DEDICATED CLUSTER COMMUNICATIONS

Exploring Routes to Tantalum(V) Alkylidene Complexes Supported by Amine Tris(phenolate) Ligands

Stanislav Groysman,[a] Israel Goldberg,[a] Moshe Kol,[a,*] Elisheva Genizi,[b] Zeev Goldschmidt[b,*]

[a] School of Chemistry, Raymond and Beverly Sackler of Exact Sciences, Tel Aviv University, Tel Aviv 69978, Israel
Fax: (+972)-3-640-9293, e-mail: moshekol@post.tau.ac.il
[b] Department of Chemistry, Bar Ilan University, Ramat Gan 52900, Israel
Fax: (+972)-3-535-1250, e-mail: goldz@mail.biu.ac.il

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Dedicated to Prof. R. R. Schrock on the occasion of his 60th birthday.

Abstract: Two basic organometallic species, tris(neopentyl)mono(neopenylidene)tantalum and pentabenzyltantalum, were evaluated as starting materials on the route to alkyl and alkylidene complexes with amine tris(phenolate) ligands. The reaction of the former with the ligand precursor proceeded *via* the addition of the O–H functionality to the Ta=C double bond at the first step, forming a sterically congested tetraneopentyl complex, that was characterized by X-ray crystallography. In contrast, the reaction of the less bulky pentabenzyltantalum with a variety of the ligand precursors led directly and in a high yield to the dibenzyl Ta(V) complexes. These species were surprisingly stable toward thermolysis, decomposing only at 120–130 °C after prolonged periods of time. The unexpected product of this decomposition was found to be a dinuclear μ-benzylidene Ta(V) complex.

Keywords: alkane elimination reaction; alkylidene complex; amine tris(phenolate); ligand design; N,O ligands; tantalum

The first Schrock-type alkylidene complex, Ta(CH-*t*-Bu)(CH_2-*t*-Bu)$_3$, was prepared in 1974.[1] Since then, the significance of the alkylidene functionality as the mediator of the olefin metathesis reaction has been widely established. Although not showing a high reactivity in metathesis, Ta(V) alkylidene complexes were extensively studied as model compounds for the formation and reactivity of metal-carbon multiple bonds.[2] Various monodentate and polydentate ligand systems that support this functionality have been introduced in recent years.[3] Recently, we began to explore the synthesis and reactivity of organometallic tantalum complexes of amine-phenolate ligands.[4,5] We found that tribenzyltantalum complexes of amine bis(phenolate) ligands may be conveniently synthesized by direct reaction between the ligand precursor and pentabenzyltantalum, and that these may be thermally converted into benzyl-benzylidene complexes, depending on the presence of an extra donor on a side arm.[4b] The related trianionic amine tris(phenolate) ligands are especially interesting since they were found to support both trigonal bipyramidal and octahedral geometries on binding to group IV and V metals, and due to their similarity to the trianionoic triamidoamine ligands (see Figure 1). The latter have been extensively studied in recent years,[6] and were shown to stabilize an axial tantalum(V) alkylidene functionality in a trigonal bipyramidal complex following a smooth α-hydrogen abstraction from a dialkyl intermediate.[7]

Several synthetic methodologies are known to lead to alkylidene complexes, including the employment of precursors that already include the alkylidene function, or by an α-elimination reaction sequence from dialkyl precursors.[3] The amine phenolate ligands are relatively acidic, and may be bound to tantalum *via* an alkane elimination starting from a suitable precursor.[4] Ta(CH-*t*-Bu)(CH_2-*t*-Bu)$_3$ is an attractive candidate for reaction with an amine tris(phenolate) ligand precursor since it already contains an alkylidene function. Two possible reactions may be envisioned to result from the two types of metal-carbon bonds of this complex. The O–H bond may add across the Ta=C double bond, generating a tetraalkyl species, that can react further, to generate complexes of the [O_3N]Ta(CH_2-*t*-Bu)$_2$- or [O_3N]Ta=C(H)-

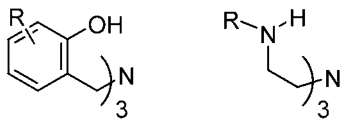

Figure 1. A schematic representation of the amine tris(phenolate) and triamidoamine ligand systems.

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t-Bu-type. Alternatively, the acidic OH functions of the ligand may react with the neopentyl ligands, eliminating the corresponding alkanes, and preserving the alkylidene function in the resulting $[O_3N]Ta{=}C(H)$-*t*-Bu-type complex.

Ta(CH-*t*-Bu)(CH_2-*t*-Bu)$_3$, prepared by Schrock's procedure,[1b] was reacted with the amine tris(phenolate) ligand precursor featuring 2,4-dimethyl substitution (Lig^1H_3) in ether at room temperature for 1 h. The ^1H NMR spectrum of the crude light-yellow solid product indicated that no starting materials remained. The solid was extracted with pentane, and cooled to −35 °C. After prolonged standing at this temperature, yellow crystals had formed whose ^1H NMR spectrum supported their assignment as the major component in the crude reaction mixture. According to the ^1H NMR spectrum, this complex (**1**) was neither a dineopentyl nor a neopentylidene complex. The solid state structure of **1** revealed a rather unexpected product of the $[H_2O_3N]Ta(CH_2$-*t*-Bu)$_4$ formula (see Figure 2), in which the strong chelate (Lig^1) binds to the metal *via* only one phenolate oxygen, while the other two are still protonated. In addition to the phenolate ligand, four neopentyl ligands are bound to the Ta(V) metal center whose geometry may be described as a distorted square-pyramidal, with one of the neopentyl groups occupying the axial position. To our knowledge, this is the first crystallographically characterized tantalum complex featuring four neopentyl groups. Notably, the nitrogen donor is not coordinating to the tantalum, signifying a highly crowded metal center.

The reactions between Ta(CH-*t*-Bu)(CH_2-*t*-Bu)$_3$ and ligand precursors bearing an acidic proton were reported to follow different routes. A reaction with HCl led to protonation of the nucleophilic alkylidene carbon, generating the tetraalkyl monochloro species.[1b] Similarly, the first step in the reaction of Ta(CH-*t*-Bu)(CH_2-*t*-Bu)$_3$ with silica was proposed to be an addition of the silanol OH bond across the Ta=C bond.[8] In contrast, Wolczanski et al. reported the whole spectrum of reactivities for different OH bearing ligands: the "silox" ligand precursor led to protonolysis of a Ta−C single bond rather than addition to a Ta=C double bond, whereas the 9-hydroxytriptycene reacted with the alkylidene function. When the ligand precursor was too bulky ("tritox"), no reaction between the O−H functionality and this metal complex took place.[9] Compound **1**, being the primary product in the reaction between the amine tris(phenolate) ligand precursor and Ta(CH-*t*-Bu)(CH_2-*t*-Bu)$_3$, undoubtedly results from the addition of one of the ligand OH groups across the Ta=C double bond. Thus, in Ta(CH-*t*-Bu)(CH_2-*t*-Bu)$_3$, the alkylidene function appears to be more reactive than the alkyl function toward the non-bulky phenol function. According to this reactivity, Ta(CH-*t*-Bu)(CH_2-*t*-Bu)$_3$ may be viewed as a masked form of "Ta(CH_2-*t*-Bu)$_5$",[10] a sterically hindered analogue of $Ta(CH_2Ph)_5$ (*vide supra*) or $Ta(CH_3)_5$,[11] since it leads to the same product that would be expected to result from "Ta(CH_2-*t*-Bu)$_5$". Apparently, the significant steric crowding at the metal center provides a sufficient kinetic stability to **1**. However, **1** is unstable in solution at room temperature, and reacts further, releasing neopentane. When longer reaction times were employed (24–72 h), a complex product mixture of various Ta(V) alkyl complexes formed. These products possessed a similar solubility in organic solvents, and therefore their separation by the regular extraction/recrystallization techniques was not successful. According to ^{13}C NMR spectroscopy, no alkylidene complexes were present among the products.

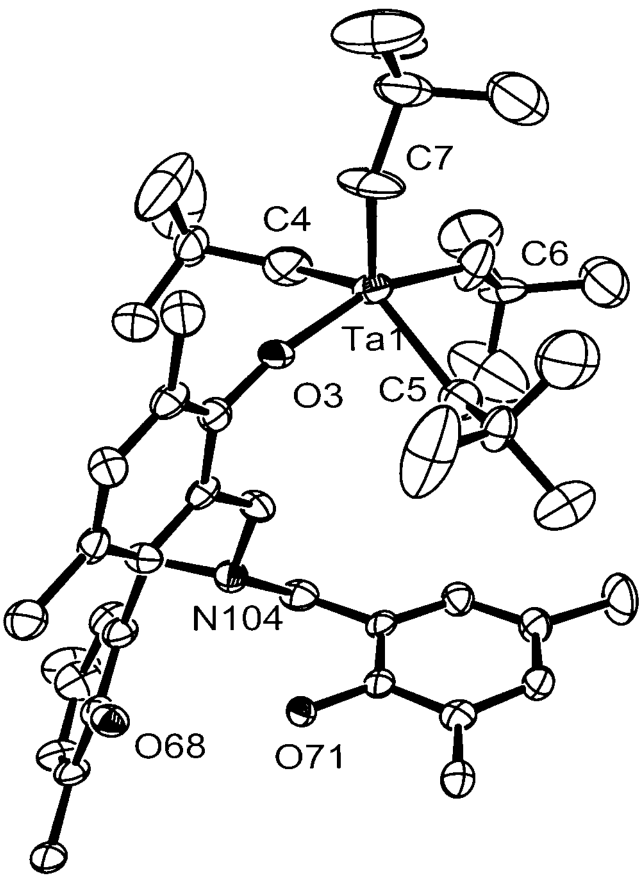
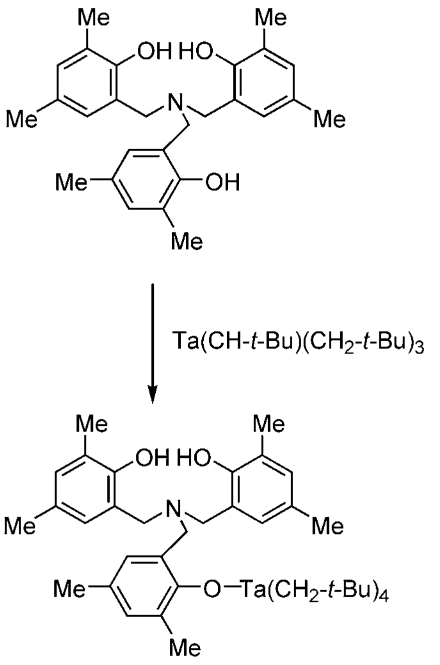


Figure 2. ORTEP representation of the molecular structure of **1** (30% probability ellipsoids). The asymmetric unit contains two crystallographically independent molecules of similar structure, only one of which is presented here. The elongated ellipsoids of the carbon atoms of the neopentyl groups reflect their orientational disorder. In addition, one of the phenolate rings (of the molecule not shown here) is partially disordered.

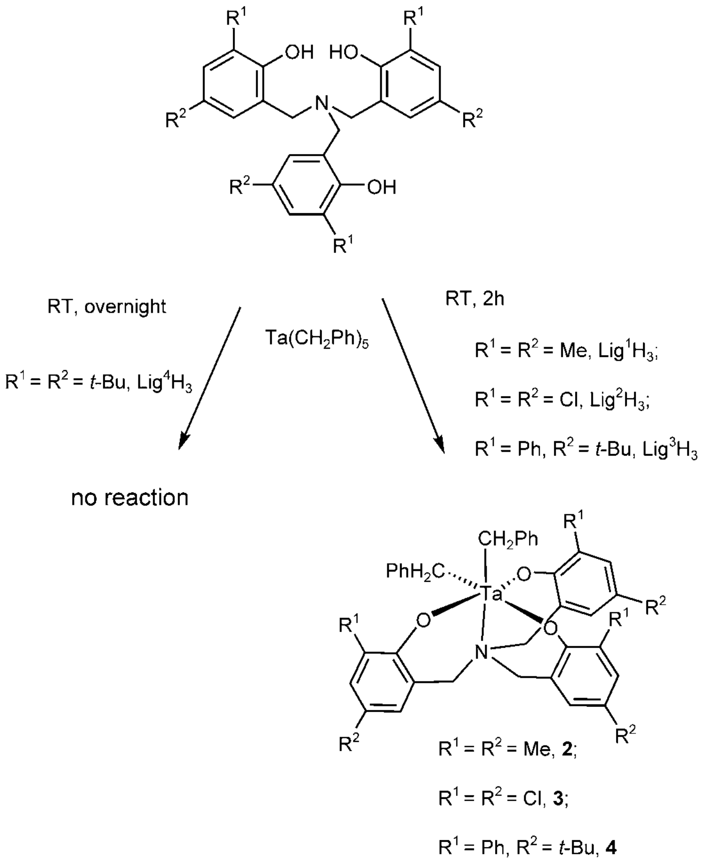
Since the Ta(CH-*t*-Bu)(CH_2-*t*-Bu)$_3$-route proved unsuccessful, we turned to a less bulky metal precursor: pentabenzyltantalum. We have previously shown that pentabenzyltantalum may be prepared directly from $TaCl_5$ and BnMgCl in a reasonable yield. Pentabenzyltantalum was shown to react quantitatively with a varie-



Scheme 1. The initial product of the reaction between Ta(CH-*t*-Bu)(CH$_2$-*t*-Bu)$_3$ and the amine tris(phenolate) ligand precursor Lig^{1}H$_3$.

ty of amine bis(phenolate) ligands, yielding tribenzyl Ta(V) complexes, that led to formation of alkyl-alkylidene complexes or to ligand β-CH activation upon thermolysis.[4b] The amine tris(phenolate) ligand precursor Lig^{1}H$_3$ reacted with pentabenzyltantalum as well, leading to the dibenzyl complex **2**.[4a] To estimate the generality of this approach, we reacted three additional amine tris(phenolate) ligand precursors, carrying chloro (Lig^{2}H$_3$), phenyl (Lig^{3}H$_3$), or *tert*-butyl (Lig^{4}H$_3$) *ortho* substituents, with pentabenzyltantalum. The reaction of the relatively non-bulky ligands (Lig^{2}H$_3$ and Lig^{3}H$_3$) with pentabenzyltantalum was fast and clean, forming the corresponding dibenzyl complexes **3**, and **4** after 2 h in a high yields. Noteworthy, the bulky amine tris(phenolate) ligand precursor, Lig^{4}H$_3$, did not react with pentabenzyltantalum under the same conditions (room temperature, toluene), even after 6 h, after which only the starting materials were observed.

The NMR spectra of **2**–**4** at room temperature were consistent with C_{3v}-symmetrical species, exhibiting three identical ligand arms and two identical benzyl groups. However, the X-ray structure of **2** revealed a hexacoordinate complex, in which the three phenolate oxygens, the two benzyl carbons, and the central (weakly bound) nitrogen donor create an *octahedral* environment around the metal center.[4a] According to VT-NMR experiments, these segments (three phenolate arms and two benzyl ligands) are equilibrated by some low-energy process(es): Upon cooling, all benzyl peaks flatten until completely disappearing at *ca.* –73 °C.[4a] In contrast to the related tribenzyl Ta(V) complexes of the amine bis(phenolate) ligands that led to the corresponding alkyl-alkylidene complexes by thermolytic α-abstraction reaction, complexes **2**–**4** were found to be relatively stable toward thermolysis. Thus, heating of **2**–**4** in toluene to *ca.* 100 °C for 1–2 h did not affect them much [in comparison, a fast decomposition of the tribenzyl amine bis(phenolate) complexes was observed at *ca.* 80 °C].[4b] When harsher conditions were employed, i.e., heating to 130 °C for *ca.* 2 h in chlorobenzene, a slow color change from yellow-brown to red-purple was observed. An inspection of the ^{1}H NMR spectra of the crude products revealed the presence of complex mixtures. It was not clear whether alkylidene formation had taken place.



Scheme 2. The reactions of Ta(CH$_2$Ph)$_5$ with the amine tris(phenolate) ligands precursors.

To determine the nature of the main product(s), we attempted recrystallization of a "model" compound **5**, a decomposition product of **2**. Slow evaporation of benzene solution of **5** resulted in formation of dark-red crystals, along with some non-crystalline beige material. The X-ray structure determination disclosed a *dinuclear* Ta complex, possessing bridging benzylidene ligands in which the geometry around each metal atom is nearly octahedral (Figure 3). Thus, the coordination mode of the amine tris(phenolate) ligand does not change, as would occur if a *mononuclear* benzylidene product

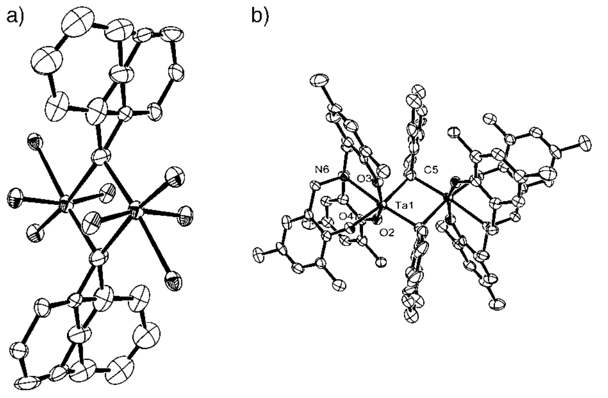
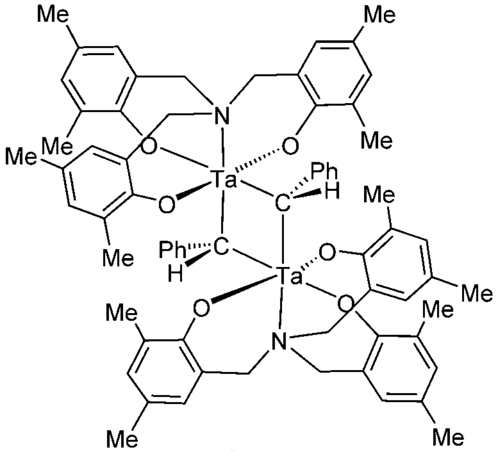
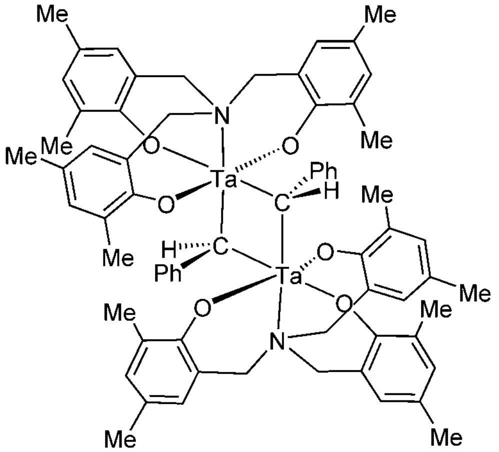


Figure 3. ORTEP representation of **5**, 50% probability. *Left:* the dinuclear complex core including both conformations of the bridging benzylidene groups. *Right:* the whole structure except for the crystallization solvent, that is omitted for clarity.



C_2-symmetry



C_i-symmetry

Figure 4. Two possible isomers of the dinuclear μ-benzylidene complex, **5**.

would have formed. Moreover, the Ta–O and the Ta–N bond lengths are similar to those in **2**.[4a] The Ta–C bond lengths are not identical, being 2.159(9) and 2.207(9) Å. As expected for a d^0 metal, the Ta–Ta distance (3.19 Å) seems to be too long to support a metal-metal bond.

Compound **5** may form either through an intramolecular α-abstraction reaction leading to a terminal alkylidene group followed by dimerization of two such units to give the bridging dinuclear species, or by an intermolecular pathway leading to it directly. The latter pathway may explain the harsh conditions required for formation of **5**. Still, the former pathway cannot be ruled out as the high activation energy may result from the instability of a pentacoordinate terminal alkylidene species. These findings are especially intriguing when compared with the facile formation of benzylidene complexes from the proposed unstable $[N_3N]Ta(CH_2Ph)_2$ complexes. Thus, the amine tris(phenolate) ligand, in contrast to the triamidoamine ligand, is not inclined to support a metal-carbon multiple bond in the axial position of a "tripodal" complex of the $[O_3N]M{=}R$-type.[12]

The structure of **5** contains two overlapping orientations of the benzylidene ligand (Figure 3, right) that may arise from two different isomers of **5** (**5a** and **5b**, see Figure 4). A "*cis*" disposition of the benzylidene phenyl groups leads to a C_2-symmetrical complex, while a "*trans*" disposition of these groups leads to a C_i-symmetrical complex.[13] In this crystal structure, **5** co-crystallizes with a C_6D_6 molecule, occupying two variable sites in the crystal grid, in accordance with the orientation of the benzylidene group: In one of its sites, deuteriobenzene overlaps with one of the orientations of the benzylidene group. On its own, the crystal structure cannot provide reliable evidence for the existence of these two isomers, since it may result from the co-crystallization of the two different enantiomers of C_2-symmetry, or two different orientations of the C_i-symmetrical isomer, at the same sites in the crystal. Yet, these isomers, if they exist, are of a diastereoisomeric relationship that should be manifested in their different spectroscopic data. Therefore, we attempted the separation of the isomers by extraction and recrystallization from different solvents.

The crude product was extracted consecutively with pentane, ether, and toluene. Red-purple crystals formed in the ethereal phase within several days at –35 °C. The ^{1}H NMR spectrum of the crystalline solid showed a *single* alkylidene species (**5a**), displaying the benzylidene signal at 8.20 ppm. In addition, the spectrum featured six different Me groups, six different aromatic protons, and three AB systems for the ligand methylene protons. The ^{13}C NMR spectrum of **5a** included a single peak for the alkylidene carbon at 212.9 ppm. The above spectroscopic data were consistent with either (C_2 and C_i) of the isomers of the dinuclear complex, proposed by the solid-state structure. No crystals formed in the toluene fraction, however, the removal of the solvent revealed a relatively clean mixture of the two alkylidene isomers (**5a** and **5b**), in *ca.* 3:1 ratio. The pentane fraction also contained both isomers (in *ca.* 1:1.5 ratio), though being contaminated by unknown impurities. According to its ^1H NMR spectrum, the second alkylidene species displaying a benzylidene proton at 8.04 ppm, 6 aromatic protons, and 6 Me groups, fits the structure of the second possible diastereoisomer of the general formula [Lig-Ta=CH(Ph)]$_2$ (**5b**). The ability to isolate and handle complex **5a** in its pure form for at least 24 hours at room temperature, indicates that these diastereoisomers do not interconvert readily.

In conclusion, both the tri(alkyl)mono(alkylidene) and homoleptic pentaalkyl Ta complexes are potential precursors for the preparation of Ta(V) alkyl complexes with amine tris(phenolate) ligand precursors. The reaction of tris(neopentyl)mono(neopenylidene)tantalum with the ligand precursor proceeded *via* the addition of the O–H functionality to the Ta=C double bond, generating the tetra(alkyl) species, that reacted further to give a mixture of Ta alkyl species. In contrast, the reaction of pentabenzyltantalum with a variety of the amine tris(phenolate) ligand precursors led cleanly to the formation of the octahedral dibenzyl Ta(V) complexes, that were found to be surprisingly stable toward a thermolytic decomposition (toluene, 100 °C, several hours). Under more severe conditions, the reaction led to the formation of unusual dinuclear Ta(V) complex, possessing bridging benzylidene ligands. Two diastereoisomers of this compound ("*cis*" and "*trans*") were observed, one of which was obtained in a pure state by recrystallization from ether. While the stability of the dibenzyl species seems to support an intermolecular α-hydrogen abstraction pathway for formation of the bridging alkylidene complexes, an intramolecular pathway cannot be ruled out.

Experimental Section

General Remarks

All manipulations of the metal complexes were performed under a dry nitrogen atmosphere in a nitrogen-filled glove-box. Ta(CH-*t*-Bu)(CH$_2$-*t*-Bu)$_3$,[1b] Ta(CH$_2$Ph)$_5$,[4a] Lig^{1}H$_3$,[14] and Lig^{4}H$_3$[14] were prepared according to previously published procedures. TaCl$_5$, PhCH$_2$MgCl (1.0 M in ether), and *t*-BuCH$_2$MgCl (1.0 M in ether) were obtained from Aldrich Inc. Solvents were purified and dried following standard procedures. NMR data were collected on Bruker AC-200 and Bruker AC-400 spectrometers, and referenced to protio impurities in benzene-d_6 (δ = 7.15 ppm) and to the ^{13}C chemical shift of benzene (δ = 128.70 ppm). Routine characterization of metal complexes consisted of ^1H, and BB ^{13}C NMR experiments, performed in C_6D_6 at 298 K. The X-ray diffraction measurements were performed on a Nonius Kappa CCD diffractometer system, using MoKα (λ = 0.7107 Å) radiation. The analyzed crystals were embedded within a drop of viscous oil and freeze-cooled to *ca.* 110 K. The structures were solved by a combination of direct methods and Fourier techniques using mostly DIRDIF software, and were refined by full-matrix least squares with SHELXL-97. Elemental analyses of the ligand precursors and of the tantalum complexes were performed in the microanalytical laboratories of the Hebrew University in Jerusalem. The analysis of the complexes consistently showed a somewhat low carbon value apparently due to air sensitivity.

Synthesis of Lig^{2}H$_3$ {2,2′,2″-[Nitrilotris(methylene)]tris(4,6-dichlorophenol)}

2,4-Dichlorophenol (4.0 g, 24.5 mmol), and hexamethylenetetramine (1.2 g, 8.5 mmol) were melted and stirred at 110 °C for 2.5 h. Hot ethanol was added to the reaction mixture and the stirring was continued until the oil was dissolved completely, and some solid started to form. The stirring was stopped and the solid was allowed to precipitate overnight. The solid was filtered, washed with ethanol and dried to give a yellow powder (1.4 g, 32% yield). This was further purified by recrystallization from 2-ethoxyethanol (or DMF) to give colorless crystals of 2,2′-[bis(methylene)imino]bis(4,6-dichlorophenol); mp 210 °C–212 °C [Lit. mp.[15] 197–198 °C]. The filtrate was evaporated to give an oil, which was triturated with methanol to give the desired compound, which was further purified by column chromatography (silica gel, chloroform). Recrystallization from chloroform gave the pure tris product as colorless plates; yield: 1.0 g (21%); mp 143–144 °C; anal. calcd. for $C_{21}H_{15}Cl_6NO_3$: C 46.53, H 2.79, N 2.58; Cl 39.24; found: C 46.12, H 2.83, N 2.54, Cl 40.01%; ^1H NMR (200 MHz, CDCl$_3$): δ = 7.23 (d, *J* = 2 Hz, 3H), 7.02 (d, *J* = 2 Hz, 3H), 5.60 (br s, 3H), 3.72 (s, 6H); ^{13}C NMR (CDCl$_3$) δ = 149.81 (3 *C*), 129.10 (3 *C*), 128.55 (3 *C*), 124.80 (3 *C*H), 124.73 (3 *C*H), 121.09 (3 *C*), 55.33 (3 *C*H$_2$); HRMS (DCI-I-Bu): *m/z* = 538.917527 ($C_{21}H_{15}Cl_6NO_3$) (M$^+$).

Synthesis of Lig^{3}H$_3$ {2,2′,2″-[Nitrilotris(methylene)]tris[4-(2,2-dimethylethyl)-6-phenyl-phenol]}

A mixture of 4-*t*-butyl-2-phenylphenol (4.53 g, 20.0 mmol), hexamethylenetetramine (0.23 g, 1.65 mmol) and 36% aqueous formaldehyde (0.84 mL, 10.0 mmol) was stirred and heated to 125 °C for 48 h. The mixture was cooled to room temperature, triturated with methanol, filtered, washed with cold methanol and dried to give the product as a pale yellow powder (2.7 g, 55% yield) which could be further purified by recrystallization from methanol; mp 174 °C; anal. calcd. for $C_{51}H_{57}NO_3$: C 83.58, H 7.85, N 1.91; found: C 83.39, H 7.96, N 1.89%; ^1H NMR (CDCl$_3$, 200 MHz): δ = 7.5–7.2 (21H, m), 3.89 (6H, s), 1.28 (27H, s); ^{13}C NMR (50.38 MHz, CDCl$_3$): δ = 150.14 (3 *C*), 142.6 (3 *C*), 138.19 (3*C*), 129.41 (6 *C*H), 128.65 (6 *C*H), 127.95 (3 *C*), 127.24 (6 *C*H), 126.77 (3 *C*H), 122.76 (3 *C*), 55.65 (3 *C*H$_2$), 34.06 (3 *C*), 31.55 (9 *C*H$_3$); HRMS (DCI-CH$_4$): *m/z* = 731.430384 ($C_{51}H_{57}NO_3$) (M$^+$).

Synthesis of 1

22 mg (0.053 mmol) of Lig^{1}H$_3$ were dissolved in ether (1 mL) and added dropwise to a stirred yellow-orange solution of

$Ta(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3$ (24 mg, 1 equiv.) in ether (1 mL). After stirring at room temperature for 1 h, a pale yellow solution was obtained. The solvent was removed under vacuum, and the bright-yellow product was analyzed by ^{1}H NMR. The crude product was extracted with pentane and toluene, and left at −35 °C. During several weeks, bright-yellow crystals of **1** were obtained in the pentane phase and were analyzed by ^{1}H NMR and X-ray diffraction analyses. ^{1}H NMR (200 MHz, C_6D_6): δ = 8.04 (s, 2H, O*H*), 7.63 (br s, 1H, Ar-*H*), 6.83 (br s, 2H, Ar-*H*), 6.75 (m, 3H, Ar-*H*), 4.10 (s, 2H, Ar-C*H*$_2$-N), 3.90 (s, 4H, Ar-C*H*$_2$-N), 2.33 (s, 3H, Ar-C*H*$_3$), 2.19 (s, 6H, Ar-C*H*$_3$), 2.17 (s, 3H, Ar-C*H*$_3$), 2.09 (s, 6H, Ar- C*H*$_3$), 1.64 [s, 8H, Ta-C*H*$_2$-C(CH$_3$)$_3$], 1.20 [s, 36H, Ta-CH$_2$-C(C*H*$_3$)$_3$]. These data were consistent with the major product (*ca.* 80%) in the crude reaction mixture. This compound was too unstable in solution at room temperature to be further characterized.

Synthesis of 2

Compound **2** was prepared as previously described.[4a] Anal. calcd. for $C_{41}H_{44}NO_3Ta$: C 63.15, H 5.69, N 1.80; found: C 62.49, H 5.82, N 1.48%.

Synthesis of 3

53 mg (0.098 mmol) of Lig^{2}H$_3$ were dissolved in toluene and added dropwise to a stirred solution of $Ta(CH_2Ph)_5$ (66 mg, 0.104 mmol). After 2 h, the yellow-brown solution was concentrated under vacuum. The resulting solid was washed with a small amount of pentane and dried under vacuum, yielding 73 mg (0.081 mmol, 83%) of **3** as yellow solid; ^{1}H NMR (200 MHz, C_6D_6): δ = 7.21 (m, 8H), 7.06 (d, *J* = 2.5 Hz, 3H), 6.88 (tt, J_1 = 6.3 Hz, J_2 = 2.4 Hz, 3H), 6.29 (d, *J* = 2.5 Hz, 3H), 2.88 (s, 4H, Ph-C*H*$_2$-Ta), 2.62 (s, Ar-C*H*$_2$-N); ^{13}C NMR (50.38 MHz, C_6D_6): δ = 153.05, 143.36, 131.55, 130.95, 130.52, 129.99, 129.44, 129.37, 129.00, 128.72, 127.86, 91.25, 61.80; anal. calcd. for $C_{35}H_{26}Cl_6NO_3Ta$: C 46.59, H 2.90, N 1.55; found: C 45.72, H 3.01, N 1.22%.

Synthesis of 4

63 mg (0.087 mmol) of Lig^{3}H$_3$ were dissolved in 2 mL of toluene and added to a stirred solution of $Ta(CH_2Ph)_5$ (56 mg, 0.088 mmol) in 1 mL of toluene. The brown reaction mixture was stirred for 2 h, after which the solvent was removed under vacuum. The resulting brown solid was washed with pentane (*ca.* 3 mL), and dried under vacuum, yielding 80 mg (0.071 mmol, 81%) of **4**; ^{1}H NMR (200 MHz, C_6D_6): δ = 7.69 (d, *J* = 7.3 Hz, 6H), 7.38 (m, 9H), 7.19 (t, *J* = 7.2 Hz, 3H), 6.89 (t, *J* = 7.5 Hz, 4H), 6.75 (d, *J* = 2.0 Hz, 3H), 6.57 (t, *J* = 7.2 Hz, 3H), 6.44 (d, *J* = 7.4 Hz, 4H), 3.31 (s, 6H, Ar-C*H*$_2$-N), 2.65 (s, 4H, Ph-C*H*$_2$-Ta), 1.26 [s, 27H, C(C*H*$_3$)$_3$]; ^{13}C NMR (50.38 MHz, C_6D_6): δ = 153.81, 149.16, 144.56, 139.97, 131.41, 130.96, 129.26, 128.46, 128.37, 128.04, 126.54, 126.27, 124.12, 79.14, 63.02, 34.89, 32.44.

Synthesis of 5

A solution of 124 mg (0.159 mmol) of **2** in chlorobenzene (1 mL) was heated to 130 °C for 1.5 h. After cooling, a deep-red solution was observed. The solvent was removed, and the resulting deep-red solid was extracted with pentane, ether, and toluene (*ca.* 2 mL each). Red-purple crystals (22 mg) that had formed in the ethereal phase were separated from the solution and dried under vacuum, leading to the single isomer **5a** in *ca.* 20% yield. ^{1}H NMR of **5a** (400 MHz, C_6D_6): δ = 8.20 [s, 2H, PhC(*H*)(Ta)$_2$], 7.24 (m, 6H), 6.93 (br s, 2H), 6.67 (br, 2H), 6.62 (br s, 2H), 6.50 (t, *J* = 7 Hz, 4H), 6.39 (br s, 2H), 6.17 (br s, 2H), 5.74 (br s, 2H), 4.37 (d, *J* = 13.3 Hz, 2H), 3.36 (d, *J* = 13.1 Hz, 2H), 3.14 (d, *J* = 12.9 Hz, 2H), 2.87 (d, *J* = 13.2 Hz, 2H), 2.59 (s, 3H, Ar-Me), 2.52 (d, *J* = 12.9 Hz, 2H, Ar-Me), *ca.* 2.42 [m (s + d), 5H], 2.25 (s, 3H, Ar-Me), 2.05 (s, 3H, Ar-Me), 1.85 (s, 3H, Ar), 1.66 (s, 3H, Ar-Me); ^{13}C NMR (100.76 MHz, C_6D_6): δ = 212.91 [Ph*C*(H)-(Ta)$_2$], 155.66, 155.55, 155.12, 150.26, 145.05, 132.50, 132.34, 131.19, 130.81, 130.48, 129.34, 129.22, 128.29, 128.22, 128.16, 128.05, 127.35, 126.28, 126.14, 125.61, 124.08, 129.34, 65.46, 65.05, 60.62, 21.47, 21.17, 20.95, 19.63, 17.19, 16.35. The remaining ethereal phase has shown no traces of additional alkylidene products. The non-crystalline solid material that was found in the pentane phase has shown the presence of both alkylidene products, according to the benzylidene signals at 8.20 and 8.04 ppm, in *ca.* 1 : 1.5 (**5a** : **5b**) ratio, in addition to some impurities. Evaporation of the toluene led to a purple solid, containing a relatively clean mixture of two alkylidene isomers, in 3 : 1 (**5a** : **5b**) ratio. The relative amount of **5b** in the mixture of **5a** and **5b** was estimated according to the following resonances: δ = 8.04 [s, 2H, PhC(*H*)(Ta)$_2$], 6.88 (br s, 2H, Ar-H), 6.76 (br s, 2H, Ar-H), 6.57 (br s, 2H, Ar-H), 6.26 (br s, 2H, Ar-H), 5.78 (br s, 2H, Ar-H), 7.54 5.78 (br s, 2H, Ar-H), 2.66 (s, 3H, Ar-Me), 2.61 (s, 3H, Ar-Me), 2.20 (s, 3H, Ar-Me), 2.09 (s, 3H, Ar-Me), 1.87 (s, 3H, Ar-Me), 1.70 (s, 3H, Ar-Me). X-ray quality crystals were obtained upon slow evaporation of a C_6D_6 solution of crude **5**.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-248942 (complex **5**) and 248943 (complex **1**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

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References and Notes

[1] a) R. R. Schrock, *J. Am. Chem. Soc.* **1974**, *96*, 6796–6797; b) R. R. Schrock, J. D. Fellmann, *J. Am. Chem. Soc.* **1978**, *100*, 3359–3370.

[2] R. R. Schrock, *Acc. Chem. Res.* **1979**, *12*, 98–104.

[3] R. R. Schrock, *Chem. Rev.* **2002**, *102*, 145–179.

[4] a) S. Groysman, I. Goldberg, M. Kol, Z. Goldschmidt, *Organometallics* **2003**, *22*, 3793–3795; b) S. Groysman, I. Goldberg, M. Kol, E. Genizi, Z. Goldschmidt, *Organometallics* **2004**, *23*, 1880–1890.

[5] For the synthesis of amine tris(phenolate) Ta(V) complexes featuring amido, chloro and alkoxo ligands, see: a) S. Groysman, S. Segal, M. Shamis, I. Goldberg, M. Kol, Z. Goldschmidt, E. Hayut-Salant, *J. Chem. Soc. Dalton Trans.* **2002**, 3425–3426; b) Y. Kim, P. N. Kapoor, J. G. Verkade, *Inorg. Chem.* **2002**, *41*, 4834–4838; c) S. Groysman, S. Segal, I. Goldberg, M. Kol, Z. Goldschmidt, *Inorg. Chem. Commun.* **2004**, *7*, 938–941.

[6] R. R. Schrock, *Acc. Chem. Res.* **1997**, *30*, 9–16.

[7] a) J. Freundlich, R. R. Schrock, W. M. Davis, *J. Am. Chem. Soc.* **1996**, *118*, 3643–3655; b) J. Freundlich, R. R. Schrock, W. M. Davis, *Organometallics* **1996**, *15*, 2777–2783.

[8] V. Dufaud, G. Niccolai, J. Thivolle-Cazat, J. M. Basset, *J. Am. Chem. Soc.* **1995**, 117, 4288–4294.

[9] R. E. LaPointe, P. T. Wolczanski, G. D. Van Duyne, *Organometallics* **1985**, *4*, 1810–1818.

[10] L. Li, M. Hung, Z. Xue *J. Am. Chem. Soc.* **1995**, 117, 12746–12750.

[11] R. R. Schrock, J. Lee, L. C. Liang, W. M. Davis, *Inorg. Chim. Acta* **1998**, #32#*270*, 353–362.

[12] However, a variety of vanadium-oxo complexes with the amine tris(phenolate) ligands have been prepared and structurally characterized, exhibiting TBP geometry at the metal center, and a double-bonded (oxo) ligand in the axial position. S. Groysman, M. Kol, unpublished results.

[13] A similar mixture of isomers was reported for the dinuclear zirconocene complex bearing bridging neopentylidene ligands: F. W. Hartner, Jr., J. Schwartz, S. M. Clift, *J. Am. Chem. Soc*. **1983**, *105*, 640–641.

[14] M. Kol, M. Shamis, I. Goldberg, Z. Goldschmidt, S. Alfi, and E. Hayut-Salant, *Inorg. Chem. Commun*. **2001**, *4*, 177–179.

[15] A. Zinke, G. Zigeuner, G. Weiss, W. Schaden, E. Wiesenberger, *Monatsh. Chem*. **1950**, 81, 999.