# Lewis Acidity of Si_6Cl_{12} and Its Role as Convenient $SiCl_2$ Source

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Ⓢ Supporting Information

ABSTRACT: The free cyclohexasilane Si_6Cl_{12} (**1**) was obtained in 66% yield from the corresponding Cl^- diadduct $[nBu_4N]_2[\mathbf{1}\cdot2Cl]$ and $AlCl_3$ in C_6H_6. The substituted cyclohexasilane $1,1\text{-}(Cl_3Si)_2Si_6Cl_{10}$ (**2**), however, cannot be liberated from $[nBu_4N]_2[\mathbf{2}\cdot2Cl]$ under comparable reaction conditions. Instead, a mixture of several products was obtained, from which the oligosilane $Si_{19}Cl_{36}$ (**3**) crystallized in low yields. X-ray crystallography revealed **3** to consist of two Si_5 rings, bridged by one silicon atom. Compound **1** possesses Lewis acidic sites above and below the ring centroid. Competition experiments reveal that their corresponding acid strengths are comparable to that of BCl_3. The reaction of **1** with 6 equiv of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (Idipp) leads to a complete breakdown of the cyclic scaffold and furnishes the dichlorosilylene adduct $Idipp\text{-}SiCl_2$.
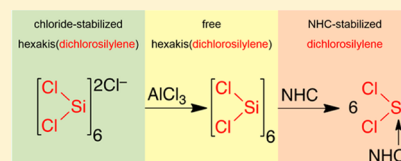
INTRODUCTION

Owing to their chemical inertness, saturated hydrocarbons have been referred to as the "noble gases of organic chemistry".[1] The homologous polysilanes, in contrast, are characterized by a pronounced dynamic covalent chemistry of their Si−Si bonds, which results in facile skeletal rearrangements and silylene extrusion/insertion reactions.[2] This reactivity can be triggered by external stimuli such as light, heat, and the presence of Lewis bases or acids.[3] With regard to photochemical reactions it is important to note that the UV/vis absorption bands of polysilanes are bathochromically shifted compared to those of structurally comparable alkanes. This observation is generally attributed to a certain degree of σ-bond delocalization present in Si chains, rings, and cages.[4]

So far, the organyl derivatives Si_nR_{2n+2} and Si_nR_{2n} with R = Me and Ph constitute the most thoroughly investigated class of polysilanes.[3,5−7] Such compounds are available from R_2SiCl_2/R_3SiCl and alkali metals through Wurtz-type coupling protocols. For obvious reasons, this convenient approach falls short on the synthesis of perchlorinated polysilanes Si_nCl_{2n+2} and Si_nCl_{2n}. The preparation of these species therefore requires a detour via the corresponding perphenylated organosilanes, which readily undergo a Ph/Cl exchange reaction upon treatment with $HCl/AlCl_3$ (for an example, see Scheme 1).[8]

Our group is particularly interested in perchloro polysilanes, because an increase in the substituents' electronegativity influences the stability of the Si−Si bonds and raises the Lewis acidity of the individual Si atoms. For example, addition of two Cl^- ions to the cyclohexasilane Si_6Cl_{12} (**1**) results in the inverse sandwich structure $[Si_6Cl_{12}\cdot2Cl]^{2-}$ ($[\mathbf{1}\cdot2Cl]^{2-}$; Figure 1),[9−11] whereas the permethylated Si_6Me_{12} does not form adducts with halide ions.[9] In terms of applications, perchloro polysilanes serve as key precursors for the preparation of analogous hydrogenated polysilanes, which are widely used for the deposition of silicon thin films.[12−14]

The use of monodisperse samples greatly facilitates investigations of macromolecular species. We therefore focused our attention on homocyclic silanes Si_nCl_{2n}. As alluded to above, the classic synthesis approach relies on the reductive dechlorination of Ph_2SiCl_2,[15−18] followed by the (Lewis) acid-mediated exchange of all phenyl substituents for chlorine atoms (Scheme 1).[8,19] The crude product resulting from the first step contains four-, five-, and six-membered rings Si_nPh_{2n} ($n = 4−6$) with Si_5Ph_{10} generally being the most abundant constituent of the reaction mixture. In order to obtain cyclosilanes Si_nCl_{2n} with uniform ring sizes, it is best to separate already the primary mixture of Si_nPh_{2n} rings by extraction and fractional crystallization. Ring-size-selective synthesis strategies, specifically for perchlorinated cyclohexasilanes, have recently been developed by Boudjouk and our group through (i) $HSiCl_3$ oligomerization with PEDETA[9] or (ii) the reaction of Si_2Cl_6 with $[nBu_4N]Cl$ in CH_2Cl_2[11] (Scheme 1; PEDETA = 1,1,4,7,7-pentaethyldiethylenetriamine). In both cases, the six-membered rings are obtained as Cl^- diadducts. While Boudjouk's protocol furnishes exclusively the unsubstituted species $[\mathbf{1}\cdot2Cl]^{2-}$, our approach also provides access to trichlorosilylated derivatives such as $[1,1\text{-}(Cl_3Si)_2Si_6Cl_{10}\cdot2Cl]^{2-}$ ($[\mathbf{2}\cdot2Cl]^{2-}$; Figure 1, Scheme 1).[10,11] $[nBu_4N]_2[\mathbf{1}\cdot2Cl]$ can easily be separated from the substituted congeners, because its crystals float on the surface of the CH_2Cl_2 solution, whereas the substituted rings can be harvested from the bottom of the reaction flask. Large quantities of $[nBu_4N]_2[\mathbf{1}\cdot2Cl]$ are best prepared from the primary mixtures of substituted Si_6 rings by temperature treatment, which results in the stripping of all Cl_3Si substituents.[11]
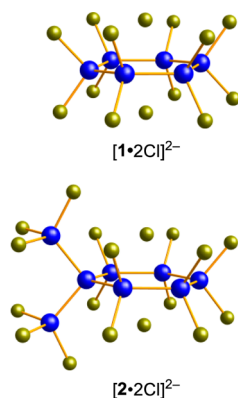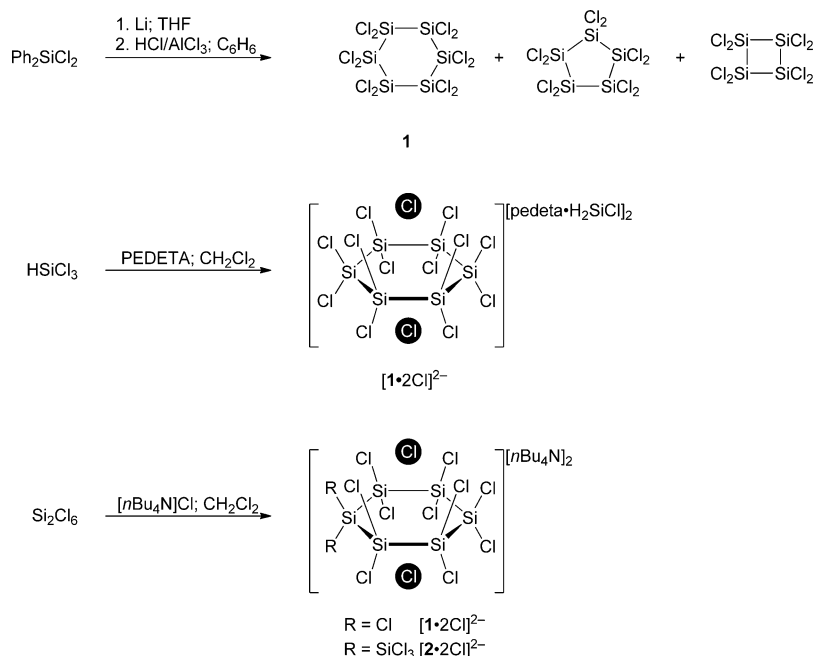
According to in situ ^{29}Si NMR spectroscopy and quantum-chemical calculations, the addition of Cl^- anions to Si_2Cl_6 creates an equilibrating mixture of several species. It is the Cl^-

Scheme 1. Known Syntheses of Perchlorinated Cyclosilanes

$[1 \cdot 2Cl]^{2-}$

R = Cl $[1 \cdot 2Cl]^{2-}$
R = SiCl$_3$ $[2 \cdot 2Cl]^{2-}$

$[1 \cdot 2Cl]^{2-}$

$[2 \cdot 2Cl]^{2-}$

Figure 1. Molecular structures of $[1 \cdot 2Cl]^{2-}$ and $[2 \cdot 2Cl]^{2-}$ obtained by X-ray crystallography.[11] Cations are omitted for clarity (Si: blue, Cl: green).

complexation that finally provides the thermodynamic thrust toward cyclohexasilane formation.[11] Yet, for a thorough investigation of perchlorinated cyclohexasilanes, as well as for many applications, it is indispensable to use the uncomplexed Si$_6$Cl$_{12}$ ring (1; Scheme 2). Until to date, the preparation of 1 via chlorodephenylation of Si$_6$Ph$_{12}$ constitutes the only viable option, but it is neither time- nor atom-economical (Scheme 1).

Boudjouk et al. obtained 1 from $[\text{pedeta} \cdot \text{H}_2\text{SiCl}]_2[1 \cdot 2Cl]$ upon hydration with LiAlH$_4$ and subsequent chlorination of the pyrophoric liquid intermediate Si$_6$H$_{12}$ with Cl$_2$ in cold (−89 °C) CH$_2$Cl$_2$.[20] Herein we report on the convenient and quantitative direct decomplexation of $[n\text{Bu}_4\text{N}]_2[1 \cdot 2Cl]$ to 1 by means of AlCl$_3$. We also provide an experimental estimate of the Lewis acidity of the acceptor sites above and below the centroid of the Si$_6$ ring. Finally, we show that 1 reacts with the N-heterocyclic carbene 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (Idipp) to give the literature-known[21,22] adduct Idipp−SiCl$_2$, which proves that Si$_6$Cl$_{12}$ is an oligomeric storage form of dichlorosilylene.

Scheme 2. Synthetic Routes to Si$_6$Cl$_{12}$ (1) via Boudjouk's Protocol or the Decomplexation of $[1 \cdot 2Cl]^{2-}$ Reported Herein[a]


$[1 \cdot 2Cl]^{2-}$

1
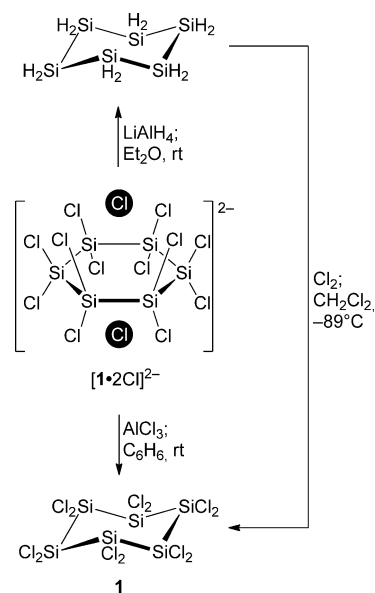
[a]Cation: $[\text{pedeta} \cdot \text{H}_2\text{SiCl}]^+$ or $[n\text{Bu}_4\text{N}]^+$.

■ RESULTS AND DISCUSSION

Preparation of Si$_6$Cl$_{12}$ (1) through Decomplexation of $[n\text{Bu}_4\text{N}]_2[1 \cdot 2Cl]$. We have chosen AlCl$_3$ for the decomplexation of $[n\text{Bu}_4\text{N}]_2[1 \cdot 2Cl]$ because this Lewis acid is also employed in the chlorodephenylation of Si$_6$Ph$_{12}$ with HCl/AlCl$_3$.[8] When the latter reaction is complete, the crude mixture contains free Si$_6$Cl$_{12}$ (1) together with $[\text{AlCl}_4]^-$ ions. Thus, the Cl$^-$ ion affinity of AlCl$_3$ is apparently larger than that of 1 or $[1 \cdot Cl]^-$ (experimental gas-phase dissociation energy for $[\text{AlCl}_4]^-$: $\Delta H^\circ = 321 \pm 12$ kJ mol^{-1}).[23]

A mixture of crystalline $[n\text{Bu}_4\text{N}]_2[\mathbf{1}\cdot2\text{Cl}]$ and 2 equiv of AlCl_3 in CD_2Cl_2 gave a clear, colorless solution within minutes. The ^{29}Si NMR spectrum of the solution confirmed the quantitative consumption of the starting material and showed exclusively one resonance at $\delta = -3.0$, assignable to the free Si_6 ring $\mathbf{1}$.[24,25] Even though this chemical shift value did not change upon cooling to $-30\ ^\circ\text{C}$, storage of the sealed NMR tube at this temperature led to the formation of colorless crystals. An X-ray analysis revealed that the crystals consisted of the
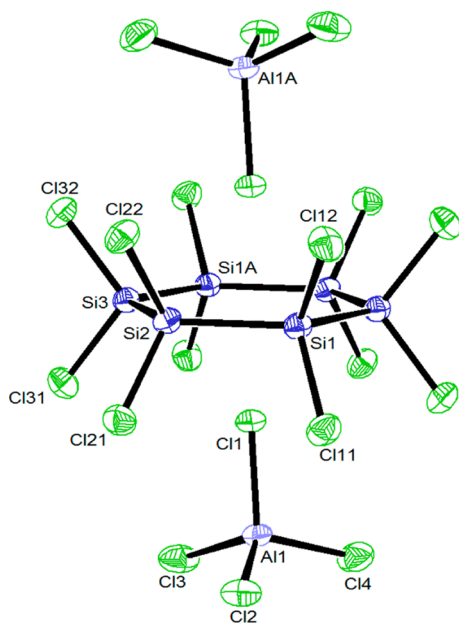
Figure 2. Molecular structure of $[n\text{Bu}_4\text{N}]_2[\mathbf{1}\cdot2\text{AlCl}_4]$ in the solid state. Cations are omitted for clarity; displacement ellipsoids are shown at the 30% probability level. Selected bond lengths [Å], atom···atom distance [Å], bond angles [deg], and torsion angles [deg]: Si(1)−Si(2) = 2.369(3), Si(1)−Si(3A) = 2.364(3), Si(2)−Si(3) = 2.367(3), Al(1)−Cl(1) = 2.192(3), Al(1)−Cl(2) = 2.114(3), Al(1)−Cl(3) = 2.116(3), Al(1)−Cl(4) = 2.117(3); Cl(1)···Cl(1A) = 4.467(3); Si(1)−Si(2)−Si(3) = 120.0(1), Si(2)−Si(1)−Si(3A) = 120.4(1), Si(2)−Si(3)−Si(1A) = 119.6(1), Si(1)−Si(2)−Si(3)−Si(1A) = −0.5(2), Si(2)−Si(3)−Si(1A)−Si(2A) = 0.6(2), Si(3)−Si(2)−Si(1)−Si(3A) = 0.6(2). Symmetry transformation used to generate equivalent atoms: A: $0.5-x$, $0.5-y$, $-z$.

diadduct $[n\text{Bu}_4\text{N}]_2[\mathbf{1}\cdot2\text{AlCl}_4]$, in which the cyclohexasilane moiety binds two $[\text{AlCl}_4]^-$ anions (Figure 2). Similar to $[n\text{Bu}_4\text{N}]_2[\mathbf{1}\cdot2\text{Cl}]$,[11,26] the Si_6 ring in $[n\text{Bu}_4\text{N}]_2[\mathbf{1}\cdot2\text{AlCl}_4]$ is planar and does not adopt the chair conformation of $\mathbf{1}$[25] in the solid state. The shortest contact between the $[\text{AlCl}_4]^-$ anion and the centroid (COG) of the six-membered ring in the centrosymmetric aggregate $[\mathbf{1}\cdot2\text{AlCl}_4]^{2-}$ amounts to Cl(1)···COG = 2.233(2) Å and is thus larger by 0.315 Å than the corresponding distance Cl$^-$···COG = 1.918(1) Å in $[\mathbf{1}\cdot2\text{Cl}]^{2-}$. This observation can be rationalized given the usual classification of $[\text{AlCl}_4]^-$ as a weakly coordinating anion[27] and the reversibility of $[\text{AlCl}_4]^-$ complexation in solution according to ^{29}Si NMR spectroscopy. Nevertheless, the interaction between $\mathbf{1}$ and $[\text{AlCl}_4]^-$ must still be sufficiently strong to compensate for the energy penalty for the planarization of the $\text{Si}_6\text{Cl}_{12}$ ring (calculated value: 50 kJ mol^{-1}).[26]

For the liberation of the free cyclohexasilane $\mathbf{1}$ on a preparative scale, finely divided solid $[n\text{Bu}_4\text{N}]_2[\mathbf{1}\cdot2\text{Cl}]$ was

added in several portions at room temperature (rt) to a suspension of 2.5 equiv of AlCl_3 in C_6H_6. After the addition was complete, the reaction mixture was stirred for 1 h, all volatiles were removed under reduced pressure, and $\mathbf{1}$ was extracted into n-hexane at elevated temperature. Crystals of $\mathbf{1}$ were grown from the hexane extract upon slow evaporation of the solvent (yield: 66%). The compound gave rise to a ^{29}Si NMR signal at $\delta = -3.0$; X-ray crystallography also confirmed the identity of $\mathbf{1}$ as $\text{Si}_6\text{Cl}_{12}$ (the molecular structure of $\text{Si}_6\text{Cl}_{12}$ is already literature known[25]).

The clean transformation of $[n\text{Bu}_4\text{N}]_2[\mathbf{1}\cdot2\text{Cl}]$ to $\mathbf{1}$ by AlCl_3 could not be taken for granted in the first place, because treatment of permethylated cyclohexasilane, $\text{Si}_6\text{Me}_{12}$, with a catalytic amount of AlCl_3 (C_6H_6, rt) leads to skeletal rearrangement furnishing (trimethylsilyl)nonamethyl-cyclopentasilane, $(\text{Me}_3\text{Si})\text{Si}_5\text{Me}_9$, in 90% yield.[28] A reaction mechanism has been proposed in which the chloropolysilane $\text{Si}_6\text{Me}_{11}\text{Cl}$, formed by initial chlorodemethylation of the starting material, acts as a key intermediate.[28] This scenario would suggest that $\mathbf{1}$ might be even more amenable to corresponding ring-contraction reactions than $\text{Si}_6\text{Me}_{12}$. We therefore monitored an equimolar mixture of $\mathbf{1}$ and AlCl_3 in C_6D_{12} by ^{29}Si NMR spectroscopy, but found the cyclohexasilane inert toward the Lewis acid in the temperature regime between rt and 80 °C (1 h).

When they revisited the AlCl_3-mediated rearrangement of $\text{Si}_6\text{Me}_{12}$, West et al. did not observe chlorosilanes at any stage of the reaction sequence.[29] Instead, they showed that the AlCl_3 catalyst needed to contain some Fe in order to be efficient. We therefore investigated next an equimolar mixture of $\mathbf{1}$ and FeCl_3 in C_6D_{12} after it had been heated to reflux temperature for 1 h. Apart from $\mathbf{1}$, we detected only trace amounts of decomposition products in the NMR spectrum. On the other hand, all our attempts to generate $\mathbf{1}$ from $[n\text{Bu}_4\text{N}]_2[\mathbf{1}\cdot2\text{Cl}]$ using FeCl_3 as the Cl$^-$-abstracting agent failed and rather resulted in complex, inseparable product mixtures (CD_2Cl_2; ^{29}Si NMR spectroscopic control).

We found it impossible to achieve a similarly selective decomplexation reaction as in the case of $[\mathbf{1}\cdot2\text{Cl}]^{2-}$ with its 1,1-disilylated congener $[\mathbf{2}\cdot2\text{Cl}]^{2-}$. According to ^{29}Si NMR spectroscopy, a variety of products are generated when AlCl_3 is added at rt to a solution of $[n\text{Bu}_4\text{N}]_2[\mathbf{2}\cdot2\text{Cl}]$ in CD_2Cl_2. After the NMR sample had been stored for 30 d, crystals of the highly branched oligosilane $\text{Si}_{19}\text{Cl}_{36}$ ($\mathbf{3}$) could be harvested. $\mathbf{3}$ is only very sparingly soluble in inert solvents, and it decomposes in THF solution. We therefore had to restrict its characterization to X-ray crystallography (Figure 3). The C_2-symmetric molecule $\mathbf{3}$ consists of two five-membered rings, connected by one silicon atom (Si(10)). The Si(10) bridge carries two additional Cl_3Si substituents; each Si_5 ring is equipped with three Cl_3Si substituents.

The perchlorinated oligosilane $\mathbf{3}$ shares common structural motifs with the permethylated species cis-1,1,2-tris-(trimethylsilyl)-4-tris(trimethylsilyl)silylhexamethylcyclopenta-silane ($\mathbf{4}$; Figure 4), which was isolated as one of four products in the Al(Fe)Cl_3-catalyzed rearrangement of octakis-(trimethylsilyl)cyclotetrasilane.[30] Even corresponding Si−Si bond lengths and Si−Si−Si bond angles of $\mathbf{3}$ and $\mathbf{4}$ are strikingly similar. Ishikawa et al.,[28] West et al.,[29] and more recently Marschner et al.[30] reported that the cyclohexasilane $\text{Si}_6\text{Me}_{12}$ can selectively be converted into the monosilylated cyclopentasilane $(\text{Me}_3\text{Si})\text{Si}_5\text{Me}_9$ by treatment with Al(Fe)Cl_3. The silylated cyclohexasilane $(\text{Me}_3\text{Si})\text{Si}_6\text{Me}_{11}$ gave the
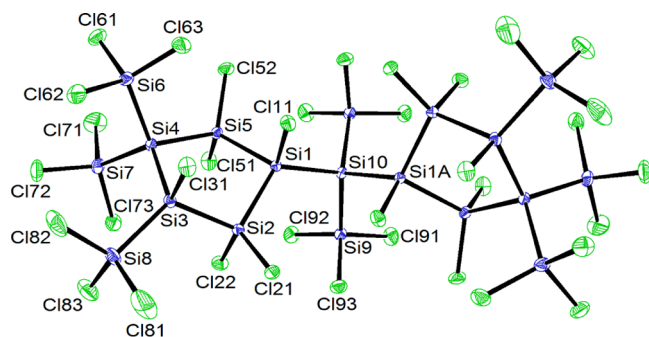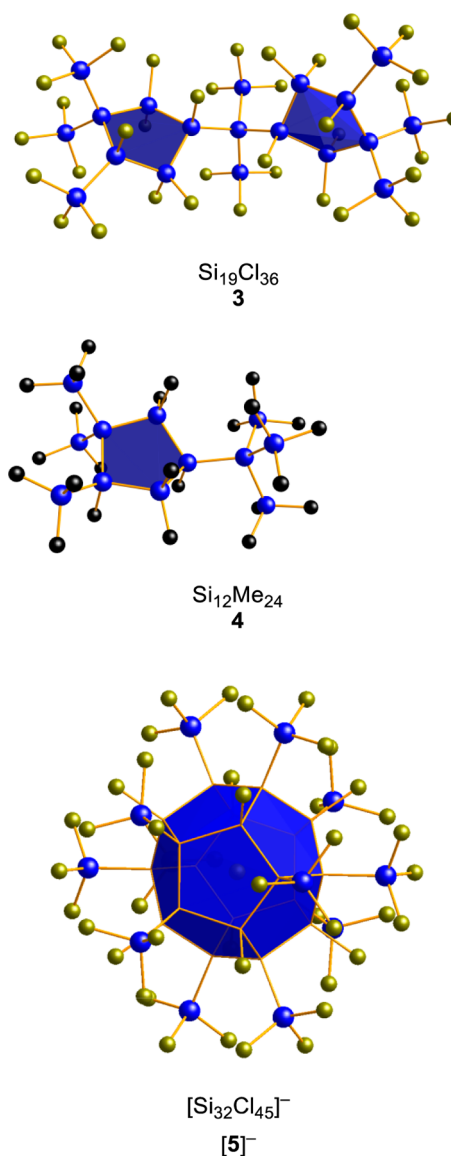
Figure 3. Molecular structure of $Si_{19}Cl_{36}$ in the solid state; displacement ellipsoids are shown at the 30% probability level. Selected bond lengths [Å], bond angles [deg], and torsion angles [deg]: Si(1)−Si(2) = 2.345(1), Si(1)−Si(5) = 2.360(1), Si(1)−Si(10) = 2.365(1), Si(2)−Si(3) = 2.339(1), Si(3)−Si(4) = 2.352(1), Si(4)−Si(5) = 2.359(1); Si(1)−Si(2)−Si(3) = 103.8(1), Si(1)−Si(5)−Si(4) = 107.5(1), Si(1)−Si(10)−Si(1A) = 105.7(1), Si(2)−Si(1)−Si(5) = 98.1(1), Si(2)−Si(1)−Si(10) = 120.9(1), Si(2)−Si(3)−Si(4) = 103.8(1), Si(3)−Si(4)−Si(5) = 104.5(1); Si(1)−Si(2)−Si(3)−Si(4) = 40.7(1), Si(1)−Si(5)−Si(4)−Si(3) = −12.9(1), Si(2)−Si(3)−Si(4)−Si(5) = −16.6(1), Si(2)−Si(1)−Si(5)−Si(4) = 36.5(1), Si(3)−Si(2)−Si(1)−Si(5) = −46.9(1). Symmetry transformation used to generate equivalent atoms: A: $1−x, y, 0.5−z$.

disubstituted cyclopentasilane $1,1-(Me_3Si)_2Si_5Me_8$. As a general feature, rearrangement reactions of permethylated cyclosilanes favored products with a geminal bis(trimethylsilyl) substitution pattern. Obviously, the formation of **3** proceeded along analogous guiding lines: The disubstituted cyclohexasilane starting material **2** furnished trisubstituted cyclopentasilane fragments. We also note that **3** contains a number of geminally substituted Si^0 centers, i.e., Si(4), Si(4A), and Si(10).

Recently, our group discovered a one-step synthesis of the siladodecahedrane $[R_4N][5]$ (Figure 4; R = Et, nBu), which starts from Si_2Cl_6 and nBu$_3$N/$[n$Bu$_4$N]Cl.[31] Now, the generation of compound **3** provides further indication that reaction cascades beginning with the Lewis base-induced disproportionation reaction of Si_2Cl_6 can ultimately be taken far beyond the preparation of perchlorinated *neo*-pentasilane (trigger: R_3N)[32] or (substituted) cyclohexasilanes (trigger: Cl^-).[10,11] With regard to the reaction mechanism leading to the formation of $[R_4N][5]$, it is revealing that the Si_6 ring of **2** can readily rearrange to furnish Cl_3Si-substituted Si_5 rings and that there appears to be a tendency of the resulting cyclo-pentasilanes to cross-link via Si bridges.

Assessment of the Lewis Acidity of Si_6Cl_{12} (1). In the planarized Si_6Cl_{12} moiety, 12 electron-withdrawing chloro substituents lead to strong Lewis acid sites above and below the positively polarized Si_6 core. Coordination of the two extra Cl^- ions in $[1·2Cl]^{2−}$ is therefore partly due to Coulomb attraction.[26,33] Electrostatic interactions likely contribute also to the bonding in $[1·2AlCl_4]^{2−}$, and we note in this context that comparable aggregates do not form when **1** cocrystallizes with CCl_4, a charge-neutral analogue of $[AlCl_4]^−$ (see the SI for details of the crystal structure of $[1/CCl_4]$). The apical anion coordination in $[1·2Cl]^{2−}$ is further stabilized through $n_{Cl} \rightarrow \sigma^*_{Si−Cl}$ interactions, by which charge density is donated from Cl^- lone pairs into Si−Cl antibonding orbitals.[11,33]

The Gutmann−Beckett acceptor number is a commonly used measure for the classification of relative Lewis acid-ities.[34,35] The calculation of acceptor numbers requires the determination of the ^{31}P NMR shift of Et_3PO in the presence

Figure 4. Molecular structures of $Si_{19}Cl_{36}$ (**3**), $Si_{12}Me_{24}$ (**4**), and the silafullerane $[Si_{32}Cl_{45}]^−$ ($[5]^−$) in the solid state. Hydrogen atoms of **4** and the $[Et_4N]^+$ cation of $[5]^−$ are omitted for clarity.

of the respective Lewis acid. Addition of Et_3PO to free **1** in C_6D_6 led to the formation of various silicon-containing species together with Et_3P (NMR spectroscopic control). This result was to be expected, because it is well known that phosphine oxides are readily reduced by Si_2Cl_6 to their corresponding phosphines.[36,37]

We next performed competition experiments to narrow down the Cl^- affinity of **1** (Table 1), because in assessing a pair of Lewis acids for comparative Lewis acid strength toward a given Lewis base, a competition experiment usually provides the most accurate information.[38] First, we determined the relative affinities of **1** and **2**. The ^{29}Si NMR spectrum of a solution of **1** and $[n$Bu$_4$N]$_2[2·2Cl]$ in CD_2Cl_2 showed an intense signal at $\delta(^{29}Si) = −21.7$, assignable to the $[1·2Cl]^{2−}$ ion. Correspondingly, $[n$Bu$_4$N]$_2[1·2Cl]$ was later isolated from the sample in almost quantitative yield. According to NMR spectroscopy, the reaction mixture did not contain notable amounts of free **2**, but a number of other, unidentified follow-up products. These results lead to the following conclusions: (i)

Table 1. Competition Experiments Performed to Gauge the Lewis Acidity and Stability of 1

entry no.	reactant	reagent	reaction conditions	result
1	$[1 \cdot 2Cl]^{2-}$	$AlCl_3$ (2 equiv)	CD_2Cl_2, rt	free **1** obtained
2	$[1 \cdot 2Cl]^{2-}$	$AlCl_3$ (2 equiv)	C_6D_{12}, 80 °C	free **1** obtained
3	$[1 \cdot 2Cl]^{2-}$	$AlCl_3$ (2 equiv)	C_6D_6, rt	free **1** obtained
4	$[1 \cdot 2Cl]^{2-}$	$AlCl_3$ (2 equiv)	C_6H_6, rt	66% **1** isolated
5	$[1 \cdot 2Cl]^{2-}$	$AlCl_3$ (1 equiv)	CD_2Cl_2, rt	rearrangement/fragmentation
6	$[1 \cdot 2Cl]^{2-}$	$AlCl_3$ (1 equiv)	C_6D_6, rt	rearrangement/fragmentation
7	$[2 \cdot 2Cl]^{2-}$	$AlCl_3$ (2 equiv)	CD_2Cl_2, rt	rearrangement/fragmentation
8	$[2 \cdot 2Cl]^{2-}$	$AlCl_3$ (2 equiv)	C_6D_6, rt	rearrangement/fragmentation
9	$[1 \cdot 2Cl]^{2-}$	$AlBr_3$ (2 equiv)	C_6D_6, rt	Cl/Br scrambling
10	$[1 \cdot 2Cl]^{2-}$	$FeCl_3$ (2 equiv)	CD_2Cl_2, rt	rearrangement/fragmentation
11	$[1 \cdot 2Cl]^{2-}$	BCl_3 (exc.)	CD_2Cl_2, rt	rearrangement/fragmentation
12	$[1 \cdot 2Cl]^{2-}$	BPh_3 (2 equiv)	CD_2Cl_2, rt	no reaction
13	$[1 \cdot 2Cl]^{2-}$	**1** (1 equiv)	CD_2Cl_2, rt	91% $[1 \cdot 2Cl]^{2-}$ isolated
14	$[2 \cdot 2Cl]^{2-}$	**1** (1 equiv)	CD_2Cl_2, rt	92% $[1 \cdot 2Cl]^{2-}$ isolated
15	**1**	$AlCl_3$ (1 equiv)	CD_2Cl_2, 50 °C, 2 h	no reaction
16	**1**	$AlCl_3$ (1 equiv)	C_6D_{12}, 80 °C, 1 h	no reaction
17	**1**	$FeCl_3$ (1 equiv)	CD_2Cl_2, 50 °C, 2 h	no reaction
18	**1**	$FeCl_3$ (1 equiv)	C_6D_{12}, 80 °C, 1 h	no reaction
19	**1**	BCl_3 (exc.)	CD_2Cl_2, rt	no reaction
20	**1**	$[nBu_4N][BCl_4]$ (exc.)	CD_2Cl_2, rt	rearrangement/fragmentation
21	**1**	Et_3PO	C_6D_6, rt	Et_3P observed

The unsubstituted cyclohexasilane **1** is a stronger Lewis acid than **2**, which can be understood on steric as well as electronic grounds, because **2** offers fewer Si–Cl antibonding orbitals for $n_{Cl} \rightarrow \sigma^*_{Si-Cl}$ donation. (ii) The degradation of free **2** already observed earlier is not solely attributable to the action of $AlCl_3$.

We therefore assumed that cyclohexasilane monoadducts, generated by the transfer of Cl^- ions, might play a decisive role for the degradation/rearrangement of the Si_6 ring. Indeed, quantum chemical calculations on $[1 \cdot Cl]^-$ unveiled a reaction path along which the extra Cl^- ion leaves the acidic pocket on top of the ring centroid to attack one of the Si atoms and open the cyclic framework. The associated energy barrier amounts to 22.7 kcal mol^{-1}.[11] To gain experimental insight into the reactivity of $[1 \cdot Cl]^-$, we recorded ^{29}Si NMR spectra on an equimolar mixture of $[nBu_4N]_2[1 \cdot 2Cl]$ and **1** in CD_2Cl_2. We did not detect the signal of the free cyclohexasilane **1**, whereas a strong resonance at $\delta(^{29}Si) = -21.7$ testified to the presence of the Cl^- diadduct $[1 \cdot 2Cl]^{2-}$. A number of further NMR signals indicated the formation of several new species. The most likely primary product of the reaction is the monoadduct $[1 \cdot Cl]^-$, which subsequently reacts further to furnish the (yet unidentified) secondary products observable in the NMR spectrum. The degradation of the Si_6 rings continues until a sufficient amount of Cl^- ions has been liberated to stabilize all remaining cyclohexasilane molecules in the form of their diadducts $[1 \cdot 2Cl]^{2-}$. Given the stoichiometric ratios employed, the amount of $[1 \cdot 2Cl]^{2-}$ should remain the same before and after the addition of **1**, which we found to be the case after sample workup. The second competition experiment thus shows that the Cl^- ion affinities of **1** and $[1 \cdot Cl]^-$ are comparable, because otherwise no reaction between **1** and $[1 \cdot 2Cl]^{2-}$ would have taken place. Contrary to **1** and $[1 \cdot 2Cl]^{2-}$, the monoadduct $[1 \cdot Cl]^-$ is not a stable compound. However, in light of the successful decomplexation of $[1 \cdot 2Cl]^{2-}$ to **1** by $AlCl_3$, the lifetime of intermediate monoadducts $[1 \cdot Cl]^-$ must be sufficiently long to enable the second Cl^- abstraction reaction. We further conclude that $[2 \cdot Cl]^-$ should be even less

stable than $[1 \cdot Cl]^-$, which is why **2** is not accessible from $[2 \cdot 2Cl]^{2-}$ and $AlCl_3$.

So far, it is obvious that the Lewis acidities of $[1 \cdot Cl]^-$ and **1** are lower than that of $AlCl_3$. To narrow the gauge, $[nBu_4N]_2[1 \cdot 2Cl]$ was also treated with BPh_3 and BCl_3 in CD_2Cl_2. In the first case, the only resonances detectable appeared at chemical shift values of $\delta(^{29}Si) = -21.7$ (cf. $[1 \cdot 2Cl]^{2-}$: $\delta = -21.7$)[11] and $\delta(^{11}B) = 67.9$ (cf. BPh_3: $\delta = 67.5$),[39] which unequivocally proves that no reaction had taken place.

In the second case, a significant amount of $[1 \cdot 2Cl]^{2-}$ was still present after 2 equiv of BCl_3 had been added. Surprisingly, however, the BCl_3 was already fully consumed at this stage (NMR spectroscopic control). The sample was therefore treated with further BCl_3, and we found that overall 4 equiv of the Lewis acid are required to quantitatively transform the Cl^- diadduct. Notably, we never observed the ^{29}Si NMR signal of free **1** in this experiment. In addition, we also performed the reverse reaction between **1** and $[nBu_4N][BCl_4]$[40] in CD_2Cl_2 and confirmed the presence of the Cl^- diadduct $[1 \cdot 2Cl]^{2-}$ in a mixture of several silicon-containing species. Even though we have not yet identified the full palette of reaction products, it can nevertheless be concluded that **1** and $[1 \cdot Cl]^-$ possess Lewis acidities similar to BCl_3 but lower than $AlCl_3$. Seemingly inconsistent with these results, BCl_3 is ranked higher than $AlCl_3$ on the scale of Childs and Gutmann–Beckett acceptor numbers.[41,42] It has, however, to be noted that different reference Lewis bases (Et_3PO vs Cl^-) can lead to different Lewis acidity estimates[38] (cf. gas-phase dissociation energies $[ECl_4]^- \rightarrow ECl_3 + Cl^-$: $\Delta H° = 321 \pm 12$ kJ mol^{-1} (E = Al), 289 ± 8 kJ mol^{-1} (E = B)[23]).

Reaction of Si_6Cl_{12} (1) with 1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene. Michl and West have reported on the isolation of dimethylsilylene ($SiMe_2$) from photolysis of Si_6Me_{12} in Ar (at 10 K) or hydrocarbon matrices (at 77 K).[43,44] Roesky and Filippou have demonstrated that dihalosilylenes can be isolated and crystallographically characterized as their N-heterocyclic carbene (NHC) adducts NHC–SiX_2 (X = Cl,[21] Br[45]).

With the aim to establish Si_6Cl_{12} (**1**) as a storage form of $SiCl_2$, we allowed **1** to react with 6 equiv of 1,3-bis(2,6-

Scheme 3. Synthesis of Idipp−SiCl₂
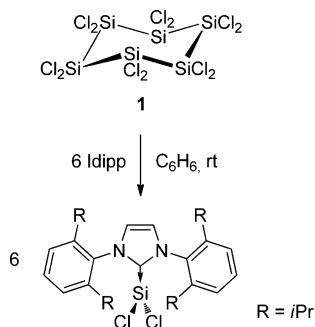
diisopropylphenyl)imidazol-2-ylidene in C_6H_6 (Scheme 3). Indeed, the quantitative formation of Idipp−SiCl₂ was observed (NMR spectroscopic control; 89% isolated yield). X-ray crystallography further confirmed the identity of the reaction product as Idipp−SiCl₂, a compound that has already been described previously by Roesky et al.[21]

In a general context, our experiment suggests **1** as a novel source of reactive $SiCl_2$. Specifically, it provides convenient access to the promising and versatile reagent Idipp−SiCl₂.[46]

■ CONCLUSION

Perchlorinated cyclohexasilane (**1**) is readily accessible from the Cl⁻ diadduct $[1·2Cl]^{2-}$ through abstraction of the extra Cl⁻ ions with $AlCl_3$. Given that $[nBu_4N]_2[1·2Cl]$ forms in one step when Si_2Cl_6 is treated with $[nBu_4N]Cl$, our overall two-step protocol provides a convenient new synthesis of **1**, which is an intensely investigated precursor for semiconductor materials. Yet, the synthesis procedure is apparently not applicable for the preparation of substituted derivatives, such as 1,1-$(Cl_3Si)_2Si_6Cl_{10}$ (**2**): Instead of **2**, the reaction between $[nBu_4N]_2[2·2Cl]$ and $AlCl_3$ furnishes a number of other (oligo)silanes, among them $Si_{19}Cl_{36}$ (**3**). On the other hand, this result also demonstrates that it is possible to go beyond the structural motif of Si_6 rings, exploiting the intrinsic fragmentation/rearrangement reactivity of perchlorinated oligosilanes. From competition experiments between **1** and $[nBu_4N]_2[1·2Cl]$ or $[nBu_4N]_2[2·2Cl]$ we further conclude (i) that the monoadducts $[1·Cl]^-$ and $[2·Cl]^-$ are unstable and subject to rearrangement and (ii) that Cl_3Si substitution of the Si_6 ring significantly reduces its Cl⁻ affinity. According to our current assessment, the Lewis acidity of free **1** is comparable to that of BCl_3. While free **1** proved to be inert toward Lewis acids (i.e., BCl_3, $AlCl_3$, $FeCl_3$) even at elevated temperatures, addition of 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene leads to the instantaneous and quantitative formation of the adduct Idipp−SiCl₂. Work is currently in progress in our laboratories to fully exploit the potential of perchlorinated cyclic silanes as $SiCl_2$ storage forms.

■ EXPERIMENTAL SECTION

General Details. All reactions were carried out under an inert-gas atmosphere (dry argon or nitrogen) using standard Schlenk or glovebox techniques. Commercially available substances were used as received. $[nBu_4N]_2[1·2Cl]$ and $[nBu_4N]_2[2·2Cl]$ were prepared according to literature procedures.[11] $AlCl_3$ was prepared from Al turnings and HCl gas.[47,48] Reaction solvents were dried over sodium

(n-hexane and C_6H_6) or CaH_2 (CH_2Cl_2) and freshly distilled prior to use. C_6D_{12}, C_6D_6, and CD_2Cl_2 were stored over molecular sieves (4 Å). NMR spectra were recorded on a Bruker Avance III HD 500 MHz spectrometer equipped with a Prodigy BBO 500 S1 probe. $^1H/^{13}C\{^1H\}$ NMR spectra were referenced against (residual) solvent signals (C_6D_{12}: 1.38 ppm/26.43 ppm, C_6D_6: 7.16 ppm/128.06 ppm, CD_2Cl_2: 5.32 ppm/53.84 ppm). ^{29}Si NMR spectra were calibrated against external $SiMe_4$ ($\delta(^{29}Si) = 0$); whenever present, $SiCl_4$ ($\delta(^{29}Si) = -18.9$) was used as internal standard.

Synthesis of Si_6Cl_{12} (1). A Schlenk tube was charged with $AlCl_3$ (145 mg, 1.09 mmol) and C_6H_6 (5 mL). Finely ground single-crystalline $[nBu_4N]_2[1·2Cl]$ (500 mg, 0.44 mmol) was added with stirring at rt in four portions at intervals of 30 min. The reaction mixture was stirred for another 1 h to obtain a clear, colorless solution. After the solvent had been removed under reduced pressure, n-hexane (5 mL) was added to the colorless solid residue. The Schlenk tube was immersed in liquid nitrogen in a Dewar flask until the solvent solidified. Thereafter, the vessel was evacuated, closed, slowly heated to 85 °C (water-bath temperature), and left at this temperature for 30 min. After the mixture had cooled to rt, it was filtered through a PTFE-syringe filter (pore size: 0.2 μm) to obtain a clear, colorless liquid. The solvent was removed from the filtrate under reduced pressure, and the colorless product was dried under dynamic vacuum for 2 h. Yield: 169 mg (0.29 mmol, 66%). ^{29}Si NMR (C_6D_6; 99.4 MHz): $\delta = -3.0$. Single crystals of $[1/CCl_4]$ were grown from a solution of **1** in CCl_4 at -30 °C. The crystals used for X-ray analysis were selected in a cold (-40 °C) stream of N_2.

Crystallization of $[nBu_4N]_2[1·2AlCl_4]$. A solution of $[nBu_4N]_2[1·2Cl]$ (115 mg, 0.10 mmol) in CD_2Cl_2 (0.6 mL) was prepared in an NMR tube. $AlCl_3$ (27 mg, 0.20 mmol) was added, and the NMR tube was vacuum-sealed. At rt, an investigation of the clear, colorless solution by ^{29}Si NMR spectroscopy showed exclusively the resonance assignable to free **1**. At -30 °C, however, colorless, X-ray quality crystals of $[nBu_4N]_2[1·2AlCl_4]$ grew within 24 h.

Formation of $Si_{19}Cl_{36}$ (3). In an NMR tube, a solid mixture of single-crystalline $[nBu_4N]_2[2·2Cl]$ (100 mg, 0.07 mmol) and $AlCl_3$ (20 mg, 0.15 mmol) was dissolved in CD_2Cl_2 (0.5 mL; *note*: $AlCl_3$ or $[nBu_4N]_2[2·2Cl]$ alone is very poorly soluble in CD_2Cl_2). The NMR tube was vacuum-sealed. A few hours later, ^{29}Si NMR spectroscopy on the colorless solution showed resonances assignable neither to the starting material $[nBu_4N]_2[2·2Cl]$ nor to the target compound **2**. Rather, the spectrum indicated the formation of a complex product mixture. The reaction solution was transferred to a screw-capped vial and stored for 30 d at rt, whereupon a few colorless, cuboid crystals of **3** precipitated. From the same sample, we also isolated crystals of $[Bu_4N][AlCl_4]$. ^{29}Si NMR data of **3** could not be acquired, because the compound is insoluble in all common inert solvents.

Synthesis of Idipp−SiCl₂. A solution of **1** (51 mg, 0.086 mmol) in C_6H_6 (2 mL) was slowly added to 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene (200 mg, 0.515 mmol) in C_6H_6 (6 mL). After the resulting yellow reaction mixture had been stirred at rt overnight, all volatiles were removed under a dynamic vacuum. The yellow solid residue was washed with n-hexane (1 mL), and the remaining pale yellow crude product recrystallized from C_6H_6. Yield: 223 mg (0.457 mmol, 89%). The identity of the reaction product as Idipp−SiCl₂ was confirmed by ^{29}Si NMR spectroscopy and X-ray crystallography. ^{29}Si NMR (C_6D_6; 99.4 MHz): $\delta = 18.7$.

X-ray Crystal Structure Determination. Single crystals of $[nBu_4N]_2[1·2AlCl_4]$, $Si_{19}Cl_{36}$ (**3**), and $1/CCl_4$ were measured on a STOE IPDS-II diffractometer with a Genix microfocus tube with mirror optics. The data were scaled using the frame-scaling procedure in the X-AREA program system.[49] All structures were solved by direct methods and refined with full-matrix least-squares on F^2 using the program SHELXL97.[50] The crystal of $[nBu_4N]_2[1·2AlCl_4]$ was nonmerohedrally twinned with a fractional contribution of 0.191(4) for the minor domain. The chlorine atoms of CCl_4 in $1/CCl_4$ are disordered over two equally occupied positions. CCDC reference numbers: 1414710 ($[nBu_4N]_2[1·2AlCl_4]$), 1414711 (**3**), and 1414712 ($1/CCl_4$).

Table 2. Selected Crystallographic Data for [*n*Bu$_4$N]$_2$[1·2AlCl$_4$], Si$_{19}$Cl$_{36}$ (3), and 1/CCl$_4$

	[*n*Bu$_4$N]$_2$[1·2AlCl$_4$]	Si$_{19}$Cl$_{36}$ (3)	1/CCl$_4$
formula	C$_{32}$H$_{72}$Al$_2$Cl$_{20}$N$_2$Si$_6$	Si$_{19}$Cl$_{36}$	CCl$_{16}$Si$_6$
M_r	1416.41	1809.91	747.75
color, shape	colorless, block	colorless, block	colorless, block
T [K]	173(2)	173(2)	173(2)
radiation, λ [Å]	Mo Kα, 0.710 73	Mo Kα, 0.710 73	Mo Kα, 0.710 73
cryst syst	monoclinic	monoclinic	trigonal
space group	$C2/c$	$C2/c$	$R\bar{3}c$
a [Å]	20.3059(13)	36.9602(14)	12.6663(11)
b [Å]	12.0325(5)	9.5908(3)	12.6663(11)
c [Å]	27.9854(17)	18.4902(7)	27.782(3)
α [deg]	90	90	90
β [deg]	103.759(5)	99.231(3)	90
γ [deg]	90	90	120
V [Å^3]	6641.5(7)	6469.5(4)	3860.1(8)
Z	4	4	6
D_{calcd} [g cm^{-3}]	1.417	1.858	1.930
$F(000)$	2912	3512	2172
μ [mm^{-1}]	0.984	1.873	1.977
cryst size [mm]	0.20 × 0.10 × 0.05	0.39 × 0.37 × 0.21	0.57 × 0.52 × 0.47
rflns collected	28 729	72 318	3307
indep rflns (R_{int})	6461 (0.0988)	9065 (0.0579)	977 (0.0498)
data/restraints/params	6461/0/281	9065/0/249	977/0/42
GOF on F^2	1.105	1.058	1.206
R_1, wR_2 [$I > 2\sigma(I)$]	0.0898, 0.2577	0.0357, 0.0819	0.0375, 0.0912
R_1, wR_2 (all data)	0.1001, 0.2635	0.0406, 0.0844	0.0400, 0.0924
largest diff peak and hole [e Å^{-3}]	0.846, −0.521	0.951, −1.067	0.523, −0.385

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01703.

> Details of the X-ray crystal structure analysis of 1/CCl$_4$ and plots of the NMR spectra of [*n*Bu$_4$N]$_2$[1·2AlCl$_4$], 1, and Idipp−SiCl$_2$ (PDF)
> Crystallographic data (CIF)

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Author Contributions

J.T. and M.M. performed the synthetic work, prepared the samples for analytics, analyzed data, and collected X-ray data; M.B. processed and refined X-ray data; H.W.L. was involved in study design; M.W. designed and supervised the experimental studies; M.W., J.T., and M.M. wrote the paper; and all the authors discussed the results and commented on the manuscript.

Notes

The authors declare no competing financial interest.

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