

Diamido Tantalum(V) Complexes Derived from a Diaza Macrocycle¹

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ABSTRACT The amido complexes [Ta{O(N)₂}(CH₂Ph)₃], (**1**), [Ta{O(N)₂}(μ-CHBu^t){μ-O(NH)N}Li], (**2**), and [Ta{O(N)₂}Cl₃], (**3**), all featuring the dianionic diamido macrocycle [O(N)₂]²⁻ originating from O(NH)₂ by deprotonation, O(NH)₂ = 3,3-dimethyl-1,5-diaza-8-oxacyclodecane, have been prepared from Ta(CH₂Ph)₅, Ta(CH₂^tBu)₃Cl₂ and TaCl₅ by alkanolysis, salt metathesis with Li₂[O(N)₂] and .Me₃SiCl elimination with O(NSiMe₃)₂, respectively. Structural analyses revealed that in (**1**) the macrocycle is facially coordinated, while (**2**) contains one dianionic, facially coordinated macrocycle and one monoanionic macrocycle coordinating one lithium atom and metallated at one of the 3-methyl groups by the Ta.

KEYWORDS Azamacrocycle, Amido, Bimetallic, Alkylidene, Tantalum

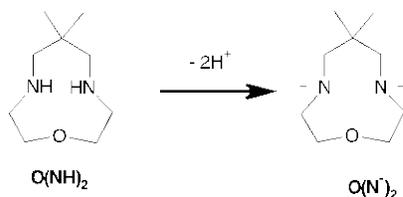
Declarations of interest: none

¹ This paper is dedicated to Professor Spyros Perlepes with best wishes on the occasion of his 65th birthday

INTRODUCTION

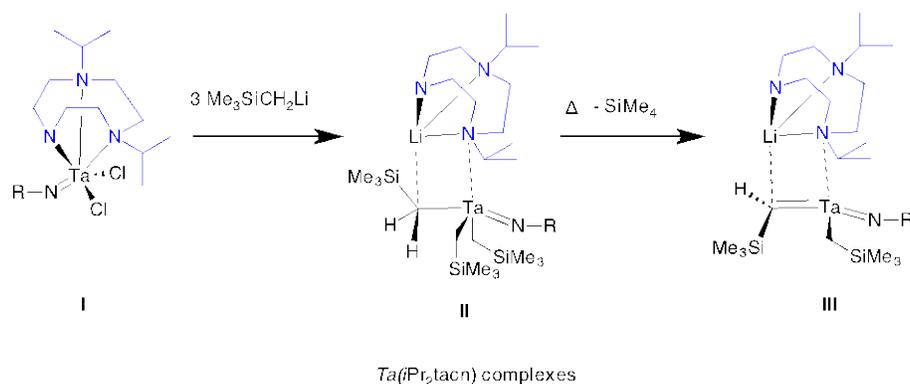
The chemistry of medium-sized tridentate macrocycles has been largely dominated by *neutral* ligands with amine, ether and/or thioether functions, facially coordinating to middle or late transition metals.¹ Peralkylated azamacrocycles with or without pendant groups have also been used with these metals.² *Mono-* and *di-anionic* aza-macrocycles with amido functions integrated in the macrocyclic rim, formally obtained by deprotonation at secondary N atom(s), have emerged as an alternative class of ancillary anionic ligands.^{3, 4} Due to the hardness of the amido donor groups, they are suitable as spectators for electrophilic, high oxidation state early transition metals and may serve as versatile, tunable (by virtue of ring size, substituents on the macrocycle rim, *etc.*) alternatives to cyclopentadienyl-, imido- and other L_nX_m type ligands, $m = 1,2$, $n =$ small integer. Catalytic applications may emerge in areas where early transition metal complexes with cyclopentadienyl, chelating, non-macrocyclic (polyamido) and imido ligands have shown potential (*e.g.* alkene polymerization and oligomerization, hydroamination of alkynes, allenes, *etc.*).^{5,6} With late transition metals *anionic* azamacrocyclic complexes are rare due to the energetically unfavourable interaction of the amido π -donors with the partially filled d-manifolds and macrocycle imposed constraints, but they may show potential as proton responsive ligands. Recently, monoanionic amidotriamine azamacrocycles Me_3TACD of the L_3X -type (obtained by the deprotonation of 1,4,7-trimethyl-1,4,7,10-tetraazacyclododecane) have been used as spectators in lanthanide chemistry, main group organometallic chemistry and the stabilization of well defined molecular magnesium hydride clusters.⁷

As part of a program aiming at developing new capping tridentate amido macrocyclic ligands, we prepared the novel oxa-aza macrocycle, 3,3-dimethyl-1,5-diaza-8-oxacyclododecane, $[O(NH)_2]$, which serves as a convenient precursor for the dianionic $[O(N^-)_2]$ by deprotonation of both secondary N atoms of the macrocyclic ring.



$O(NH)_2$ reacted with Ti(IV) and Zr(IV) dialkylamides to produce complexes in which the macrocycle functions as L_3 , L_2X and L_3X donor depending upon the conditions employed.⁴

Herein we describe Ta(V) alkyl complexes with the $[O(N^-)_2]$, which point to the versatility and possible limitations of the ligand design. Arnold obtained Ta complexes with the monoanionic $[N, N'-(iPr)_2tacn]^-$, including the complex $[TaCl_2(iPr_2tacn)(=NAr)]$ (**I**) ($Ar = 2,6-iPr_2C_6H_3$), $tacn = 1,4,7$ -triazacyclononane, which on reaction with $LiCH_2SiMe_3$ gave the unexpected $[(Me_3SiCH_2)_2(NAr)Ta(\mu-CH_2SiMe_3)(\mu-iPr_2tacn)Li]$ (**II**). Thermolysis of the latter produced *via* α -hydrogen abstraction the alkylidene complex $[(Me_3SiCH_2)(NAr)Ta(\mu-CHSiMe_3)(\mu-iPr_2tacn)Li]$, (**III**), the reactivity of which was studied in some detail, revealing behaviour associated with Schrock-type alkylidene and metallated nucleophilic carbanion (Scheme 1).^{3,8} Mountford has also described the closely related $[M(R_2tacn)Cl_2(N^iBu)]$, $M = Nb, Ta$; $R = Me$ or iPr .⁹



Scheme 1 Ta(iPr_2tacn) complexes previously described featuring bimetallic Ta/Li cores and 'masked' alkylidene ligand in **III**^{8a}

MATERIALS AND METHODS

General: ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker AV300 spectrometer and referenced to the residual proton signals from the solvent C_6D_6 . Microanalyses were undertaken by the London Metropolitan University microanalytical service.

Solvents were dried over appropriate drying agents and distilled prior to use. All preparations involving metal alkyls and amides were carried out under N_2 atmosphere using standard Schlenk techniques or in a Braun glove box. The starting materials $\text{Ta}(\text{CH}_2\text{Ph})_5$ ¹⁰ and $\text{Ta}(\text{CH}_2^t\text{Bu})_3\text{Cl}_2$ ¹¹ were prepared following literature procedures. $\text{O}(\text{NH})_2$ and $\text{O}(\text{NSiMe}_3)_2$ were obtained as described previously.⁴

[Ta{O(N)₂}(CH₂Ph)₃] (1): $\text{O}(\text{NH})_2$ (0.13 g, 0.75 mmol) and $\text{Ta}(\text{CH}_2\text{Ph})_5$ (0.49 g, 0.77 mmol) were mixed together in toluene (25 mL) at room temperature giving a dark brown solution. The mixture was heated at 60 °C for 4 h and then the solvent was removed *in vacuo* to yield a dark brown oil. This was extracted with ether (2 x 20 mL) and filtered. Evaporation of the ether gave an orange-brown residue (*ca.* 0.32 g), which by ^1H NMR analysis consists of $\text{Ta}[\text{O}(\text{N})_2](\text{CH}_2\text{Ph})_3$ with minor amounts (*ca.* 5%) of unreacted $\text{O}(\text{NH})_2$. Under these conditions no $\text{Ta}(\text{CH}_2\text{Ph})_5$ was found in the ether extract. The separation of **(1)** and the traces of unreacted $\text{O}(\text{NH})_2$ proved impossible due to their similar solubility in inert solvents and the limited thermal of **(1)** above 60 °C. Solution of this reaction mixture in C_6D_6 in a NMR tube gave, on standing after two days, X-ray quality crystals. δ_{H} (C_6D_6) (ppm): 7.25 - 7.30 and 6.80 - 6.95 (m, 15H, aromatic), 3.85 and 3.55 (m, 2H, $\text{NCH}_2\text{CH}_2\text{O}$), 3.15 and 3.05 (d, 2H, $\text{NCH}_2\text{CH}_2\text{O}$), 2.45 (s, 6H, PhCH_2), 2.37 and 2.25 (d, 4H, NCH_2CMe_2 of the macrocycle), 0.15 and 0.10 (s, 3H each, NCH_2CMe_2). δ_{C} (C_6D_6) (ppm): 148.2, 129.6, 123.4, 84.6, 76.6, 71.2, 61.6, 59.4, 57.23, 27.1, 26.1.

[{O(N)₂}Ta(μ -CH^tBu){ μ -O(NH)N}Li] (2): $\text{O}(\text{NH})_2$ (0.45 g, 2.6 mmol) was placed in a Schlenk tube and dissolved in toluene (100 mL). The solution was cooled to -78 °C, treated with $^n\text{BuLi}$ (2.5 M, 2.2 mL, 5.5 mmol), allowed to reach room temperature within 30 min and stirred for 5 h. The reaction mixture was then re-cooled to -78 °C and a solution of $\text{Ta}(\text{CH}_2^t\text{Bu})_3\text{Cl}_2$ (1.2 g, 2.6 mmol), in toluene (10 mL) was added. After completion of the addition, the mixture was allowed to reach room

temperature and stirred for further 12 h. The separated LiCl was removed by filtration and the volatiles were evaporated from the filtrate under reduced pressure. The solid residue was extracted with petrol (*ca.* 100 mL) and cooled to -35 °C to give an orange/brown solid which was isolated by filtration and dried *in vacuo*. Yield: 0.22 g, *ca.* 15% based on Ta. The solid was recrystallized from toluene at -35 °C to give crystals suitable for X-ray diffraction. The ¹H-NMR spectrum of the molecule is complicated and full assignment of the macrocyclic backbone protons was impossible. δ_{H} (C₆D₆) (ppm): 4.62 – 4.20 (m, 3H, macrocyclic backbone), 3.95 – 4.10 (ddd, 1H, macrocyclic backbone), 3.70-3.82 (m, 3H, macrocyclic backbone), 3.30 – 3.42 (m, 5H, macrocyclic backbone), 3.10 – 3.23 (m, 2H, macrocyclic backbone), 2.98 – 3.08 (m, 2H, macrocyclic backbone), 2.82 – 2.93 (m, 2H, macrocyclic backbone), 2.65-2.75 (m, 2H, macrocyclic backbone), 2.45 (ddd, 1H, macrocyclic backbone), 2.28 (s, 1H, Bu^tCH), 1.90-2.12(m, 3H, macrocyclic backbone), 1.75 (d, 1H, macrocyclic backbone), 1.45 {s, 9H, (CH₃)₃}, 1.12, 1.11 and 1.02 (s, 3H each, CH₃ of the macrocycle). Found (%): C, 46.21; H, 7.17; N, 9.22; Calculated (%) for C₂₃H₄₃LiN₄O₂Ta: C, 46.39; H, 7.28; N, 9.41.

[Ta{O(N₂)}Cl₃] (3): A solution of O(NSiMe₃)₂ (0.85 g, 2.7 mmol) in 15 mL of toluene was added to a Teflon-tapped ampoule containing TaCl₅ (0.96 g, 2.7 mmol) suspended in 15 mL of toluene. The ampoule was sealed at reduced pressure and heated overnight (oil bath set at 110 °C). After cooling to room temperature, the resulting suspension was transferred into a wider-necked Schlenk tube, the volatiles were removed under reduced pressure and the solid product was washed with toluene (20 mL) and petrol (20 mL), and dried *in vacuo*. (Yield = 1.1 g, 90%). Found (%): C, 23.64 H, 3.88 N, 6.03; Calculated (%) for C₉H₁₈Cl₃N₂OTa, C, 23.62, H, 3.97, N, 6.03. NMR data for this product could not be obtained due its poor solubility in inert solvents.

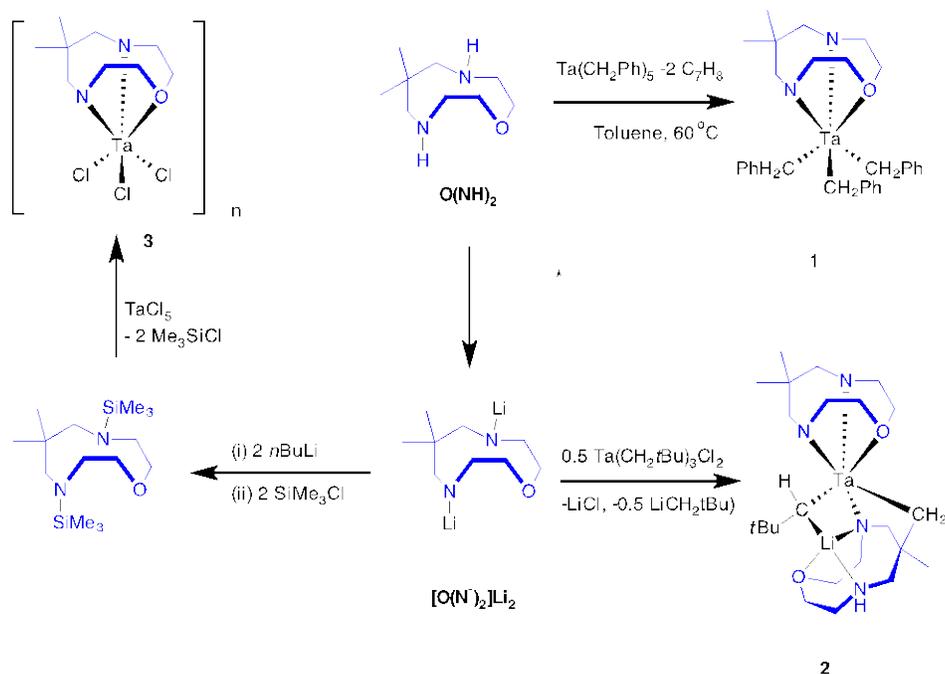
X-ray crystallography:

Details of the crystallographic data collection and refinement parameters are given in Table 1. The data were collected on a Bruker Nonius KappaCCD area detector diffractometer with rotating anode FR591 and an Oxford Cryosystems low-temperature device, operating in omega scanning mode with phi and

omega scans to fill the Ewald sphere. The crystals were mounted on a glass fiber with silicon grease, from Fomblin vacuum oil. The programs used for control and integration were Collect, Scalepack and Denzo. All solutions and refinements were performed using the WinGX package and all software packages within.^{12, 13}

RESULTS AND DISCUSSION

The complexes described in this paper and the relevant transformations leading to them are shown in Scheme 2.



Scheme 2 Complexes described herein

Metallation of the neutral 10-membered ring macrocycle O(NH)₂ was achieved by reaction with Ta(CH₂Ph)₅ in toluene. The brown oil obtained was shown by ¹H and ¹³C{¹H} NMR spectroscopy to be (**1**) with minor quantities of the unreacted macrocycle (Scheme 2). This transformation represents the first example of alkanolysis with Ta(CH₂Ph)₅ leading to a Ta-amido species. The reported formation of Ta-phenoxides by the reaction of Ta(CH₂Ph)₅ with the more acidic phenols can be slow.¹⁴

Attempts to drive the reaction to completion under more vigorous conditions led to decomposition due to the limited thermal stability of (**1**). Characterization of (**1**) was accomplished by X-ray diffraction;

brown X-ray quality crystals were formed upon standing of a C₆D₆ solution in an NMR tube. The structure is shown in Figure 1.

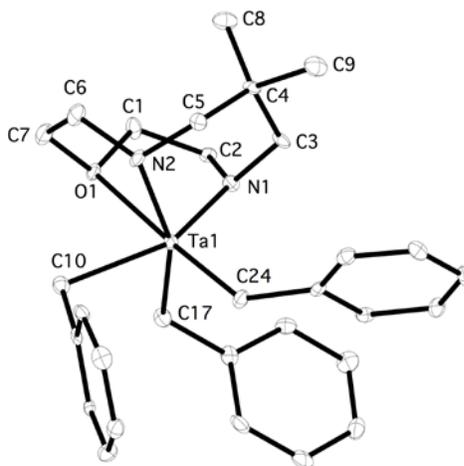


Figure 1. ORTEP representation of the structure of Ta[O(N)₂](CH₂Ph)₃ (**1**). Ellipsoids are drawn at the 30% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ta1-C10 = 2.274(6), Ta1-C17 = 2.260(6), Ta1-C24 = 2.187(6), Ta1-N1 = 1.975(5), Ta1-N2 = 1.985(5), Ta1-O1 = 2.491(4); N1-Ta1-N2 = 91.2(2), N1-Ta1-C24 = 106.5(2), N2-Ta1-C24 = 107.2(2), N1-Ta1-C17 = 150.4(2), N2-Ta1-C17 = 86.7(2), C24-Ta1-C17 = 102.3(2), N1-Ta1-C10 = 85.3(2), N2-Ta1-C10 = 145.7(2), C24-Ta1-C10 = 106.5(2), C17-Ta1-C10 = 80.1(2), N1-Ta1-O1 = 70.92(18), N2-Ta1-O1 = 71.53(17), C24-Ta1-O1 = 177.0(2), C17-Ta1-O1 = 80.44(19), C10-Ta1-O1 = 75.12(18), C2-N1-C3 = 116.3(5), C2-N1-Ta1 = 127.8(4), C3-N1-Ta1 = 109.7(4), C6-N2-C5 = 117.2(5), C6-N2-Ta1 = 123.4(4), C5-N2-Ta1 = 111.5(4).

The Ta center adopts a distorted octahedral geometry incorporating three facially coordinated benzyl ligands and one face-capping tridentate dianionic macrocycle. The Ta-N distances [1.975(5), 1.985(5) Å] and Ta-O distance [2.491(4) Å] are in accord with the proposed assignments, albeit Ta-O is rather long, suggesting a weak interaction presumably due to constraints imposed by the size of the macrocycle. The Ta-C_{benzyl} bonds *trans* to N_{amido} [2.274(6), 2.260(6) Å] are considerably longer than the

one *trans* to the ether O atom [2.187(6) Å]. Furthermore, the sum of the angles around the amido donor atoms N1 and N2 are 353.8 and 352.1°, consistent with a significant degree of π -donor character in the Ta-N bond, lead to distorted trigonal planar geometries at N1 and N2. These compare with angles at N_{amido} in the range 354.4 – 357.6° in Ti(IV) and Zr(IV) complexes involving the monoanionic macrocycle [O(NH)N]^{-4b} and 340.6 – 346.6° within Zr[O(N)₂]₂, which contains two dianionic diamido macrocycles.^{4a} Analysis of the angles subtended at Ta show that those involving 5-membered chelate rings (N-Ta-O) are very acute at 70.92(18) and 71.53(17)°, while the N-Ta-N angle (6-membered chelate) is less strained at 91.2(2)°. The C-C-Ta angles at the three benzylic carbons are unequal (126.95°, 112.95° and 99.58°). The variation of the angle at the *ipso*-C has been observed in other σ -benzylic complexes, however the correlation of an acute angle with increased electron donation of the benzyl to the metal is not straightforward.¹⁵ In (**1**) the distance of the aromatic carbons to the metal does not support any interaction. There are not any close contacts in the lattice that could account for the variation in bending. The involvement of polarization induced interactions as contributing factor at the angular distortions at the benzylic C has been proposed recently.¹⁶ Tantalum tribenzyl complexes with bulky monodentate aryloxides adopt trigonal bipyramidal geometry with equatorial benzyls,¹⁷ and with bulky chelating bis aryloxides trigonal bipyramidal with two axial and one equatorial benzyls;¹⁸ tridentate amine bis-phenolate ligands support octahedral geometry with meridional benzyls.¹⁴ Attempts to convert (**1**) to a benzyldiene complex by thermal α -abstraction led to intractable mixtures. Complex **1** is electronically unsaturated with number of 12 valence electrons.

Treatment of O(NH)₂ with 2 mol. equiv. of *n*BuLi gave Li₂[O(N)₂] *in situ*. This compound reacted with Ta(CH₂¹Bu₃)₃Cl₂ in toluene giving, following work-up, a brown solid (**2**). The ¹H-NMR spectrum of (**2**) shows three methyl and one *tert*-butyl peaks assignable to macrocyclic and neopentyl methyl protons, respectively. However, due to the lack of any symmetry, all the macrocyclic backbone protons in (**2**) are inequivalent and appear as eleven complicated multiplets, which could not be assigned even by two dimensional experiments. Further characterization of (**2**) was carried out by single crystal X-ray

diffraction. The structure (Figure 2) shows a heterobimetallic Ta/Li species with bridging amido and neopentylidene ligands.

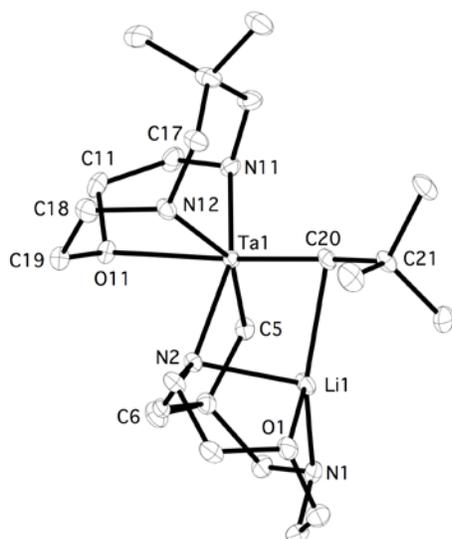
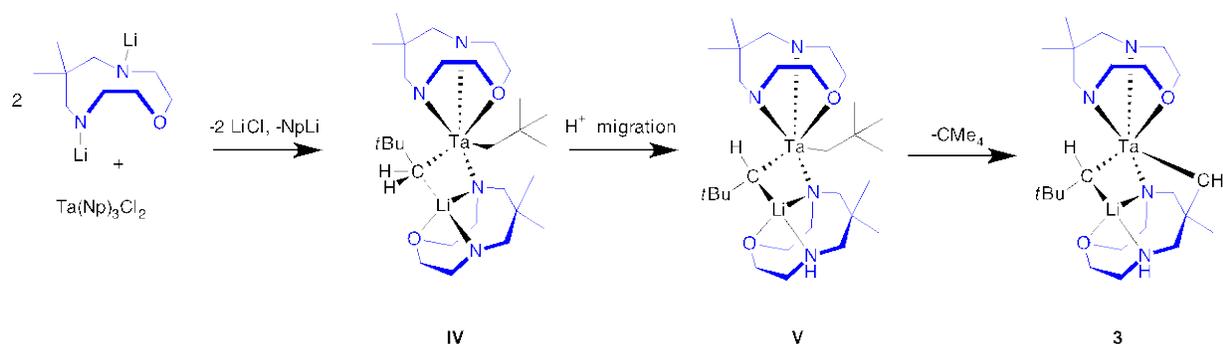


Figure 2. ORTEP representation of the structure of $[\text{O}(\text{N})_2]\text{Ta}(\mu\text{-CH}^t\text{Bu})[\mu\text{-O}(\text{NH})\text{N}]\text{Li}$ (**2**). Ellipsoids are drawn at the 30% probability level and H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): C20-Ta1 = 1.950(4), C20-Li1 = 2.371(9), N1-Li1 = 2.026(9), N2-Ta1 = 2.097(3), N2-Li1 = 2.107(9), N11-Ta1 = 2.070(4), N12-Ta1 = 2.031(4), O1-Li1 = 1.994(9), O11-Ta1 = 2.496(3), C5-Ta1 = 2.286(5), Li1...Ta1 = 2.728(8); O1-Li1-N1 = 89.5(4), O1-Li1-N2 = 86.5(4), N1-Li1-N2 103.4(4), O1-Li1-C20 = 119.7(4), N1-Li1-C20 = 149.3(5), N2-Li1-C20 = 88.7(3), 104.6(3), C20-Ta1-N12 = 104.61(19), C20-Ta1-N11 = 104.32(16), N12-Ta1-N11 = 89.80(16), C20-Ta1-N2 = 101.51(16), N12-Ta1-N2 = 93.29(15), N11-Ta1-N2 = 152.29(14), C20-Ta1-C5 = 104.11(19), N12-Ta1-C5 = 150.31(16), N11-Ta1-C5 = 90.32(15), N2-Ta1-C5 = 73.69(16), C20-Ta1-O11 = 176.11(16), N12-Ta1-O11 = 71

The Ta center is coordinated to one tridentate dianionic $[\text{O}(\text{N})_2]^{2-}$ and one $[\text{O}(\text{NH})(\text{N}^-)]$ type macrocycle. The monoanionic macrocycle also features one metallated methyl group. The Li atom is four coordinated to the ether O, the amido and the amine N atom of the bridging $[\text{O}(\text{NH})(\text{N}^-)]$ and the neopentylidene group. While the Ta-N(amido) bond distances are $\sim 0.05 - 0.10$ Å longer than in $[\text{Ta}\{\text{O}(\text{N})_2(\text{CH}_2\text{Ph})_3\}]$ described above (different *trans* ligands), the Ta-O distance and the angles at Ta

and N(amido) involving the tridentate macrocycle are very similar. Similar Ta-N_{amido} bond distances have been observed in the complexes of (*i*Pr₂tacn)⁻⁷

There is no experimental evidence in support of a mechanism for the formation of **2**. One proposal is given in Scheme 3. It includes the formation of a complex with two dianionic macrocycles and two neopentyl groups (**IV** in Scheme 3); one macrocycle is κN, κN, κO coordinated and the other only κN, the other amido and one ether groups being either dangling or coordinated to Li; the six-coordinate **IV** is more plausible over anionic 'ato' species with higher coordination numbers. Deprotonation and transfer of one α-hydrogen from the neopentyl-C to the Li-amido groups leads to the intermediate **V**; the driving force of this migration may be the high acidity of the Ta-CH₂tBu protons being in the vicinity of Ta. Finally, metallation of one of the methyls of the macrocycle by σ-bond metathesis leading to the observed product is driven by the release of strain in the coordination sphere. It is interesting to compare the spontaneous formation of **3** and the proposed steps leading to it with the behavior of **I-III**, (Scheme 1), where the less congested coordination sphere and the reduced number of amido π-donors requires more vigorous conditions for the α-elimination to occur and suppresses further ligand metallation reactions.



Scheme 3 Proposed sequence of steps leading to **3**

Finally, the bis-N, N'-trimethylsilyl functionalized macrocycle O(NSiMe₃)₂ reacted with TaCl₅ in refluxing toluene to give a very poorly soluble solid (with liberation of 2 mol. equivs. of Me₃SiCl) which, on the basis of microanalysis is formulated as [Ta{O(N₂)}Cl₃], presumably involving distorted

octahedral coordination *via* a tridentate diamido macrocycle. The very low solubility of (**3**) may be due to oligomer or polymer formation involving Cl bridging ligands.

CONCLUSIONS

Our results show that the 10-membered O(N)₂ donor macrocycle is an adaptable ligand, which can support organometallic chemistry on Ta(V). The strain imposed by the macrocycle results in amido functionalities departing from planarity a fact that could imply less metal-ligand π -bonding. The attempted introduction of two dianionic macrocycles as spectators led to unusual Ta/Li supported alkylidenes and facile C-H activation by σ -bond metathesis. The study of the scope and limitations of ON₂ and related analogues in the chemistry of other metals is a direction of future work.

ACKNOWLEDGEMENTS.

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Table 1. Crystallographic and data collection parameters

Compound	[Ta{O(N) ₂ }(CH ₂ Ph) ₃]	[{O(N) ₂ }Ta(μ-CH ^t Bu){μ-O(NH)N}Li]
CCDC Ref number	1827123	1827122
Formula	C ₃₀ H ₃₉ N ₂ OTa	C ₂₃ H ₄₆ LiN ₄ O ₂ Ta
MWt.	624.58	598.53
Crystal system	orthorhombic	monoclinic
Space group	<i>Pbca</i>	<i>P2₁/n</i>
<i>a</i> /Å	16.948(3)	13.1090(17)
<i>b</i> /Å	15.953(3)	11.8851(9)
<i>c</i> /Å	19.031(3)	17.0550(19)
α°	90	90
β°	90	97.889(9)
γ°	90	90
<i>V</i> /Å ³	5145.4(16)	2632.1(5)
<i>Z</i>	8	4
μ(Mo-Kα)/mm ⁻¹	4.298	4.200
Total no. reflns.	39383	17059
No. unique reflns.	5965	5970
<i>R</i> _{int}	0.1432	0.0866
No. of parameters	309	290
<i>R</i> 1 [<i>I</i> _o > 2σ(<i>I</i> _o)]	0.0517	0.0386
<i>R</i> 1 [all data]	0.1108	0.0848
w <i>R</i> 2 [<i>I</i> _o > 2σ(<i>I</i> _o)]	0.0688	0.0669
w <i>R</i> 2 [all data]	0.0810	0.0744

$$R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR2 = [\frac{\sum w(F_o^2 - F_c^2)^2}{\sum wF_o^4}]^{1/2}$$

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SYNOPSIS TOC. The 10-membered macrocyclic diamido ligand is a rigid face-capping 'spectator' in Ta organometallic complexes.

