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Tantalum Complexes Bearing η^1-, η^2-, and “Slipped” η^2-Pyrazolato Ligands

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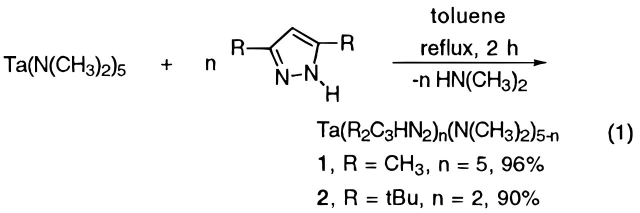
In the course of studies directed toward the deposition of metal nitride films, we have been pursuing the synthesis of early transition metal complexes that contain only nitrogen donor ligands in the coordination sphere. We recently reported the synthesis and structure of homoleptic titanium complexes bearing η^2-pyrazolato (pz) ligands.[2] These complexes are significant because they represent the first homoleptic metal complexes bearing η^2-pz ligands and because they are rare examples of η^2-pz coordination by a d-block metal.[3] Furthermore, molecular orbital calculations on the titanium complexes suggested that η^2-pz coordination should be common in early to mid d-block metal complexes.[3] Accordingly, we have continued to explore the preparation of new pz complexes. Herein we describe the synthesis and structural characterization of pentakis(3,5-dimethylpyrazolato)tantalum(V) and tris(dimethylamido)bis(3,5-di-*tert*-butylpyrazolato)tantalum(V). The former compound contains three η^2-pz ligands and two η^1-pz ligands and is the first complex to contain both types of pz binding. The latter compound has “slipped” η^2-pz ligands, where there is substantial deviation from ideal bidentate coordination. These complexes afford insight into some of the factors that affect pz ligand coordination on early transition metal centers.

Treatment of pentakis(dimethylamido)tantalum[4] with either 3,5-dimethylpyrazole[5] (5 equiv) or 3,5-di-*tert*-butylpyrazole[5] (2 equiv) in refluxing toluene for 2 h resulted in pentakis(3,5-dimethylpyrazolato)tantalum(V) (**1**, 96%) and tris(dimethylamido)bis(3,5-di-*tert*-butylpyrazolato)tantalum(V) (**2**, 90%), respectively, as yellow and red crystalline solids (eq 1).[6] Treatment of pentakis(dimethylamido)tantalum with more than 2 equiv of 3,5-di-*tert*-butylpyrazole did not lead to substitution of more dimethylamido groups, and only **2** was isolated. Complexes **1** and **2** were characterized by spectral and analytical methods as well as by X-ray structure determinations (vide infra). The ^{1}H NMR spectrum of **1** in benzene-d_6 showed only one type of pz ligand at 23 °C, while **2** revealed resonances for one type of dimethylamido ligand and one type of pz ligand in the same solvent. The ^{1}H NMR spectrum of **1** in toluene-d_8 between +20 and −80 °C showed only one type of pz ligand, indicating that the methyl sites are exchanging rapidly on the NMR time scale in this temperature range or that they have the same chemical shifts.



In order to understand the bonding involved in **1** and **2**, their X-ray crystal structures were determined.[7] Complex **1** crystallizes as a monomer with three bidentate and two monodentate pz ligands (Figure 1). The coordination environment of the tantalum atom is best described as trigonal bipyramidal, if the centers of the chelating ligands are considered as monodentate substituents. Unexpectedly, the η^1-ligands occupy equatorial

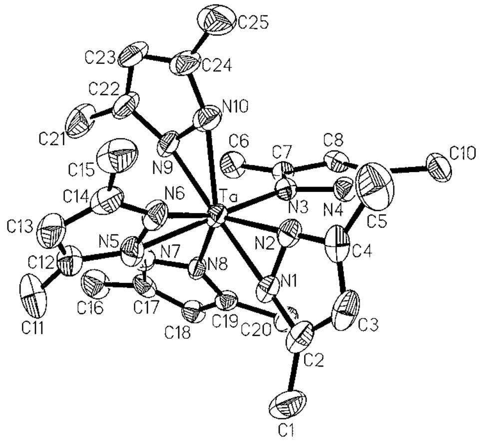


Figure 1. Perspective view Of **1** with thermal ellipsoids at the 35% probability level. Selected bond lengths (Å) and angles (deg): Ta−N(1) 2.109(7), Ta−N(2) 2.059(7), Ta−N(3) 2.162(6), Ta−N(5) 2.105(7), Ta−N(6) 2.133(6), Ta−N(8) 2.102(7), Ta−N(9) 2.076(7), Ta−N(10) 2.152(8); N(2)−Ta−N(1) 38.1(3), N(5)−Ta−N(6) 37.8(3), N(9)−Ta−N(10) 39.0(3), N(8)−Ta−N(3) 80.9(2).

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(1) (a) Wayne State University. (b) University of Windsor.

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(6) Analytical and spectral data for **1**: mp 159 °C; ^{1}H NMR (benzene-d_6, 22 °C, δ) 5.94 (s, 1 H, ring C*H*), 2.14 (s, 6 H, C*H*$_3$); ^{13}C{^{1}H} NMR (benzene-d_6, 22 °C, ppm) 146.20 (10 *C*CH$_3$), 113.07 (5 *C*H), 12.84 (10 *C*H$_3$). Anal. Calcd for $C_{25}H_{35}N_{10}Ta$: C, 45.73; H, 5.37; N, 21.33. Found: C, 45.71; H, 5.43; N, 21.37. Analytical and spectral data for **2**: mp 157 °C; ^{1}H NMR (benzene-d_6, 22 °C, δ) 6.60 (s, 1 H, ring C*H*), 3.09 (s, 9 H, 3 N(C*H*$_3$)$_2$), 1.53 (s, 18 H, 4 (C(C*H*$_3$)$_3$); ^{13}C{^{1}H} NMR (benzene-d_6, 22 °C, ppm) 157.47 (4 *C*C(CH$_3$)$_3$), 106.74 (2 ring *C*H), 48.00 (3 N(*C*H$_3$)$_2$), 31.91 (4 *C*(CH$_3$)$_3$), 31.08 (4 (C(*C*H$_3$)$_3$). Anal. Calcd for $C_{28}H_{56}N_7Ta$: C, 50.06; H, 8.40; N, 14.60. Found: C, 51.04; H, 8.32; N, 14.77.

(7) X-ray crystal data for $C_{25}H_{35}N_{10}Ta$: monoclinic, $P2_1/n$, $a = 12.382(5)$ Å, $b = 14.108(6)$ Å, $c = 17.150(4)$ Å, $\beta = 91.27(2)°$, $V = 2995(2)$ Å^3, $Z = 4$, $T = 295(2)$ K, $D_{calc} = 1.456$ g cm^{-3}, $R(F) = 3.57\%$ for 3640 independent reflections ($4° \leq 2\theta \leq 45°$). X-ray crystal data for $C_{28}H_{56}N_7Ta$: monoclinic, $P2_1/c$, $a = 10.895(5)$ Å, $b = 33.513(7)$ Å, $c = 19.279(4)$ Å, $\beta = 104.54(3)°$, $V = 6814(2)$ Å^3, $Z = 8$, $T = 295(2)$ K, $D_{calc} = 1.310$ g cm^{-3}, $R(F) = 5.08\%$ for 10382 independent reflections ($4.0° \leq 2\theta \leq 48°$). All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas all hydrogen atoms were treated as idealized contributors. All software and sources of the scattering factors are contained in the SHELXL-93 program library (G. Sheldrick, Institut für Anorganische Chemie, Tammannstrasse 4, D-37077 Göttingen, Germany). Further details on the structures of **1** and **2** are available in the Supporting Information.

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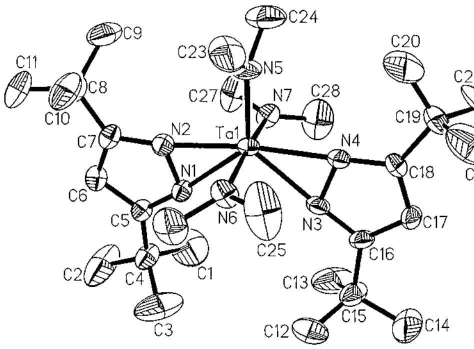

Figure 2. Perspective view of one independent molecule of **2** with thermal ellipsoids at the 35% probability level. Selected bond lengths (Å) and angles (deg): Ta(1)−N(1) 2.286(6), Ta(1)−N(2) 2.118(7), Ta(1)−N(3) 2.195(6), Ta(1)−N(4) 2.156(7), Ta(1)−N(5) 1.996(6), Ta(1)−N(6) 2.022(6), Ta(1)−N(7) 2.016(6), Ta(2)−N(1A) 2.220(7), Ta(2)−N(2A) 2.131(7), Ta(2)−N(3A) 2.117(6), Ta(2)−N(4A) 2.237(7), Ta(2)−N(5A) 1.996(7), Ta(2)−N(6A) 2.004(6), Ta(2)−N(7A) 2.021(6); N(2)−Ta(1)−N(1) 36.1(2), N(4)−Ta(1)−N(3) 37.2(2), N(5)−Ta(1)−N(7) 93.8(3), N(5)−Ta(1)−N(6) 95.7(3), N(7)−Ta(1)−N(6) 170.4(3), N(5)−Ta(1)−N(2) 94.2(3), N(5)−Ta(1)−N(4) 93.2(3).

and axial positions, rather than two axial sites adopted by tetrahydrofuran ligands in lanthanide pyrazolato complexes of the formula $\mathrm{Ln}(\eta^2\text{-pz})_3(\mathrm{THF})_2$.[8] The angles between axial and equatorial ligands range between 80.0 and 101.2°, while the angles between the axial ligands span 107.1−137.9°. The tantalum−nitrogen bond lengths in the η^2-pz ligands range between 2.059(7) and 2.152(8) Å. Within each η^2-ligand, the tantalum−nitrogen bond lengths are the same within experimental error. The tantalum−nitrogen bond lengths in the η^1-pz ligands are 2.162(6) Å (Ta−N(3)) and 2.102(7) Å (Ta−N(8)). The second nitrogen on each η^1-ligand is clearly not coordinated to the tantalum center.

Complex **2** crystallizes with two independent molecules in the asymmetric unit. The molecules are 7-coordinate monomers with differing pz coordination modes and a disordered *tert*-butyl group in one of the independent molecules. The tantalum atoms are bound to two chelating pyrazolato ligands and three dimethylamido groups (Figure 2). The geometry of **2** is distorted pentagonal bipyramidal, if two of the dimethylamido ligands are taken as the axial groups and one dimethylamido and the pz nitrogens are considered as the equatorial substituents. In the molecule containing Ta(1), the N(6)−Ta(1)−N(7) angle is 170.2(6)°, the angles between the axial and equatorial bonds range between 80 and 100°, and the angles between the equatorial ligands vary from 38 to 90°. Ideal values for pentagonal bipyramidal geometry are 180, 90, and 72°, respectively. The five equatorial nitrogen atoms and the tantalum atom define the pentagonal plane with an esd of 0.01 Å. The pz ligands in the two independent molecules of **2** show one η^2-interaction (Ta(1)−N(4) 2.157(7), Ta(1)−N(3) 2.198(7) Å) and three interactions that are best described as "slipped" η^2 (Ta(1)−N(2) 2.117(7), Ta(1)−N(1) 2.287(7); Ta(2)−N(2A) 2.134(7), Ta−N(1A) 2.221(7); Ta(2)−N(3A) 2.117(7), Ta(2)−N(4A) 2.233(7) Å). In the "slipped" η^2- ligands, one tantalum−nitrogen bond is 0.087−0.170 Å longer than the other. This type of bonding between a metal and a pz ligand has not been observed previously. The fact that both "normal" η^2- ligands and a "slipped" η^2- ligand are observed in **2** suggests that the energy difference between these forms is small.

The structures of **1** and **2** demonstrate that pz ligands prefer to bind to tantalum(V) centers in an η^2-fashion, but steric and electronic factors play a central role in determining the overall structure. In **1**, accommodation of five pz ligands leads to three η^2-pz and two η^1-pz interactions. If the η^2-pz ligand is considered to be a 4-electron donor[2] and the η^1-ligand is a 2-electron donor, then **1** is a 16-electron species. The poorer donor characteristics of an η^1-pz ligand (2-electron donor) compared to a dimethylamido ligand (planar 4-electron donor in **2**) can be illustrated by $\mathrm{Ta{-}N}_{\eta^1\text{-pz}}$ bond lengths of 2.162(6) and 2.102(7) Å versus $\mathrm{Ta{-}N}_{\mathrm{N(CH_3)_2}}$ bond lengths in **2** of 1.997(6), 2.018(6), and 2.013(6) Å. The complexes $\mathrm{M(O_2CNR_2)_5}$ (M = Nb,[9] Ta[10]) have been crystallographically characterized and are 8-coordinate, with three bidentate and two monodentate carbamato ligands. Like **1**, $\mathrm{Nb(O_2CNR_2)_5}$ has the monodentate ligands in a cis arrangement, while in $\mathrm{Ta(O_2CNR_2)_5}$ the monodentate ligands are approximately trans to one another. The formation of M(V) complexes with three bidentate and two monodentate ligands appears to be a general feature of potentially bindentate ligands with small bite angles. The sterically saturating nature of the di-*tert*-butylpyrazolato ligands in **2** allows the substitution of only two dimethylamido ligands. The "slipped" η^2-pz bonding in **2** may result from avoidance of steric interactions between two of the *tert*-butyl groups and the dimethylamido group containing N(5) or from crystal packing forces, or it could have electronic origins, since fully η^2-pz ligands would give a 20-electron molecule.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for complexes **1** and **2** are available on the Internet only. Access information is given on any current masthead page.

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