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# Enantioselective Pinacol Coupling of Aryl Aldehydes Catalyzed by Chiral Salan−Mo(IV) Complexes

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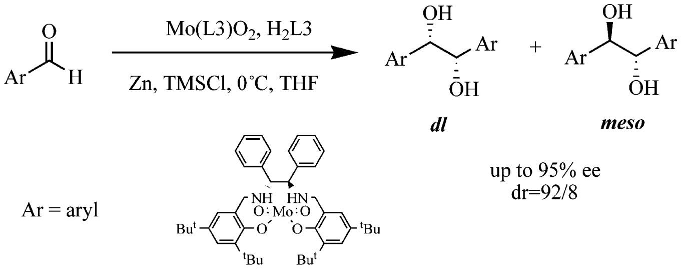

**Mo(L3)O$_2$**

Reported herein is the asymmetric pinacol coupling of aromatic aldehydes with chiral Salan−Mo(VI) dioxo complex as an effective precatalyst. Chiral diols were obtained with high diastereoselectivity and enantioselectivity up to 92/8 and 95%, respectively. The possible mechanism of the pinacol coupling reaction with the catalytic system was investigated. The X-ray crystal structure of the precatalyst Mo(L3)O$_2$ was determined and the oxidation state of the intermediate **C** was confirmed as +4 with X-ray photoelectron spectroscopy study. The proposed mechanism speculated the stereochemical outcome of the reaction, and a working model for the radical coupling of **E** was proposed, which explained the absolute configuration of the favored (*S*,*S*)-enantiomer of the *dl* isomer.

## Introduction

Chiral 1,2-diols, especially hydrobenzoins, are very useful chiral ligands[1] and auxiliaries[2] in stereoselective organic syntheses. Besides the asymmetric dihydroxylation reaction,[3] the asymmetric pinacol coupling reaction[4] was found to be one of the most direct methods to prepare chiral 1,2-diol. Although different metals such as Ce,[5] Ti,[6] U,[7] Sm,[8] Cr,[9] V,[10] Ru,[11] and In[12] have been shown to efficiently catalyze pinacol coupling

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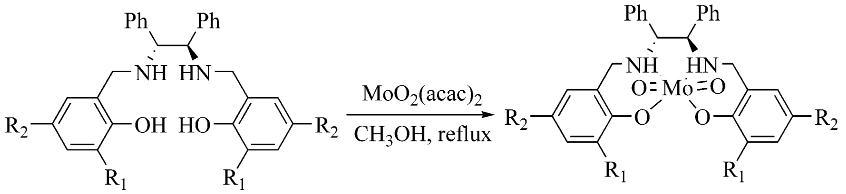
**SCHEME 1. Synthesis of Salan−Mo(VI) Dioxo Complexes**



**MoLO$_2$**

**H$_2$L**

**Mo(L1)O$_2$**: $R_1$ = H, $R_2$ = H
**Mo(L2)O$_2$**: $R_1$ = $OCH_3$, $R_2$ = H
**Mo(L3)O$_2$**: $R_1$ = *t*-Bu, $R_2$ = *t*-Bu

in diastereoselectivity study, attention was mainly focused on chiral titanium catalysts in the field of enantioselective pinacol coupling reaction.[13] More recently, Yamamoto's group developed the highly enantio- and diastereoselective pinacol coupling reaction with a chiral chromium complex TBOxCr(III)Cl as precatalyst.[14] However, other chiral metal complex catalysts but chiral chromium and titanium complexes used in asymmetric pinacol coupling reaction have not been reported.

*cis*-Dioxo complexes dominate the chemistry of molybdenum(VI), and their prevalence, ease of synthesis, and chemical attributes have led to their exploitation as oxidation catalysts, models for enzymes and surface oxides, sensors, and drug targets.[15] Although application for chiral Mo(VI) dioxo complexes in asymmetric reaction dated back the 1970's, all study was focused on oxygen atom transfer reactions, the olefin epoxidation,[16] and oxidation of sulfides.[17] To the best of our knowledge, no optically active chiral Mo(VI) dioxo complexes were used in asymmetric reactions other than the oxidative reaction.

Herein we describe the highly enantioselective pinacol coupling of aromatic aldehydes with characterized Salan−Mo(VI) dioxo complexes as precatalysts and the reaction mechanism was also investigated.

## Results and Discussion

The readily obtainable tetradentate Salan ligands, which are derived from (*R*,*R*)-1,2-diphenylethane, were chosen as the requisite ligands. As shown in Scheme 1, treatment of the chiral ligand with 1 equiv of $MoO_2(acac)_2$ in refluxing methanol provided the chiral Salan−Mo(VI) dioxo complexes in very high yield. Attempts to apply the Salan−Mo(VI) dioxo complexes in oxygen atom transfer reactions were not succeed. We found these complexes were completely ineffective in both the olefin epoxidation and oxidative reaction of sulfides. This may be attributed to the enhanced stability of the molybdenum−oxo moiety afforded by the chelate effect of the quadridentate ligands, which prevents the metal−oxo moiety from coordinating with substrates.[18]

**Asymmetric Pinacol Coupling of Aryl Aldehydes Catalyzed by Chiral Salan−Mo (IV) Complexes.** Following the protocol of the Ti-catalyzed pinacol coupling reaction, in which $Me_3SiCl$ was used as a mediator and a second metal was employed as a co-reductant. We studied the asymmetric pinacol coupling of aromatic aldehydes with the Salan−Mo(IV) complexes as precatalysts. In our preliminary investigation, we carried out the coupling of benzaldehyde using three different Salan−Mo(IV) complexes as precatalysts in THF with 10 mol

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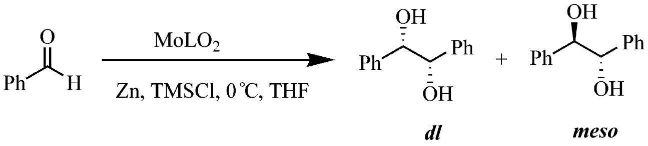
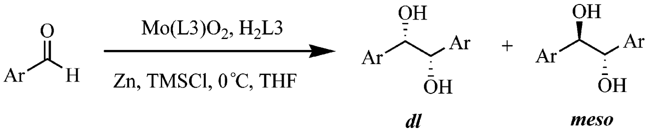
**TABLE 1. Asymmetric Pinacol Coupling Reaction of Benzaldehyde under Different Conditions**[a]



| entry | catalst (%) | sol. | reaction time (h) | yields (%)[b] | *dl*/*meso*[c] | ee[d] (%) |
|---|---|---|---|---|---|---|
| 1 | 5% Mo(L3)$O_2$ | THF | 36 | 76 | 63/35 | 25 |
| 2 | 10% Mo(L3)$O_2$ | THF | 36 | 80 | 66/34 | 68 |
| 3 | 15% Mo(L3)$O_2$ | THF | 36 | 82 | 90/10 | 86 |
| 4 | 15% Mo(L3)$O_2$ +7.5%$H_2$L3 | THF | 48 | 90 | 92/8 | 95 |
| 5 | 15% Mo(L3)$O_2$ +7.5% $H_2$L3 | hexane | 48 | 62 | 48/52 | 23 |
| 6 | 15% Mo(L3)$O_2$ +7.5% $H_2$L3 | $CH_3CN$ | 48 | 74 | 66/34 | 74 |
| 7 | 15% Mo(L3)$O_2$ +7.5% $H_2$L3 | $CH_2Cl_2$ | 48 | 58 | 88/12 | 30 |

[a] Reaction conditions: PhCHO/Zn/$Me_3SiCl$ = 1:4:2, reaction was performed at 0 °C. [b] Isolated yields. [c] Determined by $^1H$ NMR or HPLC. [d] The ee values were determined by HPLC with a Daicel Chiralcel OJ-H.

**TABLE 2. Asymmetric Pinacol Coupling Reaction of Various Aromatic Aldehydes**[a]



| entry | aldehyde (Ar) | reaction time (h) | yield (%)[b] | *dl*/*meso*[c] | ee (%) (config.)[f] |
|---|---|---|---|---|---|
| 1 | Ph | 48 | 90 | 92/8 | 95[d] (*S*,*S*) |
| 2 | *o*-$CH_3C_6H_4$ | 48 | 84 | 74/26 | 85[e] (*S*,*S*) |
| 3 | *m*-$CH_3C_6H_4$ | 48 | 80 | 82/18 | 76[d] (*S*,*S*) |
| 4 | *p*-$CH_3C_6H_4$ | 48 | 95 | 93/7 | 90[e] (*S*,*S*) |
| 5 | *p*-$BrC_6H_4$ | 36 | 88 | 73/27 | 72[e] (*S*,*S*) |
| 6 | *m*-$BrC_6H_4$ | 36 | 78 | 75/25 | 72[e] (*S*,*S*) |
| 7 | *o*-$ClC_6H_4$ | 48 | 88 | 42/58 | 84[d] (*S*,*S*) |
| 8 | *p*-$FC_6H_4$ | 36 | 65 | 78/22 | 66[e] (*S*,*S*) |
| 9 | *o*-$CF_3C_6H_4$ | 48 | 60 | 66/34 | 47[e] (*S*,*S*) |

[a] Reaction conditions: RCHO/Mo(L3)$O_2$/$H_2$L3/Zn/$Me_3SiCl$ = 1:0.15: 0.075:4:2, reaction was performed at 0 °C. [b] Isolated yields. [c] Determined by $^1H$ NMR. [d] The ee values were determined by HPLC with a Daicel Chiralcel OJ-H. [e] The ee values were determined by HPLC with a Daicel Chiralcel AD-H. [f] Absolute configuration was assigned by comparison of optical rotation reported in the literature.

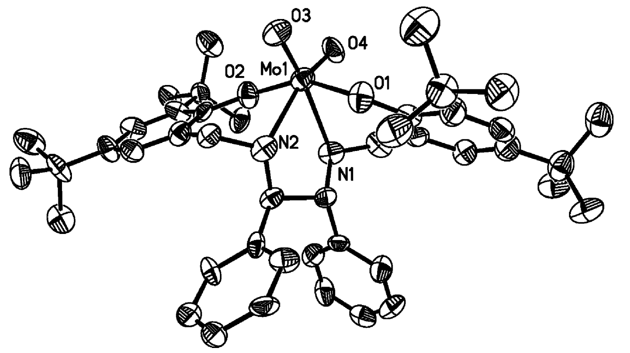


**FIGURE 1.** ORTEP diagram of Mo(L3)$O_2$ with 30% probability ellipsoids. Hydrogen atoms are omitted for clarity.

% loading, 2 equiv of $Me_3SiCl$, and 4 equiv of Zn powder as co-reductants. Mo(L1)$O_2$ and Mo(L2)$O_2$ complexes as precatalysts were not further studied for providing lower diastereoselectivity and enantioselectivity less than 30% ee. Complex Mo(L3)$O_2$ can give moderate diastereoselectivity (dr = 66/34) and enantioselectivity (ee = 43%). Change in precatalyst loading from 5, to 10, to 15 mol % was explored in the reaction (Table 1, entries 1−3). The enantioselectivity increased from 25%, to 68%, to 86% and the yield was not enhanced obviously. By further increasing the catalyst loading to 20 mol %, improvement of the enantioselectivity and yield could not be obtain. Therefore as for the concentration parameter, 15 mol % precatalysts loading was the optimal reaction condition. To our delight, the mixture of 7.5 mol % $H_2$L3 and 15 mol % Mo(L3)$O_2$ as precatalyst can afford a much better result than 15 mol % Mo(L3)$O_2$ only. Both enantioselectivity and diastereoselectivity were improved from 86% to 95% ee and 90/10 to 92/8 dr, respectively (Table 1, entries 3 and 4). In addition, a further survey of solvent revealed that THF was the most favorable solvent among all those examined. Extensive exploration showed the optimized conditions of the catalytic pinacol coupling reaction as PhCHO/Mo(L3)$O_2$/$H_2$L3/Zn/$Me_3SiCl$ = 1:0.15: 0.075:4:2 at 0 °C with THF.

On the basis of the optimal conditions established, we investigated the coupling of a variety of aromatic aldehydes to examine the scope of this catalytic system. The results are shown in Table 2. As can be seen from Table 2, steric hindrance caused a negative effect on the enantioselectivity. All the substituted aryl aldehydes (Table 2, entries 2−9) showed lower ee values than the benzaldehydes (Table 2, entry 1). Various substituted aryl aldehydes exhibited a crucial electronic effect on enantioselectivity. All benzaldehydes substituted by $CH_3$ at different positions, ortho, meta, and para, can give higher diastereoselectivity and enantioselectivity (Table 2, entries 2−4). With the enhancement of a groups' electron-withdraw capability from Br, F, and $CF_3$, the optical reactivity was reduced (Table 2, entries 5, 6, 8, and 9). It was noteworthy that the *o*-chlorobenzaldehyde afforded higher optical reactivity with enantioselectivity up to 84%, but lower diastereoselectivity (Table 2, entry 7). In most cases, the reaction's optical reactivity of aromatic aldehydes with electron-donating groups was higher than that with electron-withdraw groups in this catalytic system. In addition, the absolute configuration of the major isomers of the *dl* products was determined as (*S*,*S*).

**Studied Reaction Mechanism of Pinacol Coupling Catalyzed by Salan−Mo(IV) Complexes.** For better understanding of the reaction mechanism, the X-ray crystal structure of the precatalyst Mo(L3)$O_2$ was determined. Complexes Mo(L3)$O_2$ and $NH_4PF_6$ were dissolved in ethanol. Single crystals suitable for X-ray diffraction analysis were grown by slow evaporation from their ethanol solution for several days. The molecule structure of Mo(L3)$O_2$ is a monomer and the ORTEP diagram of Mo(L3)$O_2$ is shown in Figure 1. The X-ray structure of Mo(L3)$O_2$ exhibited that the coordination around the molybdenum atom was a highly distorted octahedral geometry in the α-cis

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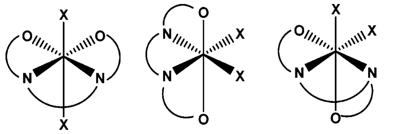
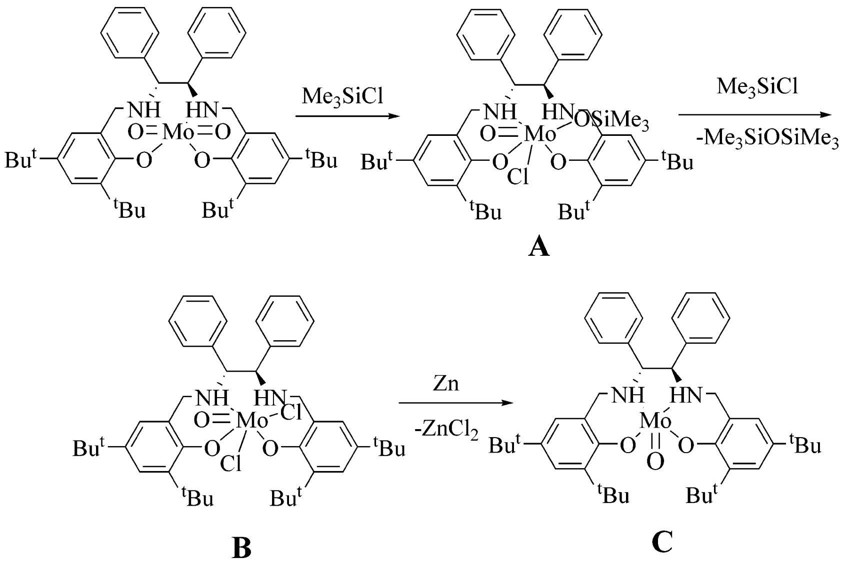
(19) Six-coordinate molybdenum complexes have three geometric isomers:



*Trans* isomer *α-cis* isomer *β-cis* isomer

**SCHEME 2. The Possible Reaction Course of $Me_3SiCl$ with Molybdenum−Dioxo Complexes and Co-reductant Zn**



configuration,[19] with the N atoms trans to the terminal double bonded oxygen atoms.

On the basis of X-ray analysis of $Mo(L3)O_2$ precatalyst, the possible mechanism of the pinacol coupling reaction catalyzed by Salan−Mo(VI) complexes was investigated.

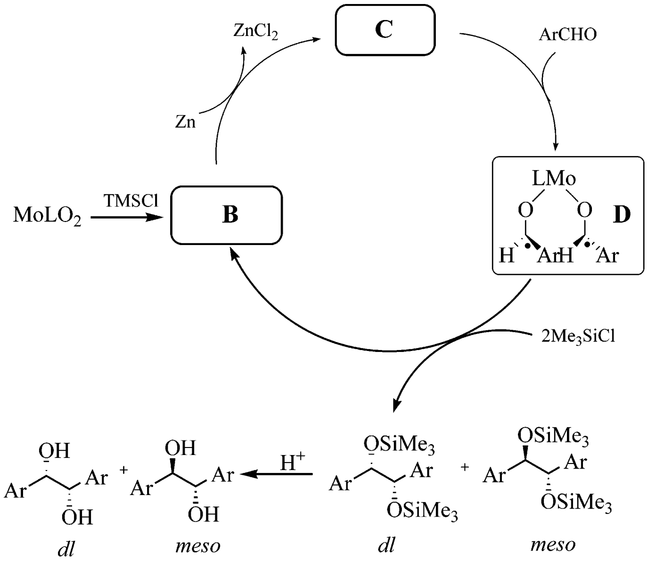
It has been reported that the treatment of the dioxomolybdenm(VI) complex with chlorosilane formed monoxomolybdenm dichloride through a two-step procedure involving a 1,2-monoaddition of the chlorosilane to a Mo═O bond and the subsequent halogenation reaction.[20] The formation of the active species in our catalytic system, based on this result, was proposed in Scheme 2. Reaction of $Mo(L3)O_2$ with 1 equiv of $Me_3SiCl$ gave the intermediate **A**, which transferred to **B** after reacting with another equivalent of $Me_3SiCl$ by nucleophilic substitution of $OSiMe_3$ with chloride. The active catalytic species **C** could be formed through the reduction of **B** with Zn metal.

X-ray photoelectron spectroscopy (XPS) has been used extensively to elucidate the electronic structure of transition metal compounds.[21] To confirm the oxidation state of the intermediate **C**, we carried out the XPS study with this catalyst system.

To the solution of $Mo(L3)O_2$ (0.115 g, 0.15 mmol) in 4 mL of anhydrous THF was added Zn powder (0.26 g, 6 mmol) under nitrogen atmosphere. The yellow mixture was stirred for 10 min at room temperature. After $Me_3SiCl$ (254 $\mu$L, 2 mmol) was added, the suspension turned red. The mixture was stirred for 12 h, and the suspension was filtered through a glass funnel. Then the solvent and excess $Me_3SiCl$ were removed in vacuum. After being dried in vacuum, the sample was ground into powder for XPS study.

The results of the XPS study on the catalyst system were shown in Figures 2 and 3, which showed the analysis of the Mo 3d and the Zn 2p spectra, respectively. Curve a in Figure 2 showed the Mo 3d experimental spectra. The peaks in the experimental spectrum were broader than that in the $Mo^{6+}$ spectrum, and a low-intensity additional peak at a binding energy of 229.4 eV was present, which indicated the presence of mixed states of molybdenum. We then deconvoluted the Mo 3d envelope to obtain the oxidation state distribution of molybdenum. The Mo 3d photoelectron spectrum of the dominant species exhibited the Mo $3d_{3/2}$ line situated at 234.6 eV and the Mo $3d_{5/2}$ component at 231.4 eV, which were accordant to the binding energy of $Mo^{6+}$ 3d (Figure 2, curve b).[23] The Mo $3d_{5/2}$ peak and Mo $3d_{3/2}$ peak of the minority species were centered at a binding energy of 229.4 and 232.5 eV, respectively, which were in a agreement with the value reported for $Mo^{4+}$ (Figure 2, curve c).[22,20b] This indicated the sample was composed of both $Mo^{6+}$ and $Mo^{4+}$ species. The corresponding Zn $2p_{3/2}$ peak would be located at 1023.3 eV, which was assigned to $Zn^{2+}$

**SCHEME 3. Proposed Mechanism for Pinacol Coupling Reaction**



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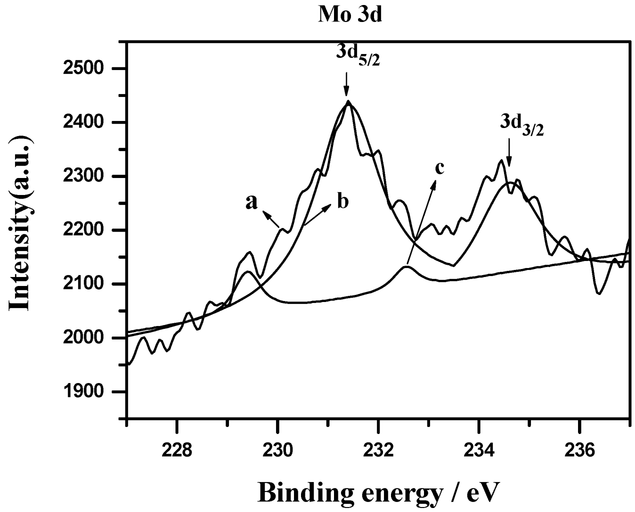


**FIGURE 2.** Deconvoluted Mo 3d spectra for the intermediate catalyst **C**: (a) experimental spectra, (b) deconvoluted curve for $Mo^{6+}$, and (c) deconvoluted curve for $Mo^{4+}$.

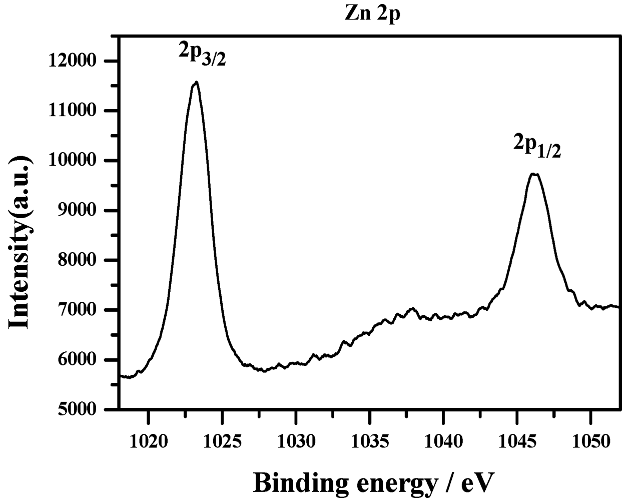


**FIGURE 3.** XPS spectra of Zn 2p for the intermediate catalyst **C**.

(Figure 3).[24] These results show that the oxidation state of molybdenum in $Mo(L3)OCl_2$ (**B**) has been partly reduced from +6 to +4, while Zn powder was oxidized to $Zn^{2+}$ in $ZnCl_2$. On the basis the XPS study, the oxidation state of molybdenum in **C** was confirmed as +4.

The proposed catalytic mechanism for the pinacol coupling reaction was shown in Scheme 3. Unlike the one-electron reducing agent such as Ti(III), Cr(II), etc. employed in the pinacol coupling reaction,[13a] the intermediate **C** was a unique two-electron reducing species. The oxygen atoms of 2 equiv of aldehydes formed a bond with molybdenum atom of the intermediate catalyst **C** to give diketyl radical intermediate **D**. The diketyl radicals were generated through two simultaneous electron transfers from the molybdenum atom to two carbonyl substrates. The oxidation state of molybdenum was changed from +4 to +6. After the coupling of the diketyl radical, and

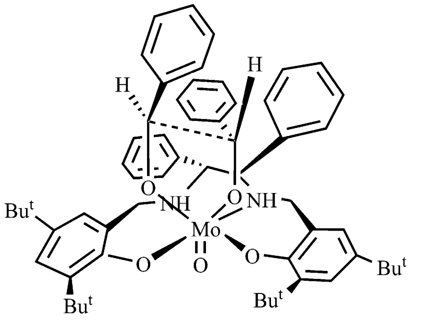
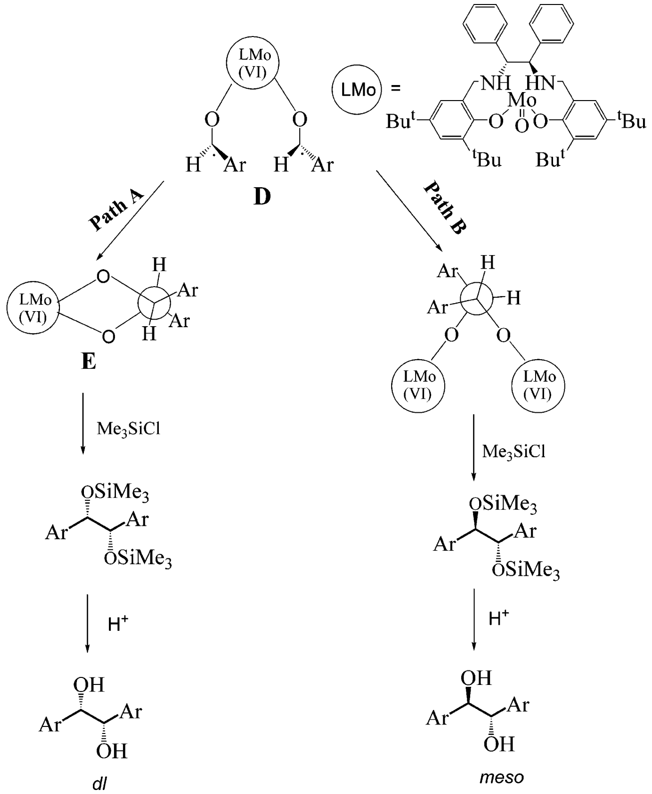


**FIGURE 4.** Proposed molecular model for **E** (formation of the (*S*,*S*)-product was favored).

**SCHEME 4. Proposed Mechanism for the Diastereoselective Pinacol Coupling Reaction**



subsequently cleavage of the Mo−O bonds with $Me_3SiCl$, the diol silyl ether was formed and the intermediate **B** was regenerated.

The *dl* and *meso* diastereoisomers were possibly formed by different coupling patterns of the ketyl radicals as indicated in Scheme 4. (i) The *dl* isomers should be produced through the intramolecular coupling of the carbon radicals (Scheme 4, Path A). The intramolecular coupling of two ketyl radicals in **D** might be more favorable to form the cyclic metal-bridged intermediate **E**, in which two aryl groups are oriented trans to each other, and resulted in the formation of the *dl* stereochemistry in the product. (ii) The intermolecular coupling of the carbon radicals should lead to the formation of the *meso* isomer, through an acyclic bimetallic intermediate (Scheme 4, Path B). The cis transition state was favorable in this case. As the intramolecular reaction of carbon radical coupling was more accessible than the intermolecular reaction, the *dl* product was predominant.

By the way, the absolute configuration (*R*,*R*)-form of the chiral ligand played a key role in the enantioselectivity. We

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proposed a working model for the radical coupling of **E**, which explained the absolute configuration of the favored enantiomer of the *dl* isomer, as shown in Figure 4. The aryl group of aldehyde oriented away from the phenyl group at the backbone of the ligand as far as possible owing to steric hindrance. This situation led to the formation of the (*S*,*S*) enantiomer of the *dl* pinacol products, and was consistent with the experimental results.

## Conclusions

The highly diasteroselective and enantioselective pinacol coupling reaction with the optically active Salan−Mo dioxo complex as an effective precatalyst was developed. The molecular structure of the precatalyst Mo(L3)$O_2$ was characterized with X-ray analysis as a monomer, with α-cis configuration coordination around the molybdenum atom. The XPS study exhibited the oxidation state of the key intermediate is +4. The possible mechanism was proposed with a two-electron reducing process. The stereochemical outcome of the reaction was speculated by the possible mechanism. Our study will provide the basis for studies on the application of chiral Mo dioxo complexes.

## Experimental Section

**Synthesis of *R*,*R*-Mo(L3)$O_2$.** *R*,*R*-$H_2$L3 (2.73 g, 5 mmol) was dissolved in methanol (40 mL), followed by the addition of $MoO_2$(acac)$_2$ (1.79 g, 5.5 mmol). The resulting brown mixture was refluxed for about 6 h with magnetic stirring. After completion of the reaction (monitored by TLC), the solvent was removed in vacuum. The crude product was purified by column chromatography on silica gel (5:1; petroleum ether/EtOAc). Yellow crystals were obtained (3.67 g, 95%). ESI-MS *m*/*z* 774 [Mo(L3)$O_2$ + H]$^+$ (40); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 1.33 (s, 18H), 1.57 (s, 18H), 3.64−3.69 (d, 2H, $J = 15$ Hz), 3.88−3.92 (m, 2H), 5.18−5.23 (d, 2H, $J = 15$ Hz), 6.70−7.38 (14H) ppm; $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 29.69, 30.48, 34.67, 35.67, 52.31, 63.91, 120.48, 126.60, 125.21, 127.61, 129.20, 129.52, 136.61, 138.39, 143.17, 157.35 ppm; IR (KBr) 2952, 1466, 1236, 909, 844, 760, 699, 555, 478 cm$^{-1}$. Anal. Calcd for $C_{44}H_{56}MoN_2O_4$: C, 68.38; H, 7.30; N, 3.62. Found: C, 68.43; H, 7.30; N, 3.91. Yellow solid and $NH_4PF_6$ were dissolved in ethanol. Crystals suitable for X-ray diffraction were grown by slow evaporation from solution for several days.

**General Procedure for Pinacol Coupling Reaction.** To a mixture of Mo(L3)$O_2$ (57.8 mg, 0.075 mmol), $H_2$L3 (24 mg, 0.0375 mmol), and Zn powder (130 mg, 3 mmol) was added anhydrous THF (2 mL) under nitrogen atmosphere. The yellow mixture was stirred for 10 min at room temperature, and then cooled to 0 °C. The freshly distilled $Me_3SiCl$ (127 μL, 1 mmol) was added and the suspension turned red. After 20 min, aldehyde (0.5 mmol) was added. The mixture was stirred at 0 °C for a specified length of time. The suspension was filtered through a glass funnel, then the filtrate was treated with 2 M HCl (5 mL) and stirred until the silyl ether was completely desilylated (monitored by TLC). The mixture was extracted with EtOAc (3 × 10 mL) and the organic phase was washed with a saturated $NaHCO_3$ solution (2 × 10 mL) and then dried over anhydrous $Na_2SO_4$. After removal of solvent under vacuum, the crude product was purified by flash chromatography on silica gel (5:1; petroleum ether/EtOAc).

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**Supporting Information Available:** Experimental procedures, spectral data for all new compounds, and crystallographic data and an X-ray crystallographic file (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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