



Research paper

The Al(I) molecule, Ph₂COAl and its anionXinxing Zhang^a, Bryan Eichhorn^b, Hansgeorg Schnöckel^c, Kit Bowen^{a,*}^a Department of Chemistry, Johns Hopkins University, Baltimore, MD 21218, USA^b Department of Chemistry, University of Maryland College Park, College Park, MD 20742, USA^c Institute of Inorganic Chemistry, Karlsruhe Institute of Technology, 76128 Karlsruhe, Germany

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ABSTRACT

We have formed the Al(I)-containing molecule, benzophenone-aluminum, i.e., Ph₂COAl, and studied it by conducting density functional theory calculations on both its neutral and anionic forms and by measuring the photoelectron spectrum of its anion. Our calculations identified two nearly iso-energetic anion isomers, (Ph₂COAl)⁻, the vertical detachment energies (VDE) of which are in excellent agreement with our photoelectron spectrum. Natural population analysis (NPA) of Ph₂COAl found the Al moiety to be positively charged by +0.81 e, indicating a strongly ionic bond between Al and Ph₂CO, i.e., Ph₂CO⁻Al⁺.

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1. Introduction

Aluminum chemistry has received significant attention in recent years as a result of interest in the reactivity of low oxidation state aluminum compounds [1,2]. Using mono-valent aluminum (I) halides, AlX (X = Cl, Br, I) as precursors [3–5], Schnöckel et al. synthesized a variety of ligated aluminum cluster compounds, molecules which themselves are low oxidation state aluminum species [1–2,6–15]. In addition to AlX, (Cp*Al)₄ (Cp* = pentamethylcyclopentadienyl) is another low oxidation state aluminum precursor that has been used to synthesize such compounds [15–25].

Al(I) precursors are indispensable reagents in the synthesis of ligated, low oxidation state, aluminum cluster compounds. Imagining other Al(I) species involves identifying electron acceptors that could serve as counterparts to X in AlX or to Cp* in (Cp*Al)₄. Benzophenone (Ph₂CO) is an attractive candidate. In solution, benzophenone readily reacts with alkali metals to form stable, dark-colored Ph₂CO⁻M⁺ (M = Li, Na, and K) solutions [26]. In the gas phase, benzophenone attaches electrons and forms parent (intact) anions, (Ph₂CO)⁻, the vertical detachment energy (VDE) of which have been measured to be 1.11 eV [27]. The stability of (Ph₂CO)⁻ arises from the delocalization of its excess electron into benzophenone's π* anti-bonding orbital.

In analogy with the alkali metals, one can envision aluminum atoms reacting with benzophenone molecules to form Ph₂CO⁻Al⁺, a Al(I) species. However, while the alkali metals are mono-valent, aluminum is normally tri-valent. The formation of AlX, which also

faced this problem, relied on aluminum's ability to avoid sp² hybridization [28] and remain mono-valent under the low reactant density (gas phase) and high temperature conditions of Schnöckel's co-condensation reactor.

In the present work, we utilized broadly analogous reaction conditions to produce the parent anion of Ph₂COAl, i.e., (Ph₂COAl)⁻. We then studied the (Ph₂COAl)⁻ anion by recording its mass spectrum, measuring its anion photoelectron spectrum, and conducting density functional theory calculations both on it and its neutral counterpart. Our primary goal in this work was the fundamental study of low oxidation state aluminum-containing molecules.

2. Experimental and theoretical methods

Anion photoelectron spectroscopy is conducted by crossing a mass-selected beam of negative ions with a fixed-frequency photon beam and energy-analyzing the resultant photodetached electrons. It is governed by the energy-conserving relationship, $h\nu = \text{EBE} + \text{EKE}$, where $h\nu$ is the photon energy, EBE is the electron binding (photodetachment transition) energy, and EKE is the electron kinetic energy. Our anion photoelectron spectrometer, which has been described previously [29], consists of a laser vaporization anion source, a linear time-of-flight mass analyzer/selector, a pulsed Nd:YAG photodetachment laser operating at 355 nm (3.49 eV), and a magnetic bottle electron energy analyzer. Photoelectron spectra were calibrated against the well-known photoelectron spectrum of Cu⁻ [30].

Parent anions of Ph₂COAl, i.e., (Ph₂COAl)⁻, were generated in a laser vaporization source. An aluminum rod was coated by a thin layer of Ph₂CO powder and then ablated by a pulsed Nd:YAG laser

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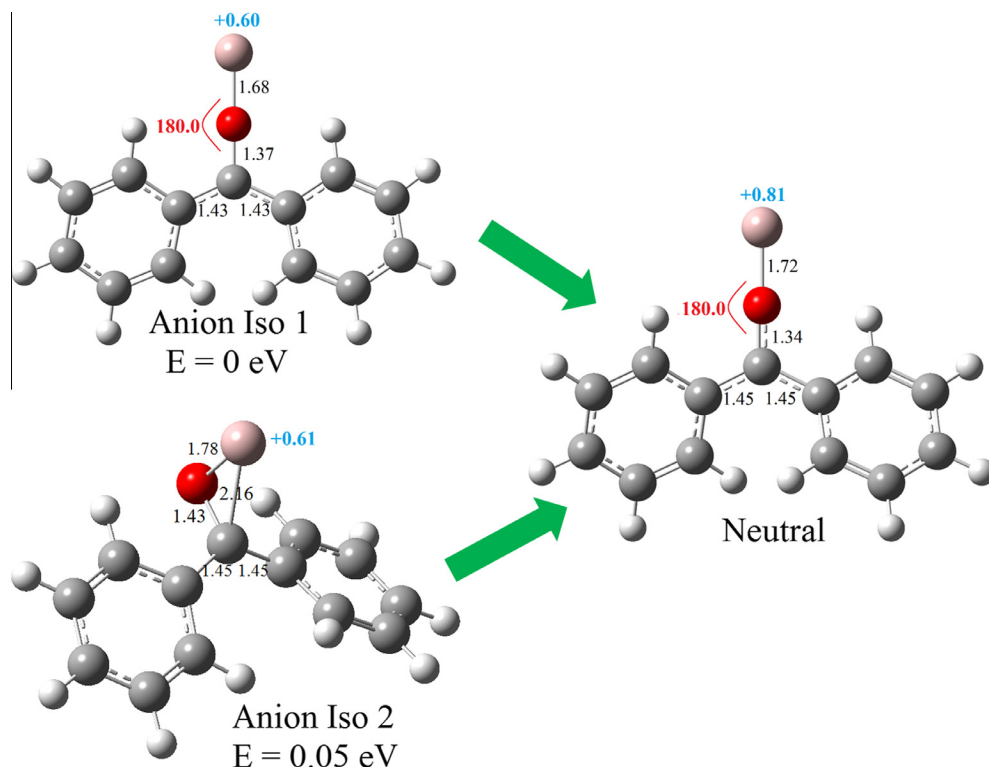


Fig. 1. Calculated structures of neutral Ph_2COAl and its two anionic isomers, **Iso 1** and **Iso 2**.

beam operating at a wavelength of 532 nm. The resulting plasma was cooled via a supersonic jet of helium gas (expansion pressure of ~ 60 psi). These source conditions, where both Ph_2CO powder and aluminum were vaporized together at high temperature, are reminiscent of those used to form AIX in Schnöckel's co-condensation reactor. Negatively-charged anions, generated in this way, then drifted into the extraction plates of the time-of-flight mass spectrometer segment of the larger apparatus, from where they were mass-selected prior to photodetachment.

Density functional theory calculations were conducted by applying Becke's three-parameter hybrid functional (B3LYP) [31–33] using the Gaussian09 software package [34] to determine the geometries of both Ph_2COAl and its anions, the vertical detachment energy (VDE) values of the two anionic isomers, the excited states of neutral Ph_2COAl , the charge distributions, and the relevant potential energy curve. All geometries, including those of the anion and its corresponding neutral molecule, were fully optimized without any geometrical constraints. The VDE value is the energy difference between the ground state of the anion and its neutral counterpart, having the same geometry as the anion. The energies for the excited states of the neutral molecule were calculated with time-dependent DFT (TDDFT) methods [35–37]. Natural population analysis (NPA), as implemented in the Gaussian09 code, was also carried out to determine the charge distributions. For comparison, the NPA charge distribution of AlCl was also calculated. The NPA method has been found to be satisfactory for calculating the charge distribution within clusters [38–44]. The potential energy curve was scanned along the Al–O coordinate with a step width of 0.05 Å. All the above calculations were performed with the 6-311++G (3df, 3pd) basis set.

3. Results and discussion

The calculated structures of neutral Ph_2COAl and its two nearly isoenergetic anionic isomers, i.e., **Iso 1** and **Iso 2**, are presented in

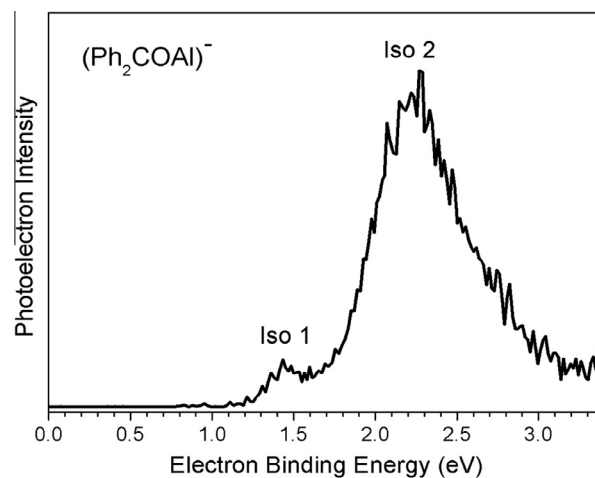


Fig. 2. Photoelectron spectrum of the $(\text{Ph}_2\text{COAl})^-$ anion, recorded with 3.49 eV photons.

Fig. 1. Bond lengths (Å) are marked in black, bond angles ($^\circ$) are in red, and the charges on Al atoms (e) are in blue. The energy difference between the two anionic isomers is only 0.05 eV, suggesting that they should be able to coexist in the ion beam. Upon photodetachment of **Iso 1** and **Iso 2**, their resulting neutral counterparts were both found to relax to the same neutral Ph_2COAl structure. This is indicated in Fig. 1 by green¹ arrows. In both anionic isomers, the Al atom bonds to the O atom of benzophenone. In **Iso 1**, the Al–O–C bond angle is 180° , while in **Iso 2**, the Al–O–C bond angle is 83.7° . This latter angle is due to the formation of an Al/O/C

¹ For interpretation of color in Fig. 1, the reader is referred to the web version of this article.

heterometalloycycle there, the result of an Al atom inserting into the C=O bond. Both the Al–O bond and the C–O bond are longer in **Iso 2** than in **Iso 1**. As in **Iso 1**, neutral Ph₂COAl also exhibits an Al–O–C bond angle of 180°, although its Al–O bond length is slightly longer. The Al–O bond length in neutral Ph₂COAl is similar to that of a free Al–O single bond, suggesting that only a single charge transfer has occurred between Al and Ph₂CO moieties during bond formation. Lastly, due to steric hindrance, the two benzene rings are out of plane, to one extent or another, in all of these structures.

The photoelectron spectrum of the (Ph₂COAl)[−] anion is presented in Fig. 2. The spectrum exhibits two broad bands, one reaching its maximum photoelectron intensity at EBE = 1.43 eV, while the other attains its maximum intensity at EBE = 2.14 eV. The rela-

Table 1
Experimental and theoretical VDE values of the two anionic isomers, **Iso 1** and **Iso 2**.

| | Expt. VDE (eV) | Theo. VDE (eV) |
|--------------|----------------|----------------|
| Iso 1 | 1.43 | 1.39 |
| Iso 2 | 2.14 | 2.00 |

Table 2
Charge distributions on the aluminum atom and on the rest of the molecule.

| | Charge on Al (e) | Charge on the rest of the molecule (e) |
|---|------------------|--|
| Ph ₂ COAl anion Iso 1 | +0.60 | −1.60 |
| Ph ₂ COAl anion Iso 2 | +0.61 | −1.61 |
| Neutral Ph ₂ COAl | +0.81 | −0.81 |
| AlCl | +0.69 | −0.69 |

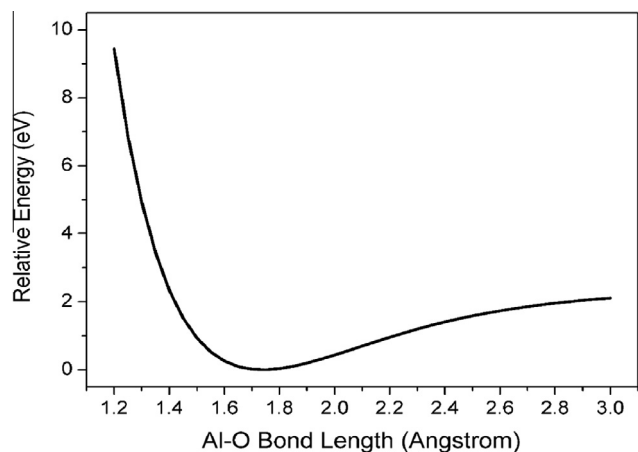


Fig. 3. Potential energy curve for neutral Ph₂COAl along the Al–O coordinate.

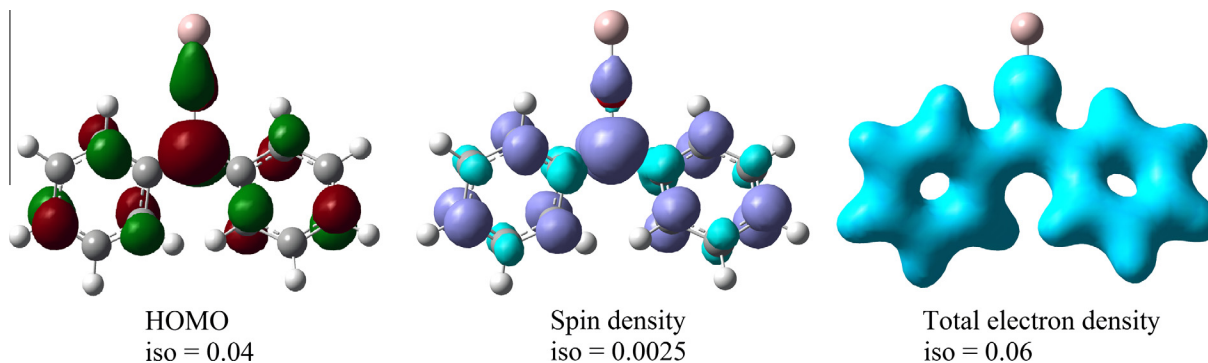


Fig. 4. The HOMO, spin density, and total electron density of the neutral Ph₂COAl molecule.

tive intensity of these two bands varied from day to day, confirming that they originated from different anions, i.e., anionic isomers. The band that maximized at EBE = 1.43 eV is due to photodetachment of anionic isomer, **Iso 1**, while the band that maximized at EBE = 2.14 eV corresponds to photodetachment of anionic isomer, **Iso 2**. These are their respective VDE values. The calculated VDE values of the anionic isomers, **Iso 1** and **Iso 2**, are 1.39 eV and 2.00 eV, respectively. Table 1 presents both experimental and theoretical VDE values, and they are in good agreement. Moreover, it is clear that the band at EBE = 2.14 eV is not due to a transition from the ground state of anionic **Iso 1** to an excited electronic state of neutral Ph₂COAl. Our TDDFT calculations found that transition to occur at EBE = 3.8 eV.

The NPA charge distributions of neutral Ph₂COAl and its two anionic isomers are tabulated in Table 2. In both anionic isomers, the Al atom has a positive charge of about +0.6 e, while the Ph₂CO moiety carries a negative charge of about −1.6 e. In neutral Ph₂COAl, the Al atom has a positive charge of +0.81 e, indicating that the bond between Al and Ph₂CO is strongly ionic. Thus, one can depict neutral Ph₂COAl as Ph₂CO[−]Al⁺. This analysis confirms that Ph₂COAl's Al moiety is essentially in its +1 oxidation state, i.e., Al (I). By comparison, the charge on Al in AlCl was calculated to be +0.69 e at the same level of theory. Ph₂COAl and AlCl are comparable molecules in this respect.

While the NPA charge distribution analysis alone confirms that Ph₂COAl is an Al(I) compound, further support for this assessment comes from inspecting Fig. 3, where the potential energy curve of Ph₂COAl is shown along its Al–O coordinate. This potential curve is relatively flat, as evidenced by Ph₂COAl's weak bond strength, i.e., ~2 eV. Fig. 3 indicates that the reaction between Ph₂CO and Al atom is thermodynamically favored without a barrier on the reaction pathway, suggesting potential synthesis of this molecule in the bulk. This story is similar to that of diatomic AlF [45–47], which is isoelectronic to the Al–O bond portion of Ph₂COAl. As is the case for AlF, Ph₂COAl is also an Al(I) species.

To obtain more insights of this Al(I) molecule, Ph₂COAl, we present its highest occupied molecular orbital (HOMO), unpaired spin density and total electron density in Fig. 4. They were plotted with different iso-values to obtain the best visual effect. The singly occupied HOMO shows a molecular orbital mainly delocalized on the Ph₂CO moiety, its distribution being consistent with the unpaired spin density, which was obtained by subtracting the total electron density of beta spin electrons from the total electron density of alpha spin electrons. The total electron density distribution again shows that the major electron density (negative charge) is on Ph₂CO, it being consistent with the NPA calculations, and further confirming the ionic nature of this Ph₂CO–Al bond.

Lastly, there is the question of whether Ph₂COAl could be utilized to make ligated aluminum clusters. The answer likely depends on the density of reactants. On the one hand, we gener-

ated copious quantities of $(\text{Ph}_2\text{COAl})^-$ anions and in all likelihood, neutral Ph_2COAl molecules in a laser vaporization source and a subsequent beam environment. On the other hand, in a higher density, traditional chemistry environment, it is worth trying to synthesize Ph_2COAl and further utilize it as a precursor for other low oxidation state Al compounds given the experimental and computational results in the current study.

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