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Preparation and Reactivity of Arylcyclopolysilanes

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The relative rate and extent of Si–Si bond cleavage by Li for octaphenylcyclotetrasilane and octa(*p*-tolyl)cyclotetrasilane were determined. In the case of the latter, cleavage of more than one Si–Si bond readily takes place. A new method for the synthesis of perarylcyclopentasilane is presented involving reaction of α,ω-dilithioperarylpolysilanes with K_2PtCl_4. The relative order of stability of permethyl-, perphenyl-, and per-*p*-tolylcyclopentasilanes, toward ring cleavage by alkali metals, is discussed in terms of aryl–silicon π bonding.

Introduction

The synthesis and characterization of deca(*p*-tolyl)cyclopentasilane is a problem which has existed in the literature for many years. Originally, Kipping and Sands reported that treatment of diphenyldichlorosilane with sodium affords "compounds A, B, and C" and characterized A to be the diradical $\cdot Si(C_6H_5)_2[Si(C_6H_5]_2Si(C_6H_5)_2\cdot$ whereas B was thought to be $Si_4[C_6H_5]_8$.[2] Several years later Kipping carried out the analogous reaction between dichlorodi(*p*-tolyl)silane and sodium and characterized the respective products as the analogous *p*-tolyl diradical and cyclotetrasilane derivatives.[3] Subsequently Gilman and co-workers conducted a series of investigations on the products derived from the reactions of alkali metals with dichlorodiphenylsilane. They found that Kipping and Sand's compound A failed to exhibit an ESR signal and that many of the characterized reaction products could be explained in terms of ring cleavage; e.g., reactions with HCl, HBr, I_2, Br_2, and $C_2H_4Cl_4$ afforded α(H),ω(halo)- or dihalooctaaryltetrasilane.[4] Accordingly, Gilman concluded that compound A, previously designated the diradical octaphenyltetrasilane, was in fact octaphenyl*cyclo*tetrasilane. Also, on the basis of characterization of reaction products, compound B was found to be decaphenylcyclopentasilane as opposed to octaphenylcyclotetrasilane.[5] By analogy Gilman further reasoned that the products in the per(*p*-tolyl) case likewise must have been octa(*p*-tolyl)cyclotetrasilane and deca(*p*-tolyl)cyclopentasilane.[6] Contrary to this suggestion we have not been able to obtain deca(*p*-tolyl)cyclopentasilane by the reported method[3] but have obtained this species by reaction of α,ω-dilithioper-*p*-tolylpolysilanes with K_2PtCl_4.

Experimental Section

Equipment. Chemical reactions and procedures were followed as previously described while molecular weight determinations were carried out with a Model 301A vapor pressure osmometer manufactured by Mechrolab Inc.[7] Individual samples were dissolved in benzene or chloroform, and results were obtained from a calibration curve determined from standard solutions of benzil ($C_6H_5COCOC_6H_5$, mol wt 210.2) dissolved in the respective solvents. Melting points were determined on a Mel-Temp melting point apparatus equipped with a 0–500 °C range thermometer. Samples were placed in Kimax-51 capillary tubes (1.6–1.8 × 100 mm) manufactured by Kimble Products.

Analyses. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y., and Galbraith Laboratories, Knoxville, Tenn. Silyllithium solutions were analyzed for percent lithium according to a method reported by Gilman and Cartledge.[8]

Chemicals. Acetonitrile, Certified ACS, Fisher Scientific Co., was dried over Linde 4A molecular sieves. **Benzene**, Certified ACS, Fisher Scientific Co., was dried over lithium aluminum hydride. **Chlorobenzene**, Certified, Fisher Scientific Co., was dried over calcium hydride. **Chloroform**, Certified ACS, Fisher Scientific Co., was dried over calcium hydride and stored over Linde 4A molecular sieves. **Cyclohexane**, Matheson Coleman and Bell, was dried over lithium aluminum hydride and stored over Linde 4A molecular sieves. **Dichlorodiphenylsilane**, PCR, Inc., was used as received. **Lithium**, wire, $^1/_8$-in. diameter, Research Organic/Inorganic Chemical Corp., was used as received. **Tetrahydrofuran**, Certified, Fisher Scientific Co., was dried over lithium aluminum hydride. **Hexachloroplatinic acid**, H_2PtCl_6, was prepared from platinum wire and aqua regia. **Potassium hexachloroplatinate**, K_2PtCl_6, was prepared from H_2PtCl_6 as described in the literature.[9] **Potassium tetrachloroplatinate**, K_2PtCl_4, was prepared as described in the literature.[9]

Octaphenylcyclotetrasilane, $Si_4(C_6H_5)_8$, was prepared from dichlorodiphenylsilane and lithium as previously described in the literature.[10] After purification by Soxhlet extraction with hot toluene, a melting point range of 319–322 °C was obtained (lit. mp 321–323 °C). Anal. Calcd: C, 79.1; H, 5.5; Si, 15.5. Found: C, 79.0; H, 5.5; Si (by difference), 15.5. Infrared data: 3060 (w), 1960 (vw, b), 1880 (vw, b), 1815 (vw, b), 1585 (w), 1486 (m), 1430 (s), 1303 (w), 1260 (w), 1190 (w), 1160 (w), 1094 (s), 1025 (w), 998 (m), 970 (vw), 910 (vw), 845 (vw), 735 (vs), 700 (vs), 695 (vs, sh), 684 (m), 678 (m, sh), 618 (vw), 531 (m), 480 (s), 469 (s), 458 (w, sh), 445 (m), 425 (m), 420 (m), and 330 (vs) cm^{-1}.

1,4-Dilithiooctaphenyltetrasilane, 1,4-$Li_2Si_4(C_6H_5)_8$, was prepared from octaphenylcyclotetrasilane and lithium as previously described in the literature.[10] The progress of the reaction could be determined according to the method described for the analysis of organolithium compounds.[8] Because no method for isolating 1,4-$Li_2Si_4(C_6H_5)_8$ has been reported, this product may only be characterized by its reaction products.[11] (A short communication by Hengge and Wolfer reports the isolation of $(C_6H_5)_8Si_4Li_2\cdot 2THF$ as a yellow-red crystalline solid; however, experimental details have not been reported.[12])

Decaphenylcyclopentasilane. Small-scale syntheses of $Si_5(C_6H_5)_{10}$ were performed as previously described utilizing 1,4-dilithiooctaphenyltetrasilane and dichlorodiphenylsilane.[11] Purification was effected by fractional crystallization with hexane from a benzene solution; mp 462–466 °C (lit. mp 466–470 °C). For larger scale syntheses, a somewhat less pure product may be obtained by modifying the reaction used in the synthesis of octaphenylcyclotetrasilane. To 300 ml of dry tetrahydrofuran under nitrogen, 8.0 g (1.1 mol) of clean, finely cut lithium wire was added. Next 126 g (0.5 mol) of diphenyldichlorosilane was added dropwise with constant stirring. After the addition was complete the mixture was allowed to stir vigorously under reflux for 40 h, affording a dark brown mixture which was subsequently filtered in air and purified in a manner analogous to that described by Gilman for $Si_5(C_6H_5)_{10}$.[13] After recrystallization from a benzene–hexane mixture 45 g (50%) of the pentamer was obtained; mp 451–456 °C. The infrared spectrum of $Si_5(C_6H_5)_{10}$ contains absorptions at 3040 (w), 1955 (w, b), 1885 (w, b), 1815 (w, b), 1770 (vw, b), 1650 (vw, b), 1580 (vw), 1565 (vw), 1480 (m), 1430 (s), 1305 (w), 1262 (w), 1192 (w), 1155 (w), 1092 (s), 1025 (w), 1000 (w), 972 (w), 915 (vw), 890 (vw), 850 (w), 735 (vs), 725 (m, sh), 699 (vw), 515 (w), 484 (s), 472 (s), 442 (w, sh), 434 (w, sh), 412 (m), 377 (m), 345 (s), 335 (m, sh), 331 (m, sh), and 325 (s) cm^{-1}.

1,5-Dilithiodecaphenylpentasilane. 1,5-$Li_2Si_5(C_6H_5)_{10}$ was prepared from decaphenylcyclopentasilane and lithium as previously described in the literature.[13] The course of the reaction could be followed in a manner analogous to that for 1,4-$Li_2Si_4(C_6H_5)_8$.

Dichloro(*p*-tolyl)silane. $Si(p\text{-}CH_3C_6H_4)_2Cl_2$ was prepared from the reaction of $SiCl_4$ with $(p\text{-}CH_3C_6H_4)MgBr$ as described in the literature.[14] The product was purified by distillation; bp 225 °C (50 mm) (lit. bp 225–226 °C (50 mm)).

Octa(*p*-tolyl)cyclotetrasilane. $Si_4(p\text{-}CH_3C_6H_4)_8$ was originally prepared by Steele and Kipping but mistakenly characterized at that time as the diradical octa(*p*-tolyl)tetrasilane.[14] With this in mind, the original synthesis was followed, with subsequent purification effected by recrystallization from benzene; mp 287–292 °C dec (lit.

mp 290–293 °C dec); yield 20%. Anal. Calcd: C, 80.0; H, 6.7; Si, 13.3; mol wt 840. Found: C, 79.4; H, 6.7; Si, 13.9 (by difference); mol wt 833. Infrared data: 3060 (w), 1595 (m), 1495 (m), 1390 (m), 1313 (m), 1255 (w), 1190 (m), 1095 (s), 1040 (w), 1021 (m), 850 (w), 800 (vs), 728 (w), 711 (m), 695 (vw), 639 (w), 624 (s), 614 (s), 495 (vs), 473 (m), 402 (w), 387 (m), 370 (m), and 329 (m) cm^{-1}.

Reaction of Octa(*p*-tolyl)cyclotetrasilane with Lithium. In a drybox a reaction bulb was charged with a known amount of $Si_4(p\text{-}CH_3C_6H_4)_8$, an excess of clean, finely cut lithium wire ($^1/_8$-in. diameter), and a Teflon spin-bar. This reaction vessel was attached to a vacuum line by means of a three-way adapter to which a tip bulb containing dry THF had been connected. The entire system was evacuated and THF added with stirring; within 10 s yellow coloration could be detected which rapidly became dark red. The extent of reaction was determined by the literature method.[8]

Attempted Reaction of the Octa(*p*-tolyl)cyclotetrasilane. Lithium Cleavage Product with Dichlorodi(*p*-tolyl)silane. $Si(p\text{-}CH_3C_6H_4)_2Cl_2$ was treated with the product obtained from the lithium cleavage of $Si_4(p\text{-}CH_3C_6H_4)_8$ in a manner analogous to that reported for the reaction of 1,4-$Li_2Si_4(C_6H_5)_8$ and $Si(C_6H_5)_2Cl_2$.[11] The only silane product obtained was a viscous yellow oil which could not be crystallized even when treated with acetonitrile or hydrocarbon solvents such as pentane or hexane.

Reaction of Potassium Tetrachloroplatinate with 1,4-Dilithiooctaphenyltetrasilane. K_2PtCl_4, 250 mg (0.60 mmol), was added to a stirred THF solution of 1,4-dilithiooctaphenyltetrasilane, 250 mg (0.45 mmol). After 4 h the original dark red color of the silyllithium solution appeared to have become darker and after 12 h the color was distinctly dark brown. After 36 h of reaction the THF was removed by distillation and insoluble alkali metal chlorides and K_2PtCl_4 were removed by filtration with benzene. The volume of the filtrate was reduced to ca. 3 ml and hexane added dropwise with stirring until a gray metallic solid separated. The mixture was filtered and the solid determined to be metallic platinum by its reaction with aqua regia to yield H_2PtCl_6. The filtrate was concentrated to ca. 2 ml and addition of hexane resulted in the precipitation of 85 mg (26%) of decaphenylcyclopentasilane which was identified by its melting point (465–470 °C; lit. mp 466–470 °C)[11] and a comparison of its ir spectrum with that of an authentic sample.

Reaction of Potassium Tetrachloroplatinate with 1,5-Dilithiodecaphenylpentasilane. This reaction was carried out in a manner analogous to that of the K_2PtCl_4 reaction with 1,4-dilithiooctaphenyltetrasilane. K_2PtCl_4, 230 mg (0.55 mmol), was added to a THF equimolar solution of 1,5-$Li_2Si(C_6H_5)_{10}$. The stirred solution was allowed to react for 24 h after which the dark brown mixture showed no further change. After the indicated workup a yield of 150 mg (30%) of decaphenylcyclopentasilane was obtained and characterized by its melting point and ir spectrum. Platinum metal and a mixture of alkali metal chlorides were also isolated.

Deca(*p*-tolyl)cyclopentasilane. Octa(*p*-tolyl)cyclotetrasilane, 1.00 g, was treated with lithium for 2 h as previously described. After filtration, 500 mg of K_2PtCl_4 was added to the silyllithium species and the contents of the flask stirred under an inert atmosphere. After 8 h the reaction mixture appeared dark brown, THF was removed by distillation, and 10 ml of benzene was added to the reaction mixture. This mixture was stirred in air for an additional 30 min and filtered to remove the insoluble lithium chloride, potassium chloride, and platinum metal. The yellow benzene filtrate was concentrated to about 2 ml and acetonitrile added, resulting in the precipitation of deca(*p*-tolyl)cyclopentasilane. Further purification was effected by fractional crystallization with benzene–acetonitrile. The total yield was 340 mg (34%); mp 308–309 °C (sealed tube). Anal. Calcd: C, 80.0; H, 6.7; Si, 13.3; mol wt 1050. Found: C, 79.4; H, 6.7; Si (by difference) 13.9; mol wt 1060. Infrared data: 3060 (w), 1598 (m), 1495 (m), 1488 (m, sh), 1421 (vw), 1390 (m), 1310 (m), 1191 (s), 1090 (s), 1040 (w), 1020 (m), 800 (vw), 737 (vw, sh), 728 (vw, sh), 722 (w), 713 (m), 675 (w), 640 (w), 620 (m), 615 (m, sh), 610 (m, sh), 503 (vw), 485 (m, sh), 478 (w, sh), 392 (m), 375 (m), 368 (m), 358 (w, sh), 352 (w, sh), and 329 (m), cm^{-1}.

Reaction of 1,4-Dilithiooctaphenyltetrasilane with Chlorobenzene. A stirred THF solution containing 1.3 mmol of 1,4-dilithiooctaphenyltetrasilane was treated with 1.00 ml of chlorobenzene. After 30 min the dark red color of the original solution appeared less intense. The reaction was allowed to proceed for 12 h after which the cloudy solution was pale yellow. THF was distilled from the reaction vessel under reduced pressure. Chloroform was added and LiCl removed from the soluble fraction by filtration. The chloroform filtrate was reduced in volume to ca. 1 ml and decaphenylcyclopentasilane precipitated on addition of hexane; its melting point and ir spectrum were identical with those of an authentic sample. The yield was 107 mg (11%). After removal of the pentamer by filtration, the filtrate was reduced in volume (ca. 1 ml) and hydrolyzed with water. A vapor-phase ir spectrum of a gas, isolated via high-vacuum fractional condensation, indicated the presence of benzene while the aqueous solution was determined to be basic.

Attempted Reaction of 1,4-Dilithiooctaphenyltetrasilane with Platinum Metal. Platinum black, 100 mg, was added to a THF solution of 1,4-$Li_2Si_4(C_6H_5)_8$, 1.3 mmol, and stirred for 12 h at 25 °C. No change in the appearance of the dark red solution was noted. The solution was filtered under inert atmosphere and the filtrate diluted to a known volume. Titration of a hydrolyzed aliquot indicated no change in the silyllithium content.

Reaction of 1,4-Dilithiooctaphenyltetrasilane with Chlorobenzene and Platinum Metal. The procedure for the reaction of 1,4-dilithiooctaphenyltetrasilane with chlorobenzene was followed except platinum black, 100 mg, was added to the silyllithium solution before the chlorobenzene. The reaction was again allowed to proceed for 12 h. Following the previously described workup, the yield of $Si_5(C_6H_5)_{10}$ was 170 mg (18%) and 95% of the original platinum was recovered.

Discussion

Arylcyclosilane Formation and Cleavage. We have attempted, without success, to prepare deca(*p*-tolyl)cyclopentasilane by the literature method which involves treatment of $Si(p\text{-tol})_2Cl_2$ with Na.[3] Rather than the cyclopentamer, we found the reaction product to consist of a 10% yield of octa(*p*-tolyl)cyclotetrasilane. Gilman reported when he investigated this same reaction, using xylene as the solvent, that no crystalline products could be isolated.[15]

The synthesis of perphenylcyclosilanes may be conveniently achieved by treatment of $(C_6H_5)_2SiCl_2$ with Li to afford octaphenylcyclotetrasilane, $Si_4(C_6H_5)_8$ (I).[10] Subsequent treatment of I with Li, to afford 1,4-dilithiooctaphenyltetrasilane, $Li_2Si_4(C_6H_5)_8$, followed by reaction with additional $(C_6H_5)_2SiCl_2$ affords decaphenylcyclopentasilane, $Si_5(C_6H_5)_{10}$.[11] However, when we carried out the analogous reaction sequence employing $(p\text{-tol})_2SiCl_2$, the corresponding cyclopentasilane did not result although octa(*p*-tolyl)cyclotetrasilane was isolated.

Because the reaction between lithium and the cyclotetrasilanes, per-*p*-tolyl and perphenyl, appeared much faster with the *p*-tolyl derivative, the extent of Si–Si bond cleavage by lithium for both cyclotetrasilane derivatives was investigated.

Reactions of Perarylcyclotetrasilane with Lithium. One may determine the extent of Si–Si bond cleavage as a consequence of reaction with Li by the method previously described.[8] This procedure was followed for both $Si_4(p\text{-tol})_8$ and $Si_4(C_6H_5)_8$ as a function of reaction time with Li, Figure 1. As indicated, the reaction of $Si_4(C_6H_5)_8$, to afford 1,4-$Li_2Si_4(C_6H_5)_8$, proceeds at a moderate rate with reaction essentially complete after 1.5 h. However, if further contact between the product and Li takes place, additional cleavage of the silicon chain results with an accompanying decreased yield of the desired product.

The reactivity of $Si_4(p\text{-tol})_8$ is much greater than that of the phenyl analogue in that after 30 s the reaction product(s) contain 150% of the Li content expected for 1,4-$Li_2Si_2(p\text{-tol})_8$; i.e., additional Si–Si bond cleavage has taken place. Therefore it is not surprising that treatment of this silyllithium product mixture with $(p\text{-tol})_2SiCl_2$ does not afford the deca(*p*-tolyl)cyclopentasilane. Isolation of the $Si_4(p\text{-tol})_8$ was achieved and is now understood based on the presence and subsequent reaction of 1,3-$Li_2Si_3(p\text{-tol})_4$ with $(p\text{-tol})_2SiCl_2$.

Silane Ring Closure with K_2PtCl_4. As part of an investigation involving cyclometallosilanes it was discovered that treatment of both 1,4-$Li_2Si_4(C_6H_5)_8$ and 1,3-$Li_2Si_5(C_6H_5)_{10}$

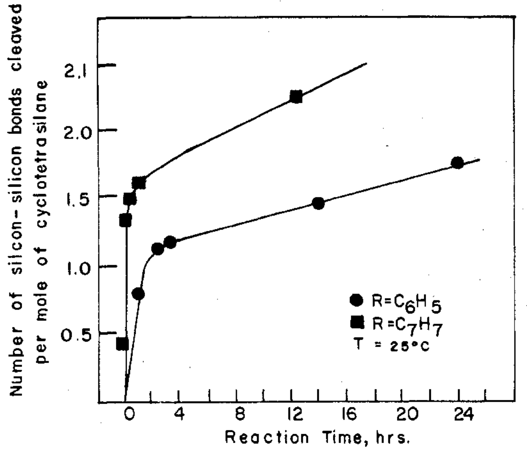


Figure 1. Relative rates of Si–Si bond cleavage of perarylcyclotetrasilanes by Li.

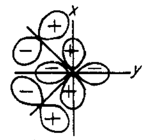
with K_2PtCl_4 affords decaphenylcyclopentasilane, $Si_5(C_6H_5)_{10}$.[16] Most likely K_2PtCl_4 functions as a lithium sink ultimately affording LiCl and the thermodynamically favored five-membered cyclosilane. Consistent with this function of K_2PtCl_4 is the fact that the pentacyclosilane formation was also achieved by treatment of 1,4-$Li_2Si_4(C_6H_5)_8$ with chlorobenzene. Platinum black was found to increase the yield of this latter reaction although platinum black had no effect in the absence of C_6H_5Cl. As previously noted, the reaction of octa(*p*-tolyl)cyclotetrasilane, Si_4(*p*-tol)$_8$, with Li results in multiple Si–Si bond cleavage. However, treatment of this mixture of silyllithio species with K_2PtCl_4 results in a 34% yield of deca(*p*-tolyl)cyclopentasilane. When a similar reaction sequence was carried out, starting with deca(*p*-tolyl)cyclopentasilane, no cyclohexasilane was isolated but rather a 30% "yield" of starting material was isolated. As in the case of the perphenylcyclosilanes, it appears that the per-*p*-tolylcyclosilane five-membered rings are favored in the reactions with K_2PtCl_4. However, in contrast to the perphenylcyclotetrasilane system, per-*p*-tolylcyclotetrasilane rapidly forms smaller dilithio chains, e.g., 1,3-Li_2Si_3(*p*-tol)$_6$, when treated with lithium. It appears likely that cyclosilane formation with K_2PtCl_4 involves the latter functioning not only as a lithium sink but also possibly as a promoter of chain lengthening prior to cyclization to afford the most thermodynamically stable five-membered silane, Si_5(*p*-tol)$_{10}$.

Stability of Cyclosilanes toward Ring Cleavage by Alkali Metals. Treatment of decamethylcyclopentasilane, $Si_5(CH_3)_{10}$, and dodecamethylcyclohexasilane, $Si_6(CH_3)_{12}$, with alkali metals in ether affords the corresponding radical anions with the stability of the five-membered radical greater than that of the six-membered ring.[17] Electron delocalization was established based on an ESR study with conjugated Si d orbitals suggested to be involved in electrodelocalization. This latter postulate is in agreement with ultraviolet absorption spectra associated with various cyclic and linear polysilanes which can be interpreted to indicate that conjugated vacant Si d orbitals comprise a low-lying excited state.[17,18]

In contrast to the reaction of permethylcyclosilanes forming radical ions, perphenyl- and per-*p*-tolylcyclosilanes undergo ring cleavage. If the inductive effect of the silicon substituent was of primary importance in stabilizing the respective radical anions, then one would expect the relative order of stabilities $C_6H_5 > CH_3C_6H_4 > CH_3$. The relative stability of the cyclopentasilane derivatives toward ring cleavage is found to be $CH_3 \gg C_6H_5 > CH_3C_6H_4$. This order may be explained when one considers the interaction of π-electron density, associated with the substituent, with vacant silicon d orbitals.

Due to the larger size of Si, as compared to C, a five-membered Si ring is planar assuming tetrahedral Si. If one defines the coordinate system, centered on Si, with the y axis coincident with the twofold axis of the five-membered Si ring and the x axis normal to the ring, then the following Si ring MO's may be constructed. Separate combinations of the five Si $3d_{x^2-y^2}$, five Si $3d_{z^2}$, and five Si $3d_{xy}$ orbitals result in three nodeless MO's with respect to ring bonding, whereas each MO comprised of five Si $3d_{yz}$ and five Si $3d_{xz}$ orbitals has one nodal plane.

Orientation of the phenyl moieties, associated with $Si_5(C_6H_5)_{10}$, to achieve minimum steric interaction results in the phenyl plane normal to the x–y plane. This orientation allows, on the basis of symmetry, overlap of aryl π-electron density with the silicon ring via the MO constructed with $d_{x^2-y^2}$ orbitals, i.e.



Utilizing this MO approach, the relative order of electron donation to the Si ring by the Si substituent would be expected to be that found experimentally, $CH_3C_6H_4 > C_6H_4 > CH_3$. It is suggested that aryl-substituted cyclosilanes undergo ring cleavage when treated with Li because there is excess charge on the silane ring (both from Li and the aryl moieties π bonding to the ring) and/or because π interaction of the aryl moieties with the silane ring results in the electron from Li being added to a silane antibonding MO, e.g., the d_{yz} or d_{xz} combinations.

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Registry No. $Si_4(C_6H_5)_8$, 1065-95-8; 1,4-$Li_2Si_4(C_6H_5)_8$, 18826-17-0; $Si_5(C_6H_5)_{10}$, 1770-54-3; 1,5-$Li_2Si_5(C_6H_5)_{10}$, 18827-08-2; Si(*p*-$CH_3C_6H_4)_2Cl_2$, 18414-38-5; Si_4(*p*-$CH_3C_6H_4)_8$, 18825-62-2; Si_5(*p*-$CH_3C_6H_4)_{10}$, 24636-37-1; chlorobenzene, 108-90-7; Li, 7439-93-2; K_2PtCl_4, 10025-99-7.

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