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COMMUNICATION

# Structural Diversity in Multinuclear Tantalum Polyhydrides Formed via Reductive Hydrogenolysis of Metal-Carbon Bonds†

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**Using $H_2$ as a reducing agent, we demonstrate controlled reduction of tri- and tetramethyl tantalum bis(*N*-heterocyclic carbene)borate complexes to yield low-valent, multinuclear tantalum polyhydrides. Reaction of a Ta(V)$Me_3$ complex with $H_2$ afforded a bimetallic, hydride-bridged Ta(IV) complex. The analogous reaction of a Ta(V)$Me_4$ complex in benzene or toluene yielded bimetallic Ta(III) complexes in which both metals are bound to the same face of a $\mu$-$\eta^4$:$\eta^4$-arene$^{2-}$ ligand.**

Low-valent early transition metal centers are strongly reducing and complexes that incorporate them have been shown to mediate challenging transformations of organic and inorganic substrates. In particular, Group 5 complexes in the $d^2$ electronic configuration have been shown to promote reduction and hydrogenation of arenes,[1-3] catalytic hydrodefluorination,[4,5] activation of $N_2$ and other small molecules,[6-11] C–C bond formation,[12-16] and cleavage of strong C–H and C–N bonds,[17-19] all across the M(III)/M(V) couple.

While low-valent early metal complexes are typically accessed via reduction of halide-containing precursors with strong alkali metal reductants,[20] such methodologies may present difficulties: the desired low-valent product is often contaminated by reductant-derived salts or over-reduced impurities, and furthermore, the metal-containing product(s) of reduction may be charged "ate" complexes or salt-contacted, coordinatively saturated species. To overcome these issues, Mashima and coworkers have recently employed silyl diene reductants for the generation of low-valent early transition metal species without concomitant salt formation.[21] Here, we target the well-known methodology of hydrogenolysis as an alternative salt-free synthetic route to access low-valent tantalum species. In this approach, a high-valent precursor containing multiple alkyl substituents is treated with dihydrogen ($H_2$), leading to the generation of easily-removable alkanes and reduction of the metal center via reductive elimination.[20,22,23] By varying the methyl substitution pattern on the high-valent precursor, we aimed to influence the extent of metal reduction: increasing the number of methyl groups leads to a greater degree of reduction. Here we report the synthesis and isolation of low-valent, multinuclear tantalum(IV) and tantalum(III) complexes, generated by hydrogenolysis, that readily reduce arene solvent molecules.

We selected a mesityl-substituted bis(*N*-heterocyclic carbene)borate ligand ($H_2B(^{Mes}Im)_2$ = bis(*N*'-mesitylimidazol-1-yl)dihydroborate)[24-26] to support the Ta metal center. *N*-Heterocyclic carbene (NHC) ligands are known to offer strong $\sigma$-donation but weak $\pi$-acceptance, so masking of low-valence via back-bonding interactions was deemed unlikely.[27] In a two-step, one-pot synthesis, akin to a procedure that we have previously reported,[26] deprotonation of the proligand with lithium diisopropylamine followed by salt metathesis with $TaMe_3Cl_2$ led to the isolation of the yellow Ta(V) trimethyl chloride complex (**1**) in 72% yield (Scheme S1). Addition of one equivalent of methyllithium to complex **1** afforded the pale yellow Ta(V) tetramethyl complex (**2**) in 84% yield (Scheme 1). The structures of complexes **1** and **2** were confirmed by X-ray crystallography (Figures S30 and S31, respectively); both complexes adopt a distorted trigonal prismatic geometry.

The addition of one atmosphere of $H_2$ to a solution of **1** in benzene resulted in formation of the dark brown, tetrahydride-bridged bimetallic Ta(IV) complex, $\{[H_2B(^{Mes}Im)_2]TaCl\}_2(\mu\text{-}H)_4$ (**3**; Scheme 1), in 75% yield. Similarly, exposing a benzene solution of **1** to one atmosphere of $D_2$ led to the formation of the corresponding tetradeuteride-bridged analog (**3-*d*$_4$**).

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Electronic Supplementary Information (ESI) available: Experimental details, NMR and IR spectra, X-ray crystallographic data, and computational methods. For ESI, crystallographic data in CIF format, and computational data in mol2 format see DOI: 10.1039/x0xx00000x

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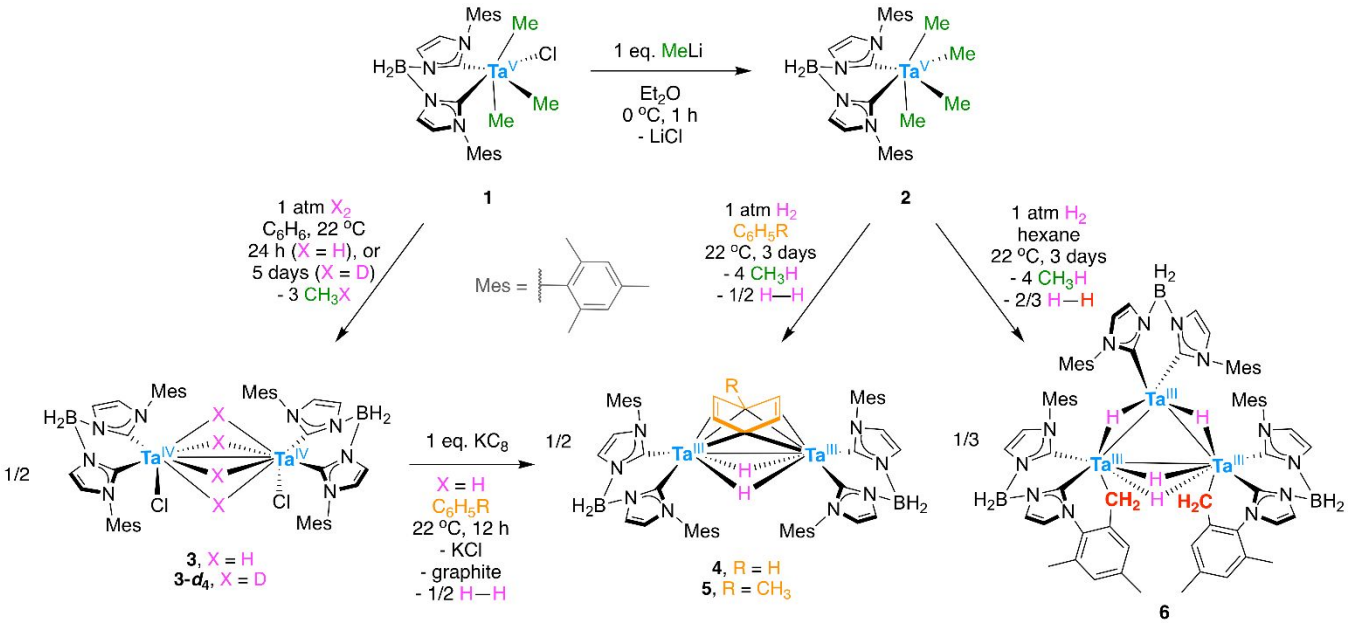


Scheme 1 Syntheses of complexes **2**, **3**, **3-$d_4$**, **4**, **5**, and **6**.

Complex **3** is diamagnetic (as observed by $^1$H NMR spectroscopy), consistent with the presence of either a bond or antiferromagnetic coupling between the two $d^1$ metal centers. At room temperature, the $^1$H NMR spectrum of **3** exhibits only broad resonances (due to dynamic processes) corresponding to the two bis(NHC)borate ligands; signals for the four bridging hydrides are not observed (Figure S9). Upon cooling to −30 °C, the resonances for the bis(NHC)borate ligands sharpen and two new signals, each integrating to two protons, appear downfield at δ 7.70 and 15.45 (Figure S10). We confirmed that these downfield resonances correspond to the bridging hydrides by obtaining $^1$H and $^2$H NMR spectra of **3-$d_4$** at −30 °C (Figures S14 and S15, respectively).

The solid-state structure of **3** is depicted in Figure 1; the complex displays approximate $C_2$ symmetry. The Ta–Ta distance of 2.5594(5) Å is within that typically found for a Ta–Ta single bond[28] and is similar to that of other structurally characterized Ta(IV) bimetallic complexes.[29-36]

While complexes **1** and **2** differ only in the identity of a single ligand (Cl vs. Me), the products they form upon hydrogenolysis are notably distinct. Under an atmosphere of $H_2$, a solution of **2** in benzene reacted to form the blue bimetallic Ta(III) complex $\{[H_2B(^{Mes}Im)_2]Ta\}_2(\mu\text{-}H)_2(\mu\text{-}\eta^4\text{:}\eta^4\text{-}C_6H_6)$ (**4**; Scheme 1; 77% yield). An X-ray diffraction study (*vide infra*) shows both metal centers bound to the same face of a bridging benzene ligand that has been reduced by two electrons. Similarly, the dark purple, toluene-bridged bimetallic Ta(III) species $\{[H_2B(^{Mes}Im)_2]Ta\}_2(\mu\text{-}H)_2(\mu\text{-}\eta^4\text{:}\eta^4\text{-}C_7H_8)$ (**5**) was obtained in 77% yield upon carrying out hydrogenolysis of **2** in toluene. The *syn*-$\mu$-$\eta^4$:$\eta^4$ arene binding mode is quite uncommon,[37-39] and, to the best of our knowledge, has never previously been formed via direct reduction of aromatic solvent. We hypothesize that reductive elimination of $H_2$ from a tetrahydride-bridged intermediate provides the two electrons that ultimately reduce arene solvent molecules.[40,41]

The $^1$H NMR spectrum of **4** displays resonances for two equivalent bis(NHC)borate ligands, two hydride ligands, and one upfield singlet integrating to six protons and assigned to the benzene ligand (Figure S17). The signal for the coordinated benzene appears far upfield of free benzene: in toluene-$d_8$, the bridging benzene hydrogens in **4** appear at δ 1.81, whereas the proton resonance for free benzene is found at δ 7.12. Similarly, the $^{13}$C NMR spectrum of **4** displays a resonance at δ 58.79 for the coordinated benzene ligand, while that for free benzene appears at δ 128.57 (Figure S18). The $^1$H NMR spectrum of **5** also displays signals for the coordinated toluene ligand that are shifted far upfield, relative to free toluene.‡ Together, these data are consistent with disruption of aromaticity and reduction of the coordinated arene ligands.[22,42] At room temperature, the benzene ligand rotates freely, as evidenced by all six protons appearing as a singlet. Upon cooling to −110 °C, the signal fully resolves into two singlets at δ 2.02 and 0.97, integrating to two and four protons, respectively (Figure S20); this dynamic process is reversible upon warming. Despite the free rotation of the benzene ring at room temperature, no

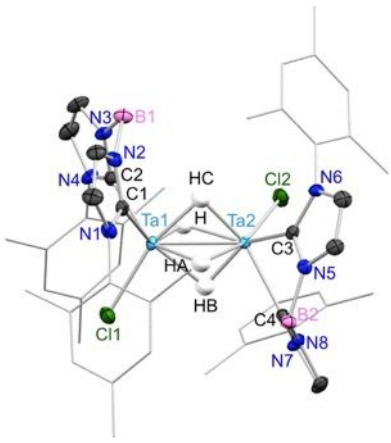


Figure 1 Crystal structure of **3** with 50% probability thermal ellipsoids. H atoms (except the bridging hydrides) and lattice solvent are excluded, and mesityl groups are depicted in wireframe.



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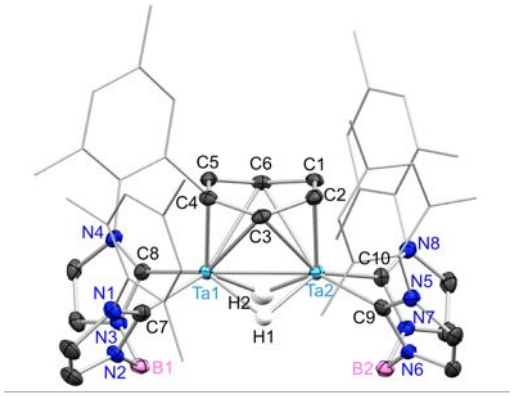


Figure 2 Crystal structure of **4** with 50% probability thermal ellipsoids. H atoms (except the bridging hydrides) are excluded, and mesityl groups are depicted in wireframe.

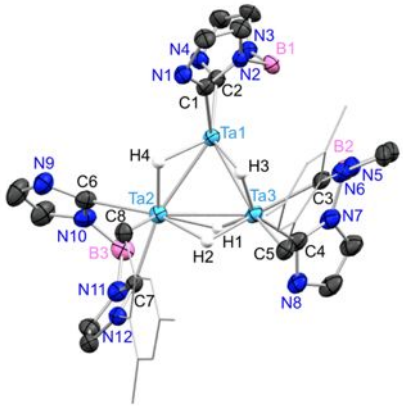


Figure 3 Crystal structure of **6** with 50% probability thermal ellipsoids. H atoms (except the bridging hydrides) and mesityl groups (except the cyclometallated groups, which are depicted in wireframe), and lattice solvent are excluded.

exchange of either the benzene or the toluene ligand with $C_6D_6$ or toluene-$d_8$ was observed, even with heating to 80 °C.

The solid-state X-ray structures of complexes **4** and **5** are both approximately $C_{2v}$ symmetric (Figures 2 and S32, respectively). The Ta–Ta distances of 2.6328(4) Å (**4**) and 2.6138(6)–2.6191(6) Å (**5**) are consistent with a bonding interaction between the two $d^2$ metal centers.[37] Metrical parameters within the arene ligands are consistent with dianionic character: the C–C bond lengths of the benzene ligand range from 1.426(5)–1.446(6) Å in **4** and are lengthened relative to that of free benzene (1.378(3) Å).[§] Similarly, the coordinated toluene ligand in **5** exhibits C–C bond lengths ranging from 1.415(7)–1.452(6) Å, compared to 1.380(6) Å in solid toluene. In both **4** and **5**, the C–C bonds of the coordinated arene are roughly equivalent in length. Both bound arenes deviate significantly from planarity, showing torsion angles of 22° and 19° in **4** and **5**, respectively. We suggest this deviation from planarity occurs to bring the arene π orbitals out of conjugation, thus avoiding an unfavorable eight-electron, Hückel antiaromatic π system.[43]

To examine the strength of the Ta-arene binding interactions, we turned to density functional theory (DFT) calculations. For computational efficiency, calculations were carried out on truncated versions of complexes **4** and **5**, denoted $\mathbf{4^{Ph}}$ and $\mathbf{5^{Ph}}$, in which the mesityl substituents have been replaced with phenyl groups. The DFT-optimized structures $\mathbf{4^{Ph}}$ and $\mathbf{5^{Ph}}$ are in good agreement with the crystallographically-determined structures of **4** and **5** (Tables S10 and S11). The structure of the hypothetical bimetallic Ta(II) complex $\{[H_2B(^{Mes}Im)_2]Ta\}_2(\mu\text{-}H)_2$ ($\mathbf{A^{Ph}}$), the species that results from removal of a neutral arene from $\mathbf{4^{Ph}}$ or $\mathbf{5^{Ph}}$, was also calculated (Figure S34). The DFT-minimized energy of $\mathbf{4^{Ph}}$ was compared to that of a combination of $\mathbf{A^{Ph}}$ and free benzene, revealing a hypothetical benzene total binding energy of –62.4 kcal/mol (Table S9). Using the same methodology, we found a toluene total binding energy of –59.8 kcal/mol for $\mathbf{5^{Ph}}$. These computational results are consistent with the observed lack of exchange between bound and free arenes. Additionally, NBO analysis of $\mathbf{4^{Ph}}$ and $\mathbf{5^{Ph}}$ confirmed the presence of a Ta–Ta single bond; this σ interaction occurs through the Ta $d_{x2-y2}$ orbitals.

Carrying out hydrogenolysis of **2** in hexane resulted in the formation of the dark purple, trimetallic Ta(III) complex (**6**), in which three Ta(III) centers are arranged in a triangle and bridged by a total of four hydride ligands (Scheme 1; 56% yield). Each metal center in **6** bears one bis(NHC)borate ligand; two of the three bis(NHC)borate ligands have cyclometallated through a mesityl methyl group concomitant with loss of $H_2$. Complex **6** presumably arises from a trimetallic species with six bridging hydrides and no cyclometallated ligands; however, while we did observe evidence for a five-hydride, mono-cyclometallated intermediate (**7**; Scheme S2), via X-ray crystallography (Figure S33), neither the five- or six-hydride bridged trimetallic species could be isolated in pure form.

The solid-state structure of **6** is depicted in Figure 3; the Ta–Ta bond lengths are longer than those in **3**, **4**, and **5**, ranging from 2.6334(7)–2.8974(7) Å. Complex **6** represents the first structurally-characterized complex containing three Ta centers linked solely by bridging hydrides, although examples of Ta triangles linked by bridging chloride,[44-46] oxo,[47] and sulfido[48] ligands have been reported.

To investigate the mechanism by which these species are formed, we reduced Ta(IV) complex **3** with two equivalents of $KC_8$ in benzene solution, resulting in the formation of Ta(III) species **4** in 70% yield; carrying out the same reaction in toluene yielded **5** in 71% yield (Scheme 1). The analogous reduction of **3** in hexane, ether, or THF led to intractable mixtures, with no **6** being observed; this suggests that the formation of **4**, **5**, and (most importantly) **6** by hydrogenolysis of **2** depends on the generation of reduced, mononuclear Ta hydride intermediates that can then aggregate (Scheme 1). Presumably, the reduced species formed by the chemical reduction of **3** is dinuclear and not prone to cleavage into mononuclear compounds: we posit this lack of mononuclear intermediates is the reason **6** does not form following the chemical reduction of **3**. Notably, reduction of **3-$d_4$** in benzene yielded the arene-bridged complex **4-$d_n$**, in which scrambling of deuterium into the ortho-mesityl-methyl positions of the bis(NHC)borate ligand has occurred (Scheme S3 and Figures S27-29); this result suggests that cyclometallation occurs reversibly upon reduction from Ta(IV) to Ta(III).

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In conclusion, we have shown that varying the degree of methyl substitution in a Ta(V) precursor influences the outcome of reduction with $H_2$. Furthermore, we show that hydrogenolysis of NHC-supported Ta tri- and tetramethyl complexes provides expedient access to low valent hydride species that readily reduce benzene and toluene. Future work will focus on functionalization and displacement of the direduced arene ligands, with the ultimate goal of rendering such a transformation catalytic.

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## Conflicts of interest

There are no conflicts to declare.

## Notes and references

‡ In $C_6D_6$, the aromatic protons of the bound toluene appear at δ 2.33, 2.05, and 1.88, and the methyl protons at δ 0.96. In free toluene, these protons appear at δ 7.13 ,7.02, and 2.11.
§ CCDC deposition # 1108749 (benzene), 1273751 (toluene).

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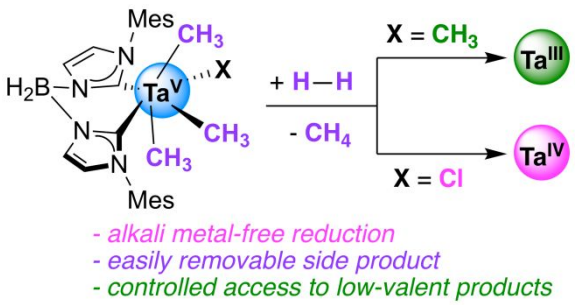


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Put the methyl to the metal: hydrogenolysis of metal-carbon bonds offers controlled access to low-valent early metal complexes.