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Asymmetric Catalytic Intramolecular Hydroamination of Aminoallenes by Tantalum Amidoalkoxide Complexes

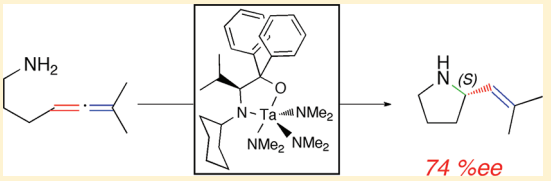
Michelle C. Hansen,[†] Carolyn A. Heusser,[†] Tarun C. Narayan,[†] Kristine E. Fong,[†] Nagiko Hara,[†] Alexander W. Kohn,[†] Alexander R. Venning,[†] Arnold L. Rheingold,[‡] and Adam R. Johnson*[,†]

[†]Department of Chemistry, Harvey Mudd College, 301 Platt Boulevard, Claremont, California 91711, United States

[‡]Department of Chemistry, University of California, San Diego, 9500 Gilman Drive, MC 0358, La Jolla, California 92093, United States

Supporting Information

ABSTRACT: A series of tantalum complexes of chiral bidentate amidoalkoxide ligands was prepared. The crystal structure of one complex, $Ta(NMe_2)_3[\text{-}OCPh_2CH(CHMe_2)N(c\text{-}C_6H_{11})\text{-}]$ was obtained. Unlike previously described titanium complexes with these ligands, which are dimeric with bridging oxygen atoms, this tantalum complex is monomeric with an approximate trigonal-bipyramidal geometry. The resulting complexes were examined for their *in situ* activity for catalytic asymmetric hydroamination/cyclization of an aminoallene. Enantioselectivities up to 80% ee were observed for the cyclization of 6-methylhepta-4,5-dienylamine to 2-(2-methylpropenyl)pyrrolidine at 135 °C with 5 mol % catalyst loading.



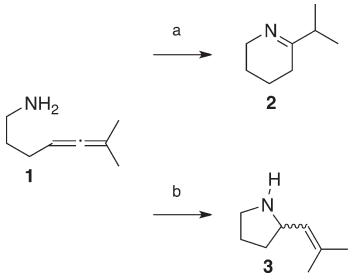
INTRODUCTION

Hydroamination, the addition of an N−H bond across an unsaturated C−C bond, is a highly atom economical method for synthesizing nitrogen-containing compounds.[1] Although the reaction is generally thermoneutral or slightly exothermic, it requires a catalyst due to the electronic repulsion between the nitrogen and the unsaturated group. Both inter- and intramolecular variations of the reaction have been reported for the hydroamination of olefins, alkynes, and allenes, and the field has been extensively reviewed for a number of metal catalyst systems including lanthanides,[2] gold,[3] early metals,[4] and rhodium and iridium.[5] More recent reviews summarize the asymmetric hydroamination reaction.[6] There have also been several recent reports of the hydroamination reaction (both inter- and intramolecular variants, with both alkyne and alkene substrates) in protic media.[7]

Hydroamination of aminoallenes has been studied for almost thirty years, and while initial reports used late metal catalysts such as silver, mercury, and palladium,[8] more recent work has focused on titanium,[9] lanthanide,[10] and gold catalysts.[11] The intramolecular hydroamination of 4,5-dienylamines (**1**, Scheme 1) can proceed by two pathways. When the addition occurs at the external double bond (path a), the reaction gives achiral tetrahydropyridine products (**2**). The corresponding addition to the internal double bond (path b) yields nitrogen-containing heterocycles with a pendant vinyl group that is available for further substitution (**3**). The resulting pyrrolidine heterocycles are chiral, and as such, there has been significant effort to develop the asymmetric hydroamination reaction for both aminoallene[11b,c,12] and aminoalkene[13] substrates.

The first example of asymmetric intramolecular hydroamination of an allene by a titanium catalyst was reported by our group in 2004 using chiral titanium amidoalkoxide complexes.[14] The dimeric complexes with bridging oxygen atoms[15] can enter the catalytic cycle proposed by Bergman[16] by reacting with the incoming substrate to form an imido complex (Scheme 2). The imido can react via a [2+2] cycloaddition reaction to form the corresponding azametallacyclobutane, and protonolysis by additional substrate regenerates the catalytically active species. The resulting pyrrolidine (**3**) was obtained in quantitative yield, but the enantioselectivity of the reaction was low, up to 16% ee. In an attempt to improve the enantioselectivity of the catalysis, bulkier alkyl groups were added to the ligands, but these new catalysts did not lead to higher enantioselectivity.[17] We also examined titanium sulfonamide alcohol complexes due to their altered electronic properties, but again found no increase in enantioselectivity.[18]

Scheme 1



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There have been some recent reports of using tantalum catalysts for hydroamination[19] and the closely related hydroaminoalkylation.[20] Bergman initially studied stoichiometric experiments with cationic tantalum complexes ($[Bn_2Ta{=}NCMe_3]^+$), suggesting that the mechanism for intermolecular alkyne hydroamination goes through the [2+2] cycloaddition mechanism seen for Ti catalysts.[19a] A later, more thorough, investigation showed that neither neutral nor cationic alkyl/imido tantalum complexes were able to directly access a [2+2] cycloaddition reaction manifold with alkynes.[21] They hypothesized that amido/imido tantalum complexes would be able to access this pathway, however. To date, no detailed mechanistic study for tantalum-catalyzed hydroamination has been carried out. We investigated catalysis with tantalum complexes of our sulfonamide alcohol ligands and found a significant increase in enantioselectivity to a maximum of 34% ee.[18] We recently reported this as the first example of asymmetric hydroamination using a group V metal catalyst. Two recent reports described the use of V, Nb, and Ta complexes for the asymmetric hydroamination of alkenes.[22] We sought to improve our results on the asymmetric hydroamination of aminoallenes by investigating catalysis using tantalum complexes of our previously reported amidoalkoxide ligands.[17]

RESULTS AND DISCUSSION

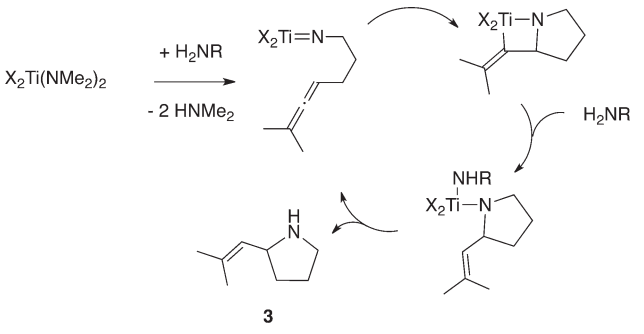
We previously reported the synthesis of a library of bidentate amino alcohols that could be readily prepared in a two-step process from commercially available chiral amino acid derivatives.[17] The ligand abbreviation indicates, in order, the amino acid derivative (valine or phenylalanine), the *N*-alkyl substituent (isopropyl, cyclohexyl, or adamantyl), and the substituent in the position α to oxygen (hydrogen, methyl, *n*-butyl, or phenyl) (Chart 1). Of the 24 ligands in the series, we were originally unable to synthesize one, L-H_2VPP.[17] However, during the course of this study we found that it is possible to prepare this ligand by using diethyl ether as solvent. The synthesis of L-H_2VPP was carried out according to the procedure outlined in Scheme 3.

As reported previously,[14,17] we have not seen evidence for the racemization of the phenylalanine- or valine-derived ligands during their synthesis. The addition of (*S*)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol to the ligands resulted in the shifting of the ligand hydrogen signals due to the formation of transient diastereomeric complexes, but we did not observe splitting of the resonances into two sets of peaks, indicating that the ligands were enantiomerically pure.[23] However, when L-H_2VPP was examined by this procedure, it was found to be partially racemized. Simulation using gNMR[24] suggested that the ligand was obtained in about a 75:25 ratio of enantiomers (50% ee). We have had significant difficulties preparing this single ligand derivative and include the results from the partially racemized ligand in this report.

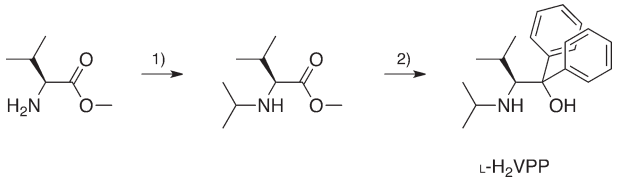
The opposite enantiomers of several ligands were also prepared according to established procedures:[17] D-H_2PCP, D-H_2VCP, D-H_2PPP, and D-H_2PPM. Significant solvent effects were observed when using phenyl Grignard reagents; in most cases, yields improved when THF was replaced with diethyl ether as the solvent, but in some cases, alkylation was achievable only using THF. Details of the modified synthetic procedures are included in the Experimental Section.

Tantalum complexes of the amidoalkoxide ligands were synthesized by protonolysis reactions and liberation of $HNMe_2$ (Scheme 4). ^{1}H NMR spectroscopy (see Supporting Information

Scheme 2

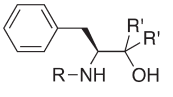


Scheme 3[a]

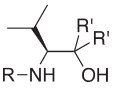


[a] Reagents and conditions: (1) $NaHCO_3$/acetone/$NaBH(OAc)_3$, (2) PhMgBr/ether.

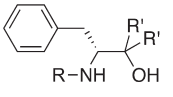
Chart 1[a]



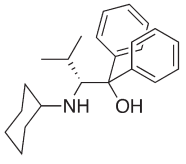
L-H_2PPH(M, B, P), R = ^{i}Pr, R' = H (Me, ^{n}Bu, Ph)
L-H_2PCH(M, B, P), R = c-C_6H_{11}, R' = H (Me, ^{n}Bu, Ph)
L-H_2PAH(M, B, P), R = 2-Ad, R' = H (Me, ^{n}Bu, Ph)



L-H_2VPH(M, B, P), R = ^{i}Pr, R' = H (Me, ^{n}Bu, Ph)
L-H_2VCH(M, B, P), R = c-C_6H_{11}, R' = H (Me, ^{n}Bu, Ph)
L-H_2VAH(M, B, P), R = 2-Ad, R' = H (Me, ^{n}Bu, Ph)



D-H_2PPM(P), R = ^{i}Pr, R' = Me(Ph)
D-H_2PCP, R = c-C_6H_{11}, R' = Ph



D-H_2VCP

[a]Ligands used in this study: ^{i}Pr = isopropyl, c-C_6H_{11} = cyclohexyl, 2-Ad = 2-adamantyl.

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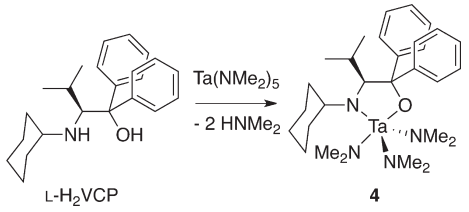
Scheme 4



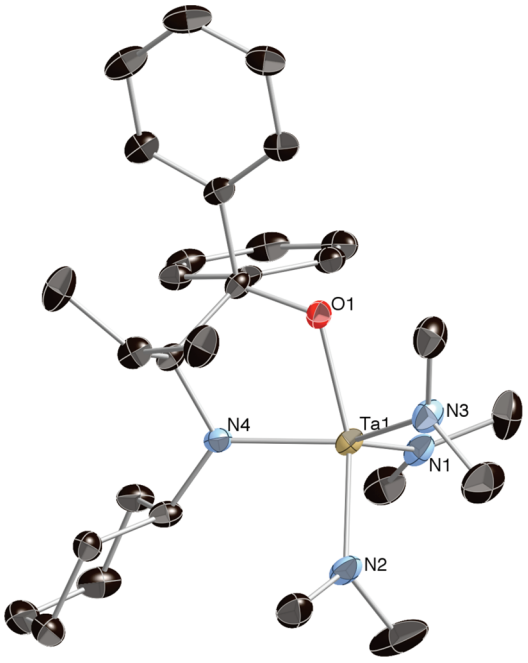


Figure 1. ORTEP of complex **4** showing 50% probability ellipsoids with partial atom-numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ta(1)−N(1) 1.958(2), Ta(1)−N(2) 1.991(2), Ta(1)−N(3) 2.014(2), Ta(1)−N(4) 2.026(2), Ta(1)−O(1) 1.9963(19), N(1)−Ta(1)−N(2) 96.20(10), N(1)−Ta(1)−N(3) 110.14(10), N(1)−Ta(1)−N(4) 114.06(10), N(1)−Ta(1)−O(1) 102.96(9), N(2)−Ta(1)−N(3) 93.76(10), N(2)−Ta(1)−N(4) 90.70(9), N(2)−Ta(1)−O(1) 159.99(9), N(3)−Ta(1)−N(4) 134.76(9), N(3)−Ta(1)−O(1) 85.11(8), N(4)−Ta(1)−O(1) 76.33(8).

for spectra and assignments) supports formation of the complexes due to shifted ligand resonances. Dimethylamine was also observed, indicating that protonolysis of the starting material by the incoming ligand took place. Almost all the tantalum complexes were oils that could not be purified. However, the reaction of $Ta(NMe_2)_5$ with L-H_2VCP in diethyl ether resulted in a solid compound, $Ta(NMe_2)_3$(VCP), **4**. Concentrating the solution by evaporation followed by storage at −35 °C resulted in the formation of crystals suitable for an X-ray crystallographic study. An ORTEP diagram and partial atom-numbering scheme of complex **4** is shown in Figure 1; crystallographic data collection parameters and refinement statistics are listed in Table 1.

The complex shown in Figure 1 adopts a slightly distorted trigonal-bipyramid structure, $R_c(x)$ = 9.8%,[25] with O(1) and N(2) in the axial positions and N(1), N(3), and N(4) in the equatorial positions. The complex is less well described as square pyramidal with apical N(1), $R_c(x)$ = 17.3%,[25] as the basal ligands exhibit significant distortions from the ideal geometry. The N4−Ta1−O1 angle exhibits a large deviation from the ideal trigonal-bipyramidal geometry due to the reduced bite angle of the chelate ring. The equatorial plane bond angles range from 110° to 134°. The sum of bond angles about each of the four nitrogen atoms is just under 360°, as expected for a strongly π-acidic metal center.

Table 1. Crystal Data and Structure Refinement for Complex 4

empirical formula	$C_{29}H_{47}N_4OTa$
fw	648.66
temperature	123(2) K
wavelength	Mo Kα, 0.71073 Å
cryst syst	orthorhombic
space group	*P*2(1)2(1)2(1)
a	9.2269(5) Å
b	16.2635(8) Å
c	19.5119(10) Å
volume	2928.0(3) Å^3
Z	4
density (calcd)	1.471 g/cm^3
absorp coeff	3.781 mm^{-1}
F(000)	1320
cryst size	0.32 × 0.30 × 0.20 mm^3
cryst color, habit	colorless block
θ range for data collection	1.63−25.42°
index ranges	$-11 \le h \le 11$, $-19 \le k \le 17$, $-23 \le l \le 13$
reflns collected	14 424
indep reflns	5384 [*R*(int) = 0.0215]
completeness to theta = 25.00°	100.0%
absorp corr	multiscan
refinement method	full-matrix least-squares on F^2
data/restraints/params	5384/0/324
goodness-of-fit on F^2	0.949
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0156, wR2 = 0.0356
R indices (all data)	R1 = 0.0165, wR2 = 0.0358
largest diff peak and hole	0.507 and −0.260 e Å^{-3}

The Ta−NMe_2 bond distances are 1.958(2), 1.991(2), and 2.014(2) Å; the Ta−N(ligand) distance is 2.026(2) Å, while the Ta−O distance is 1.9963(19) Å. These bond distances are nearly identical to those found in $Ta(NMe_2)_5$,[26] with Ta−N distances from 1.965(5) to 2.038(8) Å. The shortest bond distance in $Ta(NMe_2)_5$ is that of the apical nitrogen in its distorted square-pyramidal structure.

The Cambridge Structural Database does not contain any tantalum complexes with a bidentate amidoalkoxide ligand.[27] Rothwell reported several square-pyramidal complexes of the general form $Ta(NMe_2)_4(OAr)$;[28] each has a basal phenoxide ligand. Ta−N and Ta−O bond distances for these complexes are similar to those reported for complex **4**.

The tantalum complexes of the bidentate amidoalkoxide ligands were prepared *in situ* and examined for catalytic activity

Table 2. Hydroamination of 6-Methylhepta-4,5-dienylamine at 135 °C with Tantalum Amidoalkoxide Catalysts (5 mol %)

entry	ligand	ee/%[a]	conv/%[b]	*t*/h	entry	ligand	ee/%[a]	conv/%[b]	*t*/h
1	L-PPH	13	24	69	16	L-VPH	10	78	162
2	L-PPM	46	100	15	17	L-VPM	2	100	23
3	D-PPM	53[c]	100	20	18	L-VPB	24	39	98
4	L-PPB	1	100	23	19	L-VPP[d]	29	100	15
5	L-PPP	65	100	18	20	L-VCH	7	64	286
6	D-PPP	58[c]	100	21	21	L-VCM	3	90	46
7	L-PCH	13	35	50	22	L-VCB	8	100	43
8	L-PCM	35	100	65	23	L-VCP	74	100	18
9	L-PCB	32	100	23	24	D-VCP	79[c]	100	15
10	L-PCP	80	100	16	25	L-VAH	2	65	336
11	D-PCP	76[c]	100	15	26	L-VAM	3	44	334
12	L-PAH	6	33	116	27	L-VAB	6	100	134
13	L-PAM	2	100	24	28	L-VAP	37	91	42
14	L-PAB	24	100	115	29	none	3	100	525
15	L-PAP	25	28	230					

[a] Determined by GC using Chiraldex B-DM (±5%). [b] Determined by ^{1}H NMR spectroscopy. [c] (+)-Enantiomer was favored. [d] Ligand obtained in 50% ee.

in the hydroamination/cyclization of 6-methylhepta-4,5-dienylamine to 2-(2-methylpropenyl)pyrrolidine. All catalytic reactions were carried out at 135 °C in C_6D_6 in J. Young NMR tubes with 5 mol % catalyst loading. Reactions were monitored periodically by ^{1}H NMR spectroscopy and were quenched when complete or when no further progress was observed after 24 h. Approximately half of the reactions were complete in under 24 h, although reaction times varied greatly (from 15 to more than 300 h), and not every reaction went to 100% conversion. Enantiomeric excesses of the benzamide derivatives were determined by chiral GC-MS as reported previously.[14] Results of the catalytic study are given in Table 2.

Run-to-run repeatability of enantioselectivity values is ±5% ee, which is also approximately the error with repeat injections of the same sample. A sample that had been stored for one year was reinjected and found to have an enantioselectivity within error of the previous value, indicating that the samples do not decompose or racemize over time. Sample GC traces are included in the Supporting Information.

Several trends can be observed from the data. Pairs of ligand enantiomers give approximately equal and opposite stereoselectivity (entries 2, 3, 5, 6, 10, 11, 23, and 24), with D-enantiomers of the ligands favoring the formation of the (+)-enantiomer of the pyrrolidine product. Ligands containing primary alcohol groups tend to have extremely slow and/or low conversion to product (entries 1, 7, 12, 16, 20, and 25). None of the catalysts with a primary alcohol substituent achieved 100% conversion to product, and in most cases, the reaction stopped near 50% conversion. Ligands that had an *N*-adamantyl substituent tended to give extremely poor enantioselectivity (<6% ee) of the pyrrolidine (entries 12, 13, 25, 26, and 27), though several (entries 14, 15, and 28) produced the pyrrolidine product with moderate enantioselectivity (24−37% ee). Ligands that contain phenyl substituents α to the oxygen tended to give high enantioselectivity for the formation of the pyrrolidine product (entries 5, 6, 10, 11, 15, 19, 23, 24, and 28). The six ligands that gave the highest enantioselectivity were (in decreasing order of % ee) entries 10, 11, 23, 24, 5, and 6; these contained phenyl groups α to the oxygen and an *N*-cyclohexyl substituent (entries 10, 11, 23, and 24) or an *N*-isopropyl substituent (entries 5 and 6).

Since the enantioselectivity of the catalysis was consistently high for the L-VCP ligand (entry 23), we sought to determine the absolute stereochemistry of the pyrrolidine product. A reaction using this ligand was quenched with benzyl bromide and triethylamine to form the *N*-benzyl derivative; analysis of the derivative by polarimetry showed it to also be the (−)-enantiomer. A number of closely related pyrrolidines consistently give a negative optical rotation for the *N*-benzyl-(*S*)-enantiomer,[29] which suggests that we are also favoring the formation of the (*S*)-enantiomer of the pyrrolidine.

^{1}H NMR spectroscopy of the precatalyst solutions showed that there was usually either a slight excess of the free ligand or $Ta(NMe_2)_5$. We carried out several experiments to determine the effects (if any) of carrying out our catalytic reactions *in situ*. First, a control experiment was carried out using $Ta(NMe_2)_5$ with no added chiral ligand (entry 29). $Ta(NMe_2)_5$ does catalyze the reaction (albeit slowly, and with essentially no enantioselectivity), so it is possible that some of the reactions with slow conversion or low enantioselectivity may in fact be due to catalysis by the tantalum precursor complex instead of the amidoalkoxide complex.

We then carried out thermal stability studies of the precatalyst solutions to look for ligand redistribution or decomposition. Approximately half of our precatalyst solutions were heated at 135 °C for extended periods (>18 h), but no significant changes to the ^{1}H NMR spectra were observed over this time period; importantly, we did not notice formation of either $Ta(NMe_2)_5$ or free ligand.

Next, a more detailed study was carried out to determine the effect of either a deficiency or excess of free ligand on the catalytic reaction and enantioselectivity. About half of the ligands were examined for catalysis with ligand to metal ratios that varied from 0.6:1 to 2:1. Changing the ratio of ligand to metal does not in most cases significantly change the enantioselectivity of the reaction (see Supporting Information for details). In two cases, decreasing the ligand to metal ratio below 1:1 showed a change in enantioselectivity on the order of 20% ee (L-PPB increased to 24% ee from 1% ee, and L-VCB increased to 20% ee from 8% ee); the ligands L-PPP, D-PPP, L-PAH, L-VPB, L-VAM, and L-VAB all showed slight or no decrease in enantioselectivity with reduced L:M ratios. Increasing the L:M ratio above 1:1 significantly changed the observed enantioselectivity for three ligands (L-PPH decreased to 2% ee from 13% ee, L-PPP decreased to 21% ee from 65% ee, and L-PAP increased to 50% ee from 25% ee); the ligands D-PPP, L-VPM, and L-VAH did not exhibit significant changes in selectivity. No obvious trends are present in these data.

Finally, experiments were carried out to investigate any differences between isolated and *in situ* prepared complexes. The complexes derived from L-VCP, L-PPP, L-VAM, and L-PPH were prepared on a small scale (30−50 mg) in diethyl ether, and residual solvent and dimethylamine were removed *in vacuo*. These ligands were chosen to span a wide range of observed enantioselectivities. As the complexes (even complex **4** on this small scale) were isolated as oils, they were used as obtained in a catalytic study; the results are presented in Table 3. The observed enantioselectivities for the *in situ* and isolated complexes are almost identical for L-VCP and L-PPP (entries 1−4), while for L-VAM the isolated complex shows a slightly higher selectivity

Table 3. Comparison of Hydroamination with *in Situ* or Isolated Tantalum Amidoalkoxide Catalysts

entry	ligand		ee/%[a]	conv/%[b]	*t*/h
1	L-VCP	isolated	68	100	16
2		*in situ*[c]	74	100	18
3	L-PPP	isolated	63	38	39
4		*in situ*[c]	65	100	18
5	L-VAM	isolated	12	83	133
6		*in situ*[c]	3	44	335
7	L-PPH	isolated	8	28	135
8		*in situ*[c]	13	24	69

[a] Determined by GC using Chiraldex B-DM (±5%). [b] Determined by ^{1}H NMR spectroscopy. [c] Data from Table 2.

(entry 5) and for L-PPH the isolated complex shows a slightly lower selectivity (entry 7). The results of this and the previous experiments show that our system is robust to slight differences in L:M ratio that are hard to avoid by our *in situ* method.

We then sought to determine why some catalytic reactions stalled or were more sluggish than others. There was some ^{1}H NMR evidence that suggested that trace amounts of THF might be responsible for the reaction stalling, so we examined hydroamination with deliberately added solvents. Either THF or diethyl ether were added to a catalytic reaction using the tantalum complex of the D-PPP ligand. Addition of solvent either at the start or at approximately 25% or 75% conversion showed minimal changes in enantioselectivity and conversion and did not noticeably slow the reaction progress.

We also examined the effect of temperature on enantioselectivity by carrying out six reactions at 100 °C. Catalysts derived from L-PPH, L-PCH, and L-PAM did not react at this lower temperature. Of the remaining three ligands, L-PPP, L-VPP, and L-VPM, the time to reach 100% conversion was slower, but enantioselectivities were within error except for the reaction catalyzed by L-VPM, which gave a slightly higher selectivity of 14% ee (instead of 2% ee for the reaction at 135 °C). Our previous studies have also not shown a significant increase in enantioselectivity of the reaction at reduced temperature.[14,18]

The tantalum catalysts with ligands derived from the L-amino acids preferentially formed the (−)-enantiomer of the pyrrolidine, while titanium catalysts preferentially form the (+)-enantiomer. The tantalum catalysts in almost all cases give the pyrrolidine in higher enantiomeric excess than the corresponding titanium catalysts;[17] there are only two ligands that gave higher enantioselectivity with titanium (L-PAH and L-VAB), though even on titanium these two ligands gave low enantioselectivity (<15% ee).

We considered that the monomeric structure of the tantalum complexes, as opposed to the dimeric structure of the corresponding titanium complexes,[14] is important for the improved enantioselectivity for hydroamination. We attempted solution molecular weight determinations to verify the monomeric nature of the tantalum complexes in solution,[30] but the results have not been reproducible due to precipitation of the complexes and decomposition over the long time periods to reach equilibrium for this measurement. We are continuing to examine the system both experimentally and computationally in order to address this hypothesis.

Although the tantalum-catalyzed cyclizations reported here result in pyrrolidine products with significantly higher enantiomeric excesses than those we have previously observed with titanium, there are reports of gold(I) phosphine complexes that catalyze the intramolecular hydroamination of a number of *N*-tosylated aminoallene substrates (including the *N*-tosylated derivative of substrate **1**) with enantioselectivity above 98% ee.[11b,12] Similar results have been seen for the asymmetric cyclization of other aminoallenes with *gem*-dialkyl substituents.[11c] However, the substrates for gold catalysis all contain protecting groups on nitrogen, and no primary amine substrates were examined. Two recent reports describe the tantalum-catalyzed intramolecular hydroamination of closely related aminoalkene substrates that led to cyclized pyrrolidine products with up to 80% ee.[22] It is worth noting, however, that these substrates include *gem*-dialkyl substituents as opposed to the straight-chain aminoallenes described here.

CONCLUSIONS

Procedures for the synthesis of chiral bidentate amino alcohols were optimized, allowing for the synthesis of a new sterically bulky derivative of valine. A tantalum complex of one amido alkoxide ligand was prepared and found to be monomeric by X-ray crystallography. A series of tantalum complexes of these ligands was investigated for the *in situ* catalytic asymmetric hydroamination of aminoallenes. The L-enantiomers of the ligands preferentially form (−)-2-(2-methylpropenyl)pyrrolidine, which we tentatively assign as the (*S*)-enantiomer. The tantalum complexes catalyzed the reaction with significantly higher enantioselectivity than their titanium counterparts. Ligands containing phenyl substituents α to the alcohol oxygen tend to give the pyrrolidine product with high enantioselectivity. Future work will be aimed at establishing the mechanism of this transformation in order to better design our catalysts.

EXPERIMENTAL SECTION

General Procedures. All reagents were obtained from commercial suppliers and were purified by standard methods[31] or used as received. Ligands were prepared by literature procedures.[14,17] Solvents were purified by vacuum transfer from sodium/benzophenone (C_6D_6) or by passage through a column of activated alumina (Innovative Technology PS-400-5-MD) and stored under nitrogen. Solutions of ligands (ca. 0.05 M in C_6D_6) and 6-methylhepta-4,5-dienylamine (ca. 1.5 M in C_6D_6) for catalysis were dried over molecular sieves overnight and stored at −35 °C. All air- and/or moisture-sensitive compounds were manipulated under an atmosphere of nitrogen using standard Schlenk techniques or in a glovebox (MBraun Unilab). ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature on a Brüker Avance 400 spectrometer. Carbon assignments of complex **4** were made using DEPT experiments. Polarimetry was carried out using a JASCO P1010 instrument. GC analysis was carried out using a Hewlett-Packard 5890 Series II gas chromatograph. Mass spectra were obtained at the Mass Spectrometry Laboratory, California Institute of Technology, Pasadena, CA. Elemental analyses were performed by Columbia Analytical Services, Tucson, AZ.

L-N-Isopropyldiphenylvalinol (L-H_2VPP). L-*N*-Isopropylvaline methyl ester (490 mg, 2.83 mmol) was dissolved in diethyl ether (20 mL) and stirred under N_2. The reaction was cooled to −78 °C. Phenylmagnesium bromide (3.8 mL, 3 M in diethyl ether, 11.4 mmol) was added dropwise. The reaction was allowed to stir and warm to room temperature for approximately 40 h. The reaction was then cooled to 0 °C and quenched by the addition of 1:1 saturated ammonium chloride/deionized water (30 mL:30 mL), which gave a transparent, bright yellow solution.

The aqueous layer was washed with diethyl ether (2 × 50 mL). The combined organic layers were dried with anhydrous magnesium sulfate and concentrated to yield a white powder. Some of the product was purified by column chromatography (3% ethyl acetate, 0.5% triethylamine, 96.5% hexanes). This was combined with microcrystals obtained by slow cooling from 3:1 ethyl acetate/hexanes solution to yield a white, microcrystalline powder (82.9 mg, 0.28 mmol, 10%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (dd, 2H, J = 1.2 Hz, 8.5 Hz, *o*-Ar*H*), 7.55 (dd, 2H, J = 1.2 Hz, 8.4 Hz, *o*-Ar*H*), 7.25 (m, 4H, *m*-Ar*H*), 7.17 (m, 2H, *p*-Ar*H*), 5.75 (br s, 1H, N*H*), 3.64 (d, 1H, J = 1.8 Hz, C*H*^{i}Pr), 2.24 (m, 1H, NC*H*Me$_2$), 2.05 (m, 1H, CC*H*Me$_2$), 1.03 (d, 3H, J = 7.0 Hz, CCH*Me*Me′), 0.99 (d, 3H, J = 6.5 Hz, NCHMe*Me*′), 0.87 (d, 3H, J = 6.4 Hz, NCH*Me*Me′), 0.61 (d, 3H, J = 6.8 Hz, CCHMe*Me*′). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.4, 146.1, 128.1, 126.5, 65.4, 47.6, 28.9, 24.2, 23.4, 16.2. HRMS (EI+): calcd for $C_{20}H_{28}ON$ 298.2171, found 298.2144. $[\alpha]_D$ = −37 (*c* 2.09 g/mL, EtOAc). Mp: 111−112 °C.

Chiral Shift Study of L-H$_2$VPP. A solution of L-H$_2$VPP (0.050 M, 400 μL, 0.020 mmol) was examined by ^{1}H NMR spectroscopy. A solution of (*S*)-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol (0.18 M, 110 μL, 0.020 mmol) was added to the NMR tube, and the solution was reexamined. Additional shift reagent (2 equiv total) was added, and the solution was reexamined. A shoulder was observed on two of the four isopropyl methyl doublets. Simulation of the methyl doublets using gNMR suggested approximately 25% of the D-enantiomer or an enantiomeric excess of 50% ee.

D-N-Isopropyldimethylphenylalaninol (D-H$_2$PPM). The D-enantiomer of PPM was prepared analogously to the L-enantiomer, starting from D-*N*-isopropylphenylalanine ethyl ester hydrochloride (2.06 g, 9.6 mmol) dissolved in THF (75 mL) and methylmagnesium bromide (22 mL, 3 M in ether) to yield a yellow oil (1.9 g, 8.5 mmol, 88% yield). The product was purified by flash chromatography (5% ethyl acetate, 0.1% triethylamine, 94.9% hexanes). NMR spectroscopy confirmed the formation of the desired ligand with essentially equal and opposite optical rotation.[17] HRMS (FAB+): calcd for $C_{14}H_{24}ON$ 222.1858, found 222.1868 (M + H$^+$). $[\alpha]_D$ = +19.7 (*c* 2.18 × 10^{-2} g·mL^{-1}, EtOAc).

D-N-Isopropyldiphenylphenylalaninol (D-H$_2$PPP). The D-enantiomer of PPP was prepared analogously to the L-enantiomer,[17] starting from D-*N*-isopropylphenylalanine methyl ester[14] (0.632 g, 3.01 mmol) in diethyl ether (35 mL) and phenylmagnesium bromide (4 mL, 3 M in diethyl ether, 12 mmol) to yield pale yellow crystals that were recrystallized from hexanes (0.2777 g, 0.81 mmol, 27%). NMR spectroscopy confirmed the formation of the desired ligand with essentially equal and opposite optical rotation.[17] $[\alpha]_D$ = −3.5 (*c* 9.75 × 10^{-3} g·mL^{-1}, EtOAc).

D-N-Cyclohexyldiphenylvalinol (D-H$_2$VCP). The D-enantiomer of VCP was prepared analogously to the L-enantiomer,[17] starting from D-*N*-cyclohexylvaline methyl ester (0.878 g, 4.12 mmol) in diethyl ether (35 mL) and phenylmagnesium bromide (5.5 mL, 3 M in diethyl ether, 16.5 mmol) to yield a white powder that was recrystallized from ethanol (0.4373 g, 1.36 mmol, 33%). NMR spectroscopy confirmed the formation of the desired ligand with essentially equal and opposite optical rotation.[17] $[\alpha]_D$ = +39.0 (*c* = 1.07 × 10^{-2} g·mL^{-1}, EtOAc).

D-N-Cyclohexyldiphenylphenylalaninol (D-H$_2$PCP). The D-enantiomer of PCP was prepared analogously to the L-enantiomer,[17] starting from D-*N*-cyclohexylphenylalanine methyl ester (288.6 mg, 1.34 mmol) in diethyl ether (60 mL) and phenylmagnesium bromide (3 M in THF, 2.3 mL, 6.9 mmol) to yield an orange oil, which was purified by column chromatography (20% ethyl acetate, 80% hexanes) to yield a white solid. The solid was recrystallized from boiling ethanol to yield a white microcrystalline powder (75.8 mg, 0.20 mmol, 15%). NMR spectroscopy confirmed the formation of the desired ligand with essentially equal and opposite optical rotation.[17] $[\alpha]_D$= −6.85 (*c* 8.9 × 10^{-3} g·mL^{-1}, EtOAc).

*Tris(dimethylamide)(L-VCP)tantalum (**4**).* In the glovebox at room temperature, tantalum pentakis(dimethylamide) (520 mg, 1.29 mmol) and L-*N*-cyclohexyldiphenylvalinol (439 mg, 1.30 mmol) were dissolved in diethyl ether (10 mL), which was allowed to slowly evaporate. When approximately 2 mL of diethyl ether was remaining, the solution was allowed to stand overnight and then stored at −35 °C. The resulting light yellow crystals were collected by vacuum filtration. The slow evaporation procedure was repeated with the collected crystals to yield colorless crystals (466 mg, 0.72 mmol, 55%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.70 (d, 2H, J = 7.2 Hz, Ar*H*), 6.9−7.2 (m, 8H, Ar*H*), 4.82 (m, 1H, NC*H*^{i}Pr), 3.23 (s, 18H, N*Me*$_2$), 2.20 (m, 1H, CC*H*Me$_2$), 1.90 (d, 1H, J = 11.0 Hz, Cy*H*), 1.79 (d, 2H, J = 10.6 Hz, Cy*H*), 1.61 (d, 1H, J = 12.3 Hz, Cy*H*), 1.45 (m, 1H, Cy*H*), 1.0−1.4 (m, 6H, Cy*H*), 1.21 (d, 3H, J = 7.2 Hz, CH*Me*Me′), 0.95 (d, 3H, J = 7.4 Hz, CHMe*Me*′). ^{13}C NMR (100 MHz, C_6D_6): δ 153.2 (4°, Ar), 149.9 (4°, Ar), 127.5 (CH, Ar), 126.8 (CH, Ar), 125.7 (CH, Ar), 125.6$_9$ (CH, Ar), 94.5 (4°), 78.1 (CH), 66.2 (CH), 46.0 (CH_3, NMe_2), 38.8 (cyclohexyl CH_2), 35.8 (cyclohexyl CH_2), 34.0 (CH), 27.6 (cyclohexyl CH_2), 27.5 (cyclohexyl CH_2), 26.7 (cyclohexyl CH_2), 22.0 (isopropyl CH_3), 19.6 (isopropyl CH_3) (two of the eight aryl carbons overlap other signals). Anal. Calcd: C, 53.76; H, 7.30; N, 8.64. Found: C, 53.52; H, 7.64; N, 8.62. Mp: 138−141 °C.

General Hydroamination Procedure. Hydroamination was carried out with 5 mol % catalyst loading. Inside the glovebox, deuterated benzene (175 μL), Ta(NMe$_2$)$_5$ (100 μL of a 0.0375 M solution, 3.75 × 10^{-3} mmol), ligand (75 μL of a 0.05 M solution, 3.75 × 10^{-3} mmol), and 6-methylhepta-4,5-dienylamine (50 μL of a 1.5 M solution, 0.075 mmol, 20 equiv) were combined in a medium-walled J. Young NMR tube, and an ^{1}H NMR spectrum was taken. The tube was placed in a 135 ± 2 °C oil bath and monitored by ^{1}H NMR until the reaction reached completion or stopped converting. Percent conversion was determined by NMR spectroscopy.

Benzamide Derivative. The reaction mixture was quenched with 2-propanol (1 mL) and added to a 20 mL vial along with diethyl ether (3 mL), benzoyl chloride (9 μL, 0.08 mmol), and triethylamine (21 μL, 0.15 mmol). After stirring at room temperature for 2 h, water (1 mL) was added, the layers were separated, and the organic layer was washed with brine and dried with magnesium sulfate. The crude benzamide solution (0.2−0.5 μL) was injected on the GC capillary column (Chiraldex B-DM, 30 m × 0.25 μm, 100 °C, 8 min, 1 °C/min to 180 °C, 180 °C, 15 min). The two enantiomers were separated with retention times of approximately 135 and 136 min. The latter time corresponds to the enantiomer with negative optical rotation.

Benzyl Derivative. Benzyl bromide (9 μL, 0.08 mmol) and triethylamine (21 μL, 0.15 mmol) were added to the J. Young NMR tube of a completed hydroamination reaction (0.075 mmol). The tube was left to sit for 18 h, and a crystalline solid precipitated out of solution. 2-Propanol (100 μL) was added to the solution, which was then filtered through glass fibers in a pipet filter. The clear solution was diluted to a total volume of 2 mL with benzene. The crude solution (0.2−0.5 μL) was injected on the GC capillary column (Chiraldex B-DM, 30 m × 0.25 μm, 100 °C, 8 min, 1 °C/min to 180 °C, 180 °C, 15 min). The two enantiomers were separated with retention times of approximately 100 and 101 min. The later time corresponds to the enantiomer with negative optical rotation.

Polarimetry of N-Benzyl Derivative. Benzyl bromide (9 μL, 0.08 mmol) and triethyl amine (21 μL, 0.15 mmol) were added to the product of a hydroamination catalyzed by Ta(NMe$_2$)$_5$ and L-VCP and left to stand overnight. 2-Propanol (100 μL) was added, and the reaction mixture was filtered through glass fibers and then diluted to a total volume of 2.0 mL with benzene. The polarimetry reading (α) was −0.23°; thus the enantiomer with the longer retention time is the (−)-enantiomer. The specific rotation was calculated, considering the enantioselectivity of the reaction (53% ee for this run, as determined by GC-MS), $[\alpha]_D$ = −54 (*c* 8.08 × 10^{-3} g·mL^{-1}, benzene).

Synthesis and Isolation of Complexes for Hydroamination Study. Ta(L-VCP)$(NMe_2)_3$ (**4**) was prepared by combining $Ta(NMe_2)_5$ (34 mg, 0.085 mmol) and L-H_2VCP (30 mg, 0.089 mmol) in diethyl ether (2 mL). The solvent was removed on the vacuum line to yield a yellow oil, which was dissolved in C_6D_6 to make a hydroamination solution (1.70 mL, 0.050 M). Ta(L-PPP)$(NMe_2)_3$ was prepared similarly from $Ta(NMe_2)_5$ (39 mg, 0.097 mmol) and L-H_2PPP (35 mg, 0.10 mmol) and dissolved in C_6D_6 (1.70 mL, 0.050 M). Ta(L-VAM)-$(NMe_2)_3$ was prepared similarly from $Ta(NMe_2)_5$ (43 mg, 0.11 mmol) and L-H_2VAM (29 mg, 0.11 mmol) and dissolved in C_6D_6 (2.10 mL, 0.051 M). Ta(L-PPH)$(NMe_2)_3$ was prepared similarly from $Ta(NMe_2)_5$ (35 mg, 0.087 mmol) and L-H_2PPH (17 mg, 0.088 mmol) and dissolved in C_6D_6 (1.75 mL, 0.050 M). Hydroamination with the isolated complexes was carried out by combining deuterated benzene (275 μL), the complex solution (75 μL of a 0.05 M solution, 3.75×10^{-3} mmol), and 6-methylhepta-4,5-dienylamine (50 μL of a 1.5 M solution, 0.075 mmol, 20 equiv), and the reaction was monitored as described previously.

Hydroamination at 100 °C. Hydroamination was carried out with 5 mol % catalyst loading. Inside the glovebox, deuterated benzene (175 μL), $Ta(NMe_2)_5$ (100 μL of a 0.0375 M solution, 3.75×10^{-3} mmol), ligand (75 μL of a 0.05 M solution, 3.75×10^{-3} mmol), and 6-methylhepta-4,5-dienylamine (50 μL of a 1.5 M solution, 0.075 mmol, 20 equiv) were combined in a medium-walled J. Young NMR tube, and an ^{1}H NMR spectrum was taken. The tube was placed in a 100 ± 2 °C oil bath and monitored by ^{1}H NMR until the reaction reached completion or stopped converting. Percent conversion was determined by NMR spectroscopy. Enantioselectivity was determined as previously described.

*X-ray Crystal Structure of Tris(dimethylamide)(L-VCP)tantalum (**4**).* Suitable crystals were obtained by prolonged storage of an diethyl ether solution of **4** at −35 °C. A colorless block with approximate dimensions of 0.32 × 0.30 × 0.20 mm was used for the X-ray crystallographic analysis. The crystal was mounted on a Cryoloop with Paratone-N oil. Diffraction intensity data were collected at 123(2) K using a Brüker Apex-II CCD diffractometer equipped with a graphite monochromator and a Mo Kα fine-focus sealed tube. Crystal data and refinement parameters are summarized in Table 1. The systematic absences in the diffraction data are consistent with the orthorhombic space group $P2_12_12_1$. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. The correct absolute structure was unambiguously determined; Flack parameter = 0.002(6).[32] Data were corrected for absorption effects using SADABS.[33] All non-hydrogen atoms were refined with anisotropic displacement coefficients, and hydrogen atoms were treated as idealized contributions. All software and sources of scattering factors are contained in the SHELXTL (6.10) program package (G. Sheldrick, Brüker XRD, Madison, WI).[34] Images were generated using CrystalMaker.[35]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Additional experimental details, characterization data, and NMR spectra for the *in situ* prepared complexes, sample GC traces, and complete crystallographic data as a CIF file for compound **4** are available free of charge via the Internet at http://pubs.acs.org. CCDC 817406 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: Adam_Johnson@hmc.edu.

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