e

tter

## The platinum catalysed diboration of alkynes using 1,2-B<sub>2</sub>Cl<sub>2</sub>(NMe<sub>2</sub>)<sub>2</sub> : formation of 1-azonia-2-borata-5-borole derivatives

Kirsty M. Anderson, M. J. Gerald Lesley,\* Nicholas C. Norman,\* A. Guy Orpen and Jonathan Starbuck

The University of Bristol, School of Chemistry, Cantock's Close, Bristol, UK BS8 1TS

Received (in Montpellier, France) 6th September 1999, Accepted 22nd September 1999

The platinum catalysed diboration of alkynes using the diborane(4) compound  $1,2-B_2Cl_2(NMe_2)_2$  affords high yields of cyclic 1-azonia-2-borata-5-borole compounds, which arise from redistribution of B–Cl and B–NMe<sub>2</sub> bonds.

Transition metal borvl compounds are known to be active catalysts for the diboration of unsaturated organic substrates<sup>1</sup> although in most cases the diborane(4) compounds employed have been either  $B_2(cat)_2$  (cat = 1,2- $O_2C_6H_4$ )<sup>1,2</sup> (and alkylated derivatives thereof) or  $B_2(pin)_2$  (pin = 1,2- $O_2C_2Me_4$ ).<sup>1,3</sup> Herein we describe some preliminary results from a study of catalysed alkyne diboration<sup>4</sup> platinum using 1.2- $B_2Cl_2(NMe_2)_2$  (1)<sup>5</sup> as the diboration reagent, the chemistry of which is significantly different. Prior reactivity studies involving transition metal complexes and 1 have yielded products derived from both B-B and B-Cl activation, an example of the former being our own report of the reaction beand  $[Pt(PPh_3)_2(\eta-C_2H_4)]$ affording tween 1  $[Pt(PPh_3)_2{BCl(NMe_2)}_2]^6$  and the latter exemplified by the work of Braunschweig involving the formation of diboran(4)yl derivatives.7

The diboration of internal alkynes (2a-d) employing 1 in the presence of 5 mol% [Pt(PPh<sub>3</sub>)<sub>2</sub>( $\eta$ -C<sub>2</sub>H<sub>4</sub>)] proceeded over 24 h in toluene at 95 °C to give compounds formulated as cyclic 1-azonia-2-borata-5-borole derivatives (3a-d) in excellent yield and purity (Scheme 1).† Analytical and spectroscopic data† were in accord with the proposed structures, which, for 3a, 3c and 3d, were confirmed by X-ray crystallography.<sup>‡</sup> A view of 3c is shown in Fig. 1. Key features of the 1-azonia-2-borata-5borole structure are the presence of three- and four-coordinate boron centres [B(2) and B(1), respectively] and three- and four-coordinate nitrogen centres [N(2) and N(1), respectively].The two three-coordinate centres are associated with the shortest B-N bond [B(2)-N(2) 1.381(2) Å], consistent with a B-N double bond resulting from dative  $N \rightarrow B \pi$ -bonding. The bonds B(1)-N(1) [1.622(2) Å] and B(2)-N(1) [1.563(2) Å] are both consistent with B-N single bonds, the difference

Me<sub>2</sub>N B-B NMe<sub>2</sub> CI |Pt|, toluene, 95°C Me<sub>2</sub>N-B1--R<sup>2</sup> Me м́е 3a-f **2a**,  $R^1 = Ph$ ,  $R^2 = Me$ **2b**,  $R^1 = R^2 = Ph$ **2c**,  $R^1 = R^2 = 4 \cdot MeC_6H_4$ **2d**,  $R^1 = R^2 = 4$ -MeOC<sub>6</sub>H<sub>4</sub>  $2\mathbf{e}, \mathbf{R}^1 = n$ -octyl,  $\mathbf{R}^2 = \mathbf{H}$  $2f, R^1 = Ph, R^2 = H$ 

Scheme 1

being attributable to the coordination numbers of the two boron atoms [in the diagrams, the B(1)-N(1) bond is represented as a coordinate bond]. In all of **3a-d**, the solution NMR data are consistent with the retention of this structure in solution. In particular, the disparate <sup>11</sup>B chemical shifts are characteristic of three- and four-coordinate boron environments, and the observed inequivalence of the exocyclic amido methyl groups (at room temperature) is consistent with hindered rotation about the exocyclic B–N bond.

The mechanism by which 3a-d are formed remains unclear although an initial diboration product A, which subsequently rearranges to 3, is likely in view of the known structure of the platinum boryl catalyst precursor cis- $[Pt(PPh_3)_2\{BCl(NMe_2)\}_2]^6$  in which each boron retains the one chlorine and one amido group present in the starting diborane(4) compound 1. In relation to this study, particularly with regard to any mechanistic speculation, we note that Berndt et al. have described the uncatalysed reaction between 1 and the silyl alkynes Me<sub>3</sub>SiC=CSiMe<sub>3</sub> and PhC=CSiMe<sub>3</sub> at 150 °C. Spectroscopic data on the products formed are consistent with species containing unrearranged boryl groups but in



Fig. 1 A view of the molecular structure of **3c** with key atoms labelled. Atoms are drawn as spheres of arbitrary radius and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg) include B(1)-N(1) 1.622(2), B(2)-N(1) 1.563(2), B(2)-N(2) 1.381(2), B(1)-Cl(1) 1.894(2), B(1)-Cl(2) 1.853(2), B(1)-N(1)-B(2) 98.76(11), C(12)-B(1)-N(1) 102.32(12), C(13)-B(2)-N(1) 106.61(13), B(1)-C(12)-C(13) 109.11(13), B(2)-C(13)-C(12) 109.60(13).

which silvl/boryl rearrangement has occurred, resulting in 1,1isomers, such as  $(Me_3Si)(R)C=C[BCl(NMe_2)]_2$  (R = Ph,Me<sub>3</sub>Si).<sup>8</sup> More recently, Siebert et al. have presented spectroscopic data that reveal that alkenes derived from cis-1,2addition of B<sub>2</sub>Cl<sub>4</sub> to alkynes, for example cis-(R)- $(BCl_2)C=C(BCl_2)(R')$  (B), react with the silvl amide Me<sub>3</sub>SiNMe<sub>2</sub> to afford compounds analogous to either 3  $(R = R' = Et, Me; R = Bu^{t}, R' = H)$  or A  $(R = R' = Bu^{t}).^{9}$ Reactions between **B** and Pr<sub>2</sub><sup>i</sup>NH also afforded species of type A (R = R' = H, Me, Et; R = H, R' = Bu'). {This report<sup>9</sup> described the structure of the bromo derivative cis-(Bu<sup>t</sup>)- $[BBr(NMe_2)]C=C[BBr(NMe_2)](Bu^t)$ , a structure analogous to A, although this compound was not prepared by a route relevant to this study.} The results of Siebert et al. indicate that structures 3 and A are probably close in energy (with a subtle dependence on the nature of the R group) and our preliminary ab initio calculations<sup>10</sup> carried out on **3b** and its isomer of type A confirm that the two isomers are very close in energy.§



In contrast to the reactions of internal alkynes, terminal alkynes reacted more slowly. Thus, the platinum catalysed reaction between 1 and 1-octyne (2e) gave 3e but was complete only after three days. Reactions using phenylacetylene (2f) were incomplete even after several days although the reaction between phenylacetylene and 1 in the presence of a stoichiometric amount of  $[Pt(PPh_3)_2(\eta-C_2H_4)]$  did afford the desired product (3f) after 3 h (Scheme 1).¶ Competing activation of the CH bonds in terminal alkynes has been noted in catalytic reactions involving alkoxy substituted diborane(4) compounds with phenylacetylene.<sup>4e</sup>

The availability of crystalline 3a-d prepared in high yields under mild conditions has enabled an initial study of their reactivity to be carried out, preliminary details of which are reported here for 3c with HCl, alcohols, diols and dilithioferrocene (Scheme 2). A previous study by Siebert et al., wherein  $cis-(R)[BCl(NPr_2^i)]C=C[BCl(NPr_2^i)](R)$  (R = H, Et) was reacted with Me<sub>3</sub>SnLi affording cis-(R)[B(SnMe<sub>3</sub>)(NPr<sup>i</sup><sub>2</sub>)]- $C=C[B(SnMe_3)(NPr_2^i)](R)$ , is noted.<sup>11</sup> Thus, 3c reacts with two equiv. of HCl in Et<sub>2</sub>O to give 4 in high yield,<sup> $\parallel$ </sup> resulting from the addition of HCl across the exocyclic B-N bond. <sup>11</sup>B NMR data were consistent with the presence of two distinct four-coordinate boron centres whilst the <sup>1</sup>H NMR spectrum revealed the presence of a coordinated NHMe<sub>2</sub> amine ligand; the asymmetric boron centre [B(2)] results in inequivalent (diastereotopic) ring NMe<sub>2</sub> and coordinated NHMe<sub>2</sub> methyl environments. The structure of 4 was confirmed by X-ray



Scheme 2  $R = 4-MeC_6H_4$  (i) HCl; (ii) a, H<sub>2</sub>O/EtOH, b, H<sub>2</sub>O; (iii) 1,2-(HO)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>; (iv) [Fe(C<sub>5</sub>H<sub>4</sub>Li)<sub>2</sub>]



Fig. 2 A view of the molecular structure of 4 with key atoms labelled. Atoms are drawn as spheres of arbitrary radius and hydrogen atoms omitted for clarity with the exception of H(98). Selected bond lengths (Å) and angles (deg) include B(1)-N(1) 1.607(6), B(2)-N(1) 1.604(5), B(2)-N(2) 1.616(6), B(1)-Cl(1) 1.862(5), B(1)-Cl(2) 1.904(5), B(2)-Cl(3) 1.867(5), B(1)-N(1)-B(2) 101.3(3), C(12)-B(1)-N(1) 102.8(3), C(13)-B(2)-N(1) 101.6(3), B(1)-C(12)-C(13) 111.3(3), B(2)-C(13)-C(12) 109.7(3).

crystallography<sup>\*\*</sup> (Fig. 2). In most respects, the structure of 4 is similar to that of 3c with the exception of the environment around B(2), which now carries a chlorine and a datively bound NHMe<sub>2</sub> amine ligand; pertinent metric data are given in the caption to Fig. 2, which reveal that all B–N bond lengths are the same within experimental error, as expected for bonds between four-coordinate boron and nitrogen centres. Attempts to prepare an amine adduct of a bis(dichloroboryl)ethene derivative (*cf.*, **B** above) through addition of a second equivalent of HCl across the B(2)–N(1) bond were not successful. Thus, the reaction between 3c and 4 equiv. HCl also afforded 4 whilst with the use of 10 equiv. of HCl, significant decomposition was evident by NMR.

The addition of one equivalent of water in ethanol to a solution of 3c in toluene afforded a compound formulated as the oxaborole species 5a on the basis of the <sup>11</sup>B NMR chemical shift and the <sup>1</sup>H NMR spectrum integration (two equivalents of [NH<sub>2</sub>Me<sub>2</sub>]Cl were also produced).<sup>††</sup> In the absence of ethanol, reaction with 4 equiv. of water in toluene yielded 5b plus two equivalents of [NH2Me2]Cl.<sup>††</sup> The formulation of **5b** as an oxaborole species rather than a bis(boronic acid)<sup>12</sup>  $\{i.e., (R)[B(OH)_2]C=C[B(OH)_2](R)\}$  was confirmed by obtaining a <sup>1</sup>H NMR spectrum in CD<sub>3</sub>OD wherein an OH signal integrating to six protons was observed, corresponding to four from exchange with the  $[NH_2Me_2]^+$  cations and two from B-OH groups.<sup>‡‡</sup> Even in the presence of a large excess of water, no evidence was obtained for the formation of a bis(boronic acid) with only stilbene and boron containing compounds of unknown composition being formed. Reaction of 3c with 2.2 equiv. catechol afforded the known<sup>4e</sup> bis(catecholatoboryl) derivative 6 quantitatively according to in situ <sup>1</sup>H and <sup>11</sup>B NMR spectroscopy.

Finally, the reaction between **3c** and 1,1'-dilithioferrocene afforded a species formulated as the [4]ferrocenophane compound 7.§§ The boron chemical shift of 7 ( $\delta$  38.6) is consistent with that found for three-coordinate boron centres in related boron containing ferrocenophane derivatives, which have attracted some attention as precursors to polyferrocene polymers,<sup>13–15</sup> but the fact that the symmetrical species **7** is

formed here indicates that 3c is a synthetic equivalent of the type A structure.

## Acknowledgements

NCN and AGO thank the EPSRC for research support and Johnson Matthey Ltd. are thanked for generous supplies of platinum salts.

## Notes and references

† In a typical reaction, a solution of 1 (0.502 g, 2.78 mmol) in toluene (5 cm<sup>3</sup>) containing  $[Pt(PPh_3)_2(\eta-C_2H_4)]^{4e}$  (0.035 g, 5 mol%) was transferred to a Young's tap tube containing 2c (0.478 g, 2.32 mmol), which was then sealed and heated to 95 °C overnight. The toluene was removed in vacuo and addition of Et<sub>2</sub>O (5 cm<sup>3</sup>) resulted in the formation of a precipitate 3c (0.680 g, 76%) that was isolated by filtration and washed with hexane (3 × 5 cm<sup>3</sup>). Slow diffusion of hexane into the initial filtrate resulted in the formation of a crop of red crystals of 3c, one of which was used for X-ray crystallography. NMR data for 3c  $(C_7D_8)$ : <sup>11</sup>B-{<sup>1</sup>H}  $\delta$  34.4 (B-NMe<sub>2</sub>), 9.1 (BCl<sub>2</sub>); <sup>1</sup>H  $\delta$  7.51 (d, 2H, C-NMe<sub>2</sub>), 9.1  $C_6H_4$ ,  $J_{HH} = 8.0$  Hz), 6.89 (M, 4H,  $C_6H_4$ ), 6.87 (d, 2H,  $C_6H_4$ ,  $J_{HH} = 8.0$  Hz), 6.89 (M, 4H,  $C_6H_4$ ), 6.87 (d, 2H,  $C_6H_4$ ,  $J_{HH} = 8.0$  Hz), 2.51 (s, 6H,  $B_2NMe_2$ ), 2.11 (s, 3H, BNMe<sub>2</sub>), 2.08 (s, 3H, BNMe<sub>2</sub>), 2.03 (s, 3H,  $C_6H_4Me$ ), 2.02 (s, 3H,  $C_6H_4Me$ ); <sup>13</sup>C-{<sup>1</sup>H} 8.0 Hz), 2.03 (s, 2H,  $C_6H_4Me$ ), 2.02 (s, 3H,  $C_6H_4Me$ ); <sup>13</sup>C-{<sup>1</sup>H} 138.9, 137.3 (ipso-C), 136.2, 135.5 (p-C), 129.6, 129.4 (o-C), 129.2, 128.5 (m-C), 44.4 (B<sub>2</sub>NMe<sub>2</sub>), 42.2, 38.9 (BNMe<sub>2</sub>), 21.2, 21.1 (C<sub>6</sub>H<sub>4</sub>Me). <sup>11</sup>B, <sup>1</sup>H and <sup>13</sup>C spectra were referenced to  $BF_3 \cdot Et_2O$ ,  $Me_4Si$  and  $Me_4Si$ , respectively. HRMS (EI) for  $C_{20}H_{26}B_2Cl_2N_2$ : Calcd 384.173181, found 384.171 333. Compounds 3a, 3b and 3d were prepared similarly. Selected data for **3a**: <sup>11</sup>B-{<sup>1</sup>H} NMR ( $C_7D_8$ )  $\delta$  33.8 (B–NMe<sub>2</sub>), 9.5 (BCl<sub>2</sub>); **3b**: <sup>11</sup>B-{<sup>1</sup>H} NMR ( $C_7D_8$ )  $\delta$  34.2 (B–NMe<sub>2</sub>), 9.0 (BCl<sub>2</sub>), HRMS (EI) for  $C_{18}H_{22}B_2Cl_2N_2$ : Calcd 356.141 880, found 356.140 419; **3d**: <sup>11</sup>B-{<sup>1</sup>H} NMR (C<sub>7</sub>D<sub>8</sub>)  $\delta$  34.7 (B–NMe<sub>2</sub>), 8.7 (BCl<sub>2</sub>), HRMS (EI) for C<sub>20</sub>H<sub>26</sub>B<sub>2</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>: Calcd 416.163010, found 416.162 476. The <sup>11</sup>B resonances for the B-NMe<sub>2</sub> borons for all 3 are significantly broader than those for the BCl<sub>2</sub> borons consistent with their respective coordination geometries. Satisfactory  ${}^1\mathrm{H}$  and  ${}^{13}\mathrm{C}$ NMR data were also obtained for 3a, 3b and 3d. All alkynes were either procured commercially or prepared by literature methods.

<sup>‡</sup> Crystal data for **3a**:  $C_{13}H_{20}B_2Cl_2N_2$ , M = 296.83, monoclinic, space group  $P2_1/c$  (no. 14), a = 16.121(3), b = 7.1894(6), c = 13.5772(17) Å,  $\beta = 95.567(15)^\circ$ , U = 1566.2(4) Å<sup>3</sup>, Z = 4,  $\lambda = 0.71073$  Å,  $\mu = 0.40$  mm<sup>-1</sup>, T = 173(2) K. Crystal data for **3c**:  $C_{20}H_{26}B_2CI_2N_2$ , M = 386.95, monoclinic, space group P2/c (no. 13), a = 12.410(2), b = 12.8779(14), c = 13.0655(16) Å,  $\beta = 90.428(14)^\circ$ , U = 2088.0(5) Å<sup>3</sup>, Z = 4,  $\lambda = 0.71073$  Å,  $\mu = 0.317$  mm<sup>-1</sup>,  $D_{ealc} =$ 1.231 Mg m<sup>-3</sup>, F(000) = 816, T = 173(2) K, 4779 unique data, RI = 0.0372. Crystal data for **3d**:  $C_{20}H_{26}B_2CI_2N_2O_2$ , M = 418.95, magnetizing array group  $R_2/c$  (no. 10) monoclinic, space group  $P2_1/c$  (no. 14),  $a^2 = 10.870(3)$ , b = 12.404(2), c = 16.086(3) Å,  $\beta = 92.185(9)^\circ$ , U = 2167.3(7) Å<sup>3</sup>, Z = 4,  $\lambda = 0.71073$  Å,  $\mu = 0.32$  mm<sup>-1</sup>, T = 173(2) K.

 Gas phase energies of 3b and its type A isomer were evaluated by full geometry optimisation at the SCF 6-31G level, followed by single point energy calculations with 6-31G\*\* basis sets. At this level the acyclic A isomer is 6.9 kcal  $mol^{-1}$  more stable. We note however, that these calculations do not model any intermolecular interactions that might influence the preferred geometry in condensed phases.  $\P^{11}B$  NMR data (C<sub>7</sub>D<sub>8</sub>) for 3e:  ${}^{11}B-{}^{11}H$   $\delta$  37.9 (B–NMe<sub>2</sub>), 11.1

(BCl<sub>2</sub>); 3f: 36.2 (B-NMe<sub>2</sub>), 9.1 (BCl<sub>2</sub>). Satisfactory <sup>1</sup>H NMR data were also obtained.

|| NMR data for 4 (CD<sub>2</sub>Cl<sub>2</sub>): <sup>11</sup>B-{<sup>1</sup>H}  $\delta$  8.7 (sh), 7.3 (sh); <sup>1</sup>H  $\delta$  7.03 (d, 2H,  $C_6H_4$ ,  $J_{HH} = 8.1$  Hz), 6.96 (d, 2H,  $C_6H_4$ ,  $J_{HH} = 8.1$  Hz), 6.92 (s, 4H, C<sub>6</sub>H<sub>4</sub>), 6.59 (br s, 1H, NHMe<sub>2</sub>), 2.84 (s, 3H, NMe<sub>2</sub>), 2.74 (d, 3H, NHMe<sub>2</sub>,  ${}^{3}J_{\text{HH}} = 5.5 \text{ Hz}$ , 2.72 (s, 3H, NMe<sub>2</sub>), 2.37 (d, 3H, NHMe<sub>2</sub>,  ${}^{3}J_{\text{HH}} = 5.5 \text{ Hz}$ , 2.25 (s, 3H, C<sub>6</sub>H<sub>4</sub>Me), 2.24 (s, 3H, C<sub>6</sub>H<sub>4</sub>Me);  ${}^{13}\text{C}$ -{ ${}^{14}\text{H}$ }  $\delta$  157.8, 147.5 (BC=CB), 139.3, 138.4 (ipso-C), 135.5 (p-C), 130.3, 128.9 (o-C), 128.6, 128.5 (m-C), 49.4, 42.8, 40.1, 40.3 (NMe<sub>2</sub> and NHMe<sub>2</sub>), 21.4, 21.3 (C<sub>6</sub>H<sub>4</sub>Me).

\*\* Crystal data for 4:  $C_{20}H_{27}B_2Cl_3N_2$ , M = 423.41, monoclinic, space group  $P2_1/c$  (no. 14), a = 20.496(9), b = 9.775(4), c = 23.894(13)Å,  $\beta = 114.37(6)^\circ$ , U = 4360(3) Å<sup>3</sup>, Z = 8,  $\lambda = 0.71073$  Å,  $\mu = 0.428$  mm<sup>-1</sup>,  $D_{calc} = 1.290$  Mg m<sup>-3</sup>, F(000) = 1776, T = 173(2) K, 7670 unique data, R1 = 0.0563.

CCDC reference number 440/150. See http://www.rsc.org/

suppdata/nj/1999/1053/ for crystallographic files in .cif format. †† NMR data for **5a** (CD<sub>2</sub>Cl<sub>2</sub>): <sup>11</sup>B-{<sup>1</sup>H}  $\delta$  30.2; <sup>1</sup>H  $\delta$  7.13 (d, 4H, C<sub>6</sub>H<sub>4</sub>, J<sub>HH</sub> = 7.8 Hz), 7.02 (d, 4H, C<sub>6</sub>H<sub>4</sub>, J<sub>HH</sub> = 7.8 Hz), 4.19 (q, 4H, CH<sub>2</sub>CH<sub>3</sub>), 2.29 (s, 6H, C<sub>6</sub>H<sub>4</sub>Me), 1.31 (t, 6H, CH<sub>2</sub>CH<sub>3</sub>). **5b** (CD<sub>3</sub>OD): <sup>11</sup>B-{<sup>1</sup>H}  $\delta$  24.5; <sup>1</sup>H (including data for the [NH<sub>2</sub>Me<sub>2</sub>]<sup>+</sup> cation, see text)  $\delta$  6.91 (s, 8H, C<sub>6</sub>H<sub>4</sub>), 4.88 (s, 6H, OH), 2.69 (s, 12H, NH<sub>2</sub>Me<sub>2</sub>), 2.24 (s, 6H, C<sub>6</sub>H<sub>4</sub>Me); <sup>13</sup>C-{<sup>1</sup>H}  $\delta$  139.2 (*ipso*-C), 136.9 (*p*-C), 130.2 (*o*-C), 136.9 (*p*-C), 130.2 (*p*-C), C), 129.7 (m-C), 21.3 (C<sub>6</sub>H<sub>4</sub>Me).

<sup>‡‡</sup> Evidence for oxaborole species was also seen in the mass spectra of **3b-d**. Th<u>us, in the case of **3d**, HRMS data were obtained for the</u> species  $C(4-MeOC_6H_4)=C(4-MeOC_6H_4)B(NMe_2)OB(NMe)_2)$ . Calcd C<sub>20</sub>H<sub>26</sub>B<sub>2</sub>N<sub>2</sub>O<sub>3</sub> 364.213959, found 364.212954.

§ NMR data for 7 (CDCl<sub>3</sub>): <sup>11</sup>B-{<sup>1</sup>H}  $\delta$  38.6; <sup>1</sup>H  $\delta$  7.02 (d, 4H,  $C_6H_4$ ,  $J_{HH} = 8.6$  Hz), 6.68 (d, 4H,  $C_6H_4$ ,  $J_{HH} = 8.6$  Hz), 4.28 (br s, 4H,  $C_5H_5$ ), 4.19 (br s, 4H,  $C_5H_5$ ), 3.74 (s, 6H, NMe<sub>2</sub>), 2.98 (s, 6H,  $NMe_2$ ), 2.86 (s, 6H,  $C_6H_4Me$ ).

- 1 G. J. Irvine, M. J. G. Lesley, T. B. Marder, N. C. Norman, E. G. Robins, W. Roper, C. R. Rice, G. R. Whittell and G. J. Wright, Chem. Rev., 1998, 98, 2685; T. B. Marder and N. C. Norman, Topics in Catalysis, ed. W. Leitner and D. G. Blackmond, Baltzer Science Publishers, Amsterdam, 1998, vol. 5, p. 63.
- 2 F. J. Lawlor, N. C. Norman, N. L. Pickett, E. G. Robins, P. Nguyen, G. Lesley, T. B. Marder, J. A. Ashmore and J. C. Green, Inorg.Chem., 1998, 37, 5282.
- 3 H. Nöth, Z. Naturforsch., Teil B, 1984, 39, 1463.
- 4 (a) T. Ishiyama, N. Matsuda, N. Miyaura and A. Suzuki, J. Am. Chem. Soc., 1993, 115, 11018; (b) F. Ozaura, A. Suzuki and N. Miyaura, Organometallics, 1996, 15, 713; (c) C. N. Iverson and M. R. Smith, J. Am. Chem. Soc., 1995, 117, 4403; (d) C. N. Iverson and M. R. Smith, Organometallics, 1996, 15, 5155; (e) M. J. G. Lesley, P. Nguyen, N. J. Taylor, T. B. Marder, A. J. Scott, W. Clegg and N. C. Norman, Organometallics, 1996, 15, 5137.
- H. Nöth and W. Meister, Z. Naturforsch., Teil B, 1962, 17, 714.
- D. Curtis, M. J. G. Lesley, N. C. Norman, A. G. Orpen and J. Starbuck, J. Chem. Soc., Dalton Trans., 1999, 1687.
- H. Braunschweig, Angew. Chem., Int. Ed., 1998, 37, 1787. 8 H. Klusik, C. Pues and A. Berndt, Z. Naturforsch., Teil B, 1984,
- 39, 1042.
- 9 W. Siebert, M. Hildenbrand, P. Hornbach, G. Karger and H. Pritzkow, Z. Naturforsch., Teil B, 1989, 44, 1179.
- 10 M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzeqski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, Gaussian 94, revision D.4, Gaussian Inc., Pittsburgh, PA, 1995
- 11 P. Frankhauser, H. Pritzkow and W. Siebert, Z. Naturforsch., Teil B, 1994, 49, 250.
- 12 N. Miyaura and A. Suzuki, Chem. Rev., 1995, 95, 2457.
- 13 M. J. G. Lesley, U. Mock, N. C. Norman, A. G. Orpen, C. R. Rice and J. Starbuck, J. Organomet. Chem., 1999, 582, 116.
- 14 M. Herberhold, U. Dörfler and B. Wrackmeyer, J. Organomet. Chem., 1997, 530, 117.
- 15 H. Braunschweig, R. Dirk, M. Müller, P. Nguyen, R. Resendes, D. P. Gates and I. Manners, Angew. Chem., Int. Ed. Engl., 1997, 36, 2338.

Letter 9/07255A