Supporting Information for "A Heterotetrametallic Re-Zn-Zn-Re Complex Generated by an Anionic Rhenium(I) β-Diketiminate"

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General Considerations

All manipulations were carried out under a dry nitrogen atmosphere, either in an MBraun LabStar glovebox or on a Schlenk line using standard techniques. Toluene, diethyl ether, tetrahydrofuran, *n*-pentane, and *n*-hexane were dried by passage through a basic alumina column and were handled and stored under a dry nitrogen atmosphere in standard Strauss flasks or in the glovebox. Hexamethyldisiloxane (HMDSO) was dried over Na/benzophenone, distilled under N_2, and stored in the glovebox prior to use. Deuterated benzene and pyridine were obtained commercially, dried over an appropriate reagent (Na/benzophenone for C_6D_6, CaH_2 for pyridine-d5), and distilled prior to storage in the glovebox over 4 Å molecular sieves. Celite was dried in a 150 °C oven for 24 hours prior to storage in the glovebox. Sodium metal, silver(I) trifluoromethanesulfonate, and anhydrous zinc(II) chloride were obtained from commercial sources and stored in the glovebox. The reported compounds [ORe(η^5-Cp)(BDI)][$SnCl_3$][1] and triethylammonium tetraphenylborate[2] were synthesized using known procedures. NMR spectroscopy data were obtained on Bruker AVQ-400, AVB-400, AV-500 and AV-600 instruments. All ^{1}H and ^{13}C spectra were referenced to the residual peak of the solvent used. Select peak assignments were corroborated with ^{1}H-^{13}C HSQC experiments as necessary. Unless noted otherwise, "room temperature" and "ambient temperature" both refer to approx. 23 °C. Infrared absorption data were obtained using a Thermo Scientific Nicolet iS10 instrument, with the sample chamber under ambient atmosphere. Samples were prepared as Nujol mulls pressed between KBr plates in the glovebox.

Synthetic Procedures

Na[Re(η^5-Cp)(BDI)] (1)

In the glovebox, [ORe(η^5-Cp)(BDI)][$SnCl_3$] (2.60 g, 2.86 mmol), a pre-weighed quantity of metallic sodium (800 mg, 34.8 mmol, 12.2 eq.) cut into approximately 20 equal sized pieces, and an egg-shaped Teflon-coated stir bar were added to a 100 mL pear-shaped Schlenk flask. The flask was sealed, removed from the glovebox, and transferred onto a Schlenk line, where THF (80 mL) was added, ensuring all of the rhenium starting material was dissolved. The reaction mixture, sealed under N_2, was stirred vigorously at ambient temperature for 4 days, with an observable change in color from dark red to a deep maroon-purple color. The volatile components of the reaction mixture were removed in vacuo, and the resulting solids were extracted with 200 mL of diethyl ether. These extracts were filtered through Celite, and concentrated in vacuo to one quarter of their original volume. Hexane (100 mL) was then added, and the solution was concentrated in vacuo to half of its volume (to remove most of the remaining diethyl ether) and crystalline solids were observed. An additional aliquot of hexane (50 mL) was added to this mixture, and the diluted mother liquor was then decanted by cannula transfer. The remaining deep purple crystalline solids were washed with hexane (2 x 50 mL) and dried in vacuo to give **1** (1.36 g, 69% yield). m.p.: 161-168 °C (decomp.). ^{1}H NMR (300 MHz, C_6D_6, 298 K): 7.19 (d, 4H, BDI Ar, *J* = 7.5 Hz), 6.81 (t, 2H, BDI Ar, *J* = 7.5 Hz), 6.13 (bs, 1H, *H*C[MeC(NAr)]$_2$), 4.51 (bs, 5H, Cp), 3.74 (bs, 4H, BDI C*H*(Me)$_2$), 1.60 (bs, 6H, HC[*Me*C(NAr)]$_2$), 1.25 (bs, 12H, BDI CH(*Me*)$_2$), 1.15 (bs, 12H, BDI CH(*Me*)$_2$). ^{13}C NMR (101 MHz, C_6D_6, 298 K): 122.64 (BDI Ar), 120.51 (BDI Ar), 79.08 (Cp), 30.01 (HC[*Me*C(NAr)]$_2$), 29.42 (BDI *C*H(Me)$_2$), 25.78 (BDI CH(*Me*)$_2$), 25.59 (BDI CH(*Me*)$_2$). Due to the fluxional behavior of **1** in solution and the correspondingly low signal-to-noise ratio, we could not observe a ^{13}C NMR signal for the BDI backbone C-H group, as well as several BDI aryl signals typically observed in other Re BDI compounds. Anal. Calcd. for $ReC_{34}H_{46}N_2Na$ (**1**): C, 59.00; H, 6.70; N, 4.05 %. Found: C, 58.70; H, 7.00; N, 3.75 %.

Re(η^5-Cp)(BDI) (2)

In the glovebox, solid **1** (100 mg, 0.144 mmol) ,and silver(I) trifluoromethanesulfonate (37.1 mg, 0.144 mmol) were separately dissolved in diethyl ether (5 mL and 3 mL, respectively). The solution of AgOTf was then added to the solution of **1** with magnetic stirring. The formation of a dark grey precipitate was observed in seconds, and the dark solution became bright red in color. After being stirred for 15 min, the volatile components of the reaction mixture were removed in vacuo. The red residue was extracted with pentane (6 mL). These extracts were filtered through Celite and concentrated in vacuo prior to storage at -40 °C. The following day, **2** was isolated as red crystals (63 mg). Concentration of the mother liquor and storage at -40 °C yielded a second crop (10 mg) of similar purity. Total yield: 73 mg, 76%. m.p.: 137-141 °C (decomp.). ^{1}H NMR (400 MHz, C_6D_6, 298 K): 69.0 (bs), 38.8 (bs), 34.3 (bs), -1.5 (bs), -13.5 (bs), -22.8 (bs), -29.1 (bs). Anal. Calcd. for $ReC_{34}H_{46}N_2$ (**2**): C, 61.03; H, 6.93; N, 4.19 %. Found: C, 60.92; H, 6.91; N, 4.22 %.

Re(H)(η^5-Cp)(BDI) (3)

In the glovebox, solid **1** (100 mg, 0.144 mmol) was dissolved in THF (5 mL) and this solution was set to stir. Separately, solid triethylammonium tetraphenylborate (60.8 mg, 0.144 mmol) was dissolved in THF (4 mL), and this colorless solution was added to the stirred solution of **1**. In seconds, an emerald green solution was observed. After 15 minutes, the volatile components of the reaction mixture were removed in vacuo, giving a tacky solid residue that was triturated with 2 mL of HMDSO. The residue was then extracted with 7 mL HMDSO, and these extracts were filtered through Celite. The filtered extracts were concentrated in vacuo and stored at -40 °C to give **3** as green crystals (79 mg, 82%). m.p.: 125-128 °C. ^{1}H NMR (600 MHz, C_6D_6, 298 K): 7.11 (bs, 2H, BDI Ar), 6.95 (bs, 2H, BDI Ar), 6.93 (t, 2H, BDI Ar, *J* = 7.7 Hz), 6.40 (s, 1H, *H*C[MeC(NAr)]$_2$), 4.80 (s, 5H, Cp), 3.44 (bs, 2H, BDI C*H*(Me)$_2$), 2.80 (s, 6H, HC[*Me*C(NAr)]$_2$), 1.95 (bs, 2H, BDI C*H*(Me)$_2$), 1.22-1.00 (m, 18H, BDI CH(*Me*)$_2$), 0.91 (bs, 6H, BDI CH(*Me*)$_2$), -27.95 (s, 1H, Re-*H*). ^{13}C NMR (151 MHz, C_6D_6, 298 K): 165.42 (HC[Me*C*(NAr)]$_2$), 158.85 (BDI Ar), 139.51 (BDI Ar), 138.55 (BDI Ar), 124.94 (BDI Ar), 123.81 (BDI Ar), 122.42 (BDI Ar), 105.44 (H*C*[MeC(NAr)]$_2$), 78.67 (Cp), 29.40 (BDI *C*H(Me)$_2$), 28.15 (BDI *C*H(Me)$_2$), 25.19 (BDI CH(*Me*)$_2$), 24.74 (BDI CH(*Me*)$_2$), 24.46 (BDI CH(*Me*)$_2$), 24.16 (BDI CH(*Me*)$_2$), 23.28 (HC[*Me*C(NAr)]$_2$). FT-IR (Nujol): 2028 cm^{-1} (Re-H). Anal. Calcd. for $ReC_{34}H_{47}N_2$ (**3**): C, 60.93; H, 7.07; N, 4.18 %. Found: C, 60.79; H, 7.24; N, 4.12 %.

[ZnRe(η^5-Cp)(BDI)]$_2$ (4)

In the glovebox, solid **1** (250 mg, 0.361 mmol) was dissolved in THF (6 mL). To this stirred solution was added $ZnCl_2$ (24.6 mg, 0.181 mmol) dissolved in 4 mL THF. This mixture was stirred at ambient temperature for 30 minutes, and then its volatile components were removed in vacuo. The residue was triturated with hexane (2 x 2 mL) to remove residual THF. The dry, dark red residue was then extracted with toluene (8 mL), and these extracts were filtered through Celite. The volatile components of the filtered extracts were removed in vacuo, and then hexane (10 mL) was added to give a dark red-brown, homogeneous solution that was left to sit at room temperature. Over the course of several days, large, block-shaped green crystals formed. These crystals were isolated, washed with pentane (2 mL), and dried in vacuo to give **4** (72 mg). A second crop of **4** of similar purity (10 mg) could be isolated by a similar method, using half the volume of hexane (ca. 5 mL) in the crystallization conditions. Total yield: 82 mg, 62%. m.p.: 181-186 °C (decomp.). ^{1}H NMR (600 MHz, C_6D_6, 298 K): 7.18 (dd, 2H, BDI Ar, *J* = 7.1, 2.2 Hz), 7.06 (dd, 2H, BDI Ar, *J* = 7.5, 1.6 Hz), 7.03-6.97 (m, 6H, BDI Ar), 6.95 (t, 2H, BDI Ar, *J* = 7.6 Hz), 6.31 (s, 2H, *H*C[MeC(NAr)]$_2$), 4.51 (s, 10H, Cp), 3.79 (sept, 2H, BDI C*H*(Me)$_2$, *J* = 6.8 Hz), 3.61 (sept, 2H, BDI C*H*(Me)$_2$, *J*

= 6.8 Hz), 2.46 (s, 6H, HC[*Me*C(NAr)]$_2$), 2.42 (s, 6H, HC[*Me*C(NAr)]$_2$), 1.99-1.91 (m, 4H, BDI C*H*(Me)$_2$), 1.40 (d, 6H, BDI CH(*Me*)$_2$, *J* = 6.7 Hz), 1.28 (d, 6H, BDI CH(*Me*)$_2$, *J* z= 6.7 Hz), 1.23-1.19 (m, 12H, BDI CH(*Me*)$_2$), 1.03-1.01 (m, 12H, BDI CH(*Me*)$_2$), 0.99-0.95 (m, 12H, BDI CH(*Me*)$_2$). ^{13}C NMR (151 MHz, C_6D_6, 298 K): 159.68 (HC[Me*C*(NAr)]$_2$), 159.40 (HC[Me*C*(NAr)]$_2$), 158.22 (BDI Ar), 158.15 (BDI Ar), 140.45 (BDI Ar), 140.40 (BDI Ar), 136.91 (BDI Ar), 136.88 (BDI Ar), 124.70 (BDI Ar), 124.67 (BDI Ar), 123.96 (BDI Ar), 123.94 (BDI Ar), 122.64 (BDI Ar), 122.62 (BDI Ar), 105.10 (H*C*[MeC(NAr)]$_2$), 72.03 (Cp), 30.02 (BDI *C*H(Me)$_2$), 29.98 (BDI *C*H(Me)$_2$), 27.95 (BDI *C*H(Me)$_2$), 27.72 (BDI *C*H(Me)$_2$), 25.35 (BDI CH(*Me*)$_2$), 25.08 (BDI CH(*Me*)$_2$), 24.93 (BDI CH(*Me*)$_2$), 24.30 (BDI CH(*Me*)$_2$), 24.25 (BDI CH(*Me*)$_2$), 24.22 (BDI CH(*Me*)$_2$), 24.09 (BDI CH(*Me*)$_2$), 23.94 (HC[*Me*C(NAr)]$_2$). Anal. Calcd. for $Re_2Zn_2C_{68}H_{92}N_4$ (**4**): C, 55.59; H, 6.32; N, 3.82 %. Found: C, 55.81; H, 6.47; N, 3.59 %.

[(μ-OTf)ZnRe(η^5-Cp)(BDI)]$_2$ (5)

Solid **4** (50.0 mg, 0.0340 mmol) was dissolved in toluene (6 mL) and set to stir. Solid silver(I) trifluoromethanesulfonate (9.2 mg, 0.036 mmol) was added to this solution, and the mixture was stirred for 30 minutes at ambient temperature. The volatile components of the reaction mixture were removed and the residue was triturated with hexane (1 mL), washed with additional hexane (3 x 3 mL) to remove the **2** formed in the reaction, and finally extracted with Et_2O (8 mL). These extracts were filtered through Celite, and their volatile components were removed in vacuo. The resulting solids were washed with pentane (3 x 1 mL) to give **5** as green microcrystalline solids (16 mg, 54 %). m.p.: 153-158 ^{o}C (decomp.). ^{1}H NMR (600 MHz, C_6D_6, 298 K): 7.14 (d, 4H, BDI Ar, *J* = 8.3), 6.95-6.89 (m, 8H, BDI Ar), 6.49 (s, 2H, *H*C[MeC(NAr)]$_2$), 5.08 (s, 10H, Cp), 3.88 (sept, 4H, BDI C*H*(Me)$_2$, *J* = 6.8 Hz), 2.82 (s, 12H, HC[*Me*C(NAr)]$_2$), 1.75 (sept, 4H, BDI C*H*(Me)$_2$, *J* = 6.7 Hz), 1.57-1.48 (m, 24H, BDI CH(*Me*)$_2$), 1.01 (d, 12H, BDI CH(*Me*)$_2$, *J* = 6.7 Hz), 0.90 (d, 12H, BDI CH(*Me*)$_2$, *J* = 6.7 Hz). ^{13}C NMR (151 MHz, C_6D_6, 298 K): 159.43 (HC[Me*C*(NAr)]$_2$), 139.38 (BDI Ar), 137.95 (BDI Ar), 125.27 (BDI Ar), 124.21 (BDI Ar), 122.78 (BDI Ar), 106.88 (H*C*[MeC(NAr)]$_2$), 76.26 (Cp), 30.10 (BDI *C*H(Me)$_2$), 28.63 (BDI *C*H(Me)$_2$), 25.82 (BDI *C*H(Me)$_2$), 25.23 (BDI *C*H(Me)$_2$), 24.00 (BDI CH(*Me*)$_2$), 23.95 (HC[*Me*C(NAr)]$_2$), 23.24 (BDI CH(*Me*)$_2$). ^{19}F NMR (376 MHz, C_6D_6, 298 K): 77.22 (bs). Despite multiple attempts to obtain a satisfactory elemental analysis for **5**, we consistently observed different, very low (by 6-12%) values for its carbon content. Despite this, we believe our other characterization data supports our assignment of its composition and structure.

NMR Spectra

Figure S1. ^{1}H NMR spectrum of **1** in pyridine-d5. A residual amount of hexane is observable.

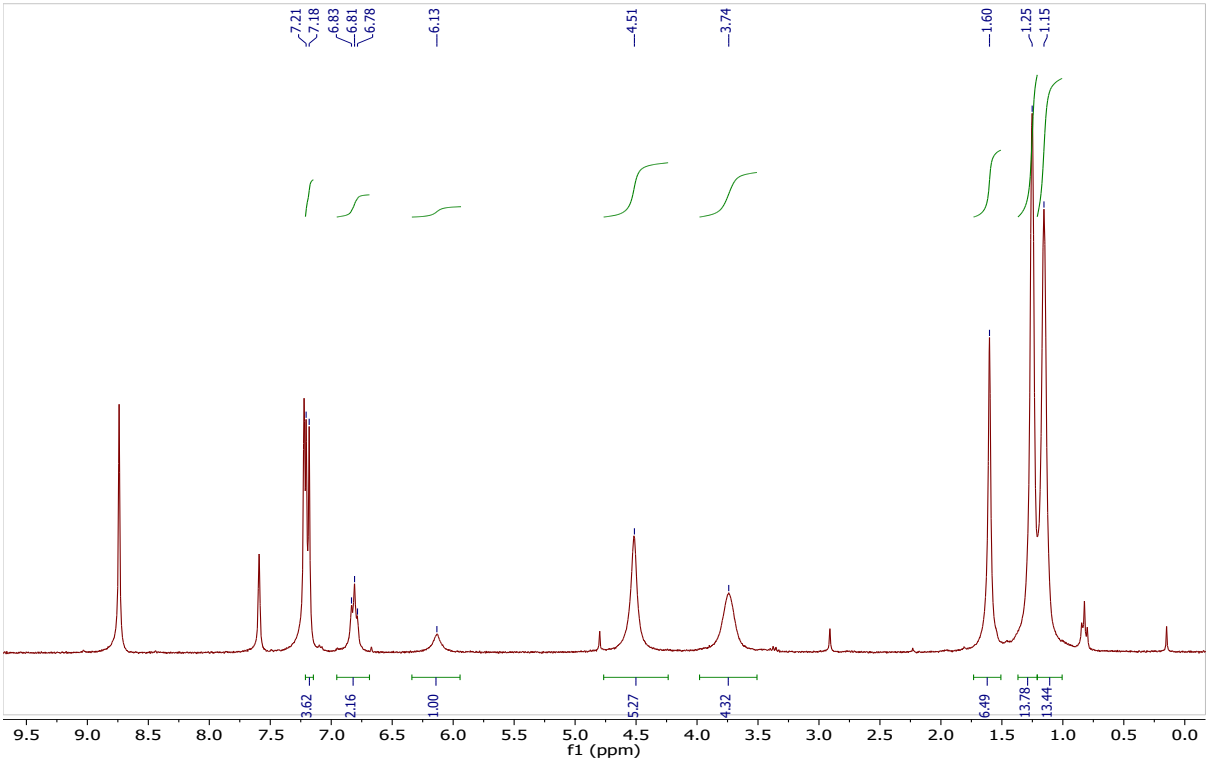


Figure S2. ^{13}C NMR spectrum of **1** in pyridine-d5. A residual amount of hexane is observable.

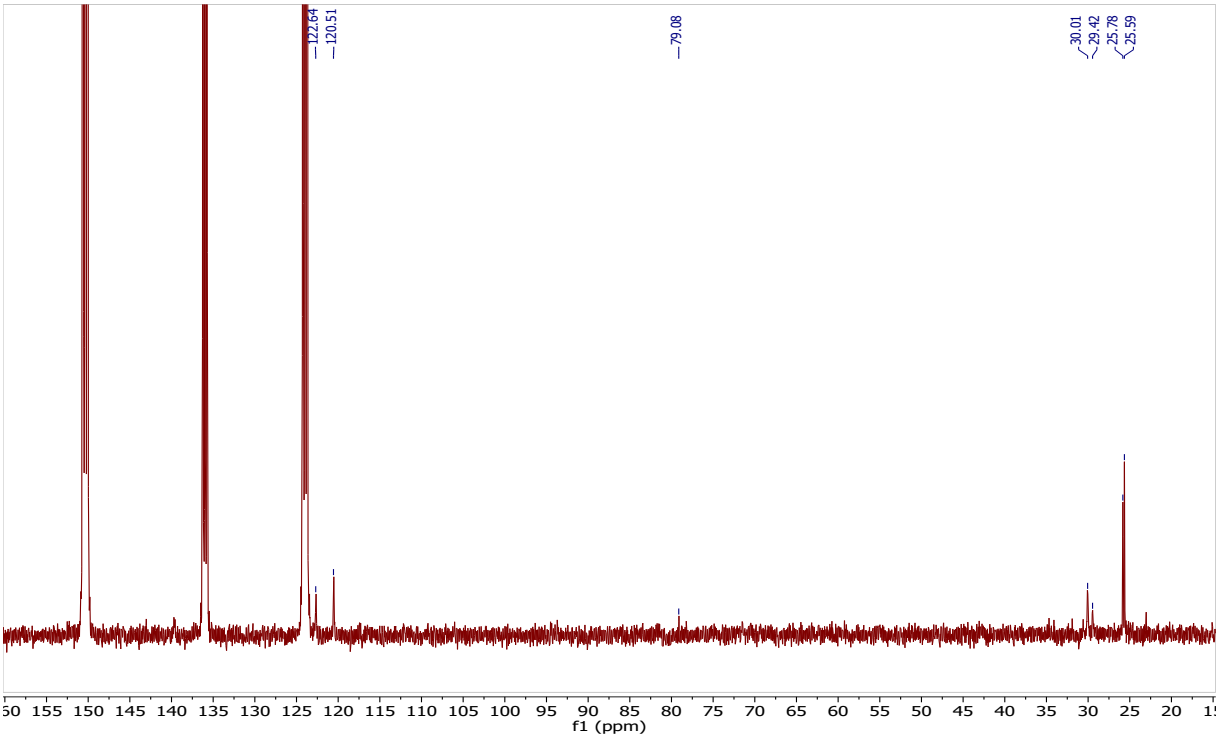


Figure S3. ^{1}H NMR spectrum of **2** in C_6D_6. Small quantities of diamagnetic products (including **3**) arising from the thermal decomposition of **2** are observable.

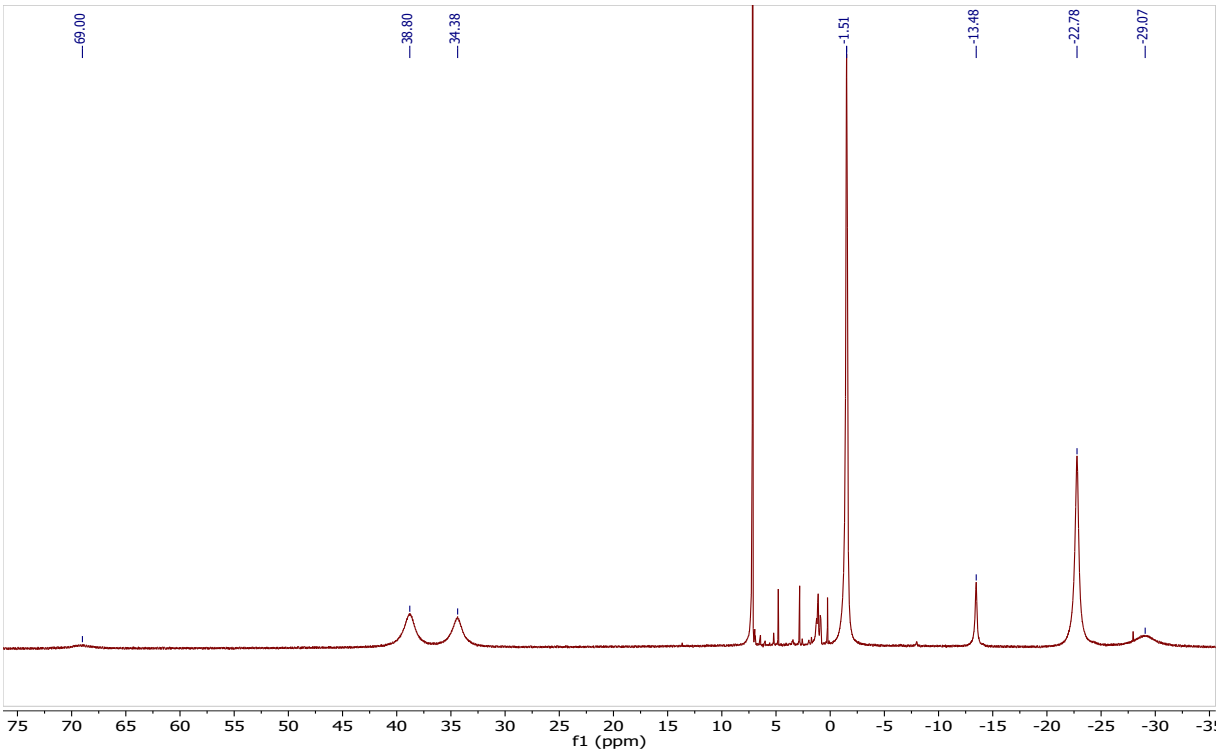


Figure S4. ^{1}H NMR spectrum of **3** in C_6D_6. A residual amount of HMDSO is observable.

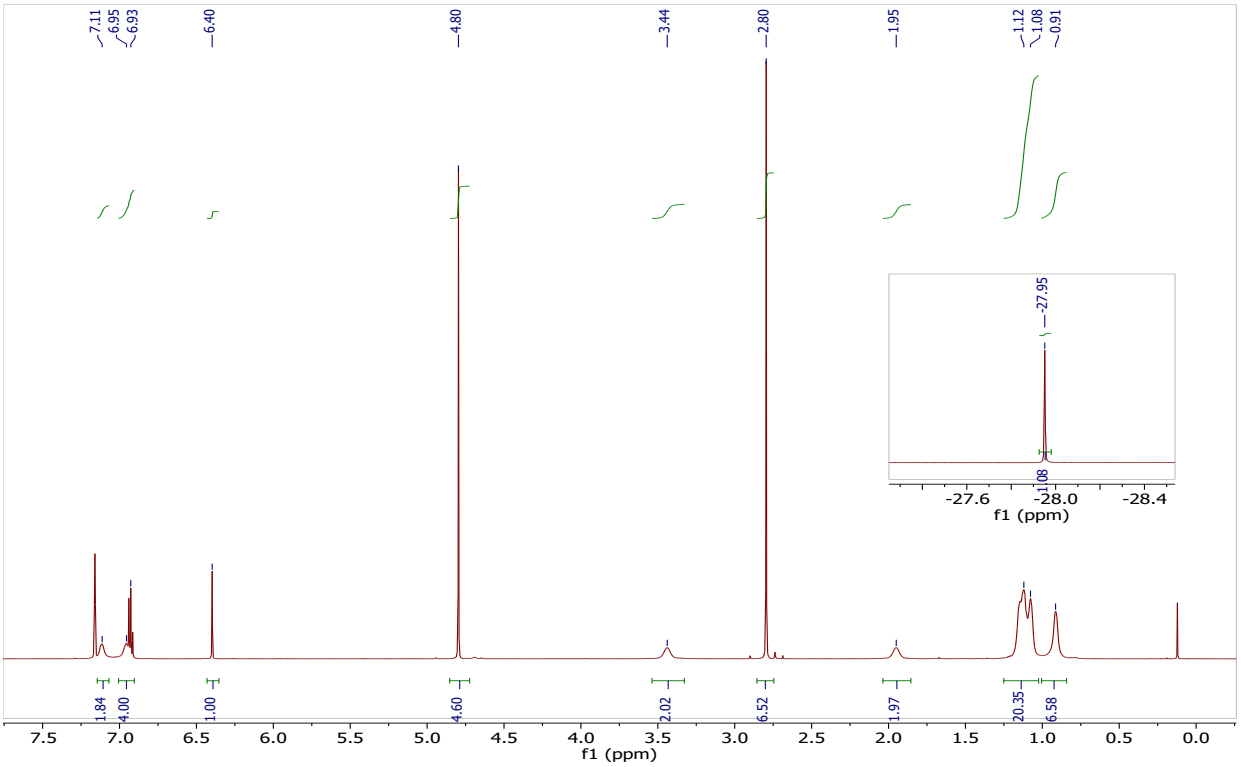


Figure S5. ^{13}C NMR spectrum of **3** in C_6D_6. A residual amount of HMDSO is observable.

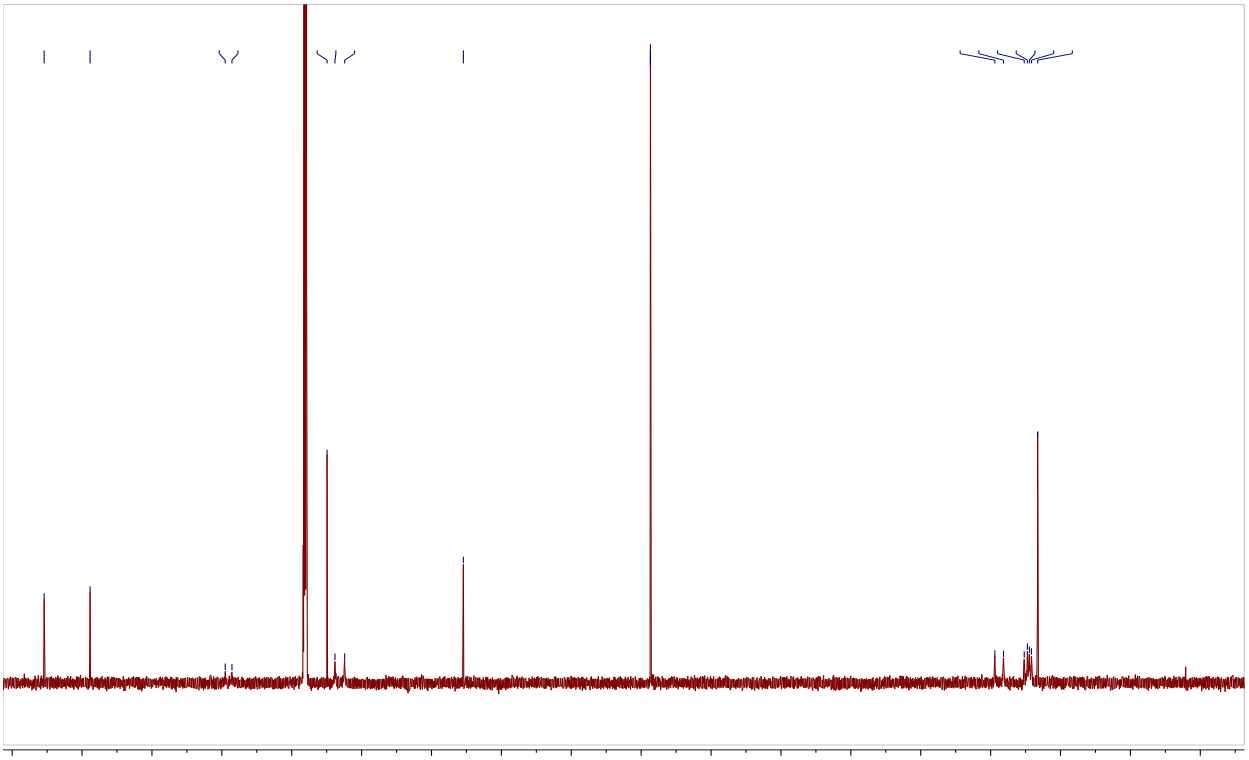


Figure S6. ^{1}H NMR spectrum of **4** in C_6D_6. A residual equivalent of *n*-hexane is observable.

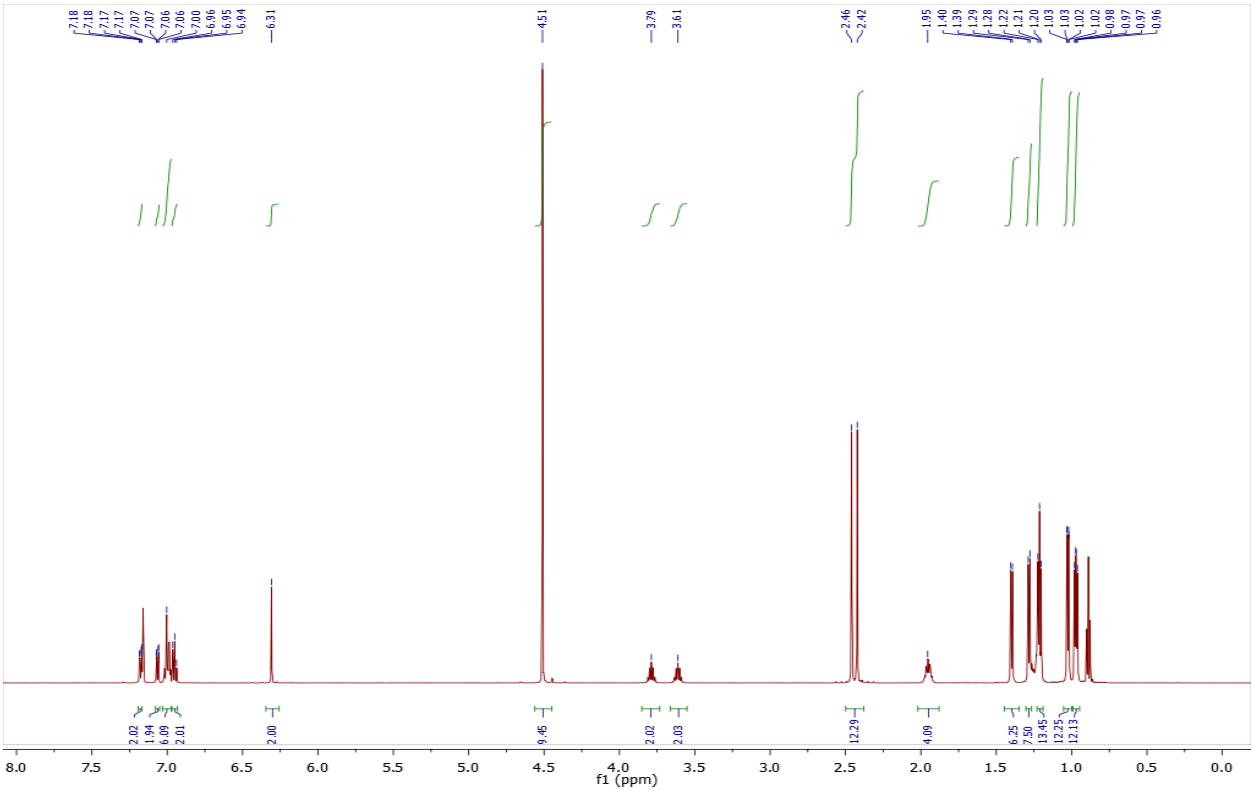


Figure S7. ^{13}C NMR spectrum of **4** in C_6D_6. A residual equivalent of *n*-hexane is observable.

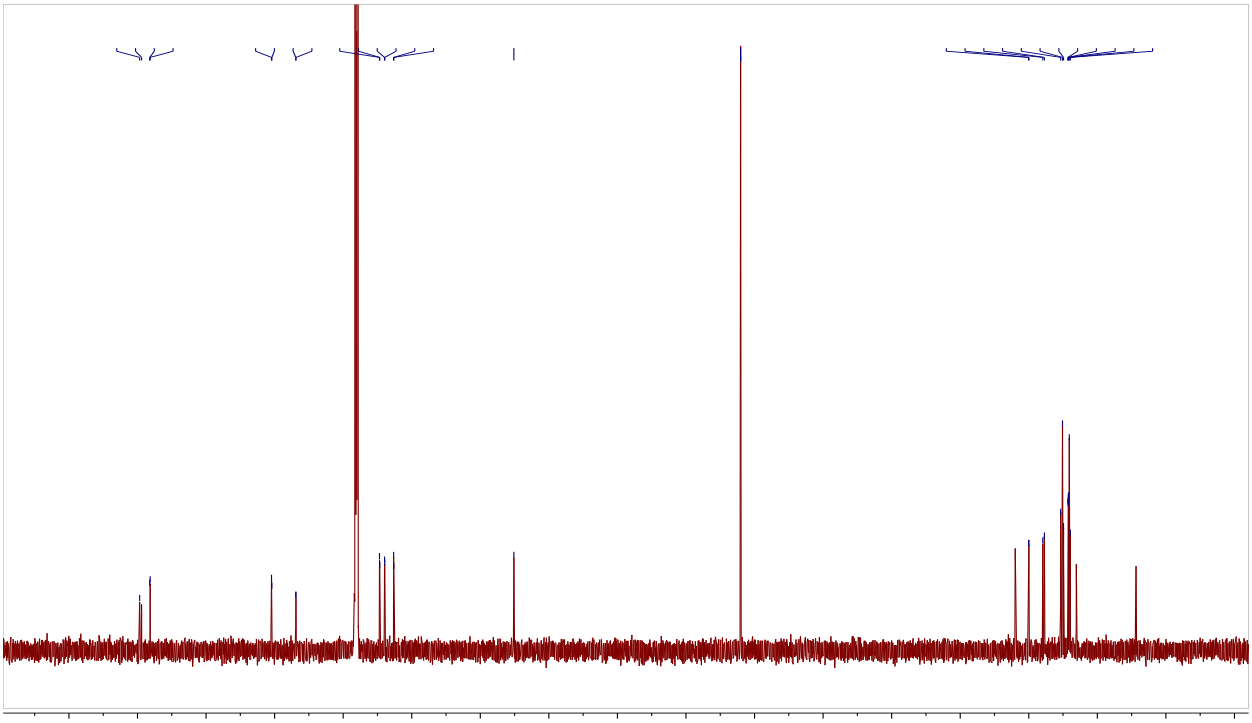


Figure S8. ^{1}H NMR spectrum of **5** in C_6D_6. A residual half equivalent of *n*-pentane and trace Et_2O are observable.

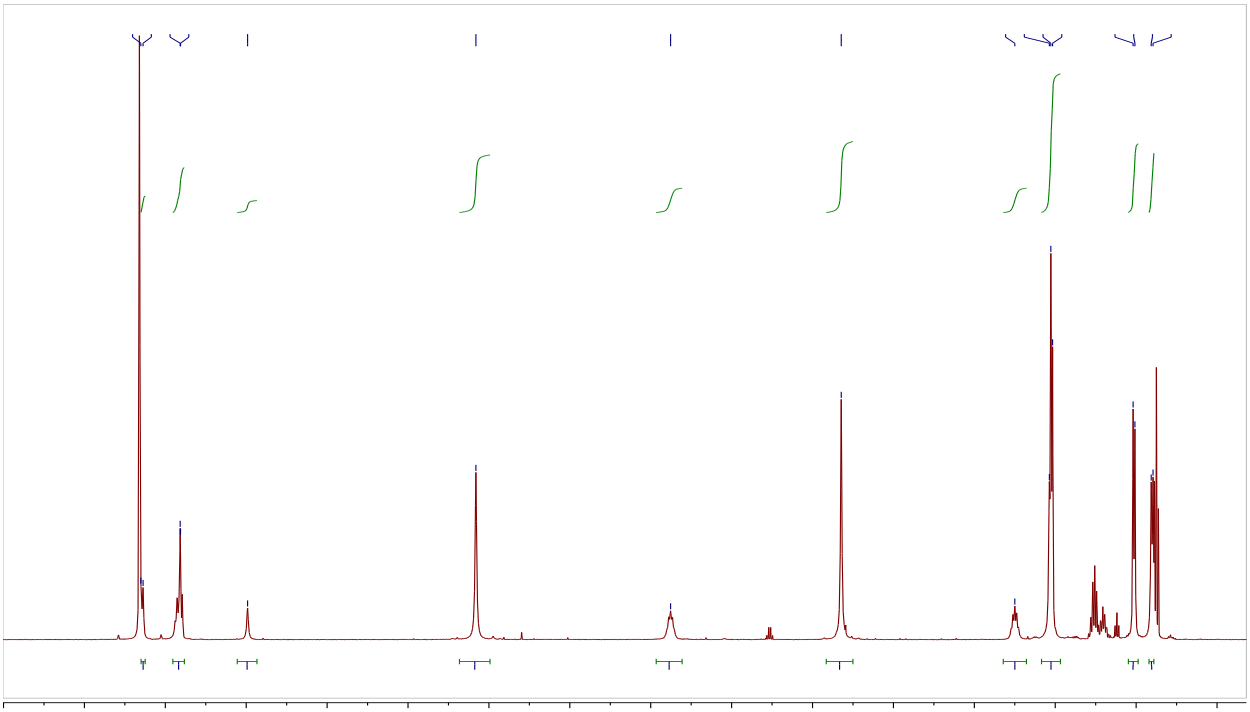


Figure S9. ^{13}C NMR spectrum of **5** in C_6D_6. A residual half equivalent of *n*-pentane is observable.

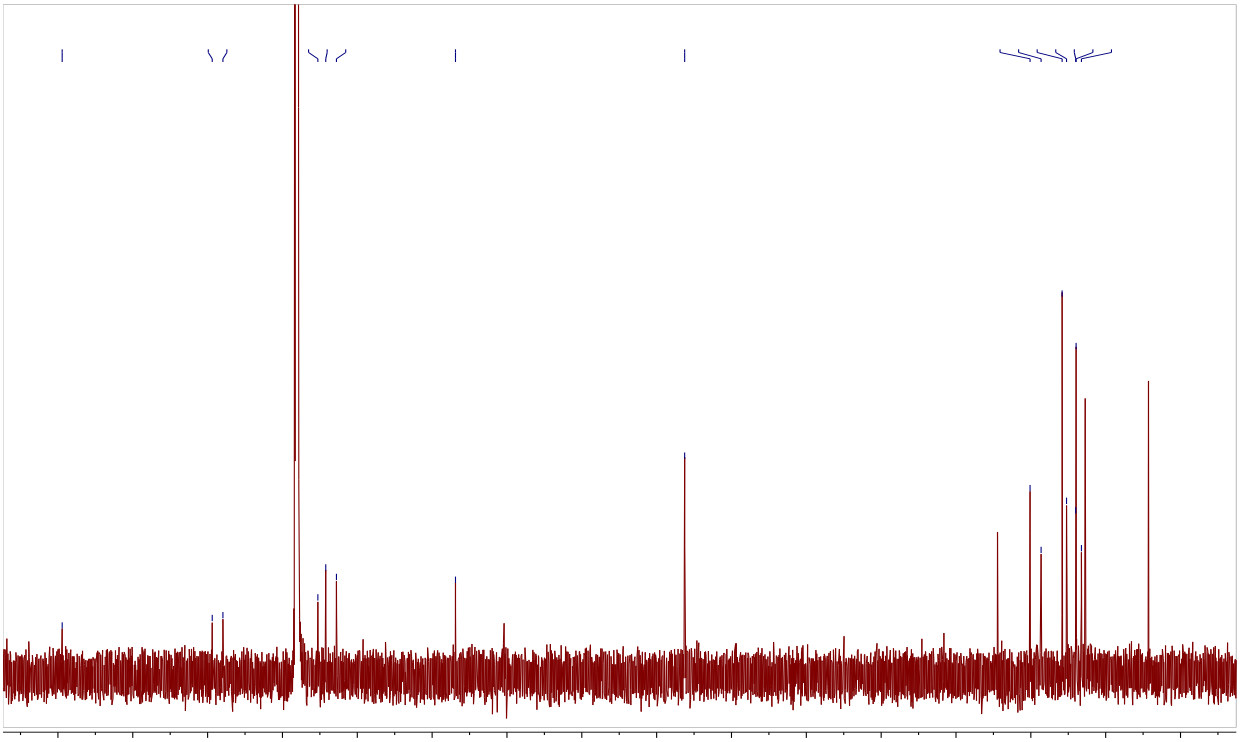
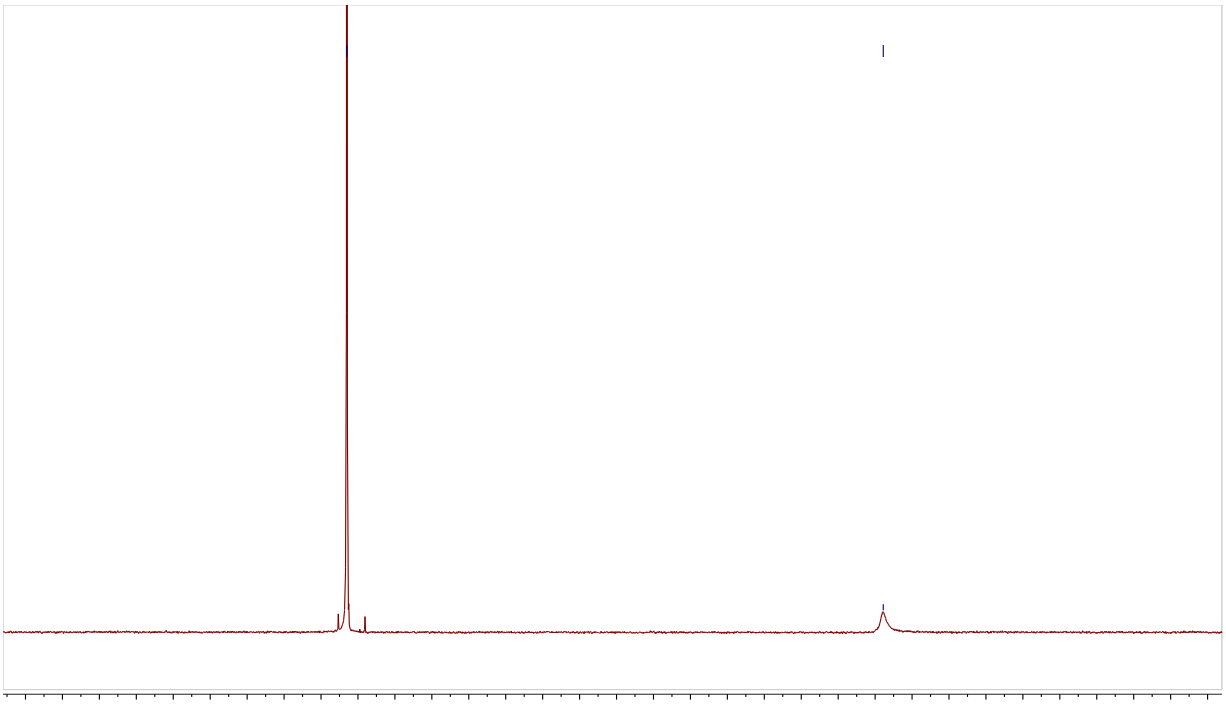


Figure S10. ^{19}F NMR spectrum of **5** in C_6D_6. A large peak for the α,α,α-trifluorotoluene internal reference is labeled at -62.70 ppm.



X-Ray Crystallographic Information

X-ray diffraction data were collected at CheXray, UC Berkeley (**1**, **2**, **4**, **5**) and the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory (**3**). At CheXray, measurements for **1** were taken using a Rigaku XtalLAB P200 instrument equipped with a rotating-anode Mo X-ray source and a Pilatus 200K detector, and the data was analyzed, reduced, and solved using the CrysAlisPro software package and Olex2 (SHELXT and SHELXL).[3,4,5] Measurements for **2**, **4**, and **5** were taken using a Bruker APEXII Quazar diffractometer equipped with a micro-focus Mo X-ray source and a Bruker APEX-II CCD detector, with data analyzed and reduced using either the Bruker APEX2 or APEX3 software package, and solutions and refinements conducted using WinGX (SHELXT and SHELXL-2014).[6,7] Measurements for **3** were taken using the ALS beam line 12.2.1, using a monochromated beam of 17 keV synchrotron radiation and a Bruker D8 diffractometer equipped with a Bruker PHOTON II CPAD detector. Diffraction data for **3** were analyzed and reduced using the Bruker APEX3 software package, and the structure was solved and refined using SHELXT and SHELXL-2014 as implemented by WinGX. All structures were collected at 100 K in a stream of dry nitrogen. In refining the structure of **4**, the SQUEEZE program in PLATON was utilized to remove electron density associated with a highly disordered hexane molecule.[8] All structures have been deposited to the Cambridge Crystallographic Data Centre (CCDC), with deposition numbers 1877453 (**1**), 1877454 (**2**), 1877455 (**3**), 1877456 (**4**), and 1877457 (**5**).

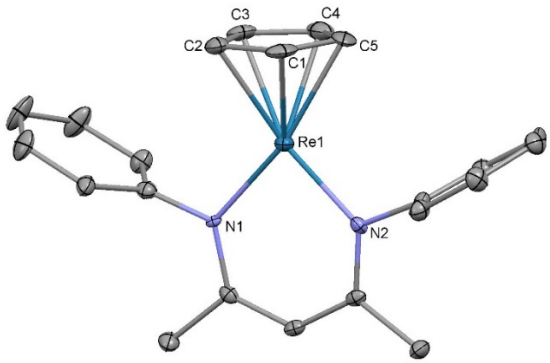


Figure S11. X-ray crystal structure of **2** with 50% probability ellipsoids. H-atoms and BDI isopropyl groups have been removed for clarity.

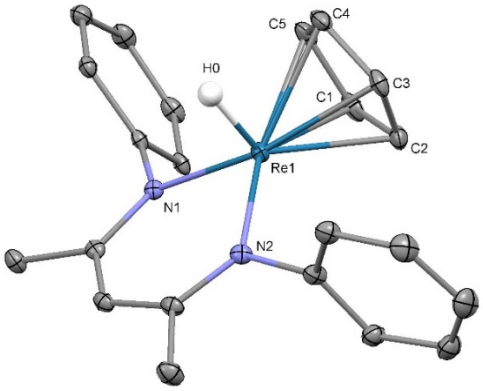


Figure S12. X-ray crystal structure of **3** with 50% probability ellipsoids. H-atoms (except for the metal hydride) and BDI isopropyl groups have been removed for clarity.

Table S1. Crystallographic details and refinement metrics.

	1	**2**	**3**	**4 • *n*-Hexane**	**5 • Et_2O**
Chemical formula	$C_{34}H_{46}N_2ORe$ Na	$C_{34}H_{46}N_2Re$	$C_{34}H_{47}N_2Re$	$C_{74}H_{106}N_4Re_2$ Zn_2	$C_{74}H_{102}N_4O_7F_6$ $S_2Re_2Zn_2$
Formula weight	691.92	668.93	669.93	1554.76	1840.85
Color, habit	Red, plank	Red, tablet	Green, block	Orange, block	Green, block
Temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	Orthorhombic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	Pnma	$P2_1/n$	P-1	P-1	P-1
a (Å)	12.1625(3)	12.5845(6)	9.6137(4)	12.6151(2)	11.9790(3)
b (Å)	21.0519(7)	18.1223(7)	12.4780(6)	12.7440(2)	12.3925(3)
c (Å)	12.4534(4)	13.8772(6)	13.2623(6)	22.8461(4)	13.8937(3)
α (°)	90	90	73.366(2)	88.556(1)	97.317(1)
β (°)	90	106.396(2)	85.413(2)	77.634(1)	109.657(1)
γ (°)	90	90	84.457(2)	73.542(1)	94.520(1)
V ($Å^3$)	3188.61(17)	3036.1(2)	1514.95(12)	3438.22(10)	1910.09(8)
Z	4	4	2	2	1
Density (Mg m^{-3})	1.441	1.463	1.469	1.502	1.600
F(000)	1400	1356	680	1578	926
Radiation Type	MoK_α	MoK_α	Synchrotron	MoK_α	MoK_α
μ (mm^{-1})	3.848	4.026	4.271	4.241	3.901
Crystal size (mm^3)	0.430 x 0.070 x 0.060	0.060 x 0.030 x 0.010	0.070 x 0.060 x 0.055	0.300 x 0.200 x 0.060	0.190 x 0.160 x 0.120
Meas. Refl.	34993	48933	16811	51839	33379
Indep. Refl.	3350	5570	6962	14109	7833
R(int)	0.1316	0.0607	0.0348	0.0360	0.0318
Final R indices	R = 0.0371	R = 0.0336	R = 0.0223	R = 0.0218	R = 0.0198
[I > 2σ(I)]	R_w = 0.0863	R_w = 0.0693	R_w = 0.558	R_w = 0.0462	R_w = 0.0411
Goodness-of-fit	1.032	1.059	1.095	0.995	1.029
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	3.307, -1.997	1.852, -0.754	0.812, -1.695	0.734, -0.728	0.628, -0.539

Computational Details and Coordinates of Optimized Structures

Calculations were carried out with the *Gaussian09* program[9] with the B3PW91-GD3BJ,[10,11] that includes dispersion effects according to the Grimme's scheme. The Zn and Re atom were treated with the corresponding Stuttgart-Dresden RECP (relativistic effective core potential) in combination with its adapted basis sets,[12] and augmented by an extra polarization function.[13] For all the remaining atoms the 6-31G(d,p) basis set was used.[14] Geometry optimizations were carried out without any symmetry restrictions. Natural population analysis (NPA) was performed using Weinhold's methodology.[15] Finally, Chemcraft is used for the visualization of the molecular orbitals.[16]

Table S2. Coordinates for the Optimized Structure of **4**.

6	12.139056000	0.695555000	15.056976000
1	11.075578000	0.502861000	15.059927000
6	12.899911000	1.248519000	16.117458000
1	12.522091000	1.499470000	17.098493000
6	14.289417000	1.308082000	15.702365000
1	15.119910000	1.606750000	16.327412000
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75	14.757839000	7.365291000	19.519242000

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