

Synthesis and Reactivity of Tantalum Alkylidene Complexes Containing the *C,N,N*-Chelating Aryldiamine Ligand [C₆H₄(CH₂N(Me)CH₂CH₂NMe₂)-2][−] (CNN). X-ray Structures of [TaCl₂(=CH-*t*-Bu)(CNN)], [Ta{(CH₂)₃-1,3}(CNN)(O-*t*-Bu)₂], and [Ta(CNN)(O-*t*-Bu)₂(H₂C=CH₂)]

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The potentially *C,N,N*-chelating anionic aryldiamine ligand [C₆H₄(CH₂N(Me)CH₂CH₂NMe₂)-2][−] (CNN) has been employed in the preparation of six-coordinate Ta(V) alkylidene complexes. The new dichloro alkylidene complex [TaCl₂(=CH-*t*-Bu)(CNN)], **2**, prepared from [TaCl₃(=CH-*t*-Bu)(THF)₂] and [Li(CNN)]₂, **1**, has been obtained as a mixture of three diastereoisomers (**2a–c**) in 51% yield. The molecular structure of the major isomer **2a**, determined by X-ray methods, shows this to be a tetragonal bipyramidal complex in which the metal coordination sphere is comprised of the *C,N,N* facially bonded CNN, two *cis*-positioned chlorides in the equatorial plane, and a neopentylidene group and the NMe₂ nitrogen donor mutually *trans*-positioned at the apices. The dialkoxide complexes [Ta(=CHR)(CNN)(O-*t*-Bu)₂] (R = *t*-Bu (**3a**), CMe₂Ph (**3b**)) have been obtained by transmetalation of [TaCl(=CHR)(O-*t*-Bu)₂(PMe₃)] with **1**. The neopentylidene complex **3a** was isolated as an analytically pure orange solid in 47% yield, whereas the neophylidene complex **3b** was isolated as an orange oil of ±90% purity. Complex **3b** reacts in pentane with ethene at room temperature to afford the tantalacyclobutane complex [Ta{(CH₂)₃-1,3}(CNN)(O-*t*-Bu)₂], **4**, which was isolated as a white solid in 81% yield. An X-ray diffraction study of **4** shows it to be a heptacoordinate pentagonal bipyramidal tantalum species in which two mutually *trans* alkoxide groups are in the apical positions; the meridional ligation is comprised of the *C,N,N*-coordination of CNN and the σ-bonded carbon atoms of the metallacycle. Reaction of **3b** in hexane at 69 °C with ethene gives a mixture of the new tantalum alkene complex [Ta(CNN)(O-*t*-Bu)₂(H₂C=CH₂)], **5**, and **4** in a 5:2 ratio. Complex **5** can be isolated from this mixture as a yellow solid by recrystallization from diethyl ether at −30 °C. The X-ray molecular structure of **5** shows it to be a pentagonal bipyramidal complex in which the array of atoms directly bonded to tantalum is like that in **4**. However, in **5**, the meridional ligation is comprised of the *C,N,N*-coordination of CNN and the two C atoms of the ethene molecule. Complexes **3b** and **4** initiate ring-opening metathesis polymerization with strained cyclic olefins; dicyclopentadiene produces cross-linked polymers, whereas norbornene produces polycyclopentamers with approximately 90% *trans*-vinylene bonds. In contrast, none of the isomers of alkylidene complex **2** show any reactivity toward either ethene or norbornene.

Introduction

Currently there is much interest in ligands that may replace the cyclopentadienyl ligand in early transition metal chemistry. Some of our efforts in this field have focussed on developing tantalum alkylidene compounds

that contain the monoanionic bis(*ortho*)-chelating aryldiamine ligand [C₆H₃(CH₂NMe₂)₂-2,6][−] (NCN), Figure 1, and this has led to the synthesis of interesting new σ-bonded aryl–tantalum complexes. In a previous paper, we reported the synthesis of the first alkylidene complex containing this ligand, i.e., [TaCl₂(=CH-*t*-Bu)(NCN)]; with propene and ethene this complex shows no metathesis reactivity, but instead, isolable alkene adduct complexes are formed *via* a reductive rearrangement of the intermediate metallacyclobutane ring.^{1a,c} The mono- and bisalkoxide analogs [TaCl₂-*n*(=CH-*t*-

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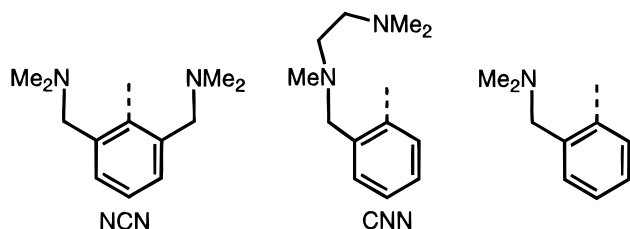


Figure 1. Different *ortho*-chelating arylamine ligands.

Bu)(NCN)(O-*t*-Bu)_{*n*}] (*n* = 1, 2) in solution have only *C,N,N*-coordination of NCN, i.e., one CH₂NMe₂ arm is not coordinated.^{1b} The reactivity of these alkoxide alkylidene complexes with simple alkenes varied from unclean reactions (probably involving reductive rearrangement) to very clean metathesis reactions.^{1b} In some cases, tantalacyclobutane complexes could be isolated, though these slowly decompose in solution in an unclean manner liberating ethene.^{1b} In the latter paper, we also described a dialkoxide tantalum alkylidene complex stabilized by the mono(*ortho*)-chelating arylamine ligand [C₆H₄CH₂NMe₂-2]⁻.^{1b}

These successful studies with NCN have promoted us to examine the potentially *C,N,N*-coordinating monoanionic ligand [C₆H₄(CH₂N(Me)CH₂CH₂NMe₂)-2]⁻ (CNN) in this field of chemistry, Figure 1. We have already shown that CNN, which can be seen as a mono(*ortho*)-chelating aryldiamine ligand, like bis(*ortho*)-chelating aryldiamine NCN, has a number of available coordination modes. Examples from late transition metal chemistry are already known in which the ligand is *C,N,N*-bonded to the metal in both a meridional fashion, e.g., [PdI(CNN)]₂,² and a pseudo-facial fashion, e.g., [Ir(CNN)(COD)]₃.³ It can furthermore function as a *C,N*-bidentate ligand, and in this case, it resembles the arylamine [C₆H₄CH₂NMe₂-2]⁻, Figure 1, with the second uncoordinated amine being considered as a well-positioned intramolecular Lewis base.

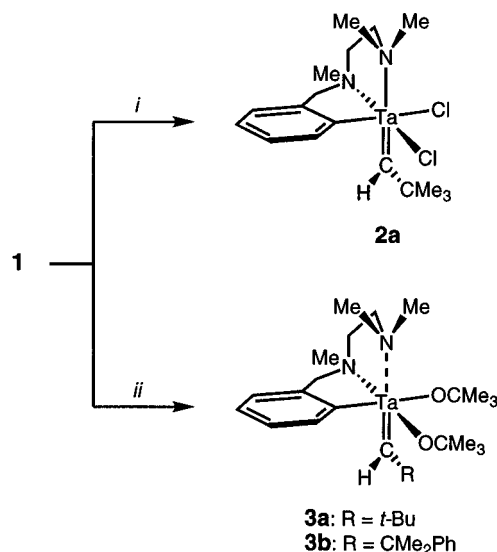
Recently, Richmond and co-workers reported the *C,N,N*-bonded tungsten(II) alkoxide and aryloxy complexes [W(CNN)(OR)(CO)₃] (R = Me, C₆H₄-4-Me, CH₂C₆H₄-4-Me) and the tungsten-tin complex [W(CNN)(SnPh₃)(CO)₃].⁴

We now report the synthesis of the first tantalum(V) CNN complexes, and the reactivity of the new dichloro and dialkoxide tantalum alkylidene complexes with ethene and strained olefins is described.

Results and Discussion

Preparation of CNN Tantalum Alkylidene Complexes. The new alkylidene complex [TaCl₂(=CH-*t*-Bu)(CNN)] (CNN = [C₆H₄(CH₂N(Me)CH₂CH₂NMe₂)-2]⁻), **2**, formed by treatment of the alkylidene complex [TaCl₃(=CH-*t*-Bu)(THF)₂]⁵ with 0.5 equiv of dimeric [Li(CNN)]₂,⁶ **1**, can be isolated as a red/purple solid mixture

Scheme 1. Synthesis of the Alkylidene Complexes **2**, **3a**, and **3b** from [Li{C₆H₄(CH₂N(Me)CH₂CH₂NMe₂)-2}]₂ (**1**)^a



^a Reaction conditions: (i) +2 [TaCl₃(=CH-*t*-Bu)(THF)₂], -2 LiCl, -4 THF, Et₂O, -78 °C; (ii) +2 [TaCl(=CHR)(O-*t*-Bu)₂(PMe₃)], -2 LiCl, -2 PMe₃, C₆H₆, room temperature, 48 h.

of three different diastereoisomers (**2a**, red, and **2b** and **2c**, purple) in a total yield of 51%. From ¹H NMR spectroscopic data (*vide infra*) this mixture was shown to have a composition **2a:2b:2c** of approximately 8:1:1.

The major isomer **2a** can be separated from the crude mixture of diastereoisomers by extraction with cold diethyl ether and can be obtained analytically pure as red block-shaped crystals by recrystallization from a saturated diethyl ether solution at -30 °C. This red diastereoisomer **2a**, which has been characterized as a six-coordinate species with the overall structure illustrated in Scheme 1, is also soluble in benzene and toluene but is insoluble in pentane or hexane. Further concentration and cooling of the supernatant diethyl ether from the crystallization of **2a** yields the pure purple diastereoisomer **2b** as small star-shaped crystals. Attempts to obtain pure **2c** from the supernatant diethyl ether of this crystallization of **2b** were unsuccessful, and NMR characterization of **2c** was carried out with a sample containing both **2b** and **2c** (*vide infra*). Complexes **2b** and **2c** as a mixture are also soluble in benzene and toluene, insoluble in pentane and hexane, and only slightly soluble in diethyl ether. Although the stereochemical identity of **2b** and **2c** is not known with absolute certainty (see later), ¹H NMR experiments have thrown some light on the interrelationship between **2a**, **2b**, and **2c**. For example, **2a** appears to thermodynamically be the most stable isomer, and a solution of **2a** in C₆H₆ for 12 h shows no traces of **2b** or **2c**. However, a solution of **2b** kept under similar conditions showed ca. 20% conversion to **2a**, i.e., **2b** may be a kinetically formed product. The slow interconversion between **2a**, **2b**, and **2c** was also shown in an experiment where the crude 8:1:1 reaction product mixture in C₆D₆ was heated for 1 h at 75 °C; after this time, there was little change in the relative integral intensities of the three species.

The new dialkoxide alkylidene complexes [Ta(=CHR)(CNN)(O-*t*-Bu)₂] (R = *t*-Bu (**3a**), CMe₂Ph (**3b**)) have been obtained by treating the phosphine alkylidene complexes [TaCl(=CHR)(O-*t*-Bu)₂(PMe₃)]⁷ (R = *t*-Bu, CMe₂-

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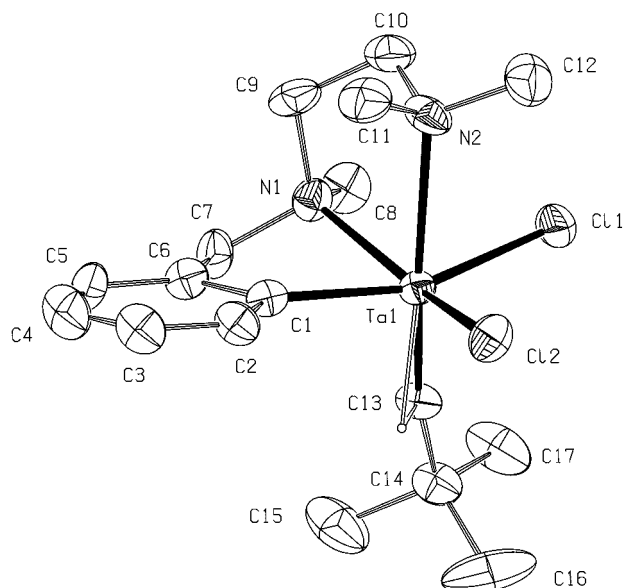


Figure 2. ORTEP²⁹ (30% probability level) drawing of [TaCl₂(=CH-*t*-Bu)(CNN)] (**2a**). Hydrogen atoms have been omitted for clarity, except for the alkylidene C_α hydrogen.

Ph) with 1 equiv of the aryllithium complex [Li(CNN)]₂,⁶ **1** (Scheme 1). The neopentylidene complex **3a** was isolated as block-shaped orange crystals from a saturated pentane solution at -30 °C in 47% yield. Attempts to crystallize the neophylidene analog **3b** failed, and this product was isolated as an air-sensitive orange oil of *ca.* 90% purity. ¹H NMR spectroscopy showed **3b** to be contaminated with small amounts of PMe₃, *tert*-butylbenzene, and the protonated ligand C₆H₅CH₂N(Me)CH₂CH₂NMe₂ (CNN-H), which could not be removed under reduced pressure. Complex **3b** was, therefore, prepared *in situ* and was used as such without further workup for the synthesis of **4** and **5** (*vide infra*). An alternative approach to obtain an alkoxide alkylidene complex by a transmetallation reaction of complex **2** with Li-O-*t*-Bu has also been attempted. However, a benzene solution of complex **2** and 2 equiv of Li-O-*t*-Bu heated for 16 h at 80 °C did not lead, on the basis of ¹H NMR measurements, to the formation of mono- or bisalkoxide complexes. This latter result contrasts with an earlier report that the NCN analog of complex **2**, i.e., [TaCl₂(=CH-*t*-Bu)(NCN)], reacts at room temperature with Li-O-*t*-Bu to afford the monoalkoxide complex [TaCl(=CH-*t*-Bu)(NCN)(O-*t*-Bu)];^{1b} this latter complex undergoes a substitution/rearrangement reaction at 80 °C to afford [Ta(=CH-*t*-Bu){C₆H₃(CH₂NMe₂)₂-2,4}(O-*t*-Bu)] in which the metal has moved from a position in between the two CH₂NMe₂ groups to a position *ortho* to one of the CH₂NMe₂ arms.⁸

Molecular Structure of Complex 2a. An X-ray structural analysis of **2a** was carried out in order to elucidate the stereochemistry of the ligand distribution around tantalum and to aid the interpretation of the NMR spectroscopic data (*vide infra*). The molecular structure of **2a** together with the adopted numbering scheme are shown in Figure 2, with relevant bond distances and bond angles being given in Table 1.

Complex **2a** is a 6-coordinate tantalum species with the arylidiamine CNN ligand pseudo-facially *C,N,N*-

Table 1. Selected Geometrical Data for **2a**

| Bond Lengths (Å) | | | |
|-------------------|-----------|--------------------|-----------|
| Ta(1)–Cl(1) | 2.428(3) | Ta(1)–N(1) | 2.310(9) |
| Ta(1)–Cl(2) | 2.374(3) | Ta(1)–N(2) | 2.479(10) |
| Ta(1)–C(1) | 2.202(11) | Ta(1)–C(13) | 1.860(11) |
| C(13)–C(14) | 1.502(16) | C(13)–H(1) | 1.01(7) |
| Ta(1)···H(100) | 1.91(9) | | |
| Bond Angles (deg) | | | |
| N(2)–Ta(1)–C(13) | 164.8(4) | C(13)–Ta(1)–Cl(1) | 89.2(3) |
| N(2)–Ta(1)–Cl(1) | 79.2(2) | C(13)–Ta(1)–N(1) | 94.7(4) |
| N(2)–Ta(1)–Cl(2) | 86.9(2) | Ta(1)–C(13)–C(14) | 168.9(9) |
| N(2)–Ta(1)–C(1) | 88.8(4) | N(1)–Ta(1)–Cl(2) | 157.1(3) |
| N(2)–Ta(1)–N(1) | 76.3(3) | N(1)–Ta(1)–C(1) | 73.7(4) |
| N(1)–Ta(1)–Cl(1) | 87.9(2) | Ta(1)–C(13)–H(100) | 77(5) |

Table 2. Relevant ¹H NMR Data for Complexes **2a**, **2b**, and **2c**^a

| complex | CMe ₃ | Ta=CH | NMe | PhCH ₂ N ^b | Ar-H _{ortho} ^c |
|-----------|------------------|-------|------------------|----------------------------------|------------------------------------|
| 2a | 1.02 | 2.79 | 1.77, 2.57, 2.76 | 3.35, 4.22 (13) | 8.34 (7) |
| 2b | 1.33 | 2.00 | 1.87, 2.61, 2.71 | 3.20, 4.42 (14) | 9.04 (6) |
| 2c | 1.32 | 2.06 | 1.80, 2.60, 2.80 | 3.18, 4.54 (14) | 8.98 (7) |

^a Recorded in C₆D₆ at 25 °C, 200.13 MHz. Chemical shifts (δ) in ppm referenced to TMS. ^b ²J(H,H) (Hz) in parentheses. ^c ³J(H,H) (Hz) in parentheses.

bonded to the metal center. The geometry around the metal in **2a** can be described as being distorted octahedral with the aryl C_{ipso}, the two chlorides, and the nitrogen donor of the NMe unit forming the meridional plane, with the nitrogen donor of the NMe₂ unit and the alkylidene C_α carbon in the axial positions. The good quality of the X-ray diffraction data for **2a** allowed the neopentylidene H_α to be located, and the alkylidene functionality shows characteristic structural features, such as a large Ta–C_α–C_β bond angle of 168.9(9)°, a small Ta–C_α–H_α angle of 77(5)°, and a short Ta=C bond length of 1.860(11) Å. These data are similar to those in other alkylidene complexes: [TaCl₂(=CH-*t*-Bu)(Cp)] (Cp = C₅H₅), Ta–C_α–C_β = 165(3)°;⁹ [TaCl₂(=CH-*t*-Bu)(NCN)], Ta–C_α–C_β = 170.6(3)°, Ta–C_α–H_α = 71(3)°, Ta=C_α = 1.938(4) Å;^{1a} [TaCl₂(=CH-*t*-Bu){OCMe(CH₂PPh₂)₂}], Ta–C_α–C_β = 152.7(5)°, Ta–C_α–H_α = 104(5)°, Ta=C_α = 1.932(7) Å;¹⁰ [Ti(Cp)(=CH-*t*-Bu){PMe₂CH₂C(O)CMe₂-*o*-C₆H₄CMe₂}], Ti–C_α–C_β = 158.7(2)°, Ti–C_α–H_α = 85(3)°, Ti=C_α = 1.911(3) Å.¹¹

Crystals of the purple diastereoisomer **2b** were unfortunately found to be unsuitable for a molecular structure determination, and we, therefore, have no information regarding the solid state stereochemistry of this isomeric species.

NMR Spectroscopy on the Alkylidene Complexes 2 and 3. Relevant ¹H NMR data for the three diastereoisomers of **2** (**2a–c**) are shown in Table 2. The ¹H NMR (200 MHz, C₆D₆, 25 °C) spectra of all of the isomers of **2** show two signals for the Me groups of the NMe₂ unit, which indicate that in solution the NMe₂ donor atom is coordinated to the metal center. No coalescence of the diastereotopic signals of the NMe₂ unit is found, even at 75 °C when **2** starts to decompose. Because **2b** and **2c** in solution slowly convert to the thermodynamically more stable isomer **2a**, we have only characterized them by ¹H NMR spectroscopy and combined with their low solubility in benzene and chloro-

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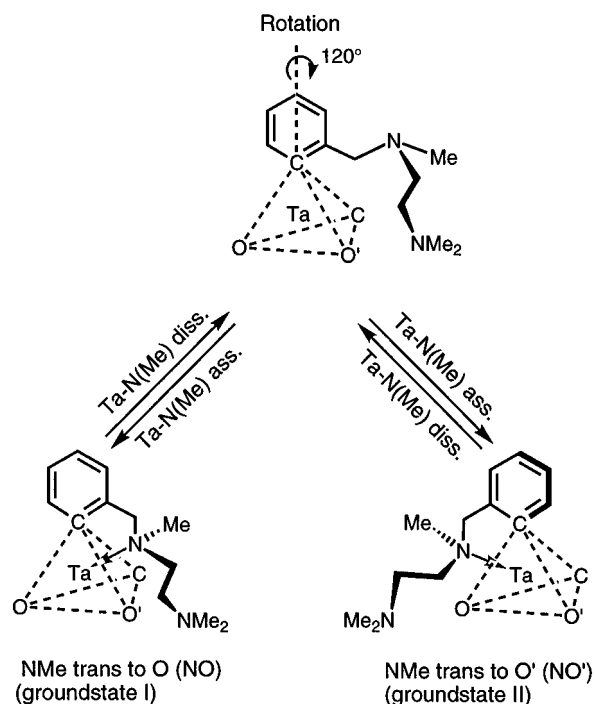
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form, attempts to study their structure by NOE spectroscopy were unsuccessful.

The ^1H NMR data for **2a** are consistent with the solid state structure, i.e., the CNN ligand is *C,N,N* facially coordinated to the metal center. With this coordination mode, one Me group of the NMe_2 unit is placed almost above the aryl ring (Figure 2) and its resonance is significantly upfield-shifted compared to the signal of the other Me group on the same nitrogen donor. In contrast, in a meridional coordination mode of CNN, it is known that the resonance positions for the three Me groups of the CNN ligand are very similar.^{2,3} This latter situation is clearly not the case for any of the three isomers of **2** (Table 2), and comparison of the NMe and NMe_2 resonances of **2a**, **2b**, and **2c** shows these species to be closely related, i.e., they are isomers with a facial coordination mode of the CNN ligand. On the basis of the other ^1H NMR data shown in Table 2, we propose that the isomers of **2** are further discriminated by different facial positions of the other ligands, namely the alkylidene functionality and the two chlorine atoms. Results from a molecular mechanics study are in agreement with this proposal (*vide infra*). In the ^{13}C NMR (50 MHz, C_6D_6 , 25 °C) spectrum of **2a**, the signal for the alkylidene carbon has a distinctive low-field value of 244.9 ppm and a low value for $^1J(\text{C,H})$ of 76 Hz, which is characteristic of this functionality.^{1,12} Low values for $^1J(\text{C,H})$ of ~ 70 Hz have recently been found in other tantalum alkylidene complexes containing various multidentate nitrogen donor ligands, see refs 12e–g for examples, and the apparent correlation of $^1J(\text{C,H})$ with the chemical shift of the alkylidene proton has been commented upon.^{12e}

The ^1H NMR spectrum for the dialkoxide complex **3a** is strongly temperature dependent, and the data are consistent with this species being fluxional in solution. At low temperature (-53 °C, toluene- d_8), there are two signals for the NMe_2 groups at 2.21 and 1.69 ppm and two signals for the *O-t*-Bu groups at 1.50 and 1.61 ppm; this data is consistent with a structure for **3a** as shown in Scheme 1. Upon raising the temperature, the NMe_2 signals coalesce at approximately -25 °C ($\Delta G^\ddagger = 49 \pm 2$ kJ·mol $^{-1}$). At room temperature, the ^1H NMR spectrum of **3a** reveals two broad signals for the *O-t*-Bu groups, one NMe_2 signal at 1.94 ppm and a well-resolved AB pattern for the $\text{ArCH}_2\text{N}(\text{Me})$ proton signals. At higher temperatures, the *O-t*-Bu signals broaden and coalescence occurs at approximately 80 °C ($\Delta G^\ddagger = 75 \pm 2$ kJ·mol $^{-1}$); at this temperature, the $\text{ArCH}_2\text{N}(\text{Me})$ signals were also broad but it was not possible to reach their coalescence temperature without decomposition of the complex. Interestingly, the value of $^1J(\text{C,H})$ for the bisalkoxide complex **3** (78 Hz) is very similar to that of dichloride complex **2a** (76 Hz).

Scheme 2. Fluxional Behavior of Complex **3a** in Solution



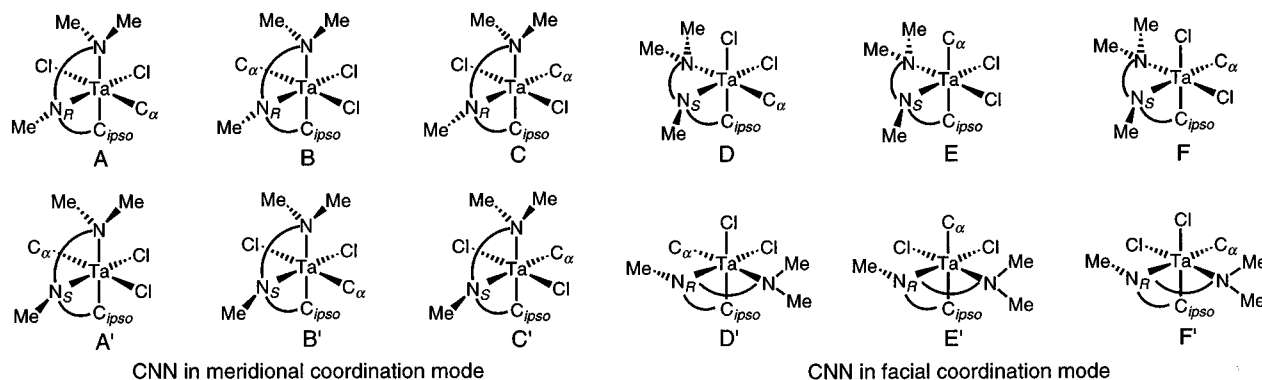
Postulated Mechanisms for the Fluxional Behavior of Complex **3a** in Solution.

Because two different values for ΔG^\ddagger are obtained for the coalescence of the NMe_2 (49 kJ·mol $^{-1}$) and *O-t*-Bu (75 kJ·mol $^{-1}$), groupings the fluxionality of **3a** must involve two different processes. A simple process that explains the equilibration of the NMe_2 signals at room temperature involves dissociation of the Ta–N(Me_2) bond, pyramidal inversion at the nitrogen atom followed by rotation around the C–N(Me_2) bond, and finally N-donor recoordination to tantalum. A more difficult process with a higher ΔG^\ddagger value that is responsible for the equilibration of the *O-t*-Bu groupings is described in detail in the following section. A possible process which might account for this equilibration is shown in Scheme 2; this process was earlier described in the literature for the complexes $[\text{Ta}(\text{=CH-}t\text{-Bu})(\text{NCN})(\text{O-}t\text{-Bu})_2]$ and $[\text{Ta}(\text{=CH-}t\text{-Bu})(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_2(\text{O-}t\text{-Bu})_2]$.^{1b}

In the ground state structure of **3a** shown in Scheme 2, the tantalum center is considered to be positioned at the center of a tetrahedral array formed by two O atoms of the *O-t*-Bu groups, the alkylidene C_α carbon, and the C_{ipso} carbon of the aryl ring. In addition, there is coordination of the N(Me) nitrogen donor of the $-\text{CH}_2\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2$ substituent to one triangular C/C/O(O') face. The postulated process starting from ground state I involves (i) Ta–N(Me) dissociation from the C–C–O' face, leading to a tetrahedral intermediate (during this process there is pyramidal inversion at the N-donor atom), (ii) a 120° wagging of the aryl group around Ta– C_{ipso} , and (iii) a face-centered nucleophilic attack of the N(Me) donor on the C–C–O plane forming ground state II (Scheme 2).^{1b} The ΔG^\ddagger value of 75 kJ·mol $^{-1}$ found for **3** is considerably higher than that found earlier for the mono- and bis(*ortho*)-chelated arylamine complexes $[\text{Ta}(\text{=CH-}t\text{-Bu})(\text{NCN})(\text{O-}t\text{-Bu})_2]$ and $[\text{Ta}(\text{=CH-}t\text{-Bu})(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)_2(\text{O-}t\text{-Bu})_2]$, which both afforded ΔG^\ddagger values of 57 ± 2 kJ·mol $^{-1}$.^{1b} This result can be explained by the expected difference in dissociation energy involved in breaking the Ta–N(Me)

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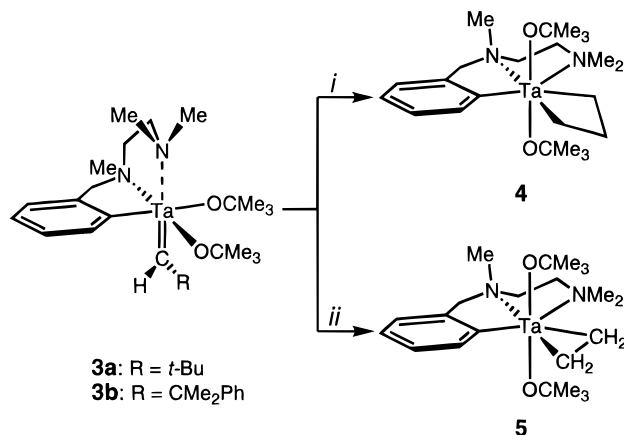
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Scheme 3. Different Stereoisomers of Complex 2. MM2 Calculations on Isomers of 2 Afforded the Following Energies E (kcal mol⁻¹): A, 15.9; B, 20.0; C, 16.1; D, 11.8; E, 14.4; F, 14.2

bond in **3a** (which is part of a chelated N(Me)CH₂CH₂-NMe₂ unit) and the breaking of a Ta-N(Me)₂ bond of a monodentate chelated unit in the latter complexes.

Molecular Mechanics Study of Complex 2. In Scheme 3 are shown all of the possible isomers of **2** with both meridional and facial *C,N,N*-coordination of CNN (having both *R* and *S* configurations of the coordinated N(Me) unit) in combination with different mutual positions of the two ligating chlorides and the alkylidene C_α atom; the alkylidene functionality can have different orientations. The meridional CNN isomers are designated **A–C** (N_R configuration) and **A'–C'** (N_S configuration) and the facial isomers **D–F** (N_R configuration) and **D'–F'** (N_S configuration). The X-ray structural analysis of **2a** (Figure 2) showed this complex to have structure **D'** in the solid state, with the alkylidene functionality orientated *anti* with respect to the aryl C_{ipso} atom. To get some additional information about possible structures of the isomers **2b** and **2c**, we turned to molecular mechanics and have calculated the minimum conformational energies of the six possible isomers **A–F** depicted in Scheme 3. The isomers **A'–F'** are the mirror images of **A–F** and have not been calculated separately, but global energy minimalization of the relative orientation of the alkylidene rotamer conformation was carried out. The results of these calculations are listed in the legend to Scheme 3. One sees from these results that for each of the three isomers having the CNN ligand meridionally bonded to the metal (**A–C**), the minimum conformational energy is approximately 2–8 kcal mol⁻¹ higher than that found for the three isomers (**D–F**) with the CNN ligand facially bonded (Scheme 3). Firstly, we find that isomer **D** (**D'**) has the lowest conformational energy of 11.8 kcal mol⁻¹, and this result is in agreement with our observations (*vide supra*), which indicate that in solution **2a** is thermodynamically the most stable form of **2**. The next most energetically stable isomers are **E** (**E'**) and **F** (**F'**), with facially bonded CNN, and this result strengthens our proposal based on the ¹H NMR data that the isomers **2b** and **2c** have this particular arrangement of the CNN ligand. Although the energy difference between **E** (**E'**) and **F** (**F'**) is only small, the fact that they coexist in solution suggests that isomerization between the forms is slow and that, therefore, there is a high thermodynamic barrier for interconversion.

Reactivity of the Alkylidene Complexes with Olefins. To test the reactivity of alkylidene species **2** toward alkenes, a benzene solution containing **2a** or a mixture of **2b** and **2c** was saturated with ethene, but after 2 days there was no evidence in either case that

Scheme 4. Formation of Complexes 4 and 5^a

^a Reaction conditions: (i) **3a,b** + 2 CH₂=CH₂, 1 atm, pentane, room temperature, -RCH=CH₂; (ii) **3b** + 2 CH₂=CH₂, 1 atm, hexane, 69 °C, -PhMe₂CCH₂CH=CH₂.

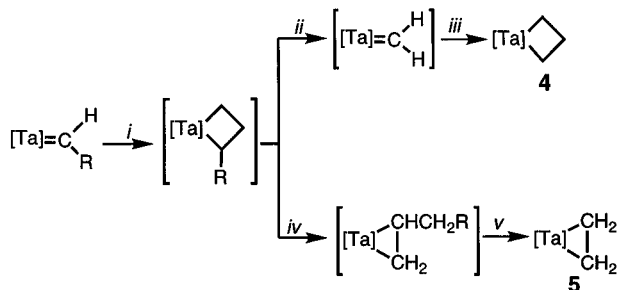
any reaction had taken place. The solution containing the mixture of **2b** and **2c** showed, as expected, the presence of **2a** from slow isomerization.

Reaction of a pentane solution of **3a** or **3b** (prepared *in situ*) with ethene at room temperature yields the new tantalacyclobutane complex [Ta{(CH₂)₃-1,3}(CNN)(O-*t*-Bu)₂], **4**, which precipitates from the solution and can be isolated in high yield (81% for **3a**) as a white solid (Scheme 4). Complex **4** is soluble in benzene, toluene, and diethyl ether, but is insoluble in pentane and hexane. Colorless needle-shaped crystals of **4** can be obtained from saturated diethyl ether solutions at -30 °C.

The supernatant pentane layer obtained after the reaction of neophylidene complex **3b** with ethene to afford **4** was collected, and the solvent was removed to afford a yellowish oil. This oil, which was further purified by bulb-to-bulb distillation, was found to contain, by GC-MS, the metathesis product 3-methyl-3-phenyl-1-butene. In contrast, the reaction of the alkylidene complex **3b** with an excess amount of the internal alkene *cis*-2-pentene (50 equiv) in benzene-*d*₆ does not afford a tantalacyclobutane complex and no metathesis product was identified.

The known alkylidene complex [Ta(=CH-*t*-Bu)(C₆H₄-CH₂NMe₂-2)(O-*t*-Bu)₂],^{1b} which contains a mono(*ortho*)-chelated arylamine was also tested for its metathesis reactivity with ethene. A pentane solution of this complex, like **3b**, also reacts with this alkene, but it is not a clean reaction and ¹H NMR spectroscopy of the reaction mixture showed a mixture of products.

Scheme 5. Postulated Mechanism for the Formation of 4 and 5 ($R = \text{CMe}_2\text{Ph}$, $[\text{Ta}] = \{\text{Ta}(\text{CNN})(\text{O}-t\text{-Bu})_2\}$)^a



^a Reaction conditions: (i) 25 °C, +C₂H₄; (ii) 25 °C, -C₁₁H₁₄; (iii) 25 °C, +C₂H₄; (iv) 69 °C; (v) 69 °C; +C₂H₄, -C₁₂H₁₆.

When ethene is bubbled through a hexane solution of the dialkoxide **3b** at 69 °C, the new alkene adduct complex $[\text{Ta}(\text{CNN})(\text{O}-t\text{-Bu})_2(\text{H}_2\text{C}=\text{CH}_2)]$, **5**, is formed together with some tantalacyclobutane complex **4** and both of these complexes precipitate directly from the solution as a yellow and white solid, respectively (Scheme 4). A ¹H NMR spectrum of the isolated crude product mixture in benzene-*d*₆ shows it to contain complexes **4** and **5** in a ratio of approximately 25:2. Bright yellow crystals of **5** can be obtained from a saturated diethyl ether solution of the crude product mixture of **4** and **5** at -30 °C. Complex **5** is soluble in diethyl ether, benzene, and toluene, but it is insoluble in pentane or hexane. In the solid state, **5** is stable under an inert atmosphere at -30 °C for months, but in diethyl ether solution at 25 °C, there is evidence of decomposition within several days.

The supernatant hexane layer from the reaction of **3b** with ethene that affords the mixture of **4** and **5** was examined for the presence of organic products. Removal of volatiles and subsequent workup as described above (synthesis of **4**) afforded a colorless oil, and GC-MS analysis of this showed the presence of both 3-methyl-3-phenyl-1-butene, which is the metathesis product, and 4-methyl-4-phenyl-1-pentene, which is the product formed after reductive rearrangement of the intermediate tantalacyclobutane ring. The formation of these organic products is explained in the following paragraph.

Proposed Mechanism for the Formation of Complexes 4 and 5. A mechanism that accounts for the formation of the tantalacyclobutane complex **4**, the ethene adduct complex **5**, and the organic products from the reaction of **3b** with ethene is presented in Scheme 5. This mechanism most likely involves an α -substituted tantalacyclobutane intermediate, which is formed by reaction of alkylidene complex **3b** with 1 equiv of ethene (step *i*). In step *ii* (at 25 °C), a metathesis reaction takes place by which 3-methyl-3-phenyl-1-butene and a methylene complex are formed. Further reaction of this latter species with ethene affords, in step *iii*, the tantalacyclobutane complex **4**. At elevated temperatures, step *iv* becomes operative in which a β -H elimination affords a hydrido alkyl complex, which then rearranges by a reductive elimination reaction to a 4-methyl-4-phenyl-1-pentene adduct complex. Subsequently, the olefin is displaced in step *v* by excess ethene to afford complex **5**. An alternative mechanism for the formation of the alkene adduct complex **5** could involve a β -H elimination of complex **4** and a reductive elimination of the resulting hydrido alkyl complex (like that shown in step *iv*) to afford a propene adduct complex;

subsequent substitution of propene for ethene gives complex **5**.

To test this alternative mechanism, a stirred benzene solution of complex **4** was warmed to 80 °C for 16 h, but after this time a ¹H NMR spectrum of the mixture showed no evidence for an alkene adduct complex, i.e., this alternative mechanism is not operative in the formation of complex **5**.

Temperature dependent reactivity of an alkylidene complex with an alkene, as described for **2b** and ethene, has been reported before by van Doorn *et al.*¹¹ When they reacted $[\text{Ti}(\text{Cp})(=\text{CH}-t\text{-Bu})(\text{PMe}_2\text{CH}_2\text{C}(\text{O})\text{CMe}_2-o\text{-C}_6\text{H}_4\text{CMe}_2)]$ with ethene at room temperature, the α -substituted titanacyclobutane $[\text{Ti}(\text{Cp})(\text{CH}(t\text{-Bu})\text{CH}_2\text{-CH}_2\text{-1,3})(\text{PMe}_2\text{CH}_2\text{C}(\text{O})\text{CMe}_2-o\text{-C}_6\text{H}_4\text{CMe}_2)]$ was formed, whereas at higher reaction temperatures, they obtained the ethene adduct complex $[\text{Ti}(\text{Cp})(\text{PMe}_2\text{CH}_2\text{C}(\text{O})\text{CMe}_2-o\text{-C}_6\text{H}_4\text{CMe}_2)(\text{H}_2\text{C}=\text{CH}_2)]$, which is formed by a mechanism similar to that shown in Scheme 5 (steps *i*, *iv*, and *v*).¹¹

Molecular Structures of Complexes 4 and 5. In order to elucidate the coordination geometry of complexes **4** and **5**, X-ray single-crystal diffraction studies have been carried out; for complex **4**, we have determined the structures of both a monoclinic modification (**4m**) and an orthorhombic modification (**4o**). The solid state molecular structures of **4m** and **5** together with the adopted numbering scheme are shown in Figure 3, with relevant bond distances and bond angles for **4** (both modifications) and **5** being collected in Table 3. The monoclinic modification of **4** (**4m**) shows two crystallographically independent molecules (1 and 2) in the asymmetric unit (Figure 3).

The structure of complexes **4** (**4m** and **4o**) and **5** are very similar. Both **4** and **5** are mononuclear pentagonal bipyramidal species with the two nitrogen donors of the $\text{N}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2$ unit, the *C*_{ipso} atom of the aryl ring, and the two carbon atoms of the metallacycle in **4** or of the ethene in **5** forming the meridional plane, with the two alkoxide groups occupying the apical positions.

The $\text{C}_\alpha\text{-M-C}_\alpha$ angles of the metallacycle for the two modifications of **4** have values of 61.4(3)°, 61.3(2)° (**4m**), and 59.5(6)° (**4o**) with a corresponding $\text{M}\cdots\text{C}_\beta$ separation of 2.868(7), 2.889(8) (**4m**), and 2.846(19) Å (**4o**). The metallacyclobutane rings in both **4o** and **4m** are almost planar, and in the four-membered $\text{Ta}(1)\text{-C}(13)\text{-C}(14)\text{-C}(15)$ ring the dihedral angle between the planes $\text{C}(13)\text{-Ta}(1)\text{-C}(15)$ and $\text{C}(13)\text{-C}(14)\text{-C}(15)$ is 26.8(6)° for **4o** and 17.8(7)° for the two independent molecules of **4m**. Metallacyclobutane complexes of Ti,¹³ Mo,¹⁴ W,¹⁵ and Ta¹⁶ are well-known and described in the literature. The geometries of such molybdenum, tungsten, and tanta-

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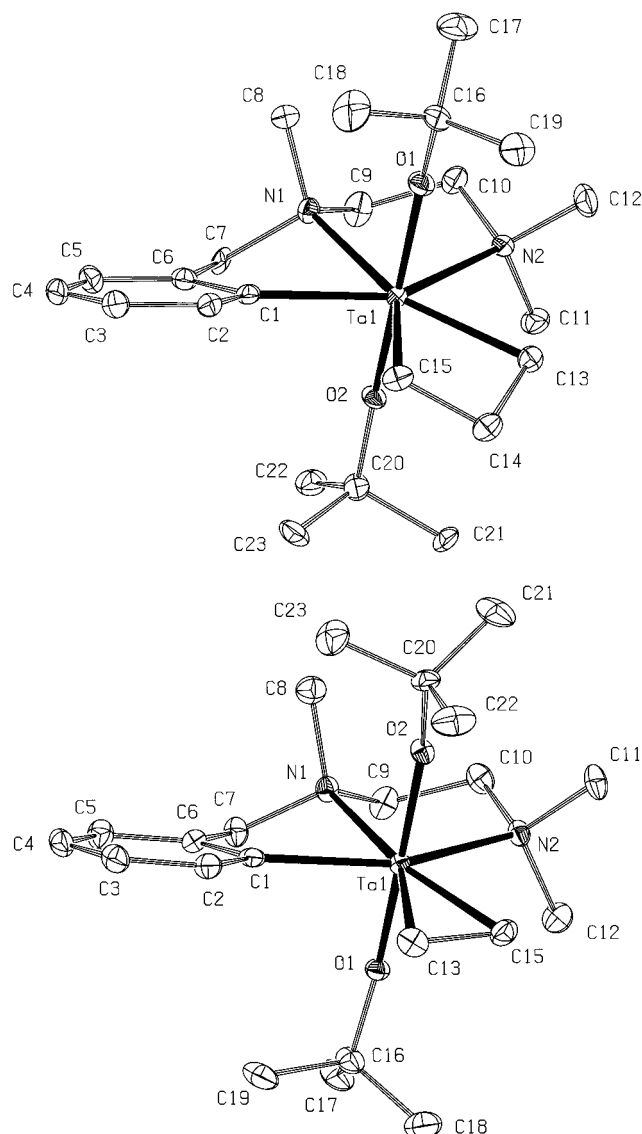


Figure 3. ORTEP²⁹ (30% probability level) drawing of (top) [Ta{(CH₂)₃-1,3}(CNN)(O-*t*-Bu)₂] (**4m**, monoclinic modification) and (bottom) [Ta(CNN)(O-*t*-Bu)₂(H₂C=CH₂)] (**5**). Hydrogen atoms have been omitted for clarity. Only one of the two independent molecules of **4m** is shown.

lum complexes fall primarily into two categories, namely square pyramidal or trigonal bipyramidal. Characteristic aspects of the metallacyclobutane ring in the square pyramidal complexes are the small C_α-M-C_α bond angles (63–65°) and large M···C_β distances (2.77–2.79 Å). For the trigonal bipyramidal complexes, the C_α-M-C_α angle becomes larger (82–84°) and M···C_β distances become smaller (2.3–2.4 Å). The first tantalacyclobutane complexes reported by Schrock and co-workers included square pyramidal [Ta{CH(Ph)CH(*t*-Bu)CH₂-1,3}(DIPP)₃] (DIPP = 2,6-diisopropylphenoxide) (C_α-M-C_α = 64.4 (9)°, M···C_β = 2.782 (24) Å) and trigonal bipyramidal [Ta{CH(C₅H₈)CHCH(*t*-Bu)-1,3}(DIPP)₃] (C_α-M-C_α = 78.7 (7)°, M···C_β = 2.382 (16) Å).^{16a} The small C_α-M-C_α angles (~60°) and large M···C_β distances (~2.8 Å) in both modifications of **4** make the metallacyclobutane ring in this complex

Table 3. Selected Bond Distances (Å) and Angles (deg) for **4m**, **4o**, and **5**

| | 4m | | 4o | 5 |
|-------------------|------------|------------|-----------|------------|
| | molecule 1 | molecule 2 | | |
| Ta(1)–O(1) | 1.902(5) | 1.907(5) | 1.867(12) | 1.912(4) |
| Ta(1)–O(2) | 1.893(5) | 1.899(5) | 1.862(13) | 1.892(4) |
| Ta(1)–C(1) | 2.281(7) | 2.286(7) | 2.220(19) | 2.235(6) |
| Ta(1)···C(14) | 2.868(7) | 2.889(8) | 2.846(19) | |
| Ta(1)–N(1) | 2.423(6) | 2.421(7) | 2.355(16) | 2.364(6) |
| Ta(1)–N(2) | 2.503(6) | 2.517(6) | 2.534(17) | 2.425(5) |
| Ta(1)–C(13) | 2.270(6) | 2.275(8) | 2.245(13) | 2.194(7) |
| Ta(1)–C(15) | 2.248(7) | 2.248(7) | 2.246(16) | 2.203(8) |
| C(13)–C(14) | 1.535(10) | 1.496(11) | 1.45(2) | |
| C(14)–C(15) | 1.514(10) | 1.515(11) | 1.47(3) | |
| C(13)–C(15) | | | | 1.491(9) |
| O(1)–Ta(1)–O(2) | 169.6(2) | 169.9(3) | 170.2(5) | 172.89(18) |
| O(1)–Ta(1)–C(13) | 93.4(3) | 92.2(2) | 93.9(6) | 92.4(2) |
| O(1)–Ta(1)–C(15) | 95.9(3) | 95.9(3) | 97.6(6) | 92.6(2) |
| O(1)–Ta(1)–C(1) | 92.6(2) | 92.2(2) | 90.9(6) | 89.5(2) |
| O(1)–Ta(1)–N(1) | 86.0(2) | 86.9(2) | 85.3(6) | 83.65(19) |
| O(1)–Ta(1)–N(2) | 85.9(2) | 86.7(2) | 85.6(5) | 85.46(17) |
| N(1)–Ta(1)–C(1) | 70.9(2) | 70.5(2) | 69.3(6) | 73.8(2) |
| N(1)–Ta(1)–C(15) | 147.6(2) | 148.0(2) | 147.9(6) | 161.7(2) |
| N(1)–Ta(1)–C(13) | 151.0(2) | 150.6(2) | 152.5(6) | 158.1(2) |
| N(1)–Ta(1)–N(2) | 72.3(2) | 72.2(2) | 71.6(5) | 74.44(19) |
| Ta(1)–O(1)–C(16) | 159.5(5) | 160.9(5) | 160.5(12) | 155.8(4) |
| Ta(1)–O(2)–C(20) | 161.9(5) | 162.5(5) | 166.4(11) | 161.9(4) |
| C(13)–Ta(1)–C(15) | 61.4(3) | 61.3(2) | 59.5(6) | 39.6(2) |
| Ta(1)–C(13)–C(14) | 95.9(4) | 97.9(5) | 98.4(11) | |
| Ta(1)–C(15)–C(14) | 97.4(4) | 98.1(5) | 97.7(11) | |
| C(13)–C(14)–C(15) | 98.3(6) | 99.6(6) | 99.2(16) | |

structurally comparable to that in the square pyramidal complexes of Mo, W, and Ta.^{14–16}

The structure of ethene complex **5** has a long olefinic C(13)–C(15) bond distance of 1.491(9) Å and short Ta(1)–C(13) and Ta(1)–C(15) distances of 2.194(7) and 2.203(8) Å. These parameters are typical for early transition metal alkene complexes and are specifically similar to those found for the neopentylethene adduct complex [TaCl₂(NCN)(H₂C=CHCH₂-*t*-Bu)], which has a C–C bond distance of 1.436(10) Å and Ta–C bond distances of 2.211(7) and 2.200(7) Å.^{1c,13} This complex was described as being a tantalacyclopentane species with tantalum in its highest oxidation state of +5, but we believe species of these type (including **5**) are better described as Ta(III)–alkene adducts.^{1c}

NMR Spectroscopy of Complexes 4 and 5. The ¹H NMR spectroscopic data for the tantalacyclobutane complex **4** and the ethene adduct complex **5** are in agreement with their pentagonal bipyramidal structures depicted in Figure 3. For example, both complexes afford two resonances for the Me groups of the diastereotopic NMe₂ unit and the ArCH₂N protons give rise to an AB pattern.

For **4**, characteristic resonances for the α-protons of the tantalacyclobutane ring are found between 0.61 and 1.58 ppm and the two β-proton resonances are found at 3.75 and 4.69 ppm. In the ¹³C NMR spectrum of **4**, this tantalacyclobutane ring provides resonances for the α- and β-carbons that have similar chemical shifts and ¹J(C,H) values close to 120 Hz, i.e., C_α, 23.7 (121 Hz) and 36.7 ppm (120 Hz); C_β, 25.0 ppm (120 Hz). These data are similar to those of the square pyramidal tantalum and tungsten metallacycle complexes with a large M···C_β separation reported by Schrock and co-workers.^{15a,16a}

For ethene adduct complex **5**, the resonances for the ethene protons are found as multiplets between 0.91 and 1.93 ppm; unfortunately, due to overlap with the O-*t*-Bu and N(Me)CH₂CH₂NMe₂ signals, we were unable to obtain reliable ²J(H,H) or ³J(H,H) values. In the ¹³C

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Table 4. Polymerization Reactions with Complexes **3b and **4**^a**

| compound | olefin monomer | temp (°C) | reaction time (h) | result | cis:trans ratio ^b |
|-------------------|--|-----------|-------------------|---------|------------------------------|
| 3b | NBE ^c | 25 | 12 | polymer | 10:90 |
| | NBE ^c | 70 | 1 | polymer | 12:88 |
| | DCPD ^d | 25 | 12 | polymer | |
| | C ₉ H ₁₂ O ₂ ^e | 70 | 12 | dec | |
| | C ₁₁ H ₁₆ O ^f | 70 | 12 | dec | |
| 4 | NBE ^c | 70 | 1 | polymer | 12:88 |
| | DCPD ^d | 70 | 1 | polymer | |
| | C ₉ H ₁₂ O ₂ ^e | 70 | 1 | dec | |
| | C ₁₁ H ₁₆ O ^f | 70 | 1 | dec | |
| [Ta] ^g | NBE ^c | 25 | instantly | polymer | 30:70 |

^a Conditions: 50 μmol of alkylidene or tantalacyclobutane in 1 mL of toluene added to 250 equiv of monomer in 10 mL of toluene. Solid polymers were obtained by quenching with benzaldehyde, precipitation with MeOH, filtration, and drying *in vacuo*. All monomeric olefin was consumed in the reaction stated, i.e., yields of polymeric material are 100%. ^b Determined by ¹H NMR (200.13 MHz, CDCl₃, 25 °C); data refers to the chloroform soluble fraction of the solid polymeric materials. ^c NBE = norbornene. ^d DCPD = dicyclopentadiene. ^e Methyl ester of bicyclo[2.2.1]hept-2-ene-2-carboxylic acid. ^f [(Bicyclo[2.2.1]hept-5-en-2-ylmethoxy)methyl]oxirane. ^g [TaCl(=CHCMe₂Ph)(O-*t*-Bu)₂(PMe₃)].

NMR spectrum of **5**, the ethene carbon resonances are found at 41.2 and 54.9 ppm with ¹J(C,H) values of 141 and 143 Hz, respectively. These ¹J(C,H) values fall at the end of the range of 142–156 Hz reported for other alkene complexes and compare well with those found for the dichloro complex [TaCl₂(NCN)(H₂C=CHCH₂-*t*-Bu)] (¹J(C,H) 145.5 and 139.2 Hz).^{1c,18}

Reactivity of Tantalum Complexes **2, **3**, and **4** with Strained Cyclic Olefins.** To study the possible ring-opening metathesis polymerization (ROMP) reactivity of the alkylidene complexes **2** and **3** and the tantalacyclobutane complex **4**, we have treated these complexes with strained cyclic olefins like norbornene and dicyclopentadiene.

The alkylidene complex **2** (mixture of isomers **2a–c**) did not show reactivity with norbornene; even after 4 days at room temperature in benzene no polymer signals were detected by ¹H NMR spectroscopy. The reactivity of complexes **2b** and **4** with acyclic olefins is similar, despite their structural differences, and both complexes show slow ROMP activity with norbornene or dicyclopentadiene at 25 °C in toluene (250 equiv of monomer converted in *ca.* 12 h); the polymerization rates can be greatly increased by performing the reactions at 70 °C (250 equiv of monomer converted in *ca.* 1 h). These results are summarized in Table 4.

Polynorbornene and polydicyclopentadiene were isolated as solid materials by quenching the reaction mixtures with benzaldehyde followed by precipitation with MeOH, filtration, and drying *in vacuo*. The polymeric material obtained from dicyclopentadiene is partially insoluble in benzene and chloroform; the insoluble fraction most probably consists of a cross-linked polymer that arises from the reaction of both olefin bonds in the starting monomer. The polynorbornene materials dissolve reasonably well in benzene and chloroform, and this has enabled us to study the *cis/trans* ratio of the vinylene bonds by ¹H NMR

Table 5. GPC Analysis of Polynorbornenes and Polydicyclopentadienes^a

| catalyst | equiv of NBE ^b | equiv of DCPD ^c | M _n | M _w /M _n |
|-----------|---------------------------|----------------------------|----------------|--------------------------------|
| 3b | 250 ^d | | 22 170 | 1.14 |
| 3b | 250 ^e | | 47 908 | 1.30 |
| 3b | | 250 ^d | 3254 | 1.23 |
| 4 | 250 ^e | | 12 243 | 1.29 |
| 4 | | 250 ^e | 31 823 | 1.26 |

^a Solid polymeric materials were prepared as indicated in Table 4. The data refer to 0.5 wt % solutions in THF (see Experimental Section). ^b NBE = norbornene. ^c DCPD = dicyclopentadiene. ^d Sample from a reaction mixture stirred for 12 h at 25 °C. ^e Sample from a reaction mixture stirred for 1 h at 70 °C.

spectroscopy (Table 4). The data in Table 4 show that when either the alkylidene complex **3b** or the tantalacyclobutane complex **4** is used as the catalyst, polycyclopentamers are obtained which contain *ca.* 90% *trans*-vinylene bonds.

The isolated polymers of norbornene and dicyclopentadiene dissolved in THF were analyzed by GPC, and the results, listed in Table 5, show that the materials obtained have low dispersities and low molecular weights. This could indicate that the system with **3b** and **4** involves living polymers, but kinetic data to substantiate this proposal is not available.

The ROMP reactivity of the alkylidene complex [TaCl(=CHCMe₂Ph)(O-*t*-Bu)₂(PMe₃)], which is the starting material for the synthesis of **3b**, was also tested with norbornene. This five-coordinate tantalum neophylidene complex in benzene solution at 25 °C polymerizes norbornene far more rapidly than **3b** and **4** (250 equiv of monomer were converted in *ca.* 2 min) and gives polycyclopentamers which contain approximately 70% *trans* vinylene bonds.

This difference in polymerization rate between a five-coordinate tantalum alkylidene complex and the six-coordinate complexes **3b** and **4** is notable, and this indicates that a free site for olefin coordination is a prerequisite. Accordingly, a likely mechanism for the reaction of the six-coordinate **3b** with a strained cyclic olefin (norbornene) involves (rate-determining) dissociation of the outer NMe₂ nitrogen donor of the CNN ligand from tantalum and subsequent coordination of the olefin to the five-coordinate tantalum center, which then leads to formation of a tantalacyclobutane. Opening of this tantalacyclobutane ring (that releases ring strain) generates an alkylidene species, which can then react further with the excess olefin to form a polymer. For the tantalacyclobutane complex **4**, the initiation step for polymerization could involve a rearrangement of the metallacycle to an "alkylidene/olefin" intermediate (as described earlier in the formation of **4**) which then loses ethene to afford a Ta=CH₂ (methylene) intermediate (Scheme 5, *vide supra*), which reacts with norbornene in the same way as described for complex **3b**. In the polymerization reaction of cyclic olefins the propagation step is very similar for complexes **2b** and **4**, and this might be the reason why the polymerization of norbornene affords in both cases polycyclopentamers with approximately 90% *trans*-vinylene bonds.

The observations here indicate that the presence of the weakly bonded NMe₂ nitrogen donor in **3b** hinders the initial coordination of the cyclic olefin to the metal by blocking a coordination site, and this reduces the reactivity of **3b** compared to that of the five-coordinate alkylidene complex [TaCl(=CHCMe₂Ph)(O-*t*-Bu)₂(PMe₃)]. The apparent necessity for dissociation of the NMe₂

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nitrogen donor from the metal center to allow polymerization to occur might also explain the lack of reactivity of the dichloro alkylidene complex **2** toward cyclic olefins. In complex **2**, both the inner N(Me) and the outer NMe₂ nitrogen donor atoms are strongly bonded to the metal center whereby it is not possible for the olefin to approach the metal center and react with the alkylidene functionality.

Conclusions

The present results show that tantalum alkylidene complexes which contain the mono(*ortho*)-chelating diamine ligand CNN are readily accessible. The dichloro complex, which contains two strong intramolecular Ta–N coordination bonds, shows no metathesis reactivity with ethene and no ROMP reactivity with norbornene. In contrast, the bisalkoxide analog, in which there is only strong Ta–N coordination of the inner N(Me) nitrogen donor atom with weak bonding of the outer NMe₂ nitrogen donor atom, shows interesting reactivity with olefins. For example, this bisalkoxide complex reacts with ethene at room temperature to give a stable tantalacyclobutane complex, and in addition, at higher temperatures, an alkene adduct complex is also formed. This complex also shows ROMP reactivity with the strained cyclic olefins norbornene and dicyclopentadiene. It seems, therefore, important for the reactivity of CNN tantalum alkylidene complexes that the coordination bond of the outer NMe₂ nitrogen donor atom to the metal should be weak in order to be able to easily create a more reactive five-coordinate alkylidene species. The results of current investigations of the reactivity of the tantalacyclobutane complex with mono-substituted olefins and small molecules like carbon monoxide and tert-butyl isocyanide will be reported in a following paper.¹⁹

Experimental Section

General. All experiments were performed in 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 AC 200 or AC 300 spectrometer; coupling constant data are from proton-coupled spectra. GC-MS measurements were carried out with a Unicam 610 instrument using electron impact (EI, 70 eV). Molecular mechanics MM2 calculations were performed with CAChe Scientific, Oxford Molecular Group, Inc., software. The complexes [Li{C₆H₄(CH₂N(Me)CH₂CH₂NMe₂)-2}]₂ (**1**),⁶ [TaCl(=CH-*t*-Bu)(O-*t*-Bu)₂(PMe₃)],⁷ and [TaCl₃(=CH-*t*-Bu)(THF)₂]⁵ were prepared according to literature procedures. The neophylidene complex [TaCl(=CHCMe₂-Ph)(O-*t*-Bu)₂(PMe₃)] was prepared as described for its neopentylidene analog starting from [TaCl₃(=CHCMe₂Ph)(PMe₃)].⁷ Ethene (Aldrich) and TaCl₅ (Alfa) were used as received. All polymer samples (0.5 wt % in THF) were analyzed by gel permeation chromatography (GPC) employing THF as eluent (flow rate: 1 mL/min) with a Waters 600E controller (490 UV 410RI detector), Maxima 820 software, and a PSS-SDV Gel Linear (5 μm) column from Stagroma. The molecular weights and polydispersities of polymers are reported relative to monodisperse polystyrene standards (Polymer Standard Services).

[TaCl₂(=CH-*t*-Bu){C₆H₄(CH₂N(Me)CH₂CH₂NMe₂)-2}], **2**. To a stirred purple solution of [TaCl₃(=CH-*t*-Bu)(THF)₂] (11.42 g, 22.7 mmol) in Et₂O (50 mL) at -78 °C was added within 1 min a solution of **1** (4.53 g, 23 mmol) in Et₂O (30 mL). The resulting mixture was allowed to warm over *ca.* 30 min to room temperature, and during this time, a brown suspension was formed. The solvent was removed *in vacuo*, and the remaining brown solid was extracted with C₆H₆ (2 × 100 mL). The combined extracts were stripped *in vacuo*, affording a brown solid which was subsequently extracted with Et₂O (2 × 100 mL). Removal of the solvent under reduced pressure followed by additional washing of the remaining red/brown solid with pentane (2 × 20 mL) afforded a red solid. Analysis of this solid by ¹H NMR spectroscopy revealed the presence of three isomers of **2** (**2a–c**), with approximately 80% of **2a** and 10% each of **2b** and **2c**; total yield 5.89 g (51%). Isomer **2a** was separated from **2b** and **2c** by an additional extraction of this solid mixture of isomers with cold Et₂O (50 mL), and slow cooling of the concentrated extract from +25 to -30 °C afforded block-shaped dark red crystals of **2a** in *ca.* 30% yield. Anal. Calcd for C₁₇H₂₉Cl₂N₂Ta (**2a**): C, 39.78; H, 5.69; N, 5.46. Found: C, 39.73; H, 5.75; N, 5.48. ¹H NMR (300 MHz, C₆D₆, 25 °C) (**2a**): δ 1.02 (s, 9 H, CMe₃), 1.70 (br m, 1 H, NCH₂CH₂N), 1.77 (s, 3 H, NMe), 2.10 (br m, 1 H, NCH₂CH₂N), 2.25 (br m, 2 H, NCH₂CH₂N), 2.57 (s, 3 H, NMe₂), 2.76 (s, 3 H, NMe₂), 2.79 (s, 1 H, Ta=CHCMe₃), 3.35 and 4.22 (d, ²J(H,H) = 13 Hz, 2 H, ArCH₂N), 7.02 (d, ³J(H,H) = 7 Hz, 1 H, ArH), 7.16 (m, 1 H, ArH), 7.27 (m, 1 H, ArH), 8.34 (d, ²J(H,H) = 7 Hz, 1 H, ArH). ¹³C{¹H} NMR (50 MHz, C₆D₆, 25 °C) (**2a**): δ 33.3 (CMe₃), 49.3 (NMe), 49.8 (NMe), 54.4 (NMe), 57.7 (NCH₂CH₂N), 58.6 (NCH₂CH₂N), 74.3 (ArCH₂N), 123.0 (Ar), 125.9 (Ar), 141.2 (Ar), 144.1 (Ar), 200.3 (C_{ipso}), 244.9 (Ta=CHCMe₃, ¹J(C,H) = 76 Hz).

Further concentration and recooling of the Et₂O solution from which **2a** was obtained afforded small amounts (*ca.* 0.5 g, 4%) of **2b** as needle-shaped purple crystals. ¹H NMR (200 MHz, C₆D₆, 25 °C) (**2b**): δ 1.28 (br m, 1 H, NCH₂CH₂N), 1.33 (s, 9 H, CMe₃), 1.49 (br m, 1 H, NCH₂CH₂N), 1.87 (s, 3 H, NMe), 2.00 (s, 1 H, Ta=CHCMe₃), 2.32 (br m, 1 H, NCH₂CH₂N), 2.61 (s, 3 H, NMe₂), 2.71 (s, 3 H, NMe₂), 2.74 (br m, 1 H, NCH₂CH₂N), 3.20 and 4.42 (d, ²J(H,H) = 14 Hz, 2 H, ArCH₂N), 6.97 (d, ³J(H,H) = 7 Hz, 1 H, ArH), 7.27 (m, 2 H, ArH), 9.04 (d, ³J(H,H) = 6 Hz, 1 H, ArH).

Complex **2c** was never isolated pure; the following selected data are from a 2:1 mixture of **2b** and **2c**. ¹H NMR (200 MHz, C₆D₆, 25 °C) (**2c**): δ 1.32 (s, 9 H, CMe₃), 1.80 (s, 3 H, NMe), 2.06 (s, 1 H, Ta=CHCMe₃), 2.60 (s, 3 H, NMe₂), 2.80 (s, 3 H, NMe₂), 3.18 and 4.54 (d, ²J(H,H) = 14 Hz, 2 H, ArCH₂N), 8.98 (d, ³J(H,H) = 7 Hz, 1 H, ArH).

[Ta(=CH-*t*-Bu){C₆H₄(CH₂N(Me)CH₂CH₂NMe₂)-2}(O-*t*-Bu)₂], **3a**. To a yellow solution of [TaCl(O-*t*-Bu)₂(=CH-*t*-Bu)(PMe₃)] (8.37 g, 17.7 mmol) in benzene (70 mL) was added within 1 min a solution of **1** (3.53 g, 17.8 mmol) in benzene (25 mL). There was an immediate color change from yellow to orange/red. The mixture was stirred for 48 h, during which time a brown suspension was formed. The solvent was removed *in vacuo*, and the remaining orange/brown oil was rigorously dried under reduced pressure to remove excess PMe₃ and 2,2-dimethylpropane. The orange/brown oil was extracted with pentane (2 × 100 mL), and the extracts were collected and concentrated *in vacuo* to *ca.* 15 mL. From this concentrated solution, the product **3a** crystallized overnight at -30 °C as block-shaped orange crystals; yield 4.25 g. The supernatant was decanted off from the crystals and concentrated further under reduced pressure; from this solution another 0.65 g of pure **3a** crystallized overnight at -30 °C; total yield 4.90 g (8.8 mmol, 47%). Anal. Calcd for C₂₅H₄₇N₂O₂Ta: C, 51.01; H, 8.05; N, 4.76. Found: C, 50.74; H, 8.11; N, 4.72. ¹H NMR (300 MHz, C₆D₆, 25 °C): δ 1.07 (br s, 9 H, CMe₃), 1.39 (br m, 2H, NCH₂CH₂N), 1.50 (br s, 9 H, OCM₃), 1.61 (br s, 9 H, OCM₃), 1.94 (s, 6 H, NMe₂), 2.42 (s, 1 H, Ta=CHCMe₃), 2.45 (br m, 2 H, NCH₂CH₂N), 2.57 (s, 3 H, NMe), 3.35 and 4.22 (d, ²J(H,H) = 13 Hz, 2 H, ArCH₂N), 7.02 (d, ³J(H,H) = 7

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Hz, 1 H, ArH), 7.16 (m, 1 H, ArH), 7.27 (m, 1 H, ArH), 8.34 (d, $^3J(\text{H,H}) = 7$ Hz, 1 H, ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, C_6D_6 , 25 °C): δ 33.6 (OCMe₃), 35.42 (CMe₃), 45.4 (CMe₃), 47.7 (NMe₂), 50.8 (NMe), 56.3 (NCH₂CH₂N), 56.7 (NCH₂CH₂N), 71.9 (ArCH₂N), 74.9 (OCMe₃), 78.0 (OCMe₃), 123.0, 123.5 (Ar), 126.0 (Ar), 140.8 (Ar), 144.4 (Ar), 199.3 (C_{ipso}), 216.4 (Ta=CHCMe₃, $^1J(\text{C,H}) = 78$ Hz).

[Ta(=CHCMe₂Ph){C₆H₄(CH₂N(Me)CH₂CH₂NMe₂)-2}-(O-*t*-Bu)₂], 3b. The synthesis of the neophylidene complex **3b** was carried out as described for its neopentylidene analog **3a**, starting from [TaCl(=CHCMe₂Ph)(O-*t*-Bu)₂(PMe₃)] (4.04 g, 7.07 mmol) and **1** (1.40 g, 7.06 mmol). After 48 h, the clear orange solution was evaporated *in vacuo* to afford the almost pure product as a red oil. This product, according to its ^1H NMR spectrum, contained trace amounts of tert-butylbenzene and O=PMe₃ that could not be removed under reduced pressure. Attempts to purify this red oil by recrystallization from a minimum amount of pentane at -30 °C were unsuccessful. Selected NMR data follow. ^1H NMR (300 MHz, C_6D_6 , 25 °C) (**3b**): δ 1.46 (s, 3 H, CMe₂Ph), 1.48 (s, 3 H, CMe₂Ph), 1.91 (s, 6 H, NMe₂), 2.41 (s, 3 H, NMe), 3.19 and 3.67 (d, $^2J(\text{H,H}) = 13$ Hz, 2 H, ArCH₂N), 8.30 (d, $^3J(\text{H,H}) = 7$ Hz, 1 H, ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, C_6D_6 , 25 °C): δ 47.7 (NMe₂), 50.8 (NMe), 71.9 (ArCH₂N), 199.3 (C_{ipso}), 216.4 (Ta=CHCMe₂-Ph, $^1J(\text{C,H}) = 78$ Hz).

[Ta{(CH₂)₃-1,3}{C₆H₄CH₂N(Me)CH₂CH₂NMe₂-2}-(O-*t*-Bu)₂], 4, from 3a. A yellow solution of **3a** (4.25 g, 7.19 mmol) in pentane (30 mL) was saturated with ethene. After about 15 min, a white solid precipitated and the suspension was stirred for an additional 1 h. Decantation of the pentane solution and subsequent drying of the solid residue under reduced pressure gave **4** as a white solid; yield 3.24 g (81%). Needle-shaped colorless crystals of **4** were obtained by slow cooling of a saturated solution in Et₂O from +25 to -30 °C. Anal. Calcd for C₂₃H₄₃N₂O₂Ta: C, 49.28; H, 7.73; N, 5.00. Found: C, 49.08; H, 7.54; N, 5.04. ^1H NMR (300 MHz, C_6D_6 , 25 °C): δ 0.61 (m, 1 H, CH₂CH₂CH₂), 0.76 (m, 1 H, CH₂CH₂CH₂), 0.87 (m, 1 H, CH₂CH₂CH₂), 1.16 (s, 9 H, OCMe₃), 1.25 (s, 9 H, OCMe₃), 1.58 (m, 1 H, NCH₂CH₂N; m, 1 H, CH₂CH₂CH₂), 1.68 (m, 1 H, NCH₂CH₂N), 2.07 (s, 3 H, NMe), 2.27 (s, 3 H, NMe), 2.28 (s, 3 H, NMe), 2.37 (m, 1 H, NCH₂CH₂N), 2.73 (m, 1 H, NCH₂CH₂N), 3.17 and 4.59 (d, $^2J(\text{H,H}) = 12$ Hz, 2 H, ArCH₂N), 3.75 (m, 1 H, CH₂CH₂CH₂), 4.69 (m, 1 H, CH₂CH₂CH₂), 7.17 (d, $^3J(\text{H,H}) = 8$ Hz, 1 H, ArH), 7.23 (t, $^3J(\text{H,H}) = 6$ Hz, 1 H, ArH), 7.39 (t, $^3J(\text{H,H}) = 7$ Hz, 1 H, ArH), 8.65 (d, $^3J(\text{H,H}) = 7$ Hz, 1 H, ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, C_6D_6 , 25 °C): δ 23.7 (CH₂CH₂CH₂, $^1J(\text{C,H}) = 121$ Hz), 25.0 (CH₂CH₂CH₂, $^1J(\text{C,H}) = 123$ Hz), 31.7 (OCMe₃), 31.9 (OCMe₃), 36.7 (CH₂CH₂CH₂, $^1J(\text{C,H}) = 120$ Hz), 46.9 (NMe), 48.9 (NMe), 50.4 (NMe), 56.7 (NCH₂CH₂N), 61.5 (NCH₂CH₂N), 70.4 (ArCH₂N), 78.8 (OCMe₃), 78.9 (OCMe₃), 122.9 (Ar), 124.7 (Ar), 126.4 (Ar), 137.5 (Ar), 148.0 (Ar), 191.5 (C_{ipso}).

[Ta{(CH₂)₃-1,3}{C₆H₄(CH₂N(Me)CH₂CH₂NMe₂)-2}-(O-*t*-Bu)₂], 4, from 3b. The neophylidene complex [Ta(=CHCMe₂-Ph){C₆H₄(CH₂N(Me)CH₂CH₂NMe₂)-2}-(O-*t*-Bu)₂], **3b**, can be formed *in situ* by a reaction of [TaCl(=CHCMe₂Ph)₂(O-*t*-Bu)₂(PMe₃)] with **1** in the same way as described for its neopentylidene analog **3a** and was isolated as an orange/red oil through removal of all volatiles *in vacuo*. Extraction of the oil with pentane (2 × 100 mL) and removal of the solvent under reduced pressure yielded **3b** as an orange oil. This orange oil was rigorously dried under reduced pressure for several hours to remove excess PMe₃ and was used without further workup in the synthesis of **4**. A solution of **3b** in pentane (100 mL) was saturated with ethene, and after *ca.* 30 min, complex **4** precipitated as a white solid from this solution. The solid was separated from the solution by decantation of the pentane layer and dried *in vacuo*. ^1H NMR spectroscopy of this solid showed it to be pure **4**. The pentane layer was evaporated under reduced pressure, and the remaining pale yellow oil was subject to bulb-to-bulb distillation to afford a colorless oil, which was shown by GC-MS to be a mixture of two organic compounds. GC-MS, *m/z*: (H₂C=CHCMe₂Ph) 146 [M]⁺, 131

[M - Me]⁺, 115 [M - 2Me]⁺; (PhCH₂N(Me)CH₂CH₂NMe₂) 192 [M]⁺, 134 [M - CH₂NMe₂]⁺.

[Ta{C₆H₄(CH₂N(Me)CH₂CH₂NMe₂)-2}-(O-*t*-Bu)₂-(H₂C=CH₂)], 5. An orange solution of **3b** in hexane (50 mL), which was synthesized *in situ* as described above, was heated to reflux and saturated with an ethene stream for 2 min. The heating source was removed, and the mixture was stirred for *ca.* 1 h at 25 °C. The mixture was reheated to reflux, and the procedure was repeated. After the mixture was stirred for *ca.* 1 h at 25 °C, during which time the color gradually changed from orange to bright-yellow, a yellow precipitate formed and the solution was then stirred for an additional 12 h at this temperature. The solid was isolated by decantation of the hexane layer and subsequent drying under reduced pressure. Analysis of the yellow solid product by ^1H NMR spectroscopy showed the presence of **4** and **5** in a ratio of 1:2.5. Block-shaped bright yellow crystals of **5** were obtained by slowly cooling down a saturated solution of the crude mixture of **4** and **5** in diethyl ether from +25 to -30 °C. Anal. Calcd for C₂₂H₄₁N₂O₂Ta: C, 48.35; H, 7.56; N, 5.13. Found: C, 48.22; H, 7.64; N, 5.11. ^1H NMR (300 MHz, C_6D_6 , 25 °C): δ 0.77 (s, 9 H, OCMe₃), 0.91 (s, 9 H, OCMe₃; m, 1 H, H₂C=CH₂), 1.25 (m, 2 H, H₂C=CH₂), 1.93 (m, 2 H, NCH₂CH₂N; m, 1 H, H₂C=CH₂), 2.27 (s, 3 H, NMe), 2.44 (s, 3 H, NMe), 2.51 (m, 1 H, NCH₂CH₂N), 2.63 (s, 3 H, NMe), 2.95 (m, 1 H, NCH₂CH₂N), 3.51 and 4.47 (d, $^2J(\text{H,H}) = 12$ Hz, 1 H, CH₂N), 7.28 (m, 2 H, ArH), 7.42 (m, 1 H, ArH), 8.98 (d, $^3J(\text{H,H}) = 7$ Hz, 1 H, ArH). $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz, C_6D_6 , 25 °C): δ 30.6 (OCMe₃), 31.2 (OCMe₃), 41.18 (H₂C=CH₂, $^1J(\text{C,H}) = 141$ Hz), 46.8 (NMe), 50.9 (NMe), 53.0 (NMe), 54.9 (H₂C=CH₂, $^1J(\text{C,H}) = 143$ Hz), 57.4 (NCH₂CH₂N), 61.5 (NCH₂CH₂N), 71.0 (ArCH₂N), 77.0 (OCMe₃), 77.3 (OCMe₃), 122.8 (Ar), 124.9 (Ar), 126.2 (Ar), 141.8 (Ar), 148.6 (Ar), 180.8 (C_{ipso}). The hexane layer, which was decanted from the reaction mixture, was evaporated under reduced pressure and subjected to bulb-to-bulb distillation to afford a colorless oil, which was subsequently analyzed by GC-MS. GC-MS, *m/z*: (H₂C=CHCMe₂Ph) 146 [M]⁺, 131 [M - Me]⁺, 116 [M - 2Me]⁺; (H₂C=CHCH₂CMe₂Ph) 160 [M]⁺, 119 [M - H₂C=CHCH₂]⁺; (PhCH₂N(Me)CH₂CH₂NMe₂) 192 [M]⁺, 134 [M - CH₂NMe₂]⁺.

X-Ray Structure Determination of 2a, 4, and 5. Crystallization of complex **4** yielded two different crystal shapes, needles and plates, which turned out to be monoclinic (**4m**) and orthorhombic (**4o**) modifications, respectively, of the same species. The crystals of the orthorhombic modification diffracted poorly (at $\theta = 24^\circ$, only 4% of the reflection data were above the 2.5 $\sigma(I)$ level), and the structure of **4o** is not illustrated in the results section.

Crystals suitable for X-ray diffraction were mounted on the tip of a glass fiber and were either transferred to an Enraf-Nonius CAD4-F diffractometer with a sealed tube at room temperature (**2a** and **4o**) or placed in the cold nitrogen stream on an Enraf-Nonius CAD4-T diffractometer on a rotating anode (**4m** and **5**). Accurate unit-cell parameters and orientation matrix were determined by least-squares fitting of the setting angles of 25 well-centered reflections (SET4).²⁰ The unit-cell parameters were checked for the presence of higher lattice symmetry.²¹ Crystal data and details on data collection and refinement are collected in Table 6. All data were collected in the $\omega/2\theta$ scan mode using Mo K α (wavelength 0.710 73 Å). Data were corrected for *Lp* effects and for the observed linear decay of the reference reflections. An empirical absorption correction was applied for all complexes (DI-FABS).²²

The structures of all complexes were solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92).²³ Complex **2a** was refined on *F* by full-matrix least-squares techniques (SHELX76).²⁴ All other structures were refined on *F*², also using full-matrix least-squares

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Table 6. Crystallographic Data for 2a, 4m, 4o, and 5

| | 2a | 4m | 4o | 5 |
|--|---|--|--|--|
| Crystal Data | | | | |
| formula | C ₁₇ H ₂₉ Cl ₂ N ₂ Ta | C ₂₃ H ₄₃ N ₂ O ₂ Ta | C ₂₃ H ₄₃ N ₂ O ₂ Ta | C ₂₂ H ₄₁ N ₂ O ₂ Ta |
| mol wt | 513.28 | 560.55 | 560.55 | 546.53 |
| cryst syst | monoclinic | monoclinic | orthorhombic | monoclinic |
| space group | <i>P</i> 2 ₁ / <i>c</i> (No. 14) | <i>P</i> 2 ₁ / <i>c</i> (No. 14) | <i>Pbca</i> (No. 61) | <i>P</i> 2 ₁ / <i>c</i> (No. 14) |
| <i>a</i> (Å) | 17.075(1) | 9.0403(5) | 14.9111(9) | 14.440(2) |
| <i>b</i> (Å) | 8.3212(4) | 16.8921(9) | 18.2260(12) | 9.2122(9) |
| <i>c</i> (Å) | 14.697(1) | 32.412(2) | 18.5459(12) | 19.495(3) |
| β (°) | 101.07(1) | 102.30(5) | 90 | 116.679(11) |
| <i>V</i> (Å ³) | 2049.3(2) | 4836.0(10) | 5040.2(6) | 2317.2(6) |
| <i>D</i> _{calcd} (g cm ⁻³) | 1.664 | 1.540 | 1.477 | 1.566 |
| <i>Z</i> | 4 | 8 | 8 | 4 |
| <i>F</i> (000) | 1008 | 2272 | 2272 | 1104 |
| μ (cm ⁻¹) | 55.6 (Mo K α) | 45.1 (Mo K α) | 43.8 (Mo K α) | 47.0 (Mo K α) |
| cryst size (mm) | 0.13 \times 0.28 \times 0.50 | 0.1 \times 0.2 \times 0.4 | 0.2 \times 0.4 \times 0.4 | 0.15 \times 0.15 \times 0.15 |
| Data Collection | | | | |
| <i>T</i> (K) | 298 | 150 | 298 | 150 |
| θ_{\min} (deg), θ_{\max} (deg) | 1.22, 27.5 | 0.64, 27.50 | 1.10, 24.20 | 1.17, 25.00 |
| SET4 θ_{\min} (deg), θ_{\max} (deg) | 9.46, 14.61 | 11.55, 13.95 | 6.76, 13.64 | 11.41, 13.97 |
| filter/monochromator | Zr filter | graphite monochromator | Zr filter | graphite monochromator |
| $\Delta\omega$ (deg) | 0.93 + 0.35 tan θ | 0.61 + 0.35 tan θ | 0.68 + 0.35 tan θ | 0.80 + 0.35 tan θ |
| hor., ver. aperture (mm) | 3.59, 4.00 | 3.00, 4.00 | 3.00, 4.00 | 3.00, 4.00 |
| X-ray exposure time (h) | 75 | 28 | 59 | 11 |
| linear decay (%) | 3 | 5 | 13 | 23 |
| reference reflns | 432; 323; 221 | 211; 222; 341 | 253; 424; 512 | 3,2,10; 353 |
| data set | -22:22, 0:10, -19:18 | 0:11, -21:0, -42:41 | 0:17, -21:0, -21:0 | -17:0, -1:10, -20:23 |
| total data | 5664 | 12 209 | 4520 | 4765 |
| total unique data | 4692 | 11 081 | 4040 | 4062 |
| no. obs data | 2331 [<i>I</i> > 2.5 σ (<i>I</i>)] | [no crit. applied] | [no crit. applied] | [no crit. applied] |
| abs corr range | 0.71–1.22 | 0.85–1.13 | 0.79–1.33 | 0.84–1.30 |
| Refinement | | | | |
| no. of refined params | 224 | 523 | 127 | 253 |
| final R1 ^a | 0.0490 [2331 <i>I</i> > 2.5 σ (<i>I</i>)] | 0.0450 [7621 <i>I</i> > 2 σ (<i>I</i>)] | 0.0874 [1215 <i>I</i> > 2 σ (<i>I</i>)] | 0.0347 [3301 <i>I</i> > 2 σ (<i>I</i>)] |
| final wR2 ^b | | 0.1072 | 0.1095 | 0.0784 |
| final <i>R</i> _w ^c | 0.0333 | | | |
| goodness of fit | 1.36 | 1.02 | 0.83 | 1.02 |
| <i>w</i> ⁻¹ ^d | $\sigma^2(F) + 0.000048 F^2$ | $\sigma^2(F^2) + (0.0475 P)^2$ | $\sigma^2(F^2) + (0.0100 P)^2$ | $\sigma^2(F^2) + (0.0412 P)^2 + 2.26 P$ |
| (Δ/σ) _{av} , (Δ/σ) _{max} | 0.040, 0.420 | 0.006, 0.562 | 0.005, 0.053 | 0.000, 0.001 |
| min and max | -1.65, 1.22 | -2.09, 1.60 | -1.74; 0.81 | -1.49, 1.37 |
| residual density (e Å ⁻³) | | | | |

^a R1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$. ^b wR2 = $[\sum \{w(F_o^2 - F_c^2)^2\} / \sum \{w(F_o^2)^2\}]^{1/2}$. ^c *R*_w = $[\sum \{w(|F_o| - |F_c|)^2\} / \sum \{w(F_o^2)\}]^{1/2}$. ^d *P* = (max(*F*_o², 0) + 2*F*_c²)/3.

techniques (SHELXL-93);²⁵ no observance criterion was applied during refinement on *F*². Hydrogen atoms were included in the refinement on calculated positions, riding on their carrier atoms, except for the alkylidene C_α hydrogen atom of complex **2a**, which was located on a difference Fourier map and subsequently included in the refinement. All methyl hydrogen atoms were refined in a rigid group, allowing for rotation around the C–C or N–C bonds. The non-hydrogen atoms of **2a**, **4m**, and **5** were refined with anisotropic thermal parameters. The data set of **4o** did not allow the anisotropic refinement of C, N, and O atoms. The hydrogen atoms of **2a** were refined with three overall isotropic thermal parameters with values of 0.110(11), 0.071(15), and 0.08(2) Å² for the hydrogen atoms of the CH₃, CH₂, and CH groups, respectively. The hydrogen atoms of the other complexes were refined with a fixed isotropic thermal parameter related to the value of the equivalent isotropic displacement parameter of their carrier atoms by a factor of 1.5 for the methyl and ethene hydrogens of **5** and a factor of 1.2 for all other hydrogen atoms.

Complex **2a** was refined using neutral atom scattering factors taken from Cromer and Mann²⁶ and anomalous dispersion corrections from Cromer and Liberman.²⁷ Neutral atom scattering factors and anomalous dispersion corrections were taken from the *International Tables for Crystallography*.²⁸ Geometrical calculations and illustrations were performed with PLATON;²⁹ all calculations were performed on a DEC station 5000 cluster.

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Supporting Information Available: Further details of structure determinations, including tables of atomic coordinates, bond lengths and angles, and thermal parameters (30 pages). Ordering information is given on any current masthead page.

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