Inorganic Chemistry

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Communication

Cyclic (Alkyl)(amino)carbene Lanthanide Amides: Synthesis, Structure, and Catalytic Selective Hydrosilylation of Alkenes

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Cite This: https://doi.org/10.1021/acs.inorgchem.1c01780

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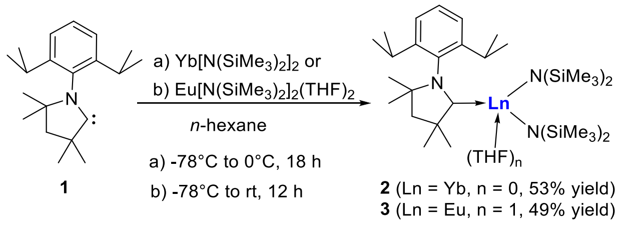
ABSTRACT: The first examples of cyclic (alkyl)(amino)carbene (CAAC) lanthanide (Ln) complexes were synthesized from the reaction of CAAC with $Yb[N(SiMe_3)_2]_2$ and $Eu[N(SiMe_3)_2]_2(THF)_2$ (THF = tetrahydrofuran). The structures of $(CAAC)Yb[N(SiMe_3)_2]_2$ (**2**) and $(CAAC)Eu[N(SiMe_3)_2]_2(THF)$ (**3**) were determined by X-ray diffraction analysis. Density functional theory calculations of **2** revealed the predominantly ionic bond between the Ln ion and CAAC. Complex **3** enabled catalytic hydrosilylation of aryl- and silylalkenes with primary and secondary silanes in high yields and Markovnikov selectivity.

Lanthanide (Ln) amides have attracted a great deal attention as catalysts for organic and polymer synthesis during the last 2 decades because of their unique activity and selectivity.[1] Many types of anionic spectator ligands have been designed to tune their stability and reactivity.[2] The readily available homoleptic amides $Ln[N(SiMe_3)_2]_n$ (n = 2, 3) have also been applied to some catalytic reactions.[3] Recently, we showed that neutral N-heterocyclic carbenes (NHCs) could bring remarkable improvement in the activity and selectivity of the lanthanide bis(amido) complex $Ln[N(SiMe_3)_2]_2$.[4] Trifonov and co-workers also reported the synthesis and catalytic behaviors of NHC complexes of $Ln[N(SiMe_3)_2]_2$.[5]

Cyclic (alkyl)(amino)carbenes (CAACs) represent different types of carbenes with great prospects developed in recent years.[6] Because of their unique electronic structures, CAACs, as both strong σ donors and π acceptors, exhibited some advantages in the stabilization of low-coordinated main-group compounds and transition-metal complexes[7,8] and in homogeneous catalysis.[9] However, to the best of our knowledge, there are no reports on CAAC lanthanide complexes.[4,5,10] In this paper, CAAC complexes of divalent ytterbium and europium amides (**2** and **3**; Scheme 1) have been synthesized and structurally characterized. The bonding between the Ln ions and CAAC was studied by X-ray diffraction analysis and density functional theory (DFT) calculations. Remarkably, CAAC-Eu^{II} complex **3** was found to catalyze the hydrosilylation of alkenes with primary and secondary silanes. The aryl-, (arylsilyl)-, (alkylsilyl)-, and (hydrosilyl)alkenes were hydrosilylated to generate the Markovnikov products in high yields with high regioselectivity.

Scheme 1. Synthesis of CAAC-Ln^{II} Bis(amido) Complexes



The reaction of solvent-free $Yb[N(SiMe_3)_2]_2$ with CAAC (**1**; Scheme 1) yielded $(CAAC)Yb[N(SiMe_3)_2]_2$ (**2**; 53% yield) as dark-green crystals. It is noted that no reaction was observed between $Yb[N(SiMe_3)_2]_2(THF)_2$ and **1**. In contrast, the reaction of **1** with $Eu[N(SiMe_3)_2]_2(THF)_2$ (**EuN**) yielded $(CAAC)Eu[N(SiMe_3)_2]_2(THF)$ (**3**) as yellow crystals in 49% yield. It is assumed that the reaction of $Ln[N(SiMe_3)_2]_2(THF)_2$ with **1** is very likely to go through a nucleophilic substitution mechanism. The relatively small Yb ion (1.02 and 1.17 Å for Yb^{II} and Eu^{II} in six coordination) in $Yb[N(SiMe_3)_2]_2(THF)_2$ could not be easily accessed by bulky CAAC.[1a]

The structure of **2** was characterized by ^1H and ^{13}C NMR and X-ray diffraction analysis. In the ^{13}C NMR spectrum of **2**, the characteristic resonance of the carbenic carbon appeared at δ = 288.4 ppm. The molecular structure of **2** is depicted in Figure 1. The Yb atom is tricoordinated and has a trigonal-pyramidal geometry. The Yb center deviates slightly from the plane N(3)−N(2)−C(1) (0.459 Å). The trigonal-pyramidal geometry of **2**, instead of a planar geometry, may optimize the overall crystal packing by minimizing the intermolecular contacts.[11] The Yb(1)−C(1) bond length of 2.672(3) Å is longer than that observed in the tricoordinated NHC-Yb^{II} bis(amido) complex $(IMes)Yb[N(SiMe_3)_2]_2$ [IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene; 2.600(3) Å].[4a] The Yb−N bond lengths [2.321(2) and 2.327(2) Å] in **2** are similar to those [2.317(3) and 2.323(2) Å] in $(IMes)Yb[N(SiMe_3)_2]_2$. The angle of N(2)−Yb(1)−N(3) [116.97(8)°] is slightly smaller than that [122.21(9)°] in (IMes)Yb[N-

Received: June 12, 2021

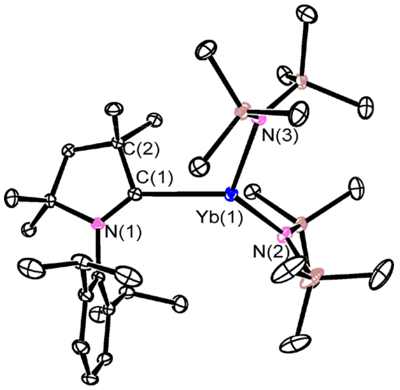


Figure 1. ORTEP representation of the X-ray structure of **2**.

(SiMe$_3$)$_2$]$_2$, showing a larger steric hindrance of CAAC than of IMes.

Because of the paramagnetic nature of the divalent Eu ion, no useful information could be obtained from the NMR spectrum of **3**. The structure of **3** was characterized by elemental and X-ray diffraction analyses. The Eu atom of **3** features a distorted tetrahedral geometry (Figure 2). The Eu−C_{CAAC} distance [2.945(3) Å] is longer than the Yb−C_{CAAC} distance because of the larger Eu^{II} ion and higher coordination number. In addition, this distance is much longer than those found in the tri- and tetracoordinated NHC-Eu^{II} bis(amido) complexes (2.722−2.808 Å).[4c] Both complexes **2** and **3** feature longer Ln−C_{CAAC} distances than the corresponding ones in NHC-Ln^{II} bis(amido) complexes, indicating the relatively weak Ln−C_{CAAC} bonding. The Eu−N bond lengths of 2.460(3) and 2.479(3) Å in **3** are comparable to those observed in tetracoordinated complexes (IMe)$_2$Eu[N(SiMe$_3$)$_2$]$_2$ and (I*i*Pr)$_2$Eu[N(SiMe$_3$)$_2$]$_2$ [2.479(5)−2.4859(11) Å].

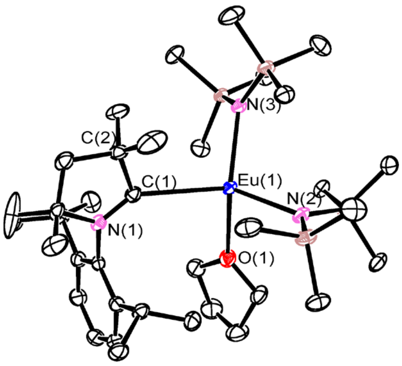


Figure 2. ORTEP representation of the X-ray structure of **3**.

To explore the nature of the Ln−C_{CAAC} bond, DFT calculations were undertaken using the PBE1PBE functional for complex **2**. The computationally optimized structure (Table S4) of **2** was in very good agreement with the crystallographically obtained structure. Natural bond orbital analyses (Figure S1) supported that most of the positive charge is located on the Yb center, portraying a predominantly ionic bond.[12] On the basis of analysis of the frontier molecular orbital for **2**, a lone pair (LP) of the carbene can be observed in the highest occupied molecular orbital (HOMO)−5 (Figure 3), which donated to the highly electropositive metal center. The natural localized molecular orbital (NLMO) calculations indicate that the Yb−C_{CAAC} bond can be represented by LP(C_{CAAC}) with 93% C 2s2p$^{1.54}$ and 4% Yb 6s6p$^{0.03}$5d$^{0.67}$ contributions with a Wiberg bond index of 0.132. The primarily electrostatic interaction is expected, given that a hard metal is interacting with a soft and polarizable carbene.[13] The lowest unoccupied molecular orbital (LUMO) of **2** is mainly the antibonding π orbital of the C(1)−N(1) bond in the CAAC.

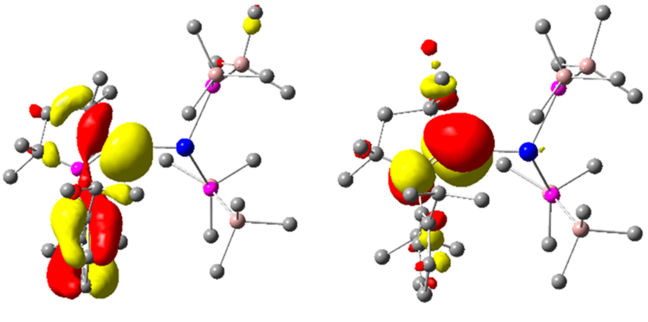

HOMO-5 LUMO

Figure 3. DFT-computed HOMO−5 and LUMO of complex **2**.

The UV−visible absorption spectra of complexes **2** and **3** (Figure 4) displayed intense absorptions at wavelengths shorter than 300 nm. The low-energy absorption of **2** (643 nm) was observed with a lower extinction coefficient (ε = 212 M^{-1} cm^{-1}) in the visible region, which is in agreement with the green color of the solution of **2**. The absorption of 643 and 316 nm for complexes **2** and **3** could be assigned to a Laporte-allowed 4f−5d transition of Ln^{II} ions.[14]

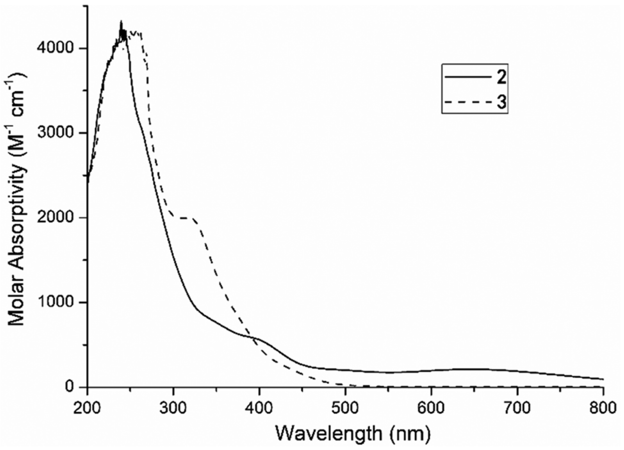
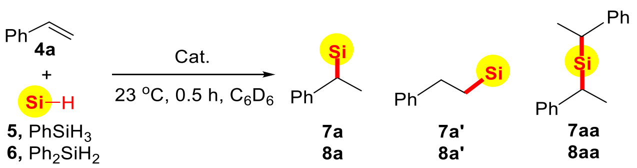


Figure 4. UV−visible absorption spectra of **2** and **3** in *n*-hexane (1 mM).

Metal-catalyzed hydrosilylation of alkenes represents the most straightforward and atom-economic protocol for the synthesis of various organosilanes, which have played important roles in organic and materials chemistry.[15] With the CAAC lanthanide amides in hand, we investigated their catalytic applications for hydrosilylation. In the first place, the catalytic hydrosilylation of styrene (**4a**) with primary silane PhSiH$_3$ (**5**) was selected as the model reaction for optimization of the conditions (Table 1, entries 1−6). A total of 1 mol % **2** (entry 1) could catalyze the hydrosilylation of **4a** in good conversion (72%) at room temperature in 0.5 h, but the anti-Markovnikov product (**7a′**) and double hydrosilylation product (**7aa**) were also yielded in about 6% selectivity

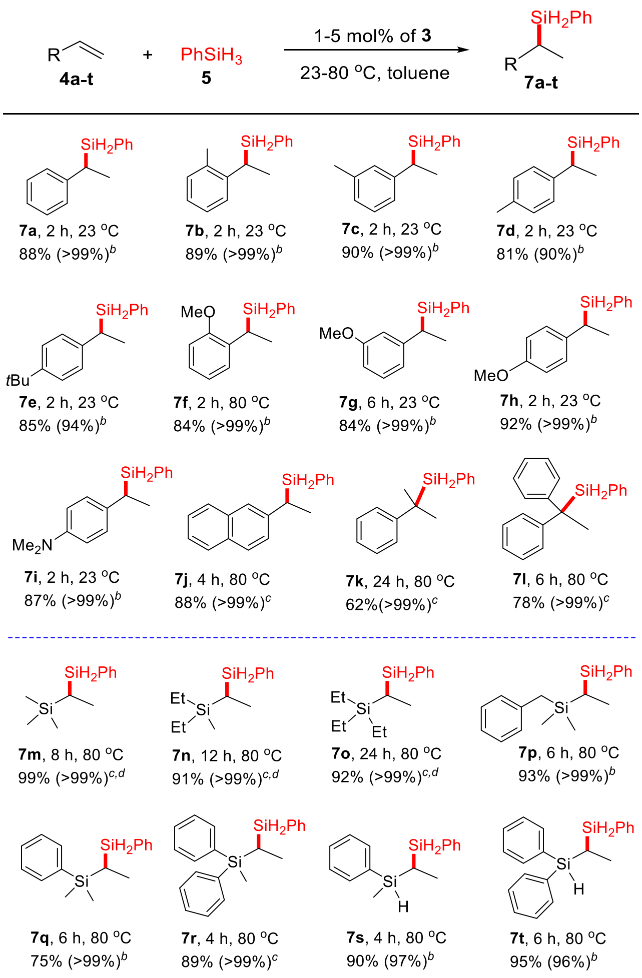
Table 1. Optimization of Reaction Conditions[a]



entry	catalyst	loading (%)	conv (%)[b]	7a/7a′/7aa[b] or 8a/8a′/8aa[b]	yield (%)[c]
1	**2**	1	72	94/4/2	55
2	**3**	1	>99	99/0/1	87
3	**3**	0.5	>99	99/0/1	87
4[d]	**EuN**	0.5	40	99/0/1	30
5	**1**	0.5	0		
6[e]	**3**	0.5	49	93/0/7	37
7[f]	**3**	1	94	91/0/9	73
8[f]	**2**	1	0		

[a] 0.01 mmol of catalyst, 0.4 mL of solvent, 1.0−2.0 mmol of **4a**, and 1.2−2.4 mmol of silane (**5** for entries 1−6 and **6** for entries 7 and 8), 23 °C, 0.5 h. [b] The conversions of **4a** and selectivity were determined by gas chromatography (GC)−mass spectrometry (MS) with a crude reaction mixture. [c] Isolated yields of **7a** and **8a**. [d] **EuN** = Eu[N(SiMe$_3$)$_2$]$_2$(THF)$_2$. [e] THF as the solvent. [f] 80 °C, 6 h.

Table 2. Eu^{II}-Catalyzed Hydrosilylation with **5**[a]



7a, 2 h, 23 °C 88% (>99%)[b]
7b, 2 h, 23 °C 89% (>99%)[b]
7c, 2 h, 23 °C 90% (>99%)[b]
7d, 2 h, 23 °C 81% (90%)[b]
7e, 2 h, 23 °C 85% (94%)[b]
7f, 2 h, 80 °C 84% (>99%)[b]
7g, 6 h, 23 °C 84% (>99%)[b]
7h, 2 h, 23 °C 92% (>99%)[b]
7i, 2 h, 23 °C 87% (>99%)[b]
7j, 4 h, 80 °C 88% (>99%)[c]
7k, 24 h, 80 °C 62%(>99%)[c]
7l, 6 h, 80 °C 78% (>99%)[c]
7m, 8 h, 80 °C 99% (>99%)[c,d]
7n, 12 h, 80 °C 91% (>99%)[c,d]
7o, 24 h, 80 °C 92% (>99%)[c,d]
7p, 6 h, 80 °C 93% (>99%)[b]
7q, 6 h, 80 °C 75% (>99%)[b]
7r, 4 h, 80 °C 89% (>99%)[c]
7s, 4 h, 80 °C 90% (97%)[b]
7t, 6 h, 80 °C 95% (96%)[b]

[a] 0.01 mmol of **3** and 0.4 mL of toluene. The percent refers to the isolated yields. The percent in brackets refers to the regioselectivity determined by GC−MS measurement of the crude reaction mixture. [b] 1.0 mmol of alkene and 1.2 mmol of **5**. [c] 0.2 mmol of alkene and 0.24 mmol of **5**. [d] Yields determined by GC−MS measurement of the crude product.

besides the major Markovnikov product (**7a**). Under the same reaction conditions, **3** (entry 2) could enable highly efficient and selective hydrosilylation reaction, leading to the quantitative production of **7a** in 99% selectivity even in 0.5 mol % catalyst loading (entry 3). For comparison, **EuN** and **1** were also examined as catalysts. Although **EuN** displayed high selectivity (99%), only 40% of **4a** could be hydrosilylated (entry 4), while CAAC was inactive for this hydrosilylation (entry 5). **4a** was hydrosilylated in moderate conversion (49%) in THF (entry 6) probably because of the interactions of the solvent molecules with Eu ion, which suppresses the coordination−insertion process of alkenes. To our delight, catalytic hydrosilylation of **4a** with the secondary silane Ph$_2$SiH$_2$ (**6**) was also carried out efficiently (94% conversion and 91% selectivity) to yield the Markovnikov product **8a** (entry 7). In sharp contrast, **2** has no activity for the same reaction (entry 8). Other silanes were tested in **4a** hydrosilylation (Table S1). n-C$_6$H$_{13}$SiH$_3$ and PhMeSiH$_2$ exhibited moderate activity (62 and 70% conversions) and good-to-poor selectivity (94 and 74%). Et$_2$SiH$_2$ was inactive with catalyst **3**.

Under the optimized conditions with **5** as the silylation reagent, a range of aryl- and silylalkenes (**4a**−**4t**) were examined. As shown in Table 2, the secondary silane products (**7a**−**7t**) were generated in good-to-high yields (62−95%) and high Markovnikov selectivity (from 90 to >99%). The regioselectivity of the arylalkenes is attributed to η^3 coordination between the Ln ion and aromatic fragment,[16] whereas that of silylalkenes might arise from polarization of the Si−C bond, in which the α-C atom with higher electron density leads to bonding with the Ln ion.[17] The catalytic protocol tolerated alkoxy (**7f**−**7h**), amino (**7i**), alkylsilyl (**7m**−**7p**), arylsilyl (**7q** and **7r**), and hydrosilyl (**7s** and **7t**) groups. Although the selective hydrosilylation of arylalkenes can be realized by a number of metal complex catalysts, the reaction for silylalkenes could only be achieved with a couple of metal catalysts.[18] Furthermore, because the alkenes containing two functional groups, like Si−H bond and double bond, preferred stepwise polymerization as monomers with transition-metal catalysts, the hydrosilylation of hydrosilylalkene has not been reported.[19] The existence of the two different hydrosilyl groups in product **7t** was confirmed by the proton-coupled ^{29}Si NMR spectrum, in which one doublet peak and one triplet peak were observed (Figure S22). Moreover, the bulky 1,1-disubstituted alkenes (α-methyl **7k** and α-phenyl **7l**) can be smoothly catalyzed by **3** to generate the Markovnikov products in 62 and 78% yields and excellent regioselectivity (>99%).

With the secondary silane **6** as the silylation reagent (Table 3), complex **3** enabled the hydrosilylation of aryl- and silylalkenes (**4a**−**i**, **4l**, **4q**, and **4s**), leading to the tertiary silane products (**8a**−**8l**) in moderate-to-high yields (49−90%) and high Markovnikov selectivity (from 90 to >99%). The arylalkenes with OMe and NMe$_2$ substituents on the phenyl rings and silylalkene with a PhMeSiH substituent can be hydrosilylated smoothly to give the regioselective products **8f**−**8i** and **8l**) in good yields (61−85%). Furthermore, complex **3** also catalyzed the hydrosilylation of bulky α-phenylstyrene with **6** (**8j**) in 49% yield and excellent regioselectivity (>99%). For complex **3**-catalyzed hydrosilylation (Tables 2 and 3), the activities of the primary silane and α-alkenes were higher than

https://doi.org/10.1021/acs.inorgchem.1c01780
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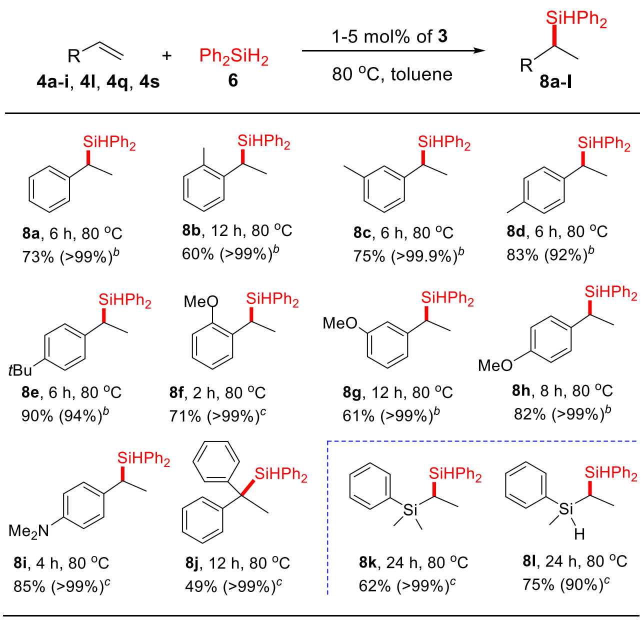
Table 3. Eu^{II}-Catalyzed Hydrosilylation with 6[a]



[a] 0.01 mmol of **3** and 0.4 mL of toluene. The percent refers to the isolated yields. The percent in brackets refers to the regioselectivity determined by GC−MS measurement of the crude reaction mixture. [b] 1.0 mmol of alkene and 1.2 mmol of **6**. [c] 0.2 mmol of alkene and 0.24 mmol of **6**.

those of the secondary silane and 1,1-disubstituted alkenes because of the steric effects. However, catalyst **3** could not catalyze the hydrosilylation of arylalkenes with halogen substituents (4-fluorostyrene, 4-chlorostyrene, and 4-bromostyrene) and alkylalkenes (1-hexene and cyclohexene). The mechanism of the hydrosilylation is proposed as the typical σ-bond metathesis/coordination−insertion catalytic cycle with a lanthanide hydride intermediate.[16,20] The product $PhSiH_2N(SiMe_3)_2$ of the σ-bond metathesis reaction between amide **3** and **5** could be observed during the hydrosilylation in an NMR tube. However, the possible CAAC-stabilized europium hydride cannot be isolated from the stoichiometric reaction of **3** with **5**. It is probably attributed to the instability of the hydride under the experimental conditions.[4a]

In summary, we have described the synthesis and characterization of the first examples of CAAC lanthanide complexes **2** and **3**. The europium complex **3** enabled selective hydrosilylation of aryl- and silylalkenes, giving Markovnikov products in high yields. Remarkably, complex **3** enabled the catalytic hydrosilylation of hydrosilylalkenes, which were more likely to polymerize with transition-metal catalysts. The high activity of **3** could be attributed to the large ionic radius of the Eu ion for alkene coordination as well as the stabilizing effect of the CAAC ligand for catalytic active species. The present results suggest the potential of the CAAC lanthanide amides in hydroelementation reactions, which are currently in progress. Moreover, optimization of the reaction conditions for low catalyst loadings and functional group tolerance is also our future target.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c01780.

Experimental procedures, crystallographic data, DFT calculations, and spectra (PDF)

Accession Codes

CCDC 2064197 and 2068390 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the National Natural Science Foundation of China (Grants 21890722, 22071123, and 21632006) for financial support. Dedicated to the 100th Anniversary of Chemistry at Nankai University.

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