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Stable Formally Zerovalent and Diamagnetic Monovalent Niobium and Tantalum Complexes Based on Diazadiene Ligands

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There has been a long-standing quest for readily available sources of zerovalent niobium and tantalum complexes. The consistent failure to generate paramagnetic 17-electron (17e) hexacarbonyl complexes $M(CO)_6$ ($M = Nb$, Ta) on a synthetic scale contrasts markedly with the availability of $V(CO)_6$[1] and also of the more highly reduced 18e complexes, $[M(CO)_6]^-$, $[M(CO)_5]^{3-}$, and $[M(CN\text{-}2,6\text{-}Me_2C_6H_3)_6]^-$.[2] Relatively pure $Ta(CO)_4(dppe)$ [dppe = 1,2-bis(diphenylphosphino)ethane], a dimer in the solid state, can be generated on a limited scale via hydride abstraction from $TaH(CO)_4(dppe)$.[3] Metal vapor techniques have yielded $M(arene)_2$[4] and $M(dmpe)_3$ [dmpe = 1,2-bis(dimethylphosphino)ethane],[5] but only $Nb(1,3,5\text{-}Me_3C_6H_3)_2$ is available via solution chemistry.[4b] There has been a brief report of M(2,2′-bipyridine)$_3$ and M(1,10-phenanthroline)$_3$,[6] but there is a clear need for more accessible routes to stable zerovalent niobium and tantalum complexes. 1,4-Diazabuta-1,3-diene (α-diimine) ligands have long been known to stabilize transition metals in low-oxidation states,[7] and there has been a recent resurgence in interest in their chemistry with the heavier group 5 metals.[8] We report herein the efficient synthesis and full characterization of *formally* zerovalent 17e niobium and tantalum complexes, M(*i*Pr$_2$-dad)$_3$, containing the readily available 1,4-diisopropyl-1,4-diazabuta-1,3-diene (*i*Pr$_2$-dad). These complexes are also oxidized to diamagnetic 16e cations [M(*i*Pr$_2$-dad)$_3$]$^+$, and the two oxidation states are investigated using density functional theory.

Addition of Na/naphthalene (5 mol equiv) in 1,2-dimethoxyethane (dme) to a dme solution of $TaCl_5$ at −60 °C generates an orange-brown slurry to which *i*Pr$_2$-dad (3.5 mol equiv) was added. Workup of the resulting dark red-brown slurry yielded Ta(*i*Pr$_2$-dad)$_3$ (**1a**) as red-brown crystals in 33% yield. Dark-green Nb(*i*Pr$_2$-dad)$_3$ (**1b**) is more conveniently obtained from $NbCl_4(thf)_2$ and Na sand in 52% yield. Reactions have been conducted repeatedly on multigram scales. **1a**,**b**, although extremely air sensitive, are indefinitely stable under an inert atmosphere up to 80 °C. Both compounds give satisfactory elemental analyses,[9] and molecular ions are observed in the mass spectra. These formally zerovalent 17e complexes behave as paramagnets with one unpaired electron ($\mu_{eff} = 1.66$ B. M. down to 11 K for **1a**). Pentane or toluene solutions (fluid or frozen) give a broad ($\Delta H_{pp} = 55$ to 26 G) esr signal centered at $g = 2.025$ (**1a**) with no resolved coupling pattern, indicating very little metal contribution to the SOMO. Dark-red **1a** shows blue-shifted UV−vis absorption bands [512 (550 sh) nm (ϵ 2800 L·mol^{-1}·cm^{-1}), 374 (6100), 304 (8900)] as compared to green **1b** [636 (2700), 434 (5300), 336 (5200)]. **1a**,**b** are isomorphous in the crystal (monoclinic, $P2/c$),[10] and **1a** adopts a distorted octahedral geometry (Figure 1) with planar *i*Pr$_2$-dad ligands. The Ta atom lies on a special position (0 y $^1/_4$), and a C_2 axis bisects the C(1)−Ta−C(1)′ angle. Ta−N bond lengths are 2.088(6), 2.096(4), and 2.100(6) Å. C−N bond lengths of 1.365(7), 1.370(9), and 1.397(8) Å and C−C bond lengths of 1.348(12) and 1.369(8) Å suggest some enediamido character. **1a**,**b** remain electron-rich, exhibiting two fully reversible single-electron processes in the CV (**1a**, −1.93 and −1.03 V vs ferrocenium/ferrocene), as well as an irreversible oxidation process (**1a**, 0.12 V). Whatever the electron density distribution within these complexes (see below), **1a**,**b** are among the very few examples of fully characterized, readily available, *formally* zerovalent Nb and Ta complexes. Both the reductant and the nature of the ligand seem crucial to the successful synthesis of **1b**, since utilization of Li, *t*Bu$_2$-dad and $NbCl_5$ (10:5:2 ratio) yields a diamagnetic dimer that displays three different coordination modes.[8e]

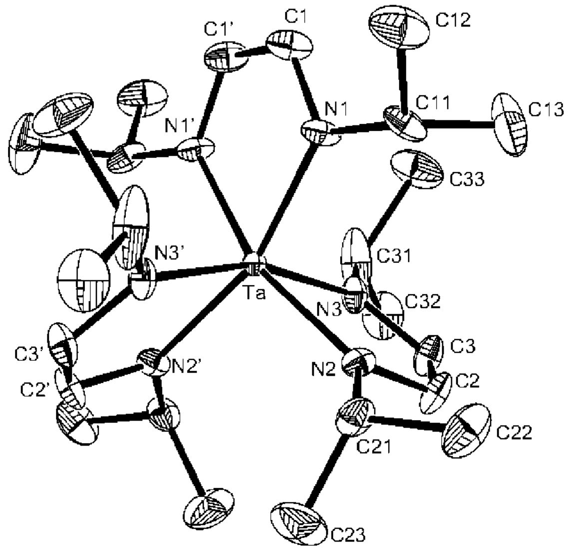

Figure 1. Molecular structure of [Ta(*i*Pr$_2$-dad)$_3$] (**1a**).

Addition of $AgBPh_4$ to **1a**,**b** generates the cation [M(*i*Pr$_2$-dad)$_3$]$^+$[BPh_4]$^-$ [M = Ta (**2a**), Nb (**2b**)] as dark-violet crystals.[11] The overall X-ray molecular structure[12] of **2a** (Figure 2) is conspicuously similar to that of **1a** although there is no special position occupied. Ta−N bond lengths vary between 2.074(2) and 2.135(2) Å, C−N bond lengths between 1.327(4) and 1.365(3) Å, and C−C bond lengths between 1.347(4)) and 1.380(4) Å. Somewhat surprisingly, the Ta−N bonds in **2a** are essentially identical to those in **1a**, but there is a small but significant shortening of the C−N bonds. Unusually for pseudo-octahedral 16e species, **2a**,**b** are diamagnetic

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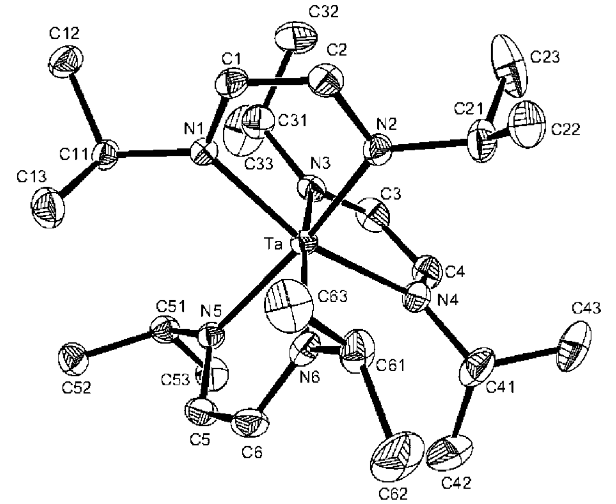

Figure 2. Molecular structure of the cation $[Ta(iPr_2\text{-dad})_3]^+$ **(2a)**.

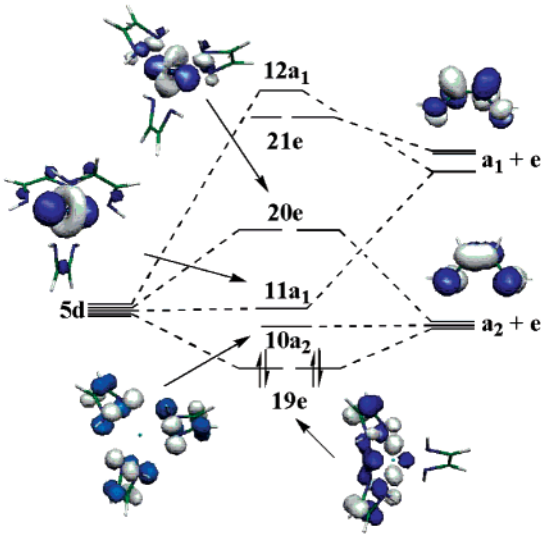

Figure 3. Frontier molecular orbitals for $[Ta(iPr_2\text{-dad})_3]^+$.

and exhibit temperature-independent (300−193 K) ^{1}H NMR spectra.[11]

A number of the experimental features described above are inconsistent with a simple pseudo-octahedral ligand field model, prompting us to examine the detailed electronic structure of these compounds using density functional theory (DFT).[13] The frontier molecular orbitals for $[Ta(dad)_3]^+$ are shown in Figure 3. The most striking feature of the orbital array is the strong splitting within the t_{2g} subset of orbitals (19e and $11a_1$). In D_3 symmetry, the LUMOs (i.e., π^*) of the three ligands transform as $a_2 + e$, as a result of which, only 19e is strongly stabilized by back-bonding, leading to the unusual diamagnetic ground state. Moreover, the relative energies of the metal- and ligand-based orbitals are such that the nonbonding combination of ligand LUMOs, $10a_2$, falls in the gap between 19e and $11a_1$ and forms the LUMO of complex **2a**. The $^2A_2$ ground state of the neutral complex, **1a**, arises from addition of a single electron to $10a_2$, indicating that the neutral complex is correctly formulated as $[Ta]^+$ $[(iPr_2\text{-dad})_3]^-$ (16e + 1e), rather than $[Ta]^0$ $[(iPr_2\text{-dad})_3]^0$ (17e). The unpaired electron has negligible metal character and is instead delocalized over the ligand array, rationalizing both the esr and magnetic behavior. The alternative formulation, where the Ta center is zerovalent, is realized in the $^2A_1$ state, resulting from promotion of the unpaired electron into the $11a_1$ orbital. This state is located some 0.64 eV above its $^2A_2$ counterpart, indicating a clear thermodynamic preference for a ligand-based redox process. This conclusion is reinforced by the optimized structural parameters (Table 1), where the redox-induced changes in bond length in the $^2A_2$ state are far more consistent with experiment than those in $^2A_1$.

Table 1. Structural Data for $Ta(iPr_2\text{-dad})_3$ and $[Ta(iPr_2\text{-dad})_3]^+$ as Determined by X-ray Diffraction (average) and by DFT Calculations (Bond Lengths in Å, Energies in eV)

	method	state	Ta–N	C–N	E_{rel}
2a	X-ray	–	2.107(2)	1.347(4)	–
	DFT	$^1A_1$	2.159	1.352	–
1a	X-ray	–	2.095(6)	1.377(9)	–
	DFT	$^2A_2$	2.156	1.371	0.0
	DFT	$^2A_1$	2.182	1.351	+0.64

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Supporting Information Available: Details of the synthesis and characterization of **1a**,**b** and **2a**,**b**; X-ray diffraction data for **1a** and **2a**; computational details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) For **1a**. Anal. Calcd for $C_{24}H_{48}N_6Ta$: C, 47.91; H, 8.04; N, 13.97. Found: C, 47.40; H, 8.03; N, 13.46. MS-CI (NH_3): *m*/*e* 602 $(M + H)^+$. CV (Bu_4NBF_4, THF, 100 $mV{\cdot}s^{-1}$): $E_{1/2}$ −1.93 [**1a**/**1a**$^{-1}$], −1.03 [**1a**$^+$/**1a**], E_p −0.12 V vs ferrocenium/ferrocene. ^{1}H NMR (dichloromethane-d_2, 300 MHz, 300 K): δ 0.29 (s, 3 H, $w_{1/2}$ 155 Hz, CH_3), −2.34 (s, 3 H, $w_{1/2}$ 90 Hz, CH_3), other signals unobserved.

(10) Crystal data for **1a**: $C_{24}H_{48}N_6Ta$, monoclinic, *P2/c*, $T = 180(2)$ K, $a = 9.955(2)$ Å, $b = 15.939(3)$ Å, $c = 9.385(2)$ Å, $\beta = 110.73(3)°$, $V = 1392.7(5)$ Å^3, $Z = 2$, R1 = 0.0227, wR2 = 0.0477 (2275 reflections, 147 parameters), GOF = 1.011.

(11) For **2a**: Anal. Calcd for $C_{48}H_{68}BN_6Ta$: C, 62.60; H, 7.44; N, 9.13. Found: C, 62.45; H, 7.42; N, 9.08. MS-CI (NH_3): *m*/*e* 601 ($[Ta(iPr_2\text{-dad})_3]^+$), MS-ES: *m*/*e* 319 ($BPh_4^-$). ^{1}H NMR (dichloromethane-d_2, 300 MHz, 300 K): δ 7.37 (br, 8 H, o-C_6H_5), 7.07 (t, 8 H, m-C_6H_5), 6.88 (t, 4 H, p-C_6H_5), 6.56 (s, 6 H, $CH{=}N$), 3.54 (septet, 6 H, $CH(CH_3)_2$), 1.29 (d, 18 H, CH_3), 1.14 (d, 18 H, CH_3).

(12) Crystal data for **2a**: $C_{48}H_{68}BN_6Ta$, monoclinic, $P2_1/n$, $T = 298(2)$ K, $a = 12.873(5)$ Å, $b = 20.883(5)$ Å, $c = 17.307(5)$ Å, $\beta = 99.215(5)°$, $V = 4593(2)$ Å^3, $Z = 4$, R1 = 0.0209, wR2 = 0.0495 (7040 reflections, 517 parameters), GOF = 1.022.

(13) DFT calculations (Amsterdam Density Functional package)[14] were performed using the gradient corrections of Becke[15a] and Perdew (BP86)[15b] Double-ζ + polarization and triple-ζ basis sets were used for main group and transition metals, respectively. Relativistic effects were included using the zeroth order relativistic approximation (ZORA). In all cases, the terminal CH_3 groups were replaced with hydrogens.

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