Synthesis of Cyclometalated Aryltantalum(V) Complexes: Amine C–H Activation via σ-Bond Metathesis

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Cyclometalated aryltantalum(V) complexes containing a five-membered Ta–C–C–C–N chelate ring can be prepared by transmetalation reactions. The 1:2 reaction of [Zn(C$_6$H$_4$CH$_2$NMe$_2$-2)$_2$] with TaCl$_5$ affords [TaCl$_4$(C$_6$H$_4$CH$_2$NMe$_2$-2)] (**1a**) in high yield. [TaCl$_4${C$_6$H$_4$CH(Me)NMe$_2$-2}] (**1b**) (*S* enantiomer) and [TaCl$_4$(C$_6$H$_3$CH$_2$NMe$_2$-2-Me-6)] (**1c**) can be prepared similarly. The reaction of **1a** and **1c** with a half-equiv of [Zn(CH$_2$Ph)$_2$] affords the monobenzyl substituted analogues [TaCl$_3$(C$_6$H$_4$CH$_2$NMe$_2$-2)(CH$_2$Ph)] (**2a**) and [TaCl$_3$(C$_6$H$_3$CH$_2$NMe$_2$-2-Me-6)(CH$_2$Ph)] (**2c**). The 2:1 reaction of [TaCl$_3$(CH$_2$Ph)$_2$] with [Zn(C$_6$H$_4$CH$_2$NMe$_2$-2)$_2$] affords the dibenzyl species [TaCl$_2$(C$_6$H$_4$CH$_2$NMe$_2$-2)(CH$_2$Ph)$_2$] (**3a**) in good yield. [TaCl$_2${C$_6$H$_4$CH(Me)NMe$_2$-2}(CH$_2$Ph)$_2$] (**3b**) and [TaCl$_2$(CH$_2$C$_6$H$_4$NMe$_2$-2)(CH$_2$Ph)$_2$] (**3d**) can be prepared similarly. An analogous transmetalation of [TaCl$_3$(CH$_2$Ph)$_2$] with $^1/_2$ [Li(1-C$_{10}$H$_6$NMe$_2$-8)]$_2$ affords [TaCl$_2$(1-C$_{10}$H$_6$NMe$_2$-8)(CH$_2$Ph)$_2$] (**3e**). [TaCl$_2$(C$_6$H$_4$CH$_2$NMe$_2$-2)(CH$_2$Ph)$_2$] (**3a**) belongs to the space group $P\bar{1}$ with a = 9.055 (2) Å, b = 9.614 (1) Å, c = 13.910 (3) Å, α = 72.93 (1)°, β = 80.91 (2)°, γ = 72.74 (1)°, and Z = 2. The overall structure is distorted octahedral with the Ta–C–C–C–N chelate ring and both benzyl ligands in the equatorial plane. In solution all complexes **3** are fluxional: at room temperature the benzyl ligands are rendered equivalent by a sequence of pseudorations that does not involve dissociation of the Ta–N coordinative bond. For **3b** and **3e** in solution rupture of the Ta–N bond (at ca. 60 °C) leads to a (stereoselective) NMe C–H activation, proceeding via a σ-bond metathesis step, that gives [TaCl$_2${C$_6$H$_4$(CH(Me)N(Me)CH$_2$)-2}(CH$_2$Ph)(THF)] (**4b**) and [TaCl$_2${1-C$_{10}$H$_6$(N(Me)CH$_2$)-8}(CH$_2$Ph)(THF)$_2$] (**4e**), respectively, in moderate yield. **4b** belongs to the space group $P\bar{1}$ with a = 9.218 (1) Å, b = 9.974 (1) Å, c = 25.930 (1) Å, α = 85.75 (1)°, β = 85.70 (2)°, γ = 64.97 (1)°, and Z = 4. The overall structure is distorted pentagonal bipyramidal. The chirality of the arylamine leads to a single, structurally characterized diastereoisomer in which intramolecular coordination of the modified amine group produces a triangular Ta–CH$_2$–N unit.

Introduction

The earliest reference to aryltantalum and arylniobium chemistry dates back to 1928! The metal pentachlorides were reported to react with arenes to give HCl and, in some cases, products that analyzed as metal aryls, e.g. TaCl$_4$(C$_6$H$_5$) and NbCl$_4$(C$_{10}$H$_7$). This report was contradicted and retracted in succession.[1] In 1940 the reaction of TaCl$_5$ with phenyl Grignards was reported to give unstable, colored solutions.[1] To date few simple aryltantalum compounds have been isolated, although some aryl "ate" complexes,[2] [Ta(Ar)$_6$]$^{n-}$, are known. Many aryltantalum complexes are labile and tend to decompose

via β-H elimination reactions forming benzyne complexes. A representative example of this reaction is found in eq 1.[3]

$$\text{via } \beta\text{-el.} \quad -\text{CH}_4 \qquad (1)$$
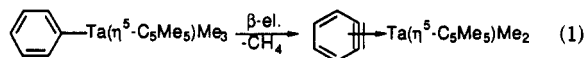
The synthesis of aryltantalum(V) complexes is possible when the aryl β-hydrogens are replaced by methyl or fluorine substituents. For example, TaCl$_3$(C$_6$F$_5$)$_2$ is known[4] and a series of tantalum mesityl complexes, TaX$_{5-n}$(Mes)$_n$ (X = Cl, Br; n = 1–3), has been reported.[5] An interesting aspect of the chemistry of the latter complexes is that the halides may be substituted to provide heteroleptic complexes containing combinations of alkyl, mesityl, and halogen ligands. However, for several mesityl complexes decomposition pathways are feasible involving a γ-H and α-H elimination sequence that converts the mesityl unit into a benzylidene derivative (eq 2).[5]

In general, ancillary ligands capable of π-bonding have a stabilizing influence on σ-bonded alkyl and aryl ligands

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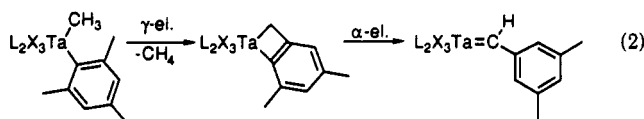† Debye Research Institute.
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$$L_2X_3Ta \xrightarrow{\gamma\text{-el.}}_{-CH_4} L_2X_3Ta \xrightarrow{\alpha\text{-el.}} L_2X_3Ta=C \quad (2)$$

Figure 1. Selected C,N-chelating ligand systems.

a b c d e

in high oxidation state early transition metal chemistry. For aryltantalum chemistry this has been illustrated by Chisholm et al., who prepared a stable tolyl complex, Ta(NMe₂)₃(p-tolyl)Br, by transmetalation of TaCl₂(NMe₂)₃ with p-tolyllithium that contained LiBr.[6] In this complex π-donation of the dimethylamido ligands to the tantalum center blocks β-H elimination pathways involving the tolyl unit.[6] Similar π-donation can also be achieved with alkoxide ligands, and phenyl complexes have recently been isolated using bulky 2,6-disubstituted aryloxide ancillaries.[7] Additionally, dicyclopentadienyltantalum systems do not require bulky alkyl groups for stability, and such complexes, which can be either diamagnetic or paramagnetic, can even tolerate β-hydrogens. Typical examples are the diphenyl complex Cp₂TaPh₂[8] and the series of homologous alkyl chain complexes Cp₂Ta(CH₂-CH₂R)(R'NC) (R = Me, Et).[9]

When tantalum alkylation or arylation is performed in a transmetalation reaction, the transmetalation agent should be selected with care. The syntheses of tantalum complexes of the type TaX₅₋ₙRₙ (1 ≤ n ≤ 5; R = methyl, benzyl, mesityl, neopentyl, (trimethylsilyl)methyl, adamantylmethyl) is illustrative. For n = 1–3, the general synthesis is by means of a transmetalation reaction between TaCl₅ and the diorganozinc compound of the chosen ligand[10] in the desired stoichiometry; the ZnR₂ compounds transfer both alkyl groups. Similar transmetalation reactions between TaCl₅ and alkyl Grignard or alkyllithium reagents lead to either overalkylation, α-H abstractions, or complex mixtures. For instance, the reaction of Zn(CH₂SiMe₃)₂ with TaCl₅ leads to TaCl₃(CH₂SiMe₃)₂ and TaCl₂(CH₂SiMe₃)₃, while the same reaction performed with a Grignard or lithium reagent leads to a bridged alkylidyne complex, (Me₃SiCH₂)₂Ta(μ-CSiMe₃)₂Ta(CH₂SiMe₃).[11] It should not be a surprise that the (nevertheless very interesting) reaction of TaCl₅ or NbCl₅ with phenyllithium produces bisbenzyne/polyphenyl derivatives in an unclean way;[12] both the choice of the arylating agent and the presence of aryl β-hydrogens augment this result.

A possible approach to overcome complications caused by β-H elimination (that seems to have been rather unexploited in tantalum chemistry) is to prepare tantalum(V) complexes by employing an aryl ligand that has
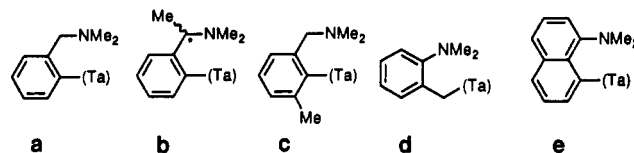
an ortho-substituent containing a heteroatom. This heteroatom may form an additional coordinative bond to the metal center and thereby enhance the kinetic stability of the organometallic complex formed.[13] In our laboratory many organometallic compounds have been studied that contain monoanionic, mono- or bis-ortho-substituted, C,N-chelating, arylamine ligands.[14] The bidentate ligands shown in Figure 1 seem well-suited for stabilizing tantalum(V) centers because they possess a hard anionic Cᵢₚₛₒ atom and a neutral tertiary N donor atom as ligating sites. Moreover, these ligands should form cyclometalated complexes which contain a five-membered chelate ring and which, therefore, are likely to be kinetically stable.[15] In addition, each of these ligands has been chosen for a special reason. When a Ta–C–C–C–N chelate ring is formed, the steric constraints within this ring will be less with the 2-[(dimethylamino)methyl]phenyl ligands a–c and the 2-(dimethylamino)benzyl ligand d than with with the more rigid ligand system e.[16] Moreover, the presence of the stereogenic center in ligand b may affect the stereospecificity of reactions occurring at the tantalum center and can also provide NMR data relating to the occurrence of nitrogen-to-tantalum coordination in solution (vide infra). In contrast to the situation with ligands a–d, the 8-(dimethylamino)-1-naphthyl ligand e has steric constraints of the naphthalene backbone which will cause the N atom to be in close proximity to the metal center even when the Ta–N bond has dissociated. Finally, the ortho-methyl substituent in ligand c is of interest because it is anticipated (and already shown in Ir and Rh chemistry[17]) that it may interfere with other ligands present in the tantalum coordination sphere.

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We have investigated the use of the arylamine systems shown in Figure 1 as appropriate chelating ligands for tantalum(V). This paper describes full details[18] of the synthesis and characterization of the resulting organotantalum complexes. Most of the cyclometalated tantalum(V) complexes reported here are thermally stable, and this aspect is particularly noteworthy for those complexes that contain an aryl-to-tantalum bond. This paper thus illustrates that organotantalum complexes gain stability not only by π-donation[6-9] but also by σ-donation.

It turns out that formation of an intramolecular Ta–C–C–C–N chelate blocks decomposition pathways and thereby causes a pronounced enhancement of the stability of the complexes reported. Upon rupture of the Ta–N coordinative bond, NMe C–H activation reactions can occur that lead to a C,C'-chelating, metal-bonded, dianionic fragment. Overall similar, but mechanistically different, NMe C–H activations have been postulated and found in late transition metal chemistry.[17]

Results and Discussion

Synthesis of Cyclometalated Tantalum(V) Chlorides. The new cyclometalated tantalum(V) complexes are prepared via transmetalation reactions using lithium- and zinc-metalated derivatives of the amine ligands a–e. The syntheses of the diorganozinc complexes of ligands **a** and **d** are already known,[19] and by analogy the reaction of the organolithium compounds of **b** or **c** with ZnCl$_2$ nicely affords the diorganozinc complexes of these ligands. Isolation of the diorganozinc complex of the naphthylamine ligand **e** by the reaction of [Li(1-C$_{10}$H$_6$NMe$_2$-8)]$_2$ with 1 equiv of ZnCl$_2$ in Et$_2$O or THF was hampered by the unexpectedly low solubility of this product. Treatment of TaCl$_5$ with a half-equiv of the diorganozinc compounds of the ligands a–c (eq 3) at low temperature in Et$_2$O affords the novel, yellow, ortho-chelated tantalum tetrachlorides **1a–1c**.

$$TaCl_5 + 1/2\ Zn(cn)_2 \xrightarrow[-78\ °C,\ -1/2\ ZnCl_2]{Et_2O} \quad (3)$$

1 a: R^1 = R^2 = H
1 b: R^1 = Me, R^2 = H (*S* -enantiomer)
1 c: R^1 = H, R^2 = Me
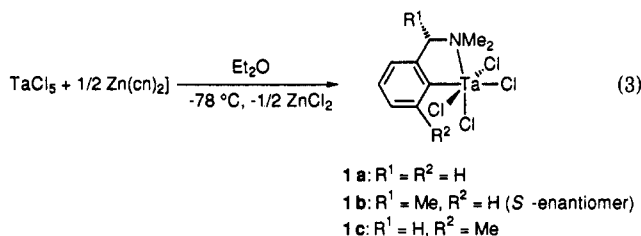
In the transmetalation reactions reported in this paper the starting diorganozinc compounds transfer both organic groups to tantalum. The complexes **1** are isolated by extraction with benzene and crystallize readily when pentane is added to the concentrated extracts; yields range from 75 to 90%. The solids can be handled for short periods in air and are thermally stable to at least 100 °C.

The red, crystalline, thermally stable, monobenzyl complexes **2** are conveniently prepared in yields ranging from 53 to 88% by treatment of the aryltantalum tetrachloride (**1a** or **1c**) with a half-equiv of Zn(CH$_2$Ph)$_2$ (eq 4).

$$TaCl_4(cn) + 1/2\ Zn(CH_2Ph)_2 \xrightarrow[-78\ °C,\ -1/2\ ZnCl_2]{Et_2O}$$

2 a: R = H
2 c: R = Me

$$(4)$$
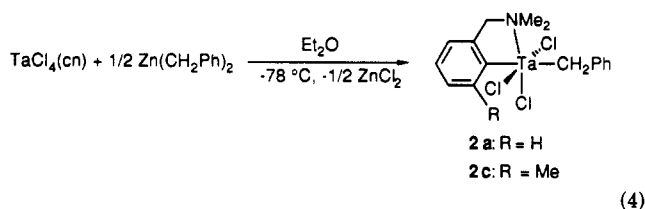
No attempts have been made to synthesize other members of class 1 or 2 since we are especially interested in the use of cyclometalated *di*alkyltantalum(V) complexes as precursors for cyclometalated tantalum alkylidene complexes.

Scheme I shows the attempted routes for the syntheses of the dibenzyl derivatives with the ligands **a–e**. The tantalum tetrachloride complex **1a** reacts smoothly in Et$_2$O at low temperature with 1 equiv of Zn(CH$_2$Ph)$_2$ to afford the red dibenzyl complex **3a** (route i). With the C$_6$H$_3$CH$_2$NMe$_2$-2-Me-6 monoanionic ligand **c**, however, the dibenzyl analogue **3c** cannot be isolated. In this case the reaction stops after the monobenzyl complex **2c** is formed (route ii). When, in an alternative approach, the diorganozinc compound of the arylamine **c** is treated with TaCl$_3$(CH$_2$Ph)$_2$, a very unclean reaction takes place (route iii). In contrast to this result, the reaction of diorganozinc compounds of **a**, **b**, and **d** with TaCl$_3$(CH$_2$Ph)$_2$ occurs smoothly in Et$_2$O at low temperature (route iv) and provides an excellent alternative route for the synthesis of dibenzyl complexes **3**.

The preparation of the dibenzyl complex **3e** (route vi) is noteworthy because, in contrast to the aryltantalum amine complexes **3a,b,d**, it can be prepared by the reaction of an organolithium compound, [Li(1-C$_{10}$H$_6$NMe$_2$-8)-(Et$_2$O)]$_2$, with TaCl$_3$(CH$_2$Ph)$_2$. Similar reactions performed with [Li{C$_6$H$_4$CH(R)NMe$_2$-2}]$_4$ (R = H, Me) or [Li(CH$_2$C$_6$H$_4$NMe$_2$-2)]$_n$ (route v) are not clean and do not afford the dibenzyl complexes **3**. Such a substantial difference in reactivity between zinc and lithium alkylating or arylating reagents is common in organotantalum chemistry.[5] This may be ascribed to the greater reactivity of lithium compounds toward substitution and reduction of tantalum halides. The reducing activity of the lithio species results from their usually high degree of association which facilitates interaggregate C–C bond coupling after electron transfer from the organolithium cluster to a tantalum species. Consequently, the difference in reactivity between dimeric [Li(1-C$_{10}$H$_6$NMe$_2$-8)(Et$_2$O)]$_2$ and tetrameric [Li{C$_6$H$_4$CH(R)NMe$_2$-2}]$_4$ (R = H, Me) or [Li(CH$_2$C$_6$H$_4$NMe$_2$-2)]$_n$ can originate from their different degree of association in diethyl ether.[20]

The red complexes **3a,d,e** can be handled and stored at room temperature whereas the thermal stability of **3b** is already low at ambient temperature. These four dibenzyl complexes react readily with water and decompose on contact with air.

The ^{1}H and ^{13}C NMR data of the tantalum amine complexes **1–3** (Tables I and II) are consistent with the structural proposals shown in eq 3 and 4 and in Scheme I. The tantalum aryl functions of ligands a–c and e provide highly characteristic lowfield C$_{ipso}$ signals (δ 215–220 ppm), and for **2** and **3** the distinctive resonances of the benzylic

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Scheme I. Synthesis of the Cyclometalated Dibenzyl Complexes 3
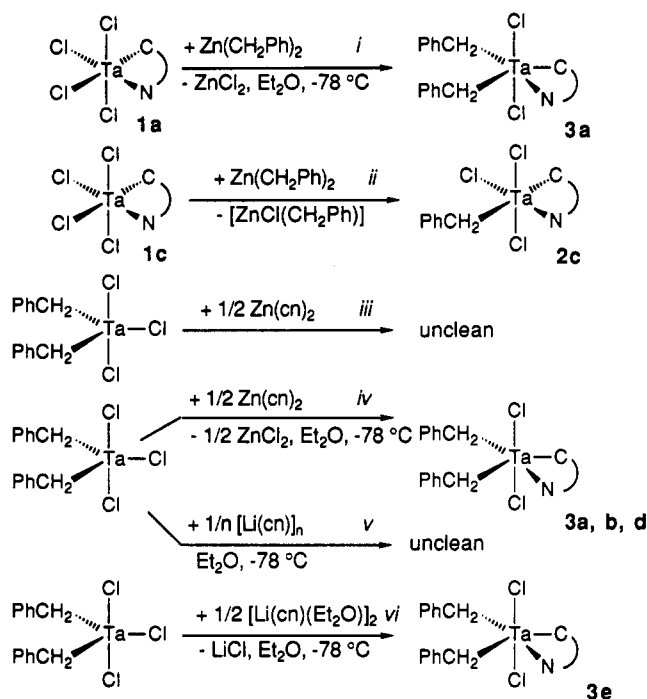
C_α carbons appear at δ 92–97 ppm. These values compare well with those of other tantalum mesityl[5] and tantalum benzyl compounds.[21]

Structure of TaCl₂(C₆H₄CH₂NMe₂-2)(CH₂Ph)₂ (3a) in the Solid State and in Solution. The ¹H NMR spectra of the dibenzyl complexes 3 show an interesting temperature dependence (vide infra), and to aid interpretation of the spectroscopic data, an X-ray structural analysis of one of these complexes was carried out. Suitable crystals of the dibenzyl complex 3a were obtained from a diethyl ether layered THF solution at –30 °C. The crystal structure involves the packing of two discrete monomeric molecules in the 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 III. The X-ray structure shows that 3a is a mononuclear tantalum species that has a distorted octahedral geometry. In this complex two chlorine atoms occupy axial trans positions with two cis-positioned C-bonded benzyl ligands in the equatorial plane. The coordination sphere is completed by the N-donor atom and the C_ipso atom of the chelating 2-[(dimethylamino)-methyl]phenyl ligand; the resulting five-memebered Ta-C-C-C-N ring is puckered. The small bite angle of the chelate ring [N(1)-Ta(1)-C(11) = 69.7 (4)°] seems to be compensated for by a rather wide angle of 115.0 (5)° between the two benzyl ligands. The distortions in the equatorial plane (see Figure 3) are such that it is possible to use an alternative description of the structure based on a distorted trigonal arrangement of the organo groups around tantalum with "supplementary" coordination of the N-donor substituent.

Noteworthy is the long tantalum-to-nitrogen bond length of 2.496 (9) Å (cf. 2.229 (6) Å in 4b; vide infra) that is similar to Sn–N bond lengths in organotin(IV) complexes

with this type of chelating ligand.[22] In 3a the Ta–N coordination results in a slight lengthening of the Ta–C_α bond of the trans-positioned benzyl ligand [Ta–C(5) = 2.24 (1) Å] compared to the other benzylic Ta–C_α bond [Ta–C(4) = 2.19 (1) Å]. Possibly, the interplay between two trans-positioned internal nucleophiles (C⁻ and N:) causes the bond lengthening along the N–Ta–C axis. The dynamic solution behavior of the related complex 3b, in which rupture of the Ta–N bond occurs at elevated temperature (vide infra), illustrates that this lengthened coordinative bond is probably weak.

In complexes 3, even with formation of the intramolecular Ta-C-C-C-N chelate ring, the electron count on the tantalum(V) center is formally only 12. The structural features of 3a show that the benzyl ligands are orientated so that the metal atom can alleviate some of its electronic deficiency. The angles $Ta-C_\alpha-C_\beta$ in the benzyl ligands are 99.2 (8) and 120.1 (8)° and deviate markedly from the expected value of 109°; cf. the mean angle of 111 (1)° in Sn(CH₂Ph)₄.[23] Due to the small $Ta-C_\alpha-C_\beta$ angle [Ta-C(4)-C(21)] in one of the benzyl ligands, its β-carbon penetrates into the tantalum coordination sphere [Ta···C(21) = 2.81 Å]. In this case the aromatic plane of the benzyl ligand is virtually perpendicular to the equatorial plane and this means that the β-carbon is well-oriented to donate π-electron density to the tantalum atom (Figure 4, structure a). Similar η^2-bonding that deviates from classical η^1-benzyl-bonding is known for complexes of the early transition metals Ti, Zr, and Hf,[24] the middle transition metals Mo and W,[25] and the actinide Th.[26] For instance, in Ti(CH₂Ph)₄ the Ti···C_β distances range from 2.61 to 3.16 Å.[23]

In the structure of 3a the larger benzyl $Ta-C_\alpha-C_\beta$ angle [Ta-C(5)-C(31)] of 120.1 (8)° is likely to be caused by steric interactions within the molecule, the C_β···Cl(1) distance being 3.19 Å. Therefore, it is inaccurate—but tempting—to describe this benzylic bonding as like that found in the structure of the 12-electron complex Ti(η^5-C₅Me₅)(CH₂Ph)₃[27] (Figure 4, structure b) which has one benzyl $Ta-C_\alpha-C_\beta$ angle of 139.0 (7)°. In this latter case the benzyl α-hydrogens have an agostic interaction with the metal leading to benzylidene-type bonding with a very short Ti–C_α bond.

NMR Studies on the Cyclometalated Tantalum Complexes. In solution (C₆D₆, 200.13 MHz) dibenzyl complexes 3 provide temperature-dependent NMR spectra that can be interpreted in terms of a fluxional process involving the NMe₂ unit. For 3b at 300 K there are two anisochronous proton resonances for the NMe groups, and the nitrogen center is therefore a stable tetrahedral array reflecting the chirality of the adjacent chiral center. This

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Table I. ^{1}H NMR Data (ppm) for the Cyclometalated Tantalum(V) Complexes[a]

complex	NMe	CH$_2$N or CH(Me)N		CH$_2$Ph (^2J(H,H), Hz)	Ar H[b]		other
		CH$_2$/CH	Me		o-H[c]	o-Me	
TaCl$_4$(C$_6$H$_4$CH$_2$NMe$_2$-2) (1a)	2.37	3.63			8.65		
TaCl$_4${(S)-C$_6$H$_4$CH(Me)NMe$_2$-2} (1b)	2.08, 2.75	4.41	0.72		8.74		
TaCl$_3$(C$_6$H$_3$CH$_2$NMe$_2$-2-Me-6) (1c)	2.37	3.79				2.87	
TaCl$_3$(C$_6$H$_4$CH$_2$NMe$_2$-2)(CH$_2$Ph) (2a)	2.35	3.82		3.05	8.84		
TaCl$_3$(C$_6$H$_3$CH$_2$NMe$_2$-2-Me-6)(CH$_2$Ph) (2c)	2.30	3.97		3.09		2.88	
TaCl$_2$(C$_6$H$_4$CH$_2$NMe$_2$-2)(CH$_2$Ph)$_2$[d] (3a)	2.09	3.65		3.14	8.12		
TaCl$_2${(R/S)-C$_6$H$_4$CH(Me)NMe$_2$-2}(CH$_2$Ph)$_2$[d] (3b)	1.86, 2.21	4.13	0.89	3.28	8.35		
TaCl$_2$(CH$_2$C$_6$H$_4$NMe$_2$-2)(CH$_2$Ph)$_2$[d] (3d)	2.50			3.08			e
TaCl$_2$(1-C$_{10}$H$_6$NMe$_2$-8)(CH$_2$Ph)$_2$[d] (3e)	2.57			3.45	8.02		
TaCl$_2${C$_6$H$_4$(CH(Me)N(Me)CH$_2$)-2}(CH$_2$Ph)(THF) (4b)	2.79	4.08	1.10	3.46, 4.96 (13)	8.42		f
TaCl$_2${1-C$_{10}$H$_6$NMeCH$_2$-8}(CH$_2$Ph)(THF)$_2$ (4e)	3.18			3.50, 5.36 (13)[g]	8.72		h

[a] Spectra were obtained in benzene-d_6 at 298 K, 200.13 MHz. Chemical shifts are indirectly referenced to SiMe$_4$ using solvent signals. [b] Other aryl resonances between 6.5 and 7.5 ppm. [c] Doublet with $7 \leq {}^3J$(H,H) ≤ 9 Hz. [d] Slow-exchange limit value for the benzyl protons in the following: **3a**, 3.05 (s, 2H), 3.22 (s, 2H); **3b**, 3.00 (m, 2H), 3.31 (d, ^2J(H,H) = 13 Hz, 1H), 3.53 (d, 1H); **3d**, 2.90 (s, 2H), 3.10 (s, 2H); **3e**, 3.33 (s, 2H), 3.47 (s, 2H). [e] 3.55 (CH$_2$C$_6$H$_4$N). [f] 1.93, 2.48 (AB, 2H, ^2J(H,H) = 10 Hz, TaCH$_2$N); 1.24, 3.61 (m, THF). [g] Poorly resolved. [h] 2.95, 3.02 (AB, 2H, ^2J(H,H) = 10 Hz, TaCH$_2$N); 1.16, 3.50 (m, THF).

Table II. Relevant ^{13}C NMR Data (ppm) for the Cyclometalated Tantalum(V) Complexes[a]

complex	NMe	CH$_2$N or CH(Me)N		CH$_2$Ph[b]	Ar C		other
		CH$_2$/CH	Me		C$_{ipso}$	o-Me	
1a	52.8	73.4			216.6		
1b	44.0, 50.1	72.6	11.1		220.1		
1c	52.9	73.4			219.7	28.7	
2a	52.3	75.7		93.6	215.5		
2c	51.6	76.0		97.4	217.1	28.3	
3a	48.2	72.2		94.6	215.7		
3b[c]	36.5, 42.0	68.8	10.2	91.7, 94.6	217.3		
3d	48.5			92.0			d
3e	49.1			95.2	214.8		
4b	51.0	73.4	16.0	96.0 (br)	208.8		e
4e	48.6			102.5 (br)	206.4		f

[a] Unless otherwise specified, spectra were obtained in benzene-d_6 at 298 K, 50.32 MHz. Chemical shifts are indirectly referenced to SiMe$_4$ using solvent signals. [b] Resonances for Ph ring between 120 and 140 ppm not assigned. [c] In toluene-d_8 at 213 K. [d] 93.2 (CH$_2$C$_6$H$_4$N). [e] 25.6, 71.6 (THF), 96.6 (br, TaCH$_2$N). [f] 25.5, 70.6 (THF), 117.8 (br, TaCH$_2$N).

Table III. Relevant Data for the Geometry of TaCl$_2$(C$_6$H$_4$CH$_2$NMe$_2$-2)(CH$_2$Ph)$_2$ (3a)

Bond Lengths (Å)

Ta(1)–Cl(1)	2.312 (3)	C(1)–C(12)	1.48 (2)
Ta(1)–Cl(2)	2.335 (3)	N(1)–C(1)	1.46 (2)
Ta(1)–N(1)	2.496 (9)	N(1)–C(2)	1.49 (2)
Ta(1)–C(4)	2.19 (1)	N(1)–C(3)	1.49 (2)
Ta(1)–C(5)	2.24 (1)	C(4)–C(21)	1.46 (2)
Ta(1)–C(11)	2.15 (1)	C(5)–C(31)	1.51 (2)

Bond Angles (deg)

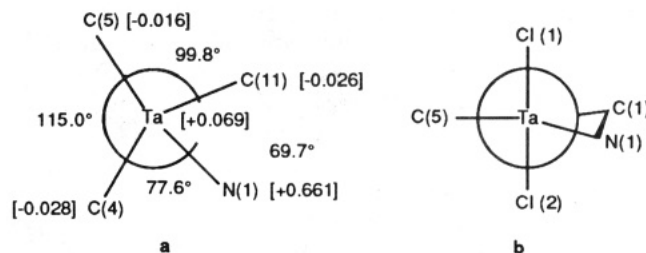|			
Cl(1)–Ta(1)–Cl(2)	176.36 (8)	N(1)–Ta(1)–C(4)	77.6 (4)
Cl(1)–Ta(1)–N(1)	80.7 (2)	N(1)–Ta(1)–C(11)	69.7 (4)
Cl(1)–Ta(1)–C(4)	91.9 (3)	N(1)–Ta(1)–C(5)	163.7 (4)
Cl(1)–Ta(1)–C(11)	95.8 (3)	C(4)–Ta(1)–C(5)	115.0 (5)
Ta(1)–C(4)–C(21)	99.2 (8)	C(5)–Ta(1)–C(11)	99.8 (4)
Ta(1)–C(5)–C(31)	120.1 (8)		

Figure 3. (a) Projection [Cl(1)–Ta(1)–Cl(2)] showing interligand angles (deg) and deviations (Å) in **3a** from the least-squares plane defined by Ta, C(4), C(5), and C(11). (b) Newman projection [Ta(1)–C(11)]. The benzylic atom C(4) is omitted for clarity.
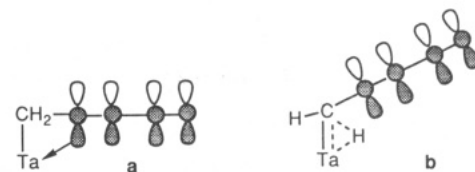

Figure 2. Structure of TaCl$_2$(C$_6$H$_4$CH$_2$NMe$_2$-2)(CH$_2$Ph)$_2$ (**3a**) in the crystal: ORTEP drawing with 30% probability ellipsoids.

Figure 4. Distorted benzyl bonding: (a) η^2-type; (b) "benzylidene"-type.

means that both pyramidal inversion of the nitrogen center is blocked and rotation around the C–NMe$_2$ bond is hindered, i.e., the tantalum–nitrogen interaction is stable on the NMR time scale, and that in solution the complexes have a five-membered Ta–C–C–C–N chelate ring as also found in the solid state (cf. **3a**).

Upon an increase of the temperature, these NMe resonances of **3b** broaden and eventually coalesce at 333 K. For the related tetrachloro complex **1b**, coalescence of the resonances of the NMe$_2$ unit does not occur under 353 K (the highest temperature employed). A likely process that renders the two NMe groups of **3b** homotopic at elevated temperatures involves dissociation of the Ta–N
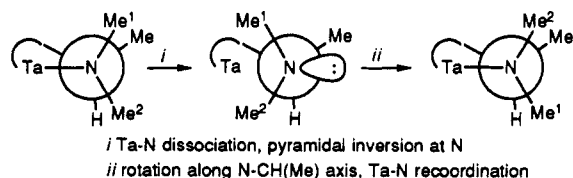
i Ta-N dissociation, pyramidal inversion at N

ii rotation along N-CH(Me) axis, Ta-N recoordination

Figure 5. Newman projection [N–CH(Me)] showing the Ta–N dissociation/association process rendering the NMe groups homotopic in **3b**.

Table IV. Fluxional Processes in the Dibenzyltantalum Complexes 3

complex	T_c (K)^a	$\Delta G^{\ddagger}$ (kJ·mol^{-1})^b	process
3a	253	49.7 ± 2	exchange of benzyl
3b	253	51.4 ± 2^c	ligands
3d	237	50.2 ± 2	
3e	208	41.0 ± 2	
3b	333	69.4 ± 2	Ta–N dissociation/ association

^{a} Data were obtained from the ^{1}H NMR spectra (toluene-d_8, 200.13 MHz) using the chemical shift differences of the proton resonances in the slow-exchange limit. ^{b} $\Delta G^{\ddagger} = 19.10 T_c\{9.97 + \log (T_c/\delta\nu)\}$. ^{c} Mean value obtained from two AB patterns both with ^2J(H,H) = 13 Hz; $\Delta\nu = 62$ and 106 Hz.

coordinative bond, since this allows pyramidal inversion at nitrogen, and rotation around the C–NMe$_2$ bond followed by recoordination of the N-donor atom to tantalum. This sequence is shown in Figure 5.

The easier coalescence of the NMe resonances of the dibenzyl complex **3b** compared to the tetrachloride **1b** is indicative of a stronger coordinative Ta–N bond in the latter caused by the greater Lewis acidity of its tantalum center.

In addition to Ta–N dissociation/association all complexes **3** exhibit below room temperature another fluxional process involving their benzyl ligands. At room temperature the benzylic C$_\alpha$ protons give rise to one sharp resonance in the range δ 3.05–3.45 ppm, which splits at low temperature into either two distinct signals (for **3a,d,e**) or two partially overlapping AB patterns (**3b**). In the temperature range where this fluxionality is evident the signals for the NMe$_2$ units are unaffected and the nitrogen donor atom is coordinatively bonded to tantalum on the NMR time scale (vide supra). The $\Delta G^{\ddagger}$ values for the fluxional process involving the benzyl ligands (Table IV) are virtually independent of the arylamine ligand present; for example the difference in $\Delta G^{\ddagger}$ for this process between **3a** and **3e** is only ca. 8 kJ·mol^{-1}. From this observation and from the fact that the $\Delta G^{\ddagger}$ for the dissociation of the Ta–N bond (69.4 ± 2 kJ·mol^{-1} for **3b**) is substantially greater than $\Delta G^{\ddagger}$ for the exchange of the benzyl ligands (51.4 ± 2 kJ·mol^{-1} for **3b**), we can conclude that the underlying process is not correlated to Ta–N association/dissociation. Furthermore, we found no concentration dependence for this fluxionality and deduce that the benzyl exchange occurs intramolecularly. The benzyl ligands are probably rendered equivalent by an overall positional exchange of the C$_{ipso}$ and the nitrogen donor of the amine ligand. This result can be achieved by a sequence of Ray–Dutt or Bailar twists,[28] during which a Ta–N interaction is retained.

NMe C–H Activation in TaCl$_2${C$_6$H$_4$CH(Me)NMe$_2$-2}(CH$_2$Ph)$_2$ (3b) and TaCl$_2$(1-C$_{10}$H$_6$NMe$_2$-8)(CH$_2$Ph)$_2$

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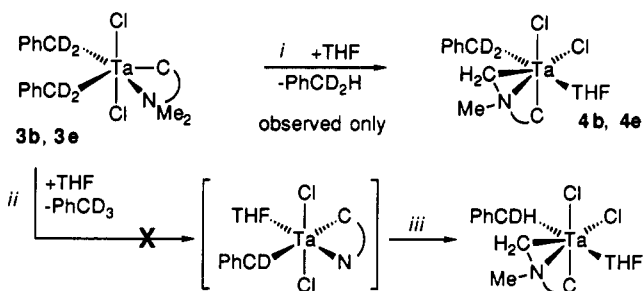
(3e). At reflux in tetrahydrofuran (THF) the dibenzyl complexes **3b,e** are converted within 1 h, with concomitant formation of toluene, to the new complexes **4b,e** that are isolated as red microcrystalline THF adducts in 60 and 34% yield, respectively (eq 5). The complexes can be
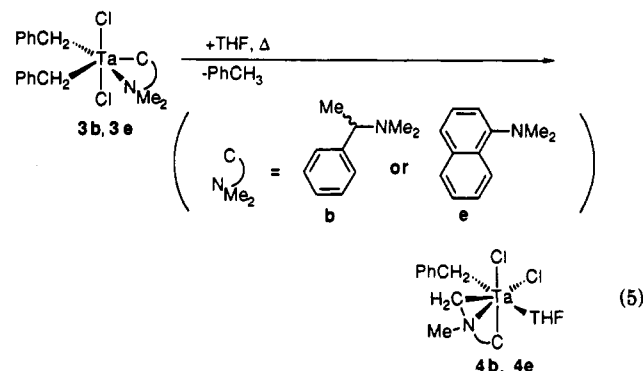
handled for short periods in air but are moisture-sensitive; the ^{1}H NMR data (Tables I and II) are characteristic and consistent with the presence of a new NCH$_2$ unit; i.e., C–H activation has taken place within one of the NMe groups of the dibenzyl complexes **3b,e**. Similar thermolysis experiments performed with **3a,d** showed that C–H activation occurred, but the reaction results in a complex mixture of organometallic species which have not been identified.

The course of the C–H activation reaction of the dibenzyl complexes **3b,e** to **4b,e**, respectively, has been followed by ^{1}H NMR (200.13 MHz, 4:1 C$_6$D$_6$/THF-d_8), and in neither case were reaction intermediates observed. At room temperature **3b** exhibits two anisochronous NMe resonances at 1.72 and 2.08 ppm. Upon warming of the solution, these two signals broaden and eventually coalesce at 333 K ($\Delta G^{\ddagger} = 69.4 \pm 2$ kJ·mol^{-1}); i.e., there is a fluxional process involving dissociation of the Ta–N bond. At about the same temperature a NMe C–H activation reaction takes place (**3b** starts converting to **4b**) with the concomitant formation of toluene. This activation, which is *overall* the abstraction of a hydrogen atom of a NMe group by a benzyl group, can result if one of the methyl groups of the amine penetrates into the tantalum inner coordination sphere. The temperature where rupture/formation of the Ta–N bond becomes fast on the (200 MHz) NMR time scale is also that where the NMe C–H activation occurs, but these processes are not directly connected. Each Ta–N dissociation does not necessarily trigger an NMe C–H activation sequence: the Ta–N dissociation is only a prelude to a second step in which the NMe group must penetrate the tantalum coordination sphere. In this ^{1}H NMR experiment, **4b** is formed in about 80% yield together with traces of some other diastereoisomers. This result clearly shows the stereoselectivity of the observed reactions. The conversion of the dibenzyl complex **3e** to **4e** occurs in a similar way, but in this case the NMR experiment does not allow the observation of dynamic behavior of the NMe$_2$ unit of **3e** (due to the absence of a chiral label in the amine ligand **e**).

In solution the dibenzyl complex **3a** also undergoes a C–H activation reaction similar to that of **3b**; however, for **3a** substantial formation of toluene begins at higher temperatures (ca. 353 K). Under these conditions the organometallic product of the C–H activation reaction is seen (^{1}H NMR, 200 MHz) only as a thermally unstable

Scheme II. Probing Possible Reaction Key Steps of NMe C–H Activation by Deuterium Labeling

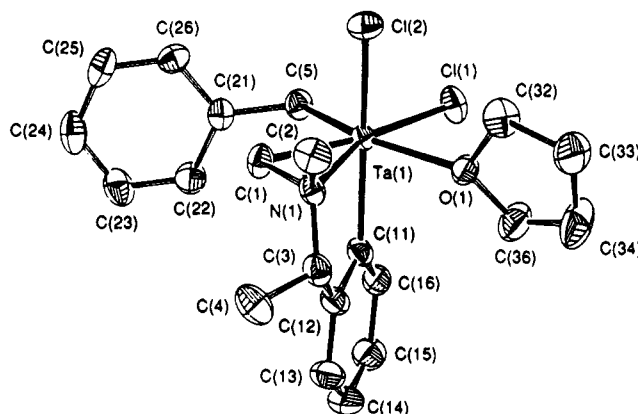*i*, σ-bond metathesis; *ii*, α-H abstraction; *iii*, alkylidene mediated NMe C–H activation.

Figure 6. ORTEP plot of one of the enantiomers of **4b** with S-configuration at the benzylic carbon atom of the arylamine function (30% probability thermal ellipsoids).

species. Thermolysis of the dibenzyl complex **3d** affords toluene and uncharacterized products. The thermal stability of the complexes **3** decreases in the order **3a** ~ **3d** > **3e** ≫ **3b**. The much lower thermal stability of **3b** compared to the other complexes is probably a direct result of the steric interference between one of the NMe groups and the Me substituent at the benzylic position of the amine ligand (Figure 5). When the amine unit is coordinated to tantalum, this inteference is pronounced and presumably weakens the Ta–N bond. Such steric hinder is absent in **3a,d,e** and results in a stronger coordinative Ta–N bond and higher thermal stability of these complexes. Further evidence for the weakening of a M–N coordinative bond by an alkyl substituent at the benzylic position of an ortho-metalated benzylamine ligand is found in organotin chemistry:[29] in SnBr{C₆H₄CH(R)NMe₂-2}(Me)(Ph) the Sn–N bond lengthens as R becomes bulkier [R = Me, Sn–N = 2.476 (7) Å; R = *t*-Bu, Sn–N = 2.552 (5) Å].

The NMR experiments performed with the dibenzyl complexes **3b,e** do not reveal whether the NMe hydrogen atom is abstracted either directly by a benzyl ligand, i.e. a one-step σ-bond metathesis reaction (Scheme II, step i), or indirectly by a two-step process involving a previously formed benzylidene group, i.e. alkylidene-mediated C–H activation (Scheme II, steps ii and iii). Many examples of both mechanistic routes are known in organotantalum chemistry. The σ-bond metathesis route is operative in not only the α-hydrogen abstraction reaction[30] that converts dialkyltantalum complexes to alkylidene tantalum complexes but also in many other 4-center C–H activation reactions.[31] Alkylidene-mediated C–H activation is known for tantalum alkylidene species because the α-carbon is very nucleophilic[32] and capable of abstracting protons from both inter- and intramolecular sources.

In order to find out which mechanistic route is being followed, an NMR study was carried out using the dibenzyl complex **3b** or **3e** with CD₂Ph instead of CH₂Ph ligands. As is shown in Scheme II, the toluene formed in the course of the NMe C–H activation reaction will now be either

PhCD₂H (σ-bond metathesis route) or PhCD₃ (the alkylidene-mediated route). The C–H activation reaction performed using **3b** or **3e** with CD₂Ph ligands produces 1 equiv of PhCD₂H only. In the case of **3e** an additional GC/MS analysis of the reaction volatiles confirmed this result and no PhCD₃ was detected. This study proves that the key step in the NMe C–H activation reaction is the direct abstraction of an NMe hydrogen atom by a benzyl ligand. Although alkylidene formation might have been expected for **3e**, because the 8-(dimethylamino)-1-naphthyl ligand keeps its NMe₂ unit in close proximity to the tantalum center,[16] this does not occur. The probable reason why this is not so is that the naphthylamine ligand **e** has the nitrogen donor attached to a completely sp²-hybridized carbon skeleton. This leads to a wider C,N bite angle and also allows the nitrogen lone pair to donate its electron density to the aromatic system. These factors, in combination, facilitate flipping around the C–NMe₂ bond and thus promote NMe C–H activation.

Molecular Geometry and Crystal Structure of TaCl₂{C₆H₄(CH(Me)N(Me)CH₂)-2}(CH₂Ph)(THF) (4b). In order to elucidate the stereochemistry of the ligand distribution around tantalum and the bonding in the TaCH₂N unit, an X-ray structural analysis of **4b** was carried out. Suitable crystals of **4b** were obtained from a diethyl ether solution at –30 °C. The crystal structure comprises the packing of two pairs of enantiomers in a triclinic unit cell. An ORTEP drawing of **4b**, along with the adopted numbering scheme, is shown in Figure 6; selected bond distances and angles are listed in Table V. The determined structure shows **4b** to be a mononuclear tantalum(V) species TaCl₂{C₆H₄(CH(Me)N(Me)CH₂)-2}(CH₂Ph)(THF) that has a distorted pentagonal bipyramidal geometry in which a chlorine atom [Cl(2)] and the ipso carbon atom [C(11)] of the arylamine occupy the apical positions. Coordinated to tantalum in the pentagonal plane are a chlorine atom [Cl(1)], THF [O(1)-bonded], a benzyl group [C(5)-bonded], and both the nitrogen [N(1)] and the carbon [C(1)] of the NCH₂ functionality of the C₆H₄(CH(Me)N(Me)CH₂)-2 ligand.

An interesting structural aspect is the intramolecular coordination of the NCH₂ group; this generates a triangular Ta–C–N unit [∠C(1)–Ta–N(1) = 38.7 (2)°] that is best described as a Ta–CH₂ σ-bond [Ta–C(1) = 2.158 (8) Å] combined with a donative N→Ta interaction [Ta–N(1) = 2.229 (6) Å]. Structural data for a recently published

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Table V. Relevant Data for the Geometry of Ta{C_6H_4(CH(Me)N(Me)CH$_2$)-2}(CH$_2$Ph)Cl$_2$(THF) (4b)

	mol 1	mol 2		mol 1	mol 2
		Bond Lengths (Å)			
Ta(1)–Cl(1)	2.406 (2)	2.392 (2)	N(1)–C(1)	1.455 (9)	1.451 (9)
Ta(1)–Cl(2)	2.386 (2)	2.379 (2)	N(1)–C(2)	1.50 (1)	1.49 (1)
Ta(1)–O(1)	2.343 (4)	2.330 (5)	N(1)–C(3)	1.48 (1)	1.503 (9)
Ta(1)–N(1)	2.229 (6)	2.224 (6)	C(3)–C(4)	1.51 (1)	1.52 (1)
Ta(1)–C(1)	2.158 (8)	2.162 (8)	C(5)–C(21)	1.50 (9)	1.52 (1)
Ta(1)–C(5)	2.211 (7)	2.215 (7)			
Ta(1)–C(11)	2.158 (7)	2.183 (7)			
		Bond Angles (deg)			
Cl(1)–Ta(1)–Cl(2)	95.95 (7)	102.50 (7)	C(1)–Ta(1)–C(5)	82.0 (3)	80.2 (3)
Cl(1)–Ta(1)–O(1)	79.1 (1)	79.5 (1)	C(1)–Ta(1)–N(1)	38.7 (2)	38.6 (2)
Cl(1)–Ta(1)–N(1)	159.3 (2)	156.4 (2)	N(1)–Ta(1)–O(1)	81.1 (2)	82.2 (2)
Cl(1)–Ta(1)–C(5)	78.8 (2)	83.2 (2)	C(1)–N(1)–C(2)	115.8 (6)	116.3 (6)
Cl(1)–Ta(1)–C(11)	96.9 (2)	94.1 (2)	C(2)–N(1)–C(3)	111.1 (6)	109.8 (6)
Cl(2)–Ta(1)–O(1)	86.7 (2)	80.9 (1)	Cl(2)–Ta(1)–N(1)	89.1 (2)	89.2 (2)
Cl(2)–Ta(1)–C(1)	90.1 (2)	94.1 (2)	Cl(2)–Ta(1)–C(5)	100.3 (2)	87.2 (2)
Cl(2)–Ta(1)–C(11)	162.1 (2)	159.5 (2)			

yttrium complex[33] with a bridging $C_6H_4CH_2N$(Me)(CH$_2$-μ)-2 functionality seem to make this description more general. On the basis of both geometrical and spectroscopic considerations, this latter formulation seems preferable to an alternative involving complexation of an iminium ion (>N$^+$=CH$_2$) to Ta(III), the N(1)–C(1) distance of 1.455 (9) Å being characteristic for a single N–C bond. In this new tantalaazacyclopropane unit bent bonds allow the nitrogen lone pair, which is not directly orientated to the metal center, to become involved in bonding to tantalum. Related NMe C–H-activation reactions have been found in tantalum amido chemistry, where C–H activation generates similar Ta–C–N units. Obviously, in the latter units the nitrogen atom forms an additional covalent bond to the tantalum center.[34]

In 4b the large Ta–C$_\alpha$–C$_\beta$ angle of 124.1 (5)° afforded by the benzyl ligand is close to the larger of the angles found in the dibenzyl complex 3a [i.e. 120.1 (8)°] and seems again to be caused by steric repulsions within the molecule, the C$_\beta$···C(1) distance being 2.90 Å. Alleviation of electronic deficiency of the tantalum center by unusual benzylic bonding (see Figure 4) is more unlikely in this structure than in that of the dibenzyl complex 3a because of the higher formal electron count on the tantalum (14e for 4b versus 12e for 3a).

It is interesting from a synthetic point of view that the solution NMR data and the X-ray structure of 4b correspond to the enantiomeric pair of only one of the several theoretically possible diastereoisomers. Without taking account of the N–Ta coordinative bond, the Bailar method[35] describes this complex as an octahedral species of the type M(AB)cde$_2$ for which seven diasteroisomers are possible. However, the presence of the chiral benzylic carbon atom centre [C(3)] of the amine ligand and coordination of the nitrogen centre [N(1)] to tantalum augment the number of diastereoisomers to a total of 24. In spite of this large number the structurally characterized one is obtained in good yield, and therefore, the overall formation of 4b from 3b is not only chemoselective but also very stereoselective. The isolated isomer is the only one in which there is optimal synergism resulting from

electron-withdrawing chlorine atoms being in positions trans to the hardest electron-donating substituents (C$_{ipso}$ and the NCH$_2$ unit).

Conclusions

The results presented clearly show that tantalum compounds with an intramolecularly coordinating N-donor ligand site are readily accessible. The scope of the adopted synthetic methods includes cyclometalated tantalum complexes in which the chelate rings have different steric constraints. In general, the cyclometalated complexes have good thermal stability as long as the five-membered Ta–C–C–C–N chelate ring remains intact.

NMR evidence and deuterium labeling studies show that rupture of the Ta–N coordinative bond of the dibenzyl complexes 3 can result in a (stereoselective) NMe C–H activation that proceeds via a σ-bond metathesis step. Relief of steric strain in a sterically crowded molecule seems to be the driving force behind the NMe C–H activation process just as it is the driving force in α-hydrogen abstraction reactions of dialkyltantalum complexes leading to alkylidene species. However, for the dibenzyl complexes 3 the (stereoselective) NMe C–H activation step leading to tantala(V)azacyclopropane species provides a new reaction pathway that is favored above the expected route that leads to benzylidene formation.

Experimental Section

TaCl$_3$-(CH$_2$Ph)$_2$,[21] Zn(C$_6$H$_4$CH$_2$NMe$_2$-2)$_2$,[19] Zn(CH$_2$C$_6$H$_4$NMe$_2$-2)$_2$,[19] and [Li(1-C$_{10}$H$_6$NMe$_2$-8)(Et$_2$O)]$_2$[20c] were prepared according to literature procedures. The partially deuterated complexes TaCl$_2$-{C$_6$H$_4$CH(Me)NMe$_2$-2}(CD$_2$Ph)$_2$ and TaCl$_2$(1-C$_{10}$H$_6$NMe$_2$-8)-(CD$_2$Ph)$_2$ were synthesized in analogy to 3b,e, respectively, using TaCl$_3$(CD$_2$Ph)$_2$[21] instead of TaCl$_3$(CH$_2$Ph)$_2$. The amine C$_6$H$_5$-CH(Me)NMe$_2$ (S or R/S) was synthesized via a conventional Eschweiler–Clarke procedure starting with the commercially available enantiomer or racemic mixture of C$_6$H$_5$CH(Me)NH$_2$. The preparation of Zn{C$_6$H$_4$CH(Me)NMe$_2$-2}$_2$ is similar to that of Zn(C$_6$H$_4$CH$_2$NMe$_2$-2)$_2$.[19]

Synthesis of Zn(C$_6$H$_3$CH$_2$NMe$_2$-2-Me-6)$_2$. To a stirred solution of BrC$_6$H$_3$CH$_2$NMe$_2$-2-Me-6 (17 g, 74 mmol) in Et$_2$O (150 mL) at –78 °C was slowly added a solution of 1.5 M

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n-butyllithium (50 mL, 75 mmol). The reaction mixture was stirred at 20 °C for 1 h and subsequently cooled to -78 °C. ZnCl₂ (5.0 g, 38 mmol) in Et₂O (25 mL) was added. The solvent was stripped of at 20 °C and the residue extracted with C₆H₆ (3 × 50 mL). The solvent was removed from the extracts in vacuo, and the residue was recrystallized from pentane (~100 mL) at -30 °C; yield 12 g (91%) of white crystalline Zn(C₆H₃CH₂NMe₂-2-Me-6)₂. ¹H NMR (200.13 MHz, toluene-d₈, 298 K): δ 1.90 (s, 12, NCH₃), 2.58 (s, 6, ArCH₃), 2.98 and 3.61 (AB, J = 14 Hz, 4, CH₂N), 7.0 (m, 6, ArH).

Synthesis of TaCl₄(C₆H₄CH₂NMe₂-2) (1a). To a stirred suspension of TaCl₅ (3.43 g, 9.58 mmol) in Et₂O (30 mL) at -78 °C was added over 1 min a solution of Zn(C₆H₄CH₂NMe₂-2)₂ (1.49 g, 4.46 mmol) in Et₂O (10 mL). After the initially yellow suspension was warmed to 20 °C, a yellow solution resulted from which the solvent was removed in vacuo. The sticky residue was triturated with hexane and subsequently extracted with C₆H₆ (3 × 30 mL). The volume of the combined extracts was reduced in vacuo to ca. 10 mL. Pentane (200 mL) was added, and the product crystallized out as bright yellow needles after 2 h at -30 °C; yield 3.43 g (91%). Anal. Calcd for TaC₉H₁₂NCl₄: C, 23.66; H, 2.65; N, 3.07. Found: C, 24.16; H, 2.80; N, 3.07.

Synthesis of TaCl₄{(S)-C₆H₄CH(Me)NMe₂-2} (1b). The procedure is the same as that for TaCl₄(C₆H₄CH₂NMe₂-2) except that 1.37 g (3.82 mmol) of TaCl₅ and 0.69 g (1.91 mmol) of Zn{(S)-C₆H₄CH(Me)NMe₂-2}₂ yielded 1.27 g (76%) of yellow microcrystalline TaCl₄{(S)-C₆H₄CH(Me)NMe₂-2} after 18 h at -30 °C.

Synthesis of TaCl₄(C₆H₃CH₂NMe₂-2-Me-6) (1c). The procedure is the same as that for TaCl₄(C₆H₄CH₂NMe₂-2) except that 4.87 g (13.6 mmol) of TaCl₅ and 2.37 g (6.55 mmol) of Zn(C₆H₃CH₂NMe₂-2-Me-6)₂ yielded 4.39 g (76%) of yellow microcrystalline TaCl₄(C₆H₃CH₂NMe₂-2-Me-6) after 18 h at -30 °C. Anal. Calcd for TaC₁₀H₁₄NCl₄: C, 25.50; H, 3.00; N, 2.97. Found: C, 25.20; H, 2.95; N, 2.74.

Synthesis of TaCl₃(C₆H₄CH₂NMe₂-2)(CH₂Ph) (2a). To a stirred solution of TaCl₄(C₆H₄CH₂NMe₂-2) (2.52 g, 5.94 mmol) in Et₂O (30 mL) at -78 °C was added over 5 min a solution of Zn(CH₂Ph)₂ (0.80 g, 3.2 mmol) in Et₂O (10 mL). The initially yellow solution was allowed to warm to 20 °C giving a red solution from which the solvent was removed in vacuo. The resulting red oil was triturated with hexane and subsequently extracted with C₆H₆ (2 × 30 mL). The volume of the combined extracts was reduced in vacuo to ca. 10 mL. Pentane (200 mL) was added, and the product crystallized out as bright red needles after 18 h at -30 °C; yield 1.60 g (53%).

Synthesis of TaCl₃(C₆H₃CH₂NMe₂-2-Me-6)(CH₂Ph) (2c). The procedure is the same as that for TaCl₃(C₆H₄CH₂NMe₂-2)(CH₂Ph) except that 0.54 g (1.1 mmol) of TaCl₄(C₆H₃CH₂NMe₂-2-Me-6) and 0.37 g (1.5 mmol) of Zn(CH₂Ph)₂ yielded 0.51 g (88%) of red crystalline TaCl₃(C₆H₃CH₂NMe₂-2-Me-6)(CH₂Ph) after 18 h at -30 °C. Anal. Calcd for TaC₁₇H₂₁NCl₃: C, 38.70; H, 4.20; N, 2.65. Found: C, 38.55; H, 4.10; N, 2.65.

Synthesis of TaCl₂(C₆H₄CH₂NMe₂-2)(CH₂Ph)₂ (3a) (Improved Procedure). A solution of Zn(C₆H₄CH₂NMe₂-2)₂ (1.12 g, 3.37 mmol) in Et₂O (20 mL) was added over 1 min to a stirred suspension of TaCl₃(CH₂Ph)₂ (2.90 g, 6.18 mmol) in Et₂O (50 mL) at -78 °C. After the addition, the resulting orange suspension was allowed to warm to room temperature giving a dark red solution from which the solvent was removed under reduced pressure. The residue was extracted with C₆H₆ (2 × 30 mL). The combined extracts were concentrated in vacuo to 20 mL and layered with pentane (80 mL). After the solution was left standing at -20 °C for 18 h, the product crystallized out as red needles that were isolated by decantation and subsequently dried in vacuo; yield 2.37 g (68%). Anal. Calcd for TaC₂₃H₂₆Cl₂N: C, 48.61; H, 4.61; N, 2.46; Cl, 12.49. Found: C, 46.70; H, 4.67; N, 2.61; Cl, 13.01.

Synthesis of TaCl₂{(R/S)-C₆H₄CH(Me)NMe₂-2}(CH₂Ph)₂ (3b). The procedure is the same as that for TaCl₂(C₆H₄CH₂NMe₂-2)(CH₂Ph)₂ except that 3.62 g (7.71 mmol) of TaCl₃(CH₂Ph)₂ and 1.40 g (3.87 mmol) of Zn{(R/S)-C₆H₄CH(Me)NMe₂-2}₂ yielded 3.33 g (74%) of orange TaCl₂{(R/S)-C₆H₄CH(Me)NMe₂-

2}(CH₂Ph)₂. Note: due to the thermal instability of the product, the workup procedure must be carried out at ~0 °C; the crystallization step was omitted, and the product was washed with pentane (2 × 30 mL). This experimental procedure gives best results when completed within 2 h. The product can be stored at -30 °C for months without noticeable decomposition.

Synthesis of TaCl₂(CH₂C₆H₄NMe₂-2)(CH₂Ph)₂ (3d). The procedure is the same as that for TaCl₂(C₆H₄CH₂NMe₂-2)(CH₂Ph)₂ except that 1.87 g (3.98 mmol) of TaCl₃(CH₂Ph)₂ and 0.66 g (1.98 mmol) of Zn(CH₂C₆H₄NMe₂-2)₂ yielded 1.13 g (50%) of orange/red TaCl₂(CH₂C₆H₄NMe₂-2)(CH₂Ph)₂.

Synthesis of TaCl₂(1-C₁₀H₆NMe₂-8)(CH₂Ph)₂ (3e). The procedure is the same as that for TaCl₂(C₆H₄CH₂NMe₂-2)(CH₂Ph)₂ except that 4.15 g (8.84 mmol) of TaCl₃(CH₂Ph)₂ and 1.90 g (7.96 mmol) of [Li(1-C₁₀H₆NMe₂-8)(Et₂O)]₂ yielded 2.93 g (62%) of orange TaCl₂(1-C₁₀H₆NMe₂-8)(CH₂Ph)₂. Note: [Li(1-C₁₀H₆NMe₂-8)(Et₂O)]₂ was added as a suspension in Et₂O.

Synthesis of TaCl₂{C₆H₄(CH(Me)N(Me)CH₂)-2}-(CH₂Ph)(THF) (4b). A solution of 3b (1.63 g, 2.80 mmol, R/S) in THF (20 mL) was heated at 58 °C for 75 min. The resulting red solution was allowed to cool down to room temperature and was layered with ca. 50 mL of Et₂O. After the solution was left standing at -30 °C for several days, microcrystalline, red TaCl₂{C₆H₄(CH(Me)N(Me)CH₂)-2}(CH₂Ph)(THF)₂.₃ was isolated by decantation. Repeated washing with pentane to remove excess THF and drying in vacuo yielded 0.95 g (60%) of pure red product. Anal. Calcd for C₂₁H₂₈Cl₂NOTa: C, 44.86; H, 5.02; N, 2.49. Found: C, 44.73; H, 4.84; N, 2.39.

Synthesis of TaCl₂(1-C₁₀H₆NMeCH₂-8)(CH₂Ph)(THF)₂ (4e). A solution of 3e (2.45 g, 4.03 mmol) in THF (20 mL) was heated under gentle reflux for 1.5 h. The resulting red solution was allowed to cool down to room temperature and was concentrated in vacuo to ca. 5 mL. The turbid solution was filtered, and Et₂O vapor was allowed to diffuse into the solution over a period of several days, first at room temperature and later at -30 °C. Yield: 0.91 g (34%) of microcrystalline, dark-red TaCl₂(1-C₁₀H₆NMeCH₂-8)(CH₂Ph)(THF)₂.

Crystal Structure Determination of 3a. Transparent red crystals of 3a, Ta(C₆H₄CH₂NMe₂-2)(CH₂Ph)₂Cl₂, C₂₃H₂₆Cl₂NTa, formed with M_r = 568.32, triclinic space group $P\bar{1}$, a = 9.055 (2) Å, b = 9.614 (1), c = 13.910 (3) Å, α = 72.93 (1)°, β = 80.91 (2),

Table VI. 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 Å²
Ta(1)	0.06555 (5)	0.37315 (4)	0.27775 (3)	0.0389 (1)
Cl(1)	-0.0714 (3)	0.4622 (3)	0.1353 (2)	0.0560 (9)
Cl(2)	0.2138 (3)	0.2935 (3)	0.4165 (2)	0.068 (1)
N(1)	0.029 (1)	0.1309 (9)	0.2673 (7)	0.059 (3)
C(1)	-0.137 (2)	0.143 (1)	0.287 (1)	0.076 (5)
C(2)	0.112 (2)	0.009 (1)	0.350 (1)	0.081 (5)
C(3)	0.081 (2)	0.079 (2)	0.174 (1)	0.095 (6)
C(4)	0.279 (1)	0.282 (1)	0.1931 (9)	0.061 (4)
C(5)	0.026 (1)	0.613 (1)	0.2808 (9)	0.052 (3)
C(11)	-0.124 (1)	0.317 (1)	0.3816 (8)	0.054 (3)
C(12)	-0.201 (1)	0.219 (1)	0.3698 (8)	0.060 (4)
C(13)	-0.333 (2)	0.195 (2)	0.431 (1)	0.083 (5)
C(14)	-0.391 (2)	0.270 (2)	0.505 (1)	0.088 (5)
C(15)	-0.317 (2)	0.366 (2)	0.518 (1)	0.087 (5)
C(16)	-0.184 (1)	0.389 (1)	0.4606 (8)	0.063 (4)
C(21)	0.341 (1)	0.414 (1)	0.1613 (8)	0.049 (3)
C(22)	0.440 (1)	0.436 (2)	0.2204 (9)	0.072 (5)
C(23)	0.489 (2)	0.569 (2)	0.191 (1)	0.092 (7)
C(24)	0.440 (2)	0.677 (2)	0.104 (1)	0.092 (6)
C(25)	0.347 (2)	0.657 (2)	0.045 (1)	0.083 (5)
C(26)	0.297 (1)	0.527 (1)	0.0740 (8)	0.062 (4)
C(31)	-0.112 (1)	0.733 (1)	0.2339 (8)	0.048 (3)
C(32)	-0.103 (2)	0.812 (1)	0.1298 (9)	0.066 (4)
C(33)	-0.228 (2)	0.925 (1)	0.0901 (9)	0.076 (5)
C(34)	-0.364 (1)	0.964 (1)	0.146 (1)	0.072 (4)
C(35)	-0.376 (2)	0.887 (1)	0.245 (1)	0.073 (4)
C(36)	-0.248 (1)	0.774 (1)	0.2887 (8)	0.057 (4)

ª $U(eq) = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.

Table VII. Final Coordinates and Equivalent Isotropic Thermal Parameters and Their Esd's in Parentheses for the Non-H Atoms of 4b[a]

atom	x	y	z	$U(eq),$[a] Å^2
		Molecule 1		
Ta(1)	0.32746 (3)	0.27683 (3)	0.11755 (1)	0.0378 (1)
Cl(1)	0.1725 (2)	0.1855 (2)	0.17672 (8)	0.0606 (6)
Cl(2)	0.2539 (2)	0.2081 (2)	0.04076 (8)	0.0680 (7)
O(1)	0.5072 (5)	0.0276 (4)	0.1288 (2)	0.053 (2)
N(1)	0.5406 (6)	0.2860 (6)	0.0736 (2)	0.047 (2)
C(1)	0.4024 (8)	0.4288 (8)	0.0722 (3)	0.056 (2)
C(2)	0.6003 (9)	0.216 (1)	0.0224 (3)	0.068 (3)
C(3)	0.6749 (8)	0.2740 (8)	0.1041 (3)	0.056 (2)
C(4)	0.766 (1)	0.360 (1)	0.0798 (4)	0.085 (4)
C(5)	0.1124 (7)	0.4833 (7)	0.1333 (3)	0.048 (2)
C(11)	0.4663 (7)	0.3098 (7)	0.1747 (3)	0.047 (2)
C(12)	0.6158 (8)	0.3098 (7)	0.1592 (3)	0.052 (2)
C(13)	0.7046 (9)	0.3391 (9)	0.1941 (4)	0.073 (3)
C(14)	0.645 (1)	0.369 (1)	0.2452 (4)	0.081 (4)
C(15)	0.500 (1)	0.3719 (9)	0.2602 (3)	0.070 (3)
C(16)	0.4097 (8)	0.3422 (7)	0.2263 (3)	0.054 (2)
C(21)	0.0969 (7)	0.6352 (7)	0.1156 (3)	0.045 (2)
C(22)	0.1474 (9)	0.7176 (8)	0.1449 (3)	0.060 (3)
C(23)	0.136 (1)	0.8543 (8)	0.1284 (3)	0.069 (3)
C(24)	0.067 (1)	0.9197 (8)	0.0827 (3)	0.070 (3)
C(25)	0.0142 (9)	0.8411 (9)	0.0524 (3)	0.066 (3)
C(26)	0.0293 (7)	0.7022 (8)	0.0680 (3)	0.055 (2)
C(33)	0.6068 (5)	−0.2295 (4)	0.1239 (2)	0.105 (2)
C(34)	0.6532 (5)	−0.1972 (4)	0.1750 (2)	0.110 (5)
C(32)[b]	0.5095 (5)	−0.0852 (4)	0.0956 (2)	0.083 (6)
C(36)[b]	0.5548 (5)	−0.0350 (4)	0.1810 (2)	0.090 (7)
C(31)[c]	0.5767 (5)	−0.0889 (4)	0.0922 (2)	0.09 (1)
C(35)[c]	0.6067 (5)	−0.0337 (4)	0.1732 (2)	0.11 (2)
		Molecule 2		
Ta(2)	0.15237 (3)	0.23638 (3)	0.64051 (1)	0.0388 (1)
Cl(3)	0.2612 (2)	0.2754 (2)	0.55705 (7)	0.0614 (6)
Cl(4)	0.3864 (2)	0.0880 (2)	0.68608 (8)	0.0629 (6)
O(2)	0.2152 (6)	0.0097 (5)	0.6048 (2)	0.062 (2)
N(2)	0.0101 (6)	0.1564 (6)	0.6973 (2)	0.046 (2)
C(6)	−0.0009 (8)	0.2998 (8)	0.7100 (3)	0.051 (2)
C(7)	0.0861 (9)	0.0315 (9)	0.7359 (3)	0.072 (3)
C(8)	−0.1396 (7)	0.1529 (7)	0.6794 (3)	0.045 (2)
C(9)	−0.2689 (9)	0.1858 (9)	0.7228 (3)	0.062 (3)
C(10)	0.1916 (8)	0.4312 (7)	0.6593 (3)	0.052 (2)
C(41)	−0.0812 (7)	0.3053 (7)	0.6077 (2)	0.040 (2)
C(42)	−0.1914 (7)	0.2556 (6)	0.6320 (2)	0.041 (2)
C(43)	−0.3423 (7)	0.2932 (8)	0.6139 (3)	0.054 (2)
C(44)	−0.3881 (8)	0.3880 (8)	0.5696 (3)	0.061 (3)
C(45)	−0.2825 (8)	0.4386 (8)	0.5443 (3)	0.055 (2)
C(46)	−0.1334 (8)	0.3991 (8)	0.5627 (3)	0.053 (2)
C(51)	0.0526 (9)	0.5771 (8)	0.6454 (3)	0.054 (3)
C(52)	0.028 (1)	0.6359 (9)	0.5951 (3)	0.068 (3)
C(53)	−0.105 (1)	0.7677 (9)	0.5829 (4)	0.081 (3)
C(54)	−0.209 (1)	0.845 (1)	0.6221 (4)	0.083 (4)
C(55)	−0.185 (1)	0.7907 (9)	0.6723 (4)	0.079 (3)
C(56)	−0.0583 (9)	0.6592 (8)	0.6836 (3)	0.061 (3)
C(63)	0.2463 (6)	−0.1210 (5)	0.5325 (2)	0.174 (8)
C(64)	0.3710 (6)	−0.2024 (5)	0.5615 (2)	0.25 (1)
C(62)[d]	0.1239 (6)	−0.0401 (5)	0.5741 (2)	0.16 (2)
C(66)[d]	0.3171 (6)	−0.1455 (5)	0.6148 (2)	0.21 (2)
C(61)[e]	0.1291 (6)	0.0129 (5)	0.5594 (2)	0.071 (7)
C(65)[e]	0.3835 (6)	−0.0857 (5)	0.5913 (2)	0.102 (9)

[a] See footnote *a* of Table VI. [b] Major disorder (65.4%). [c] Minor disorder (34.6%). [d] Major disorder (50.3%). [e] Minor disorder (49.7%).

$\gamma = 72.74$ (1)°, $V = 1102.1$ (4) Å^3, $Z = 2$, $D_c = 1.712$ g cm^{-3}, and μ(Mo Kα) = 51.8 cm^{-1}. A block-shaped crystal (0.15 × 0.20 × 0.63 mm) of **3a**, mounted in a Lindemann glass capillary, was used for data collection on an Enraf-Nonius CAD-4 diffractometer

with Zr-filtered Mo Kα radiation ($\theta_{max} = 28$°). The cell parameters were derived from the 25 SET 4 setting angles with $8 < \theta < 13$°. The triclinic unit cell was checked for the presence of higher symmetry.[36] Intensity data were corrected for Lp, a small linear decay of 6%, and absorption (correction range 0.74/1.45) (DIFABS).[37] The structure was solved with the PATT option of SHELXS-86[38] and refined by full-matrix least-squares techniques on F (SHELX-76).[39] All H atoms, except the H atoms on C(4) and C(5), which were found in a difference Fourier map, were introduced at calculated positions with C–H = 0.98 Å and refined riding on their carrier atom. Full-matrix least-squares refinement converged at final values $R = 0.049$, $R_w = 0.057$, and $w^{-1} = [\sigma^2(F) + 0.001363F^2]$ for 3427 unique reflections with $I \geq 2.5\sigma(I)$. Four common isotropic thermal parameters for H atoms were used. Scattering factors were taken from Cromer and Mann,[40] and anomalous dispersion corrections, from Cromer and Liberman.[41] Final coordinates of the non-hydrogen atoms are given in Table VI.

Crystal Structure Determination of 4b. Transparent red crystals of **4b**, TaCl$_2$|C$_6$H$_4$CH(Me)N(Me)CH$_2$-2|(CH$_2$Ph)(THF), C$_{21}$H$_{28}$Cl$_2$NOTa, formed with $M_r = 562.32$, triclinic space group $P\bar{1}$, $a = 9.218$ (1) Å, $b = 9.974$ (1) Å, $c = 25.930$ (1) Å, $\alpha = 85.75$ (1)°, $\beta = 85.70$ (2)°, $\gamma = 64.97$ (1)°, $V = 2151.7$ (4) Å^3, $Z = 4$, $D_c = 1.73$ g cm^{-3}, and μ(Mo Kα) = 53.1 cm^{-1}. A block-shaped crystal (0.26 × 0.43 × 0.87 mm) of **4b**, mounted in a Lindemann glass capillary, was used for data collection on an Enraf-Nonius CAD-4 diffractometer with Zr-filtered Mo Kα radiation ($\theta_{max} = 27.5$°). The cell parameters were derived from the 25 SET4 setting angles with $14 < \theta < 20$°. The triclinic unit cell was checked for the presence of higher symmetry.[36] Intensity data were corrected for Lp and absorption (correction range 0.73/1.24) (DIFABS).[37] The structure was solved with the PATT option of SHELXS-86[38] and refined by full-matrix least-square techniques on F (SHELX-76).[39] All H atoms were introduced at calculated positions with C–H = 0.98 Å and refined riding on their carrier atom. A disorder model was used to describe the disorder of the tetrahydrofuran rings of both independent molecules. Full-matrix least-squares refinement converged at final values $R = 0.035$, $R_w = 0.041$, and $w^{-1} = \sigma^2(F)$ for 7175 unique reflections with $I \geq 2.5\sigma(I)$. Four common isotropic thermal parameters for H atoms were used. Scattering factors were taken from Cromer and Mann,[40] and anomalous dispersion corrections, from Cromer and Liberman.[41] Final coordinates of the non-hydrogen atoms are given in Table VII.

Supplementary Material Available: For **3a** and **4b**, tables of anisotropic thermal parameters, hydrogen atom positions and isotropic thermal parameters, all bond distances, and all bond angles (12 pages). Ordering information is given on any current masthead page.

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