Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Multi-electron Reduction of Diazoalkane and Azide Compounds via Reversible Cyclometalation in Ditantalum Complexes

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Experimenral Section

Experimental Section

General procedures

All manipulations were carried out using standard Schlenk techniques or in a glove-box under argon atmosphere. Anhydrous hexane, pentane and toluene were dried by passage through two columns of activated alumina and a Q-5 column, while anhydrous THF and DME were dried by passage through two columns of activated alumina. Anhydrous benzene and deuterated benzene (benzene-d_6) were dried and degassed over a potassium mirror prior to use. Deuterated tetrahydrofuran (THF-d_8) and deuterated toluene (toluene-d_8) were distilled from calcium hydride prior to use. The starting complex $[M(DME)_2][\{(OOCO)Ta\}_2(\mu\text{-}H)_3]$ (M = K (**1-K**), Na (**1-Na**)) were prepared by the literature procedure.[1] ^{1}H, ^{13}C and ^{15}N NMR spectra were recorded on JEOL ECX-400 spectrometer. All spectra were referenced to residual protiosolvent (^{1}H, C_6D_5H in C_6D_6, ^{1}H (δ) = 7.15; C_4D_7HO in THF-d_8, ^{1}H (δ) = 3.58), solvent (^{13}C) or nitromethane (^{15}N) resonances. IR spectra were recorded on JASCO FT/IR-410 spectrometer. Elemental analyses (C, H, and N) were carried out on an Elementar VarioMicroCube.

Synthesis of $[K(DME)_4][\{(OOO)Ta\}_2(\mu\text{-}N)(\mu\text{-}NCH_2SiMe_3)]$ (2)

Trimethylsilyldiazomethane (2.0 M in hexane, 120 μL, 228 μmol) was added to a THF (20 mL) solution of **1-K** (360 mg, 228 μmol) at room temperature. The mixture was stirred for 30 h at room temperature, during which time a color of the solution gradually changed from yellow to red to light yellow. After removal of volatiles under vacuum, the yellow residue was extracted with DME (2 mL). The solution was filtrated and layered with hexane to afford **2** as colorless crystals (201 mg, 107 μmol, 47%).

^{1}H NMR (400 MHz, C_6D_6): δ 0.49 (s, 9H, SiMe_3), 1.16 (s, 9H, *t*Bu), 1.20 (s, 9H, *t*Bu), 1.35 (s, 9H, *t*Bu), 1.40 (s, 18H, *t*Bu), 1.51 (s, 9H, *t*Bu), 2.00 (s, 3H, *p*Me), 2.09 (s, 3H, *p*Me), 2.31 (s, 6H, *p*Me), 2.99 (s, 24H, DME), 3.43 (s, 16H, DME), 3.40 (d, $^2J_{HH}$ = 12 Hz, 1H, CH_2), 3.50 (d, $^2J_{HH}$ = 14 Hz, 1H, CH_2), 3.61 (d, $^2J_{HH}$ = 13 Hz, 1H, CH_2), 3.63 (d, $^2J_{HH}$ = 13 Hz, 1H, CH_2), 4.26 (d, $^2J_{HH}$ = 14 Hz, 1H, CH_2), 5.10 (d, $^2J_{HH}$ = 13 Hz, 1H, CH_2), 5.24 (d, $^2J_{HH}$ = 12 Hz, 1H, CH_2), 5.50 (d, $^2J_{HH}$ = 13 Hz, 1H, CH_2), 5.69 (d, $^2J_{HH}$ = 15 Hz, 1H, NCH_2SiMe_3), 6.36 (d, $^2J_{HH}$ = 15 Hz, 1H, NCH_2SiMe_3), 6.83 (s, 1H, Ar*H*), 6.27 (s, 1H, Ar*H*), 6.85 (s, 1H, Ar*H*), 6.87 (s, 1H, Ar*H*), 6.92 (s, 1H, Ar*H*), 7.03 (s, 1H, Ar*H*), 7.06 (s, 1H, Ar*H*), 7.13 (s, 1H, Ar*H*), 7.14 (s, 1H, Ar*H*), 7.24 (s, 1H, Ar*H*), 7.27 (s, 1H, Ar*H*), 7.36 (s, 1H, Ar*H*). ^{13}C NMR (100 MHz, C_6D_6): δ 0.03 (Si*Me*$_3$), 20.7, 21.0 (3C) (*p*Me), 30.0, 31.6, 31.7, 31.8, 31.9, 32.0 (C*Me*$_3$), 33.9 (CH$_2$), 34.1, 34.2 (3C) (*C*Me$_3$), 34.8 (2C) (CH$_2$), 35.1 (2C), 35.4, 35.5 (*C*Me$_3$) 37.1 (CH$_2$), 53.2 (N*C*H$_2$SiMe$_3$), 58.6, 71.7 (DME), 123.2, 124.2, 124.4, 125.1, 125.2, 125.3, 126.1, 126.3, 126.5, 126.7, 127.2, 128.2, 128.8, 129.2, 129.6, 130.0, 130.2, 130.3, 130.9, 131.1, 132.0, 133.2, 134.9, 135.9, 138.7, 139.5, 139.6, 140.2, 142.2, 142.6, 156.1, 156.6, 158.8, 158.9, 160.3, 160.4 (Ar). Anal. Calcd for $C_{88}H_{137}KN_2O_{14}SiTa_2$: C, 56.34; H, 7.36; N, 1.49. Found: C, 56.61; H, 7.45; N, 1.36.

Synthesis of [K(DME)$_4$][{(OOO)Ta(NSiMe$_3$)}{(OCOO)Ta} (μ-H)$_2$] (3)

To a toluene (30 mL) solution of **1-K** (542 mg, 342 μmol) was added azidotrimethylsilane (62.5 μL, 477 μmol). After stirring for 3 h at room temperature, the solution was evaporated to dryness. The residue was extracted with DME (0.5 mL). The solution was filtered and layered with pentane, giving **3** as yellow powder (467 mg, 253 μmol, 74%).

^{1}H NMR (400 MHz, C_6D_6): δ 0.75 (s, 9H, SiMe$_3$), 0.87 (br, 18H, *t*Bu), 1.12 (s, 9H, *t*Bu), 1.59 (br, 9H, *t*Bu), 1.67 (br, 18H, *t*Bu), 2.18 (br, 3H, *p*Me), 2.21 (s, 6H, *p*Me), 2.31 (br, 3H, *p*Me), 3.28 (d, $^2J_{HH}$ = 13 Hz, 2H, C*H*$_2$), 3.94 (br, 1H, C*H* or C*H*$_2$), 5.22 (br, 1H, C*H* or C*H*$_2$), 5.35 (d, $^2J_{HH}$ = 13 Hz, 2H, C*H*$_2$), 5.46 (br, 1H, C*H* or C*H*$_2$), 6.55 (s, 1H, Ar*H*), 6.72 (s, 1H, Ar*H*), 6.75 (br, 1H, Ar*H*), 6.88 (s, 1H, Ar*H*), 6.94 (br, 2H, Ar*H*), 6.99 (s, 1H, Ar*H*), 7.05 (br, 1H, Ar*H*), 7.06 (br, 1H, Ar*H*), 7.14 (br, 1H, Ar*H*), 7.34 (br, 1H, Ar*H*), 14.05 (br, 2H, TaH). ^{13}C NMR (100 MHz, toluene-*d*$_8$): δ 4.81 (Si*Me*$_3$), 14.5, 14.6 (2C), 23.0, 23.3 (2C, *p*Me), 30.4-32.2 (br, *C*Me$_3$ and C*Me*$_3$), 33.33–35.6 (br, CH$_2$), 57.7, 70.4 (DME), 122.2–163.0 (Ar). Anal. Calcd for $C_{87}H_{136}KNO_{14}SiTa_2$: C, 56.51; H, 7.41; N, 0.76. Found: C, 56.61; H, 7.17; N, 1.06.

Synthesis of [K(DME)][{(OOO)Ta(NSiMe$_3$)}{(OOO)Ta} (μ-NSiMe$_3$)(μ-H)] (4)

To a toluene (10 mL) solution of **3** (89.0 mg, 48.1 μmol) at room temperature was added azidotrimethylsilane (18.5 μL, 141 μmol). The mixture was warmed to 60 ˚C and stirred for 15 h. After volatiles were removed under vacuum, the residue was washed with pentane to give **4** as pale yellow powder (69.0 mg, 41.4 μmol, 86%).

^{1}H NMR (400 MHz, C_6D_6): δ 0.57 (s, 9H, SiMe$_3$), 0.65 (s, 9H, SiMe$_3$), 1.03 (s, 9H, *t*Bu), 1.09 (s, 9H, *t*Bu), 1.40 (s, 9H, *t*Bu), 1.53 (s, 9H, *t*Bu), 1.79 (s, 9H, *t*Bu), 1.82 (s, 9H, *t*Bu), 1.99 (s, 3H, *p*Me), 2.09 (s, 3H, *p*Me), 2.18 (s, 3H, *p*Me), 2.30 (s, 3H, *p*Me), 2.50 (s, 6H, DME), 2.65 (s, 4H, DME), 3.04 (d, $^2J_{HH}$ = 13 Hz, 1H, C*H*$_2$), 3.57 (d, $^2J_{HH}$ = 13 Hz, 2H, C*H*$_2$), 3.65 (d, $^2J_{HH}$ = 13 Hz, 1H, CH$_2$), 4.53 (d, $^2J_{HH}$ = 13 Hz, 1H, C*H*$_2$), 5.09 (d, $^2J_{HH}$ = 13 Hz, 1H, C*H*$_2$), 5.52 (d, $^2J_{HH}$ = 13 Hz, 1H, C*H*$_2$), 6.43 (d, $^2J_{HH}$ = 12 Hz, 1H, C*H*$_2$), 6.75 (s, 1H, Ar*H*), 6.87 (s, 1H, Ar*H*), 6.99 (s, 2H, Ar*H*), 7.06 (s, 3H, Ar*H*), 7.10 (s, 2H, Ar*H*), 7.18 (s, 2H, Ar*H*), 7.29 (s, 1H, Ar*H*), 12.64 (s, 1H, Ta*H*). ^{13}C NMR (100 MHz, C$_6$D$_6$): δ 5.86 (Si*Me*$_3$), 6.23 (Si*Me*$_3$), 20.6, 20.8, 20.9, 21.3 (*p*Me), 31.5, 31.6, 31.7, 32.7, 32.3 (C*Me*$_3$), 33.9 (2C, *C*Me$_3$), 34.4 (CH$_2$), 34.7 (C*Me*$_3$), 35.8 (CH$_2$), 35.9 (5C, *C*Me$_3$ + CH$_2$), 36.9 (*C*Me$_3$), 58.2, 71.0 (DME), 122.7, 123.0, 123.9, 124.4, 124.8, 126.2, 126.3 (2C), 126.4 (2C), 126.5, 126.8, 127.1, 127.3, 128.2, 128.7, 129.2, 129.6, 131.4, 134.7, 134.8, 135.2 (2C), 137.8, 139.8, 144.5, 144.6, 144.8, 149.3, 155.1, 155.9, 157.8, 158.5, 159.4, 160.4, 160.7 (Ar). Anal. Calcd for $C_{78}H_{115}KN_2O_8Si_2Ta_2$: C, 56.24; H, 6.96; N, 1.68. Found: C, 56.48; H, 7.09; N, 1.68

Synthesis of [{(OOO)Ta}{(OCOO)Ta}(μ-N) (μ-H)$_2$ {Na(DME)}$_2$] (5)

To a THF (30 mL) solution of **1-Na** (450 mg, 288 μmol) was added sodium azide (105 mg, 1.62 mmol). The mixture was stirred for 3 days at room temperature. The solution was evaporated to dryness. The pale yellow residue was dissolved in DME (10 mL) and filtrated. The filtrate was layered with hexane at -30 °C to give **5** as pale yellow powder (287 mg), which contains **5** and **6** in an 80:20 ratio.

For **5**: ^{1}H NMR (400 MHz, C$_6$D$_6$): δ 11.99 (br, 1H, Ta*H*), 12.88 (br, 1H, Ta*H*). Crystal data: $C_{76}H_{107}NNa_2O_{10}Ta_2$, monoclinic, $P2_1/n$, a = 18.0182(10) Å, b = 19.153(10) Å, c = 27.749(15) Å, β = 90.058(7) °, V = 9576(7) Å^3, Z = 4, D_c = 1.112 g cm^{-3}.

Synthesis of [Na(DME)$_3$][{(OOO)Ta(H)}{(OCO)Ta(μ-O)} (μ-N) {Na(DME)$_2$}] (6)

To a THF (30 mL) solution of **1-Na** (252 mg, 161 μmol) was added sodium azide (25.0 mg, 385 μmol). The mixture was warmed to 50 °C and stirred for 15 h. The solution was evaporated to dryness. The pale yellow residue was dissolved in DME (5 mL) and filtrated. The filtrate was layered with hexane to give **6** as colorless crystals (145 mg, 77.6 μmol, 48%).

^{1}H NMR (400 MHz, C$_6$D$_6$): δ 1.15 (s, 9H, *t*Bu), 1.31 (s, 9H, *t*Bu), 1.37 (s, 9H, *t*Bu), 1.44 (s, 9H, *t*Bu), 1.56 (s, 9H, *t*Bu), 1.73 (s, 9H, *t*Bu), 2.24 (s, 3H, *p*Me), 2.27 (s, 3H, *p*Me), 2.33 (s, 3H, *p*Me), 2.46 (s, 3H, *p*Me), 2.79 (d, $^2J_{HH}$ = 13 Hz, 2H, C*H*$_2$), 3.00 (s, 20H, DME), 3.12 (d, $^2J_{HH}$ = 13 Hz, 1H, C*H*$_2$), 3.16 (s, 30H, DME), 3.50 (d, $^2J_{HH}$ = 13 Hz, 1H, C*H*$_2$), 3.53 (d, $^2J_{HH}$ = 13 Hz, 2H, C*H*$_2$), 4.01 (d, $^2J_{HH}$ = 13 Hz, 1H, C*H*$_2$), 4.32 (d, $^2J_{HH}$ = 13 Hz, 1H, C*H*$_2$), 4.45 (d, $^2J_{HH}$ = 13 Hz, 1H, C*H*$_2$), 5.23 (d, $^2J_{HH}$ = 15 Hz, 1H, C*H*$_2$), 6.90 (s, 1H, Ar*H*), 6.95 (s, 1H, Ar*H*), 6.97 (s, 2H, Ar*H*), 7.00 (s, 1H, Ar*H*), 7.11 (s, 1H, Ar*H*), 7.20 (s,1H, Ar*H*), 7.21 (s, 1H, Ar*H*), 7.33 (s, 1H, Ar*H*), 7.35 (s, 1H, Ar*H*), 7.49 (s, 1H, Ar*H*), 7.51 (s, 1H, Ar*H*), 15.71 (s, 1H, Ta*H*). IR (cm^{-1}; Nujol mull): 843 (s, $\nu_{Ta=O}$), 1010 (s, $\nu_{Ta–N}$), 1734 (br, $\nu_{Ta–H}$). Anal. Calcd for $C_{88}H_{137}NNaO_{16}Ta_2$: C, 56.43; H, 7.37; N, 0.75. Found: C, 56.53; H, 7.09; N, 0.96. Solubility constraints prevent us from aquiring the ^{13}C NMR spectrum of **6**.

Synthesis of [Na(DME)$_3$][{(OOO)Ta(H)}{(OCO)Ta(μ-O)} (μ-N^{15}) {Na(DME)$_2$}] (6-^{15}N)

The same procedure as used for **6** was followed. Addition of Na^{15}NNN to THF solution of **1-Na** afforded **6-^{15}N** as white powder. No changes to the ^{1}H NMR spectrum were observed. ^{15}N NMR (40 MHz, C_6D_6): δ 152. IR (cm^{-1}; Nujol mull): 842 (s, ν_{Ta-O}), 985 (s, ν_{Ta-15N}), 1011 (s, ν_{Ta-N}), 1732 (br, ν_{Ta-H}).

X-ray Crystallography

Crystallographic data for are summarized Table S1 for **2**, **3**, **4**, and **6**. Single crystals of **2**, **3**, **4**, **5** and **6** were obtained from DME/hexane, THF/hexane, toluene/pentane, DME/pentane and benzene, repectively. Crystals of these complexes immersed in mineral oil on nylon loop and transferred to a Rigaku Saturn CCD system for **2**, **5** and **6**, and to a Rigaku Mercury CCD system for **3** and **4** equipped with a Rigaku GNNP low-temperature device. Data were collected under cold nitrogen stream (123 K) using graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å). Equivalent reflections were merged, and the images were processed with the CrystalClear (Rigaku) Program. Corrections for Lorentz-polarization effects and absorption were performed.

All calculations were performed using SHELXS[2] and SHELXL[3]. The structures were solved by Patterson and Fourier transform methods. For **2**, one of DME molecules coordinated to K was disordered over two positions and using a rigid group model. For **3**, 9767 Friedel pairs were used to determine the absolute structure, and the Flack parameter refined to 0.001(8), indicating by the successful refinement of the model. For **4**, four sites occupied by pentane were identified in the asymmetric unit. Two of these sites were fully occupied by two pentane molecules. The other sites contains considerably disordered pentane molecules and were treated by SQUEEZE as a diffuse contribution.[4, 5] In the void space, a contribution of 84 e$^-$ per unit cell was found and taken to represent 0.5 pentane molecules for each Ta_2 complex, giving a total of 2.5 pentane in the asymmetric unit. For **6**, two of *tert*-butyl groups were disordered over two positions. In addition, an asymmetric unit contains four benzene molecules, two of which were disordered over two positions and refined using a rigid group model. All non-hydrogen atoms atoms are refined anisotropically, with exception of disordered atoms, which were refined isotropically. All carbon-bound hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. In the case of metal-bound hydrides, the positions of these atoms were found in the Fourier map. The positions of these hydrides were refined although the thermal parameters remained fixed.

These results were checked using the IUCR's CheckCIF routine. The alerts in the output are related to the disorder of *tert*-butyl groups, DME molecules, THF molecules and crystal solvents. The large values of the second parameter on the SHELXL weighting are due to the poor quality of crystals.

References

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(2) SHELXS-97, G. M. Sheldrick, Program for Crystal Structure Determination; University of Göttingen, Göttingen, Germany (1997).

(3) SHELXL-97, G. M. Sheldrick, Program for Crystal Structure Determination; University of Göttingen, Göttingen, Germany (1997).

(4) A. L. Spek, *Acta Cryst.* 2009, **D65**, 148-155.

(5) P. van der Sluis, A. L. Spek, *Acta Cryst.* 1990, **A46**, 194-201.

Table S1. Crystallographic Data for **2**, **3**, **4** and **6**.

	2	**3**	**4**
Formula	$C_{88}H_{137}KN2O_{14}SiTa_2$	$C_{95}H_{144}KNO_{12}SiTa_2$	$C_{90.5}H_{145}KN_2O_8Si_2Ta_2$
M	1876.09	1921.20	1846.27
T/K	123(2)	123(2)	123(2)
Color	colorless	yellow	colorless
Crystal size/mm^3	0.11 x 0.03 x 0.03	0.07 x 0.05 x 0.04	0.15 x 0.12 x 0.06
Crystal system	*Triclinic*	*Orthorhombic*	*Monoclinic*
Space group	P-1 (No. 2)	$P2_12_12_1$ (No. 19)	$P2_1/n$ (No. 14)
a/Å	14.205(2)	14.635(2)	14.4755(10)
b/Å	14.235(2)	17.948(3)	30.724(2)
c/Å	23.253(4)	35.657(5)	22.0497(12)
α/°	96.844(2)	90	90
β/°	93.925(3)	90	94.990(3)
γ/°	99.634(3)	90	90
V/Å^3	4583.7(13)	9366(2)	9769.3(11)
Z	2	4	4
D_c/g cm^{-3}	1.359	1.363	1.255
μ/mm^{-1}	2.502	2.449	2.354
Reflections collected	57423	96270	101648
Independent reflections (R_{int})	20932 (0.0576)	21410 (0.0661)	22455 (0.0920)
Refined parameters	998	948	910
Goodness-of-fit on F^2	1.109	1.117	1.160
R_1 [$I > 2\sigma(I)$][a]	0.0626	0.0539	0.0751
wR_2 (all data)[b]	0.1562	0.1308	0.1925
Largest diff. peak and hole/e Å^{-3}	3.604 and −1.758	1.334 and −1.814	2.662 and −2.995

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[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$, [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{0.5}$

Table S1. Crystallographic Data for **2**, **3**, **4** and **6**. (Cont.)

	6
Formula	$C_{220}H_{290}N_2Na_4O_{24}Ta_4$
M	4162.30
T/K	123(2)
Color	colorless
Crystal size/mm^3	0.11 x 0.04 x 0.03
Crystal system	*Monoclinic*
Space group	$P2_1/n$ (No. 14)
a/Å	16.9098(17)
b/Å	29.072(3)
c/Å	21.836(2)
α/°	90
β/°	103.6045(16)
γ/°	90
V/Å^3	10433.5(18)
Z	2
D_c/g cm^{-3}	1.325
μ/mm^{-1}	2.162
Reflections collected	129240
Independent reflections (R_{int})	23897 (0.0845)
Refined parameters	1106
Goodness-of-fit on F^2	1.125
R_1 [$I > 2\sigma(I)$][a]	0.0716
wR_2 (all data)[b]	0.1652
Largest diff. peak and hole/e Å^{-3}	3.067 and −1.633

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[a] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$, [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{0.5}$

Fig. S1 Structure of the anion part of **2**. H atoms, methyl and tert-butyl groups omitted.

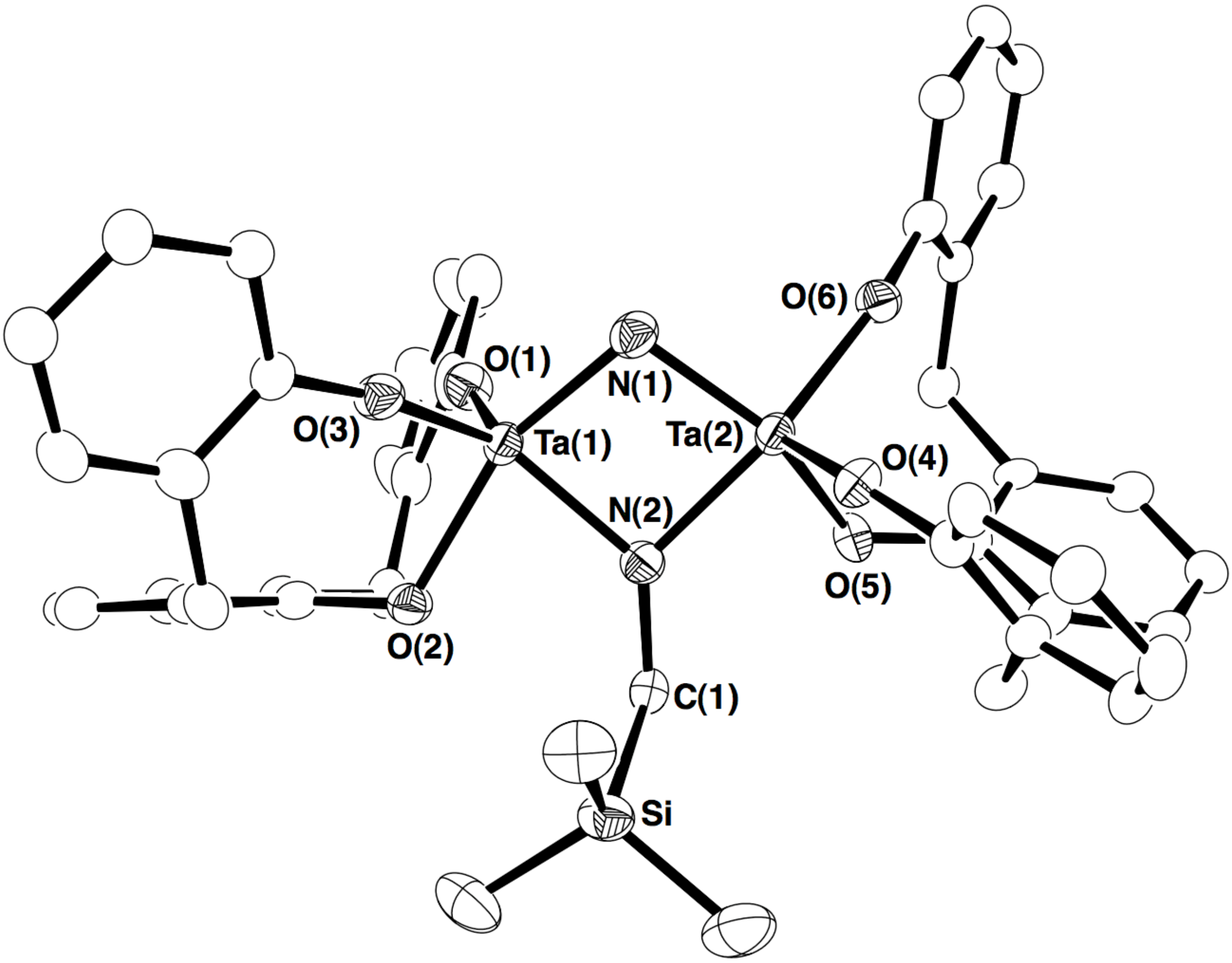

Fig. S2 Structure of the anion part of **3**. C–bound H atoms, methyl and tert-butyl groups omitted.

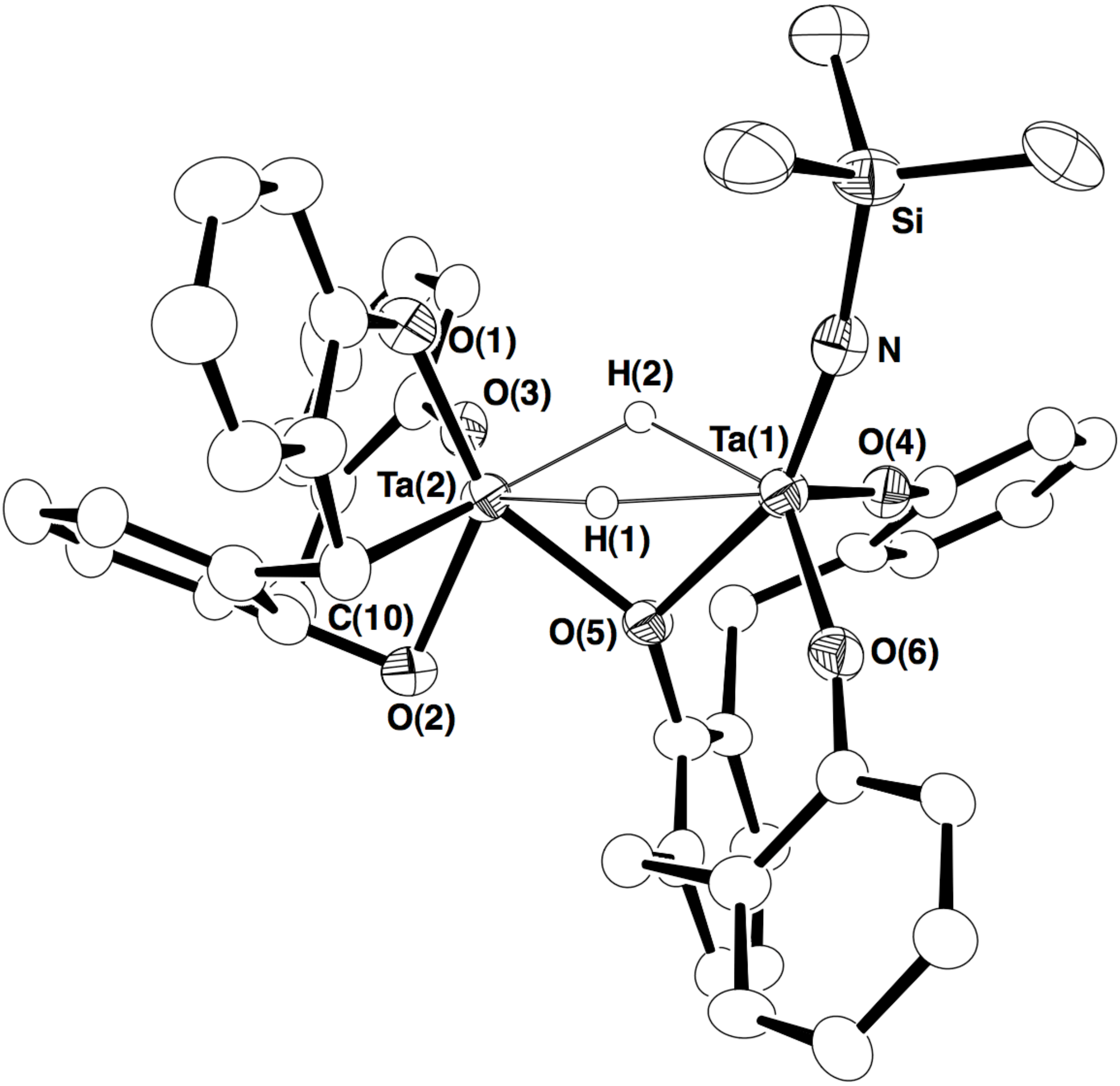

Fig. S3 Structure of the anion part of **4**. C–bound H atoms, methyl and tert-butyl groups omitted.

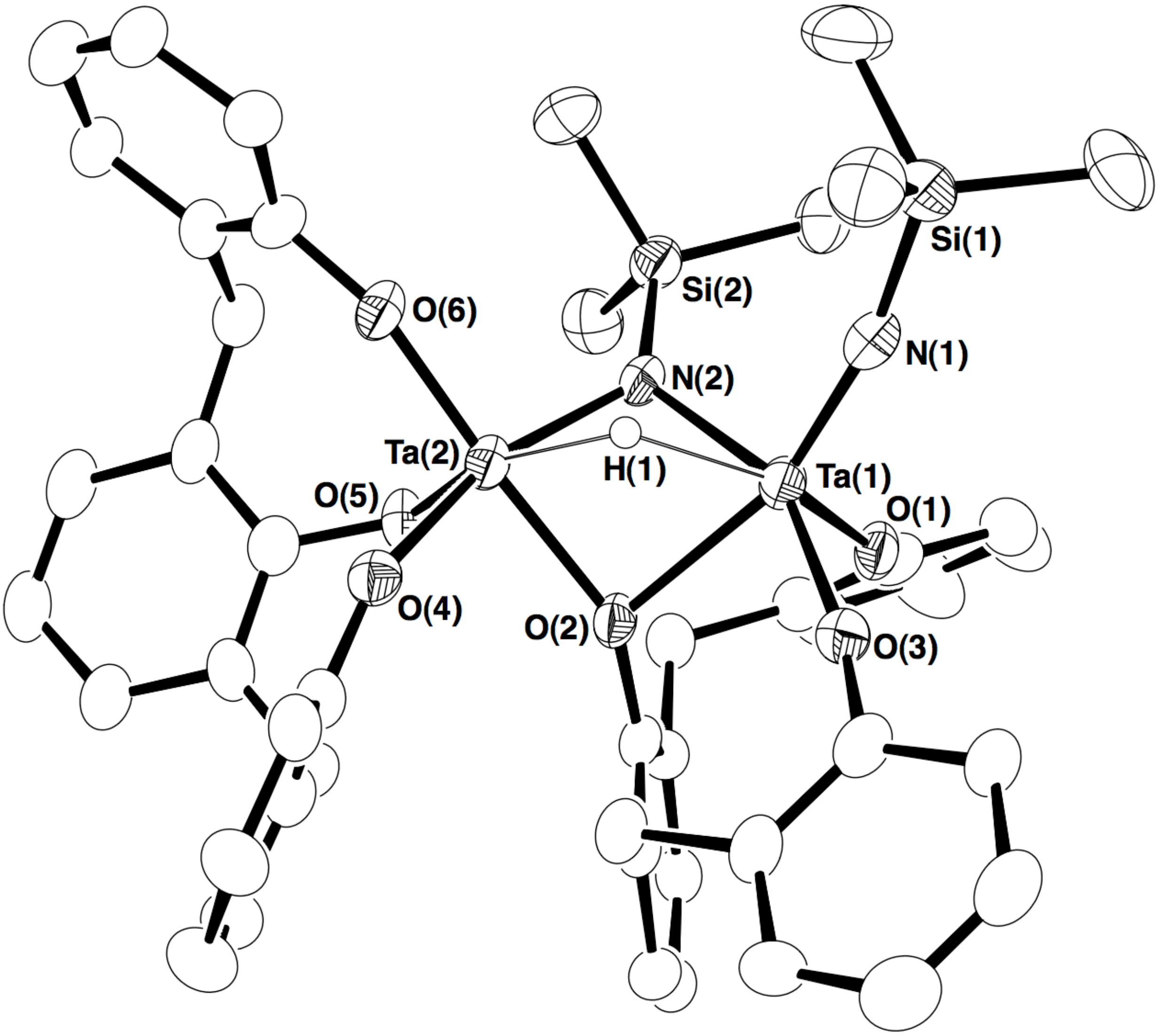

Fig. S4 Structure of **5**. H atoms, methyl and tert-butyl groups omitted.

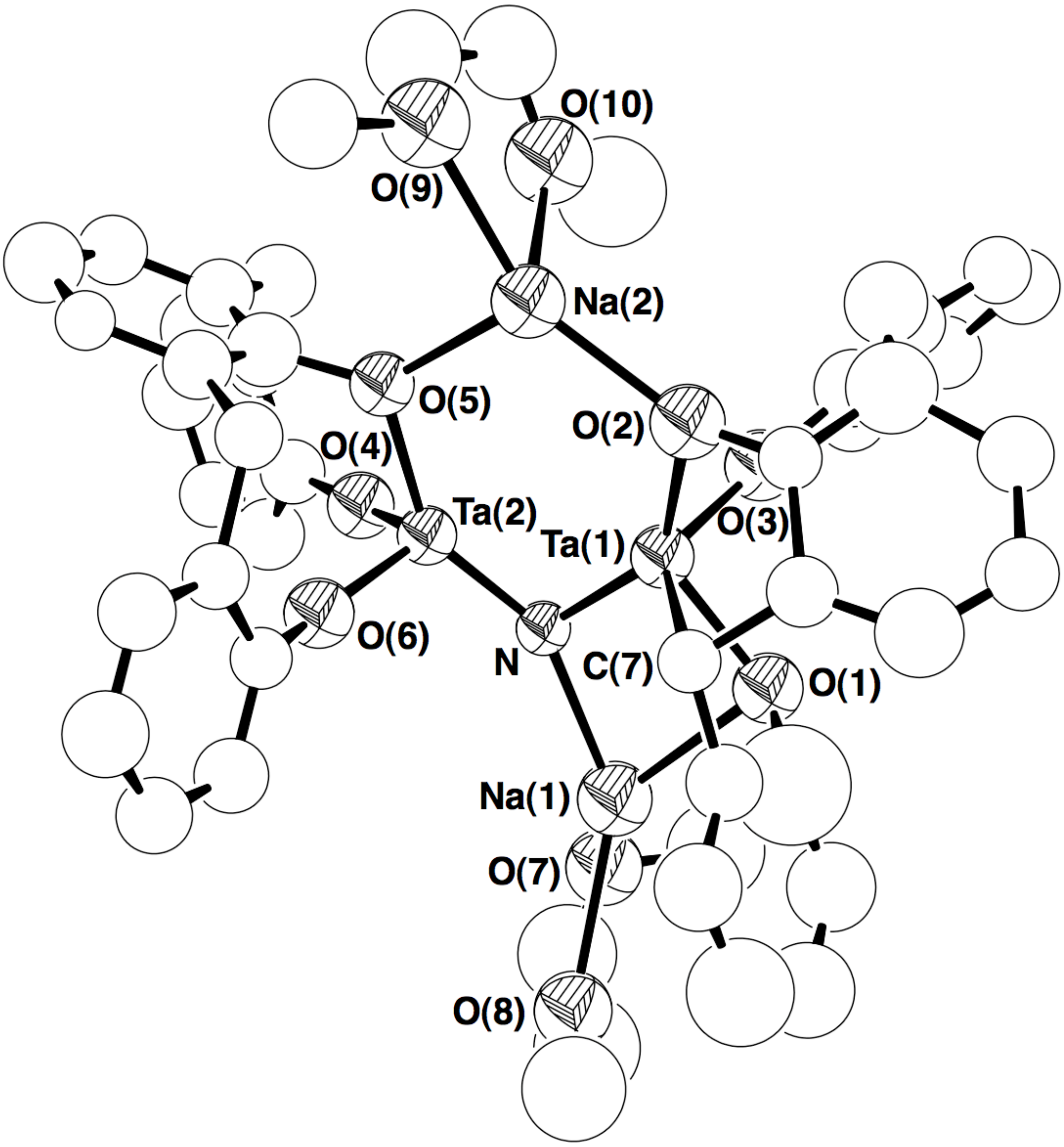

Fig. S5 Structure of the anion part of **6**. C–bound H atoms, methyl and tert-butyl groups omitted.