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Supporting Information for:

New Reactivity at the Silicon Bridge in Sila[1]ferrocenophanes

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Additional Figures

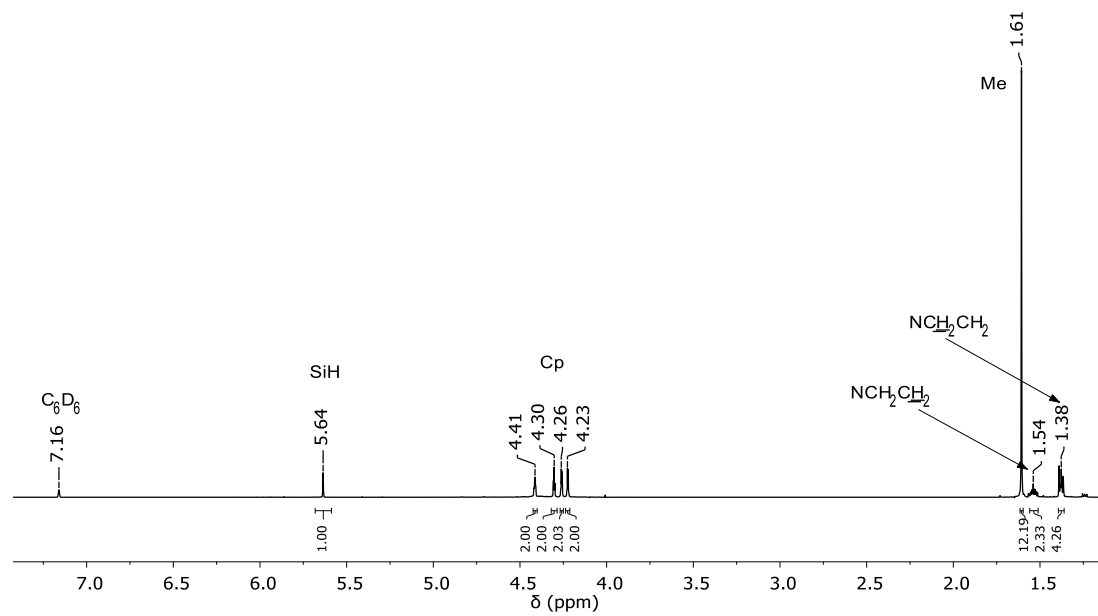


Figure S1. ^1H NMR (500 MHz, C_6D_6) spectrum of **12**.

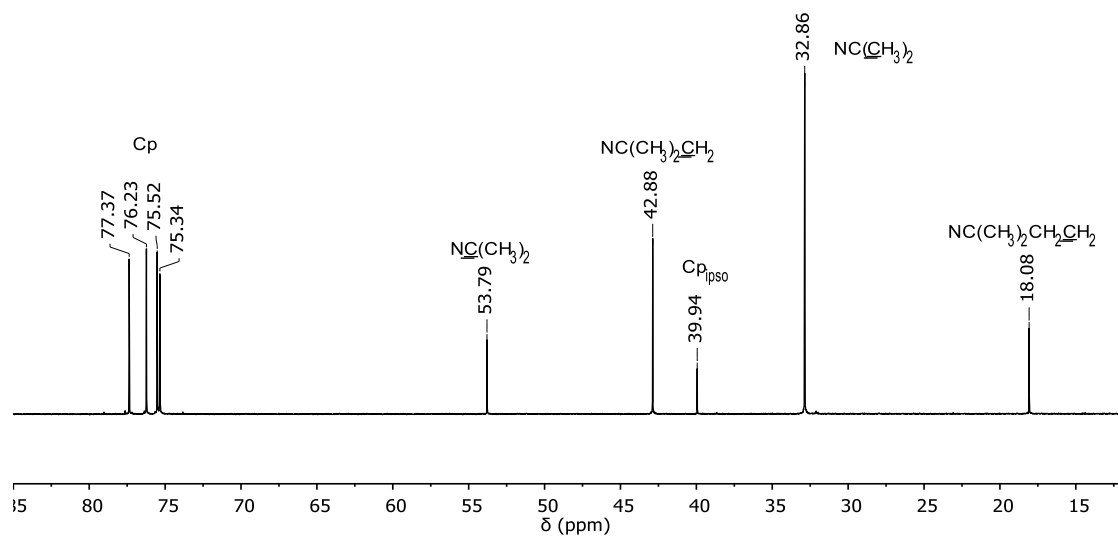


Figure S2. ^{13}C NMR (500 MHz, C_6D_6) spectrum of **12**.

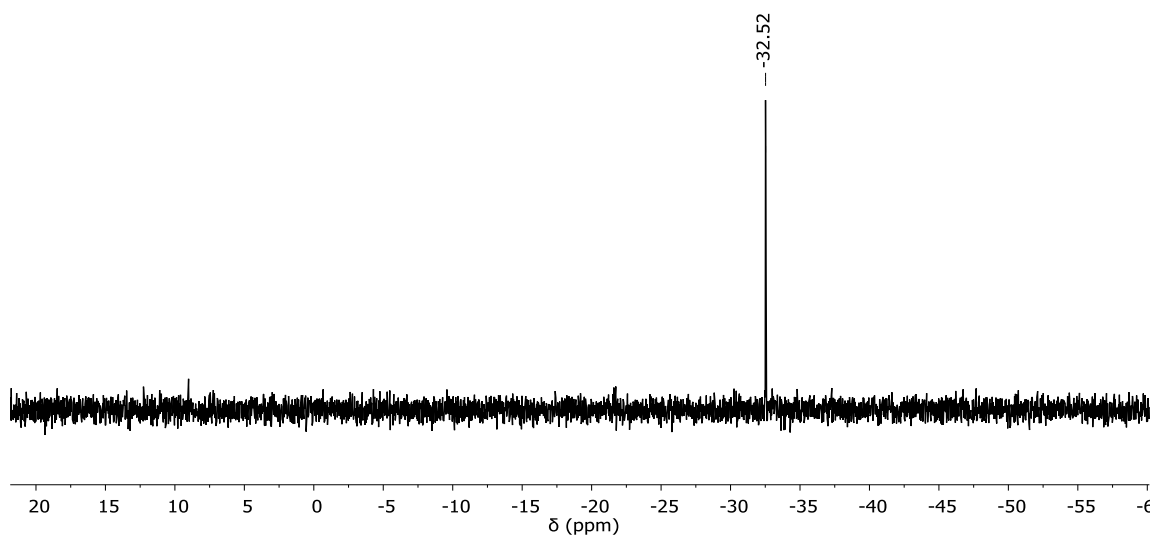


Figure S3. $^{29}\text{Si}\{^1\text{H}\}$ NMR (500 MHz, C_6D_6) spectrum of **12**.

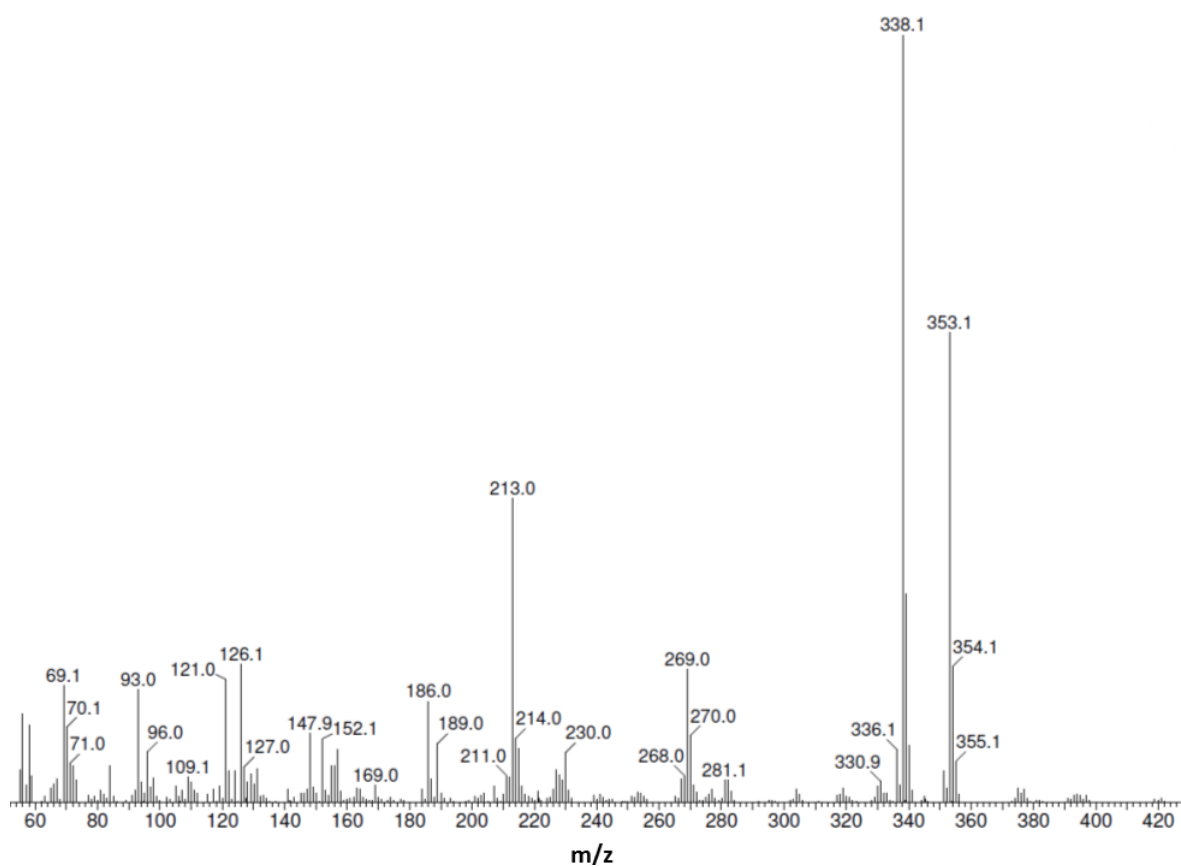


Figure S4. Positive ion mode EI mass spectrum of a 1,2-difluorobenzene solution of **12**.

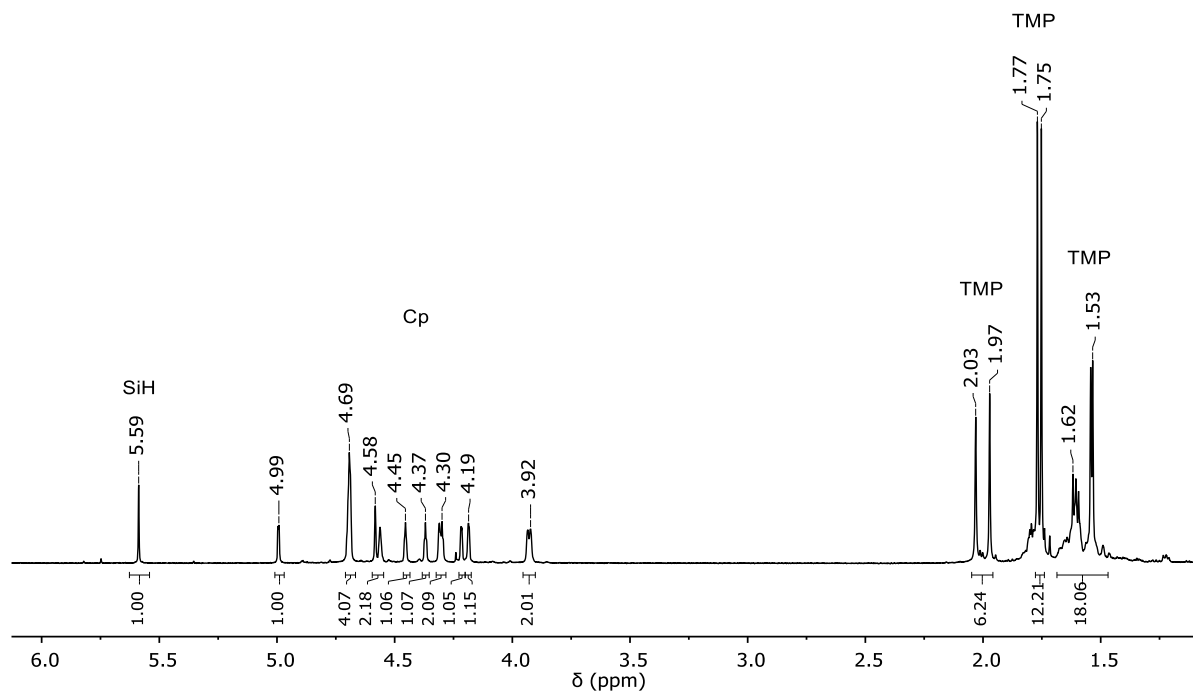


Figure S5. ^1H NMR (500 MHz, C_6D_6) spectrum of $[13][\text{B}(\text{C}_6\text{F}_5)_4]$.

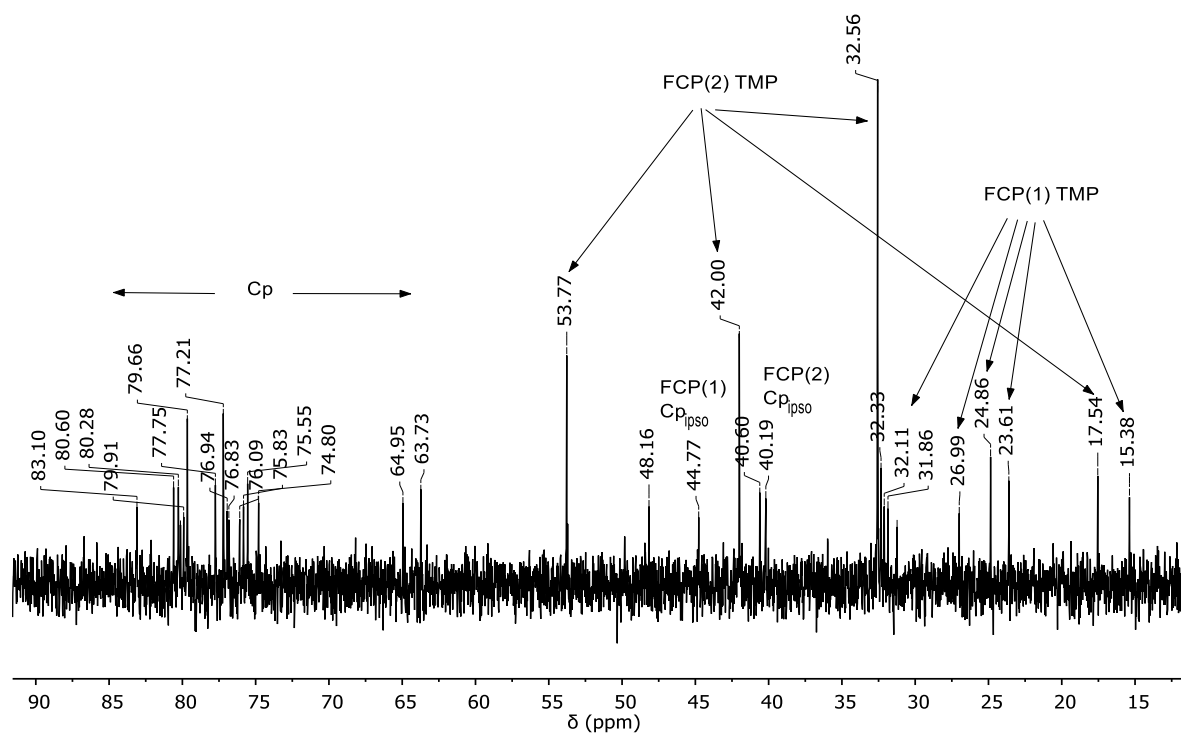


Figure S6. ^{13}C NMR (500 MHz, C_6D_6) spectrum of $[13][\text{B}(\text{C}_6\text{F}_5)_4]$.

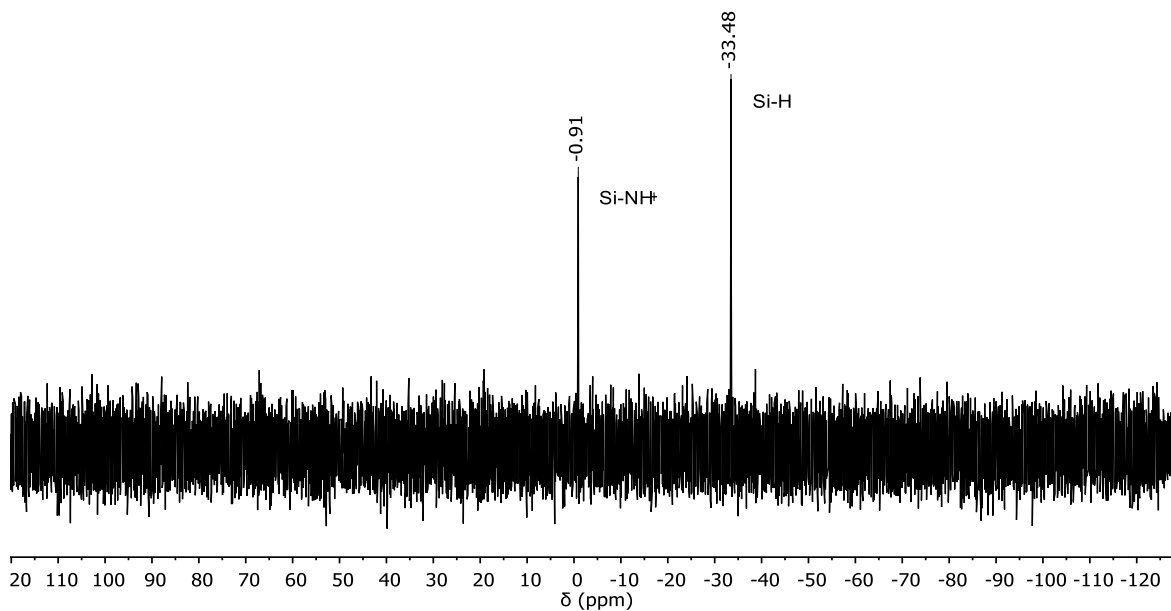


Figure S7. $^{29}\text{Si}\{^1\text{H}\}$ NMR (500 MHz, C_6D_6) spectrum of $[\mathbf{13}][\text{B}(\text{C}_6\text{F}_5)_4]$.

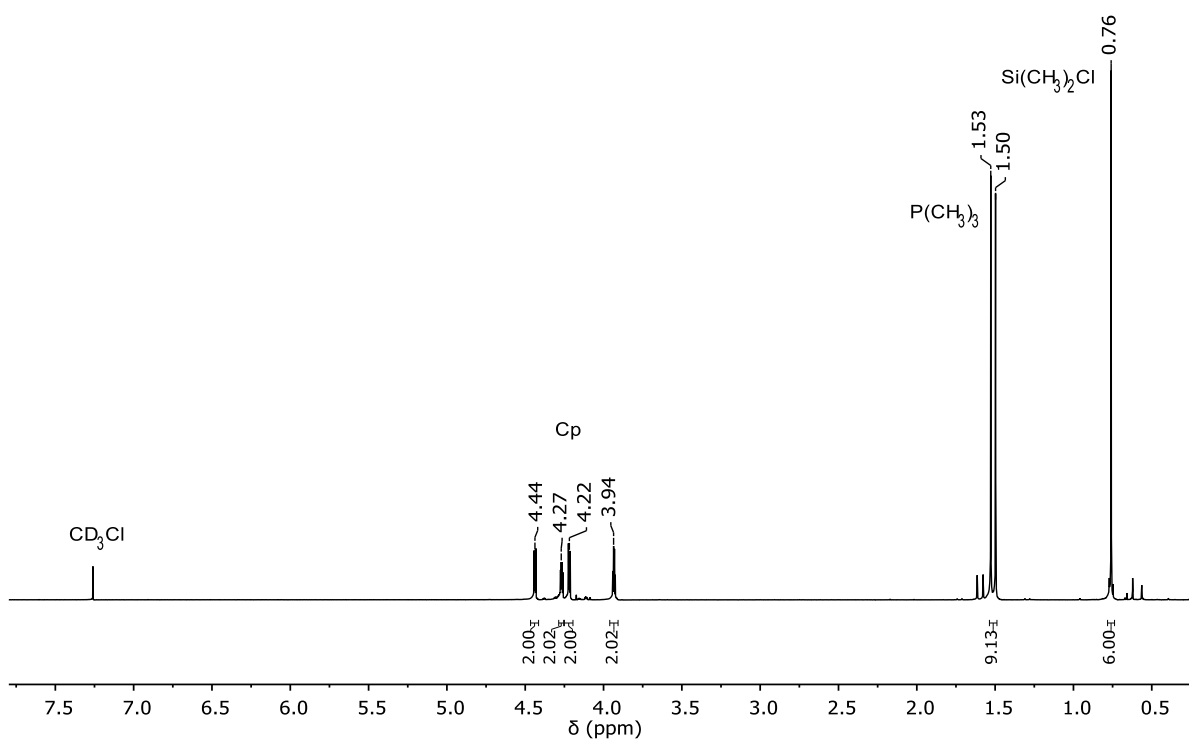


Figure S8. ^1H NMR (300 MHz, CDCl_3) spectrum of **14**.

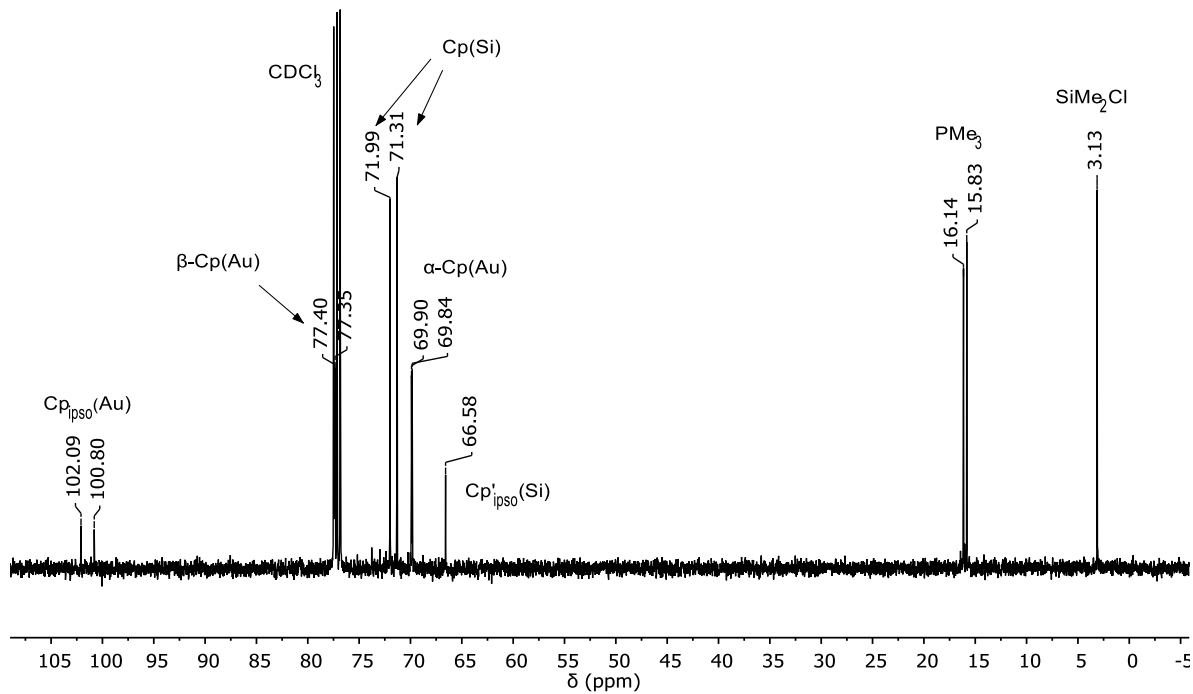


Figure S9. ^{13}C NMR (400 MHz, CDCl_3) spectrum of **14**.

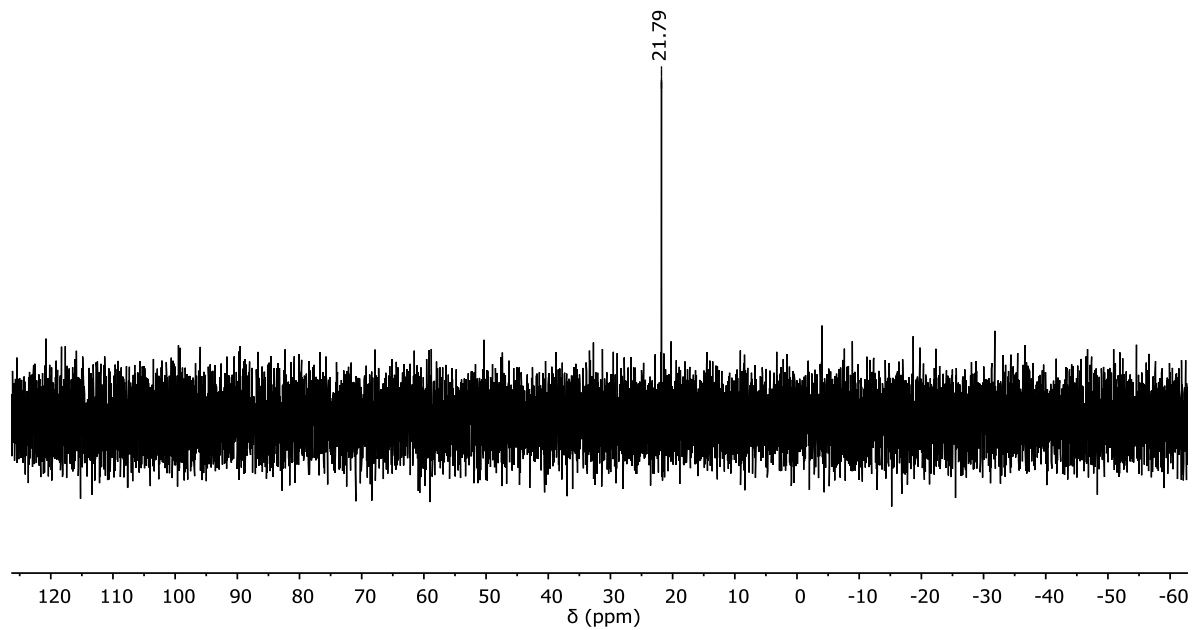


Figure S10. $^{29}\text{Si}\{^1\text{H}\}$ NMR (500 MHz, CDCl_3) spectrum of **14**.

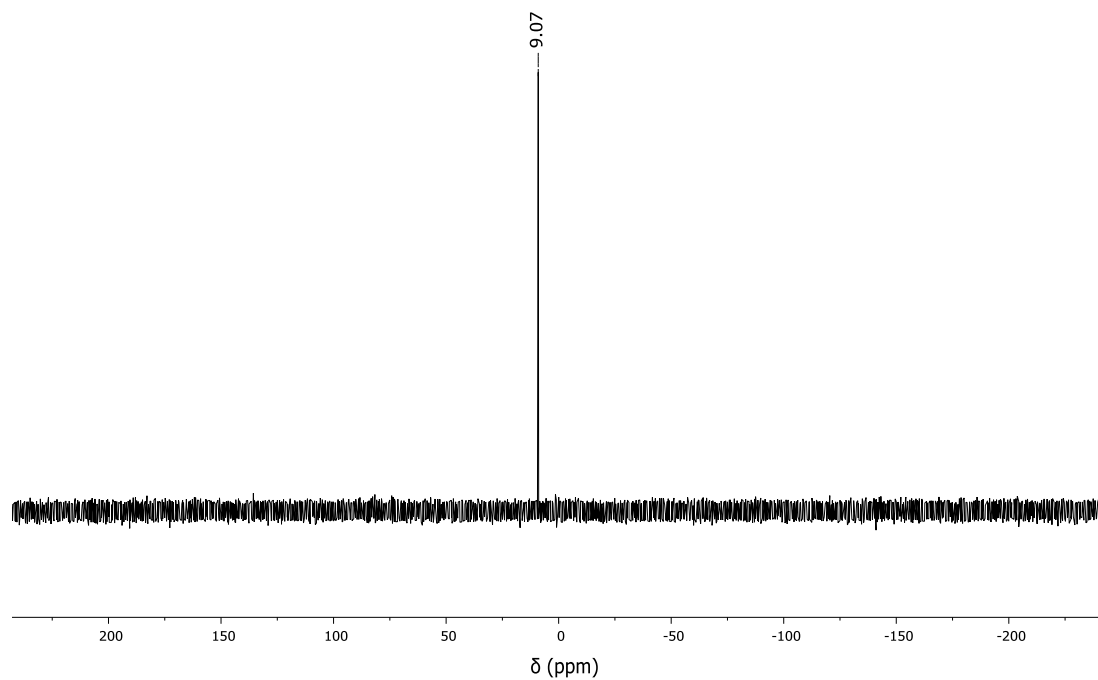
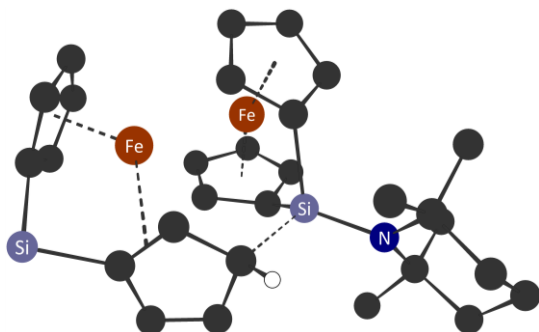


Figure S11. $^{31}\text{P}\{^1\text{H}\}$ NMR (400 MHz, CDCl_3) spectrum of **14**.

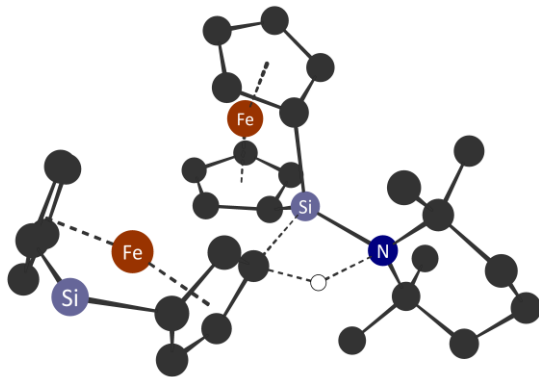
Calculated Atomic Coordinates



E(BS1) = -2007.39901094 a.u.

	x	y	z
Fe1	-0.542615	-1.926971	0.181282
Fe2	-2.529669	0.053901	-0.230374
Si1	1.209722	0.278343	0.015648
Si2	-3.823694	2.916772	-0.010384
N1	2.923557	0.514201	-0.057389
C1	0.505190	-0.955040	-1.278140
C2	0.959218	-2.313219	-1.223490
C3	-0.883946	-1.048072	-1.683786
C4	-0.100121	-3.200510	-1.549633
C5	-1.238804	-2.424199	-1.845465
C6	0.720353	-2.019584	1.841185
C7	0.411659	-0.670269	1.471761
C8	-0.461961	-2.700531	2.235506
C9	-1.018856	-0.543477	1.684938
C10	-1.536491	-1.790932	2.151746
C11	3.834777	0.239772	1.111823
C12	3.549701	0.712152	-1.421314
C13	5.089488	1.132681	1.061351
C14	4.791238	1.614514	-1.318475
C15	5.793322	1.139341	-0.283751
C16	0.262873	1.966237	-0.079704
C17	0.075800	2.571550	1.265910
C18	-1.116679	2.014091	-0.659918
C19	-4.236486	-0.957362	-1.162222
C20	-4.309561	-1.127312	0.233625
C21	-4.245730	0.435402	-1.446048
C22	3.924844	-0.626267	-2.080113
C23	-4.367779	1.142968	-0.210413
C24	2.601297	1.446725	-2.384341
C25	-1.223085	2.899551	1.455277
C26	-4.380818	0.169164	0.827375
C27	-1.982287	2.598226	0.242618
C28	3.143278	0.599594	2.435817

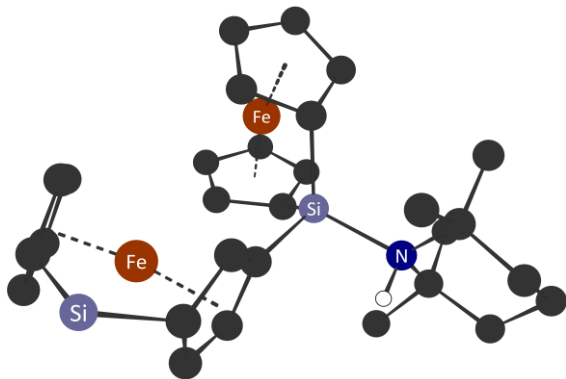
C29	4.275494	-1.236526	1.176795
H1	1.941341	-2.625273	-0.887608
H2	-1.507187	-0.217288	-2.019256
H3	-0.044869	-4.280778	-1.557692
H4	-2.198192	-2.804798	-2.165465
H5	1.693037	-2.486503	1.765388
H6	-0.524034	-3.736272	2.541177
H7	-1.562163	0.400812	1.690750
H8	-2.564280	-1.989856	2.423409
H9	5.761454	0.795396	1.858920
H10	4.792842	2.161496	1.305455
H11	5.243008	1.678438	-2.314415
H12	4.463093	2.626986	-1.047453
H13	6.656985	1.810392	-0.252910
H14	6.180318	0.145767	-0.540378
H15	0.872221	2.702081	1.988779
H16	-1.311255	1.894012	-1.722759
H17	-1.647792	3.343770	2.348339
H18	-4.156821	-1.750178	-1.894007
H19	-4.303166	-2.075833	0.753402
H20	-4.190203	0.883586	-2.430779
H21	-4.425136	0.377947	1.890039
H22	0.945568	2.572453	-0.688396
H23	3.027802	-1.192544	-2.343034
H24	4.478516	-0.441604	-3.006701
H25	4.549777	-1.249033	-1.439109
H26	1.648834	0.932488	-2.546965
H27	2.415433	2.473345	-2.055339
H28	3.091200	1.508635	-3.360602
H29	3.897169	0.613698	3.228852
H30	2.709927	1.603422	2.380401
H31	2.371673	-0.108238	2.738438
H32	3.450565	-1.903831	0.909835
H33	5.107655	-1.457534	0.504723
H34	4.604971	-1.486424	2.190836
H35	-4.391646	3.557044	1.191528
H36	-4.082091	3.680996	-1.246493



E(BS1) = -2007.36483544 a.u.

	x	y	z
Fe1	0.276755	2.747276	0.153989
Fe2	-2.555296	-0.649248	-0.359539
Si1	1.044043	0.161835	-0.020173
Si2	-3.916270	-2.803069	0.890599
N1	2.349963	-1.100818	-0.039413
C1	0.746662	1.253709	1.478644
C2	1.559336	2.412278	1.762541
C3	-0.609643	1.667095	1.737104
C4	0.722141	3.483316	2.159441
C5	-0.620525	3.023242	2.143113
C6	1.661969	2.677559	-1.404297
C7	0.855232	1.481342	-1.350670
C8	0.832993	3.791014	-1.682396
C9	-0.491593	1.922679	-1.629957
C10	-0.499995	3.324499	-1.820915
C11	3.206035	-1.224666	-1.287001
C12	2.943701	-1.514890	1.297684
C13	4.021867	-2.528431	-1.267109
C14	3.760675	-2.808882	1.147520
C15	4.781594	-2.760038	0.026087
C16	1.812564	-1.846233	2.282777
C17	-3.696360	1.138238	0.117485
C18	-4.097008	0.655874	-1.157064
C19	-3.900813	0.105607	1.066522
C20	-0.310066	-1.211099	-0.246764
C21	-0.915885	-1.627621	-1.518266
C22	-1.169675	-1.822093	0.774451
C23	-1.959776	-2.508952	-1.256562
C24	-2.156476	-2.630437	0.177771
C25	-4.551911	-0.676761	-0.986819
C26	-4.427363	-1.051255	0.392681

C27	3.816658	-0.412584	1.910375
C28	4.146686	-0.025417	-1.454614
C29	2.298614	-1.320208	-2.522703
H1	2.630265	2.488037	1.622775
H2	-1.483338	1.048806	1.584942
H3	1.052435	4.477746	2.426920
H4	-1.494848	3.603428	2.406324
H5	2.720301	2.747713	-1.190354
H6	1.163948	4.816867	-1.770363
H7	-1.369742	1.289476	-1.646297
H8	-1.367164	3.930585	-2.046337
H9	4.696283	-2.502038	-2.129868
H10	3.336530	-3.372392	-1.423624
H11	4.235219	-3.008659	2.114187
H12	3.068203	-3.639138	0.953520
H13	5.330324	-3.704997	-0.025345
H14	5.528166	-1.975880	0.198732
H15	-0.560516	-1.339117	-2.499974
H16	-1.056175	-1.661425	1.841311
H17	-2.576528	-2.984153	-2.010433
H18	-3.280915	2.118480	0.320261
H19	-4.071733	1.207695	-2.087380
H20	-3.652984	0.157759	2.120395
H21	-4.870668	-1.333677	-1.787392
H22	0.862951	-1.713987	-0.215395
H23	3.235852	0.495199	2.085864
H24	4.193908	-0.747908	2.881694
H25	4.678988	-0.163151	1.290616
H26	1.189565	-0.983219	2.534585
H27	1.183130	-2.655404	1.897433
H28	2.259956	-2.197937	3.217044
H29	2.925838	-1.495311	-3.401887
H30	1.617293	-2.173173	-2.434387
H31	1.726358	-0.408391	-2.713468
H32	3.591960	0.914659	-1.415736
H33	4.929354	0.002504	-0.695138
H34	4.635578	-0.076397	-2.432578
H35	-4.677973	-3.844187	0.175117
H36	-3.884124	-2.985449	2.354134



E(BS1) = -2007.43953459 a.u.

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Fe1	0.513567	2.712385	0.216729
Fe2	-2.720732	-0.579900	-0.398012
Si1	-4.101302	-2.637799	0.856303
Si2	0.897773	0.075741	-0.031783
N1	2.286313	-1.301278	-0.129896
C1	0.858400	1.148130	1.504788
C2	1.787034	2.215714	1.790431
C3	-0.450374	1.691320	1.796554
C4	1.069340	3.354467	2.229393
C5	-0.313129	3.031210	2.228795
C6	1.822625	2.552088	-1.399091
C7	0.908038	1.436310	-1.332041
C8	1.093896	3.744348	-1.621427
C9	-0.404133	2.011401	-1.549815
C10	-0.282086	3.410845	-1.709853
C11	3.297475	-1.175999	-1.292444
C12	2.839029	-1.815049	1.229652
C13	4.154663	-2.451149	-1.372248
C14	3.656811	-3.086748	0.962291
C15	4.771394	-2.886892	-0.052595
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C17	-1.064187	-1.500733	-1.495003
C18	-1.362064	-1.665008	0.775114
C19	-2.109697	-2.418948	-1.248884
C20	-2.330144	-2.528847	0.168611
C21	-3.757717	1.275343	0.072713
C22	-4.202683	0.801176	-1.191890
C23	-4.004738	0.259515	1.031573
C24	-4.722772	-0.504538	-1.005238
C25	-4.598769	-0.875610	0.377901
C26	1.644123	-2.189907	2.107959

C27	4.172644	0.069061	-1.101619
C28	3.682486	-0.762729	1.943711
C29	2.500041	-1.101030	-2.601126
H1	2.859103	2.188250	1.637581
H2	-1.388398	1.174672	1.634635
H3	1.502469	4.304217	2.512469
H4	-1.121224	3.691018	2.514420
H5	2.892119	2.520692	-1.249376
H6	1.518432	4.735440	-1.706443
H7	-1.338429	1.464797	-1.525465
H8	-1.096126	4.103180	-1.877174
H9	4.924346	-2.266511	-2.129674
H10	3.529248	-3.269002	-1.756920
H11	4.052621	-3.425757	1.924970
H12	2.980007	-3.877674	0.607142
H13	5.318854	-3.822508	-0.195783
H14	5.501120	-2.154346	0.310174
H15	-0.704805	-1.195540	-2.471355
H16	-1.286273	-1.472066	1.840153
H17	-2.709340	-2.897743	-2.013820
H18	-3.311433	2.243368	0.267283
H19	-4.164197	1.343239	-2.127576
H20	-3.734170	0.304835	2.080434
H21	-5.087515	-1.150449	-1.794794
H22	1.684726	-2.082885	-0.426328
H23	3.092264	0.116422	2.202023
H24	4.030017	-1.203115	2.883145
H25	4.564693	-0.455356	1.383101
H26	1.066878	-1.315455	2.419904
H27	0.978814	-2.901672	1.607452
H28	2.025823	-2.670213	3.013443
H29	3.201919	-1.228359	-3.430522
H30	1.770420	-1.917529	-2.665058
H31	1.986539	-0.150103	-2.741294
H32	3.683225	0.821937	-0.477349
H33	5.131960	-0.169479	-0.636717
H34	4.379912	0.524224	-2.074232
H35	-4.890272	-3.659247	0.138285
H36	-4.094340	-2.838361	2.320672

Crystallographic Data

Compound	12	[13][B(C₆F₅)₄]	14
Empirical formula	C ₁₉ H ₂₇ FeNSi	C ₆₂ H ₅₃ BF ₂₀ Fe ₂ N ₂ Si ₂	C ₁₅ H ₂₃ AuClFePSi
Formula weight	353.35	1384.75	550.66
Temperature/K	100.0	100.0	100.0
Crystal system	orthorhombic	monoclinic	triclinic
Space group	<i>Iba</i> 2	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1
<i>a</i> /Å	13.6524(4)	11.5252(5)	7.473(5)
<i>b</i> /Å	27.8481(10)	26.6215(10)	9.660(7)
<i>c</i> /Å	8.8550(3)	18.4948(7)	12.930(9)
α /°	90	90	76.909(16)
β /°	90	91.736(3)	81.91(2)
γ /°	90	90	80.681(14)
Volume/Å ³	3366.6(2)	5671.9(4)	891.9(11)
Z	1	4	2
$\rho_{\text{calc}}/\text{cm}^3$	1.394	1.622	2.050
μ/mm^{-1}	0.964	0.664	9.323
F(000)	1.394	2816.0	528.0
Crystal size/mm ³	0.55×0.30×0.11	0.02×0.02×0.02	0.1×0.08×0.07
Radiation	Mo K α ($\lambda = 0.71073$)	Mo K α ($\lambda = 0.71073$)	Mo K α ($\lambda = 0.71073$)
2 θ range for data collection/°	2.924 to 55.848	2.682 to 51.362	4.368 to 58.99
Index ranges	-17 ≤ <i>h</i> ≤ 17, -36 ≤ <i>k</i> ≤ 34, -10 ≤ <i>l</i> ≤ 11	-14 ≤ <i>h</i> ≤ 14, -32 ≤ <i>k</i> ≤ 32, -22 ≤ <i>l</i> ≤ 22	-10 ≤ <i>h</i> ≤ 10, -13 ≤ <i>k</i> ≤ 13, -17 ≤ <i>l</i> ≤ 17
Reflections collected	14677	85664	29657
Independent reflections	3733 [<i>R</i> _{int} = 0.0310, <i>R</i> _{sigma} = 0.0336]	10766 [<i>R</i> _{int} = 0.1593, <i>R</i> _{sigma} = 0.0919]	4960 [<i>R</i> _{int} = 0.0281, <i>R</i> _{sigma} = 0.0205]
Data/restraints/parameters	3733/1/207	10766/0/810	4960/0/186
Goodness-of-fit on F ²	1.046	1.011	1.062
Final R indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0250, <i>wR</i> ₂ = 0.0581	<i>R</i> ₁ = 0.0555, <i>wR</i> ₂ = 0.1201	<i>R</i> ₁ = 0.0154, <i>wR</i> ₂ = 0.0330
Final R indexes [all data]	<i>R</i> ₁ = 0.0276, <i>wR</i> ₂ = 0.0592	<i>R</i> ₁ = 0.1208, <i>wR</i> ₂ = 0.1506	<i>R</i> ₁ = 0.0185, <i>wR</i> ₂ = 0.0338
Largest diff. peak/hole/e Å ⁻³	0.34/-0.20	1.32/-0.74	1.02/-0.46
Flack parameter	0.018(10)	N/A	N/A

Table S1. Crystallographic data for **12**, **[13][B(C₆F₅)₄]** and **14**.

Compound	[Fe(NCMe) ₆][B(C ₆ F ₅) ₄] ₂	[Fe(NCMe) ₆][B ₁₂ Cl ₁₂]
Empirical formula	C ₆₀ H ₁₈ B ₂ F ₄₀ FeN ₆	C ₆₂ H ₅₃ BF ₂₀ Fe ₂ N ₂ Si ₂
Formula weight	1660.23	857.3245
Temperature/K	100.0	100.0
Crystal system	orthorhombic	trigonal
Space group	<i>Pnma</i>	<i>R-3m</i>
a/Å	17.9405(3)	11.3371(2)
b/Å	24.5421(4)	11.3371(2)
c/Å	14.0694(2)	23.9716(4)
α/°	90	90
β/°	90	90
γ/°	90	120
Volume/Å ³	6194.72(17)	2668.28(8)
Z	8	4
ρ _{calc} /cm ³	14.242	1.6005
μ/mm ⁻¹	3.297	1.346
F(000)	26112.0	1272.6
Crystal size/mm ³	0.13×0.09×0.05	0.09×0.15×0.14
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2θ range for data collection/°	3.318 to 53.528	4.48 to 55.14
Index ranges	-22 ≤ h ≤ 22, -31 ≤ k ≤ 27, -17 ≤ l ≤ 17	-13 ≤ h ≤ 14, -14 ≤ k ≤ 11, -31 ≤ l ≤ 30
Reflections collected	48712	7988
Independent reflections	6747 [R _{int} = 0.0328, R _{sigma} = 0.0190]	800 [R _{int} = 0.0390, R _{sigma} = 0.0175]
Data/restraints/parameters	6747/0/516	800/0/45
Goodness-of-fit on F ²	0.937	1.015
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0307, wR ₂ = 0.1090	R ₁ = 0.0232, wR ₂ = 0.0574
Final R indexes [all data]	R ₁ = 0.0397, wR ₂ = 0.1181	R ₁ = 0.0275, wR ₂ = 0.0594
Largest diff. peak/hole/e Å ⁻³	0.33/-0.47	0.45/-0.45
Flack parameter	N/A	N/A

Table S2. Crystallographic data for [Fe(NCMe)₆][B(C₆F₅)₄]₂ and [Fe(NCMe)₆][B₁₂Cl₁₂].