Four-electron reduction of dinitrogen during solution disproportionation of the organodimetallic (η-$C_5Me_4R)_2Ta_2(\mu$-Cl$)_4$ (R = Me, Et) to a new μ-η^1,η^1-N_2 complex and odd-electron organotrimetallic cluster

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$(C_5Me_5R)_2Ta_2Cl_4$ (d^2–d^2) disproportionates under dinitrogen to $[(C_5Me_4R)TaCl_2]_2(\mu$-$N_2)$ and the D_{3h} cluster cation $(C_5Me_4R)_3Ta_3(\mu$-$Cl)_6^+$ with anionic $(C_5Me_4R)TaCl_4^-$.

There is strong interest in modelling[1–4] transition metal intermediates and clusters[5] involved in reductive cleavage of N_2 by nitrogenase.[6,7] Chemically important observations include side-on bonded[8,9] and semi-bridging η^1,η^2-N_2-coordination[10] and reductive cleavage,[11–13] bimetallic protonation,[14] hydroboration,[15] hydrosilylation,[16] and hydrogenation/cleavage of N_2.[17] Crystallographic studies of nitrogenases suggest that coordination of N_2 to multiple Fe atoms precedes cleavage, though N_2 coordination/reduction at the Mo center remains plausible.[18]

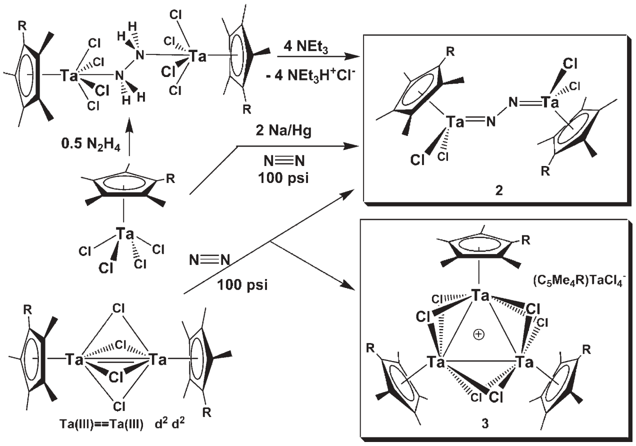
μ-η^1,η^1-Dinitrogen coordination is the predominant dinuclear coordination mode, often with lengthened N–N bonds, M=N multiple bonding, and bent M=N–N linkages. Formal descriptions of these N_2 ligands range from N_2^0 to N_2^{2-} to hydrazido N_2^{4-}. For the latter, which is common for second- and third-row early transition metals, the N–N distances are the longest.[2,4] Group 5 transition metal μ-η^1,η^1-N_2 complexes have been prepared by azine–alkylidene metathesis,[19] N_2 addition to mid-valent mononuclear complexes,[20–23] addition of silylated hydrazines to metal chlorides,[24] and reduction of mononuclear complexes under N_2.[25] Organodimetallic μ-η^1,η^1-N_2 complexes are few compared to dinuclear μ-N_2 complexes that lack metal–carbon bonding.[4,19,20,24]

$(C_5Me_4R)_2Ta_2(\mu$-$Cl)_4$ (**1a**, R = Me, Cp*; **1b**, R = Et, Cp″), a reactive[26] d^2–d^2 organoditantalum(III) complex,[27] is stable as a solid but disproportionates in toluene under N_2. Major products are the new organoditantalum(V) $[(C_5Me_4R)TaCl_2]_2(\mu$-$N_2)$ (**2a**, Cp*, 50%; **2b**, R = Et) and the novel organotrimetallic cluster $(C_5Me_4R)_3Ta_3(\mu$-$Cl)_6^+$ with a $(C_5Me_4R)TaCl_4^-$ anion (**3a**, Cp*, 32%; **3b**, R = Et) (Scheme 1).† Reduction of Cp^*TaCl_4 with Na/Hg under N_2 (PhMe, 100 psi)‡ forms **2a** in 52% yield. Dehydrochlorination (Et_3N, 1,2-$Cl_2C_2H_4$, 60 °C, 2 d) of hydrazine adduct $[(C_5Me_4R)TaCl_4]_2(\mu$-$N_2H_4)$, **4**, prepared in >90% yield from anhydrous N_2H_4 and $(C_5Me_4R)TaCl_4$ in CH_2Cl_2, gives **2** quantitatively. The ^{1}H NMR spectrum of **2b** is consistent with mirror plane symmetry. The ^{15}N NMR resonance ($CDCl_3$) of **2a** at δ 367.9 (NH_4Cl internal reference corrected to NH_3(l)) is similar to those of other μ-N_2 ditantalum complexes.[28]

Nitrogenation of a **1a**/**1b** mixture in toluene gave **2a**, cross product $Cp^*Cp''Ta_2Cl_4(N_2)$ (**2c**) and **2b** in the 1 : 2 : 1 ratio expected for nitrogenation of mononuclear intermediates (*e.g.*, $(C_5Me_4R)TaCl_2(PhMe)$). However, control studies on the reaction timescale showed that, while **1a** and **1b** do not exchange C_5Me_4R groups, **2a** and **2b** scramble to give **2c**. Therefore, it is not known whether N_2 complexation to **1** or to mononuclear intermediates leads to **2**.

Single-crystal diffractometry on **2b**§ established that the N_2 ligand was bound in a μ-η^1,η^1 fashion (Fig. 1). The Ta(1)=N(1) distance, 1.804(3) Å, is consistent with the imido-like linkage of a μ-N_2^{4-} ligand. The N(1)–N(1′) distance, 1.280(6) Å, is near the upper end of reported μ-η^1,η^1-N_2 complexes,[4] and the Ta(1)=N(1)–N(1A) angle of 166.3(4)° is smaller than usual.

The electronic structure of **2a** (with C_5H_5 replacing Cp*) was examined *via* GAMESS.[29] The structure was optimized under C_{2h} symmetry at the RHF(d) level, and SBK effective core potentials[30]



Scheme 1

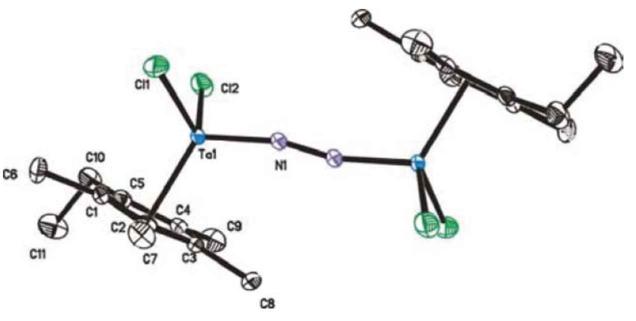


Fig. 1 Thermal ellipsoid (35% probability level) plot of $[(C_5Me_4Et)TaCl_2]_2(\mu$-$N_2)$ (**2b**).

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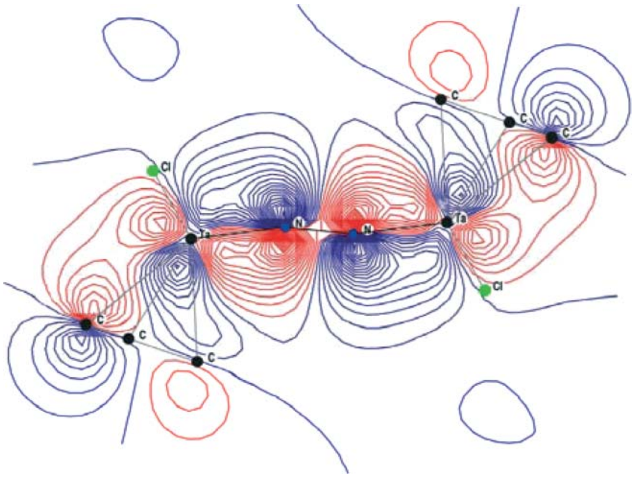

Fig. 2 Contour plot of HOMO for $[(C_5H_5)TaCl_2]_2(\mu\text{-}N_2)$.

were used for all non-H atoms. The Ta–N–N angle was varied in 5° increments and the structures reoptimized. The Walsh diagram showed a shallow potential well around the equilibrium geometry, with a HOMO–LUMO gap of 9.2 eV. The HOMO (Fig. 2) is N–N π^* and Ta$=$N π in character, whereas the LUMO (Fig. 3) is N–N π and Ta$=$N π^*. Thus, oxidation or reduction would strengthen the N–N bond in the absence of structural change.

Complex **3a** is paramagnetic, with ^{1}H chemical shifts (C_6D_6) of δ 22.0 (cation) and δ 49.8 (anion), and gives broad, featureless EPR spectra. The ^{1}H NMR spectrum of **3b** showed multiplicities consistent with mirror plane symmetry. The **3b** cation has an equilateral triangular Ta_3 core (Fig. 4) in the solid-state,¶ with two μ-Cl per edge, average Ta–Ta distance of 3.172[4] Å, Ta–Cl–Ta angle of 80.0[1]°, and Ta–Ta–Ta angle of 60.0[1]°. The anionic $Cp''TaCl_4^-$ structure differs from that of neutral $Cp''TaCl_4$.[31]

The Ta(IV) anion of **3** can be removed by permethylation with MeLi ($\geqslant$7 equiv.), leading to $(C_5Me_4R)_3Ta_3(\mu\text{-}Cl)_6{}^+Cl^-$ (**4**) and hexane-soluble $(C_5Me_4R)TaMe_4$. Preliminary structure determination on twinned **4a** crystals showed a similar cluster cation.

Organotrimetallic Group 4–6 clusters have attracted theoretical interest.[32] Group 5 halide clusters with arene[33] or cyclopentadienyl[34] ligands are uncommon in comparison to late metal clusters with π-acid ligands, and odd-electron organotrimetallics have unusual electronic and magnetic properties. We are interested in whether the trinuclear cation can be reduced.

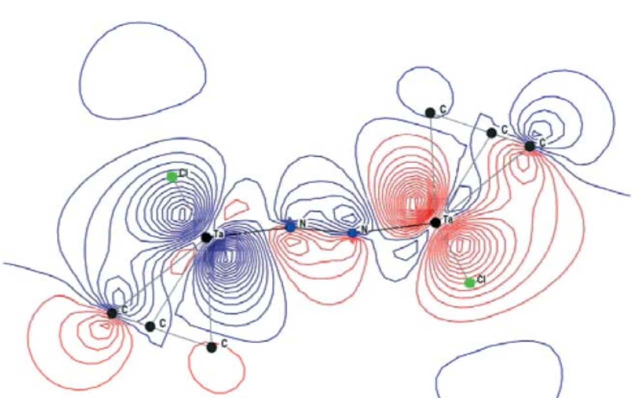

Fig. 3 Contour plot of LUMO for $[(C_5H_5)TaCl_2]_2(\mu\text{-}N_2)$.

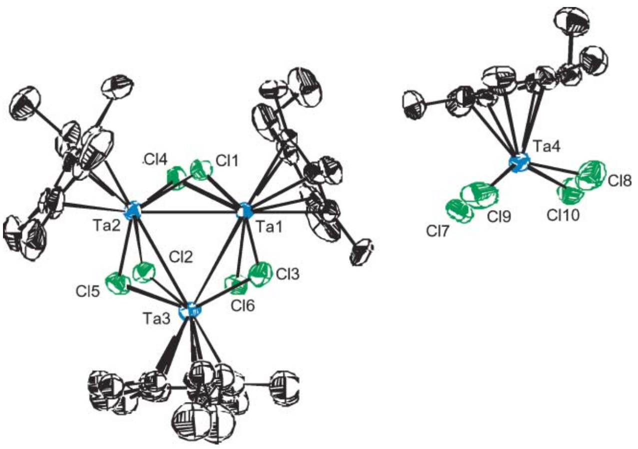

Fig. 4 Thermal ellipsoid (35% probability level) plot of $[Cp''_3Ta_3Cl_6]^+[Cp''TaCl_4]^-$ (**3b**); one disordered Cp″ shown in both orientations.

We are further examining the mechanisms of N_2 addition to **1** and scrambling between **2a** and **2b**, and reactions of **2** with protic reagents. Metathesis of **2a** with excess MeLi or $NaOCMe_3$ affords $[(C_5Me_4R)TaMe_2]_2(\mu\text{-}N_2)$ and $[(C_5Me_4R)TaCl(OCMe_3)]_2(\mu\text{-}N_2)$, respectively, showing that **2** is a soluble synthon for functionalization in organic solvents. These derivatives offer additional possibilities for small molecule reactivity studies.

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Notes and references

† $Cp^*{}_2Ta_2Cl_4$ (1.577 g, 2.04 mmol) in toluene (22 mL) was stirred for two days under N_2/He. The solution changed from bright green to brown, and a dark precipitate formed. The solid was filtered off, washed with toluene, and dried *in vacuo* to give a light green powder; weight = 0.535 g (32% yield of **3a** based on **1a**). The filtrate was concentrated to ~5 mL volume and cooled to −35 °C overnight. A red-brown solid was filtered off, washed with hexane and then cold toluene, and dried *in vacuo*; weight = 0.814 g (50% yield of **2a** based on **1a**).

‡ Cp^*TaCl_4 (1.5 g, 3.3 mmol) in PhMe was combined with 40.1 g (0.413%, 7.20 mmol) Na/Hg. The mixture was stirred under N_2 (100 psi) in a pressure bottle for 2 d and then filtered through Celite to give a red-brown solution. Solvent was removed *in vacuo* and the solid washed with cold hexane (3 mL) and dried *in vacuo*; weight = 0.67 g (52% yield **2a** based on Cp^*TaCl_4).

§ Crystallographic data (**2b**): $C_{22}H_{34}Cl_4N_2Ta_2$, $M = 830.21$, monoclinic, $a = 12.071(1)$ Å, $b = 9.030(1)$ Å, $c = 12.447(1)$ Å, $\beta = 95.86(1)°$, $V = 1349.6(2)$ Å^3, $T = 190$ K, $P2_1/n$, $Z = 2$, $\mu = 8.510$ mm^{-1}, 24923 reflections measured, 3098 independent reflections, $R1 = 0.0230$, $wR2 = 0.0542$.

¶ Crystallographic data (**3b**): $C_{44}H_{68}Cl_{10}Ta_4$, $M = 1675.28$, orthorhombic, $a = 19.223(4)$ Å, $b = 21.597(4)$ Å, $c = 12.671(3)$ Å, $V = 5261(2)$ Å^3, $T = 210$ K, $P2_12_12_1$, $Z = 4$, $\mu = 8.830$ mm^{-1}, 9549 reflections measured, 7165 independent reflections, $R1 = 0.0259$, $wR2 = 0.0602$. CCDC 274833 and 274834. See http://dx.doi.org/10.1039/b508148c for crystallographic data in CIF or other electronic format.

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