Group 13 M\textsuperscript{I} compounds often disproportionate into M\textsuperscript{0} and M\textsuperscript{III}. Here, however, we show that the reaction of the M\textsuperscript{I} salt of the weakly coordinating alkoxyaluminate \([\text{Ga}(\text{C}_6\text{H}_5\text{F})_2]\text{Al}(\text{ORF})_4]\text{C}_0\) with \(2,2^\prime\)-bipyridine (bipy) yields the paramagnetic and distorted octahedral \([\text{Ga}(\text{bipy})_3]^2+\{[\text{Al}(\text{ORF})_4]\text{C}_0\}_2\) complex salt. While the latter appears to be a Ga\textsuperscript{II} compound, both, EPR and DFT investigations assign a ligand-centred \([\text{GaIII}(\text{bipy})_3]\text{K}^2+\{[\text{Al}(\text{ORF})_4]\text{C}_0\}_2\) radical dication. Surprisingly, the application of the heavier homologue \([\text{InI}(\text{C}_6\text{H}_5\text{F})_2]\text{Al}(\text{ORF})_4]\text{C}_0\) leads to aggregation and formation of the homo-nuclear cationic triangular and rhombic \([\text{In3}(\text{bipy})_6]^3+\), \([\text{In3}(\text{bipy})_5]^3+\) and \([\text{In4}(\text{bipy})_6]^4+\) metal atom clusters. Typically, such clusters are formed under strongly reductive conditions. Analysing the unexpected redox-neutral cationic cluster formation, DFT studies suggest a stepwise formation of the clusters, possibly via their triplet state and further investigations attribute the overall driving force of the reactions to the strong In – In bonds and the high lattice enthalpies of the resultant ligand stabilized \([\text{M3}^3+\{[\text{Al}(\text{ORF})_4]\text{C}_0\}_3\] and \([\text{M4}^4+\{[\text{Al}(\text{ORF})_4]\text{C}_0\}_4\] salts.
In 1966, F. A. Cotton defined the term metal atom cluster compound as ‘those containing a finite group of metal atoms which are held together entirely, mainly, or at least to a significant extent, by bonds directly between the metal atoms even though some non-metal atoms may be associated intimately with the cluster’. Meanwhile, the term cluster has been expanded, describing various ensembles of bonded atoms (both metal and non-metal) or molecules, thus including compounds such as the boranes and carboranes, Zintl-like phases, salt-like clusters as well as metalloid clusters. Among the many routes leading to metal atom cluster compounds, the reductive and anionic syntheses prevail: such clusters are typically electron deficient and have a strong demand for additional electrons that can be provided by reductants such as alkaline metals or through electron transfer reactions like disproportionations.

Alternatively, aggregation can be achieved by applying strong donor ligands: for example, the carbene-mediated formation of the neutral P₃₂ non-metal cluster. Though the different approaches have yielded a vast number of neutral and anionic cluster compounds, the redox-neutral synthesis of cationic clusters by low-valent cation aggregation has not been reported to our knowledge. Thus, univalent group 13 metal salts such as—partly hypothetic—M⁺⁺⁺(A⁻)₃ (M = Al, Ga, In, Tl; A = Cl, [AsF₆]⁻, [Al(ORF)₄]⁺ with R = C(CF₃)₃) could in principle aggregate, yielding the electron precise [M₃⁺⁺⁺(A⁻)₃]₃⁺⁺⁺ cluster salt (Fig. 1, right).

The simple M⁺⁺⁺Cl⁻ salts however, are prone to disproportionate to elemental M⁰ and M⁳⁺(Cl⁻)₄, due to the high and favourable lattice energies of MCl₃ (Fig. 1, left). Thus, AICl₃ is only known as a gas phase molecule, and a hypothetical salt Al⁺⁺⁺Cl⁻ would disproportionate to elemental Al⁰ and AlCl₃ (solid-state reaction enthalpy ΔHₚₚ(solid) = –396 kJ mol⁻¹, cf. Born-Haber-Fajans Cycle (BHFC), Supplementary Fig. 9). For the heavier element indium on the other hand, the oxidation state +1 is more favourable due to inert pair effects and the known salt In⁺⁺⁺Cl⁻ (refs 11,12) is stable towards disproportionation by +31 kJ mol⁻¹ (BHFC, Supplementary Fig. 9). Yet, the alternative formation of the metal atom cluster [M₃⁺⁺⁺(A⁻)₃]⁺⁺⁺ is hampered by the lower lattice energies of [M₃⁺⁺⁺(A⁻)₃] compared with M⁺⁺⁺(A⁻)₃ and, most of all, the very distinct Coulomb repulsion (Fig. 1, right). Thus, a gaseous triangular [M₃⁺⁺⁺]⁺⁺⁺ cluster would Coulomb-explode, releasing +1,544 kJ mol⁻¹ Coulomb energy at a typical M–M distance of 270 pm. The cluster formation, however, becomes favoured for larger anions A⁻: that is, the difference of the estimated lattice enthalpies (ΔHₚₚ) of the In₃⁺⁺⁺(A⁻)₃ and [In₃⁺⁺⁺(A⁻)₃] salts is +697 kJ mol⁻¹ for Cl⁻ (V = 0.047 nm³), +281 kJ mol⁻¹ for [AsF₆]⁻ (V = 0.110 nm³) but only +26 kJ mol⁻¹ for [Al(ORF)₄]⁻ (V = 0.758 nm³; Supplementary Tables 10 and 11). Overall, salts with very large anions like [Al(ORF)₄]⁻ and ligands, allowing for a delocalization and thus ‘dilution’ of the positive charge on [M₃⁺⁺⁺]⁺⁺⁺, may support cationic cluster formation. Yet, the question remains: what are suitable Ga¹/In¹ sources to perform such a chemistry?

Stabilizing gallium in its low oxidation states (<III) has been an objective since the 1,930 s. (ref. 13) Subvalent gallium halides Ga[III][GaIII₅X₄] (X = Cl, Br and I)⁵¹, ‘Ga’ (refs 15,16) and metastable, donor stabilized GaCl solutions⁶ are important milestones and to this day used as starting material for further Ga chemistry; for example, arené, Cp⁻⁻⁻ complexes (Cp⁺; Cp = C₅H₅ and Cp⁺⁺⁺ = C₅M₆), (ref. 18) N-heterocyclic carbene (NHC) analogues of Ga, or metalloidal gallium clusters⁷. In addition, the neutral Ga–Cp/Cp⁺ complexes as well as the galla-NHC analogues have been applied as ligands for transition-metals.⁸ Due to the strongly coordinating halide anions, however, Ga[III][GaIII₅X₄] and ‘Ga’ are prone to com- and disproportionation reactions.⁹–¹² Donor-free GaCl and related compounds are only accessible at very low temperatures using elaborated matrix isolation techniques. Simple indium halides InX (X = Cl, Br and I)¹¹,¹² are stable at ambient conditions (vide supra). In contrast to the Ga III systems, the halide anions can be replaced for weakly coordinating anions (WCA) of different sizes including [BF₄]⁻ (ref. 23), [OTF]⁻ (TfO = SO₂CF₂)²⁴, [PF₆]⁻ (P = P, As, Sb)²⁵ and Al(ORF)₄⁻ (TfO = C(FCF₃)₂)²⁶ Various In¹–Cp complexes²² have also been used as catalysts in organic syntheses. Their group introduced a simple route to univalent gallium and indium salts of the weakly coordinating In(ORF)₄⁻ anion, by oxidizing elemental gallium and indium with Ag⁺⁺⁺[Al(ORF)₄]⁻ in fluorobenzene (C₆H₅F)²⁸,²⁹. Under inert conditions, the [M(C₆H₅F)₂]⁺⁺⁺[Al(ORF)₄]⁻ salts (M = Ga (1), In (2)) are stable, soluble in aromatic solvents (preferably fluorinated), and a potent starting material for further Ga and In chemistry: for example, phosphine²⁹, crown ether³⁰, carbene³¹ and N-heterocyclic arene³² complexes. In addition, the [Ga(arene)₁₂]⁺⁺⁺ complexes (arene = C₆H₆F, mesitylene, diphenylethane, m-terphenyl) are highly efficient isobutylen polymerization catalysts.³³,³⁴

Herein we report on the surprising reactions of [M(C₆H₅F)₂]⁺⁺⁺[Al(ORF)₄]⁻ salts mainly with 2,2’-bipyridyl (bipy), but also with the bipy-relative 1,10-phenanthroline (phen).

**Results**

### Orienting quantum-chemical calculations.

In contrast to the anionic chelating N-ligands for univalent gallium and indium, for example, guanidinates, diazabutadienes, β-diketiminetetrazol or tris(pyrazolyl)hydroborates (Tp)⁴⁰, neutral N-ligands, like pyridine derivatives, were shown to only stabilize the +1 oxidation state of indium³⁹, but not of gallium⁴¹. Applying [Ga(C₆H₅F)₂]⁺⁺⁺[Al(ORF)₄]⁻ (1), however, we were able to isolate the first gallium(I) complexes with simple N-ligands, such as pyrazine and di-tert-butylmethylpyridine. To expand the scope to neutral chelating N-ligands, we investigated the thermodynamics of potential ligand exchange reactions of the [M(C₆H₅F)₂]⁺⁺⁺ complexes (M = Ga, In) and 1 to 3 equivalents bipy. All turned out to be exothermic/exergonic by at least −146 kJ mol⁻¹ (Supplementary Table 9). Thus, it appeared interesting to test the reactions.

**Reaction of [Ga¹⁺⁺⁺(C₆H₅F)₂]⁺⁺⁺[Al(ORF)₄]⁻ with bipy.** On mixing colourless solutions of 1 and bipy (2.00 eq) in ortho-difluorobenzene (o-C₆H₅F₃), an unexpected distinct change in colour towards moss-green was observed (Supplementary Data 1–7). To promote crystallization, the reaction mixture was concentrated by slowly removing the volatiles under reduced pressure. During this process, the formation of a black precipitate was observed, while the colour of the solution remained green. Applying C₆H₅F as

![Figure 1 | Disproportionation versus cationic cluster formation of univalent group 13 metal salts M⁺⁺⁺A⁻. Generally, the disproportionation is favoured over the cluster formation due to the much higher lattice energies of the M³⁺⁺⁺(A⁻)₃ salt.](image)
yet, and more importantly, the SOMO is primarily located on the bipy ligand, corresponding to a $\text{Ga}^{III} \{ \text{bipy} \}_3^{2+}$ complex, that is, a $[\text{Ga}^{III} \{ \text{bipy} \}_3^{2+}]$ complex.

For earlier reported Ga$^{II}$ compounds have proven to be mixed-valent species$^{14}$ or diamagnetic dimers$^{44}$ Aldridge et al. recently reported on a thermally robust monomeric Ga$^{II}$ compound: $[\text{Ga}^{II} \{ \text{B} (\text{N} (\text{C}_6\text{H}_3-2,3-\text{F})_2) \}_2]^{2+}$ In this Ga$^{II}$ molecule, the metal atom is coordinated in a bent fashion by two boryl ligands and over 70% of the unpaired spin density is located on the metal. The related $[\text{Ga} \{ \text{dabab} \}_2]^{2+}$ complex$^{46}$ (dabab = 1,4-di-tert-butyl-1,4-diazabutadiene) on the other hand, is correctly described as a Ga$^{III}$ cation coordinated by one singly and one doubly reduced dabab ligand$^{19}$,$^{20}$,$^{29}$,$^{30}$ A related description could account for $32^{+}$, that is, a $[\text{Ga}^{III} \{ \text{bipy} \}_3^{2+}]$ complex, and therefore we conducted electron paramagnetic resonance (EPR) spectroscopy measurements of solutions of 3 in o-C$_6$H$_4$F$_2$ (Fig. 3). Both, the isotropic g-value ($g_{iso} = 2.0024$) being close to that of the free electron and the low anisotropy$^{47}$,$^{48}$ speak in favour of a ligand-centred spin system. This assumption is further supported by the low hyperfine coupling constant $A^{69}\text{Ga} = 21$ MHz, thus being in good agreement with studies by Kaim et al.$^{47}$ and clearly differing from the above mentioned metal-centred spin system $[\text{Ga}^{II} \{ \text{B} (\text{N} (\text{C}_6\text{H}_3-2,3-\text{iPr}) \text{CH})_2 \}_2]^{2+}$ (cf. $A^{69}\text{Ga} = 670$ MHz$^{45}$). Furthermore, we applied density functional theory (DFT) calculations to compute the singly occupied molecular orbitals (Fig. 2, inset) and the spin density of $32^{+}$ (Fig. 3, inset). We chose
the hybrid B3LYP/SV(P) method, as it yielded good agreements between calculated and experimental bond lengths of $3^{2+}$ (Fig. 2), and the main absorption maximum ($\lambda_{max}$) in measured (302 nm) and simulated (296 nm) ultraviolet-visible spectra (Supplementary Fig. 5). These bands are reminiscent of the absorption of the related $[\text{Ru}^{3+} \text{(bipy)}_2(\text{bipy}^*)]^2^2$ complex$^{31}$ (cf. $\lambda_{max} = 373$ nm). Beyond featuring a similarly distorted octahedral coordination mode as its single-crystal congeners, the singly occupied molecular orbitals of the geometry-optimized $3^{2+}$ is solely located on the bipy ligands (Fig. 2) and only 3.0% of the spin is located at the gallium cation (Fig. 3). Overall, the experimental results (X-ray powder diffraction, EPR and ultraviolet-visible) and the DFT studies are in very good agreement and clearly assign a $[\text{Ga}^{3+}[(\text{bipy})_3]^\bullet]^2^2$ complex as correct formulation of $3^{2+}$. To our knowledge, $3$ is the first reported single-crystal structure of a p-block metal complex, featuring a bipy radical anion as ligand (cf. the few examples of alkali-metal salts of bipy radicals and diamons of Goicoechea et al. as well as Wieghardt’s extensive work on transition-metal complexes of bipy$^{32,33}$).

**Reaction of $[\text{In}^1(\text{C}_6\text{H}_5\text{F})_2]^{4+}$ with $[\text{Al(OR F)}_4]^{-}$ with bipy.** Due to the redox instability of $1$, we additionally reacted the heavier, more redox-stable homologue $[\text{In}^1(\text{C}_6\text{H}_5\text{F})_2]^{4+}[\text{Al(OR F)}_4]^{-}$ (2) with bipy. While the isolation of single crystals from highly concentrated, yellowish solutions of 2 and bipy (2.00 eq or 1.63 eq) in $\text{C}_6\text{H}_5\text{F}$ was straightforward, the composition of the isolated crystals depended on the amount of bipy employed as well as the crystallization procedure. Overall, we were surprised not to isolate any of the predicted $[\text{In}^{\text{bipy}}]_3^{3+}$ complexes (cf. Supplementary Table 9), but the very first homonuclear cationic triangular or rhombic $\text{In}^1$ clusters: $[\text{In}^{\text{bipy}}]_3^{3+}[\text{Al(OR F)}_4]^{-}$ $[\text{In}^{\text{bipy}}]_3^{3+}$ $[\text{Al(OR F)}_4]^{-}$ $[\text{In}^{\text{bipy}}]_3^{3+}$ $[\text{Al(OR F)}_4]^{-}$ $[\text{In}^{\text{bipy}}]_3^{3+}$ $[\text{Al(OR F)}_4]^{-}$. As above, the direct interaction between the cationic clusters and the $[\text{Al(OR F)}_4]^{-}$ anions is negligible and the latter are therefore not shown in Fig. 4. For the synthesis of 4, 2.04 equivalents of bipy were applied. In $3^{3+}$, each $\text{In}^{3+}$ is coordinated in a distorted octahedral fashion, or in other words, three tetragonal pyramidal N-coordinated $[\text{In}^{\text{bipy}}]_3^{3+}$ fragments interact with each other, thus forming the observed triangular cationic $\text{In}^1$ cluster. While the $\text{In}1 - \text{In}2$ and $\text{In}1 - \text{In}3$ bond lengths are very similar ($266.07(4)$ and $266.98(5)$ pm, respectively), the $\text{In}2 - \text{In}3$ distance is elongated by 11-12 pm. All three distances are well within the sum of the van der Waals radii$^{2,43}$ (386 pm) and among the shortest compared to the manifold of reported organometallic and inorganic compounds that feature $\text{In} - \text{In}$ bonds (Table 1 and Supplementary Table 15).

Reducing the amount of bipy from 2.00 to 1.63 equivalents, we obtained compound 5. Though the molecular structure of $5^{3+}$ resembles the one of $4^{3+}$, one bipy ligand now acts as bridging N-ligand between two $\text{In}^1$ cations, thus resulting in a more twisted arrangement of the two pyridine rings. These findings are likely attributable to the reduced amount of bipy employed and correspond well with the stoichiometry of the reaction (cf. $\langle 5$ bipy ligands$/3 \text{ In}^1$ cations $\rangle \approx 1.67$). Hence, only $\text{In}2$ is coordinated in a distorted octahedral fashion, while $\text{In}1$ and $\text{In}3$ are coordinated in distorted trigonal bipyramidal fashions. The very short $\text{In}1 - \text{In}2$ bond lengths (Table 1) are similar within 3 pm (av. $\text{In}1 - \text{In}2$ distance of 268.18(5) pm), thus resulting in an almost equilateral triangle. For 6, 2.00 equivalents of bipy were applied. Yet, and different to the synthesis of 4, the reaction mixture was additionally concentrated under reduced pressure, leading to the cationic planar $\text{In}^1$ rhomb $6^{4+}$. While the coordination modes of $\text{In}2$ and $\text{In}4$ resemble the ones of the $\text{In}^1$ cations in $4^{3+}$ and $\text{In}2$ in $5^{3+}$, $\text{In}1$ and $\text{In}3$ are pentacoordinated, interacting with only one bipy ligand and featuring three $\text{In} - \text{In}$ contacts. The peripheral $\text{In}1 - \text{In}3$ bond lengths only deviate by 5 pm (av. $\text{In}1 - \text{In}3$ distance $= 277.99(14)$ pm) and are, with the exception of the $259.65(12)$ pm the shortest $\text{In}1 - \text{In}3$ distance on the other hand, is with $259.65(12)$ pm the shortest $\text{In}1 - \text{In}3$ bond that, to our knowledge, has been reported (the only shorter $\text{In}1 - \text{In}3$ bond derives from the structural relative seven, see below) (Table 1 and Supplementary Table 15).

Overall and despite the vast literature on compounds containing $\text{In} - \text{In}$ bonds, the cationic molecular and univalent structures of 4, 5 and 6 are unique. Somewhat related to 6 is the $[\text{In}4_{1/2}\text{Cp}_2\text{MnO}_2(\text{CO})_2\text{P}_2]\text{In}^{3+}$ $[\text{Al(OR F)}_4]^{-}$ salt reported by Scheer et al.$^{26}$ Herein, the $\text{In}1$ cations form a similar rhombic arrangement, but with intermetallic distances that are at least 60 pm longer (shortest $\text{In}1 - \text{In}3$ distance: 348.2 pm). These findings must be due to the different ligand system, as the group used the same $[\text{Al(OR F)}_4]^{-}$ anion: that is, the interactions seem to be weakly dispersive rather than covalent. The remaining known
caticonic compounds are purely inorganic (cf. Supplementary Table 15) and while some of them feature similar In–In bond lengths, their chain-like substructures differ significantly. Though featuring a related geometry, the reported anionic triangular cyclogallanes differ in their electronic structures: that is, they are only accessible via reductive routes and feature delocalized cationic compounds are unstable in solution, while the InI clusters are unstable in solution, while the InI clusters are unable to solvate bipy, thus speaking for a fragmentation of the cationic indium clusters in solution. The solution of the crystalline residue of 7 and 8 yielded a complex multiplet pattern in the aromatic region, which is likely attributable to different fragments of both sets of single crystals. From the multinuclear NMR studies we suggest that the cationic InI clusters are unstable in solution, while the [Al(OR)₅]⁺ anions stay intact. The dissociation of the cationic InI clusters is probably attributable to the distinct Coulomb repulsion of the In–In bonded individual [In(N-ligand)]₂⁺ units constituting 4³⁺, 5³⁺, 6⁴⁺ and 7⁴⁺ (cf. DFT studies below).

### Multinuclear solution NMR spectroscopy

All obtained single crystals were dissolved in o-C₆H₄F₂ and investigated by ¹H, ¹⁴N, ¹⁹F, ²⁷Al, ⁷¹Ga and ¹¹⁵In NMR spectroscopy. While the ¹⁴N, ⁷¹Ga and ¹¹⁵In NMR spectra featured no resonances, thus being in good agreement with earlier reported σ-coordinated complexes of Ga⁺ and In⁺ (28, 29, 31, 32), one singlet in the ¹⁹F NMR and ²⁷Al NMR spectra at −74.9 p.p.m. and +33.8 p.p.m., respectively, revealed the intactness of the [Al(OR)₅]⁺ anions. In the case of the mixed crystalline residue of 7 and 8, the ¹⁹F NMR spectrum additionally featured the triplet of a tris-monoamide, which was clearly detectable in the low-field region. Finally, the ¹H NMR spectra provided primary information on the stability of the obtained cationic complexes in solution: that is, the solution of 3 featured very weak and broad resonances due to the paramagnetic nature of 3²⁺ (cf. EPR studies). Solutions of 4, 5 and 6 featured multiplets attributable to solvated bipy, thus speaking for a fragmentation of the cationic indium clusters in solution. The solution of the crystalline residue of 7 and 8 yielded a complex multiplet pattern in the aromatic region, which is likely attributable to different fragments of both sets of single crystals. From the multinuclear NMR studies we suggest that the cationic InI clusters are unstable in solution, while the [Al(OR)₅]⁺ anions stay intact. The dissociation of the cationic InI clusters is probably attributable to the distinct Coulomb repulsion of the In–In bonded individual [In(N-ligand)]₂⁺ units constituting 4³⁺, 5³⁺, 6⁴⁺ and 7⁴⁺ (cf. DFT studies below).
From an energetic point of view, the singlet-triplet route appears to be more conceivable, as the singlet-triplet gaps are distinctively smaller than the corresponding 4s/5s-4p/5p energy gaps (Table 2; cf. DFT studies by Macdonald et al.63). In addition and considering the distribution of spin densities, the triplet states of the [M(bipy)]2+ complexes offer important insights into the metal-dependent redox stabilities: that is, for gallium the tetrahedral [Ga3+] {[(bipy)2]2+} complex forms and for indium the tetragonal pyramidal [In2+ (bipy)(bipy)+] complex. Hence, only the latter should be able to stepwise cyclotrimerize, while the former is labile and disproportionate.

In this context, the choice of the redox-active ligand is crucial and for indium, bipy seems to be the perfect match as it enables metal-dependent redox stabilities: that is, for gallium the tetrahedral [Ga3+] {[(bipy)2]2+} complex forms and for indium the tetragonal pyramidal [In2+ (bipy)(bipy)+] complex. Hence, only the latter should be able to stepwise cyclotrimerize, while the former is labile and disproportionate.

Finally, we attempted to calculate the molecular structures of $\sigma^+_4$, $\rho^+_3$ and $\sigma^+_6$. Though we implemented the conductor-like screening model65 with an infinite permittivity and dispersive interactions (D3), the cationic In clusters fragmented due to the distinct Coulomb repulsion. However, we were able to calculate dicaticonic fragments in their triplet state, such as $\sigma^+_3$–$\sigma^+_6$ (Fig. 7, inset). With an average spin-density distribution of 32% at each indium atom, the latter could be seen as a reaction intermediate of the univalent indium clusters, thus supporting a stepwise cluster formation (for further dicaticonic fragments see Supplementary Fig. 10). Furthermore, we assessed the gas-phase thermodynamics ($\Delta H^\circ$ (gas), Table 3) of the formations of $\sigma^+_4$, $\rho^+_3$ and $\sigma^+_6$ from BHFCs and setting $\Delta H^\circ$ solid in a worst-case scenario to $\pm 0$ kJ mol$^{-1}$ (Supplementary Fig. 8). The endothermic values are attributable to the above-mentioned Coulomb repulsion and very well correspond to the large exothermicity of the Coulomb
explosion of $4^{3+}$ with formation of three $[\text{In}(\text{bipy})_2]^+$ monocations in the gas phase and assessed via a suitable BHFC as $-466 \text{ kJ mol}^{-1}$ (Table 3 and Supplementary Fig. 8).

This is in agreement with single-point DFT calculations on the frozen configuration of solid $4^{3+}$, Coulomb exploding to give three $[\text{In}(\text{bipy})_2]^+$ monocations cut out of this cyclic trimer solid-state structure. B3LYP and BHLYP suggest this gas phase process to be favoured by $-684$ and $-705 \text{ kJ mol}^{-1}$, respectively. A non-ligand- supported triangular $[\text{In}_3]^{3+}$ cluster ($d_{\text{In-In}} = 270 \text{ pm}$) was calculated to Coulomb explode at the same level with $-1,447/-1,459 \text{ kJ mol}^{-1}$, Supplementary Table 13). Overall, the formation of the ligand supported $[\text{In}_3]^{3+}/[\text{In}_2]^+$ clusters seems to be only

possible through the application of matching ligands and ultimately is a solid-state-driven phenomenon. Both, bipy and phen lead to a pronounced decrease of the Coulomb repulsion within the clusters by diluting the positive charges on the In$^+$ cations to the ligand backbone, and contributing enough negative charge to yield ligand stabilized $[\text{In}_3]^{3+}(\text{A}^-)$ and $[\text{In}_2]^{4+}(\text{A}^-)$ salts with short In$-$In bonds. This corresponds to a ligand-to-metal charge transfer. The calculated high $\Delta_{\text{HUM}}^R$ values of $-1,438$ (4), $-1,444$ (5) and $-2,266 \text{ kJ mol}^{-1}$ (6) further stabilize the salts$^{66}$. Together, the charge transfer leading to favourable metal-metal bond strengths, in combination with the lattice enthalpy gain are sufficient to overcome the strong Coulomb repulsion active in gaseous and solution phases. Last, it should be noted that for the central $[\text{In}_4]^{4+}$ cluster core with eight valence electrons deriving from four In$^+$ cations, the stability of $6^{4+}$ and $7^{4+}$ would be in agreement with the Jellium model$^{67}$.
Discussion

The reaction of I and 2,2’-bipyridine resulted in a disproportionation of the former, thus yielding the monomeric and paramagnetic [Ga(bipy)$_3$]$^{3+}$ complex. Herein, the gallium cation is coordinated in a distorted octahedral fashion, and EPR and DFT studies reveal a ligand-centred radical: that is, a [GaIII(bipy)$_3$]$^{3+}$ complex. Applying the higher homologue 2 on the other hand, we isolated the first homonuclear cationic triangular and rhombic clusters of univalent indium: [In$_4$]$_4$$^{2+}$ and [In$_7$]$_7$$^{2+}$. Herein, the In$^3+$ cations are coordinated by one, 1.5 or two chelating bipy/phen ligands. To our knowledge, the In – In distances (258.1 and 259.7 pm) within the In – In bridges in the rhombic clusters are the shortest that have been reported so far. DFT studies suggest a stepwise formation of the clusters via their triplet state and an alternate ambiphilic route seems to be energetically less favourable. The general driving force for this cationic cluster formation is attributable to relatively strong In – In bonds, reduction of Coulomb repulsion by introduction of a suitable ligand and ligand-to-metal charge transfer in combination with the high lattice enthalpies of the resultant ligand stabilized [M$_3$]$^{3+}$ and [M$_4$]$^{4+}$ salts. We are convinced that this is a general phenomenon, which could be used as a pathway to cationic metal atom cluster formation of subvalent metal ions in combination with strong but sterically accessible (chelating?) ligands.

Methods

General experimental procedures. All manipulations were performed using Schlenk or glove box techniques in an argon atmosphere (H$_2$O and O$_2$ < 1 pp.m.). o-C$_6$H$_4$F$_2$ and C$_6$H$_5$F$_2$ were dried over CaH$_2$ distilled and had H$_2$O contents below 5 pp.m. (Karl-Fischer titrations). Because the obtained compounds contain large amounts of fluorine in chemically very stable CF$_3$ groups, standard combustion analyses have proven to be incomplete. Characterizations of novel compounds were therefore done on the basis of single-crystal X-ray analysis and multinuclear NMR spectroscopy. As the highly symmetric and perfluorinated [Al(ORF)$_4$]$_2$ complex. Applying the heavier homologue of yellow and red indium monochloride. Acta Crystallogr., Sect. B: Struct. Sci. 34, 3333–3335 (1978).

Brühl, A. & Ortner, G. Die Sulfide des Galliums. Monatsh. Chem. 56, 358–364 (1930).

Tuck, D. G. Gallium and indium dihalides: a classical structural problem. Polyhedron 9, 377–386 (1990).

Eiker, R. J. & Jones, C. ‘Ga$:’ a versatile reagent for the synthetic chemist. Dalton Trans. 1341–1348 (2005).

Malbrecht, B. J., Dube, J. W., Williams, M. J. & Ragogna, P. J. Addressing the chemical socber of ‘Ga’: benefits of solid-state analysis aiding in the synthesis of P →Ga coordination compounds. Inorg. Chem. 53, 9644–9656 (2014).

Schmidbaur, H. Arene complexes of univalent gallium, indium, and thallium. Angew. Chem. Int. Ed. Engl. 24, 893–904 (1985).

Schenk, C., Köppe, R., Schnöckel, H. & Schnöckel, A. A convenient synthesis of cyclopentadienyngallium—the awakening of a sleeping beauty in organometallic chemistry. Eur. J. Inorg. Chem. 2011, 3681–3685 (2011).

Asay, M., Jones, C. & Driess, M. N-Heterocyclic carbene analogues with low-valent group 13 and group 14 elements: syntheses, structures, and reactivities of a new generation of multitaleded ligands. Angew. Chem. 111, 354–396 (2011).

Dange, D., Choong, S. L., Schenk, C., Stach, A. & Jones, C. Synthesis and characterisation of anionic and neutral gallium(I) N-heterocyclic carbene analogues. Dalton Trans. 41, 9304–9315 (2012).

Linti, G. & Schnöckel, H. Low valent gallium and aluminium compounds—structural variety and coordination modes to transition metal fragments. Coord. Chem. Rev. 206-207, 285–319 (2000).

Pardee, J. A. J. & Downs, A. J. Development of the chemistry of indium in formal oxidation states lower than +3. Chem. Rev. 107, 2–45 (2007).

Fitz, H. & Müller, B. G. InBF$_4$: das erste komplexe Fluorid mit Indium(I). Z. Anorg. Allg. Chem. 623, 579–582 (1997).

Macdonald, C. L. B., Corrente, A. M., Andrews, C. G., Taylor, A. & Ellis, B. D. Indium(I) trifluoromethanesulfonate and other soluble salts for univalent indium chemistry. Chem. Commun. 250–251 (2004).

Maze, Z. Indium(I) hexafluoropropionate (InPF$_6$: P = As, Sb). Eur. J. Inorg. Chem. 2005, 3983–3987 (2011).

Welsch, S., Bodenstein, M., Dušek, M., Sieker, M. & Scheer, M. A novel soluble In$^3+$ precursor for P$_2$ ligand coordination chemistry. Chem. Eur. J. 16, 13041–13045 (2010).

Schneider, U. & Kobayashi, S. Low oxidation state indium-catalyzed C–C Bond formation. Acc. Chem. Res. 45, 1331–1344 (2012).

Slattery, J. M., Higelin, A., Bayer, T. & Krossing, I. A simple route to univalent gallium salts of weakly coordinating anions. Angew. Chem. Int. Ed. 49, 3228–3231 (2010).

Higelin, A., Sachs, U., Keller, S. & Krossing, I. Univalent gallium and indium phosphane complexes: from pyramidal M[PPh$_3$)$_3$]$_2$ to carbene-organobutyl $M$[P(PBu$_3$)$_3$]$_2$ (M = Ga, In) Complexes. Chem. Eur. J. 18, 10029–10034 (2012).

Higelin, A., Haber, C., Meier, S. & Krossing, I. Unusual cationic crown ether complexes of gallium(I) and indium(I). Dalton Trans. 41, 12011–12015 (2012).

Higelin, A., Keller, S., Göhringer, C., Jones, C. & Krossing, I. Unusual Tiled carbene coordination in carbene complexes of gallium(I) and indium(I). Angew. Chem. Int. Ed. 52, 4941–4944 (2013).

Lichtenthaler, M. R. et al. σ- or τ-coordination? Complexes of univalent gallium salts with aromatic nitrogen bases. Eur. J. Inorg. Chem. 2014, 4335–4341 (2014).

Lichtenthaler, M. R. et al. Univalent gallium salts of weakly coordinating anions: effective initiators/catalysts for the synthesis of highly reactive polyisobutylene. Organometallics 32, 6725–6735 (2013).
43. Lichtenthaler, M. R. et al. Univalent gallium complexes of simple and ansa-Arene ligands: effects on the polymerization of isobutylene. *Chem. Eur. J.*, 21, 1555–1565 (2015).

44. Jones, C. Bulky Guanidinates for the stabilization of low oxidation state metallacycles. *Coord. Chem. Rev.* 254, 1273–1289 (2010).

45. Baker, R. I., Farley, R. D., Jones, C., Kloth, M. & Murphy, D. M. The reactivity of diazabutadienes toward low oxidation state Group 13 iodides and the synthesis of a new gallium(I) carbene analogue. *J. Chem. Soc., Dalton Trans.* 3844–3850 (2002).

46. Tsai, Y.-C. The chemistry of univalent metal β-diketimines. *Coord. Chem. Rev.* 256, 722–758 (2012).

47. Reger, D. L. Poly(pyrazolyl)borate complexes of gallium and indium. *Coord. Chem. Rev.* 147, 571–595 (1996).

48. Jurca, T., Lummis, J., Burchell, T. J., Gorelsky, S. I. & Richeson, D. S. Capturing $^{35}$P monomers in a neutral weakly coordinating environment. *J. Am. Chem. Soc.* 131, 4608–4609 (2009).

49. Baker, R. I., Jones, C., Kloth, M. & Mills, D. P. The reactivity of gallium(I) and indium(I) halides towards bipyridines, terpyridines, imino-substituted pyridines and bis(imino)acnaphthenes. *New J. Chem.* 28, 207–213 (2004).

50. Tuononen, T. et al. Disproportionation and formation in the coordination of ‘Gal’ with bis(imino)pyridines. *Dalton Trans.* 39, 1266–1272 (2010).

51. Bondi, A. van der Waals volumes and Radii. *J. Phys. Chem.* 68, 441–451 (1964).

52. Mantinia, M., Chamberlin, A. C., Valero, R., Cramer, C. J. & Truhlar, D. G. Consistent van der Waals Radii for the whole main group. *J. Phys. Chem. A* 113, 5806–5812 (2009).

53. Baker, R. I., Bettenrup, H. & Jones, C. The reactivity of primary and secondary amines, secondary phosphines and N-heterocyclic carbanes toward Group 13 metal(I) halides. *Eur. J. Inorg. Chem.* 2003, 2446–2451 (2003).

54. Protchenko, A. V. et al. Stable GaX₄, InX₄ and TIX₄ radicals. *Nat. Chem.* 6, 315–319 (2014).

55. Cloke, F. G. N., Hanson, G. R., Henderson, M. J., Hitchcock, P. B. & Raston, C. L. Synthesis and X-ray crystal structure of the first homoleptic main group diazadiene complex, bis(1,4-di-t-butyl-1,4-diazabuta-1,3-diene) gallium. *J. Chem. Soc., Chem. Commun.* 1002–1003 (1989).

56. Kaim, W. & Matheis, W. Bis(1,4-di-t-butyl-1,4-diazabuta-1,4-diene)gallium is not a gallium(II) compound. *J. Chem. Soc., Chem. Commun.* 597–598 (1991).

57. Baker, R. I. et al. An EPR and ENDOR Investigation of a Series of Diazabutadiene-complexes. *Chem. Eur. J.* 11, 2972–2982 (2005).

58. Tuononen, H. M. & Armstrong, A. F. Theoretical investigation of paramagnetic diazabutadiene gallium(III) – pi centogen complexes: insights into the interpretation and simulation of electron paramagnetic resonance spectra. *Inorg. Chem. Acta,* 44, 8277–8284 (2005).

59. Tuononen, T. et al. Armstrong, A. F. Theoretical investigation of paramagnetic group 13 diazabutadiene radical ions into the prediction and interpretation of EPR spectroscopy parameters. *Dalton Trans.* 1885–1894 (2006).

60. Záliš, S. et al. Origin of electronic absorption spectra of MLCT-excited and one-electron reduced 2,2'-bipyridine and 1,10-phenanthroline complexes. *Inorg. Chem. Acta* 374, 578–583 (2011).

61. Peer, R. J., Bettenrup, H. M., Denning, M. S. & Goicoechea, J. M. Synthesis and characterization of alkali-metal salts of 2,2'-bipyridine and 1,10-phenanthroline complexes. *Eur. J. Inorg. Chem.* 1002–1003 (1989).

62. Wang, M., Weyhermueller, T., England, J. & Wieghardt, K. Molecular and metallacycles. *Coord. Chem. Rev.* 1273–1289 (2010).

63. Allan, C. J., Cooper, B. F. T., Cowley, H. J., Rawson, J. M. & Macdonald, C. L. B. Electro-oxidation and electronic properties of the (1,4-diaza-1,3-dibutyl)gallium. *Eur. J. Inorg. Chem.* 133, 577–582 (1978).

64. Wang, M., Weyhermueller, T., England, J. & Wieghardt, K. Molecular and metallacycles. *Coord. Chem. Rev.* 12763–12776 (2013).

65. Wang, M., Weyhermueller, T., England, J. & Wieghardt, K. Molecular and metallacycles. *Angew. Chem. Int. Ed.* 38, 1948–1952 (1999).

66. Wang, M., Weyhermueller, T., England, J. & Wieghardt, K. Molecular and metallacycles. *Rev. Mod. Phys.* 65, 677–732 (1993).

67. Weil, J. A. & Bolton, J. R. In Electron Paramagnetic Resonance 583, John Wiley & Sons, Inc., 2006.

68. Dedieu, A. & Hoffmann, R. Platinum(0)-platinum(0) dimers. Bonding relationships in a d10-d10 system. *J. Am. Chem. Soc.* 100, 2074–2079 (1978).

Acknowledgements

This work was supported by the Albert-Ludwigs-Universitat Freiburg and by the DFG in the Normverfahren. We would like to thank Fadime Bitgül and Dr Harald Scherer for the measurement of the NMR spectra, B. Sc. Bounahid Benkhil for his support regarding single-crystal X-ray analysis, Dr Michael Schwarz and Prof. Dr Caroline Röhr for their support during the attempted preparation of single-crystalline EPR samples. This work is dedicated to the occasion of the 60th birthday of Prof. Dr. Manfred Scherer in Regensburg.

Author contributions

M.R.L. initiated and coordinated the project, conducted the synthesis of 4, 5, 6, 7 and 8, synthesized the 3rd characterization of the obtained compounds, performed the DFT calculations and wrote the manuscript with assistance of I.K., during his apprenticeship and under the supervision of M.R.L. J.S. performed the synthesis of 1 and 3. D.K. contributed valuable support in solving and refining the single-crystal structures; L.H., E.S. and S.W. conducted the EPR measurements of 3, contributed the simulated spectra and drafted the EPR-related part of the manuscript. S.W. also revised the completed manuscript; During his bachelor thesis and under the supervision of M.R.L., J.H. performed the synthesis of 2; D.H. provided important advice regarding the DFT calculations and revised the manuscript; I.K. directed the project, conceived the central ideas concerning the formation of the reported compounds and drafted parts of the manuscript.

Additional information

Accession codes: The X-ray crystallographic coordinates for structures reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition numbers CCDC 1032681 (3), CCDC 1032680 (4), CCDC 1033048 (5), CCDC 1032732 (6), CCDC 1034231 (7) and CCDC 1034089 (8). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary Information accompanies this paper at http://www.nature.com/naturecommunications

Competing financial interests: The authors declare no competing financial interests.

Reprints and permission information is available online at http://npg.nature.com/reprintsandpermissions/.

How to cite this article: Lichtenthaler, M. R. et al. Cationic cluster formation versus disproportionation of low-valent indium and gallium complexes of 2,2'-bipyridine. *Nat. Commun.* 6:8288 doi: 10.1038/ncomms9288 (2015).