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Configurational Preferences and Alkylidene-Centered Reactivity of Tantalum Alkoxide Complexes Containing an Aryldiamine Spectator Ligand[†]

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Transmetalation of Ta(=CH-*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,6}Cl_2 with LiO-*t*-Bu or KOMe affords monoalkoxide complexes Ta(=CH-*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,6}Cl(OR) (R = *t*-Bu, Me) in moderate yield. The *tert*-butoxide complex Ta(=CH-*t*-Bu)){$C_6H_3(CH_2NMe_2)_2$-2,6}Cl(O-*t*-Bu) reacts with (trimethylsilyl)ethene to afford a (trimethylsilyl)methylidene analogue *via* a quantitative alkene metathesis reaction. Transmetalation of Ta(=CH-*t*-Bu)Cl(O-*t*-Bu)$_2$(PMe_3) with $^1/_2$ equiv of [Li{$C_6H_3(CH_2NMe_2)_2$-2,6}]$_2$ gives the dialkoxide complex Ta(=CH-*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,6}(O-*t*-Bu)$_2$, **3d**, in moderate yield. Complex **3d** belongs to space group $P\bar{1}$ with $a = 9.3519(5)$ Å, $b = 9.4443(3)$ Å, $c = 18.1110(9)$ Å, $\alpha = 90.432(3)°$, $\beta = 100.241(4)°$, $\gamma = 116.593(3)°$, and $Z = 2$. The pentacoordinate tantalum center in **3d** has a distorted trigonal bipyramidal geometry with one of the NMe_2 units of the C,N-bidentate bonded aryldiamine (Ta−N(2) = 2.415(3) Å) and one of the alkoxide ligands in axial positions, while the second *o*-CH_2NMe_2 substituent is free (Ta···N(1) = 3.426(3) Å) but still *trans*-oriented to the alkylidene carbon atom. Complex **3d** reacts with (trimethylsilyl)ethene to afford its (trimethylsilyl)methylidene analogue. A dialkoxide complex, Ta(=CH-*t*-Bu)($C_6H_4CH_2NMe_2$-2)(O-*t*-Bu)$_2$, **3b**, that is related to **3d** but which contains only one *o*-amino substituent, can be prepared in a one-pot procedure by a sequence of transmetalation reactions starting from Ta(=CH-*t*-Bu)Cl_3(THF)$_2$ (THF = tetrahydrofuran), Zn($C_6H_4CH_2NMe_2$-2)$_2$, and LiO-*t*-Bu. All alkoxide complexes are fluxional in solution at room temperature and undergo dissociation/association processes involving the coordinative Ta−N bonds of the arylamine ligands.

Introduction

In research directed to the study of the influence of ligand geometry on metal-centered reactivity, we have used a monoanionic, potentially terdentate, aryldiamine ligand, {$C_6H_3(CH_2NMe_2)_2$-2,6}$^-$ (=NCN) to enhance the kinetic stability of organotransition metal complexes. With this aryldiamine ligand it has been possible to (i) stabilize organometallic compounds in which the metal has an unusual oxidation state, *e.g.* Fe(III),[1] Co(II),[2] and Ni(III),[3a] (ii) trap organometallic species that are proposed to be intermediates in basic reactions, for example organoplatinum compounds in which a diiodine molecule is coordinated end-on to platinum as a first step in oxidative-addition reactions,[4] (iii) use organonickel(II) compounds as catalysts in the selective Kharasch addition of polyhaloalkanes to alkenes,[5] and (iv) establish an unexpected reactivity of organocopper compounds toward alkynes.[6]

Figure 1 shows the reported bonding modes of the NCN ligand to a transition metal center.[1−14] The coordination mode of the NCN ligand is not limited to N,C,N-terdentate bonding (structures **C** and **D**) since noncoordination of one or two nitrogen donors allows it to bond either C,N-bidentate or even C-monodentate to a metal center (structures **B** and **A**, respectively). In principle, competition between intramolecular N-coordination of the NCN ligand and intermolecular coordination of suitable substrates is possible and this can provide a method to allow appropriate substrates to penetrate into the metal coordination sphere. The resulting substrate recognition may provide a basis for selective metal-mediated conversions.

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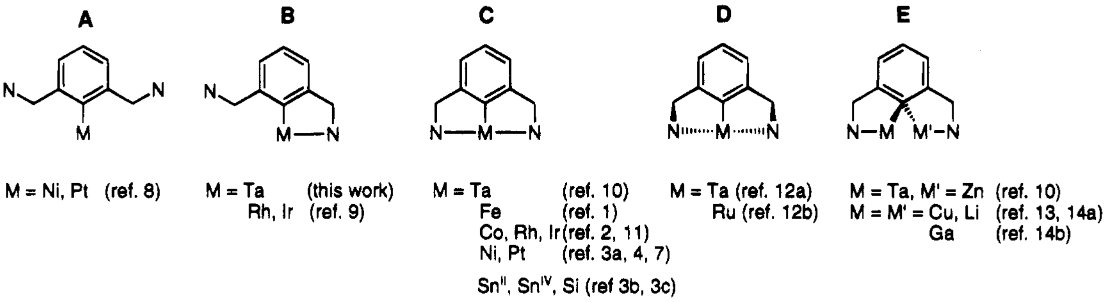
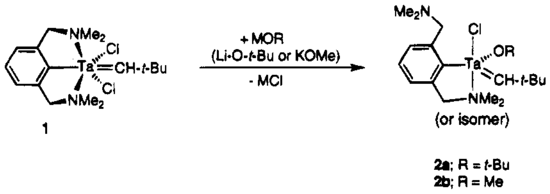


Figure 1. Reported bonding modes of the $\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}^-$ monoanion to transition metal centers with an indication of the metals involved.

The NCN ligand has been demonstrated to be extremely flexible in its coordination modes to a tantalum center, and the bonding modes **B** to **E** (see Figure 1) are known.[10,12a] This stimulated us to use the NCN monoanion to probe the possibility of achieving ligand-geometry-tuned metal reactivity in tantalum chemistry. For such research, alkene metathesis is a challenging reaction[15] that is well-documented in tantalum–alkylidene chemistry.[16,17] In a previous paper we described a tantalum alkylidene complex which contains the NCN ligand, Ta(=CH-*t*-Bu)(NCN)Cl_2, **1**,[12a] but which is not active in alkene metathesis reactions. In this paper we report the synthetic methods that lead to some mono- and dialkoxide derivatives of this complex. The alkylidene-centered reactivity of these alkoxide complexes with simple alkenes involves alkene metathesis reactions and some kinetic reaction control by the NCN ligand.

Results

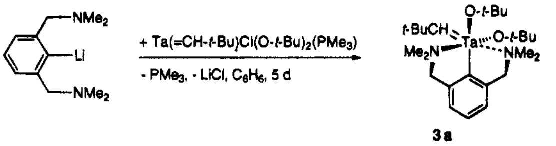
Synthesis of Tantalum Alkoxide Complexes Containing the NCN Ligand. Reaction of Ta(=CH-*t*-Bu)$\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}Cl_2$,[12a] **1**, with LiO-*t*-Bu in benzene gives a slow but very clean transmetalation in which one of the halogen atoms is substituted by a *tert*-butoxide ligand (eq 1) to provide the purple monoalkoxide complex Ta(=CH-*t*-Bu)$\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}$Cl(O-*t*-Bu), **2a**. The isolated yield of **2a** is only moderate (49%) because of its high solubility in apolar organic solvents (~1 g of **2a** dissolves in 1 mL of hexane) that hinders the crystallization step in its workup procedure.



(1)

In a way similar to that for the formation of **2a**, the neopentylidene complex **1** undergoes a clean transmetalation reaction with KOMe in Et_2O to afford the purple monoalkoxide complex Ta(=CH-*t*-Bu)$\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}$Cl(OMe), **2b**, in high yield (eq 1). Both monoalkoxide complexes **2** turn white on exposure to air but can be stored intact for months under a nitrogen atmosphere at room temperature.

When the reaction of **1** is performed with more than 1 equiv of the alkoxide reagent, either LiO-*t*-Bu or KOMe, no dialkoxide complexes are formed; *i.e* only monosubstituted **2a** or **2b** is obtained. In order to overcome this limitation we have tried an alternative synthesis for dialkoxides involving the transmetalation reaction between a dialkoxide tantalum alkylidene halide complex and the NCN monoanion. A suitable starting material is the phosphine complex Ta(=CH-*t*-Bu)Cl(O-*t*-Bu)$_2$(PMe$_3$)[16] that gives a clean—but slow—transmetalation reaction with [Li$\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}$]$_2$[18] in benzene to afford the yellow dialkoxide complex Ta(=CH-*t*-Bu)$\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}$(O-*t*-Bu)$_2$, **3a**, in moderate yield (eq 2). From hexane, complex **3a** crystallizes nicely in large, yellow parallellepipeda that readily decompose on contact with air but which



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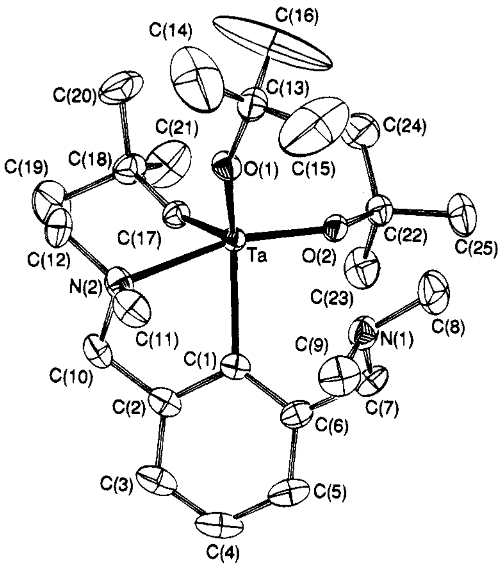
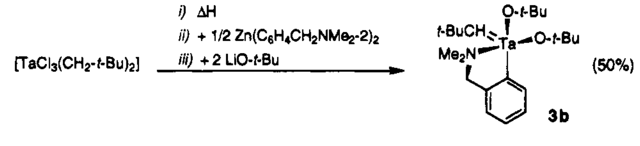


Figure 2. Structure of Ta(=CH-*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,6}(O-*t*-Bu)$_2$, **3a**, in the crystal; ORTEP drawing with 30% probability ellipsoids.

Scheme 1. One-Pot Procedure for the Synthesis of the Dialkoxide Complex 3b



i) Et_2O / THF (4 : 1), 20 °C; -CMe_4. *ii)* Et_2O, -78 °C; - 1/2 $ZnCl_2$, -2 THF. *iii)* Et_2O, 20 °C; - 2 LiCl .

can be stored intact for months under a nitrogen atmosphere at room temperature. Interestingly, a yellow dialkoxide complex Ta(=CH-*t*-Bu)($C_6H_4CH_2NMe_2$-2)(O-*t*-Bu)$_2$, **3b**, which is closely related to the dialkoxide **3a** but which contains the arylmonoamine ligand ($C_6H_4CH_2NMe_2$-2)$^-$, can be prepared readily in a one-pot procedure by a sequence of transmetalation reactions between Ta(=CH-*t*-Bu)Cl_3(THF)$_2$ (THF = tetrahydrofuran),[19] Zn($C_6H_4CH_2NMe_2$-2)$_2$,[20] and LiO-*t*-Bu (Scheme 1). The physical properties of dialkoxide complexes **3a** and **3b** are very similar.

Molecular Geometry and Crystal Structure of Ta(=CH-*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,6}(O-*t*-Bu)$_2$, 3a. An X-ray structural analysis of **3a** was carried out in order to elucidate the stereochemistry of the ligand distribution around tantalum and to aid interpretation of the temperature dependent spectroscopic data (*vide infra*). Suitable crystals of the dialkoxide complex **3a** were obtained by slowly cooling a pentane solution down to −30 °C. The crystal structure of **3a** involves the packing of two discrete mononuclear molecules in a triclinic unit cell. An ORTEP drawing of **3a**, along with the adopted numbering scheme, is shown in Figure 2; selected bond distances and angles are given in Table 1. The structure determination shows **3a** to be a mononuclear, pentacoordinate tantalum species Ta(=CH-*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,6}(O-*t*-Bu)$_2$ with a ligand array that is in between square pyramidal and trigonal bipyramidal (63% along the Berry pseudorotation coordinate toward the latter).[21] When the structure is described as trigonal bipyramidal, one of the NMe_2 units of the aryldiamine ligand [N(2)] and one of the alkoxide ligands [bonded *via* O(2)] occupy the axial positions [∠N(2)−Ta−O(2) = 163.73(11)°]. The equatorial plane contains the other alkoxide ligand [bonded *via* O(1)], the neopentylidene unit [bonded *via* C(17)], and the *ipso* carbon atom [C(1)] of the aryldiamine ligand. The ligands in the equatorial plane bend toward the neopentylidene unit: ∠C(1)−Ta−C(17) = 106.44(17)°, ∠O(1)−Ta−C(17) = 113.36(17)°. The other NMe_2 unit does not coordinate to the tantalum center [Ta···N(1) = 3.426(3) Å] but its free electron pair does seem to be directed toward the metal. The structural data for the neopentylidene grouping are in the same range as those found for other tantalum neopentylidene complexes.[22,23] These include the typically large Ta−C_α−C_β angle of 159.5(4)° and the short Ta=C_α bond length of 1.914(4) Å.

Table 1. Selected Data on the Geometry of 3a

	Bond Lengths (Å)		
Ta−O(1)	1.872(3)	O(1)−C(13)	1.417(6)
Ta−O(2)	1.914(3)	O(2)−C(22)	1.435(5)
Ta−N(2)	2.415(3)	C(17)−C(18)	1.512(6)
Ta···N(1)	3.426(3)	Ta−C(1)	2.242(4)
Ta−C(17)	1.914(4)		
	Bond Angles (deg)		
N(2)−Ta−O(2)	163.73(11)	Ta−O(1)−C(13)	154.9(3)
C(1)−Ta−C(17)	106.44(17)	Ta−O(2)−C(22)	141.6(2)
C(17)−Ta−O(1)	113.36(17)	Ta−C(17)−C(18)	159.5(4)
C(1)−Ta−O(1)	130.33(13)	C(17)−Ta−O(2)	103.67(15)
C(17)−Ta−N(2)	88.96(15)	N(2)−Ta···N(1)	99.70(10)
C(1)−Ta···N(1)	58.18(13)	O(2)−Ta···N(1)	64.84(9)

NMR Spectroscopy on the Alkoxide Complexes. The ^1H and ^{13}C NMR data of the alkylidene complexes **2** and **3** and some of their (trimethylsilyl)methylidene analogues (*vide infra*) are given in Tables 2 and 3. The NMR data are consistent with formulation of the complexes as tantalum alkylidenes containing an arylamine ligand that is at least monodentate bonded to tantalum with the aryl C_{ipso} atom. Characteristic for each complex is the low-field ^{13}C aryl C_{ipso} signal at δ 191−205 that compares nicely with data for other tantalum aryl complexes.[10,12,24] The alkylidene resonances at δ 225−267 together with their comparatively small $^1J(C_\alpha,H)$ values of 85−113 Hz are typical of electron-deficient alkylidene complexes.[25]

Table 2. Relevant ^1H NMR Data for the Cyclometalated Tantalum Alkylidene Complexes 1−3[a]

complex	CH_2N[b]	NMe	Ta=CH−	other
Ta(CH-*t*-Bu)(NCN)Cl_2 (**1**)	3.61, 4.36 (14)	2.58, 2.85	2.61	1.24 [C-*t*-Bu]
Ta(CH-*t*-Bu)(NCN)Cl(O-*t*-Bu)[c] (**2a**)	3.71,[d] 4.61[d]	2.85	5.86	1.19 [C-*t*-Bu] 1.48 [O-*t*-*Bu*]
Ta(CH-*t*-Bu)(NCN)Cl(OMe)[c] (**2b**)	3.68, 4.55 (14)	2.87	5.84	1.19 [C-*t*-Bu] 4.34 [OMe]
Ta($CHSiMe_3$)(NCN)Cl(O-*t*-Bu) (**2c**)	3.10 (12.6), 4.23,[d] 4.82[d]	2.43	6.96	1.49 [O-*t*-*Bu*] 0.49 [Si*Me*$_3$]
Ta(CH-*t*-Bu)(NCN)(O-*t*-Bu)$_2$ (**3a**)	3.31,[d] 4.76[d]	2.26	3.20	1.27 [C-*t*-Bu] 1.48 [O-*t*-*Bu*]
Ta(CH-*t*-Bu)(CN)(O-*t*-Bu)$_2$[f] (**3b**)	3.75[d]	2.32	3.17	1.26 [C-*t*-Bu] 1.50 [O-*t*-*Bu*]
Ta($CHSiMe_3$)(NCN)(O-*t*-Bu)$_2$[e] (**3c**)	3.9[g]	2.17	5.41	1.43 [O-*t*-*Bu*] 0.39 [Si*Me*$_3$]

[a] Measured in C_6D_6 at 298 K (unless otherwise stated), 200.13 MHz. Chemical shifts (δ ppm) indirectly referenced to $SiMe_4$ using solvent signals. NCN = $C_6H_3(CH_2NMe_2)_2$-2,6. [b] $^2J(H,H)$ (Hz) in parentheses. [c] In $CDCl_3$. [d] Unresolved, broad signals due to fluxionality; see text. [e] Data for *in situ* generated complex. [f] CN = $C_6H_4CH_2NMe_2$-2. [g] Very broad resonance, $\Delta\nu_{1/2}$ = 200 Hz.

Table 3. ^{13}C NMR Data for the Cyclometalated Tantalum Complexes 1−3[a]

	aryl							
complex	C(1)	C(2,6)	C(3,5)	C(4)	CH_2	NMe	Ta=CH(ZMe$_3$)[b]	O-*t*-Bu[c]
Ta(=CH-*t*-Bu)(NCN)Cl$_2$[d] (**1**)	195.4	147.5	122.5	128.9	73.2	49.3, 59.4	253.5 (78), 46.5, 34.2	
Ta(=CH-*t*-Bu)(NCN)Cl(O-*t*-Bu) (**2a**)	204.1	149	122.8	*e*	69.5	50.6	266.7 (88),[f] 42.2, 37.0	83.3, 31.8
Ta(=CH-*t*-Bu)(NCN)Cl(OMe)[d] (**2b**)	204.0	148.9	122.0	128.8	69.9	51.4	265.8 (113), 43.4, 36.1	62.6[g]
Ta(=CHSiMe$_3$)(NCN)Cl(O-*t*-Bu) (**2c**)	204.7	150	122.3, 123.0	129.0	69.6	51.4	238.3 (111), *h*, 4.55	83.2, 31.9
Ta(=CH-*t*-Bu)(NCN)(O-*t*-Bu)$_2$ (**3a**)	191.5	149.8	125.8, 126.6	*e*	68.9	46.8	224.5 (85), 44.9, 35.8	77.9, 33.1
Ta(=CH-*t*-Bu)(CN)(O-*t*-Bu)$_2$[i] (**3b**)	190.5				70.7	48.6	225.1 (97), 44.7, 35.8	77.7, 33.3

[a] In C_6D_6 at 298 K (unless otherwise stated), 50.32 or 75.47 MHz. Chemical shifts (δ, ppm) indirectly referenced to SiMe$_4$ using solvent signals. [b] Data sequence: C_α, C_β, C_γ; $^1J(C_\alpha,H)$ (Hz) in parentheses. [c] Data sequence: C_α, C_β. [d] In $CDCl_3$. [e] Resonance masked by solvent signal. [f] *J* value of major isomer at −60 °C in $CDCl_3$. [g] OMe resonance. [h] C_β not present. [i] CN = $C_6H_4CH_2NMe_2$-2.

Table 4. Relevant ^1H NMR Data for the Alkoxide Complexes in the Slow Exchange Limit[a]

compd	solvent	CH_2N[b]	NMe	Ta=CH−	other
2a, major[c]	$CDCl_3$	4.29 (2), 4.85 (2)	2.98 (6), 3.28 (6)	5.58	*d*
2a, minor[e]	$CDCl_3$	3.49 (1), 4.72 (1), 3.68 (1), 4.43 (1)	2.47 (3), 2.51 (3), 3.06 (6)	6.20	*f*
2a	toluene-d_8	2.96[g] (2), 4.09 (1), 4.90 (1)	1.99 (6), 2.66 (3), 3.11 (3)	6.13	*h*
2a	THF-d_8	3.61 (1), 4.82 (1), 3.88 (1), 4.58 (1)	3.60 (3), 2.65 (3), 3.20 (6)	6.27	*i*
2b	$CDCl_3$	3.77 (2), 4.39 (1), 4.72 (1)	2.68 (6), 3.04 (3), 3.21 (3)	6.10	*j*
2c	toluene-d_8	2.81 (1), 2.97 (1), 4.02 (1), 4.81 (1)	1.87 (3), 2.01 (3), 2.71 (3), 3.10 (3)	~7.0[k]	*l*
3a[m]	toluene-d_8	3.01 (1), 3.15 (1), 4.73 (1), 4.88 (1)	1.88 (3), 2.23 (6), 2.66 (3)	3.17	*n*
3b	toluene-d_8	3.06 (1), 4.30 (1)	1.91 (3), 2.65 (3)	3.14	*o*

[a] Chemical shifts (δ, ppm) indirectly referenced to SiMe$_4$ using solvent signals; measured at 213 K (200.13 MHz) unless otherwise stated with the number of protons per resonance given in parentheses. [b] Unless otherwise indicated, all resonances appear as doublets with $12 \le {}^2J(H,H) \le 14$ Hz. [c] Relevant ^{13}C NMR data (50.32 MHz): δ 50.4, 59.2 (NMe), 74.2 (CH_2N), 254.9 (Ta=C−, $^1J(C,H) = 88$ Hz). [d] 1.03 [CH-*t*-*Bu*], 1.56 [O-*t*-Bu]. [e] Relevant ^{13}C NMR data (50.32 MHz): δ 48.8, 50.8, 51.5, 52.3 (NMe), 68.9, 69.2 (CH_2N), 270.8 (Ta=C−, $^1J(C,H) = 107$ Hz). [f] 1.13 [CH-*t*-*Bu*], 1.38 [O-*t*-Bu]. [g] Triplet; $^2J(H,H) = 13$ Hz. [h] 1.45 [CH-*t*-*Bu*], 1.57 [O-*t*-Bu]. [i] 1.33 [CH-*t*-*Bu*], 1.52 [O-*t*-Bu]. [j] 1.17 [CH-*t*-*Bu*], 4.31 [OMe]. [k] Obscured by aryl H. [l] 0.63 [CHSi*Me*$_3$], 1.48 [O-*t*-Bu]. [m] At 200 K. [n] 1.39 [CH-*t*-*Bu*], 1.23, 1.65 [O-*t*-Bu]. [o] 1.19 [CH-*t*-*Bu*], 1.34, 1.64 [O-*t*-Bu].

The NMR spectra of the alkoxide complexes **2** and **3** are strongly temperature dependent and are consistent with these species being fluxional in solution (see Discussion); the low temperature (200−213 K) ^1H NMR data for the complexes are given in Table 4. For complexes **2** at room temperature only one methyl resonance is observed for the NMe_2 units while the CH_2N units give rise to unresolved or poorly resolved patterns. At low temperatures two to four NMe resonances are observed and all CH_2N units give rise to well-resolved doublets or AB patterns. At −60 °C in $CDCl_3$, the monoalkoxide complex Ta(=CH-*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,6}Cl(O-*t*-Bu), **2a**, exists as two isomers in a 1:3 ratio (see Figure 3) which is concentration independent in the range 0.05−1 M. Characteristic for the major isomer are two methyl resonances for the NMe_2 units at δ 2.98 (6H) and 3.28 (6H) and a single AB pattern (4H) for the CH_2N units (see Table 4). The minor isomer gives rise to three methyl resonances for the NMe_2 units at δ 2.47 (3H), 2.51 (3H), and 3.06 (6H) and two AB patterns for the CH_2N units. In a ^1H NOE-difference experiment (Figure 3), irradiation into the neopentylidene H_α resonance of the major isomer at δ 5.58 causes a decrease in the intensity of the neopentylidene H_α resonance of the minor isomer at δ 6.20. The intensities of the other resonances remain unaffected. The two isomers are, thus, interconverting on the laboratory time scale. At −60 °C in THF-d_8 or toluene-d_8 only one isomer is observed (see Table 4) with three methyl resonances in a 1:1:2 ratio for the NMe_2 units. For the other alkoxide complexes listed in Table 4 only one isomer is observed at low temperature.

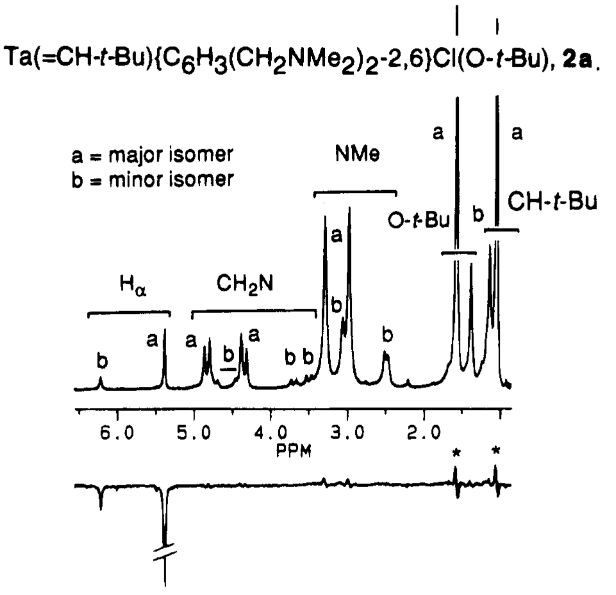


Figure 3. (Top trace) ^1H NMR spectrum (200.13 MHz, $CDCl_3$) of the two isomers of the monoalkoxide complex **2a** at −60 °C. (Bottom trace) NOE-difference spectrum obtained by irradiation into the alkylidene H_α resonance of the major isomer. (* = subtraction artifact.)

The ^1H NMR spectra (200.13 MHz, toluene-d_8) of the dialkoxide complexes **3** are very simple at room temperature (see Figure 4): only one sharp resonance is observed for both O-*t*-Bu groups, and the NMe_2 units also give only one resonance. At −60 °C, the signal for the O-*t*-Bu groups is split into two singlets; at this

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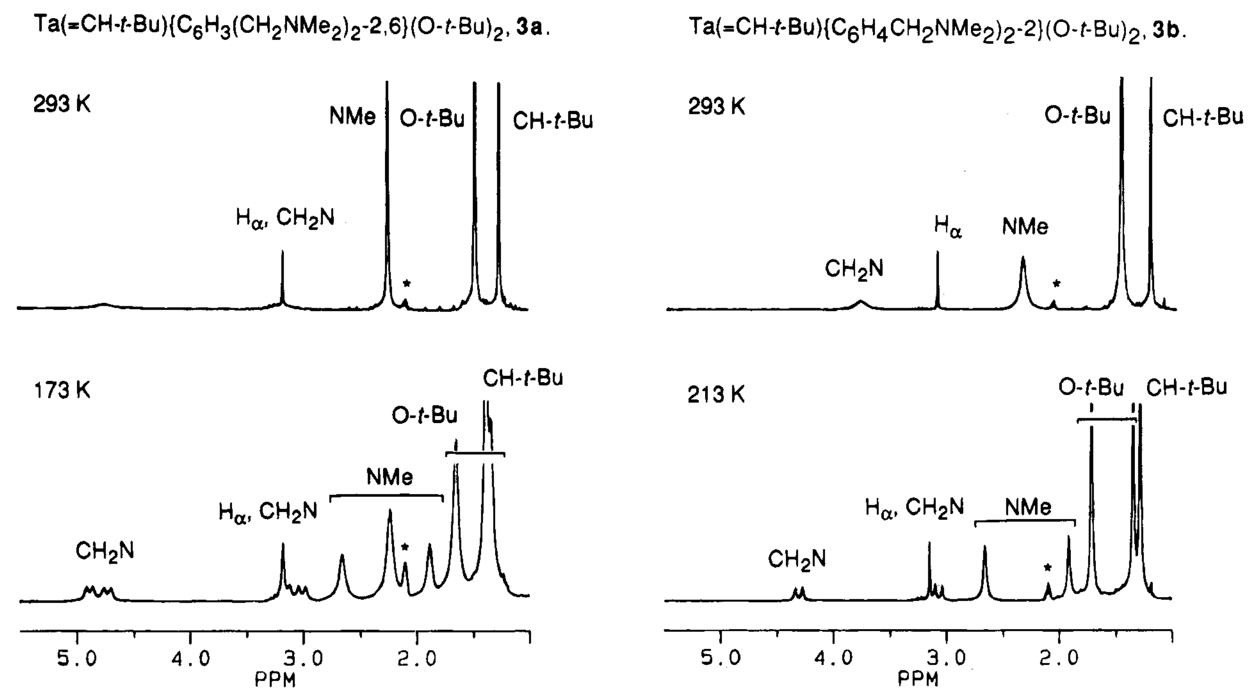

Ta(=CH-t-Bu){$C_6H_3(CH_2NMe_2)_2$-2,6}(O-t-Bu)$_2$, **3a**. Ta(=CH-t-Bu){$C_6H_4CH_2NMe_2$)$_2$-2}(O-t-Bu)$_2$, **3b**.

Figure 4. ^1H NMR spectra (200.13 MHz, toluene-d_8) of the dialkoxide complexes **3** at different temperatures. See the text and Table 4. (* = solvent.)

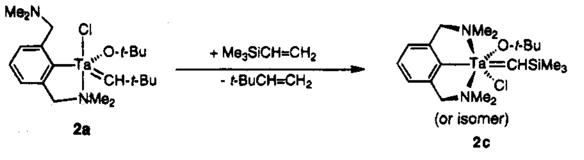
Table 5. Fluxional Processes in the Dialkoxide Tantalum Complexes 3

complex	grouping	T_c (K)	$\Delta G^{\ddagger}$ (kJ·mol^{-1})[a]
3a	O-*t*-Bu	230	47 ± 2
3a	NMe_2	230	45 ± 2
3a	CH_2N	213	44 ± 2
3a	CH_2N	300	57 ± 2
3b	O-*t*-Bu	260	53 ± 2
3b	NMe_2	273	53 ± 2
3b	CH_2N	273	52 ± 2

[a] Data calculated from ^1H NMR spectra (toluene-d_8, 200.13 MHz) using the chemical shift differences of the proton resonances in the slow exchange limit.

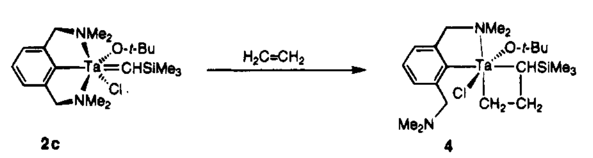
temperature the NMe_2 unit of the monoamine complex Ta(=CH-t-Bu)($C_6H_4CH_2NMe_2$-2)(O-t-Bu)$_2$, **3b**, gives two resonances while the two NMe_2 units of the aryldiamine complex Ta(=CH-t-Bu){$C_6H_3(CH_2NMe_2)_2$-2,6}(O-t-Bu)$_2$, **3a**, afford three distinct resonances with relative intensities 1:1:2 (Figure 4). In a ^1H NOE-difference experiment performed with **3a** (−70 °C, toluene-d_8), irradiation into the NMe resonance at δ 2.33 (6H) causes a clear decrease in the intensities of the other NMe resonances at δ 1.88 (3H) and 2.66 (3H); these data are used later (see Discussion) to help propose the solution structure for this complex. The initially broad signals for the CH_2N functions change upon lowering the temperature and split into one AB pattern for **3b** and (*via* one AB pattern) finally into two AB patterns for **3a**. Table 5 gives a listing of the parameters that quantify the observed processes.

Preliminary Study of the Reactivity of the Alkoxide Complexes with Simple Alkenes. The *tert*-butoxide complex Ta(=CH-t-Bu){$C_6H_3(CH_2NMe_2)_2$-2,6}Cl(O-t-Bu), **2a**, reacts at low temperature (*ca.* −60 °C) with ethene in either THF, toluene, or chloroform to generate a yellow complex that decomposes at ±0 °C in an unclean fashion without liberating any alkenes. In contrast the methoxide analogue Ta(=CH-t-Bu){$C_6H_3(CH_2NMe_2)_2$-2,6}Cl(OMe), **2b**, gives directly at −60 °C an unclean reaction with ethene. With (trimethylsilyl)ethene **2a** gives a clean reaction at 20 °C that leads to the quantitative formation of *tert*-butylethene and an orange alkylidene complex, Ta(=$CHSiMe_3$){$C_6H_3(CH_2NMe_2)_2$-2,6}Cl(O-t-Bu), **2c** (eq 3).



(3)

The alkylidene complex **2c** reacts instantaneously with ethene at room temperature in benzene or pentane to afford a tantalacyclobutane complex, Ta{CH($SiMe_3$)CH_2CH_2-1,3}{$C_6H_3(CH_2NMe_2)_2$-2,6}Cl(O-t-Bu), **4** (eq 4)



(4)

which could be characterized by ^1H and ^{13}C NMR but which decomposes slowly in solution in an unclean fashion liberating ethene (in C_6D_6 ~20% decomposition in 18 h at 20 °C). Complex **4** was successfully recrystallized from hexane at low temperature as thin plates that were, however, unsuitable for an X-ray diffraction study.

With (trimethylsilyl)ethene **3a** reacts slowly (~70% conversion in 22 h) with liberation of t-BuCH=CH_2 to produce the expected (trimethylsilyl)methylidene complex Ta(=$CHSiMe_3$){$C_6H_3(CH_2NMe_2)_2$-2,6}(O-t-Bu)$_2$, **3c**.

Discussion

Coordination of NCN and Fluxionality in the Alkoxide Complexes 2 and 3. Fluxionality and different isomers of electron-deficient tantalum alkylidene complexes are common. For example, complexes of the type Ta(=CHR)Cl_3(L)$_2$ (R = Ph, t-Bu; L = phosphine, pyridine, THF) exist in solution as inter-

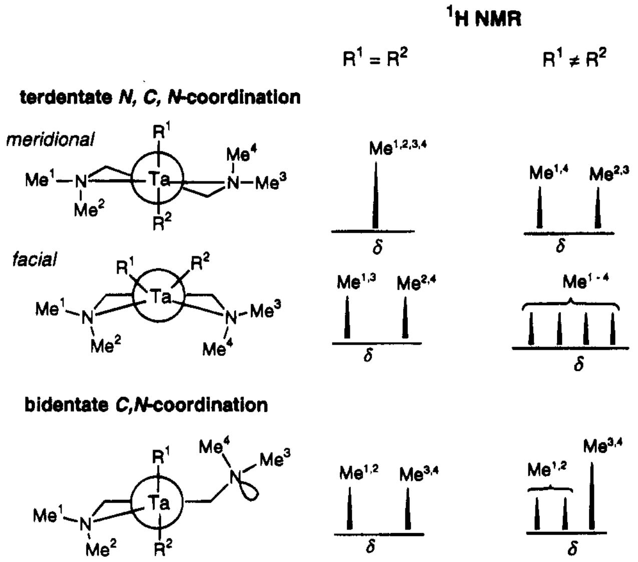


Figure 5. Discrimination of N,C,N bonding modes in complexes **2** and **3** by analysis of the ¹H NMR NMe resonances. In the meridional N,C,N bonding case fast flipping of the five-membered chelate is assumed to occur and this generates the given equivalence between pairs of Me groups.[8a]

converting isomers that have either a *trans,mer* or a *cis,mer* coordination of the ligand L. For these complexes it has proven difficult to rationalize the observed isomer ratio that is a function not only of the substituent R and the ligand L, but also of the solvent.[19] For the monoalkoxide substituted neopentylidene complex Ta(=CH-*t*-Bu)Cl$_2$(O-*t*-Bu)(PMe$_3$)$_2$, that is related to the monoalkoxide NCN complexes **2**, two isomers have been reported with the major one having *trans*-positioned phosphine ligands; the position of the alkoxide ligand is unknown (either equatorial or axial).[16] Fluxionality of tantalum alkoxide complexes is generally more pronounced than that of isoelectronic tantalum halide complexes and is due to p$\pi \rightarrow$ dπ electron donation of the alkoxide ligands to the metal center (*vide infra*). This electron donation provides a way for the tantalum center to alleviate the increased electron deficiency that results from dissociation of a coordinative Ta—L bond. The electronic properties of the alkoxide ligands thus assist (entropy favored) Ta—L dissociation.

For complexes Ta(=CH-*t*-Bu){C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}Cl(OR), **2**, and Ta(=CH-*t*-Bu){C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}(OR)$_2$, **3c,d**, inspection of the number and the intensity of the methyl resonances of the NMe$_2$ units in their slow exchange limit (Table 4), allows an unambiguous determination of the NCN coordination mode as either N,C,N-terdentate or C,N-bidentate (Figure 5). With facial terdentate N,C,N-coordination the two NMe$_2$ units can give rise to either two or four methyl resonances depending on the positioning of the other three ligands; similarly, with meridional terdentate N,C,N-coordination the two NMe$_2$ units can give rise to either one or two methyl resonances.[8a] With C,N-bidentate coordination of NCN there are two possibilities of either two NMe resonances in a ratio of 1:1 or of three resonances in a 1:1:2 ratio. In the latter case the signal with higher intensity is from the noncoordinating NMe$_2$ unit that can render its methyl groupings homotopic by a process involving pyramidal inversion at the nitrogen center followed by 180° rotation around the ArCH$_2$—NMe$_2$ bond.

On this basis it can be concluded from Table 4 that at low temperatures the coordination mode of NCN is N,C,N-facial terdentate for **2c**, while it is C,N-bidentate not only for the minor isomer of **2a** but also for **2b**, **3a**, and **3b** and N,C,N-meridional terdentate for the major isomer of **2a**.

Interconversion of the Isomers of Ta(=CH-*t*-Bu){C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}Cl(O-*t*-Bu), 2a. From the NOE-difference experiment performed with **2a** in CDCl$_3$ (see Figure 3), it is clear that these isomers interconvert on the NOE time scale and thus the laboratory time scale even at −60 °C. Although we conclude that the isomers interconvert by a process involving dissociation/association of one of the Ta—N coordinative bonds, without structural data for an isomer of **2a**, any detailed explanation for this process is speculative. A tentative explanation is that the isomers are based on two different conformations of the bulky neopentylidene ligand and that changes in steric hindrance between it and one of the NMe$_2$ units upon going from one isomer to the other leads to Ta—N dissociation/association. Support for such a postulate comes from the recent finding of alkylidene rotamers.[26]

Structure of the Dialkoxide Complexes 3 in the Solid State and in Solution. When the structure of the dialkoxide complex **3a** is compared with that of the related dichloride complex Ta(=CH-*t*-Bu){C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}Cl$_2$, **1**, one sees that their coordination geometries are related but differ with respect to the positioning of the neopentylidene unit (Figure 6). In the dichloride complex **1**, which contains an NCN ligand that is a pseudofacially terdentate N,C,N bonded ligand,

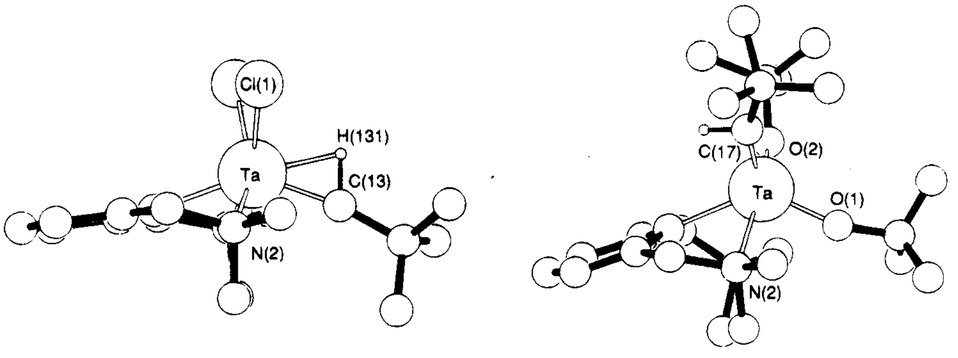


Figure 6. Drawings showing (left) the terdentate N,C,N coordination of NCN in the dichloride complex **1** [Ta—N = 2.345(4), 2.373(4) Å] and (right) the bidentate N,C coordination mode of NCN in the dialkoxide complex **3a** [Ta—N = 2.415(3), Ta⋯N = 3.426(3) Å].

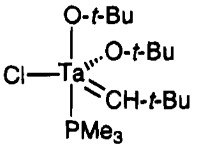


Figure 7. Schematic drawing of $Ta(=CH\text{-}t\text{-}Bu)Cl(O\text{-}t\text{-}Bu)_2(PMe_3)$.

the chlorine atoms are *trans* to the two NMe_2 units and the alkylidene α-C atom is *trans* to C_{ipso} of the NCN system. The facial N,C,N bonding originates from the *trans* influence of the neopentylidene function that would strongly weaken a tantalum-to-carbon bond located exactly *trans* to the alkylidene group ($\angle C_{ipso}-Ta-C_\alpha = 139°$).[22] The other possible geometry contains an alkylidene group *trans* positioned to one of the NMe_2 units but this would cause steric hindrance between the *t*-Bu group of the alkylidene group and the NMe_2 units. In contrast, in the dialkoxide complex **3a** the neopentylidene unit is *trans* to one of the NMe_2 units. In this case the alkoxide groups are as bulky as the alkylidene group, so for steric reasons there is no preference in having either an alkoxide or alkylidene group *cis* to the NMe_2 units. Electronically, the geometry with the alkylidene group *trans* to one of the NMe_2 units leads to lengthening of the Ta—N bond (and C,N-bidentate bonding of NCN as in **3a**): the alkylidene group *trans* to $M-C_{ipso}$ would weaken this bond because of the *trans* influence of the alkylidene group. It is interesting to note that in the structure of **1** the NCN ligand is present in a conformation that is strikingly comparable with the conformation of this aryldiamine ligand when it is facially bonded (N—Ta- - -N = 99.70(10)°). A view along the aryl plane of NCN for both **1** and **3a** shows this point clearly. An obvious difference is the presence of two equal M—N bonds of 2.345(4) Å in **1** and one short and one long M—N bond in **3a**, but the facial conformation of NCN remains, suggesting that the facial orientation may be a ground state configuration for the NCN anion in Ta—NCN chemistry.[40]

The trigonal bipyramidal coordination geometry as found for the alkylidene complex **3a** (eq 2) is favored in many alkylidene complexes[22] and is, for example, similar to the one proposed for a related dialkoxide complex, $Ta(=CH\text{-}t\text{-}Bu)Cl(O\text{-}t\text{-}Bu)_2(PMe_3)$ (see Figure 7).[16] The large Ta—O—C angles and the short Ta—O distances in the structure of **3a** [∠Ta—O(1)—C(13) = 154.9°, Ta—O(1) = 1.872 Å; ∠Ta—O(2)—C(22) = 141.6°, Ta—O(2) = 1.914 Å] are comparable to those in other tantalum alkoxide complexes [the angles range from 144.8 to 167.6° and bond lengths range from 1.897 to 1.903 Å].[27,28] The larger M—O—C angles and shorter M—O distances[29] in these complexes originate from $p\pi \rightarrow d\pi$ electron donation from one or two of the oxygen lone pairs to vacant d-orbitals on tantalum, leading to tantalum—oxygen π-bonds.[30] The overlap of the filled oxygen p-orbitals with empty metal d-orbitals thus gives rise to additional π^2 to π^4 interactions; without such additional coordination the complexes **3** would be very electron-deficient 12-electron complexes. In this respect $Zr(OC\text{-}t\text{-}Bu_3)_2X_2$[31] is an extreme case that can even be regarded as an analogue of $ZrCp_2X_2$ with each OC-*t*-Bu_3 ligand donating 5 electrons to Zr. The short Zr—O distance of 1.895 Å and the large Zr—O—C angle of 169° are consistent with a high degree of electron donation from the alkoxide ligands to the metal. In addition, there is a correlation between M—O distances and M—O—C angles as a function of the presence and accessibility of empty metal d-orbitals in molybdenum alkoxide complexes.[30] When no d-orbitals are available, for instance because they are used for metal-to-metal bonding as in $Mo_2(OR)_4L_4$ complexes, the M—O—C angle decreases to 120° and the M—O bond length is increased by 0.1 Å. The fact that for the present tantalum complex **3a** the Ta—O(1) bond length is smaller compared to Ta—O(2) and the Ta—O(1)—C(13) angle is larger compared to Ta—O(2)—C(1) indicates that there is more $p\pi \rightarrow d\pi$ electron donation between the oxygen lone pairs of the alkoxide *trans* to the C_{ipso} than for the alkoxide *trans* to the nitrogen donor. This could be due to $d\pi \rightarrow \pi^*$ electron donation from filled d-orbitals on tantalum to the antibonding orbitals of the aromatic ring.

The strongly temperature dependent solution ^1H NMR spectra of the dialkoxide complexes **3** (see Figure 4) are indicative of fluxional behavior. The NOE-difference experiment performed with **3a** showed that the coordinating and uncoordinated NMe_2 units are equilibrating, *i.e.* the fluxionality involves a Ta—N dissociation/association process. A detailed discussion of this observation is easiest when the fluxionality of the monoamine complex **3b** is described first and used as a basis for comparison with the more complex fluxional processes that occur with the diamine complex **3a**.

The fluxionality of **3b** (and **3a**) involves equilibration of the O-*t*-Bu, CH_2N, and NMe_2 groupings present in the molecule. Moreover the equilibrations of these groupings are likely to occur in a concerted fashion since they are associated with the same value of $\Delta G^\ddagger$ of 53 $kJ\cdot mol^{-1}$ (see Table 5). A process that provides a way to racemize two enantiomeric forms of **3b** and thus to render all the diastereotopic groups in this complex homotopic is shown in Scheme 2 and involves (i) Ta—N dissociation from the Ta—C—O′ plane, leading to a "tetrahedral" intermediate, (ii) 180° wagging around $Ta-C_{ipso}$, and (iii) face-centered nucleophilic attack on the Ta—C—O plane. A similar process is likely to occur in the related complex **3a** (Scheme 2, process i) and can be associated with a slightly higher value of $\Delta G^\ddagger$ (57 $kJ\cdot mol^{-1}$, see Table 5). However, since **3a** contains a

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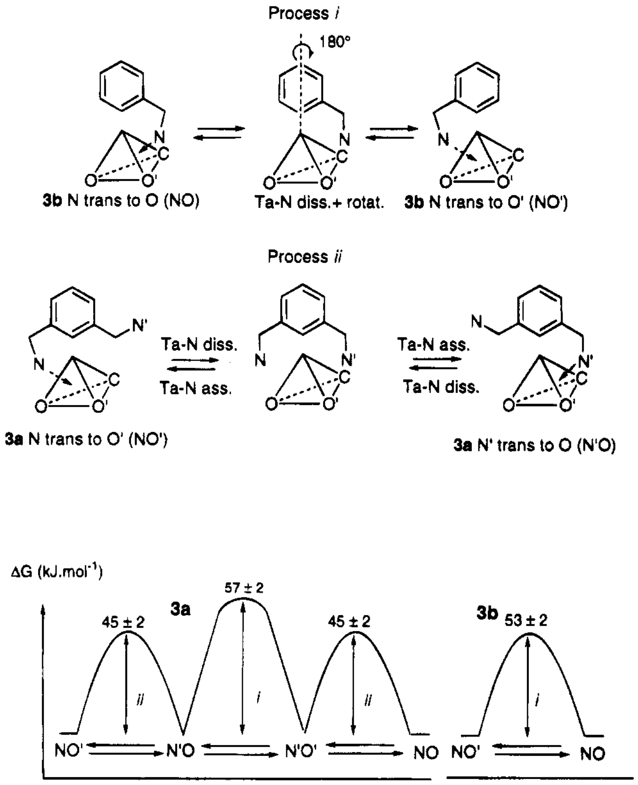
Scheme 2. Proposed Fluxionality Mechanism of the Dialkoxide Complexes 3



second nitrogen donor a more facile process is also possible that involves dissociation of one of the N donors from the Ta—C—O′ plane, leading to the same tetrahedral intermediate followed by face-centered attack of the other N donor on the Ta—C—O plane (Scheme 2, process ii). Since this process does not involve wagging of an uncoordinated amine ligand, a lower value of the corresponding $\Delta G^{\ddagger}$ may be expected ($\Delta G^{\ddagger} = 45$ kJ·mol^{-1}).

Alkylidene-Centered Reactivity of the Alkoxide Complexes 2 and 3. The reactivity of the alkoxide complexes **2** and **3** with simple alkenes (eqs 3 and 4) varies from unclean (probably reductive rearrangement) reactions to very clean alkene metathesis reactions. The overall effect of substituting chlorine atoms by alkoxide ligands allows tuning of the reactivity of the tantalum alkylidene complexes in essentially the same way as reported by Schrock and co-workers.[16,32]

The reactions with (trimethylsilyl)ethene are noteworthy. In order to produce the metathesis product *t*-BuCH=CH$_2$ together with a new alkylidene group (Ta=CHSiMe$_3$) the reaction of the alkoxide complexes **2** and **3a** with $Me_3SiCH{=}CH_2$ have to proceed in such a way that the C_β atom of the $Me_3SiCH{=}CH_2$ molecule binds to the tantalum center. This seems somewhat unanticipated because it results in a further concentration of bulky groups in the tantalum coordination sphere, but it is possible that placing a *t*-Bu and a SiMe$_3$ group next to one another on a metallocyclobutane ring is more sterically unfavorable than to have both substituents α to the metal center. Since the reaction, nevertheless, proceeds very quickly and without the formation of organic products from other possible metallacyclobutane intermediates, it is likely that the driving force for this reaction originates in electronic rather than steric effects; *i.e.* the Si atom in the newly formed alkylidene group stabilizes the negative charge on the nucleophilic alkylidene C_α atom.[32]

Conclusions

The findings presented here show that the NCN monoanion is an adequate spectator ligand for the study of tantalum alkylidene-centered reactivity with respect to alkene metathesis. The use of this ligand has allowed a structural study of fluxional tantalum alkylidene complexes. At the same time, it has become clear that the NCN ligand is flexible enough in its coordination modes to generate a vacant coordination site at a tantalum center that allows a substrate molecule to bind to the metal and undergo a metal-mediated reaction.

Experimental Section

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 provided by the Institute of Applied Chemistry (TNO), Zeist, The Netherlands, or by Dornis and Kolbe, Mülheim a. d. Ruhr, Germany; ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC200 or AC300 spectrometer. Ta(=CH-*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,6}Cl$_2$,[12] Ta(=CH-*t*-Bu)Cl(O-*t*-Bu)$_2$(PMe$_3$),[16] and [Li{$C_6H_3(CH_2NMe_2)_2$-2,6}]$_2$[18] were prepared according to literature procedures. High purity ethene was obtained from Aldrich and used as received. (Trimethylsilyl)ethene was dried on 4-Å molecular sieves.

Ta(=CH-*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,6}Cl(O-*t*-Bu), 2a. A purple solution of Ta(=CH-*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,6}Cl$_2$ (2.89 g, 5.63 mmol) and LiO-*t*-Bu (0.46 g, 5.7 mmol) in benzene (*ca.* 100 mL) was stirred for 5 days. The resulting suspension was stripped *in vacuo* to a red oil that was subsequently extracted with hexane (3 × 30 mL). The combined extracts were concentrated *in vacuo* to *ca.* 3 mL from which the product crystallized overnight at −30 °C as small purple needles; yield 1.58 g (49%). (The same product was obtained when 2 equiv of LiO-*t*-Bu were used.) Anal. Calcd for $C_{21}H_{38}N_2ClOTa$: C, 45.78; H, 6.95; N, 5.08. Found: C, 44.89; H, 6.99; N, 4.98.

Ta(=CH-*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,6}Cl(OMe), 2b. A purple suspension of Ta(=CH-*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,6}Cl$_2$ (1.31 g, 2.55 mmol) and KOMe (0.34 g, 4.85 mmol) in Et$_2$O (*ca.* 100 mL) was stirred overnight. The resulting suspension was filtered and the solvent removed from the filtrate *in vacuo* to give 1.10 g (85%) of purple product that was pure by ^{1}H NMR spectroscopy.

Ta(=CHSiMe$_3$){$C_6H_3(CH_2NMe_2)_2$-2,6}Cl(O-*t*-Bu), 2c. To a stirred purple solution of Ta(=CH-*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,6}Cl(O-*t*-Bu) (1.71 g, 3.10 mmol) in Et$_2$O (50 mL) was added $Me_3SiCH{=}CH_2$ (0.96 mL, 6.2 mmol). The mixture was stirred for 18 h during which time the color gradually changed to orange. All volatiles were subsequently removed *in vacuo* and the remaining orange spongy material was triturated with hexane to provide a powder that was dried *in vacuo*, giving 1.64 g (93%) of orange product **2c** that was pure by ^{1}H NMR spectroscopy. When this experiment was performed in an NMR tube using C_6D_6 as solvent, 1 equiv of **2c** together with 1 equiv of *t*-Bu-CH=CH$_2$ (identified by comparison with an authentic sample) were formed quantitatively within 3 h. Anal. Calcd for $C_{20}H_{38}N_2ClOSiTa$: C, 42.36; H, 6.76; N, 4.94. Found: C, 41.47; H, 6.33; N, 4.89.

Ta(=CH-*t*-Bu){$C_6H_3(CH_2NMe_2)_2$-2,6}(O-*t*-Bu)$_2$, 3a. A yellow solution of Ta(=CH-*t*-Bu)Cl(O-*t*-Bu)$_2$(PMe$_3$) (2.41 g, 4.74 mmol) and [Li{$C_6H_3(CH_2NMe_2)_2$-2,6}]$_2$ (0.95 g, 4.80 mmol) in benzene (100 mL) was stirred for 1 week. During this period, the color of the solution gradually changed to orange and a precipitate of LiCl was formed. The solvent was removed *in*

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Table 6. Crystal Data and Details of the Structure Determination of 3a

(a) Crystal Data	
formula	$C_{25}H_{47}N_2O_2Ta$
mol wt	588.60
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a, b, c (Å)	9.3519(5), 9.4443(3), 18.1110(9)
α, β, γ (deg)	90.432(3), 100.241(4), 116.593(3)
V (Å^3)	1400.68(11)
Z	2
D_{calc} (g cm^{-3})	1.3955(1)
$F(000)$	600.0
μ (cm^{-1})	39.0
cryst size (mm)	0.33 × 0.40 × 0.50
(b) Data Collection	
temp (K)	295
$\theta_{min}, \theta_{max}$	1.15, 27.49
radiation; λ (Å)	Mo Kα (Zr-filtered); 0.710 73
$\Delta\omega$ (deg)	$0.80 + 0.35 \tan\theta$
hor and vert aperture (mm)	3.0, 4.0
no. of ref reflns	3
total no. of data	6815
total no. of unique data	6428
no. of obsd data	5724 [$I > 2.5\sigma(I)$]
abs corr range	0.85−1.32
(c) Refinement	
N_{ref}, N_{par}	5723, 365
weighting scheme	$w = 1.0/\sigma^2(F)$
Final R, wR, S	0.0271, 0.0260, 1.19
max and av shift/error	0.5661/0.0193
min and max resd density (e/Å^3)	−1.44, 1.20 (near Ta)

Table 7. Final Coordinates and Equivalent Isotropic Thermal Parameters and Their Esd's in Parentheses for the Non-H Atoms of 3a

atom	x	y	z	U(eq)^a (Å^2)
Ta	1.05142(2)	0.44212(2)	0.25744(1)	0.0317(1)
O(1)	0.8659(3)	0.4697(3)	0.25927(15)	0.0487(9)
O(2)	0.9985(3)	0.2442(3)	0.30006(13)	0.0394(8)
N(1)	0.8118(4)	0.1089(4)	0.1338(2)	0.0566(12)
N(2)	1.0966(4)	0.6441(4)	0.17094(18)	0.0493(11)
C(1)	1.1395(4)	0.3822(5)	0.16010(19)	0.0396(13)
C(2)	1.2424(4)	0.5126(6)	0.1268(2)	0.0481(14)
C(3)	1.3201(5)	0.4967(8)	0.0709(2)	0.0646(16)
C(4)	1.2926(6)	0.3480(9)	0.0456(3)	0.075(2)
C(5)	1.1787(6)	0.2163(7)	0.0708(3)	0.0649(19)
C(6)	1.1001(5)	0.2322(5)	0.1263(2)	0.0474(14)
C(7)	0.9572(6)	0.0859(6)	0.1442(3)	0.0549(17)
C(8)	0.6826(7)	−0.0222(7)	0.1619(4)	0.089(2)
C(9)	0.7552(6)	0.1236(8)	0.0556(3)	0.0804(19)
C(10)	1.2531(5)	0.6702(6)	0.1501(3)	0.0533(16)
C(11)	0.9661(6)	0.5889(8)	0.1019(3)	0.0660(19)
C(12)	1.1106(7)	0.7924(6)	0.2037(3)	0.0692(19)
C(13)	0.7127(5)	0.4314(6)	0.2779(3)	0.0566(16)
C(14)	0.6575(11)	0.5439(13)	0.2538(7)	0.215(7)
C(15)	0.5991(9)	0.2858(12)	0.2424(8)	0.306(11)
C(16)	0.7264(12)	0.427(2)	0.3558(5)	0.354(14)
C(17)	1.2418(5)	0.5912(5)	0.3268(2)	0.0418(12)
C(18)	1.3459(5)	0.7194(5)	0.3910(2)	0.0552(14)
C(19)	1.4705(7)	0.8675(7)	0.3629(3)	0.105(2)
C(20)	1.2341(7)	0.7641(8)	0.4276(3)	0.091(2)
C(21)	1.4385(7)	0.6621(8)	0.4504(3)	0.100(3)
C(22)	1.0545(5)	0.1763(5)	0.3623(2)	0.0500(16)
C(23)	1.2255(7)	0.2024(8)	0.3586(3)	0.073(2)
C(24)	1.0546(9)	0.2559(8)	0.4353(3)	0.084(3)
C(25)	0.9412(8)	0.0005(7)	0.3555(4)	0.079(2)

^{a} $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*\mathbf{a}_i\mathbf{a}_j$.

vacuo, and the resulting brown oil was extracted with hexane (100 mL). The extract was concentrated *in vacuo* to *ca.* 40 mL. From this extract, the product crystallized overnight at −30 °C together with traces of a red byproduct. Recrystallization from hexane at −30 °C afforded analytically pure yellow product **3a**; yield 1.39 g (50%). Anal. Calcd for $C_{25}H_{47}N_2O_2Ta$: C, 51.01; H, 8.05; N, 4.76. Found: C, 50.38; H, 7.39; N, 4.78.

Ta(=CH-*t*-Bu){$C_6H_4CH_2NMe_2$-2}(O-*t*-Bu)$_2$, 3b (One-Pot Procedure). Yellow Ta(CH_2-*t*-Bu)$_2Cl_3$ (2.62 g, 6.10 mmol) dissolved in 50 mL of Et_2O/THF (4:1) was stirred for 18 h to give a purple solution of Ta(=CH-*t*-Bu)Cl_3(THF)$_2$. After removing the solvent *in vacuo* and replacing it by pure Et_2O (50 mL), the solution was cooled to −78 °C. Zn($C_6H_4CH_2NMe_2$-2)$_2$ (0.99 g, 2.97 mmol) in Et_2O (10 mL) was added in 1 min, and the mixture was allowed to warm to 20 °C. To the resulting dark-purple solution was added LiO-*t*-Bu (1.49 g, 18.6 mmol) in Et_2O (20 mL) in 5 min, so generating a yellow suspension from which volatiles were stripped *in vacuo*. The remaining sticky solid was triturated with hexane, dried rigorously *in vacuo*, and subsequently extracted with hexane (50 mL), leaving 1.40 g of a white residue. The yellow extract was concentrated *in vacuo* to 10 mL, from which the product **3b** crystallized overnight at −30 °C as block-shaped yellow crystals; yield 1.63 g (52%). Anal. Calcd for $C_{22}H_{40}NO_2Ta$: C, 49.71; H, 7.59; N, 2.64. Found: C, 49.52; H, 7.50; N, 2.71.

Ta{CH($SiMe_3$)CH_2CH_2-1,3}{C_6H_3(CH_2NMe_2)$_2$-2,6}Cl(O-*t*-Bu), 4 (in Situ). An NMR tube was charged with an orange solution of Ta(=CHSiMe$_3$){C_6H_3(CH_2NMe_2)$_2$-2,6}Cl(O-*t*-Bu) (*ca.* 100 mg) in C_6D_6 (0.5 mL). For 10 s, ethene was passed through, causing the solution to change color almost immediately to yellow. ^{1}H and ^{13}C NMR measurements showed that the product **4** was formed quantitatively. In solution, the product slowly decomposes (*ca.* 20%/18 h) in an unclean way, liberating ethene. ^{1}H NMR (200.13 MHz, C_6D_6, 24 °C, TMS): δ 0.58 [s, 9 H, CH(Si*Me*$_3$)], 0.87 [s, 9 H, O-*t*-Bu], 1.0−1.19 [m, 3 H, TaC*H*$_2$C*H*$_2$−], 2.16 (3 H), 2.50 (6 H), 2.58 (3 H) [s, N(C*H*$_3$)$_2$], 2.5 [(partially obscured by NMe) m, 1 H, TaC*H*$_2$-CH$_2$−], 3.11 [t, ^2J(HH) = 13 Hz, 2H, C*H*$_2$N], 4.27 and 5.02 [d, ^2J(HH) = 13 Hz, 2 H, C*H*$_2$N], 3.43 [m, 1 H, TaC*H*(SiMe$_3$)], 6.94−7.17 (m, 3 H, ArH). ^{13}C{^{1}H} NMR (50.32 MHz, C_6D_6, 24 °C, TMS): δ 1.8 [CH(Si*Me*$_3$)], 23.1 (TaCH$_2$*C*H$_2$−), 29.5 [OC-(*C*H$_3$)$_3$], 48.6, 50.1, 50.9 [N(CH$_3$)$_2$], 54.3 (Ta*C*H$_2$CH$_2$−), 55.1 [Ta*C*H(SiMe$_3$)], 73.9 and 74.0 (CH$_2$N), 83.9 [O*C*(CH$_3$)$_3$], 201.2 (C$_{ipso}$ of C_6H_3).

Crystal Structure Determination of 3a. Crystal data and numerical details of the structure determination are given in Table 6. A yellow crystal of **3a** was mounted under nitrogen in a Lindemann glass capillary and transferred to an Enraf-Nonius CAD4T diffractometer on a rotating anode (50 kV, 200 mA) with graphite monochromated Mo Kα radiation. Unit cell parameters were determined from a least-squares treatment of the SET4 setting angles of 25 reflections in the range $11 < \theta < 14°$ and were checked for the presence of higher lattice symmetry.[33] All data were collected with the $\omega/2\theta$ scan mode. Data were corrected for *Lp* and for the small linear decay of 2% of the reference reflections. An absorption correction was applied using the DIFABS method[34] (correction range 0.85: 1.32). The structure was solved using standard Patterson methods (SHELXS-86)[35] and subsequent difference Fourier synthesis and refined by full-matrix least-squares techniques on F (SHELX76).[36] Most H atoms were introduced on calculated positions (C−H = 0.98 Å) and included in the refinement riding on their carrier atoms (an exception is the alkylidene proton that was located from a difference Fourier map and refined). All non-hydrogen atoms were refined with anisotropic thermal parameters. Weights were introduced in the final refinement cycles. Scattering factors were taken from Cromer and Mann[37] and corrected for anomalous dispersion.[38] All calculations were carried out on a DEC 5000 system. Geometrical calculations and illustrations were done with PLATON.[39] Final coordinates of the non-hydrogen atoms of **3a** are given in Table 7.

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Supplementary Material Available: Tables of anisotropic thermal parameters, all H atom parameters, bond lengths, and bond angles (9 pages). Ordering information is given on any current masthead page.

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(40) Computational studies on the planar and facial conformations of the NCN monoanion are underway.