## *SUPPORTING INFORMATION*

# Metal-Rich Oxametallaboranes of Group 5 Metals: Synthesis and Structure of a Face-Fused $\mu_7$-Boride Cluster

*Rini Prakash[†], Anangsha De[†], Bakthavachalam Kirubakaran[†] and Sundargopal Ghosh[†]**

[†]*Department of Chemistry, Indian Institute of Technology Madras, Chennai, 600 036, India.*

*Fax: +91 44-22574202; Tel: +91 44- 22574230; E-mail: sghosh@iitm.ac.in*

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## I Supplementary Data

**Table S1.** Crystallographic data and structure refinement information for compounds **1**, **3** and **4**.

| | **1** | **3** | **4** |
|---|---|---|---|
| CCCDC no. | 1862624 | 1862625 | 1862626 |
| Empirical formula | $C_{20}H_{38}B_4Nb_2O$ | $C_{30}H_{42}B_4Nb_2O_{11}Ru_4$ | $C_{28}H_{38}B_4Ta_2O_9Ru_3$ |
| Formula weight | 523.56 | 1211.98 | 1226.93 |
| Crystal system | triclinic | orthorhombic | triclinic |
| Space group | *P*-1 | $P2_12_12_1$ | *P*-1 |
| *a* (Å) | 8.7671(4) | 13.0386(4) | 10.2153(12) |
| *b* (Å) | 10.3397(5) | 16.0508(4) | 11.4968(14) |
| *c* (Å) | 15.2338(6) | 19.5876(6) | 16.636(2) |
| *α* (°) | 70.838(2) | 90 | 85.258(6) |
| *β* (°) | 77.033(2) | 90 | 88.641(5) |
| *γ* (°) | 73.132(2) | 90 | 68.509(5) |
| V (Å$^3$) | 1235.49(10) | 4099.3(2) | 1811.7(4) |
| *Z* | 2 | 4 | 2 |
| $D_{calc}$(g/cm$^3$) | 1.407 | 1.961 | 2.249 |
| *F* (000) | 536 | 2344 | 720 |
| *μ* (mm$^{-1}$) | 0.934 | 2.027 | 7.284 |
| θ Range (°) | 2.9−24.8 | 2.26−25.12 | 3.24−25.68 |
| no. of reflections collected | 4349 | 7120 | 6345 |
| no. of unique reflns [$I > 2\sigma(I)$] | 2919 | 6204 | 4730 |
| goodness−of−fit on $F^2$ | 1.037 | 1.053 | 1.030 |
| R1, *w*R2 [$I > 2\sigma(I)$] | 0.0883, 0.1982 | 0.0452, 0.0733 | 0.0691, 0.0797 |
| R1, *w*R2 (all data) | 0.0609, 0.1695 | 0.0342, 0.0674 | 0.0414, 0.0716 |

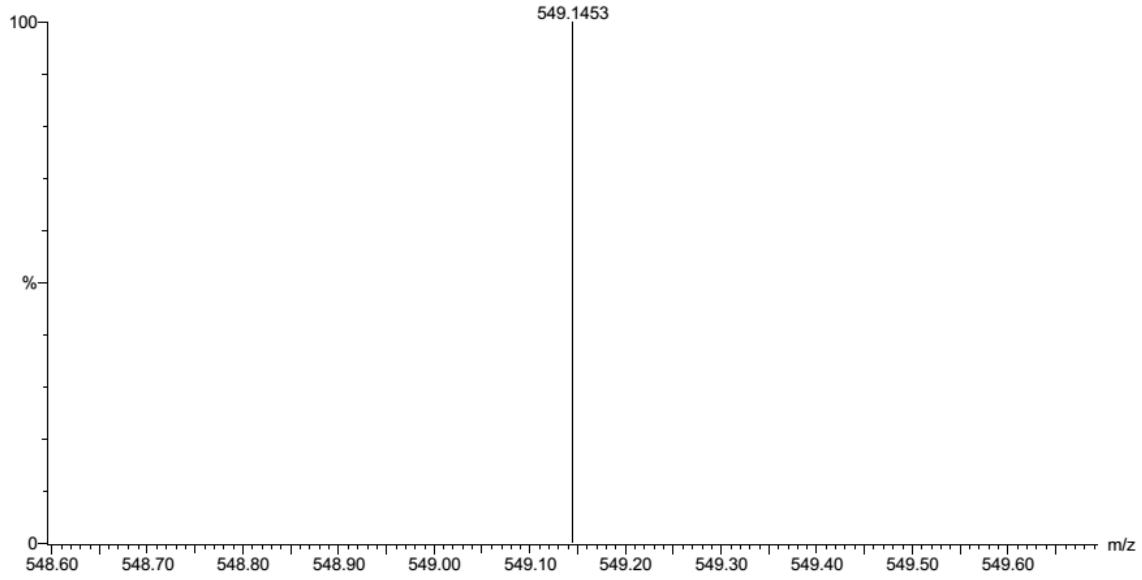
## II Spectroscopic details

**Elemental Composition Report** **Page 1**

**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
59 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-20 H: 0-40 B: 0-4 O: 0-1 Na: 0-1 Nb: 0-2

SGG-NBO
28022018-04-SGG-NBO 4 (0.101) AM (Cen,5, 80.00, Ar,5000.0,0.00,1.00); Sb (1,40.00 ); Sm (Mn, 1x0.00); Cm (2:4) TOF MS ES+
2.24e+003




| | | | | | | |
|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | |
| Maximum: | | 5.0 | 10.0 | 50.0 | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 549.1453 | 549.1477 | -2.4 | -4.4 | 2.5 | n/a | C20 H40 B4 O Na Nb2 |

**Fig. S1.** HRMS spectrum of **1**

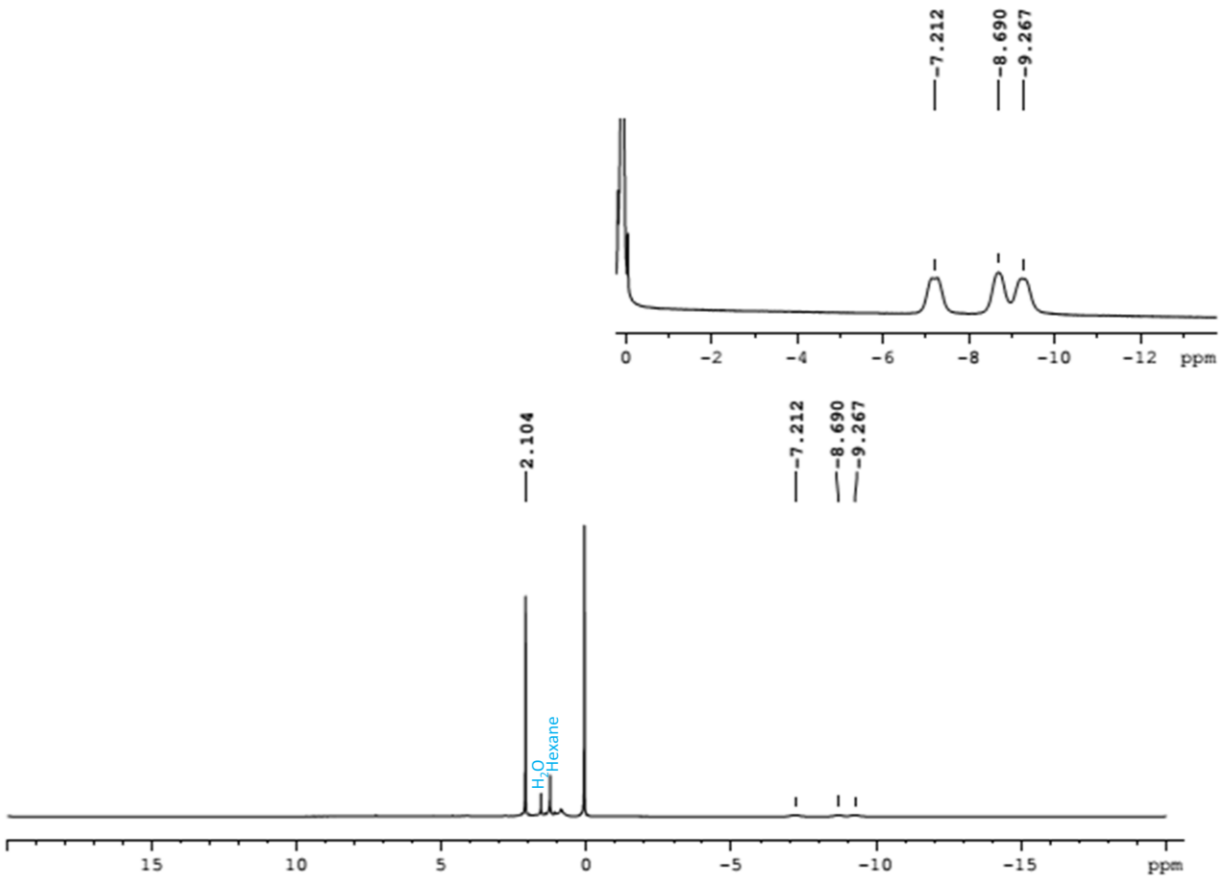



**Fig. S2.** $^{1}H$ NMR spectrum of **1** in $CDCl_3$

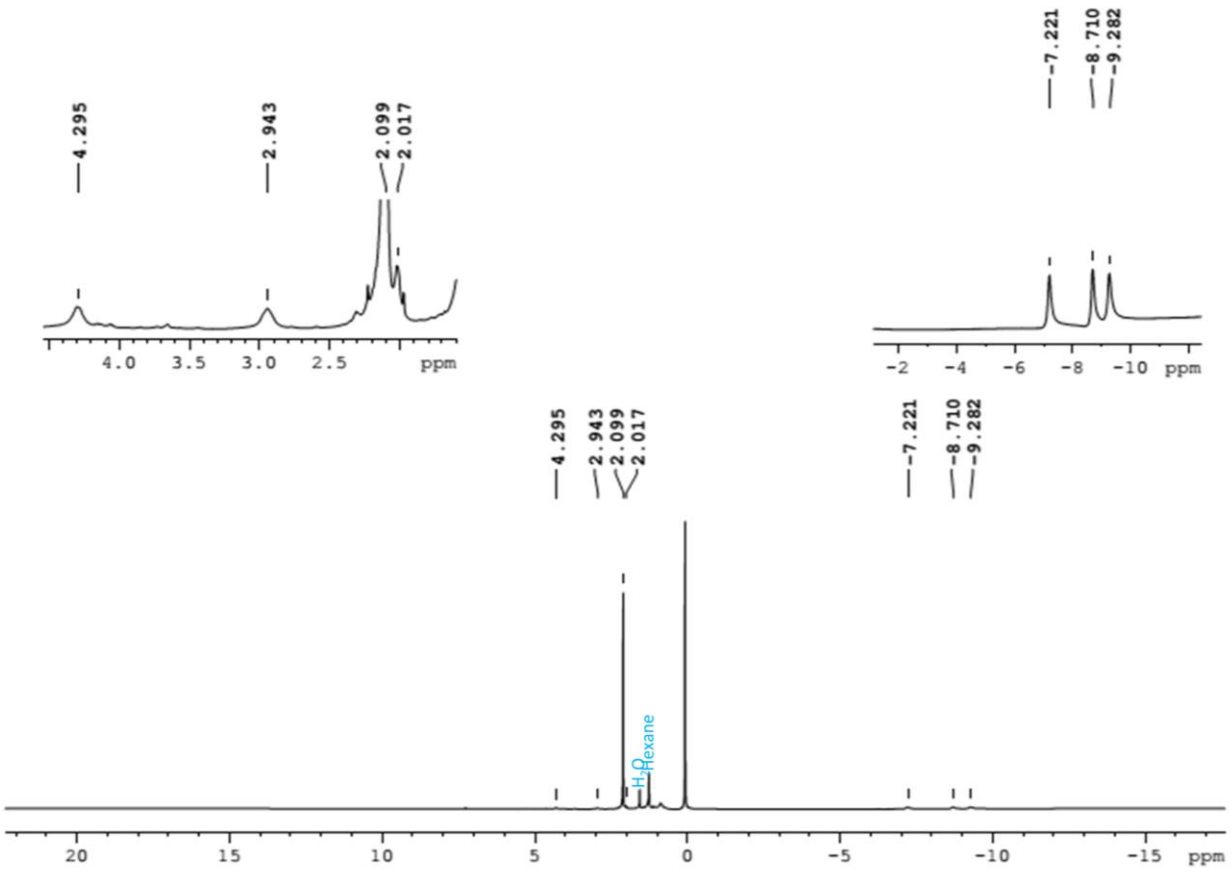



**Fig. S3.** $^{1}H\{^{11}B\}$ NMR spectrum of **1** in $CDCl_3$

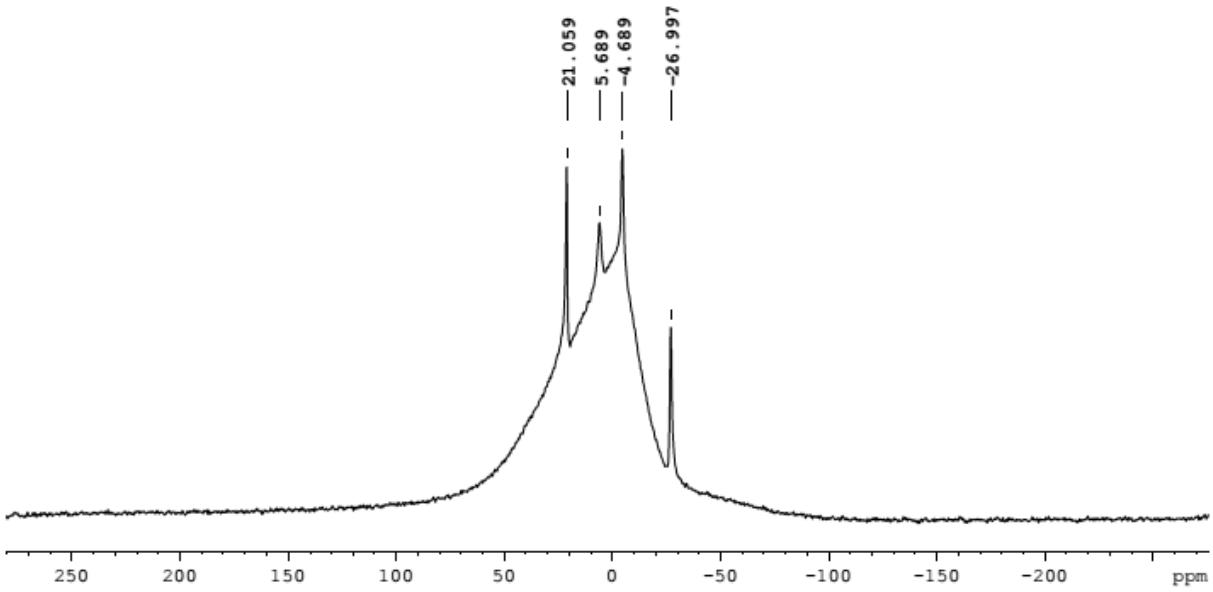



**Fig. S4.** $^{11}B\{^{1}H\}$ NMR spectrum of **1** in $CDCl_3$

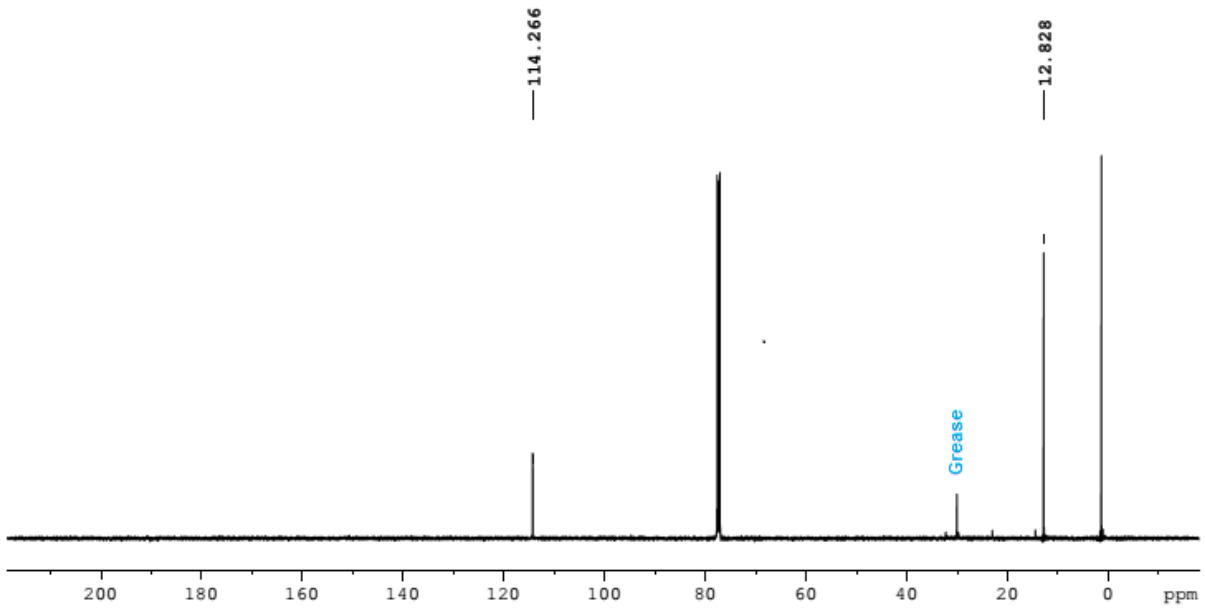



**Fig. S5.** $^{13}C\{^{1}H\}$ NMR spectrum of **1** in $CDCl_3$

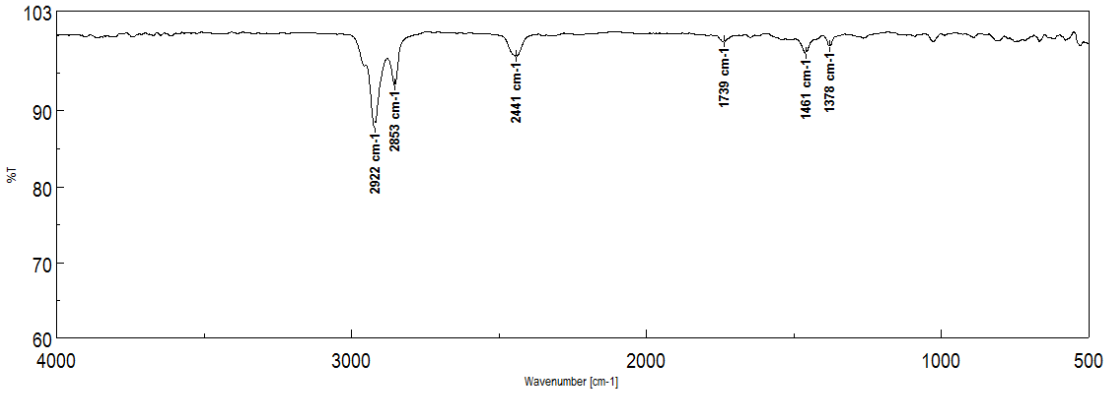



**Fig. S6.** IR spectrum of **1** in $CH_2Cl_2$

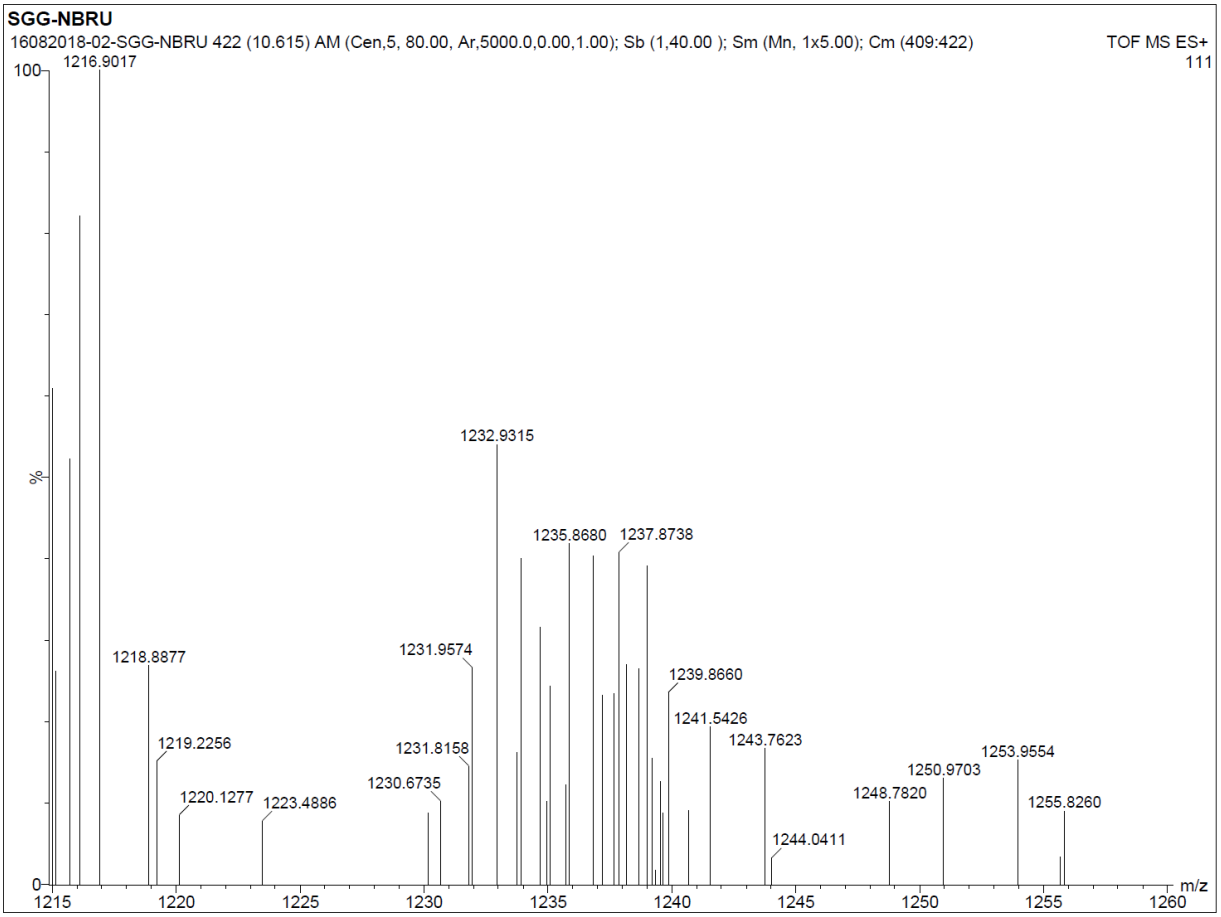



**Fig. S7.** ESI-MS spectrum of **3**

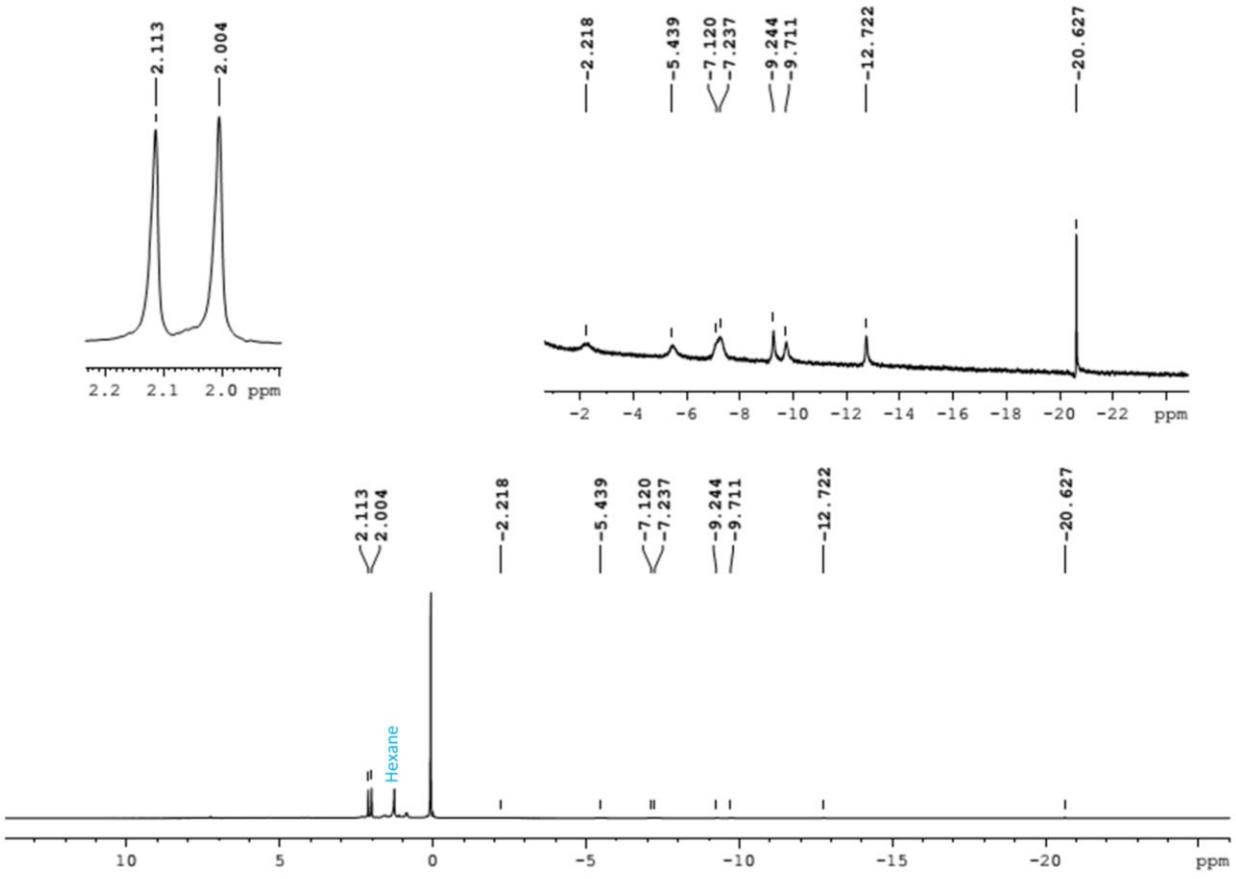



**Fig. S8.** $^{1}$H NMR spectrum of **3** in $CDCl_3$

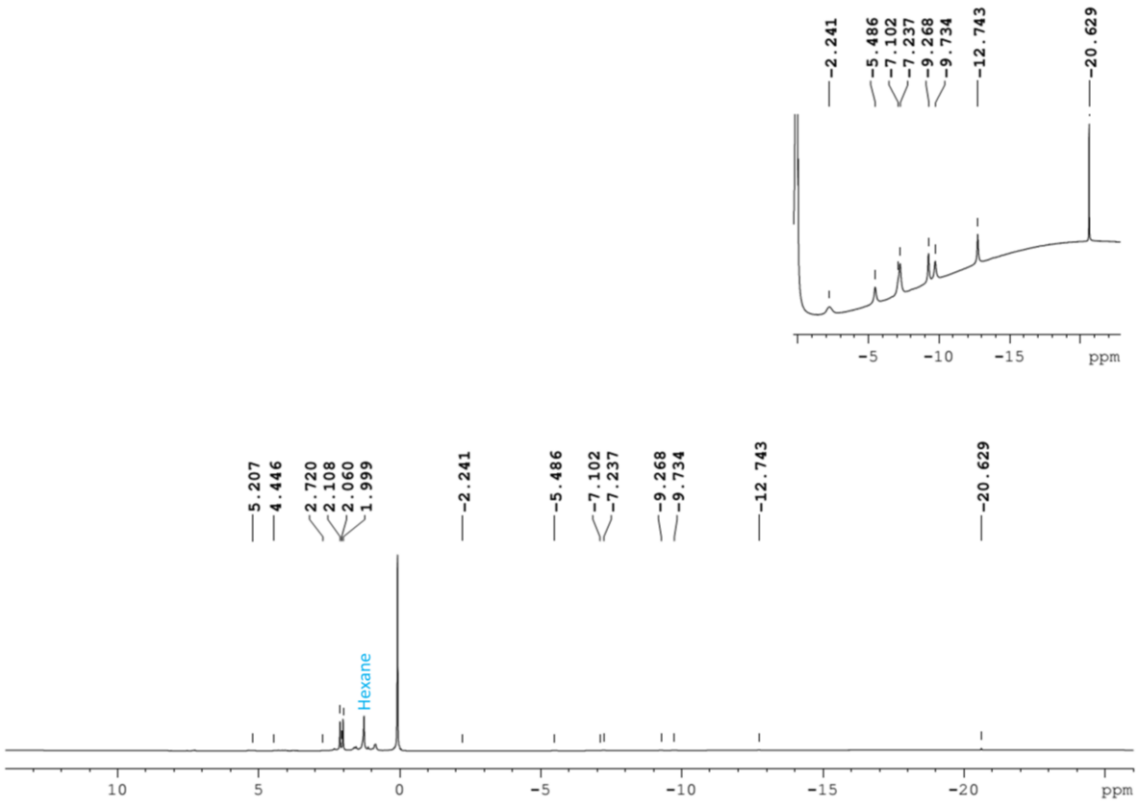



**Fig. S9.** $^{1}H\{^{11}B\}$ spectrum of **3** in $CDCl_3$

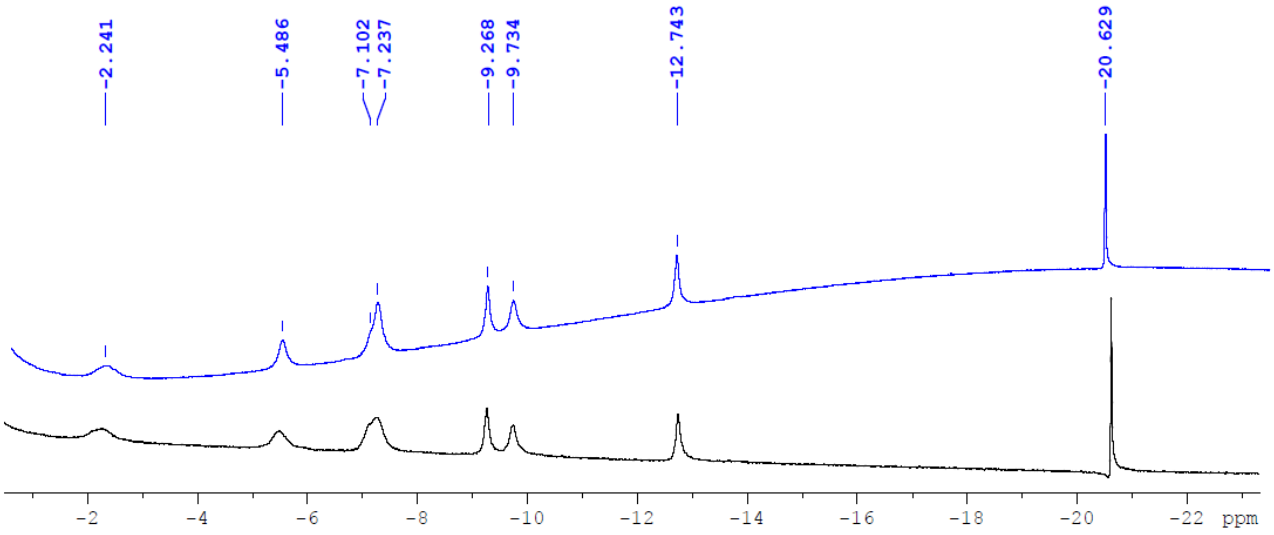



**Fig. S10.** Stacked $^{1}H$ (black) and $^{1}H\{^{11}B\}$ spectra of **3**

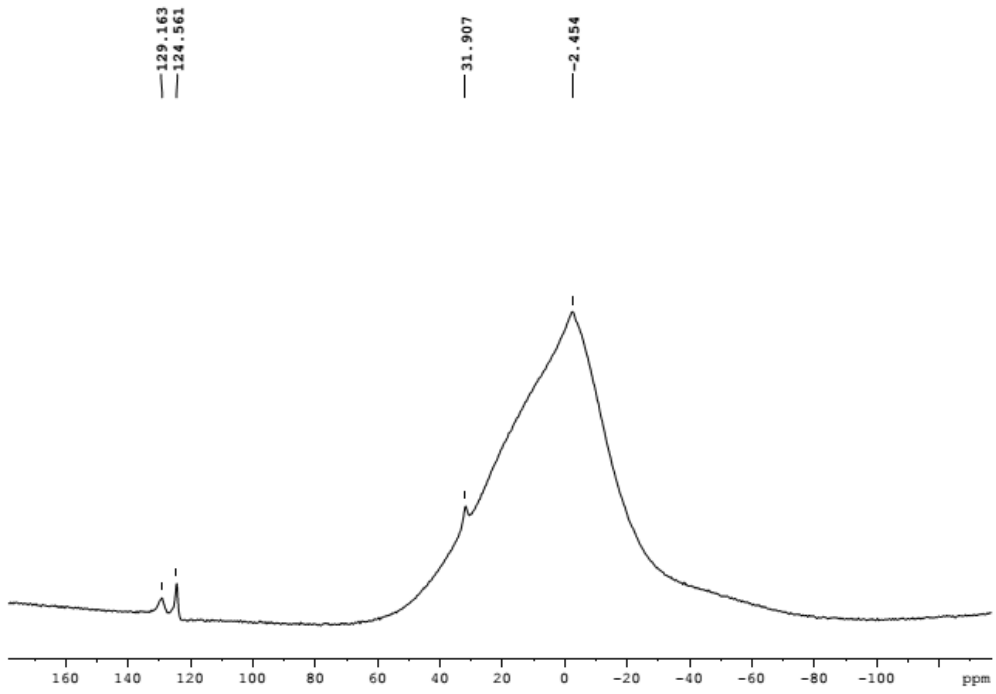



**Fig. S11.** $^{11}B\{^{1}H\}$ spectrum of **3** in $CDCl_3$

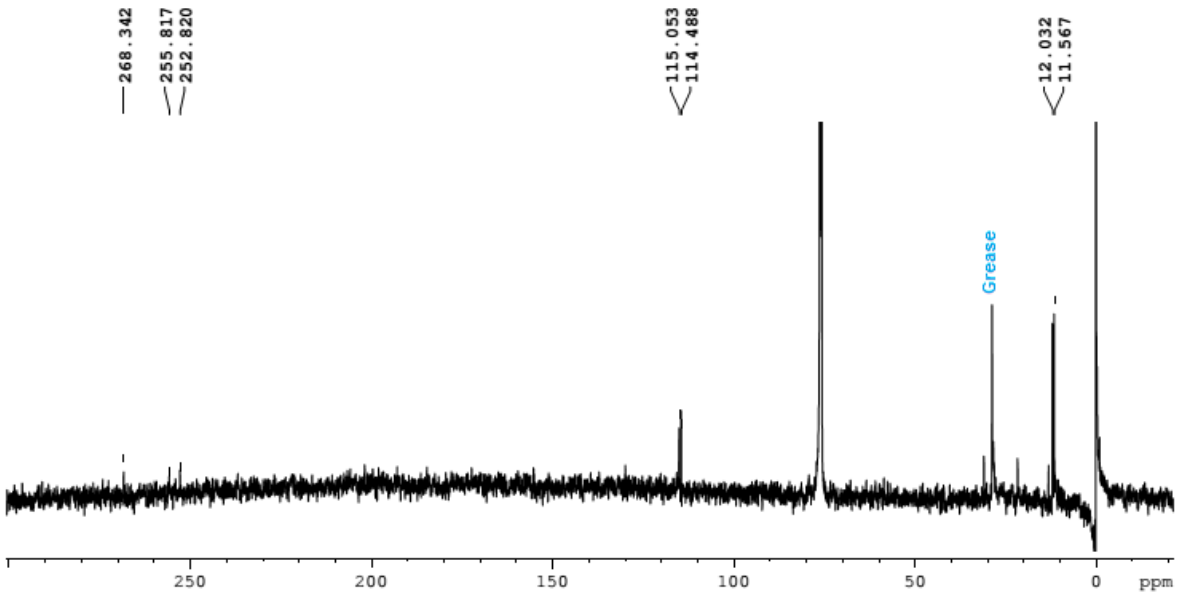



**Fig. S12.** $^{13}C\{^{1}H\}$ spectrum of **3** in $CDCl_3$

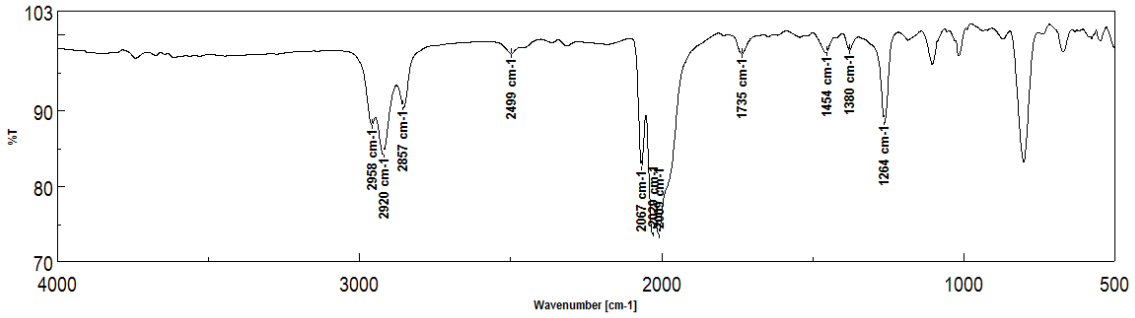


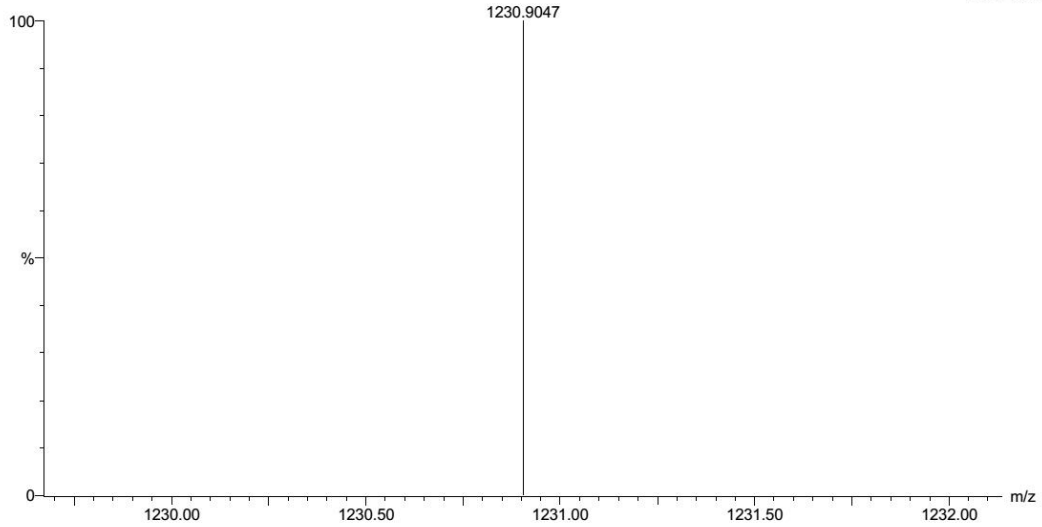

**Fig. S13.** IR spectrum of **3** in $CH_2Cl_2$

**Elemental Composition Report** **Page 1**

**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Odd and Even Electron Ions
595 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-28 H: 0-39 B: 0-4 O: 0-9 Ru: 0-3 Ta: 0-2

SGG-TARU
16082018-01-SGG-TARU 306 (7.698) AM (Cen,5, 80.00, Ar,5000.0,0.00,1.00); Sb (1,40.00 ); Sm (Mn, 1x0.00); Cm (267:306) TOF MS ES+
7.30e+003




| | | | | | | |
|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | |
| Maximum: | | 5.0 | 10.0 | 50.0 | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 1230.9047 | 1230.9057 | -1.0 | -0.8 | 12.5 | n/a | C28 H39 B4 O9 Ru3 Ta2 |

**Fig. S14.** HRMS spectrum of **4**

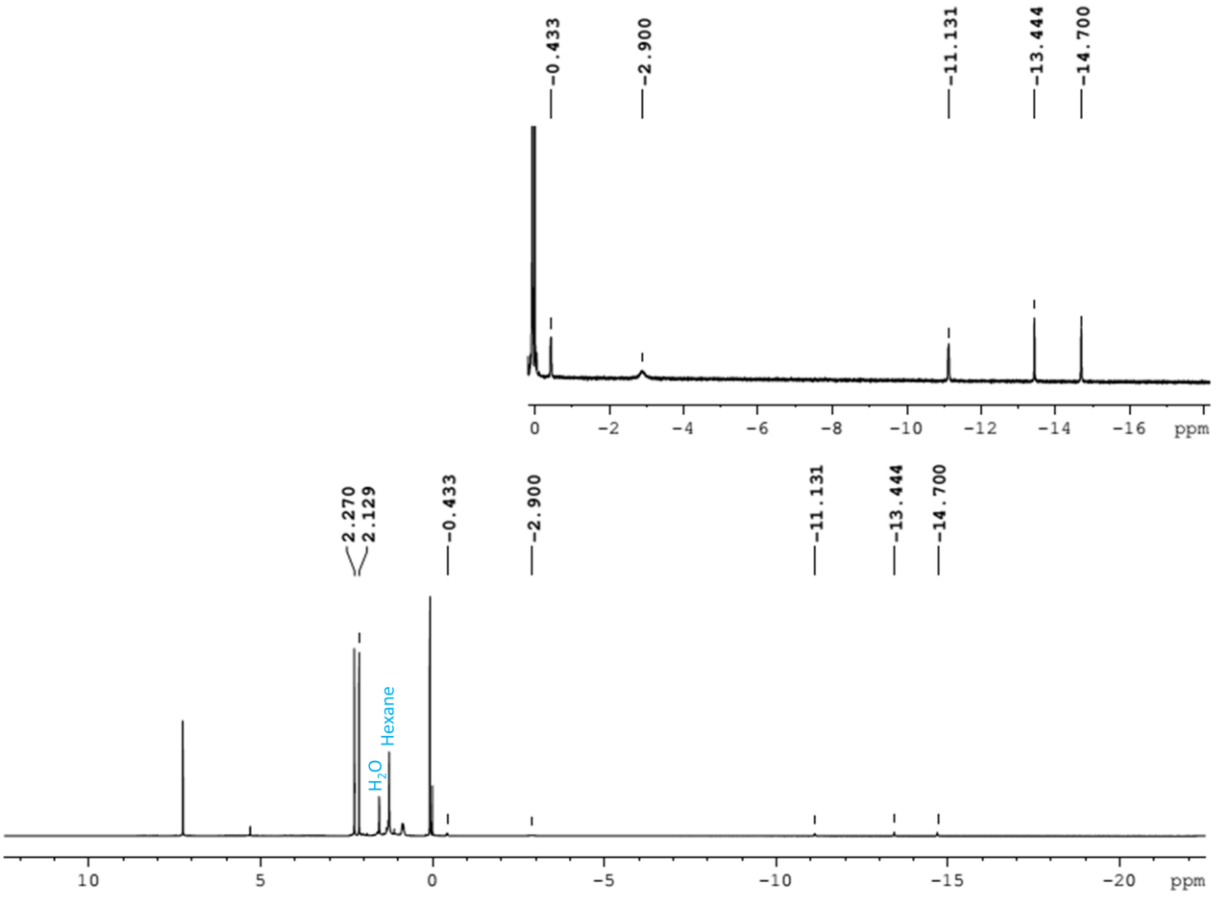



**Fig. S15.** $^{1}$H NMR spectrum of **4** in $CDCl_3$

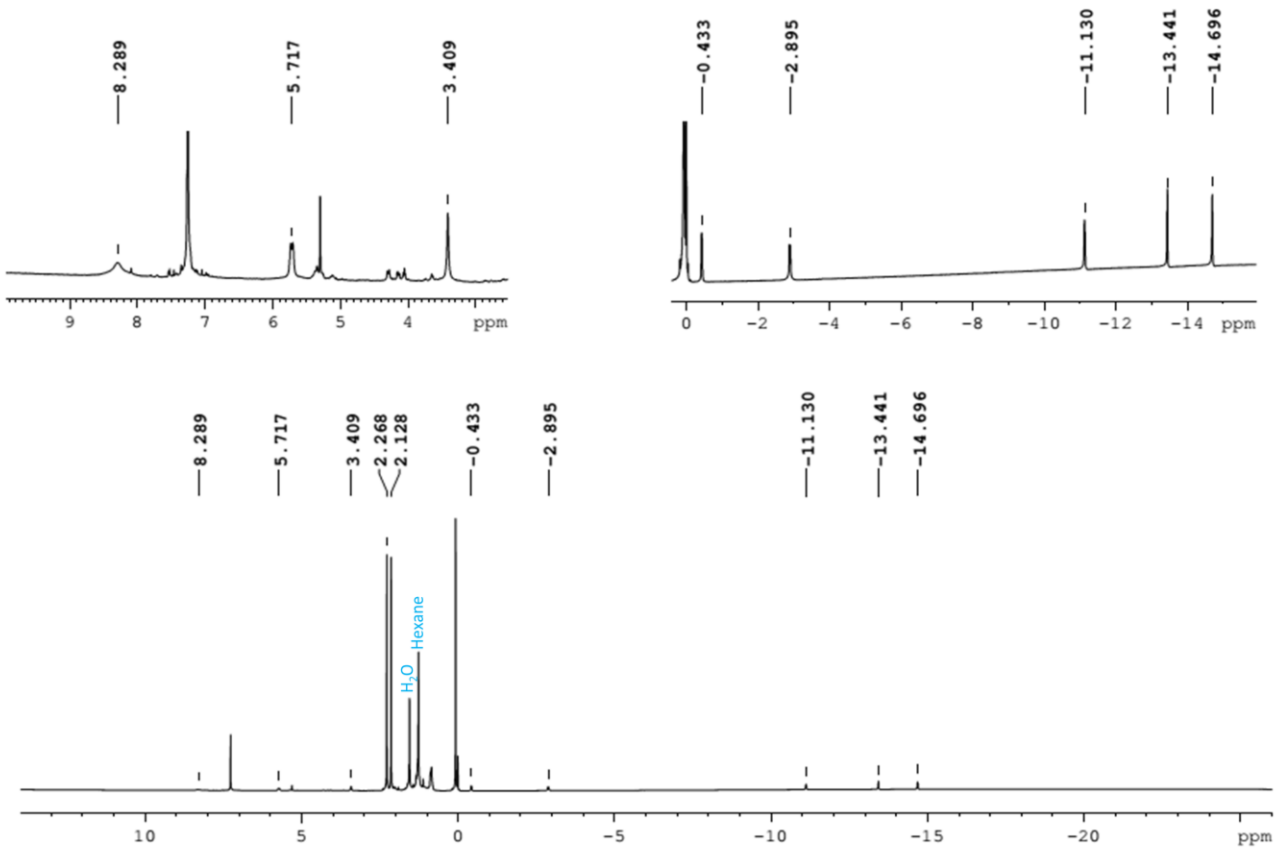



**Fig. S16.** $^{1}H\{^{11}B\}$ spectrum of **4** in $CDCl_3$

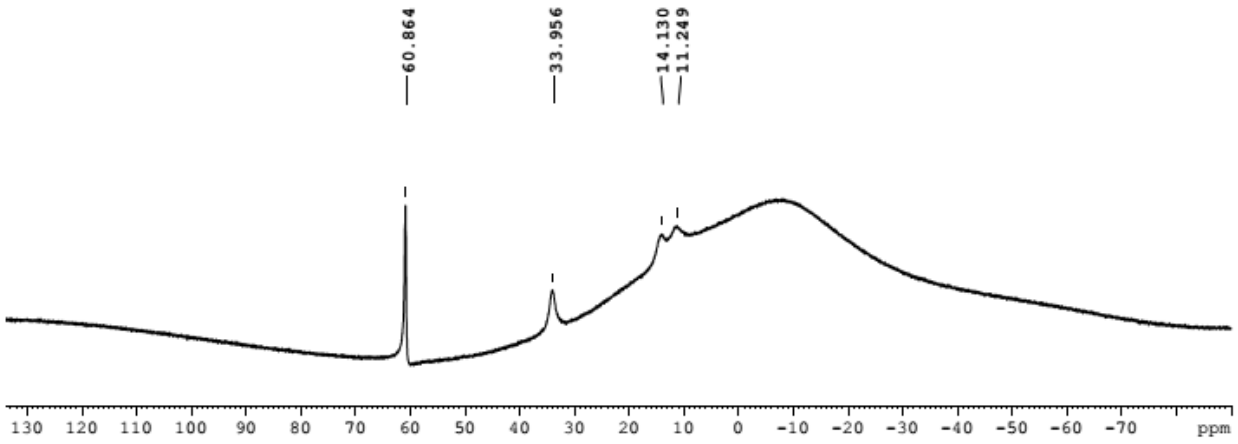



**Fig. S17.** $^{11}B\{^{1}H\}$ spectrum of **4** in $CDCl_3$

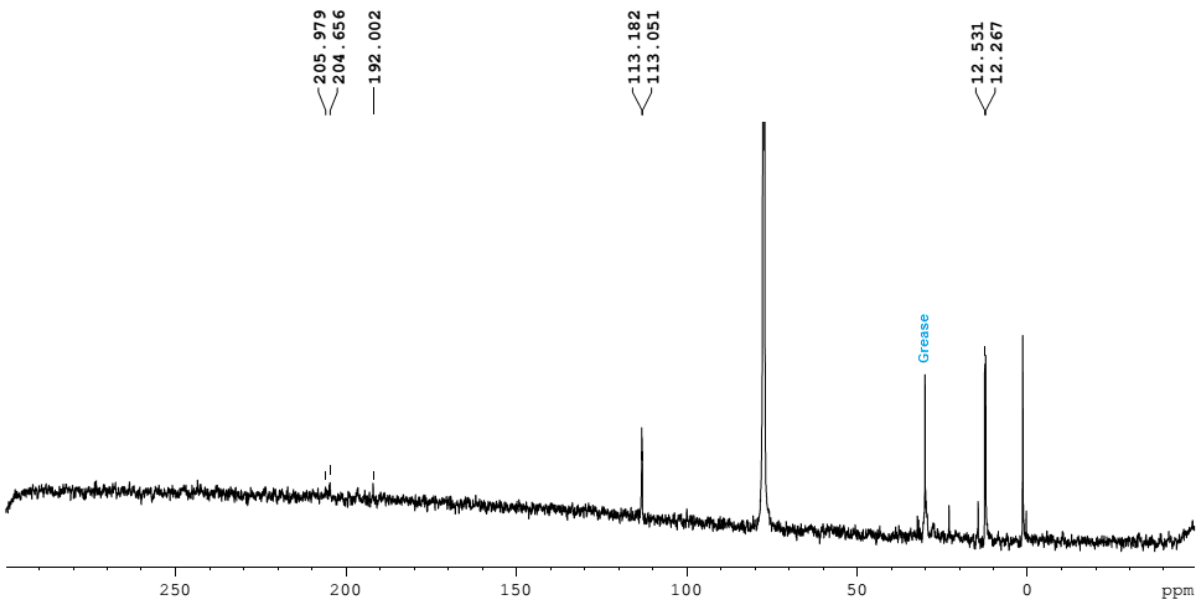



**Fig. S18.** $^{13}C\{^{1}H\}$ spectrum of **4** in $CDCl_3$

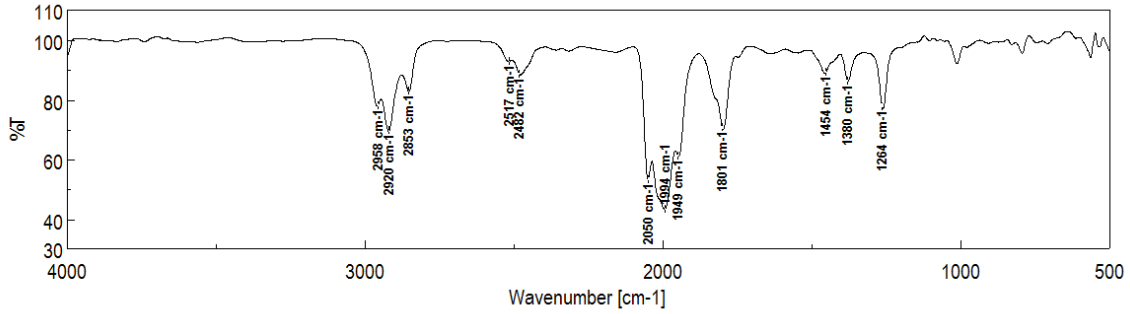



**Fig. S19.** IR spectrum of **4** in $CH_2Cl_2$

## III Computational Data

**Table S2.** Selected bond parameters for the compound **1'** (**1'**: Cp analogue of **1**) and their Wiberg bond indices (WBI)

| | Expt. | Theo. | WBI |
|---|---|---|---|
| Nb1-Nb2 | 2.746 | 2.769 | 0.9763 |
| B2-O1 | 1.454 | 1.405 | 0.8239 |
| B1-B2 | 1.702 | 1.749 | 0.5765 |
| B4-B3 | 1.704 | 1.765 | 0.6663 |
| Nb1-O1 | 2.106 | 2.154 | 0.5863 |
| Nb2-O1 | 2.103 | 2.154 | 0.5863 |
| Nb1-B1 | 2.365 | 2.398 | 0.5076 |
| Nb1-B2 | 2.421 | 2.395 | 0.4053 |
| Nb2-B1 | 2.378 | 2.399 | 0.5074 |
| Nb2-B2 | 2.409 | 2.395 | 0.4055 |
| Nb1-B3 | 2.403 | 2.477 | 0.4097 |
| Nb1-B4 | 2.372 | 2.431 | 0.4385 |
| Nb2-B3 | 2.408 | 2.477 | 0.4094 |
| Nb2-B4 | 2.411 | 2.432 | 0.4383 |

**Table S3.** Experimentally observed and calculated $^{11}B$ chemical shifts of **1'**.

| | Expt. | Theo. |
|---|---|---|
| B1 | 21.05 | 23.27 |
| B2 | 5.68 | 0.44 |
| B3 | −26.99 | −24.86 |
| B4 | −4.6 | −4.49 |

**Table S4**. Calculated (DFT) energies of the HOMO and LUMO (eV) and HOMO-LUMO gaps (ΔE = $E_{LUMO}$-$E_{HOMO}$, eV) for compounds **I', 1'**and **2'.**

| Compound | **I'** | **1'** | **2'** |
|---|---|---|---|
| HOMO | −5.63 | −5.43 | −5.25 |
| LUMO | −2.49 | −1.99 | −1.71 |
| ΔE | 3.14 | 3.44 | 3.54 |

**Table S5**. Calculated natural charges (q) and natural valence population (Pop) of **I'**, **1'**and **2'**.

| | **I'** | | **1'** | | **2'** | |
|---|---|---|---|---|---|---|
| | q | pop | q | pop | q | pop |
| B1 | -0.23 | 3.20 | -0.29 | 3.27 | -0.34 | 3.32 |
| B2 | 0.57 | 2.39 | 0.48 | 2.49 | 0.39 | 2.57 |
| B3 | -0.31 | 3.29 | -0.33 | 3.31 | -0.37 | 3.35 |
| B4 | -0.17 | 3.14 | -0.23 | 3.21 | -0.29 | 3.25 |
| O | -0.56 | 6.55 | -0.63 | 6.61 | -0.70 | 6.69 |
| M1 | -0.46 | 5.42 | -0.15 | 5.14 | 0.15 | 4.81 |
| M2 | -0.46 | 5.42 | -0.15 | 5.14 | 0.15 | 4.81 |

**Table S6.** Electron density, $\rho(r)$, Laplacian of electron density, $\nabla^2\rho(r)$, total energy density, H(r), potential energy density, V(r) and kinetic energy density, G(r) in a.u. of selected bond critical points (BCPs) of **1'**.

| BCP | $\rho(r)$ | $\nabla^2\rho(r)$ | H(r) | V(r) | G(r) |
|---|---|---|---|---|---|
| Nb1-Nb2 | 0.0708 | −0.0559 | −0.0315 | −0.049 | 0.0175 |
| B3-B4 | 0.136 | −0.283 | −0.0854 | −0.100 | 0.0147 |
| B2-O | 0.1945 | 0.4204 | −0.1551 | −0.415 | 0.260 |
| Nb1-O | 0.067 | 0.325 | −0.0016 | −0.0846 | −0.0829 |
| Nb2-O | 0.0727 | 0.291 | −0.0056 | −0.0842 | −0.0786 |

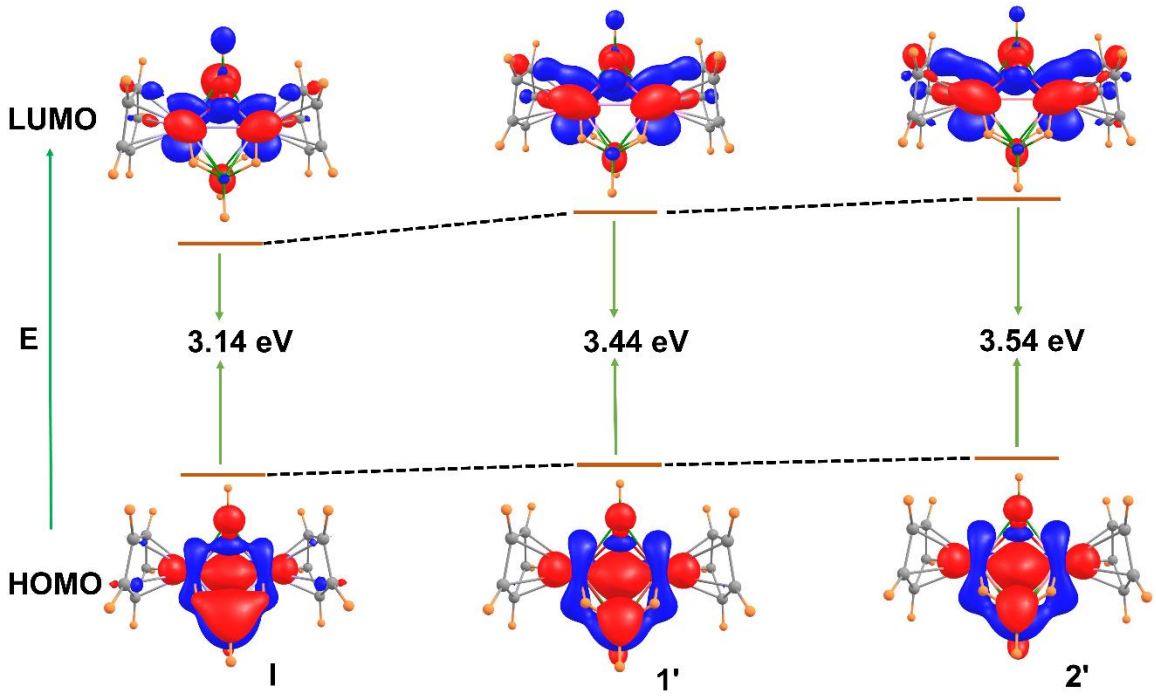



**Fig. S20.** Frontier molecular orbital (MO) diagram of **I'**, **1'** and **2'**. Isosurfaces are plotted at an isovalue of 0.04 $a_0^{-3/2}$.

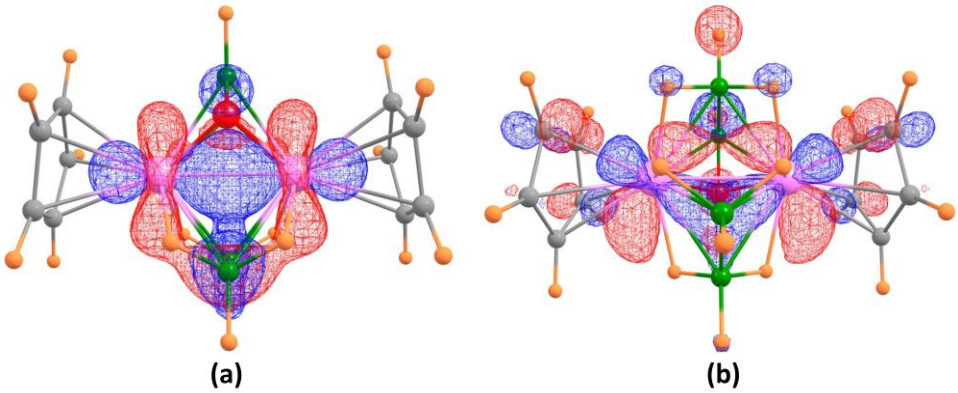



**Fig. 21**. M−M double bonding interactions in **1'**.

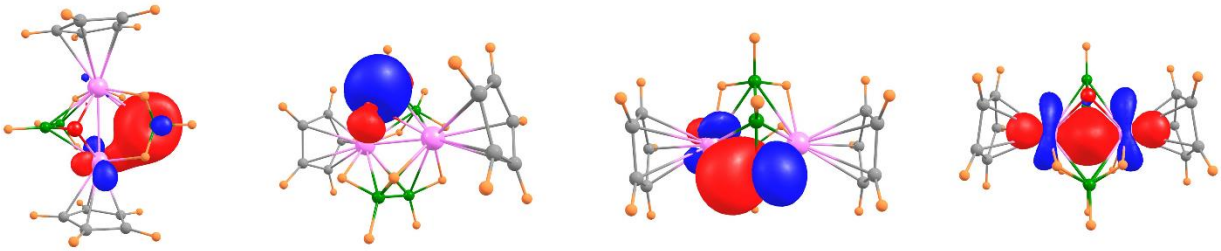



**Fig. S22.** Selected bonding diagrams of **1'** and their occupation number (ON) as obtained from NBO analysis [(a) 3c-2e B4-B3-Nb1 bond, (b) B2-O1 bond, (c) Nb1-O1 bond and (d) Nb1-Nb2 bond]. Isosurfaces are plotted at an isovalue of 0.04 $a_0^{-3/2}$.

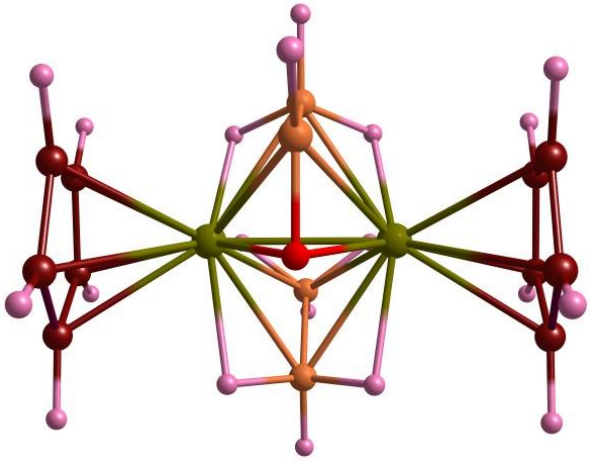


**Fig. 23.** Optimized geometry of compound **I'**.
T. E. = −711.3647 a. u.

Cartesian coordinates for the calculated structure of **I'** (in Å).

| | | | |
|---|---|---|---|
| C | -3.37059300 | 0.94344000 | -0.48603700 |
| C | -3.20514200 | 0.83723800 | 0.92485700 |
| C | -2.98011100 | -0.53513600 | 1.24862100 |
| C | -3.03597800 | -1.29258700 | 0.03650100 |
| C | -3.27806800 | -0.37471100 | -1.03872400 |
| C | 3.27807400 | -0.37468500 | -1.03872500 |
| C | 3.03588900 | -1.29261500 | 0.03642000 |
| C | 2.98000200 | -0.53521600 | 1.24856700 |
| C | 3.20516100 | 0.83717800 | 0.92492300 |
| C | 3.37071100 | 0.94342500 | -0.48594400 |
| B | -0.00010900 | 1.79010900 | -1.04024100 |
| B | -0.00012500 | 1.89860500 | 0.69004800 |
| O | 0.00002100 | -0.71917100 | 1.20868500 |
| B | 0.00007600 | -1.75901400 | 0.29535800 |
| B | 0.00007100 | -1.33811400 | -1.37743100 |
| H | -0.00059600 | 2.83381000 | -1.66064900 |
| H | 1.03154600 | 1.19295600 | -1.53125600 |
| H | -1.03078700 | 1.19167000 | -1.53181700 |
| H | 0.00026400 | 3.07105200 | 1.00729800 |
| H | 0.00005800 | -2.91919900 | 0.64491200 |
| H | 0.00044800 | -2.33408500 | -2.06865400 |
| H | 1.02491300 | -0.65236100 | -1.75191400 |
| H | -1.02537900 | -0.65323500 | -1.75179500 |
| H | -0.96088100 | 1.35999900 | 1.28898700 |
| H | 0.96068900 | 1.35998200 | 1.28899800 |

| | | | |
|---|---|---|---|
| H | 3.20199800 | 1.66896100 | 1.63021700 |
| H | 3.52687900 | 1.86624400 | -1.04606100 |
| H | 3.37679000 | -0.63398900 | -2.09351700 |
| H | 2.91474000 | -2.37212600 | -0.05633500 |
| H | 2.75720200 | -0.92883000 | 2.24112700 |
| H | -2.91483900 | -2.37210800 | -0.05617000 |
| H | -3.37679000 | -0.63412400 | -2.09348800 |
| H | -3.52666200 | 1.86626100 | -1.04617600 |
| H | -3.20190800 | 1.66909600 | 1.63006500 |
| H | -2.75741500 | -0.92872400 | 2.24121200 |
| V | 1.25837300 | 0.09148800 | -0.13076700 |
| V | -1.25835900 | 0.09139100 | -0.13079300 |

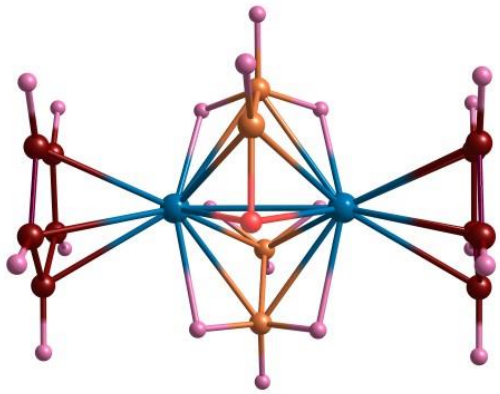


**Fig. S24.** Optimized geometry of compound **1'**.
T. E. = −682.0168 a. u.

Cartesian coordinates for the calculated structure of **1'** (in Å).

| | | | |
|---|---|---|---|
| C | -3.66744946 | 0.92340954 | -0.44768861 |
| C | -3.49649064 | 0.81095150 | 0.96520411 |
| C | -3.28330997 | -0.56883273 | 1.28417478 |
| C | -3.34586632 | -1.32202235 | 0.06586907 |
| C | -3.57689802 | -0.39487452 | -1.00821345 |
| C | 3.57709161 | -0.39254212 | -1.00882123 |
| C | 3.34678346 | -1.32170349 | 0.06368069 |
| C | 3.28390534 | -0.57069731 | 1.28328578 |
| C | 3.49604037 | 0.80974643 | 0.96671649 |
| C | 3.66665991 | 0.92483614 | -0.44604253 |
| B | 0.00051729 | 1.87006843 | -1.00652356 |

| | | | |
|---|---|---|---|
| B | 0.00071660 | 1.94288433 | 0.75769571 |
| O | -0.00021166 | -0.82959350 | 1.26384533 |
| B | -0.00066006 | -1.83306039 | 0.28005370 |
| B | -0.00024765 | -1.38486420 | -1.41137966 |
| H | 0.00105743 | 2.93862509 | -1.58063819 |
| H | 1.04062650 | 1.30431443 | -1.55627023 |
| H | -1.04085737 | 1.30579745 | -1.55558448 |
| H | 0.00076377 | 3.09806060 | 1.12308589 |
| H | -0.00083765 | -3.00429219 | 0.58153499 |
| H | -0.00094574 | -2.38930647 | -2.08816366 |
| H | 1.04244417 | -0.70038934 | -1.83950353 |
| H | -1.04200479 | -0.69896289 | -1.83963895 |
| H | -0.97041245 | 1.39595251 | 1.37064027 |
| H | 0.97111716 | 1.39549866 | 1.37115037 |
| H | 3.49338316 | 1.63664230 | 1.67904016 |
| H | 3.83576963 | 1.85047581 | -0.99863272 |
| H | 3.68785865 | -0.64695796 | -2.06400179 |
| H | 3.25094850 | -2.40384419 | -0.03260924 |
| H | 3.09613919 | -0.97762215 | 2.27845315 |
| H | -3.24942269 | -2.40426871 | -0.02855841 |
| H | -3.68760934 | -0.65122867 | -2.06293026 |
| H | -3.83718504 | 1.84797794 | -1.00188700 |
| H | -3.49435754 | 1.63913769 | 1.67603100 |
| H | -3.09543329 | -0.97393127 | 2.28006020 |
| Nb | 1.38464212 | 0.08152340 | -0.11255720 |
| Nb | -1.38473426 | 0.08214250 | -0.11257845 |

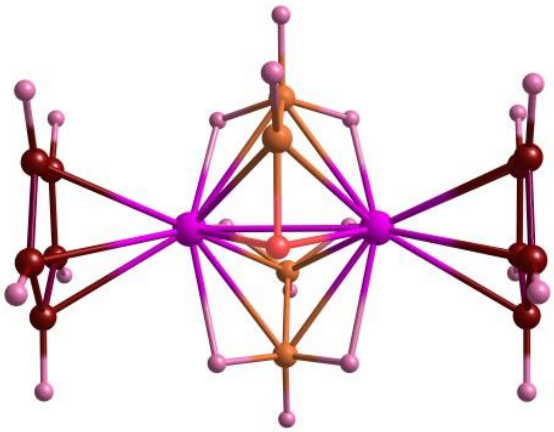


**Fig. S25.** Optimized geometry of compound **2'**.
T. E. = −682.1233 a. u.

Cartesian coordinates for the calculated structure of **2'** (in Å).

| | | | |
|---|---|---|---|
| C | -3.68354000 | 0.91546600 | -0.38281500 |
| C | -3.50613200 | 0.76741900 | 1.02699200 |
| C | -3.29583100 | -0.62044500 | 1.31151500 |
| C | -3.36599200 | -1.34437800 | 0.07437000 |
| C | -3.60104200 | -0.39010800 | -0.97647700 |
| C | 3.60099400 | -0.38966400 | -0.97664100 |
| C | 3.36630700 | -1.34417200 | 0.07408400 |
| C | 3.29614300 | -0.62049400 | 1.31137400 |
| C | 3.50603500 | 0.76745200 | 1.02705100 |
| C | 3.68321400 | 0.91581600 | -0.38276300 |
| B | 0.00009600 | 1.84569600 | -0.96479000 |
| B | 0.00025700 | 1.91782600 | 0.79830100 |
| O | -0.00019600 | -0.84390400 | 1.27653800 |
| B | -0.00029700 | -1.85579700 | 0.28229400 |
| B | -0.00011100 | -1.37912500 | -1.39220500 |
| Ta | -1.39675000 | 0.06165500 | -0.08812300 |
| Ta | 1.39675300 | 0.06140100 | -0.08805400 |
| H | 0.00055800 | 2.91218100 | -1.54190800 |
| H | 1.05490100 | 1.29516000 | -1.51950000 |
| H | -1.05513000 | 1.29590500 | -1.51931500 |
| H | 0.00015900 | 3.06543500 | 1.18279700 |
| H | -0.00034400 | -3.02512900 | 0.58827100 |
| H | -0.00040700 | -2.37118400 | -2.08667200 |
| H | 1.05484600 | -0.69203700 | -1.82587200 |
| H | -1.05457400 | -0.69136500 | -1.82603200 |
| H | -0.96977200 | 1.36208300 | 1.40865000 |
| H | 0.97003200 | 1.36199600 | 1.40883700 |
| H | 3.49837400 | 1.57768400 | 1.75840200 |
| H | 3.85652100 | 1.85417200 | -0.91219800 |
| H | 3.72385500 | -0.62026000 | -2.03588600 |
| H | 3.27791800 | -2.42451600 | -0.04621300 |
| H | 3.10687500 | -1.05122900 | 2.29626900 |
| H | -3.27715500 | -2.42470200 | -0.04574800 |
| H | -3.72393200 | -0.62084000 | -2.03569100 |
| H | -3.85714400 | 1.85362500 | -0.91250600 |
| H | -3.49856100 | 1.57770600 | 1.75828100 |
| H | -3.10629800 | -1.05090000 | 2.29648100 |