Electronic supplementary materials *Mendeleev Commun.*, 2023, **33**, 167–170

Reactivity of digallane toward nitrogen-containing compounds

Tatyana S. Koptseva, Natalia L. Bazyakina, Evgeny V. Baranov and Igor L. Fedushkin

Table of contents

Experimental

General information.

Compounds **2-6** are sensitive to air and moisture. Therefore all manipulations concerning their preparation and identification were carried out under vacuum using glass ampoules. Toluene was dried over sodium/benzophenone, hexane was dried over sodium and condensed under vacuum in the flasks just prior to use. Benzene-d_6, toluene-d_8, and THF-d_8 were dried over sodium/benzophenone at ambient temperature and condensed under vacuum into the NMR tubes that contained the sample. The IR-spectra were recorded on a FSM-1201 spectrometer, the ^{1}H NMR – on BrukerDPX-200, Bruker Avance NEO 300, Bruker Advance III 400 spectrometers. Elemental analysis was performed on a Vario EL Cube analyzer. Compound **1** was prepared according to a literature procedure. [I. L. Fedushkin *et al*., *Chem. Eur. J.*, 2010, **16**, 7563].

[(dpp-bian)(NH_3)Ga–Ga(NH_3)(dpp-bian)] (2). To a frozen solution of **1** (*in situ* from 0.5 g, 1.0 mmol of dpp-bian and excess of gallium metal) in toluene (30 ml), 1 equiv of gaseous NH_3 (0.022 g, 1.0 mmol) was added. The resulting green solution was left for 24 h at 25 °C. Green crystals of compound **2** were separated by decantation, washed with cold toluene and dried in vacuum. Yield 0.48 g (82%). Anal. calcd. for $C_{72}H_{86}Ga_2N_6$ (1174.90): C, 73.60; H, 7.38; N 7.15. Found: C 73.56; H 7.36; N 7.13.

^{1}H NMR (300 MHz, C_4D_8O, 298 K): δ 7.22-7.10 (m, 4H), 6.94 (d, 4H J = 7.0), 6.71 (pseudo t, 4H, J = 7.0), 5.67 (d, 4H, J = 7.0), 3.43 (sept, 8H, J = 7.0), 2.31 (s, 3H, toluene), 2.26 (s, 6H), 0.94 (d, 24H, J = 7.0), 0.90 (d, 24H, J = 7.0).

A low solubility of **2** prevented recording its ^{13}C NMR spectrum.

IR (Nujol): 3375 m, 3272 m, 3360 m, 1922 w, 1851 w, 1777 w, 1652 m, 1613 m, 1589 s, 1516 s, 1435 s, 1355 w, 1327 s, 1258 s, 1204 s, 1182 w, 1134 w, 1117 w, 1103 w, 1061 m, 1030 w, 998 w, 961 w, 937 m, 922 s, 900 s, 859 w, 811 s, 802 m, 779 w, 761 s, 728 m, 694 w, 682 w, 667 w, 646 m, 622 m, 571 m, 547 m, 515 m cm^{-1}.

[(dpp-bian)Ga(NC_4H_8)(HNC_4H_8)] (3). To crystalline **1** (0.57 g, 0.5 mmol), an excess of pyrrolidine (17.32 g, 243.9 mmol) was added. The ampule was sealed and heated at 50 °C. Unreacted pyrrolidine was removed by evaporation *in vacuo*. The remaining precipitate was dissolved in toluene/hexane (20 :2 ml/ml) and allowed to stand at 25 °C for 24 h. Blue crystals of compound **3** were separated by decantation, washed with cold toluene and dried in

vacuum. Yield 0.38 g (53 %). Anal. calcd. for $C_{44}H_{57}GaN_4$ (711.65): C 74.25, H 8.07, N 7.87. Found: C 74.23, H 8.06, N 7.87.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 7.24-7.18 (m, 4H), 7.14-7.09 (m, 4H), 7.07-6.99 (m, 5H), 6.84 (d, 1H, J = 7.0), 6.82 (d, 1H, J = 7.0), 6.11 (d, 2H, J = 7.0), 3.62 (sept, 2H, J = 7.0), 3.56 (sept, 2H, J = 7.0), 2.76-2.54 (m, 3H), 2.47 (br. s, 2H), 2.11 (s, 3H), 1.46-1.32 (m, 2H), 1.30 (d, 6H, J = 7.0), 1.26 (br.s, 5H), 1.14 (d, 6H, J = 7.0), 0.96 (br.s, 5H), 0.92 (d, 6H, J = 7.0), 0.78 (d, 6H, J = 7.0).

^{13}C NMR (100.6 MHz, C_6D_6, 298 K): 148.31, 145.54, 136.06, 128.96, 128.19, 126.81, 126.77, 126.72, 125.31, 124.64, 123.32, 122.38, 117.53, 46.70, 27.88, 27.59, 25.15, 24.85, 24.00, 23.18.

IR (Nujol): 3275 w, 1614 w, 1604 w, 1590 m, 1511 s, 1435 s, 1326 s,1360 w, 1310 s, 1256 s, 1207 m, 1183 m, 1161 w, 1133 w, 1112 w, 1103 w, 1082 w, 1058 w, 1035 m, 1000 m, 935 m, 898 s, 879 s, 870 s, 809 s, 805 s, 762 s, 780 w, 763 w, 748 w, 729 s, 694 w, 684 w, 667 w, 645 w, 628 w, 621 w, 552 w, 537 w, 515 w, 464 w cm^{-1}.

[(dpp-bian)(HNC$_4$H$_8$)Ga–Ga(dpp-bian)] (4). To a solution of **1** (*in situ* from 0.5 g, 1.0 mmol of dpp-bian and excess of gallium metal) in toluene (30 ml) pyrrolidine (0.07 g, 1.0 mmol) was added. To the resulting brown solution hexane (30 ml) was added, and this was allowed to stand at 25 °C for 24 h. Brown crystals of compound **4** were separated by decantation, washed with cold toluene and dried in vacuum. Yield 0.42 g (63%). Anal. calcd. for $C_{85.5}H_{107}Ga_2N_5$ (1344.19): C 76.39, H 8.02, N 5.21. Found: C 76.36, H 7.98, N 5.20.

^{1}H NMR (200 MHz, C_7D_8, 298 K): δ 7.30-6.95 (m, 16H), 6.81 (pseudo t, 4H, J = 7.0), 6.10 (d, 4H, J = 7.0), 3.53 (sept, 8H, J = 7.0), 2.38 (br.s., 4H), 1.21 (br.s, 5H), 1.05 (d, 24H, J = 7.0), 0.99 (d, 24H, J = 7.0).

IR (Nujol): 3292 w, 1640 m, 1613 w, 1592 m, 1515 s, 1446 s, 1436 s, 1351 s, 1328 s, 1314 m, 1276 w, 1252 s, 1207 w, 1178 m, 1158 w, 1134 w, 1112 m, 1055 m, 1040 m, 1034 m, 1000 w, 964 w, 934 m, 925 s, 899 m, 876 w, 835 m, 812 s, 803 m, 799 m, 787 m, 762 s, 750 s, 733 m, 694 w, 681 w, 668 w, 648 w, 628 w, 618 w, 592 w, 549 w, 533 w, 518 w cm^{-1}.

[(dpp-bian)(HNC$_4$H$_8$)Ga–Ga(HNC$_4$H$_8$)(dpp-bian)] (5). To a solution of **1** (*in situ* from 0.5 g, 1.0 mmol of dpp-bian and excess of gallium metal) in toluene (30 ml), pyrrolidine (2.59 g, 36.0 mmol) was added. The resulting brown solution was left at 25 °C for 24 h. Green crystals of compound **5** were separated by decantation, washed with cold toluene and dried in vacuum. Yield 0.49 g (76%). Anal. calcd. for $C_{80}H_{98}Ga_2N_6$ (1283.08): C 74.88, H 7.70, N 6.55. Found: C 74.85, H 7.67, N 6.54.

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 7.31-7.21 (m, 6H), 7.18 (s, 6H), 7.06 (d, 4H, J = 7.0), 6.84 (d, 2H, J = 7.0), 6.82 (d, 2H, J = 7.0), 6.17 (d, 4H, J = 7.0), 3.58 (sept, 8H, J = 7.0), 2.46 (br.s., 8H), 1.09 (d, 32H, J = 7.0), 1.01 (d, 26H, J = 7.0).

^{13}C NMR (100.6 MHz, C_6D_6, 298 K): 146.65, 145.41, 143.79, 136.36, 135.22, 128.89, 127.48, 126.75, 124.84, 124.53, 124.44, 118.92, 47.41, 29.11, 25.72, 25.18.

IR (Nujol): 3278 m, 1611 m, 1588 m, 1515 s, 1435 s, 1397 w, 1378 s, 1359 m, 1326 s, 1308 s, 1252 s, 1205 m, 1184 m, 1134 m, 1108 m, 1057 m, 1043 s, 1035 w, 999 w, 936 s, 919 s, 905 m, 897 m, 884 m, 815 s, 807 s, 800 s, 781 w, 760 s, 730 w, 683 m, 669 w, 644 w, 622 m, 610 w, 548 w, 515 w. cm^{-1}.

[(dpp-bian)Ga(C_5H_5N)(*μ*-O)Ga(C_5H_5N)(dpp-bian)] (6). To a frozen solution of **1** (*in situ* from 0.5 g, 1.0 mmol of dpp-bian and excess of gallium metal) in toluene (30 ml) pyridine (0.5 g, 6.3 mmol) and 1 equiv of gaseous N_2O (0.022 g, 1.0 mmol) were added. The ampule was sealed and heated at 80 °C. Within 30 min, the reaction mixture turned from dark blue to light blue. The resulting solution was left at 25 °C for 24 h. Blue crystals of compound **6** were separated by decantation, washed with cold toluene and dried in vacuum. Yield 0.55 g (74%). Anal. calcd. for $C_{97}H_{105}Ga_2N_6O$ (1510.30): C, 77.14; H, 7.01; N 5.56. Found: C 77.11; H 6.98; N 5.55.

^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 8.33-7.51 (m, 4H), 7.29-7.15 (m, 10H), 7.09-6.94 (m, 10H), 6.89-679 (m, 5H), 6.77-6.69 (m, 2H), 6.25-613 (m, 7H), 3.75 (br.s., 8H), 2.98 (br.s., 8H), 1.10 (d, 12H, J = 6.6), 1.00 (d, 12H, J = 6.6), 0.76 (br.s., 8H), 0.53 (d, 12H, J = 6.6).

Low solubility of **6** prevented recording its ^{13}C NMR spectrum.

IR (Nujol): 1946 w, 1665 w, 1610 s, 1591 m, 1573 w, 1514 s, 1434 s, 1337 s, 1259 s, 1211 s, 1183 m, 1157 w, 1136 w, 1110 m, 1063 s, 1047 s, 1033 w, 1017 m, 999 m, 912 s, 826 w, 809 s, 761 s, 722 w, 700 s, 678 s, 645 s, 621 m, 549 w, 537 w, 516 m, 497 w cm^{-1}.

Table S1. Crystal data and structure refinement details for compounds **2-6**.

	2	**3**	**4**	**5**	**6**
Empirical Formula	$C_{72}H_{86}Ga_2N_6$	$C_{44}H_{57}GaN_4$	$C_{85.5}H_{107}Ga_2N_5$	$C_{80}H_{98}Ga_2N_6$	$C_{97}H_{105}Ga_2N_6O$
M	1174.90	711.65	1344.19	1283.08	1510.30
T/K	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal System	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Monoclinic
Space Group	$P2_1/n$	$P2_1/c$	P-1	$Pnma$	$P2_1/n$
a/Å	13.7390(7)	10.5539(9)	12.0662(16)	27.7611(11)	16.2793(8)
b/Å	13.9627(7)	20.4624(13)	13.0749(17)	21.1364(9)	24.1339(12)
c/Å	16.0243(8)	17.8849(13)	26.069(4)	11.5765(5)	21.3756(10)
α/deg	90	90	104.388(2)	90	90
β/deg	99.337(2)	102.900(8)	91.883(3)	90	101.791(2)
γ/deg	90	90	113.391(2)	90	90
V/Å^3	3033.3(3)	3764.9(5)	3616.2(9)	6792.7(5)	8220.9(7)
Z	2	4	2	4	4
d_{calc}/Mg m^{-3}	1.286	1.256	1.234	1.255	1.220
μ(Mo Kα)/mm^{-1}	0.936	0.767	0.794	0.842	0.707
F(000)	1244	1520	1434	2728	3196
Crystal Size/mm	0.20 × 0.16 × 0.02	0.20 × 0.15 × 0.05	0.20 × 0.20 × 0.15	0.10 × 0.10 × 0.05	0.55 × 0.30 × 0.16
θ range/deg	2.13 – 25.67	3.07–27.00	2.15 – 27.00	2.42 – 26.09	2.12 –28.00
Limiting indices	–16 ≤ h ≤ 16 –17 ≤ k ≤ 17 –19 ≤ l ≤ 19	–13 ≤ *h* ≤ 13 –26 ≤ *k* ≤ 25 –22 ≤ *l* ≤ 22	–15 ≤ *h* ≤ 15 –16 ≤ *k* ≤ 16 –33 ≤ *l* ≤ 33	–34 ≤ *h* ≤ 34 –26 ≤ *k* ≤ 26 –14 ≤ *l* ≤ 14	-21 ≤ h ≤ 21 -31 ≤ k ≤ 31 -28 ≤ l ≤ 28
Reflections Collected/ Unique	37318 / 5747	19366 / 8207	34726 / 15654	113783 / 6780	186385 / 19415
R_{int}	0.0769	0.0526	0.0823	0.0607	0.0578
Data/Restraints/ Parameters	5747 / 13 / 387	8207 / 8 / 463	15654 / 125 / 897	6780 / 134 / 471	19415 / 114 / 1029
S(F^2)	1.030	1.031	1.031	1.040	1.073
R_1 / wR_2 (I>2σ(I))	0.0545 / 0.1023	0.0582 / 0.1386	0.0683 / 0.1647	0.0409 / 0.0898	0.0619 / 0.1098
R_1 / wR_2 (all data)	0.0918 / 0.1174	0.1051 / 0.1568	0.1145 / 0.1795	0.0536 / 0.0951	0.0815 / 0.1157
Larg. Diff. Peak and Hole/e Å^{-3}	0.664 / -0.749	0.774 / –0.548	1.364 / –1.051	0.610 / –0.653	0.736 / -0.927

Table S2. Selected bond lengths [Å] and angles [°] for complexes **2-6**.

Bond	**2**	**Bond**	**3**
Ga(1)–N(1)	1.922(3)	Ga(1)–N(1)	1.905(3)
Ga(1)–N(2)	1.920(3)	Ga(1)–N(2)	1.901(3)
Ga(1)–N(3)	2.143(4)	Ga(1)–N(3)	2.059(3)
N(1)–C(1)	1.404(4)	Ga(1)–N(4)	1.832(4)
N(2)–C(2)	1.392(4)	N(1)–C(1)	1.389(4)
C(1)–C(2)	1.383(5)	N(2)–C(2)	1.400(4)
Ga(1)-Ga(1)’	2.4421(7)	C(1)–C(2)	1.384(5)
Angle		**Angle**	
N(1)–Ga(1)–N(2)	90.64(12)	N(1)–Ga(1)–N(2)	90.90(12)
N(2)–Ga(1)–N(3)	95.98(13)	N(4)–Ga(1)–N(3)	102.64(17)
N(1)–Ga(1)–N(3)	94.87(13)	N(2)–Ga(1)–N(3)	109.85(11)
N(3)–Ga(1)–Ga(1)’	107.19(10)	N(4)–Ga(1)–N(1)	126.35(16)

Bond	**4**	**Bond**	**5**
Ga(1)–N(1)	1.896(3)	Ga(1)–N(1)	1.9304(17)
Ga(1)–N(2)	1.908(3)	Ga(1)–N(5)	2.118(3)
Ga(1)–N(5)	2.066(3)	N(1)–C(1)	1.403(3)
N(1)–C(1)	1.402(4)	C(1)–C(1)’	1.368(5)
N(2)–C(2)	1.395(5)	Ga(1)–Ga(2)	2.4695(5)
C(1)–C(2)	1.363(5)	Ga(2)–N(2)	1.9310(17)
Ga(1)–Ga(2)	2.4167(6)	Ga(2)–N(6)	2.117(3)
Ga(2)–N(4)	1.882(3)	N(2)–C(20)	1.399(3)
Ga(2)–N(3)	1.887(3)	C(20)–C(20)’	1.373(4)
N(3)–C(37)	1.385(5)		
N(4)–C(38)	1.385(5)		
C(37)–C(38)	1.390(5)		
Angle		**Angle**	
N(1)–Ga(1)–N(2)	90.74(13)	N(1)–Ga(1)–N(1)’	90.32(11)
N(5)–Ga(1)–Ga(2)	102.84(10)	N(5)–Ga(1)–Ga(2)	104.01(9)
N(4)–Ga(2)–N(3)	89.90(13)	N(2)–Ga(2)–N(2)’	90.11(10)

Bond	**6**	**Bond**	**6**
Ga(1)–N(1)	1.901(2)	C(1)–C(2)	1.374(4)
Ga(1)–N(2)	1.917(2)	Ga(1)–O(1)	1.756(2)
Ga(1)-N(5)	2.049(2)	Ga(2)–O(1)	1.757(2)
N(1)–C(1)	1.397(3)		
N(2)–C(2)	1.394(3)		
Ga(2)–N(3)	1.907(2)	**Angle**	**6**
Ga(2)–N(4)	1.896(2)	Ga(1)–O(1)–Ga(2)	172.21(14)
Ga(2)–N(6)	2.038(2)	N(1)–Ga(1)–N(2)	91.80(10)
N(3)–C(37)	1.395(3)	O(1)–Ga(1)–N(5)	100.53(9)
N(4)–C(38)	1.401(3)	N(4)–Ga(2)–N(3)	91.93(9)
C(37)–C(38)	1.373(4)	O(1)–Ga(2)–N(6)	102.69(9)

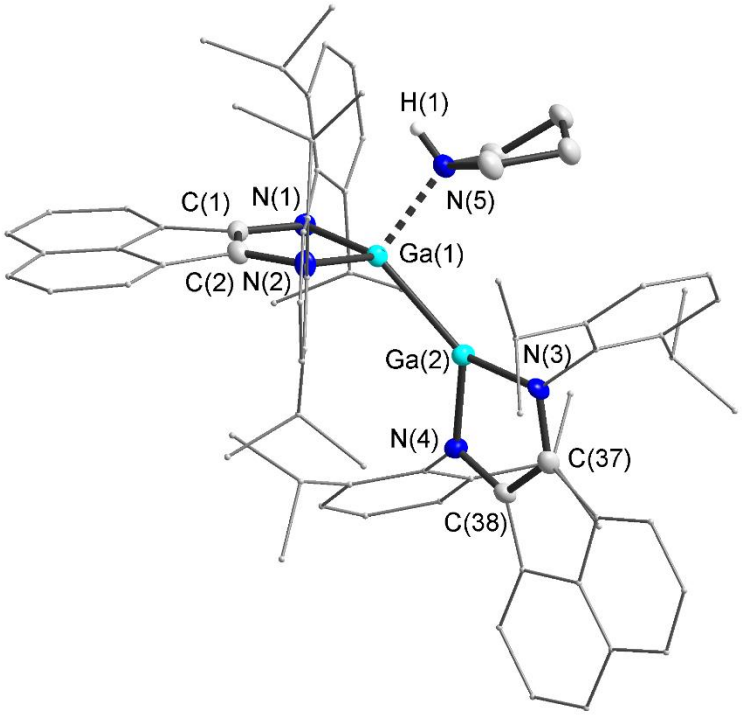

Figure S1. Molecular structure of **4**. Thermal ellipsoids drawn at 50% probability level.

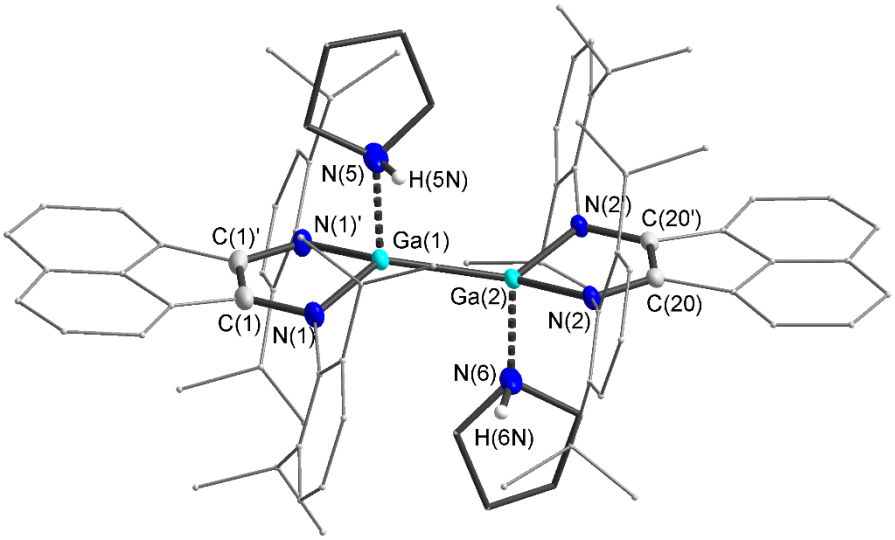

Figure S2. Molecular structure of **5**. Thermal ellipsoids drawn at 50% probability level.

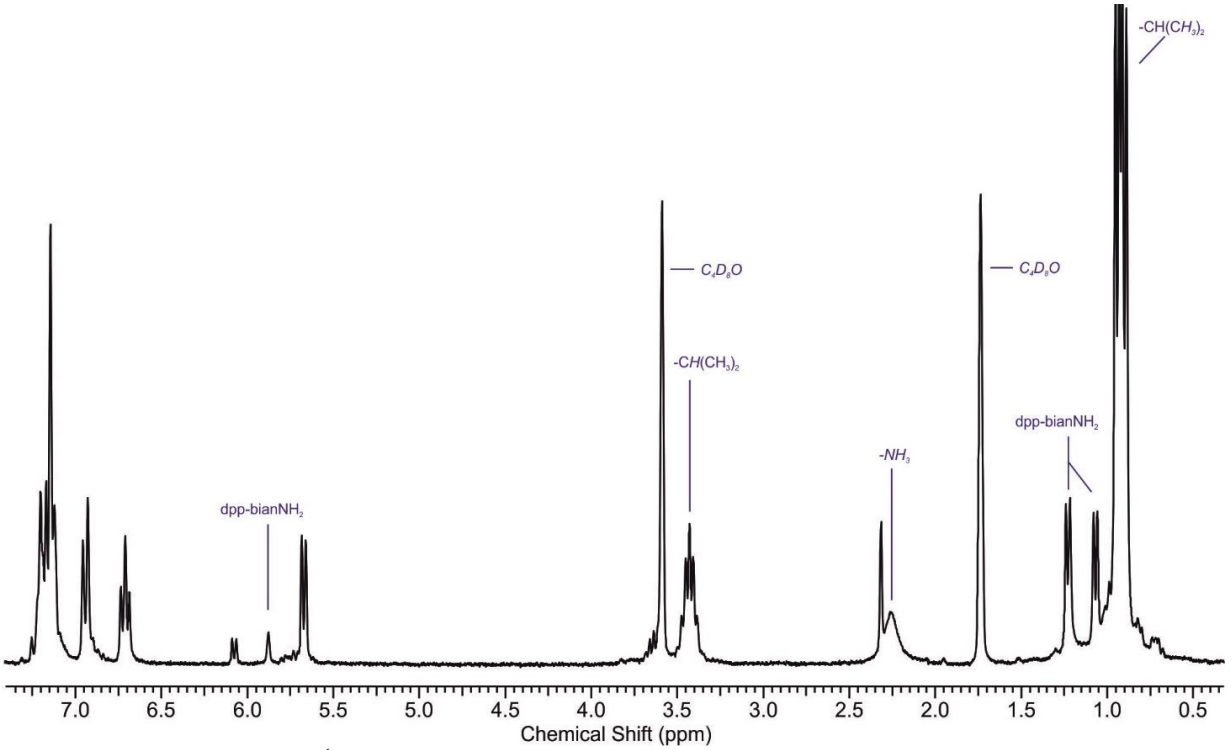

Figure S3. ^{1}H NMR spectrum of complex **2** (300 MHz, C_4D_8O, 298 K).
Minor signals in the NMR spectrum belong to dpp-bianNH$_2$ (hydrolysis product of compound **2**).

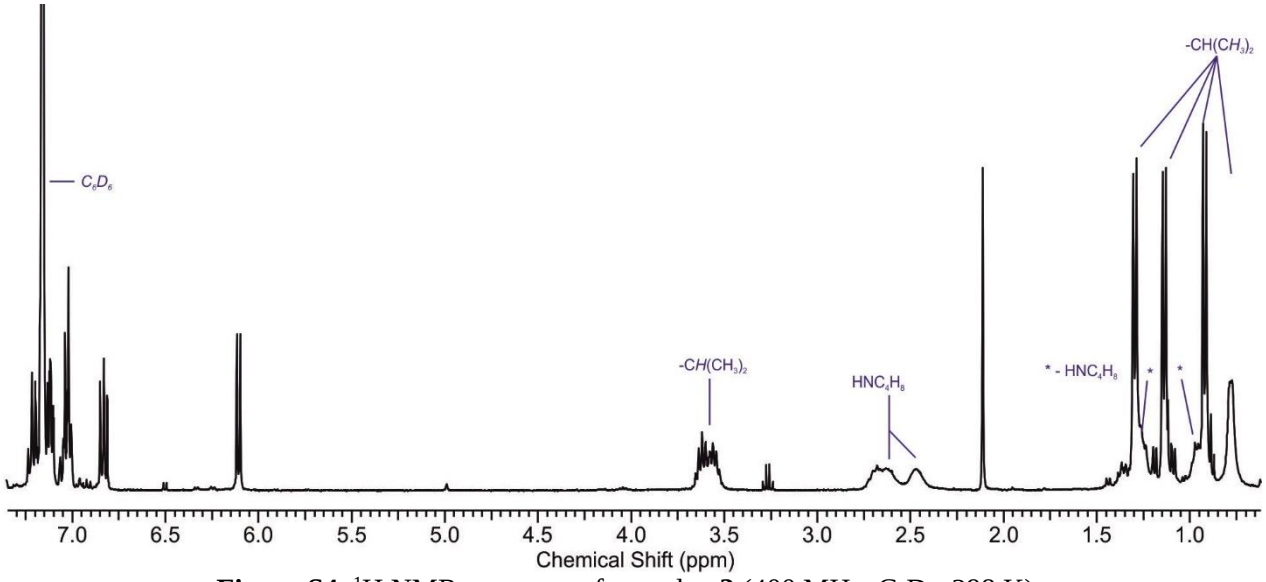

Figure S4. ^{1}H NMR spectrum of complex **3** (400 MHz, C_6D_6, 298 K).

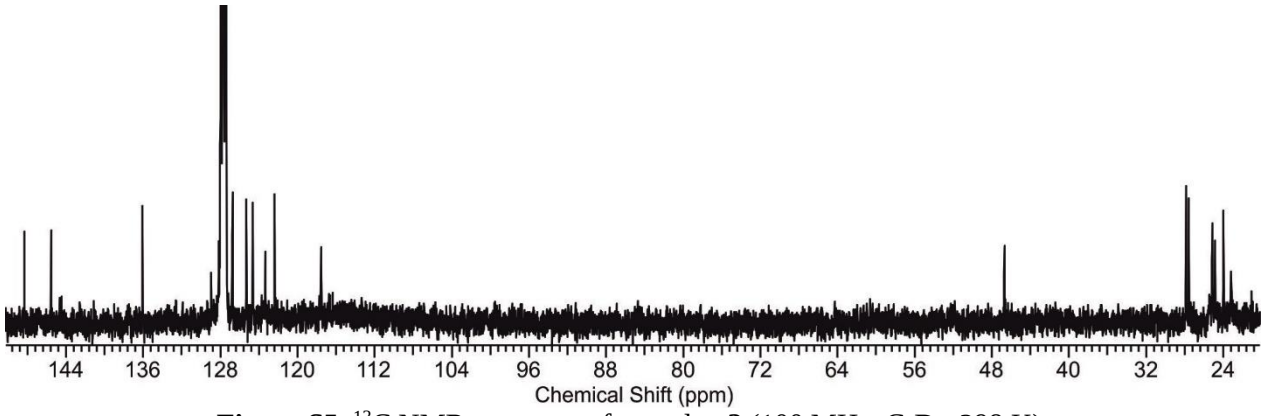

Figure S5. ^{13}C NMR spectrum of complex **3** (100 MHz, C_6D_6, 298 K).

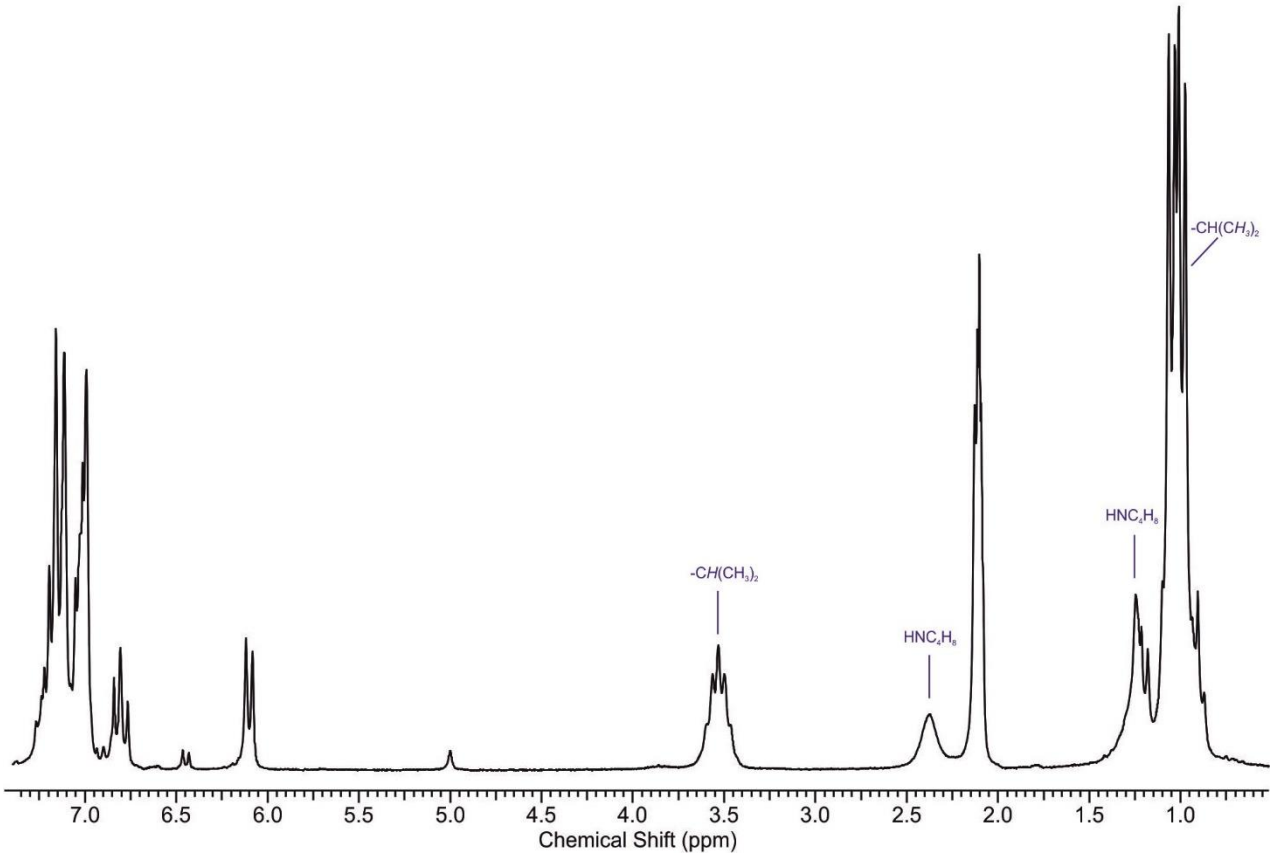

Figure S6. ^{1}H NMR spectrum of complex **4** (200 MHz, C_7D_8, 298 K).

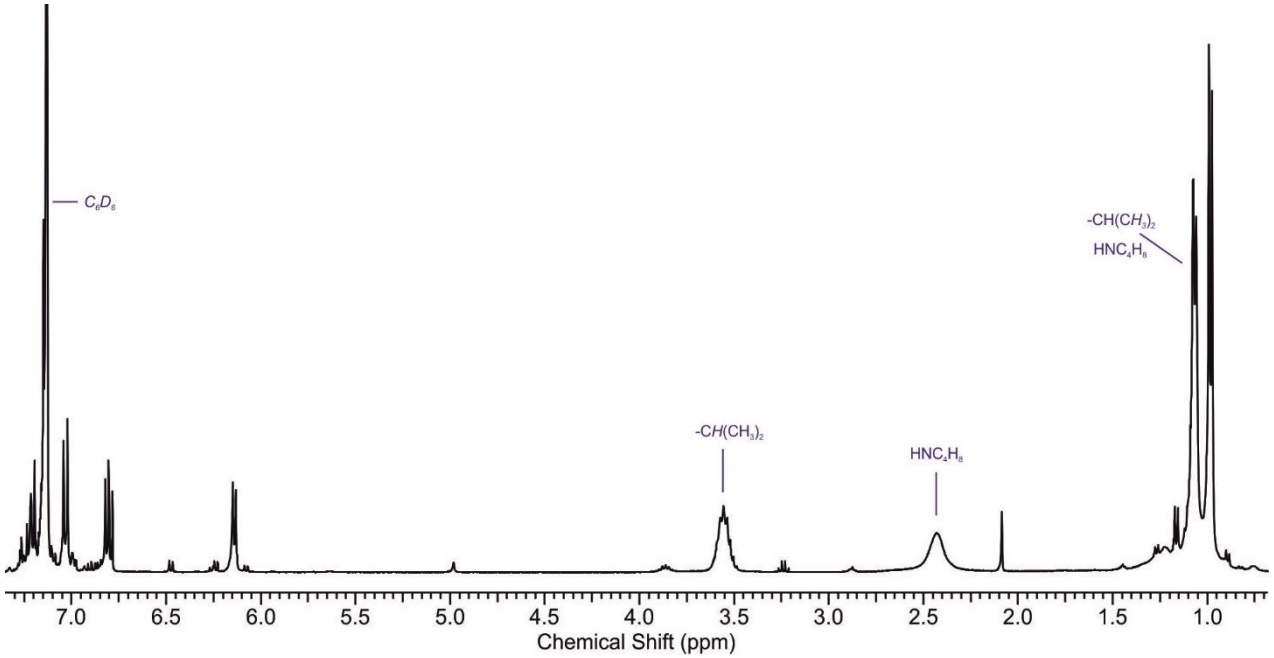

Figure S7. ^{1}H NMR spectrum of complex **5** (400 MHz, C_6D_6, 298 K).

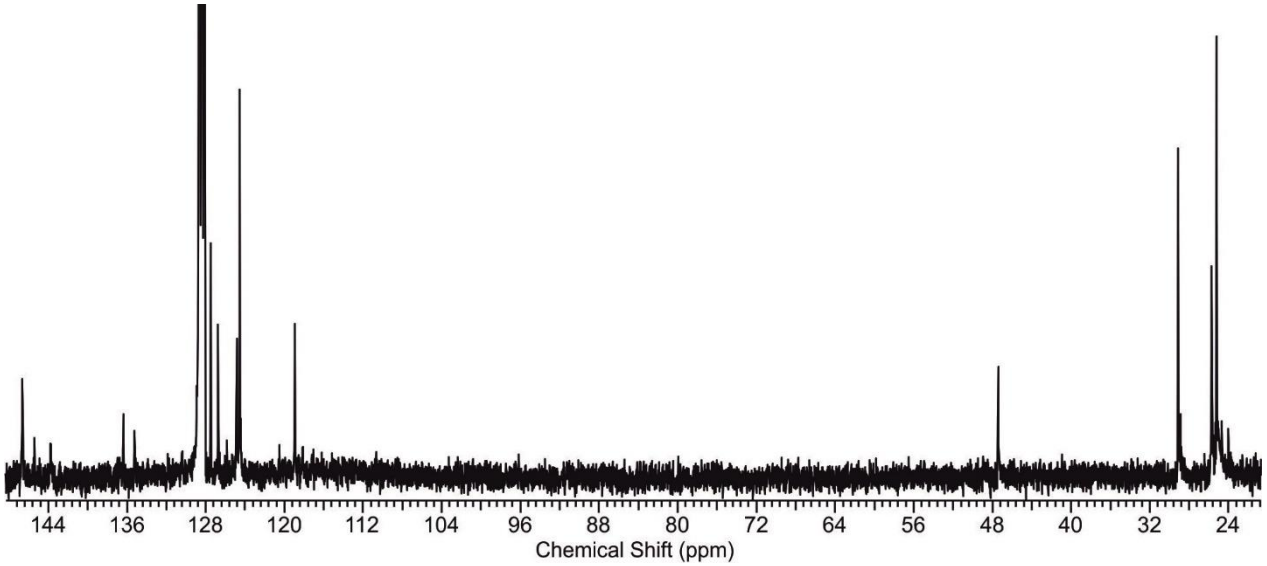

Figure S8. ^{13}C NMR spectrum of complex **5** (100 MHz, C_6D_6, 298 K).

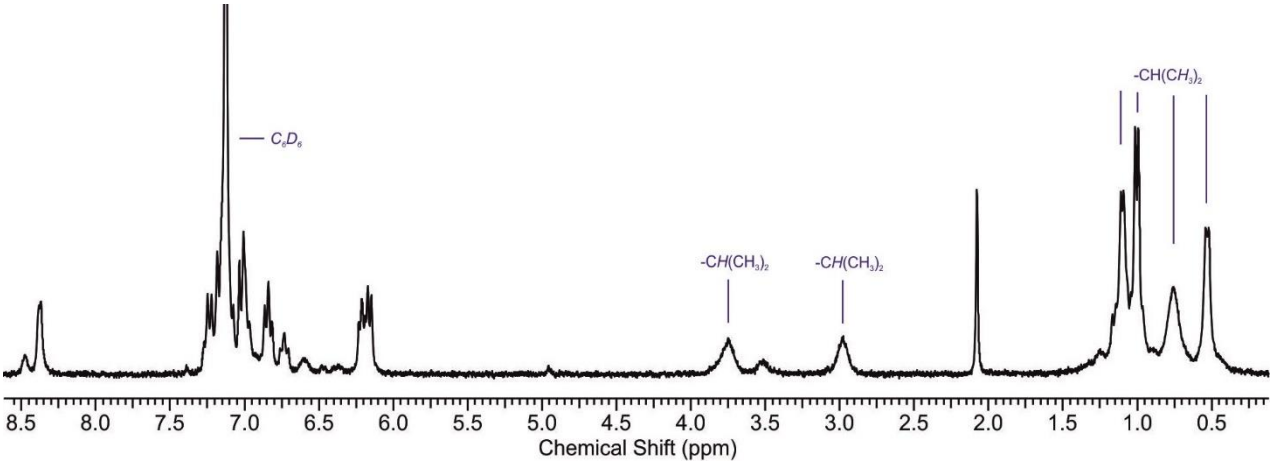

Figure S9. ^{1}H NMR spectrum of complex **6** (300 MHz, C_6D_6, 298 K).