

Isolation and Chemistry of Tantalum(V) Compounds Containing Two Resolved 3,3'-Disubstituted-1,1'-bi-2,2'-Naphthoxide Ligands

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Reaction of dimeric $[(Et_2N)_2Cl_2Ta(\mu-Cl)_2TaCl_2(NEt_2)_2]$ with $(R)-[H_2O_2C_{20}H_{10}(R)_{2-3,3'}]$ ($R = SiMe_3, SiMe_2Ph, SiMePh_2, \text{ or } SiPh_3$) produces the 3,3'-dialkyl-1,1'-bi-2,2'-naphthoxide complexes $(R,R)-[H_2NET_2][Ta(O_2C_{20}H_{10}\{R\}_{2-3,3'})_2Cl_2]$ ($R = SiMe_3, (R,R)\text{-1}; SiMe_2Ph, (R,R)\text{-2}; SiMePh_2, (R,R)\text{-3}; SiPh_3, (R,R)\text{-4}$). Structural studies of the $SiMe_3$ derivative $(R,R)\text{-1}$ show a pseudo-octahedral anion with mutually *cis* chloride ligands. Although NMR studies indicate that the anion of $(R,R)\text{-1}$ is stable in DMSO- d_6 , an equilibrium mixture is observed in C_6D_6 solution with the neutral complex $(R,R)-[Ta(O_2C_{20}H_{10}(SiMe_3)_{2-3,3'})_2Cl]$, $(R,R)\text{-1a}$, and $[H_2NET_2]Cl$. The temperature dependence of the equilibrium has been studied. Addition of $[^nBu_4N]Cl$ to a mixture of $(R,R)\text{-1}/(R,R)\text{-1a}$ in C_6D_6 is shown (1H NMR) to shift the equilibrium toward $(R,R)\text{-1}$. Alkylation of $(R,R)\text{-1}$ with Grignard reagents RMgCl results in formation of the five-coordinate $(R,R)-[Ta(O_2C_{20}H_{10}\{SiMe_3\}_{2-3,3'})_2R']$ ($R' = CH_2SiMe_3, (R,R)\text{-5}; CH_2Ph, (R,R)\text{-6}; c-C_5H_9, (R,R)\text{-7}$).

Introduction

The use of bulky aryloxy ligands for supporting stoichiometric and catalytic chemistry at early transition metal centers continues to be an important area in inorganic/organometallic chemistry.¹ In the case of the group 5 metals niobium and tantalum, the mixed chloro/aryloxy species $[M(OAr)_xCl_{5-x}]$ ($OAr = 2,6$ -disubstituted phenoxides) are important starting materials for exploring the chemistry of these elements. In particular, the stoichiometric and catalytic reactivity of d^0 -alkyl- and hydridoaryloxides^{2,3} has been well developed, particularly involving their use as precursors/catalysts for arene hydrogenation. These developments have led us to attempt the synthesis of chiral analogues of known

niobium and tantalum aryloxy compounds with the goal of carrying out asymmetric transformations. Yamamoto *et al.* have achieved the isolation and resolution of C_2 -symmetric, chiral monodentate aryloxy ligands.⁴ We have also synthesized and studied potentially chiral 2,6-di(1-naphthyl)phenoxide ligands and explored some of their reaction chemistry.^{2m-o} However, low yields and the difficulty of resolution of these materials have hampered this effort.

The readily resolved 2,2'-dihydroxy-1,1'-binaphthyl (BINOL) ligand is one of the most important chiral auxiliaries in chemistry.⁵ The unsubstituted BINOL has been used in a vast number of asymmetric catalytic applications, although in some of these applications the exact nature (molecularity) of the active species is uncertain. To help control solubility and increase the chiral impact and steric size of the ligand, various strategies have been devised to introduce substituents at the 3,3'-positions. These bulkier ligands have also been applied to asymmetric syntheses and have been instrumental in allowing the isolation and characterization of discrete molecular species. In particular, Mikami *et al.* have applied a compound formulated as $[(\text{binaphthoxide})TiCl_2]$ to numerous organic transformations.⁶ Heppert and co-workers have managed to structurally characterize and better understand the molecularity, dynamics, and bonding modes of Ti(IV) derivatives of

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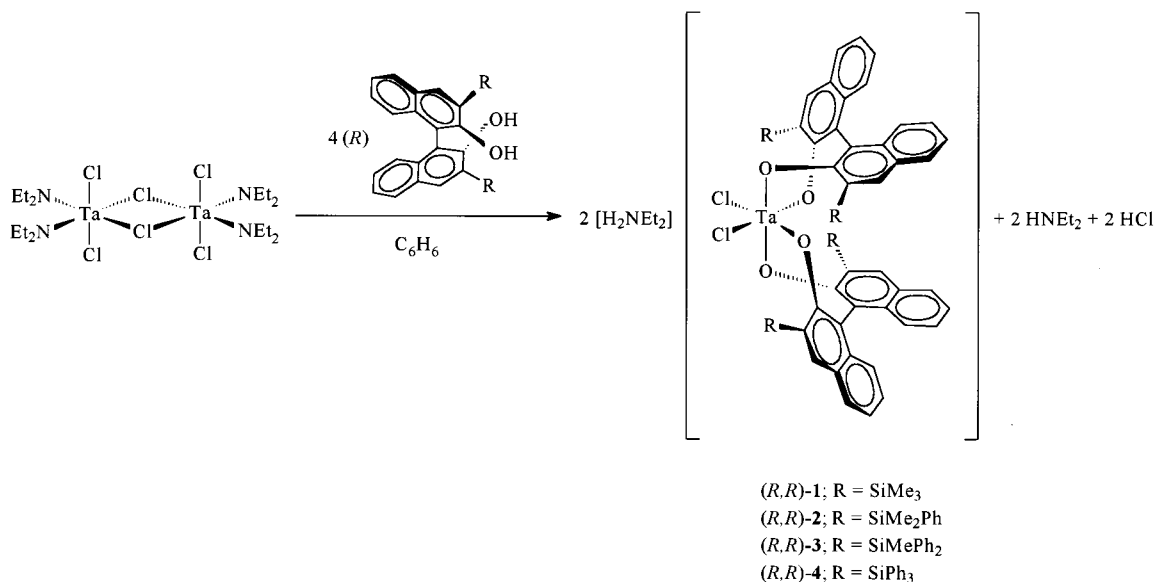
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Scheme 1



substituted binaphthoxide ligands.⁷ Schaverien has shown that binaphthoxide derivatives of Ti and Zr will produce isotactic poly(α -olefins) when activated with MAO.⁸ Heppert has also studied a number of molybdenum and tungsten complexes containing these ligands.⁹ Schrock has reported the application of binaphthoxide ligands containing bulky 3,3'-substituents to give well-defined, asymmetric metathesis catalysts.¹⁰

However, there appears to be little reported on the chemistry of Nb and Ta binaphthoxide complexes, and hence we decided to investigate potential routes to complexes of these metals containing this bis(aryloxy) chiral auxiliary. We have used the synthetic methodology of Snieckus¹¹ to obtain gram quantities of the resolved ligands [H₂O₂C₂₀H₁₀(R)₂-3,3'] (R = SiMe₃, SiMe₂Ph, SiMePh₂, SiPh₃). Preliminary studies of the reaction of simple metal halides with either these parent BINOLs or their dilithio derivatives have proven disappointing. However, the use of dialkylamido precursors has proven to be a convenient approach to introducing the chiral ligands into the metal coordination sphere. In this paper we report on the reactivity of the dimeric compound [(Et₂N)₂Cl₂Ta(μ -Cl)₂TaCl₂(NEt₂)₂] shown by

Wigley *et al.* to contain an edge-shared bis(octahedral) structure with terminal diethylamido groups located *trans* to the bridging chloride ligands.¹²

Results and Discussion

Synthesis and Structural Studies. Reaction of the dimer [(Et₂N)₂Cl₂Ta(μ -Cl)₂TaCl₂(NEt₂)₂] with (*R*)-3,3'-bis(trimethylsilyl)-1,1'-bi-2,2'-naphthol proceeds rapidly in hydrocarbon solvents. However, the reaction is not straightforward. Addition of 1 equiv. of (*R*)-3,3'-bis(trimethylsilyl)-1,1'-bi-2,2'-naphthol per Ta results in a product mixture that did not contain expected mono-(binaphthoxide) products such as [Ta(O₂C₂₀H₁₀{SiMe₃}₂-3,3')Cl₃]. Spectroscopic (¹H NMR in C₆D₆) characterization of the product mixture obtained indicated the presence of unreacted reagent [(Et₂N)₂Cl₂Ta(μ -Cl)₂TaCl₂(NEt₂)₂] and an equilibrium mixture (*vide infra*) of two new tantalum compounds (*R,R*)-**1** and (*R,R*)-**1a**. The reaction of 2 equiv. of (*R*)-3,3'-bis(trimethylsilyl)-2,2'-bi-1,1'-naphthol per Ta results in the clean (NMR) formation of (*R,R*)-**1**/*R,R*)-**1a**. Hence it appears that any mono(binaphthoxide) intermediates that are formed react more rapidly with (*R*)-3,3'-bis(trimethylsilyl)-1,1'-bi-2,2'-naphthol than does [(Et₂N)₂Cl₂Ta(μ -Cl)₂TaCl₂(NEt₂)₂].

Slow cooling of a hot, concentrated benzene solution of the clean product mixture resulted in X-ray quality crystals of a single morphology. Analysis by X-ray diffraction showed them to contain the salt (*R,R*)-[H₂NEt₂][Ta(O₂C₂₀H₁₀{SiMe₃}₂-3,3')Cl₂], (*R,R*)-**1** (Scheme 1). An ORTEP diagram of the anion of (*R,R*)-**1** is shown in Figure 1, and selected bond distances and angles are listed in Table 1. The anion is a six-coordinate *pseudo*-octahedral complex of Ta(V), with two binaphthoxide ligands bound to the metal center in a bidentate fashion. The two chlorine atoms are in a mutually *cis*-arrangement. The average Ta–O bond distance is 1.92 Å, while the average Ta–Cl distance is 2.46 Å. The average acute O–Ta–O bond angle is 92.7°, and the Cl–Ta–Cl angle

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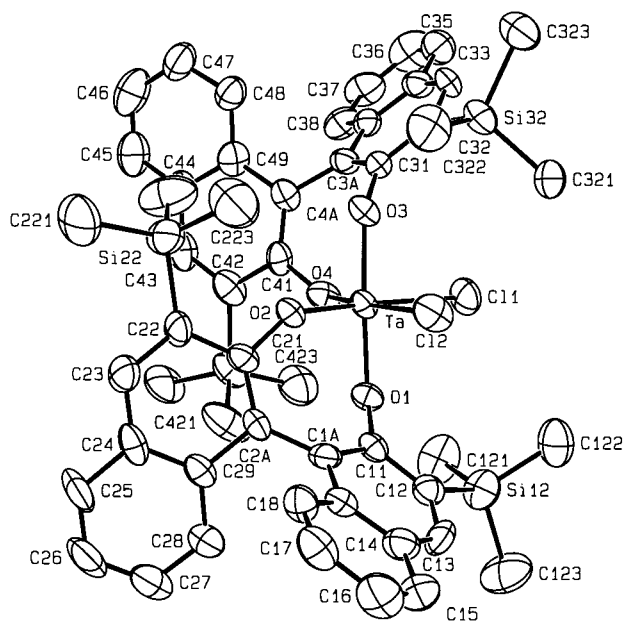


Figure 1. ORTEP diagram for the anion of $[\text{H}_2\text{NET}_2][\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiMe}_3\}_2\text{-}3,3')_2\text{Cl}_2]$, (*R,R*)-**1**. Thermal ellipsoids are drawn at 50% probability.

Table 1. Selected Bond Distances (Å) and Angles (deg) for $[\text{H}_2\text{NET}_2][\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiMe}_3\}_2\text{-}3,3')_2\text{Cl}_2]$, (*R,R*)-**1**· C_6H_6

Ta–O(1)	1.945(4)	Ta–O(2)	1.880(4)
Ta–O(3)	1.945(4)	Ta–O(4)	1.896(4)
Ta–Cl(1)	2.456(2)	Ta–Cl(2)	2.454(2)
O(1)–Ta–O(2)	90.0(2)	O(1)–Ta–O(3)	177.6(2)
O(1)–Ta–O(4)	91.6(2)	O(2)–Ta–O(3)	92.3(2)
O(2)–Ta–O(4)	100.8(2)	O(3)–Ta–O(4)	88.8(2)
O(1)–Ta–Cl(1)	89.2(2)	O(1)–Ta–Cl(2)	89.6(2)
O(2)–Ta–Cl(1)	170.6(2)	O(2)–Ta–Cl(2)	86.0(2)
O(3)–Ta–Cl(1)	88.4(2)	O(3)–Ta–Cl(2)	89.8(2)
O(4)–Ta–Cl(1)	88.6(2)	O(4)–Ta–Cl(2)	173.2(2)
Cl(1)–Ta–Cl(2)	84.65(7)		

is 84.6°. The O(2)–Ta–O(4) angle is significantly larger than the others, likely resulting from the steric repulsion of the two bulky binaphthoxide ligands. The Ta–O bond length in (*R,R*)-**1** is slightly longer than that of the neutral complex (*S*)- $[\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiMe}_3\}_2\text{-}3,3')\text{-}(\text{NMe}_2)_3(\text{HNMe}_2)]$.¹³ This is likely due to the anionic charge of (*R,R*)-**1**, which reduces π -bonding between the binaphthoxide ligands and the metal center, resulting in a longer Ta–O bond. An average bond length of 1.89 Å was found for the Ta–O bond of $[\text{H}_2\text{NMe}_2](\text{S})\text{-}[\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiMe}_3\}_2\text{-}3,3')\text{Cl}_4]$, which also contains an anionic tantalum binaphthoxide complex.¹³ Complex (*R,R*)-**1** is the only structurally characterized bis(binaphthoxide) complex of tantalum. A complex, $\text{H}[\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{12})_3]$, has been reported which was not structurally characterized.¹⁴

Related compounds (*R,R*)-**2**–**4** were prepared from $[(\text{Et}_2\text{N})_2\text{Cl}_2\text{Ta}(\mu\text{-Cl})_2\text{TaCl}_2(\text{NEt}_2)_2]$ and (*R*)-3,3'-dimethylphenylsilyl-1,1'-bi-2,2'-naphthol, (*R*)-3,3'-methylphenylsilyl-1,1'-bi-2,2'-naphthol, and (*R*)-3,3'-triphenylsilyl-1,1'-bi-2,2'-naphthol, respectively, as shown in Scheme 1. Complex **2** exhibits diminished solubility in C_6D_6

relative to (*R,R*)-**1**, and complexes (*R,R*)-**3** and (*R,R*)-**4** are increasingly less soluble.

Solution Studies. The ^1H NMR spectrum of the crystals of (*R,R*)-**1** in $\text{DMSO-}d_6$ exhibits two resonances in the aromatic region at δ 7.98 and 7.53 ppm, which can be assigned to the 4,4'-hydrogens of a coordinated binaphthoxide ligand, and two sharp peaks at δ 0.49 and -0.29 ppm attributable to two distinct sets of trimethylsilyl groups (Table 2). The solid state structure of (*R,R*)-**1** can be used to rationalize the ^1H NMR spectrum in $\text{DMSO-}d_6$. There are two groups of magnetically and chemically inequivalent 4,4'-hydrogen atoms, one group pointing in toward the chiral pocket and one group pointing away. Similarly, two trimethylsilyl groups point into the chiral pocket and two lie away from the metal center. The SiMe_3 resonance at δ 0.49 ppm corresponds to the groups pointing away from the metal, which are slightly deshielded by the magnetic anisotropy of the naphthyl rings. Similarly, the resonance at δ 7.53 ppm is assigned to the 4,4'-hydrogens that point toward the chiral pocket.

The ^{13}C NMR of (*R,R*)-**1** in $\text{DMSO-}d_6$ exhibits 20 distinct resonances for the carbon atoms of the binaphthyl rings. Two peaks at δ 163.0 and 160.4 ppm are assigned to the carbons bound to oxygen, while the upfield features at δ 21.7 and 13.8 ppm are assigned to the carbon atoms bound to silicon. The ^1H and ^{13}C NMR data indicate that the two binaphthoxide ligands are equivalent on the NMR time scale.

The ^1H NMR spectrum of (*R,R*)-**1** in C_6D_6 is more complex than that in $\text{DMSO-}d_6$. There are three distinct resonances for the 4,4'-hydrogens, as well as three peaks for the SiMe_3 groups. This indicates the presence of another binaphthoxide-containing complex in solution. We believe complex (*R,R*)-**1** undergoes an equilibrium between the six-coordinate salt complex that exists in the solid state and a neutral, five-coordinate species $[\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiMe}_3\}_2\text{-}3,3')_2\text{Cl}]$, (*R,R*)-**1a**, as shown in Scheme 2.

Upon addition of $[\text{Bu}_4\text{N}]\text{Cl}$ to an NMR sample of (*R,R*)-**1**/*(R,R)*-**1a** in C_6D_6 , the partially soluble material completely dissolves and the resonances due to neutral (*R,R*)-**1a** at δ 8.19 and 0.66 ppm disappear, while those due to (*R,R*)-**1** at δ 8.22, 7.83, 0.91, and 0.09 ppm remain. Surprisingly, addition of $[\text{Bu}_4\text{N}]\text{Br}$ results in the mixed-halide complex $[\text{H}_2\text{NET}_2][\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\text{-}3,3'\text{-}\{\text{SiMe}_3\}_2)_2\text{ClBr}]$, which exhibits resonances identical to those using $[\text{Bu}_4\text{N}]\text{Cl}$ despite the presence of a less electronegative halide ligand. Although we are unable to provide a definite explanation for this effect, it appears the incoming bromide anion drives the equilibrium to the left as well. Furthermore, complex (*R,R*)-**1a** is expected to exhibit two resonances for both the 4,4'-hydrogens and the trimethylsilyl groups. However, the presence of one feature for each group indicates that (*R,R*)-**1a** is fluxional on the NMR time scale, while conformational rigidity seems to be enforced in the salt (*R,R*)-**1** by the presence of a second chloride ligand.

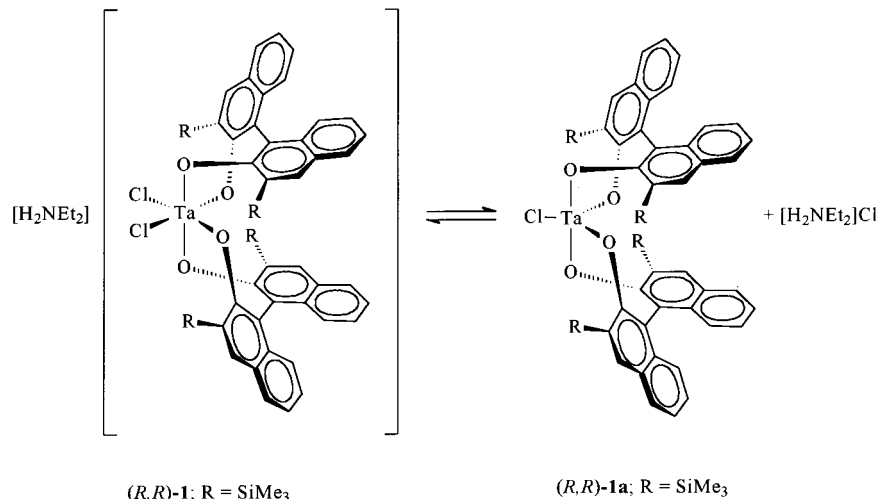
Variable-temperature NMR experiments over the temperature range -90 to $+90$ °C on (*R,R*)-**1** in toluene- d_8 also confirm the existence of the equilibrium process. At very low temperatures (-90 °C), the spectrum lacks distinct features due to the low solubility of **1** in toluene, but at -70 °C, an approximate 1:1 mixture of (*R,R*)-**1**

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Table 2. ^1H NMR Data for Complexes (*R,R*)-1-(*R,R*)-7

species	solvent	δ (4,4'-hydrogens)	δ (alkylsilyl groups)
$[\text{H}_2\text{NET}_2][\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiMe}_3\}_{2-3,3'})_2\text{Cl}_2]$ (<i>R,R</i>)-1	C_6D_6	8.22, 8.19, 7.83	0.91, 0.66, 0.09
	DMSO- d_6	7.98, 7.53	0.49, -0.29
$[\text{H}_2\text{NET}_2][\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiMe}_2\text{Ph}\}_{2-3,3'})_2\text{Cl}_2]$ (<i>R,R</i>)-2	C_6D_6	8.07, 7.98, 7.91, 7.89	0.89, 0.88, 0.87, 0.85, 0.71, -0.15
	DMSO- d_6	7.80, 7.78, 7.73, 7.71	0.90, 0.84, 0.36, -0.53
$[\text{H}_2\text{NET}_2][\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiMePh}_2\}_{2-3,3'})_2\text{Cl}_2]$ (<i>R,R</i>)-3	DMSO- d_6	8.45, 7.70	0.90, 0.42
$[\text{H}_2\text{NET}_2][\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiPh}_3\}_{2-3,3'})_2\text{Cl}_2]$ (<i>R,R</i>)-4	DMSO- d_6	8.75, 7.83	
$[\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiMe}_3\}_{2-3,3'})_2(\text{CH}_2\text{SiMe}_3)]$ (<i>R,R</i>)-5	C_6D_6	8.24, 8.00	0.56, 0.16, -0.18
$[\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiMe}_3\}_{2-3,3'})_2(\text{CH}_2\text{C}_6\text{H}_5)]$ (<i>R,R</i>)-6	C_6D_6	8.02, 7.89	0.37, 0.14
$[\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiMe}_3\}_{2-3,3'})_2(\text{CH}_2\text{C}_5\text{H}_9)]$ (<i>R,R</i>)-7	C_6D_6	8.23, 8.21, 8.03, 8.00	0.53, 0.49, 0.15, 0.14

Scheme 2

and (*R,R*)-1a becomes evident. At -50°C , the resonances become sharp and distinctive, and they increase in intensity across the range between -40 and $+30^\circ\text{C}$ with little change in the relative intensities for (*R,R*)-1 and (*R,R*)-1a. Above $+30^\circ\text{C}$, the peaks at δ 8.10 and 0.60 ppm begin to decrease in intensity, indicating the predominance of the salt (*R,R*)-1, and by $+90^\circ\text{C}$, the resonances of (*R,R*)-1a are very low in intensity. This is likely the result of the increased solubility of $[\text{H}_2\text{NET}_2][\text{Cl}]$ at higher temperatures, which drives the equilibrium to the left.

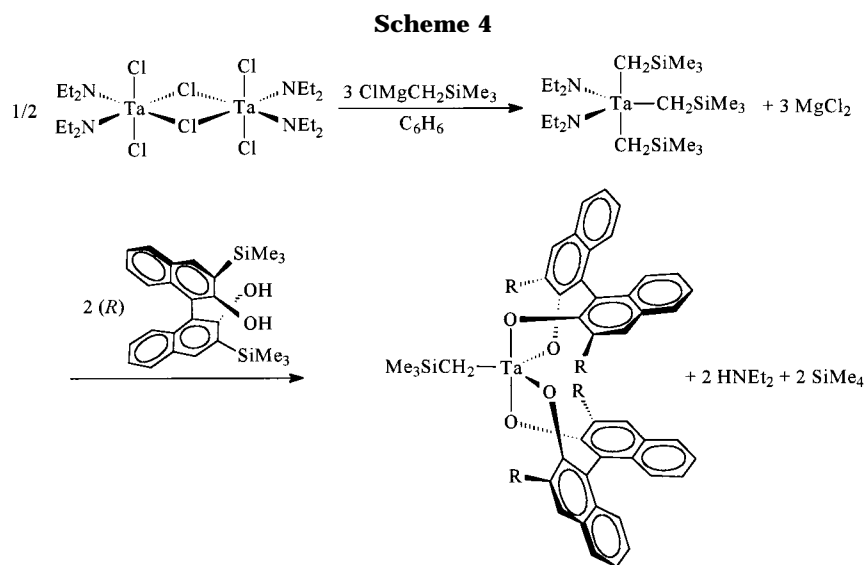
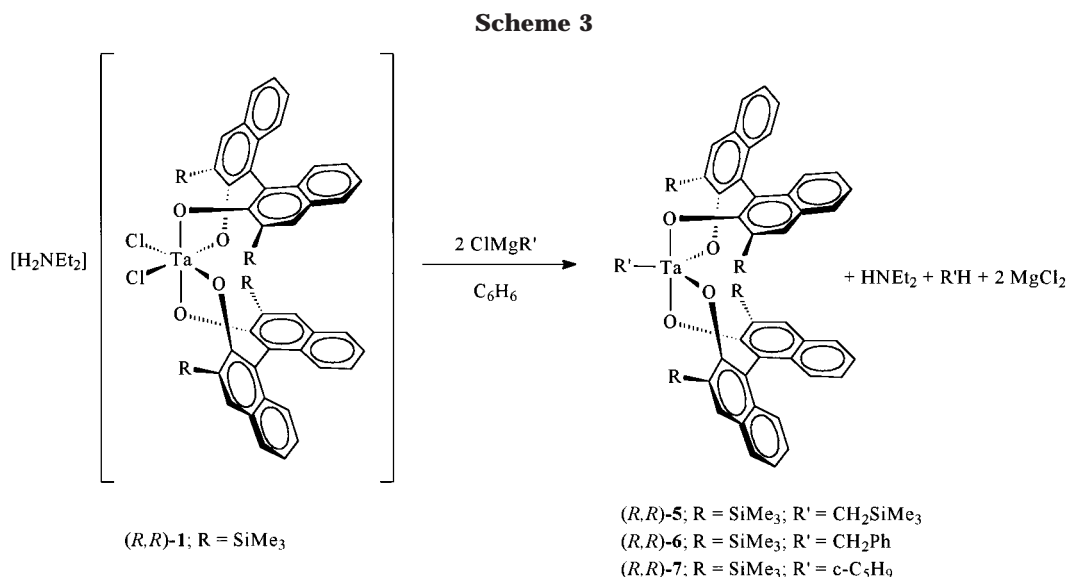
Compound (*R,R*)-2 is a salt with the formula $[\text{H}_2\text{NET}_2][\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{Me}_2\text{PhSi}\}_{2-3,3'})_2\text{Cl}_2]$, which exhibits resonances for the diethylammonium cation identical to (*R,R*)-1. Similar to (*R,R*)-1, the NMR spectrum of (*R,R*)-2 contains two features for the 4,4'-hydrogens of the binaphthoxide ligands, as well as four distinct signals for the magnetically nonequivalent Me_2PhSi groups (Table 2). Compound (*R,R*)-2 also appears to undergo an equilibrium process similar to (*R,R*)-1. The ^1H NMR spectrum in C_6D_6 exhibits three 4,4'-hydrogen resonances and six features for the Me_2PhSi groups (Table 2). The ^1H and ^{13}C NMR spectra of (*R,R*)-3 and (*R,R*)-4 in DMSO- d_6 indicate that these materials are also salts with the formulas $[\text{H}_2\text{NET}_2][\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{MePh}_2\text{Si}\}_{2-3,3'})_2\text{Cl}_2]$ and $[\text{H}_2\text{NET}_2][\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{Ph}_3\text{Si}\}_{2-3,3'})_2\text{Cl}_2]$, respectively. The limited solubility of both (*R,R*)-3 and (*R,R*)-4 in C_6D_6 precluded NMR studies in this solvent.

Alkylation Studies. Reaction of (*R,R*)-1 with 2.2 equiv. of $\text{ClMgCH}_2\text{SiMe}_3$ cleanly produces the neutral complex $[\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiMe}_3\}_{2-3,3'})_2\text{CH}_2\text{SiMe}_3]$, (*R,R*)-5, as shown in Scheme 3. The excess Grignard reagent deprotonates the $[\text{H}_2\text{NET}_2]^+$ cation, resulting in the formation of HNET $_2$ and SiMe $_4$ (which are removed *in*

vacuo) and MgCl_2 . Two resonances at δ 8.24 and 8.00 ppm in the ^1H NMR spectrum of (*R,R*)-5 correspond to the 4,4'-hydrogens, and three peaks in the alkylsilyl region at δ 0.56, 0.16, and -0.18 ppm (intensity ratio 2:2:1) arise from the two nonequivalent trimethylsilyl groups on the binaphthoxide ligands and the CH_2SiMe_3 group, respectively. The diastereotopic hydrogens of the CH_2SiMe_3 group result in an AX pattern, with resonances at δ 2.09 and 1.47 ppm and a coupling constant of 12.3 Hz.

Two additional alkyl species, $[\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiMe}_3\}_{2-3,3'})_2(\text{CH}_2\text{C}_6\text{H}_5)]$, (*R,R*)-6, and $[\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiMe}_3\}_{2-3,3'})_2(\text{c-C}_5\text{H}_9)]$, (*R,R*)-7, were prepared from (*R,R*)-1 and $\text{ClMgCH}_2\text{C}_6\text{H}_5$ or ClMgC_5H_9 , respectively, as shown in Scheme 3. The ^1H NMR of the benzyl derivative (*R,R*)-6 contains two peaks for the 4,4' aromatic hydrogens at δ 8.02 and 7.89 ppm and peaks for the trimethylsilyl groups at δ 0.37 and 0.14 ppm (Table 2). The diastereotopic CH_2 hydrogens again result in an AX pattern, with doublets at 3.57 and 3.19 ppm and a coupling constant of 14.7 Hz.

The ^1H NMR spectrum of (*R,R*)-7 contains four resonances for the 4,4' aromatic protons and four features for the trimethylsilyl groups (Table 2). Incorporation of the cyclopentyl ligand removes C_2 symmetry from the molecule, which is present in both (*R,R*)-5 and (*R,R*)-6, resulting in all four $-\text{SiMe}_3$ groups and all four 4,4'-hydrogens being nonequivalent. Nine distinct features are observed for the protons attached to the cyclopentyl ring. A signal for the proton bound to the α -carbon appears at δ 2.90 ppm and appears as a multiplet, close to the predicted triplet of triplets. Additionally, four SiMe $_3$ peaks are observed in the ^{13}C NMR of (*R,R*)-7, further indicating the absence of C_2 symmetry in this complex.



The preparation of (R,R)-5 was attempted by an alternate strategy, as illustrated in Scheme 4. The dimer [(Et₂N)₂Cl₂Ta(μ-Cl)₂TaCl₂(NEt₂)₂] was reacted with 3 equiv. of ClMgCH₂SiMe₃ in an attempt to prepare the mixed amide alkyl complex [Ta(NEt₂)₂(CH₂SiMe₃)₃]. The ¹H NMR of the product suggested the desired complex was present, but that it was one component of a mixture of species. Treatment of the crude reaction mixture with 2 equiv. of (R)-3,3'-bis(trimethylsilyl)-1,1'-bi-2,2'-naphthol also yielded (R,R)-5, but again as a component of a mixture of products.

Attempts to isolate (R,R)-5 in pure form from the reaction mixture by successive recrystallization were unsuccessful. However, colorless crystals were isolated which were determined to be [H₂NEt₂]₂[Mg(O₂C₂₀H₁₀{SiMe₃}₂-3,3')Cl₂], (R,R)-8. An ORTEP plot of the anion is shown in Figure 2, and selected bond distances and angles are listed in Table 3. Binaphthoxide complexes of magnesium are rare, and only one series of Mg-binaphthoxide complexes has been reported, (S)-Li₂[Mg(O₂C₂₀H₁₂)R₂] (R = CH₃, C₂H₅, *n*-C₄H₉, *t*-C₄H₉, CH₂=CHCH₂, C₆H₅, CH₂=CH, or Me₃SiCC).¹⁵ To our

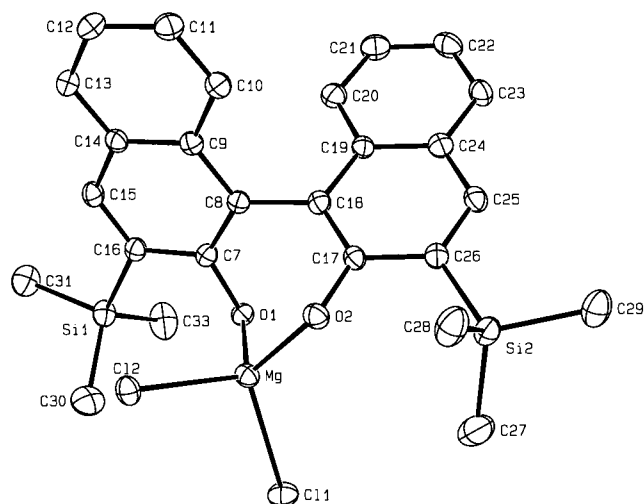


Figure 2. ORTEP diagram for the anion of [H₂NEt₂]₂[Mg(O₂C₂₀H₁₀{SiMe₃}₂-3,3')Cl₂], (R,R)-8. Thermal ellipsoids are drawn at 50% probability.

knowledge, complex (R,R)-8 represents the only structurally characterized example of a material of this type. The environment about the magnesium atom ap-

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Table 3. Selected Bond Distances (Å) and Angles (deg) for $[\text{H}_2\text{NET}_2]_2[\text{Mg}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiMe}_3\}_2\text{-3,3'})\text{Cl}_2]\cdot\text{C}_6\text{H}_6$, (*R,R*)-8**· C_6H_6**

Mg–O(1)	1.979(2)	Mg–O(2)	1.912(2)
Mg–Cl(1)	2.348(1)	Mg–Cl(2)	2.3906(9)
O(1)–Mg–O(2)	99.44(7)	O(1)–Mg–Cl(1)	109.15(5)
O(1)–Mg–Cl(2)	116.06(6)	O(2)–Mg–Cl(1)	118.29(6)
O(2)–Mg–Cl(2)	108.10(6)	Cl(1)–Mg–Cl(2)	106.21(4)

proaches tetrahedral, and the average Mg–O and Mg–Cl bond lengths are 1.95 and 2.37 Å, respectively.

Experimental Section

General Remarks. All manipulations were carried out using standard syringe, Schlenk line, and glovebox techniques.¹⁶ Benzene, toluene, ether, THF, and hexane were dried over sodium benzophenone ketyl and were freshly distilled before use. Pentane was dried over sodium ribbon. The reagents $[(\text{Et}_2\text{N})_2\text{Cl}_2\text{Ta}(\mu\text{-Cl})_2\text{TaCl}_2(\text{NET}_2)_2]$,⁴ (*R*)-3,3'-trimethylsilyl-1,1'-bi-2,2'-naphthol, (*R*)-3,3'-dimethylphenylsilyl-1,1'-bi-2,2'-naphthol, (*R*)-3,3'-methylphenylsilyl-1,1'-bi-2,2'-naphthol, and (*R*)-3,3'-triphenylsilyl-1,1'-bi-2,2'-naphthol^{11,17} were prepared according to literature procedures or slight variations thereof. Trimethylsilylmethylmagnesium chloride (1.0 M solution in Et_2O), benzylmagnesium chloride (2.0 M solution in THF), and cyclopentylmagnesium chloride (2.0 M solution in Et_2O) were purchased from Aldrich and used as received. ¹H NMR spectra were recorded on a Varian INOVA-300 NMR spectrometer or a Bruker DRX-500 NMR spectrometer and were referenced to residual protio solvent. ¹³C NMR spectra were recorded on a Bruker DRX-500 NMR spectrometer at 125.7 MHz and were internally referenced to the solvent signal. Elemental analyses were carried out in house at Purdue University. The low percentage of carbon found in some of these analyses (typically by 2–3%) is due to the formation of carbide species, which is typical for early transition metal organometallic compounds.

Synthesis of $[\text{H}_2\text{NET}_2][\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiMe}_3\}_2\text{-3,3'})_2\text{Cl}_2]$, (*R,R*)-1**.** The complex $[(\text{Et}_2\text{N})_2\text{Cl}_2\text{Ta}(\mu\text{-Cl})_2\text{TaCl}_2(\text{NET}_2)_2]$ (1.87 g, 2.17 mmol) was dissolved in 25 mL of benzene. To this was added (*R*)-3,3'-trimethylsilyl-1,1'-bi-2,2'-naphthol (3.92 g, 9.10 mmol) in 15 mL of benzene dropwise over 10 min. The resulting solution was stirred for 18 h, resulting in the formation of an orange-red precipitate. The volume of the solution was reduced to approximately 10 mL *in vacuo* and was then heated to reflux and allowed to cool slowly. After 3 h, orange crystals had formed. These were isolated by filtration, washed with 4 × 10 mL of pentane, and dried *in vacuo* to yield 3.87 g (75%) of (*R,R*)-**1**. ¹H NMR (C_6D_6 , 25 °C, 300 MHz): δ 8.21 (s), 8.19 (s), 7.82 (s) (4,4'-aromatic H); 7.68 (d, *J* = 8.1 Hz), 7.60 (d, *J* = 3.9 Hz), 7.57 (d, *J* = 3.9 Hz) (7,7'-aromatic H); 7.11–6.62 (m, aromatics), 1.51 (pseudosept, $\text{H}_2\text{NCH}_2\text{CH}_3$); 0.91 (s, $\text{Si}(\text{CH}_3)_3$); 0.88 (t, *J* = 7.3 Hz, $\text{H}_2\text{NCH}_2\text{CH}_3$); 0.65 (s, $\text{Si}(\text{CH}_3)_3$); 0.09 (s, $\text{Si}(\text{CH}_3)_3$). ¹H NMR (DMSO-*d*₆, 25 °C, 500 MHz): δ 8.50 (br s, 2H $\text{H}_2\text{NCH}_2\text{CH}_3$); 7.98 (s, 2H); 7.80 (d, 2H, *J* = 8.1 Hz); 7.74 (d, 2H, *J* = 8.1 Hz); 7.53 (s, 2H); 7.35 (s, 2H); 7.13 (t, 2H, *J* = 7.5 Hz); 7.10 (t, 2H, *J* = 7.5 Hz); 6.95 (t, 2H, *J* = 7.2 Hz); 6.88 (t, 2H, *J* = 7.2 Hz); 6.53 (d, 2H, *J* = 8.4 Hz); 6.29 (d, 2H, *J* = 8.4 Hz); 2.89 (pseudosept, 4H, $\text{H}_2\text{N}(\text{CH}_2\text{CH}_3)_2$); 1.16 (t, 6H, *J* = 7.2 Hz); 0.49 (s, 18H, $\text{Si}(\text{CH}_3)_3$); –0.29 (s, 18H, $\text{Si}(\text{CH}_3)_3$). ¹³C NMR (DMSO-*d*₆, 25 °C, 125.7 MHz): δ 163.0, 160.4, 136.2, 135.6, 134.2, 131.2, 130.5, 129.2, 128.6, 127.5, 127.3, 126.7, 126.1, 125.0, 122.6,

122.0, 117.8, 116.0, 41.2, 21.7, 13.8, 10.9, 0.7, –0.7. Anal. Calcd for $\text{C}_{66}\text{H}_{74}\text{Cl}_2\text{NO}_4\text{Si}_4\text{Ta}$ [**1**· C_6H_6]: C, 59.03; H, 5.91; N, 1.11; Cl, 5.62. Found: C, 58.79; H, 5.97; N, 1.17; Cl, 5.84.

Synthesis of $[\text{H}_2\text{NET}_2][\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiMe}_2\text{Ph}\}_2\text{-3,3'})_2\text{Cl}_2]$, (*R,R*)-2**.** In a manner analogous to the synthesis of (*R,R*)-**1**, $[(\text{Et}_2\text{N})_2\text{Cl}_2\text{Ta}(\mu\text{-Cl})_2\text{TaCl}_2(\text{NET}_2)_2]$ (0.561 g, 0.649 mmol) was reacted with (*R*)-3,3'-(dimethylphenylsilyl)-1,1'-bi-2,2'-naphthol (1.52 g, 2.73 mmol) to yield 0.74 g (79%) of (*R,R*)-**2**. ¹H NMR (C_6D_6 , 25 °C, 300 MHz): δ 8.42 (s), 8.31 (s), 7.98 (s), 7.92 (s), 7.84 (s), 7.68 (m), 7.53 (s), 7.34–6.66 (m, aromatics); 2.12 (s) 1.72 (br s), 1.44(s), 1.29 (s, $\text{Si}(\text{CH}_3)_3$), 0.89 (s, $\text{Si}(\text{CH}_3)_3$), 0.88 (s, $\text{Si}(\text{CH}_3)_3$), 0.87 (s, $\text{Si}(\text{CH}_3)_3$), 0.85(s, $\text{Si}(\text{CH}_3)_3$), 0.52 (br s), –0.15 (s, $\text{Si}(\text{CH}_3)_3$). ¹H NMR (DMSO-*d*₆, 25 °C, 500 MHz): 8.52 (br, 2 H, H_2NET_2); 7.80 (s, 2 H); 7.78 (s, 2 H); 7.72 (br, 4H); 7.51–6.85 (m, 28 H, aromatics); 6.71 (d, 2 H *J* = 8.5 Hz); 6.25 (d, 2 H, *J* = 8.5 Hz); 2.89 (pseudosept, 4 H, $\text{H}_2\text{N}(\text{CH}_2\text{CH}_3)_2$); 1.17 (t, 6 H, *J* = 7.0 Hz, $\text{H}_2\text{N}(\text{CH}_2\text{CH}_3)_2$); 0.92 (s, $\text{SiPh}(\text{CH}_3)_2$); 0.85 (s, $\text{SiPh}(\text{CH}_3)_2$); 0.37 (s, $\text{SiPh}(\text{CH}_3)_2$); –0.52 (s, $\text{SiPh}(\text{CH}_3)_2$). ¹³C NMR (DMSO-*d*₆, 25 °C, 125.7 MHz): δ 163.0, 160.2, 140.1, 139.8, 136.9, 135.5, 135.2, 134.7, 134.5, 133.2, 130.1, 129.3, 128.2, 128.0, 127.9, 127.7, 127.5, 127.2, 126.5, 126.0, 125.4, 125.0, 123.0, 122.4, 117.2, 116.7, 41.2, 11.0, –1.1, –1.5, –1.6, –3.5. Anal. Calcd for $\text{C}_{76}\text{H}_{76}\text{Cl}_2\text{NO}_4\text{Si}_4\text{Ta}$: C, 63.76; H, 5.35. Found: C, 62.31; H, 5.75.

Synthesis of $[\text{H}_2\text{NET}_2][\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiMePh}_2\}_2\text{-3,3'})_2\text{Cl}_2]$, (*R,R*)-3**.** In a manner analogous to the synthesis of (*R,R*)-**1**, $[(\text{Et}_2\text{N})_2\text{Cl}_2\text{Ta}(\mu\text{-Cl})_2\text{TaCl}_2(\text{NET}_2)_2]$ (0.208 g, 0.242 mmol) was reacted with (*R*)-3,3'-(methylphenylsilyl)-1,1'-bi-2,2'-naphthol (0.690 g, 1.01 mmol) to yield 0.65 g (79%) of (*R,R*)-**3**. ¹H NMR (DMSO-*d*₆, 25 °C, 500 MHz): 8.65 (br, H_2NET_2); 8.46 (s); 7.70–6.64 (m, aromatics); 2.88 (pseudosept, $\text{H}_2\text{N}(\text{CH}_2\text{CH}_3)_2$); 1.17 (t, *J* = 7.2 Hz, $\text{H}_2\text{N}(\text{CH}_2\text{CH}_3)_2$); 0.90 (s, $\text{SiPh}_2(\text{CH}_3)$); 0.42 (s, $\text{SiPh}_2(\text{CH}_3)$). ¹³C NMR (DMSO-*d*₆, 25 °C, 125.7 MHz): δ 163.4, 158.2, 138.8, 138.6, 136.9, 136.8, 135.3, 135.2, 135.2, 135.0, 134.9, 134.8, 134.7, 134.4, 126.1, 129.0, 128.9, 128.3, 127.9, 127.7, 127.6, 127.5, 127.3, 127.1, 126.7, 125.6, 123.7, 122.4, 112.2, 39.8, 11.0, –2.1, –2.4, –2.8, –3.2. Anal. Calcd for $\text{C}_{96}\text{H}_{84}\text{Cl}_2\text{NO}_4\text{Si}_4\text{Ta}$: C, 68.64; H, 5.04. Found: C, 66.59; H, 5.64.

Synthesis of $[\text{H}_2\text{NET}_2][\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiPh}_3\}_2\text{-3,3'})_2\text{Cl}_2]$, (*R,R*)-4**.** In a manner analogous to the synthesis of (*R,R*)-**1**, $[(\text{Et}_2\text{N})_2\text{Cl}_2\text{Ta}(\mu\text{-Cl})_2\text{TaCl}_2(\text{NET}_2)_2]$ (0.200 g, 0.231 mmol) was reacted with (*R*)-3,3'-(triphenylsilyl)-1,1'-bi-2,2'-naphthol (0.778 g, 0.969 mmol) to yield 0.56 g (73%) of (*R,R*)-**4**. ¹H NMR (DMSO-*d*₆, 25 °C, 300 MHz): δ 8.75 (s); 8.70 (br s); 7.83–7.52 (m, aromatics); 7.42–7.03 (m, aromatics); 2.88 (pseudosept, $\text{H}_2\text{N}(\text{CH}_2\text{CH}_3)_2$); 0.86 (t, *J* = 7.2 Hz, $\text{H}_2\text{N}(\text{CH}_2\text{CH}_3)_2$).

Synthesis of $[\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiMe}_3\}_2\text{-3,3'})_2(\text{CH}_2\text{SiMe}_3)]$, (*R,R*)-5**.** Compound (*R,R*)-**1** (0.552 g, 0.466 mmol) was suspended in 10 mL of benzene. A 1.0 M ethereal solution of $\text{ClMgCH}_2\text{SiMe}_3$ (1.1 mL) was added via syringe. All materials dissolved, and the reaction mixture changed from orange to yellow over a period of 2 h with stirring. The solution was filtered through Celite, and the solvent was removed *in vacuo* to yield 0.43 g (83%) of (*R,R*)-**5** as a yellow powder. ¹H NMR (C_6D_6 , 25 °C, 300 MHz): 8.24 (s, 2 H); 8.00 (s, 2 H); 7.71 (d, 2 H *J* = 8.1 Hz); 7.63 (d, 2 H, *J* = 8.1 Hz); 7.19–6.80 (m, 12 H, aromatics); 2.09 (d, 1 H, *J* = 12.3 Hz, CH_2SiMe_3); 1.47 (d, 1 H, *J* = 12.3 Hz, CH_2SiMe_3); 0.56 (s, 18 H, BINOL- SiMe_3); 0.16 (s, 18 H, BINOL- SiMe_3); –0.18 (s, 9 H, $\text{CH}_2\text{Si}(\text{CH}_3)_3$). ¹³C NMR (C_6D_6 , 25 °C, 125.7 MHz): 160.9, 160.5, 137.8, 137.6, 136.5, 136.0, 131.6, 131.4, 131.0, 130.3, 128.9, 127.7, 127.6, 127.5, 127.3, 124.9, 124.6, 119.1, 117.4, 71.8, 4.1, 1.7, –0.1. Anal. Calcd for $\text{C}_{56}\text{H}_{67}\text{O}_4\text{Si}_5\text{Ta}$: C, 59.76; H, 6.00. Found: C, 57.80; H, 6.30.

Synthesis of $[\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiMe}_3\}_2\text{-3,3'})_2(\text{CH}_2\text{C}_6\text{H}_5)]$, (*R,R*)-6**.** To a suspension of (*R,R*)-**1** (0.310 g, 0.262 mmol) in benzene was added 0.6 mL of $\text{ClMgCH}_2\text{C}_6\text{H}_5$ (2.0 M in THF). After stirring for 2 h, the reaction mixture had become yellow. The solution was filtered through Celite, and the solvent was removed *in vacuo* to yield 0.20 g (69%) of (*R,R*)-**6** as a dark

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yellow solid. ^1H NMR (C_6D_6 , 25 °C, 300 MHz): δ 8.02 (s, 2 H); 7.89 (s, 2H); 7.63 (d, 4 H, $J = 8.1$ Hz); 7.19–6.36 (m, 17 H, aromatics); 3.57 (d, 1 H, $J = 14.7$, $\text{CH}_2\text{C}_6\text{H}_5$); 3.19 (d, 1 H, $J = 14.7$, $\text{CH}_2\text{C}_6\text{H}_5$); 0.37 (s, 18 H, $\text{Si}(\text{CH}_3)_3$); 0.14 (s, 18 H, $\text{Si}(\text{CH}_3)_3$). ^{13}C NMR (C_6D_6 , 25 °C, 125.7 MHz): δ 160.6, 159.8, 140.3, 139.5, 137.3, 137.1, 131.3, 129.5, 129.0, 128.8, 128.7, 127.8, 127.5, 127.1, 127.0, 126.8, 126.6, 124.7, 124.1, 119.0, 116.2, 79.3, 67.8, 33.5, 0.9, –0.7. Anal. Calcd for $\text{C}_{59}\text{H}_{63}\text{O}_4\text{Si}_4\text{Ta}$: C, 62.74; H, 5.62. Found: C, 59.32; H, 6.10.

Synthesis of $[\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiMe}_3\}_2\text{3,3'})_2(\text{C}_5\text{H}_9)]$, (*R,R*)-7. To a suspension of (*R,R*)-1 in 10 mL of benzene was added 0.4 mL of ClMgC_5H_9 (2.0 M in Et_2O). The reaction mixture became yellow after 2 h of stirring. The solution was filtered through Celite, and the solvent was removed *in vacuo* to yield 0.32 g (80%) of (*R,R*)-7 as a yellow-brown solid. ^1H NMR (C_6D_6 , 25 °C, 300 MHz): δ 8.23 (s, 1 H); 8.21 (s, 1 H); 8.03 (s, 1 H); 8.00 (s, 1 H); 7.73–7.61 (m, 4 H, aromatics); 7.15–7.00 (m, 8 H, aromatics); 6.86–6.76 (m, 4 H, aromatics); 2.89 (m, 1 H, H-C_α); 2.30 (m, 1 H); 2.02 (m, 1 H); 1.70 (m, 1 H); 1.52 (m, 1 H); 1.41 (m, 1 H); 0.92 (m, 1 H); 0.73 (m, 1 H); 0.29 (m, 1 H); 0.53 (s, $\text{Si}(\text{CH}_3)_3$); 0.47 (s, $\text{Si}(\text{CH}_3)_3$); 0.16 (s, $\text{Si}(\text{CH}_3)_3$); 0.15 (s, $\text{Si}(\text{CH}_3)_3$). ^{13}C NMR (C_6D_6 , 25 °C, 125.7 MHz): δ 160.2, 159.9, 138.6, 137.4, 136.9, 136.8, 135.8, 135.6, 130.7, 130.3, 129.9, 129.2, 128.9, 128.5, 128.8, 127.4, 127.2, 127.1, 126.8, 124.9, 124.4, 124.2, 119.0, 117.0, 33.9, 32.9, 28.4, 27.7, 1.4, 1.3, –0.5, –0.9. Anal. Calcd for $\text{C}_{57}\text{H}_{65}\text{O}_4\text{Si}_4\text{Ta}$: C, 61.82; H, 5.92. Found: C, 59.10; H, 5.86.

Alternate Synthesis of $[\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiPh}_3\}_2\text{3,3'})_2(\text{CH}_2\text{-SiMe}_3)]$, (*R,R*)-5. A flask was charged with $[\text{Ta}(\text{NET}_2)_2\text{Cl}_3]_2$ (1.32 g, 1.53 mmol). The solid was dissolved in 15 mL of benzene and 10.5 mL of $\text{ClMgCH}_2\text{SiMe}_3$ (1.0 M in Et_2O) was added dropwise at 0 °C. The reaction mixture was stirred at room temperature for 18 h. The solvent was removed *in vacuo* to yield a thick red-brown oil. This was redissolved in 20 mL of benzene, and (*R*)-3,3'-trimethylsilyl-1,1'-bi-2,2'-naphthol (2.76 g, 6.41 mmol) in 10 mL of benzene was added dropwise. The solution was stirred for 12 h, filtered through Celite, and dried *in vacuo*. The product was recrystallized from hot benzene (10 mL) to yield a yellow powder. Further recrystallization from benzene yielded colorless blocklike crystals, which were determined to be $[\text{H}_2\text{NET}_2]_2[\text{Mg}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiMe}_3\}_2\text{3,3'})\text{Cl}_2]$, (*R*)-8. ^1H NMR (C_6D_6 , 300 MHz): δ 8.19 (s), 7.74 (d, $J = 7.8$ Hz); 7.11–6.82 (m, aromatics); 1.87 (pseudosept, $\text{H}_2\text{N}(\text{CH}_2\text{CH}_3)_2$); 0.89 (t, $J = 6.3$ Hz, $\text{H}_2\text{N}(\text{CH}_2\text{CH}_3)_2$), 0.74 (s, $\text{Si}(\text{CH}_3)_3$).

X-ray Data Collection and Reduction. Crystal data and data collection parameters are contained in Table 4. A suitable crystal was mounted on a glass fiber in a random orientation under a cold stream of dry nitrogen. Preliminary examination and final data collection were performed with Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) on a Nonius KappaCCD. Lorentz and polarization corrections were applied to the data.¹⁸ An empiri-

Table 4. Crystallographic Data for $[\text{H}_2\text{NET}_2][\text{Ta}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiMe}_3\}_2\text{3,3'})_2\text{Cl}_2]$, (*R,R*)-1, and $[\text{H}_2\text{NET}_2]_2[\text{Mg}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiMe}_3\}_2\text{3,3'})\text{Cl}_2]$, (*R*)-8

	(<i>R,R</i>)-1·C ₆ H ₆	(<i>R</i>)-8·C ₆ H ₆
formula	C ₆₆ H ₇₄ Cl ₂ NO ₄ Si ₄ Ta	C ₄₀ H ₅₈ Cl ₂ MgN ₂ O ₂ Si ₂
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (#19)	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (#19)
<i>a</i> , Å	15.8407(2)	11.5471(2)
<i>b</i> , Å	16.1199(2)	14.8484(3)
<i>c</i> , Å	31.0956(6)	24.8848(6)
α , deg	90	90
β , deg	90	90
γ , deg	90	90
<i>V</i> , Å ³	7940.3(4)	4266.6(3)
<i>Z</i>	4	4
ρ_{calc} , g cm ⁻³	1.055	1.168
temperature, K	220	150
radiation	Mo $K\alpha$ (0.71073 Å)	Mo $K\alpha$ (0.71073 Å)
(wavelength)		
<i>R</i>	0.048	0.045
<i>R</i> _w	0.095	0.085

cal absorption correction using SCALEPACK was applied.¹⁹ Intensities of equivalent reflections were averaged. The structure was solved using the structure solution program PATTY in DIRDIF92.²⁰ The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined in full-matrix least-squares where the function minimized was $\sum w(|F_o|^2 - |F_c|^2)^2$ and the weight *w* is defined as $w = 1/[\sigma^2(F_o^2) + (0.0585P)^2 + 1.4064P]$, where $P = (F_o^2 + 2F_c^2)/3$. Scattering factors were taken from the International Tables for Crystallography.²¹ Refinement was performed on a AlphaServer 2100 using SHELX-97.²² Crystallographic drawings were done using the program ORTEP.²³

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Supporting Information Available: X-ray crystallographic files in CIF format for (*R,R*)-1 and (*R,R*)-8, and NMR spectra for complexes 2–7 are available. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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