

Articles

Alkylidene-Centered Rearrangement of a Tantalum Alkylidene Alkoxide Species with the N,C,N-Bis-*ortho*-chelated 1,2,6-Trisubstituted Aryldiamine Ligand $[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}]^-$ to a Product with a C,N-Mono-*ortho*-chelated 1,2,4-Trisubstituted Aryldiamine Ligand. X-ray Molecular Structure of $[\text{TaCl}(\text{=CH-}t\text{-Bu})\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,4}\}(\text{O-}t\text{-Bu})]^\dagger$

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 $\text{LiO-}t\text{-Bu}$ with $[\text{TaCl}_2(\text{=CH-}t\text{-Bu})\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}\}]$ (**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 $[\text{Ta}(\text{=CH-}t\text{-Bu})\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,4}\}(\text{O-}t\text{-Bu})_2]$ (**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 $[\text{TaCl}(\text{=CH-}t\text{-Bu})\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}\}(\text{O-}t\text{-Bu})]$ (**3**) to the rearranged intermediate $[\text{TaCl}(\text{=CH-}t\text{-Bu})\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,4}\}(\text{O-}t\text{-Bu})]$ (**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 $\text{LiO-}t\text{-Bu}$ at room temperature. Complex **4** is obtained exclusively, as revealed by ^1H 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 $\text{Ta}=\text{C}(\text{H})\text{-}t\text{-Bu}$ moiety; $\Delta G^\ddagger = 71 \text{ kJ mol}^{-1}$. 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 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 ($\text{Ta}\cdots\text{N} = 2.629(4) \text{ \AA}$), providing incipient $\eta^3(\text{N,C,N})$ facial bonding of the aryldiamine ligand. The structure of **3** also shows a pseudo-parallel orientation of the alkylidene $\text{C}_\alpha\text{-H}_\alpha$ bond and the $\text{C}_{\text{ipso}}\text{-Ta}$ 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 $\alpha\text{-H}$ 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 re-

mains 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 $\alpha\text{-H}$ abstraction reactions with alkyl and aryl C–H bonds.² In particular, we have found intramolecular NMe_2 C–H bond activation when the tantalum benzyl complexes $[\text{TaCl}_2\{\text{C}_6\text{H}_4\text{CH}(\text{Me})\text{NMe}_2\text{-2}\}(\text{CH}_2\text{Ph})_2]$ and $[\text{TaCl}_2\{1\text{-}$

* 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.

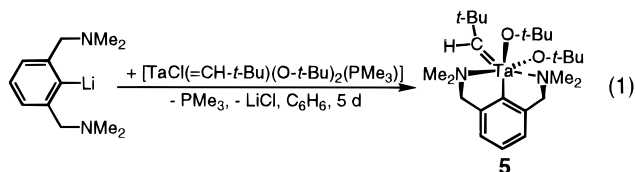
[®] Abstract published in *Advance ACS Abstracts*, August 15, 1997.

(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.

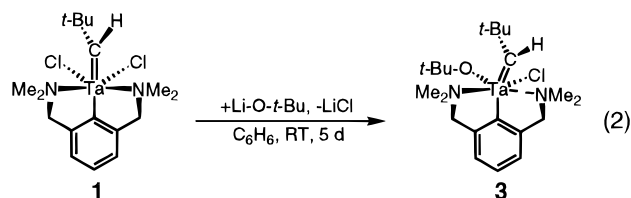
$C_{10}H_6NMe_2-8\}(CH_2Ph)_2]$ are heated in tetrahydrofuran (THF); these reactions afford the tantalum(V)azacyclopropane species $[TaCl_2\{C_6H_4(CH(Me)N(Me)CH_2-2\}(CH_2Ph)(THF)]$ and $[TaCl_2\{1-C_{10}H_6(N(Me)CH_2-8\}(CH_2Ph)(THF)_2]$, respectively.^{2a} Recently Royo and co-workers have reported 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 $[Cp^*TaCl_2\{C_6H_4CH_2N(Me)CH_2-2\}]$ ($Cp^* = C_5Me_5$) 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 $[Cp^*TaCl\{C_6H_4CH_2NMe_2-2\}\{C_6H_4CH_2N(Me)CH_2-2\}]$.^{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 $\eta^2(N,C)$ -chelated 1,2,6-trisubstituted aryl-diamine 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 aryl-diamine is now 1,2,4-trisubstituted and again $\eta^2(N,C)$ -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 aryl-diamine 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 $[Ir\{C_6H_3(CH_2NMe_2)_2-2-Me-6\}(COD)]$ with a 6-Me grouping, which on heating irreversibly forms $[Ir\{C_6H_3(CH_2NMe_2)_2-2-Me-4\}(COD)]$.³

We are now studying the reactivity of high-oxidation-state tantalum alkylidene complexes stabilized by the aryl-diamine 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 $\eta^2(C,N)$ bidentate or as an $\eta^3(N,C,N)$ 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}



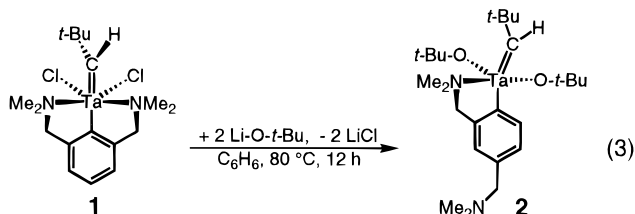
A problem with the preparation of **5** by this route is not only that this reaction takes 1 week to reach completion but also that the product is isolated in low yield. In an alternative approach to obtain **5**, we reacted dichloride complex **1** with lithium *tert*-butoxide, but even after 1 week 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}



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 aryl-diamine 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



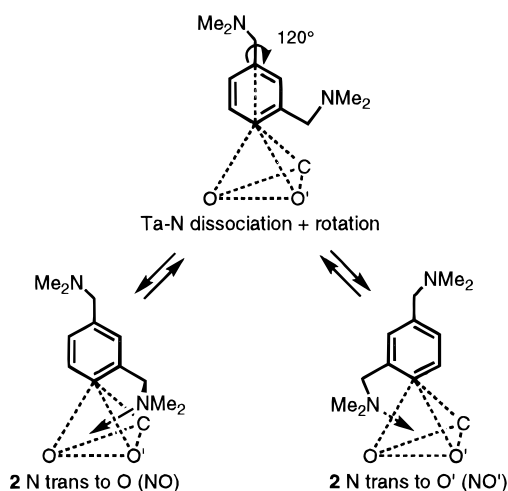
large block-shaped yellow crystals by slow cooling of a saturated pentane solution from +25 to –30 °C. Although the synthesis of **2** is very efficient, the isolated yield of **2** is only moderate (69%), since its high solubility in nonpolar organic solvents hinders the crystallization step.

The ¹H NMR spectrum of the rearrangement product **2** at room temperature (benzene-*d*₆) shows broadened signals for the NMe₂ and the CH₂ groups of one CH₂-NMe₂ 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

(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) Booi, 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 $\eta^2(\text{C},\text{N})$ coordination mode of the aryl ligand. This is in contrast to the 1,2,6-trisubstituted pattern of the aryldiamine and $\eta^3(\text{N},\text{C},\text{N})$ 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 ($^2J(\text{H},\text{H}) = 12$ 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 ΔG^\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.

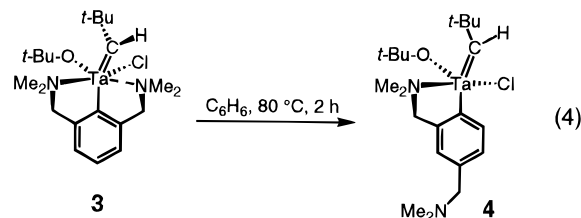
In the ground-state structure the tantalum center is considered to be positioned at the center of a tetrahedral ligand array formed by two O atoms, the alkylidene C_α , and the σ -bonded C atom of the aryldiamine ligand with additional coordination of the nitrogen donor of the coordinating CH_2NMe_2 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 $\text{C}_{\text{ipso}}\text{--C}_\alpha\text{--O'}$ 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 $\text{C}_{\text{ipso}}\text{--Ta}$ axis, and that allows a face-centered nucleophilic attack of the nitrogen donor on the $\text{C}_{\text{ipso}}\text{--C}_\alpha\text{--O}$ face. A similar mechanism has been reported to explain the fluxional behavior of an *ortho*-chelated *N,N*-

dimethylbenzylamine analog of **2**, i.e. $[\text{Ta}(\text{=CH-}t\text{-Bu})\{\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\}_2(\text{O-}t\text{-Bu})_2]$.^{4b}

The ¹³C 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 $^1J(\text{C},\text{H})$ 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 ¹H 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 $[\text{TaCl}(\text{=CH-}t\text{-Bu})\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\}_2(\text{O-}t\text{-Bu})]$ (**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 $[\text{TaCl}(\text{=CH-}t\text{-Bu})\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\}_2(\text{O-}t\text{-Bu})]$ (**3**). A benzene solution of the mono(alkoxide) complex $[\text{TaCl}(\text{=CH-}t\text{-Bu})\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\}_2(\text{O-}t\text{-Bu})]$ (**3**)^{4b} at 80 °C is unstable and after *ca.* 2 h (as monitored by ¹H NMR) is converted exclusively into the isomeric complex $[\text{TaCl}(\text{=CH-}t\text{-Bu})\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\}_2(\text{O-}t\text{-Bu})]$ (**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.

The ¹H 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 ¹H 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 ¹H NMR (200.13 MHz) spectra show that the two isomers start to interconvert and coalescence of various resonances occurs (*CH-t-Bu*, $T_c = 370$

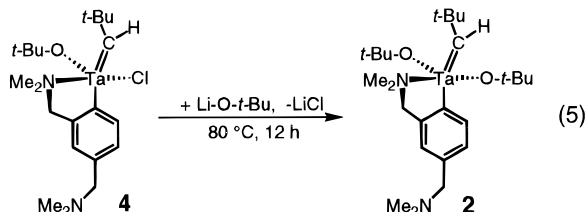
(5) (a) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210. (b) Wallace, K. C.; Liu, A. H.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 4964. (c) Schrock, R. R. *Acc. Chem. Res.* **1986**, *19*, 98 and references therein.

K, $\Delta G^\ddagger = 71 \pm 2 \text{ kJ mol}^{-1}$; CH-*t*-Bu, $T_c = 355 \text{ K}$, $\Delta G^\ddagger = 71 \pm 2 \text{ kJ mol}^{-1}$; O-*t*-Bu, $T_c = 360 \text{ K}$, $\Delta G^\ddagger = 73 \pm 2 \text{ kJ mol}^{-1}$). In the ^1H NMR spectrum at 375 K the broad (coalesced) alkylidene H_α 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 $[\text{Cp}_2\text{Ta}(=\text{CHPh})\text{CH}_2\text{Ph}]$ and $[\text{Cp}_2\text{TaCl}(=\text{CH-}t\text{-Bu})]$, where ΔG^\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 $^1J(\text{C},\text{H})$ 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.



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 $[\text{TaCl}(=\text{CH-}t\text{-Bu})\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\cdot 2,6\}(\text{O-}t\text{-Bu})]$ (3**).** The molecular structure of mono(alkoxide) complex **3** together with the adopted numbering scheme is shown in Figure 1, with

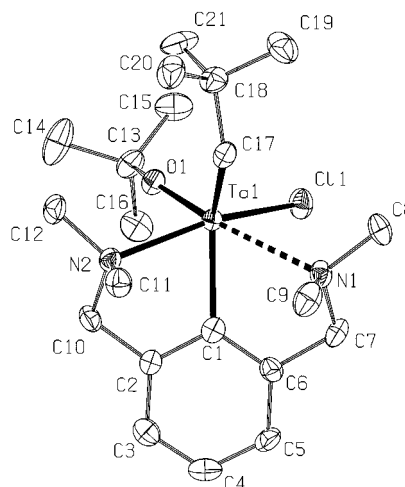


Figure 1. ORTEP thermal motion ellipsoid plot¹² (drawn at 50% probability level) of $[\text{TaCl}(=\text{CH-}t\text{-Bu})\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\cdot 2,6\}(\text{O-}t\text{-Bu})]$ (**3**).

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)

bond distances and bond angles being given in Table 1. 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 (Cl1) 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 $\eta^2(\text{C},\text{N})$ 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 $\eta^3(\text{N},\text{C},\text{N})$ (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 $[\text{TaCl}_2(=\text{CH-}t\text{-Bu})\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\cdot 2,6\}]$ (**1**) and bis(alkoxide) complex $[\text{Ta}(=\text{CH-}t\text{-Bu})\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\cdot 2,6\}(\text{O-}t\text{-Bu})_2]$ (**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.

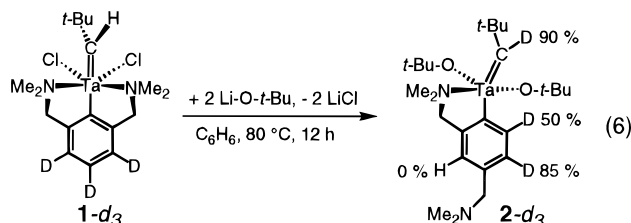
For the alkylidene function of **3** the Ta–C17–C18 angle of 140.7(5)° is considerably smaller than corresponding angles of 170.6(3) and 159.5(5)° in dichloride complex **1**^{4a} and bis(alkoxide) complex **5**,^{4b} respectively, which contain distorted alkylidene functionalities.^{6c,7} This Ta–C $_{\alpha}$ –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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complexes reported previously by our group, i.e. 138.5-(11) $^{\circ}$ for $[\text{W}(\text{=CHSiMe}_3)\{\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\}_2(\text{=NPh})(\text{CH}_2\text{SiMe}_3)]$ and 136.4(3) $^{\circ}$ for $[\text{W}(\text{=CHSiMe}_3)\{\text{OCPh}_2\{[2\text{-py}]\}(\text{=NPh})(\text{CH}_2\text{SiMe}_3)\}_2]$.^{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 $-60\text{ }^{\circ}\text{C}$ can be seen by ^1H 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 $[\text{TaCl}_2(\text{=CH-}t\text{-Bu})\{\text{C}_6\text{D}_3(\text{CH}_2\text{NMe}_2)_2\}_2$ 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 $\text{C}_{\text{ipso}}(\text{Ta})$ position and an originally $\text{C}_{\text{ortho}}\text{--H}$ 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 $[\text{TaCl}_2(\text{=CH-}t\text{-Bu})\{\text{C}_6\text{D}_3(\text{CH}_2\text{NMe}_2)_2\}_2]$ (**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 $\text{C}_6\text{H}_3\text{Me}_2\text{-1,3-Br-2}$, from which it was synthesized.

The reaction of **1-*d*₃** with $\text{LiO-}t\text{-Bu}$ (eq 6) affords the complex $[\text{Ta}(\text{=CD-}t\text{-Bu})\{\text{C}_6\text{D}_2\text{H}(\text{CH}_2\text{NMe}_2)_2\}_2(\text{O-}t\text{-Bu})_2]$ (**2-*d*₃**), whose ^1H NMR spectrum (298 K, 200.13 MHz, C_6D_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_6D_6) a C–D triplet ($^1J(\text{C},\text{D}) = 12\text{ Hz}$) for the alkylidene carbon further underlines the formation of a $\text{C}_{\alpha}\text{--D}$ 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 $\text{LiO-}t\text{-Bu}$ 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 $80\text{ }^{\circ}\text{C}$ 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

Scheme 2. Rearrangement via Alkylidene C–H Bond Activation

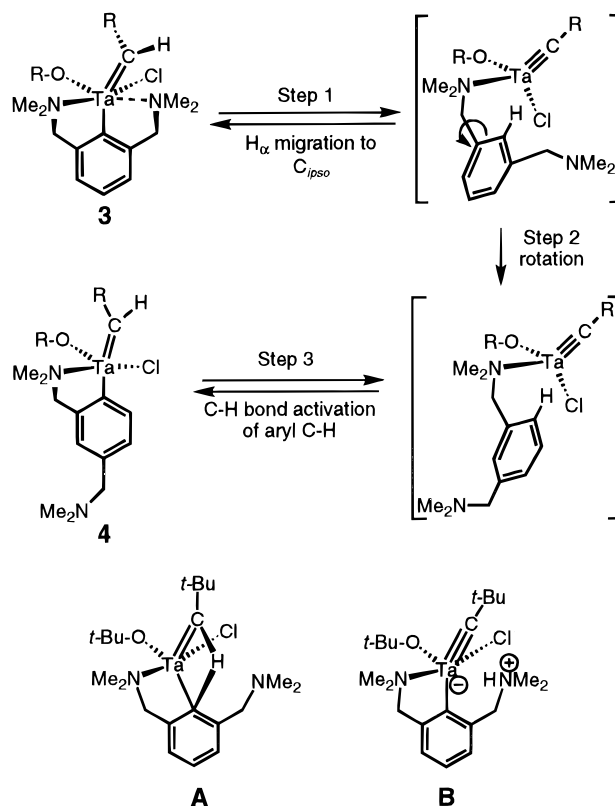


Figure 2. Transition state **A** and intermediate **B** proposed in the mechanistic schemes for rearrangement of **3** to **4**.

intermediates for the rearrangement reaction, as shown in Scheme 2.

A description of the three consecutive steps from **3** to **4** follows. In step 1 there is an overall migration of H_{α} of the alkylidene $\text{C}_{\alpha}\text{--H}_{\alpha}$ bond to C_{ipso} of the former $\text{Ta-}t\text{-Bu}$ bond to form an alkylidyne arene intermediate. In the case of a concerted mechanism involving a four-membered $\text{Ta-}t\text{-Bu-C}_{\alpha}\text{-C}_{\text{ipso}}$ metallacyclic transition state (not depicted), this step can only occur when the alkylidene C_{α} 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 $\text{C}_{\alpha}\text{--Ta-}t\text{-Bu}$ angle from $131.3(2)^{\circ}$ (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 $[\text{TaCl}_2\{\mu\text{-C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\}_2\{\mu\text{-C-}t\text{-Bu}\}\text{ZnCl}]$ (**6**), illustrated schematically in Figure 3,⁸ in which ZnCl is seen to occupy a position analogous to that of the alkylidene H_{α} 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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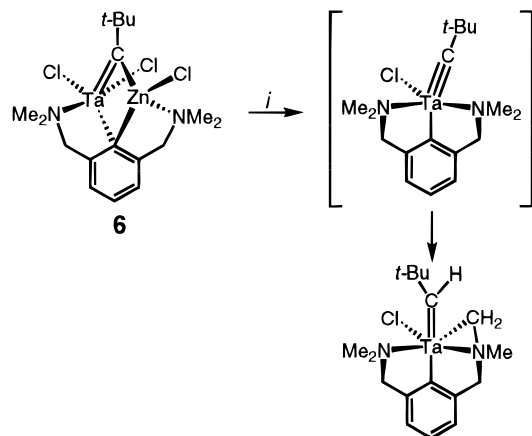


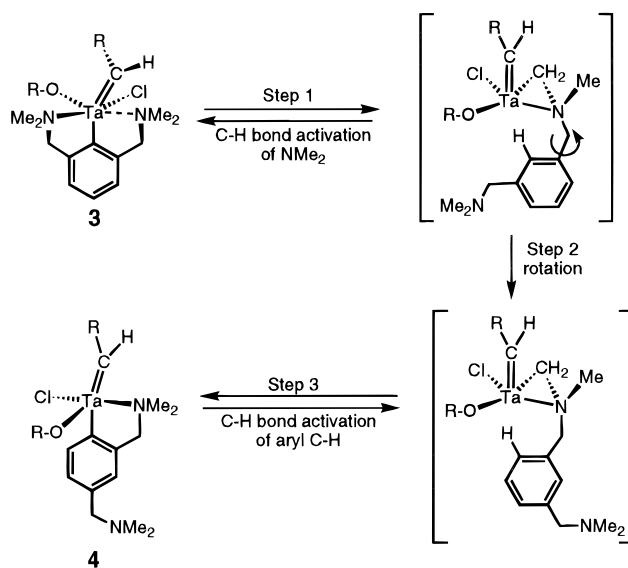
Figure 3. Schematic structure of **6** and its reactivity with tmeda. Reaction conditions: (i) +tmeda, - [ZnCl₂(tmeda)], C₆H₆, 60 °C.

tions in alkylidene/alkylidyne complexes. In this description one of the weakly coordinated *ortho* amine N donor atoms in **3** acts as an *intramolecular* 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 CH₂NMe₂ group, as shown in proposed intermediate **B**. This idea that a reaction can be assisted by a CH₂NMe₂ 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 NMe₂ group^{4b} and the bulk of the *tert*-butyl groups does not allow this NMe₂ 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) CH₂NMe₂ 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.

It is worth recalling that treatment of the bimetallic tantalum–zinc alkylidyne complex [TaCl₂{μ-C₆H₃(CH₂NMe₂)₂₋₂, 6'}(μ-C-*t*-Bu)ZnCl] (**6**), shown in Figure 3, with Me₂NCH₂CH₂NMe₂ (tmeda) at 60 °C leads to a clean

Scheme 3. Rearrangement via NMe₂ C–H Bond Activation



and quick elimination of [ZnCl₂(tmeda)] with concomitant formation of the yellow tantalum alkylidene complex [TaCl(=CH-*t*-Bu){C₆H₃(CH₂N(Me)CH₂)-2-(CH₂NMe₂)-6}].⁸ This latter reaction involves the presence of a mononuclear square-pyramidal tantalum alkylidyne complex that, after elimination of ZnCl₂, 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 NMe₂ 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 NMe₂ 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 CH₂NMe₂ substituent whereby a triangular Ta–CH₂–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–CH₂ 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 NMe₂ C–H bond activation like that shown in Scheme 3 was observed in the isomerization rearrangement reactions of the η²(C,N) 1,2,6-trisubstituted aryl-diamine species [Ir^I{C₆H₃(CH₂NMe₂)₂₋₂, 6'}(COD)] and [Ru^{II}Cl{C₆H₃(CH₂NMe₂)₂₋₂, 6'}{η⁶-(CH₃C₆H₄CH(CH₃)₂)}]^{10b} that afford their η²(C,N) 1,2,4-trisubstituted aryl-diamine products [Ir{C₆H₃(CH₂NMe₂)₂₋₂, 4'}(COD)]³ and [RuCl{C₆H₃(CH₂NMe₂)₂₋₂, 4'}{η⁶-(CH₃C₆H₄CH(CH₃)₂)}]^{10b} respectively. Although in principle the mechanism in Scheme 3 is feasible during the rear-

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(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.

rament 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 $[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6]^-$ 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 NMe₂ 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 *intramolecular* 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 ¹³C NMR spectra were recorded on a Bruker AC200 or AC300 spectrometer; ¹J(C,H) data are from separately recorded proton-coupled spectra. The complexes $[\text{TaCl}_2(\text{=CH-}t\text{-Bu})\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6\}]$ (**1**) and $[\text{TaCl}(\text{=CH-}t\text{-Bu})\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6\}(\text{O-}t\text{-Bu})]$ (**3**) were prepared according to literature procedures.^{4a,b}

$[\text{Ta}(\text{=CH-}t\text{-Bu})\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,4\}(\text{O-}t\text{-Bu})_2]$ (2**) (One-Pot Procedure).** A purple solution of $[\text{TaCl}_2(\text{=CH-}t\text{-Bu})\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6\}]$ (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 $\text{C}_{25}\text{H}_{47}\text{N}_2\text{O}_2\text{Ta}$: 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, CHCMe_3), 1.48 (s, 18 H, OCMe_3), 2.25 (s, 6 H, NMe_2), 2.64 (br s, 6 H, NMe_2), 3.01 (s, 1 H, CHCMe_3), 3.37 (s, 2 H, ArCH_2N), 4.02 (br s, 2 H, ArCH_2N), 7.08 (m + s, 2 H, *m*-Ar), 8.47 (d, ²J(H,H) = 7 Hz, 1 H, *o*-H). ¹³C{¹H} NMR (50.32 MHz, benzene-*d*₆, 25 °C, TMS): δ 33.4 (OCMe_3), 35.8 (CHCMe_3), 44.7 (NMe_2), 45.7 (NMe_2), 48.7 (OCMe_3), 65.0 (ArCH_2N), 70.7 (ArCH_2N), 77.6 (CHCMe_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 (CHCMe_3 , ¹J(C,H) = 90 Hz).

$[\text{Ta}(\text{=CH-}t\text{-Bu})\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,4\}(\text{O-}t\text{-Bu})_2]$ (2**) (Starting from **4**).** A yellow solution of $[\text{TaCl}_2(\text{=CH-}t\text{-Bu})\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,4\}(\text{O-}t\text{-Bu})]$ (**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

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

Crystal Data	
formula	$\text{C}_{21}\text{H}_{38}\text{ClN}_2\text{O}_2\text{Ta}$
mol wt	550.95
cryst syst	orthorhombic
space group	<i>Pbca</i> (No. 61)
<i>a</i> (Å)	17.9176(10)
<i>b</i> (Å)	12.3038(10)
<i>c</i> (Å)	21.7338(11)
<i>V</i> (Å ³)	4791.3(5)
<i>Z</i>	8
<i>d</i> _{calcd} (g cm ^{–3})	1.528
<i>F</i> (000)	2208
μ (cm ^{–1})	47.1 (Mo K α)
cryst size (mm)	0.18 × 0.30 × 0.43
Data Collection	
<i>T</i> (K)	150
X-ray exposure time (h)	9.2
wavelength, Å	0.710 73 (Mo K α 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,	5773, 5476, 0.0627
no. of unique data, <i>R</i> _{int}	
no. of obsd data (<i>I</i> > 2.0 σ (<i>I</i>))	3641
transmissn cor range	0.518–1.000
Refinement	
<i>N</i> _{ref} , <i>N</i> _{par}	5476, 248
<i>R</i> , <i>wR</i> ₂ , <i>S</i>	0.0414, 0.0801, 1.04
weight (<i>w</i>)	$1/(\sigma^2(F_o^2) + (0.0250P)^2 + 2.5317P)^a$
max and av shift/error	0.001, 0.000
min, max resd dens (e Å ^{–3})	–0.93, +0.63
^a $P = (F_o^2 + 2F_c^2)/3$.	

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%).

$[\text{TaCl}(\text{=CH-}t\text{-Bu})\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,4\}(\text{O-}t\text{-Bu})]$ (4**).** A purple solution of $[\text{TaCl}_2(\text{=CH-}t\text{-Bu})\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6\}(\text{O-}t\text{-Bu})]$ (**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 $\text{C}_{21}\text{H}_{38}\text{N}_2\text{O}_2\text{ClTa}$: 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, CHCMe_3), 1.20 (s, 9 H, CHCMe_3), 1.33 (s, 9 H, OCMe_3), 1.51 (s, 9 H, OCMe_3), 1.91 (s, 3 H, NMe_2), 2.02 (s, 3 H, NMe_2), 2.14 (s, 6 H, NMe_2), 2.16 (s, 6 H, NMe_2), 2.58 (s, 3 H, NMe_2), 2.59 (s, 3 H, NMe_2), 3.21 (d, 1 H, ²J(H,H) = 13 Hz, ArCH_2N), 3.28 (d, 1 H, ²J(H,H) = 14 Hz, ArCH_2N), 3.31 (s, 2 H, ArCH_2N), 3.35 (s, 2 H, ArCH_2N), 4.12 (d, 1 H, ²J(H,H) = 13 Hz, ArCH_2N), 4.39 (d, 1 H, ²J(H,H) = 14 Hz, ArCH_2N), 4.71 (s, 1 H, CHCMe_3), 5.34 (s, 1 H, CHCMe_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). ¹³C{¹H} NMR (50.32 MHz, benzene-*d*₆, 25 °C, TMS) (two diastereoisomers): δ 29.6 (CHCMe_3), 31.8 (OCMe_3), 32.2 (OCMe_3), 34.5 (CHCMe_3), 34.6 (CHCMe_3), 35.8 (CHCMe_3), 45.3 (NMe_2), 45.5 (NMe_2), 45.6 (NMe_2), 46.9 (NMe_2), 51.8 (NMe_2), 51.8 (NMe_2), 64.8 (ArCH_2N), 66.0 (ArCH_2N), 71.0 (ArCH_2N), 73.4 (ArCH_2N), 82.8 (OCMe_3), 84.8 (OCMe_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*-

O), 148.3 (*o*-C), 193.9 (C_{ipso}), 194.3 (C_{ipso}), 245.3 (CHCMe₃, $^1J(\text{C,H}) = 96$ Hz), 249.3 (CHCMe₃, $^1J(\text{C,H}) = 95$ Hz).

[TaCl₂(=CH-*t*-Bu){C₆D₃(CH₂NMe₂)₂-2,6}] (1-*d*₃). C₆H₃-Me₂-1,3-Br-2 was deuterated with D₂O and D₂SO₄ according to a literature procedure⁷ to afford C₆D₃Me₂-1,3-Br-2 with *ca.* 80% deuterium enrichment of the three aryl hydrogens. The compound C₆D₃Me₂-1,3-Br-2 was used for the successive synthesis (four further steps) of [TaCl₂(=CH-*t*-Bu){C₆D₃(CH₂NMe₂)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 [TaCl₂(=CH-*t*-Bu){C₆D₃(CH₂NMe₂)₂-2,6}] (1-*d*₃) with LiO-*t*-Bu. The alkylidene complex [TaCl₂(=CH-*t*-Bu){C₆D₃(CH₂NMe₂)₂-2,6}] was reacted with 2 equiv of LiO-*t*-Bu, as described above for its non-deuterated analog. ¹³C NMR (50.32 MHz, benzene-*d*₆, 25 °C) showed a triplet for the tantalum alkylidene carbon at 224.0 ppm ($^1J(\text{C,D}) = 12$ 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 < θ < 13.9°. The reflection data were corrected for absorption

with DIFABS¹¹ as implemented in PLATON.¹² The structure was solved with automated Patterson/Fourier techniques using DIRDIF92¹³ 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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