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1,2-Dimetallic Compounds

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$InCl_3$-Catalyzed Synthesis of 1,2-Dimetallic Compounds by Direct Insertion of Aluminum or Zinc Powder**

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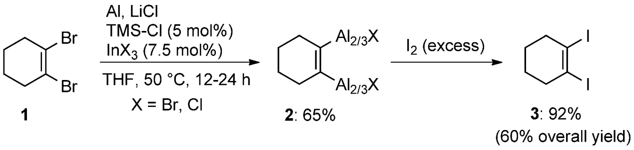
Organometallic species containing two carbon–metal bonds in the same molecule (dimetallic compounds) often show special reactivity patterns and offer unique synthetic applications.[1] The chemical properties of such organometallic species depend on the nature of the two metals and their topological proximity.[2] Whereas 1,*n*-dimetallic species ($n=1$, 3–6)[3] have been prepared by several methods and efficiently employed as multi-coupling reagents,[4] the preparation of organometallic compounds bearing two adjacent carbon–metal bonds (1,2-dimetallic species) in general is difficult. The reduction of acetylenes with lithium metal at low temperatures (−78 °C) has furnished 1,2-dilithioalkenes.[5] Transmetalations, or transition-metal-catalyzed trapping of arynes, have led to 1,2-dimetallic species derived from boron,[6] aluminum,[7] tin,[8] and silicon.[9] However, the direct insertion of a metal into a 1,2-dihalide, such as 1,2-dibromobenzene, would be the most straightforward method to generate a 1,2-dimetallic compound, but all attempts so far have proved to be highly problematic.[10] Owing to the thermal instability of the intermediately formed β-halo organometallic compound, side reactions occur, leading to low yield of the 1,2-dimetallic species.[11] The best results to date have been obtained using a zinc insertion into aromatic iodides in a polar solvent,[12] under ultrasound irradiation,[13] or with electrochemical assistance.[14] Because of the similar electronegativity of Al (1.66) and Zn (1.65),[15] we envisioned the synthesis of 1,2-dimetallic reagents by aluminum insertion. As Takai[16] and others[17] have shown recently, aluminum inserts readily into different unsaturated halides after activation of the metal surface by various additives, of which $InCl_3$ was especially effective.

Thus, in preliminary experiments we treated 1,2-dibromocyclohexene (**1**) with Al powder (3 equiv), LiCl (3 equiv), 5 % TMS-Cl,[18] and 7.5 % $InCl_3$ in THF. Within 24 h at 50 °C we obtained the cyclohexenyl 1,2-dimetallic compound **2** in 65 % yield.[19,20] The reagent reacted almost quantitatively in a second step with iodine, furnishing 1,2-diiodocyclohexane (**3**) in 92 % yield (Scheme 1). No reaction occurred between the dibromide **1** and Al powder in the absence of either LiCl or $InCl_3$, indicating that both salts are required for the insertion of Al powder.



Scheme 1. Preparation of the dialuminum reagent **2**.[21] THF = tetrahydrofuran, TMS = trimethylsilyl.

To prove the formation of a 1,2-dimetallic reagent and gain information about the structure of the dimetallic intermediate, we conducted ESI mass spectrometric experiments.[22] Interestingly, these experiments showed that several aluminates are formed during the insertion reaction (Figure 1, **A**–**C**).[23] The main charged component (Figure 1, **A**) produced by the insertion reaction, corresponded to the sum formula $[C_{10}H_{16}Al_2BrCl_4O]^-$ ($m/z=427$).[24] The simulated isotope pattern is in good agreement with the measured pattern.

The proposed structure of the aluminate is derived from the measured *m/z* values and analysis of the fragmentation

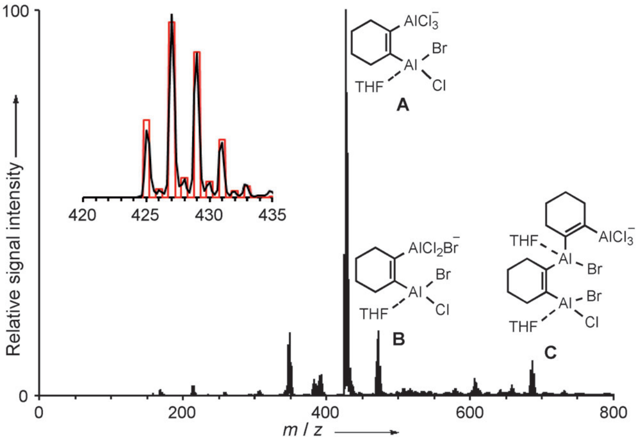


Figure 1. Negative-ion-mode ESI mass spectrum of a circa 10 mM solution of the products formed by reaction of **1** with Al powder in the presence of LiCl and $InCl_3$ in THF (*m/z* ratios of the most abundant isotopologues: **A**: 427 $[C_{10}H_{16}Al_2BrCl_4O]^-$; **B**: 473 $[C_{10}H_{16}Al_2Br_2Cl_3O]^-$; **C**: 687 $[C_{20}H_{32}Al_3Br_2Cl_4O_2]^-$). Inset: measured (line, black) and simulated isotope pattern (bars, red) of **A**.

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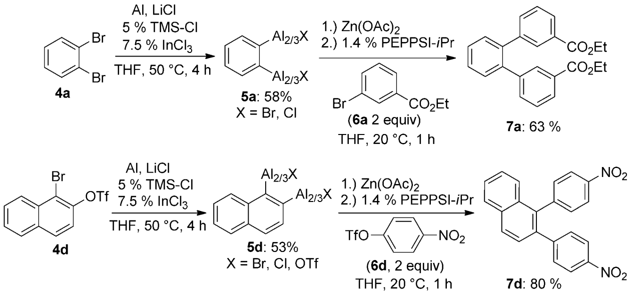
patterns obtained from collision-induced dissociation (CID) experiments. Remarkably, one aluminum atom in the dimetallic species remains uncharged and is complexed by THF, which could be verified by using deuterated THF as solvent.[25] The exchange of a chlorine by a bromine atom leads to the related species **B**.[26] A dimeric structure was also detected (Figure 1, **C**).

The synthesis of **2** could be extended to various aromatic 1,2-dibromides of type **4** (Table 1). Thus, the addition of 1,2-dibromobenzene (**4a**) to Al (3 equiv), LiCl (3 equiv), and 7.5% InCl$_3$ in THF furnished the expected dialuminum reagent **5a** in about 58% yield[20] (50°C, 4 h). Again, ESI mass spectrometric analysis indicated that several aluminates are produced.[25] This 1,2-dimetallic reagent **5a** reacted well with ethyl 3-bromobenzoate (**6a**) in a Pd-catalyzed cross-coupling reaction in the presence of Zn(OAc)$_2$ and 1.4% PEPPSI-*i*Pr,[27] affording the diester **7a** in 63% yield (Scheme 2).[28] Similarly, 3,4-dibromotoluene (**4b**) and 3,4-dibromo-*o*-xylene (**4c**) were converted into the corresponding 1,2-dimetallic reagents in 54–61% yield.[20] After transmetalation with Zn(OAc)$_2$, these reagents reacted in an allylation reaction (10% CuCN·2LiCl)[29] with 2-(bromomethyl) ethyl acrylate[30] (**6b**), and in a Liebeskind–Srogl acylation[31] (1.4% PEPPSI-*i*Pr) with the thioester (**6c**) providing the bis(acrylate) **7b** and the heterocyclic diketone **7c** in 70–93% yield (Table 1, entries 1 and 2).

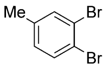
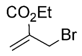
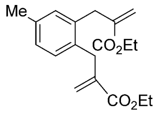
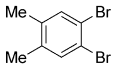
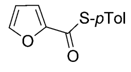
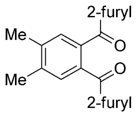
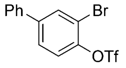
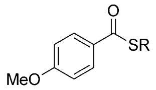
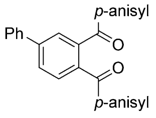
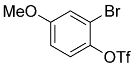
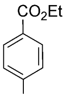
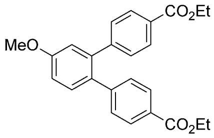
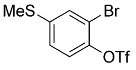
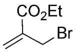
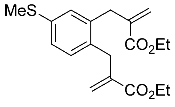
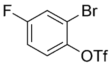
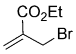
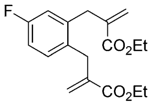
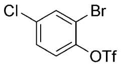
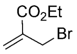
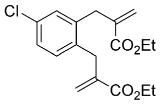
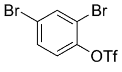
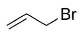
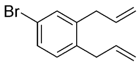
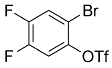
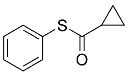
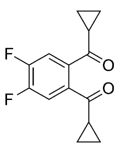


Scheme 2. Preparation of 1,2-dimetallic reagents **5a** and **5d** and subsequent cross-coupling reactions.

Remarkably, using the same insertion conditions, readily available aromatic *ortho*-bromotriflates[32] also afforded a variety of 1,2-dimetallic reagents. Thus, the naphthalene derivative **4d** led to the dimetallic species **5d** in 53% yield[20] (4 h, 50°C), which was converted into the dinitro-substituted terphenyl **7d** by a Pd-catalyzed cross-coupling reaction with 4-nitrophenyl triflate (**6d**) in the presence of Zn(OAc)$_2$ (80%; Scheme 2). ESI mass spectrometric analysis proved again the formation of a mixture of aluminates.[25]

Several other electron-rich aromatic triflates (**4e–g**) underwent a smooth insertion, furnishing 1,2-dialuminum reagents in 50–60% yield.[20] After transmetalation with Zn(OAc)$_2$, these reagents could be readily functionalized in Cu- or Pd-catalyzed reactions, leading to the bis-functionalized aromatic products (**7e–g**) in 64–87% yield (Table 1, entries 3–5). In the case of electron-deficient aromatic triflates (**4h–k**), the typical reaction conditions led to aryne

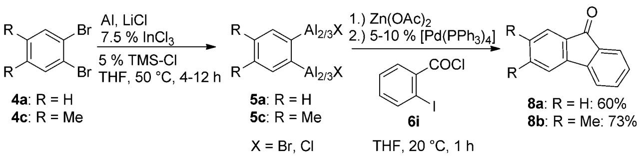
Table 1: InCl$_3$-catalyzed insertion of Al powder into substrates **4** and subsequent functionalization affording products **7**.

Entry	Substrate	Time[a] Yield[b]	Electrophile[c]	Product[d]
1	 **4b**	12 h 54%	 **6b**	 **7b**: 93%[f]
2	 **4c**	12 h 61%	 **6c**	 **7c**: 70%[e]
3	 **4e**	12 h 51%	 **6e**: R = *p*-Cl-Ph	 **7e**: 66%[e]
4	 **4f**	12 h 58%	 **6f**	 **7f**: 87%[e]
5	 **4g**	12 h 55%	 **6b**	 **7g**: 64%[f]
6	 **4h**	12 h 66%	 **6b**	 **7h**: 65%[f,g]
7	 **4i**	8 h 40%	 **6b**	 **7i**: 84%[f,g]
8	 **4j**	6 h 38%	 **6g**	 **7j**: 61%[f,g]
9	 **4k**	6 h 45%	 **6h**	 **7k**: 44%[e,g]

[a] Reaction time for completion at 50°C. [b] Yield determined by GC-analysis of iodolyzed reaction aliquots. [c] Up to 200% of electrophile was used. [d] Yield of isolated analytically pure compounds. [e] 1.4% PEPPSI-*i*Pr was used. [f] 10% CuCN·2LiCl was added. [g] No LiCl was used.

formation, and no dimetallic reagent was obtained. However, performing the aluminum insertion in the absence of LiCl smoothly produced (50 °C, 6–12 h) the 1,2-dimetallic species, although in somewhat lower yields (38–66 %).[20] Again, Cu-mediated or Pd-catalyzed reactions led to *ortho*-functionalized aromatics (**7h–k**) in 44–84 % yield (Table 1, entries 6–9).

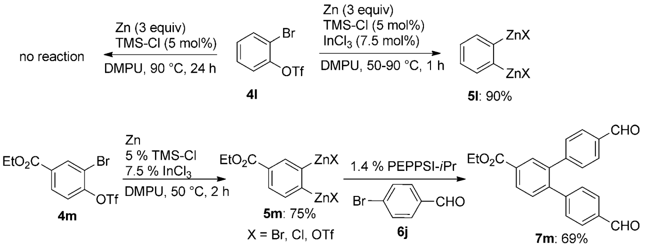
Moreover, cyclization reactions could be achieved using the 1,2-dimetallic species. Thus, the dialuminum reagent **5a** reacted with 2-iodobenzoyl chloride (**6i**) in the presence of $Zn(OAc)_2$ and 5–10 % $[Pd(PPh_3)_4]$ in an acylation followed by a cross-coupling reaction, furnishing 9*H*-fluorenone (**8a**; 20 °C, 1 h) in 60 % yield (Scheme 3). In an analogous way, the dimetallic species **5c** also underwent the ring-closure, leading to the fluorenone derivative **8b** in 73 % yield (Scheme 3).



Scheme 3. Preparation of 1,2-dimetallic species **5a**, **5c** and subsequent acylation/cross-coupling sequence affording 9*H*-fluorenone derivatives **8a**, **8b**.

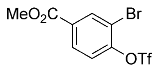
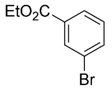
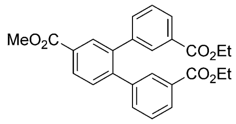
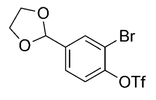
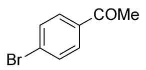
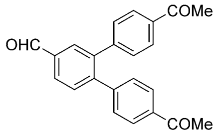
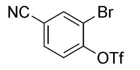
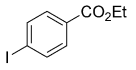
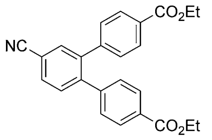
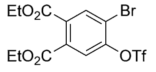
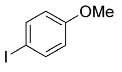
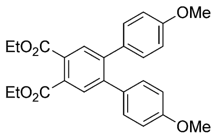
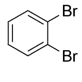
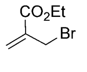
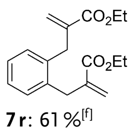
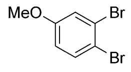
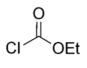
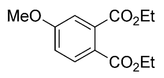
As $InCl_3$ proved to be effective in generating 1,2-dialuminum reagents, we also investigated whether it could mediate the reaction of Zn powder with the readily available 2-bromophenyl triflate (**4l**) in *N*,*N'*-dimethylpropyleneurea (DMPU) at 90 °C to give the corresponding 1,2-dizinc reagent (Scheme 4). The addition of 7.5 % $InCl_3$ furnished the 1,2-dimetallic zinc reagent **5l** (50 °C, 1 h) in 90 % yield,[20] whereas the zinc insertion into the bromotriflate **4l** does not proceed in the absence of $InCl_3$.[33]

Remarkably, using this $InCl_3$ catalysis, even highly functionalized 1,2-dizinc dimetallic species could be prepared under relatively mild conditions. Thus, the reaction of the functionalized triflate **4m** with Zn powder (3 equiv) and 7.5 % $InCl_3$ furnished an ester-substituted 1,2-dizinc **5m** reagent (50 °C, 2 h) in 75 % yield[20] in DMPU. Cross-coupling with 4-bromobenzaldehyde (**6j**, 1.4 %, PEPPSI-*i*Pr)[27] led to the highly functionalized terphenyl **7m** in 69 % yield (Scheme 4). A sensitive methyl ester (**4n**) was also compatible with the reaction conditions (50 °C, 2 h) and the functionalized dimetallic compound underwent a Negishi cross-coupling[34] with ethyl 3-bromobenzoate (**6a**), furnishing the triester **7n** in 61 % yield (Table 2, entry 1). Ketones and aldehydes were not tolerated under the insertion conditions. However, the protected aldehyde **4o** reacted well with Zn powder in the presence of 7.5 % $InCl_3$ and led to the 1,2-dizinc reagent in 60 % yield.[20] Negishi cross-coupling[34] followed by acetal cleavage afforded the aldehyde **7o** in 60 % yield (Table 2, entry 2). Even dimetallic species bearing a cyano or two ester groups could be readily prepared, and afforded highly functionalized terphenyls (**7p–q**) in 55–69 % yield after cross-coupling reactions (Table 2, entries 3 and 4). Moreover, aromatic dibromides also underwent a smooth Zn insertion in the presence of 7.5 % $InCl_3$. Thus, 1,2-dibromobenzene (**4a**) or an electron-rich 3,4-dibromoanisole (**4r**) furnished dimetallic reagents that could be converted into the 1,2-disubsti-



Scheme 4. Reaction of the bromotriflates **4l** and **4m** with Zn powder in the absence and in the presence of catalytic amounts of $InCl_3$.

Table 2: $InCl_3$-catalyzed Zn insertion into substrates **4** and subsequent functionalization leading to products **7**.

Entry	Substrate	Time[a] Yield[b]	Electrophile[c]	Product[d]
1	 **4n**	2 h 70%	 **6a**	 **7n**: 61%[e]
2	 **4o**	2 h 60%	 **6k**	 **7o**: 60%[e]
3	 **4p**	2 h 57%	 **6f**	 **7p**: 55%[e]
4	 **4q**	2 h 45%	 **6l**	 **7q**: 69%[e]
5	 **4r**	2 h 59%	 **6b**	 **7r**: 61%[f]
6	 **4s**	2 h 59%	 **6m**	 **7s**: 72%[g]

[a] Reaction time for completion at 50 °C. [b] Yield determined by GC-analysis of iodolyzed reaction aliquots [c] Up to 200 % of electrophile was used. [d] Yield of isolated analytically pure compounds. [e] 1.4 % PEPPSI-*i*Pr. [f] 10 % CuCN·2 LiCl was added. [g] 5 % $[Pd(PPh_3)_4]$ was used.

tuted aromatic species **7r,s** in 61–72 % yield (Table 2, entries 5 and 6).

We speculate that the formation of the dimetallic reagents proceeds over an intermediately generated aryne, as both aluminum and zinc are known not to insert into carbon–triflate bonds. This hypothesis is also supported by the fact that 1,2-dibromocyclopentene furnished exclusively a monometallic reagent (elimination to the strained cyclopentyne does not occur). We propose that the triflate plays, as usual, the role of a leaving group,[35] generating an aryne that is trapped by low-valent zinc or aluminum at the metal surface, providing the corresponding 1,2-dimetallic species. In all cases, aryne-derived side-products were observed.

In summary, we have demonstrated that a catalytic amount of InCl$_3$ dramatically enhances the insertion of aluminum and zinc powder, allowing the preparation of 1,2-dimetallic species of aluminum or zinc by direct insertion using commercially available metal powders under mild conditions. These 1,2-dimetallic species react in Cu- or Pd-catalyzed reactions, affording various interesting *ortho*-bisfunctionalized aromatics for potential pharmaceutical or materials science applications. The reactivity of such organometallic species can be used for the synthesis of fluorenone derivatives. Further synthetic extensions of this method as well as mechanistic studies are currently being performed in our laboratories.

Experimental Section

Typical procedure: Preparation of **8b**: LiCl (254 mg, 6 mmol), InCl$_3$ (33 mg, 0.15 mmol), and Al powder (162 mg, 6 mmol) were placed in an argon-flushed Schlenk flask, followed by THF (4 mL) along with the internal standard. 3,4-Dibromo-*o*-xylene (**4c**, 417 mg, 2 mmol) was added in one portion and the reaction mixture stirred at 50 °C for 12 h. Iodolysis indicated a yield of 51 % dimetallic reagent. The aluminum powder was allowed to settle down and the dimetallic solution was transferred to another flask. [Pd(PPh$_3$)$_4$] (88 mg, 0.076 mmol) and 2-iodobenzoyl chloride (**6i**, 850 mg, 3 mmol) were added and the reaction mixture was stirred for 1 h at 20 °C. Standard aqueous workup and flash column chromatographical purification (isohexane) afforded **8b** as yellow solid (158 mg, 73 %).

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[20] The yield was determined by GC analysis of iodolyzed reaction aliquots in THF.

[21] The insertion of aluminum usually leads to a mixture of organometallic species, namely R_2AlX and $RAlX_2$. These combined give $R_3Al_2Cl_3$, which is shortened to $RAl_{2/3}X$.

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[24] The m/z ratio is given for the most abundant isotopologue.

[25] See the Supporting Information.

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Communications

1,2-Dimetallic Compounds

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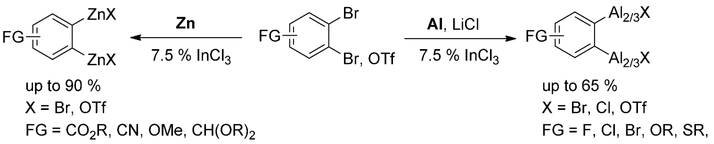
P. Knochel* ______ ■■■■–■■■■

InCl$_3$-Catalyzed Synthesis of 1,2-Dimetallic Compounds by Direct Insertion of Aluminum or Zinc Powder



In-sertion of metal: Catalytic amounts of InCl$_3$ allow the insertion of aluminum and zinc powder into aromatic 1,2-dibromides or 1,2-bromotriflates (see scheme). These 1,2-dimetallic species can undergo Cu or Pd-catalyzed acylations, allylations, or cross-couplings.