Group VI metal aminoborylene complex-catalyzed demercuration reactions of bis(alkynyl)mercurials†

Leonardo Apostolico,[a] Holger Braunschweig,*[a] Andrew G. Crawford,[b] Thomas Herbst[a] and Daniela Rais[a]

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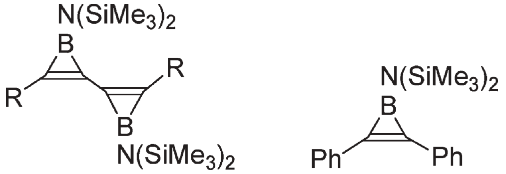
The first catalytic application of the Group VI metal borylene complexes [$(CO)_5M{=}BN(SiMe_3)_2$] involves the demercuration reaction of bis(alkynyl)mercurials, [$Hg(C{\equiv}CR)_2$], with formation of a series of buta-1,3-diynes.

Since their first synthesis in 1998,[1a] the reactivity of Group VI metal terminal aminoborylene complexes [$(CO)_5M{=}BN(SiMe_3)_2$] (M = Cr, **1**; M = Mo, **2**; M = W, **3**)[1b] has been investigated in some detail.[2] A particularly useful property of these compounds is their ability to transfer the aminoborylene moiety from the Group VI element to other transition metals, under thermal or photolytic conditions, depending on the borylene acceptor.[3] Recently, successful borylene transfer was achieved employing alkynes as borylene acceptors, allowing for a new, high yielding synthesis of a number of borirenes.[3c] In light of the interesting photophysical properties displayed by boron-containing conjugated materials,[4] and with a view to incorporating a heavy metal into such frameworks, we wondered about the possibility of transferring the borylene moiety to transition metal alkynyl complexes. Mercury alkynyls [$Hg(C{\equiv}CR)_2$] (**4**) were initially chosen, principally on the basis of their linear, and thus sterically unhindered, geometry.[5] Upon irradiation of equimolar amounts of chromium complex **1** and [$Hg(C{\equiv}CPh)_2$] (**4a**) in C_6D_6, spectroscopic evidence for the formation of a new boron-containing species, **5**, was obtained.[6] However, the similarity of the ^{11}B NMR chemical shift of **5** (δ = 24.0) to that of the bisborirene **6a** (δ = 28.0) and the borirene **6b** (δ = 25.0), respectively (Fig. 1),[3c] along with the presence of metallic mercury in the reaction vessel, led us to hypothesize an unexpected outcome of the reaction. Indeed, a first control experiment showed that heating equimolar amounts of **1** and **4a** in C_6H_6 at 90 °C resulted in the formation of $PhC{\equiv}C{-}C{\equiv}CPh$ (**7a**) along with elemental mercury and recovery of **1**. Since the borylene fragment would not transfer in the absence of irradiation,[3c] **1** was photolyzed in a second control experiment in the presence of the diyne **7a**, thus leading to the bisborirene compound **5**. Hence, we assumed that the aforementioned photolysis of **1** and **4a** proceeded not only with transfer of the borylene to the C–C triple bond, but interestingly also with formation of an intermediate diyne obtained by demercuration of **4a**.



R = Ph, **5**
R = $SiMe_3$, **6a**

6b

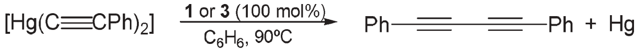
Fig. 1 Bis(borirenes) **5**, **6a** and borirene **6b**.

Herein, we describe the aminoborylene complex-catalyzed demercuration reaction of [$Hg(C{\equiv}CR)_2$]. This represents the very first catalytic application of borylene complexes, and the first instance in which a transition metal complex with a direct metal–boron bond participates in a catalytic cycle in which the boron-based ligand is not transferred to a substrate.

The stoichiometric reaction described in Scheme 1 was monitored by ^1H and $^{11}B\{^1H\}$ NMR spectroscopy.

This revealed gradual consumption of **4a**, simultaneous formation of **7a** and the presence of **1** (or **3**) as the only boron-containing compound. The ^1H NMR and GC-MS data for **7a** were perfectly consistent with those obtained from an authentic sample. To establish the scope of the transformation, the reaction was performed with a range of complexes [$Hg(C{\equiv}CR)_2$] (R = C_6H_4-4-Me, **4b**; C_6H_4-4-OMe, **4c**; C_6H_4-4-NMe_2, **4d**), under the same conditions. Choosing a convenient substitution pattern on the alkynyl ligand allowed monitoring of the reaction using ^1H NMR spectroscopy. Gradual disappearance of the methyl resonance of the [$Hg(C{\equiv}CR)_2$] complexes was noted, with the simultaneous appearance of the corresponding signal for the buta-1,3-diynes. The values obtained, compared with those of authentic samples, proved formation of the buta-1,3-diynes, which could then be isolated in moderate yields (Table 1, a).[7a,b] As reported in Table 1‡, different reaction times reflect a dependence on the electronic properties of the alkynyl ligands.

Having ascertained the thermal stability of [$Hg(C{\equiv}CR)_2$] (**4**) under the reaction conditions, formation of $RC{\equiv}C{-}C{\equiv}CR$ (**7**) and recovery of unreacted aminoborylene complex **1** led us to believe that **1** could play a catalytic role in the demercuration process. To verify our hypothesis, the same reactions were performed with a



$$[Hg(C{\equiv}CPh)_2] \xrightarrow[C_6H_6,\ 90°C]{1\ or\ 3\ (100\ mol\%)} Ph{-}C{\equiv}C{-}C{\equiv}C{-}Ph + Hg$$

4a **7a**

Scheme 1 Stoichiometric demercuration reaction of [$Hg(C{\equiv}CPh)_2$].

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[a] *Institut für Anorganische Chemie, Julius-Maximilians-Universität, Würzburg, Am Hubland, 97074 Würzburg, Germany. E-mail: h.braunschweig@mail.uni-wuerzburg.de; Fax: (+49)931-888-4623; Tel: (+49)931-888-5260*
[b] *Department of Chemistry, University Science Laboratories, South Road, Durham, UK DH1 3LE*

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Table 1 Synthesis of buta-1,3-diynes *via* stoichiometric (a) and catalytic (b) demercuration reactions of $[Hg(C\equiv CR)_2]$

R	4	7	Time/h	Yield (%)
C_6H_5	**4a**	**7a**	32[a]	62[a]
			91[b]	65[b]
C_6H_4-4-Me	**4b**	**7b**	21[a]	64[a]
			70[b]	66[b]
C_6H_4-4-OMe	**4c**	**7c**	11[a]	47[a]
			34[b]	51[b]
C_6H_4-4-NMe_2	**4d**	**7d**	1.5[a]	52[a]
			11[b]	55[b]

[a] Stoichiometric reaction conditions: **4** (0.066 mmol), **1** (0.066 mmol), C_6H_6 (1.5 mL), 90 °C. [b] Catalytic reaction conditions: **4** (0.066 mmol), **1** (0.0066 mmol), C_6H_6 (1.5 mL), 90 °C.

catalytic amount (10 mol%) of **1**. In all cases, the reactions reached full conversion as judged from ^1H NMR spectroscopy of the reaction mixture and the absence of soluble degradation products, demonstrating that **1** catalyzes the demercuration of bis(alkynyl)-mercurials (Table 1, b).

All reactions were also performed with tungsten complex **3**, yielding comparable results to those obtained with **1**. Furthermore, control experiments with $[Cr(CO)_6]$ proved that the hexacarbonyl complex showed no catalytic activity. Bis(alkynyl)mercurials find application primarily as air and moisture stable transalkynylating reagents for transition metal,[8] lanthanide[9] and main group element compounds.[10] Demercuration reactions of these species have been described as a means to access conjugated diynes, as well as more complex systems.[11] Hence, Takagi *et al.* studied the Rh-catalyzed demercuration of a range of organomercurials, including $[Hg(C\equiv CPh)_2]$, to give the corresponding diyne $PhC\equiv C–C\equiv CPh$ (**7a**).[11b] Later Hill and co-workers extended the range of suitable mercury alkynyl reagents, noting extrusion of elementary mercury from $[Hg(C\equiv CR)_2]$ and consequent formation of buta-1,3-diynes as the result of a catalytic process involving complexes of Rh, Ru and Os,[11c,d] and elegantly applied the protocol to the synthesis of dimetallaoctatetraynes.[11e–g] The reactions reported herein demonstrate that earlier transition metal complexes are also capable of effecting demercuration reactions, when possessing an aminoborylene ligand. However, while for later transition metals a catalytic cycle involving conventional steps, such as oxidative addition, extrusion of mercury with organyl group transfer and reductive elimination, was established, favoured by the electronic and coordinative unsaturation of the metal complexes involved, it is unlikely that such a cycle applies to the 18-electron borylene species. Efforts devoted to a clarification of the operative mechanism are under way.

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Notes and references

‡ Aminoborylene complexes **1**[1a] and **3**[1a] and bis(alkynyl)mercurials $[Hg(C\equiv CR)_2]$,[5] were prepared according to literature procedures. The spectroscopic data for compounds **7** are in full agreement with those reported in the literature.[7a,b]

General procedure for the catalytic formation of buta-1,3-diynes (7). Solid **1** (0.0024 g, 0.0066 mmol) was added to a solution of $[Hg(C\equiv CR)_2]$ (0.066 mmol) in benzene (1.5 mL). The mixture was heated at 90 °C until the reaction had reached completion (as judged from GC-MS spectra, see Table 1 for reaction times). The solvent was then removed. Complex **1** and small amounts of $[Cr(CO)_6]$ were removed by high vacuum sublimation. Crystals of **7** were obtained upon extraction of the diynes from the residue with hexane, filtration and subsequent crystallization (see Table 1 for isolated yields).

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