Boron Ligands

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A T-Shaped Platinum(II) Boryl Complex as the Precursor to a Platinum Compound with a Base-Stabilized Borylene Ligand**

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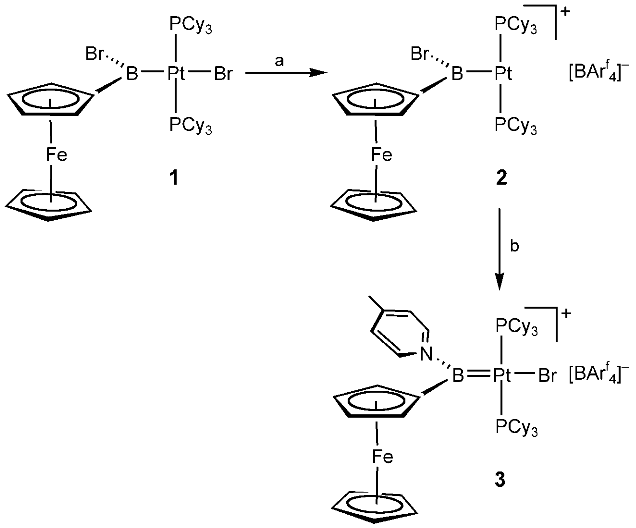
Transition-metal boryl complexes constitute an abundant and important class of boron-containing transition-metal compounds,[1] in view of their intermediacy in the catalyzed hydro-[2] and diboration[3] of unsaturated organic substrates, as well as the selective C–H bond activation of alkanes and arenes.[4] A number of synthetic routes have been applied to the generation of boryl complexes.[1] Among these, that involving B–X (X = Cl, Br) bond oxidative addition has seldom been employed, and examples of rhodium and iridium,[5] palladium,[6] and platinum[7] boryl complexes synthesized in this fashion have only relatively recently appeared in the literature.

We previously reported the synthesis of *trans*-$[(\mathrm{Cy_3P})_2\mathrm{Pt(Br)\{B(Fc)Br\}}]$ (Fc = ferrocenyl, Cy = cyclohexyl) (**1**) by reaction of $[\mathrm{Pt(PCy_3)_2}]$ with $\mathrm{FcBBr_2}$.[7b] A remarkable structural feature of crystalline **1** is the rather long Pt–Br bond length (2.6183(8) Å), which provides an indication of the high *trans* influence of the B(Fc)Br group. Indeed, on account of its strong σ-donor character, the boryl ligand exerts a higher *trans*-labilizing influence[8] than that of other σ donors, such as hydrido[7a,9] and stannyl groups,[6a] or π acceptors, such as CO.[10] Herein, we demonstrate how strongly this property influences the reactivity of **1**. Thus, the reaction of **1** with $\mathrm{Na[BAr^f_4]}$ ($\mathrm{Ar^f} = 3{,}5\text{-}\mathrm{C_6H_3(CF_3)_2}$) leads to the T-shaped, three-coordinate platinum complex *trans*-$[(\mathrm{Cy_3P})_2\mathrm{Pt\{B(Fc)Br\}}][\mathrm{BAr^f_4}]$ (**2**). Such a species constitutes the precursor to the cationic, base-stabilized borylene complex *trans*-$[(\mathrm{Cy_3P})_2\mathrm{Pt(Br)\{B(Fc)(NC_5H_4\text{-}4\text{-}Me)\}}][\mathrm{BAr^f_4}]$ (**3**), which is obtained upon addition of 4-methylpyridine, via an overall 1,2-bromide migration from the boron center to the platinum center.



Scheme 1. a) $\mathrm{Na[BAr^f_4]}$ in $\mathrm{CD_2Cl_2}$; b) 4-methylpyridine in $\mathrm{CD_2Cl_2}$.

Treatment of a solution of **1** in $\mathrm{CD_2Cl_2}$ with $\mathrm{Na[BAr^f_4]}$ led to an immediate color change from bright orange to cherry red, with concomitant precipitation of NaBr (Scheme 1, a). The $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum of the reaction mixture conclusively revealed the quantitative formation of a new compound within a few minutes, with the presence of a single signal at $\delta = 41.7$ ppm ($^1J(\mathrm{P,Pt}) = 2914$ Hz), strongly downfield shifted with respect to that of **1** ($\delta = 21.5$ ppm, $^1J(\mathrm{P,Pt}) = 2892$ Hz).

In the ^{1}H NMR spectrum, two broad signals for the protons of the $[\mathrm{BAr^f_4}]^-$ ion appeared at $\delta = 7.74$ and 7.58 ppm, alongside a new set of signals for the ferrocenylboryl ligand, namely two multiplets at $\delta = 4.71$ ppm (2H) and $\delta = 4.52$ ppm (2H), and a singlet at $\delta = 4.26$ ppm (5H). Surprisingly, no resonance signal was observed in the $^{11}\mathrm{B}\{^1\mathrm{H}\}$ NMR spectrum, probably due to broadening of the signal as a consequence of unresolved coupling to the platinum and phosphorus nuclei.[11]

Orange bricklike crystals of **2** were obtained by layering a solution of the complex in $\mathrm{CD_2Cl_2}$ with hexane and cooling the solution to −36 °C. The X-ray diffraction study performed

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on a suitable single crystal confirmed that complex **2** was a three-coordinate platinum(II) boryl compound that displayed a distorted T-shaped geometry (P1-Pt1-P2 162.96(3)°; Figure 1).[12]

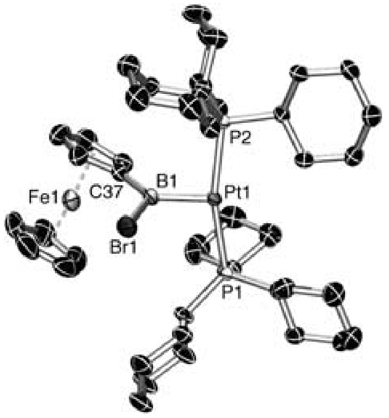

Figure 1. Molecular structure of **2**. Hydrogen atoms and the $[BAr^f_4]^-$ ion were omitted for clarity. Selected bond lengths [Å] and angle [°]: Pt1–B1 1.966(4), Pt1–P2 2.3071(8), Pt1–P1 2.3323(8), B1–Br1 1.955(4); P1-Pt1-P2 162.96(3).

Despite the absence of a ligand *trans* to the boryl group, the B1–Pt1 distance (1.966(4) Å) in **2** is, unexpectedly, only slightly shorter than that in crystalline **1** (1.9963(34) Å).[7b] This is presumably a consequence of the steric bulk of the tricyclohexylphosphane ligands, which prevents a closer approach of the boryl group to the metal center. The threefold coordination at the platinum center in the cationic portion of **2** is remarkable. It is well-established that the highly unsaturated, Lewis acidic nature of the metal center in 14-electron d^8 ML_3 compounds greatly enhances the reactivity of these species, leading to interactions even with weak nucleophiles, such as solvent molecules, weakly coordinating anions,[13] or agostic C–H bonds.[14] In **2**, however, no such interaction is observed. Particularly noteworthy is the absence of any efficient agostic interaction between the metal center and the C–H bonds of the cyclohexyl groups. The shortest Pt···H–C distance is 2.542 Å (Pt···C–H 3.117 Å), which is considerably longer than corresponding distances in the complexes $[PtMe(PiPr_3)_2][1\text{-H-}closo\text{-}CB_{11}Me_{11}]$ (Pt–H 2.24, Pt–C 2.859 Å)[14g] and $[Pt\{P(2,6\text{-}Me_2C_6H_3)Cy_2\}\{\kappa^2\text{-}P,C\text{-}P(2\text{-}Me\text{-}6\text{-}CH_2\text{-}C_6H_3)Cy_2\}][BAr^f_4]$ (Pt–C 2.432 Å)[14f] and in the range of those observed in truly three-coordinate *neutral* palladium complexes, in which the presence of agostic interactions was excluded.[15] Indeed, theoretical calculations on 14-electron d^8 ML_3 boryl complexes of the type $[(R_3P)_2Rh(BX_2)]$ support the reluctance of such compounds to bind C–H bonds in the site opposite to the boryl group, owing to the extremely strong *trans* influence of the boryl ligand.[16] Thus, compound **2** represents a structurally characterized example of this class of complexes, and provides experimental confirmation of what was predicted from theoretical studies.

The absence of agostic interactions in **2** was supported by density functional calculations[17] and variable-temperature NMR studies. No appreciable change in the NMR spectra of **2** was observed upon cooling the sample to −60 °C. At lower temperatures, the signal in ^1H NMR spectrum at $\delta = 4.52$ ppm for two of the ferrocenyl protons broadened. At −90 °C, coalescence occurred, consistent with restricted rotation of the ferrocenyl group around the B–C(Fc) bond. Concomitant broadening of the initial singlet at $\delta = 41.7$ ppm was observed in the $^{31}P\{^1H\}$ NMR spectrum, and two separate broad signals at $\delta = 42.5$ and 38.3 ppm could be detected at −90 °C. However, none of these processes was accompanied by the appearance of a high-field resonance signal that could be assigned to an agostic hydrogen atom, suggesting the decreased fluxionality of the molecule at low temperatures as the likely origin of the spectral phenomena.

The bulky tricyclohexylphosphane ligands and the high *trans*-labilizing boryl ligand cooperate to inhibit coordination of more efficient nucleophiles, such as THF or CH_3CN, at the platinum center. Negligible decomposition of a solution of **2** in CD_2Cl_2 containing an excess (> 10 equiv) of THF or CH_3CN was observed by NMR spectroscopy over the course of 24 h. Upon addition of the stronger Lewis base 4-methylpyridine, however, gradual darkening of the solution from cherry red to dark purple occurred within 2 h, and the predominant formation of a new species, **3**, which incorporated the added ligand was observed by NMR spectroscopy. Although binding of the pyridine unit to the platinum center might have been expected, on account of the electronic unsaturation at the metal center and its affinity for nitrogen donors,[13b–d] an X-ray diffraction study[12] performed on purple crystals of **3** revealed a different outcome of the reaction. As displayed in Figure 2, the constitution of complex **3** is that of a four-coordinate, cationic *trans*-bis(tricyclohexylphosphino)platinum complex, with the two remaining sites occupied by a bromide ligand and a 4-methylpyridine-stabilized ferrocenylborylene moiety. As such, **3** represents a unique example of a cationic[18] platinum(II) borylene complex and a rare instance of a base-stabilized borylene

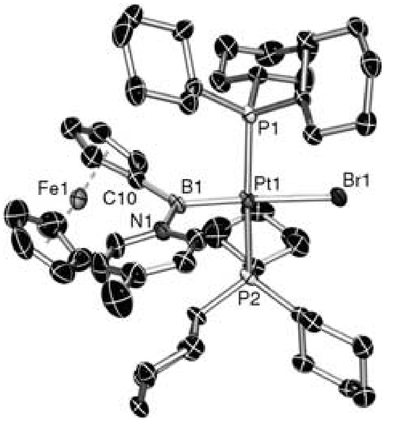

Figure 2. Molecular structure of **3**. The hydrogen atoms and the $[BAr^f_4]^-$ ion have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Pt1–B1 2.014(5), Pt1–P2 2.3452(11), Pt1–P1 2.3564(11), Pt1–Br1 2.6057(5), N1–B1 1.582(6); P2-Pt1-P1 171.83(4), C10-B1-N1 114.4(4), C10-B1-Pt1 131.0(3), N1-B1-Pt1 113.6(3).

compound.[10b,19] Previously, Roper et al. described formation of the only other reported organic base-stabilized borylene compounds, upon reaction of the osmium dichloroboryl precursor $[Os(BCl_2)Cl(CO)(PPh_3)_2]$ with 8-aminoquinoline[10b] or 2-aminopyridine.[19a] In analogy with the formation of the osmium system, it can be inferred that formation of **3** occurs by a Lewis base induced, formal 1,2-halide shift from boron to platinum, by which a strong B−N bond (B1−N1 1.582(6) Å) is formed within the borylene moiety and concomitantly the coordinative unsaturation at the metal center is relieved upon coordination of the bromide ligand. The latter appears to be an important factor. For example, intramolecular, particularly α-hydrogen, migrations within organometallic compounds are thought to be kinetically favorable, if through the shift a coordinatively unsaturated species can be converted into coordinatively more strongly saturated compound.[20] This principle, which plays a significant role in organometallic chemistry,[21] provided a viable route to silylene complexes of platinum.[22] The isolation of complex **3** and of the osmium compounds demonstrates that analogous 1,2-halide migrations might be similarly powerful synthetic tools in borylene chemistry.[23]

In contrast to the very short Fe−B distance (1.792(8) Å) in $[(\eta^5\text{-}C_5Me_5)(OC)_2Fe{=}BMes][BAr^f_4]$ (Mes = 2,4,6-$Me_3C_6H_2$),[18] the only other reported cationic terminal borylene complex, the Pt1−B1 distance (2.014(5) Å) in **3** is only slightly longer than that in the three-coordinate platinum precursor **2** (1.966(4) Å) and comparable to that in the four-coordinate boryl compound **1** (1.9963(34) Å).[7b] This is in line with the increased coordination number at the metal center and the enhanced steric congestion at the boron center.

Nonetheless, it must be stated that the comparable Pt−B bond lengths and angles at boron in the T-shaped complex **2** and the tetracoordinate complex **3** make the description of **2** as a boryl and of **3** as a borylene complex somewhat ambiguous. A similar ambiguity was pointed out by Roper et al. with regard to the "boryl" character of their base-stabilized borylene compounds of osmium,[10b,19a] and found to apply to base-stabilized silylene compounds, whose silylene character was judged to be limited.[24a,c] Hence, while the utilized description of complex **3** is based on the formalism that defines the B−R group a borylene, and hence a B(L)R group, where L is a Lewis base, a base-stabilized borylene ligand, this is only one of the possible descriptions. Elucidation of the bonding interactions that characterize complex **3** awaits theoretical calculations and reactivity studies, both of which are currently in progress.

The increased steric congestion at the boron center brought about by the coordination of pyridine is likely to be responsible for the nearly orthogonal disposition (78.42(13)°) of the plane of the borylene ligand with respect to the coordination plane of the platinum center. An analogous orientation of the boron-containing group was observed in the molecular structures of the boryl complexes **1** and **2**, as well as in those of square-planar platinum carbene[25] and silylene[24b] compounds, and attributed to steric interactions with the phosphane ligands. The Pt1−Br1 distance (2.6057(5) Å) in **3** is rather long and comparable to that in the neutral boryl complex **1** (2.6183(8) Å), in line with the high *trans* influence of the boron-containing ligand.

The spectroscopic data of complex **3** were in agreement with its solid-state structure. The $^{31}P\{^1H\}$ NMR spectrum exhibited a singlet at $\delta = 25.0$ ppm ($^1J(P,Pt) = 2554$ Hz), strongly high-field-shifted with respect to the corresponding signal of **2**. In the room-temperature ^1H NMR spectrum, broad signals were observed at $\delta = 7.90$ and 7.82 ppm for two of the 4-methylpyridine protons, as well as at $\delta = 4.54$ ppm for two of the ferrocenyl protons and for some of the cyclohexyl protons; this indicates slow hindered rotation of the methylpyridine ligands and of the ferrocenyl groups around the B−N and B−C bonds, respectively, with respect to the NMR time scale. At −20 °C, the four pyridine protons gave rise to two overlapping doublets at $\delta = 10.45$–10.42 ppm and two more doublets at $\delta = 7.92$ and 7.79 ppm ($^3J(H,H) = 6$ Hz). Only after the sample had been cooled to −60 °C were four separate signals for the four protons of the boron-bound cyclopentadienyl ring observed at $\delta = 4.92$, 4.88, 4.73, and 4.04 ppm. Finally, as for complex **2**, extreme broadening of the resonance in the $^{11}B\{^1H\}$ NMR spectrum of **3** prevented observation of a detectable signal.

In conclusion, we have described the synthesis of the T-shaped, three-coordinate boryl complex *trans*-$[(Cy_3P)_2Pt\{B(Fc)Br\}][BAr^f_4]$ (**2**) and its conversion into the cationic base-stabilized borylene complex *trans*-$[(Cy_3P)_2Pt(Br)\{B(Fc)(NC_5H_4\text{-}4\text{-}Me)\}][BAr^f_4]$ (**3**) by an overall 1,2-migration of bromide from the boron to the platinum center. Experiments aimed at verifying the generality of this approach to the synthesis of borylene complexes, as well as at exploiting the high *trans* influence of the boryl ligand to access highly unsaturated compounds are currently underway.

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[1] a) H. Braunschweig, *Angew. Chem.* **1998**, *110*, 1882–1898; *Angew. Chem. Int. Ed.* **1998**, *37*, 1786–1801; b) G. J. Irvine, M. G. J. Lesley, T. B. Marder, N. C. Norman, C. R. Rice, E. G. Robins, W. R. Roper, G. R. Whittell, L. J. Wright, *Chem. Rev.* **1998**, *98*, 2685–2722; c) H. Braunschweig, M. Colling, *Coord. Chem. Rev.* **2001**, *223*, 1–51; d) S. Aldridge, D. L. Coombs, *Coord. Chem. Rev.* **2004**, *248*, 535–559.

[2] a) K. Burgess, M. J. Ohlmeyer, *Chem. Rev.* **1991**, *91*, 1179–1191; b) I. Beletskaya, A. Pelter, *Tetrahedron* **1997**, *53*, 4957–5026.

[3] T. B. Marder, N. C. Norman, *Top. Catal.* **1998**, *5*, 63–73.

[4] a) J.-Y. Cho, M. K. Tse, D. Holmes, R. E. Maleczka, Jr., M. R. Smith III, *Science* **2002**, *295*, 305–308; b) T. Ishiyama, N. Miyaura, *J. Organomet. Chem.* **2003**, *680*, 3–11; c) T. Ishiyama, Y. Nobuta, J. F. Hartwig, N. Miyaura, *Chem. Commun.* **2003**, 2924–2925; d) D. N. Coventry, A. S. Batsanov, A. E. Goeta, J. A. K. Howard, T. B. Marder, R. N. Perutz, *Chem. Commun.* **2005**, 2172–2174; e) J. F. Hartwig, K. S. Cook, M. Hapke, C. D. Incarvito, Y. Fan, C. E. Webster, M. B. Hall, *J. Am. Chem. Soc.* **2005**, *127*, 2538–2552, and references therein.

[5] F. E. S. Souza, P. Nguyen, T. B. Marder, A. J. Scott, W. Clegg, *Inorg. Chim. Acta* **2005**, *358*, 1501–1509.

[6] a) S.-Y. Onozawa, Y. Hatanaka, T. Sakakura, S. Shimada, M. Tanaka, *Organometallics* **1996**, *15*, 5450–5452; b) S.-Y. Onozawa, M. Tanaka, *Organometallics* **2001**, *20*, 2956–2958.

[7] a) W. Clegg, F. J. Lawlor, G. Lesley, T. B. Marder, N. C. Norman, A. G. Orpen, M. J. Quayle, G. C. Rice, A. J. Scott, F. E. S. Souza, *J. Organomet. Chem.* **1998**, *550*, 183–192; b) H. Braunschweig, K. Radacki, D. Rais, F. Seeler, *Organometallics* **2004**, *23*, 5545–5549.

[8] a) G. Sivignon, P. Fleurat-Lessard, J.-M. Onno, F. Volatron, *Inorg. Chem.* **2002**, *41*, 6656–6661; b) K. C. Lam, W. H. Lam, Z. Lin, T. B. Marder, N. C. Norman, *Inorg. Chem.* **2004**, *43*, 2541–2547.

[9] C. Dai, G. Stringer, T. B. Marder, R. T. Baker, A. J. Scott, W. Clegg, N. C. Norman, *Can. J. Chem.* **1996**, *74*, 2026–2031.

[10] a) C. E. F. Rickard, W. R. Roper, A. Williamson, L. J. Wright, *Organometallics* **1998**, *17*, 4869–4874; b) G. J. Irvine, C. E. F. Rickard, W. R. Roper, A. Williamson, L. G. Wright, *Angew. Chem.* **2000**, *112*, 978–980; *Angew. Chem. Int. Ed.* **2000**, *39*, 948–950.

[11] C. N. Iverson, M. R. Smith III, *J. Am. Chem. Soc.* **1995**, *117*, 4403–4404.

[12] Crystal data for **2**: $C_{78}H_{87}B_2BrF_{24}FeP_2Pt \cdot 1.5\,CH_2Cl_2 \cdot 0.25\,C_6H_{14}$, orange brick, $0.093 \times 0.210 \times 0.250$ mm^3, triclinic, space group $P\bar{1}$, $a = 12.8443(9)$, $b = 17.7059(12)$, $c = 19.5664(13)$ Å, $\alpha = 102.7860(10)$, $\beta = 91.0560(10)$, $\gamma = 91.9000(10)^\circ$, $V = 4335.5(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.566$ g cm^{-3}, $T = 173(2)$ K; Bruker-Apex platform with CCD detector, graphite-monochromated $Mo_{K\alpha}$ radiation, $2\theta_{max} = 52.79$; 39023 reflections, 17675 independent ($R_{int} = 0.0266$), direct methods, absorption correction SADABS ($\mu = 2.462$ cm^{-1}). Residual electron density was attributed to 1.5 dichloromethane and 0.25 hexane molecules per asymmetric unit. Refinement on split positions, and DFIX, DANG, and DELU restraints were applied to all solvents molecules. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined on idealized positions. $R_1 = 0.0347$ ($I > 2\sigma$), $wR_2 = 0.0885$ (all data), GoF = 1.044, restrained GoF = 1.046, max/min residual electron density: $2.059/-0.485 \times 10^{30}$ e m^{-3}. Crystal data for **3**: $C_{84}H_{94}NB_2BrF_{24}FeP_2Pt$, red plate, $0.06 \times 0.15 \times 0.30$ mm^3, triclinic, space group $P\bar{1}$, $a = 14.2217(17)$, $b = 15.7319(19)$, $c = 21.014(3)$ Å, $\alpha = 110.284(2)$, $\beta = 103.702(2)$, $\gamma = 93.827(2)^\circ$, $V = 4226.9(9)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.562$ g cm^{-3}, $T = 173(2)$ K; Bruker-Apex platform with CCD detector, graphite-monochromated $Mo_{K\alpha}$ radiation, $2\theta_{max} = 52.08$; 35533 reflections, 16491 independent ($R_{int} = 0.0287$), absorption correction SADABS ($\mu = 2.432$ cm^{-1}). The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined on idealized positions. $R_1 = 0.0412$ ($I > 2\sigma$), $wR_2 = 0.0995$ (all data), GoF = 1.068, max/min residual electron density: $1.833/-1.362 \times 10^{30}$ e m^{-3}. CCDC-271343 (**2**) and CCDC-271344 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[13] a) M. D. Butts, B. L. Scott, G. J. Kubas, *J. Am. Chem. Soc.* **1996**, *118*, 11831–11843; b) S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169–1204; c) H. A. Zhong, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **2002**, *124*, 1378–1399; d) U. Fekl, K. I. Goldberg, *Adv. Inorg. Chem.* **2003**, *54*, 259–320.

[14] a) F. M. Conroy-Lewis, L. Mole, A. D. Redhouse, S. A. Litster, J. L. Spencer, *J. Chem. Soc. Chem. Commun.* **1991**, 1601–1603; b) L. Mole, J. L. Spencer, N. Carr, A. G. Orpen, *Organometallics* **1991**, *10*, 49–52; c) N. Carr, L. Mole, A. G. Orpen, J. L. Spencer, *J. Chem. Soc. Dalton Trans.* **1992**, 2653–2662; d) J. L. Spencer, G. S. Mhinzi, *J. Chem. Soc. Dalton Trans.* **1995**, 3819–3824; e) L. Huff Shultz, M. Brookhart, *Organometallics* **2001**, *20*, 3975–3982; f) W. Baratta, S. Stoccoro, A. Doppiu, E. Herdtweck, A. Zucca, P. Rigo, *Angew. Chem.* **2003**, *115*, 109–113; *Angew. Chem. Int. Ed.* **2003**, *42*, 105–108; g) M. J. Ingleson, M. F. Mahon, A. S. Weller, *Chem. Commun.* **2004**, 2398–2399.

[15] J. P. Stambuli, M. Bühl, J. F. Hartwig, *J. Am. Chem. Soc.* **2002**, *124*, 9346–9347.

[16] W. H. Lam, K. C. Lam, Z. Lin, S. Shimada, R. N. Perutz, T. B. Marder, *Dalton Trans.* **2004**, 1556–1562.

[17] See Supporting Information.

[18] For the only other example of cationic terminal borylene complex, see: D. L. Coombs, S. Aldridge, C. Jones, D. J. Willock, *J. Am. Chem. Soc.* **2003**, *125*, 6356–6357.

[19] a) C. E. F. Rickard, W. R. Roper, A. Williamson, J. L. Wright, *Organometallics* **2002**, *21*, 4862–4872; b) For an example of terminal borylene complex stabilized by a transition metal-base, see: H. Braunschweig, D. Rais, K. Uttinger, *Angew. Chem.* **2005**, *117*, 3829–3832; *Angew. Chem. Int. Ed.* **2005**, *44*, 3763–3766.

[20] a) R. J. Goddard, R. Hoffman, E. D. Temmis, *J. Am. Chem. Soc.* **1980**, *102*, 7667–7676; b) T. Ziegler, L. Versluis, V. Tschinke, *J. Am. Chem. Soc.* **1986**, *108*, 612–617.

[21] R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals*, Wiley, New York, 2nd ed., **1994**.

[22] a) G. P. Mitchell, T. D. Tilley, *J. Am. Chem. Soc.* **1998**, *120*, 7635–7636; b) G. P. Mitchell, T. D. Tilley, *Angew. Chem.* **1998**, *110*, 2602–2605; *Angew. Chem. Int. Ed.* **1998**, *37*, 2524–2526.

[23] We wish to point out that the definition "1,2-halide migration" refers here to the overall outcome of the reaction that from compound **2** leads to compound **3**, and is not intended to hold any mechanistic implication which, in the absence of appropriate studies, would only be purely speculative.

[24] a) T. D. Tilley in *The Silicon-Heteroatom Bond* (Eds.: S. Patai, Z. Rappaport), Wiley, New York, **1991**, chaps. 9 and 10; b) S. D. Grumbine, T. D. Tilley, *J. Am. Chem. Soc.* **1993**, *115*, 7884–7885; c) S. K. Grumbine, D. A. Straus, T. D. Tilley, A. L. Rheingold, *Polyhedron* **1995**, *14*, 127–148, and references therein.

[25] U. Schubert, *Coord. Chem. Rev.* **1984**, *55*, 261–286.