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1,2-Halosilane vs. 1,2-alkylborane elimination from (boryl)(silyl) complexes of iron: switching between borylenes and silylenes just by changing the alkyl group[†]

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Reaction of different combinations of aryl(dihalo)boranes and trialkylsilyl iron metallates, a route previously used to prepare a terminal iron arylborylene complex, is found to lead to three distinct new reaction outcomes, including unselective decomposition, an inert iron(11) (boryl)(silyl) complex, and a dinuclear bis(µ-silylene) complex. The latter result is to our knowledge the first example of a 1,2-alkylborane elimination, in contrast to the facile and ubiquitous 1,1-alkylborane elimination observed from (alkyl)(boryl) transition metal complexes, and is also a novel route to bridging silylene complexes.

The 1,2-elimination of halotriorganylsilanes (SiXR₃) from 1-halo-2silyl-functionalised molecules is often a highly favored reaction, due to the creation of a thermodynamically-stable silicon– halide bond ($\Delta H_{\text{SiX}} = 565$ (F), 381 (Cl), 310 (Br) kJ mol⁻¹).¹ This technique, often induced thermally, has been applied throughout organic and main-group chemistry in order to create multiple bonds in specific positions (Fig. 1A), such as in the formation of strained alkenes from 1-halo-2-silylalkanes,² iminophosphines (RN=PR') from *P*-halo-*N*-silylaminophosphines,³ iminoboranes (RN=BR') from *B*-halo-*N*-silylaminoboranes,⁴ as well as the related syntheses of transition metal iminoboryl,⁵ oxoboryl,⁶ and alkylideneboryl complexes.⁷

Another facile elimination reaction is the reductive elimination of an alkylborane from a transition metal center (*i.e.* 1,1-alkylborane elimination; Fig. 1B). This process is the final step in the catalytic hydroboration, diboration and C–H borylation protocols,⁸ and is such a facile process that only one stable transition metal (alkyl)(boryl) complex has been isolated.⁹ However, borane elimination from a two-atom system, analogous to the 1,2-halosilane elimination, is much more rare,¹⁰ and to our knowledge no 1,2-alkylborane elimination (Fig. 1C) has yet been observed. This is despite the considerable driving force



Fig. 1 Elimination reactions of relevance to this study.

provided by the creation of a very strong boron-carbon bond $(\Delta H_{\rm BC} = 372 \text{ kJ mol}^{-1}).^{1}$

In 2012 we reported the synthesis of a zerovalent iron borylene complex from the combination of a trialkylsilyl iron metallate and a bulky aryldihaloborane (bottom, Fig. 1A), *via* a presumed tandem salt elimination/1,2-halosilane elimination process.¹¹ However, recent experiments in our laboratories have shown that minor alterations of the halide and alkyl groups of the

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starting materials in this reaction lead to vastly different outcomes. While one combination of iron metallate and halosilane leads to unselective decomposition, another leads to the isolation of an iron(π) (boryl)(silyl) complex, and another to a dinuclear bis(μ -silylene) complex *via* the aforementioned unprecedented 1,2-alkylborane elimination. These results are reported herein.

The synthesis of the terminal borylene complex [Fe(BDur)-(CO)₃(PMe₃)] (**4b**, Fig. 2; Dur = 2,3,5,6-tetramethylphenyl), reported in 2012 by our group,¹¹ was presumed to follow from an initial salt elimination step where the trialkylsilyl iron metallate K[Fe(CO)₃(PMe₃)(SiMe₃)] (**1a**) attacks the borane BBr₂Dur (**2b**), leading to the presumed intermediate boryl complex *mer*-[Fe(BBrDur)(CO)₃(PMe₃)(SiMe₃)] (**3b**), followed by conventional bromosilane elimination. In an attempt to detect or isolate the presumed iron(II) (boryl)(silyl) intermediate, the dichloroborane BCl₂Dur (**2a**) was instead treated with **1a**, leading to a brown solid (**3a**). That the reaction had not led to a terminal borylene complex was evident from the much more low-frequency ¹¹B and ³¹P NMR signals of **3a** ($\delta_{\rm B}$ 114.2; $\delta_{\rm P}$ 2.4) compared to those of **4b** ($\delta_{\rm B}$ 146; $\delta_{\rm P}$ 17.6).¹¹ The similarity of the ¹¹B and ³¹P NMR data of **3a** ($\delta_{\rm B}$ 114.2; $\delta_{\rm P}$ 2.4) to that of the



Fig. 2 Various outcomes of the reactions of trialkylsilyl iron metallates **1a,b** with aryldihaloboranes **2a,b**.

previously-published¹² iron(II) (boryl)(gallyl) complex *mer*-[Fe(BClDur)(CO)₃(GaCl₂)(PMe₃)] ($\delta_{\rm B}$ 113; $\delta_{\rm P}$ 0.6) indicated that **3a** was a trimethylsilyl derivative thereof: *mer*-[Fe(BClDur)(CO)₃-(PMe₃)(SiMe₃)]. A doublet resonance was also observed in the ²⁹Si NMR spectrum of **3a** ($\delta_{\rm Si}$ 16.7, ² $J_{\rm SiP}$ = 12.0) reflecting ²⁹Si-³¹P coupling. A single-crystal X-ray diffraction study of **3a** (Fig. 3) confirmed its connectivity and showed it to be isostructural to *mer*-[Fe(BClDur)(CO)₃(GaCl₂)(PMe₃)] (however, lacking the dimerisation



Fig. 3 Crystallographically-derived molecular structure of [Fe(BClDur)-(CO)₃(PMe₃)(SiMe₃)] (**3a**), [Fe₂(CO)₆(PMe₃)₂(μ -SiEt₂)₂] (**6c**) and [Fe₂(CO)₄(μ -CO)-(PMe₃)₂(μ -SiEt₂)₂] (**7c**). Thermal ellipsoids drawn at the 50% probability level. Relevant bond lengths [Å] and angles [deg] for **3a**: Fe-P 2.2706(5), Fe-Si 2.4527(5), Fe-B 2.036(2), B-Cl 1.816(2), B-C 1.584(2); Si-Fe-B 92.55(5). For **6c**: Fe1-Fe2 3.8758(6), Fe1-Si1 2.3908(5), Fe1-Si2 2.4506(6), Fe1-P1 2.2385(5), Si1-Si2 2.9019(6); C1-Fe1-C2 161.22(8), Si1-Fe1-P1 178.07(2), Fe1-Si1-Fe2 106.36(2). For **7c**: Fe1-Fe2 2.6171(4), Fe1-Si1 2.3399(7), Fe1-Si2 2.3281(6), Fe1-P1 2.2264(7) Fe1-C1 1.955(2), Si1-Si2 3.2593(9); Si1-Fe1-P1 171.64(3), Fe2-Si1-Fe1 68.54(2), Fe2-Si2-Fe1 68.09(2).

caused by the dichlorogallyl ligand of the latter complex). The phosphine, silyl and boryl ligands of **3a** adopt a meridional arrangement, with the phosphine and boryl ligands mutually *trans*. It should be noted also that **3a** was not observed to convert further to a terminal borylene (or any other) complex, even at elevated temperatures.

At this point, we turned our attention back to the presumably more-reactive dibromoborane BBr₂Dur (2b), combining it with $K[Fe(CO)_3(PMe_3)(SiEt_3)]$ (1b) at room temperature. To our surprise, ¹¹B and ³¹P NMR of the reaction mixture showed a mixture of compounds including what was clearly the iron (boryl)(silyl) complex 3c based on its effectively identical NMR data ($\delta_{\rm B}$ 114.2; $\delta_{\rm P}$ 2.3) to that of 3a, as well as a number of other signals. No NMR signals corresponding to a terminal borylene akin to 4b were observed. However, 3c was found to convert further over time. Upon reducing the volume of the hexane solution, yellow crystals precipitated, which showed single ³¹P NMR (δ_P 9.6) and ²⁹Si NMR (δ_{si} 29.8) signals but no appreciable ¹¹B NMR resonance. The identity of the compound was ascertained from single-crystal X-ray diffraction, which showed it to be the dinuclear bis(μ -silvlene) complex mer, mer-[Fe₂(CO)₆(PMe₃)₂(μ -SiEt₂)₂] (6c, Fig. 2 and 3; yield 25%). The Fe-Fe (3.8758(6) Å) and Si-Si (2.9019(6) Å) distances of 6c are significantly longer than those of two previously-published iron bis(µ-silylene) octacarbonyl complexes,¹³ giving the impression of a much more dilated Fe_2Si_2 core in 6c. However, the silvlene ligands of 6c are much less symmetrically bound to the iron atoms (Fe1-Si1 2.3908(5), Fe1-Si2 2.4506(6) Å) than in the literature complexes. The ²⁹Si NMR resonance of **6c** (δ_{si} 29.8) was also found to be in line with that of the previously-reported bridging bis(dialkylsilylene) complex $[Fe(\mu-SiMe_2)(CO)_4]_2 (\delta_{Si} 17.8).^{13}$

Reduction of the mother liquor from which 6c crystallised under vacuum led to a black solid. Sublimation of this solid gave a white solid containing the borane BBrEtDur ($\sim 80 \text{ mol}\%$ by ¹H and ¹¹B NMR; $\delta_{\rm B}$ 81.1), as well as a small amount of the zerovalent iron complexes $[Fe(CO)_4(PMe_3)]$ ($\delta_P \sim 34$) and $[Fe(CO)_3(PMe_3)_2]$ $(\delta_{\rm P} \sim 39)$.¹⁴ All attempts to isolate BBrEtDur were hampered by cocrystallisation or cosublimation of the aforementioned iron(0) phosphine complexes. However, its presence was confirmed by ¹H and ¹¹B NMR spectroscopy of the solid obtained by crystallisation, as well as GCMS, where peaks corresponding to its hydrolysis product BEtDur(OH) were observed. An attempt to independently synthesise BBrEtDur by addition of ethyl magnesium bromide to BBr₂Dur was unsuccessful, but addition of ethyllithium to BBr₂Dur gave a mixture with signals corresponding to those of BEt₂Dur and the presumed BBrEtDur, thus providing convincing evidence for the identity of the latter.

The identification of the product **3c** from this reaction is a clear indicator that the initial salt elimination step occurs as in the reaction to form the isolated complex **3a**. From here, however, the reaction pathway deviates from those forming **3a** and **4b**. The alkylborane BBrEtDur is eliminated instead of the halosilane SiBrEt₃, leading to the mononuclear terminal silylene complex¹⁵ **5c**, which dimerises to form the bridging bis(μ -silylene) complex **6c**. The dimerisation of terminal silylene and related borylene complexes has precedence in the literature.¹³

The observation of small amounts of $[Fe(CO)_4(PMe_3)]$ and $[Fe(CO)_3(PMe_3)_2]$ suggest the possibility of reductive elimination of a silylborane from **3c**. Although the silylborane was not observed, it cannot be conclusively ruled out. Oxidative addition of a B–Si bond (*i.e.* the reverse reaction) to zerovalent palladium or platinum complexes has been calculated by Sakaki and coworkers¹⁶ to be strongly exothermic and proceed with either a very small or no activation barrier, in marked contrast to the difficult oxidative addition of the relatively inert B–C bond. Thus the very small amounts – or complete absence – of reductive elimination products from complexes **3a–c** can be ascribed to the generally disfavored reductive elimination of silylboranes from transition metal (boryl)(silyl) complexes.

Under photolytic conditions, the dinuclear complex 6c was observed to extrude one carbonyl ligand and form the triplybridged diiron complex 7c (Fig. 2). This complex showed little change in its ³¹P NMR data (δ_P 10.1) from precursor 6c, but significant complication of the carbonyl region of its IR spectrum. A massively high-frequency-shifted broadened singlet with unresolved coupling was observed in the ²⁹Si NMR spectrum of 7c (δ_{si} 190.44), in comparison to that of its precursor 6c (δ_{si} 29.8). A single-crystal X-ray diffraction study of 7c (Fig. 3) confirmed its structure, which contains significantly shorter Fe-Fe (2.6171(4) Å), and longer Si-Si (3.2593(9) Å), distances than those of 6c. This also dictates much more acute Fe-Si-Fe angles in 7c (68.54(2), 68.09(2)°) than in 6c (106.36(2)°), which could explain the large difference in the chemical shifts of the 29Si NMR resonances of the two complexes. The silvlene ligands of 7c are now much more symmetrically bound, as is the bridging carbonyl ligand.

The photolysis of dinuclear bis(μ -silylene) complexes of the form $[Fe_2(CO)_6L_2(\mu$ -SiR₂)₂] to release one carbonyl, leading to triply-bridged $[Fe_2(\mu$ -CO)(CO)₄L₂(μ -SiR₂)₂] complexes, is also well-documented in the literature.¹⁷ However, **7c** is to our knowledge the first bis(μ -silylene) complex with a carbonyl ligand bridging the two metals to be structurally authenticated. It should also be noted that the combination of the triethylsilyl complex K[Fe(CO)₃(PMe₃)(SiEt₃)] (**1b**) with the dichloroborane BCl₂Dur (**2a**) led only to the formation of many unidentifiable products (Fig. 2).

Unfortunately, attempts to split the bis(μ -silylene) into mononuclear complexes using large excesses of Lewis bases (DABCO, 4-dimethylaminopyridine or PMe₃) were unsuccessful, in contrast to published reports.¹³

In conclusion, the generation of the bis(μ -silylene) complex **6c**, to our knowledge, is first example of an 1,2-alkylborane elimination, in marked contrast to the vast precedence of 1,1-alkylborane eliminations from transition metals (*i.e.* reductive eliminations), and also represents a novel route to silylene complexes. To our surprise, while methyl substituents on the silyl ligands lead to halosilane elimination and a borylene complex, ethyl substituents appear to promote alkylborane elimination to the complete exclusion of halosilane elimination. Overall, the four permutations of the two different iron metallates (**1a,b**) and two different dihalodurylboranes (**2a,b**) led to four unique outcomes: unselective decomposition, an inert iron(π) (boryl)(silyl) complex, a terminal borylene complex, ¹¹ and a dinuclear bis(μ -silylene) complex.

A small amount of reductive elimination from one (boryl)(silyl) complex was also inferred from the detection of simple monovalent iron carbonyl-phosphine complexes. The bulky duryl group appears to be integral to this chemistry, by providing steric shielding of the boron atom while simultaneously denying it the π electron density needed to quench its electron deficiency, thus allowing unusual reactions with small groups. Given the subtle differences between methyl and ethyl groups, the distinct reactivity difference observed is surprising. While the proposal of a mechanism would be premature, the results appear to rule out a radical mechanism, which would presumably favour a methyl shift over an ethyl shift in accordance with the noted differences in the relative willingness of methyl and ethyl groups to undergo radical processes.¹⁸

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