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Ta(V) complexes of a bulky amine tris(phenolate) ligand: steric inhibition vs. chelate effect

Stanislav Groysman^a, Sharon Segal^a, Israel Goldberg^a, Moshe Kol^{a,*}, Zeev Goldschmidt^{b,*}

^a Raymond and Beverly Sackler Faculty of Exact Sciences, School of Chemistry, Tel Aviv University, Tel Aviv, 69978 Israel ^b Department of Chemistry, Bar-Ilan University, Ramat Gan, 52900 Israel

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Abstract

The reactivity of a bulky amine tris(phenolate) ligand toward $Ta(NMe_2)_5$ was investigated. The reaction leading to the final product LigTa(NMe_2)_2 was slow and proceeded via an unusual dinuclear complex. The X-ray structures of both complexes were solved. Significantly, although the reaction of $Ta(OEt)_5$ with that ligand precursor is slow as well, no dinuclear intermediate is observed during the reaction course.

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A number of tetradentate trianionic ligands of tripodal geometry have been reported in the last two decades. Noteworthy members are the triamido-amine $[N_3N]$ ligands family, that has been extensively studied [1,2], and the amine tris(phenolate) ligands family introduced more recently to the early transition metals realm. Whereas complexes of the former with a variety of early transition metals were prepared, and their reactivity potential explored [2,3], the chemistry of the latter ligands has been investigated less thoroughly [4–8], being focused mainly on Group IV metals [5,6]. Recently, we and others have begun extending this chemistry to Group V metals [7,8].



One ligand of this family, bearing methyl groups on the 2, 4 positions of the phenolate rings (Lig^1H_3) was shown to undergo a fast and nearly quantitative reaction with a variety of Ta(V) metal precursors, such as Ta(NMe₂)₅ [8b], Ta(OEt)₅ [8b], Ta(OMe)₅ [7b] and Ta(CH₂Ph)₅ [8b]. The reactions ultimately led to the formation of octahedral complexes of the Lig¹TaX₂ type (Fig. 1). Lig¹H₃ is the only tripodal ligand of this framework reported thus far in relation to Group V metals. As the atomic radius of Ta(V) is smaller than its Group IV analogues, we were interested to reveal how the steric pressure affect the binding of this ligand family around tantalum. Therefore, we decided to explore the reactivity of the sterically

^{*} Corresponding authors. Tel.: +972-3-6407392; fax: +972-3-6409293 (M. Kol).

E-mail addresses: moshekol@post.tau.ac.il (M. Kol), goldz@mail. biu.ac.il (Z. Goldschmidt).

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Fig. 1. X = OEt, OMe, NMe₂, CH₂Ph.

crowded analogue, Lig^2H_3 , carrying bulky *t*-Bu substituents in the *ortho* (*para*) positions of the phenolate rings. This ligand was previously employed in Ti(IV) chemistry [5,6b], however, the coordination chemistry of this ligand with group V metals and, in particular with Ta(V) has not been described before.

Our first attempt to prepare Ta(V) complexes of this ligand relied on Ta(CH₂Ph)₅, a readily available organometallic precursor [8b]. However, even after long reaction times, the products mixture consisted mainly of the unreacted starting materials. Therefore, we turned to the more traditional metal precursor, Ta(NMe₂)₅ [9]. As previously reported, the reaction of Ta(NMe₂)₅ with the less bulky ligand Lig¹H₃ proceeded smoothly when the reagents were mixed in ether at RT, and after 2 h, no starting materials were detected in the reaction mixture [8b]. In contrast, Lig^2H_3 led to the formation of several products. Under the same reaction conditions, the products mixture consisted of three species: the desired product A, the unreacted ligand precursor Lig^2H_3 , and an additional product **B** (Scheme 1). On the other hand, no traces of Ta(NMe₂)₅ were observed among the products. Employing longer reaction times led to a higher portion of A in the products mixture and when the reaction was allowed to proceed for three days, no other products besides A were detected. Therefore, we propose that for the sterically crowded ligand Lig^2H_3 , the formation of the expected mononuclear complex A may take place via some sort of long-lived, relatively stable intermediate B.

A was characterized by means of ¹H and ¹³C NMR, that indicate a regular C_s -symmetrical complex $Lig^2Ta(NMe_2)_2$ [10]. The ¹H NMR spectrum of A exhibits two groups of aryl protons and two groups of *t*-Bu





Fig. 2. ORTEP representation of **B**, 50% probability ellipsoids. Selected bond lengths (Å): Ta1–O2 1.933(3); Ta1–O3 1.944(3); Ta1–O4 2.029(3); Ta1–N5 2.002(4); Ta1–N6 2.019(3); Ta1–N7 2.387(3).

substituents, of the relative intensity 2:1. The dimethylamido groups, lying on the mirror plane, appear as two distinct signals. Four of the six benzyl protons appear as an AB system, while the other two, being reflected by the mirror plane, give rise to a sharp singlet. In addition, A was characterized by means of X-ray crystallography [11]. The crystal structure of A reveals a mononuclear octahedral complex $Lig^2Ta(NMe_2)_2$ (Fig. 2). As may be expected, the amine tris(phenolate) ligand binds to the metal in a tetradentate fashion and the two remaining dimethylamido groups occupy mutually cis positions. We have previously reported that the "labile" ligands X in $Lig^{1}TaX_{2}$ (X = OEt, NMe₂) exhibit different reactivities, attributed to the trans influence of the phenolate oxygen vs. the central amine donor. This different trans influence was expressed in different Ta-X bond lengths, i.e., Ta- $X_{trans-amine} < Ta - X_{trans-phenolate}$ [8b]. In contrast, the Ta-X bond lengths in A are very similar $(2.002_{trans-amine} \text{ vs.})$ $2.019_{trans-phenolate}$), probably due to the steric pressure imposed by three t-Bu groups inside the "phenolates pocket". To minimize repulsive steric interaction, the top dimethylamido unit is rotated to a conformation that seems to reduce its ability for π -donation (for an "unrotated" dimethylamido group in B see below). A lesser degree of π -donation by this dimethylamido nitrogen (N5) in A may explain a relatively short trans Ta-N7 bond (2.387 A).

In contrast to **A**, the nature of **B** was much less obvious. To identify the structure of this intermediate, we isolated bright-yellow crystals of **B** by fractional crystallization from pentane [12]. Its ¹H NMR spectrum displayed two groups of aromatic protons and two groups of *t*-Bu substituents, each having a relative intensity of 2:1. The NMe₂ region was somewhat more complicated, featuring four signals of relative intensities of 4:1:1:1. Single crystals of **B** were obtained by crystallization from cold pentane, and its X-ray structure was solved [13,14], revealing an unusual dinuclear



Fig. 3. ORTEP representation of B, 40% probability ellipsoids. The H atoms, a disordered pentane molecule, and the disorder in *t*-Bu groups are omitted for clarity. Selected bond lengths (Å): Ta1–O3 1.947(5); Ta1–O4 1.928(5); Ta1–N5 2.028(6); Ta1–N6 1.970(6); Ta1–N7 2.067(6); Ta1–N8 2.571(6); Ta2–O9 1.952(6); Ta2–N10 2.000(7); Ta2–N11 2.027(6); Ta2–N12 2.026(7); Ta2–N13 1.952(6).

complex, in which two Ta(V) centers are bound to one amine tris(phenolate) ligand (Fig. 3). The structure of **B** may be roughly divided into two segments, interconnected by the ligand backbone, designated as [Ta1] and [Ta2]. The metal center in [Ta1] is hexa-coordinate, with an [ONO] ligand fragment and three NMe₂ groups each bound in a mer fashion forming a nearly perfect octahedral geometry. The remaining phenolate group binds to the second, penta-coordinate [Ta2], along with four NMe₂ groups. The geometry of this segment is nearly square-pyramidal, with the phenolate oxygen lying in the basal plane, and one of the dimethylamido nitrogens (N11) occupying the axial position. The phenolate oxygens in the two segments exhibit a different binding mode: the Ta–O–C bond angles in the [Ta1] segment are substantially narrower (142-145°) than their counterpart in the [Ta2] segment, which is almost linear (174°).

The orientation of the central NMe₂ ligand in [Ta1] is noteworthy, as it may shed light on the inertness of **B**. To avoid overlapping, the Me groups of the "central" NMe₂ ligand move as far as possible from the *ortho t*-Bu substituents. Thus, one of the dimethylamido methyl groups has to point directly toward the *ortho*-substituent of the "incoming" (third) phenolate on the reaction pathway leading to **A**. This repulsive interaction may be responsible for the relative inertness of this intermediate [14]. Interestingly, the dimethylamido nitrogen (N6) seems to interact strongly with the metal via π -donation (Ta1–N 1.971 Å), thus lengthening the *trans* Ta–N bond (2.571 Å).

$$Lig^{2}H_{3}$$
 +Ta(OEt)₅ \xrightarrow{slow} $Lig^{2}Ta(OEt)_{2}$
Scheme 2.

In addition to Ta(NMe₂)₅, Ta(OEt)₅ may also serve as a suitable metal precursor. The differences between these two are the reduced basicity, as well as the reduced steric bulk of the ethoxy ligand, in comparison to the dimethylamino ligand. According to the NMR spectra, the reaction of the ligand precursor with $Ta(OEt)_5$ (in ether at RT) led to the slow formation of the expected mononuclear di(ethoxy) complex $Lig^2Ta(OEt)_2$ (C). However, for this metal precursor, no dinuclear intermediate was detected. Thus, after 2-3 h, the reaction mixture consisted exclusively of the final product and both starting materials, in the relative ratios of 2:1:1. Carrying out the reaction for 2 d leads to a high-yield formation of white C, contaminated by the traces of the ligand precursor and the metal precursor (<10%). Pure $Lig^{2}Ta(OEt)_{2}$ was obtained upon recrystallization from pentane in ca. 50% yield [15], and is proposed to be isostructural with A according to its spectroscopic data scheme 2.

In conclusion, we have shown that an amine tris(phenolate) ligand carrying bulky *t*-Bu substituents can wrap around a Ta(V) center, leading to an octahedral Lig²TaX₂ (**A**) complex, provided that a suitable precursor is employed (Ta(NMe₂)₅ or Ta(OEt)₅). Even with such a precursor, the reaction is slow and may go through an intermediate dinuclear complex Lig²Ta₂X₇ (**B**, X = NMe₂), in which two Ta(V) centers are in different environments. When the "leaving" ligand X is less easily protonated, and less bulky (OEt vs. NMe₂), a kinetic product analogous to the intermediate **B** is not observed in the products mixture. We are currently investigating the reactivity of these species.

Supplementary information

Crystallographic data for complexes **A** and **B** have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publications No. CCDC 238150 and No. CCDC 238151. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

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- [9] D.C. Bradley, I.M. Thomas, Can. J. Chemistry 40 (1962) 1355.
- [10] Preparation of A: Evaporation of the pentane solution after crystallization of B (see [12]) led to 186 mg (0.20 mmol, 64%) of pure A. ¹H NMR (C₆D₆, 200 MHz) δ 7.48 (d, J = 2.4 Hz, 2H), 7.19 (d, J = 2.6 Hz, 1H), 6.98 (d, J = 2.4 Hz, 2H), 6.27 (d, J = 2.4 Hz, 1H), 4.00 (d, J = 13.5 Hz, 2H, ArC(H)H), 3.91 (s, 6H, N(CH₃)₂), 3.31 (s, 6H, N(CH₃)₂), 3.04 (s, 2H), 2.96 (d, J = 13.6 Hz, 2H) 1.61 (s, 18H, C(CH₃)₃), 1.53 (s, 9H, C(CH₃)₃), 1.39 (s, 18H, C(CH₃)₃), 1.23 (s, 9H, C(CH₃)₃).
- [11] Crystal data for A: $C_{48}H_{78}N_3O_3Ta$, M = 938.09, monoclinic, $P2_1/c$, a = 15.8440(2), b = 15.8290(2), c = 19.9410(2) Å, $\beta = 102.9840(5)^\circ$, V = 4873.23(10) Å³, Z = 4, $\mu = 2.296$ mm⁻¹, T = 110 K. Final agreement factors were: $R_1 = 0.0370$ for 9318 rflns with $I > 2\sigma(I)$, and $R_1 = 0.0529$ for all 11,514 rflns.
- [12] 212 mg (0.31 mmol) of Lig²H₃ in ca. 5 mL of ether were added to the yellow ether solution of Ta(NMe₂)₅ (125 mg, 0.31 mmol).

After 2.5 h the solvent was evaporated, leading to 315 mg of a crude yellow product. Recrystallization from pentane led to yellow crystals that contain essentially pure **B** (75 mg, 18% yield). ¹H NMR (C₆D₆, 200 MHz) δ 8.24 (br s, 1H), 7.58 (br s, 1H), 7.55 (d, J = 2.5 Hz, 2H), 6.92 (d, J = 2.5 Hz, 2H), 4.89 (d, J = 12.5 Hz, 2H), 4.44 (d, J = 12.4 Hz, 2H), 3.85 (s, 6H, N(CH₃)₂), 3.45 (s, 6H, N(CH₃)₂), 3.37 (s, 6H, N(CH₃)₂), 3.17 (s, 2H), 2.98 (s, 24 H, four N(CH₃)₂), 1.77 (s, 18H, *t*-Bu), 1.53 (s, 9H, *t*-Bu), 1.50 (s, 9H, *t*-Bu), 1.24 (s, 18H, *t*-Bu).

- [13] Crystal data for **B**: $C_{64}H_{120}N_8O_3Ta$, M = 1411.58, triclinic, P_{-1} , a = 13.7350(3), b = 14.0700(3), c = 20.7800(7) Å, $\alpha = 93.6480(9)$, $\beta = 104.5320(9)$, $\gamma = 114.6211(19)^\circ$, V = 3468.74(16)Å³, Z = 2, $\mu = 3.198$ mm⁻¹, T = 110 K. Final agreement factors were: $R_1 = 0.0614$ for 9717 rflns with $I > 2\sigma(I)$, and $R_1 = 0.1225$ for all 15.987 rflns.
- [14] A somewhat similar structure of a Ta(V) complex with tris[(2indonyl)methyl]amine ligand was reported. That tetradentate [3–] ligand coordinates to the metal in a tridentate [2–] fashion, leaving 3 dimethylamido groups on the Ta. However, the fourth, unbound, ligand arm was still protonated in that case. The authors explained the structure by a reduced π-donating ability of that ligand J.M. Tanski, G. Parkin, Inorg. Chem. 42 (2003) 264.
- [15] 0.17 mmol of Ta(OEt)₅ in ether were added to a stirred solution of an equimolar amount of Lig²H₃ (0.17 mmol in ether). The reaction was stirred at RT for 2.3 h, after which time the solvent was evaporated. The ¹H NMR spectrum of the crude product consisted of Lig²Ta(OEt)₂, Ta(OEt)₅, and Lig²H₃, in relative intensities of 2:1:1, thus indicating the formation of Lig²Ta(OEt)₂ in ca. 50%. The off-white product was extracted with pentane (ca. 2 mL), filtered through Celite, and left in the freezer overnight. White powder (72 mg) was separated from the pentane solution, and dried in vacuo, leading to the pure Lig²Ta(OEt)₂ (0.08 mmol, 47%). ¹H NMR (C₆D₆, 200 MHz) δ 7.60 (d, J = 2.4 Hz, 1H), 7.52 (d, J = 2.4 Hz, 2H), 6.93 (d, J = 2.2 Hz, 2H), 6.81 (d, J = 2.4 Hz, 1H), 4.90 (q, J = 7.0 Hz, 2H), ca.3.6 (q + br s, J = 7.0 Hz, 8H), 1.77 (s, 9H), 1.64 (s, 18H), 1.47 (t, J = 7.0 Hz, 3H), 1.40 (s, 9H), 1.36 (s, 18H), 0.53 (t, J = 7.0 Hz, 3H).