**What Singles out Aluminyl Anions? A Comparative Computational Study of the Carbon Dioxide Insertion Reaction in Gold—Aluminyl, —Gallyl, and —Indyl Complexes**

Diego Sorbelli,* Leonardo Belpassi,* and Paola Belanzoni*

**ABSTRACT:** Anionic aluminum(I) anions ("aluminyls") are the most recent discovery along Group 13 anions, and the understanding of the unconventional reactivity they are able to induce at a coordinated metal site is at an early stage. A striking example is the efficient insertion of carbon dioxide into the Au—Al bond of a gold—aluminyl complex. The reaction occurs via a cooperative mechanism, with the gold—aluminum bond being the actual nucleophile and the Al site also behaving as an electrophile. In the complex, the Au—Al bond has been shown to be mainly of an electron-sharing nature, with the two metal fragments displaying a diradical-like reactivity with CO$_2$. In this work, the analogous reactivity with isostructural Au—X complexes (X = Al, Ga, and In) is computationally explored. We demonstrate that a kinetically and thermodynamically favorable reactivity with CO$_2$ may only be expected for the gold—aluminyl complex. The Au—Al bond nature, which features the most (nonpolar) electron-sharing character among the Group 13 anions analyzed here, is responsible for its highest efficiency. The radical-like reactivity appears to be a key ingredient to stabilize the CO$_2$ insertion product. This investigation elucidates the special role of Al in these hetero-binuclear compounds, providing new insights into the peculiar electronic structure of aluminyls, which may help for the rational control of their unprecedented reactivity toward carbon dioxide.

**INTRODUCTION**

The problems connected with the increasing concentration of carbon dioxide in the atmosphere require a continuous effort toward the exploration of efficient and novel solutions for its capture and reduction. Among these, CO$_2$ capture with transition metal (TM) complexes is surely one of the most interesting, due to the well-known ability of TMs of activating structurally simple TM complexes bearing CO$_2$ also offer an ideal playground for characterizing in detail the CO$_2$ activation mechanisms.

In this framework, the exceptional reactivity of a molecular gold—aluminyl complex, [Bu$_4$PAnAu(NON)] (NON = 4,5-bis(2,6-diisopropylanilido)-2,7-dibutyl-9,9-dimethylxanthene, complex I) was recently reported, in which I was easily capable of capturing carbon dioxide at room temperature by inserting it into the Au—Al bond, yielding insertion product II (Scheme 1).3

Product II, with the CO$_2$ carbon atom coordinated to Au, was considered to be a probe for a nucleophilic reactivity at the gold site, due to the presence of a supposedly strongly polarized Au—Al bond, despite gold complexes being widely known for their electrophilic behavior.4−7 This became even more surprising when the CO$_2$ insertion into a slightly polarized copper—aluminyl bond was reported, featuring the same CO$_2$ insertion mode.8 Since a mechanistic description for the formation of II was missing, we have recently embarked in a thorough computational exploration of the reaction mechanism and of the nature of the Au—aluminyl bond in I.9 Our study revealed the bimetallic (Au—Al) activation of CO$_2$ with the Au—Al bond being the actual nucleophilic site with the reaction and Al also assisting the activation with the electrophilicity induced by its vacant valence 3p$_z$ orbital. We showed that the Au—Al bond is of the electron-sharing type, with Au and Al cooperatively inserting CO$_2$ with a radical-like reactivity.9

In accordance with above reactivity, a zinc—aluminyl complex featuring a highly covalent electron-rich Al—Zn bond was recently found to react with CO$_2$ forming an insertion product analogous to II.10 Following our work, a combined experimental and theoretical paper on the insertion of CO$_2$ into Cu—Al, Ag—Al, and Au—Al bonds appeared in the literature, showing a similar reaction mechanism also for Cu and Ag,11 in agreement with the TM—Al bond behaving as a nucleophilic site.

**Received:** November 16, 2021  
**Published:** January 6, 2022
Scheme 1. Complexes in This Worka

This novel and unexpected reactivity of aluminyls raises questions, mainly about the peculiar chemical nature of the aluminyl and its implications for a rational design of similar bimetallic compounds capable of reacting with carbon dioxide in analogous conditions. While the very recent aluminyls12 surely represent promising species for this aim, analogue Group 13 anions (boryls, gallyls) have been known for a longer time:12

Indeed, six-membered heterocyclic boryls have not been synthesized yet.25,26 However, aluminyl, gallyl, and indyl have a much larger singlet–triplet energy gap,23,24 which makes the synthesis of the corresponding heterocyclic anions (boryls, gallyls) have been known for a longer time:12

The aim of this work is to analyze and characterize systematically any analogy/difference between aluminyls and their heavier Group 13 analogues in the framework of the carbon dioxide insertion reaction. We computationally study here the insertion of CO2 in the model complexes I3 (Scheme 1). These complexes feature an Al, Ga and In anion with the same heterocyclic ring structure (XNON), X= Al, Ga, and In) combined with a common [tBu3PAu+] gold moiety. It is worth reminding that the aluminyl and indyl ligands in complexes IAl and IIn have been actually synthesized and characterized experimentally21,22 and that similar heterocyclic structures appear to be reasonably accessible for Ga. Analogous boryl complex IAl has not been included in this work since the constrained six-member heterocyclic ring structure (BNON) represents a poorly realistic model complex, not directly comparable to the aluminyl, gallyl, and indyl analogues. We mention that the experimentally accessible coinage-metal–boryl complexes possess mainly acyclic (such as the very recent gold boryl complex bearing a boryl with two o-tolyl substituents)14 or five-membered structures.15,24,27 A comparative study of the electronic structure of boryl/aluminyl anions, including a systematic analysis of the structural and substituent effects, is currently under way in our laboratory.

By exploring the reaction mechanism for the CO2 insertion and carrying out an extensive electronic structure analysis, we will highlight that despite all the complexes (IAl, IGa, and IIn) proceed toward the CO2 insertion with the same mechanism observed for complex I the reaction is kinetically and thermodynamically significantly disfavored for IGa and IIn complexes with respect to IAl. Upon detailed analysis, this is explained by the higher electron-sharing character of the Au–Al bond, which makes it a suitable active site for attacking CO2. A radical-like reactivity is shown here to be fundamental for stabilizing the CO2 insertion product.

■ RESULTS AND DISCUSSION

Reaction Mechanism. For CO2 insertion into the Au–Al bond of the [tBu3PAuAl(NON)] complex I, we found a two-step mechanism characterized (i) by a nucleophilic attack to the CO2 carbon atom performed by the Au–Al bond also assisted by the electrophilic Al "empty" p orbital, followed (ii) by a rearrangement driven by an electrophilic attack to the oxygen atom of CO2 by the aluminum center, leading to the formation...
of the insertion product where the CO₂ carbon atom is coordinated to gold and both the CO₂ oxygen atoms are coordinated to Al (complex II, see Scheme 1). Transition states and intermediate structures pointed out a radical-like insertion of CO₂ in the Au−Al bond, which was consistently shown to have mainly an electron-sharing character. In the following, we applied the same systematic computational strategy used in ref 9, that is, density functional theory (DFT) with inclusion of scalar relativistic effects, solvation (toluene), and dispersion corrections (see the “Computational Details” section), for the study of CO₂ insertion into the Au−X bond in complexes I (X = Al, Ga, and In) analogously to [tBu₃PAuAl(NON)], complexes I have been slightly simplified at the NON site by replacing the two Dipp substituents on the nitrogen atoms with phenyl groups (denoted as NON'). This modeling has been shown to give good agreement with available experimental geometrical data for complex I in ref 9.

The free energy profiles for all systems are shown in Figure 1. For the reader’s convenience we also include the reaction profile for the gold−aluminyl [tBu₃PAuAl(NON')] complex reported in ref 9. Optimized structures of reactants (RC), transition states (TSI, TSII), intermediates (INT), and products (PC) for [tBu₃PAuAl(NON')] and [tBu₃PAuX(NON')] (X = Al, Ga, and In) complexes are sketched with selected geometrical parameters in Figure 2, whereas fully optimized geometries for all the species involved in the whole path are reported in Figures S1−S4. Calculations of the singlet−triplet energy gap in [X(NON')]− (X = Al, Ga, and In) anions show that these systems are stable. In particular, it is large for [Al(NON')]− (1.47 eV) and even increases from [Ga(NON')]− to [In(NON')]− (2.14 and 2.23 eV, respectively).

The nucleophilic attack to the CO₂ carbon atom has a relatively low activation free energy barrier for all the complexes, with the lowest value for complex IAl (ΔG° = 6.6 kcal/mol), the highest for complex IGa (ΔG° = 16.2 kcal/mol), and intermediate for complexes I and IIn (ΔG° = 10.9 and 13.7 kcal/mol, respectively) (see Table S1 for the imaginary frequency values of TSI).

The nucleophilic attack to the CO₂ carbon atom has a relatively low activation free energy barrier for all the complexes, with the lowest value for complex IAl (ΔG° = 6.6 kcal/mol), the highest for complex IGa (ΔG° = 16.2 kcal/mol), and intermediate for complexes I and IIn (ΔG° = 10.9 and 13.7 kcal/mol, respectively) (see Table S1 for the imaginary frequency values of TSI).

The nucleophilic attack to the CO₂ carbon atom has a relatively low activation free energy barrier for all the complexes, with the lowest value for complex IAl (ΔG° = 6.6 kcal/mol), the highest for complex IGa (ΔG° = 16.2 kcal/mol), and intermediate for complexes I and IIn (ΔG° = 10.9 and 13.7 kcal/mol, respectively) (see Table S1 for the imaginary frequency values of TSI).

The nucleophilic attack to the CO₂ carbon atom has a relatively low activation free energy barrier for all the complexes, with the lowest value for complex IAl (ΔG° = 6.6 kcal/mol), the highest for complex IGa (ΔG° = 16.2 kcal/mol), and intermediate for complexes I and IIn (ΔG° = 10.9 and 13.7 kcal/mol, respectively) (see Table S1 for the imaginary frequency values of TSI).
found for the other systems to 160°. Thus, the structure of TSI\textsuperscript{Al} is quite unique and apparently difficult to rationalize, both in terms of structure and energy profile along the whole reaction path, particularly in light of its similarity to complex I. We will return on this interesting point at the end of this section.

The formation of intermediate INT\textsuperscript{X} shows substantial differences between systems containing Al and those involving the heavier Group 13 elements. INT\textsuperscript{X} is stabilized with respect to TSI\textsuperscript{X} by 20.5 and 17.1 kcal/mol for I and I\textsuperscript{Al}, respectively, and by only 6.2 and 0.2 kcal/mol for I\textsuperscript{Ga} and I\textsuperscript{In}, respectively, thus resulting in an exergonic step for I and I\textsuperscript{Al}, an endergonic step for I\textsuperscript{Ga} and a highly endergonic step for I\textsuperscript{In}. Nonetheless, the INT\textsuperscript{X} structures share some common features: (i) a slightly increased Au–X bond distance and (ii) an almost linear coordination of the 'Bu\textsubscript{3}PAu moiety to the carbon atom of CO\textsubscript{2}. Similar structures are also observed for transition states TSI\textsuperscript{X} (see Table S1 for imaginary frequency values of TSI\textsuperscript{Al}), in which the Au–X bond is significantly elongated and the second oxygen of CO\textsubscript{2} is approaching X. However, while for TSI\textsuperscript{II} and TSI\textsuperscript{Al} similar lower activation barriers are found (12.0 and 13.3 kcal/mol, respectively), TSI\textsuperscript{Ga} and TSI\textsuperscript{In} lie at a much higher energy, with corresponding higher ΔG\textsuperscript{Z} values (17.3 and 16.4 kcal/mol, respectively), suggesting that the INT\textsuperscript{X} to PC\textsuperscript{X} conversion would be less favorable for I\textsuperscript{Ga} and I\textsuperscript{In}. Remarkably, the reverse step from INT\textsuperscript{X} to RC\textsuperscript{X} is expected to be kinetically favorable for Ga and, particularly, for In, predicting that the reaction of I\textsuperscript{Ga} and I\textsuperscript{In} with CO\textsubscript{2} to give insertion products I\textsuperscript{Ga} and I\textsuperscript{In} is not feasible neither kinetically nor thermodynamically. Product complex PC\textsuperscript{X} (corresponding to compounds II and II\textsuperscript{X} in Scheme 1) has been calculated to be stable for I and I\textsuperscript{Al} (−13.2 and −14.2 kcal/mol, respectively) and highly unstable for I\textsuperscript{Ga} and I\textsuperscript{In} (15.6 and 19.1 kcal/mol, respectively). In our previous study, we investigated the possibility that the product complexes INT\textsuperscript{X} evolution to CO elimination\textsuperscript{3} and we found that the resulting oxide complex [′Bu\textsubscript{3}PAuOAl(NON\textsuperscript{′})][CO] is highly unstable (ΔG = 16.6 kcal/mol). Here, the corresponding [′Bu\textsubscript{3}PAuOX(NON\textsuperscript{′})][CO] (X = Al, Ga, and In) complexes have also been calculated to be unstable with ΔG = 14.9, 37.2, and 46.3 kcal/mol, respectively, consistent with the recent results reported in ref 11.

It can be clearly surmised that upon substitution of the Group 13 element the reactivity with CO\textsubscript{2} becomes much more difficult, thus signaling that key differences in the Au–X bond nature should be expected. However, before proceeding in the following sections to detail a comparative analysis of the electronic structures and nature of the Au–X bond in complexes I\textsuperscript{X}, precisely in order to rationalize these findings, we briefly return on the eye-catching differences in the transition state structures of I and I\textsuperscript{Al} (TSI\textsuperscript{X} and TSI\textsuperscript{Al}, respectively). This point is particularly interesting since the degree of activation of CO\textsubscript{2} is often monitored by following its bending distortion along the reaction path. For instance, in heterogeneous catalysis studies, the bending of the OCO angle in the surface-adsorbed CO\textsubscript{2} molecule relative to the gas-phase value of 180° (linear) has been proposed\textsuperscript{35} and widely accepted as a good indicator of activation. The interpretative framework lies on the fact that upon reduction the gas-phase CO\textsubscript{2} accepts electron charge in its molecule relative to the gas-phase value of 180° (linear) has been proposed\textsuperscript{35} and widely accepted as a good indicator of activation. The interpretative framework lies on the fact that upon reduction the gas-phase CO\textsubscript{2} accepts electron charge in its

Figure 2. Selected interatomic distances (in Å) and bond angles (degrees) are given with the sketched TSI, TSI\textsuperscript{X}, INT, INT\textsuperscript{X}, TSI\textsuperscript{II}, and PC, PC\textsuperscript{X} structures of I and I\textsuperscript{X} (X = Al, Ga, and In) complexes.
To clarify this issue, we explored the topology of the potential energy surface (PES) around each TS, by varying the Au–C and Al–O distances in the 2.90–2.40 and 2.60–2.30 Å ranges, respectively. The PES around TSI is shown in Figure 3.

We also explored the PES of carbon dioxide constrained at the geometry of the corresponding structure. The results for TSI are reported in Figure 4. The results for the other systems are
depicted in Figures S5–S7, and all the numerical values are reported in Tables S2–S5.

The analysis of the PES in Figure 3 is illuminating. It clearly shows that this bimetallic CO$_2$ activation occurs in a PES which is very flat around TSI in a wide range of interfragment distances, indicating that similar energies correspond to very different structures. Indeed, the energy varies overall in the tight 3 kcal/mol range. This becomes emblematic when considering the structure of CO$_2$ in each structure sampled along this PES cut (Figure 4). The CO$_2$ bending angle varies significantly along the PES and, in particular, tightens in the direction of both shorter Au–C and Al–O distances. As shown in Figure 4, these changes cause the associated distortion penalty of in-adduct CO$_2$ to increase in a much wider range (30 kcal/mol). In other words, in different structures the orbital interactions between I and CO$_2$ always efficiently counterbalance the variable and increasing distortion penalty of CO$_2$.

The complexity of the PES is further confirmed by the fact that we could locate an alternative transition state structure for complex I (TSI') with a very different structure with respect to TSI (CO$_2$ bending angles and the Au–C and Al–O distances are 159.5° and 2.818 and 2.314 Å for the former and 146.3° and 2.403 and 2.569 Å for the latter, respectively) which lies extremely close in energy (TSI’ is 2.2 and 0.9 kcal/mol higher than TSI in terms of electronic and Gibbs' free energy, respectively) and is almost isostructural with TSI$_{Al}$. Visualization of the vibrational modes associated with the imaginary frequency of TSI’ (~212.5 cm$^{-1}$) indicates (analogous to TSI) a concerted transition state associated with a vibrational mode involving Au–C, Al–O, and Al–C interactions. We should also mention that in ref 11, using a different computational protocol, a transition state has been reported which is very similar to that of TSI’ in Figure 3, consistent with the very flat PES we show here.

The PES around TSI$_{Al}$ (Figure S5) is also flat: Along the same scanned range of Al–O and Au–C distances around TSI$_{Al}$, an overall variation of 6 kcal/mol is observed, and as can be envisaged by the numerical data reported in Table S3, this range is even tighter right around TSI$_{Al}$. In the 2.550–2.900 Å and 2.300–2.600 Å ranges for the Au–C and Al–O distances, respectively, two structures with substantial geometrical differences (particularly concerning the CO$_2$ structure) have been found with a variation of less than 3 kcal/mol in the electronic energy. Concerning the PESs for TSI$_{Ga}$ and TSI$_{In}$, less flat PESs are found, with a variation of 7 and 8 kcal/mol in the overall scanned range, respectively, showing a steeper topology in the closest region to TSI$_{Al}$ (see Figures S6 and S7 and Tables S4 and S5), and suggesting that the orbital interactions between I$_{Ga}$ and I$_{In}$ and CO$_2$ may not be strong enough to efficiently counterbalance the geometrical distortion of CO$_2$.

Notably, as shown in Figure 2, the O–C–O angle is very similar for all the complexes at the INTX structure (124.1, 123.5,...
and 125.4° for INT\textsuperscript{Al}, INT\textsuperscript{Ga} and INT\textsuperscript{In}, respectively, and 124.6° for INT\textsuperscript{I}.\textsuperscript{9} Clearly, this indicates that, as for the intermediate structure, the bending angle of CO\textsubscript{2} does not represent a good parameter for quantitatively evaluating the capability of the different complexes of activating carbon dioxide, probably due to the cooperative role of Au and X in reacting with CO\textsubscript{2} (\textit{vide infra}). Very interestingly, these results are in nice agreement with the recent finding that the decrease of the OCO angle is not an appropriate indicator of CO\textsubscript{2} activation on semiconductor oxides.\textsuperscript{30} As a final remark, we should note that despite the change in the coordination at Al from a tridentate N,O,N\textsuperscript{−} to a bidentate N,N\textsuperscript{−} scaffold in 1 and 1\textsuperscript{d} very similar free energy reaction profiles and PES topology at the TSI have been found. Previous computational results on the electronic structures of the parent naked aluminyls\textsuperscript{12} suggested a possible role of the oxygen atom in the [Al(NON)]\textsuperscript{−} anion and a reduced N-to-Al \textit{z} donation (‘folded’ nonplanar [Al(NON)]\textsuperscript{−} vs planar [Al(NON)]\textsuperscript{−}), which seem here to have only a negligible effect on the reactivity of their gold complexes. A detailed analysis of the N-to-Al \textit{z} donation issue in the aluminyl scaffolds is still lacking, and it certainly deserves to be further investigated.

**Electronic Structure/Reactivity Relationship.** To further investigate the effect of the substitution of the Group 13 element on the reactivity discussed above, a comparative analysis of the electronic structure of the transition states and stationary points has been carried out. Several theoretical methods have been applied. In particular, we employed the Activation Strain Model (ASM), Energy Decomposition Analysis (EDA) in combination with ETS-NOCV, Charge Displacement (CD) analysis, and dual descriptors for chemical reactivity.

We start by decomposing the electronic energy reaction path connecting each RC\textsubscript{X} with the corresponding TSI\textsuperscript{X} and INT\textsuperscript{X} using the ASM,\textsuperscript{31–33} which decomposes the path into two contributions: the distortion penalty \(\Delta E_{\text{dist}}\) of the increasingly deformed reactants and the interaction \(\Delta E_{\text{int}}\) between these deformed reactants (see the Supporting Information for details). The ASM allows to get insights into the factors involved in the stabilization/destabilization of TSI\textsuperscript{X} and INT\textsuperscript{X} structures. The main results are reported in Figure 5 (\(\Delta E\) energy profile, \(\Delta E_{\text{stab}}\) and \(\Delta E_{\text{int}}\) in panels a–c, respectively) and discussed below. All the numerical ASM results are reported in Tables S6 and S7.

Upon inspection of Figure 5, we see that the activation barrier for 1\textsuperscript{Al} is the lowest (5.6 kcal/mol) due to an overall small distortion penalty (8.3 kcal/mol), which is efficiently counterbalanced by a small interaction stabilization (−2.7 kcal/mol). For 1\textsuperscript{Ga} and 1\textsuperscript{In}, the interaction stabilization (−12.5 and −12.4 kcal/mol, respectively) is not able to efficiently counterbalance the larger distortion penalty (26.1 and 27.5 kcal/mol, respectively), yielding higher activation barriers (13.6 and 15.1 kcal/mol), consistently with the \(\Delta G^\#\) values discussed in the previous section. As a comparison, the electronic energy activation barrier for 1 (8.9 kcal/mol) was found to result from a 21.8 kcal/mol distortion penalty efficiently counteracted by a −12.9 interaction stabilization.\textsuperscript{7} A complementary picture arises from the analysis of the differences between the three complexes at INT\textsuperscript{X}, where CO\textsubscript{2} presents a similar degree of distortion. Indeed, as it can be surmised from Figure 5a, the formation of INT\textsuperscript{Al} is only favored for X = Al (\(\Delta E = −17.9\) kcal/mol), whereas formation of INT\textsuperscript{Ga} and INT\textsuperscript{In} is energetically disfavored (\(\Delta E = +4.7\) and +10.6 kcal/mol, respectively). This is due to the increased distortion penalty which is differently counterbalanced by the interaction stabilization for the three complexes. As it can be seen from Figure Sb, from RC\textsuperscript{X} to INT\textsuperscript{X} a similarly increased distortion penalty is observed for all the three complexes, with I\textsuperscript{Al} having a slightly less increased penalty at INT\textsuperscript{Al} with respect to INT\textsuperscript{Ga} and INT\textsuperscript{In} (\(\Delta E_{\text{dist}}\) increases up to 85.4, 83.0, and 74.5 kcal/mol for I\textsuperscript{Al}, I\textsuperscript{Ga}, and I\textsuperscript{In}, respectively), consistent with the slightly less bent CO\textsubscript{2} structure in INT\textsuperscript{Al} (see Figure 2). The interaction stabilization, however, is significantly different, and the extent of the stabilization decreases sharply on going from INT\textsuperscript{Al} (\(\Delta E_{\text{int}} = −100.9\)) to INT\textsuperscript{Ga} (\(\Delta E_{\text{int}} = −80.7\) kcal/mol) and INT\textsuperscript{In} (\(\Delta E_{\text{int}} = −63.9\) kcal/mol).

To shed light on the nature of the interactions taking place when CO\textsubscript{2} approaches I\textsuperscript{Al}, we resort to the use of the EDA,\textsuperscript{44,45} and we applied the ETS-NOCV\textsuperscript{36} approach also in combination with the CD\textsuperscript{37}−\textsuperscript{39} function on both TSI\textsuperscript{X} and INT\textsuperscript{X} structures. All the results are reported in Tables S8–S9 and Figures S8–S14. The isodensity pictures of the main NOCV deformation orbitals associated with INT\textsuperscript{Al} are reported in Figure 5d.

By analyzing the nature of the interactions occurring at the three TSI\textsuperscript{X} and INT\textsuperscript{X}, the interaction scheme between CO\textsubscript{2} and the [Bu\textsubscript{3}PnAu(Al(NON))\textsuperscript{−}] is qualitatively unaltered, following the same scheme reported in ref 9 for TSI (see Figures S8–S14). As an example, for INT\textsuperscript{Al} in Figure 5d the interaction between the CO\textsubscript{2} and I\textsuperscript{Al} consists mainly of two opposite charge fluxes: a charge transfer from the Au–X bond toward the LUMO of CO\textsubscript{2} (\(\Delta \rho_{\text{p}}\)) and a charge transfer toward the vacant valence \(\rho_{\text{p}}\) orbital of the Group 13 element from the HOMO of CO\textsubscript{2} (\(\Delta \rho_{\text{p}}\)). We mention that the presence of these two active sites, namely, the Au–X bond and the \(\rho_{\text{p}}\) orbital of X as nucleophile and electrophilic centers, respectively, can be also visualized in the plot of the dual descriptors (nucleophilicity and electrophilicity) for chemical reactivity, introduced by Morell et al.\textsuperscript{40} (see Figure S15).

The decomposition into the donor and acceptor NOCV orbitals provides a clear picture of the nature of the molecular orbitals (MOs) involved in the interactions depicted above and points out significant differences between the systems under study. Concerning the NOCV deformation density \(\Delta \rho_{\text{f}}\) (see Figures S8, S10, and S12), in all cases the main acceptor MO is the LUMO of CO\textsubscript{2} while the main donor MOs are high-lying \(\sigma\) bonding molecular orbitals of the Au–X complex (namely, HOMO–1 for I\textsuperscript{Al} and I\textsuperscript{Ga} and HOMO–2 for I\textsuperscript{In}). However, a quantitative inspection of the atomic composition of these donor MOs reveals that the donor features of complexes I\textsuperscript{Ga} and I\textsuperscript{In} differ from those of I\textsuperscript{Al}. Indeed, as shown by the data reported in Table S10, while the energy of the MOs which mainly contribute to the donor NOCV is comparable for all three complexes, their atomic composition varies significantly. The plot and composition of the main donor MO of I\textsuperscript{Al} (HOMO–1, see Figure S8) clearly suggest an Au–Al-centered \(\sigma\) MO (overall 23.4 and 14.4% contribution from valence s and p orbitals of Au and Al, respectively). However, the HOMO–1 of I\textsuperscript{Ga} and HOMO–2 of I\textsuperscript{In} (main donor MOs, see Figures S10 and S12, respectively) are less centered on Au and Ga (16.0 and 4.8% contribution from Ga and Au, respectively) and on Au and In (17.0 and 8.2% contribution from In and Au, respectively), thus indicating a delocalization on the [(NON)]\textsuperscript{−} backbone and suggesting possibly less electron-rich (and less nucleophilic) Au–Ga and Au–In bonds. We quantitatively inspected the extent of the interaction and charge transfer occurring between the CO\textsubscript{2} and different complexes at INT\textsuperscript{X} by relying on the EDA, ETS-NOCV, and CD-NOCV approaches. The results are reported in Tables 1 and S9 and Figure S14.
decomposition of NOCVs into MOs presented above suggests that the element does change on descending along the Group. The results show that the interaction between Au and the Group 13 element X (X = Al, Ga, and In) Interaction in Intermediates INT\textsuperscript{Al}, INT\textsuperscript{Ga}, and INT\textsuperscript{In}, Respectively.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
 & INT\textsuperscript{Al} & INT\textsuperscript{Ga} & INT\textsuperscript{In} \\
\hline
$\Delta E_{\text{oi}}$ & $-272.9$ & $-246.2$ & $-193.8$ \\
$\Delta E_{\text{oi}}^\dagger$ & $-225.3$ & $-204.0$ & $-159.0$ \\
$\Delta E_{\text{oi}}^\ddagger$ & $-11.1$ & $-11.9$ & $-9.8$ \\
ICT\textsuperscript{Al} & 0.67 & 0.61 & 0.60 \\
ICT\textsuperscript{Ga} & 0.07 & 0.07 & 0.07 \\
ICT\textsuperscript{In} & 0.07 & 0.07 & 0.07 \\
$\Delta E$ & $-105.9$ & $-84.8$ & $-68.1$ \\
\hline
\end{tabular}
\caption{Main Results of the EDA, ETS-NOCV, and CD Analyses of the [CO\textsubscript{2}]−[Bu\textsubscript{3}PAu(X\textsuperscript{18}NON')] (X = Al, Ga, and In) Interaction in Intermediates INT\textsuperscript{Al}, INT\textsuperscript{Ga}, and INT\textsuperscript{In}, Respectively\textsuperscript{a}}
\end{table}

\textsuperscript{a}Energies are given in kcal/mol; charge transfer (CT) values are given in electrons (e).

From a quantitative perspective, data in Table 1 show that the activation process is favored for INT\textsuperscript{Al} over INT\textsuperscript{Ga} and INT\textsuperscript{In}. A much stronger interaction between INT\textsuperscript{Al} and CO\textsubscript{2} is observed at INT\textsuperscript{Al} (−105.9 kcal/mol) with respect to INT\textsuperscript{Ga} and INT\textsuperscript{In} (−84.8 and −68.1 kcal/mol). The same trend can be noticed for the orbital interaction energy $\Delta E_{\text{oi}}$ and the Au–X bond-to-CO\textsubscript{2} charge transfer (ICT)\textsuperscript{Al} values (0.67, 0.61, and 0.60 e for INT\textsuperscript{Al}, INT\textsuperscript{Ga}, and INT\textsuperscript{In}, respectively), in Table 1. Remarkably, the three complexes display very similar $\Delta E_{\text{oi}}^\dagger$ and ICT\textsuperscript{Al} values. These results show that the interaction between Au and the Group 13 element does change on descending along the group. The decomposition of NOCVs into MOs presented above suggests that Ga and In may feature a more polarized Au–X\textsuperscript{III} bond, which would be consistent with the weaker interaction between Au and the Group 13 element X. It consists mainly of two components that act in opposite directions: a gold-to-X ($\Delta \rho_{1\alpha}$) and an X-to-gold ($\Delta \rho_{1\beta}$) charge transfer of spherical ($\sigma$) symmetry. In addition to these, two collective gold-to-X $\pi$ back-donation components are also envisioned in each case (see Figures S16 S21), although their contribution is considerably smaller.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig6}
\caption{Isodensity surfaces (isodensity value 2 me/a\textsubscript{0}) of the main NOCV deformation densities ($\Delta \rho_{1\alpha}$ and $\Delta \rho_{1\beta}$) for the interaction between doublet [Bu\textsubscript{3}PAu] and [X\textsuperscript{18}NON’] fragments (X = Al, Ga, and In) in complexes INT\textsuperscript{Al}, INT\textsuperscript{Ga}, and INT\textsuperscript{In}. The charge flux is shown as red \rightarrow blue.}
\end{figure}

Features of the Au–X (X = Al, Ga, and In) Bond and the Impact on the Diradical-like Reactivity. The analysis of the features of the bond between gold and the Group 13 fragments may shed light into the differences in the reactivity observed above. To this aim we use a three-pronged approach: (i) We analyze the nature of the Au–X bond in complexes INT with the CD-NOCV and ETS-NOCV approaches in order to identify the basic nature of the Au–X in these complexes and the degree of polarization on descending along the Group 13. This method has been successfully applied to complex I where revealed the existence of an electron-sharing Au–Al bond. (ii) We assess the variability in the electronic structure of the [X\textsuperscript{18}NON’] fragments, by relying on the tools of conceptual DFT\textsuperscript{41,42} (i.e., studying the nature of the lone pairs of the anions by calculating their gas phase proton affinity and quantitatively comparing their HOMO energy). (iii) To assess the radical-like behavior of complexes INT\textsuperscript{Al} (if any) and its impact on the formation of the products INT\textsuperscript{Al}, we model the reactivity of the radical fragments [X\textsuperscript{18}NON’] and [Bu\textsubscript{3}PAu] with carbon dioxide.

In order to apply the CD-NOCV and ETS-NOCV approaches in a consistent way it is important to determine the most suitable fragmentation (i.e., charged singlet or neutral doublet [Bu\textsubscript{3}PAu] and [X\textsuperscript{18}NON’] fragments) for the most accurate description of the bond. Such an assessment, carried out with the protocol reported in refs 43 and 44, which is based on a comparative EDA, is shown in Tables S11–S13. It demonstrates that for all the complexes the most appropriate fragments for describing the Au–X bond are the neutral doublet fragments [Bu\textsubscript{3}PAu] and [X\textsuperscript{18}NON’]; since this fragmentation provides both the smaller orbital interaction and total interaction energies. Application of the NOCV-CD approach allows to quantify the differences between the three Au–X bonds, as shown in Figures 6 and 7 and Table 2. The complete results of the NOCV-CD analysis using neutral doublet fragments are reported in Table S14 and Figures S16–S21.

From a qualitative perspective, the bond picture between the [Bu\textsubscript{3}PAu] and [X\textsuperscript{18}NON’] fragments does not change upon substitution of the Group 13 element X. It consists mainly of two components that act in opposite directions: a gold-to-X ($\Delta \rho_{1\alpha}$) and an X-to-gold ($\Delta \rho_{1\beta}$) charge transfer of spherical ($\sigma$) symmetry. In addition to these, two collective gold-to-X $\pi$ back-donation components are also envisioned in each case (see Figures S16–S21), although their contribution is considerably smaller.

From a quantitative point of view, however, the amount of the two opposite charge fluxes changes substantially on descending along Group 13, as it can be clearly seen from the shape and extent of the CD-NOCV curves in Figure 7 and data in Table 2. By comparing the CD-NOCV curves, it is very clear that the gold-to-X ($\Delta \rho_{1\alpha}$) charge transfer increases in the order Al < Ga < In, thus suggesting that the polarization of the Au–X bond may increase on descending along the group. Quantitatively, for
the \( \text{[Al(}^{\text{NON}}\text{)]}^- \) fragment, we see indeed that the two fluxes are practically equivalent (associated CT values of \(-0.31\) and \(-0.30\) e for \( \Delta \rho_{\text{Cu}}^\alpha \) and \( \Delta \rho_{\text{Cu}}^\beta \), respectively), resulting in an overall very small net charge transfer \((-0.01)\) e that can be ascribed to the presence of a slightly polarized electron-sharing Au=Al bond. This picture is also very similar to that of the \( \text{[Bu}_3\text{P} \text{Au}]^- \text{[Al(}^{\text{NON}}\text{)]}^- \) bond reported in ref 9 and to that of a nonpolar covalent bond system, such as the homonuclear \( \text{Au}_2 \) molecule (see Figure S8 in the Supporting Information of ref 9).

For the bond involving the \( \text{[Ga(}^{\text{NON}}\text{)]}^- \) fragment, while the extent of the Ga-to-Au donation remains practically unaltered (0.29 e), the \( \Delta \rho_{\text{Cu}}^\beta \) component related to the Au-to-Ga charge increases \((-0.37)\) e, thus representing a more polarized \( \text{Au}^\text{III} \text{-Ga}^\text{III} \) bond (net charge transfer \(-0.08)\) e. For the \( \text{[Bu}_3\text{P} \text{Au}]^- \text{[In(}^{\text{NON}}\text{)]}^- \) bond, the difference is even more pronounced, with a CT\(^\beta \) of \(-0.42\) e for the donation toward indium and a more negative net charge transfer \((-0.16)\) e. The associated \( \Delta E_{\text{st}}^{\beta} \) values follow the same trend, with \( \text{Ga}^\text{III} \) having the less negative value \((-33.1)\) kcal/mol which increases for both \( \text{Ga}^\text{I} \) and \( \text{In}^\text{I} \) \((-45.7)\) and \(-4.3)\) kcal/mol, respectively.

The different tendency of Al, Ga, and In to form electron-sharing type bonds with Au can be further inferred by relying on the tools of conceptual DFT\(^{44,45}\) (see the “Methodology” section in the Supporting Information for details). By using global DFT descriptors (Table S15) on the neutral species, one can easily see that \( \text{[Ga(}^{\text{NON}}\text{)]}^- \) and \( \text{[In(}^{\text{NON}}\text{)]}^- \) are more likely to retain the negative charge with respect to the \( \text{[Al(}^{\text{NON}}\text{)]}^- \) fragment. For instance, the electrophilicity \( (\omega^-) \) index peaks at the indium fragment \((2.58)\) and descends toward gallium \((2.15)\) and more rapidly toward the \( \text{[Al(}^{\text{NON}}\text{)]}^- \) fragment \((1.68)\), consistent with the increased tendency of gallium and indium fragments to accept electrons from gold. The nucleophilicity \( (\omega^+) \) index follows, coherently, the opposite trend, decreasing from Al toward In \((values\) are \(0.17, 0.14,\) and \(0.13)\) for Al, Ga, and In fragments, respectively.

The evaluation of the strength and basicity of the lone pair of the \( \text{[X(}^{\text{NON}}\text{)]}^- \) anions also gives an idea of the different nature of these species.\(^{45}\) On the basis of the gas phase proton affinity and the corresponding HOMO energy and composition properties, the \( \text{[Al(}^{\text{NON}}\text{)]}^- \) fragment emerges as the most reactive and basic anion \((proton\) affinity \(-354.5)\) kcal/mol vs \(-334.8\) and \(-294.2\) kcal/mol for \( \text{[Ga(}^{\text{NON}}\text{)]}^- \) and \( \text{[In(}^{\text{NON}}\text{)]}^- \)\), respectively, see Table S16). The peculiarity of the \( \text{[Al(}^{\text{NON}}\text{)]}^- \) lone pair with respect to those of \( \text{[Ga(}^{\text{NON}}\text{)]}^- \) and \( \text{[In(}^{\text{NON}}\text{)]}^- \) is immediately evident by inspection of the isodensity pictures of the corresponding HOMOs, reported in Figure 8.

The \( \text{[Al(}^{\text{NON}}\text{)]}^- \) HOMO is very diffuse and mainly centered at the Al site, whereas on descending toward Ga and In, the HOMO becomes much less diffuse and more delocalized on the \( (\text{NON})^- \) ligand. The HOMO energy and nature for these anions are also consistent with this trend and with the proton affinities trend: the HOMO energy for the aluminyl is the highest \((-0.356)\) eV, whereas gallyl and indyl anions have more stabilized HOMOs \((-1.095\) and \(-1.320)\) eV, respectively), thus reflecting the higher basic character of the aluminyl. Consistently, while the aluminyl HOMO has atomic contributions mostly from s and p orbitals of Al (more than 80%), the gallyl and indyl HOMO contains analogous contributions, but to a much lesser extent (in both cases below 50%), thus

\[
\begin{array}{|c|c|c|c|c|}
\hline
\text{X} & \Delta E_{\text{st}}^{\alpha} & CT^{\alpha} & \Delta E_{\text{st}}^{\beta} & CT^{\beta} \\
\hline
\text{Al} & -33.1 & -0.31 & -23.4 & 0.30 \\
\text{Ga} & -47.4 & -0.37 & -21.5 & 0.29 \\
\text{In} & -45.3 & -0.42 & -20.3 & 0.26 \\
\hline
\end{array}
\]

\(\Delta E_{\text{st}}^{\alpha,\beta}\) values are associated to the first NOCV deformation density and to the corresponding \(\alpha\) and \(\beta\) components of the interaction between neutral doublet \(\text{[Bu}_3\text{P} \text{Au}]^- \text{[X(}^{\text{NON}}\text{)]}^- \) fragments \((X = \text{Al, Ga, and In})\) for complexes \(\text{I}^\text{I}, \text{I}^\text{II}\) and \(\text{I}^\text{III}\).
indicating more ligand-centered MOs, coherently with their lower basic power and reactivity (see Table S16). On the basis of these results, two canonical resonance structures can be drawn for explaining the changing bonding scheme, as depicted in Scheme 2.

Structure a in Scheme 2 represents a purely electron-sharing bond between Au and X, while canonical structure b refers to a polarized dative-type bond in which the fragment bearing X behaves more like a ligand toward gold. On the basis of the CD-NOCV analysis, it is clear that in complex IAl an almost pure electron-sharing type bond between Au and Al occurs, with structure a being the dominant one. Such a bond is only slightly polarized, which is consistent with its remarkable ability of activating carbon dioxide as a nucleophile (see also the previous discussion in ref 9 and on the mechanism depicted in the previous section). Indeed, for the [′Bu3PAuC=OAl(NON)′] complex, the electron-sharing character of the Au–Al bond was strictly related to the two fragments behaving cooperatively like radicals for the carbon dioxide insertion, leading to the ′[′Bu3PAuCO2Al(NON)′] product. Since a similar insertion product has been also calculated for complexes [IAl, IGa, and IIn], an analogous geometric and energetic assessment of the radical-like behavior can be carried out.

From a structural perspective, optimization of the open shell radical [CO2X(NON)−]− (X = Al, Ga, and In) anions. Isovalue is 30 me/a0.

**Figure 8.** Isodensity pictures of the HOMO of the three [X(NON)−]− (X = Al, Ga, and In) anions. Isovalue is 30 me/a0.

At this stage, it is worth investigating if such differences in the Au–X bond reflect into differences on the radical-like behavior of the fragments (which is an expected behavior, at least for complex IAl, based on the results reported in ref 9 and on the mechanism depicted in the previous section). Indeed, for the [′Bu3PAuAl(NON)′] complex, the electron-sharing character of the Au–Al bond was strictly related to the two fragments behaving cooperatively like radicals for the carbon dioxide insertion, leading to the [′Bu3PAuCO2Al(NON)′] product. Since a similar insertion product has been also calculated for complexes [IAl, IGa, and IIn], an analogous geometric and energetic assessment of the radical-like behavior can be carried out.

From a structural perspective, optimization of the open shell radical [CO2X(NON)−]− (X = Al, Ga, and In) anions. Isovalue is 30 me/a0.

**Figure 8.** Isodensity pictures of the HOMO of the three [X(NON)−]− (X = Al, Ga, and In) anions. Isovalue is 30 me/a0.

At this stage, it is worth investigating if such differences in the Au–X bond reflect into differences on the radical-like behavior of the fragments (which is an expected behavior, at least for complex IAl, based on the results reported in ref 9 and on the mechanism depicted in the previous section). Indeed, for the [′Bu3PAuAl(NON)′] complex, the electron-sharing character of the Au–Al bond was strictly related to the two fragments behaving cooperatively like radicals for the carbon dioxide insertion, leading to the [′Bu3PAuCO2Al(NON)′] product. Since a similar insertion product has been also calculated for complexes [IAl, IGa, and IIn], an analogous geometric and energetic assessment of the radical-like behavior can be carried out.

From a structural perspective, optimization of the open shell radical [CO2X(NON)−]− (X = Al, Ga, and In) anions. Isovalue is 30 me/a0.

**Figure 8.** Isodensity pictures of the HOMO of the three [X(NON)−]− (X = Al, Ga, and In) anions. Isovalue is 30 me/a0.

At this stage, it is worth investigating if such differences in the Au–X bond reflect into differences on the radical-like behavior of the fragments (which is an expected behavior, at least for complex IAl, based on the results reported in ref 9 and on the mechanism depicted in the previous section). Indeed, for the [′Bu3PAuAl(NON)′] complex, the electron-sharing character of the Au–Al bond was strictly related to the two fragments behaving cooperatively like radicals for the carbon dioxide insertion, leading to the [′Bu3PAuCO2Al(NON)′] product. Since a similar insertion product has been also calculated for complexes [IAl, IGa, and IIn], an analogous geometric and energetic assessment of the radical-like behavior can be carried out.

At this stage, it is worth investigating if such differences in the Au–X bond reflect into differences on the radical-like behavior of the fragments (which is an expected behavior, at least for complex IAl, based on the results reported in ref 9 and on the mechanism depicted in the previous section). Indeed, for the [′Bu3PAuAl(NON)′] complex, the electron-sharing character of the Au–Al bond was strictly related to the two fragments behaving cooperatively like radicals for the carbon dioxide insertion, leading to the [′Bu3PAuCO2Al(NON)′] product. Since a similar insertion product has been also calculated for complexes [IAl, IGa, and IIn], an analogous geometric and energetic assessment of the radical-like behavior can be carried out.

From a structural perspective, optimization of the open shell radical [CO2X(NON)−]− (X = Al, Ga, and In) anions. Isovalue is 30 me/a0.

**Figure 8.** Isodensity pictures of the HOMO of the three [X(NON)−]− (X = Al, Ga, and In) anions. Isovalue is 30 me/a0.

At this stage, it is worth investigating if such differences in the Au–X bond reflect into differences on the radical-like behavior of the fragments (which is an expected behavior, at least for complex IAl, based on the results reported in ref 9 and on the mechanism depicted in the previous section). Indeed, for the [′Bu3PAuAl(NON)′] complex, the electron-sharing character of the Au–Al bond was strictly related to the two fragments behaving cooperatively like radicals for the carbon dioxide insertion, leading to the [′Bu3PAuCO2Al(NON)′] product. Since a similar insertion product has been also calculated for complexes [IAl, IGa, and IIn], an analogous geometric and energetic assessment of the radical-like behavior can be carried out.

From a structural perspective, optimization of the open shell radical [CO2X(NON)−]− (X = Al, Ga, and In) anions. Isovalue is 30 me/a0.

**Figure 8.** Isodensity pictures of the HOMO of the three [X(NON)−]− (X = Al, Ga, and In) anions. Isovalue is 30 me/a0.

At this stage, it is worth investigating if such differences in the Au–X bond reflect into differences on the radical-like behavior of the fragments (which is an expected behavior, at least for complex IAl, based on the results reported in ref 9 and on the mechanism depicted in the previous section). Indeed, for the [′Bu3PAuAl(NON)′] complex, the electron-sharing character of the Au–Al bond was strictly related to the two fragments behaving cooperatively like radicals for the carbon dioxide insertion, leading to the [′Bu3PAuCO2Al(NON)′] product. Since a similar insertion product has been also calculated for complexes [IAl, IGa, and IIn], an analogous geometric and energetic assessment of the radical-like behavior can be carried out.

From a structural perspective, optimization of the open shell radical [CO2X(NON)−]− (X = Al, Ga, and In) anions. Isovalue is 30 me/a0.

**Figure 8.** Isodensity pictures of the HOMO of the three [X(NON)−]− (X = Al, Ga, and In) anions. Isovalue is 30 me/a0.

At this stage, it is worth investigating if such differences in the Au–X bond reflect into differences on the radical-like behavior of the fragments (which is an expected behavior, at least for complex IAl, based on the results reported in ref 9 and on the mechanism depicted in the previous section). Indeed, for the [′Bu3PAuAl(NON)′] complex, the electron-sharing character of the Au–Al bond was strictly related to the two fragments behaving cooperatively like radicals for the carbon dioxide insertion, leading to the [′Bu3PAuCO2Al(NON)′] product. Since a similar insertion product has been also calculated for complexes [IAl, IGa, and IIn], an analogous geometric and energetic assessment of the radical-like behavior can be carried out.

From a structural perspective, optimization of the open shell radical [CO2X(NON)−]− (X = Al, Ga, and In) anions. Isovalue is 30 me/a0.

**Figure 8.** Isodensity pictures of the HOMO of the three [X(NON)−]− (X = Al, Ga, and In) anions. Isovalue is 30 me/a0.
important in terms of reactivity is the energy separation between the key occupied and unoccupied MOs (HOMO −1 and LUMO for IAl, HOMO −2 and LUMO for IGa and In), which is very similar for all the three complexes. However, a correlation can be found for the occupied donor MO energies, with IAl showing the highest energy donor HOMO −1 (−5.01 eV), and IGa and In showing a lower energy donor HOMO −2 (−5.29 and −5.34 eV, respectively), consistent with the lowest first step barrier calculated for IAl.

Finally, the possibility that the gold–aluminyl complex would be better described as a diradical rather than a closed-shell singlet has been explored. The reaction profile for complex I has been calculated at the open-shell (unrestricted) singlet level, attaining the same geometries and energies as those calculated at closed-shell (restricted) one, whereas the triplet spin reaction profile is much higher in energy. For instance, the electronic energy difference between the singlet and triplet spin states for complex I is 66.6 kcal/mol.

Table 3. Reaction Energies (ΔE) for Exchange (i) and Association (ii) and (iii) Reactions Involving Open Shell Neutral Radical [X(SiNON′)]· (X = Al, Ga, and In) and [tBu3PAu]· Fragments Reacting with CO2

| reaction  | ΔE (kcal/mol) |
|-----------|---------------|
|           | X = Al  | X = Ga  | X = In  |
| (i)       | −2.2    | 17.9    | 27.5    |
| (ii)      | −12.5   | 7.7     | 17.3    |
| (iii)     |         | [tBu3PAu]· | −10.3   |

In this work, we have computationally investigated the reactivity toward carbon dioxide and the electronic structure of a series of isostructural gold complexes, in which the gold center is coordinated to a heterocyclic anion of Group 13 elements (Al, Ga, and In).

Both the reaction mechanism and the trends in the electronic structure along the reaction path of all the complexes reveal that the gold–aluminyl complex represents a peculiar case. Indeed, it features the lowest activation barriers and is the only complex for which the insertion product formation is calculated to be exothermic. This different reactivity with CO2 reflects changes in the electronic structure of these compounds upon element substitution. By investigating the interactions taking place along the reaction path, it clearly emerges that while in all the cases the same mechanism is observed (i.e., Au–X bond acting as a nucleophilic site coupled with the vacant npz orbital of the Group 13 element behaving as an electrophilic site), the gold–aluminyl bond is the most apolar electron-sharing-type bond featuring an enhanced capacity of activating and stabilizing carbon dioxide. All the other Au–X bonds show a decreasing electron-sharing character with an increasing Auδ+ − Xδ− polarization when descending along the group toward the heavier elements Ga and In, which, in turn, makes the activation of CO2 much harder both kinetically and thermodynamically. Aluminyl anion is so special because of the highly electron-sharing nature of the Au–Al bond. The decreasing electron-sharing character for gallyl and indyl gold complexes accounts for the endergonic formation of their carbon dioxide insertion products, thus showing that a radical-like reactivity is crucial for CO2 capture.

This work fits in the framework of new perspectives on this novel and unconventional reactivity, highlighting the singularity...
of the aluminyl anions and, more generally, revealing that the kinetics and thermodynamics of TM–X cooperative processes for the activation of carbon dioxide are strictly related to the degree of the electron-sharing character of the TM–X bond, which represents a critical factor for the rational control of this reactivity. In an even more general framework, we also find that carbon dioxide bending is not a good indicator of its activation, similar to what is currently emerging in heterogeneous catalysis, making these TM–X complexes promising good models for studying CO$_2$ fixation into nucleophilic/electrophilic sites-containing heterogeneous catalysts.

**COMPUTATIONAL DETAILS**

All geometry optimizations and frequency calculations on optimized structures (minima with zero imaginary frequencies and transition states with one imaginary frequency) for the CO$_2$ insertion into the [Bu$_3$PAuX(SiNON)]$^-$ (X = Al, Ga, and In) complexes reaction have been carried out using the Amsterdam Density Functional (ADF) code, 46,47 in combination with the related Quantum-regions Inter-connected by Local Description (QUILD) program. 48 The PBE 49 GGA exchange-correlation (XC) functional, the TZ2P basis set with a Hamiltonian 50 small frozen core approximation for all atoms, the ZORA Hamiltonian 50–52 for treating scalar relativistic effects, and the Grimme’s D3-BJ dispersion correction were used. 53,54 Solvent effects were modeled employing the Conductor-like Screening Model (COSMO) with the default parameters for toluene as implemented in the ADF code. 55 The same computational setup has also been used for the EDA, CD-NOVC, and ASM calculations and for computing the radical reactions between [X(SiNON)]$^-$, [CO$_2$]$,^-$ and [Bu$_3$PAu]$_2$ fragments. Gas-phase calculation of conceptual DFT descriptors and proton affinities have been carried out by excluding solvent effects from the same computational protocol. This protocol has been used successfully in refs 3 and 9 to study the [Bu$_3$PAuAl(NON)]$^-$ and [Bu$_3$PAuCO$_2$Al(NON)]$^-$ complexes. For further details and description of the methods used in this work, see the “Methodology” section in the Supporting Information.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c03579.

Methodology, imaginary frequencies of TSI$^-$ and TSII$^-$, energies associated with the PESs, ASM results, EDA, ETS-NOVC and NOCV-CD analysis of TSI$^-$ and INT$^-$, energy and composition of donor MOs of T$_3^-$, comparative EDA for complexes T$_1$, NOCV results on T$_1$, conceptual DFT results on Au and X fragments, proton affinity and anion’s HOMO analysis of [X(SiNON)]$^-$, optimized structures of T$_1$, RC$_3^-$, TSI$^-$, INT$^-$, TIS$^-$, and PC$_3$ complexes, PESs around T$_1$, NOCV analysis of TS$_1$, NOCV analysis of INT$^-$, dual descriptor plots, CD-NOVC results on T$_1$, schematic geometries of radical [CO$_2$X(SiNON)]$^-$ fragments, spin densities of [X(SiNON)]$^-$ radicals, xyz coordinates of all structures (PDF).

**AUTHOR INFORMATION**

Corresponding Authors

Diego Sorbelli – Department of Chemistry, Biology and Biotechnologies, University of Perugia, 06123 Perugia, Italy; orcid.org/0000-0002-1348-1371; Email: diegosorbelli00@gmail.com

Leonardo Belpassi – CNR Institute of Chemical Science and Technologies “Giulio Natta” (CNR-SCITEC), 06123 Perugia, Italy; orcid.org/0000-0002-2888-4990; Email: leonardo.belpassi@cnr.it

Paola Belanzoni – Department of Chemistry, Biology and Biotechnologies, University of Perugia, 06123 Perugia, Italy; CNR Institute of Chemical Science and Technologies “Giulio Natta” (CNR-SCITEC), 06123 Perugia, Italy; orcid.org/0000-0002-1286-9294; Email: paola.belanzoni@unipg.it

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c03579

**Author Contributions**

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors thank the Ministero dell’Università e della Ricerca (MUR, project AMIS, through the program “Dipartimenti di Eccellenza –2018–2022”) for funding, and P.B. acknowledges additional support from the University of Perugia through “Fondo Ricerca di Base 2019”.

**REFERENCES**

1. Global Monitoring Laboratory. Carbon Cycle Greenhouse Gases. https://gml.noaa.gov/ccgg/.
2. Paparo, A.; Okuda, J. Carbon Dioxide Complexes: Bonding Modes and Synthetic Methods. Coord. Chem. Rev. 2017, 334, 136–149.
3. Hicks, J.; Mansikkamäki, Å.; Vasko, P.; Goicoechea, J. M.; Aldridge, S. A Nucleophilic Gold Complex. Nat. Chem. 2019, 11 (3), 237–241.
4. Obradors, C.; Echarvaren, A. M. Intriguing Mechanistic Labyrinths in Gold(1) Catalysis. Chem. Commun. 2014, 50, 16–28.
5. Wang, Y.-M.; Lackner, A. D.; Toste, F. D. Development of Catalysts and Ligands for Enantioselective Gold Catalysis. Acc. Chem. Res. 2014, 47 (3), 889–901.
6. Hashmi, A. S. K. Dual Gold Catalysis. Acc. Chem. Res. 2014, 47 (3), 864–876.
7. Zhang, L. A Non-Diazoo Approach to α-Oxo Gold Carbenes via Gold-Catalyzed Alkyn Oxidation. Acc. Chem. Res. 2014, 47 (3), 877–886.
8. Liu, H.; Schwamm, R. J.; Hill, M. S.; Mohon, M. F.; McMullin, C. L.; Rajabi, N. A. Ambiphilic Al–Cu Bonding. Angew. Chem., Int. Ed. 2021, 60 (26), 14390–14393.
9. Sorbrelli, D.; Belpassi, L.; Belanzoni, P. Reactivity of a Gold-Aluminyl Complex with Carbon Dioxide: A Nucleophilic Gold? J. Am. Chem. Soc. 2021, 143 (36), 14433–14437.
10. Roy, M. M. D.; Hicks, J.; Vasko, P.; Heilmann, A.; Baston, A.; Goicoechea, J. M.; Aldridge, S. Probing the Extremes of Covalency in M–Al Bonds: Lithium and Zinc Aluminyl Compounds. Angew. Chem., Int. Ed. 2021, 60 (41), 22301–22306.
11. McManus, C.; Hicks, J.; Cui, X.; Zhao, L.; Frenking, G.; Goicoechea, J. M.; Aldridge, S. Coinage Metal Aluminyl Complexes: Probing Regiochemistry and Mechanism in the Insertion and Reduction of Carbon Dioxide. Chem. Sci. 2021, 12 (40), 13458–13468.
12. Hicks, J.; Vasko, P.; Goicoechea, J. M.; Aldridge, S. The Aluminyl Anion: A New Generation of Aluminium Nucleophile. Angew. Chem., Int. Ed. 2021, 60 (4), 1702–1713.
13. Schmidt, E. S.; Jockisch, A.; Schmidbaur, H. A Carbonate Anion with Low-Valent Gallium as a Heteroatom in a Quasi-Aromatic Imidazolide Anion. J. Am. Chem. Soc. 2019, 121 (41), 9758–9759.
14. Kempter, A.; Gemel, C.; Fischer, R. A. Insertion of Ga(DDP) into the Au–Cl Bond of (PPh$_3$)$_2$AuCl: A First Structurally Characterized Au–Ga Bond. Inorg. Chem. 2005, 44 (2), 163–165.
Catalysis in the Reduction of CO₂ to CO.

Syntheses, Structures, and Reactivities of a New Generation of Analogues with Low-Valent Group 13 and Group 14 Elements: Reactivity of Group 13 Metal(I) Heterocycles.

Surf. Sci. Rep.

Ghiringhelli, L.; Levchenko, S.; Sche.

M. Indyllithium and the Indyl Anion [InL]

Reactivity of the Gold Atom in a Diarylborylgold(I) Complex toward Curiosities to Versatile Reagents in Synthesis.

Coord. Chem. Rev.

Developments in Transition Metal Boryl Complexes: An Overview.

Copper(I) Boryl Complexes.

Inorganic Chemistry pubs.acs.org/IC

Reactivity of Group 11 Borylmetal Transition-Metal Chlorides To Form Boryl Complexes: Syntheses, Spectroscopic, and Structural Studies on Group 13 Borylmetal Complexes. Angew. Chem., Int. Ed. 2007, 46 (35), 6710–6713.

Segawa, Y.; Yamashita, M.; Nozaki, K. Boryl Anion Attacks Transition-Metal Chlorides To Form Boryl Complexes: Syntheses, Spectroscopic, and Structural Studies on Group 11 Borylmetal Complexes. Angew. Chem., Int. Ed. 2007, 46 (35), 6710–6713.

Segawa, Y.; Yamashita, M.; Nozaki, K. Borylilium: Isolation, Characterization, and Reactivity as a Boryl Anion. Science 2006, 314 (5796), 113–115.

Weber, L. 1,3,2-Diazaborolyl Anions – From Laboratory Curiosities to Versatile Reagents in Synthesis. Eur. J. Inorg. Chem. 2017, 2017 (29), 3461–3488.

Suzuki, A.; Guo, X.; Lin, Z.; Yamashita, M. Nucleophilic Reactivity of the Gold Atom in a Diarylborylgold(I) Complex toward Polar Multiple Bonds. Chem. Sci. 2021, 12 (3), 917–928.

Te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J. A.; Snijders, J. G.; Ziegler, T. Chemistry with Functional Theory. Computational Molecular Science 2018, 8, 1345.

J. Chem. Phys.

Ziegler, T.; Rauk, A. On the Calculation of Bonding Energies by Energy Decomposition Analysis. J. Chem. Theory Comput. 2008, 4 (5), 154.

J. Comput. Chem.

Swart, M.; Bickelhaupt, F. M. QUILD: QUantum-Regions Displacement Analysis via Natural Orbitals for Chemical Valence: Charge Transfer Effects in Coordination Chemistry. J. Chem. Phys. 2015, 142 (8), 084112.

Bistoni, G.; Bistoni, F.; Tarantelli, F. Advances in Charge Displacement Analysis. J. Chem. Theory Comput. 2016, 12 (3), 1236–1244.

Morell, C.; Grand, A.; Toro-Labbé, A. New Dual Descriptor for Chemical Reactivity. J. Phys. Chem. A 2005, 109 (1), 205–212.

Chernette, H. Chemical Reactivity Indexes in Density Functional Theory. J. Comput. Chem. 1999, 20 (1), 129–154.

Geerlings, P.; De Proft, F.; Langenaeker, W. Conceptual Density Functional Theory. Chem. Rev. 2003, 103 (5), 1793–1873.

Zhao, L.; von Hopfgarten, M.; Andrade, D. M.; Frenking, G. Energy Decomposition Analysis. Wiley Interdisciplinary Reviews: Computational Molecular Science 2018, 8, 1345.

J. Comput. Chem.

Rahm, M.; Christe, K. O. Quantifying the Nature of Lone Pair Domains. ChemPhysChem 2013, 14 (16), 3714–3725.

ADF Manual, ADF Program System Release 2014; SCM, Theoretical Chemistry, Vrije Universiteit: Amsterdam, The Netherlands, 1993.

Chem. Rev.

te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. A.; Snijders, J. G.; Ziegler, T. Chemistry with ADF. J. Comput. Chem. 2001, 22 (9), 931–967.

Bistoni, G.; Infante, I.; Tarantelli, F.; Visscher, L. The Chemical Correspondence of Formal Oxidation Numbers, Lewis Structures, and Reactivity. Eur. J. Inorg. Chem. 2002, 1854–1863.

Chen, C.-H.; Tsai, M.-L.; Su, M.-D. Theoretical Study of the Reactivities of Neutral Six-Membered Carbene Analogues of the Group 13 Elements. Organometallics 2006, 25 (11), 2766–2773.

Kaur, U.; Saha, K.; Gayen, S.; Ghosh, S. Contemporary Developments in Transition Metal Boryl Complexes: An Overview. Coord. Chem. Rev. 2021, 446, 214106.

The singlet–triplet energy gap has also been calculated for the model six-membered N-heterocyclic boryl anion (0.71 eV), and it is consistent with the expected much lower stability of this anion compared with its heavier homologues.

Freund, H. J.; Roberts, M. W. Surface Chemistry of Carbon Dioxide. Surf. Sci. Rep. 1996, 25 (8), 225–273.

Mazheika, A.; Wang, Y.; Valero, R.; Vines, F.; Illas, F.; Ghiringhelli, L.; Levchenko, S.; Scheffler, M. Artificial-Intelligence-Driven Discovery of Catalyst “Genes” with Application to CO₂ Activation on Semiconductor Oxides. In Review (preprint), August 26, 2021, DOI: 10.21203/rs.3.rs-845882/v1.

Fernández, I.; Bickelhaupt, F. M. The Activation Strand Model and Molecular Orbital Theory: Understanding and Designing Chemical Reactions. Chem. Soc. Rev. 2014, 43, 4953.

Bickelhaupt, F. M.; Houk, K. N. Analyzing Reaction Rates with the Distortion/Interaction-Activation Strand Model. Angew. Chem. Int. Ed. 2017, 56 (34), 10070–10086.

Vermeeren, P.; van der Lubbe, S. C. C.; Fonseca Guerra, C.; Bickelhaupt, F. M.; Hamlin, T. A. Understanding Chemical Reactivity Using the Activation Strand Model. Nat. Protoc. 2020, 15 (2), 649–667.

Ziegler, T.; Rauk, A. On the Calculation of Bonding Energies by the Hartree Fock Slater Method. Theor. Chim. Acta 1977, 46 (1), 1–10.

Morokuma, K. Molecular Orbital Studies of Hydrogen Bonds. III. C = O···H−O Hydrogen Bond in H₂CO···H₂O and H₂CO···ZH·O. J. Chem. Phys. 1971, 55 (3), 1236–1244.

Mitrojak, M. P.; Michalak, A.; Ziegler, T. A Combined Charge and Energy Decomposition Scheme for Bond Formulation. J. Chem. Theory Comput. 2009, 5 (4), 962–975.

Belpassi, L.; Infante, I; Tarantelli, F.; Visscher, L. The Chemical Bond between Au(1) and the Noble Gases. Comparative Study of NgAuF and NgAu ‘ (Ng = Ar, Kr, Xe) by Density Functional and Coupled Cluster Methods. J. Am. Chem. Soc. 2008, 130 (3), 1048–1060.

Bistoni, G.; Rampino, S.; Tarantelli, F.; Belpassi, L. Charge-Displacement Analysis via Natural Orbitals for Chemical Valence: Charge Transfer Effects in Coordination Chemistry. J. Chem. Phys. 2014, 120 (20), 084112.

J. Am. Chem. Soc.

Ziegler, T.; Rauk, A. On the Calculation of Bonding Energies by Energy Decomposition Analysis. J. Chem. Phys. 1977, 66 (1), 1869.

J. Chem. Phys.

Suzuki, A.; Guo, X.; Lin, Z.; Yamashita, M. Nucleophilic Reactivity of the Gold Atom in a Diarylborylgold(I) Complex toward Polar Multiple Bonds. Chem. Sci. 2021, 12 (3), 917–928.

Te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. A.; Snijders, J. G.; Ziegler, T. Chemistry with ADF. J. Comput. Chem. 2001, 22 (9), 931–967.

Bistoni, G.; Bistoni, F.; Tarantelli, F. Advances in Charge Displacement Analysis. J. Chem. Theory Comput. 2016, 12 (3), 1236–1244.

Morell, C.; Grand, A.; Toro-Labbé, A. New Dual Descriptor for Chemical Reactivity. J. Phys. Chem. A 2005, 109 (1), 205–212.

Chernette, H. Chemical Reactivity Indexes in Density Functional Theory. J. Comput. Chem. 1999, 20 (1), 129–154.

Geerlings, P.; De Proft, F.; Langenaeker, W. Conceptual Density Functional Theory. Chem. Rev. 2003, 103 (5), 1793–1873.

Zhao, L.; von Hopfgarten, M.; Andrade, D. M.; Frenking, G. Energy Decomposition Analysis. Wiley Interdisciplinary Reviews: Computational Molecular Science 2018, 8, 1345.

J. Comput. Chem.

Rahm, M.; Christe, K. O. Quantifying the Nature of Lone Pair Domains. ChemPhysChem 2013, 14 (16), 3714–3725.

ADF Manual, ADF Program System Release 2014; SCM, Theoretical Chemistry, Vrije Universiteit: Amsterdam, The Netherlands, 1993.