# Dynamic Stereochemistry of Terminally Substituted π-Allyl Complexes of Molybdenum with the Tp′ Ligand: NMR Evidence for π−σ−π Interconversion†

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*Summary: NMR spectroscopic evidence is provided for a π−σ−π interconversion in fluxional, mono- and 1,3-disubstituted π-allyl molybdenum complexes containing the hydrotris(3,5-dimethylpyrazolyl)borate ligand.*



## Introduction

Stereochemical nonrigidity in molybdenum(II) π-allyl complexes has been widely studied.[1] In $CpMo(CO)_2$−π-allyl complexes, the nonrigidity is attributed[2] to rotation of the allyl group about the metal−π-allyl axis (*exo*/*endo* orientation). In Tp (hydrotris(pyrazolyl)borate) or Tp′ (hydrotris(3,5-dimethylpyrazolyl)borate) analogs, the nonrigidity is often attributed[3] to a *trigonal twist*[4] of the tridentate ligand. The line shapes of the NMR signals change when the interconversion of conformers is slow on the NMR time scale. In these examples, the *syn*/*anti* relationship of the substituents on the allyl group remains unchanged. When a *syn*-substituent is converted to an *anti*-substituent in an isomerization process, a σ-allyl intermediate is mandatory,[5] implying that the π-allyl group undergoes isomerization by a π−σ−π process (Chart 1).

In a recent definitive paper, Liebeskind[6] has reported extensive structural and conformational data on $TpMo(CO)_2$−π-allyl complexes. The barrier to *syn*/*anti* interconversion in many of those complexes was high enough to permit the preparation and observation of individual stereoisomers by NMR spectroscopy. In this paper, we present variable-temperature proton NMR data consistent with a π−σ−π isomerization of the allyl group π-bonded to a $Tp'(CO)_2Mo(II)$ moiety. The barrier height in these complexes is consistently low, such that two stereoisomers could be observed only at subambient temperatures.

## Results and Discussion

The synthesis and structure of complex **1** has been reported earlier.[7] The $^1H$ NMR spectrum (400 MHz) of this complex at 20 °C consisted of only one set of signals. This was interpreted in terms of the structure obtained from the X-ray diffraction studies. The structure revealed a significant distortion of the allyl orientation from its commonly observed position[8] in similar molybdenum π-allyl complexes. This deviation was correlated to the relatively deshielded central proton signal observed in the $^1H$ NMR spectrum as a diagnostic feature.

As the temperature was lowered, extensive broadening of the signals was observed until the peaks completely decoalesced and a well-resolved spectrum was obtained at −80 °C (Figure 1). The signals now represent two sets of isostructural but isomeric species present in a ratio of 2.2:1. The peaks due to each species were identified by careful analysis of the COSY spectrum recorded at low temperature. The most dramatic difference was observed for the two phenyl ring proton sets. While the signals due to the phenyl ring of the major isomer (identified as the *anti*-phenyl ring) exhibited three sets of multiplets at 7.54, 7.38, and 7.27 ppm (2:2:1), the *syn*-phenyl proton signals showed five distinct signals at 7.19, 7.07, 6.87, 6.59, and 5.66 ppm. The high-field signal at 5.66 ppm was assigned to an *ortho*-proton (coupled only with the proton at 6.59 ppm) which was placed close to a pyrazole ring (a tilted aromatic ring flanked by two pyrazole rings is observed in the crystal structure) and was thereby affected by the anisotropic effect of a shielding ring current. The assignment of the *syn*/*anti*-phenyl groups was made based on the identification of the relevant allyl proton signals. For instance, the major isomer with an *anti*-phenyl group displayed signals due to the *syn*-benzylic proton at 3.40 ppm ($J_{syn/central} = 7.08$ Hz), the central proton at 6.03 ppm (m), a *syn*-proton at 2.70 ppm ($J_{syn/central} = 4.96$ Hz), and another *anti*-proton at 2.10 ppm ($J_{anti/central} = 12.76$ Hz). We found that the pattern of signals for the aromatic protons in a *syn* or *anti* orientation remains consistent throughout the series (*vide infra*).

It was now clear that the proton NMR spectrum recorded at 20 °C actually represented an exchange-averaged spectrum. The central proton of the allyl

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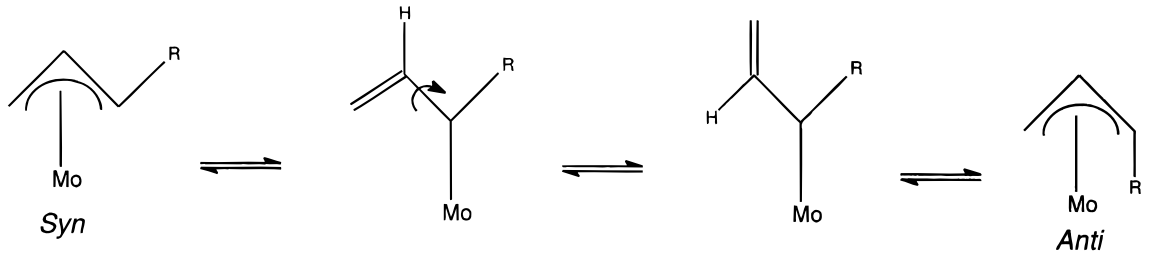
**Chart 1**



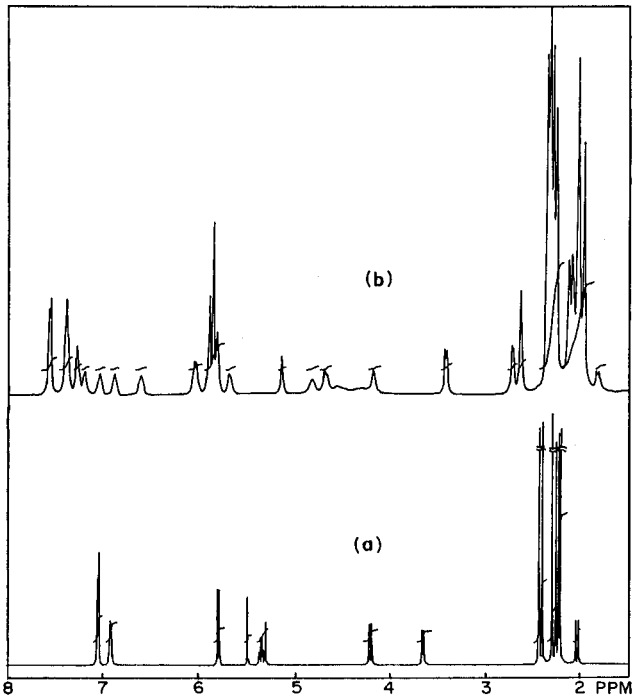




**Figure 1.** $^1$H NMR spectrum of complex **1** in $CD_2Cl_2$: (a) at 20 °C; (b) at −80 °C.

group appeared at 6.03 (major isomer) and 4.79 ppm (minor isomer), indicating that the distortion of the allyl orientation persists in both of the isomers (more in the major isomer). The crystal structure revealed the structure of the minor isomer alone. The dynamic NMR spectral pattern is consistent with a $\pi-\sigma-\pi$ interconversion that leads to the isomerization involving the allylic substituent.[9] We found that this trend was present in a set of isostructural 1,3-disubstituted $\pi$-allyl complexes **2**−**4** (Chart 2). Throughout the series, however, the central proton of the terminally substituted allyl groups was distinctly deshielded in comparison with Tp analogs;[6] more deshielding reflects a greater steric strain resulting from a picket-fence interaction with the 3-methyl groups leading to a greater deviation from the usual orientation of the allyl group.

The complex **2** was prepared from the reaction of $(CH_3CN)_3Mo(CO)_3$ and 3-acetoxy-1,3-diphenylprop-2-ene, followed by ligand exchange. Complexes **3**−**5** were prepared from the corresponding allyl halides and $(CH_3CN)_3Mo(CO)_3$, followed by ligand exchange. All complexes were purified by column chromatography, followed by recrystallization, to afford analytically pure samples.

(9) In the Tp series, the barrier of interconversion is high, *e.g.*, the *anti*-Ph isomer was independently synthesised and isolated from *Z*-cinnamyl acetate, characterized by $^1$H NMR spectroscopy, and converted to the *syn*-Ph isomer at 120 °C; see ref 6.

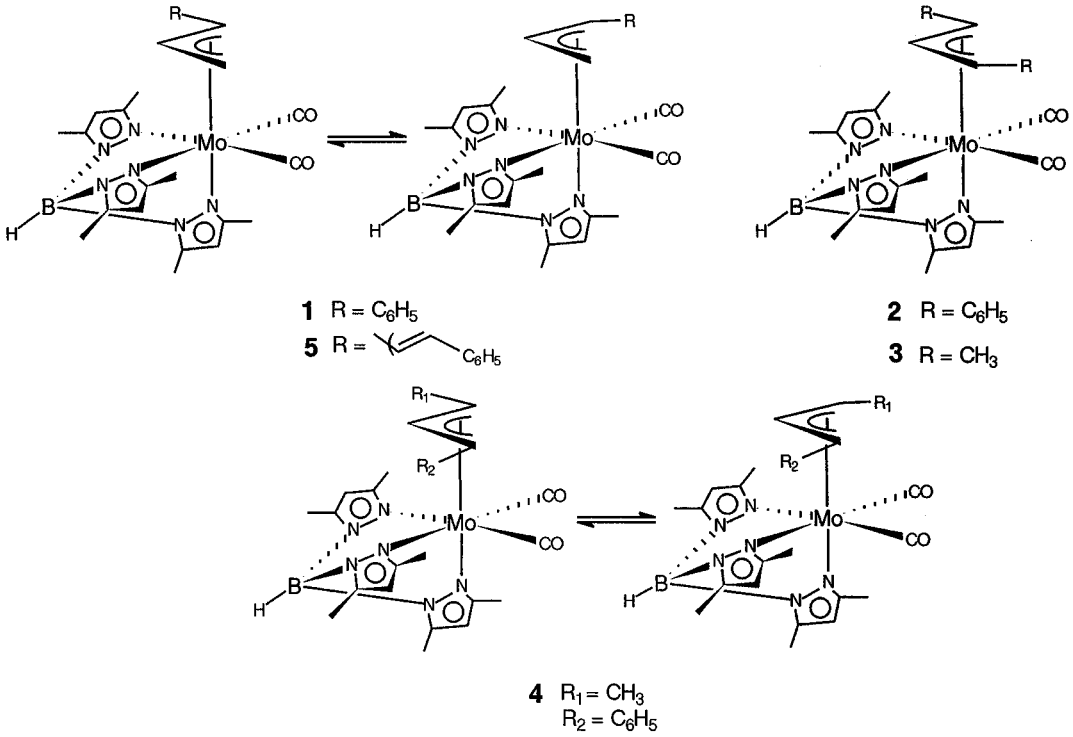
At 20 °C, an averaged spectrum was observed for complex **2** (Figure 2). The aromatic protons appeared as broad multiplets at 7.14−7.04 ppm, the pyrazole 4-H at 5.78 and 5.55 ppm (1:2), the central allyl proton at 6.27 ppm, the two benzylic allyl protons at 3.91 ppm (broad doublet), and the four methyl signals at 2.37, 2.31, 2.14, and 2.03 ppm (2:1:2:1). The symmetrical, averaged structure (at 0 °C) was also evident from the existence of only one $^{13}$C NMR signal for CO at 234.5 ppm.

Extensive decoalescence of the $^1$H NMR signals was observed as the sample was cooled in the NMR probe. At −70 °C, sharp signals were obtained, which permitted assignment of individual peaks by the use of a COSY spectrum recorded also at that temperature. The spectrum revealed the presence of only one type of molecule. The two aromatic proton sets appeared as described above for complex **1**. One set consisted of three peaks at 7.63, 7.42, and 7.28 ppm (2:2:1). The other set had five clear signals at 7.47, 7.04, 6.88, 6.59, and 5.11 ppm. The former indicated an *anti*-phenyl group and the latter a *syn*-phenyl group. The central allyl proton appears at 6.32 ppm, indicating no change from the spectrum recorded at ambient temperature. The structure of complex **2** was thus assigned to be as shown, with one phenyl ring in the *syn* (*anti*-benzylic proton at 4.00 ppm, $J_{anti/central} = 11.04$ Hz) and the other in the *anti* (*syn*-benzylic proton at 3.66 ppm, $J_{syn/central} = 7.28$ Hz) configuration. This structure, in turn, confirmed the previous assignment of the phenyl group orientation in complex **1**.

The proton NMR spectrum of the 1,3-dimethylallyl complex **3** recorded at −40 °C revealed the presence of essentially one isomer. As described in the case of complex **2**, it has one methyl group in the *syn* (2.23 ppm) and the other in *anti* (0.85 ppm) orientation. The central proton of the allyl group is less deshielded in this case and appears at 5.01 ppm. The room temperature spectrum showed broad features indicating an averaging of the signals. Taken together, the spectral data of both complexes **2** and **3** indicate that the dynamic process involved site-exchange of the allyl substituents between the *syn* and *anti* orientation, though the overall structures remain the same because of the symmetry of the ligand.

In complex **4**, one terminus of the allyl group contains a phenyl ring and the other terminus contains a methyl substituent. From the proton NMR spectrum at room temperature, the presence of two isomers in unequal amounts (2:1) can be ascertained. In this series, this is the only complex that displayed sharp signals, except in the aromatic region, such that two isomers could be observed at ambient temperature. Two clusters of multiplets due to the aromatic protons of the two isomers decoalesced to five signals each on cooling to

**Chart 2**



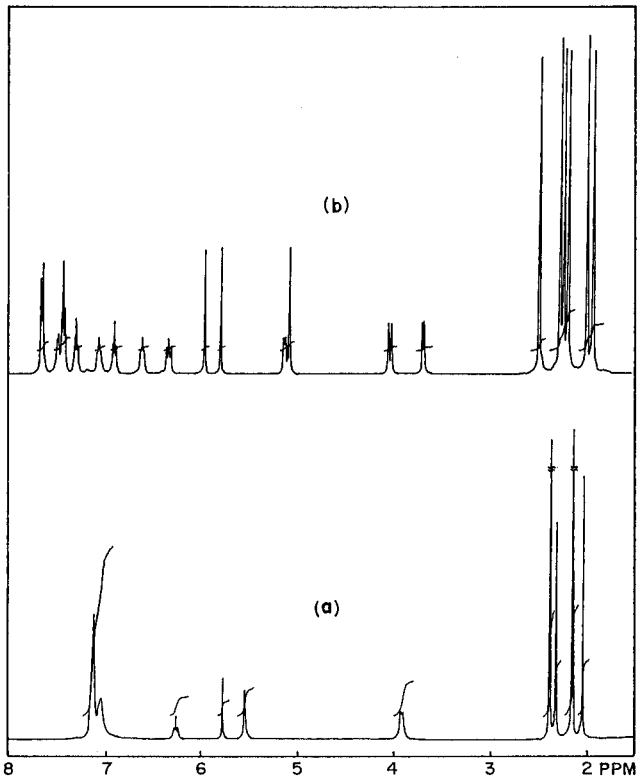




**Figure 2.** $^1$H NMR spectrum of complex **2** in $CD_2Cl_2$: (a) at 20 °C; (b) at −70 °C.

−70 °C. It was clearly evident from the signal pattern of the aromatic protons that in both of the isomers, the rings were *syn* oriented (Chart 2). The methyl group was placed *syn* (2.34 ppm) in one isomer and *anti* (1.43 ppm) in the other. The corresponding methine protons appeared at 2.81 and 5.10 ppm, respectively. The benzylic methine protons appeared at 3.78 ppm for the major isomer and 5.13 ppm for the minor isomer. The central proton of the allyl group appeared at 5.60 (major isomer) and 4.90 ppm (minor isomer). Four carbonyl carbon signals corresponding to the two isomers appeared in the $^{13}$C NMR spectrum at 233.65 and 232.06 ppm (major) and 236.10 and 228.25 ppm (minor), respectively.

Additional support for the assignment of five separate signals to a *syn*-phenyl group was provided by complex **5**, which has a double bond between the allyl and phenyl group.[10] The proton NMR spectrum of this complex at room temperature displayed two sets of isomers in the ratio of 2:1 (Chart 2) in which the *syn*-substituted isomer was the major one. The phenyl proton signals appeared as a complex multiplet between 7.13 and 7.32 ppm, and in both isomers, the phenyl ring was placed away from the pyrazole groups. The central proton of the allyl group appeared at 5.30−5.37 ppm in the major isomer and at 4.42 ppm in the minor isomer, indicating lesser distortion of the allyl group.

## Conclusions

In summary, the variable temperature proton NMR spectra of a set of Tp′Mo(CO)$_2$−$\pi$-allyl complexes provided clear evidence that the fluxionality of these molecules originated from a $\pi$−$\sigma$−$\pi$ interconversion of the $\pi$-allyl group as reflected in the *syn*/*anti* interconversion of the terminal allyl substituents, but the barrier heights were generally low compared to the isostructural Tp complexes described by Liebeskind.[6]

## Experimental Section

All reactions were carried out under a positive pressure of dry argon. Acetonitrile was purified by distillation over calcium hydride. The progress of the reaction was monitored by analytical thin layer chromatography with TLC plates precoated with silica gel $F_{254}$(Merck). Column chromatography of the molybdenum complexes was carried out with silica gel

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obtained from Merck (230−400 mesh, 9385 grade) under argon or nitrogen pressure. The IR spectra were recorded as Nujol mulls on an ATI Mattson, UK, model RS-1 FT-IR. The $^1$H NMR spectra were recorded in $CDCl_3$ or $CD_2Cl_2$ on a Bruker AC 400 spectrometer. $^{13}$C NMR spectra were recorded in $CDCl_3$ or $CD_2Cl_2$ on a Bruker AC (100.6 MHz) spectrometer. All NMR data were expressed as parts per million (ppm) downfield of tetramethylsilane. All melting points (recorded on a Thermonik Campbell melting point apparatus) are uncorrected and are recorded on the Celsius scale. Elemental analyses (C, H ,N) were performed by Dr. S. Y. Kulkarni and his group at NCL on a Carlo-Erba 1100 automatic analyzer. The ligand sodium hydrotris(3,5-dimethylpyrazolyl)borate was prepared by a reported method.[11]

**General Method of Complexation.** A suspension of $Mo(CO)_6$ (2 mmol) in freshly distilled acetonitrile (30 mL) was refluxed for 6 h. The golden solution of the resultant tris(acetonitrile) $Mo(CO)_3$ complex was then treated with freshly distilled allyl chloride (2.1 mmol), and the solution was refluxed for another 15 min. The reaction mixture was cooled to room temperature, and volume of the solution was reduced to approximately 5 mL under reduced pressure. A solution of the ligand (2.1 mmol) in $CH_2Cl_2$ (10 mL) was then added to the reaction mixture with vigorous stirring, and stirring was continued for 1.5 h. The reaction mixture was then concentrated and subjected to column chromatography to isolate the desired complex. Crystallization afforded analytically pure samples.

**Low-Temperature $^1$H NMR of complex 1** (400 MHz, $CD_2Cl_2$, −80 °C): two isomers were present in a ratio of 2.2:1. Major isomer: $\delta$ 1.90−2.30 (6s, 18H), 2.10 (d, 1H, $J$ = 12.76 Hz), 2.70 (d, 1H, $J$ = 4.96 Hz), 3.40 (d, 1H, $J$ = 7.08 Hz), 5.79−5.88 (m, 3H), 6.03 (m, 1H), 7.27 (m, 1H), 7.38 (m, 2H), 7.54 (m, 2H). Minor isomer: $\delta$ 1.90−2.30 (5s, 15H), 1.82 (d, 1H, $J$ = 9.72 Hz), 2.62 (s, 3H), 4.17 (m, 1H), 4.65 (d, 1H, $J$ = 10 Hz), 4.79 (m, 1H), 5.66 (m, 1H), 5.79−5.88 (m, 3H), 6.59 (m, 1H), 6.87 (m, 1H), 7.07 (m, 1H), 7.19 (m, 1H).

**Preparation of Complex 2.** Molybdenum hexacarbonyl (0.528 g, 2 mmol) was refluxed in acetonitrile (30 mL) to afford the tris(acetonitrile) $Mo(CO)_3$ complex. 3-Acetoxy-1,3-diphenyl-prop-2-ene[6] (0.544 g, 2.2 mmol) was added to the refluxing solution, and it was further refluxed for 16 h. The ligand (0.704 g, 2.2 mmol) was then added to the solution at room temperature and stirred for 1 h. Pure complex **2** was obtained by column chromatography (10% EtOAc−petroleum ether). Recrystallization from $CH_2Cl_2$/MeOH afforded shiny black crystals (0.17 g, 13%). Mp: 185 °C (dec). IR: 2510 (w), 1940 (s), 1839 (s), 1543 (m) cm$^{-1}$. $^1$H NMR (400 MHz, $CD_2Cl_2$, −70 °C): $\delta$ 1.89 (s, 3H), 1.95 (s, 3H), 2.20 (s, 3H), 2.23 (s, 3H), 2.29 (s, 3H), 2.45 (s, 3H), 3.66 (d, 1H, $J$ = 7.28 Hz), 4.00 (d, 1H, $J$ = 11.04), 5.06 (s, 1H), 5.11 (d, 1H, $J$ = 7.12 Hz), 5.78 (s, 1H), 5.94 (s, 1H), 6.32 (dd, 1H, $J$ = 7.94, 10.54 Hz), 6.59 (t, 1H, $J$ = 8.04 Hz), 6.88 (t, 1H, $J$ = 7.24 Hz), 7.04 (m, 1H), 7.28 (m, 1H), 7.42 (t, 2H, $J$ = 7.48 Hz), 7.47 (d, 1H, $J$ = 7.12 Hz), 7.63 (d, 2H, $J$ = 7.6 Hz). $^{13}$C NMR (100.6 MHz, $CD_2Cl_2$, −70 °C): $\delta$ 12.7, 13.2, 13.5, 15.2, 15.3, 16.5, 68.3, 83, 88.2, 106.4, 106.6, 107.8, 126.7, 126.9, 127.2, 128.1, 137.7, 140.4, 145.1, 145.4, 146.7, 150.4, 151.4, 152.7, 232.9, 233.9. Anal. Calcd for $C_{32}H_{35}BMoN_6O_2$: C, 59.81; H, 5.45; N, 13.08. Found: C, 59.85; H, 5.69; N, 12.84.

**Preparation of Complex 3.** Complex **3** was prepared from molybdenum hexacarbonyl (0.528 g, 2 mmol), acetonitrile (30 mL), 4-chloropent-2-ene[12] (0.418 g, 4 mmol), and the ligand (0.8 g, 2.5 mmol). The pure complex was obtained by column chromatography (25% EtOAc−petroleum ether) and was recrystallized from $CH_2Cl_2$−petroleum ether to obtain red crystals (0.530 g, 51%). Mp: 161 °C (dec). IR: 2530 (w), 1916 (s), 1820 (s), 1543 (m) cm$^{-1}$. $^1$H NMR (400 MHz, $CD_2Cl_2$, −40 °C): $\delta$ 0.85 (d, 3H, $J$ = 6.16 Hz), 1.90 (s, 3H), 2.21 (s, 3H), 2.23 (d, 3H, $J$ = 5.84 Hz), 2.26 (s, 3H), 2.29 (s, 3H), 2.31 (s, 3H), 2.34 (s, 3H), 2.54 (m, 1H), 2.87 (m, 1H), 5.01 (dd, 1H, $J$ = 6.78, 10.46 Hz), 5.81 (s, 1H), 5.83 (s, 1H), 5.85 (s, 1H). $^{13}$C NMR (100.6 MHz, $CD_2Cl_2$, −60 °C): $\delta$ 12.1, 12.3, 12.4, 13.7, 14.2, 14.8, 15.1, 19.8, 64.3, 87.6, 91.5, 105.6, 106.0, 106.6, 143.8, 145.0, 145.4, 149.5, 150.7, 151.3, 231.4, 232.9. Anal. Calcd for $C_{22}H_{31}BMoN_6O_2$: C, 50.96; H, 5.98; N, 16.21. Found: C, 50.42; H. 5.81; N, 15.81.

**Preparation of Complex 4.** From $Mo(CO)_6$ (0.528 g, 2 mmol), acetonitrile (30 mL), 3-chloro-1-phenylbutene[12] (0.350 g, 2.1 mmol), and ligand (0.704 g, 2.2 mmol), the pure complex **4** was obtained by column chromatography (30% $CH_2Cl_2$−petroleum ether). Recrystallization from $CH_2Cl_2$/MeOH yielded shiny black crystals (0.175 g, 15%). Mp: 189 °C (dec). IR: 2520 (w), 1909 (s), 1811 (s), 1544 (m) cm$^{-1}$. $^1$H NMR (400 MHz, $CD_2Cl_2$, −70 °C): two isomers were present in the ratio of 2:1. Major isomer: $\delta$ 1.76 (s, 3H), 2.01−2.45 (5s, 15H), 2.34 (d, 3H, $J$ = 6.64 Hz), 2.81 (m, 1H), 3.78 (d, 1H, $J$ = 11 Hz), 5.06 (brs, 1H), 5.10 (m, 1H), 5.60 (m, 1H), 5.87 (s, 1H), 5.90 (s, 1H), 6.50 (m, 1H), 6.60 (m, 1H), 7.05 (m, 1H), 7.35 (m, 1H). $^{13}$C NMR (100.6 MHz, $CD_2Cl_2$, −70 °C): $\delta$ 12.23, 12.69, 12.79, 13.00, 14.37, 15.08, 20.52, 65.46, 86.28, 86.92, 105.61, 106.02, 107.05, 125.82, 126.29, 126.37, 126.71, 127.01, 137.42, 144.44, 144.69, 146.26, 149.82, 150.82, 152.15, 232.06, 233.65. Minor isomer. $^1$H NMR: $\delta$ 1.43 (d, 3H, $J$ = 5.96 Hz), 2.05−2.65 (6s, 18H), 4.90 (m, 1H), 5.10 (m, 1H), 5.13 (d, 1H, $J$ = 11.2 Hz), 5.31 (s, 1H), 5.60 (m, 1H), 5.83 (s, 1H), 5.85 (s, 1H), 6.50 (m, 1H), 6.60 (m, 1H), 7.05 (m, 1H), 7.25 (m, 1H). $^{13}$C NMR: $\delta$ 12.11, 12.55, 14.37, 14.67, 15.72, 16.26, 17.24, 66.32, 84.12, 96.07, 105.90, 106.17, 107.53, 125.06, 125.82, 125.94, 126.86, 128.58, 138.36, 144.44, 144.90, 151.55, 151.83, 153.16, 228.25, 236.10. Anal. Calcd for $C_{27}H_{33}BMoN_6O_2$: C, 55.86; H, 5.73; N, 14.48. Found: C, 55.20; H, 5.53; N, 13.96.

**Preparation of Complex 5.** From $Mo(CO)_6$ (0.528 g, 2 mmol), acetonitrile (30 mL), 1-chloro-5-phenyl-pent-2,4-diene[13] (0.535 g, 3 mmol), and ligand (0.8 g, 2.5 mmol), the pure complex **5** was obtained by column chromatography (10% $CH_2Cl_2$−petroleum ether) and recrystallized from $CH_2Cl_2$/MeOH to obtain shiny black crystals (0.177 g, 18%). Mp: 184 °C (dec). IR: 2545 (w), 1932 (s), 1821 (s), 1546 (m) cm$^{-1}$. $^1$H NMR (400 MHz, $CDCl_3$, 20 °C): two isomers were present in the ratio of 2:1. Major isomer: $\delta$ 2.09 (m, 1H), 2.26 (s, 3H), 2.31 (s, 3H), 2.32 (s, 3H), 2.33 (s, 3H), 2.34 (s, 3H), 2.35 (s, 3H), 3.10 (d, 1H, $J$ = 6.32 Hz), 3.57 (t, 1H, $J$ = 9.40 Hz), 5.30−5.37 (m, 1H), 5.73 (s, 1H), 5.75 (s, 1H), 5.78 (s, 1H), 6.45 (d, 1H, $J$ = 15.56 Hz), 6.63 (dd, 1H, $J$ = 10.2, 15.52 Hz), 7.13−7.32 (m, 5H). Minor isomer: $\delta$ 1.97 (s, 3H), 2.12 (s, 3H), 2.13 (s, 3H), 2.46 (s, 3H), 2.57 (s, 3H), 2.81 (s, 3H), 3.22 (d, 1H, $J$ = 10.96 Hz), 3.62 (d, 1H, $J$ = 7.4 Hz), 4.42 (m, 1H), 5.28−5.34 (m, 1H), 5.35 (m, 1H), 5.72 (s, 1H), 5.76 (s, 1H), 5.79 (s, 1H), 6.68 (d, 1H, $J$ = 14.56 Hz), 7.13−7.32 (m, 5H). $^{13}$C NMR (100.6 MHz, $CDCl_3$, 21 °C): $\delta$ 12.6, 12.9, 14.7, 14.9, 15.4, 15.5, 16.2, 60.7, 61.9, 79.7, 82.1, 83.1, 87.4, 106.6, 106.7, 107.2, 107.4, 107.9, 108.0, 126.2, 126.3, 126.8, 127.0, 127.2, 128.4, 129.8, 130.0, 130.5, 137.6, 137.8, 143.9, 144.4, 144.5, 145.0, 145.2, 151.0, 151.8, 152.0, 153.2, 154.1, 228.5, 232.1, 232.8, 233.9. Anal. Calcd for $C_{28}H_{33}BMoN_6O_2$: C, 56.75; H, 5.57; N, 14.18. Found: C, 56.85; H, 5.74; N, 13.81.

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**Supporting Information Available:** $^1$H, COSY, and $^{13}$C NMR spectra of all the complexes (20 pages). Ordering information is given on any current masthead page.

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