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Reversible Coordination of Boron–, Aluminum–, Zinc–, Magnesium–, and Calcium–Hydrogen Bonds to Bent {CuL₂} Fragments: Heavy σ Complexes of the Lightest Coinage Metal

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Supporting Information

ABSTRACT: A series of copper(I) complexes bearing electron-deficient β -diketiminate ligands have been prepared. The study includes [{{ArNC(CR₃)}₂CH}-Cu(η^2 -toluene)_n] (Ar = Mes, R = F, n = 0.5, [1₂·tol]; Ar = C₆F₅, R = Me, n = 1, [2·tol]; Ar = 2,6-Cl₂C₆H₃, R = H, n = 0.5, [3₂·tol]). Reactions of [1-3_n·tol] with boranes, alanes, a zinc hydride, a magnesium hydride, and a calcium hydride generate the corresponding σ complexes ([1-3·B], [3·B'], [3·AI], [3·AI'], [1-3·Zn], [1·Mg], and [1·Ca]). These species all form reversibly, being in equilibrium with the arene solvates in solution. With the exception of the calcium complex, the complexes have



all been characterized by single-crystal X-ray diffraction studies. In solution, the σ -hydride of the aluminum, zinc, magnesium, and calcium derivatives resonates between -0.12 and -1.77 ppm (C_6D_6 or toluene- d_8 , 193–298 K). For the σ -borane complexes, the hydrides are observed as a single resonance between 2 and 3.5 ppm (C_6D_6 , 298 K) and bridging and terminal hydrides rapidly exchange on the NMR time scale even at 193 K. Quantification of the solution dynamics by van't Hoff analysis yields expectedly small values of ΔH° and negative values of ΔS° consistent with weak binding and a reversible process that does not involve aggregation of the copper species. The donor–acceptor complexes can be rationalized in terms of the Dewar–Chatt–Duncanson model. Density functional theory calculations show that the donation of σ -M–H (or E–H) electrons into the 4s-based orbital (LUMO or LUMO+1) of the copper fragment is accompanied by weak back-donation from a d_{xz} -based orbital (HOMO or HOMO–1) into the σ^* -M–H (or E–H) orbital.

INTRODUCTION

Bond-breaking processes are intimately related to the binding of substrates to transition-metal centers. Reversible coordination of a σ bond of a substrate to the metal is a key step in a number of catalytic reactions, with bond breaking often occurring by oxidative addition to the transition metal.¹⁻⁶ Despite growing applications in catalysis,^{7,8} there is limited precedent for the coordination of element–hydrogen or element–element bonds to the coinage metals (element = C, Si, Sn, B; metal = Cu, Ag, Au). This discrepancy is in stark contrast to earlier members of the transition-metal series.^{9–13}

In its simplest form, the coordination of σ bonds to transition metals can be considered within the Dewar–Chatt–Duncanson bonding model. As such, the common occurrence of the 1+ oxidation state in group 11 complexes and the associated d¹⁰ configuration of the metal may go some way to account for the lack of observable and isolable σ complexes: In these complexes, no unoccupied metal-based d orbitals are available to accept electron density from the σ bond. Nevertheless, a handful of σ complexes of the coinage metals have been reported in the past few years, and a number of approaches to stabilize these species have emerged (Figure 1).

Bourissou and co-workers have adopted a chelation strategy to prepare and isolate σ complexes of copper(I) (Figure 1a). *Intramolecular* coordination and activation of Si–Si, Si–H, and Sn–Sn bonds, within trans-coordinating phosphine frameworks, at copper(I) and gold(I) have been reported.^{14–16} In the case of an Sn-Sn analogue, oxidative addition of the Sn-Sn bond was observed, allowing isolation and characterization of the corresponding copper(III) distannyl complex.¹⁷ While the oxidative addition of σ -(Si-Si) bonds within similar copper complexes has not been observed, this reaction is known to occur in both an intra- and an intermolecular sense at gold(I).^{14,18} Using chelation as a means to force coordination, claims have been made for agostic interactions in complexes of copper(II) bearing chelating organic ligands. While the intramolecular interaction between a C-H bond of a chiral ephedrine ligand and a copper(II) center was initially classified as agostic,¹⁹ careful reanalysis shows that its description as a multicenter intramolecular hydrogen bond is more accurate.²⁰ Similarly, weak and primarily electrostatic interactions in copper(I) and copper(II) complexes have been classified as anagostic.^{21–23} Only in 2010 was convincing experimental (electron paramagnetic resonance) and computational support (density functional theory) for a C-H agostic interaction with a copper(II) azamacrocycle provided by Stack and coworkers.²⁴

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Figure 1. Strategies to stabilize σ complexes of the coinage metals.

A comparable trend of speculation, followed by unambiguous characterization, can be found for gold(I) and gold(III) agostic complexes,²⁵ with Bourrisou and co-workers recently carrying out low-temperature spectroscopic characterization and computational modeling of a square-planar gold d⁸ complex possessing an agostic C–H ligand (Figure 1a).²⁶ Dihydrogen complexes of the coinage metals are essentially unknown in the condensed phase; although those of copper(I) have been considered as intermediates in the catalytic hydrogenation of CO_2^{27} and semihydrogenation of alkynes with bimetallic catalysts,²⁸ those of gold(I) have been proposed as high-energy intermediates in alkene hydrogenation based on DFT calculations.²⁹

An alternative strategy adopted to prepare σ complexes of the coinage metals is to maximize the number of binding events (Figure 1b). This approach has been argued as a means to stabilize notoriously weak *intermolecular* σ -alkane complexes of transition metals.³⁰ Through deviation from a 1:1 ratio of transition metal/ σ bond, the number of potential interactions, and the binding enthalpy, can be maximized. Two cationic copper(I) diborane complexes have been isolated in which the diborane coordinates to the metal through two σ -B–H bonds (Figure 1b).^{31,32}

Through a serendipitous discovery, we found that copper(I) β -diketiminate complexes are well suited for substrate binding (Figure 1c). The bent {CuL₂} fragment possess an accessible lowest unoccupied molecular orbital (LUMO or LUMO+1) that is largely 4s in character and oriented between the flanking arms of the ligand. The symmetry and energy of the 4s-based orbital circumvents the problem of available d orbitals because it is capable of accepting electron density from a σ -(E–H) bond; similarly. the highest occupied molecular orbital (HOMO or HOMO-1) is of suitable symmetry to backdonate into the σ^* -(E–H) orbital (Figure 1d). We have communicated that the reversible *intermolecular* binding of σ -

boranes, σ -alanes, and σ -zincanes to these copper(I) fragments is possible. By increasing the ionicity of the element-hydrogen (element = boron) bond to include metal-hydrogen (metal = aluminum, zinc) bonds, we have found that the binding energy may be maximized. This has allowed the isolation and characterization of previously inaccessible types of heterobimetallic complexes that may be classified as σ complexes of copper(I).^{33,34} Here we report a full account of experimental and theoretical work detailing the preparation and properties of copper σ complexes of the heavier main-group elements including the first description of the reversible binding of a magnesium hydride and a calcium hydride to copper(I).

EXPERIMENTAL PROCEDURES

General experimental procedures, the preparation of the proligands $L^{1}H = \{MesNC(CF_{3})\}_{2}CH$, $L^{2}H = \{C_{6}F_{3}NC(Me)\}_{2}CH$, and $L^{3}H = \{2,6\text{-}Cl_{2}C_{6}H_{3}NCMe\}_{2}CH$, the main-group complexes [BDIMg^IOEt_{2}], [BDIZnH], and [BDIMg(μ -H)]_2 (BDI = $\{2,6\text{-}^{i}Pr_{2}C_{6}H_{3}NCMe\}_{2}CH$), and associated multinuclear NMR and single-crystal X-ray diffraction data are detailed in the Supporting Information.

Synthesis of [1₂·tol]. In a glovebox, [CuMes]_n (n = 4, 5; 262 mg, 1.4 mmol, 1.2 equiv) was dissolved in toluene (13 mL). The proligand L¹H was added to the reaction mixture as a solid (534 mg, 1.2 mmol, 1 equiv), and the mixture turned bright red. The solution was stirred for 3 days at 80 °C and then allowed to cool to room temperature, and any precipitate was allowed to settle. The solution was filtered through glass fiber, and slow evaporation of the solvent yielded [1₂·tol] as an orange crystalline solid (468 mg, 0.85 mmol, 71%). ¹H NMR (C₆D₆, 500 MHz, 298 K): δ 1.97 (s, 12H), 2.11 (s, 1.3H, tol), 2.19 (s, 6H), 6.07 (s, 1H), 6.82 (s, 4H), 7.01–7.16 (m, 2H). ¹³C NMR (C₆D₆, 125 MHz, 298 K): δ 18.7, 21.0, 21.4 (tol), 83.4, 122.0 (q, ¹J_{C-F} = 288.0 Hz), 125.7 (tol), 128.6 (tol), 128.8, 129.3 (tol), 129.9, 133.4, 137.9 (tol), 145.3, 152.6 (q, ²J_{C-F} = 24.9 Hz). ¹⁹F NMR (C₆D₆, 470.4 MHz, 298 K): δ -64.88 (s, 6F). Elem anal. Calcd for C₅₃H₅₀Cu₂F₁₂N₄: C, 57.97; H, 4.59; N, 5.10. Found: C, 57.89; H, 4.68; N, 5.03.

Synthesis of [2-tol]. In a glovebox, $[CuMes]_n$ (n = 4, 5; 508 mg, 2.8 mmol, 1.2 equiv) was dissolved in toluene (30 mL). The proligand

L²H was added to the reaction mixture as a solid (998 mg, 2.3 mmol, 1 equiv), at which point the mixture turned bright red. The solution was stirred overnight at 25 °C, and the now green solution was diluted with toluene (20 mL) and filtered through glass fiber. The solvent volume was reduced to ca. 10 mL, upon which point crystallization of a light-green solid was observed. The product was isolated by filtration and dried in vacuo to give [**2tol**] as a light-green crystalline solid (764 mg, 1.3 mmol, 56%). ¹H NMR (C₆D₆, 298 K, 500 MHz): δ 1.49 (s, 6H), 2.12 (s, 2.5H, tol), 4.73 (s, 1H), 7.01–7.13 (m, 3.7H). ¹³C NMR (C₆D₆, 298 K, 125 MHz): δ 21.4 (tol), 23.7, 97.4, 125.7 (tol), 127.2 (tm, ²*J*_{C-F} = 15.8 Hz), 128.5 (tol), 129.4 (tol), 137.5 (dm, ¹*J*_{C-F} = 248.2 Hz), 137.9 (tol), 137.9 (dm, ¹*J*_{C-F} = 248.2 Hz), 141.3 (dm, ¹*J*_{C-F} = 242.4 Hz), 166.9. ¹⁹F NMR (C₆D₆, 298 K, 470.4 MHz): δ – 164.0 (td, 4F, ³*J*_{F-F} = 23.1 Hz, ⁴*J*_{F-F} = 5.3 Hz), -162.9 (t, 2F, ³*J*_{F-F} = 21.9 Hz), -150.5 (dd, 4F, ³*J*_{F-F} = 25.6 HZ, ⁴*J*_{F-F} = 5.3 Hz). Elem anal. Calcd for C₄₁H₂₂Cu₂F₂₀N₄: C, 45.89; H, 2.06; N, 5.20. Found: C, 45.90; H, 19.5; N, 5.11.

Synthesis of [1·B]. In a glovebox, [12·tol] (61 mg, 0.055 mmol, 1 equiv) was weighed into a vial and dissolved in toluene (1.5 mL). Similarly, $H_3B\cdot L$ (L = 2-methylpyridine; 12 mg, 0.11 mmol, 2 equiv) was weighed and dissolved in toluene (1.5 mL). The solution containing H3B·L was added dropwise over 5 min to the stirred solution of [12·tol]. The reaction mixture was stirred for 1 h at 25 °C. The green solution was filtered using a glass fiber and concentrated in vacuo to 1/4 of its original volume before *n*-heptane (1.5 mL) was added. The reaction mixture was left at -35 °C overnight to give yellow crystals of [1·B] (53 mg, 0.088 mmol, 80%). At room temperature, the equilibrium remains in fast exchange, and NMR data are given as such. ¹H NMR (C_6D_6 , 298 K, 500 MHz): δ 1.99 (br s, 3H, $Ar-Me_B$), 2.08 (br s, 6H, Me_{Cu}), 2.22 (br s, 12H, $Ar-Me_{Cu}$), 2.98 (br m, 3H, B-(H)₃-Cu), 5.94 (t, 1H, ${}^{3}J_{H-H} = 7.3$ Hz, Ar-H_B), 5.98 (d, 1H, ${}^{3}J_{H-H} = 7.3$ Hz, ${}_{B}Ar-H$), 6.17 (s, 1H, CH_{Cu}), 6.47 (td, 1H, ${}^{3}J_{H-H}$ = 5.0 Hz, ${}^{4}J_{H-H}$ = 1.5 Hz, Ar-H_B), 6.66 (s, 4H, Ar-H_{Cu}), 7.01-7.13, 7.55 (br s, 1H Ar-H_B). 13 C NMR (C₆D₆, 298 K, 125 MHz): δ 18.8, 20.9, 22.2, 83.4 (sept, ${}^{3}J_{C-F} = 5.2$ Hz), 121.3 (q, ${}^{1}J_{C-F} = 288.7$ Hz), 126.3, 128.7, 129.3, 129.5, 132.2, 138.5, 146.6, 148.0, 151.9 (q, ${}^2J_{C-F}$ 25.7 Hz), 156.9. ¹¹B NMR (C_6D_6 , 298 K, 160.4 MHz): δ –18.0 (br). $^{19}\mathrm{F}$ NMR (C₆D₆, 470.4 MHz, 298 K): δ –64.6. Elem anal. Calcd for C₂₉H₂₃BCuF₆N₃: C, 56.92; H, 5.44; N, 6.87. Found: C, 56.84; H, 5.45; N, 6.90.

Synthesis of [2·B]. In a glovebox, [2·tol] (64 mg, 0.11 mmol, 1 equiv) was weighed into a vial and dissolved in toluene (1.5 mL). Similarly, $H_3B \cdot L$ (L = 2-methylpyridine; 12 mg, 0.11 mmol, 1 equiv) was weighed and dissolved in toluene (1.5 mL). The solution containing H3B·L was added dropwise over 5 min to the stirred solution of [2·tol]. The reaction mixture was stirred for 1 h at 25 °C. The green solution was filtered using a glass fiber and concentrated in vacuo to 1/4 of its original volume before *n*-heptane (1.5 mL) was added. The reaction mixture was left at -35 °C overnight to give yellow crystals of [2·B] (0.042 g, 0.069 mmol, 62%). At room temperature, the equilibrium remains in fast exchange, and NMR data are given as such. ¹H NMR (C_6D_6 , 298 K, 500 MHz): δ 1.65 (s, 6H, Me_{Cu}), 1.97 (s, 3H, Me_{B}), 3.07 (br m, 3H, B-(H)₃-Cu), 4.92 (s, 1H, CH_{Cu}), 5.96 (t, 1H, ${}^{3}J_{H-H}$ = 7.6 Hz, Ar- H_{B}), 6.00 (d, 1H, ${}^{3}J_{H-H}$ = 7.6 Hz, $Ar-H_B$), 6.51 (br t, 1H, ${}^{3}J_{H-H}$ = 7.6 Hz, $Ar-H_B$), 7.62 (br d, 1H, ${}^{3}J_{H-H} = 5.8$ Hz, Ar $-H_{B}$). ${}^{13}C$ NMR (C₆D₆, 298 K, 125 MHz): δ 21.9, 23.2, 97.7, 122.1, 126.6, 136.8 (dm, ${}^{1}J_{C-F} = 250.7$ Hz), 138.0 (dm, ${}^{1}J_{C-F} = 250.7$ Hz), 139.4, 140.2 (dm, ${}^{1}J_{C-F} = 239.0$ Hz). ¹¹B NMR (C₆D₆, 298 K, 160.4 MHz): δ -19.7 (br). ¹⁹F NMR (C₆D₆, 376.5 MHz, 298 K): δ –166.1 (t, 2F, ${}^{3}J_{F-F}$ = 21.5 Hz), –164.8 (t, 4F, ${}^{3}J_{F-F}$ = 23.5 Hz), -151.2 (d, 2F, ${}^{3}J_{F-F} = 23.1$ Hz). Elem anal. Calcd for C23H16BCuF10N3: C, 46.06; H, 2.86; N, 7.01. Found: C, 46.17; H, 2.79; N, 7.07.

Synthesis of $[1\cdot Zn]$. In a glovebox, $[1_2 \cdot tol]$ (61 g, 0.055 mmol, 1 equiv) was weighed into a vial and dissolved in toluene (1.5 mL). Similarly, BDIZnH (53 mg, 0.11 mmol, 2 equiv) was weighed and dissolved in toluene (1.5 mL). The solution containing BDIZnH was added dropwise over 5 min to the stirred solution of $[1_2 \cdot tol]$. The reaction mixture was allowed to warm to 25 °C and stirred for 30 min. The orange solution was filtered using a glass fiber and concentrated in

vacuo to 1/4 of its original volume before *n*-heptane (3 mL) was added. The reaction mixture was left at -35 °C overnight to give orange crystals of [1·Zn] (63 mg, 0.07 mmol, 58%). At room temperature, the equilibrium remains in fast exchange, and NMR data are given as such. ¹H NMR (C_6D_6 , 298 K, 500 MHz): δ 1.16 (d, 12H, ³ J_{H-H} = 6.8 Hz, $_{Zn}$ CHMe₂), 1.25 (d, 12H, $^{3}J_{H-H}$ = 6.8 Hz, $_{Zn}$ CHMe₂), 1.68 (s, 6H, Me_{Zn}), 1.97 (s, 12H, Ar-Me_{Cu}), 2.19 (s, 6H, Ar-Me_{Cu}), 3.16 (hept, 4H, ${}^{3}J_{H-H} = 6.8$ Hz, ${}_{Zn}CHMe_{2}$), 5.01 (s, 1H, CH_{Zn}), 6.08 (s, 1H, CH_{Cu}), 6.81 (s, 4H, Ar H_{Cu}) 6.99–7.15 (m, 6H, Ar H_{Zn}). ¹³C NMR (C₆D₆, 298 K, 125 MHz): δ 18.7, 21.0, 23.2, 23.5, 24.8, 28.5, 83.6, 96.1, 120.9 (q, ${}^{1}J_{C-F}$ = 287.9 Hz), 124.0, 126.3, 128.8, 130.0, 133.4, 141.8, 144.6, 145.4, 152.6 (q, ${}^{2}J_{C-F} = 25.4$ Hz), 168.2. ${}^{19}F$ NMR $(C_6D_6, 298 \text{ K}, 470.7 \text{ MHz})$: δ -64.8. At low temperature, the equilibrium enters the slow-exchange regime, and NMR data are given as such. ¹H NMR (C_7D_{8} , 195 K, 500 MHz): δ –0.40 (s, 1H), 0.98 (br d, 12H, _{Zn}CHMe₂), 1.04 (br d, 12H, _{Zn}CHMe₂), 1.39 (br s, 6H, Me_{Zn}), 2.10 (s, 6H, Ar- Me_{Cu}), 2.19 (s, 12H, Ar- Me_{Cu}), 2.84 (br m, 4H, _{Zn}CHMe₂), 4.76 (s, 1H, CH_{Zn}), 6.46 (s, 1H, CH_{Cu}), 6.64 (s, 4H, ArH_{Cu}), 6.87–6.98 (m, 6H, ArH_{Zn}). ¹³C NMR (C_7D_8 , 193 K, 125 MHz): δ 18.6, 21.0, 23.6, 24.1, 25.3, 32.6, 83.1, 97.4, 121.0 (q, ${}^{1}J_{C-F}$ = 287.9 Hz), 126.2, 126.5, 130.1, 133.3, 141.6, 142.6, 145.8, 146.3, 152.4 (m), 168.3. ¹⁹F NMR (C₇D₈, 193 K, 407.4 MHz): δ –63.3. Elem anal. Calcd for C52H65CuF6ZnN4: C, 63.15; H, 6.62; N, 5.66. Found: C, 63.14; H, 6.58; N, 5.75.

Synthesis of [2·Zn]. In a glovebox, [2·tol] (64 mg, 0.11 mmol, 1 equiv) was weighed into a vial and dissolved in toluene (0.75 mL). Similarly, BDIZnH (53 mg, 0.11 mmol, 1 equiv) was weighed and dissolved in toluene (0.75 mL). The solution containing the copper complex was cooled to $-35\ ^\circ C$ with stirring. After 10 min, the solution containing BDIZnH was added dropwise to the stirred reaction mixture. The reaction mixture was allowed to warm to 25 °C and stirred for 30 min. The light-green solution was filtered using a glass filter and the solvent removed under vacuum to 1/4 of its original volume. n-Heptane (1.5 mL) was added and the reaction mixture stored at -35 °C for 3 days to give multiple crops of light-green crystals of [2·Zn] (combined yield: 27 mg, 0.028 mmol, 25%). At room temperature, the equilibrium remains in fast exchange, and NMR data are given as such. ¹H NMR (C_6D_6 , 298 K, 500 MHz): δ 1.07 (d, 12H, ${}^{3}J_{H-H}$ = 6.8 Hz, ${}_{Zn}$ CHMe₂), 1.12 (d, 12H, ${}^{3}J_{H-H}$ = 6.8 Hz, _{Zn}CHMe₂), 1.45 (s, 6H, Me_{Zn}), 1.50 (s, 6H, Me_{Cu}), 2.97 (hept, 4H, ${}^{3}J_{H-H} = 6.8 \text{ Hz}_{7n} \text{CHMe}_{2}$, 4.82 (s, 1H, CH_{Cu}), 4.92 (s, 1H, CH_{7n}), 7.04–7.15 (m, 6H, ArH). ¹³C NMR (C_6D_6 , 298 K, 125 MHz); δ 23.4, 23.5, 24.4, 28.6, 97.4, 98.8, 124.0, 125.6 (m), 126.7, 129.3 (br s), 137.6 (dm, ${}^{1}J_{C-F}$ = 249.6 Hz), 138.1 (dm, ${}^{1}J_{C-F}$ = 246.5 Hz), 141.3 (dm, ${}^{1}J_{C-F}$ = 242.2 Hz), 141.6, 143.6, 166.7, 169.1. ¹⁹F NMR (C₆D₆, 298 K, 470.7 MHz): δ -150.0 (d, 4F, ${}^{3}J_{F-F}$ = 23.0 Hz), -163.3 (t, 4F, ${}^{3}J_{F-F}$ = 23.0 Hz), -164.5 (br m, 2F). Elem anal. Calcd for $C_{46}H_{49}CuF_{10}N_4Zn$: C, 56.56; H, 5.06; N, 5.74. Found: C, 56.42; H, 5.04; N, 5.66.

Synthesis of [1·Mg]. In a glovebox, [1, tol] (61 mg, 0.055 mmol, 1 equiv) was weighed into a vial and dissolved in toluene (1.5 mL). Similarly, $[BDIMg(\mu-H)]_2$ (49 mg, 0.11 mmol, 2 equiv) was weighed and dissolved in toluene (1.5 mL). Vials containing both complexes were placed in the glovebox freezer and cooled to -35 °C. After 20 min, the solution containing BDIMgH was added dropwise over 5 min to the stirred reaction mixture at -35 °C and was left to stir at this temperature for 30 min. The solvent volume was reduced in vacuo, with stirring, to 1/4 of its original volume, before the addition of cold *n*heptane (3 mL). The orange crude reaction mixture was stored at -35°C overnight to give red crystals of [1·Mg] (30 mg, 0.032 mmol, 29%). At room temperature, the complex is unstable, and thus NMR data are given at 193 K. ¹H NMR (C_7D_8 , 193 K, 500 MHz): δ –1.94 (s, 1H), 0.92 (br d, 12H, CHMe₂), 1.04 (br d, 12H, CHMe₂), 1.39 (s, 6H, Me_{Mg}), 1.98 (s, 12H, Ar-Me_{Cu}), 2.19 (s, 6H, Ar-Me_{Cu}), 2.77 (br sept, 4H, $CHMe_2$), 4.66 (s, 1H, CH_{Mg}), 6.41 (s, 1H, CH_{Cu}), 6.65 (s, 4H, ArH_{Cu}) 6.90–6.99 (m, 6H, ArH_{Zn}). ¹³C NMR (C₇D₈, 193 K, 125 MHz): δ 18.9, 20.9, 23.0, 23.9, 24.8, 83.1, 95.9, 121.0 (m), 129.8, 131.9, 133.1, 136.0, 141.2, 143.0, 144.6, 146.9, 151.6 (m), 169.8. ¹⁹F NMR (C_7D_{84} 193 K, 470.4 MHz): δ -63.4. Elem anal. Calcd for

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 $\rm C_{52}H_{65}CuF_6MgN_4:$ C, 65.89; H, 6.91; N, 5.91. Found: C, 65.75; H, 6.95; N, 6.00.

L²MgBDI. Method A. In a glovebox, $[BDIMg(\mu-H)]_2$ (0.024 g, 0.055 mmol, 1 equiv) was weighed into a vial and dissolved in toluene (0.75 mL). Similarly, [2-tol] (0.032 g, 0.055 mmol, 1 equiv) was weighed and dissolved in toluene (0.75 mL). The solution containing the copper complex was cooled to -35 °C and, after 10 min, added dropwise to the solution containing $[BDIMg(\mu-H)]_2$. The reaction mixture was allowed to warm to 25 °C and stirred for 30 min. The dark-brown solution was filtered using a glass fiber and the solvent reduced under vacuum to 1/4 of its original volume. *n*-Hexane (1.5 mL) was added, and the reaction mixture was then stored at -35 °C overnight to give colorless crystals of L²MgBDI, which was submitted for single-crystal X-ray diffraction without further analysis.

Method B. In a glovebox, KHMDS (88 mg, 0.44 mmol, 1 equiv) was weighed into a vial, and toluene (6 mL) was added to create a suspension. Similarly, L^2H (189 mg, 0.44 mmol, 1 equiv) was weighed and dissolved in toluene (6 mL). The solution containing KHMDS was added to the solution containing the ligand, and a yellow precipitate was formed. The reaction was left to stir for 15 min and the precipitate left to settle overnight before the solvent was first decanted, then removed in vacuo to give L^2K as a yellow powder (171 mg, 0.37 $\,$ mmol, 83%), and used without further purification. To a suspension of L²K (102 mg, 0.22 mmol, 1 equiv) in toluene (3 mL) was added BDIMg^I(OEt₂) (135 mg, 0.22 mmol, 1 equiv) to give a colorless, cloudy solution. The solution was left to stir for 30 min before the precipitate was left to settle overnight filtered through glass fiber, and the solvent was removed in vacuo to give a crude as an off-white powder. The crude was recrystallized from *n*-hexane (3 mL) at -35 °C to give white crystals of L²MgBDI (67 mg, 0.077 mmol, 35%). ¹H NMR (C₆D₆, 298 K, 500 MHž): δ 1.06 (d, 6H, ${}^{3}J_{H-H} = 6.8$ Hz), 1.09 (d, 6H, ${}^{3}J_{H-H} = 6.8$ Hz), 1.22 (s, 3H), 1.28 (d, 6H, ${}^{3}J_{H-H} = 6.8$ Hz), 1.36 (d, 6H, ${}^{3}J_{H-H} = 6.8$ Hz), 1.52 (s, 6H), 1.63 (s, 3H), 2.90 (sept, 2H, ${}^{3}J_{H-H} = 6.8 \text{ Hz}$), 3.19 (sept, 2H, ${}^{3}J_{H-H} = 6.8 \text{ Hz}$), 4.48 (s, 1H), 4.81 (s, 1H), 7.00-7.16 (m, 6H). ${}^{13}\text{C}$ NMR (C₆D₆, 298 K, 125 MHz): δ 24.4, 24.6, 25.1, 25.4, 25.4, 28.4, 29.0, 29.0, 94.0, 100.0, 123.6 (br t), 123.9, 124.3, 125.4, 125.6 (br t), 137.1 (br t), 139.1 (br t), 140.7 (br d), 141.7 (br d), 141.9, 142.6 (br d), 142.8, 143.7 (br d), 144.8, 171.2, 172.2, 172.4. ¹⁹F NMR (C₆D₆, 298 K, 470.7 MHz): δ –143.6 (d, 2F, ${}^{3}J_{F-F} = 23.5 \text{ Hz}$, $-147.4 \text{ (dd, 2F, }{}^{3}J_{F-F} = 23.5 \text{ Hz}$, ${}^{4}J_{F-F} = 4.7 \text{ Hz}$), $-161.4 \text{ (t, 1F, }{}^{3}J_{F-F} = 23.5 \text{ Hz}$), $-161.7 \text{ (t, 1F, }{}^{3}J_{F-F} = 18.8 \text{ Hz}$), $-162.8 \text{ (td, 2F, }{}^{3}J_{F-F} = 23.5 \text{ Hz}$, ${}^{4}J_{F-F} = 4.7 \text{ Hz}$), $-164.3 \text{ (td, 2F, }{}^{3}J_{F-F}$ = 23.5 Hz, ${}^{4}J_{F-F}$ = 4.7 Hz). Elem anal. Calcd for C₄₆H₄₈F₁₀MgN₄: C, 63.42; H, 5.55; N, 6.43. Found: C, 63.37; H, 5.67; N, 6.34.

RESULTS

Preparation of Copper(I) Arene Complexes (1-3, tol) Containing {CuL₂} Fragments (1–3). Copper(I) complexes supported by β -diketiminate ligands have found widespread applications as reagents for small-molecule activation (O₂ and N₂) and catalysts for alkane functionalization under oxidative conditions (azide, dialkylperoxide, and diazoalkanes).^{7,35–39} As part of these studies, a number of groups have prepared and studied fluorinated derivatives of the β -diketiminate ligands.⁴⁰⁻⁴⁴ For example, in 2003 Sadighi and co-workers reported the isolation of a series of complexes with CF₃ groups on the backbone of the β -diketiminate ligand and/or in the meta positions of the aromatic flanking groups.⁴¹ Below, we extend the series of known ligands to new members and investigate the effect of the inclusion of fluorinated electronwithdrawing groups on stabilization of the corresponding σ complexes of copper(I).

Condensation of mesitylamine with 1,1,1,5,5,5-hexafluoroacetylacetone in the presence of TiCl₄ afforded a mixture of the symmetric β -diketiminate L¹H and the asymmetric monocondensation L¹H product, which could be separated by column chromatography. The decafluorinated and tetrachlorinated ligand precursors, L^2H and L^3H , respectively, were prepared by condensation reactions, as described in the literature.^{45,46} The reaction of each of the β -diketiminate ligand precursors with 1.2–1.4 equiv of [CuMes]_n (n = 4, 5) in a toluene solution generated a series of η^2 -coordinated toluene copper(I) adducts in 56–71% isolated yield (Scheme 1).

Scheme 1. Preparation of Copper(I) Arene Complexes



Two well-known coordination modes are observed in the solid-state structures of these complexes: $[1_2 \cdot tol]$ formed an inverse sandwich complex, while $[2 \cdot tol]$ is monomeric (Figure 2). A dimeric structure is also found for $[3_2 \cdot tol]$ reported by Warren and co-workers⁴⁷ and an analogue in which the chlorine atoms are replaced by methyl groups.⁴⁸ Similarly, the analogue of $[1_2 \cdot tol]$ with methyl groups in place of trifluoromethyl groups on the β -diketiminate backbone is dinunclear in the solid state.⁴⁹ In contrast, precedent for the monomeric structure of $[2 \cdot tol]$ can be found in heavily fluorinated copper(I) complexes reported by Sadighi and co-workers.⁴¹

Complex [2-tol] crystallizes with the copper(I) center disordered over two sites. The coordinated toluene molecule remains planar and lies perpendicular to the copper(I) center. C-C bond lengths of the η^2 ligand increase from the mononuclear ($[2 \cdot tol]$, 1.384(6) Å) to the inverse sandwich complex ([1, tol], 1.400(3) and 1.430(3) Å). A comparison to the average bond length in toluene (1.39 Å) suggests little π back-bonding from the copper to the arene, with the cumulative effect of two transition-metal centers required to begin to see any lengthening of the C-C distances. Consideration of these new structures in the context of known mononuclear and dinuclear (inverse sandwich) species^{41,47-49} reveals no clear trend correlating the sterics or electronics of the ligand and the observed level of solvation. The nuclearity is a likely a reflection of the precise crystallization conditions for each sample. On the basis of CHN analysis of [2·tol] and the careful and repeated preparation of the complexes described herein, it appears that desolvation occurs upon extended drying of these samples in the solid state. In all cases, the inverse sandwich complexes form, with the two copper centers bound to adjacent positions of the aromatic system.

We have previously shown that in a toluene or benzene solution the monomeric species [3·tol], not dinuclear [3₂·tol], is present, as evidenced by a comparison of the diffusion coefficient (0.989 × 10⁻⁹ m² s⁻¹) measured by DOSY NMR studies against that for the control sample [3·cyclohexene] (0.967 × 10⁻⁹ m² s⁻¹). The data correspond with solution hydrodynamic radii of 4.1-4.2 Å. In a benzene solution, DOSY experiments on [1₂·tol] and [2·tol] return similar hydrodynamic radii (4.4-4.5 Å) and leave little doubt that in arene solvents monomers persist. It is worth noting that Warren and co-workers have previously suggested that



Figure 2. Crystal structures (a) [1, tol] and (b) $[2 \cdot tol]$ and (c) selected bond angles (deg) and bond lengths (Å).



Figure 3. Carbonyl stretching frequencies of selected copper(I) β -diketiminate complexes.

 $[{(MesNCMe)_2CH}Cu]_2$ ·tol forms both monomeric and dimeric species in a benzene solution.⁴⁹

To gain insight into the electron density at copper(I) within the series, the carbonyl complexes were formed by reactions of $[1_2$ ·tol], [2·tol], and $[3_2$ ·tol] with CO. The results of these experiments are presented in Figure 3, alongside relevant literature.⁴¹ As previously concluded,⁴¹ increased levels of fluorination lead to higher frequency carbonyl stretches, signifying increasingly electron-deficient metal centers.

Reversible Coordination of B–H Bonds to Copper(I). Four-coordinate boranes reversibly bind to 3 in a toluene or benzene solution. Isolation of these species has allowed characterization of the binding event as an η^2 , η^2 -coordination mode and the reaction products as bis- σ complexes containing a four-center four-electron interaction.^{50–53} In a toluene solution, [1·tol] and [2·tol] react reversibly with H₃B·L to generate the corresponding bis- σ complexes (Scheme 2). We have previously demonstrated that [3·tol] reacts with H₃B·L (L

Scheme 2. Reversible Reactions of [1·tol], [2·tol], and [3·tol] with H_3B ·L (L = 2-Methylpyridine)



= NEt₃, 2-methylpyridine, and NHEt₂), leading to the formation of a copper(0) mirror and amine-borane dehydrocoupling in the case of the substrate bearing both acidic and hydridic positions.³⁴ In no case has any data been collected to support a single η^2 -binding mode analogous to those found in zinc, magnesium, and aluminum complexes of these ligands. Initial attempts to isolate HBpin or HBcat complexes of these copper(I) fragments have proven unsuccessful.

Single crystals of $[1 \cdot B]$ and $[2 \cdot B]$ could be grown from toluene/*n*-heptane mixtures at -35 °C, affording data of quality that allowed the hydride positions to be determined from a difference electron density map. Both structures show Cu-H and B-H(Cu) distances within experimental error (Figure 4). While the terminal B–H distances are slightly shorter than the bridging hydrides, IR data collected in the solid state do not suggest that any significant "B-H bond activation" occurs within these complexes. This latter statement is supported by DFT calculations (vide infra, Figure 13). The B-H stretching frequencies are consistent across the series and similar to those of the free borane occurring as broad overlapping peaks in the region 2400-2500 cm⁻¹. The Cu---B distances are consistent across the series of complexes (Figure 4c). One noticeable difference between the structures of $[1 \cdot B]$ and $[2 \cdot B]$ is found in the π - π -stacking interaction of the 2-methylpyridine group and an aryl group of the β -diketiminate ligand. Despite the two aromatic rings being a similar distance apart in both complexes ($[1 \cdot B]$, 4.2 Å; $[2 \cdot B]$ 4.1 Å), the angle between the planes created by each aromatic ring differs ([1·B], 40°; [2·B], 15°).



Figure 4. Crystal structures of (a) [1·B] and (b) [2·B] and (c) selected bond lengths (Å) for these complexes and [3·B].

Previously reported $[3\cdot B]$ also shows only a small torsion angle between the two planes of 14° .³⁴ In combination, the data suggest that a π - π -stacking interaction between the electronrich 2-methylpyridine and electron-poor 2,6-pentafluorophenyl moieties is present.

Upon dissolution of crystalline samples of $[1 \cdot B]$, $[2 \cdot B]$, or $[\mathbf{3}\cdot\mathbf{B}]$ in a toluene- d_8 or C_6D_6 solution, the equilibrium between copper(I) σ -borane and copper(I) arene complexes represented in Scheme 2 is established. Fast exchange is observed at 298 K; both ¹¹B{¹H} chemical shifts (δ : [**1**·**B**], -18.0 ppm; [**2**·**B**], -19.7 ppm; [3·B], -15.5 ppm) and the ¹H NMR chemical shift of the broad quartet assigned to the hydride resonances (δ: [1·B], 2.98 ppm; [2·B], 3.07 ppm; [3·B], 3.27 ppm) are time-averaged contributions of the two sides of the equilibrium. While variable-temperature NMR data across the 193-298 K temperature range on samples of $[3\cdot B]$ in toluene- d_8 revealed that the slow-exchange regime could be reached at 193 K, van't Hoff analysis could not be performed on these samples because of the limited number of data points in which all components of the equilibrium mixture could be accurately quantified. Samples of [2·B] remained in the fast-exchange regime down to 193 K. In contrast, data recorded on the analogue $[3 \cdot B']$ (B' = H₃B·NEt₃) allowed quantification of the equilibrium represented in Scheme 2: $\Delta H^{\circ} = -1.40(4)$ kcal mol⁻¹, $\Delta S^{\circ} =$ -5.9(2) cal K⁻¹ mol⁻¹, and $\Delta G^{\circ} = +0.17(3)$ kcal mol⁻¹. In all cases, even at the lowest temperature, rapid exchange was found to occur between the bridging and terminal hydride ligands.

Taken in combination, the thermodynamic and characterization data are consistent with a very weak binding of the borane to the copper(I) center. In line with this hypothesis, solutions of $[1\cdot B]$ and $[2\cdot B]$ react readily with CO under 1 atm at room temperature, affording the copper(I) carbonyl complexes $[1\cdot CO]$ and $[2\cdot CO]$, respectively, and $H_3B\cdot L$.

Reversible Coordination of Al–H Bonds to Cu(l). Two distinct coordination modes are observed in the formation of σ complexes of copper(I) with alanes.³³ These appear to be dependent on the nature of the aluminum center. While the copper(I) center sits within the wedge formed by the AlH₂ group in the four-coordinate aluminum center within [3·Al], it sits outside this wedge for its five-coordinate analogue [3·Al'] (Figure 5). The Cu--Al separations are significantly different in these two complexes, taking values of 2.6143(7) and 3.1231(5) Å for [3·Al] and [3·Al'], respectively. Despite the potential for the AlH₂ unit to bind to copper by the η^2 ; η^2 -coordination mode observed for the borane analogue, this has yet to be experimentally observed, and both crystallographically characterized adducts show a single η^2 -coordination. For [3·Al], the



coordinated Al–H bond sits clearly in the plane of the {CuL₂} fragment, in direct contrast to the aforementioned borane complexes, where both coordinated B–H bonds are orthogonal to the plane of the β -diketiminate ligand.

σ-Complex formation was found to be reversible. Crossover experiments show that [3·AI] reacts with Al' to form [3·AI'] and Al and vice versa. van't Hoff analysis on a sample of [3·AI'] in toluene- d_8 allowed quantification of the thermodynamics of alane binding with $\Delta H^\circ = -1.75(9)$ kcal mol⁻¹ and $\Delta S^\circ =$ -5.0(2) cal K⁻¹ mol⁻¹. Further experiments demonstrated that the position of the equilibrium was dependent on the solvent, and for the reaction of [3·AI'] + arene to form [3·arene] + Al', it takes relative values of 12.2, 1.6, and 1.0 for 1,2difluorobenzene, toluene, and benzene, respectively.

Reversible Coordination of Zn–H Bonds to Copper(I). The monomeric three-coordinate zinc hydride complex BDIZnH reversibly binds to the copper(I) fragments described herein. While data are again consistent with fast and reversible coordination in solution, crystalline samples of [1·Zn], [2·Zn], and [3·Zn] could be isolated from hydrocarbon solutions (Scheme 3). The structure of [3·Zn] was reported previously and showed a remarkable short Cu---Zn distance (vide infra).³³

Single crystals of $[1\cdot Zn]$ or $[2\cdot Zn]$ could be grown from toluene/*n*-heptane mixtures at -35 °C, affording data of high enough quality to locate the positions of the hydrides from a

Scheme 3. Reversible Reaction of [1·tol], [2·tol], and [3·tol] with BDIZnH





Figure 6. Crystal structures of (a) [1·Zn] and (b) [2·Zn] and (c) selected bond lengths (Å) for these complexes and [3·Zn].

difference electron density map. The data are presented in Figure 6 and compared against the known structure of [3·Zn]. A notable difference between the structures of [1·Zn], [2·Zn], and [3·Zn] lies within the Cu---Zn distances: these range between 2.4684(5) and 2.6884(4) Å. We have previously used the formal shortness ratio (fsr) to gain insight into the electronic structures of three-center two-electron TM-H-Zn bonds.⁵⁴ The fsr normalizes the metal---metal bond length with respect to the sum of the single-bond radii.⁵⁵ In the current case, fsr values are consistent with the formulation as weakly bound σ complexes ([1·Zn], fsr = 1.06; [2·Zn], fsr = 1.11; [2•Zn], fsr = 1.02).

The coordination geometry at copper shows considerable flexibility across the series. While the N-Cu-Zn bond angles found within $[1\cdot Zn]$ and $[2\cdot Zn]$ suggest a distorted trigonalplanar coordination site for the copper in [3·Zn], data are reminiscent of a minimal perturbation toward T-shaped geometry (with respect to the heavy atoms). Because the N-Cu-N bite angle of the {CuL₂} fragment remains nearly constant throughout the series (97-99°), the changes in the geometry are most easily quantified by considering the difference in the two N-Cu-Zn angles for each complex ([1·Zn], $\Delta = 6.5^{\circ}$; [2·Zn], $\Delta = 0^{\circ}$; [2·Zn], $\Delta = 17^{\circ}$), with the larger Δ values representing a distortion from trigonal planar toward T-shaped (ideal geometry $\Delta = 90^{\circ}$). Notably the distortion toward T-shaped increases with decreasing TM---Zn separation (i.e., fsr) and requires a torsional rotation of the β diketiminate ligands out of plane with one another in order to accommodate the approach of the two metals (Figure 7). The solid-state structures tolerate approximately $\pm 5\%$ variance in the Cu---Zn distance, and as the Zn-H ligand gains a closer approach to copper, the geometry at copper bends from trigonal planar to T-shaped.



Figure 7. Graphical representation of the coordination geometries at copper in $[1-3\cdot Zn]$. Torsion = smallest N-Cu-Zn-N dihedral angle.

The Cu–H and Zn–H distances are all within error and in the ranges 1.47(4)–1.53(3) and 1.51(3)–1.63(3) Å, respectively. For comparison the Zn–H distance in BDIZnH takes a value of 1.46(2) Å similar to those found in $[1-3\cdot Zn]$.⁵⁶ It should be noted that the hydride atom in $[2\cdot Zn]$ is disordered over two sites related by a C_2 rotation and has been modeled to have 50% occupancy in both positions. The Cu–H distances are notably shorter than those found in the corresponding σ borane complexes (vide supra). We have previously shown that very short TM---M separations are required to expose a significant elongation of the Zn–H bond.⁵⁴

Dissolving crystals of $[1\cdot \mathbf{Zn}]$ in toluene- d_8 reestablishes an equilibrium between $[1 \cdot tol] + BDIZnH$ and $[1 \cdot Zn] + toluene$. Fast exchange between all species is observed at 298 K, with the ¹H NMR chemical shift of the broad singlet at δ = 3.88 ppm assigned to the time-averaged resonance of coordinated and uncoordinated hydrides. Upon cooling a sample of $[1\cdot \mathbf{Zn}]$ in toluene- d_8 to 233 K, decoalescence occurs, and both sides of the equilibrium resolve (see the Supporting Information). At 193 K, a sharp singlet at $\delta = -0.44$ ppm is seen, corresponding to the σ -hydride of [1·Zn]. Similarly, upon generation of [2· Zn] in situ, fast exchange of the equilibrium components is observed at 298 K, with the ¹H NMR chemical shift of the broad singlet at $\delta = -0.22$ ppm assigned to a time-averaged σ hydride resonance. Upon cooling, the equilibrium mixture still remains in fast exchange; however, the hydride resonance sharpens and shifts increasingly upfield as the temperature is lowered, ultimately observed as a sharp singlet at $\delta = -0.64$ ppm at 193 K. We previously reported that [3·Zn] demonstrated a hydride resonance at $\delta = -0.55$ ppm in toluene-d₈ at 193 K.

van't Hoff analysis on $[\mathbf{1}\cdot\mathbf{Zn}]$ in toluene- d_8 allowed quantification of the thermodynamics of the equilibrium. These data are compared against those obtained for samples of $[\mathbf{3}\cdot\mathbf{Zn}]$ and $[\mathbf{3}\cdot\mathbf{B}']$ in the same solvent across similar temperature ranges in Table 1. Table 1 also depicts the characteristic hydride NMR resonances, stability measurements (half-lives), and qualitative data for the rate of exchange of the σ complex and toluene adduct for the entire series of copper(I) complexes isolated to date, data that are discussed further below. A crossover experiment was performed in order to confirm the reversibility of the reaction. Upon the addition of 1 equiv of BDIMgH to a 37 mM sample of $[\mathbf{1}\cdot\mathbf{Zn}]$ in toluene- d_8 , the formation of $[\mathbf{1}\cdot\mathbf{Mg}]$ was observed (vide infra).

Table 1. Selected ¹H NMR, Thermodynamic, and Stability Data on Copper(I) σ Complexes

	σ -hydride				
complex	$\delta/{ m ppm}$	fwhm/Hz	exchange kinetics ^a	van't Hoff analysis"	$t_{1/2}^{\ \ b}$
[1·B]	2.98 (298 K)	С			>1 years
[2·B]	3.07 (298 K)	с	fast exchange above 193 K		>140 days
[3·B]	3.27 (298 K)	с	slow exchange below 213 K		
[3·B ′]	2.25 (298 K)	с	slow exchange below 243 K	$\Delta H^{\circ} = -1.40(4), \ \Delta S^{\circ} = -5.9(2), \ \Delta G^{\circ}_{298 \text{ K}} = +0.17(3)$	
[3·Al]	d	d	fast exchange above 193 K		
[3·Al′]	-0.12 (193 K)	47	slow exchange below 353 K	$\Delta H^{\circ} = -1.75(9), \ \Delta S^{\circ} = -5.0(2), \ \Delta G^{\circ}_{298 \text{ K}} = -0.23(4)$	
[1·Zn]	-0.40 (195 K)	8	slow exchange below 233 K	$\Delta H^{\circ} = -4.92(11), \ \Delta S^{\circ} = -27.6(6), \ \Delta G^{\circ}_{298 \text{ K}} = +3.31(5)$	60 days
[2·Zn]	-0.64 (193 K)	8	fast exchange above 193 K		24 days
[3·Zn]	-0.55 (193 K)	8	slow exchange below 243 K	$\Delta H^{\circ} = -2.47(9), \ \Delta S^{\circ} = -10.8(4), \ \Delta G^{\circ}_{298 \text{ K}} = +0.65(8)$	
[1·Mg]	-1.77 (298 K)	4	fast exchange above 193 K		3.5 h
[1•Ca]	-0.36 (298 K)	10	fast exchange at 298 K		10.5 h

^{*a*}Data were measured in toluene- d_8 or C₆D₆ solvent at 37 mM, ΔH° and ΔG° given as kcal mol⁻¹ and ΔS° given as cal K⁻¹ mol⁻¹, and errors measured using least-squares regression. ^{*b*} $t_{1/2}$ values were recorded at ambient temperature against a ferrocene internal standard, and those for **1**·**Zn** and **2**·**Zn** can be fitted to first-order kinetics. ^{*c*}Because of coupling to both ¹⁰B and ¹¹B nuclei, the fwhm has not been recorded. ^{*d*}Hydride resonance was not observed across the 193–298 K range.





Reversible Coordination of Mg–H and Ca–H Bonds to Copper(I) (Decomposition Pathways). Although dimeric molecular magnesium and calcium hydrides react with copper(I) arene complexes, the products of these reactions are unstable (Scheme 5). They readily decompose at room



temperature within a few hours in a hydrocarbon solution. Despite the apparent capricious nature of Cu–H–Mg and Cu– H–Ca three-center two-electron bonds stabilized by β diketiminate ligand frameworks, a single complex has been isolated and crystallographically characterized (Figure 8a). Additional complexes have been generated in situ and characterized by multinuclear NMR spectroscopy (Scheme 4).

 $[1\cdot Mg]$ could be prepared and isolated as a crystalline solid provided reactions were conducted with stirring at -35 °C in the freezer of a glovebox, followed by low-temperature workup and direct crystallization at this temperature. While $[1\cdot Mg]$ can be generated at higher temperature, these preparations lead to small amounts of decomposition that hampered purification of the product. Single crystals of $[1\cdot Mg]$ could be grown from toluene/*n*-heptane mixtures at -35 °C, and the quality of the data was such that the hydride position could not be located



Figure 8. (a) Crystal structure of $[1 \cdot Mg]$. Selected bond angles (deg) and bond lengths (Å): Mg-Cu 2.905(2), Mg-N 2.008(4), Cu-N 1.975(4); N-Mg-N 96.8(2), N-Cu-N 98.4(2), N-Mg-Cu 131.61(12). (b) Crystal structure of $[L^2MgBDI]$.

(Figure 8a). The Cu---Mg separation is 2.905(2) Å. The metal---metal distance is slightly longer than the equatorial Cu-Mg bonds [2.754(4) Å] found within a $[Cu_4MgPh_6]$ cluster but significantly shorter than nonbonding Cu---Mg axial interactions with the same species [3.828 (4) Å].⁵⁷ The Mg–N lengths and N–Mg–N angles found within $[1\cdotMg]$ are within





Figure 9. (a) Qualitative MO diagram for a $C_{2\nu}$ {CuL₂} fragment with a π -donor ligand. (b) Selected calculated MOs for copper(I) fragment 3. (c) Energies (in eV) of the 4a₁ and 2b₁ orbitals for each copper(I) fragment.



Figure 10. (a) Qualitative MO diagram for a combination of the $C_{2\nu}$ {CuL₂} fragment with a σ -(H–H) bond. (b) Selected calculated MOs for theoretical [3·H₂].

the range of those found within the parent hydride $[BDIMgH]_2$ [Mg-N, 2.008(4)-2.071(4) Å; N-Mg-N, 96.8(2)-96.5(2)°].

The analogous synthesis of σ complexes of calcium via reaction of the copper(I) complexes with $[BDICa(\mu-H)\cdot THF]_2$ was attempted but did not lead to isolable products. These complexes were extremely unstable in solution. The most stable complex in this series, $[1\cdotCa]$, has $t_{1/2} = 10.5$ h at room temperature in C₆D₆. Experimental evidence for the proposed formation of $[1\cdotCa]$ comes from a loss of the diagnostic calcium hydride resonance at $\delta = 4.45$ ppm (C₆D₆, 298 K) in $[BDICa(\mu-H)\cdot THF]_2$ and the formation of new species in which the σ -hydride resonates as a broad singlet at $\delta = -0.30$ ppm (toluene- d_8 , 298 K).⁵⁸ Decomposition reactions of the complexes possessing Cu– H–Mg and Cu–H–Ca moieties occur with the formation of a copper(0) mirror on the wall of any vessel storing solutions of these species and often small amounts of H₂, as observed by ¹H NMR. The reaction of [2·tol] with 0.5 equiv of [BDIMg(μ -H)]₂ allows a conclusion on at least one possible decomposition pathway. In this case, while the formation of [2·Mg] was not observed, the tetrahedral magnesium complex bearing two β -diketiminate ligands [L²MgBDI] was generated cleanly. The composition of the latter complex was confirmed by an independent synthesis. It most likely arises from a ligandexchange reaction between copper and magnesium generating "Cu–H" and [L²MgBDI] in situ; the former readily decomposes to H₂ and copper(0). Further experimental support for this hypothesis has been gathered during reactions of phosphine-ligated copper(I) complexes with $[BDIMg(\mu-H)]_2$, which proceed to give not only the expected ligand-exchange products but Stryker's reagent $[HCu(PPh_3)]_6$.⁵⁹

DISCUSSION: THEORY AND EXPERIMENT

 σ complexes of the late transition metals are often discussed in the context of the Dewar-Chatt-Duncanson model. Donation from the E-H bond to a vacant d orbital is accompanied by back-donation from a filled d orbital to the E-H σ^* orbital. The electron configurations of the copper(I) fragments, however, preclude the involvement of vacant d orbitals. The qualitative molecular orbital (MO) diagram for a $C_{2\nu}$ -symmetric d^{10} ML₂ complex containing a π -donating ligand matches well with DFT calculations performed on naked two-coordinate copper complexes 1-3 (Figure 9a).⁶⁰ A number of groups have considered Walsh diagrams for linear-to-bent deformation of d¹⁰ ML₂ complexes.^{61,62} For gold(I) complexes, the bending has been proposed to be an important stereoelectronic requirement for efficient back-donation upon binding of small molecules and can ultimately lead to oxidative addition reactions.⁶³ σ -Borane complexes of a bent d¹⁰ {NiL₂} complex have also been reported.⁶⁴

Considering a dihydrogen complex as a prototypical representation for E–H or M–H bonding, for 3 the LUMO is 4s-based and suitable for overlap with the σ -(H–H) orbital, while the HOMO–1, consisting of an out-of-phase combination of the d_{yz} orbital and antisymmetric ligand SALC (symmetry-adapted linear combination), is suitable for backdonation into the σ^* -(H–H) orbital. Filled and empty b₂-symmetric orbitals remain essentially nonbonding with respect to the H₂ fragment (Figure 10).

Quantification of the donor-acceptor interactions by calculations using the ω B97X-D functional and a hybrid 6,31-G/SDD basis set was achieved using second-order perturbation theory. In all cases, the donor-acceptor contribution from the σ -(M-H) \rightarrow Cu 4s orbital is far more significant than that from Cu(3d) $\rightarrow \sigma^*$ -(M-H) (Figure 11a). In comparison within a series for Zn-H, it appears that, as the filled 2b₁ orbital of {CuL₂} is destabilized, the back-bonding contribution becomes slightly more significant. It is noteworthy that this theoretical argument is supported by the experimental data in which the Cu--Zn distance decreases across the series 3 < 1 <

(a)_					(b) AI	
(u)	{CuL ₂ }	M–H	σ(M–H) donation <i>(kcai</i>	o⁺(M–H) back-donation f <i>mot¹)</i>	(b) AI 1.59 H AI $\frac{2.60}{105^{\circ}}$ Cu =	$\xrightarrow{H} 1.59$ 1.66Al $H / 133^{\circ}$
	3	B–H	47	3	1.72 H 1.56	1.60 2.99
	2	B–H	49	2	$\Delta \mathbf{G}^{\circ} = 0$	Cu ∆ G°= 3.7 kcal mol -1
	1	B–H	49	2	$\Delta \mathbf{H}^{o} = 0$	∆H°= 5.4 kcal mol ⁻¹
	3	AI–H	85	17	(c) ΔΙ	
	3	Al'–H	54	5	H 1.61	H 1.61
	3	Zn–H	144	22	1.68 H 164°	H 171° 1.61 H 3.28
	2	Zn–H	124	19		Cu
	1	Zn–H	142	19	∆ G °=0	∆G°= 2.4 kcal mol ⁻¹
	1	Mg–H	136	10	$\Delta H^{o} = 0$	$\Delta H^{\circ} = 2.2 \text{ kcal mol}^{-1}$

Figure 11. (a) Calculated donor–acceptor contributions from secondorder perturbation theory. (b) Relative energies of isomers of [3·Al] and [3·Al'].

2 as the coordination geometry at copper deviates from trigonal toward T-shaped (Figure 7). Considering the hydride atom as a discrete ligand, the latter geometry could be described as square-planar and the increased back-donation an indication of a tiny perturbation toward a d^8 copper(III) species. The geometries of β -diketiminate copper(I) complexes of ethylene have been rationalized using similar MO arguments, and the ligands are believed to be coplanar because of back-donation from copper(I) into the π^* orbital of the alkene.⁶⁵ Similarly, the orthogonal relationship between the substituents of the carbene and the β -diketiminate plane in [L₂Cu=CR₂] complexes originates from the overlap of the filled d orbital with an empty p orbital of the CR_2 moiety.^{49,66} More in-depth analysis combining X-ray absorption spectroscopy and theoretical methods that model multiconfigurational ground states suggests that back-donation in β -diketiminate copper(I) complexes of nitrosobenzene, diazine, and dioxygen can be considered in terms of the weighting of the $[Cu^+(\eta^2-L_2)]$, $[Cu^{2+}(\eta^2-L_2^{-1})]$, and $[Cu^{3+}(\eta^2-L_2^{-2})]$ configurations. A bias to increasing the copper(II) contribution to the ground state occurs as the ligand atoms become more electronegative and can be considered as an alternative description of increased back-donation.67

For $[3 \cdot AI']$, the copper(I) fragment sits outside the wedge made by the AlH₂ group and disrupts the orbital overlap required for back-donation (Figure 11c). A comparison of the coordination modes in $[3 \cdot AI']$ and $[3 \cdot AI]$ by computational methods provides some insight into the small stabilization afforded by back-bonding. The Gibbs free energies of each binding mode were explored using gas-phase calculations using the initial geometries about the Cu–H–Al group from the solid-state data but varying the ligands on aluminum. For $[3 \cdot$ AI], the isomer geometry in which the {CuL₂} fragment sits inside the H₂Al wedge is 3.7 kcal mol⁻¹ more stable than the geometry in which it sits outside the wedge (Figure 11b). The additional stabilization afforded by back-bonding is also manifest in the second-order perturbation theory data for $[3 \cdot$ AI'] and $[3 \cdot AI]$.

Attempts to calculate both geometries for [3·Al'] repeatedly returned two minima of similar stability, in both of which the $\{CuL_2\}$ fragment sits outside the AlH₂ wedge (Figure 11c). Consideration of the aluminum fragments reveals that the first empty orbital of appropriate symmetry for accepting electron density comprised of a contribution from σ^* -(Al-H) is destabilized (LUMO+6 = +0.149 eV for Al; LUMO+4 = +0.161 eV for Al') upon an increase in the coordination number. This orbital destabilization provides an explanation for the observed change in geometry. As the coordination number increases from that found in [3·Al] to that in [3·Al'], the electronic structure of the alane becomes unsuitable for backdonation. Similar conclusions have been made during the comparison of the coordination chemistry of three- and fourcoordinate boranes.^{68–70} Attempts to find minima in which the AlH₂ unit engages in the bis-coordination mode, including optimization of the solid-state structure of $[3 \cdot B']$, in which the boron atom was replaced by aluminum, failed and slipped to the experimentally observed η^2 -coordination.

MO analysis of the η^2 ; η^2 -coordination mode found in σ borane complexes of the {CuL₂} fragment provides an explanation for the experimental tetrahedral geometry. In order to preserve the symmetry, BH₄⁻ was used as an approximation of the σ -borane ligand.⁷¹ Simplified qualitative analysis combines filled a₁-, b₁-, and b₂-symmetric orbitals of the



Figure 12. (a) Qualitative MO diagram for the combination of the $C_{2\nu}$ {CuL₂} fragment with a BH₄⁻ unit d/p mixing not drawn. (b) Selected calculated MOs for theoretical [3·BH₄]⁻. (c) Energy as a function of the dihedral angle.

 BH_4^- SALCs with the frontier orbital {CuL₂} fragment (Figure 12). Because no significant back-bonding occurs in this system, the approximation that unoccupied ligand orbitals are not important for constructing an MO diagram is likely to be valid. The totally a1-symmetric ligand SALC remains essentially nonbonding. The preference for tetrahedral geometry can be rationalized by considering the b₁- and b₂-symmetric orbitals of the newly formed MOs. While d/p mixing can occur in both the b_2 - and b_1 -symmetric orbitals, the former are stabilized to a greater extent than the latter because of the relatively low energy of the $4p_{\nu}$ orbital (+0.127 eV in 3) with respect to the $4p_x$ orbital (+0.184 eV in 3). In the resulting MO diagram and in quantitative calculations on theoretical $[3 \cdot BH_4]^-$, the b₂symmetric MOs (HOMO-1 and HOMO-12) are stabilized relative to the b_1 -symmetric MOs (HOMO and HOMO-6). Hence, there is a preference for the coordinated BH₂ unit to sit orthogonal to the $\{CuL_2\}$ plane. The twist from tetrahedral to planar was investigated by single-point calculations in which the N-Cu-H-B torsion angle was varied incrementally from +90° to 0° . These calculations reveal that the planar geometry is 4.7 kcal mol⁻¹ higher in energy than the observed tetrahedral ground state and is actually a maximum on the potential energy surface (Figure 12c).

The changes as a function of the ligand were evaluated by inspection of the Wiberg bond indices (WBIs) from natural bond orbital (NBO) calculations with the DFT method and quantum theory of atoms in molecules (QTAIM) calculations; the former data exclude the important ionic component of the bonding, which will be discussed further below (vide infra). Comparisons of the WBIs for the series $[1-3\cdot B]$ and $[1-3\cdot Zn]$ are presented in Figure 13. The electronic structures of these complexes were found to be highly insensitive to the nature of the ligand, despite the apparent variation in the Cu---Zn distance in the solid-state structures of the latter series. QTAIM calculations on the zinc series lead to a similar conclusion and



show the expected bond critical paths between Zn–H and H– Cu with only subtle differences between the densities at the bond critical points. The NBO data, however, clearly outline the increased back-donation to the planar Cu–H–Zn fragment compared to the tetrahedral Cu–H₂–B one, even with the reduced covalent contribution to the bonding expected for the more electropositive zinc atom.

As the ionicity of the donating bond is increased from B–H to M–H (M = Al, Mg, Zn, Ca), the electrostatic contribution to the bonding becomes increasingly important. This ionic contribution undoubtedly leads to an increase in the enthalpy of binding relative to the coordination of silanes and boranes and is likely the reason for the increased stability and ease of isolation of heavy σ complexes of copper(I) (M = Al, Zn, Mg) over their lighter counterparts (E = Si, H, C). Only by increasing the number of binding events (E = B) or reducing the entropy of the system (E = C) through the use of chelating ligands have σ or agostic complexes of copper(I) been isolated. The ionic contribution to the bonding can be inferred from the natural population analysis (NPA) charge on the bridging hydride ligand, which is presented in Table 2.

We have previously reported that the binding energies of ligands to $\{CuL_2\}$ fragments modeled with the B3pw91

Table 2. Calculated NPA Charges on the Products $[1\cdot M]$ and Gas-phase Calculations Using the ω B97x-D Functional and Hybrid 6,31-G (C, H, N, Cl, and F) and SDD (Cu, Al, Zn, and Mg) Basis Sets

${CuL_2} M-H$	[1·M] NPA charges for H, M
Zn-H	-0.46, +1.38
Al-H	-0.26, +1.42
Al'-H	-0.45, +1.39
Mg-H	-0.57, +1.09

functional and a hybrid basis set (6,31+Gd,p/LanL2DZ) are increasingly exergonic across the series $C_6F_6 < H-B < H-Si < C_6H_6 < H-Zn < H-Al$. Data are reproduced with the methods described herein and for the heavier σ complexes suggest that magnesium hydride binding is similarly favorable to alane binding to both 1 and 3 (Table 3). A comparison of the

Table 3. Calculated Gibbs Free Energies (kcal mol⁻¹, 298.15 K) for the Reaction of M–H with 1 or 3 and Gas-Phase Calculations Using the ω B97x-D Functional and Hybrid 6,31-G (C, H, N, Cl, and F) and SDD (Cu, Al, Zn, and Mg) Basis Sets

$\{CuL_2\}$ M–H	1	3
Zn-H	-25.5	-21.2
Al-H	-29.6	-21.7
Al'-H	-30.2	-23.8
Mg-H	-29.4	-24.7

calculated Gibbs free energy of binding of Zn to 1 or 3 to form either [1·Zn] or [3·Zn] suggests that the former should be more favorable. This prediction contrasts the experimental equilibrium data on the reaction of [1·tol] and [3·tol] with BDIZnH, which take values of $\Delta G^{\circ}_{298 \text{ K}} = 3.31(5)$ kcal mol⁻¹ and $\Delta G^{\circ}_{298 \text{ K}} = +0.65(8)$, respectively. The reaction of [3·tol] with Al'-H has an experimental $\Delta G^{\circ}_{298 \text{ K}} = -0.23(4)$ kcal mol⁻¹; this finding is consistent with the DFT studies (Table 3), and the five-coordinate alane binds more tightly than the zincane to this ligand fragment. Hence, while the calculations predict some trends, despite considering long-range dispersion forces in the functional, due to the small energy differences involved, they do not yet accurately or quantitative model the thermodynamics of the binding events.

Intramolecular noncovalent interactions between the substituents on copper and either boron or M (M = Al, Zn, Mg, Ca) likely play an important role in stabilizing the weakly bound σ complexes described herein. The structure of [2·B] shows a clear π - π -stacking interaction, while those of $[1-2\cdot$ Zn] are replete with C-F---H-C and C-H---H-C interactions. This is evidenced from the close contacts in solid-state data and further emphasized because of the clear but weak bond critical paths in the QTAIM data. The noncovalent interactions in $[1-3\cdot Zn]$ may be estimated by single-point calculations using the ω b97x and ω B97x-D functionals. The latter method includes a long-range dispersion correction and may more accurately capture weak intramolecular forces than the former. Power and others have begun to consistently argue the importance of dispersion forces in stabilizing both transition-metal and main-group complexes stabilized by bulky hydrocarbon ligands.⁷² These experiments reveal that inclusion of the dispersion correction results in stabilization of the heterobimetallic complexes by 12-15 kcal mol⁻¹, and it can

be concluded that noncovalent interactions are likely to play an important part in adduct formation.

SUMMARY AND CONCLUSIONS

In summary, we have reported the preparation, characterization, and solution dynamics of a series of new σ complexes of copper(I), which contain either three-center two-electron (Cu-H-Al, Cu-H-Zn, Cu-H-Mg, or Cu-H-Al) or fourcenter four-electron (Cu-H₂B) bonds. The bonding within these complexes can be viewed within the Dewar-Chatt-Duncanson model. Formation of a bent d^{10} {CuL₂} fragment is essential to produce fragment MOs of suitable symmetry and energy to overlap with B-H or M-H (M = Al, Zn, Mg) bonds. Substrate binding is weak, and in solution, the σ complexes readily undergo ligand exchange with a toluene or benzene solvent. Consideration of simplified qualitative MO diagrams allows rationalization of the observed solid-state structures, including the diverse geometries found at copper. In all cases, the donation of electron density from the ligand to a largely 4sbased orbital of the {CuL₂} fragment greatly outweighs backdonation from a 3d_{xz}-based orbital to the ligand. Calculations suggest that dispersion forces (capturing noncovalent interactions such as $\pi - \pi$ stacking and C-F---H-C bonds) play an important part in stabilizing the new molecular species reported herein. In combination, the data suggest that modification of the σ -donating ability of the ligand and the L-Cu-L angle within bent {CuL₂} fragments, along with fine-tuning of ligand---ligand interactions, may all be important design features for the preparation of new σ complexes of copper(I).

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b00182.

Experimental procedures, synthesis of L1H, crossover experiment, variable-temperature and decomposition NMR experiments, details of the DFT studies, singlecrystal X-ray data, Z matrices, and multinuclear NMR spectra (in addition, electronic versions of the NMR spectra as as .mnova and .mnpub files along with coordinates for the optimized DFT structures are available at DOI:10.14469/hpc/2074) (PDF) X-ray crystallographic data (CIF)

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Notes

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