Supplementary Information

Heterobimetallic Unsaturated Silicon Clusters (Siliconoids) with Transition Metal-Expanded Scaffolds

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KEYWORDS: siliconoids • heterobimetallic • low-valent • clusters • anions

Abstract: We report a heterobimetallical unsaturated silicon cluster (siliconoid) with a formally anionic Group 9 metal vertex (Ir) in close contact to the lithium counter-cation, thus constituting a rare example of transition metal-lithium interactions. The anionic cluster is obtained by reductive chloride elimination from the corresponding neutral siliconoid complex of iridium(I) chloride with lithium/naphtalene. The previously exohedral transition metal center is fully incorporated into the siliconoid cluster scaffold giving rise to an irida- heterosiliconoid reminiscent of the corresponding homonuclear Si_7 species. Despite the formal negative charge at the iridium center, the nucleophilic site is on one of the adjacent silicon vertices judging from the reactivity toward Group 4 metallocene dichlorides, Cp_2MCl_2 (M = Zr, Hf). Under elimination of LiCl, the Cp_2MCl moieties in the heterobimetallic products are installed as pending functionalities under retention of the literally uncompromised iridasiliconoid core.

DOI:

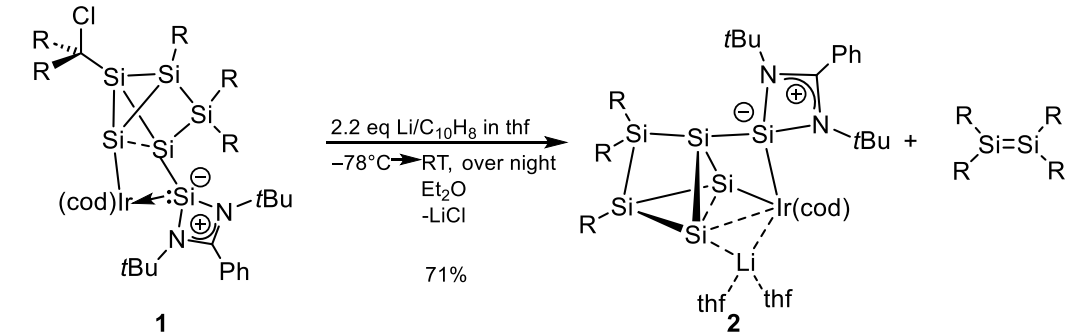
Content

1 Experimental Procedures

All manipulations were carried out under a protective atmosphere of argon, by using a glovebox or standard Schlenk techniques. Solvents were dried and degassed by reflux over sodium/benzophenone under argon. [D_6]-benzene (C_6D_6) was dried over potassium mirror and distilled under argon prior to use. NMR spectra were recorded on a Bruker Avance IV 400 NMR spectrometer (^{1}H = 400.13 MHz, ^{7}Li = 155.51 MHz, ^{13}C = 100.6 MHz, ^{29}Si = 79.5 MHz). The ^{1}H and ^{13}C{1H} NMR spectra were referenced to the residual proton and natural abundance ^{13}C resonances of the deuterated solvent and chemical shifts were reported relative to $SiMe_4$ (C_6D_6: δ^1H = 7.16 ppm and δ^{13}C = 128.06 ppm). Solid State NMR spectra were measured on a Bruker Avance III 400 WB spectrometer (^{7}Li = 155.57 MHz, ^{29}Si =79.53 MHz). UV-Vis spectra were recorded on a Shimadzu UV-2600 spectrometer in quartz cells with a path length of 0.1 cm and Infrared spectra on a Shimadzu IR Affinity-1S spectrometer in a platinum ATR diamond cell. Elemental analyses were performed on an elemental analyzer Leco CHN-900 and/or an elementar vario Micro Cube. Mass spectrometry was measured on a Bruker SolariX 7 Tesla MALDI/ESI/APPI FTICR imaging MS. Melting points were determined under argon in NMR tubes and are uncorrected. The molten samples were examined by NMR spectroscopy to confirm whether decomposition had occurred upon melting. Crystallographic data of the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk). Group 9 transition metal siliconoid hybrid **1** was prepared following the literature protocol.[S1]

2 Preparation, data and spectra (NMR, UV-Vis)

2.1 Preparation of Si_6Ir-Li 2



Supplementary Scheme S1: Synthesis of the iridasiliconoid **2** (R = 2,4,6-triisopropylphenyl, cod = cyclooctadienyl).

Iridium siliconoid complex **1**[S1] (720 mg 0.42 mmol, 1.0 eq) is dissolved in 10 mL diethyl ether. After cooling the solution to –78°C, a freshly prepared lithium/naphthalene solution (1.8 mL, 0.93 mmol, 2.21 eq) in thf is added dropwise to the precooled mixture at –78°C. The resulting brown reaction mixture is allowed to warm to ambient temperature under stirring overnight. All volatiles are removed under reduced

pressure. The dark-red-brown residue is filtered from 20 mL of hexane and washed 3x with 3 mL hexane. The solvent of the filtrate is distilled off under reduced pressure and the residue is dried thoroughly. This affords iridasiliconoid **2** as a dark-red-brown crystalline solid in a yield of 71% (627 mg, 0.30 mmol) along with thf (1.9 eq), naphthalene ($C_{10}H_8$, 1.6 eq) and Tip_4-disilene (0.35 eq) according to the ^{1}H NMR. Depending on crystallization conditions different amounts of thf, naphthalene and disilene co-crystallize. Single crystals of **2** were obtained as red blocks from a concentrated solution of **2** in hexane at –26°C.

^{1}H NMR (400.13 MHz, C_6D_6, 300 K) δ = 7.356 (d, $^3J_{HH}$ = 1.56 Hz, 1H, Ar-*H*), 7.270 (d, $^3J_{HH}$ = 1.56 Hz, 1H Ar-*H*), 7.205– 7.184 (m, 1H, Ar-*H*), 7.138 (d, $^3J_{HH}$ = 1.32 Hz, 1H, Ar-*H*), 7.053 (d, $^3J_{HH}$ = 1.32 Hz, 1H, Ar-*H*), 6.981 (d, $^3J_{HH}$ = 1.60 Hz, 1H, Ar-*H*), 6.939 – 6.906 (m, 3H, Ar-*H*), 6.849 – 6.809 (m, 1H, Ar-*H*), 6.535 (sept, $^3J_{HH}$ = 6.69 Hz, 1H, Ar-*H*), 5.257 (sept, $^3J_{HH}$ = 6.69 Hz, 1H, Tip-*i*Pr-C*H*), 5.039 (sept, $^3J_{HH}$ = 6.59 Hz, 1H, Tip-*i*Pr-C*H*), 4.382 – 4.317 (m, 3H, Tip-*i*Pr-C*H*), 3.884 – 3.806 (m, 3H, Tip-*i*Pr-C*H* overlapping with COD-C*H*), 2.591 – 3.558 (m, 8H, thf), 3.239 (sept, $^3J_{HH}$ = 6.56 Hz, 1H, Tip-*i*Pr-C*H*), 2.861 – 2.751 (m, 3H, Tip-*i*Pr-C*H* overlapping with COD-C*H*), 2.317 – 2.267 (m, 6H, COD-CH_2), 2.233 – 2.194 (m, 3H, Tip-*i*Pr-C*H* overlapping with COD-CH_2), 1.937 (d, $^3J_{HH}$ = 6.56 Hz, 3H, Tip-*i*Pr-CH_3), 1.748 – 1.718 (m, 9H, Tip-*i*Pr-CH_3), 1.583 (dd, $^3J_{HH}$ = 6.56 Hz, $^3J_{HH}$ = 4.56 Hz, 6H, Tip-*i*Pr-CH_3), 1.507 (d, $^3J_{HH}$ = 6.57 Hz, 3H, Tip-*i*Pr-CH_3), 1.401 (s, 9H, PhC(N(C(CH_3)$_3$)$_2$Si), 1.373 – 1.340 (m, 7H, Tip-*i*Pr-CH_3), 1.295 (s, 9H, PhC(N(C(CH_3)$_3$)$_2$Si), 1.275 (d, $^3J_{HH}$ = 1.58 Hz, 2H, Tip-*i*Pr-CH_3), 1.258 (d, $^3J_{HH}$ = 1.11 Hz, 2H, Tip-*i*Pr-CH_3), 1.241 (d, $^3J_{HH}$ = 1.34 Hz, 3H, Tip-*i*Pr-CH_3), 1.231 – 1.225 (m, 4H, Tip-*i*Pr-CH_3), 1.211 (d, $^3J_{HH}$ = 2.61 Hz, 3H, Tip-*i*Pr-CH_3), 0.861 (d, $^3J_{HH}$ = 6.72 Hz, 3H, Tip-*i*Pr-CH_3), 0.776 (t, $^3J_{HH}$ = 6.26 Hz, 6H Tip-*i*Pr-CH_3), 0.466 (d, $^3J_{HH}$ = 6.46 Hz, 3H, Tip-*i*Pr-CH_3) ppm.

^{13}C NMR (100.61 MHz, C_6D_6, 300 K) δ = 168.62 (s, 1C, Ph*C*(N(C(CH$_3$)$_3$)$_2$Si), 153.61, 153.50, 153.18, 152.67, 152.10, 151.94, 148.68, 148.24, 147.76, 144.68, 143.51, 141.83, 133.53 (s, 1C, each Ar-*C*), 129.90, 128.35, 128.11, 128.06, 127.87, 125.90 (s, 1C, each Ar-*C*H), 122.48, 122.46 (each s, 2C, COD-*C*H), 122.06, 120.85, 120.60, 119.52 (s, 1C, each Ar-*C*H), 68.51 (s, 2C, thf), 56.40 (s, 1C, PhC(N(*C*(CH$_3$)$_3$)$_2$Si), 54.13 (s, 1C, PhC(N(*C*(CH$_3$)$_3$)$_2$Si), 35.49, 35.19, 34.84, 34.73, 34.64 (each s, 1C, Tip-*i*Pr-*C*H), 33.73 (s, 3C, PhC(N(C(*C*H$_3$)$_3$)$_2$Si), 33.15, 33.03, 32.66, 32.20 (each s, Tip-*i*Pr-*C*H), 31.78 (s, 3C, PhC(N(C(*C*H$_3$)$_3$)$_2$Si), 29.25 (s, 2C, COD-*C*H$_2$), 28.81 (s, 1C, Tip-*i*Pr-*C*H$_3$), 27.62 (s, 2C, COD-*C*H$_2$), 27.38 (each s, 1C, Tip-*i*Pr-*C*H$_3$), 25.47 (s, 2C, thf), 25.36, 25.22, 24.83, 24.63, 24.57, 24.47, 24.41(each s, 1C, Tip-*i*Pr-*C*H$_3$), 24.36 (s, 2C, Tip-*i*Pr-*C*H$_3$), 24.20, 24.22, 24.13, 24.08, 23.72, 23.09, 21.30 (each s, 1C, Tip-*i*Pr-*C*H$_3$) ppm.

^{7}Li NMR (155.51 MHz, C_6D_6, 300 K) δ = 5.99 (s, *Li*), 1.12 (brs, *Li*) ppm.

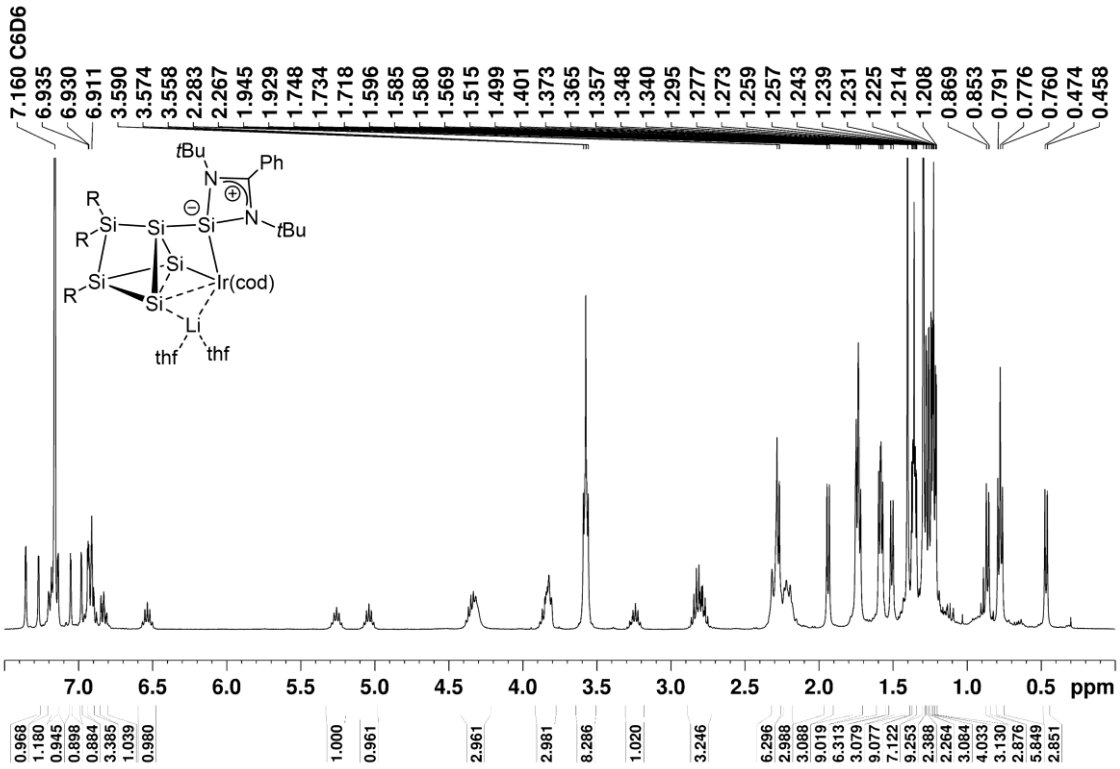
^{29}Si NMR (79.49 MHz, C_6D_6, 300 K) δ = 152.8 (s, *Si*Tip), 108.2 (s, Ph*C*(N(C(CH$_3$)$_3$)$_2$*Si*), 36.0 (s, *Si*Tip$_2$), –103.2 (s, unsubstituted *Si*), –184.0 (s, unsubstituted *Si*), –226.3 (brs, *Si*Li) ppm.

Elemental analysis: calculated for $C_{76}H_{120}Si_6N_2O_2IrLi$: C:62.46%; H: 8.28%; N: 1.92%. Found: C: 62.48%; H: 7.28%; N: 1.51%. The lower values compared to those calculated are quite common for unsaturated silicon clusters due to incomplete combustion typically attributed to the formation of silicon

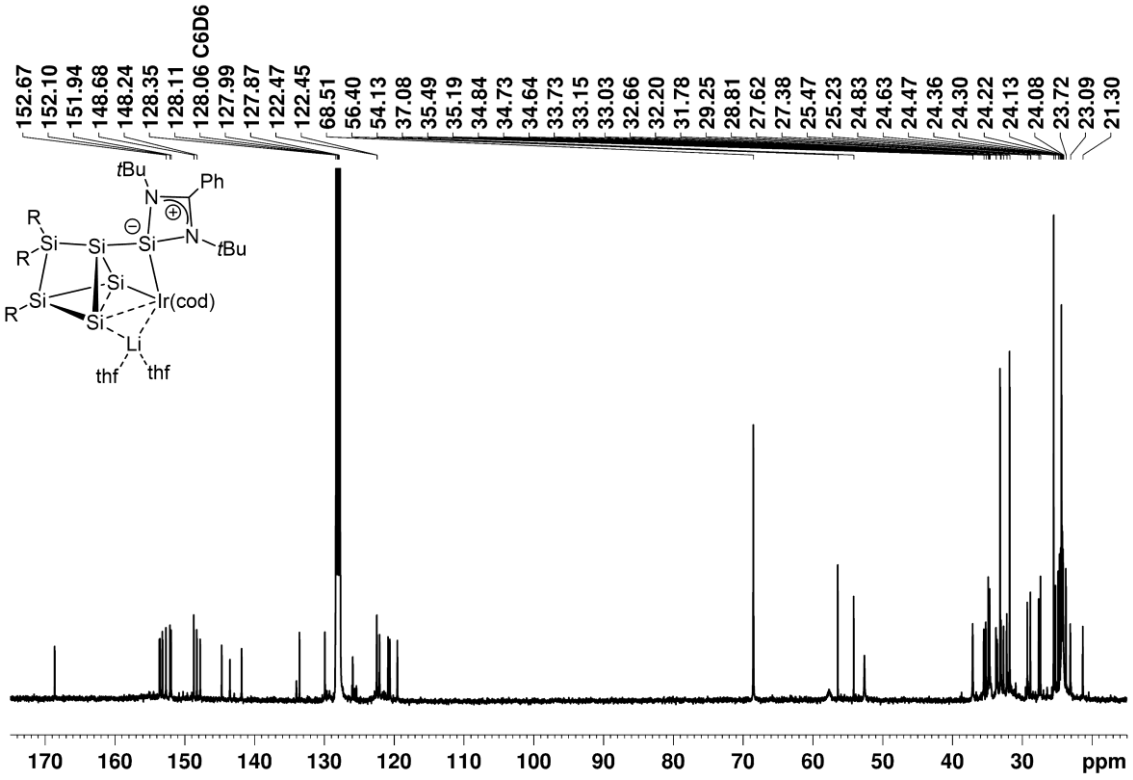
carbides and/or nitrides. In addition, elemental analysis has come under scrutiny because of highly variable results of bona fide identical samples.[S2]

UV-Vis (hexane): λ (ε [M^{-1} cm^{-1}]) = 543 (2860), .425 (7660) nm.

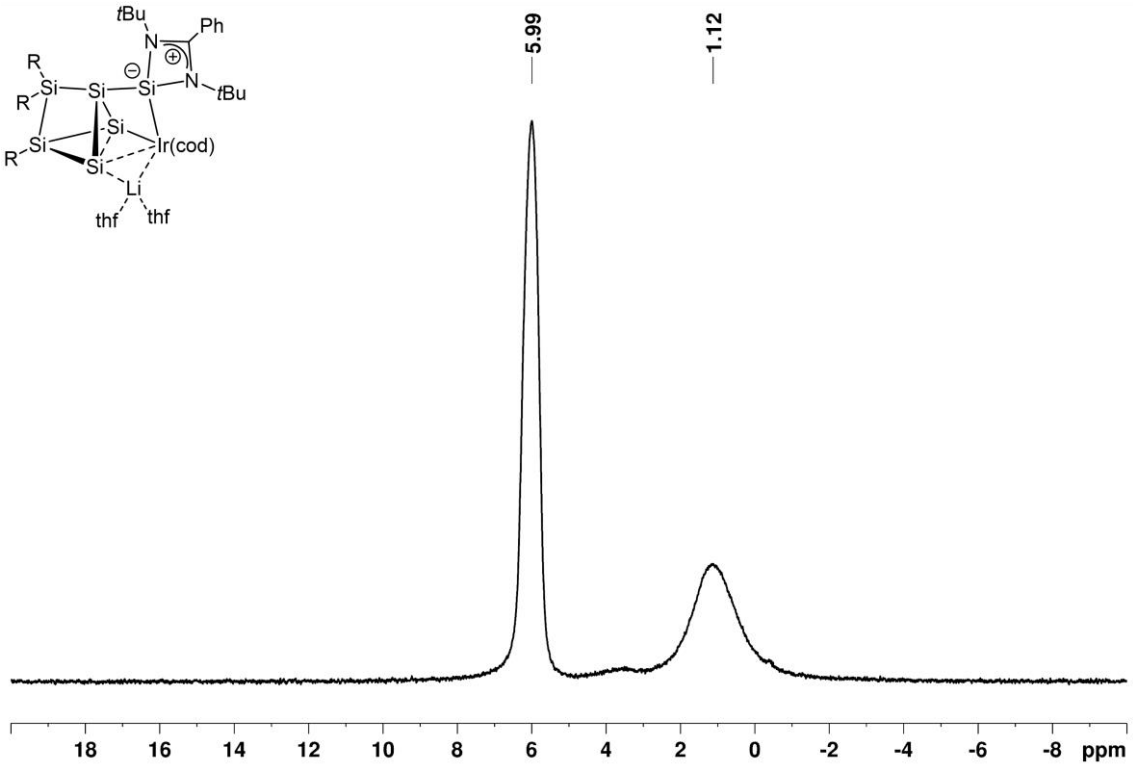
Melting Point: Decomposition under color change to a dark-brown/black solid was observed starting from 145°C with subsequent melting of the dark solid from 178°C-186°C.



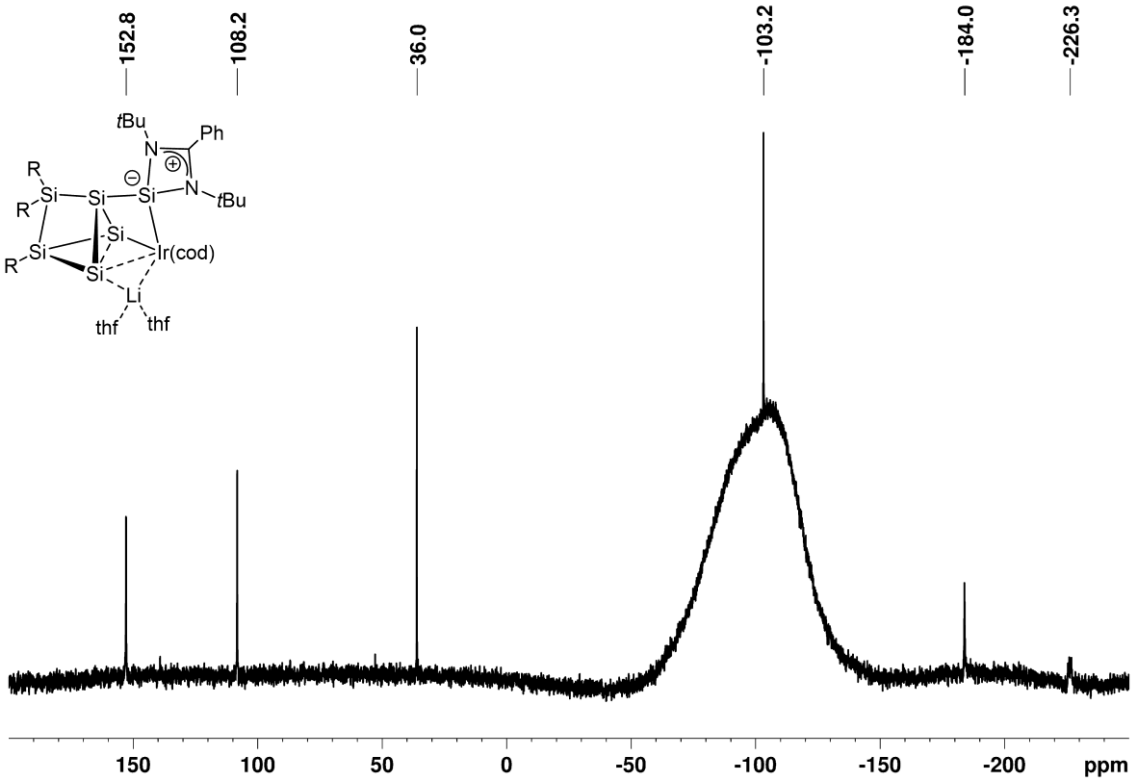
Supplementary Figure S1. ^{1}H NMR spectrum of **2** in C_6D_6 (400.13 MHz, 300 K).



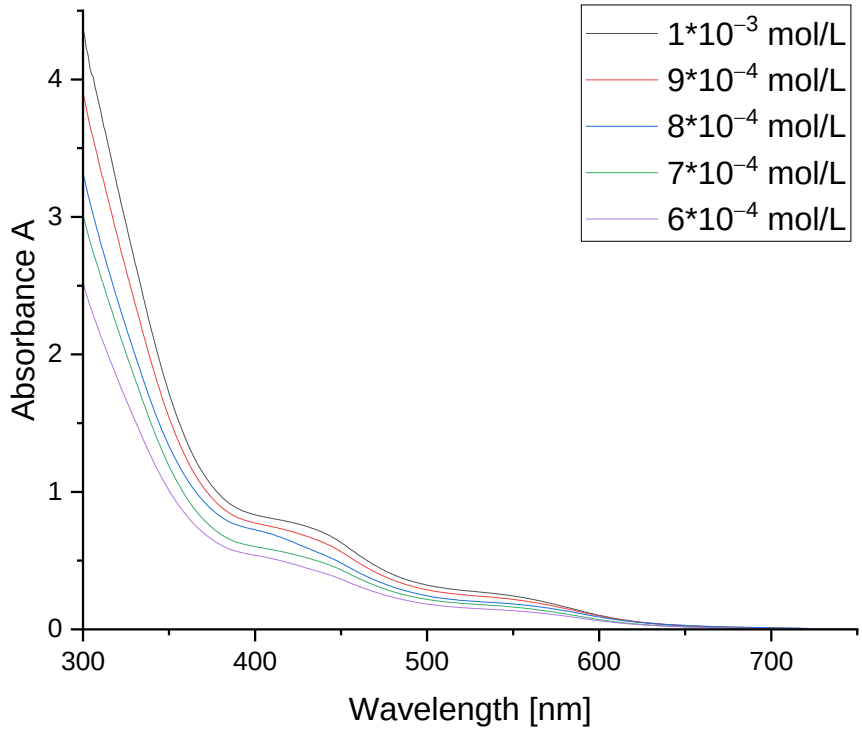
Supplementary Figure S2. ^{13}C NMR spectrum of **2** in C_6D_6 (100.61 MHz, 300 K).



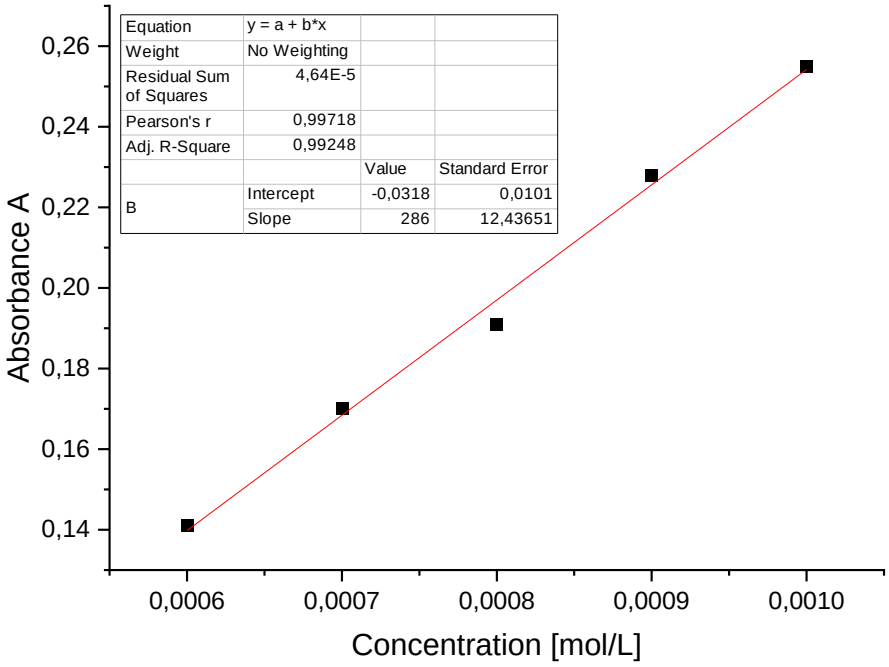
Supplementary Figure S3. ^{7}Li NMR spectrum of **2** in C_6D_6 (155.51 MHz, 300 K).



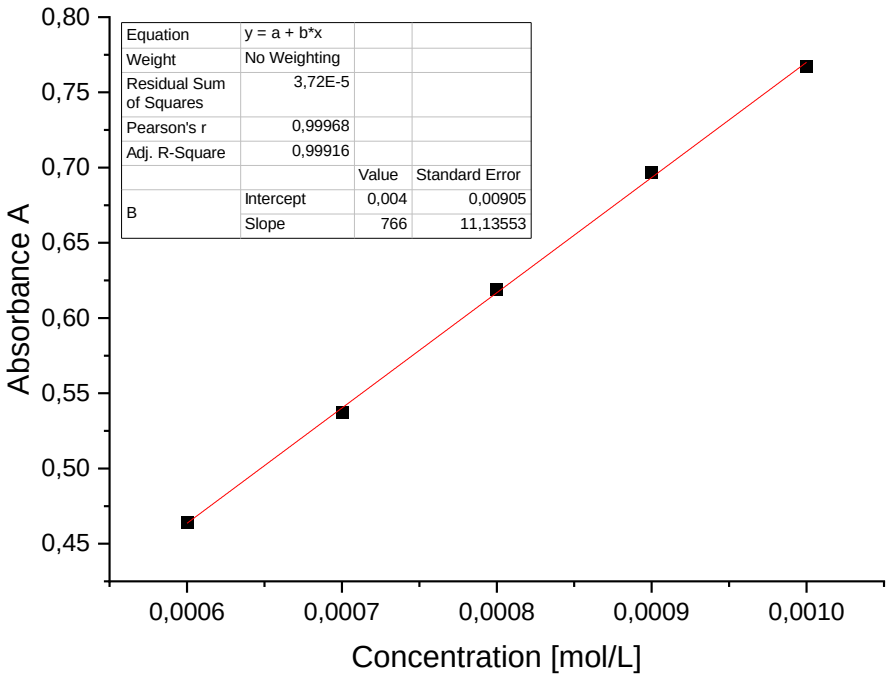
Supplementary Figure S4. ^{29}Si NMR spectrum of **2** in C_6D_6 (79.49 MHz, 300 K).



Supplementary Figure S5. UV-Vis spectra of Si_6Ir-Li complex **2** in hexane at different concentrations.

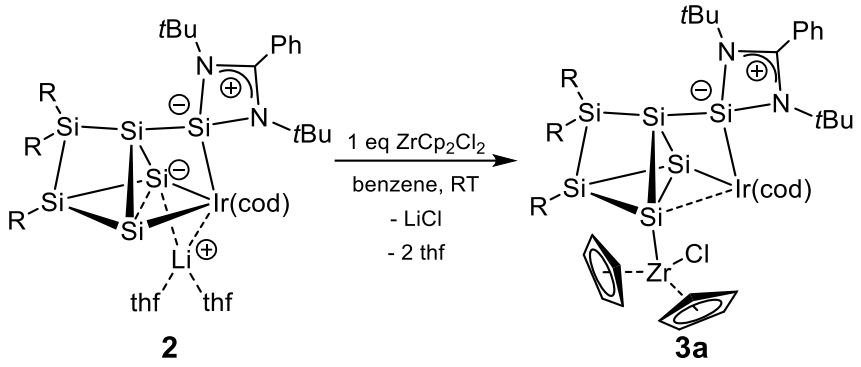


Supplementary Figure S6. Determination of the extinction coefficient $\varepsilon = 2860\ M^{-1}\ cm^{-1}$ of **2** by linear regression at $\lambda_{max} = 543$ nm against the concentration.



Supplementary Figure S7. Determination of the extinction coefficient $\varepsilon = 7660\ M^{-1}\ cm^{-1}$ of **2** by linear regression at $\lambda_{max} = 425$ nm against the concentration.

2.2 Preparation of Si_6Ir-Zr complex 3a



M = 1461.48 g/mol 292.32 g/mol 1567.12 g/mol

Supplementary Scheme S2. Synthesis of zirconium/iridium siliconoid **3a** (R = 2,4,6-triisopropylphenyl, cod = cyclooctadienyl).

Iridasiliconoid **2** (249 mg, 0.15 mmol, 1.0 eq) is treated with $ZrCp_2Cl_2$ (43.2 mg, 0.15 mmol, 1.0 eq) in 2 mL benzene. After the dark-green solution is stirred 20 minutes at room temperature, all volatiles are removed under reduced pressure and the black-green residue is extracted from 2 mL hexane and washed 3x with 2 mL hexane each. The dark-green-brown filtrate is concentrated and kept overnight, first at –26°C, then at room temperature for crystallization. Removal of the mother liquor and drying of the dark-green-brown crystals yields 32.8 mg (0.021 mmol; 14%) of the zirconium/iridium siliconoid **3a**. The yields are compromised by the competing formation of an unidentified side product, which could be due to the elimination of CpLi according to residual ^{1}H and ^{13}C NMR signals in the spectra of **3a** (5.869/ 114.3 ppm), as well as the co-crystallization of the starting material $ZrCp_2Cl_2$ that cannot be separated completely. Attempts to detect CpLi by ^{7}Li NMR remained unsuccessful.

^{1}H NMR (400.13 MHz, C_6D_6, 300 K) δ = 7.283 (d, $^{4}J_{HH}$ = 1.61 Hz, 1H, Ar-*H*), 7.258 (d, $^{4}J_{HH}$ = 1.46 Hz, 1H, Ar-*H*), 7.1919 – 7.176 (m, 4H, Ar-*H*), 7.101 (d, $^{4}J_{HH}$ = 1.41 Hz,1H, Ar-*H*), 7.056 – 7.033 (m, 1H, Ar-*H*), 6.960 – 6.940 (m, 1H, Ar-*H*), 6.926 (d, $^{4}J_{HH}$ = 1.58 Hz, 1H, Ar-*H*), 6.853 (d, $^{4}J_{HH}$ = 1.43 Hz, 1H, Ar-*H*), 6.297 (s, 5H, Cp-C*H*), 6.230(s, 5H, Cp-C*H*), 6.013 ($ZrCp_2Cl_2$), 5.869 (CpLi?), 5.573 (sept, $^{3}J_{HH}$ = 6.63 Hz, 1H, Tip-*i*Pr-C*H*), 5.487 (sept, $^{3}J_{HH}$ = 6.78 Hz, 1H, Tip-*i*Pr-C*H*), 4.826 (sept, $^{3}J_{HH}$ = 6.50 Hz, 1H, Tip-*i*Pr-C*H*), 4.506 (m, 1H, COD-C*H*), 4.074 (sept, $^{3}J_{HH}$ = 6.59 Hz, 1H, Tip-*i*Pr-C*H*), 3.957 (m, 1H, COD-C*H*), 3.752 (m, 1H, COD-C*H*), 3.648 (sept, 1H, $^{3}J_{HH}$ = 6.65 Hz, Tip-*i*Pr-C*H*), 2.980 (sept, $^{3}J_{HH}$ = 6.47 Hz, 1H, Tip-*i*Pr-C*H*), 2.824 – 2.641 (m, 6H, Tip-*i*Pr-C*H* overlapping with COD-CH_2), 2.422 (m, 1H, COD-C*H*), 2.217 – 2.122 (m, 5H, Tip-*i*Pr-C*H* overlapping with d, $^{3}J_{HH}$ = 6.35 Hz, 3H, Tip-*i*Pr-CH_3), 1.898 – 1.813 (m, 8H, COD-CH_2 overlapping with Tip-*i*Pr-CH_3 (1.890, d, $^{3}J_{HH}$ = 6.47 Hz, 3H; 1.822, d, $^{3}J_{HH}$ = 6.70 Hz, 3H)), 1.773 (d, $^{3}J_{HH}$ = 6.81 Hz, 3H, Tip-*i*Pr-CH_3), 1.694 (d, $^{3}J_{HH}$ = 6.70 Hz, 3H, Tip-*i*Pr-CH_3), 1.449 (dd, $^{3}J_{HH}$ = 10.63, 6.67 Hz, 3H, Tip-*i*Pr-CH_3), 1.366 (d, $^{3}J_{HH}$ = 6.49 Hz, 6H, Tip-*i*Pr-CH_3), 1.257 (s, 9H, PhC(N(C(CH_3)$_3$)$_2$Si), 1.230 (d, $^{4}J_{HH}$ = 1.75 Hz, 3H, Tip-*i*Pr-CH_3), 1.214 – 1.182 (m, 15H, Tip-*i*Pr-CH_3), 1.095 (s, 9H, PhC(N(C(CH_3)$_3$)$_2$Si), 1.028 (d, $^{3}J_{HH}$ = 6.61 Hz, 3H, Tip-*i*Pr-CH_3), 0.925 (d, $^{3}J_{HH}$ = 6.58 Hz,

3H, Tip-*i*Pr-C*H*$_3$), 0.889 (t, 2H, hexane), 0.489 (d, $^3J_{HH}$ = 6.58 Hz, 3H, Tip-*i*Pr-C*H*$_3$), 0.197 (d, $^3J_{HH}$ = 6.30 Hz, 3H, Tip-*i*Pr-C*H*$_3$) ppm.

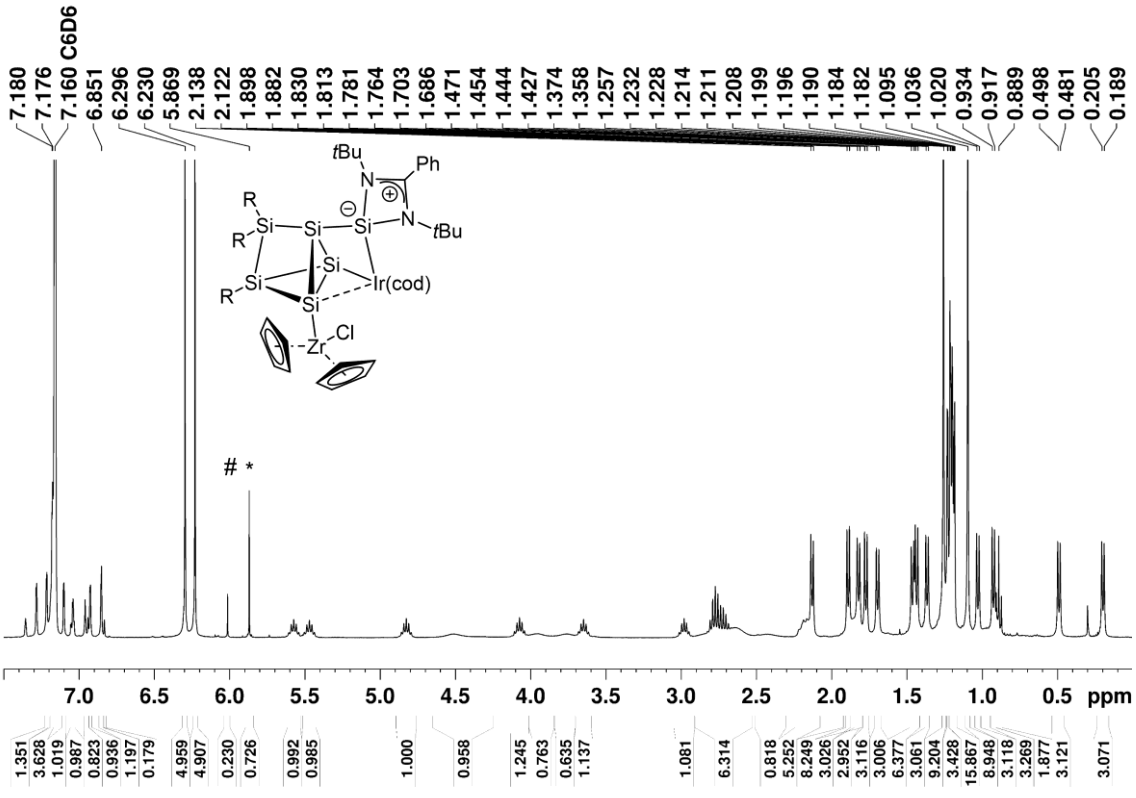
^{13}C NMR (100.61 MHz, C_6D_6, 300 K) δ = 169.72 (s, 1C, Ph*C*(N(C(*C*H$_3$)$_3$)$_2$Si), 154.11, 154.07, 153.97, 153.64, 153.36, 153.05, 149.80, 149.07, 148.06, 146.79, 141.46, 139.13, 133.03 (each s, 1C, Ar-*C*), 130.12, 128.10, 127.86, 123.74 (each s, Ar-*C*H), 122.67(s, 4C, COD-*C*H), 121.63, 121.10, 120.46 (each s, 1C, Ar-*C*H), 115.65 ($ZrCp_2Cl_2$), 114.32 (CpLi?), 112.07, 110.96 (each s, 10C, Cp-*C*H), 55.67 (s, 1C, PhC(N(*C*(CH$_3$)$_3$)$_2$Si), 54.38 (s, 1C, PhC(N(*C*(CH$_3$)$_3$)$_2$Si), 36.03, 35.55, 34.85 (each s, 1C, Tip-*i*Pr-*C*H), 34.57 – 34.46 (m, 4C, Tip-*i*Pr-*C*H), 33.06, 32.63 (each s, 1C, Tip-*i*Pr-*C*H), 32.37, 32.22(each s, 3C, PhC(N(C(*C*H$_3$)$_3$)$_2$Si), 31.90 (s, hexane), 29.33, 27.96, 27.40, 26.85 (each s, 1C, Tip-*i*Pr-*C*H$_3$), 26.64 (brs, 2C, COD-*C*H$_2$), 25.96, 25.37 (each s, 1C, Tip-*i*Pr-*C*H$_3$), 25.25 (brs, 2C, COD-*C*H$_2$), 25.05, 24.45 (each s, 1C, Tip-*i*Pr-*C*H$_3$), 24.21 – 24.06 (m, 9C, Tip-*i*Pr-*C*H$_3$), 23.82 (s, 1C, Tip-*i*Pr-*C*H$_3$), 22.99 14.30 (s, hexane) ppm.

^{29}Si NMR: (79.49 MHz, C_6D_6, 300 K) δ = 73.8 (brs, *Si*Tip), 73.5 (s, Ph*C*(N(C(CH$_3$)$_3$)$_2$*Si*), 52.8 (Tip$_2$Si=SiTip$_2$) 30.5 (s, *Si*Tip$_2$), −40.9 (s, unsubstituted *Si* (Si3)), −77.9 (s, *Si*Zr), −131.9 (s, unsubstituted *Si*) ppm.

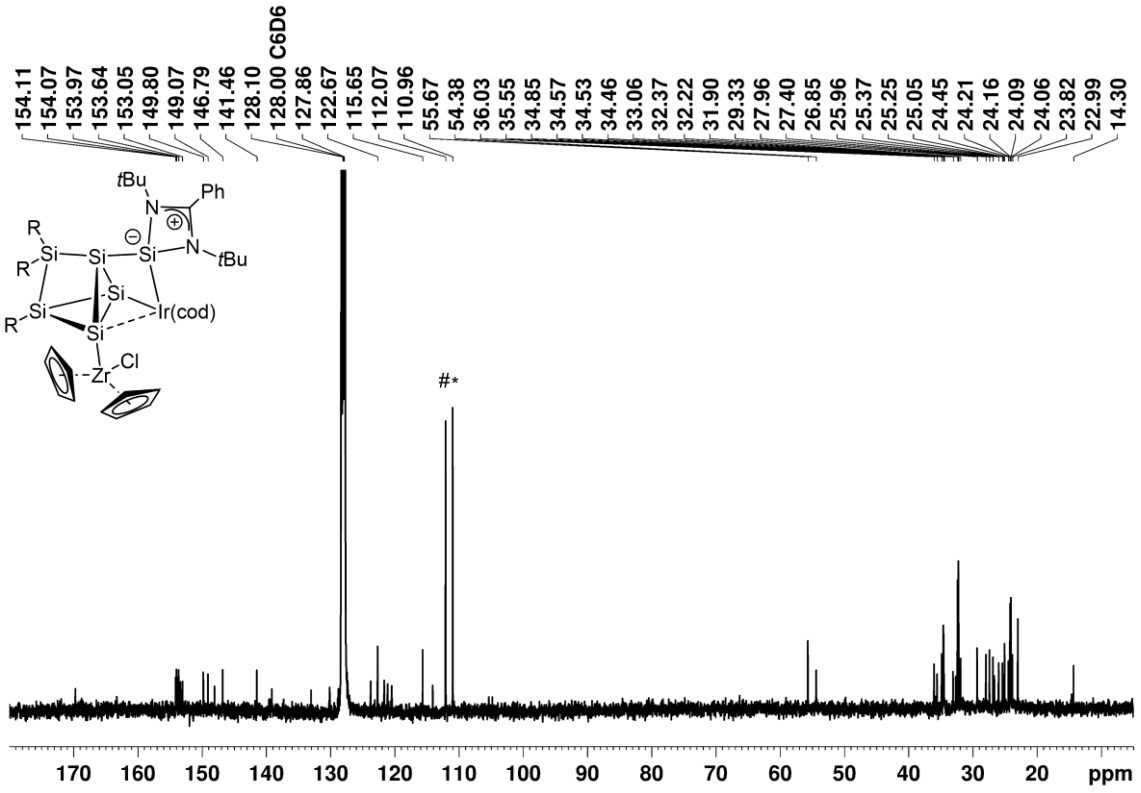
UV-Vis (in hexane)**:** λ (ε [M^{-1} cm^{-1}]) = 601 (3389), 426 (6911), 354 (17431) nm.

Elemental analysis calculated for $C_{78}H_{114}ClIrN_2Si_6Zr$: C: 59.78 %, H: 7.33 %, N: 1.79 %. Found: C: 59.56 %, H: 7.23 %, N: 1.54 %.

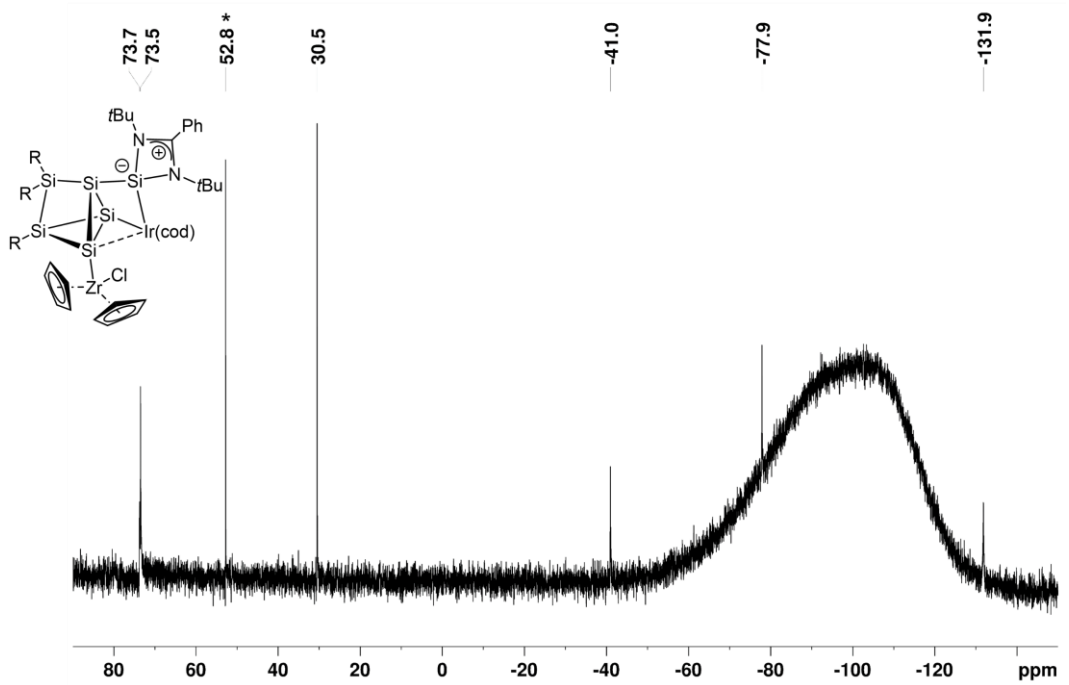
Melting point: 310°C.



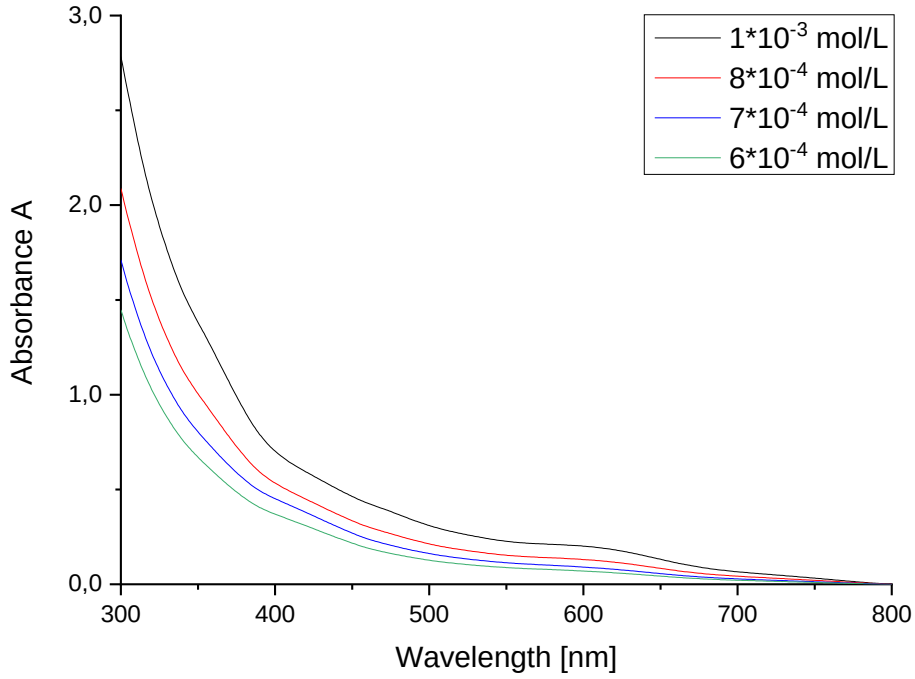
Supplementary Figure S8. ^{1}H NMR spectrum of **3a** in C_6D_6 (400.13 MHz, 300 K), #,* impurities, likely # = Cp_2ZrCl_2, * = CpLi.



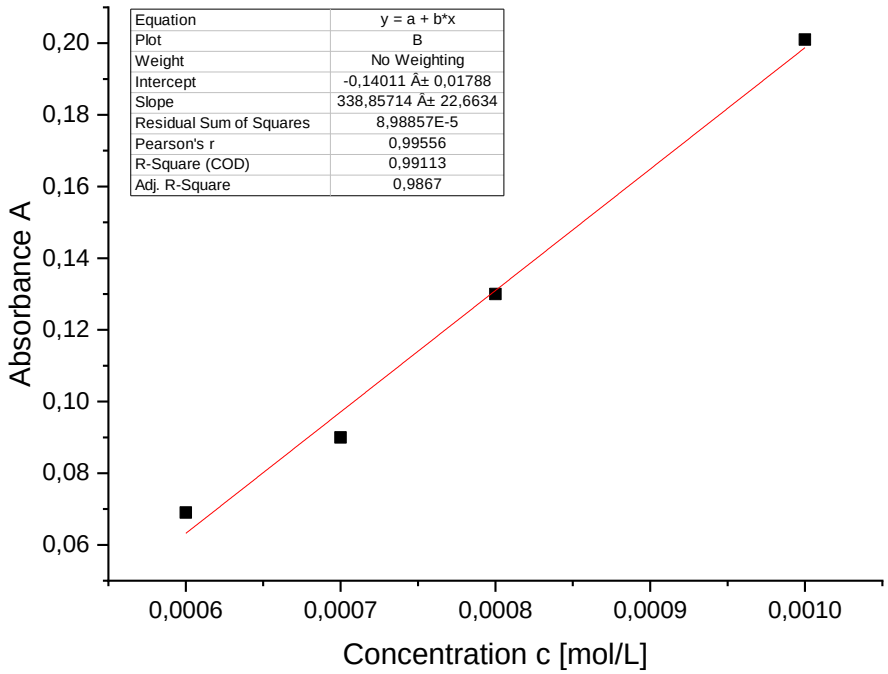
Supplementary Figure S9. ^{13}C NMR spectrum of **3a** in C_6D_6 (100.61 MHz, 300 K), #,* impurities, likely # = Cp_2ZrCl_2, * = CpLi.



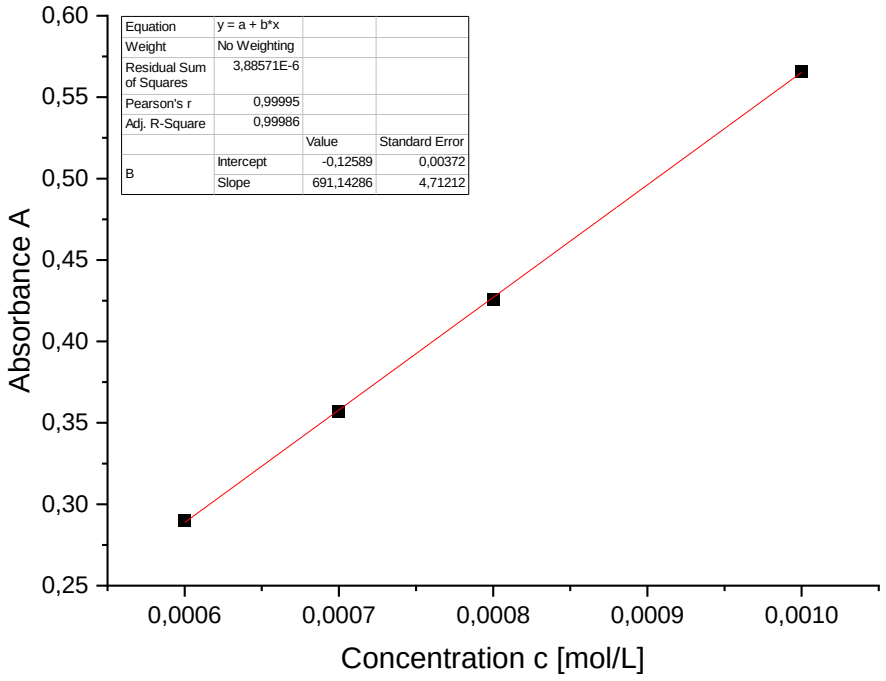
Supplementary Figure S10. ^{29}Si NMR spectrum of **3a** in C_6D_6 (79.49 MHz, 300 K), impurity * = residual $Tip_2Si{=}SiTip_2$.



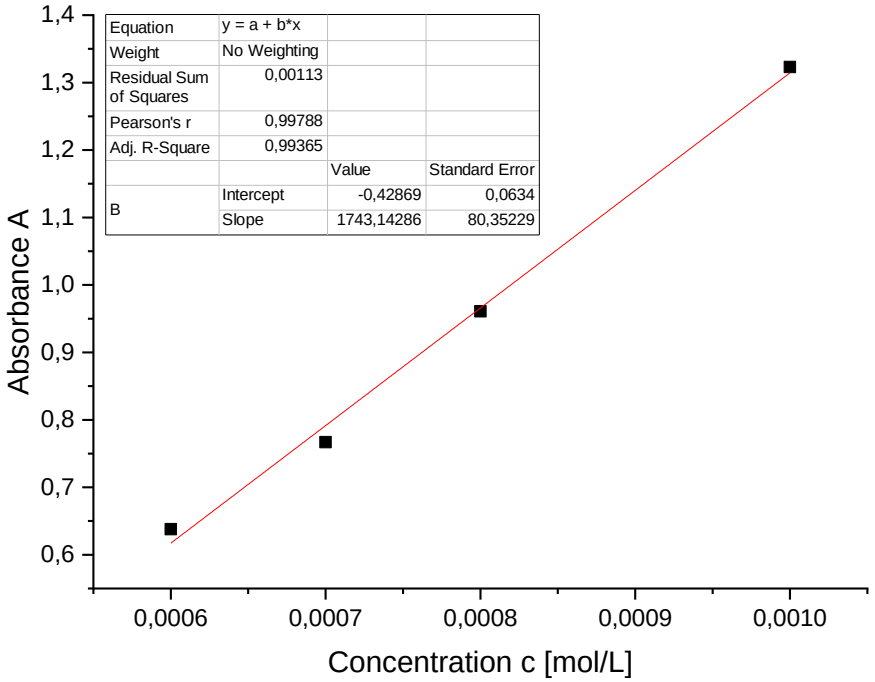
Supplementary Figure S11. UV-Vis spectra of zirconium complex **3a** in hexane at different concentrations.



Supplementary Figure S12. Determination of the extinction ε = 3389 M^{-1} cm^{-1} of **3a** by linear regression at λ_{max} = 601 nm.

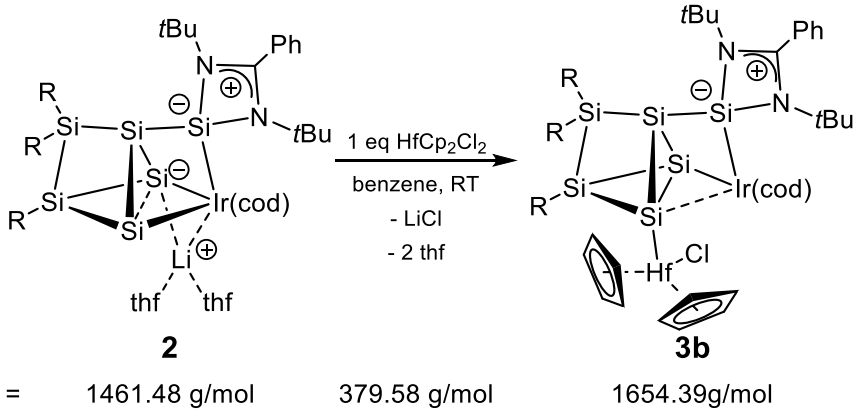


Supplementary Figure S13. Determination of the extinction ε = 6911 M^{-1} cm^{-1} of **3a** by linear regression at λ = 426 nm.



Supplementary Figure S14. Determination of the extinction ε = 17431 M^{-1} cm^{-1} of **3a** by linear regression at λ = 354 nm.

2.3 Preparation of Si_6Ir-Hf complex 3b



Supplementary Scheme S3. Synthesis of the hafnium complex **3b** (R = 2,4,6-triisopropylphenyl, cod = cyclooctadienyl).

Hafnocene dichloride (49.6 mg (0.13 mmol, 1.08°eq.) is added to iridasiliconoid **2** (249 mg, 0.15 mmol, 1.0 eq.) in 3 mL benzene. The reaction mixture is stirred for 1.5 hours at room temperature and afterwards the solvent of the brown-orange solution is removed under reduced pressure. The dark-red residue is filtered from 3 mL hexane and washed with 5 mL hexane in total. Afterwards, the red-brown filtrate is concentrated and kept at room temperature for crystallization overnight. The mother liquor is removed *via* cannula and the crystals are dried under reduced pressure to afford 68.4 mg (0.041 mmol; 32%) of hafnium/iridium siliconoid **3b** as dark-violet-brown crystals. The yields are compromised by the competing formation of an unidentified side product, which could be due to the elimination of CpLi according to residual ^{1}H and ^{13}C NMR signals in the spectra of **3b** (5.810 ppm/ 112.85 ppm), as well as the co-crystallization of the starting material $HfCp_2Cl_2$ that cannot be separated completely. Residual naphthalene ($C_{10}H_8$) in the NMR spectra stems from the reduction step with lithium/naphthalene to **2** that could not be completely removed by sublimation and subsequent crystallization.

^{1}H NMR (400.13 MHz, C_6D_6, 300 K) δ = 7.627 (q, 0.2H, $C_{10}H_8$), 7.276 (d, $^{4}J_{HH}$ = 1.65 Hz, 1H, Ar-*H*), 7.251 (q, 0.2H, $C_{10}H_8$), 7.190 (dd, $^{3}J_{HH}$ = 8.05 Hz, $^{4}J_{HH}$ = 1.29 Hz, 3H, Ar-*H*), 7.103 (d, $^{4}J_{HH}$ = 1.50 Hz,1H, Ar-*H*), 7.007 – 7.053 (m, 1H, Ar-*H*), 6.967 – 6.946 (m, 2H, Ar-*H*), 6.917 (d, $^{4}J_{HH}$ = 1.58 Hz, 1H, Ar-*H*), 6.856 (d, $^{4}J_{HH}$ = 1.58 Hz, 2H, Ar-*H*), 6.171 (s, 5H, Cp-C*H*), 6.137 (s, 5H, Cp-C*H*), 5.925 ($HfCp_2Cl_2$), 5.810 (CpLi?), 5.531 (sept, $^{3}J_{HH}$ = 6.60 Hz, 1H, Tip-*i*Pr-C*H*), 5.441 (sept, $^{3}J_{HH}$ = 6.73 Hz, 1H, Tip-*i*Pr-C*H*), 4.847 (sept, $^{3}J_{HH}$ = 6.56 Hz, 1H, Tip-*i*Pr-C*H*), 4.584 – 4.274 (m, 1H, COD-C*H*) 4.068 (sept, $^{3}J_{HH}$ = 6.58 Hz, 1H, Tip-*i*Pr-C*H*), 3.998 – 3.727 (m, 1H, COD-C*H*), 3.633 (sept, $^{3}J_{HH}$ = 6.58 Hz, 1H, Tip-*i*Pr-C*H*), 2.965 (sept, $^{3}J_{HH}$ = 6.48 Hz, 1H, Tip-*i*Pr-C*H*), 2.801 – 2.630 (m, 8H, Tip-*i*Pr-C*H* overlapping with COD-C*H* and COD-CH_2), 2.122 (d, $^{3}J_{HH}$ = 6.39 Hz, 3H, Tip-*i*Pr-CH_3), 1.880 (d, $^{3}J_{HH}$ = 6.39 Hz, 3H, Tip-*i*Pr-CH_3), 1.817 (d, $^{3}J_{HH}$ = 6.70 Hz, 3H, Tip-*i*Pr-CH_3), 1.743 (d, $^{3}J_{HH}$ = 6.70 Hz, 3H, Tip-*i*Pr-CH_3), 1.672 (d, $^{3}J_{HH}$ = 6.70 Hz, 3H, Tip-*i*Pr-CH_3), 1.466 (d, $^{3}J_{HH}$ = 6.68 Hz, 3H, COD-CH_2 overlapping with Tip-*i*Pr-CH_3), 1.421 (t, $^{3}J_{HH}$ = 6.77 Hz, 6H, Tip-*i*Pr-CH_3), 1.254 (s, 9H, PhC(N(C(CH_3)$_3$)$_2$Si), 1.228 – 1.174 (m, 23H, Tip-*i*Pr-CH_3 overlapping with COD-CH_2), 1.106 (s, 9H, PhC(N(C(CH_3)$_3$)$_2$Si), 1.032 (d, $^{3}J_{HH}$ = 6.65 Hz, 3H, Tip-*i*Pr-

C*H*$_3$), 0.937 (d, $^3J_{HH}$ = 6.56 Hz, 3H, Tip-*i*Pr-C*H*$_3$), 0.886 (t, 2H, hexane), 0.481 (d, $^3J_{HH}$ = 6.56 Hz, 3H, Tip-*i*Pr-C*H*$_3$), 0.181 (d, $^3J_{HH}$ = 6.32 Hz, 3H, Tip-*i*Pr-C*H*$_3$) ppm.

^{13}C NMR (100.61 MHz, C_6D_6, 300 K) δ = 169.73 (s, 1C, Ph*C*(N(C(*C*H$_3$)$_3$)$_2$Si), 154.29, 154.13, 154.05, 153.80, 153.41, 153.05, 149.71, 149.04, 148.08, 146.91, 142.03, 138.97, 133.10 (each s, 1C, Ar-*C*), 130.32, 129.83, 128.92, 128.12, 127.88, 127.55, 126.01, 123.75 (each s, 1C, Ar-*C*H), 122.66 (s, 2C, COD-*C*H), 122.62 (s, 2C, COD-*C*H), 121.65, 121.20, 120.41 (each s, 1C, Ar-*C*H), 114.32 ($HfCp_2Cl_2$), 112.85 (CpLi?), 111.11, 110.20 (each s, each 5C, Cp-*C*H), 55.70 (s, 1C, PhC(N(*C*(CH$_3$)$_3$)$_2$Si), 54.33 (s, 1C, PhC(N(*C*(CH$_3$)$_3$)$_2$Si), 36.05, 35.61, 34.84 (each s, 1C, Tip-*i*Pr-*C*H), 34.60 – 34.50 (m, 4C, Tip-*i*Pr-*C*H), 33.22, 32.59 (each s, 1C, Tip-*i*Pr-*C*H), 32.46, 32.30 (each s, 3C, PhC(N(C(*C*H$_3$)$_3$)$_2$Si), 31.90 (s, hexane), 29.36, 28.08 (each s, 1C, Tip-*i*Pr-*C*H$_3$), 27.43 (s, 2C, COD-C*H*$_2$), 27.21, 26.65, 26.06 (each s, 1C, Tip-*i*Pr-*C*H$_3$), 25.59 (s, 2C, COD-C*H*$_2$), 25.53, 25.10, 24.47, 24.24 – 24.10 (m, 9C, Tip-*i*Pr-*C*H$_3$), 23.81 (s, 1C, Tip-*i*Pr-*C*H$_3$), 23.00, 14.32 (each s, hexane) ppm.

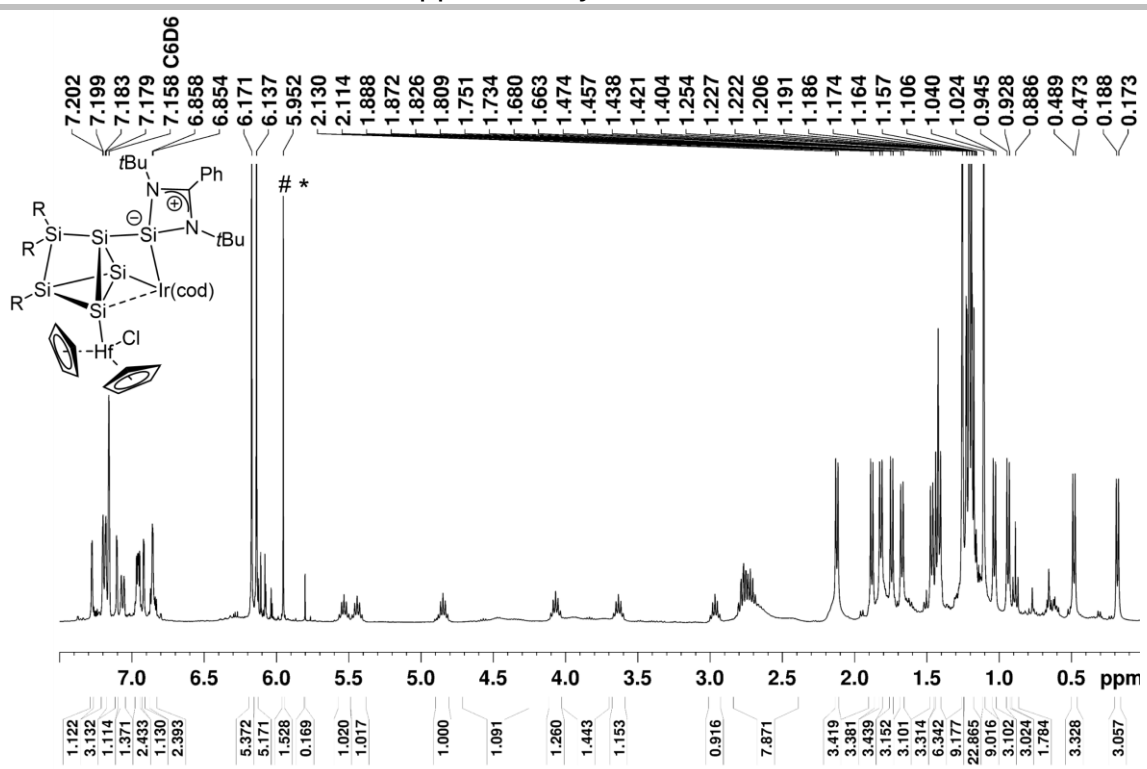
^{29}Si NMR (79.49 MHz, C_6D_6, 300 K) δ = 75.9 (s, *Si*Tip), 68.1 (bs, PhC(N(C(CH$_3$)$_3$)$_2$*Si*), 29.9 (s, *Si*Tip$_2$), −36.6 (s, *Si*Hf), −90.4 (s, *Si*Ir), −131.1 (s, unsubstituted *Si*) ppm.

CP-MAS ^{29}Si-NMR (79.53 MHz, 13KHz, 300K) δ = 65.5 (s, *Si*Tip and PhC(N(C(CH$_3$)$_3$)$_2$*Si*), 28.4 (s, *Si*Tip$_2$), −26.3 (s, unsubstituted *Si* (Si3)), −87.0 (s, *Si*Hf), −140.8 (s, unsubstituted *Si*), ppm.

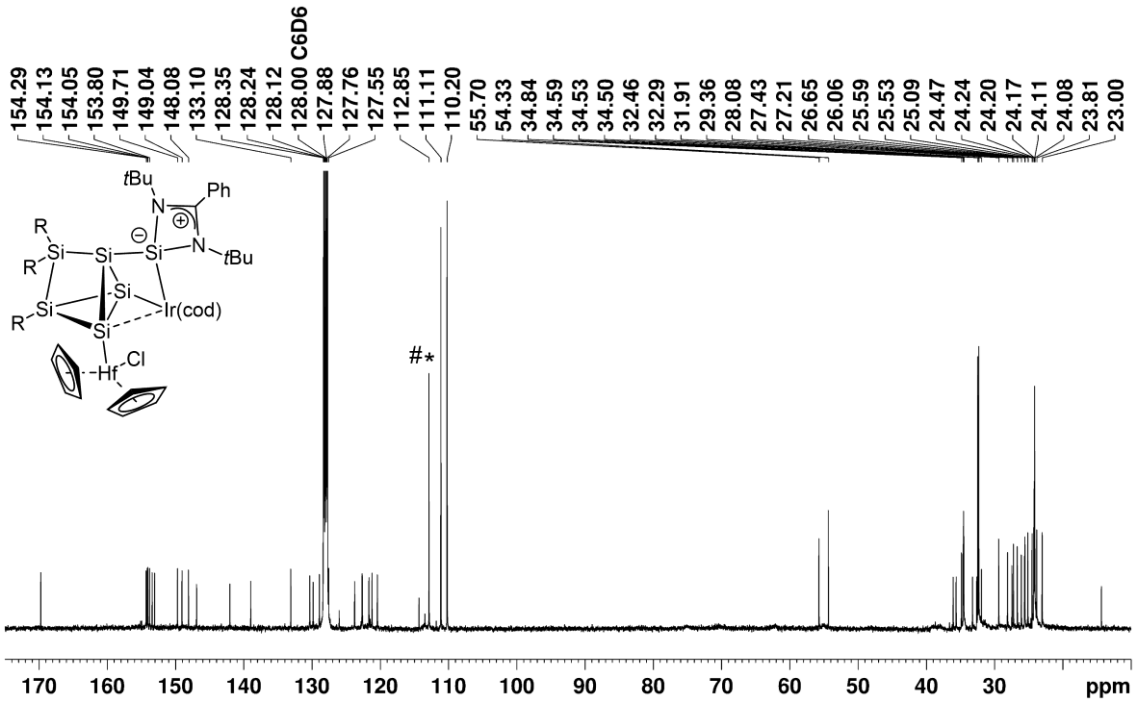
UV-Vis (in hexane)**:** λ (ε [M^{-1} cm^{-1}]) = 647 (1257), 524 (5303), 437 (6871), 340 (20960) nm.

Elemental analysis: calculated for $C_{78}H_{114}ClHfIrN_2Si_6$: C: 56.63 %, H: 6.95 %, N: 1.69 %. Found: C: 55.18 %, H: 6.72 %, N: 1.36 %. The lower values compared to those calculated are quite common for unsaturated silicon clusters due to incomplete combustion typically attributed to the formation of silicon carbides and/or nitrides. In addition, elemental analysis has come under scrutiny because of highly variable results of bona fide identical samples.[S2]

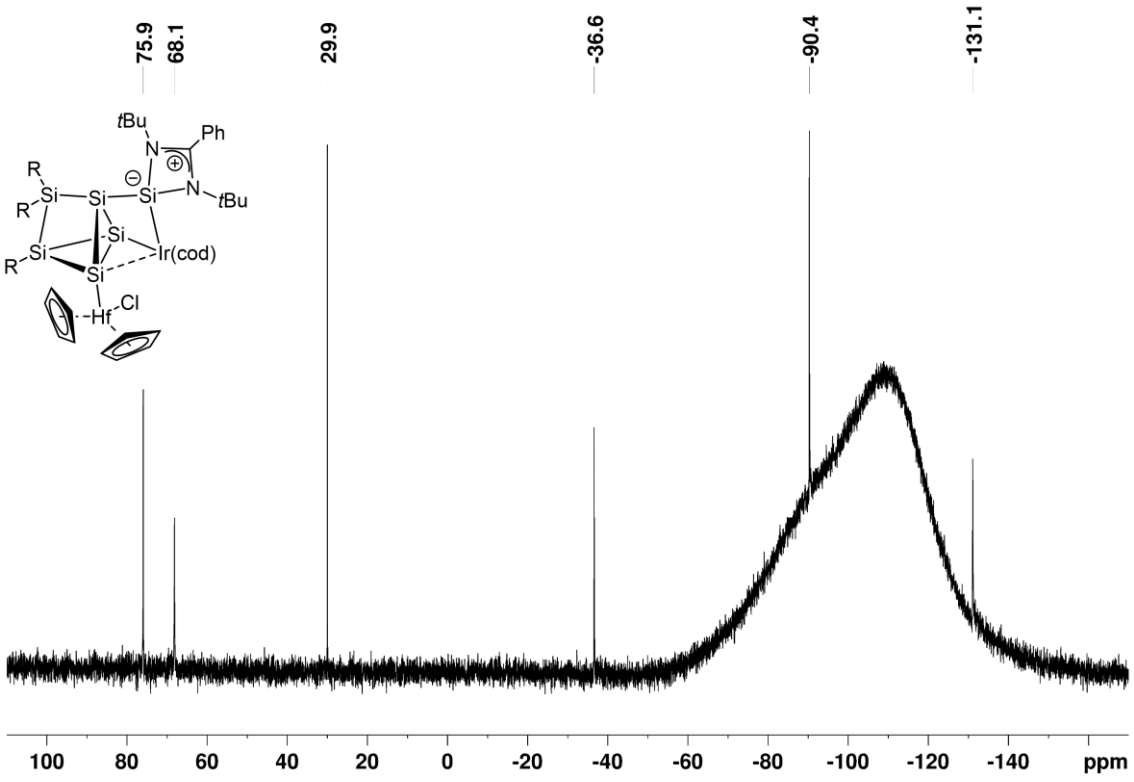
Melting point: 300°C.



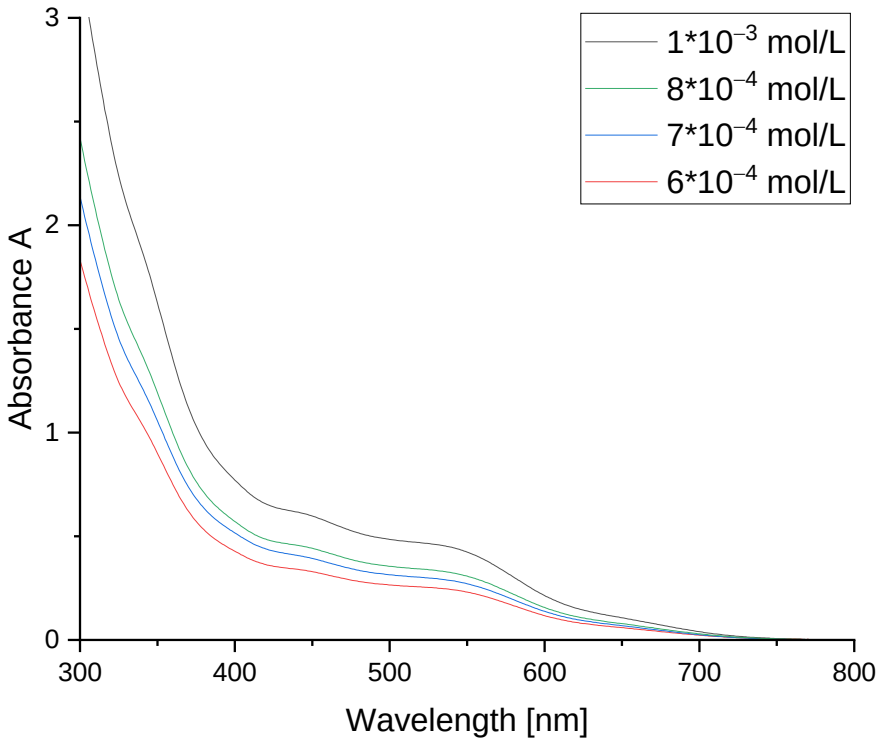
Supplementary Figure S15. ^{1}H NMR spectrum of **3b** in C_6D_6 (400.13 MHz, 300 K), #,* impurities, likely # = Cp_2HfCl_2, * = CpLi.



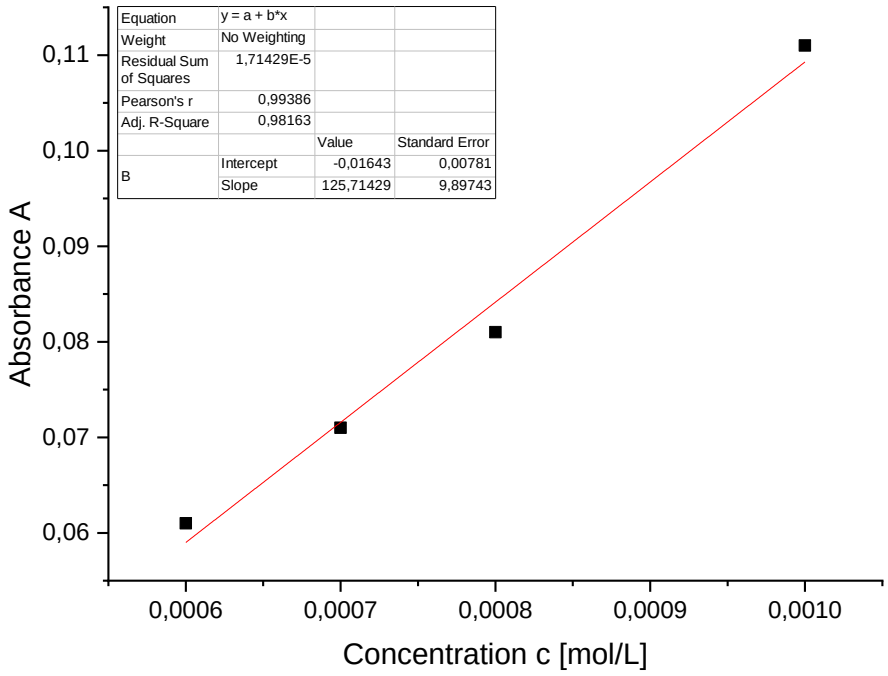
Supplementary Figure S16. ^{13}C NMR spectrum of **3b** in C_6D_6 (100.61 MHz, 300 K), #,* impurities, likely # = Cp_2HfCl_2, * = CpLi.



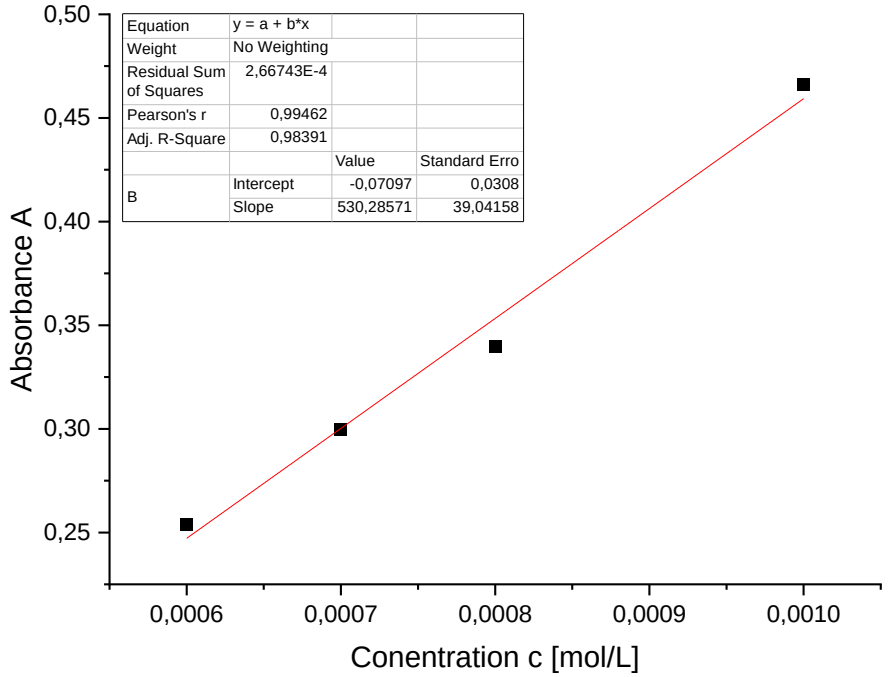
Supplementary Figure S17. ^{29}Si NMR spectrum of **3b** in C_6D_6 (79.49 MHz, 300 K).



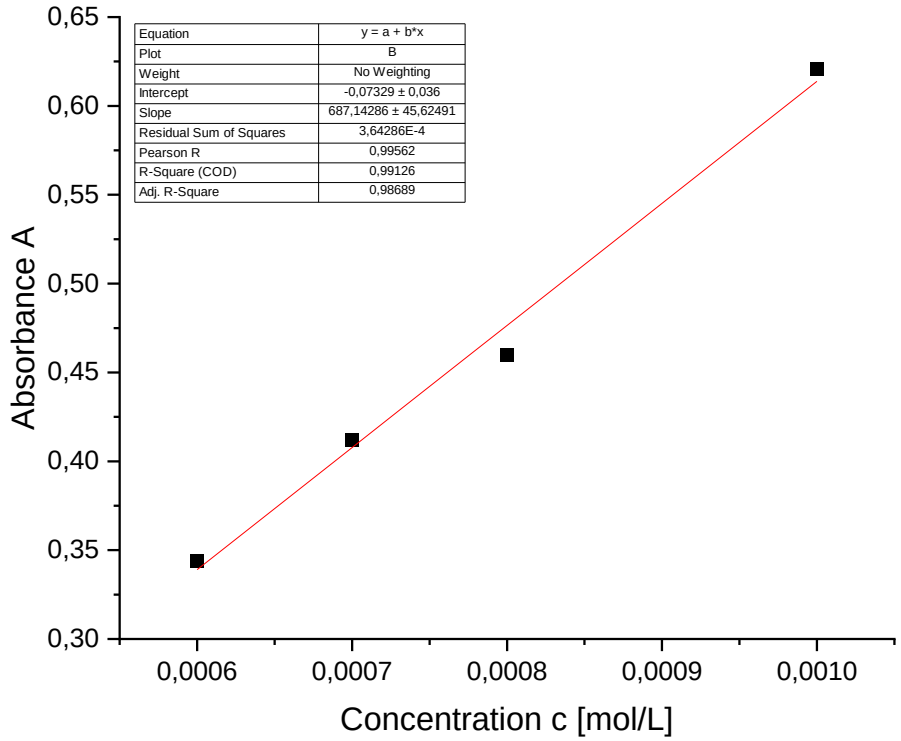
Supplementary Figure S18. UV-Vis spectra of hafnium complex **3b** in hexane at different concentrations.



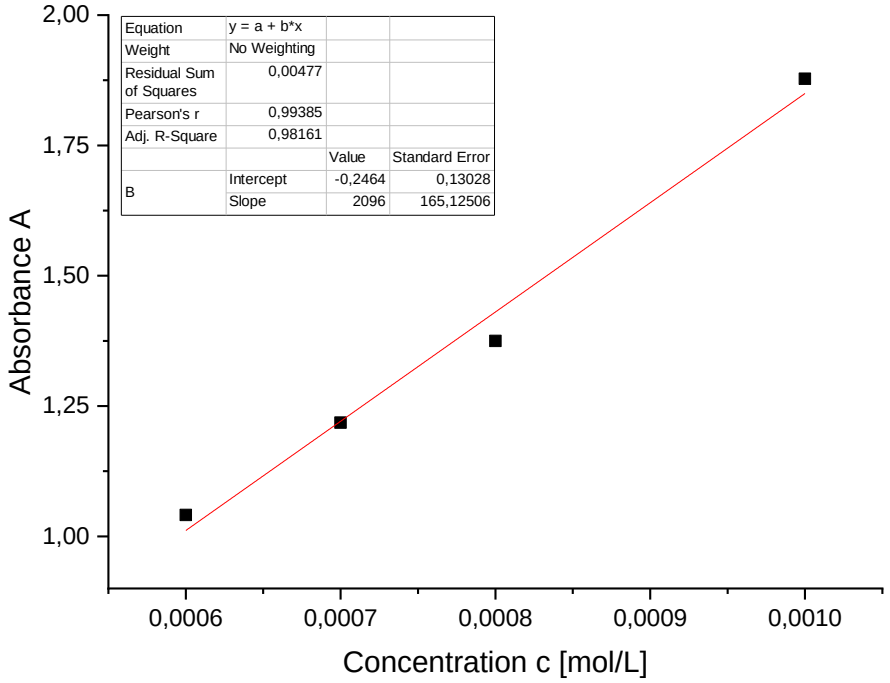
Supplementary Figure S19. Determination of the extinction ε = 1257 M^{-1} cm^{-1} of **3b** by linear regression at λ_{max} = 647 nm.



Supplementary Figure S20. of the extinction ε = 5303 M^{-1} cm^{-1} of **3b** by linear regression at λ = 524 nm.



Supplementary Figure S21. Determination of the extinction ε = 6871 M^{-1} cm^{-1} of **3b** by linear regression at λ = 437 nm.



Supplementary Figure S22. Determination of the extinction ε = 20960 M^{-1} cm^{-1} of **3b** by linear regression at λ = 340 nm.

3 Details on X-Ray Diffraction Studies

Crystallographic data

The data set was collected using a Bruker D8 Venture diffractometer with a microfocus sealed tube and a Photon II detector. Graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) was used. Data were collected at 122(2) K (**2**) or 133(2) K (**3a,b**) and corrected for absorption effects using the multi-scan method. The structures were solved by direct methods using SHELXS-97 (**2**)[S4a] or SHELXT (**3a,b**)[S4b] and were refined by full matrix least squares calculations on F^2 (SHELXL 2018[S5]) in the graphical user interface Shelxle.[S6] The refinement of the two structures **3a** and **3b** was each extended with the BOND$H command of SHELX to introduce the C-C-H angles and the C-H distances in the cif-file and then refined again. After the refinement, the two structures **3a** and **3b** each show one increased residual electron density peak near a non-heavy atom. This could be an indication of twinning, although neither TwinRotMat (PLATON)[S7] detected a twin law nor was non-merohedral twinning observed in the reciprocal space.

Acknowledgments

Instrumentation and technical assistance for this work were provided by the Service Center X-ray Diffraction, with financial support from Saarland University and German Science Foundation (project number INST 256/506-1).

3.1 Solid State Structure of Si_6Ir-Li 2

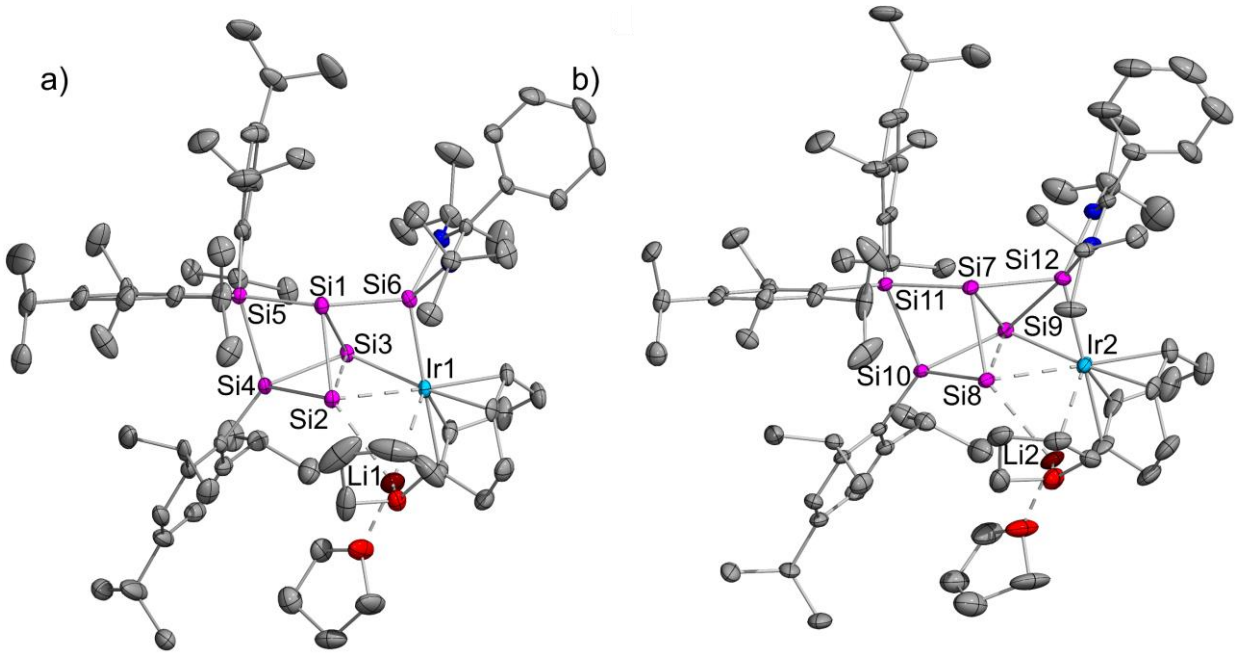
Refinement

All non H-atoms were located in the electron density maps and refined anisotropically. C-bound H atoms were placed in positions of optimized geometry and treated as riding atoms. Their isotropic displacement parameters were coupled to the corresponding carrier atoms by a factor of 1.2 (CH, CH2) or 1.5 (CH3). *Disorder*: Two isopropyl-groups (fvar 2: 0.60/0.40; fvar 4: 0.70/0.30), one tert.butyl-group (fvar 5: 0.65/0.35) and a part of the coordinated thf molecule (fvar 3: 0.61/0.39) are split over two positions.

Supplementary Table S1. Crystal data and structure refinement for $Si_5NHSiIrLi$ **2** (CCDC: 2447272).

Empirical formula	C76 H120 Ir Li N2 O2 Si6	
Formula weight	1461.41	
Temperature	122(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 14.3574(10) Å	α = 75.099(2)°.
	b = 22.2591(14) Å	β = 88.548(2)°.
	c = 25.9243(17) Å	γ = 77.283(2)°.

Volume	7805.7(9) $Å^3$
Z	4
Density (calculated)	1.244 Mg/m^3
Absorption coefficient	1.846 mm^{-1}
F(000)	3080
Crystal size	0.510 x 0.144 x 0.060 mm^3
Theta range for data collection	0.971 to 27.986°.
Index ranges	-18<=h<=18, -29<=k<=29, -34<=l<=34
Reflections collected	114921
Independent reflections	37415 [R(int) = 0.0547]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5737
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	37415 / 171 / 1715
Goodness-of-fit on F^2	1.025
Final R indices [I>2sigma(I)]	R1 = 0.0442, wR2 = 0.1001
R indices (all data)	R1 = 0.0702, wR2 = 0.1089
Largest diff. peak and hole	1.717 and -2.350 $e.Å^{-3}$



Supplementary Figure S23. Molecular structure of iridasiliconoid **2** in the solid state (a) molecule 1, b) molecule 2). Hydrogen atoms are omitted for clarity. Thermal ellipsoids represent 50% probability.

Supplementary Table S2. Comparison of the bonding parameters in molecule 1 and 2 of iridasiliconoid **2** and averaged arithmetic values.

Molecule 1		Molecule 2		Arithmetic Mean Values
Atoms	**Distance [Å]**	**Atoms**	**Distance [Å]**	**Distance [Å]**
Ir1-Si2	2.658(1)	Ir2-Si8	2.623(1)	2.641(1)
Ir1-Si3	2.404(1)	Ir2-Si9	2.417(1)	2.411(1)
Ir1-Si6	2.343(1)	Ir2-Si12	2.345(1)	2.344(1)
Ir1-Li1	2.880(8)	Ir2-Li2	2.880(8)	2.880(8)
Si1-Si2	2.327(2)	Si7-Si8	2.327(2)	2.327(2)
Si1-Si3	2.438(2)	Si7-Si9	2.408(2)	2.423(2)
Si1-Si5	2.317(2)	Si7-Si11	2.324(2)	2.321(2)
Si1-Si6	2.286(2)	Si7-Si12	2.284(2)	2.285(2)
Si2-Si3	2.466(2)	Si8-Si9	2.484(2)	2.475(2)
Si2-Si4	2.400(2)	Si8-Si10	2.375(2)	2.388(2)
Si2-Li1	2.617(8)	Si8-Li2	2.605(7)	2.611(8)
Si3-Si4	2.321(1)	Si9-Si10	2.341(2)	2.331(2)
Si4-Si5	2.405(2)	Si10-Si11	2.399(1)	2.402(2)
Atoms	**Angle [°]**	**Atoms**	**Angle [°]**	**Angle [°]**
Si5-Si1-Si6	146.2(6)	Si11-Si7-Si12	153.5(7)	149.9(7)
Si6-Ir1-Li1	125.1(2)	Si12-Ir2-Li2	120.3(2)	122.7(2)
Si3-Ir1-Li1	105.8(2)	Si9-Ir2-Li2	108.2(2)	107.1(2)
Si2-Ir1-Li1	56.2(2)	Si8-Ir2-Li2	56.3(2)	56.3(2)
Si3-Si2-Li1	112.4(2)	Si9-Si8-Li2	115.3(2)	113.9(2)
Si6-Ir-Si3	68.4(4)	Si12-Ir2-Si9	69.9(4)	69.2(4)

3.2 Solid State Structure of Si6Ir-Zr 3a

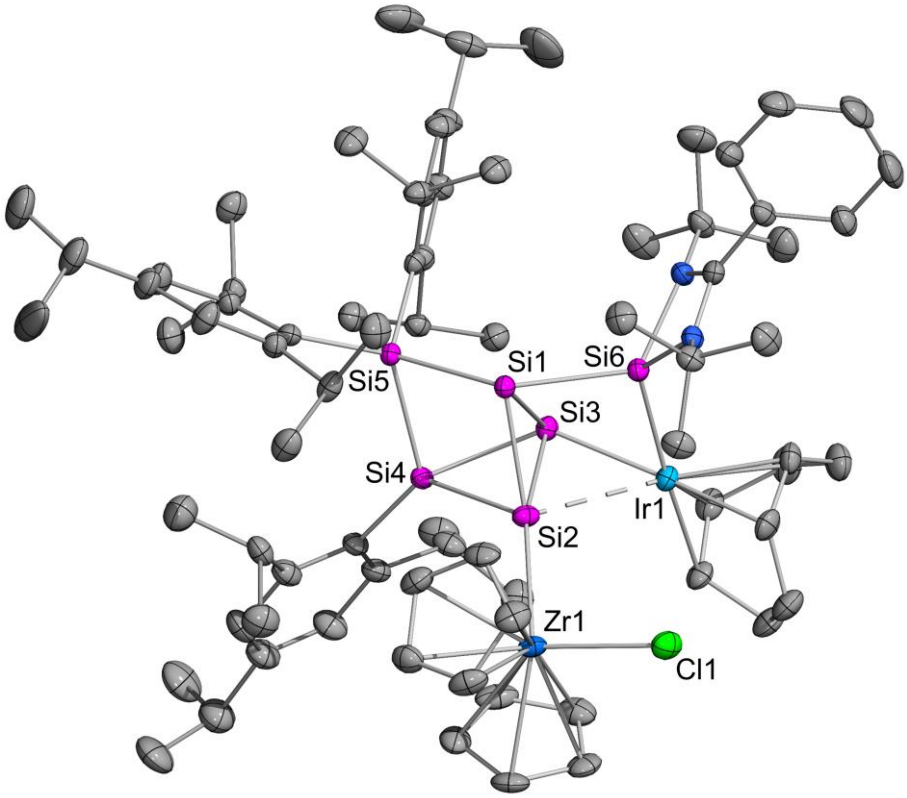
Refinement

All non H-atoms were located on the electron density maps and refined anisotropically. C-bound H atoms were placed in positions of optimized geometry and treated as riding atoms. Their isotropic displacement parameters were coupled to the corresponding carrier atoms by a factor of 1.2 (CH, CH2) or 1.5 (CH3). *Disorder*: One of the isopropyl groups (C28a C30a and C28b C30b) was split over two positions. Its occupancy factors refined to 81.1% for the major component. Some residual electron density (3.11 $Å^3$) was found near (2.28 Å) a isopropyl group (C23) of the Tip substituent due to unmodelled disorder.

Supplementary Table S3. Crystal data and structure refinement for zirconium complex **3a** (CCDC: 2447286).

Empirical formula	C78 H114 Cl Ir N2 Si6 Zr	
Formula weight	1567.12	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 13.0066(6) Å	α = 85.640(2)°.
	b = 16.0638(8)) Å	β = 73.327(2)°.
	c = 20.4956(10) Å	γ = 70.671(2)°.
Volume	3870.1(3) $Å^3$	

Z	2
Density (calculated)	1.345 Mg/m^3
Absorption coefficient	2.021 mm^{-1}
F(000)	1628
Crystal size	0.176 x 0.109 x 0.064 mm^3
Theta range for data collection	2.075 to 25.681°
Index ranges	-15<=h<=15, -19<=k<=19, -24<=l<=24
Reflections collected	137646
Independent reflections	14647 [R(int) = 0.0688]
Completeness to theta = 25.027°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7455 and 0.6989
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14647 / 87 / 856
Goodness-of-fit on F^2	1.057
Final R indices [I>2sigma(I)]	R1 = 0.0306, wR2 = 0.0629
R indices (all data)	R1 = 0.0383, wR2 = 0.0665
Largest diff. peak and hole	3.312 and –0.598 e.Å^{-3}



Supplementary Figure S24. Molecular structure of the zirconium complex **3a** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids represent 50% probability.

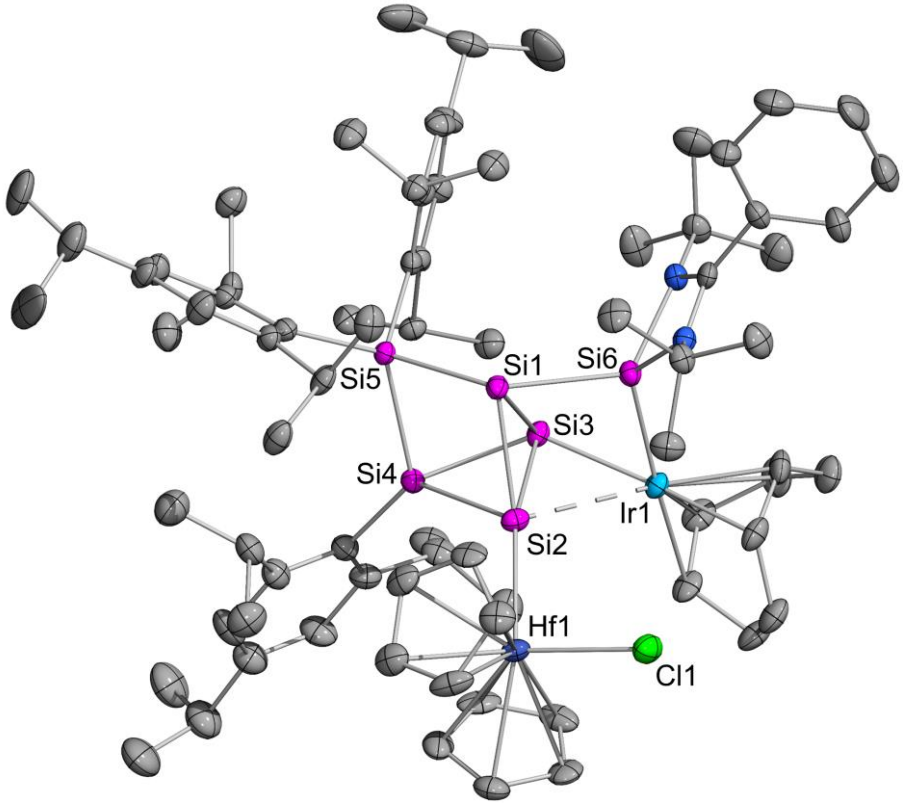
3.3 Solid State Structure of Si6Ir-Hf 3b

Refinement

All non H-atoms were located on the electron density maps and refined anisotropically. C-bound H atoms were placed in positions of optimized geometry and treated as riding atoms. Their isotropic displacement parameters were coupled to the corresponding carrier atoms by a factor of 1.2 (CH, CH2) or 1.5 (CH3). Disorder: One of the isopropyl groups is split over two positions. Its occupancy factors refined to 78 % and 22 %, respectively.

Supplementary Table S4. Crystal data and structure refinement for hafnium complex **3b** (CCDC: 2447266).

Empirical formula	C78 H114 Cl Hf Ir N2 Si6	
Formula weight	1654.39	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.9983(9) Å	α = 85.512(3)°.
	b = 16.0655(12) Å	β = 73.304(3)°.
	c = 20.4888(14) Å	γ = 70.764(3)°.
Volume	3868.7(5) $Å^3$	
Z	2	
Density (calculated)	1.420 Mg/m^3	
Absorption coefficient	3.228 mm^{-1}	
F(000)	1692	
Crystal size	0.172 x 0.138 x 0.074 mm^3	
Theta range for data collection	2.076 to 25.027°	
Index ranges	-15<=h<=15, -19<=k<=19, -24<=l<=24	
Reflections collected	106012	
Independent reflections	13360 [R(int) = 0.0607]	
Completeness to theta = 25.027°	97.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7455 and 0.6256	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13360 / 87 / 852	
Goodness-of-fit on F^2	1.107	
Final R indices [I>2sigma(I)]	R1 = 0.0331, wR2 = 0.0644	
R indices (all data)	R1 = 0.0469, wR2 = 0.0698	
Largest diff. peak and hole	2.548 and –1.354 $e.Å^{-3}$	



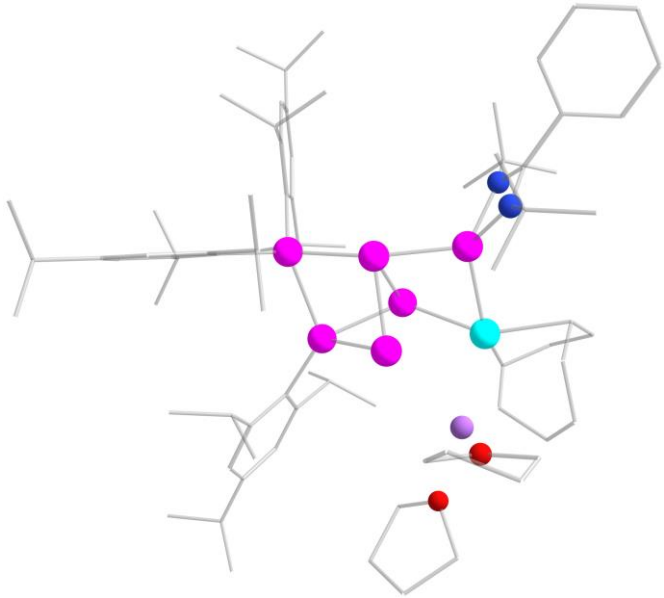
Supplementary Figure S25. Molecular structure of the hafnium complex **3b** in the solid state. Hydrogen atoms are omitted for clarity. Thermal ellipsoids represent 50% probability.

4 DFT Calculations

Computations were carried out with orca 5.0.4/6.0.1[S8] and the Gaussian 16 program package.[S9] Structural optimizations in the gas-phase, frequency analyses and single point calculations were performed at the B3LYP or PBE0/def2TZVPP level of theory [S10,11] for **2** and **3a,b** including the dispersion correction by Grimme.[S12] Tighter than default convergence had to be chosen for the scf (thightscf) in the TD-DFT calculation for **2**. Implicit correction for solvation effects (solvents: hexane or benzene) were investigated with the CPCM model for geometry optimizations for spectroscopy calculations.[S13]
Pictures of Kohn-Sham orbitals were displayed with ChemCraft 1.8.[S14]

4.1 Si_6Ir-Li 2

4.1.1 Optimization and single point



Supplementary Figure S26. Optimized molecular structure of Si_6Ir-Li **2** at the PBE0/def2-TZVPP level of theory.[S10c-e,11] Hydrogen atoms omitted for clarity.

Supplementary Table S5. Coordinates of the optimized geometry of Si_6Ir-Li **2** at the PBE0/def2-TZVPP level of theory.[S10c-e,11]

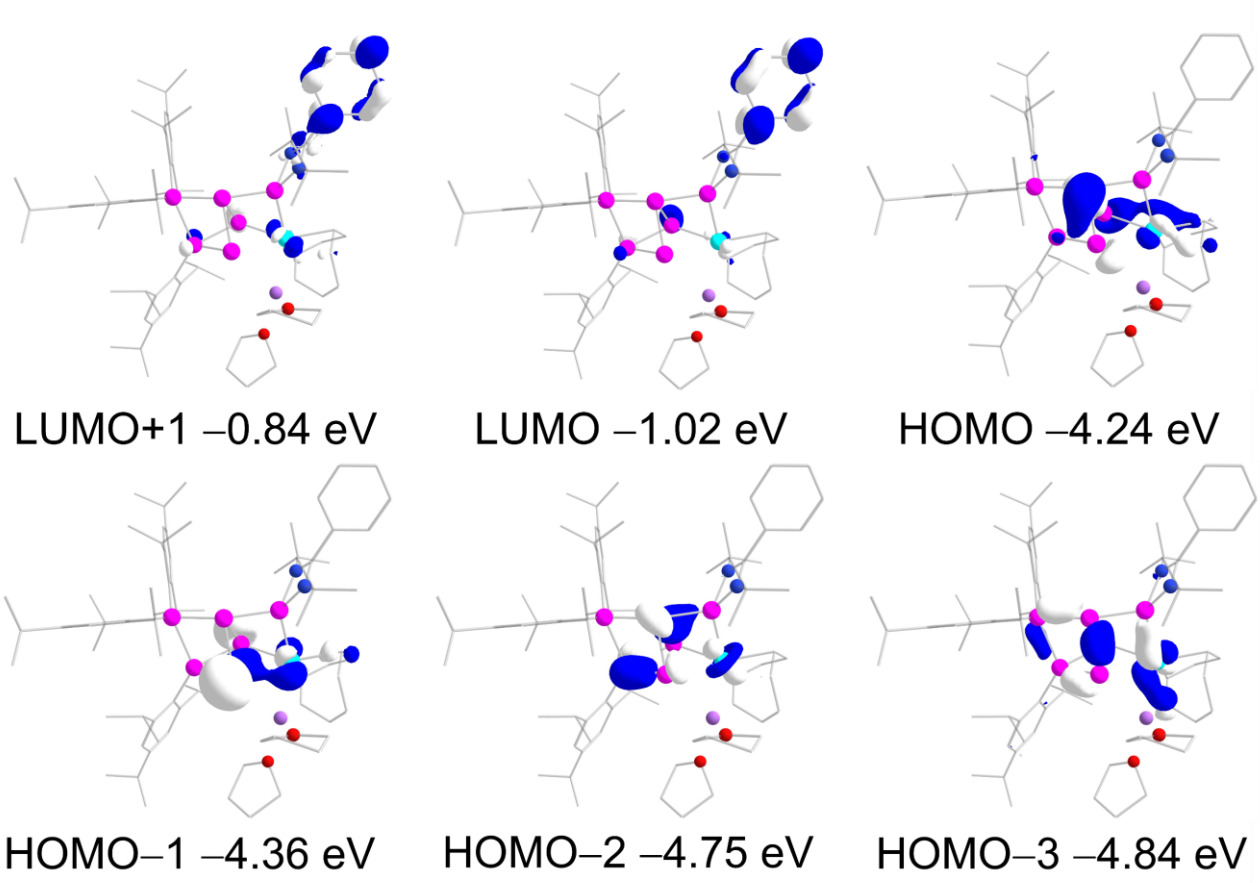
N	-4.003520	1.429997	-0.641711
N	-4.079205	0.511421	1.304294
Ir	-2.236352	-1.939778	-0.977011
Si	-0.566039	0.799395	0.538374
Si	0.006983	-1.467187	0.607132
Si	-0.486513	-0.353416	-1.564285
Si	1.713660	-0.476850	-0.741557
Si	1.509895	1.829638	0.109458
Si	-2.731759	0.177280	0.001477
C	-4.343464	-2.458043	-1.215834
H	-4.987477	-1.654359	-0.877117
C	-4.715009	-2.994602	-2.597061
H	-5.023935	-4.040604	-2.523957
H	-5.591585	-2.458305	-2.967219
C	-3.565450	-2.841285	-3.607125
H	-3.636641	-3.603863	-4.395877
H	-3.659058	-1.876972	-4.110048
C	-2.192354	-2.884098	-2.967422
H	-1.427516	-2.413509	-3.571432
C	-1.752323	-3.871596	-2.060260
H	-0.688535	-4.068889	-2.057884
C	3.318908	-1.444840	-1.247983
C	3.571022	-1.858713	-2.578651
C	4.659912	-2.687962	-2.857690
H	4.835500	-3.001199	-3.879889

C	5.536577	-3.126850	-1.875282
C	5.294568	-2.706129	-0.571726
H	5.966063	-3.026419	0.215501
C	4.218696	-1.884005	-0.239873
C	2.678465	-1.463832	-3.749296
H	2.032455	-0.652496	-3.413143
C	3.471281	-0.951365	-4.961368
H	2.792101	-0.543380	-5.712404
H	4.040733	-1.748367	-5.442772
H	4.173885	-0.167793	-4.677325
C	1.759910	-2.622866	-4.166178
H	1.149386	-2.962184	-3.329811
H	2.342859	-3.473242	-4.527944
H	1.086358	-2.311663	-4.967733
C	6.717046	-4.016385	-2.226552
H	6.655861	-4.212244	-3.301253
C	8.060032	-3.317165	-1.964810
H	8.121207	-2.370050	-2.502095
H	8.892057	-3.946767	-2.287903
H	8.195571	-3.105905	-0.902363
C	6.657535	-5.374139	-1.510460
H	6.721592	-5.254747	-0.427059
H	7.487539	-6.011801	-1.822513
H	5.726326	-5.897111	-1.733602
C	4.056162	-1.517025	1.233526
H	3.268771	-0.765102	1.305542
C	5.323855	-0.900058	1.842209
H	5.677262	-0.051472	1.260108
H	6.135951	-1.627211	1.906472
H	5.117432	-0.545709	2.853168
C	3.607689	-2.727145	2.068307
H	3.481309	-2.443197	3.115376
H	4.352808	-3.525157	2.028224
H	2.656515	-3.120914	1.709807
C	2.832752	2.244912	1.489651
C	4.102763	2.727161	1.078752
C	5.085887	3.030404	2.022680
H	6.043821	3.404966	1.681350
C	4.889447	2.870155	3.385269
C	3.652450	2.383617	3.788091
H	3.467024	2.241595	4.845629
C	2.632622	2.070607	2.888721
C	4.482022	2.964008	-0.381195
H	3.648764	2.645552	-1.003881
C	5.696713	2.134184	-0.826163
H	5.510654	1.066211	-0.717522
H	6.590766	2.383231	-0.252156

H	5.919306	2.326560	-1.877801
C	4.712060	4.458527	-0.660637
H	4.948112	4.623626	-1.713434
H	5.546354	4.843449	-0.071303
H	3.827160	5.046443	-0.418612
C	5.982148	3.218983	4.380872
H	6.849135	3.543272	3.797505
C	5.576802	4.390708	5.288524
H	5.298376	5.266082	4.700369
H	6.401206	4.671188	5.947926
H	4.723711	4.126635	5.916737
C	6.418734	2.004955	5.215061
H	5.598589	1.633000	5.832341
H	7.240900	2.271581	5.882844
H	6.752095	1.186366	4.576071
C	1.341821	1.544296	3.513522
H	0.604927	1.432399	2.721416
C	0.742682	2.503792	4.554693
H	0.606315	3.505790	4.149079
H	1.372556	2.589512	5.442182
H	-0.232953	2.137375	4.882274
C	1.534259	0.150308	4.130056
H	0.592776	-0.209560	4.552016
H	2.276200	0.168650	4.931554
H	1.856878	-0.569759	3.379421
C	1.209805	3.455553	-0.934243
C	0.687789	4.581180	-0.237459
C	0.416209	5.770517	-0.912013
H	0.027356	6.608719	-0.346858
C	0.623248	5.917724	-2.277436
C	1.114261	4.814699	-2.957336
H	1.274810	4.902136	-4.025285
C	1.411616	3.601909	-2.329211
C	0.370056	4.576868	1.256348
H	0.647356	3.608415	1.663856
C	1.184825	5.628490	2.025092
H	0.941997	6.641615	1.699937
H	2.254645	5.476274	1.882823
H	0.977275	5.569116	3.095393
C	-1.135764	4.743593	1.517418
H	-1.498473	5.714086	1.173319
H	-1.348311	4.669867	2.586672
H	-1.707394	3.968589	1.004432
C	0.346209	7.223095	-3.002746
H	0.493224	7.028041	-4.069307
C	1.343882	8.319557	-2.595685
H	1.174317	9.231378	-3.172817

H	2.372333	7.997182	-2.762909
H	1.242042	8.570286	-1.537764
C	-1.100501	7.704086	-2.819767
H	-1.310300	7.945738	-1.776051
H	-1.813207	6.940803	-3.134923
H	-1.283235	8.604911	-3.409598
C	1.938401	2.500260	-3.244059
H	2.173544	1.634916	-2.623879
C	3.225078	2.910421	-3.981702
H	3.049742	3.751457	-4.654389
H	3.594479	2.080874	-4.585667
H	4.013954	3.200490	-3.289955
C	0.872781	2.060769	-4.260655
H	-0.034256	1.724762	-3.760673
H	1.244285	1.236690	-4.871878
H	0.610011	2.880007	-4.932989
C	-4.712936	1.356685	0.490071
C	-4.326117	2.098154	-1.928969
H	-5.635332	3.726968	-1.238846
C	-3.077760	2.022998	-2.814077
H	-3.284317	2.508679	-3.768393
H	-2.791169	0.991322	-3.006745
H	-2.231596	2.527219	-2.348662
C	-5.478757	1.364936	-2.637046
H	-5.232029	0.312768	-2.776975
H	-5.653702	1.807808	-3.619139
C	-4.680503	3.582760	-1.737329
H	-4.744638	4.060178	-2.716149
H	-3.904777	4.093085	-1.165721
H	-6.407342	1.435048	-2.072192
C	-4.336932	0.143680	2.713194
C	-4.251506	1.369639	3.639919
H	-5.059670	2.074116	3.458057
H	-3.300206	1.884138	3.501557
H	-4.318073	1.049750	4.681387
C	-3.238004	-0.844244	3.124725
H	-3.403068	-1.156122	4.157119
H	-5.782265	-1.398216	2.191408
H	-2.250179	-0.390905	3.051959
C	-5.702070	-0.548062	2.870070
H	-5.813262	-0.915633	3.891932
H	-6.528516	0.130999	2.671872
H	-3.240992	-1.725862	2.486132
C	-8.392187	2.207549	0.790604
C	-8.339940	3.470619	1.368932
C	-7.217820	1.519470	0.506739
H	-9.254256	4.005335	1.589878

H	-7.264950	0.533962	0.063617
C	-7.107176	4.044568	1.661356
C	-5.977847	2.090815	0.795252
H	-7.057761	5.028381	2.109001
C	-5.932958	3.359745	1.375627
H	-4.976779	3.814520	1.595801
H	-9.347189	1.754388	0.559591
C	-3.789520	-3.278426	-0.185321
H	-4.089584	-3.041862	0.831797
C	-3.496066	-4.756421	-0.392533
H	-2.982058	-5.137396	0.496735
H	-4.430003	-5.334497	-0.439442
C	-2.630389	-5.046376	-1.638967
H	-1.992278	-5.909387	-1.438136
H	-3.269206	-5.345221	-2.472905
Li	-1.039881	-3.832940	0.808605
C	-2.288139	-4.987424	4.845261
C	-2.659124	-4.854159	3.370520
C	-0.443321	-4.054753	3.670226
C	-1.175986	-3.943360	4.999800
H	-1.903072	-5.987167	5.055226
H	-3.438518	-4.105328	3.216322
H	-2.984260	-5.792458	2.920604
H	0.022811	-3.130149	3.333614
H	-1.600096	-2.945322	5.116176
H	-0.521824	-4.136250	5.848813
H	-3.140495	-4.811422	5.500074
H	0.310995	-4.846432	3.691884
O	-1.458494	-4.413907	2.696278
C	1.686256	-6.966105	1.151639
C	0.222324	-6.652002	0.851462
C	1.391904	-5.186400	-0.490212
C	2.455561	-6.129296	0.101809
H	1.899911	-8.031996	1.082041
H	-0.433242	-6.685344	1.718558
H	-0.177925	-7.315125	0.075388
H	1.111049	-5.490508	-1.501960
H	3.267584	-5.569190	0.559013
H	2.886655	-6.757607	-0.676268
H	1.937962	-6.638917	2.160328
O	0.235055	-5.304148	0.366895
H	1.681527	-4.138992	-0.502534



Supplementary Figure S27. Selected molecular orbitals of Si_6Ir-Li **2** at the PBE0/def2-TZVPP level of theory.[S10c-e,11]

4.1.2 Experimental vs. calculated NMR shifts

Supplementary Table S6. Comparison of experimental vs. calculated NMR chemical shifts for compound **2** at the PBE0/def2-TZVPP level of theory.[S10c-e,11]

	Exp. **2** $\delta(^{29}Si)$ [ppm]	Calc. **2** $\delta(^{29}Si)$ [ppm]
Si4 (SiTip)	149.6	163.8
Si6 (NHSi)	109.3	63.8
Si5 (SiTip2)	34.7	56.5
Si3 (unsubstituted)	−104.0	−125.6
Si1 (unsubstituted)	−178.4	−132.4
Si2 (SiLi)	−230.7	−228.1

4.1.3 TD-DFT calculations

Supplementary Table S7. Transition Energy, wavelength, and oscillator strengths of the electronic transition of **2** calculated at the TD-PBE0/def2-TZVPP[S10c-e,11] level of theory (the 354th orbital is the highest occupied orbital (HOMO), the 355th orbital is the lowest unoccupied orbital (LUMO) shown in Supplementary Figure S27).

STATE 1:	E= 0.086317 au	2.349 eV	18944.5 cm**-1	<S**2> = 0.000000
352a -> 355a :	0.025043 (c= -0.15825039)			
353a -> 355a :	0.119009 (c= 0.34497659)			

354a -> 355a : 0.780130 (c= -0.88324964)
354a -> 356a : 0.041454 (c= 0.20360142)

STATE 2: E= 0.096573 au 2.628 eV 21195.3 cm**-1 <S**2> = 0.000000
352a -> 355a : 0.014257 (c= -0.11940426)
353a -> 355a : 0.747358 (c= -0.86449849)
353a -> 356a : 0.045571 (c= 0.21347460)
354a -> 355a : 0.105743 (c= -0.32518084)

STATE 3: E= 0.104750 au 2.850 eV 22990.0 cm**-1 <S**2> = 0.000000
350a -> 355a : 0.016180 (c= -0.12720221)
351a -> 355a : 0.465084 (c= -0.68197088)
351a -> 356a : 0.033331 (c= 0.18256717)
352a -> 355a : 0.252146 (c= 0.50214093)
352a -> 356a : 0.019937 (c= -0.14119824)
354a -> 355a : 0.024805 (c= -0.15749643)
354a -> 358a : 0.126904 (c= -0.35623528)

STATE 4: E= 0.106014 au 2.885 eV 23267.4 cm**-1 <S**2> = 0.000000
350a -> 355a : 0.010256 (c= -0.10127226)
351a -> 355a : 0.054853 (c= -0.23420798)
352a -> 355a : 0.057100 (c= 0.23895615)
353a -> 358a : 0.012092 (c= -0.10996332)
354a -> 356a : 0.015019 (c= -0.12255032)
354a -> 358a : 0.777601 (c= 0.88181668)
354a -> 359a : 0.010213 (c= -0.10105993)
354a -> 360a : 0.011501 (c= -0.10724418)

STATE 5: E= 0.108957 au 2.965 eV 23913.3 cm**-1 <S**2> = 0.000000
350a -> 355a : 0.019609 (c= -0.14003041)
351a -> 355a : 0.351928 (c= 0.59323535)
351a -> 356a : 0.026662 (c= -0.16328523)
351a -> 358a : 0.011981 (c= -0.10945658)
352a -> 355a : 0.392372 (c= 0.62639634)
352a -> 356a : 0.029236 (c= -0.17098616)
353a -> 358a : 0.019052 (c= 0.13802776)
354a -> 355a : 0.025053 (c= -0.15828021)
354a -> 356a : 0.049962 (c= -0.22352213)

STATE 6: E= 0.110015 au 2.994 eV 24145.4 cm**-1 <S**2> = 0.000000
350a -> 355a : 0.037823 (c= -0.19448192)

352a -> 355a : 0.042958 (c= 0.20726424)
354a -> 355a : 0.030581 (c= 0.17487438)
354a -> 356a : 0.824560 (c= 0.90805287)
354a -> 359a : 0.012751 (c= -0.11291919)

STATE 7: E= 0.112359 au 3.057 eV 24659.9 cm**-1 <S**2> = 0.000000
350a -> 355a : 0.015053 (c= 0.12268916)
353a -> 355a : 0.013355 (c= -0.11556420)
353a -> 356a : 0.031876 (c= -0.17853884)
353a -> 358a : 0.842142 (c= 0.91768291)
353a -> 359a : 0.010692 (c= -0.10340175)
353a -> 360a : 0.013885 (c= -0.11783457)
354a -> 358a : 0.017342 (c= 0.13169027)

STATE 8: E= 0.114068 au 3.104 eV 25034.9 cm**-1 <S**2> = 0.000000
350a -> 355a : 0.785383 (c= -0.88621826)
350a -> 356a : 0.049204 (c= 0.22182005)
352a -> 355a : 0.057413 (c= -0.23961054)
353a -> 356a : 0.010010 (c= -0.10004820)
353a -> 358a : 0.013348 (c= 0.11553288)
354a -> 356a : 0.018957 (c= -0.13768535)
354a -> 360a : 0.010756 (c= 0.10371112)

STATE 9: E= 0.115253 au 3.136 eV 25295.2 cm**-1 <S**2> = 0.000000
353a -> 355a : 0.051500 (c= -0.22693617)
353a -> 356a : 0.866596 (c= -0.93091126)
353a -> 358a : 0.029305 (c= -0.17118788)
353a -> 359a : 0.022462 (c= 0.14987372)

STATE 10: E= 0.118964 au 3.237 eV 26109.5 cm**-1 <S**2> = 0.000000
354a -> 357a : 0.981156 (c= -0.99053304)

STATE 11: E= 0.120989 au 3.292 eV 26554.0 cm**-1 <S**2> = 0.000000
354a -> 356a : 0.016082 (c= 0.12681322)
354a -> 357a : 0.013803 (c= -0.11748776)
354a -> 358a : 0.030064 (c= 0.17338990)
354a -> 359a : 0.753038 (c= 0.86777759)
354a -> 360a : 0.129971 (c= 0.36051552)

STATE 12: E= 0.124346 au 3.384 eV 27290.8 cm**-1 <S**2> = 0.000000
353a -> 357a : 0.969806 (c= -0.98478707)

353a -> 359a : 0.019472 (c= -0.13954308)

STATE 13: E= 0.124716 au 3.394 eV 27372.1 cm**-1 <S**2> = 0.000000
351a -> 358a : 0.014575 (c= 0.12072508)
352a -> 358a : 0.445379 (c= 0.66736718)
352a -> 359a : 0.019287 (c= -0.13887882)
353a -> 360a : 0.013934 (c= -0.11804188)
354a -> 359a : 0.067341 (c= -0.25950080)
354a -> 360a : 0.330854 (c= 0.57519917)
354a -> 361a : 0.032958 (c= 0.18154363)
354a -> 366a : 0.010713 (c= -0.10350341)

STATE 14: E= 0.125753 au 3.422 eV 27599.6 cm**-1 <S**2> = 0.000000
349a -> 355a : 0.014350 (c= -0.11979132)
351a -> 358a : 0.020051 (c= 0.14160023)
352a -> 358a : 0.114345 (c= 0.33814949)
353a -> 357a : 0.016480 (c= 0.12837497)
353a -> 359a : 0.565328 (c= -0.75188312)
354a -> 359a : 0.011531 (c= 0.10738452)
354a -> 360a : 0.172566 (c= -0.41541117)

STATE 15: E= 0.126005 au 3.429 eV 27654.9 cm**-1 <S**2> = 0.000000
351a -> 358a : 0.064877 (c= -0.25470905)
352a -> 358a : 0.220097 (c= -0.46914493)
353a -> 358a : 0.023479 (c= -0.15322880)
353a -> 359a : 0.305257 (c= -0.55250083)
353a -> 360a : 0.091149 (c= -0.30190838)
354a -> 359a : 0.071144 (c= -0.26672823)
354a -> 360a : 0.132795 (c= 0.36441020)

STATE 16: E= 0.127564 au 3.471 eV 27997.0 cm**-1 <S**2> = 0.000000
347a -> 355a : 0.039910 (c= 0.19977598)
349a -> 355a : 0.661326 (c= -0.81321924)
349a -> 356a : 0.045193 (c= 0.21258682)
351a -> 358a : 0.071443 (c= -0.26728895)
352a -> 355a : 0.011627 (c= -0.10782631)
352a -> 356a : 0.077182 (c= -0.27781689)

STATE 17: E= 0.128860 au 3.506 eV 28281.5 cm**-1 <S**2> = 0.000000
351a -> 358a : 0.229111 (c= -0.47865547)
352a -> 356a : 0.035456 (c= 0.18829799)

353a -> 360a : 0.547197 (c= 0.73972744)
353a -> 361a : 0.031999 (c= 0.17888132)
353a -> 366a : 0.013761 (c= -0.11730625)
353a -> 367a : 0.018366 (c= 0.13552191)
354a -> 360a : 0.029094 (c= 0.17056934)

STATE 18: E= 0.129402 au 3.521 eV 28400.5 cm**-1 <S**2> = 0.000000
349a -> 355a : 0.092068 (c= -0.30342664)
351a -> 358a : 0.014480 (c= 0.12033186)
352a -> 355a : 0.049633 (c= 0.22278529)
352a -> 356a : 0.749328 (c= 0.86563734)
352a -> 359a : 0.013173 (c= -0.11477157)
353a -> 360a : 0.014373 (c= -0.11988929)

STATE 19: E= 0.130273 au 3.545 eV 28591.6 cm**-1 <S**2> = 0.000000
349a -> 355a : 0.018787 (c= 0.13706747)
350a -> 358a : 0.110574 (c= -0.33252732)
351a -> 358a : 0.383557 (c= -0.61931951)
352a -> 356a : 0.025613 (c= 0.16004060)
352a -> 358a : 0.088379 (c= 0.29728551)
353a -> 359a : 0.013837 (c= 0.11763114)
353a -> 360a : 0.127553 (c= -0.35714528)
353a -> 361a : 0.014923 (c= -0.12215982)
354a -> 360a : 0.052368 (c= -0.22883978)

STATE 20: E= 0.132199 au 3.597 eV 29014.4 cm**-1 <S**2> = 0.000000
351a -> 355a : 0.065982 (c= 0.25686865)
351a -> 356a : 0.877305 (c= 0.93664552)
351a -> 359a : 0.010405 (c= -0.10200492)

STATE 21: E= 0.134330 au 3.655 eV 29482.1 cm**-1 <S**2> = 0.000000
350a -> 358a : 0.026559 (c= -0.16296928)
353a -> 361a : 0.019816 (c= -0.14076905)
354a -> 360a : 0.028544 (c= -0.16894829)
354a -> 361a : 0.845602 (c= 0.91956618)

STATE 22: E= 0.137756 au 3.749 eV 30234.0 cm**-1 <S**2> = 0.000000
350a -> 358a : 0.345112 (c= 0.58746230)
350a -> 359a : 0.018897 (c= -0.13746523)
351a -> 358a : 0.045931 (c= -0.21431531)
352a -> 355a : 0.011729 (c= -0.10830108)

352a -> 357a : 0.064097 (c= -0.25317344)
352a -> 359a : 0.344302 (c= -0.58677228)
354a -> 360a : 0.015036 (c= -0.12262134)
354a -> 361a : 0.029557 (c= 0.17192251)
354a -> 366a : 0.014344 (c= -0.11976806)

STATE 23: E= 0.138378 au 3.765 eV 30370.5 cm**-1 <S**2> = 0.000000
350a -> 356a : 0.010723 (c= 0.10355355)
350a -> 358a : 0.204649 (c= 0.45238107)
350a -> 359a : 0.010135 (c= -0.10067306)
351a -> 358a : 0.023051 (c= -0.15182562)
352a -> 357a : 0.506833 (c= 0.71192205)
352a -> 358a : 0.015600 (c= 0.12489905)
352a -> 359a : 0.116432 (c= 0.34122081)
354a -> 362a : 0.012447 (c= -0.11156446)

STATE 24: E= 0.138701 au 3.774 eV 30441.4 cm**-1 <S**2> = 0.000000
350a -> 356a : 0.011927 (c= 0.10921232)
350a -> 358a : 0.072656 (c= 0.26954714)
352a -> 357a : 0.412662 (c= -0.64238777)
352a -> 359a : 0.362965 (c= 0.60246600)
353a -> 361a : 0.040729 (c= -0.20181333)
354a -> 362a : 0.013586 (c= -0.11656028)

STATE 25: E= 0.139017 au 3.783 eV 30510.7 cm**-1 <S**2> = 0.000000
352a -> 359a : 0.019837 (c= -0.14084325)
353a -> 360a : 0.036589 (c= 0.19128162)
353a -> 361a : 0.764663 (c= -0.87445015)
354a -> 361a : 0.022762 (c= -0.15087061)
354a -> 362a : 0.059779 (c= 0.24449698)
354a -> 363a : 0.013945 (c= -0.11808899)
354a -> 366a : 0.028617 (c= -0.16916633)

STATE 26: E= 0.139187 au 3.787 eV 30548.0 cm**-1 <S**2> = 0.000000
348a -> 355a : 0.028458 (c= -0.16869502)
349a -> 356a : 0.010898 (c= -0.10439428)
350a -> 355a : 0.041592 (c= -0.20394196)
350a -> 356a : 0.651378 (c= -0.80708011)
350a -> 358a : 0.030954 (c= 0.17593842)
351a -> 359a : 0.014616 (c= 0.12089761)
353a -> 361a : 0.019892 (c= -0.14104055)

354a -> 362a : 0.072182 (c= -0.26866640)
354a -> 363a : 0.012642 (c= 0.11243498)
354a -> 366a : 0.040198 (c= 0.20049416)

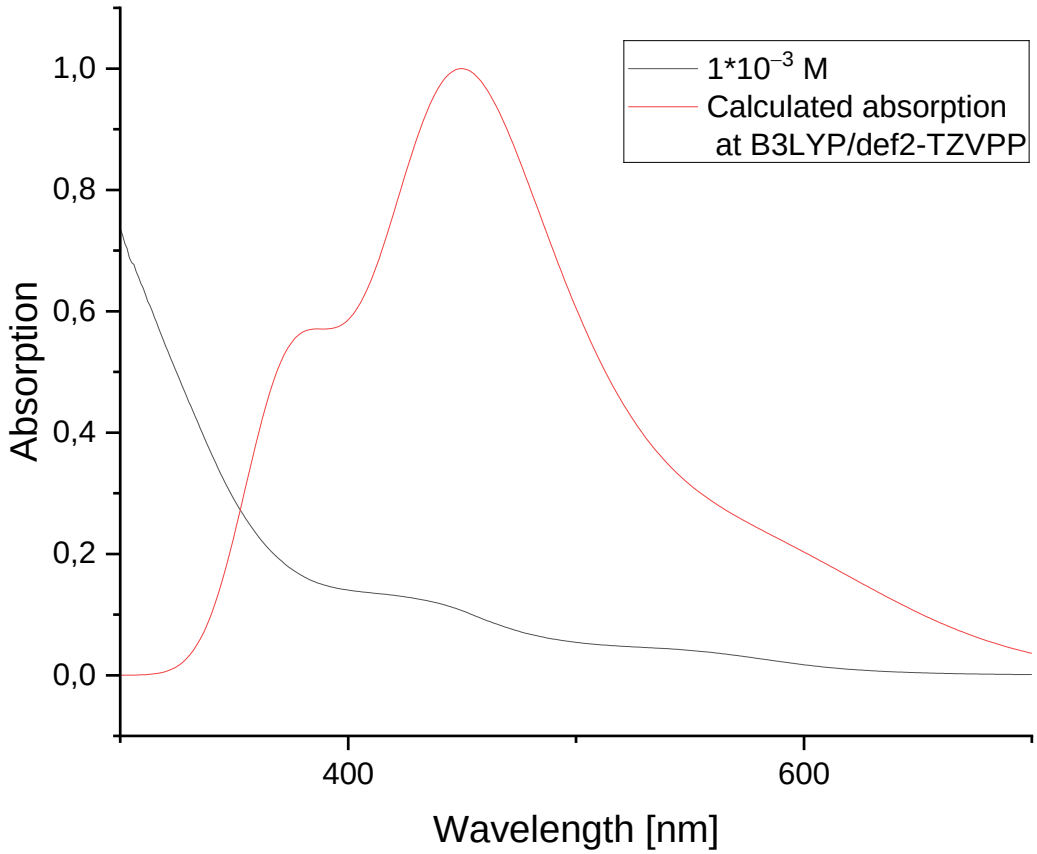
STATE 27: E= 0.139592 au 3.798 eV 30637.0 cm**-1 <S**2> = 0.000000
350a -> 356a : 0.163182 (c= -0.40395741)
351a -> 358a : 0.021900 (c= -0.14798785)
352a -> 359a : 0.038625 (c= 0.19653250)
353a -> 361a : 0.055918 (c= 0.23646950)
354a -> 362a : 0.366002 (c= 0.60498063)
354a -> 363a : 0.058170 (c= -0.24118380)
354a -> 364a : 0.017157 (c= -0.13098629)
354a -> 366a : 0.174603 (c= -0.41785562)

STATE 28: E= 0.141513 au 3.851 eV 31058.5 cm**-1 <S**2> = 0.000000
351a -> 357a : 0.942699 (c= -0.97092702)
351a -> 359a : 0.010075 (c= -0.10037312)
352a -> 360a : 0.016365 (c= 0.12792736)

STATE 29: E= 0.141879 au 3.861 eV 31138.7 cm**-1 <S**2> = 0.000000
346a -> 355a : 0.027680 (c= 0.16637325)
348a -> 355a : 0.127126 (c= 0.35654793)
348a -> 356a : 0.011794 (c= -0.10859997)
350a -> 356a : 0.031828 (c= -0.17840275)
350a -> 358a : 0.029644 (c= -0.17217409)
351a -> 357a : 0.023325 (c= 0.15272371)
351a -> 359a : 0.034896 (c= -0.18680355)
352a -> 360a : 0.170343 (c= 0.41272682)
352a -> 361a : 0.012851 (c= 0.11336076)
353a -> 362a : 0.016007 (c= 0.12651889)
354a -> 360a : 0.012649 (c= -0.11246591)
354a -> 362a : 0.190834 (c= -0.43684517)
354a -> 363a : 0.049295 (c= -0.22202381)
354a -> 364a : 0.012456 (c= 0.11160587)
354a -> 366a : 0.098772 (c= -0.31428010)
354a -> 367a : 0.050926 (c= 0.22566726)

STATE 30: E= 0.142029 au 3.865 eV 31171.7 cm**-1 <S**2> = 0.000000
351a -> 357a : 0.017573 (c= 0.13256295)
351a -> 359a : 0.060322 (c= -0.24560437)
351a -> 360a : 0.021520 (c= -0.14669851)

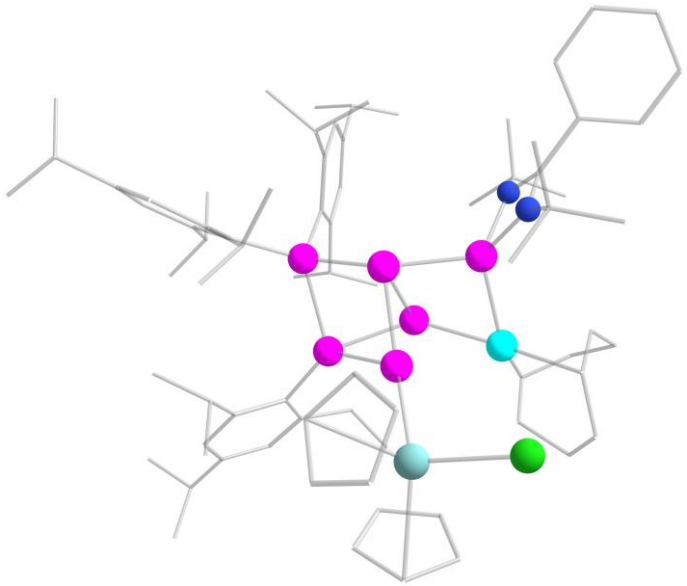
352a -> 359a : 0.017418 (c= -0.13197614)
352a -> 360a : 0.358032 (c= 0.59835763)
352a -> 361a : 0.013260 (c= 0.11515231)
353a -> 366a : 0.037428 (c= -0.19346226)
354a -> 362a : 0.055759 (c= 0.23613413)
354a -> 363a : 0.068299 (c= 0.26134051)
354a -> 364a : 0.019393 (c= -0.13925826)
354a -> 366a : 0.142448 (c= 0.37742323)
354a -> 367a : 0.055738 (c= -0.23608940)



Supplementary Figure S28. Experimental vs. calculated UV-Vis absorption bands of compound **2** at the PBE0/def2-TZVPP[S10c-e,11] level of theory.

4.2 Si_6Ir-Zr 3a

4.2.1 Optimization and single point



Supplementary Figure S29. Optimized molecular structure of Si_6Ir-Zr **3a** at the PBE0P/def2-TZVPP level of theory.[S10c-e,11] Hydrogen atoms omitted for clarity.

Supplementary Table S8. Coordinates of the optimized geometry of Si_6Ir-Zr **3a** at the PBE0P/def2-TZVPP level of theory.[S10c-e,11]

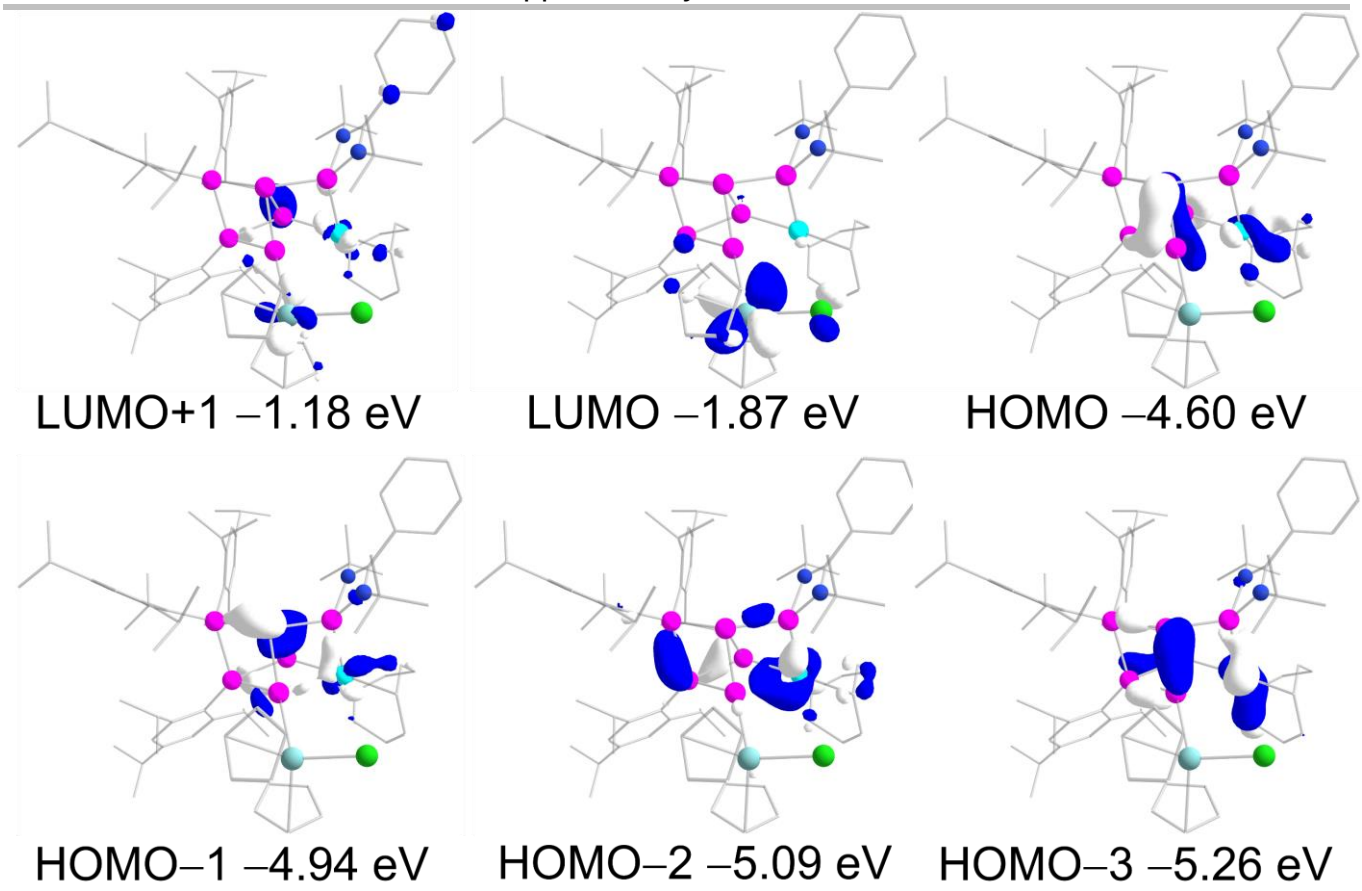
Ir	-2.772602	-0.703089	-1.303284
Zr	-1.380561	-3.857932	1.770778
Cl	-3.796549	-3.706606	2.033641
Si	1.916248	1.177483	0.366894
Si	-0.324514	0.704357	0.935874
Si	-2.475699	1.131262	0.140038
Si	-0.526737	0.006905	-1.407384
Si	-0.604042	-1.548621	0.403805
Si	1.474809	-0.938050	-0.694749
N	-3.707687	1.747736	1.419813
N	-3.034639	2.870210	-0.277799
C	1.885793	2.837591	-0.636828
C	1.623595	4.006194	0.117407
C	1.601962	5.254805	-0.497965
H	1.403045	6.134523	0.106614
C	1.835448	5.419332	-1.851273
C	2.079227	4.272864	-2.589598
H	2.259466	4.366595	-3.655326
C	2.106474	3.000719	-2.025602
C	2.376890	1.865722	-2.998844
H	2.384682	0.929517	-2.432946
C	1.269624	1.768924	-4.046545
H	1.471259	0.953132	-4.742459
H	1.200703	2.689792	-4.630413
H	0.296214	1.591859	-3.585819

C	3.726713	1.991881	-3.705852
H	4.556800	2.039273	-3.003152
H	3.768097	2.885651	-4.332782
H	3.889059	1.128390	-4.354709
C	1.349396	3.997346	1.609783
H	1.411993	2.966143	1.958172
C	2.387746	4.793308	2.395925
H	2.188691	4.719707	3.467898
H	2.367317	5.852217	2.126808
H	3.394606	4.415755	2.213550
C	-0.064618	4.480111	1.924726
H	-0.260476	4.409498	2.998323
H	-0.808511	3.877808	1.398516
H	-0.202036	5.524238	1.631110
C	1.828744	6.790173	-2.485573
H	1.607055	7.507471	-1.687916
C	0.737346	6.922606	-3.544788
H	-0.246911	6.702018	-3.127762
H	0.909430	6.233557	-4.375198
H	0.716609	7.935757	-3.953491
C	3.195281	7.149502	-3.064457
H	3.975223	7.089754	-2.303418
H	3.188673	8.164356	-3.469469
H	3.469175	6.470019	-3.875103
C	3.383574	1.363773	1.623421
C	3.255831	1.123397	3.011412
C	4.273250	1.506696	3.881996
H	4.141557	1.348551	4.947266
C	5.459844	2.070558	3.448163
C	5.622473	2.212944	2.080131
H	6.558059	2.606914	1.697697
C	4.625602	1.874943	1.171337
C	4.976653	2.068050	-0.292584
H	4.124379	1.739202	-0.888860
C	6.168757	1.209912	-0.717746
H	7.060694	1.442659	-0.132093
H	6.409997	1.393955	-1.767626
H	5.962005	0.145036	-0.608980
C	5.241021	3.537173	-0.616716
H	4.379734	4.159889	-0.373804
H	5.462509	3.666050	-1.678325
H	6.100772	3.909125	-0.054337
C	2.066678	0.421438	3.644558
H	1.475923	-0.021793	2.837780
C	1.155043	1.376811	4.411209
H	0.338233	0.826333	4.885631
H	0.711657	2.127299	3.756427

H	1.708281	1.897015	5.197321
C	2.512396	-0.711360	4.569031
H	3.035464	-0.331859	5.448710
H	3.185426	-1.404136	4.060672
H	1.648523	-1.273590	4.926282
H	8.569489	1.986897	4.972655
H	7.172168	4.291071	3.402997
C	2.831428	-2.045337	-1.482852
C	3.857018	-2.563077	-0.660324
C	4.914133	-3.268791	-1.225226
H	5.691079	-3.656679	-0.574859
C	5.000787	-3.501585	-2.588336
C	3.970458	-3.027132	-3.385984
H	4.016853	-3.221746	-4.451197
C	2.891261	-2.318458	-2.869218
C	1.772040	-1.923186	-3.810716
H	1.348662	-0.985224	-3.439170
C	2.206654	-1.698524	-5.253813
H	3.063859	-1.026412	-5.325561
H	1.383481	-1.261859	-5.823432
H	2.471714	-2.634825	-5.750840
C	0.656018	-2.965207	-3.763127
H	0.239506	-3.045681	-2.758103
H	1.032047	-3.948402	-4.058205
H	-0.157016	-2.693436	-4.440844
C	3.825242	-2.469672	0.854798
H	3.006137	-1.795912	1.135433
C	5.105574	-1.915206	1.469725
H	5.019049	-1.885809	2.558049
H	5.309611	-0.901180	1.132239
H	5.969640	-2.538629	1.229417
C	3.521017	-3.847577	1.442697
H	4.300152	-4.562727	1.168837
H	2.570875	-4.232343	1.070666
H	3.478841	-3.806612	2.534260
C	6.162514	-4.254733	-3.192349
H	5.979403	-4.307487	-4.270818
C	6.247354	-5.685860	-2.666769
H	5.316272	-6.228082	-2.840854
H	6.445230	-5.699253	-1.592245
H	7.057074	-6.229817	-3.158920
C	7.482806	-3.517423	-2.980887
H	7.724712	-3.443097	-1.917994
H	7.439316	-2.503915	-3.383294
H	8.302910	-4.046296	-3.472315
C	-3.866679	2.890431	0.765677
C	-4.797147	3.988097	1.132507

C	-6.127777	3.948079	0.729639
H	-6.487482	3.109680	0.145585
C	-6.992243	4.977237	1.073304
H	-8.025780	4.938922	0.751724
C	-6.535503	6.047833	1.826383
H	-7.211635	6.850028	2.095682
C	-5.209548	6.088539	2.235094
H	-4.847371	6.921653	2.824926
C	-4.342654	5.065579	1.888584
H	-3.306560	5.099951	2.202729
C	-2.989501	3.753227	-1.456580
C	-1.741673	3.383629	-2.245854
H	-0.841677	3.503173	-1.640561
H	-1.655465	4.032340	-3.118855
H	-1.793037	2.348975	-2.585526
C	-2.890714	5.229547	-1.075551
H	-3.798678	5.604894	-0.607696
H	-2.721546	5.812849	-1.982889
H	-2.047954	5.400346	-0.403772
C	-4.221025	3.517240	-2.331644
H	-4.300962	2.460446	-2.588931
H	-4.138876	4.093371	-3.255909
H	-5.137014	3.827390	-1.826240
C	-4.285706	1.269579	2.680936
C	-4.094817	2.277081	3.814636
H	-4.393693	1.816356	4.758389
H	-4.698636	3.172622	3.677516
H	-3.045418	2.567280	3.896003
C	-3.536206	-0.006069	3.042421
H	-3.964953	-0.439844	3.947186
H	-2.482608	0.212703	3.221446
H	-3.598524	-0.748462	2.245427
C	-5.769916	0.946471	2.506983
H	-6.152786	0.474247	3.414049
H	-5.920105	0.255985	1.675509
H	-6.357523	1.846868	2.326086
C	-2.988788	-1.079903	-3.436278
H	-2.069322	-0.786810	-3.932950
C	-2.991967	-2.337905	-2.812996
H	-2.066981	-2.897949	-2.883804
C	-4.254036	-3.152633	-2.621292
H	-4.006160	-4.215990	-2.679943
H	-4.933102	-2.968918	-3.458447
C	-4.949307	-2.870365	-1.285660
H	-6.030968	-3.050797	-1.369192
H	-4.586034	-3.573057	-0.535073
C	-4.690460	-1.482295	-0.755870

H	-4.844221	-1.399477	0.317274
C	-4.869718	-0.304240	-1.535167
H	-5.162994	0.589686	-0.991095
C	-5.367496	-0.345640	-2.970083
H	-5.988632	0.532082	-3.166947
H	-6.024404	-1.208501	-3.106028
C	-4.212815	-0.381791	-3.971244
H	-4.525712	-0.848154	-4.916375
H	-3.922217	0.641749	-4.221250
C	-0.155413	-4.777274	-0.241350
H	0.591539	-4.178605	-0.738900
C	-1.535637	-4.827389	-0.558507
H	-2.030876	-4.229493	-1.305602
C	-2.148090	-5.755906	0.299325
H	-3.198726	-5.994976	0.325815
C	-1.165508	-6.255311	1.180047
H	-1.320665	-6.989669	1.956045
C	0.072650	-5.663602	0.824691
H	1.028316	-5.873372	1.277361
C	-1.207519	-4.495955	4.179735
H	-1.774395	-5.347208	4.525215
C	0.111629	-4.519305	3.672635
H	0.732045	-5.395142	3.570159
C	0.466511	-3.206047	3.319213
H	1.396832	-2.890607	2.877720
C	-0.620317	-2.357175	3.647510
H	-0.652306	-1.292768	3.478538
C	-1.641215	-3.150675	4.189187
H	-2.614561	-2.807415	4.497767
C	6.530897	2.486029	4.428098
C	7.829629	1.711167	4.217419
H	7.663490	0.634222	4.278277
H	8.261213	1.926970	3.237232
C	6.783140	3.991407	4.379100
H	7.517148	4.284628	5.133584
H	5.865034	4.553781	4.558064
H	6.156982	2.242633	5.428480



Supplementary Figure S30. Selected molecular orbitals of Si_6Ir-Zr **3a** at the PBE0/def2-TZVPP level of theory.[S10c-e,11]

4.2.2 Experimental vs. calculated NMR shifts

Supplementary Table S9. Comparison of experimental vs. calculated NMR chemical shifts for compound **3a** at the PBE0//def2-TZVPP level of theory.[S10c-e,11]

	Exp. **3a** $\delta(^{29}Si)$ [ppm]	Calc. **3a** $\delta(^{29}Si)$ [ppm]
Si4 (SiTip)	73.7	83.8
Si6 (NHSi)	73.5	61.9
Si5 (SiTip2)	30.5	33.4
Si3 (unsubstituted)	−41.0	−30.1
Si1 (unsubstituted)	−131.9	−168.5
Si2 (SiZr)	−77.9	−67.5

4.2.3 TD-DFT calculations

Supplementary Table S10. Transition Energy, wavelength, and oscillator strengths of the electronic transition of **3a** calculated at the TD-PBE0/def2-TZVPP level of theory [S10c-e,11] (the 362nd orbital is the highest occupied orbital (HOMO), the 363th ortbital is the lowest unoccupied orbital (LUMO) shown in Supplementary Figure S30).

STATE 1:	E=	0.071609 au	1.949 eV	15716.3 cm**-1 <S**2> =	0.000000 Mult 1

361a -> 363a : 0.019195 (c= 0.13854517)
362a -> 363a : 0.953738 (c= -0.97659500)

STATE 2: E= 0.084446 au 2.298 eV 18533.8 cm**-1 <S**2> = 0.000000 Mult 1
359a -> 363a : 0.015308 (c= -0.12372531)
360a -> 364a : 0.011827 (c= -0.10875261)
361a -> 363a : 0.904576 (c= 0.95109195)
362a -> 363a : 0.013776 (c= 0.11737081)

STATE 3: E= 0.088659 au 2.413 eV 19458.4 cm**-1 <S**2> = 0.000000 Mult 1
359a -> 363a : 0.015795 (c= -0.12567712)
360a -> 363a : 0.923408 (c= -0.96094111)
362a -> 364a : 0.023071 (c= -0.15189298)

STATE 4: E= 0.094816 au 2.580 eV 20809.7 cm**-1 <S**2> = 0.000000 Mult 1
359a -> 363a : 0.332066 (c= 0.57625152)
360a -> 363a : 0.040628 (c= -0.20156421)
361a -> 364a : 0.033317 (c= -0.18252949)
362a -> 364a : 0.541875 (c= 0.73612148)

STATE 5: E= 0.095664 au 2.603 eV 20995.8 cm**-1 <S**2> = 0.000000 Mult 1
358a -> 363a : 0.017314 (c= 0.13158133)
359a -> 363a : 0.590452 (c= 0.76840856)
361a -> 363a : 0.019978 (c= 0.14134219)
361a -> 364a : 0.076287 (c= 0.27620150)
362a -> 364a : 0.251996 (c= -0.50199221)

STATE 6: E= 0.105162 au 2.862 eV 23080.4 cm**-1 <S**2> = 0.000000 Mult 1
358a -> 363a : 0.259338 (c= 0.50925207)
360a -> 364a : 0.044669 (c= -0.21135063)
361a -> 364a : 0.334792 (c= 0.57861211)
362a -> 364a : 0.057306 (c= 0.23938674)
362a -> 365a : 0.116020 (c= 0.34061647)
362a -> 366a : 0.130542 (c= -0.36130564)

STATE 7: E= 0.105215 au 2.863 eV 23091.9 cm**-1 <S**2> = 0.000000 Mult 1
358a -> 363a : 0.173954 (c= -0.41707775)
360a -> 364a : 0.078194 (c= 0.27963181)
361a -> 364a : 0.010484 (c= -0.10239000)
362a -> 364a : 0.038022 (c= -0.19499212)
362a -> 365a : 0.279291 (c= 0.52848009)

362a -> 366a : 0.359093 (c= -0.59924391)

STATE 8: E= 0.107119 au 2.915 eV 23509.9 cm**-1 <S**2> = 0.000000 Mult 1
358a -> 363a : 0.346484 (c= 0.58862855)
360a -> 364a : 0.029883 (c= -0.17286784)
361a -> 364a : 0.468631 (c= -0.68456661)
362a -> 364a : 0.024569 (c= -0.15674439)
362a -> 365a : 0.017036 (c= 0.13052142)
362a -> 366a : 0.034447 (c= -0.18560011)
362a -> 368a : 0.010478 (c= 0.10236081)

STATE 9: E= 0.109612 au 2.983 eV 24057.0 cm**-1 <S**2> = 0.000000 Mult 1
357a -> 363a : 0.019329 (c= 0.13902718)
358a -> 363a : 0.119060 (c= 0.34505030)
358a -> 364a : 0.035246 (c= -0.18773889)
360a -> 364a : 0.668865 (c= 0.81784182)
360a -> 366a : 0.029476 (c= 0.17168508)
362a -> 365a : 0.015196 (c= -0.12327061)
362a -> 368a : 0.010019 (c= 0.10009392)

STATE 10: E= 0.113326 au 3.084 eV 24872.3 cm**-1 <S**2> = 0.000000 Mult 1
357a -> 363a : 0.888255 (c= 0.94247278)
357a -> 364a : 0.042537 (c= -0.20624501)
358a -> 364a : 0.014451 (c= 0.12021435)
360a -> 364a : 0.013647 (c= -0.11682052)

STATE 11: E= 0.116013 au 3.157 eV 25461.8 cm**-1 <S**2> = 0.000000 Mult 1
359a -> 364a : 0.120074 (c= -0.34651674)
360a -> 364a : 0.010220 (c= 0.10109173)
362a -> 365a : 0.334847 (c= 0.57865945)
362a -> 366a : 0.204107 (c= 0.45178251)
362a -> 368a : 0.276003 (c= -0.52535963)

STATE 12: E= 0.116720 au 3.176 eV 25617.0 cm**-1 <S**2> = 0.000000 Mult 1
359a -> 364a : 0.685810 (c= 0.82813658)
360a -> 364a : 0.014403 (c= -0.12001300)
361a -> 365a : 0.031568 (c= 0.17767272)
361a -> 366a : 0.035763 (c= -0.18911237)
362a -> 365a : 0.057454 (c= 0.23969515)
362a -> 366a : 0.089514 (c= 0.29918825)

STATE 13: E= 0.117557 au 3.199 eV 25800.7 cm**-1 <S**2> = 0.000000 Mult 1
360a -> 366a : 0.016530 (c= 0.12856962)
361a -> 365a : 0.388279 (c= -0.62312062)
361a -> 366a : 0.372863 (c= 0.61062546)
362a -> 365a : 0.026004 (c= 0.16125697)
362a -> 366a : 0.050146 (c= 0.22393192)
362a -> 368a : 0.030489 (c= 0.17460985)
362a -> 369a : 0.015845 (c= -0.12587510)

STATE 14: E= 0.119777 au 3.259 eV 26288.1 cm**-1 <S**2> = 0.000000 Mult 1
357a -> 364a : 0.010857 (c= -0.10419790)
358a -> 364a : 0.014806 (c= -0.12168181)
359a -> 364a : 0.059183 (c= 0.24327639)
359a -> 366a : 0.011810 (c= 0.10867245)
360a -> 366a : 0.010392 (c= 0.10194210)
361a -> 365a : 0.023730 (c= -0.15404677)
361a -> 366a : 0.036683 (c= 0.19152935)
362a -> 365a : 0.080793 (c= -0.28424164)
362a -> 366a : 0.091053 (c= -0.30174989)
362a -> 368a : 0.510997 (c= -0.71484057)
362a -> 369a : 0.050747 (c= 0.22527077)
362a -> 370a : 0.015874 (c= -0.12599083)

STATE 15: E= 0.123975 au 3.374 eV 27209.4 cm**-1 <S**2> = 0.000000 Mult 1
357a -> 363a : 0.014281 (c= -0.11950374)
357a -> 364a : 0.033102 (c= -0.18193987)
358a -> 364a : 0.531155 (c= 0.72880370)
358a -> 368a : 0.012590 (c= 0.11220475)
360a -> 364a : 0.012914 (c= 0.11364015)
360a -> 365a : 0.157312 (c= -0.39662515)
360a -> 366a : 0.154434 (c= 0.39298097)

STATE 16: E= 0.125978 au 3.428 eV 27649.0 cm**-1 <S**2> = 0.000000 Mult 1
357a -> 364a : 0.020745 (c= 0.14403039)
358a -> 363a : 0.010930 (c= -0.10454847)
358a -> 364a : 0.232464 (c= -0.48214473)
359a -> 364a : 0.014518 (c= -0.12049222)
359a -> 365a : 0.034481 (c= -0.18568983)
359a -> 366a : 0.027523 (c= 0.16589911)
360a -> 364a : 0.041689 (c= -0.20417950)
360a -> 365a : 0.160854 (c= -0.40106651)

360a -> 366a : 0.229444 (c= 0.47900302)
361a -> 366a : 0.064162 (c= -0.25330279)
361a -> 368a : 0.056242 (c= 0.23715309)
362a -> 368a : 0.013184 (c= 0.11482094)

STATE 17: E= 0.127872 au 3.480 eV 28064.7 cm**-1 <S**2> = 0.000000 Mult 1
355a -> 363a : 0.033602 (c= 0.18330908)
356a -> 363a : 0.044796 (c= 0.21164997)
359a -> 365a : 0.044949 (c= -0.21201200)
359a -> 366a : 0.038263 (c= 0.19560860)
360a -> 365a : 0.012549 (c= -0.11202091)
360a -> 366a : 0.012131 (c= 0.11014267)
361a -> 365a : 0.277755 (c= 0.52702463)
361a -> 366a : 0.185179 (c= 0.43032458)
361a -> 368a : 0.241633 (c= -0.49156182)
362a -> 371a : 0.016820 (c= 0.12969339)

STATE 18: E= 0.128835 au 3.506 eV 28275.9 cm**-1 <S**2> = 0.000000 Mult 1
355a -> 363a : 0.013379 (c= 0.11566600)
356a -> 363a : 0.032336 (c= 0.17982194)
357a -> 364a : 0.021321 (c= 0.14601704)
361a -> 366a : 0.014654 (c= -0.12105524)
362a -> 365a : 0.026209 (c= -0.16189198)
362a -> 367a : 0.099999 (c= -0.31622581)
362a -> 368a : 0.079433 (c= -0.28183869)
362a -> 369a : 0.598805 (c= -0.77382471)
362a -> 370a : 0.035876 (c= 0.18941038)

STATE 19: E= 0.129461 au 3.523 eV 28413.5 cm**-1 <S**2> = 0.000000 Mult 1
355a -> 363a : 0.088705 (c= 0.29783380)
356a -> 363a : 0.230214 (c= 0.47980612)
357a -> 364a : 0.086785 (c= 0.29459262)
358a -> 364a : 0.022498 (c= 0.14999230)
359a -> 365a : 0.014023 (c= -0.11841778)
359a -> 366a : 0.027982 (c= 0.16727724)
360a -> 365a : 0.013588 (c= 0.11656782)
360a -> 366a : 0.014262 (c= -0.11942491)
361a -> 365a : 0.069564 (c= -0.26375029)
361a -> 366a : 0.050366 (c= -0.22442306)
362a -> 367a : 0.259808 (c= 0.50971361)
362a -> 369a : 0.010713 (c= 0.10350124)

STATE 20: E= 0.129619 au 3.527 eV 28448.1 cm**-1 <S**2> = 0.000000 Mult 1
356a -> 363a : 0.029359 (c= 0.17134389)
357a -> 364a : 0.015318 (c= 0.12376653)
359a -> 366a : 0.013798 (c= 0.11746558)
361a -> 365a : 0.039490 (c= -0.19872087)
361a -> 366a : 0.027613 (c= -0.16617029)
362a -> 367a : 0.607536 (c= -0.77944610)
362a -> 369a : 0.183961 (c= 0.42890679)

STATE 21: E= 0.130541 au 3.552 eV 28650.4 cm**-1 <S**2> = 0.000000 Mult 1
355a -> 363a : 0.113750 (c= -0.33726860)
356a -> 363a : 0.206794 (c= -0.45474568)
357a -> 364a : 0.070694 (c= 0.26588327)
359a -> 365a : 0.030849 (c= -0.17563787)
359a -> 366a : 0.029334 (c= 0.17127041)
361a -> 365a : 0.036397 (c= -0.19077871)
361a -> 366a : 0.042209 (c= -0.20544744)
361a -> 368a : 0.198461 (c= -0.44549007)
361a -> 369a : 0.046418 (c= 0.21544793)
361a -> 370a : 0.010642 (c= -0.10316014)
362a -> 367a : 0.010497 (c= 0.10245602)
362a -> 370a : 0.080357 (c= 0.28347320)
362a -> 372a : 0.013426 (c= -0.11587208)

STATE 22: E= 0.131093 au 3.567 eV 28771.5 cm**-1 <S**2> = 0.000000 Mult 1
355a -> 363a : 0.055922 (c= 0.23647763)
359a -> 365a : 0.189057 (c= 0.43480668)
359a -> 366a : 0.221193 (c= -0.47031159)
359a -> 368a : 0.011474 (c= 0.10711905)
360a -> 365a : 0.069897 (c= -0.26438100)
360a -> 368a : 0.048146 (c= 0.21942301)
361a -> 365a : 0.010054 (c= -0.10026921)
361a -> 366a : 0.020698 (c= -0.14386773)
361a -> 368a : 0.143522 (c= -0.37884299)
361a -> 369a : 0.037140 (c= 0.19271830)
362a -> 370a : 0.076125 (c= -0.27590757)
362a -> 371a : 0.032470 (c= 0.18019504)

STATE 23: E= 0.131685 au 3.583 eV 28901.6 cm**-1 <S**2> = 0.000000 Mult 1
355a -> 364a : 0.011726 (c= -0.10828795)

356a -> 363a : 0.040749 (c= -0.20186450)
357a -> 363a : 0.018122 (c= 0.13461954)
357a -> 364a : 0.524503 (c= 0.72422585)
358a -> 364a : 0.046343 (c= 0.21527406)
361a -> 365a : 0.018749 (c= 0.13692594)
361a -> 366a : 0.061061 (c= 0.24710528)
361a -> 368a : 0.086775 (c= 0.29457585)
361a -> 369a : 0.026039 (c= -0.16136607)
362a -> 370a : 0.040852 (c= -0.20211805)

STATE 24: E= 0.132270 au 3.599 eV 29030.0 cm**-1 <S**2> = 0.000000 Mult 1
352a -> 363a : 0.016358 (c= 0.12789743)
353a -> 363a : 0.038427 (c= -0.19602826)
354a -> 363a : 0.014203 (c= 0.11917750)
355a -> 363a : 0.491048 (c= -0.70074811)
356a -> 363a : 0.210196 (c= 0.45847109)
361a -> 368a : 0.018051 (c= -0.13435408)
362a -> 370a : 0.109300 (c= -0.33060543)
362a -> 372a : 0.013361 (c= 0.11559191)

STATE 25: E= 0.132665 au 3.610 eV 29116.7 cm**-1 <S**2> = 0.000000 Mult 1
355a -> 363a : 0.022992 (c= 0.15163044)
356a -> 363a : 0.093001 (c= -0.30496041)
359a -> 365a : 0.036197 (c= -0.19025423)
359a -> 366a : 0.052828 (c= 0.22984258)
360a -> 365a : 0.047765 (c= 0.21855252)
360a -> 368a : 0.075416 (c= -0.27461981)
361a -> 368a : 0.035151 (c= -0.18748493)
362a -> 369a : 0.046259 (c= -0.21507983)
362a -> 370a : 0.446553 (c= -0.66824648)
362a -> 372a : 0.048099 (c= 0.21931382)

STATE 26: E= 0.134604 au 3.663 eV 29542.2 cm**-1 <S**2> = 0.000000 Mult 1
359a -> 365a : 0.012276 (c= -0.11079660)
359a -> 366a : 0.012239 (c= 0.11063226)
360a -> 365a : 0.169278 (c= -0.41143461)
360a -> 366a : 0.112920 (c= -0.33603535)
360a -> 368a : 0.139520 (c= 0.37352379)
362a -> 371a : 0.426562 (c= -0.65311680)
362a -> 372a : 0.023812 (c= 0.15431006)

STATE 27: E= 0.135317 au 3.682 eV 29698.6 cm**-1 <S**2> = 0.000000 Mult 1
359a -> 366a : 0.040362 (c= -0.20090359)
360a -> 364a : 0.011572 (c= -0.10757237)
360a -> 365a : 0.184478 (c= 0.42950851)
360a -> 366a : 0.299500 (c= 0.54726608)
360a -> 369a : 0.012743 (c= -0.11288299)
360a -> 370a : 0.019103 (c= 0.13821386)
361a -> 368a : 0.020117 (c= -0.14183333)
362a -> 370a : 0.015714 (c= 0.12535417)
362a -> 371a : 0.283599 (c= -0.53254042)

STATE 28: E= 0.138632 au 3.772 eV 30426.3 cm**-1 <S**2> = 0.000000 Mult 1
347a -> 363a : 0.108792 (c= 0.32983692)
348a -> 363a : 0.048221 (c= -0.21959392)
358a -> 364a : 0.011313 (c= -0.10636470)
358a -> 365a : 0.063137 (c= 0.25127120)
358a -> 366a : 0.073189 (c= -0.27053404)
359a -> 368a : 0.019600 (c= -0.14000008)
360a -> 365a : 0.039346 (c= -0.19835907)
360a -> 366a : 0.018359 (c= -0.13549438)
360a -> 368a : 0.252498 (c= -0.50249188)
360a -> 369a : 0.020992 (c= 0.14488661)
361a -> 368a : 0.046436 (c= -0.21548933)
361a -> 369a : 0.015246 (c= -0.12347655)
362a -> 370a : 0.019499 (c= 0.13963758)
362a -> 372a : 0.041327 (c= 0.20328922)
362a -> 373a : 0.038985 (c= -0.19744545)
362a -> 374a : 0.014022 (c= 0.11841650)
362a -> 376a : 0.023298 (c= 0.15263530)

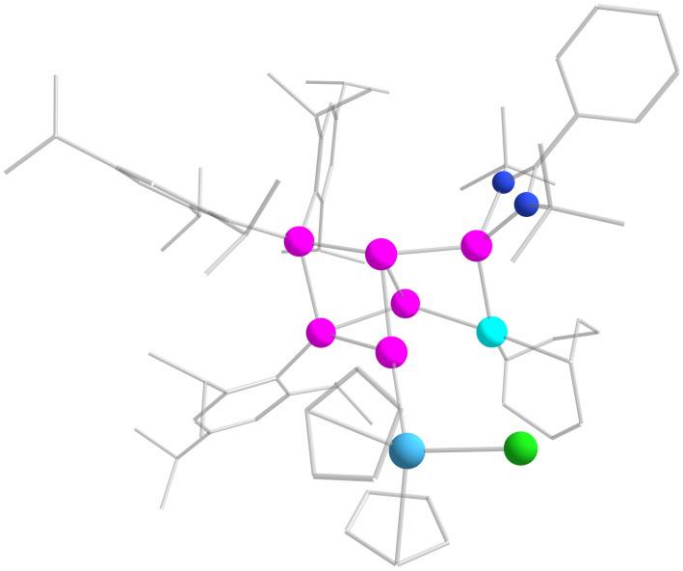
STATE 29: E= 0.139279 au 3.790 eV 30568.1 cm**-1 <S**2> = 0.000000 Mult 1
347a -> 363a : 0.047832 (c= -0.21870447)
348a -> 363a : 0.021815 (c= 0.14769741)
359a -> 365a : 0.063896 (c= 0.25277640)
359a -> 366a : 0.041671 (c= 0.20413393)
359a -> 368a : 0.040201 (c= -0.20050162)
361a -> 365a : 0.026161 (c= -0.16174271)
361a -> 366a : 0.015942 (c= -0.12626203)
361a -> 368a : 0.066317 (c= -0.25752029)
361a -> 369a : 0.536908 (c= -0.73274009)
361a -> 370a : 0.038248 (c= 0.19556970)

STATE 30: E= 0.139477 au 3.795 eV 30611.7 cm**-1 <S**2> = 0.000000 Mult 1

347a -> 363a : 0.194081 (c= -0.44054641)
348a -> 363a : 0.095111 (c= 0.30840027)
358a -> 365a : 0.042766 (c= -0.20679897)
358a -> 366a : 0.046778 (c= 0.21628170)
359a -> 366a : 0.016272 (c= -0.12756212)
360a -> 365a : 0.015330 (c= -0.12381328)
360a -> 366a : 0.018581 (c= -0.13631390)
360a -> 368a : 0.318397 (c= -0.56426701)
360a -> 369a : 0.019070 (c= 0.13809432)
361a -> 371a : 0.012282 (c= 0.11082600)
362a -> 371a : 0.041620 (c= -0.20401069)
362a -> 372a : 0.033998 (c= -0.18438651)

4.3 Si_6Ir-Hf 3b

4.3.1 Optimization and single point



Supplementary Figure S31. Optimized molecular structure of Si_6Ir-Hf **3b** at the PBE0P/def2-TZVPP level of theory.[S10c-e,11] Hydrogen atoms omitted for clarity.

Supplementary Table S11. Coordinates of the optimized geometry of Si_6Ir-Hf **3b** at the PBE0P/def2-TZVPP level of theory.[S10c-e,11]

Ir	-2.781759	-0.693964	-1.311847
Hf	-1.348342	-3.867825	1.766341
Cl	-3.752587	-3.688491	2.003664
Si	1.910778	1.174832	0.369569
Si	-0.331178	0.704093	0.937334
Si	-2.479464	1.135648	0.136028
Si	-0.531039	0.003012	-1.404239

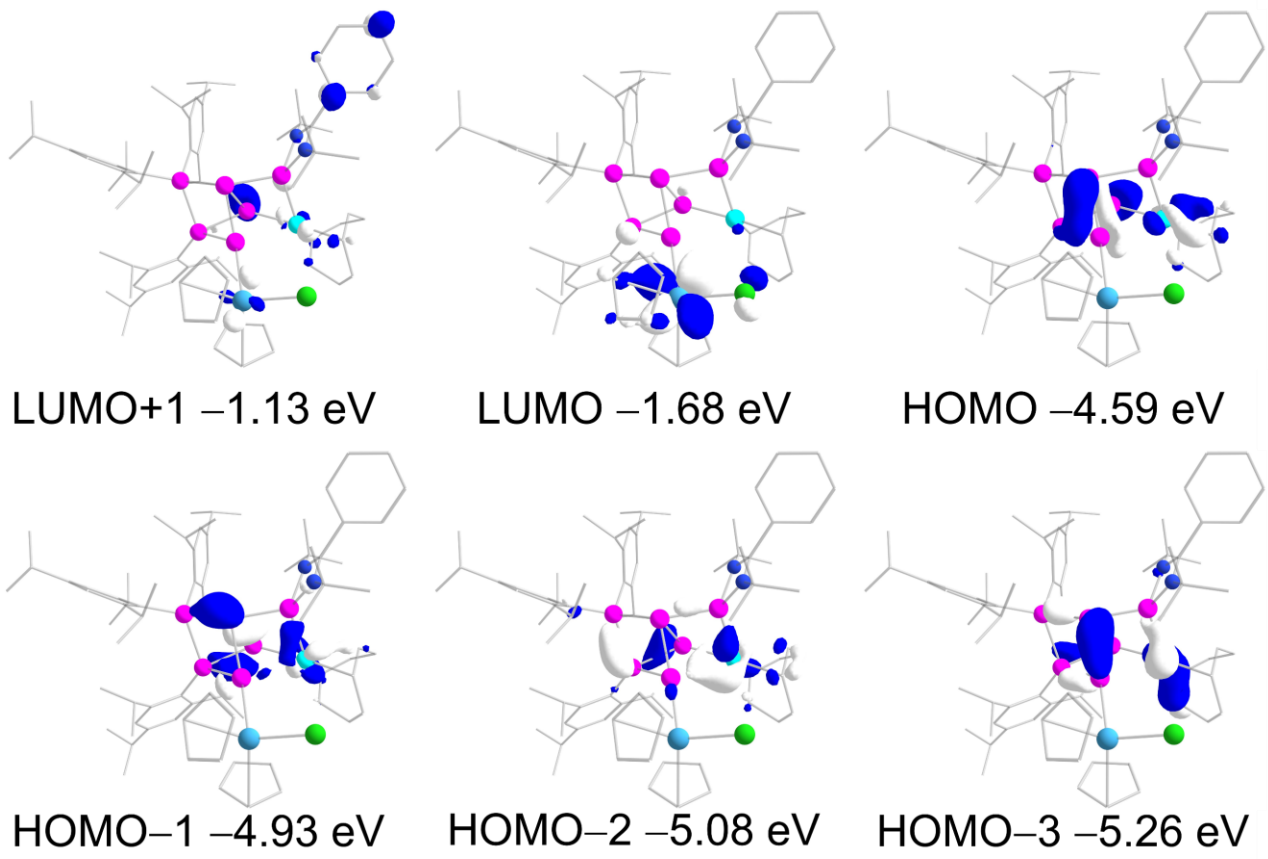
Si	-0.608607	-1.549300	0.409242
Si	1.469558	-0.942879	-0.687385
N	-3.709029	1.753105	1.417949
N	-3.035134	2.876123	-0.278958
C	1.880738	2.833882	-0.636101
C	1.619590	4.003408	0.117070
C	1.599481	5.251507	-0.499384
H	1.401244	6.131978	0.104337
C	1.833421	5.414596	-1.852782
C	2.076020	4.267222	-2.590091
H	2.256424	4.359828	-3.655888
C	2.101802	2.995549	-2.024952
C	2.371597	1.859227	-2.996828
H	2.378183	0.923697	-2.429877
C	1.264691	1.762311	-4.044913
H	1.465725	0.945370	-4.739649
H	1.197159	2.682493	-4.630036
H	0.290893	1.586945	-3.584411
C	3.721855	1.983264	-3.703423
H	4.551722	2.031030	-3.000475
H	3.764228	2.876029	-4.331710
H	3.883782	1.118615	-4.350867
C	1.344394	3.996163	1.609323
H	1.405173	2.965161	1.958590
C	2.383324	4.791215	2.395647
H	2.183115	4.718871	3.467495
H	2.364828	5.849927	2.125607
H	3.389758	4.411906	2.214596
C	-0.069078	4.481268	1.922971
H	-0.265670	4.411900	2.996529
H	-0.813499	3.879590	1.396833
H	-0.204800	5.525338	1.628345
C	1.828679	6.784948	-2.488109
H	1.608069	7.503153	-1.690967
C	0.737410	6.918201	-3.547338
H	-0.247126	6.699464	-3.130015
H	0.908357	6.228195	-4.377184
H	0.718204	7.931049	-3.956871
C	3.195707	7.141829	-3.067344
H	3.975625	7.081500	-2.306324
H	3.190557	8.156385	-3.473128
H	3.468521	6.461322	-3.877490
C	3.378082	1.364595	1.625859
C	3.249912	1.126608	3.014185
C	4.266341	1.512691	3.884676
H	4.134137	1.356607	4.950185
C	5.452746	2.076641	3.450470

C	5.616078	2.216455	2.082269
H	6.551613	2.610362	1.699628
C	4.619885	1.876223	1.173531
C	4.971580	2.067824	-0.290487
H	4.120074	1.737218	-0.886841
C	6.165182	1.211053	-0.714157
H	7.056322	1.445400	-0.127921
H	6.407051	1.395078	-1.763890
H	5.959993	0.145924	-0.605235
C	5.234465	3.536900	-0.616103
H	4.372707	4.159089	-0.373639
H	5.455653	3.664906	-1.677881
H	6.093988	3.910110	-0.054208
C	2.061425	0.424019	3.647877
H	1.471627	-0.021352	2.841520
C	1.148242	1.379220	4.412899
H	0.331814	0.828456	4.887676
H	0.704227	2.128393	3.757042
H	1.700570	1.900968	5.198650
C	2.508957	-0.706496	4.574282
H	3.031953	-0.324680	5.453001
H	3.182837	-1.399141	4.066891
H	1.646201	-1.269284	4.933218
H	8.558780	1.989916	4.981611
H	7.173744	4.291496	3.397449
C	2.826127	-2.050194	-1.476747
C	3.854411	-2.566018	-0.656284
C	4.912162	-3.269155	-1.223325
H	5.691125	-3.655355	-0.574341
C	4.997154	-3.501247	-2.586577
C	3.964235	-3.029072	-3.382198
H	4.008914	-3.223758	-4.447453
C	2.884235	-2.323181	-2.863347
C	1.762362	-1.930927	-3.802962
H	1.338600	-0.992898	-3.432080
C	2.193157	-1.708295	-5.247517
H	3.049638	-1.035631	-5.322645
H	1.368189	-1.273189	-5.815709
H	2.457676	-2.645217	-5.743684
C	0.647923	-2.974402	-3.750880
H	0.233631	-3.053360	-2.744783
H	1.024710	-3.957664	-4.044772
H	-0.166802	-2.705097	-4.427540
C	3.826147	-2.473646	0.859110
H	3.003229	-1.805753	1.142470
C	5.104493	-1.910917	1.470715
H	5.020905	-1.883062	2.559331

H	5.300764	-0.895243	1.133712
H	5.972062	-2.528206	1.227179
C	3.534094	-3.854106	1.447271
H	4.316264	-4.563980	1.168469
H	2.584407	-4.244882	1.080547
H	3.498010	-3.814638	2.539094
C	6.159006	-4.252454	-3.192717
H	5.974484	-4.304626	-4.270968
C	6.246195	-5.683870	-2.668319
H	5.315552	-6.227061	-2.841719
H	6.445304	-5.697795	-1.594028
H	7.055978	-6.226505	-3.161791
C	7.478698	-3.513757	-2.982484
H	7.722024	-3.440023	-1.919876
H	7.433452	-2.499970	-3.383987
H	8.298741	-4.041255	-3.475488
C	-3.866357	2.896817	0.765232
C	-4.794583	3.995778	1.133923
C	-6.125808	3.957972	0.732694
H	-6.487458	3.120385	0.148680
C	-6.988352	4.988163	1.078033
H	-8.022354	4.951501	0.757765
C	-6.529163	6.057570	1.831328
H	-7.203829	6.860497	2.102125
C	-5.202682	6.096024	2.238494
H	-4.838614	6.928155	2.828556
C	-4.337671	5.072038	1.890241
H	-3.301138	5.104786	2.203121
C	-2.990111	3.759156	-1.457724
C	-1.743272	3.387943	-2.247830
H	-0.842653	3.507979	-1.643600
H	-1.657713	4.035389	-3.121828
H	-1.795466	2.352789	-2.585881
C	-2.889584	5.235362	-1.076755
H	-3.796956	5.611648	-0.608473
H	-2.720289	5.818454	-1.984206
H	-2.046346	5.405319	-0.405398
C	-4.222504	3.524540	-2.331915
H	-4.303105	2.468092	-2.590341
H	-4.140896	4.101675	-3.255604
H	-5.137941	3.834521	-1.825401
C	-4.284582	1.275251	2.680238
C	-4.086341	2.280852	3.814404
H	-4.384395	1.820677	4.758703
H	-4.686817	3.178999	3.679539
H	-3.035448	2.566435	3.892808
C	-3.539004	-0.003896	3.037985

H	-3.968041	-0.437721	3.942651
H	-2.484081	0.209733	3.215719
H	-3.605101	-0.744289	2.239488
C	-5.770550	0.957876	2.510599
H	-6.152583	0.486995	3.418733
H	-5.925586	0.268125	1.679391
H	-6.355352	1.860428	2.331434
C	-2.994799	-1.074868	-3.444038
H	-2.073336	-0.785576	-3.939286
C	-3.002334	-2.331046	-2.817000
H	-2.078346	-2.893064	-2.884986
C	-4.265179	-3.144165	-2.624281
H	-4.015814	-4.207609	-2.673300
H	-4.940904	-2.967250	-3.465734
C	-4.967252	-2.852647	-1.293771
H	-6.049670	-3.024989	-1.384681
H	-4.614784	-3.556490	-0.539309
C	-4.702005	-1.464892	-0.766164
H	-4.858430	-1.378357	0.306319
C	-4.875923	-0.288191	-1.549025
H	-5.167287	0.608405	-1.008298
C	-5.371893	-0.333689	-2.984394
H	-5.992333	0.543616	-3.185299
H	-6.028786	-1.196862	-3.118689
C	-4.215376	-0.374079	-3.983072
H	-4.527492	-0.840710	-4.928325
H	-3.921339	0.648389	-4.233499
C	-0.111748	-4.793738	-0.238639
H	0.643673	-4.196229	-0.725185
C	-1.489799	-4.830253	-0.567813
H	-1.973678	-4.226096	-1.317426
C	-2.117262	-5.755824	0.282655
H	-3.169912	-5.986778	0.298990
C	-1.145937	-6.266770	1.170516
H	-1.313387	-7.004384	1.940798
C	0.100673	-5.686292	0.825313
H	1.050872	-5.905753	1.284765
C	-1.193153	-4.520837	4.175019
H	-1.762430	-5.372280	4.516064
C	0.129889	-4.544438	3.677316
H	0.748681	-5.421232	3.574113
C	0.489434	-3.230389	3.331572
H	1.423137	-2.915065	2.897187
C	-0.598144	-2.380226	3.657195
H	-0.627753	-1.314934	3.493015
C	-1.623496	-3.174033	4.189806
H	-2.597400	-2.829778	4.495457

C	6.523148	2.493987	4.430289
C	7.819285	1.712923	4.226459
H	7.648735	0.637002	4.293017
H	8.253616	1.921375	3.245875
C	6.781201	3.998063	4.374034
H	7.514484	4.292373	5.128795
H	5.864786	4.564780	4.547924
H	6.146363	2.257233	5.431188



Supplementary Figure S32. Selected molecular orbitals of Si_6Ir-Hf **3b** at the PBE0/def2-TZVPP[S10c-e,11] level of theory.

4.3.2 Experimental vs. calculated NMR shifts

Supplementary Table S12. Comparison of experimental vs. calculated NMR chemical shifts for compound **3b** at the PBE0/def2-TZVPPlevel of theory.[S10c-e,11]

	Exp. **3b** $\delta(^{29}Si)$ [ppm]	Calc. **3b** $\delta(^{29}Si)$ [ppm]
Si4 (SiTip)	75.9	78.6
Si6 (NHSi)	68.2	60.6
Si5 (SiTip2)	29.9	34.3
Si3 (unsubstituted)	−36.7	−46.2
Si1 (unsubstituted)	−131.2	−167.4
Si2 (SiHf)	−90.4	−91.1

4.3.3 TD-DFT calculations

Supplementary Table S13. Transition Energy, wavelength, and oscillator strengths of the electronic transition of **3b** calculated at the TD-B3LYP/def2-TZVPP[S10b-e,11] level of theory (the 362nd orbital is the highest occupied orbital (HOMO), the 363th orbital is the lowest unoccupied orbital (LUMO) shown in Supplementary Figure S32).

STATE 1: E= 0.072633 au 1.976 eV 15941.0 cm**-1 <S**2> = 0.000000 Mult 1
361a -> 363a : 0.022796 (c= -0.15098219)
362a -> 363a : 0.953327 (c= -0.97638481)

STATE 2: E= 0.085082 au 2.315 eV 18673.4 cm**-1 <S**2> = 0.000000 Mult 1
361a -> 363a : 0.911679 (c= -0.95481893)
362a -> 363a : 0.016656 (c= 0.12905775)
362a -> 364a : 0.013836 (c= 0.11762739)

STATE 3: E= 0.089824 au 2.444 eV 19714.0 cm**-1 <S**2> = 0.000000 Mult 1
359a -> 363a : 0.010113 (c= -0.10056234)
360a -> 363a : 0.931440 (c= -0.96511158)
362a -> 364a : 0.036533 (c= 0.19113692)

STATE 4: E= 0.093266 au 2.538 eV 20469.6 cm**-1 <S**2> = 0.000000 Mult 1
359a -> 363a : 0.017545 (c= 0.13245713)
360a -> 363a : 0.037595 (c= -0.19389483)
361a -> 363a : 0.015740 (c= -0.12546017)
361a -> 364a : 0.100259 (c= -0.31663674)
362a -> 364a : 0.755468 (c= -0.86917652)
362a -> 365a : 0.023055 (c= 0.15183871)

STATE 5: E= 0.096377 au 2.623 eV 21152.3 cm**-1 <S**2> = 0.000000 Mult 1
359a -> 363a : 0.907501 (c= 0.95262848)
361a -> 364a : 0.037874 (c= 0.19461188)

STATE 6: E= 0.102248 au 2.782 eV 22440.8 cm**-1 <S**2> = 0.000000 Mult 1
360a -> 364a : 0.016981 (c= -0.13031091)
362a -> 364a : 0.017790 (c= -0.13337916)
362a -> 365a : 0.060375 (c= -0.24571240)
362a -> 366a : 0.863639 (c= -0.92932186)

STATE 7: E= 0.104048 au 2.831 eV 22836.0 cm**-1 <S**2> = 0.000000 Mult 1
358a -> 363a : 0.019159 (c= 0.13841661)
359a -> 363a : 0.019632 (c= 0.14011413)
360a -> 364a : 0.027540 (c= 0.16595298)

360a -> 366a : 0.011882 (c= -0.10900261)
361a -> 364a : 0.722006 (c= -0.84970940)
361a -> 365a : 0.025586 (c= 0.15995525)
362a -> 364a : 0.105698 (c= 0.32511191)

STATE 8: E= 0.106890 au 2.909 eV 23459.7 cm**-1 <S**2> = 0.000000 Mult 1
358a -> 363a : 0.294718 (c= 0.54287933)
360a -> 364a : 0.540311 (c= 0.73505854)
360a -> 365a : 0.018195 (c= -0.13488769)
361a -> 364a : 0.039618 (c= 0.19904151)
362a -> 365a : 0.026307 (c= -0.16219460)

STATE 9: E= 0.107466 au 2.924 eV 23586.1 cm**-1 <S**2> = 0.000000 Mult 1
358a -> 363a : 0.119015 (c= -0.34498586)
362a -> 364a : 0.017819 (c= -0.13348912)
362a -> 365a : 0.733011 (c= -0.85616076)
362a -> 366a : 0.062672 (c= 0.25034372)
362a -> 368a : 0.024334 (c= -0.15599408)

STATE 10: E= 0.108710 au 2.958 eV 23859.0 cm**-1 <S**2> = 0.000000 Mult 1
358a -> 363a : 0.487458 (c= -0.69818198)
358a -> 364a : 0.019696 (c= 0.14034078)
360a -> 364a : 0.256347 (c= 0.50630721)
360a -> 366a : 0.031917 (c= 0.17865299)
361a -> 366a : 0.010269 (c= -0.10133849)
362a -> 365a : 0.108211 (c= 0.32895488)
362a -> 366a : 0.021925 (c= -0.14807115)

STATE 11: E= 0.113122 au 3.078 eV 24827.4 cm**-1 <S**2> = 0.000000 Mult 1
357a -> 363a : 0.903968 (c= 0.95077211)
357a -> 364a : 0.033921 (c= -0.18417538)
358a -> 364a : 0.014626 (c= 0.12093847)
361a -> 366a : 0.014797 (c= 0.12164333)

STATE 12: E= 0.114633 au 3.119 eV 25159.1 cm**-1 <S**2> = 0.000000 Mult 1
357a -> 363a : 0.013049 (c= 0.11423317)
359a -> 364a : 0.322843 (c= 0.56819273)
359a -> 365a : 0.016336 (c= -0.12781345)
360a -> 364a : 0.021359 (c= -0.14614841)
361a -> 365a : 0.084003 (c= -0.28983346)
361a -> 366a : 0.481894 (c= -0.69418618)

STATE 13: E= 0.114928 au 3.127 eV 25223.9 cm**-1 <S**2> = 0.000000 Mult 1
359a -> 364a : 0.398748 (c= -0.63146482)
359a -> 365a : 0.017597 (c= 0.13265343)
360a -> 366a : 0.017024 (c= -0.13047692)
361a -> 365a : 0.041628 (c= -0.20402970)
361a -> 366a : 0.252825 (c= -0.50281741)
362a -> 368a : 0.153477 (c= 0.39176163)
362a -> 369a : 0.040198 (c= -0.20049344)

STATE 14: E= 0.116210 au 3.162 eV 25505.1 cm**-1 <S**2> = 0.000000 Mult 1
359a -> 364a : 0.146265 (c= -0.38244564)
359a -> 366a : 0.011671 (c= -0.10803056)
360a -> 366a : 0.016157 (c= -0.12711159)
361a -> 366a : 0.026413 (c= -0.16252075)
362a -> 368a : 0.683351 (c= -0.82665052)
362a -> 369a : 0.031682 (c= 0.17799465)

STATE 15: E= 0.118243 au 3.218 eV 25951.4 cm**-1 <S**2> = 0.000000 Mult 1
362a -> 367a : 0.992677 (c= -0.99633183)

STATE 16: E= 0.119201 au 3.244 eV 26161.5 cm**-1 <S**2> = 0.000000 Mult 1
361a -> 364a : 0.027480 (c= 0.16577006)
361a -> 365a : 0.770219 (c= 0.87762150)
361a -> 366a : 0.131726 (c= -0.36294085)
361a -> 368a : 0.016095 (c= 0.12686454)
361a -> 369a : 0.010325 (c= 0.10161247)

STATE 17: E= 0.121328 au 3.301 eV 26628.4 cm**-1 <S**2> = 0.000000 Mult 1
357a -> 364a : 0.013106 (c= -0.11448186)
358a -> 364a : 0.106868 (c= 0.32690748)
359a -> 366a : 0.012647 (c= -0.11245702)
360a -> 365a : 0.042496 (c= -0.20614585)
360a -> 366a : 0.235104 (c= -0.48487574)
362a -> 368a : 0.054190 (c= 0.23278830)
362a -> 369a : 0.426362 (c= 0.65296371)
362a -> 370a : 0.029352 (c= -0.17132477)

STATE 18: E= 0.122079 au 3.322 eV 26793.2 cm**-1 <S**2> = 0.000000 Mult 1
357a -> 364a : 0.013163 (c= 0.11473032)
358a -> 364a : 0.345700 (c= -0.58796260)

358a -> 365a : 0.014031 (c= 0.11845193)
360a -> 365a : 0.022241 (c= 0.14913438)
360a -> 366a : 0.130376 (c= 0.36107683)
362a -> 365a : 0.011616 (c= -0.10777852)
362a -> 368a : 0.019489 (c= 0.13960269)
362a -> 369a : 0.346253 (c= 0.58843306)
362a -> 370a : 0.027842 (c= -0.16685976)

STATE 19: E= 0.123831 au 3.370 eV 27177.8 cm**-1 <S**2> = 0.000000 Mult 1
357a -> 364a : 0.021487 (c= -0.14658508)
358a -> 363a : 0.017598 (c= 0.13265714)
358a -> 364a : 0.286501 (c= 0.53525752)
358a -> 365a : 0.012238 (c= -0.11062463)
359a -> 365a : 0.015481 (c= 0.12442104)
359a -> 366a : 0.046150 (c= 0.21482665)
360a -> 364a : 0.026143 (c= -0.16168815)
360a -> 366a : 0.339050 (c= 0.58227959)
361a -> 368a : 0.037004 (c= 0.19236344)
362a -> 369a : 0.049923 (c= 0.22343486)
362a -> 370a : 0.035898 (c= 0.18946723)

STATE 20: E= 0.125766 au 3.422 eV 27602.4 cm**-1 <S**2> = 0.000000 Mult 1
359a -> 365a : 0.019270 (c= 0.13881560)
359a -> 366a : 0.094787 (c= 0.30787490)
360a -> 364a : 0.012889 (c= -0.11352986)
360a -> 365a : 0.335546 (c= -0.57926371)
360a -> 366a : 0.022374 (c= 0.14958047)
362a -> 369a : 0.024698 (c= -0.15715518)
362a -> 370a : 0.413754 (c= -0.64323723)
362a -> 371a : 0.018867 (c= 0.13735569)

STATE 21: E= 0.126208 au 3.434 eV 27699.5 cm**-1 <S**2> = 0.000000 Mult 1
358a -> 364a : 0.041208 (c= 0.20299655)
359a -> 366a : 0.024001 (c= 0.15492184)
360a -> 365a : 0.515165 (c= 0.71775024)
360a -> 366a : 0.018004 (c= -0.13417986)
360a -> 368a : 0.017829 (c= 0.13352583)
361a -> 368a : 0.023339 (c= 0.15277016)
362a -> 370a : 0.296459 (c= -0.54448094)

STATE 22: E= 0.126818 au 3.451 eV 27833.3 cm**-1 <S**2> = 0.000000 Mult 1

356a -> 363a : 0.017324 (c= 0.13162037)
357a -> 364a : 0.095495 (c= 0.30902289)
359a -> 365a : 0.020907 (c= -0.14459179)
359a -> 366a : 0.188392 (c= -0.43404180)
361a -> 368a : 0.508257 (c= 0.71292147)
361a -> 369a : 0.053711 (c= -0.23175711)

STATE 23: E= 0.128463 au 3.496 eV 28194.3 cm**-1 <S**2> = 0.000000 Mult 1
356a -> 363a : 0.018461 (c= -0.13587264)
357a -> 363a : 0.012078 (c= -0.10990179)
357a -> 364a : 0.417862 (c= -0.64642237)
357a -> 365a : 0.016746 (c= 0.12940580)
358a -> 364a : 0.067010 (c= -0.25886241)
359a -> 364a : 0.013090 (c= 0.11441118)
359a -> 366a : 0.054258 (c= 0.23293385)
360a -> 366a : 0.028500 (c= -0.16882027)
360a -> 368a : 0.010802 (c= -0.10393375)
361a -> 368a : 0.219967 (c= 0.46900635)
361a -> 369a : 0.029307 (c= -0.17119315)
362a -> 370a : 0.011870 (c= 0.10895129)

STATE 24: E= 0.129639 au 3.528 eV 28452.5 cm**-1 <S**2> = 0.000000 Mult 1
355a -> 363a : 0.010472 (c= -0.10233326)
356a -> 363a : 0.041724 (c= 0.20426422)
357a -> 364a : 0.230261 (c= -0.47985487)
357a -> 365a : 0.011291 (c= 0.10625894)
359a -> 365a : 0.012425 (c= -0.11146552)
359a -> 366a : 0.290258 (c= -0.53875629)
360a -> 366a : 0.067843 (c= 0.26046690)
360a -> 368a : 0.083167 (c= 0.28838629)
361a -> 367a : 0.010760 (c= -0.10372920)
361a -> 368a : 0.013232 (c= -0.11503168)
361a -> 369a : 0.011943 (c= 0.10928379)
362a -> 369a : 0.012215 (c= -0.11052157)
362a -> 370a : 0.058510 (c= -0.24188854)

STATE 25: E= 0.129824 au 3.533 eV 28493.1 cm**-1 <S**2> = 0.000000 Mult 1
361a -> 367a : 0.976110 (c= 0.98798277)

STATE 26: E= 0.130964 au 3.564 eV 28743.2 cm**-1 <S**2> = 0.000000 Mult 1
355a -> 363a : 0.017358 (c= -0.13175000)

356a -> 363a : 0.252944 (c= 0.50293543)
359a -> 365a : 0.066190 (c= -0.25727480)
359a -> 366a : 0.045194 (c= 0.21258807)
360a -> 368a : 0.037273 (c= -0.19306263)
361a -> 369a : 0.029278 (c= -0.17110721)
362a -> 371a : 0.465348 (c= -0.68216395)

STATE 27: E= 0.131191 au 3.570 eV 28793.1 cm**-1 <S**2> = 0.000000 Mult 1
355a -> 363a : 0.167804 (c= -0.40963887)
356a -> 363a : 0.362585 (c= 0.60215013)
359a -> 365a : 0.131184 (c= 0.36219288)
362a -> 370a : 0.034572 (c= 0.18593598)
362a -> 371a : 0.178961 (c= 0.42303779)
362a -> 374a : 0.014666 (c= 0.12110411)
362a -> 375a : 0.010027 (c= 0.10013609)

STATE 28: E= 0.131716 au 3.584 eV 28908.4 cm**-1 <S**2> = 0.000000 Mult 1
355a -> 363a : 0.085306 (c= -0.29207143)
356a -> 363a : 0.042784 (c= -0.20684408)
359a -> 364a : 0.021106 (c= 0.14528062)
359a -> 365a : 0.354039 (c= 0.59501142)
359a -> 366a : 0.036386 (c= -0.19075225)
361a -> 368a : 0.027478 (c= 0.16576543)
361a -> 369a : 0.139360 (c= 0.37330943)
362a -> 371a : 0.205806 (c= -0.45365849)

STATE 29: E= 0.132057 au 3.593 eV 28983.2 cm**-1 <S**2> = 0.000000 Mult 1
355a -> 363a : 0.093866 (c= 0.30637557)
356a -> 363a : 0.093629 (c= 0.30598904)
359a -> 365a : 0.027220 (c= -0.16498505)
359a -> 366a : 0.026062 (c= 0.16143696)
361a -> 365a : 0.021727 (c= -0.14740207)
361a -> 368a : 0.070883 (c= 0.26623801)
361a -> 369a : 0.566299 (c= 0.75252865)
361a -> 370a : 0.027865 (c= -0.16692690)

STATE 30: E= 0.132558 au 3.607 eV 29093.1 cm**-1 <S**2> = 0.000000 Mult 1
354a -> 363a : 0.032152 (c= 0.17931093)
355a -> 363a : 0.445208 (c= 0.66723936)
356a -> 363a : 0.086140 (c= 0.29349547)
359a -> 365a : 0.240376 (c= 0.49028178)

359a -> 366a : 0.026830 (c= -0.16379813)

360a -> 368a : 0.012655 (c= 0.11249298)

361a -> 369a : 0.058625 (c= -0.24212626)

4.4 Summary of calculated TD-DFT data of 2-3b

Supplementary Table S14. Extended comparison of wavelengths λ_{max}, oscillator strengths f, and excitation energy E from experimental and TD-DFT calculations for iridasiliconoid salt **2** and the bimetallic compounds **3a,b**.

	Experimental		**TD-DFT**			
	λ_{max} (nm)	Excitation energy E (eV)	λ_{max} (nm)	Excitation energy E (eV)	Oscillator strength f	Transitions (% contribution)
2	543	2.283	528	2.349	0.0388	HOMO−2→LUMO (2.5) HOMO−1→LUMO (11.9) HOMO→LUMO (78.0) HOMO→LUMO+1 (4.1)
	425	2.917	430	2.885	0.0201	HOMO−4→LUMO (1.0) HOMO−3→LUMO (5.5) HOMO−2→LUMO (5.7) HOMO−1→LUMO+3 (1.2) HOMO→LUMO+1 (1.5) HOMO→LUMO+3 (77.8) HOMO→LUMO+4 (1.0) HOMO→LUMO+5 (1.2)
			418	2.965	0.0592	HOMO−4→LUMO (2.0) HOMO−3→LUMO (35.2) HOMO−3→LUMO+1 (2.7) HOMO−3→LUMO+3 (1.2) HOMO−2→LUMO (39.2) HOMO−2→LUMO+1 (2.9) HOMO−1→LUMO+3 (1.9) HOMO→LUMO (2.5) HOMO→LUMO+1 (1.2)
3a	601	2.063	636	1.949	0.0181	HOMO−1→LUMO (1.9) HOMO→LUMO (95.4)
	426	2.910	425	2.915	0.0540	HOMO−4→LUMO (34.6) HOMO−2→LUMO+1 (3.0) HOMO−1→LUMO+1 (46.9)

						HOMO→LUMO+1 (2.5) HOMO→LUMO+2 (1.7) HOMO→LUMO+3 (3.4) HOMO→LUMO+5 (1.0)
	354	3.502	354	3.506	0.002341513	HOMO−7→LUMO (1.3) HOMO−6→LUMO (3.2) HOMO−5→LUMO+1 (2.1) HOMO−1→LUMO+3 (1.5) HOMO→LUMO+2 (2.6) HOMO→LUMO+4 (10.0) HOMO→LUMO+5 (7.9) HOMO→LUMO+6 (59.9) HOMO→LUMO+7 (3.6)
3b	647	1.916	627	1.976	0.0179	HOMO−1→LUMO (2.3) HOMO→LUMO (95.3)
	524	2.366	536	2.315	0.0645	HOMO−1→LUMO (91.2) HOMO→LUMO (1.7) HOMO→LUMO+1 (1.4)
	340	3.647	344	3.607	0.00306	HOMO−8→LUMO (3.2) HOMO−7→LUMO (44.5) HOMO−6→LUMO (8.6) HOMO−3→LUMO+2 (24.0) HOMO−3→LUMO+3 (2.7) HOMO−2→LUMO+5 (1.3) HOMO−1→LUMO+6 (5.9)

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