Synthesis, Structure and Bonding in Pentagonal Bipyramidal Cluster Compounds Containing a cyclo-Sn\textsubscript{5} Ring, [(CO)\textsubscript{3}MSn\textsubscript{5}M(CO)\textsubscript{3}]\textsuperscript{14–} (M = Cr, Mo)

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Abstract: In this paper, we report the synthesis and structural characterisation of two hetero-metallic clusters, [(CO)\textsubscript{3}CrSn\textsubscript{5}Cr(CO)\textsubscript{3}]\textsuperscript{14–} and [(CO)\textsubscript{3}MoSn\textsubscript{5}Mo(CO)\textsubscript{3}]\textsuperscript{14–}, both of which have a pentagonal bipyramidal core. The structures are similar to that of previously reported [(CO)\textsubscript{3}MoPb\textsubscript{3}Mo(CO)\textsubscript{3}]\textsuperscript{18–} and our analysis of the bonding suggests that they are best formulated as containing Sn\textsubscript{5}\textsuperscript{4–} rings bridging two zerovalent M(CO)\textsubscript{3} fragments. The electronic structure is compared to two isovalent M\textsubscript{2}E\textsubscript{5} clusters, [CpCrP\textsubscript{5}CrCp]\textsuperscript{−} and Tl\textsubscript{7}\textsuperscript{−}, both of which show clear evidence for trans-annular bonds between the apical atoms that is not immediately obvious in the title clusters. Our analysis shows that the balance between E-E and M-M bonding is a delicate one, and shifts in the relative energies of the orbitals on the E\textsubscript{5} and M\textsubscript{2} fragments generate a continuum of bonding situations linked by the degree of localisation of the cluster LUMO.

Keywords: Zintl clusters; X-ray crystallography; Density Functional Theory

1. Introduction

The chemistry of cyclo-Pn\textsubscript{5} rings of the pnictogens is now well established, and many coordination compounds of P\textsubscript{5}\textsuperscript{−} and its heavier congeners, As\textsubscript{5}\textsuperscript{−} and Sb\textsubscript{5}\textsuperscript{−}, have been reported in the literature [1–3]. These are of interest from a synthetic perspective, but also in the context of the isolobal relationship between Pn and CH [4,5] which can be used, for example, to rationalise the very similar structural chemistry of complexes of P\textsubscript{5}\textsuperscript{−} and C\textsubscript{5}H\textsubscript{5} [6]. Rather less common are cyclo-Tl\textsubscript{5} rings containing the tetrel elements Si, Ge, Sn and Pb. An iso-electronic relationship to P\textsubscript{5}\textsuperscript{−} would require a formal charge of −6, and indeed Todorov and Sevov have reported both Sn\textsubscript{5}\textsuperscript{6−} and Pb\textsubscript{5}\textsuperscript{6−} in a family of Zintl phases, Na\textsubscript{8}BaPb\textsubscript{6}, Na\textsubscript{8}BaSn\textsubscript{6} and Na\textsubscript{8}EuSn\textsubscript{6}, Figure 1, (where charge balance is maintained by the presence of an isolated Tl\textsuperscript{4+} ion in the unit cell in addition to a Tl\textsubscript{5}\textsuperscript{5−} ring) [7]. Lighter homologues such as Si\textsubscript{5}\textsuperscript{6−} and Ge\textsubscript{5}\textsuperscript{6−} have an even longer history, having been identified in binary phases such as Li\textsubscript{12}Si\textsubscript{7} and Li\textsubscript{11}Ge\textsubscript{6} as far back as the late 1970s [8–10]. The stability of the planar Tl\textsubscript{5}\textsuperscript{6−} rings can be rationalised either on the grounds of aromaticity (the rings have 6 \pi electrons), or in terms of Wade’s rules (the clusters have a 2n + 6 = 16 skeletal electron count or, equivalently, a total valence electron count of 4n + 6 = 26, consistent with a 5-vertex \textit{arachno} cluster based on a pentagonal bipyramid with two missing \textit{trans} vertices) [11]. These two perspectives, both equally valid, highlight the important point that the bonding in ring and cluster compounds of the heavier main group elements is complex, and different interpretations are often possible.
Inorganics 2022, 10, 75

Figure 1. Examples of pentagonal bipyramidal cluster architectures from the transition metal series and main-group: (a) cyclo-T₂₆⁵⁻ (Tt = Si, Sn, Pb; M = alkali, alkaline- or rare-earth metals); (b) Tl₇⁷⁻ in the binary phase K₁₀Tl₇ [12]; (c) [(CO)₃MoPb₅Mo(CO)₃]⁴⁻ [13], (d) [(CO)₃MSn₅M(CO)₃]⁴⁻ (M = Cr, Mo), this work and (e) [CpCrP₅CrCp]⁰⁻ [14].

Soon after Sevov’s report of the Sn₆⁻ and Pb₆⁻ rings [7], Fässler, Kaupp and coworkers described the synthesis of a molecular analogue, [(CO)₃MoPb₅Mo(CO)₃]⁴⁺, which they formulated as a Pb₄⁻⁵ ring bridging two neutral Mo(CO)₃ fragments [13]. The 4π electron count is now consistent with anti-aromatic, rather than aromatic, character, but the Pb-Pb bond lengths in this cluster (3.0138–3.0647 Å) are nevertheless marginally shorter than those in the aromatic (6π) Pb₆⁻⁻ unit in Na₈BaPb₆ (3.047–3.117 Å). An analysis of the electronic structure reveals very substantial transfer of charge from the Pb₄⁻⁵ ring to the Mo(CO)₃ fragments, such that the most intense C-O stretching frequency (1737 cm⁻¹) is substantially reduced from the value of 1960 cm⁻¹ in the precursor, (mesitylene)Mo(CO)₃ [15], and this covalency clearly precludes a simple correlation between bond lengths and formal charge on the five-membered ring. Gholiee et al. have, more recently, published a detailed computational survey of the family of pentagonal bipyramidal clusters with general formula [(CO)₃ME₅M(CO)₃]⁴⁻, M = Cr, Mo, W, E = Si, Ge, Sn and Pb [16]. Their analysis, using the M06-2X functional in combination with a def2-TZVPP basis, concurs with the conclusion from Fässler and Kaupp, that there is substantial charge transfer from the formally Tt₄⁻⁵ ring to the M(CO)₃ fragments, such that the former actually carries a positive natural charge: clearly the formal charge is at best a first approximation, and the balance between M-M, M-Tt and Tt-Tt bonding is a delicate one.

In this paper, we report the synthesis and structural characterisation of two tin analogues of Fässler’s lead cluster, [(CO)₃MSn₅M(CO)₃]⁴⁻, M = Cr (1) and Mo (2), both of which were included in Gholiee’s computational survey [16]. Both compounds are formed from the reaction of K₄Sn₉ with the organometallic precursors M(MeCN)₃(CO)₃ (M = Cr, Mo), and both feature a planar cyclo-Sn₅ motif capped by two M(CO)₃ fragments. This new structural data provides a platform to consider the general features of bonding in the family of pentagonal bipyramids. In the final section of this paper, we take the opportunity to compare these two new clusters to closely related species that share the pentagonal bipyramidal architecture, and to compare the different electron-counting models that have been applied in this context.

2. Materials and Methods

All manipulations and reactions were performed under a dry nitrogen atmosphere in the glove box. Ethylenediamine (en) (99%, Sigma-Aldrich, Beijing, China), and N, N-Dimethylformamide (Sigma-Aldrich, 99.8%) were freshly distilled and
stored under nitrogen before use. Toluene (Sigma-Aldrich, 99.8%) was distilled from sodium/benzophenone under nitrogen and stored under nitrogen. The [2.2.2]crypt (4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo (8.8.8) hexacosane) (98%), and 18-Crown-6 (1,4,7,10,13,16-Hexaoxacyclooctadecane) (99%), both purchased from Sigma-Aldrich, were dried in vacuum for 12 h prior to use. K₄Sn₉ was synthesised by heating a mixture of K and Sn (K: 99%, Sn: 99.99%, both from Aladdin (Shanghai, China)) at 850 °C for 48 h in a tubular tantalum container and then cooling to room temperature at a rate of 10 °C/h. Finally, black powders were obtained. The M(MeCN)₃(CO)₃ (M = Cr, Mo) starting materials were synthesised according to literature procedures [17].

2.1. Synthesis of K₂(en)₃[K([2.2.2]-crypt)]₂[Cr(CO)₃Sn₅Cr(CO)₃]·2en, (1)

K₄Sn₉ (100 mg, 0.817 mmol) and [2.2.2]crypt (150 mg, 0.399 mmol) were dissolved in 3 mL en solution in a 10 mL vial, and the mixture was stirred vigorously for 30 min at room temperature. The organometallic precursor Cr(MeCN)₃(CO)₃ (30 mg 0.116 mmol) was then added and stirring continued for 3 h at room temperature. The resulting red-brown solution was centrifuged and filtered with standard glass wool, then carefully layered with 3 mL toluene. After 5 days, small dark-brown needle-like crystals of 1 (Figure S1, left) were observed in the bottom of the test tube in approximately 26% yield (based on precursor Cr(MeCN)₃(CO)₃ used).

2.2. Synthesis of K[K(18-crown-6)]₃[Mo(CO)₃Sn₅Mo(CO)₃] (2)

K₄Sn₉ (100 mg, 0.817 mmol) and 18-Crown-6 (105 mg, 0.397 mmol) were dissolved in 3 mL en solution in a 10 mL vial, and the mixture was stirred vigorously for 30 min at room temperature. The organometallic precursor Mo(MeCN)₃(CO)₃ (35 mg 0.116 mmol) was then added and stirring continued for 4 h at room temperature. The resulting red-brown solution was centrifuged and filtered with standard glass wool, then carefully layered with 3 mL toluene. After 7 days, dark-brown needle-like crystals of 2 (Figure S1, right) were observed in the bottom of the test tube in approximately 19% yield (based on precursor Mo(MeCN)₃(CO)₃ used).

2.3. X-ray Diffraction

Suitable crystals of 1 and 2 were selected for X-ray diffraction analyses. Crystallographic data were collected on Rigaku XtalAB Pro MM007 DW diffractometer with graphite monochromated Cu Ka radiation (λ = 1.54184 Å). The structures of crystals 1 (Figures S2 and S3) and 2 (Figures S4 and S5) were solved using direct methods and then refined using SHELXL-2014 and OLEX2 [18,19]. All the non-hydrogen atoms were refined anisotropically, except for those in the split positions. The uncoordinated solvent molecules in 1 and 2 could not be modeled properly, so the solvent molecules are removed using SQUEEZE in PLATON [20]. The cluster anion in 1 has a disordered structure which was solved by the Split SAME process [19]. The unique bond angles and distances were constrained by Dfix order. We use the SIMU order to limit the anisotropic displacement parameters of the interconnected atoms to be similar. A summary of the crystallographic data for the title compounds is listed in Table S1, and selected bond distances and bond angles are given in Table S2. CCDC entries CCDC-2122111 and CCDC-2122112 for compounds 1 and 2 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (accessed on 15 November 2021).

2.4. Electrospray Ionisation Mass Spectrometry (ESI-MS)

Negative ion mode ESI-MS of a MeCN solution made up from crystals of 1 were measured on an LTQ linear ion trap spectrometer by Agilent Technologies ESI-TOF-MS (6230). The spray voltage was 5.48 kV and the capillary temperature was maintained at 300 °C. The capillary voltage was 30 V. The samples were prepared inside a glove box and
very rapidly transferred to the spectrometer in an airtight syringe by direct infusion with a Harvard syringe pump at 0.2 mL/min.

2.5. Energy Dispersive X-ray (EDX) Analysis

EDX analysis was performed to support the elemental composition proposed in the XRD experiment. These were carried out using a scanning electron microscope (Hitachi S-4800) equipped with a Bruker AXS XFlash detector 4010. Data acquisition was performed with an acceleration voltage of 20 kV and an accumulation time of 150 s (Figures S8 and S9).

2.6. Computational Details

All DFT calculations were performed using the ORCA 5.0.1 software [21,22]. A range of functionals was considered, including the generalised gradient approximation (GGA) functional proposed by Perdew, Burke and Ernzerhof (PBE) [23], the hybrid B3LYP [24–26], the meta-hybrid M06-2X [27] and the double-hybrid, B2PLYP [28,29]. Scalar relativistic effects were included using the zeroth-order relativistic approximation (ZORA) [30–32]. A valence triple-zeta polarised relativistically recontracted Karlsruhe basis set (ZORA-def2-TZVP) [33–35] was employed for H, C and O and segmented all-electron relativistically contracted (SARC) basis sets were used for heavier elements. The RI-J approximation to the Coulomb integrals (J) was made using the (SARC/J) [34–36] auxiliary basis set appropriate for ZORA calculations. The conductor-like polarisable continuum mode (CPCM) was implemented taking water as a solvent with dielectric constant (ε) 80.4 to model the confining potential of the cation lattice [37–40]. The multiwf1 package was used to analyse the topology of the electron density and to compute bond orders [41]. Graphics containing molecular structures were generated using Chemcraft [42].

3. Results

3.1. Synthesis and Structural Characterisation

The synthesis of both 1 and 2 was achieved by reacting a transition metal carbonyl precursor, M(MeCN)₃(CO)₅, with K₅Sn₉ in the presence of a chelating ligand, 18-Crown-6 or [2.2.2]-crypt, that binds K⁺ cations in the final product. In initial tests, both chelating ligands were used with both transition metals, but in the case of 18-Crown-6 with Cr or [2.2.2]-crypt with Mo, the major products were the known clusters [M(CO)₅Sn₉]₄⁻ [43], rather than the Sn₅-containing species. The influence of the chelating ligand most likely reflects subtle differences in the solubility of the two competing anions with cations of different size. X-ray diffraction analysis reveals that crystallises in the triclinic space group P1 and contains a [(CO)₃CrSnSnCr(CO)₃]₄⁻ anion with two isolated K⁺ ions and two [K([2.2.2]-crypt)]⁺ cations per cluster (Figures S2 and S3). The anionic clusters are arranged in approximately linear chains, with the K⁺ ions bridging adjacent units via four K⁺-O (CO) contacts of ~2.85 Å. The coordination sphere of the K⁺ ions is completed by a single chelating en ligand. The K⁺ ions chelated by [K([2.2.2]-crypt)]⁺ are separated from the centroid of the cluster by distances in excess of 7 Å. 2 (Figures S4 and S5) crystallises in the monoclinic space group P2₁/c with three [K(18-Crown-6)]⁺ cations and one further, isolated, K⁺ in the unit cell in addition to the [(CO)₃MoSn₅Mo(CO)₃]¹⁻ anion. The isolated K⁺ cations form bridges between adjacent cluster units, in this case via three K⁺-O (CO) contacts between 2.70 Å and 3.45 Å as well as three short K⁺-Sn contacts to the equatorial rings. These short K⁺-Sn contacts are responsible for the small distortion of the Sn₅ ring away from a perfect pentagon. The structures of the two anions are shown in Figure 2 and further details are given in Supporting Information, Figures S2–S5. The [(CO)₃MSn₅M(CO)₅]₄⁻ anions (M = Cr, 1; Mo, 2) are, like the Pb analogue [13], pentagonal bipyramids with a Sn₅ ring capped by two M(CO)₅ fragments at the vertices. The M–M distances along the principal axis are 2.948(9) Å and 3.1393(5) Å in 1 and 2, respectively. Fässler and co-workers have emphasised the point that the Mo-Mo distance of 3.2156(8) Å in [(CO)₅MPh₃M(CO)₅]¹⁻ is longer than that in unambiguously Mo-Mo bonded species such as [Mo₂(CO)₁₀]²⁻ (Mo-Mo = 3.123 Å) [44]. The corresponding Mo-Mo distance of 3.1393(5) Å in the Sn₅ analogue, 2, is,
however, almost identical to that in \([\text{Mo}_2(\text{CO})_{10}]^{2-}\) while the Cr-Cr distance of 2.948(9) Å in 1 is shorter than that in \([\text{Cr}_2(\text{CO})_{10}]^{2-}\), 2.970 Å [44]. The unambiguous identification of metal-metal bonds in systems with bridging ligands is notoriously difficult, as illustrated by the spirited debate over the existence or otherwise of an Fe-Fe bond in \(\text{Fe}_2(\text{CO})_9\) [45–47], but in this case, it seems clear, at least, that direct metal-metal bonding cannot be excluded a priori based on the structural data alone. The Sn\(_5\) rings are almost perfectly planar, with the sums of the interior angles close to the ideal value of 540° (1: 539.850°; 2: 539.928°). The Sn–Sn bond lengths in 1 (av. 2.878 Å) and 2 (av. 2.934 Å) (Figure 2) bracket the values in the Sn\(_5^6\) – clusters: 2.883 Å in Na\(_8\)EuSn\(_5\), 2.921 Å in Na\(_8\)BaSn\(_5\), again highlighting the absence of a simple relationship between bond length and formal charge [7].

![Molecular structure of the anions \((\text{CO})_3\text{CrSn}_5\text{Cr(\text{CO})}_3\)^{4-} and \((\text{CO})_3\text{MoSn}_5\text{Mo(\text{CO})}_3\)^{4-} in compounds 1 and 2, respectively.](image)

**Figure 2.** Molecular structure of the anions \((\text{CO})_3\text{CrSn}_5\text{Cr(\text{CO})}_3\)^{4-} and \((\text{CO})_3\text{MoSn}_5\text{Mo(\text{CO})}_3\)^{4-} in compounds 1 and 2, respectively. Thermal ellipsoids are drawn at the 50% probability level.

### 3.2. ESI-MS

The ESI-MS of an acetonitrile solution of 1 shown in Figure 3 shows peaks at \(m/z = 865.3735\) and 1281.5919, identified as \([\text{Cr}_2\text{Sn}(\text{CO})_6]^–\) and \([\text{HK}(2.2.2-\text{crypt})\text{Cr}_2\text{Sn}(\text{CO})_6]^–\), respectively. No other small fragment peaks were found, indicating that compound 1 is relatively stable in acetonitrile solution under mass spectrometry conditions, albeit with a much reduced overall charge compared to the anion present in the crystal. Very similar features are apparent in the spectrum of 2 (Figures S6 and S7), where a prominent peak assigned to \([\text{K}(18–\text{Crown}–6)\text{Mo}_2\text{Sn}_5(\text{CO})_6]^–\) is observed at \(m/z \sim 1256\).

### 3.3. Electronic Structure Analysis

Optimised structural parameters for the two Sn\(_5\) clusters \((\text{CO})_3\text{MSn}_5\text{M(\text{CO})}_3\)^{4-}, \(M = \text{Cr, Mo}\), are compared in Table 1, along with corresponding values for Fässler’s Pb\(_5\) cluster [13], using a range of exchange-correlation functionals. The gradient corrected functional (PBE) give somewhat shorter M-M bonds than their hybrid counterparts (B3LYP) [26], which is a relatively common observation in systems with weak metal–metal bonds [48]. In contrast, the double hybrid function B2PLYP [28,29] predicts M-M bond lengths that are shorter than any of the other functionals, and indeed even shorter than the experimental values. Despite the functional dependence of the absolute bond lengths, the calculations replicate the important trends in the crystallographic data, irrespective of functional. Within the pair of Sn\(_5\) clusters, the optimised Cr-Cr bond length is \(\sim 0.2\) Å shorter than the Mo-Mo bond and the Sn-Sn bonds in the Sn\(_5\) ring are \(\sim 0.05\) Å shorter in the Cr complex than its Mo counterpart. Likewise, the elongation of the Mo-Mo distance in \([\text{Mo}(\text{CO})_3\text{Pb}_5\text{Mo(\text{CO})}_3]^4–\) vs. \((\text{CO})_3\text{MoSn}_5\text{Mo(\text{CO})}_3]^4–\) seen in the X-ray data is reproduced across all functionals.
Figure 3. Negative-ion mode ESI-MS spectra of a freshly prepared solution of 1 in MeCN. The region of the spectrum corresponding to \([\text{Cr}_2\text{Sn}_5(\text{CO})_6]^–\) is expanded (Top: measured spectrum. Bottom: calculated spectrum).

Table 1. Optimised bond lengths for \([\text{(CO)}_3\text{MSn}_5\text{M(CO)}_3]^4–\), \(M = \text{Cr, Mo and Pb}\) and \([\text{(CO)}_3\text{MoPb}_5\text{Mo(CO)}_3]^4–\) for PBE, B3LYP, M062X and B2PLYP functionals.

|                 | M-M       | M-Tt      | Tt-Tt     |
|-----------------|-----------|-----------|-----------|
| \([\text{(CO)}_3\text{CrSn}_5\text{Cr(CO)}_3]^4–\)| X-ray     | 2.95      | 2.86      | 2.88      |
|                 | PBE       | 2.97      | 2.88      | 2.91      |
|                 | B3LYP     | 3.07      | 2.91      | 2.91      |
|                 | M062X     | 2.97      | 2.86      | 2.88      |
|                 | B2PLYP    | 2.85      | 2.87      | 2.93      |
| \([\text{(CO)}_3\text{MoSn}_5\text{Mo(CO)}_3]^4–\)| X-ray     | 3.14      | 2.95      | 2.93      |
|                 | PBE       | 3.19      | 2.99      | 2.98      |
|                 | B3LYP     | 3.27      | 3.02      | 2.98      |
|                 | M062X     | 3.20      | 2.97      | 2.95      |
|                 | B2PLYP    | 3.15      | 2.98      | 2.97      |
| \([\text{(CO)}_3\text{MoPb}_5\text{Mo(CO)}_3]^4–\)| X-ray     | 3.21      | 3.05      | 3.04      |
|                 | PBE       | 3.22      | 3.08      | 3.09      |
|                 | B3LYP     | 3.31      | 3.11      | 3.10      |
|                 | B2PLYP    | 3.17      | 3.06      | 3.09      |

A schematic molecular orbital diagram showing the interaction between a Sn$_5^{4–}$ fragment and a (CO)$_3$M–M(CO)$_3$ unit is summarised in Figure 4. Quantitative versions for both clusters are shown in the Supporting Information, Figure S10. Note that the orbitals of the Sn$_5^{4–}$ ring are labelled according to $D_{5h}$ point symmetry while those of M(CO)$_3$ and (CO)$_3$M–M(CO)$_3$ are labelled according to $C_{3v}$ and $D_{3h}$, respectively. The complete cluster has only $C_{s}$ point symmetry. The bonding interaction between the Sn$_5^{4–}$ ring and the transition metal center is dominated by charge transfer from the highest occupied orbitals on Sn$_5^{4–}$ with Sn-Sn $\sigma$ ($e'_1$) and Sn-Sn $\pi$ ($e''_2$) character, which overlap with in- and out-of-phase combinations of the degenerate LUMO of M(CO)$_3$ ($2e'$ and $2e''$, respectively) to generate near-degenerate pairs with $a'$ and $a''$ symmetry ($(5a',3a''),(6a',4a'')$). The air- and moisture-sensitivity of both 1 and 2 has precluded the measurement of infra-red spectra for either, but our computed C-O stretching frequencies (1712 cm$^{-1}$ and 1744 cm$^{-1}$ for 1 and 2, respectively) indicate a similar red-shift to that observed in the Pb$_5$ analogue (measured, 1737 cm$^{-1}$ [13], calculated 1744 cm$^{-1}$). In addition, there is a further significant interaction between the out-of-phase combination of $d_{z^2}$ orbitals and the Sn$_5\pi a''_2$ orbital, which destabilises the antibonding combination to the extent that it constitutes the LUMO.
of the complex (8a′). This LUMO, an iso-surface plot which is shown in Figure 4, is clearly localised primarily on the Sn₅ ring, with relatively minor contributions from the out-of-phase combination of Cr d₂ orbitals.

**Figure 4.** Schematic molecular orbital diagram for [(CO)₃MSn₅M(CO)₃]⁴⁻. Note that the orbitals of the M(CO)₃, M₂(CO)₆ and Sn₅ fragments are labelled according to C₃ᵥ, D₃h and D₅h point symmetry, respectively. The cluster itself has only C₅ point symmetry.

4. Discussion

**Electron-Counting and Metal–Metal Bonding in Pentagonal Bipyramidal Clusters**

In order to place these new Sn₅ clusters into an appropriate context, it is useful to compare them to other 7-vertex cluster compounds with the same or similar formal electron counts. A useful point of comparison is with the 7-vertex main-group clusters Tl₄Bi₃³⁻ and Tl₇⁷⁻, the former synthesised recently by Dehnen [49] and co-workers and the latter by Corbett and co-workers in 2000 [12]. The [Tl₄Bi₃]³⁻ cluster has a total valence-electron count of 4n + 2 = 30, a skeletal-electron count of 2n + 2 = 16, and is a classically closo cluster with a distance of 4.086(3) Å between the two apical Tl atoms. Corbett’s Tl₇⁻ cluster, in contrast, has two electrons fewer (4n = 28) and is compressed along the principal axis, generating a short trans-annular Ti-Tl bond of 3.4622(9) Å. Its a′′₂-symmetric LUMO (the counterpart of which is occupied in [Tl₄Bi₃]³⁻), shown in Figure 5, has Ti-Tl π⁺ character around the equator, just like the LUMOs of [(CO)₃MSn₅M(CO)₃]⁴⁻, but also substantial Ti 6s character on the apical Tl atoms, and it is this feature that gives rise to the direct Ti-Tl bond [12,50].
How can we reconcile the well-established Wade’s rules electron-counting model used in these main-group clusters with the electronic structure of \([\text{(CO)}_3\text{MSn}_5\text{M(CO)}_3]^{4-}\)? Fässler and Kaupp formulated the skeletal electron count as \(2n = 14\), treating the Mo(CO)_3 fragment as a zero-electron donor. The assumption here is that the occupied 3d orbitals, including the 3d\(_{z^2}\) orbitals aligned along the principal axis, are not involved in the cluster bonding. The linear combinations of 3d\(_{z^2}\) are, however, the direct analogues of the 6s radial lone pairs in \([\text{Tl}_4\text{Bi}_3]^{7-}\), and if we do include these we reach a total-electron count of 28 (=4n), highlighting an isolobal analogy to Tl\(_7\)\(^{7-}\). So why, then, do we consider a trans-annular Tl-Tl bond to be present in the main-group cluster, but not in \([\text{(CO)}_3\text{MSn}_5\text{Cr(CO)}_3]^{4-}\)? The resolution to this question lies in the nature of the LUMO, and in particular its distribution over the five atoms of the equatorial ring and the two along the principal axis. To understand the significance of this orbital, we note that the hypothetical 30-electron (closo) clusters, \([\text{(CO)}_2\text{MSn}_5\text{Cr(CO)}_3]^{6-}\), can be formulated without ambiguity as a Sn\(_{6-}\) ring bridging two M\(_0\)(CO)_3 fragments, with no trans-annular bond. If the LUMO of the 28-electron cluster is an out-of-phase combination of orbitals on the apical atoms, a trans-annular bond is fully developed while the equatorial five-membered ring retains the full complement of six \(\pi\) electrons. At the opposite extreme, if the LUMO is localised entirely in the equatorial plane, the electron deficiency is accommodated in an anti-aromatic 4\(\pi\) ring while both in- and out-of-phase combinations of 3d\(_{z^2}\) are occupied, annihilating the trans-annular bond. The LUMOs shown in Figure 5 suggest that the amplitude of the LUMO is indeed shifted towards the apical atoms in Tl\(_7\)\(^{7-}\) compared to \([\text{(CO)}_3\text{CrSn}_5\text{Cr(CO)}_3]^{4-}\), justifying the rather different descriptions of bonding applied in the two cases. An even more extreme example of a trans-annular bond can be found in the P\(_5\)-bridged clusters, \(\text{CpCr}_5\text{CrCp}\) and \(\text{Cp'}\text{CrP}_5\text{CrCp'}\) and their one-electron reduced analogues (Figure 1e) [14,51]. The neutral Cp cluster has a Cr-Cr separation is 2.69(1) Å, considerably shorter than that in 1, and Hoffmann’s analysis of the bonding [52] concludes that there is indeed Cr-Cr bonding present. The one-electron reduced analogue \([\text{CpCrP}_5\text{CrCp}]^{-}\) noted in Scherer’s original report of the synthesis of the Cp\(^*\) compound [14] is particularly interesting in the present context because its total valence electron count of 28 establishes a further isolobal relationship to both Tl\(_7\)\(^{7-}\) and \([\text{(CO)}_3\text{CrSn}_5\text{Cr(CO)}_3]^{4-}\). The optimised structure of \([\text{CpCrP}_5\text{CrCp}]^{-}\) is summarised in Table 2, with full cartesian coordinates given in the Supplementary Materials: the Cr-Cr bond length of 2.61 Å is indicative of an even stronger Cr-Cr interaction than in the neutral species. The 28 available electrons in \([\text{CpCrP}_5\text{CrCp}]^{-}\) can either be partitioned to give a 6\(\pi\)-electron P\(_5\)\(^-\) ring and two d\(_5\) CpCr fragments (and hence a Cr-Cr bond) or, alternatively, as a 4\(\pi\)-electron P\(_5\)\(^+\) ring with two d\(_6\) CpCr\(^-\) fragments (and hence no Cr-Cr bond). The LUMO, shown in Figure 5c, is clearly strongly localised on the apical Cr atoms with relatively minor contributions on the equatorial P\(_5\) ring, confirming that the electron-deficiency is accommodated on the apical atoms.
An important point to take from this analysis is that there is no black-and-white distinction between the electronic structure models for [(CO)$_3$CrSn$_5$Cr(CO)$_3$]$^{4-}$, [CpCrP$_5$CrCp]$^-$ and Tl$_7^{-}$. All three share a common skeletal-electron count of 28, two fewer than the closo count of 30, and they constitute a continuum of situations defined by the shape of the LUMO, and hence by the way that the electron deficiency (relative to the closo form) is accommodated. In terms of the molecular orbital diagram shown in Figure 4, the limiting cases defined by [(CO)$_3$CrSn$_5$Cr(CO)$_3$]$^{4-}$ and [CpCrP$_5$CrCp]$^-$ are connected by a shift in the relative energies of the metal- and E$_5$-based fragments. A downward shift of the orbitals on the E$_5$ ring will increase the metal $d_{z^2}$ character in the LUMO, increasing the importance of the trans-annular bonded resonance form while an upward shift increases the contribution of the anti-aromatic 4π configuration. The Quantum Theory of Atoms in Molecules (QTAIM) offers an alternative perspective on the nature of the bonding in these systems, although we note that the separation of metal–metal and metal–ligand bonding remains far from simple [53]. The delocalisation index, $\delta$, offers a direct measure of Cr-Cr bond strength, and the values of 0.40 and 0.93 for [(CO)$_3$CrSn$_5$Cr(CO)$_3$]$^{4-}$ and [CpCrP$_5$CrCp]$^-$, respectively, correlate directly with the computed values for the Mayer bond order (0.39 and 0.72) extracted from the wavefunction itself (Table 2). A survey of the topology of the electron density identifies bond critical points (BCPs) midway between the Cr centres for both [(CO)$_3$CrSn$_5$Cr(CO)$_3$]$^{4-}$ and [CpCrP$_5$CrCp]$^-$ (see molecular graphs in Figure 5), but the electron density at the BCP ($\rho_{BCP}$) is considerably larger for the latter (0.055) than the former (0.028). Following Macchi’s classification of the local indicators of bond type [54], the balance between kinetic ($G_b$) and potential ($V_b$) energies is consistent with an open-shell-type interaction in both cases, although the local dominance of $V_b$ over $G_b$ in [CpCrP$_5$CrCp]$^-$ is indicative of enhanced covalent Cr-Cr character. All of the indicators, structural and electronic, are therefore consistent with the conclusion that Cr-Cr bonding is considerably stronger in [CpCrP$_5$CrCp]$^-$ than it is in [(CO)$_3$CrSn$_5$Cr(CO)$_3$]$^{4-}$. The Mayer bond order, delocalisation index and properties of the trans-annular BCP for the Tl$_7^{-}$ cluster suggest that it sits closer to [(CO)$_3$CrSn$_5$Cr(CO)$_3$]$^{4-}$ than to [CpCrP$_5$CrCp]$^-$ on this spectrum of bond types.

Figure 5. Contour plots of the LUMOs of (a) [(CO)$_3$CrSn$_5$Cr(CO)$_3$]$^{4-}$, (b) [CpCrP$_5$CrCp]$^-$ and (c) Tl$_7^{-}$ and the corresponding molecular graphs. Bond Critical Points (BCPs) are shown in the molecular graphs as orange dots.
Table 2. Comparison of Mayer bond orders (BO) and QTAIM parameters for the trans-Annular M-M Bond Critical Points (BCPs) for 28-electron M₂E₅ clusters, [(CO)₃Sn₅Cr(CO)₃]⁴⁻, [CpCrP₅CrCp]⁻, and Tl₇⁻.

|                  | [(CO)₃Sn₅Cr(CO)₃]⁴⁻ | [CpCrP₅CrCp]⁻ | Tl₇⁻⁻ |
|------------------|---------------------|---------------|--------|
| \( r_{M-M} / \text{Å} \) | 2.97                | 2.62          | 3.32   |
| BO \( M-M \)     | 0.39                | 0.72          | 0.31   |
| \( \delta M-M \) | 0.40                | 0.93          | 0.52   |
| \( \rho_{BCP} / \text{au} \) | 0.028               | 0.055         | 0.020  |
| \( G_B / \text{au} \) | 0.010               | 0.026         | 0.009  |
| \( V_B / \text{au} \) | -0.015              | -0.045        | -0.010 |

5. Conclusions

In this paper we have reported the synthesis and structural characterisation of two new cluster compounds, [(CO)₃Sn₅M(CO)₃]⁴⁻, \( M = \text{Cr, Mo} \), which feature a pair of zerovalent M(CO)₃ fragments bridged by a cyclo-Sn₅ unit. The Sn clusters are isostructural with the Pb analogue, [(CO)₃MoPb₅Mo(CO)₃]⁴⁻, reported previously by Fässler and co-workers. The LUMOs of both clusters have dominant Sn-Sn \( \pi \) character, consistent with their formulation as Sn₅⁻⁻ rings coordinated to two zero-valent M(CO)₃ fragments. The electronic structure makes a striking contrast with the isoelectronic [CpCrP₅CrCp]⁻ anion, where the relative energies of the orbitals on the E₅ and M₂ fragments are reversed, causing the LUMO to have dominant Cr-Cr \( \sigma^* \) rather than Sn-Sn \( \pi \) character. The Tl₇⁻⁻ cluster is isolobal with both clusters, and the axial compression in this hypo-electronic cluster is strikingly reminiscent of the short Cr-Cr bond in [CpCrP₅CrCp]⁻. These three 28-electron clusters therefore mark three distinct points on a continuum between two limits where (i) the LUMO is localised in the equatorial E₅ ring (as in [(CO)₃Sn₅M(CO)₃]⁴⁻), and (ii) the LUMO is localised on the M₂ caps, forming a trans-annular bond (as in [CpCrP₅CrCp]⁻). This continuum perspective establishes a link between apparently quite different electron-counting models.

Supplementary Materials: The following Supplementary Materials can be downloaded at: https://www.mdpi.com/article/10.3390/inorganics10060075/s1, Details of the crystallographic analysis (Figures S1–S5 and Tables S1 and S2), the ESI for 2 (Figures S6 and S7) and EDX (Figures S8 and S9) experiments. Cartesian coordinates of the optimized structures are given in Supporting Information, and quantitative MO diagrams for 1 and 2 are presented in Figure S10.

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Abbreviations

The following abbreviations are used in this manuscript:

DFT   Density Functional Theory
QTAIM Quantum Theory of Atoms in Molecules
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