

Unexpected formation of a trinuclear complex containing a Ta(IV)-Ta(IV) bond in the reactions of Bu^tN=Ta(NMe₂)₃ with silanes

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Supplementary information

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Experimental Section and NMR Studies of the Structure of 4

General procedures. Unless noted, all manipulations were carried out under a dry and oxygen-free nitrogen atmosphere with the use of glovebox or Schlenk techniques. All solvents were purified by distillation from potassium/benzophenone ketyl. Benzene- d_6 and toluene- d_8 were dried and stored over activated molecular sieves under nitrogen. TaCl_5 (Strem), LiNMe_2 (Aldrich), and Me_3SiCl (Acros) were used as received. Bu^tNH_2 (Acros) was refluxed over NaOH and distilled. ^1H , VT- ^1H , ^2H , and ^{13}C NMR spectra were recorded on a Bruker Avance 400 Fourier transform spectrometer. HMBC, HSQC, and NOESY 2D NMR spectra were recorded on Varian VNMRS 500 MHz spectrometer. FT-IR spectra were recorded on Varian 4100 FT-IR (Excalibur series) spectrometer. Electrochemical cyclic voltammogram (CV) were recorded on (CH Instrument) electrochemical workstation (CHI 650a). UV-Vis spectra were recorded on 8452A diode array spectrophotometer (Hewlett Packard). Elemental analyses were conducted by Complete Analysis Laboratories, Inc., Parsippany, NJ.

Preparation of $\text{Ta}_3(\mu\text{-H})(\mu\text{-NMe}_2)(\mu\text{-NBu}^t)_2(=\text{NBu}^t)(\text{NMe}_2)_5$ (2) and $\text{Ta}_2\text{H}_2(\mu\text{-NMe}_2)_2(\text{NMe}_2)_2(=\text{NBu}^t)_2$ (3).

Reaction of $\text{Bu}^t\text{N}=\text{Ta}(\text{NMe}_2)_3$ with H_3SiPh . To $\text{Bu}^t\text{N}=\text{Ta}(\text{NMe}_2)_3$ (5.566 g, 14.48 mmol) in toluene (15 mL) in a Schlenk flask (50 mL) with stirring at 23 °C was added 2/3 equiv of H_3SiPh (1.045 g, 9.655 mmol) in toluene (10 mL) in a Schlenk tube in a period of 13 min. The pale-yellow solution turned red immediately, giving off bubbles. After the solution was stirred at 23 °C for another 16 min, volatiles were stripped off in vacuo for 3 h to give a red solid residue. It was dissolved in hexanes to form a clear solution which was concentrated for crystallization at -32 °C. Red crystals (2.060 g, 2.016 mmol, 42% yield based on Ta) of **2** were isolated next day. ^1H NMR of **2** (benzene- d_6 , 399.79 MHz, 23 °C) δ 7.69 (s, 1H, Ta-H), 3.75 (s, 3H, NMe_aMe_b on Ta1. See Fig. 1 copied below for the atom labeling), 3.18 (s, 24H, NMe_2), 2.87 (s, 3H, $\mu\text{-NMe}_c\text{Me}_d$), 2.78 (s, 3H, $\mu\text{-NMe}_c\text{Me}_d$), 2.30 (s, 3H, NMe_aMe_b), 1.79 (s, 18H, $\mu\text{-NCMe}_3$), 1.47 (s, 9H, NCMe_3).

^{13}C NMR of **2** (benzene- d_6 , 100.53 MHz, 23 °C) δ 68.67 (s, $\mu\text{-NCMe}_3$), 64.91 (s, NCMe_3), 53.40 (s, NMe_aMe_b), 49.86 (s, NMe_2), 48.21 (s, $\mu\text{-NMe}_2$), 37.89 (s, NMe_aMe_b), 36.13 (s, $\mu\text{-NCMe}_3$), 35.90 (s, NCMe_3). ^1H NMR of **2** (toluene- d_8 , 399.79 MHz, 23 °C) δ 7.64 (s, 1H, Ta-H), 3.73 (s, 3H, NMe_aMe_b), 3.18 (s, 24H, NMe_2), 2.89 (s, 3H, $\mu\text{-NMe}_c\text{Me}_d$), 2.77 (s, 3H, $\mu\text{-NMe}_c\text{Me}_d$), 2.29 (s, 3H, NMe_aMe_b), 1.76 (s, 18H, $\mu\text{-NCMe}_3$), 1.40 (s, 9H, NCMe_3). ^{13}C NMR of **2** (toluene- d_8 , 100.53 MHz, 23 °C) δ 68.79 (s, $\mu\text{-NCMe}_3$), 65.02 (s, NCMe_3), 53.47 (s, NMe_aMe_b), 49.93 (s, NMe_2), 48.28 (s, $\mu\text{-NMe}_2$), 37.96 (s, NMe_aMe_b), 36.18 (s, $\mu\text{-NCMe}_3$), 35.15 (s, NCMe_3). Anal. Calcd for $\text{C}_{24}\text{H}_{64}\text{N}_9\text{Ta}_3$: C, 28.21; H, 6.31; N, 12.34. Found: C, 27.90; H, 6.43; N, 12.18.

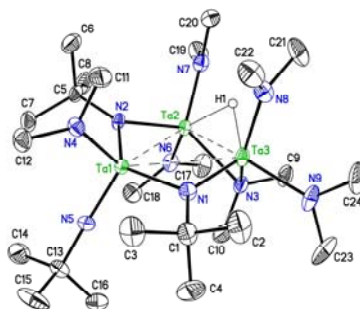


Fig. 1 ORTEP view of **2** with ellipsoids at 30% probability.

After crystals of **2** were isolated, the supernatant solution was concentrated and put at -32 °C for crystallization. Needle-like colorless crystals of **3** were isolated (310 mg, 0.454 mmol, 6% yield based on Ta). ^1H NMR of **3** (toluene- d_8 , 400.25 MHz, 23 °C) δ 6.69 (s, 2H, Ta-H), 4.11 (s, 6H, $\mu\text{-NMe}_a\text{Me}_b$), 3.85 (s, 6H, $\mu\text{-NMe}_a\text{Me}_b$), 3.46 (6H, NMe_cMe_d), 3.45 (6H, NMe_cMe_d), 1.40 (s, 18H, NCMe_3). ^{13}C NMR of **3** (toluene- d_8 , 100.65 MHz, 23 °C) δ 64.89 (NCMe_3), 58.59, 57.77, 56.97, 56.67 (NMe_aMe_b , NMe_aMe_b , NMe_cMe_d , NMe_cMe_d), 35.17 (NCMe_3). Anal. Calcd for $\text{C}_{16}\text{H}_{44}\text{N}_6\text{Ta}_2$: C, 28.16; H, 6.50; N, 12.31. Found: C, 28.05; H, 6.59; N, 12.22.

Reaction of $\text{Bu}^t\text{N}=\text{Ta}(\text{NMe}_2)_3$ with H_2SiMePh . Two equiv of H_2SiMePh (0.636 g, 5.60 mmol) in toluene (10 mL) in a Schlenk tube was added to $\text{Bu}^t\text{N}=\text{Ta}(\text{NMe}_2)_3$ (1.000 g, 2.602 mmol) in toluene (10 mL) in a Schlenk flask (50 mL) with stirring at 23 °C in a period of 13 min. The pale-

yellow solution turned red. After the solution was stirred at 23 °C for another 13 min, volatiles were stripped off in vacuo for 1.5 h to give a red solid residue. It was dissolved in hexanes to form a clear solution which was concentrated for crystallization at -32 °C. Red crystals (0.367 g, 0.359 mmol, 41% yield based on Ta) of **2** were collected next day. Another needle-like colorless crystals of **3** (68 mg, ca 8% yield based on Ta) were collected from the remaining concentrated supernatant solution.

Preparation of Ta₃(μ-D)(μ-NMe₂)(μ=NBu^t)₂(=NBu^t)(NMe₂)₅ (2-d₁**).** To Bu^tN=Ta(NMe₂)₃ (0.665 g, 1.730 mmol) in toluene (10 mL) in a Schlenk flask (125 mL) with stirring at 23 °C was added dropwise 2 equiv of D₂SiMePh (0.430 mg, 3.460 mmol) in toluene (10 mL) dissolved in a Schlenk tube over a period of 13 min. The color of the solution changed to red from pale-yellow slowly. After the solution was stirred at 23 °C for additional 18 min, volatiles were stripped off in vacuo for 1.5 h to give a red viscous residue. The residue was dissolved in hexanes, and the solution was concentrated. Cooling at -32 °C gave red crystals (0.228 g, 0.223 mmol, 39% yield based on Ta) of **2-d₁** in two days. ¹H NMR of **2-d₁** (toluene-*d*₈, 399.71 MHz, 23 °C) δ 3.71 (s, 3H, NMe_aMe_b), 3.17 (s, 24H, NMe₂), 2.88 (s, 3H, μ-NMe_aMe_b), 2.77 (s, 3H, μ-NMe_aMe_b), 2.27 (s, 3H, NMe_aMe_b), 1.75 (s, 18H, μ-NCMe₃), 1.41 (s, 9H, NCMe₃). ²H NMR of **2-d₁** (toluene-*d*₈, 61.36 MHz, 23 °C) δ 7.55 (s, 1D, Ta-D). ¹³C NMR of **2-d₁** (toluene-*d*₈, 100.51 MHz, 23 °C) δ 68.79 (s, μ-NCMe₃), 65.02 (s, NCMe₃), 53.43 (s, NMe_aMe_b), 49.83 (s, NMe₂), 48.27 (s, μ-NMe₂), 37.89 (s, NMe_aMe_b), 36.19 (s, μ-NCMe₃), 35.16 (s, NCMe₃).

Preparation of Ta₃(μ₃-O)(H)(μ=NBu^t)(μ-NMe₂)₂(NMe₂)₄(=NBu^t)₂ (4**).** **2** (0.631 g, 0.618 mmol) in toluene (5 mL) in a Schlenk tube was frozen with liquid nitrogen and pumped for 5 min. After liquid nitrogen was removed and the frozen red solid melted, 1 equiv of O₂ (15 mL, 1 atm, 0.618 mmol) was added. The red solution was then stirred for ca. 3 h at 23 °C. The red color faded, giving a yellow solution. The solution was transferred to a smaller Schlenk flask and volatiles were removed to give a yellow viscous residue. Hexanes were added, dissolving the residue for

crystallization at $-32\text{ }^{\circ}\text{C}$. Yellow crystals of **4** were isolated in ca. two months (0.102 g, 0.098 mmol, 16% yield). ^1H NMR of **4** (benzene- d_6 , 400.25 MHz, $23\text{ }^{\circ}\text{C}$) δ 6.98 (s, 1H, Ta-H), 4.19 (s, 3H, NMe_iMe_j), 4.07 (s, 3H, NMe_eMe_f), 3.62 [s, 6H, $\text{N}(\text{Me}_a)_2$], 3.51 (s, 3H, NMe_eMe_f), 3.37 (s, 3H, $\mu\text{-NMe}_c\text{Me}_d$), 3.33 (s, 3H, NMe_iMe_j), 3.32 (s, 3H, $\mu\text{-NMe}_g\text{Me}_h$), 3.31 [s, 6H, $\text{N}(\text{Me}_b)_2$], 3.22 (s, 3H, $\mu\text{-NMe}_g\text{Me}_h$), 2.77 (s, 3H, $\mu\text{-NMe}_c\text{Me}_d$), 1.45 [s, 9H, $\text{NC}(\text{Me}_m)_3$], 1.43 [s, 9H, $\text{NC}(\text{Me}_l)_3$], 1.34 [s, 9H, $\mu\text{-NC}(\text{Me}_k)_3$]. ^{13}C NMR of **4** (benzene- d_6 , 100.65 MHz, $23\text{ }^{\circ}\text{C}$) δ 63.15 [s, $\text{NC}(\text{Me}_l)_3$], 62.27 [s, $\text{NC}(\text{Me}_m)_3$], 59.69 [s, $\mu\text{-NC}(\text{Me}_k)_3$], 57.57 (s, NMe_iMe_j), 57.30 (s, NMe_eMe_f), 56.18 (s, $\mu\text{-NMe}_g\text{Me}_h$), 53.80 (s, $\mu\text{-NMe}_c\text{Me}_d$), 51.72 (s, $\mu\text{-NMe}_g\text{Me}_h$), 50.31 [s, $\text{N}(\text{Me}_a)_2$], 48.11 [s, $\text{N}(\text{Me}_b)_2$], 47.72 (s, NMe_iMe_j), 47.60 (s, NMe_eMe_f), 44.92 (s, $\mu\text{-NMe}_c\text{Me}_d$), 34.92 [s, $\text{NC}(\text{Me}_m)_3$], 34.39 [s, $\text{NC}(\text{Me}_l)_3$], 30.22 [s, $\mu\text{-NC}(\text{Me}_k)_3$]. Anal. Calcd for $\text{C}_{24}\text{H}_{64}\text{N}_9\text{OTa}_3$: C, 27.78; H, 6.22; N, 12.15. Found: C, 27.69; H, 6.12; N, 12.11.

NMR studies give the structure of **4** in Chart 1. After 2D HSQC (Fig. S8) was used to establish the correlations between ^1H and ^{13}C atoms that are bound to each other,⁵ HMBC (Fig. S9 and S10) provided correlations between: (1) protons of one Me group and the C atom of the other Me group in the same -NMe_2 ligand - the H and C atoms are three bonds away; (2) the hydride ligand and vicinal C atoms with dihedral angles of ca. 180° (and thus strong couplings).^{S1} These C atoms are the Me_d and Me_a groups (Fig. S10). No correlation between the hydride ligand and the Me_e (or Me_f) group was observed, and the HMBC spectrum (Fig. S10) showed only a weak peak between the hydride and the Me_g group. The HMBC spectrum and the much longer H1-Ta1 distance in the structure of **4** discussed above point to either a terminal hydride ligand or an unsymmetrical bridging hydride that binds much more strongly with Ta2 than with Ta1. The NOESY spectrum reveals H atoms that are spatially close, and it (Fig. S11-S13) indicates that the hydride ligand is close to the Me_a , Me_c , Me_g , and Me_m groups.

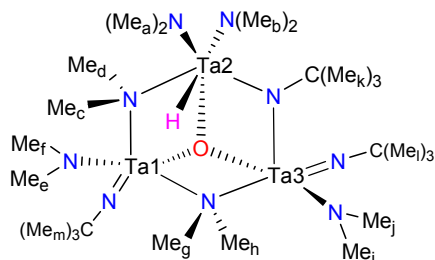


Chart 1. Structure of **4** based on 1D and 2D NMR studies.

FT-IR measurement of **2 and **2-d₁**.** KBr (96.4 mg) pellet was prepared under nitrogen atmosphere and scanned as background. **2** (2 mg) was ground with KBr (96.4 mg) and pressed into a pellet. A broad band of Ta-H stretch was observed at 1628 cm^{-1} (Fig. S3). The IR sample of **2-d₁** (2 mg) was similarly prepared and its spectrum is given in Fig. S3. The Ta-D stretch was obscured by other peaks.

Electrochemical cyclic voltammogram (CV) of **2.** In a glovebox, 0.10 M of $(\text{Bu}^n_4\text{N})\text{PF}_6$ (electrolyte, 387.4 mg, 1.00 mmol) and 1.0 M of **2** (10.2 mg, 10 mmol) were made in CHCl_3 (10 mL) in a cell with three electrodes (working electrode: glassy carbon; counter electrode: platinum wire; reference electrode: Ag/AgCl wire). The cell was then put into an Erlenmeyer flask (1000 mL) with a rubber stopper. Three wires went through the stopper for power connection. The whole set-up was taken out the glove box and quickly connected to a CHI electrochemical workstation. Two peaks at -0.089 and 0.22 V during the oxidation (Fig. S5) are consistent with the presence of a Ta-Ta bond in **2**. The oxidation is essentially irreversible.

UV-Vis measurement of **2.** **2** (9.1 mg, $8.9\ \mu\text{mol}$) was dissolved in hexanes (4.0 mL) to form a red solution. Part of the solution (0.4 mL) was transferred into a cuvette and additional hexanes (4 mL) was added to the cuvette to give a final solution (0.202 mM) for UV-Vis measurement. Another cuvette loaded with hexanes (4.4 mL) was prepared as background. The sample was scanned for three times. The spectra are given in Fig. S7.

The new complex **2** is red. d^0 complexes are usually colorless or lightly colored as a result of their UV absorption. The absorption at 450 nm suggests the presence of d electrons in **2**.

Determination of X-ray crystal structures of 2 and 4. The data for the X-ray crystal structures of **2** and **4** were collected on a Bruker-AXS APEX diffractometer equipped with a CCD area detector fitted with an upgraded Nicolet LT-2 low temperature device. The data were obtained using a graphite-monochromated Mo source (K_{α} radiation, 0.71073 Å). Suitable crystals were coated with paratone oil (Exxon) and mounted on loops under a stream of nitrogen at the data collection temperature. The structures were solved by direct methods. Non-hydrogen atoms were anisotropically refined. All hydrogen atoms were treated as idealized contributions. Empirical absorption correction was performed with SADABS.^{S2a} In addition the global refinements for the unit cells and data reductions of the structure was performed using the Saint program (version 6.02). All calculations were performed using SHELXTL (version 5.1) proprietary software package.^{S2b}

Computational details. In the isolated trinuclear Ta cluster complex **2**, a Ta(IV)-Ta(IV) bond can be formally assigned. To better understand the nature of the Ta-Ta bonding interactions, we carried out density functional theory calculations at the B3LYP level. In our calculations, *tert*-butyl groups were replaced by CH₃. Important structural parameters calculated for the model cluster complex **2A** are shown in Fig. 2, together with the experimental ones obtained from the X-ray diffraction study. The calculated geometry reproduced well the experimental structure. Overall, the metal-ligand bonds were better reproduced while the metal-metal bonds were slightly overestimated. The shorter bond of Ta(2)-Ta(3) versus Ta(1)-Ta(2)/Ta(1)-Ta(3) was also well reproduced.

The highest occupied molecular orbital (HOMO) shown in Fig. 4 illustrates the metal-metal bonding interactions in the trinuclear Ta cluster complex. Interestingly, the two metal d electrons in the cluster complex occupy an orbital that delocalizes significantly onto the three

metal centers. On the basis of the calculation results, we conclude a three-center-two-electron bond for the trinuclear Ta cluster complex.

Fig. 4 also shows the plot of the lowest unoccupied molecular orbital (LUMO). The LUMO shows a bonding interaction between d orbitals of Ta(2) and Ta(3). Clearly, d-d transition is responsible for the absorption peak at 450 nm observed in the visible spectrum (Fig. S7). The time-dependent B3LYP (TD-B3LYP) calculation gives the lowest excited state at a wavelength of 494 nm, a value close to the experimentally observed one.

Molecular geometry of the trinuclear Ta cluster complex **2**, in which the *tert*-butyl groups were modeled by CH₃, was optimized at the Becke3LYP level of density functional theory.^{S3} The Ta atom was described using the LANL2DZ basis set with the Hay and Wadt effective core potential (ECP).^{S4} The 6-31G basis set was used for other atoms.^{S5} All calculations were performed with Gaussian 03 packages.^{S6}

To test the basis set dependence of the calculated Ta-Ta bond distances, we also employed the SDD basis set^{S7} with Stuttgart potentials for Ta to carry out the geometry optimization for the trinuclear Ta cluster complex **2A**, a model for **2**. Comparison of the calculated bond distances obtained based on the LANL2DZ and SDD basis sets was made (Fig. S1). Both basis sets reproduce well the experimental structure. The LANL2DZ basis gives slightly better results in reproducing the Ta-Ta distances.

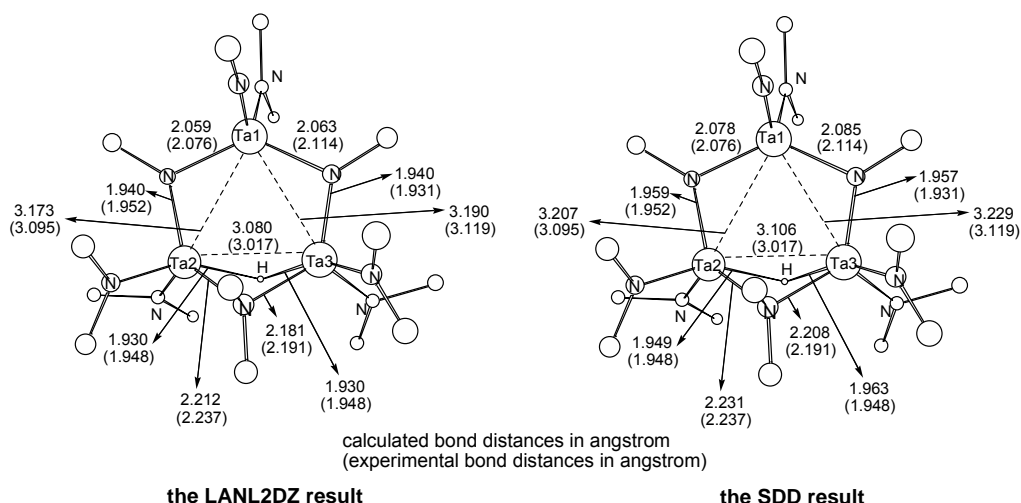


Fig. S1 Comparison of the results using the LANL2DZ and SDD basis sets.

References

- (S1) For the dependence of vicinal couplings on dihedral angles, see, e.g., H. Friebolin, in *Basic One- and Two-Dimensional NMR Spectroscopy*, Wiley-VCH, Weinheim, 2005, pp. 90-93.
- (S2) (a) G. M. Sheldrick, *SADABS, A Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen, Göttingen, Germany, 2000; (b) G. M. Sheldrick, *SHELXL-97, A Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1997.
- (S3) (a) A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B* 1988, **37**, 785; (c) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.* 1994, **98**, 11623.
- (S4) (a) P. J. Hay and W. R. Wadt, *J. Chem. Phys.* 1985, **82**, 299; (b) W. R. Wadt and P. J. Hay, *J. Chem. Phys.* 1985, **82**, 284.
- (S5) P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta* 1973, **28**, 213.
- (S6) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T., Jr. 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, 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 D01; Gaussian, Inc.: Pittsburgh, PA, 2003.

(S7) (a) A. Bergner, M. Dolg, W. Kuechle, H. Stoll and H. Preuss, *Mol. Phys.* 1993, **80**, 1431; (b) M. Dolg, U. Wedig, H. Stoll and H. Preuss, *J. Chem. Phys.* 1987, **86**, 866.

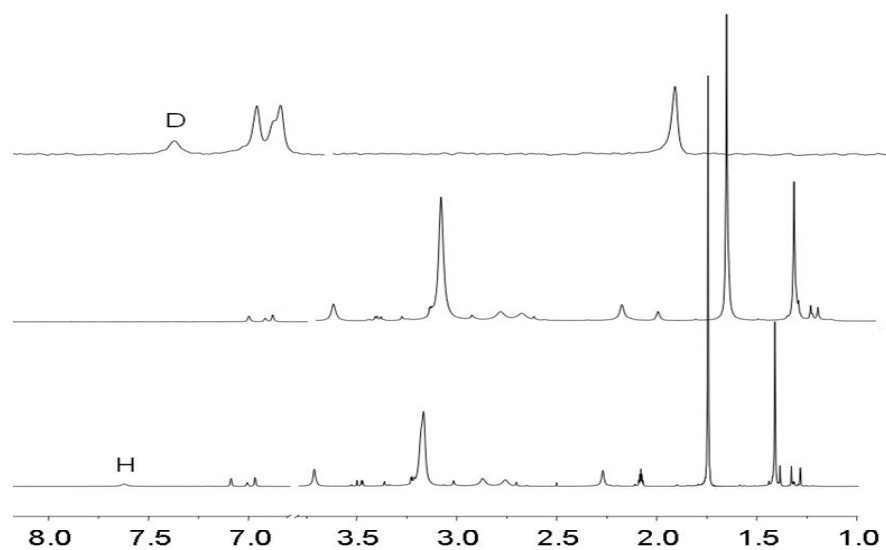


Fig. S2 ^1H NMR spectrum of **2** (bottom) and **2- d_1** (middle) in $\text{toluene-}d_8$. ^2H NMR spectrum of **2- d_1** (top) in toluene. All were acquired at 23 °C.

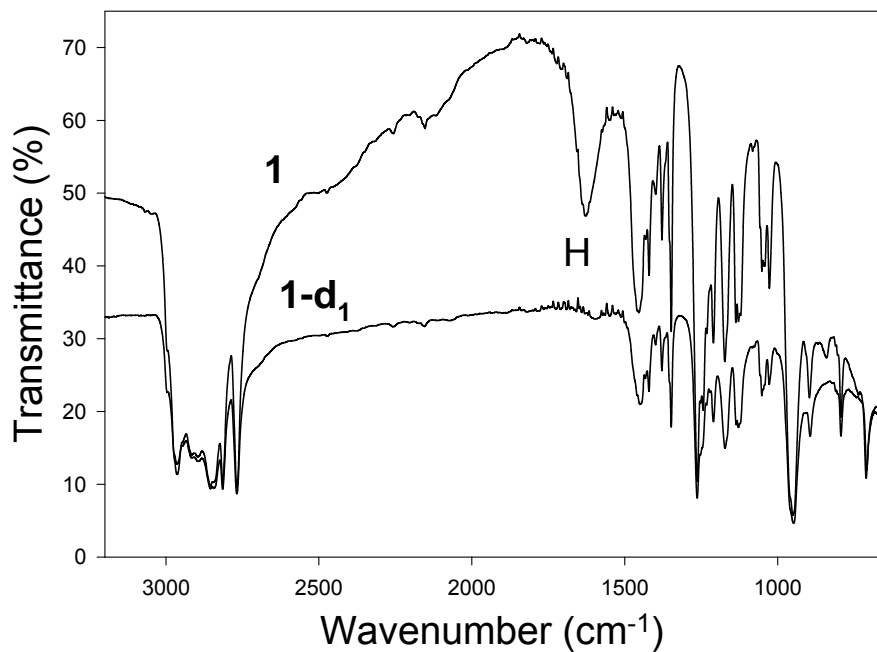


Fig. S3 FT-IR spectra of **2** (top) and **2- d_1** (bottom).

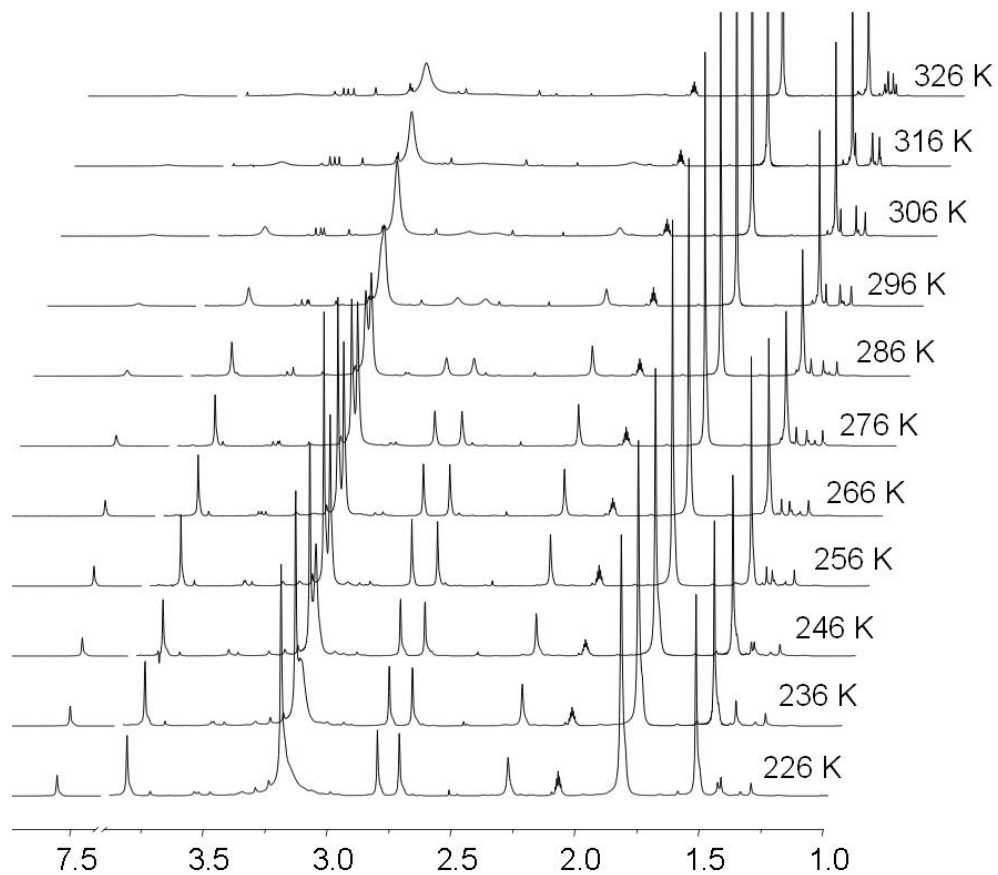


Fig. S4 Variable-temperature ^1H NMR spectra of **2** (226-326 K).

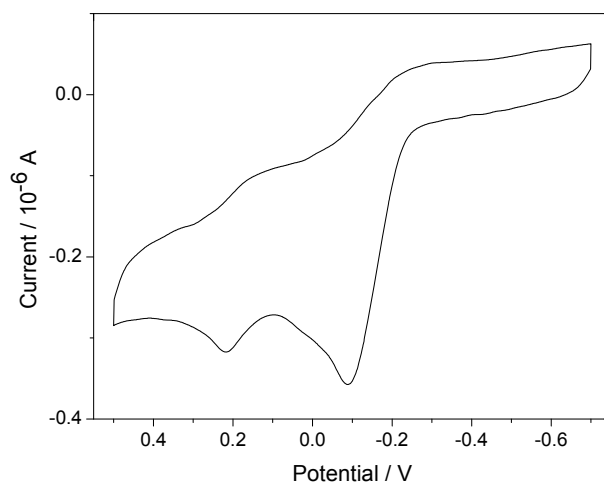


Fig. S5 Cyclic voltammetry (CV) showing irreversible oxidation of **2** at -0.089 and 0.22 V (vs. Ag/AgCl). For the CV experiment: [**2**]: 1.0 mM; solvent: HCCl₃; electrolyte: 0.10 M (Buⁿ₄N)PF₆; scan rate: 100 mV/s (working electrode: glassy carbon; reference electrode: Ag/AgCl; counter electrode: Pt).

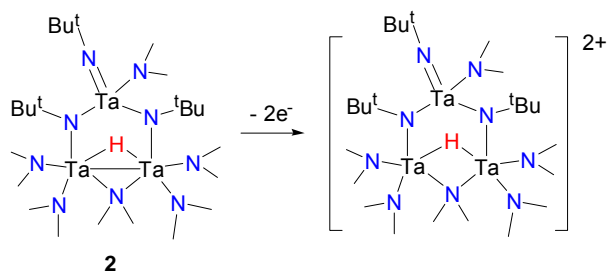


Fig. S6 Postulated oxidation of **2** in the CV experiments.

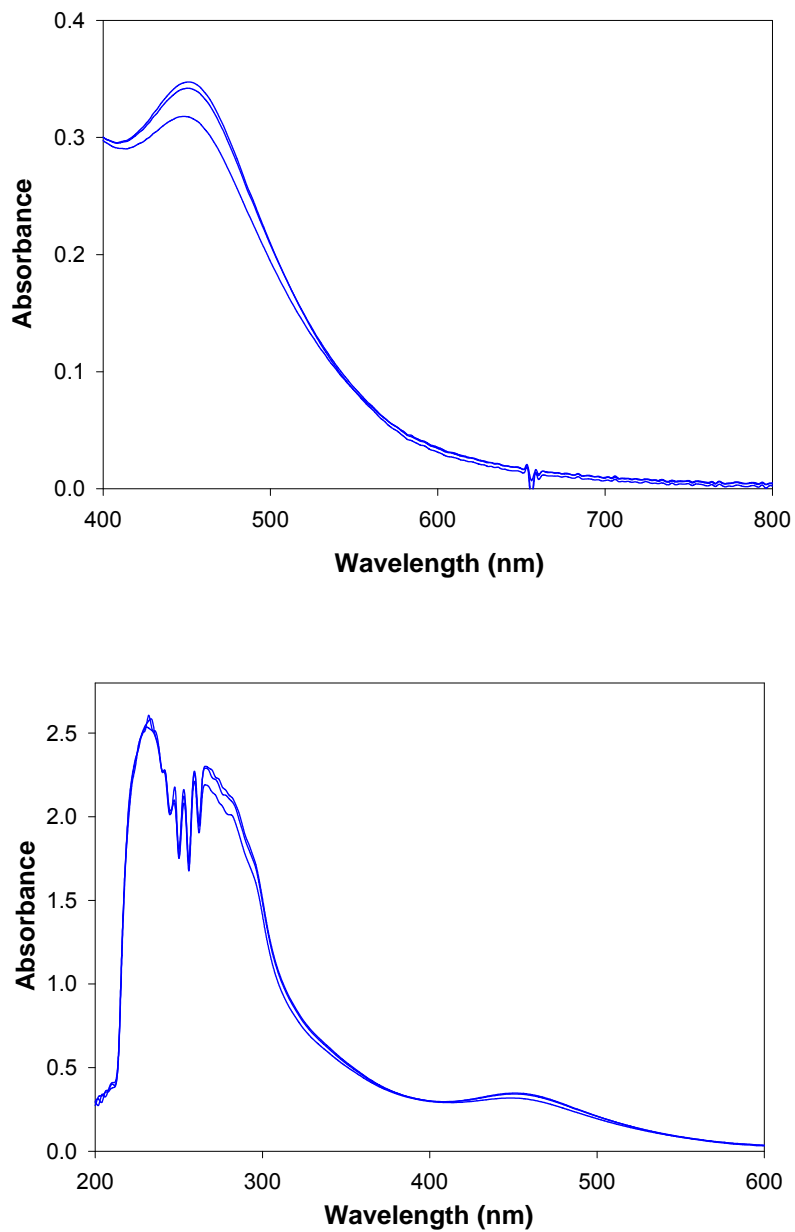


Fig. S7 UV-Vis spectrum of **2** (0.202 mM in hexanes). Up: 400-800 nm; Bottom: 200-600 nm. Three scans were obtained of the sample, and the three spectra are given.



Fig. S8 HSQC (Heteronuclear Single Quantum Coherence) spectrum of **4** (benzene- d_6 , 26 °C). It gives the correlation between ^1H and ^{13}C atoms that are bound to each other. f1 and f2 are ^{13}C and ^1H NMR axes, respectively.

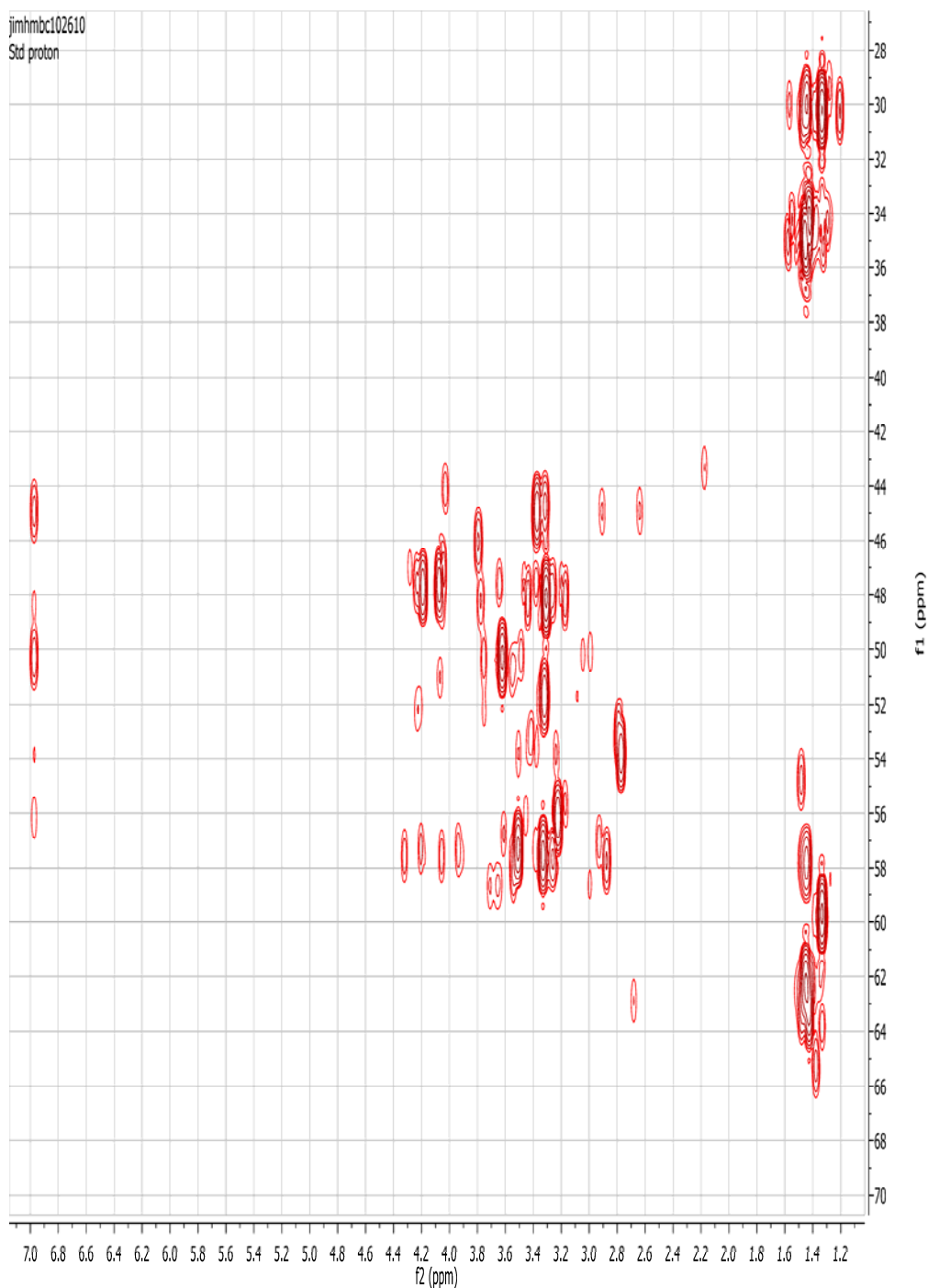


Fig. S9 HMBC (Heteronuclear Multiple Bond Correlation) spectrum of **4** (benzene- d_6 , 26 °C), providing correlations between protons and carbons over two and three bonds.

This spectrum reveals the correlations of: (1) Protons of one Me group with the C atom of the other Me group in the same $-NMe_2$ ligand - The H and C atoms are three bonds away; (2) Hydride ligand with vicinal C atoms (three bonds away) with dihedral angles of ca. 180° .¹¹ f1 and f2 are ^{13}C and 1H NMR axes, respectively.

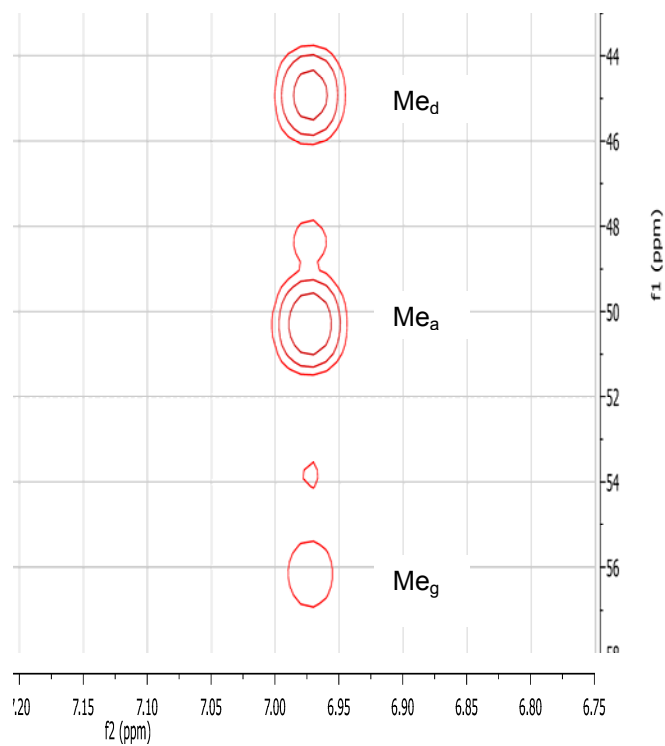


Fig. S10 HMBC spectrum of **4** (benzene- d_6 , 26 °C) around the hydride region. f1 and f2 are ^{13}C and ^1H NMR axes, respectively. This portion of the spectrum highlights the correlations of the hydride ligand with vicinal C atoms (three bonds away) with dihedral angles of ca. 180° .¹¹

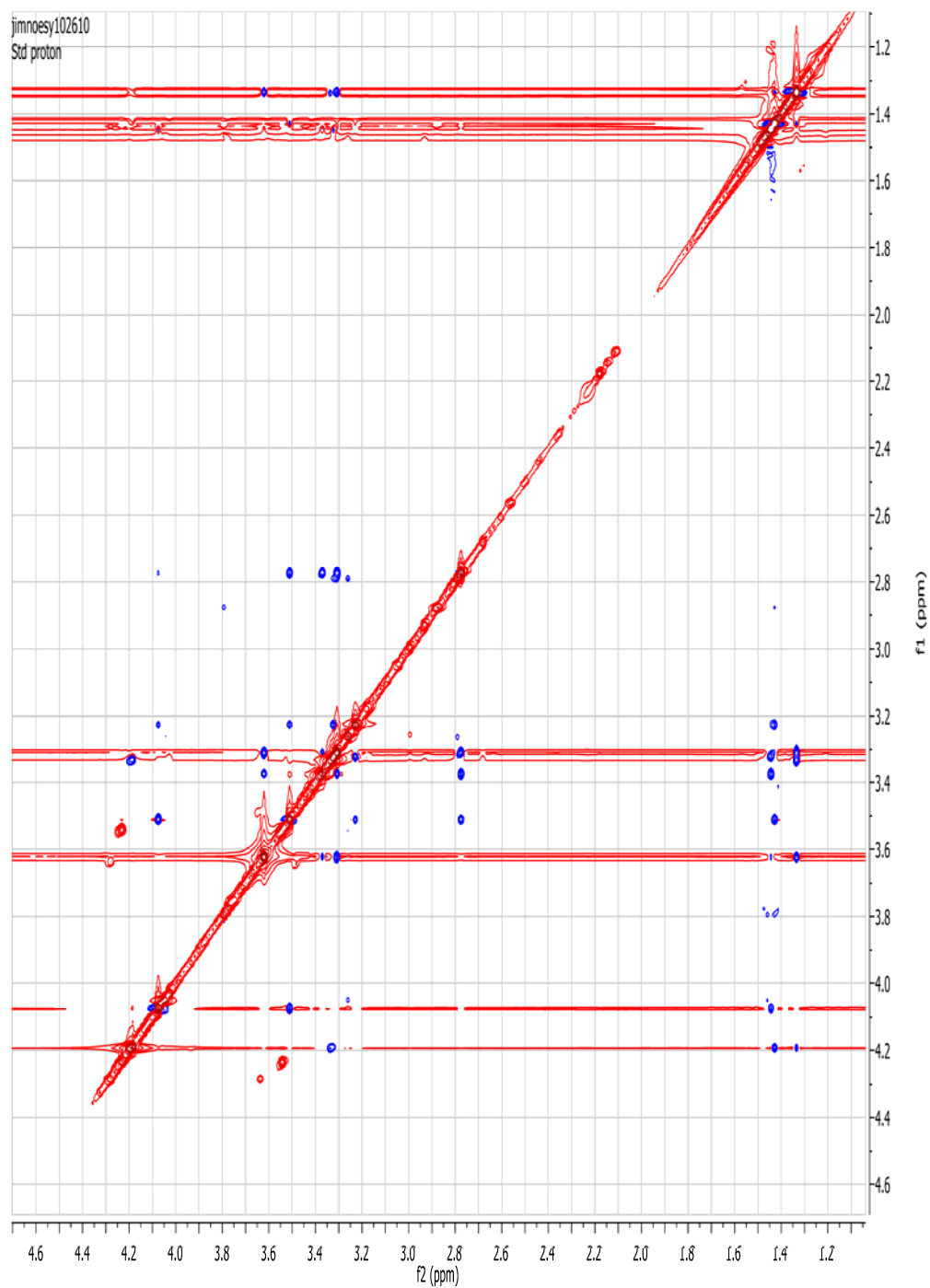


Fig. S11 NOESY (Nuclear Overhauser Enhancement Spectroscopy) spectrum of **4** (benzene-*d*₆, 26 °C), Part 1. Cross-peaks connect resonances of H atoms that are spatially close. Both f1 and f2 are ¹H NMR axes.

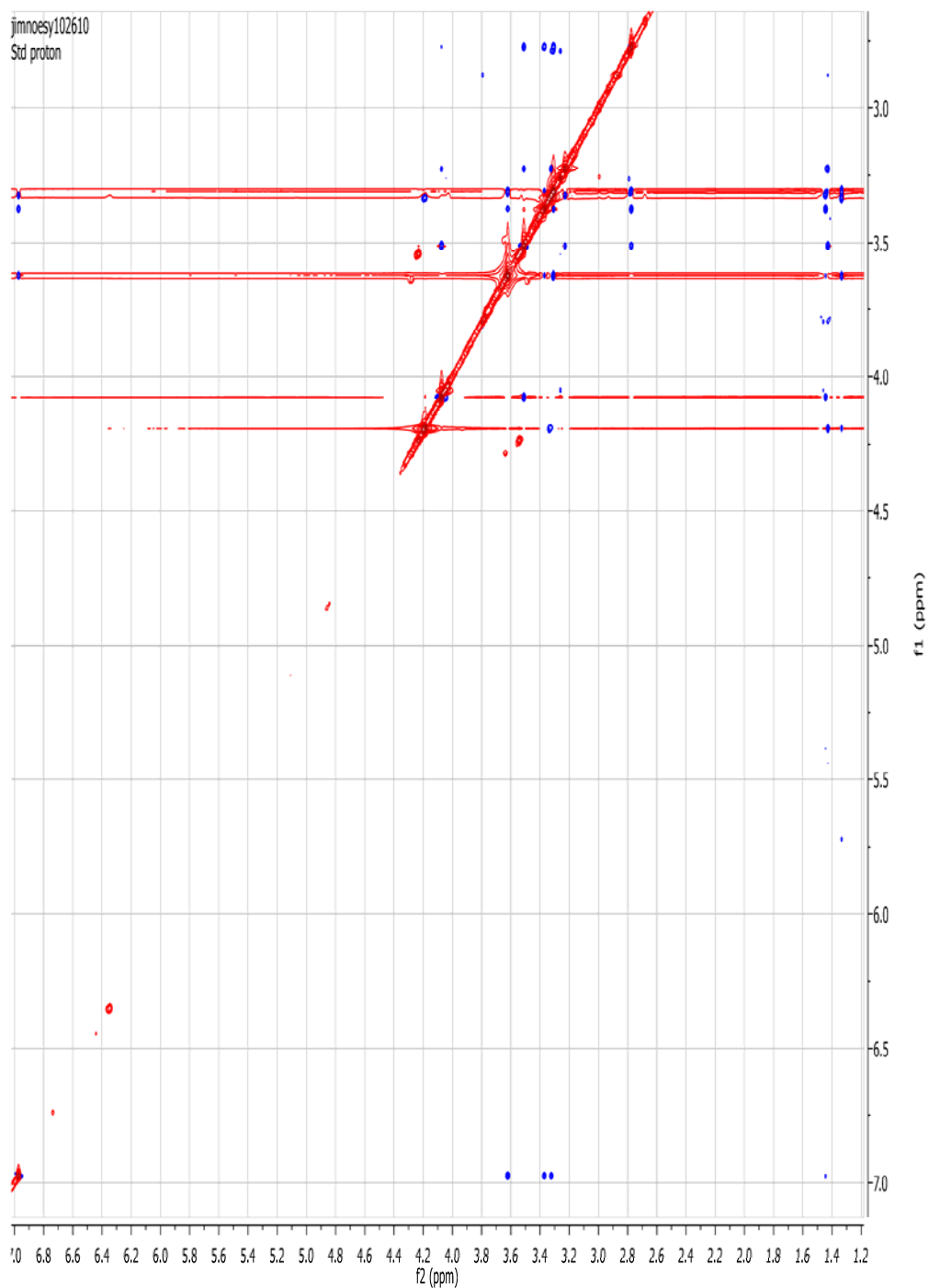


Fig. S12 NOESY (Nuclear Overhauser Enhancement Spectroscopy) spectrum of **4** (benzene-*d*₆, 26 °C), Part 2. Cross-peaks connect resonances of H atoms that are spatially close. Both f1 and f2 are ¹H NMR axes.

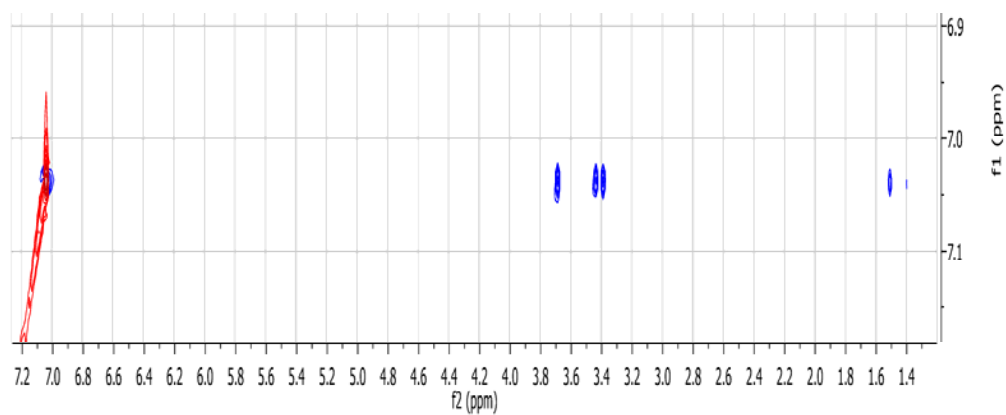


Fig. S13 NOESY (Nuclear Overhauser Enhancement Spectroscopy) spectrum of **4** (benzene- d_6 , 26 °C), Part 3 near the hydride region on f1. Cross-peaks connect resonances of the hydride ligand with H atoms that are spatially close. Both f1 and f2 are ^1H NMR axes.

Table S1. Crystal data and structure refinement for **2**.

Empirical formula	C ₂₄ H ₆₄ N ₉ Ta ₃	
Formula weight	1021.69	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pna2(1)	
Unit cell dimensions	<i>a</i> = 21.270(11) Å	$\alpha = 90^\circ$
	<i>b</i> = 9.700(5) Å	$\beta = 90^\circ$
	<i>c</i> = 17.118(9) Å	$\gamma = 90^\circ$
Volume	3532(3) Å ³	
Z	4	
Density (calculated)	1.922 Mg/m ³	
Absorption coefficient	9.298 mm ⁻¹	
<i>F</i> (000)	1960	
Crystal size	0.20 x 0.20 x 0.05 mm ³	
Theta range for data collection	1.91 to 28.36°	
Index ranges	-27 ≤ <i>h</i> ≤ 27, -12 ≤ <i>k</i> ≤ 12, -21 ≤ <i>l</i> ≤ 22	
Reflections collected	35048	
Independent reflections	8156 [<i>R</i> (int) = 0.0322]	
Completeness to theta = 28.36°	95.2%	
Max. and min. transmission	0.6535 and 0.2578	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	8156 / 1 / 349	
Goodness-of-fit on <i>F</i> ²	1.020	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0158, w <i>R</i> 2 = 0.0349	
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0166, w <i>R</i> 2 = 0.0351	
Absolute structure parameter	-0.001(6)	
Largest diff. peak and hole	0.897 and -1.394 e.Å ⁻³	

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
Ta(1)	6419(1)	5724(1)	3557(1)	14(1)
Ta(2)	6217(1)	4971(1)	5296(1)	14(1)
Ta(3)	7528(1)	4799(1)	4628(1)	18(1)
N(1)	7411(1)	5662(3)	3622(2)	20(1)
N(2)	5734(1)	5029(2)	4326(2)	16(1)
N(3)	7122(1)	6044(3)	5569(2)	22(1)
N(4)	6272(1)	4650(3)	2576(2)	19(1)
N(5)	6206(1)	7463(2)	3329(2)	19(1)
N(6)	5758(1)	6438(3)	5904(2)	22(1)
N(7)	5948(1)	3226(3)	5822(2)	21(1)
N(8)	7733(1)	2845(3)	4372(2)	25(1)
N(9)	8401(2)	5337(4)	5004(2)	32(1)
C(1)	7851(2)	6325(4)	3046(2)	27(1)
C(2)	8493(2)	5615(5)	3046(3)	44(1)
C(3)	7583(2)	6299(5)	2228(2)	38(1)
C(4)	7937(2)	7832(4)	3297(3)	43(1)
C(5)	5070(2)	4629(3)	4141(2)	21(1)
C(6)	5078(2)	3174(4)	3795(2)	31(1)
C(7)	4784(2)	5614(4)	3546(3)	30(1)
C(8)	4653(2)	4630(4)	4874(2)	32(1)
C(9)	7358(2)	5723(4)	6367(2)	29(1)
C(10)	7071(2)	7552(3)	5470(2)	30(1)
C(11)	6466(2)	3212(3)	2591(2)	31(1)
C(12)	6062(2)	5052(4)	1801(2)	28(1)
C(13)	6031(2)	8885(3)	3173(2)	24(1)
C(14)	5312(2)	9064(4)	3189(3)	41(1)
C(15)	6277(3)	9293(4)	2366(3)	46(1)
C(16)	6310(2)	9817(4)	3815(3)	37(1)
C(17)	5824(2)	6609(4)	6749(2)	36(1)
C(18)	5421(2)	7614(4)	5585(2)	33(1)

C(19)	5496(2)	3176(4)	6472(2)	33(1)
C(20)	6090(2)	1828(4)	5566(2)	28(1)
C(21)	7775(2)	1796(4)	4981(2)	38(1)
C(22)	7902(2)	2256(4)	3618(3)	36(1)
C(23)	8638(2)	6677(5)	5273(3)	48(1)
C(24)	8939(2)	4371(5)	4983(3)	42(1)

Table S3. Bond lengths (Å) and angles (deg) for **2**.

Ta(1)-N(5)	1.789(3)	C(1)-C(2)	1.530(5)
Ta(1)-N(4)	2.001(3)	C(1)-C(4)	1.534(5)
Ta(1)-N(2)	2.076(3)	C(2)-H(2A)	0.9800
Ta(1)-N(1)	2.114(3)	C(2)-H(2B)	0.9800
Ta(1)-Ta(2)	3.0950(15)	C(2)-H(2C)	0.9800
Ta(1)-Ta(3)	3.1190(11)	C(3)-H(3A)	0.9800
Ta(2)-N(2)	1.953(3)	C(3)-H(3B)	0.9800
Ta(2)-N(7)	2.002(3)	C(3)-H(3C)	0.9800
Ta(2)-N(6)	2.016(3)	C(4)-H(4A)	0.9800
Ta(2)-N(3)	2.237(3)	C(4)-H(4B)	0.9800
Ta(2)-Ta(3)	3.0173(13)	C(4)-H(4C)	0.9800
Ta(2)-H(1)	1.95(4)	C(5)-C(7)	1.524(5)
Ta(3)-N(1)	1.930(3)	C(5)-C(6)	1.531(5)
Ta(3)-N(8)	1.994(3)	C(5)-C(8)	1.535(5)
Ta(3)-N(9)	2.034(3)	C(6)-H(6A)	0.9800
Ta(3)-N(3)	2.191(3)	C(6)-H(6B)	0.9800
Ta(3)-H(1)	1.86(4)	C(6)-H(6C)	0.9800
N(1)-C(1)	1.505(4)	C(7)-H(7A)	0.9800
N(2)-C(5)	1.498(4)	C(7)-H(7B)	0.9800
N(3)-C(10)	1.476(4)	C(7)-H(7C)	0.9800
N(3)-C(9)	1.489(5)	C(8)-H(8A)	0.9800
N(4)-C(12)	1.453(5)	C(8)-H(8B)	0.9800
N(4)-C(11)	1.455(4)	C(8)-H(8C)	0.9800
N(5)-C(13)	1.454(4)	C(9)-H(9A)	0.9800
N(6)-C(18)	1.455(5)	C(9)-H(9B)	0.9800
N(6)-C(17)	1.462(5)	C(9)-H(9C)	0.9800
N(7)-C(20)	1.457(5)	C(10)-H(10A)	0.9800
N(7)-C(19)	1.470(5)	C(10)-H(10B)	0.9800
N(8)-C(22)	1.458(5)	C(10)-H(10C)	0.9800
N(8)-C(21)	1.459(4)	C(11)-H(11A)	0.9800
N(9)-C(23)	1.468(6)	C(11)-H(11B)	0.9800
N(9)-C(24)	1.479(5)	C(11)-H(11C)	0.9800
C(1)-C(3)	1.511(5)	C(12)-H(12A)	0.9800

C(12)-H(12B)	0.9800	C(23)-H(23B)	0.9800
C(12)-H(12C)	0.9800	C(24)-H(24D)	0.9800
C(13)-C(15)	1.530(5)	C(24)-H(24A)	0.9800
C(13)-C(14)	1.539(5)	C(24)-H(24B)	0.9800
C(13)-C(16)	1.541(6)	N(5)-Ta(1)-N(4)	105.58(12)
C(14)-H(14A)	0.9800	N(5)-Ta(1)-N(2)	105.52(11)
C(14)-H(14B)	0.9800	N(4)-Ta(1)-N(2)	104.67(12)
C(14)-H(14C)	0.9800	N(5)-Ta(1)-N(1)	106.89(11)
C(15)-H(15A)	0.9800	N(4)-Ta(1)-N(1)	100.70(12)
C(15)-H(15B)	0.9800	N(2)-Ta(1)-N(1)	131.10(12)
C(15)-H(15C)	0.9800	N(5)-Ta(1)-Ta(2)	113.41(9)
C(16)-H(16A)	0.9800	N(4)-Ta(1)-Ta(2)	131.50(9)
C(16)-H(16B)	0.9800	N(2)-Ta(1)-Ta(2)	38.38(8)
C(16)-H(16C)	0.9800	N(1)-Ta(1)-Ta(2)	94.62(9)
C(17)-H(17A)	0.9800	N(5)-Ta(1)-Ta(3)	126.18(9)
C(17)-H(17B)	0.9800	N(4)-Ta(1)-Ta(3)	117.49(8)
C(17)-H(17C)	0.9800	N(2)-Ta(1)-Ta(3)	93.68(9)
C(18)-H(18A)	0.9800	N(1)-Ta(1)-Ta(3)	37.42(9)
C(18)-H(18B)	0.9800	Ta(2)-Ta(1)-Ta(3)	58.10(2)
C(18)-H(18C)	0.9800	N(2)-Ta(2)-N(7)	104.85(11)
C(19)-H(19A)	0.9800	N(2)-Ta(2)-N(6)	99.46(12)
C(19)-H(19B)	0.9800	N(7)-Ta(2)-N(6)	103.04(12)
C(19)-H(19C)	0.9800	N(2)-Ta(2)-N(3)	128.08(11)
C(20)-H(20A)	0.9800	N(7)-Ta(2)-N(3)	123.08(11)
C(20)-H(20B)	0.9800	N(6)-Ta(2)-N(3)	88.84(12)
C(20)-H(20C)	0.9800	N(2)-Ta(2)-Ta(3)	99.52(9)
C(21)-H(21A)	0.9800	N(7)-Ta(2)-Ta(3)	112.87(8)
C(21)-H(21B)	0.9800	N(6)-Ta(2)-Ta(3)	133.00(8)
C(21)-H(21C)	0.9800	N(3)-Ta(2)-Ta(3)	46.40(8)
C(22)-H(22A)	0.9800	N(2)-Ta(2)-Ta(1)	41.30(8)
C(22)-H(22B)	0.9800	N(7)-Ta(2)-Ta(1)	132.26(8)
C(22)-H(22D)	0.9800	N(6)-Ta(2)-Ta(1)	113.42(9)
C(23)-H(23A)	0.9800	N(3)-Ta(2)-Ta(1)	88.39(8)
C(23)-H(23D)	0.9800	Ta(3)-Ta(2)-Ta(1)	61.349(10)

N(2)-Ta(2)-H(1)	109.2(11)	C(10)-N(3)-Ta(3)	119.4(2)
N(7)-Ta(2)-H(1)	76.4(11)	C(9)-N(3)-Ta(3)	115.3(2)
N(6)-Ta(2)-H(1)	150.6(11)	C(10)-N(3)-Ta(2)	111.9(2)
N(3)-Ta(2)-H(1)	68.4(11)	C(9)-N(3)-Ta(2)	112.6(2)
Ta(3)-Ta(2)-H(1)	36.4(11)	Ta(3)-N(3)-Ta(2)	85.90(10)
Ta(1)-Ta(2)-H(1)	85.4(11)	C(12)-N(4)-C(11)	111.1(3)
N(1)-Ta(3)-N(8)	104.20(13)	C(12)-N(4)-Ta(1)	132.4(2)
N(1)-Ta(3)-N(9)	106.78(13)	C(11)-N(4)-Ta(1)	116.1(2)
N(8)-Ta(3)-N(9)	96.48(13)	C(13)-N(5)-Ta(1)	178.0(3)
N(1)-Ta(3)-N(3)	111.47(12)	C(18)-N(6)-C(17)	109.3(3)
N(8)-Ta(3)-N(3)	140.50(11)	C(18)-N(6)-Ta(2)	126.7(2)
N(9)-Ta(3)-N(3)	89.17(13)	C(17)-N(6)-Ta(2)	123.0(2)
N(1)-Ta(3)-Ta(2)	101.25(8)	C(20)-N(7)-C(19)	109.4(3)
N(8)-Ta(3)-Ta(2)	109.76(8)	C(20)-N(7)-Ta(2)	126.3(2)
N(9)-Ta(3)-Ta(2)	135.19(10)	C(19)-N(7)-Ta(2)	123.7(2)
N(3)-Ta(3)-Ta(2)	47.70(7)	C(22)-N(8)-C(21)	110.1(3)
N(1)-Ta(3)-Ta(1)	41.73(8)	C(22)-N(8)-Ta(3)	128.4(2)
N(8)-Ta(3)-Ta(1)	108.10(9)	C(21)-N(8)-Ta(3)	121.4(2)
N(9)-Ta(3)-Ta(1)	143.41(10)	C(23)-N(9)-C(24)	107.7(3)
N(3)-Ta(3)-Ta(1)	88.61(8)	C(23)-N(9)-Ta(3)	129.7(3)
Ta(2)-Ta(3)-Ta(1)	60.55(3)	C(24)-N(9)-Ta(3)	122.4(3)
N(1)-Ta(3)-H(1)	126.0(11)	N(1)-C(1)-C(3)	111.5(3)
N(8)-Ta(3)-H(1)	74.6(11)	N(1)-C(1)-C(2)	111.3(3)
N(9)-Ta(3)-H(1)	127.2(11)	C(3)-C(1)-C(2)	109.2(3)
N(3)-Ta(3)-H(1)	71.0(11)	N(1)-C(1)-C(4)	107.3(3)
Ta(2)-Ta(3)-H(1)	38.6(11)	C(3)-C(1)-C(4)	108.7(3)
Ta(1)-Ta(3)-H(1)	86.2(11)	C(2)-C(1)-C(4)	108.8(3)
C(1)-N(1)-Ta(3)	133.6(2)	C(1)-C(2)-H(2A)	109.5
C(1)-N(1)-Ta(1)	125.0(2)	C(1)-C(2)-H(2B)	109.5
Ta(3)-N(1)-Ta(1)	100.85(13)	H(2A)-C(2)-H(2B)	109.5
C(5)-N(2)-Ta(2)	131.9(2)	C(1)-C(2)-H(2C)	109.5
C(5)-N(2)-Ta(1)	127.7(2)	H(2A)-C(2)-H(2C)	109.5
Ta(2)-N(2)-Ta(1)	100.32(12)	H(2B)-C(2)-H(2C)	109.5
C(10)-N(3)-C(9)	109.7(3)	C(1)-C(3)-H(3A)	109.5

C(1)-C(3)-H(3B)	109.5	H(8B)-C(8)-H(8C)	109.5
H(3A)-C(3)-H(3B)	109.5	N(3)-C(9)-H(9A)	109.5
C(1)-C(3)-H(3C)	109.5	N(3)-C(9)-H(9B)	109.5
H(3A)-C(3)-H(3C)	109.5	H(9A)-C(9)-H(9B)	109.5
H(3B)-C(3)-H(3C)	109.5	N(3)-C(9)-H(9C)	109.5
C(1)-C(4)-H(4A)	109.5	H(9A)-C(9)-H(9C)	109.5
C(1)-C(4)-H(4B)	109.5	H(9B)-C(9)-H(9C)	109.5
H(4A)-C(4)-H(4B)	109.5	N(3)-C(10)-H(10A)	109.5
C(1)-C(4)-H(4C)	109.5	N(3)-C(10)-H(10B)	109.5
H(4A)-C(4)-H(4C)	109.5	H(10A)-C(10)-H(10B)	109.5
H(4B)-C(4)-H(4C)	109.5	N(3)-C(10)-H(10C)	109.5
N(2)-C(5)-C(7)	110.8(3)	H(10A)-C(10)-H(10C)	109.5
N(2)-C(5)-C(6)	108.1(3)	H(10B)-C(10)-H(10C)	109.5
C(7)-C(5)-C(6)	108.9(3)	N(4)-C(11)-H(11A)	109.5
N(2)-C(5)-C(8)	111.8(3)	N(4)-C(11)-H(11B)	109.5
C(7)-C(5)-C(8)	108.4(3)	H(11A)-C(11)-H(11B)	109.5
C(6)-C(5)-C(8)	108.9(3)	N(4)-C(11)-H(11C)	109.5
C(5)-C(6)-H(6A)	109.5	H(11A)-C(11)-H(11C)	109.5
C(5)-C(6)-H(6B)	109.5	H(11B)-C(11)-H(11C)	109.5
H(6A)-C(6)-H(6B)	109.5	N(4)-C(12)-H(12A)	109.5
C(5)-C(6)-H(6C)	109.5	N(4)-C(12)-H(12B)	109.5
H(6A)-C(6)-H(6C)	109.5	H(12A)-C(12)-H(12B)	109.5
H(6B)-C(6)-H(6C)	109.5	N(4)-C(12)-H(12C)	109.5
C(5)-C(7)-H(7A)	109.5	H(12A)-C(12)-H(12C)	109.5
C(5)-C(7)-H(7B)	109.5	H(12B)-C(12)-H(12C)	109.5
H(7A)-C(7)-H(7B)	109.5	N(5)-C(13)-C(15)	108.9(3)
C(5)-C(7)-H(7C)	109.5	N(5)-C(13)-C(14)	111.0(3)
H(7A)-C(7)-H(7C)	109.5	C(15)-C(13)-C(14)	109.0(4)
H(7B)-C(7)-H(7C)	109.5	N(5)-C(13)-C(16)	109.1(3)
C(5)-C(8)-H(8A)	109.5	C(15)-C(13)-C(16)	111.2(3)
C(5)-C(8)-H(8B)	109.5	C(14)-C(13)-C(16)	107.7(3)
H(8A)-C(8)-H(8B)	109.5	C(13)-C(14)-H(14A)	109.5
C(5)-C(8)-H(8C)	109.5	C(13)-C(14)-H(14B)	109.5
H(8A)-C(8)-H(8C)	109.5	H(14A)-C(14)-H(14B)	109.5

C(13)-C(14)-H(14C)	109.5	H(19B)-C(19)-H(19C)	109.5
H(14A)-C(14)-H(14C)	109.5	N(7)-C(20)-H(20A)	109.5
H(14B)-C(14)-H(14C)	109.5	N(7)-C(20)-H(20B)	109.5
C(13)-C(15)-H(15A)	109.5	H(20A)-C(20)-H(20B)	109.5
C(13)-C(15)-H(15B)	109.5	N(7)-C(20)-H(20C)	109.5
H(15A)-C(15)-H(15B)	109.5	H(20A)-C(20)-H(20C)	109.5
C(13)-C(15)-H(15C)	109.5	H(20B)-C(20)-H(20C)	109.5
H(15A)-C(15)-H(15C)	109.5	N(8)-C(21)-H(21A)	109.5
H(15B)-C(15)-H(15C)	109.5	N(8)-C(21)-H(21B)	109.5
C(13)-C(16)-H(16A)	109.5	H(21A)-C(21)-H(21B)	109.5
C(13)-C(16)-H(16B)	109.5	N(8)-C(21)-H(21C)	109.5
H(16A)-C(16)-H(16B)	109.5	H(21A)-C(21)-H(21C)	109.5
C(13)-C(16)-H(16C)	109.5	H(21B)-C(21)-H(21C)	109.5
H(16A)-C(16)-H(16C)	109.5	N(8)-C(22)-H(22A)	109.5
H(16B)-C(16)-H(16C)	109.5	N(8)-C(22)-H(22B)	109.5
N(6)-C(17)-H(17A)	109.5	H(22A)-C(22)-H(22B)	109.5
N(6)-C(17)-H(17B)	109.5	N(8)-C(22)-H(22D)	109.5
H(17A)-C(17)-H(17B)	109.5	H(22A)-C(22)-H(22D)	109.5
N(6)-C(17)-H(17C)	109.5	H(22B)-C(22)-H(22D)	109.5
H(17A)-C(17)-H(17C)	109.5	N(9)-C(23)-H(23A)	109.5
H(17B)-C(17)-H(17C)	109.5	N(9)-C(23)-H(23D)	109.5
N(6)-C(18)-H(18A)	109.5	H(23A)-C(23)-H(23D)	109.5
N(6)-C(18)-H(18B)	109.5	N(9)-C(23)-H(23B)	109.5
H(18A)-C(18)-H(18B)	109.5	H(23A)-C(23)-H(23B)	109.5
N(6)-C(18)-H(18C)	109.5	H(23D)-C(23)-H(23B)	109.5
H(18A)-C(18)-H(18C)	109.5	N(9)-C(24)-H(24D)	109.5
H(18B)-C(18)-H(18C)	109.5	N(9)-C(24)-H(24A)	109.5
N(7)-C(19)-H(19A)	109.5	H(24D)-C(24)-H(24A)	109.5
N(7)-C(19)-H(19B)	109.5	N(9)-C(24)-H(24B)	109.5
H(19A)-C(19)-H(19B)	109.5	H(24D)-C(24)-H(24B)	109.5
N(7)-C(19)-H(19C)	109.5	H(24A)-C(24)-H(24B)	109.5
H(19A)-C(19)-H(19C)	109.5		

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + \dots + 2hka^*b^*U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ta(1)	13(1)	16(1)	12(1)	1(1)	1(1)	-1(1)
Ta(2)	12(1)	19(1)	12(1)	0(1)	0(1)	0(1)
Ta(3)	11(1)	25(1)	16(1)	2(1)	0(1)	0(1)
N(1)	16(1)	26(1)	19(2)	4(1)	4(1)	-2(1)
N(2)	10(1)	22(1)	16(2)	1(1)	0(1)	-1(1)
N(3)	20(2)	26(1)	20(2)	0(1)	-6(1)	-3(1)
N(4)	23(2)	19(1)	16(2)	0(1)	0(1)	3(1)
N(5)	22(1)	15(1)	20(2)	1(1)	2(1)	0(1)
N(6)	19(1)	28(1)	19(2)	-4(1)	2(1)	2(1)
N(7)	17(1)	26(1)	19(2)	1(1)	2(1)	-2(1)
N(8)	20(2)	28(1)	26(2)	3(1)	6(1)	5(1)
N(9)	14(2)	50(2)	32(2)	-3(2)	-3(1)	-3(1)
C(1)	17(2)	37(2)	28(2)	11(2)	5(2)	-1(2)
C(2)	19(2)	72(3)	39(3)	22(2)	12(2)	4(2)
C(3)	28(2)	61(3)	24(2)	14(2)	12(2)	-1(2)
C(4)	34(2)	42(2)	54(3)	9(2)	7(2)	-16(2)
C(5)	11(2)	26(2)	26(2)	2(1)	-4(1)	-3(1)
C(6)	26(2)	31(2)	36(2)	-4(2)	-4(2)	-6(2)
C(7)	18(2)	38(2)	33(2)	11(2)	-7(2)	-3(1)
C(8)	19(2)	50(2)	27(2)	-1(2)	0(2)	-7(2)
C(9)	27(2)	42(2)	19(2)	1(2)	-9(2)	-6(2)
C(10)	25(2)	28(2)	36(2)	-3(2)	-1(2)	-5(2)
C(11)	40(2)	20(2)	32(2)	-7(2)	-4(2)	4(2)
C(12)	35(2)	31(2)	17(2)	-1(2)	-5(2)	2(2)
C(13)	28(2)	19(2)	25(2)	4(1)	3(2)	3(1)
C(14)	32(2)	24(2)	66(3)	5(2)	-8(2)	8(2)
C(15)	81(4)	25(2)	31(3)	12(2)	19(2)	7(2)
C(16)	45(3)	21(2)	46(3)	-1(2)	-8(2)	-4(2)
C(17)	34(2)	51(2)	23(2)	-9(2)	2(2)	2(2)
C(18)	28(2)	30(2)	41(2)	-5(2)	0(2)	8(2)

C(19)	30(2)	40(2)	28(2)	11(2)	10(2)	4(2)
C(20)	26(2)	26(2)	32(2)	1(2)	-1(2)	-4(2)
C(21)	29(2)	43(2)	41(2)	16(2)	7(2)	16(2)
C(22)	36(2)	36(2)	35(2)	0(2)	10(2)	9(2)
C(23)	21(2)	65(3)	60(3)	-13(3)	-2(2)	-19(2)
C(24)	16(2)	68(3)	41(3)	9(2)	-1(2)	5(2)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2**.

	x	y	z	$U(\text{eq})$
H(1)	6936(18)	3750(40)	5160(20)	26
H(2A)	8443	4649	2892	65
H(2B)	8675	5660	3572	65
H(2C)	8773	6082	2676	65
H(3A)	7496	5344	2076	57
H(3B)	7888	6702	1864	57
H(3C)	7193	6834	2214	57
H(4A)	7525	8277	3339	65
H(4B)	8192	8318	2908	65
H(4C)	8149	7862	3805	65
H(6A)	5319	3177	3307	46
H(6B)	4646	2875	3689	46
H(6C)	5275	2538	4167	46
H(7A)	5029	5581	3061	45
H(7B)	4790	6554	3755	45
H(7C)	4349	5341	3438	45
H(8A)	4678	5532	5129	48
H(8B)	4798	3914	5235	48
H(8C)	4217	4443	4724	48
H(9A)	7801	5990	6407	44
H(9B)	7317	4732	6466	44
H(9C)	7112	6236	6754	44
H(10A)	7488	7970	5516	44
H(10B)	6794	7930	5874	44
H(10C)	6896	7758	4953	44
H(11A)	6108	2624	2451	46
H(11B)	6613	2973	3116	46
H(11C)	6807	3070	2215	46
H(12A)	6399	4881	1423	42
H(12B)	5955	6035	1800	42

H(12C)	5691	4511	1657	42
H(14A)	5122	8498	2778	61
H(14B)	5206	10035	3100	61
H(14C)	5150	8773	3699	61
H(15A)	6071	8727	1966	69
H(15B)	6732	9144	2345	69
H(15C)	6185	10268	2269	69
H(16A)	6770	9771	3795	56
H(16B)	6164	9501	4328	56
H(16C)	6174	10770	3730	56
H(17A)	5406	6687	6987	54
H(17B)	6066	7446	6859	54
H(17C)	6043	5808	6968	54
H(18A)	4994	7636	5800	50
H(18B)	5400	7531	5015	50
H(18C)	5641	8466	5724	50
H(19A)	5130	2625	6318	49
H(19B)	5360	4114	6602	49
H(19C)	5696	2757	6929	49
H(20A)	6270	1305	6002	42
H(20B)	6392	1860	5135	42
H(20C)	5702	1378	5390	42
H(21A)	8198	1392	4979	57
H(21B)	7464	1073	4881	57
H(21C)	7693	2218	5491	57
H(22A)	7653	1422	3525	54
H(22B)	8350	2020	3616	54
H(22D)	7817	2929	3204	54
H(23A)	8783	6596	5814	73
H(23D)	8300	7362	5244	73
H(23B)	8988	6969	4939	73
H(24D)	9112	4269	5511	63
H(24A)	9264	4733	4633	63
H(24B)	8796	3471	4793	63

Table S6. Crystal data and structure refinement for **4**.

Empirical formula	$C_{24}H_{64}N_9OTa_3$	
Formula weight	1037.69	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2(1)2(1)2(1)$	
Unit cell dimensions	$a = 9.289(4)$ Å	$\alpha = 90^\circ$
	$b = 17.389(7)$ Å	$\beta = 90^\circ$
	$c = 23.143(9)$ Å	$\gamma = 90^\circ$
Volume	$3738(2)$ Å ³	
Z	4	
Density (calculated)	1.844 Mg/m ³	
Absorption coefficient	8.787 mm ⁻¹	
$F(000)$	1992	
Crystal size	0.40 x 0.20 x 0.20 mm ³	
Theta range for data collection	1.46 to 27.50°	
Index ranges	$-11 \leq h \leq 12, -22 \leq k \leq 22, -29 \leq l \leq 30$	
Reflections collected	38925	
Independent reflections	8559 [$R(\text{int}) = 0.0675$]	
Completeness to theta = 27.50°	100.0%	
Max. and min. transmission	0.2724 and 0.1269	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8559 / 42 / 345	
Goodness-of-fit on F^2	1.071	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0394, wR2 = 0.1076$	
R indices (all data)	$R1 = 0.0404, wR2 = 0.1082$	
Absolute structure parameter	0.20(2)	
Extinction coefficient	0.00023(6)	
Largest diff. peak and hole	6.897 and -0.829 e.Å ⁻³	

Table S7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ta(1)	5909(1)	9523(1)	309(1)	28(1)
Ta(2)	6977(1)	10878(1)	1027(1)	30(1)
Ta(3)	6084(1)	9436(1)	1796(1)	28(1)
O(1)	7240(6)	9744(3)	1062(3)	30(1)
N(1)	7243(9)	10545(5)	87(3)	40(2)
N(2)	4829(8)	8942(5)	1049(3)	34(2)
N(3)	6924(9)	10586(4)	1959(3)	36(2)
N(4)	4521(8)	9541(5)	-223(3)	36(2)
N(5)	7128(9)	8677(5)	14(3)	38(2)
N(6)	5930(11)	11874(5)	912(4)	45(2)
N(7)	9026(10)	11245(5)	1039(4)	50(2)
N(8)	4443(11)	9417(5)	2361(4)	50(2)
N(9)	7228(10)	8692(4)	2072(3)	35(2)
C(1)	8697(13)	10301(8)	-93(5)	56(3)
C(2)	6617(16)	11100(8)	-324(5)	60(3)
C(3)	3260(10)	9102(10)	1076(5)	66(4)
C(4)	4970(14)	8112(6)	1026(5)	53(3)
C(5)	7044(14)	11081(6)	2497(5)	47(2)
C(6)	8394(17)	10819(8)	2808(6)	72(4)
C(7)	5731(19)	10994(8)	2881(5)	67(4)
C(8)	7249(16)	11910(7)	2325(6)	60(3)
C(9)	3305(10)	9680(6)	-605(4)	51(3)
C(10)	2320(20)	10264(10)	-313(9)	54(4)
C(11)	2430(30)	8986(10)	-769(11)	78(6)
C(12)	3860(20)	10061(13)	-1160(7)	69(5)
C(10B)	2550(30)	10440(10)	-536(12)	54(4)
C(11B)	2200(30)	9039(13)	-496(14)	78(6)
C(12B)	3790(30)	9596(17)	-1229(7)	69(5)
C(13)	8461(12)	8404(7)	261(6)	56(3)

C(14)	6838(15)	8201(7)	-505(5)	56(3)
C(15)	4300(17)	11936(9)	850(7)	75(4)
C(16)	6619(18)	12645(6)	846(6)	62(4)
C(17)	9868(19)	11732(10)	659(7)	84(5)
C(18)	10101(15)	10861(9)	1458(6)	74(4)
C(19)	3154(15)	9871(8)	2339(6)	60(3)
C(20)	4322(17)	8881(8)	2868(5)	64(4)
C(21)	8322(12)	8178(5)	2287(4)	52(3)
C(22)	7650(20)	7381(8)	2355(8)	62(5)
C(23)	8910(20)	8429(12)	2869(6)	77(6)
C(24)	9580(20)	8104(13)	1865(8)	83(6)
C(22B)	8190(50)	7362(11)	2071(15)	62(5)
C(23B)	8270(50)	8170(20)	2947(6)	77(6)
C(24B)	9760(30)	8510(20)	2100(18)	83(6)

Table S8. Bond lengths (Å) and angles (deg) for **4**.

Ta(1)-N(4)	1.784(7)	C(5)-C(6)	1.516(18)
Ta(1)-N(5)	1.978(8)	C(5)-C(7)	1.516(19)
Ta(1)-O(1)	2.170(6)	C(9)-C(10B)	1.504(9)
Ta(1)-N(1)	2.227(9)	C(9)-C(11)	1.504(9)
Ta(1)-N(2)	2.227(8)	C(9)-C(12B)	1.520(9)
Ta(2)-H(1)	1.89(8)	C(9)-C(10)	1.526(9)
Ta(2)-O(1)	1.989(6)	C(9)-C(12)	1.532(9)
Ta(2)-N(6)	2.003(8)	C(9)-C(11B)	1.538(10)
Ta(2)-N(7)	2.008(9)	C(21)-C(22B)	1.510(10)
Ta(2)-N(3)	2.217(8)	C(21)-C(23)	1.518(9)
Ta(2)-N(1)	2.265(8)	C(21)-C(24B)	1.516(10)
Ta(3)-N(9)	1.793(8)	C(21)-C(24)	1.527(9)
Ta(3)-N(8)	2.008(10)	C(21)-C(22)	1.528(9)
Ta(3)-O(1)	2.080(6)	C(21)-C(23B)	1.527(10)
Ta(3)-N(3)	2.180(7)	N(4)-Ta(1)-N(5)	100.8(3)
Ta(3)-N(2)	2.256(7)	N(4)-Ta(1)-O(1)	164.4(3)
N(1)-C(1)	1.475(14)	N(5)-Ta(1)-O(1)	94.7(3)
N(1)-C(2)	1.473(14)	N(4)-Ta(1)-N(1)	103.2(4)
N(2)-C(4)	1.449(14)	N(5)-Ta(1)-N(1)	101.2(3)
N(2)-C(3)	1.485(13)	O(1)-Ta(1)-N(1)	74.2(3)
N(3)-C(5)	1.517(12)	N(4)-Ta(1)-N(2)	102.3(3)
N(4)-C(9)	1.455(11)	N(5)-Ta(1)-N(2)	100.7(3)
N(5)-C(13)	1.444(13)	O(1)-Ta(1)-N(2)	73.7(2)
N(5)-C(14)	1.485(13)	N(1)-Ta(1)-N(2)	142.3(3)
N(6)-C(16)	1.494(14)	H(1)-Ta(2)-O(1)	79(3)
N(6)-C(15)	1.525(18)	H(1)-Ta(2)-N(6)	79(3)
N(7)-C(17)	1.450(15)	O(1)-Ta(2)-N(6)	157.2(3)
N(7)-C(18)	1.545(18)	H(1)-Ta(2)-N(7)	162(2)
N(8)-C(19)	1.435(16)	O(1)-Ta(2)-N(7)	101.4(3)
N(8)-C(20)	1.503(13)	N(6)-Ta(2)-N(7)	100.8(4)
N(9)-C(21)	1.441(12)	H(1)-Ta(2)-N(3)	103(2)
C(5)-C(8)	1.508(16)	O(1)-Ta(2)-N(3)	74.7(3)

N(6)-Ta(2)-N(3)	108.4(3)	Ta(3)-N(3)-Ta(2)	92.8(3)
N(7)-Ta(2)-N(3)	94.6(4)	C(9)-N(4)-Ta(1)	169.7(7)
H(1)-Ta(2)-N(1)	73(2)	C(13)-N(5)-C(14)	107.0(8)
O(1)-Ta(2)-N(1)	76.9(3)	C(13)-N(5)-Ta(1)	126.8(7)
N(6)-Ta(2)-N(1)	98.4(3)	C(14)-N(5)-Ta(1)	126.2(7)
N(7)-Ta(2)-N(1)	89.5(4)	C(16)-N(6)-C(15)	110.6(10)
N(3)-Ta(2)-N(1)	151.5(3)	C(16)-N(6)-Ta(2)	125.6(9)
N(9)-Ta(3)-N(8)	101.9(4)	C(15)-N(6)-Ta(2)	123.8(8)
N(9)-Ta(3)-O(1)	99.8(3)	C(17)-N(7)-C(18)	106.6(11)
N(8)-Ta(3)-O(1)	158.1(3)	C(17)-N(7)-Ta(2)	133.5(10)
N(9)-Ta(3)-N(3)	112.9(3)	C(18)-N(7)-Ta(2)	119.0(7)
N(8)-Ta(3)-N(3)	100.1(4)	C(19)-N(8)-C(20)	107.9(10)
O(1)-Ta(3)-N(3)	73.8(3)	C(19)-N(8)-Ta(3)	126.9(7)
N(9)-Ta(3)-N(2)	107.7(3)	C(20)-N(8)-Ta(3)	125.1(8)
N(8)-Ta(3)-N(2)	95.7(4)	C(21)-N(9)-Ta(3)	171.2(7)
O(1)-Ta(3)-N(2)	74.8(3)	N(3)-C(5)-C(8)	109.5(9)
N(3)-Ta(3)-N(2)	131.9(3)	N(3)-C(5)-C(6)	106.3(9)
Ta(2)-O(1)-Ta(3)	103.0(3)	C(8)-C(5)-C(6)	107.9(11)
Ta(2)-O(1)-Ta(1)	94.1(2)	N(3)-C(5)-C(7)	111.4(9)
Ta(3)-O(1)-Ta(1)	108.4(2)	C(8)-C(5)-C(7)	110.6(11)
C(1)-N(1)-C(2)	111.6(9)	C(6)-C(5)-C(7)	110.9(11)
C(1)-N(1)-Ta(1)	110.2(7)	N(4)-C(9)-C(10B)	116.2(13)
C(2)-N(1)-Ta(1)	116.8(7)	N(4)-C(9)-C(11)	116.2(14)
C(1)-N(1)-Ta(2)	116.3(7)	C(10B)-C(9)-C(11)	118.7(17)
C(2)-N(1)-Ta(2)	114.1(7)	N(4)-C(9)-C(12B)	109.2(14)
Ta(1)-N(1)-Ta(2)	85.5(3)	C(10B)-C(9)-C(12B)	108.9(9)
C(4)-N(2)-C(3)	106.1(9)	C(11)-C(9)-C(12B)	81.1(12)
C(4)-N(2)-Ta(1)	112.5(7)	N(4)-C(9)-C(10)	107.9(10)
C(3)-N(2)-Ta(1)	112.9(8)	C(10B)-C(9)-C(10)	24.3(10)
C(4)-N(2)-Ta(3)	111.2(7)	C(11)-C(9)-C(10)	108.7(8)
C(3)-N(2)-Ta(3)	113.8(7)	C(12B)-C(9)-C(10)	131.6(14)
Ta(1)-N(2)-Ta(3)	100.5(3)	N(4)-C(9)-C(12)	108.8(12)
C(5)-N(3)-Ta(3)	133.5(7)	C(10B)-C(9)-C(12)	82.2(11)
C(5)-N(3)-Ta(2)	131.9(6)	C(11)-C(9)-C(12)	108.5(8)

C(12B)-C(9)-C(12)	31.4(10)	C(22B)-C(21)-C(24)	76.7(15)
C(10)-C(9)-C(12)	106.5(8)	C(23)-C(21)-C(24)	108.5(8)
N(4)-C(9)-C(11B)	107.4(15)	C(24B)-C(21)-C(24)	34.6(14)
C(10B)-C(9)-C(11B)	107.9(9)	N(9)-C(21)-C(22)	108.1(11)
C(11)-C(9)-C(11B)	25.6(12)	C(22B)-C(21)-C(22)	31.6(14)
C(12B)-C(9)-C(11B)	106.7(9)	C(23)-C(21)-C(22)	108.4(8)
C(10)-C(9)-C(11B)	90.4(12)	C(24B)-C(21)-C(22)	137.0(19)
C(12)-C(9)-C(11B)	132.5(15)	C(24)-C(21)-C(22)	107.5(8)
N(9)-C(21)-C(22B)	114.3(17)	N(9)-C(21)-C(23B)	109.1(19)
N(9)-C(21)-C(23)	112.5(12)	C(22B)-C(21)-C(23B)	108.7(10)
C(22B)-C(21)-C(23)	126.3(18)	C(23)-C(21)-C(23B)	29.1(15)
N(9)-C(21)-C(24B)	107(2)	C(24B)-C(21)-C(23B)	108.3(10)
C(22B)-C(21)-C(24B)	109.4(10)	C(24)-C(21)-C(23B)	132(2)
C(23)-C(21)-C(24B)	80.0(16)	C(22)-C(21)-C(23B)	82.9(14)
N(9)-C(21)-C(24)	111.7(12)		

Symmetry transformations used to generate equivalent atoms

Table S9. Anisotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^*2U^{11} + \dots + 2hka^*b^*U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ta(1)	27(1)	33(1)	24(1)	-4(1)	-1(1)	7(1)
Ta(2)	36(1)	24(1)	31(1)	4(1)	-2(1)	-2(1)
Ta(3)	37(1)	24(1)	24(1)	1(1)	-2(1)	-3(1)
O(1)	27(3)	25(3)	36(3)	0(2)	4(2)	2(2)
N(1)	40(4)	44(4)	36(4)	4(3)	9(3)	-3(4)
N(2)	31(4)	40(4)	30(3)	-6(3)	-8(3)	-4(3)
N(3)	42(4)	21(3)	43(4)	-9(3)	-6(3)	-4(3)
N(4)	35(4)	50(5)	23(3)	-4(3)	-4(3)	18(3)
N(5)	36(4)	43(4)	35(4)	1(3)	6(3)	16(4)
N(6)	64(6)	28(4)	43(5)	4(3)	2(4)	11(4)
N(7)	51(5)	40(4)	59(5)	6(4)	2(5)	-20(4)
N(8)	65(6)	37(4)	47(5)	13(4)	10(4)	8(4)
N(9)	54(5)	22(3)	31(4)	9(3)	-12(3)	0(3)
C(1)	44(6)	75(8)	49(6)	4(6)	17(5)	2(6)
C(2)	80(9)	64(7)	35(5)	12(5)	-5(6)	-3(6)
C(3)	25(5)	124(12)	48(6)	-16(8)	9(4)	-16(6)
C(4)	65(7)	43(5)	52(6)	-10(5)	-1(6)	-24(5)
C(5)	62(7)	33(5)	46(6)	-13(4)	-6(5)	-3(5)
C(6)	97(11)	63(8)	58(7)	-21(6)	-51(7)	7(8)
C(7)	112(12)	60(7)	29(5)	-17(5)	15(6)	-21(8)
C(8)	77(9)	38(6)	66(7)	-15(5)	-14(7)	-1(6)
C(9)	40(5)	84(8)	28(4)	-8(5)	-10(4)	19(5)
C(13)	41(6)	52(6)	74(8)	-13(6)	-8(6)	20(5)
C(14)	69(8)	47(6)	52(6)	-14(5)	-4(6)	34(6)
C(15)	77(10)	56(8)	94(11)	-6(7)	-12(8)	24(7)
C(16)	100(11)	20(4)	68(8)	4(4)	-9(7)	-4(5)
C(17)	87(11)	88(11)	76(9)	6(8)	19(9)	-49(10)
C(18)	54(7)	84(10)	84(9)	-34(8)	-17(7)	-20(7)
C(19)	62(7)	54(7)	63(7)	-1(6)	22(6)	-4(6)

C(20)	88(10)	60(7)	44(6)	24(5)	18(6)	-13(7)
C(21)	56(7)	37(5)	62(7)	7(5)	-18(5)	12(5)

Table S10. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4**.

	x	y	z	$U(\text{eq})$
H(1A)	9262	10754	-204	84
H(1B)	8622	9950	-422	84
H(1C)	9172	10038	230	84
H(2A)	6655	10885	-715	89
H(2B)	7166	11580	-311	89
H(2C)	5613	11201	-218	89
H(3A)	2889	8955	1456	99
H(3B)	2764	8805	776	99
H(3C)	3092	9652	1012	99
H(4C)	4527	7920	670	80
H(4D)	4486	7883	1360	80
H(4E)	5992	7973	1031	80
H(6A)	9234	10913	2562	108
H(6B)	8323	10269	2893	108
H(6C)	8497	11107	3170	108
H(7A)	5600	10450	2980	100
H(7B)	4878	11181	2675	100
H(7C)	5868	11294	3235	100
H(8A)	6396	12089	2115	90
H(8B)	8098	11955	2076	90
H(8C)	7385	12224	2672	90
H(10A)	1909	10038	38	82
H(10B)	1540	10406	-578	82
H(10C)	2874	10724	-212	82
H(11A)	2056	8740	-419	117
H(11B)	3034	8622	-981	117
H(11C)	1621	9146	-1014	117
H(12A)	4522	10477	-1060	104
H(12B)	3040	10271	-1377	104

H(12C)	4355	9678	-1397	104
H(10D)	1966	10431	-185	82
H(10E)	1934	10533	-872	82
H(10F)	3271	10851	-508	82
H(11D)	2093	8957	-79	117
H(11E)	2522	8563	-679	117
H(11F)	1264	9191	-659	117
H(12D)	3709	9057	-1348	104
H(12E)	4800	9760	-1263	104
H(12F)	3189	9917	-1479	104
H(13A)	9251	8500	-11	84
H(13B)	8387	7851	336	84
H(13C)	8650	8676	624	84
H(14A)	6715	7662	-390	84
H(14B)	7649	8242	-774	84
H(14C)	5958	8383	-695	84
H(15A)	4039	11907	440	113
H(15B)	3974	12428	1010	113
H(15C)	3840	11513	1060	113
H(16A)	6158	13012	1110	94
H(16B)	6505	12824	447	94
H(16C)	7646	12607	939	94
H(17A)	10786	11481	571	125
H(17B)	10050	12226	849	125
H(17C)	9335	11819	299	125
H(18A)	10762	11250	1611	111
H(18B)	10651	10466	1252	111
H(18C)	9573	10623	1778	111
H(19A)	3016	10133	2709	89
H(19B)	2327	9536	2262	89
H(19C)	3238	10254	2030	89
H(20A)	3352	8660	2880	96
H(20B)	4503	9166	3226	96
H(20C)	5032	8467	2829	96

H(22A)	7460	7162	1973	94
H(22B)	6751	7423	2572	94
H(22C)	8322	7046	2565	94
H(23A)	9675	8810	2811	116
H(23B)	9305	7982	3073	116
H(23C)	8136	8657	3099	116
H(24A)	9215	8136	1468	124
H(24B)	10056	7608	1922	124
H(24C)	10266	8522	1933	124
H(22D)	8189	7360	1648	94
H(22E)	7293	7136	2214	94
H(22F)	9009	7059	2212	94
H(23D)	8678	8653	3095	116
H(23E)	8834	7737	3092	116
H(23F)	7271	8123	3075	116
H(24D)	9797	8535	1678	124
H(24E)	10539	8179	2242	124
H(24F)	9871	9027	2261	124
H(1)	5170(90)	10530(50)	760(30)	7(19)
