ORGANOMETALLICS

Note

Borole-Derived Spirocyclic Tetraorganoborate

Holger Braunschweig,* Christian Hörl, Florian Hupp, Krzysztof Radacki, and Johannes Wahler

Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany

Supporting Information

ABSTRACT: Preparation of a novel conjugated tetraorganoborate is presented in a facile two-step procedure. Successful utilization as a halide abstraction reagent is demonstrated in a metathesis reaction with the platinum(II) boryl complex $[(Cy_3P)_2Pt(Br)(BC_4Ph_4)]$, which was obtained by oxidative addition of 1-bromo-2,3,4,5-tetraphenylborole to a platinum(0) species. The novel compounds were investigated by means of spectroscopic and X-ray diffraction techniques.



Steric protection of the central structural motif is crucial for the synthesis of boroles, a class of highly reactive compounds that show a rich chemistry driven by inherent antiaromatic destabilization.¹ Recently, we isolated 1-bromo-2,3,4,5-tetraphenylborole $(1)^2$ and 1-chloro-2,3,4,5-tetraphenylborole (2)^{3,4} which serve as useful precursors for other borole derivatives and borole-related chemistry (Chart 1).⁵ Examples

Chart 1. 1-Haloboroles 1-3, Perfluorinated Spiroborate 6, and Spiro[4.4]nonatetraene (7)



for the versatile reactivity of the B-C bond in 2 include substitution reactions,^{3,5} halide abstraction,³ oxidative addition to platinum(0),⁶ and reduction processes.^{4,7} However, all efforts to extend this series by 1-fluoro-2,3,4,5-tetraphenylborole (3) via the common synthetic methods (tin-boron exchange reaction, salt elimination)⁸ met with no success so far. In this contribution we present the synthesis of a perphenylated spirocyclic tetraorganoborate (4) obtained from the reaction of $[BF_3 \cdot Et_2O]$ with 1,2,3,4-tetraphenyl-1,4dilithio-1,3-butadiene (5). The latter is readily accessible by reductive dimerization of diphenylacetylene using lithium metal.⁸ In addition, the facile application of 4 as a halide abstraction reagent is demonstrated.

RESULTS AND DISCUSSION

Reaction of excess $[BF_3 \cdot Et_2O]$ with 5 at low temperature (-78 °C) gives a complex mixture of products. However, salt elimination reaction of $[BF_2 \cdot Et_2O]$ with two equivalents of 5 yields lithium-1,2,3,4,6,7,8,9-octaphenyl-5-boraspiro[4.4]nona-1,3,6,8-tetraenide (4) as an isolable compound (Scheme 1).



The latter constitutes a tetraorganocycloborate where the central boron atom is located in the spiro position connecting two 1,2,3,4-tetraphenyl-1,3-butadiene moieties. The related neutral group 14 derivatives with Si, Ge, Sn, and Pb in the spiro position have been reported earlier.9 After optimization of the reaction conditions, 4 was obtained in yields of 58% as a bright yellow solid containing three equivalents of Et₂O deduced from elemental analysis and ¹H NMR spectroscopy. A similar reaction has been reported between perfluorinated 2,2'-dilithio-1,1'-biphenyl and BCl₃ to form the analogue spirocyclic borafluorene derivative 6 (Chart 1), which is considered as an activator for zirconocene-catalyzed ethylene polymerization.¹⁰ The ¹¹B NMR resonance of 4 was found at δ = -1.4 ppm thus, in the range of sp³-hybridized boron in tetrahedral geometry. However, the resonance is significantly shifted to higher frequency by about 10 to 20 ppm compared to organocycloborate derivatives comprising a saturated organic backbone¹¹ or the acyclic tetravinylborate (Li[B(CH=CH₂)₄], $\delta = -16.1$ ppm).¹² This is presumably a consequence of spiro-

Received: November 8, 2012 Published: November 28, 2012

conjugation effects, which are discussed for the neutral isoelectronic spiro[4.4]nonatetraene (7).¹³

Single crystals suitable for X-ray diffraction were obtained by diffusion of diethyl ether into a solution of 4 in thf. The solidstate analysis reveals a separated ion pair with the lithium cation being coordinated by four thf molecules (Figure 1). The



Figure 1. Molecular structure of $4(thf)_4$ in the solid state with additional solvent molecule (thf) and hydrogen atoms omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [deg]: B1–C1 1.627(2), B1–C4 1.637(2), B1–C5 1.635(2), B1–C8 1.623(2), C1–C2 1.368(2), C2–C3 1.481(2), C3–C4 1.365(2), C5–C6 1.365(2), C6–C7 1.480(2), C7–C8 1.363(2); C1–B1–C4 100.1(2), C1–B1–C5 112.2(2), C1–B1–C8 115.3(2), C4–B1–C5 114.3(2), C4–B1–C8 116.6(2), C5–B1–C8 99.1(2), B1–C1–C2 107.9(2), C1–C2–C3 112.0(2), C2–C3–C4 111.8(2), C3–C4–B1 108.0(2).

anionic moiety shows an idealized D_{2d} symmetry, and the fused five-membered rings are essentially planar with an interplanar torsion angle of 89.7(1)°. The B–C bond distances (1.623(2) to 1.637(2) Å) as well as the C–C single (1.480(2) to 1.481(2) Å) and C=C double bonds (1.363(2) to 1.368(2) Å) of the spirocycle are comparable to those found in Lewis acid–base adducts of boroles with various Lewis bases.^{2a,3,7,14}

Hence, the structure resembles that of a conjugated butadiene moiety similar to *E,E-1,2,3,4*-tetraphenyl-1,3-butadiene (C–C: 1.483(2) Å; C=C: 1.353(2) Å).¹⁵ The anionic boron center is well-shielded, and in principle, charge delocalization should be possible over the entire conjugated system.

As a suitable target to probe a potential applicability of 4 in organometallic synthesis, we chose the platinum(II) boryl complex (8) obtained by oxidative addition of 1 to $[Pt(PCy_3)_2]$ (Cy = cyclohexyl). As reported earlier, halide abstraction from the chloro derivative $[(Cy_3P)_2Pt(Cl)(BC_4Ph_4)]$ (9) affords the cationic T-shaped complex $10[B(Ar^F)_4]$ (Ar^F = C₆H₃-3,5- $(CF_3)_2$) when Na[B(Ar^F)₄] is used in a metathesis reaction.^{6,16} The oxidative addition of the B–Br bond of 1 to $[Pt(PCy_3)_2]$ proceeds readily at ambient temperature, as indicated by a rapid color change from deep purple to dark red (8: λ_{max} = 487 nm) upon addition of $[Pt(PCy_3)_2]$ to a solution of 1 (Scheme 2). After extraction of the crude product, 8 was obtained as red crystals suitable for X-ray diffraction. The ¹¹B NMR resonance was found at $\delta = 93.4$ ppm as a broad signal in the expected range for a borole system in η^1 -coordination to platinum(II).⁶ The ³¹P{¹H} NMR resonance at δ = 34.6 ppm (¹J_{Pt-P} = 2942 Hz) is in agreement with a planar trans-Pt(II) boryl complex.¹⁷ Structural analysis substantiates the observed spectroscopic findings, and the structural parameters are very similar to those found for 9 (Figure 2).⁶

The metathesis reaction of **4** with **8** was conveniently accomplished in benzene solution supported by the good



Scheme 2. Synthesis of the Platinum-Substituted Boroles 8

Figure 2. Molecular structure of 8 in the solid state with hydrogen atoms omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [deg]: Pt1–P1 2.351(1), Pt1–P2 2.356(1), Pt1–Br 2.640(1), Pt1–B1 1.996(3), B1–C1 1.624(4), B1–C4 1.620(4), C1–C2 1.361(4), C2–C3 1.525(4), C3–C4 1.350(4), B1–Pt1–Br1 174.7(1), P1–Pt1–P2 172.2(1).

solubility of both compounds (Scheme 2). The product $10[B(C_4Ph_4)_2]$ precipitated from solution along with LiBr. After filtration and extraction, the product was recrystallized from CH₂Cl₂/hexane at -30 °C to give a reddish-brown solid of $10[B(C_4Ph_4)_2]$ in 85% yield. According to ¹H NMR spectroscopy and elemental analysis the product includes 1.5 equivalents of CH₂Cl₂. The ¹¹B NMR resonance of the borole unit was detected at $\delta = 63.9$ ppm as an extremely broad signal, whereas the ¹¹B NMR signal of the anion ($\delta = -1.7$ ppm) remains almost unaltered compared to 4. The ³¹P{¹H} NMR resonance detected at δ = 53.5 ppm (¹J_{Pt-P} = 2848 Hz) is consistent with formation of the cationic T-shaped 14-electron complex.^{6,16} The lowest energy electronic absorption was observed at $\lambda_{\text{max}} = 521 \text{ nm}$ to be almost identical to that found for $10[B(\text{Ar}^F)_4]$ ($\lambda_{\text{max}} = 524 \text{ nm}$).⁶ Hence, substitution of the counteranion has no striking effect on the absorption properties of the cationic moiety. This can be judged as an indication of similar coordinating properties between the novel anion and $[B(Ar^{F})_{4}]^{-}$ in the present case. The absorption bands of the anion are also very similar in 4 ($\lambda_{max} = 356$ nm) and $10[B(C_4Ph_4)_2] (\lambda_{max} = 358 \text{ nm}).$

Slow diffusion of hexane into a solution of $10[B(C_4Ph_4)_2]$ in CH_2Cl_2 yielded single crystals suitable for X-ray diffraction (Figure 3). As expected from the spectroscopic data, the ion pair is well-separated in the solid state. The cationic T-shaped fragment shows a nearly planar coordination of platinum as well

Organometallics



Figure 3. Molecular structure of $10[B(C_4Ph_4)_2]$ in the solid state with additional solvent molecules (CH_2Cl_2) and hydrogen atoms omitted for clarity. Thermal ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [deg]: B1–C1 1.628(5), B1–C4 1.621(5), B1–C5 1.629(5), B1–C8 1.628(5), C1–C2 1.365(4), C2–C3 1.474(4), C3–C4 1.355(4), C5–C6 1.369(5), C6–C7 1.478(4), C7–C8 1.355(4), Pt1–B2 1.953(3), Pt1–P1 2.328(1), Pt1–P2 2.330(1), B2–C9 1.584(4), B2–C12 1.578(5), C9–C10 1.352(4), C10–C11 1.518(4), C11–C12 1.353(4); C1–B1–C4 99.4(3), C1–B1–C5 123.5(3), C1–B1–C8 108.4(3), C4–B1–C5 112.1(3), C4–B1–C8 114.5(3), C5–B1–C8 99.6(3), P1–P1–P2 166.4(1), B2–Pt1–P1 95.1(1), B2–Pt1–P2 98.5(1).

as a planar borole ring with bond lengths and angles similar to those found in $10[B(Ar^F)_4]$.⁶ The anionic moiety of $10[B(C_4Ph_4)_2]$ displays significant distortion of the central spirocyclic framework in comparison to 4. This is indicated by a decreased interplanar torsion angle of 82.7(2)° between the fused C₄B rings, resulting in C–B–C angles ranging from $108.4(3)^\circ$ to $123.5(3)^\circ$ in $10[B(C_4Ph_4)_2]$ compared with $112.2(2)^\circ$ to $116.6(2)^\circ$ in 4. The bond distances show no unusual deviation. Considering the spectroscopic findings in solution, this structural change is most likely caused by crystalpacking effects.

CONCLUSION

In conclusion, we have reported a two-step synthesis protocol and concomitant characterization of the novel borate salt 4 consisting of a bulky perphenylated spirocyclic tetraorganoborate. In particular, it was demonstrated that 4 can be effectively employed as a halide abstraction reagent. According to this, reaction with the platinum boryl complex 8 results in formation of the cationic T-shaped derivative $10[B(C_4Ph_4)_2]$ in high yield. The structural and spectroscopic parallels of $10[B-(C_4Ph_4)_2]$ and $10[B(Ar^F)_4]$ give a first indication of possible applications. The facile access and good solubility of 4 as well as the tendency of its derivatives to form single crystals of good quality are considered to be advantageous in a variety of reactions. Further research will include investigations of the scope of 4 in related reactions and catalysis

EXPERIMENTAL SECTION

General Considerations. All syntheses were carried out under an argon atmosphere with standard Schlenk and glovebox techniques. 1-Bromo-2,3,4,5-tetraphenylborole (1),^{2a} 1,4-dilithio-1,2,3,4-tetraphenylbuta-1,3-diene containing 0.5 equivalent of diethyl ether (**5**),⁸ and $[Pt(PCy_3)_2]^{18}$ were prepared according to published procedures. $[BF_3:Et_2O]$ was freshly distilled prior to use. Hexane, benzene, tetrahydrofuran (thf), and diethyl ether were dried by distillation over sodium, and dichloromethane (dcm) was dried by distillation over P_2O_5 under argon and stored over molecular sieves. C_6D_6 and CD_2Cl_2 were degassed by three freeze–pump–thaw cycles and stored over molecular sieves. NMR spectra were recorded on a Bruker Avance 500 NMR spectrometer (500 MHz for ¹H, 160 MHz for ¹¹B, 202 MHz for ³¹P{¹H}, 194 MHz for ⁷Li, 126 MHz for ¹³C{¹H}) at 296 K. Chemical shifts (δ) are given in ppm and are referenced against external Me₄Si (¹¹H, ¹³C), $[BF_3:Et_2O]$ (¹¹B), 85% H₃PO₄ (³¹P), and 1 M LiCl (⁷Li).

Synthesis of $[Li(Et_2O)_3][B(C_4Ph_4)_2]$ (4). A solution of $[BF_3 \cdot Et_2O]$ (257 mg, 1.81 mmol) in benzene (3 mL) was added dropwise to a solution of 5 (1.00 g, 2.45 mmol) in benzene (15 mL) within 5 min at RT. The mixture was stirred for 22 h, resulting in formation of a colorless precipitate and a brown solution. After filtration, all volatiles were removed under vacuum. Et₂O (3 mL) was added to give a dark brown oil that started to crystallize within minutes. The yellow solid (682 mg, 716 mmol, 58%) was filtered, washed with Et_2O (3 × 2 mL), and dried under vacuum. Single crystals of $[Li(thf)_4][B(C_4Ph_4)_2]$ $(4(thf)_4)$ suitable for X-ray diffraction were obtained by diffusion of Et₂O into a solution of 4 in thf. 4 shows a good solubility in benzene and thf as well as a poor solubility in Et_2O. ^1H NMR (500 MHz, C₆D₆): δ 6.87-6.92 (m, 8H, C₆H₅), 6.96-6.99 (m, 8H, C₆H₅), 7.04-7.11 (m, 16H, C₆H₅), 7.51–7.52 (m, 8H, C₆H₅). ¹¹B NMR (160 MHz, C₆D₆): δ –1.4. ¹³C{¹H} NMR (126 MHz, C₆D₆): δ 125.67, 126.05, 127.91, 128.35, 129.37, 130.56 (CH), 140.53, 143.42, 152.49, 156.99 (br) (C). ⁷Li NMR (194 MHz, C₆D₆): δ –1.8. λ_{max} (ε) = 356 nm (34 490 L mol⁻¹ cm⁻¹; measured in Et₂O). Anal. Calcd (%) for C₆₈H₇₀BLiO₃: C 85.70; H 7.40. Found: C 85.41; H 7.09.

Synthesis of [(Cy₃P)₂Pt(Br)(BC₄Ph₄)] (8). A solution of [Pt- $(PCy_3)_2$] (30.0 mg, 39.7 μ mol) in benzene (0.4 mL) was added dropwise to a stirred solution of 1 (20.0 mg, 44.7 μ mol) in benzene (0.3 mL) at RT, resulting in an immediate color change from deep purple to dark red. After 10 min the solvent was removed under vacuum, and the residue was extracted with hexane $(4 \times 0.3 \text{ mL})$. Within 5 h red crystals (suitable for X-ray diffraction) of 8 (33.2 mg, 24.9 μ mol, 63%) containing 1.5 equivalents of hexane were obtained from the solution. The product was washed with hexane (0.3 mL) and dried under vacuum. $^1\hat{H}$ NMR (500 MHz, $C_6D_6):$ δ 1.19–1.38 (m, 18H, Cy), 1.64-1.77 (m, 31H, Cy), 2.18 (br s, 11H, Cy), 2.79 (br s, 6H, Cy), 6.91-7.00 (m, 12H, C₆H₅), 7.12-7.15 (m, 4H, C₆H₅), 7.87-7.89 (m, 4H, C_6H_5). ¹¹B NMR (160 MHz, C_6D_6): δ 93.4 (br). ¹³C{¹H} NMR (126 MHz, C_6D_6): δ 26.85, 28.14 (m), 31.13 (m) (CH₂), 37.86 (m), 125.80, 126.83, 127.45, 127.90, 130.00, 132.37 (CH), 138.36, 141.45, 142.77, 154.86 (C). ³¹P{¹H} NMR (202 MHz, C_6D_6): δ 34.6 (s, ${}^{1}J_{P-Pt}$ = 2942 Hz). λ_{max} (ϵ) = 487 nm (1407 L mol⁻¹ cm⁻¹; measured in CH₂Cl₂). Anal. Calcd (%) for C₇₃H₁₀₇BBrP₂Pt: C 65.81; H 8.09. Found: C 65.90; H 8.09.

Synthesis of $[(Cy_3P)_2Pt(BC_4Ph_4)][B(C_4Ph_4)_2]$ (10[B(C₄Ph_4)_2]). A solution of 4 (15.1 mg, 15.8 µmol) in benzene (0.5 mL) was added dropwise to a stirred solution of 8 (20.0 mg, 15.5 µmol) in benzene (0.5 mL) at RT, resulting in an immediate color change from dark red to reddish-brown. After 1 h the mixture was cooled to $-30 \,^{\circ}$ C, and after warming to RT a reddish solid precipitated. The solid was filtered, washed with benzene (3 × 0.3 mL), and dried under vacuum. After extraction with dcm (0.5 mL), hexane (0.5 mL) was diffused into the solution at $-30 \,^{\circ}$ C to yield 10[B(C₄Ph_4)_2] (26.0 mg, 13.2 µmol, 85%) as a reddish-brown solid containing 1.5 equivalents of dcm. Single crystals suitable for X-ray diffraction were obtained by the same method. ¹H NMR (500 MHz, CD₂Cl₂): δ 1.19–1.42 (m, 30H, Cy), 1.79–1.87 (m, 18H, Cy), 2.00–2.02 (m, 12H, Cy), 2.19–2.24 (m, 6H, Cy), 6.66–6.68 (m, 4H, C₆H₅), 6.74–7.78 (m, 4H, C₆H₅), 6.87–6.96 (m, 20H, C₆H₅), 6.99–7.07 (m, 20H, C₆H₅), 7.15–7.25 (m, 12H, Cy).

C₆H₅). ¹¹B NMR (160 MHz, CD₂Cl₂): δ –1.7, 63.9 (br). ¹³C{¹H} NMR (126 MHz, CD₂Cl₂): δ 26.13, 27.42 (vt, N = $|^{2}J_{C-P} + {}^{4}J_{C-P}| = 11.6$ Hz), 30.97 (CH₂), 35.27 (vt, N = $|^{1}J_{C-P} + {}^{3}J_{C-P}| = 27.0$ Hz), 122.73, 124.36, 126.64, 127.22, 127.26, 128.12, 128.26, 128.55, 129.39, 129.52, 130.19, 130.94 (CH), 135.56, 136.37 (br), 138.87, 144.14, 145.64, 149.32, 158.18, 161.15 (br) (C). {}^{31}P{}^{1}H NMR (202 MHz, CD₂Cl₂): δ 53.5 (s, ${}^{1}J_{P-Pt} = 2848$ Hz). λ_{max} (ε) = 521 nm (831 L mol⁻¹ cm⁻¹), 358 nm (27 620 L mol⁻¹ cm⁻¹; measured in CH₂Cl₂). Anal. Calcd (%) for C_{121.5}H₁₂₉B₂Cl₃P₂Pt: C 73.91, H 6.59. Found: C 73.88, H 6.68.

ASSOCIATED CONTENT

Supporting Information

Experimental details including X-ray crystallographic data (CIF files) and UV/vis spectra of 4, 8, and $10[B(C_4Ph_4)_2]$. This material is available free of charge via the Internet at http:// pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Fax: (+49) 931-31-84623. E-mail: h.braunschweig@uniwuerzburg.de.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are grateful to the German Science Foundation (DFG) for financial support.

REFERENCES

(1) (a) Eisch, J. J.; Hota, N. K.; Kozima, S. J. Am. Chem. Soc. **1969**, 91, 4575–4577. (b) Braunschweig, H.; Fernández, I.; Frenking, G.; Kupfer, T. Angew. Chem., Int. Ed. **2008**, 47, 1951–1954.

(2) (a) Braunschweig, H.; Chiu, C.-W.; Damme, A.; Ferkinghoff, K.; Kraft, K.; Radacki, K.; Wahler, J. *Organometallics* **2011**, *30*, 3210–3216. (b) Fan, C.; Piers, W. E.; Parvez, M. Angew. Chem., Int. Ed. **2009**, *48*, 2955–2958.

(3) Braunschweig, H.; Kupfer, T. Chem. Commun. 2008, 4487–4489.
(4) Braunschweig, H.; Chiu, C.-W.; Wahler, J.; Radacki, K.; Kupfer, T. Chem.—Eur. J. 2010, 16, 12229–12233.

(5) (a) Braunschweig, H.; Kupfer, T. Chem. Commun. 2011, 47, 10903–10914. (b) Braunschweig, H.; Dyakonov, V.; Jimenez-Halla, J. O. C.; Kraft, K.; Krummenacher, I.; Radacki, K.; Sperlich, A.; Wahler, J. Angew. Chem., Int. Ed. 2012, 51, 2977–2980.

(6) Braunschweig, H.; Chiu, C.-W.; Radacki, K.; Brenner, P. Chem. Commun. 2010, 46, 916–918.

(7) Braunschweig, H.; Chiu, C.-W.; Radacki, K.; Kupfer, T. Angew. Chem., Int. Ed. 2010, 49, 2041–2044.

(8) Eisch, J. J.; Galle, J. E.; Kozima, S. J. Am. Chem. Soc. 1986, 108, 379–385.

(9) (a) Timokhin, V. I.; Guzei, I. A.; West, R. Silicon Chem. 2005, 3, 239–242. (b) Leavitt, F. C.; Manuel, T. A.; Johnson, F.; Matternas, L. U.; Lehman, D. S. J. Am. Chem. Soc. 1960, 82, 5099–5102. (c) Curtis, M. D. J. Am. Chem. Soc. 1969, 91, 6011–6017. (d) Van Beelen, D. C.; Wolters, J.; Van der Gen, A. Recl. Trav. Chim. Pays-Bas 1979, 98, 437–440.

(10) Chen, E. Y-X.; Marks, T. J. Chem. Rev. 2000, 100, 1391–1434.
(11) (a) Braunschweig, H.; D'Andola, G.; Welton, T.; White, A. J. P. Chem. Commun. 2004, 1738–1739. (b) Braunschweig, H.; D'Andola, G.; Welton, T.; White, A. J. P. Chem.—Eur. J. 2006, 12, 600–606.

(12) Thompson, R. J.; Davis, J. C. Inorg. Chem. 1965, 4, 1464–1467.
(13) (a) Simmons, H. E.; Fukunaga, T. J. Am. Chem. Soc. 1967, 89, 5208–5215. (b) Semmelhack, M. F.; Foos, J. S.; Katz, S. J. Am. Chem. Soc. 1973, 95, 7325–7336. (c) Haumann, T.; Benet-Buchholz, J.; Boese, R. J. Mol. Struct. 1996, 374, 299–304.

(14) (a) Ansorg, K.; Braunschweig, H.; Chiu, C.-W.; Engels, B.; Gamon, D.; Hügel, M.; Kupfer, T.; Radacki, K. Angew. Chem., Int. Ed. **2011**, *50*, 2833–2836. (b) Braunschweig, H.; Damme, A.; Gamon, D.; Kupfer, T.; Radacki, K. *Inorg. Chem.* **2011**, *50*, 4250–4252. (c) Fukazawa, A.; Dutton, J.; Fan, C.; Mercier, L. G.; Houghton, A. Y.; Wu, Q.; Piers, W. E.; Parvez, M. *Chem. Sci.* **2012**, *3*, 1814–1818. (15) López-Serrano, J.; Duckett, S. B.; Dunne, J. P.; Godard, C.; Whitwood, A. C. *Dalton Trans.* **2008**, *26*, 4270–4281.

(16) (a) Braunschweig, H.; Radacki, K.; Rais, D.; Scheschkewitz, D. Angew. Chem., Int. Ed. **2005**, 44, 5651–5654. (b) Braunschweig, H.; Radacki, K.; Uttinger, K. Chem.—Eur. J. **2008**, 14, 7858–7866.

(17) Braunschweig, H.; Brenner, P.; Müller, A.; Radacki, K.; Rais, D.; Uttinger, K. *Chem.—Eur. J.* **2007**, *13*, 7171–7176.

(18) Yoshida, T.; Otsuka, S. Inorg. Synth. 1979, 19, 101-107.