Metal Complexes Bearing Terminal Borylene Ligands

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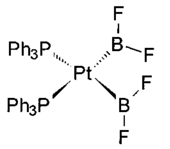
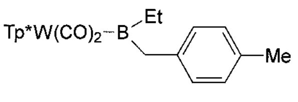
The understanding of metal–boron interactions and the challenge to build metal–boron (M–B) bonds provide extremely intriguing research areas in theoretical chemistry as well as in solid-state and molecular chemistry. The development of metallapolyboranes[1] and metallacarboranes,[2] compounds in which M–B multicenter bonds play a decisive role, began already in the 1960s. In addition, metal hydridoborates have been characterized more precisely,[3] simple neutral boranes or anionic borates[4] have served as π-donor ligands in transition metal complexes, and more recently fascinating complexes with interstitial boron atoms were described.[5] There have been early attempts at the synthesis of molecules with M–B two-electron, two-center (2e/2c) bonds,[6] and at that time complexes with borylene ligands (boranediyl, RB) were already considered.[7] However, the products obtained in these early experiments most probably do not possess metal–boron bonds, at least the physical data are by no means conclusive. There are also some doubts regarding the M–B σ bond for the majority of complexes for which it is suggested that a basic metal center interacts with a borane. Results pertinent to M–B 2e/2c bonds supported by direct structural evidence were only reported very recently,[8] and this work is primarily related to the investigation of metal-catalyzed hydroboration[9] and diboration of alkenes and alkynes.[10] A recent example representative for numerous similar complexes (in particular with catecholboryl groups[8]) is complex **1**,[11] an intermediate of the diboration. There are rather few examples for complexes in which a diorganoboryl group is linked to the metal (e.g., **2**;[12] Tp* = tris(3,5-dimethylpyrazol-1-yl)hydroborate), whereas it appears that the access to complexes bearing aminoboryl groups at the metal[8] is more facile (e.g., **3**[13]). Since it proved possible to prepare μ_2-borylene derivatives (e.g., **4**;[14] Cp′ = C_5H_4Me), the question of complexes with terminal borylene ligands was re-opened.



1



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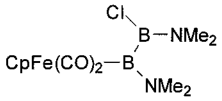

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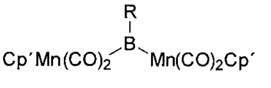
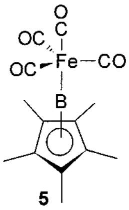


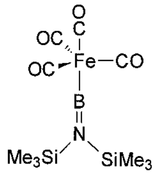
4a, R = NMe$_2$
4b, R = *t*Bu

Complexes with terminal borylene ligands have become a further milestone in the chemistry of metal–boron compounds. The synthesis and structural characterization of such complexes containing one terminal borylene ligand each has been reported recently.[15, 16] Cowley et al.[15] have obtained and fully characterized the tetracarbonyliron complex **5** from the reaction of $C_5Me_5BCl_2$ with $K_2[Fe(CO)_4]$. Braunschweig et al.[16] have mentioned the existence of an analogous complex **6** (not fully characterized), and have described the pentacarbonylchromium- and -tungsten complexes **7**.



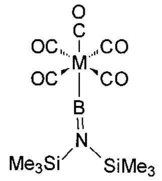
5

$\delta(^{11}B) = -35.3$



6

$\delta(^{11}B) = +88.2$



7

$\delta(^{11}B) = +92.3$ (M = Cr), 86.6 (M = W)

The bonding in **5** is similar to that in the homologous aluminum compound;[17] the boron atom possesses the formal oxidation number +1 and functions as a weak π acceptor. The chemical shift $\delta(^{11}B) = -35.3$ lies in the range typical of apical ^{11}B nuclei in *nido*-carboranes. However, to date there is no carbon derivative which can be compared directly with **5**. The question of the relative contributions of canonical structures is more important for **6** and **7** than for **5**. Thus, a carbyne-like canonical structure $[Ar^*Ga{\equiv}Fe(CO)_4]$ has been discussed for $[Ar^*GaFe(CO)_4]$[18] (Ar* = 2,6-bis(2,4,6-triisopropylphenyl)phenyl). Such a structure may play a role for complexes with terminal RB ligands (R = alkyl, aryl); however, these complexes have not been obtained as yet. The comparison of **6** and **7** with vinylidene complexes is evident, considering the isoelectronic substitution of BN by CC. The short B–N bond (133.8(8) pm) in **7** with M = W supports this argumentation.

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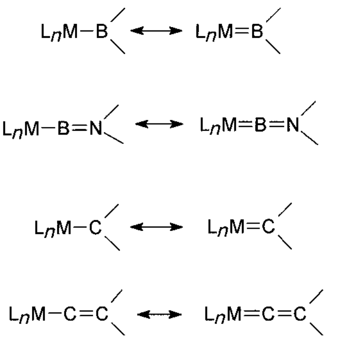
The ^{11}B resonances of **6** and **7** at low field are typical of the low-coordinate ^{11}B nuclei and their integration into the BN π system. An even more reduced magnetic shielding of ^{11}B nuclei can be predicted for the unknown complexes L_nM-BR (R = alkyl, aryl) (c.f. $\delta(^{11}B)$ values for **4** with $R = NMe_2$ (+103) and R = *t*Bu (+170)[14]). The weak π-acceptor properties of the $BN(SiMe_3)_2$ ligand are reflected by the length of the W–B bond in **7** (215.1(7) pm; 8 pm longer than in **2**[12]), and also by the $\tilde{\nu}(CO)$ frequencies which are shifted to lower wavenumbers in **7** with respect to comparable vinylidene complexes.

The comparison of the boryl metal complexes with carbene complexes and of the borylidene complexes **6** and **7** with vinylidene complexes reveal analogous bonding situations. The contribution arising from the canonical structure with the M=B bond is always significantly less important than from the one with the M=C bond (Scheme 1).



Scheme 1. Comparison of the possible canonical structures of metal complexes with borylene ligands with those of the corresponding carbon analogues.

Future efforts will focus on the synthesis of complexes with terminal borylene ligands RB (R = alkyl, aryl), the possibility of linking two or even more terminal borylene ligands to one metal atom, and on attempts to combine a variety of other ligands with terminal borylene ligands at the metal center. The enormous synthetic potential of boron chemistry and of transition metal chemistry have to be explored for these new systems, and this will almost certainly guarantee some surprises.

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