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Aluminacyclopropene–phosphine complex: a carbene-exchange reagent†

Huihui Xu,^{†a} José Miguel León Baeza,^{†ab} Antoine Baceiredo,^a René Segundo Rojas Guerrero,^{†b} Nathalie Saffon-Merceron,^c Vicenç Branchadell^{†d} and Tsuyoshi Kato^{†*a}

N-heterocyclic carbenes (NHCs) are extensively used as auxiliary ligands or organocatalysts thanks to their remarkable stability. However, due to their high structural stability, applications involving skeletal modifications without losing the low-valent nature (carbene exchange reactions) remain extremely rare. We report here that aluminacyclopropene–phosphine complex **1** promotes original “carbene-to-carbene” transformations of stable carbenes. Indeed, the Al(III)–phosphine Lewis pair complex **1**, due to its high ring strain, is able to react with NHC **2** to produce a cyclopropenyldiene (**4**), via atomic carbon transfer from the NHC to the η^2 -coordinated alkyne fragment, within the coordination sphere of the Al(III) center. Moreover, the complex **1** transforms the stable (diamino)cyclopropenyldiene **7** into a more reactive acyclic (amino)carbene **8**, which has been isolated in crystalline form.

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Introduction

Stable carbenes, featuring a divalent carbon center well stabilized by substitution and structural effects, have become indispensable tools in chemistry due to their ease of handling and synthetic usefulness as reagents with the properties of great modularity through substitution patterns. A large variety of stable carbenes, such as N-heterocyclic carbenes (NHCs), are now available and found in applications, mainly as chemical reagents, ligands¹ and organocatalysts.² Usually, their reactions take place at the divalent carbon center, accompanied by its oxidation [C(II) $\rightarrow$ C(IV) transformation], without skeletal modifications. Although still rare, reactions involving skeletal modifications, which enable them to be used as unique low-valent carbon sources, are also emerging. Indeed, Tobisu *et al.* have recently demonstrated that the C(II) atom of NHCs can be used as a formal atomic carbon [“C(0)”] source, showing the reaction of NHCs with acrylamides *via* single carbon atom doping annulation to form a γ -lactam and release of diimine

(Fig. 1(a)).³ More recently, Radius' group also described the reaction of NHCs as an atomic carbon source with $\text{Me}_3\text{N}\cdot\text{AlH}_3$ to produce ethylene and a diaminoalane dimer (Fig. 1(b)).⁴ Such

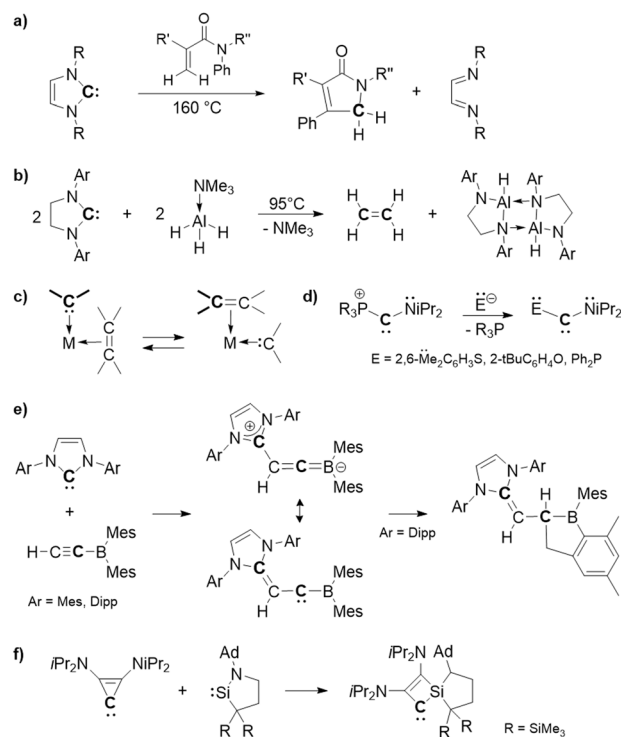


Fig. 1 Applications of stable cyclic carbenes as atomic carbon sources (a and b) and carbene-to-carbene transformations (c–f).

^aLaboratoire Hétérochimie Fondamentale et Appliquée (UMR 5069), Université de Toulouse, CNRS, 118 Route de Narbonne, F-31062 Toulouse, France. E-mail: tsuyoshi.kato@utoulouse.fr

^bDepartamento de Química Inorgánica, Facultad de Química y de Farmacia, Pontificia Universidad Católica de Chile, Casilla 306, Santiago 22, Chile. E-mail: rrojasg@uc.cl

^cInstitut de Chimie de Toulouse (FR 2599), Université de Toulouse, CNRS, 118 Route de Narbonne, F-31062 Toulouse, France

^dDepartament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain

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‡ These authors contributed equally to this work.

behavior of NHCs is rather surprising, given their high framework stability and limited examples of ring structure modifications,^{5–8} in agreement with their current extensive applications as persistent ligands and organocatalysts.^{1,2}

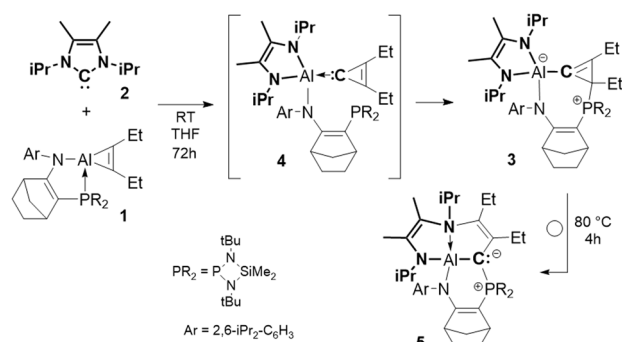
In addition to these $[C(II)/C(0) \rightarrow C(IV)]$ transformations, reactions without losing their divalent nature could be expected, allowing the synthesis of new carbenes (carbene-to-carbene transformations). However, although the olefin metathesis is a well-known catalytic process that promotes the interchange of carbenes in the coordination sphere of a transition metal (Fig. 1(c)), such a transformation with stable carbenes is rather uncommon. A rare example is the substitution reaction at the carbene center of (phosphonio)(amino)carbene, reported by Bertrand *et al.*, allowing the synthesis of various stable push-push carbenes from a single carbene precursor (Fig. 1(d)).⁹ Braunschweig described a reaction of an NHC with a borylacetylene to generate a zwitterionic allene, whose central carbon exhibits carbene-type reactivity, despite no skeletal modification involved in this process (Fig. 1(e)).¹⁰ Koike and Iwamoto also successfully synthesized a stable cyclobutenylidene *via* carbene-to-carbene ring expansion of stable diaminocyclopropenylidene through its reaction with a cyclic (amino)(alkyl)silylene (Fig. 1(f)).¹¹ We report here a unique behavior of strained $Al(III)$ -phosphine Lewis pair complex **1** being able to promote “carbene-to-carbene” transformations of stable carbenes (NHC **2** and cyclopropenylidene **7**) *via* skeletal recasting.

Results and discussion

As demonstrated by the work of Radius' group, the use of $Al(III)$ compounds is a viable strategy to achieve skeletal modifications of NHCs by overcoming their excessive framework stability.^{4–8,12} Hence, we considered the use of phosphine-aluminocyclopropene Lewis pair complex **1**, expecting greater reactivity thanks to the high ring strain of the three-membered cyclic structure.¹³ Indeed, aluminocyclopropene **1**, a formal η^2 -alkyne–alumylene complex,^{14,15} reacts at room temperature (RT) with NHC **2** to give the $Al(III)$ complex **3** featuring a phosphine-supported cyclopropenylidene moiety (Scheme 1). Formally, to obtain **3**, both C–N bonds of the NHC were cleaved and the divalent carbon atom was transferred to the η^2 -coordinated

alkyne fragment at the aluminum center to generate the transient cyclopropenylidene– $Al(III)$ complex **4**, which is stabilized by the coordination of the phosphine ligand. The resulting complex **3** is stable at RT and was isolated as brown crystals in good yield (58%) from a pentane solution at $-30^\circ C$.

The ^{31}P -NMR spectrum of **3** displays only a sharp signal at 68.0 ppm, indicating that the reaction proceeds in a diastereoselective manner. In the ^{13}C -NMR spectrum, the signal of the sp^2 -C atom attached to the Al center could not be observed at either $25^\circ C$ or $-70^\circ C$, probably due to a broadening of the signal induced by the C–Al connection. However, a HMBBC experiment yielded a correlation between a carbon signal at 119.2 ppm and the proton signal of CH_2 -ethyl groups. The other three-membered ring sp^2 - and sp^3 -carbon atoms were observed at 130.1 ppm (singlet) and at 26.3 ppm (doublet, $^1J_{CP} = 108.0$ Hz), respectively. The X-ray structure of **3** confirms the presence of an Al center substituted by diamino and cyclopropenyl moieties and the migration of the phosphine ligand from Al to the carbon center of the cyclopropenyl group to form a seven-membered ring (Fig. 2-left). The Al–C1 bond distance [1.959(1) Å] corresponds to covalent Al–C(sp^2) single bonds. In contrast, the elongated Al–N1 bond [1.936(1) Å] relative to other Al–N bonds [Al–N2 1.841(1) Å and Al–N3 1.842(1) Å] is probably due to its dative bond character enhanced by the π -attracting effect of the phosphonio group in addition to the steric repulsion between the two bulky groups, the Dipp substituent and the diamino moiety. As expected, the computationally optimized structure of cyclopropenylidene complex **4** exhibits an elongated Al–C1 bond [2.031 Å] and a shorter Al–N1 bond [1.889 Å] (Fig. 2, right) compared to those observed for **3**. Certainly, due to the aromatic character of the cyclopropenylidene fragment in **4**,¹⁶ the stabilization energy gained by the phosphine coordination to give **3** is relatively small ($\Delta G_{4 \rightarrow 3} = -16.2$ kcal mol $^{-1}$, Fig. 3), suggesting a possible equilibrium between complexes **3** and **4**. However, all efforts to find a suitable reactivity of **3** to



Scheme 1 The synthesis of phosphine-stabilized cyclopropenylidene $Al(III)$ complex **3** and its isomerization into polycyclic $Al(III)$ complex **5**.

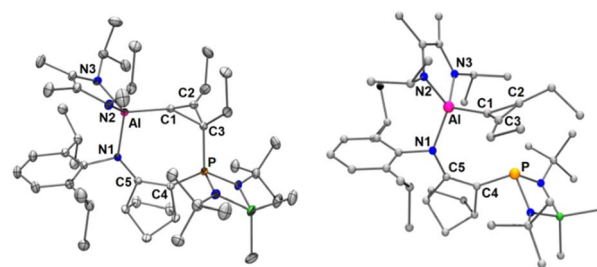


Fig. 2 Molecular structure of **3** obtained by X-ray diffraction analysis (left). Thermal ellipsoids represent 30% probability. Structure of **4** calculated at the M06-2X/6-31G(d) level of theory (right). H and disordered atoms are omitted from both structures for clarity. Selected bond lengths [Å] and angles [°]: **3**: Al–N2 1.841(1), Al–N3 1.842(1), N1–Al 1.936(1), Al–C1 1.959(1), C1–C2 1.298(2), C2–C3 1.501(2), C3–C1 1.583(2), C3–P 1.789(1), C3–C1–C2 61.89(8), C1–C2–C3 68.44(9), C2–C3–C1 49.67(7), N1–Al–C1 99.10(4), C1–C3–P 114.98(8), C2–C3–P 118.76(9), C3–P–C4 113.47(5), P–C4–C5 138.62(9), C4–C5–N1 135.32(10), C5–N1–Al 131.69(7). $\Sigma^\circ N2 = 340.90^\circ$. $\Sigma^\circ N3 = 352.62^\circ$. $\Sigma^\circ C1 = 355.39^\circ$. **4**: Al–N2 1.831, Al–N3 1.840, N1–Al 1.889, Al–C1 2.031, C1–C2 1.392, C2–C3 1.346, C3–C1 1.397. $\Sigma^\circ C1 = 355.39^\circ$.



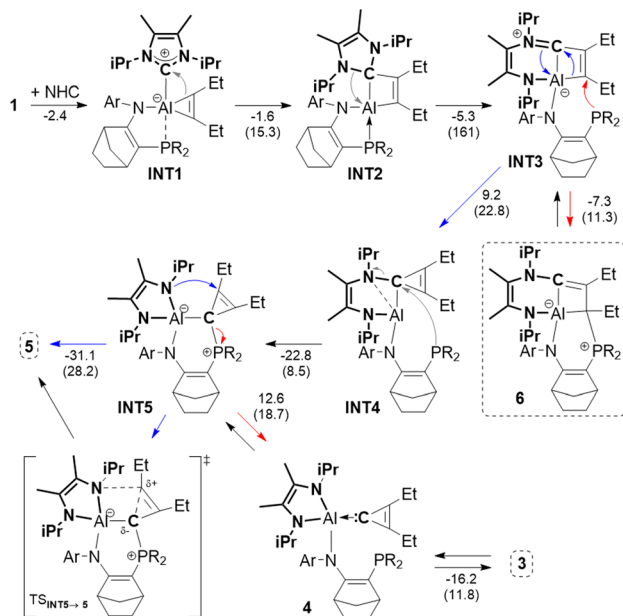


Fig. 3 Calculated pathway for the reaction of **1** with NHC **2** (M06-2X/Def2TZVP//M06-2X/6-31G(d) level). Gibbs energies of intermediates (and transition states) are in kcal mol⁻¹. Compounds **3**, **5** and **6**, outlined by a dotted line, are isolable.

experimentally prove the generation of intermediate **4** in order to use it as a source of cyclopropenylidene have failed.

The transformation of **1**/NHC into **4** can be regarded as a single atomic carbon transfer from the NHC to the η^2 -coordinated alkyne ligand of the Al(III) complex **1**, resulting in a formal carbene exchange reaction from NHC to cyclopropenylidene (Fig. 3). DFT calculations predict that the reaction starts with the coordination of NHC to the Al center of **1** (INT1), which triggers two ring expansion reactions consecutively, first in the three-membered aluminocyclopropene ring and then in the NHC-five-membered ring, affording bicyclic intermediate INT3. Further isomerization of INT3 via two successive ring contractions, involving two 1,2-migrations of ethylene carbon (Al $\rightarrow$ C) (INT4) and the amino group (C $\rightarrow$ Al) in opposite directions from the previous ones, promoted by the phosphine ligand, to generate cyclopropenylidene INT5 formally stabilized by an Al(III)–phosphine Lewis pair. Then, the phosphine ligand migration, via the intermediacy of cyclopropenylidene–Al(III) complex **4**, gives the more stable isomer **3**. All steps, except for the transformation of INT3 to INT4 via a ring-contraction to form a three-membered ring ($\Delta G_{\text{INT3} \rightarrow \text{INT4}} = +15.0$ kcal mol⁻¹), are exergonic processes, and this carbene exchange reaction is thermodynamically favored ($\Delta G_{\text{1+2} \rightarrow \text{3}} = -20.3$ kcal mol⁻¹). A related reaction of NHC-supported aluminocyclopropene, proceeding in a similar way, has been recently reported by Liu *et al.*¹⁷ As expected by the following endergonic and rate-determining steps (INT3 $\rightarrow$ INT4 and INT5 $\rightarrow$ **4**, respectively) for further evolution, INT3 should be a relatively long-lived intermediate. Indeed, monitoring the reaction by ³¹P-NMR spectroscopy allowed the detection of a signal at 61.0 ppm corresponding to the fused-tricyclic compound **6**,

which is the phosphine-stabilized form of INT3. Complex **6** has been successfully isolated by crystallization from the reaction mixture in pentane solution at -30 °C, and its structure was confirmed by X-ray diffraction analysis (Fig. 4, right). Given the poorly exergonic nature of INT3 $\rightarrow$ **6** transformation ($\Delta G_{\text{INT3} \rightarrow \text{6}} = -7.3$ kcal mol⁻¹), this stabilization process is expected to be reversible. Indeed, although **6** is stable at -40 °C in THF and can be fully characterized by NMR, it isomerizes into Al(III) complex **3** at RT in C₆D₆. This experimental result is in good agreement with the reaction pathway predicted by calculations.

Complex **3** is stable at room temperature, but it evolves above 60 °C (4 h at 80 °C) via a fusion of three- and five-membered rings, affording the tricyclic Al(III)-substituted phosphonium ylide **5** (Scheme 1). The ³¹P-NMR chemical shift of **5** (10.7 ppm) is high-field shifted compared to those of isomers **3** and **6** (68.0 and 61.0 ppm, respectively). The ¹³C-NMR spectrum exhibits a large doublet signal at 56.1 ppm, corresponding to the Al-ylidic carbon atom, with a large phosphorus–carbon coupling constant ($^1J_{\text{CP}} = 115.1$ Hz). The X-ray structure of **5** reveals a fused tricyclic structure with a tetracoordinated Al center (Fig. 4, left). Calculations on the reaction pathway predict that the reaction starts with the reformation of less stable isomer INT5 from **3** with the migration of the phosphine ligand through **4** and then INT5 undergoes a ring fusion via a formal substitution reaction at the vinyl carbon of the cyclopropylidene moiety by the adjacent amino group of the diamino ligand to directly produce the final tricyclic Al(III) complex **5** (Fig. 3). Careful analysis of the transition state (TS_{INT5 $\rightarrow$ 5}) indicates that the ring fusion is triggered by ring opening of cyclopropylidene, formally activated by an Al/P Lewis pair, via heterolytic C–C bond cleavage (Fig. 3) and therefore, the high ring strain of the cyclopropylidene moiety is an important driving force for such a peculiar rearrangement.

In marked contrast to the reaction of aluminocyclopropene–phosphine complex **1** with NHC **2** generating a carbene complex, its reaction with stable (diamino)cyclopropenylidene **7** affords an

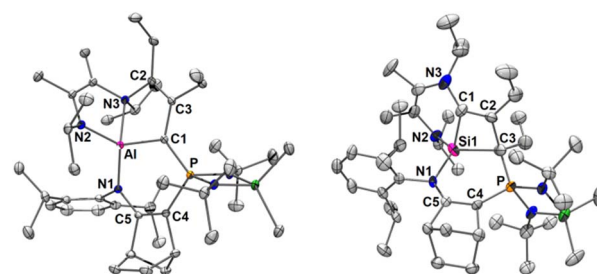


Fig. 4 Molecular structures of **5** (left) and **6** (right). Thermal ellipsoids represent 30% probability. H and disordered atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **5**: Al–N1 1.886(2), Al–N2 1.850(2), Al–N3 2.026(2), Al–C1 1.895(2), C1–C3 1.463(2), C3–C2 1.361(3), C2–N3 1.507(2), C1–P 1.670(2), N3–Al–C1 90.96(7), N3–Al–N2 86.66(6), N1–Al–C1 108.23(7), N1–Al–N2 120.12(7), Al–C1–C3 104.68(12), Al–C1–P 122.76(10), P–C1–C3 131.03(13). **6**: C1–N3 1.398(9), C1–Al 1.849(8), Al–N2 1.821(7), Al–C3 2.145(8), C3–C2 1.534(10), C2–C1 1.400(10), C3–P 1.824(8), N1–Al 1.865(6), Al–C3–C2 82.6(4), C3–C2–C1 106.5(7), C2–C1–N3 135.2(8), C2–C1–Al 98.0(5), C1–Al–C3 71.7(3).

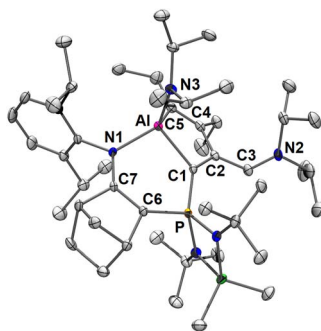
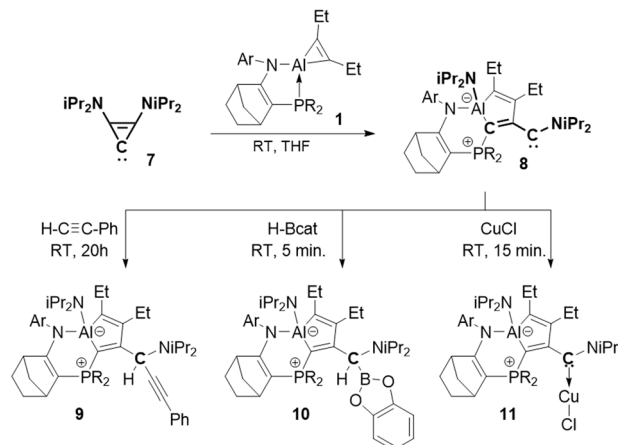


Fig. 5 Molecular structure of **8**. Thermal ellipsoids represent 30% probability. H and disordered atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Al–C1 1.992(2), C1–C2 1.401(3), C1–P 1.708(2), C2–C3 1.415(3), C3–N2 1.285(3), C2–C4 1.518(3), C4–C5 1.355(3), C5–Al 1.990(2), N1–Al 1.917(2), Al–N3 1.845(2), C2–C3–N2 125.7(2). Torsion angles [°]: C1–C2–C3–N3 104.5(3).

acyclic (amino)carbene **8**, as a mixture of two diastereomers (80 : 20). Carbene **8** is stable at RT and was isolated as red crystals from a concentrated pentane solution at $-25\text{ }^{\circ}\text{C}$ (yield: 85%). The ^{31}P -NMR spectrum exhibits two singlet signals corresponding to the two diastereomers at 20.1 ppm and 22.5 ppm, respectively, with an 80 : 20 ratio. In the ^{13}C -NMR spectrum, two doublet signals corresponding to the carbene carbon atom appear at 296 ppm ($J_{\text{CP}} = 17.6\text{ Hz}$) and 301 ppm ($J_{\text{CP}} = 17.6\text{ Hz}$), respectively, chemical shifts within the range of (amino)carbenes.^{18–21} The X-ray structure of **8** (Fig. 5) exhibits a short C3–N2 bond length [1.285(3) Å], indicating double bond character, and a planar geometry around the N2 atom ($\Sigma\text{N}2^{\circ}: 360^{\circ}$). These are consistent with the stabilization of carbene by π -electron donation from the amino group. The (amino)carbene **8** also shows a widened carbene angle [125.7(2) $^{\circ}$] and a shorter C2–C3 bond [1.415(3) Å] compared to those of previously reported (amino)(aryl)carbenes [$\text{C}_{\text{aryl}}\text{--C}_{\text{carbene}}\text{--N}$: 117.9–121.0 $^{\circ}$ and $\text{C}_{\text{aryl}}\text{--C}_{\text{carbene}}$: 1.453–1.469 Å].¹⁸ This suggests an enhanced π -interaction of the carbene lone pair with the adjacent phosphonio-substituted Al-heterocycle with a strong π -attracting character. Indeed, the ^{13}C -NMR signal for the C1 atom adjacent to the P/Al atoms (102.0 ppm) is upfield shifted compared to those observed for its derivatives **9–11** (137.8–140.1 ppm). Hence, **8** is regarded as a push–pull carbene rather than a push–spectator carbene. As expected, with a singlet-triplet energy gap ($\Delta E_{\text{S-T}} = 31.0\text{ kcal mol}^{-1}$) of **8** much smaller than that of the starting cyclopropenylidene **7** ($\Delta E_{\text{S-T}} = 70.6\text{ kcal mol}^{-1}$), the (amino)carbene **8** exhibits enhanced ambiphilic reactivity.

Indeed, **8** reacts with phenylacetylene and catecholborane, through C–H and B–H bond activation, respectively, to give the corresponding 1,1-adducts **9** and **10** (Scheme 2), in a manner similar to that of previously reported (amino)carbenes.^{22,23} Their formation was easily monitored using the characteristic ^1H -NMR signals of the newly formed C–H group at the carbene center [**9**: 5.20 ppm and **10**: 4.53 ppm]. The structure of **9** was confirmed by X-ray diffraction analysis (see ESI, Fig. S6†). The reaction of **8** with CuCl at RT affords the corresponding Cu(I)-complex **11**, which has been isolated as orange crystals from a toluene solution at $-30\text{ }^{\circ}\text{C}$ (yield: 82%). The ^{13}C -NMR



Scheme 2 The reaction of **1** with stable cyclopropenylidene **7** and reactions of (amino)carbene **8**.

spectrum exhibits a characteristic signal for the Cu(I)-complexed (amino)carbene at 244.4 ppm ($J_{\text{CP}} = 14.4\text{ Hz}$), upfield shifted relative to that of the free-carbene **8** (296 and 301 ppm).²⁴ The molecular structure of complex **11** was confirmed by X-ray diffraction analysis (see ESI, Fig. S7†).

According to DFT calculations on the reaction pathway, the reaction starts with a formal insertion of cyclopropenylidene **7** into the Al–C bond of aluminocyclopropene **1**, which proceeds in two steps, through the carbene $\rightarrow$ Al coordination (INT6) followed by the expansion of the aluminocyclopropene ring *via* the 1,2-migration of the vinyl carbon from Al to the $\text{C}_{\text{carbene}}$ atoms to form the corresponding spirocyclic intermediate INT7 (Fig. 6). Of particular interest, although slightly endergonic ($\Delta G_{\text{INT7} \rightarrow \text{INT8}} = 2.5\text{ kcal mol}^{-1}$), the amino-substituted cyclopropene ring in INT7 readily opens to generate the corresponding (vinyl)(amino)carbene INT8, which then intramolecularly reacts with the adjacent aluminocyclobutene moiety *via* formal C–C bond activation to produce a bicyclic cyclopropene INT9. The resulting INT9 then undergoes the migration of the amino group towards the Al

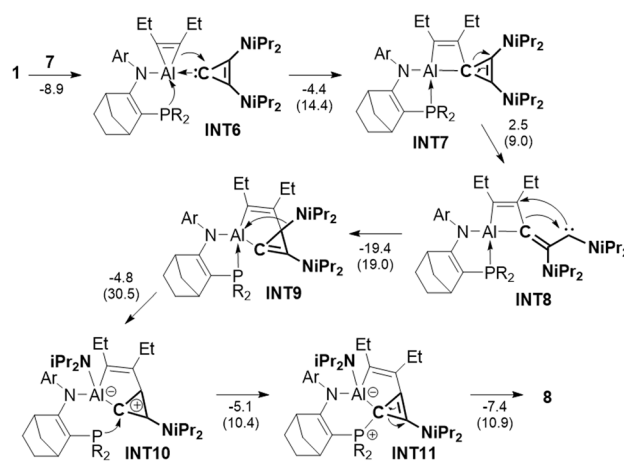


Fig. 6 Calculated pathway for the reaction of **1** with bis(diisopropylamino)cyclopropenylidene **7** (M06-2X/Def2TZVP//M06-2X/6-31G(d) level). Gibbs energies of intermediates (and transition states) are in kcal mol $^{-1}$.

center to generate the zwitterionic cyclopropenium ion **INT10**. Subsequent stabilization of **INT10** by the phosphine coordination again generates an amino-substituted cyclopropene intermediate **INT11**, analogous to **INT7**, which also opens to give the experimentally obtained stable (amino)carbene **8**. Certainly, due to the ring strain release of two three-membered rings, the reaction is strongly exergonic ($\Delta G_{1+7 \rightarrow 8} = -47.2 \text{ kcal mol}^{-1}$) and all steps, except for the carbene formation step (**INT7** $\rightarrow$ **INT8**), are exergonic processes with a highest reaction barrier of $24.4 \text{ kcal mol}^{-1}$ (**INT9** $\rightarrow$ **INT10**), which is in good agreement with the experimentally observed reaction at RT to form **8**.

Although several transition metal-involved skeletal modifications of stable (amino)cyclopropenylidene **7** are known, none of them affords a carbene derivative.²⁵ To date, only one example of “carbene-to-carbene” transformation of **7** has been reported by Koike and Iwamoto (Fig. 1(f)).¹¹ Without any doubt, the most interesting transformation found in this pathway is the easy generation of (amino)carbenes (**INT8** and **8**) from amino-substituted cyclopropene precursors (**INT7** and **INT11**), also regarded as donor-acceptor complexes of cyclopropenylidenes. This implies the possibility to use such a transformation to develop an original way to activate stable (amino)cyclopropenylidenes using Lewis pairs.

Conclusions

In conclusion, we have demonstrated that the Lewis pair complex of aluminacyclopropene with phosphine **1** can be used as a carbene-exchange reagent, which promotes “carbene-to-carbene” transformations of stable carbenes *via* skeletal recasting. Indeed, **1** reacts with a structurally stable NHC to produce a “more strained” cyclopropenylidene (**4**) *via* atomic carbon transfer from the NHC to the η^2 -coordinated alkyne fragment, within the coordination sphere of the Al(III) center. DFT calculations indicate that the transformation proceeds step-by-step ring expansions and contractions around the transferring carbon atom, and, indeed, one of the intermediates, **6** (“frozen” form of **INT6** by phosphine coordination), was successfully isolated and fully characterized. Moreover, the Al(III)-phosphine complex **1** is also able to transform the stable (diamino)cyclopropenylidene **7** into an isolable acyclic (amino)carbene **8**, which exhibits enhanced ambiphilic reactivity. As demonstrated by the numerous studies on stable mono-amino carbenes, featuring a broad range of electronic properties, the new stable amino-carbene **8**, readily available from (diamino)cyclopropenylidene **7**, has an enhanced ambiphilic character and holds promising applications in synthesis and catalysis. Further studies on the applications of this new method to activate stable carbenes, through “carbene-to-carbene” transformations promoted by Al/P Lewis pair complexes, are under active investigation. In addition, the expansion of reactivity of new carbenes (**4**) (the equilibrium species of **3**)/**8** is currently being studied.

Data availability

All experimental and computational data associated with this work are available in the ESI.†

Author contributions

Huihui Xu and José Miguel León Baeza carried out the synthetic experiments and analyzed the experimental data. Nathalie Saffon-Merceron assisted in the XRD refinement of the compounds. Vıcenç Branchadell performed the DFT calculations. Tsuyoshi Kato, Antoine Baceiredo and René Segundo Rojas Guerrero supervised the work and edited the manuscript. The manuscript was written through the contribution of all authors.

Conflicts of interest

There are no conflicts to declare.

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