Articles

Alkylidene-Centered Rearrangement of a Tantalum Alkylidene Alkoxide Species with the N,C,N-Bis-*ortho*-chelated 1,2,6-Trisubstituted Aryldiamine Ligand $[\mathrm{C_6H_3(CH_2NMe_2)_2}\text{-}2,6]^-$ to a Product with a C,N-Mono-*ortho*-chelated 1,2,4-Trisubstituted Aryldiamine Ligand. X-ray Molecular Structure of $[\mathrm{TaCl({=}CH}\text{-}t\text{-}\mathrm{Bu})\{\mathrm{C_6H_3(CH_2NMe_2)_2}\text{-}2,4\}(\mathrm{O}\text{-}t\text{-}\mathrm{Bu})]$[†]

Marco H. P. Rietveld,[‡] Elzebé G. Klumpers,[‡] Johann T. B. H. Jastrzebski,[‡]
David M. Grove,[‡] Nora Veldman,[§] Anthony L. Spek,[§,∥] and Gerard van Koten*[,‡]

Debye Institute, Department of Metal-Mediated Synthesis,
and Bijvoet Center for Biomolecular Research, Department of Crystal and Structural
Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

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The reaction of 2 equiv of LiO-*t*-Bu with $[\mathrm{TaCl_2({=}CH}\text{-}t\text{-}\mathrm{Bu})\{\mathrm{C_6H_3(CH_2NMe_2)_2}\text{-}2,6\}]$ (**1**), in which there is an N,C,N-chelated 1,2,6-trisubstituted aryldiamine ligand, affords in a one-pot procedure at 80 °C the new rearranged product $[\mathrm{Ta({=}CH}\text{-}t\text{-}\mathrm{Bu})\{\mathrm{C_6H_3(CH_2NMe_2)_2}\text{-}2,4\}(\mathrm{O}\text{-}t\text{-}\mathrm{Bu})_2]$ (**2**), in which there is a C,N-chelated 1,2,4-trisubstituted aryldiamine ligand. Complex **2** is a yellow solid that has been isolated in 69% yield. The reaction mechanism for the formation of **2** involves a crucial isomerization of the intermediate $[\mathrm{TaCl({=}CH}\text{-}t\text{-}\mathrm{Bu})\{\mathrm{C_6H_3(CH_2NMe_2)_2}\text{-}2,6\}(\mathrm{O}\text{-}t\text{-}\mathrm{Bu})]$ (**3**) to the rearranged intermediate $[\mathrm{TaCl({=}CH}\text{-}t\text{-}\mathrm{Bu})\{\mathrm{C_6H_3(CH_2NMe_2)_2}\text{-}2,4\}(\mathrm{O}\text{-}t\text{-}\mathrm{Bu})]$ (**4**). The intermediate complexes **3** and **4** have been independently prepared and characterized. The known complex **3** can be obtained by reaction of **1** with LiO-*t*-Bu at room temperature. Complex **4** is obtained exclusively, as revealed by ^{1}H NMR spectroscopy, by heating a benzene solution of **3** to 80 °C and has been isolated as a purple solid in 77% yield. In solution **4** exists as two rotational isomers for the Ta═C(H)-*t*-Bu moiety; $\Delta G^{\ddagger} = 71$ kJ mol^{-1}. The X-ray molecular structure of **3** shows it to be a pentacoordinate Ta(V) species in which the aryl C_{ipso} atom, the alkylidene functionality, and the alkoxide group define the meridional plane of a trigonal bipyramid, with one of the $\mathrm{NMe_2}$ nitrogen donors of the C,N-bidentate-bonded aryldiamine and the chloride occupying the axial positions. The lone pair of the N-donor atom of the second *ortho* amine substituent is oriented toward Ta (Ta···N = 2.629.4 Å), providing incipient η^3(N,C,N) facial bonding of the aryldiamine ligand. The structure of **3** also shows a pseudo-parallel orientation of the alkylidene $\mathrm{C}_\alpha-\mathrm{H}_\alpha$ bond and the $\mathrm{C}_{ipso}-\mathrm{Ta}$ bond that points to potential C−H activation *via* a four-membered metallacyclic ring that contains Ta, C_{ipso}, C_α, and H_α. The involvement of the alkylidene functionality in the sequence of highly regiospecific C−H bond-making and -breaking processes necessary to produce complex **4** from **3** was confirmed by deuterium-labeling experiments. The mechanism probably involves an α-H abstraction from the alkylidene moiety in **3** (assisted by the weakly coordinated dimethylamino group) that leads to an intermediate which has a geometry similar to that of a known aryltantalum(V) zinc alkylidene adduct.

Introduction

The activation of C−H bonds by metal species remains a topic of current interest,[1] and there are many interesting examples where complexes of early transition metals such as tantalum give intermolecular σ-bond metathesis reactions or intramolecular α−H abstraction reactions with alkyl and aryl C−H bonds.[2] In particular, we have found intramolecular N*Me*$_2$ C−H bond activation when the tantalum benzyl complexes $[\mathrm{TaCl_2\{C_6H_4CH(Me)NMe_2\text{-}2\}(CH_2Ph)_2}]$ and $[\mathrm{TaCl_2}\{1\text{-}$

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[*] To whom correspondence should be addressed.

[†] In this paper concerning an aryl ligand rearrangement, the metal center (which is σ-bonded to the aromatic ring at the 1 (C_{ipso})-position) is explicitly considered to be one of the three ring substituents.

[‡] Debye Institute.

[§] Bijvoet Center for Biomolecular Research.

[∥] Address correspondence pertaining to crystallographic studies to this author.

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(1) (a) Green, M. L. H.; O'Hare, D. *Pure Appl. Chem.* **1985**, *57*, 1897. (b) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403 and references therein.

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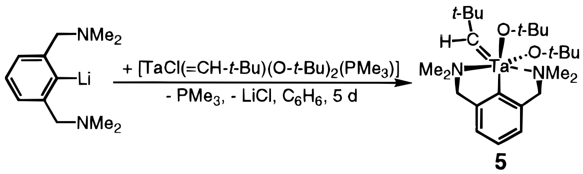
$C_{10}H_6NMe_2$-8}$(CH_2Ph)_2$] are heated in tetrahydrofuran (THF); these reactions afford the tantala(V)azacyclopropane species [$TaCl_2${C_6H_4(CH(Me)N(Me)CH_2)-2}(CH_2Ph)(THF)] and [$TaCl_2${1-$C_{10}H_6$(N(Me)CH_2)-8}(CH_2Ph)(THF)$_2$], respectively.[2a] Recently Royo and co-workers have reported a similar C−H bond activation of an Me group of the [$C_6H_4CH_2NMe_2$-2]$^-$ ligand in the formation of the cyclometalated complex [Cp*$TaCl_2${$C_6H_4CH_2$N(Me)CH_2-2}] (Cp* = C_5Me_5) from the reaction of the trichloroaryltantalum(V) complex [Cp*$TaCl_3${$C_6H_4CH_2NMe_2$-2}] with [Li{$C_6H_4CH_2NMe_2$-2}].[2b] Further reaction of this cyclometalated complex with 2 equiv of [Li{$C_6H_4CH_2NMe_2$-2}] afforded the cyclometalated alkylidene complex [Cp*TaCl{$C_6H_4CH_2NMe_2$-2}{$C_6H_4CH_2$N(Me)CH-2}].[2b] van der Zeijden *et al.* have reported that the Ir(I) complex [Ir{$C_6H_3(CH_2NMe_2)_2$-2,*6*}(COD)], which contains an η^2(N,C)-chelated 1,2,6-trisubstituted aryldiamine ligand, when heated to 60 °C in hexane undergoes an irreversible isomerization to form [Ir{$C_6H_3(CH_2NMe_2)_2$-2,*4*}(COD)], in which the aryldiamine is now 1,2,4-trisubstituted and again η^2(N,C)-bonded.[3] In this unusual rearrangement reaction the late transition metal iridium moves from a position *ortho* to both $-CH_2NMe_2$ coordination arms of the aryldiamine ligand [$C_6H_3(CH_2NMe_2)_2$-2,*6*]$^-$ to a position *ortho* to only one of these arms. This process involves prior decoordination of a dimethylamino group followed by an oxidative addition of one of the NMe C−H bonds of the [$C_6H_3(CH_2NMe_2)_2$-2,6]$^-$ ligand. Relief from steric crowding around the metal center, which affords the free 6-CH_2NMe_2 substituent, appears to be the driving force for the reaction. Note that the same type of rearrangement was found for [Ir{$C_6H_3(CH_2NMe_2)$-2-Me-6}(COD)] with a 6-Me grouping, which on heating irreversibly forms [Ir{$C_6H_3(CH_2NMe_2)$-2-Me-4}(COD)].[3]

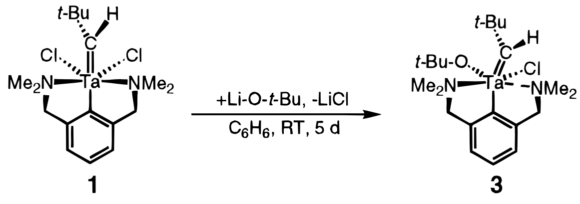
We are now studying the reactivity of high-oxidation-state tantalum alkylidene complexes stabilized by the aryldiamine ligand [$C_6H_3(CH_2NMe_2)_2$-2,6]$^-$, which, depending on whether one or both of the CH_2NMe_2 substituents is coordinated, can function either as an η^2(C,N) bidentate or as an η^3(N,C,N) tridentate ligand.

The dichloro neopentylidene complex [$TaCl_2$(=CH-*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,*6*}] (**1**) is regrettably not active as an alkene metathesis catalyst.[4a] In contrast to the dichloride complex **1**, the bis(alkoxide) analog [Ta(=CH-*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,*6*}(O-*t*-Bu)$_2$] (**5**), which was prepared *via* a transmetalation reaction of [Li{$C_6H_3(CH_2NMe_2)_2$-2,*6*}]$_2$ with [TaCl(=CH-*t*-Bu)(O-*t*-Bu)$_2$(PMe_3)] (eq 1), does show metathesis reactivity with olefins.[4b]



(1)

A problem with the preparation of **5** by this route is not only that this reaction takes 1 week to reach completion but also that the product is isolated in low yield. In an alternative approach to obtain **5**, we reacted dichloride complex **1** with lithium *tert*-butoxide, but even after 1 week at room temperature, only the mono(alkoxide) product [TaCl(=CH-*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,*6*}(O-*t*-Bu)] (**3**) was formed (eq 2).[4b]

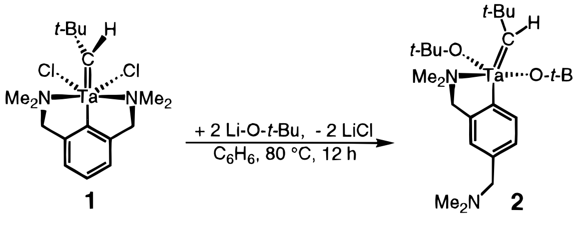


(2)

In this paper we report on an attempt to synthesize the bis(alkoxide) **5** by reaction of the dichloride **1** with lithium *tert*-butoxide at higher temperature that, unexpectedly, results in the formation of the bis(alkoxide) product [Ta(=CH-*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,*4*}(O-*t*-Bu)$_2$] (**2**), in which the 1,2,6-trisubstituted aryldiamine has rearranged to a 1,2,4-trisubstituted system. The reaction pathway and mechanism for the different C−H bond-breaking and -making processes involved in this reaction are discussed on the basis of deuterium-labeling experiments and the reactivity of separately synthesized intermediate species.

Results and Discussion

Preparation and Characterization of [Ta(=CH-*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,*4*}(O-*t*-Bu)$_2$] (2). Reaction of purple [$TaCl_2$(=CH-*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,*6*}] (**1**)[4a] with 2 equiv of lithium *tert*-butoxide in benzene at 80 °C yields the yellow bis(alkoxide) rearrangement product [Ta(=CH-*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,*4*}(O-*t*-Bu)$_2$] (**2**), as illustrated in eq 3. Complex **2** has been isolated as large block-shaped yellow crystals by slow cooling of a saturated pentane solution from +25 to −30 °C. Although the synthesis of **2** is very efficient, the isolated yield of **2** is only moderate (69%), since its high solubility in nonpolar organic solvents hinders the crystallization step.



(3)

The ^{1}H NMR spectrum of the rearrangement product **2** at room temperature (benzene-d_6) shows broadened signals for the NMe_2 and the CH_2 groups of one CH_2NMe_2 substituent at δ 2.64 and 4.02 ppm, respectively, and these data are indicative of coordination to the metal center and some degree of complex fluxionality

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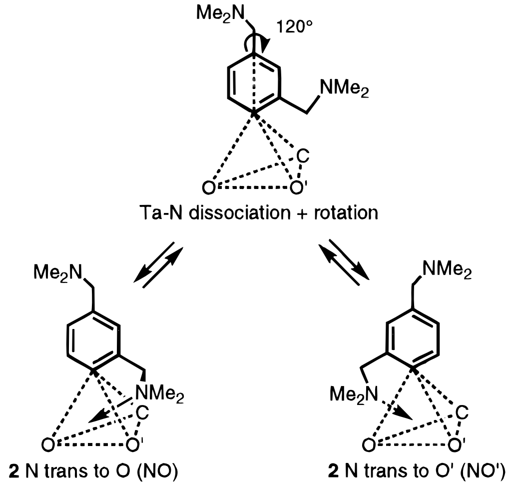
(2) (a) Abbenhuis, H. C. L.; Belzen, R.; Grove, D. M.; Klomp, A. J. A.; van Mier, G. P. M.; Spek, A. L.; van Koten, G. *Organometallics* **1993**, *12*, 210. (b) Castro, I.; Galakhov, M. V.; Gómez, M.; Gómez-Sal, P.; Royo, P. *Organometallics* **1996**, *15*, 1362. (c) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203. (d) Booij, M.; Kiers, N. H.; Meetsma, A.; Teuben, J. H.; Smeets, W. J. J.; Spek, A. L. *Organometallics* **1989**, *8*, 2454. (e) Chamberlain, L.; Keddington, J.; Rothwell, I. P. *Organometallics* **1982**, *1*, 1538. (f) Chamberlain, L. R.; Kerschner, J. L.; Rothwell, A. P.; Rothwell, I. P.; Huffman, J. *J. Am. Chem. Soc.* **1987**, *109*, 6471. (g) van Doorn, J. A.; van der Heijden, H.; Orpen, A. G. *Organometallics* **1994**, *13*, 4271. (h) van der Heijden, H.; Hessen, B. *J. Chem. Soc., Chem. Commun.* **1995**, 145.

(3) van der Zeijden, A. A. H.; van Koten, G.; Luijk, R.; Nordemann, R. A.; Spek, A. L. *Organometallics* **1988**, *7*, 1549.

(4) (a) Abbenhuis, H. C. L.; Feiken, N.; Grove, D. M.; Jastrzebski, J. T. B. H.; Kooijman, H.; van der Sluis, P.; Smeets, W. J. J.; Spek, A. L; van Koten, G. *J. Am. Chem. Soc.* **1992**, *114*, 9773. (b) Abbenhuis, H. C. L.; Rietveld, M. H. P.; Haarman, H. F.; Hogerheide, M. P.; Spek, A. L.; van Koten, G. *Organometallics* **1994**, *13*, 3259.

Scheme 1. Postulated Fluxional Process for 2 in Solution[a]



[a] Ta is considered to be at the center of the tetrahedron.

(see below). The second CH_2NMe_2 substituent is, on the basis of its CH_2 and NMe_2 resonances at 2.25 and 3.37 ppm, respectively, not coordinated to the metal center. There is a low-field doublet signal at 8.47 ppm that is characteristic of an aromatic hydrogen atom positioned *ortho* to the tantalum$-C_{ipso}$ bond, and this is in accordance with a 1,2,4-trisubstituted arene ring and a bidentate η^2(C,N)coordination mode of the aryl ligand. This is in contrast to the 1,2,6-trisubstituted pattern of the aryldiamine and η^3(N,C,N) bonding in starting material **1**.

At low temperature (toluene-d_8, 224 K) the coordinated CH_2NMe_2 substituent of **2** affords two NMe_2 signals at 1.95 and 2.65 ppm, and the CH_2 protons give rise to a well-resolved AB pattern at 3.22 and 4.33 ppm (^2J(H,H) = 12 Hz). At this temperature there are also two O-*t*-Bu signals at 1.33 and 1.70 ppm. When the temperature of this solution is raised, the resonances of the coordinated CH_2NMe_2 and O-*t*-Bu groups broaden and the CH_2, NMe_2, and O-*t*-Bu groupings eventually become homotopic (CH_2, $T_c = 275$ K, $\Delta G^{\ddagger} = 51 \pm 2$ kJ mol^{-1}; NMe_2, $T_c = 275$ K, $\Delta G^{\ddagger} = 52 \pm 2$ kJ mol^{-1}; O-*t*-Bu, $T_c = 275$ K, $\Delta G^{\ddagger} = 54 \pm 2$ kJ mol^{-1}).

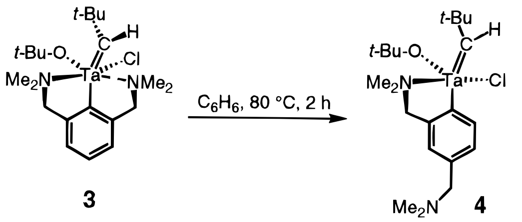
Since the equilibration of the different groups is associated with almost the same $\Delta G^{\ddagger}$ value of *ca.* 53 kJ mol^{-1}, the fluxionality in **2** is likely to be a single concerted process. A process which accounts for this fluxional behavior of **2** is shown in Scheme 1.

In the ground-state structure the tantalum center is considered to be positioned at the center of a tetrahedral ligand array formed by two O atoms, the alkylidene C_α, and the σ-bonded C atom of the aryldiamine ligand with additional coordination of the nitrogen donor of the coordinating CH_2NMe_2 substituent to a triangular C/C/O face. The first step in the postulated process is Ta$-$N dissociation of the coordinated nitrogen donor from the $C_{ipso}-C_\alpha-O'$ face, leading to an intermediate in which the aryldiamine ligand is only bonded to the metal by C_{ipso}, i.e., monodentate C-coordination. This is then followed by a rotation of the aryl group around the $C_{ipso}$$-$Ta axis, and that allows a face-centered nucleophilic attack of the nitrogen donor on the $C_{ipso}-C_\alpha-O$ face. A similar mechanism has been reported to explain the fluxional behavior of an *ortho*-chelated *N*,*N'*-dimethylbenzylamine analog of **2**, i.e. [Ta(=CH-*t*-Bu)-{$C_6H_4CH_2NMe_2$-2}(O-*t*-Bu)$_2$].[4b]

The ^{13}C NMR (50.32 MHz, C_6D_6, 25 °C) spectrum of **2** shows a low-field signal for the aryl C_{ipso} atom at 189.7 ppm in a region that is characteristic of an aryl carbon atom that is directly bonded to tantalum.[2a,b,4] The alkylidene resonance is found at 224.9 ppm, and its low ^1J(C,H) value of 90 Hz is typical for electron-deficient alkylidene complexes.[5]

To test whether the dichloride species **1** can also isomerize to a rearrangement product, a solution of **1** was heated at reflux in benzene for 12 h, but a ^{1}H NMR spectrum of a sample taken from the reaction mixture showed that no reaction had occurred. This means that in the one-pot procedure for the preparation of complex **2** (eq 3) the rearrangement reaction probably occurs in another intermediate species. Therefore, we suspected that it was the mono(alkoxide) complex [TaCl(=CH-*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,*6*}(O-*t*-Bu)] (**3**), which can be prepared independently by reaction of **1** with LiO-*t*-Bu at room temperature (eq 2),[4b] that would be the rearrangement intermediate. The thermal stability of this complex has been studied, and the results are described in the following section.

Isomerization of the Monoalkoxide Alkylidene Complex [TaCl(=CH-*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,*6*}-(O-*t*-Bu)] (3). A benzene solution of the mono(alkoxide) complex [TaCl(=CH-*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,*6*}(O-*t*-Bu)] (**3**)[4b] at 80 °C is unstable and after *ca.* 2 h (as monitored by ^{1}H NMR) is converted exclusively into the isomeric complex [TaCl(=CH-*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,*4*}(O-*t*-Bu)] (**4**; eq 4), which has a 1,2,4-disubstituted aryldiamine ligand. Complex **4** has been isolated almost quantitatively as a yellow solid, and it is very soluble in polar and apolar organic solvents. The product can be recrystallized as needle-shaped yellow crystals by cooling of a saturated hexane solution of **4** from +25 to −30 °C in 77% yield.



(4)

The ^{1}H NMR (200.13 MHz, toluene-d_8) spectrum of **4** at room temperature reveals the presence of two isomers in a 1:1 ratio, with each isomer affording two signals for the metal-bonded NMe_2 group and a well-resolved AB pattern for the CH_2 group. There are two doublet signals present at 8.17 and 8.82 ppm, which indicate that in both isomers there is an aromatic hydrogen atom positioned *ortho* to the Ta$-C_{ipso}$ bond. These and other ^{1}H NMR data are consistent with the presence of a 1,2,4-trisubstituted arene ring.

When the temperature of a solution of **4** in toluene-d_8 is raised, the ^{1}H NMR (200.13 MHz) spectra show that the two isomers start to interconvert and coalescence of various resonances occurs (C*H*-*t*-Bu, $T_c = 370$

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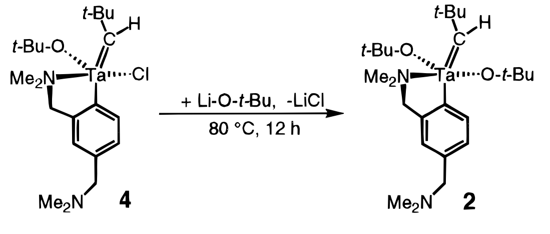
(5) (a) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210. (b) Wallace, K. C.; Liu, A. H.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 4964. (c) Schrock, R. R. *Acc. Chem. Res.* **1986**, *19*, 98 and references therein.

K, $\Delta G^{\ddagger} = 71 \pm 2$ kJ mol^{-1}; CH-*t*-Bu, $T_c = 355$ K, $\Delta G^{\ddagger} = 71 \pm 2$ kJ mol^{-1}; O-*t*-Bu, $T_c = 360$ K, $\Delta G^{\ddagger} = 73 \pm 2$ kJ mol^{-1}). In the ^{1}H NMR spectrum at 375 K the broad (coalesced) alkylidene H$_\alpha$ signal is at 4.85 ppm.

The two isomers for **4** originate from restricted rotation of the alkylidene double bond, and many examples of alkylidene complexes which exist in different rotameric forms are documented in the literature.[6,7] The activation energy for the rotamer interconversion in **4** is approximately 71 kJ mol^{-1}, and the process might involve simple rotation of the alkylidene functionality, as was demonstrated to be occurring in the tetrahedral tantalum complexes [$Cp_2Ta({=}CHPh)CH_2Ph$)] and [$Cp_2TaCl({=}CH$-*t*-Bu)], where $\Delta G^{\ddagger}$ values of 80 and 70 kJ mol^{-1}, respectively, were measured.[6e] For steric reasons rotation of an alkylidene is more favorable in a tetrahedral complex than in a trigonal-bipyramidal complex and rotation of the alkylidene in five-coordinate **4** is more likely to occur after Ta−N dissociation of the single coordinating CH_2NMe_2 substituent.[6a]

The ^{13}C NMR (50.32 MHz, C_6D_6, 25 °C) spectrum for **4** shows two isomers with two characteristic low-field signals for aryl C$_{ipso}$ atoms at 193.9 and 194.3 ppm, and these values compare nicely with data for other tantalum aryl complexes.[2a,b,4] The alkylidene resonance positions at 245.3 and 249.3 ppm, with ^1J(C,H) values of 96 and 95 Hz, respectively, are typical for electron-deficient alkylidene complexes.[4,5]

To test whether it would be possible to convert the mono(alkoxide) rearrangement product **4** into the bis(alkoxide) rearrangement product **2**, we have reacted **4** with LiO-*t*-Bu in benzene at 80 °C, and this indeed affords **2** (eq 5), which could be isolated in 50% yield.



(5)

On the basis of the above results, it is most likely that in the one-pot conversion of **1** to **2** the aryldiamine rearrangement reaction takes place from intermediate **3**, i.e. the monochloro mono(alkoxide) species (eq 3). In order to help understand why it is this particular complex which gives such a rearrangement reaction, we have carried out a crystallographic solid-state structure determination of complex **3**.

Molecular Structure of [TaCl(=CH-*t*-Bu){C_6H_3-(CH_2NMe_2)$_2$-2,*6*}(O-*t*-Bu)] (3). The molecular structure of mono(alkoxide) complex **3** together with the adopted numbering scheme is shown in Figure 1, with bond distances and bond angles being given in Table 1.

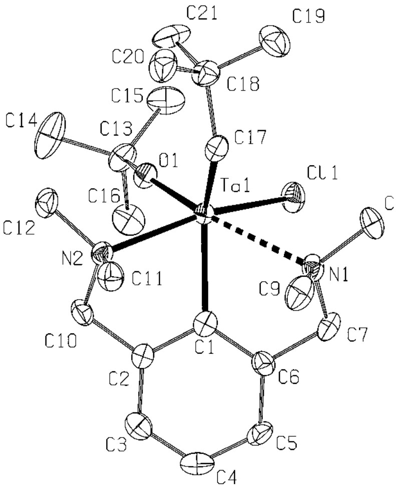


Figure 1. ORTEP thermal motion ellipsoid plot[12] (drawn at 50% probability level) of [TaCl(=CH-*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,6}(O-*t*-Bu)] (**3**).

Table 1. Selected Geometrical Details of 3

Bond Distances (Å)			
Ta−Cl1	2.4451(15)	Ta−N2	2.359(5)
Ta−C1	2.189(6)	Ta---N1	2.629(4)
Ta−C17	1.962(7)	Ta−O1	1.867(4)
Bond Angles (deg)			
Cl1−Ta−O1	86.04(12)	O1−Ta−C17	108.5(2)
Cl1−Ta−N2	158.10(13)	N2−Ta−C1	70.92(19)
Cl1−Ta−C1	97.01(17)	N2−Ta−C17	92.1(2)
Cl1−Ta−C17	109.24(19)	C1−Ta−C17	131.3(2)
O1−Ta−N2	82.58(16)	Ta−O1−C13	155.9(4)
O1−Ta−C1	113.73(19)	Ta−C17−C18	140.7(5)
Cl1−Ta−N1	75.33(11)	N1−Ta−N2	113.59(15)
O1−Ta−N1	160.95(16)	N1−Ta−C1	65.66(17)

The metal center has a pentacoordinate geometry which can be described as being distorted trigonal-bipyramidal. The axial positions are occupied by the chlorine atom (Cl) and the N-donor atom (N2) of one of the CH_2NMe_2 substituents. The trigonal plane is defined by the O atom (O1) of the O-*t*-Bu group, the C atom (C17) of the alkylidene, and the aryl C$_{ipso}$ atom (C1). In this description the aryldiamine is formally η^2(C,N) chelate-bonded but the positioning of the second CH_2NMe_2 substituent is noteworthy, since the lone pair of the N-donor atom (N1) is orientated toward the metal center such that the Ta−N(1) separation is 2.629(4) Å. This situation represents incipient η^3(N,C,N) (facial) bonding of the aryldiamine. The structure shows a short Ta=C bond distance of 1.962(7) Å, and this value is similar to those of 1.938(4) and 1.914(4) Å found in the dichloride complex [$TaCl_2$(=CH-*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,*6*}] (**1**) and bis(alkoxide) complex [Ta(=CH-*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,*6*}(O-*t*-Bu)$_2$] (**5**), respectively.[4a,b] It is important to emphasize here that the Ta=C bond in mono(alkoxide) complex **3** is adjacent to the weakly bonded N-donor atom N1, whereas in bis(alkoxide) complex **5** the Ta=C bond is positioned approximately opposite to the weakly bonded N-donor atom.

For the alkylidene function of **3** the Ta−C17−C18 angle of 140.7(5)° is considerably smaller than corresponding angles of 170.6(3) and 159.5(5)° in dichloride complex **1**[4a] and bis(alkoxide) complex **5**,[4b] respectively, which contain distorted alkylidene functionalities.[6c,7] This Ta−C$_\alpha$−C$_\beta$ angle of 140.7(5)° in **3** is comparable to the W−C$_\alpha$−C$_\beta$ angle in the tungsten alkylidene

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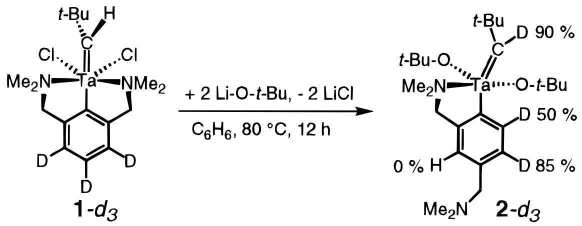
[6] (a) Schrock, R. R.; Crowe, W. E.; Bazan, G. C.; DiMare, M.; O'Regan, M. B.; Schofield, M. *Organometallics* **1991**, *10*, 1832. (b) Vaughan, W. M.; Abboud, K. A.; Boncella, J. M. *Organometallics* **1995**, *14*, 1567. (c) van der Schaaf, P. A.; Abbenhuis, R. A. T. M.; van der Noort, W. P. A.; de Graaf, R.; Grove, D. M.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1994**, *13*, 1433. (d) Sodupe, M.; Lluch, J. M.; Olivia, A.; Bertrán, J. *Organometallics* **1989**, *8*, 1837. (e) Schrock, R. R.; Messerle, L. W.; Wood, C. D.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 3793.

[7] (a) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988. (b) van der Schaaf, P. A.; Hogerheide, M. P.; Grove, D. M.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1992**, 717. (c) Buijink, J. F.; Teuben, J. H.; Kooijman, H.; Spek, A. L. *Organometallics* **1994**, *13*, 2922.

complexes reported previously by our group, i.e. 138.5(11)° for [W(=CHSiMe$_3$){C$_6$H$_4$CH$_2$NMe$_2$-2}(=NPh)(CH$_2$SiMe$_3$)] and 136.4(3)° for [W(=CHSiMe$_3$){OCPh$_2$([2]-py)}(=NPh)(CH$_2$SiMe$_3$)].[6c,7b] Interestingly, the latter complex was isolated as a mixture of *syn* and *anti* rotamers. It is worth recalling that Abbenhuis *et al.* reported that complex **3** in CDCl$_3$ solution at −60 °C can be seen by ^{1}H NMR spectroscopy to exist as two isomers and that these interconvert on the laboratory time scale at this temperature;[4b] this behavior could be explained in terms of two alkylidene rotamers for **3**.[4b]

Reaction of [TaCl$_2$(=CH-*t*-Bu){C$_6$D$_3$(CH$_2$NMe$_2$)$_2$-2,*6*}] with Lithium *tert*-Butoxide. It is clear that during the aryldiamine rearrangement reaction which occurs when **1** is transformed to **2** an aryl C−H bond is formed at the original C$_{ipso}$(Ta) position and an originally C$_{ortho}$−H bond has to be activated and broken to form the new C−Ta bond. To gain more information about the mechanism of this process, a reaction was carried out between the deuterated aryldiamine complex [TaCl$_2$(=CH-*t*-Bu){C$_6$D$_3$(CH$_2$NMe$_2$)$_2$-2,*6*}] (**1**-*d*$_3$), which has an overall deuterium enrichment of *ca.* 75% of the aryl positions, and lithium *tert*-butoxide (eq 6). It should be noted that the *para* hydrogen in **1**-*d*$_3$ has a significantly lower deuterium enrichment (*ca.* 50%) than the *ortho* hydrogens (*ca.* 50% versus 80%, respectively) due to unequal deuteration of these positions in the organic compound C$_6$H$_3$Me$_2$-1,3-Br-2, from which it was synthesized.

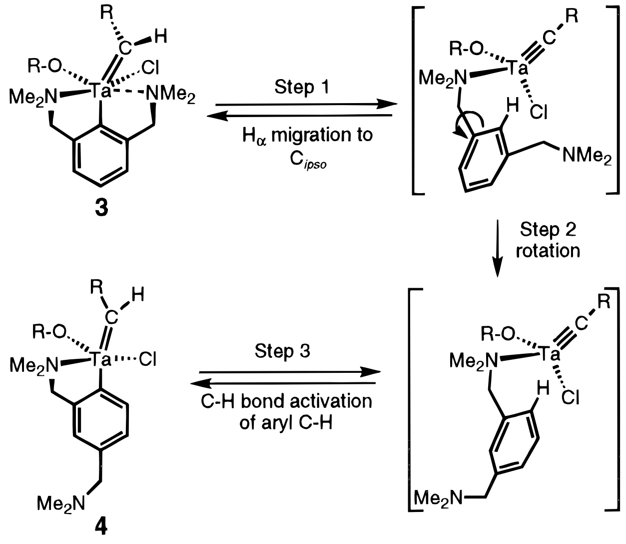


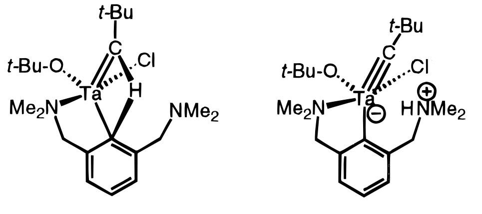
(6)

The reaction of **1**-*d*$_3$ with LiO-*t*-Bu (eq 6) affords the complex [Ta(=CD-*t*-Bu){C$_6$D$_2$H(CH$_2$NMe$_2$)$_2$-2,*6*}(O-*t*-Bu)$_2$] (**2**-*d*$_3$), whose ^{1}H NMR spectrum (298 K, 200.13 MHz, C$_6$D$_6$) shows a very weak signal at 3.01 ppm for an alkylidene hydrogen, consistent with the product being predominantly the one with a deuterium atom in the alkylidene function. Moreover, in the ^{13}C NMR spectrum (298 K, 50.32 MHz, C$_6$D$_6$) a C−D triplet (^1J(C,D) = 12 Hz) for the alkylidene carbon further underlines the formation of a C$_\alpha$−D functionality. We found no evidence for incorporation of deuterium in other parts of the aryldiamine ligand system. To exclude the possibility that this reaction might involve intermolecular C−D bond activation of the deuterated solvent, complex **1** was reacted with LiO-*t*-Bu in benzene-*d*$_6$, but this afforded the product **2** and provided no spectroscopic evidence for deuterium incorporation.

Mechanism for the Substitution and Rearrangement Reaction. We have found that the mono(alkoxide) **3** is thermally unstable and at 80 °C a 1,2,6- to 1,2,4-aryldiamine rearrangement reaction takes place which must involve a number of C−H bond activation steps and which also involves the alkylidene functionality. In combination with the X-ray molecular structure of **3** (Figure 1), which shows that the alkylidene functionality is positioned pseudo-*cis* to the aryl C$_{ipso}$ atom in the solid state, we postulate a sequence of intermediates for the rearrangement reaction, as shown in Scheme 2.

Scheme 2. Rearrangment *via* Alkylidene C−H Bond Activation





A B

Figure 2. Transition state **A** and intermediate **B** proposed in the mechanistic schemes for rearrangement of **3** to **4**.

A description of the three consecutive steps from **3** to **4** follows. In step 1 there is an overall migration of H$_\alpha$ of the alkylidene C$_\alpha$−H$_\alpha$ bond to C$_{ipso}$ of the former Ta−C$_{ipso}$ bond to form an alkylidyne arene intermediate. In the case of a concerted mechanism involving a four-membered Ta−C$_\alpha$−H$_\alpha$−C$_{ipso}$ metallacyclic transition state (not depicted), this step can only occur when the alkylidene C$_\alpha$ and the aryl C$_{ipso}$ carbon atoms are in mutually *cis* positions, and this situation is found in the solid-state structure of **3.** Furthermore, as stated in our earlier publication,[4b] solution fluxionality within complex **3** may involve a tetrahedral Ta geometry that would reduce the C$_\alpha$−Ta−C$_{ipso}$ angle from 131.3(2)° (Table 1) to *ca.* 109° and in this situation the transition state **A**, as depicted in Figure 2, becomes feasible. The structure of this transition state **A** derived from **3** is related to that of the bimetallic Ta−Zn alkylidyne complex [TaCl$_2${μ-C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,*6*}(μ-C-*t*-Bu)ZnCl] (**6**), illustrated schematically in Figure 3,[8] in which ZnCl is seen to occupy a position analogous to that of the alkylidene H$_\alpha$ atom in Figure 2.

However, the structural features of **6** can also be used to support an alternative explanation for the involvement of the alkylidene functionality in the aryl ligand rearrangement and proton migration that occurs on going from **3** to **4.** This explanation, which was kindly brought to our attention by one of the reviewers of this paper, is based on known base-catalyzed proton migra-

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(8) Abbenhuis, H. C. L.; Feiken, N.; Haarman, H. F.; Grove, D. M.; Horn, E.; Spek, A. L.; Pfeffer, M.; van Koten, G. *Organometallics* **1993**, *12*, 2227.

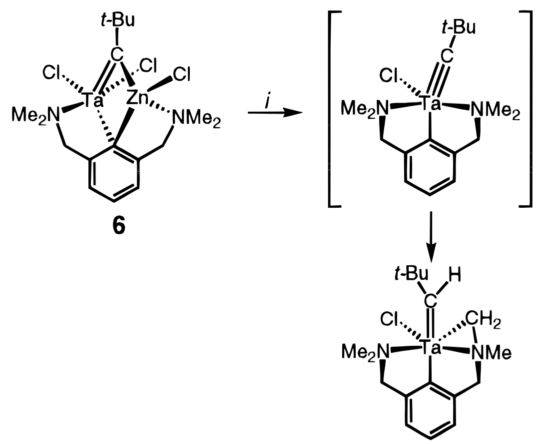
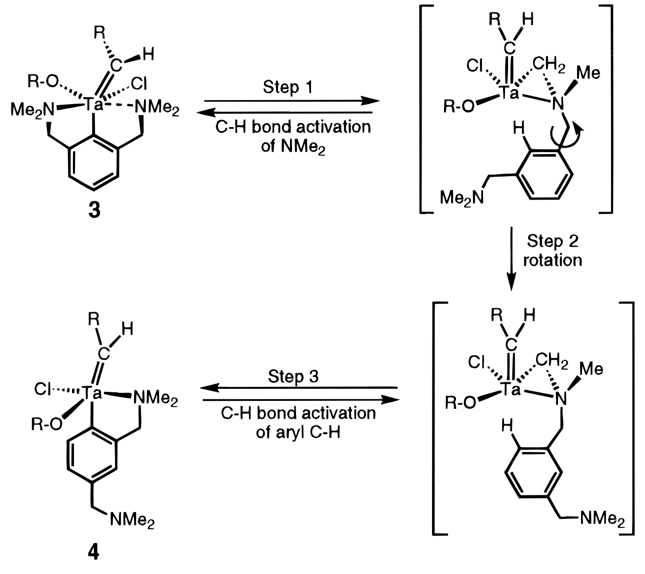


Figure 3. Schematic structure of **6** and its reactivity with tmeda. Reaction conditions: (i) +tmeda, − $[ZnCl_2(tmeda)]$, C_6H_6, 60 °C.

tions in alkylidene/alkylidyne complexes. In this description one of the weakly coordinated *ortho* amine N donor atoms in **3** acts as an *intra*molecular base that mediates the proton migration process. This process would involve either an intermediate similar to **A** but now with additional involvement of the N-donor atom (*cf*. Zn−N coordination in **6**) or the formation of a zwitterionic situation comprising a tantalate alkylidyne moiety and a protonated CH_2NHMe_2 group, as shown in proposed intermediate **B**. This idea that a reaction can be assisted by a CH_2NMe_2 group functioning as an intramolecular base has been proposed by us in earlier studies to be an important aspect of rearrangement mechanisms of certain arylpalladium species.[9] The fact that the bis(*tert*-butoxy) complex **5** does not undergo rearrangement similar to that of the chloro *tert*-butoxy complex **3** is consistent with the proposal of selective protonation of C_{ipso} in the tantalate moiety of **B**. In complex **5** (see stereochemistry in eq 1) the alkylidene function is approximately trans to the weakly coordinated NMe_2 group[4b] and the bulk of the *tert*-butyl groups does not allow this NMe_2 group to approach close enough to the alkylidene proton (in neither **A** nor **B**) to facilitate transfer.

In step 2 of the proposed rearrangement mechanism the tantalum alkylidyne arene intermediate species undergoes a reorganization (through simple bond rotation) whereby the alkylidyne function now comes to lie closer to the less sterically hindered part of the aryl ring away from the uncoordinated (bulky) CH_2NMe_2 substituent. Step 3 involves a C−H bond activation of the arene ring by this alkylidyne to form the alkylidene complex **4**; this process can be seen to be very much like the reverse of step 1. Although all steps depicted in Scheme 1 are formally reversible, it is step 3, in which the steric repulsion of the 6-substituent of the aryl ring and the metal is relieved, that is in practice likely to be almost irreversible and this will drive the reaction to completion.

Scheme 3. Rearrangment *via* NMe_2 C−H Bond Activation



It is worth recalling that treatment of the bimetallic tantalum−zinc alkylidyne complex $[TaCl_2\{\mu\text{-}C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(\mu\text{-}C\text{-}t\text{-}Bu)ZnCl]$ (**6**), shown in Figure 3, with $Me_2NCH_2CH_2NMe_2$ (tmeda) at 60 °C leads to a clean and quick elimination of $[ZnCl_2(tmeda)]$ with concomitant formation of the yellow tantalum alkylidene complex $[TaCl(=CH\text{-}t\text{-}Bu)\{C_6H_3(CH_2N(Me)CH_2)\text{-}2\text{-}(CH_2NMe_2)\text{-}6\}]$.[8] This latter reaction involves the presence of a mononuclear square-pyramidal tantalum alkylidyne complex that, after elimination of $ZnCl_2$, gives a NMe C−H activation and formation of an alkylidene functionality.[8] Surprisingly, although in the mechanism shown in Scheme 2 an alkylidyne intermediate is also involved, no evidence for a C−H bond activation of one of the NMe_2 groups could be found. This is unexpected, since many examples of stereoselective NMe C−H activation have been reported by our group[2a,3,10] and by others.[2b]

An alternative mechanism for the conversion of **3** to **4** that involves a NMe_2 C−H activation is shown in Scheme 3. In this mechanism step 1 involves a C−H bond activation of one of the Me groups of a noncoordinated CH_2NMe_2 substituent whereby a triangular $Ta{-}CH_2{-}N$ unit is formed and the proton is transferred to C_{ipso} of the aryl skeleton; i.e., the $Ta{-}C_{ipso}$ bond is broken. In step 2 there is bond rotation and the alkylidene complex moiety moves to a less sterically hindered position on the aromatic ring in much the same way as depicted in Scheme 2. Step 3 involves a C−H bond activation by which the $Ta{-}CH_2$ bond is broken and a $Ta{-}C_{ipso}$ bond is formed. The driving force in this mechanism has the same steric origin as that of the mechanism shown in Scheme 2.

A NMe_2 C−H bond activation like that shown in Scheme 3 was observed in the isomerization rearrangement reactions of the η^2(C,N) 1,2,6-trisubstituted aryldiamine species $[Ir^I\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(COD)]$ and $[Ru^{II}Cl\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}\{\eta^6\text{-}(CH_3C_6H_4CH(CH_3)_2)\}]$[10b] that afford their η^2(C,N) 1,2,4-trisubstituted aryldiamine products $[Ir\{C_6H_3(CH_2NMe_2)_2\text{-}2,4\}(COD)]$[3] and $[RuCl\{C_6H_3(CH_2NMe_2)_2\text{-}2,4\}\{\eta^6\text{-}(CH_3C_6H_4CH(CH_3)_2\}]$,[10b] respectively. Although in principle the mechanism in Scheme 3 is feasible during the rear-

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(9) (a) Valk, J. M.; Maassarani, F.; van der Sluis, P.; Spek, A. L.; Boersma, J.; van Koten, G. *Organometallics* **1994**, *13*, 2320. (b) Markies, B. A.; Wijkens, P.; Kooijman, H.; Spek, A. L.; Boersma, J.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1992**, 1420.

(10) (a) Wehman-Ooyevaar, I. C. M.; Lutweiler, I. F.; Vatter, K.; Grove, D. M.; Smeets, W. J. J.; Horn, E.; Spek, A. L.; van Koten, G. *Inorg. Chem. Acta* **1987**, *139*, 67. (b) Steenwinkel, P.; van Koten, G; Spek, A. L. To be submitted for publication.

rangement of **1** to **2**, we do not believe it is operative, on the basis of the absence of deuterium incorporation in any Me group of the coordinated CH_2NMe_2 arm in product **2** when **1**-d_3 was reacted with LiO-*t*-Bu (*vide supra*).

Conclusions

The $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$ ligand not only acts as a spectator ligand in organometallic complexes but can also become involved in intramolecular C−H bond activation processes, and with iridium and ruthenium species these processes can result in ligand isomerization. The mechanism for these reactions involves an oxidative-addition step of a C−H bond on one of the NMe_2 groups. Here we have shown that not only a late transition metal but also an early transition metal can give a similar isomerization reaction and that other groups such as an alkylidene functionality can be involved in the various C−H bond activation steps. In the alkylidene/aryl proton migration step the CH_2NMe_2 group functions as an *intra*molecular Lewis base, mediating the α-H abstraction from the alkylidene to give an alkylidyne tantalum intermediate. A further crucial step in this rearrangement involves a unique activation of an aryl C−H bond by the alkylidenetantalum moiety.

Experimental Section

General Details. All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were stored over sodium benzophenone ketyl and distilled prior to use. Elemental analyses were carried out by Dornis und Kolbe, Microanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC200 or AC300 spectrometer; $^1J(C,H)$ data are from separately recorded proton-coupled spectra. The complexes $[TaCl_2({=}CH\text{-}t\text{-}Bu)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ (**1**) and $[TaCl({=}CH\text{-}t\text{-}Bu)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(O\text{-}t\text{-}Bu)]$ (**3**) were prepared according to literature procedures.[4a,b]

$[Ta({=}CH\text{-}t\text{-}Bu)\{C_6H_3(CH_2NMe_2)_2\text{-}2,4\}(O\text{-}t\text{-}Bu)_2]$ (2) (One-Pot Procedure). A purple solution of $[TaCl_2({=}CH\text{-}t\text{-}Bu)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ (3.33 g, 6.49 mmol) and LiO-*t*-Bu (1.13 g, 14 mmol) in C_6H_6 (50 mL) was stirred at 80 °C for 12 h. During this period the color of the reaction mixture gradually changed from purple to yellow and a white precipitate was formed. The solvent was removed *in vacuo*, and the remaining orange sticky residue was extracted with pentane (3 × 20 mL). The combined extracts were concentrated *in vacuo* to 5 mL and from the resulting yellow solution the product **2** crystallized overnight at −30 °C as small needle-shaped yellow crystals; yield 2.67 g (69%). Anal. Calcd for $C_{25}H_{47}N_2O_2Ta$: C, 51.01; H, 8.05; N, 4.76. Found: C, 50.79; H, 8.12; N, 4.68. ^1H NMR (200.13 MHz, benzene-d_6, 25 °C, TMS): δ 1.15 (s, 9 H, CHC*Me*$_3$), 1.48 (s, 18 H, OC*Me*$_3$), 2.25 (s, 6 H, N*Me*$_2$), 2.64 (br s, 6 H, N*Me*$_2$), 3.01 (s, 1 H, C*H*CMe$_3$), 3.37 (s, 2 H, ArC*H*$_2$N), 4.02 (br s, 2 H, ArC*H*$_2$N), 7.08 (m + s, 2 H, *m*-Ar), 8.47 (d, $^2J(H,H)$ = 7 Hz, 1 H, *o*-H). $^{13}C\{^1H\}$ NMR (50.32 MHz, benzene-d_6, 25 °C, TMS): δ 33.4 (OC*Me*$_3$), 35.8 (CHC*Me*$_3$), 44.7 (N*Me*$_2$), 45.7 (N*Me*$_2$), 48.7 (O*C*Me$_3$), 65.0 (Ar*C*H$_2$N), 70.7 (Ar*C*H$_2$N), 77.6 (CH*C*Me$_3$), 124.6 (*m-C*), 127.5 (*m-C*), 138.5 (*o-C*), 144.3 (*p-C*), 149.3 (*o-C*), 189.7 (C_{ipso}), 224.9 (*C*HCMe$_3$, $^1J(C,H)$ = 90 Hz).

$[Ta({=}CH\text{-}t\text{-}Bu)\{C_6H_3(CH_2NMe_2)_2\text{-}2,4\}(O\text{-}t\text{-}Bu)_2]$ (2) (Starting from 4). A yellow solution of $[TaCl_2({=}CH\text{-}t\text{-}Bu)\{C_6H_3(CH_2NMe_2)_2\text{-}2,4\}(O\text{-}t\text{-}Bu)]$ (**4**; 0.30 g, 0.61 mmol) and LiO-*t*-Bu (0.05 g, 0.61 mmol) in benzene (50 mL) was stirred for 12 h at 80 °C, and during this time a white precipitate gradually formed. The solvent was removed *in vacuo*, and the orange/yellow sticky residue was extracted with pentane (3 × 20 mL). The combined extracts were concentrated to 5 mL *in vacuo*, and from the remaining yellow solution, the product **2** crystallized overnight as needle-shaped yellow crystals at −30 °C; yield 0.18 g (50%).

Table 2. Experimental Data for the X-ray Diffraction Study of 3

Crystal Data	
formula	$C_{21}H_{38}ClN_2OTa$
mol wt	550.95
cryst syst	orthorhombic
space group	*Pbca* (No. 61)
a (Å)	17.9176(10)
b (Å)	12.3038(10)
c (Å)	21.7338(11)
V (Å^3)	4791.3(5)
Z	8
d_{calcd} (g cm^{-3})	1.528
F(000)	2208
μ (cm^{-1})	47.1 (Mo Kα)
cryst size (mm)	0.18 × 0.30 × 0.43
Data Collection	
T (K)	150
X-ray exposure time (h)	9.2
wavelength, Å	0.710 73 (Mo Kα with graphite monochromator)
θ_{min}, θ_{max} (deg)	1.9, 27.5
scan type, scan (deg)	ω, 0.60 + 0.35 tan θ
horiz and vert aperture (mm)	2.04, 4.00
ref rflns	−1,5,−2; −2,−3,−3, −3,−2,5
data set	−23 to 0; −15 to 0; −10 to +28
total no. of data, no. of unique data, R_{int}	5773, 5476, 0.0627
no. of obsd data ($I > 2.0\sigma(I)$)	3641
transmissn cor range	0.518−1.000
Refinement	
N_{ref}, N_{par}	5476, 248
R, wR_2, S	0.0414, 0.0801, 1.04
weight (w)	$1/(\sigma^2(F_o^2) + (0.0250P)^2 + 2.5317P)$[a]
max and av shift/error	0.001, 0.000
min, max resd dens (e Å^{-3})	−0.93, +0.63

[a] $P = (F_o^2 + 2F_c^2)/3$.

$[TaCl({=}CH\text{-}t\text{-}Bu)\{C_6H_3(CH_2NMe_2)_2\text{-}2,4\}(O\text{-}t\text{-}Bu)]$ (4). A purple solution of $[TaCl({=}CH\text{-}t\text{-}Bu)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(O\text{-}t\text{-}Bu)]$ (**3**; 1.53 g, 3.1 mmol) was stirred in benzene (50 mL) at 80 °C for 2 h. During this time the color of the solution gradually changed from purple to pale yellow. The solvent was removed *in vacuo*, affording an orange oil which was subsequently extracted with pentane (3 × 20 mL), and the combined extracts were concentrated *in vacuo* to 5 mL. From the resulting yellow-orange solution the product **4** crystallized overnight as needle-shaped yellow crystals at −30 °C; yield 1.15 g (77%). The product **4** was isolated as a mixture of two diastereoisomers in a 1:1 ratio. Anal. Calcd for $C_{21}H_{38}N_2ClOTa$: C, 45.78; H, 6.95; N, 5.08. Found: C, 45.62; H, 6.98; N, 5.07. ^1H NMR (200.13 MHz, benzene-d_6, 25 °C, TMS) (two diastereoisomers): δ 1.12 (s, 9 H, CHC*Me*$_3$), 1.20 (s, 9 H, CHC*Me*$_3$), 1.33 (s, 9 H, OC*Me*$_3$), 1.51 (s, 9 H, OC*Me*$_3$), 1.91 (s, 3 H, N*Me*$_2$), 2.02 (s, 3 H, N*Me*$_2$), 2.14 (s, 6 H, N*Me*$_2$), 2.16 (s, 6 H, N*Me*$_2$), 2.58 (s, 3 H, N*Me*$_2$), 2.59 (s, 3 H, N*Me*$_2$), 3.21 (d, 1 H, $^2J(H,H)$ = 13 Hz, ArC*H*$_2$N), 3.28 (d, 1 H, $^2J(H,H)$ = 14 Hz, ArC*H*$_2$N), 3.31 (s, 2 H, ArC*H*$_2$N), 3.35 (s, 2 H, ArC*H*$_2$N), 4.12 (d, 1 H, $^2J(H,H)$ = 13 Hz, ArC*H*$_2$N), 4.39 (d, 1 H, $^2J(H,H)$ = 14 Hz, ArC*H*$_2$N), 4.71 (s, 1 H, C*H*CMe$_3$), 5.34 (s, 1 H, C*H*CMe$_3$), 7.16−7.29 (m, 4 H, Ar *H*), 8.17 (d, 1 H, $^2J(H,H)$ = 7 Hz, *o-H*), 8.82 (d, 1 H, $^2J(H,H)$ = 7 Hz, *o-H*). $^{13}C\{^1H\}$ NMR (50.32 MHz, benzene-d_6, 25 °C, TMS) (two diastereoisomers): δ 29.6 (CHC*Me*$_3$), 31.8 (OC*Me*$_3$), 32.2 (OC*Me*$_3$), 34.5 (CHC*Me*$_3$), 34.6 (CHC*Me*$_3$), 35.8 (CHC*Me*$_3$), 45.3 (N*Me*$_2$), 45.5 (N*Me*$_2$), 45.6 (N*Me*$_2$), 46.9 (N*Me*$_2$), 51.8 (N*Me*$_2$), 51.8 (N*Me*$_2$), 64.8 (Ar*C*H$_2$N), 66.0 (Ar*C*H$_2$N), 71.0 (Ar*C*H$_2$N), 73.4 (Ar*C*H$_2$N), 82.8 (O*C*Me$_3$), 84.8 (O*C*Me$_3$), 124.2 (*m-C*), 124.5 (*m-C*), 126.6 (*m-C*), 127.6 (*m-C*), 137.3 (*o-C*), 139.6 (*o-C*), 140.7 (*p-C*), 144.7 (*p-C*), 145.9 (*o-*

C), 148.3 (*o*-*C*), 193.9 (C_{ipso}), 194.3 (C_{ipso}), 245.3 (*C*HCMe$_3$, ^1J(C,H) = 96 Hz), 249.3 (*C*HCMe$_3$, ^1J(C,H) = 95 Hz).

[TaCl$_2$(=CH-*t*-Bu){C$_6$D$_3$(CH$_2$NMe$_2$)$_2$-2,*6*}] (1-*d*$_3$). C$_6$H$_3$-Me$_2$-1,3-Br-2 was deuterated with D$_2$O and D$_2$SO$_4$ according to a literature procedure[7] to afford C$_6$D$_3$Me$_2$-1,3-Br-2 with *ca.* 80% deuterium enrichment of the three aryl hydrogens. The compound C$_6$D$_3$Me$_2$-1,3-Br-2 was used for the successive synthesis (four further steps) of [TaCl$_2$(=CH-*t*-Bu){C$_6$D$_3$(CH$_2$-NMe$_2$)$_2$-2,*6*}], as described for its non-deuterated analog,[4a] with a total deuterium enrichment of *ca.* 80% of the three aromatic hydrogens.

Reaction of [TaCl$_2$(=CH-*t*-Bu){C$_6$D$_3$(CH$_2$NMe$_2$)$_2$-2,*6*}] (1-*d*$_3$) with LiO-*t*-Bu. The alkylidene complex [TaCl$_2$(=CH-*t*-Bu){C$_6$D$_3$(CH$_2$NMe$_2$)$_2$-2,*6*}] was reacted with 2 equiv of LiO-*t*-Bu, as described above for its non-deuterated analog. ^{13}C NMR (50.32 MHz, benzene-*d*$_6$, 25 °C) showed a triplet for the tantalum alkylidene carbon at 224.0 ppm (^1J(C,D) = 12 Hz).

Crystal Structure Refinement of Complex 3. Crystals of **3** suitable for an X-ray crystallographic study were obtained as described in the literature[4b] from a saturated hexane solution of **3** at −30 °C. Numerical data concerning the structure determination have been collected in Table 2. X-ray data were collected for a transparent red crystal glued on top of a glass fiber on an Enraf-Nonius CAD4T diffractometer having a rotating anode. Accurate unit cell parameters were derived from setting angles of 25 reflections in the range $11.4 < \theta < 13.9°$. The reflection data were corrected for absorption with DIFABS[11] as implemented in PLATON.[12] The structure was solved with automated Patterson/Fourier techniques using DIRDIF92[13] and refined on F^2 with SHELXL-93.[14] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms with U_{iso} related to U_{eq} of the atom they are attached to.

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Supporting Information Available: Further details of the structure determination, including tables of atomic coordinates, bond lengths and angles, and thermal parameters (7 pages). Ordering information is given on any current masthead page.

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