Oxidative Homocoupling of Diheteroaryl- or Diarylmanganese Reagents Generated via Directed Manganation Using TMP_2Mn

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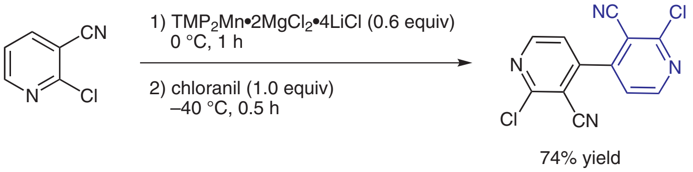

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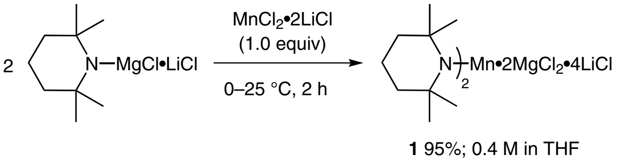
Abstract We report an oxidative homocoupling of diheteroaryl or diarylmanganese reagents prepared by directed manganation using $TMP_2Mn{\cdot}2MgCl_2{\cdot}4LiCl$. The resulting diorganomanganese reagents can efficiently undergo an oxidative dimerization leading to the homocoupling products in good yields. Remarkably, a number of functional groups, as well as sensitive heterocycles are tolerated using this metalation–dimerization procedure.

Key words homocoupling, manganese, metalation, dimerization, oxidation

The biaryl motif can be found in a broad array of natural products, pharmaceuticals, agrochemicals, and materials.[2] Thus, an increasing number of methods for their synthesis have been described. Homo- and cross-coupling reactions are most commonly used to construct these biaryl structures. Many symmetrical biaryls can be obtained by the palladium-[3] or nickel-catalyzed[4] homocoupling of ArX (X = I, Br, Cl, OTf) in the presence of an oxidizing agent. However, metal catalysts together with the ligands are often expensive or toxic.[5] Oxidative homocoupling of aryl-metal reagents displays another efficient synthetic method for the construction of symmetrical biaryls.[6] Although many organometallic reagents (ArMet; Met = Mg, Zn, Mn) can be used for this reaction, Grignard reagents remain the most convenient choice for large-scale preparations due to their economical preparation directly from the corresponding aryl halides.[7] So far, only few metalation–dimerization procedures have been described.[8] Herein, we report a convenient oxidative homocoupling of various diheteroaryl- or diaryl-manganese reagents prepared by a directed C–H metalation using the sterically hindered base $TMP_2Mn{\cdot}2MgCl_2{\cdot}4LiCl$[9] (**1**, Scheme 1; TMP = 2,2,6,6-tetramethylpiperidyl).

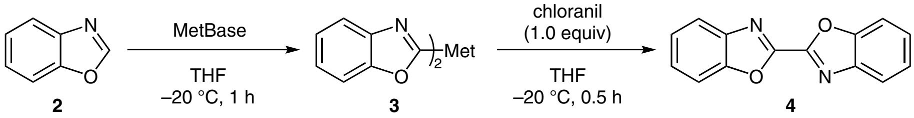


Scheme 1 Preparation of $TMP_2Mn{\cdot}2MgCl_2{\cdot}4LiCl$

In preliminary experiments, we have examined the oxidative homocoupling of various mono- or diheteroarylmetal species **3** generated via a direct metalation of benzoxazole (**2**) followed by an oxidative dimerization using chloranil[10] (Table 1). First experiments metalating with *n*-BuLi,[11] or metalating with *n*-BuLi followed by a transmetalation with either $ZnCl_2$ (0.5 equiv) or $MgCl_2$ (0.5 equiv) and subsequent oxidation using chloranil (1.0 equiv) only gave poor results (Table 1, entries 1–3). An improvement was achieved when transmetalating the aryllithium species with $MnCl_2{\cdot}2LiCl$ (0.5 equiv), which led to the desired product **4** in 47% yield after oxidation (Table 1, entry 4).

The C–H zincation of benzoxazole (**2**) with either $TMPZnCl{\cdot}LiCl$[12] or $TMP_2Zn{\cdot}2MgCl_2{\cdot}2LiCl$[13] followed by oxidation with chloranil at –20 °C did not lead to any product formation (Table 1, entries 5 and 6). Switching to the magnesium bases $TMPMgCl{\cdot}LiCl$[14] or $TMP_2Mg{\cdot}2LiCl$[15] at –20 °C also did not improve the result (Table 1, entries 7 and 8). Finally, it was found that the directed manganation of **2** using $TMP_2Mn{\cdot}2MgCl_2{\cdot}4LiCl$ (**1**, 0.6 equiv, –20 °C, 1 h) followed by an oxidation with chloranil (1.0 equiv, –20 °C) gave the best results leading to the heterobiaryl **4** in 79% isolated yield (Table 1, entry 9).[15]

Table 1 Homocoupling of Benzoxazole (**2**)



Entry	MetBase[a]	Additive[b]	GC yield of **4** (%)[c]
1	*n*-BuLi	–	0
2	*n*-BuLi	$ZnCl_2$	0
3	*n*-BuLi	$MgCl_2$	traces
4	*n*-BuLi	$MnCl_2\cdot 2LiCl$	47
5	TMPZnCl·LiCl	–	–
6	$TMP_2Zn\cdot 2MgCl_2\cdot 2LiCl$	–	–
7	TMPMgCl·LiCl	–	–
8	$TMP_2Mg\cdot 2LiCl$	–	–
9	$TMP_2Mn\cdot 2MgCl_2\cdot 4LiCl$	–	84 (79)[d]

[a] Conditions: 1.1 equiv of the metallic base was used, however, in entries 6, 8, and 9 only 0.6 equiv were used.
[b] Conditions: 0.5 equiv were used.
[c] Tetradecane ($C_{14}H_{30}$) was used as an internal standard.
[d] Isolated yield.

With these optimized conditions in hand, we applied this method to the dimerization of a broad range of heterocycles. The reaction scope proved to be general, and various substituted heterocycles could efficiently be homocoupled in 61–81% yield (Table 2). Remarkably, 2,3- and 3,6-disubstituted pyridines were smoothly dimerized to furnish the expected products **6a**–**e** in up to 74% yield.

Noteworthy is the metalation of 2-chloro-3-cyanopyridine, as its direct magnesiation or lithiation is difficult using other bases, such as TMPLi, $TMP_2Mg\cdot 2LiCl$, or TMPMgCl·LiCl and usually only leads to decomposition of the starting material. However, its manganation using $TMP_2Mn\cdot 2MgCl_2\cdot 4LiCl$ (**1**, 0.6 equiv) proceeded smoothly within four hours at 0 °C and afforded the corresponding diorganomanganese **5a**. Oxidative dimerization using chloranil (1.0 equiv, –40 °C) furnished the desired bipyridine **6a**[16] in 74% yield (Table 2, entry 1). Additionally, various electron-withdrawing groups, such as CF_3, F, and Cl, were tolerated under these reaction conditions, leading to the corresponding products **6b**–**e** in 61–71% yield (Table 2, entries 2–5). 3,6-Disubstituted pyridazines were also smoothly metalated using **1** (0 °C, 1 h) and gave the desired biaryls **6f**,**g**)[16] in 61–67% yield after oxidation of the corresponding manganese species **5f**,**g** (Table 2, entries 6 and 7). The metalation of benzofuran or benzothiophene using $TMP_2Mn\cdot 2MgCl_2\cdot 4LiCl$ (**1**, 0.6 equiv) was complete within five hours at 0 °C, providing the corresponding manganese reagents **5h**,**i**, that smoothly underwent the oxidative dimerization using chloranil (1.0 equiv, –40 °C) leading to the homocoupling products **6h**,**i** in 74–77% yield (Table 2, entries 8 and 9). Similarly, 1-methyl-benzimidazole was manganated using **1** (0.6 equiv, 0 °C, 6 h) to afford the manganese reagent **5j**, which undergoes oxidative dimerization leading to the expected product **6j** in 81% yield (Table 2, entry 12).

Table 2 Oxidative Homocoupling of Diheteroarylmanganese Reagents

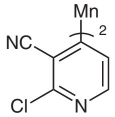
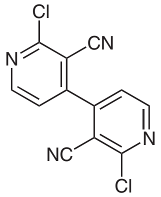
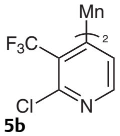
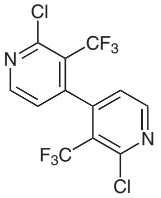
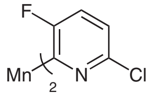
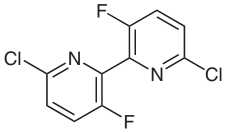
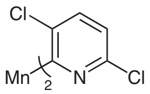
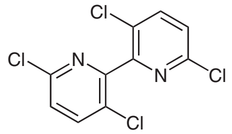
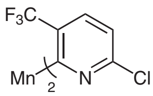
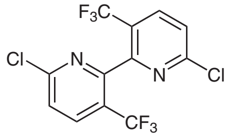
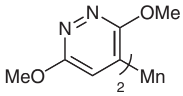
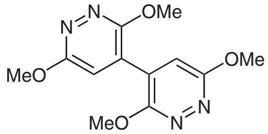
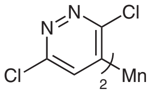
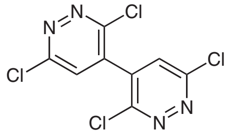
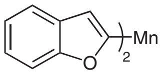
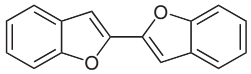
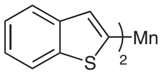
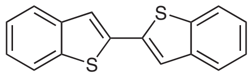
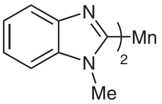
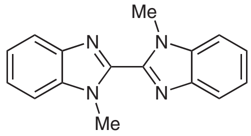
Entry	Manganese reagent[a]	Yield of product **6** (%)[b]
1	 **5a**	 **6a** 74
2	 **5b**	 **6b** 71
3	 **5c**	 **6c** 64

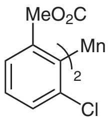
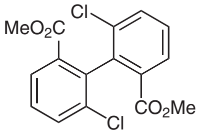
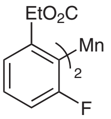
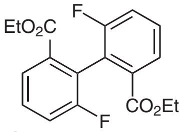
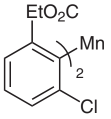
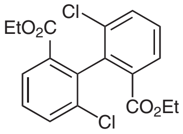
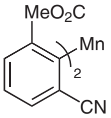
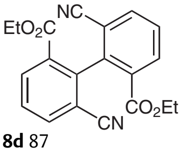
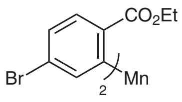
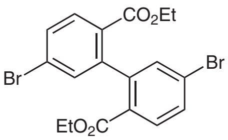
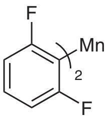
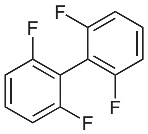
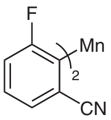
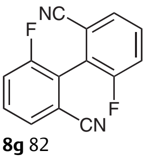
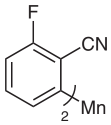
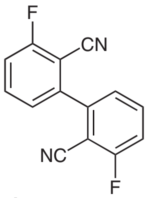
Table 2 (continued)

Entry	Manganese reagent[a]	Yield of product **6** (%)[b]
4	 **5d**	 **6d** 63
5	 **5e**	 **6e** 61
6	 **5f**	 **6f** 67
7	 **5g**	 **6g** 61
8	 **5h**	 **6h** 74
9	 **5i**	 **6i** 77
10	 **5j**	 **6j** 81

[a] $MgCl_2$ and LiCl are omitted for the sake of clarity.
[b] Isolated yield.

Additionally, a range of polyfunctional arenes have been dimerized in 51–97% yield using this method (Table 3). Thus, the directed manganation of methyl 3-chlorobenzoate with TMP$_2$Mn·2MgCl$_2$·4LiCl (**1**, 0.6 equiv, 0 °C, 6 h) and subsequent oxidation of the resulting manganese reagent **7a** using chloranil (1.0 equiv) at –40 °C gave the desired bisarene **8a** in 76% yield (Table 3, entry 1). Similarly, 3-substituted ethyl benzoates were deprotonated and dimerized to afford the desired products **8b–d**[16] in up to 97% yield, while tolerating various functionalities such as F, Cl, and sensitive cyano groups (Table 3, entries 2–4). The manganation of ethyl 4-bromobenzoate also proceeded smoothly leading to

Table 3 Oxidative Homocoupling of Arylmanganese Reagents

Entry	Manganese reagent[a]	Yield of product **8** (%)[b]
1	 **7a**	 **8a** 76
2	 **7b**	 **8b** 97
3	 **7c**	 **8c** 70
4	 **7d**	 **8d** 87
5	 **7e**	 **8e** 53
6	 **7f**	 **8f** 51
7	 **7g**	 **8g** 82
8	 **7h**	 **8h** 81

[a] $MgCl_2$ and LiCl are omitted for the sake of clarity.
[b] Isolated yield.

the manganese reagent **7e** which can dimerize to give **8e** in 53% yield (Table 3, entry 5). The metalation of 1,3-difluorobenzene using **1** (0.6 equiv, 0 °C, 6 h) followed by the oxidation of the manganese reagent **7f** using chloranil (1.0 equiv, –40 °C, 0.5 h) gave the polyfluorinated product **8f** in 51% yield (Table 3, entry 6). Additionally, 3-fluorobenzonitrile and 2-fluorobenzonitrile could be manganated efficiently using $\text{TMP}_2\text{Mn}\cdot 2\text{MgCl}_2\cdot 4\text{LiCl}$ (**1**, 0.6 equiv, 0 °C, 6 h). The subsequent homocoupling with chloranil (1.0 equiv) at –40 °C gave the fluorobenzonitriles **8g**,**h** in up to 82% yield (Table 3, entries 7 and 8).

In summary, we have reported a convenient directed manganation–dimerization procedure for various polyfunctional arenes and heterocycles. This oxidative homocoupling using chloranil tolerates various functional groups, such as esters, halides, and nitriles, and proceeds at convenient temperatures (–20 to –40 °C). Thus, various functionalized diaryl- and diheteroaryl-manganese reagents have been used successfully to prepare polyfunctionalized biaryl and biheteroaryl compounds. Further application towards the synthesis of natural products is under way in our laboratories.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1380424.

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(1) These authors contributed equally to this work.

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(16) **General Procedure for the Metalation and Homocoupling of (Hetero)arenes**

A dried and argon-flushed Schlenk tube is charged with the corresponding substrate (1.0 mmol, 1.0 equiv) and dissolved in THF (1.0 mL). $TMP_2Mn·2MgCl_2·4LiCl$ (1.5 mL, 0.6 mmol, 0.6 equiv, 0.40 M solution in THF) is added dropwise at the given temperature and stirred until a reaction aliquot quenched with iodine in THF showed full consumption of the starting material. Then, the reaction mixture is cooled to the given temperature, and chloranil (1.0 mmol, 1.0 equiv) dissolved in THF (4.0 mL) is added dropwise. The reaction is stirred for 0.5 h and is then quenched with sat. aq NH_4Cl solution and extracted with CH_2Cl_2 (3 × 25 mL). The crude product is purified by column chromatography on silica to yield the corresponding title compound.

Characterization of Typical Homocoupling Products 2,2′-Dichloro-[4,4′-bipyridine]-3,3′-dicarbonitrile (6a)

White solid; yield 74%, 102 mg; mp 197–199 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.79 (d, *J* = 5.0 Hz, 2 H), 7.49 (d, *J* = 5.0 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.6, 153.0, 148.6, 122.2, 112.8, 109.5 ppm. FT-IR (ATR): ν = 2253, 1565, 1545, 1525, 1470, 1440, 1369, 1209, 1090, 904, 840, 807, 725, 690 cm^{-1}. HRMS (EI): *m/z* $[M]^+$ calcd for $C_{12}H_4Cl_2N_4$: 273.9813; found: 273.9809.

3,3′,6,6′-Tetramethoxy-4,4′-bipyridazine (6f)

Off-white solid; yield 67%, 95 mg; mp 230–232 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.02 (s, 2 H), 4.09 (s, 6 H), 4.04 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.9, 158.7, 126.5, 121.1, 55.0, 54.8 ppm. FT-IR (ATR): ν = 3020, 2999, 2958, 1690, 1679, 1608, 1569, 1526, 1469, 1452, 1390, 1363, 1341, 1264, 1244, 1206, 1183, 1176, 1130, 1109, 1008, 999, 907, 899, 887, 828, 768, 756, 712, 676, 662 cm^{-1}. HRMS (EI): *m/z* $[M]^+$ calcd for $C_{12}H_{14}N_4O_4$: 278.1015; found: 278.1010.

Diethyl 6,6′-Dicyano-[1,1′-biphenyl]-2,2′-dicarboxylate (8d)

Yellowish solid; yield 87%, 153 mg; mp 180–182 °C. ^1H NMR (600 MHz, $CDCl_3$): δ = 8.38 (dd, *J*= 8.0, 1.3 Hz, 2 H), 7.93 (dd, *J*= 7.8, 1.3 Hz, 2 H), 7.66 (t, *J*= 7.9 Hz, 2 H), 4.11 (q, *J* = 7.1 Hz, 4 H), 1.08 (t, *J* = 7.2 Hz, 6 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 164.3, 143.4, 136.0, 134.7, 130.5, 129.1, 116.3, 114.3, 61.6, 13.7 ppm. FT-IR (ATR): ν = 2985, 2255, 2231, 1717, 1578, 1477, 1447, 1428, 1393, 1368, 1288, 1273, 1182, 1148, 1103, 1020, 905, 865, 829, 763, 727 cm^{-1}. HRMS (EI): *m/z* $[M]^+$ calcd for $C_{20}H_{16}N_2O_4$: 348.1110; found: 348.1102.