

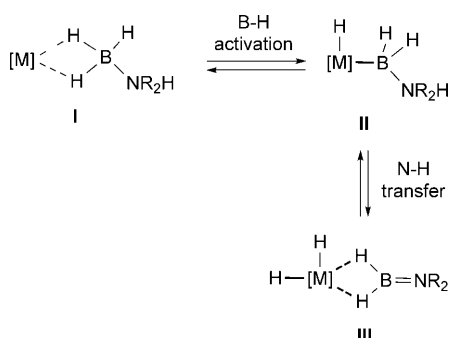
B–H Activation at a Rhodium(I) Center: Isolation of a Bimetallic Complex Relevant to the Transition-Metal-Catalyzed Dehydrocoupling of Amine–Boranes**

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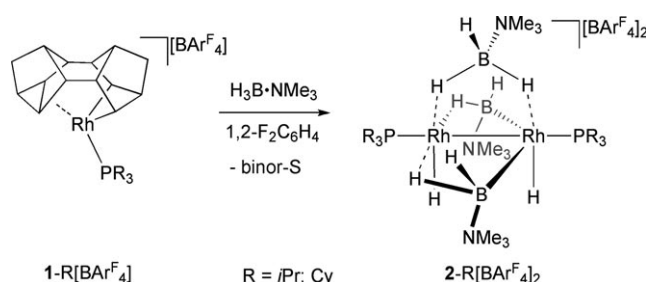
In memory of Daniela Rais

The transition-metal-catalyzed dehydrocoupling of amine–boranes and phosphine–boranes ($\text{H}_3\text{B}\cdot\text{EHR}_2$; $\text{E} = \text{N}, \text{P}$; $\text{R} = \text{H}$, alkyl, aryl) to form oligomeric and polymeric materials, with the concomitant release of H_2 , is attracting considerable attention owing to the control that the metal fragment imposes on the kinetics and product distributions involved in these processes. This has particular relevance to chemical hydrogen storage as a future energy vector and the synthesis of new Group 13/15 polymeric materials that show useful physical and electronic properties.^[1,2]

There are a growing number of transition metal systems that have been reported to effect the dehydrocoupling of amine–boranes ($\text{H}_3\text{B}\cdot\text{NR}_2\text{H}$).^[3–11] For homogeneous systems, two different mechanistic scenarios have been proposed on the basis of experimental and computational studies: inner-sphere,^[5,8,12] in which the metal center takes part in BH/NH activation (stepwise or concerted), and outer-sphere,^[9] which is conceptually related to alcohol oxidation using transition metal catalysts. For an inner-sphere mechanism that involves initial B–H activation at the metal center, suggested intermediates include metal amine–borane sigma complexes (**I**) and the products of B–H activation (oxidative addition), namely base-stabilized boryl compounds (**II**).



Despite their central role, the chemistry of complexes such as **I** is only now beginning to be explored, although model species incorporating $\text{H}_3\text{B}\cdot\text{EMe}_3$ ($\text{E} = \text{N}, \text{P}$) were reported 10 years ago by Shimoi and co-workers.^[13] We have recently described the isolation, structural characterization, and subsequent reactivity of a number of sigma complexes of type **I** using the $\{\text{Rh}(\text{P}i\text{Bu}_3)_2\}^+$ and $\{\text{Rh}(\text{P}(\text{C}_5\text{H}_9)_2(\eta^2\text{-C}_5\text{H}_7))\}^+$ 12-electron fragments.^[6–8] Amine–borane complexes of type **III**, which contain the $\{\text{Rh}(\text{P}i\text{Bu}_3)_2\}^+$ metal fragment, have also been spectroscopically characterized.^[6,8] Closely related ruthenium η^2 -sigma complexes of H_2BR ($\text{R} = \text{H}$, alkyl, aryl) have recently been reported.^[14] As far as we are aware, however, there are no reports of products that result directly from B–H activation (**II**). Although oxidative addition of three-coordinate borane species is well-established,^[15] oxidative addition of four-coordinate, base-stabilized borane compounds is less common.^[16] Base-stabilized boryl compounds are known,^[17] but the key hydrido complexes (**II**) remain elusive. The isolation of such complexes would thus be significant. Herein, we report the synthesis of such species, dinuclear metal–metal bonded complexes with base-stabilized boryl and hydride ligands (**II**), which result from B–H activation at monometallic rhodium(I) fragments. The formation of these metal–metal bonded complexes also has significance with regard to colloidal^[18] or cluster^[10,11] rhodium(0) catalysts, which form by reduction of monometallic rhodium(I) precursors by amine–boranes, providing insight into the bonding modes of amine–boranes at more than one metal center.^[2,11]



We have previously reported on the rhodium(III) complexes $[\text{Rh}(\text{PR}_3)(\text{binor-S})][\text{Bar}^{\text{F}}_4]$ (**1-R[Bar^F₄]**), where $\text{R} = \text{Cy}, i\text{Pr}$; binor-S = norbornadiene dimer, $\text{C}_{14}\text{H}_{16}$; $\text{Ar}^{\text{F}} = \text{C}_6\text{H}_3(\text{CF}_3)_2$, that contain a ligand that adopts a C–C sigma interaction with the metal.^[19] These complexes act as a latent source of the $\{\text{Rh}(\text{PR}_3)\}^+$ fragment by reductive

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elimination of binor-S on addition of Lewis bases.^[19,20] Addition of $\text{H}_3\text{B}\cdot\text{NMe}_3$ to $\mathbf{1}\text{-R}[\text{BAR}^{\text{F}}_4]$ results in the slow (ca. 2 h) formation of the dimeric complexes $[\text{Rh}_2(\text{PR}_3)_2(\text{H})_2(\mu\text{-H}_2\text{BNMe}_3)_2(\mu\text{-H}_3\text{B}\cdot\text{NMe}_3)][\text{BAR}^{\text{F}}_4]_2$ ($\mathbf{2}\text{-R}[\text{BAR}^{\text{F}}_4]_2$), which are isolated as air-sensitive crystalline solids in greater than 70 % yield. These complexes were characterized by NMR spectroscopy, X-ray crystallography, and ESI-MS. The solid-state structure of $\mathbf{2}\text{-Cy}[\text{BAR}^{\text{F}}_4]_2$ was of sufficient quality that the hydrogen atoms associated with the metal and boron centers were reliably located (Figure 1). The X-ray crystal structure

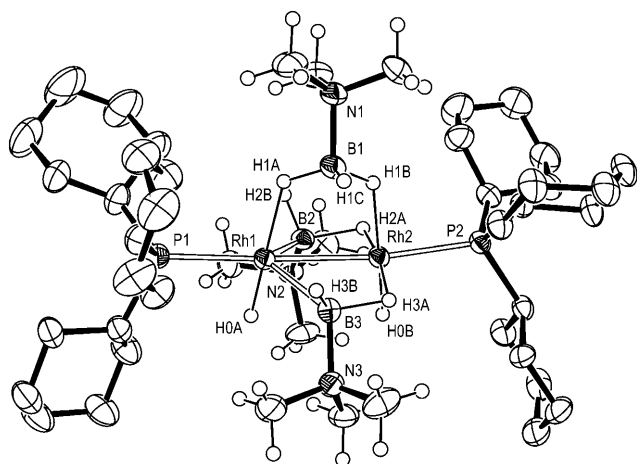
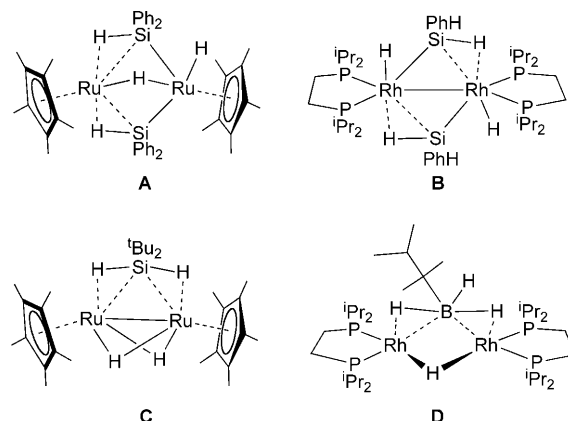


Figure 1. Solid-state structure of $\mathbf{2}\text{-Cy}^{2+}$. Thermal ellipsoids set at 50 % probability; phosphine H-atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh1–Rh2 2.6292(4), Rh1–P1 2.4025(10), Rh2–P2 2.3559(10), Rh1–B1 2.747(5), Rh1–B2 2.086(4), Rh1–B3 2.086(4), Rh2–B1 2.757(5), Rh2–B2 2.217(4), Rh2–B3 2.233(4), Rh1–H0A 1.46(4), Rh2–H0B 1.50(4), Rh1–H1A 1.88(5), Rh2–H1B 1.86(5), B1–H1A 1.21(5), B1–H1B 1.22(5), B1–H1C 1.15(5), B2–H2A 1.43(5), B2–H2B 1.12(5), B3–H3A 1.34(5), B3–H3B 1.10(5), P1–Rh1–Rh2 176.55(3), Rh1–Rh2–P2 171.91(3).

of $\mathbf{2}\text{-iPr}[\text{BAR}^{\text{F}}_4]_2$ was also obtained, but, owing to extensive disorder, only the gross heavy-atom core could be located. The solution-phase NMR data for both dimeric complexes are essentially the same, indicating similar structures.

In the solid-state, $\mathbf{2}\text{-Cy}^{2+}$ exists as a dicationic dimer formed from two $[\text{Rh}(\text{PCy}_3)]^+$ fragments that are bridged by three $\text{H}_3\text{B}\cdot\text{NMe}_3$ ligands. Two of these ligands have undergone B–H activation, which results in two ligands in which amine–boranes (B2 and B3) form both a σ -bond (base-stabilized boryl ligand) to Rh1, and an α -B agostic^[21] B–H interaction with Rh2 (Figure 1). The third $\text{H}_3\text{B}\cdot\text{NMe}_3$ ligand remains intact and bridges both metal atoms by two three-center–two-electron (3c–2e) interactions. The Rh–B distances reflect these different bonding modes, viz. Rh1–B3 2.086(4) Å, Rh2–B3 2.233(4) and Rh1–B1 2.747(5) Å. The first two bonds are consistent with those that have been reported previously,^[22,23] whereas the amine–borane bridging two metal centers is, as far as we are aware, unique. The related ditantalum BH_3 adduct,^[24] and monomeric rhodium(III) sigma complex of $\text{H}_3\text{B}\cdot\text{NHMe}_2$,^[6] both have much shorter M–B distances (ca. 2.3 Å). The Rh–Rh distance (2.6292(4) Å) is consistent with a Rh–Rh single bond, albeit a

short one. Although this is a new motif in metal–boron chemistry, corresponding silyl and hydridoborate complexes have been reported that show closely related bonding motifs to both the σ /agostic interaction (**A**^[25] and **B**^[26]) and the

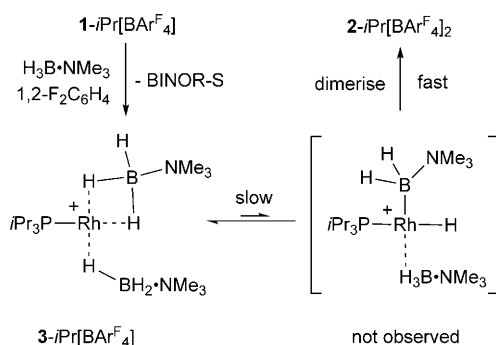


bridging σ ligand (**C**^[27] and **D**^[23]). Preliminary calculations afforded the same structural core as is observed experimentally, and the calculated bond orders are consistent with the proposed structure (see Supporting Information); a starting structure that places one boryl ligand at each metal center, such as the silyl ligands in **B**, optimizes to the experimentally observed structure, with both on the same metal (similar to complex **A**).

In solution, the solid-state structures are retained. For example, in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\mathbf{2}\text{-iPr}[\text{BAR}^{\text{F}}_4]_2$, two different ^{31}P environments are observed that show coupling to both rhodium atoms, thus confirming the M–M bond. At 298 K, the high-field region of the ^1H NMR spectrum shows four signals. Two integral 1H resonances at $\delta = -17.75$ ppm and $\delta = -21.16$ ppm do not sharpen on ^{11}B decoupling; this observation, combined with their chemical shift, identifies them as rhodium hydrides (e.g., H0A and H0B, Figure 1). The equivalent α -B agostic hydrogen atoms (e.g., H3A), assigned to a signal at $\delta = -9.46$ ppm (br, 2H), do not exchange with the terminal B–H atoms (e.g., H3B), which are observed at $\delta = 5.45$ ppm (vbr, 2H). Thus, these 3c–2e interactions appear to be relatively strong. The intact σ ligand hydrogen atoms (e.g., H1A, H1B, and H1C) are observed as a broad 3H signal at $\delta = -3.56$ ppm, demonstrating site-exchange between bridging and terminal B–H motifs. Cooling the NMR sample down slows this site exchange process; at 200 K this resonance resolves into two signals, which are observed at $\delta = -1.90$ (vbr, approx. 2H) and -8.31 ppm (br, 1H). At 190 K, the former resonance splits into a very broad signal at $\delta = -3.90$ ppm, and another that is presumably also very broad and could not be definitively assigned. The latter peak remains essentially unchanged. These observations support a mechanism that involves two site-exchange processes; one that makes all three B–H groups equivalent, and a second, with a lower energy barrier, that exchanges just two B–H groups. The chemical shifts for the other hydride signals remain unchanged on cooling, although one of the rhodium hydrides resolves into a sharp doublet of doublets at 273 K. The ^{11}B NMR spectrum shows two environments at $\delta = +37.3$ and -9.6 ppm in an approximate 2:1 ratio. These resonances

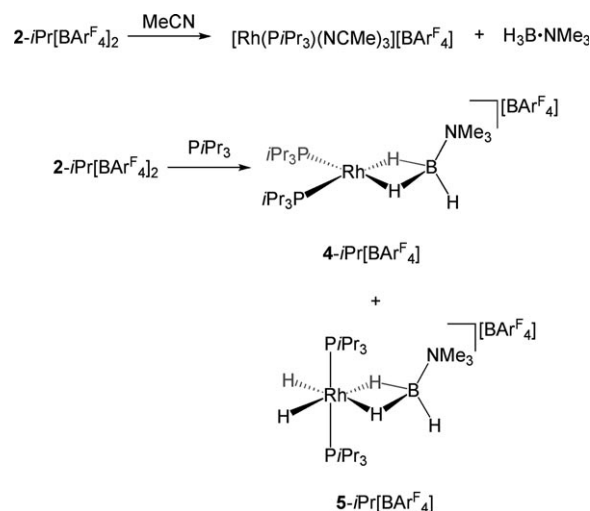
are assigned to the base-stabilized boryl (B2/B3) and borane (B1) ligands, respectively.^[28] ESI-MS shows a strong molecular-ion peak for $[2\text{-}i\text{Pr}[\text{BAR}^{\text{F}}_4]]^+$ ($m/z = 1608.5$, calcd 1608.5), thus confirming the empirical formula.

Monitoring of the formation of $2\text{-}i\text{Pr}[\text{BAR}^{\text{F}}_4]_2$ in situ by NMR spectroscopy indicates the formation of a rhodium(I) intermediate upon addition of $\text{H}_3\text{B}\cdot\text{NMe}_3$ to $1\text{-}i\text{Pr}[\text{BAR}^{\text{F}}_4]$, with the concomitant elimination of binor-S. The reaction then proceeds (1.5 h, see the Supporting Information) to afford $2\text{-}i\text{Pr}[\text{BAR}^{\text{F}}_4]_2$ as the only observed product. NMR spectroscopy and in situ ESI-MS studies identified this intermediate as $[\text{Rh}(\text{PiPr}_3)(\text{H}_3\text{B}\cdot\text{NMe}_3)_2][\text{BAR}^{\text{F}}_4]$ ($3\text{-}i\text{Pr}[\text{BAR}^{\text{F}}_4]$). Notably, broad signals are observed at $\delta = -3.25$ ppm (6H) in the ^1H NMR spectrum, at $\delta = 8.3$ ppm in the ^{11}B NMR spectrum, and a doublet is observed at $\delta = 85.0$ ppm ($J_{\text{RhP}} = 169$ Hz) in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum; cooling the sample to 190 K does not change these spectra significantly. ESI-MS shows the molecular ion for $3\text{-}i\text{Pr}^+$, $m/z = 409.26$ (calcd 409.26). $3\text{-}i\text{Pr}[\text{BAR}^{\text{F}}_4]$ presumably proceeds to $2\text{-}i\text{Pr}[\text{BAR}^{\text{F}}_4]_2$ by B–H oxidative addition, followed by dimerization and then isomerization of the rhodium(III) hydrido boryl compound. Precedent for the suggested bis-(amine–borane) binding mode in $3\text{-}i\text{Pr}[\text{BAR}^{\text{F}}_4]$ comes from the recently reported rhodium(I) complex $[\text{Rh}(\text{P}(\text{C}_5\text{H}_9)_2)(\eta^2\text{-C}_3\text{H}_7)(\eta^2\text{-H}_3\text{B}\cdot\text{NMe}_3)(\eta^1\text{-H}_3\text{B}\cdot\text{NMe}_3)][\text{BAR}^{\text{F}}_4]$.^[7]

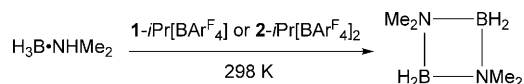


Crossover experiments between $2\text{-}i\text{Pr}[\text{BAR}^{\text{F}}_4]_2$ and $2\text{-Cy}[\text{BAR}^{\text{F}}_4]_2$ show that the Rh–Rh bond remains intact on the laboratory timescale, with no mixed-phosphine species observed. However, addition of relatively strong Lewis bases results in fragmentation of the dimeric motif. Addition of acetonitrile results in elimination of $\text{H}_3\text{B}\cdot\text{NMe}_3$ and the formation of a rhodium(I) complex, which was tentatively assigned as $[\text{Rh}(\text{PiPr}_3)(\text{NCMe})_3][\text{BAR}^{\text{F}}_4]$. This result demonstrates that the B–H activation of $\text{H}_3\text{B}\cdot\text{NMe}_3$ is reversible. Addition of PiPr_3 to $2\text{-}i\text{Pr}[\text{BAR}^{\text{F}}_4]_2$ gives a 1:1 mixture of rhodium(I) and rhodium(III) complexes, $4\text{-}i\text{Pr}[\text{BAR}^{\text{F}}_4]$ and $5\text{-}i\text{Pr}[\text{BAR}^{\text{F}}_4]$ respectively, each with a coordinated $\text{H}_3\text{B}\cdot\text{NMe}_3$ group. Independent synthesis confirmed their assignment (for their solid-state structures, see the Supporting Information), and they are closely related to the recently reported PiBu_3 analogues.^[6,8] The mechanism for the formation of $5\text{-}i\text{Pr}[\text{BAR}^{\text{F}}_4]$ is yet to be determined.

Complexes $2\text{-R}[\text{BAR}^{\text{F}}_4]_2$ do not undergo dehydrocoupling owing to the lack of an NH proton. In contrast, addition of



$\text{H}_3\text{B}\cdot\text{NHMe}_2$ to $2\text{-}i\text{Pr}[\text{BAR}^{\text{F}}_4]_2$ (20 mol % rhodium, 15 h, 100 % conversion) does result in slow dehydrocoupling and the formation of $(\text{H}_2\text{BNMe}_2)_2$.^[3] Free $\text{H}_3\text{B}\cdot\text{NMe}_3$ is formed at the onset of catalysis, demonstrating exchange of the amine–boranes. Complex $1\text{-}i\text{Pr}[\text{BAR}^{\text{F}}_4]$ is also a competent catalyst, with quantitative conversion occurring in a shorter reaction time (5 h). Mercury poisoning experiments showed no inhibition in rate, thus suggesting a homogenous process. Although a number of species are present in solution (as observed by NMR spectroscopy) during these catalytic runs we have not been able to definitively assign them to analogues of either $2\text{-}i\text{Pr}[\text{BAR}^{\text{F}}_4]_2$ or $3\text{-}i\text{Pr}[\text{BAR}^{\text{F}}_4]$, and so cannot comment on their role in the mechanism of $\text{H}_3\text{B}\cdot\text{NHMe}_2$ dehydrocoupling.



In conclusion, we report complexes arising from B–H activation of an amine–borane at a low-valent, late transition metal center, that show a unique dimeric motif with three different amine–borane activation modes. The isolation of these dimeric complexes and the observation of rhodium(I) intermediates during their formation provide a link between homogenous and colloidal heterogeneous rhodium systems used in the dehydrocoupling reactions of amine–boranes and is thus significant to both areas.

Experimental Section

A solution of $1\text{-}i\text{Pr}[\text{BAR}^{\text{F}}_4]$ (67 mg, 0.051 mmol) and $\text{H}_3\text{B}\cdot\text{NMe}_3$ (7.5 mg, 0.103 mmol) in 1,2-difluorobenzene (2 mL) was stirred at room temperature for 20 min. Layering with pentane and cooling to 5 °C afforded $2\text{-}i\text{Pr}[\text{BAR}^{\text{F}}_4]_2$ as pale yellow crystals (1,2-difluorobenzene solvate). Yield: 0.058 g (88 %). ^1H NMR (CD_2Cl_2 , 500 MHz): $\delta = 7.68\text{--}7.79$ (m, 16H, BAR^{F}_4), 7.56 (br, 8H, BAR^{F}_4), 5.45 (vbr, fwhm = 360 Hz, 2H, terminal- H_2BNMe_3); fwhm = full width at half maximum), 2.76 (s, 18H, H_2BNMe_3), 2.51 (s, 9H, $\text{H}_3\text{B}\cdot\text{NMe}_3$), 2.26 (apparent octet, $J = 7$ Hz, 6H, PCHMe_2), 1.32 (br, 36H, PCHMe_2), -3.56 (vbr, fwhm = 220 Hz, 3H, $\text{H}_3\text{B}\cdot\text{NMe}_3$), -9.46 (vbr, fwhm = 110 Hz, 2H, B -agostic- H_2BNMe_3), -17.75 (m, 1H, RhH - $(\text{BH}_2\text{NMe}_3)_2$), -21.16 ppm (br, 1H, RhH); ^{11}B NMR (CD_2Cl_2 ,

160 MHz): $\delta = 37.3$ (br, 2B, H_2BNMe_3), -6.6 (s, 2B, BAR^F_4), -9.6 ppm (br, 1B, $H_3B \cdot NMe_3$); $^{31}P\{^1H\}$ NMR (CD_2Cl_2 , 202 MHz): $\delta = 69.0$ (dd, 1P, $^1J_{RHP} = 104$ Hz, $^2J_{RHP} = 68$ Hz, $RhPiPr_3$), 58.1 ppm (dd, 1P, $^1J_{RHP} = 124$ Hz, $^2J_{RHP} = 59$ Hz, $RhPiPr_3(BH_3NMe_3)_2$); ESI-MS ($1.2 \cdot F_2C_6H_4$, 60 °C, 4.5 kV) positive ion: m/z , 1608.4868 [$M + (BAR^F_4)^+$] (calcd 1608.4709); IR (KBr): $\nu(BH)$ 2484 (w), 2383 (w); $\nu(Rh-HB)$ 2026 cm^{-1} (br, s); Anal. calcd for $C_{97}H_{106}B_5F_{50}N_3P_3Rh_2 \cdot C_6H_4F_2$ (2585.66 $g \cdot mol^{-1}$): C 45.06, H 4.13, N 1.63; found: C 45.27, H 4.36, N 1.82. **2-Cy**[BAR^F_4]₂ was prepared in an analogous manner in 70 % yield. Full details of the synthesis, characterization, and reactivity of **2-R**[BAR^F_4]₂ and **3-*i*Pr**[BAR^F_4] are provided in the Supporting Information.

Crystallographic data for **2-Cy**[BAR^F_4]₂: $C_{109}H_{126}B_5F_{48}N_3P_3Rh_2$, $M_r = 2711.94$, pale yellow block, $0.28 \times 0.22 \times 0.20$ mm³, triclinic, $P\bar{1}$, $a = 17.21390(10)$, $b = 17.64870(10)$, $c = 22.98490(10)$ Å, $\alpha = 81.6540(3)$, $\beta = 82.6968(3)$, $\gamma = 70.3695(2)^\circ$, $V = 6484.33(6)$ Å³, $Z = 2$, $\rho_{calcd} = 1.389$ g cm⁻³, $\mu = 0.392$ mm⁻¹, KappaCCD, $Mo_{K\alpha}$ radiation $\lambda = 0.71073$ Å, $T = 150(2)$ K, $5.11 \leq \theta \leq 26.37^\circ$, 47732 reflections, 26301 unique ($R_{int} = 0.0202$), Final $GoF = 1.073$, $R1$ ($I > 2\sigma(I)$) = 0.0526, $wR2$ (all data) = 0.1520. H0A, H0B, H1A, H1B, H1C, H2A, H2B, H3A, and H3B were located on the Fourier difference map and freely refined (isotropic displacement parameters were fixed to ride on the parent atoms). CCDC 747860 contains 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.

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- [1] a) T. B. Marder, *Angew. Chem.* **2007**, *119*, 8262–8264; *Angew. Chem. Int. Ed.* **2007**, *46*, 8116–8118; b) C. W. Hamilton, R. T. Baker, A. Staubitz, I. Manners, *Chem. Soc. Rev.* **2009**, *38*, 279–293; c) F. H. Stephens, V. Pons, R. T. Baker, *Dalton Trans.* **2007**, 2613–2626.
- [2] T. J. Clark, K. Lee, I. Manners, *Chem. Eur. J.* **2006**, *12*, 8634–8648.
- [3] C. A. Jaska, K. Temple, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **2003**, *125*, 9424–9434.
- [4] a) T. J. Clark, C. A. Russell, I. Manners, *J. Am. Chem. Soc.* **2006**, *128*, 9582–9583; b) A. Staubitz, A. P. Soto, I. Manners, *Angew. Chem.* **2008**, *120*, 6308–6311; *Angew. Chem. Int. Ed.* **2008**, *47*, 6212–6215; c) M. E. Sloan, T. J. Clark, I. Manners, *Inorg. Chem.* **2009**, *48*, 2429–2435; d) D. Pun, E. Lobkovsky, P. J. Chirik, *Chem. Commun.* **2007**, 3297–3299; e) M. C. Denney, V. Pons, T. J. Hebden, D. M. Heinekey, K. I. Goldberg, *J. Am. Chem. Soc.* **2006**, *128*, 12048–12049; f) B. L. Dietrich, K. I. Goldberg, D. M. Heinekey, T. Autrey, J. C. Linehan, *Inorg. Chem.* **2008**, *47*, 8583–8585; g) Y. Jiang, O. Blaque, T. Fox, C. M. Frech, H. Berke, *Organometallics* **2009**, *28*, 5493–5504.
- [5] a) R. J. Keaton, J. M. Blacquiere, R. T. Baker, *J. Am. Chem. Soc.* **2007**, *129*, 1844–1845; b) V. Pons, R. T. Baker, N. K. Szymczak, D. J. Heldebrant, J. C. Linehan, M. H. Matus, D. J. Grant, D. A. Dixon, *Chem. Commun.* **2008**, 6597–6599.
- [6] T. M. Douglas, A. B. Chaplin, A. S. Weller, *J. Am. Chem. Soc.* **2008**, *130*, 14432–14433.
- [7] R. Dallanegra, A. B. Chaplin, A. S. Weller, *Angew. Chem.* **2009**, *121*, 7007–7010; *Angew. Chem. Int. Ed.* **2009**, *48*, 6875–6878.
- [8] T. M. Douglas, A. B. Chaplin, A. S. Weller, X. Yang, M. B. Hall, *J. Am. Chem. Soc.* **2009**, *131*, 15440–15456.
- [9] a) N. Blaquiere, S. Diallo-Garcia, S. I. Gorelsky, D. A. Black, K. Fagnou, *J. Am. Chem. Soc.* **2008**, *130*, 14034–14035; b) M. Käß, A. Friedrich, M. Drees, S. Schneider, *Angew. Chem.* **2009**, *121*, 922–924; *Angew. Chem. Int. Ed.* **2009**, *48*, 905–907.
- [10] J. L. Fulton, J. C. Linehan, T. Autrey, M. Balasubramanian, Y. Chen, N. K. Szymczak, *J. Am. Chem. Soc.* **2007**, *129*, 11936–11949.
- [11] R. Rousseau, G. K. Schenter, J. L. Fulton, J. C. Linehan, M. H. Engelhard, T. Autrey, *J. Am. Chem. Soc.* **2009**, *131*, 10516–10524.
- [12] a) A. Paul, C. B. Musgrave, *Angew. Chem.* **2007**, *119*, 8301–8304; *Angew. Chem. Int. Ed.* **2007**, *46*, 8153–8156; b) X. Z. Yang, M. B. Hall, *J. Am. Chem. Soc.* **2008**, *130*, 1798–1799; c) P. M. Zimmerman, A. Paul, Z. Y. Zhang, C. B. Musgrave, *Angew. Chem.* **2009**, *121*, 2235–2239; *Angew. Chem. Int. Ed.* **2009**, *48*, 2201–2205.
- [13] M. Shimoi, S. Nagai, M. Ichikawa, Y. Kawano, K. Katoh, M. Uruichi, H. Ogino, *J. Am. Chem. Soc.* **1999**, *121*, 11704–11712.
- [14] G. Alcaraz, E. Clot, U. Helmstedt, L. Vendier, S. Sabo-Etienne, *J. Am. Chem. Soc.* **2007**, *129*, 8704–8705.
- [15] 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. Aldridge, D. L. Coombs, *Coord. Chem. Rev.* **2004**, *248*, 535–559.
- [16] a) I. R. Crossley, A. F. Hill, A. C. Willis, *Organometallics* **2005**, *24*, 1062–1064; b) Reaction of $H_3B \cdot L$ with an Ir^I centre occurs via an intermediate tentatively suggested to be the product of oxidative addition: A. Rossin, M. Caporali, L. Gonsalvi, A. Guerri, A. Lledós, M. Peruzzini, F. Zanobini, *Eur. J. Inorg. Chem.* **2009**, 3055–3059.
- [17] a) S. Aldridge, D. L. Kays, *Struct. Bonding (Berlin)* **2008**, *130*, 29–122; b) Y. Kawano, T. Yasue, M. Shimoi, *J. Am. Chem. Soc.* **1999**, *121*, 11744–11750; c) H. Nakazawa, M. Ohba, M. Itazaki, *Organometallics* **2006**, *25*, 2903–2905; d) D. J. Elliot, C. J. Levy, R. J. Puddephatt, D. G. Holah, A. N. Hughes, V. R. Magnuson, I. M. Moser, *Inorg. Chem.* **1990**, *29*, 5014–5015; e) H. Braunschweig, K. Radacki, F. Seeler, G. R. Whittell, *Organometallics* **2004**, *23*, 4178–4180.
- [18] a) C. A. Jaska, T. J. Clark, S. B. Clendenning, D. Grozea, A. Turak, Z.-H. Lu, I. Manners, *J. Am. Chem. Soc.* **2005**, *127*, 5116–5124; b) C. A. Jaska, I. Manners, *J. Am. Chem. Soc.* **2004**, *126*, 9776–9785; c) M. Zahmakiran, S. O'Ààzkar, *Inorg. Chem.* **2009**, *48*, 8955–8964.
- [19] S. Brayshaw, J. Green, G. Kociok-Köhn, E. Sceats, A. Weller, *Angew. Chem.* **2006**, *118*, 466–470; *Angew. Chem. Int. Ed.* **2006**, *45*, 452–456.
- [20] A. B. Chaplin, A. I. Poblador-Bahamonde, H. A. Sparkes, J. A. K. Howard, S. A. Macgregor, A. S. Weller, *Chem. Commun.* **2009**, 244–246.
- [21] a) J. Spielmann, S. Harder, *J. Am. Chem. Soc.* **2009**, *131*, 5064–5065; b) T. D. Forster, H. M. Tuononen, M. Parvez, R. Roesler, *J. Am. Chem. Soc.* **2009**, *131*, 6689–6691.
- [22] a) C. Dai, G. Stringer, T. B. Marder, A. J. Scott, W. Clegg, N. C. Norman, *Inorg. Chem.* **1997**, *36*, 272–273; b) P. E. Behnken, T. B. Marder, R. T. Baker, C. B. Knobler, M. R. Thompson, M. F. Hawthorne, *J. Am. Chem. Soc.* **1985**, *107*, 932–940.
- [23] R. T. Baker, D. W. Ovenall, R. L. Harlow, S. A. Westcott, N. J. Taylor, T. B. Marder, *Organometallics* **2002**, *21*, 3028–3030.
- [24] F. A. Cotton, C. A. Murillo, X. P. Wang, *J. Am. Chem. Soc.* **1998**, *120*, 9594–9599.
- [25] H. Suzuki, T. Takao, M. Tanaka, Y. Morooka, *J. Chem. Soc. Chem. Commun.* **1992**, 476–478.
- [26] M. D. Fryzuk, L. Rosenberg, S. J. Rettig, *Inorg. Chim. Acta* **1994**, *222*, 345–364.
- [27] T. Takao, S. Yoshida, H. Suzuki, M. Tanaka, *Organometallics* **1995**, *14*, 3855–3868.
- [28] G. Alcaraz, S. Sabo-Etienne, *Coord. Chem. Rev.* **2008**, *252*, 2395–2409.