Organic & Biomolecular Chemistry

Electronic Supplementary Information

Platinum-catalyzed reactions between Si-H groups as a new method for cross-linking of silicones

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1. Materials and methods

α,ω-di(trimethylsiloxy)polymethylhydroxylsiloxane (**PMHS**) (the number-average molecular weight M_n=1700–3200, viscosity 12–45 cSt, Aldrich) and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution 0.1 M in xylene were purchased from commercial suppliers, fully characterized by NMR spectroscopy before usage (Fig.2S–3S, ESI) and used as received. Anhydrous solvents were freshly distilled (benzene over Na/benzophenone CH_2Cl_2, over CaH_2). *cis*-[$PtCl_2(BnCN)_2$] was prepared according to the published methods [1,2].

NMR spectra were recorded on a commercial instrument (400.13 MHz for ^{1}H, 100.61 MHz for ^{13}C, 79.50 MHz for ^{29}Si) in $CDCl_3$. Chemical shifts are given in δ-values [ppm] referenced to the residual signals of non-deuterated solvent ($CHCl_3$): δ 7.26 (^{1}H) and 77.2 (^{13}C).

Solid-state NMR spectra were obtained using either a Bruker Avance III WB 400 operating at 400.23 MHz for ^{1}H (16 scans), 100.64 MHz for ^{13}C (2000 scans) and 79.51 MHz for ^{29}Si (2000 scans). They were obtained under magic-angle spinning conditions with spin-rates around 12500 Hz. ^{13}C and ^{29}Si SSNMR spectra were recorded with cross-polarization (typically with a recycle delay of 2.0 s and a contact time of 2.00 ms) and direct excitation (typically with a recycle delay of 5.0 s) with ^{1}H decoupling. ^{1}H spectra were obtained with direct excitation. Samples were run as-prepared and spectral referencing is with respect to external, neat tetramethylsilane.

2. Cross-linking procedure

PMHS (500 mg) and 4.5 mL of a previously prepared 10^{-4} M solution of the catalyst (Karstedt's catalyst in freshly distilled benzene was made from a commercially available 0.1 M solution of Karstedt's catalyst in xylene; *cis*-[$PtCl_2(BnCN)_2$] in CH_2Cl_2) were mixed together in a tube. The mixture was being stirred for 5 min, and was poured into a polytetrafluoroethylene mold measuring 12 cm length × 12 mm width × 3 mm height and cross-linked at RT for one day followed by drying at 80 °C for 5 h. The final concentration of the catalyst in **PMHS** was 10^{-3} M.

The stepwise procedure of the silicone cross-linking is shown in Fig. 1S.

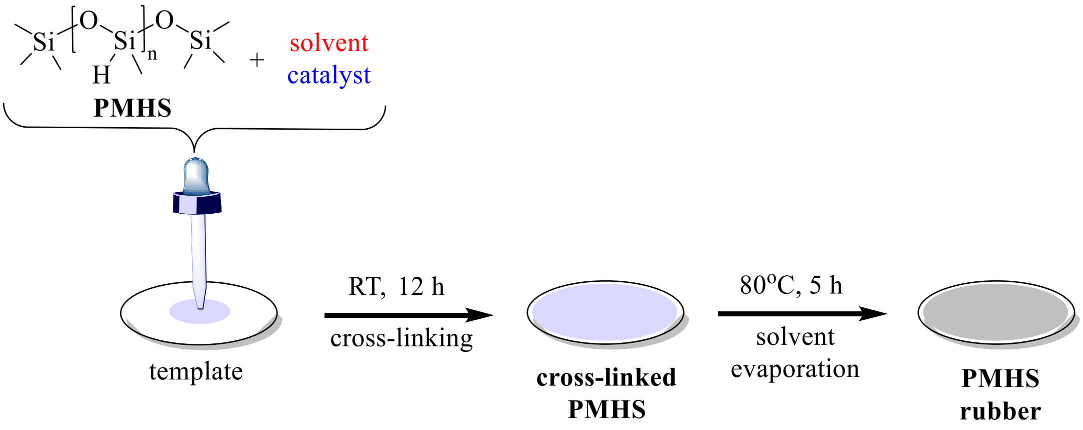


Fig. 1S. Schematic displaying the stepwise procedure for the cross-linking of **PMHS**.

3. NMR spectra of polysiloxanes

2.1. PMHS

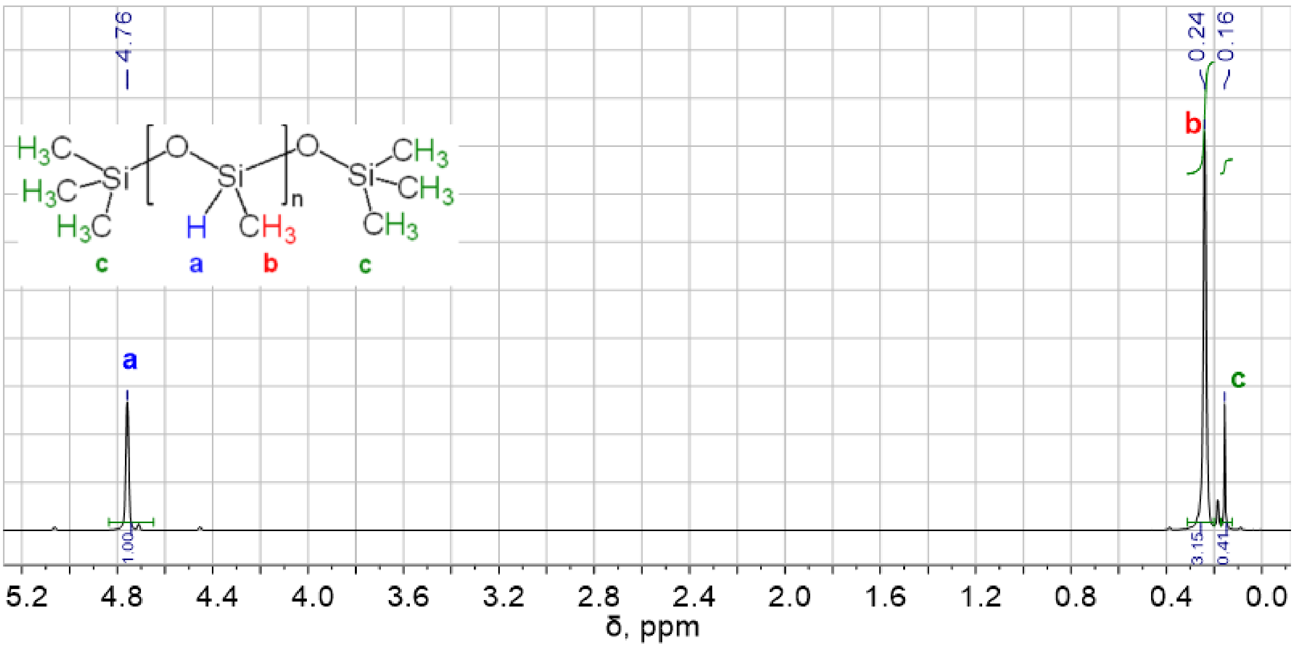


Fig. 2S. The NMR ^{1}H of **PMHS** (before cross-linking).

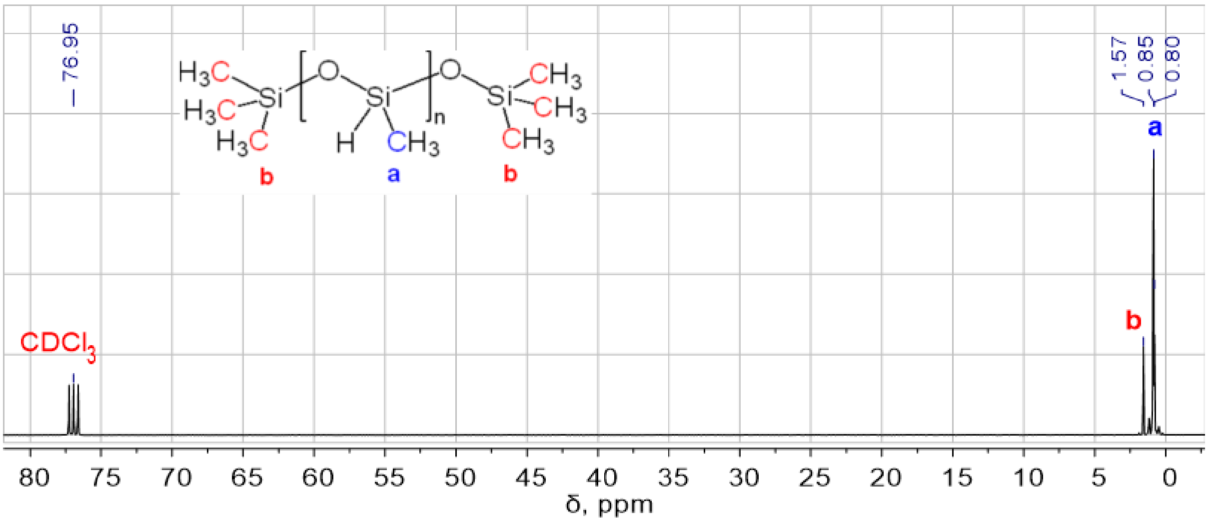


Fig. 3S. The NMR ^{13}C of **PMHS** (before cross-linking).

2.2. Cross-linked PMHS by Karstedt's catalyst

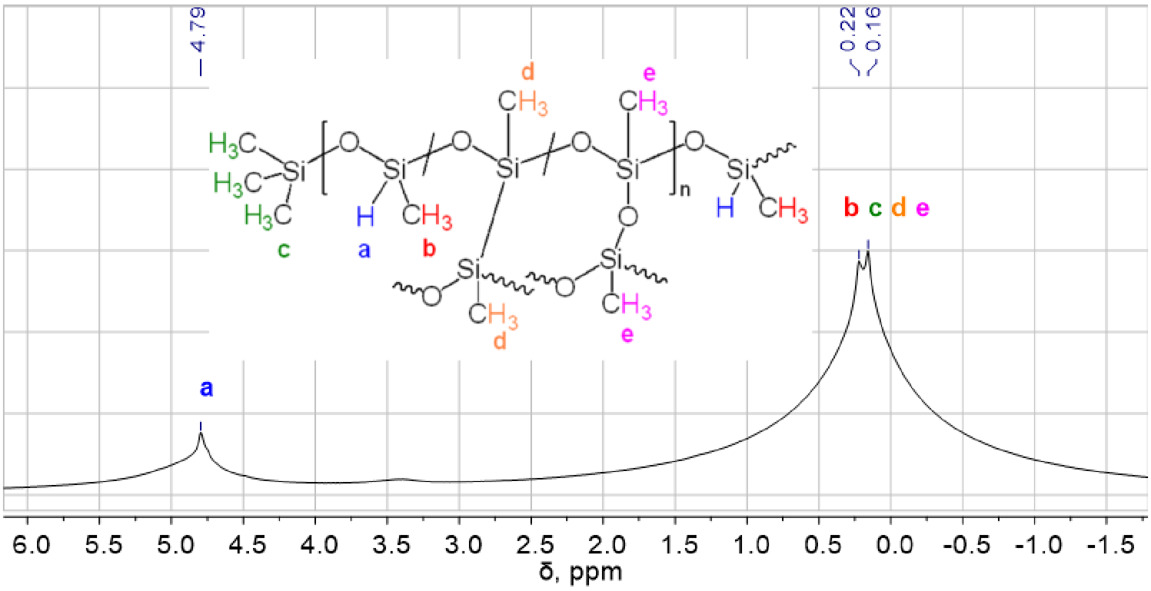


Fig. 4S. The SSNMR ^{1}H of cross-linked **PMHS** (10^{-3} M Karstedt's catalyst).

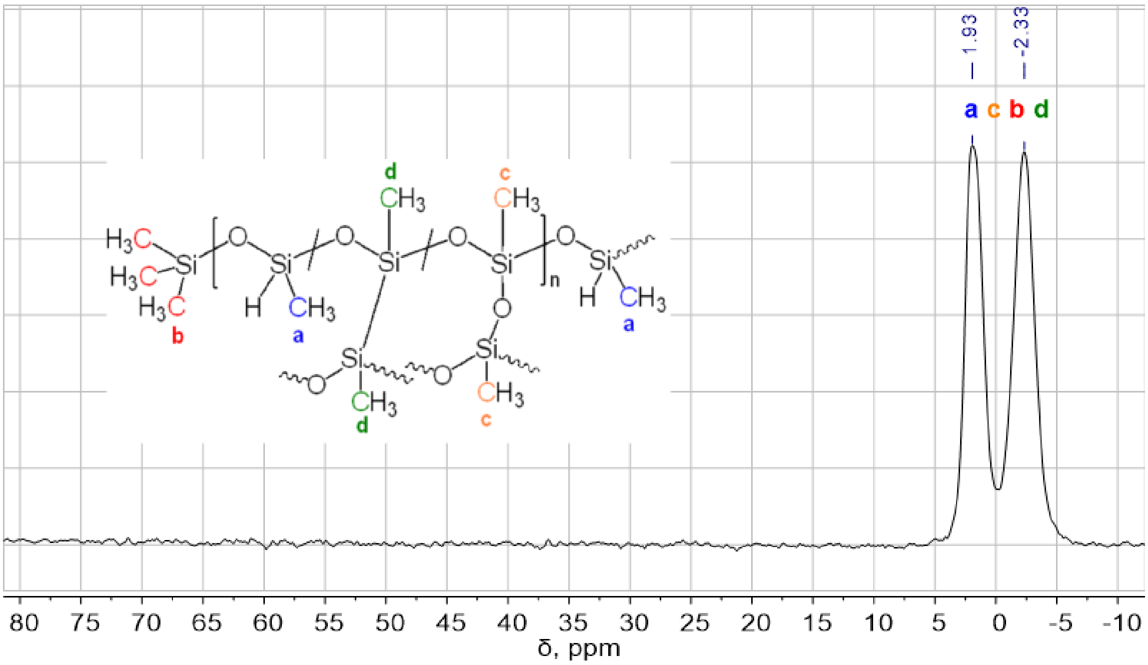


Fig. 5S. The SSNMR ^{13}C of cross-linked **PMHS** (10^{-3} M Karstedt's catalyst).

2.3. Cross-linked PMHS by cis-[$PtCl_2(BnCN)_2$]

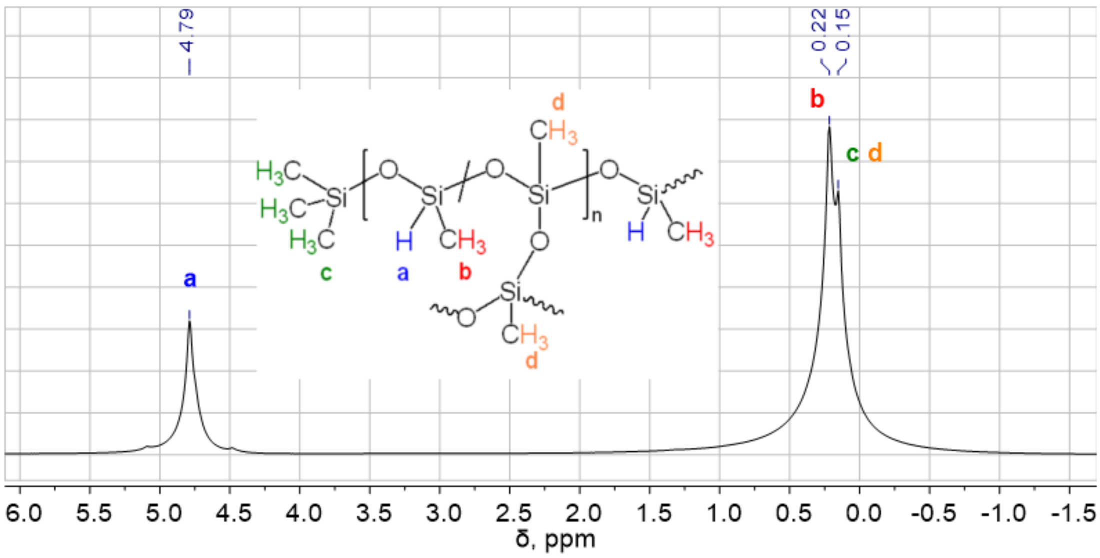


Fig. 6S. The SSNMR ^{1}H of cross-linked **PMHS** (10^{-3} M *cis*-[$PtCl_2(BnCN)_2$]).

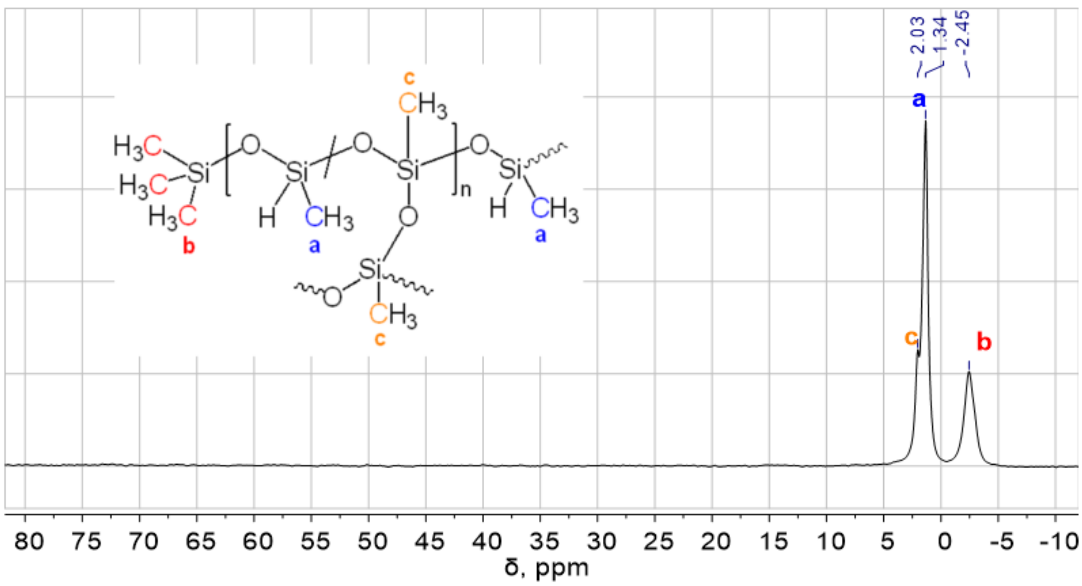
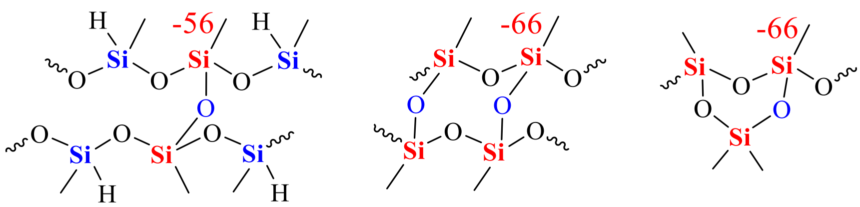


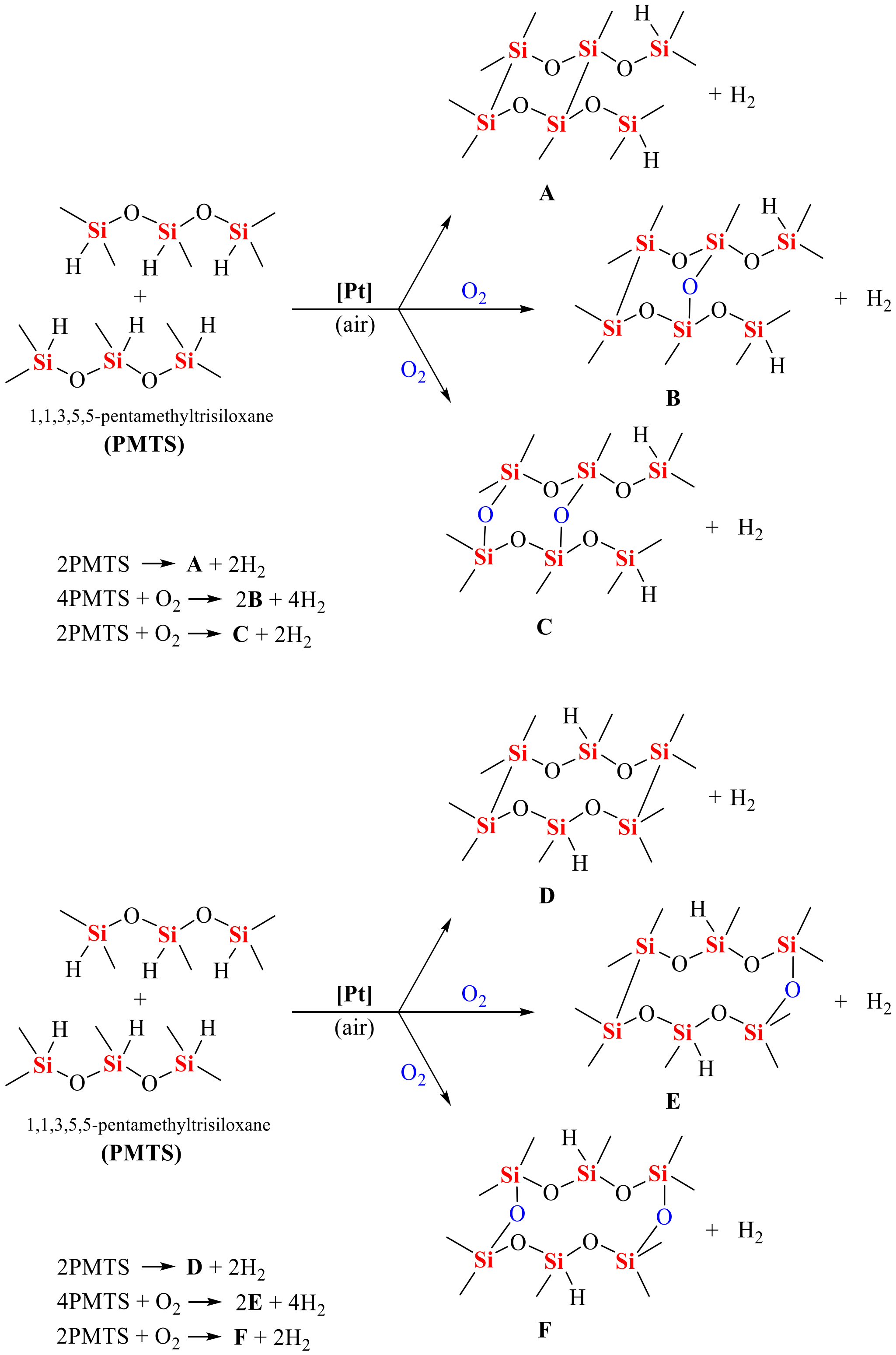
Fig. 7S. The SSNMR ^{13}C of cross-linked **PMHS** (10^{-3} M *cis*-[$PtCl_2(BnCN)_2$]).



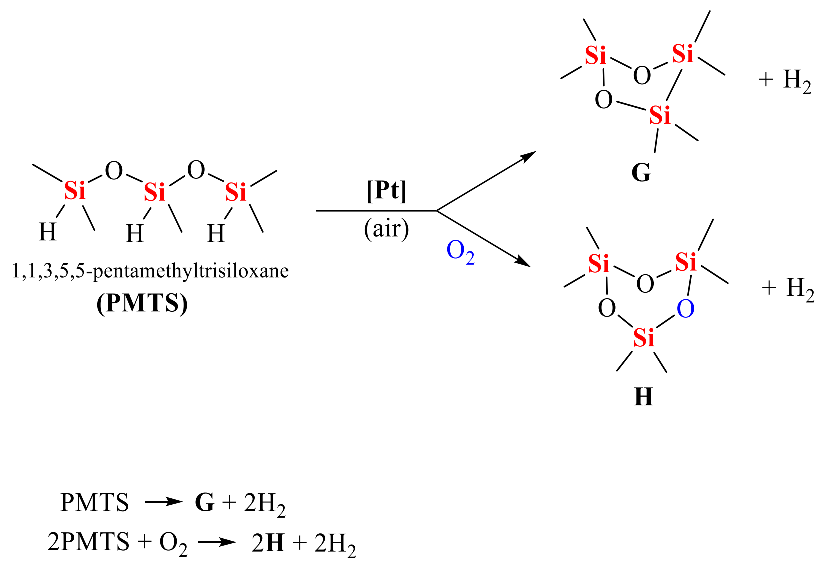
Scheme 1S. Possible cross-linking structures of O-trisubstituted Si atom and their ^{29}Si chemical shifts.

4. Quantum chemical modeling

3.1. Model reactions



Scheme 2S. Model Si-Si coupling reactions between **PMTS** molecules.



Scheme 3S. Model Si-Si coupling reactions – cyclization of **PMTS**.

3.2. Quantum chemical calculations

Computational details. The full geometry optimization of all model structures has been carried out at the DFT level of theory using the global hybrid functional M06-2X (54% of Hartree–Fock exchange, specifically developed for main group thermochemistry) [3] with the help of Gaussian-09 program package [4]. The standard 6-31G* basis sets were used for all atoms. No symmetry restrictions have been applied during the geometry optimization procedure. The Hessian matrices were calculated analytically for all optimized model structures to prove the location of correct minima on the potential energy surface (no imaginary frequencies) and to estimate the thermodynamic parameters, the latter being calculated at 25 °C (Table 2S). The Cartesian atomic coordinates for all optimized equilibrium model structures are presented in Table 3S.

Table 1S. Calculated total energies, enthalpies, Gibbs free energies (in Hartree), and entropies (in cal/mol•K) for optimized equilibrium model structures (E, H, G, and S, respectively).

Model structure	E	H	G	S
PMTS	-1220.23859519	-1219.995016	-1220.064368	145.965
H_2	-1.16356550545	-1.149957	-1.164733	31.099
O_2	-150.258154385	-150.250765	-150.274023	48.951
A	-2438.12805851	-2437.675556	-2437.776094	211.600

B	-2513.45120139	-2512.992350	-2513.096078	218.313
C	-2588.77261534	-2588.307859	-2588.411784	218.728
D	-2438.13424682	-2437.681918	-2437.782127	210.908
E	-2513.45028098	-2512.991468	-2513.094546	216.945
F	-2588.76706725	-2588.302074	-2588.404841	216.291
G	-1219.04768005	-1218.822504	-1218.884293	130.046
H	-1294.37035061	-1294.139211	-1294.203634	135.589

Table 2S. Cartesian atomic coordinates for optimized equilibrium model structures. Nuclear charges of elements are shown in the second column.

Model structure	Charge	X	Y	Z
PMTS				
	14	2.825948	-0.489984	-0.487360
	8	1.304993	-0.368839	0.167076
	14	0.002656	0.624263	0.030192
	8	-1.360521	-0.251889	0.300633
	14	-2.829600	-0.478421	-0.441324
	6	3.632107	1.203193	-0.500607
	6	0.123323	1.994009	1.284632
	6	3.807156	-1.698866	0.543806
	6	-3.691974	1.177139	-0.615756
	6	-3.829926	-1.656704	0.606790
	1	2.710025	-0.984551	-1.885194
	1	-0.044617	1.174207	-1.353730
	1	-2.606101	-1.055854	-1.794434
	1	3.040132	1.920424	-1.079969
	1	3.733366	1.594640	0.517386
	1	4.631961	1.163450	-0.945568
	1	-0.743816	2.659725	1.227863
	1	0.166187	1.578628	2.296270
	1	1.025268	2.594568	1.125776

	1	3.303805	-2.668413	0.597814
	1	3.926616	-1.324609	1.565420
	1	4.804832	-1.856418	0.121128
	1	-4.666888	1.069930	-1.102677
	1	-3.094556	1.871392	-1.216555
	1	-3.854059	1.634783	0.365915
	1	-4.811278	-1.843358	0.158404
	1	-3.987820	-1.240286	1.606692
	1	-3.319015	-2.617074	0.719496
H_2				
	1	0.000000	0.000000	0.368264
	1	0.000000	0.000000	-0.368264
O_2				
	8	0.000000	0.000000	0.598700
	8	0.000000	0.000000	-0.598700
A				
	14	-0.282208	2.217249	-0.592403
	14	1.993917	1.636324	-0.426907
	8	-1.038009	1.547188	0.750213
	14	-1.015344	-0.014081	1.329807
	14	1.206179	-0.793438	1.350295
	8	-1.906697	-0.978559	0.314962
	14	-3.504827	-1.047697	-0.147672
	8	2.100711	0.128674	0.292790
	8	1.299891	-2.358895	0.832590
	14	1.455150	-2.981353	-0.708012
	6	-0.514811	4.077042	-0.496415
	6	-1.807206	0.022949	3.023079
	6	-3.565508	-1.723501	-1.890636
	6	-4.282382	0.656056	-0.060456
	6	2.866036	1.533009	-2.086782

	6	2.881752	2.884496	0.664929
	6	1.962081	-0.695547	3.054647
	6	3.257006	-2.948195	-1.213002
	6	0.425902	-1.972955	-1.908252
	6	-1.083241	1.553339	-2.161479
	1	-4.221965	-1.965937	0.776268
	1	0.952668	-4.376664	-0.649692
	1	-1.579706	4.332566	-0.512958
	1	-0.034330	4.577488	-1.344567
	1	-0.084337	4.482402	0.424391
	1	-1.877236	-0.984062	3.447018
	1	-2.819429	0.439261	2.969840
	1	-1.227863	0.645507	3.712546
	1	-4.600134	-1.849938	-2.226508
	1	-3.066651	-1.040874	-2.587358
	1	-3.067948	-2.695961	-1.957257
	1	-3.759375	1.351217	-0.725019
	1	-4.237451	1.074135	0.950277
	1	-5.334425	0.620429	-0.363628
	1	2.879845	2.510521	-2.582176
	1	3.904213	1.210739	-1.950562
	1	2.378771	0.821625	-2.761285
	1	2.886861	3.878194	0.202673
	1	2.395404	2.974331	1.642389
	1	3.921194	2.583249	0.833706
	1	1.435274	-1.347368	3.758971
	1	3.010319	-1.009267	3.019311
	1	1.925646	0.327818	3.444048
	1	3.401191	-3.374428	-2.211441
	1	3.609796	-1.911142	-1.227599
	1	3.881142	-3.508439	-0.510638

	1	-0.593842	-1.852618	-1.527621
	1	0.863276	-0.974490	-2.031132
	1	0.378182	-2.443311	-2.896176
	1	-1.163253	0.461558	-2.120145
	1	-0.491166	1.813907	-3.046347
	1	-2.089751	1.964068	-2.299082
B				
	14	-2.610432	0.951965	-0.490345
	14	-2.664637	-1.389449	-0.509226
	8	-1.824399	1.361915	0.940646
	14	-0.228764	1.339944	1.320843
	14	0.275458	-1.683306	0.439005
	8	0.537401	2.507981	0.456738
	14	2.036658	2.672928	-0.245246
	8	-1.067752	-1.897755	-0.468831
	8	1.563967	-2.070166	-0.493689
	14	3.195339	-2.261640	-0.226424
	8	0.427367	-0.103168	0.873172
	6	-4.305444	1.752734	-0.440045
	6	-1.597518	1.596904	-1.937034
	6	-0.012227	1.599020	3.140161
	6	2.161562	4.418050	-0.901633
	6	2.271779	1.420768	-1.620241
	6	-3.442716	-2.129946	-2.046698
	6	-3.533636	-2.029420	1.032181
	6	0.220636	-2.735436	1.970413
	6	3.796851	-0.951267	0.970649
	6	4.060150	-2.142746	-1.877102
	1	3.072408	2.448420	0.802163
	1	3.414542	-3.606733	0.372595
	1	-4.212406	2.842626	-0.391058

	1	-4.886394	1.500862	-1.333875
	1	-4.870933	1.423333	0.437105
	1	-0.626755	1.089014	-1.971004
	1	-2.105161	1.417920	-2.891198
	1	-1.410895	2.671580	-1.835464
	1	-0.427497	2.561660	3.450450
	1	-0.516735	0.810814	3.706980
	1	1.049697	1.582754	3.404388
	1	3.137906	4.594924	-1.364655
	1	1.391617	4.592698	-1.660420
	1	2.022880	5.154417	-0.105117
	1	3.323835	1.377070	-1.925823
	1	1.965816	0.420398	-1.293428
	1	1.677548	1.685567	-2.501145
	1	-3.398441	-3.223452	-2.011646
	1	-4.494467	-1.835302	-2.133275
	1	-2.921029	-1.801152	-2.950585
	1	-3.127549	-1.558653	1.934430
	1	-4.606072	-1.807070	0.998287
	1	-3.415077	-3.114174	1.129994
	1	-0.652111	-2.489028	2.584095
	1	1.113427	-2.583626	2.586627
	1	0.163357	-3.797256	1.713268
	1	4.865432	-1.070071	1.179489
	1	3.639727	0.053005	0.563588
	1	3.261513	-1.004546	1.924928
	1	3.668985	-2.886599	-2.577134
	1	3.904909	-1.152800	-2.317743
	1	5.137915	-2.305217	-1.773507
C				
	14	2.876337	0.248486	-0.172505

	14	0.740409	2.314870	-0.906612
	8	2.123896	-0.345264	1.181698
	14	0.812093	-1.286726	1.482392
	14	-1.145942	1.134175	1.186529
	8	0.773714	-2.520021	0.399594
	14	-0.185592	-2.968045	-0.885310
	8	-0.011519	2.141946	0.564624
	8	-2.413290	1.118306	0.148042
	14	-3.874920	0.373642	-0.114749
	8	-0.564450	-0.404246	1.278495
	8	1.759726	1.024189	-1.121207
	6	4.175009	1.444514	0.426731
	6	3.572900	-1.144686	-1.190803
	6	0.773415	-4.195935	-1.919151
	6	-0.661552	-1.454327	-1.880523
	6	1.721489	3.898376	-0.836542
	6	-0.506801	2.303382	-2.287879
	6	-1.648772	1.721301	2.870084
	6	-3.823297	-1.378317	0.541411
	6	-4.199004	0.417015	-1.955362
	6	0.918954	-1.942062	3.208910
	1	-1.407393	-3.629650	-0.355650
	1	-4.922512	1.144613	0.607085
	1	3.742528	2.159461	1.134123
	1	4.979983	0.913940	0.945283
	1	4.617087	2.006519	-0.402157
	1	4.098566	-0.763605	-2.071838
	1	4.271556	-1.751495	-0.606970
	1	2.767143	-1.801820	-1.532672
	1	0.142717	-4.605254	-2.715470
	1	1.645063	-3.729515	-2.388731

	1	1.127647	-5.029982	-1.306298
	1	-1.234132	-1.726114	-2.774688
	1	0.231028	-0.901390	-2.197816
	1	-1.267533	-0.772578	-1.273369
	1	2.377458	3.916084	0.039110
	1	2.344677	4.011338	-1.729536
	1	1.056948	4.765846	-0.773825
	1	-0.019577	2.442315	-3.258218
	1	-1.055659	1.357243	-2.310716
	1	-1.238071	3.106406	-2.150496
	1	-2.082227	2.724030	2.820290
	1	-2.394102	1.048200	3.306098
	1	-0.788744	1.755469	3.545560
	1	-4.795423	-1.870080	0.429254
	1	-3.077900	-1.974330	0.004439
	1	-3.556181	-1.398441	1.603296
	1	-3.441382	-0.165757	-2.490120
	1	-4.161197	1.443043	-2.333833
	1	-5.181800	0.000265	-2.198637
	1	1.005828	-1.124560	3.930611
	1	1.794471	-2.587941	3.320146
	1	0.029071	-2.526723	3.458089
D				
	14	1.421323	1.402239	-0.729564
	14	2.664328	0.295026	0.917878
	8	-0.202778	1.436110	-0.321257
	14	-1.574034	2.239646	-0.767848
	14	1.591208	-2.415227	0.269495
	8	-2.832745	1.287391	-0.292730
	14	-2.761002	-0.082289	0.681465
	14	-1.375795	-1.661283	-0.354372

	8	2.808784	-1.329981	0.509622
	8	0.209909	-1.519799	0.161894
	6	1.995047	3.191174	-0.912530
	6	-4.511573	-0.757507	0.783871
	6	1.633510	0.538969	-2.387077
	6	-1.668299	3.897244	0.074753
	6	-2.162120	0.433778	2.386418
	6	4.410643	0.986782	0.950225
	6	1.869787	0.436260	2.614412
	6	1.902967	-3.388898	-1.289502
	6	-1.954897	-3.412843	0.044883
	6	-1.445425	-1.415349	-2.218420
	1	-1.604173	2.383032	-2.245961
	1	1.498275	-3.321189	1.440062
	1	1.849072	3.757373	0.013866
	1	1.440317	3.701413	-1.709588
	1	3.059433	3.238110	-1.169491
	1	-4.882452	-1.061614	-0.200209
	1	-4.553737	-1.629980	1.445437
	1	-5.194314	0.001564	1.179464
	1	2.687763	0.541008	-2.687142
	1	1.300739	-0.501761	-2.326474
	1	1.055143	1.035589	-3.174716
	1	-2.626386	4.386037	-0.126549
	1	-1.574384	3.771218	1.158732
	1	-0.867723	4.564646	-0.260711
	1	-2.868953	1.131186	2.849805
	1	-2.043400	-0.425059	3.056110
	1	-1.191157	0.932810	2.301665
	1	4.886632	0.911128	-0.032851
	1	4.407226	2.042396	1.244089

	1	5.030351	0.436080	1.665492
	1	2.510239	0.001558	3.389283
	1	1.677349	1.482555	2.877384
	1	0.911311	-0.093177	2.622785
	1	2.003494	-2.724577	-2.153875
	1	1.085947	-4.090486	-1.491487
	1	2.828161	-3.967823	-1.204784
	1	-1.875802	-3.624590	1.116625
	1	-3.001261	-3.556206	-0.247813
	1	-1.358667	-4.163039	-0.488056
	1	-2.458972	-1.606904	-2.589185
	1	-1.175741	-0.391458	-2.499036
	1	-0.761928	-2.100840	-2.734071
E				
	14	-1.173147	-1.560975	0.718331
	14	-2.855810	-0.569029	-0.582494
	8	0.138304	-1.786220	-0.301734
	14	1.669989	-2.377550	-0.165726
	14	-2.177329	2.364057	0.090052
	8	2.766359	-1.165006	-0.378451
	14	3.165675	0.232715	0.420511
	14	0.854252	2.076062	-0.480127
	8	-2.655005	1.075855	-0.815833
	8	-0.553716	2.297311	0.359661
	8	1.838150	1.206822	0.523294
	6	-0.614911	-0.631207	2.253095
	6	-1.794785	-3.260050	1.253575
	6	1.958150	-3.655560	-1.482016
	6	4.491689	1.071052	-0.586940
	6	-2.837447	-1.363496	-2.281240
	6	-4.524058	-0.855656	0.243827

	6	-3.027783	2.359366	1.746267
	6	1.630924	3.742623	-0.796784
	6	0.529500	1.127217	-2.052797
	6	3.697137	-0.166834	2.160359
	1	1.834770	-2.932288	1.206827
	1	-2.490392	3.578890	-0.696240
	1	0.201933	-1.182893	2.735255
	1	-1.429748	-0.552582	2.982345
	1	-0.253695	0.374858	2.017554
	1	-2.100930	-3.866893	0.394743
	1	-1.007497	-3.805586	1.786960
	1	-2.653799	-3.171624	1.928265
	1	2.976272	-4.052420	-1.434068
	1	1.812859	-3.209316	-2.470738
	1	1.256222	-4.488688	-1.379641
	1	4.145040	1.242679	-1.612103
	1	4.762567	2.039495	-0.153886
	1	5.395826	0.457005	-0.642651
	1	-1.865759	-1.220707	-2.763525
	1	-3.025291	-2.440877	-2.215214
	1	-3.607391	-0.921546	-2.922339
	1	-5.324945	-0.379948	-0.332445
	1	-4.552099	-0.446279	1.259475
	1	-4.745834	-1.926912	0.308258
	1	-4.116191	2.383110	1.631904
	1	-2.763054	1.456278	2.307574
	1	-2.726186	3.221493	2.348592
	1	1.808493	4.265231	0.148187
	1	2.591214	3.642115	-1.314204
	1	0.980646	4.371073	-1.414074
	1	-0.228255	1.621843	-2.670122

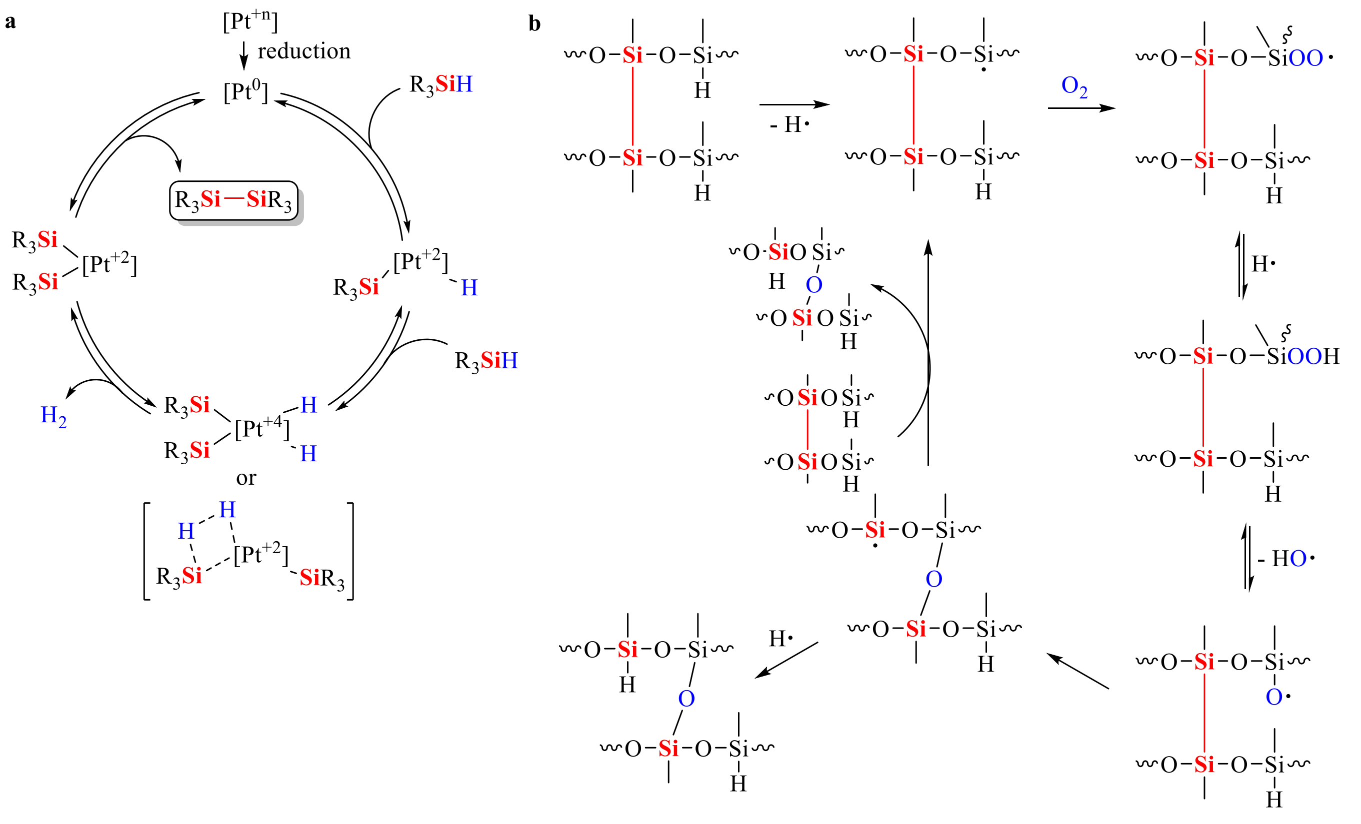
	1	0.177389	0.117183	-1.815708
	1	1.444752	1.030087	-2.648166
	1	2.877783	-0.639734	2.711850
	1	3.981070	0.740559	2.701961
	1	4.550203	-0.852356	2.168140
F				
	14	-3.316476	-0.002721	0.403763
	14	-1.094572	2.123651	0.471505
	8	-2.731321	-0.880981	-0.869708
	14	-1.318676	-1.453852	-1.484098
	14	1.239800	1.544321	-1.444114
	8	-0.158360	-1.384393	-0.305656
	14	1.114554	-2.200384	0.364665
	14	3.206375	0.176367	0.463624
	8	-0.315084	1.660901	-0.916656
	8	2.254907	1.387652	-0.146533
	8	2.471936	-1.280631	0.212378
	8	-2.619694	1.496624	0.423665
	6	0.751575	-2.491073	2.173031
	6	-1.241413	3.979973	0.507800
	6	-0.161804	1.440021	1.937363
	6	1.696023	3.099031	-2.361071
	6	3.437813	0.471420	2.289292
	6	4.821374	0.145189	-0.465013
	6	-1.612112	-3.217936	-2.014024
	6	1.443191	-3.799915	-0.536050
	6	-2.901574	-0.899875	1.989636
	6	-5.143154	0.221720	0.143384
	1	-0.908506	-0.622740	-2.632139
	1	1.358828	0.346281	-2.304299
	1	0.593912	-1.551617	2.713279

	1	-0.148849	-3.101929	2.299339
	1	1.585423	-3.014425	2.652563
	1	-1.753495	4.339771	-0.389669
	1	-1.810347	4.315003	1.380565
	1	-0.252883	4.450153	0.547572
	1	0.768570	1.993903	2.096794
	1	-0.755321	1.468766	2.856769
	1	0.103446	0.398020	1.724210
	1	1.007944	3.278360	-3.192638
	1	1.650620	3.964649	-1.691991
	1	2.712430	3.036463	-2.762246
	1	2.488153	0.397609	2.828276
	1	3.853175	1.467192	2.475232
	1	4.125592	-0.266746	2.714461
	1	5.483565	-0.640885	-0.089452
	1	4.642704	-0.048416	-1.528002
	1	5.344283	1.102809	-0.378614
	1	-1.855039	-3.849658	-1.152616
	1	-2.460320	-3.258545	-2.704881
	1	-0.742564	-3.648653	-2.519528
	1	1.652476	-3.616713	-1.595038
	1	0.600045	-4.494085	-0.468375
	1	2.322081	-4.292049	-0.106962
	1	-1.822466	-1.078396	2.050397
	1	-3.200247	-0.322282	2.870320
	1	-3.404023	-1.871979	2.033899
	1	-5.327012	0.758505	-0.791975
	1	-5.653512	-0.744492	0.085579
	1	-5.591312	0.798096	0.958340
G				
	6	-0.899621	-1.992027	1.755018

	14	-0.729360	-1.177044	0.071250
	6	-1.872525	-2.017573	-1.156705
	14	-0.729595	1.176948	0.071352
	6	-1.872512	2.017249	-1.156995
	6	-0.900932	1.991564	1.755196
	8	0.866979	-1.327453	-0.459042
	14	1.842662	0.000225	-0.688578
	8	0.866863	1.327736	-0.458259
	6	3.232726	0.000295	0.546973
	1	-0.671803	-3.061272	1.691367
	1	-1.918937	-1.886129	2.141808
	1	-0.215122	-1.545788	2.483363
	1	-2.918316	-1.925794	-0.843882
	1	-1.777835	-1.578855	-2.154570
	1	-1.635925	-3.084009	-1.234021
	1	-1.636942	3.083988	-1.233265
	1	-1.776348	1.579386	-2.155097
	1	-2.918519	1.924115	-0.845314
	1	-1.920116	1.884075	2.141910
	1	-0.674705	3.061156	1.691789
	1	-0.215828	1.546149	2.483472
	1	2.355025	0.000650	-2.076020
	1	3.866198	-0.884191	0.428715
	1	3.860582	0.889494	0.434174
	1	2.833133	-0.004099	1.566712
H				
	6	2.165997	-0.582081	1.792309
	14	1.512098	-0.677120	0.048592
	6	2.617841	-1.655620	-1.080209
	14	-1.512298	-0.676683	0.048566
	6	-2.166605	-0.581644	1.792130

	6	-2.618239	-1.654674	-1.080469
	8	1.337248	0.867447	-0.543029
	14	0.000318	1.824364	-0.739198
	8	-1.336890	0.867920	-0.542796
	6	0.000697	3.177394	0.536808
	8	-0.000211	-1.364248	0.067542
	1	2.252842	-1.578011	2.237790
	1	3.152317	-0.108395	1.820848
	1	1.493235	0.009542	2.422798
	1	2.753939	-2.674356	-0.703974
	1	3.604126	-1.189334	-1.165388
	1	2.185315	-1.719968	-2.082829
	1	-2.253716	-1.577563	2.237577
	1	-1.494074	0.009964	2.422871
	1	-3.152911	-0.107892	1.820257
	1	-2.754484	-2.673501	-0.704528
	1	-2.185795	-1.718805	-2.083138
	1	-3.604458	-1.188212	-1.165459
	1	0.000335	2.368364	-2.112419
	1	0.887897	3.810790	0.441138
	1	-0.885880	3.811622	0.440906
	1	0.000362	2.748702	1.544951

5. Mechanisms of the Si-O-Si cross-links formation



Scheme 4S. Proposed catalytic cycle of Si-Si coupling [5–10] (**a**) and mechanism of autoxidation [11] (**b**).

6. Swelling and density measurements

The density determination of the cross-linked polysiloxanes. The weight of the empty pycnometer, previously washed out by rinsing with distilled water and thoroughly dried, is determined. The pycnometer is filled with distilled water up to the mark and the mass of the pycnometer with water (m_1) is measured. The mass of a solid polymer (m) (total weight of around 10 pellets) is determined. The solid polymer is immersed in the pycnometer with water (all weighed pellets) so that no air bubbles remained on the pellets. Excess water is removed using filter paper (up to the mark) and the mass of the pycnometer with water and solid (m_2) is determined. The density of the solid polymer (ρ) is calculated by using the following equation:

$$\rho = \frac{m}{m_1 + m - m_2} \cdot \rho_0. \tag{1}$$

where ρ_0 – the density of distilled water corresponding to the air temperature in the room (at RT ρ_0 = 0.997 g/mL).

The density of the cross-linked **PMHSs** with *cis*-[$PtCl_2(BnCN)_2$] (**1**) is 1.04±0.01 g/mL, with Karstedt's catalyst (**2**) is 1.05±0.01 g/mL, respectively.

Swelling measurements. A typical sample of obtained cross-linked silicone rubber (cylindrical disk of 10 mm diameter and 1 mm thickness) is weighed for evaluating the initial dry weight (m_{unex}). The solvent (125 ml of toluene) is added to a round bottom flask, which is attached to a Soxhlet extractor and reflux condenser. The sample is loaded into the thimble, which is placed inside the Soxhlet extractor. The solvent is refluxed using the heating element. The condensate drips into the Soxhlet extractor containing the silicone sample, which swells by toluene. The process of swelling is carried out for 12 h. Then the sample is plunged into a sealed bottle with another toluene (50 mL) and wait for 12 h. The sample is extracted and gently wiped to remove the liquid solvent, which is present on the sample surface and immediately weighed (m_s). The sample is then dried overnight at RT and then 2 h at 60 C under reduced pressure and reweighed (m_{ex}). The soluble fraction (w_{sol}) and the volume fraction of the polymer in the swollen sample (υ) are calculated as follows:

$$w\ (\%) = \frac{m_{unex} - m_{ex}}{m_{unex}} \cdot 100, \tag{2}$$

$$v = \left[1 + \frac{m_s - m_{ex}}{m_{ex}} \cdot \frac{\rho_p}{\rho_s}\right]^{-1}\ , \tag{3}$$

where ρ_s and ρ_p are the solvent (toluene, 0.87 g/mL) and polymers (cross-linked **PMHS** with *cis*-$[PtCl_2(BnCN)_2]$, 1.04 g/mL; cross-linked **PMHS** with Karstedt’s catalyst, 1.05 g/mL) densities, respectively. The swelling experiments are carried out three times for each test.

7. Notes and references

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