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#### Introduction

As the area of heterobimetallic chemistry continues to attract attention,<sup>1–8</sup> it is of importance to consider heterobinuclear complexes that feature earth's most abundant metal, aluminium. Indeed, studying complexes with direct Al–M bonds has become a frontier area of research with applications in areas such as catalysis<sup>9–12</sup> and small molecule activation.<sup>13–20</sup> As these applications continue to emerge, it becomes increasingly important to understand the nature of Al–M bonding itself. Canonically, heterobinuclear complexes pairing d-block

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Complexes with Al–M bonds (M = transition metal) have emerged as platforms for discovering new reaction chemistry either through cooperative bond activation behaviour of the heterobinuclear unit or by modifying the properties of the M site through its interaction with the Al centre. Therefore, elucidating the nature of Al–M bonding is critical to advancing this research area and typically involves careful theoretical modelling. This Frontier article reviews selected recent case studies that included theoretical treatments of Al–M bonds, specifically highlighting complexes capable of cooperative CO<sub>2</sub> activation and focusing on extracting lessons particular to the Al–M sub-field that will inform future studies with theoretical/computational components.

> elements with aluminium are viewed as featuring electropositive aluminium centres serving as donor atoms (aluminyl "metalloligands") towards transition metal sites. According to this model, the unique reactivity of the transition metal site is imparted by this unconventional bond polarity *vis á vis* traditional coordination complexes with electronegative donor atoms. This bonding motif is certainly valid in some cases but may not be universal to all Al–M complexes.

> In this context, elucidating the electronic structures of Al–M bonds is critical. Because gaining this understanding will necessarily involve theoretical analysis, it is important to identify aspects of Al–M bonding that require special treatment theoretically.<sup>21</sup> Lessons learnt from such case studies will inform future research in this frontier area. In this Frontier article, we briefly review selected recent cases to summarise



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some important lessons that have emerged. We have chosen to use Al-M complexes that capture CO<sub>2</sub> as a venue. In the domain of anthropogenic greenhouse gases, carbon dioxide  $(CO_2)$  stands out as the primary contributor to global warming.<sup>22</sup> As atmospheric CO<sub>2</sub> levels continue to rise, there is an increasing urgency for developing innovative strategies to capture and valorise CO<sub>2</sub> to mitigate its environmental impact.<sup>23,24</sup> Transition metal complexes have long been known to present promising pathways for CO<sub>2</sub> capture due, in part to their ability to access multiple oxidation states during smallmolecule activation.<sup>25,26</sup> In addition to mononuclear and homobinuclear compounds, CO<sub>2</sub> activation by heterobinuclear complexes, particularly those combining main group and transition metal systems, continues to be an area of focus dating back to seminal observations by Floriani.27,28 As discussed herein, our group and several others have recently studied CO<sub>2</sub> activation with heterobinuclear complexes pairing d-block elements (e.g. Fe, Cu, Ag, Au) with aluminium.

# Nucleophilic Al–M (M = coinage metal) complexes: covalent *vs.* polarised bonding

#### Initial discovery & assignment of nucleophilic Au(-I)

In an influential 2019 report,<sup>29</sup> Hicks *et al.* synthesised (NON) Al-AuP<sup>t</sup>Bu<sub>3</sub> (1) by reacting the Al(I) nucleophile, K[Al(NON)], with the Au(1) complex, <sup>t</sup>Bu<sub>3</sub>PAuI (Scheme 1). The resulting Al-Au bond was found to be the shortest on record (2.40 Å). The Al-N and Al-O bond distances in 1 being shorter than in the K [Al(NON)] precursor was attributed by the authors to 2e<sup>-</sup> oxidation of Al(1) to Al(11) during the formation of 1. However, contributions of molecular charge (i.e., transforming an anion to a neutral species) to these bond contractions were not considered at the time. The authors' preliminary model for the short Al-Au interaction in **1** was that of a polarised  $Al^{\delta^+}-Au^{\delta^-}$ bond, *i.e.* resembling a strong  $[(NON)Al]^+ \leftarrow [AuP^tBu_3]^-$  dative interaction, based on the dramatically higher electronegativity of atomic Au (2.54) compared to atomic Al (1.61) on the Pauling scale. The implication that complex 1 contains a  $[AuP^tBu_3]^-$  fragment, and thus a gold centre with formally Au (-I) (auride) character, was provocative since most sub-valent

transition metal centres require stabilisation by strong  $\pi$ -acids like CO.<sup>30</sup>

The nature of the putatively  $Al^{\delta+}-Au^{\delta-}$  bond was investigated computationally in the same study using density functional theory (DFT), quantum theory of atoms in molecules (OTAIM), and natural orbitals for chemical valence (NOCV) calculations. QTAIM is a conceptual framework used in theoretical chemistry to understand the electronic structure of molecules through analysis of electron density distribution and topology.<sup>31,32</sup> In this case, partial atomic charges were assigned from OTAIM calculations based on the integration of electron density over each atomic basin found within the overall density map. NOCV is a method that identifies the natural bond orbitals (NBOs,<sup>33</sup> *i.e.*, localised wavefunctions resembling canonical Lewis structures) predominantly involved in chemical bonding.<sup>34</sup> Like in QTAIM, the NOCV orbitals are derived from analysis of the total electron density of the molecule rather than from arbitrary basis functions sometimes used in standard DFT and NBO calculations.

Comparison of QTAIM partial atomic charges for 1 to those of its synthetic precursors indicated transfer of ~1.6e<sup>-</sup> from  $[Al(NON)]^{-}$  to  $[AuP^{t}Bu_{3}]^{+}$  during Al-Au bond formation.<sup>29</sup> The most significant Al/Au NOCV interaction in 1 compared to its synthetic precursor fragments was calculated to be a  $\sigma$ -bond assigned by the authors as Al-to-Au lone pair donation. These two observations were used to justify the formal 2e<sup>-</sup> oxidation of Al(I) to Al(III) and formal  $2e^{-1}$  reduction of Au(I) to Au(-I) during formation of 1. However, one can argue that these analyses were biased because they relied on comparison of 1 to starting fragments defined by the theorists. In other words, the authors based their interpretations of NOCV and QTAIM calculations on comparison of 1 to its ionised fragments, [Al(NON)]- and  $[AuP^tBu_3]^+$ . However, DFT calculations disclosed in the same study instead indicated that the lowest energy pathway (by 37-62 kcal  $mol^{-1}$ <sup>35</sup> for Al-Au cleavage is not heterolytic but homolytic, *i.e.* to [Al(NON)] and [AuP<sup>t</sup>Bu<sub>3</sub>] fragments.<sup>29</sup> Thus, in contrast to the theoretical analyses described above and to use the authors' own words written in the article's ESI, "the bonding interaction should rather be considered as a conventional covalent bond instead of a coordination or some other dative bond". The further refinement of the bonding model for complex 1 as involving a highly covalent bond between formally  $Al(\pi)$  and Au(0) centres would emerge in later studies (see below).



Scheme 1 Synthesis and reactivity of a nucleophilic Al–Au bond originally reported by Hicks et al.<sup>29</sup> dipp = 2,6-di-iso-propylphenyl.

Based on the observations above and the fact that the QTAIM charge at the Au centre in 1 was calculated to be quite negative (-0.82 au), the authors hypothesised that complex 1 would be nucleophilic at gold, in stark contrast to the typical electrophilic chemistry of molecular gold complexes. Addition of  $CO_2$  gas to 1 resulted in metallacarboxylate species 2 in which the Au centre is C-bound to  $CO_2$  (Scheme 1). This reaction outcome was used by the authors as further evidence for the presence of a nucleophilic centre with Au(-I) character in 1 that had added to the electrophilic carbon centre of CO<sub>2</sub>. However, soon afterwards, the same team as well as Liu et al. showed that CO<sub>2</sub> inserts readily into corresponding Al-Ag, Al-Cu, and Al-Zn bonds (Fig. 1).<sup>36-39</sup> These lighter analogues were calculated to feature significantly less Al-M polarisation and less accumulation of negative charge on the d-block metal; yet, they reacted as (or more) efficiently with  $CO_2$  as 1. In the most extreme case, an Al-Zn bond was calculated to accumulate positive charge of 1.26 au on Zn and still react with CO<sub>2</sub> to form a metallcarboxylate species with a C-bound Zn centre.39 In other words, efficient CO2 activation to form AlO<sub>2</sub>C-M bonds does not correlate with nor require negative charge accumulation at M, thus negating the only experimental evidence for the presence of a nucleophilic Au(-I)-like ion in **1**. Indeed, as later pointed out by Sorbelli *et al.*,<sup>35</sup> even homobinuclear complexes (i.e., inherently apolar metal-metal bonds) efficiently insert CO<sub>2</sub> to form analogous metallacarboxvlate structures.

#### Re-interpretation as a covalent, nucleophilic Al-Au bond

In 2021, Sorbelli *et al.* revisited the computational analysis of **1** and its  $CO_2$  reactivity using DFT, extended transition state natural orbitals for chemical valence (ETS-NOCV), and charge displacement (CD) calculations.<sup>35</sup> ETS-NOCV is a theoretical method that combines aspects of both transition state theory

and NOCV analysis, essentially calculating changes in NOCV distributions occurring along a reaction coordinate.<sup>40</sup> CD further partitions this data into partial atomic charge contributions from individual components of the molecule(s).<sup>41</sup> Relatedly, the CD-NOCV method breaks down partial atomic charge density contributions that, together, comprise a covalent interaction.<sup>42</sup>

In their report,<sup>35</sup> the Sorbelli *et al.* disfavoured the nucleophilic auride model for **1**, instead proposing that **1** contains a highly covalent Al–Au bond that, itself, serves as the nucleophilic electron pair towards CO<sub>2</sub>. The previous use of Pauling electronegativity values to formulate a polarised  $Al^{\delta+}-Au^{\delta-}$ bond was contradicted by noting that the ionisation energies of the [Al(NON)]<sup>\*</sup> and [AuP<sup>t</sup>Bu<sub>3</sub>]<sup>\*</sup> fragments are calculated to be nearly identical (2.53 and 2.56 eV, respectively). The previous use of partial atomic charge calculations to support the  $Al^{\delta+}$ –  $Au^{\delta-}$  proposal was also called into question by noting that the partial atomic charge at Au in **1** varies from –0.83 to +0.22 au depending on the charge partitioning scheme used in the calculations.<sup>43</sup>

The overall CD-NOCV analysis of the Al–Au bond in **1** indicated only slight polarisation of  $0.05e^-$  towards the Au centre.<sup>35</sup> This was partitioned into two charge fluxes, one from Au towards Al and the other from Al towards Au, that approximately counterbalanced each other (Fig. 2). Based on these observations and others, the authors assigned the Al–Au bond in **1** as involving formally Al(II) and Au(0) centres engaged in a bond with a high degree of covalency. Based on the bidirectional charge fluxes apparent by CD-NOCV, the authors also chose to describe the nature of **1** as "diradical-like" despite the calculated Al–Au bond energy of 83 kcal mol<sup>-1</sup> precluding the formation of any radicals at standard conditions.<sup>35,44</sup> Indeed, complete active space self-consistent field (CASSCF) calculations (known to be more accurate than DFT) later reported



**Fig. 1** Selected Al–M bonds known to insert  $CO_2$  to form metallacarboxylates with *C*-bound M centres.<sup>29,36–39</sup> dipp = 2,6-di-isopropylphenyl.



**Fig. 2** CD-NOCV curves for the interaction between [Al(NON)]<sup>•</sup> and [AuP<sup>t</sup>Bu<sub>3</sub>]<sup>•</sup> fragments, with isodensity surfaces (1 me<sup>-</sup> a<sub>0</sub><sup>-3</sup>) shown for the two main deformation densities contributing to Al-Au bonding (charge flux: red  $\rightarrow$  blue). Image reproduced with permission from Sorbelli et al.<sup>35</sup>

by Guo *et al.* indicated that the contributions of open-shell configurations are small and that the active electrons remain paired throughout the  $CO_2$  activation pathway.<sup>45</sup> Thus, description of the chemistry of **1** as "diradical-like" is questionable, in our view.

In the 2021 study by Sorbelli *et al.*, the reaction pathway for **1** and CO<sub>2</sub> converting to **2** was calculated.<sup>35</sup> The calculated mechanism is, effectively, a [2 + 2] cycloaddition involving the Al–Au  $\sigma$ -bonding pair and one of the CO<sub>2</sub>  $\pi$ -bonding pairs, followed by rearrangement from  $\kappa^1$ -to  $\kappa^2$ -metallcarboxylate binding to aluminium. Interestingly, the calculated [2 + 2] transition state structure features the carbon centre of CO<sub>2</sub> interacting with *both* Au and Al (M–C Mayer bond orders of 0.26 and 0.16, respectively), consistent with the Al–Au bond (and not a formal auride centre) acting as the nucleophilic electron pair. An analogous transition state geometry was calculated in 2022 by Guo *et al.* (Fig. 3), who also found that the Al–C interaction is even more significant at the transition state for the reaction of an Al–Cu analogue.<sup>45</sup> ETS-NOCV calculations by Sorbelli *et al.* indicated that the major interaction



Fig. 3 Calculated transition state for CO<sub>2</sub> activation by  $1.^{35,44,45}$  Image reproduced with permission from Guo *et al.*<sup>45</sup>

during  $CO_2$  activation by 1 involves the transfer of electron density (0.33e<sup>-</sup>) from both Al and Au (specifically, from the Al-Au  $\sigma$ -bond region) to CO<sub>2</sub> (specifically, its LUMO).<sup>35</sup> Intrinsic bond orbital (IBO) calculations, which track changes in NBOs as a function of intrinsic reaction coordinate,<sup>46</sup> were performed by Guo et al.<sup>45</sup> The results (Fig. 4) agree with the results of Sorbelli et al. conceptually and are readily interpreted as involving flow of two reactive electron pairs: transformation of the Al-Au σ-bonding orbital into an Al-C σbonding orbital, and transformation of the  $CO_2$   $\pi$ -bonding orbital into an Al-O o-bonding orbital. Collectively, these computational models converge on the concept of the Al-Au σbond being the nucleophilic electron pair that adds to the  $CO_2$ carbon centre via a [2 + 2]-like transition state, with the C-bound rather than O-bound aurocarboxylate forming due to a secondary Lewis acid/base interaction between the Al site and the  $CO_2$  oxygen centre rather than being indicative of nucleophilic character at any individual atom within 1.

#### Cooperative CO<sub>2</sub> activation at a weak Al–Fe bond: frustrated radical pair behaviour

For about a decade (2012–2022), our group had studied (NHC) Cu–Fp complexes (NHC = *N*-heterocyclic carbene, Fp = FeCp (CO)<sub>2</sub>) with reactive Cu–Fe bonds.<sup>5,47,48</sup> All physical and computational data indicated that such complexes contained polar Cu<sup> $\delta+$ </sup>-Fe<sup> $\delta-$ </sup> bonds with Wiberg bond orders<sup>49</sup> of <0.5 and with



Fig. 4 IBO analysis of the reaction between 1 and CO<sub>2</sub>. Image reproduced with permission from Guo et al.<sup>45</sup>



Scheme 2 Synthesis and reactivity of a weak, covalent Al–Fe bond reported by Sinhababu *et al.*<sup>59</sup> dipp = 2,6-di-iso-propylphenyl.

an accumulation of negative charge at the Fe centres.<sup>50–52</sup> (Note that the proposed  $Cu^{\delta^+}$ –Fe<sup> $\delta^-$ </sup> polarisation opposes the relative Pauling electronegativity values: Cu, 1.90; Fe, 1.83.) As such, depending on reaction conditions, we typically proposed either that (NHC)Cu–Fp complexes react as Fe(0) nucleophiles (akin to the auride proposal of Hicks *et al.* discussed above) or that they dissociate heterolytically to reveal [(NHC)Cu]<sup>+</sup>[Fp]<sup>-</sup> ion pairs with frustrated Lewis pair (FLP)<sup>53,54</sup> behaviour.<sup>47,55–58</sup>

In 2022, our group synthesised LAl(Me)Fp (3) by reacting the metallonucleophile, KFp, with the Al(III)  $\beta$ -diketiminate complex, LAl(Me)I (Scheme 2, L =  $HC[MeCNdipp]_2^-$ , dipp = 2,6-di-iso-propylphenyl).<sup>59</sup> The resulting Al–Fe bond was found to be among the shortest on record (2.48 Å). Computational modelling revealed that the Al-Fe bond is significantly more covalent than the previously studied Cu-Fe systems, with a Wiberg bond order of >0.8 based on NBO calculations and with relatively less accumulation of negative charge at Fe according to theoretical QTAIM analysis. Moreover, whereas the heterolytic bond dissociation energy (BDE) of 3 to  $[LAlMe]^{+}[Fp]^{-}$  was calculated to be quite high (59 kcal mol<sup>-1</sup>), homolytic dissociation of 3 to the [LAIMe]'/[Fp]' radical pair was calculated to be energetically accessible (25 kcal  $mol^{-1}$ ) at standard conditions. Thus, while the polar Cu-Fe bonds previously studied by our group were viewed as masked FLPs, the covalent Al-Fe bond in 3 can be regarded as a masked frustrated radical pair (FRP).<sup>60-62</sup> Due to the covalent nature of the Al-Fe bond, oxidation state assignments have not been proposed in the literature for 3 and, arguably, are irrelevant to understanding chemical reactivity.

Exposure of **3** to  $CO_2$  gas provided metallacarboxylate species **4** (Scheme 2).<sup>59</sup> The mechanism for this transformation proposed by Sinhababu *et al.* is shown in Scheme 2. A reasonable pathway was calculated by DFT and, in accord with recent findings by Mears *et al.* on an Al–Cu system,<sup>21</sup> required the use of dispersion corrections to the DFT functional along with the inclusion of all ligand substituents (as opposed to use of simplified models). In the proposed mechanism, spontaneous homolytic Al–Fe dissociation from **3** releases [Fp]<sup>•</sup> and forms [LAlMe]<sup>•</sup> intermediate **A.** While the [LAlMe]<sup>•</sup> formula would indicate an Al( $\pi$ ) formal oxidation state, DFT calculation of spin density indicated that **A** is better assigned as having an Al( $\pi$ ) centre bound to the 1e<sup>-</sup> reduced form of L. As such, the redox non-innocence of L must contribute significantly to the low homolytic BDE of **3**. Coordination of CO<sub>2</sub> to the Lewis acidic Al( $\pi$ ) site in **A** produces [LAl(Me)(O=C=O)]<sup>•</sup> intermediate **B**. Finally, net 2e<sup>-</sup> reduction of CO<sub>2</sub> involves coupled delivery of 1e<sup>-</sup> from the non-innocent L ligand and 1e<sup>-</sup> from [Fp]<sup>•</sup> to generate  $\kappa^1$ -metallacarboxylate **C**, which rearranges to  $\kappa^2$ isomer **4**.

In support of this mechanistic proposal, a synthetic model of B, namely [LAl(Me)(O=CPh2)], was isolated experimentally by replacing CO<sub>2</sub> with benzophenone and characterised spectroscopically.59 An alternative mechanism involving heterolytic dissociation of 3 to the [LAIMe]<sup>+</sup>[Fp]<sup>-</sup> ion pair followed by FLPlike CO2 activation was ruled out based on the high heterolytic BDE calculated by DFT (see above) as well as FRP-like regioselectivity during ring opening of propylene oxide by 3.63 A concerted, [2 + 2]-like mechanism (such as that discussed in the previous section for 1 proposed by Sorbelli et al. and Guo et al.) involving direct engagement of  $CO_2$  with the covalent Al-Fe bond of 3 was ruled out based on the large and positive entropy of activation for CO2 insertion measured experimentally, as well as the fact that the Al-Fe homolytic BDE was computed to be lower than the [2 + 2] activation energy by  $\sim 15 \text{ kcal mol}^{-1}$ .

#### Conclusions

Since heterobinuclear metal-metal bonds between p-block and d-block metals are historically less studied than metalmetal bonds between two d-block metals, it is unsurprising that frontier Al–M complexes like **1** and **3** would challenge traditional bonding paradigms, require careful iterations of interpretation and re-interpretation, and give rise to unconventional reaction pathways. As briefly reviewed here, complex **1** was originally assigned as having a polar  $Al^{\delta+}-Au^{\delta-}$  bond featuring a nucleophilic gold centre assigned as formally Au(-I). Subsequent re-evaluations led to reassignment as a covalently bonded, nucleophilic [Al–Au] unit best formulated as involving formal  $Al(\pi)$  and Au(0) centres. Lessons from the analysis of **1** and its reaction pathways informed studies of Al–Fe complex **3**, which in turn provided additional lessons for the community to consider.

When analysing the nature of Al–M bonds, certain trends may be emerging based on case studies presented here:

• Al–M bonds tend to be more covalent than analogous M–M bonds involving only d-block metals. This may be due to the stronger valence orbital overlap imparted by greater s/p character at aluminium relative to predominantly d character of a transition metal substitute.

• These covalent Al–M bonds are best analysed theoretically relative to their neutral (radical) fragments, even if they are synthesised from ionic precursors experimentally. Often, this is evident by comparing homolytic *vs.* heterolytic BDEs computationally.

• Atomic electronegativity values can be misleading since they do not necessarily reflect the properties of an atom in a molecular setting.

• Partial atomic charge calculations are method-dependent,<sup>43</sup> making their absolute values sometimes misleading. It is more appropriate to focus on trends in partial atomic charges across a series of interrelated compounds.

• Al–M bonds can involve anomalously high levels of dispersion forces.<sup>21</sup> Partly for this reason, it can be useful to base theoretical analyses on full molecules rather than truncated model systems.

Additionally, some lessons emerge from these case studies regarding the analysis of reaction pathways (*e.g.*  $CO_2$  activation):

• For CO<sub>2</sub> activation by Al–M bonds, it is not necessary for there to be an accumulation of negative charge at M. Additionally, the formation of a *C*-bound metallacarboxylate does not necessarily imply that the M centre is, by itself, a nucleophilic site.

• For covalently bonded [Al-M] units, the assignment of oxidation states can be irrelevant or even misleading for interpreting reactivity behaviour. A parallel can be drawn to the Enemark-Feltham system for analysing covalent [M-NO]<sup>n</sup> units.<sup>64</sup>

• When making proposals about reaction mechanisms, it is more reliable to analyse *changes* in computed parameters over an entire reaction coordinate rather than focusing on the reactant Al–M bond itself.

• Where possible, one should measure experimental observables (*e.g.*, activation parameters) reporting on the nature of a transition state to validate theoretical conclusions and help rule out alternative mechanisms.

Given the vibrant activity in the Al–M space, we expect new discoveries in small molecule activation and catalysis to continue emerging from studies of these fascinating metal–metal bonds. We hope that the brief reflection presented here will aid this research community as it continues to progress.

### Author contributions

S. M. S. S. conceptualised the article and wrote the first draft. N. P. M. edited the manuscript and acquired funding.

#### Data availability

No primary research results have been included and no new data were generated as part of this review.

## Conflicts of interest

There are no conflicts to declare.

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