Stereo- and Regiocontrolled Construction of Trisubstituted Piperidines Using a $TpMo(CO)_2$(Dihydropyridine) Scaffold (Tp = Hydridotrispyrazolylborate)

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Cationic $TpMo(CO)_2$(dihydropyridine) complexes (Tp = hydridotrispyrazolylborate), readily generated from 3-oxo-3,6-dihydro-2*H*-pyridine-1-carboxylic acid benzyl ester, represent scaffolds from which (by judicious choice of demetalation conditions) either 2,3,6- or 2,5,6-trisubstituted-1,2,3,6-tetrahydropyridines can be prepared in a regio- and stereodefined way.

Introduction

The sequential, multistep, stereo- and regiocontrolled functionalization−demetalation of stoichiometric transition metal π-complexes has received considerable attention as a means of producing highly substituted organic molecules.[1−14] Stoichiometric π-complexes of molybdenum bound to polyene ligands are especially well suited to this task.[1,15,16] In this regard, hydridotris(1-pyrazolyl)borate (Tp)[17−19] used in place of the more commonly studied cyclopentadienyl (Cp) auxiliary ligand has significantly extended the applicability of the molybdenum-based methodology.[6,8,20−25] In particular, the $TpMo(CO)_2$ ligand set has rendered useful the functionalization of a variety oxygen-containing heterocyclic systems.[8,23,26] Since the core units of a vast number of biologically active synthetic and natural products are nitrogen-containing heterocycles,[27] the $TpMo(CO)_2$-based synthetic methodology could prove of use in the stereocontrolled construction of these systems, also. To that effect, we report herein the synthesis, functionalization, and demetalation of a chiral, racemic $TpMo(CO)_2$(dihydropyridine) complex and its use in the synthesis of 2,3,6-trisubstituted tetrahydropyridines and piperidines. These studies represent a prelude to current efforts to develop an enantiocontrolled synthesis of substituted piperidines, the full details of which will be reported in due course.

Results and Discussion

Formation of 2,3,6-Trisubstituted $TpMo(CO)_2(\eta^3$-allyl) Complexes. Molybdenum π-allyl complex **2** was derived from dihydropyridinone **1b** (Scheme 1), which was prepared from the known **1a** by exchange of *N*-protecting groups. Dihydropyridinone **1a** was available on large scale in three steps from commercially available *N*-benzylglycine ethyl ester through a modification of a literature procedure.[28,29] The previously described[22] oxidative addition of $Mo(DMF)_3(CO)_3$ to an enone followed by *O*-methylation was used to generate molybdenum complex **2** (the *O*-silylated material was too labile to be of use, while *O*-acetylation gave a complex that could not be converted into a cationic diene complex by hydride abstraction). The robust *O*-methyl complex **2** proved to be a useful starting point for the synthesis of a variety substituted piperidines.

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Scheme 1. Generation of Dihydropyridine Complex 3 from Dihydropyridone 1b

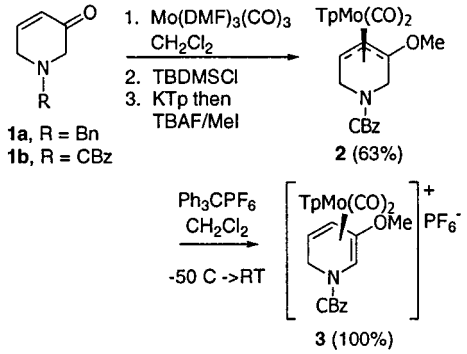
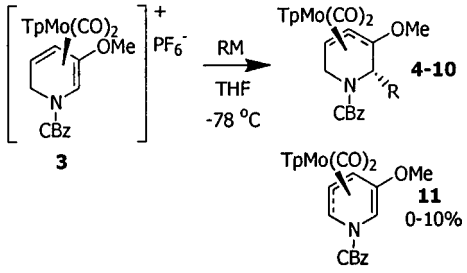


Table 1. Nucleophilic Functionalization of Dihydropyridine Complex 3



compd	RM	yield (%)
4	MeMgBr	83
5	EtMgBr	71
6	BnMgBr	77
7	VinylMgBr	67
8	PhMgBr	66
9	$LiCH_2CO_2Et$	52
10	AllylMgBr	69

Complex **2** underwent hydride abstraction using Ph_3CPF_6 and gave the cationic diene complex **3** in quantitative yield (Scheme 1). In this hydride abstraction, the exclusive formation of the cross-conjugated system over the alternate linearly conjugated regioisomer is consistent with Pearson's earlier studies of stoichiometric organoiron π-complexes, where frontier molecular orbital arguments were used to rationalize the selectivity.[7] In the present case, the regiochemistry of the hydride abstraction was established through the examination of ^{1}H NMR coupling constants. The C-2 proton appears as a broad singlet at 7.60 ppm, and the protons at C-4 and C-5 are observed as a doublet (δ = 5.60 ppm, J = 8.4 Hz) and an apparent doublet of doublets (δ = 5.44 ppm, J = 8.4 and 3.2 Hz), respectively.

Treatment of cationic complex **3** with various Grignard reagents and a lithium enolate gave the anticipated nucleophilic addition products **4**−**10** in good yield, along with small amounts of the corresponding neutral η^3-pentadienyl complex **11**, formed by competitive deprotonation of **3** (Table 1). Although sensitive to silica gel, the derived products **4**−**10** were readily purified by chromatography using basic alumina. Consistent with earlier studies of the analogous Cp- and $TpMo(CO)_2$(dihydropyran) complexes,[10,11,26] the addition of nucleophiles to the dihydropyridinone complexes was regio- and stereocontrolled, giving only the products from nucleophilic attack at the end of the coordinated diene adjacent to the *N*-heteroatom, and anti to the molybdenum moiety.

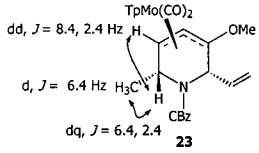
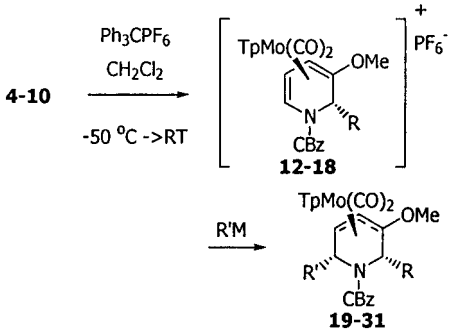


Figure 1. ^{1}H NMR Analysis of compound **23** substitution pattern.

Table 2. Synthesis of 2,3,6-Trisubstituted Dihydropyridinyl Complexes



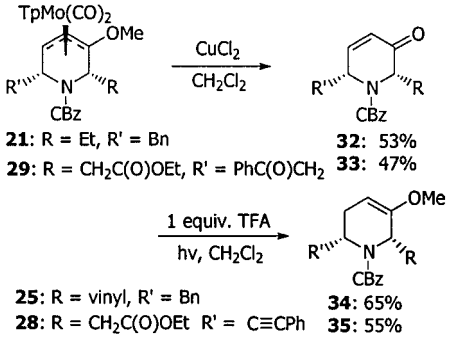
compd	R	compd, yield (%)	R′M	compd, yield (%)
4	methyl	**12** (90)	vinylMgBr	**19** (62)
5	ethyl	**13** (94)	phenylMgBr	**20** (43)
			BnMgBr	**21** (76)
6	benzyl	**14** (94)	EtMgBr	**22** (66)
7	vinyl	**15** (86)	MeMgBr	**23** (76)
			EtMgBr	**24** (78)
			BnMgBr	**25** (75)
8	phenyl	**16** (84)	vinylMgBr	**26** (55)
			EtMgBr	**27** (73)
9	CH_2CO_2Et	**17** (78)	PhC≡CLi	**28** (58)
			$PhC(OLi)=CH_2$	**29** (43)
10	allyl	**18** (68)	PhC≡CLi	**30** (67)
			$PhC(OLi)=CH_2$	**31** (54)

The structures were determined through two-dimensional ^{1}H NMR analysis (vide infra).

Further functionalization of the dihydropyridine scaffold was achieved through a selective second hydride abstraction from tetrahydropyridinyl complexes **4**−**10**, which gave the corresponding cationic dienes **12**−**18** (Table 2). In this second regiocontrolled hydride abstraction, only the C−H bond that is situated anti to the $TpMo(CO)_2$ moiety is properly oriented and accessible to the triphenylcarbenium for abstraction. The derived cationic diene complexes **12**−**18** underwent a second nucleophilic addition with commercially available Grignard reagents, two lithium enolates, and one lithium acetylide, giving only a single isolable product in each case. Although the yields for the second addition were slightly reduced from those of the first, the remainder of the mass balance was an intractable polar material that was easily removed by basic alumina chromatography.

Both termini of the coordinated dienes **12**−**18** are available for nucleophilic attack. The site of the second nucleophilic addition was determined through a study of compound **23** (Figure 1) whose ^{1}H NMR spectrum showed doublets at both 1.43 and 1.42 ppm (rotamers) with J = 6.4 Hz, which were assigned to the methyl substituent. The corresponding COSY spectrum allowed identification of a doublet of quartets (J = 6.4 and 2.4 Hz) at 4.56 and 4.48 ppm (rotamers) to which the doublet was coupled. This methyne was in turn coupled to one

Scheme 2. Oxidative and Protic Decomplexation of Dihydropyridinyl Complexes



of the terminal π-allyl protons, which was observed as a doublet of doublets (J = 8.4 and 2.4 Hz) at 3.98 and 3.92 ppm (rotamers). These data unambiguously confirm addition of the nucleophile α to nitrogen not oxygen, and consequently confirm the regiochemistry of the first nucleophilic addition.

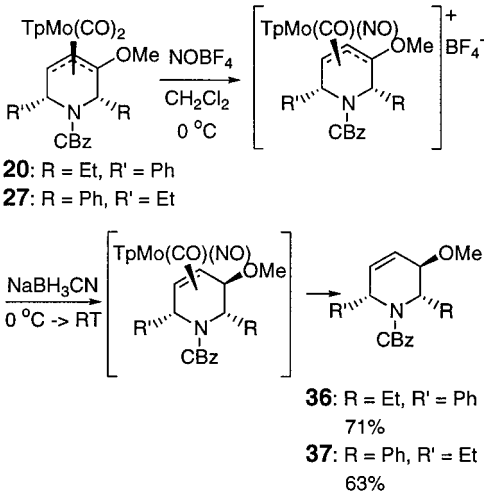
Decomplexation of 2,3,6-Trisubstituted TpMo(CO)$_2$(η^3-allyl) Complexes. Three different decomplexation protocols were explored: an oxidative decomplexation,[30] a photolytic protodemetalation,[31,32] and a reductive decomplexation using CO → NO$^+$ exchange to activate the metal complex prior to hydride addition.[26] Each of these protocols gave a unique array of functionality, each of which has potential utility for further synthetic manipulations.

Oxidative decomplexation of compounds **21** and **29** with cupric chloride (6 equiv) gave the corresponding enones **32** and **33** in moderate yield, as shown in Scheme 2, but the procedure was not general. Attempted oxidative decomplexation of other complexes led to decomposition or epimerization of the stereocenters. While direct protodemetalation with TFA in CH_2Cl_2 was not successful, a photoinduced protodemetalation protocol gave the desired tetrahydropyridines. Irradiation (350 nm lamp) through Pyrex of a 0.005 M solution of compound **25** or **28** in CH_2Cl_2 solution in the presence of 1 equiv of trifluoroacetic acid gave the desired protodemetalation products **34** and **35**.

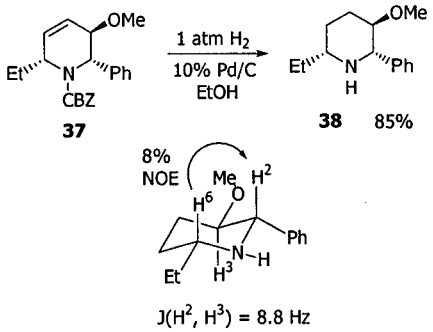
Treatment of a TpMo(CO)$_2$(η^3-allyl) complex with nitrosonium tetrafluoroborate generates a cationic TpMo(CO)(NO)(eta-3-allyl) complex that is susceptible to nucleophilic attack.[25,26] Application of this activation procedure to TpMo(CO)$_2$(dihydropyridinyl) complexes **20** and **27** followed by reduction of the intermediate cationic η^3-allyl complex with $NaBH_3CN$ gave tetrahydropyridines **36** and **37** as shown in Scheme 3. Note that either of two isomeric tetrahydropyridines can be prepared by application of the pertinent decomplexation protocol (**34** and **35** in Scheme 2 or **36** and **37** in Scheme 3).

Delivery of the hydride nucleophile at C3 of complexes **20** and **27** in Scheme 3 (adjacent to the methoxy substituent and anti to the molybdenum[11]) was rigorously established through a careful examination of the coupling constants of the trisubstituted piperidine **38**. Piperidine **38** was produced from tetrahydropyridine **37** upon treatment under one atmosphere of hydrogen in the presence of 10 mol % of palladium on carbon (Scheme 4). Examination of the ^{1}H NMR spectrum of **38** revealed a coupling constant of 8.8 Hz between H2 and H3, which is consistent with a trans diaxial relationship[33] and implies a chair conformation for **38** in which the phenyl group occupies an equatorial position. If the ethyl group at the 6-position is cis to the phenyl group, as expected, the protons at C2 and C6 should be 1,3-diaxial. To confirm this an NOE difference spectrum was obtained. Irradiation of H2 or H6 gave an 8% enhancement of the other, supporting the assigned relative stereochemistry depicted for compound **38** shown in Scheme 4.

Scheme 3. Regio- and Stereocontrolled Decomplexations



Scheme 4 ^{1}H NMR Analysis of Compound 23 Substitution Pattern



Conclusions

A strategy for the stereocontrolled placement of three substituents around a π-coordinated dihydropyridinyl-metal−ligand auxiliary has been described. This facile, sequential introduction of substituents to a late, common heterocyclic scaffold suggests that this methodological sequence would be amenable to the generation of libraries of analogous tetrahydropyridines and piperidines for use in screening and structure−activity relationship studies. Optimization of the reaction sequences, generalization of the substituents beyond those demonstrated in this work, and expansion of the methodology to the synthesis of enantiomerically pure molybdenum complexes are currently under active investigation. A general synthesis of enantiomerically pure trisubstituted piperidines using this methodology will be reported in due course.

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Experimental Section

General Methods. All reactions were performed under a positive pressure of nitrogen, in flame-dried glassware. All solvents were dried over 4 Å molecular sieves and titrated with a Fisher Coulomatic Karl Fischer titrator prior to use. Solvents were degassed by purging with nitrogen. Analytical thin-layer chromatography (TLC) was performed on glass plates precoated with Merck F_{254} silica gel 60, 0.25 mm thickness, and visualized by UV light and a 5% solution of phosphomolybdic acid in ethanol. Column chromatography was performed with mixtures of hexane and ethyl acetate on Aldrich aluminum oxide, activated basic, Brockman I, under a positive pressure of nitrogen. ***Presentation of the ^{1}H and ^{13}C NMR spectra of the N−Cbz protected π-allylmolybdenum and cationic diene complexes requires comment.*** *These compounds show multiple and sometimes broadened resonances because of urethane* ***and*** *allylmolybdenum conformational isomers. Therefore, ^{1}H NMR and ^{13}C NMR spectra of all η-3 allylmolybdenum complexes were run in DMSO-d_6 at 80 °C, ^{1}H NMR and ^{13}C NMR spectra of all η-4 cationic diene complexes were run at room temperature in CD_2Cl_2, and ^{1}H NMR spectra of all final decomplexed organic products were run in DMSO-d_6 at 60 °C. Depending on the structure, only partial coalescence was sometimes achieved in spectra taken at 60−80 °C, and either too many or two few (from significant broadening) signals were observed. ^{1}H NMR spectra of organic products (**32**−**37**) were taken at 60 °C to achieve full coalescence of the urethane rotamers that are present at room temperature.*

Reagents. Potassium hydridotris(1-pyrazolyl)borate was prepared by the method of Trofimenko.[34] $(DMF)_3Mo(CO)_3$ was prepared according to a literature procedure.[35] Triphenylcarbenium hexafluorophosphate was freshly prepared from triphenylmethanol and hexafluorophosphoric acid following a literature procedure.[7] Phenylacetylene and acetophenone were purchased from Aldrich Chemical Co. and dried over 4 Å molecular sieves. Nitrosonium tetrafluoroborate, sodium borohydride, methylmagnesium bromide, ethylmagnesium bromide, vinylmagnesium bromide, phenylmagnesium bromide, and benzylmagnesium bromide were purchased from Aldrich Chemical Co. and used as received.

Benzyl 1,6-Dihydro-3(2*H*)-pyridinone-1-carboxylate, 1b. To an oven-dried 100 mL round-bottomed flask equipped with a magnetic stirring bar was added 1-benzyl-1,6-dihydro-3(2*H*)-pyridinone (**1a**)[28,29] (4.69 g, 25.19 mmol, 1.0 equiv) and 50 mL of dry CH_2Cl_2. The resulting solution was cooled to 0 °C in an ice/water bath, and benzyl chloroformate (7.2 mL, 50.37 mmol, 2.0 equiv) was added via syringe. After warming slowly to room temperature, the mixture was stirred for an additional 12 h. Solvent was removed in vacuo, and the resulting oil was purified by medium-pressure chromatography (silica gel, 10−25% ethyl acetate in hexane) to give **1b** as a yellow oil (5.01 g, 23.43 mmol, 93%). TLC (silica gel, 50% ethyl acetate in hexanes, R_f = 0.43); IR ($CDCl_3$, KBr, cm^{-1}): 1695 (sh, s). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36 (m, 5 H), 7.01 (br m, 1 H), 6.19 (dt, *J* = 10.8, 2.2 Hz, 1 H), 5.17 (s, 2 H), 4.31 (s, 2 H), 4.20 (s, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.6, 154.9, 146.9, 136.0, 128.6, 128.4, 128.3, 128.1, 127.5, 67.8, 51.6, 51.2, 43.0. Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06; O, 20.76. Found: C, 67.39; H, 5.70; N, 6.02.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]-[(3*R,4*R**,5*S**)-(1-benzyloxycarbonyl)-η-(3,4,5)-3-methoxy-1,2,5,6-tetrahydropyridin-3-yl]molybdenum, 2**. To an oven-dried 250 mL Schlenk tube equipped with a magnetic stirring bar was added $Mo(DMF)_3(CO)_3$[35] (11.16 g, 0.026 mol, 1.0 equiv) and 90 mL of dry, degassed CH_2Cl_2. To the resulting green suspension was added a solution of **1b** (5.99 g, 0.026 mol, 1.0 equiv) in 5 mL of dry, degassed CH_2Cl_2, followed by addition of *tert*-butyldimethylsilyl chloride (4.21 g, 0.026 mol, 1.0 equiv) as a solid. The resulting deep red solution was allowed to stir at room temperature for 18 h, and then potassium hydridotrispyrazolylborate (7.05 g, 0.026 mol, 1.0 equiv) was added as a solid. After stirring the resulting brown suspension at room temperature for 0.5 h, tetrabutylammonium fluoride trihydrate (22.05 g, 0.070 mol, 2.5 equiv) was added as a solid. This was stirred for 0.5 h, methyl iodide (34.8 mL, 0.559 mol, 20.0 equiv) was added, and the mixture was allowed to stir for 3 days. The resulting black suspension was filtered through a large plug of basic alumina eluting with 50% ethyl acetate in hexane, and the solvents were removed in vacuo. The resulting brown residue was occluded onto Celite and purified by basic alumina chromatography to give molybdenum complex **2** as an orange, foamy solid (9.90 g, 0.016 mol, 63%). TLC (silica gel, 25% ethyl acetate in hexanes, R_f = 0.18); mp 173−176 °C with decomp (THF/hexanes, 1:4); IR (CH_2Cl_2, KBr, cm^{-1}): 2486 (m), 1930 (sh, s), 1840 (sh, s), 1699 (sh, m). ^{1}H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.28 (d, *J* = 1.6 Hz, 1 H), 7.89 (d, *J* = 1.6 Hz, 1 H), 7.87 (d, *J* = 1.6 Hz, 1 H), 7.83 (d, *J* = 1.6 Hz, 1 H), 7.66 (d, *J* = 1.6 Hz, 2 H), 7.34 (m, 5 H), 6.34 (s, 1 H), 6.31 (s, 1 H), 6.29 (s, 1 H), 5.07 (br m, 2 H), 4.39 (d, *J* = 16.0 Hz, 1 H), 4.25 (d, *J* = 7.2 Hz, 1 H), 4.12 (dd, *J* = 13.6, 2.8 Hz, 1 H), 3.76 (d, *J* = 8.0 Hz, 2 H), 3.50 (br s, 1 H), 3.11 (s, 3 H). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): δ 229.5, 227.4, 153.8, 145.7, 143.7, 140.6, 136.6, 136.5, 135.9, 134.8, 127.9, 127.2, 126.9, 105.6, 105.4, 105.3, 65.9, 56.2, 54.9, 44.2, 41.3, 41.2, 40.1 (only 23 of 25 signals were found). Anal. Calcd for $C_{25}H_{26}N_7O_5BMo$: C, 49.12; H, 4.29; N, 16.04; O, 13.09; B, 1.77; Mo, 15.69. Found: C, 49.12; H, 4.36; N, 16.13.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]-[(2*R,3*R**,4*R**,5*S**)-(1-benzyloxycarbonyl) η-(2,3,4,5)-3-methoxy-1,2-dihydropyridine]molybdenum Hexafluorophosphate, 3**. To a 100 mL round-bottomed flask equipped with a stirring bar were added complex **2** (5.82 g, 9.55 mmol, 1.0 equiv) and 10 mL of dry CH_2Cl_2. This solution was cooled to −50 °C in a dry ice/acetone bath, and triphenylcarbenium hexafluorophosphate (4.45 g, 11.46 mmol, 1.1 equiv) was added all at once as a solid. The solution was allowed to warm slowly to room temperature over 2 h. The resulting red/brown suspension was diluted with 80 mL of Et_2O, and the solvent was removed from the resulting precipitate via filter-tip cannulation. The solid was redissolved in 5 mL of CH_2Cl_2 and precipitated once again from solution by addition of 80 mL of Et_2O. The solvent was again removed from the precipitate via filter-tip cannulation, and the resulting solids were washed three times with 10 mL portions of Et_2O. The product was dried under vacuum to give cationic molybdenum complex **3** as a red/brown powder (7.20 g, 9.55 mmol, 100%): mp 117−122 °C with decomp; IR (CH_2Cl_2, KBr, cm^{-1}): 2506 (w), 2020 (sh, s), 1956 (sh, s), 1723 (m). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.39 (d, *J* = 2.0 Hz, 1 H), 7.93 (d, *J* = 2.0 Hz, 1 H), 7.85 (d, *J* = 2.0 Hz, 1 H), 7.80 (d, *J* = 2.0 Hz, 1 H), 7.66 (d, *J* = 2.0 Hz, 1 H), 7.60 (br s, 1 H), 7.58 (br s, 1 H), 7.40 (m, 5 H), 6.46 (br t, *J* = 2.0 Hz, 1 H), 6.42 (br t, *J* = 2.0 Hz, 1 H), 6.40 (br t, *J* = 2.0 Hz, 1 H), 5.60 (br d, *J* = 8.4 Hz, 1 H), 5.44 (dd, *J* = 8.4, 3.2 Hz, 1 H), 5.25 (s, 2 H), 3.73 (A of AB quartet, *J* = 14.8 Hz, 1 H), 3.61 (B of AB quartet, *J* = 14.8 Hz, 1 H), 3.00 (s, 3 H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 217.4, 146.4, 145.9, 143.8, 139.2, 138.6, 137.1, 135.4, 133.7, 129.8, 129.3, 129.2, 128.8, 126.8, 108.5, 107.9, 107.8, 94.8, 82.1, 69.9, 66.2, 56.3, 44.8 (only 23 of 25 signals were found). HRMS (FAB) calcd for $C_{25}H_{25}N_7O_5BMo$: 612.1065. Found: 612.1064.

Synthesis of 4−10 from Cationic Complex 3. (η)-Dicarbonyl[hydridotris(1-pyrazolyl)borato][(2S*,3R*,4R*,5S*)-(1-benzyloxycarbonyl) η-(3,4,5)-2-methyl-3-methoxy-1,2,5,6-tetrahydropyridin-3-yl]molybdenum, 4. To a 100 mL Schlenk tube equipped with a magnetic stirring bar were added cationic complex **3** (2.0 g, 2.66 mmol, 1.0 equiv) and 25 mL dry THF. The resulting red/brown solution was cooled to −78 °C in a dry ice/acetone bath. To this cooled solution was added a 3 M solution of methylmagnesium bromide in THF (0.97 mL, 2.92 mmol, 1.1 equiv) dropwise by syringe. The resulting mixture was allowed to stir at −78 °C for 0.5 h. The cold reaction mixture was then poured over a plug of basic alumina, which was then washed with 50% ethyl acetate in hexane. The solvent was removed in vacuo, and the resulting

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foamy orange solid was occluded onto Celite and purified by basic alumina chromatography to give **4** as an orange solid (1.37 g, 2.21 mmol, 83%). TLC (silica gel, 25% ethyl acetate in hexane, $R_f = 0.30$); mp 111−114 °C with decomp; IR (CH_2Cl_2, KBr, cm^{-1}): 2486 (w), 1932 (sh, s), 1840 (sh, s), 1695 (sh, m). ^1H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.29 (d, $J = 1.6$ Hz, 1 H), 7.89 (s, 1 H), 7.88 (d, $J = 1.6$ Hz, 1 H), 7.84 (d, $J = 2.0$ Hz, 1 H), 7.76 (s, 2 H), 7.36 (m, 5 H), 6.34 (s, 1 H), 6.32 (s, 1 H), 6.29 (s, 1 H), 5.13 (A of AB quartet, $J = 12.4$ Hz, 0.4 H), 5.08 (A of AB quartet, $J = 12.4$ Hz, 0.6 H), 5.04 (B of AB quartet, $J = 12.4$ Hz, 0.6 H), 4.95 (B of AB quartet, $J = 12.4$ Hz, 0.4 H), 4.55 (m, 1 H), 4.25 (d, $J = 8.0$ Hz, 0.6 H), 4.21 (d, $J = 8.0$ Hz, 0.4 H), 4.06 (s, 0.4 H), 4.02 (s, 0.6 H), 3.75 (d, $J = 4.0$ Hz, 0.6 H), 3.73 (d, $J = 4.0$ Hz, 0.4 H), 3.56 (d, $J = 14.4$ Hz, 0.6 H), 3.48 (d, $J = 14.4$ Hz, 0.4 H), 3.05 (s, 1.2 H), 2.98 (s, 1.8 H), 1.35 (d, $J = 6.4$ Hz, 3 H). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): δ 229.9, 227.3, 153.4, 152.9, 145.6, 143.9, 140.6, 140.5, 140.0, 136.6, 136.0, 134.8, 128.4, 127.9, 127.3, 127.2, 127.1, 126.8, 105.7, 105.5, 105.4, 66.0, 65.7, 56.1, 54.9, 53.8, 53.2, 50.2, 49.9, 19.1. Anal. Calcd for $C_{26}H_{28}N_7O_5BMo$: C, 49.94; H, 4.51; N, 15.68; O, 12.79; B, 1.73; Mo, 15.34. Found: C, 49.88; H, 4.56; N, 15.46.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]-[(2*S,3*R**,4*R**,5*S**)-(1-benzyloxycarbonyl)-η-(3,4,5)-2-ethyl-3-methoxy-1,2,5,6-tetrahydropyridin-3-yl]molybdenum, 5**. Complex **3** (1.0 g, 1.33 mmol, 1.0 equiv) in 15 mL dry THF at −78 °C was treated with a 1 M solution of ethylmagnesium bromide in THF (1.46 mL, 1.46 mmol, 1.1 equiv) to give, after workup and basic alumina chromatography, **5** as an orange solid (0.6044 g, 0.94 mmol, 71%). TLC (silica gel, 25% ethyl acetate in hexanes, $R_f = 0.38$); mp 171−175 °C with decomp (THF/hexane, 1:4); IR (CH_2Cl_2, KBr, cm^{-1}): 2483 (m), 1931 (sh, s), 1842 (sh, s), 1693 (sh, m). ^1H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.28 (s, 1 H), 7.88 (m, 2 H), 7.84 (d, $J = 2.0$ Hz, 1 H), 7.77 (d, $J = 2.4$ Hz, 1 H), 7.74 (s, 1 H), 7.34 (m, 5 H), 6.34 (s, 1 H), 6.32 (s, 1 H), 6.28 (s, 1 H), 5.10 (A of AB quartet, $J = 12.4$ Hz, 0.6 H), 5.06 (s, 0.8 H), 4.91 (B of AB quartet, $J = 12.4$ Hz, 0.6 H), 4.55 (br m, 1 H), 4.25 (d, $J = 8.2$ Hz, 0.6 H), 4.21 (d, $J = 8.2$ Hz, 0.4 H), 4.13 (t, $J = 12.8$ Hz, 1 H), 3.79 (t, $J = 7.8$ Hz, 1 H), 3.60 (d, $J = 14.2$ Hz, 0.4 H), 3.50 (d, $J = 14.2$ Hz, 0.6 H), 3.01 (s, 1.2 H), 2.93 (s, 1.8 H), 1.99 (br m, 1.2 H), 1.71 (br m, 0.8 H), 0.94 (t, $J = 7.6$ Hz, 1.2 H), 0.89 (t, $J =$ Hz, 1.6 H). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz):[36] δ 153.9, 153.4, 145.7, 143.9, 140.7, 140.5, 136.7, 136.0, 135.6, 134.9, 128.0, 127.9, 127.4, 127.3, 126.9, 105.7, 105.6, 105.5, 66.1, 65.8, 57.0, 55.2, 54.6, 53.6, 53.1, 27.9, 27.4, 10.3. Anal. Calcd for $C_{27}H_{30}N_7O_5BMo$: C, 50.72; H, 4.73; N, 15.34; O, 12.51; B, 1.69; Mo, 15.01. Found: C, 50.84; H, 4.82; N, 15.21.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]-[(2*S,3*R**,4*R**,5*S**)-(1-benzyloxycarbonyl)-η-(3,4,5)-2-benzyl-3-methoxy-1,2,5,6-tetrahydropyridin-3-yl]molybdenum, 6**. Complex **3** (1.0 g, 1.33 mmol, 1.0 equiv) in 15 mL dry THF −78 °C was treated with a 1 M solution of benzylmagnesium bromide in THF (1.46 mL, 1.46 mmol, 1.1 equiv) to give, after workup and basic alumina chromatography, **6** as an orange solid (0.721 g, 1.02 mmol, 77%). TLC (silica gel, 25% ethyl acetate in hexanes, $R_f = 0.25$); mp 111−113 °C with decomp (THF/hexanes, 1:4); IR (CH_2Cl_2, KBr, cm^{-1}): 2484 (m), 1932 (sh, s), 1842 (sh, s), 1694 (sh, m). ^1H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.26 (d, $J = 2.4$ Hz, 1 H), 7.88 (d, $J = 2.0$ Hz, 1 H), 7.84 (d, $J = 2.4$ Hz, 1 H), 7.75 (s, 1 H), 7.24 (m, 12 H), 6.32 (t, $J = 2.4$ Hz, 1 H), 6.30 (t, $J = 2.4$ Hz, 1 H), 6.28 (t, $J = 2.4$ Hz, 1 H), 5.04 (A of AB quartet, $J = 12.8$ Hz, 0.33 H), 4.97 (B of AB quartet, $J = 12.8$ Hz, 0.33 H), 4.79 (m, 2.68 H), 4.53 (B of AB quartet, $J = 12.4$ Hz, 0.66 H), 4.17 (d, $J = 8.4$ Hz, 0.66 H), 4.10 (d, $J = 8.4$ Hz, 0.33 H), 4.02 (dd, $J = 13.2$, 2.4 Hz, 0.66 H), 3.92 (d, $J = 14.0$ Hz, 0.33 H), 3.76 (t, $J = 7.6$ Hz, 1 H), 2.90 (m, 2 H), 3.00 (s, 1 H), 2.98 (s, 2 H). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz):[36] δ 153.6, 145.6, 144.0, 140.6, 137.6, 136.6, 136.3, 136.0, 134.8, 134.3, 129.4, 129.2, 127.9, 127.8, 127.7, 127.2, 126.9, 126.0, 105.7, 105.5, 65.9, 57.0, 56.1, 54.5, 54.3, 53.4. Anal. Calcd for $C_{32}H_{32}N_7O_5BMo$: C, 54.80; H, 4.60; N, 13.98; O, 11.41; B, 1.54; Mo, 13.68. Found: C, 54.57; H, 4.66; N, 13.76.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]-[(2*S,3*R**,4*R**,5*S**)-(1-benzyloxycarbonyl) η-(3,4,5)-2-ethenyl-3-methoxy-1,2,5,6-tetrahydropyridin-3-yl]molybdenum, 7**. Complex **3** (0.250 g, 0.33 mmol, 1.0 equiv) in 25 mL dry THF −78 °C was treated with a 1 M solution of vinylmagnesium bromide in THF (0.37 mL, 0.37 mmol, 1.1 equiv) to give, after workup and basic alumina chromatography, **7** as an orange solid (0.141 g, 0.22 mmol, 67%). TLC (silica gel, 25% ethyl acetate in hexanes, $R_f = 0.30$); mp 100−104 °C with decomp; IR (CH_2Cl_2, KBr, cm^{-1}): 2485 (w), 1932 (sh, s), 1844 (sh, s), 1699 (sh, m). ^1H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.32 (s, 1 H), 7.92 (s, 1 H), 7.87 (s, 1 H), 7.84 (s, 1 H), 7.80 (s, 1 H), 7.77 (s, 1 H), 7.34 (m, 5 H), 6.35 (s, 1 H), 6.32 (s, 1 H), 6.28 (s, 1 H), 5.96 (m, 1 H), 5.11 (m, 5 H), 4.28 (d, $J = 8.0$ Hz, 0.6 H), 4.23 (d, $J = 8.0$ Hz, 0.4 H), 4.09 (s, 0.4 H), 4.05 (s, 0.6 H), 3.83 (t, $J = 6.6$ Hz, 1 H), 3.56 (d, $J = 13.8$ Hz, 0.4 H), 3.48 (d, $J = 13.8$ Hz, 0.6 H), 3.03 (s, 1.2 H), 2.95 (s, 1.8 H). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): δ 230.0, 227.4, 153.7, 153.0, 145.7, 144.0, 140.8, 140.6, 136.6, 136.0, 135.8, 135.4, 134.8, 131.5, 130.9, 127.9, 127.3, 127.0, 126.9, 116.7, 116.4, 105.8, 105.6, 105.4, 66.1, 65.9, 56.6, 56.4, 55.7, 54.9, 54.0, 53.3. Anal. Calcd for $C_{27}H_{28}N_7O_5BMo$: C, 50.89; H, 4.43; N, 15.38; O, 12.55; B, 1.70; Mo, 15.05. Found: C, 50.70; H, 4.55; N, 15.17.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]-[(2*S,3*R**,4*R**,5*S**)-(1-benzyloxycarbonyl)-η-(3,4,5)-2-phenyl-3-methyoxy-1,2,5,6-tetrahydropyridin-3-yl]molybdenum, 8**. Complex **3** (0.250 g, 0.33 mmol, 1.0 equiv) in 5 mL of dry THF −78 °C was treated with a 1 M solution of phenylmagnesium bromide in THF (0.37 mL, 0.37 mmol, 1.1 equiv) to give, after workup and basic alumina chromatography, **8** as an orange solid (0.150 g, 0.22 mmol, 66%). TLC (silica gel, 25% ethyl acetate in hexanes, $R_f = 0.24$); mp 194−198 °C with decomp; IR (CH_2Cl_2, KBr, cm^{-1}): 2484 (w), 1935 (sh, s), 1844 (sh, s), 1695 (sh, m). ^1H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.36 (s, 1 H), 7.99 (s, 1 H), 7.87 (s, 2 H), 7.82 (d, $J = 9.2$ Hz, 1 H), 7.78 (s, 2 H), 7.62 (d, $J = 7.6$ Hz, 1 H), 7.34 (m, 8 H), 6.35 (s, 2 H), 6.26 (s, 1 H), 5.59 (s, 0.46 H), 5.55 (s, 0.54 H), 5.06 (A of AB quartet, $J = 12.4$ Hz, 1 H), 4.96 (B of AB quartet, $J = 12.4$ Hz, 0.54 H), 4.94 (B of AB quartet, $J = 12.4$ Hz, 0.46 H), 4.44 (d, $J = 8.2$ Hz, 0.54 H), 4.39 (d, $J = 8.2$ Hz, 0.46 H), 4.12 (m, 2 H), 3.69 (s, 0.54 H), 3.65 (s, 0.46 H), 2.78 (s, 1.38 H), 2.68 (s, 1.62 H). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): δ 229.8, 227.5, 227.2, 153.5, 152.8, 145.8, 144.1, 140.7, 140.6, 140.5, 140.0, 136.6, 136.4, 136.3, 136.0, 134.8, 131.5, 131.0, 128.0, 127.8, 127.4, 127.3, 127.2, 127.1, 126.8, 126.7, 105.8, 105.6, 105.4, 66.2, 65.9, 58.3, 57.8, 57.7, 57.6, 54.5, 53.3, 52.7. Anal. Calcd for $C_{31}H_{30}N_7O_5BMo$: C, 54.17; H, 4.40; N, 14.26; O, 11.64; B, 1.57; Mo, 13.96. Found: C, 54.16; H, 4.40; N, 14.27.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]-[(2*S,3*R**,4*R**,5*S**)-(1-benzyloxycarbonyl)-η-(3,4,5)-2-ethoxycarbonylmethyl-3-methoxy-1,2,5,6-tetrahydropyridin-3-yl]molybdenum, 9**. Lithioethyl acetate was generated: THF (10 mL) and diisopropylamine (0.94 mL, 6.73 mmol, 1.4 equiv) in a 25 mL round-bottomed flask at −78 °C were treated with *n*-butyllithium (2.71 mL, 2.48 M in hexanes, 6.73 mmol, 1.4 equiv). After 1 h at −78 °C, ethyl acetate (0.66 mL, 6.37 mmol, 1.4 equiv) was added by syringe, and the mixture was allowed to stir for 1 h at −78 °C. Then, the lithioethyl acetate was cannulated into a solution of complex **3** (1.12 g, 1.49 mmol, 1.0 equiv) in 40 mL of dry THF at −78 °C. The resulting mixture was allowed to stir at −78 °C for 0.5 h. Workup and basic alumina chromatography delivered **9** as an orange solid (1.751 g, 2.50 mmol, 52%). TLC (silica gel, 25% ethyl acetate in hexanes, $R_f = 0.19$); mp 135 °C with decomp; IR (CH_2Cl_2, KBr, cm^{-1}): 2483 (w), 1935 (sh, s), 1846 (sh, s), 1732 (sh, m), 1699 (sh, m). ^1H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.29 (s, 1 H), 7.89 (d, $J = 2.4$ Hz, 2 H), 7.85 (d, $J = 2.4$ Hz, 1 H), 7.76 (s, 1 H), 7.74 (s, 0.44 H), 7.72 (s, 0.56 H), 7.34 (m, 5 H), 6.33 (t, $J = 2.4$ Hz, 2 H), 6.29 (t, $J = 2.4$ Hz, 1 H), 5.09 (A of AB quartet, $J = 12.8$ Hz, 0.56 H), 5.06 (A of AB quartet, $J = 12.8$ Hz, 0.44 H), 5.04 (B of AB quartet, $J = 12.8$ Hz, 0.56 H), 4.98 (B of AB quartet, $J = 12.8$ Hz, 0.44 H), 4.93 (t, $J = 6.0$ Hz, 0.56 H),

(36) ^{13}C signals for the CO ligands were not found under the conditions of the NMR experiment.

4.87 (t, J = 6.0 Hz, 0.44 H), 4.30 (d, J = 8.0 Hz, 0.56 H), 4.26 (d, J = 8.0 Hz, 0.44 H), 4.04 (m, 2.44 H), 3.93 (m, 0.56 H), 3.77 (d, J = 8.0 Hz, 1 H), 3.57 (d, J = 13.2 Hz, 0.44 H), 3.49 (d, J = 13.2 Hz, 0.56 H), 2.92 (s, 1.32 H), 2.87 (s, 1.68 H), 2.68 (m, 2 H), 1.22 (t, J = 7.2 Hz, 1.32 H), 1.14 (t, J = 7.2 Hz, 1.68 H). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): δ 230.0, 229.6, 227.2, 226.8, 169.8, 169.7, 153.4, 153.1, 145.7, 144.0, 140.5, 136.8, 136.6, 136.4, 136.1, 134.9, 132.4, 132.2, 128.0, 127.4, 127.1, 126.9, 105.8, 105.7, 105.6, 66.3, 66.0, 59.8, 56.6, 54.8, 53.0, 52.9, 52.6, 13.7, 13.6. Anal. Calcd for $C_{29}H_{32}N_7O_7BMo$: C, 49.95; H, 4.63; N, 14.06; O, 16.06; B, 1.55; Mo, 13.76. Found: C, 50.16; H, 4.64; N, 13.82.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]-[(2*S,3*R**,4*R**,5*S**)-(1-benzyloxycarbonyl)-η-(3,4,5)-2-(1-propenyl)-3-methoxy-1,2,5,6-tetrahydropyridin-3-yl]molybdenum, 10**. Complex **3** (1.12 g, 1.49 mmol, 1.0 equiv) in 20 mL of dry THF −78 °C was treated with a 1 M solution of allylmagnesium bromide in THF (1.78 mL, 1.78 mmol, 1.2 equiv) to give, after workup and basic alumina chromatography, **10** as an orange solid (0.666 g, 1.02 mmol, 69%). TLC (silica gel, 25% ethyl acetate in hexanes, R_f = 0.35); mp 85 °C with decomp; IR (CH_2Cl_2, KBr, cm^{-1}): 2484 (w), 1932 (sh, s), 1843 (sh, s), 1695 (sh, m). ^{1}H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.28 (t, J = 2.0 Hz, 1 H), 7.89 (d, J = 2.0 Hz, 1 H), 7.88 (d, J = 2.0 Hz, 1 H), 7.84 (d, J = 2.0 Hz, 1 H), 7.76 (m, 2 H), 7.36 (m, 4 H), 7.32 (m, 1 H), 6.32 (m, 2 H), 6.28 (m, 1 H), 5.91 (dt, J = 10.0, 7.2 Hz, 0.42 H), 5.81 (dt, J = 10.0, 7.2 Hz, 0.58 H), 5.10 (A of AB quartet, J = 12.4 Hz, 0.42 H), 5.01 (m, 3.16 H), 4.92 (B of AB quartet, J = 12.4 Hz, 0.42 H), 4.65 (t, J = 6.4 Hz, 0.42 H), 4.64 (t, J = 6.4 Hz, 0.58 H), 4.26 (d, J = 8.2 Hz, 0.58 H), 4.22 (d, J = 8.2 Hz, 0.42 H), 4.11 (dd, J = 9.2, 2.4 Hz, 0.42 H), 4.07 (dd, J = 9.2, 2.4 Hz, 0.58 H), 3.78 (t, J = 8.4 Hz, 1 H), 3.62 (dd, J = 14.0, 1.6 Hz, 0.42 H), 3.52 (dd, J = 14.0, 1.6 Hz, 0.58 H), 2.97 (s, 1.26 H), 2.90 (s, 1.74 H), 2.67 (m, 1 H), 2.53 (m, 1 H). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): δ 230.2, 230.0, 227.5, 227.2, 153.7, 153.3, 145.7, 144.0, 140.7, 140.5, 136.7, 136.5, 136.1, 134.9, 134.5, 134.4, 134.1, 133.7, 128.0, 127.9, 127.4, 127.3, 126.9, 117.3, 117.2, 105.8, 105.6, 105.5, 66.1, 65.8, 59.4, 57.0, 54.5, 54.3, 54.2, 53.9, 53.8, 53.3, 53.0. Anal. Calcd for $C_{28}H_{30}N_7O_5BMo$: C, 51.63; H, 4.64; N, 15.05; O, 12.28; B, 1.66; Mo, 14.73. Found: C, 51.80; H, 4.67; N, 14.81.

Characterization of Side-product 11, (±)-Dicarbonyl-[hydridotris(1-pyrazolyl)borato][1*S,2*S**,3*R**)-(1-benzyloxycarbonyl) η-(1,2,3)-4-methoxy-1,2-tetrahydropyridin-2-yl]molybdenum.** To a 100 mL Schlenk tube equipped with a magnetic stirring bar were added **3** (2.0 g, 2.66 mmol, 1.0 equiv) and 25 mL of dry THF. The resulting red/brown solution was cooled to −78 °C in a dry ice/acetone bath. To this cooled solution was added a 3 M solution of methylmagnesium bromide in THF (0.97 mL, 2.92 mmol, 1.1 equiv) dropwise by syringe. The resulting mixture was allowed to stir at −78 °C for 0.5 h. The cold reaction mixture was then poured over a plug of basic alumina, which was then washed with 50% ethyl acetate in hexane. The solvent was removed in vacuo, and the resulting foamy orange solid was occluded onto Celite and purified by basic alumina chromatography. Product **11** was isolated by collection of the least polar orange band, giving a bright orange solid (0.16 g, 0.27 mmol, 10%): mp = 118−120 °C (EtOAc/hexane); R_f = 0.54 (EtOAc/hexane, 1:2); IR (KBr, cm^{-1}): 1925 (s), 1832 (s), 1701 (s); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.42 (d, J = 2.1 Hz, 0.3 H), 8.21 (t, J = 2.4 Hz, 0.7 H), 7.73 (d, J = 1.8 Hz, 0.5 H), 7.70 (d, J = 2.1 Hz, 0.5 H), 7.68 (d, J = 2.1 Hz, 0.25 H), 7.61 (d, J = 2.4 Hz, 0.25 H), 7.59 (d, J = 2.4 Hz, 0.25 H), 7.57 (d, J = 2.1 Hz, 0.25 H), 7.53 (d, J = 2.1 Hz, 1 H), 7.51 (d, J = 1.8 Hz, 0.5 H), 7.48 (d, J = 2.4 Hz, 0.5 H), 7.46 (d, J = 2.1 Hz, 0.5 H), 7.42 (d, J = 2.1 Hz, 0.5 H), 7.40−7.37 (m, 2 H), 7.26−7.19 (m, 5 H), 6.26 (t, J = 2.1 Hz, 0.5 H), 6.20−6.17 (m, 1.5 H), 5.90−5.88 (m, 0.7 H), 5.72 (s, br, 0.3 H), 5.40−5.26 (m, 2 H), 4.62 (dd, J = 5.2 Hz, J = 0.3 Hz, 1 H), 3.64 (s, 1.5 H), 3.58 (s, 1.5 H), 2.84 (t, J = 6.0 Hz, 0.5 H), 2.72 (t, J = 6.0 Hz, 0.5 H); ^{13}C NMR (100 MHz, $CDCl_3$) 229.93, 229.26, 223.17, 222.54, 153.48, 153.11, 151.46, 150.75, 146.36, 145.07, 143.89, 140.48, 140.32, 136.2, 136.17, 136.05, 136.00, 134.65, 129.37, 128.95, 128.85, 128.77, 128.48, 128.23, 106.02, 105.67 (2 carbons), 92.43, 92.34, 92.01, 90.91, 69.47, 68.52, 59.47, 58.99, 55.70, 55.57, 51.92, 51.41; Anal. Calcd for $C_{25}H_{24}BMoN_7O_5$: C, 49.28; H, 3.97; N, 16.09. Found: C, 49.03; H, 3.95, N, 16.05.

Generation of Cationic Complexes 12−18.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]-[(2*S,3*R**,4*R**,5*S**,6*S**)-(1-benzyloxycarbonyl)-η-(3,4,5,6)-2-methyl-3-methoxy-1,2-dihydropyridine]molybdenum Hexafluorophosphate, 12**. To a 100 mL round-bottomed flask equipped with a stirring bar were added **4** (3.60 g, 5.78 mmol, 1.0 equiv) and 10 mL of dry CH_2Cl_2. This solution was cooled to −50 °C in a dry ice/acetone bath and treated with triphenylcarbenium hexafluorophosphate (2.47 g, 6.35 mmol, 1.1 equiv) all at once as a solid. The solution was allowed to warm slowly to room temperature over 2 h. The resulting red/brown suspension was diluted with 80 mL of Et_2O, and the solvent was removed from the resulting precipitate via filter-tip cannulation. The solid was the redissolved in 5 mL of CH_2Cl_2 and precipitated once again from solution by addition of 80 mL of Et_2O. The solvent was again removed from the precipitate via filter-tip cannulation, and the resulting solids were washed three times with 10 mL portions of Et_2O. The product was dried under vacuum to give **12** as a red/brown powder (3.95 g, 5.20 mmol, 90%). mp 98−101 °C with decomp; IR (CH_2Cl_2, KBr, cm^{-1}): 2506 (w), 2053 (sh, s), 2053 (m), 1935 (sh, s), 1730 (m). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.12 (br s, 1 H), 7.91 (br s, 1 H), 7.81 (br s, 2 H), 7.75 (br s, 1 H), 7.57 (br s, 1 H), 7.50 (d, J = 5.6 Hz, 1 H), 7.41 (m, 5 H), 6.40 (br s, 3 H), 5.45 (t, J = 4.8 Hz, 1 H), 5.31 (s, 2 H), 5.04 (br s, 1 H), 4.12 (q, J = 6.4 Hz, 1 H), 3.30 (s, 3 H), 1.62 (d, J = 6.4 Hz, 3 H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 219.2, 152.8, 147.2, 144.5, 143.5, 139.4, 138.2, 135.1, 129.5, 129.3, 129.2, 108.0, 100.2, 70.4, 69.3, 62.3, 58.7, 51.6, 21.3. Anal. Calcd for $C_{26}H_{27}N_7O_5BMoPF_6$: C, 40.60; H, 3.54; N, 12.75; O, 10.40; B, 1.41; Mo, 12.47; P, 4.03; F, 14.82. Found: C, 40.51; H, 3.49; N, 12.81.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]-[(2*S,3*R**,4*R**,5*S**,6*S**)-(1-benzyloxycarbonyl)-η-(3,4,5,6)-2-ethyl-3-methoxy-1,2-dihydropyridine]molybdenum Hexafluorophosphate, 13**. Complex **5** (0.545 g, 0.85 mmol, 1.0 equiv) in 5 mL of dry CH_2Cl_2 was treated with triphenylcarbenium hexafluorophosphate (0.365 g, 0.94 mmol, 1.1 equiv) and gave, after workup, **13** as a red/brown powder (0.623 g, 0.80 mmol, 94%). mp 117−119 °C with decomp; IR (CH_2Cl_2, KBr, cm^{-1}): 2507 (w), 2052 (sh, s), 2006 (m), 1933 (sh, s), 1732. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.11 (br s, 1 H), 7.90 (br s, 1 H), 7.82 (br s, 1 H), 7.78 (br s, 1 H), 7.57 (d, J = 5.2 Hz, 1 H), 7.51 (br s, 2 H), 7.42 (m, 5 H), 6.40 (br s, 3 H), 5.48 (br s, 1 H), 5.34 (s, 2 H), 5.09 (br s, 1 H), 4.17 (app t, J = 3.2 Hz, 1 H), 3.26 (s, 3 H), 2.27 (m, 1 H), 2.03 (m, 1 H), 0.85 (t, J = 7.6 Hz, 3 H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 219.0, 153.0, 147.1, 144.4, 143.4, 139.4, 138.2, 135.1, 129.6, 129.4, 129.2, 129.1, 127.9, 127.7, 108.0, 101.0, 70.4, 70.3, 62.1, 58.6, 56.1, 27.4, 8.0. Anal. Calcd for $C_{27}H_{29}N_7O_5F_6PBMo$: C, 41.40; H, 3.73; N, 12.52; O, 10.21; F, 14.55; P, 3.95; B, 1.38; Mo, 12.25. Found: C, 41.29; H, 3.69; N, 12.59.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]-[(2*S,3*R**,4*R**,5*S**,6*S**)-(1-benzyloxycarbonyl)-η-(3,4,5,6)-2-benzyl-3-methoxy-1,2-dihydropyridine]molybdenum Hexafluorophosphate, 14.** Complex **6** (0.726 g, 1.04 mmol, 1.0 equiv) in 5 mL of dry CH_2Cl_2 was treated with triphenylcarbenium hexafluorophosphate (0.484 g, 1.25 mmol, 1.1 equiv) and gave, after workup, **14** as a red/brown powder (0.823 g, 0.98 mmol, 94%): mp 100−103 °C with decomp; IR (CH_2Cl_2, KBr, cm^{-1}): 2512 (w), 2053 (sh, s), 2007 (m), 1936 (sh, s), 1729 (m). ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.11 (br s, 1 H), 7.90 (br s, 1 H), 7.82 (br s, 1 H), 7.78 (br s, 1 H), 7.57 (d, J = 5.2 Hz, 1 H), 7.51 (br s, 2 H), 7.42 (m, 5 H), 7.35 (m, 5 H) 6.40 (br s, 3 H), 5.48 (br s, 1 H), 5.34 (s, 2 H), 5.09 (br s, 1 H), 4.17 (app t, J = 3.2 Hz, 1 H), 3.26 (s, 3 H), 2.70 (m, 2 H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 218.7, 152.9, 147.1, 144.6, 143.2, 139.5, 138.3, 135.1, 133.9, 130.2, 129.6, 129.5, 129.4, 129.3, 128.5, 127.9, 127.7, 108.0, 98.2, 70.7, 61.6, 58.3, 56.4, 39.7. Anal. Calcd for $C_{32}H_{31}N_7O_5F_6BMoP$: C, 45.47; H, 3.70; N, 11.60; O, 9.46; F, 13.48; B, 1.28; Mo, 11.35; P, 3.66. Found: C, 45.17; H, 3.74; N, 11.45.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]-[(2*S,3*R**,4*R**,5*S**,6*S**)-(1-benzyloxycarbonyl)-η-(3,4,5,6)-2-ethenyl-3-methoxy-1,2-dihydropyridine]molybdenum Hexafluorophosphate, 15.** Complex **7** (0.119 g, 0.19 mmol, 1.0 equiv) in 5 mL of dry CH_2Cl_2 was treated with triphenylcarbenium hexafluorophosphate (0.087 g, 0.23 mmol, 1.1 equiv) and gave, after workup, **15** as a red/brown powder (0.116 g, 0.16 mmol, 86%). mp 99−101 °C with decomp; IR (CH_2Cl_2, KBr, cm^{-1}): 2506 (w), 2055 (sh, s), 2008 (m), 1935 (sh, s), 1731 (m). ^1H NMR (CD_2Cl_2, 400 MHz): δ 8.15 (br s, 1 H), 7.90 (br s, 1 H), 7.83 (br s, 1 H), 7.76 (br s, 1 H), 7.62 (m, 2 H), 7.58 (br s, 1 H), 7.40 (m, 5 H), 6.42 (br s, 3 H), 5.70 (m, 1 H), 5.54 (s, 1 H), 5.49 (s, 1 H), 5.46 (s, 1 H), 5.30 (s, 2 H), 5.08 (br s, 1 H), 4.58 (br s, 1 H), 3.27 (s, 3 H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 218.7, 161.0, 147.2, 144.8, 143.4, 139.5, 138.1, 135.0, 131.8, 129.6, 129.4, 129.2, 129.1, 127.9, 127.7, 122.9, 108.0, 100.1, 70.5, 66.2, 58.7, 57.2. HRMS (FAB) calcd for $C_{27}H_{27}N_7O_5BMo$: 638.1221. Found: 638.1412.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]-[(2*S,3*R**,4*R**,5*S**,6*S**)-(1-benzyloxycarbonyl)-η-(3,4,5,6)-2-phenyl-3-methoxy-1,2-dihydropyridine]molybdenum Hexafluorophosphate, 16.** Complex **8** (0.412 g, 0.60 mmol, 1.0 equiv) in 5 mL of dry CH_2Cl_2 was treated with triphenylcarbenium hexafluorophosphate (0.256 g, 0.66 mmol, 1.1 equiv) and gave, after workup, **16** as a red/brown powder (0.419 g, 0.50 mmol, 84%): mp 194−198 °C with decomp; IR (CH_2Cl_2, KBr, cm^{-1}): 2506 (w), 2057 (sh, s), 2011 (m), 1937 (sh, s), 1732 (m). ^1H NMR (CD_2Cl_2, 400 MHz): δ 8.15 (br s, 1 H), 7.95 (br s, 1 H), 7.85 (br s, 1 H), 7.80 (br s, 1 H), 7.69 (d, J = 5.6 Hz, 1 H), 7.40 (m, 10 H), 7.32 (br s, 2 H), 6.43 (br s, 3 H), 5.87 (br s, 1 H), 5.32 (br s, 1 H), 5.18 (s, 2 H), 4.97 (br s, 1 H), 2.94 (s, 3 H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 218.4, 165.3, 147.2, 144.7, 144.4, 143.5, 139.7, 138.3, 135.9, 134.9, 130.1, 129.8, 129.6, 129.1, 129.0, 128.8, 127.9, 127.7, 126.8, 108.1, 99.0, 70.2, 70.0, 66.2, 61.9, 59.3, 58.5, 57.3. HRMS (FAB) calcd for $C_{31}H_{29}N_7O_5BMo$: 688.1378. Found: 688.1377.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]-[(2*S,3*R**,4*R**,5*S**,6*S**)-(1-benzyloxycarbonyl)-η-(3,4,5,6)-2-ethoxycarbonylmethyl-3-methoxy-1,2-dihydropyridine]-molybdenum Hexafluorophosphate, 17.** Complex **9** (1.107 g, 1.59 mmol, 1.0 equiv) in 5 mL of dry CH_2Cl_2 was treated with triphenylcarbenium hexafluorophosphate (0.740 g, 1.91 mmol, 1.1 equiv) and gave, after workup, **17** as a red/brown powder (1.05 g, 1.24 mmol, 78%). mp 89−91 °C with decomp; IR (CH_2Cl_2, KBr, cm^{-1}): 2507 (w), 2055 (sh, s), 2016 (m), 1939 (sh, s), 1734 (sh, s). ^1H NMR (CD_2Cl_2, 400.MHz): δ 8.11 (br s, 1 H), 7.93 (br s, 1 H), 7.85 (br s, 1 H), 7.84 (br s, 1 H), 7.81 (br s, 1 H), 7.80 (br s, 1 H), 7.56 (br s, 1 H), 7.42 (m, 5 H), 6.41 (br s, 3 H), 5.57 (br s, 1 H), 5.35 (s, 2 H), 5.03 (br s, 1 H), 4.36 (t, J = 4.0 Hz, 1 H), 4.14 (q, J = 7.2 Hz, 2 H), 3.22 (s, 3 H), 3.07 (m, 2 H), 1.25 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 218.0, 169.0, 152.9, 147.2, 144.4, 143.4, 139.7, 138.3, 134.9, 129.5, 129.2, 129.1, 108.1, 99.3, 70.7, 70.6, 66.3, 62.1, 61.7, 58.7, 38.7, 14.4. Anal. Calcd for $C_{29}H_{31}N_7O_7F_6PBMo$: C, 41.40; H, 3.71; N, 11.65; O, 13.31; F, 13.55; P, 3.68; B, 1.28; Mo, 11.40. Found: C, 41.58; H, 3.83; N, 11.37.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]-[(2*S,3*R**,4*R**,5*S**,6*S**)-(1-benzyloxycarbonyl)-η-(3,4,5,6)-2-(1-propenyl)-3-methoxy-1,2-dihydropyridine]molybdenum Hexafluorophosphate, 18.** Complex **10** (0.198 g, 0.30 mmol, 1.0 equiv) in 5 mL of dry CH_2Cl_2 was treated with triphenylcarbenium hexafluorophosphate (0.142 g, 0.37 mmol, 1.2 equiv) and gave, after workup, **18** as a red/brown powder (0.165 g, 0.20 mmol, 68%). mp 92−95 °C with decomp; IR (CH_2Cl_2, KBr, cm^{-1}): 2509 (w), 2053 (sh, m), 2021 (sh, s), 1951 (sh, s), 1717 (m). ^1H NMR (CD_2Cl_2, 400 MHz): δ 8.11 (s, 1 H), 7.90 (s, 1 H), 7.82 (s, 1 H), 7.75 (s, 1 H), 7.70 (s, 1 H), 7.54 (s, 1 H), 7.48 (d, J = 5.4 Hz, 1 H), 7.42 (m, 5 H), 6.41 (br s, 3 H), 5.64 (m, 1 H), 5.41 (t, J = 5.4 Hz, 1 H), 5.34 (s, 2 H), 5.24 (d, J = 10.0 Hz, 1 H), 5.10 (d, J = 17.2 Hz, 1 H), 5.02 (br s, 1 H), 4.22 (br s, 1 H), 3.20 (s, 3 H), 2.95 (m, 1 H), 2.74 (m, 1 H). ^{13}C NMR (CD_2Cl_2, 100 MHz): δ 218.7, 147.1, 144.5, 143.4, 139.6, 138.2, 135.0, 130.3, 129.6, 129.5, 129.3, 129.2, 128.6, 127.9, 127.7, 121.5, 108.0, 100.0, 70.7, 70.5, 66.3, 58.3, 55.4. HRMS (FAB+) calcd for $C_{28}H_{29}N_7O_5BMo$: 652.1378. Found: 652.1396.

Synthesis of 19−31 from Cationic Complexes 12−18.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]-[(2*S,3*R**,4*R**,5*S**,6*R**)-(1-benzyloxycarbonyl)-η-(3,4,5)-2-methyl-3-methoxy-6-ethenyl-1,2,5,6-tetrahydropyridin-3-yl]molybdenum, 19**. To a 50 mL Schlenk tube equipped with a magnetic stirring bar were added **12** (0.400 g, 0.52 mmol, 1.0 equiv) and 25 mL of dry THF. The resulting red/brown solution was cooled to −78 °C in a dry ice/acetone bath. To this cooled solution was added a 1 M solution of vinylmagnesium bromide in THF (0.63 mL, 0.63 mmol, 1.2 equiv) dropwise by syringe. The resulting mixture was allowed to stir at −78 °C for 0.5 h. The cold reaction mixture was then poured over a plug of basic alumina, which was then washed with 50% ethyl acetate in hexane. The solvent was removed in vacuo, and the resulting foamy orange solid was occluded onto Celite and purified by basic alumina chromatography to give **19** as an orange solid (0.211 g, 0.32 mmol, 62%). TLC (silica gel, 25% ethyl acetate in hexanes, R_f = 0.35); mp 91−95 °C with decomp; IR (CH_2Cl_2, KBr, cm^{-1}): 2483 (w), 1933 (sh, s), 1840 (sh, s), 1694 (sh, m). ^1H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.28 (s, 1 H), 7.89 (s, 2 H), 7.85 (s, 1 H), 7.77 (s, 1 H), 7.73 (s, 1 H), 7.36 (s, 4 H), 7.32 (s, 1 H), 6.34 (s, 1 H), 6.31 (s, 2 H), 6.05 (m, 1 H), 5.44 (d, J = 17.2 Hz, 0.5 H), 5.32 (d, J = 17.2 Hz, 0.5 H), 5.08 (m, 3 H), 4.78 (d, J = 5.8 Hz, 0.5 H), 4.75 (d, J = 5.8 Hz, 0.5 H), 4.64 (m, 1 H), 4.28 (d, J = 7.6 Hz, 0.5 H), 4.22 (d, J = 7.6 Hz, 0.5 H), 3.80 (d, J = 8.0 Hz, 1 H), 3.00 (s, 1.5 H), 2.93 (s, 1.5 H), 1.44 (d, J = 6.8 Hz, 3 H). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): δ 231.0, 230.8, 227.3, 227.0, 153.4, 153.0, 145.7, 143.9, 141.6, 141.4, 140.7, 140.5, 136.7, 136.5, 136.0, 134.9, 128.0, 127.9, 127.4, 127.3, 127.1, 126.8, 115.9, 115.7, 105.7, 105.6, 105.5, 66.1, 65.9, 56.7, 56.0, 55.8, 54.7, 54.0, 53.6, 50.5, 50.2, 23.1, 22.2. Anal. Calcd for $C_{28}H_{30}N_7O_5BMo$: C, 51.63; H, 4.64; N, 15.05; O, 12.28; B, 1.66; Mo, 14.73. Found: C, 51.90; H, 4.71; N, 14.79.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]-[(2*S,3*R**,4*R**,5*S**,6*R**)-(1-benzyloxycarbonyl)-η-(3,4,5)-2-ethyl-3-methoxy-6-phenyl-1,2,5,6-tetrahydropyridin-3-yl]molybdenum, 20**. Cationic complex **13** (0.400 g, 0.51 mmol, 1.0 equiv) in 25 mL dry THF at −78 °C was treated with a 1 M solution of phenylmagnesium bromide in THF (0.66 mL, 0.66 mmol, 1.3 equiv) and gave, after workup and basic alumina chromatography, **20** as an orange solid (0.156 g, 0.22 mmol, 43%). TLC (silica gel, 25% ethyl acetate in hexanes, R_f = 0.43); mp 120−123 °C with decomp; IR (CH_2Cl_2, KBr, cm^{-1}): 2485 (w), 1933 (sh, s), 1841 (sh, s), 1690 (sh, m). ^1H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.30 (d, J = 1.6 Hz, 0.65 H), 8.29 (d, J = 1.6 Hz, 0.35 H), 7.98 (s, 0.65 H), 7.96 (s, 0.35 H), 7.92 (d, J = 1.6 Hz, 1 H), 7.88 (s, 1.05 H), 7.87 (s, 1.95 H), 7.78 (m, 3 H), 7.36 (m, 7 H), 6.35 (t, J = 1.6 Hz, 1 H), 6.32 (t, J = 1.6 Hz, 1 H), 6.31 (t, J = 1.6 Hz, 1 H), 5.69 (d, J = 1.6 Hz, 0.65 H), 5.56 (d, J = 1.6 Hz, 0.35 H), 5.23 (A of AB quartet, J = 12.4 Hz, 0.35 H), 5.16 (A of AB quartet, J = 12.4 Hz, 0.65 H), 5.13 (B of AB quartet, J = 12.4 Hz, 0.35 H), 4.94 (B of AB quartet, J = 12.4 Hz, 0.65 H), 4.58 (d, J = 7.6 Hz, 0.35 H), 4.57 (d, J = 7.6 Hz, 0.65 H), 4.54 (d, J = 4.0 Hz, 0.35 H), 4.52 (d, J = 4.0 Hz, 0.65 H), 4.14 (s, 0.65 H), 4.12 (s, 0.35 H), 3.02 (s, 1.05 H), 2.95 (s, 1.95 H), 1.72 (m, 0.7 H), 1.08 (m, 1.3 H), 0.67 (t, J = 7.6 Hz, 1.05 H), 0.54 (t, J = 7.6 Hz, 1.95 H). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): δ 231.2, 227.5, 227.1, 154.8, 153.7, 145.6, 144.1, 143.6, 140.9, 140.8, 137.8, 136.7, 136.5, 136.3, 136.0, 134.9, 128.4, 127.9, 127.8, 127.7, 127.5, 127.0, 105.7, 105.5, 66.5, 66.3, 57.1, 56.9, 56.2, 55.9, 55.2, 54.7, 53.6, 53.1, 30.5, 30.4, 11.6, 11.4. Anal. Calcd for $C_{33}H_{34}N_7O_5BMo$: C, 55.40; H, 4.79; N, 13.70; O, 11.18; B, 1.51; Mo, 13.41. Found: C, 55.47; H, 4.82; N, 13.58.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]-[(2*S,3*R**,4*R**,5*S**,6*R**)-(1-benzyloxycarbonyl)-η-(3,4,5)-2-ethyl-3-methoxy-6-benzyl-1,2,5,6-tetrahydropyridin-3-yl]molybdenum, 21**. Cationic complex **13** (0.400 g, 0.51 mmol, 1.0 equiv) in 25 mL of dry THF at −78 °C was treated with a 1 M solution of benzylmagnesium bromide in THF (0.66 mL, 0.66 mmol, 1.3 equiv) and gave, after workup and basic alumina chromatography, **21** as an orange solid (0.282 g, 0.39 mmol, 76%). TLC (silica gel, 25% ethyl acetate in hexanes, R_f = 0.38); mp 100−105 °C with decomp; IR (CH_2Cl_2, KBr, cm^{-1}):

2484 (w), 1933 (sh, s), 1841 (sh, s), 1692 (sh, m). ^{1}H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.22 (s, 1 H), 7.88 (d, J = 2.0 Hz, 1 H), 7.83 (d, J = 2.0 Hz, 1 H), 7.78 (s, 1 H), 7.74 (s, 1 H), 7.34 (m, 11 H), 6.30 (s, 3 H), 5.50 (A of AB quartet, J = 12.4 Hz, 0.5 H), 5.02 (A of AB quartet, J = 12.4 Hz, 0.5 H), 4.95 (B of AB quartet, J = 12.4 Hz, 0.5 H), 4.94 (B of AB quartet, J = 12.4 Hz, 0.5 H), 4.52 (m, 2 H), 3.96 (m, 1 H), 3.77 (d, J = 5.6 Hz, 0.5 H), 3.75 (d, J = 5.6 Hz, 0.5 H), 3.03 (m, 2 H), 3.03 (s, 1.5 H), 2.96 (s, 1.5 H), 2.14 (m, 1 H), 1.77 (m, 1 H), 1.12 (t, J = 7.6 Hz, 1.5 H), 0.99 (t, J = 7.6 Hz, 1.5 H). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): δ 231.0, 230.7, 227.4, 227.1, 154.0, 153.5, 145.7, 144.0, 139.4, 139.2, 138.6, 138.5, 137.4, 137.0, 136.7, 136.6, 136.4, 136.1, 134.9, 128.9, 128.8, 128.1, 128.0, 127.9, 127.8, 127.4, 127.3, 127.1, 126.1, 105.7, 105.5, 66.2, 66.1, 56.6, 55.9, 55.6, 54.7, 54.1, 53.7, 46.0, 45.4, 32.7, 32.5, 12.6, 12.4. Anal. Calcd for $C_{34}H_{36}N_7O_5BMo$: C, 55.98; H, 4.97; N, 13.44; O, 10.97; B, 1.48; Mo, 13.15. Found: C, 56.03; H, 4.99; N, 13.34.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]-[(2*S,3*R**,4*R**,5*S**,6*R**)-(1-benzyloxycarbonyl)- η-(3,4,5)-2-benzyl-3-methoxy-6-ethyl-1,2,5,6-tetrahydropyridin-3-yl-1-carboxylate]molybdenum, 22**. Cationic complex **14** (0.250 g, 0.30 mmol, 1.0 equiv) in 10 of mL dry THF at −78 °C was treated with a 1 M solution of ethylmagnesium bromide in THF (0.36 mL, 0.36 mmol, 1.2 equiv) and gave, after workup and basic alumina chromatography, **22** as an orange solid (0.143 g, 0.20 mmol, 66%). TLC (silica gel, 25% ethyl acetate in hexane, R_f = 0.38); mp 107−111 °C with decomp; IR (CH_2Cl_2, KBr, cm^{-1}): 2487 (w), 1931 (sh, s), 1838 (sh, s), 1691 (sh, m). ^{1}H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.25 (s, 0.56 H), 8.24 (s, 0.44 H), 7.90 (s, 1 H), 7.84 (s, 2 H), 7.73 (s, 1 H), 7.51 (s, 1 H), 7.28 (m, 10 H), 6.32 (d, J = 2.0 Hz, 2 H), 6.20 (s, 1 H), 5.10 (s, 0.9 H), 4.93 (s, 1.1 H), 4.82 (br m, 1 H), 4.33 (t, J = 8.4 Hz, 0.56 H), 4.29 (t, J = 8.4 Hz, 0.44 H), 4.26 (t, J = 6.8 Hz, 0.56 H), 4.20 (t, J = 6.8 Hz, 0.44 H), 3.72 (d, J = 2.8 Hz, 0.56 H), 3.70 (d, J = 2.8 Hz, 0.44 H), 3.07 (m, 2 H), 2.80 (s, 1.33 H), 2.77 (s, 1.67 H), 1.89 (m, 0.88 H), 1.77 (m, 1.22 H), 1.10 (t, J = 7.2 Hz, 1.67 H), 1.00 (t, J = 7.2 Hz, 1.33 H). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): δ 230.7, 227.4, 153.8, 153.5, 145.6, 143.7, 140.2, 139.7, 137.4, 137.0, 136.5, 136.2, 135.9, 134.8, 128.6, 128.4, 127.8, 127.5, 127.4, 127.2, 126.9, 125.4, 105.5, 66.4, 65.9, 57.1, 57.0, 55.9, 54.2, 53.8, 53.6, 45.8, 45.6, 33.2, 33.011.4. Anal. Calcd for $C_{34}H_{36}N_7O_5BMo$: C, 55.98; H, 4.97; N, 13.44; O, 10.97; B, 1.48; Mo, 13.15. Found: C, 55.87; H, 5.01; N, 13.31.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]-[(2*S,3*R**,4*R**,5*S**,6*R**)-(1-benzyloxycarbonyl)- η-(3,4,5)-2-ethenyl-3-methoxy-6-methyl-1,2,5,6-tetrahydropyridin-3-yl]molybdenum, 23**. Cationic complex **15** (0.05 g, 0.064 mmol, 1.0 equiv) in 25 mL of dry THF at −78 °C was treated with a 1.0 M solution of methylmagnesium bromide in THF (0.02 mL, 0.071 mmol, 1.1 equiv) and gave, after workup and basic alumina chromatography, **23** as an orange solid (0.032 g, 0.049 mmol, 76%). TLC (silica gel, 25% ethyl acetate in hexane, R_f = 0.32); mp 95−100 °C with decomp; IR (CH_2Cl_2, KBr, cm^{-1}): 2484 (w), 1932 (sh, s), 1842 (sh, s), 1692 (sh, m). ^{1}H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.30 (d, J = 2.0 Hz, 1 H), 7.98 (d, J = 2.0 Hz, 0.43 H), 7.96 (d, J = 2.0 Hz, 0.57 H), 7.88 (br s, 1 H), 7.85 (d, J = 2.0 Hz, 1 H), 7.83 (d, J = 2.0 Hz, 1 H), 7.77 (d, J = 2.0 Hz, 1 H), 7.33 (m, 5 H), 6.33 (m, 2 H), 6.28 (m, 1 H), 5.93 (m, 1 H), 5.38 (d, J = 17.2 Hz, 0.43 H), 5.25 (d, J = 10.4 Hz, 0.43 H), 5.20 (d, J = 10.4 Hz, 0.57 H), 5.19 (d, J = 17.2 Hz, 0.57 H), 5.09 (A of AB quartet, J = 14.8 Hz, 0.57 H), 5.07 (br s, 1 H), 5.02 (A of AB quartet, J = 10.4 Hz, 0.43 H), 4.98 (B of AB quartet, J = 10.4 Hz, 0.57 H), 4.96 (B of AB quartet, J = 14.8 Hz, 0.57 H), 4.38 (m, 1 H), 4.33 (dd, J = 8.0, 2.2 Hz, 0.57 H), 4.28 (dd, J = 8.0, 2.2 Hz, 0.43 H), 3.81 (d, J = 8.0 Hz, 0.43 H), 3.79 (d, J = 8.0 Hz, 0.57 H), 3.02 (s, 1.29 H), 2.92 (s, 1.71 H), 1.43 (d, J = 6.4 Hz, 1.29 H), 1.42 (d, J = 6.4 Hz, 1.71 H). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): δ 230.5, 227.5, 153.5, 152.9, 145.8, 144.1, 141.0, 140.7, 138.9, 138.6, 136.7, 136.5, 136.1, 135.0, 131.4, 130.5, 128.0, 127.9, 127.4, 127.2, 126.9, 118.3, 117.9, 105.8, 105.5, 66.1, 65.9, 60.5, 59.6, 56.8, 56.4, 56.2, 54.7, 47.7, 25.9, 25.2. Anal. Calcd for $C_{28}H_{30}N_7O_5BMo$: C, 51.63; H, 4.64; N, 15.05; O, 12.28; B, 1.66; Mo, 14.73. Found: C, 51.81; H, 4.83; N, 14.76.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]-[(2*S,3*R**,4*R**,5*S**,6*R**)-(1-benzyloxycarbonyl)- η-(3,4,5)-2-ethenyl-3-methoxy-6-ethyl-1,2,5,6-tetrahydropyridin-3-yl]molybdenum, 24**. Cationic complex **15** (0.400 g, 0.51 mmol, 1.0 equiv) in 25 mL of dry THF at −78 °C was treated with a 1 M solution of ethylmagnesium bromide in THF (0.53 mL, 0.53 mmol, 1.2 equiv) and gave, after workup and basic alumina chromatography, **24** as an orange solid (0.263 g, 0.40 mmol, 78%). TLC (silica gel, 25% ethyl acetate in hexanes, R_f = 0.34); mp 89−94 °C with decomp; IR (CH_2Cl_2, KBr, cm^{-1}): 2486 (w), 1933 (sh, s), 1841 (sh, s), 1693 (sh, m). ^{1}H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.29 (s, 1 H), 7.91 (s, 1 H), 7.87 (s, 1 H), 7.84 (s, 1 H), 7.81 (s, 1 H), 7.76 (s, 1 H), 7.52 (m, 5 H), 6.33 (s, 2 H), 6.28 (s, 1 H), 5.89 (m, 1 H), 5.44 (d, J = 17.2 Hz, 0.44 H), 5.09 (m, 4.44 H), 4.32 (d, J = 8.2 Hz, 0.56 H), 4.27 (d, J = 8.2 Hz, 0.44 H), 4.22 (t, J = 6.2 Hz, 0.56 H), 4.17 (t, J = 6.2 Hz, 0.44 H), 3.81 (d, J = 3.8 Hz, 0.56 H), 3.79 (d, J = 3.8 Hz, 0.44 H), 3.01 (s, 1.32 H), 2.91 (s, 1.68 H), 1.87 (m, 1.12 H), 1.67 (m, 0.88 H), 1.00 (t, J = 7.2 Hz, 1.68 H), 0.93 (t, J = 7.2 Hz, 1.32 H). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): δ 230.2, 227.5, 153.9, 153.4, 145.7, 144.0, 140.7, 140.5, 138.7, 138.5, 136.5, 136.0, 134.8, 132.4, 131.8, 127.8, 127.2, 127.1, 127.0, 118.3, 117.9, 105.7, 105.5, 105.4, 65.9, 58.6, 57.7, 56.8, 56.4, 56.1, 54.5, 53.4, 53.2, 33.3, 33.1, 11.1. Anal. Calcd for $C_{29}H_{32}N_7O_5BMo$: C, 52.35; H, 4.85; N, 14.74; O, 12.02; B, 1.62; Mo, 14.42. Found: C, 52.63; H, 4.95; N, 14.47.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]-[(2*S,3*R**,4*R**,5*S**,6*R**)-(1-benzyloxycarbonyl)- η-(3,4,5)-2-ethenyl-3-methoxy-6-benzyl-1,2,5,6-tetrahydropyridin-3-yl]molybdenum, 25**. Cationic complex **15** (0.15 g, 0.19 mmol, 1.0 equiv) in 10 mL of dry THF at −78 °C was treated with a 1 M solution of benzylmagnesium bromide in THF (0.23 mL, 0.23 mmol, 1.2 equiv) and gave, after workup and basic alumina chromatography, **25** as an orange solid 0.103 g, 0.14 mmol, 75%). TLC (silica gel, 25% ethyl acetate in hexanes, R_f = 0.35); mp 106−109 °C with decomp; IR (CH_2Cl_2, KBr, cm^{-1}): 2486 (w), 1933 (sh, s), 1843 (sh, s), 1693 (sh, m). ^{1}H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.27 (s, 1 H), 7.87 (s, 1 H), 7.84 (d, J = 2.0 Hz, 2 H), 7.75 (s, 1 H), 7.33 (m, 11 H), 6.32 (t, J = 2.0 Hz, 1 H), 6.30 (t, J = 2.0 Hz, 2 H), 6.05 (m, 1 H), 5.40 (m, 2 H), 4.95 (m, 4 H), 4.46 (m, 1 H), 4.05 (dd, J = 8.0, 2.0 Hz, 0.57 H), 4.01 (dd, J = 8.0, 2.0 Hz, 0.43 H), 3.90 (d, J = 7.8 Hz, 1 H), 3.09 (s, 1.71 H), 2.99 (s, 1.29 H), 3.01 (m, 1 H). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): δ 230.1, 227.4, 153.6, 153.0, 145.8, 144.1, 139.8, 139.4, 138.7, 138.6, 136.7, 136.4, 136.2, 134.9, 132.1, 131.2, 128.8, 128.7, 128.1, 128.0, 127.9, 127.8, 127.3, 127.1, 127.0, 126.0, 125.9, 118.7, 118.2, 105.8, 105.6, 10.5, 66.2, 66.0, 57.7, 56.8, 56.5, 56.4, 56.2, 54.7, 54.1, 53.8, 46.1, 45.6. Anal. Calcd for $C_{34}H_{34}N_7O_5BMo$: C, 56.14; H, 4.71; N, 13.48; O, 11.00; B, 1.49; Mo, 13.19. Found: C, 56.40; H, 4.82; N, 13.23.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]-[(2*S,3*R**,4*R**,5*S**,6*R**)-(1-benzyloxycarbonyl)- η-(3,4,5)-2-phenyl-3-methoxy-6-ethenyl-1,2,5,6-tetrahydropyridin-3-yl]molybdenum, 26**. Cationic complex **16** (0.15 g, 0.18 mmol, 1.0 equiv) in 10 mL of dry THF at −78 °C was treated with a 1 M solution of vinylmagnesium bromide in THF (0.22 mL, 0.22 mmol, 1.2 equiv) and gave, after workup and basic alumina chromatography, **26** as an orange solid (0.071 g, 0.1 mmol, 55%). TLC (silica gel, 25% ethyl acetate in hexanes, R_f = 0.36); mp 116−119 °C with decomp; IR (CH_2Cl_2, KBr, cm^{-1}): 2486 (w), 1934 (sh, s), 1844 (sh, s), 1694 (sh, m). ^{1}H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.34 (d, J = 1.6 Hz, 1 H), 8.01 (s, 1 H), 7.88 (m, 2 H), 7.79 (m, 2 H), 7.69 (d, J = 7.2 Hz, 1 H), 7.49 (m, 1 H), 7.31 (m, 8 H), 6.36 (m, 2 H), 6.26 (t, J = 1.6 Hz, 1 H), 5.86 (m, 1 H), 5.78 (s, 0.5 H), 5.70 (s, 0.5 H), 5.24 (d, J = 17.2 Hz, 0.5 H), 5.03 (m, 4 H), 4.87 (d, J = 6.0 Hz, 0.5 H), 4.81 (d, J = 6.0 Hz, 0.5 H), 4.46 (dd, J = 8.0, 2.0 Hz, 0.5 H), 4.37 (dd, J = 8.0, 2.0 Hz, 0.5 H), 2.80 (s, 1.5 H), 2.66 (s, 1.5 H). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): δ 230.9, 227.2, 153.6, 153.3, 145.7, 144.2, 141.1, 140.9, 140.7, 140.5, 140.4, 136.7, 136.4, 136.1, 134.9, 131.2, 129.9, 128.5, 128.3, 127.9, 127.8, 127.6, 127.5, 127.4, 127.2, 126.8, 115.9, 115.7, 105.8, 105.6, 105.5, 66.5, 66.1, 58.5, 58.4, 58.2, 57.3, 56.3, 54.5. Anal. Calcd for $C_{33}H_{32}N_7O_5BMo$: C, 55.56; H, 4.52; N, 13.74; O, 11.21; B, 1.52; Mo, 13.45. Found: C, 55.37; H, 4.64; N, 13.47.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]-[(2*S,3*R**,4*R**,5*S**,6*R**)-(1-benzyloxycarbonyl)-η-(3,4,5)-2-phenyl-3-methoxy-6-ethyl-1,2,5,6-tetrahydropyridin-3-yl]molybdenum, 27**. Cationic complex **16** (0.400 g, 0.48 mmol, 1.0 equiv) in 25 mL of dry THF at −78 °C was treated with a 1 M solution of vinylmagnesium bromide in THF (0.53 mL, 0.53 mmol, 1.1 equiv) and gave, after workup and basic alumina chromatography, **27** as an orange solid (0.252 g, 0.35 mmol, 73%). TLC (silica gel, 25% ethyl acetate in hexane, R_f = 0.43); mp 117−120 °C with decomp; IR (CH_2Cl_2, KBr, cm^{-1}): 2483 (w), 1934 (sh, s), 1842 (sh, s), 1693 (sh, m). ^1H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.32 (s, 1 H), 7.98 (d, *J* = 2.4 Hz, 1 H), 7.88 (d, *J* = 1.6 Hz, 2 H), 7.78 (m, 4 H), 7.55 (m, 1 H), 7.32 (m, 7 H), 6.36 (s, 2 H), 6.26 (s, 1 H), 5.85 (s, 0.56 H), 5.77 (s, 0.44 H), 5.17 (A of AB quartet, *J* = 12.4 Hz, 0.44 H), 5.07 (A of AB quartet, *J* = 12.4 Hz, 0.56 H), 5.03 (B of AB quartet, *J* = 12.4 Hz, 0.56 H), 4.98 (B of AB quartet, *J* = 12.4 Hz, 0.44 H), 4.42 (dd, *J* = 8.4, 2.0 Hz, 0.44 H), 4.36 (dd, *J* = 8.4, 2.0 Hz, 0.56 H), 4.28 (t, *J* = 7.4 Hz, 0.44 H), 4.20 (t, *J* = 7.4 Hz, 0.56 H), 4.17 (d, *J* = 8.4 Hz, 0.56 H), 4.13 (d, *J* = 8.4 Hz, 0.44 H), 2.86 (s, 1.68 H), 2.71 (s, 1.32 H), 1.77 (m, 0.88 H), 1.49 (m, 1.12 H), 0.68 (t, *J* = 7.4 Hz, 1.32 H), 0.55 (t, *J* = 7.4 Hz, 1.68 H). ^{13}C NMR ($(CD_3)_2SO$, 400 MHz): δ 230.7, 227.4, 154.0, 153.9, 145.7, 144.1, 141.5, 140.8, 140.5, 136.6, 136.4, 136.3, 136.0, 134.8, 131.6, 130.7, 128.2, 128.0, 127.9, 127.8, 127.6, 127.5, 127.5, 127.3, 127.1, 127.0, 105.7, 105.6, 105.5, 66.4, 66.1, 58.7, 58.5, 58.4, 57.6, 57.5, 56.7, 53.9, 53.5, 31.9, 10.7, 10.6. Anal. Calcd for $C_{33}H_{34}N_7O_5BMo$: C, 55.40; H, 4.79; N, 13.70; O, 11.18; B, 1.51; Mo, 13.41. Found: C, 55.34; H, 4.82; N, 13.62.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]-[(2*S,3*R**,4*R**,5*S**,6*R**)-(1-benzyloxycarbonyl)-η-(3,4,5)-2-ethoxycarbonylmethyl-3-methoxy-6-phenylethynyl-1,2,5,6-tetrahydropyridin-3-yl]molybdenum, 28**. Cationic complex **17** (0.200 g, 0.24 mmol, 1.0 equiv) in 4 mL of dry THF at −78 °C was treated with lithium phenylacetylide (generated from phenylacetylene (0.031 mL, 0.29 mmol, 1.2 equiv) in 4 mL of THF and *n*-butyllithium (0.12 mL, 2.42 M in hexanes, 0.29 mmol, 1.2 equiv) at −78 °C) to give, after workup and basic alumina chromatography, **28** as an orange solid (0.110 g, 0.14 mmol, 58%). TLC (silica gel, 25% ethyl acetate in hexanes, R_f = 0.20); mp 102−105 °C with decomp; IR (CH_2Cl_2, KBr, cm^{-1}): 2489 (w), 1939 (sh, s), 1850 (sh, s), 1731 (sh, m), 1700 (sh, m). ^1H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.30 (d, *J* = 2.0 Hz, 1 H), 8.00 (s, 1 H), 7.91 (d, *J* = 2.0 Hz, 1 H), 7.86 (d, *J* = 2.0 Hz, 1 H), 7.78 (s, 1 H), 7.72 (s, 0.5 H), 7.70 (s, 0.5 H), 7.40 (m, 10 H), 6.33 (m, 3 H), 5.13 (m, 4 H), 4.60 (dd, *J* = 8.0, 2.0 Hz, 0.5 H), 4.57 (dd, *J* = 8.0, 2.0 Hz, 0.5 H), 4.02 (m, 2 H), 3.89 (s, 0.5 H), 3.87 (s, 0.5 H), 2.99 (m, 2 H), 2.91 (s, 1.5 H), 2.88 (s, 1.5 H), 1.21 (t, *J* = 7.2 Hz, 1.5 H), 1.13 (t, *J* = 7.2 Hz, 1.5 H). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): δ 230.4, 230.0, 226.5, 226.1, 169.7, 169.6, 153.2, 152.6, 145.8, 144.0, 140.9, 137.0, 136.4, 136.2, 136.0, 135.1, 133.8, 133.2, 131.4, 131.0, 128.4, 127.9, 127.4, 127.1, 126.9, 126.7, 122.0, 121.9, 105.9, 105.7, 91.5, 91.3, 82.8, 82.6, 66.8, 66.3, 59.7, 56.1, 55.1, 54.8, 53.0, 52.9, 43.0, 42.6, 42.0, 41.1, 13.7. Anal. Calcd for $C_{37}H_{36}N_7O_7$-BMo: C, 55.73; H, 4.55; N, 12.29; O, 14.04; B, 1.36; Mo, 12.03. Found: C, 55.85; H, 4.71; N, 12.31.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]-[(2*S,3*R**,4*R**,5*S**,6*R**)-(1-benzyloxycarbonyl)-η-(3,4,5)-2-ethoxycarbonylmethyl-3-methoxy-6-(2-oxo-2-phenyl-ethyl)-1,2,5,6-tetrahydropyridin-3-yl]molybdenum, 29**. Cationic complex **17** (0.200 g, 0.24 mmol, 1.0 equiv) in 4 mL of dry THF at −78 °C was treated via cannula with lithioacetophenone (generated by addition of acetophenone (0.40 mL, 0.33 mmol, 1.4 equiv) to lithium diisopropylamide, prepared from diisopropylamine (0.047 mL, 0.33 mmol, 1.4 equiv), 4 mL of THF, and *n*-butyllithium (0.14 mL, 2.42 M in hexanes, 0.33 mmol, 1.4 equiv) at −78 °C). Workup and basic alumina chromatography gave **29** as an orange solid (0.083 g, 0.10 mmol, 43%). TLC (silica gel, 25% ethyl acetate in hexanes, R_f = 0.17); mp 98−100 °C with decomp; IR (CH_2Cl_2, KBr, cm^{-1}): 2487 (w), 1938 (sh, s), 1846 (sh, s), 1732 (sh, m), 1698 (sh, m). ^1H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.29 (d, *J* = 2.0 Hz, 0.55 H), 8.27 (d, *J* = 2.0 Hz, 0.45 H), 8.10 (s, 0.45 H), 8.08 (d, *J* = 2.0 Hz, 0.55 H), 8.04 (s, 0.45 H), 8.02 (d, *J* = 2.0 Hz, 0.55 H), 7.89 (d, *J* = 2.0 Hz, 1 H), 7.86 (s, 1 H), 7.77 (s, 1 H), 7.60 (m, 4 H), 7.34 (m, 4 H), 7.19 (m, 2 H), 6.32 (m, 3 H), 5.17 (dd, *J* = 8.4, 3.6 Hz, 0.45 H), 5.07 (m, 1.55 H), 5.00 (A of AB quartet, *J* = 13.2 Hz, 0.55 H), 4.87 (m, 0.9 H), 4.79 (B of AB quartet, *J* = 13.2 Hz, 0.55 H), 4.43 (dd, *J* = 8.4, 2.4 Hz, 1 H), 4.09 (m, 3 H), 3.74 (m, 1 H), 3.72 (dd, *J* = 8.4, 1.6 Hz, 1 H), 3.33 (dd, *J* = 16.4, 4.8 Hz, 0.55 H), 3.28 (dd, *J* = 16.4, 4.8 Hz, 0.45 H), 2.91 (s, 1.35 H), 2.90 (m, 1 H), 2.87 (s, 1.65 H), 1.25 (t, *J* = 7.0 Hz, 1.35 H), 1.17 (t, *J* = 7.0 Hz, 1.65 H). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): δ 230.5, 230.2, 226.8, 226.4, 197.8, 197.6, 170.1, 169.9, 153.3, 152.8, 145.8, 143.9, 140.1, 140.0, 136.8, 136.6, 136.3, 136.2, 135.0, 133.4, 132.9, 132.7, 128.4, 127.9, 127.8, 127.4, 127.3, 127.1, 126.9, 126.5, 105.9, 105.7, 105.6, 66.3, 65.8, 63.2, 60.1, 59.6, 57.3, 57.1, 55.8, 55.6, 54.9, 54.3, 52.4, 52.3, 49.0, 48.7, 48.0, 47.6, 43.4, 42.413.9, 13.8. Anal. Calcd for $C_{37}H_{38}N_7O_8BMo$: C, 54.50; H, 4.70; N, 12.02; O, 15.70; B, 1.33; Mo, 11.76. Found: C, 54.22; H, 4.77; N, 12.30.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]-[(2*S,3*R**,4*R**,5*S**,6*R**)-(1-benzyloxycarbonyl)-η-(3,4,5)-2-(1-propenyl)-3-methoxy-6-phenylethynyl-1,2,5,6-tetrahydropyridin-3-yl]molybdenum, 30**. Cationic complex **18** (0.200 g, 0.25 mmol, 1.0 equiv) in 4 mL of dry THF was treated with lithium phenylacetylide (generated from phenylacetylene (0.033 mL, 0.30 mmol, 1.2 equiv) in 4 mL of THF and *n*-butyllithium (0.13 mL, 2.42 M in hexanes, 0.30 mmol, 1.2 equiv) at −78 °C) to give, after workup and basic alumina chromatography, **30** as an orange solid (0.126 g, 0.17 mmol, 67%). TLC (silica gel, 25%ethyl acetate in hexanes, R_f = 0.45); mp 103 °C with decomp; IR (CH_2Cl_2, KBr, cm^{-1}): 2484 (w), 1936 (sh, s), 1846 (sh, s), 1699 (sh, m). ^1H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.28 (s, 1 H), 8.00 (s, 1 H), 7.91 (d, *J* = 2.4 Hz, 1 H), 7.86 (d, *J* = 2.4 Hz, 1 H), 7.78 (d, *J* = 2.4 Hz, 1 H), 7.51 (d, *J* = 2.4 Hz, 1 H), 7.35 (m, 10 H), 6.35 (t, *J* = 2.4 Hz, 1 H), 6.32 (t, *J* = 2.4 Hz, 1 H), 6.30 (t, *J* = 2.4 Hz, 1 H), 6.01 (dt, *J* = 17.0, 7.2 Hz, 0.38 H), 5.88 (dt, *J* = 17.0, 7.2 Hz, 0.62 H), 5.21 (dd, *J* = 10.8, 2.4 Hz, 1 H), 5.10 (A of AB quartet, *J* = 12.8 Hz, 1 H), 5.07 (d, *J* = 14.0 Hz, 1 H), 4.97 (B of AB quartet, *J* = 12.8 Hz, 1 H), 4.92 (app t, *J* = 9.6 Hz, 1 H), 4.71 (m, 1 H), 4.54 (dd, *J* = 8.0, 2.4 Hz, 0.62 H), 4.50 (dd, *J* = 8.0, 2.4 Hz, 0.38 H), 3.86 (d, *J* = 8.0 Hz, 0.62 H), 3.84 (d, *J* = 8.0 Hz, 0.38 H), 3.00 (s, 1.14 H), 2.95 (s, 1.86 H), 2.89 (m, 2 H). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): δ 230.8, 230.5, 226.9, 226.4, 153.7, 152.8, 145.7, 144.1, 141.0, 136.9, 136.6, 136.2, 136.1, 135.7, 135.5, 135.0, 134.9, 131.0, 128.4, 128.0, 127.9, 127.6, 127.4, 126.8, 122.1, 116.3, 115.9, 105.9, 105.7, 92.1, 91.9, 82.7, 82.4, 66.6, 66.2, 56.6, 55.2, 54.8, 54.6 42.9, 42.5, 41.2. Anal. Calcd for $C_{36}H_{34}N_7O_5BMo$: C, 57.54; H, 4.56; N, 13.05; O, 10.65; B, 1.44; Mo, 12.77. Found: C, 57.35; H, 4.71; N, 12.98.

(±)-Dicarbonyl[hydridotris(1-pyrazolyl)borato]-[(2*S,3*R**,4*R**,5*S**,6*R**)-(1-benzyloxycarbonyl)-η-(3,4,5)-2-(1-propenyl)-3-methoxy-6-(2-oxo-2-phenyl-ethyl)-1,2,5,6-tetrahydropyridin-3-yl]molybdenum, 31**. Cationic complex **18** (0.200 g, 0.25 mmol, 1.0 equiv) in 4 mL of dry at −78 °C was treated via cannula with lithioacetophenone (generated by addition of acetophenone (0.41 mL, 0.35 mmol, 1.4 equiv) to lithium diisopropylamide, prepared from diisopropylamine (0.05 mL, 0.35 mmol, 1.4 equiv), 4 mL of THF, and *n*-butyllithium (0.15 mL, 2.42 M in hexanes, 0.35 mmol, 1.4 equiv) at −78 °C). Workup and basic alumina chromatography gave **31** as an orange solid (0.103 g, 0.14 mmol, 54%). TLC (silica gel, 25% ethyl acetate in hexanes, R_f = 0.33); mp 92 °C with decomp; IR (CH_2Cl_2, KBr, cm^{-1}): 2487 (w), 1934 (sh, s), 1842 (sh, s), 1696 (sh, m). ^1H NMR ($(CD_3)_2SO$, 400 MHz): δ 8.28 (d, *J* = 1.6 Hz, 0.56 H), 8.26 (d, *J* = 1.6 Hz, 0.44 H), 8.08 (s, 0.44 H), 8.07 (s, 0.56 H), 8.01 (s, 0.44 H), 8.00 (s, 0.56 H), 7.89 (d, *J* = 2.0 Hz, 2 H), 7.85 (d, *J* = 2.0 Hz, 1 H), 7.63 (m, 5 H), 7.28 (m, 5 H), 6.34 (t, *J* = 2.0 Hz, 1 H), 6.31 (t, *J* = 2.0 Hz, 1 H), 6.29 (m, 1 H), 6.04 (m, 0.44 H), 5.85 (m, 0.56 H), 5.03 (m, 5 H), 4.70 (q, *J* = 6.0 Hz, 1 H), 4.36 (s, 0.44 H), 4.34 (s, 0.56 H), 3.79 (t, *J* = 8.0 Hz, 0.44 H), 3.73 (d, *J* = 4.8 Hz, 0.56 H), 3.71 (d, *J* = 4.8 Hz, 0.44 H), 3.66 (t, *J* = 8.0 Hz, 0.56 H), 3.35 (dd, *J* = 16.0, 3.6 Hz, 0.56 H), 3.29 (dd, *J* = 16.0, 3.6 Hz, 0.44 H), 3.00 (s, 0.87 H), 2.98 (s, 0.45 H), 2.94 (s, 1.11 H), 2.92 (s, 0.57 H), 2.83 (m, 1 H), 2.66 (m, 1H). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz): δ 230.5, 227.5, 227.4, 227.1, 197.8, 197.7, 153.7,

153.1, 145.8, 144.0, 140.2, 140.0, 136.8, 136.6, 136.5, 136.3, 136.2, 135.1, 135.0, 134.4, 134.1, 133.7, 133.0, 128.5, 128.0, 127.8, 127.7, 127.6, 127.4, 127.1, 126.9, 126.6, 117.2, 116.1, 115.8, 105.9, 105.6, 66.3, 65.8, 58.0, 57.4, 57.0, 56.1, 55.9, 54.6, 48.8, 48.6, 48.0, 43.2, 42.7. Anal. Calcd for $C_{36}H_{36}N_7O_6BMo$: C, 56.19; H, 4.72; N, 12.74; O, 12.48; B, 1.40; Mo, 12.47. Found: C, 55.94; H, 4.90; N, 12.83.

Decomplexation Studies.

(±)-(2*S,6*R**)-6-Benzyl-2-ethyl-3-oxo-3,6-dihydro-2*H*-pyridine-1-carboxylic Acid Benzyl Ester, 32**. To a 10-mL round-bottomed flask equipped with a stirring bar were added molybdenum complex **21** (0.081 g, 0.11 mmol, 1.0 equiv) and 1 mL dry CH_2Cl_2. Cupric chloride (0.066 g, 0.67 mmol, 6.0 equiv) was added as a solid, and the reaction mixture was allowed to stir at room temperature for 15 min. The resulting green suspension was added directly to a flash silica gel column and eluted with 25% ethyl acetate in hexanes to give enone **32** as a colorless oil (0.021 g, 0.06 mmol, 53%). TLC (silica gel, 25% ethyl acetate in hexanes, $R_f = 0.68$); IR ($CDCl_3$, KBr, cm^{-1}): 3091 (w), 3068 (w), 3034 (w), 2973 (w), 2936 (w), 2879 (w), 1685 (sh, s). ^1H NMR ($(CD_3)_2SO$, 400 MHz): δ 7.40 (m, 5 H), 7.26 (m, 5 H), 6.85 (dd, $J = 10.8$, 4.4 Hz, 1 H), 6.04 (dd, $J = 10.8$, 2.4 Hz, 1 H), 5.15 (m, 2 H), 4.87 (m, 1 H), 4.42 (app t, $J = 8.0$ Hz, 1 H), 3.19 (m, 1 H), 2.91 (dd, $J = 12.8$, 10.4 Hz, 1 H), 1.68 (m, 2 H), 0.92 (m, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 195.4, 155.4, 155.2, 148.2, 147.1, 137.3, 136.1, 134.4, 130.3, 129.8, 129.6, 129.5, 129.2, 129.0, 128.9, 128.8, 128.7, 128.5, 128.3, 128.2, 128.1, 127.5, 127.4, 127.3, 125.0, 124.8, 68.4, 68.2, 67.9, 64.1, 61.9, 61.4, 55.0, 42.9, 28.8, 10.9, 10.8. HRMS (EI) calcd for $C_{22}H_{23}NO_3$: 349.1678. Found: 349.1682.

(±)-(2*S,6*R**)-2-Ethoxycarbonylmethyl-3-oxo-6-(2-oxo-2-phenyl-ethyl)-3,6-dihydro-2*H*-pyridine-1-carboxylic Acid Benzyl Ester, 33**. In a similar fashion, molybdenum complex **29** (0.096 g, 0.12 mmol, 1.0 equiv) in 1 mL of dry CH_2Cl_2 was treated with cupric chloride (0.070 g, 0.71 mmol, 6.0 equiv). Flash silica gel chromatography (25% ethyl acetate in hexanes) gave enone **33** as a colorless oil (0.024 g, 0.06 mmol, 47%). TLC (silica gel, 25% ethyl acetate in hexanes, $R_f = 0.34$); IR ($CDCl_3$, KBr, cm^{-1}): 1731 (sh, s), 1686 (sh, s). ^1H NMR ($(CD_3)_2SO$, 400 MHz): δ 7.97 (d, $J = 7.6$ Hz, 2 H), 7.67 (tt, $J = 7.6$, 1.2 Hz, 1 H), 7.54 (t, $J = 7.6$ Hz, 2 H), 7.30 (m, 5 H), 7.22 (dd, $J = 10.4$, 4.8 Hz, 1 H), 6.12 (dd, $J = 10.4$, 2.0 Hz, 1 H), 5.29 (dtd, $J = 9.2$, 4.5, 2.0 Hz, 1 H), 5.10 (s, 2 H), 4.95 (t, $J = 6.8$ Hz, 1 H), 4.03 (q, $J = 7.2$ Hz, 2 H), 3.68 (dd, $J = 17.3$, 9.2 Hz, 1 H), 3.51 (dd, $J = 17.2$, 3.8 Hz, 1 H), 2.85 (dd, $J = 14.7$, 7.0 Hz, 1 H), 2.75 (dd, $J = 14.7$, 7.2 Hz, 1 H), 1.16 (t, $J = 7.2$ Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 197.2, 193.3, 170.2, 170.3, 154.8, 150.1, 149.3, 136.3, 135.8, 133.9, 129.3, 129.0, 128.8, 128.5, 128.3, 68.2, 61.4, 57.3, 49.1, 44.6, 43.7, 39.7, 39.0, 14.3. HRMS (EI) calcd for $C_{25}H_{25}NO_6$: 435.1682. Found: 435.1675.

(±)-(2*S,6*S**)-2-Benzyl-5-methoxy-6-ethenyl-3,6-dihydro-2*H*-pyridine-1-carboxylic Acid Benzyl Ester, 34**. To a 25-mL resealable Pyrex Schlenk tube were added molybdenum complex **25** (0.060 g, 0.083 mmol, 1.0 equiv), 15 mL of dry CH_2Cl_2, and trifluoroacetic acid (0.0094 g, 0.083 mmol, 1.0 equiv). The flask was placed in a UV reactor equipped with 350 nm lamps and irradiated for 24 h. The mixture was then occluded onto silica and purified by medium-pressure chromatography (SiO_2, 10% ethyl acetate in hexanes) to give **34** as a colorless oil (0.019 g, 0.054 mmol, 65%). TLC (silica gel, 10% ethyl acetate in hexanes, $R_f = 0.46$); IR ($CDCl_3$, KBr, cm^{-1}): 3089 (w), 3068 (w), 3032 (w), 2957 (w), 2940 (w), 2907 (w), 2857 (w), 2839 (w), 1686 (sh, s). ^1H NMR ($(CD_3)_2SO$, 400 MHz): δ 7.27 (m, 10 H), 5.88 (ddd, $J = 17.0$, 10.3, 6.8 Hz, 1 H), 5.19 (d, $J = 14.8$ Hz, 1 H), 5.15 (d, $J = 8.8$ Hz, 1 H), 5.12 (s, 2 H), 4.81 (m, 2 H), 4.55 (q, $J = 7.2$ Hz, 1 H), 3.21 (s, 3 H), 2.80 (m, 2 H), 2.22 (ddt, $J = 16.4$, 6.8, 2.8 Hz, 1 H), 1.98 (dd, $J = 17.8$, 5.0 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz, significant broadening of some absorptions precluded an accurate signal count): δ 155.6, 151.9, 139.6, 136.8, 136.1, 129.5, 129.0, 128.7, 128.6, 128.3, 128.2, 126.5, 118.3, 89.7, 67.5, 55.2, 54.7, 50.8, 40.7, 24.4. HRMS (EI) calcd for $C_{23}H_{25}NO_3$: 363.1834. Found: 363.1832.

(±)-(2*S,6*S**)-6-Ethoxycarbonylmethyl-5-methoxy-2-phenylethynyl-3,6-dihydro-2*H*-pyridine-1-carboxylic Acid Benzyl Ester, 35**. In a similar fashion, molybdenum complex **28** (0.043 g, 0.054 mmol, 1.0 equiv) in 15 mL of dry CH_2Cl_2 containing trifluoroacetic acid (0.006 g, 0.083 mmol, 1.0 equiv) was irradiated for 24 h. The mixture was then occluded onto silica and purified by silica MPLC (10% ethyl acetate in hexanes) to give **35** as a colorless oil (0.023 g, 0.030 mmol, 55%). TLC (silica gel, 25% ethyl acetate in hexanes, $R_f = 0.48$); IR (CH_2Cl_2, KBr, cm^{-1}): 3071 (w), 3037 (w), 2984 (w), 2961 (w), 2941 (w), 2908 (w), 2853 (w), 1730 (sh, s), 1699 (sh, s). ^1H NMR ($(CD_3)_2SO$, 400 MHz): δ 7.35 (m, 10 H), 5.47 (d, $J = 5.2$ Hz, 1 H), 5.20 (A of AB quartet, $J = 12.8$ Hz, 1 H), 5.12 (B of AB quartet, $J = 12.8$ Hz, 1 H), 4.89 (d, $J = 6.0$ Hz, 1 H), 4.82 (app t, $J = 6.4$ Hz, 1 H), 4.00 (m, 2 H), 3.52 (s, 3 H), 3.20 (m, 1 H), 2.89 (app t, $J = 5.2$ Hz, 1 H), 2.59 (m, 1 H), 2.37 (dd, $J = 16.6$, 6.4 Hz, 1 H), 1.14 (m, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.5, 171.0, 155.9, 155.6, 153.6, 136.7, 136.5, 132.0, 131.7, 128.8, 128.7, 128.6, 128.5, 128.3, 128.2, 128.1, 128.0, 126.6, 123.2, 123.0, 90.3, 89.8, 89.4, 82.5, 81.1, 67.8, 67.6, 60.5, 54.9, 54.7, 52.3, 50.9, 44.8, 29.4, 27.6, 14.4. HRMS (EI) calcd for $C_{26}H_{27}NO_5$: 433.1889. Found: 433.1895.

(±)-(2*S,3*R**,6*S**)-2-Ethyl-3-methoxy-6-phenyl-3,6-dihydro-2*H*-pyridine-1-carboxylic Acid Benzyl Ester, 36**. To a 10 mL round-bottomed flask equipped with stirring bar was added the molybdenum complex **20** (0.077 g, 0.108 mmol, 1.0 equiv) and 1 mL of dry CH_2Cl_2. The solution was cooled to 0 °C in an ice/water bath and treated with nitrosonium tetrafluoroborate (0.038 g, 0.32 mmol, 3.0 equiv). The reaction mixture was allowed to stir at 0 °C for 1 h, and then a solution of sodium cyanoborohydride (0.024 g, 0.38 mmol, 3.5 equiv) in 1 mL of THF was added by cannula. The resulting mixture was allowed to warm to room temperature, stirred for 1.5 h, and then filtered through a plug of silica gel eluting with 50% ethyl acetate in hexanes. The resulting crude product was purified by medium-pressure chromatography (SiO_2, 25% ethyl acetate in hexanes) to give **36** as a colorless oil (0.027 g, 0.077 mmol, 71%). TLC (silica gel, 25% ethyl acetate in hexanes, $R_f = 0.64$); IR ($CDCl_3$, KBr, cm^{-1}): 3091 (w), 3068 (w), 3037 (w), 2970 (w), 2936 (w), 2880 (w), 2094 (w), 2824 (w), 1687 (sh, s). ^1H NMR ($(CD_3)_2SO$, 400 MHz): δ 7.30 (m, 10 H), 6.28 (br d, $J = 8.8$ Hz, 1 H), 6.14 (ddd, $J = 8.8$, 6.0, 2.0 Hz, 1 H), 5.67 (br s, 1 H), 5.20 (A of AB quartet, $J = 12.8$ Hz, 1 H), 5.12 (B of AB quartet, $J = 12.8$ Hz, 1 H), 4.46 (br t, $J = 7.2$ Hz, 1 H), 3.64 (d, $J = 5.2$ Hz, 1 H), 3.25 (s, 3 H), 1.24 (m, 2 H), 0.55 (br s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.1, 156.8, 141.7, 137.1, 136.6, 131.2, 128.6, 128.4, 128.1, 127.8, 127.5, 123.7, 77.4, 74.3, 73.9, 67.5, 56.5, 56.1, 54.8, 54.0, 53.4, 25.9, 25.6, 11.0, 10.8. HRMS (EI) calcd for $C_{22}H_{25}O_3N$: 351.1834. Found: 351.1826.

(±)-(2*S,3*R**,6*R**)-6-Ethyl-3-methoxy-2-phenyl-3,6-dihydro-2*H*-pyridine-1-carboxylic Acid Benzyl Ester, 37**. In a similar fashion, molybdenum complex **27** (0.050 g, 0.070 mmol, 1.0 equiv) in 1 mL of dry CH_2Cl_2 at 0 °C was treated with nitrosonium tetrafluoroborate (0.025 g, 0.21 mmol, 3.0 equiv). Treatment with sodium cyanoborohydride (0.015 g, 0.25 mmol, 3.5 equiv) in 1 mL of THF followed by workup and chromatography (25% ethyl acetate in hexanes) gave **37** as a colorless oil (0.015 g, 0.044 mmol, 63%). TLC (silica gel, 25% ethyl acetate in hexanes, $R_f = 0.50$); IR (CH_2Cl_2, KBr, cm^{-1}): 3032 (w), 2968 (w), 2932 (w), 2875 (w), 2819 (w), 1688 (sh, s). ^1H NMR ($(CD_3)_2SO$, 400 MHz): δ 7.33 (m, 10 H), 6.20 (ddd, $J = 10.4$, 5.6, 2.8 Hz, 1 H), 6.02 (dd, $J = 10.4$, 3.6 Hz, 1 H), 5.69 (s, 1 H), 5.24 (A of AB quartet, $J = 12.8$ Hz, 1 H), 5.19 (B of AB quartet, $J = 12.8$ Hz, 1 H), 4.28 (dd, $J = 5.4$, 1.4 Hz, 1 H), 4.27 (m, 1 H), 3.21 (s, 3 H), 0.89 (m, 2 H), 0.62 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.6, 136.9, 133.2, 128.8, 128.7, 128.6, 128.5, 128.3, 128.1, 128.0, 127.6, 122.2, 72.5, 68.2, 67.6, 56.8, 54.9, 54.1, 53.3, 27.4, 11.4, 11.2. Anal. Calcd for $C_{22}H_{25}NO_3$: C, 75.19; H, 7.17; N, 3.99; O, 13.66. Found: C, 74.92; H, 7.02; N, 4.06.

(±)-(2*S,3*R**,6*R**)-6-Ethyl-3-methoxy-2-phenyl-piperidine, 38**. In a 25 mL round-bottomed flask, a solution of compound **37** (0.062 g, 0.18 mmol, 1 equiv) in 10 mL of anhydrous ethanol and 10% palladium on carbon (0.019 g, 0.017 mmol, 0.10 equiv) was purged with hydrogen gas for 10 min. The reaction mixture was then allowed to stir under 1 atm of hydrogen overnight. The solid catalyst was then

removed by filtration, and the solvent evaporated to give **38** as a colorless oil (0.033 g, 0.14 mmol, 85%). TLC (silica gel, 25% ethyl acetate in hexanes, $R_f = 0.48$); IR ($CDCl_3$, KBr, cm^{-1}): 3155 (sh, m), 2983 (w), 2934 (w), 2899 (w). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.35 (m, 5 H), 3.47 (d, $J = 8.8$ Hz, 1 H), 3.16 (ddd, $J = 10.4, 8.8, 4.4$ Hz, 1 H), 3.02 (s, 3 H), 2.56 (app ddd, $J = 17.1, 6.4, 2.4$ Hz, 1 H), 2.27 (dq, $J = 10.4, 4.0$ Hz, 1 H), 1.81 (dq, $J = 8.4, 3.2$ Hz, 1 H), 1.75 (m, 4 H), 0.90 (t, $J = 7.6$ Hz, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 143.9, 129.2, 129.1, 128.4, 83.3, 68.7, 59.7, 58.3, 31.9, 31.7, 30.4, 11.7. HRMS (EI) calcd for $C_{14}H_{21}ON$: 219.1623. Found: 219.1615.

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Supporting Information Available: Photocopies of ^1H and ^{13}C NMR spectra of compounds **3**, **15**, **16**, **18**, **32**−**38**. This material is available free of charge via the Internet at http://pubs.acs.org.

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