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Deprotonative metalation of substituted aromatics using mixed lithium–cobalt combinations

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ABSTRACT

The deprotonation of anisole was attempted using different homo- and heteroleptic TMP/Bu mixed lithium–cobalt combinations. Using iodine to intercept the metalated anisole, an optimization of the reaction conditions showed that in THF at room temperature 2 equiv of base were required to suppress the formation of the corresponding 2,2′-dimer. The origin of the dimer was not identified, but its formation was favored with allyl bromide as electrophile. The metalated anisole was efficiently trapped using iodine, anisaldehyde, and chlorodiphenylphosphine, and moderately employing benzophenone, and benzoyl chloride. 1,2-, 1,3-, and 1,4-dimethoxybenzene were similarly converted regioselectively to the corresponding iodides. It was observed that 2-methoxy- and 2,6-dimethoxypyridine were more prone to dimerization than the corresponding benzenes when treated similarly. Involving ethyl benzoate in the metalation–iodination sequence showed that the method was not suitable to functionalize substrates bearing reactive functions.

1. Introduction

The deprotonative metalation using lithium bases has been widely used as a powerful method for the regioselective functionalization of aromatic compounds.[1] The use of metal additives in order to get more efficient or more chemoselective bases (synergic superbases) is a challenging field. Pioneer studies, respectively, carried out in the groups of Schlosser[2] and Lochmann[3] with LIC–KOR, mixture of butyllithium (LIC) and potassium *tert*-butoxide (KOR), and by Caubère, Gros and Fort[4] in the pyridine series with BuLi–LiDMAE (DMAE=2-dimethylaminoethoxide) and Me_3SiCH_2Li–LiDMAE merged alkyllithiums and alkali-metal alkoxides. More recently, the use of other $(R)_n(R')_{n'}MLi$-type bases, with M being different from an alkali-metal (e.g., M=Mg, Al, Cr, Mn, Cu, Zn), has been described by different groups for their ability to deprotonate aromatic compounds,[5] and notably anisole.[6] In 2009, Klett, Mulvey and co-workers showed that it is possible to design sodium-iron(II) bases, and extended the ability to deprotonate to group 8 ate compounds.[7] The same year, Wunderlich and Knochel showed that ferration can be achieved using salt-solubilized $(TMP)_2Fe\cdot 2MgCl_2\cdot 4LiCl$ (TMP=2,2,6,6-tetramethylpiperidino).[8]

We recently accomplished the room temperature deprotometalation of a large range of substrates including sensitive heterocycles and functionalized benzenes using newly developed lithium–zinc,[9] lithium–cadmium,[10] and lithium–copper(I)[11] combinations, in situ prepared from $MCl_2\cdot$TMEDA (M=Zn, Cd or Cu, TMEDA=*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) and lithium reagents (alkyllithiums or lithium amides). The studies performed using lithium–zinc and lithium–cadmium combinations have notably shown that the more efficient bases were obtained by mixing the metal salt with 3 equiv of LiTMP.[9d,10g] A main drawback of the methods developed being the lack of reactivity of such generated arylmetals in direct trapping with electrophiles, we turned to other bimetallic combinations in order to identify candidates able to perform efficient deprotonations, but also to allow direct functionalizations. We here describe the first aromatic deproto-metalations using lithium–cobalt combinations.

2. Results and discussion

The synthesis of organocobalt ate compounds is well-documented in the literature. They are in general obtained by transmetalation of organolithium[12] or -magnesium[13] reagents with cobalt(II) halides. Examples are Me_3CoLi,[12a] $Me_4CoLi_2(TMEDA)_2$,[12b] and $(R_3SiCH_2)_4Co(MgCl)_2$ (R_3Si=Me_3Si, $MePh_2Si$, $^tBuMe_2Si$).[13] The access to mixed lithium–cobalt amides is far less documented, but seems possible similarly.[14] We first consider the use of $CoCl_2\cdot$TMEDA chelate[15] in order to manipulate a salt less hygroscopic than $CoCl_2$, but attempts to prepare it failing in giving good microanalyses, we

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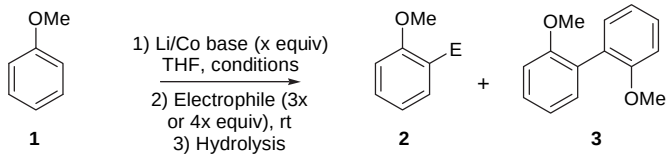
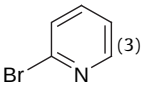
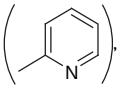
turned to $CoBr_2$.[16] We prepared different lithium–cobalt combinations by mixing the cobalt salt with 3 or 4 equiv of a lithium compound, either LiTMP or mixtures with butyllithium, at 0 °C. We chose anisole (**1**) as substrate to check the ability to deprotonate of the mixtures (Table 1).

Table 1
Optimization of anisole metalation using a lithium/cobalt base



Entry	Li/Co base (*x*)	Conditions	Electrophile (3*x* or 4*x*)	**2** (E), yield (%)	Yield of **3**[a] (%)
1[b]	$CoBr_2$ (1)+LiTMP (3)	25 °C, 2 h	I_2 (3)	**2a** (I), 54	17
2	$CoBr_2$ (1)+LiTMP (3)	0 °C, 2 h	I_2 (3)	**2a** (I), 12	5
3	$CoBr_2$ (1)+LiTMP (3)	0 °C, 4 h	I_2 (3)	**2a** (I), 13	24
4	$CoBr_2$ (1)+LiTMP (3)	45 °C, 2 h	I_2 (3)	**2a** (I), 49	20
5	$CoBr_2$ (1)+LiTMP (3)	rt,[c] 2 h	I_2 (3)	**2a** (I), 59[d]	—[e]
6	$CoBr_2$ (1)+LiTMP (3)	rt, 30 min	I_2 (3)	**2a** (I), 43	21
7	$CoBr_2$ (1)+LiTMP (3)	rt, 4 h	I_2 (3)	**2a** (I), 57	—[e]
8	$CoBr_2$ (1)+LiTMP (3)	rt, 20 h	I_2 (3)	**2a** (I), 38	34
9	$CoBr_2$ (0.5)+LiTMP (1.5)	rt, 2 to 20 h	I_2 (1.5)	**2a** (I), —[f]	—[f]
10	$CoBr_2$ (1.5)+LiTMP (4.5)	rt, 30 min	I_2 (4.5)	**2a** (I), 54	16
11	$CoBr_2$ (2)+LiTMP (6)	rt, 2 h	I_2 (6)	**2a** (I), 93	—[e]
12	$CoBr_2$ (2)+LiTMP (6)	rt, 30 min	I_2 (6)	**2a** (I), 93	5
13	$CoBr_2$ (1)+BuLi (3)	rt, 2 h	I_2 (3)	**2a** (I), 0	0
14	$CoBr_2$ (1)+LiTMP (1)+BuLi (2)	rt, 2 h	I_2 (3)	**2a** (I), 0	0
15	$CoBr_2$ (1)+LiTMP (2)+BuLi (1)	rt, 2 h	I_2 (3)	**2a** (I), 0	0
16	$CoBr_2$ (1)+LiTMP (1)+BuLi (3)	rt, 2 h	I_2 (4)	**2a** (I), 0	0
17	$CoBr_2$ (1)+LiTMP (2)+BuLi (2)	rt, 2 h	I_2 (4)	**2a** (I), 0	0
18	$CoBr_2$ (1)+LiTMP (3)+BuLi (1)	rt, 2 h	I_2 (4)	**2a** (I), 19	35
19	$CoBr_2$ (1)+LiTMP (3)	rt, 2 h	H_2O (3)	**1** (H), —	14[g]
20	$CoBr_2$ (1)+LiTMP (3)	rt, 2 h	$BrCH_2CH{=}CH_2$ (3)	**2b** ($CH_2CH{=}CH_2$), 6[h]	38
21	$CoBr_2$ (1)+LiTMP (3)	rt, 2 h	 (3)	**2c**  , 14% (16)[i]	19 (26)[i]

[a] The rest is in general anisole.
[b] Yields of 9 and 0% using LiTMP and $(TMP)_2Co$, respectively, under the same reaction conditions.
[c] Between 17 and 23 °C.
[d] Yield of 39% in the presence of 1 equiv of TMEDA.
[e] Not quantified.
[f] Low conversion and significant formation of dimer.
[g] Twelve percent using degassed THF.
[h] The high volatility of the compound could be partly responsible for the low yield obtained.
[i] Trapping step performed at 50 °C instead of rt.

Using LiTMP (1 equiv) or $(TMP)_2Co$ (1 equiv, in situ generated from $CoBr_2$ and 2 equiv of LiTMP) in tetrahydrofuran (THF) at room temperature for 2 h, and then iodine, anisole (**1**) was converted into the 2-iodo derivative **2a** in 9 or 0% yield, respectively. In contrast, when treated with an in situ prepared mixture of $CoBr_2$ (1 equiv) and LiTMP (3 equiv) at 25 °C for 2 h, anisole (**1**) was readily *ortho*-metalated, a result evidenced with the formation of **2a** in 54% yield after purification (entry 1). Lowering the reaction temperature to 0 °C resulted in a low conversion, even after 4 h reaction time (entries 2 and 3). When performed at 45 °C, the metalation step worked as at 25 °C, affording **2a** in 50% yield (entry 4). It is known that labile ligands can play a role on the course of reactions.[9a] To check a possible effect, the reaction was performed at room temperature in the presence of 1 equiv of TMEDA; the 39 and 59% yields, respectively, obtained with and without TMEDA indicates the deleterious influence of this ligand, uninteresting in this case (entry 5). The impact of the reaction time was next considered. It was observed that reducing the reaction time to 30 min resulted in a lower 43% yield (entry 6). Extending the reaction time to 4 h did not bring any improvement (entry 7), but after 20 h the yield was significantly reduced to 38% (entry 8). The effect of the base amount was then studied. Using 0.5 equiv of $CoBr_2$ and 1.5 equiv of LiTMP led to low conversions, whatever the reaction time (entry 9). It was possible to find again the 54% yield already obtained (entry 1) by using 1.5 equiv of $CoBr_2$ and 4.5 equiv of LiTMP, and a 30 min reaction time (entry 10). The best result (93% yield) was obtained using 2 equiv of $CoBr_2$ and 6 equiv of LiTMP (entry 11), allowing to reduce the reaction time to 30 min (entry 12).

As previously noted in a lesser extent in other bimetallic series,[9d,10g] putative $Bu_3CoLi{\cdot}2LiBr$ (entry 13), $Bu_2Co(TMP)Li{\cdot}2LiBr$ (entry 14), and $BuCo(TMP)_2Li{\cdot}2LiBr$ (entry 15) alkyl/amino combinations are not able to deprotonate anisole (**1**). Higher-order ate compounds being in general more reactive than lower-order ones,[17] reactions were attempted using putative $Bu_3Co(TMP)Li_2{\cdot}2LiBr$ (entry 16), $Bu_2Co(TMP)_2Li_2{\cdot}2LiBr$ (entry 17), and $BuCo(TMP)_3Li_2{\cdot}2LiBr$ (entry 18). The iodide **2a** was only isolated in 19% yield in the last reaction, due to the competitive formation of 2,2′-dimethoxybiphenyl (**3**) in 35% yield.

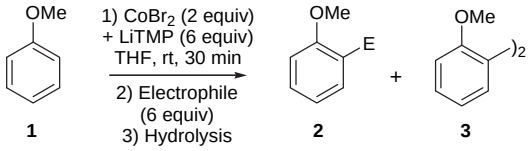
The formation of the dimer **3** has been observed in all the experiments where metalation took place, but in various yields. Its formation does not seem to depend on the deprotonation

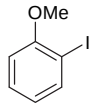
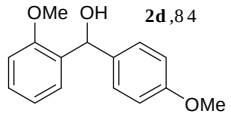
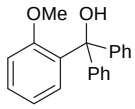
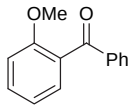
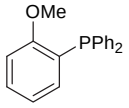
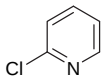
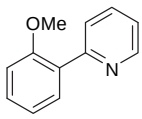
temperature (entries 1–4), but seems to be favored with long contact times (entry 8). In addition, it is clear that the use of 2 equiv of base prevents its formation (entries 11 and 12), as if it formed intramolecularly. Using water instead of iodine to trap the metalated anisole derivative also resulted in the formation of **3** in a similar 14% yield (entry 19). Thus, if cross-coupling with the iodide **2**,[12c,18] and iodine-mediated oxidation[19] can be proposed to explain the formation of **3**, alternative ways without recourse to them exist. A possible in situ partial reduction of Co(II) species to Co (I) due to the presence of metal amides is possible,[20] but would not lead to a dimer in the absence of an halide.[21] Even if the use of degassed THF did not change significantly the result (entry 19),[22] a possible role of dissolved oxygen cannot be ruled out.[19] An alternative explanation could be the presence of a metal impurity in $CoBr_2$ for which the corresponding diaryl metal ate compounds is prone to dimerization. Using allyl bromide instead of iodine (or water) to quench the metalated anisole derivative produced the dimer **3** in 38% yield, and 2-allylanisole (**2b**) in 6% yield besides (Entry 20). One-electron transfers from cobalt(II) ate compounds to allyl bromide are possible pathways,[23] and dimerization from the generated Co(III) species bearing two aryl groups[18a] appears as a possible pathway to explain the formation of **3** in this case (Scheme 1). Other electrophiles favor the dimerization. For example, the use of 2-bromopyridine in order to convert the metalated anisole into the cross-coupling product **2c** was similarly threatened by a significant formation of **3** (entry 21).

The optimized conditions in hands, the use of different electrophiles was attempted (Table 2). Anisaldehyde led to the corresponding alcohol **2d** in a satisfying yield (entry 2). The alcohol **2e** and ketone **2f** were produced in moderate yields upon interception with benzophenone and benzoyl chloride, respectively (entries 3 and 4). The phosphine **2g** was obtained satisfactorily using chlorodiphenylphosphine, but the cross-coupled derivative **2c** was isolated in a low 25% yield due to a significant formation of **3** (entry 6).

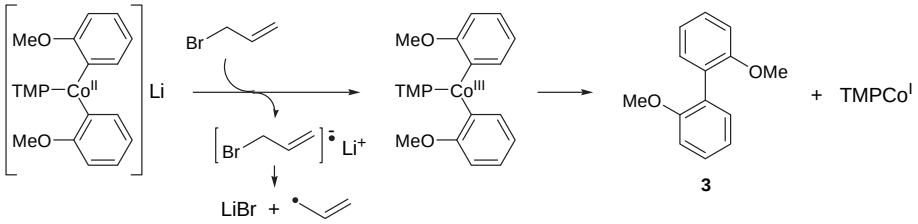
The method was then extended to other aromatic substrates (Table 3). Starting from 1,4-dimethoxybenzene (**4**) and using iodine as electrophile, the expected derivative **5a** was obtained in a correct yield provided that 2 equiv of base were used (entries 1–3). It was noted that a longer reaction time favored the co-formation of diiodides. Trapping with allyl bromide resulted in a significant formation of the dimer **6** whereas the expected allylated compound **5b** was isolated in a low 6% yield (entry 4). These results are similar to those obtained from anisole (**1**). Benefiting from a greater activation, 1,3-dimethoxybenzene (**7**) was quantitatively converted to the iodide **8a** (entry 5). Using allyl bromide instead of iodine yielded the derivative **8b** in a low yield due to a significant recovery of starting material; in this case, the corresponding dimer **9** was isolated in a low 6% yield (entry 6). The behavior of 1,2-dimethoxybenzene (**10**) is similar to that of 1,4-dimethoxybenzene (**4**); the formation of the corresponding dimer **12** was suppressed by reducing the reaction time to 30 min (entries 7 and 8). Trapping using allyl bromide led to a significant formation of the dimer **12**, limiting the yield of the allylated derivative **11b** to 23% (entry 9). 1,2,3-Trimethoxybenzene (**13**) led to the expected iodide **14** in a moderate 33% yield, due to a significant recovery of starting material (entry 10). Performed with 2-methoxypyridine (**15**), the reaction led to a more important formation of dimer than starting from methoxybenzenes. The iodide resulting from a regioselective metalation next to the methoxy group was isolated in a moderate 43% yield (entries 11 and 12). Except an increased conversion, a similar result was observed from 2,6-dimethoxypyridine (**18**) (entry 13). The method is not suitable to functionalize substrates bearing reactive functions. Indeed, using ethyl benzoate (**21**), side reactions with the ester function only allowed the expected iodide **22** to be obtained in maximum 22% yield (entries 14 and 15). A deprotonative metalation followed by a cross-coupling reaction was carried out from thiophene. Using 1 equiv of base (in order to avoid 2,5-dideprotonation),[9d] the expected cross-coupled compound was isolated, but in a low 19% yield (entry 16).

Table 2
Electrophilic trapping of metalated anisole



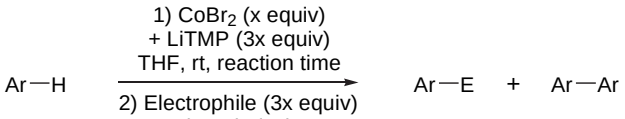
Entry	Electrophile	**2**, Yield (%)	Yield of **3** (%)
1	I_2	 **2a**, 93	5
2	4-$MeOC_6H_4$–CHO	 **2d**, 84	15
3	PhC(O)Ph	 **2e**, 45	10
4	PhC(O)Cl	 **2f**, 30	16
5	Ph_2PCl	 **2g**, 82	15
6[a]		 **2c**, 25 (19)[c]	—[b] (33)[c]

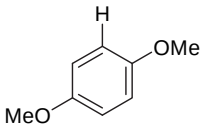
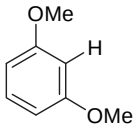
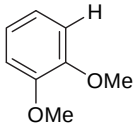
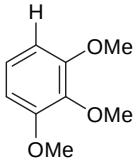
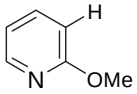
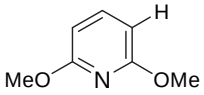
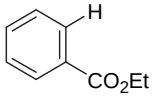
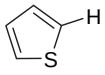
[a] Trapping step performed at 50 °C instead of rt.
[b] Not quantified.
[c] Using 1 equiv of base.



Scheme 1. Possible pathway for the formation of **3** from the metalated anisole derivative.

Table 3
Extension to other aromatic substrates including heterocycles



Entry	Ar–H		*x*	Reaction time	Electrophile	Ar–E (E), yield	Ar–Ar, yield
1	**4**:		0.5	2 h	I_2	**5a** (I), 10%	**6**, 22%
2			1	2 h	I_2	**5a** (I), 45%	—[a]
3			2	30 min	I_2	**5a** (I), 76%	**6**, 10%
4			2	30 min	$BrCH_2CH{=}CH_2$	**5b** ($CH_2CH{=}CH_2$), 6%	**6**, 33%
5	**7**:		2	30 min	I_2	**8a** (I), 97%	
6			2	30 min	$BrCH_2CH{=}CH_2$	**8b** ($CH_2CH{=}CH_2$), 14%	**9**, 6%
7	**10**:		2	2 h	I_2	**11a** (I), 76%	**12**, 17%
8			2	30 min	I_2	**11a** (I), 74%	**12**, 0%
9			2	30 min	$BrCH_2CH{=}CH_2$	**11b** ($CH_2CH{=}CH_2$), 23%	**12**, 62%
10	**13**:		2	30 min	I_2	**14** (I), 33%	
11	**15**:		1	2 h	I_2	**16** (I), 11%	**17**, 19%
12			2	2 h	I_2	**16** (I), 43%	**17**, 14%
13	**18**:		2	30 min	I_2	**19** (I), 64%	**20**, 34%
14	**21**:		1	2 h	I_2	**22** (I), 14%	—[a]
15			2	2 h	I_2	**22** (I), 22%	—[a]
16[b]	**23**:		1	2 h	4-IC_6H_4OMe	**24** (4-C_6H_4OMe), 19%	—[a]

[a] Not quantified.
[b] Using 1 equiv of base.

3. Conclusion

Like the other lithium–metal combinations, the mixture of $CoBr_2$ and 3 equiv of LiTMP behaves synergically, but compared with the previously described 'all-TMP' lithium–zinc[9] and lithium–cadmium[10] combinations, the base obtained by combining $CoBr_2$ with 3 equiv of LiTMP is less efficient as far as both conversion and chemoselectivity are concerned. For example, starting from anisole (**1**), the iodide **2a** was isolated in 84% and 75% yields using 0.5 equiv of the lithium–zinc and lithium–cadmium combinations, respectively, against 59% under the same conditions using 1 equiv of the lithium-cobalt one. Concerning the metalation of methoxybenzenes, its efficiency more looks like that of the reported 'all-TMP' Gilman-type lithium–copper(I) combination.[11] Nevertheless, the reactivity exhibited by the generated arylmetal species has been improved using lithium–cobalt bases.

In conclusion, compared with the previously reported 'all-TMP' reagents, the combination here presented allows more efficient direct trappings for the generated arylmetal compounds, but lacks both efficiency and chemoselectivity. Studies are under development to identify more suitable lithium–metal systems.

4. Experimental section

4.1. General procedure A (deprotonation using 2 equiv $CoBr_2$ and 6 equiv LiTMP followed by trapping using I_2)

To a stirred cooled (0 °C) solution of 2,2,6,6-tetramethylpiperidine (4.1 mL, 24 mmol) in THF (8 mL) were added BuLi (1.6 M hexanes solution, 24 mmol) and, 5 min later, $CoBr_2$ (1.7 g, 8.0 mmol). The mixture was stirred for 10 min at 0 °C before introduction of the substrate (4.0 mmol). After 2 h at room

temperature, a solution of I_2 (6.1 g, 24 mmol) in THF (7 mL) was added. The mixture was stirred overnight before addition of an aq saturated solution of $Na_2S_2O_3$ (10 mL) and extraction with EtOAc (3×20 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure.

*4.1.1. 2-Iodoanisole (**2a**).* Compound **2a** was obtained according to the general procedure A starting from anisole (0.44 mL), but reducing the metalation reaction time to 30 min, and was isolated after purification by flash chromatography on silica gel (eluent: heptane/CH_2Cl_2 95/5) as a colorless oil (93% yield). The analyses are as described previously.[10a]

*4.1.2. 2-Iodo-1,4-dimethoxybenzene (**5a**).* Compound **5a** was obtained according to the general procedure A starting from 1,4-dimethoxybenzene (0.55 g), but reducing the metalation reaction time to 30 min, and was isolated after purification by flash chromatography on silica gel (eluent: heptane/AcOEt 97/3) as a yellow solid (76% yield): mp <50 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.74 (s, 3H), 3.81 (s, 3H), 6.94 (d, 1H, J=8.9 Hz), 6.85 (dd, 1H, J=2.9 and 8.9 Hz), 7.33 (d, 1H, J=2.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.2, 152.6, 124.7, 114.6, 111.5, 85.9, 56.9, 55.8. These data are analogous to those previously described.[24]

*4.1.3. 2,2′,5,5′-Tetramethoxybiphenyl (**6**).* Compound **6** was obtained according to the general procedure A starting from 1,4-dimethoxybenzene (0.55 g), but using 2,2,6,6-tetramethylpiperidine (1.0 mL, 6.0 mmol), BuLi (6.0 mmol), and $CoBr_2$ (0.42 g, 2.0 mmol). It was isolated after purification by flash chromatography on silica gel (eluent: heptane/AcOEt 88/12) as a red solid (22% yield): mp 94–95 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.73 (s, 6H), 3.78 (s, 6H), 6.83–6.88 (m, 4H), 6.91 (dd, 2H, J=1.0 and 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.3 (2C), 151.1 (2C), 128.6 (2C), 117.1 (2C), 113.4 (2C), 112.4 (2C), 56.6 (2C), 55.7 (2C). These data are analogous to those previously described.[25]

*4.1.4. 2-Iodo-1,3-dimethoxybenzene (**8a**).* Compound **8a** was obtained according to the general procedure A starting from 1,3-dimethoxybenzene (0.55 g), but reducing the metalation reaction time to 30 min, and was isolated after purification by flash chromatography on silica gel (eluent: heptane/AcOEt 60/40) as a white solid (97% yield): mp 106 °C (lit.[26] 100 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.88 (s, 6H), 6.49 (d, 2H, J=8.2 Hz), 7.25 (t, 1H, J=8.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.4 (2C), 129.7, 104.0 (2C), 77.5, 56.5 (2C).

*4.1.5. 1-Iodo-2,3-dimethoxybenzene (**11a**).* Compound **11a** was obtained according to the general procedure A starting from veratrole (0.50 mL), and was isolated after purification by flash chromatography on silica gel (eluent: heptane/AcOEt 98/2) as a yellow solid (76% yield). The analyses are as described previously.[10a]

*4.1.6. 1-Iodo-2,3,4-trimethoxybenzene (**14**).* Compound **14** was obtained according to the general procedure A starting from 1,2,3-trimethoxybenzene (0.68 g), but reducing the metalation reaction time to 30 min, and was isolated after purification by flash chromatography on silica gel (eluent: heptane/CH_2Cl_2 50/50) as a light yellow solid (33% yield): mp <50 °C (lit.[27] 42 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.84 (s, 3H), 3.86 (s, 3H), 3.87 (s, 3H), 6.49 (d, 1H, J=8.8 Hz), 7.40 (d, 1H, J=8.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.3, 153.3, 142.6, 132.5, 109.7, 81.2, 60.9, 60.8, 56.1.

*4.1.7. 3-Iodo-2-methoxypyridine (**16**).* Compound **16** was obtained according to the general procedure A starting from 2-methoxypyridine (0.42 mL), and was isolated after purification by flash chromatography on silica gel (eluent: heptane/Et_2O 85/15) as a white solid (43% yield): mp 64 °C (lit.[28] 66 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.98 (s, 3H), 6.64 (dd, 1H, J=4.8 and 7.5 Hz), 8.02 (dd, 1H, J=1.7 and 7.5 Hz), 8.11 (dd, 1H, 1.7 and 4.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.8, 147.9, 146.4, 118.1, 79.7, 54.6.

*4.1.8. 2,2′-Dimethoxybipyridine (**17**).* Compound **17** was obtained according to the general procedure A starting from 2-methoxypyridine (0.42 mL), but using 2,2,6,6-tetramethylpiperidine (2.0 mL, 12 mmol), BuLi (12 mmol), and $CoBr_2$ (0.84 g, 4.0 mmol). It was isolated after purification by flash chromatography on silica gel (eluent: heptane/AcOEt 98/2) as a light yellow solid (19% yield): mp 104 °C (lit.[29] 139–140 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.92 (s, 6H), 6.95 (dd, 2H, J=5.0 and 7.2 Hz), 7.59 (dd, 2H, J=1.9 and 7.2 Hz), 8.18 (dd, 2H, J=1.9 and 5.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.1 (2C), 146.2 (2C), 139.5 (2C), 119.8 (2C), 116.4 (2C), 53.5 (2C).

*4.1.9. 3-Iodo-2,6-dimethoxypyridine (**19**)[30].* Compound **19** was obtained according to the general procedure A starting from 2,6-dimethoxypyridine (0.53 mL), but reducing the metalation reaction time to 30 min, and was isolated after purification by flash chromatography on silica gel (eluent: heptane/AcOEt 98/2) as a brown solid (64% yield): mp <50 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.88 (s, 3H), 3.95 (s, 3H), 6.13 (d, 1H, J=8.2 Hz), 7.78 (d, 1H, J=8.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.2, 160.5, 149.3, 103.4, 65.5, 54.3, 53.5; HRMS calcd for $C_7H_8INNaO_2$ [$(M+Na)^{+\bullet}$] 287.9497 and $C_7H_9INO_2$ [$(M+H)^{+\bullet}$] 265.9678, found 287.9492 and 265.9680, respectively.

*4.1.10. 2,2′,6,6′-Tetramethoxy-3,3′-bipyridine (**20**)[30].* Compound **20** was obtained according to the general procedure A starting from 2,6-dimethoxypyridine (0.53 mL), but reducing the metalation reaction time to 30 min, and was isolated after purification by flash chromatography on silica gel (eluent: heptane/AcOEt 96/4) as a white solid (34% yield): mp 144.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.92 (s, 6H), 3.94 (s, 6H), 6.36 (d, 2H, J=8.0 Hz), 7.52 (d, 2H, J=8.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.0 (2C), 159.6 (2C), 142.5 (2C), 110.5 (2C), 100.4 (2C), 53.4 (2C), 53.3 (2C); HRMS calcd for $C_{14}H_{16}N_2NaO_4$ [$(M+Na)^{+\bullet}$] 299.1008 and $C_{14}H_{17}N_2O_4$ [$(M+H)^{+\bullet}$] 277.1188, found 299.1007 and 277.1192, respectively.

*4.1.11. Ethyl 2-iodobenzoate (**22**).* Compound **22** was obtained according to the general procedure A starting from ethyl benzoate (0.61 mL), and was isolated after purification by flash chromatography on silica gel (eluent: heptane/AcOEt 98/2) as a yellow oil (22% yield): ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.41 (t, 3H, J=7.1 Hz), 4.39 (q, 2H, J=7.1 Hz), 7.14 (td, 1H, J=1.7 and 7.8 Hz), 7.39 (td, 1H, J=1.7 and 7.9 Hz), 7.79 (dd, 1H, J=1.7 and 7.8 Hz), 7.98 (dd, 1H, J=1.0 and 7.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5, 141.1, 135.4, 132.4, 130.7, 127.8, 93.9, 61.6, 14.1. These data are analogous to those previously described.[31]

4.2. General procedure B (deprotonation using 2 equiv $CoBr_2$ and 6 equiv LiTMP followed by trapping with an electrophile ≠ I_2)

To a stirred cooled (0 °C) solution of 2,2,6,6-tetramethylpiperidine (4.1 mL, 24 mmol) in THF (8 mL) were added BuLi (1.6 M hexanes solution, 24 mmol) and, 5 min later, $CoBr_2$ (1.7 g, 8.0 mmol). The mixture was stirred for 10 min at 0 °C before introduction of the substrate (4.0 mmol). After 30 min at room temperature, the electrophile (24 mmol) was added. The mixture was stirred overnight before addition of H_2O (10 mL) and extraction with EtOAc (3×20 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure.

*4.2.1. 2-Allylanisole (**2b**).* Compound **2b** was obtained according to the general procedure B (in this case, an extended reaction time of 2 h was used, and the following amounts for 2,2,6,6-tetramethylpiperidine (2.0 mL, 12 mmol), BuLi (12 mmol), and $CoBr_2$

(0.84 g, 4.0 mmol) were used) starting from anisole (0.44 mL), and using allyl bromide (1.0 mL, 12 mmol). Compound **2b** was isolated after purification by flash chromatography on silica gel (eluent: heptane/CH_2Cl_2 92/8) as a colorless oil (6% yield). The analyses are as described previously.[10e]

*4.2.2. 2,2′-Dimethoxybiphenyl (**3**).* Compound **3** was obtained according to the general procedure B (in this case, an extended reaction time of 2 h was used, and the following amounts for 2,2,6,6-tetramethylpiperidine (2.0 mL, 12 mmol), BuLi (12 mmol) and $CoBr_2$ (0.84 g, 4.0 mmol) were used) starting from anisole (0.44 mL), and using allyl bromide (1.0 mL, 12 mmol). Compound **3** was isolated after purification by flash chromatography on silica gel (eluent: heptane/CH_2Cl_2 50/50) as a white solid (38% yield): mp 158–160 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.80 (s, 6H), 7.07–6.99 (m, 4H), 7.28 (dd, 2H, J=1.7 and 7.4 Hz), 7.36 (td, 2H, J=1.7 and 8.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.9 (2C), 131.4 (2C), 128.5 (2C), 127.7 (2C), 120.2 (2C), 111.0 (2C), 55.6 (2C). These data are analogous to those previously described.[32]

*4.2.3. (2-Methoxyphenyl)(4-methoxyphenyl)methanol (**2d**).* Compound **2d** was obtained according to the general procedure B starting from anisole (0.44 mL), and using anisaldehyde (3.0 mL). It was isolated after purification by flash chromatography on silica gel (eluent: heptane/CH_2Cl_2 40/60) as a light yellow oil (84% yield). The analyses are as described previously.[9d]

*4.2.4. (2-Methoxyphenyl)diphenylmethanol (**2e**).* Compound **2e** was obtained according to the general procedure B starting from anisole (0.44 mL), and using benzophenone (4.4 g). It was isolated after purification by flash chromatography on silica gel (eluent: heptane/Et_2O 90/10) as a white solid (45% yield): mp 114.5 °C (lit.[33] 111–113 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.81 (s, 3H), 7.08–7.01 (m, 2H), 7.40–7.18 (m, 7H), 7.66–7.49 (m, 3H), 7.83–7.87 (m, 2H), OH not seen; ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.9, 144.1, 131.3, 128.5 (4C), 128.5, 127.7, 127.1 (4C), 126.8, 120.2, 110.9, 82.9, 55.5.

*4.2.5. 2-Methoxybenzophenone (**2f**).* Compound **2f** was obtained according to the general procedure B starting from anisole (0.44 mL), and using benzoyl chloride (2.8 mL). It was isolated after purification by flash chromatography on silica gel (eluent: heptane/CH_2Cl_2 50/50) as a white solid (30% yield): mp <50 °C (lit.[34] 35–37 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.72 (s, 3H), 6.98–7.07 (m, 2H), 7.34–7.58 (m, 5H), 7.79–7.83 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.4, 157.3, 137.7, 132.9, 131.8, 129.8 (2C), 129.5, 128.8, 128.1 (2C), 120.4, 111.4, 55.5.

*4.2.6. (2-Methoxyphenyl)diphenylphosphine (**2g**).* Compound **2g** was obtained according to the general procedure B starting from anisole (0.44 mL), and using chlorodiphenylphosphine (4.3 mL). Due to its suspected easy oxidation, all the solvents were degassed before use. It was isolated after purification by flash chromatography on silica gel (eluent: heptane/CH_2Cl_2 85/15) as a white solid (82% yield): mp 123 °C (lit.[35] 118 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.76 (s, 3H), 6.69–6.73 (m, 1H), 6.86–6.95 (m, 2H), 7.28–7.39 (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.0 (d, J_P=15 Hz), 136.6 (d, 2C, J_P=10 Hz), 133.8 (d, 4C, J_P=20 Hz), 133.5 (d, J_P=0.7 Hz), 130.2, 128.4 (2C), 128.3 (d, 4C, J_P=12 Hz), 125.5 (d, J_P=12 Hz), 120.9 (d, J_P=0.8 Hz), 110.1 (d, J_P=1.7 Hz), 55.5 (d, J_P=0.7); ^{31}P NMR (75 MHz, $CDCl_3$): δ −16.8; HRMS calcd for $C_{19}H_{17}NaOP$ [$(M+Na)^{+\bullet}$] 315.0915 and $C_{19}H_{18}OP$ [$(M+H)^{+\bullet}$] 293.1095, found 315.0913 and 293.1094, respectively.

*4.2.7. 2-(2-Methoxyphenyl)pyridine (**2c**).* Compound **2c** was obtained according to the general procedure B, but performing the trapping step at 50 °C, starting from anisole (0.44 mL), and using 2-chloropyridine (2.3 mL). It was isolated after purification by flash chromatography on silica gel (eluent: heptane/AcOEt 90/10) as a yellow oil (25% yield). The analyses are as described previously.[9d]

*4.2.8. 2-Allyl-1,4-dimethoxybenzene (**5b**).* Compound **5b** was obtained according to the general procedure B starting from 1,4-dimethoxybenzene (0.55 g), and using allyl bromide (2.1 mL). It was isolated after purification by flash chromatography on silica gel (eluent: heptane/EtOAc 98/2) as a colorless oil (6% yield): ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.36 (d, 2H, J=6.6 Hz), 3.76 (s, 3H), 3.78 (s, 3H), 5.01–5.14 (m, 2H), 6.10–5.90 (m, 1H), 6.92–6.68 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.5, 151.5, 136.7, 129.8, 116.1, 115.5, 111.4, 111.3, 56.0, 55.6, 34.2. The ^{1}H NMR data are analogous to those described.[36]

*4.2.9. 2-Allyl-1,3-dimethoxybenzene (**8b**)*[37]. Compound **8b** was obtained according to the general procedure B starting from 1,3-dimethoxybenzene (0.55 g), and using allyl bromide (2.1 mL). It was isolated after purification by flash chromatography on silica gel (eluent: heptane/CH_2Cl_2 90/10) as a colorless oil (14% yield): ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.42 (dt, 2H, J=1.5 and 6.1 Hz), 3.81 (s, 6H), 4.90–5.00 (m, 2H), 5.89–6.02 (m, 1H), 6.56 (d, 2H, J=8.3 Hz), 7.14 (t, 1H, J=8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.2 (2C), 136.8, 127.0, 116.5, 113.9, 103.8 (2C), 55.8 (2C), 27.1.

*4.2.10. 2,2′,6,6′-Tetramethoxybiphenyl (**9**).* Compound **9** was obtained according to the general procedure B starting from 1,3-dimethoxybenzene (0.55 g), and using allyl bromide (2.1 mL). It was isolated after purification by flash chromatography on silica gel (eluent: heptane/CH_2Cl_2 30/70) as a white solid (6% yield): mp 176 °C (lit.[37] 174–175 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.72 (s, 12H), 6.65 (d, 4H, J=8.3 Hz), 7.29 (t, 2H, J=8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.3 (4C), 128.6 (2C), 112.5 (2C), 104.4 (4C), 56.1 (4C). These data are analogous to those previously described.[38]

*4.2.11. 1-Allyl-2,3-dimethoxybenzene (**11b**)*[39]. Compound **11b** was obtained according to the general procedure B starting from veratrole (0.50 mL), and using allyl bromide (2.1 mL). It was isolated after purification by flash chromatography on silica gel (eluent: heptane/AcOEt 98/2) as a colorless oil (23% yield): ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.42 (d, 2H, J=6.5 Hz), 3.81 (s, 3H), 3.86 (s, 3H), 5.02–5.10 (m, 2H), 5.91–6.05 (m, 1H), 6.76–6.81 (m, 2H), 7.00 (t, 1H, J=7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.7, 147.0, 137.2, 133.9, 123.8, 121.9, 115.4, 110.4, 60.5, 55.6, 33.9.

*4.2.12. 2,2′,3,3′-Tetramethoxybiphenyl (**12**).* Compound **12** was obtained according to the general procedure B starting from veratrole (0.50 mL), and using allyl bromide (2.1 mL). It was isolated after purification by flash chromatography on silica gel (eluent: heptane/AcOEt 88/12) as a white solid (62% yield): mp 106–108 °C (lit.[40] 104–105 °C); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.65 (s, 6H), 3.90 (s, 6H), 6.87 (dd, 2H, J=1.6 and 7.6 Hz), 6.93 (dd, 2H, J=1.6 and 8.2 Hz), 7.08 (dd, 2H, J=7.6 and 8.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.7 (2C), 146.7 (2C), 132.8 (2C), 123.2 (2C), 123.2 (2C), 111.5 (2C), 60.5 (2C), 55.7 (2C); HRMS calcd for $C_{16}H_{18}NaO_4$ [$(M+Na)^{+\bullet}$] 297.1103 and $C_{16}H_{18}KO_4$ [$(M+K)^{+\bullet}$] 313.0842, found 297.1104 and 313.0854, respectively.

*4.2.13. 2-(4-Methoxyphenyl)thiophene (**24**).* Compound **24** was obtained according to the general procedure B starting from thiophene (0.32 g), but using 2,2,6,6-tetramethylpiperidine (2.0 mL, 12 mmol), BuLi (12 mmol), and $CoBr_2$ (0.84 g, 4.0 mmol). It was isolated after purification by flash chromatography on silica gel (eluent: heptane) as a yellow solid (19% yield). The analyses are as described previously.[10e]

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