Electronic Supplementary Information

Gallium complexes with α-diimine and phenazine in various reduced states

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Experimental

General Considerations: All of the reactions and manipulations of air- and moisture-sensitive compounds were carried out under argon or nitrogen with standard Schlenk or drybox techniques. The solvents (THF and toluene) were dried using appropriate methods and were distilled under argon prior to use. Benzene-d_6 was dried over Na/K alloy. The α-diimine ligand L was prepared according to literature procedures.[1] Sodium metal, anhydrous gallium chloride ($GaCl_3$) and phenazine (Phz) were purchased from Alfa Aesar. NMR spectra were recorded on a Mercury Plus-400 spectrometer in benzene-d_6. Elemental analyses were performed with an Elementar VarioEL III instrument. EPR spectra were recorded on a Bruker EMX-10/12 spectrometer in THF. IR spectra were recorded using a Nicolet AVATAR 360 FT-IR spectrometer.

$[(L^{ipr})^{2-}Ga^{II}(\mu_3\text{-}Cl)Na(Et_2O)]_2$ (2). Sodium metal (0.046 g, 2.0 mmol) was added to the diethyl ether (30 mL) solution of $L^{\bullet-}GaCl_2$ (0.542 g, 1.0 mmol)[2] and the mixture was stirred for 2 d. The resulting mixture was filtered and the filtrate was concentrated to about 5 mL and stored at ca. –20 ℃ for several days to yield the product as yellow crystals (0.290 g, 45%). Decomposed at 197 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 ℃, TMS): δ = 1.03 (Et_2O), 1.36 (m, 48H, CH(CH_3)$_2$), 2.09 (s, 12H, CCH_3), 3.15 (Et_2O), 3.88 (m, 8H, CH(CH$_3$)$_2$), 7.12-7.14 (m, 4 H, *p*-ArH), 7.24 ppm (d, 8 H, J = 7.2 Hz, *m*-ArH). ^{13}C NMR (100.6 MHz, C_6D_6, 25 ℃, TMS): δ = 16.4 (N-CCH_3), 24.4 (CH(CH_3)$_2$), 26.1 (CH(CH_3)$_2$), 27.5 ($CH(CH_3)_2$), 28.3 (THF), 68.5 (THF), 121.7 (*p*-C_6H_3), 123.0 (*m*-C_6H_3), 123.6 (*o*-C_6H_3), 147.2 (*i*-C_6H_3), 149.1 ppm (N-CCH_3); elemental analysis calcd (%) for $C_{64}H_{100}Cl_2Ga_2N_4Na_2O_2{\cdot}Et_2O$ (1287.92): C, 63.41; H, 8.61; N, 4.35. Found: C, 63.05; H, 8.55; N, 4.82.

$[(L(THF)Ga)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N,N\text{-}Phz)]$ (3). Phz (0.090 g, 0.5 mmol) was added to a solution of the digallane **2** (0.5 mmol) in 30 mL of THF, and the greenish-yellow color of **2** completely changed to brown within 0.5 hour. The solution was stirred for 6 days at ambient temperature. X-ray quality red crystals of **2** were grown from toluene at −20 ℃ after several days (0.350 g, 47%). ^{1}H NMR (400 MHz, C_6D_6, δ/ppm): 1.11 (THF), 1.34 (d, 24H, J = 7.2 Hz, CH(CH_3)$_2$), 1.42 (d, 24H, J = 7.2 Hz, CH(CH_3)$_2$), 2.11 (s, 12H, CCH_3), 3.25 (m, 8H, CH(CH$_3$)$_2$), 3.56 (THF), 5.70 (m, 4H, $C_{12}H_8N_2$) 6.46 (m, 4H, $C_{12}H_8N_2$), 7.00−7.35 (m, Ar-H). ^{13}C NMR (C_6D_6, δ/ppm): 15.4 (N-CCH_3), 25.6 (CH(CH_3)$_2$), 25.6 (THF), 30.0 ($CH(CH_3)_2$), 65.7 (THF), 110.0 ($C_{12}H_8N_2$), 121.2 ($C_{12}H_8N_2$), 127.4, 127.7, 128.1, 129.2, 131.1 (Ar-C), 144.8 (N-CCH_3). IR (KBr, ν/cm^{-1}): 2961s, 2927m, 2868m, 1635w, 1565w, 1479s, 1383m, 1360m, 1297s, 1137m, 1033w, 817w, 794w, 742s. Anal. Calcd for $C_{68}H_{88}Ga_2N_6{\cdot}5C_4H_8O$ (1489.4): C, 70.96; H, 8.66; N, 5.64. Found: C, 70.62; H, 8.74; N, 5.73.

[LGa(Phz)$_2$Na(THF)$_3$Na(THF)$_2$){μ_2-Na(THF)$_2$}]$_2$ (4). Phz (0.360 g, 2.0 mmol) was added to a solution of **2** (0.5 mmol) in 30 mL of THF. Further reduction of the mixture by 6.0 equiv of Na (0.069 g, 3.0 mmol) yielded the product **4**. Single crystals were grown from a THF solution at −20 ℃. Purple-red crystals (0.876 g, 52%). ^{1}H NMR (400 MHz, C_6D_6, δ/ppm): 1.07 (d, 12H, J = 7.2 Hz, CH(CH_3)$_2$), 1.21 (THF), 1.22 (d, 12H, J = 7.2 Hz, CH(CH_3)$_2$), 1.89 (s, 6H, CCH_3), 3.06 (m, 4H, CH(CH$_3$)$_2$), 3.32 (THF), 5.41 (m, 4H, $C_{12}H_8N_2$), 5.55 (m, 4H, $C_{12}H_8N_2$), 5.75 (m, 4H, $C_{12}H_8N_2$), 6.20 (m, 4H, $C_{12}H_8N_2$), 6.80−7.20 (m, Ar-H). IR (KBr, ν/cm^{-1}): 2961s, 2927m, 2870m, 1913w, 1640m, 1511s, 1478s, 1434m, 1362m, 1382w, 1300s, 1186w, 1118s, 819w, 742s. Anal. Calcd for 2[($C_{52}H_{56}GaN_6Na_3$)·7C_4H_8O·3C_7H_8] (3369.7): C, 72.00; H, 8.14; N, 4.99. Found: C, 72.02; H, 8.44; N, 4.54.

[L$_{-H}$Ga(Phz)$_2$] (5). A solution of $GaCl_3$ (0.176 g, 1.0 mmol) in THF (30 mL) was added to a rigorously stirred solution of L$_{-H}$Na [prepared in situ from L (0.40 g, 1.0 mmol) and NaH (0.024 1.0 mmol) in 30 mL THF]. The mixture was stirred for 1 day at room temperature, which was followed by addition of 2.0 equiv of Phz·Na (the singly reduced form of Phz; 0.42 g, 2.0 mmol). The mixture was filtered and the filtrate was concentrated to about 5 mL and stored at about −20 ℃ to yield purple-red crystals of the product (0.426 g, 46%). EPR (THF, 293 K): g = 2.005. IR (KBr, ν/cm^{-1}): 3026s, 2920s, 2871m, 2734w, 1942w, 1802w, 1604s, 1495s, 1460s, 1379m, 1178w, 1081s,1030s, 895w, 727s, 694s, 520w, 464s. Anal. Calcd for $C_{52}H_{55}GaN_6$·C_7H_8 (925.87): C, 76.53; H, 6.86; N, 9.08. Found: C, 76.09; H, 6.46; N, 9.25.

X-ray Crystal Structure Determination. Diffraction data for the complexes **2**–**5** (sealed in thin glass tubes) were collected on a Bruker SMART APEX II diffractometer at at low temperature (173 K) with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An empirical absorption correction using SADABS was applied for all data.[3] The structures were solved by direct methods using the SHELXS program.[4] All non-hydrogen atoms were refined anisotropically by full-matrix least squares on F^2 by the use of the program SHELXL.[4] Hydrogen atoms bonded to carbon were included in idealized geometric positions with thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Crystallographic data and refinement details for **2**–**5** are given in Table S1. CCDC 697665 (complex **2**) and 977582–977584 (**3**–**5**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data and refinement details for compounds **2**–**5**.

compound	**2**	**3**·3THF	**4**·6toluene	**5**·toluene
empirical formula	$C_{68}H_{110}Cl_2Ga_2N_4Na_2O_3$	$C_{68}H_{88}Ga_2N_6{\cdot}5C_4H_8O$	$2[(C_{52}H_{56}GaN_6Na_3){\cdot}7C_4H_8O{\cdot}3C_7H_8]$	$C_{52}H_{55}GaN_6{\cdot}C_7H_8$
Fw	1287.92	1489.40	3369.7	925.87
crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	*C*2/*c*	*P2(1)/c*	*P2(1)/n*	*P2(1)/c*
a /Å	22.583(3)	11.056(4)	13.014(2)	11.018(2)
b /Å	14.543(2)	24.846(9)	35.213(5)	24.049(4)
c /Å	22.793(4)	15.591(6)	20.564(3)	19.699(3)
α / °	90	90	90	90
β / °	106.309(4)	92.912(6)	95.481(2)	104.139(2)
γ / °	90	90	90	90
V /Å^3	7184.8(18)	4277(3)	9381(3)	5062(2)
Z	4	2	4	4
D_{calc} /g cm^{-3}	1.189	1.156	1.193	1.215
F (000)	0.47 × 0.41 × 0.35	1600	3616	1960
μ /mm^{-1}	2784	0.681	0.364	0.588
θ range	0.880	2.10−25.18	1.53−25.05	1.69−25.11
reflns collected	18030	28048	16369	32736
independent reflns	6518	7585	16369	8913
observed reflns	0.0991	4770	1031	5665
R(int)	2967	0.0765	0.0701	0.0743
R_1; wR_2 [$I > 2\sigma(I)$]	0.0817; 0.1656	0.0537, 0.1176	0.0694, 0.1468	0.0557, 0.1084
R_1; wR_2 (all data)	0.1605; 0.1802	0.0994, 0.1345	0.1061, 0.1644	0.1048, 0.1273
GOF (F^2)	1.071	1.032	1.075	1.001

DFT computations

The model compounds $[L'_2(Ga)_2(\mu_3\text{-}Cl)_2Na_2(H_2O)_2]$ (L' = $[PhNCH]_2$, **2H**), $[(L'(H_2O)Ga)_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N,N\text{-}Phz)]$ (**3H**), and $[L'Ga(Phz)_2Na(H_2O)_3Na(H_2O)_2\{\mu_2\text{-}Na(H_2O)_2\}]_2$ (**4H**), wherein the 2,6-diisopropylphenyl groups on the nitrogen atoms were replaced by phenyl groups and the THF molecules by H_2O, were used for the products **2**–**4**, respectively, in the DFT computations. The structure optimization and NBO bonding analysis for the model compounds **2H**–**4H** were carried out at the DFT (B3LYP) level with the 6-31G* basis sets using the Gaussian 03 program.[5] The B3LYP method is a hybrid of the HF and DFT methods, incorporating Becke's three-parameter exchange functional (B3)[6] with the Lee, Yang, and Parr (LYP) correlation functional. Geometry optimizations

gave bond distances that were in good agreement with the X-ray structures. Bonding analyses were performed by means of natural bond orbital (NBO) analysis and natural population analysis (NPA). Wiberg bond indices (WBI) were evaluated with Weinhold's natural bond orbital method.[7]

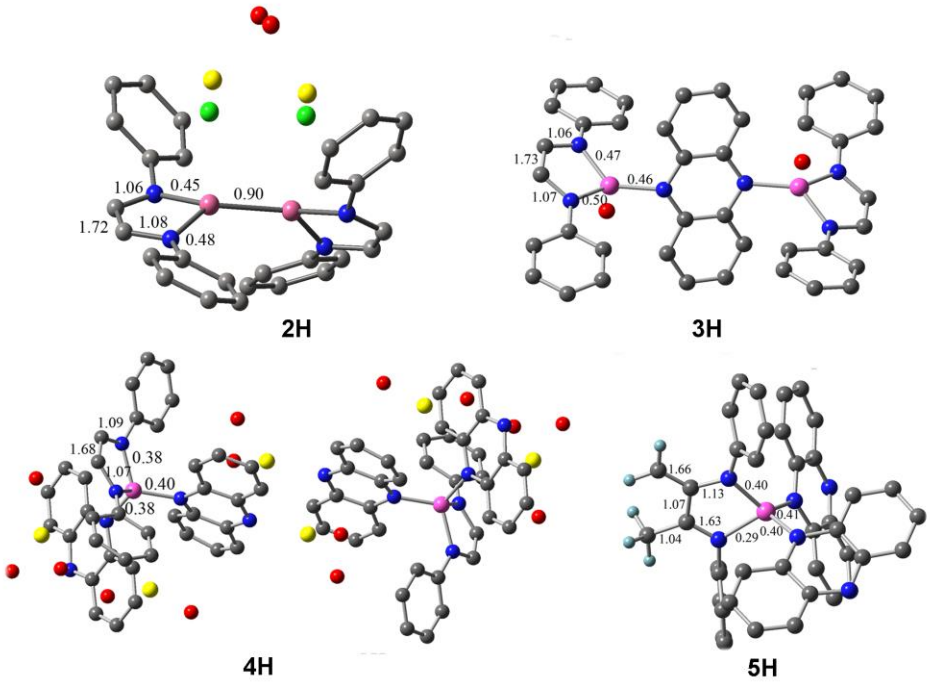

Fig. S1. Optimized structures of **2H**–**5H** and their selected bond orders.

A simplified model [{L'Ga^{II}(μ_3-Cl)Na(H_2O)}$_2$] (**2H**) was used to evaluate the electronic structure of the Ga−Ga-bonded compound **2**. The optimized structure is very close to that from X-ray diffraction. The theoretical Ga–Ga distance (2.435 Å) compares well with that observed for **2** (2.452(2) Å), but is longer than the theoretical Ga–Ga distance for Ga_2(Ar-bian)$_2$ (2.29 Å, Ar-bian = *o*,*o'*-C_6H_5-bis(imino)acenaphthene) at the B3LYP/6-31G* level. The NBO analysis revealed a Ga–Ga single bond with 66.04% s, 33.73% p, and 0.23% d character and a Wiberg bond index (WBI) of 0.90. The HOMO–6 (Fig. S2) represents the Ga–Ga bond. The natural charge on Ga is 1.114. Moreover, there is a lot increase of the total negative charge on the α-diimine ligand L, from –0.461 (**1H**) to –1.300 (**2H**).

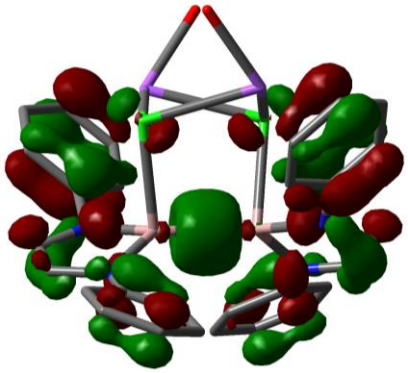

Fig. S2. The Ga–Ga bonding orbital (HOMO–6) of model compound **2H** from DFT computations.

DFT studies were carried out to elucidate the electronic structure of **3** at the B3LYP/6-31G* level by using a model compound [(L′(H_2O)Ga)$_2$(μ-η^1:η^1-N,N-Phz)] (**3H**; L′ = [PhNCH]$_2$). The natural charge on Ga (1.80) is more positive than in **2H** (1.11), confirming the formal oxidation state of Ga to be +3. The bridging Phz ligand bears a negative charge of −1.27 consistent with a dianion. Meanwhile, the total negative charge on the α-diimine L is almost the same in **2H** (−1.30) and **3H** (−1.28) (Table S2). The charge density on the N atoms (Fig. S3) indicates their electron-rich character, which favors the coordination to the Lewis acidic gallium(III) centers.

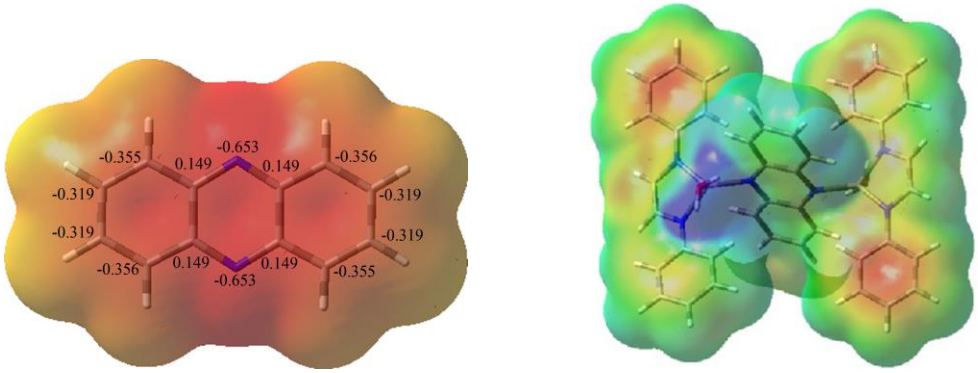

Fig. S3. Charge distribution for the 6-31g*-optimized Phz^{2-} (left) and compound **3** (right).

The simplified model compound [L′Ga(Phz)$_2$Na(H_2O)$_3$Na(H_2O)$_2${μ$_2$-Na(H_2O)$_2$}]$_2$ (**4H**) (L′ = [PhNCH]$_2$) was used in the DFT studies (Fig. S1). The computed Ga–N_{Phz} (1.959 and 1.932 Å) distances compare well with the experimental values (1.951(3) and 1.929(3) Å), with an average σ-bond order of 0.39. Meanwhile, each Phz fragment accumulates negative partial charges of −1.50 and −1.47, indicating the dianionic state of Phz. The NPA charge on the Ga atom (1.82) is also similar to **3H** (1.80).

The electronic structure of **5** was further studied by DFT methods on the simplified model compound [L'_{-H}Ga(Phz)$_2$] (L'_{-H} = PhN–C(=CH_2)–C(–Me)=NPh; **5H**, Fig. S1) and also on the full molecule of **5**, in the open-shell singlet and triplet spin states, respectively. The optimized geometries and harmonic vibrational frequencies were computed at the B3LYP exchange-correlation functional. In order to test the basis set dependence of the data, both 6-31g(d)[8] and LanL2DZ effective core potentials together with corresponding valence basis sets[9] were used. The results demonstrate that the triplet spin state and open-shell singlet state arising from the two Phz radicals are very close in energy (Table S3). NPA of **5H** shows that the Phz ligands have negative charges of –0.67 and –0.68, respectively. These values are remarkably smaller than that in **3H** (–1.28 and –1.27) and **4H** (–1.50 and –1.47). Meanwhile, the Ga atom has a significant positive charge (1.87) and the charge on the α-diimine ligand is –0.52.

Table S2. Natural charges of the model compounds **2H**–**5H** at the B3LYP/6-31G* level.

	2H	**3H**	**4H**	**5H**
Ga	1.11	1.80	1.83	1.87
L	−1.30	−1.28	−1.35	−0.52
Phz		−1.27	−1.50, −1.47	−0.67, −0.68

Table S3. Relative energies of compound **5** (simplified model and full molecule) in the high spin state and spin broken symmetry state. Basis: type I, 6-31g(d); II, LanL2DZ.

Spin multiplicity	Structure	Basis	Energy (E, a.u.)	ΔE (kJ/mol)	Gibbs free energy (G, a.u.)	ΔG (kJ/mol)
1	simplified	I	−3794.4567716	0.00	−3793.915353	3.20
3	simplified	I	−3794.4567875	0	−3793.916395	0
1	simplified	II	−1873.2617929	0.00	−1872.718455	2.56
3	simplified	II	−1873.2618047	0	−1872.719515	0
1	full	II	−2344.9313376	0.00	−2344.062291	2.56
3	full	II	−2344.9313513	0	−2344.063342	0

Magnetic Properties

Magnetic susceptibility data were measured from powder sample of **5** in the temperature range 2–300 K using a Quantum Design MPMS-XL7 SQUID magnetometer. The measured data fit to Equation (1) corresponding to the modified Bleany–Bowers singlet–triplet model[10].

$$\chi_{\mathrm{M}} = (1-\rho)\frac{2Ng^2\beta^2}{kT} \times \frac{1}{3+e^{-2J/kT}} + \frac{Ng^2\beta^2}{2kT}\rho \qquad (1)$$

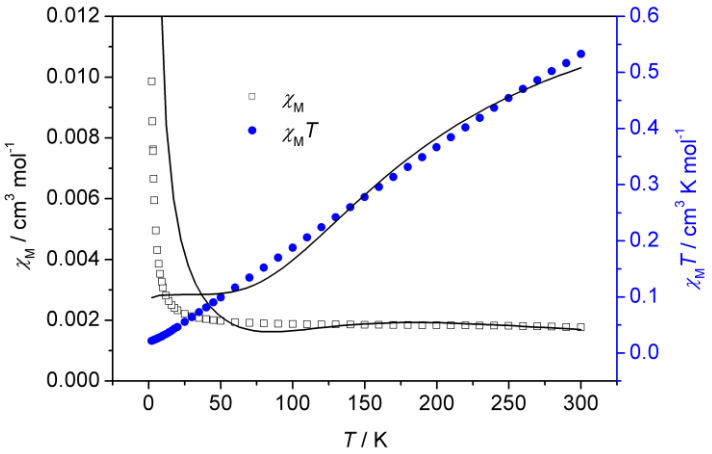

Fig. S4 curves of χ_{M} and $\chi_{\mathrm{M}}T$ versus T for **5**. Solid lines are the fitting curves according to Bleaney−Bowers equation.

From Figure S4 we can see that in the whole temperature range from room temperature to 2 K, $\chi_{\mathrm{M}}T$ continuously and slowly decreases with cooling, suggesting that the coupling between spins is dependent on the temperature and there may exist thermal depopulation of spins in the S = 1 state. Namely, at higher temperatures for example above 300 K, the complex shows paramagnetic state with noninteracting spins. Contrarily, below 300 K, the antiferromagnetic coupling between spins leads to a ground state of S = 0. The magnetic data can be fitted roughly by a dimer model with $S_1 = S_2 = 1/2$ and Hamiltonian $\hat{\mathrm{H}} = -2J\vec{\mathrm{S}}_1 \cdot \vec{\mathrm{S}}_2$ to estimate the coupling interaction. For this dimer system, the eigenvalue of $\hat{\mathrm{H}}$ is $E(S_{\mathrm{T}}, S) = -J[S_{\mathrm{T}}(S_{\mathrm{T}}+1)-2S(S+1)]$. According to the fitting results, we can obtain the energy of the low-lying states, $E(0, 1/2)$ = −191 cm^{-1} and $E(1, 1/2)$ = −63.6 cm^{-1}, respectively. Careful fitting with Bleaney−Bowers equation[10] gave a singlet−triplet energy gap ($\Delta E_{\mathrm{S-T}}$ = −0.078 kcal/mol) that agrees with the DFT calculated value (−0.01 kcal/mol) at the UB3LYP/6-31G(d) level. It indicates that the ground state spin is zero for this complex and the antiferromagnetic coupling between spins dominates the magnetic properties.

Table S4. Cartesian coordinates of the optimized geometry for **2H**.

Ga	-0.89808800	0.82208500	-0.67125500	C	0.00502900	-3.45988200	0.32692500
Cl	-1.75079100	0.53280800	1.86725200	C	-1.39491600	-3.21918900	0.38077400
Na	0.48648500	1.89977500	2.60227600	C	-2.20621100	-3.87699000	1.31130400
N	-0.79475100	2.74132800	-0.56178800	H	-3.27630800	-3.67124800	1.31478800
N	-2.53700600	1.00837300	-1.61875500	C	-1.66121700	-4.80574600	2.21675500
O	1.83297900	1.34368400	4.39833400	H	-2.29739300	-5.32487500	2.93125700
C	-2.03966600	3.23757000	-0.99286400	C	-0.28187400	-5.06908600	2.15946200
C	-2.91188800	2.35510400	-1.54845600	H	0.16297100	-5.78901900	2.84670700
C	-0.00502900	3.45988200	0.32692500	C	0.54220700	-4.41027600	1.23800700
C	1.39491600	3.21918900	0.38077400	C	3.42245400	-0.01718500	-2.06090700
C	2.20621100	3.87699000	1.31130400	C	2.91188800	1.20233800	-2.56434700
H	3.27630800	3.67124800	1.31478800	C	3.76569300	2.21834800	-3.00162500
C	1.66121700	4.80574600	2.21675500	H	3.33690400	3.14244500	-3.38918300
H	2.29739300	5.32487500	2.93125700	C	5.15897500	2.04723600	-2.96707200
C	0.28187400	5.06908600	2.15946200	H	5.82377600	2.83502300	-3.31759200
H	-0.16297100	5.78901900	2.84670700	C	5.67567200	0.83885600	-2.47796700
C	-0.54220700	4.41027600	1.23800700	H	6.75421200	0.68592700	-2.43502600
C	-3.42245400	0.01718500	-2.06090700	C	4.82737400	-0.17764500	-2.02315400
C	-2.91188800	-1.20233800	-2.56434700	H	-1.61285100	4.60193100	1.23374900
C	-3.76569300	-2.21834800	-3.00162500	H	1.84525600	2.53496200	-0.33570400
H	-3.33690400	-3.14244500	-3.38918300	H	-1.83249400	-1.33349100	-2.64663900
C	-5.15897500	-2.04723600	-2.96707200	H	-5.25736900	1.08790100	-1.61084800
H	-5.82377600	-2.83502300	-3.31759200	H	1.61285100	-4.60193100	1.23374900
C	-5.67567200	-0.83885600	-2.47796700	H	-1.84525600	-2.53496200	-0.33570400
H	-6.75421200	-0.68592700	-2.43502600	H	1.83249400	1.33349100	-2.64663900
C	-4.82737400	0.17764500	-2.02315400	H	5.25736900	-1.08790100	-1.61084800
Ga	0.89808800	-0.82208500	-0.67125500	H	2.50741800	1.72708400	4.97592500
Cl	1.75079100	-0.53280800	1.86725200	H	2.24795700	0.58616900	3.94027100
Na	-0.48648500	-1.89977500	2.60227600	H	-2.24795700	-0.58616900	3.94027100
N	0.79475100	-2.74132800	-0.56178800	H	-2.50741800	-1.72708400	4.97592500
N	2.53700600	-1.00837300	-1.61875500	H	3.84440900	-2.67686500	-2.00270500
O	-1.83297900	-1.34368400	4.39833400	H	2.22808500	-4.30774500	-0.96828500
C	2.03966600	-3.23757000	-0.99286400	H	-2.22808500	4.30774500	-0.96828500
C	2.91188800	-2.35510400	-1.54845600	H	-3.84440900	2.67686500	-2.00270500

Table S5. Cartesian coordinates of the optimized geometry for **3H**.

Ga	1.14272500	-3.07810500	0.19896300	H	-5.39996700	0.56053200	-2.15382100
N	0.51150300	-4.53616000	-0.82760900	C	-5.06861400	4.30995700	-1.24799700
N	2.85404000	-3.85527900	0.27380400	C	-6.21661500	3.84150900	-1.88595000
C	1.60695000	-5.39531300	-1.03097300	H	-7.00764000	4.54637300	-2.13089000
C	2.78815000	-5.04628300	-0.47302200	C	-6.35286100	2.49489200	-2.22405600
C	4.02018800	-3.42957700	0.91788500	H	-7.24867200	2.13691300	-2.72292100
C	4.16670200	-2.07066400	1.26425000	C	1.21509100	6.23413700	1.28456600
C	5.31399900	-1.61595600	1.90667400	C	0.81229800	4.90646500	1.01851800
H	5.39996700	-0.56053200	2.15382100	C	1.82914800	3.92784400	0.89439000
C	5.06861400	-4.30995700	1.24799700	C	3.55718000	5.57858300	1.31277000
C	6.21661500	-3.84150900	1.88595000	H	4.60487200	5.83811300	1.43016000
H	7.00764000	-4.54637300	2.13089000	C	3.17333500	4.26323200	1.04520900
C	6.35286100	-2.49489200	2.22405600	H	3.92536000	3.48227100	0.96198600
H	7.24867200	-2.13691300	2.72292100	C	2.56261700	6.55208000	1.43524500
C	-1.21509100	-6.23413700	-1.28456600	H	2.83784300	7.58409800	1.63984800
C	-0.81229800	-4.90646500	-1.01851800	O	0.07145900	3.55502400	-1.81137400
C	-1.82914800	-3.92784400	-0.89439000	N	-0.73130100	1.21988500	-0.10253300
C	-3.55718000	-5.57858300	-1.31277000	C	-0.40435300	0.48251400	-1.25353100
H	-4.60487200	-5.83811300	-1.43016000	C	-0.40491300	0.68071000	1.15926200
C	-3.17333500	-4.26323200	-1.04520900	C	-0.83685800	0.89511600	-2.52408300
H	-3.92536000	-3.48227100	-0.96198600	H	-1.58108600	1.68620200	-2.60327900
C	-2.56261700	-6.55208000	-1.43524500	C	-0.42838900	0.23515700	-3.69326000
H	-2.83784300	-7.58409800	-1.63984800	H	-0.79094900	0.57944000	-4.65712200
O	-0.07145900	-3.55502400	1.81137400	C	-0.82421800	1.30801900	2.33566400
N	0.73130100	-1.21988500	0.10253300	H	-1.48702600	2.16778700	2.27133800
C	0.40435300	-0.48251400	1.25353100	C	0.42623700	-0.85344600	-3.59820400
C	0.40491300	-0.68071000	-1.15926200	H	0.77097700	-1.37174600	-4.48743200
C	0.83685800	-0.89511600	2.52408300	H	3.69828300	-5.60525400	-0.64956900
H	1.58108600	-1.68620200	2.60327900	H	1.50125200	-6.25563200	-1.68013900
C	0.42838900	-0.23515700	3.69326000	H	-1.50125200	6.25563200	1.68013900
H	0.79094900	-0.57944000	4.65712200	H	-3.69828300	5.60525400	0.64956900
C	0.82421800	-1.30801900	-2.33566400	H	0.47146400	7.02064200	1.35128200
H	1.48702600	-2.16778700	-2.27133800	H	1.55176400	2.88206700	0.77486600
C	-0.42623700	0.85344600	3.59820400	H	3.39288500	-1.36073400	0.98431200
H	-0.77097700	1.37174600	4.48743200	H	4.97425900	-5.36927900	1.03345800
Ga	-1.14272500	3.07810500	-0.19896300	H	-1.55176400	-2.88206700	-0.77486600
N	-0.51150300	4.53616000	0.82760900	H	-0.47146400	-7.02064200	-1.35128200
N	-2.85404000	3.85527900	-0.27380400	H	-4.97425900	5.36927900	-1.03345800
C	-1.60695000	5.39531300	1.03097300	H	-3.39288500	1.36073400	-0.98431200
C	-2.78815000	5.04628300	0.47302200	H	-0.87466300	-3.97471400	1.43935200
C	-4.02018800	3.42957700	-0.91788500	H	-0.34277800	-2.76744300	2.32974800
C	-4.16670200	2.07066400	-1.26425000	H	0.34277800	2.76744300	-2.32974800
C	-5.31399900	1.61595600	-1.90667400	H	0.87466300	3.97471400	-1.43935200

Table S6. Cartesian coordinates of the optimized geometry for **4H**.

Ga	6.14848900	-0.81871400	-0.54325600	C	2.92059400	-1.83181000	-3.54411000
Na	0.63080400	-1.54485200	0.46061500	H	3.24886900	-2.51956200	-4.31776100
Na	5.52093100	3.09466000	2.73999000	C	1.66592400	-1.23816200	-3.60080500
Na	9.93263600	0.61343400	-0.22412200	H	0.98383200	-1.45710000	-4.41807000
O	1.73331500	-3.30932500	-0.49772600	C	1.27619100	-0.35734300	-2.58517500
O	1.73543100	-1.73771400	2.51681300	H	0.28570700	0.08809100	-2.61135900
O	4.12089100	4.18494900	1.33190600	C	2.11368200	-0.03905400	-1.50208100
O	7.07213300	3.15797400	4.37603800	C	3.72843900	0.29980700	0.72806100
O	11.09750000	1.91214600	1.24215800	C	4.33767900	0.26226200	1.98744000
O	9.93202300	-1.66755800	-0.18279600	H	5.24044200	-0.31894000	2.13425800
O	9.46175400	2.07900400	-1.91429700	C	3.82407100	0.98325600	3.10020300
N	6.42402700	-2.73298700	-0.52563000	H	4.30683100	0.88777000	4.07088400
N	7.02433800	-0.78673600	-2.29439700	C	2.67271000	1.74680700	2.93614200
N	4.28344500	-0.33654600	-0.39311100	H	2.26148000	2.32371800	3.76158700
N	1.63370300	0.78201300	-0.48159000	C	2.01209800	1.75192400	1.69515900
N	7.20924900	0.26280900	0.69950700	H	1.07818800	2.29976100	1.59194100
N	8.64677200	2.03098100	2.48460300	C	2.44322400	0.95467000	0.60380400
C	7.32018800	-3.02796600	-1.55987900	C	7.80231500	-0.22754600	1.89583100
C	7.63255100	-2.03960400	-2.43650200	C	7.73452100	-1.58253900	2.24722400
C	5.67783200	-3.72617500	0.09592200	H	7.19469400	-2.27393600	1.61284600
C	5.74997900	-5.09296400	-0.26038800	C	8.36503600	-2.07919900	3.39937900
C	4.99023800	-6.05308200	0.40455800	H	8.29111100	-3.13782500	3.63102000
H	5.07449700	-7.09268200	0.09685700	C	9.06191300	-1.21273900	4.23216300
C	4.12193000	-5.70072700	1.43941600	H	9.55795000	-1.57801400	5.12721300
H	3.53379500	-6.45440900	1.95426500	C	9.12289500	0.14539300	3.90536500
C	4.02983600	-4.35152900	1.79656300	H	9.67492700	0.84120700	4.53323500
H	3.35908800	-4.03908400	2.59303500	C	8.51194600	0.66276400	2.75335200
C	4.78417100	-3.38245800	1.13722600	C	7.17259200	1.66275300	0.53329000
C	7.10654800	0.13700100	-3.33312200	C	6.46375200	2.25559300	-0.51695800
C	6.03272900	1.01589700	-3.59723400	H	5.86838900	1.63117600	-1.16892200
C	6.10014700	1.94920700	-4.62699800	C	6.51715200	3.63850700	-0.78586000
H	5.24516300	2.59629600	-4.80830300	H	6.00240900	4.03338200	-1.65790400
C	7.23200800	2.04693500	-5.44221800	C	7.25918900	4.46593000	0.05492400
H	7.27609400	2.77351000	-6.24783100	H	7.32331700	5.53498000	-0.12859800
C	8.29597700	1.17519100	-5.21053400	C	7.92786100	3.90479200	1.15197000
H	9.18447700	1.21968800	-5.83602600	H	8.51272400	4.53282200	1.81992900
C	8.24327100	0.23822300	-4.17385800	C	7.92498700	2.51526500	1.41091600
C	3.41093700	-0.63326400	-1.46534600	Ga	-6.14848900	0.81871400	0.54325600
C	3.78159900	-1.52927900	-2.47604000	Na	-0.63080400	1.54485200	-0.46061500
H	4.75760100	-1.99897700	-2.44068900	Na	-5.52093100	-3.09466000	-2.73999000

Na	-9.93263600	-0.61343400	0.22412200	C	-3.72843900	-0.29980700	-0.72806100
O	-1.73331500	3.30932500	0.49772600	C	-4.33767900	-0.26226200	-1.98744000
O	-1.73543100	1.73771400	-2.51681300	H	-5.24044200	0.31894000	-2.13425800
O	-4.12089100	-4.18494900	-1.33190600	C	-3.82407100	-0.98325600	-3.10020300
O	-7.07213300	-3.15797400	-4.37603800	H	-4.30683100	-0.88777000	-4.07088400
O	-11.09750000	-1.91214600	-1.24215800	C	-2.67271000	-1.74680700	-2.93614200
O	-9.93202300	1.66755800	0.18279600	H	-2.26148000	-2.32371800	-3.76158700
O	-9.46175400	-2.07900400	1.91429700	C	-2.01209800	-1.75192400	-1.69515900
N	-6.42402700	2.73298700	0.52563000	H	-1.07818800	-2.29976100	-1.59194100
N	-7.02433800	0.78673600	2.29439700	C	-2.44322400	-0.95467000	-0.60380400
N	-4.28344500	0.33654600	0.39311100	C	-7.80231500	0.22754600	-1.89583100
N	-1.63370300	-0.78201300	0.48159000	C	-7.73452100	1.58253900	-2.24722400
N	-7.20924900	-0.26280900	-0.69950700	H	-7.19469400	2.27393600	-1.61284600
N	-8.64677200	-2.03098100	-2.48460300	C	-8.36503600	2.07919900	-3.39937900
C	-7.32018800	3.02796600	1.55987900	H	-8.29111100	3.13782500	-3.63102000
C	-7.63255100	2.03960400	2.43650200	C	-9.06191300	1.21273900	-4.23216300
C	-5.67783200	3.72617500	-0.09592200	H	-9.55795000	1.57801400	-5.12721300
C	-5.74997900	5.09296400	0.26038800	C	-9.12289500	-0.14539300	-3.90536500
C	-4.99023800	6.05308200	-0.40455800	H	-9.67492700	-0.84120700	-4.53323500
H	-5.07449700	7.09268200	-0.09685700	C	-8.51194600	-0.66276400	-2.75335200
C	-4.12193000	5.70072700	-1.43941600	C	-7.17259200	-1.66275300	-0.53329000
H	-3.53379500	6.45440900	-1.95426500	C	-6.46375200	-2.25559300	0.51695800
C	-4.02983600	4.35152900	-1.79656300	H	-5.86838900	-1.63117600	1.16892200
H	-3.35908800	4.03908400	-2.59303500	C	-6.51715200	-3.63850700	0.78586000
C	-4.78417100	3.38245800	-1.13722600	H	-6.00240900	-4.03338200	1.65790400
C	-7.10654800	-0.13700100	3.33312200	C	-7.25918900	-4.46593000	-0.05492400
C	-6.03272900	-1.01589700	3.59723400	H	-7.32331700	-5.53498000	0.12859800
C	-6.10014700	-1.94920700	4.62699800	C	-7.92786100	-3.90479200	-1.15197000
H	-5.24516300	-2.59629600	4.80830300	H	-8.51272400	-4.53282200	-1.81992900
C	-7.23200800	-2.04693500	5.44221800	C	-7.92498700	-2.51526500	-1.41091600
H	-7.27609400	-2.77351000	6.24783100	H	9.56713200	-1.90061300	0.69161700
C	-8.29597700	-1.17519100	5.21053400	H	9.29196700	-2.06527200	-0.81320600
H	-9.18447700	-1.21968800	5.83602600	H	10.33762200	2.09713100	1.87155200
C	-8.24327100	-0.23822300	4.17385800	H	11.37001000	2.78178700	0.91285300
C	-3.41093700	0.63326400	1.46534600	H	8.71503200	2.63407300	-1.62477100
C	-3.78159900	1.52927900	2.47604000	H	9.14016000	1.67849500	-2.74613400
H	-4.75760100	1.99897700	2.44068900	H	8.27626200	-2.22980400	-3.28778800
C	-2.92059400	1.83181000	3.54411000	H	7.74289900	-4.02148800	-1.65317000
H	-3.24886900	2.51956200	4.31776100	H	4.69217200	-2.34859600	1.44746600
C	-1.66592400	1.23816200	3.60080500	H	6.38245300	-5.40979400	-1.08156300
H	-0.98383200	1.45710000	4.41807000	H	5.11322200	0.91280200	-3.03087700
C	-1.27619100	0.35734300	2.58517500	H	9.08999100	-0.42495400	-4.01892600
H	-0.28570700	-0.08809100	2.61135900	H	3.38485000	3.55242000	1.20550600
C	-2.11368200	0.03905400	1.50208100	H	4.62068100	4.17658200	0.49435200

H	7.08130200	2.58813200	5.15896000	H	-7.08130200	-2.58813200	-5.15896000
H	7.83963900	2.81891900	3.80628700	H	-9.29196700	2.06527200	0.81320600
H	-2.22810900	3.01380700	1.28462300	H	-9.56713200	1.90061300	-0.69161700
H	-2.41789700	3.69262600	-0.08173400	H	-11.37001000	-2.78178700	-0.91285300
H	-2.50953700	1.14031000	-2.51452000	H	-10.33762200	-2.09713100	-1.87155200
H	-1.27080100	1.54187600	-3.34440800	H	-9.14016000	-1.67849500	2.74613400
H	1.27080100	-1.54187600	3.34440800	H	-8.71503200	-2.63407300	1.62477100
H	2.50953700	-1.14031000	2.51452000	H	-7.74289900	4.02148800	1.65317000
H	2.41789700	-3.69262600	0.08173400	H	-8.27626200	2.22980400	3.28778800
H	2.22810900	-3.01380700	-1.28462300	H	-6.38245300	5.40979400	1.08156300
H	-4.62068100	-4.17658200	-0.49435200	H	-4.69217200	2.34859600	-1.44746600
H	-3.38485000	-3.55242000	-1.20550600	H	-9.08999100	0.42495400	4.01892600
H	-7.83963900	-2.81891900	-3.80628700	H	-5.11322200	-0.91280200	3.03087700

Table S7. Cartesian coordinates of the optimized geometry for **5H**.

Ga	-0.36098100	0.04127300	-0.36113300	H	-5.43398800	-1.47525800	1.01522800
N	0.58516900	-0.37981700	-2.09235400	C	-5.84756900	0.40894500	0.05238500
N	-1.90775100	0.11233500	-1.46769300	H	-6.85410300	0.48800700	0.45347900
N	0.63624500	1.56192300	0.29868400	C	-5.34367400	1.40715600	-0.78388100
N	2.24422300	3.82500200	1.00600600	H	-5.95449400	2.27085200	-1.03324000
N	-0.50772000	-1.36207800	0.95087200	C	-4.04795900	1.31013300	-1.29092500
N	0.14275100	-3.31092500	2.93338100	C	3.79022000	-0.02232300	1.47757300
C	-0.21856500	-0.32204300	-3.11576200	H	4.19502700	-1.01979400	1.62135600
C	-1.65372000	-0.08747900	-2.81314300	C	4.56920700	1.10656700	1.77547300
C	0.25241600	-0.49520700	-4.53340500	H	5.58328000	0.98852200	2.14726600
H	1.32800200	-0.65880200	-4.57964000	C	4.03228500	2.36915200	1.60369100
H	0.00299800	0.39140700	-5.12453800	H	4.59627800	3.26811300	1.83292200
H	-0.25325400	-1.34966200	-4.99380500	C	2.70923000	2.55345400	1.12996400
C	-2.56199200	-0.13735500	-3.82009500	C	1.92772500	1.39324600	0.80836300
H	-3.61925300	-0.00015900	-3.63191700	C	2.49153600	0.12180800	1.00294000
H	-2.26546700	-0.32956800	-4.84148900	H	1.91444400	-0.77268900	0.79517700
C	1.99988400	-0.59767700	-2.23543700	C	0.11175200	2.85404600	0.27298000
C	2.84294900	0.47978900	-2.52077700	C	0.95003300	3.96453100	0.61836100
C	4.21878900	0.26949500	-2.60817700	C	0.39910900	5.26926600	0.55867300
H	4.87453400	1.10755500	-2.82495800	H	1.06065700	6.09007800	0.81813400
C	4.74996300	-1.00515400	-2.40439300	C	-0.92158200	5.48211500	0.20398900
H	5.82250400	-1.16387200	-2.46851700	H	-1.32380200	6.49099500	0.17406500
C	3.90061200	-2.07340400	-2.11069100	C	-1.74092700	4.38511700	-0.10474100
H	4.30809000	-3.06687100	-1.94640600	H	-2.78451300	4.53535500	-0.36727300
C	2.52277200	-1.87501100	-2.01578900	C	-1.22625300	3.09363300	-0.07066500
C	-3.24570300	0.19886500	-0.98714500	H	-1.87073800	2.25921100	-0.31347100
C	-3.75655600	-0.79937400	-0.14552700	C	-0.47095400	-4.52096200	-1.01713200
C	-5.05016000	-0.69235700	0.36684700	H	-0.68039100	-4.85755200	-2.02898600

C	-0.05056700	-5.43863200	-0.04184700	H	0.11065200	-2.44368800	5.35334700
H	0.08842200	-6.48467700	-0.30053200	C	-0.55938200	-0.40933000	5.05556300
C	0.16111700	-5.00889100	1.25692900	H	-0.55892800	-0.15556800	6.11187700
H	0.46027400	-5.69436300	2.04386800	C	-0.96078000	0.54282500	4.10374700
C	-0.02634700	-3.65395900	1.62932200	H	-1.28068300	1.53103900	4.42091600
C	-0.39635000	-2.71175400	0.61125000	C	-0.95270700	0.22988700	2.74932900
C	-0.64200900	-3.17599800	-0.69282800	H	-1.29837100	0.97164700	2.03544700
H	-1.01191000	-2.49208100	-1.44895100	H	1.85326200	-2.69420200	-1.77175800
C	-0.55236500	-1.04094000	2.31041200	H	2.42068500	1.47022000	-2.66150400
C	-0.18583500	-2.03482500	3.27427600	H	-3.14876700	-1.67105200	0.07345900
C	-0.18283900	-1.67533300	4.64476400	H	-3.64930100	2.09016800	-1.93352100

References

1. H. A. Zhong, J. A. Labinger and J. E. Bercaw, *J. Am. Chem. Soc*., 2002, **124**, 1378.
2. Y. Liu, S. Li, X.-J. Yang, Q.-S. Li, Y. Xie, H. F. Schaefer and B. Wu, *J. Organomet. Chem.*, 2011, **696**, 1450.
3. G. M. Sheldrick, *Program SADABS: Area-Detector Absorption Correction*; University of Göttingen, Germany, 1996.
4. G. M. Sheldrick, *SHELXS-97 and SHELXL-97*, Programs for Crystal Structure Analysis; University of Göttingen, Germany, 1997.
5. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian 03, Revision E.01, Gaussian, Inc., Wallingford CT, 2004.
6. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
7. (a) K. B. Wiberg, *Tetrahedron*, 1968, **24**, 1083; (b) A. E. Reed, L.A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899.
8. M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, *J. Chem. Phys.*, 1982, **77**, 3654.
9. W. R. Wadt and P. J. Hay, *J. Chem. Phys*., 1985, **82**, 284.
10. B . Bleaney, K. D. Bowers, *Proc. R. Soc. London Ser. A* 1952, **214**, 451.