Synthesis of the Tantalum Hydride Complex (*R,R*)-[Ta($O_2C_{20}H_{10}${$SiMe_3$}$_2$-3,3′)$_2$(H)] and Reactivity with Aldehydes, Ketones, Acetylenes, and Related Substrates: A Reagent for the Asymmetric Hydrogenation of Prochiral Carbonyl Species†

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The tantalum phenyl complex (*R,R*)-[Ta($O_2C_{20}H_{10}${$SiMe_3$}$_2$-3,3′)$_2$(Ph)], (*R,R*)-**1**, has been prepared from [H_2NEt_2][Ta($O_2C_{20}H_{10}${$SiMe_3$}$_2$-3,3′)$_2Cl_2$] and has been employed for the synthesis of the hydride species (*R,R*)-[Ta($O_2C_{20}H_{10}${$SiMe_3$}$_2$-3,3′)$_2$(H)], (*R,R*)-**2**, by reaction with diisobutylaluminum hydride (DIBAL-H). The reaction proceeds cleanly and in high yield. Compound (*R,R*)-**2** undergoes clean reactions with acetophenone and benzaldehyde-*d* to give alkoxide complexes that are chiral at the α-carbon. The progress of these reactions was monitored by ^{13}C NMR spectroscopy. An X-ray crystal structure of one of the products (*R,R,R*)/(*R,R,S*)-[Ta($O_2C_{20}H_{10}${$SiMe_3$}$_2$-3,3′)$_2$(OCH{CH_3}{Ph})(O=C{CH_3}{Ph})] was obtained, and the catalytic conversion of benzaldehyde-*d* to benzyl alcohol-*d* was carried out using (*R,R*)-**2**. The hydride complex also reacts with acetylenes to give vinyl metal complexes, with 2,6-dimethylphenyl isocyanide to give an iminoformyl complex, and with allene to yield a labile η^3-π-allyl species.

Introduction

Mono- and dihydride complexes of the heavy group 5 metals niobium and tantalum with ancilliary aryloxide ligation have been shown to function as catalysts for the hydrogenation of unsaturated hydrocarbons.[1–5] Previous work has focused on hydrogenation reactions using species containing achiral aryl ligands, although (*S*)-[Ta($O_2C_{20}H_{10}$-3,3′-{$SiMe_3$}$_2$)(H)(Cl)$_2$(PMe_3)$_2$], which contains a resolved chiral binaphthoxide ligand, has been recently prepared and has the potential to function as an asymmetric hydrogenation catalyst.[6] Although the binaphthoxide ligand is an important chiral auxiliary in complexes of titanium, substantially fewer examples of related heavy group 5 complexes have been reported.[7–11] We have prepared and characterized the salt complex (*R,R*)-[H_2NEt_2][Ta($O_2C_{20}H_{10}${$SiMe_3$}$_2$-3,3′)$_2Cl_2$], which serves as a precursor for various organometallic species of the formula (*R,R*)-[Ta($O_2C_{20}H_{10}${$SiMe_3$}$_2$-3,3′)$_2$(R)] (R = CH_2SiMe_3, CH_2Ph, or *c*-C_5H_9).[12] We now wish to report the use of (*R,R*)-[H_2NEt_2][Ta($O_2C_{20}H_{10}${$SiMe_3$}$_2$-3,3′)$_2Cl_2$] for the preparation of a hydride complex that contains two resolved binaphthoxide ligands and serves as a hydrogenation agent for aldehydes, ketones, and acetylenes.

Results and Discussion

The phenyl complex (*R,R*)-[Ta($O_2C_{20}H_{10}${$SiMe_3$}$_2$-3,3′)$_2$(Ph)], (*R,R*)-**1**, was prepared by the reaction of PhMgCl with (*R,R*)-[H_2NEt_2][Ta($O_2C_{20}H_{10}${$SiMe_3$}$_2$-3,3′)$_2Cl_2$] via the method used for the preparation of the alkyl complexes (*R,R*)-[Ta($O_2C_{20}H_{10}${$SiMe_3$}$_2$-3,3′)$_2$(R)] (R = CH_2SiMe_3, CH_2Ph, or *c*-C_5H_9), as shown in Scheme 1.[12] The identity of (*R,R*)-**1** was confirmed by NMR spectroscopy which indicates the presence of one phenyl group attached to the tantalum metal center. Complex (*R,R*)-**1** was subsequently converted to the hydride species (*R,R*)-[Ta($O_2C_{20}H_{10}${$SiMe_3$}$_2$-3,3′)$_2$(H)], (*R,R*)-**2**, by reaction with diisobutylaluminum hydride (DIBAL-H) as shown in Scheme 1. Other methods for the

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† Dedicated to the memory of Professor Ian P. Rothwell.

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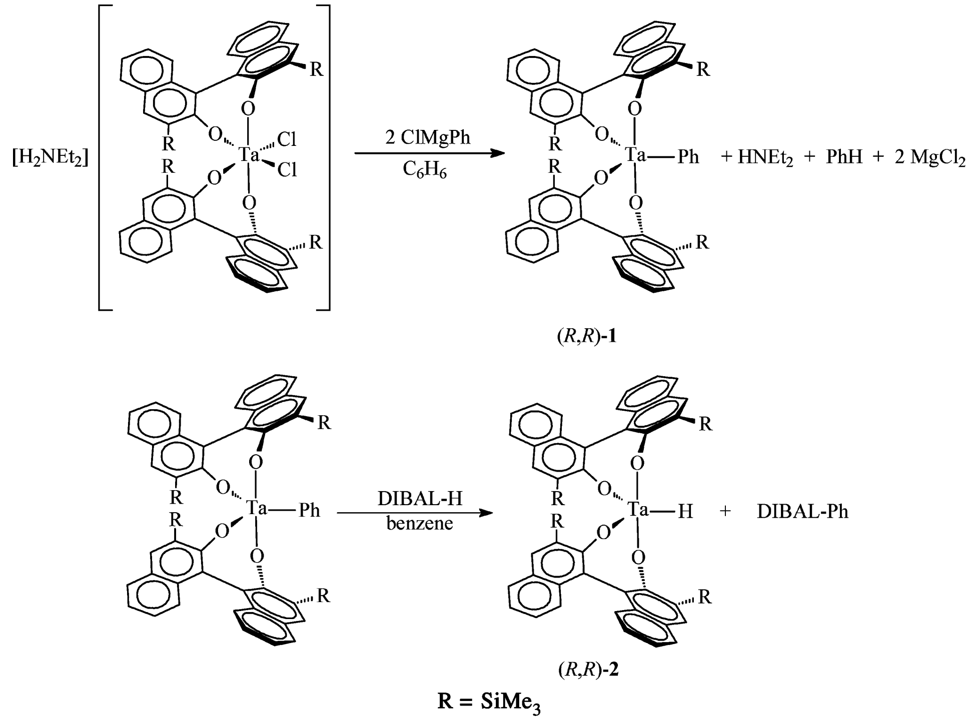
Scheme 1



conversion of alkyl species to hydride species previously employed in our research group, including reaction of the alkyl with Bu_3SnH or pressurization to 1200 psi with hydrogen gas,[4,6] were unsuccessful for the conversion of (*R*,*R*)-**1** to (*R*,*R*)-**2**. Furthermore, although the phenyl derivative (*R*,*R*)-**1** could be converted to (*R*,*R*)-**2**, the other alkyl species (*R*,*R*)-$[Ta(O_2C_{20}H_{10}\{SiMe_3\}_2\text{-}3,3')_2(R)]$ (R = CH_2SiMe_3, CH_2Ph, or *c*-C_5H_9) did not yield the hydride under identical reaction conditions. The fact that only (*R*,*R*)-**1** can be used for the preparation (*R*,*R*)-**2** is likely due to the increased lability of the phenyl ligand versus the alkyl ligands in these tantalum complexes, which was demonstrated for the elimination of RH from $(^tBu_3SiNH)_2RTa{=}NSi^tBu_3$ complexes.[13]

Complex (*R*,*R*)-**2** was identified as a five-coordinate tantalum(V) monohydride complex by ^1H NMR spectroscopy and elemental analysis. The singlet resonance for the hydride proton appears very far downfield at δ 21.5 ppm due to the highly deshielding nature of the electropositive tantalum(V) metal center. The related complex $[Ta(O_2C_{20}H_{10}\{SiMe_3\}_2\text{-}3,3')(H)(Cl)_2(PMe_3)_2]$ exhibits a similar chemical shift for the hydride proton at δ 22.0 ppm.[6] However, while the latter is six-coordinate and coordinatively saturated, (*R*,*R*)-**2** contains a vacant coordination site. Introduction of trimethylphosphine to a solution of (*R*,*R*)-**2** results in coordination of the phosphine as shown by ^1H and ^{31}P NMR spectroscopy, but this ligand is labile and dissociates upon exposure of a solution of this adduct to vacuum. Dimethylphenylphosphine and other sterically unencumbering phosphines exhibit similar effects, but triphenylphosphine does not coordinate to the metal center. The presence of a vacant coordination site is advantageous since complexation of unsaturated species can occur, which could be followed by insertion of these substrates into the Ta−H bond. Indeed, complex (*R*,*R*)-**2** was found to undergo clean insertion reactions with the prochiral substances acetophenone and benzaldehyde-*d* to give alkoxides and also yielded organometallic species via reaction with alkynes and isocyanides.

The reaction of (*R*,*R*)-**2** with acetophenone leads to a complex mixture of products as shown by ^1H NMR spectroscopy. There are nine sharp features in the alkylsilyl region: four resonances of equal intensity appearing between 0.51 and 0.42 ppm, a sharp peak at 0.32 ppm, and an additional set of four resonances of equal intensity between 0.21 and 0.14 ppm. The peak at 0.32 ppm is approximately twice the intensity of each of the other eight peaks. The ^{13}C NMR spectrum of the product is also extremely complex. To identify the species formed in this reaction, the progress of the reaction of (*R*,*R*)-**2** with acetophenone ^{13}C-enriched at the carbonyl carbon was monitored by ^{13}C NMR spectroscopy, and the reactivity is summarized in Scheme 2.

When the ratio of acetophenone-^{13}C to (*R*,*R*)-**2** was 1.5:1, the initial spectrum indicated the presence of four distinct complexes in solution: the six-coordinate species (*R*,*R*,*R*)-**3** and (*R*,*R*,*S*)-**3** and the five-coordinate species (*R*,*R*,*R*)-**3a** and (*R*,*R*,*S*)-**3a**. The two signals for the coordinated ketone carbon appear downfield at δ 212.0 and 211.3 ppm, while those for the four alkoxide carbons are observed at δ 83.6, 83.3, 82.7, and 80.3 ppm. The alkoxide resonances for (*R*,*R*,*R*)-**3** and(*R*,*R*,*S*)-**3** at δ 82.7 and 80.3 ppm are shifted slightly upfield relative to the corresponding five-coordinate complexes due to the presence of the coordinated ketone. A broad feature at 200.4 ppm corresponding to free acetophenone-^{13}C was also observed. Addition of (*R*,*R*)-**2** to the NMR tube resulted in the consumption of the free acetophenone-^{13}C and the disappearance of complexes (*R*,*R*,*R*)-**3** and (*R*,*R*,*S*)-**3**. The resonances for the alkoxides (*R*,*R*,*R*)-**3a** and (*R*,*R*,*S*)-**3a** shift downfield to δ 85.5 and 84.6 ppm

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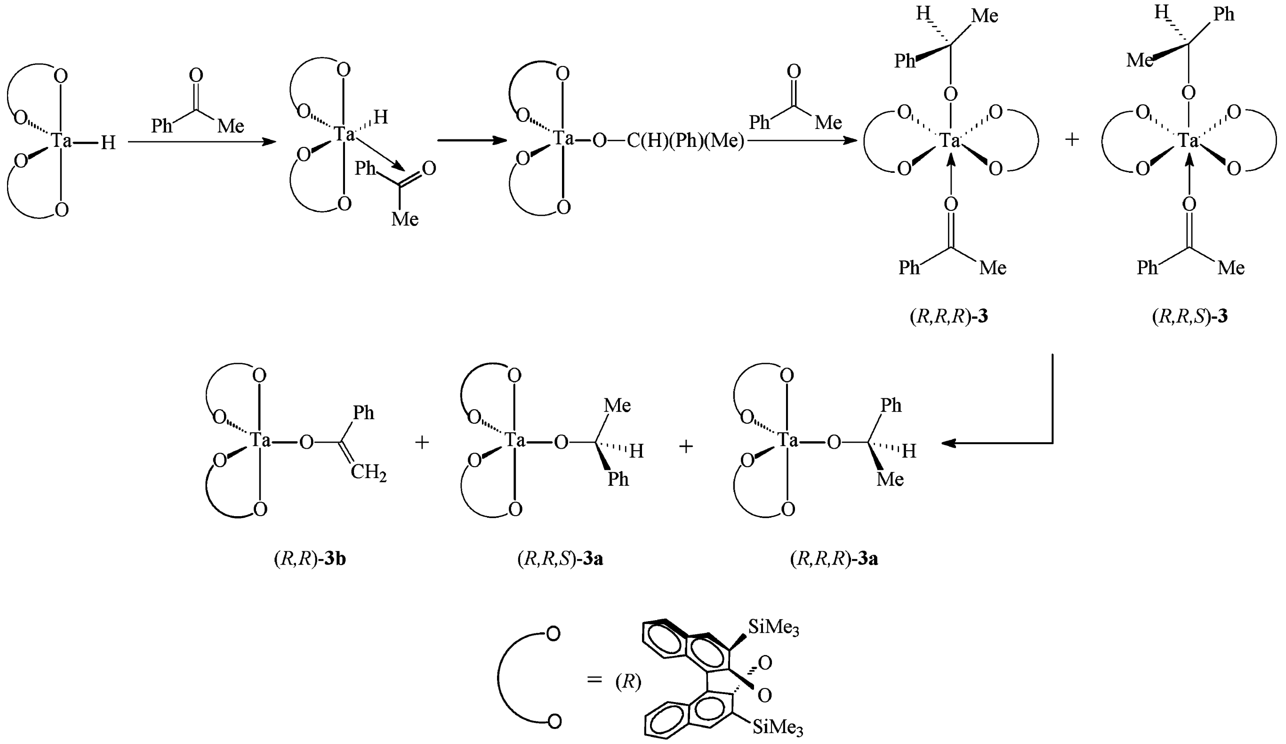
Scheme 2



due to the absence of coordinating acetophenone. A new peak at δ 160.6 ppm also appeared upon addition of excess (*R*,*R*)-**2**, which corresponds to the tantalum enolate complex (*R*,*R*)-**3b**. This chemical shift observed for (*R*,*R*)-**3b** is similar to that observed for metal enolates of titanium, zirconium, and ruthenium.[14−19]

A diastereomeric mixture of (*R*,*R*,*R*)-**3** and (*R*,*R*,*S*)-**3** was obtained on a preparative scale by reaction of (*R*,*R*)-**2** with an excess (4 equiv) of nonenriched acetophenone followed by careful evaporation of the solvent to avoid loss of coordinated acetophenone. An X-ray crystal structure of (*R*,*R*,*R*)-**3**/(*R*,*R*,*S*)-**3** was obtained, and an ORTEP plot is shown in Figure 1. Selected bond lengths and angles are collected in Table 1. Complex (*R*,*R*,*R*)-**3**/(*R*,*R*,*S*)-**3** consists of a tantalum atom surrounded by two resolved chelating binaphthoxide ligands as well as a 1-phenylethoxide ligand. A molecule of acetophenone is coordinated to the tantalum metal center in a *trans*-fashion relative to the alkoxide ligand, and the environment about the tantalum atom is approximately square bipyramidal. The Ta(1)−O(6) bond length is 1.806(5) Å, which is typical for a tantalum−alkoxide bond, while the Ta(1)−O(5) bond length is 2.205(5) Å to the coordinated acetophenone molecule.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for (*R*,*R*,*R*)/(*R*,*R*,*S*)-[Ta($O_2C_{20}H_{10}\{SiMe_3\}_2$-3,3′)$_2$(OCH(Me)(Ph))(O=C(Me)(Ph)]·$2C_6H_6$, (*R*,*R*,*R*)-3/(*R*,*R*,*S*)-3

Ta(1)−O(1)	1.988(5)	Ta(1)−O(4)	1.936(6)
Ta(1)−O(2)	1.998(5)	Ta(1)−O(5)	2.205(5)
Ta(1)−O(3)	1.981(5)	Ta(1)−O(6)	1.806(5)
O(5)−C(50)	1.32(1)	O(6)−C(60)	1.28(1)
O(1)−Ta(1)−O(2)	89.4(2)	O(2)−Ta(1)−O(6)	89.9(2)
O(1)−Ta(1)−O(3)	91.3(2)	O(3)−Ta(1)−O(4)	91.0(2)
O(1)−Ta(1)−O(4)	159.2(2)	O(3)−Ta(1)−O(5)	79.9(2)
O(1)−Ta(1)−O(5)	79.7(2)	O(3)−Ta(1)−O(6)	99.4(2)
O(1)−Ta(1)−O(6)	101.1(2)	O(4)−Ta(1)−O(5)	90.2(2)
O(2)−Ta(1)−O(3)	93.7(2)	O(4)−Ta(1)−O(6)	92.4(2)
O(2)−Ta(1)−O(4)	174.3(2)	O(5)−Ta(1)−O(6)	177.3(3)
O(2)−Ta(1)−O(5)	87.5(2)	O(5)−C(50)−C(51)	115.7(9)
O(5)−C(50)−C(57)	118.3(9)	C(51)−C(50)−C(57)	120.4(8)
O(6)−C(60)−C(61)	118.0(9)	O(6)−C(60)−C(67)	119.1(9)
C(61)−C(60)−C(67)	121.8(9)		

There are two types of crystallographic disorder present in the structure of (*R*,*R*,*R*)-**3**/(*R*,*R*,*S*)-**3**. The 1-phenylethoxide ligand and the coordinated acetophenone ligand are disordered with one another such that two tantalum atoms with relative occupancies of 0.5 are present. The C(61)−C(60)−C(67), O(6)−C(60)−C(61), and O(6)−C(60)−C(67) angles of the alkoxide moiety are 121.8(9)°, 118.0(9)°, and 121.8(9)° (respectively), indicating the environment about the C(60) atom is approximately planar. Since the 1-phenylalkoxide ligand is also disordered between the *R*- and *S*-configurations in a 1:1 ratio, an average structure results with a planar configuration at C(60) instead of the expected tetrahedral environment. The proton attached to C(60) was not detected crystallographically as a result of these two distortions, as each hydrogen position has an occupancy of 0.25. The geometry of the coordinated acetophenone molecule is as expected, and the O(5)−Ta(1)−O(6) angle of 177.3(3)° indicates the 1-phenylalkoxide ligand and the acetophenone ligand are diposed in an approximately linear orientation.

The reaction of (*R*,*R*)-**2** with benzaldehyde to give the corresponding benzyl alkoxide was investigated by NMR

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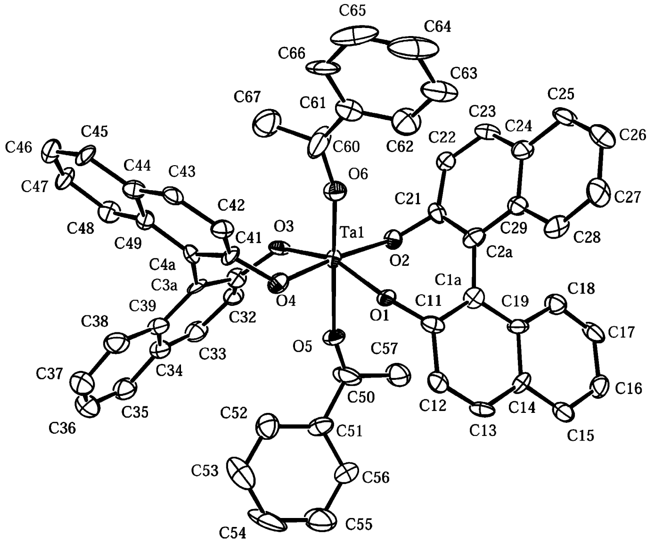


Figure 1. ORTEP diagram of (*R*,*R*,*R*)-**3**/(*R*,*R*,*S*)-**3**. Thermal ellipsoids are drawn at 50% probability. The 3,3′-SiMe$_3$ groups are not shown for clarity.

spectroscopy using benzaldehyde-*d*, unlabeled material, and material ^{13}C-enriched at the carbonyl carbon. The three ^{1}H NMR spectra are shown in Figure 2. The spectrum for the unlabeled material exhibits four lines due to the diastereotopic protons attached to the α-carbon (J = 8.1 Hz), which are further split into two sets of four lines when the ^{13}C-enriched benzaldehyde was employed ($J_{\mathrm{H-H}}$ = 8.1 Hz, $J_{\mathrm{C-H}}$ = 32.7 and 16.8 Hz). Reaction of (*R*,*R*)-**2** with benzaldehyde-*d* resulted in a ^{1}H NMR spectrum exhibiting two resonances at δ 4.93 and 4.83 ppm with an intensity ratio of 9:1. As the alkoxide ligand is now chiral at the α-carbon, two diastereomeric complexes are expected, and the greater intensity for the peak at δ 4.93 ppm indicates one species is favored over the other. When the enantiomer of (*R*,*R*)-**2** is used, the reverse pattern can be observed. Reaction of (*S*,*S*)-**2** with benzaldehyde-*d* results in a similar pattern with two peaks at δ 4.93 and 4.83 in a ratio of 1:9. Therefore, this process provides one diastereomer in 80% excess, which is greater than that obtained using Ru-, Os-, Rh-, and Ir-based systems[20,21] but less than that obtained with a Ti-based system.[22]

Titration of (*R*,*R*)-**2** with the ^{13}C-enriched benzaldehyde indicates that a mixture of species is formed as was found when acetophenone was employed as the substrate. When the ratio of (*R*,*R*)-**2** to the benzaldehyde is large, one peak is observed at δ 78.2 ppm in the ^{13}C NMR spectrum, but when the ratio is slightly less than 1:1, a second feature is observed at δ 198.6 ppm, indicating the formation of a six-coordinate species that contains an alkoxide ligand and a coordinated benzaldehyde ligand. This peak increases in intensity and becomes broadened as subsequent aliquots are added, indicating that the coordinated benzaldehyde ligand is in a state of dissociative equilibrium. This is also manifested in the ^{1}H NMR spectra, as all features are very broad when even a slight excess of the benzaldehyde is employed.

Addition of 6 mol % of (*R*,*R*)-**2** to a solution of benzaldehyde-*d* in benzene followed by addition of 1 equiv (relative to benzaldehyde-*d*) of DIBAL-H and subsequent hydrolysis after 12 h yields a mixture of the free benzyl alcohol-*d* and 3,3′-bis(trimethylsilyl)-1,1′-bi-2,2′-naphthol, which can be separated by preparative TLC. The benzyl alcohol-*d* was isolated in 52% yield and was characterized by mass spectrometry (EI), which exhibited a peak for the parent molecular ion as well as fragmentation of the CHO group. Thus, the conversion of benzaldehyde-*d* to benzyl-1-*d* alcohol deuterated at the α-carbon can be carried out catalytically. The

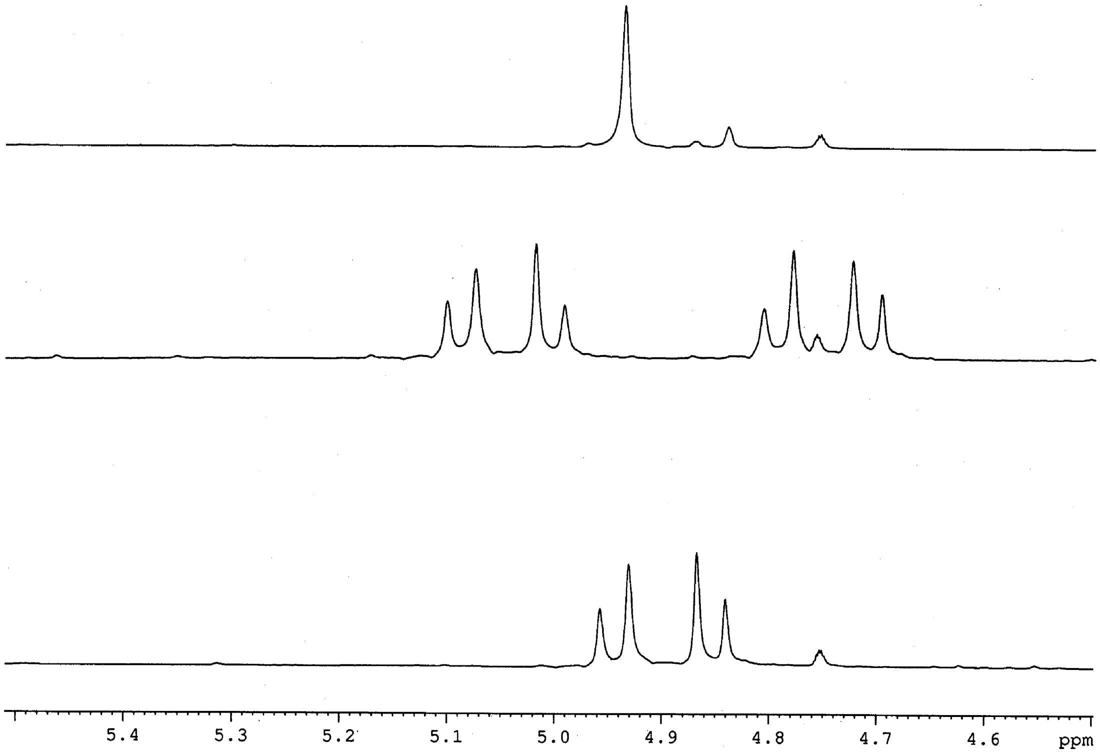
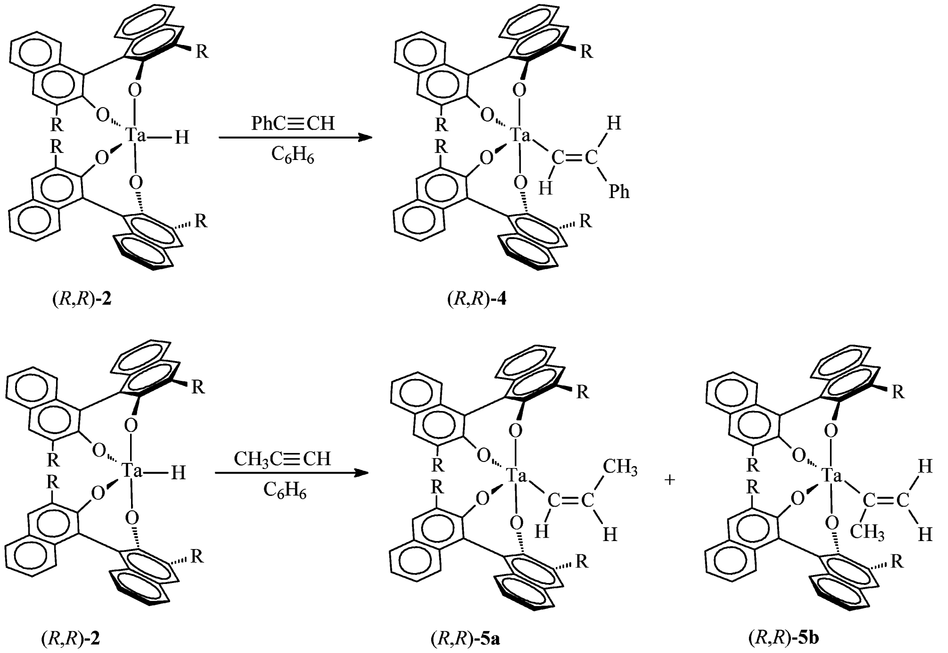


Figure 2. ^{1}H NMR spectra for the reaction of (*R*,*R*)-**2** with benzaldehyde (bottom), benzaldehyde ^{13}C-enriched at the carbonyl carbon (middle), and benzaldehyde-*d* (top).

Scheme 3



R = SiMe$_3$

product of this reaction was converted to the benzyl ester of α-methoxy-α-(trifluoromethyl)phenylacetic acid (MTPA, Mosher's acid),[21,23,24] and the ^{1}H NMR spectrum was recorded to determine the stereochemical outcome of hydride transfer reaction.[25] The ratio of the *R*-isomer to the *S*-isomer is 93:7, and thus the *R*-isomer is present in an 86% enantiomeric excess. This is superior to that reported for the conversion of benzaldehyde-*d* to benzyl-1-*d* alcohol using a catalyst system generated in situ from (1*R*,2*S*)-(+)-*cis*-1-amino-2-indanol and (*p*-cymeneRuCl$_2$)$_2$, (*p*-cymeneOsCl$_2$), (Cp*RuCl$_2$)$_2$, or (Cp*IrCl$_2$)$_2$, which ranged from 54 to 63%.[21] However, the reduction of benzaldehyde to benzyl-1-*d* alcohol using Bu$_3$SnD and a resolved titanium binaphthoxide system resulted in an ee of 94% of the *S*-isomer,[22] and reduction of benzaldehyde-*d* using a chiral ruthenium catalyst in the presence of ^{t}BuOK gave an ee of 98% of the *R*-isomer.[20]

Compound (*R*,*R*)-**2** also reacts with acetylenic species to give vinyl metal complexes as shown in Scheme 3. Reaction of (*R*,*R*)-**2** with phenylacetylene cleanly gives the phenylethylene tantalum complex (*R*,*R*)-**4**. Resonances in the ^{1}H NMR spectrum of (*R*,*R*)-**4** for the two protons attached to the vinylic carbon atoms appear as doublets (J = 18.9 Hz) at δ 8.51 and 6.42 ppm. The coupling constant of 18.9 Hz indicates the alkene moiety is present in the *E*-configuration, and there is no evidence for the presence of the *Z*-isomer. A similar ligand disposition was observed in the reaction of [Ta(OC$_6$H$_3{}^t$Bu$_2$-2,6)$_2$(H)$_2$Cl(PMePh$_2$)] with phenylacetylene, which yields a cyclometalated product also containing an ethenyl group in the *E*-configuration.[3]

The downfield resonance in the ^{1}H NMR spectrum of (*R*,*R*)-**4** can be attributed to the proton that is proximal to the metal center, while the upfield resonance arises from the terminal proton. The hydride ligand of (*R*,*R*)-**2** is transferred from the tantalum atom to the terminal position, as shown by a deuterium-labeling experiment. Reaction of (*R*,*R*)-**2** with phenylacetylene-d_6 gives a ^{1}H NMR spectrum similar to that obtained for the protio species. However, the resonance at δ 8.51 ppm is no longer present and the doublet at δ 6.42 ppm has collapsed to a singlet, indicating that the upfield resonance must arise from the hydride of (*R*,*R*)-**2**.

The reaction of (*R*,*R*)-**2** with propyne yields a mixture of two products resulting from addition of the hydride ligand to either the terminal carbon or the internal carbon of propyne. In the first complex, (*R*,*R*)-**5a**, the methyl group is distal to the tantalum and appears as a doublet at 1.24 ppm (J = 6.0 Hz). The proton proximal to the tantalum metal center appears as a doublet of quartets centered at 5.55 ppm with coupling constants of 6.0 Hz, resulting from coupling to the methyl group and 18.0 Hz resulting from coupling to the other proton. In the second complex, (*R*,*R*)-**5b**, the methyl group is proximal to the tantalum, giving rise to a singlet at 1.81 ppm. The vinylic protons appear at 5.91 and 4.99 ppm with the downfield resonance corresponding to the proton *trans* to the methyl group. The two complexes are present in an approximate 4:1 ratio (for (*R*,*R*)-**5a**:(*R*,*R*)-**5b**), indicating the addition of the hydride to the internal carbon of propyne is favored.

In addition to reactions with acetylenic substrates, complex (*R*,*R*)-**2** also undergoes insertion of 2,6-dimethylphenyl isocyanide into the Ta−H bond to give the η^2-metal iminoformyl complex (*R*,*R*)-**6** (Scheme 4). The ^{1}H NMR spectrum of (*R*,*R*)-**6** exhibits a singlet appearing far downfield at δ 11.49 ppm attributed to the proton bound to the nitrogen atom of the iminoformyl moiety. The dramatic downfield shift is likely attributable to the interaction of the lone pair of electrons on nitrogen with the tantalum metal center, resulting in a substan-

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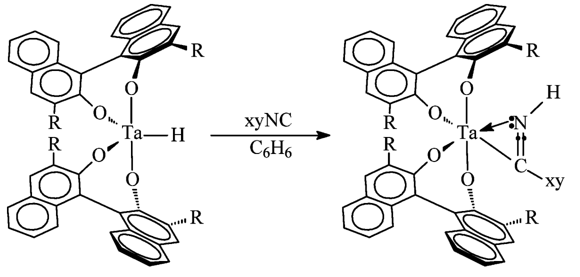
Scheme 4



(*R*,*R*)-**2** (*R*,*R*)-**6**

R = SiMe$_3$

xy = 2,6-dimethylphenyl

tial deshielding effect. The ^{13}C NMR resonance for the carbon bound to the tantalum metal center also appears downfield at δ 239.5 ppm. This value is similar to that found for the cyclometalated tantalum iminoacyl species [Ta(OC$_6$H$_3$^{t}Bu$_2$-2,6)(OC$_6$H$_3$^{t}BuCMe$_2$CH$_2$-η^2-C=Nxy)(Ph-CH=CH-η^2-C=Nxy)Cl], which appears at δ 243.0 ppm,[3] although other tantalum η^2-iminoacyl complexes exhibit a variety of chemical shifts for this carbon atom, depending on the nature of the ligands attached to the metal center.[26,27]

The reaction of (*R*,*R*)-**2** with allene was also investigated. An atmosphere of allene was introduced into a NMR tube containing a solution of (*R*,*R*)-**2** in C$_6$D$_6$, and an immediate reaction was observed resulting in the allyl complex (*R*,*R*)-**7**. A doublet at δ 3.48 ppm (J = 10.8 Hz) and a pentet at δ 6.18 ppm (J = 10.8 Hz) were observed in the ^{1}H NMR spectrum of (*R*,*R*)-**7**, corresponding to the terminal protons and central proton, respectively. The ^{1}H NMR spectrum indicates that the allyl ligand is η^3-bound rather than η^1-bound, which would result in four distinct resonances.[28] Furthermore, the presence of one doublet for the terminal protons indicates the allyl moiety undergoes free rotation at room temperature. The process is extremely fast, and two distinct doublets for the *syn*- and *anti*-protons do not appear even at − 80 °C.[29,30] Attempts to synthesize (*R*,*R*)-**7** on a preparative scale were not successful because the complex is not stable in the absence of an allene atmosphere. Introduction of a nitrogen atmosphere results in rapid decomposition of the product. This observation, in conjunction with the spectroscopic evidence, suggests that the allyl ligand is only weakly bound to the tantalum metal center.

Conclusions

The tantalum bis(binaphthoxide) hydride complex (*R*,*R*)-**2** can be prepared in excellent yield in two steps from [H$_2$NEt$_2$][Ta(O$_2$C$_{20}$H$_{10}$\{SiMe$_3$\}$_2$-3,3′)$_2$Cl$_2$]. This material reacts readily with prochiral ketones to give metal complexes containing chiral alkoxide ligands and serves for the catalytic conversion of benzaldehyde-*d* to benzyl-1-*d* alcohol, giving the *R*-isomer in an 86% enantiomeric excess. Complex (*R*,*R*)-**2** also reacts with phenylacetylene and propyne to give the corresponding vinyl metal complexes and with 2,6-dimethylphenyl isocyanide to give an iminoformyl complex. This species also hydrogenates allene, but the resulting product is labile and cannot be obtained on a preparative scale. Although (*R*,*R*)-**2** reacts readily with these substrates, it is unfortantely unreactive toward alkenes. Reactions of (*R*,*R*)-**2** with styrene and butadiene occurred only very slowly at room temperature.

Experimental Section

General Procedures. All manipulations were carried out using standard Schlenk line, glovebox, and syringe techniques.[31] The compound [H$_2$NEt$_2$][Ta(O$_2$C$_{20}$H$_{10}$\{SiMe$_3$\}$_2$-3,3′)$_2$-Cl$_2$] was prepared according to a previously published procedure.[12] Reagents were purchased from Aldrich and used without further purification. Solvents were purified using an Innovative Technologies solvent purification system. ^{1}H NMR spectra were recorded at 300 MHz and referenced to residual protio solvent. ^{13}C NMR spectra were recorded at 125.9 MHz and referenced to the solvent. Elemental analyses and EI mass spectrometry were carried out in-house at Purdue University.

Preparation of [Ta(O$_2$C$_{20}$H$_{10}$\{SiMe$_3$\}$_2$-3,3′)$_2$(C$_6$H$_5$)], (*R*,*R*)-1. To a suspension of [H$_2$NEt$_2$][Ta(O$_2$C$_{20}$H$_{10}$\{SiMe$_3$\}$_2$-3,3′)$_2$Cl$_2$] (4.95 g, 4.18 mmol) in benzene (50 mL) was added a solution of PhMgCl (2.0 M in THF) via syringe. The reaction mixture became homogeneous and was subsequently stirred for 3 h, after which time a white precipitate was present. The volatiles were removed *in vacuo*, and the resulting solid was suspended in 20 mL of benzene. Filtration through Celite and evaporation of the solvent afforded 3.41 g (74%) of (*R*,*R*)-**1** as an orange solid. ^{1}H NMR (C$_6$D$_6$, 25 °C, 300 MHz): δ 8.18 (s, 2 H, 4,4′-*H*), 7.91 (s, 2 H, 4,4′-*H*), 7.64 (pseudo q, 4 H, 6,6′-*H*), 7.14−6.74 (m, 17 H, aromatics), 0.58 (s, 18 H, Si(C*H*$_3$)$_3$), 0.06 (s, 18 H, Si(C*H*$_3$)$_3$) ppm. ^{13}C NMR (C$_6$D$_6$, 25 °C, 125.7 MHz): δ 161.7, 161.4, 142.0, 138.2, 137.7, 137.5, 137.1, 131.4, 131.1, 130.3, 129.7, 129.4, 128.9, 127.8, 127.5, 127.0, 126.9, 126.0, 124.8, 124.2, 25.1, 21.8, 1.35, −0.3 ppm.

Preparation of [Ta(O$_2$C$_{20}$H$_{10}$\{SiMe$_3$\}$_2$-3,3′)$_2$(H)], (*R*,*R*)-2. To a solution of (*R*,*R*)-**1** (1.15 g, 1.03 mmol) in benzene (10 mL) was added a solution of diisobutylaluminum hydride (1.27 mL, 1.0 M in hexane, 1.27 mmol). The solution was stirred for 2 h, after which time the solvent was removed in vacuo. The resulting solid was suspended in 10 mL of hexane, and the suspension was filtered. The filter cake was washed with 5 × 5 mL of hexane and dried *in vacuo* to yield 0.85 g (79%) of (*R*,*R*)-**2** as a gray solid. IR (Nujol mull): 1633.8 cm^{-1} ($\nu_{\mathrm{Ta-H}}$). ^{1}H NMR (C$_6$D$_6$, 25 °C, 300 MHz): δ 21.5 (s, 1 H, Ta-*H*), 8.17 (s, 2 H, 4,4′-*H*), 8.02 (s, 2 H, 4,4′-*H*) 7.66 (pseudo q, 4 H, 6,6′-*H*), 7.19−6.77 (m, 12 H, aromatics), 0.44 (s, 18 H, Si(C*H*$_3$)$_3$), 0.11 (s, 18 H, Si(C*H*$_3$)$_3$) ppm. ^{13}C NMR (C$_6$D$_6$, 25 °C, 125.7 MHz): δ 159.9, 159.6, 138.5, 137.6, 136.0, 135.5, 131.7, 131.3, 130.8, 128.9, 127.7, 127.5, 125.4, 124.7, 119.1, 116.7, 23.1, 14.7, 1.3, −0.5 ppm. Anal. Calcd for C$_{52}$H$_{57}$O$_4$Si$_4$Ta: C, 60.09; H, 5.53. Found: C, 60.04; H, 5.85.

Preparation of [Ta(O$_2$C$_{20}$H$_{10}$\{SiMe$_3$\}$_2$-3,3′)$_2$(OCH(Me)-(Ph))(O=C(Me)(Ph)], (*R*,*R*,*R*)-3/(*R*,*R*,*S*)-3. To a solution of (*R*,*R*)-**2** (0.53 g, 0.51 mmol) in benzene (15 mL) was added acetophenone (0.50 mL, 0.51 g, 4.2 mmol). The resulting deep red solution was stirred for 18 h, and the solvent was removed *in vacuo*. The resulting oily red solid was redissovled in benzene (5 mL), and the solution was layered with hexane (15 mL), resulting in the formation of a brown precipitate. The solution was filtered and the volatiles were removed from the

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filtrate in vacuo to yield a viscous red liquid. To this was added hexane (5 mL), and the mixture was heated until all of the oil dissolved. The solution was allowed to cool overnight, after which time a dark oil separated from the solution. The mother liquor was decanted, and the volatiles were removed *in vacuo*, resulting in a red oil, which slowly crystallized. The resulting solid was identified to be a diasteromeric mixture of (*R*,*R*,*R*)-**3** and (*R*,*R*,*S*)-**3**. Yield: 0.41 g (63%).

Reaction of (*R*,*R*)-2 with Benzaldehyde. A solution of (*R*,*R*)-**2** (0.060 g, 0.058 mmol) in C_6D_6 (0.5 mL) was prepared and placed in an NMR tube. To this solution was added benzaldehyde (5.9 μL, 0.059 mmol) via microliter syringe. The tube was shaken, and the progress of the reaction was monitored by ^{1}H NMR spectroscopy.

Reaction of (*R*,*R*)-2 with Benzaldehyde-*d*. A solution of (*R*,*R*)-**2** (0.080 g, 0.076 mmol) in C_6D_6 (0.5 mL) was prepared and placed in an NMR tube. To this solution was added benzaldehyde-*d* (7.9 μL, 0.078 mmol) via microliter syringe. The tube was shaken, and the progress of the reaction was monitored by ^{1}H NMR spectroscopy.

Titration of (*R*,*R*)-2 with Benzaldehyde-*carbonyl*-^{13}C. A solution of (*R*,*R*)-**2** (0.15 g, 0.14 mmol) in C_6D_6 (0.5 mL) was prepared and placed in an NMR tube. To this solution was added 10 equiv of benzaldehyde-*carbonyl*-^{13}C (140 μL, 1.37 mmol) in aliquots of 7.0 μL. The progress of the reaction was monitored using ^{13}C NMR spectroscopy.

Catalytic Preparation of Benzyl Alcohol-*d* Using (*R*,*R*)-2. To a solution of benzaldehyde-*d* (0.50 mL, 4.92 mmol) in benzene (15 mL) was added a solution of (*R*,*R*)-**2** (0.32 g, 0.31 mmol) in benzene (5 mL) followed by a 1.0 M solution of DIBAL-H (5.0 mL, 0.50 mmol) in hexane. The reaction mixture was stirred for 12 h under N_2. The flask was opened in air, and deionized water (10 mL) was added, resulting in the formation of a white solid. The suspension was filtered, and the filter cake was washed with hexane (5 × 5 mL). The organic layer was separated, and the aqueous phase was washed with hexane (3 × 5 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and filtered, and the volatiles were removed *in vacuo* to yield a yellow oil. The product was purified by preparative thin-layer chromatography (95:5 hexane/ethyl acetate eluent). The band containing the product was scraped off, and the product was extracted from the silica using acetone, which was subsequently removed *in vacuo* to yield benzyl alcohol-*d* (0.28 g, 54%) as a pale yellow oil. ^{1}H NMR (C_6D_6, 25 °C, 300 MHz): δ 7.17−7.07 (m, 5 H, aromatics), 4.29 (s, 1 H, PhC*H*DOH), 3.12 (br s, 1 H, −O*H*). ^{13}C NMR (C_6D_6, 25 °C, 125.7 MHz): δ 140.9 (*ipso*-C), 128.4 (*meta*-C), 127.4 (*para*-C), 126.7 (*ortho*-C), 65.2 (t, J_{C-D} = 26.1 Hz, Ph-*C*HD(OH)). MS (EI): *m*/*z* 108 (M^+), 79 (M^+ − CHO).

Preparation of [Ta($O_2C_{20}H_{10}${$SiMe_3$}$_2$-3,3′)$_2$(CH=CHC$_6$H$_5$)],(*R*,*R*)-4. To a solution of (*R*,*R*)-**2** (0.20 g, 0.19 mmol) in benzene (10 mL) was added phenylacetylene (0.030 mL, 0.028 g, 0.32 mmol) via syringe. The reaction mixture became reddish in color and was stirred for 6 h. The volatiles were removed *in vacuo* to yield 0.16 g (73%) of (*R*,*R*)-**5** as an orange solid. ^{1}H NMR (C_6D_6, 25 °C, 300 MHz): δ 8.51 (d, *J* = 18.9 Hz, 1 H, TaC*H*=CHPh) 8.22 (s, 2 H, 4,4′-*H*), 8.09 (s, 2 H, 4,4′-*H*), 7.78−7.68 (m, aromatics, 6 H) 7.55−6.85 (m, aromatics, 15 H), 6.42 (d, *J* = 18.9 Hz, 1 H, TaCH=C*H*Ph), 0.33 (s, 18 H, Si(C*H*$_3$)$_3$), 0.20 (s, 18 H, Si(C*H*$_3$)$_3$) ppm. ^{13}C NMR (C_6D_6, 25 °C, 125.7 MHz): δ 189.9 Ta(*C*H=CHPh), 161.1 (TaO*C*), 160.3 (TaO*C*), 148.0, 137.5, 137.2, 136.6, 135.6, 135.5, 132.3, 131.2, 131.1, 130.9, 130.2, 129.7, 129.0, 128.8, 128.7, 128.5, 127.6, 127.6, 127.4, 127.2, 127.1, 127.0, 124.7, 124.3, 83.9, 77.8, −2.9, −5.5 ppm. Anal. Calcd for $C_{60}H_{63}O_4Si_4Ta$: C, 63.13; H, 5.56. Found: C, 62.35; H, 5.53.

Preparation of [Ta($O_2C_{20}H_{10}${$SiMe_3$}$_2$-3,3′)$_2$(CD=CHC$_6$D$_5$)]. To a solution of (*R*,*R*)-**2** (0.070 g, 0.067 mmol) in benzene-*d*$_6$ (0.5 mL) in an NMR tube was added phenylacetylene-*d*$_6$ (10 μL, 0.010 g, 0.094 mmol) via microliter syringe. The tube was shaken and then allowed to sit at room temperature for 3 h. ^{1}H NMR (C_6D_6, 25 °C, 300 MHz): δ 8.22 (s, 2 H, 4,4′-*H*), 8.09 (s, 2 H, 4,4′-*H*), 7.78−7.68 (m, aromatics, 6 H), 7.76 (d, *J* = 8.1 Hz, 2 H, 6,6′-*H*), 7.70 (d, *J* = 8.1 Hz, 2 H, 6,6′-*H*), 6.42 (s, 1 H, TaCD=C*H*Ph), 0.33 (s, 18 H, Si(C*H*$_3$)$_3$), 0.20 (s, 18 H, Si(C*H*$_3$)$_3$) ppm.

Preparation of [Ta($O_2C_{20}H_{10}${$SiMe_3$}$_2$-3,3′)$_2$(C(H)=C(H)-CH$_3$)], (*R*,*R*)-5a/(*R*,*R*)-5b. Compound (*R*,*R*)-**2** (0.32 g, 0.31 mmol) was dissolved in benzene (15 mL) in a Schlenk flask. The solution was freeze−thaw−degassed three times, then an atmosphere (730 Torr) of propyne was introduced into the flask. The solution was allowed to thaw and was subsequently stirred for 3 h. The solution was filtered through Celite to remove a small amount of precipitate, and the volatiles were removed *in vacuo* to yield a yellow solid, which was redissolved in benzene (5 mL). The solution was layered with hexane (10 mL) to give a yellow solid, which was isolated and washed with hexane (3 × 5 mL) to yield (*R*,*R*)-**5** as yellow crystals (0.16 g, 47%). Compound (*R*,*R*)-**5** is present as a mixture of the *E*- and *Z*-isomers. For (*R*,*R*)-**5a**: ^{1}H NMR δ 8.23 (s, 2 H, 4,4′-*H*), 8.04 (s, 2 H, 4,4′-*H*), 7.77−7.65 (m, X H, aromatics), 7.19−6.78 (m, X H, aromatics), 5.55 (doublet of quartets, Ta−C(H)=C(*H*)-CH$_3$), *J* = 6.0 and 18.0 Hz), 1.23 (d, *J* = 6.0 Hz, Ta−C(H)=C(H)C*H*$_3$), 0.44 (s, 18H, Si(C*H*$_3$)$_3$), 0.17 (s, 18H, Si(C*H*$_3$)$_3$) ppm. For (*R*,*R*)-**5b**: ^{1}H NMR δ 8.20 (s, 2 H, 4,4′-*H*), 7.98 (s, 2 H, 4,4′-*H*), 7.77−7.65 (m, X H, aromatics), 7.19−6.78 (m, X H, aromatics), 5.91 (s, 1 H, Ta−CH$_3$=C*H*$_2$), 4.99 (s, 1 H, Ta−CH$_3$=C*H*$_2$), 1.81 (s, 3H, Ta−C*H*$_3$=CH$_2$), 0.49 (s, 18H, Si(C*H*$_3$)$_3$), 0.14 (s, 18H, Si(C*H*$_3$)$_3$) ppm. Anal. Calcd for $C_{55}H_{61}O_4Si_4Ta$: C, 61.20; H, 5.70. Found: C, 60.93; H, 5.75.

Preparation of [Ta($O_2C_{20}H_{10}${$SiMe_3$}$_2$-3,3′)$_2$(C(H)=NC$_6$H$_2$Me$_2$-2,6)], (*R*,*R*)-6. To a solution of 0.43 g (0.41 mmol) of (*R*,*R*)-**2** in benzene (15 mL) was added a solution of 2,6-dimethylisocyanide (0.055 g, 0.42 mmol) in benzene (5 mL). The solution became dark red and was stirred 14 h. The volatiles were removed, and the resulting red solid was redissolved in benzene (5 mL). This solution was layered with hexane (10 mL), resulting in the precipitation of a gray solid. The solution was filtered, and the volatiles were removed from the filtrate, yielding 0.37 g (77%) of (*R*,*R*)-**6** as a red solid. ^{1}H NMR (C_6D_6, 25 °C, 300 MHz): δ 11.5 (s, 1 H, Ta−C(*H*)=Nxy), 8.14 (s, 2 H, 4,4′-*H*), 7.81 (s, 2 H, 4,4′-*H*), 7.74 (d, *J* = 8.1 Hz, 2 H, 6,6′-*H*), 7.44 (d, *J* = 8.1 Hz, 2 H, 6,6′-*H*), 7.18−6.29 (m, 15 H, aromatics), 2.21 (s, 6 H, *o*-C*H*$_3$), 0.29 (s, 18 H, Si(C*H*$_3$)$_3$), 0.25 (s, 18 H, Si(C*H*$_3$)$_3$) ppm. ^{13}C NMR (C_6D_6, 25 °C, 125.7 MHz): δ 239.5 (Ta−*C*=Nxy), 163.2 (TaO*C*), 160.7 (TaO*C*), 152.8 (ipso-*C*N), 145.8, 141.7, 140.9, 137.0, 136.4, 132.5, 131.8, 130.6, 129.7, 129.5, 129.3, 129.1, 128.9, 128.3, 127.9, 127.4, 127.2, 126.7, 123.8, 123.4, 122.6, 117.8, 117.6, 36.9 (*o*-*C*H$_3$), 36.3 (*o*-*C*H$_3$), 1.0 (−Si(*C*H$_3$)$_3$), 0.8 (−Si(*C*H$_3$)$_3$), −0.9 (−Si(*C*H$_3$)$_3$), −0.8 (−Si(*C*H$_3$)$_3$) ppm. Anal. Calcd for $C_{61}H_{66}NO_4Si_4Ta$: C, 62.59; H, 5.68. Found: C, 62.48; H, 6.34.

Reaction of (*R*,*R*)-2 with Allene. A solution of (*R*,*R*)-**2** (0.075 g, 0.072 mmol) in C_6D_6 (0.7 mL) was placed in a J. Young NMR tube. The solution was freeze−thaw−degassed three times, and then 740 Torr of allene was introduced into the tube. The solution was allowed to thaw, and the tube was shaken. ^{1}H NMR: δ 8.23 (s, 2 H, 4,4′-*H*), 8.02 (s, 2 H, 4,4′-*H*), 7.70 (pseudo q, 4 H, 6,6′-*H*), 7.18−6.81 (m, 10 H, aromatics), 6.18 (p, *J* = 10.8 Hz, 1 H CH$_2$C*H*CH$_2$), 3.48 (d, *J* = 10.8 Hz, 4H, C*H*$_2$CHC*H*$_2$), 0.54 (s, 18 H, Si(C*H*$_3$)$_3$), 0.15 (s, 18 H, Si(C*H*$_3$)$_3$) ppm.

X-ray Structure Determination. Crystal data and data collection parameters are contained in Table 2. 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 Kα radiation (λ = 0.71073 Å) on a Nonius KappaCCD. Lorentz and polarization corrections were applied to the data.[32] An empiri-

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Table 2. Crystallographic Data for Compound (*R*,*R*,*R*)-3/(*R*,*R*,*S*)-3·2C_6H_6

formula	$C_{80}H_{84}O_6Si_4Ta$
space group	$P2_12_12_1$ (#19)
a, Å	15.9939(7)
b, Å	17.5689(4)
c, Å	25.6582(9)
α, deg	90
β, deg	90
γ, deg	90
V, Å^3	7209.9(4)
Z	4
ρ_{calc}, g cm^{-3}	1.322
temperature, K	150
radiation (wavelength)	Mo Kα (0.71073 Å)
R	0.090
R_w	0.118

cal absorption correction using SCALEPACK was applied.[33] Intensities of equivalent reflections were averaged. The structure was solved using the structure solution program PATTY in DIRDIF92.[34] 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.[35] Refinement was performed on a AlphaServer 2100 using SHELX-97.[36] Crystallographic drawings were done using the programs ORTEP-3.[37]

Supporting Information Available: Crystallographic data for (*R,R,R*-**3**)/(*R*,*R*,*S*-**3**) in .cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050633S

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