

Supporting Information

for

A Stable Silylene with a σ^2 , π - Butadiene Ligand

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Experimental part

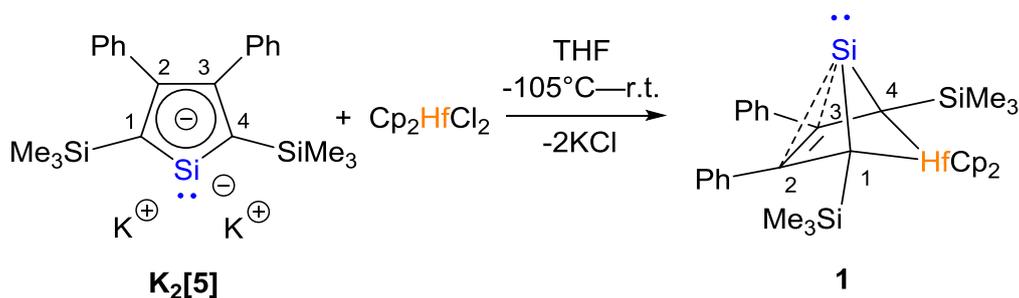
General. All reactions were performed under a controlled dry argon or nitrogen atmosphere using a high-vacuum line, standard Schlenk techniques, and a MBraun glovebox. The used glassware was dried in an oven at 140 °C and evacuated prior to use. Tetrahydrofuran (THF) was pre-dried over potassium hydroxide (KOH) and distilled. The solvents THF, diethylether (Et₂O), benzene and *n*-pentane were dried over sodium/potassium alloy and distilled under nitrogen prior to use. Toluene was dried over sodium and distilled under nitrogen prior to use. Deuterated benzene-d₆ was dried over sodium/potassium alloy, distilled and stored over molecular sieve (4 Å). All used standard chemicals were obtained from commercial suppliers and used as delivered if not mentioned otherwise. For new compounds, all available NMR spectra are provided.

NMR spectroscopy. NMR spectra were recorded on Bruker Avance 500 and Bruker Avance III 500 spectrometers. ¹H NMR spectra were calibrated against the residual proton signal of the solvent as internal reference (benzene-d₆: δ¹H(C₆D₅H) = 7.20; acetone-d₆: δ¹H((CD₃)(CD₂H)CO) = 2.05) and ¹³C{¹H} NMR spectra by using the central line of the solvent signal (benzene-d₆: δ¹³C(C₆D₆) = 128.0; acetone-d₆: δ¹³C((CD₃)₂CO) = 29.8, 206.3). The ²⁹Si{¹H} NMR inverse gated spectra were recorded with a relaxation delay D1 = 10 s. The ²⁹Si{¹H} INEPT spectra were recorded with the combination of D3 = 0.0086 s and D4 = 0.0313 s.

IR spectroscopy: IR spectra were recorded on a Bruker Tensor 27 instrument at room temperature.

Mass spectrometry: High resolution mass spectra were recorded on a Thermo SCIENTIFIC DFS.

The synthesis of silylene 1:



Scheme S1.

Silylene 1. A THF (6 mL) solution of hafnocene dichloride (200 mg, 0.447 mmol) was slowly added to a red-brown THF solution (10 mL) of $K_2[5]^{[1]}$ (203.3 mg, 0.447 mmol) at $-105^\circ C$. The reaction mixture was allowed to warm to room temperature after 0.5 h and then stirred for another 1.5 h to form a dark red solution. The solvent was removed under vacuum and the residue was re-dissolved in 10 mL pentane and the filtrate was concentrated to 3 mL. Another 1 mL THF was added to the red-brown solution and the mixture solution was kept at $-30^\circ C$ for one night to afford orange crystals of silylene **1**. (Yield: 85 mg (27.7 %)).

1H NMR (499.87 MHz, 305.0 K, C_6D_6): δ = 7.00–7.04 (m, 2H, Ph), 6.93–6.96 (m, 2H, Ph), 6.88–6.91 (m, 4H, Ph), 6.83–6.86 (m, 2H, Ph), 5.84 (s, 5H, Cp), 5.73 (s, 5H, Cp), 0.08 (s, 18H, $Si(CH_3)_3$).

$^{13}C\{^1H\}$ NMR (125.71 MHz, 305.0 K, C_6D_6): δ = 143.1 (2x C_{Ph}), 141.0 (Ph), 128.9 (Ph), 128.4 (Ph), 127.6 (Ph), 127.5 (Ph), 127.0 (Ph), 110.0 (2x C_{Si}), 105.0 (Cp), 104.2 (Cp), 4.2 ($Si(CH_3)_3$).

$^{29}Si\{^1H\}$ NMR (99.31 MHz, 305.0 K, C_6D_6): δ = -155.2 (silylene), -2.9 ($Si(CH_3)_3$).

HRMS (70 eV, Cl) m/z [M] $^+$ Calcd for $C_{32}H_{38}HfSi_3$: 686.1741 Found: 686.1739.

UV-vis (*n*-hexane solution) [nm]: λ = 252, 292(sh), 388.

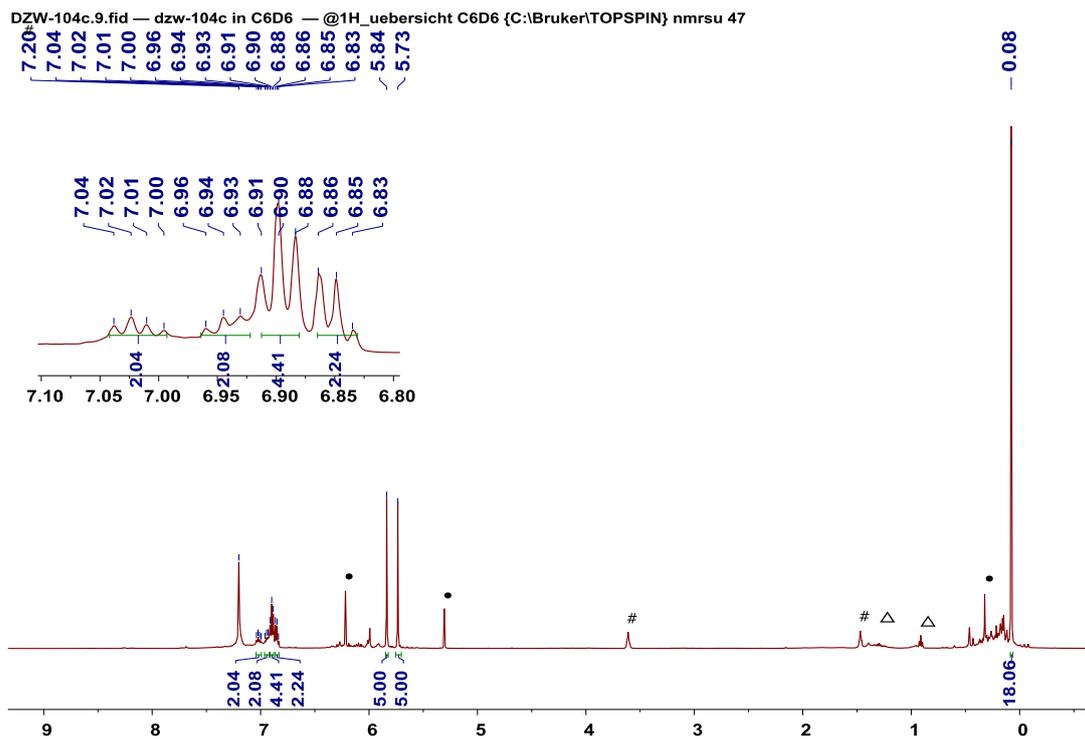


Figure S1a. ^1H NMR (499.87 MHz, 305.0 K, C_6D_6) spectrum of silylene **1**. (# THF, Δ pentane, \bullet not identified impurities)

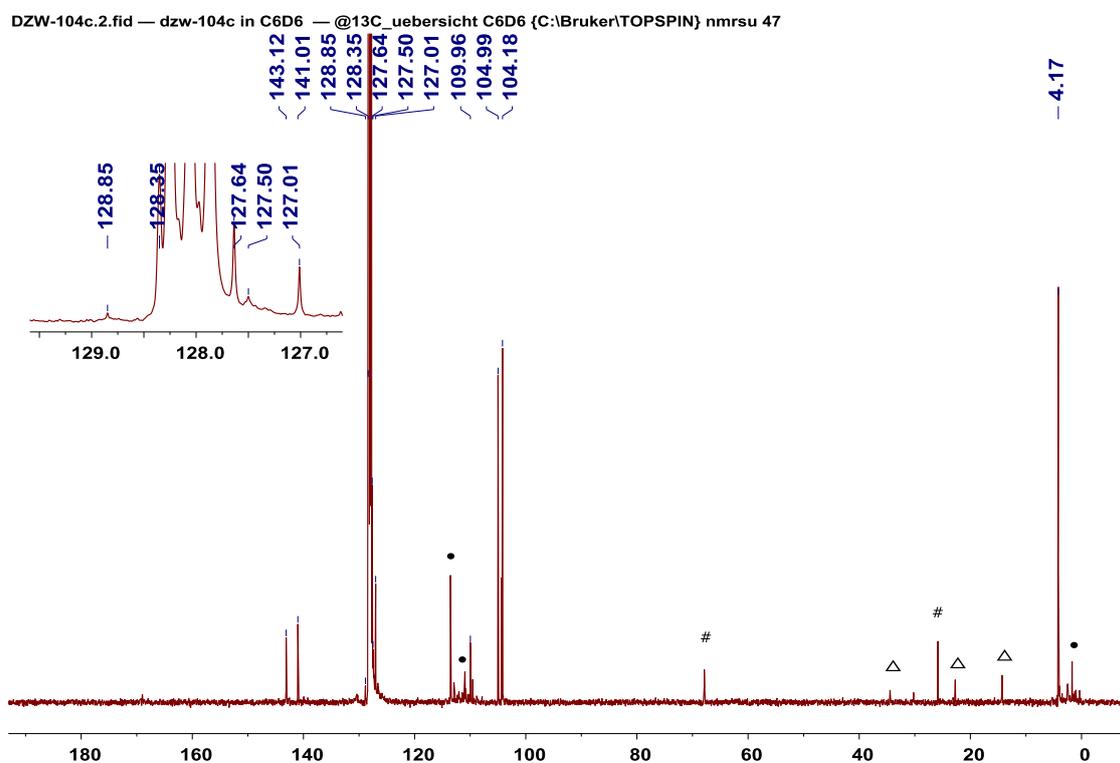


Figure S1b. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.71 MHz, 305.0 K, C_6D_6) spectrum of silylene **1**. (# THF, Δ pentane, \bullet not identified impurities)

DZW-104c.6.fid — dzw-104c in C6D6 — @29Si_zgig_400ppm C6D6 {C:\Bruker\TOPSPIN} nmrsu 47

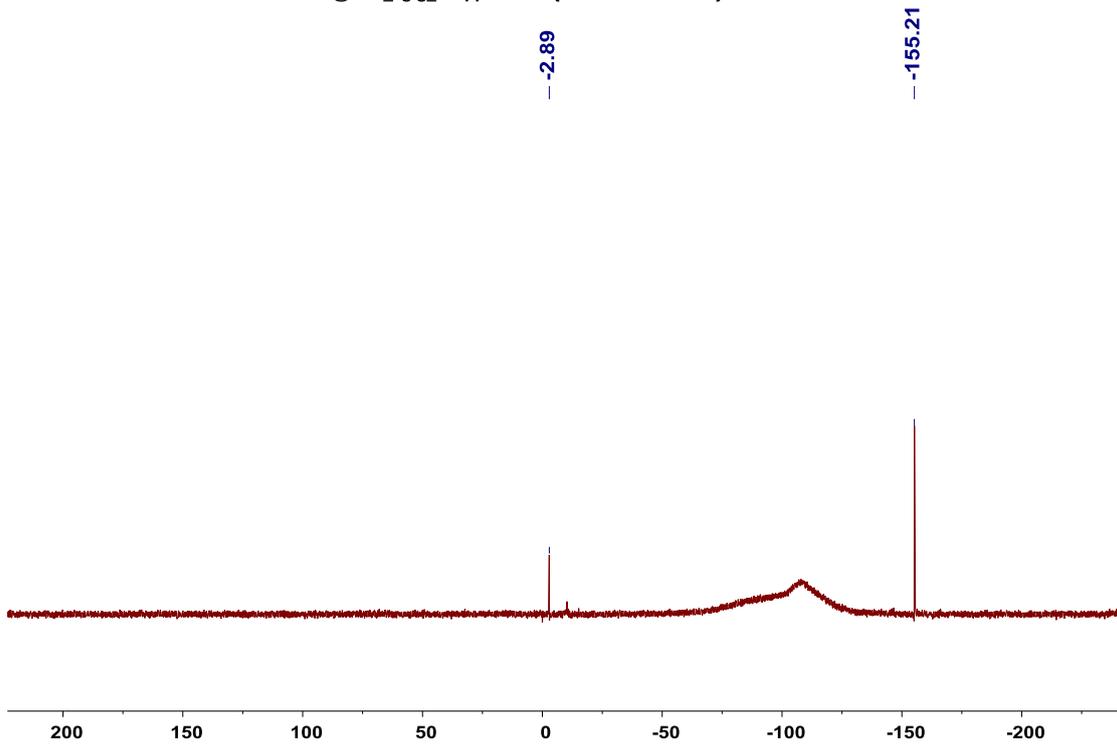


Figure S1c. $^{29}\text{Si}\{^1\text{H}\}$ NMR (99.31 MHz, 305.0 K, C_6D_6) spectrum of silylene **1**.

DZW-104c.7.ser — dzw-104c in C6D6 — @29Si_HMBCGP C6D6 {C:\Bruker\TOPSPIN} nmrsu 47

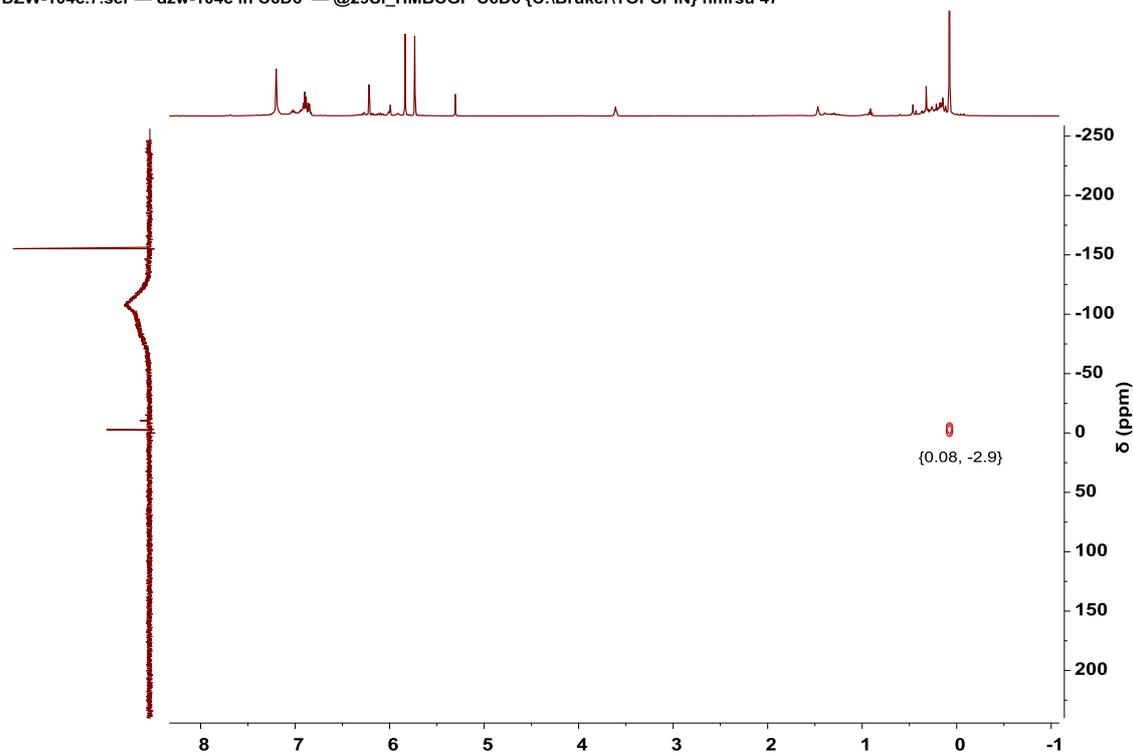


Figure S1d. $^1\text{H}^{29}\text{Si}$ HMBC NMR (99.31 MHz, 305.0 K, C_6D_6) spectrum of silylene **1**.

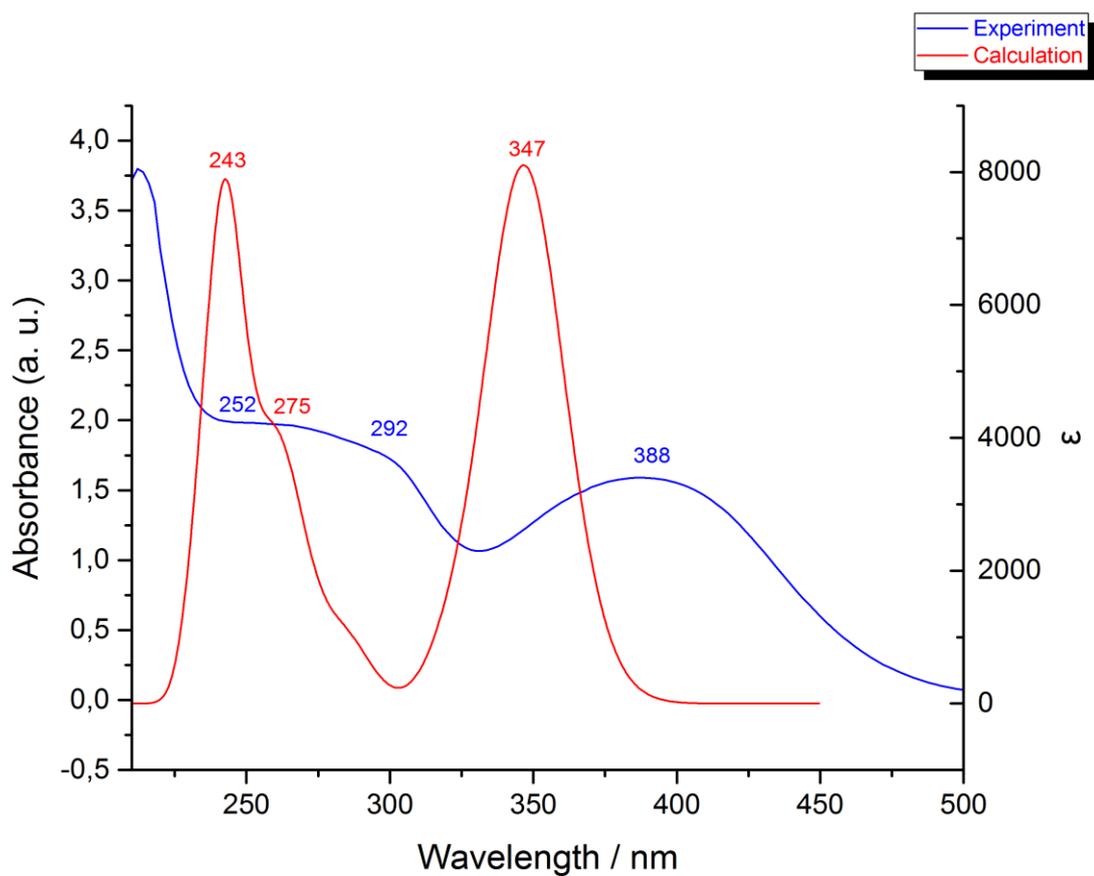
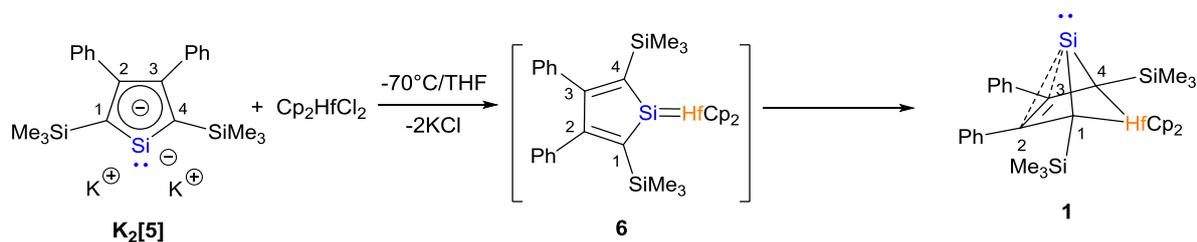


Figure S1e. UV-vis spectra of silylene **1** (in n-hexane). (blue trace, $\lambda = 200\text{-}500$ nm) and calculated gas phase UV-vis spectra of silylene **1** (red trace, $\lambda = 200\text{-}450$ nm, first 15 excited states were collected. For display of the calculated spectra a natural line width of 0.15 eV was assumed). (Calculated at TD/M062X/def2-tzvp //M062X/def2-tzvp)

Reaction of $K_2[5]$ with Cp_2HfCl_2 , NMR experiment.



Scheme S2.

A THF (2 mL) solution of hafnocene dichloride (200 mg, 0.447 mmol) was slowly added to a red-brown THF solution (5 mL) of $K_2[5]$ (203.3 mg, 0.447 mmol) at $-105^\circ C$. Then the reaction mixture was allowed to warm to $-70^\circ C$. The obtained solution was stirred for 10 min at $-70^\circ C$ and transferred in a J-Young NMR tube with acetone- d_6 capillary. The NMR tube was kept at $-70^\circ C$ and the NMR was measured at this temperature. Hafnium-silylene complex **6** was detected as a temperature sensitive intermediate in nearly quantitative yield. After that, the temperature was allowed to warm to $30^\circ C$. The ^{29}Si -NMR spectra showed no differences between $-70^\circ C$ and $-30^\circ C$. The residual reaction mixture was slowly warmed to room temperature and stirred for 2 h at this temperature. After removal of the THF solvent under reduced pressure, the red-brown solid residue was re-dissolved in C_6D_6 for NMR measurement. The final product silylene **1** was observed by NMR spectra in a suitable yield.

1H NMR (499.87 MHz, 203.0 K, acetone- d_6 /THF): δ = 6.97–6.69 (m, 10H, Ph), 6.4 (s, 10H, Cp), 0.23 (s, 18H, $Si(CH_3)_3$).

$^{13}C\{^1H\}$ NMR (125.71 MHz, 203.0 K, acetone- d_6 /THF): δ = 153.5 (2x C_{Ph}), 146.4 (2x C_{Si}), 140.3, 130.7, 129.3, 122.8, 120.0 (Ph), 108.0 (Cp), 2.71 ($Si(CH_3)_3$).

$^{29}Si\{^1H\}$ NMR (99.31 MHz, 203.0 K, acetone- d_6 /THF): δ = -14.5 ($CSi(CH_3)_3$), 164.5 ($Si=Hf$).

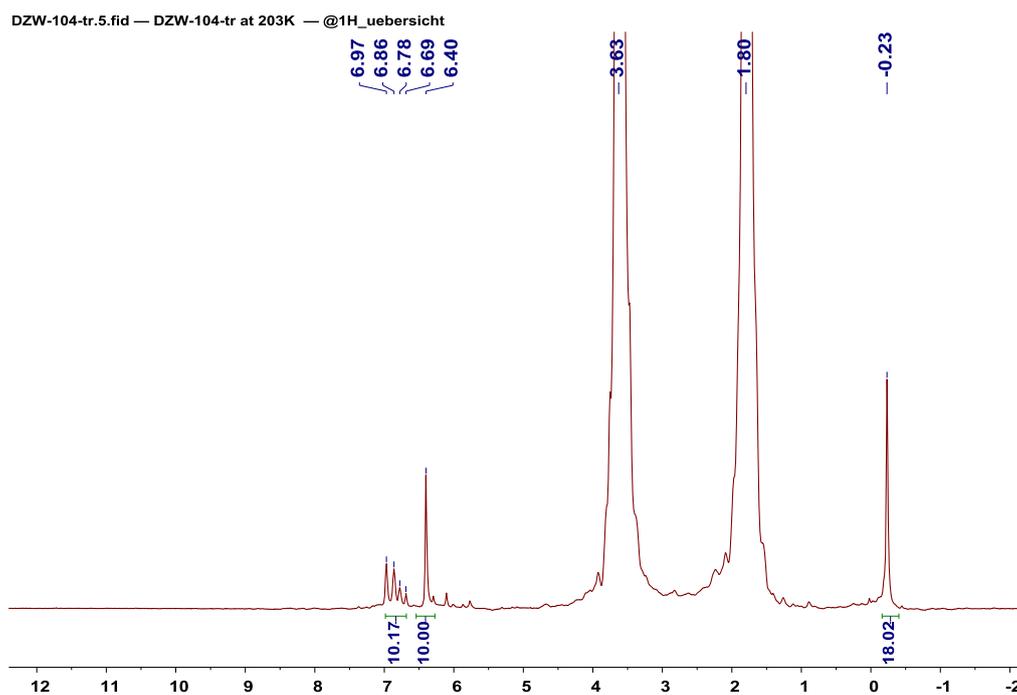


Figure S2a. ^1H NMR (499.87 MHz, 203.0 K, acetone- d_6 /THF) spectrum of hafnium-silylene complex **6**.

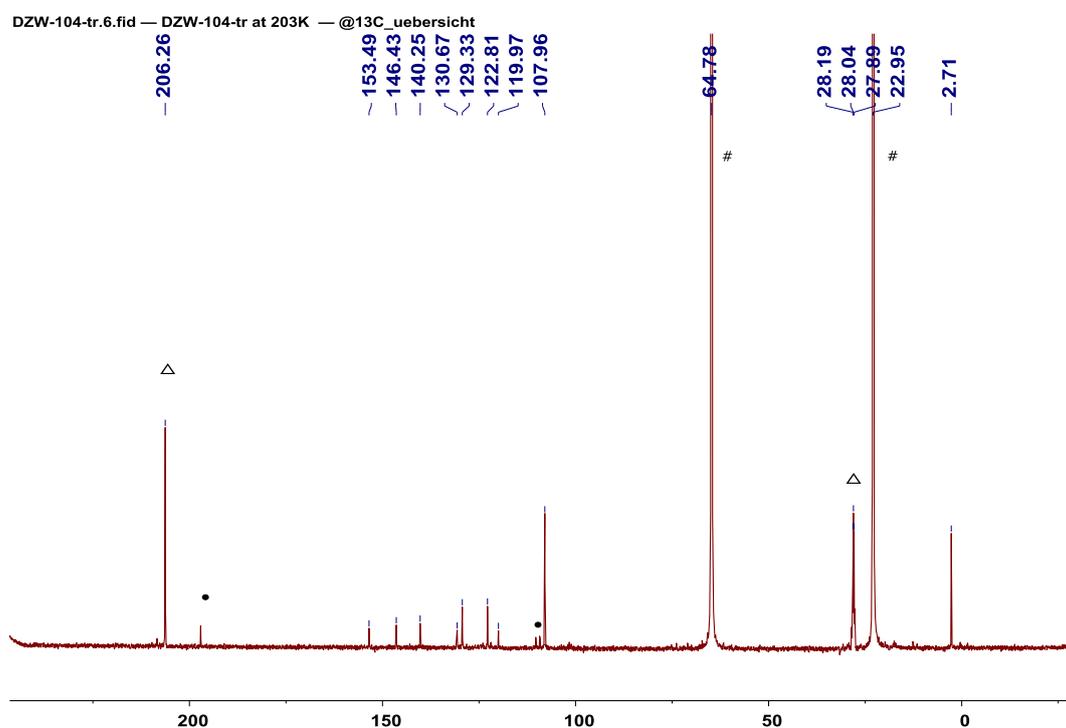


Figure S2b. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.71 MHz, 203.0 K, acetone- d_6 /THF) spectrum of hafnium-silylene complex **6**. (# THF, Δ acetone, \bullet not identified impurities)

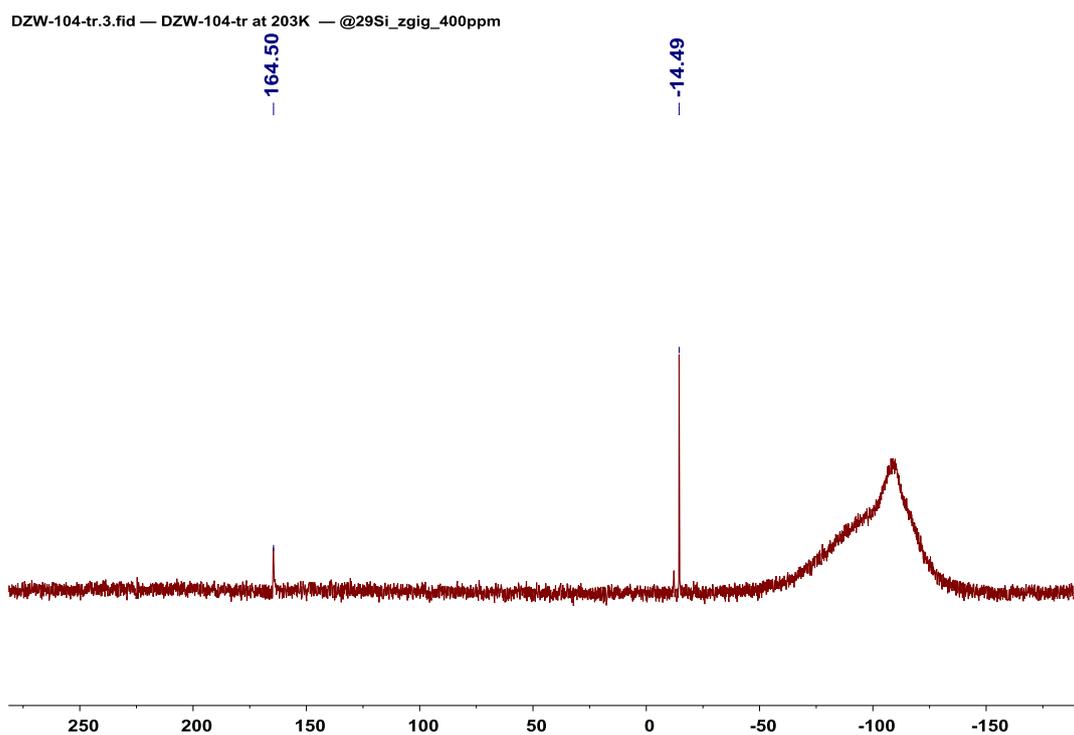


Figure S2c. $^{29}\text{Si}\{^1\text{H}\}$ NMR (99.31 MHz, 203.0 K, acetone- d_6 /THF) spectrum of hafnium-silylene complex **6**.

Details of X-ray Analysis of silylene 1

Single crystal X-ray data were measured on a Bruker AXS Apex II diffractometer (Mo-K α radiation, λ = 0.71073 Å, Kappa 4 circle goniometer, Bruker Apex II detector). The crystal was kept at 100.0 K during data collection. Absorption corrections based on symmetry-related measurements (multi-scan) were performed with the program SADABS.^[2] The structures were solved with the program SHELXS and refined with SHELXL.^[3] Pertinent data are summarized in Table S1.

Table S1. Crystal data and structure refinement for **1 THF**.

Identification code	dzw104	
Empirical formula	C ₃₆ H ₄₆ Hf O Si ₃	
Formula weight	757.49	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	a = 39.330(3) Å	α = 90°.
	b = 7.9638(6) Å	β = 93.2487 (15)°.
	c = 10.8208(8) Å	γ = 90°.
Volume	2624.7(4) Å ³	
Z	4	
Density (calculated)	1.487 Mg/m ³	
Absorption coefficient	3.216 mm ⁻¹	
F(000)	1536	
Crystal size	0.200 x 0.120 x 0.050 mm ³	
Theta range for data collection	1.885 to 34.971°	
Index ranges	-61 ≤ h ≤ 63, -12 ≤ k ≤ 12, -17 ≤ l ≤ 17	
Reflections collected	84101	
Independent reflections	14867 (R(int) = 0.0400)	
Observed reflections (I > 2(I))	14078	
Completeness to theta = 25.026°	100.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.8969 and 0.5133	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	14867 / 1 / 421	
Goodness-of-fit on F ²	1.095	
Final R indices (I > 2σ(I))	R1 = 0.0246, wR2 = 0.0505	
R indices (all data)	R1 = 0.0274, wR2 = 0.0512	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.077 and -3.114 e.Å ⁻³	

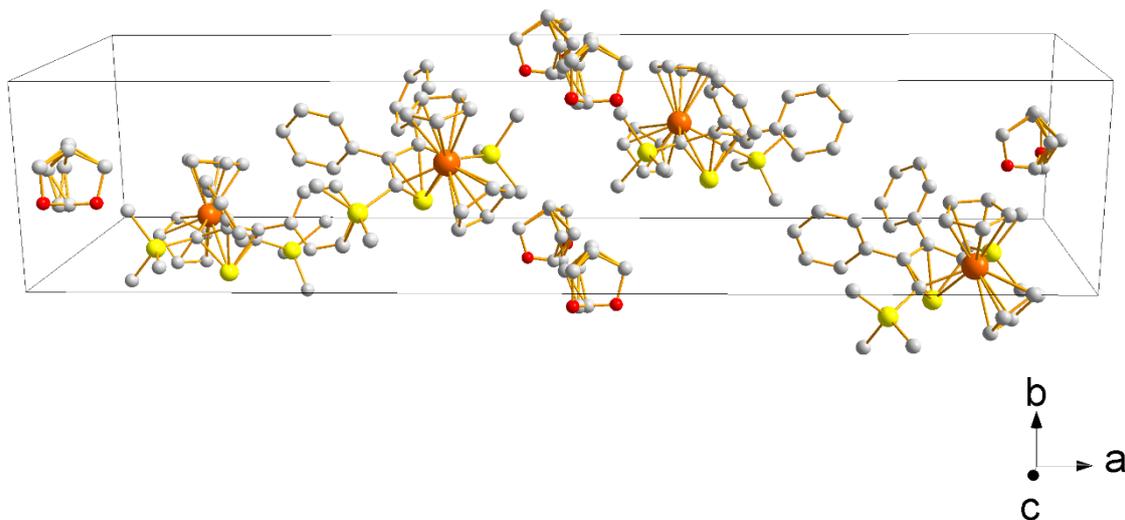


Figure S3. Packing diagram of silylene **1** THF in the crystal (view along the c-axis, hydrogen atoms are omitted for clarity and THF molecules are disordered).

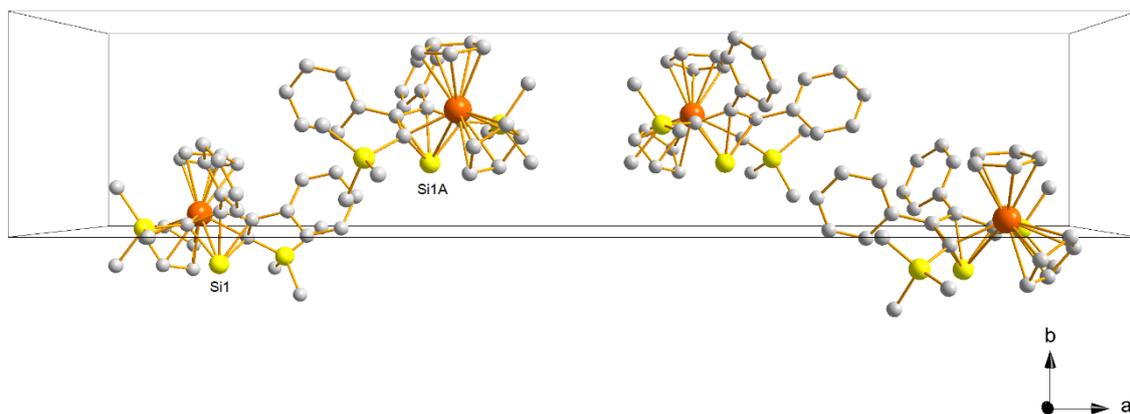
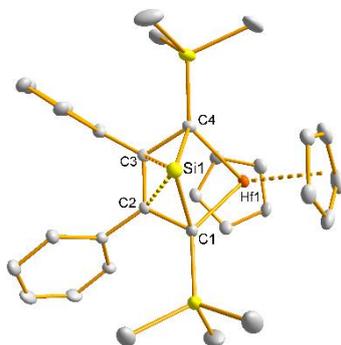
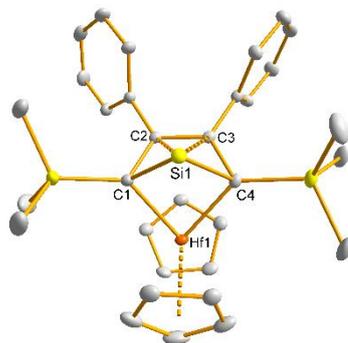


Figure S4. Packing diagram of silylene **1** in the crystal, the closest distance between Si1 and Si1A is 1002.2(13) pm. (view along the c-axis, hydrogen atoms and solvent molecules are omitted for clarity).

Top view



Side view



Flap angles

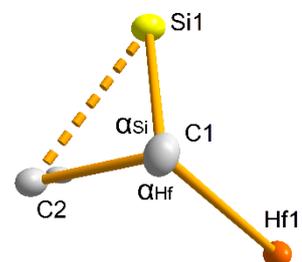


Figure S5. Molecular structure of silylene **1** in the crystal. Hydrogen atoms and solvent molecules are omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected atom distances [pm] and angles [°], mean values from three independent molecules: Si1 – C1 199.0(3), Si1 – C2 214.5(3), Si1 – C3 217.1(4), Si1 – C4 198.8(3), Si1 – Hf1 293.9(9), C1 – C2 148.8(4), C2 – C3 1423.6(4), C3 – C4 148.4(4), C1 – Hf1 221.7(3), C4 – Hf1 221.0(3), α (Ge) 94.9, α (Hf) 128.3.

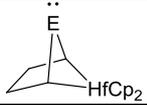
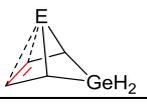
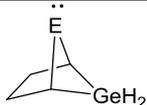
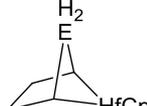
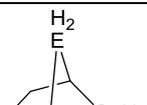
Computational Details

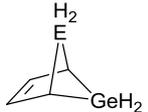
All quantum chemical calculations were carried out using the Gaussian09 package.^[4] The NBO analyses^[5] were performed with the Version 6.0 of the NBO program which was implemented in the G09 D.01 version of the Gaussian program.^[6] The AIMALL program was used to perform the QTAIM analysis.^[7]

The molecular structure optimizations were performed using the M06-2X functional^[8] along with the def2-tzvp basis set for all elements.^[9] For the elements Sn, Hf and Pb the corresponding pseudo potentials were applied.^[9] Every stationary point was identified by a subsequent frequency calculation as minimum (Number of imaginary frequencies (NIMAG): 0). The SCF energies (E(SCF)) and the absolute computed Gibbs free energies at T = 298.15 K and p = 0.101 MPa (1 atm) in the gas phase (G^{298}) are given in Table S1 for all optimized molecular structures obtained with this method. NMR chemical shift computations were performed using the GIAO method as implemented in Gaussian 09 and the M06-L functional along with the def2-tzvp basis set for molecular structures obtained at the M06-2X/def2-tzvp level of theory.^[10, 11]

For the NBO analysis, the M06-2X functional along with a def2-tzvp basis set/pseudo potentials was used to generate the density to be analysed. For the QTAIM analysis single point calculations using an all-electron basis set for Hf, Sn, Pb (ADZP)^[12] and for Ge, C, H the def2-tzvp basis set.^[13] Table S3 summarizes relevant data from these analysis. For comparison, data of related standard compound (Scheme S3) are given as well. Figure S6 shows the calculated molecular graphs for the carbene analogues **1a** – **4a**.

Table S2. Calculated absolute energies, E(SCF), and free enthalpies at 298 K, G^{298} for compounds of interest.

Compound	Method/basis set	E(SCF) [a.u.]	NIMAG, ZPVE [kJ mol ⁻¹]	G^{298} [a.u.]
1	M06-2X/def2tzvp	-2158.74158	0, 1583	-2158.20715
2		-3562.81533	0, 1298	-3562.38400
3		-2319.34129	0, 2031	-2318.64392
6		-2158.67347	0, 1585	-2158.14219
6(THF)		-2391.15617	0, 1902	-2390.51016
THF		-232.43049	0, 309	-232.34106
8		-477.63065	0, 178	-477.58975
1a		-879.14616	0, 617	-879.14616
2a		-2666.87326	0, 616	-2666.68247
3a		-804.10348	0, 614	-803.91435
4a		-782.61294	0, 610	-782.42660
				
E = Si		-880.50593	0, 678	-880.29010
E = Ge		-2668.04755	0, 677	-2667.83356
E = Sn		-805.27608	0, 673	-805.06237
E = Pb		-783.78053	0, 671	-783.56836
				
E = Si		-2522.45139	0, 218	-2522.39854
E = Ge		-4309.99300	0, 216	-4309.94215
E = Sn		-2447.22569	0, 216	-2447.17662
E = Pb		-2425.73575	0, 212	-2425.68800
				
E = Si		-2523.63096	0, 278	-2523.55622
E = Ge		-4311.17299	0, 275	-4311.10062
E = Sn		-2448.40602	0, 274	-2448.33519
E = Pb		-2426.91175	0, 273	-2426.84188
				
E = Si		-881.73532	0, 727	-881.50011
E = Ge		-2669.24390	0, 723	-2669.01105
E = Sn		-806.44405	0, 715	-806.21522
E = Pb		-784.90747	0, 710	-784.68156
				
E = Si		-2524.87378	0, 325	-2524.78120
E = Ge		-4312.38752	0, 320	-4312.29780
E = Sn		-2449.58837	0, 312	-2449.50263

E = Pb		-2428.04774	0, 308	-2427.96542
				
E = Si		-2523.65167	0, 261	-2523.58274
E = Ge		-4311.16588	0, 257	-4311.09981
E = Sn		-2448.37264	0, 249	-2448.31036
E = Pb		- not a stationary point -		

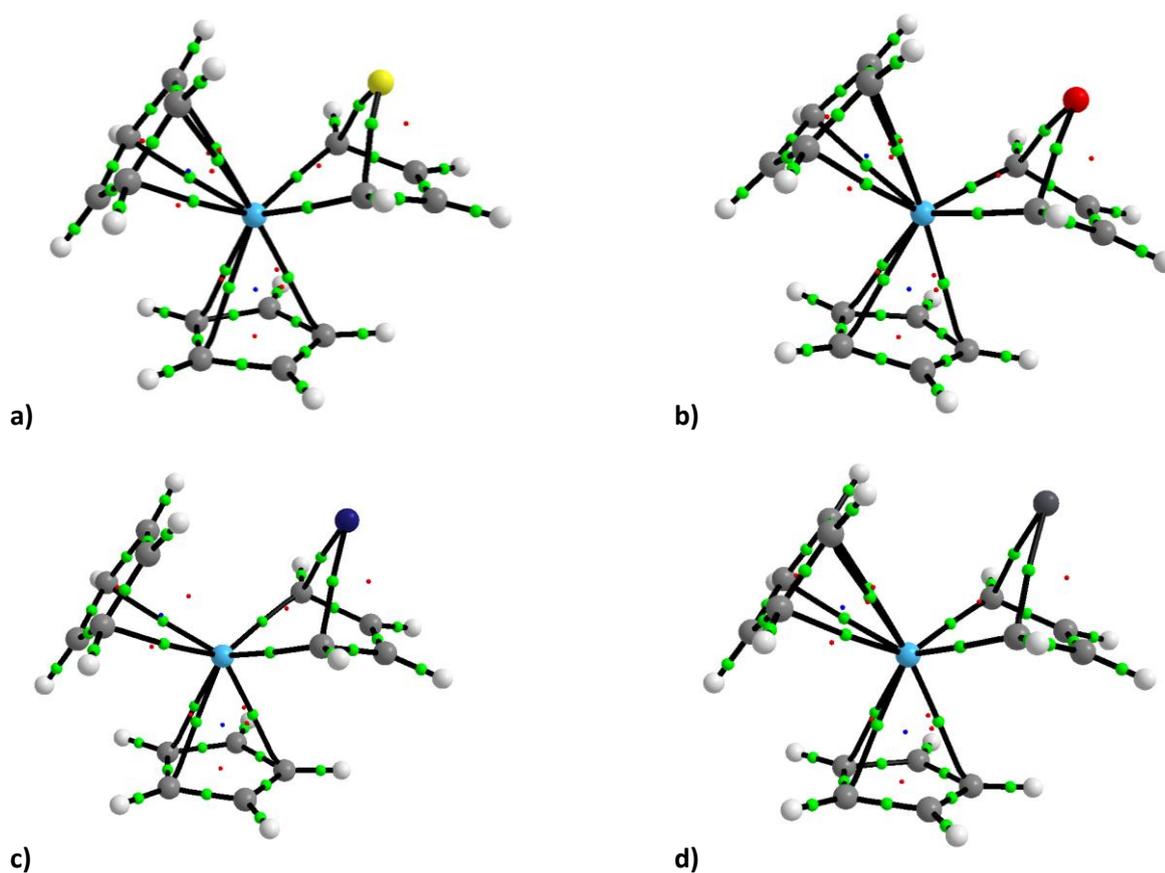
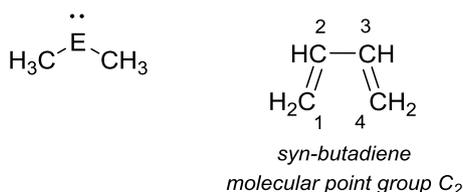


Figure S6: Molecular graphs of carbene analogues **1a** – **4a** based on QTAIM analysis (M062X/ADZP(Hf,Sn, Pb),def2tzvpp(Ge,Si,C,H)//M06-2X/def2-tzvp). Black lines indicate bond paths, green circles represent bond critical points, and small red circles are ring critical points. a) silylene **1a**, b) germylene **2a**, c) stannylene **3a**, d) plumbylene **4a**.



Scheme S3. Model compounds relevant for Table S3 (E = Si, Ge, Sn Pb).

Table S3. Relevant data from NBO and QTAIM analysis.

	1a E = Si	2a E = Ge	3a E = Sn	4a E = Pb	Me ₂ Si	Me ₂ Ge	Me ₂ Sn	Me ₂ Pb	<i>syn</i> - C ₄ H ₆
NBO									
C ¹ - C ² [pm]	145.8	145.6	145.7	145.2					132.8
WBI (C ¹ - C ²)	1.18	1.21	1.22	1.24					1.94
C ² - C ³ [pm]	141.2	141.8	141.8	142.1					146.9
WBI (C ² - C ³)	1.38	1.38	1.39	1.38					1.08
E - C ^{1/4} [pm]	201.8	213.6	232.3	242.9	189.9	200.3	220.0	228.8	
WBI (E - C ^{1/4})	0.58	0.54	0.50	0.49	0.80	0.75	0.73	0.75	
E - C ^{2/3} [pm]	209.5	219.4	240.4	250.0					
WBI (E - C ^{2/3})	0.30	0.27	0.27	0.24					
occupation (σ(E - C ¹)) [a.u.]	1.71	1.68	1.67	1.65	1.99	1.98	1.99	1.99	
occupation (π*(C ² - C ³)) [a.u.]	0.40	0.42	0.42	0.43					0.05
occupation (π(C ² - C ³))	1.66	1.68	1.70	1.69					1.95
occupation (np(E)) [a.u.]	0.30	0.27	0.24	0.23	0.04	0.04	0.03	0.02	
QTAIM									
C ¹ - C ²									
ρ [a.u.]	0.268	0.271	0.271	0.274					0.354
∇ ² ρ [a.u.]	-0.632	-0.654	-0.664	-0.672					-1.097
ε	0.167	0.143	0.126	0.133					0.298
C ² - C ³									
ρ [a.u.]	0.303	0.300	0.301	0.299					0.275
∇ ² ρ [a.u.]	-0.820	-0.816	-0.832	-0.815					-0.763
ε	0.242	0.218	0.200	0.210					0.051

References

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