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O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski,
and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

More detailed discussion on formation of $1^{\bullet+}$, $2^{\bullet+}$ and $3^{\bullet+}$

Efficient generation of the radical cations of **1** – **3** for time-resolved absorption measurements was achieved via photo-induced electron transfer using a positively charged sensitizer (Figure S1): irradiation of N-methyl quinolinium (NMQ; 355 nm) in the presence of a co-sensitizer (toluene) yields the formation of toluene radical cation in high yields, even in apolar solvents.⁴⁹ Electron transfer to toluene radical cation from the more easily oxidizable Si compounds then yields $1^{\bullet+}$, $2^{\bullet+}$ and $3^{\bullet+}$, respectively. At high concentrations of toluene (1 M), this yields a highly efficient (quantum yield > 80%) and complete (no toluene radical cations left over) formation of the radical cations of **1** – **3** within 50 ns, which was suitable for this study. This method is highly superior over direct irradiation methods, which yield significant

amounts of photochemical side products, as below 300 nm photo-ionization competes with direct homolytic Si-H bond cleavage.

Figure S1. Photoinduced electron transfer reactions yielding **1^{•+}**, **2^{•+}** and **3^{•+}**.

Characterization of **1^{•+}**, **2^{•+}** and **3^{•+}**

The oxidation potentials of the models were obtained by cyclic voltammetry to ensure efficient electron transfer from the silanes to toluene^{•+} ($E_{\text{ox}}(\text{toluene}) = 2.32 \text{ V}$ vs. Ag/AgCl).⁵⁰ Since the oxidation was irreversible peak potentials E_p were determined. From the results it becomes clear that all three compounds have a sufficiently lower oxidation potential than toluene (1.34 to 1.67 V vs Ag/AgCl). In more detail it shows that **1**, with the smallest silicon ‘backbone’, has the highest potential. Interestingly **3** has a slightly higher oxidation potential than **2**, while having more silicon atoms. This may be explained by differences in the effective conjugation lengths although both molecules have five silicon atoms bound in a row. Sigma conjugation in branched polysilanes is highly dependent on the conformation of the silicon backbone. Anti-conformation of the silicon atoms contributes the most to conjugation, whereas small dihedral angles (syn to gauche) do not contribute significantly.⁵¹ Due to steric hindrance of the bulky TMS groups, **3** can not fully optimize the σ delocalization to the degree available for **2**, which encounters less steric hindrance due to the presence of four rather than six TMS groups. This steric effect is visible in the bond angle between the central Si and the two adjacent Si atoms. For **2** and **3**, this was calculated (B3LYP/6-311G(d,p)) to be 118° and 132°,

respectively, i.e. significantly larger than the 109° for unstrained sp^3 Si atoms. While for **2** no experimental value is known, the calculated value for **3** is in good agreement with X-ray diffraction data that yield 128.3° .⁴⁷ Calculated vertical ionization potentials (Table 1), obtained from the difference in absolute energies between the optimized neutral species and the corresponding radical cation in that geometry, confirm the significantly higher oxidation potential found for **1**. For **2** and **3**, the calculated potentials are close to each other, with the ordering in line with the experimental data. Finally, also the ordering of the ease of oxidation obtained using Koopmans' theorem⁵² (Table 3, bottom row) correlates nicely with the oxidation potentials found.

The effect of the steric hindrance is also visible in Figure S2, which shows the relaxed geometries of the radical cations. In **1**^{•+} two of the three Si-Si bonds are lengthened significantly more than the third bond (from 2.38 Å in the neutral precursor **1** to 2.50/2.50 and 2.40 Å, respectively). The charge is also predominantly present on the TMS moieties that are bound by a more lengthened Si-Si bond (from 0.027 in the precursor molecule **1** to 0.385 and 0.202 for the more and less lengthened Si-Si bonds, respectively). Also the angle $\angle\text{Si2-Si1-Si3}$ becomes smaller going from 113° to 99° as the radical cation is formed, while the other angles, $\angle\text{Si2-Si1-Si4}$ and $\angle\text{Si3-Si1-Si4}$, increase from 113° to 118° . Also **2**^{•+} shows relaxation of the central angle $\angle\text{Si2-Si1-Si3}$, as it decreases from 118° to 107° . The positive charge on the molecule is mainly localized on the TMS groups (from 0.062 in the precursor molecule **2** to 0.260 and 0.231 for the TMS moieties centered on atoms Si5 and Si7, respectively, and to 0.149 and 0.150 for those on Si4 and Si6, respectively). Most charge is localized on the TMS groups that are part of the w-shaped silicon chain (Si5-Si2-Si1-Si3-Si7). This is also shown by the Si-Si bond orders, which are about 0.77 in this chain and 0.89 for the remaining two Si-Si bonds. Also bond lengths are

increased from 2.38 to 2.44 Å in this chain, whereas the other bonds are only marginally lengthened to 2.40 Å. The w-shape (dihedrals: 7-3-1-2, 143°; 3-1-2-5, 147°) is distinctive for the previously mentioned σ conjugation in silicon chains. Silicon atoms bound in this conformation can attribute to the conjugation and thus stabilize the molecule.

The geometry of $\mathbf{3}^{\bullet+}$ resembles that of $\mathbf{2}^{\bullet+}$, including the relaxation of the angle strain ($\angle\text{Si2-Si1-Si3}$ = from 132° in the neutral to 119° in the radical cation) and the w-shaped chain. The conjugated ‘backbone’ shows a better anti-conformation than $\mathbf{2}^{\bullet+}$ (dihedrals: $\angle\text{8-3-1-2}$ = 172°; $\angle\text{3-1-2-5}$ = 154°). However, bond orders show that the charge is mainly localized on two TMS-groups on Si5 and Si8. This is also reflected by the bond lengths, which are longer for Si3-Si8 and Si2-Si5 (2.49 Å) than for Si1-Si3 and Si1-Si2 (2.45 Å). The bonds not significantly involved in the sigma conjugation are only slightly longer (2.42 Å) than in the neutral molecule (2.39 - 2.40 Å).

Figure S2. Silicon backbones and relevant carbon and hydrogen atoms of relaxed geometries of $1^{\bullet+}$, $2^{\bullet+}$ and $3^{\bullet+}$. Bond distances and Wiberg bond orders (between parentheses) are depicted near the corresponding bonds (B3LYP/6-311++G(2d,2p)//B3LYP/6-311G(d,p) calculations).

Estimation of barrier energies

Table S1. Gibb's free activation barriers for the reactions of $2^{\bullet+}$ and $3^{\bullet+}$ with various

nucleophiles, estimated using $k(T) = \frac{k_B T}{h} e^{\frac{-G_{act}}{RT}}$.

Entry	Nucleophile	$G_{act}, 2^{\bullet+}$	$G_{act}, 3^{\bullet+}$
1	1-Decene	18.3	9.0
2	1-Decyne	17.7	8.5
3	H ₂ O	-	7.2
4	1-Undecanol	16.1	7.4
5	1-Undecanal	15.6	7.1
6	1-Undecanoic acid	16.3	7.4
7	1-Decanethiol	-	< 6.5
8	1-Bromohexane	-	> 10.6
9	10-Undecenoic acid	-	7.4
10	10-Undecynoic acid	-	7.5
11	10-Undecenal	-	6.9
12	10-Undecynal	-	7.0

Activation barriers in kcal mol⁻¹.

Optimized geometries

Cartesian coordinates of the radical cations of **1**, **2** and **3** as obtained after optimization at the B3LYP/6-311G(d,p) level of theory:

Optimized geometry **1**^{•+}:

Charge = 1 Multiplicity = 2

Si	-0.17793600	-0.02774100	-0.69623100
H	-0.11302800	-0.06359800	-2.18807800
Si	1.39245800	-1.84665100	0.00700300
Si	1.19672000	1.94040500	0.01308100
Si	-2.46964900	-0.09132900	0.01256800
C	1.93841200	-1.64248000	1.78722500
H	2.45837700	-2.55645800	2.09694400
H	1.09578800	-1.50055800	2.46765900
H	2.63769200	-0.81425900	1.91900000
C	2.80655500	-1.90791400	-1.21945200
H	3.39205400	-2.81437600	-1.02398800
H	3.48131100	-1.05591400	-1.12768400
H	2.45161700	-1.96114600	-2.25096900
C	0.20463800	-3.29883700	-0.21215100
H	0.79340500	-4.20745100	-0.02775200
H	-0.20155900	-3.37030700	-1.22275700
H	-0.61773300	-3.28407300	0.50455100
C	0.86434400	2.23097100	1.83470400
H	1.35785800	3.16477300	2.12945300
H	1.27018800	1.43629800	2.46395700
H	-0.19936100	2.33917000	2.05585200
C	0.36851400	3.20709700	-1.11566600
H	0.83970700	4.17354500	-0.89101700
H	-0.70312300	3.31128300	-0.94065500
H	0.53608500	2.99329200	-2.17281100
C	3.01892800	1.76252500	-0.37761100
H	3.49727800	2.73273700	-0.19775800
H	3.19742100	1.50097500	-1.42270000
H	3.52168600	1.03344300	0.26038200
C	-3.29940000	-1.46249000	-0.98080900
H	-4.36084700	-1.50255000	-0.71424800
H	-2.87347600	-2.44729200	-0.77585300
H	-3.23699300	-1.28041200	-2.05653700
C	-2.55754500	-0.42889800	1.86505900
H	-3.60662900	-0.44786400	2.17794400
H	-2.05770500	0.34381300	2.45493400
H	-2.12394000	-1.39544800	2.13447100
C	-3.23789900	1.58230500	-0.40124300
H	-4.30711000	1.54515700	-0.16738400
H	-3.14414900	1.83133500	-1.46108200
H	-2.80638300	2.39662600	0.18587800

Optimized geometry **2^{•+}**:

Charge = 1 Multiplicity = 2

Si	-5.44892	-2.46919	1.23437
Si	-4.08198	-0.61915	0.55986
Si	-4.26153	0.04262	-1.80369
Si	-1.72334	-1.17009	0.45429
H	-1.02146	-0.3455	-0.56976
Si	-0.74119	-0.46613	2.56013
Si	0.98273	-2.17566	2.85295
Si	0.12677	1.7581	2.33534
C	-1.5688	-2.98069	-0.0622
H	-2.06226	-3.13701	-1.02485
H	-0.51894	-3.25603	-0.18855
H	-2.01767	-3.65893	0.66458
C	-3.3987	1.70069	-2.02707
H	-3.57003	2.05603	-3.04917
H	-3.78761	2.46279	-1.34741
H	-2.31873	1.62614	-1.88208
C	-3.56867	-1.2577	-2.9747
H	-2.48356	-1.35479	-2.89481
H	-4.01809	-2.24198	-2.82223
H	-3.79144	-0.95489	-4.00378
C	-6.13009	0.22429	-2.04363
H	-6.57422	0.94852	-1.35721
H	-6.30388	0.5873	-3.06369
H	-6.6593	-0.72503	-1.93713
C	-4.51771	0.92212	1.57686
H	-5.54327	1.22584	1.34648
H	-4.48324	0.70999	2.64845
H	-3.86144	1.76707	1.36704
C	-7.18473	-1.76891	1.49741
H	-7.6004	-1.33085	0.58651
H	-7.85666	-2.57518	1.80961
H	-7.20463	-1.00534	2.27932
C	-4.81294	-3.19347	2.86136
H	-4.79211	-2.44756	3.66005
H	-5.48313	-3.99698	3.18413
H	-3.81209	-3.62289	2.76758
C	-5.48077	-3.80361	-0.10156
H	-4.49727	-4.24494	-0.28007
H	-6.149	-4.61213	0.21238
H	-5.85923	-3.42367	-1.05414
C	-1.91291	-0.61103	4.0503
H	-2.69148	0.15515	4.0238
H	-2.39098	-1.59017	4.11336
H	-1.34489	-0.45613	4.97255
C	0.17297	-3.83323	3.24188
H	-0.36375	-4.24947	2.38719
H	0.9514	-4.55222	3.51993
H	-0.52065	-3.76354	4.08352

C	1.95002	-1.57071	4.36408
H	2.70192	-2.33039	4.60797
H	2.47888	-0.6341	4.17631
H	1.31687	-1.44106	5.24465
C	2.13058	-2.30208	1.36398
H	2.58389	-1.34151	1.10972
H	2.94406	-2.99517	1.60474
H	1.63299	-2.68683	0.47124
C	-1.17302	2.94828	1.65154
H	-0.73836	3.95137	1.58839
H	-1.50102	2.67206	0.6462
H	-2.05124	3.01597	2.29828
C	1.62304	1.73783	1.18302
H	1.37398	1.35805	0.18853
H	2.00146	2.75765	1.05896
H	2.44279	1.134	1.58014
C	0.6264	2.31814	4.07059
H	-0.23065	2.34926	4.74854
H	1.38543	1.67132	4.51689
H	1.04365	3.3293	4.02136

Optimized geometry 3^{++} :

Charge = 1 Multiplicity = 2

Si	-0.09409	-0.33728	1.21875
H	-0.10744	0.69082	2.29398
Si	-2.15435	0.07631	-0.02092
Si	2.06203	-0.07557	0.06681
Si	-2.54322	-1.29114	-1.95576
Si	-3.65114	-0.75743	1.78737
Si	-2.50981	2.44847	-0.33973
Si	2.63748	1.76769	-1.39633
Si	2.79767	-2.13405	-0.96428
Si	3.26639	0.42375	2.19483
C	-0.10026	-2.04169	2.04522
H	0.88446	-2.29106	2.44118
H	-0.38631	-2.83036	1.34939
H	-0.80052	-2.04983	2.88278
C	-4.40043	-1.30591	-2.31785
H	-4.57349	-1.83883	-3.25877
H	-4.81147	-0.29976	-2.43333
H	-4.97313	-1.82097	-1.54316
C	-1.95598	-3.06371	-1.64956
H	-2.18161	-3.67458	-2.53006
H	-2.44953	-3.52839	-0.79351
H	-0.87667	-3.11636	-1.48705
C	-1.63854	-0.60213	-3.46405
H	-1.78126	-1.28522	-4.30816
H	-0.56438	-0.50368	-3.29593
H	-2.0242	0.37479	-3.76172
C	-5.39046	-0.18979	1.30707
H	-6.08706	-0.71334	1.97319
H	-5.66155	-0.44767	0.28218
H	-5.53697	0.88021	1.44758
C	-3.18679	-0.01009	3.45546
H	-3.94772	-0.29668	4.19005
H	-3.15998	1.08165	3.42192
H	-2.22286	-0.35812	3.83066
C	-3.67397	-2.64243	1.86732
H	-4.34127	-2.93074	2.68803
H	-2.70329	-3.09787	2.06076
H	-4.08241	-3.07897	0.95301
C	-2.70008	2.86035	-2.17548
H	-2.86985	3.93743	-2.27898
H	-3.56187	2.35346	-2.61785
H	-1.82004	2.60906	-2.77041
C	-4.07772	3.049	0.5324
H	-4.13318	4.13503	0.39964
H	-4.07551	2.85371	1.60701
H	-4.98681	2.62311	0.10347
C	-1.05351	3.4073	0.38783
H	-1.22536	4.48076	0.25714

H	-0.11468	3.16168	-0.10966
H	-0.93266	3.21897	1.45756
C	2.84098	3.40628	-0.47472
H	3.01562	4.19611	-1.21337
H	3.70603	3.39428	0.1924
H	1.96734	3.69561	0.11128
C	4.28796	1.37479	-2.23392
H	4.5492	2.21918	-2.88116
H	4.24078	0.48518	-2.86556
H	5.10715	1.24616	-1.52328
C	1.32572	1.95044	-2.74423
H	1.59961	2.78799	-3.39472
H	0.33448	2.1572	-2.33885
H	1.25825	1.05714	-3.36901
C	2.2805	-2.1564	-2.78305
H	2.65799	-3.07277	-3.24914
H	2.68911	-1.31346	-3.34515
H	1.19534	-2.15125	-2.90903
C	2.14578	-3.69647	-0.12597
H	2.61025	-4.56156	-0.61153
H	1.065	-3.81466	-0.21984
H	2.40202	-3.74318	0.93481
C	4.68795	-2.18294	-0.85322
H	5.03979	-3.05334	-1.41783
H	5.03486	-2.3041	0.17597
H	5.16948	-1.30042	-1.27691
C	3.25071	-1.04908	3.37096
H	3.98051	-0.84828	4.16409
H	3.54501	-1.98504	2.89092
H	2.28288	-1.19382	3.85438
C	5.04223	0.7411	1.62487
H	5.63615	0.94897	2.52319
H	5.12707	1.60702	0.96721
H	5.48767	-0.12001	1.12513
C	2.58634	1.94869	3.06277
H	3.25654	2.19165	3.89531
H	1.5916	1.78041	3.47839
H	2.54303	2.82207	2.41027