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Tetravalent niobium alkyls and enolate stabilized by anionic organic amides

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Dedicated to Professor Vol'pin in recognition of his outstanding contribution to organometallic chemistry

Abstract

The lithium amide $[3,5-Me_2PhN(Ad)]Li+Et_2O$ reacts with NbCl₄(THF)₂ to give $[3,5-Me_2PhN(Ad)]$, NbCl (1). Reactions of 1 with PhLi and MeLi produced the corresponding alkyl derivatives $[3,5-Me_2PhN(Ad)]$, NbR (R=Ph (2a), Me (2b)). Attempts to prepare a neophyl niobium derivative led instead to the formation of the corresponding enolate $[3,5-Me_2PhN(Ad)]$, Nb(OCH=CH₂) (3), arising from the cleavage of THF. (1) 1998 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Niobium complexes; Amide complexes; Alkyl complexes; Enolate complexes

1. Introduction

The metal-promoted cleavage of the C–X bond is an important feature of the chemistry of transition metals [1]. Dehydro-desulfurization [2], -deoxygenation [3] and -denitrogenation [4] of crude oil, catalytic degradation of halocarbons [5], catalysis and extrusion of nitrogen and ammonia from organic compounds [6] are just the most prominent examples of several reactions which involve this process. Since these remarkable transformations are limited to diversifed examples involving a range of different metals in different oxidation states, it is difficult at this stage to rationalize the factors which promote this type of behavior.

Recent work has demonstrated that medium valent niobium complexes are capable of cleaving N–C single and double bonds [7]. This behavior emphasizes the exceptionally high reactivity of these metal species which may be an important factor in the perspective of rendering these transformations catalytic [8]. More recently, we found that during attempts to prepare di- and trivalent niobium and tantalum amides it was possible not only to cleave the amide N–C bond but also to form either nitrido- or oxo- derivatives, via N₂ cleavage or deo.ygenation of THF respectively [9], depending on the nature of the metal and of the ligand organic substituents. While rationalizing this reactivity is not possible at this early stage, further investigation into this behavior will certainly help to shed some light on the understanding of this remarkable behavior.

Nitrogen donor based ligands (formamidinate, amides, porphyrinogens, etc.) have proven to be versatile supporting molecules in the chemistry of low valent early transition metals [10], allowing the stabilization of the low and medium oxidation states [11]. The possibility of adjusting the electronic features and steric hindrance around the transition metal via a virtually unlimited choice of organic substituents attached to the nitrogen donor atom is the most versatile characteristic of these ligands. For example, sterically demanding anionic organic amides were recently employed as ligands for metals in a number of remarkable transformations, which include dinitrogen cleavage [12], formation of stable and reactive nitrides [13] and of heterodimetallic structures [14].

The remarkable robustness of these ligands prompted us to probe their use in preparing low-valent niobium complexes which may work as substrates for further reactivity studies in the area of C-X bond activation. In order to achieve this goal, there are two possible strategies. The most obvious consists of the utilization of metal complexes which already contain the metal in the desired oxidation state. So far, this strategy was not successful in preparing low valent homoleptic Nb amides and only transformations leading to oxidation of the metal center have been obtained [9.15]. As an alternative,

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we have now probed synthetic routes to suitable Nb(IV) amide derivatives which are amenable to further reduction and which can undergo further functionalization. In this work we describe the preparation of a novel (amide)₃NbCl complex and its transformation to the corresponding alkyl derivatives and enolate obtained from THF cleavage. For this particular purpose, we have selected the sterically demanding [3,5-Me₂PhN(Ad)] anion [16] as a ligand system, which has proven versatile for the preparation and characterization of several transition metal complexes in a variety of oxidation states [9,16]. Herein we describe our finding.

2. Results and discussion

The starting complex $[3,5-Me_2PhN(Ad)]_3NbCl (1)$ was prepared in good yield and in crystalline form via direct reaction of NbCl₄(THF)₂ [17] with $[3,5-Me_2PhN(Ad)]$ -Li(ether) [16] (Scheme 1). The complex is paramagnetic with a magnetic moment as expected for the d¹ electronic configuration of tetravalent niobium. Combustion analysis data were consistent with the proposed formulation, and the IR spectrum clearly showed the bands characteristic of the ligand system. While qualitative tests to reveal the presence of chloride failed, the presence of this element and the Nb/ Cl ratio were conclusively elucidated by X-ray fluorescence. A single crystal X-ray crystal structure revealed the chemical connectivity [16c].

The structure of complex 1 consists of discrete monomeric units (Fig. 1). The coordination geometry around the niobium atom is tetrahedral and is defined by three nitrogen atoms of three amide groups and one chlorine atom (Cl-Nb-N(1) = 100.39(8), Cl-Nb-N(2) = 117.45(7), Cl-Nb-N(3) = 103.67(8), N(1)-Nb-N(2) = 114.1(1), N(1)-Nb-N(3) = 115.4(1), N(2)-Nb-N(3) = 105.7(1)°, respectively). The Nb-N (Nb-N(1) = 1.998(3), Nb-N(2) = 2.030(3), Nb-N(3) = 1.984(3) Å, respectively) and Nb-Cl (Nb-Cl = 2.3780(8) Å) distances are as expected and the distortion of the geometry around the metal center is likely to be ascribed to the steric bulk introduced by the three large amide groups. The coordination geometry around the amide nitrogen atom is trigonal planar (Nb-N(1)-C(6)



= 116.9(2), Nb–N(1)–C(11) = 128.7(2), C(6)–N(1)– C(11) = 113.3(2)°, respectively), probably resulting from some extent of N \rightarrow Nb π -bonding. Each of the planes containing the trigonal nitrogen atoms is nearly perpendicular to the N₃ plane with the organic substituents located on the two sides. In particular, the three adamantyl groups are on the same side of the Nb–CI moiety while the three aromatic rings are situated on the opposite side.

Attempts to replace the chlorine atom attached to niobium were carried out with alkyl lithium derivatives. Attempts made with PhLi and MeLi yielded the corresponding [3,5-Me₂Ph(Ad)N]₃NbR derivatives (R = Ph (2a), Me (2b)). The reactions were carried out in diethyl ether by stirring for 24 h at room temperature. Both compounds were isolated in crystalline form as purple-violet, very air-sensitive materials. In both cases, the magnetic moments calculated for the formulations indicated by combustion analysis data were in agreement with the d¹ electronic configuration of Nb(IV).

The structure of the phenyl derivative 2a revealed a monomeric complex with an arrangement similar to that of complex 1 (Fig. 2). Even in this case, the geometry around the metal center is slightly distorted tetrahedral (N(1)-Nb-N(2) = 110.74(7), N(1)-Nb-N(3) = 124.39(7), N(2)-Nb-N(3) = $107.23(7)^\circ$, respectively), and is defined by the three N atoms of the three amides and one carbon of the phenyl group (C(66)-Nb-N(1)=99.43(8), C(66)- $Nb-N(2) = 117.48(7), C(66)-Nb(1)-N(3) = 97.35(7)^{\circ},$ respectively). The Nb-N distances are in the expected range (Nb-N(1) = 2.026(2), Nb-N(2) = 2.024(2), Nb-N(3) =2.006(2) A, respectively) and compare well with those of 1. The coordination geometry around the amide nitrogen atom is trigonal planar as usual (Nb-N(1)-C(6) = 126.0(1), Nb- $N(1)-C(11) = 121.3(1), C(6)-N(1)-C(11) = 112.7(2)^{\circ},$ respectively). The Nb-C distance (Nb(1)-C(66) =2.201(2) A) fails in the expected range and compares well with that of [(Me₃Si)₂N]₂NbPhCl [18]. Although the tetrahedral arrangement of the metal center in complexes 1 and



Fig. 1. ORTEP plot of 1. Thermal ellipsoids are drawn at the 30% probability level.



Fig. 2. ORTEP plot of 2a. Thermal ellipsoids are drawn at the 30% probability level.

2a is rather similar, the three amide groups orient their organic susbituents in a different manner with respect to the N_3 plane. In the present case, only one amide group points its adamantyl substituents toward the Nb–Ph group. The other two amide ligands place instead two phenyl groups in the same direction and the adamantyl groups on the opposite side.

In the case of the methyl derivative **2b**, it was not possible to grow analytically pure crystals of suitable size for X-ray diffraction analysis. However, a co-crystallite **1/2b** (20:80) was obtained in suitable crystalline form and used to elucidate the connectivity of **2b** (Fig. 3). As expected, the complex is almost isostructural with **1** even though it belongs to a different crystal system (orthorhombic versus monoclinic).

An attempt to replace the chlorine atom in complex 1 was also carried out with NfLi ($Nf = CH_2CMe_2Ph$). The reaction took a remarkably different pathway in this particular case. While reactions carried out in either hexane or diethyl ether gave no reaction even upon long reflux and stirring, a reasonably fast reaction was observed upon refluxing in THF. A dark purple crystalline material was isolated in reasonable yield. Combustion analysis data and the IR spectrum clearly showed the absence of the neophyl ligand. The IR spectrum also showed the presence of a rather intense band at 1643 cm⁻¹. Given the paranagnetism of this complex, we have undertaken an X-ray crystal structure to elucidate the connectivity. Combustion analysis data as well as the magnetic moments were in agreement with the formulation as obtained from the X-ray structure.

The structure revealed the complex to be a unique case of monomeric enolate niobium ¹ complex (Fig. 4). The molecular structure of complex 3 is similar to those of the other complexes reported in this work and features a monomeric, distorted tetrahedral niobium atom (O-Nb-N(1) =



Fig. 3. ORTEP plot of 2b. Thermal ellipsoids are drawn at the 30% probability level.



Fig. 4. ORTEP plot of 3. Thermal ellipsoids are drawn at the 30% probability level.

O-Nb-N(2) = 114.1(2),O-Nb-N(3) =101.0(2), 108.2(2), N(1)-Nb-N(2) = 115.2(2), N(1)-Nb-N(3) =110.9(2), N(2)-Nb-N(3) = $107.2(2)^{\circ}$, respectively), surrounded by three amides (Nb-N(1) = 2.003(4), Nb-N(2) = 2.939(4), Nb-N(3) = 1.998(4) Å, respectively) and one enolate group (Nb-O=1.955(3) Å). The orientation of two of the three amides, with the adamantyl groups pointing on the same side as Nb with respect to the N3 plane and the aromatic groups on the opposite side, is very similar to that observed for complexes 1 and 2b. However, the third amide group is nearly coplanar with the N3 plane. The enolate group was found to be disordered over two positions with a relative occupancy of 60:40. In the first conformation, the geometrical parameters are in good agreement with those expected for an enolate function [20]. The O-C distance $(O-C(1^*) = 1.35(2) \text{ Å})$ is consistent with a partial multiple bond character while the C-C distance $(C(1^*) C(2^*) = 1.26(2)$ Å) is in agreement with the presence of a

¹ To the best of our knowledge there are only two claims of a Nb-enolate type complexes, see Ref. [19].

C-C double bond. Accordingly, the bond angle of the enolate moiety $(O-C(1^*)-C(2^*) = 126(2)^\circ)$ is as expected for the sp² hybridization of the carbon atom. In the second position the enolate function is also bent $(O-C(1')-C(2') = 119(2)^\circ)$. However, the bond distances are slightly longer (O-C(1') = 1.42(3), C(1')-C(2') = 1.33(4) Å, respectively).

The cleavage of THF to form the enolate function poses some interesting mechanistic questions. There are basically two possibilities. In the first scenario, a Nb-Nf complex formed in situ reacts with THF. Under the reaction conditions employed, the subsequent reaction forms a mixture of t-BuPh, ethylene and 3. Accordingly, all of these products were found present in the reaction mixture in substantial amounts. Similar to the case of yttrium alkyl derivatives [20], the reaction is probably initiated by the Nf moiety which abstracts a proton from THF (Scheme 1). The corresponding anion triggers the internal transformation and ring cleavage thus forming the final products. However, since in the present case it was not possible to isolate the (amide) NbNf derivative and given that the reaction must be carried out in THF to avoid recovering of large amount of unreacted starting materials, we cannot exclude the second possibility that the enolate function is actually generated by the direct reaction of NfLi with THF. Subsequent reaction with 1 would originate the final complex 3. Thus, in a blank experiment we have boiled a solution of NfLi in THF in a sealed vessel and formed a significant amount of ethylene, no H₂ and no ethane. However, from a qualitative point of view this reaction is significantly slower than the reaction carried out in the presence of 1, thus giving some support to the idea that the formation of 3 is indeed promoted by the niobium center.

Regardless of the pathway through which the Nb-enolate function is generated, complex **3** represents the first case of a structurally characterized niobium enolate. Further studies to explore the reactivity of this moiety are in progress.

3. Experimental

All operations were performed under an inert atmosphere by using standard Schlenck techniques. [NbCl₄(THF)₂] [17], neophyl iithium [21], phenyl lithium [22] and [3,5-Me2PhN(Ad)]Li·Et2O (Ad=adamantyl) [16] were prepared according to published procedures. Solvents were dried with the appropriate drying agents and distilled prior to use. Infrared spectra were recorded on a Mattson 9000 FTIR instrument from Nujol mulls prepared in a drybox. Samples for magnetic susceptibility measurements were prepared inside a drybox and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. The magnetic moments were calculated by standard methods [23], and corrections for underlying diamagnetism were applied to the data [24]. Elemental analyses were carried out with a Perkin Elmer 2400 CHN analyzer.

3.1. Preparation of [3,5-Me₂PhN(Ad)]₃NbCl(1)

A suspension of NbCl₄(THF)₂ (3.0 g, 7.9 mmol) in diethyl ether (200 ml) was stirred with [3,5-Me₂-PhN(Ad)]Li·Et₂O (8.0 g, 23.8 mmol) at room temperature. The mixture slowly turned brownish purple. After stirring for 8 h at room temperature, purplish microcrystalline product separated. The crude product was isolated by filtration and extracted with toluene (100 ml) to eliminate lithium chloride. The resulting clear solution was concentrated, added with 50 ml of diethyl ether and allowed to stand at -30° C for 2 days. Dark purple crystals of 1 were obtained (3.8 g, 4.3 mmol, 53%). IR (Nujol mull, NaCl, cm⁻¹) v: 1589s, 1354w, 1303s, 1291s, 1261m, 1190w, 1153m, 1105m, 1068s, 1027s, 989w, 950m, 924s, 887w, 850m, 802m, 707m, 689s. $\mu_{eff} = 1.60 \mu_{B}$. *Anal.* Calc. for C₅₄H₇₂N₃NbCl: C, 72.75; H, 8.14; N, 4.71. Found: C, 72.57; H, 7.94; N, 4.56%.

3.2. Preparation of [3,5-Me₂PhN(Ad)]₃NbPh] (2a)

A suspension of $[3,5-Me_2PhN(Ad)]_3NbCl]$ (1) (1.5 g, 1.7 mmol) in diethyl ether (100 ml) was treated with PhLi (0.20 g, 2.4 mmol) at room temperature. The color of the solution slowly changed from dark purple to violet during the 24 h of stirring, with the precipitation of some lithium chloride. The mixture was filtered and evaporated to dryness. The residue was dissolved in hexane (100 ml), concentrated and cooled to -30° C. Moderately air sensitive dark violet crystals of **2a** were isolated by filtration (0.9 g, 1.0 mmol, 57%). IR (Nujol mull, NaCl, cm⁻¹) ν : 1598s, 1582s, 1353m. 1302s, 1287s, 1186w, 1152s, 1103m, 1071s, 1028s, 984m, 948s, 922s, 890m, 851s, 814w, 787w, 762w, 729m, 711s, 693s. μ_{eff} = 1.68 μ_{B} . Anal. Calc. for C₆₀H₇₇N₃Nb: C, 77.22; H, 8.32; N, 4.50. Found: C, 77.20; H, 8.55; N, 4.64%.

3.3. Preparation of [3,5-Me2PhN(Ad)] NbMe (2b)

A suspension of [3,5-Me₂PhN(Ad)]₃NbCl (1) (1.5 g, 1.7 mmol) in diethyl ether (100 ml) was treated with a solution of MeLi in the same solvent (1.4 M solution 1.2 ml, 1.7 mmol) at room temperature. The color of the solution changed from dark purple to violet in a few hours with precipitation of some lithium chloride. After 24 h, the mixture was filtered, concentrated and cooled to - 30°C. Dark violet extremely air sensitive crystals of 2b were obtained which were collected by filtration (0.5 g). A second crop (0.4 g)was obtained upon evaporation of ether and crystallization of the residue from hexane (overall yield 0.9 g, 1.0 mmol, 61%). IR (Nujol mull, NaCl, cm⁻¹) v: 1586s, 1352m, 1303s, 1290s, 1153s, 1106w, 1072s, 1028m, 988w, 950m, 923s, 948w, 813w, 708m, 687s. $\mu_{eff} = 1.72 \ \mu_{B}$. Anal. Calc. for C₅₅H₇₅N₃Nb: C, 75.83; H, 8.68; N, 4.82. Found: C, 77.20; H, 8.55; N, 4.64%.

3.4. Preparation of $[3,5-Me_2PhN(Ad)]_3Nb(OCH=CH_2)(3)$

A solution of $[3,5-Me_2PhN(Ad)]_3NbCl]$ (1) (0.8 g, 0.9 mmol) in THF (50 ml) was treated with freshly prepared neophyl lithium (0.3 g, 2.2 mmol) at room temperature. The solution was boiled for 10 min and then stirred at room temperature for 24 h without observing any apparent color change. The solvent was evaporated to dryness and the residue was extracted with diethyl ether (40 ml). Dark purple crystals of **3** were obtained upon allowing the solution standing at room temperature for 2 days (0.3 g, 0.3 mmol, 31%).

Table 1 Crystal data and structure analysis results

IR (Nujol mull, NaCl, cm⁻¹) ν : 1643m, 1593s, 1520w, 1354m, 1342w, 1303s, 1292s, 1191s, 1174s, 1157s, 1103m, 1071s, 1028m, 989m, 950m, 922s, 876w, 849m, 813s, 710m, 690s. $\mu_{eff} = 1.69 \mu_B$. Anal. Calc. for C₅₆H₇₅N₃NbO: C, 74.81; H, 8.41; N, 4.67. Found: C, 75.08; H, 8.48; N, 4.75%.

3.5. X-ray crystallography

Crystal data collection and refinement parameters are given in Table 1. Suitable crystals were selected and mounted with a viscous oil on thin glass fiber of the goniometric head of a

Compound	1	2a	2b	3
Formula	C ₁ H ₂ ,CIN,Nb	C _{N0} H ₇₇ N ₃ Nb	C _{54.79} H _{74.36} Cl _{0.35} N ₃ Nb	C50H75N3NDO
Formula weight	891.51	933.16	875.52	899.10
Lattice	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	P2;/c	Pna2	P2,/c
a (Å)	12.7949(1)	10.679(2)	20.9643(2)	13.627(3)
b (Å)	19.5091(3)	19.850(4)	17.9067(2)	18.713(4)
c (Å)	18.9156(2)	23.150(5)	12.4894(1)	18.851(4)
β(°)	103.3(3)	98.24(3)		97.03(3)
V (Å ³)	4594.48(9)	4857(2)	4688.54(8)	4771(2)
Z	4	4	4	4
Radiation (Ka (Å))	Мо	Mo	Мо	Мо
T(K)	163(2)	163(2)	153(2)	163(2)
D_{calc} (g cm ⁻³)	1.289	1.276	1.240	1.252
μ_{eale} (cm ⁻¹)	3.60	2.90	3.08	2.94
Foon	1900	1996	1875	1924
R ., R, 2 h	0.0507, 0.1275	0.0384, 0.0913	0.039, 0.1042	0.0547, 0.1433
GOF	1.002	1.004	1.037	1.125

 ${}^{a}R = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|.$

^b $R_{\rm w} = [(\Sigma (F_{\rm o} - F_{\rm s})^2 / \Sigma w F_{\rm o}^2)]^{1/2}.$

Table 2

Selected bond distances (Å) and angles (°)

1		2a		2b		3	
Nb-Cl	2.3780(8)	Nb-N(1)	2.026(2)	Nb-C(1)Cl)	2.302(2)	NbO	1.955(3)
Nb-N(1)	1.998(3)	Nb-N(2)	2.024(2)	Nb-N(i)	2.001(3)	Nb-N(1)	2.003(4)
Nb-N(2)	2.030(3)	Nb-N(3)	2.006(2)	Nb-N(2)	2.034(3)	Nb-N(2)	2.039(4)
Nb-N(3)	1.984(3)	Nb-C(66)	2.201(2)	Nb-N(3)	1.996(3)	Nb-N(3)	1.998(4)
						0-C(1)	1.42(3)
						0-C(1*)	1.35(2)
						C(1)-C(2)	1.33(4)
						C(1*)-C(2*)	1.26(2)
Cl-Nb-N(1)	100.39(8)	N(1)-Nb-C(66)	99.43(8)	C(1)-Nb-N(1)	98.4(1)	O-Nb-N(1)	101.0(2)
Cl-Nb-N(2)	117.45(7)	N(1)-Nb-N(2)	110.74(7)	C(1) - Nb - N(2)	116.0(1)	O-Nb-N(2)	114.1(2)
Cl-Nb-N(3)	103.67(8)	N(1)-Nb-N(3)	124.39(7)	C(1)-Nb-N(3)	103.0(1)	N(1)=Nb=N(2)	115.2(2)
N1-Nb-N(2)	114.1(1)	N(2)-Nb-C(66)	117.48(7)	N(1)-Nb-N(2)	114.7(1)	N(1)-Nb-N(3)	110.9(2)
N1-Nb-N(3)	115.4(1)	N(2)-Nb-N(3)	107.23(7)	N(1)NbN(3)	116.9(1)	C(6)-N(1)-C(11)	112.9(4)
N2-Nb-N(3)	105.7(1)	N(3)-Nb-C(66)	97.35(7)	N(2)-Nb-N(3)	107.3(1)	Nb-O-C(1)	144(1)
Nb-N(1)-C(6)	116.9(2)	Nb-C(66)-C(61)	118.3(2)	Nb-N(1)-C(6)	116.3(2)	0-C(1)-C(2)	119(2)
Nb-N(1)-C(11)	128.7(2)	Nb-C(66)-C(65)	125.3(2)	Nb-N(1)-C(11)	129.8(2)	Nb-O-C(1*)	134.8(7)
C(6)-N(1)-C(11)	113.2(2)	Nb-N(1)-C(6)	126.0(1)	C(6)-N(1)-C(11)	112.8(3)	0-C(1*) -℃(2 *)	126(2)
		Nb-N(1)-C(11)	121.3(1)	N(2)NbN(3)	107.2(2)		
		C(6)-N(1)-C(11)	112.7(2)	Nb-N(1)-C(6)	116.6(3)		
		C(65)-C(66)-C(61)	116.1(2)	Nb-N(1)-C(11)	128.2(3)		

Siemens CCD diffractometer and cooled to the data collection temperature. Cell parameters were obtained from 60 data frames representing different sections of the Ewald sphere and refined using the entire diffraction data sets. Absorption corrections based on redundant data with different effective azimuthal angles were applied. The systematic absences and cell parameters were uniquely consistent for the reported space groups for 2a and 3, and consistent with Pna2, and Pnma for 1 and 2b. Since a molecular mirror plane is possible, the centric option was thoroughly explored but only the solution in Pna2, yielded chemically reasonable and computationally stable results of refinement. The structures were solved using sharpened Patterson maps, completed with Fourier synthesis and refined using full-matrix, least-squares procedures based on $|F|^2$. Structure 2b was refined as a coincident co-crystallized structure with 80/20 methyl/chloride site occupancy distribution. The olefinic ligand in 3 was located in two disordered positions with a 60/40 site occupancy distribution. All the non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were treated as idealized contributions. All software and sources of atomic scattering factors are contained in the SHELXTL (5.03) program library [25]. Selected bond distances and bond angles are given in Table 2. For a listing of atomic coordinates and thermal parameters see Section 4.

4. Supplementary material

Table of crystal data with details of structure solution and refinement, listing of atomic coordinates, anisotropic thermal parameters, bond distances and angles for 1, 2a, 2b and 3 are available from the authors upon request.

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