A Bimetallic Tantalum–Zinc Complex with an Ancillary Aryldiamine Ligand as Precursor for a Reactive Alkylidyne Species: Alkylidyne-Mediated C–H Activation and a Palladium-Mediated Alkylidyne Functionalization

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The 1:1 reaction of $TaCl_2\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(\equiv CH\text{-}t\text{-}Bu)$ with neopentylzinc chloride affords the bimetallic complex $TaCl_2\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(\mu\text{-}C\text{-}t\text{-}Bu)(\mu\text{-}ZnCl)$ (2) in high yield. Crystals of 2 belong to the space group $P2_12_12_1$ with $a = 9.725(2)$ Å, $b = 10.436(2)$ Å, $c = 20.766(3)$ Å, $Z = 4$, $M_r = 613.11$, $V = 2107.5(7)$ Å^3, ρ(calcd) = 1.932 g·cm^{-3}. The pentacoordinate tantalum center has a coordination geometry between trigonal bipyramidal and square pyramidal while the zinc center has a distorted tetrahedral ligand array; the alkylidyne functionality and the aryl *ipso*-carbon bridge between the zinc and tantalum centers. The p-orbital at C_{ipso} of the aryldiamine ligand forms a 2-electron bond to the zinc center, and this aryldiamine ancillary thus functions as an 8-electron donor. The reaction of 2 with tmeda at 60 °C leads to elimination of zinc chloride and formation of the alkylidene complex $TaCl\{C_6H_3(CH_2N(Me)CH_2)\text{-}2\text{-}(CH_2\text{-}NMe_2)\text{-}6\}(\equiv CH\text{-}t\text{-}Bu)$; this is an alkylidyne-mediated activation reaction of a methyl C–H bond in a NMe$_2$ group. In the presence of $[Pd(C_6H_4CH_2NMe_2\text{-}2)(\mu\text{-}X)]_2$ (X = Cl, I) the reaction of bimetallic 2 with tmeda $[Me_2N(CH_2)_2NMe_2]$ appears to generate $TaCl_2(C_6H_4CH_2NMe_2\text{-}2)[\equiv C(t\text{-}Bu)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ and, as such, is an unanticipated, new palladium-mediated alkylidyne functionalization reaction.

Introduction

The reactivity of the metal—carbon triple bond in carbyne complexes[1] has been studied by several groups. Principal aims have been either the use of the carbyne fragment as a building block in organic synthesis or the use of the metal—carbon triple bond as a sterically hindered heteroacetylene, for example, in cluster synthesis.[2,3] In particular there has been extensive employment of the isolobal analogy[4] between group 6 metallacarbynes and alkynes to guide the synthesis of polymetallic compounds, whereby one adds M(≡CR)(L)(CO)$_2$ (L = 6-electron ligand) complexes to coordinatively unsaturated metal species.[2] Very few studies, however, report the use of this concept to achieve C—C bond formation.[5,6] Recently, it has been shown that low oxidation state tungsten and molybdenum carbyne complexes containing either cyclopentadienyl or tripod ligands can react with [Pd(C$_6$H$_4$-CH$_2$NMe$_2$-2)(μ-X)]$_2$ (X = Cl, I) to give organometallic products wherein there is a new C—C bond formed through insertion of a W≡C or Mo≡C bond into a Pd—C bond.[6] Compared to such low oxidation state carbyne complexes, higher oxidation state alkylidyne species should have a

more reactive nucleophilic M≡C unit[7,8] that may be more likely to participate in C—C bond formation reactions. However, reactions between high oxidation state metal alkylidyne complexes and late transition metal species containing a metal-to-carbon bond do not seem to have been investigated so far.

In a previous paper, we reported the synthesis of a high oxidation state tantalum alkylidene complex, TaCl$_2$-{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}(≡CH-*t*-Bu) (1),[9b] that contains a monoanionic aryldiamine ancillary ligand that markedly enhances the kinetic stability of this complex by forming intramolecular Ta–C–C–C–N chelate rings. In this

(3) In organotantalum chemistry, however, a number of heterobimetallic and -polymetallic complexes have been reported, but none of the synthetic methods employed here involves a reaction with a tantalum alkylidyne complex. Heterometallics that contain an 18-electron dicyclopentadienyltantalum fragment are well-represented.[3a–d] The remaining heterometallic tantalum complexes reported are either saltlike derivatives of the hexacarbonyltantalate anion,[3e–h] Lewis-acid stabilized tantalum alkylidene[3h] and alkylidyne complexes[10,18] or heterobimetallic complexes in which a specially designed ligand system binds two metal centers; ligand systems used in this field are (oxyalkyl)phosphines[3j] and a bis-(tetramethylcyclopentadienyl)ethane ligand.[3k] (a) Budzelaar, P. H. M.; van der Zeijden, A. A. H.; Boersma, J.; van der Kerk, G. J. M.; Spek, A. L.; Duisenberg, A. J. M. *Organometallics* 1984, *3*, 159. (b) Harris, D. H.; Keppie, S. A.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* 1973, 1653. (c) Perrey, D.; Leblanc, J. C.; Moise, C.; Martin-Gil, J. *J. Organomet. Chem.* 1991, *412*, 363. (d) Jacobsen, E. N.; Goldberg, K. I.; Bergmann, R. G. *J. Am. Chem. Soc.* 1988, *110*, 3706. (e) Werner, R. P. M.; Filbey, A. H.; Manastyrskyj, S. A. *Inorg. Chem.* 1964, *3*, 298. (f) Ellis, J. E.; Davidson, A. *Inorg. Synth.* 1976, *16*, 68. (g) Davidson, A.; Ellis, J. E. *J. Organomet. Chem.* 1972, *36*, 113. (h) Keblys, K. A.; Dubeck, M. *Inorg. Chem.* 1964, *3*, 1646. (i) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* 1978, *100*, 2389. (j) Baxter, S. M.; Wolczanski, P. T. *Organometallics* 1990, *9*, 2498. (k) Buzinkai, J. F.; Schrock, R. R. *Inorg. Chem.* 1989, *28*, 2837.

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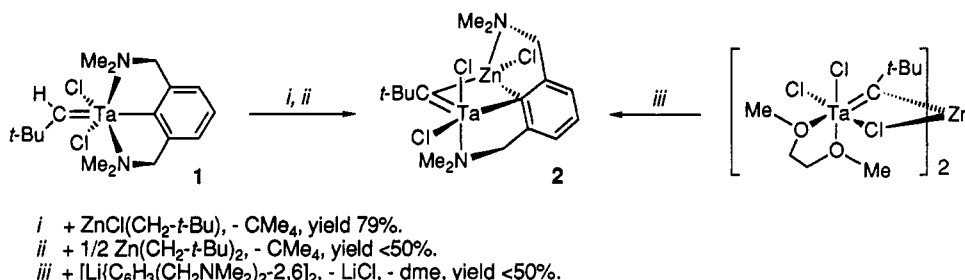† Debye Research Institute, University of Utrecht.
‡ Bijvoet Research Institute, University of Utrecht.
§ Université Louis Pasteur.

(1) Fischer, H.; Hoffmann, P.; Kreissl, F. R.; Schrock, R. R.; Schubert, U.; Weiss, K., Eds. *Carbyne Complexes*; Verlag Chemie: Weinheim, 1988.
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Scheme I. Routes to the Bimetallic Tantalum–Zinc Complex 2

i + ZnCl(CH₂-*t*-Bu), - CMe₄, yield 79%.
ii + 1/2 Zn(CH₂-*t*-Bu)₂, - CMe₄, yield <50%.
iii + [Li{C₆H₃(CH₂NMe₂)₂-2,6]₂, - LiCl, - dme, yield <50%.

paper we report a synthetic approach that converts 1 into a Lewis-acid stabilized alkylidyne species. We also show examples of various tantalum alkylidyne-mediated reactions, including the intramolecular activation of a C—H bond in a NMe₂ group and the unprecedented functionalization of an alkylidyne fragment obtained with a cyclometalated palladium species.

Results

Synthesis of a Bimetallic Tantalum–Zinc Complex.

The 1:1 reaction of the alkylidene complex TaCl₂-{C₆H₃(CH₂NMe₂)₂-2,6}(=CH-*t*-Bu) (1) with neopentylzinc chloride, a mild base, leads to alkylidene α-H abstraction that affords the red, bimetallic, neopentylidyne complex TaCl₂{C₆H₃(CH₂NMe₂)₂-2,6}(μ-C-*t*-Bu)(μ-ZnCl) (2) in high yield (Scheme I, route *i*). When, instead, this α-H abstraction is performed with 0.5 equiv of dineopentylzinc, complex 2 is formed in less than 50% yield (Scheme I, route *ii*). In an alternative approach, the transmetalation reaction of the trimetallic ditantalum–zinc complex {TaCl₂(μ-C-*t*-Bu)(dme)}₂Zn(μ-Cl)₂[10] (dme = MeO(CH₂)₂-OMe) with the aryllithium compound [Li{C₆H₃(CH₂-NMe₂)₂-2,6]₂[11] also affords bimetallic 2 but in low yield (Scheme I, route *iii*). Bimetallic 2 can be easily isolated from the reaction mixtures by evaporation of the solvent and subsequent extraction of the solid residue with benzene; the complex crystallizes in large red needles from benzene/pentane solutions. The solid compound is thermally stable to at least 80 °C and can be safely handled for short periods in air. Cryoscopic molecular weight measurements show that 2 is monomeric in benzene.

The ¹H (200.13 MHz) and ¹³C (50.32 MHz) NMR data of 2 in C₆D₆ are not temperature dependent to at least 80 °C (the highest temperature employed) and are consistent with its formulation as shown in Scheme I. The ¹H NMR spectrum contains four anisochronous methyl resonances for the two NMe₂ units of the aryldiamine ligand and an

AX pattern for each of the two CH₂N units. Since there are also four ¹³C NMR resonances for the NMe₂ units, one can conclude that each nitrogen center is a stable tetrahedral array that reflects the molecular asymmetry present. This can only occur when both pyramidal inversion of the nitrogen center is blocked and when rotation around the C—NMe₂ bond is hindered. This means that in 2 the tantalum–nitrogen and the zinc–nitrogen interactions are stable on the NMR time scale and that in solution it has a structure with stable five-membered Ta–C–C–C–N and Zn–C–C–C–N chelate rings. The ¹³C NMR spectrum contains a resonance at δ 295.4 ppm for the bridging alkylidyne α-carbon. The resonance for the bridging C_ipso atom of the monoanionic aryldiamine ligand is at δ 175.2 and is to a higher field of the nonbridging C_ipso atom resonances in other aryltantalum complexes[9] that are found in the range 190 ≤ δ ≤ 210.

Solid State Structure and Molecular Geometry of TaCl₂{C₆H₃(CH₂NMe₂)₂-2,6}(μ-C-*t*-Bu)(μ-ZnCl) (2). In order to elucidate the stereochemistry of the ligand distribution around the metal centers and to obtain information about the bonding modes of both the aryldiamine ligand and the alkylidyne unit, an X-ray structural analysis of 2 has been carried out. Suitable crystals were grown from a benzene solution of 2 into which pentane vapor was allowed to diffuse slowly.[12] The crystal structure of 2 involves the packing of four discrete monomers in an orthorhombic unit cell. An ORTEP drawing of 2, along with the adopted numbering scheme is shown in Figure 1; selected bond lengths and angles are listed in Table I. The structure determination shows 2 to be a bimetallic species in which the metal atoms of a TaCl₂ and a ZnCl unit are bridged by a neopentylidyne (≡C-*t*-Bu) unit *via* carbyne carbon C(13) and an aryldiamine (C₆H₃(CH₂-NMe₂)₂-2,6) ligand *via* C_ipso atom C(9). The aryldiamine ligand further coordinates through the N-donor atoms of its two CH₂NMe₂ arms, one to each metal, to complete the coordination sphere of the two metal centers. The resulting coordination geometry around zinc is distorted tetrahedral and that around tantalum is between trigonal bipyramidal and square pyramidal (70% along the Berry pseudorotation coordinate toward the latter).[13] The C(9)-based aryl ligand bridge between zinc and tantalum is very asymmetric: the angle made by the Ta—Zn vector with the least squares plane through the aryl carbon atoms is 65.2(2)° and deviates markedly from the 90° expected for a symmetrically bridging aryl system (see Figure 2).

C—H Bond Activation Reaction of a NMe₂ Group in 2. Treatment of bimetallic 2 with one or more equivalents of tmeda [=Me₂N(CH₂)₂NMe₂] at 60 °C leads

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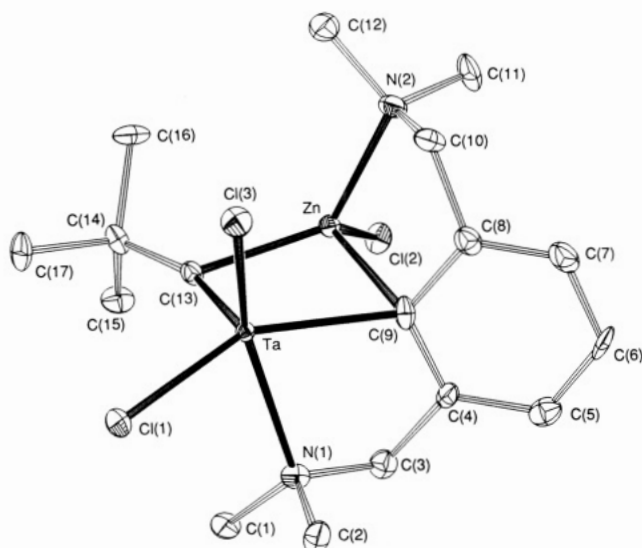
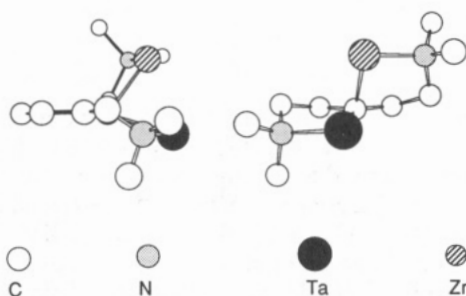**Figure 1.** ORTEP drawing of the structure of **2** in the crystal, with 50% probability ellipsoids.

Figure 2. Bridging aryldiamine ligand in the bimetallic complex **2**. The other ligands have been omitted for clarity. Left: view along the C(4)–C(8) axis (aryl carbon atoms perpendicular to the plane of drawing). Right: approximate view along Ta–C_{ipso}.

Table I. Relevant Data for the Geometry of 2

Bond Lengths (Å)			
Ta–Cl(1)	2.3830(15)	Ta–Cl(3)	2.3628(16)
Ta–C(9)	2.321(6)	Ta–C(13)	1.862(6)
Ta–N(1)	2.313(6)	Ta···Zn	2.729(1)
Zn–Cl(2)	2.214(2)	Zn–C(9)	2.258(6)
Zn–C(13)	2.114(6)	Zn–N(2)	2.101(5)

Bond Angles (deg)			
Cl(1)–Ta–N(1)	83.69(15)	N(1)–Ta–C(9)	75.0(2)
C(9)–Ta–Cl(3)	95.79(16)	C(9)–Ta–C(13)	102.5(2)
Cl(1)–Ta–Cl(3)	91.90(5)	Ta–C(13)–C(14)	158.5(4)
Cl(1)–Ta–C(13)	103.04(18)	C(9)–Zn–C(13)	96.9(2)
C(9)–Zn–Cl(2)	117.71(17)	C(9)–Zn–N(2)	86.7(2)
N(2)–Zn–Cl(2)	108.49(15)	Cl(2)–Zn–C(13)	118.51(15)

to clean and quick elimination of $ZnCl_2$ (as $ZnCl_2$(tmeda)) with concomitant formation of a tantalum neopentylidene complex **3** characterized as $TaCl\{C_6H_3(CH_2N(Me)CH_2)$-2-$(CH_2NMe_2)-6\}$(=$CH$-$t$-Bu) (Scheme II, route *i*). The elimination of $ZnCl_2$ from **2** could not be achieved by an analogous reaction with dme or by tetrahydrofuran (THF) at reflux for 4 h. Complex **3** can be regarded as a product that arises from a postulated intermediate $TaCl\{C_6H_3(CH_2NMe_2)_2$-2,6$\}$(=$C$-$t$-Bu) (**6**) by a hydrogen atom abstraction from a methyl group of a NMe_2 unit by the Ta≡C function. In an alternative approach, **3** can be prepared by the reaction of the alkylidene complex **1** with 1 equiv of MeLi in THF at low temperature (Scheme II, route *ii*). The remaining chlorine atom of the alkylidene complex **3** can be substituted by a *tert*-butoxide ligand in a clean

transmetalation reaction with LiO-t-Bu, leading to the halogen-free alkylidene complex $Ta(O$-t-Bu$)\{C_6H_3$-$(CH_2N(Me)CH_2)$-2-(CH_2NMe_2)-6$\}$(=CH-t-Bu) (**4**) in high yield (Scheme II, route *v*). The yellow alkylidene complexes **3** and **4** are air-sensitive but thermally quite stable, and they can be stored intact for months under a nitrogen atmosphere.

The ^{1}H (300.13 MHz) and ^{13}C (75.74 MHz) NMR data of **3** and **4** in C_6D_6 are consistent with their formulations as shown in Scheme II. As a result of the C—H activation reaction (*vide supra*), they both contain an aryldiamine ligand with one NMe_2 and one NMe unit, and the corresponding three methyl group resonances are observed either at ambient temperature (**3**) or at lower temperature (**4**). For complex **4** the two anisochronous ^{1}H NMR resonances for the NMe_2 unit coalesce at 20 °C (toluene-d_8). In the ^{1}H NMR spectra of both **3** and **4** the three $CH_2(N)$ moieties present each provide an AB pattern. A high-field AX pattern (δ 3.0 and 1.3) with a small ${}^2J(H,H)$ of 10 Hz can be assigned to the new Ta—CH_2—N unit that has resulted from the C—H activation reaction; the Ta—CH_2—N unit in the related, and structurally characterized, complex $TaCl_2\{C_6H_4(CH(Me)N(Me)CH_2)-2\}$-$(CH_2Ph)$(THF) provides similar NMR data.[14] To gain insight into the bonding in the triangular Ta—CH_2—N unit, proton-coupled ^{13}C NMR spectra have been measured for **3** and **4** and these provided ${}^1J(C,H)$ values of 146 and 141 Hz, respectively; these are close to the ${}^1J(C,H)$ value of 135 Hz in the Ar—CH_2N units. The NMR data of the C_α alkylidene atom of the =CH-t-Bu unit in **3** (δ 253.1, ${}^1J(C_\alpha,H)$ = 91 Hz) and in **4** (δ 250.3, ${}^1J(C_\alpha,H)$ = 96 Hz) are typical for electron-deficient alkylidene complexes.[15]

The reactivity of the alkylidene complexes **3** and **4** toward alkenes is very low. In C_6D_6 complexes **3** and **4** react slowly with ethene and neopentylethene (4,4-dimethylpent-1-ene) is liberated, but the reaction is not clean; no trace of the metathesis product *tert*-butylethene (3,3-dimethylbut-1-ene) was detected. The formation of neopentylethene is indicative of a reductive rearrangement occurring in an intermediate tantalacyclobutane complex (as is regularly observed in tantalum alkylidene-mediated reactions[16]) and has not been further investigated.
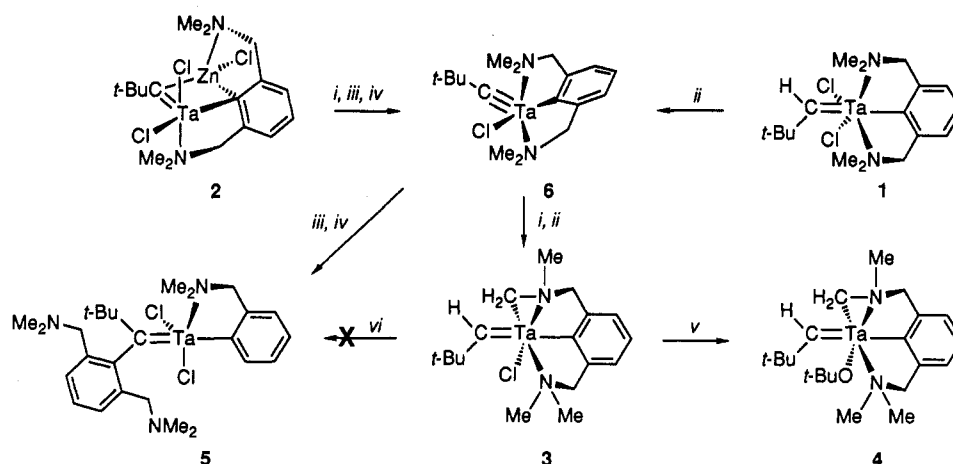
Evidence for a Palladium-Mediated Synthesis of a Functionalized Tantalum Alkylidene Complex. Bimetallic **2** does not react with $[Pd(C_6H_4CH_2NMe_2$-2$)(\mu$-X$)]_2$ (X = Cl, I) in either toluene or THF. When, however, the tmeda-induced elimination of $ZnCl_2$ from bimetallic **2** is performed in the presence of these dimeric palladium complexes the final product isolated in low yield is a blue complex **5** (Scheme II, routes *iii* and *iv*) and not **3** (the product of a C—H activation reaction). Complex **5** is air-sensitive and slightly thermally unstable but can be stored intact under a nitrogen atmosphere at –30 °C. For **5** the ^{1}H and ^{13}C NMR data (*vide infra*) are consistent with a proposed formulation of $TaCl_2(C_6H_4CH_2NMe_2$-2$)[$=$C(t$-

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Scheme II. Alkylidyne-Mediated Alkylidene Syntheses

i   + tmeda (benzene, 60 °C) , - ZnCl$_2$(tmeda), yield 69%.

ii   + LiMe (THF, -78 °C) , - CH$_4$, - LiCl, yield 40%.

iii + tmeda, + [Pd(C$_6$H$_4$CH$_2$NMe$_2$-2)(μ-I)]$_2$, - ZnCl(I)(tmeda), - Pd^0, yield ~50%.

iv   + tmeda, + [Pd(C$_6$H$_4$CH$_2$NMe$_2$-2)(μ-Cl)]$_2$, - ZnCl$_2$(tmeda), - Pd^0, yield ~20%.

v   + LiO-*t*-Bu, -LiCl, yield 100 %.

vi   + [Pd(C$_6$H$_4$CH$_2$NMe$_2$-2)(μ-X)]$_2$ (X = I, Cl) unclean reaction.

Bu){C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}]. This is a neopentylidene complex in which the alkylidene α-hydrogen atom of a =CH-*t*-Bu unit (present in 1) has been substituted by a C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6, aryldiamine, group. Note that regardless of the starting palladium complex the only halide present in isolated 5 is chloride (see Discussion). Attempts to obtain crystals of 5 suitable for X-ray analysis failed since the complex invariably crystallized in thin fibers. When bimetallic 2 was reacted with tmeda in the presence of ClC$_6$H$_4$CH$_2$NMe$_2$-2, instead of [Pd(C$_6$H$_4$CH$_2$-NMe$_2$-2)(μ-X)]$_2$ (X = Cl, I), no 5 was formed. Under the same conditions as those that resulted in the formation of 5, TaCl{C$_6$H$_3$(CH$_2$N(Me)CH$_2$)-2-(CH$_2$NMe$_2$)-6}(=CH-*t*-Bu) (3) also reacts with [PdX(C$_6$H$_4$CH$_2$NMe$_2$-2)]$_2$ (X = Cl, I) but this reaction results in a complex mixture of unidentified organometallic species that does not contain 5 (Scheme II, route *vi*).

Further evidence for our postulated structure of 5 comes from a FAB mass spectrum of the organic products obtained by hydrolysis of complex 5. This spectrum showed mainly parent ions that could be attributed to the protonated forms of the arylamine C$_6$H$_5$CH$_2$NMe$_2$-2 (*m/e* = 136.1) and the neopentyl–aryldiamine CH$_2$(*t*-Bu){C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6} (*m/e* = 263.2). After similar deuterolysis, a FAB mass spectrum was obtained with peaks attributable to C$_6$H$_4$DCH$_2$NMe$_2$-2 and CD$_2$(*t*-Bu){C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}; the incorporation of one and two deuterium atoms, respectively, in these products is consistent with the deuterolysis of a Ta—C single bond and a Ta=C double bond in complex 5.

The ^{1}H NMR spectrum of 5 (300.13 MHz, C$_6$D$_6$, 25 °C) is given in Figure 3 and shows four anisochronous resonances for N-bonded methyl groups in a 1:1:2:2 ratio and three AB patterns for the CH$_2$N units in accord with the formulation TaCl$_2$(C$_6$H$_4$CH$_2$NMe$_2$-2)[=C(*t*-Bu)-{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}], as shown in Scheme II. To reach this conclusion, it is necessary to make the reasonable assumptions that on the NMR time scale only the NMe$_2$ unit of the arylmonoamine C$_6$H$_4$CH$_2$NMe$_2$-2 forms a coordinative bond to the tantalum center and that on this time scale the tantalum center is a chiral entity that does

not racemize. In order to facilitate the assignments of the ^{1}H and ^{13}C NMR data of 5 and to probe the mechanism by which it is formed from bimetallic 2, we have carried out a deuterium labeling experiment. The *d$_3$* analogue of 2, TaCl$_2${C$_6$D$_3$(CH$_2$NMe$_2$)$_2$-2,6}(μ-C-*t*-Bu)(μ-ZnCl), was prepared (see Experimental Section) and reacted with tmeda and [Pd(C$_6$H$_4$CH$_2$NMe$_2$-2)(μ-I)]$_2$. This reaction gave TaCl$_2$(C$_6$H$_4$CH$_2$NMe$_2$-2)[=C(*t*-Bu){C$_6$D$_3$(CH$_2$NMe$_2$)$_2$-2,6}], and no products with deuterium incorporated in another part of the complex were found (see Figure 3). Comparison of the ^{1}H NMR spectra of 5 and its *d$_3$* analogue allows assignment of all the aromatic resonances present. In this functionalized alkylidene complex 5 the low-field aryl resonance for one proton of the aryldiamine at δ 8.36 is a remarkable feature for which we have no explanation. Inspection of the aryl resonance multiplicities shows that the C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6 ligand is intact, and this excludes an interpretation based on isomerization to a 2,4-disubstituted aryldiamine ligand, as encountered in late transition metal chemistry.[17] The ^{13}C NMR resonance of the alkylidene α-carbon in 5 is located at δ 278 and that of the C$_{ipso}$ atom of C$_6$H$_4$CH$_2$NMe$_2$-2 is at δ 203.8; these values are characteristic for tantalum aryl[9] and tantalum alkylidene[15] complexes, respectively. Consistent with the postulated formulation of 5 these two resonances appear as singlets in the proton-coupled ^{13}C NMR spectrum.

Discussion

Synthesis and Structure of Bimetallic 2. Most known tantalum (and some tungsten) alkylidyne complexes contain a Lewis acid,[10,18] e.g. Li$^+$, ZnCl$^+$, Zn^{2+}, or Al^{3+} that becomes incorporated as a direct result of the preparative method used. The alkylidene α-H atom of a precursor alkylidene complex has a relatively high acidity that allows its abstraction (as a proton) by a metal alkyl

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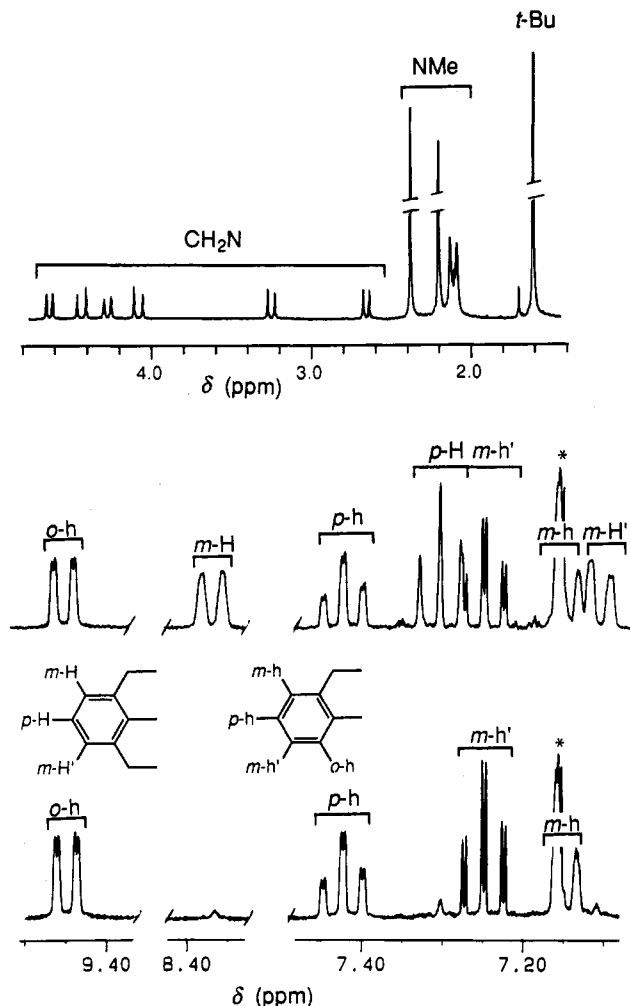
Figure 3. Top: highfield part of the ^{1}H NMR (C_6D_6, 300.13 MHz) spectrum of the alkylidene complex $TaCl_2(C_6H_4CH_2-NMe_2-2)[=C(t\text{-}Bu)\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]$ **(5)**. Middle: aromatic resonances of **5** and their assignments. Bottom: corresponding resonances in the d_3 complex containing a $\{C_6D_3(CH_2NMe_2)_2\text{-}2,6\}$ function. (* denotes solvent.)
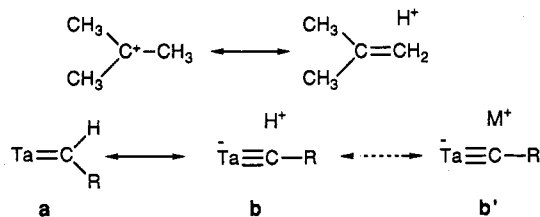

Figure 4. Hyperconjugation accounting for the structural features of the *tert*-butyl cation (top) and by analogy for the structures of the alkylidene complexes (bottom).

compound under mild conditions. This acidity of alkylidene α-H atoms is a feature of high oxidation state, electron-deficient, early transition metal alkylidenes in which the metal withdraws electron density from the alkylidene C_α–H_α bond. This situation using a hyperconjugation description results in a mesomer in which the alkylidene α-carbon is triply bonded to the metal center and the alkylidene C_α–H_α bond is weakened (Figure 4, mesomer b). Similar hyperconjugation is well-known in carbocation chemistry, *e.g.* the *tert*-butyl cation (see also Figure 4), and is used to explain short C–C bonds and lengthened C–H linkages.[19] Although this model for

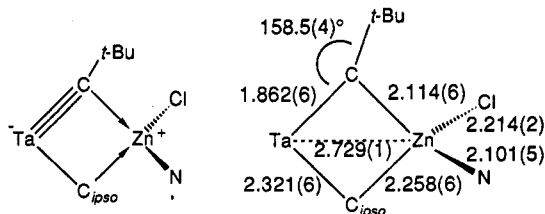(19) Hehre, W. J. *Acc. Chem. Res.* **1975**, *8*, 369.

Figure 5. Left: main resonance structure including the coordinative bonds that account for the structural features of bimetallic **2**. Right: bond lengths (Å) in the Ta–C–Zn–C fragment.

describing metal-to-carbon alkylidene bonding has been refined by theoretical studies,[20] even in this simple form it accounts for all the structural and spectroscopic features of tantalum alkylidene complexes:[15] (i) the Ta–C_α–C_β angle is typically in the range 150–170° and is much larger than the 120° expected for a formally sp^2-hybridized α-carbon; (ii) the Ta–C_α–H_α angle (70–80°) is small, the C_α–H_α bond (~1.30 Å) is lengthened, and the value of $^1J(C_\alpha$–$H_\alpha)$ is small (70–130 Hz); (iii) the Ta–C_α bond is so short (1.8–2.0 Å) that its range overlaps that of the Ta–C_α bond lengths in tantalum alkylidyne complexes. In 18-electron tantalum alkylidene complexes that do not contain an electron-deficient tantalum center, the resonance structure a (Figure 4) becomes more important and consequently larger Ta–C_α bond lengths and smaller Ta–C_α–C_β angles are found.[21] Replacing the proton in resonance structure b by a metal cation affords an isoelectronic structure b′ (Figure 4) that can be used to describe Lewis-acid-containing alkylidyne complexes; here the hyperconjugative valence structure b′ is especially important due to the ability of the Lewis acid to bear a significant positive charge.

For bimetallic $TaCl_2\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(\mu\text{-}C\text{-}t\text{-}Bu)$-$(\mu\text{-}ZnCl)$ **(2)** the structural data of the Ta($\mu\text{-}C\text{-}t\text{-}Bu$)Zn unit could be interpreted as a Ta=C-t-Bu fragment combined with a Zn—C σ-bond, i.e. as a zincaalkylidene complex. However, we favor a description with a Ta≡C-t-Bu fragment and a C→Zn donative interaction from a filled p-orbital on C_α (Figure 5), not only because it is in line with the hyperconjugation model but also because it best shows this complex as a precursor to a Lewis-acid-free alkylidyne complex and thus accounts for its observed reactivity. In this description of **2** there are interesting Lewis-base interactions present that lead to an 18-electron count for zinc and to a 14-electron count for tantalum. In detail there are three coordinative bonds to the cationic $ZnCl^+$ moiety: the lone pair of one of the nitrogen donors of the aryldiamine ligand, a filled p-orbital of the alkylidyne C_α, and a filled p-orbital of the aryldiamine C_{ipso} (*vide infra*). In **2** the bridging interaction of C_{ipso} and the orientation of the aryldiamine ring are such that the p-orbital at C_{ipso} is directed toward the zinc center while the Ta atom is almost in line with the C_{ipso}—C_{para} vector of the aryldiamine ligand (Figure 2). Consequently, the bonding of the bridging C_{ipso} is then described as being a 2-electron Ta—C_{ipso} σ-bond with electron donation of the filled p-orbital of C_{ipso} to the zinc center to form a

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coordinative Zn—C_{ipso} bond. This latter structural feature is like that of the early stages in the attack of an electrophile E^+ on a benzene ring, i.e. the formation of a π-complex in which effectively 2-electron donation from the benzene ring to E^+ occurs.

As in 2 there is also 2-electron donation from an aryl p-orbital to a metal center in the recently reported structure of the arene adduct cis-Pd$(C_6F_5)_2(C_6H_5CH_2$-$NMe_2)$.[22] This palladium complex and 2 thus mimic an initial stage of electrophilic attack at an aryl carbon atom that does not lead to substantial deformation of the aryl moiety. We have previously reported platinum complexes that contain a σ-metal-substituted arenonium ion in which rehybridization of an sp²-C center has already taken place[23] and which therefore mimic a later stage in electrophilic attack at an aryl carbon atom.

Spectroscopic evidence for the participation of the C_{ipso} p-orbital in bonding to the zinc center is provided by the unusual ¹³C NMR C_{ipso} resonance value of δ 175.2. This value deviates from those found for C_{ipso} atoms either in tantalum compounds with the same aryldiamine ligand or in tantalum mesityl compounds ($190 \le \delta \le 210$[9]) where the low-field resonance arises from aryl-to-tantalum bonding in which there is additional electron donation from the filled p-orbital on C_{ipso} to empty d-orbitals on the (electron-deficient) tantalum center. As a result a resonance structure can be drawn in which C_{ipso} is doubly bonded to the tantalum, i.e. like the bonding in a tantalum alkylidene fragment, and it is known empirically that the formation of such a carbon-to-metal multiple bond results in a typically low-field carbon resonance of δ 200–400. In bimetallic 2 the situation is different, the filled p-orbital of C_{ipso} is directed toward a zinc center and, thereby, its p-electron density cannot be donated to tantalum so that a high-field shift of C_{ipso} results.

This 4-electron three-center Ta–C_{ipso}–Zn bonding described above is preferred by us over an alternative 2-electron three-center (2e–3c) description. Examples of both types of aryl bonding and borderline cases are well-documented in arylmagnesium,[24] -copper, and -cuprate chemistry.[25-27] For instance, in polynuclear arylcopper complexes of the type $[Cu(C_6H_2R_3$-2,4,6)]$_4$ (R = Me, i-Pr, Ph) an increase in the bulk of the ortho substituents is known to change the nature of the Cu–C_{ipso} bonding from a symmetrical 2e–3c bonding mode in the trimethyl complex,[25] via asymmetric bonding in the triisopropyl complex (described as either 2e–2c Cu–C_{ipso} bonding and Cu–C_{ipso} π-donation),[26] to purely 2e–2c Cu–C_{ipso} bonding in the triphenyl complex.[27] Overall, the aryldiamine ligand in bimetallic 2 participates in a 4-electron three-center bond involving C_{ipso} and in coordinative Ta–N and Zn–N bonds so that this ligand is an 8-electron donor. Such a high electron donating capacity makes the $C_6H_3(CH_2$-$NMe_2)_2$-2,6 monoanion an excellent ancillary ligand, that

is capable of stabilizing high oxidation states of early transition metal centers.

Alkylidyne-Mediated C–H Bond Activation in a NMe Unit. The preparation of an alkylidene species TaCl$\{C_6H_3(CH_2N(Me)CH_2)$-2-(CH_2NMe_2)-6$\}$(=CH-t-Bu) (3) both from the bimetallic alkylidyne complex 2 by addition of tmeda and from the neopentylidene complex TaCl$_2\{C_6H_3(CH_2NMe_2)_2$-2,6$\}$(=CH-t-Bu) by reaction with MeLi as base points to the common intermediacy of a very reactive Lewis-acid-free alkylidyne species TaCl-$\{C_6H_3(CH_2NMe_2)_2$-2,6$\}$(≡C-t-Bu) (6). This intermediate arises in the reaction of 2 with tmeda by elimination of ZnCl$_2$(tmeda) (Scheme II, route i) and in the reaction of 1 with MeLi by abstraction of the α-H atom with formation of LiCl and CH$_4$ (Scheme II, route ii). In this postulated alkylidyne intermediate 6 there then follows an alkylidyne-mediated proton abstraction from one of the nitrogen-bonded methyl groups of the aryldiamine ligand (NMe C–H activation) to afford alkylidene species 3. It has been reported that a similar Lewis-acid-free alkylidyne is probably generated in situ from the reaction of the trimetallic complex $\{TaCl_2(\mu$-C-t-Bu)(dme)$\}_2Zn(\mu$-Cl)$_2$ with alkynes that is accompanied by elimination of ZnCl$_2$ and dme.[28]

On the basis of the substantial, and well-documented, trans influence of a neopentylidyne unit[29] the intermediate alkylidyne species 6 probably has a square pyramidal structure with the neopentylidyne function in the apical position and the tridentate-bonded aryldiamine ligand and the remaining chlorine atom in the basal plane. In this structure both NMe$_2$ units of the aryldiamine ligand are cis-positioned relative to the neopentylidyne unit and this arrangement is ideal for an alkylidyne-mediated abstraction of a hydrogen atom from a C—H bond in a NMe unit; this reaction is likely to occur via a multicenter pathway. Many analogous multicenter C—H activation reactions have been documented in the area of high-valent early transition metal chemistry,[30] and activation by alkyl, alkylidene, and benzyne groups is possible.[31] For instance, Rothwell and co-workers have shown that the ligands 2,6-di-tert-butylphenoxide and 2,6-diphenylphenoxide can undergo intramolecular activation of their aliphatic and aromatic C—H bonds at d⁰ metal centers.[32] We have already reported a stereoselective C—H activation reaction in a NMe unit of the dibenzyltantalum complex TaCl$_2$-$\{C_6H_4(CH(Me)NMe_2)$-2$\}$(CH$_2$Ph)$_2$ that occurs via a multicentered σ-bond metathesis and that leads to the formation of a triangular Ta—CH$_2$—N unit[14] like that in

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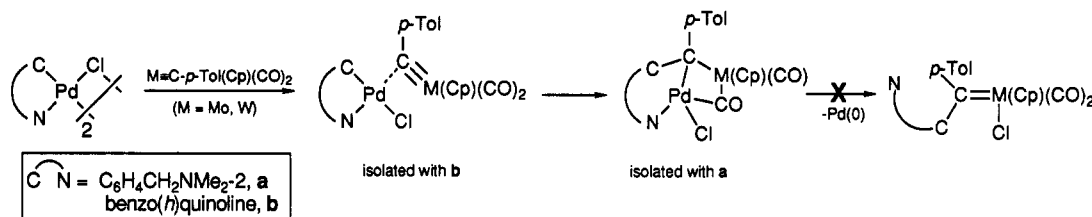
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Scheme III. Reported Reactivity of Low-Valent Carbene Complexes with Cyclometalated Palladium Compounds

3 and 4.[14] Structurally similar triangular Ta—CH₂—P and Ta=CH—P units have also been reported.[33]

The formation of the functionalized alkylidene complex TaCl₂(C₆H₄CH₂NMe₂-2)[=C(*t*-Bu){C₆H₃(CH₂NMe₂)₂-2,6}] (5) from 2 with tmeda and [Pd(C₆H₄CH₂NMe₂-2)-(μ-X)]₂ can also be explained by assuming 6 to be a key intermediate. However, details of this route are far from clear and the absence of the diiodo or iodo/chloro analogue of 5 clearly indicates that halogen exchange processes are important and that ZnXCl species invariably provide one of the chlorine atoms present in 5; in combination with the long reaction times employed and the heterogeneous nature of the reaction medium it is not inconsistent that the better yield of dichloro complex 5 was obtained with [Pd(C₆H₄CH₂NMe₂-2)(μ-I)]₂ as starting material. Complex 5 can be thought of as arising from insertion of the alkylidyne unit of 6 into the Ta—C$_{ipso}$ bond of the aryldiamine, formally a reductive elimination reaction. Complementary to this reductive step, the C₆H₄CH₂-NMe₂-2 grouping and a chlorine atom are transferred to the tantalum center in an oxidative fashion, formally an oxidative addition of an aryl chloride to a tantalum(III) center. However, the mechanism and exact role played by the palladium center in the overall formation of 5 are not fully understood; among unsolved points are the incorporation of two Cl atoms in the product even when [Pd(C₆H₄CH₂NMe₂-2)(μ-I)]₂ is used and the fact that simple reaction of the aryl chloride ClC₆H₄CH₂NMe₂-2 with 2 in the presence of tmeda does not afford 5 at all.

Nevertheless, the conversion of 2 to 5 is a new example illustrating the potential of palladium-mediated functionalization of an alkylidyne complex. Among other examples are the recently reported reactions of low-valent carbyne complexes M≡C-*p*-Tol(Cp)(CO)₂ (M = Mo, W) with cyclometalated palladium compounds (Scheme III)[6b] that afford heterobimetallic species which are either adducts of the palladium moiety to a metal carbyne or products resulting from insertion of the M≡C triple bond into a Pd—C bond. Reductive elimination from the latter would result in complexes containing functionalized alkylidene units as in 5, but this has so far not be achieved (possibly due to the stabilizing influence of the CO ligands).

Conclusions

The synthetically easily accessible bimetallic tantalum-zinc complex 2 is an excellent precursor for a very reactive alkylidyne species and provides insight into the versatility of aryl-to-metal bonding. The ancillary C₆H₃(CH₂NMe₂)₂-2,6 aryldiamine ligand in 2 acts as an unanticipated 8-electron donor with a demonstrated ability to stabilize

"state of the art" early transition metal species. Under specific conditions, this aryldiamine can act as a proton donor by converting one of its NMe₂ units into a new anionic N,C-chelating fragment: N(Me)CH₂⁻. Starting from bimetallic 2, a completely new method for functionalized alkylidenes seems to be possible.

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, or by Dornis and Kolbe, Mülheim a.d. Ruhr; ¹H and ¹³C NMR spectra were recorded on Bruker AC200 or AC300 spectrometers. Mass spectra for the hydrolysis/deuterolysis products of 5 were obtained from C₆D₆/pryridine-*d*₅ solutions on a VG Analytical ZAB HF mass spectrometer using FAB ionization with thioglycerol as matrix. TaCl₂{C₆H₃(CH₂NMe₂)₂-2,6}(=CH-*t*-Bu) was prepared according to a literature procedure.[9b]

TaCl₂{C₆H₃(CH₂NMe₂)₂-2,6}(μ-C-*t*-Bu)(μ-ZnCl) (2). A purple suspension of TaCl₂{C₆H₃(CH₂NMe₂)₂-2,6}(=CH-*t*-Bu) (6.31 g, 12.3 mmol) in a solution of ZnCl₂ (0.97 g, 7.12 mmol) and Zn(CH₂-*t*-Bu)₂ (1.28 g, 6.16 mmol) in Et₂O (100 mL) was stirred at 20 °C for 5 days. The solvent was removed *in vacuo* and the sticky residue triturated with hexane. The resulting red powder was extracted with warm (50 °C) benzene (150 mL). The extract was concentrated *in vacuo* to *ca.* 50 mL and layered with pentane (200 mL). After standing at 20 °C for 3 days, large red crystals of the product could be isolated; yield: 5.94 g (79%). Anal. Calcd for C₁₇H₃₈N₂Cl₃TaZn: C, 33.30; H, 4.60; N, 4.57. Found: C, 32.81; H, 4.82; N, 4.42. ¹H NMR (200.13 MHz, C₆D₆, 25 °C, TMS): δ 1.55 (s, 9 H, *t*-Bu), 1.75, 1.94, 2.42, and 2.71 (s, 4 × 3 H, NCH₃), 2.26, 2.33, 4.43, and 5.03 [d, ²*J*(H,H) = 13 Hz, 4 × 1 H, CH₂N], 6.62 (dd, 2 H, *m*-C₆H₃), 6.97 (t, 1 H, *p*-C₆H₃). ¹³C{¹H} NMR (50.32 MHz, C₆D₆, 25 °C, TMS): δ 35.2 [C(CH₃)₃], 51.2 [*C*(CH₃)₃], 47.4, 47.9, 48.1, and 54.0 (NCH₃), 67.0 and 71.6 (CH₂N), 175.2 (C$_{ipso}$ of C₆H₃), 295.4 (C-*t*-Bu).

TaCl{C₆H₃(CH₂N(Me)CH₂)-2-(CH₂NMe₂)-6}(=CH-*t*-Bu) (3). Route i. To a stirred purple solution of TaCl₂{C₆H₃(CH₂NMe₂)₂-2,6}(μ-C-*t*-Bu)(μ-ZnCl) (0.65 g, 1.1 mmol) in benzene (100 mL) at 62 °C was added tmeda (1.7 mL, 7.4 mmol). Within 30 min at 62 °C, the color of the mixture changed to yellow-brown. After stirring for 18 h at room temperature, the solvent was removed *in vacuo* leaving a brown spongy material that was extracted with hexane (1 × 100 mL). The solvent was removed from the extract *in vacuo*, leaving 0.48 g (92%) of crude brown product. Subsequent crystallization from warm (60 °C) hexane (50 mL) gave 0.35 g (69%) of 3 as large block-shaped yellow crystals.

Route ii. To a stirred purple solution of TaCl₂{C₆H₃(CH₂-NMe₂)₂-2,6}(=CH-*t*-Bu) (0.71 g, 1.4 mmol) in THF (100 mL) at -108 °C was added 0.9 mL of a 1.6 M solution of LiMe in hexane (1.4 mmol). The resulting solution was allowed to warm to room temperature during which time the color gradually changed to brown-red. The solvent was removed *in vacuo* affording a solid that was suspended in hexane (100 mL) and stirred for 2 days. Subsequent hot filtration (60 °C) gave an orange filtrate that was concentrated *in vacuo* to *ca.* 40 mL. From this concentrated solution, yellow 3 crystallized readily at -30 °C; yield 0.26 g (40%).

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Table II. Crystal Data and Details of the Structure Determination of 2

(a) Crystal Data

formula	$C_{17}H_{28}Cl_3N_2TaZn$
mol wt	613.11
cryst syst	orthorhombic
space group	$P2_12_12_1$ (No. 19)
a, b, c (Å)	9.725(2), 10.436(2), 20.766(3)
V (Å^3)	2107.5(7)
Z	4
D_{calc} (g cm^{-3})	1.932(1)
$F(000)$	1192
μ (cm^{-1})	66.8
cryst size (mm)	0.37 × 0.63 × 0.80

(b) Data Collection

temp (K)	100
$\theta_{min}, \theta_{max}$	1.0, 29.4
scan type	$\omega/2\theta$
radiation, λ (Å)	Mo Kα, 0.710 73
$\Delta\omega$ (deg)	$0.81 + 0.35 \tan\theta$
hor and vert aperture (mm)	2.83, 5.0
ref reflns	−4,4,0; 4,0,−4; 0,4,−4
data set	−12 to +13, 0–14, −24 to 0
total no of data, no. of unique data	5481, 4851
no. of obsd data	4746 $[I > 2.5\sigma(I)]$

(c) Refinement

N_{ref}, N_{par}	4746, 219
weighting scheme	$w = 1.0/[\sigma^2(F) + 0.0017F^2]$
final R, R_w, S	0.034, 0.054, 2.69
max/av shift/error	0.09/0.01
min/max resd dens (e/Å^3)	−1.8/1.6 (near heavy atoms)

Anal. Calcd for $C_{17}H_{28}N_2ClTa$: C, 42.82; H, 5.92; N, 5.88. Found: C, 42.75; H, 5.94; N, 5.81. ^{1}H NMR (300.13 MHz, C$_6$D$_6$, 24 °C, TMS): δ 0.90 (s, 1 H, C*H*-t-Bu), 1.17 (s, 9 H, CH-*t*-*Bu*), 1.32 and 3.18 [2 d, ^2J(HH) = 9.6 Hz, 2 × 1 H, TaC*H*$_2$N], 2.07, 2.85, and 2.97 [3 s, 3 × 3 H, N(C*H*$_3$)], 3.20 and 4.09 [2 d, ^2J(HH) = 15.7 Hz, 2 × 1 H, C*H*$_2$N], 3.32 and 4.47 [2 d, ^2J(HH) = 12.9 Hz, 2 × 1 H, C*H*$_2$N], 6.98 (dd, 2 H, *m*-C$_6$H$_3$), 7.14 (t, 1 H, *p*-C$_6$H$_3$). ^{13}C$\{^1$H$\}$ NMR (50.32 MHz, C$_6$D$_6$, 24 °C, TMS): δ 34.4 [C(H)C-(C*H*$_3$)$_3$], 46.3 [C(H)*C*(CH$_3$)$_3$], 46.9, 52.2, and 58.6 [N(CH$_3$)], 73.3 (CH$_2$N), 84.5 (Ta—CH$_2$N), 193.1 (C$_{ipso}$ of C$_6$H$_3$), 253.1 [*C*(H)-*t*-Bu, $^1J(^{13}$C—^{1}H) = 91 Hz].

Ta(O-*t*-Bu){C$_6$H$_3$(CH$_2$N(Me)CH$_2$)-2-(CH$_2$NMe$_2$)-6}(=CH-*t*-Bu) (4). A yellow solution of 3 (1.27 g, 2.66 mmol) and LiO-*t*-Bu (0.22 g, 2.7 mmol) in hexane (100 mL) was stirred for 2 h at 40 °C and then for 3 h at 20 °C. The LiCl precipitate that formed was filtered off and the solvent removed from the filtrate *in vacuo*, leaving crude yellow product 4 in quantitative yield. The compound can be purified by recrystallization from a minimum of hexane. Anal. Calcd for $C_{21}H_{37}N_2OTa$: C, 49.03; H, 7.25; N, 5.44. Found: C, 48.29; H, 7.20; N, 5.36. ^{1}H NMR (300.13 MHz, C$_6$D$_6$, 24 °C, TMS): δ 1.29 (s, 9 H, CH-*t*-*Bu*), 1.41 (s, 9 H, O-*t*-Bu), 1.37 and 2.91 [2 d, ^2J(HH) = 9.8 Hz, 2 × 1 H, TaC*H*$_2$N], 2.4 [br s, 6 H, N(C*H*$_3$)$_2$], 3.03 (s, 3 H, NC*H*$_3$), 3.35 (s, 1 H, C*H*-*t*-Bu), 3.47 and 4.02 [2 d, ^2J(HH) = 13.0 Hz, 2 × 1 H, C*H*$_2$N], 3.57 and 4.18 [2 d, ^2J(HH) = 15.7 Hz, 2 × 1 H, C*H*$_2$N], 7.02 (d, 2 H, *m*-C$_6$H$_3$), 7.18 (t, 1 H, *p*-C$_6$H$_3$). ^{13}C$\{^1$H$\}$ NMR (75.47 MHz, C$_6$D$_6$, 24 °C, TMS): δ 34.0 [C(H)C(C*H*$_3$)$_3$], 35.2 [OC(C*H*$_3$)$_3$], 45.2 [C(H)*C*(CH$_3$)$_3$], 47.7 (br), 51.1 (br), and 58.4 [N(CH$_3$)], 70.0 and 73.6 (CH$_2$N), 76.6 (Ta—CH$_2$N), 77.4 [O*C*(CH$_3$)$_3$], 194.8 (C$_{ipso}$ of C$_6$H$_3$), 250.3 [*C*(H)-*t*-Bu, $^1J(^{13}$C—^{1}H) = 96 Hz].

TaCl$_2$(C$_6$H$_4$CH$_2$NMe$_2$-2)[=C(*t*-Bu){C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}] (5). [Pd(C$_6$H$_4$CH$_2$NMe$_2$-2)(μ-I)]$_2$ (0.86 g, 2.3 mmol) was suspended in a stirred solution of TaCl$_2${C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}-(μ-C-*t*-Bu)(μ-ZnCl) (1.16 g, 1.89 mmol) in THF (35 mL). A slight excess of tmeda (0.40 mL, 2.65 mmol) was added, and the stirred brown suspension gradually blackened during 15 h. The solvent was removed *in vacuo* and the remaining sticky solid triturated with hexane. Subsequent extraction with hexane (2 × 75 mL) followed by removal of the solvent *in vacuo* gave the crude blue-purple product in *ca*. 50% yield. Compound 5 can be obtained spectroscopically pure (by ^{1}H and ^{13}C NMR) after repeated recrystallization from pentane. Anal. Calcd for $C_{28}H_{38}N_3Cl_2Ta$:

Table III. Final Coordinates and Equivalent Isotropic Thermal Parameters and Their Esd's in Parentheses for the Non-H Atoms of 2

atom	x	y	z	$U(eq)^a$ (Å^2)
Ta	0.25757(2)	0.09897(2)	0.10272(1)	0.0080(1)
Zn	0.07764(6)	−0.08956(6)	0.13719(3)	0.0101(2)
Cl(1)	0.47610(14)	0.20202(14)	0.10627(7)	0.0169(4)
Cl(2)	0.05270(15)	−0.30019(13)	0.13180(7)	0.0152(4)
Cl(3)	0.14493(16)	0.28458(14)	0.14096(8)	0.0180(4)
N(1)	0.3543(6)	−0.0137(5)	0.0182(3)	0.0130(12)
N(2)	−0.1148(5)	−0.0075(5)	0.1576(3)	0.0160(12)
C(1)	0.4832(6)	−0.0813(7)	0.0350(3)	0.0197(17)
C(2)	0.3836(7)	0.0826(6)	−0.0342(3)	0.0190(17)
C(3)	0.2550(6)	−0.1074(5)	−0.0074(3)	0.0163(17)
C(4)	0.1133(7)	−0.0497(6)	−0.0103(3)	0.0143(17)
C(5)	0.0255(7)	−0.0724(6)	−0.0629(3)	0.0190(17)
C(6)	−0.1084(7)	−0.0275(6)	−0.0612(3)	0.0187(17)
C(7)	−0.1550(7)	0.0337(7)	−0.0060(3)	0.0227(19)
C(8)	−0.0692(6)	0.0558(6)	0.0460(3)	0.0163(17)
C(9)	0.0722(6)	0.0218(6)	0.0440(3)	0.0147(16)
C(10)	−0.1296(6)	0.0979(6)	0.1105(3)	0.0170(16)
C(11)	−0.2240(7)	−0.1028(6)	0.1492(3)	0.0220(16)
C(12)	−0.1225(7)	0.0455(7)	0.2248(3)	0.0203(17)
C(13)	0.2659(6)	−0.0150(5)	0.1715(3)	0.0117(14)
C(14)	0.3177(6)	−0.0754(6)	0.2319(3)	0.0143(14)
C(15)	0.3864(6)	−0.2045(6)	0.2163(3)	0.0170(17)
C(16)	0.2020(7)	−0.0968(7)	0.2803(3)	0.0197(17)
C(17)	0.4263(7)	0.0154(6)	0.2619(3)	0.0197(17)

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

C, 48.46; H, 5.94; N, 6.52. Found: C, 46.42; H, 5.81; N, 6.48.[34] ^{1}H NMR (300.13 MHz, C$_6$D$_6$, 25 °C, TMS): δ 1.57 (s, 9 H, *t*-Bu), 2.07, 2.11, 2.18, and 2.36 (4 s, 18 H, NMe), 2.65 and 4.64 (d, ^2J = 11.8 Hz, 2 × 1 H, CH$_2$N), 3.24 and 4.27 (2 d, ^2J = 13.1 Hz, 2 × 1 H, CH$_2$N), 4.07 and 4.43 (2 d, ^2J = 16.4 Hz, 2 × 1 H, CH$_2$N), 7.26 (m, 5 H, ArH), 8.36 (d, ^3J = 7.6 Hz, 1 H, *o*-H of C$_6$H$_3$), 9.44 (dd, ^3J = 7.3 Hz, ^4J = 1.0 Hz, 1 H, *o*-H of C$_6$H$_4$). ^{13}C$\{^1$H$\}$ NMR (75.47 MHz, C$_6$D$_6$, 25 °C, TMS): δ 36.5 [C(CH$_3$)$_3$], 47.3 [*C*(CH$_3$)$_3$], 46.3, 48.4, 50.8, and 51.8 (NCH$_3$), 66.0, 71.1, and 71.7 (CH$_2$N), 125.2–158.6 (ArC), 203.8 (C$_{ipso}$ of C$_6$H$_4$), 278.4 (*C*-*t*-Bu).

Hydrolysis and Deuterolysis of 5. A stirred blue solution of 5 (ca. 10 mg) in C$_6$D$_6$ (0.5 mL) was treated with a drop of H$_2$O or D$_2$O whereupon instantaneous decolorization occurred and a white precipitate formed. A drop of pyridine-*d$_5$* was added and the mixture filtered through Celite to afford a colorless solution that was used for the FAB measurements.

C$_6$D$_3$Me$_2$-1,3-Br-2. A vigorously stirred mixture of 2-bromo-1,3-dimethylbenzene (37 g), D$_2$SO$_4$ (22 mL), and D$_2$O (6 mL) was heated at reflux for 3 × 1 min. (Prolonged reflux leads to thermal decomposition.) The reaction mixture was stirred at 20 °C for 18 h, and the resulting gray slush was diluted with 50 mL of H$_2$O. The organic product was subsequently extracted with CCl$_4$ (3 × 50 mL), dried over Na$_2$SO$_4$, and purified by distillation; yield 20 g of C$_6$D$_3$Me$_2$-1,3-Br-2 with 90% deuterium enrichment of the three aryl hydrogens.

TaCl$_2$(C$_6$H$_4$CH$_2$NMe$_2$-2)[=C(*t*-Bu){C$_6$D$_3$(CH$_2$NMe$_2$)$_2$-2,6}]. C$_6$D$_3$Me$_2$-1,3-Br as prepared above was used for the successive synthesis (six further steps) of TaCl$_2$(C$_6$H$_4$CH$_2$NMe$_2$-2)[=C(*t*-Bu){C$_6$D$_3$(CH$_2$NMe$_2$)$_2$-2,6}] as described for its non-deuterated analogue 5.

Crystal Structure Determination of 2. Crystal data and numerical details of the structure determination of 2 are given in Table II. X-ray data were collected for a red-brown crystal mounted on a glass fiber at 100 K on an Enraf-Nonius CAD4 diffractometer with Zr-filtered Mo Kα radiation. The cell parameters were derived from the 25 SET4 setting angles with $15 < \theta < 18°$. Intensity data were corrected for *Lp*, a small linear decay of 1%, and absorption (corrections 0.76:1.39) (DIFABS).[35]

(34) An explanation for the too low C, H, N values found for this new complex is the incorporation of a little ZnCl$_2$ that is coordinated by the "free" CH$_2$NMe$_2$ functions. Anal. Calcd for 5·0.2 ZnCl$_2$: C, 46.49; H, 5.70; N, 6.26.

(35) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

The structure was solved for the heavy atoms with the TREF option of SHELXS-86[36] and subsequent difference Fourier syntheses and refined by full-matrix least squares techniques on F.[37] All H-atoms were introduced at calculated positions with C–H = 1.08 Å and refined riding on their carrier atom. Convergence was reached at $R = 0.034$, $R_w = 0.054$. Weights were based on counting statistics. One common isotropic thermal parameter for H-atoms was used. Scattering factors were taken from Cromer and Mann,[38] and anomalous dispersion corrections, from Cromer and Liberman.[39] Refinement of the enantiomorphous model resulted in the slightly higher $R = 0.036$. Geometrical calculations and illustrations were done with the program PLATON.[40] All calculations were carried out on a MicroVax-II cluster. Final coordinates of the non-hydrogen atoms of 2 are given in Table III.

Supplementary Material Available: For 2, tables of hydrogen atom positions and isotropic thermal parameters, anisotropic thermal parameters, and complete bond distances and angles (5 pages). Ordering information is available on any current masthead page.

OM9300991

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(40) Spek, A. L. *Acta Crystallogr., Sect. A* **1990**, *46*, C34.