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2-Triorgano-silyl, -germyl, -stannyl and -plumbyl derivatives of 1,3-diisopropyl-benzo-1,3,2-diazaborolidine and related compounds and their reactions with $(\eta^2\text{-}C_2H_4)Pt(PPh_3)_2$†§

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A series of 1,3-diisopropyl-benzo-1,3,2-diazaborolidines 1–6 carrying ER_3 substituents of Group 14 at the boron atom (E = C, Si, Ge, Sn, Pb; R = Me, Ph) have been prepared. Their molecular structures have been determined. As expected, the B–E bond length increases along this series. Moreover, the orientation of the isopropyl groups relative to the ER_3 substituent is influenced by the steric demand of these substituents. The ^{11}B NMR data show a deshielding of the boron nucleus as the atomic weight of E increases. Oxidative addition reactions with $(\eta^2\text{-}C_2H_4)Pt(PPh_3)_2$ were successful only for the bromo derivative 1 and the trimethylstannyl derivative 5a; they failed for the triphenylsilyl, triphenylgermyl and triphenylstannyl compounds, indicating that steric effects play an important role in the successful oxidative addition to boryl-substituted bis(triphenylphosphane)platinum(II) complexes. The triphenylplumbyl derivative 6 reacted with $(\eta^2\text{-}C_2H_4)Pt(PPh_3)_2$ to give *cis*- and *trans*-diphenyl-bis(triphenylphosphane)platinum besides $Ph(Ph_3P)Pt(PPh_3)_2$. Obviously, the Pb–C bond is more reactive than the Pb–B bond. *Cis*-Platinum–boryl complexes were also obtained from $(Me_2N)_2B\text{–}SnMe_3$ and $(Me_2N)_2B\text{–}GeMe_3$ while the boranes $tmpB(SnMe_3)_2$ and $^iPr_2NB(SnMe_3)_2$ were unreactive. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: boryl–platinum complexes; benzo-1,3,2-diazaborolidines; Ge–B bond; Sn–B bond; X-ray structures

INTRODUCTION

The transition-metal-catalyzed additions of homoatomic bonds, such as Si–Si,[1–10] Sn–Sn[11–13] and B–B,[14–18] to unsaturated organic substrates is now well established as a powerful method for preparing reactive intermediates useful in synthetic organic chemistry. Meanwhile, similar reactions with compounds having bonds between elements of two different main group elements are gaining increased interest for the same purpose. For instance, palladium- or platinum-catalyzed additions of compounds featuring B–Si,[19–22] B–Sn[23–27] or Si–Sn[28–30] bonds have been shown to be extremely versatile. For example, the addition of B–Sn bonds to dienes yields a variety of carbocycles, even strained ones.[30] The great advantage of these reactions is their high regio- and stereo-selectivity. Therefore, the resulting heteroatom-bearing organic compounds have proved to be versatile intermediates in synthetic organic chemistry and allow numerous applications.

Oxidative additions of the B–E bonds (E = Si, Sn) to the metal center of low valent transition metal complexes have been proposed as key elementary steps to generate active species for these reactions. The oxidative addition-products are, however, with only few exceptions, so far unknown.[28] A theoretical study by Sakaki *et al.*[31] systematically investigated the addition of B–C, B–Si, B–Ge and B–Sn bonds to platinum(0) and palladium(0) complexes. According to these calculations, the transition metal products containing M–E

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†Dedicated to Professor Thomas P. Fehlner on the occasion of his 65th birthday, in recognition of his outstanding contributions to organometallic and inorganic chemistry.

§ Contribution to the Chemistry of boron, part 250. For part 249 see Braun U, Habereder T, Nöth H, Piotrowsky H, Warchhold M. *Eur. J. Inorg. Chem.* 2002; 1132.

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bonds (M: transition metal atom; E: main group element atom) are proposed to be rather stable except for the B–C addition, as the activation energies for the oxidative additions are generally low.

Systematic experimental studies of oxidative additions of B–E bonds (E = C, Si, Ge, Sn, Pb) to low valent organo-transition-metal fragments are, however, limited due to the lack of suitable B–E starting materials. For instance, a fully characterized series of simple compounds of the type $R_2B–ER_3$ (E = Group 14 element; R = Me) is, as yet, unknown. This is due to the decreasing stability of these compounds for the heavier representatives, particularly plumbylboranes. No stable compound having a B–Pb bond has been published so far.[32,33] In contrast, stannylboranes are readily accessible for electronically stabilized boron centers.[34–44]

The first part of this paper describes the synthesis of a series of diazaborolidines bearing B–C, B–Si, B–Ge, B–Sn and B–Pb bonds. The second part reports reactions of these compounds with $(\eta^2\text{-}C_2H_4)Pt(PPh_3)_2$.

SYNTHESIS

Because boron-bonded amino groups allow a stabilization of B–E bonds (both kinetically and thermodynamically) we chose the benzodiazaborolidinyl fragment for the purpose of obtaining a series of comparable compounds to the Group 14 derivatives, as we know that incorporation of the boron atom into a ring system adds additional stability. Thus, a series of bis(amino)boranes (**2**–**6**) were prepared from 2-bromo-(1,3-diisopropyl)benzo-1,3,2-diazaborolidine (**1**; obtained by standard methods, analogous to the preparation of 1,3,2-benzimidazolborole)[45] utilizing its metathesis with R_3ELi compounds. In a similar reaction, the triphenylgermyl-substituted benzodioxaborolane **7** was also obtained (Scheme 1).

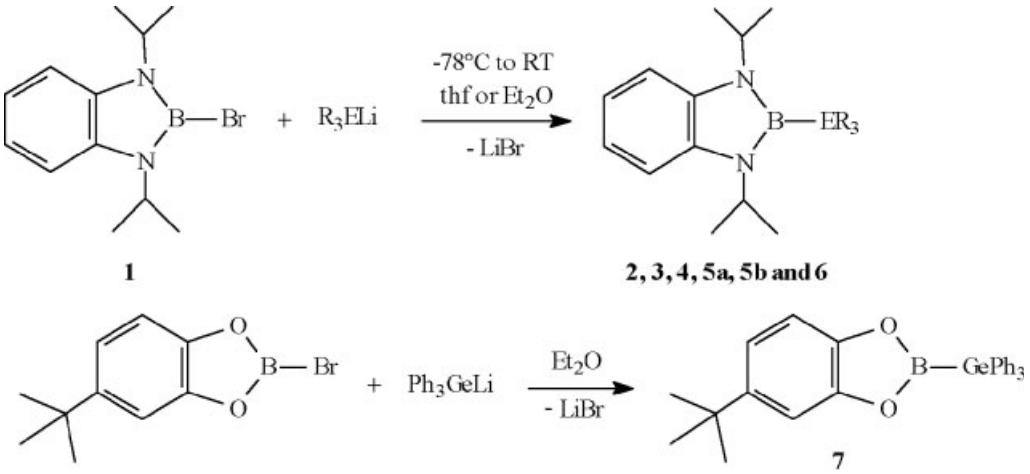
Compared with bis(dimethylamino)borane halides, the slightly strained five-membered ring system of benzodiazaborolidine allows halide replacement even at low temperatures, and it was expected that the products would be stabilized electronically via the two nitrogen atoms and sterically by the two diisopropyl groups. Another advantage of the heterocyclic fragment is that its derivatives crystallize readily. Compounds **2** to **7** were obtained in good to excellent yields, and, moreover, compounds **2, 3, 4, 5a, 5b** and **7** were obtained as single crystals. Although attempts to obtain single crystals of the lead compound **6** failed, it was nevertheless possible to isolate it as a polycrystalline material. Therefore, its powder diffraction pattern was determined, and it was fully characterized by NMR methods.

NMR DATA

^{11}B NMR data for compounds **2**–**6** are summarized in Table 1. One notes that the boron atom is deshielded with increasing atomic weight of the Group 14 atom. In particular, the chemical shift of the lead compound **6** is striking. This is an indication that the shielding is influenced primary by the spin-orbit-induced heavy-atom effect[48] of the heavy atom in question. However, there is almost no difference in the shielding between the *tert*-butyl and the trimethylsilyl derivative, in spite of an electronegativity difference between carbon and silicon of 0.9 units.

Table 1. ^{11}B NMR spectroscopic data for compounds **2**, **3**, **4**, **5a**, **5b** and **6**

	2	**3**	**4**	**5a**	**5b**	**6**
$\delta^{11}B$	29.5	29.9	30.5	32.8	32.4	39.6
$^1J(BE)$ (Hz)	—	—	—	970	962	1450



Scheme 1. ER_3 = CMe_3 (**2**), $SiPh_3$ (**3**), $GePh_3$ (**4**), $SnMe_3$ (**5a**). $SnPh_3$ (**5b**), $PbPh_3$ (**6**).

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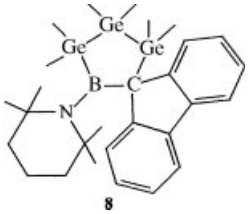

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This trend is much more regular than in the series of 1,3-dimethyl-2-halo-diazaborolidines, where the most electropositive halide iodine leads to the better shielding within the series [$(CH_2NMe)_2BF$: $\delta^{11}B = 23.4$; $(CH_2NMe)_2BCl$: $\delta^{11}B = 27.0$; $(CH_2NMe)_2BBr$: $\delta^{11}B = 24.8$; $(CH_2NMe)_2BI$: $\delta^{11}B = 21.3$].[48] Nevertheless, the observed tendency in compounds **2** to **6** agrees with earlier reports about boryl compounds of Group 14 elements.[48] A simple explanation on the basis of a +I effect of the Group 14 element substituents that could cause a decreasing π back-bonding from the nitrogen atoms resulting in a deshielding of the boron atoms is not justified because this argument stands in contrast to the observed B–N bond lengths, assessed from X-ray structure analysis (Table 2), as the B–N bond lengths for **3** to **5** differ only by 2 ppm. Therefore, the increase of B–E bond lengths has the most significant influence on the shielding, and this can be better explained by NMR shielding tensors by proper spin-orbit-induced heavy-atom effects on NMR chemical shifts, as shown for many organic iodo compounds.[46–47] Another interesting aspect of the ^{11}B NMR spectroscopic data is the observed $^1J_{BE}$ coupling constants. Owing to the relative abundance and sensitivity of the NMR active isotopes of Group 14, satellites in the ^{11}B NMR spectrum were observed only for the tin and lead compounds **5** and **6**. The observation of the NMR signals for the heteroatoms was more difficult, as the signals are significantly broad due to the quadrupole moment of the directly bonded boron atom. The phenyl groups of **5b** and **6** add to this trend. Consequently, the expected quartet signal in the ^{119}Sn spectrum was found only for **5a**, not for **5b** (see Figs 1 and 2), and no signal in the ^{207}Pb NMR spectrum for **6** could be detected.

Table 2. Selected bonding parameters of the benzodiazaborolidines **2** to **5** (E = C, Si, Ge, Sn)

	2	3	4	5a	5b
B(1)–E(1) (°)	1.612(3)	1.978(4)	2.061(4)	2.250(7)	2.265(4)
B(1)–N(1) (°)	1.449(3)	1.414(4)	1.435(4)	1.423(8)	1.412(5)
B(1)–N(2) (°)	1.449(3)	1.404(4)	1.433(4)	1.421(7)	1.430(5)
N(1)–B(1)–N(2) (°)	105.4(2)	104.8(3)	106.4(3)	106.5(5)	106.6(3)
E(1)–B(1)–N(1) (°)	124.3(2)	123.2(2)	122.9(2)	124.4(4)	122.9(3)
E(1)–B(1)–N(2) (°)	130.2(2)	131.5(3)	130.0(2)	128.9(4)	130.5(3)

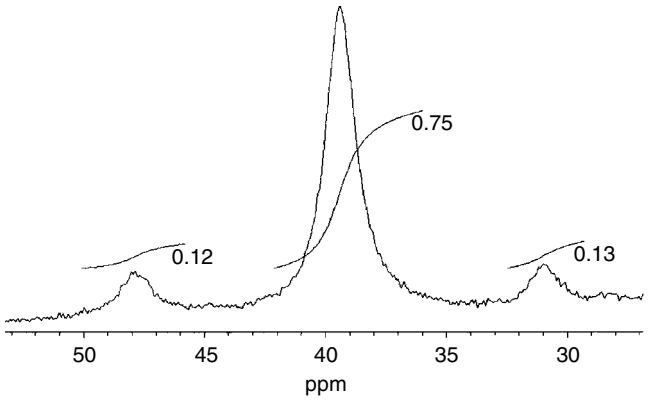

Figure 1. ^{11}B NMR spectrum of **6**.

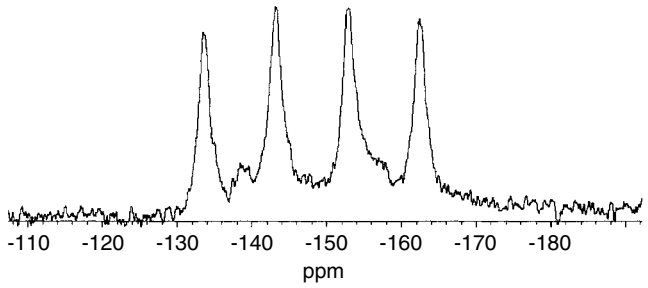

Figure 2. ^{119}Sn NMR spectrum of **5a**.

MOLECULAR STRUCTURES

The molecular structures of **2, 3, 4, 5a** and **5b** in the solid state are all similar (Figs 3–7). As expected, the

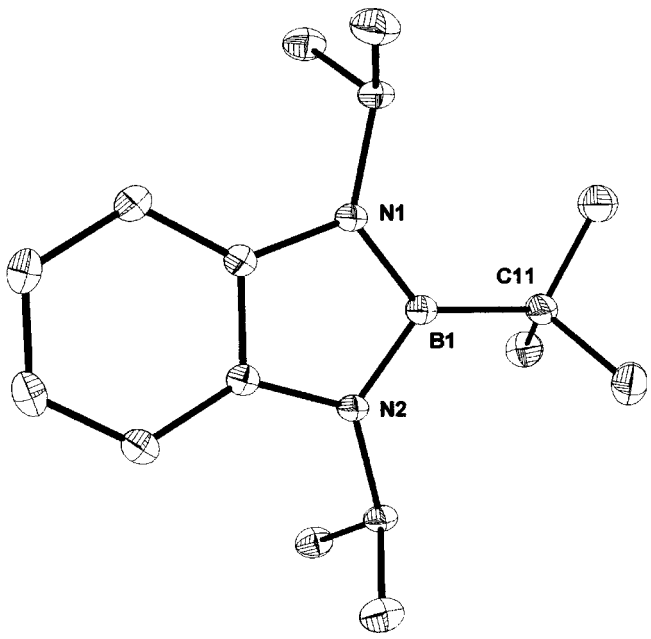

Figure 3. Molecular structure of **2** in the crystal. ORTEP plot with 25% probability ellipsoids.

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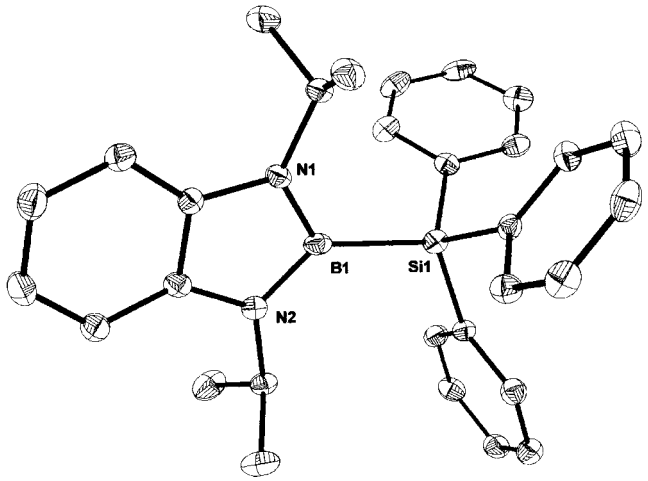

Figure 4. Molecular structure of **3** in the crystal. ORTEP plot with 25% probability ellipsoids.

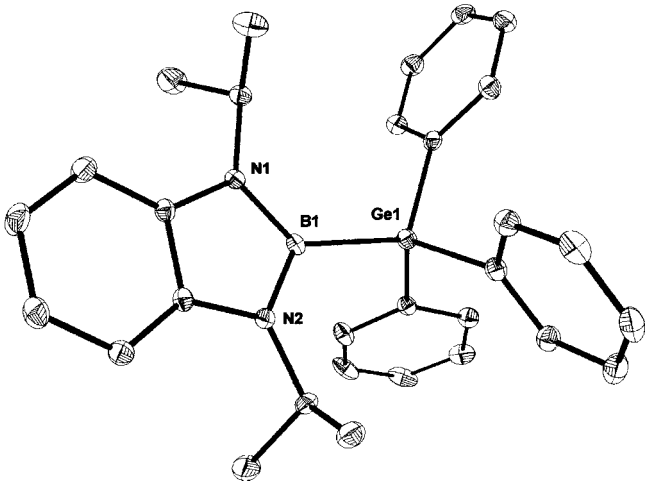

Figure 5. Molecular structure of **4** in the crystal. ORTEP plot with 25% probability ellipsoids.

bonding parameters of the 1,3-(diisopropyl)-benzo-1,3,2-diazaborolidine fragments are almost identical. Thus, the B–N bonds and the N–B–N angles do not change systematically with the increasing B–E distance. In each case the isopropyl group is bent away from the R_3E fragment, except for compound **5b**. This is surprising, because for **3, 4** and **5b** a different conformation results for the latter in spite of the fact that in each case triphenyl element groups are the substituents at the boron atom. This conformation is not retained in solution because the isopropyl groups are equivalent, as shown by the NMR data.

Although the B–N bond lengths differ at most by 3.7 pm, there seems to be a correlation between the B–N bond length and the electronegativity of the element E. Thus, the carbon atom-substituted compound **2** (χ(C) = 2.50) shows the longest B–N bonds (B–N = 1.449 Å), whereas

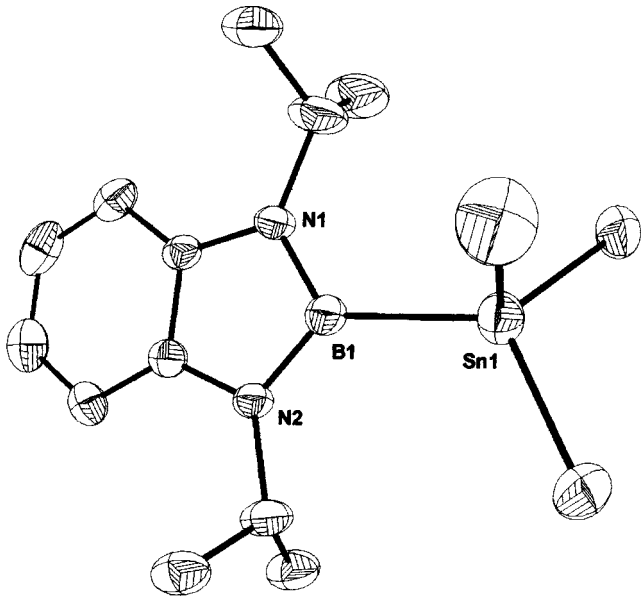

Figure 6. Molecular structure of **5a** in the crystal. ORTEP plot with 25% probability ellipsoids.

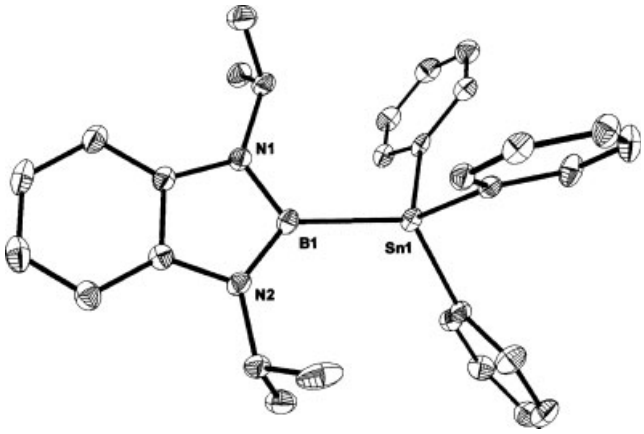

Figure 7. Molecular structure of **5b** in the crystal. ORTEP plot with 25% probability ellipsoids.

the tin- and silicon-substituted compounds **3** and **5b** [χ(Sn) = 1.72, χ(Si) = 1.74, electronegativities according to Rochow[49]] show the shortest B–N bonds. As expected, the benzodiazaborolidine unit is planar. And it is remarkable that the bond angles E–B–N(1) and E–B–N(2) are not equal but differ, particularly for the Ph_3E compounds, by 7.1 to 8.3°, showing that the ER_3 group is not bound symmetrically to the diaminoborane unit of the diazaborolidine, irrespective of the configuration resulting from different orientations of the isopropyl groups. We assume that this results from a packing effect.

The increase of B–E bond lengths along the series **2** to **5** was to be expected. As far as the B–Ge bond is concerned, it is significantly shorter than for the cyclic

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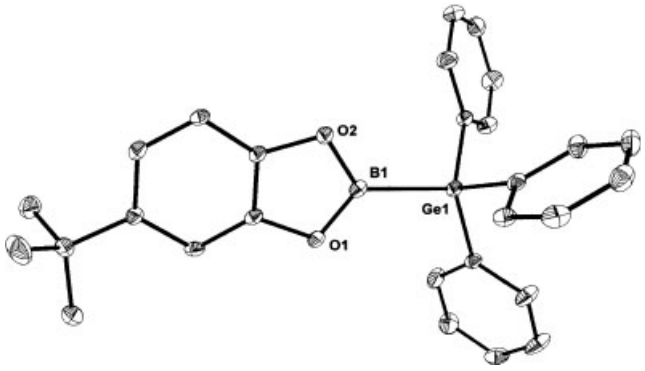

Figure 8. Molecular structure of **7** in ORTEP description; thermal ellipsoids are shown at a 25% probability level. Selected interatomic distances (Å) and angles (°): Ge(1)–B(1) 2.054(2), B(1)–O(2) 1.383(3), B(1)–O(1) 1.384(3); O(2)–B(1)–O(1) 111.3(2), O(2)–B(1)–Ge(1) 123.5(2), O(1)–B(1)–Ge(1) 125.1(2).

germylborane **8**,[50] which is 2.17(1) Å, the only Ge–B distance so far reported.

The B–Ge distance in **7**, 2.054(2) Å, is even shorter than in **4** (Fig. 8). The main reason for these short bonds seems to be due to an absence of steric interaction of the R_3E group with the strained diazaborolidine or dioxaborolane fragments.

A similar situation is also found for the B–Si and B–Sn bond length of **3, 5a** and **5b**. All these B–E bonds are among the shortest determined so far.[56,57] Since we were only able to obtain the plumbylborane **6** as a polycrystalline material, we measured its powder X-ray diffraction pattern. According to the powder diagrams for **5b** and **6**,‡ both compounds are isomorphous. However, although the data could easily be indexed, the structure of **6** could not be reliably determined due to the complexity of the structure and the high electron density at the lead atom. Therefore, we were unable to obtain data for the B–Pb bond length.

OXIDATIVE ADDITION REACTIONS

Several reactions of the new diazaborolidine compounds, particularly with $(\eta^2\text{-}C_2H_4)Pt(PPh_3)_2$, have been studied. Very different results were obtained, although we had expected that because of the similarity of the starting materials their behavior would be rather monotonous. The results are summarized in Scheme 2.

2-Bromo-1,3-diisopropyl-benzo-1,3,2-diazaborolidine (**1**; bdiabo-bromide) reacts with $(\eta^2\text{-}C_2H_4)Pt(PPh_3)_2$[58] to give *trans*-[Pt(bdiabo)Br$(PPh_3)_2$] (**9**), which was unambiguously identified by the NMR spectroscopic data: $\delta^{11}B = 27.9$ (line width, $h_{1/2} = 1180$ Hz) and $\delta^{31}P = 25.0$ ($^1J_{PPt} = 3066$ Hz). This corresponds with results observed for the reaction of $(\eta^2\text{-}C_2H_4)Pt(PPh_3)_2$ with catecholbromo borane.[59] The favored formation of the *trans* geometry can easily be understood as a consequence of the relative ordering of the *trans* influence for the ligands ($BR_2 > PPh_3 > Br$). Compound **9** shows a very low solubility in solvents like toluene or hexane. Attempts to dissolve **9** in $CHCl_3$ led to decomposition. The only product obtained from $CHCl_3$ solutions was *trans*-[PtH(Br)$(PPh_3)_2$] (**10**).#

Attempts to react compounds **3**, **4** or **5b** with $(\eta^2\text{-}C_2H_4)Pt(PPh_3)_2$ failed, even with gentle warming. In contrast, the reaction of **5a** with $(\eta^2\text{-}C_2H_4)Pt(PPh_3)_2$ yielded *cis*-[Pt(bdiabo)$(SnMe_3)(PPh_3)_2$] (**11**) in good yield. The different behavior of **5a** and **5b** may be explained by a better steric shielding of the B–Sn bond in **5b**. An electronic effect is less likely, as the bond lengths, the bond angles and the ^{11}B shifts are very similar for both compounds. NMR data of complex **11** are very informative, as it shows no symmetry and possesses seven different magnetically active nuclei. Consequently, the NMR spectra are complex due to the coupling between these atoms. Hence, many coupling constants could be determined. The ^{11}B NMR spectrum shows a broad signal at $\delta^{11}B = 44.7$ ($h_{1/2} = 1000$ Hz). This resonance proves the presence of a B–Pt bond. Compared with the boron NMR signal of **9** ($\delta^{11}B = 27.9$), the remarkable low field shift for **11** is striking. A double doublet is observed in the ^{119}Sn NMR spectrum, $\delta^{119}Sn = -48.4$ (dd, $^2J_{PSn} = 1462$ Hz, $^2J_{PSn} = 150$ Hz), confirming that the tin atom stands *cis* ($^2J_{PSn} = 150$ Hz) as well as *trans* ($^2J_{PSn} = 1462$ Hz) to one PPh_3 ligand. Moreover, the ^{119}Sn NMR signal shows the expected satellites $^1J_{PtSn} = 10\,130$ Hz. Consequently, the ^{31}P NMR spectrum exhibits two sets of signals: one very broad set at $\delta^{31}P = 30.2$ ($^1J_{PPt} = 1560$ Hz, $^2J_{PSn} = 150$ Hz) and a sharp one at $\delta^{31}P = 27.4$ (m, $^1J_{PPt} = 2448$ Hz, $^2J_{PP} = 17$ Hz, $^2J_{P^{119}Sn} = 1462$ Hz, $^2J_{P^{117}Sn} = 1431$ Hz). Owing to the observed coupling constants (see Figs 9 and 10), the broad signal set can be assigned to the phosphorus atom *trans* to the boron atom.

Surprisingly, the ^{31}P NMR data of **11**, especially the coupling $^2J_{PSn}$, differs significantly from the data of the *cis* complex $[(Ph_3P)_2Pt(SnMe_3)(Bcat)]$ (cat = catecholate), which was reported to be formed by the reaction of $[(Ph_3P)_2Pt(Bcat)_2]$ and Me_6Sn_2.[59] Since the structure of **11** was confirmed by X-ray crystallography too, there is no doubt that the observed NMR spectroscopic data originate from compound **11**. The ^1H and ^{13}C NMR spectra show two sets of signals for the isopropyl groups, indicating a hindered rotation about the B–Pt bond, whereas the methyl groups attached to the tin

‡ Data were obtained with a STOE powder diffractometer Stadi P (Debey Scherrer geometry) using Cu Kα radiation ($\lambda = 154.05$ pm). The intensities were measured with a linear PSD area detector. For the solution of the structure the programs WinXPOW (Fa. STOE)[51] GUFI[52] EXTRA[53] und GSAS[54] were employed.

Compound **10** was identified by X-ray structure determination. There is one toluene molecule besides **10** in the asymmetric unit. The structure of **10** is not shown here. Monoclinic cell parameters: $a = 9.2467(5)$ Å, $b = 18.588(1)$ Å, $c = 21.926(1)$ Å, $\beta = 96.634(1)°$, $V = 3743.4(4)$ Å^3, $Z = 4$. Structural data have also been deposited with the Cambridge Crystallographic Data Centre (CCDC).

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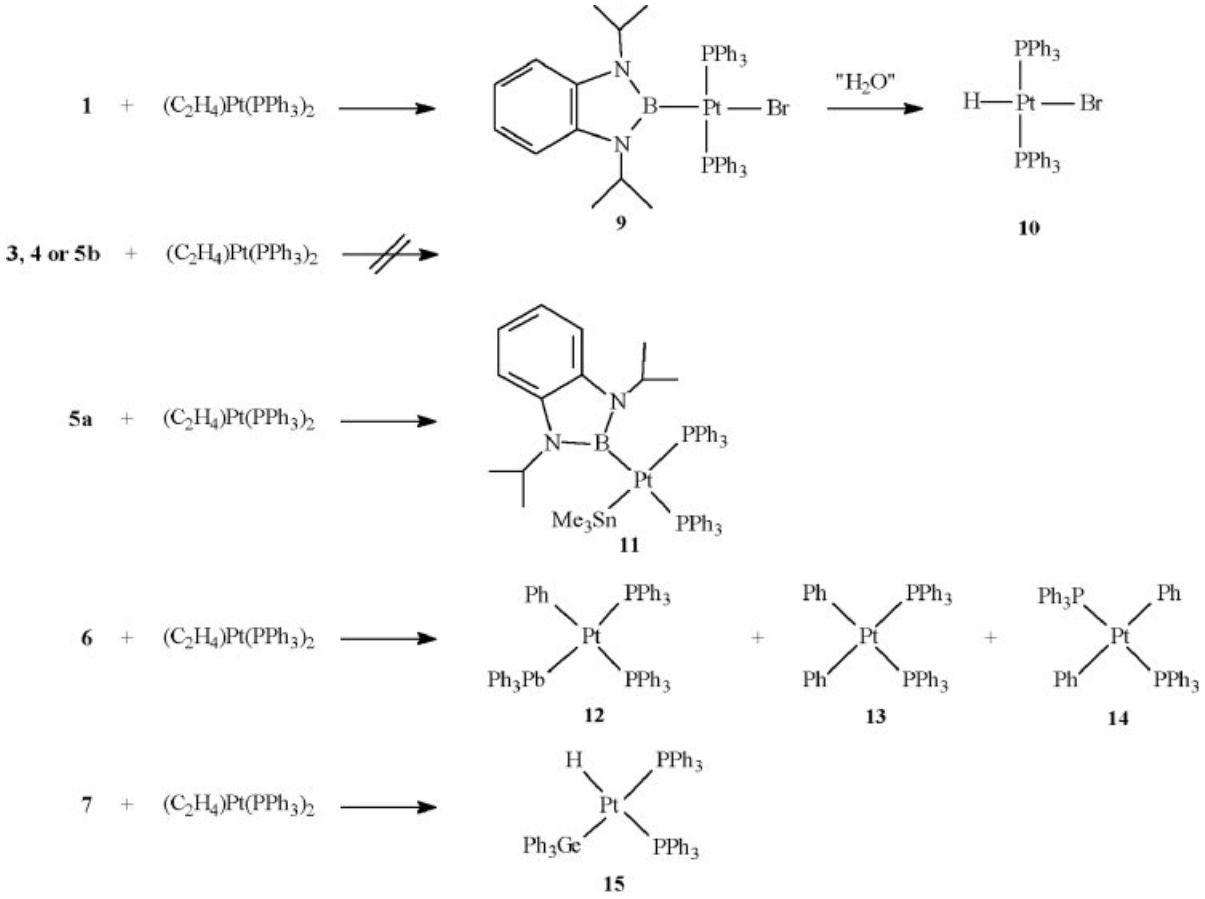

Scheme 2.

atom give rise to only one set of signals, thereby indicating free rotation about the Pt–Sn bond. This leads to the conclusion, that the hindered rotation of the B–Pt bond may be due to steric effects and/or π back-bonding from the platinum atom to the boron atom.

The reaction of **6** with $(\eta^2\text{-}C_2H_4)Pt(PPh_3)_2$ did not generate a new platinum–boryl complex; rather, the known compounds **12**, **13** and **14** were formed.[60–62] Their mechanism of formation remains unclear, especially as we were not able to isolate and identify a boron-containing product. But, as compounds **12**, **13** and **14**[&] are also obtained from the reaction of $(\eta^2\text{-}C_2H_4)Pt(PPh_3)_2$ with Ph_6Pb_2,[60] it is likely that the platinum fragment prefers to insert in the C–Pb bond.

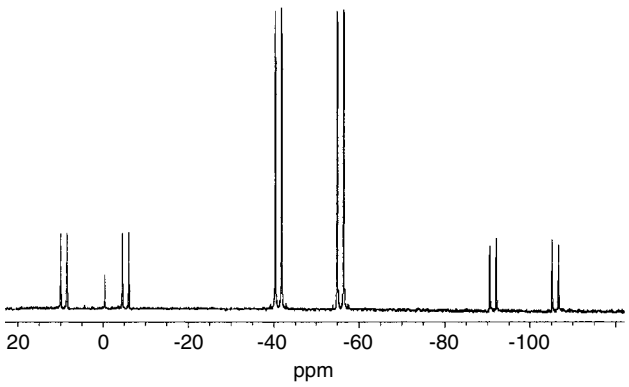

Figure 9. ^{119}Sn NMR spectrum of **11**.

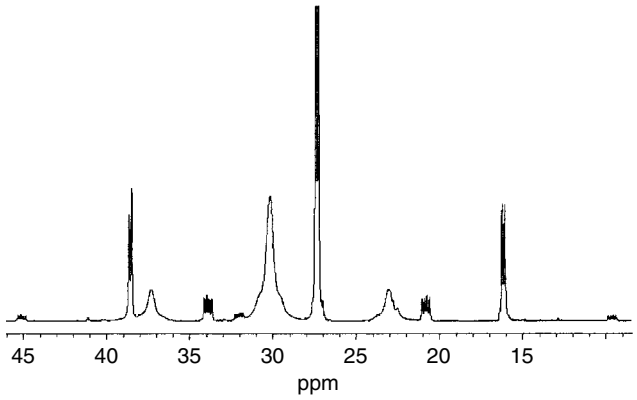

Figure 10. ^{31}P NMR spectrum of **11**.

[&] The cell of compound **14** contains one toluene molecule per asymmetric unit. Monoclinic cell parameters: $a = 22.216(3)$ Å, $b = 10.539(2)$ Å, $c = 18.036(2)$ Å, $\beta = 92.707(2)°$, $V = 34218(1)$ Å^3, $Z = 4$. The structural data are deposited with the CCDC.

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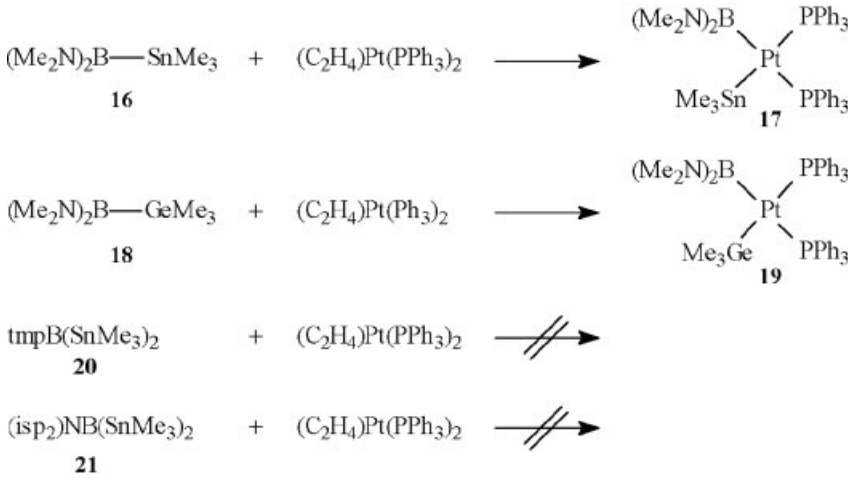

Scheme 3.

Table 3. Selected NMR spectroscopic data for compounds **17** and **19**

Compound	δ^{11}B	δ^{31}P(*trans*-B)	δ^{31}P(*cis*-B)	δ^{119}Sn
17	45.6	$\delta = 32.1$ ^2J(PSn) = 146 Hz ^1J(PPt) = 1392 Hz	$\delta = 31.0$ ^1J(PPt) = 2681 Hz ^2J(P^{119}Sn) = 1509 Hz ^2J(P^{117}Sn) = 11 438 Hz ^3J(PP) = 15 Hz	$\delta = -28.4$ ^2J(PSn) = 146 Hz ^2J(PSn) = 1508 Hz ^1J(SnPt) = 12 470 Hz
18	46.7	$\delta = 31.8$ ^1J(PPt) = 1200 Hz	$\delta = 31.2$ ^1J(PPt) = 2220 Hz ^3J(PP) = 15 Hz	

The reaction of **7** with (η^2-C_2H_4)Pt(PPh_3)$_2$ also gives an unexpected product. The only platinum-containing product was the hydrido complex **15**, a compound that was obtained directly by reacting Ph_3GeH with (η^2-C_2H_4)Pt(PPh_3)$_2$. As **7** was provided as a crystalline material, and as we were able to reproduce the reaction several times, the presence of Ph_3GeH as an impurity of **7** could be excluded.

In addition, some reactions of (η^2-C_2H_4)Pt(PPh_3)$_2$ with other Group 14 boryl compounds, which are readily available, were studied and allowed the synthesis of further boryl platinum complexes. The results are summarized in Scheme 3.

Once again, it transpired that only a few of the Group 14 boryls were suitable for oxidative addition reactions with (η^2-C_2H_4)Pt(PPh_3)$_2$. Thus, the stannylborane **16** and the germylborane **18** produce the oxidative addition complexes with the Pt(PPh_3)$_2$ fragment in excellent yields, whereas the bis(stannyl)boranes **20** and **21** were inert under similar reaction conditions. We attribute the failure of oxidative addition to the better steric shielding of the boron atom by the rather bulky amino groups of **20** and **21**. The structures of the platinum complexes **17** and **19** could both be deduced from NMR spectroscopy and by X-ray crystallography.

Selected NMR spectroscopic data for **17** and **19** are summarized in Table 3. The data for **17** are very similar to those of **11**. The almost identical ^{11}B NMR shifts (**11**: $\delta^{11}B = 44.7$; **17**: $\delta^{11}B = 45.6$) were unexpected, because the starting materials show a significant difference in the ^{11}B shielding ($(Me_2N)B-SnMe_3$: $\delta^{11}B = 39.0$; **5a**: $\delta^{11}B = 32.8$). Obviously, the electronic environment at the boron atom in the boryl platinum complexes is influenced by the platinum center, whereas the BN_2 unit of the boryl group is of less importance. Another interesting feature of the NMR data is that both the ^{1}H and ^{13}C NMR spectra show only one set of signals for the dimethylamino groups, consistent with a free rotation about the B–Pt and the B–N bonds. For compounds **17** and **19**, a strong π back-bonding from the platinum to the boron atom can be ruled out. It seems to be quite clear that the benzodiazaboryl compounds are more reactive than the bis(dialkylamino)boron compounds $(Me_2N)_2B-ER_3$, and this can be attributed to the strain at the boron atom in the heterocycle, which makes the boron center more Lewis acidic.

Whereas the stannylborane **16** reacts easily with (η^2-C_2H_4)Pt(PPh_3)$_2$ by oxidative addition, neither Pd(PPh_3)$_4$ nor

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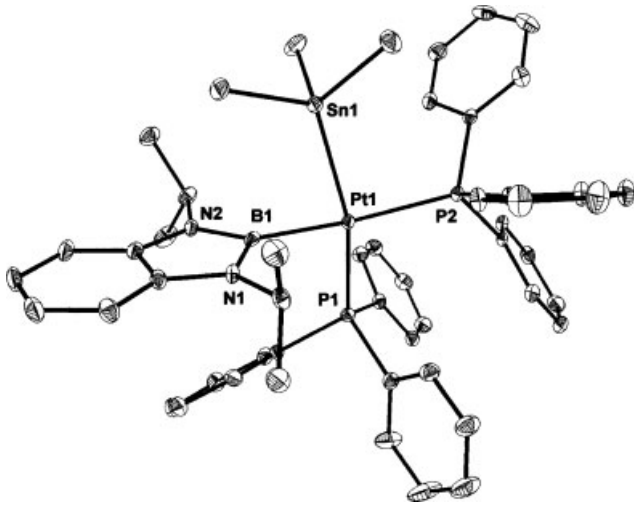

Figure 11. Molecular structure of **11** in the crystal; thermal ellipsoids are shown at a 25% probability level. Selected bond lengths (Å) and bond angles (°): Pt(1)–B(1) 2.085(6), Pt(1)–P(1) 2.301(1), Pt(1)–P(2) 2.376(1), Pt(1)–Sn(1) 2.6339(4), B(1)–N(2) 1.446(8), B(1)–N(1) 1.454(7); B(1)–Pt(1)–P(1) 90.5(2), B(1)–Pt(1)–P(2) 165.7(2), P(1)–Pt(1)–P(2) 99.74(5), B(1)–Pt(1)–Sn(1) 77.9(2), P(1)–Pt(1)–Sn(1) 164.62(4), P(2)–Pt(1)–Sn(1) 93.50(3), N(2)–B(1)–N(1) 105.1(5), N(2)–B(1)–Pt(1) 131.2(4), N(1)–B(1)–Pt(1) 123.5(4).

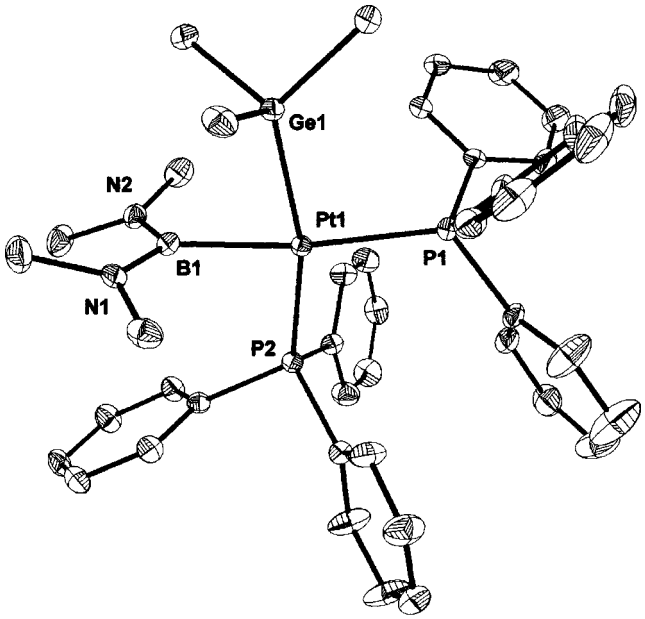

Figure 12. Molecular structure of **19** in ORTEP description; thermal ellipsoids are shown at a 25% probability level. Selected bond lengths (Å) and bond angles (°): Pt(1)–B(1) 2.139(6), Pt(1)–P(1) 2.377(1), Pt(1)–P(2) 2.304(1), Pt(1)–Ge(1) 2.470(1), N(1)–B(1) 1.418(8), N(2)–B(1) 1.422(7); B(1)–Pt(1)–P(1) 172.5(2), B(1)–Pt(1)–P(2) 87.0(2), P(1)–Pt(1)–P(2) 99.25(5), B(1)–Pt(1)–Ge(1) 78.7(2), P(1)–Pt(1)–Ge(1) 95.03(4), P(2)–Pt(1)–Ge(1) 165.72(4), N(2)–B(1)–N(1) 120.7(5), N(1)–B(1)–Pt(1) 120.7(4), N(2)–B(1)–Pt(1) 118.5(4).

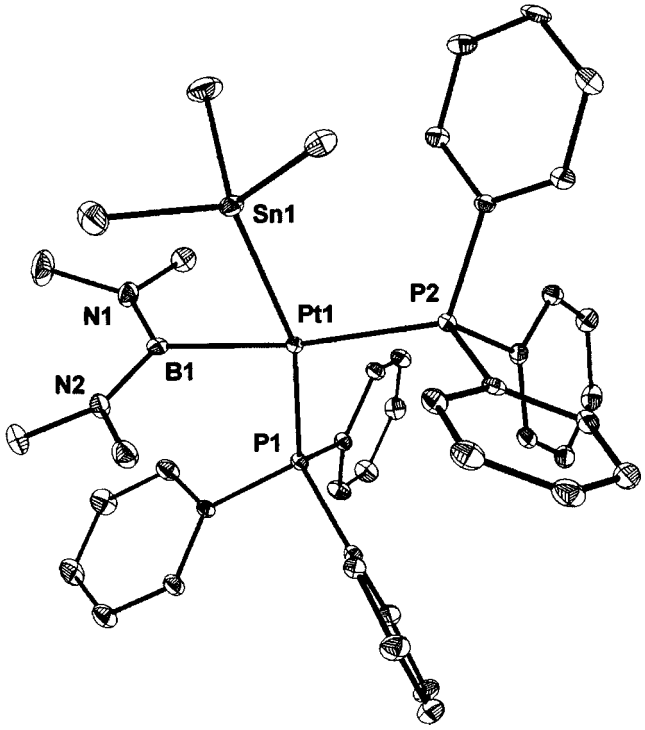

Figure 13. ORTEP plot of the molecular structure of **17** in the crystal; thermal ellipsoids are shown at a 25% probability level. Selected bond lengths (Å) and bond angles (°): Pt(1)–B(1) 2.136(4), Pt(1)–P(1) 2.303(1), Pt(1)–P(2) 2.369(1), Pt(1)–Sn(1) 2.6289(6), N(1)–B(1) 1.435(5), N(2)–B(1) 1.420(5); B(1)–Pt(1)–P(1) 87.6(1), B(1)–Pt(1)–P(2) 170.3(1), P(1)–Pt(1)–P(2) 102.15(4), B(1)–Pt(1)–Sn(1) 74.4(1), P(1)–Pt(1)–Sn(1) 161.63(2), P(2)–Pt(1)–Sn(1) 95.92(3), N(2)–B(1)–N(1) 121.6(3), N(1)–B(1)–Pt(1) 118.5(3), N(2)–B(1)–Pt(1) 119.8(3).

$(Ph_3P)_3RhCl$ are suitable reactants. This is not expected, as palladium complexes proved to be extremely good catalysts for borylstannylation reactions. Moreover, it is well known that stannyl–boryl–palladium complexes are stable compounds.[28–30] We assume that the low reactivity of **16** towards $Pd(PPh_3)_4$ and $(Ph_3P)_3RhCl$ can be explained be steric hindrance. Therefore, using less bulky ligands with the palladium or rhodium complexes may well provide a proper route to boryl–palladium and boryl–rhodium complexes.

MOLECULAR STRUCTURE OF THE PLATINUM COMPLEXES

Compounds **11**, **17** and **19** (see Figs 11,12 and 13) all exhibit a *cis* orientation of the Ph_3P ligands with a planar geometry around the platinum atom. The repulsion minimized by the near-perpendicular orientation of the BN_2 unit to the mean $BPtP_2$ plane results in only minor distortions from planarity. In compound **11** the N_2B plane stands exactly orthogonal

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to the platinum plane, $N_2B/PPtSn = 90°$, whereas for compounds **17** and **19** the interplanar angles $N_2B/PPtSn$ are 82.6° and $N_2B/PPtGe$ 82.2° respectively. This arrangement of the diazaborolidinyl group generates small B–Pt–P, B–Pt–Sn or B–Pt–Ge angles. Moreover, the orthogonal orientation of the boryl ligand meets the orbital requirement for an overlap between the filled platinum d_{xy} orbital and the empty *p*-orbital at the boron atoms. This results in Pt–B distances of Pt(1)–B(1) = 2.085(6) Å for **11**, Pt(1)–B(1) = 2.139(6) Å for **17** and Pt(1)–B(1) = 2.136(4) Å for **19**. Known Pt–B bond lengths range from 2.031 to 2.100 Å.[63] *trans*-$PtCl(PPh_3)_2(1,2\text{-}O_2BC_6H_4)$ shows the shortest Pt–B bond length so far (2.008 Å).[59] These short bonds are found in platinum complexes carrying dioxoborolanyl or catecholboryl groups. The longer Pt–B bonds in **11**, **17** and **19** are most likely the consequence of B–N π back-bonding, which competes with possible Pt–B π back-bonding. The Pt–P bond length *trans* to the boryl ligands is slightly longer than the bond length for the phosphane *trans* to the stannyl or germyl group. This indicates some *trans* influence for the boryl ligand due to the BN stabilized boryl groups. On the other hand, the influence of the Pt–B bond on the B–N bond induces comparatively longer B–N bonds than are usually observed for diaminoboranes. This effect can be seen by comparing these distances in **11** [B(1)–N(2) = 1.446(8) Å and B(1)–N(1) 1.454(7) Å] with those of **5a** [B(1)–N(1) = 1.423(8) Å and B1–N(2) = 2.421(7) Å]. For a further insight into the bonding situation, however, a theoretical analysis is necessary. Compounds **17** and **19** possess B–N bonds with an average bond length of ~1.42 Å. The interplanar angles between the NMe_2 groups and the boryl group are only 21.1°, allowing good BN-π overlap.

The molecular structure of complex **15** (see Fig. 14) does not exhibit any unusual detail. A planar geometry (sum of angles at platinum equals 360°), typical for d^8 complexes, is realized. The hydrogen atom attached to the platinum was found in the difference Fourier plot, but its position could not be properly refined. The bond lengths Pt–P(1) and Pt–P(2) are comparable, indicating that the *trans* influence of the Ph_3Ge group is of the same kind as the hydrogen ligand. The Pt–Ge atom distance of 2.440(4) Å lies within the expected range.[63] The angles at the platinum center are determined mainly by the different space requirements of the hydrogen atom compared with the spacious Ph_3Ge or Ph_3P groups. This leads to significant deviations from 90° bond angles: P(2)–Pt(1)–P(1) = 104.92(3)°, P(2)–Pt(1)–Ge(1) = 159.27(2)° and P(1)–Pt(1)–Ge(1) = 95.20(2)°. These values show that the Ph_3Ge group demands less space than a Ph_3P group. This is in line with the relatively long Pt–Ge bond length, compared with the Pt–P bond length.

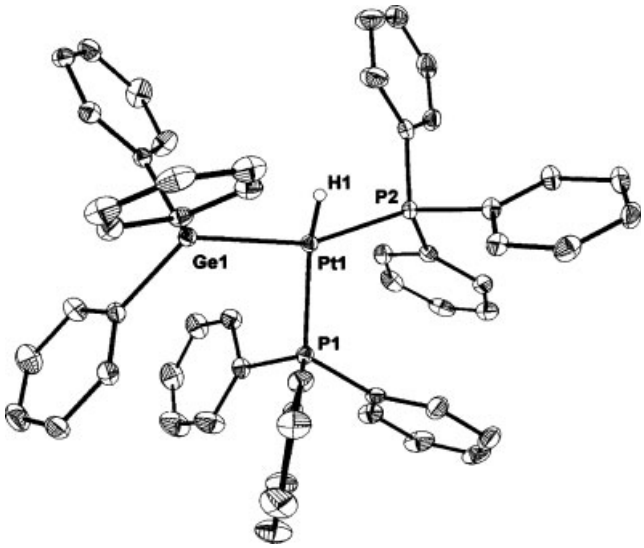

Figure 14. ORTEP plot of the molecular structure of **15** in the crystal; thermal ellipsoids are shown at a 25% probability level. Selected bonds lengths (Å) and bond angles (°): Pt(1)–P(2) 2.2917(8), Pt(1)–P(1) 2.3082(8), Pt(1)–Ge(1) 2.4400(4); P(2)–Pt(1)–P(1) 104.92(3), P(2)–Pt(1)–Ge(1) 159.27(2), P(1)–Pt(1)–Ge(1) 95.20(2).

EXPERIMENTAL

General

All experimental manipulations were conducted under anhydrous conditions in an atmosphere of dry dinitrogen or argon gas employing standard Schlenk and vacuum line techniques. Solvents were dried by conventional methods. Starting materials were prepared by literature methods. NMR: Jeol 270 and 400 and Bruker 200 spectrometers [standards: tetramethylsilane (^1H, ^{13}C), external $BF_3{\cdot}OEt_2$ (^{11}B), external 85% H_3PO_4 (^{31}P) and external $SnMe_4$ (^{119}Sn)]. X-ray structure determinations: Siemens P4 diffractometer equipped with an area detector, Mo K_α radiation, graphite monochromator, LT device.

2-*tert*-Butyl-1,3-di(isopropyl)-benzo-1,3,2-diazaborolidine (2)

To a stirred solution of 2-bromo-1,3-di(isopropyl)-benzo-1,3,2-diazaborolidine (**1**) (0.52 g, 1.5 mmol) in hexane (20 ml was added *tert*-butyllithium (1 ml, 1.5 M solution in hexane) at 0 °C. A colorless precipitate formed immediately. After stirring for 1 day at ambient temperature, the solid was removed by filtration. The volume of the filtrate was reduced and the solution kept at −30 °C The crystals that formed within a few days were isolated. Yield: 0.35 g (90%) of **2**, colorless prisms, which decomposed at 122 °C. ^1H NMR (270 MHz, C_6D_6): $\delta = 1.28$ (s, 9H, $CCH_3)_3$), 1.36 (d, 12H, $^3J_{HH} = 7.2$ Hz, $CH(CH_3)_2$), 4.64 (m, $^3J_{HH} = 7.2$ Hz, 2H, $CH(CH_3)_2$), 7.03 (dd, $^3J_{HH} = 6.0$ Hz, $^4J_{HH} = 3.0$ Hz, 2H, CH-arom), 7.29 (dd, $^3J_{HH} = 6.0$ Hz, $^4J_{HH} = 3.0$ Hz, 2H, CH-arom). ^{13}C NMR (100 MHz, C_6D_6): $\delta = 20.8$ ($CH(CH_3)_2$), 30.7 ($C(CH_3)_3$), 45.3 ($CH(CH_3)_2$), 113.0, 117.7, 136.6 (all C-arom). ^{11}B NMR (64 MHz, C_6D_6): $\delta = 29.5$ ($h_{1/2} = 165$ Hz). Anal. Found: C, 74.39; H, 10.75; N, 10.72. Calc. for $C_{16}H_{27}BN_2$ (258.2): C, 74.43; H, 10.54; N, 10.85%.

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2-Triphenylsilyl-1,3-di(isopropyl)-benzo-1,3,2-diazaborolidine (3)

A stirred suspension of Lithium powder (0.13 g, 20.0 mmol) in tetrahydrofuran (THF; ~40 ml) was treated with triphenylsilylchloride (0.45 g, 1.5 mmol) and stirred at ambient temperature for 12 h. The solid was then removed by filtration and the filtrate cooled to −78 °C. Subsequently, **1** (0.36 g, 1.3 mmol) dissolved in hexane (20 ml) was added. After stirring for 1 h at ambient temperature, all volatile components were removed *in vacuo*. The solid, brownish residue was treated with hexane (50 ml). After filtration the solvent was slowly evaporated in a vacuum to afford solid, pure **3** (0.36 g, 62%) decomposing at ~145 °C. ^{1}H NMR (400 MHz, C_6D_6): $\delta = 1.17$ (d, 12H, $^3J_{HH} = 6.9$ Hz, $CH(CH_3)_2$), 4.19 (m, $^3J_{HH} = 6.9$ Hz, 2H, $CH(CH_3)_2$), 7.06 (dd, $^3J_{HH} = 6.0$ Hz, $^4J_{HH} = 3.2$ Hz, 2H, CH-arom), 7.19 (m, 9H, m-Ph-H, p-Ph-H), 7.30 (dd, $^3J_{HH} = 6.0$ Hz, $^4J_{HH} = 3.2$ Hz, 2H, CH-arom), 7.80 (m, 6H, *o*-Ph-H). ^{13}C NMR (100 MHz, C_6D_6): $\delta = 21.3$ ($CH(CH_3)_2$), 48.0 ($CH(CH_3)_2$), 113.2, 118.5, 128.1, 129.1, 136.5, 137.0, 137.6 (all C-arom). ^{11}B NMR (64 MHz, C_6D_6): $\delta = 29.9$ ($h_{1/2} = 225$ Hz). Anal. Found: C, 78.35; H, 7.21; N, 5.98. Calc. for $C_{30}H_{33}BN_2Si$ (460.5): C, 78.25; H, 7.22; N, 6.08%.

2-Triphenylgermyl-1,3-di(isopropyl)-benzo-1,3,2-diazaborolidine (4)

Ph_3GeLi (2.4 mmol)[68] was freshly prepared in 40 ml of diethyl ether. The solution was stirred and cooled to −78 °C, and then treated with a solution of **1** (0.67 g, 2.4 mmol) in hexane (20 ml). After stirring for 1 h at ambient temperature, all volatile components were removed *in vacuo* and the solid residue treated with hexane. The filtrate was cooled to −30 °C. The crystals that settled within a few days were isolated. Yield: 0.98 g (81%) of **4**, colorless prisms, m.p. 158 °C. ^{1}H NMR (400 MHz, C_6D_6): $\delta = 1.18$ (d, $^3J_{HH} = 7.0$ Hz, 12H, $CH(CH_3)_2$), 4.26 (m, $^3J_{HH} = 7.0$ Hz, 2H, $CH(CH_3)_2$), 7.05 (dd, $^3J_{HH} = 7.0$ Hz, $^4J_{HH} = 2.9$ Hz, 2H, C*H*-arom), 7.19 (m, 9H, *m*-Ph-*H* and *p*-Ph-*H*), 7.30 (dd, $^3J_{HH} = 7.0$ Hz, $^4J_{HH} = 2.9$ Hz, 2H, C*H*-arom), 7.72 (m, 6H, *o*-Ph-*H*). ^{13}C NMR (100 MHz, C_6D_6) $\delta = 21.4$ ($CH(CH_3)_2$), 48.1 ($CH(CH_3)_2$), 113.1, 118.6, 128.3, 128.5, 135.7, 137.5, 139.5 (all *C*-arom). ^{11}B NMR (64 MHz, C_6D_6): $\delta = 30.5$ ($h_{1/2} = 160$ Hz). Anal. Found: C, 70.74; H, 6.51; N, 5.37. Calc. for $C_{30}H_{33}BGeN_2$ (505.0): C, 71.35; H, 6.59; N, 5.55%.

2-Trimethylstannyl-1,3-di(isopropyl)-benzo-1,3,2-diazaborolidine (5a)

To a stirred solution of freshly prepared Me_3SnLi[69] (6.6 mmol) in ~40 ml of THF was slowly added at 0 °C to a solution of **1** (1.7 g, 6.0 mmol) in 25 ml of diethyl ether. After stirring for 1 h at ambient temperature, all volatile components were removed *in vacuo*. The black solid residue was treated with 40 ml of hexane. The resulting suspension was subjected to filtration and the filtrate reduced in volume to ~20 ml. Colorless prisms settled within 3 days from the filtrate kept at −30 °C. Yield: 1.85 g of **5a** (85%), m.p. 69 °C with decomposition. ^{1}H NMR (400 MHz, C_6D_6): $\delta = 0.37$ (d, $^2J_{HSn} = 45.8$ Hz, 9H, $Sn(CH_3)_3$), 1.32 (d, $^3J_{HH} = 7.1$ Hz, 12H, $CH(CH_3)_2$), 4.27 (m, $^3J_{HH} = 7.1$ Hz, 2H, $CH(CH_3)_2$), 7.06 (dd, $^3J_{HH} = 6.0$ Hz, $^4J_{HH} = 3.2$ Hz, 2H, C*H*-arom), 7.18 (dd, $^3J_{HH} = 6.0$ Hz, $^4J_{HH} = 3.2$ Hz, 2H, C*H*-arom). ^{13}C NMR (100 MHz, C_6D_6) $\delta = -9.6$ (m, $^1J_{CSn} = 274.6$ and $^1J_{CSn} = 287.0$ Hz, $Sn(CH_3)_3$), 22.7 ($CH(CH_3)_2$), 48.6 ($CH(CH_3)_2$), 111.7, 118.9, 128.3, 137.8 (all *C*-arom). ^{11}B NMR (64 MHz, C_6D_6): $\delta = 32.8$ (d, $^1J_{Bsn} = 950$ Hz, $h_{1/2} = 150$ Hz). ^{119}Sn NMR (149 MHz, C_6D_6): −147.5 (q, $^1J_{Bsn} = 976$ Hz). Anal. Found: C, 49.15; H, 7.38; N, 7.59. Calc. for $C_{15}H_{27}BN_2Sn$ (364.9). C, 49.37; H, 7.46; N, 7.68%.

2-Triphenylstannyl-1,3-di(isopropyl)-benzo-1,3,2-diazaborolidine (5b)

To a stirred solution of freshly prepared Ph_3SnLi[70] (2.5 mmol in 50 ml of THF) was slowly added at −78 °C a solution of **1** (0.56 g, 2.0 mmol) in hexane (20 ml). After stirring for 1 h at ambient temperature, all volatile components were removed *in vacuo*. The solid residue was treated with hexane (50 ml) and the undissolved material removed by filtration. The filtrate was then brought to 20 ml and cooled to −30 °C. Within a few days, colorless prisms of **5b** settled. Yield: 0.95 g of **5b** (86%), m.p. 126 °C. ^{1}H NMR (400 MHz, C_6D_6): $\delta = 1.24$ (d, $^3J_{HH} = 7.0$ Hz, 12H, $CH(CH_3)_2$), 4.38 (m, $^3J_{HH} = 7.0$ Hz, 2H, $CH(CH_3)_2$), 7.05 (dd, $^3J_{HH} = 7.0$ Hz, $^4J_{HH} = 2.8$ Hz, 2H, C*H*-arom), 7.16–7.28 (m, 11H, C*H*-arom, *m*-Ph-*H*, *p*-Ph-*H*), 7.72 (ddd, 6H, $^3J_{HH} = 6.6$ Hz, $^4J_{HH} = 1.4$ Hz, $^3J_{HSn} = 47.3$ Hz, *o*-Ph-*H*). ^{13}C NMR (100 MHz, C_6D_6): $\delta = 22.1$ ($CH(CH_3)_2$), 49.1 ($CH(CH_3)_2$), 112.4, 118.8, 128.6, 129.4, 137.7, 137.5, 140.9 (all *C*-arom). ^{11}B NMR (64 MHz, C_6D_6): $\delta = 32.4$ (d, $^1J_{Bsn} = 962$ Hz, $h_{1/2} = 300$ Hz). ^{119}Sn NMR (149 MHz, C_6D_6): no signal observed. Anal. Found: C, 64.13; H, 5.76; N, 4.83. Calc. for $C_{30}H_{33}BN_2Sn$ (551.1): C, 65.38; H, 6.04; N, 5.08%.

2-Triphenylplumbyl-1,3-di(isopropyl)-benzo-1,3,2-diazaborolidine (6)

Hexaphenyldilead (1.4 g, 1.6 mmol) was dissolved in ~40 ml of THF. At 0 °C a phenyl lithium solution in diethyl ether (1.6 mmol) was added. After stirring for 1 h a precipitate of Ph_4Pb had formed. The suspension was cooled to −78 °C and treated with **1** (0.44 g, 1.6 mmol). After stirring for 1 h at ambient temperature, the solution was analyzed by ^{11}B NMR spectroscopy: $\delta^{11}B = 40.4$ (d, $^1J_{BPb} = 1450$ Hz, $h_{1/2} = 150$ Hz) (50%), 25.3 ($h_{1/2} = 140$ Hz) (30%) and $\delta^{11}B = 23.0$ ($h_{1/2} = 140$ Hz) (20%). All volatile components were removed from the suspension *in vacuo*. Then the solid residue was extracted with 40 ml of hexane. After reducing the volume of the filtrate to ~20 ml it was kept at −30 °C. This afforded 0.41 g (40%) of pure **6** in the form of a polycrystalline solid, m.p. 114 °C, decomposed ^{1}H NMR (400 MHz, C_6D_6): $\delta = 1.24$ (d, 12H, $^3J_{HH} = 6.9$ Hz, $CH(CH_3)_2$), 4.39 (m, $^3J_{HH} = 6.9$ Hz,

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2H, C*H*(CH_3)$_2$), 7.06 (dd, $^3J_{HH}$ = 6.0 Hz, $^4J_{HH}$ = 3.2 Hz, 2H, C*H*-arom), 7.15–7.25 (m, 11H, C*H*-arom, *m*-Ph-*H*, *p*-Ph-*H*), 7.82 (ddd, 6H, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.2 Hz, $^3J_{HPb}$ = 66.1 Hz, *o*-Ph-*H*). ^{13}C NMR (100 MHz, C_6D_6): δ = 22.2 (CH(CH_3)$_2$), 49.2 (*C*H(CH_3)$_2$), 112.3, 119.1, 129.4 (J_{CPb} = 63 Hz), 129.9, 138.3 (J_{CPb} = 60 Hz), 150.2 (J_{CPb} = 301 Hz) (all *C*-arom). ^{11}B NMR (64 MHz, C_6D_6): δ = 39.6 (d, $^1J_{BPb}$ = 1450 Hz, $h_{1/2}$ = 150 Hz). ^{207}Pb NMR (149 MHz, C_6D_6): no signal observed. Anal. Found: C, 55.12; H, 5.46; N, 4.28. Calc. for $C_{30}H_{33}BN_2Pb$ (639.6): C, 56.34; H, 5.20; N, 4.38%.

2-Triphenylgermyl-(4-*tert*-butyl-catecholato)borane (7)

Ph_3GeLi (1.84 mmol) was prepared freshly in ~50 ml of diethyl ether. The stirred solution was treated at −78 °C with a solution of 2-bromocatecholborane (0.47 g, 1.84 mmol) in 20 ml of toluene. All volatile components were removed after several hours *in vacuo* from the cold suspension. The residue was treated with 20 ml of toluene and filtered. The filtrate was layered with 20 ml of hexane. This afforded at ambient temperature 0.39 g (45%) of **7** as colorless prisms, m.p. 150 °C ^{1}H NMR (400 MHz, C_6D_6): δ = 1.16 (s, 9H, C(CH_3)$_3$), 6.78–7.02 (m, 3H, *H*-arom), 7.16 (m, 9H, *m*-Ph-*H* and *p*-Ph-*H*), 7.76 (m, 6H, *o*-Ph-*H*). ^{13}C NMR (100 MHz, C_6D_6): δ = 31.7 (C(*C*H_3)$_3$), 34.6 (*C*(CH_3)$_3$), 109.7, 111.0, 118.7, 128.8, 130.6, 135.1, 135.5, 145.3, 146.8, 148.9 (all *C*-arom). ^{11}B NMR (64 MHz, hexane): δ = 38.3 ($h_{1/2}$ = 300 Hz). Anal. Found: C, 69.54; H, 4.96 Calc. for $C_{28}H_{27}BGeO_2$ (480.2): C, 70.22; H, 5.68%.

Reaction of 1 with (η^2-C_2H_4) Pt(PPh_3)$_2$

A solution of (η^2-C_2H_4)Pt(PPh_3)$_2$[58] (0.74 g, 1.0 mmol) in toluene (40 ml) was treated with **1** (0.32 g, 1.0 mmol) and stirred for 1 day at ambient temperature. Within this period a brown solid was formed. This was isolated and washed twice with hexane and identified as *trans*-bromo-(1,3-diisopropyl)-1,3,2-diazaborolidin-2-yl-bis(triphenylphosphane)platinum(II) **9**. Yield (crude product): 0.84 g (76%), m.p. >200 °C, decomposed ^{1}H NMR (270 MHz, $CDCl_3$): δ = 0.59 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CHCH_3), 4.48 (m, $^3J_{HH}$ = 6.8 Hz, 2H, NCH_3), 6.70 (dd, $^3J_{HH}$ = 5.9 Hz, $^4J_{HH}$ = 3.1 Hz, 2H, C*H*-arom), 6.81 (dd, $^3J_{HH}$ = 5.9 Hz, $^4J_{HH}$ = 3.1 Hz, 2H, C*H*-arom), 7.14–7.73 (m, 30H, Ph-*H*). ^{13}C NMR (100 MHz, $CDCl_3$): 20.2 (CH(*C*H_3)$_2$, 48.5 (*C*H(CH_3)$_2$), 110.3, 116.2, 118.8, 127.9, 130.2, 134.8 (broad), 138.1 (all *C*-arom). ^{31}P NMR (109 MHz, $CDCl_3$): δ = 25.0 ($^1J_{PPt}$ = 3066 Hz). ^{11}B NMR (64 MHz, $CDCl_3$): δ = 27.9 ($h_{1/2}$ = 1180 Hz). Anal. Found: C, 56.94; H, 5.07; Br 7.83; N, 2.44. Calc. for $C_{48}H_{48}BBrP_2Pt$ (1091.3): C, 57.61; H, 4.83; Br 7.99; N, 2.80%.

Attempts to crystallize **9** from $CHCl_3$–hexane failed. Instead, *trans*-(bromo)(hydrido)bis(triphenylphosphane) platinum(II)·toluene, (**10**) was isolated. Yield: 0.64 g (71%), m.p. >200 °C, decomposed ^{1}H NMR (270 MHz, C_6D_6): δ = 7.00 (m, broad, 18H, Ph-*H*), 7.89 (m, broad, 12H, Ph-*H*). ^{13}C NMR (100 MHz, C_6D_6): 127.9, 128.2 (t, $^1J_{CP}$ = 11.1 Hz), 130.2, 134.9 (t, $^1J_{CP}$ = 13.0 Hz) (all *C*-arom). ^{31}P NMR (109 MHz, C_6D_6): δ = 28.3 ($^1J_{PPt}$ = 2990 Hz). Anal. Found: C, 57.85; H, 4.34; Br, 8.92. Calc. for $C_{43}H_{39}BrP_2Pt$ (891.1): C, 57.85; H, 4.40; Br 8.95%.

Reaction of 3, 4 and 5b with (η^2-C_2H_4) Pt(PPh_3)$_2$

Equimolar amounts of (η^2-C_2H_4)Pt(PPh_3)$_2$ and **3** (or **4** or **5b**) (1 mmol each) were dissolved in toluene (20 ml). The solutions were stirred for 10 days. No reactions were observed, as only the unreacted platinum complex was detected: δ^{31}P = 35.2 ($^1J_{PtP}$ = 3745 Hz).

cis-1,3-Di(isopropyl-benzo-1,3,2-diazaborolidine-2-yl)-(trimethylstannyl)(bis(triphenylphosphane)platinum(II) (11)

A solution of (η^2-C_2H_4)Pt(PPh_3)$_2$ (0.74 g, 1.0 mmol) in toluene (40 ml) was treated with 0.33 g of **5a**. After stirring at ambient temperature for 3 days the precipitate that had formed was isolated by filtration. The solid was washed twice with some hexane, and its solution in $CHCl_3$ (30 ml) was layered with hexane (30 ml). After standing for some days, 0.94 g (87%) of **11** was isolated as colorless crystals, m.p. >156 °C, decomposed. ^{1}H NMR (270 MHz, $CDCl_3$): δ = −0.43 (m, $^2J_{SnH}$ = 38.9 Hz, $^3J_{PtH}$ = 8.6 Hz, 9H, Sn(CH_3)$_3$), 0.95 (d, $^3J_{HH}$ = 6.8 Hz, 6H, CHCH_3), 1.63 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CHCH_3), 4.81 (m, $^3J_{HH}$ = 6.7 Hz, 2H, NCH_3), 6.83 (dd, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 2.8 Hz, 2H, C*H*-arom), 7.05 (dd, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 2.8 Hz, 2H, C*H*-arom), 7.19–7.43 (m, 30H, Ph-*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ = −3.7 (m, $^3J_{CP}$ = 3.9 Hz, $^3J_{CP}$ = 7.9 Hz, $^2J_{PtC}$ = 85 Hz, $^1J_{SnC}$ = 215 Hz, Sn(CH_3)$_3$), 22.7 (CH(*C*H_3)$_2$), 31.7 (CH(CH_3)$_2$), 48.6 (broad, *C*H(CH_3)$_2$), 110.0, 116.2, 118.8, 127.7, 129.2, 129.4, 133.9 (broad, P*C*), 134.6, 134.7, 136.0 (d, J = 3.2 Hz), 136.4 (d, J = 3.2 Hz), 139.7 (m) (all *C*-arom). ^{11}B NMR (64 MHz, $CDCl_3$): δ = 44.7 ($h_{1/2}$ = 1000 Hz). ^{119}Sn NMR (149 MHz, $CDCl_3$): −48.4 (m, $^2J_{PSn}$ = 1462 Hz, $^2J_{PSn}$ = 150 Hz, $^1J_{PtSn}$ = 10 130 Hz). ^{31}P NMR (109 MHz, $CDCl_3$): δ = 27.4 (m, $^1J_{PPt}$ = 2448 Hz, $^2J_{PP}$ = 17 Hz, $^2J_{P^{119}Sn}$ = 1462 Hz, $^2J_{P^{117}Sn}$ = 1431 Hz), 30.2 (broad, $^1J_{PPt}$ = 1560 Hz, $^2J_{PSn}$ = 150 Hz). Anal. Found: C, 55.34; H, 4.65; N, 2.40. Calc. for $C_{51}H_{57}BN_2P_2PtSn$ (1085.3): C, 56.48; H, 5.30; N, 2.58%.

Reaction of 6 with (η^2-C_2H_4) Pt(PPh_3)$_2$

(η^2-C_2H_4)Pt(PPh_3)$_2$ (0.3 g, 0.4 mmol) was dissolved in toluene (25 ml) and treated with **6** (0.2 g, 0.33 mmol). A black solid was formed immediately. The solution was investigated with ^{31}P NMR spectroscopy. The following products were detected: *cis*-(Ph)$_2$(Ph_3P)$_2$Pt, δ^{31}P = 19.5 ($^1J_{PPt}$ = 1734 Hz);[61] *trans*-(Ph)$_2$(Ph_3P)$_2$Pt, δ^{31}P = 21.6 ($^1J_{PPt}$ = 3201 Hz)[61] and *cis*-(Ph)(Ph)(Ph_3Pb)(Ph_3P)$_2$Pt, δ^{31}P = 21.4 ($^1J_{PPt}$ = 1990 Hz, $^2J_{PPb}$ = 252 Hz, $^3J_{PP}$ = 13 Hz); 28.6 ($^1J_{PPt}$ = 2979 Hz, $^2J_{PPb}$ = 3368 Hz, $^3J_{PP}$ = 12 Hz).[62] Attempts to separate these products by fractional crystallization yielded only crystalline *trans*-(Ph)$_2$(Ph_3P)$_2$Pt, which was identified by X-ray structure analysis.

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cis-Triphenylgermyl(hydrido)bis(triphenylphosphane)platinum(II) (15)

7 (0.57 g, 1.14 mmol) was dissolved in toluene (40 ml) and treated with (η^2-C_2H_4)Pt(PPh_3)$_2$ (0.85 g, 1.14 mmol). After stirring for 1 day at ambient temperature the solution was reduced to 20 ml and layered with hexane (20 ml). From the solution, orange crystals separated, affording 0.84 g of **15** (74%), which were identified by X-ray structure analysis. No boron-containing compound could be isolated. ^{31}P NMR (162 MHz, D_8C_7) : $\delta = 32.3$ (dd, $^1J_{PtP} = 2497$ Hz, $^2J_{PP} = 10$ Hz), 33.7 (dd, $^1J_{PtP} = 2177$ Hz, $^2J_{PP} = 10$ Hz). Anal. Found: C, 62.23; H, 4.09. Calc. for $C_{54}H_{46}GeP_2Pt$ (1012.6): C, 62.87; H, 4.58%.

Attempts to dissolve **15** in $CHCl_3$ lead to decomposition. In the ^{31}P NMR spectrum the formation of *cis*-di(chloro)-bis(triphenylphosphane)platinum(II), $\delta^{31}P = 14.9$ (d, $^1J_{PtP} = 2804$ Hz), was detected.

cis-Bis(dimethylamino)boryl-(trimethylstannyl)-bis(triphenylphosphane)platinum(II) (17)

(η^2-C_2H_4)Pt(PPh_3)$_2$ (0.93 g, 1.28 mmol) was dissolved in 50 ml of toluene and the solution treated with **16**[65] (0.34 g, 1.28 mmol). After stirring for 10 days, NMR spectroscopy showed a quantitative reaction. The solution was reduced to 10 ml *in vacuo* and layered with 20 ml of hexane. This resulted in crystalline **17** (0.62 g, 45%), m.p. ~170 °C with decomposition. ^{1}H NMR (270 MHz, C_6D_6): $\delta = 0.15$ (d, 9H, $^1J_{SnH} = 32.6$ Hz, Sn(CH_3)$_3$), 2.80 (s, 12H, NCH_3), 6.88 (m, broad, 18H, Ph-*H*), 7.46 (m, broad, 12H, Ph-*H*). ^{13}C NMR (100 MHz, C_6D_6): $\delta = -3.7$ (m, $^3J_{CP} = 3.9$ Hz, $^3J_{CP} = 8.7$ Hz, $^2J_{PtC} = 105$ Hz, Sn(CH_3)$_3$), 43.0 (NCH_3), 125.4, 127.3, 127.7, 127.9, 130.0, 128.3, 129.1, 129.2 (*C*-arom), 134.3 (dd, $^3J_{CPt} = 16$ Hz, $^2J_{CP} = 13.2$ Hz, *o*-*C*-PPh_3), 134.8 (dd, $^3J_{CPt} = 18$ Hz, $^2J_{CP} = 13$ Hz, *o*-*C*-PPh_3), 137.6 (*C*-arom). ^{11}B NMR (64 MHz, C_6D_6): $\delta = 45.7$ ($h_{1/2} = 1040$ Hz). ^{119}Sn NMR (149 MHz, C_6D_6): −28.4 (ddd, $^2J_{PSn} = 1508$ Hz, $^2J_{PSn} = 146$ Hz, $^1J_{SnPt} = 12\,470$ Hz). ^{31}P NMR (109 MHz, C_6D_6): $\delta = 31.0$ ($^1J_{PPt} = 2681$ Hz, $^2J_{PP} = 15$ Hz, $^2J_{P^{119}Sn} = 1509$ Hz, $^2J_{P^{117}Sn} = 1438$ Hz), 32.1 (broad, $^1J_{PPt} = 1392$ Hz, $^2J_{PSn} = 146$ Hz). Anal. Found: C, 50.79; H, 4.95; N, 2.61. Calc. for $C_{43}H_{51}BN_2P_2PtSn$ (983.2): C, 52.57; H, 5.23; N 2.85%.

cis-Bis(dimethylamino)boryl-(trimethylgermyl)-bis(triphenylphosphane)platinum(II) (19)

(η^2-C_2H_4)Pt(PPh_3)$_2$ (0.75 g, 1.0 mmol) was dissolved in ~40 ml of toluene and treated with 5 ml of a crude sample of $(Me_2N)_2B$–$GeMe_3$[64] (this guarantees at least a tenfold excess). The progress of the reaction was followed by ^{31}P NMR spectroscopy. After 10 weeks, no more starting material could be detected. Then the solution was reduced to 20 ml and layered with 20 ml of hexane. This afforded within several days 0.86 g (91%) of **19** as colorless prisms, m.p. ~175 °C with decomposition. ^{1}H NMR (270 MHz, C_6D_6): $\delta = 0.46$ (d, $^2J_{PtH} = 18$ Hz, 9H, Ge(CH_3)$_3$), 2.85 (s, broad, 12H, NCH_3), 6.87 (m, broad, 18H, Ph-*H*), 7.52 (m, broad, 12H, Ph-*H*). ^{13}C NMR (100 MHz, C_6D_6): $\delta = 7.4$ (ddd, $^2J_{CPt} = 97$ Hz, $^3J_{CP} = 8.5$ Hz, $^3J_{CP} = 4.5$ Hz, Ge(CH_3)$_3$), 43.1 (NCH_3), 127.3, 127.4, 127.5, 127.7, 128.1, 129.0, 129.1 (all *C*-arom), 134.5 (dd, $^3J_{CPt} = 16$ Hz, $^2J_{CP} = 13.5$ Hz, *o*-Ph), 134.9 (dd, $^3J_{CPt} = 13$ Hz, $^2J_{CP} = 13.5$ Hz, *o*-Ph), 136.4 (m), 136.8 (m), 137.2 (m), 137.5 (m) (all *C*-arom). ^{11}B NMR (64 MHz, C_6D_6): $\delta = 46.7$ ($h_{1/2} = 1020$ Hz). ^{31}P NMR (109 MHz, C_6D_6): $\delta = 31.2$ ($^1J_{PPt} = 2220$ Hz, $^2J_{PP} = 15$ Hz, P *cis* B), 31.8 (broad, $^1J_{PPt} = 1200$ Hz, P *trans* B). Anal. Found: C, 54.68; H, 5.75; N, 2.94. Calc. for $C_{43}H_{51}BGeN_2P_2Pt$ (937.2): C, 55.16; H, 5.49; N, 2.99%.

Reactions of (η^2-C_2H_4) Pt(PPh_3)$_2$ with bis(stannyl)aminoboranes

(η^2-C_2H_4)Pt(PPh_3)$_2$ (0.69 g, 0.93 mmol) was dissolved in 20 ml of toluene and slowly treated with tmpB($SnMe_3$)$_2$ (**20**)[66] (0.45 g, 0.95 mmol). The solution was stirred for 10 days. No reaction was observed, as only starting materials were detected: $\delta^{31}P = 35.2$ ($^1J_{PtP} = 3745$ Hz), $\delta^{11}B = 68.4$ ($^1J_{SnB} = 650$ Hz). The analogous observation was made for a possible reaction between 0.74 g (1.0 mmol) (η^2-C_2H_4)Pt(PPh_3)$_2$ and (^{i}Pr$_2$N)B($SnMe_2$)$_2$ (**21**):[66] $\delta^{31}P = 35.2$ ($^1J_{PtP} = 3745$ Hz), $\delta^{11}B = 64.3$ ($^1J_{SnB} = 650$ Hz).

Reaction between 16 and tetrakis(triphenylphosphane)palladium(0) or tris(triphenylphosphane)rhodium(I) chloride

$(Me_2N)_2B$–$SnMe_3$ (**16**; 0.225 g, 0.84 mmol) was dissolved in 20 ml of toluene and treated with tetrakis(triphenylphosphane)palladium(0) (0.97 g, 0.84 mmol). No reaction was observed within 10 weeks at ambient temperature. Only starting material was detected: $\delta^{11}B = 39.2$ ($^1J_{SnB} = 940$ Hz, $h_{1/2} = 100$ Hz). The same result was obtained for the reaction between **16** (0.10 g, 0.40 mmol) and tris(triphenylphosphane) rhodium(I) chloride (0.33 g, 0.36 mmol).

X-ray structure determinations

The single crystals were covered with perfluoropolyether oil and suitable specimens selected and mounted on a glass fiber. Cell dimensions were determined from the reflections on 15 frames each at four different χ and ψ settings by changing ψ by 0.3° per frame at 193 K. Data collection was performed in the hemisphere mode of the SMART[70] program at 193 K by collecting a total of 1264 frames. Data reduction was performed using the program SAINT.[70] No absorption correction was applied. The structures were solved by direct or Patterson methods (SHELXTL-97).[70] Non-hydrogen atoms were refined anisotropically (SHELXTL-97) and C–H hydrogen atoms placed in calculated positions by applying a riding model in the refinement. Crystallographic data relating to the data collection and refinement are summarized in Table 4. Additional crystallographic data for the structures are deposited with the CCDC as supplementary publications, numbers CCDC 202 889–202 894 (**2**–**7**) and 202 953–202 958 (Pt complexes). They can be obtained free of charge on

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Table 4. Crystallographic data and data referring to data collection and refinement

	2	3	4	5a	5b	7	15	11	17	19
Chemical formula	$C_{13}H_{26}BN_2$	$C_{30}H_{33}BN_2Si$	$C_{30}H_{33}BGeN_2$	$C_{15}H_{27}BN_2Sn$	$C_{30}H_{33}BN_2Sn$	$C_{28}H_{27}BGeO_2$	$C_{54}H_{46}GeP_2Pt$	$C_{51}H_{57}BN_2P_2PtSn$	$C_{50}H_{59}BN_2P_2PtSn$	$C_{43}H_{51}BGeN_2P_2Pt$
Formula weight	221.17	460.48	504.98	364.89	551.08	478.90	1024.53	1084.52	1074.52	936.29
Crystal size (mm^3)	0.2 × 0.2 × 0.3	0.1 × 0.1 × 0.2	0.1 × 0.3 × 0.3	0.2 × 0.2 × 0.25	0.1 × 0.2 × 0.2	0.2 × 0.3 × 0.4	0.0 × 0.2 × 0.3	0.05 × 0.2 × 0.3	0.15 × 0.2 × 0.3	0.2 × 0.2 × 0.3
Crystal system	Monoclinic	Monoclinic	Monoclinic	Tetragonal	Orthorhombic	Triclinic	Orthorhombic	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/m$	$P2_1/n$	$P2_1/n$	$I4_1/a$	$Pna2_1$	$P\bar{1}$	$P2_12_12_1$	$P2_1/n$	$P\bar{1}$	*Pbca*
a (Å)	9.1014(8)	15.175(3)	15.6274(2)	25.8258(2)	14.4486(8)	10.0263(3)	13.5223(16)	10.4067(2)	11.709(2)	16.189(1)
b (Å)	9.6352(9)	10.649(2)	10.9076(2)	25.8258(2)	22.1601(13)	11.5147(3)	17.812(2)	23.3306(4)	12.050(3)	19.360(1)
c (Å)	9.4194(8)	15.876(3)	16.2883(1)	10.8076(1)	8.3176(5)	12.3255(3)	18.752(2)	19.569 40(10)	18.124(4)	25.911(2)
α (°)	90	90	90	90	90	108.230(1)	90	90	102.305(7)	90
β (°)	106.837(2)	106.024(3)	106.428(2)	90	90	96.843(1)	90	92.262(1)0	96.281(8)	90
γ (°)	90	90	90	90	90	111.831(1)	90	90	110.740(8)	90
V ($Å^3$)	790.6(1)	2466.0(9)	2665.57(6)	7208.4(1)	2663.1(3)	1209.05(6)	4516.5(9)	4747.64(12)	2288.2(9)	8121.1(8)
Z	4	4	4	16	4	2	4	4	2	8
ρ(calcd) ($Mg\,m^3$)	1.858	1.240	1.258	1.345	1.374	1.315	1.507	1.517	1.560	1.532
μ (mm^{-1})	0.107	0.117	1.169	1.408	0.980	1.289	3.866	3.572	3.705	4.292
F(000)	492	984	1056	2976	1128	496	2040	2160	1072	3744
Index range	$-11 \le h \le 11$ $-12 \le k \le 12$ $-12 \le l \le 9$	$-19 \le h \le 19$ $-13 \le k \le 13$ $-20 \le l \le 21$	$-19 \le h \le 17$ $-13 \le k \le 13$ $-20 \le l \le 22$	$-32 \le h \le 32$ $-27 \le k \le 34$ $-14 \le l \le 14$	$-18 \le h \le 17$ $-27 \le k \le 27$ $-10 \le l \le 10$	$-13 \le h \le 8$ $-14 \le k \le 14$ $-15 \le l \le 15$	$-16 \le h \le 16$ $-22 \le k \le 22$ $-19 \le l \le 24$	$-11 \le h \le 13$ $-30 \le k \le 30$ $-25 \le l \le 25$	$-14 \le h \le 14$ $-15 \le k \le 15$ $-22 \le l \le 22$	$-20 \le h \le 20$ $-19 \le k \le 26$ $-33 \le l \le 33$
2θ (°)	55.90	59.90	58.24	59.00	58.60	57.56	56.34	58.42	58.74	58.66
Temperature (K)	193	193(2)	173	183(2)	183	183	193	173(2)	183(2)	193
Refl. collected	4626	15 379	15 206	20 556	15 214	7080	23 255	26 805	13 773	45 506
Refl. unique	1508	5384	4776	4060	5590	3809	8074	8880	7393	8584
Refl. observed (4σ)	1177	2303	3611	2822	4102	3428	7597	7006	6918	5562
R_{int}	0.0324	0.1357	0.0562	0.0350	0.0409	0.0150	0.0199	0.0469	0.0170	0.0874
No. variables	110	311	311	179	315	292	524	530	522	458
Weighting scheme[a] *x*/*y*	0.088/0.156	0.050	0.018/2.459	0.049/37.085	0.021	0.032/0.456	0.028	0.024/12.117	0.0469/0.8439	0.037
GOF	1.055	0.929	1.107	1.048	0.976	1.030	1.012	1.073	1.056	1.025
Final *R* (4σ)	0.0496	0.0687	0.0425	0.0560	0.0339	0.0256	0.0191	0.0404	0.0277	0.0381
Final wR_2	0.1408	0.1144	0.0717	0.1221	0.0500	0.0627	0.0429	0.0734	0.0694	0.0716
Largest residual peak ($e^-/Å^{-3}$]	0.341	0.315	0.297	1.115	0.356	0.286	0.775	1.107	1.207	1.506

[a] $w^{-1} = s^2F_o^2 + (xP)^2 + yP$; $P = (F_o^2 + 2F_c^2)/3$.

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REFERENCES

1. Sakurai H, Kamiyama Y, Nakadaira Y. *J. Am. Chem. Soc.* 1975; **97**: 931.
2. Watanabe H, Kobayashi M, Higuchi K, Nagai J. *J. Organometal Chem.* 1980; **51**: 186.
3. Hayashi T, Kobayashi T, Kowamoto AM, Yamashita H, Tanaka M. *Organometallics* 1990; **9**: 280.
4. Ito Y, Suginome M, Murakami M. *J. Org. Chem.* 1991; **56**: 1948.
5. Yamashita H, Catellani M, Tanaka M. *Chem. Lett.* 1991; 241.
6. Tsuji Y, Lago RM, Tomohiro S, Tsuneishi H. *Organometallics* 1992; **11**: 2353.
7. Murakami M, Suginome M, Fujimoto K, Nakamura H, Andersson PG, Ito Y. *J. Am. Chem. Soc.* 1993; **111**: 6487.
8. Yamashita H, Reddy NP, Tanaka M. *Chem. Lett.* 1993; 315.
9. Ozawa F, Sugawara M, Hayashi T. *Organometallics* 1994; **13**: 3237.
10. Obora Y, Tsuji Y, Kakehi T, Kobayashi M, Shinkai Y. *J. Chem. Soc. Perkin Trans.* 1995; 599.
11. Mitchell TN, Amamria A, Killing H, Rutschow DJ. *J. Organometal Chem.* 1983; **C45**: 241.
12. Killing H, Mitchell TN. *Organometallics* 1984; **3**: 1318.
13. Piers E, Skerlj RT. *J. Chem. Soc. Chem. Commun.* 1986; 626.
14. Chenard BL, Van Zyl CM. *J. Org. Chem.* 1986; **51**: 3561.
15. Mitchell TN, Wickenkamp R, Amamria A, Dicke R, Schneider U. *J. Org. Chem.* 1987; **52**: 868.
16. Tsuji Y, Obora Y. *J. Am. Chem. Soc.* 1991; **113**: 9368.
17. Murakami M, Amii H, Takizawa N, Ito Y. *Organometallics* 1993; **12**: 4223.
18. Obora Y, Tsuji Y, Asayama M, Kawamura T. *Organometallics* 1993; **12**: 4697.
19. Ishiyama T, Matsuda N, Miyaura N, Suzuki A. *J. Am. Chem. Soc.* 1993; **115**: 11 018.
20. Iverson CN, Smith MR. *J. Am. Chem. Soc.* 1995; **117**: 4403.
21. Ishiyama T, Matsuda N, Murata M, Ozawa F, Suzuki A, Miyaura N. *Organometallics* 1996; **15**: 713.
22. Bluhm M, Maderna A, Pritzkow H, Bethke S, Gleiter R, Siebert W. *Eur. J. Inorg. Chem.* 1999; 1693.
23. Suginome M, Nakamura H, Ito Y. *J. Chem. Soc. Chem. Commun.* 1996; 2777.
24. Suginome M, Nakamura H, Ito Y. *Angew. Chem.* 1997; **109**: 2626; *Angew. Chem. Int. Ed. Engl.* 1997; **36**: 2516.
25. Suginome M, Ohmori Y, Ito Y. *Synlett.* 1999; **10**: 1567.
26. Onozawa S, Hatanaka Y, Tanaka M. *Chem. Commun.* 1999; **10**: 1863.
27. Han LB, Tanaka M. *Chem. Commun.* 1999; **10**: 395.
28. a) Onozawa S, Hatanaka Y, Sakakura T, Shimada S, Tanaka M. *Organometallics* 1996; **15**: 5450.
29. Onozawa S, Hatanaka Y, Tanaka M. *Tetrahedron Lett.* 1998; **39**: 9043.
30. Onozawa S, Hatanaka Y, Choi N, Tanaka M. *Organometallics* 1997; **16**: 5389.
31. Sakaki S, Kai S, Sugimato M. *Organometallics* 1999; **18**: 4825.
32. Kennedy JD, McFarlane W, Wrackmeyer B. *Inorg. Chem.* 1976; **15**: 1299.
33. Horchler K, Wrackmeyer B. *Z. Naturforsch. Teil B* 1989; **44**: 1195.
34. Nöth H, Hermannsdörfer K. *Angew. Chem.* 1964; **76**: 377; *Angew. Chem. Int. Ed. Engl.* 1964; **3**: 377.
35. Niedenzu K, Rothgery E. *Synth. Inorg. Met. Org. Chem.* 1972; **2**: 1.
36. Bradley EB, Herber RH, Busse PJ, Niedenzu K. *J. Organometal. Chem.* 1973; **52**: 297.
37. Kennedy JD, McFarlane W, Pyne G, Wrackmeyer B. *J. Chem. Soc. Dalton Trans.* 1975; 386.
38. Kennedy JD, McFarlane W, Wrackmeyer B. *Inorg. Chem.* 1976; **15**: 1299.
39. Biffar W, Nöth H, Pommering H, Schwerthöffer R, Storch W, Wrackmeyer B. *Chem. Ber.* 1981; **114**: 49.
40. Fußstetter H, Nöth H, Wrackmeyer B, McFarlane W. *Chem. Ber.* 1977; **110**: 3172.
41. Nöth H, Schwerthöffer R. *Chem. Ber.* 1981; **114**: 3056.
42. Sharma S, Oehlschlager A. *Tetrahedron Lett.* 1988; **29**: 261 .
43. Corey L, Singh S, Oehlschlager A. *Can. J. Chem.* 1987; **65**: 1821.
44. Frankhauser P, Pritzkow H, Siebert W. *Z. Naturforsch. Teil B* 1994; **49**: 250.
45. Padilla-Martinez II, Andrade-Lopez N, Gama-Goicochea M, Aguilar-Cruz E, Cruz A, Contrereas R, Tlahuext H. *Heteroat. Chem.* 1996; **5**: 323.
46. Kaup M, Malkina OL, Malin V, Pykkö P. *Chem. Eur. J.* 1998; **4**: 4.
47. Kaup M, Malkina OL, Malin V, Pykkö P. *J. Phys. Chem.* 1995; **99**: 606.
48. Nöth H, Wrackmeyer B. In *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds, NMR Principles and Progress*, vol. 14, Diehl R, Fluck E, Kosfeld R (eds). Springer: Heidelberg, New York, 1973.
49. Holleman A, Wiberg N. *Holleman-Wiberg: Lehrbuch der Anorganischen Chemie*, 101st edn. Walter de Gruyter: Berlin, 1995.
50. Mayer EP, Nöth H, Rattay W, Wietelmann U. *Chem. Ber.* 1992; **125**: 401.
51. STOE WinXPow. Version 1.03, Fa. STOE & Cie GmbH, Darmstadt, 1998.
52. Dinnebier RE. NONIUS-GUFI 5.00, Bayreuth, 1997.
53. Altomare A, Burla M, Giacovazzo G, Guagliardi A, Moliterni A, Polidori G. *J. Appl. Crystallogr.* 1995; **28**: 842.
54. Larson A, von Dreele R. GSAS, General Structure Analysis System, Los Alamos National Laboratory, 1997.
55. Wong W-C, Wong C-M, Pritzkow H, Siebert W. *Z. Naturforsch. Teil B* 1990; **45**: 1597.
56. Paetzold P, Hahnfeld D, Englert U, Wojnowski W, Dreczewski B, Pawelec Z, Walz L. *Chem. Ber.* 1992; **125**: 1073.
57. Blumenthal A, Bissinger P, Schmidbaur H. *J. Organometal. Chem.* 1993; **462**: 107.
58. Nagel U. *Chem. Ber.* 1982; **115**: 1198.
59. Clegg W, Lawlor FJ, Lesly G, Marder TB, Norman NC, Orpen AG, Quayle MJ, Rice CR, Scott AJ, Souza FES. *J. Organometal. Chem.* 1998; **550**: 183.
60. Iverson CN, Smith MR III. *Organometallics* 1996; **15**: 5155.
61. Ertl J, Debaerdemaeker T, Brune H. *Chem. Ber.* 1982; **115**: 3860.
62. Carr S, Colton R, Dakternieks D. *J. Organometal. Chem.* 1982; **240**: 143.
63. Gee R, Powell H. *J. Am. Chem. Soc.* 1971; **93**: 1965.
64. Hermannsdörfer K. PhD thesis, University of Munich, 1965.
65. Nöth H, Schwerthöffer R. *Chem. Ber.* 1981; **114**: 3056.
66. Horchler K. Diploma thesis, University of Munich, 1987.
67. Irvine GJ, Lesley MJG, Marder TB, Norman NC, Rice CR, Robbins EG, Roper WR, Whittell GR, Wright LJ. *Chem. Rev.* 1988; **98**: 2685.
68. Tamborski C, Ford F, Soloski E. *J. Org. Chem.* 1963; **28**: 237.
69. Wittig G, Meyer FJ, Lange G. *Liebigs Ann. Chem.* 1951; **571**: 167.
70. Still W. *J. Am. Chem. Soc.* 1978; **100**: 1481.
71. SMART, SAINT, *SHELXTL*, Version 5. Siemens X-ray Analytic Instruments, Madison, 1994.

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