Transition-Metal Complexes of Heavier Cyclopropenes: Non-Dewar–Chatt–Duncanson Coordination and Facile Si=Ge Functionalization

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ABSTRACT: Transition-metal complexes of cyclopropenes occur as fleeting intermediates of numerous metal-catalyzed organic transformations. A heavier analogue has now been obtained from the reaction of an NHC-stabilized silagermenylidene, bis(1,5-cyclooctadiene)nickel(0), and 1 equiv of N-heterocyclic carbene (NHC). The residual chloro functionality at the germanium end of the coordinated Ge=Si moiety of the thus formed 1*H*-disilagermirene is easily exchanged by treatment with anionic nucleophiles, which provides access to a series of differently substituted Si_2Ge-cyclopropenes as nickel complexes in excellent yields. NMR spectroscopic data, X-ray crystallographic analysis, and DFT calculations indicate a coordination mode different from the metallacyclopropane and π-complex extremes of the Dewar−Chatt−Duncanson model: the σ-component of the Ge=Si double bond acts as donor and acceptor, leaving behind a nearly unsupported Si−Ge π-bond.

Since the first purported synthesis almost 100 years ago, cyclopropenes **I** continue to attract considerable interest as the smallest unsaturated ring compounds.[1] Their 2-fold degree of unsaturation (double bond, strained ring) allows for different types of rearrangements as well as ring opening, addition, and cycloaddition reactions to a manifold of structural motifs.[1] The coordination chemistry of acyclic and cyclic olefins is a cornerstone of homogeneous catalysis[2] and unsurprisingly has been the subject of numerous studies in the case of cyclopropenes as well.[3] The increased π-density of the double bond turns cyclopropenes into attractive ligands for π-electrophilic transition metals with a bonding situation between the extremes of π-complexes of type **II** and bicyclo[1.1.0]metallabutanes **III** (Chart 1).[3]

The analogous transition-metal complexes of heavier cyclopropenes (also known as cyclotrimetallenes)[4] have not been realized thus far, although the use of sterically and electronically stabilizing substituents has enabled the isolation of a number of free heavier cyclopropenes **IV** in the last few decades.[4−11] Several routes toward homonuclear heavier cyclopropenes, including reductive dehalogenation,[8] condensation/salt elimination reactions,[9] and valence isomerizations,[10] have been developed. In contrast, only a handful of heteronuclear cyclotrimetallenes such as 1*H*-disilagermirenes[11] **V** are known. Heavier cyclotrimetallenes exhibit highly versatile reactivities toward a range of substrates.[4] While the addition and cycloaddition reactions across the E=E (E = Si, Ge) double bond provide facile access to a pool of new silicon- and germanium-based cyclic and bicyclic compounds,[12] insertion reactions into the three-membered ring afford ring-expanded products.[13] The oxidation of cyclotrimetallenes yields stable silyl and germyl cations with a Hückel-type aromatic 2-π-electron system.[14] The ring-opening reaction of a cyclotrisilene toward either transient or isolable disilenylsilylenes (referred to as the "silicon version of vinyl carbene") occurs through interaction with suitable bases or nucleophiles.[15] Despite the significant progress with regard to functionalized open-chain alkene homologues of heavier group 14 elements,[16] the presence of functional groups in heavier cyclopropenes is so far restricted to the saturated ring atom, as for instance in halo cyclotrigermenes **VI**.[9e] The introduction of functional groups directly at the heavier double bond remains elusive, as it is hampered by the indispensable requirement of two sterically demanding substituents for efficient kinetic stabilization and sufficiently tamed reactivity.
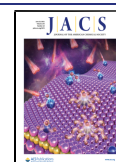
Chart 1. Literature-Known Motifs of Cyclopropenes I, Their Transition Metal Complexes II and III, and Heavier Cyclopropenes IV−VI[a]
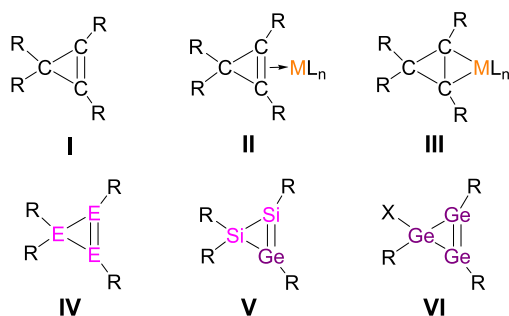
[a]E = Si, Ge, Sn; R = aryl, alkyl, silyl groups; X = Cl, Br, I; ML_n = transition-metal fragments.

We now report the synthesis and isolation of a stable transition-metal complex of a heavier cyclopropene with a chloro substituent at the germanium end of the coordinated Ge=Si bond. As we demonstrate with a set of proof of principle reactions, the presence of the residual leaving group allows for facile postcoordination functionalization.

We anticipated that the reported rearrangement of the scaffold of NHC-coordinated silylsilagermenylidene **1**[17] upon treatment with nucleophiles to either isomeric cyclic germylenes or the corresponding heavier cyclopropene[11c,d] would also occur in the coordination sphere of a suitable transition metal despite the preceding isolation of a terminal complex of **1** and the $Fe(CO)_4$ fragment.[17] We chose nickel(0) as the transition-metal center for its considerably better back-donation ability in comparison to iron(0).[18]

Indeed, treatment of NHC-stabilized silagermenylidene **1**[17] and $Ni(COD)_2$ in combination with a further 1 equiv of NHC affords the desired disilagermirene-nickel complex **2a** with a residual chloro functionality at the germanium center in 66% yield (Scheme 1).[19] The ^{29}Si NMR spectrum of **2a** in $[D_6]$-

Scheme 1. Synthesis of Disilagermirene-Nickel Complex 2a[a]
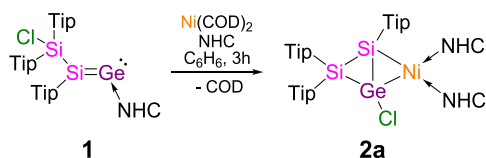
[a]Tip = 2,4,6-iPr$_3$C$_6$H$_2$; NHC = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene; COD = cyclooctadiene.

benzene shows two signals at δ 41.0 (SiTip$_2$), 34.1 (SiTip) in a 1:1 ratio. While the signal assigned to SiTip is observed at slightly higher field in comparison to an isolable peraryl-substituted cyclotrisilene (c-Si$_3$Tip$_4$: $\delta(^{29}Si)$ 42.5),[8c] that assigned to SiTip$_2$ is remarkably downfield shifted (c-Si$_3$Tip$_4$: $\delta(^{29}Si)$ −23.2). The similar chemical shifts observed in the ^{29}Si CP-MAS NMR spectrum (δ 48.4 (SiTip$_2$), 44.0 (SiTip)) suggest closely resembling structures of **2a** in solution and the solid state. Two downfield signals in the $^{13}C\{^1H\}$ NMR spectrum in $[D_6]$-benzene at δ 192.9 and 186.9 in the typical region for NHC-nickel complexes[20] are assigned to the carbenic NHC carbon atoms and confirm the presence of two Ni-bonded NHC ligands, one of which apparently originated from the germanium center. The UV/vis spectrum in n-hexane (Figure S7) shows the longest wavelength absorption band at λ_{max} = 456 nm (ε = 3610 L mol^{-1} cm^{-1}), which is remarkably red shifted in comparison to c-Si$_3$Tip$_4$ (λ_{max} = 413 nm)[8c] and the bis(NHC) η^2-disilene nickel complex (λ_{max} = 409 nm) reported by Eisenhut and Inoue.[20]

The molecular structure of **2a** as determined by X-ray diffraction on single crystals (Figure 1) shows a bicyclo[1.1.0]-metallabutane-like butterfly structure in which 1H-disilagermirene is bonded side-on to nickel. The coordination by two NHC ligands with a C1−Ni1−C12 angle of 100.0(7)° and a Si1−Ni1−Ge1 angle of 63.9(1)° completes the distorted-square-planar coordination environment of the 16e$^-$ nickel center. The substituents at the bridgehead positions adopt a cisoid conformation with a dihedral angle of 23.3(1)° (C23−Si1−Ge1−Cl1). The Si1−Ge1 bond in **2a** of 2.397(5) Å is almost identical with that of a hafnocene complex of an acyclic silagermene (2.398 Å),[21a] while the Si1−Ni1 bond of 2.269(5)
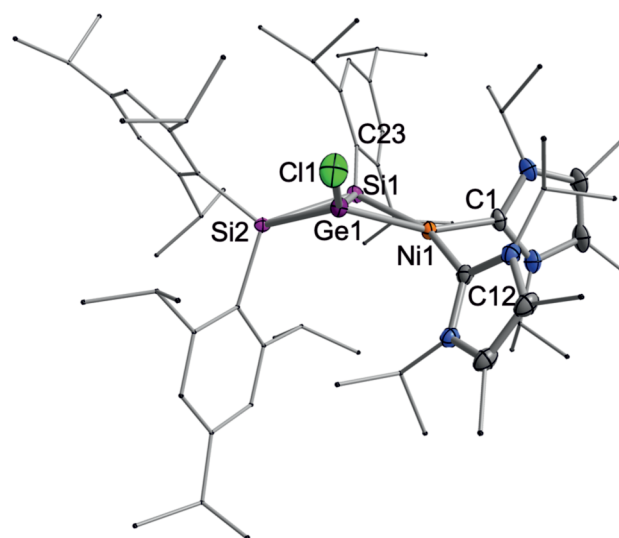
Figure 1. Molecular structure of **2a** in the solid state. Hydrogen atoms and cocrystallized solvent are omitted for clarity; thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å): Si1−Ge1 2.397(5), Ge1−Si2 2.336(4), Si1−Si2 2.378(6), Si1−Ni1 2.269(5), Ge1−Ni1 2.261(3), Ge1−Cl1 2.256(4).

Å is significantly shorter than that of an acyclic η^2-disilene nickel complex (2.300 Å).[20] The interflap angle (ϕ) of 143.83(3)° between the two three-membered rings that constitute the bicyclo[1.1.0]metallabutane skeleton is slightly larger than that of a bicyclo[1.1.0]1,3-disilabutane (ϕ = 141.1°).[22]

The sum of bond angles (excluding metal coordination) in **2a** ($\sum\angle$Si1 = 325.70° and $\sum\angle$Ge1 = 343.03°) deviates substantially from the 360° expected for a π-complex according to the Dewar−Chatt−Duncanson model,[23] indicating a major contribution of the bicyclo[1.1.0]metallabutane-like butterfly structure to the ground state of **2a**. The elongated Si1−Ge1 bond (2.397(5) Å) in **2a** in comparison to Si=Ge doubly bonded species known in the literature (2.220−2.276 Å)[24] further corroborates this interpretation. Accordingly, the bent-back angles θ (θ_{Si1} = 31.05(5)° and θ_{Ge1} = 25.85(3)°) are comparable to those reported for metallacyclopropane-like structures (9.2−35.1°)[20,25] and are significantly larger than those found in disilene π-complexes (4.4−9.7°).[26] Additional evidence for a bicyclo[1.1.0]metallabutane structure is garnered from the fact that the Si1−Ni1 bond of 2.269(5) Å and the Ge1−Ni1 bond of 2.261(3) Å in **2a** compare well with those of σ-bonded silyl and germyl groups connected to nickel (2.283[27] and 2.249 Å,[28] respectively).

To gather more insight into the electronic structure of complex **2a**, density functional theory (DFT) calculations were performed at the M06-2X(D3)/def2-SV(P)//BP86(D3BJ)/def2-SVP level of theory. The HOMO is dominated by a π-type interaction resulting from the in-phase combination of the bridgehead silicon 3p and germanium 4p orbitals (Figure 2). In notable contrast to all reported cases of transition-metal complexes of heavier alkenes, the interaction with a d orbital at the nickel center is antibonding in nature, albeit weak. The HOMO-1 is largely composed of a σ-bonding interaction between [Ni(NHC)$_2$] and the disilagermirene fragment, suggesting that the bonding in **2a** may be best described as an unprecedented complexation of the σ-component of the double bond of a cyclopropene-like ligand, while the π-bond
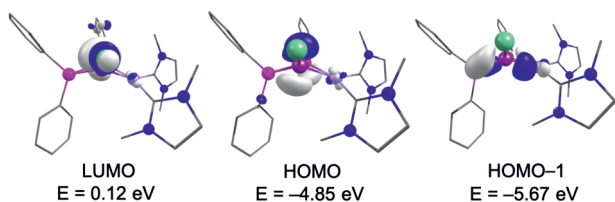
Figure 2. Selected Kohn−Sham molecular orbitals of **2a** (contour value 0.062). Hydrogen atoms and methyl and isopropyl groups are omitted for clarity.

remains only marginally perturbed. Compound **2a** thus represents a rare example of a compound featuring a π-type single bond without a clearly defined supporting σ-bond.[29] Similar modes of interaction in group 14 systems have so far only been described for transition-metal-free 1,3-cyclobutanediyl analogues.[30] Indeed, a natural bond orbital (NBO) analysis (Figure 3) indicates that the bridgehead Si1−Ge1
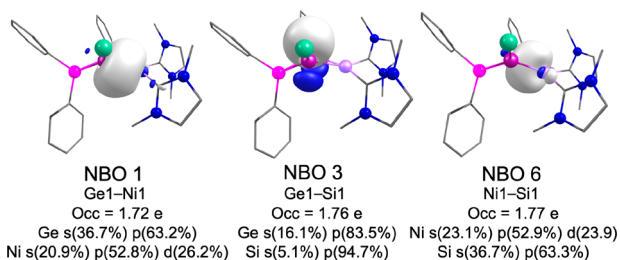

Figure 3. Selected NBO orbitals of **2a** (contour value 0.043). Hydrogen atoms and methyl and isopropyl groups are omitted for clarity.

bond is formed predominantly by the interactions of p orbitals of π-type according to visual inspection (Si 94.7%; Ge 83.5%). The NBO analysis also confirms that two σ-bonding orbitals are responsible for the interaction of the disilagermirene unit with the bridging $[Ni(NHC)_2]$ moiety. According to the TD-DFT simulated UV/vis spectrum (Figure S43), the almost unsupported π-bond between Si and Ge accounts for the longest wavelength absorption band at $\lambda_{max,calcd}$ = 467 nm (HOMO → LUMO, 72% contribution), in good agreement with the experimental value ($\lambda_{max,exptl}$ = 456 nm). The observed red shift can therefore be attributed to the increased energy of the Si−Ge π-bond due to the aforementioned antibonding interaction with the nickel center. To obtain further confirmation on the structure of **2a**, ^{29}Si NMR chemical shifts were calculated at the OLYP/def2-TZV(P)//BP86/def2-SVP level of theory. The good agreement between the experimentally observed and calculated values ($\delta(^{29}$Si$)_{exptl}$ 41.0, 34.1 and $\delta(^{29}$Si$)_{calcd}$ 53.1, 25.7) in addition to the solid-state NMR provides further corroboration for the integrity of **2a** in solution (see above).

The LUMO (Figure 2) shows a partial contribution from the antibonding Ge−Cl σ*-orbitals, which predisposes the germanium center as a potential site for nucleophilic attack. The chloro functionality in **2a** thus offers the unprecedented opportunity for postcoordination functionalization, and hence a set of three representative nucleophilic substitution reactions was performed as a proof of principle. The treatment of **2a** with an equimolar amount of phenyllithium (PhLi) produces the peraryl-substituted disilagermirene-nickel complex **2b** in 82% yield (Scheme 2).

Scheme 2. Synthesis of Functionalized Disilagermirene-Nickel Complexes 2b−d^a
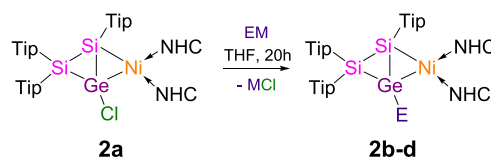
^{a}Tip = 2,4,6-iPr$_3$C$_6$H$_2$; NHC = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene; EM = PhLi, tBuOK, Ph$_2$PLi; **2b**, E = Ph; **2c**, E = OtBu; **2d**, E = PPh$_2$.

Complex **2b** has surprising thermal stability even at 180 °C. The ^{29}Si NMR resonances of **2b** in $[D_6]$-benzene at δ 3.7 (SiTip$_2$) and −38.9 (SiTip) are shifted upfield in comparison to **2a** and are in good agreement with the calculated ^{29}Si NMR chemical shifts ($\delta(^{29}$Si$)_{calcd}$ −5.7, − 22.7; see Table S7). The replacement of the chloro functionality by the phenyl group in **2b** causes an additional strong red shift of the longest-wavelength UV/vis absorption (Figure S15) to λ_{max} = 578 nm (ε = 740 L mol^{-1} cm^{-1}), in excellent agreement with the TD-DFT calculated value of $\lambda_{max,calcd}$ = 579 nm (for details see the Supporting Information).

Similarly, the reaction of **2a** with potassium $tert$-butoxide affords the alkoxy-functionalized disilagermirene-nickel complex **2c** as a red solid in 78% yield. The ^{29}Si NMR resonances of **2c** at δ 22.0 (SiTip$_2$) and −6.7 (SiTip) in $[D_6]$-benzene are between those of the chloro derivative **2a** and phenyl-substituted **2b** and are in good agreement with the calculated ^{29}Si NMR chemical shifts ($\delta(^{29}$Si$)_{calcd}$ 10.5, 4.9; see Table S10). The red color of **2c** is due to the longest-wavelength absorption in the UV/vis spectrum (Figure S24) at λ_{max} = 411 nm (ε = 6400 L mol^{-1} cm^{-1}; for calculated values see the Supporting Information). The molecular structure of **2c** on the basis of an X-ray crystal structure analysis confirms the constitution of an alkoxy-substituted disilagermirene-nickel complex (Figure 4), but due to poor data, we refrain from discussing the bond parameters.
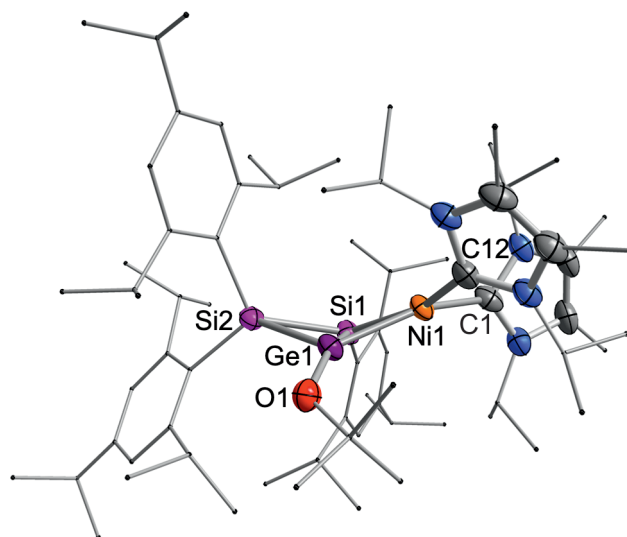

Figure 4. Molecular structure of **2c** in the solid state. Hydrogen atoms and cocrystallized solvent are omitted for clarity; thermal ellipsoids are shown at 50% probability.

Finally, the reaction of **2a** with an equimolar amount of lithium diphenylphosphanide (Ph$_2$PLi) furnishes the phosphanyl-substituted disilagermirene-nickel complex **2d** in 70% yield (Scheme 2). The ^{31}P NMR spectrum in [D_6]-benzene shows a signal at δ 10.1 with two pairs of silicon satellites due to coupling to both ^{29}Si nuclei. The ^{31}P CP-MAS NMR spectrum shows an almost identical signal at δ 8.5, thereby proving the structural identity of **2d** in solution and the solid state. The ^{29}Si NMR spectrum in [D_6]-benzene exhibits two doublets at δ 12.1 (*Si*Tip$_2$) and -0.2 (*Si*Tip), which are comparable to the ^{29}Si CP-MAS NMR chemical shifts as well (δ(^{29}Si) 14.8, 4.3). Curiously, the coupling constant to *Si*Tip ($^2J_{P, Si}$ = 12.1 Hz) is smaller in comparison to that to *Si*Tip$_2$ ($^2J_{P, Si}$ = 23.6 Hz), which, however, is not uncommon for small ring systems due to the additive contributions of different coupling pathways. The TD-DFT simulated UV/vis spectrum predicts the longest-wavelength absorption band at $\lambda_{max,calcd}$ = 426 nm, which is blue-shifted in comparison to the experimental value ($\lambda_{max,exptl}$ = 477 nm) (Figure S36) and is assigned mostly to the HOMO → LUMO transition as in the cases of **2a−c** (Table S12).

A single-crystal X-ray diffraction analysis confirms the constitution of **2d** as a phosphanyl-substituted disilagermirene-nickel complex (Figure 5). While the Si1−Ni1 bond of
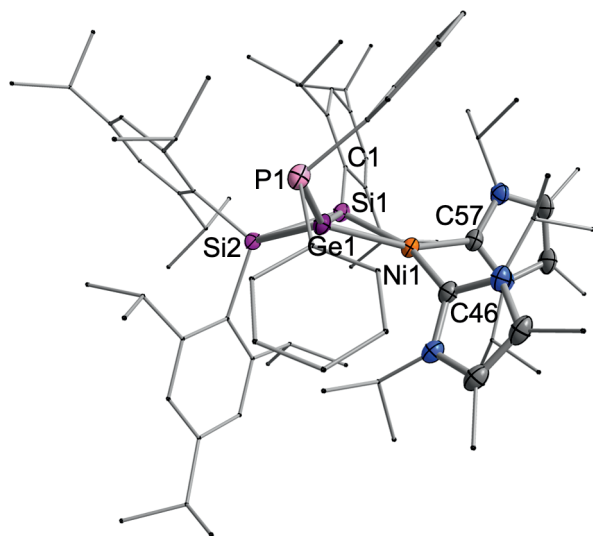

Figure 5. Molecular structure of **2d** in the solid state. Hydrogen atoms and cocrystallized solvent are omitted for clarity; thermal ellipsoids are shown at 50% probability. Selected bond lengths (Å): Si1−Ge1 2.432(4), Ge1−Si2 2.380(4), Si1−Si2 2.332(5), Si1−Ni1 2.258(4), Ge1−Ni1 2.323(2), Ge1−P1 2.379(4).

2.258(4) Å is similar, the Ge1−Ni1 bond of 2.323(2) Å is elongated in comparison to complex **2a** (2.269 and 2.261 Å, respectively), presumably as a consequence of the repulsive interaction induced by the bulky diphenylphosphanyl group. Accordingly, the Si1−Ge1 bond of 2.432(4) Å is also longer than in **2a**. As in complex **2a**, both substituents at the bridgehead positions adopt a *cisoid* conformation, albeit with a smaller C1−Si1−Ge1−P1 dihedral angle of 7.2(1)°. The interflap angle (ϕ) of 143.05(2)° is close to those of **2a** (ϕ = 143.83°) and bicyclo[1.1.0]1,3-disilabutane (ϕ = 141.1°).[22] The substitution of Cl with a PPh$_2$ unit in **2d** results in a more pronounced pyramidalization of the germanium atom, as reflected by the sum of bond angles (excluding metal

coordination) ($\sum\angle$Ge1 = 330.90°). The large bent-back angles θ (θ_{Si1} = 31.02(4)° and θ_{Ge1} = 30.70(2)°) further confirm the bicyclo[1.1.0]metallabutane character of **2d**.

In conclusion, the reaction of NHC-stabilized silagermenylidene with Ni(COD)$_2$ in the presence of 1 equiv of N-heterocyclic carbene (NHC) afforded the first examples of transition-metal complexes of a heavier cyclopropene analogue. The stabilization brought to the 1*H*-disilagermirene by coordination to the transition-metal center allows for the presence of a functional group directly attached to the coordinated Si=Ge bond, which has so far been impossible in the case of free heavier cyclopropenes. The 16e$^-$ bicyclo[1.1.0]metallabutane-like butterfly complex **2a** can be cleanly converted to the differently functionalized cyclo-disilagermene-metal complexes **2b−d** by simple treatment with the corresponding anionic nucleophiles, offering various possibilities for further manipulations such as the incorporation of a second transition-metal center or an assembly to supramolecular aggregates. DFT calculations on **2a** suggest a nearly unsupported π-type single bond between the bridgehead silicon and germanium atoms, demonstrating the higher propensity of σ-bonding electrons for donation to the nickel center in comparison to the π-bond. With this, a novel coordination mode of alkene-like ligands to transition metals is proposed outside the scope of the widely popular Dewar−Chatt−Duncanson model.[23]

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.1c04419.

> Experimental procedures, NMR, CP-MAS NMR, and UV−vis spectra, X-ray crystallographic data, and computational details (PDF)

Accession Codes

CCDC 2071403 and 2071405 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.

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