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# Structural and spectroscopic studies of three-coordinate copper(I) supported by bis(phosphino)borate ligands

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Dedicated to Professor Malcolm H. Green, an inspiring organometallic chemist

#### Abstract

The bis(phosphino)borates  $[(p^{-t}BuPh)_2B(CH_2PPh_2)_2][ASN]$  (1[ASN]; ASN = 5-azonia-spiro[4.4]nonane),  $[Ph_2B(CH_2P'Pr_2)_2]$ -Li(THF)<sub>2</sub> (2[Li]), and  $[(3,5-Me_2Ph)_2B(CH_2P'Bu_2)_2]^{-}$  (3[Li] and 3[Tl]) react with copper(I) reagents to generate anionic and neutral complexes. Reaction of 1[ASN] with CuI provides the 1:1 adduct  $[[(p^{-t}BuPh)_2B(CH_2PPh_2)_2]CuI][ASN]$  (4). CuCl reacts with 3[Li] in THF to afford  $[[(3,5-Me_2Ph)_2B(CH_2P'Bu_2)_2]CuCI][Li(THF)_4]$  (5), along with a minor byproduct, the three-coordinate bis(phosphine) adduct {(3,5-Me\_2Ph)\_B(CH\_2P'Bu\_2)\_2}CuCl (6). An analogous neutral complex, {PhB(CH\_2P'Bu\_2)\_2}CuCl (7), can be synthesized directly by reacting CuCl with the neutral phosphino borane PhB(CH\_2P'Bu\_2)\_2. Reaction of the substituted copper(I) halide Me<sub>2</sub>S · CuBr with 3[Tl] provides the anionic dimer complex [{[(3,5-Me\_2Ph)\_2B(CH\_2P'Bu\_2)\_2]Cu(NCCH\_3) (10) are prepared by the reactions between [Cu(CH<sub>3</sub>CN)<sub>4</sub>][PF<sub>6</sub>] and 2[Li] or 3[Li], respectively. Neutral 10 is a useful precursor to several other neutral species via substitution of the labile acetonitrile ligand, including [(3,5-Me\_2Ph)\_2B(CH\_2P'Bu\_2)\_2]Cu(PMe\_2Ph)(11), [(3,5-Me\_2Ph)\_2B(CH\_2P'Bu\_2)\_2]Cu(CO) (15), are frustrated by the high lability of the CO ligand. The solid-state crystal structures of complexes 6, 8, 9, 10, and 11 have been determined and are described.

Keywords: Zwitterions; Monoanionic ligands; Phosphines; Syntheses; Structures; Boron

### 1. Introduction

Copper(I) complexes play a significant role in many catalytic and stoichiometric processes, including catalytic hydrocarbon functionalization reactions [1], catalytic oxidation reactions [2], and biomimetic dioxygen activation [3]. Several well-defined copper(I) systems have been developed recently using ligands designed to

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control both steric and electronic factors that dictate overall reactivity profiles. These include modified bis- and tris(pyrazolyl)borates [4],  $\beta$ -diketiminates [5], *N*-heterocyclic carbenes [6], and a host of other nitrogenous ligands [7].

We recently reported the synthesis of a new family of bis(phosphino)borate ligands that are both sterically and electronically tunable [8]. These ligands are anionic relatives to the better known bis(pyrazolyl)borate and  $\beta$ -diketiminate ligands, and their fundamental coordination chemistry is therefore of comparative interest. In this contribution, we introduce a series of well-defined copper(I) complexes supported by monoanionic

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Fig. 1. Bis(phosphino)borate ligands used to prepare copper(I) complexes.

bis(phosphino)borates. The aim of this initial study is to develop reliable protocols for the generation and isolation of these new copper species, to establish their structural characterization, and to assess their ligand substitution chemistry. In this context, we examine the copper(I) coordination chemistry of the three bis(phosphino)borate ligands:  $[(p-^{t}BuPh)_{2}B(CH_{2}P (1[ASN]), [Ph_2B(CH_2P^iPr_2)_2]Li(THF)_2$  $Ph_2)_2[[ASN]]$ (2[Li]), and  $[(3,5-Me_2Ph)_2B(CH_2P^tBu_2)_2]^-$  (3[Li]) and 3[T1]) (Fig. 1). In particular, we emphasize the use of the sterically encumbered *tert*-butyl phosphine ligand 3 due to its ability to enforce three-coordinate geometries for a host of copper(I) complexes. Our hope is that the complexes described will serve as useful "[BP<sub>2</sub>]Cu<sup>1</sup>(L)" sources in the context of future group transfer studies.

#### 2. Experimental

### 2.1. General considerations

General procedures were performed according to previously published methods [9]. The compounds  $[(p^{-t}BuPh)_2B(CH_2PPh_2)_2][ASN]$  (1[ASN]), [Ph<sub>2</sub>B (CH<sub>2</sub>P<sup>i</sup>Pr<sub>2</sub>)<sub>2</sub>]Li(THF)<sub>2</sub> (2[Li]), [(3,5-Me\_2Ph)\_2B(CH\_2P'<sup>-</sup> Bu<sub>2</sub>)<sub>2</sub>]Li(OEt<sub>2</sub>) (3[Li]), [(3,5-Me\_2Ph)\_2B(CH\_2P'Bu\_2)\_2]Tl (3[Tl]), and Me<sub>3</sub>P=S were prepared by published methods [8]. 'BuNC was distilled under dinitrogen and dried over 3 Å molecular sieves prior to use. 2,6-Lutidine was sparged with dinitrogen and then dried with CaH<sub>2</sub> and distilled under dinitrogen. PhB(CH<sub>2</sub>P'Bu<sub>2</sub>)<sub>2</sub> was generated by the addition of PhBCl<sub>2</sub> to a cold ethereal suspension of  $LiCH_2P'Bu_2$ .<sup>1</sup> All other reagents were purchased from commercial vendors and used without further purification.

#### 2.2. Syntheses of complexes

### 2.2.1. $[[(p^{-t}BuPh)_2B(CH_2PPh_2)_2]CuI][ASN]$ (4)

Solid CuI (83.6 mg, 439 µmol) and [(p-<sup>t</sup>BuPh)<sub>2</sub> B(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>][ASN] (351.8 mg, 438.7 µmol) were combined with THF (4 mL) and ethanol (0.3 mL). The reaction mixture was stirred for 2.5 h. Volatiles were removed under reduced pressure. The resulting solids were washed with diethyl ether (3 mL) and dried under reduced pressure, providing analytically pure white 4 (432.8 mg, 99.4%). <sup>1</sup>H NMR (300 MHz, acetone-d<sub>6</sub>):  $\delta$ 7.60 (m, 8H), 7.12 (m, 16H), 6.82 (d, 4H), 3.69 (m, 8H), 2.24 (m, 8H), 1.76 (br, 4H), 1.21 (s, 16H).  $^{13}C{^{1}H}$  NMR (75.4 MHz, acetone-d<sub>6</sub>):  $\delta$  162.7 (br), 144.55, 141.80 (d,  ${}^{1}J_{P-C} = 12.3$  Hz), 141.64 (d,  ${}^{1}J_{P-C} = 12.3$  Hz), 133.83, 133.71 (d,  ${}^{2}J_{P-C} = 8.0$  Hz), 133.60 (d,  ${}^{2}J_{P-C} = 8.0$  Hz), 128.72, 128.49 (d,  ${}^{3}J_{P-C} = 4.3$  Hz), 128.43 (d,  ${}^{3}J_{P-C} = 4.0$  Hz), 123.51, 63.78 (t,  $(CH_2CH_2)_2N$ ,  ${}^1J_{N-C} = 3.4$  Hz), 34.42 (Ph- $C(CH_3)_3$ ), 32.15 (Ph- $C(CH_3)_3$ ), 22.84 ( $(CH_2CH_2)_2N$ ), 22.0 (br, B(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz, acetone-d<sub>6</sub>):  $\delta$  -13.08. <sup>11</sup>B{<sup>1</sup>H} NMR (128.3 MHz, acetone-d<sub>6</sub>):  $\delta$  –12.5. Anal. Calc. for C<sub>54</sub>H<sub>66</sub>BCuINP<sub>2</sub>: C, 65.36; H, 6.70; N, 1.41. Found: C, 65.08; H, 6.94; N, 1.21%.

# 2.2.2. $[[(3,5-Me_2Ph)_2B(CH_2P^tBu_2)_2]CuCl][Li(THF)_4]$ (5)

Solid CuCl (26.5 mg, 268 µmol) was suspended in THF (1.5 mL), stirred vigorously, and a THF solution (4 mL) of  $[(3,5-Me_2Ph)_2B(CH_2P'Bu_2)_2]Li(OEt_2)$  (166.2 mg, 268.2 µmol) was then added to the stirring suspension. After stirring for 24 h, analysis by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy revealed the formation of one major product, along with two minor byproducts. The reaction mixture was then filtered. The resulting filtrate was concentrated under reduced pressure to 0.5 mL. Vapor diffusion of petroleum ether into the THF solution provided white crystalline solids over several days. The isolated solids were dried under reduced pressure to provide the major product, [[(3,5-Me\_2Ph)\_2B(CH\_2P'Bu\_2)\_2]-CuCl][Li(THF)\_4] (163.9 mg, 65.5%). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>/THF-d<sub>8</sub>, 6:1):  $\delta$  7.59 (s, 4H, *ortho*-

<sup>&</sup>lt;sup>1</sup> The synthesis of PhB(CH<sub>2</sub>P'Bu<sub>2</sub>)<sub>2</sub> and its use as a ligand building block to other borate ligands will be reported separately (C.M. Thomas, J.C. Peters, manuscript in preparation). Key characterization data for PhB(CH<sub>2</sub>P'Bu<sub>2</sub>)<sub>2</sub>: <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 8.02$  (m, 2H, *o*-Ph), 7.27 (m, 3H, *m*, *p*-Ph), 2.27 (d, <sup>2</sup>J<sub>P-H</sub> = 5.7 Hz, CH<sub>2</sub>), 1.12 (d, <sup>2</sup>J<sub>P-H</sub> = 10.5 Hz, 36 H, 'Bu). <sup>31</sup>P NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 38.4$  (s). *Anal.* Calc. for C<sub>24</sub>H<sub>45</sub>BP<sub>2</sub>: C, 70.93; H, 11.16. Found: C, 69.32; H, 10.60%.

 $(Me_2C_6H_3)_2B)$ , 6.62 (s, 2H, para- $(Me_2C_6H_3)_2B)$ , 3.54 (m, 16H,  $(CH_2CH_2)_2O$ ) 2.29 (s, 12H,  $((CH_3)_2C_6H_3)_2B$ ), 1.92 (br, 4H,  $B(CH_2P^tBu_2)_2$ ), 1.45 (m, 16H,  $(CH_2CH_2)_2O$  1.32 (d, 18H,  $P(C(CH_3)_3)_2$ ,  ${}^3J_{P-H} = 5.7$ Hz), 1.30 (d, 18H,  $P(C(CH_3)_3)_2$ ,  ${}^{3}J_{P-H} = 6.3$  Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz, C<sub>6</sub>D<sub>6</sub>/THF-d<sub>8</sub>, 6:1):  $\delta$ 167.3 (br,  $ipso-(Me_2C_6H_3)_2B),$ 134.52 (meta- $(Me_2C_6H_3)_2B)$ , 131.89 (*ortho*- $(Me_2C_6H_3)_2B$ ), 124.50 (para-(Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>B), 68.17 ((CH<sub>2</sub>C H<sub>2</sub>)<sub>2</sub>O), 34.22 (d,  ${}^{1}J_{\text{P-C}} = 4.6$ Hz), 34.16  $CH_2P(C(CH_3)_3)_2,$ (d.  ${}^{1}J_{\rm P-C} = 4.6$  $CH_2P(C(CH_3)_3)_2,$ Hz), 31.05 (br,  $CH_2P(C(CH_3)_3)_2)$ , 30.92 (br,  $CH_2P(C(CH_3)_3)_2)$ , 26.17 ((C H<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O), 22.68 (((CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>B), 14.7 (br, BC H<sub>2</sub>P). <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz, C<sub>6</sub>D<sub>6</sub>/THF-d<sub>8</sub>, 6:1):  $\delta$  33.31. <sup>11</sup>B{<sup>1</sup>H} NMR (128.3 MHz, C<sub>6</sub>D<sub>6</sub>/THF-d<sub>8</sub>, 6:1):  $\delta$  -14.0. Anal. Calc. for C<sub>50</sub>H<sub>90</sub>BClCuLiO<sub>4</sub>P<sub>2</sub>: C, 64.38; H, 9.71. Found: C, 64.30; H, 9.70%.

### 2.2.3. $\{(3,5-Me_2Ph)B(CH_2P^tBu_2)_2\}CuCl(6)$

Yellow crystals of the minor byproduct, **6**, were isolated from a separate reaction, carried-out in an analogous fashion to that used in the preparation of **5**, by petroleum ether diffusion into a THF solution of the crude reaction mixture. A <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the solution prior to crystallization showed **6** to be present as approximately 15% of the observed diamagnetic phosphorus containing products. <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz, THF):  $\delta$  23.75. The identity of **6** was established by XRD analysis (see Fig. 2), and by comparison to the spectral properties of independently prepared **7**.

### 2.2.4. $\{PhB(CH_2P^tBu_2)_2\}CuCl(7)$

Solid PhB(CH<sub>2</sub>P'Bu<sub>2</sub>)<sub>2</sub> 1 (25.4 mg, 62.5  $\mu$ mol) and CuCl (6.2 mg, 63  $\mu$ mol) were combined in THF (4 mL) and stirred for 1 h, forming a homogeneous yellow



Fig. 2. Displacement ellipsoid representation (50%) of  $\{(3,5-Me_2Ph)B(CH_2P'Bu_2)_2\}$ CuCl (6). Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): P1–Cu, 2.2433(11); P2–Cu, 2.2481(12); Cl–Cu, 2.2183(12); B–Cu, 3.639(5); P1–Cu–P2, 108.55(5); P1–Cu–Cl, 129.28(5); P2–Cu–Cl, 121.93(5).

solution. The solution was filtered, and volatiles were removed under reduced pressure, forming microcrystalline yellow {PhB(CH<sub>2</sub>P'Bu<sub>2</sub>)<sub>2</sub>}CuCl (30.7 mg, 97.2%). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.88 (m, 2H), 7.28 (m, 3H), 1.73 (br, 4H, B(CH<sub>2</sub>P'Bu<sub>2</sub>)<sub>2</sub>), 1.22 (d, 18H, P(C(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>P-H</sub> = 6.3 Hz), 1.20 (d, 18H, P(C(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>P-H</sub> = 6.6 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  134.60, 133.29, 129.05, 34.47 (m, CH<sub>2</sub>P(C(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>), 29.82 (m, CH<sub>2</sub>P(C(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>), 18.8 (br, BC H<sub>2</sub>P). <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  23.11. <sup>11</sup>B{<sup>1</sup>H} NMR (160.4 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  75.2. *Anal.* Calc. for C<sub>24</sub>H<sub>45</sub>BClCuP<sub>2</sub>: C, 57.04; H, 8.98. Found: C, 57.40; H, 8.67%.

# 2.2.5. $[\{[(3,5-Me_2Ph)_2B(CH_2P^tBu_2)_2]Cu\}_2(\mu-Br)]Tl$ (8)

Solid Me<sub>2</sub>S · CuBr (16.2 mg, 78.8 µmol) was suspended in THF (3 mL). While stirring, a THF solution (9 mL) of  $[(3,5-\text{Me}_2\text{Ph})_2\text{B}(\text{CH}_2\text{P}^t\text{Bu}_2)_2]\text{Tl}$  (58.6 mg, 78.8 umol) was added dropwise. Upon completing the addition, the reaction mixture was stirred for 15 min. The reaction mixture was filtered, removing white and gray solids. The resulting solution was concentrated under reduced pressure to 1 mL. Vapor diffusion of petroleum ether into the THF solution provided colorless crystals over several days. The crystals were dried under reduced pressure to provide 8 (28.7 mg, 48.9%). <sup>1</sup>H NMR (300 MHz, THF-d<sub>8</sub>):  $\delta$  7.03 (s, 4H, ortho-(Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>B), 6.34 (s, 2H,  $para-(Me_2C_6H_3)_2B)$ , 2.11 (s, 12H,  $((CH_3)_2C_6H_3)_2B)$ , 1.53 (br, 4H, B( $CH_2P^tBu)_2$ ), 1.12 (d, 18H,  $P(C(CH_3)_3)_2$ ,  ${}^{3}J_{P-H} = 6.3$  Hz), 1.10 (d, 18H,  $P(C(CH_3)_3)_2$ ,  ${}^{3}J_{P-H} = 6.0$  Hz).  ${}^{13}C{}^{1}H{}$  NMR (75.4 MHz, THF-d<sub>8</sub>): δ 167 (br), 134.58, 131.50, 124.35, 34.34 (d,  $CH_2P(C(CH_3)_3)_2$ ,  ${}^1J_{P-C} = 6.0$  Hz), 34.26 (d,  $CH_2P(C (CH_3)_3)_2$ ,  ${}^1J_{P-C} = 6.4 Hz$ , 30.99 (d, 30.9) $H_{3}_{3}_{2}_{2}, {}^{2}J_{P-C} = 3.7 \text{ Hz}, 22.31 (((CH_{3})_{2}C_{6}H_{3})_{2}B), 14.8$ (br, BC H<sub>2</sub>P).  ${}^{31}P{}^{1}H{}$  NMR (121.4 MHz, THF- $d_8$ ):  $\delta$ 38.79. <sup>11</sup>B{<sup>1</sup>H} NMR (128.3 MHz, THF-d<sub>8</sub>):  $\delta$  –14.4. Anal. Calc. for C<sub>68</sub>H<sub>116</sub>B<sub>2</sub>BrCu<sub>2</sub>P<sub>4</sub>Tl: C, 54.79; H, 7.84. Found: C, 55.17; H, 7.55%.

#### 2.2.6. $[Ph_2B(CH_2P^iPr_2)_2]Cu(NCCH_3)$ (9)

Solid  $[Ph_2B(CH_2P'Pr_2)_2]Li(THF)_2$  (157.5 mg, 272.2 µmol) and solid  $[Cu(CH_3CN)_4][PF_6]$  (101.5 mg, 272.3 µmol) were combined in Et<sub>2</sub>O (4 mL). The reaction mixture was stirred for 30 min, forming a pale yellow solution. Volatiles were removed under reduced pressure, providing pale yellow solids. The solids were washed with acetonitrile (3 × 0.5 mL). The resulting solids were dissolved in THF (3 mL) and filtered. Removal of volatiles under reduced pressure provided white solids that analyzed as  $[Ph_2B(CH_2P'Pr_2)_2]Cu(NCCH_3)$  (62.7 mg, 43.3%). Crystals for an X-ray diffraction experiment were grown by vapor diffusion of petroleum ether into a THF solution of **9**. <sup>1</sup>H NMR (300 MHz, THF-d<sub>8</sub>):  $\delta$ 

7.30 (br, 4H), 6.90 (t, 4H,  ${}^{3}J_{H-H} = 7.2$  Hz), 6.72 (t, 2H, 6.9 Hz), 2.206 (s, 3H, CH<sub>3</sub>CN), 1.73 (m, 4H, P(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>), 1.21 (br, 4H, BCH<sub>2</sub>P), 1.07 (dd, 12H, P(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>), J = 7.2, 15 Hz), 0.87 (dd, 12H, P(CH(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>), J = 6.9, 13.2 Hz).  ${}^{13}C{}^{1}H{}$  NMR (75.4 MHz, THF-d<sub>8</sub>):  $\delta$  166 (br), 133.55, 126.84, 124.24 (CH<sub>3</sub>CN), 123.88, 21.6 (m, P(CH(CH<sub>3</sub>)<sub>2</sub>)), 19.34 P(CH(CH<sub>3</sub>)<sub>2</sub>), 17.10 (q, BCH<sub>2</sub>P,  ${}^{1}J_{B-C} = 41$  Hz), 1.52 (CH<sub>3</sub>CN).  ${}^{31}P{}^{1}H{}$  NMR (121.4 MHz, THF-d<sub>8</sub>):  $\delta$  17.83.  ${}^{11}B{}^{1}H{}$  NMR (160.4 MHz, THF-d<sub>8</sub>):  $\delta$  -14.4. IR: (KBr (s), cm<sup>-1</sup>)  $v_{CN} = 2265$  (w). *Anal.* Calc. for C<sub>28</sub>H<sub>45</sub>BCuNP<sub>2</sub>: C, 63.22; H, 8.53; N, 2.63. Found: C, 63.27; H, 8.73, N, 2.84%.

2.2.7.  $[(3,5-Me_2Ph)_2B(CH_2P^tBu_2)_2]Cu(NCCH_3)$  (10)

White  $[(3,5-Me_2Ph)_2B(CH_2P^tBu_2)_2]Li(OEt_2)$  (323.1 mg, 521.4 µmol) and [Cu(CH<sub>3</sub>CN)<sub>4</sub>][PF<sub>6</sub>] (194.4 mg, 521.6 µmol) were combined, and diethyl ether (10 mL) was added. The reaction mixture was stirred vigorously for 40 min. Volatiles were removed under reduced pressure, providing pale yellow solids. The solids were washed with acetonitrile  $(3 \times 0.8 \text{ mL})$ , and then dissolved in THF (5 mL) and filtered. The resulting solution was concentrated to dryness under reduced pressure, providing fine white, analytically pure 10 (280.8 mg, 83.6%). Crystals of 10 were grown by vapor diffusion of petroleum ether into a THF solution of 10. <sup>1</sup>H NMR (300 MHz, THF-d<sub>8</sub>):  $\delta$  7.01 (s, 4H, ortho- $(Me_2C_6H_3)_2B)$ , 6.33 (s, 2H, para- $(Me_2C_6H_3)_2B)$ , 2.28 (s, 3H, Cu-NCCH<sub>3</sub>), 2.11 (s, 12H,  $((CH_3)_2C_6H_3)_2B)$ , 1.51 (br s, 4H, B(CH<sub>2</sub>P'Bu)<sub>2</sub>), 1.12 (d, 18H,  $P(C(CH_3)_3)_2)$ , 1.10 (d, 18H,  $P(C(CH_3)_3)_2)$ . <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz, THF- $d_8$ ):  $\delta$  166.7 (br q,  ${}^{1}J_{B-C} = 44$ Hz), 134.43, 131.59, 124.87 (Cu-NCCH<sub>3</sub>), 124.27, 34.32 (d,  $P(C(CH_3)_3)_2$ ,  ${}^1J_{P-C} = 6.0$  Hz), 34.24 (d,  $P(C(CH_3)_3)_2$ ,  ${}^1J_{P-C} = 6.0$  Hz), 30.85 (d,  $P(C(CH_3)_3)_2$ ,  ${}^{2}J_{P-C} = 4.3$  Hz), 30.79 (d, P(C(CH\_{3})\_{3})\_{2},  ${}^{2}J_{P-C} = 4.3$ Hz), 22.34 ((CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>B, 14.22 (br q, B(CH<sub>2</sub>P<sup>t</sup>Bu)<sub>2</sub>,  ${}^{1}J_{B-C} = 42$  Hz), 1.59 (Cu-NCCH<sub>3</sub>).  ${}^{31}P{}^{1}H{}$  NMR (121.4 MHz, THF- $d_8$ ):  $\delta$  36.4. <sup>11</sup>B{<sup>1</sup>H} NMR (128.3 MHz, THF-d<sub>8</sub>):  $\delta$ -14.2. IR: (KBr (s), cm<sup>-1</sup>)  $v_{\rm CN} = 2267$  (w). Anal. Calc. for C<sub>36</sub>H<sub>61</sub>BCuNP<sub>2</sub>: C, 67.12; H, 9.54; N, 2.17. Found: C, 66.98; H, 9.55; N, 2.43%.

2.2.8.  $[(3,5-Me_2Ph)_2B(CH_2P^tBu_2)_2]Cu(PMe_2Ph)$  (11)

A THF solution (2 mL) of Me<sub>2</sub>PPh (12.8  $\mu$ L, 90.0  $\mu$ mol) was added to solid **10** (58.0 mg, 90.0  $\mu$ mol), providing a colorless solution. After 15 min, the solution was concentrated to dryness under reduced pressure. The resulting white solids were washed with petroleum ether (3 × 1 mL) and dried under reduced pressure, providing analytically pure white **11** (61.8 mg, 92.7%). Crystals of **11** were grown by vapor diffusion of petroleum ether into a THF solution of **11**. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.68 (s, 4H, *ortho*-(Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>B), 6.96–7.14

(m, 5H, P(C<sub>6</sub>H<sub>5</sub>)), 6.74 (s, 2H, *para*-(Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>B), 2.37 (s, 12H, ((CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>B), 1.93 (br, 4H, B(CH<sub>2</sub>P<sup>*i*</sup>Bu)<sub>2</sub>), 1.07 (m, 42H, P(C(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub> and P(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.7 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ 166.85 (q, <sup>1</sup>J<sub>B-C</sub> = 54 Hz), 135.33, 131.72, 130.65 (d, J<sub>P-C</sub> = 12 Hz), 130.12, 129.48 (d, J<sub>P-C</sub> = 8.3 Hz), 125.30, 34.38 (d, P(C(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>, <sup>1</sup>J<sub>P-C</sub> = 6.0 Hz), 34.30 (d, P(C(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>, <sup>1</sup>J<sub>P-C</sub> = 6.0 Hz), 31.04 (d, P(C(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>, <sup>2</sup>J<sub>P-C</sub> = 4.1 Hz), 30.99 (d, P(C(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>, <sup>2</sup>J<sub>P-C</sub> = 4.0 Hz), 22.99 (((CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>B), 15.49 (d, P(CH<sub>3</sub>)<sub>2</sub>, <sup>1</sup>J<sub>P-C</sub> = 18 Hz), 14.09 (br q, B(CH<sub>2</sub>P'Bu)<sub>2</sub>, <sup>1</sup>J<sub>B-C</sub> = 43 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ 40.81 (d, 2P, CH<sub>2</sub>P<sup>*i*</sup>Bu<sub>2</sub>, <sup>2</sup>J<sub>P-P</sub> = 79 Hz), -36.22 (t, 1P, P Me<sub>2</sub>Ph, <sup>2</sup>J<sub>P-P</sub> = 79 Hz). <sup>11</sup>B{<sup>1</sup>H} NMR (128.3 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  -14.4. *Anal.* Calc. for C<sub>42</sub>H<sub>69</sub>BCuP<sub>3</sub>: C, 68.05; H, 9.38. Found: C, 67.87; H, 9.17%.

2.2.9.  $[(3,5-Me_2Ph)_2B(CH_2P^tBu_2)_2]Cu(S = PMe_3)$  (12)

Solid Me<sub>3</sub>P = S (8.8 mg, 81  $\mu$ mol) and 10 (52.1 mg, 80.9 µmol) were dissolved in THF (2 mL). After 15 min, the reaction mixture was filtered and concentrated to dryness under reduced pressure. The resulting white solids were washed with petroleum ether  $(3 \times 1 \text{ mL})$ and dried under reduced pressure, producing analytically pure white 12 (49.2 mg, 85.6%). <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ ):  $\delta$  7.73 (s, 4H, ortho-(Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>B), 6.75  $para-(Me_2C_6H_3)_2B),$ 2.39 2H, (s, 12H, (s,  $((CH_3)_2C_6H_3)_2B)$ , 2.03 (br s, 4H,  $B(CH_2P^tBu)_2)$ , 1.29 (m, 36H,  $P(C(CH_3)_3)_2$ ), 0.90 (d, 9H,  $S=P(CH_3)_3$ ,  ${}^{2}J_{P-H} = 13$  Hz).  ${}^{13}C{}^{1}H$  NMR (75.4 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ 134.76, 131.33, 124.71, 34.10 (br, P(C(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>), 30.64 (m, P(C(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>), 30.25 (d, S = P(CH<sub>3</sub>)<sub>3</sub>,  ${}^{1}J_{P-C} = 6.7$ Hz), 22.47 (((CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>B).  ${}^{31}P{}^{1}H{}$  NMR (121.4 MHz,  $C_6D_6$ ):  $\delta$  35.05 (s, 2P, CH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>), 26.48 (s, 1P,  $S = P Me_3$ ). <sup>11</sup>B{<sup>1</sup>H} NMR (128.3 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ -14.3. Anal. Calc. for C<sub>37</sub>H<sub>67</sub>BCuP<sub>3</sub>S: C, 62.48; H, 9.49. Found: C, 62.28; H, 9.25%.

# 2.2.10. $[(3,5-Me_2Ph)_2B(CH_2P^tBu_2)_2]Cu(2,6-lutidine)$ (13)

Solid 10 (51.7 mg, 80.3 µmol) was dissolved in THF (2 mL). An aliquot of 2,6-lutidine (9.6 µL, 83 µmol) was added to the reaction mixture, providing a pale yellow solution. After 15 min, the solution was concentrated to dryness under reduced pressure. The resulting white solids were washed with petroleum ether  $(3 \times 1)$ mL) and dried under reduced pressure, providing analytically pure pale yellow 13 (48.9 mg, 85.8%). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 7.67 (s, 4H, ortho-6.76 1H,  $para-Me_2C_5H_3N$ ,  $(Me_2C_6H_3)_2B),$ (t,  ${}^{3}J_{H-H} = 7.5$  Hz), 6.75 (s, 2H, *para*-(Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>B), 6.32 (d, 2H, meta-Me<sub>2</sub>C<sub>5</sub> $H_3$ N,  ${}^{3}J_{H-H}$  = 7.5 Hz), 2.50 (s, 6H,  $(CH_3)_2C_5H_3N$ , 2.38 (s, 12H,  $((CH_3)_2C_6H_3)_2B$ ), 1.99 (br s, 4H,  $B(CH_2P^tBu)_2$ ), 1.14 (d, 18H,  $P(C(CH_3)_3)_2$ ,  ${}^{3}J_{P-H} = 5.7$  Hz), 1.12 (d, 18H,  $P(C(CH_{3})_{3})_{2}$ ,  ${}^{3}J_{P-H} = 6.3 \text{ Hz}$ .  ${}^{13}C\{{}^{1}H\}$  NMR (75.4 MHz, C<sub>6</sub>D<sub>6</sub>):

2905

δ 166.2 (br), 156.98, 137.62, 135.12, 132.57, 125.33, 122.55, 34.17 (d, P(C(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>, <sup>1</sup>J<sub>P-C</sub> = 5.4 Hz), 34.09 (d, P(C(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>, <sup>1</sup>J<sub>P-C</sub> = 5.7 Hz), 31.05 (d, P(C(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>, <sup>2</sup>J<sub>P-C</sub> = 4.3 Hz), 31.00 (d, P(C(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>, <sup>2</sup>J<sub>P-C</sub> = 4.0 Hz), 26.70 (*o*,*o*-(CH<sub>3</sub>)<sub>2</sub>C<sub>5</sub>H<sub>5</sub>N), 22.97 (((CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>B), 14.88 (br q, B(CH<sub>2</sub>P'Bu)<sub>2</sub>, <sup>1</sup>J<sub>B-C</sub> = 40 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz, C<sub>6</sub>D<sub>6</sub>): δ 36.10. <sup>11</sup>B{<sup>1</sup>H} NMR (128.3 MHz, C<sub>6</sub>D<sub>6</sub>): δ -14.1. *Anal.* Calc. for C<sub>41</sub>H<sub>67</sub>BCuNP<sub>2</sub>: C, 69.33; H, 9.51; N, 1.97. Found: C, 68.94; H, 9.14; N, 2.09%.

## 2.2.11. $[(3,5-Me_2Ph)_2B(CH_2P^tBu_2)_2]Cu(CN^tBu)$ (14)

A THF solution (2 mL) of tert-butyl isonitrile (11.8  $\mu$ L, 104  $\mu$ mol) was added to solid 10 (66.3 mg, 103 µmol), providing a colorless solution. After 15 min, the solution was concentrated to dryness under reduced pressure. The resulting white solids were washed with petroleum ether  $(3 \times 1 \text{ mL})$  and dried under reduced pressure, providing analytically pure white 14 (63.9 mg, 90.4%). <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ ):  $\delta$  7.68 (s, 4H, ortho-( $Me_2C_6H_3$ )<sub>2</sub>B), 6.74 (s, 2H, para-(Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>B), 2.38 (s, 12H, ((CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>B), 1.94 (br s, 4H,  $B(CH_2P^tBu)_2$ ), 1.24 (d, 18H,  $P(C(CH_3)_3)_2$ ,  ${}^{3}J_{P-H} = 6.6$  Hz), 1.22 (d, 18H,  $P(C(CH_{3})_{3})_{2}$ ,  ${}^{3}J_{P-H} = 6.0$  Hz), 0.77 (s, 9H, Cu-CNC(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (75.4 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  166.7 (br q,  ${}^{1}J_{B-C} = 45$  Hz), 144.26 (br, Cu-*C*N<sup>*t*</sup>Bu), 135.25, 131.91, 125.30, 57.02 (Cu-CNC(CH<sub>3</sub>)<sub>3</sub>), 34.46 (d, P(C(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>,  ${}^{1}J_{P-C} = 6.3$  Hz), 34.38 (d,  $P(C(CH_3)_3)_2$ ,  ${}^{1}J_{P-C} = 6.0$ Hz), 30.97 (d, P(C(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>,  ${}^{2}J_{P-C} = 4.0$  Hz), 30.92 (d,  $P(C(CH_3)_3)_2$ ,  ${}^2J_{P-C} = 4.0$  Hz), 29.99 (Cu-CNC(CH\_3)\_3), 22.98 (((CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>B), 12.84 (br q, B(CH<sub>2</sub>P'Bu)<sub>2</sub>,  ${}^{1}J_{B-C} = 41$  Hz).  ${}^{31}P{}^{1}H{}$  NMR (121.4 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$ 38.07. <sup>11</sup>B{<sup>1</sup>H} NMR (128.3 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  –13.6. IR:  $(CH_2Cl_2/KBr, cm^{-1}) v_{CN} = 2162$  (st). Anal. Calc. for C<sub>39</sub>H<sub>67</sub>BCuNP<sub>2</sub>: C, 68.26; H, 9.84; N, 2.04. Found: C, 68.01; H, 9.81; N, 2.24%.

# 2.2.12. $[(3,5-Me_2Ph)_2B(CH_2P^tBu_2)_2]Cu(CO)$ (15)

(a) Solid **10** (11.3 mg, 17.5 µmol) was dissolved in THF- $d_8$  (0.7 mL) and placed in a J. Young NMR tube. The tube was partially evacuated. CO gas (approximately 1 atm) was introduced to the J. Young tube, and the tube was sealed. The solution was analyzed by NMR spectroscopy. <sup>1</sup>H NMR (300 MHz, THF- $d_8$ ):  $\delta$  7.00 (s, 4H, ortho-(Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>B), 6.36 (s, 2H, para-(Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>B), 2.12 (s, 12H, ((CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>B), 2.03 (s, 3H, CH<sub>3</sub>CN), 1.53 (br, 4H, B(CH<sub>2</sub>P'Bu)<sub>2</sub>), 1.14 (d, 18H, P(C(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>P-H</sub> = 6.3 Hz), 1.12 (d, 18H, P(C(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>, <sup>1</sup>J<sub>P-C</sub> = 7.2 Hz), 30.72 (br, P(C(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>), 22.28 (((CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>B), 12.76 (br q, B(CH<sub>2</sub>P<sup>t</sup>Bu)<sub>2</sub>, <sup>1</sup>J<sub>P-C</sub> = 42 Hz), 1.01 (CH<sub>3</sub>CN).

<sup>31</sup>P{<sup>1</sup>H} NMR (121.4 MHz, THF- $d_8$ ):  $\delta$  42.33. <sup>11</sup>B{<sup>1</sup>H} NMR (128.3 MHz, THF- $d_8$ ):  $\delta$  –13.9.

(b) In a 25 mL Schlenk flask, solid **10** (14.3 mg, 22.2 µmol) was dissolved in THF (1.5 mL) with a stirbar. The solution was stirred under a stream of CO gas until dry, producing pale green solids. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.56 (s, 4H, *ortho*-(Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>B), 6.72 (s, 2H, *para*-(Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>B), 2.35 (s, 12H, ((CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>B), 1.86 (br, 4H, B(CH<sub>2</sub>P<sup>t</sup>Bu)<sub>2</sub>), 1.07 (d, 18H, P(C(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>P-H</sub> = 6.3 Hz), 1.12 (d, 18H, P(C(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>, <sup>3</sup>J<sub>P-H</sub> = 6.3 Hz). IR: (THF/KBr, cm<sup>-1</sup>) v<sub>CO</sub> = 2084 (st).

#### 2.3. X-ray crystallography

The general X-ray experimental procedure was performed according previously published methods [9]. Crystallographic information is provided in Table 1. The structures of  $8 \cdot \text{THF} \cdot \text{pentane}$  and  $10 \cdot 0.56 \text{THF} \cdot 0.22$  pentane contained sites of disordered solvent molecules.

## 3. Results and discussion

#### 3.1. Copper(I) complexes containing halides

The formation of low-coordinate copper complexes using bis(phosphino)borate ligands was examined using several Cu(II) precursors, such as  $CuCl_2 \cdot 0.8THF$  [10], anhydrous Cu(OAc)<sub>2</sub>, and Cu(OTf)<sub>2</sub>. As has been observed in previous efforts to develop Cu(II)-phosphine chemistry [11], we found that Cu(II) was easily reduced to Cu(I) in the presence these reducing phosphine ligands to provide ill-defined degradation products. In comparison, copper(I) starting materials provide in many cases clean 1:1 adducts with monoanionic bis(phosphino)borate ligands. Anionic complexes of copper(I) halides were prepared using both the phenyl substituted phosphine ligand  $[(p^{-t}BuPh)_2B(CH_2PPh_2)_2]^{-1}$  (1) and the *tert*-butyl substituted phosphine ligand  $[(3,5-Me_2Ph)_2]$  $B(CH_2P^tBu_2)_2$  (3). For example, reacting 1[ASN] with CuI in THF/EtOH solution resulted in the near quantitative generation of  $[[(p^{-t}BuPh)_2B(CH_2PPh_2)_2]CuI][ASN]$ (4), which could be isolated in high yield (Eq. (1)). Reactions using the [Ph<sub>2</sub>B(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>][ASN] ligand [8] provided similar results with CuI and CuCl; however, the presence of *tert*-butyl substituents in the backbone of the ligand framework increases the hydrocarbon solubility of these complexes.



X-ray diffraction experimental details for 6,  $8 \cdot THF \cdot pentane$ , 9,  $10 \cdot 0.56THF \cdot 0.22pentane$ , and 11

Table 1

Compound	6	8 · THF · pentane	9	10 · 0.56THF · 0.22pentane	11
CCDC ID	238116	238119	238120	238118	238117
Empirical formula	C26H49BClCuP2	$C_{68}H_{116}B_2BrCu_2P_4Tl \cdot C_5 \cdot C_4O$	C28H45BCuNP2	$C_{36}H_{61}BCuNP_2 \cdot 0.56(C_4O) \cdot 0.22(C_5)$	C42H69BCuP3
Formula weight	533.39	1490.54 · 124.02	531.94	644.18 · 49.76	741.23
Crystal description	yellow block	colorless rod	colorless block	colorless block	colorless block
Crystal size (mm)	$0.19 \times 0.19 \times 0.19$	$0.33 \times 0.18 \times 0.13$	$0.25 \times 0.21 \times 0.19$	$0.26 \times 0.26 \times 0.19$	$0.34 \times 0.27 \times 0.21$
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	triclinic
Space group	$P2_{1}2_{1}2_{1}$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P\overline{1}$
Unit cell dimensions					
a (Å)	7.3748(8)	12.3182(11)	13.4206(9)	9.9223(8)	12.6936(12)
b (Å)	11.7329(13)	24.799(2)	15.8317(11)	21.5707(18)	16.8198(16)
<i>c</i> (Å)	33.404(4)	27.773(3)	14.1571(9)	19.7938(17)	20.773(2)
α (°)	90	90	90	90	104.598(2)
β (°)	90	95.881(2)	98.3490(10)	100.6480(10)	92.772(2)
γ (°)	90	90	90	90	90.192(2)
$V(\text{\AA}^3)$	2890.4(6)	8439.5(13)	2976.1(3)	4163.5(6)	4286.3(7)
Ζ	4	4	4	4	4
$D_{\rm calc}({\rm g \ cm}^{-3})$	1.226	1.271	1.187	1.107	1.149
$\mu (\mathrm{mm}^{-1})$	0.971	2.991	0.857	0.628	0.648
<i>T</i> (K)	98	98	98	98	98
Radiation $\lambda$ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Reflections collected	17622	127436	17391	72447	26776
Unique data/parameters	6558/295	20450/775	6028/307	9928/418	18540/883
$R_1, wR_2 (I > 2\sigma(I))$	0.0565, 0.1037	0.0723, 0.1467	0.0349, 0.0738	0.0530, 0.1100	0.0469, 0.0753
Goodness-of-fit	1.386	2.302	1.401	2.087	1.240
Largest difference peak and hole (e $Å^{-3}$ )	0.987 and -0.825	2.510 and -1.144	0.676 and -0.295	0.867 and -0.449	0.808 and -0.559

 $\overline{R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR_2} = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$ 

Similar attempts to prepare 1:1 adducts of copper(I) halides using the alkyl substituted phosphine ligands 2[Li] or 3[Li] gave more complicated results. For example, the reaction of copper(I) iodide with either 2[Li] or 3[Li] resulted in the immediate precipitation of black sediment with concomitant phosphine degradation, ascertained by  ${}^{31}P{}^{1}H$  and  ${}^{11}B{}^{1}H$  NMR spectroscopies. By contrast, combining copper(I) chloride and 3[Li] in THF solution provided one major product  $({}^{31}P{}^{1}H{})$ NMR). Spectroscopic and elemental analysis proved formation consistent with the of [[(3,5- $Me_2Ph_2B(CH_2P^tBu_2)_2[CuCl][Li(THF)_4]$  (5) (Eq. (2)). The clean preparation of copper(I) halides using the alkyl substituted phosphine ligands 2 and 3 appears to require a less redox susceptible copper(I) synthon (i.e., CuCl instead of CuI).



A significant body of work on {P<sub>2</sub>CuX} complexes (P = phosphine, X = Cl, Br, I) shows that their coordination geometry can vary between three-coordinate (P<sub>2</sub>CuX) or four-coordinate with bridging halides ({P<sub>2</sub>Cu( $\mu$ -X)}<sub>2</sub>) [12,13]. For some phosphines, such as PPh<sub>3</sub>, structural data have been obtained for both forms [12b,12c]. A related example containing the *tert*-butyl substituted chelating bis(phosphine) ligand dtbpe (dtbpe = <sup>*t*</sup>Bu<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>P'Bu<sub>2</sub>) provided the dimeric structure {(dtbpe)Cu( $\mu$ -Cl)}<sub>2</sub> [14]. It is therefore possible that 4 and 5 exist as either three-coordinate monomers, or four-coordinate, bridged dimers in solution. An equilibrium mixture of the two conformations may also prevail in solution.

The reaction between 3[Li] and several copper(I) halide reagents provides a common secondary product. For instance, the reaction between 3[Li] and CuCl provided a mixture of three phosphine containing products  $(^{31}P\{^{1}H\} NMR)$ . Along with the formation of the dominant product 5 (>80%), two minor products were observed. One of the minor products proved to be isolable by fractional crystallization, and XRD analysis of crystals thus obtained established its identity as  $\{(3,5)$  $Me_2Ph)B(CH_2P^tBu_2)_2$ CuCl (6) (Fig. 2). Neutral 6 results from the loss of an aryl ring from the borate ligand, generating a neutral bis(phosphino)borane ligated to copper(I) chloride. Potentially related examples of (phosphino)borate ligand degradation have been observed previously [15]. In all of these cases, a boron-carbon bond is cleaved at the boron-methylene link. The present example demonstrates that the boron-aryl link is also susceptible to cleavage.

The spectroscopic identification of **6** was supported by the independent synthesis of a structurally analogous species, {PhB(CH<sub>2</sub>P'Bu<sub>2</sub>)<sub>2</sub>}CuCl (7). The reaction between the neutral borane PhB(CH<sub>2</sub>P'Bu<sub>2</sub>)<sub>2</sub> and CuCl in THF solution provided a high yield route to **7** (97% yield) 1. The phosphine precursor PhB(CH<sub>2</sub>P'Bu<sub>2</sub>)<sub>2</sub> was readily generated by the addition of two equiv of LiCH<sub>2</sub>P'Bu<sub>2</sub> to PhBCl<sub>2</sub> in diethyl ether. Neutral **7** has two important spectroscopic features. First, its <sup>11</sup>B{<sup>1</sup>H} NMR spectrum (singlet at 75.2 ppm) confirms the three-coordinate nature of the boron atom [16]. Second, the <sup>31</sup>P{<sup>1</sup>H} NMR chemical shift of **7** (23.11 ppm) is consistent with the resonance ascribed to **6** (23.75 ppm).

To circumvent ligand degradation pathways, alternative copper(I) sources and the use of thallium phosphine reagents were examined. Upon addition of a THF solution of **3**[TI] to Me<sub>2</sub>S · CuBr, thallium bromide precipitated from solution. NMR analysis of the reaction solution showed one major product. XRD analysis of crystals obtained from the reaction solution provided the unexpected molecular structure, [{[(3,5-Me<sub>2</sub>Ph)<sub>2</sub>B(CH<sub>2</sub>P'Bu<sub>2</sub>)<sub>2</sub>]Cu}<sub>2</sub>( $\mu$ -Br)]Tl (**8**), shown in Fig. 3. As is evident, only one-half of an equivalent of TlBr is lost in the reaction (Eq. (3)).



The structure of 8 shows two copper centers connected by a linear bromide bridge, thus providing a monoanionic dinuclear copper species with one thallium counter-cation. A common plane cuts through each of the phosphine, copper, bromide, and boron atoms of 8. The chelate phosphine ligand exists in its typical twisted boat conformation [8,17]. In the molecular structure, the thallium atom resides in the pocket formed by the two aryl rings of the borate anion. This thallium coordination environment is similar to that observed in the molecular structure of [Ph<sub>2</sub>B(CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>]Tl (3[T1]) [8]. Halide-bridged systems are well known for copper(I), although there are few structurally characterized examples of copper centers bridged by a single halide [18]. This example appears to be structurally unique amongst phosphine-coordinated copper(I) species. In addition, all previous structurally characterized exhibit a copper-halide-copper angle that is significantly bent. The present example contains a linear halide bridge  $(Cu1-Br-Cu2 = 178.00(6)^{\circ})$ . Attempts to induce loss of TlBr in solution by the addition of a donor ligand to 8, such as PMe<sub>3</sub>, pyridine, or acetonitrile, have not been successful.



Fig. 3. Displacement ellipsoid representation (50%) of  $[\{[(3,5-Me_2Ph)_2B(CH_2P'Bu_2)_2]Cu\}_2(\mu-Br)]Tl \cdot THF \cdot pentane$  (8 · THF · pentane). Hydrogen atoms and solvent molecules are omitted for clarity. Selected interatomic distances (Å) and angles (°): P1–Cu1, 2.238(2); P2–Cu1, 2.230(2); P3–Cu2, 2.235(2); P4–Cu2, 2.231(2); Cu1–Br, 2.3660(12); Cu2–Br, 2.3638(12); B1–Cu1, 3.819(8); B2–Cu2, 3.829(8) and P1–Cu1–P2, 110.67(7); P1–Cu1–Br, 125.55(7); P2–Cu1–Br, 123.78(7); P3–Cu2–P4, 110.60(7); P3–Cu2–Br, 124.63(7); P4–Cu2–Br, 124.70(7); Cu1–Br–Cu2, 178.00(6).

# 3.2. Neutral three-coordinate acetonitrile copper(I) complexes

To access more substitutionally labile copper(I) complexes, the copper(I) reagent  $[Cu(CH_3CN)_4][PF_6]$  proved effective. Reaction of the alkyl-substituted phosphine ligands 2[Li] or 3[Li] with [Cu(CH<sub>3</sub>CN)<sub>4</sub>][PF<sub>6</sub>] in THF solution led to rapid formation of the three-coordinate products  $[Ph_2B(CH_2P'Pr_2)_2]Cu(NCCH_3)$  (9) and [(3,5- $Me_2Ph_2B(CH_2P^tBu_2)_2Cu(NCCH_3)$  (10) (Eqs. (4) and (5)). Isolated yields of pure 9 were low (ca. 40%) due to the difficulty in separating  $[Li(solvent)_x][PF_6]$  from 9. In comparison, 10 was isolated in much higher yield (80%). Both compounds have been thoroughly characterized by NMR spectroscopy and elemental analysis. The IR spectra for 9 and 10 show  $v_{\rm CN}$  bands at 2265 and 2267  $\rm cm^{-1}$ , respectively. These stretches are consistent with acetonitrile acting as a weakly bound  $\sigma$ -donor. Previously reported IR data for phosphine-coordinated copper(I) acetonitrile complexes show a wide range of C $\equiv$ N stretching frequencies (2268–2361 cm<sup>-1</sup>), all of which are above the value for the free ligand (CH<sub>3</sub>CN, thin film on KBr:  $2253 \text{ cm}^{-1}$ ) [19].



An X-ray diffraction study verified the threecoordinate nature of **9** (Fig. 4). The bis(phosphino)borate ligand is again in a twisted boat conformation. Two parameters of further note from the molecular structure of **9** are the B–Cu distance and the nature of the coordinated acetonitrile ligand. In other structures of transition metal complexes coordinated by bis(phosphino) borate ligands, the B–Cu distance in the twistedboat conformation has typically been observed at B–M = 3.91-4.12 Å (M = Fe, Co, Rh, Pd, Pt). In the structure of **9** and the other three-coordinate structures presented in the present study, the B–M distance is relatively short (**9**: B–Cu = 3.823(2) Å). This is due to an



Fig. 4. Displacement ellipsoid representation (50%) of  $[Ph_2B(CH_2P'Pr_2)_2]Cu(NCCH_3)$  (9). Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): P1–Cu, 2.2349(6); P2–Cu, 2.2556(6); Cu–N, 1.934(2); B–Cu, 3.823(2) and P1–Cu–P2, 103.35(2); P1–Cu–N, 133.25(5); P2–Cu–N, 118.98(5).



Fig. 5. Displacement ellipsoid representation (50%) of  $[(3,5-Me_2Ph)_2B(CH_2P'Bu_2)_2]Cu(NCCH_3) \cdot 0.56THF \cdot 0.22pentane (10 \cdot 0.56 THF \cdot 0.22pentane). Hydrogen atoms and solvent molecules are omitted for clarity. Selected interatomic distances (Å) and angles (°): P1–Cu, 2.2421(8); P2–Cu, 2.2333(8); Cu–N, 1.930(2); B–Cu, 3.861(3) and P1–Cu–P2, 108.55(3); P1–Cu–N, 124.94(7); P2–Cu–N, 126.49(7).$ 

expansion of the P–M–P angle  $(103.35(2)^\circ)$  that results from the three-coordinate structure and the sterically small acetonitrile ligand. The acetonitrile ligand of **9** adopts a distorted coordination mode. Rather than bisecting the P–Cu–P linkage, the nitrile is canted below the plane of these three atoms, favoring one side of the  $C_2$  axis. This is likely a solid-state phenomenon: the solution spectra of **9** are consistent with a molecule that contains a  $C_2$  axis.

An X-ray diffraction study carried out on 10 also shows a trigonal planar three-coordinate copper center (Fig. 5). The structural parameters of 10 are guite similar to those found for 9, with two minor differences. First, the acetonitrile ligand is coincident with the  $C_2$  axis of the molecule and thus colinear with the B-Cu vector. Second, the P-Cu-P angle is modestly wider  $(108.55(3)^{\circ})$  than that observed in 9  $(103.35(2)^{\circ})$ . The slightly wider bite angle of the bis(phosphine) does not result in a corresponding contraction of the B-Cu distance; instead, a slight increase in the B-Cu distance of 10 as compared to 9 (3.861(3) vs. 3.823(2) Å) is observed. The acetonitrile compounds 9 and 10 are structurally distinctive examples of monomeric, phosphine-supported nitrile adducts of 3-coordinate copper(I). A few related examples of phosphine-coordinated copper nitrile complexes have been structurally characterized previously [20]. These examples are each either four-coordinate, or contain multiple metal centers (e.g., Cu<sub>2</sub> or RhCu).

# 3.3. Substitution chemistry of the sterically encumbered complex 10

The well-defined three-coordinate acetonitrile complexes 9 and 10 serve as useful precursors to other three coordinate donor adduct complexes. Accordingly, replacement of the labile acetonitrile complex 10 is affected by a variety of donor ligands (Eq. (6)). Reaction of 10 with dimethylphosphine (PMe<sub>2</sub>Ph), trimethylphosphine sulfide (S=PMe<sub>3</sub>), 2,6-lutidine, and tertbutylisonitrile ('BuNC) in THF solution provides the corresponding complexes [(3,5-Me<sub>2</sub>Ph)<sub>2</sub>B(CH<sub>2</sub>P<sup>t</sup>Bu<sub>2</sub>)<sub>2</sub>]-Cu(PMe<sub>2</sub>Ph) (11),  $[(3,5-Me_2Ph)_2B(CH_2P^tBu_2)_2]$ - $Cu(S=PMe_3)$  (12),  $[(3,5-Me_2Ph)_2B(CH_2P^tBu_2)_2]Cu(2,6$ lutidine) (13), and  $[(3,5-Me_2Ph)_2B(CH_2P^tBu_2)_2]Cu(CN^{t-1})$ Bu) (14). All of these products can be isolated in high yield (85–95%) and the reactions are complete in less than 15 min at ambient temperature. In addition to PMe<sub>2</sub>Ph, several other phosphine donors were also examined. Triethylphosphine provided a well-defined three-coordinate adduct complex, whereas PMePh<sub>2</sub> provided a mixture of the expected three-coordinate adduct complex and also a second, unidentified diamagnetic product. PPh<sub>3</sub> does not substitute the acetonitrile ligand of 10, presumably due to steric congestion. Addition of the phosphite ligand  $P(OPh)_3$  gradually consumes 10, but results in overall complex degradation to ill-defined products. Substitution reactions of 10 by simple olefins was also surveyed. No reaction was observed (<sup>1</sup>H and  ${}^{31}P{}^{1}H$  NMR) between **10** and the potentially  $\eta^2$ -donors ethylene, 1-hexene, styrene, and azobenzene (1-10 equiv) in THF solution. This lack of reactivity is consistent with previous literature studies that suggest that copper(I) complexes supported by phosphine ligands do not form stable olefin adducts readily. Those that have been observed have typically required the presence of a large excess of the olefin [21] or chelation effects [22] to provide a Cu-olefin adduct species.



The tris(phosphine) complex **11** was structurally characterized by X-ray diffraction, verifying its threecoordinate geometry (Fig. 6). The structural parameters of **11** reflect the incorporation of a more sterically demanding phosphine donor ligand relative to the acetonitrile ligand of **10**. For example, the P–Cu–P angle is reduced (103.87(3)° in **11** versus 108.55(3)° in **10**) and the B–Cu distance is increased (3.972(3) Åin **11** versus 3.861(3) Å in **10**). Also, the average P–Cu bond lengths for the bis(phosphino)borate ligand are modestly longer (2.27 Å in **11** versus 2.24 Å in **10**), likely reflecting the greater electron-releasing nature of PMe<sub>2</sub>Ph as compared to acetonitrile.

Neutral 11 is similar to previous structurally characterized  $P_3Cu$  complexes (P = trialkyl phosphine). Several



Fig. 6. Displacement ellipsoid representation (50%) of [(3,5-Me<sub>2</sub>Ph)<sub>2</sub>B(CH<sub>2</sub>P'Bu<sub>2</sub>)<sub>2</sub>]Cu(PMe<sub>2</sub>Ph) (11). Second molecule in the asymmetric unit and hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): P1-Cu1, 2.2714(8); P2-Cu1, 2.2707(8); Cu1-P3, 2.2477(8); B1-Cu1, 3.972(3) and P1-Cu1-P2, 103.87(3); P1-Cu1-P3, 127.29(3); P2-Cu1-P3, 128.84(3).

structures reported for  $[(Ph_3P)_3Cu]^+$  [23] and the related  $[{(p-MeOPh)_3P}_3Cu]^+$  cation [24] have shown a mean Cu-P length of 2.295 Å and P-Cu-P angles near 120°. Also, Mathey and coworkers reported a macrocyclic P<sub>3</sub>-phosphinine ligand system in which a copper center lies in a distorted trigonal planar coordination geometry [25]. Additionally, there are two reports of bimetallic  $[Cu_2(\eta^1:\eta^1-L_2)_3]^{2+}$  (L<sub>2</sub> = dmpm, (Ph<sub>2</sub>P)<sub>2</sub>py), where the copper centers are both in highly symmetric trigonal planar environments [26]. The structures of these homoleptic phosphine adducts are relatively  $C_3$  symmetric, whereas the structure of 11 is better described as  $C_{2v}$ due to the geometric constraint imposed by the chelated bis(phosphine) ligand. A similarly distorted structure has been reported for dicationic [{(dppf)Cu}<sub>2</sub>( $\eta^1$ : $\eta^1$ dppf)]<sup>2+</sup> [27], which has Cu–P bond lengths of 2.280 Å, 2.283 Å, and 2.260 Å and P-Cu-P angles of 124.6°, 123.4°, and 111.3°.

A complex related to 11 is the phosphine sulfide adduct  $[(3,5-Me_2Ph)_2B(CH_2P^tBu_2)_2]Cu(S=PMe_3)$  (12). A structurally related species has been reported:  $[{(dppf)Cu}_2(\eta^1:\eta^1-dppfS_2)][BF_4]_2$  [28]. Complex 12 exhibits remarkably poor solubility (<5 mg/mL) in benzene and THF solution, distinct from 11, 13, and 14.

Similar to 12, the lutidine derivative [(3,5- $Me_2Ph)_2B(CH_2P^tBu_2)_2]Cu(2,6-lutidine)$  (13) contains an uncommon coordination environment for copper(I). The sterically hindered pyridines 2,6-lutidine and 2,4,6collidine have been used previously to prepare two- and three-coordinate copper complexes [29-32]. In almost all of these cases, the complexes are homoleptic pyridine cations, or include a single halide or pseudo-halide donor [29–31]. One notable exception reported by Omary et al. [32] is the fluorinated bis(pyrazolyl)borate derivative,  $[H_2B(3,5-(CF_3)_2Pz)_2]Cu(2,4,6-collidine)$ . Similar to 13, the monoanionic borate-based  $[H_2B(3,5-(CF_3)_2Pz)_2]^{-1}$ provides a neutral, three-coordinate copper(I) center.

The isonitrile complex  $[(3,5-Me_2Ph)_2B(CH_2P^tBu_2)_2]$ - $Cu(CN^{t}Bu)$  (14) is structurally distinct in that it represents what is to our knowledge the only example of a phosphine-supported, three-coordinate monoisonitrile complex of copper(I). Four-coordinate copper(I) complexes featuring terminal isocyanide ligands more typically feature either three phosphine ligands and one isonitrile ligand, or two phosphines and two isocyanide ligands [33–37]. A key spectroscopic feature of metalbound isocyanides is their infrared signature. The infrared spectrum of 14 shows a  $v_{\rm CN}$  band at 2162 cm<sup>-1</sup>. This value is presented in Table 2 along with several other previously reported copper(I) complexes containing a single tert-butyl isonitrile ligand [38–43]. As can be seen, most of the examples have  $v_{\rm CN}$  values greater than that observed for free CN'Bu. This increase in the  $C \equiv N$ stretching frequency has been attributed to both poor back-donation from the copper d-orbitals into the ligand  $\pi^*$  orbitals, and to a strong  $\sigma$ -donor effect that polarizes the C=N bond [44,45]. Thus, the isonitrile ligand in 14 can be considered as primarily a strong  $\sigma$ donor in this context.

We also surveyed the generation of a monocarbonyl copper complex analogous to 14. To our knowledge, there are as yet no examples of well-defined copper carbonyl complexes supported by phosphine ligands. This is consistent with the observations of related isonitrile complexes, where copper(I) has been characterized as a relatively poor  $\pi$ -donor. We have found that the reaction between 10 and excess CO gas results in the formation of an unstable carbonyl adduct species that can be formulated as  $[(3,5-Me_2Ph)_2B(CH_2P^tBu_2)_2]Cu(CO)$  (15). In THF solution, excess carbon monoxide appears to displace the acetonitrile ligand, resulting in a shift in the <sup>31</sup>P{<sup>1</sup>H} NMR resonance from 36.4 to 42.3 ppm. If CO is removed under vacuum, the acetonitrile adduct is

Infrared resonances (v<sub>CN</sub>) for some copper(I) monoisonitrile complexes

Complex	$v_{\rm CN}~({\rm cm}^{-1})$	Ref
$[HB{3,5-(CF_3)_2pz}_3]Cu(CN'Bu)$	2196 <sup>a</sup>	[38]
[(Ph <sub>3</sub> P) <sub>3</sub> Cu(CNEt)][BF <sub>4</sub> ]	2193 <sup>b</sup>	[37]
CpCu(CN <sup><i>t</i></sup> Bu)	2170 <sup>a</sup>	[39]
$[(3,5-Me_2Ph)_2B(CH_2P'Bu_2)_2]Cu(CN'Bu)$ (14)	2162 <sup>c</sup>	
$[HB(Pz)_3]Cu(CN'Bu)$	2155 <sup>d</sup>	[40]
$[CpCo{P(OMe)_2O}_3]Cu(CN'Bu)$	2148 <sup>a</sup>	[41]
$[\kappa^3 - B(Pz)_4]Cu(CN^tBu)$	2140 <sup>d</sup>	[42]
<sup><i>i</i></sup> BuNC	2138 <sup>e</sup>	[19]
( <sup>t</sup> BuO)Cu(CN <sup>t</sup> Bu)	2102 <sup>b</sup>	[43]
<sup>a</sup> KBr		

<sup>b</sup> Nujol.

° THF/KBr. <sup>d</sup> Not reported.

<sup>e</sup> Neat.

regenerated as indicated by the return of the 36.4 ppm resonance. Infrared analysis of green solids isolated by drying a sample of 10 under a stream of CO gas revealed a single infrared band at 2084  $\text{cm}^{-1}$ , consistent with a metal-bound monocarbonyl species. The carbonyl species 15 is not stable in the absence of excess CO, apparently decaying to solvent-bound species with concomitant loss of CO. For instance, if a THF solution of 10 is dried under a stream of CO gas, the resulting pale green solids that are isolated display a  ${}^{31}P{}^{1}H$  NMR resonance at 44 ppm upon dissolution in benzene- $d_6$ . This resonance gradually disappears unless a blanket of CO is preserved above the NMR sample solution. A single new resonance grows in at 38 ppm, which may be indicative of a benzene solvent adduct of Cu(I). The lability of the putative monocarbonyl species is consistent with previous observations for phosphine-supported copper [20n].

$$10 \xrightarrow{+ CO}_{- CO} (3,5-Me_2Ph)_2B \xrightarrow{+ Cu - CO}_{+ Bu_2} (7)$$

In summation, we have prepared and characterized several neutral and anionic copper complexes supported by chelating, monoanionic bis(phosphino)borate ligands. In particular, the sterically encumbered *tert*-butyl substituted bidentate phosphine **3** is useful for stabilizing three-coordinate species with a host of donor ligands occupying the third coordination site. The substitution chemistry of the available to the acetonitrile complex **10** is key to the preparation of numerous donor adduct complexes in this series. These synthons should expand the reaction chemistry available to neutral and anionic phosphine-chelated copper(I) systems. In particular, the 3-coordinate systems described may serve as useful entry points to group transfer reactions that would generate [BP<sub>2</sub>]Cu<sup>III</sup> = E species.

#### 4. Supplementary material

Crystallographic data for the structural analyses have been deposited at the Cambridge Crystallographic Data Centre, CCDC numbers 238116 (6), 238119 ( $8 \cdot$  THF  $\cdot$  pentane), 238120 (9), 238118 (10  $\cdot$  0.56 THF  $\cdot$  0.22 pentane), and 238117 (11). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc. cam.ac.uk or http://www.ccdc.cam.ac.uk).

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