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Preparation of the First Ditantalum(III) Complex Containing a Ta−Ta Bond without Bridging Ligands

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Anionic organic amides have proven to be versatile ligands in the chemistry of di- and trivalent vanadium. In addition to the stabilization of rare V−N_2−V moieties,[1] these ligands can be involved in a number of vanadium metal center mediated transformations which include C−H σ-bond metathesis,[2] H-transfer,[3] dinitrogen cleavage,[4] azide coordination,[5] stabilization of alkyl groups,[6] and formation of metallacycles.[7] These observations prompted us to study the chemistry of low-valent niobium and tantalum amides for which only little information is available in terms of preparation and characterization.[8]

We have recently reported that the reaction of $[NbCl_4(THF)_2]$ with Cy_2NLi affords a Nb(V) niobaaziridine complex where the metallacycle is formed *via* C−H σ-bond activation.[9] Given the potential offered by this type of reactivity, we are currently attempting to expand the accessibility to medium-valent Ta−amide derivatives through preparation of complexes with the formula $[(R_2N)_nTaCl_{(5-n)}]$, which may work as a starting material for further reduction. In this paper, we describe our preliminary observations.

The reaction of $TaCl_5$ with 4 equiv of Cy_2NLi in diethyl ether at −78 °C gave, upon mixing, an instantaneous color change and formation of a brown-reddish mixture.[10] After elimination of a small amount of insoluble white material, replacement of the solvent with toluene, and cooling at −30 °C, the solution yielded bright yellow needles (Figure 1). Combustion analysis and X-ray fluorescence data were in agreement with the formulation $[(Cy_2N)_2TaCl](CyNC_6H_{10})$ (**1**). The IR spectrum was superimposable with that of the previously described niobium derivative,[9] thus suggesting that the two compounds may be isostructural. In agreement with the above formulation, the ^{1}H-NMR spectrum of complex **1** showed two different multiplets for the cyclohexyl C−H *ipso* hydrogens in a ratio of 1:4. The ^{13}C-NMR spectrum showed a resonance at 86.0 ppm due to a quaternary carbon atom, thus confirming that indeed one *ipso* carbon was deprotonated.

Complex **1** is both isostructural and isomorphous[11] with the previously reported Nb derivative.[9] The salient feature of its crystal structure is the metalation of one cyclohexyl to form a tantalaaziridine ring, along with the presence of two fairly short contacts between the tantalum metal center and the *ipso* hydrogen of two cyclohexyl of two amide groups (Figure 1). Similar to the case of the isostructural niobium derivatives, the Ta−N distance of the tantalaaziridine ring is slightly but significantly shorter than the Ta−C distance, which is a probable result of the steric interaction between the two bulky amide groups.

Deep-red air-sensitive crystals of a second complex were present in a second crop of crystals of **1** obtained from the mother liquor after concentration and cooling. The size of the crystals was sufficiently large to allow their separation under a microscope and to isolate a small but analytically pure sample. This second species was the only product that was isolated from a similar preparation carried out in toluene rather than in ether.[12] Combustion analysis and X-ray fluorescence data were in agreement with the formulation $[(Cy_2N)_2TaCl]$ (**2**). Chemical degradation experiments carried out either with H_2O or with 4 equiv of anhydrous HCl in a closed vessel connected to a Toepler pump did not yield hydrogen gas, thus ruling out the presence of hydride functions.

An X-ray crystal structure determination revealed that complex **2** is dimeric[13] and composed of two pyramidal $[(Cy_2N)_2TaCl]$ moieties linked together only by a direct Ta−Ta bond [Ta(1)−Ta(2) = 2.8484(7) Å]. Taking into consideration the

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[10] Complex **1**. Freshly sublimed $TaCl_5$ (2.20 g, 6.14 mmol) was added to ether (75 mL) at −78 °C. After about 5 min, $LiNCy_2$ was added to the nearly colorless suspension. The color of the reaction mixture rapidly changed to yellowish brown. The mixture was allowed to warm up slowly to room temperature, and stirring was continued for additional 2 h. A pale yellow fine solid, precipitated during this period, was isolated by filtration. The solid was extracted with toluene and cooled to −30 °C, yielding a pale yellow crystalline **1** (1.6 g, 34.4%). The brownish mother liquor was concentrated and cooled, upon which pale yellow crystals of **1** were obtained. This crop was found to be contaminated by a small amount of red crystals of **2**. Elemental anal. Calcd (Found) for $C_{36}H_{65}TaN_3Cl$: C, 57.17 (57.01); H, 8.66 (8.54); N, 5.56 (5.38). IR (Nujol, KBr plates, cm^{-1}) ν: 1648 (w), 1344 (m), 1330 (w), 1258 (s), 1204 (m), 1161 (s), 1147 (s), 1105 (s), 1024 (s), 979 (w), 947 (s), 892 (s), 843 (m), 803 (m), 781 (m), 724 (w), 686 (m), 619 (w), 585 (w). ^{1}H-NMR (C_6D_6, 500 MHz, 25 °C) δ: 3.78 (m, 1H, C−H cyclohexyl), 3.42 (m, 4H, C−H cyclohexyl), 1.7 (series of multiplets, 60H, CH_2 cyclohexyl). ^{13}C-NMR (C_6D_6, 125 MHz, 25 °C) δ: 86.0, 66.2, 58.1, 41.0, 38.1, 37.1, 29.7, 29.5, 29.1, 28.7, 28.0, 27.0, 26.87.

[11] Crystal data. **1**: $C_{36}H_{65}N_3TaCl$, fw 756.33, triclinic $P{-}1$, a = 10.074(1) Å, b = 18.813(2) Å, c = 9.731(1) Å, α = 93.82(1)°, β = 105.41(2)°, γ = 88.32(1)°, V = 1773.8(7) Å^3, Z = 2, D_{calc} = 1.416 g/cm^3, F_{000} = 784, μ = 31.64 cm^{-1}, T = −145 °C, R = 0.058, R_w = 0.072, GoF = 3.45 for 355 parameters and 4412 reflections out of 5151 unique. Non-hydrogen atom positions were located and refined anisotropically with the exception of N2, C24, and C25, which show a tendency to become nonpositive definite. Hydrogen atoms were introduced at their idealized positions.

[12] Freshly sublimed $TaCl_5$ (1.97 g, 5.5 mmol) was suspended in toluene (50 mL) at −78 °C. Treatment of the resulting pale yellow suspension with $LiNCy_2$ (4.31 g, 23 mmol) caused a sudden color change to purple, then to dark red, and finally to reddish brown. The solution was stirred for 5 h and left undisturbed for a further 5 h. The solution was filtered and the solvent evaporated *in vacuo* to yield a reddish-brown solid residue. The solid was extracted with hexane, and the solution was filtered, concentrated to small volume (40 mL), and cooled to −30 °C, upon which reddish black crystals of **2** separated (0.45 g, 0.4 mmol, 14%). An additional crop was obtained upon cooling the mother liquor to −78 °C (overall yield 31%). Elemental anal. Calcd (Found) for $C_{48}H_{88}Ta_2N_4Cl_2$: C, 49.96 (49.71); H, 7.69 (7.55); N, 4.85 (4.78). IR (Nujol, KBr windows, cm^{-1}) ν: 1574 (br w), 1345 (m), 1255 (m), 1160 (m), 1143 (w), 1104 (s), 1025 (s), 980 (w), 945 (s), 892 (m), 842 (m), 804 (m), 780 (m), 683 (m), 523 (w). ^{1}H-NMR (C_6D_6, 500 MHz, 25 °C) δ: 3.48 (tt, 1H, C−H cyclohexyl), 3.35 (tt, 1H, C−H cyclohexyl), 2.6, 2.25, 1.8, 1.6, 1.35, 1.20, 1.0 (series of multiplets, 20H, CH_2 cyclohexyl). ^{13}C-NMR (C_6D_6, 125 MHz, 25 °C) δ: 57.72, 53.13, 34.86, 27.16, 26.98, 26.72, 25.97, 25.92.

[13] Crystal data. **2**: $C_{48}H_{88}N_4Cl_2Ta_2$, fw 1154.05, monoclinic $C2/c$, a = 48.833(1) Å, b = 10.960(1) Å, c = 22.317(1) Å, β = 95.99(1)°, V = 11879(2) Å^3, Z = 8, D_{calc} = 1.290 g/cm^3, F_{000} = 4672, μ = 37.58 cm^{-1}, T = −140 °C, R = 0.047, R_w = 0.058, GoF = 1.95 for 498 parameters and 5458 reflections out of 7904 unique. Non-hydrogen atom positions were located and refined either isotropically or anisotropically. Hydrogen atoms were introduced at their idealized positions.

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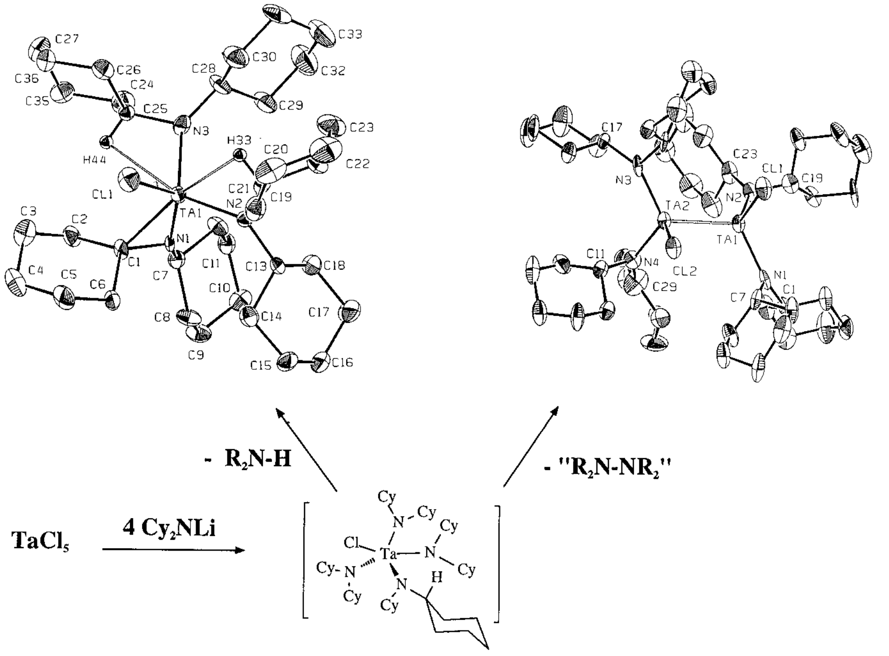

Figure 1. Complexes **1** and **2**. Thermal ellipsoids are drawn at the 50% probability level. (Left) ORTEP plot of **1**. Selected bond distances (Å) and angles (deg): Ta(1)−Cl(1) = 2.389(3), Ta(1)−N(1) = 1.937(8), Ta(1)−N(2) = 1.966(8), Ta(1)−N(3) = 1.969(9), Ta(1)−C(1) = 2.16(1), Ta(1)−H(33) = 2.632, Ta(1)−H(44) = 2.528, C(1)−N(1) = 1.46(1), N(1)−C(7) = 1.46(1), Cl(1)−Ta(1)−N(1) = 132.0(3), Cl(1)−Ta(1)−C(1) = 91.2(3), Cl(1)−Ta(1)−N(2) = 101.5(3), Cl(1)−Ta(1)−N(3) = 100.9(3), N(1)−Ta(1)−C(1) = 41.2(4), N(1)−Ta(1)−N(2) = 100.0(3), N(1)−Ta(1)−N(3) = 108.6(4), N(2)−Ta(1)−N(3) = 113.8(4). (Right) ORTEP plot of **2**. Selected bond distances (Å) and angles (deg): Ta(1)−Ta(2) = 2.8484(7), Ta(1)−Cl(1) = 2.401(3), Ta(1)−N(1) = 2.28(1), Ta(1)−N(2) = 2.08(1), Ta(2)−Cl(2) = 2.453(3), Ta(2)−N(3) = 2.25(1), Ta(2)−N(4) = 2.05(1), Cl(1)−Ta(1)−Ta(2) = 96.32(9), Cl(1)−Ta(1)−N(1) = 108.2(3), Cl(1)−Ta(1)−N(2) = 103.7(3), N(1)−Ta(1)−N(2) = 114.9(4), N(1)−Ta(1)−Ta(2) = 115.9(2), N(2)−Ta(1)−Ta(2) = 115.0(3), Cl(1)−Ta(1)−Ta(2)−Cl(2) = 57.0(1).

Ta−Ta bond, each Ta atom is in a slightly distorted tetrahedral coordination geometry. The distortion is probably due to the steric hindrance introduced by the two bulky amides. Accordingly, the two $(Cy_2N)_2TaCl$ moieties are staggered with respect to each other. However, the two chlorine atoms are *gauche*- rather than *anti*-positioned as it would be expected on the basis of steric repulsion minimization. This may be the result of the two agostic interactions formed by each Ta center with two *ipso* hydrogens [Ta···H distances range from 2.644 to 2.791 Å].

Complex **2** provides the first example of a ditantalum(III) species with an unsupported Ta−Ta bond and the second example in the chemistry of tantalum.[14] The Ta−Ta distance is significantly longer than that of the tetravalent $[(silox)_2TaH_2]_2$[14] and is perhaps in agreement with the presence of a Ta−Ta single bond. In addition to the long intermetallic distance, the staggered conformation makes the presence of a significant Ta−Ta δ-bond unlikely. The ^{1}H- and ^{13}C-NMR spectra show only two different types of cyclohexyl groups in the ratio 1:1, thus indicating that only the rotation along the Ta−N bond is slow in solution.

The fact that a 1:4 stoichiometric ratio is necessary for the formation of the two complexes may be tentatively rationalized by assuming the existence of two different decomposition pathways for an initially formed $[(Cy_2N)_4TaCl]$ intermediate. While the formation of **1** is achieved *via* proton abstraction, the *formal* reductive elimination of hydrazine yields **2**.[15] In this second case, the stability of the Ta−Ta bond is likely to provide the necessary thermodynamic driving force. The possibility that **2** could be derived from **1** *via* reductive elimination of $CyN{=}C_6H_{10}$ is excluded by the observation that **1** is thermally robust and can be heated at 80 °C for a few days without appreciable modification of the NMR spectrum.

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Supporting Information Available: Listings of atomic coordinates, thermal parameters, bond distances, and bond angles for **1** and **2** (36 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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