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η^3−η^5 Interconversion vs Weak Bonding Interactions in Neutral Molybdenum(II) Complexes[†]

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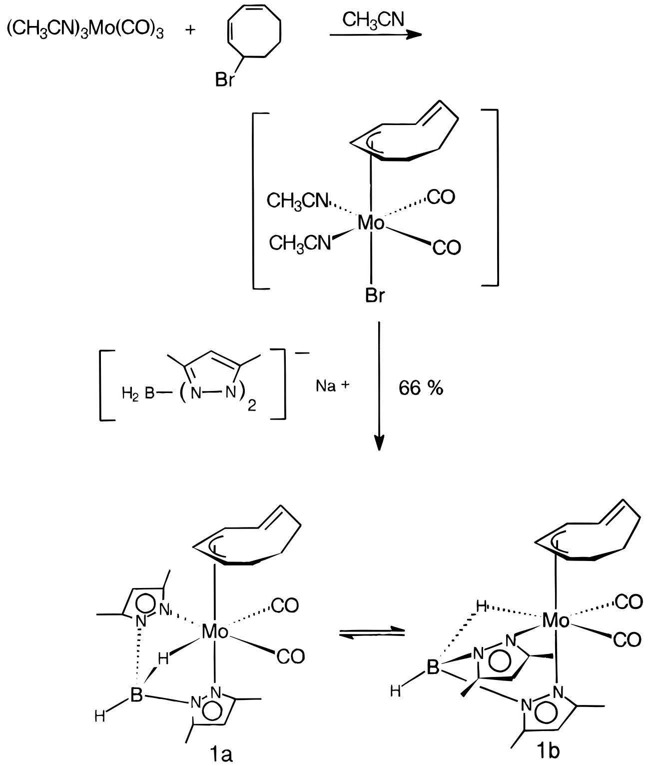
In a set of structurally related Mo(II) π-allyl complexes with a conjugated double bond appended to the allyl group, a weak bonding interaction such as B−H−Mo or C−H−Mo appears to prevent η^3 to η^5 interconversion. Structural assignments are made on the basis of NMR data, and crystal structure solutions are carried out for two of the complexes.

Introduction

Numerous examples are known[1] for the interconversion of a pentadienyl ligand from an η^1 to η^3 to η^5 coordination mode. In molybdenum(II) complexes, a pattern already exists.[2] In the absence of a donor ligand, a cationic 16e η^3-pentadienyl complex slips readily to a η^5-pentadienyl structure; a donor solvent can reverse this interconversion back to the η^3 mode,[3] indicating a delicate energy balance in such a process. In a neutral, formally 16e complex such as (dihydrobis(3,5-dimethylpyrazolyl)borato)(η^3-cycloheptatrienyl)dicarbonylmolybdenum(II), interconversion to η^5 coordination appears to be precluded by a B−H−Mo bonding interaction.[4] As detailed in this paper, not only was our present attempt to effect an interconversion in neutral cyclooctadienyl derivatives frustrated by a B−H−Mo bridge that was replaced by a B−O−Mo bond on reaction with benzaldehyde but also a weak C−H−Mo agostic[6] interaction was found to prohibit η^3−η^5 interconversion in a structurally related complex.

Scheme 1



Results and Discussion

Complex **1** was synthesized from 1-bromocycloocta-2,4-diene,[7] Mo(CO)$_6$, and sodium dihydridobis(3,5-dimethyl-1-pyrazolyl)borate (Scheme 1) and purified by column chromatography. It was obtained as an air-stable, red, crystalline solid with good solubility in common organic solvents. The proton NMR spectral lines, which were broad at room temperature, became well-resolved as the temperature was lowered (−30 °C) to reveal the presence of two equally populated conformers. Assignment of the pentadienyl protons in each conformer was made by the use of a 2D spectrum. It was clear that an η^3-allyl rather than η^5-pentadienyl coordination was present. Coupling correlations allowed us to confirm, for instance, that the multiplets at 4.10 and 4.20 ppm are associated with the central π-allyl proton of the two conformers. In one conformer, the two *syn* protons appeared at 4.45 and 4.57 ppm as a multiplet and a broad doublet, respectively. These protons in the other conformer appeared at 4.10 and 4.75 ppm with similar multiplicity. The olefinic protons appeared together at 5.30 ppm (both conformers) as a

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(7) See ref 3f.

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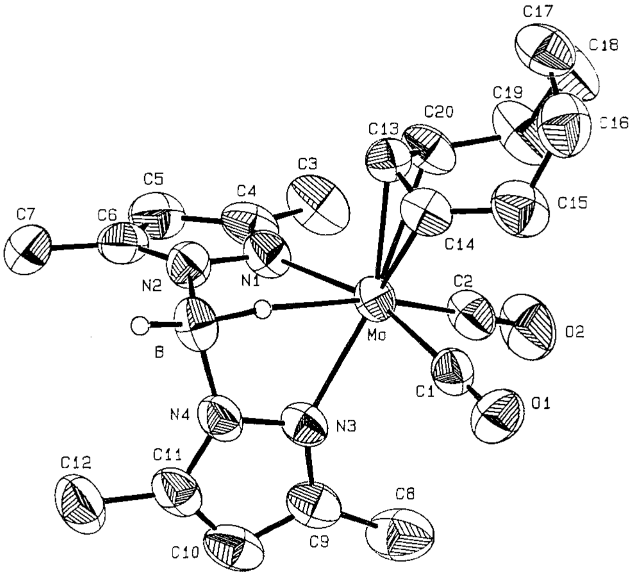


Figure 1. ORTEP view of the molecular structure of **1**.

Table 1. X-ray Crystallographic Data and Structure Refinement for $C_{20}H_{27}BMoN_4O_2$ (1) and $C_{27}H_{33}BMoN_4O_3$ (2)

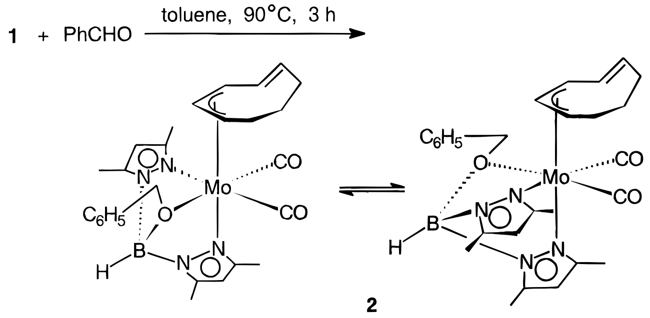
	1	2
formula	$C_{20}H_{27}BMoN_4O_2$	$C_{27}H_{33}BMoN_4O_3$
fw	462.21	568.32
cryst syst	orthorhombic	monoclinic
space group	$Pc2_1n$	$P2_1/n$
a (Å)	8.486(2)	22.194(5)
b (Å)	12.296(3)	10.493(2)
c (Å)	20.476(3)	23.562(4)
β (deg)	90	96.058(10)
V (Å^3)	2136.5(8)	5456(2)
Z	4	8
D_{calcd} (Mg m^{-3})	1.437	1.384
μ (mm^{-1})	0.636	0.515
F(000)	952	2352
cryst size (mm)	0.06 × 0.22 × 0.32	0.25 × 0.40 × 1.15
radiation	Mo Kα (λ = 0.709 30 Å)	Mo Kα (λ = 0.709 30 Å)
temp (K)	293(2)	293(2)
scan type	$\omega/2\theta$	$\omega/2\theta$
scan width (deg)	0.8 + 0.35 tan θ	0.8 + 0.35 tan θ
2θ range (deg)	1.99–23.45	1.20–23.46
no. of rflns obsd	1668 (R(int) = 0.0000)	8030 (R(int) = 0.0000)
no. of params varied	260	657
GOF	1.084	1.223
R ($I > 2\sigma(I)$)	0.0258	0.0524
R_w ($I > 2\sigma(I)$)	0.0691	0.1432
largest diff peak and hole	0.272, −0.360	1.550, −0.933

multiplet and at 6.35 and 6.55 ppm as two peaks (doublet of doublets). The proton that bridges boron and molybdenum appeared as a broad signal at −1.65 ppm. Two sets of CO signals were observed (227.2, 229.4, 233.9, and 235.9 ppm) in the ^{13}C NMR spectrum of this complex, consistent with the presence of two conformers. No change in the spectra was observed after the complex was heated under reflux in toluene or methanol for 3 h.

The X-ray crystal structure of the complex **1** confirmed the η^3-dienyl assignment (Figure 1, Table 1). Only one conformer was observed in the crystalline state. The structure is best described as a distorted octahedron.

The bond between molybdenum and the pyrazole nitrogen *trans* to the allyl moiety is shorter (2.17 Å) than the other Mo−N bond (2.22 Å). Location of the hydrogen involved in the B−H−Mo bond was ascertained by the difference Fourier method. The B−H distance of the bridging hydrogen is longer (1.15 Å) than the nonbridging B−H bond (1.11 Å). The Mo−H bond length was 1.95 Å, typical of a bridging hydride rather than a metal hydride.[8] The central carbon of the allyl system is nearest to molybdenum (2.22 Å, as compared to Mo−C14 = 2.35 Å and Mo−C20 = 2.42 Å). While the sp^2 character of the allyl carbons is reflected in the bond angle (C14−C13−C20 = 122.5°), deviation from planarity of the π-allyl group was evident from the relevant dihedral angles (C15−C14−C13−C20 = 44.8°; C14−C13−C20−C19 = −43.4°). The C18−C19 bond was assigned to be the olefinic bond (1.39 Å); considerable puckering was evident around this bond as well (C17−C18−C19−C20 = 36.6°). Such deviations probably are intrinsic to the cyclooctane ring.

Scheme 2



Treatment of this complex with an excess of benzaldehyde (toluene, 90 °C, 3 h) produced the new complex **2** (Scheme 2).

The ^{1}H NMR spectrum revealed that only one benzyl group was present, and the molecule existed in two distinct conformations in solution (^{13}C NMR peaks for CO at 228.5, 231.0, 231.7, and 232.8 ppm are consistent with this). The ^{1}H NMR peaks due to the conformers being present in unequal amounts (1.6:1) could be assigned with the help of the COSY spectrum. The B−H proton signal was absent in the usual region of −0.9 to −2.6 ppm, which suggested the possible absence of a B−H−Mo bond.[9] The pentadienyl proton signals were similar in overall pattern to that described above (except minor variations), allowing us to conclude that there was no interconversion to the η^5 coordination mode. This was clear from the crystal structure (Figure

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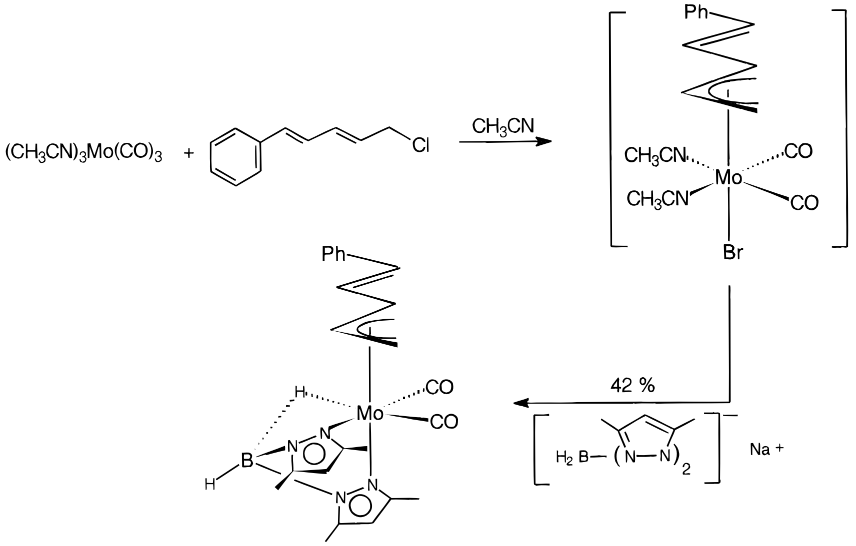
[8] Representative B−H distances are as follows. (a) B−H−Mo = 1.33 Å, B−H$_t$ = 0.94 and 1.02 Å in CpMo(CO)$_2${P(Ph){N[Si-(CH$_3$)$_3$]}(μ-H-BH$_2$): McNamara, W. F.; Duesler, E. N.; Paine, R. T.; Ortiz, J. V.; Kölle, P.; Nöth, H. *Organometallics* **1986,** *5*, 380. B−H$_t$ = 1.196 Å, B−H$_{br}$ = 1.339 Å in B_2H_6: Bartell, L. S.; Carroll, B. L. *J. Chem. Phys.* **1965**, *42*, 1135. Representative Mo−H distances in Mo-(II) hydride: 1.63 Å; in $C_5Me_5(CO)_2(CN^tBu)MoH$: Alt, H. G.; Engelhardt, H. E.; Frister, T.; Rogers, R. D. *J. Organomet. Chem.* **1989**, *366*, 297. 1.436 Å; in Tp′Mo(CO)$_3$H: Protasiewicz, J. D.; Theopold, K. H. *J. Am. Chem. Soc.* **1993**, *115*, 5559. Representative bridged Mo(II) hydride, Mo$_1$−H = 1.76 Å and Mo$_2$−H = 1.93 Å in [(Ph$_3$P)$_2$N]$^+$[Mo$_2$(CO)$_{10}$(μ-H)]: Petersen, J. L.; Masino, A. *J. Organomet. Chem.* **1981**, *208*, 55.

[9] Rarely has the ^{1}H chemical shift of B−H protons in pyrazolylborate complexes been reported. Trofimenko reported the chemical shift of BH$_2$ in the dipyrazolylborate ligand in the region 1.0−6.0 ppm: Trofimenko, S. *Inorg. Chem.* **1969**, *8*, 1714. Similar chemical shift values for BH$_2$ were reported for tin complexes: Reger, D. L.; Knox, S. J.; Huff, M. F.; Rheingold, A. L.; Haggerty, B. S. *Inorg. Chem.* **1991**, *30*, 1754. For the complexes reported in this paper, the B−H proton resonance is observed only when it is a bridging proton between B and Mo; a terminal B−H as in complex **2** is not observed.

Scheme 3



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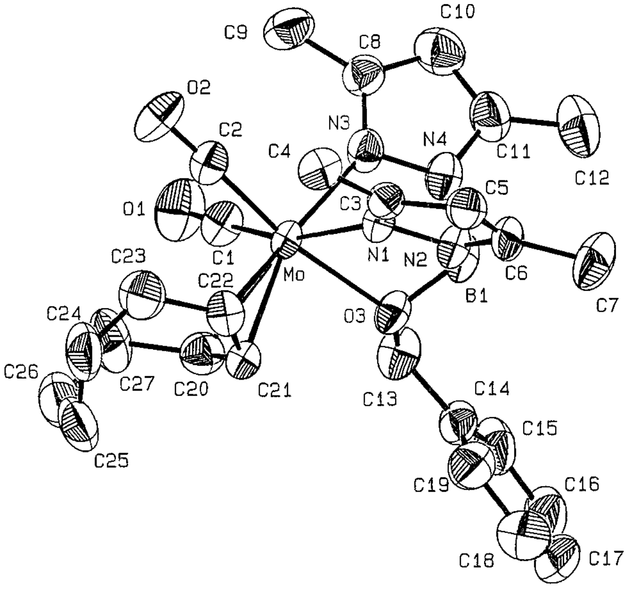

Figure 2. ORTEP view of the molecular structure of **2**.

2). The complex **2** did not react with benzaldehyde any further.

The ORTEP diagram shows one out of a pair of enantiomeric molecules present in one asymmetric unit. The molybdenum center is coordinated to two pyrazole donors and the oxygen atom of the new benzyloxy group (Mo−O3 = 2.29 and 2.30 Å). In molybdenum chemistry, this is a new structural type with a B−O−Mo bridge.[10] This mode of ligation did not appreciably change the conformation of the six-membered pyrazole chelate. Even the conformation of the eight-membered ring was not significantly different. The free double bond of the η^3-dienyl group was on the same side as the pyrazole, as in the structure of complex **1**.

Two possible intramolecular processes can account for the dynamic behavior of these complexes. A *trigonal twist*,[11] well-established for this ligand system,[12] can probably explain the dynamic NMR spectra for both these complexes. Also, the structural isomerism in complexes **1** and **2** can be viewed as interchange of positions of the double bond and the π-allyl group in the cyclic carbon ligand. Alternatively, in complex **1**, a boat−boat interconversion involving the six-membered ring containing molybdenum and two pyrazoles may be significant,[13] but it seems less probable since it involves cleavage and reconstitution of the B−H−Mo bridge.

Interconversion was not observed with an acyclic π-system either. Complex **3** was prepared from the appropriate halide by following an established procedure[14] (Scheme 3).

In the structure of the product, the cinnamyl side chain has been placed on the less sterically congested site, since only one conformer was observed.[15] The complex was characterized by NMR spectroscopy (^{1}H, ^{13}C, and COSY).

An interesting ligand derived from 9-BBN and developed by Trofimenko[16] was used to find whether a C−H−Mo interaction is strong enough to compete with a η^5-dienyl coordination mode in these complexes. Complex **4** was prepared by the usual method (Scheme 4).

In the ^{1}H NMR spectrum, no significant change was observed in the temperature range of −50 to +50 °C, except that minimal line broadening was observed at low temperature and the peaks were slightly sharper at +50 °C. Therefore, coupling constants were determined from decoupling experiments at +50 °C, while a connectivity relationship was deduced from the 2D spectrum recorded at 25 °C. The C−H−Mo agostic

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[10] (a) Gorrell, I. B.; Looney, A.; Parkin, G.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, *112*, 4068. (b) See ref 5.

[11] (a) Faller, J. W.; Haitko, D. A.; Adams, R. D.; Chodosh, D. F. *J. Am. Chem. Soc.* **1977**, *99*, 1654. (b) Faller, J. W.; Haitko, D. A.; Adams, R. D.; Chodosh, D. F. *J. Am. Chem. Soc.* **1979**, *101*, 865.

[12] (a) Trofimenko, S. *Inorg. Chem.* **1970**, *9*, 2493. (b) Shiu, K. B.; Liou, K. S.; Cheng, C. P.; Fang, B. R.; Wang, Y.; Lee, G. H.; Vong, W. J. *Organometallics* **1989**, *8*, 1219.

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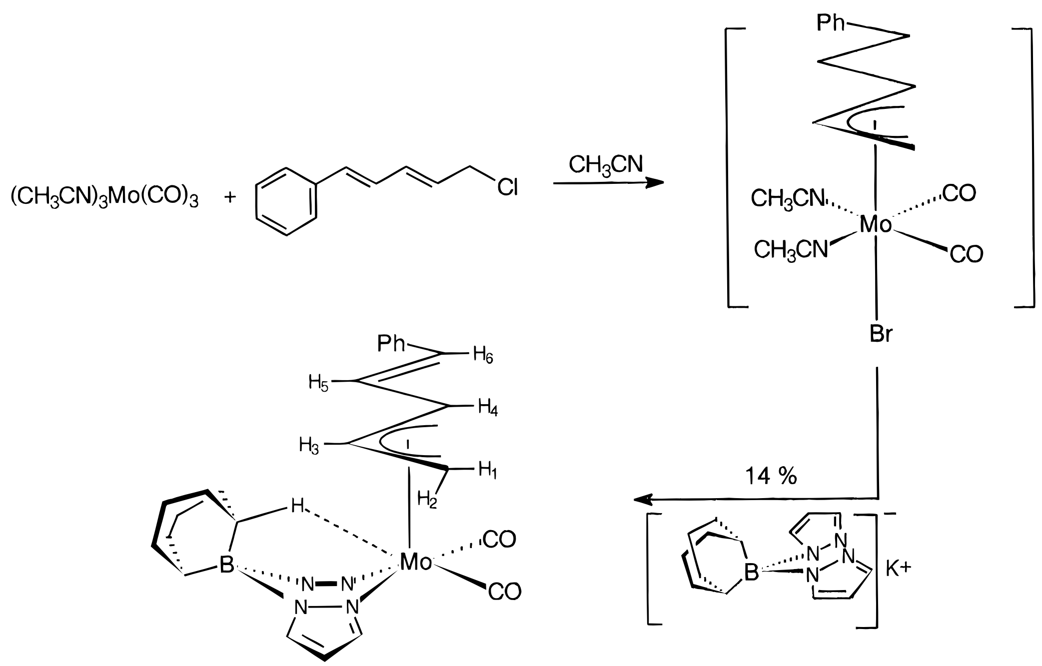
[14] (a) Lee, G. H.; Peng, S. M.; Liu, F. C.; Mu, D.; Liu, R. S. *Organometallics* **1989**, *8*, 402. (b) Paz-Sandoval, M. A.; Sauvedra, P. J.; Powell, P. *J. Organomet. Chem.* **1990**, *387*, 265.

[15] The present assignment of the orientation of allyl group is supported by an NOE difference experiment on an isostructural π-crotyl complex; 0.5% NOE is observed between a pyrazole 3-methyl group and the proximal *syn*-allyl proton: Chowdhury, S. K.; Samuel, A. G. Unpublished results.

[16] Trofimenko, S.; Calabrese, J. C.; Thompson, J. S. *Inorg. Chem.* **1992**, *31*, 974.

Scheme 4



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interaction was clearly evident from the one proton signal at −5.10 ppm, and typical signals indicated an η^3-dienyl coordination rather than an η^5 mode. A doublet of a triplet at 4.30 ppm (J = 10.0, 6.9 Hz) was assigned to the central π-allyl proton (H3). The coupling of H3 with H4 was 10.1 Hz, which established their *anti* relationship. The *syn* methylene proton (H2) at 3.81 ppm appeared as a doublet (J = 6.78 Hz), coupled with H3. The *anti* protons H1 and H4 appeared at 1.80 (merged with methylene protons) and 2.74 (triplet, J = 10.1 Hz, due to the same coupling with H3 and H5), respectively. The protons of the *trans* double bond appeared at 6.55 (H5) as a doublet of doublets (J = 10.5, 15.6 Hz) and at 6.87 (H6) as a doublet (J = 15.6 Hz). The ^{13}C NMR spectrum recorded at 100.6 MHz (24 °C), however, showed considerable line broadening for certain carbons as a result of stereochemical nonrigidity. For instance, signals due to two allyl carbons were not observed at all, and two methylene signals at 20.4 and 35.7 ppm were barely visible above the base line.

In summary, these results seem to vindicate the notion that the η^5-dienyl (other than Cp or indenyl) complex of dicarbonylmolybdenum(II) is not significantly more stable than the η^3-dienyl complex. Possible interconversion from η^3 to η^5 coordination can be effectively prevented by weak, intramolecular three-center−two-electron bonds such as agostic B−H−Mo and C−H−Mo interactions. Theoretical calculations on a related palladium complex carried out by Mingos,[17] with reference to a set of complexes prepared by Maitlis,[18] prompted a similar conclusion.

Experimental Section

All reactions were carried out under a positive pressure of dry argon. Acetonitrile was purified by distillation from calcium hydride. The progress of the reaction was monitored by analytical thin-layer chromatography with TLC plates precoated with silica gel 60 F_{254} (Merck). Column chromatography of molybdenum complexes was carried out with silica gel obtained from Merck (230−400 mesh, 9385 grade) under argon or nitrogen pressure. The IR spectra were recorded as Nujol mulls on a Perkin-Elmer Infracord spectrophotometer, Model 1600 FT-IR. The ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker AC-200; ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker AC-200 and AC-400 FT NMR spectrometers at 50.3 and 100.6 MHz, respectively. All NMR data were expressed as parts per million downfield from 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 ligands sodium dihydridobis(3,5-dimethylpyrazol-1-yl)borate[12a] (L) and potassium (cyclooctane-1,5-diyl)bis(pyrazol-1-yl)borate[16] (L′) were prepared by reported methods.

Preparation of Complex 1. A suspension of molybdenum hexacarbonyl (0.528 g, 2 mmol) was heated in acetonitrile (30 mL) under reflux for 6 h to afford a golden yellow solution of the (acetonitrile)$_3$Mo(CO)$_3$ complex. The tris(acetonitrile) complex was treated with 1-bromocycloocta-2,4-diene (0.467 g, 2.5 mmol) and the mixture slowly cooled to room temperature. The volume of the reaction mixture was reduced to 5 mL, and it was then diluted with dichloromethane (15 mL). The ligand L (0.497 g, 2.2 mmol) was added to the reaction mixture, and it was stirred for 1.5 h at room temperature to afford a red solution. The pure complex **1** was obtained by column chromatography (10% dichloromethane−90% petroleum ether) and recrystallized from dichloromethane−petroleum ether to obtain hexagonal red crystals (0.613 g, 66%). Mp: 189 °C dec. IR: 2475 (m), 2017 (m), 1933 (s), 1842 (s), 1537 (m) cm^{-1}. ^{1}H NMR (−30 °C, 200 MHz): conformer A, 4.1 (m, 1H), 4.45 (m, 1H), 4.57 (brd, 1H), 5.3 (m, 1H), 6.35 (dd, 1H, J = 10.2, 2.4 Hz); conformer B, 4.1 (m, 1H), 4.2 (m, 1H), 4.75 (brd, 1H), 5.3 (m, 1H), 6.55 (dd, 1H, J = 10.2, 2.4 Hz); bridging H for two conformers of B−H−Mo appeared as a broad hump at −1.65 ppm; methyl protons appeared at 2.1 (s, 6H), 2.15 (s, 6H), 2.35 (s, 3H), 2.4 (s, 3H), 2.7 (s, 3H), 2.75 (s, 3H); 12 methylene protons appeared as broad humps at 0.7, 1.25, 1.65, 2.1, 2.35, 2.85; 4 pyrazole protons appeared at 5.65 (s, 1H), 5.7 (s, 1H) 5.8 (s, 2H). ^{13}C NMR (25 °C, 50.3

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[17] Mingos, D. M. P.; Nurse, C. R. *J. Organomet. Chem.* **1980**, *184*, 281.

[18] Mann, B. E.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1976**, 1058.

MHz): 10.7, 10.8, 14, 24.9, 25.1, 28.4, 31.5, 32.1, 63.6, 66, 77.6, 78.4, 80.4, 82.4, 105.7, 126.7, 127, 134.8, 135, 142.8, 144.5, 149.9, 152.7, 152.9, 227.2, 229.4, 233.9, 235.9. Anal. Calcd for $C_{20}H_{27}BMoN_4O_2$: C, 51.97; H, 5.89; N, 12.12. Found: C, 51.29; H, 6.00; N, 11.80.

Preparation of Complex 2. Complex **1** (0.25 g, 0.54 mmol) was dissolved in toluene (7 mL) at room temperature. Benzaldehyde (0.06 mL, 0.95 mmol) was added dropwise into this solution. The temperature was slowly raised to 90−95 °C with constant stirring and maintained at that temperature for 3 h. The reaction mixture was then cooled to room temperature, and toluene was removed under reduced pressure. Complex **2** was isolated by column chromatography (8% ethyl acetate−92% petroleum ether) and recrystallized from dichloromethane−pentane as orange crystals (0.26 g, 85%). Mp: 149 °C dec. IR: 2468 (m), 1927 (s), 1834 (s), 1541 (m) cm^{-1}. ^1H NMR (25 °C, 200 MHz): conformer A, 2.15 (s, 6H), 2.47 (s, 3H), 2.85 (s, 3H), 3.65 (m, 1H), 3.95 (m, 1H), 4.8 (m, 1H), 5.3 (m, 1H), 6.6 (dd, 1H, $J = 11.2$, 2.6 Hz); conformer B, 2.17 (s, 6H), 2.42 (s, 3H), 2.90 (s, 3H), 3.8 (m, 1H), 4.2 (brd, 1H), 4.4 (m, 1H), 5.3 (m, 1H), 6.3 (dd, 1H, $J = 11.2$, 2.6 Hz); 12 methylene protons appeared as complex multiplets at 0.80, 1.25, 1.5, 2.05, 2.25, 2.35, 2.75; 4 pyrazole protons at 5.67, 5.75, 5.82; four benzylic protons at 4.4−4.8; 10 phenyl protons at 7.35. ^{13}C NMR (25 °C, 75.2 MHz): 11.7, 11.9, 14.8, 24.5, 24.7, 27.8, 28.3, 31.0, 31.2, 67.9, 69.1, 72.8, 73.0, 77.4, 78.9, 80.0, 80.8, 81.3, 105.8, 106.3, 126.0, 126.3, 126.5, 127.2, 128.0, 128.3, 128.5, 134.6, 134.7, 139.4, 142.3, 143.4, 143.5, 150.7, 153.1, 153.3, 228.5, 231.0, 231.7, 232.8. Anal. Calcd for $C_{27}H_{33}BMoN_4O_3$: C, 57.06; H, 5.85; N, 9.86. Found: C, 56.78; H, 5.15; N, 9.76.

Preparation of Complex 3. The complex **3** was prepared using the same procedure as described for **1** from molybdenum hexacarbonyl (0.528 g, 2 mmol), acetonitrile (25 mL), 1-chloro-5-phenyl-2,4-pentadiene (0.393 g, 2.2 mmol) and the ligand L (0.497 g, 2.2 mmol). The pure red complex **3** was obtained by column chromatography (20% dichloromethane−80% petroleum ether). It was recrystallized from dichloromethane−petroleum ether (0.424 g, 42%). Mp: 199 °C dec. IR: 2476 (m), 2013 (m), 1946 (s), 1856 (s), 1537 (m) cm^{-1}. ^1H NMR (25 °C, 200 MHz): −1.95 (broad hump, 1H), 1.81 (d, 1H, $J = 11.2$ Hz), 2.12 (s, 3H), 2.18 (s, 3H), 2.35 (s, 3H), 2.58 (t, 1H, $J = 9.8$ Hz), 2.70 (s, 3H), 3.77 (d, 1H, $J = 7.3$ Hz), 4.32 (m, 1H), 5.69 (s, 1H), 5.72 (s, 1H), 6.55 (m, 1H), 6.77 (d, 1H, $J = 15.5$ Hz), 7.34 (m, 5H). ^{13}C NMR (25 °C, 50.3 MHz): 10.6, 10.8, 13.8, 13.9, 61.9, 71.9, 79.1, 105.7, 105.9, 126.6, 127.4, 128.8, 129.1, 131.7, 137.7, 143.0, 144.5, 149.9, 152.6, 227.8, 233.7. Anal. Calcd for $C_{23}H_{27}BMoN_4O_2$: C, 55.45; H, 5.46; N, 11.24. Found: C, 55.38; H, 5.68; N, 11.32.

Preparation of Complex 4. The complex **4** was prepared using the same procedure as for **3** from molybdenum hexacarbonyl (0.195 g, 0.73 mmol), 1-chloro-5-phenyl-2,4-pentadiene (0.196 g, 1.1 mmol), the ligand L′ (0.294 g, 1 mmol), and acetonitrile (15 mL). The pure orange complex **4** (0.055 g, 14%) was obtained by column chromatography (30% dichloromethane−70% petroleum ether) and was recrystallized from dichloromethane−petroleum ether. Mp: 175 °C dec. IR: 1939 (s), 1852 (s) cm^{-1}. ^1H NMR (50 °C, 200 MHz): −5.1 (s, 1H), 0.85−2.1 (br, 13H), 1.9 (m, 1H), 2.74 (t, 1H, $J = 10.12$ Hz), 3.81 (d, 1H, $J = 6.78$ Hz), 4.3 (dt, 1H, $J = 10.0$, 6.9 Hz), 6.17 (t, 1H, $J = 2.17$ Hz), 6.21 (t, 1H, $J = 2.1$ Hz), 6.55 (dd, 1H, $J = 10.5$, 15.6 Hz), 6.87 (d, 1H, $J = 15.6$ Hz), 7.2−7.5 (m, 7H), 7.86 (d, 1H, $J = 1.99$ Hz), 8.25 (d, 1H, $J = 1.87$). ^{13}C NMR (21 °C, 100.6 MHz): 20.4, 24.3, 24.7, 30.8, 30.9, 32.2, 32.5, 35.7, 79.4, 105.2, 105.5, 126.4, 127.6, 128.7, 129.0, 131.4, 133.0, 133.4, 137.1, 142.8, 145.8, 229.9, 230.2. Anal. Calcd for $C_{27}H_{31}BMoN_4O_2$: C, 58.93; H, 5.68; N, 10.18. Found: C, 58.36; H, 6.05; N, 9.88.

X-ray Structure Solution of Complexes 1 and 2. The crystals of complex **1** were grown from dichloromethane−petroleum ether. Diffraction data were collected on an Enraf-Nonius CAD-4F single-crystal X-ray diffractometer for both crystals. Unit cell dimensions were determined using 25 machine-centered reflections in the range $17 \leq \theta \leq 28°$. Reflections were measured with the index ranges $0 \leq h \leq 9$, $0 \leq k \leq 13$, $0 \leq l \leq 22$. The average scan speed was 1° min^{-1}, and the $\omega/2\theta$ scan mode was used for the complex. The structure was solved using Multan-80 and NRCVAX[19] programs. Least-squares refinement of scale factors and positional and anisotropic thermal parameters for non-hydrogen atoms were carried out using SHELXL-93.[20] Coordinates of hydrogen atoms were geometrically determined and confirmed by difference Fourier analysis. Refinements were carried out for hydrogens attached to boron, and the rest were held fixed. The weighting scheme was $w = 1/[\sigma^2(F_o)^2 + (0.0539P)^2 + 0.3873P]$, where $P = (F_o^2 + 2F_c^2)/3$. The refinement converged to $R = 0.0258$ for 1668 observed reflections.

The crystals of complex **2** was grown from dichloromethane−pentane. Unit cell dimensions were determined using 25 machine-centered reflections in the range $18 \leq \theta \leq 25°$. Reflections were measured with the index ranges $-24 \leq h \leq 24$, $0 \leq k \leq 11$, $0 \leq l \leq 26$. The average scan speed was 1° min^{-1}, and the $\omega/2\theta$ scan mode was used. The structure of the complex was solved using SHELXS-86. Least-squares refinement of scale factors and positional and anisotropic thermal parameters for non-hydrogen atoms were carried out using SHELXL-93. Coordinates of hydrogen atoms were taken from a difference Fourier electron density map and held fixed during refinement, except for hydrogens attached to boron. The weighting scheme was $w = 1/[\sigma^2(F_o)^2 + (0.0882P)^2 + 12.1947P]$, where $P = (F_o^2 + 2F_c^2)/3$. The refinement converged to $R = 0.0524$ for 8030 observed reflections.

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Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters, unit cell and packing diagrams for complexes **1** and **2**, and a diagram of two molecules in one asymmetric unit for complex **2** (19 pages). Ordering information is given on any current masthead page.

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