

Supporting Information

**Breaking Carbon-Chlorine Bonds with the Unconventional Lewis Acid
Dodecachlorocyclohexasilane**

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Table of Contents

1. Experimental.....	3
2. References	19

1. Experimental

Characterization of Materials

Single crystal X-ray diffraction data of the compound $[\text{Tr}^+]_2[\text{Si}_6\text{Cl}_{14}^{2-}]$ were collected on a Bruker Apex Duo diffractometer with an Apex 2 CCD area detector at $T = 110\text{K}$. Cu radiation was used. Data was processed (integration and absorption correction) with Bruker's software APEX3 version 2016.9-0. Olex2, version 1.2.9 software package,¹ was used to solve the structure with the ShelXT structure solution program² followed by structure refinement with the ShelXL refinement package³ using least squares minimization. The samples were protected from atmospheric $\text{H}_2\text{O}/\text{O}_2$ by immersing in NVH type oil prior to transfer from the glove box to the instrument.

FTIR spectra were recorded using a Thermo Scientific Nicolet 8700 FT-IR. FTIR samples used KBr pellets which were prepared in a dry, inert atmosphere. Due to the air-sensitive nature of the materials being characterized, the samples were transferred to the FTIR in a dry, inert atmosphere and quickly transferred to the instrument, while the chamber was being flushed with dry N_2 . Raman spectra were recorded using a Horiba Jobin Yvon Aramis Confocal Raman imaging system which was equipped with 532 and 785 nm lasers. The samples were protected from the atmosphere by sandwiching them between two quartz plates and sealing the edges with Krytox grease.

Preparation of Starting Materials

Starting materials were reagent grade or higher, unless otherwise noted. $\text{Si}_6\text{Cl}_{12}$ (**1**) was prepared two ways using modified procedures from literature.⁴ The origin of **1** had no observable effect on experiments when used as a starting material. All manipulations were performed in a dry, oxygen free atmosphere due to the $\text{H}_2\text{O}/\text{O}_2$ sensitive nature of the starting materials (particularly **1** which readily reacts with H_2O). A dry and oxygen free atmosphere was maintained by performing manipulations in a rigorously controlled, N_2 filled glove box ($\text{O}_2 < 0.1$ ppm; $\text{H}_2\text{O} <$

0.1 ppm) or by using standard Schlenk line techniques. Glassware was dried at 150°C for >2 h and transferred into the glove box while hot to prevent atmospheric H₂O from condensing on the glass.

Solvents were deoxygenated by sparging with N₂ while stirring for >2 h. They were then dried using literature protocols, which included passing over neutral alumina and/or storage over 3 Å or 4 Å molecular sieves.⁵ The sieves were dried at 300°C under a vacuum of <50 mTorr for >12 h and stored under a dry, inert atmosphere before use.

Synthesis of [BnPh₃P⁺]₂[EDIPA-H⁺]₂[Si₆H_nCl_{14-n}²⁻][Cl⁻]₂·4CH₂Cl₂

Synthesis of a dianion salt was the initial step in producing **1**. [BnPh₃P⁺]₂[EDIPA-H⁺]₂[Si₆H_nCl_{14-n}²⁻][Cl⁻]₂·4CH₂Cl₂ was prepared by repeating the following procedure. A reaction vessel was fitted with a -10°C condenser and charged with Ph₃BnPCl (51.19 g, 131.6 mmol), 1,2-dimethoxyethane (1.19 g, 13.2 mmol), N, N-diisopropylethylamine (51.2 g, 396 mmol) and 150 mL CH₂Cl₂. HSiCl₃ (67.0 mL, 664 mmol) was added via addition funnel over 30 min while stirring. A heat of ~50°C was applied and reflux was controlled at ≤1 drop/sec. Heating was stopped after 72 h and product (59.72 g) was isolated via cold filtration after precipitation at -28°C for 21 h.

Synthesis of [BnPh₃P⁺]₂[Si₆H_nCl_{14-n}²⁻] and [BnPh₃P⁺]₂[Si₆Cl₁₄²⁻]

[BnPh₃P⁺]₂[EDIPA-H⁺]₂[Si₆H_nCl_{14-n}²⁻][Cl⁻]₂·4CH₂Cl₂ was co-crystallized with superfluous [EDIPA-H⁺], [Cl] and solvent which were removed by recrystallization from CHCl₃. The mixed salt (124.9 g) was dissolved in 625 mL CHCl₃. This initially formed a solution which precipitated white solids within 5 min. The mixture was stirred for 1 h then undisturbed for 15 min. The precipitate was filtered via glass frit and washed 3x with 80 mL CHCl₃ (-9°C) to yield 45.6g of [BnPh₃P⁺]₂[Si₆H_nCl_{14-n}²⁻].

The Si₆ ring in [BnPh₃P⁺]₂[Si₆H_nCl_{14-n}²⁻] contained partial hydride substitution on Si (undesirable for synthesis of **1**) which were exchanged with chlorine by reaction with trityl chloride. [BnPh₃P⁺]₂[Si₆H_nCl_{14-n}²⁻] (4.990 g) of was reacted with trityl chloride (3.048 g, 10.93 mmol) in 160 mL CH₂Cl₂. The reaction mixture was stirred for 24 h. Afterwards, 160 mL hexanes were added to the reaction mixture to facilitate complete precipitation of [Ph₃BnP⁺]₂[Si₆Cl₁₄²⁻]. The mixture was stirred an additional 5 min and then undisturbed for 2 h. The reaction was filtered via frit and washed 3x with 20 mL CHCl₃ (-28°C). [BnPh₃P⁺]₂[Si₆Cl₁₄²⁻] (4.905 g, 3.576 mmol) was isolated following 1.5 h drying under vacuum (98.3% yield by weight).

Synthesis of Si₆Cl₁₂ (**1**)

The first method used to prepare **1** was a slightly modified version of that reported by Boudjouk et al.^{4a} In short, chlorine gas was bubbled through a chilled solution (-89°C) of Si₆H₁₂ (0.400 g, 2.22 mmol) in 20 mL CH₂Cl₂, producing Si₆Cl₁₂ and HCl byproduct. Crude Si₆Cl₁₂ was isolated as a white solid after removal of CH₂Cl₂ and HCl via vacuum. The crude Si₆Cl₁₂ was purified by dissolution in hexane. Insoluble material was removed by filtration and Si₆Cl₁₂ was crystallized from the resulting filtrate, giving 0.923g (70% yield) product.

The second method used to prepare **1** was a modified version of that reported by Wagner et al. in which AlCl₃ is used to abstract the axial chlorides from [Si₆Cl₁₄²⁻].^{4b} A high pressure reaction vessel was charged with AlCl₃ (5.86 g, 43.9 mmol) and 200.0 mL benzene. [BnPh₃P⁺]₂[Si₆Cl₁₄²⁻] (24.1 g, 17.6 mmol) was added to the reaction mixture in quarter increments every 15 min. The solvent was removed via vacuum, revealing green/yellow solids. The solids were dried an additional 30 min following complete solvent removal. The solids were charged with 200 mL n-heptane and stirred for 30 min while heating at 95°C. After returning to room temperature the

mother liquor was decanted and filtered through a 0.2 μm PTFE filter. The solvent was removed from the filtrate via vacuum to give $\text{Si}_6\text{Cl}_{12}$ (9.38 g, 15.8 mmol, 89.9% yield).

Preparations of $[\text{Tr}^+]_2[\text{Si}_6\text{Cl}_{14}^{2-}]$

The reaction of $\text{Si}_6\text{Cl}_{12}$ with TrCl in hexane or halogenated solvents caused the rapid precipitation of yellow solids which had characteristics of the desired $[\text{Tr}^+]_2[\text{Si}_6\text{Cl}_{14}^{2-}]$ according to FTIR, Raman and elemental analysis (EA). However, to produce crystals that were diffractable the reaction had to be slowed down by adding $\text{C}_2\text{H}_4(\text{CN})_2$. Addition of $\text{C}_2\text{H}_4(\text{CN})_2$ to the reaction enabled higher quality crystal formation but had the tradeoff of lowering the yield from 90.3% to 13%. FTIR data for $[\text{Tr}^+]_2[\text{Si}_6\text{Cl}_{14}^{2-}]$ was the same, whether or not $\text{C}_2\text{H}_4(\text{CN})_2$ was used, confirming that none of the $\text{C}_2\text{H}_4(\text{CN})_2$ contaminated the bulk sample. Adducts of the form $\text{Si}_6\text{Cl}_{12} \cdot \text{C}_2\text{H}_4(\text{CN})_2$ have characteristic $\text{C}\equiv\text{N}$ stretching bands in the region of 2250 cm^{-1} ,⁶ which were absent from both spectra (figure S1).

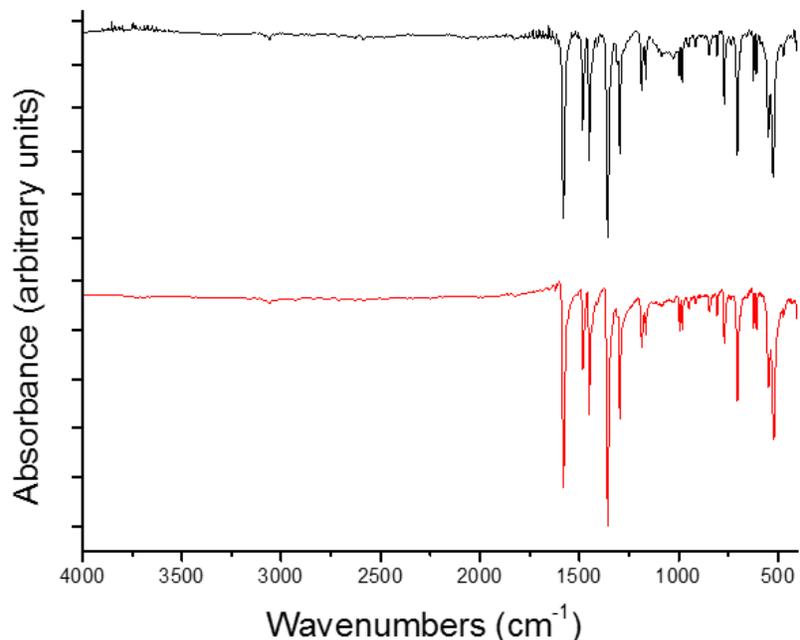


Figure S1. FTIR data for $[\text{Tr}^+]_2[\text{Si}_6\text{Cl}_{14}^{2-}]$ produced in the absence of $\text{C}_2\text{H}_4(\text{CN})_2$ (black) and in the presence of $\text{C}_2\text{H}_4(\text{CN})_2$ (red). The latter did not show characteristic $\text{C}\equiv\text{N}$ stretching for the $\text{Si}_6\text{Cl}_{12}\cdot\text{C}_2\text{H}_4(\text{CN})_2$ coordination polymer at 2250 cm^{-1} ,⁶ indicating that none of the $\text{C}_2\text{H}_4(\text{CN})_2$ made it into the bulk sample.

Synthesis of $[\text{Tr}^+]_2[\text{Si}_6\text{Cl}_{14}^{2-}]$ from $\text{Si}_6\text{Cl}_{12}$ and TrCl in Hexanes

$\text{Si}_6\text{Cl}_{12}$ (67 mg, 0.11 mmol) was dissolved in 0.50 mL hexanes (95% n-hexane) forming a colorless solution. TrCl (66.4 mg, 0.238 mmol) was dissolved in 2.50 mL hexanes. Adding a drop of the TrCl solution to the $\text{Si}_6\text{Cl}_{12}$ solution resulted in the immediate precipitation of yellow solids. The remaining TrCl solution was added all at once, causing the rapid precipitation of yellow solids and changing the mother liquor to an orange solution. The reaction mixture was stirred an additional 5 min prior to filtering the solids and washing 8x with 2 mL hexanes. The solids were dried under vacuum for 15 min, leaving a yellow fine powder (118 mg). Theoretical elemental

analysis: C, 39.64; H, 2.63; Cl, 43.10; Si, 14.63. Experimental elemental analysis: C, 37.49; H, 2.69; Cl, 40.23; Si, 15.4.

FTIR data confirmed the presence of the $[\text{Tr}^+]$ ion in the product (table S1). There are numerous FTIR signatures for the $[\text{Tr}^+]$ that differentiate it from the neutral Tr organic group, as summarized in the table.⁷

Table S1. Observed and calculated FTIR frequencies with corresponding assignments for TrCl , $[\text{Tr}^+][\text{AlCl}_4^-]$, $[\text{Tr}^+]_2[\text{Si}_6\text{Cl}_{14}^{2-}]$ and $[\text{Tr}^+]_2[\text{Si}_6\text{Br}_{14}^{2-}]^*$.

Assignment	Trityl Chloride			$[\text{Tr}][\text{AlCl}_4]$		$[\text{Tr}]_2[\text{Si}_6\text{Cl}_{14}]$	$[\text{Tr}]_2[\text{Si}_6\text{Br}_{14}]^*$
	Calc ⁷	Exp ⁷	Exp	Calc ⁷	Exp ⁷	Exp	Exp
C-C stretch	1616	1597 m	1595 w	1599	1583 s	1579 s	1579 s
C-C stretch	1596	1582 m	1581 w	1569	1562 w	----	1558 w
C-C stretch	1499	1488 s	1489 m	1488	1483 m	1483 m	1481 m
Asym Me def C-C stretch	1449	1445 s	1444 m	1450	----	1450 m	1448 s
Sym Me def C-H bend ()	1338	1336 sh	----	----	----	----	----
C-C stretch	1314	1318 m	1317 w	----	----	1309 w	----
C-H bend ()	----	----	----	1327	1295 s	1296 m	1296 m
Asym C- Φ stretch	1196	1215 m	1215 w	1357	1358 s	1356 s	1358 s
C-H bend ()	1190	1182 m	1182 w	1189	1186 s	1188 m	1184 m
C-H bend ()	1163	1158 m	1157 w	1172	1166 m	1167 m	1167 w
Sym C- Φ stretch	1142	1147 m	1147 w	1182	----	----	----
C-H bend ()	1090	1082 m	1082 w	1098	1089 vw	1088 vw	----
C-H bend ()	1036	1033 m	1034 w	1028	1030 m	1026 vw	1028 w
C-H bend (\perp)	----	----	----	1009	----	----	----
Me def ring breathe	996	1001 m	1001 w	989	996 m	997 m	995 m
C-H bend (\perp)	986	988 vw	----	985	980 w	984 m	982 w
C-H bend (\perp)	972	975 vw	----	----	----	----	----
C-H bend (\perp)	932	931 m	931 w	956	952 vw	951 w	----
C-H bend (\perp)	926	924 w	----	952	949 vw	----	949 w
C- Φ def	891	895 m	893 w	910	916 w	916 w	914 w
C-H bend (\perp)	845	848 m	849 w	843	842 w	847 w	843 w
C-H bend (\perp)	841	843 sh	----	----	----	----	----
C-H bend (\perp)/C-Cl stretch	805	821 m	822 w	----	----	----	----
C-H bend (\perp)	----	----	810 w	808	806 m	806 m	806 w
C-H bend (\perp)	758	758 s	758 m	770	768 sh	771 m	768 m
C-H bend (\perp)	----	762 sh	----	----	----	----	----
C-Cl stretch	728	747 s	746 m	----	----	----	----
C-Cl stretch	----	736 s	737 m	----	----	----	735 w
C-C-C bend (\perp)	697	698 s	698 s	705	----	704 m	702 m
C-C-C bend ()/C-Cl stretch	660	667 s	667 m	----	----	----	----
C-C-C bend (\perp)	----	----	660 m	659	660 w	----	660 w
C-C-C bend ()	627	627 s	627 m	622	623 m	623 m	623 m
C-C-C bend ()	618	918 m	617 m	609	609 m	607 m	607 m
C-C-C bend (\perp)/Me def	509	508 m	507 w	----	----	----	----

Literature values and peak assignments come from work reported by Eide et al.⁷ (s = sharp, m = medium, w = weak, sh = shoulder). Values marked with “----” mean no peak was present at this location. * Reaction product of $\text{Si}_6\text{Br}_{12}$ and TrBr .

Preparation of Diffrangible $[\text{Tr}^+]_2[\text{Si}_6\text{Cl}_{14}^{2-}]$ Crystals

To facilitate crystal formation, the reaction mixture was not stirred throughout the course of the reaction. $\text{Si}_6\text{Cl}_{12}$ (25 mg, 0.042 mmol) was dissolved in 0.50 mL 1,2-dichloroethane (DCE), forming a yellow solution. Separately, $\text{C}_2\text{H}_4(\text{CN})_2$ (7 mg, 0.09 mmol) was dissolved in 0.50 mL DCE, forming a colorless solution. Both solutions were separately heated to 80°C , with the $\text{Si}_6\text{Cl}_{12}$ solution changing to colorless in <5 min. The $\text{C}_2\text{H}_4(\text{CN})_2$ solution was added to the $\text{Si}_6\text{Cl}_{12}$ solution in one addition, resulting in the precipitation of a small amount of white solid. The particulate did not go into solution after 5 min at 80°C . An additional 1.00 mL DCE was added which dissolved the solids and instantly changed the solution color from colorless to yellow. The color faded, however, returning to colorless in <5 min at 80°C . The reaction mixture was returned to room temperature. No precipitate formed at room temperature and the reaction solution remained colorless.

Separately, trityl chloride (23 mg, 0.084 mmol) was dissolved in 0.50 mL DCE, forming a light-yellow solution. The TrCl solution was added to the reaction solution over 5 min. Each addition caused the instantaneous creation of yellow color that slowly diffused throughout the reaction.

The reaction solution was undisturbed following the TrCl addition, during which time the color changed to orange. Dark yellow crystals slowly precipitated, first becoming visible after 45 min. After 1.5 h significant quantities were formed. The reaction mixture was undisturbed for an additional 45 min for a total reaction time of 2.25 h.

The mother liquor was decanted from the crystalline material and the solids were washed 3x with 1 mL DCE at room temperature. The crystals were stored under high viscosity oil. Storage overnight at room temperature caused some brown color to appear but the crystals appeared

unchanged when viewed under an optical microscope. The crystals were transferred to a glove box freezer at -28°C. After 3 weeks storage, the color changed further to green/brown but the crystals still appeared unchanged under magnification. A transparent dark yellow single crystal, .09 x 0.10 x 0.16 mm³, was isolated and characterized via XRD, confirming the generation of [Tr⁺]₂[Si₆Cl₁₄²⁻]. Crystal structure solution and refinement details are shown in table S2.

Table S2. X-ray crystallographic data for [Tr⁺]₂[Si₆Cl₁₄²⁻]

Formula	Si ₆ Cl ₁₄ C ₃₈ H ₃₀
FW	1151.46
Cryst. size_max [mm]	0.163
Cryst. size_mid [mm]	0.104
Cryst. size_min [mm]	0.09
Cryst. system	trigonal
Space Group, Z	R -3
a [Å]	16.7524(6)
b [Å]	16.7524(6)
c [Å]	14.8211(6)
α [°]	90
β [°]	90
γ [°]	120
V [Å ³]	3602.2(3)
ρ _{calc} [g/cm ³]	1.592
μ [mm ⁻¹]	9.046
Radiation Type	CuKα
F(000)	1740
No of measured refl.	6637
No of indep. refl.	1417
No of refl. (I ≥ 2σ)	1293
Resolution [Å]	0.84
R1/wR2 (I ≥ 2σ) ^a [%]	2.84/7.31
R1/wR2 (all data) [%]	3.13/7.50

^a R1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$, wR2 = $[\sum w[(F_o)^2 - (F_c)^2]^2 / \sum w(F_o)^2]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$, $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$ where $P = [(F_o)^2 + 2(F_c)^2] / 3$ and A, B coefficients are A (B) = 0.0408 (3.8402).

Yield Determination for Diffrangible [Tr⁺]₂[Si₆Cl₁₄²⁻] Crystal Preparation

The synthesis of [Tr⁺]₂[Si₆Cl₁₄²⁻] with C₂H₄(CN)₂ was repeated with the same reaction conditions at a 4x larger scale so that a yield could be collected. To facilitate crystal formation, the reaction mixture was not stirred throughout the course of the reaction. Si₆Cl₁₂ (110 mg, 0.185 mmol) was dissolved in 6.60 mL DCE, forming a yellow solution with a small amount of insoluble particulate. Separately, C₂H₄(CN)₂ (31 mg, 0.387 mmol) was dissolved in 2.20 mL DCE, forming

a colorless solution. Both solutions were heated to 80°C. The $\text{Si}_6\text{Cl}_{12}$ solution changed to light yellow in <5 min, with most of the solid going into solution. The $\text{C}_2\text{H}_4(\text{CN})_2$ solution was added to the $\text{Si}_6\text{Cl}_{12}$ solution in one addition, causing the color to change to yellow instantly. The color changed back to light yellow in <5 min at 80°C. The reaction mixture was returned to room temperature, with neither of the starting materials precipitating. The insoluble particulate was removed via filtration with a 0.2 μm PTFE filter.

Separately, TrCl (103 mg, 0.369 mmol) was dissolved in 2.20 mL DCE, forming a light-yellow solution. The TrCl solution was added to the reaction solution over 5 min. Each addition caused the instantaneous formation of a yellow solution that slowly diffused throughout the reaction. By the end of the addition the reaction had become orange colored with a small amount of precipitated crystals.

The reaction mixture was undisturbed following the TrCl addition, during which time more crystals gradually precipitated. A significant amount of crystals had precipitated after 1.5 h. Viewing the crystals under a 10x microscope revealed them to be highly clustered. The reaction mixture was undisturbed for an additional 45 min, giving a total reaction time of 2.25 h.

The mother liquor was decanted from the crystals and the solids were washed 3x with 4.5 mL DCE. The solids were dried under vacuum for 45 min, giving dark yellow crystals of $[\text{Tr}^+]_2[\text{Si}_6\text{Cl}_{14}^{2-}]$ (28 mg, 13% yield).

Additional Reactions

Attempted Dissolution and Crystallization of $[\text{Tr}^+]_2[\text{Si}_6\text{Cl}_{14}^{2-}]$ in 1,2-DCE

$[\text{Tr}^+]_2[\text{Si}_6\text{Cl}_{14}^{2-}]$ (55.13 mg, 0.0479 mmol) that was prepared in hexanes was stirred in ~4 mL DCE. The mother liquor changed to an orange solution after 12 h of stirring, although, some $[\text{Tr}^+]_2[\text{Si}_6\text{Cl}_{14}^{2-}]$ remained unchanged. One third of the mother liquor was removed and stirring

was continued. After an additional 24 h stirring the mixture had completely changed to an orange solution. The solution was heated to 80°C and additional $[\text{Tr}^+]_2[\text{Si}_6\text{Cl}_{14}^{2-}]$ (~75 mg, ~0.065 mmol) was added. The mixture had completely changed to an orange solution in less than 30 min. No precipitation occurred after storing the solution at -28°C for 5.5 h. Again, $[\text{Tr}^+]_2[\text{Si}_6\text{Cl}_{14}^{2-}]$ (~75 mg, ~0.065 mmol) was added to the solution which dissolved after stirring at 80°C. The solution became an increasingly darker shade of orange as more $[\text{Tr}^+]_2[\text{Si}_6\text{Cl}_{14}^{2-}]$ was added. Storage at -28°C for 3 days changed the color to a slightly lighter shade of orange but no solids precipitated. The DCE was removed by heating the solution at ~100°C for 10 min, revealing an orange gel.

Attempted Metathesis Reaction of $[\text{Tr}^+][\text{BF}_4^-]$ and $[\text{nBu}_4\text{N}^+]_2[\text{Si}_6\text{Cl}_{14}^{2-}]$ in CH_2Cl_2

This reaction was performed to see if an ionic exchange would occur between $[\text{Tr}^+][\text{BF}_4^-]$ and $[\text{nBu}_4\text{N}^+]_2[\text{Si}_6\text{Cl}_{14}^{2-}]$ to precipitate $[\text{Tr}^+]_2[\text{Si}_6\text{Cl}_{14}^{2-}]$. However, no reaction was observed when these reagents were mixed.

A yellow solution of $[\text{Tr}^+][\text{BF}_4^-]$ (17.34 mg, 0.053 mmol) in ~1.25 mL CH_2Cl_2 was prepared. A colorless solution of $[\text{nBu}_4\text{N}^+]_2[\text{Si}_6\text{Cl}_{14}^{2-}]$ (23.15 mg, 0.020 mmol) in ~1.25 mL CH_2Cl_2 was also prepared. The solutions were combined and there was no observable change after 5 min of stirring at room temperature. Storage at -28°C for 1 h did not result in any precipitation.

Reaction of Benzyl Chloride (BnCl) and $\text{Si}_6\text{Cl}_{12}$ in Hexanes

BnCl and $\text{Si}_6\text{Cl}_{12}$ were reacted in hexanes to see if the tropylium salt, $[\text{Bn}^+]_2[\text{Si}_6\text{Cl}_{14}^{2-}]$ could be prepared. BnCl (0.066 g, 0.52 mmol) was dissolved in 1.00 mL hexanes, forming a colorless solution. $\text{Si}_6\text{Cl}_{12}$ (0.149 g, 0.251 mmol) was dissolved in 5.00 mL hexanes, forming a light-yellow

solution. The two solutions were combined under stirring but there was no immediate reaction. No color change or precipitation was observed after stirring the solution for 18 h at room temperature.

Reaction of Benzyl Chloride (BnCl) and $\text{Si}_6\text{Cl}_{12}$ in CD_2Cl_2

BnCl and $\text{Si}_6\text{Cl}_{12}$ were combined in CD_2Cl_2 to determine by NMR if a reaction was occurring. $\text{Si}_6\text{Cl}_{12}$ (49.63 mg, 0.08356 mmol) and BnCl (21.3 mg, 0.168 mmol) were combined in 0.300 mL CD_2Cl_2 , initially forming a clear solution. Over the next 1 h, the reaction mixture changed to a salmon color and a small amount of white solids precipitated. The solution became slightly darker after an additional 43 h, upon which time a ^1H -NMR was collected. The spectrum did not show the characteristic tropylium peak (9.25 ppm) but did show peak broadening for the chemical shifts at 7.0 and 3.9 ppm for BnCl (figure S2).

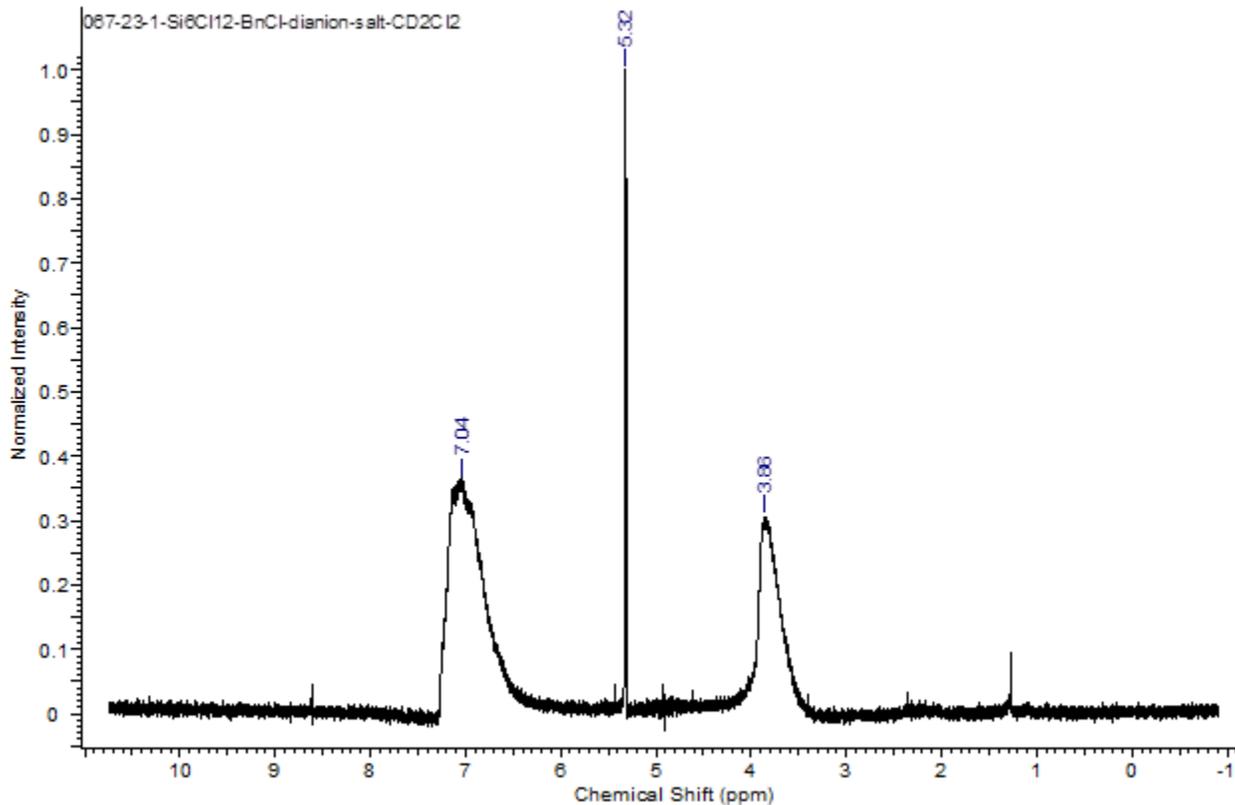


Figure S2. ^1H NMR spectrum for the reaction of $\text{Si}_6\text{Cl}_{12}$ and BnCl in CD_2Cl_2 .

Reaction of Benzhydryl Chloride (BzhCl) and Si₆Cl₁₂ in Hexanes

BzhCl and Si₆Cl₁₂ were reacted in hexanes to see if [Bzh⁺]₂[Si₆Cl₁₄²⁻] could be prepared. BzhCl (0.108 g, 0.532 mmol) was dissolved in 1.00 mL hexanes, forming a light-yellow solution. Si₆Cl₁₂ (0.151 g, 0.254 mmol) was dissolved in 5.00 mL hexanes, forming a light-yellow solution. The solutions were combined while stirring. Within 1 min this produced a salmon colored solution. The reaction color became more saturated over the next 10 min. No more changes were observed after an additional 30 min after which the reaction mixture was stored at -28°C. After 15 min at -28°C, a small amount of red solids had precipitated. Returning the reaction mixture to room temperature caused more solids to precipitate. Solvent was slowly removed from the reaction mixture via a vacuum to give 0.216 g of red solids. The solids did not readily decompose upon exposure to the atmosphere.

Reaction of Benzhydryl Chloride (BzhCl) and Si₆Cl₁₂ in DCM

BzhCl and Si₆Cl₁₂ were reacted in DCM to see if [Bzh⁺]₂[Si₆Cl₁₄²⁻] could be prepared. BzhCl (48.74 mg, 0.2405 mmol) was added to a solution of Si₆Cl₁₂ (51.52 mg, 0.0867 mmol) in 0.5 mL DCM. Over the next 40 min the reaction mixture changed from a yellow solution to a dark brown solution. The reaction turned green over the next 24 h. No solids precipitated after 24 h storage at -28°C. The solvent was removed via a vacuum producing a viscous, dark green solution.

Reaction of Triphenylbromomethane (TrBr) and Si₆Br₁₂ in DCM

TrBr and Si₆Br₁₂ were reacted in DCM to determine if [Tr⁺]₂[Si₆Br₁₄²⁻] could be prepared. Si₆Br₁₂ (20.20 mg, 0.0180 mmol) was dissolved in 1.00 mL DCM. TrBr (11.86 mg, 0.0367 mmol) was dissolved in 0.500 mL DCM. Dropwise addition of the TrBr solution to the Si₆Br₁₂ solution initially resulted in the formation of a yellow solution. Further addition caused orange solids to precipitate while changing the mother liquor to orange. The mixture was filtered after <5 min

stirring, washed 4x with 1.5 mL DCM and dried under vacuum for 30 min, giving 26.31 mg of orange solids. Raman data showed the totally symmetric Si-Si stretching mode shifting from 185 cm^{-1} for $\text{Si}_6\text{Br}_{12}$ to 173 cm^{-1} for the isolated solid indicating that the $[\text{Si}_6\text{Br}_{14}^{2-}]$ dianion was in the product (figure S3). FTIR data for the product showed the presence of the $[\text{Tr}^+]$ (table S1), further indicating that its composition is the intended $[\text{Tr}^+]_2[\text{Si}_6\text{Br}_{14}^{2-}]$.

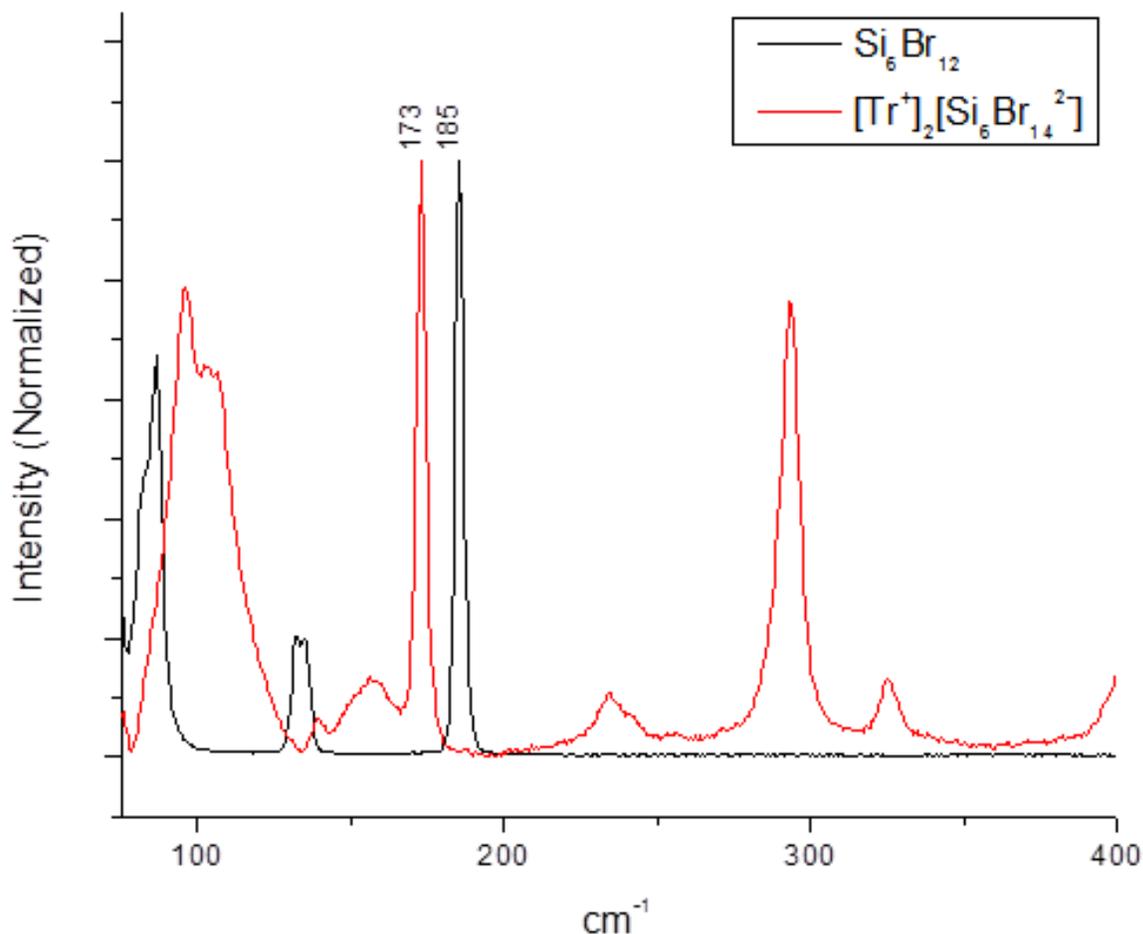


Figure S3: Raman data for $\text{Si}_6\text{Br}_{12}$ (black) and product of $\text{TrBr} + \text{Si}_6\text{Br}_{12}$ (red).

Attempted Preparation of Diffrangible $[\text{Tr}^+]_2[\text{Si}_6\text{Br}_{14}^{2-}]$ Crystals

A reaction was attempted to produce diffrangible $[\text{Tr}^+]_2[\text{Si}_6\text{Br}_{14}^{2-}]$ crystals in the same manner as that of $[\text{Tr}^+]_2[\text{Si}_6\text{Cl}_{14}^{2-}]$. Unfortunately, the addition of succinonitrile did not adequately slow the reaction of TrBr and $\text{Si}_6\text{Br}_{12}$ so a X-ray structure has not been obtained.

$\text{Si}_6\text{Br}_{12}$ (0.051 g, 0.045 mmol) was dissolved in 4.00 mL DCE, forming a light-yellow solution. TrBr (0.029 g, 0.090 mmol) was dissolved in 4.00 mL DCE, forming a light-yellow solution. $\text{C}_2\text{H}_4(\text{CN})_2$ (0.352 g, 4.40 mmol) was dissolved in 10.00 mL DCE, forming a colorless solution. The $\text{Si}_6\text{Br}_{12}$ and $\text{C}_2\text{H}_4(\text{CN})_2$ solutions were heated to 80°C and combined, instantly creating a yellow solution which became colorless within 5 min. The solution was returned to room temperature with no changes.

The TrBr solution was added to the $\text{C}_2\text{H}_4(\text{CN})_2/\text{Si}_6\text{Br}_{12}$ solution over 2 h. Addition of the TrBr solution caused the reaction solution to become yellow until approximately one half of the reagent was added at which point addition caused precipitation of orange solids. The mother liquor gradually changed from yellow to orange during the addition. The reaction mixture was undisturbed for 20 h with no observable change. The mother liquor was decanted, and the solids washed 2x with 2.00 mL DCE. The product was subsequently stored under high viscosity oil until X-ray characterization. The solid material had the appearance of clustered crystals under an optical microscope but XRD analysis of the sample was unsuccessful.

Comparison of $[\text{Tr}^+]_2[\text{Si}_6\text{Cl}_{14}^{2-}]$ Ion Properties with Other Experimental Examples

Table S3. Geometric parameters of $[\text{Si}_6\text{Cl}_{14}^{2-}]$ from experimental examples.

Compound	R.M.S ^(a)	$d_{\text{avg}}(\text{Si-Si})$	$d_{\text{avg}}(\text{Si-Cl}_{\text{eq}})$	$d(\text{Centroid-Cl}_{\text{ax}})$	$d_{\text{avg}}(\text{Si-Cl}_{\text{ax}})$
$[\text{Ph}_4\text{P}]_2[\text{Si}_6\text{Cl}_{14}]^6$	0.000	2.325	2.090	1.923	3.02
$[\text{EDIPA-H}]_2[\text{Si}_6\text{Cl}_{14}]^{(b) 6}$	0.002	2.339	2.077	1.957	3.05
$[\text{Ph}_4\text{P}]_2[\text{Si}_6\text{Cl}_{14}]^8$	0.003	2.314	2.082	1.904	2.997
$[\text{EDIPA-H}]_2[\text{Si}_6\text{Cl}_{14}]^{(c) 6}$	0.003	2.330	2.069	1.997	3.07
$[\text{nBu}_4\text{N}]_2[\text{Si}_6\text{Cl}_{12} \cdot 2\text{AlCl}_4]^{4b}$	0.003	2.367	2.052	2.233	3.25
$[\text{Et}_4\text{N}]_2[\text{Si}_6\text{Cl}_{14}]^9$	0.007	2.321	2.079	1.867	2.98
$[\text{R}]_2[\text{Si}_6\text{Cl}_{14}]^{(d) 10}$	0.007	2.322	2.075	1.930	3.02
$[\text{PEDETA-H}_2\text{SiCl}]_2[\text{Si}_6\text{Cl}_{14}]^{11}$	0.031	2.320	2.078	1.904	3.00
$[\text{Ph}_3\text{BnP}]_2[\text{Si}_6\text{Cl}_{14}]^9$	0.041	2.321	2.079	1.905	3.00
$[\text{nBu}_4\text{N}][\text{nBu}_3\text{Me}][\text{Si}_6\text{Cl}_{14}]^9$	0.047	2.326	2.077	1.894	3.00
	0.015	2.321	2.079	1.914	3.01
$[\text{Ph}_3\text{C}]_2[\text{Si}_6\text{Cl}_{14}]$	0.066	2.325	2.082	1.917	3.01

^(a) Root mean square deviation of ring ^(b) P 2₁/n space group ^(c) $\overline{\text{R } 3}$ space group ^(d) R = 2-(dimethylamino)-N, N, N-trimethylethanaminium.

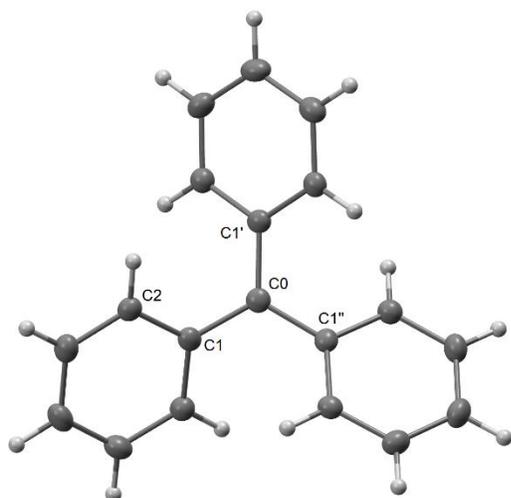


Figure S4. Structure of $[\text{Tr}^+]$ from $[\text{Tr}^+]_2[\text{Si}_6\text{Cl}_{14}^{2-}]$. Carbon labels added for defining geometric parameters of triphenyl carbenium ions in table S4.

Table S4. Geometric parameters of triphenyl carbenium ion from experimental examples.

Compound	d(C0-C1) ^(a)	$\Sigma\angle\text{C0}^{(b)}$	d(C0-plane) ^(c)	$\alpha^{(d)}$
[Ph ₃ C][GaCl ₄] ¹²	1.444	360.0	0.0003	32.3
	1.442	360.0	0.0001	32.0
[Ph ₃ C][AlCl ₄] ¹²	1.443	360.1	0.0005	32.3
	1.443	360.2	0.0001	32.1
[Ph ₃ C][BCl ₄] ¹²	1.443	360.2	0.0005	34.2
[Ph ₃ C] ₂ [AsF ₆] ¹²	1.445	360.1	0.0120	35.7
[Ph ₃ C] ₂ [SbF ₆] ¹²	1.445	360.2	0.0150	28.6
[Ph ₃ C] ₂ [PF ₆] ¹²	1.447	360.1	0.0160	31.9
[Ph ₃ C] ₂ [Si ₆ Cl ₁₄]	1.447	359.7	0.0470	30.3

^(a) Distance between atoms C0 and C1 (figure S4) ^(b) Sum of bond angles around C0 (figure S4) ^(c) Distance between C0 and plane composed of C1, C1' and C1'' (figure S4) ^(d) Dihedral angle between C1'-C0-C1-C2 (figure S4).

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