

# Synthesis and Reactivity of a Molybdenum(IV) $\eta^4$ -Butadiene Complex

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Molybdenum olefin complexes of the type  $[\text{Mo}(\text{NPh})(\eta^2\text{-olefin})(o\text{-}(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4)]$  (olefin = propene (**1a**), isobutene (**1b**)) reacted with butadiene gas, affording  $[\text{Mo}(\text{NPh})(\eta^4\text{-H}_2\text{C}=\text{CHCH}=\text{CH}_2)(o\text{-}(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4)]$  (**2**), a molybdenum  $\eta^4$ -butadiene complex. The crystal structure of **2** is reported. Treatment of **2** with 1 equiv of 2-butyne afforded  $[\text{Mo}(\text{NPh})(\eta^4\text{-CH}_2\text{CH}=\text{C}(\text{CH}_3)\text{C}(\text{CH}_3)=\text{CHCH}_2)(o\text{-}(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4)]$  (**3**) by  $^1\text{H}$  NMR spectroscopy. Two intermediates arising during the progress of the reaction were trapped at low temperature and characterized as the isomeric  $\eta^3$ -allyl metallacycles [*syn*- $\text{Mo}(\text{NPh})(\text{C}(\text{CH}_3)=\text{C}(\text{CH}_3)\text{CH}_2\text{-CHCHCH}_2)(o\text{-}(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4)]$  and [*anti*- $\text{Mo}(\text{NPh})(\text{C}(\text{CH}_3)=\text{C}(\text{CH}_3)\text{CH}_2\text{CHCHCH}_2)(o\text{-}(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4)]$  (**4a,b**, respectively) by NMR spectroscopy. Complex **3** was made independently by reaction of **1b** with 1,2-dimethyl-1,4-cyclohexadiene, and the crystal structure of **3** is reported. Treatment of **2** with 2 equiv of 2-butyne afforded 1,2-dimethyl-1,4-cyclohexadiene as an organic product with concomitant formation of  $[\text{Mo}(\text{NPh})(\eta^2\text{-alkyne})(o\text{-}(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4)]$  (alkyne = 2-butyne; **5**) by  $^1\text{H}$  NMR spectroscopy. Reaction of **1b** with 2-butyne also affords **5**, and the X-ray structure of **5** is reported.

## Introduction

Low-valent zirconium(0) butadiene complexes with bidentate phosphine ligands were among the first well-characterized examples of group 4 metal butadiene complexes.<sup>1</sup> The well-known, higher valent, base-free group 4 metallocene transition-metal butadiene complexes were independently synthesized by both Erker<sup>2</sup> and Nakamura<sup>3</sup> (Scheme 1). Among the striking structural characteristics of these complexes is the ability of the butadiene fragment to coordinate to the metallocene core in *cis* and *trans* modes and the dynamic envelope shift isomerization process associated with the *cis* coordination mode. The structure and bonding of the *cis*-butadiene complex varies between the  $\pi^2$  and the  $\sigma^2, \pi$  designation depending on the substitution of the butadiene ligand and the identity of the metal. To date there are several examples of structurally characterized group 4 and 5 *cis*-<sup>4</sup> and *trans*-butadiene<sup>5</sup> metal complexes, the *cisoid* conformation being the most common.

(1) (a) Datta, S.; Wreford, S. S.; Beatty, R. P.; McNeese, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 1053. (b) Beatty, R. P.; Datta, S.; Wreford, S. S. *Inorg. Chem.* **1979**, *18*, 3139.

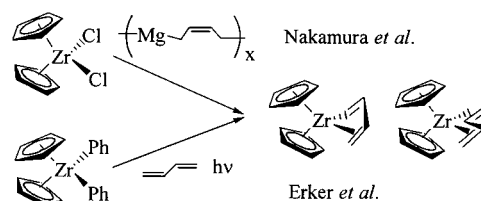
(2) Erker, G.; Wicher, J.; Engel, K.; Rosenfeldt, F.; Dietrich, W.; Kruger, C. *J. Am. Chem. Soc.* **1980**, *102*, 6346.

(3) (a) Yasuda, H.; Kajihara, Y.; Mashima, K.; Lee, K.; Nakamura, A. *Chem. Lett.* **1981**, 519. (b) Yasuda, H.; Kajihara, Y.; Mashima, K.; Lee, K.; Nakamura, A. *Organometallics* **1982**, *1*, 388.

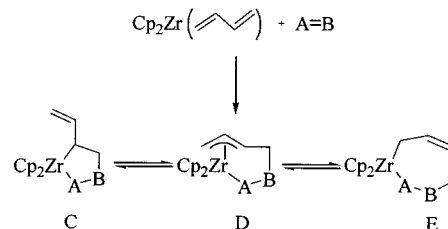
(4) For a Cambridge Structural Database compilation of group 3, 4, and 5  $\eta^4$ -*cis* transition-metal butadiene complexes see: Dahlmann, M.; Erker, G.; Frohlich, R.; Meyer, O. *Organometallics* **1999**, *18*, 4459 (supporting information).

(5) For a compilation of examples see: (a) Wang, L.-S.; Fettingner, J. C.; Poli, R. *J. Am. Chem. Soc.* **1997**, *119*, 4453. (b) Mashima, K.; Fukumoto, H.; Tani, K.; Haga, M.; Nakamura, A. *Organometallics* **1998**, *17*, 410 and references therein. (c) Strauch, H. C.; Erker, G.; Frohlich, R. *Organometallics* **1998**, *17*, 5746.

## Scheme 1



## Scheme 2



The characteristic reactivity of group 4 and 5 butadiene complexes involves reactions with unsaturated substrates such as carbonyl compounds, nitriles, and alkynes.<sup>6</sup> This reactivity is typified by  $\text{Cp}_2\text{Zr}(\text{butadiene})$ , where C–C coupling of the unsaturated substrate with a terminal butadiene carbon results in metallacyclic complexes (C–E; Scheme 2). In some cases the interconversion of these metallacyclic compounds can be followed experimentally. The metallacycles are generally stable, and hydrolysis protocols are required to free useful acyclic organic products from the metal center. In sharp contrast, later transition metals (groups 9 and

(6) Selected examples: see Dahlmann, M.; Erker, G.; Frohlich, R.; Meyer, O. *Organometallics* **1999**, *18*, 4459.

**Table 1. Crystal Data and Data Collection and Structure Refinement Details for 2, 3, and 5**

	<b>2</b>	<b>3</b>	<b>5</b>
empirical formula	C <sub>22</sub> H <sub>33</sub> MoN <sub>3</sub> Si <sub>2</sub> ·CH <sub>2</sub> Cl <sub>2</sub>	C <sub>26</sub> H <sub>39</sub> MoN <sub>3</sub> Si <sub>2</sub>	C <sub>22</sub> H <sub>33</sub> MoN <sub>3</sub> Si <sub>2</sub>
fw	576.56	545.72	491.63
space group	P2 <sub>1</sub> /n	P2 <sub>1</sub> /c	P1
a (Å)	11.9736(6)	16.031(1)	10.7483(5)
b (Å)	15.8844(8)	10.0300(8)	10.8358(6)
c (Å)	14.5066(7)	16.906(1)	12.3049(6)
$\alpha$ (deg)			77.788(1)
$\beta$ (deg)	95.324(1)	93.351(1)	64.377(1)
$\gamma$ (deg)			77.812(1)
V <sub>c</sub> (Å <sup>3</sup> )	2747.2(2)	2713.7(4)	1251.2(1)
D <sub>c</sub> (Mg m <sup>-3</sup> )	1.394	1.336	1.305
Z	4	4	2
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	0.775	0.590	0.632
final R indices	R1 = 0.0307, wR2 = 0.0755 (5170)	R1 = 0.0356, wR2 = 0.0907 (5487)	R1 = 0.0275, wR2 = 0.0719 (5120)
R indices (all data)	R1 = 0.0408, wR2 = 0.0815	R1 = 0.0409, wR2 = 0.0947	R1 = 0.0304, wR2 = 0.0742

10) catalyze the intermolecular 4 + 2 cycloaddition of nonactivated substrates,<sup>7</sup> while related transition-metal-catalyzed cycloisomerization reactions constitute a rapidly developing area of research.<sup>7a,8</sup>

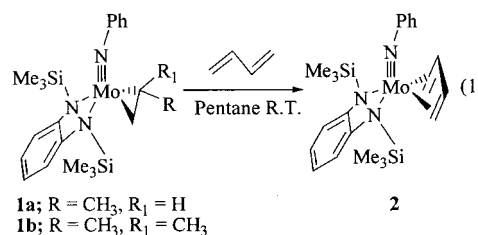
Reports concerning the synthesis and characterization of group 6 transition metal butadiene complexes are not as common as those of the earlier groups.<sup>9</sup> Furthermore, reactivity of these group 6 butadiene complexes differs from the well-explored reaction chemistry associated with the group 4 and 5 butadiene complexes and the catalytic cycloisomerization reactions of the later metals.<sup>9</sup>

The synthesis, structural characterization, and reactivity studies of a monomeric, diamagnetic molyb-

denum(IV) *cis*-butadiene complex, [Mo(NPh)( $\eta^4$ -H<sub>2</sub>C=CHCH=CH<sub>2</sub>)(*o*-(Me<sub>3</sub>SiN)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)] (**2**), is discussed below. While structurally similar to other molybdenum butadiene complexes, the reactivity of **2** departs from these, showing similarities to both early- and late-transition-metal reactivity.

## Results and Discussion

**Synthesis of the High-Valent, Base-Free,  $\eta^4$ -Butadiene Complex [Mo(NPh)( $\eta^4$ -H<sub>2</sub>C=CHCH=CH<sub>2</sub>)(*o*-(Me<sub>3</sub>SiN)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)] (**2**).** Treatment of a pentane solution of [Mo(NPh)( $\eta^2$ -propene)(*o*-(Me<sub>3</sub>SiN)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)] (**1a**) or [Mo(NPh)( $\eta^2$ -isobutene)(*o*-(Me<sub>3</sub>SiN)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)] (**1b**) with molecular butadiene affords the  $\eta^4$ -*cis*-butadiene complex [Mo(NPh)( $\eta^4$ -H<sub>2</sub>C=CHCH=CH<sub>2</sub>)(*o*-(Me<sub>3</sub>SiN)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)] (**2**) in good yield (eq 1). Decomposition of **2** occurs within



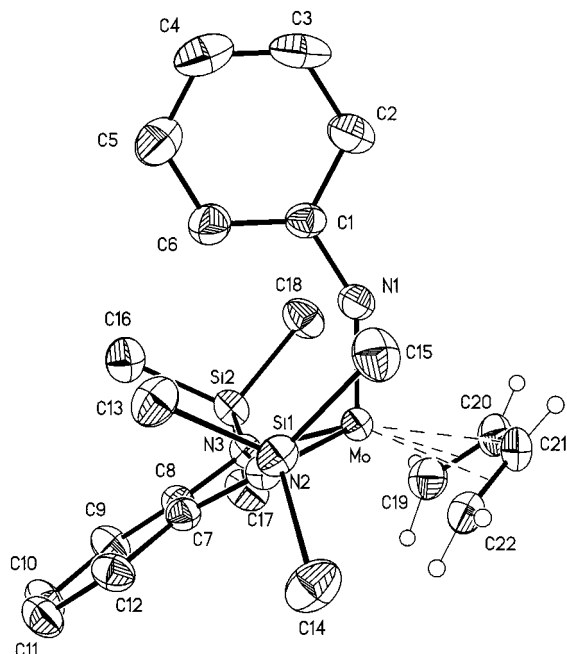
4 h at room temperature, affording an intractable mixture as determined by <sup>1</sup>H NMR spectroscopy. If kept at -30 °C in the solid state, **2** does not decompose appreciably over an 8 month period, as noted by <sup>1</sup>H NMR spectroscopy.

An X-ray crystallographic study was carried out on a single crystal of **2** grown from a -30 °C solution of pentane/methylene chloride. The crystal data and details of the structure refinement are summarized in Table 1. The butadiene complex crystallizes in a monoclinic unit cell with one molecule of methylene chloride. The molecular structure of **2**, accompanied by selected bond lengths and angles, is shown in Figure 1. The butadiene fragment clearly adopts a *cis* arrangement when bound to the metal center. The metal to terminal butadiene carbon atom distances of 2.254(3) Å (Mo-C(19)) and 2.257(2) Å (Mo-C(22)) and the Mo-C(20) and Mo-C(21) bond lengths of 2.336(2) and 2.355(2) Å, respectively, support a  $\pi^2, \eta^4$ -butadiene bonding motif for **2**. Other molybdenum butadiene complexes adopt similar bonding modes.<sup>9</sup> Within the butadiene fragment the similar C(19)-C(20), C(20)-C(21), and C(21)-C(22)

(7) (a) Hilt, G.; du Mesnil, F.-X. *Tetrahedron Lett.* **2000**, *41*, 6757. (b) Paik, S.-J.; Son, S. U.; Chung, Y. K. *Org. Lett.* **1999**, *13*, 2045. (c) Matsuda, I.; Shibata, M.; Sato, S.; Izumi, Y. *Tetrahedron Lett.* **1987**, 3361. (d) tom Dieck, H.; Diercks, R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 778. (e) Mach, K.; Antropiusová, H.; Petrusová, L.; Turecek, F.; Hanus, V. *J. Organomet. Chem.* **1985**, *289*, 331. (f) Murakami, M.; Ubukata, M.; Itami, K.; Ito, Y. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 16. (g) Murakami, M.; Itami, K.; Ito, Y. *J. Am. Chem. Soc.* **1997**, *119*, 7163.

(8) (a) Wender, P. A.; Jenkins, T. E. *J. Am. Chem. Soc.* **1989**, *111*, 6432. (b) Jolly, R. S.; Luedtke, G.; Sheehan, D.; Livinghouse, T. *J. Am. Chem. Soc.* **1990**, *112*, 4965. (c) Wender, P. A.; Smith, T. E. *J. Org. Chem.* **1996**, *61*, 824. (d) McKinsty, L.; Livinghouse, T. *Tetrahedron* **1994**, *50*, 6145. (e) O'Mahony, D. J. R.; Belanger, D. B.; Livinghouse, T. *Synlett* **1998**, 443. (f) Gilbertson, S. R.; Hoge, G. S. *Tetrahedron Lett.* **1998**, *39*, 2075. (g) Gilbertson, S. R.; Hoge, G. S.; Genov, D. G. *J. Org. Chem.* **1998**, *63*, 10077. (h) Kumar, K.; Jolly, R. S. *Tetrahedron Lett.* **1998**, *39*, 3047. For a review of transition-metal-mediated cycloaddition reactions see: Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49.

(9) Homoleptic Mo(d<sup>6</sup>) butadiene and derivative complexes (synthesis and structure): (a) Skell, P. S.; Van Dam, E. M.; Silvon, M. P. *J. Am. Chem. Soc.* **1974**, *96*, 626. (b) Skell, P. S.; McGlinchy, M. J. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 195. (c) Gausing, W.; Wilke, G. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 186. (d) Bogdanovic, B.; Bonnemann, H.; Goddard, R.; Startsev, A.; Wallis, J. M. *J. Organomet. Chem.* **1986**, *299*, 347. (e) Yun, S. S.; Kang, S. K.; Suh, I.-H.; Choi, Y. D.; Chang, I. S. *Organometallics* **1991**, *10*, 2509. Nonhomoleptic systems (synthesis and reactivity): (f) Le Grogne, E.; Poli, R.; Richard, P. *Organometallics* **2000**, *19*, 3842. (g) Poli, R.; Wang, L.-S. *Polyhedron* **1998**, *17*, 3689. (h) Wang, L.-S.; Fetting, J. C.; Poli, R.; Meunier-Prest, R. *Organometallics* **1998**, *17*, 2692. (i) Galindo, A.; Gutierrez, E.; Monge, A.; Paneque, M.; Pastor, A.; Perez, P. J.; Rogers, R. D.; Carmona, E. *J. Chem. Soc., Dalton Trans.* **1995**, *23*, 3801. (j) Kingsbury, K. B.; Carter, J. D.; Mc-Elwee-White, L.; Ostrander, R. L.; Rheingold, A. L. *Organometallics* **1994**, *13*, 1635. (k) Vong, W.-J.; Peng, S.-M.; Lin, S.-H.; Lin, W.-J.; Liu, R.-S. *J. Am. Chem. Soc.* **1991**, *113*, 573. (l) Benyunes, S. A.; Binelli, A.; Green, M.; Grimshire, M. J. *J. Chem. Soc., Dalton Trans.* **1991**, 895. (m) Hunter, A. D.; Legzdins, P.; Einstein, F. W. B.; Willis, A. C.; Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.* **1986**, *108*, 3843. (n) Davidson, J. L.; Davidson, K.; Lindsell, W. E.; Murrall, N. W.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1677. (o) Brookhart, M.; Cox, K.; Cloke, F. G. N.; Green, J. C.; Green, M. L. H.; Hare, M. P.; Bashkin, J.; Derome, A.; Grebenik, P. D. *J. Chem. Soc., Dalton Trans.* **1985**, 423. (p) Hunter, A. D.; Legzdins, P.; Nurse, C. R.; Einstein, F. W. B.; Willis, A. C. *J. Am. Chem. Soc.* **1985**, *107*, 1791.

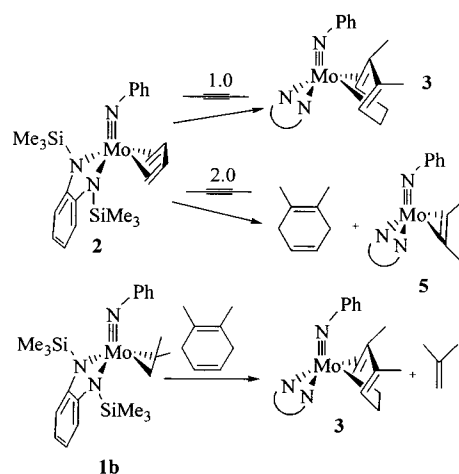


**Figure 1.** Thermal ellipsoid plot of **2** (50% probability thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Mo–N(1), 1.7517(19); Mo–N(2), 2.0556(17); Mo–N(3), 2.0536(18); Mo–C(19), 2.254(3); Mo–C(20), 2.336(2); Mo–C(21), 2.355(2); Mo–C(22), 2.257(2); C(19)–C(20), 1.401(4); C(20)–C(21), 1.397(4); C(21)–C(22), 1.405(4); C(19)–C(20)–C(21), 124.4(2); C(20)–C(21)–C(22), 123.3(2).

bond lengths of 1.401(4), 1.397(4), and 1.405(4) Å, respectively, also support a  $\pi^2, \eta^4$ -bonding mode for **2**. The Mo–N(1) length of 1.7517(19) Å is typical of a Mo–N triple-bond interaction and is comparable to the Mo–N(1) lengths in similar complexes.<sup>10</sup>

It is common practice to use the  $^1J(\text{C}–\text{H})$  coupling constants to determine the relative degree of  $\text{sp}^2$ – $\text{sp}^3$  hybridization of the coordinated diene carbons in metal butadiene complexes. By determination of the relative degree of hybridization of the diene carbon atoms, the structure, in terms of butadiene bonding, can be assigned a position somewhere between the two extremes  $\pi^2$  and  $\sigma^2, \pi$ . Using Newton's semiempirical rule,<sup>11</sup> it is possible to calculate the percent s character of carbon atoms in the dienes and, hence, the hybridization. The value of  $n$  for the carbons at diene termini reaches 2.8–2.9 (132–128 Hz) when the molecule adopts a  $\sigma^2, \pi$  type structure, while the value is in the range of 2.1–2.3 (165–154 Hz) in the case of a  $\pi^2$  complex.<sup>12</sup> We have assigned the observed triplet in the  $^{13}\text{C}$  NMR spectrum of **2** at 75.0 ppm to the terminal butadiene carbons, and the observed 158 Hz coupling constant is in good

**Scheme 3**



agreement with the formulation of **2** as a  $\pi^2$ -butadiene complex. In light of these results regarding **2**, the formal oxidation state at the metal center is best represented by Mo(IV).

**Reactivity of the Molybdenum Butadiene Complex with 2-Butyne.** The reactivity of **2** with 1 or 2 equiv of 2-butyne was explored. Proton NMR spectra of these reaction mixtures revealed the formation of two intermediates that disappear within 30 min at room temperature, giving rise to the final products, as outlined in Scheme 3. Reaction of **2** with 1 equiv of 2-butyne afforded the molybdenum 2,3-dimethyl-1,3-cyclohexadiene complex **3** by  $^1\text{H}$  NMR spectroscopy, while reaction with 2 equiv of 2-butyne gave 1,2-dimethyl-1,4-cyclohexadiene and a molybdenum  $\eta^2$ -alkyne complex (**5**) by  $^1\text{H}$  NMR spectroscopy (this alkyne complex has been synthesized independently, vide infra). Complex **3** was prepared independently by treatment of **1b** with excess 1,2-dimethyl-1,4-cyclohexadiene (Scheme 3). In addition the 2,3-dimethyl-1,3-cyclohexadiene ligand in **3** is not displaced by 2-butyne at room temperature by  $^1\text{H}$  NMR spectroscopy.

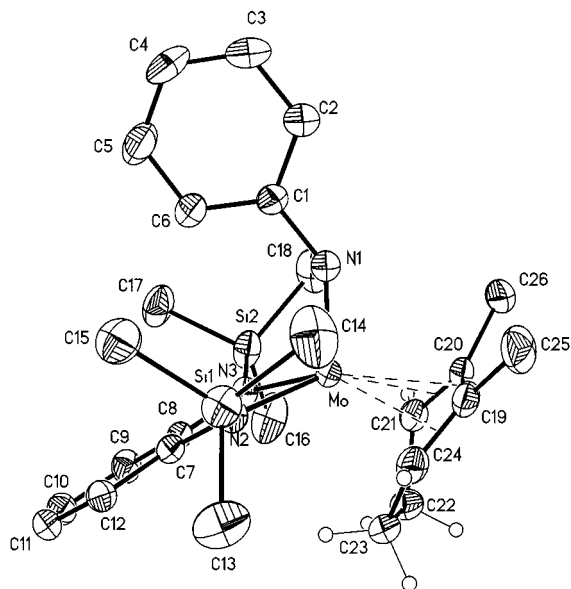
The identity of **3** was confirmed by X-ray structural analysis (Figure 2) and NMR spectroscopy. The crystal data and details of the structure refinement are summarized in Table 1. In **3** the metal is bound to the 2,3-dimethyl-1,3-cyclohexadiene in an  $\eta^4$  mode reminiscent of **2**. The C–C distances for C(21)–C(20), C(20)–C(19), and C(19)–C(24) in **3** (1.418(3), 1.418(3), and 1.405(3) Å respectively), as well as the metal–carbon bond lengths, are similar to the corresponding distances in **2**. The Mo–N(1) distance of 1.7686(18) Å is consistent with a molybdenum–nitrogen triple bond interaction.<sup>10</sup> The Mo–N(2) and N(3) amide distances of 2.0561(18) and 2.0492(17) Å, respectively, are within the range expected for Mo–N single bonds.<sup>10(e),(f),(g)</sup> Complex **3** is stable in solution at room temperature for weeks. We attribute the difference in stabilities between **2** and **3** in part to steric crowding around the metal center in **3**.

When **2** is treated with 1 equiv of 2-butyne at  $-20$  °C, the accumulation of two metal-containing species is observed by  $^1\text{H}$  NMR spectroscopy over 24 h. These species are the fleeting intermediates observed during this reaction at room temperature and are stable at  $-20$  °C for extended periods of time (over 2 days). An array of two-dimensional NMR spectroscopic techniques was

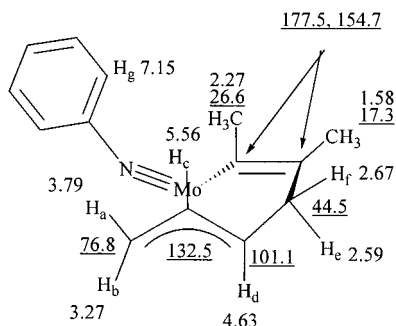
(10) (a) Dyer, P. W.; Gibson, V. C.; Howard, J. A. K.; Whittle, B.; Wilson, C. *Polyhedron* **1995**, *14*, 103. (b) Dyer, P. W.; Gibson, V. C.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **1995**, 3313. (c) Dyer, P. W.; Gibson, V. C.; Howard, J. A. K.; Whittle, B.; Wilson, C. *J. Chem. Soc., Chem. Commun.* **1992**, 1666. (d) Bryson, N.; Youinou, M. T.; Osborn, J. A. *Organometallics* **1991**, *10*, 3389. (e) Cameron, T. M.; Ortiz, C. G.; Abboud, K. A.; Boncella, J. M.; Baker, R. T.; Scott, B. L. *Chem. Commun.* **2000**, 573. (f) Ortiz, C. G.; Abboud, K. A.; Cameron, T. M.; Boncella, J. M. *Chem. Commun.* **2001**, 247. (g) Cameron, T. M.; Ortiz, C. G.; Ghiviriga, I.; Abboud, K. A.; Boncella, J. M. *Organometallics* **2001**, *20*, 2032.

(11) Newton, M. D.; Schulmann, T. M.; Manus, M. M. *J. Am. Chem. Soc.* **1974**, *96*, 17.

(12) Yamamoto, H.; Yasuda, H.; Tatsumi, K.; Lee, K.; Nakamura, A.; Chen, J.; Kai, Y.; Kasai, N. *Organometallics* **1989**, *8*, 105.

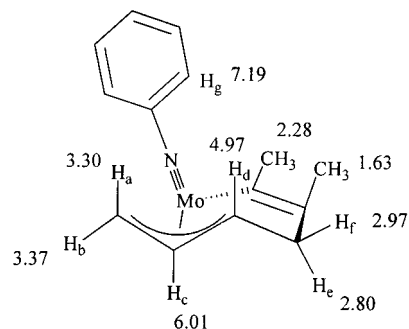


**Figure 2.** Molecular structure of **3** (50% probability thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Mo–N(1), 1.7686(18); Mo–N(2), 2.0561(18); Mo–N(3), 2.0492(17); Mo–C(21), 2.258(2); Mo–C(20), 2.342(2); Mo–C(19), 2.402(2); Mo–C(24), 2.274(2); C(21)–C(20), 1.418(3); C(20)–C(19), 1.418(3); C(24)–C(19), 1.405(3); C(24)–C(23), 1.518(3); C(23)–C(22), 1.542(3); C(22)–C(21), 1.525(3).



**Figure 3.** Structure of intermediate **4a**, a molybdenum  $\eta^3$ -allyl metallacycle. The proton and carbon resonances are assigned to corresponding atoms (carbon resonances are underlined). The chelating ligand has been omitted for clarity.

used to elucidate the structures of these intermediates. The intermediates consist of two isomeric complexes present in a 4:1 ratio. The major intermediate (**4a**) has been characterized as a *syn*  $\eta^3$ -allyl metallacyclic system, and the results of the structural elucidation study are presented in Figure 3. The metallacycle  $H_a$ –C and  $H_b$ –C  $^1J(C$ – $H)$  values of ca. 160 Hz are consistent with an  $sp^2$  hybridization of the carbon resonance at 76.8 ppm. This, along with the lack of resolved coupling between  $H_a$  and  $H_b$ , supports the existence of an  $\eta^3$ -allyl functionality. The chemical shifts of the remaining allyl proton and carbon nuclei also support the allyl fragment in **4a**. The sequence of the protons which display multiplets was seen in the DQCOSY spectrum. NOE's with the methylene protons at 2.59 and 2.67 ppm identified the methyl at 1.58 ppm as the one close to the methylene. The protonated carbons were assigned to the corresponding protons on the basis of the GHMQC spectrum. The GHMBC spectrum displayed the long-



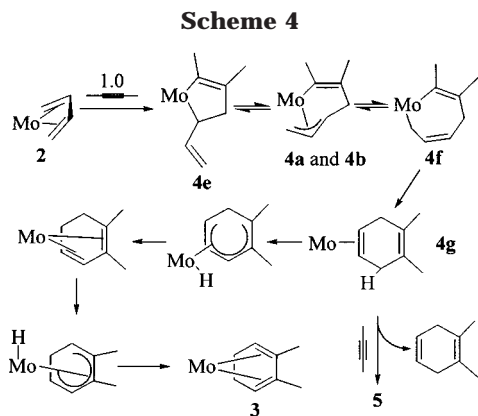
**Figure 4.** Structure of **4b**, a molybdenum  $\eta^3$ -allyl metallacycle. Only proton resonances are assigned. The chelating ligand has been omitted for clarity.

range couplings between the quaternary carbons at 177.5 and 154.7 ppm and the protons of both the methylene and the methyl groups, which confirm the metallacycle fragment. The relative sizes of the NOE's place  $H_b$ ,  $H_d$ , and  $H_e$  on one side of the cycle and  $H_a$ ,  $H_c$ , and  $H_f$  on the other side. In **4a**  $H_a$ ,  $H_c$ , and  $H_f$  showed NOE's to the aromatic proton  $H_g$ . We state that  $H_g$  is an ortho phenyl imido proton and not a phenylene proton because in the DQCOSY spectrum they displayed a phenyl coupling pattern (7.15 ppm ( $H_g$ )–6.98 ppm–6.79 ppm). Therefore,  $H_c$  occupies a *syn* relationship with respect to the phenyl imido group. This intermediate metallacyclic  $\pi$ -allyl system most likely arises from C–C coupling at the conjugated diene terminus. The minor species also consists of a metallacyclic  $\pi$ -allyl system (**4b**) which is very similar to that in **4a** (Figure 4). Metallacycle **4b** differs from **4a** in that in **4b** the central allyl proton  $H_c$  is anti with respect to the phenyl imido group, as revealed by the NOE's of  $H_g$  at 7.19 ppm and  $H_a$ ,  $H_d$ , and  $H_f$ . The details of the structural elucidation of **4b** are similar to those of **4a**; however, the low concentration of **4b** in solution prevented the assignment of the  $^{13}C$  chemical shifts of the metallacycle fragment from the GHMQC and GHMBC spectra. The NOESY spectrum did not display any exchange peaks between **4a** and **4b** at  $-20$  °C.

There has been extensive mechanistic work by Erker et al. and Nakamura et al. on the reactivity of group 4 metallocene derivatives of 1,3-butadienes with unsaturated substrates. The pathway favored for such reactions involves coupling of the unsaturated moiety with one of the diene double bonds, producing a 2-vinyl metallacyclopentane species (C in Scheme 2). This species can then isomerize as shown in Scheme 2.

It thus seems reasonable to propose that **2** reacts with 2-butyne to give **4e**, which does not accumulate to any detectable levels by  $^1H$  NMR spectroscopy (Scheme 4). Intermediate **4e** rapidly rearranges, affording **4a** and **4b**, which can be observed at low temperature. At room temperature **4a**, **4b**, or some combination of the two most likely rearranges to form **4f**, which rapidly generates **4g** via reductive elimination. Isomerization of **4g** ultimately results in the formation of **3**.<sup>13</sup> The production of **3** from treatment of the olefin complex **1b** with excess 1,2-dimethyl-1,4-cyclohexadiene gives evidence supporting formation of **4g** in the proposed mechanism.

The difference in product distribution when 2 equiv of 2-butyne reacts with **2** can be rationalized on the basis of the proposed mechanism in Scheme 4. Excess



2-butyne competes for the metal center with the 1,2-dimethyl-1,4-cyclohexadiene ligand in **4g**, liberating free 1,2-dimethyl-1,4-cyclohexadiene and forming **5** as the metal-containing product.

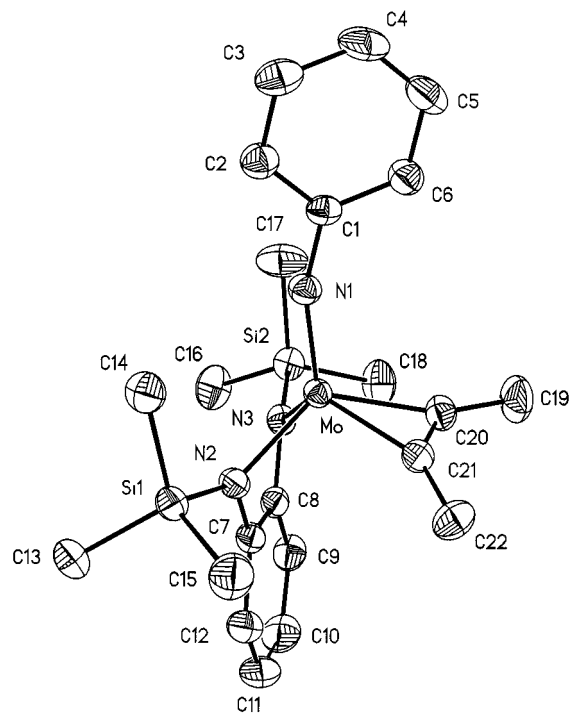
**Synthesis of the Molybdenum 2-Butyne Complex [Mo(NPh)( $\eta^2$ -2-butyne)(*o*-(Me<sub>3</sub>SiN)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)] (**5**).** Treatment of a pentane solution of **1b** with 2-butyne affords the  $\eta^2$ -2-butyne complex [Mo(NPh)( $\eta^2$ -2-butyne)(*o*-(Me<sub>3</sub>SiN)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)] (**5**). This alkyne complex is not stable in solution at room temperature and decomposes, affording an intractable mixture by <sup>1</sup>H NMR spectroscopy. At  $-30^\circ\text{C}$  **5** is stable for a brief period of time and X-ray-quality crystals can be grown overnight, allowing us to perform a single-crystal X-ray diffraction study. The crystal data and details of the structure refinement are summarized in Table 3 and a thermal ellipsoid plot of **5** along with selected bond lengths and angles is displayed in Figure 5. Complex **5** adopts a square-pyramidal geometry in which the imido group occupies the apical position. The metal–imido interaction (Mo–N(1), 1.7511(17) Å) is consistent with a metal–nitrogen triple-bond interaction,<sup>10</sup> and the molybdenum amide contacts are consistent with metal–nitrogen single-bond interactions.<sup>10e–g</sup> The C(21)–C(20) bond length of 1.297(3) Å and bond angles C(21)–C(20)–C(19) ( $137.3(2)^\circ$ ) and C(20)–C(21)–C(22) ( $140.2(2)^\circ$ ) support a considerable amount of sp<sup>2</sup> character of carbons C(20) and C(21). The metal-coordinated 2-butyne carbons of **5** resonate at 181.5 ppm in the <sup>13</sup>C NMR spectrum. On the basis of this chemical shift the 2-butyne ligand is best viewed as donating more than 2e to the metal center.<sup>14</sup> We have been able to generate a variety of  $\eta^2$ -alkyne complexes of disubstituted alkynes that show similar trends in bonding. We are currently in the process of investigating the bonding in these compounds via DFT studies. These results will be reported separately.

### Conclusion

We have characterized a cis molybdenum butadiene complex with structural characteristics similar to those

(13) (a) Along these lines we have observed that **1b** catalyzes the isomerization of allylanisole to *trans*- $\beta$ -methylstyrene. Although no hydride species are detected in solution for these isomerization reactions, we have isolated hydride complexes of a closely related tungsten system<sup>13b</sup> and have spectroscopically observed a molybdenum PMe<sub>3</sub> stabilized dihydrogen complex of this system (manuscript in preparation). (b) Boncella, J. M.; Wang, S.-Y. S.; VanderLende, D. D. *J. Organomet. Chem.* **1999**, 591, 8.

(14) (a) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, 102, 3288. (b) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, 102, 1532. (c) Tatsumi, K.; Hoffmann, R.; Templeton, J. L. *Inorg. Chem.* **1982**, 21, 466.



**Figure 5.** Molecular structure of **5** (50% probability thermal ellipsoids). Selected bond lengths (Å) and angles (deg): Mo–N(1), 1.7511(17); Mo–N(2), 2.0314(16); Mo–N(3), 2.0014(16); Mo–C(20), 2.056(2); Mo–C(21), 2.052(2); C(20)–C(21), 1.297(3); C(20)–C(21)–C(22),  $140.2(2)^\circ$ ; C(21)–C(20)–C(19),  $137.3(2)^\circ$ .

of other group 6 metal butadiene complexes. The reactivity of our butadiene complex is comparable to the reactivity of early-metal butadiene complexes. Our system is unique in that unlike group 4 chemistry, where the final products of butadiene substrate C–C coupling are metallacyclic, our system is governed by a reductive-elimination step, resulting in formation of a metal 1,3-cyclohexadiene complex. Additional studies into the reactivity of this butadiene complex with other unsaturated organics are underway.

### Experimental Section

**General Methods.** All reactions were conducted under a dry argon atmosphere using standard Schlenk techniques, and all compounds were handled in a nitrogen-filled drybox. All solvents were distilled under nitrogen from sodium or sodium benzophenone ketyl or passed over activated alumina, stored over molecular sieves, and degassed prior to use. Complexes **1a** and **1b** were synthesized according to published procedure.<sup>10g</sup> NMR spectra were obtained on a Varian Gemini 300, VXR 300, or Mercury 300 instrument with C<sub>6</sub>D<sub>6</sub>, C<sub>7</sub>D<sub>8</sub>, and CDCl<sub>3</sub> as solvents, as noted, and referenced to residual solvent peaks. A Varian Inova 500 equipped with an indirect detection probe was used as indicated for the GHMQC,<sup>15</sup> GHMBC,<sup>16</sup> and NOESY<sup>17</sup> experiments.

**Synthesis and Characterization of [Mo(NPh)( $\eta^4$ -H<sub>2</sub>C=CHCH=CH<sub>2</sub>)(*o*-(Me<sub>3</sub>SiN)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>)] (**2**).** In a typical procedure butadiene gas (ca. 15 psi) was added to a degassed flask containing a green solution of **1a** (0.42 g, 0.88 mmol) in

(15) Bodenhausen, G.; Ruben, D. J. *Chem. Phys. Lett.* **1980**, 69, 185.

(16) Bax, A.; Summers, M. F. *J. Am. Chem. Soc.* **1986**, 108, 2093.

(17) (a) States, D. J.; Haberkorn, R. A.; Ruben, D. J. *J. Magn. Reson.* **1982**, 48, 286. (b) Bodenhausen, G.; Kogler, H.; Ernest, R. R. *J. Magn. Reson.* **1984**, 58, 370. (c) Wider, G.; Macura, S.; Kumar, A.; Ernst, R. R.; Wuthrich, K. *J. Magn. Reson.* **1984**, 56, 207.

pentane. The mixture was stirred for 10 min and concentrated in vacuo, affording **2** as a green solid in 90% yield. Complex **2** decomposes rapidly in solution at room temperature and is best stored as a solid at  $-30\text{ }^\circ\text{C}$  under an inert atmosphere.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ; room temperature):  $\delta$  0.33 (18H,  $\text{SiMe}_3$ ), 0.33 (ov, 2 H, butadiene protons), 4.20 (mult, 2 H, butadiene protons), 5.49 (mult, 2 H, butadiene protons), 6.7–7.0 (ov, mult, 7 H), 7.23 (m, 2 H, aromatic protons).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ; room temperature):  $\delta$  4.7, 75.0, 114.7, 117.9, 119.0, 119.4, 127.3, 129.3, 152.8, 158.9.  $^1\text{H}$  NMR ( $\text{C}_7\text{D}_8$ ;  $-30\text{ }^\circ\text{C}$ ; assigned via GHMQC; 500 MHz):  $\delta$  0.13 (br, mult, 2 H, terminal butadiene protons), 0.33 (br, 18 H,  $\text{SiMe}_3$ ), 4.21 (br, m, 2 H, terminal butadiene protons), 5.53 (br, mult, 2 H, internal butadiene protons), 6.69 (t, 8.0 Hz, para proton), 6.72 (d, 8.0 Hz, ortho protons), 6.85 (t, 8.0 Hz, meta proton), 6.94 (m, 2 H,  $\sigma$ - $(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4$  protons), 7.25 (m, 2 H,  $\sigma$ - $(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4$  protons).  $^{13}\text{C}$  NMR ( $\text{C}_7\text{D}_8$ ;  $-30\text{ }^\circ\text{C}$ ; assigned via GHMQC and  $J_{\text{CH}}$  from the gated decoupled  $^{13}\text{C}$  NMR spectrum):  $\delta$  4.2 (q, 122 Hz,  $\text{Si}(\text{CH}_3)_3$ ), 75.0 (br, t, 158 Hz, butadiene terminal carbon), 114.4 (d, 164 Hz, butadiene internal carbon), 117.3 (d, 147 Hz), 118.3 (d of d, 157 Hz, 8 Hz), 118.7 (d, 162 Hz), 126.9, 128.8, 152.3 (t, 7 Hz), 158.3 (t, 8 Hz). Because of the thermal instability of **2**, elemental analysis was not possible.

**Synthesis and Characterization of  $[\text{Mo}(\text{NPh})(\eta^4\text{-2,3-dimethyl-1,3-cyclohexadiene})(\sigma\text{-}(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4)]$  (**3**).** 1,2-Dimethyl-1,4-cyclohexadiene (0.145 g, 1.33 mmol) was added to a stirred solution of **1b** (0.660 g, 1.33 mmol) in pentane. This mixture was stirred for 5 days and then concentrated under reduced pressure, affording **3** in 76% yield. Analytically pure **3** can be obtained by washing the solid with pentane at room temperature. Anal. Calcd for  $\text{C}_{26}\text{H}_{39}\text{MoN}_3\text{Si}_2$ : C, 57.22; H, 7.20; N, 7.70. Found: C, 57.08; H, 7.26; N, 7.52.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ; room temperature; 500 MHz; assigned by GHMQC, GHMBC, and NOESY):  $\delta$  0.32 (18 H,  $\text{SiMe}_3$ ), 0.31 (ov, 2 H, cyclohexadiene methylene protons), 1.45 (br, mult, 2 H, cyclohexadiene methylene protons), 2.05 (*Me*), 4.59 (br, C=C(*H*)), 6.68 (ortho protons), 6.73 (para proton), 6.83 (m, 2 H,  $\sigma$ - $(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4$  protons), 6.93 (meta protons), 7.16 (m, 2 H,  $\sigma$ - $(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4$  protons).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ; room temperature; 500 MHz; assigned by GHMQC and GHMBC):  $\delta$  3.6 ( $\text{Si}(\text{CH}_3)_3$ ), 18.4 ( $\text{CH}_2$ ), 22.0 (*Me*), 87.4 (C=C(H)), 117.3 ( $\sigma$ - $(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4$ ), 117.6 (ortho carbon), 118.2 ( $\sigma$ - $(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4$ ), 126.0 (para carbon), 126.2 (C=C(H)), 128.7 (*meta* carbon), 153.3 (*ipso*,  $\sigma$ - $(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4$ ), 158.7 (*ipso*, phenyl).

**Formation of **3** by Treatment of **2** with 2-Butyne.** An NMR tube containing **2** (136.3 mg, 27.7 mmol) in  $\text{C}_6\text{D}_6$  was charged with 2-butyne (21.7  $\mu\text{L}$ , 27.7 mmol) at room temperature. The reaction was complete after 30 min. Complex **3** is observed in the  $^1\text{H}$  NMR spectrum of the reaction mixture.

**Synthesis and Characterization of Intermediates **4a** and **4b**.** An NMR tube containing **2** (136.3 mgs, 27.7 mmol) in cold  $\text{C}_7\text{D}_8$  was charged with 2-butyne (21.7  $\mu\text{L}$ , 27.7 mmol) at room temperature. The mixture was frozen with liquid nitrogen after 1 min and placed in a cooled ( $-20\text{ }^\circ\text{C}$ ) NMR probe. All 2D spectra (GHMQC, GHMBC, NOESY, DQCOSY, and TOCSY) were acquired at  $-20\text{ }^\circ\text{C}$  on an Inova 500. For selected  $^1\text{H}$  and  $^{13}\text{C}$  NMR data for **4a** and **4b** see Figures 4 and 5.

**Synthesis and Characterization of  $[\text{Mo}(\text{NPh})(\eta^2\text{-CH}_3\text{-CCCH}_3)(\sigma\text{-}(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4)]$  (**5**).** To a stirred solution of **1b** (0.340 g, 6.880 mmol) in pentane was added 2-butyne (0.0373 g, 6.880 mmol). The reaction mixture was stirred for 10 min, and **5** was isolated as a red solid upon concentration of the reaction mixture under reduced pressure (yield 76%). Complex **5** is not stable in solution at room temperature and also decomposes in solution at  $-30\text{ }^\circ\text{C}$  overnight.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ; room temperature):  $\delta$  0.45 (18 H,  $\text{SiMe}_3$ ), 2.17 (6 H,  $\text{CH}_3\text{-CCCH}_3$ ), 6.9–7.2 (ov, mult, 9 H).  $^{13}\text{C}$  NMR ( $\text{C}_7\text{D}_7$ ;  $-25\text{ }^\circ\text{C}$ ):  $\delta$  1.8, 17.8, 121.9, 123.3, 123.8, 124.1, 157.8, 181.5. Two resonances are overlapping with solvent. Because of the thermal instability of **5** elemental analysis was not possible.

**Formation of **5** and 1,2-Dimethyl-1,4-cyclohexadiene by Treatment of **2** with 2 Equiv of 2-Butyne.** An NMR tube containing **2** (136.3 mg, 27.7 mmol) in  $\text{C}_6\text{D}_6$  was charged with 2-butyne (43.4  $\mu\text{L}$ , 55.4 mmol) at room temperature. The reaction is complete after 30 min. Complex **5** and 1,2-dimethyl-1,4-cyclohexadiene are observed in the  $^1\text{H}$  NMR spectrum of the reaction mixture.

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**Supporting Information Available:** Tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for **2**, **3**, and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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