From an Al₄-Cluster to Al⁺ Complexes: Lessons on Metalloidal Clustering

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From an Al₄-Cluster to Al⁺ Complexes: Lessons on Metalloidal Clustering

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Abstract

Low-valent aluminium compounds are among the most reactive and widely researched main-group compounds. Since the isolation of [(AlCp^{*})₄] in 1991 as the first stable, molecular Al^I compound, a variety of highly reactive neutral or anionic low-valent aluminium complexes were developed. In particular, the strongly basic alumanyl anions allowed for nucleophilic activation of a large variety of small molecules and formation of elusive transition-metal complexes. By contrast, an accessible cationic, low-valent aluminium compound combining the nucleophilicity of low-valent compounds with the electrophilicity of aluminium is hitherto unknown. Here, we report the synthesis of [Al(AlCp^{*})₃]⁺[Al(OR^F)₄][−] (R^F = C(CF₃)₃) via a simple metathesis route. Unexpectedly, the complex ion forms a dimer in the solid state and in concentrated solutions. Addition of Lewis bases results in monomerization and coordination to the unique formal Al⁺ atom giving [(L)_xAl(AlCp^{*})₃]⁺ salts with L = hexaphenylcarbodiphosphorane (cdp; x = 1), tetramethylethylenediamine (tmeda; x = 1) and 4-dimethylamino-pyridine (dmap; x = 3). Depending on the donor strength of the ligand added, the Al⁺–AlCp^{*} bonds in the [(L)_xAl(AlCp^{*})₃]⁺ cluster cations can be finely tuned between very strong (L = nothing) to very weak and approaching isolated [Al(L)₃]⁺ ions (L = dmap). We anticipate our easily accessible low-valent aluminium cation salts to be the starting point for investigation and potential application of this unusual compound class. In particular, the ambiphilic reactivity of the cationic, low-valent compounds will be studied. Moreover, knowledge gained from the stabilization of the reported complex salts is expected to facilitate the isolation and application of novel cationic, low-valent Al complexes.

Introduction

Thirty years ago Schnöckel reported the milestone-discovery of the first room temperature-stable, molecular Al^I complex [(Al^ICp^{*})₄] **1**¹. Although being tetrameric in the solid state and in solution at ambient temperatures, [(Al^ICp^{*})₄] partially dissociates into monomeric Al^ICp^{*} upon heating above 30°C². Since then, intrigued by the desire to mimic redox catalysis achievable with transition metal catalysts, the synthesis of low-valent main-group complexes has grown into a major field of chemical research^{3,4,5,6}. In particular, aluminium compounds in the oxidation state +1 have been studied intensively^{7–9}. Following the preparation of **1**, meta-stable Al^IX-

solutions^{10,11} granted access to extraordinarily aluminium-rich clusters, e.g. $[\text{Al}_{77}\{\text{N}(\text{SiMe}_3)_2\}_{20}]^{2-12}$ and $[\text{Al}_{50}(\text{Cp}^*)_{12}]^{13}$. The first stable, monomeric Al^{I} complex **II** was reported by Roesky in 2000¹⁴. Monomeric $\text{Al}^{\text{I}}\text{Cp}^{\text{R}}$ **III** ($\text{Cp}^{\text{R}} = \text{C}_5\text{H}_2^t\text{Bu}_3$)¹⁵ as well as the monomeric alanediy **IV** only followed recently¹⁶. Intriguingly, Aldridge and co-workers expanded the field of Al^{I} complexes with the anionic aluminy **V**,^{17,18} followed by various amido-substituted aluminy compounds^{19–21} as well as the recent highly nucleophilic, alkyl-substituted aluminy anion **VI**²² and a cyclic (alkyl)(amino)aluminy anion²³. These low-valent aluminium compounds **I** to **VI** allowed for a variety of small molecule activation reactions *via* oxidative additions, e.g. into C–H or C=O bonds^{7,8,17}.

Figure 1: Hitherto reported neutral and anionic Al^{I} -compounds **I** to **VI** together with the solitary low-valent aluminium cation **VII**. Here, we introduce the low-valent aluminium salt $[\text{Al}(\text{AlCp}^*)_3]^+[\text{pf}]^-$ **1** ($[\text{pf}]^- = [\text{Al}(\text{OR}^{\text{F}})_4]^-$; $\text{R}^{\text{F}} = \text{C}(\text{CF}_3)_3$).

Despite this decade-long thorough research on low-valent aluminium compounds, only one example for a cationic, low-valent aluminium compound was found by serendipity as the salt $[\text{Al}_5\text{Br}_6 \cdot (\text{thf})_6]^+[\text{Al}_5\text{Br}_8 \cdot (\text{thf})_4]^-$ (**VII**, $\text{thf} = \text{tetrahydrofuran}$)²⁴. However, **VII** cannot be prepared with a rational synthesis. Yet, cationic low-valent aluminium compounds are highly aspiring due to a potential transition-metal like ambiphilic reactivity²⁵. Examples for a similar ambiphilicity were already reported for the more developed chemistry of cationic low-valent gallium and indium compounds^{26–29}. Such cationic low-valent group 13 complexes profit from a more pronounced electrophilicity compared to their neutral analogues. Moreover, the stabilisation of the lower oxidation state induced by positive charge is an aspiring strategy to control reductive eliminations at low-valent main-group elements with first examples reported for cationic complexes of Ga and Ge^{30–32}.

Here, we present the synthesis and full characterization of the cationic, low-valent aluminium complex salt $[\text{Al}(\text{AlCp}^*)_3]^+[\text{pf}]^-$ **1** ($[\text{pf}]^- = [\text{Al}(\text{OR}^{\text{F}})_4]^-$; $\text{R}^{\text{F}} = \text{C}(\text{CF}_3)_3$), accessible *via* a simple metathesis procedure. A first study on its reactions with strong donor ligands is included.

Results and Discussion

Synthesis of $[\text{Al}(\text{AlCp}^*)_3]^+[\text{pf}]^-$ **1.** Numerous previous attempts aiming at the synthesis of cationic, low-valent aluminium compounds *via* oxidative or reductive procedures have proven unsuccessful²⁵. Hence, $[(\text{Al}^{\text{I}}\text{Cp}^*)_4]$ was chosen as easily accessible starting material already in the correct oxidation state³³. Intriguingly, upon reaction of $[(\text{Al}^{\text{I}}\text{Cp}^*)_4]$ with $\text{Li}[\text{pf}]$ in 1,2-difluorobenzene (1,2-DFB), a colour change from yellow to red is observed instantly. The NMR spectra of the reaction mixture indicate the complete consumption of $[(\text{AlCp}^*)_4]$ and crystallization of the reaction mixture yielded $[\text{Al}(\text{AlCp}^*)_3]^+[\text{pf}]^-$ **1** as dark-purple crystals (Figure 2). However, in first experiments, precipitation of LiCp^* was not observed and the product was significantly contaminated with various, unidentifiable lithium-containing compounds as determined by means of ^7Li NMR spectroscopy (Electronic supporting information, ESI S-Figure 6). After extraction of the crude product in 1,3-DFB, precipitation of the by-products was observed, and pure $[\text{Al}(\text{AlCp}^*)_3]^+[\text{pf}]^-$ **1** could be isolated in 33 % yield as dark-purple crystals (Figure 2).

Characterization. Single-crystal X-ray diffraction analysis (scXRD) revealed a trigonal pyramidal geometry at the unique aluminium atom (Figure 2). Average Al–Al bond lengths in known tetrahedral $[(\text{AlR})_4]$ complexes range from 2.602(2) Å in $[(\text{Al}\{\text{Si}(\text{SiMe}_3)_3\})_4]$ ³⁴ to 2.770(5) Å in $[(\text{Al}^{\text{I}}\text{Cp}^*)_4]$ ¹. In the molecular structure of **1**, the average bond lengths between the $\text{Al}^{\text{I}}\text{Cp}^*$ moieties and the unique aluminium atom are significantly shortened to an average value of 2.546(2) Å. Moreover, the distances between the Al atoms of the $\text{Al}^{\text{I}}\text{Cp}^*$ fragments are elongated to secondary bonds at 3.044(2) Å (av.). Hence, a strong bonding interaction between the Al atoms of the $\text{Al}^{\text{I}}\text{Cp}^*$ fragments can be precluded, and complex **1** could be described as an aluminium cation Al^+ accepting three strongly bound neutral $\text{Al}^{\text{I}}\text{Cp}^*$ ligands (*vide infra*). Intriguingly, scXRD revealed the presence of two independent dimer structures of **1** in the unit cell (Figure 2e). In one of those, a nearly ideal eclipsed conformation of the $\text{Al}^{\text{I}}\text{Cp}^*$ units in $[(\text{Cp}^*\text{Al}^{\text{I}})_3\text{Al}-(\text{Al}^{\text{I}}\text{Cp}^*)_3]^{2+}$ is present with an Al–Al distance of 2.838(2) Å. This dimer dication $[\text{Al}_8(\text{Cp}^*)_6]^{2+}$, although two electrons in deficit, strongly resembles Schnöckel's neutral $[\text{Ga}_8\text{R}_6]$ cluster ($\text{R} = \text{C}(\text{SiMe}_3)_3$)³⁵, which he defined as an ideal model for a 2e2c metal-metal bond. Yet, in the second unit the Al_4 -pyramids are tilted against one another resulting in a longer Al–Al distance of 3.005(2) Å. Related trans-bent structures are observed for main group donor-acceptor dimers³. With both geometries observed in the same crystal, the bonding modes between the two “naked” aluminium atoms need to be energetically comparable.

Figure 2: a) Reaction equation (1) for the synthesis of $[\text{Al}(\text{AlCp}^*)_4]^+[\text{pf}]^-$ **1**. b) Molecular structure of a $[\text{Al}(\text{AlCp}^*)_4]^+$ unit. Hydrogen atoms and $[\text{pf}]^-$ anion omitted for clarity. Thermal displacement of the ellipsoids was set at 50 % probability. Selected interatomic distances [Å]: Al(1)–AlCp*(av.) 2.546(2), Al(1)–AlCp* (range) 2.534(1)–2.575(2), Cp*Al–AlCp*(av.) 3.044(2), Cp*Al–AlCp* 2.998(2)–3.101(1). c) ^{27}Al NMR spectrum (78 MHz, 1,2-DFB, 300 K) of **1**. The decomposition product $[\text{Al}^{\text{III}}(\text{Cp}^*)_2]^+$ of **1** generates the weak ^{27}Al resonance at $\delta = -114$ ppm. A broad signal at $\delta = 66$ ppm originates from the NMR probe head. d) Dark-purple crystals of **1**. e) Molecular structures of the dimeric $[\text{Al}_8(\text{Cp}^*)_6]^{2+}$ units. Hydrogen atoms and $[\text{pf}]^-$ anion omitted for clarity. Thermal displacement of the ellipsoids was set at 50 % probability. f) UVVIS spectra of a solution of **1** in 1,2-DFB ($c = 19 \text{ mg mL}^{-1}$) measured at room temperature (yellow) and at -40°C (purple).

Solid-state UV/VIS-spectroscopy revealed the HOMO-LUMO gap of the dark-purple crystalline solid **1** including the dimer dications as 1.74–1.92 eV (645–725 nm), depending on the method of determination (ESI; S-Figures 17–20). Intriguingly, solutions of **1** in 1,2-DFB and 1,3-DFB show distinct colour changes from yellow to deep purple upon concentration or cooling of the reaction mixture. In the UV/VIS spectrum of **1**, the colour change is accompanied by the appearance of a broad UV/VIS-absorption band at $\lambda = 564 \text{ nm}$ (Figure 2f). The experimental spectrum of the purple solution is in line with the TD-DFT computed spectrum of the dimer with the short Al–Al bond as observed in the molecular structure of **1** ($\lambda_{\text{comp.}} = 581 \text{ nm}$, bp86-d3bj/def2-svp, ESI, S-Figure 62). By contrast, the computation of the UV/VIS spectrum of the monomer does not include a band above 500 nm. Hence, an equilibrium between a purple $[\text{Al}_8(\text{Cp}^*)_6]^{2+}[\text{pf}]_-2$ dimer and its corresponding yellow monomer is postulated, with the dimer being favoured at lower temperatures and higher concentrations. On the basis of the experimental data, an excess of the monomer at STP conditions is suggested to yield an equilibration constant of about $K_{\text{dim.,1,2-DFB}}^0 = 0.1$ and thus a Gibbs free energy of $\Delta G_{1,2\text{-DFB}}^0 = -6 \text{ kJ mol}^{-1}$. This hypothesis agrees with DFT calculations (bp86-d3bj/def2-svp), which suggest the dimerization in 1,2-DFB and 1,3-DFB solution to be exergonic at ambient

Figure 4: a) Molecular structures of isolated Al_4 cluster cations. Thermal displacement of ellipsoids set at 50 % probability. Hydrogen atoms and $[\text{pfl}]^-$ anions omitted for clarity. Selected bond lengths [Å]: **3⁺**: Al1-N1 2.118(3), Al1-N2 2.162(2), Al1-Al2 2.724(1), Al1-Al3 2.629(1), Al1-Al4 2.731(1), Al2-Al3 2.755(1), Al2-Al4 2.806(1), Al3-Al4 2.786(1). **4⁺**: Al1-C1 2.041(2), Al1-Al2 2.704(1), Al1-Al3 2.622(1), Al1-Al4 2.659(1), Al2-Al3 2.762(1), Al2-Al4 2.755(1), Al3-Al4 2.801(1). **5⁺**: Al1-N1 2.045(2), Al1-N2 2.037(2), Al1-N3 2.040(2), Al1-Al2 2.797(1), Al1-Al3 2.796(1), Al1-Al4 2.815(1), Al2-Al3 2.673(1), Al2-Al4 2.661(1), Al3-Al4 2.678(1).

The $\text{Al}_\text{L}-\text{Al}_{\text{Cp}^*}$ bonds of $[(\text{tmeda})\text{Al}(\text{Al}^{\text{I}}\text{Cp}^*)_3]^+[\text{pfl}]^-$ **3** and $[(\text{cdp})\text{Al}(\text{Al}^{\text{I}}\text{Cp}^*)_3]^+[\text{pfl}]^-$ **4** are asymmetric and significantly elongated compared to **1⁺**. With $\text{Al}_\text{L}-\text{Al}_{\text{Cp}^*}$ bond lengths ranging from 2.628(1) Å to 2.727(1) Å in **3⁺** and from 2.754(1) to 2.801(1) Å in **4⁺**, they correspond to distances in known $[(\text{AlL})_4]$ complexes (ESI, S-Table 1). Moreover, the $\text{Al}_{\text{Cp}^*}-\text{Al}_{\text{Cp}^*}$ distances shrink to 2.787 Å for **3⁺** and 2.773 Å for **4⁺** (av.). Hence, the covalent bonding between the Al_{Cp^*} atoms is reconstituted in the complexes. Notably, the Al–Al bond lengths change upon complexation is even more pronounced in the complex $[(\text{dmap})_3\text{Al}(\text{AlCp}^*)_3]^+[\text{pfl}]^-$ **5**. Here, the average $\text{Al}_\text{L}-\text{Al}_{\text{Cp}^*}$ bond length of 2.802(1) Å is even larger than the average $\text{Al}_{\text{Cp}^*}-\text{Al}_{\text{Cp}^*}$ bond lengths of 2.670(1) Å. Hence, with coordination of dmap as a strong donor-ligand, an inversion of the relative Al–Al bonds in the asymmetric Al_4 complexes compared to **1⁺** could be achieved and apparently **5⁺** is already very close to an isolated $[\text{Al}(\text{L})_3]^+$ complex ion. These structural changes of the cationic Al_4 clusters are also reflected in the ^{27}Al NMR spectra. For **3⁺** and **4⁺**, the resonances of the aluminium atoms of the AlCp^* moieties are shifted high-field compared to **1** to $\delta_{\text{exp.}} = -65$ ppm ($\delta_{\text{calc.}} = -66$ ppm) and $\delta_{\text{exp.}} = -59$ ppm ($\delta_{\text{calc.}} = -59$ ppm) respectively. However, only for the tmeda-complex an NMR signal of the unique Al atom can be observed at $\delta_{\text{exp.}} = 48$ ppm ($\delta_{\text{calc.}} = 9$ ppm). Intriguingly, upon dissolution of **5** in 1,2-DFB, the orange solution shows an NMR signal at $\delta_{\text{exp.}} = -83$ ppm, fitting to the calculated value of $\delta_{\text{calc.}} = -86$ ppm. Yet, already after a few minutes, a ^{27}Al NMR resonance at $\delta = -79$ ppm, indicative for the formation of free $[(\text{AlCp}^*)_4]$, was observed. After two weeks at room temperature, the colour of the solution changed to yellow and only the ^{27}Al NMR resonance of $[(\text{AlCp}^*)_4]$ was detected. Hence, the thermodynamics for the breakup of the tetrameric clusters in a

monomeric Al species of type $[\text{Al}(\text{L})]^+$ ($\text{L} = \text{tmeda}, \text{cdp}, (\text{dmap})_3$) and an $[(\text{AlCp}^*)_3]$ -trimer were investigated by DFT calculations. Here, the dmap-complex **5**⁺ was computed to be more prone to a decomposition compared to **4**⁺ and **5**⁺ (**3**⁺: $\Delta G_{1,2\text{-DFB}}^0 = 237 \text{ kJ mol}^{-1}$, **4**⁺: $\Delta G_{1,2\text{-DFB}}^0 = 245 \text{ kJ mol}^{-1}$, **5**⁺: $\Delta G_{1,2\text{-DFB}}^0 = 229 \text{ kJ mol}^{-1}$).⁴² Hence, **5** is unstable at room temperature in solution and decomposes into $[(\text{AlCp}^*)_4]$ and potentially a cationic aluminium complex, which could not be identified on the basis of the NMR-spectroscopic analysis or be isolated, yet.

DFT Investigations of Structure and Bonding of **1**, **3** to **5**

To investigate the bonding situation of **1** as well as of the cationic clusters **3**–**5**, supporting DFT calculations were performed at the pbe0-d3bj/def2-tzvpp//bp86-d3bj/def2-svp level of theory. In the monomeric $[\text{Al}(\text{AlCp}^*)_3]^+$ unit, the $3s^2$ like lone-pair orbital at the formally cationic aluminium atom resides as HOMO–2 at an energy of -8.55 eV . The HOMO and HOMO–1 (-8.50 eV) are degenerate and present an interaction of the lone-pair orbitals of the AlCp^* moieties with the $3p_x$ - and $3p_y$ -orbitals at the unique Al atom (Figure 5a).

Figure 5: a) Kohn-Sham orbitals (isovalue 0.05) for **1**⁺ calculated at pbe0-d3bj/def2-tzvpp//bp86-d3bj/def2-svp level of DFT. b) Plots of deformation densities $\Delta\rho_{(1)}/\Delta\rho_{(4)}$ of the pairwise orbital interaction in **1**⁺ (isovalue 0.001) associated with energy terms $\Delta E_{\text{Orb}(1)}/\Delta E_{\text{Orb}(4)}$ (values in kcal mol^{–1}). The plot of deformation density $\Delta\rho_{(2)}$ with $\Delta E_{\text{Orb}(1)} = -55.62 \text{ kcal mol}^{-1}$ (32%) shows a deformation density similar to $\Delta\rho_{(1)}$ (ESI, S-Figure 65). Charge flows from yellow to purple. c) Plots of deformation densities $\Delta\rho_{(1)}/\Delta\rho_{(2)}$ of the pairwise orbital interaction in **5**⁺ (isovalue 0.001) associated with energy terms $\Delta E_{\text{Orb}(1)}/\Delta E_{\text{Orb}(2)}$ (values in kcal mol^{–1}). The plot of deformation density $\Delta\rho_{(3)}$ with $\Delta E_{\text{Orb}(3)} = -18.96 \text{ kcal mol}^{-1}$ (16%) shows a deformation density similar to $\Delta\rho_{(2)}$ (ESI, S-Figure 66). Charge flows from yellow to purple.

The LUMO (−4.32 eV) of **1**⁺ has strong 3p_z-character, whereas LUMO+1 and LUMO+2 are dominated by the 3p_x- and 3p_y-orbitals of the unique Al⁺ atom. Upon dimerization, interactions of the HOMO−2 with the LUMO as well as of the HOMO/−1 orbitals with the LUMO/−1 orbitals is expected to yield σ- and π-bonding interactions respectively, which is supported by the computed frontier orbitals of the [Al₈(Cp^{*})₈]²⁺ dimer (ESI, S-Figure 61). These frontier orbital considerations agree with the two observed bonding modes of the dimer dication in the solid-state structure of **1**. For more detail, an energy decomposition analysis combined with natural orbitals for chemical valence (EDA-NOCV; Figure 5b) was performed as promoted by Frenking and co-workers in recent years⁴³. The majority of the total orbital interaction energy between the Al⁺ and (Al⁺Cp^{*})₃-fragment in **1** stems from donation of electron density from the lone-pair orbitals of the Al⁺Cp^{*}-units into the 3p_x- and 3p_y-orbital at the unique aluminium atom (64 %). Hence and in agreement with our deduction from structure and chemistry, **1**⁺ is best described as a cationic aluminium atom, which is coordinated by three strongly electron donating Al⁺Cp^{*} substituents. This assignment agrees to the absence of bond critical points (BCPs) between the Al_{Cp^{*}} atoms in the QTAIM-analysis of **1**⁺ (ESI, Section 3; QTAIM = quantum theory of atoms in molecules). Yet, the situation changes upon complexation of the unique aluminium atom. Here, the orbital interaction terms associated with the delocalisation of the lone-pair of the unique Al atom into the (Al⁺Cp^{*})₃ fragment increase significantly in the order **3**⁺ < **4**⁺ < **5**⁺, while the energy terms associated with the electron donation from the (Al⁺Cp^{*})₃ unit into the 3p-orbitals of the [(L)_xAl⁺] moiety ((L)_x = (tmeda), (cdp), (dmap)₃)) decrease in the same sequence. In **5**⁺, the energy term of the delocalisation of the lone pair orbital at (dmap)₃Al⁺ into the (Al⁺Cp^{*})₃ fragment even becomes the dominant contribution to the total orbital interaction energies (52 %). Consequently, the role of the Al⁺Cp^{*} units can be altered decisively upon complexation of the unique Al atom in **1**: While the Al⁺Cp^{*} units mainly act as Lewis bases in **1**⁺, the Al⁺Cp^{*} units become increasingly Lewis-acidic in the isolated clusters. These trends are in-line with the observed inversion of the Al–Al bond lengths in the molecular structure of **5**⁺. These results are supported by the computed QTAIM charges at the unique Al atoms. For **1**⁺, the QTAIM charge at the unique Al atom of +0.58 reflects the charge delocalisation onto the strongly Lewis basic Al⁺Cp^{*} units. In comparison to the QTAIM analysis of [(Al⁺Cp^{*})₄] (*q*_{Cp^{*}} = −0.84, *q*_{Al} = +0.84), particularly the negative partial charges at the Cp^{*} substituents decrease in **1**⁺ (*q*_{Cp^{*}} = −0.65, *q*_{AlCp^{*}} = +0.79). Nevertheless, a significant positive charge remains at the unique Al atom. Whereas for **3**⁺ and **4**⁺ only a marginal increase of the QTAIM-charges to 0.63 and 0.68 compared to **1**⁺ is calculated, the dmap-ligated Al-atom in **5**⁺ bears a highly positive charge of *q*_{Al} = 1.17 and can be denoted as a cationic, low-valent aluminium atom. Consequently, **5**⁺ may act as source of a cationic, monomeric Al⁺ as will be studied in future research.

Conclusion

In summary, we report the synthesis of a cationic, low-valent aluminium compound $[\text{Al}(\text{AlCp}^*)_3]^+[\text{pf}]^-$ **1** accessible on gram-scale via a simple metathesis route. Indicating an ambiphilic reactivity, crystallographic as well as UV/VIS spectrometric and computational studies reveal the dimeric structure $[\text{Al}_2(\text{AlCp}^*)_6]^{2+}([\text{pf}]^-)_2$ of **1** in the solid state as well as in solution at high concentration and low-temperature. Addition of Lewis bases to solutions of **1** allows for the synthesis of various cluster cations of type $[(\text{L})_x\text{Al}(\text{AlCp}^*)_3]^+[\text{pf}]^-$ ($(\text{L})_x = (\text{tmeda})$, (cdp) , $(\text{dmap})_3$). Their solid-state structures, NMR shifts and computational studies demonstrate that the dominating bonding interactions can be fine-tuned by the donor strength of the added ligands. This effect is maximised in the highly asymmetric dmap-substituted cluster. Consequently, this salt may potentially be used as a synthon for a $[\text{Al}(\text{L})_3]^+$ -salt, which due to its cationic nature potentially may be able to conduct reversible oxidative addition and reductive elimination chemistry with small molecules.

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