# Reactivity of $[Ce(NR_2)_3]$ (R = $SiMe_3$) with Prospective Carbon-Atom Transfer Reagents

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**Abstract**

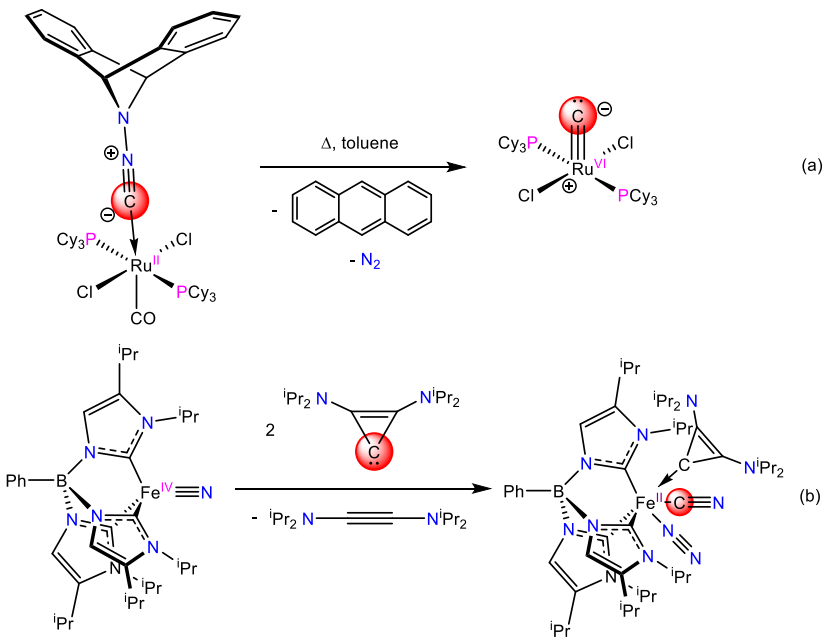
Herein, we report the synthesis, characterization, and reactivity of the *N*-(isocyanoimine)triphenylphosphine ($CNNPPh_3$) and bis(diisopropylamino)cyclopropenylidene (BAC) adducts of $[Ce(NR_2)_3]$ (R = $SiMe_3$), namely, $[(NR_2)_3Ce(CNNPPh_3)]$ (**1**) and $[(NR_2)_3Ce(BAC)]$ (**2**). Photolysis of **1** with a 380 nm LED source for 1 month results in clean formation of $[(NR_2)_3Ce(NCNPPh_3)]$ (**3**), via reorganization of the nitrilimine ligand to its carbodiimide isomer. Photolysis of **2** with a 365 nm LED source results in formation of the methylenecyclopropene species, $[(^iPr_2N)_2C_3C(N^iPr_2)(CCN^iPr_2)]$ (**5**), via the formal dimerization and rearrangement of two BAC fragments. Compound **5** can also be generated under catalytic conditions by performing the photolysis of BAC in the presence of 10 mol% $[Ce(NR_2)_3]$.

## Introduction

While cerium *N*-heterocyclic carbene (NHC) complexes are now relatively common,[1-4] cerium complexes containing Schrock- or Fischer-type carbenes are essentially unknown. Likewise, cerium carbides and alkylidynes are also unknown. That said, some progress has been made toward the generation of Ce-C multiple bonds in recent years. For example, Liddle and co-workers have reported the synthesis of the cerium methanediide complexes, $[Ce(BIPM^{TMS})(ODipp)_2]$ and $[Ce(BIPM^{TMS})_2]$ ($BIPM^{TMS} = [C(PPh_2NR)_2]^{2-}$, R = $SiMe_3$; Dipp = 2,6-diisopropylphenyl).[5-8] More recently, Zhu and co-workers ligated the carbodiphosphorane, $C(PPh_3)_2$, to Ce(III),[9, 10] forming $[BrCe(CDP)_2][BPh_4]_2$. DFT calculations revealed that the Ce-C bond in this complex consisted of a strong σ-interaction and a weak π-interaction.

In the past few years, a number of carbon-atom transfers reagents have been identified, which could, in principle, be employed to generate an elusive Ce-C multiple bond. For example, Cummins and co-workers demonstrated that 7-isocyano-7-azadibenzonorbornadiene ($CN_2C_{14}H_{10}$) could be used in a C-atom transfer reaction to synthesize the ruthenium carbide complex, $[RuCl_2(C)(PCy_3)_2]$, via loss of $N_2$ and anthracene (Scheme 1a).[11] In addition, Smith and co-workers demonstrated that bis(diisopropylamino)cyclopropenylidene (BAC) can transfer a carbon atom to the iron(IV) nitride, $[\{PhB(^iPr_2Im)_3\}Fe(N)]$ ($^iPr_2Im$ = 1,2-diisopropylimidazolylidene), resulting in formation of a cyanide complex concomitant with loss of bis(diisopropylamino)acetylene (Scheme 1b).[12]

**Scheme 1.** Previous examples of carbon-atom transfer




Generally speaking, the use of these carbon-atom transfer reagents requires a reducing metal complex to effect C-atom transfer.[12, 13] Cerium(III) is not usually considered to be a good reductant, as it prefers the 3+ oxidation state;[14, 15] however, it has recently been shown that photolysis of cerium(III) results in the generation of a substantially more reducing metal center.[16] For example, Schelter and co-workers reported that photolysis of $[Ce(NR_2)_3]$ (R = $SiMe_3$) resulted in formation of a relatively long-lived excited state.[17, 18] This excited state species is strongly reducing, and can elicit homolytic cleavage of the C-Cl bond in $PhCH_2Cl$, resulting in formation of $[Ce(Cl)(NR_2)_3]$ and bibenzyl.[17] Since then, Ce(III) has been shown to facilitate a variety of photo-mediated transformations, including aryl coupling and borylation reactions.[18-21] In addition, our group reported that photolysis of a cerium nitrate complex, [Li(2,2,2-cryptand)][Ce($\kappa^2$-$O_2NO$)$(NR_2)_3$], resulted in formation of the terminal Ce=O complex, [Li(2,2,2-cryptand)][Ce(O)$(NR_2)_3$], via formal loss of $NO_2$.[22] Motivated by these past results, we hypothesized that ligation of a carbon-atom transfer reagent to cerium(III), followed by photolysis,

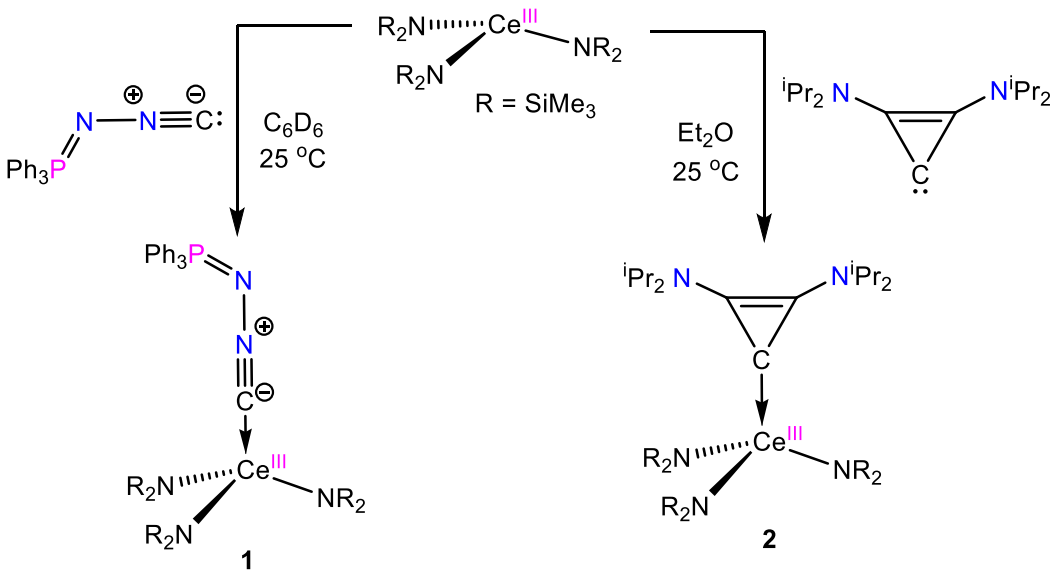
could induce either partial or complete carbon atom transfer and allow access to novel Ce(IV) organometallics.

Herein, we describe the ligation of two prospective carbon-atom transfer reagents, N-(isocyanoimine)triphenylphosphine ($CNNPPh_3$), a much more easily synthesized relative of 7-isocyano-7-azadibenzonorbornadiene, and bis(diisopropylamino)cyclopropenylidene (BAC), to the well-known Ce(III) tris(amide) complex, [$Ce(NR_2)_3$], along with an investigation of their photolytic chemistry. While carbon-atom transfer from BAC and $CNNPPh_3$ is nominally a $4e^-$ redox process,[11, 12] and each Ce(III) center can provide only one electron, we envisioned that cooperative reactivity of multiple Ce(III) centers could give rise to unique alkylidene- or carbide-containing complexes or clusters.

**Results and Discussion**

**Synthesis and characterization of 1 and 2.** Reaction of $CNNPPh_3$ with [$Ce(NR_2)_3$] (R = $SiMe_3$) in benzene-$d_6$ affords the Ce(III) isocyanoimine adduct, [$(NR_2)_3Ce(CNNPPh_3)$] (**1**), which can be isolated as pale yellow plates in 51% yield after work-up (Scheme 2). The $^1H$ NMR spectrum of the isolated material in benzene-$d_6$ features a broad resonance at -0.55 ppm, which is assignable to the $SiMe_3$ environment (Figure S1). In addition, resonances at 2.88, 5.43, and 6.00 ppm, are assignable to the *o*-, *m*-, and *p*-aryl protons of the three phenyl groups, respectively. The $^{31}P\{^1H\}$ NMR spectrum displays a sharp resonance at 8.59 ppm (Figure S2), which is shifted upfield from the signal observed for free $CNNPPh_3$ (25.7 ppm in benzene-$d_6$, Figure S19). Finally, **1** features a sharp $\nu_{CN}$ mode at 2117 $cm^{-1}$ in its IR spectrum (Figure S20), which is substantially blue-shifted from that observed for the free ligand ($\nu_{CN}$ = 2067 $cm^{-1}$).[23]

**Scheme 2.** Synthesis of Ce(III) carbene complexes **1** and **2**


R2N Ce III NR2
R2N
R = SiMe3
C6D6
25 °C
Et2O
25 °C
iPr2 N NiPr2
C
Ph3P
N
N
C
1
2

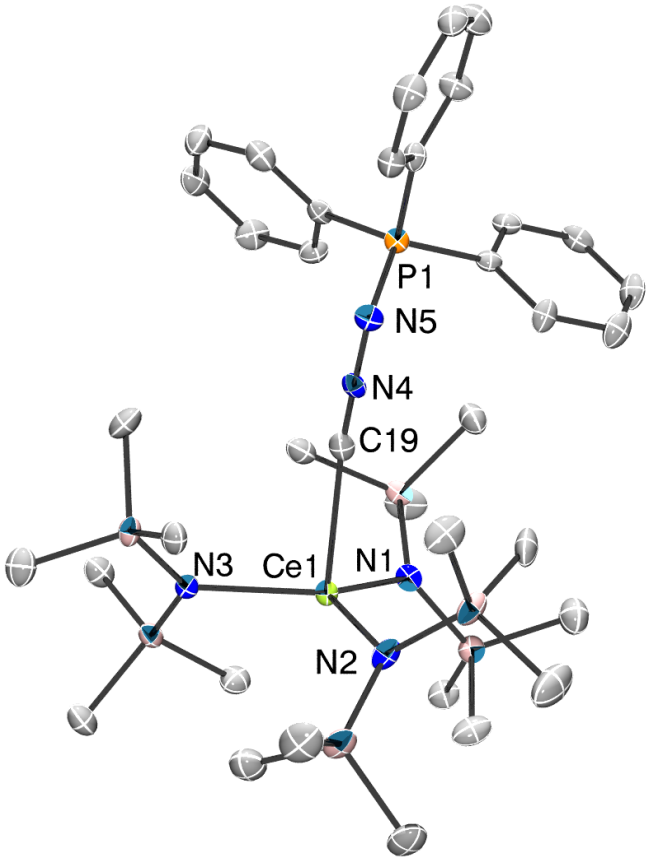

P1
N5
N4
C19
N3
Ce1
N1
N2

**Figure 1.** Solid-state molecular structure of **1**, shown with 50% probability ellipsoids. Hydrogen atoms removed for clarity. Selected bond lengths (Å) and angles (°): Ce1-N1 = 2.369(4), Ce1-N2 = 2.360(4), Ce1-N3 = 2.355(4), Ce1-C19 = 2.669(5), C19-N4 = 1.152(6), N4-N5 = 1.343(5), N5-P1 = 1.624(4), N1-Ce1-N2 = 116.7(1), N1-Ce1-N3 = 119.5(1), N2-Ce1-N3 = 121.1(1).

The connectivity of complex **1** was verified by X-ray crystallography (Figure 1; see ESI for complete structural details). Complex **1** crystallizes in the triclinic space group *P*-1 and features a pseudo-tetrahedral geometry about the cerium center. Its Ce-$N_{amide}$ distances (av. Ce-N = 2.36 Å) are consistent with the Ce-N distances reported for other Ce(III) amide complexes.[22, 24-27] Moreover, its Ce-C distance (Ce1-C19 = 2.669(5) Å) is slightly shorter than those seen in previously reported Ce(III)-isocyanide and Ce(III)-NHC complexes. For example, the Ce(III) isocyanide complexes, [$(CpMe)_3Ce(CN^tBu)$] and [$Cp'_3Ce(CN^tBu)$] (Cp' = 1,3-$(Me_3Si)_2C_5H_3$) feature Ce-C bond lengths of 2.79(3) and 2.87(3) Å, respectively.[28] For further comparison, the Ce(III)-NHC complexes, [$Cp^*_2CeI(C_3Me_4N_2)$] and [$(C_5H_4{}^tBu)_3Ce(C_3Me_4N_2)$] feature Ce-C distances of 2.724(4) Å and 2.797(4) Å, respectively.[4] Finally, the C-N (1.152(6) Å) and N-N (1.343(5) Å) distances in **1** are similar to those observed in the free ligand (C-N = 1.153(4) Å; N-N = 1.345(4) Å),[29] as well as a previously isolated Cr(0) complex, [$(OC)_5Cr(CNNPPh_3)$] (C-N = 1.150(4) Å; N-N = 1.346(3) Å),[29] suggesting minimal disruption of the nitrilimine fragment upon coordination to Ce(III).

Reaction of [$Ce(NR_2)_3$] with 1 equiv of bis(diisopropylamino)cyclopropenylidene (BAC) in $Et_2O$ results in a rapid color change from deep yellow to orange (Scheme 2). Work up of the reaction mixture, followed by crystallization from pentane/hexamethyldisiloxane (HMDSO), results in the isolation of [$(NR_2)_3Ce(BAC)$] (**2**) as yellow blocks in 60% yield. The $^1H$ NMR spectrum of **2** exhibits broad resonances at 3.12, 0.81, and 0.01 ppm, which are assignable to a

BAC methine environment and two BAC isopropyl methyl environments, respectively. In addition, a broad singlet at -2.25 ppm is assignable to the $SiMe_3$ proton environment. The chemical shift of the $SiMe_3$ groups, along with a broadening of all resonances, is consistent with the presence of a paramagnetic Ce(III) metal center.

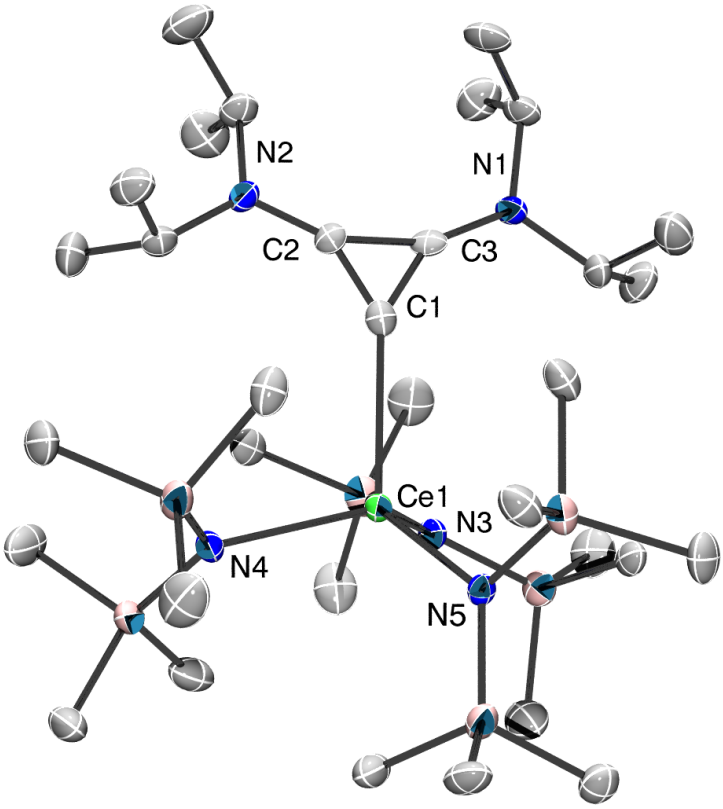



**Figure 2.** Solid-state molecular structure of **2**, shown with 50% probability ellipsoids. Hydrogen atoms removed for clarity. Selected bond lengths (Å) and angles (°): Ce1-N3 = 2.371(3), Ce1-N4 = 2.380(3), Ce1-N5 = 2.384(3), Ce1-C1 = 2.669(4), C1-C2 = 1.380(5), C1-C3 = 1.393(5), C2-C3 = 1.365(5), N3-Ce1-N4 = 121.1(1), N3-Ce1-N5 = 113.7(1), N4-Ce1-N5 = 104.1(1).

Complex **2** crystalizes in the monoclinic space group $P2_1/c$ and features a pseudo-tetrahedral geometry about the cerium(III) center (Figure 2). The Ce-$N_{amide}$ distances (av. Ce-N = 2.38 Å) are similar to Ce-N distances reported for other cerium(III) amide complexes,[22, 24-27] while the Ce-

$C_{BAC}$ bond length (2.669(4) Å) is slightly longer than those reported for other Ce(III)-NHC adducts,[4] but similar to that of complex **1**. The C1-C2 and C1-C3 distances are 1.380(5) and 1.393(5) Å, respectively, which are comparable to those of the free ligand (1.405(3) Å).[30] The C2-C3 distances in complex **2** (1.365(5) Å) and free ligand (1.344(3) Å) are also comparable.

The UV-vis spectrum of **1** in $Et_2O$ features a broad absorption at 397 nm ($\varepsilon$ = 562 $M^{-1}cm^{-1}$) (Figure 3), and is similar to that reported for $[Ce(NR_2)_3]$.[17] We have assigned the absorption to a metal-based $4f \rightarrow 5d_z^2$ transition, by analogy with the assignments reported for $[Ce(NR_2)_3]$ and other $CeX_3$-type complexes.[20, 21, 31] For comparison, the $4f \rightarrow 5d_z^2$ and $4f \rightarrow 5d_{xz/yz}$ transitions for $[Ce(NR_2)_3]$ occur at 413 nm and 341 nm, respectively. We attribute the *ca*. 16 nm blue shift observed for the $4f \rightarrow 5d_z^2$ transition in **1** to an increase in energy of the $5d_z^2$ orbital due to electron donation by the $CNNPPh_3$ ligand. The UV-vis spectrum of **2** features a broad absorption at 343 nm ($\varepsilon$ = 352 $M^{-1}cm^{-1}$), along with a prominent shoulder at ca. 380 nm (Figure 3), which we have tentatively assigned to the $4f \rightarrow 5d_{xz/yz}$ and $4f \rightarrow 5d_z^2$ transitions, respectively. The latter assignment is significantly blue shifted with respect to that reported for $[Ce(NR_2)_3]$,[17] a consequence of donation from the strongly-donating BAC ligand to the $5d_z^2$ orbital.

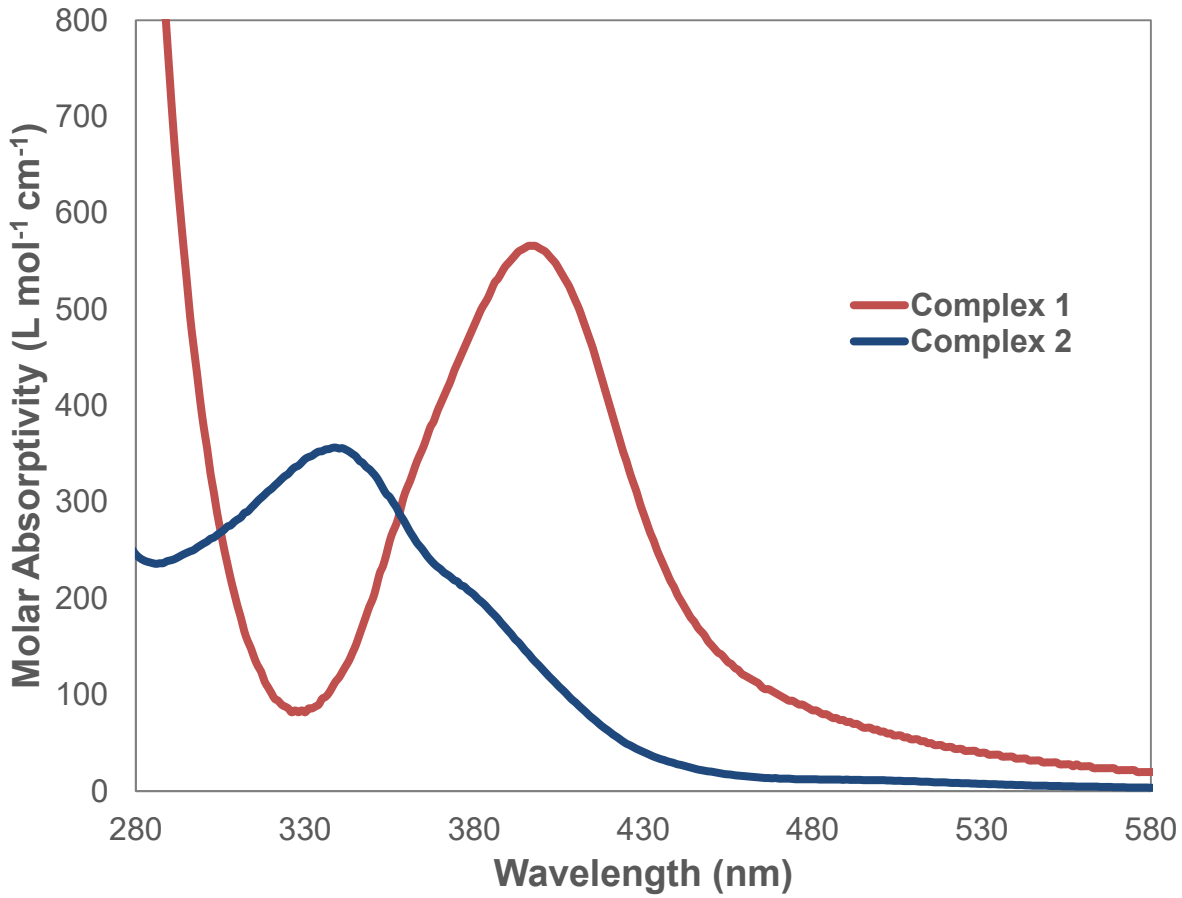
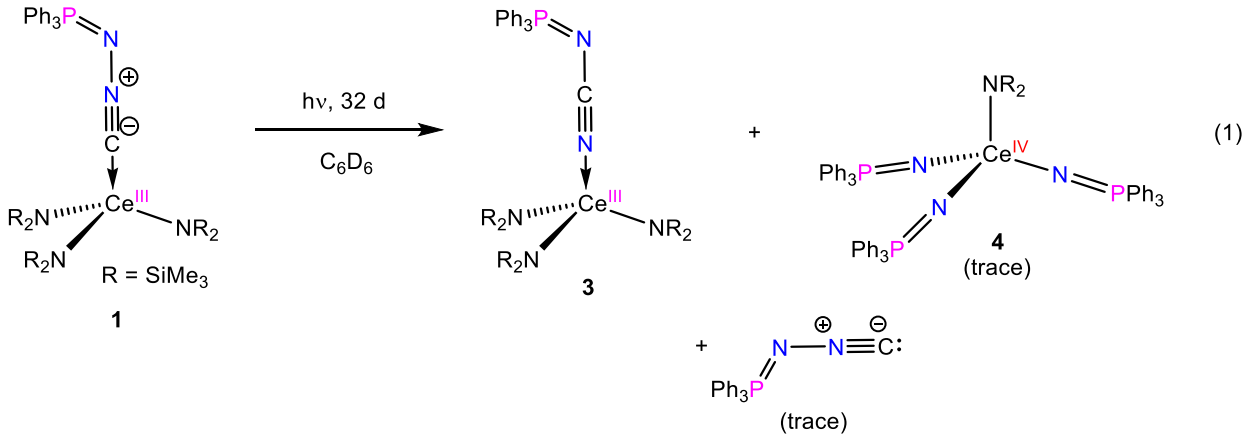



**Figure 3.** UV-vis spectra of complexes **1** (0.31 mM, $\lambda_{max}$ = 397 nm, ε = 562 L·mol$^{-1}$·cm$^{-1}$) and **2** (0.49 mM, $\lambda_{max}$ = 343 nm, ε = 352 L·mol$^{-1}$·cm$^{-1}$) in diethyl ether and benzene, respectively.

**Photochemical Reactivity of 1 and 2.** Given the similar optical properties of **1** and [Ce(NR$_2$)$_3$], we hypothesized that photolysis of **1** would also generate a highly reducing photo-excited state, which could initiate a C-atom or nitrilimine transfer to the Ce center. To this end, photolysis of a benzene-$d_6$ solution of **1** at 380 nm resulted in a very gradual color change from yellow to orange (eq 1). Complete conversion was achieved after 1 month of photolysis. A $^1$H NMR spectrum of this sample revealed the presence of a new SiMe$_3$ resonance at -0.36 ppm, as well as new phenyl resonances at 3.11, 5.53, and 6.05 ppm, which correspond to the *o*-, *m*-, and *p*-aryl protons,

respectively (Figure S6). These resonances as assignable to the carbodiimide complex, $[(NR_2)_3Ce(NCNPPh_3)]$ (**3**). Moreover, the $^{31}P\{^1H\}$ NMR spectrum of this sample features a new resonance at 7.26 ppm, which is assignable to complex **3**. Also present in this spectrum are minor resonances at -26.37 and 22.4 ppm, which are assignable to an unidentified product and free $CNNPPh_3$, respectively (Figure S7). In addition, we observe a minor resonance at -1.26 ppm, which we have tentatively assigned to the Ce(IV) phosphiniminato complex, $[(NR_2)Ce(NPPh_3)_3]$ (**4**) (see below for more details).




Work-up of the reaction mixture resulted in the isolation of pale-yellow blocks of **3**, which could be isolated in 52% crystalline yield. Complex **3** crystallizes in the triclinic space group *P*-1 and features a pseudo-tetrahedral geometry about the cerium center (Figure 4). The Ce-$N_{nitrile}$ distance (Ce1-N4 = 2.50(2) Å) in **3** is notably shorter that the Ce-C distance in **1**. This decrease likely reflects the greater electronegativity of nitrogen, which makes it a better donor to the highly electropositive $Ce^{3+}$ center. For comparison, the Ce(III) benzonitrile complex, $[Ce\{CH(SiMe_3)_2\}_3(NCPh)]$, features a Ce-N distance of 2.607(4) Å, while $[Cp^*_3Ce(NC^tBu)_2]$ features an average Ce-N distance of 2.64 Å.[32, 33] The N-C (1.159(3) Å) and C-N (1.297(3) Å) distances in **3** are similar to those observed in the free ligand (N-C = 1.151(9) Å; C-N = 1.301(7) Å), as well as a previously isolated Pd(II) complex, $[PdCl_2(NCNPPh_3)_2]$ (N-C = 1.151(4) Å; C-N

= 1.292(4) Å).[34, 35] These values are indistinguishable from the N-C and N-N distances observed for **1**, demonstrating that X-ray crystallography cannot be used to discriminate between the nitrilimine and carbodiimide fragments. However, the IR spectrum of **3** features intense $\nu_{CN}$ modes at 2150 $cm^{-1}$ and 2177 $cm^{-1}$ (Figures S22-S23). Their positions and relative intensities are consistent with those reported for other (*N*-cyanoimino)triphenylphosphine complexes.[29, 35]

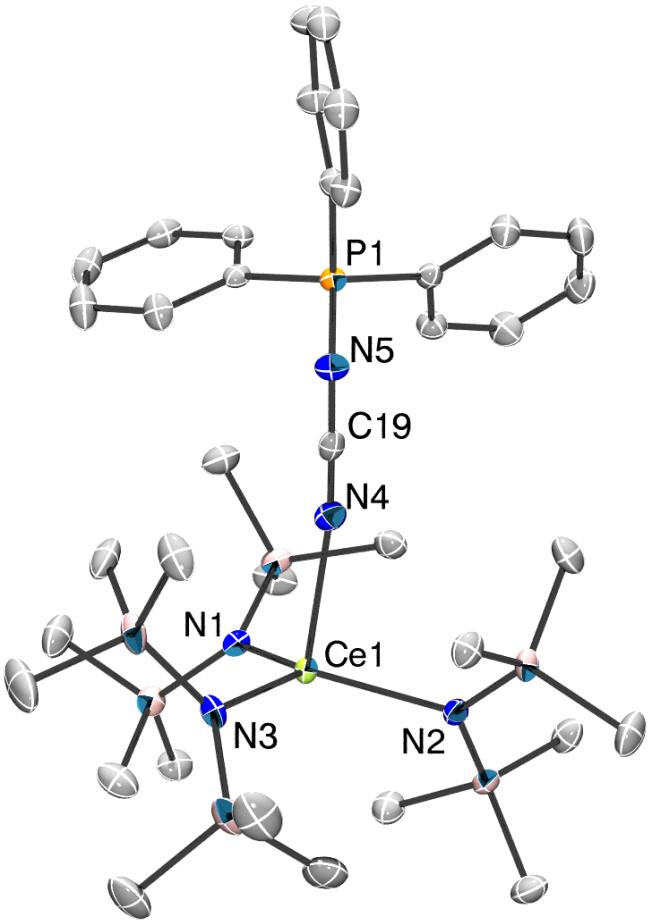



**Figure 4.** Solid-state molecular structure of **3**, shown with 50% probability ellipsoids. Hydrogen atoms removed for clarity. Selected bond lengths (Å) and angles (°): Ce1-N1 = 2.371(2), Ce1-N2 = 2.366(2), Ce1-N3 = 2.362(2), Ce1-N4 = 2.50(2), N4-C19 = 1.159(3), C19-N5 = 1.297(3), N5-P1 = 1.62(2), N1-Ce1-N2 = 118.69(6), N1-Ce1-N3 = 116.48(6), N2-Ce1-N3 = 120.14(6), N4-Ce1-N1 = 101.56(6), N4-Ce1-N2 = 96.76(6), N4-Ce1-N3 = 93.41(6).

In one instance, during an attempted crystallization of **3** we also observed the deposition of a few yellow-orange blocks, which were subsequently identified as the Ce(IV) phosphiniminato complex, $[(NR_2)Ce(NPPh_3)_3]$ (**4**), by X-ray crystallography (Figure 5). Complex **4** crystallizes in the orthorhombic space group *P*bca and features a pseudo-tetrahedral geometry about the cerium center. The $Ce\text{-}N_{amide}$ distance is 2.39(2) Å, which is comparable with the $Ce\text{-}N_{amide}$ distances reported for other Ce amide complexes.[22, 24-27] Not surprisingly, the $Ce\text{-}N_{phosphiniminato}$ bonds in **4** are much shorter (av. Ce-N = 2.12 Å), reflecting the stronger donating ability of the phosphiniminato ligand. In addition, complex **4** features an average N-P distance of 1.57 Å. For comparison, the recently reported homoleptic Ce(IV) phosphiminato complex $[Ce(NP(pip)_3)_4]$ (pip = piperidinyl, $NC_5H_{10}$) features average Ce-N and N-P distances of 2.20 Å and 1.42 Å, respectively.[36] Only a few crystals of complex **4** could be isolated, so it was not characterized further.

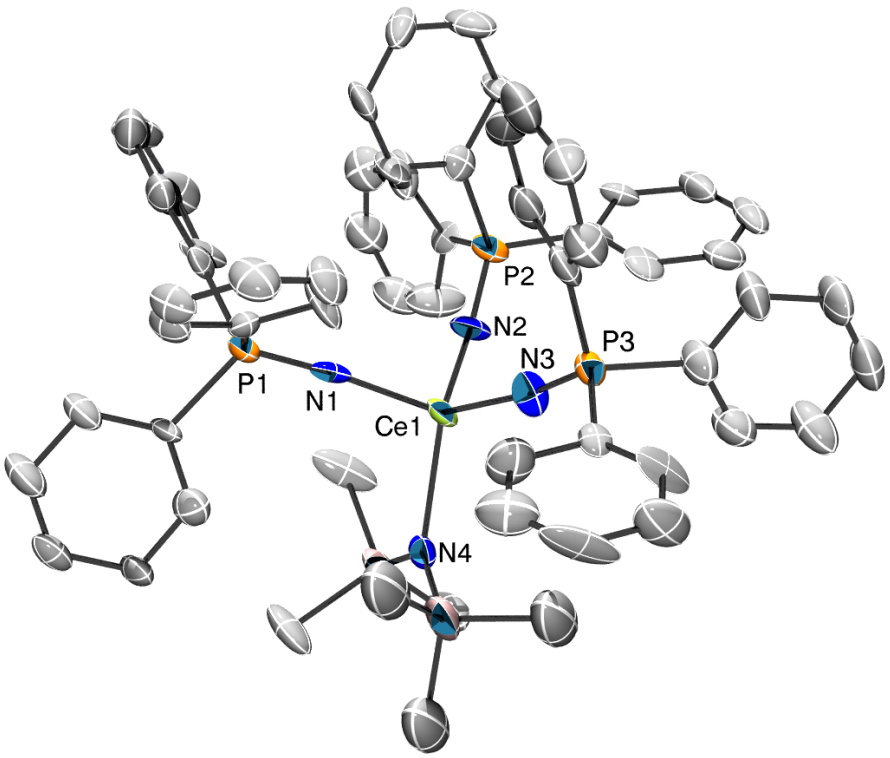



**Figure 5.** Solid-state molecular structure of **4**, shown with 50% probability ellipsoids. Hydrogen atoms removed for clarity. Selected bond lengths (Å) and angles (°): Ce1-N4 = 2.39(2), Ce-N1 = 2.131(16), Ce-N2 = 2.100(17), Ce-N3 = 2.120(16), N1-P1 = 1.582(17), N2-P2 = 1.564(16), N3-P3 = 1.552(17), N2-Ce-N4 = 125.9(6).

Complex **3** can also be generated upon thermolysis of a $C_6D_6$ solution of **1** at 42 ºC for 3 d; however, under these conditions the reaction is not as selective. In particular, we observe the formation of increased amounts of complex **4**, according to the $^{31}P\{^1H\}$ NMR spectrum (Figure S14). Finally, control experiments reveal that free $CNNPPh_3$ is stable to both the photolytic and thermolytic conditions employed in this study (Figures S15-S18), demonstrating the need for Ce(III) to effect the isomerization. For comparison, both the photochemical and thermal isomerization of metal-bound nitrilimines are known,[29, 37-40] although there are only a few

examples reported for the f-elements. In particular, Liddle and co-workers observed that the uranium nitrilimine complex, $[U(tren^{TMS})\{\mu\text{-}N(SiMe_3)NC\}]_2$ ($tren^{TMS}$ = $N(CH_2CH_2NSiMe_3)_3$], cleanly converted to the nitrile complex, $[U\{N(CH_2CH_2NSiMe_3)_2(\mu\text{-}CH_2CH_2NC{\equiv}N)\}\{N(SiMe_3)_2\}]_2$ upon photolysis.[41] Clearly, N-N bond cleavage and isomerization is the preferred route of reactivity for $CNNPPh_3$, unlike Cummins' 7-isocyano-7-azadibenzonorbornadiene, which likely has a substantially larger thermodynamic driving force for C-atom transfer.[11]

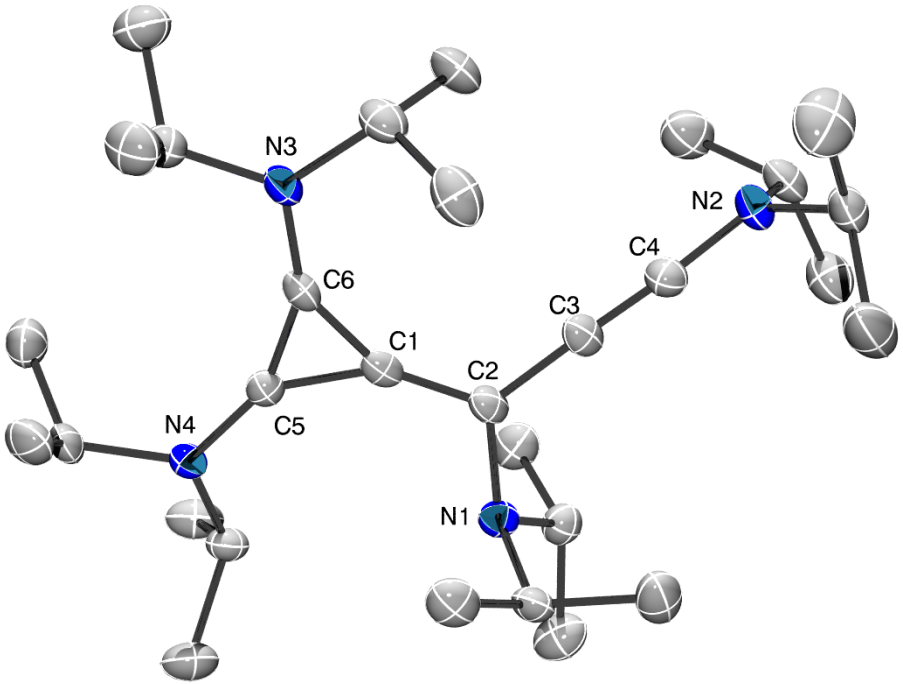
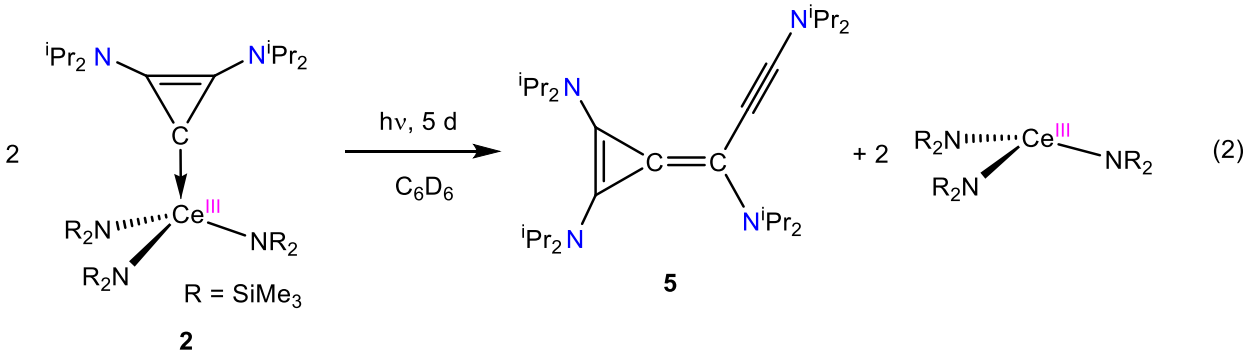



**Figure 6.** Solid-state molecular structure of **5**, shown with 50% probability ellipsoids. Hydrogen atoms removed for clarity. Selected bond lengths (Å) and angles (°): C1-C2 = 1.370(3), C1-C5 = 1.408(3), C1-C6 = 1.418(3), C2-C3 = 1.403(3), C6-C5 = 1.359(3), C6-N3 = 1.363(3), C5-N4 = 1.358(3), C2-N1 = 1.478(3), C4-N2 = 1.355(3), C3-C4 = 1.211(3), C6-C1-C2 = 153.6(2), C5-C1-

C6 = 57.5(2), C5-C1-C2 = 148.9(3) C4-N2-C22 = 118.4(2), C4-N2-C21 = 116.8(2), C22-N2-C21 = 117.5(2).

We also explored the photolysis of complex **2**. Photolysis of a benzene-$d_6$ solution of **2**, in an NMR tube equipped with a J-Young valve, using a 365 nm LED lightstrip slowly generated a new diamagnetic product, according to the $^1$H NMR spectrum. This spectrum features four new magnetically inequivalent diisopropylamino groups, as evidenced by septets at 4.37, 3.61, 3.59, and 3.00 ppm. Also present in this spectrum is free [$Ce(NR_2)_3$], as evidenced by a broad singlet at -3.38 ppm (eq 2 and Figure S8). The new diamagnetic product was identified as the methylenecyclopropeneyne, [($^i$Pr$_2$N)$_2$C$_3$C(N$^i$Pr$_2$)(CCN$^i$Pr$_2$)] (**5**), by X-ray crystallography, which is evidently formed by a photo-induced dimerization of the BAC ligand.




Compound **5** crystalizes in the monoclinic space group $P2_1/c$ (Figure 6). The C1-C2 (1.370(3) Å) and C6-C5 (1.359(3) Å) distances are somewhat longer than those expected for a C-C double bond, whereas the C1-C5 (1.408(3) Å) and C1-C6 (1.418(3) Å) distances are shorter than those expected for a C-C single bond (Figure 7). Overall, these metrical parameters are evidence of mesoionic character in **5**. For comparison, the metrical parameters of the methylenecyclopropene unit in **5** are essentially identical with those previously reported for 4,4-dicyano-2,3-

diphenyltriafulvene (Figure 7),[42] which was also thought to feature considerable mesoionic character.[43]

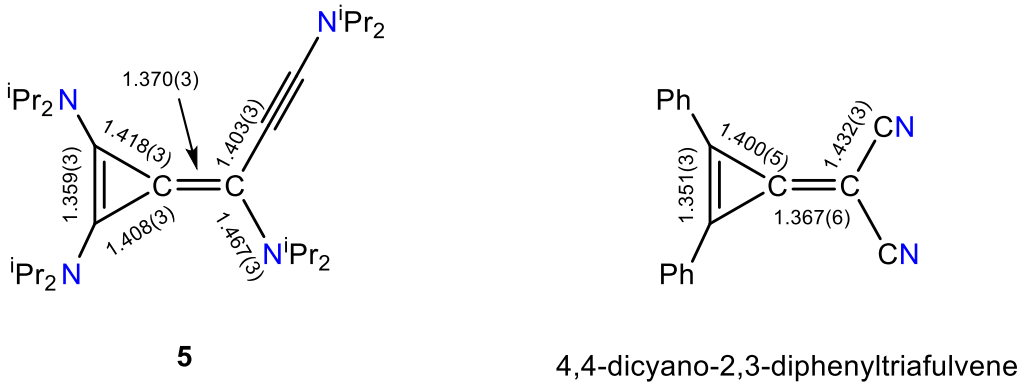


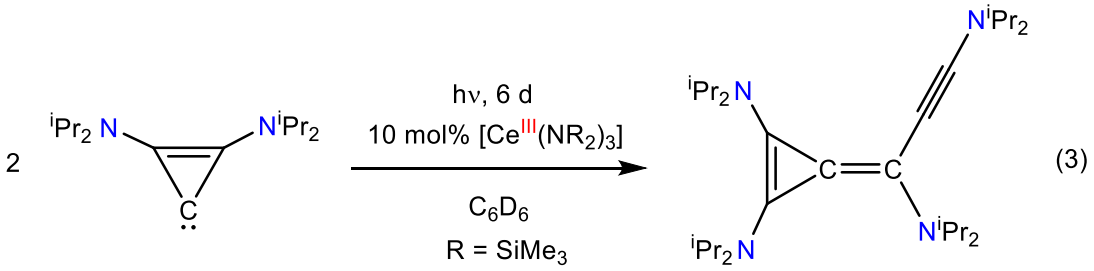

**Figure 7.** Comparison of the metrical parameters of **5** and 4,4-dicyano-2,3-diphenyltriafulvene.[42] Bond lengths are reported in Å.

The unsubstituted methylenecyclopropene fragment is highly reactive and has only been observed at low temperatures (ca. -95 °C).[44-47] Alkyl-substituted methylenecyclopropenes are somewhat more stable, but still decompose quickly at ambient temperatures.[48] In contrast, **5** shows no evidence of decomposition at room temperature even over the course of several weeks. No doubt, the enhanced thermal stability of **5** is due to its strongly donating diisopropylamino substituents. Similar thermal stability is seen with Bertrand's tetra(amino)-substituted methylenecyclopropene, likely for similar reasons.[49] That said, **5** is still highly reactive. For instance, attempts to isolate and purify **5** using an aqueous work-up result in its complete decomposition, which is likely initiated by protonation at C2. Because of this reactivity, and its similar solubility with [Ce(NR$_2$)$_3$], we were unable to isolate analytically pure samples of **5**.

To rationalize the formation of **5**, we hypothesize that photolysis of **2** results in a redox-mediated ring opening of the BAC fragment, followed by a 1,2-nitrogen shift to generate a

transient Ce(III) amino alkynyl carbene, [Ce($^i$Pr$_2$N*C*C≡C*N*$^i$Pr$_2$)(NR$_2$)$_3$], which subsequently reacts with the BAC fragment in unreacted **2** to form the cross-coupled product **5** and regenerate [Ce(NR$_2$)$_3$]. In support of this proposed mechanism, we note that Bertrand has previously observed coupling of the highly nucleophilic BAC to both cyclic alkyl(amino) carbenes (CAACs) and six- and seven-membered diamido carbenes (DACs).[49] In addition, Bertrand has also reported the ring opening of BAC fragment.[49, 50]

The reformation of [Ce(NR$_2$)$_3$] during the photolysis of **2** suggests that **5** could be generated in a catalytic manner. To test this hypothesis, we photolyzed a $C_6D_6$ solution of BAC in the presence of 10 mol% [Ce(NR$_2$)$_3$] (eq 3). Exposure of this mixture to blue light from a 365 nm LED lightstrip, over the course of 6 d, resulted in 90% conversion of BAC to **5** (Figure S9). Control experiments reveal that the formation of **5** is, in fact, catalyzed by [Ce(NR$_2$)$_3$]. For instance, photolysis of a benzene-$d_6$ solution of BAC alone for 20 h resulted in partial decomposition of the BAC starting material, according to $^1$H NMR spectroscopy (Figure S12), but no formation of **5**. Likewise, thermolysis of **2** at 50 °C for 2 d, in the absence of light, resulted in partial decomposition of **2**, but no formation of **5**, according to the $^1$H NMR spectrum of the reaction mixture (Figure S11).



(3)

## Conclusions

In summary, we have explored the coordination chemistry of [Ce(NR$_2$)$_3$] with two prospective C-atom transfer reagents, *N*-(isocyanoimine)triphenylphosphine (CNNPPh$_3$) and

bis(diisopropylamino)cyclopropenylidene (BAC). Photolysis of the resulting adducts, [$(NR_2)_3Ce(CNNPPh_3)$] (**1**) and [$(NR_2)_3Ce(BAC)$] (**2**), does not result in the originally envisioned carbon-atom transfer, but instead results in ligand rearrangement. In the case of *N*-(isocyanoimine)triphenylphosphine, we isolate [$(NR_2)_3Ce(NCNPPh_3)$] (**3**), the product of nitrilimine rearrangement to its carbodiimide isomer. In the case of BAC, we isolate the methylenecyclopropene species, [$(^iPr_2N)_2C_3C(N^iPr_2)(CCN^iPr_2)$] (**5**), which is generated by the formal dimerization and rearrangement of two BAC fragments. While ultimately unsuccessful in our efforts to generate either a cerium carbide or alkylidene complex, this work expands the scope of Ce(III)-mediated photochemistry, which is an emerging area of photocatalysis. In addition, we have discovered a new synthetic pathway to the highly reactive methylenecyclopropene fragment, which is of interest for its insights into aromaticity, as well as its use as a precursor to spiro-compounds.[51-55]

ASSOCIATED CONTENT

**Supporting Information**. Experimental procedures, crystallographic details (as CIF files), and spectral data for complexes **1**-**5**. See DOI:

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**Notes**

The authors declare no competing financial interest.

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SYNOPSIS

Photolysis of bis(diisopropylamino)cyclopropenylidene (BAC) in the presence of 10 mol% $[Ce(NR_2)_3]$ (R = $SiMe_3$) results in formation of a thermally-stable methylenecyclopropeneyne, $[(^iPr_2N)_2C_3C(N^iPr_2)(CCN^iPr_2)]$.