Articles

An Easily Accessed Molybdenum Lewis Acid as a Catalyst for Imine Aziridination

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The complex [MoCl(η^3-C_3H_5)$(CO)_2$(phen)] was prepared in a one-pot manner from Mo$(CO)_6$, allyl chloride, and 1,10-phenanthroline (phen). This complex reacted with AgOTf to afford [Mo(OTf)(η^3-C_3H_5)$(CO)_2$(phen)] (**1**). The reaction of **1** with NaBAr′$_4$ (Ar′ = 3,5-bis(trifluoromethyl)phenyl) in CH_2Cl_2 yielded a solution that catalyzed (1% load of the catalyst) the reaction of ethyl diazoacetate with *N*-benzylideneaniline to give a mixture of *cis*-(carboxyethyl)-1,3-diphenylaziridine and two enamines. Replacement of phen by chiral ligands based on *trans*-1,2-diaminocyclohexane failed to induce asymmetry on the obtained aziridine.

Introduction

Organic molecules with heteroatoms bearing lone electron pairs can be activated toward different stoichiometric or catalytic processes by coordination to Lewis acids.[1] Main-group Lewis acids are the most widely used, although transition-metal or lanthanide chlorides or triflates have been increasingly applied.[2]

More sophisticated transition-metal complexes[3] offer little or no compensation in exchange for their multistep preparation and higher cost. Lewis acidic reagents based on group 6 metal carbonyl complexes, which are the most pertinent to the work described here, include [W$(SbF_6)(CO)_3$(NO)(PMe_3)][3a,4b] and aldehyde adducts of {MCp$(CO)_3$}$^+$ [3a] or {MTp(CO)(RC≡CMe)}$^+$ [4c,d] fragments (M = Mo, W).[4]

Pseudooctahedral [MoX(η^3-allyl)$(CO)_2$(N−N)] (X = halide, N−N = 2,2′-bipyridine, 1,10-phenanthroline)[5] are inexpensive compounds that can be easily prepared, can be handled in the air for short periods of time, and are compatible with the presence of water in their solutions.[6]

Curtis found that the cationic 16-electron fragment {Mo(η^3-allyl)$(CO)_2$(N−N)}$^+$ (N−N = bipy) acts as a strong Lewis acid.[7] We felt that if a straightforward and clean method were available for the generation of fragments of this kind or the related [Mo(S)(η^3-allyl)$(CO)_2$(N−N)]$^+$ solvates, these species could be attractive Lewis acidic reagents. Here we report our results on the generation of these molybdenum cationic compounds and their application to the catalytic synthesis of aziridines from *N*-benzylideneaniline (BDA) and ethyl diazoacetate (EDA).[8]

Results and Discussion

Cationic [Mo(S)(η^3-allyl)$(CO)_2$(N−N)]$^+$ complexes have been generated by treatment of the halo precursors [MoX(η^3-allyl)$(CO)_2$(N−N)] with silver tetrafluoroborate.[9] The resulting solutions may be poorly defined regarding their use in catalysis, since traces of silver

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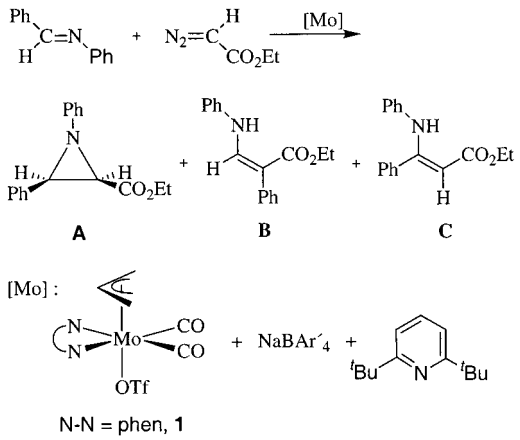
salts may act as Lewis acids as well,[3a] and the isolation of the cationic labile complexes in a pure state proved difficult. In addition, the tetrafluoroborate anion is known to participate in hydrolyses and fluoride transfer pathways, which can result in catalyst deactivation.[10]

The complex [Mo(OTf)(η^3-C_3H_5)$(CO)_2$(phen)] (**1**) is synthesized by the reaction of silver triflate with [MoCl(η^3-C_3H_5)$(CO)_2$(phen)], which in turn can be prepared in a one-pot manner from $Mo(CO)_6$, allyl chloride, and 1,10-phenanthroline (see Experimental Section). The neutral complex **1** could be purified by crystallization to remove traces of silver salts. We found that **1** does not catalyze the reaction of BDA and EDA, a fact that we attribute to insufficient lability of the triflate group in **1**.

The reaction of the salt $NaBAr'_4$ (Ar′ = 3,5-bis(trifluoromethyl)phenyl)[11] with covalent triflato complexes in CH_2Cl_2 solution was used by Bergman[12] and Caulton[13] for the generation of cationic dichloromethane complexes. Addition of $NaBAr'_4$ to a CH_2Cl_2 solution of **1** caused it to become cloudy, due to the formation of insoluble sodium triflate. The ν_{CO} bands of the resulting solution were shifted to higher wavenumbers, as expected for the formation of a cationic species (ν_{CO} 1963, 1875 cm^{-1} vs 1948, 1864 cm^{-1} for **1**). This solution was found to catalyze the reaction of BDA and EDA in CH_2Cl_2 at 20 °C. Thus, in the presence of 1% of the catalyst, EDA reacted with BDA in 8 h to afford a mixture of *cis*-(carboxyethyl)-1,3-diphenylaziridine (**A**) and enamines **B** and **C** (aziridine:enamine = 1:1) (see Scheme 1 and Experimental Section). The formation of enamines as byproducts in Lewis acid catalyzed syntheses of aziridines has been previously noted and has been explained by a 1,2-shift of either a hydrogen or an alkyl group.[8b]

Scheme 1



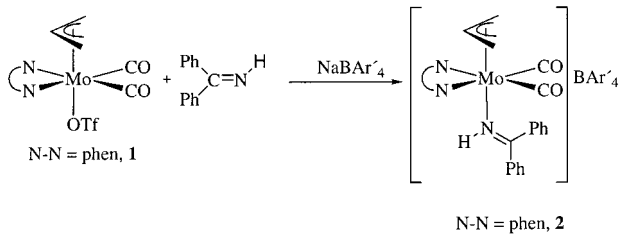
In the absence of BDA, the solution obtained by mixing **1** and $NaBAr'_4$ in CH_2Cl_2 did not catalyze the decomposition of EDA. Accordingly, diethyl fumarate and diethyl maleate were absent in the aziridine−enamine mixture obtained in the catalytic reaction. Therefore, a mechanism involving carbene intermediates can be, in principle, excluded.[14]

All our attempts to isolate the product of the reaction between **1** and $NaBAr'_4$ failed, and only broad noninformative bands could be observed in the ^1H NMR spectrum. We attribute this to the extremely labile nature of the resulting species. Furthermore, more than one cationic complex could be present, CH_2Cl_2 and water being obvious possible ligands in Mo solvates.

Addition of BDA to the CH_2Cl_2 solutions resulting from the mixture of **1** and $NaBAr'_4$ did not make possible the isolation of any pure compound either.

On the other hand, when benzophenone imine was added instead, the imine complex [Mo(HN=CPh_2)(η^3-C_3H_5)$(CO)_2$(phen)]BAr'_4 (**2**) could be isolated and characterized by microanalysis and IR and NMR (^1H and ^{13}C) spectroscopy (see Scheme 2 and Experimental Section).

Scheme 2



This confirms that one or more labile complexes [Mo(S)(η^3-C_3H_5)$(CO)_2$(phen)]BAr'_4 are present in the catalytically active solutions obtained from the reaction of the triflato complex **1** and $NaBAr'_4$ in CH_2Cl_2.

The fact that benzophenone imine, but not BDA, allowed the isolation of an imine complex is not surprising in view of the previously known chemistry of transition-metal complexes with monodentate imine ligands. Thus, whereas adducts of N−H imines can be obtained with relative ease,[15] coordination of N−CH_3 imines required more forcing conditions[15a] and, to our knowledge, no N-bound transition-metal BDA complex has been reported, reflecting the importance of the steric hindrance caused by the substituent on the nitrogen atom.[16] It was suggested above that [Mo(OH_2)(η^3-C_3H_5)$(CO)_2$(phen)]$^+$ could be present in the catalytic solution. Such a cationic aquo complex can show a significant Brønsted acidity. To suppress its possible effect on the catalysis, 2,6-di-*tert*-butylpyridine was added to the precatalyst (see Experimental Section). This hindered, noncoordinating base has been used by several groups

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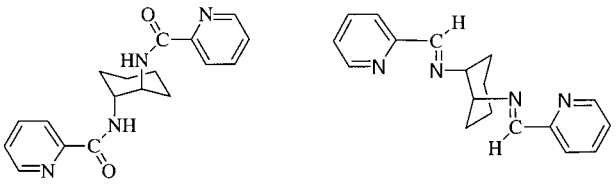
Table 1. Crystal Data and Refinement Details for Complexes 3−5

	3	4	5
formula	$C_{28}H_{30}Cl_2Mo_2N_4O_6$	$C_{26}H_{20}Mo_2N_4O_8 \cdot CH_2Cl_2$	$C_{28}H_{30}Cl_2Mo_2N_4O_4 \cdot CH_2Cl_2$
fw	781.34	793.27	834.27
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2/c$	$P\bar{1}$
a, Å	15.978(11)	15.7554(14)	11.1246(19)
b, Å	15.24(3)	8.8730(8)	12.823(2)
c, Å	13.721(6)	23.293(2)	12.928(2)
α, deg	90	90	82.526(3)
β, deg	113.04(4)	103.182	69.071(3)
γ, deg	90	90	83.352(3)
V, Å^3	3074(6)	3170.4(5)	1703.1(5)
Z	4	4	2
T, K	200(2)	293(2)	299(2)
D_c, g cm^{-3}	1.688	1.662	1.627
F(000)	1568	1576	836
λ(Mo Kα), Å	0.710 73	0.710 73	0.710 73
cryst size, mm	0.13 × 0.13 × 0.10	0.08 × 0.22 × 0.35	0.10 × 0.15 × 0.20
μ, mm^{-1}	1.037	1.012	1.089
scan range, deg	$1.38 \le \theta \le 26.01$	$1.33 \le \theta \le 23.27$	$1.61 \le \theta \le 23.26$
abs cor	ψ scan	SADABS	SADABS
no of rflns measd	6303	13 874	7760
no of indep rflns	6037	4557	4865
no. of data/restraints/params	6037/0/379	4557/3/394	4865/0/388
goodness of fit on F^2	0.962	1.037	1.0037
R1/wR2 ($I > 2\sigma(I)$)	0.0438/0.0965	0.0475/0.1376	0.0396/0.1089
R1/wR2 (all data)	0.1396/0.1230	0.0522/0.1428	0.0470/0.1150

Chart 1. Ligands L_{N2O2} and L_{N4}



L_{N2O2} L_{N4}

as a proton scavenger in Lewis acid catalyzed reactions.[3a] Its addition did not have an appreciable effect on the Mo-catalyzed aziridination. Hence, we assume that a Lewis acid, but not a Brønsted acid, is the catalytically active species.

We wanted to explore the possibility of enantioselective catalytic aziridine synthesis[17] using cationic complexes of the type described above.

The chiral ligand *trans*-1,2-bis(2-pyridinecarboxamide)cyclohexane (**L_{N2O2}**; Chart 1) has been recently employed by Trost in combination with the labile complex $[Mo(CO)_3(NCMe)_3]$ for asymmetric molybdenum-catalyzed allylic alkylation.[18]

Equimolar mixtures of $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)_2]$ and **L_{N2O2}** in CH_2Cl_2 were treated sequentially with silver triflate and, after filtration to remove AgCl, with $NaBAr'_4$ and 2,6-di-*tert*-butylpyridine. The resulting solution was found to catalyze the reaction of BDA and EDA to afford aziridine−enamine mixtures analogous to those obtained with the achiral phen catalyst. The shift reagent $[Eu(hfc)_3]$[19] was added to the CD_2Cl_2 solutions of the resulting aziridines to separate the signals due to each enantiomer in the ^{1}H NMR spectrum, which were then integrated. No observable enantiomeric excess was found.

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(19) hfc = tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato], europium(III) derivative.

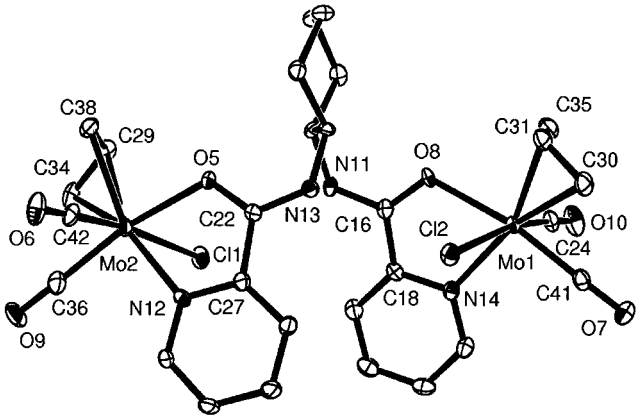
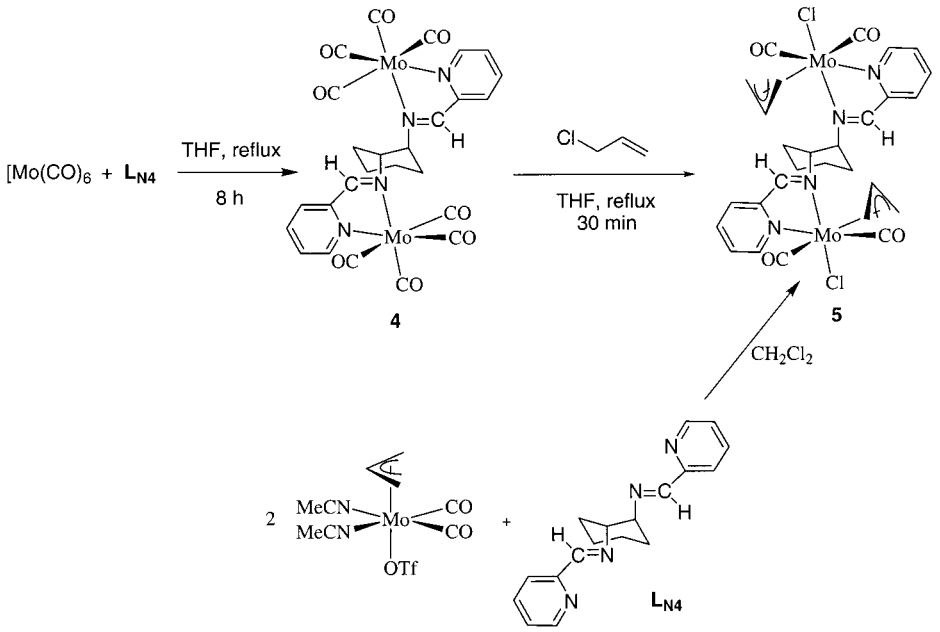


Figure 1. Molecular structure and numbering scheme of **3** with hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å): Mo(1)−C(30) = 2.346(7), Mo(1)−C(31) = 2.203(7), Mo(1)−C(35) = 2.285(8), Mo(1)−C(24) = 1.933(7), Mo(1)−C(41) = 1.931(7), Mo(1)−Cl(2) = 2.570(2), Mo(1)−N(14) = 2.226(6), Mo(1)−O(8) = 2.209(4).

We thought that knowing the structure of the catalyst would help to rationalize this lack of asymmetric induction. However, repeated attempts to obtain X-ray-quality crystals of a cationic complex from the catalytically active solutions were unsuccessful. We then turned our attention to the neutral precatalyst resulting from the reaction of $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(NCMe)_2]$ and **L_{N2O2}**. Our attempts at crystallization using these equimolar mixtures failed. We observed that the IR spectrum of the solution in the 2200−1800 cm^{-1} region, consistent with the occurrence of a single species **3**, remained the same when a **L_{N2O2}**:Mo = 1:2 ratio was employed (ν_{CO} 1936, 1845 cm^{-1}). Red crystals of compound **3**, with an IR spectrum identical with that of the mother solution, were obtained by slow diffusion of hexanes into a solution of the 1:2 mixture in CH_2Cl_2. We therefore concluded that **3** has a **L_{N2O2}**:Mo = 1:2 ratio and that

Scheme 3



the difficulty experienced trying to grow crystals from the 1:1 solution was due to the presence of a mixture of **3** and free $\mathbf{L_{N2O2}}$ in it.

The structure of **3** was determined by X-ray diffraction (Figure 1 and Table 1). Its molecule consists of two identical {MoCl(η^3-C_3H_5)$(CO)_2$} units bridged by one $\mathbf{L_{N2O2}}$ ligand, which chelates the molybdenum atom through the oxygen and the pyridine nitrogen. The coordination geometry around each molybdenum can be described as approximately octahedral, with the allyl group and the two CO ligands defining one face of the octahedron. This is common to most known [MoX(η^3-allyl)$(CO)_2$(L−L)] compounds,[20] as are the orientation of the allyl ligand, with its open face pointing toward the carbonyls,[21] and the acute OC−Mo−CO angles.[22] The Cl and oxygen donor atoms are trans to the CO groups, and the pyridine nitrogen is trans to the allyl ligand.

To our knowledge, the bimetallic complex **3** is the first complex of the ligand $\mathbf{L_{N2O2}}$ to be structurally characterized. The crystal structures of Cu(II) and Ni(II) complexes of the doubly deprotonated form of $\mathbf{L_{N2O2}}$ have been reported,[23] and in both complexes, the ligand acts as a tetradentate species through the four nitrogens toward a single metal. The structure found for **3** was somewhat unexpected, since a carbonyl oxygen should be a poor ligand for an organometallic fragment. A structurally related bridge bis(chelate) involving coordination of a carbonyl oxygen and a phosphine to each metal has been recently reported.[24] The structure of the bis(pyridylamide) complex **3** shows that the molybdenum atom is far from the stereogenic centers, and the chiral ligand does not surround the metal, as was suggested to occur in the Mo/$\mathbf{L_{N2O2}}$ catalyzed allylic alkylation.[18]

The bis(bidentate) Schiff-base ligand *trans*-1,2-bis(2-pyridylimine)cyclohexane ($\mathbf{L_{N4}}$; Chart 1), also based on *trans*-1,2-diaminocyclohexane, has been recently used by Puddephatt in the field of platinum chemistry.[25] This ligand features four potential donor nitrogens, two of which are directly bonded to the stereogenic carbons.

The neutral compound [{MoCl(η^3-C_3H_5)$(CO)_2$}$_2$(μ-$\mathbf{L_{N4}}$)] (**5**) was prepared by two methods: (a) the reaction of $\mathbf{L_{N4}}$ with [Mo$(CO)_6$] to yield [{Mo$(CO)_4$}$_2$(μ-$\mathbf{L_{N4}}$)] (**4**), followed by oxidative addition of allyl chloride, and (b) the reaction of $\mathbf{L_{N4}}$ with [MoCl(η^3-C_3H_5)$(CO)_2$$(NCMe)_2$] (see Scheme 3).

The structures of the molybdenum(0) tetracarbonyl complex **4** and the molybdenum(II) dicarbonyl complex **5** were determined by X-ray diffraction, and the results are shown in Figure 2. In both complexes, $\mathbf{L_{N4}}$ bridges two molybdenum atoms, chelating each one through one imine and one pyridine. A pseudooctahedral geometry was found for the molybdenum atoms of **5**, with the two carbonyls and the allyl group in a facial disposition. Unlike the case in **3**, now the CO ligands are trans to the Cl and pyridine donors, whereas the allyl group is trans to the imine.

The chloro complex **5** was treated with AgOTf, and the resulting triflato complex was treated with NaBAr′$_4$ and 2,6-di-*tert*-butylpyridine in CH_2Cl_2. The resulting solution was found to catalyze the aziridination of BDA and EDA. Dissappointingly, no asymmetric induction was found in the products. A search of chiral ligands able to catalyze the asymmetric synthesis of aziridines employing cationic molybdenum complexes continues in this laboratory, as well as an exploration of these molybdenum compounds as catalysts for other reactions.

Experimental Section

General Procedures. General conditions and the labeling scheme for the BAr′$_4$ anion were given elsewhere.[26]

Synthesis of [Mo(OTf)(η^3-C_3H_5)$(CO)_2$(phen)] (1). A mixture of the chloro complex [MoCl(η^3-C_3H_5)$(CO)_2$(phen)] (0.10

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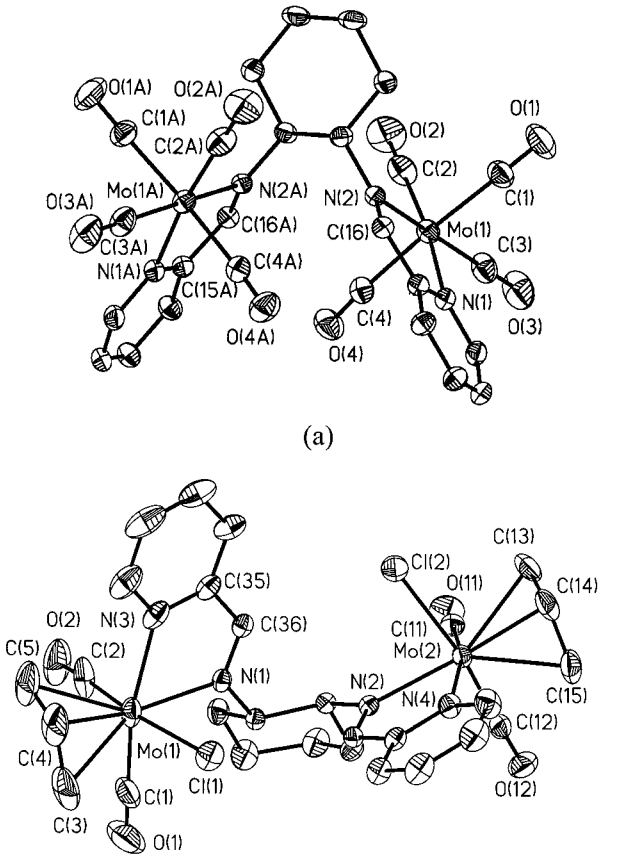

Figure 2. (a) Molecular structure and numbering scheme of **4** with hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å): Mo(1)−C(1) = 2.040(7), Mo(1)−C(2) = 1.964(7), Mo(1)−C(3) = 1.947(7), Mo(1)−C(4) = 2.034(6), Mo(1)−N(1) = 2.249(4), Mo(1)−N(2) = 2.277(4). (b) Molecular structure and numbering scheme of **5** with hydrogen atoms omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. Mo(1)−C(1) = 1.973(7), Mo(1)−C(2) = 1.974(7), Mo(1)−C(3) = 2.330(7), Mo(1)−C(4) = 2.192(6), Mo(1)−C(5) = 2.308(6), Mo(1)−Cl = 2.5511(14), Mo(1)−N(1) = 2.232(3), Mo(1)−N(3) = 2.282(5).

g, 0.24 mmol), AgOTf (0.063 g, 0.24 mmol), and acetone (1 mL) was stirred in the dark for 2 h. The solvent was removed under vacuum, and the residue was extracted in CH_2Cl_2 (30 mL) and filtered through Celite. The solvent was evaporated under reduced pressure, hexane was added, and the complex **1** was obtained as a red precipitate (0.11 g, 86%). IR (CH_2Cl_2; cm^{-1}): 1948, 1864 (ν_{CO}). ^1H NMR (CD_2Cl_2; δ): 9.54, 8.62, 8.04, and 8.00 (m, 2H each, phen), 4.24 (m, 1H, CH of η^3-C_3H_5), 3.90 (d (6.4), 2H, H_{syn}), 1.70 (d (9.7), 2H, H_{anti}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2; δ): 225.72 (CO), 152.96, 144.90, 139.29, 130.34, 127.74, and 125.59 (phen), 73.81 (C^2 of η^3-C_3H_5), 55.92 (C^1 and C^3 of η^3-C_3H_5). ^{19}F NMR (CD_2Cl_2; δ): −79.21. Anal. Calcd for $C_{16}H_{13}F_3MoN_2O_5S$: C, 41.39; H, 2.51; N, 5.36. Found: C, 41.13; H, 2.49; N, 5.29.

Aziridination Reaction. To a solution of **1** (6 mg, 0.01 mmol) in 20 mL of CH_2Cl_2 was added $NaBAr'_4$ (10 mg, 0.01 mmol), and the mixture was stirred for 15 min. 2,6-Di-*tert*-butylpyridine (5 μL, 0.02 mmol) was added, and then BDA (208 mg, 1.15 mmol) and EDA (0.12 mL, 1.15 mmol) were added. The mixture was stirred under nitrogen for 8 h, and then the volatiles were removed in vacuo. The remaining solid was dissolved in CH_2Cl_2 and filtered (Celite). ^1H NMR showed a mixture of *cis*-carboxyethyl-1,3-diphenylaziridine (**A**; 55%, ^1H NMR integration) and enamines **B** and **C** (Scheme 1). *cis*-(Carboxyethyl)-1,3-diphenylaziridine (**A**): ^1H NMR ($CDCl_3$; δ) 1.03 (t, 3H, J = 7.05 Hz, CH_3), 3.25 (d, 1H, J = 6.8 Hz, CHPh), 3.63 (d, 1H, J = 6.8 Hz, CHCO), 3.97−4.13 (m, 2H, CH_2), 6.90−7.58 (m, 10H, C_6H_5).

Synthesis of [Mo(HN=CPh$_2$)(η^3-C$_3$H$_5$)(CO)$_2$(phen)]BAr′$_4$ (2). To a solution of **1** (0.060 g, 0.11 mmol) in CH_2Cl_2 (20 mL) was added $NaBAr'_4$ (0.11 g, 0.11 mmol) and benzophenone imine (19 μL, 0.11 mmol). The mixture was stirred for 1 h at room temperature and filtered via cannula. The solution was concentrated by in vacuo evaporation to a volume of 5 mL. Addition of hexane (20 mL) caused the precipitation of **2** as a red solid, which was washed with hexane (3 × 10 mL) and dried under reduced pressure. Yield: 0.09 g, 78%. IR (CH_2Cl_2; cm^{-1}): 1963, 1875 (ν_{CO}). ^1H NMR (CD_2Cl_2; δ): 8.92, 8.53, 7.96, and 7.43 (m, 2H each, phen), 8.85 (s, br, 1H, imine N−H), 7.75 (m, 8H, H−C_o), 7.55 (m, 4H, H−C_p), 7.09 (m, 6H, 2Ph), 6.18 (m, 4H, 2Ph), 3.50 (d (6.5), 2H, H_{syn}), 2.96 (m, 1H, CH of η^3-C_3H_5), 1.77 (d (9.7), 2H, H_{anti}). $^{13}C\{^1H\}$ NMR (CD_2Cl_2; δ): 223.51 (CO), 186.70 (C=N), 162.13 (q (49.79), C_i), 152.89, 144.26, 139.52, 129.34, 129.03, and 128.32 (phen), 135.16 (C_o), 128.16 (q (31.1), C_m), 124.94 (q (272.5), CF_3), 117.87 (C_p), 74.26 (C^2 of η^3-C_3H_5), 60.37 (C^1 and C^3 of η^3-C_3H_5). Anal. Calcd for $C_{62}H_{36}BF_{24}MoN_3O_2$: C, 52.53; H, 2.56; N, 2.96. Found: C, 52.41; H, 2.48; N, 2.71.

Synthesis of 3. To a solution of [MoCl(η^3-C_3H_5)(CO)$_2$-(NCMe)$_2$] (0.10 g, 0.32 mmol) in CH_2Cl_2 (30 mL) was added the ligand $\mathbf{L_{N2O2}}$ (0.052 g, 0.16 mmol). The reaction mixture was stirred for 15 min at room temperature. The solvent was removed, and the residue was washed twice with hexane (20 mL). Recrystallization from CH_2Cl_2/hexanes yielded 0.12 g of **1** (95%) in two crops as red crystals. IR (CH_2Cl_2; cm^{-1}): 1936, 1845 (ν_{CO}). ^1H NMR (CD_2Cl_2; δ): δ 9.36 (s, br, 2H, Cy−NH), 9.08, 7.99, 7.83, 7.61 (m, 2H each, pyridine H), 3.84 (m, 4H, Cy + allyl), 3.43 (s, br, 2H, allyl), 2.22 (m, 2H, allyl), 1.95 (m, Cy + allyl), 1.43 (m, 6H, Cy + allyl). Anal. Calcd for $C_{28}H_{30}$-$Cl_2Mo_2N_4O_6$: C, 43.04; H, 3.87; N, 7.17. Found: C, 42.91; H, 4.02; N, 7.21.

Synthesis of 4. A stirred suspension of [Mo(CO)$_6$] (0.10 g, 0.38 mmol) and $\mathbf{L_{N4}}$ (0.055 g, 0.19 mmol) in THF (30 mL) was heated to reflux under nitrogen for 8 h, giving a purple solution. The solvent was evaporated to dryness. The residue was extracted with CH_2Cl_2 and filtered through Celite. The volatiles were removed in vacuo, and the residue was washed with hexane (3 × 10 mL). Slow diffusion of hexane into a solution of **4** in CH_2Cl_2 at room temperature produced red crystals. A single crystal obtained in this way was used for the X-ray analysis. Yield: 0.106 g, 79%. IR (CH_2Cl_2; cm^{-1}): 2016, 1908, 1877, 1836 (ν_{CO}). ^1H NMR (CD_2Cl_2; δ): 8.98 (m, 2H), 8.82 (s, 2H, N=CH), 7.83 (m, 2H), 7.75 (m, 2H), 7.38 (m, 2H), 4.48 (m, 2H, NCH), 2.00 (m, 6H), 1.93 (m, 2H). Anal. Calcd for $C_{26}H_{20}Cl_2Mo_2N_4O_8$: C, 44.09; H, 2.85; N, 7.91. Found: C, 44.21; H, 2.77; N, 7.85.

Synthesis of 5. (a) From [MoCl(η^3-C$_3$H$_5$)(CO)$_2$(NCMe)$_2$]. To a solution of [MoCl(η^3-C_3H_5)(CO)$_2$(NCMe)$_2$] (0.10 g, 0.32 mmol) in CH_2Cl_2 (20 mL) was added the ligand $\mathbf{L_{N4}}$ (0.047 g, 0.16 mmol). Inmediately the initially yellow solution turned red. The mixture was stirred for 30 min. Pure **5** was obtained by slow diffusion of hexane into a solution of **5** in CH_2Cl_2 at −20 °C. One of the resulting crystals was used for the X-ray determination. Yield: 0.097 g, 81%. IR (CH_2Cl_2; cm^{-1}): 1937, 1852 (ν_{CO}). ^1H NMR (CD_2Cl_2; δ): 8.98 (m, 2H), 8.37 (s, 2H, N=CH), 8.02 (m, 2H), 7.69 (m, 2H), 7.35 (m, 2H), 3.88 (m, 2H, NCH), 3.16 (d (J = 6.2 Hz), 2H, H_{syn}), 2.27 (m, 6H), 1.57 (d (J = 9.1), 2H, H_{anti}), 1.26 (m, 2H). Anal. Calcd for $C_{28}H_{30}Cl_2$-$Mo_2N_4O_4$: C, 44.88; H, 4.03; N, 7.48. Found: C, 45.06; H, 4.17; N, 7.29.

(b) From Compound 4. To a solution of **4** (0.07 g, 0.09 mmol) in THF (20 mL) was added allyl chloride (0.1 mL, 1.23

(26) Morales, D.; Pérez, J.; Riera, L.; Riera, V.; Miguel, D. *Organometallics* **2001**, *20*, 4517.

mmol), and the mixture was heated to reflux for 45 min. The solvent was evaporated to dryness. The residue was extracted with CH_2Cl_2 and filtered through Celite. The solvent was evaporated under reduced pressure, hexane was added, and the complex **5** was obtained as a red precipitate. Yield: 0.059 g, 87%. The product exhibits the same spectroscopic properties as the compound obtained in (a).

Aziridination reactions using compounds **3** and **5** were conducted as described above for the achiral complex obtained from **1**.

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Supporting Information Available: Text giving a general description of crystal structure determination for compounds **3**−**5** and tables giving positional and thermal parameters, bond distances, and bond angles for **3**, **5**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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