ELECTRONIC SUPPLEMENTARY INFORMATION

DT-ART-05-2019-001853

Mesityl(amidinato)tetrylenes as ligands in iridium(I) and iridium(III) complexes: Silicon versus germanium and simple κ^1-coordination versus cyclometallation

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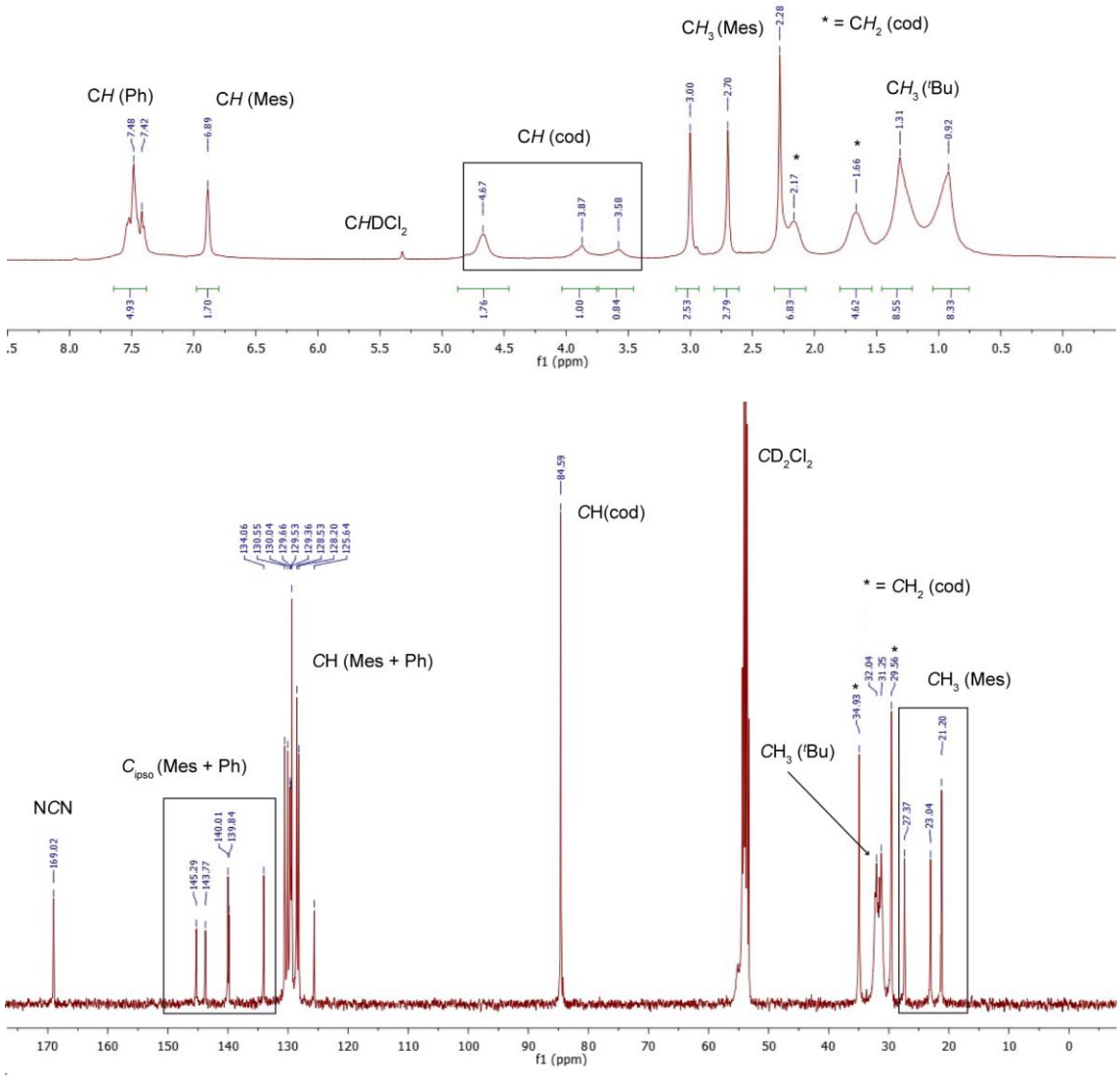

Fig. S1 ^{1}H (top, 400.1 MHz) and ^{13}C{^{1}H} (bottom, 100.6 MHz) NMR spectra (CD_2Cl_2, 293 K) of [IrCl(η^4-cod){κ^1*Ge*-Ge(^{t}Bu$_2$bzam)Mes}] (**2$_{Ge}$**).

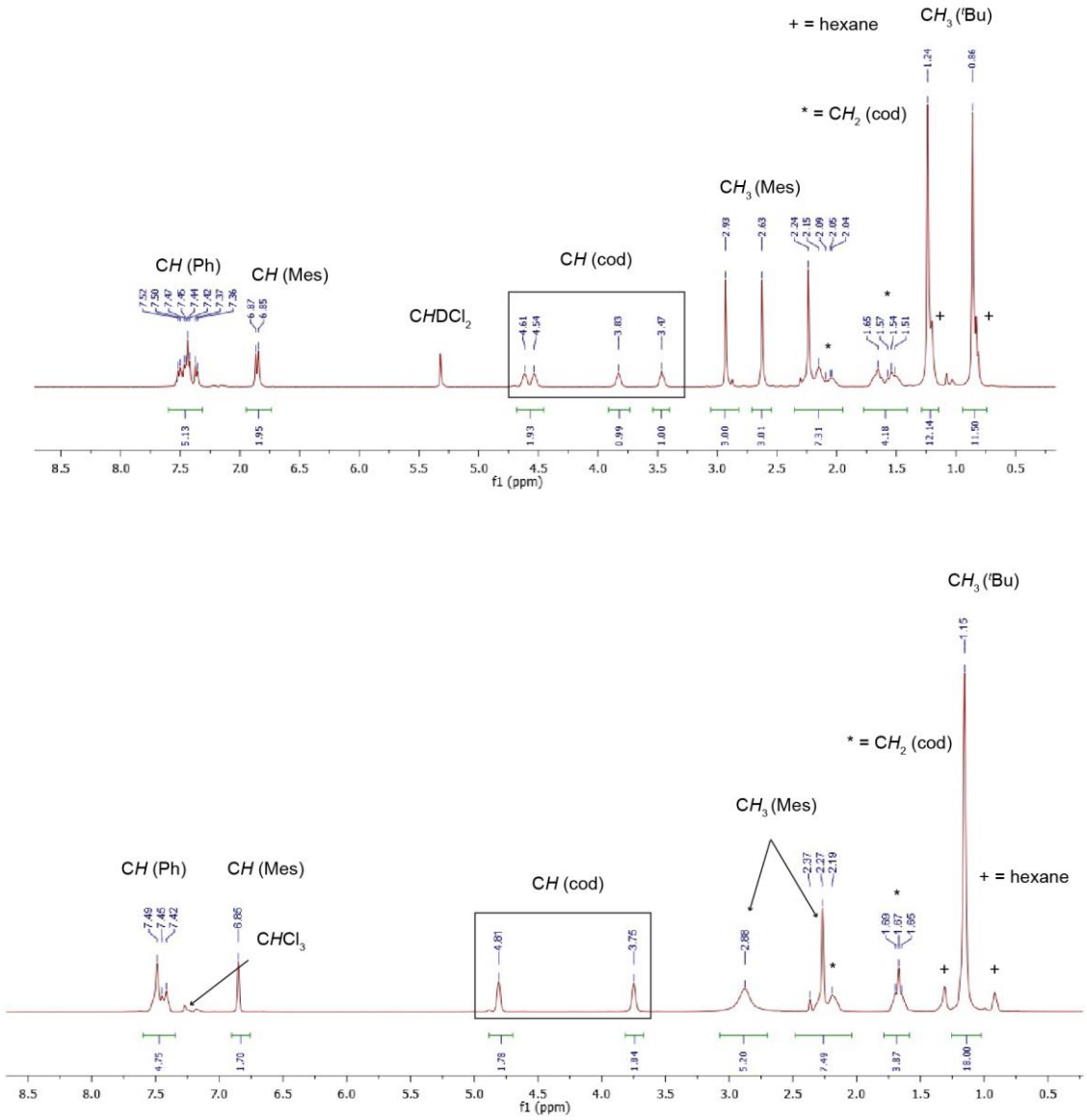

Fig. S2 ^{1}H NMR spectra of [IrCl(η^{4}-cod){κ^{1}*Ge*-Ge(^{t}Bu$_{2}$bzam)Mes}] (**2$_{Ge}$**) at 233 K (top, 400.1 MHz; CD_2Cl_2) and at 333 K (bottom, 400.1 MHz; $CDCl_3$).

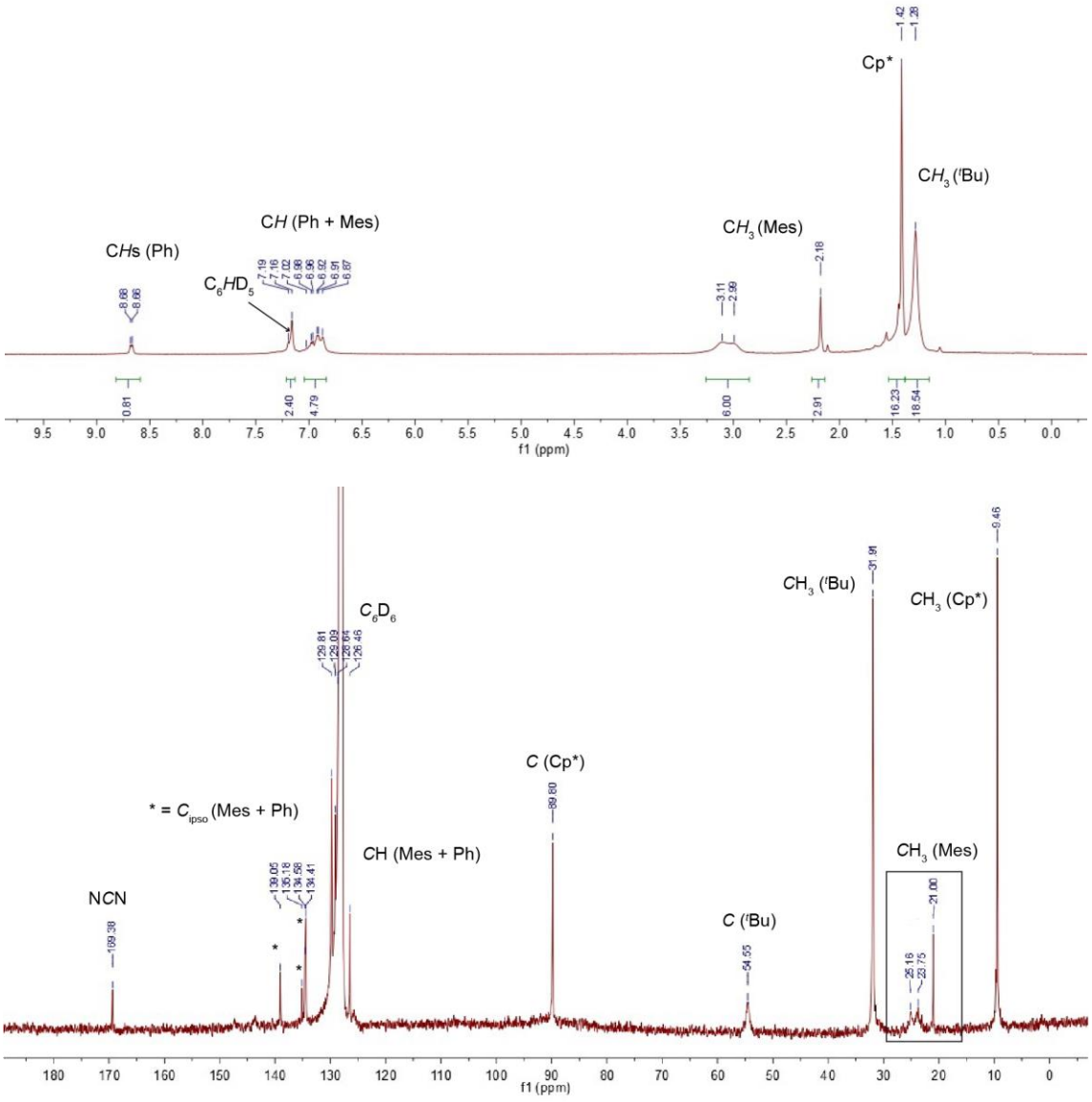

Fig. S3 ^{1}H (top, 400.1 MHz) and ^{13}C{^{1}H} (bottom, 100.6 MHz) NMR spectra (C_6D_6, 293 K) of [$IrCl_2$(η^5-Cp*){κ^1*Ge*-Ge(^{t}Bu$_2$bzam)Mes}] (**3$_{Ge}$**).

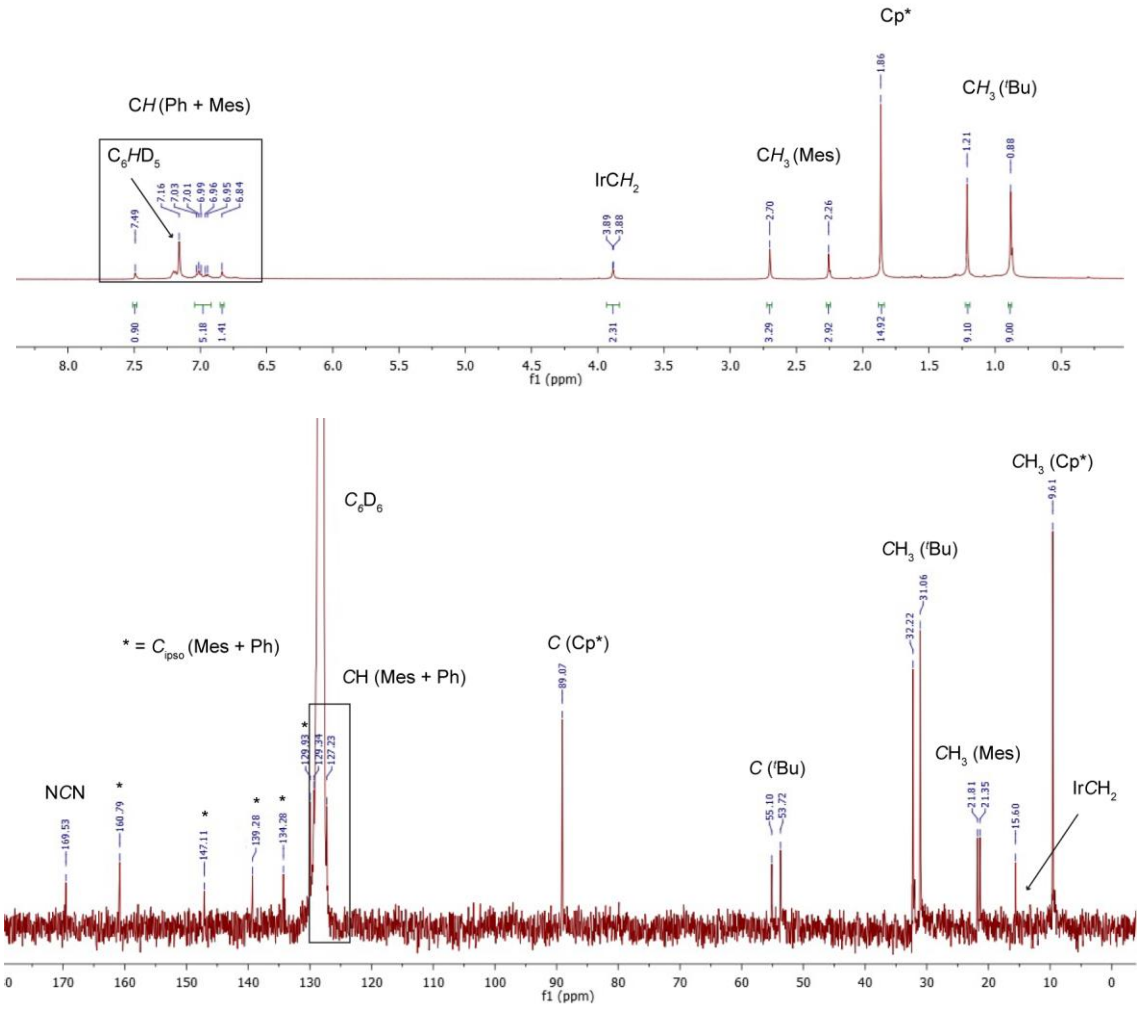

Fig. S4 ^{1}H (top, 400.1 MHz) and ^{13}C{^{1}H} (bottom, 100.6 MHz) NMR spectra (C_6D_6, 293 K) of [IrCl(η^5-Cp*){κ^2*C,Ge*-Ge(^{t}Bu$_2$bzam)($CH_2C_6H_2Me_2$)}] (**5$_{Ge}$**).

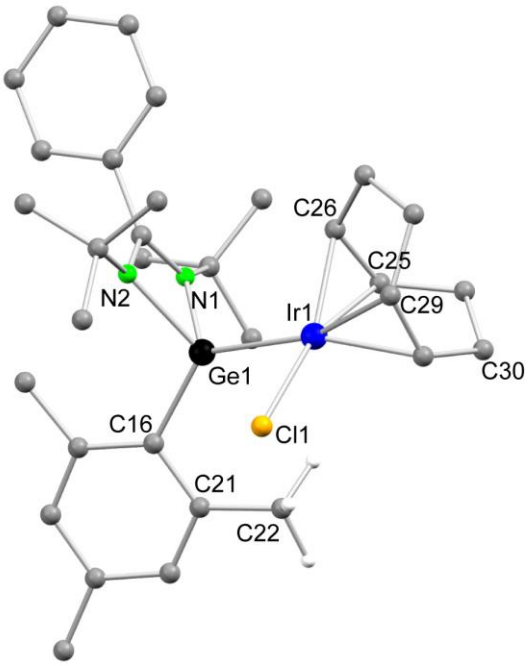

Fig. S5 DFT-optimized structure of [IrCl(η⁴-cod){κ¹*Ge*-Ge(ᵗBu₂bzam)Mes}] (**2$_{Ge}$**; H atoms, except those on C22 atom, have been omitted for clarity). Selected bond lengths (Å) and angles (º): Ir1−Ge1 2.457, Ir1−Cl1 2.388, Ir1−C25 2.113, Ir1−C26 2.092, Ir1−C29 2.179, Ir1−C30 2.160, Ge1−C16 1.974, C16−C21 1.416, C21−C22 1.512, C22···Ir1 3.644; Cl1−Ir1−Ge1 87.81, C16−Ge1−Ir1−Cl1 −50.75.

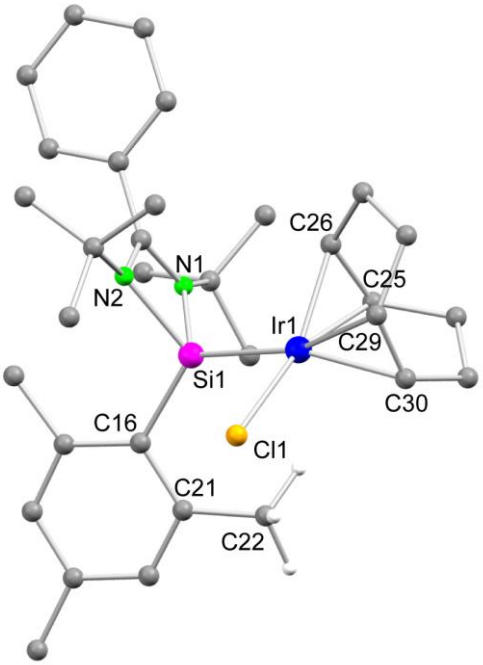

Fig. S6 DFT-optimized structure of [IrCl(η⁴-cod){κ¹*Si*-Si(ᵗBu₂bzam)Mes}] (**2$_{Si}$**; H , except those on C22 atom, have been omitted for clarity). Selected bond lengths (Å) and angles (º): Ir1−Si1 2.376, Ir1−Cl1 2.391, Ir1−C25 2.112, Ir1−C26 2.092, Ir1−C29 2.211, Ir1−C30 2.192, Si1−C16 1.906, C16−C21 1.420, C21−C22 1.510, C22···Ir1 3.514; Cl1−Ir1−Si1 88.34, C16−Si1−Ir1−Cl1 −49.34.

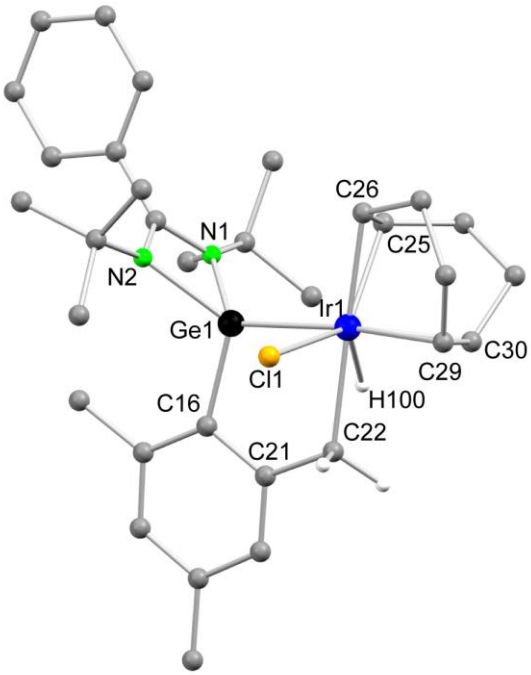

Fig. S7 DFT-optimized structure of **TS_{Ge}** (H atoms, except those on C22 and Ir atoms, have been omitted for clarity). Selected bond lengths (Å) and angles (º): Ir1−Ge1 2.387, Ir1−Cl1 2.532, Ir1−C25 2.126, Ir1−C26 2.123, Ir1−C29 2.201, Ir1−C30 2.210, Ge1−C16 1.943, C16−C21 1.407, C21−C22 1.518, C22−Ir1 2.283, Ir1−H100 1.631, C22···H100 1.466; Cl1−Ir1−Ge1 85.76, Cl1−Ir1−H100 125.17, Cl1−Ir1−C22 86.15.

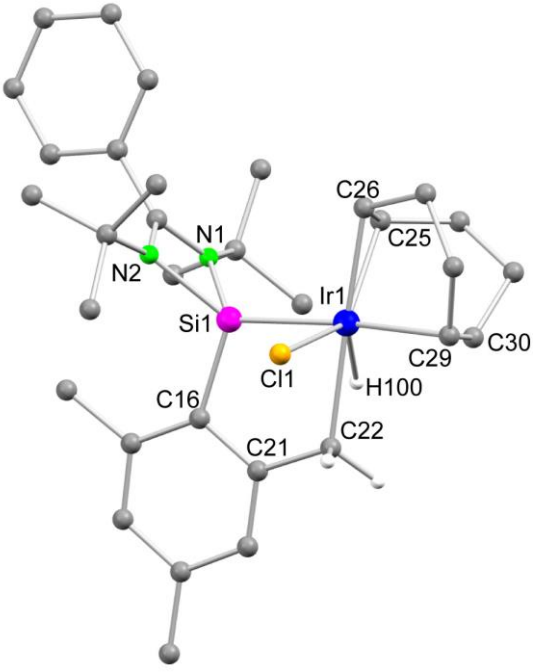

Fig. S8 DFT-optimized structure of **TS_{Si}** (H atoms, except those on C22 and Ir atoms, have been omitted for clarity). Selected bond lengths (Å) and angles (º): Ir1−Si1 2.308, Ir1−Cl1 2.533, Ir1−C25 2.120, Ir1−C26 2.120, Ir1−C29 2.251, Ir1−C30 2.264, Si1−C16 1.876, C16−C21 1.408, C21−C22 1.514, C22−Ir1 2.285, Ir1−H100 1.634; C22···H100 1.450; Cl1−Ir1−Si1 87.70, Cl1−Ir1−H100 124.21, Cl1−Ir1−C22 85.48.

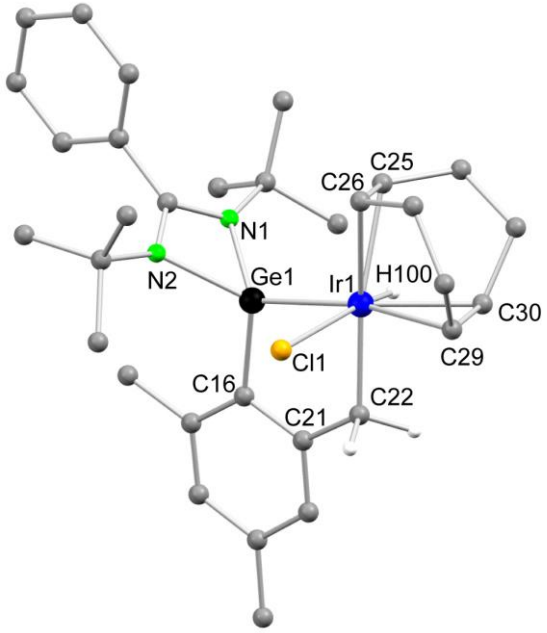

Fig. S9 DFT-optimized structure of [IrClH(η⁴-cod){κ²*C*,*Ge*-Ge(ᵗBu₂bzam)(CH₂C₆H₂Me₂)}] (**4**$_{\mathbf{Ge}}$; H atoms, except those on C22 and Ir atoms, have been omitted for clarity). Selected bond lengths (Å) and angles (º): Ir1−Ge1 2.379, Ir1−Cl1 2.516, Ir1−C25 2.226, Ir1−C26 2.224, Ir1−C29 2.217, Ir1−C30 2.217, Ge1−C16 1.929, C16−C21 1.405, C21−C22 1.525, C22−Ir1 2.124, Ir1−H100 1.579; Cl1−Ir1−Ge1 87.06, Cl1−Ir1−H100 161.08, Cl1−Ir1−C22 85.44.

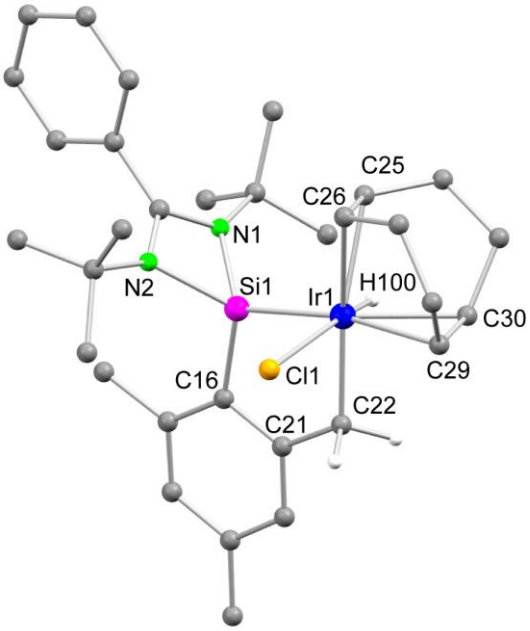

Fig. S10 DFT-optimized structure of [IrClH(η⁴-cod){κ²*C*,*Si*-Si(ᵗBu₂bzam)(CH₂C₆H₂Me₂)}] (**4**$_{\mathbf{Si}}$; H atoms, except those on C22 and Ir atoms, have been omitted for clarity). Selected bond lengths (Å) and angles (º): Ir1−Si1 2.302, Ir1−Cl1 2.517, Ir1−C25 2.219, Ir1−C26 2.239, Ir1−C29 2.265, Ir1−C30 2.259, Si1−C16 1.860, C16−C21 1.406, C21−C22 1.520, C22−Ir1 2.120, Ir1−H100 1.576; Cl1−Ir1−Si1 89.70, Cl1−Ir1−H100 161.57, Cl1−Ir1−C22 85.33.

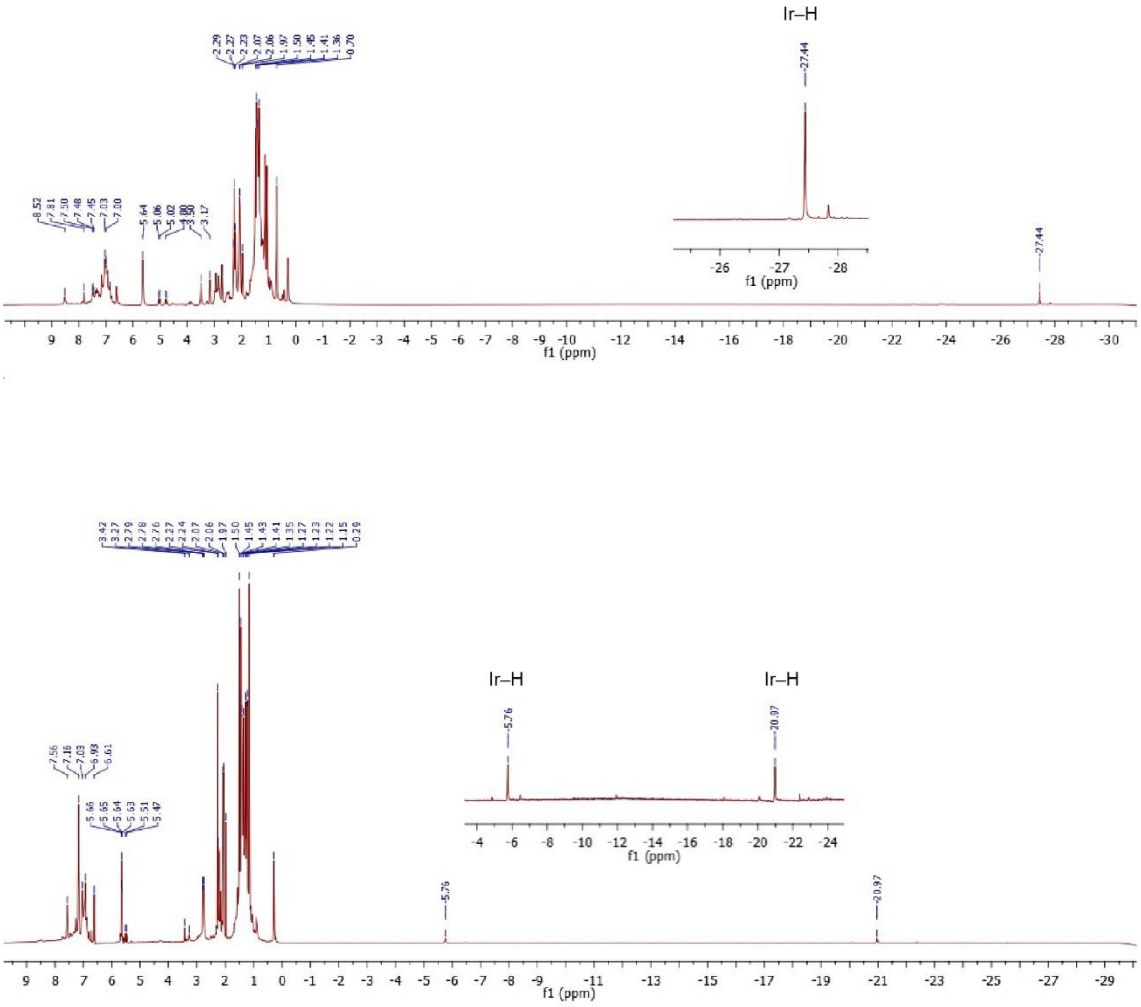

Fig. S11 ^{1}H (400.1 MHz; C_6D_6, 293 K) NMR spectra obtained by stirring in a J. Young NMR tube a C_6D_6 solution of $[Ir_2(\mu\text{-}Cl)_2(\eta^2\text{-}coe)_4]$ (22 mg, 0.025 mmol) and **1_{Ge}** at (42 mg, 0.10 mmol) for 15 minutes at room temperature (top) and for 1 h at 70 ºC (bottom).

Table S1 DFT-optimized atomic coordinates for **2_{Ge}**.

C	-0.612429	1.031147	2.884184
H	0.477146	0.923811	2.767362
H	-0.831628	1.088130	3.960114
H	-0.916132	1.978579	2.414831
C	-2.861919	0.077307	2.403583
H	-3.167518	0.990992	1.871614
H	-3.112006	0.204501	3.467984
H	-3.446355	-0.770787	2.022289
C	-0.940887	-1.453004	2.961813
H	-1.499386	-2.316740	2.575220
H	-1.148470	-1.372795	4.040015
H	0.134001	-1.644288	2.830394
C	-1.352166	-0.155376	2.252599
C	-1.376459	-0.897060	-0.195226
C	-2.285487	-2.073896	-0.115273
C	-3.657905	-1.912047	-0.318109
H	-4.059344	-0.918563	-0.525614
C	-4.505078	-3.015454	-0.266254
H	-5.576311	-2.883361	-0.425331
C	-3.983733	-4.285624	-0.020196
H	-4.648058	-5.150741	0.014088
C	-2.614118	-4.448865	0.181027
H	-2.201377	-5.440384	0.372896
C	-1.764904	-3.344872	0.137452
H	-0.692495	-3.469324	0.298844
C	-0.725439	-1.002426	-2.663438
C	-0.242168	0.126890	-3.580850
H	-0.986595	0.935577	-3.638044
H	-0.082754	-0.260738	-4.597811
H	0.712499	0.550405	-3.233044
C	0.313314	-2.132109	-2.650460
H	1.290864	-1.751865	-2.314520
H	0.430014	-2.554870	-3.660350
H	0.000877	-2.944064	-1.976358
C	-2.070783	-1.524696	-3.187388
H	-2.392019	-2.444886	-2.682320
H	-1.970089	-1.749777	-4.259745
H	-2.860080	-0.766044	-3.071864
C	-0.330260	2.668563	-0.290906
C	0.548207	3.664004	0.200452
C	0.113291	4.990104	0.282927
H	0.804166	5.746271	0.666029
C	-1.166947	5.375182	-0.105845
C	-2.031408	4.383630	-0.566600
H	-3.048916	4.658286	-0.859215
C	-1.643243	3.044648	-0.660428
C	1.957393	3.366539	0.659415
H	2.399137	4.250619	1.139163
H	2.597012	3.078408	-0.188288
H	1.996855	2.539820	1.385405
C	-1.596753	6.817556	-0.050743
H	-1.383000	7.321328	-1.007577
H	-1.062014	7.366623	0.737670
H	-2.676574	6.910367	0.135626
C	-2.679993	2.059222	-1.142188
H	-2.346587	1.516212	-2.035271
H	-3.620970	2.573419	-1.380517
H	-2.892653	1.304812	-0.370453
C	2.642898	-0.892647	1.555123
H	1.918002	-0.402767	2.212041
C	2.106373	-1.817614	0.603178
H	1.018384	-1.956924	0.628088
C	2.841227	-3.037564	0.080016
H	2.263979	-3.427013	-0.773558
H	2.854571	-3.840181	0.840307
C	4.269001	-2.707456	-0.388640
H	4.991897	-2.870384	0.425112
H	4.560962	-3.396340	-1.194316
C	4.382386	-1.276339	-0.892676
H	4.513821	-1.155984	-1.972392
C	4.785613	-0.196769	-0.088243
H	5.220288	0.666134	-0.602793
C	5.102363	-0.286029	1.389953
H	6.097691	-0.742698	1.539990
H	5.173038	0.744119	1.771818
C	4.026707	-1.045664	2.184856
H	3.999452	-0.661782	3.215320
H	4.282178	-2.113424	2.272424
Cl	3.029524	1.374396	-2.259125
Ge	0.355070	0.816962	-0.303605
Ir	2.650315	-0.055621	-0.385172
N	-0.951273	-0.169934	0.836854
N	-0.845853	-0.406779	-1.317314

Energy= -3998.27651332 hartree

Table S2 DFT-optimized atomic coordinates for **2_{Si}**.

C	-0.415504	1.082565	2.901468
H	0.645739	0.816958	2.786165
H	-0.628612	1.164495	3.976904
H	-0.573705	2.067450	2.438445
C	-2.781262	0.491249	2.405464
H	-2.931950	1.449284	1.885540
H	-3.019496	0.641193	3.469542
H	-3.488356	-0.248916	2.006693
C	-1.127389	-1.323342	2.969624
H	-1.820490	-2.084061	2.584243
H	-1.316941	-1.211476	4.048170
H	-0.098298	-1.686637	2.835334
C	-1.325690	0.025231	2.264952
C	-1.460257	-0.727377	-0.179147
C	-2.500938	-1.787243	-0.097398
C	-3.846367	-1.461310	-0.283617
H	-4.128029	-0.425477	-0.480568
C	-4.817518	-2.457199	-0.232362
H	-5.867191	-2.199090	-0.379900
C	-4.447955	-3.782316	-0.002261
H	-5.209408	-4.562995	0.032634
C	-3.105288	-4.108656	0.182471
H	-2.812601	-5.144060	0.362578
C	-2.131222	-3.113579	0.137713
H	-1.079323	-3.364508	0.285252
C	-0.826052	-0.868250	-2.652069
C	-0.258998	0.222059	-3.567620
H	-0.935849	1.087976	-3.622208
H	-0.137803	-0.177600	-4.585230
H	0.727166	0.566702	-3.223723
C	0.097711	-2.092643	-2.673663
H	1.114874	-1.808924	-2.361507
H	0.143005	-2.517450	-3.688125
H	-0.273295	-2.873693	-1.992244
C	-2.226002	-1.253521	-3.149368
H	-2.618923	-2.152966	-2.657857
H	-2.168567	-1.461971	-4.228094
H	-2.942154	-0.430836	-3.001347
C	-0.014632	2.573500	-0.259086
C	0.971948	3.452358	0.260768
C	0.723383	4.826657	0.315998
H	1.497239	5.484164	0.721807
C	-0.472604	5.383752	-0.127219
C	-1.451092	4.514806	-0.603560
H	-2.410325	4.924972	-0.931974
C	-1.252416	3.133184	-0.667186
C	2.309256	2.986208	0.790125
H	2.792740	3.789985	1.363171
H	2.977657	2.699815	-0.035235
H	2.224962	2.108928	1.448448
C	-0.693974	6.872974	-0.102351
H	-0.261730	7.342921	-1.000952
H	-0.214339	7.335767	0.772716
H	-1.765103	7.121091	-0.080668
C	-2.422272	2.308847	-1.150908
H	-2.170187	1.707854	-2.032484
H	-3.269207	2.958962	-1.409353
H	-2.762730	1.610868	-0.371741
C	2.470273	-1.207553	1.540836
H	1.805356	-0.680443	2.230438
C	1.834457	-2.055683	0.576740
H	0.739808	-2.107732	0.629486
C	2.447579	-3.325903	0.016493
H	1.826789	-3.643034	-0.836278
H	2.395268	-4.142796	0.760129

C	3.895813	-3.125427	-0.465239
H	4.607865	-3.381782	0.333585
H	4.107119	-3.820146	-1.291045
C	4.151120	-1.703491	-0.938216
H	4.262426	-1.565778	-2.017799
C	4.663962	-0.689338	-0.122834
H	5.156167	0.148112	-0.626987
C	4.976001	-0.828279	1.351761
H	5.930091	-1.368644	1.491097
H	5.134420	0.186062	1.749419
C	3.843962	-1.506608	2.141372
H	3.868899	-1.152757	3.182806
H	4.000991	-2.595528	2.194403
Cl	3.034057	1.099849	-2.227233
Si	0.379918	0.708663	-0.268999
Ir	2.517885	-0.322635	-0.376133
N	-0.933633	-0.054251	0.847072
N	-0.860200	-0.291572	-1.290064

Energy= -2210.73182095 hartree

Table S3 DFT-optimized atomic coordinates for **TS_{Ge}**.

C	0.627290	0.571976	-3.142060
H	-0.151468	-0.174161	-2.929152
H	0.746550	0.656208	-4.232000
H	0.281700	1.544591	-2.757331
C	2.401290	-1.192063	-3.034067
H	3.401022	-1.470844	-2.674791
H	2.435962	-1.160996	-4.133788
H	1.689770	-1.977174	-2.737713
C	3.013398	1.239384	-2.836643
H	2.685166	2.232904	-2.497027
H	3.161596	1.285496	-3.926506
H	3.984157	1.008170	-2.376347
C	1.960563	0.175874	-2.495368
C	2.468352	-0.209184	-0.011677
C	3.816928	-0.829162	-0.106630
C	3.928018	-2.221220	-0.139928
H	3.025843	-2.835384	-0.116764
C	5.185328	-2.815471	-0.209535
H	5.270484	-3.902914	-0.235184
C	6.331965	-2.022078	-0.247175
H	7.316629	-2.489095	-0.301511
C	6.219710	-0.632632	-0.216188
H	7.115441	-0.010000	-0.242058
C	4.963753	-0.034834	-0.144778
H	4.870469	1.051810	-0.100826
C	2.080849	-0.293967	2.528266
C	1.523587	-1.695476	2.810076
H	0.437145	-1.717105	2.635871
H	1.706502	-1.972789	3.859728
H	2.013242	-2.444772	2.168294
C	1.329174	0.742378	3.372165
H	1.736053	1.751841	3.207426
H	1.436646	0.501033	4.440017
H	0.253577	0.740438	3.138621
C	3.572661	-0.225950	2.876770
H	4.153369	-1.041503	2.426433
H	3.679788	-0.304208	3.968867
H	4.010656	0.733231	2.560697
C	-0.220178	2.434672	0.101900
C	0.685638	3.514368	0.163465
C	0.204342	4.810278	-0.001882
H	0.904997	5.649326	0.041574
C	-1.154059	5.066981	-0.230114
C	-2.034291	3.990787	-0.283072
H	-3.098354	4.175917	-0.455561
C	-1.590572	2.672760	-0.108926
C	-2.617114	1.555167	-0.121533
H	-3.441917	1.815847	-0.804886
H	-3.060416	1.471236	0.882542
C	-1.645298	6.483034	-0.384901
H	-0.966674	7.076353	-1.015912
H	-1.702646	6.983612	0.595229
H	-2.647630	6.515446	-0.834383
C	2.156979	3.289577	0.407014
H	2.711859	4.237808	0.400763
H	2.589635	2.633974	-0.362974
H	2.326393	2.796770	1.375333
C	-1.089170	-2.168278	-1.179909
H	-0.038727	-1.994663	-1.438534
C	-1.328833	-2.649002	0.156728
H	-0.439843	-2.764961	0.783414
C	-2.466953	-3.609725	0.509498
H	-2.143898	-4.255110	1.338961
H	-2.660254	-4.289404	-0.336595
C	-3.750857	-2.871077	0.930938
H	-4.644423	-3.493873	0.742162
H	-3.711553	-2.684127	2.013085
C	-3.914032	-1.519361	0.264867
H	-4.526815	-0.804447	0.821627
C	-3.714494	-1.277692	-1.103548
H	-4.188918	-0.379654	-1.510798
C	-3.431404	-2.375913	-2.122121
H	-3.871004	-3.319028	-1.765614
H	-3.952359	-2.134947	-3.060368
C	-1.930264	-2.542521	-2.386955
H	-1.635138	-1.879744	-3.216602
H	-1.699993	-3.572885	-2.716162
Cl	-2.034381	-0.321499	2.522321
Ir	-1.923260	-0.616297	0.009577
N	1.704804	0.143336	-1.045796
N	1.811130	0.055480	1.118952
Ge	0.165751	0.530959	0.145215
H	-2.096565	0.579988	-1.085143

Energy= - 3998.23446997 hartree

Table S4 DFT-optimized atomic coordinates for **TS_{Si}**.

C	0.533897	0.598170	-3.129094
H	-0.224350	-0.175190	-2.948353
H	0.672979	0.714343	-4.213693
H	0.150876	1.549365	-2.727493
C	2.367921	-1.106778	-3.035051
H	3.375012	-1.355355	-2.674092
H	2.410832	-1.045824	-4.133056
H	1.685622	-1.926492	-2.765887
C	2.887119	1.339256	-2.770979
H	2.509803	2.313285	-2.426645
H	3.059635	1.406219	-3.855986
H	3.855051	1.139627	-2.289761
C	1.869017	0.230319	-2.471381
C	2.364873	-0.228820	0.006368
C	3.695835	-0.881255	-0.086546
C	3.769437	-2.275950	-0.111510
H	2.851660	-2.865921	-0.076290
C	5.010999	-2.901184	-0.189811
H	5.068851	-3.990486	-0.210093
C	6.176665	-2.136857	-0.242995
H	7.148761	-2.628664	-0.304162
C	6.100487	-0.744876	-0.217859
H	7.011551	-0.145658	-0.254471
C	4.860878	-0.115164	-0.138896
H	4.795786	0.973584	-0.098261
C	1.944739	-0.282028	2.544190
C	1.356677	-1.663804	2.854877
H	0.269451	-1.661471	2.687927
H	1.543404	-1.924668	3.907964
H	1.824126	-2.435875	2.223232
C	1.222813	0.788839	3.370237
H	1.667182	1.782035	3.205607
H	1.313036	0.549740	4.440192
H	0.150848	0.823616	3.126265
C	3.439067	-0.244197	2.885158
H	3.997938	-1.083696	2.451408
H	3.546499	-0.302152	3.978358
H	3.901224	0.696862	2.549353
C	-0.126935	2.399260	0.104582
C	0.813856	3.450761	0.208149
C	0.385292	4.765285	0.047533
H	1.114675	5.576836	0.126599
C	-0.954528	5.078698	-0.217792
C	-1.870954	4.037621	-0.314493
H	-2.922340	4.262221	-0.515694

C	-1.479348	2.702882	-0.145560
C	-2.536438	1.620932	-0.212092
H	-3.311218	1.897385	-0.946639
H	-3.042499	1.555030	0.762777
C	-1.384117	6.515154	-0.365637
H	-0.682486	7.080036	-0.997727
H	-1.414490	7.014586	0.616163
H	-2.385827	6.593335	-0.810825
C	2.272412	3.187943	0.492418
H	2.841702	4.126684	0.535626
H	2.724000	2.554474	-0.284719
H	2.403713	2.662705	1.448507
C	-1.033418	-2.118956	-1.166008
H	0.016783	-1.967214	-1.438011
C	-1.260767	-2.576430	0.184957
H	-0.361447	-2.700977	0.794909
C	-2.393214	-3.536510	0.560284
H	-2.068004	-4.156023	1.408820
H	-2.575790	-4.242562	-0.266880
C	-3.688855	-2.805339	0.959319
H	-4.571101	-3.448823	0.787158
H	-3.654202	-2.588410	2.035916
C	-3.880095	-1.475907	0.259104
H	-4.470140	-0.740888	0.813114
C	-3.688571	-1.261194	-1.104218
H	-4.143807	-0.361143	-1.527930
C	-3.382112	-2.372277	-2.098568
H	-3.811007	-3.313854	-1.725255
H	-3.903608	-2.156634	-3.042825
C	-1.878544	-2.529021	-2.359478
H	-1.592792	-1.886485	-3.208356
H	-1.641946	-3.565603	-2.664842
Cl	-2.096279	-0.171473	2.492991
Ir	-1.845946	-0.547239	0.001020
N	1.605482	0.155772	-1.022909
N	1.685505	0.042441	1.124230
Si	0.180900	0.549108	0.133582
H	-2.013397	0.624114	-1.125960

Energy= - 2210.69713658 hartree

Table S5 DFT-optimized atomic coordinates for **4_{Ge}**.

C	0.191922	0.155754	-3.122111
H	-0.623257	-0.529774	-2.851823
H	0.341958	0.104888	-4.210288
H	-0.120436	1.179520	-2.862421
C	1.838520	-1.680318	-2.721306
H	2.807626	-1.973038	-2.295665
H	1.897416	-1.813200	-3.812429
H	1.066100	-2.363447	-2.337502
C	2.610488	0.708730	-2.871724
H	2.360781	1.759973	-2.664707
H	2.748481	0.599981	-3.958505
H	3.567875	0.469851	-2.389911
C	1.486841	-0.222119	-2.394818
C	1.970297	-0.274907	0.115762
C	3.329548	-0.880210	0.109551
C	3.466275	-2.259476	0.281916
H	2.575137	-2.880933	0.387370
C	4.734535	-2.833743	0.314100
H	4.838648	-3.911151	0.450411
C	5.867728	-2.032386	0.175874
H	6.860949	-2.483169	0.205474
C	5.730727	-0.655682	0.002043
H	6.615618	-0.026190	-0.102405
C	4.463660	-0.078614	-0.031098
H	4.351271	1.000658	-0.148945
C	1.588136	-0.043976	2.646364
C	1.131601	-1.428408	3.123973
H	0.052239	-1.552687	2.948980
H	1.316792	-1.538897	4.203609
H	1.685145	-2.224040	2.601192
C	0.761165	1.044495	3.342059
H	1.078225	2.046994	3.016412
H	0.896882	0.975407	4.431396
H	-0.311511	0.919303	3.131255
C	3.070167	0.179951	2.972382
H	3.711558	-0.646930	2.640430
H	3.178409	0.267812	4.063687
H	3.438827	1.113644	2.520262
C	-0.745408	2.360277	0.071852
C	0.123590	3.469592	0.029301
C	-0.422872	4.742963	-0.086150
H	0.241744	5.611269	-0.126072
C	-1.810853	4.938275	-0.157977
C	-2.647638	3.828378	-0.109244
H	-3.731198	3.970856	-0.161125
C	-2.139931	2.524987	0.013734
C	-3.116704	1.358625	0.115980
H	-3.880418	1.501520	-0.670561
H	-3.645815	1.482613	1.076857
C	-2.374769	6.332634	-0.255616
H	-1.768189	6.965582	-0.920397
H	-2.388285	6.816708	0.734410
H	-3.406551	6.324469	-0.635127
C	1.618459	3.287738	0.111121
H	2.148075	4.238679	-0.041100
H	1.970323	2.570668	-0.646603
H	1.913717	2.883224	1.092519
C	-1.634807	-2.555502	-0.720671
H	-0.569286	-2.412746	-0.923301
C	-2.004045	-2.798447	0.604031
H	-1.208410	-2.775643	1.351100
C	-3.261941	-3.558404	1.010076
H	-3.050067	-4.105488	1.939356
H	-3.479831	-4.325951	0.250815
C	-4.487557	-2.653835	1.241280
H	-5.421807	-3.221031	1.074132
H	-4.492515	-2.326957	2.289380
C	-4.496094	-1.401706	0.390841
H	-5.069945	-0.569196	0.808708
C	-4.219732	-1.364135	-0.981309
H	-4.606548	-0.505783	-1.535991
C	-3.943830	-2.610823	-1.815336
H	-4.499815	-3.457453	-1.384906
H	-4.359287	-2.459994	-2.822462
C	-2.449431	-2.957073	-1.934084
H	-2.027352	-2.433423	-2.806375
H	-2.320936	-4.036938	-2.130101
Cl	-2.464844	-0.455568	2.621515
Ir	-2.428265	-0.650646	0.112983
N	1.216024	-0.033157	-0.959191
N	1.297579	0.088225	1.205544
Ge	-0.336681	0.480734	0.178011
H	-2.194238	-0.301743	-1.408656

Energy= -3998.26381044 hartree

Table S6 DFT-optimized atomic coordinates for **4_{Si}**.

C	0.093642	0.239695	-3.112603
H	-0.672762	-0.526202	-2.935790
H	0.281749	0.301227	-4.194240
H	-0.305582	1.208524	-2.774310
C	1.831470	-1.522083	-2.771483
H	2.819010	-1.776930	-2.364318
H	1.890763	-1.599012	-3.867882
H	1.102075	-2.266477	-2.418476
C	2.468651	0.911322	-2.796947
H	2.135383	1.937954	-2.585817
H	2.655633	0.831055	-3.878644
H	3.421106	0.731137	-2.280495
C	1.394667	-0.103480	-2.380635
C	1.868755	-0.280087	0.128034
C	3.209918	-0.919850	0.112895
C	3.302898	-2.305905	0.259707
H	2.392855	-2.900659	0.357223
C	4.553085	-2.918777	0.274063
H	4.624812	-4.001212	0.389905
C	5.709633	-2.150063	0.143974
H	6.688641	-2.631528	0.158584
C	5.615084	-0.766549	-0.001998
H	6.518861	-0.163119	-0.098315
C	4.366639	-0.149780	-0.016903
H	4.287769	0.934850	-0.108793

C	1.460175	-0.071995	2.656876
C	0.982738	-1.452174	3.124428
H	-0.100807	-1.552392	2.962964
H	1.181067	-1.576008	4.200195
H	1.514785	-2.252565	2.586416
C	0.652593	1.026206	3.359235
H	1.000244	2.026142	3.058618
H	0.773916	0.931952	4.448443
H	-0.419596	0.932635	3.132515
C	2.946372	0.121679	2.982039
H	3.570781	-0.716243	2.644996
H	3.055873	0.200908	4.073747
H	3.334378	1.050710	2.536301
C	-0.680651	2.316359	0.104502
C	0.206730	3.417423	0.109908
C	-0.312316	4.700466	-0.010188
H	0.368536	5.557112	-0.009384
C	-1.693448	4.925057	-0.133690
C	-2.551179	3.832210	-0.125245
H	-3.629814	3.993361	-0.210265
C	-2.068388	2.519224	-0.000227
C	-3.053457	1.362255	0.053049
H	-3.769968	1.494976	-0.778845
H	-3.638689	1.490085	0.980358
C	-2.217157	6.332578	-0.259262
H	-1.758374	6.850347	-1.116222
H	-1.980371	6.920752	0.641667
H	-3.307305	6.346922	-0.395908
C	1.695437	3.221781	0.256327
H	2.234172	4.176641	0.182305
H	2.087136	2.547234	-0.519095
H	1.939885	2.764880	1.227266
C	-1.496385	-2.527719	-0.689960
H	-0.425860	-2.380382	-0.860122
C	-1.907392	-2.765815	0.625700
H	-1.134657	-2.737036	1.395126
C	-3.163600	-3.548385	0.995070
H	-2.976759	-4.071760	1.943198
H	-3.328484	-4.337351	0.243746
C	-4.425401	-2.678380	1.159757
H	-5.331998	-3.278791	0.961443
H	-4.485537	-2.339182	2.201984
C	-4.440967	-1.437957	0.293642
H	-5.027045	-0.604247	0.689738
C	-4.109452	-1.405733	-1.057886
H	-4.466287	-0.550027	-1.635416
C	-3.766939	-2.651165	-1.866040
H	-4.314881	-3.508009	-1.446855
H	-4.148266	-2.522118	-2.889543
C	-2.260580	-2.960245	-1.925923
H	-1.820923	-2.437868	-2.790095
H	-2.100207	-4.038793	-2.106034
Cl	-2.534932	-0.423552	2.602895
Ir	-2.333154	-0.631169	0.103008
N	1.110300	0.003856	-0.936951
N	1.180117	0.073362	1.213084
Si	-0.325573	0.492772	0.183702
H	-2.043222	-0.286899	-1.407805

Energy= -2210.72705378 hartree

Table S7 Crystal, measurement and refinement data for the compounds studied by X-ray diffraction.

	2$_{Ge}$·2(CH_2Cl_2)	**5**$_{Ge}$
formula	$C_{32}H_{46}ClGeIrN_2$·2(CH_2Cl_2)	$C_{34}H_{48}ClGeIrN_2$
fw	928.80	784.98
cryst syst	triclinic	monoclinic
space group	*P*–1	*P*21/n
a, Å	11.1461(4)	10.6239(1)
b, Å	12.3199(6)	18.5431(2)
c, Å	15.3703(5)	17.4300(2)
α, deg	82.470(3)	90
β, deg	79.687(3)	105.333(1)
γ, deg	67.955(4)	90
V, Å^3	1920.0(1)	3311.49(6)
Z	2	4
F(000)	924	1568
D_{calcd}, g cm^{-3}	1.607	1.575
μ, mm^{-1} (Cu Kα)	10.961	9.695
cryst size, mm	0.33 x 0.19 x 0.12	0.20 x 0.10 x 0.06
T, K	150(2)	151(2)
θ range, deg	2.93 to 69.65	3.55 to 69.45
min./max. *h*, *k*, *l*	–13/13, –14/14, –17/18	–12/12, –22/20, –20/21
no. collected reflns	20395	15223
no. unique reflns	7107	6121
no. reflns with $I > 2\sigma(I)$	6603	5711
no. params/restraints	425/22	365/0
GOF (on F^2)	1.022	1.057
R_1 (on *F*, $I > 2\sigma(I)$)	0.045	0.026
wR_2 (on F^2, all data)	0.120	0.069
min./max. $\Delta\rho$, e Å^{-3}	–2.020/1.414	–0.819/1.661
CCDC dep. no.	1911673	1911674