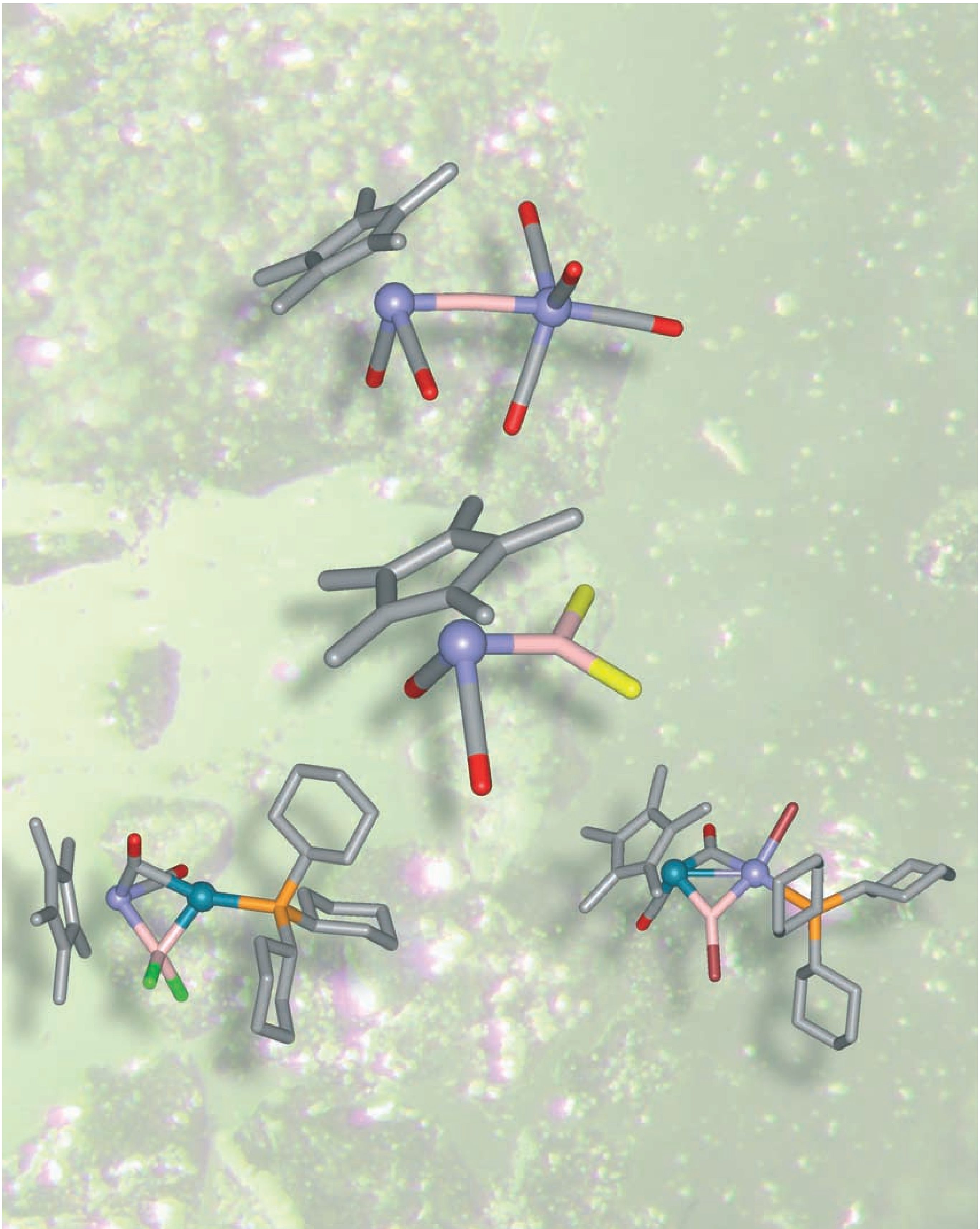

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Boron as a Bridging Ligand

Holger Braunschweig* and George R. Whittell[a]

Abstract: The Lewis acidity of [(η^5-C_5R_5)Fe(CO)$_2$(BX_2)] (**1**: R = H, X = Cl) and the robust nature of the constituent Fe–B bond have been demonstrated by reaction with 4-methylpyridine to yield the corresponding Lewis acid–base adduct. These properties have subsequently been utilised in the construction of heterodinuclear bridging borylene, bridging boryl and μ_2-boride complexes from analogues **3** (R = Me, X = Br) and **5** (R = Me, X = Cl). All the bimetallic species so formed exhibited unprecedented coordination modes for boron.

Keywords: boron · coordination modes · Lewis acids · transition metals

Introduction

Carbon-based π-acceptor ligands have a multifaceted role in organometallic chemistry, in as much as they can serve as either spectator ligands, sites of reactivity themselves or become involved in metal-centred processes.[1] The actual function exhibited can often be understood by consideration of the frontier orbital interactions between the transition-metal–ligand fragment and the ligand of interest.[2] For ligands that bind to the metal centre through a single carbon atom, π acidity can result in the formation of metal–carbon multiple bonds,[3] and the varying contributions of the σ and π components to this interaction still remain the subject of theoretical study.[4] In such ligands, a LUMO of double degeneracy, as in CO and $[CH]^+$, results in both orbitals being capable of accepting electron density back from the metal centre (Figure 1a).[1,3b] In C=CH_2, however, this degeneracy is lost as a result of the lower symmetry and the ligand acts a single-faced π acceptor (Figure 1b).[5] Both the number of π-accepting faces and the formal hybridisation of the donor atom provide a convenient method of classifying these ligands. Nonetheless, one feature common to all these groups is the ability to adopt bridging coordination modes in polymetallic complexes.[1,5,6]

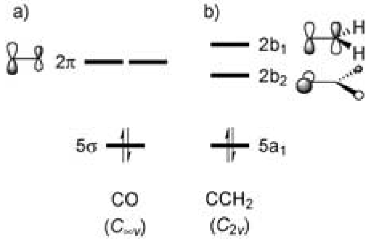

Figure 1. Qualitative molecular orbital diagrams for a) CO and b) C=CH_2.

In contrast to the case of carbon, the "organometallic" chemistry of boron-based ligands remains somewhat in its infancy. Nonetheless, the last fifteen years have seen considerable advances, predominantly in the field of transition-metal–boryl (L_nM–BR_2) chemistry.[7] This progress has, in no small part, been due to the implication of such complexes in important organic transformations, such as transition-metal-catalysed hydroboration[8] and selective C–H bond activation.[9] When compared to the carbon analogue (carbene), however, the roles of the boryl ligand in reaction chemistry are much more limited. Although a number of ligand exchange reactions at the metal centre have been described in which the metal–boron bond remains intact,[7] the chemistry of these complexes is generally characterised by loss of the boryl moiety, and examples of boron-centred reactivity remain extremely rare (vide infra).[10] More recently, complexes of amino- and arylborylenes (L_nM=BR),[11] which are comparable to vinylidene ligands,[5] have been reported and at least the former appear to contain a relatively robust metal–boron linkage.[12] Double-faced boron-based ligands, isolobal to carbonyl and carbyne, have only been successfully prepared in the case of [{(η^5-C_5H_5)Mn(CO)$_2$}$_2$(μ-B*t*Bu)][13] and [(CO)$_5$Cr{BSi(SiMe$_3$)$_3$}],[14] in which the absence of a π-

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donating substituent on boron afforded highly reactive species. Furthermore, the range of coordination modes observed for these ligand types is considerably smaller than that observed for the carbon analogues, with only borylene complexes exhibiting both terminal and bridging coordination modes.[11] Undoubtedly, one reason for the difference in the number of complexes reported with boron- and carbon-based ligands is the different synthetic strategies that must be adopted. Carbon monoxide and N-heterocyclic carbenes are kinetically stable as free molecules and this enables the facile synthesis of both carbonyl[1] and Fischer carbene complexes,[15] respectively, which in turn can serve as precursors for other ligand types. This has no parallel in transition-metal–boron chemistry in which all the ligands have to be formed and stabilised within the coordination sphere of the central metal. The availability of building-blocks from which a range of boron-based ligand types can be accessed is therefore essential to the growth of this field. We herein summarise recent advances in our research group concerning the use of half-sandwich iron–dihaloboryl complexes as precursors to a range of hitherto unprecedented types of classically bonded boron ligands.

Building Blocks

Almost one year ago, we reported[16] the structural characterisation of the dichloroboryl complex, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(BCl_2)]$ (**1**), originally prepared by Aldridge et al.[17] Although the synthesis represented a simple extension of the established route to half-sandwich iron–boryl complexes, the subsequent chemistry proved unprecedented. The reaction of **1** with 4-methylpyridine afforded the Lewis acid–base adduct, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(BCl_2{\cdot}NC_5H_4\text{-}4\text{-}Me)]$ (**2**), which despite representing a fundamental reaction for boranes, was unknown for transition-metal–boryl complexes.[16] The reason for this was probably twofold. Firstly, the vast majority of boryl complexes that had been prepared previously incorporated strongly π-donating substituents at boron and were thus too weakly Lewis acidic to form acid–base adducts.[7] Secondly, only a few transition-metal–boryl complexes retain the metal–boron linkage through boron-centred reactivity.[10] The former point is well demonstrated by the reluctance of even the difluoroboryl complexes reported by Norman to form Lewis acid–base adducts, although here steric factors may also play a role.[18] Of particular relevance to compound **1** is that the complex which exhibits the most extensive boron-centred reactivity reported to date is also a dichloroboryl complex, namely $[Os(BCl_2)Cl(CO)(PPh_3)_2]$.[19] This compound has been utilised by Roper and Wright[19] as a synthon to produce, most notably, tethered boryl and base-stabilised borylene complexes, although no attempt to form a Lewis acid–base adduct has been reported.

Abstract in German: *Die Lewisacidität von* $[(\eta^5\text{-}C_5R_5)Fe(CO)_2(BX_2)]$ *(**1**: R=H, X=Cl) und die Stabilität der Fe–B Bindung konnte durch die Reaktion mit 4-Methylpyridin zu dem entsprechenden Lewis Säure-Base Addukt belegt werden. Ausgehend von den analogen Komplexen **3** (R=Me, X=Br) und **5** (R=Me, X=Cl) wurden diese Eigenschaften für die Darstellung von heterodinuclear verbrückenden Borylenen, verbrückten Borylkomplexen und* μ_2*-Borid-Komplexen genutzt. Alle diese dimetallischen Komplexe weisen bislang beispiellose Koordinationsmodi für Bor auf.*

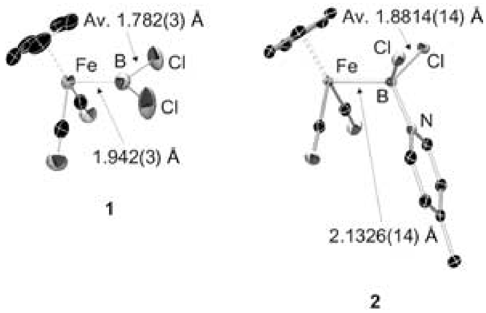


Figure 2. Molecular structures of compounds **1** and **2** (displacement ellipsoids are drawn at 50 % probability).

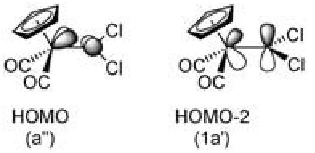


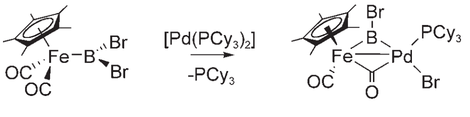
Figure 3. Relative orientations arising from overlap of the HOMO and HOMO−2 of the $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^+$ fragment with the vacant p orbital on boron.

A comparison of the molecular structures of complexes **1** and **2** revealed a 10 % elongation of the Fe–B bond upon coordination of the base (Figure 2). This was greater than that determined to arise from rehybridisation at boron (5.6 %) and thus it was concluded that the Fe–B bonding interaction in **1** must contain a significant π contribution. That the orientation of the single-faced boryl ligand in this complex would only allow π overlap with the HOMO−2 of the metal–ligand fragment and not the HOMO (Figure 3), together with the shortest Fe–B distance determined for a half-sandwich iron–boryl complex, was taken as evidence for the absence of any orientational preference in complexes of this type. These findings offered important experimental confirmation of both the high π acidity of the BCl_2 ligand and the low barrier to rotation about the Fe–B bond in such compounds, predicted previously by DFT studies.[20] Although the association of a significant π component with a low barrier to rotation about that bond may appear contradictory, calculations on a model system indicated that the π contribution to bonding was comparable for either orientation.[20] The origin of the low rotational barrier about the Fe–B bond, therefore, is more likely the near degeneracy of the mutually perpendicular donor orbitals rather than the absence of a π interaction.

The realisation that this boryl complex could undergo boron-centred reactivity with retention of the metal–boron linkage, and thus behave more like a borane than a boryl, led us to utilise this boryl compound in a number of reactions with transition metal centres that are known for boranes.

New Coordination Modes

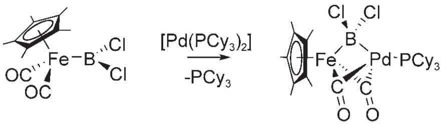
Bridging borylene complexes have traditionally been prepared by salt-elimination reactions between anionic transition-metal compounds and either dihaloboranes or dihalodiboranes.[11] These methods, however, have only afforded homobimetallic compounds. Attempts to prepare heterobimetallic examples from dihaloboranes by sequential salt-elimination steps with anionic complexes of different metals have proved unsuccessful due to differences in the nucleophilicity of the anions on changing the metal.[10] A new approach to these systems was thus clearly required. The oxidative addition of boron-halide bonds to low-valent transition-metal centres has been reported[21] and extension to dihaloboryl compounds would provide access to a heterobimetallic bridging borylene complex. Treatment of the dibromoboryl complex $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(BBr_2)]$ (**3**) with $[Pd(PCy_3)_2]$ afforded not only the first heterobimetallic bridging borylene compound, $[(\eta^5\text{-}C_5Me_5)Fe(CO)(\mu\text{-}CO)(\mu\text{-}BBr)PdBr(PCy_3)]$ (**4**), but also the first example of a bromoborylene ligand (Scheme 1).[22] Spectroscopic data suggested that the bromoborylene and the bromide ligands occupied mutually *trans* coordination sites at the palladium centre. This geometry differs from that observed in the structurally characterised ferrocenylborylene analogue, in which the borylene and bromide ligands are in a *cis* conformation.[22] The difference was attributed to greater steric bulk of the ferrocenyl group with respect to that of bromide destabilising the configuration in which the borylene and the extremely large PCy_3 ligand are mutually *cis*.



3 **4**

Scheme 1. Synthesis of the heterobinuclear bridging bromoborylene complex **4**.

It is interesting that when the reaction was repeated with the dichloroboryl species $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(BCl_2)]$ (**5**) oxidative addition did not occur. Instead, the novel symmetrically bridged boryl species $[(\eta^5\text{-}C_5Me_5)Fe(\mu\text{-}CO)_2(\mu\text{-}BCl_2)Pd(PCy_3)]$ (**6**) was formed (Scheme 2).[23] The difference in reactivity may be attributed to the increased thermodynamic strength of the B–Cl bond relative to that of B–Br and as such compound **6** may be viewed as a point along the B–X bond oxidative-addition reaction coordinate. Analysis of the X-ray structural data suggested that although electronically saturated at iron, the boryl compound behaves as a π acid by utilising the in plane π* orbitals of the μ-CO ligands and the vacant p orbital at boron, thus accepting electron density from the electronically unsaturated Pd-(PCy_3) fragment. This is a similar bonding situation to that previously proposed to account for the existence of semi-bridging carbonyls in the binuclear complex $[Cr(\mu\text{-}CO)_2(CO)(\eta^6\text{-}C_6H_6)Rh(CO)(\eta^5\text{-}C_5H_5)]$, on the basis of EHMO calculations.[24] Although bridging boryl complexes have been reported previously by Norman and Marder,[25] these compounds are highly asymmetric with respect to the two metal–boron interactions. This asymmetry can be attributed to the relatively low Lewis acidity of the boron centre, arising from the strongly π-donating catecholato substituents, leading to a weak metal–boron dative interaction. Thus, the reason why the novel symmetrical bridging mode is adopted in **6** would again appear to result from the high Lewis acidity of the dichloroboryl ligand. As a consequence of the dative interaction between the Pd centre and boron, this compound has some similarity to late transition-metal boratranes, for example $[Ru\{B(mt)_3\}(CO)(PPh_3)]$ (mt = 2-sulfanyl-1-methylazole).[26] The Pd→B bond in **6**, however, is only supported by two buttresses instead of the three common to boratranes. Furthermore, **6** may also be viewed as an analogue of the 4-methylpyridine adduct **2**, albeit with a transition-metal complex base.

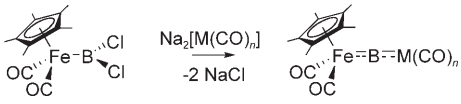


5 **6**

Scheme 2. Synthesis of the bridging dichloroboryl complex **6**.

Having demonstrated that the half-sandwich iron–dihaloboryl complexes could mimic both the Lewis acid–base and oxidative-addition chemistry of haloboranes, we ventured to explore further the transition-metal-based chemistry. The reaction of dihaloboranes with dianionic transition-metal carbonylates has proven the most general synthetic route to terminal borylene complexes.[11] From the six base-free examples known at the time, it appeared that, in addition to coordination, the presence of a strong π-donating substituent $\{\eta^5\text{-}C_5Me_5$, $N(SiMe_3)_2$ or 2,4,6-$Me_3C_6H_2\}$ at boron was required for stabilisation.[11] The hypersilylborylene complex, $[(CO)_5Cr\{BSi(SiMe_3)_3\}]$,[14] was the only example not to possess this feature and was thermally less stable as a result. Thus, with the knowledge that the iron–ligand fragment is a notable π base to boron, at least in the case of [(η5-

$C_5H_5)Fe(CO)_2(BCl_2)]$ (vide supra), we investigated the reaction of **1** with $Na_2[Cr(CO)_5]$. Although $^{11}B\{^1H\}$ NMR spectroscopy on the reaction mixture revealed a resonance at a chemical shift comparable to that computed for the desired complex, $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\mu_2\text{-}B)Cr(CO)_5]$, the product proved too thermally labile to be isolated. Increasing thermal stability by formal exchange of the cyclopentadienyl ligand for pentamethylcyclopentadienyl, however, afforded an isolable compound, namely $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(\mu_2\text{-}B)Cr(CO)_5]$ (**7**, Scheme 3).[27] An extension of this methodology also yielded the homobimetallic analogue, $[(\eta^5\text{-}C_5Me_5)Fe(CO)_2(\mu_2\text{-}B)Fe(CO)_4]$ (**8**). Both compounds exhibit particularly deshielded ^{11}B NMR resonances ($\delta = 204.7$, 190.9 ppm for **7** and **8**, respectively), comparable with those found for boron when interstitial within a transition-metal–ligand cluster.[28] Similarly low-field shifted resonances, however, have been observed in the ^{13}C NMR spectra of μ_2-carbide complexes, for example δ 446.3 ppm for $[(Cy_3P)_2(Cl)_2Ru{\equiv}C{-}Mo(CO)_5]$.[29] The molecular structures of both **7** and **8** were determined by single-crystal X-ray diffraction and both compounds contained an unprecedented linear M-B-M′ unit (M = Cr, M′ = Fe for **7**; M = M′ = Fe for **8**). A comparison of the bond lengths within this substructure with those reported for both proposed Cr–B and Fe–B single and double bonds suggested that this is probably best described by a model in which both bonds possess a partial π component, as opposed to localised single and double bonds.



4

7 (M = Cr, *n* = 5)
8 (M = Fe, *n* = 4)

Scheme 3. Syntheses of the μ_2-boride complexes **7** and **8**.

Conclusions and Outlook

It has been demonstrated that dihaloboryl complexes can serve as synthons for bimetallic systems in which the boron atom adopts a coordination mode that has not previously been accessible. Despite these advances, however, many challenges are still apparent in the field. With every new coordination mode comes the question of how best to describe the associated bonding picture and none of the compounds described have been subjected to quantum chemical studies. More fundamental, however, is that there is still relatively little experimental evidence that can be used to assess the nature of the bond between monovalent boron and transition metals. Although a number of theoretical studies have been published, more definitive experimental evidence is required. Such information is likely to be best provided by an experimental electron-density study. Finally, for the "organometallic" chemistry of these boron-based systems to be further extended, complexes need to be prepared that contain a range of other ligands at the metal centre. This has generally been limited to carbonyl and cyclopentadienyl groups due to the synthetic procedures employed. The heterodinuclear bridging borylene (vide supra) is actually the first compound to contain a halide and this may open the door to further functionalisation at the metal.

Acknowledgements

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