

two heavy bromine atom substituents may induce rapid relaxation within the doublet manifold, thus providing a further nonradiative pathway for relaxation of the excited radical. The heavy atom effects of point c are the most likely cause of the efficient excited-state relaxation.

Acknowledgment. We thank Arezou Azarani for preparing several of the substituted benzhydrols and S. E. Sugamori and G. M. Charette for technical assistance. Fluorescence spectra for a variety of the diphenylketyl radicals were initially recorded by Dr. D. J. Lougnot.

Use of an Aryldiamine Pincer Ligand in the Study of Tantalum Alkylidene-Centered Reactivity: Tantalum-Mediated Alkene Synthesis via Reductive Rearrangements and Wittig-Type Reactions

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Abstract: The potentially terdentate, monoanionic aryldiamine ligand $[C_6H_3(CH_2NMe_2)_2-2,6]^-$ provides an excellent tool for the study of tantalum alkylidene-centered reactivity. Transmetalation of $[TaCl_3(CH-t-Bu)(THF)_2]$ with $1/2[Li\{C_6H_3(CH_2NMe_2)_2-2,6\}_2]$ affords the alkylidene complex $[TaCl_2\{C_6H_3(CH_2NMe_2)_2-2,6\}(CH-t-Bu)]$ (**1**) in 90% yield. Complex **1** belongs to the space group *Cc* with $a = 12.983$ (2) Å, $b = 12.384$ (1) Å, $c = 11.969$ (1) Å, $\beta = 95.43$ (1)°, and $Z = 4$. The hexacoordinate tantalum center in **1** has an irregular ligand array in which the aryldiamine ligand adopts a new pseudofacial N,C,N-coordination mode. A Wittig-type reaction of the alkylidene complex **1** with acetone or benzaldehyde affords $[TaCl_2\{C_6H_3(CH_2NMe_2)_2-2,6\}(\mu-O)]_2$ (**2**) in virtually quantitative yield. A similar reaction of **1** with $PhCH=NR$ affords $[TaCl_2\{C_6H_3(CH_2NMe_2)_2-2,6\}(NR)]$ ($R = Me, SiMe_3$). Complex **2** belongs to the space group *Pc* with $a = 10.800$ (4) Å, $b = 11.804$ (3) Å, $c = 12.539$ (4) Å, $\beta = 108.67$ (3)°, and $Z = 2$. Complex **2** is a dimer with bridging oxo functions and has a distorted pentagonal bipyramidal ligand array around each tantalum center. Complex **1** with ethene and propene gives a rearrangement reaction that affords alkene adducts $[TaCl_2\{C_6H_3(CH_2NMe_2)_2-2,6\}(H_2C=CHR)]$ ($R = CH_2-t-Bu$ and Me, respectively). $[TaCl_2\{C_6H_3(CH_2NMe_2)_2-2,6\}(H_2C=CHCH_2-t-Bu)]$ belongs to the space group *P1* with $a = 8.320$ (1) Å, $b = 9.041$ (2) Å, $c = 14.054$ (3) Å, $\alpha = 94.53$ (2)°, $\beta = 90.75$ (2)°, $\gamma = 92.86$ (2)°, and $Z = 2$. The overall structure is distorted pentagonal bipyramidal. The chirality in the coordinated alkene determines the conformation of both five-membered Ta-C-C-C-N chelate rings. NMR experiments show the alkene complexes to be rigid in solution; the bonding of the alkene to the metal center is best described as resulting in a metallacyclopropane unit.

Introduction

Multidentate ligand systems, both cyclic¹ and acyclic,² can be designed to bind transition metals in a predictable manner. The steric constraints of such ligands and the nature of the donor atoms determine to a large extent the stability and properties of the metal complexes. In the special case of bis-ortho chelation, a terdentate monoanionic aryl ligand like $[C_6H_3(CH_2NMe_2)_2-2,6]^-$ (= NCN) partially encapsulates the complexed metal but still leaves sufficient distinctly positioned sites for the resulting complex to serve as a model compound for the study of elementary reaction processes.³ It has now been established that otherwise unstable or even transient stages in these processes are stabilized by the NCN ligand and can be isolated.⁴

A terdentate bonded NCN unit is a six-electron donor, just like the commonly employed η^5 -cyclopentadienyl ligand. These ligands, in octahedral complexes, are complementary in their coordination chemistry in the sense that an η^5 -bonded cyclopentadienyl ligand provides facial coordination, while the NCN ligand is designed to adopt a meridional bonding mode (Figure 1).⁵

In late transition metal chemistry, the three hard donor atoms of the NCN monoanion have been shown to enhance the nu-

cleophilic character of Ni(II) and Pt(II) centers, as well as to stabilize the higher formal oxidation states of Ni(III) and Pt(IV).⁶

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Table I. Relevant ^1H NMR Data (ppm) of the Cyclometalated Tantalum Complexes^a

	complex	CH_2N^b	NMe	other
1	$\text{TaCl}_2[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-}2,6](\text{CHCMe}_3)$	4.26, 4.72 (14)	2.84, 3.43 ^c	1.21 [CHCMe_3], 2.61 [CHCMe_3]
2	$[\text{TaCl}_2[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-}2,6](\mu\text{-O})_2]$	4.5 br ^d	2.95 ^d	
3a	$\text{TaCl}_2[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-}2,6](\text{NMe})$	4.23, 4.61 (13)	2.80, 3.22	4.38 [NMe]
3b	$\text{TaCl}_2[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-}2,6](\text{NSiMe}_3)^f$	4.10, 4.47 (13)	2.92, 3.08	0.19 [NSiMe_3]
4a	$\text{TaCl}_2[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-}2,6](\text{H}_2\text{C}=\text{CHCH}_2\text{CMe}_3)^e$	3.64, 3.68 (12) 4.49, 4.61 (12)	2.35, 2.42, 3.27, 3.45	g
4b	$\text{TaCl}_2[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-}2,6](\text{H}_2\text{C}=\text{CHMe})^e$	3.70, 3.77 (14) 4.51 (14) ⁱ	2.38, 2.46, 3.30, 3.37	h

^aUnless otherwise specified, spectra were obtained in CDCl_3 at 298 K, 200.13 MHz. Chemical shifts are indirectly referenced to SiMe_4 using solvent signals. ^b $^2J(\text{H,H})$ in parentheses. ^cData in C_6D_6 : 2.58, 2.82; $T_c = 305$ K. ^dData at 243 K: $\delta = 4.03, 4.93$ [d, $^2J(\text{H,H}) = 14$ Hz, CH_2N], 2.88, 2.95 (s, NMe); $T_c(\text{CH}_2\text{N}) = 300$ K, $T_c(\text{NMe}) = 266$ K. ^eIn C_6D_6 . ^fNMR data of in situ generated complex. ^gData for the *t*- $\text{BuCH}_2\text{CH}=\text{CH}_2$ unit: $\delta = 1.33$ (s, 9 H, CH_2 -*t*-Bu), 2.12 and 2.97 (dd, 2 H, CH_2 -*t*-Bu), 3.10 and 4.06 (m, $^2J_{\text{gem}} = 6.7$ Hz, $^3J_{\text{cis}} = 10.8$ Hz, $^3J_{\text{trans}} = 12.4$ Hz, 2 H, $\text{H}_2\text{C}=\text{CH}$ -). ^hData for the $\text{MeCH}=\text{CH}_2$ unit: $\delta = 2.98$ and 3.99 (dd, $^2J_{\text{gem}} = 7.2$ Hz, $^3J_{\text{cis}} = 11.0$ Hz, $^3J_{\text{trans}} = 12.9$ Hz, 2 H, $\text{H}_2\text{C}=\text{CH}$ -), 3.58 (d, $^3J(\text{H,H}) = 6.2$ Hz, 3 H, $\text{H}_2\text{C}=\text{CHCH}_3$), 4.51 (m, 1 H, $\text{H}_2\text{C}=\text{CH}$ -). ⁱTriplet with intensity 2 H.

Table II. ^{13}C NMR Data (ppm) of the Cyclometalated Tantalum Complexes^a

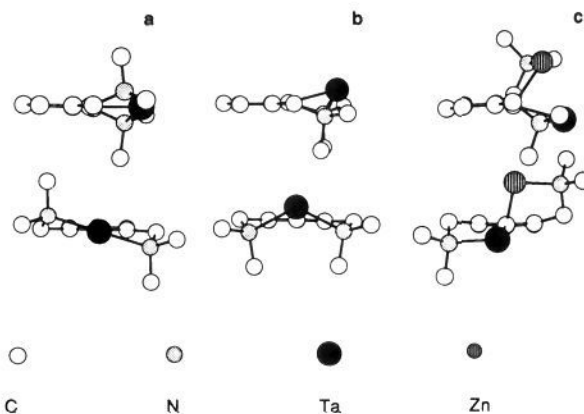
compd	aryl C				CH_2N	NMe	other
	C(1)	C(2,6)	C(3,5)	C(4)			
1	195.4	147.5	122.5	128.9	73.2	49.3, 59.4	253.5 [CHCMe_3], 46.5 [CHCMe_3], 34.2 [CHCMe_3]
2	201.7	146.5	122.3	126.9	71.9	51.1	
3	195.5	145.4	122.3	127.4	73.8	48.9, 55.9	47.1 [$\text{Ta}=\text{NMe}$]
4a ^b	204.7	144.5	121.6	129.5	78.3	52.6, 52.7	95.2 [$\text{H}_2\text{C}=\text{C}$ -], 87.6 [$\text{H}_2\text{C}=\text{C}$ -], 58.6
					78.6	54.4, 55.6	[$=\text{CH}-\text{CH}_2$ -], 40.7 [$-\text{CCMe}_3$], 30.5 [CMe_3]
4b ^b	204.7	144.7	121.7	129.6	78.1	52.7, 53.2	92.4 [$\text{H}_2\text{C}=\text{C}$ -], 86.1 [$\text{H}_2\text{C}=\text{C}$ -]
					78.5	55.1, 55.9	28.9 [$=\text{CHMe}$]

^aUnless otherwise specified, spectra were obtained in CDCl_3 at 298 K, 50.32 or 75.47 MHz. Chemical shifts are indirectly referenced to SiMe_4 using solvent signals. ^bIn C_6D_6 .

**Figure 1.** Preferences in coordination modes of the NCN monoanion and η^5 -cyclopentadienyl.

These properties would seem to make the NCN ligand also well-suited for the stabilization of high-oxidation-state early-transition-metal centers.

We have investigated the use of the monoanionic NCN ligand in organotantalum chemistry and found that it can be used as an excellent spectator ligand that stabilizes and controls tantalum-centered reactions. Moreover, from our work in tantalum chemistry, it is clear that the NCN ligand is even more versatile in its coordination modes to a metal center than we anticipated. Figure 2 shows some examples from tantalum chemistry where the ligand adopts, in addition to meridional bonding (structure a), a new pseudofacial coordination mode (structure b) or an asymmetric bridging position between two metal centers⁷ (structure c). In addition, we have found bidentate C,N-coordination modes of the NCN ligand in tantalum chemistry with one amine function uncoordinated (an example is $\text{Ta}(\text{O}-t\text{-Bu})_2(\text{NCN})(\text{CH}-t\text{-Bu})$ that will be described in another paper⁸). Other examples of such bidentate C,N-coordination⁹ and even monodentate C-coordination¹⁰ have previously been documented in the coordination

**Figure 2.** Reported bonding modes of the terdentate NCN ligand to tantalum centers: a, meridional bonding (this work); b, pseudofacial bonding (this work); c, bridging between tantalum and zinc.⁷ Bottom line views are projections along the $\text{C}_{\text{ipso}}-\text{C}(4)$ axis; top line views are projections side-on to the aryl ring approximately perpendicular to the $\text{C}_{\text{ipso}}-\text{C}(4)$ axis.

chemistry of the NCN monoanion with late transition metals (Rh, Ir, Ni, and Pt).^{9,10}

Previously, we have briefly reported on the incorporation of the NCN ligand into a tantalum complex that also contains a reactive alkylidene function.¹¹ In this paper we report the full synthetic details of this complex and other NCN-ligand-containing tantalum complexes that are prepared via alkylidene-centered processes involving Wittig-type reactions and reductive rearrangements.

Results

Synthesis of a Cyclometalated Tantalum Alkylidene Complex. The purple neopentylidene complex $\text{TaCl}_3(\text{CH}-t\text{-Bu})(\text{THF})_2$ (THF = tetrahydrofuran) is an ideal starting material for the

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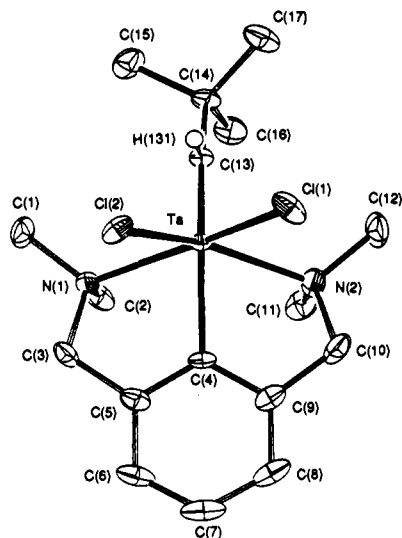
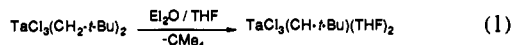


Figure 3. Molecular structure of $\text{TaCl}_2[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-2,6}](\text{CH-}t\text{-Bu})$ (1); ORTEP drawing with 50% probability ellipsoids.

synthesis of new alkylidene complexes because it can be prepared quantitatively in situ under very mild conditions starting from yellow dineopentyltantalum(V) trichloride (eq 1).¹² Moreover,



this neopentylidene complex contains weakly bonded THF ligands that can be easily displaced by other P and N donors.¹²

The organolithium compound of the NCN ligand, i.e. $[\text{Li}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-2,6}\}]_2$, reacts at low temperature in Et_2O with $\text{TaCl}_3(\text{CH-}t\text{-Bu})(\text{THF})_2$ to afford the purple neopentylidene complex $\text{TaCl}_2[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-2,6}](\text{CH-}t\text{-Bu})$ (1), which can be isolated in 90% yield (eq 2).

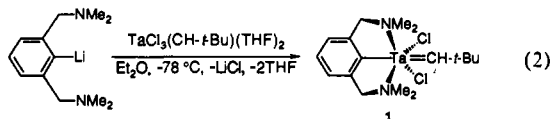


Table III. Relevant Data on the Geometry of 1

Bond Lengths (Å)			
Ta-Cl(1)	2.4247 (11)	Ta-Cl(2)	2.4313 (11)
Ta-N(1)	2.345 (4)	Ta-N(2)	2.373 (4)
Ta-C(4)	2.154 (4)	Ta-C(13)	1.938 (4)
C(13)-C(14)	1.515 (5)	C(13)-H(131)	1.09 (6)
Bond Angles (deg)			
Cl(1)-Ta-Cl(2)	79.51 (4)	N(1)-Ta-N(2)	118.63 (14)
Cl(1)-Ta-N(1)	157.71 (11)	N(1)-Ta-C(4)	70.66 (14)
Cl(1)-Ta-N(2)	79.35 (12)	N(1)-Ta-C(13)	91.08 (14)
Cl(1)-Ta-C(4)	107.44 (10)	C(4)-Ta-C(13)	139.01 (15)
Cl(1)-Ta-C(13)	102.65 (11)	Ta-C(13)-C(14)	170.6 (3)
Ta-C(13)-H(131)	71 (3)		

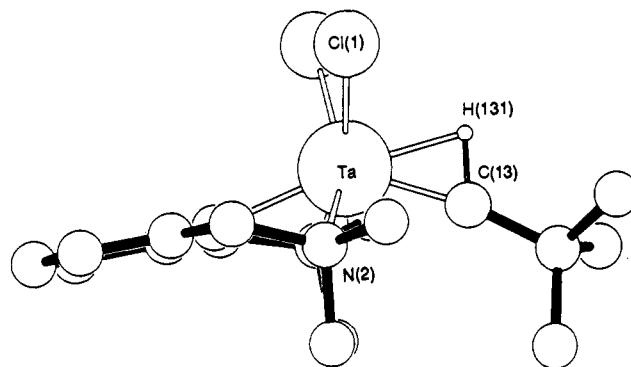


Figure 4. Plot of the neopentylidene complex 1 (aryl ring perpendicular to the plane) showing the pseudofacial coordination mode of the aryldiamine ligand and structural features of the neopentylidene unit.

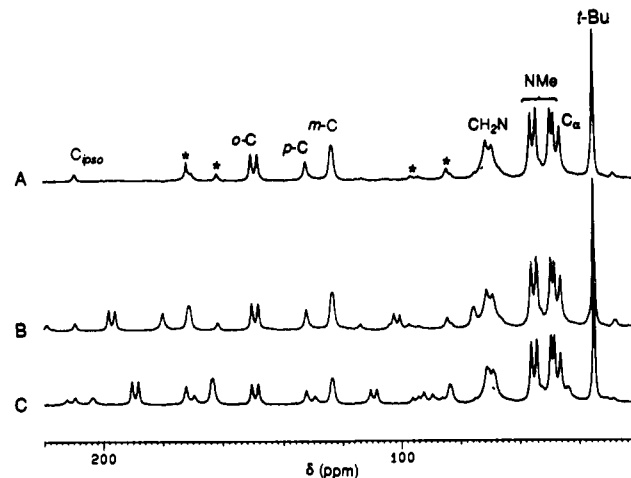


Figure 5. The 125.7-MHz CP/MAS $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of $\text{TaCl}_2[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-2,6}](\text{CH-}t\text{-Bu})$ (1); A, computed spectrum with suppressed spinning sidebands derived from two spectra obtained with different spinning frequencies (*, residual side bands); B, spectrum obtained with a spinning frequency of 6.024 kHz; C, spectrum obtained with a spinning frequency of 5.025 kHz.

The neopentylidene complex 1 is thermally stable at room temperature, and the solid can even be safely handled for short periods in air. Batches of 1 in quantities up to 30 g have been prepared without difficulty using conventional Schlenk equipment. The ^1H and ^{13}C NMR data of the complex (see Tables I and II) are indicative for the presence of a neopentylidene functionality and terdentate N,C,N-coordination of the $[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-2,6}]$ aryldiamine ligand.

Molecular Geometry and Crystal Structure of $\text{TaCl}_2(\text{NCN})-(\text{CH-}t\text{-Bu})$ (1). An X-ray structural analysis of 1 was carried out in order to elucidate the stereochemistry of the ligand distribution around tantalum and to aid the interpretation of the temperature-dependent spectroscopic data (vide infra). Suitable crystals of 1 were grown from a benzene solution into which pentane vapor was allowed to diffuse slowly. The structure of 1 involves the packing of four discrete mononuclear molecules in the unit cell. An ORTEP drawing of 1, along with the adopted numbering scheme is shown in Figure 3; selected bond distances and angles are given in Table III. The structure determination shows 1 to be a hexacoordinate tantalum species $\text{TaCl}_2[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_{2-2,6}](\text{CH-}t\text{-Bu})$ with an irregular ligand array. The best least-squares coordination plane is described by Ta, Cl(1), Cl(2), N(1), and N(2) with two mutually cis chlorine atoms [$\angle\text{Cl}(1)-\text{Ta}-\text{Cl}(2) = 79.51 (4)^\circ$] and two pseudo-cis-positioned nitrogen donor atoms [$\angle\text{N}(1)-\text{Ta}-\text{N}(2) = 118.63 (14)^\circ$]. Coordinated to tantalum on opposite sides of this plane are the ipso carbon atom of the aryldiamine ligand [C(4)] and the α -carbon

atom [C(13)] of the neopentylidene grouping [$\angle\text{C}_{\text{ipso}}-\text{Ta}-\text{C}_\alpha = 139.01 (15)^\circ$]. The conformation of the aryldiamine unit is such that it has adopted a pseudofacial bonding mode to the metal center (see also Figure 4).

The bonding mode of the neopentylidene grouping in 1 is more clearly shown in a projection of the molecule given in Figure 4; structural data for this unit are in the same ranges as those found for other tantalum neopentylidene complexes.^{13,14} These include the characteristically large $\text{Ta}-\text{C}_\alpha-\text{C}_\beta$ angle of $170.6 (3)^\circ$, the

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Table IV. Summary of the Wittig-Type Reactivity of $\text{TaCl}_2[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}](\text{CH-}i\text{-Bu})$ (**1**)^a

substrate	reaction time ^b	organic product (cis/trans) ^c	organometallic product ^d
PhC(H)=O	<60 s	$\text{PhC(H)=C(H)-}i\text{-Bu}$ (45/55)	2 $[\text{TaCl}_2(\mu\text{-O})(\text{NCN})]_2$
$\text{Me}_2\text{C=O}$	~1 h	$\text{Me}_2\text{C=C(H)-}i\text{-Bu}$	2 $[\text{TaCl}_2(\mu\text{-O})(\text{NCN})]_2$
PhC(H)=NMe	24 h	$\text{PhC(H)=C(H)-}i\text{-Bu}$ (70/30) ^e	3a $\text{TaCl}_2(\text{NMe})(\text{NCN})$
PhC(H)=NSiMe_3	~15 d ($t_{1/2}$)	$\text{PhC(H)=C(H)-}i\text{-Bu}$ (45/55)	3b $\text{TaCl}_2(\text{NSiMe}_3)(\text{NCN})$

^a Reactions were run in sealed NMR tubes using CDCl_3 as solvent with the given substrate in excess. ^b Time for >95% conversion of 1 equiv of substrate per equivalent of complex **1**. ^c Isomer ratios were obtained by integration of ^1H NMR (200.13 MHz) signals. ^d See Tables I and II for the NMR data of the inorganic products. ^e These products were identified by GC/MS analysis and by comparison of ^1H NMR data of the mixture with those reported for the pure compounds.³⁰

Table V. Selected Geometrical Data for **2**

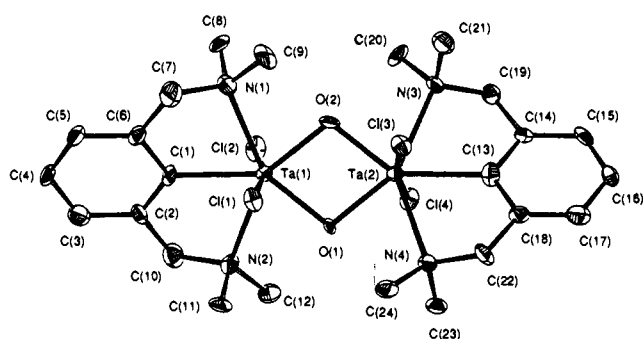
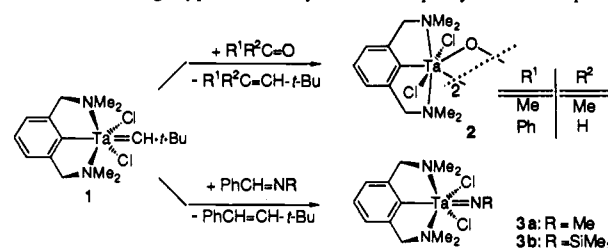
around Ta(1)				around Ta(2)			
Bond Lengths (Å)							
Ta-Cl(1)	2.387 (3)	Ta-Cl(2)	2.396 (3)	Ta-Cl(3)	2.408 (3)	Ta-Cl(4)	2.381 (3)
Ta-N(1)	2.417 (9)	Ta-N(2)	2.394 (9)	Ta-N(3)	2.423 (8)	Ta-N(4)	2.426 (8)
Ta-C(1)	2.223 (10)	Ta-O(1)	1.944 (7)	Ta-C(13)	2.224 (11)	Ta-O(1)	1.942 (6)
Ta-O(2)	1.936 (7)	Ta(1)-Ta(2)	3.0339 (13)	Ta-O(2)	1.936 (8)		
Bond Angles (deg)							
Cl(1)-Ta-Cl(2)	168.90 (12)	N(1)-Ta-N(2)	139.3 (3)	Cl(3)-Ta-Cl(4)	168.82 (10)	N(3)-Ta-N(4)	139.6 (3)
Cl(1)-Ta-N(1)	79.4 (2)	N(1)-Ta-C(1)	69.9 (3)	Cl(3)-Ta-N(3)	79.4 (2)	N(3)-Ta-C(13)	69.3 (3)
Cl(1)-Ta-N(2)	95.1 (2)	N(2)-Ta-O(1)	74.0 (3)	Cl(3)-Ta-N(4)	98.3 (2)	N(4)-Ta-O(1)	74.0 (3)
C(1)-Ta-N(2)	69.5 (3)	O(1)-Ta-O(2)	77.0 (3)	C(13)-Ta-N(4)	70.3 (3)	O(1)-Ta-O(2)	77.1 (3)

small $\text{Ta-C}_\alpha\text{-H}_\alpha$ angle of $71(3)^\circ$, and a short Ta=C_α bond length of 1.938 (4) Å (cf. the $\text{Ta-C}(4)$ single-bond length of 2.154 (4) Å). The high quality of the X-ray diffraction data allowed location of the neopentylidene H_α during the structure refinement.

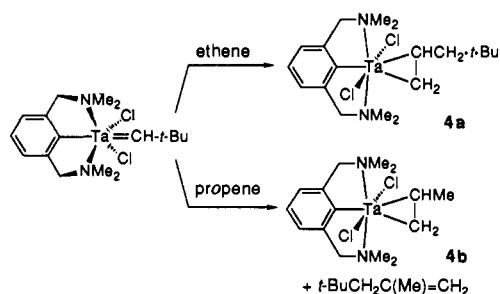
NMR Spectroscopy on **1 in the Solid State and in Solution.** The solid-state CP/MAS $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (125.7 MHz) of the neopentylidene complex **1** is shown in Figure 5. Characteristic for the rigid terdentate coordination of the aryldiamine ligand are the four anisochronous methyl resonances for the diastereotopic NMe_2 units at δ 48.4, 49.6, 54.3, and 56.2. The spectrum does not clearly show a resonance for the neopentylidene C_α although this may be the broad ($\Delta\nu_{1/2} \sim 600$ Hz) signal that seems to be present at δ 250. In solution the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** (50.32 MHz, CDCl_3) still shows the NMe_2 units to be diastereotopic but some of the resonances present in the solid-state spectrum are absent (see Discussion) and only two methyl resonances (at δ 49.3 and 59.4) are observed for the NMe_2 units (see Table II). The solution ^1H NMR spectrum of **1** (200.13 MHz) in CDCl_3 also has two distinct methyl resonances for the diastereotopic NMe_2 units (at δ 2.84 and 3.43). In C_6D_6 , however, these two ^1H NMR resonances are broad at 298 K (δ 2.58 and 2.82) and coalesce at 305 K ($\Delta G^\ddagger = 63 \pm 2$ kJ·mol⁻¹). Coalescence of the AB pattern of the CH_2N groups ($\Delta\delta = 0.75$ ppm) was not observed up to 353 K (the highest temperature employed), i.e., $\Delta G^\ddagger > 71$ kJ·mol⁻¹.

Wittig-Type Reactivity of $\text{TaCl}_2(\text{NCN})(\text{CH-}i\text{-Bu})$ (1**).** The neopentylidene complex **1** reacts with either an aldehyde (PhCHO) or a ketone (Me_2CO) to afford the white oxo complex **2** and an alkene ($\text{PhHC=CH-}i\text{-Bu}$ or $\text{Me}_2\text{C=CH-}i\text{-Bu}$, respectively) that can be seen as the product of a metal-mediated Wittig reaction (Scheme I). With an imine (PhCH=NR , $\text{R} = \text{Me}, \text{SiMe}_3$), **1** also reacts in a Wittig sense to give a green imido complex **3** and again a new alkene (Scheme I). In these clean reactions, 1 equiv of an aldehyde, ketone, or imine is converted to 1 equiv of $\text{R}^1\text{R}^2\text{C=CH-}i\text{-Bu}$ per equivalent of the neopentylidene complex **1**. It is also possible to convert the imido complex **3a** to the oxo complex **2** by treating it with benzophenone (Scheme I). These Wittig-type reactions thus proceed in the direction $\text{Ta=C} \rightarrow \text{Ta=NR} \rightarrow \text{Ta=O}$. The yields of the organometallic products are virtually quantitative, and these reactions provide an easy entry into cyclometalated tantalum oxo or imido chemistry although the reaction rates are low (see Table IV). Both the oxo complex **2** and the imido complex **3a** are thermally stable and can be safely handled in air for short periods.

Molecular Geometry and Crystal Structure of $[\text{TaCl}_2(\text{NCN})(\mu\text{-O})]_2$ (2**).** Suitable crystals of **2** were grown from a diethyl ether

**Figure 6.** Molecular structure of $[\text{TaCl}_2[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-2,6}](\mu\text{-O})]_2$ (**2**); ORTEP drawing with 50% probability ellipsoids.**Scheme I.** Wittig-Type Reactivity of the Neopentylidene Complex **1**

solution into which pentane vapor was allowed to diffuse slowly. The crystal structure of **2** involves the packing of two dinuclear molecules in the unit cell. An ORTEP drawing of **2**, along with the adopted numbering scheme is shown in Figure 6; selected bond distances and angles are given in Table V. The structure determination shows **2** to be a dinuclear, heptacoordinate tantalum complex with a distorted pentagonal bipyramidal coordination geometry around each tantalum center. The pentagonal plane contains two bridging oxo functions [O(1) and O(2)] that produce a flat square $\text{Ta}(\mu\text{-O})_2\text{Ta}$ unit together with a terdentate coordinated aryldiamine ligand [bonding via C(1), N(1), and N(2) to Ta(1) and via C(13), N(3), and N(4) to Ta(2)]. The axial trans-positioned chlorine atoms [Cl(1), Cl(2), Cl(3), and Cl(4)] complete the coordination sphere of both metal centers. The tantalum atoms are pentavalent, and consequently direct metal-metal bonds are not required to interpret the structure. The tantalum-tantalum distance of 3.0339 (13) Å is significantly longer than those of 2.6 to 2.8 Å normally found in Ta-Ta bonded systems.¹⁵ The nonlinear Ta-O-Ta arrangement found in the

Scheme II. Alkylidene-Centered Rearrangement Reactions of **1** with Small Alkenes

structure of **2** is also found in a "disrupted formyl" complex,¹⁶ a butterfly oxo cluster,¹⁷ and several trinuclear tantalum oxide species.¹⁸ It is also assumed to exist in the structure of the isolectronic, cyclopentadienyl complex $[\text{TaCl}_2(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-O})]_2$.¹⁹ These nonlinear bridges are generally found in more complex tantalum oxo systems, simpler systems having linear Ta—O—Ta units.²⁰

Reactivity of $\text{TaCl}_2(\text{NCN})(\text{CH-}t\text{-Bu})$ (1**) with Alkenes.** Generally the reactivity of the neopentylidene complex **1** toward alkenes is low. Screening experiments in CDCl_3 showed no reaction with *tert*-butylethene (not even after 6 months), styrene, or 1-pentene. However, with an excess of ethene and propene, **1** reacts to give the emerald green alkene adducts $\text{TaCl}_2\{(\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-}2,6)(\text{H}_2\text{C}=\text{CHR})\}$ (**4a**, R = $\text{CH}_2\text{-}t\text{-Bu}$, and **4b**, R = Me, respectively) in high yields (Scheme II). In the reaction with ethene, the neopentylethene formed remains bonded to the tantalum center, while the *t*-Bu- $\text{CH}_2\text{C}(\text{Me})=\text{CH}_2$ formed in the reaction of **1** with propene is displaced by propene, giving **4b**. The complexes **4** can be obtained pure by crystallization from hexane. They are moisture-sensitive, but the solids can be handled for short periods in air; they slowly decompose at room temperature, in particular the propene adduct **4b**, liberating the coordinated alkene. At -30°C , the complexes can be stored intact for months.

In order to gain insight into the nature of the alkene bonding in complexes **4**, several spectroscopic experiments have been performed. The higher order olefinic ^1H NMR patterns of **4a** have been accurately simulated, thereby facilitating a detailed analysis of all coupling relationships in the neopentylethene unit (see supplementary material). The most important olefinic H—H coupling constants thus obtained are $^2J_{\text{gem}} = 6.7$, $^3J_{\text{cis}} = 10.8$, and $^3J_{\text{trans}} = 12.4$ Hz; the values for the olefinic $^1J(^{13}\text{C}, ^1\text{H})$ of **4a** are 145.5 Hz ($\text{H}_2\text{C}=\text{CH-}$) and 139.2 Hz ($\text{H}_2\text{C}=\text{CH-}$). For **4a**, the value of the olefinic $^1J(^{13}\text{C}, ^{13}\text{C})$, obtained from an INADEQUATE experiment (see supplementary material), is 34 Hz.

When treated with excess D_2O in CDCl_3 or C_6D_6 , the alkene complex **4a** forms the alkane *t*-Bu- $\text{CH}_2\text{CHDCH}_2\text{D}$ as was shown by ^1H and ^{13}C NMR and by a GC/MS analysis of the reaction volatiles. Similarly, the reaction of **4a** with H_2O produced *t*-Bu- $\text{CH}_2\text{CH}_2\text{CH}_3$; no alkene was liberated. The other signals in the NMR spectra of the reaction mixtures can be assigned to the free diamine $\text{C}_6\text{H}_4(\text{CH}_2\text{NMe}_2)_2\text{-}1,3$ or $\text{C}_6\text{H}_3\text{D}(\text{CH}_2\text{NMe}_2)_2\text{-}1,3$.

Crystal Structure and Molecular Geometry of $\text{TaCl}_2(\text{NCN})(\text{H}_2\text{C}=\text{CHCH}_2\text{-}t\text{-Bu})$ (4a**).** Suitable crystals of **4a** were grown from a pentane solution that was cooled down to -30°C over a period of 3 days. The crystal structure of **4a** involves the

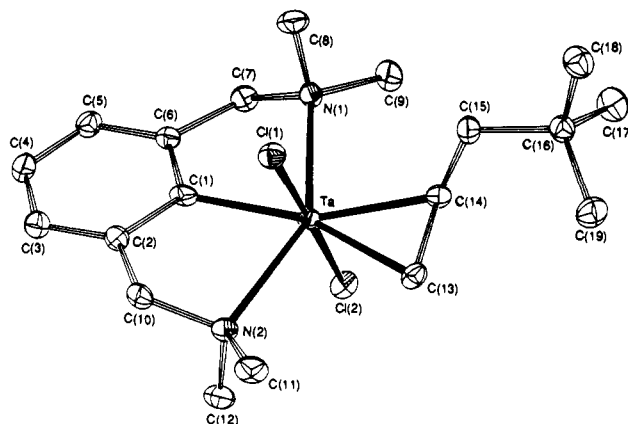


Figure 7. Molecular structure of $\text{TaCl}_2\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-}2,6\}(\text{CH}_2=\text{CHCH}_2\text{-}t\text{-Bu})$ (**4a**); ORTEP drawing (50% probability ellipsoids) of one of the enantiomers of **4a** with *S*-configuration at C(14) and λ -conformation of the Ta—C—C—N chelate rings.

Table VI. Relevant Data on the Geometry of **4a**

Bond Lengths (Å)			
Ta—Cl(1)	2.3702 (18)	Ta—Cl(2)	2.3608 (18)
Ta—N(1)	2.353 (6)	Ta—N(2)	2.372 (6)
Ta—C(1)	2.165 (7)	Ta—C(13)	2.200 (7)
Ta—C(14)	2.211 (7)	C(13)—C(14)	1.436 (10)
C(14)—C(15)	1.519 (10)	C(15)—C(16)	1.545 (10)
Bond Angles (deg)			
Cl(1)—Ta—Cl(2)	178.76 (7)	N(1)—Ta—N(2)	145.0 (2)
Cl(1)—Ta—N(1)	95.28 (15)	N(1)—Ta—C(1)	72.6 (2)
Cl(1)—Ta—N(2)	84.12 (15)	N(1)—Ta—C(13)	126.2 (2)
Cl(1)—Ta—C(1)	87.07 (18)	N(1)—Ta—C(14)	88.5 (2)
Cl(1)—Ta—C(13)	88.9 (2)	C(13)—Ta—C(14)	38.0 (3)
Cl(1)—Ta—C(14)	87.91 (19)		

packing of a pair of enantiomers of one diastereoisomer in a triclinic unit cell. An ORTEP drawing of **4a**, along with the adopted numbering scheme is shown in Figure 7; selected bond lengths and angles are given in Table VI. The structure determination shows **4a** to be a mononuclear, distorted pentagonal bipyramidal tantalum species $\text{TaCl}_2\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-}2,6\}(\text{H}_2\text{C}=\text{CHCH}_2\text{-}t\text{-Bu})$. In this complex there are two chlorine atoms [Cl(1) and Cl(2)] that occupy the axial trans positions. The equatorial plane contains the coordinated olefin ($\text{H}_2\text{C}=\text{CHCH}_2\text{-}t\text{-Bu}$) [bonding via C(13) and C(14)] together with C(1), N(1), and N(2) of the terdentate aryldiamine that covers three adjacent sites in this plane. Both five-membered Ta—C—C—N chelate rings are puckered. The olefinic bond is considerably lengthened upon coordination to tantalum [C(13)—C(14) = 1.436 (10) Å].

Reactivity of $\text{TaCl}_2(\text{NCN})(\text{H}_2\text{C}=\text{CHMe})$ (4b**) with Alkenes.** Since the propene adduct **4b** is thermally the most unstable of the alkene adducts **4**, we hoped that it would be a promising candidate for reactions with other alkenes. Therefore, some screening reactions with **4b** dissolved in C_6D_6 were carried out, followed by ^1H NMR analysis of the solutions after 18 h at room temperature. In none of these experiments did **4b** react with excess of either butadiene, cyclooctadiene, allyl bromide, acrylonitrile, or allyl cyanide. Neither was propene liberated from the complex (no displacement by another alkene) nor did any reaction take place that led to the formation of tantalacyclopentane complexes (a well-known reaction in low-valent tantalum chemistry^{21–23}). However, **4b** does enter into a very slow reaction with C_2H_4 that seems to give a mixture of two isomeric tantalacyclopentane complexes which have not been studied in detail.

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Discussion

Synthesis, Structure, and Alkylidene-Centered Reactivity of the Cyclometalated Tantalum Neopentylidene Complex (1). The transmetalation reaction with the terdentate NCN monoanion that gives neopentylidene complex **1** (eq 2) is straightforward. However, attempted syntheses of tantalum alkylidene complexes containing the potentially C,N-bidentate ligand $(C_6H_4CH_2NMe_2)^-$ met with complications. The reaction of the organolithium reagent $[Li(C_6H_4CH_2NMe_2)]_4$ with $TaCl_3(CH-t-Bu)(THF)_2$ is unclean, and no alkylidene complex could be isolated. Under similar conditions, the transmetalation with 0.5 equiv of $Zn(C_6H_4CH_2NMe_2)_2$ is clean and successful but the resulting tantalum species binds the $ZnCl_2$ formed and the resulting product is a sticky oil that could not be crystallized.

An interesting aspect of the structure of the neopentylidene complex **1** is that the aryldiamine ligand $\{C_6H_3(CH_2NMe_2)_2-2,6\}^-$ has adopted a previously unreported pseudofacial NCN bonding mode to the metal center (see Figure 4). This contrasts with the situation in octahedral organometallic complexes of the late transition metals where this ligand adopts meridional coordination with N-M-N angles of typically $161-163^\circ$.⁵ The facial NCN bonding originates from the trans influence of the neopentylidene function that would strongly weaken a tantalum-to-carbon bond located exactly trans to the alkylidene unit. An example of such a weakening trans influence is found in the structural features of the dimeric neopentylidene complex $[TaCl_3(CH-t-Bu)(PMe_3)]_2$, which contains two bridging chlorine atoms;¹³ one of these chlorine atoms is located trans to the neopentylidene unit, and its bond to tantalum [2.815 (2) Å] is considerably longer than that of the other bridging chlorine [2.448 (2) Å].

Additional evidence for the pronounced trans influence of an alkylidene function is found in a theoretical study on the conformational preferences in the methylidene complex $Cl_4W=CH_2$.²⁴ Extended Hückel and ab initio methods predict a trigonal bipyramidal coordination geometry with the methylidene unit in an equatorial position. Upon optimization of the coordination geometry, the chlorine substituents in the equatorial plane were found to bend away from the position trans to the methylidene unit ($\angle Cl_{eq}-W-Cl_{eq} = 140^\circ$ instead of 120°).

In the neopentylidene complex **1** the aryldiamine seems to alleviate the weakening of its Ta-C_{ipso} bond by placing the carbon atom away from an apical position, so resulting in the observed pseudofacial coordination mode of the aryldiamine ligand [$\angle C(4)-Ta-C(13) = 139.01(15)^\circ$]. The NCN ligand in **1** now covers a similar set of coordination sites, and donates the same number of bonding electrons, as an η^5 -bonded cyclopentadienyl system (see Figure 1). The temperature dependency of the ¹H NMR spectrum of **1** is indicative for fluxionality involving the NMe groups of the aryldiamine ligand. At room temperature, the observation of two anisochronous methyl resonances for the NMe₂ units is consistent with the solid-state structure of **1** (regardless of whether alkylidene rotation is assumed to be fast or slow on the NMR time scale, vide infra). At higher temperatures, the resonances of the NMe₂ units coalesce ($\Delta G^\ddagger = 63 \pm 2$ kJ·mol⁻¹) as the result of a process involving dissociation/association of the NMe₂ units. The methyl groups of each NMe₂ unit can be easily rendered homotopic by the successive steps: dissociation of the Ta-N bond, pyramidal inversion at the nitrogen atom, 180° rotation around the CH₂-NMe₂ bond, and recoordination of the nitrogen donor to tantalum. Since ΔG^\ddagger for the coalescence of the CH₂N groups is much larger than that for the NMe₂ units, it can be concluded that the observed fluxionality does not include any process that affects the stereochemistry of the tantalum center; i.e., exchange of other ligands around the tantalum center does not take place. The lability of the Ta-N coordinative bonds probably originates in the unusual sterically hindered pseudofacial bonding mode of the terdentate aryldiamine ligand to tantalum.

The solid-state CP/MAS ¹³C{¹H} NMR spectrum of the neopentylidene complex **1** does not show a clear resonance for the

neopentylidene C_α [possibly related to the tantalum quadrupole ($Q = 3.10 \cdot 10^{-28}$ m²) and spin ($I = 7/2$)] but is otherwise consistent with the crystal structure of **1**. The chemical shift data of the solid-state spectrum compare nicely with those obtained in solution, but (with the exception of C_{ipso} and C_{para}) all the resonances of the aryldiamine ligand are doubled in the solid-state spectrum. The underlying asymmetry cannot be explained when only one molecule of **1** is taken into account, since the molecular structure of **1** has a pseudomirror plane (see Figure 3), containing C(7), C(4), Ta, and C(13). However, inspection of the molecular packing in the crystal structure of **1** shows that the molecules are aligned in such a way that the intramolecular pseudosymmetry plane does not exist on an intermolecular scale. For instance, from Figure 3 it might be concluded that the pseudomirror plane in the molecule would render C(2) of one of the NMe₂ units equivalent to C(11) of the other NMe₂ unit (and C(1) equivalent to C(12) by analogy). However, the 4-Å coordination sphere around C(2) contains the aryl grouping of a neighboring molecule, while the same coordination sphere around C(11) is empty. Therefore, the ¹³C NMR spectrum of **1** will show two distinct signals for C(2) and C(11) in the solid state, while, in solution, when all molecules have become isolated species, both carbons are equivalent and give rise to only one resonance. The doubling of the other signals in the ¹³C NMR spectrum of **1** on going from solution to the solid state can be explained in the same way.

The difference in the number of resonances present in the solid-state and solution ¹³C NMR spectra of the alkylidene complex **1** cannot be explained by arguments involving rotation around the alkylidene Ta=C_α bond. Since the neopentylidene unit lies in the molecular pseudomirror plane, the molecular symmetry will be the same when alkylidene rotation is either blocked (cf. the solid-state spectrum) or fast on the NMR time scale (a possibility in solution). In fact, the barrier for alkylidene rotation is expected to be low in the 14-electron alkylidene complex **1**, since alkylidene rotation is not sterically hindered or prevented by electronic arguments: the electron-deficient tantalum center has empty low-lying π -orbitals perpendicular to those used for alkylidene-to-tantalum π -bonding. A similar electronic argument has been used to explain why the barrier for alkene rotation in 14-electron monocyclopentadienyltantalum alkene complexes²¹ is very low, while it is too high for alkene rotation to be observed in 18-electron dicyclopentadienyltantalum alkene complexes, even on the laboratory time scale.²⁵

Additional evidence for free alkylidene rotation in electron-deficient tantalum complexes comes from the dynamic behavior of the 10-electron alkylidene complex $Ta(OC_6H_3-t-Bu_2-2,6)_2-(CHSiMe_3)(CH_2SiMe_3)$.²⁶ In the solid state, the complex has nonequivalent aryl oxide ligands and diastereotopic Ta-CH₂SiMe₃ methylene protons due to the orientation of the alkylidene substituent. However, for this alkylidene complex, the ¹H NMR spectra could only be explained by assuming facile alkylidene rotation.

The neopentylidene complex **1** reacts with carbonyl compounds and imines; here not only the nucleophilicity of the alkylidene unit²⁷ but also the affinity of the metal center for oxygen and nitrogen ligands contribute to the driving force of the reaction. Wittig-type reactivity is a typical characteristic of Schrock-type alkylidene complexes and has been exploited in many carbonyl olefination reactions.²⁸ In addition, applications in the synthesis of some complex and highly functionalized natural products are known.²⁹

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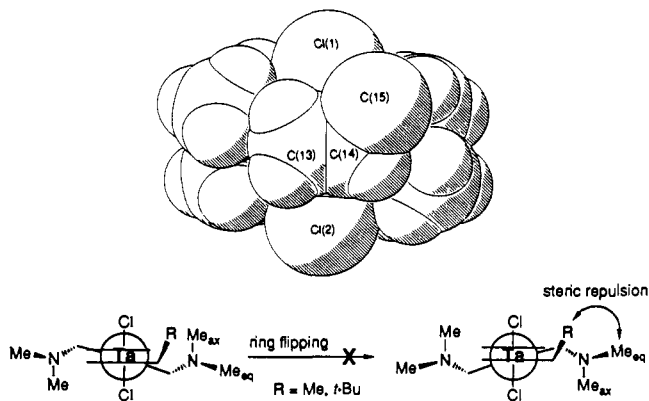


Figure 8. Top trace: Space-filling drawing of the neopentylethene adduct **4a** showing the crowded coordination sphere around the alkene function (the *t*-Bu unit and the hydrogen atoms on C(15) have been omitted for clarity). Bottom trace: Chirality in the alkene unit in complexes **4** which freezes out the ring flipping of the NCN ligand.

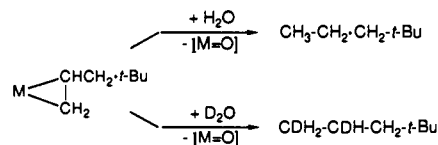
A well-documented example of Wittig-type reactivity in organotantalum chemistry provided by Schrock is the neopentylidene complex $\text{Ta}(\text{CH}_2\text{-}t\text{-Bu})_3(\text{CH-}t\text{-Bu})$, that converts aldehydes, ketones, esters, amides, and even CO_2 into neopentylidene derivatives.³⁰ However, the tantalum oxo complex formed in this case is supposed to be an undefined polymer. This contrasts to the situation with the Wittig-type reactions of **1** reported here that lead to the very stable dimeric oxo complex **2** and to the imido complexes **3** that can be readily characterized.

The (limited) reactions of the neopentylidene complex **1** with simple alkenes do not lead to products of alkene metathesis reactions but instead lead to reductive rearrangement products (Scheme II). Although these rearrangements have been well-documented in organotantalum chemistry,^{21,31} we now provide the first example where the reaction product remains trapped in the metal coordination sphere and is not subject to displacement or chemical attack. This nicely illustrates the potential of the ancillary NCN ligand to stabilize an otherwise transient stage in a tantalum alkylidene-centered reaction. Nevertheless, the fact that an alkylidene-centered reaction occurs proves that the NCN ligand does leave enough coordination sites for the occurrence of elementary reaction sequences.

Structure of $\text{TaCl}_2(\text{NCN})(\text{H}_2\text{C}=\text{CHCH}_2\text{-}t\text{-Bu})$ (4a**) and Reactivity of the Alkene Complexes **4**.** In the molecular structure of the alkene complex **4a** (Figure 7), coordination of the prochiral neopentylethene to tantalum results in the formation of a chiral center [C(14)] in the olefinic backbone. Interestingly, the neopentylethene coordination freezes out the ring flipping of both puckered five-membered Ta-C-C-N chelate rings. The configuration at the chiral atom C(14) determines the conformation of the chelate rings: an *S*-configuration at C(14) leads to a λ -configuration of the chelate rings, while an *R*-configuration at C(14) leads to a corresponding δ -conformation. As a result of the synergy between the two stereogenic elements, only one diastereoisomer of **4a** (and its enantiomer) has been found. Molecular modeling shows that the conformation of the ring puckering in **4a** is difficult to change for steric reasons. For instance, if the conformation of the chelate ring could be changed from λ to δ (i.e. by ring flipping) with the configuration at C(14) remaining *S*, the intramolecular distance between C(15) and one of the equatorial NMe groupings [(C(9))] would change from 3.43 to 2.95 Å. This would lead to severe steric repulsion between the neopentylidene ligand and the aryldiamine ligand (see Figure 8).

The neopentylethene function in the structure of **4a** is incorporated in a remarkably close-packed ligand array around the

Scheme III. Expected Organic Hydrolysis Products of a (Neopentyl)-Metallacyclopropane Species



tantalum center that is enclosed by Cl(1), Cl(2), and both NMe₂ units of the aryldiamine ligand (see Figure 8). In the solid-state structure, intramolecular contacts are already present between Cl(1)···H(151) [C(15)], C(14)···H(93) [C(9)], C(15)···H(82) [C(8)], and C(15)···H(93) [C(9)]. As a consequence of the limited docking area, even small substituents introduced at the neopentylethene unit will cause severe steric interference in the tantalum coordination sphere. For instance when the olefinic hydrogen on C(14) is substituted by a methyl group, this substituent experiences a significant steric repulsion from one of the equatorial NMe groups of the aryldiamine ligand [(C(9))···Me-substituent would be 2.77 Å]. This explains why the "methyl-substituted neopentylethene" *t*-Bu-CH₂C(Me)=CH₂, formed in the rearrangement reaction of the neopentylidene complex **1** with propene (Scheme II), is expelled from the tantalum coordination sphere and replaced by a sterically less-demanding propene ligand. The rigid encapsulation of the tantalum center in the alkene complexes **4** provides a rationale for the limited reactivity of the propene adduct **4b** with a variety of alkenes.

In **4a**, the short distances of the olefinic carbons C(13) and C(14) to tantalum [2.200 (7) and 2.211 (7) Å, respectively], that are in the same range as those found for anionic sp³-carbon to tantalum bonds, together with the long olefinic C-C bond [1.436 (10) Å] are characteristic for early-transition-metal alkene complexes: cf. Ta(C₅Me₅)(CH-*t*-Bu)(C₂H₄)(PMe₃)¹³ [Ta-C = 2.228 (3) and 2.285 (3); C-C = 1.477 (4) Å] or Nb(C₅Me₅)₂(H₂C=CPh)(H)³² [Nb-C = 2.289 (4) and 2.309 (4); C-C = 1.431 (6) Å]. The structural data of the bonded neopentylethene in **4a** are such that it is acceptable to describe the structure as a tantalum(V)cyclopropane with tantalum in its highest oxidation state (5+). A similar structure may be assumed to exist for the propene complex **4b**, the ¹H and ¹³C NMR data of both complexes being very similar (see Tables I and II).

Chemical evidence for metallacyclopropane-type reactivity of the alkene complexes **4** comes from the reaction of **4a** with D₂O or H₂O. The alkane formed in these reactions is in fact the expected hydrolysis product of a 1,2-dianionic alkanediyltantalum complex (Scheme III).

In the experiment using D₂O, the neopentane-*d*₂ formed was shown to have a deuterium atom at C¹ and C² of the former neopentylethene unit. A similar result (but obtained under more forcing conditions) known from the literature is the reaction of the ethene complex Ta(η⁵-C₅H₅)₂(H)(C₂H₄) with anhydrous HCl that produces ethane.³³

Spectroscopic Experiments with Relation to the Nature of the Alkene Bonding in Complexes **4.** The ¹H NMR spectrum of the alkene complex **4a** (200.13 MHz, C₆D₆) is consistent with the solid-state structure of **4a** and is not temperature dependent to at least 80 °C. (However, at higher temperatures, unclean thermal decomposition of the complex with release of neopentylethene occurs.) Characteristic for the rigid terdentate coordination of the aryldiamine ligand are the four anisochronous methyl resonances for the NMe₂ units at δ 2.35, 2.42, 3.27, and 3.45.

Well-resolved olefinic multiplets shifted to high field are indicative for the η²-bonded neopentylethene function (Table I). The nonfluxionality underlying the temperature-independent ¹H NMR of **4a** provides further evidence for a very high rotational barrier of the neopentylethene ligand about the metal-alkene axis and also for the frozen conformation of the Ta-C-C-N chelate rings in solution. The rigidity of this 14-electron alkene complex (which

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Table VII. Crystal Data and Details of the Structure Determinations of the Cyclometalated Tantalum Complexes

	1	2	4a
(a) Crystal Data			
formula	C ₁₇ H ₂₉ Cl ₂ N ₂ Ta	C ₂₄ H ₃₈ Cl ₄ N ₄ O ₂ Ta ₂	C ₁₉ H ₃₃ Cl ₂ N ₂ Ta
mol. wt	513.28	918.30	541.34
cryst syst	monoclinic	monoclinic	triclinic
space grp	Cc (No. 9)	Pc (No. 7)	P1 (No. 2)
a, b, c (Å)	12.983 (2), 12.384 (1), 11.969 (1)	10.800 (4), 11.804 (3), 12.539 (4)	8.320 (1), 9.041 (2), 14.054 (3)
α, β, γ (deg)	90, 95.43 (1), 90	90, 108.67 (3), 90	94.53 (2), 90.75 (2), 92.86 (2)
V (Å ³)	1915.8 (3)	1514.5 (9)	1052.4 (4)
Z	4	2	2
D _{calc} (g·cm ⁻³)	1.779	2.014	1.708
F(000), electrons	1008	880	536
μ (cm ⁻¹)	59.5	75.2	54.2
cryst size (mm)	0.50 × 0.32 × 0.31	0.15 × 0.12 × 0.10	0.60 × 0.20 × 0.11
(b) Data Collection			
temp (K)	100	100	100
θ _{min} , θ _{max} (deg)	1.00, 27.5	1.72, 27.5	1.45, 30.26
radiation, λ (Å)	Mo Kα (Zr-filtered), 0.71073	Mo Kα (Zr-filtered), 0.71073	Mo Kα (Zr-filtered), 0.71073
Δω (deg)	0.60 + 0.35 tan θ	0.65 + 0.35 tan θ	0.61 + 0.35 tan θ
hor and vert aperture (mm)	3.0, 5.0	3.0, 5.0	2.5, 5.0
X-ray exposure time (h)	59	86	110
linear decay (%)	4.2	14	2.5
ref reflections	-4,0,0; -4,-4,-1; -1,1,-1	031; 204; 320	-2,0,-3; 3,2,-2; -3,3,2
data set	h -16/0; k -16/16; l -15/15	h 0/14; k -11/15; l -16/15	h -11/0; k -12/12; l -19/19
total data	4579	5775	6983
total unique data	2287	3635	6013
obsd data	2246 [I > 2.5σ(I)]	3535 [I > 2.5σ(I)]	5267 [I > 2.5σ(I)]
absorption correction range	2.70-5.59	0.79-1.24 (DIFABS)	1.69-4.51
(c) Refinement			
no. of refined parameters	222	348	239
weighting scheme	w = 1.0/σ ² (F)	w = 1.0/[σ ² (F) + 0.000898F ²]	w = 1.0/σ ² (F)
final R, R _w , S	0.014, 0.015, 1.58	0.034, 0.051	0.043, 0.051, 2.96
isotr therm par H-atoms (Å ²)	0.035 (3)	0.0275 (13)	0.028 (4)
(Δ/σ) _{av} in final cycle	0.063	0.048	0.002
min and max resd dens (e/Å ³)	-0.89, 0.67	-1.89, 2.23 (near Ta)	-4.09, 3.37 (near Ta)

has a steric origin, vide supra) is in contrast to the rotational lability of another 14-electron tantalum alkene complex, TaCl₂(η⁵-C₅Me₅)(C₂H₄),²¹ for which ethene rotation occurs at room temperature on the NMR time scale [ΔG[‡](rot) = 39 kJ·mol⁻¹]. In the latter case, ethene rotation can occur easily because there is an empty orbital with π-symmetry and suitable energy at the metal perpendicular to the one used for alkene bonding and because there seem to be no limiting steric constraints. The relevance of the electronic argument is again illustrated in the behavior of the 18-electron tantalum alkene complex Ta(η⁵-C₅H₅)₂(H)(C₂H₄),³³ for which ethene rotation is not observed on the NMR time scale to at least 120 °C; this is in accord with the absence of a suitable empty orbital with π-symmetry. Rotation of the neopentylethene unit in **4a** however does not occur, even though it would be allowed on electronic arguments, because of the steric repulsion between the alkene carbons C(13) and C(14) and the chlorine atoms that would result from a 90° rotation of the alkene unit (that would bring C(13) and C(14) within a distance of 2.7 Å from the chlorine atoms).

The values obtained for the olefinic H-H coupling constants in **4a** and **4b** compare nicely with those for a series of dicyclopentadienylniobium and -tantalum complexes.³² However, these data do not allow one to make a conclusion regarding how to describe the complexation of the alkene to tantalum (i.e., as a tantalum(III) alkene adduct or as a tantalum(V)cyclopropane species) because there is considerable overlap in the ranges of the H-H coupling constants of alkenes and cyclopropanes. In order to gain a better insight into the nature of the alkene bonding in the complexes **4**, some other NMR experiments with the neopentylethene complex **4a** have been performed. The olefinic ¹J(¹³C,¹H) values are smaller than those in a free alkene but close to the range of 142-156 Hz reported for other tantalum alkene complexes.^{21-23,33,34} The diagnostic value of the data is low in

an evaluation of the nature of the olefinic bonding in **4a**, ¹J(¹³C,¹H) values in alkenes being close to those in cyclopropanes.³⁵ A comparison, however, of the J(H,H), J(C,H), and the X-ray data (vide supra) of the alkene function of **4a** with other tantalum alkene complexes shows that the alkene bonding present in this complex is like that found in many other early-transition-metal complexes. A clear indication of the electron density distribution within the neopentylethene function is available from the value of ¹J(¹³C,¹³C), which ranges from typically 15 Hz in cyclopropanes to 67 Hz in alkenes. For **4a**, the value of the olefinic ¹J(¹³C,¹³C) is 34 Hz, which is more like the ¹J(sp³-C,sp³-C) in alkanes (~34 Hz) and cyclopropanes (~15 Hz) than the ¹J(sp²-C,sp²-C) in alkenes (~68 Hz).³⁵ The extent of spⁿ hybridization for the carbon atoms in the Ta(η²-C-C) unit of **4a** can be roughly calculated to be n = 2.7 using Newton's semiempirical equation.³⁶ This finding argues for the structure of **4a** to be described as a tantalum(V)cyclopropane species in solution. This conclusion is supported by a recent photoelectron study on M(η²-C₅H₅)₂(η²-C₂H₄)(H) (M = Nb, Ta).³⁷

Conclusions

The potentially terdentate, monoanionic aryldiamine ligand {C₆H₃(CH₂NMe₂)₂-2,6}⁻ provides an excellent tool for the study of tantalum alkylidene-centered reactivity. The aryldiamine ligand exhibits a great flexibility in its coordination modes to a tantalum center and both normal meridional and unprecedented pseudofacial coordination are possible. The aryldiamine ligand is chemically inert in a variety of alkylidene-centered reactions and assists in the isolation of otherwise reactive tantalum alkene adducts and affords dimeric tantalum oxo species rather than often encountered

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polynuclear structures. The NCN ancillary is a rational option in early-transition-metal chemistry that even allows interesting analogies with ubiquitous cyclopentadienyl chemistry.

Experimental Section

General Comments. All experiments were performed in a dry nitrogen atmosphere using standard Schlenk techniques. Solvents were stored over sodium benzophenone ketyl and distilled prior to use. Elemental analyses were provided by the Institute of Applied Chemistry (TNO), Zeist, The Netherlands; ^1H and ^{13}C NMR spectra were recorded on a Bruker AC200 or AC300 spectrometer. The $^{13}\text{C}\{^1\text{H}\}$ INADEQUATE NMR spectrum was recorded (10^4 scans) on a Bruker AC200 spectrometer using a standard pulse sequence and a 10-mm NMR tube containing 2 g of complex **4a** in 4 mL of C_6D_6 . $\text{TaCl}_3(\text{CH}-t\text{-Bu})(\text{THF})_2$ ¹² and $[\text{Li}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6\}]_2$ ³⁸ were prepared according to literature procedures. High purity ethene and propene were obtained from Aldrich and used as received; resublimed TaCl_5 was obtained from Alfa, and neopentyl chloride was prepared from 2,2-dimethyl-1-propanol by treating it in a conventional way with $[\text{Me}_2\text{N}=\text{CHCl}]\text{Cl}$.⁴⁶

Synthesis of $\text{TaCl}_3[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6](\text{CH}-t\text{-Bu})$ (1). To a stirred purple solution of $\text{TaCl}_3(\text{CH}-t\text{-Bu})(\text{THF})_2$ (9.68 g, 19.3 mmol) in Et_2O (75 mL) at -78°C was added within 1 min a solution of $[\text{Li}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6\}]_2$ (3.81 g, 19.2 mmol) in Et_2O (25 mL). The resulting solution was allowed to warm up to room temperature, and during this time, a purple precipitate formed. The solvent was removed in vacuo, and the remaining solid was extracted with C_6H_6 (3×50 mL). The combined extracts were stripped in vacuo to give a solid that was washed with Et_2O (3×50 mL) and dried in vacuo, leaving 8.89 g (90%) of purple product. The complex can be crystallized from a pentane-layered C_6H_6 solution. Anal. Calcd for $\text{C}_{17}\text{H}_{29}\text{Cl}_2\text{N}_2\text{Ta}$: C, 39.78; H, 5.69; N, 5.46. Found: C, 39.35; H, 5.49; N, 4.95. CP/MAS $^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, 25°C , adamantane): $\delta = 35.2$ [$\text{C}(\text{CH}_3)_3$], 46.4 [$\text{C}(\text{CH}_3)_3$], 48.4, 49.6, 54.3, and 56.2 [$\text{N}(\text{CH}_2)_2$], 69.3 and 71.4 (CH_2N), 209.4 (ipso C of C_6H_3).

Synthesis of $[\text{TaCl}_3[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6](\mu\text{-O})]$ (2). To a stirred suspension of purple $\text{TaCl}_3[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6](\text{CH}-t\text{-Bu})$ (4.29 g, 8.36 mmol) in Et_2O (50 mL) was added acetone (0.55 mL, 7.49 mmol). Within a few minutes the color of the mixture changed to yellow. After the reaction mixture was stirred overnight, the Et_2O was decanted and the remaining solid was washed twice with Et_2O (2×25 mL) and dried in vacuo to give 2.62 g (76%) of white product. The complex can be crystallized from pentane-layered Et_2O solutions.

Synthesis of $\text{TaCl}_3[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6](\text{NMe})$ (3a). A suspension of purple $\text{TaCl}_3[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6](\text{CH}-t\text{-Bu})$ (0.79 g, 1.54 mmol) in Et_2O (50 mL) with $\text{PhC}(\text{H})=\text{NMe}$ (0.20 g, 1.68 mmol) was stirred for 6 days. The solvent was removed in vacuo from the resulting green suspension, and the remaining solid was washed twice with Et_2O (2×10 mL). Subsequent drying in vacuo gave 0.64 g (88%) of yellow-green product. The complexes can be crystallized from Et_2O . Anal. Calcd for $\text{C}_{13}\text{H}_{22}\text{Cl}_2\text{N}_3\text{Ta}$: C, 33.07; H, 4.70; N, 8.90. Found: C, 33.01; H, 4.70; N, 8.79.

Synthesis of $\text{TaCl}_3[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6](\text{H}_2\text{C}=\text{CHCH}_2-t\text{-Bu})$ (4a). A purple suspension of $\text{TaCl}_3[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6](\text{CH}-t\text{-Bu})$ (2.07 g, 4.03 mmol) in pentane (100 mL) saturated with ethene at 20°C was stirred for 24 h. The resulting green turbid solution was filtered, and the solvent was removed from the filtrate in vacuo to give 1.75 g (80%) of emerald green product. The complex can be crystallized from a minimum of pentane (~ 10 mL/g). Anal. Calcd for $\text{C}_{19}\text{H}_{33}\text{Cl}_2\text{N}_2\text{Ta}$: C, 42.16; H, 6.14; N, 5.17. Found: C, 42.07; H, 6.36; N, 5.31.

Synthesis of $\text{TaCl}_3[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6](\text{H}_2\text{C}=\text{CHMe})$ (4b). A purple solution of $\text{TaCl}_3[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6](\text{CH}-t\text{-Bu})$ (2.02 g, 3.94 mmol) in 100 mL of C_6H_6 /pentane (20/80) saturated with propene at

20°C was stirred for 1 week. The resulting green solution was stripped in vacuo to give a sticky residue that was extracted with pentane (3×100 mL). The combined extracts were concentrated in vacuo to ca. 25 mL, from which the product crystallized overnight at -78°C as block-shaped green crystals; yield 1.75 g (83%). The solid is only moderately thermally stable.

Structure Determination and Refinement of 1, 2, and 4a. Crystal data and numerical details of the structure determinations are given in Table VII. The crystals were glued on top of a glass fiber and transferred to an Enraf-Nonius CAD4 diffractometer for data collection at 100 K. Unit cell parameters were determined from a least-squares treatment of the SET4 setting angles of 25 reflections and were checked for the presence of higher lattice symmetry.³⁹ All data were collected in $\omega/2\theta$ scan mode. Data were corrected for L_p , for the observed linear decay of the reference reflections, and for absorption using Gaussian integration (1 and 4a) or the DIFABS⁴⁰ method (2); redundant data were merged into a unique dataset. The structures were solved with either standard Patterson methods (2 and 4a) or with direct methods (1) (SHELXS86⁴¹) and subsequent difference Fourier analyses. Refinement on F was carried out by full matrix least-squares techniques. H-atoms were introduced on calculated positions [$\text{C}-\text{H} = 0.98 \text{ \AA}$] and included in the refinement riding on their carrier atoms (except for H131 in complex 1, that was located from a difference Fourier map and refined). All non-H atoms were refined with anisotropic thermal parameters; H-atoms were refined with one common isotropic thermal parameter. Weights were introduced in the final refinement cycles. The absolute structures of 1 and 2 were checked by refinement with opposite f' anomalous dispersion contributions, resulting in $R = 0.024$ and $R_w = 0.030$ for 1 and $R = 0.041$ and $R_w = 0.061$ for 2. Neutral atom scattering factors were taken from ref 42 and corrected for anomalous dispersion.⁴³ All calculations were performed with SHELX76⁴⁴ and the EUCLID package⁴⁵ (geometrical calculations and illustrations) on a MicroVAX cluster. Final coordinates of all atoms of 1, 2, and 4a are given in the supplementary material.

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Supplementary Material Available: Tables of hydrogen atom fractional coordinates and isotropic thermal parameters, non-hydrogen atom final coordinates with both equivalent isotropic thermal parameters and anisotropic thermal parameters, all bond distances, and all bond angles for 1, 2, and 4a (Tables S1–S15), an analysis of the simulation of the ^1H NMR resonances for the olefinic protons of $[\text{TaCl}_3[\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2-2,6](\text{CH}_2=\text{CHCH}_2-t\text{-Bu})]$ (4a), and a $^{13}\text{C}\{^1\text{H}\}$ INADEQUATE NMR spectrum of the neopentylethene unit of 4a (20 pages); listings of observed and calculated structure factors for 1, 2, and 4a (74 pages). Ordering information is given on any current masthead page.

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