Odd-electron \(\sigma\)-bonds, where the electrons are delocalized between two atoms, can occur as two-center/one-electron (2c/1e) or two-center/three-electron (2c/3e) interactions. Proposed by Pauling in 1931, \(^1\) odd-electron \(\sigma\)-bonds have garnered attention because of their fundamental importance to chemical bonding and their relationship to radical species generated during oxidative stress in biological systems. \(^2\)–\(^4\) Examples of compounds exhibiting odd-electron bonding are typically homonuclear (like \(\text{H}_2^+\), \(\text{He}_2^+\), \(\text{K}_2\)) and alkali metal dimers) and transiently stable, limiting them to spectroscopic characterization. \(^1\)–\(^3\), \(^11\)–\(^13\), \(^15\)–\(^18\)

The first solid-state structure of a formally one-electron \(\sigma\)-bond was a tetraphosphabenzenyl species (Fig. 1a) which was formed by the coupling of two diphosphirenyl radicals. \(^19\) Following this discovery, the formation of discrete 2c/1e \(\sigma\)-bonds, where the odd-electron is delocalized between two homonuclear main group centers, was reported for B-B and then extended to P-P. \(^8\)–\(^17\), \(^20\) Of note, the first solid-state structure of a B-B compound was reported in only 2014 (Fig. 1b). \(^21\) Examples of 2c/1e \(\sigma\)-bonds between the heavier Group 13 congeners are even more lacking because of the greater propensity for their unpaired spins to couple, forming larger more stable clusters. \(^8\) To our knowledge, there are only three structurally characterized examples of odd-electron bonds for the heavy Group 13 atoms, \(^22\) and these examples are all homonuclear \(\pi\)-radicals (Fig. 1c). \(^23\)–\(^26\)

Heteronuclear odd-electron \(\sigma\)-bonds are also rare. The Cu(TPB) complex, where TPB is a trisphosphinoborane, is the single structural example of a 2c/1e bond between heterotogens (Fig. 1d). \(^27\) The authors described the bonding as \(\text{Cu} \cdots \text{B}\), where the unpaired electron is heavily polarized toward B. A theoretical study predicted that such a bond would also exist between Cu and Al, but no heavier analogues of Cu(TPB) have been
synthesized to date.28 Furthermore, the heavier Group 13 elements by virtue of their lower electronegativity compared to B should facilitate greater covalent interactions with the Cu center.

Hence, we sought to target formally zerovalent Cu complexes supported by Al(III) or Ga(III) as an extension of the previously reported isoelectronic nickelate species and Cu(TPB).29 Herein, we describe the synthesis, structure, spectroscopic characterization, and DFT calculations of cationic [CuML]⁺ complexes (L = [N((o-C6H4)NCH2PiPr2)3]3−; M = Al and Ga) as well as their one-electron reduced metalloradical counterparts that feature discrete 2c/1e bonds.

Results and discussion

Synthesis and cyclic voltammetry

Initial synthetic attempts to produce cationic [CuML]⁺ complexes via metatation of ML with a copper halide followed by halide abstraction produced intractable mixtures. Hence, we sought an alternative Cu(i) precursor that eschews the halide and has labile ligands, such as [Cu(COD)]⁺ (COD = 1,5-cyclooctadiene and A = counteranion). This cation has received little attention as a precursor to low-coordinate copper complexes, and has labile ligands, such as [Cu(COD)2]⁺ (COD = 2,4,6-trimethylphenyl) with [(H(OEt2)]⁺ BArF⁻ (ref. 33 and 34) in the presence of excess COD (see ESI for details, Fig. S1†). Gratifyingly, [Cu(COD)]₂⁺ reacted with the metalloligands AlL or GaL in PhF to provide [Cu(COD)2]AlL or [Cu(COD)2]GaL in good yields as yellow or orange powders, respectively (Scheme 1, Fig. S3–S22†).

Cyclic voltammetry (CV) studies of both [Cu(COD)2]AlL and [Cu(COD)2]GaL suggested that {CuM}¹⁺ complexes are accessible at low potentials (Fig. S31–36†). The CV of [1]BARF₄ reveals a single reduction event at −2.03 V vs. [FeCp₂]²⁺, which corresponds to the [CuAlL]⁺⁻ redox couple. The CV of [2]BARF₄ shows two single-electron reductions at −1.79 V and −2.42 V vs. [FeCp₂]²⁺, which correspond to the [CuGaL]⁺⁻ and [CuGaL]³⁺⁻ redox couples, respectively. Of note, Cu(TBP) was described to exhibit a similar CV profile to 2⁺⁻. Unfortunately, the second redox event for [1]BARF₄ was not observed.³⁶ Scan rate studies indicate that the [CuML]⁺⁻ redox couple is reversible for both bimetallic species, while the [CuGaL]³⁺⁻ redox process observed for [2] BARF₄ is quasi-reversible (Fig. S32 and S34–S35†). For comparison, the Group 13 metalloligands and the mononuclear complex, [Cu(LH₄)]BARF₄, exhibit no reversible redox processes in a similar potential window (Fig. S23–S30 and S37†), which suggests that the Cu–M unit may be necessary for accessing the reduced Cu states. Furthermore, the formal substitution of Al with Ga shifts the [CuML]⁺⁻ redox couple by more than 200 mV. With this electrochemical insight, we sought to prepare the reduced [CuM]⁻¹ species. Chemical reduction of [1]BARF₄ or [2] BARF₄ was accomplished using KC₈ to generate CuAlL (1⁻⁻) and CuGaL (2⁻⁻), respectively. However, high-yielding syntheses of 1⁻⁻ and 2⁻⁻ were achieved by first metataling ML with CuBr to generate an in situ Cu(i) halide complex followed by addition of KC₈ in THF at −78 °C (Scheme 1). The resultant reductions produced deeply colored maroon (1⁻⁻) and dark red (2⁻⁻) solutions, from which the products were purified by removing all volatiles and then extracting into benzene.

X-ray crystallography

While [1]BARF₄ and [2]BARF₄ could be isolated, diffraction-quality crystals of these species were not readily obtained. To this end, we sought to incorporate the highly crystalline dodecachlorododecaborate anion ([B₁₂Cl₁₂]⁻²). X-ray quality crystals of [1][B₁₂Cl₁₂] and [2][B₁₂Cl₁₂] were achieved by the oxidation of 1⁻⁻ and 2⁻⁻, respectively, with Ag₂[B₁₂Cl₁₂].³⁷–³⁹ Crystals of the neutral copper species were grown from saturated Et₂O at −30 °C (1⁻⁻) or tolune/pentane vapor diffusion at room temperature (2⁻⁻). The solid-state structures of the four copper-Group 13 complexes are shown in Fig. 2, and the structural metrics are summarized in Table 1.

The structures of [1][B₁₂Cl₁₂] and [2][B₁₂Cl₁₂] reveal weak to nonexistent Cu(i)–M interactions as their Cu–M distances of 2.6239(8) and 2.5737(5) Å, respectively, are longer than the sum of the metals’ covalent radii (c.f. 2.53 and 2.54 Å, respectively).⁴⁰,⁴¹ The formal shortness ratio (r),⁴² which is defined as the ratio of the metal–metal bond length to the sum of the single-bond covalent radii⁴¹ was also calculated: 1.04 for [1][B₁₂Cl₁₂] and 1.01 for [2][B₁₂Cl₁₂]. The strength of the copper-Group 13 donor–acceptor interaction in [1][B₁₂Cl₁₂] and [2][B₁₂Cl₁₂] is much weaker compared to the corresponding isoelectronic neutral Ni(0)⁴⁴ and anionic Co(−)⁴⁵ bimetallics, which have r values < 1, because the localized cationic charge on the Cu center should render it a weaker donor. The Cu center is nearly trigonal planar with minimal perturbation due to the Group 13 ion as both Σ(δC–P–Cu) and Σ(δNeq(M–Neq)) approach 360°. For comparison, mononuclear [Cu(LH₄)]BARF₄,

Scheme 1  Synthesis of heterobimetallic copper-Group 13 complexes.
of 0.90–0.91. The greater \( r \) values for \( 1^\text{red} \) and \( 2^\text{red} \) are expected considering that their bonding involves only one electron. Another indication of a metal–metal interaction is the pyramidalization of the Group 13 center as indicated by the \( \sum (\angle N_{\text{eq}} - M - N_{\text{ap}}) \) values of 355.01(1)\(^a\) and 350.36(4)\(^a\) for \( 1^\text{red} \) and \( 2^\text{red} \), respectively, as both the M-to-(N3-plane) and M–N\text{ap} distances increase as the M center moves closer to Cu.\(^{29} \)

The local coordination environment around the Cu center also changes, with the slight lowering of the Cu center into the P3-plane and the contraction of the Cu–P bonds upon reduction to the \{Cu–M\}\(^{11} \) core. The Cu–P bond contraction is consistent with an increased Cu electron density that more strongly \( \pi \)-backbonds into the phosphine ligands. Moreover, the significant perturbation of the Group 13 centers suggests their direct participation in stabilizing the reduced \{Cu–M\}\(^{11} \) core, presumably via bonding interactions to the Cu center.

### EPR spectroscopy

To gain insight into the radical nature of the one-electron bonds, room-temperature EPR spectra were collected for solutions of \( 1^\text{red} \) and \( 2^\text{red} \) in a 1 : 1 solvent mixture of 2-MeTHF and toluene (Fig. 3). Complex \( 1^\text{red} \) gave rise to a complex signal centered at \( g \sim 2.0 \), which corresponds to a highly overlapped manifold of hyperfine lines that can be decomposed into a leading \( 1 : 1 : 1 : 1 : 1 : 1 \) sextet due to hyperfine coupling (hfc) of the electronic spin \( S = 1/2 \) with \( ^{27}\text{Al} \) nuclei (\( I = 5/2 \), 100% natural abundance) and additional splitting of each of these hyperfine transitions into two \( 1 : 1 : 1 \) quartets due to additional coupling to the isotopes \( ^{63}\text{Cu} \) and \( ^{65}\text{Cu} \) on the copper site (\( I = 3/2 \) both, with 69.2% and 30.8% natural abundance, respectively). The corresponding combined hyperfine transitions are assigned by stick spectrum shown on top of Fig. 3. The experimental spectrum was well modeled using an isotropic \( g \) value of 2.007 and three isotropic hyperfine values (\( A, \text{in MHz} \): 269.7 (\( ^{27}\text{Al} \)), 171.4 (\( ^{63}\text{Cu} \)), and 182.6 (\( ^{65}\text{Cu} \)).

Complex \( 2^\text{red} \) likewise exhibited a complex signal with an isotropic \( g \) value of 2.002, which was well modeled as a combined hyperfine splitting of \( 1 : 1 : 1 \) quartets into \( 1 : 1 : 1 : 1 : 1 : 1 \) quartets due to dominating hfc with \( ^{69/71}\text{Ga} \) (\( I = 3/2 \)) and weaker coupling with \( ^{63/65}\text{Cu} \) (also \( I = 3/2 \)). The two larger quartets arise from the distinct couplings to the two naturally abundant Ga isotopes with \( A(^{69}\text{Ga}) = 1199.3 \text{ MHz} \) (60.1%) and \( A(^{71}\text{Ga}) = 1524.3 \text{ MHz} \) (39.9%), while the smaller quartets result from the similar coupling to the two Cu isotopes: \( A(^{63}\text{Cu}) = 128.9 \text{ MHz} \) and \( A(^{65}\text{Cu}) = 137.3 \text{ MHz} \). Furthermore, superhyperfine coupling was observed at the superimposed \( m_I = -1/2 \) transition for both the \( ^{69}\text{Ga} \) and \( ^{71}\text{Ga} \) quartets (inset of Fig. 3). A reasonable fitting was obtained by including the hyperfine interaction of three equivalent \( ^{31}\text{P} \) nuclei (\( I = 1/2 \), \( A = 29.4 \text{ MHz} \)), three equivalent \( ^{14}\text{N} \) (\( I = 1, A = 20.1 \text{ MHz} \)), and one unique \( ^{14}\text{N} \) (\( A = 3.5 \text{ MHz} \)). The simulation is consistent with the ligand’s three equivalent amido donors and one apical amine donor.\(^{29} \)

The distribution of the unpaired spin density across the Cu and Group 13 valence orbitals in the \{Cu–M\}\(^{11} \) core can be evaluated by comparing the corresponding experimental \( A_{iso} \) values

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**Table 1** Structural metrics including bond lengths (Å) and angles (°) for complexes \([\text{Cu} \text{LH}_3]_2\), \([\text{Cu} \text{LH}_3]_2\) and \([\text{Cu} \text{LH}_3]_2\) and \([\text{Cu} \text{LH}_3]_2\).

| Parameter | \([\text{Cu} \text{LH}_3]_2\) | \([\text{Cu} \text{LH}_3]_2\) | \([\text{Cu} \text{LH}_3]_2\) |
|-----------|-----------------|-----------------|-----------------|
| M–Cu      | 2.6239(8)       | 2.5298(4)       | 2.5373(5)       |
| \( r^a \) | 1.04            | 1.00            | 1.01            |
| Cu–P      | 2.2925(4)\(^b\) | 2.2487(7)\(^f\) | 2.2994(3)\(^f\) |
| M–N\text{eq}\(^b\) | 1.85469(12) | 1.8915(1)\(^f\) | 1.9059(14)\(^f\) |
| M–N\text{ap}\(^b\) | 2.000(2) | 2.0836(1) | 2.069(3) |
| Cu-to-P3-plane | 0.188 | 0.118 | 0.180 |
| M-to-N1-plane | 0.07 | 0.246 | 0.142 |
| \( \Sigma (\text{P–Cu–P}) \) | 358.02(1) | 359.18(2) | 358.19(2) |
| \( \Sigma (\text{N\text{eq}–M–N\text{ap}}) \) | 359.47(1) | 355.01(1) | 358.36(2) |

\( ^a \) Ratio of the Cu–Al/Ga bond length to the sum the Cu and Al/Ga Alvarez covalent radii.\(^{29} \) \( ^b \) Trigonal space group only display one value by symmetry.\(^{29} \) Average of three unique values.

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exhibits nearly perfect trigonal symmetry in the solid state (\( \Sigma (\text{P–Cu–P}) = 359.96(2) \)) and Cu-to-P3-plane = 0.027 Å, Table S2 and Fig. S2\(^\dagger \)). The average Cu–P bond length in \([\text{Cu} \text{LH}_3]_2\) \( \text{BAr}^6 \) of 2.3001(4) Å is similar to that of \([\text{Cu} \text{LH}_3]_2\) and \([\text{Cu} \text{LH}_3]_2\), which indicates that all three complexes possess a Cu(\( \sigma \)) d\(^{10} \) center.

After reduction to \( 1^\text{red} \) and \( 2^\text{red} \), the Cu–M bond contracts significantly by 0.094 Å (\( r = 1.00 \) and 0.120 Å (\( r = 0.97 \), respectively, indicating an increase in the metal–metal bonding. Of relevance, bonding between copper and a Group 13 centers have been structurally characterized within clusters\(^{29} \) and unsupported complexes\(^{29} \) although these prior examples do not feature odd-electron bonds. In comparison to \( 1^\text{red} \) and \( 2^\text{red} \), the known Cu–Al\(^{29} \) and Cu–Ga\(^{29} \) complexes have lower \( r \) values

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**Fig. 2** Solid-state structures of \([\text{Cu} \text{LH}_3]_2\), \([\text{Cu} \text{LH}_3]_2\), \([\text{Cu} \text{LH}_3]_2\), \([\text{Cu} \text{LH}_3]_2\), and \([\text{Cu} \text{LH}_3]_2\). Thermal ellipsoids are depicted at 50% probability. Counteranions, co-crystallized solvated molecules, and hydrogen atoms are omitted for clarity.
transitions of 6528 red hyper even smaller contributions of 2.9 and 2.2% in 166 MHz. We found that the 27Al 3pz character is much greater at collected (Fig. S43 and S46). However, only in the former case were we able to model the axial signal and thus extract the 27Al hyperfine pattern at the superimposed m1 = −1/2 69Ga/71Ga-transitions of 2red. Microwave power and modulation amplitudes used for 1red and 2red are 0.7 and 21.3 mW, and 0.98 and 0.50 mT, respectively. See ESI† for additional EPR spectra and details.

with tabulated reference values (aiso) for each specific elemental orbital.34 Using the reference values for a localized valence s-based spin for Al (3911 MHz) and Ga (12,210 MHz), the 27Al 4s and the 69Ga 4s character in 1red and 2red, respectively, were found to be small at 6.9 and 9.8%, respectively.34 A similar calculation was performed for the 63Cu 4s orbital (aiso = 5995 MHz) resulting in even smaller contributions of 2.9 and 2.2% in 1red and 2red respectively. The frozen EPR spectra of 1red and 2red were also collected (Fig. S43 and S46†). However, only in the former case were we able to model the axial signal and thus extract the 27Al hyperfine tensor, A = [229.6, 229.6, 325.4] MHz. The anisotropic component of the hfc tensor, defined as b = (A1, A2, A3), (A1 − A2, A1 − A3) = [−32, −32, 64] MHz, was then compared to that of a fully localized spin in an Al 3p orbital, where b^0 = [−83, −83, 166] MHz. We found that the 27Al 3p character is much greater at 38%. Similarly, the 63Cu 4p contribution was found to be 19.9%. The total estimated spin density between Cu and Al is ca. 67%, wherein the majority of the unpaired spin likely resides in the bonding axis between the two metals.

Only a handful of formal Cu(0) complexes are known in the literature, and they exhibit a range of isotropic A(iso) values. The complexes Cu(PMe3)3 and Cu(TPB) have A(63Cu) values of 120 and 191 MHz, respectively, which compare well to those measured for 1red and 2red.57,58 For other literature complexes, the A(63Cu) values are significantly smaller (<30 MHz) because the unpaired spin is strongly delocalized over the ligand. For example, CuMe2(CAAC)2 (CAAC = cyclic [alkyl][amino]carbene) displayed a small A(63Cu) coupling of 22.2 MHz, and the DFT-calculated spin density revealed that the majority of the spin density resides in the Ccarbene–N π-bond.59 Similarly, the unpaired spin in Cu(B3P2) (B3P2 = diphosphine–diborane-thracene) was proposed to reside on the redox-active ligand core as no Cu hyperfine was discerned.36

Further comparison can be made with hfc to the Group 13 supporting ions with 27Al and 69Ga hyperfine values for 1red and 2red of 269.7 and 1199.3 MHz, respectively. Due to their highly unstable nature, examples of mononuclear Al(u) and Ga(u) radicals are sparse. Both alane and gallane radical anions display isotropic hfc with their respective Group 13 centers with values of 432.2 MHz for [AlH3]− and 1179.5 MHz for [GaH3]−.57,58 In contrast, the more bulky [Al(SiMe3Bu2)3]− and [Ga(SiMe3Bu2)3]− complexes exhibit much smaller isotropic hfc of 174.0 and 346.9 MHz, respectively.59 Larger hfc in main group radicals has been shown to be directly related to increased s-character via pyramidalization.57,58,60,61 The hyperfine values of 1red and 2red are closer to those of [MH3]− because the Group 13 ions are similarly pyramidalized57,58 and correspondingly different from [Al(SiMe3Bu2)3]−, which is more planar (Σ (α-Si–M–Si): 358.4°).62 Lastly, direct comparison to isoelectronic [NiML]2− analogues show similar hfc to 27Al (219.7 MHz) and 69Ga (1050 MHz).29

Theoretical computations
To further elucidate the electronic structure of these species, theoretical calculations were performed using Kohn–Sham density functional theory (KS-DFT). Geometry optimizations were performed on the structures without truncation using the M06-L functional63 with def2-series basis sets63 and strong agreement was found between the optimized geometries and the X-ray structures (Table S3 and S4†). Based on the in depth study by Hedegård et al.,64 the PBE0 (ref. 65 and 66) functional in conjunction with def2-TZVP and def2/J basis sets67 were used to determine the EPR parameters with spin–orbit coupling included. The DFT-calculated EPR parameters also matched well to the experimental g and isotropic A values, as well as the anisotropic A tensors, when available (Fig. 3, Tables S12 and S13†). The good agreement further supports the validity of the calculated electronic structures as models for the experimental species.

Examination of the molecular orbitals (MOs) of cationic species [Cu(LH3)]+, [1]+, and [2]+ revealed five doubly filled d-orbitals as expected for trigonal Cu(i) species. In both bimetallics, the lowest unoccupied molecular orbital (LUMO, Fig. 4)
was found to be a hybrid MO containing large contributions from the empty Cu 4p z and Group 13 ns and np z-orbitals. The neutral radical species 1 red and 2 red each contain a singly occupied molecular orbital (SOMO) that is similar to the LUMO of the cations, suggesting that one-electron reduction of the cations results in occupancy of the LUMO. The SOMO of 1 red contains major contributions from Cu (8.4%), Al (33.8%), and P (35.2%). Similarly, the SOMO for 2 red possesses contributions from Cu (12.7%), Ga (32.0%), and P (35.2%).

The contributions of the Group 13 atoms to the SOMOs have significant s-character (ca. 19% for each species), while the Cu center only possesses contributions from the 4p z. The s/p-mixing predicted to be present at both Al and Ga likely contributes to the pyramidalization of the Group 13 center. This result is consistent with the greater hfc values observed in the EPR spectra (vide supra). Notably, the P contribution nearly doubles upon reduction (from ca. 17% to 35% for both 1 red and 2 red), further indicating the importance of the ancillary ligand in supporting the more electron-rich Cu center.

The Mulliken spin density of 1 red and 2 red revealed delocalization across Cu, Al/Ga, P, and N atoms as visualized through spin-density plots (Fig. 4, Table S11†). Comparison of spin densities between the two metal pockets CuP3 : M N3 revealed equal spin delocalization between the two metal pockets, which matches well with the experimental EPR hfc values.

Conclusion

In summary, two cationic copper-Group 13 complexes were synthesized and their subsequent reduction provided access to unusual 17 e \{-Cu-M\} 11 complexes. These radical species are characterized by short Cu–M bond lengths and exhibit significant hfc to Cu, M, and P atoms, collectively consistent with the highly covalent nature of SOMOs that involve both metal centers and the ancillary ligand donor atoms. These neutral radical \{Cu–M\} 11 species possess rarely observed 2c/1e σ-bonds and are the first report of any such bond for the heavier elements Al and Ga. Along with the previously reported Cu(TPB), 1 red and 2 red complete a triad of copper-Group 13 complexes that demonstrate an increase in Cu bonding character and Cu–M covalency when traversing down the group in the order B < Al < Ga. Investigation of the metalloradical reactivity of these bimetals is ongoing.

Data availability

Additional data for synthesis, characterization, and DFT calculations are available in the ESI.† The combined XYZ coordinates of DFT-optimized geometries have been uploaded as ESI.†

Author contributions

BJG and MVV performed the experimental work supervised by CCL. TRS performed the theoretical calculations supervised by LG. MJD assisted with the EPR data collection, and EB assisted with the EPR analysis and interpretation. VGY provided X-ray support. The original draft was written by BJG with guidance from CCL, and all authors edited the manuscript.

Conflicts of interest

There are no conflicts to declare.
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