## Reactivity of $[MCl(\eta^3-allyl)(CO)_2(N-N)]$ Complexes (M = Mo, W; N-N = bipy, phen) toward Alkyl and Acetylide Anions

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The reactions of  $[MoCl(\eta^3-allyl)(CO)_2(N-N)]$  (N-N = bipy, phen) and of the related tungsten complexes with  $MgR_2$  reagents (R = Me, Et, Bz) gave as single products the new alkyls  $[M(R)(\eta^3-allyl)(CO)_2(N-N)]$  (**3**–**9**), which have the alkyl and allyl groups in trans positions. Related alkynyls  $[M(C \equiv CR)(\eta^3 - allyl)(CO)_2(N-N)]$  with R = Ph, SiMe<sub>3</sub>, H (**10–15**) were obtained similarly employing alkaline acetylides.

## Introduction

Despite the extensive research carried out on the organometallic chemistry of Mo(II) and W(II) halocarbonyl complexes,<sup>1</sup> alkyl and alkynyl derivatives are nearly limited to fragments containing cyclopentadienyl ligands.<sup>2</sup>

The metathesis between a halocomplex and a main group organometallic such as an organolithium or organomagnesium reagent is often used to create new metal-carbon bonds.<sup>3</sup> However, this route can be hampered by the presence of ligands able to (a) act as alternative sites of the nucleophilic attack or (b) undergo intramolecular migration of an initially formed alkyl ligand. The presence of the carbonyl ligand itself can bring about this problem. Thus, Carmona found that  $\eta^2$ -acyls are the only products of the reaction between halocarbonyl Mo(II) phosphine complexes with carbanionic reagents, presumably via the intermediacy of alkyl carbonyl complexes.<sup>4</sup>

For  $[MoX(\eta^3-allyl)(CO)_2(L-L)]$  (X = anionic ligand, L-L = neutral chelate) compounds, the allyl group is a potential target of the alkylation,<sup>5</sup> and this reaction has an added interest since molybdenum carbonyl complexes catalyze the alkylation of allylic electrophiles.<sup>6</sup> This is believed to occur by oxidative addition to an electron-rich zerovalent species to give a Mo(II)  $\eta^3$ -allyl complex. Subsequent alkylation either directly to the allyl or to the metal followed by an alkyl-to-allyl

migration with concomitant reductive elimination of the resulting olefin would complete the cycle.<sup>7</sup>

In Trost's seminal paper  $[MoX(\eta^3-allyl)(CO)_2(L-L)]$ complexes were reported to react with stabilized carbanions to afford olefins.<sup>6a</sup> However, the reactivity of these complexes toward nonstabilized carbanions remains unexplored.<sup>8</sup> This work reports our studies in this area.9

## **Results and Discussion**

The reaction of  $[MoCl(\eta^3-C_3H_5)(CO)_2(bipy)]^{10}$  (1a) with MgMe<sub>2</sub> in THF afforded the methyl complex [Mo(CH<sub>3</sub>)- $(\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>(bipy)] (**3a**). Its spectroscopic data include two similarly intense bands at wavenumbers lower than in **1a**, indicating the persistence of a *cis*-Mo(CO)<sub>2</sub> unit,

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<sup>(8)</sup> The only such reaction reported is that of  $[MoX(\eta^3-C_3H_5)(CO)_2^-(DAB)]$  (X = Cl, Br; DAB = N,N-dialkylethanediimine) with MeLi or MeMgI, which afforded unidentified decomposition products: Hsieh, A. T. T.; West, B. O. J. Organomet. Chem. 1976, 112, 285. The possibility of nucleophilic attack to the metal was suggested: Curtis, M. D.; Fotinos, N. A. J. Organomet. Chem. 1984, 272, 43. Trost found results suggesting attack to the metal by the less bulky malonate anions: Trost, B. M.; Lautens, M. J. Am. Chem. Soc. **1987**, 109, 1469. For another example of at-the-metal attack by a soft nucleophile, see: Faller, J. W.; Linebarrier, D. Organometallics 1988, 7, 1670.

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a low-frequency <sup>1</sup>H NMR singlet, typical of a metalbound methyl group, and a pattern of two doublets and one multiplet in <sup>1</sup>H NMR, diagnostic of a static (without fast equilibration to  $\eta^1$ )  $\eta^3$ -C<sub>3</sub>H<sub>5</sub> group like the one present in **1a**. The set of four multiplets for the bipy hydrogens, together with the equivalence of the two syn hydrogens and of the two anti hydrogens, maintained when the temperature was lowered to 190 K,<sup>11</sup> is consistent with the existence of a mirror plane, and therefore, the structure depicted in Scheme 1 can be assigned to **3a**.

15

н

w

phen

Related ethyl (**4a**) and benzyl (**5a**) derivatives, as well as the three analogues with N-N = phen (compounds **3b**, **4b**, and **5b**), and the methyl (**6**), ethyl (**7**), and benzyl (**8**) tungsten phen complexes were prepared.

These alkylations took place selectively at the metal, and neither acyl complexes nor allylic alkylation products were formed.

The higher solubility of the phen complexes allowed their <sup>13</sup>C NMR spectra to be acquired. The spectra of the new complexes indicate a structure like that of **3a**. These compounds are the first [Mo(R)( $\eta^3$ -allyl)(CO)<sub>2</sub>L<sub>2</sub>] derivatives and add to the very few examples of alkyl carbonyl molybdenum and tungsten complexes without cyclopentadienyl ligands.<sup>12</sup> The lower  $\nu_{CO}$  values for the tungsten complexes reflect the more electron-rich nature of the third-row metal.<sup>12a</sup>

The new alkyls can be handled in the air for short periods of time without noticeable decomposition, are stable in nonchlorinated solvents, and are moderately sensitive toward air and moisture. Their reflux in THF (6 h) did not cause elimination of alkyl-allyl coupling products, probably reflecting a configurational stability that keeps the hydrocarbyl ligands on distant sites of the molecule. The stability of the ethyl complexes toward  $\beta$ -elimination can be attributed to the lack of facile dissociation processes in these electron-precise compounds.<sup>13</sup> As a result of this saturation, the new alkyls do not react with nucleophiles.<sup>14</sup> Thus, treatment with carbon monoxide (bubbling for 1 h at room temperature) or trimethylphosphine (5 equiv, 70 h at room temperature) does not induce alkyl migration to the proximate CO ligands. The same reason can explain the inertness of the new alkyls toward unsaturated organic electrophiles such as *p*-tolyl isocyanate and carbon disulfide, which typically insert into metal-carbon bonds,<sup>15</sup> since insertion usually requires previous coordination of the unsaturated molecule. The new alkyls do not react with weak acids such as methanol or phenylacetylene (5 equiv, 20 h in acetone- $d_6$  solution at room temperature). Triflic acid or benzenethiol selectively protonates the alkyl-molybdenum bond, yielding  $[Mo(X)(\eta^3-allyl)(CO)_2(N-N)]$  (X = OTf, SPh) complexes and the alkane. This selectivity is remarkable, since the allyl protonation of Mo( $\eta^3$ -allyl) complexes has been used to generate a vacant coordination site.<sup>16</sup>

The alkyl complexes underwent a transformation to their chloroprecursors in chlorinated solvents. Our attempts to grow single crystals of the new alkyls from toluene, THF, or acetone solutions failed. Dark green single crystals could be grown by slow diffusion of hexane into concentrated solutions of the methyl complexes **3a** and **3b** in CH<sub>2</sub>Cl<sub>2</sub>, but they were found to consist of Mo–CH<sub>3</sub> and Mo–Cl mixtures.<sup>17–19</sup>

We found that  $[Mo(CH_3)(\eta^3-methallyl)(CO)_2(phen)]$ (9), prepared as described for **3a**, crystallized free from the chlorinated companion. An X-ray diffraction determination (Figure 1 and Table 1) showed 9 to be isostructural with **3a**, **3b**, and known  $[MoX(\eta^3-allyl)-(CO)_2(N-N)]$  complexes,<sup>1</sup> having the alkyl and allyl groups on opposite sides of the equatorial plane defined by the two carbonyls and the two nitrogen atoms, and the allyl oriented with the wingtip carbons pointing toward the carbonyls,<sup>20</sup> resulting in  $C_s$  symmetry.

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<sup>(11)</sup> In complexes  $[MoX(\eta^3-allyl)(CO)_2(P-P)]$  (X = halide, P-P = bidentate phosphine), a dynamic process fast at room temperature in the NMR time scale lends an apparent  $C_s$  symmetry to the molecule. However, the low-temperature NMR spectra indicate that one P is trans to a CO ligand and the other P is trans to the allyl, a geometry also found in the solid-state structure: Faller, J. W.; Haitko, D. A.; Adams, R. D.; Chodosh, D. F. *J. Am. Chem. Soc.* **1979**, *101*, 865.

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<sup>(14)</sup> Reactivity of  $[MoCl(\eta^3-allyl)(CO)_2(NCMe)_2]$  with excess trialkylphosphines is known to cause reductive elimination to yield Mo(0) complexes: Clark, D. A.; Jones, D. L.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1998**, 565.

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<sup>(17)</sup> For an example of a mixture of isostructural Mo-Cl and Mo-CH<sub>3</sub> complexes in single crystals, see: Cotton, F. A.; Wiesinger, K. *Inorg. Chem.* **1990**, *29*, 2594.



**Figure 1.** Molecular structure and numbering scheme of **9**. Selected bond lengths (Å) and angles (deg): Mo(1)–C(1) 2.339(3); C(2)–Mo(1)–C(1) 88.31(11), C(3)–Mo(1)–C(1) 87.87(9); N(1)–Mo(1)–C(1) 79.18(9); N(2)–Mo(1)–C(1) 75.95(8).

Table 1. Crystal Data and Refinement Details for<br/>Complexes 9 and 10

	9	10
formula	$C_{19}H_{18}MoN_2O_2 \\$	C <sub>23</sub> H <sub>18</sub> MoN <sub>2</sub> O <sub>2</sub> · 1/2CH <sub>2</sub> Cl <sub>2</sub>
fw	402.29	492.80
cry syst	monoclinic	triclinic
space group	$P2_{1}/c$	<i>P</i> 1
a, Å	8.8017(4)	8.673(2)
<i>b</i> , Å	13.2357(6)	10.337(2)
<i>c</i> , Å	15.1162(7)	12.355(3)
α, deg	90	96.58(2)
$\beta$ , deg	99.669(1)	98.95(2)
$\gamma$ , deg	90	100.32(2)
<i>V</i> , Å <sup>3</sup>	1735.97(14)	1064.8(4)
Ζ	4	2
Т, К	293(2)	293(2)
$D_{\rm c}$ , g cm <sup>-3</sup>	1.539	1.537
<i>F</i> (000)	816	498
λ(Μο Κα), Å	0.71073	0.71073
cryst size, mm	$0.24\times0.15\times0.11$	$0.23 \times 0.17 \times 0.10$
$\mu$ , mm <sup>-1</sup>	0.768	0.763
scan range, deg	$2.06 \le \theta \le 23.24$	$1.69 \le  heta \le 25.97$
no of reflns measd	10 810	4379
no of ind reflns	2492	4379
no. of data/restraints/	2492/0/220	4379/3/635
params	1 007	1 000
goodness-of-fit on $F^{2}$	1.00/	1.033
$K_1/K_{W2} [I \ge 2\sigma(I)]$	0.0222/0.0641	0.0370/0.0853
$R_1/R_{w2}$ (all data)	0.0239/0.0656	0.0788/0.1010

Unlike for **3a** and **3b**, the metrical data of **9** could be determined with considerable accuracy.<sup>21</sup> The Mo– $C_{methyl}$  distance (2.339(3) Å) is one of the longer ones found for mononuclear molybdenum methyl complexes.<sup>22</sup>

We wished to study the reactivity of  $[MoCl(\eta^3-ally])-(CO)_2(N-N)]$  complexes with other carbanions. We wanted to know whether the softer character of acetylides would translate into a regiochemistry different from that found for alkyl anions (see above). Otherwise, acetylide attack to the metal would yield alkynyl complexes. Molybdenum and tungsten alkynyls without cyclopolyenyl ligands are rare.<sup>23</sup>



**Figure 2.** Molecular structure and numbering scheme of **10**. Selected bond lengths (Å) and angles (deg): Mo–C(3) 2.16(2); C(4)–C(41) 1.49(3); C(3)–C(4) 1.20(3); Mo–C(3)–C(4) 169.6(19); C(3)–C(4)–C(41) 174(2).

The reaction of **1a** with lithium phenylacetylide afforded the alkynyl complex  $[Mo(C \equiv CPh)(\eta^3-allyl)-(CO)_2(bipy)]$  (**10**) as the only product. Its IR spectrum displayed two strong  $\nu_{CO}$  bands and a weak band at 2077 cm<sup>-1</sup> assigned to the acetylenic C–C stretching.<sup>2,23</sup> The <sup>1</sup>H NMR spectrum **10** shows, in addition to the phenyl multiplets, sets of bipy and allyl signals such as those found for the alkyl compounds **3**–**5**, indicating a similar geometry. The limited solubility of **10** precluded the observation of the acetylenic carbons in the <sup>13</sup>C NMR spectrum (see Experimental Section). The structure of **10** was determined by X-ray diffraction (see Figure 2 and Table 1).

The results confirm the geometry inferred from spectroscopic data. In particular, the distance between the two acetylenic carbons (1.20(3) Å) and the alignment of those atoms, the ipso carbon, and the molybdenum atom  $(Mo-C(3)-C(4) = 170(2)^{\circ}, C(3)-C(4)-C(41) = 174(2)^{\circ})$  are typical of alkynyl complexes.<sup>2b,24</sup>

<sup>(20)</sup> Curtis, M. D.; Eisenstein, O. Organometallics 1984, 3, 887.

<sup>(21)</sup> However, we have to recognize that the presence of a low level of the chloro complex as an impurity in the crystal of **9**, which would have resulted in an elongated apparent Mo– $C_{methyl}$  distance and would have been compatible with normal thermal parameters and with high precision, is difficult to rule out conclusively; see p 375 of ref 19. We did not detect the presence of the chloro complex in our analytic or spectroscopic data.

<sup>(22)</sup> Most Mo- $C_{alkyl}$  bond lengths are within the range 2.131–2.264 Å: Schrauzer, G. N.; Hughes, L. A.; Strampach, N.; Robinson, P. R.; Schlemper, E. O. *Organometallics* **1982**, *1*, 44. For a very recent paper containing structural data of several molybdenum methyl complexes, see: Sharp, W. B.; Daff, P. J.; McNeil, W. S.; Legzdins, P. *J. Am. Chem. Soc.* **2001**, *123*, 6272. For Mo–CH<sub>3</sub> distances longer than the one found in **9**, see: (a) Sharp, W. B.; Daff, P. J.; McNeil, W. S.; Legzdins, P. *J. Am. Chem. Soc.* **2001**, *123*, 6272. (b) Churchill, M. R. *Perspectives in Coordination Chemistry*; Dunitz, J., Ibers, J. A., Eds.; Wiley: New York, 1970; Vol. 3, p **9**1.

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The complex  $[Mo(C \equiv CSiMe_3)(\eta^3 - allyl)(CO)_2(bipy)]$  (11) was prepared in a similar way and characterized spectroscopically. The acetylenic C-C IR stretching appears as a weak band at 2075 cm<sup>-1</sup>.25 The signals of the acetylenic carbons could be observed in <sup>13</sup>C NMR as low-intensity singlets at 161.82 and 117.60 ppm, assigned to the Mo- and Si-bonded carbons, respectively, by comparison with known complexes.<sup>26</sup>

The ethynyl derivative  $[Mo(C \equiv CH)(\eta^3 - allyl)(CO)_2 -$ (bipy)] (14a) was synthesized by reaction of 1a with excess sodium acetylide. In addition to the two  $\nu_{CO}$ bands at 1947 and 1855 cm<sup>-1</sup>, the IR of **14a** shows an absorption at 1933 cm<sup>-1</sup>, attributed to the acetylenic C-C stretching. The ethynyl hydrogen occurs at 2.12 ppm in the <sup>1</sup>H NMR, and the two acetylenic carbons as weak signals at 100.61 and 79.92 ppm in the <sup>13</sup>C NMR. The complex  $[Mo(C \equiv CH)(\eta^3 - allyl)(CO)_2(phen)]$  (14b) and the tungsten alkynyls  $[W(C \equiv CPh)(\eta^3 - allyl)(CO)_2 -$ (phen)] (12),  $[W(C \equiv CSiMe_3)(\eta^3 - allyl)(CO)_2(phen)]$  (13), and  $[W(C \equiv CH)(\eta^3 - allyl)(CO)_2(phen)]$  (15) were prepared analogously and characterized spectroscopically (see **Experimental Section**).

In each reaction, the alkynyl complex was found to be the only product. The new alkynyls are, like the alkyls **3–9**, reluctant to eliminate C–C coupling products when heated for hours in THF.

## **Experimental Section**

General procedures were given elsewhere.9

X-ray Crystallographic Analyses. The crystal of 9 was measured on a Bruker AXS SMART 1000 CCD diffractometer. Raw frame data were integrated with the SAINT<sup>27</sup> program. The structure was solved by direct methods with SHELXTL.<sup>28</sup> A semiempirical absorption correction was applied with SAD-ABS.<sup>29</sup> All non-hydrogen atoms were refined as riding atoms, with a common thermal parameter. All calculations were made with SHELXTL.

The crystal of 10 was measured on a Nonius CAD4 diffractometer. On all reflections, a profile analysis was performed.<sup>30</sup> Symmetry-equivalent and other redundant reflections were averaged and drift, Lorentz, and polarization corrections were applied. The structure was solved by Patterson methods using DIRDIF-96.<sup>31</sup> Isotropic least-squares refinement on  $F^2$  was performed using SHELXL97.32 An empirical absorption correction was applied at this stage, using XABS2.<sup>33</sup> All the H atoms were located by Fourier synthesis. During the final

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stages of the refinement, all positional parameters and the anisotropic temperature factors of all the non-H atoms were refined using SHELXL97.32 The H atoms were isotropically refined. Plots were made with the EUCLID package.<sup>34</sup> Geometrical calculations were made with PARST.35

**Synthesis of [W(CH<sub>3</sub>)**( $\eta^{3}$ -C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>(phen)] (6). To a solution of 2<sup>36</sup> (0.10 g, 0.20 mmol) in THF (20 mL) was added MgMe<sub>2</sub> (0.20 mmol, 0.7 mL of a 0.29 M solution in Et<sub>2</sub>O). The color of the solution changed immediately from orange to blue. After stirring for 15 min, the solvent was removed under vacuum. The residue was redissolved in toluene and filtered through Celite. Solvent evaporation afforded 0.064 g of 6 (67%) as a blue solid. IR (CH<sub>2</sub>Cl<sub>2</sub>): 1914, 1820 (v<sub>CO</sub>). <sup>1</sup>H NMR (CD<sub>2</sub>-Cl<sub>2</sub>): 9.08, 8.48, 8.01 and 7.75 [m, 2H each, phen], 2.70 [d (5.9), 2H, H<sub>syn</sub>], 2.04 [m, 1H, CH of η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>], 1.64 [d (8.3), 2H, H<sub>anti</sub>], -0.83 [s, 3H W-*CH*<sub>3</sub>]. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 227.97 [CO], 150.97, 144.66, 135.33, 130.22, 127.00 and 124.36 [phen], 65.84  $[C^2 \text{ of } \eta^3 - C_3H_5], 43.30 [C^1 \text{ and } C^3 \text{ of } \eta^3 - C_3H_5], 14.90 [W-CH_3].$ Anal. Calcd for C18H16N2O2W: C, 62.08; H, 4.34; N, 6.06. Found: C, 61.78; H, 4.29; N, 6.13.

Synthesis of  $[W(CH_2CH_3)(\eta^3-C_3H_5)(CO)_2(phen)]$  (7). 7 was obtained from 2 (0.10 g, 0.20 mmol) and MgEt<sub>2</sub> (1.14 mL of a 0.21 M solution in Et<sub>2</sub>O, 0.24 mmol). Yield: 0.057 g, 65% (dark blue solid). IR (CH<sub>2</sub>Cl<sub>2</sub>): 1917, 1826 (v<sub>CO</sub>). <sup>1</sup>H NMR (CD<sub>2</sub>-Cl<sub>2</sub>): 9.02, 8.44, 7.97 and 7.74 [m, 2H each, phen], 2.71 [d (6.2), 2H, H<sub>syn</sub>], 2.66 [m, 1H, CH of  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>], 1.47 [t (7.8), 3H, W-CH<sub>2</sub>CH<sub>3</sub>], 1.35 [d (8.2), 2H, H<sub>anti</sub>], -0.34 [q (7.8), 2H, Mo-CH<sub>2</sub>CH<sub>3</sub>]. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 227.87 [CO], 150.92, 143.36, 136.34, 127.06, 124.97 and 124.01 [phen], 67.63 [ $C^2$  of  $\eta^3$ - $C_3H_5$ ], 45.01 [C<sup>1</sup> and C<sup>3</sup> of  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>], 24.41 [Mo-CH<sub>2</sub>CH<sub>3</sub>], 14.17 [Mo-*CH*<sub>2</sub>CH<sub>3</sub>]. Anal. Calcd for C<sub>19</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>W: C, 46.55; H, 3.70; N, 5.71. Found: C, 46.48; H, 3.59; N, 5.81.

Synthesis of  $[W(CH_2C_6H_5)(\eta^3-C_3H_5)(CO)_2(phen)]$  (8). 8 was obtained from 2 (0.10 g, 0.20 mmol) and MgBz<sub>2</sub> (0.6 mL of a 0.34 M solution in THF, 0.20 mmol). Yield of 8 as a dark blue solid: 0.082 g, 74%. IR (CH<sub>2</sub>Cl<sub>2</sub>): 1917, 1827 (v<sub>CO</sub>). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 8.96, 8.34, 7.85 and 7.65 [m, 2H each, phen], 6.26 [m, 3H, C<sub>6</sub>H<sub>5</sub>], 6.19 [m, 2H, C<sub>6</sub>H<sub>5</sub>], 2.72 [d (6.1), 2H, H<sub>syn</sub>], 1.95 [s, 2H, W-CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>], 1.87 [m, 1H, CH of  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>], 1.66 [d (8.4), 2H, H<sub>anti</sub>]. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 226.82 [CO], 151.50, 142.31, 135.63, 130.61, 128.85, 128.69, 127.56, 126.26, 125.10 and 124.79 [phen and  $C_6H_5$ ], 65.67 [C<sup>2</sup> of  $\eta^3$ - $C_3H_5$ ], 45.10 [C<sup>1</sup> and C<sup>3</sup> of  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>], 38.24 [W-CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]. Anal. Calcd for C<sub>24</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>W: C, 52.19; H, 3.65; N, 5.07. Found: C, 51.93; H, 3.72; N, 5.05.

Synthesis of  $[Mo(CH_3)(\eta^3-methallyl)(CO)_2(phen)]$  (9). **9** was obtained from  $1c^{37}$  (0.10 g, 0.24 mmol) and MgMe<sub>2</sub> (0.9 mL of a 0.29 M solution in Et<sub>2</sub>O, 0.24 mmol). Slow diffusion of hexane into a solution of 9 in THF (10 mL) at -20 °C afforded dark blue crystals of 9, one of which was used for the X-ray analysis. Yield: 0.080, 84%. IR (CH<sub>2</sub>Cl<sub>2</sub>): 1921, 1831 (v<sub>CO</sub>). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 8.91, 8.39, 7.97 and 7.71 [m, 2H each, phen], 2.55 [s, 2H, H<sub>syn</sub>], 1.56 [s, 2H, H<sub>anti</sub>], 0.59 [s, 3H, CH<sub>3</sub> of methallyl], -0.72 [s, 3H, Mo-CH<sub>3</sub>]. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 235.80 [CO], 151.24, 144.20, 135.48, 130.57, 127.48 and 124.16 [phen], 83.32 [C<sup>2</sup> of methallyl], 53.48 [C<sup>1</sup> and C<sup>3</sup> of methallyl], 18.86 [CH<sub>3</sub> of methallyl], 11.15. [Mo-CH<sub>3</sub>]. Anal. Calcd for  $C_{19}H_{18}MoN_2O_2{:}\ C,\ 56.73;\ H,\ 4.51;\ N,\ 6.96.\ Found:\ C,\ 56.81;$ H, 4.49; N, 6.73.

Synthesis of [Mo(C=CPh)( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>(bipy)] (10). To a solution of phenylacetylene (51  $\mu$ L, 0.46 mmol) in THF (10 mL) cooled to 195 K was added "BuLi (0.35 mL of 1.6 M solution in hexane, 0.56 mmol), and the resulting solution of LiC=CPh was transferred via cannula into a solution of 1a (0.10 g, 0.26 mmol) in THF (20 mL). The mixture was allowed to reach room temperature and stirred for 45 min. The

<sup>(25)</sup> IR data of trimethylsilylacetylide complexes have been collected in the Supporting Information of: John, K. D.; Hopkins, M. D. Organometallics 1997, 16, 4948.

<sup>(27)</sup> SAINT + SAX area detector integration program, version 6.02; Bruker AXS, Inc.: Madison, WI, 1999.

<sup>(34)</sup> Spek, A. L. The EUCLID Package. In Computational Crystal*lography*; Sayre, D., Ed.; Clerendon Press: Oxford, 1982; p 528. (35) Nardelli, M. *Comput. Chem* **1983**, *7*, 95.

<sup>(36)</sup> Brisdon, B. J.; Griffin, G. F. J. Chem. Soc., Dalton Trans. 1975, 1999

resulting dark red solution was evaporated in vacuo, and the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and filtered through diatomaceous earth. Pure **10** was obtained by slow diffusion of hexane into a CH<sub>2</sub>Cl<sub>2</sub> solution at 250 K. One of the resulting dark red crystals was used for the X-ray determination. Yield: 0.070 g, 67%. IR (CH<sub>2</sub>Cl<sub>2</sub>): 2077 ( $\nu_{C=C}$ ); 1939, 1852 ( $\nu_{CO}$ ). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 8.72, 8.01, 7.95 and 7.44 [m, 2H each, bipy], 6.97 [m, 3H, C<sub>6</sub>H<sub>5</sub>], 6.77 [m, 2H, C<sub>6</sub>H<sub>5</sub>], 3.30 [m, 1H, CH of  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>], 3.15 [d (6.6), 2H, H<sub>syn</sub>], 1.69 [d (9.7), 2H, H<sub>antl</sub>]. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 229.38 [CO], 154.01, 152.43, 138.06, 137.37, 131.02, 127.94, 125.82, 125.18 and 122.31 [bipy and C<sub>6</sub>H<sub>5</sub>], 78.22 [C<sup>2</sup> of  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>], 56.76 [C<sup>1</sup> and C<sup>3</sup> of  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>]. Anal. Calcd for C<sub>23</sub>H<sub>18</sub>MoN<sub>2</sub>O<sub>2</sub>: C, 61.34; H, 4.03; N, 6.22. Found: C, 61.47; H, 3.92; N, 5.98.

Synthesis of  $[Mo(C \equiv CSiMe_3)(\eta^3 - C_3H_5)(CO)_2(bipy)]$  (11). To a solution of 1a (0.10 g, 0.26 mmol) in THF cooled to 195 K was added a LiC=CSiMe<sub>3</sub> solution prepared in situ by reaction of HC≡CSiMe<sub>3</sub> (74 µL, 0.52 mmol) and <sup>n</sup>BuLi (0.83 mL of a 1.6 M solution in hexane, 0.52 mmol) in THF at 195 K. The mixture was stirred for 1 h, and the workup was as described for 10. Compound 11 was obtained as a red-brown solid. Yield: 0.080 g, 70%. IR (CH<sub>2</sub>Cl<sub>2</sub>): 2015 ( $\nu_{C=C}$ ); 1937, 1850 ( $\nu_{CO}$ ). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 8.64, 8.13, 7.98 and 7.42 [m, 2H each, bipy], 3.42 [m, 1H, CH of  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>], 3.15 [d (6.6), 2H, H<sub>syn</sub>], 1.64 [d (9.9), 2H, H<sub>anti</sub>], -0.38 [s, 9H, Mo-C=CSi(CH<sub>3</sub>)<sub>3</sub>]. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 229.69 [CO], 154.22, 152.33, 137.96, 152.67 and 122.18 [bipy], 161.82 [Mo-C≡C], 117.60 [Mo-C≡C], 78.00  $[C^2 \text{ of } \eta^3 - C_3H_5]$ , 56.71  $[C^1 \text{ and } C^3 \text{ of } \eta^3 - C_3H_5]$ , 1.13  $[Mo-C \equiv CSi-$ (CH<sub>3</sub>)<sub>3</sub>]. Anal. Calcd for C<sub>20</sub>H<sub>22</sub>MoN<sub>2</sub>O<sub>2</sub>Si: C, 53.81; H, 4.97; N, 6.27. Found: C, 54.02; H, 4.95; N, 6.31.

**[W(C=CPh)**( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>(**phen)**] (12). Compound 12 was prepared as described above for 10, from 2 (0.10 g, 0.20 mmol) and LiC=CPh (0.40 mmol). Yield (brown solid): 0.090 g, 78%. IR (CH<sub>2</sub>Cl<sub>2</sub>): 2082 ( $\nu_{C=C}$ ); 1929, 1838 ( $\nu_{CO}$ ). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 9.18, 8.53, 8.00 and 7.81 [m, 2H each, phen], 6.87 [m, 3H, C<sub>6</sub>H<sub>5</sub>], 6.48 [m, 2H, C<sub>6</sub>H<sub>5</sub>], 3.19 [d (6.4), 2H, H<sub>syrl</sub>], 2.34 [m, 1H, CH of  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>], 1.94 [d (9.4), 2H, H<sub>antf</sub>]. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 221.76 [CO], 152.36, 146.52, 137.23, 130.82, 130.63, 127.84, 127.65, 127.51, 125.46 and 125.34 [phen and C<sub>6</sub>H<sub>5</sub>], 139.59 [W-*C*=C], 116.32 [W-C=*C*], 70.60 [C<sup>2</sup> of  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>], 40.81 [C<sup>1</sup> and C<sup>3</sup> of  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>]. Anal. Calcd for C<sub>23</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>W: C, 53.40; H, 3.23; N, 4.98. Found: C, 53.16; H, 3.19; N, 5.04.

**[W(C=CSiMe<sub>3</sub>)**( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>(phen)] (13). Compound 13 was prepared analogously from 2 (0.10 g, 0.20 mmol) and LiC≡ CSiMe<sub>3</sub> (0.40 mmol). Yield: 0.100 g, 85% (red-brown solid). IR (CH<sub>2</sub>Cl<sub>2</sub>): 2027 ( $\nu_{C=C}$ ); 1934, 1850 ( $\nu_{CO}$ ). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 9.08, 8.50, 7.97 and 7.74 [m, 2H each, phen], 3.18 [d (6.6), 2H, H<sub>syn</sub>], 2.43 [m, 1H, CH of  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>], 1.87 [d (9.7), 2H, H<sub>anti</sub>], -0.27 [s, 9H, W-C=CSi(CH<sub>3</sub>)<sub>3</sub>]. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 222.15 [CO], 152.25, 146.80, 137.09, 130.74, 127.49 and 125.32 [phen], 117.98 [W-*C*=C], 93.34 [W-C=*C*], 70.28 [C<sup>2</sup> of  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>], 48.67 [C<sup>1</sup> and C<sup>3</sup> of  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>], 1.18 [W-C≡CSi(*C*H<sub>3</sub>)<sub>3</sub>]. Anal. Calcd for C<sub>22</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub>SiW: C, 47.32; H, 3.97; N, 5.02. Found: C, 47.61; H, 4.07; N, 4.96.

 $[Mo(C \equiv CH)(\eta^3 - C_3H_5)(CO)_2(bipy)]$  (14a). To a suspension of 0.30 g (large excess) of NaC=CH (previously washed with hexane from the mineral oil accompanying the commercial product) in THF was added a solution of  $[MoCl(\eta^3-C_3H_5)(CO)_2-$ (bipy)] (1a) (0.10 g, 0.26 mmol) in THF. The mixture was stirred for 3 h, and then the volatiles were removed in vacuo. The residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (30 mL) and filtered through diatomaceous earth, and the resulting solution was concentrated by in vacuo evaporation to a volume of 10 mL. Addition of hexane (30 mL) caused the precipitation of 14a as a red microcrystalline solid, which was dried under reduced pressure. Yield: 0.060 g, 66%. IR (CH<sub>2</sub>Cl<sub>2</sub>): 1933 (v<sub>C=C</sub>); 1947, 1855 (v<sub>CO</sub>). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 8.82, 8.14, 7.99 and 7.52 [m, 2H each, bipy], 3.19 [d (6.7), 2H,  $H_{syn}$ ], 3.06 [m, 1H, CH of  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>], 2.12 [s, 1H, Mo-C=CH], 1.64 [d (9.6), 2H, H<sub>anti</sub>]. <sup>13</sup>C-{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 228.79 [CO], 152.16, 137.23, 130.29, 127.47 and 124.83 [bipy], 100.61 [Mo-C≡C], 79.92 [Mo-C≡C], 77.06 [C<sup>2</sup> of  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>], 56.45 [C<sup>1</sup> and C<sup>3</sup> of  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>]. Anal. Calcd for C<sub>17</sub>H<sub>14</sub>MoN<sub>2</sub>O<sub>2</sub>: C, 54.56; H, 3.77; N, 7.48. Found: C, 54.49; H, 3.81; N, 7.46. 14b and 15 were prepared analogously.

**[W(C=CH)**( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>(**phen**)] (15). 15 was prepared from [WCl( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)(CO)<sub>2</sub>(**phen**)] (2) (0.10 g, 0.20 mmol) and NaC=CH. Yield: 0.08 g, 86% (dark red solid). IR (CH<sub>2</sub>Cl<sub>2</sub>): 1929 ( $\nu_{C=C}$ ); 1950, 1841 ( $\nu_{CO}$ ). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 9.12, 8.52, 7.99 and 7.79 [m, 2H each, phen], 3.10 [d (6.3), 2H, H<sub>syn</sub>], 2.12 [s, 1H, W-C=C*H*], 2.02 [m, 1H, CH of  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>], 1.88 [d (9.1), 2H, H<sub>anti</sub>]. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): 221.42 [CO], 152.35, 146.35, 137.27, 130.69, 127.72 and 125.53 [phen], 131.38 [Mo-*C*=C], 102.17 [Mo-C=*C*], 70.39 [C<sup>2</sup> of  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>], 40.47 [C<sup>1</sup> and C<sup>3</sup> of  $\eta^3$ -C<sub>3</sub>H<sub>5</sub>]. Anal. Calcd for C<sub>19</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>W: C, 46.94; H, 2.90; N, 5.76. Found: C, 46.96; H, 2.97; N, 5.68.

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**Supporting Information Available:** Complete details for the synthesis of alkylating reagents, complexes 1-5,  $[MoI(\eta^3-C_3H_5)(CO)_2(phen)]$ , and  $[Mo(C=CH)(\eta^3-C_3H_5)(CO)_2(phen)]$  (**14b**), and tables giving positional and thermal parameters and bond distances and angles for **9** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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