Supporting Information for

Synthesis of (*E*)-1,4-disilsesquioxylsubstituted but-1-en-3-ynes via platinum-catalyzed dimerization of ethynylsiloxysilsesquioxanes

Patrycja Żak,^{a,*} Małgorzata Bołt,^a Beata Dudziec^{a,b} and Maciej Kubicki^a

 ^a Department of Organometallic Chemistry, Faculty of Chemistry, Adam Mickiewicz University in Poznań, Umultowska 89b, 61-614 Poznań, Poland, e-mail: pkw@amu.edu.pl
^b Centre for Advanced Technologies, Adam Mickiewicz University in Poznań, Umultowska 89c, 61-614 Poznań, Poland

1. NMR spectra of all isolated compounds	S2
1.1. NMR spectra of compounds A-C	S2
1.2. NMR spectra of platinum complex I	S5
1.3. NMR spectra of isolated products H-K	S6
2. SambVca2.0 calculation	S12
3. UV-Vis absorption spectra of G, enyn-SiMe3 and products H-K in DCM solution	S13
4. X-ray analysis	S14
5. References	S16

1. NMR spectra of all isolated compounds



1.1. NMR spectra of compounds A-C

Fig S1. ¹H NMR (400 MHz, CDCl₃) of compound **A**. Signal at 1.50 ppm derives from water from CDCl₃.



Fig S2. ^{13}C NMR (100 MHz, CDCl_3) of compound A

Compound B



Fig S3. ¹H NMR (400 MHz, CDCl₃) of compound B.



Fig S4. 13 C NMR (100 MHz, CDCl₃) of compound **B**.



Fig S5. ¹H NMR (400 MHz, CDCl₃) of compound **C**.



Fig S6. $^{\rm 13}C$ NMR (100 MHz, CDCl₃) of compound $\boldsymbol{C}.$

1.2. NMR spectra of platinum complex I



Fig S8. ¹³C NMR (100 MHz, CDCl₃) of complex I.



Fig S9. ²⁹Si NMR (79 MHz, CDCl₃) of complex I.

1.3. NMR spectra of isolated products H-K



Fig S10. ¹H NMR (400 MHz, CDCl₃) of product **H**. Signals at 0.00 ppm and 1.50 ppm derive from TMS and water from CDCl₃, respectively.

S6



Fig S11. 13 C NMR (100 MHz, CDCl₃) of product H.



Fig S12. ^{29}Si NMR (79 MHz, CDCl_3) of product H.



Fig S13. ¹H NMR (400 MHz, CDCl₃) of product I. Signal at 1.50 ppm derives from water from CDCl₃.



Fig S14. ¹³C NMR (100 MHz, CDCl₃) of product I.



100 80 60 40 20 0 -10 f1 (ppm) -90 -150 200 180 160 140 120 -30 -50 -70 -120 -180

Fig S15. 29 Si NMR (79 MHz, CDCl₃) of product I.



Fig S16. ¹H NMR (400 MHz, CDCl₃) of product J. Signal at 1.50 ppm derives from water from CDCl₃.





Fig S18. $^{\rm 29}Si$ NMR (79 MHz, CDCl₃) of product J.



Fig S19. ¹H NMR (400 MHz, CDCl₃) of product K.



Fig S20. $^{\rm 13}C$ NMR (100 MHz, CDCl_3) of product K.



Fig S21. ²⁹Si NMR (79 MHz, CDCl₃) of product K.

2. SambVca2.0 calculation



V Free	VB	Buried	V Total		V Exact	
82.0	g	97.5 179.5		,	1	L79.6
%V_Fre	e	%V_Bur			% Tot/Ex	
45.7		54.3			100.0	
Quadrant	V_f	V_b	V_t	%	V_f	%V_b
SW	19.4	25.5	44.9	4	3.2	56.8
NW	21.2	23.7	44.9	4	7.2	52.8
NE	16.3	28.6	44.8	3	6.2	63.8
SE	25.2	19.7	44.9	5	6.1	43.9

Fig S21. Steric map of platinum complex I and SambVca.2.0 calculation^[S1]

3. UV-Vis absorption spectra of G, enyn-SiMe₃ and products H-K in DCM solution



Fig S22. UV-VIS spectra of enyn-SiMe₃



Fig S23. UV-VIS spectra of ethynyl–POSS G



Fig S24. UV-VIS spectra of product H



Fig S25. UV-VIS spectra of product I



Fig S26. UV-VIS spectra of product J



Fig S27. UV-VIS spectra of product K

4. X-ray analysis

Diffraction data were collected by the ω -scan technique at room temperature (**A**, **B**) or at 100(1) K (**I**) on Rigaku XCalibur four-circle diffractometer with EOS CCD detector and graphite-monochromated MoK_{α} radiation (λ =0.71073 Å). The data were corrected for

Lorentz-polarization as well as for absorption effects.^[52] Precise unit-cell parameters were determined by a least-squares fit of 6596 (**A**), 4857 (**B**) and 12169 (**I**) reflections of the highest intensity, chosen from the whole experiment. The structures were solved with SHELXT-2013^[S3] and refined with the full-matrix least-squares procedure on F² by SHELXL-2013.^[S4] All non-hydrogen atoms were refined anisotropically, in (**I**) positions of hydrogen atoms in vinyl groups were found in difference Fourier maps, all other hydrogen atoms were placed in idealized positions and refined as 'riding model' with isotropic displacement parameters set at 1.2 (1.5 for CH₃) times U_{eg} of appropriate carrier atoms.

Crystal data: **A**: C₄₅H₃₇N, M_r = 591.75, monoclinic, P2₁/c, a = 24.9074(7) Å, b = 5.97709(17) Å, c = 23.3822(7) Å, β = 105.949(3)^o, V = 3347.00(17) Å³, Z = 4, F(000) = 1256, d_x = 1.174 g·cm⁻³, μ = 0.067 mm⁻¹. 24618 reflections collected up to 2 Θ = 25.0°, of which 5871 independent (R_{int} = 0.029), 4416 with I>2 σ (I). Final R(F) [I>2 σ (I)] = 0.045, wR(F²) [I>2 σ (I)] = 0.106, R(F) [all data] = 0.067, wR(F²) [all data] = 0.117, S = 1.05, max/min $\Delta \rho$ = 0.18/-0.19 e·Å⁻³.



Fig S28. A perspective view of the compound **A**; ellipsoids are drawn at the 50% probability level, hydrogen atoms are shown as spheres of arbitrary radii.

Crystal data: **B**: C₉₂H₇₂N₂, M_r = 1205.51, monoclinic, P2₁/c, a = 9.6590(2) Å, b = 18.2142(4) Å, c = 20.0321(4) Å, β = 97.331(2)^e, V = 3495.46(13) Å³, Z = 2, F(000) = 1276, d_x = 1.145 g·cm⁻³, μ = 0.065 mm⁻¹. 13666 reflections collected up to 2 Θ = 26.6°, of which 6730 independent (R_{int} = 0.019), 4763 with I>2 σ (I). Final R(F) [I>2 σ (I)] = 0.046, wR(F²) [I>2 σ (I)] = 0.105, R(F) [all data] = 0.069, wR(F²) [all data] = 0.119, S = 1.03, max/min $\Delta \rho$ = 0.13/-0.12 e·Å⁻³.



Fig S29. A perspective view of the compound **B**; ellipsoids are drawn at the 30% probability level; hydrogen atoms are shown as spheres of arbitrary radii. Inversion center lies in the middlepoint of the central C=C bond.

Crystal data: I: $C_{101}H_{90}N_2OPtSi_2$, $M_r = 1599.01$, monoclinic, $P2_1/n$, a = 15.0517(3) Å, b = 26.5860(5) Å, c = 19.6409(4) Å, $\beta = 92.6396(17)^{\circ}$, V = 7851.3(3) Å³, Z = 4, F(000) = 3296, $d_x = 1.353$ g·cm⁻³, $\mu = 1.870$ mm⁻¹. 35394 reflections collected up to $2\Theta = 28.5^{\circ}$, of which 16924 independent ($R_{int} = 0.029$), 13814 with $I > 2\sigma(I)$. Final R(F) [$I > 2\sigma(I)$] = 0.032, $wR(F^2)$ [$I > 2\sigma(I)$] = 0.061, R(F) [all data] = 0.047, $wR(F^2)$ [all data] = 0.067, S = 1.03, max/min $\Delta \rho = 1.09/-1.09$ e·Å⁻³.

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, Nos. CCDC-1855772 (**A**), CCDC-1855773 (**B**) and CCDC-1865768 (**I**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; e-mail: deposit@ccdc.cam.ac.uk, or www: www.ccdc.cam.ac.uk.

5. References

- ^[S1] a) A. Poater, B. Cosenza, A. Correa, S. Giudice, F. Ragone, V. Scarano, L. Cavallo, Eur. J. Inor. Chem., **2009**, 1759-1766; b) A. Poater, F. Ragone, S. Giudice, C. Costabile, R. Dorta, S. P. Nolan, L. Cavallo, Organometallics, **2008**, 27, 2679-2681; c) A. Poater, F. Ragone, R. Mariz, R. Dorta, L. Cavallo, Chem. Eur. J., **2010**, 16, 14348–14353.
- ^[S2] Agilent Technologies, CrysAlis PRO (Version 1.171.33.36d), Agilent Technologies Ltd, **2011**.
- ^[S3] G. M. Sheldrick, Acta Crystallogr., **2015**, A71, 3-8.
- ^[S4] G. M. Sheldrick, *Acta Crystallogr.*, **2015**, C71, 3-8.