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Tantalum(V) complexes of an amine triphenolate ligand: a dramatic difference in reactivity between the two labile positions†

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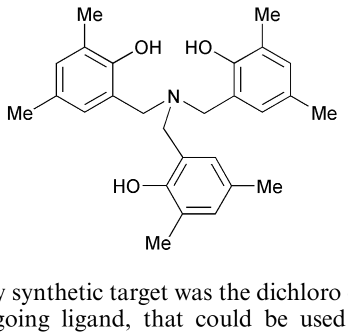
A tetradentate trianionic amine triphenolate ligand leads to octahedral Ta(V) complexes of C_s-symmetry, in which the two labile positions that are in *cis* geometry exhibit a dramatic difference in reactivity, the position *trans* to a phenoxy group being the active one.

There is a growing interest in the chemistry of early transition metal complexes of chelating alkoxide and aryloxide ligands. Substantial work has been done on Group IV metals since complexes of that family proved to be versatile precatalysts for α-olefin polymerization.[1–3] The chemistry of Group V metals (particularly Ta) was explored mostly with monodentate phenolate ligands,[4,5] whereas the use of chelating phenolates is still rare.[4d,6,7]

Recently we introduced the family of dianionic amine bis(phenolate) ligands for the Group IV triad.[3] Tetradentate ligands of that family, namely, those possessing an 'extra donor' on the sidearm led to octahedral complexes in which the two labile groups are in *cis* configuration.[3a,b] This geometry was found to be crucial for the high polymerization activity of the resulting zirconium and hafnium catalysts and the living polymerization of the titanium catalysts.[3c–f] In order to obtain Group V metal complexes of a similar geometry, tetradentate trianionic ligands are required. These may be obtained by replacing the neutral donor on the sidearm with an anionic one. Amine triphenolate ligands are especially attractive candidates because of their straightforward synthesis.[8] Even though they have been utilized for preparing several types of compounds,[7,9,10] the synthesis of Group V complexes featuring two labile groups (*e.g.* dichloro or dialkyl complexes) has not been reported. Herein we describe the chemistry of LigMX^{1}X^2 complexes of Ta(V) with the amine tri(2,4-dimethylphenolate) ligand, and demonstrate a strong differentiation between these two labile groups in the resulting complexes.



Our primary synthetic target was the dichloro complex of Ta with the foregoing ligand, that could be used as a starting material for preparing dialkyl complexes, or used directly as a precatalyst for polymerization. The direct reaction of the ligand precursor (LigH$_3$) or its lithium salt with tantalum pentachloride led to an inseparable mixture of products. An alternative synthetic pathway (developed for the titanium complexes of the dianionic ligands)[3c,f] involves synthesis of bis(alkoxy) precursors, that may be transformed to dichloro complexes by various chlorinating agents, such as Me$_3$SiCl, Et$_3$N·HCl or HCl.

Addition of the amine triphenolate ligand precursor to Ta(OEt)$_5$ resulted in quantitative formation of the bis(ethoxy) complex **1a** (Scheme 1). In the ^{1}H NMR spectrum of **1a** the protons of the amine triphenolate ligand appear as two sets in a 2 : 1 ratio, and the two ethoxy groups are different from one another. This is consistent with an octahedral complex of C_s-symmetry on the NMR timescale, whose symmetry plane includes the metal, the nitrogen donor, the 'middle' phenolate group, and the two ethoxy groups, and reflects the two remaining phenolate groups. The protons of the methylene group bound to the middle phenolate appear as a singlet whereas the protons of the methylene groups bound to the lateral phenolates appear as an AB system, thus supporting the proposed symmetry. This C_s-symmetry, in which the two labile groups are distinct, stands in sharp contrast to the C_3-symmetry of the various [N$_3$N]TaX$_2$ complexes, in which the two X groups (X = Me, Cl) are equivalent.[11] The crystal structure of **1a** ‡ (Fig. 1) reveals a distorted octahedral geometry with the two ethoxy ligands in *cis* configuration. The ethoxy ligand *trans* to the amine donor binds more tightly to the metal than the ethoxy ligand *trans* to the middle phenolate group [1.863(4) Å *vs.* 1.927(4) Å].

$$\mathrm{LigH_3 + Ta(OEt)_5 \longrightarrow LigTa(OEt)_2}$$
$$\mathrm{LigTa(OEt)_2 + 2\ Me_3SiCl \longrightarrow LigTa(OEt)(Cl)}$$
$$\mathrm{LigTa(OEt)(Cl) + 10\ Me_3SiCl \ \cancel{\longrightarrow}\ LigTaCl_2}$$

Scheme 1

Subsequently, **1a** was reacted with 2 equiv. of Me$_3$SiCl. Surprisingly, only one of the ethoxy groups was exchanged, leading to the mono(chloro)-mono(ethoxy) complex **1b** in quantitative yield (Scheme 1). **1b** does not undergo further substitution with a large excess of Me$_3$SiCl over days, and even strong chlorinating reagents such as Et$_3$N·HCl or HCl failed to do so. This marked differentiation is especially striking when taking into account the similar reactivity of the two alkoxy groups in the analogous titanium complex [ONNO]Ti(OiPr)$_2$.[3c] The crystal structure of **1b** indicated that its overall geometry is similar to that of **1a** and that the remaining ethoxy ligand is *trans* to the amine donor (Fig. 2). The differentiation may stem from the stronger labilizing ability of the *trans* phenolate group relative to the amine donor.[4b,12] This may also explain the difference in Ta–OEt bond distances in **1a**.

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† Electronic supplementary information (ESI) available: synthetic and spectroscopic data for all complexes. See http://www.rsc.org/suppdata/dt/b2/b206759e/

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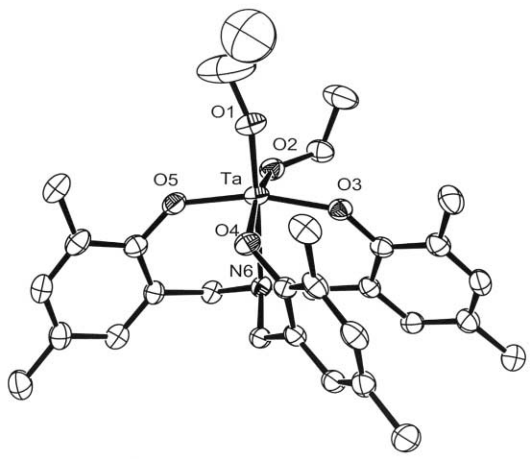

Fig. 1 Crystal structure of **1a**. Selected bond distances (Å): Ta–O1 1.863(4), Ta–O2 1.927(4), Ta–O3 1.938(3), Ta–O4 1.984(3), Ta–O5 1.931(4), Ta–N6 2.398(4).

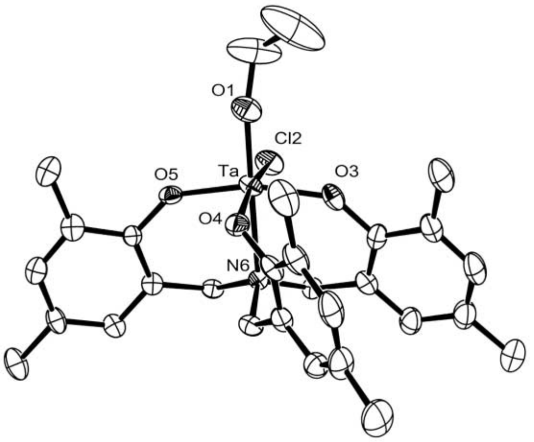

Fig. 2 Crystal structure of **1b**. Selected bond distances (Å): Ta–O1 1.865(6), Ta–Cl2 2.400(2), Ta–O3 1.911(5), Ta–O4 1.951(5), Ta–O5 1.916(5), Ta–N6 2.399(6).

As the dichloro complex is not accessible *via* the chlorinating reaction of the ethoxy precursor, we sought an alternative starting material. $Ta(NMe_2)_5$ appears to be a better candidate since dimethylamido groups are more readily replaced than alkoxo groups. Reacting the ligand precursor with $Ta(NMe_2)_5$[13] led to the desired diamido complex **2a** in quantitative yield (Scheme 2). The ^1H NMR spectrum of **2a** supports its C_s-symmetry.

$$\mathrm{LigH_3 + Ta(NMe_2)_5 \longrightarrow LigTa(NMe_2)_2}$$

$$\mathrm{LigTa(NMe_2)_2 + 2\ Me_3SiCl \longrightarrow LigTa(NMe_2)(Cl)}$$

$$\mathrm{LigTa(NMe_2)(Cl) + 10\ Me_3SiCl \longrightarrow LigTaCl_2}$$

Scheme 2

In analogy to **1a**, addition of 2 equiv. of Me_3SiCl to **2a** led to the quantitative formation of the mono(chloro)-mono(dimethylamido) complex **2b** within two hours (Scheme 2). Based on the above, we propose that the remaining dimethylamido ligand is *trans* to the amine donor. It can be seen clearly that even the strong base (amide) is resistant to electrophilic reagents when occupying this position. However, unlike **1b**, **2b** can be reacted further. Reaction of **2b** with 10 equiv. of Me_3SiCl over 4 days (Scheme 2) produced an approximately equimolar mixture of **2b** and the dichloro complex **2c**, that can be easily purified by pentane extraction of **2b**. The proton spectrum of **2c** is consistent with the spectra of all previous complexes supporting the formation of an octahedral complex of C_s-symmetry in which the two labile chloro groups are in *cis* configuration.

In conclusion, we have shown that the amine triphenolate ligand wraps around the Ta(V) center to afford octahedral complexes of C_s-symmetry, whose two labile positions exhibit a marked difference in reactivity. We are currently investigating the catalytic potential of these complexes.

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Notes and references

‡ Crystal data for $C_{31}H_{40}NO_5Ta{\cdot}0.5C_5H_{12}$ **1a**: $M = 723.66$, monoclinic, space group $P2_1/c$ (no. 14), $a = 17.0690(2)$, $b = 20.5620(7)$, $c = 9.4240(6)$ Å, $\beta = 98.849(2)°$, $V = 3268.2(2)$ Å^3, $Z = 4$, $\mu = 3.402$ mm^{-1}, $T = 110$ K. Final agreement factors were: $R1 = 0.0433$ for 6303 unique reflections with $I > 2\sigma(I)$, 0.0570 for all 7547 independent reflections. The unit cell contains two molecules of pentane located on, and severely disordered about, the centres of inversion, as indicated by the appearance of four residual peaks in the electron density map. Their structure could not be properly modelled.

For $C_{29}H_{35}NO_4ClTa{\cdot}C_5H_{12}$ **1b**: $M = 750.13$, monoclinic, space group $P2_1/c$ (no. 14), $a = 17.1150(4)$, $b = 20.2450(10)$, $c = 9.5900(9)$ Å, $\beta = 91.766(4)°$, $V = 3321.3(4)$ Å^3, $Z = 4$, $\mu = 3.426$ mm^{-1}, $T = 110$ K. Final agreement factors were: $R1 = 0.0540$ for 4940 unique reflections with $I > 2\sigma(I)$, 0.0725 for all 6046 independent reflections. The asymmetric unit of the refined structural model contains one molecule of partly disordered pentane. CCDC reference numbers 189674 and 189675. See http://www.rsc.org/suppdata/dt/b2/b206759e/ for crystallographic data in CIF or other electronic format.

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