Chemical Science

ROYAL SOCIETY OF CHEMISTRY

EDGE ARTICLE

View Article Online
View Journal | View Issue

Cite this: *Chem. Sci.*, 2022, **13**, 7587

All publication charges for this article have been paid for by the Royal Society of Chemistry

Received 23rd March 2022
Accepted 3rd June 2022

DOI: 10.1039/d2sc01690g

rsc.li/chemical-science

Highly selective addition of cyclosilanes to alkynes enabling new conjugated materials†

Qifeng Jiang, Alexandra F. Gittens, Sydnee Wong, Maxime A. Siegler and Rebekka S. Klausen *

Main group organometallic compounds can exhibit unusual optical properties arising from hybrid σ,π-conjugation. While linear silanes are extensively studied, the shortage of methods for the controlled synthesis of well-defined cyclic materials has precluded the study of cyclic conjugation. Herein we report that Ru-catalyzed addition of cyclosilanes to aryl acetylenes (hydrosilylation) proceeds with high chemoselectivity, regioselectivity, and diastereoselectivity, affording complex organosilanes that absorb visible light. We further show that the hydrosilylation products are useful building blocks towards novel conjugated polymers.

Introduction

We report the synthesis of visible-light absorbing organocyclosilanes *via* Ru-catalyzed chemoselective, regioselective, and diastereoselective hydrosilylation. While extraordinary progress in predicting and controlling selectivity in organic reactions has been made, the development of similar insights for main group molecules is in its infancy. This lack of synthetic control limits the discovery of structure–property relationships in main group materials. For example, while linear oligosilanes (*e.g.*, Ar(SiMe)$_n$Ar) capped with aromatic end groups have been extensively studied for molecular electronics,[1,2] metal–organic framework (MOF) secondary building units,[3] charge transport,[4] photoinduced charge transfer,[5–7] and nonlinear optical properties,[8–10] there has been very limited investigation of cyclic σ,π-conjugation,[11] as cyclosilanes are typically synthesized by methods[12–14] that restrict functional group diversity on an organic fragment. Nonetheless, the well-established conformation-dependence of σ-conjugation[15] strongly suggests that the restricted degrees of freedom in cyclosilanes should give rise to properties distinct from linear oligosilanes.

Our group is interested in the synthesis and properties of (macro)molecular mimics of crystalline silicon and we have described new approaches to the selective synthesis of materials based on cyclohexasilanes. We reported the five-step synthesis and chemoselective polymerization of the cyclohexasilane building blocks **1,4Si$_6$** and **1,3Si$_6$**,[16–21] as well as the seven-step stereocontrolled synthesis of *cis*- and *trans*-**Si$_{10}$H$_4$** (Fig. 1).[22] These works have led to new insights, such as the discovery that the diastereomeric siladecalins have vastly different absorption spectra arising from configuration- and conformation-dependent σ-conjugation.

We envisioned an alternative approach to functionalized cyclosilanes *via* derivatization of the Si–H bond of our building blocks,[23] but confronted several challenges. First, the Me$_3$Si–SiMe$_3$ bond is weaker than a H$_3$C–CH$_3$ bond (BDE: 79 *vs.* 90 kcal mol^{-1})[24] and cross-reactive with reagents for Si–H functionalization; Pd- and Pt-complexes like Karstedt's catalyst fragment Si–Si bonds.[25–27] Second, while the targeted cyclosilanes exhibit *cis*/*trans* diastereoisomerism, Si–C bonds are longer than C–C bonds,[28] potentially diminishing the steric factors often implicated in asymmetric stereoinduction. Third, the tetrafunctional cyclosilanes pose a significant selectivity challenge: the reaction of **1,4Si$_6$** and phenylacetylene could provide more than 40 distinct products arising from mono-, di-, tri-, or tetra-functionalization (*E*)/(*Z*)-geometric isomers, α/β-addition, or *cis*/*trans* diastereoisomerism.

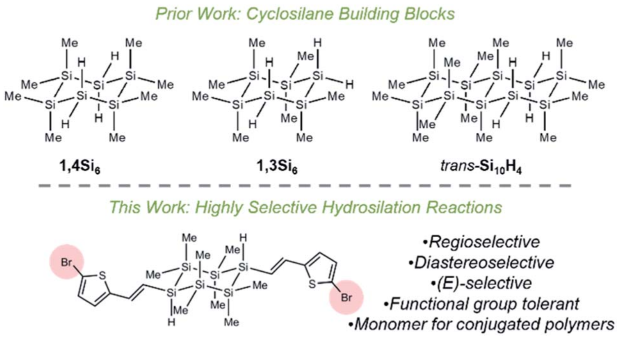


Fig. 1 Highly selective reactions between cyclosilane building blocks and functionalized acetylenes.

Department of Chemistry, Johns Hopkins University, 3400 N. Charles St, Baltimore, MD 21218, USA. E-mail: Klausen@jhu.edu

† Electronic supplementary information (ESI) available. CCDC 2158546–2158549. For ESI and crystallographic data in CIF or other electronic format see **https://doi.org/10.1039/d2sc01690g**

We report herein the extraordinarily selective outcome of the RuHCl(CO)(PPh$_3$)$_3$-catalyzed[29] reaction between cyclosilanes and aryl acetylenes. We observed perfect regioselectivity for 1,4-difunctionalization and β-addition and perfect (*E*)-selectivity. Products were isolated as a single diastereomer or as a mixture (*ca.* 2 : 1) favoring the thermodynamic isomer. The hydrosilylation is highly functional group tolerant: no Si–Si bond cleavage occurred, and functional group tolerance was high. These syntheses enabled a broad probe of the influence of substituent effects, structural isomerism, and configuration on conjugation in organocyclosilanes, which revealed bathochromic shifts relative to starting materials. We also expect the work herein to expand additional frontiers for the study of conjugated materials. As initial examples, we report the synthesis of novel thienyl-silane conjugated polymers derived from a *trans*-1,4-bis(thienylvinyl)cyclosilane copolymerized with other dibromo building blocks. The polymers not only absorb visible light, but are also an entry to stereoregular polysilanes, a class of materials where control of tacticity has been a long-standing challenge.

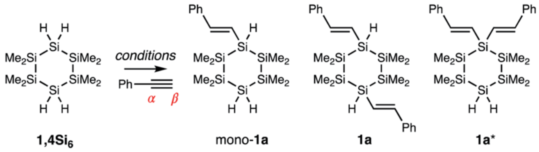
Results and discussion

Investigation of regio- and diastereoselectivity

Hydrosilylation is widely used in the industrial preparation of silicones (*e.g.*, Si–O polymers).[30–33] The application of hydrosilylation to oligo- and polysilanes (*e.g.*, Si–Si polymers) has been of interest since at least the 1960's,[34] but as documented by Rosenberg,[35] free-radical[36–38] and many transition-metal catalyzed[34,39] hydrosilylations are accompanied by partial to extensive Si–Si cleavage. Borane Lewis acids are useful for Si–H/X–H dehydrocoupling and Si–H/X═C hydrosilylation without skeletal fragmentation.[23,40,41] Recently, Kyushin reported Ru-catalyzed (*E*)- or (*Z*)-selective hydrosilylation of alkynes and hydrooligosilanes without Si–Si bond cleavage.[29,42]

We envisioned that (*E*)-selective addition of cyclosilanes to alkynes could yield σ,π-conjugated cyclosilanes. As Kyushin's study focused on linear monohydrosilanes like H–SiMe$_2$SiMe$_2$-Ph, our initial focus was regioselectivity with tetrafunctional **1,4Si$_6$** (Table 1 and Fig. 2a). It was unclear if replacement of one Si–H bond with a vinyl group would enforce selectivity for the 1,1′- or 1,4-functionalized product in the second Si–H replacement. The success of monohydrosilanes suggested the feasibility of fully alkylated Si centers, such as **1a***. A first attempt with 2.50 equivalents of phenylacetylene and 5 mol% RuHCl(CO)(PPh$_3$)$_3$ resulted in mono-**1a** (22%) and 1,4-difunctionalized **1a** (9%), as determined by ^{1}H NMR spectroscopy. No 1,1′-difunctionalized **1a*** was observed. Further optimization of solvent and catalyst loading led to increased conversion to **1a** without residual mono-**1a** (entry 6). 1,1′-Difunctionalization was not observed even with excess phenylacetylene (entry 7). The mechanistic origin of the selectivity for monofunctionalization could have steric or electronic origins, but the mechanism is not yet clear. In all cases, the ^{1}H NMR spectra were consistent with Si-addition to the phenylacetylene β-position (Table 1), as α-addition would result in a 1,1-disubsituted alkene.

Table 1 Optimization of the RuHCl(CO)(PPh$_3$)$_3$-catalyzed reaction between phenylacetylene and **1,4Si$_6$**[a]



Entry	[Catalyst][b]	Solvent	Time	Conversion[c] Mono-**1a**	**1a**	**1a***
1	5 mol%	Toluene	7 d	22%	9%	0%
2[d]	10 mol%	Toluene	24 h	42%	50%	0%
3	5 mol%	DCM	24 h	61%	39%	0%
4	10 mol%	DCM	24 h	17%	83%	0%
5[e]	10 mol%	DCM	24 h	45%	25%	0%
6	20 mol%	DCM	2 h	0%	100%	0%
7[f]	20 mol%	DCM	2 h	0%	100%	0%

[a] The reactions were carried out with 0.171 mmol of **1,4Si$_6$** and 0.428 mmol of phenylacetylene in 1 mL of solvent at room temperature under nitrogen protection unless noted. [b] RuHCl(CO)(PPh$_3$)$_3$ loading was relative to **1,4Si$_6$**. [c] The conversion was determined by ^{1}H NMR spectra of reaction aliquots. [d] The reaction was carried out at 60 °C. [e] The reactions were carried out with 0.171 mmol of **1,4Si$_6$** and 0.171 mmol of phenylacetylene. [f] The reactions were carried out with 0.171 mmol of **1,4Si$_6$** and 1.026 mmol of phenylacetylene.

Having established regioselectivity, we investigated (*E*)-selectivity and diastereoselectivity under the optimized conditions. **1a** was isolated in 89% yield as a 65 : 35 mixture of two isomeric products, assigned to the *trans* and *cis* diastereomers (Fig. 2a). The isomers were not separable by silica gel chromatography, but recrystallization afforded pure *trans*-**1a** (X-ray crystal structure, Fig. 2b), which was confirmed as the major diastereomer. The X-ray crystal structure also confirmed that hydrosilylation proceeded without skeletal rearrangement and with (*E*)- and β-selectivity. In the solid state, *trans*-**1a** adopted a chair conformation with both styryl groups at equatorial positions. This was the expected thermodynamic isomer, in which 1,3-diaxial interactions were minimized.

The recrystallization filtrate was enriched in the minor product, which was assigned to *cis*-**1a** based on symmetry consistent with 1,4-difunctionalization. The *ca.* 1 : 3 *trans* : *cis* ratio was stable over time but could not be further increased by silica gel column chromatography. The coupling constants of the vinylic peak *a*/*a*′ (d, $J = 18.7$ Hz, Fig. 2c) and *b*/*b*′ (dd, $J = 5.2$, 18.7 Hz) were consistent with an (*E*)-alkene. ^{1}H–^{29}Si HSQC and ^{29}Si INEPT + spectroscopy (Fig. S and S2†) allowed assignment of the *Si*Me$_2$ and *Si*H resonances (Fig. 2d).

Substrate scope

Having established selectivity with **1,4Si$_6$**, we investigated substrate scope (Fig. 3). With a variety of 4-substituted phenylacetylenes, 1,4-bis(styryl)cyclohexasilanes were obtained in high isolated yield and without erosion in regio- or diastereoselectivity, as shown by X-ray crystallography (Fig. S3†). This

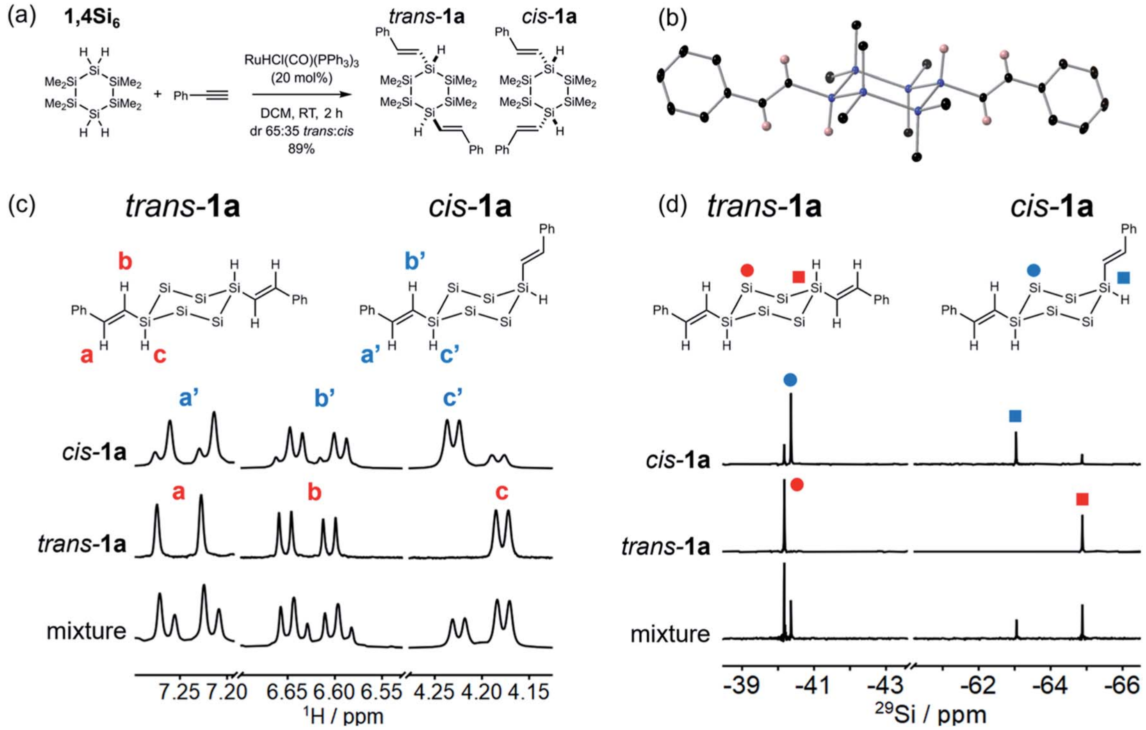


Fig. 2 (a) Synthesis of *trans* and *cis*-**1a** *via* hydrosilylation of phenylacetylene with **1,4Si$_6$** catalyzed by RuHCl(CO)(PPh$_3$)$_3$. (b) Displacement ellipsoid plot (30% probability level) of *trans*-**1a** at 110(2) K. Blue = Si, black = C, pink = H. Hydrogens on methyl and phenyl groups were omitted for clarity. Ellipsoids 30% probability. (c) Cropped ^{1}H NMR spectra (400 MHz, C$_6$D$_6$) comparing (top to bottom) *cis*-**1a** (dr 25 : 75 *trans* : *cis*), *trans*-**1a**, and the as-isolated mixture of isomers. (d) Cropped ^{29}Si {^{1}H} DEPT spectra (79 MHz, C$_6$D$_6$) comparing (top to bottom) *cis*-**1a** (dr 25 : 75 *trans* : *cis*), *trans*-**1a**, and the as-isolated mixture of isomers. DEPT = distortionless enhancement by polarization transfer. The methyl groups are omitted for clarity.

provided σ,π-hybrids functionalized with halogens (**1b–c**), electron donating groups (**1d–f**) and moderately electron withdrawing groups (**1g–h**).

The functional groups selected for investigation in Fig. 3 were chosen on the basis of potential applications. Sulfur was tolerated in thiomethyl **1d** and thienyl **1i–j**, of relevance to molecular electronics.[43] Functional groups that would not be tolerated by the reductive coupling methods traditionally used to prepare cyclosilanes from dihalosilanes were also successfully incorporated, such as methyl ester **1h.** Benzoate esters are useful intermediates to a variety of other oxygenated functionality, such as carboxylic acids that have been employed as MOF ligands.[3] In addition, halogenated products (*e.g.*, **1b** and **1j**) are suitable for catalytic cross-coupling (*vide infra*). Low conversion was observed with strongly electron-withdrawing substituents (*e.g.*, 4-nitro and 4-cyanophenylacetylene) and an electron-poor heterocycle (4-ethynylpyridine).

We also explored the cyclosilane scope. Regioselectivity was maintained (Fig. 3), yielding 1,3- or 1,4-difunctionalized products instead of 1,1′-difunctionalized cyclosilanes. No skeletal decomposition was observed and perfect (*E*)- and β-selectivities were retained. Interestingly, *cis*-**Si$_{10}$H$_4$** underwent slow reaction with phenylacetylene (<5% conversion in 24 hours).

The cyclosilane exerted a striking effect on diastereoselectivity. While diastereomeric ratios (dr) *ca.* 2 : 1 were observed for all **1,4Si$_6$**-derived products, the dr decreased to *ca.* 1 : 1 for **1,3Si$_6$** and increased dramatically for *trans*-**Si$_{10}$H$_4$**, where only one diastereomer could be detected by ^{1}H NMR spectroscopy (Fig. S4†). An X-ray crystal structure of **3a** confirmed assignment to the *trans* diastereomer (Fig. 4) with diequatorial styryl groups. Like *trans*-decalin, *trans*-**Si$_{10}$H$_4$** is conformationally locked,[22] suggesting that hydrosilylation is selective for the equatorial Si–H bond. The reduced diastereoselectivity with **1,3Si$_6$** and **1,4Si$_6$** was attributed to rapid ring inversion[44–46] in a mono-functionalized intermediate (Fig. 5). Therefore, we expect that the equilibrium between equatorial and axial conformers in mono-functionalized intermediates should determine the dr in difunctionalized products.

UV-vis absorbance spectra

We obtained UV-vis spectra of the bis(styryl)cyclosilanes. Comparison of *trans*-**1a** to starting materials showed a 50- to 100 nm red-shift relative to purely π- or σ-conjugated materials (Fig. 6a). DFT calculations showed that the *trans*-**1a** HOMO was delocalized across the entire molecule (Fig. S5†). We also compared the UV-vis spectra of *trans*- and *cis*-**1a**, finding that relative configuration did not strongly influence absorbance in solution (Fig. 6b). This observation facilitated comparison of all three cyclosilanes (Fig. 6c). While 1,4- and 1,3-difunctionalized **1a** and **2a** were similar in onset of absorption, siladecalin-derived **3a** was red-shifted by *ca.* 30 nm. We also noted the bathochromic influence of thienyl relative to phenyl substitution (Fig. 6d). Additional UV-spectra for selected compounds can be found in the ESI (Fig. S6†).

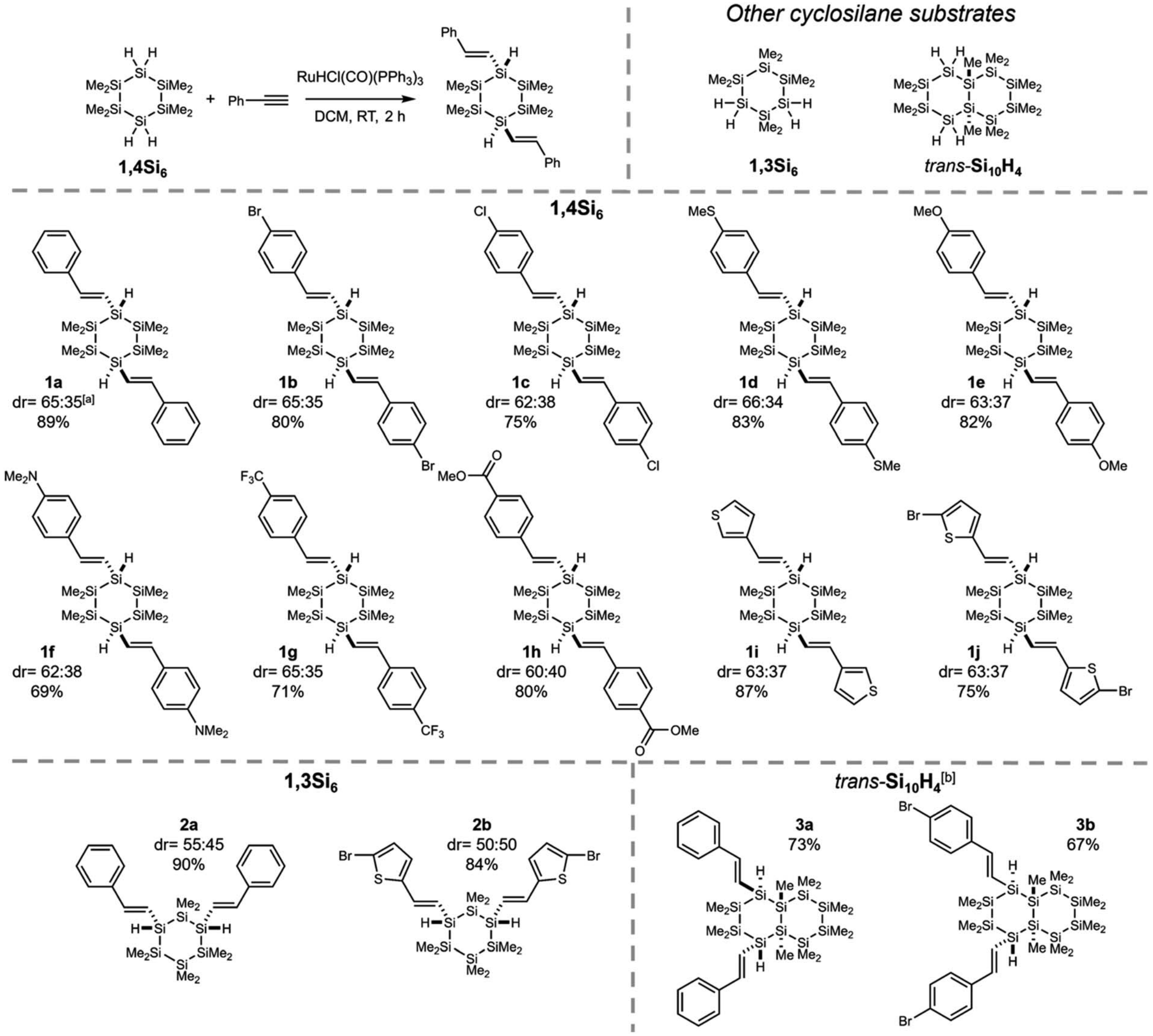


Fig. 3 Substrate scope of hydrosilylation of alkynes with cyclosilanes. For **1,4Si$_6$**, major diastereomers are shown. [a]dr determined by ^{1}H NMR spectroscopy. Isolated yields are reported. [b]Only the *trans* diastereomer was detected.

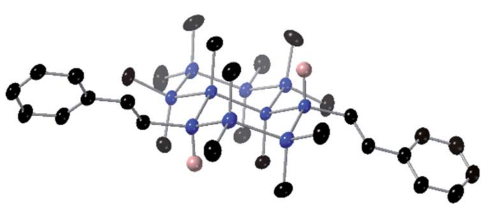


Fig. 4 Displacement ellipsoid plot (30% probability level) of **3a** at 173(2) K. Blue = Si, black = C, pink = H. Hydrogens on methyl and phenyl groups were omitted for clarity.

Stereoregular conjugated polymer synthesis

The extended conjugation observed in hybrid molecules suggested a new conjugated polymer design: stereoregular copolymers alternating in σ- and π-conjugated motifs could be prepared *via* copolymerization of a dibrominated building block (*e.g.*, *trans*-**1b** or *trans*-**1j**) with an appropriate comonomer. Polymers containing Si–Si bonds can be largely divided into two types: polysilanes (*e.g.*, poly(SiR$_2$))[47,48] and σ,π-copolymers (*e.g.*, poly(Ar(SiMe$_2$)$_n$Ar)).[49,50] Polysilanes in which the alkyl substituents are not the same (*e.g.*, poly(SiR′R″), R′ ≠ R″) are stereogenic at each Si atom, but assignment and control of polysilane tacticity is a long-standing problem with no general solution.[51–56] Use of a stereochemically pre-defined monomer appeals to avoid issues of control of relative configuration during polymerization.

We found that treatment of dibromo *trans*-**1j** (dr 90 : 10 *trans* : *cis*) with stoichiometric *i*-PrMgCl resulted in quantitative Mg–halogen exchange.[57] The intermediate α,ω-dimagnesiocyclosilane underwent Kumada cross-coupling with 2-bromothiophene, yielding *trans*-**1k** in 100% conversion (86% isolated yield) and without cyclosilane skeletal rearrangement or erosion of relative configuration (Fig. 7a). The novel polymer **P1** (M_n = 6706 g mol^{-1}, $M_w/M_n = 2.63$, Fig. S7†) was prepared by Kumada polycondensation of 2,5-dibromothiophene with the α,ω-dimagnesiocyclosilane derived from *trans*-**1j** (Fig. 7b). The

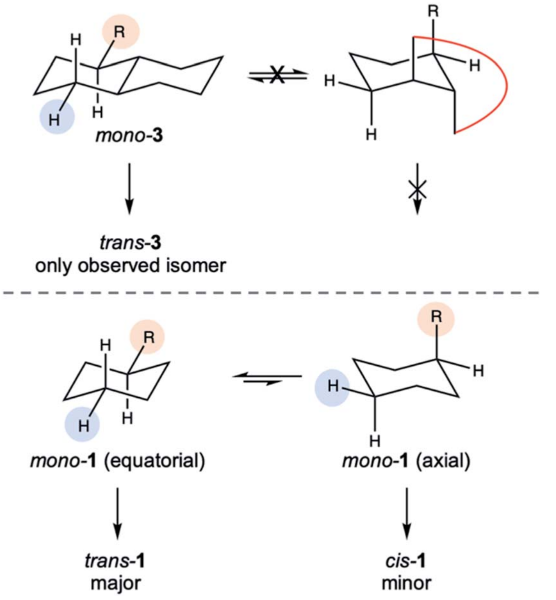


Fig. 5 Model for stereoinduction. Hydrosilylation is highly selective for the equatorial proton (blue circle). Interconversion of axial and equatorial conformers (substituent labelled with orange circle) of a monofunctionalized intermediate determines the *trans* : *cis* ratio of difunctionalized products.

dibromo building blocks could in principle serve as either a precursor to a nucleophile for Kumada polymerization, as showed above in the synthesis of **P1**, but also as the electrophile. We therefore also synthesized copolymer **P2** in which Mg–halogen exchange of *trans*-**1j** was followed by Kumada polycondensation with dibromo *trans*-**1b** ($M_n = 5075$ g mol^{-1}, $M_w/M_n = 2.43$, Fig. 7c). We note that residual catalysts were observed in both **P1** and **P2** by NMR, and further purification will be investigated in the future.

The **P1** onset of absorption (510 nm) was 140 nm red-shifted from *trans*-**1j** itself and 50 nm from *trans*-**1k** (Fig. 7d), validating the hypothesis that σ,π-mixing could be extended across a conjugated polymer chain. Comparison of the UV-vis spectra showed that **P1** was red-shifted relative to **P2**. This was attributed to the difference between dithienyl and phenyl-thienyl units, as we showed (Fig. 6d) that molecular thienyl cyclosilanes were red-shifted relative to phenylsilanes. The all organic conjugated polymer PTVT (poly(thienylenevinylenethienyl)) exhibited a similar absorbance spectrum relative to **P1** despite a much longer degree of polymerization (PTVT: $\lambda_{\max} = 430$ nm, $\lambda_{\text{onset}} = 550$ nm, $M_n = 21\,000$ g mol^{-1}).[58]

These initial studies on conjugated polymer synthesis highlight the utility of stereodefined σ,π-hybrid materials, as well as the stability of relative configuration to subsequent

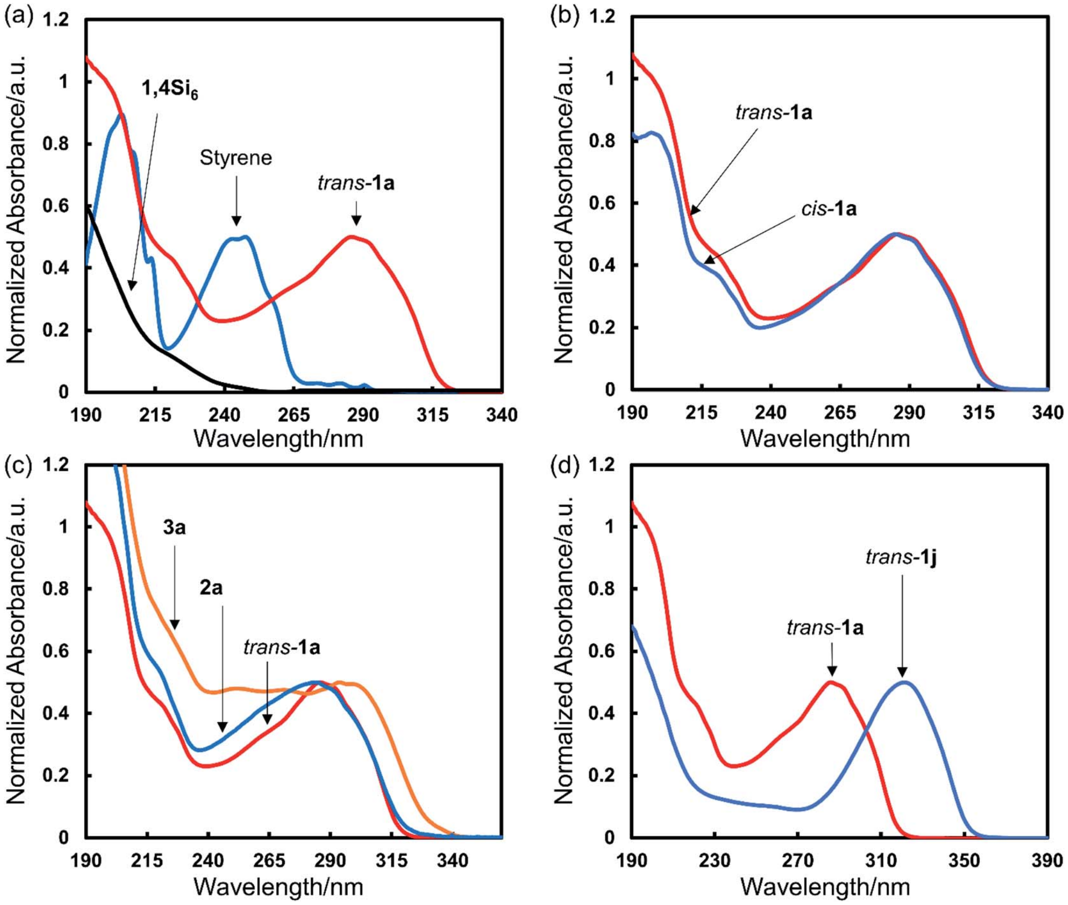


Fig. 6 UV-vis spectra with normalized absorbance ([compound] = 10^{-5} M, in *n*-pentane). (a) Comparison to starting material. Red: *trans*-**1a**; black: **1,4Si$_6$**; blue: styrene. (b) Influence of configuration. Red: *trans*-**1a**; blue: *cis*-**1a** (dr 25 : 75 *trans* : *cis*). (c) Cyclosilane comparison. Red: *trans*-**1a**; blue: **2a** (dr 55 : 45 *trans* : *cis*); orange: **3a**. (d) Heterocycle effect. Red: *trans*-**1a**; blue: **1j** (dr 90 : 10 *trans* : *cis*).

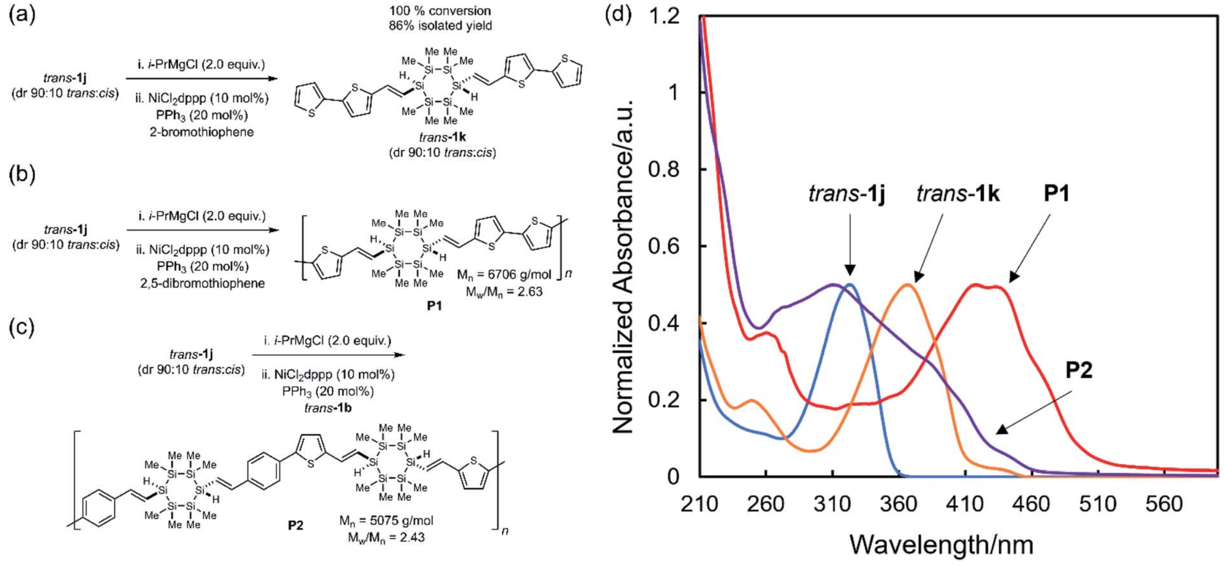


Fig. 7 (a) Model reaction: Kumada cross-coupling of *trans*-**1j** and 2-bromothiophene. (b) Kumada polycondensation synthesis of **P1**. (c) Kumada polycondensation synthesis of **P2**. (d) Comparison of UV-vis spectra of *trans*-**1j** (blue), *trans*-**1k** (orange), **P1** (red) and **P2** (purple) in THF. [*trans*-**1j**] = 10^{-5} M, [*trans*-**1k**] = 10^{-5} M, [**P1**] = 0.03 g L^{-1}, [**P2**] = 0.03 g L^{-1}.

chemical functionalization. Future work will examine the impact of stereoregularity on physical properties, as tactic polymers can demonstrate enhanced mechanical, thermal, and other properties relative to atactic.[59]

Conclusions

We demonstrated that Ru-catalyzed addition of tetrafunctional cyclosilanes to functionalized alkynes proceeded with high selectivity across several parameters: chemoselectivity for Si–H over Si–Si bonds, regioselectivity with respect to both cyclosilane and alkyne, and high (*E*)/(*Z*) and *cis*/*trans* diastereoselectivity. Broad functional group tolerance was exhibited, providing a complex organocyclosilanes bearing reactive functional groups challenging to incorporate by other means. The diverse functional groups incorporated open up several new possible directions, from MOF synthesis to molecular electronics. We also demonstrated that these synthetic achievements enabled the first broad investigation of structure–property relationships in σ,π-hybrid cyclosilanes, which revealed visible light absorption dependent on both the cyclosilane and arene identity. As exemplified by the Kumada polycondensation herein, we expect the results of this study to inspire new approaches to stereoregular conjugated materials combining σ- and π-conjugated motifs. We believe this contribution will continue to expand possibilities for the selective synthesis of complex materials from the main group.

Author contributions

R. S. K. conceived and supervised the work. Q. J., A. F. G., S. W. and M. A. S. carried out the investigation. All authors contributed to manuscript preparation.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This research was primarily supported by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences, under Award No. DE-SC0020681 (building block synthesis, structural characterization). DFT calculations were conducted using scientific computing services at the Maryland Advanced Research Computing Center (MARCC). CPMAS spectroscopy was made possible through the National Science Foundation Major Research Instrumentation grant CHE-2018176.

Notes and references

1 R. S. Klausen, J. R. Widawsky, M. L. Steigerwald, L. Venkataraman and C. Nuckolls, *J. Am. Chem. Soc.*, 2012, **134**, 4541–4544.

2 T. A. Su, H. Li, R. S. Klausen, J. R. Widawsky, A. Batra, M. L. Steigerwald, L. Venkataraman and C. Nuckolls, *J. Am. Chem. Soc.*, 2016, **138**, 7791–7795.

3 D. A. Burns, E. M. Press, M. A. Siegler, R. S. Klausen and V. S. Thoi, *Angew. Chem., Int. Ed.*, 2020, **59**, 763–768.

4 S. Surampudi, M. L. Yeh, M. A. Siegler, J. F. M. Hardigree, T. A. Kasl, H. E. Katz and R. S. Klausen, *Chem. Sci.*, 2015, **6**, 1905–1909.

5 J. Zhou, S. K. Surampudi, A. E. Bragg and R. S. Klausen, *Chem. –Eur. J.*, 2016, **22**, 6204–6207.

6 J. Zhou, C. P. Folster, S. K. Surampudi, D. Jimenez, R. S. Klausen and A. E. Bragg, *Dalton Trans.*, 2017, **46**, 8716–8726.

7 B. J. Barrett, D. Jimenez, R. S. Klausen and A. E. Bragg, *J. Phys. Chem. B*, 2021, **125**, 8460–8471.
8 H. K. Sharma, K. H. Pannell, I. Ledoux, J. Zyss, A. Ceccanti and P. Zanello, *Organometallics*, 2000, **19**, 770–774.
9 M. Shimada, Y. Yamanoi, T. Matsushita, T. Kondo, E. Nishibori, A. Hatakeyama, K. Sugimoto and H. Nishihara, *J. Am. Chem. Soc.*, 2015, **137**, 1024–1027.
10 M. Shimada, M. Tsuchiya, R. Sakamoto, Y. Yamanoi, E. Nishibori, K. Sugimoto and H. Nishihara, *Angew. Chem., Int. Ed.*, 2016, **55**, 3022–3026.
11 R. Emanuelsson, H. Löfås, A. Wallner, D. Nauroozi, J. Baumgartner, C. Marschner, R. Ahuja, S. Ott, A. Grigoriev and H. Ottosson, *Chem. –Eur. J.*, 2014, **20**, 9304–9311.
12 E. A. Carberry and R. West, *J. Am. Chem. Soc.*, 1969, **91**, 5440–5446.
13 R. Fischer, T. Konopa, S. Ully, J. Baumgartner and C. Marschner, *J. Organomet. Chem.*, 2003, **685**, 79–92.
14 D. Y. Larkin, A. A. Korlyukov, E. V. Matukhina, M. I. Buzin, N. A. Chernyavskaya, M. Y. Antipin and A. I. Chernyavskii, *Russ. Chem. Bull.*, 2005, **54**, 1612–1622.
15 A. Bande and J. Michl, *Chem. –Eur. J.*, 2009, **15**, 8504–8517.
16 E. M. Press, E. A. Marro, S. K. Surampudi, M. A. Siegler, J. A. Tang and R. S. Klausen, *Angew. Chem., Int. Ed.*, 2017, **56**, 568–572.
17 E. A. Marro and R. S. Klausen, *Chem. Mater.*, 2019, **31**, 2202–2211.
18 E. A. Marro, E. M. Press, M. A. Siegler and R. S. Klausen, *J. Am. Chem. Soc.*, 2018, **140**, 5976–5986.
19 C. P. Folster and R. S. Klausen, *Polym. Chem.*, 2018, **9**, 1938–1941.
20 Q. Jiang, S. Wong and R. S. Klausen, *Polym. Chem.*, 2021, **12**, 4785–4794.
21 R. W. Dorn, E. A. Marro, M. P. Hanrahan, R. S. Klausen and A. J. Rossini, *Chem. Mater.*, 2019, **31**, 9168–9178.
22 E. A. Marro, C. P. Folster, E. M. Press, H. Im, J. T. Ferguson, M. A. Siegler and R. S. Klausen, *J. Am. Chem. Soc.*, 2019, **141**, 17926–17936.
23 D. J. Harrison, D. R. Edwards, R. McDonald and L. Rosenberg, *Dalton Trans.*, 2008, 3401–3411.
24 R. Walsh, *Acc. Chem. Res.*, 1981, **14**, 246–252.
25 M. Suginome and Y. Ito, *Chem. Rev.*, 2000, **100**, 3221–3256.
26 H. K. Sharma and K. H. Pannell, *Chem. Rev.*, 1995, **95**, 1351–1374.
27 C. He, S. Chen, J. Zhu, J. Ke and Y. Li, *Angew. Chem., Int. Ed.*, 2022, **61**, e202117820.
28 G. K. Min, D. Hernández and T. Skrydstrup, *Acc. Chem. Res.*, 2013, **46**, 457–470.
29 K. ichiro Kanno, Y. Aikawa and S. Kyushin, *Tetrahedron Lett.*, 2020, **61**, 152274.
30 D. Troegel and J. Stohrer, *Coord. Chem. Rev.*, 2011, **255**, 1440–1459.
31 A. M. Tondreau, C. C. H. Atienza, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. P. Delis and P. J. Chirik, *Science*, 2012, **335**, 567–570.
32 Y. Nakajima and S. Shimada, *RSC Adv.*, 2015, **5**, 20603–20616.
33 H.-H. Moretto, M. Schulze and G. Wagner, *Ullmann's Encycl. Ind. Chem.*, 2012, 675–712.
34 K. Yamamoto, M. Kumada, I. Nakajima, K. Maeda and N. Imaki, *J. Organomet. Chem.*, 1968, **13**, 329–341.
35 K. C. Song, K. M. Lee, N. Van Nghia, W. Y. Sung, Y. Do and M. H. Lee, *Organometallics*, 2013, **32**, 817–823.
36 J. P. Banovetz, Y. L. Hsiao and R. M. Waymouth, *J. Am. Chem. Soc.*, 1993, **115**, 2540–2541.
37 Y. L. Hsiao and R. M. Waymouth, *J. Am. Chem. Soc.*, 1994, **116**, 9779–9780.
38 R. Shankar and V. Shahi, *J. Organomet. Chem.*, 2008, **693**, 307–315.
39 L. Sacarescu, A. Siokou, G. Sacarescu, M. Simionescu and I. Mangalagiu, *Macromolecules*, 2008, **41**, 1019–1024.
40 P. T. K. Lee, M. K. Skjel and L. Rosenberg, *Organometallics*, 2013, **32**, 1575–1578.
41 P. T. K. Lee and L. Rosenberg, *Dalton Trans.*, 2017, **46**, 8818–8826.
42 K. ichiro Kanno, S. Noguchi, Y. Ono, S. Egawa, N. Otsuka, M. Mita and S. Kyushin, *J. Organomet. Chem.*, 2022, **961**, 122234.
43 T. A. Su, H. Li, R. S. Klausen, N. T. Kim, M. Neupane, J. L. Leighton, M. L. Steigerwald, L. Venkataraman and C. Nuckolls, *Acc. Chem. Res.*, 2017, **50**, 1088–1095.
44 G. Tekautz, A. Binter, K. Hassler and M. Flock, *ChemPhysChem*, 2006, **7**, 421–429.
45 D. Casarini, L. Lunazzi and A. Mazzanti, *Tetrahedron*, 1998, **54**, 13181–13184.
46 D. Casarini, L. Lunazzi and A. Mazzanti, *J. Org. Chem.*, 1998, **63**, 9125–9127.
47 R. D. Miller and J. Michl, *Chem. Rev.*, 1989, **89**, 1359–1410.
48 R. S. Klausen and E. Ballestero-Martínez, in *Comprehensive Organometallic Chemistry IV*, Elsevier, 2021.
49 M. C. Fang, A. Watanabe and M. Matsuda, *Macromolecules*, 1996, **29**, 6807–6813.
50 Y. Morisaki, F. Fujimura and Y. Chujo, *Organometallics*, 2003, **22**, 3553–3557.
51 J. P. Banovetz, K. M. Stein and R. M. Waymouth, *Organometallics*, 1991, **10**, 3430–3432.
52 N. Choi, S. Y. Onozawa, T. Sakakura and M. Tanaka, *Organometallics*, 1997, **16**, 2765–2767.
53 B. J. Grimmond and J. Y. Corey, *Organometallics*, 2000, **19**, 3776–3783.
54 V. K. Dioumaev, K. Rahimian, F. Gauvin and J. F. Harrod, *Organometallics*, 1999, **18**, 2249–2255.
55 E. Fossum and K. Matyjaszewski, *Macromolecules*, 1995, **28**, 1618–1625.
56 J. Maxka, F. K. Mitter, D. R. Powell and R. West, *Organometallics*, 1991, **10**, 660–664.
57 P. Knochel, W. Dohle, N. Gommermann, F. F. Kneisel, F. Kopp, T. Korn, I. Sapountzis and V. A. Vu, *Angew. Chem., Int. Ed.*, 2003, **42**, 4302–4320.
58 R. Toyoshima, K. Akagi and H. Shirakawa, *Synth. Met.*, 1997, **84**, 431–432.
59 J. C. Worch, H. Prydderch, S. Jimaja, P. Bexis, M. L. Becker and A. P. Dove, *Nat. Rev. Chem.*, 2019, **3**, 514–535.