Electronic Supplementary Material (ESI) for Dalton Transactions.

Germylone-Bridged bimetallic Ir and Rh complexes

Supporting Information

Contents

1. Synthesis of compounds 2–4 and their spectral data

General considerations: All reactions were performed under an atmosphere of argon or nitrogen by using standard Schlenk or dry box techniques; solvents were dried over Na metal, K metal or CaH_2. Reagents were of analytical grade, obtained from commercial suppliers and used without further purification. ^{1}H and ^{13}C NMR spectra were obtained with a Bruker AVIII 400MHz BBFO1 spectrometer at 298 K unless otherwise stated. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. Coupling constants *J* are given in Hz. Electrospray ionization (ESI) mass spectra were obtained at the Mass Spectrometry Laboratory at the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured with an OpticMelt Stanford Research System. IR spectra were measured with the Bruker Alpha-FT-IR Spectrometer with an ECO-ATR module. Elemental analyses were performed on a 2400 Series II CHNS/O Elemental Analysis instrument. Compound **1** was synthesized following the reported procedure.[S1]

Compound 2: Benzene (15 mL) was added to a mixture of **1** (143 mg, 0.3 mmol) and $[Ir(COD)Cl]_2$ (200 mg, 0.3 mmol) at room temperature. Immediately, the color changed to deep red. After completion of the reaction, all the solvent was removed in vacuum to afford a red solid as the crude product. Recrystallization of **2** by slow evaporation of a saturated benzene solution gave the red crystalline product. (295 mg, 86%). M.p.:138 ^{o}C (decomposed); ^{1}H NMR (THF-d_8, 400 MHz, 298 K): δ 6.86 (s, 2H,

Ar-C*H*), 4.51 (t, *J* = 8.8 Hz, 2H, NCH_2), 4.48−4.44 (m, 2H, COD-C*H*), 4.19−4.13 (m, 2H, COD-C*H*), 4.06 (t, *J* = 8.7 Hz, 2H, NCH_2), 3.93−3.89 (m, 2H, COD-C*H*), 3.33−3.30 (m, 2H, COD-C*H*), 2.76 (s, 6H, Ar-CH_3), 2.58 (br, 6H, Ad-CH_2), 2.27 (s, 3H, Ar-CH_3), 2.20 (br, 3H, Ad-C*H*), 2.01−1.88 (m, 8H, COD-CH_2), 1.85−1.79 (m, 6H, Ad-CH_2), 1.44−1.38 (m, 2H, COD-CH_2), 1.34−1.29 (m, 2H, COD-CH_2), 1.28 (s, 9H, C(CH_3)$_3$), 1.20−1.13 (m, 2H, COD-CH_2), 1.10−1.02 (m, 2H, COD-CH_2); ^{13}C{^{1}H} NMR (C_6D_6, 100 MHz, 298 K): 215.3 ($C_{carbene}$), 164.4 (*C*=N), 139.8 (C_{Ar}), 136.2 (C_{Ar}), 133.7 (C_{Ar}), 129.4 (C_{Ar}), 81.1 (COD-C*H*), 79.2 (COD-C*H*), 59.6 (Ad-*q*), 48.8 (N*C*H$_2$), 47.7 (N*C*H$_2$), 45.6 (COD-C*H*), 44.5 (COD-C*H*), 40.4 (Ad-*C*H$_2$), 40.1 (*C*(CH$_3$)$_3$), 37.1 (COD-CH_2), 36.9 (Ad-*C*H$_2$), 34.3 (COD-CH_2), 31.1 (COD-CH_2), 30.8 (Ad-*C*H), 29.7 (C(*C*H$_3$)$_3$), 27.7 (COD-CH_2), 21.1 (Ar-*C*H$_3$), 20.7 (Ar-*C*H$_3$); HRMS (ESI): *m/z* calcd for $C_{43}H_{64}N_3Cl_2Ge^{191}Ir^{193}Ir$: 1150.2925 [(*M*+*H*)]$^+$; found: 1150.2925; Elemental analysis: calcd. [%] for $C_{47}H_{71}Cl_2GeN_3Ir_2O$ (**2**+THF): C 46.19, H 5.86, N 3.44; found: C 46.36, H 5.59, N 3.51.

Compound 3: Benzene (20 mL) was added to a mixture of **1** (250 mg, 0.52 mmol) and [Rh(COD)Cl]$_2$ (258 mg, 0.52 mmol) at room temperature, and the solution was stirred overnight. After that, all the solvent was removed in vacuum to afford a red solid as the crude product. Slow evaporation of a toluene solution of **3** at room temperature resulted in the red crystalline solid as the targeted compound. (389 mg, 77%). M.p.:125 ^{o}C (decomposed); ^{1}H NMR (C_6D_6, 400 MHz, 298 K): ^{1}H NMR (C_6D_6, 400 MHz, 298 K): δ 6.94 (s, 2H, Ar-C*H*), 4.94 (m, 2H, COD-C*H*), 4.65 (m, 2H,

COD-C*H*), 4.46 (t, J = 8.7 Hz, 2H, NCH_2), 4.12 (m, 2H, COD-C*H*), 3.96 (t, J = 8.7 Hz, 2H, NCH_2), 3.53 (m, 2H, COD-C*H*), 3.06 (s, 6H,Ar-CH_3), 2.75 (m, 6H, Ad-CH_2), 2.30−2.28 (m, 6H, Ar-CH_3 & Ad-C*H*), 2.26−1.97 (m, 8H, COD-CH_2), 1.94−1.67 (m, 10H, Ad-CH_2 & COD-CH_2), 1.59−1.51 (m, 2H, COD-CH_2), 1.48−1.39 (m, 2H, COD-CH_2), 1.26 (s, 9H, C(CH_3)$_3$); ^{13}C{^{1}H} NMR (THF-d$_8$, 100 MHz, 298 K): δ 215.8 ($C_{carbene}$), 163.3 (*C*=N), 140.2 (Mes), 136.1(Mes), 133.9(Mes), 129.3(Mes), 96.4 (d, *J* = 7.7 Hz, COD-*C*H), 94.8 (d, *J* = 7.7 Hz, COD-*C*H), 61.2 (d, *J* = 14.2 Hz, COD-*C*H), 60.6 (d, *J* = 14.8 Hz, COD-*C*H), 59.2 (Ad-*q*), 48.9 (N*C*H$_2$), 47.8 (N*C*H$_2$), 40.2 (Ad-*C*H$_2$), 40.1 (*C*(CH$_3$)$_3$), 37.1 (Ad-*C*H$_2$), 36.3 (COD-*C*H$_2$), 33.5 (COD-*C*H$_2$), 30.9 (Ad-*C*H), 30.3 (COD-*C*H$_2$), 29.4 (C(*C*H$_3$)$_3$), 27.3 (COD-*C*H$_2$), 24.1 (Mes-*C*H$_3$), 20.8 (Mes-*C*H$_3$); HRMS (ESI): *m/z* calcd for $C_{43}H_{64}Cl_2GeN_3Rh_2$: 972.1799. [(*M*+*H*)]$^+$; found: 972.1802; Elemental analysis: calcd. [%] for $C_{43}H_{63}Cl_2GeN_3Rh_2$: C 53.17, H 6.54, N 4.33; found: C 53.55, H 6.60, N 4.35.

Compound 4: An acetonitrile solution of [Rh(COD)Cl]$_2$ (31 mg, 0.062 mmol) in the J. Young NMR tube was degassed using a freeze-pump-thaw method, and then CO (1 bar) was introduced. After 10 mins, the solvent was removed under vacuum to give a pale white solid, which was further dissolved in benzene (3 mL) followed by addition of **1** (30 mg, 0.063 mmol). Immediately, the solution changed to deep red color, which was kept still at room temperature over two days to result in the formation of **4** as a deep red crystalline solid (46 mg, 45%). **4** does not dissolve in the common organic solvents such as benzene, fluorobenzene, THF, acetonitrile, chloroform and DMSO whereas it slightly dissolves in DCM. However, **4** in DCM gradually decompose at room temperature over 2 hrs. M.p.:147 ^{o}C (decomposed); ^{1}H

NMR(DCM-d_2): δ 6.76 (s, 2H, Mes), 6.67 (s, 2H, Mes), 4.93 (m, 2H, COD-C*H*), 4.61 (m, 4H, COD-C*H* & N-CH_2), 4.29 (m, 2H, N-CH_3), 4.12 (m, 2H, N-CH_3), 3.93 (m, 2H, N-CH_3), 3.77 (m, 2H, N-CH_3), 3.60 (m, 2H, COD-C*H*), 3.09 (s, 6H, Mes-CH_3), 2.87 (d, J = 10.8 Hz, 6H, Ad-CH_2), 2.69 (s, 6H, Mes-CH_3), 2.24−2.16 (m, 18H, Ad-C*H*, COD-CH_2 & Mes-CH_3), 2.00 (m, 2H, COD-CH_2), 1.82−1.67 (m, 18H, Ad-CH_2 & COD-CH_2), 1.25 (s, 18H, C(CH_3)$_3$); ^{13}C{^{1}H} NMR(DCM-d_2): δ 215.0 ($C_{carbene}$), 157.7 (C=N), 138.7 (Mes), 135.1 (Mes), 132.7 (Mes), 131.5 (Mes), 94.0 (d, *J* = 7.6 Hz, COD-*C*H), 93.1 (d, *J* = 8.1 Hz, COD-*C*H), 66.3 (d, *J* = 15.4 Hz, COD-*C*H), 63.0 (d, *J* = 15.0 Hz, COD-*C*H), 59.1 (Ad-*q*), 48.0 (N*C*H$_2$), 47.1 (N*C*H$_2$), 39.3 (Ad-*C*H$_2$ & *C*(CH$_3$)$_3$), 36.0 (Ad-*C*H$_2$), 34.0 (COD-*C*H$_2$), 33.8 (COD-*C*H$_2$), 29.9 (Ad-*C*H), 29.3 (C(*C*H$_3$)$_3$), 28.9 (COD-*C*H$_2$), 28.1 (COD-*C*H$_2$), 23.4 (Mes-*C*H$_3$), 21.9 (Mes-*C*H$_3$), 20.4 (Mes-*C*H$_3$), the carbon resonance signal of CO was not resolved; HRMS (ESI): m/z calcd for $C_{35}H_{51}GeN_3Rh$: 690.2350. [*(M-RhCOCl)/2-Cl*]$^+$; found: 690.2328. *Despite several attempts, the Elemental Analysis of compound **4** was failed, which is probably due to the instability of **4** under the condition.

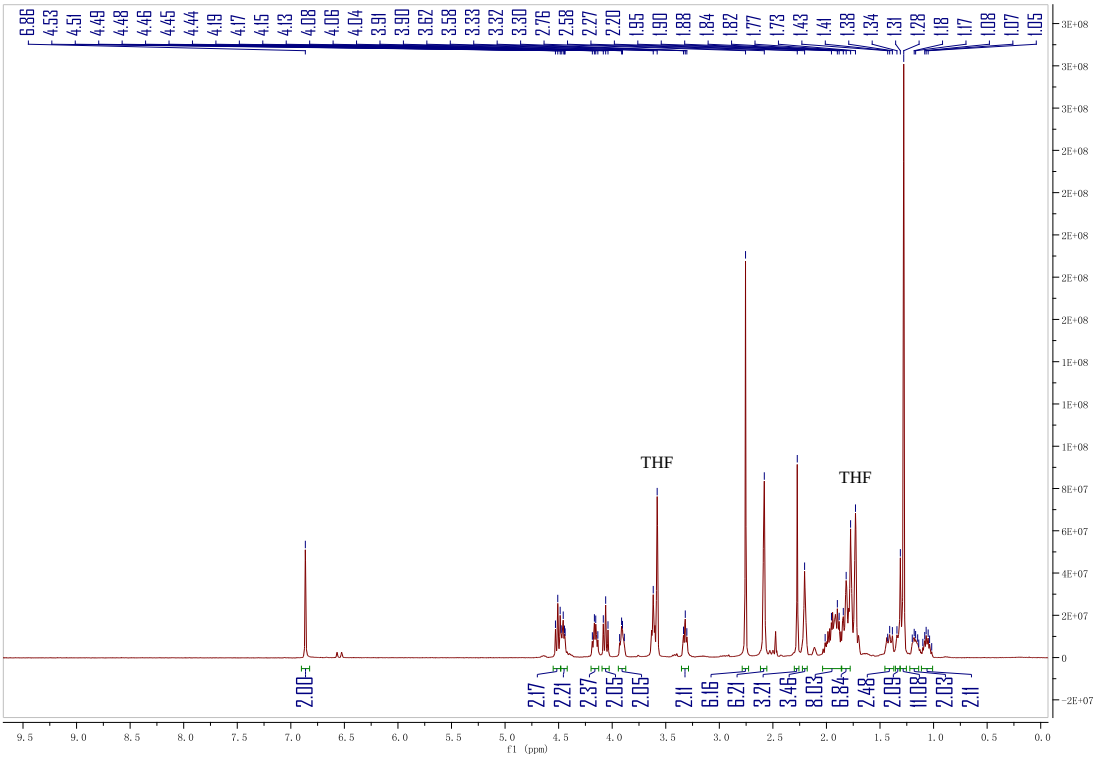


Figure S1: ^{1}H NMR spectrum of **2**.

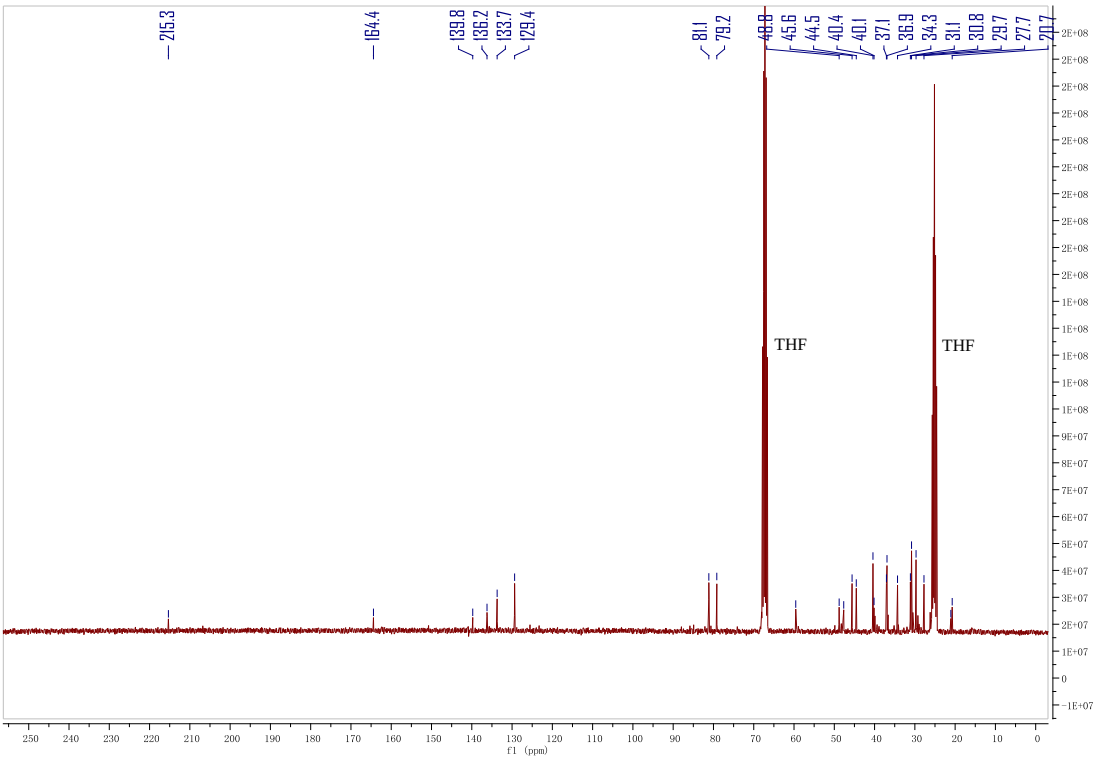


Figure S2: ^{13}C{^{1}H} NMR spectrum of **2**.

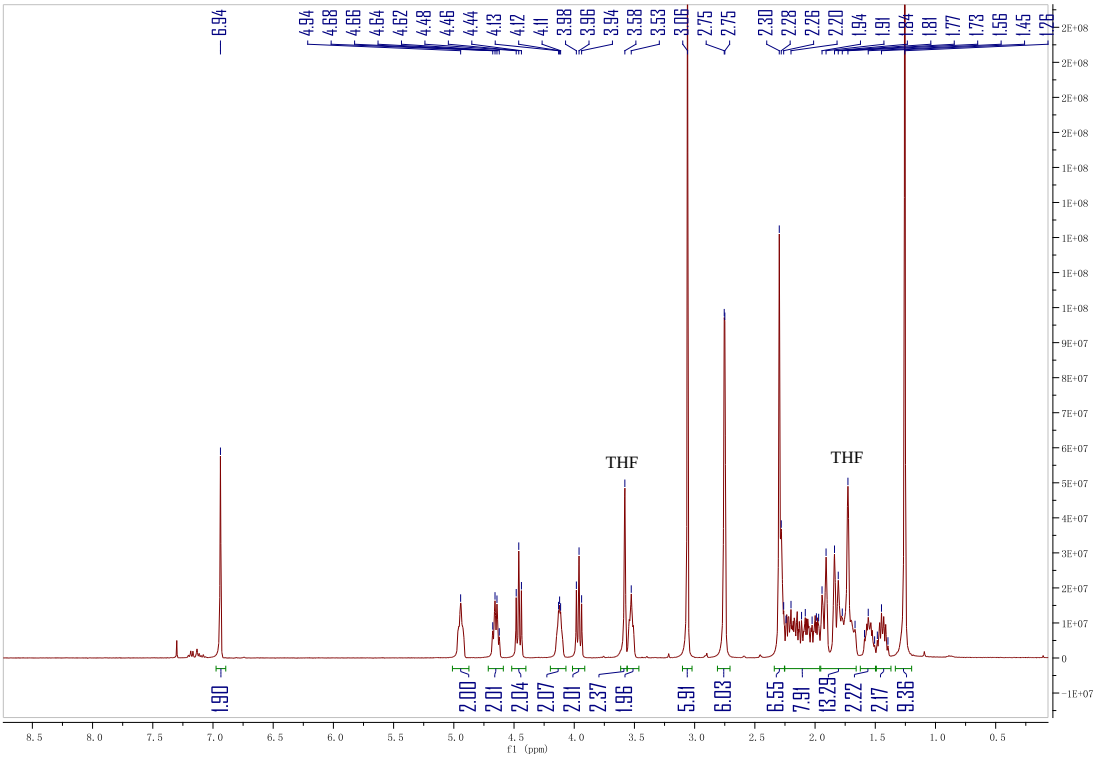


Figure S3: ^{1}H NMR spectrum of **3**.

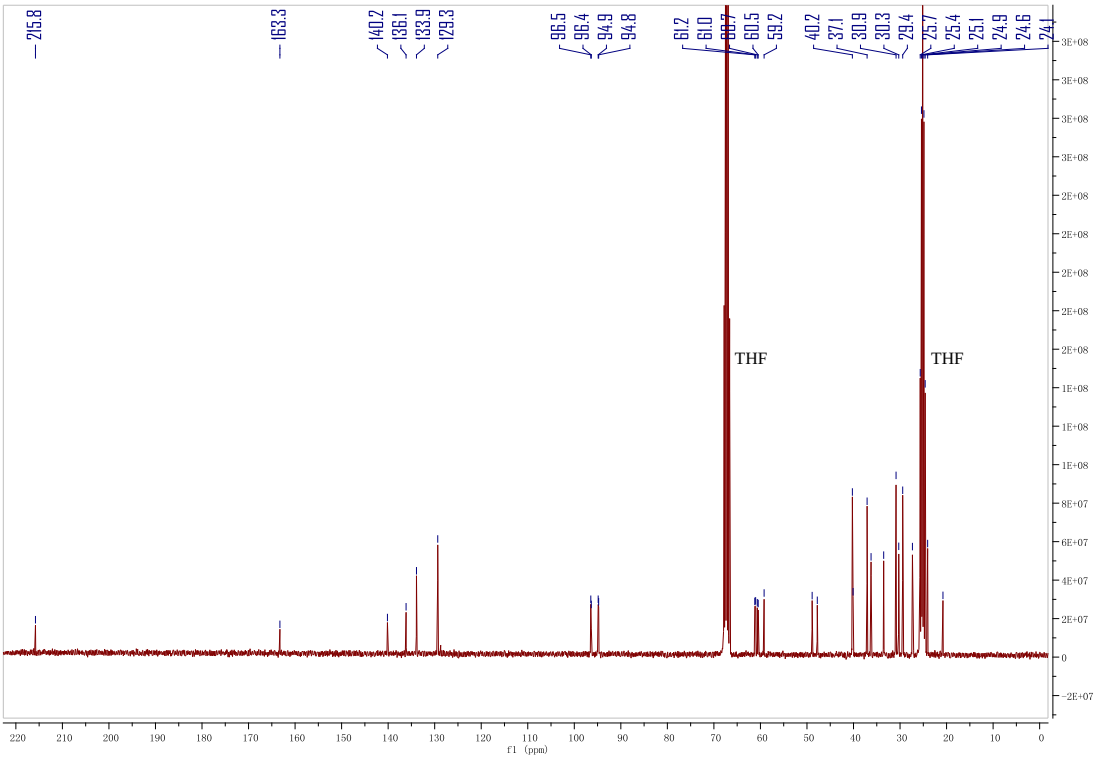


Figure S4: ^{13}C{^{1}H} NMR spectrum of **3**.

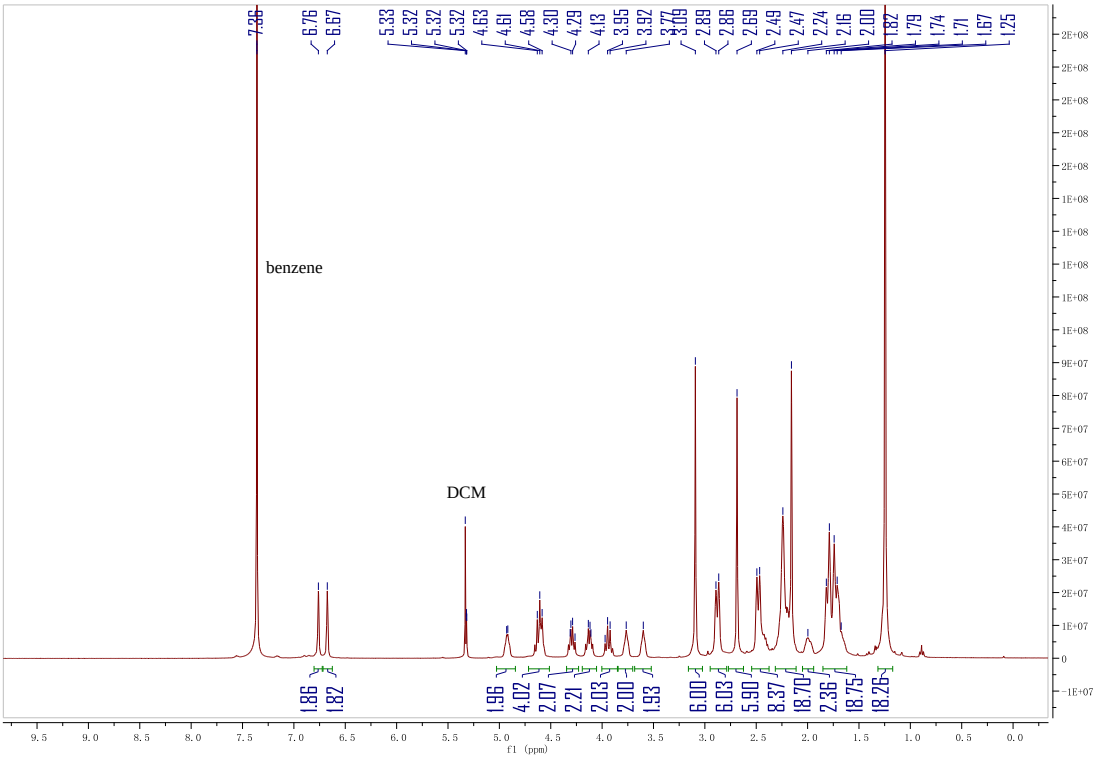


Figure S5: ^{1}H NMR spectrum of **4**.

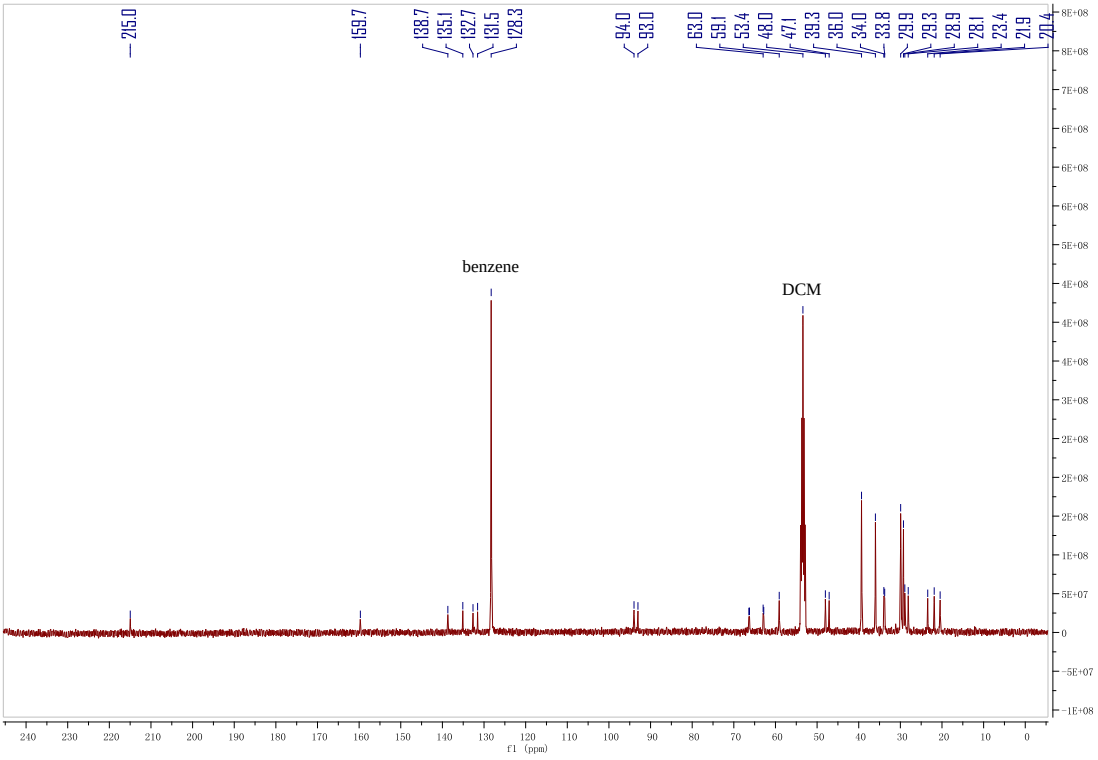


Figure S6: ^{13}C{^{1}H} NMR spectrum of **4**.

2. Crystal structure parameters

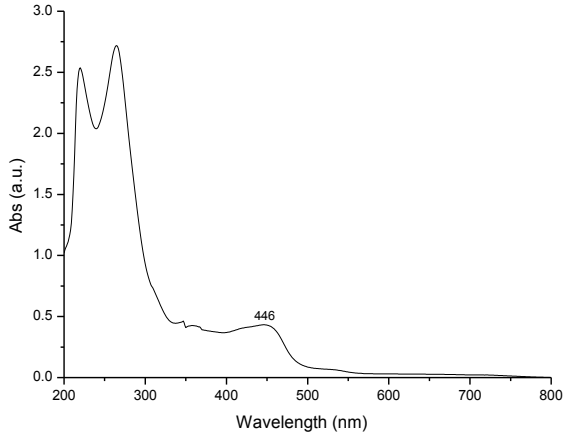
X-ray data collection and structural refinement. Intensity data for compounds **2**−**4** was collected using a Bruker APEX II diffractometer. The structures were solved by direct phase determination (SHELX-2013) and refined for all data by full-matrix least squares methods on *F2*.[S2] All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride in their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations. CCDC; 1889621-1889623 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif.

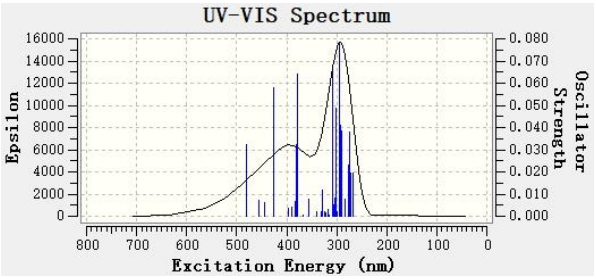
Table S1 Crystallographic data for compounds **2**−**4**.

Compounds	**2**	**3**•(toluene)$_{0.5}$	**4**•(benzene)$_{3.5}$
Formula	$C_{43}H_{63}Cl_2GeIr_2N_3$	$C_{46.50}H_{67}Cl_2GeN_3Rh_2$	$C_{92}H_{123}Cl_3Ge_2N_6OR_3$
Fw	1149.85	1017.34	1889.22
Cryst syst	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	Pbca	$P2_1/c$
Size (mm^3)	0.160 x 0.180 x 0.220	0.060 x 0.220 x 0.240	0.060 x 0.100 x 0.120
T, K	153(2)	100(2)	100(2)
a, Å	12.4041(4)	12.0092(2)	12.1630(3)
b, Å	14.8542(5)	22.8477(5)	23.7267(4)
c, Å	22.8415(8)	31.5357(6)	29.4161(5)
α, deg	90	90	90
β, deg	94.2923(18)	90	90.9225(7)
γ, deg	90	90	90

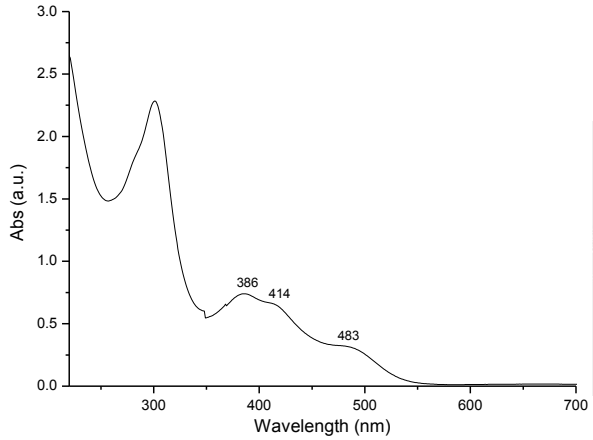
V, $Å^3$	4196.8(2)	8652.8(3)	8488.0(3)
Z	4	8	4
d_{calcd} $g \cdot cm^{-3}$	1.820	1.562	1.478
μ, mm^{-1}	7.199	1.604	1.416
Refl collected	15842	142040	126986
T_{max}/T_{min}	0.3920/0.3000	0.9100/0.6990	0.9200/0.8480
N_{measd}	12977	15751	27057
$[R_{int}]$	0.0902	0.1002	0.0960
R [I>2sigma(I)]	0.0465	0.0428	0.0482
R_w[I>2sigma(I)]	0.0907	0.0736	0.0800
GOF	1.037	1.041	1.041
Largest diff. peak/hole[$e \cdot Å^{-3}$]	1.476/-1.367	0.916/-0.927	1.348/-1.143

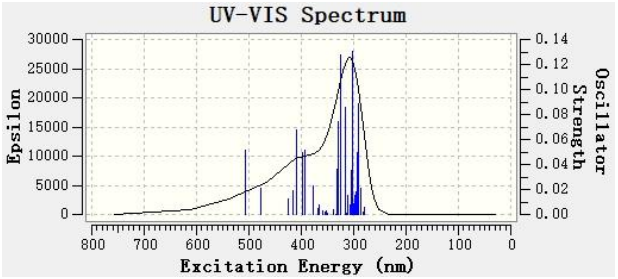
3. UV -Vis spectra for 2 and 3





Excited State 1: 2.5812 eV, 480.33 nm, f=0.0323, HOMO→LUMO.
Excited State 4: 2.9029 eV, 427.10 nm, f=0.0577, HOMO-1→LUMO+1.





Excited State 1: 2.4423 eV, 507.65 nm f=0.0510, HOMO→LUMO.
Excited State 6: 3.0320 eV, 408.92 nm, f=0.0674, HOMO-2→LUMO.
Excited State 7: 3.1110 eV, 398.54 nm, f=0.0491, HOMO-1→LUMO, HOMO-1→LUMO+1 HOMO→LUMO+2.
Excited State 8: 3.1489 eV, 393.74 nm, f=0.0516, HOMO-1→LUMO+1, HOMO→LUMO+3.

4. IR spectrum for 4

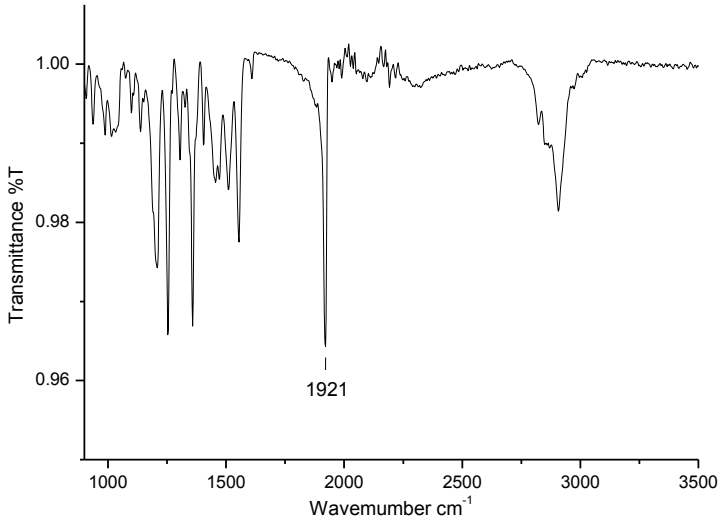
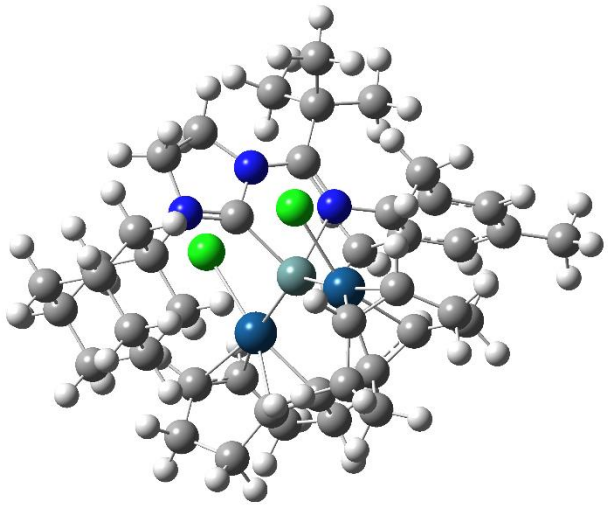


Figure S7: The IR spectrum of **4** in the solid state.

5. Theoretical calculation

Gaussian 09 was used for all density functional theory (DFT) calculations.[S3] Geometry optimization, frequency calculations and natural bond order (NBO) analysis of compound **2**, **3** were performed at the B3LYP/6-311G(d,p) level of theory, with the LANL2TZ(f) pseudo-potential applied for the metal atoms.

Figure S8: Calculated optimized structures for **2**.



2

2

Ir	0.659242	-2.212911	-0.973221	C	-1.309833	-0.872367	2.657138
Ir	-0.661935	2.387054	-0.470773	C	-2.142584	-1.377424	3.870315
Ge	-0.182051	-0.042784	0.094263	C	-1.517025	-2.690337	4.426000
C	0.821808	-0.088646	1.851893	C	-2.196594	-0.271934	4.957452
C	2.124220	-0.066620	3.753493	C	-3.612564	-1.727952	3.549372
C	0.904573	-0.929093	4.024651	C	-3.038267	-0.765805	0.903539

C	-3.884396	0.357166	0.959196
C	-3.476749	1.643505	1.624643
C	-5.146877	0.266458	0.366956
C	-5.586568	-0.886370	-0.280624
C	-6.965861	-0.963054	-0.889562
C	-4.721182	-1.978380	-0.318906
C	-3.450495	-1.948109	0.260980
C	-2.585144	-3.177194	0.204432
C	3.257409	0.602654	1.551037
C	3.763052	1.910223	2.206127
C	4.363467	-0.479554	1.631521
C	2.945754	0.870200	0.069461
C	4.215113	1.366078	-0.655470
C	5.314683	0.292287	-0.568593
C	5.634727	0.019239	0.912435
C	6.129430	1.317785	1.579419
C	5.034035	2.397544	1.480190
C	4.707534	2.669072	-0.000040
C	1.028654	-1.296950	-2.853168
C	-0.313947	-1.786560	-2.798819
C	-0.802695	-3.040591	-3.505294

C	0.116615	-4.262826	-3.274357
C	0.843973	-4.195461	-1.938369
C	2.122006	-3.637158	-1.769089
C	2.937052	-2.991455	-2.871290
C	2.128138	-1.960375	-3.687679
C	-2.126601	1.956894	-1.930855
C	-0.850633	2.017457	-2.568692
C	-0.407796	3.179389	-3.460884
C	0.363076	4.253606	-2.665754
C	-0.096490	4.356159	-1.225984
C	-1.434031	4.438338	-0.803302
C	-2.627819	4.459096	-1.747594
C	-3.186718	3.041715	-2.016618
Cl	1.038174	-3.234914	1.202516
Cl	0.115815	3.061474	1.722194
N	2.050583	0.118867	2.288580
N	0.030761	-0.554300	2.886761
N	-1.696672	-0.667137	1.431107
H	2.057482	0.908846	4.243607
H	3.048329	-0.557852	4.049190
H	1.146691	-1.989472	3.938225

H	0.460091	-0.716485	4.989431
H	-1.244284	-3.373619	3.618982
H	-2.261509	-3.186558	5.051897
H	-0.638688	-2.533843	5.046038
H	-1.225085	0.125869	5.244092
H	-2.668541	-0.683162	5.853502
H	-2.803222	0.569643	4.618423
H	-4.183662	-0.884632	3.170975
H	-4.074441	-2.045684	4.487718
H	-3.701823	-2.552693	2.844675
H	-4.341701	2.294758	1.762033
H	-2.737006	2.176867	1.012485
H	-3.006056	1.490874	2.596673
H	-5.802216	1.130380	0.418423
H	-7.681040	-1.408600	-0.189481
H	-6.968684	-1.577632	-1.792847
H	-7.339907	0.028421	-1.153416
H	-5.040258	-2.893027	-0.809024
H	-3.131005	-4.007891	-0.246232
H	-2.239912	-3.491638	1.192123
H	-1.673832	-3.001728	-0.382934

H	2.970571	2.661713	2.159606
H	4.000093	1.739754	3.261728
H	4.610447	-0.701548	2.674743
H	3.993906	-1.404407	1.179779
H	2.158442	1.623833	-0.016606
H	2.592208	-0.052768	-0.403348
H	3.960072	1.552425	-1.703283
H	4.982247	-0.629182	-1.058388
H	6.216071	0.629519	-1.092664
H	6.406500	-0.753655	0.989081
H	6.381507	1.130913	2.630065
H	7.045690	1.664804	1.089323
H	5.378592	3.319901	1.958819
H	5.597532	3.040478	-0.520568
H	3.938844	3.444619	-0.078768
H	1.158859	-0.223640	-2.748363
H	-1.101848	-1.045258	-2.681309
H	-0.930165	-2.853168	-4.581169
H	-1.800467	-3.266924	-3.117711
H	-0.482930	-5.176487	-3.307418
H	0.842912	-4.350092	-4.086885

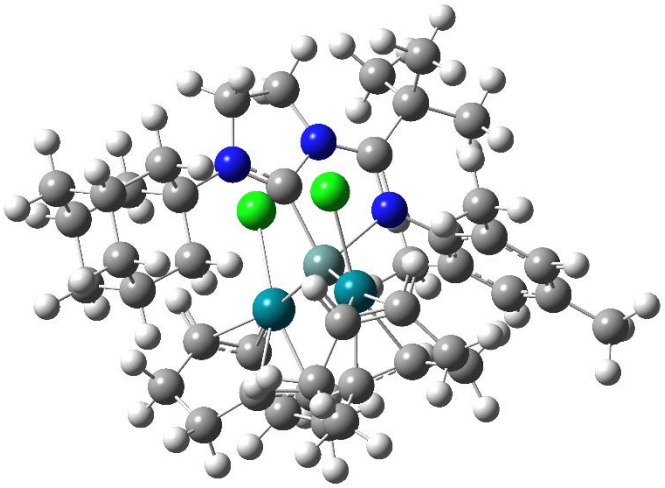
H	0.524755	-4.911249	-1.186790
H	2.696417	-3.984147	-0.915175
H	3.361509	-3.759686	-3.533285
H	3.789209	-2.491310	-2.402366
H	2.805276	-1.189565	-4.065999
H	1.690079	-2.430756	-4.572790
H	-2.556589	0.966826	-1.786933
H	-0.414652	1.068385	-2.855566
H	-1.275091	3.619864	-3.960665

H	0.232204	2.794405	-4.259698
H	1.426085	3.995886	-2.653122
H	0.289561	5.231895	-3.162060
H	0.652794	4.730110	-0.533619
H	-1.603357	4.849088	0.187192
H	-2.350352	4.942347	-2.688042
H	-3.415130	5.079729	-1.311239
H	-3.951802	2.812278	-1.269354
H	-3.693958	3.006583	-2.991594

Table S2 Selected bond distances (in Å) and angles (in degrees) as measured and calculated for **2**.

	Measured	Calculated
Ge1-Ir1	2.4954(6)	2.5606
Ge1-Ir2	2.4942(6)	2.5404
Ir1-Cl1	2.3793(13)	2.4335
Ir2-Cl2	2.3643(13)	2.4226
Ge1-C1	1.985(5)	2.0246
Ge1-N3	2.044(4)	2.1145
C1-N2	1.387(6)	1.3833
C4-N3	1.298(6)	1.3019
C4-N2	1.389(7)	1.3968
Ir2-Ge1-Ir1	144.04(2)	141.26
C1-Ge1-N3	79.52(18)	78.44
N2-C1-Ge1	111.5(3)	111.93
N3-C4-N2	113.0(4)	113.83
C1-N2-C4	119.4(4)	120.17
C4-N3-Ge1	116.5(3)	115.41

Figure S9: Calculated optimized structures for **3**.



3

3

C	0.813051	-0.200364	1.735498
C	2.119243	-0.315093	3.630594
C	0.843071	-1.096393	3.886651
C	-1.363039	-0.841938	2.533297
C	-3.079593	-0.547787	0.784137
C	-3.571398	-1.672191	0.096791
C	-2.789475	-2.952899	-0.007849
C	-4.843668	-1.595216	-0.476980
C	-5.632362	-0.449816	-0.394659
C	-6.990854	-0.387081	-1.049658
C	-5.115495	0.644481	0.297701

C	-3.849361	0.626518	0.887117
C	-3.362896	1.842220	1.629524
C	-2.226719	-1.335044	3.728632
C	-3.715164	-1.578350	3.395526
C	-2.208923	-0.271130	4.857402
C	-1.684713	-2.704209	4.236068
C	3.296852	0.284929	1.436055
C	4.261581	-0.928044	1.425208
C	5.571592	-0.544335	0.706248
C	6.234950	0.639568	1.437646
C	5.280860	1.850518	1.430115

C	3.970728	1.479354	2.153942
C	2.995867	0.683343	-0.018404
C	4.304364	1.064817	-0.742833
C	4.967228	2.253110	-0.022357
C	5.262964	-0.139971	-0.747127
C	-0.655229	2.273307	-2.577689
C	-1.926110	2.230425	-1.970922
C	-2.927010	3.369627	-1.941315
C	-2.303072	4.746650	-1.611511
C	-1.125605	4.646752	-0.658761
C	0.195928	4.532984	-1.049711
C	0.700039	4.443966	-2.473862
C	-0.113225	3.471206	-3.355423
C	0.471397	-4.199059	-2.247433
C	1.778731	-3.793846	-2.053394
C	2.661919	-3.130742	-3.088265
C	1.961541	-1.990014	-3.860457
C	0.915895	-1.250938	-3.025996
C	-0.452649	-1.594460	-2.983591
C	-1.088734	-2.778240	-3.687419
C	-0.277967	-4.089958	-3.563320

Cl	0.367088	2.949175	1.813059
Cl	0.791498	-3.322638	1.004941
Ge	-0.189805	-0.012419	-0.002253
N	-1.736306	-0.564160	1.314495
N	-0.006105	-0.630541	2.764806
N	2.056097	-0.094371	2.171292
Rh	-0.461521	2.478594	-0.439046
Rh	0.467877	-2.198606	-1.158324
H	2.119147	0.652767	4.139896
H	3.007800	-0.875319	3.913299
H	1.009083	-2.168380	3.769285
H	0.418447	-0.877901	4.859114
H	-3.378935	-3.720575	-0.512255
H	-2.486827	-3.340304	0.967646
H	-1.856487	-2.806706	-0.565918
H	-5.227765	-2.468571	-0.995056
H	-6.917171	0.007132	-2.069027
H	-7.670374	0.265389	-0.496390
H	-7.448024	-1.376997	-1.114322
H	-5.714456	1.545092	0.391761
H	-4.124735	2.623393	1.623061

H	-2.450209	2.246190	1.179234
H	-3.119325	1.624502	2.671986
H	-4.199483	-1.900133	4.321058
H	-3.856099	-2.369024	2.660611
H	-4.230535	-0.686762	3.048817
H	-2.763406	0.619572	4.557247
H	-1.212969	0.054772	5.150282
H	-2.700057	-0.687405	5.740839
H	-0.809804	-2.619733	4.875277
H	-1.433980	-3.366047	3.404501
H	-2.465336	-3.183954	4.830029
H	3.768771	-1.771575	0.933304
H	4.493801	-1.242498	2.447996
H	6.244141	-1.408420	0.715355
H	7.179088	0.901323	0.947335
H	6.479247	0.357819	2.468738
H	5.745758	2.691366	1.955067
H	4.200676	1.219315	3.192524
H	3.275828	2.323500	2.168756
H	2.302226	1.527796	-0.033255
H	2.527559	-0.158998	-0.538817

H	4.058320	1.346780	-1.771553
H	4.301493	3.122211	-0.036114
H	5.888267	2.542206	-0.541253
H	4.810615	-0.980924	-1.283672
H	6.190297	0.115627	-1.272164
H	-0.233932	1.322898	-2.881169
H	-2.392694	1.253665	-1.865135
H	-3.471245	3.421560	-2.896182
H	-3.676483	3.128293	-1.182856
H	-3.069466	5.384314	-1.161997
H	-1.993790	5.251006	-2.530099
H	-1.308465	4.922695	0.374343
H	0.948447	4.755144	-0.300087
H	0.725361	5.442878	-2.933149
H	1.738722	4.103959	-2.434158
H	0.526438	3.108556	-4.165098
H	-0.938229	3.997879	-3.842751
H	0.043402	-4.853806	-1.495376
H	2.287920	-4.178649	-1.176392
H	3.054490	-3.879054	-3.791776
H	3.532717	-2.724502	-2.566149

H	2.717885	-1.274448	-4.194994
H	1.497793	-2.376679	-4.772289
H	1.163364	-0.211385	-2.834327
H	-1.156859	-0.788297	-2.793825

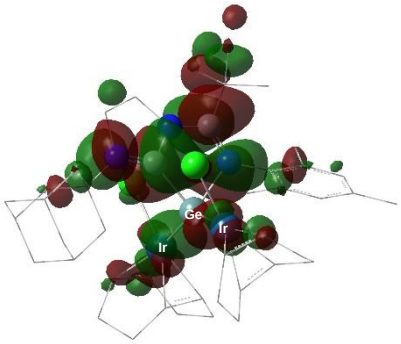
H	-1.266490	-2.543337	-4.747418
H	-2.077381	-2.929537	-3.244219
H	-0.960953	-4.939287	-3.653729
H	0.423613	-4.179983	-4.396069

Table S3 Selected bond distances (in Å) and angles (in degrees) as measured and calculated for **3.**

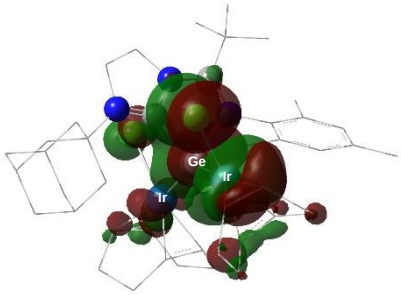
	Measured	Calculated
Ge1-Rh1	2.4912(3)	2.5436
Ge1-Rh2	2.5029(3)	2.5590
Rh1-Cl1	2.3921(7)	2.4454
Rh2-Cl2	2.4150(7)	2.4593
Ge1-C1	1.984(3)	2.0152
Ge1-N1	2.044(2)	2.1047
C1-N2	1.385(3)	1.3840
C4-N1	1.303(3)	1.3046
C4-N2	1.392(3)	1.3927
Rh1-Ge1-Rh2	142.383(13)	141.863
C1-Ge1-N1	78.91(10)	78.56
N2-C1-Ge1	112.69(18)	112.07
N1-C4-N2	112.9(2)	113.69
C4-N1-Ge1	116.88(18)	115.47
C1-N2-C4	118.4(2)	120.01

Figure S10: Plots of the frontier orbitals of compounds **2** and **3**. Orbital energies (in eV) are shown in parentheses.

2:

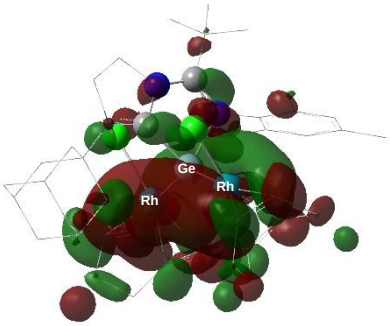


LUMO (−1.6436)

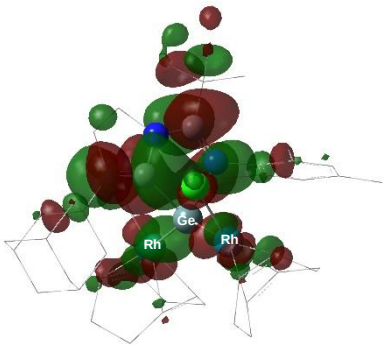


HOMO-2 (−5.3389)

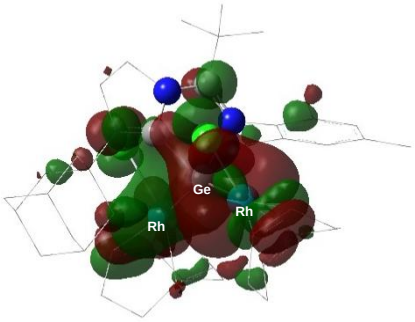
3:



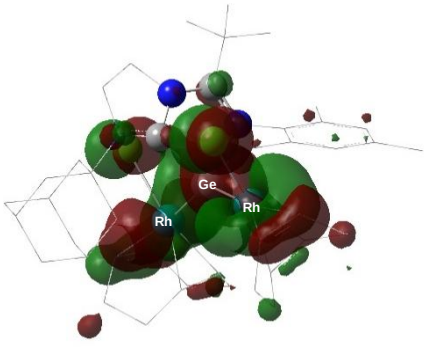
LUMO+1 (−0.8090)



LUMO (−1.6033)



HOMO (−4.6727)



HOMO-2 (−5.3046)

Table S4 The NPA charges of **2** calculated at the B3LYP/6-311G(d,p) level of theory, with the LANL2TZ(f) pseudo-potential applied for the Ir atom.

Atom	No	Natural Charge	Core	Valence	Rydberg	Total
Ir	1	-0.44271	67.97178	9.42751	0.04342	77.44271
Ir	2	-0.46023	67.97175	9.44474	0.04373	77.46023
Ge	3	1.23757	28.00000	2.72718	0.03525	30.76243
C	4	0.13742	1.99914	3.81447	0.04897	5.86258
C	5	-0.18910	1.99942	4.17371	0.01597	6.18910
C	6	-0.19001	1.99941	4.17486	0.01574	6.19001
C	7	0.55985	1.99894	3.40674	0.03447	5.44015
C	8	-0.07162	1.99933	4.05866	0.01363	6.07162
C	9	-0.58293	1.99942	4.57213	0.01138	6.58293
C	10	-0.57265	1.99943	4.56196	0.01126	6.57265
C	11	-0.58172	1.99945	4.56987	0.01240	6.58172
C	12	0.11820	1.99881	3.86200	0.02099	5.88180
C	13	-0.00293	1.99907	3.98811	0.01574	6.00293
C	14	-0.58959	1.99940	4.57941	0.01077	6.58959
C	15	-0.21917	1.99908	4.20526	0.01483	6.21917
C	16	0.00056	1.99916	3.98544	0.01484	5.99944
C	17	-0.59003	1.99944	4.58174	0.00885	6.59003
C	18	-0.21525	1.99909	4.20150	0.01466	6.21525
C	19	-0.00055	1.99907	3.98618	0.01530	6.00055
C	20	-0.58752	1.99941	4.57784	0.01027	6.58752
C	21	0.19859	1.99924	3.78039	0.02177	5.80141
C	22	-0.41618	1.99932	4.40057	0.01629	6.41618
C	23	-0.40660	1.99933	4.39081	0.01646	6.40660
C	24	-0.43093	1.99931	4.41393	0.01768	6.43093
C	25	-0.18746	1.99942	4.17130	0.01675	6.18746
C	26	-0.39127	1.99941	4.37650	0.01536	6.39127
C	27	-0.19425	1.99942	4.17804	0.01679	6.19425
C	28	-0.39174	1.99941	4.37672	0.01561	6.39174
C	29	-0.19316	1.99942	4.17700	0.01674	6.19316
C	30	-0.39125	1.99941	4.37645	0.01540	6.39125
C	31	-0.21152	1.99892	4.18887	0.02372	6.21152
C	32	-0.19739	1.99893	4.17457	0.02389	6.19739
C	33	-0.39376	1.99941	4.37869	0.01566	6.39376
C	34	-0.40280	1.99941	4.38905	0.01434	6.40280
C	35	-0.21331	1.99898	4.18972	0.02461	6.21331
C	36	-0.19422	1.99897	4.17044	0.02481	6.19422
C	37	-0.39924	1.99941	4.38456	0.01528	6.39924

C	38	-0.39674	1.99942	4.38255	0.01477	6.39674
C	39	-0.19108	1.99892	4.16833	0.02382	6.19108
C	40	-0.21143	1.99893	4.18853	0.02397	6.21143
C	41	-0.39663	1.99942	4.38249	0.01471	6.39663
C	42	-0.39854	1.99941	4.38376	0.01536	6.39854
C	43	-0.18672	1.99896	4.16284	0.02492	6.18672
C	44	-0.22184	1.99898	4.19804	0.02482	6.22184
C	45	-0.40212	1.99941	4.38848	0.01423	6.40212
C	46	-0.39504	1.99941	4.38003	0.01560	6.39504
Cl	47	-0.44626	10.00000	7.43707	0.00919	17.44626
Cl	48	-0.42567	10.00000	7.41568	0.00999	17.42567
N	49	-0.40428	1.99918	5.38502	0.02007	7.40428
N	50	-0.44277	1.99916	5.43092	0.01269	7.44277
N	51	-0.63203	1.99927	5.61326	0.01950	7.63203
H	52	0.20552	0.00000	0.79219	0.00228	0.79448
H	53	0.21451	0.00000	0.78378	0.00171	0.78549
H	54	0.22299	0.00000	0.77452	0.00249	0.77701
H	55	0.21026	0.00000	0.78760	0.00214	0.78974
H	56	0.22653	0.00000	0.77194	0.00153	0.77347
H	57	0.20789	0.00000	0.79036	0.00175	0.79211
H	58	0.19837	0.00000	0.80031	0.00132	0.80163
H	59	0.19637	0.00000	0.80228	0.00135	0.80363
H	60	0.20694	0.00000	0.79129	0.00177	0.79306
H	61	0.21178	0.00000	0.78688	0.00135	0.78822
H	62	0.21843	0.00000	0.77979	0.00178	0.78157
H	63	0.20224	0.00000	0.79574	0.00202	0.79776
H	64	0.21519	0.00000	0.78289	0.00192	0.78481
H	65	0.20380	0.00000	0.79478	0.00143	0.79620
H	66	0.24809	0.00000	0.74925	0.00266	0.75191
H	67	0.20410	0.00000	0.79345	0.00245	0.79590
H	68	0.19981	0.00000	0.79738	0.00281	0.80019
H	69	0.20969	0.00000	0.78887	0.00144	0.79031
H	70	0.20715	0.00000	0.79155	0.00130	0.79285
H	71	0.20574	0.00000	0.79299	0.00128	0.79426
H	72	0.19915	0.00000	0.79814	0.00271	0.80085
H	73	0.20245	0.00000	0.79613	0.00143	0.79755
H	74	0.21181	0.00000	0.78616	0.00203	0.78819
H	75	0.24139	0.00000	0.75530	0.00331	0.75861
H	76	0.23829	0.00000	0.75991	0.00180	0.76171
H	77	0.19221	0.00000	0.80534	0.00245	0.80779
H	78	0.19070	0.00000	0.80639	0.00292	0.80930
H	79	0.22527	0.00000	0.77258	0.00215	0.77473
H	80	0.24213	0.00000	0.75365	0.00423	0.75787
H	81	0.23489	0.00000	0.76081	0.00430	0.76511

H	82	0.21015	0.00000	0.78723	0.00262	0.78985
H	83	0.20190	0.00000	0.79564	0.00246	0.79810
H	84	0.19757	0.00000	0.79998	0.00244	0.80243
H	85	0.20807	0.00000	0.78978	0.00214	0.79193
H	86	0.19436	0.00000	0.80358	0.00206	0.80564
H	87	0.19950	0.00000	0.79813	0.00237	0.80050
H	88	0.20875	0.00000	0.78913	0.00212	0.79125
H	89	0.19687	0.00000	0.80070	0.00242	0.80313
H	90	0.20683	0.00000	0.79133	0.00184	0.79317
H	91	0.21094	0.00000	0.78617	0.00289	0.78906
H	92	0.21305	0.00000	0.78416	0.00279	0.78695
H	93	0.20212	0.00000	0.79528	0.00259	0.79788
H	94	0.19945	0.00000	0.79837	0.00217	0.80055
H	95	0.20746	0.00000	0.79079	0.00175	0.79254
H	96	0.19588	0.00000	0.80179	0.00232	0.80412
H	97	0.23027	0.00000	0.76826	0.00147	0.76973
H	98	0.23230	0.00000	0.76574	0.00196	0.76770
H	99	0.20607	0.00000	0.79133	0.00260	0.79393
H	100	0.19945	0.00000	0.79836	0.00219	0.80055
H	101	0.20359	0.00000	0.79461	0.00179	0.79641
H	102	0.19493	0.00000	0.80272	0.00235	0.80507
H	103	0.21408	0.00000	0.78279	0.00312	0.78592
H	104	0.21242	0.00000	0.78492	0.00266	0.78758
H	105	0.19389	0.00000	0.80380	0.00230	0.80611
H	106	0.20378	0.00000	0.79449	0.00173	0.79622
H	107	0.20139	0.00000	0.79692	0.00169	0.79861
H	108	0.20557	0.00000	0.79188	0.00256	0.79443
H	109	0.23012	0.00000	0.76780	0.00208	0.76988
H	110	0.23142	0.00000	0.76711	0.00148	0.76858
H	111	0.19558	0.00000	0.80211	0.00231	0.80442
H	112	0.20678	0.00000	0.79148	0.00175	0.79322
H	113	0.19992	0.00000	0.79784	0.00225	0.80008
H	114	0.20189	0.00000	0.79553	0.00258	0.79811
* Total *		-0.00000	275.90884	284.98591	1.10525	562.00000

Table S5 The NPA charges of **3** calculated at the B3LYP/6-311G(d,p) level of theory, with the LANL2TZ(f) pseudo-potential applied for the Ir atom.

Atom	No	Natural Charge	Core	Valence	Rydberg	Total
C	1	0.11491	1.99914	3.83646	0.04949	5.88509
C	2	-0.18887	1.99943	4.17355	0.01589	6.18887
C	3	-0.19000	1.99941	4.17480	0.01579	6.19000
C	4	0.55756	1.99893	3.40756	0.03595	5.44244
C	5	0.12072	1.99881	3.85935	0.02112	5.87928
C	6	-0.00077	1.99907	3.98632	0.01539	6.00077
C	7	-0.58384	1.99941	4.57414	0.01030	6.58384
C	8	-0.21587	1.99909	4.20215	0.01464	6.21587
C	9	-0.00062	1.99916	3.98660	0.01485	6.00062
C	10	-0.58986	1.99944	4.58160	0.00882	6.58986
C	11	-0.21977	1.99908	4.20588	0.01481	6.21977
C	12	-0.00376	1.99908	3.98884	0.01584	6.00376
C	13	-0.58807	1.99941	4.57810	0.01056	6.58807
C	14	-0.07103	1.99933	4.05811	0.01359	6.07103
C	15	-0.58173	1.99945	4.56992	0.01236	6.58173
C	16	-0.57134	1.99943	4.56067	0.01124	6.57134
C	17	-0.58378	1.99942	4.57293	0.01142	6.58378
C	18	0.19885	1.99925	3.78001	0.02189	5.80115
C	19	-0.40707	1.99933	4.39117	0.01657	6.40707
C	20	-0.19510	1.99942	4.17886	0.01682	6.19510
C	21	-0.39137	1.99941	4.37639	0.01557	6.39137
C	22	-0.19326	1.99942	4.17711	0.01674	6.19326
C	23	-0.41567	1.99933	4.39999	0.01636	6.41567
C	24	-0.42571	1.99931	4.40878	0.01762	6.42571
C	25	-0.18773	1.99942	4.17164	0.01668	6.18773
C	26	-0.39101	1.99941	4.37618	0.01543	6.39101
C	27	-0.39124	1.99941	4.37658	0.01525	6.39124
C	28	-0.19375	1.99886	4.17234	0.02256	6.19375
C	29	-0.17243	1.99886	4.15087	0.02270	6.17243
C	30	-0.39670	1.99940	4.38196	0.01535	6.39670
C	31	-0.40464	1.99941	4.39121	0.01402	6.40464
C	32	-0.19585	1.99896	4.17300	0.02389	6.19585
C	33	-0.17278	1.99894	4.14947	0.02437	6.17278
C	34	-0.40252	1.99940	4.38791	0.01520	6.40252
C	35	-0.39722	1.99941	4.38340	0.01440	6.39722
C	36	-0.19233	1.99896	4.16955	0.02383	6.19233
C	37	-0.17626	1.99895	4.15310	0.02421	6.17626

C	38	-0.40322	1.99940	4.38863	0.01519	6.40322
C	39	-0.39745	1.99941	4.38353	0.01451	6.39745
C	40	-0.19309	1.99884	4.17178	0.02247	6.19309
C	41	-0.17945	1.99884	4.15768	0.02293	6.17945
C	42	-0.39527	1.99940	4.38047	0.01540	6.39527
C	43	-0.40509	1.99941	4.39156	0.01413	6.40509
Cl	44	-0.48083	10.00000	7.47341	0.00742	17.48083
Cl	45	-0.50254	10.00000	7.49585	0.00669	17.50254
Ge	46	1.24776	28.00000	2.71765	0.03459	30.75224
N	47	-0.64889	1.99928	5.62983	0.01978	7.64889
N	48	-0.43990	1.99915	5.42765	0.01311	7.43990
N	49	-0.40682	1.99918	5.38671	0.02093	7.40682
Rh	50	-0.47774	35.97427	9.46694	0.03653	45.47774
Rh	51	-0.47364	35.97418	9.46439	0.03506	45.47364
H	52	0.20708	0.00000	0.79064	0.00228	0.79292
H	53	0.21300	0.00000	0.78524	0.00175	0.78700
H	54	0.22476	0.00000	0.77275	0.00249	0.77524
H	55	0.20939	0.00000	0.78846	0.00215	0.79061
H	56	0.20147	0.00000	0.79712	0.00141	0.79853
H	57	0.21500	0.00000	0.78301	0.00199	0.78500
H	58	0.23683	0.00000	0.75972	0.00344	0.76317
H	59	0.19871	0.00000	0.79855	0.00273	0.80129
H	60	0.21142	0.00000	0.78711	0.00147	0.78858
H	61	0.20536	0.00000	0.79334	0.00130	0.79464
H	62	0.20511	0.00000	0.79360	0.00130	0.79489
H	63	0.19924	0.00000	0.79799	0.00277	0.80076
H	64	0.20295	0.00000	0.79575	0.00131	0.79705
H	65	0.24682	0.00000	0.75052	0.00265	0.75318
H	66	0.20317	0.00000	0.79475	0.00208	0.79683
H	67	0.20233	0.00000	0.79564	0.00203	0.79767
H	68	0.21456	0.00000	0.78349	0.00195	0.78544
H	69	0.21686	0.00000	0.78123	0.00191	0.78314
H	70	0.20941	0.00000	0.78878	0.00181	0.79059
H	71	0.19743	0.00000	0.80121	0.00135	0.80257
H	72	0.20594	0.00000	0.79228	0.00178	0.79406
H	73	0.19840	0.00000	0.80027	0.00133	0.80160
H	74	0.22923	0.00000	0.76926	0.00150	0.77077
H	75	0.20681	0.00000	0.79144	0.00175	0.79319
H	76	0.22812	0.00000	0.76985	0.00203	0.77188
H	77	0.19156	0.00000	0.80557	0.00287	0.80844
H	78	0.20792	0.00000	0.78991	0.00218	0.79208
H	79	0.19878	0.00000	0.79884	0.00238	0.80122
H	80	0.19469	0.00000	0.80324	0.00207	0.80531
H	81	0.20845	0.00000	0.78943	0.00212	0.79155

H	82	0.19314	0.00000	0.80442	0.00244	0.80686
H	83	0.23773	0.00000	0.76046	0.00181	0.76227
H	84	0.24104	0.00000	0.75489	0.00407	0.75896
H	85	0.22997	0.00000	0.76590	0.00413	0.77003
H	86	0.20824	0.00000	0.78914	0.00262	0.79176
H	87	0.20581	0.00000	0.79234	0.00185	0.79419
H	88	0.19649	0.00000	0.80108	0.00243	0.80351
H	89	0.19901	0.00000	0.79771	0.00328	0.80099
H	90	0.19707	0.00000	0.80034	0.00259	0.80293
H	91	0.21511	0.00000	0.78227	0.00262	0.78489
H	92	0.21741	0.00000	0.77958	0.00302	0.78259
H	93	0.20387	0.00000	0.79340	0.00272	0.79613
H	94	0.20365	0.00000	0.79420	0.00215	0.79635
H	95	0.20877	0.00000	0.78949	0.00174	0.79123
H	96	0.19632	0.00000	0.80141	0.00227	0.80368
H	97	0.23488	0.00000	0.76366	0.00147	0.76512
H	98	0.23683	0.00000	0.76151	0.00166	0.76317
H	99	0.20805	0.00000	0.78937	0.00259	0.79195
H	100	0.20338	0.00000	0.79494	0.00168	0.79662
H	101	0.20515	0.00000	0.79309	0.00176	0.79485
H	102	0.19522	0.00000	0.80246	0.00232	0.80478
H	103	0.23332	0.00000	0.76526	0.00142	0.76668
H	104	0.23951	0.00000	0.75889	0.00159	0.76049
H	105	0.20901	0.00000	0.78846	0.00253	0.79099
H	106	0.20254	0.00000	0.79580	0.00166	0.79746
H	107	0.20509	0.00000	0.79309	0.00182	0.79491
H	108	0.19626	0.00000	0.80139	0.00235	0.80374
H	109	0.21322	0.00000	0.78405	0.00273	0.78678
H	110	0.21643	0.00000	0.78071	0.00286	0.78357
H	111	0.20440	0.00000	0.79290	0.00270	0.79560
H	112	0.20222	0.00000	0.79570	0.00208	0.79778
H	113	0.20938	0.00000	0.78888	0.00173	0.79062
H	114	0.19677	0.00000	0.80098	0.00226	0.80323
* Total *		0.00000	211.91329	285.00932	1.07739	498.00000

6. References

[S1] Su, B.; Ganguly, R.; Li, Y.; Kinjo, R. *Angew. Chem., Int. Ed.* 2014, **53**, 13106−13109.

[S2] Bruker AXS SHELXTL, Madison, WI; *SHELX-97G*. M. Sheldrick, Acta Crystallogr. A, 2008, **64**, 112–122, *SHELX-2013*, http://shelx.uni-ac. gwdg.de/SHELX/index.php.

[S3] Gaussian 09, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A. Jr.,; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.;Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2010**.