solid in 93% isolated yield. The desired product was confirmed by ESI-(HR)MS and NMR. ^{1}H NMR (500 MHz, C_6D_6) δ 6.98 – 6.95 (m, 3H), 6.84 (t, *J* = 7.4 Hz, 1H), 6.61 (d, *J* = 7.6 Hz, 2H), 4.14 (d, *J* = 12.0 Hz, 2H), 3.73 (d, *J* = 13.2 Hz, 2H), 3.65 (d, *J* = 11.8 Hz, 2H), 3.59 (d, *J* = 14.3 Hz, 2H), 2.84 (s, 3H), 1.15 (s, 18H). ^{13}C NMR (126 MHz, C_6D_6) δ 161.15, 138.55, 135.08, 130.98, 128.68, 124.74, 120.32, 56.10, 53.73, 27.73, 18.17. ESI-(HR)MS of the product from methanol solution (*m*/*z*): calculated for M^*H^+, $C_{24}H_{35}N_3$, 366.2904; found 366.2884.

$^{t\mathrm{Bu}}$N3C*i*Pr. 28.3 mg (0.05 mmol) of (**$^{t\mathrm{Bu}}$N3C**)$Mn^{III}Br_2$ (**1**) was dissolved in 2 mL of THF. Then, 15.6 mg of TEMPO (2 equiv), and 75 μL of isopropylmagnesium chloride (2.0 M in THF, 3 equiv) was added to the mixture and stirred at room temperature in glove box for 16 h. The mixture was quenched by addition of a saturated aqueous solution of ammonium chloride (0.2 mL), then a 2 mL saturated solution of K_2CO_3 was added to it and vigorously stirred for 30 minutes. The mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed with saturated brine (15 mL) and dried over Na_2SO_4. The ethyl acetate was completely evaporated by a rotavapor and the solid left was isolated by a short flash column chromatography on silica gel with DCM/MeOH (15/1) to provide **$^{t\mathrm{Bu}}$N3C*i*Pr** (9.2 mg, 47%).^{1}H NMR (500 MHz, C_6D_6) δ 7.00-6.97 (m, 3H), 6.66-6.63 (m, 3H), 4.13-4.09 (m, 2H), 3.92-3.88 (m, 4H), 3.77-3.71 (m, 2H), 3.59-3.55 (m, 1H), 1.83 (s, 6H), 1.19 (s, 18H). ^{13}C NMR (126 MHz, C_6D_6) δ 160.99, 138.61, 134.65, 131.85, 125.12, 120.54, 57.72, 56.01, 31.26, 28.00, 24.55, 23.39. ESI-(HR)MS of the product from methanol solution (*m*/*z*): calculated for $[M+H]^+$, $C_{26}H_{39}N_3$, 394.3217; found *m*/*z* 394.3215.

$^{t\mathrm{Bu}}$N3CC$_3$H$_5$. 28.3 mg (0.05 mmol) of (**$^{t\mathrm{Bu}}$N3C**)$Mn^{III}Br_2$ (**1**) was dissolved in 2 mL of THF. Then, 15.6 mg of TEMPO (2 equiv), and 150 μL of allylmagnesium bromide (1 M in diethyl ether, 3 equiv) were added to the mixture and stirred at room temperature for 16 h. The vial was then taken out of the glovebox and quenched by addition of a saturated aqueous solution of ammonium chloride (0.2 mL), then a 2 mL saturated solution of K_2CO_3 was added to it and vigorously stirred for 30 minutes. The mixture was extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with brine (15 mL) and dried over Na_2SO_4. The solvent was removed by rotary evaporation and a 72% yield of product **$^{t\mathrm{Bu}}$N3CC$_3$H$_5$** was obtained and confirmed by the NMR spectrum. This product was not stable and decomposed after isolation from column chromatography, but it was stable in solution for a few days. ^{1}H NMR (400 MHz, C_6D_6) δ 7.01-6.97 (m, 3H), 6.92-6.88 (m, 1H), 6.60 (d, *J* = 7.6 Hz, 2H), 6.20-6.11 (m, 1H), 5.06-5.05 (m, 2H), 4.58 (d, *J* = 5.5 Hz, 2H), 4.22 (d, *J* = 12.0 Hz, 2H), 3.71 (d, *J* = 14.5 Hz, 2H), 3.63-3.59 (m, 4H), 1.14 (s, 18H). ^{13}C NMR (101 MHz, C_6D_6) δ 161.15, 140.06, 138.32, 135.18, 131.80, 125.42, 120.34, 114.28, 56.09, 55.70, 53.66, 33.98, 27.65.ESI-(HR)MS of the product from methanol solution (*m*/*z*): calculated for $[M+H]^+$, $C_{26}H_{37}N_3$, *m*/*z* 392.3060; found 392.3058.

$^{t\mathrm{Bu}}$N3CPh. 28.3 mg (0.05 mmol) of (**$^{t\mathrm{Bu}}$N3C**)$Mn^{III}Br_2$ (**1**) was dissolved in 2 mL of tetrahydrofuran. Then, 15.6 mg of TEMPO (2 equiv), and 50 μl of phenylmagnesium bromide (3 M in diethyl ether, 3 equiv) was added and stirred at room temperature in a glovebox for 16 h. The vial was then taken out of the glovebox and quenched by addition of a saturated aqueous solution of ammonium chloride (0.2 mL), then a 2 mL saturated solution of K_2CO_3 was added to it and vigorously stirred for 30 minutes. The mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed with saturated brine (15 mL) and dried over Na_2SO_4. The solvent was removed by rotary evaporation and a 71% yield was showed from crude NMR using 1,3,5-trimethoxybenzene as an internal standard. The crude product was purified by flash column chromatography on silica gel (DCM/MeOH, 20:1) to provide **$^{t\mathrm{Bu}}$N3CC$_6$H$_5$** (12.8 mg, 60%) as a white solid. ^{1}H NMR (500 MHz, C_6D_6) δ 9.81 (d, *J* = 7.1 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.25-7.22 (m, 2H), 7.01-6.96 (m, 4H), 6.81 (t, *J* = 7.5 Hz, 1H), 6.66 (s, 2H), 3.85 (s, 4H), 3.76 (s, 4H), 1.00 (s, 18H). ^{13}C NMR (126 MHz, C_6D_6) δ 161.54, 142.04, 137.93, 134.84, 132.04, 130.97, 128.89, 127.57, 127.22, 126.64, 120.30, 56.75, 55.92, 53.29, 27.72. ESI-(HR)MS of the product from methanol solution (*m*/*z*): calculated for $[M+H]^+$, $C_{29}H_{38}N_3$, *m*/*z* 428.3060; found 428.3049.

$^{t\mathrm{Bu}}$N3CC$_6$F$_5$. 28.3 mg (0.05 mmol) of ^{t}(**$^{t\mathrm{Bu}}$N3C**)$Mn^{III}Br_2$ (**1**) was weighed out in a scintillation vial inside a glovebox and 2 mL of benzene was added and stirred for 20 min at RT. To the red solution, 600 μl (0.3 mmol) of pentafluorophenylmagnesium bromide solution (0.5 M in diethyl ether, 6 equiv) was added in one portion and the mixture was allowed to stir for 40 hours at 80 °C over which time period the color of the solution gradually changed to brown and the reaction was stopped. The vial was then taken out of the glovebox and then 2 mL of a saturated aqueous solution of K_2CO_3 was added to it and vigorously stirred for 30 minutes. The aqueous solution was extracted with ethyl acetate, filtered and then dried over anhydrous Na_2SO_4. The

ethyl acetate was completely evaporated by a rotavapor and the solid left was isolated by a short flash column chromatography on silica gel with hexane/ethyl acetate (2/1 ~ 1.5/1) to provide $^{t\mathrm{Bu}}$**N3CC$_6$F$_5$** (12.6 mg, 49%). ^{1}H NMR (400 MHz, C_6D_6) δ 7.10-7.04 (m, 3H, ArH), 6.95 (t, *J* = 7.6 Hz, 1H, ArH), 6.49 (d, *J* = 7.6 Hz, 2H, ArH), 3.70-3.65 (m, 2H, CH_2), 3.54-3.46 (m, 4H, CH_2), 3.27-3.21 (m, 2H, CH_2), 0.85 (s, 18H). ^{13}C NMR (126 MHz, C_6D_6) δ 161.06, 146.14, 141.11, 135.29, 131.90, 128.68, 119.95, 56.21, 54.70, 53.52, 27.09. ^{19}F NMR (376 MHz, C_6D_6) δ -106.51, -117.34, -138.00 (dt, *J* = 25.4, 6.1 Hz), -158.34, -164.83 (d, *J* = 111.4 Hz). ^{19}F NMR (376 MHz, C_6D_6) δ -106.5, -117.3, -138.0 (dt, *J* = 25.4, 6.1 Hz), -158.3, -164.8 (d, *J* = 111.4 Hz). ESI-(HR)MS of the product from methanol solution (*m*/*z*): calculated for $[M+H]^+$, $C_{29}H_{33}F_5N_3$, *m*/*z* 518.2589; found 518.2601.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental details and characterization data (PDF). CCDC deposition numbers 2056056-2056057, 2056899 contain the supplementary crystallographic data for this paper.

AUTHOR INFORMATION

Corresponding Author

Julia R. Khusnutdinova – *Coordination Chemistry and Catalysis Unit, Okinawa Institute of Science and Technology Graduate University, 1919-1 Tancha, Onna-son, Okinawa, 904-0495 Japan*; orcid.org/0000-0002-5911-4382; Email: julia.k@oist.jp

Authors

Yu-Tao He – *Coordination Chemistry and Catalysis Unit, Okinawa Institute of Science and Technology Graduate University, 1919-1 Tancha, Onna-son, Okinawa, 904-0495 Japan*; orcid.org/0000-0001-5280-8448

Ayumu Karimata – *Coordination Chemistry and Catalysis Unit, Okinawa Institute of Science and Technology Graduate University, 1919-1 Tancha, Onna-son, Okinawa, 904-0495 Japan;* orcid.org/0000-0003-0323-2256

Olga Gladkovskaya – *Coordination Chemistry and Catalysis Unit, Okinawa Institute of Science and Technology Graduate University, 1919-1 Tancha, Onna-son, Okinawa, 904-0495 Japan*

Eugene Khaskin – *Coordination Chemistry and Catalysis Unit, Okinawa Institute of Science and Technology Graduate University, 1919-1 Tancha, Onna-son, Okinawa, 904-0495 Japan*; orcid.org/0000-0003-1790-704X

Robert R. Fayzullin – *Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center, Russian Academy of Sciences, 8 Arbuzov Street, Kazan 420088, Russian Federation;* orcid.org/0000-0002-3740-9833

Abir Sarbajna – *Coordination Chemistry and Catalysis Unit, Okinawa Institute of Science and Technology Graduate University, 1919-1 Tancha, Onna-son, Okinawa, 904-0495 Japan*; orcid.org/0000-0003-2478-5044

Notes

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