Borylene Complexes

DOI: 10.1002/anie.200801756

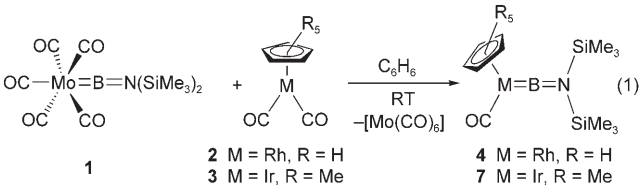
Borylene Transfer under Thermal Conditions for the Synthesis of Rhodium and Iridium Borylene Complexes**

Holger Braunschweig, Melanie Forster, Thomas Kupfer, and Fabian Seeler*

The recent development of the photochemical transfer of borylene ligands from chromium and tungsten borylene complexes to inorganic,[1] and more recently, organic[2] substrates has shown the "**:**BX" fragment to be a useful synthon. As is the case for many reactive species, the feisty nature of the difficult-to-generate free borylenes[3] is tempered by coordination to a transition metal, so that their reactivity, which is reminiscent of the neighboring carbene species,[4] can be harnessed in conventional syntheses.

In particular, the above-mentioned transfer reaction has proven a boon for the synthesis of borylenes with other metal centers, and has uncovered a surprising synthesis of borirenes from terminal or internal alkynes. However, with the exception of one example,[5] this reaction requires activation by UV light, and is thus limited to photochemically inert substrates. Herein we describe the use of a terminal molybdenum borylene complex[6] which performs this task without irradiation and at ambient temperatures. This new reactivity is borne out in the synthesis of the first terminal borylene complexes of the Group 9 elements rhodium and iridium. These two metals have been the subject of intense investigation regarding their application in catalytic borylation reactions. A variety of boryl complexes have therefore been prepared,[7] however their complexes with lower-coordinate boron have been overlooked owing to the lack of reliable synthetic routes. The complexes presented herein go some way in addressing this deficiency.

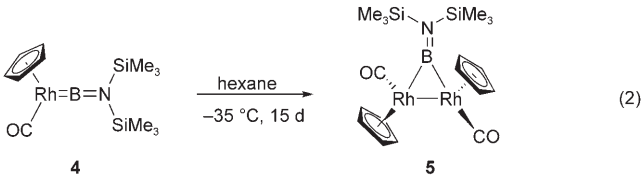
When the rhodium dicarbonyl complex **2** was added to an equimolar amount of **1** in C_6D_6 at ambient temperature, multinuclear NMR spectroscopy revealed gradual consumption of the starting materials within 16 h and formation of what appeared to be the terminal borylene species [(η^5-C_5H_5)(OC)Rh=BN($SiMe_3$)$_2$] (**4**) with concomitant generation of [$Mo(CO)_6$], as indicated by a resonance at $\delta = 201.49$ ppm in the ^{13}C NMR spectrum for the latter [Eq. (1)]. After workup, **4** was isolated as an analytically pure dark orange oil in 67% yield.



The ^{11}B{^{1}H} NMR spectrum of **4** features a broad signal at $\delta = 75$ ppm ($\omega_{1/2} = 309$ Hz) which is shifted upfield relative to the signal for **1** ($\delta = 91$ ppm),[6] suggesting the formation of a terminal borylene species.[8] The ^{1}H NMR spectrum shows a singlet for the trimethylsilyl group at $\delta = 0.21$ ppm, which is deshielded with respect to that of the molybdenum borylene precursor ($\delta = 0.15$ ppm).[6] A single conspicuous band at $\tilde{\nu} = 1955$ cm^{-1} in the solution IR spectrum of **4** suggests that a lone CO ligand at rhodium was terminally coordinated. Unfortunately, owing to its oily consistency, it was not possible to obtain single crystals of **4** suitable for X-ray diffraction.

Borylene **4** is unstable in solution, which was revealed by ^{11}B{^{1}H} NMR spectroscopy. The ^{11}B{^{1}H} NMR spectrum indicated the formation of a new boron-containing product even under mild conditions (hexane at −35 °C). Conversion into the new product was complete after about 15 days, at which point red crystals of [{(η^5-C_5H_5)(OC)Rh}$_2${μ-BN($SiMe_3$)$_2$}] (**5**) were isolated [Eq. (2)]. The rather moderate yield of 37% for **5** is in agreement with its formation in a nonstoichiometric reaction reminiscent of its cobalt congener.[9]

The ^{1}H NMR spectrum of **5** has one singlet for the trimethylsilyl group at $\delta = 0.36$ ppm, which is deshielded with regard to that of the terminal precursor **4** ($\delta = 0.21$ ppm). A



downfield-shifted broad singlet at $\delta = 90$ ppm ($\omega_{1/2} = 1577$ Hz) in the ^{11}B{^{1}H} NMR spectrum indicates the formation of a new bridged borylene compound.[8]

The atom connectivity of **5** was conclusively determined by performing a single-crystal X-ray diffraction study (Figure 1). The complex crystallizes in the monoclinic space group *C*2/c.[10] Two {(η^5-C_5H_5)Rh(CO)} units are linked through a metal–metal bond and a bridged borylene ligand. The borylene complex **5** has an *anti* orientation of the (η^5-C_5H_5) and CO groups with respect to the Rh_2B plane. These three atoms form an isosceles triangle in which the B–Rh distances are 2.054(2) Å and the Rh–Rh distance is

[*] Prof. Dr. H. Braunschweig, M. Forster, Dr. T. Kupfer, Dr. F. Seeler
Institut für Anorganische Chemie
Julius-Maximilians-Universität Würzburg
Am Hubland, 97074 Würzburg (Germany)
Fax: (+49) 931-888-4623
E-mail: h.braunschweig@mail.uni-wuerzburg.de
Homepage: http://www-anorganik.chemie.uni-wuerzburg.de/Braunschweig/index.html

[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

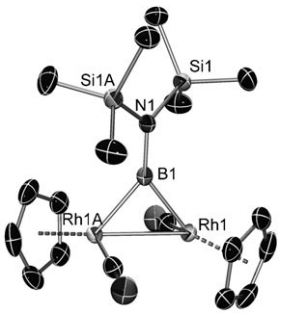


Figure 1. Molecular structure of **5** in the solid state. Bond lengths [Å] and angles [°]: B1–Rh1 2.054(2), B1–Rh1A 2.054(2), B1–N1 1.399(3), Rh1–Rh1A 2.668(3); Rh1-B1-N1-Si1 41.72(2), N1-B1-Rh1 139.51(5), N1-B1-Rh1A 139.51(5), B1-Rh1-Rh1A 49.51(6), B1-Rh1A-Rh1 49.51(6). Thermal ellipsoids are set at 50% probability, and hydrogen atoms are omitted for clarity.

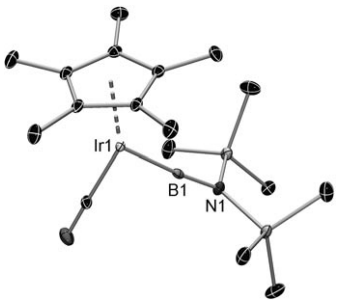


Figure 2. Molecular structure of **7** in the solid state. Bond lengths [Å] and angles [°]: B1–Ir1 1.892(3), B1–N1 1.365(4); Ir1-B1-N1 175.9(3). Thermal ellipsoids are set at 50% probability. Hydrogen atoms are omitted for clarity.

2.668(3) Å. The B–Rh bond length is similar to analogous distances found in the bridged bisborylene complex $[Rh_4\{\mu\text{-}BN(SiMe_3)_2\}_2(\mu\text{-}Cl)_4(\mu\text{-}CO)(CO)_4]$, which features two three-coordinate boron atoms linked to two rhodium centers (2.004(3) Å, 2.076(3) Å, 2.051(3) Å).[5] The molecular geometry also closely resembles that of the methylene-bridged rhodium complex $[(\mu\text{-}CH_2)\{(\eta^5\text{-}C_5H_5)Rh(CO)\}_2]$.[11] Herein the remarkably short Rh–Rh distance of 2.665(1) Å also indicates the presence of a metal–metal bond, which is consistent with the description of this class of compounds as dimetallacyclopropanes. The presence of the bulky trimethylsilyl groups imposes a twist of the Si1-B1-Si1A moiety with respect to the Rh1-B1-Rh1A unit (41.72(2)°), as was previously observed in the bridged borylene complex $[\{(\eta^5\text{-}C_5H_4Me)Fe(CO)\}_2(\mu\text{-}CO)\{\mu\text{-}BN(SiMe_3)_2\}]$ (**6**; 53(1)°). Thus, in connection with the elongated B–N distance of 1.412(4) Å, less effective backbonding from the nitrogen to the boron atom can be assumed in **6.**[12] However, the B1–N1 bond (1.399(6) Å) of **5** is only slightly longer than that observed in the bridged manganese borylene complex $[(\mu\text{-}BNMe_2)\{(\eta^5\text{-}C_5H_5)Mn(CO)_2\}_2]$ (1.390(1) Å),[13] indicating significant double-bond character of the B–N linkage.

As **4** can be regarded as an unstable terminal borylene complex, we focused our attention on the transfer of the borylene unit to a sterically more demanding late transition metal system to protect the borylene fragment from scavenging a second metal centre. We chose $[(\eta^5\text{-}C_5Me_5)Ir(CO)_2]$ (**3**) because of the electron-rich and sterically demanding nature of the iridium fragment owing to its bulky $(\eta^5\text{-}C_5Me_5)$ substituent [Eq. (1)].

Monitoring the reaction of equimolar amounts of **1** and **3** in C_6D_6 at ambient temperature by multinuclear NMR spectroscopy showed consumption of the starting materials within 20 h and formation of a new species, which we assigned as $[(\eta^5\text{-}C_5Me_5)(OC)Ir{=}BN(SiMe_3)_2]$ (**7**), with concomitant formation of $[Mo(CO)_6]$, as indicated by ^{13}C NMR spectroscopy.

The $^{11}B\{^1H\}$ NMR spectrum of **7** has a broad singlet at $\delta =$ 67 ppm ($\omega_{1/2} = 145$ Hz), which is shifted upfield with regard to the signal of the starting material **1** ($\delta = 91$ ppm),[6] suggesting, as in the case of **4**, the formation of a terminal borylene complex.[8] The ^1H NMR spectrum shows one new singlet for the trimethylsilyl group at $\delta = 0.26$ ppm, which is very slightly deshielded realtive to that of the terminal borylene **1** ($\delta =$ 0.15 ppm).[6]

The proposed constitution of **7** was confirmed by single-crystal X-ray diffraction (Figure 2). Crystals of **7** were obtained by cooling a concentrated hexane solution to −70 °C; the complex crystallizes in the monoclinic space group $P2_1/n$.[10]

The Ir1–B1 bond of **7** (1.892(3) Å) is significantly shorter than bonds of known iridium boryl complexes (1.991(6)–2.093(7) Å)[14] and is consistent with a borylene complex. The Ir1–B1 bond (1.892(3) Å) is very similar to the distance of the Ir=C double bond in the related half-sandwich iridum carbene complex $[(\eta^5\text{-}C_5H_5)Ir(=CPh_2)(P\mathit{i}Pr_3)]$ (1.904(5) Å),[15] but significantly longer than that of terminal borylene complex $[(\eta^5\text{-}C_5H_5)Mn(=BCMe_3)(CO)_2]$ (1.809(9) Å).[16] The central Ir-B-N axis is slightly bent, having an angle of 175.9(3)°. The short B–N bond length (1.365(4) Å), together with the trigonal-planar geometry of the nitrogen atom, shows the presence of a B=N double bond. The overall geometry of the M-B-N moiety in **7** resembles that of the only other structurally characterized neutral terminal half-sandwich aminoborylene complex $[(\eta^5\text{-}C_5H_5)(OC)_3V{=}BN(SiMe_3)_2]$[1b] (V=B 1.959(6) Å) and corresponds, together with the NMR spectroscopic data, to the description of a metal–boron bonding picture consisting of a strong B–M σ donation and somewhat weaker M–B π back donation.

Herein we have reported on the unprecedented borylene transfer based on molybdenum borylene complex **1** at ambient temperature, a discovery that could allow borylene transfer to thermally and/or photochemically unstable precursors. The result is the formation of the first terminal borylene complexes of rhodium and iridium, and indeed the first borylene complex of iridium.

Experimental Section

All manipulations were conducted under an atmosphere of dry argon, either inside a glove box or employing standard Schlenk techniques.

4: An orange-colored solution of **1** (0.21 g, 0.50 mmol) and **2** (0.13 g, 0.50 mmol) in benzene (3 mL) was stirred at ambient temperature for 16 h. The solvent of the reaction mixture was then removed in vacuo. The resulting dark orange oily residue was dissolved in toluene (3 mL) and stored at −35 °C for 17 h to separate $[Mo(CO)_6]$. After filtration, all volatiles were removed in vacuo. The

resulting dark orange oil was dissolved in hexane (2 mL) with subsequent filtration. The solvent was removed in vacuo and **4** was isolated as an analytically pure dark orange oil (0.12 g, 67%). ^{1}H NMR (500 MHz, C_6D_6, 25 °C, TMS): $\delta = 5.34$ (d, $^2J_{Rh,H} = 0.5$ Hz, 5H, C_5H_5), 0.21 ppm (s, 18H, SiMe_3); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 25 °C): $\delta = 194.90$ (d, $^1J_{Rh,C} = 88.0$ Hz, *C*O), 87.25 (d, $^1J_{Rh,C} = 13.0$ Hz, C_5H_5), 3.50 ppm (s, SiMe_3); ^{11}B{^{1}H} NMR (64 MHz, C_6D_6, 25 °C): $\delta =$ 75 ppm (br s, $\omega_{1/2} = 309$ Hz). IR (toluene): $\tilde{\nu} = 1955$ cm^{-1} (C=O). C,H,N analysis (%) calcd for $C_{11}H_{23}NBRhOSi_2$: C 37.20, H 6.53, N 3.94; found: C 37.37, H 6.45, N 3.31.

5: Compound **4** (0.05 g, 0.14 mmol) was dissolved in hexane (1 mL) and stored at −35 °C for 15 d to yield a dark red crystalline solid. The solid was dissolved in hexane (2 mL), filtered, and the dark red solution was cooled to −35 °C. **5** was isolated as red crystals (0.03 g, 37%). ^{1}H NMR (500 MHz, C_6D_6, 25 °C, TMS): $\delta = 5.28$ (d, 5H, C_5H_5), 0.36 (s, 18H, SiMe_3); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 25 °C): $\delta = 191.59$ (d, $^1J_{Rh,C} = 126.3$ Hz, *C*O), 90.66 (s, C_5H_5), 5.89 ppm (s, SiMe_3); ^{11}B{^{1}H} NMR (64 MHz, C_6D_6, 25 °C): $\delta = 90$ ppm (br s, $\omega_{1/2} = 1577$ Hz). IR (toluene): $\tilde{\nu} = 1975$ cm^{-1}, (C=O). C,H,N analysis (%) calcd for $C_{18}H_{28}NBRh_2O_2Si_2$: C 38.39, H 5.01, N 2.49; found: C 37.91, H 4.90, N 2.34.

7: A dark brown solution of **1** (0.21 g, 0.50 mmol) and **3** (0.20 g, 0.50 mmol) in benzene (3 mL) was stirred at ambient temperature for 20 h. The solvent was then removed in vacuo. All impurities were removed by sublimation, and the resulting yellow solid was dissolved in hexane (2 mL). After filtration, the solution was cooled to −70 °C, leading to formation of orange crystals of **7** (0.13 g, 48%). ^{1}H NMR (500 MHz, C_6D_6, 25 °C, TMS): $\delta = 2.12$ (s, 15H, C_5Me_5), 0.26 ppm (s, 18H, SiMe_3); ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, 25 °C): $\delta = 181.94$ (s, *C*O), 96.23 (s, C_5Me_5), 11.78 (s, C_5Me_5), 3.29 ppm (s, SiMe_3); ^{11}B{^{1}H} NMR (64 MHz, C_6D_6, 25 °C, TMS): $\delta = 67$ ppm (br s, $\omega_{1/2} =$ 145 Hz). IR (toluene): $\tilde{\nu} = 1945$ cm^{-1} (C=O). C,H,N analysis (%) calcd for $C_{17}H_{33}NBIrOSi_2$: C 38.77, H 6.32, N 2.66; found: C 38.50, H 6.15, N 2.65.

Received: April 15, 2008
Published online: July 4, 2008

Keywords: boron · borylene complexes · iridium · rhodium

[1] a) H. Braunschweig, M. Colling, C. Kollann, H. G. Stammler, B. Neumann, *Angew. Chem.* **2001**, *113*, 2359 – 2361; *Angew. Chem. Int. Ed.* **2001**, *40*, 2298 – 2300; b) H. Braunschweig, M. Colling, C. Hu, K. Radacki, *Angew. Chem.* **2003**, *115*, 215 – 218; *Angew. Chem. Int. Ed.* **2003**, *42*, 205 – 208; c) H. Braunschweig, M. Forster, K. Radacki, F. Seeler, G. R. Whittell, *Angew. Chem.* **2007**, *119*, 5304 – 5306; *Angew. Chem. Int. Ed.* **2007**, *46*, 5212 – 5214.

[2] a) H. Braunschweig, T. Herbst, D. Rais, F. Seeler, *Angew. Chem.* **2005**, *117*, 7627 – 7629; *Angew. Chem. Int. Ed.* **2005**, *44*, 7461 – 7463; b) H. Braunschweig, I. Fernandez, G. Frenking, K. Radacki, F. Seeler, *Angew. Chem.* **2007**, *119*, 5307 – 5310; *Angew. Chem. Int. Ed.* **2007**, *46*, 5215 – 5218; for specific reviews on borylene complexes see: c) H. Braunschweig, M. Colling, *J. Organomet. Chem.* **2000**, *614–615*, 18 – 26; d) H. Braunschweig, M. Colling, *Eur. J. Inorg. Chem.* **2003**, 393 – 403; e) H. Braunschweig, *Adv. Organomet. Chem.* **2004**, *51*, 163 – 192; f) H. Braunschweig, D. Rais, *Heteroat. Chem.* **2005**, *16*, 566 – 571.

[3] a) P. L. Timms, *J. Am. Chem. Soc.* **1967**, *89*, 1629 – 1632; b) P. L. Timms, *Acc. Chem. Res.* **1973**, *6*, 118 – 123; c) B. Pachaly, R. West, *Angew. Chem.* **1984**, *96*, 444 – 445; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 454 – 455; d) P. L. Timms, *J. Am. Chem. Soc.* **1968**, *90*, 4585 – 4589.

[4] a) H. Braunschweig, M. Burzler, K. Radacki, F. Seeler, *Angew. Chem.* **2007**, *119*, 8217 – 8219; *Angew. Chem. Int. Ed.* **2007**, *46*, 8071 – 8073; b) D. L. Kays (née Coombs), J. K. Day, L. L. Ooi, S. Aldridge, *Angew. Chem.* **2005**, *117*, 7623 – 7626; *Angew. Chem. Int. Ed.* **2005**, *44*, 7457 – 7460; c) D. L. Kays (née Coombs), J. K. Day, S. Aldridge, R. W. Harrington, W. Clegg, *Angew. Chem.* **2006**, *118*, 3593 – 3596; *Angew. Chem. Int. Ed.* **2006**, *45*, 3513 – 3516.

[5] H. Braunschweig, M. Forster, K. Radacki, *Angew. Chem.* **2006**, *118*, 2187 – 2189; *Angew. Chem. Int. Ed.* **2006**, *45*, 2132 – 2134.

[6] B. Blank, M. Colling-Hendelkens, C. Kollann, K. Radacki, D. Rais, K. Uttinger, G. R. Whittell, H. Braunschweig, *Chem. Eur. J.* **2007**, *13*, 4770 – 4781.

[7] a) H. Braunschweig, C. Kollann, D. Rais, *Angew. Chem.* **2006**, *118*, 5380 – 5400; *Angew. Chem. Int. Ed.* **2006**, *45*, 5254 – 5274; b) G. J. Irvine, M. J. G. 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) S. Aldridge, D. L. Coombs, *Coord. Chem. Rev.* **2004**, *248*, 535 – 559.

[8] H. Braunschweig, M. Colling, *Coord. Chem. Rev.* **2001**, *223*, 1 – 51.

[9] Two equivalents of **4** form the dinuclear species **5** with formal loss of one equivalent of the borylene [BN(SiMe$_3$)$_2$]. Data from NMR spectroscopy did not provide conclusive evidence as to the fate of this fragment.

[10] The crystal data for **5** and **7** were collected on a Bruker APEX diffractometer with a CCD area detector and multilayer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved by using direct methods, refined with the Shelx software package (G. Sheldrick, *Acta Crystallogr. Sect. A* **2007**, *64*, 112 – 122) and expanded by using Fourier techniques. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and were included in structure factor calculations. Crystal data for **5**: $C_{18}H_{28}BNO_2Si_2Rh_2$ $M_r =$ 563.22, red blocks, $0.29 \times 0.22 \times 0.18$ mm^3, monoclinic, space group $P2_1/n$, $a = 14.9400(12)$, $b = 9.5316(7)$, $c = 15.6173(12)$ Å, $\beta = 99.8600(10)°$, $V = 2191.1(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.707$ mg m^{-3}, $\mu = 1.628$ mm^{-1}, $F(000) = 1128$, $T = 173(2)$ K, $R_1 = 0.0182$, $wR^2 =$ 0.0447, 2171 independent reflections ($2\Phi = 52.14°$) and 119 parameters. Crystal data for **7**: $C_{17}H_{33}BIrNOSi_2$, $M_r = 526.63$, red block, $0.25 \times 0.12 \times 0.08$ mm^3, monoclinic, space group $P2_1$, $a =$ 8.6070(2), $b = 11.9484(3)$, $c = 10.9962(2)$ Å, $\beta = 99.9350(10)°$, $V = 1113.89(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.570$ g cm^{-3}, $\mu = 6.104$ mm^{-1}, $F(000) = 520$, $T = 101(2)$ K, $R_1 = 0.0137$, $wR^2 = 0.0330$, Flack parameter = 0.0633(41), 4215 independent reflections ($2\Phi =$ 52.02°) and 219 parameters. CCDC-684930 (**5**) and CCDC-684931 (**7**) 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.

[11] W. A. Herrmann, C. Krueger, R. Goddard, I. Bernal, *J. Organomet. Chem.* **1977**, *140*, 73 – 89.

[12] H. Braunschweig, C. Kollann, U. Englert, *Eur. J. Inorg. Chem.* **1998**, 465 – 468.

[13] H. Braunschweig, T. Wagner, *Angew. Chem.* **1995**, *107*, 904 – 905; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 825 – 826.

[14] a) R. T. Baker, D. W. Ovenall, J. C. Calabrese, S. A. Westcott, N. J. Taylor, I. D. Williams, T. B. Marder, *J. Am. Chem. Soc.* **1990**, *112*, 9399 – 9400; b) S. A. Westcott, T. B. Marder, R. T. Baker, J. C. Calabrese, *Can. J. Chem.* **1993**, *71*, 930 – 936; c) W. Clegg, F. J. Lawlor, T. B. Marder, P. Nguyen, N. C. Norman, A. G. Orpen, M. J. Quayle, C. R. Rice, E. G. Robins, A. J. Scott, F. E. S. Souza, G. Stringer, G. R. Whittell, *J. Chem. Soc. Dalton Trans.* **1998**, 301 – 310.

[15] D. A. Ortmann, B. Weberndoerfer, K. Ilg, M. Laubender, H. Werner, *Organometallics* **2002**, *21*, 2369 – 2381.

[16] H. Braunschweig, M. Burzler, T. Kupfer, K. Radacki, F. Seeler, *Angew. Chem.* **2007**, *119*, 7932 – 7934; *Angew. Chem. Int. Ed.* **2007**, *46*, 7785 – 7787.

