every 50 reflections. Correction for Lorentz–polarization effects and linear decay were applied.

On the basis of regular extinctions, the space group was determined as $C2/c$. The structure was determined by direct methods (SHELXS-86). Full-matrix least-squares refinement with SHELX-76 (non-hydrogen atoms with anisotropic temperature factors; hydrogen atoms on calculated positions and refined with a riding model; correction for extinction with the SHELX-76 method) converged to $R(F) = 0.054$ and $R(wF) = 0.059$ with $w = 1/\sigma^2(F)$ and 470 refined parameters. Neutral-atom scattering factors[9] were used for all atoms. Anomalous dispersion factors were taken from Cromer and Liberman.[10] Calculations were performed on a MicroVax-II computer using the programs SHELXS-86,[11] SHELX-76,[12] and the EUCLID package[13] (geometric calculations and graphics).

Ab Initio Calculations. Ab initio calculations were performed on a Cyber 205 and a Convex C120 computer using the program GAMESS.[14] Geometries were located by spin-restricted Hartree–Fock (RHF) optimization with use of the SV 3-21G or SV 6-31G* basis set. The H_2O molecules in 3 and 4 (Figure 4) were placed at a distance of 2.0 Å from Li, and their geometries were fixed at the minimum energy structure for H_2O in an SV 3-21G basis: O–H = 0.967 Å and H–O–H = 107.7°. Average and maximum gradients of 0.0005 and 0.00075, respectively, were taken as the convergence criteria.

Acknowledgment. Part of the ab initio calculations were performed on a Cyber 205 computer of SARA (Amsterdam). We thank the Dutch Supercomputing Working Group (WGS) for an allowance of computer time.

Supplementary Material Available: Tables of bond distances and angles, torsion angles, anisotropic thermal parameters, and hydrogen positional and thermal parameters (8 pages); a table of observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

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Carbon Monoxide Induced Allyl Coupling from $Mo_2(\mu_2\text{-}\eta^3\text{-allyl})_2(\eta^3\text{-allyl})_2$ Yielding the Labile Complex $Mo(CO)_4(\eta^4\text{-1,5-hexadiene})$

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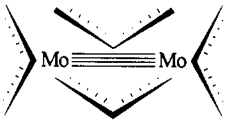
Summary: Carbon monoxide induces the reductive elimination of two pairs of allylic ligands from $Mo_2(\mu_2\text{-}\eta^3\text{-allyl})_2(\eta^3\text{-allyl})_2$ with the accompanying cleavage of the Mo–Mo quadruple bond. $Mo(\eta^4\text{-1,5-hexadiene})(CO)_4$ is obtained from the reaction of 8 equiv of CO with $Mo_2(\mu_2\text{-}\eta^3\text{-allyl})_2(\eta^3\text{-allyl})_2$. Structural data for and the reactivity of $Mo(\eta^4\text{-1,5-hexadiene})(CO)_4$ suggest that 1,5-hexadiene is bound very weakly to molybdenum.

Since its discovery,[1] tetraallyldimolybdenum, $Mo_2(\mu_2\text{-}\eta^3\text{-allyl})_2(\eta^3\text{-allyl})_2$, has been utilized as a precursor to heterogeneous catalysts.[2,3] It is a Mo(II) dimer containing a quadruple metal–metal bond. It is considerably more reactive than most Mo(II) dimers due partially to the reactivity of its pendent allylic ligands. It is unique in that its four allylic ligands are coordinated through two different bonding modes: two π-allyls are bridging the Mo–Mo quadruple bond with each π-allyl in the remaining pair binding to a single molybdenum atom.[4] Exchange of allyls between bridging and terminal positions is not observed even at 80 °C.[5]



$Mo_2(endo\text{-}\mu_2\text{-}\eta^3\text{-allyl})(exo\text{-}\mu_2\text{-}\eta^3\text{-allyl})(endo\text{-}\eta^3\text{-allyl})_2$

A goal of our research is to investigate the reactivity pathways of this molybdenum dimer and related multiply bonded metal dimers bridged by η^3-allylic ligands. Of special interest is the synergic relationship between the bridging allyls and the multiple metal–metal bond. We report here the reaction of tetraalylldimolybdenum with carbon monoxide.

Results and Discussion

Reaction of $Mo_2(\mu_2\text{-}\eta^3\text{-allyl})_2(\eta^3\text{-allyl})_2$ with Carbon Monoxide. $Mo_2(\mu_2\text{-}\eta^3\text{-allyl})_2(\eta^3\text{-allyl})_2$ reacts completely with an excess of carbon monoxide within 10–15 min at ambient temperature to form $Mo(CO)_6$ and 1,5-hexadiene:

$$Mo_2(\mu_2\text{-}\eta^3\text{-}C_3H_5)_2(\eta^3\text{-}C_3H_5)_2 + 12CO \rightarrow 2C_6H_{10} + 2Mo(CO)_6 \quad (1)$$

Carbon monoxide induces the reductive elimination of two pairs of allylic ligands with the accompanying cleavage of the Mo–Mo quadruple bond. The cleavage of multiple metal–metal bonds induced by π-acceptor ligands such as CO, NO, and CNR has been widely reported. Such reac-

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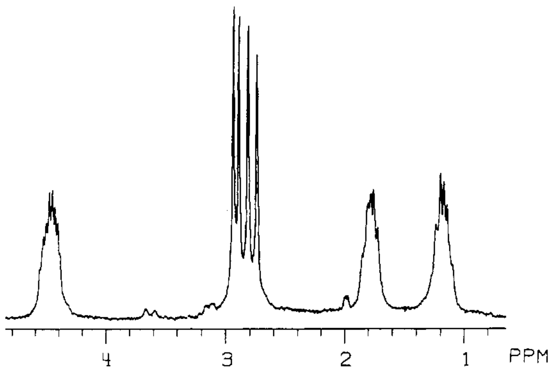


Figure 1. ^1H NMR spectrum (200 MHz) of $Mo(CO)_4(\eta^4$-1,5-hexadiene) in benzene-d_6.

tions include cleavage of both Mo–Mo triple[6] and quadruple bonds.[7] The most relevant precedent is the reaction of carbon monoxide with $Mo_2Me_4(PR_3)_4$, which yields $Mo(CO)_{6-x}(PR_3)_x$ (x = 0–3) and acetone as products.[8] In the latter reaction, as well as in reaction 1, it is uncertain whether the reductive elimination step occurs before or after Mo–Mo bond cleavage.

In some cases, intermediates have been isolated and characterized that lie along the pathway toward CO-induced metal–metal bond cleavage.[6] When $Mo_2(\mu_2\text{-}\eta^3\text{-allyl})_2(\eta^3\text{-allyl})_2$ is titrated with known quantities of carbon monoxide at ambient temperature, an intermediate is formed, which is observable by ^1H NMR spectroscopy. This species predominates when 8 equiv of carbon monoxide have been added: the green to violet color characteristic of the various isomers of $Mo_2(\mu_2\text{-}\eta^3\text{-allyl})_2(\eta^3\text{-allyl})_2$[9] is replaced by the light yellow color of the newly formed complex $Mo(CO)_4(\eta^4$-1,5-hexadiene):

$$Mo_2(\mu_2\text{-}\eta^3\text{-}C_3H_5)_2(\eta^3\text{-}C_3H_5)_2 + 8CO \rightarrow 2Mo(CO)_4(\eta^4\text{-1,5-hexadiene}) \quad (2)$$

Upon further addition of carbon monoxide, uncoordinated 1,5-hexadiene begins to predominate as the proton-containing product.

Structural Characterization of $Mo(\eta^4$-1,5-hexadiene)$(CO)_4$. The ^1H and ^{13}C NMR spectra are consistent with a structure that contains a mirror plane as the sole nonidentity element of symmetry. The ^{13}C NMR resonance at 215.2 ppm, which corresponds to the two equivalent equatorial carbonyl carbons (C_{eq}), has twice the intensity of the resonances assigned to the two nonequivalent axial carbonyl carbons, C_{ax} and C_{ax}', found at 212.6 and 215.3 ppm, respectively. The three resonances at 32.1, 73.5, and 100.0 ppm are assigned to carbons C_γ, C_α, and C_β, respectively, of the coordinated 1,5-hexadiene. The ^1H NMR spectrum of $Mo(\eta^4$-1,5-hexadiene)$(CO)_4$ is found in Figure 1. The multiplet at 4.46 ppm is coupled to the remaining four resonances and thus assigned as H_5. The doublets at 2.77 and 2.90 ppm are assigned as trans (H_3) and cis (H_4) to H_5 due to the magnitude of their coupling constants of 15.0 and 9.2 Hz, respectfully. The multiplets at 1.16 and 1.77 ppm are assigned to the two pairs of geminal methylene protons, H_1 and H_2. The complexity of the latter two resonances is consistent with the second-order AA′XX′YY′ ($H_5H_{5'}H_2H_{2'}H_1H_{1'}$) coupling pattern expected for the proposed structure.

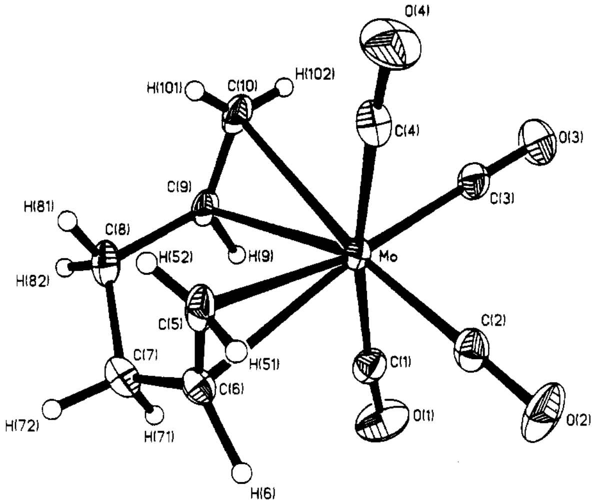
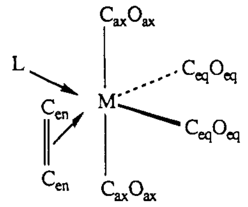


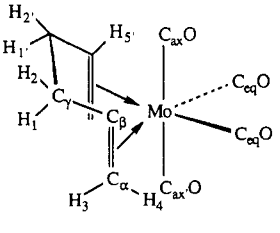
Figure 2. Molecular structure for $Mo(CO)_4(\eta^4$-1,5-hexadiene) showing the labeling scheme. Selected bond distances (Å) and angles (deg): Mo–C(1), 2.038 (5); Mo–C(2), 1.961 (4); Mo–C(3), 1.978 (4); Mo–C(4), 2.052 (5); Mo–C(5), 2.440 (5); Mo–C(6), 2.481 (4); Mo–C(9), 2.530 (4); Mo–C(10) ,2.513 (5); C(5)–C(6), 1.357 (7); C(9)–C(10), 1.348 (6); C(1)–Mo–C(4), 170.7 (2); C(6)–Mo–C(9), 73.6 (1); C(5)–Mo–C(10), 89.6 (2); C(5)–C(6)–C(7), 122.6 (4); C(6)–C(7)–C(8), 113.0 (3); C(7)–C(8)–C(9), 113.6 (3); C(8)–C(9)–C(10), 124.5 (4).

Table I. Bond Distances (Å)[a] for Olefin Complexes of the Group VI Metal Tetracarbonyls



bond	*cis*-(η^4-1,5-hexadiene)Mo-$(CO)_4$	*cis*-(η^3-Me_2POC-HPhCH=CH_2)Mo-$(CO)_4$[b]	*cis*-(η^4-norbornadiene)-$W(CO)_4$[c]	*trans*-(η^2-CH_2=$CHCO_2$-$Me)_2W$-$(CO)_4$[d]
M–C_{ax}	2.05 (1)	2.04 (1)	2.04 (1)	2.04 (1)
C_{ax}–O_{ax}	1.13 (1)	1.14 (1)	1.14 (1)	1.15 (1)
M–C_{eq}	1.97 (1)	1.98 (1)[e]	1.99 (1)	
C_{eq}–O_{eq}	1.14 (1)	1.16 (1)[e]	1.15 (2)	
M–C_{en}	2.49 (2)	2.41 (2)	2.41 (1)	2.30 (1)
C_{en}–C_{en}	1.35 (1)	1.37 (1)	1.39 (1)	1.41 (1)

[a] Several values are an average of two or more bonds lengths. [b] From ref 11. [c] From ref 12. [d] From ref 20. [e] Values pertain only to the carbonyl bound trans to the coordinated vinyl group.



$Mo(CO)_4(\eta^4$-1,5-hexadiene)

The NMR data for $Mo(\eta^4$-1,5-hexadiene)$(CO)_4$ are consistent with its X-ray crystal structure (see Figure 2). The pertinent structural data are compared to those obtained recently for the related cis complexes ($\eta^1(P),\eta^2(C{=}C)$-$Me_2POCHPhCH{=}CH_2)(CO)_4$[10] and W($\eta^4$-nor-

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bornadiene)$(CO)_4$,[11] in Table I. In all structures, the M–C_{ax} bonds are longer and the C_{ax}–O_{ax} bonds are shorter than the corresponding bonds of the equatorial carbonyls, M–C_{eq} and C_{eq}–O_{eq}. Thus, the coordinated olefins compete less efficiently as π acceptors than carbonyls with trans-coordinated ligands.[12]

We are unaware of a crystal structure for Mo(η^4-norbornadiene)$(CO)_4$. However, atomic and crystal radii for Mo and W are generally very similar.[13] Thus, a comparison of the relative bond lengths between the one tungsten and two molybdenum complexes in Table I is informative. For example, the olefin bonds, C_{en}–C_{en}, are shorter in Mo(η^4-1,5-hexadiene)$(CO)_4$ than in the other complexes, suggesting weaker metal–olefin π-back-bonding in the former. This 0.02–0.04 Å difference in bond length is significant, since the coordinated olefin bonds of 1,5-hexadiene are only 0.01 Å longer than those typically found for uncoordinated double bonds (1.34 Å).[14] In addition, the metal–olefin bonds, M–C_{en}, are 0.08 Å longer in Mo(η^4-1,5-hexadiene)$(CO)_4$ than they are in the other two complexes whereas the metal–carbonyl bonds trans to the coordinated diene, M–C_{eq}, are 0.01–0.02 Å shorter. Thus, bonding to the carbonyls trans to the metal–olefin bonds in Mo(η^4-1,5-hexadiene)$(CO)_4$ is strengthened in order to compensate for the weak metal–olefin bonding.

Diene Instability/Lability in Mo(η^4-1,5-hexadiene)$(CO)_4$. The aforementioned structural data suggest that the 1,5-hexadiene moiety in Mo(η^4-1,5-hexadiene)-$(CO)_4$ is bound very weakly to molybdenum. This is consistent with the fact that the complex is thermally unstable above 30 °C. Mo(η^4-norbornadiene)$(CO)_4$ is commonly used in the synthesis of other $Mo(CO)_4L_2$ complexes.[15,16] The instability of the 1,5-hexadiene ligand coordinated to molybdenum is even greater than that of norbornadiene.[17] For example, through ^{1}H NMR spectroscopy, it was observed that the addition of 1.6 equiv of norbornadiene to 0.25 M Mo(1,5-hexadiene)$(CO)_4$ causes complete displacement of 1,5-hexadiene in benzene-d_6 at 18 °C, forming Mo(η^4-norbornadiene)$(CO)_4$. This establishes a lower limit of K_{eq} for the equilibrium in (3) of 1.6

$$\text{Mo}(\eta^4\text{-1,5-hexadiene})(\text{CO})_4 + \text{norbornadiene} \rightarrow \text{Mo}(\eta^4\text{-norbornadiene})(\text{CO})_4 + \text{1,5-hexadiene} \quad (3)$$

× 10^2. In addition, there is no ^{1}H NMR evidence for the displacement of norbornadiene in Mo(η^4-norbornadiene)$(CO)_4$ (0.5 M) by a 6-fold excess of added 1,5-hexadiene under similar conditions. Considering the large value of K_{eq} and the value of the observed rate constants in the forward direction (discussed below), one cannot assume that this reverse reaction has reached equilibrium.

The 1,5-hexadiene moiety is also relatively labile. The reaction of 8.5 equiv of norbornadiene with 0.24 M Mo(η^4-1,5-hexadiene)$(CO)_4$ in benzene-d_6 at 18 °C occurs with a half-life of 29 ± 2 s. In addition, the displacement of 1,5-hexadiene from Mo(η^4-1,5-hexadiene)$(CO)_4$ (0.24 M) in benzene-d_6 at 28 °C utilizing 10 equiv of pyridine is complete within 60 s ($t_{1/2} < 10$ s). As a rate comparison, the $t_{1/2}$ for the displacement of norbornadiene from Mo(η^4-norbornadiene)$(CO)_4$ (1.1×10^{-3} M) utilizing a 10-fold excess of $P(OPh)_3$ in n-heptane at 28.3 °C is 2.2×10^3 s.[17]

It is unfortunate that a direct comparison cannot be made between the bond lengths of Mo(η^4-1,5-hexadiene)$(CO)_4$ and Mo(η^4-norbornadiene)$(CO)_4$. Such data would be valuable in understanding the greater instability of diene binding in the former. The metal–olefin bonding in Mo(η^4-norbornadiene)$(CO)_4$ is expected to be somewhat weaker than in its tungsten analogue because, for example, the ground-state bond enthalpy for η^6-cycloheptatriene dissociation from (η^6-cycloheptatriene)$W(CO)_3$ of 311 kJ/mol is markedly higher than that for its molybdenum analogue of 264 kJ/mol.[17] Also, the rate of diene displacement by $P(OPh)_3$ at 46.5 °C is 130 times slower for W(η^4-norbornadiene)$(CO)_4$ than it is for Mo(η^4-norbornadiene)$(CO)_4$.[17] The diene displacement equilibrium (3) may lie far to the right not only due to an inherent weakness in the metal–olefin bonding in Mo(η^4-1,5-hexadiene)$(CO)_4$ but also due to a gain in entropy; i.e., rotation about the C–C single bonds of 1,5-hexadiene is severely limited when coordinated to molybdenum whereas there is virtually no difference in this rotational freedom for coordinated vs uncoordinated norbornadiene.

trans-(η^2-Alkene)$_2$M$(CO)_4$ complexes tend to be more stable than their cis counterparts since two olefins in a trans-orthogonal orientation do not compete for metal dπ electron density owing to their single-faced π-acceptor character.[18] This is apparent in a comparison of the bond distances for *trans*-$(CH_2{=}CHCO_2Me)_2W(CO)_4$ with those of the cis complexes in Table I.[19]

Mo(η^4-1,5-hexadiene)$(CO)_4$ should prove to be one of the most labile and least stable (η^2-alkene)$_2$M$(CO)_4$ or (η^4-diene)M$(CO)_4$ complexes to be isolated. This acyclic diene is forced to bind in the cis as opposed to the trans geometry, thus weakening its metal–olefin bonds by binding trans to a carbonyl. In addition, the 1,5-hexadiene moiety loses considerably more entropy upon binding than cyclic dienes such as norbornadiene or cyclooctadiene. Efforts are underway to determine the potential of Mo(η^4-1,5-hexadiene)$(CO)_4$ as a starting material in the synthesis of $Mo(CO)_4L_2$, where L is a very weak Lewis base.

Efforts are also underway to determine further details of the mechanism of CO-induced allyl coupling from Mo_2(μ_2-η^3-allyl)$_2$(η^3-allyl)$_2$.

Experimental Section

General Considerations. All reactions were carried out under a dry and oxygen-free atmosphere of N_2 by using standard Schlenk techniques. Samples were handled in a Vacuum Atmospheres Co. Dry Lab System. Pentane and hexane were refluxed over Na–K alloy for at least 16 h before use. Diethyl ether was dried over sodium benzophenone ketyl. All solvents were collected and stored over 3-Å molecular sieves. Organic reagents were procured commercially and purged with nitrogen before use. Carbon monoxide was used as purchased. Molybdenum hexacarbonyl was purchased from Pressure Chemical. Tetrakis(acetato)dimolybdenum[20] and allylmagnesium chloride[21] were prepared according to literature procedures. Tetraallyldimolybdenum can be synthesized by utilizing $MoCl_5$,[4] $MoCl_3$,[22] or $Mo_2(OOCCH_3)_4$[23]

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as the molybdenum source. The latter method was found to be most suitable for this application.

Physical Techniques. Infrared spectra were recorded on a Perkin-Elmer 599B spectrophotometer as Nujol mulls between NaCl plates. NMR spectra were recorded on a Nicolet NT-200 spectrometer at 200 and 50 MHz for ^1H and ^{13}C, respectively, using C_6D_6 as the solvent. All ^1H NMR chemical shifts are in ppm relative to the C_6D_5H singlet set at 7.13 ppm, whereas ^{13}C chemical shifts are relative to the C_6D_6 triplet at 128.0 ppm. Difference homodecoupling spectroscopy was utilized to resolve ^1H–^1H coupling for more complicated spectra with overlapping multiplets.[24] Mass spectra were obtained on a Finnigan Mat TSQ-70 mass spectrometer in the electron-impact ionization (EI) mode. The samples were introduced quickly on a direct-exposure solid probe before insertion into the source vacuum lock.

Titrations of $Mo_2(\mu_2\text{-}\eta^3\text{-allyl})_2(\eta^3\text{-allyl})_2$ with Carbon Monoxide. Typically, the addition of 6 equiv of CO via a gastight syringe to a hydrocarbon solution of $Mo_2(\mu_2\text{-}\eta^3\text{-allyl})_2(\eta^3\text{-allyl})_2$ is accompanied by a green to violet color transition.[9] A violet to yellow color transition occurs upon addition of 2 additional equiv of CO (8 total equiv). The reaction solution becomes colorless upon addition of further carbon monoxide.

$Mo(\eta^4\text{-1,5-hexadiene})(CO)_4$. $Mo(CO)_4(\eta^4\text{-1,5-hexadiene})$ can be isolated when, by using a gastight syringe, 8 equiv of carbon monoxide is added to 0.5 g (1.4 mmol) of $Mo_2(\mu_2\text{-}\eta^3\text{-allyl})_2(\eta^3\text{-allyl})_2$ in 80 mL of pentane at 18–20 °C over a period of 2 h. The solution is then filtered through Celite, reduced in volume to ≈15 mL, and cooled slowly to −15 °C over a 24-h period. A 77% yield (0.39 g) of light yellow crystals has been collected. The mass spectrum of $Mo(\eta^4\text{-1,5-hexadiene})(CO)_4$ is dominated by its molecular ion peaks and that of free 1,5-hexadiene. IR (Nujol): ν_{CO} 2024, 1958, 1948, 1908 cm^{-1}. ^1H NMR: δ 4.46 (multiplet, 2 H_5), 2.90 (doublet, 9.2 Hz, 2 H_4), 2.77 (doublet, 15 Hz, 2 H_3), 1.77 (multiplet, 2 $H_{allylic}$), 1.16 (multiplet, 2 $H'_{allylic}$). ^{13}C NMR: δ 215.35 (1 C_{ax}), 215.22 (2 C_{eq}), 212.56 (1 C_{ax}), 99.97 (2 C_α), 73.54 (2 C_β), 32.12 (2 C_γ). The thermal instability of this complex did not allow for an accurate elemental analysis.

$Mo(CO)_6$ from $Mo_2(\mu_2\text{-}\eta^3\text{-allyl})_2(\eta^3\text{-allyl})_2$. Excess carbon monoxide was bubbled through a solution of 0.5 g (1.4 mmol) of $Mo_2(\mu_2\text{-}\eta^3\text{-allyl})_2(\eta^3\text{-allyl})_2$ in 80 mL of pentane at 0 °C. The color of solution was transformed from dark green to colorless within 10–15 minutes. The volume of solution was reduced to ≈15 mL, and white rhombic crystals were produced upon cooling of this solution to −15 °C overnight. The overall yield was 90%. ^{13}C NMR: δ 201 ppm. IR: ν_{CO} 1988 cm^{-1} (s).

$Mo(CO)_4(py)_2$ from $Mo(1,5\text{-hexadiene})(CO)_4$. In a 100-mL Schlenk flask, approximately 0.3 mL (4 mmol) of pyridine was added to 0.4 g (1.38 mmol) of $Mo(1,5\text{-hexadiene})(CO)_4$ in 70 mL of pentane. The yellow solution was transformed immediately into a red suspension. The suspended solid was trapped on Celite by filtration of the red slurry through a Celite-loaded Schlenk filter and was washed twice with dry pentane. The product was collected by washing the Celite with acetone. The resulting solution was cooled to −15 °C and, after 24 h, yielded yellow rhombic crystals of $Mo(pyridine)_2(CO)_4$ in high yield. IR: 2002 (s), 1868 (s), 1820 (s), 1600 (w), 1226 (w), 1208 (w), 1146 (w), 1030 (m), 747 (s), 690 (s), 638 (w) cm^{-1}. ^1H NMR (acetone-d_6): δ 8.76 (d of d, 6.3 and 1.6 Hz, 2 H, ortho py), 7.49 (d of d, 7.8 and 6.3 Hz, 2 H, meta py), 7.98 (t of t, 7.8 and 1.6 Hz, 1 H). Elemental analysis: C:H:N = 46.05%:2.72%:7.59% (theoretical: 45.92%:2.75%:7.65%).

Estimate of $t_{1/2}$ for the Reaction of Pyridine with $Mo(1,5\text{-hexadiene})(CO)_4$. To a 0.5-mL, 0.25 M solution of $Mo(1,5\text{-hexadiene})(CO)_4$ in benzene-d_6 contained in a 5-mm NMR tube with a septum cap was added at 28 °C a 10-fold molar excess (0.1 mL) of pyridine. The reaction was essentially complete before or during the NMR acquisition (≈60 s). The upper limit of the half-life of the reaction, $t_{1/2} < 10$ s, was estimated by assuming that the reaction must have undergone at least 6 half-lives during the acquisition time for the $Mo(1,5\text{-hexadiene})(CO)_4$ resonances to be unobservable.

Lower Limit for K_{eq} for Equilibrium 3. To a 0.5-ml, 0.25 M solution of $Mo(1,5\text{-hexadiene})(CO)_4$ in benzene-d_6 contained in a 5-mm NMR tube with a septum cap was added at 18 °C a 1.6 molar excess (0.019 mL) of norbornadiene. Via ^1H NMR spectroscopy, it was observed that norbornadiene caused the complete displacement of 1,5-hexadiene from $Mo(1,5\text{-hexadiene})(CO)_4$ within a period of 0.5 h. Assuming that no less than 1% of the initial $Mo(1,5\text{-hexadiene})(CO)_4$ could be observed visually, K_{eq} was estimated to be greater than 1.7×10^2. The addition of a 6-fold molar excess (0.15 mL) of 1,5-hexadiene to a 0.5-mL, 0.5 M solution of $Mo(\eta^4\text{-norbornadiene})(CO)_4$ yielded no ^1H NMR evidence for the displacement of norbornadiene in $Mo(\eta^4\text{-norbornadiene})(CO)_4$ forming $Mo(1,5\text{-hexadiene})(CO)_4$. ^1H NMR (free 1,5-hexadiene): δ 5.68 (multiplet, 2 H_5), 4.93 (doublet, 18 Hz, 2 H_3), 4.91 (doublet, 9.4 Hz, 2 H_4), 1.98 (multiplet, 4 $H_{allylic}$). ^1H NMR (free norbornadiene): δ 6.63 (s, 4 H_{vinyl}), 3.35 (s, 2 $H_{bridgehead}$), 1.926 (s, $H_{methylene}$). ^1H NMR ($Mo(norbornadiene)(CO)_4$): δ 4.23 (AA′BB′ multiplet, 4 H_{vinyl}), 2.93 (broad s, 2 $H_{bridgehead}$), 0.626 (s, $H_{methylene}$).

Kinetic Measurements for the Reaction of Norbornadiene with $Mo(1,5\text{-hexadiene})(CO)_4$. To a 0.5-mL, 0.14 M solution of $Mo(1,5\text{-hexadiene})(CO)_4$ in benzene-d_6 contained in a 5-mm NMR tube with a septum cap was added at 18 °C an 8.5 molar excess (0.060 mL) of norbornadiene. Ten ^1H NMR spectra were acquired at 22.8-s intervals. Concentration versus time data were derived from (a) the change in integrated area of the resonance at 4.46 ppm ($Mo(1,5\text{-hexadiene})(CO)_4$) relative to the C_6D_5H peak at 7.13 ppm, (b) peak integration ratios of the free and coordinated 1,5-hexadiene multiplets centered at 5.68 and 4.46 ppm, respectively, (c) integration ratios of 2 times the integral of the $Mo(1,5\text{-hexadiene})(CO)_4$ doublet at 2.77 ppm relative to the sum of the integrals of the 1,5-hexadiene doublets at 4.93 and 4.91 ppm, respectively, and (d) integration ratios of twice the $Mo(1,5\text{-hexadiene})(CO)_4$ 2.77 ppm doublet integration relative to the coordinated norbornadiene resonance at 4.23 ppm. The observed rate constants thus derived were self-consistent, yielding an observed pseudo-first-order rate constant of 2.4 ± 0.2 s^{-1}.

X-ray Crystallography. Crystal data for $Mo(\eta^4\text{-1,5-hexadiene})(CO)_4$, $C_{10}H_{10}O_4Mo$, were collected at 233 K, by using an automatic Nicolet R3m/V diffractometer and Mo Kα radiation. The complex crystallizes in the monoclinic space group $P2_1/c$ with cell constants a = 11.800 (6) Å, b, 7.540 (4) Å, c = 12.509 (4) Å, β = 91.32 (3)°, V = 1112.7 (9) Å^3, Z = 4, and $R(F)$ = 2.19%. A total of 1456 independent reflections in the range $3.0 \leq 2\theta \leq 45.0°$ were collected. Three standard reflections were collected after every 100 reflections. The structure was solved by direct methods programs used in SHELXTL-PLUS[25] and subsequent difference Fourier methods. Final full-matrix least-squares refinement (SHELXTL-PLUS) using 1355 observed reflections with $F > 6.0\sigma(F)$ converged to R = 0.022 and R_w = 0.037. All non-H atoms were refined anisotropically. All hydrogen atoms were placed into calculated positions with fixed isotropic temperature factors. The function being minimized was $\sum w(F_o - F_c)^2$ with the weight used being $w^{-1} = \sigma^2(F) + 0.0001F^2$. Scattering factors for C, H, O, and Mo were those stored in SHELXTL-PLUS.

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Supplementary Material Available: Tables of structure determination data, positional and thermal parameters (Table S1A), anisotropic temperature factors (Table S1B), bond lengths (Table S2), bond angles (Table S3), torsion angles (Table S4), and H atom coordinates and isotropic displacement parameters (Table S5) (6 pages); a listing of observed and calculated structure factors (Table S6) (6 pages). Ordering information is given on any current masthead page.

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