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

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Received August 27, 2001

The reactions of [MoCl(η^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)(η^3-allyl)$(CO)_2$(N−N)] (**3**−**9**), which have the alkyl and allyl groups in trans positions. Related alkynyls [M(C≡CR)(η^3-allyl)$(CO)_2$(N−N)] with R = Ph, $SiMe_3$, H (**10**−**15**) were obtained similarly employing alkaline acetylides.

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Published on March 16, 2002 on http://pubs.acs.org | doi: 10.1021/om0107800

Introduction

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

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.[3] 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 η^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.[4]

For [MoX(η^3-allyl)$(CO)_2$(L−L)] (X = anionic ligand, L−L = neutral chelate) compounds, the allyl group is a potential target of the alkylation,[5] and this reaction has an added interest since molybdenum carbonyl complexes catalyze the alkylation of allylic electrophiles.[6] This is believed to occur by oxidative addition to an electron-rich zerovalent species to give a Mo(II) η^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.[7]

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

Results and Discussion

The reaction of [MoCl(η^3-C_3H_5)$(CO)_2$(bipy)][10] (**1a**) with $MgMe_2$ in THF afforded the methyl complex [Mo(CH_3)(η^3-C_3H_5)$(CO)_2$(bipy)] (**3a**). Its spectroscopic data include two similarly intense bands at wavenumbers lower than in **1a**, indicating the persistence of a *cis*-Mo$(CO)_2$ unit,

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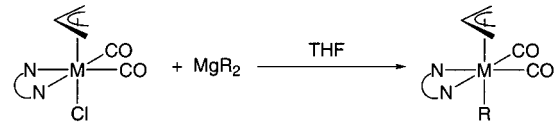
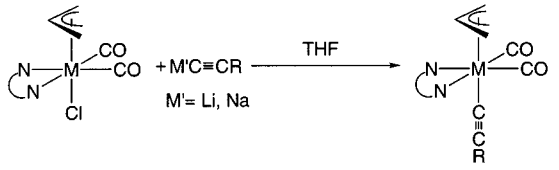
Scheme 1



	M	N-N
1a	Mo	bipy
1b	Mo	phen
2	W	phen

	R	M	N-N
3a	CH_3	Mo	bipy
3b	CH_3	Mo	phen
4a	CH_2CH_3	Mo	bipy
4b	CH_2CH_3	Mo	phen
5a	$CH_2C_6H_5$	Mo	bipy
5b	$CH_2C_6H_5$	Mo	phen
6	CH_3	W	phen
7	CH_2CH_3	W	phen
8	$CH_2C_6H_5$	W	phen

Scheme 2



	M	N-N
1a	Mo	bipy
1b	Mo	phen
2	W	phen

	R	M	N-N
10	C_6H_5	Mo	bipy
11	$SiMe_3$	Mo	bipy
12	C_6H_5	W	phen
13	$SiMe_3$	W	phen
14a	H	Mo	bipy
14b	H	Mo	phen
15	H	W	phen

a low-frequency ^{1}H NMR singlet, typical of a metal-bound methyl group, and a pattern of two doublets and one multiplet in ^{1}H NMR, diagnostic of a static (without fast equilibration to η^1) η^3-C_3H_5 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,[11] is consistent with the existence of a mirror plane, and therefore, the structure depicted in Scheme 1 can be assigned to **3a**.

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 ^{13}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)(η^3-allyl)$(CO)_2L_2$] derivatives and add to the very few examples of alkyl carbonyl molybdenum and tungsten complexes without cyclopentadienyl ligands.[12] The lower ν_{CO} values for the tungsten complexes reflect the more electron-rich nature of the third-row metal.[12a]

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 β-elimination can be attributed to the lack of facile dissociation processes in these electron-precise compounds.[13] As a result of this saturation, the new alkyls do not react with nucleophiles.[14] 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,[15] 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)(η^3-allyl)$(CO)_2$(N−N)] (X = OTf, SPh) complexes and the alkane. This selectivity is remarkable, since the allyl protonation of Mo(η^3-allyl) complexes has been used to generate a vacant coordination site.[16]

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_2Cl_2, but they were found to consist of Mo−CH_3 and Mo−Cl mixtures.[17−19]

We found that [Mo(CH_3)(η^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(η^3-allyl)-$(CO)_2$(N−N)] complexes,[1] 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,[20] resulting in C_s symmetry.

(11) In complexes [MoX(η^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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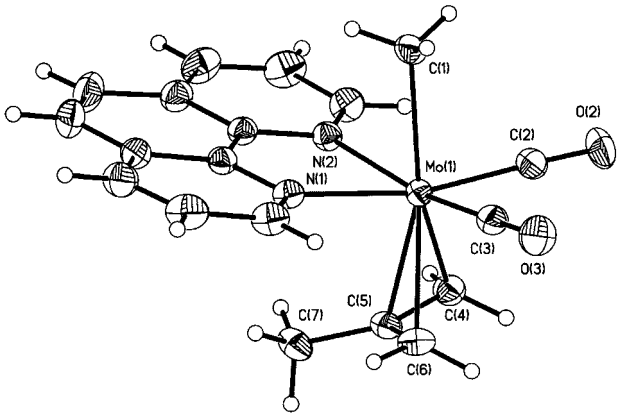

Figure 1. Molecular structure and numbering scheme of **9**. Selected bond lengths (Å) and angles (deg): Mo(1)−C(1) 2.339(3); C(2)−Mo(1)−C(1) 88.31(11), C(3)−Mo(1)−C(1) 87.87(9); N(1)−Mo(1)−C(1) 79.18(9); N(2)−Mo(1)−C(1) 75.95(8).

Table 1. Crystal Data and Refinement Details for Complexes 9 and 10

	9	**10**
formula	$C_{19}H_{18}MoN_2O_2$	$C_{23}H_{18}MoN_2O_2 \cdot 1/2CH_2Cl_2$
fw	402.29	492.80
cry syst	monoclinic	triclinic
space group	$P2_1/c$	$P1$
a, Å	8.8017(4)	8.673(2)
b, Å	13.2357(6)	10.337(2)
c, Å	15.1162(7)	12.355(3)
α, deg	90	96.58(2)
β, deg	99.669(1)	98.95(2)
γ, deg	90	100.32(2)
V, Å^3	1735.97(14)	1064.8(4)
Z	4	2
T, K	293(2)	293(2)
D_c, g cm^{-3}	1.539	1.537
F(000)	816	498
λ(Mo Kα), Å	0.71073	0.71073
cryst size, mm	0.24 × 0.15 × 0.11	0.23 × 0.17 × 0.10
μ, mm^{-1}	0.768	0.763
scan range, deg	$2.06 \le \theta \le 23.24$	$1.69 \le \theta \le 25.97$
no of reflns measd	10 810	4379
no of ind reflns	2492	4379
no. of data/restraints/params	2492/0/220	4379/3/635
goodness-of-fit on F^2	1.007	1.033
R_1/R_{w2} [$I > 2\sigma(I)$]	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.[21] The Mo−C_{methyl} distance (2.339(3) Å) is one of the longer ones found for mononuclear molybdenum methyl complexes.[22]

We wished to study the reactivity of [MoCl(η^3-allyl)-$(CO)_2$(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.[23]

(20) Curtis, M. D.; Eisenstein, O. *Organometallics* **1984**, *3*, 887.

(21) 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.

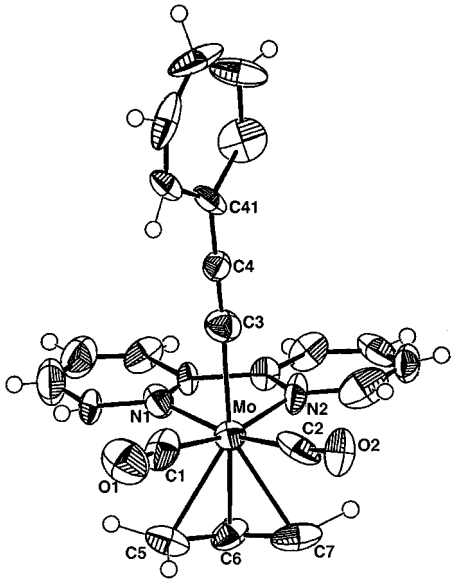

Figure 2. Molecular structure and numbering scheme of **10**. Selected bond lengths (Å) and angles (deg): Mo−C(3) 2.16(2); C(4)−C(41) 1.49(3); C(3)−C(4) 1.20(3); Mo−C(3)−C(4) 169.6(19); C(3)−C(4)−C(41) 174(2).

The reaction of **1a** with lithium phenylacetylide afforded the alkynyl complex [Mo(C≡CPh)(η^3-allyl)-$(CO)_2$(bipy)] (**10**) as the only product. Its IR spectrum displayed two strong ν_{CO} bands and a weak band at 2077 cm^{-1} assigned to the acetylenic C−C stretching.[2,23] The ^{1}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 ^{13}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)°, C(3)−C(4)−C(41) = 174(2)°) are typical of alkynyl complexes.[2b,24]

(22) 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_3 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 91.

(23) Gamasa, M. P.; Gimeno, J.; Zhang, L.; Lanfranchi, M.; Tiripicchio, A. *J. Organomet. Chem.* **1996**, *514*, 287.

(24) For crystallographically characterized molybdenum complexes having terminal alkynyl ligands, see ref 23 and: (a) Buang, N. A.; Hughes, D. L.; Kashef, N.; Richards, R. L.; Pombeiro, A. J. L. *J. Organomet. Chem.* **1987**, *323*, C47. (b) Beddoes, R. L.; Bitcon, C.; Ricalton, A.; Whiteley, M. W. *J. Organomet. Chem.* **1989**, *367*, 85. (c) Pombeiro, A. J. L.; Hills, A.; Hughes, D. L.; Richards, R. L. *J. Organomet. Chem.* **1990**, *398*, C15. (d) Beddoes, R. L.; Bitcon, C.; Whiteley, M. W. *J. Organomet. Chem.* **1991**, *402*, C85. (e) Hills, A.; Hughes, D. L.; Kashef, N.; Lemos, M. A. N. D. A.; Pombeiro, A. J. L.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1992**, 1775. (f) Stoner, T. C.; Geib, S. J.; Hopkins, M. D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 409. (g) Stoner, T. C.; Schaefer, W. P.; Marsh, R. E.; Hopkins, M. D. *J. Cluster Sci.* **1994**, *5*, 107. (h) John, K. D.; Geib, S. J.; Hopkins, M. D. *Organometallics* **1996**, *15*, 4357.

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The complex [Mo(C≡CSiMe$_3$)(η^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^{-1}.[25] The signals of the acetylenic carbons could be observed in ^{13}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.[26]

The ethynyl derivative [Mo(C≡CH)(η^3-allyl)(CO)$_2$-(bipy)] (**14a**) was synthesized by reaction of **1a** with excess sodium acetylide. In addition to the two ν_{CO} bands at 1947 and 1855 cm^{-1}, the IR of **14a** shows an absorption at 1933 cm^{-1}, attributed to the acetylenic C−C stretching. The ethynyl hydrogen occurs at 2.12 ppm in the ^{1}H NMR, and the two acetylenic carbons as weak signals at 100.61 and 79.92 ppm in the ^{13}C NMR. The complex [Mo(C≡CH)(η^3-allyl)(CO)$_2$(phen)] (**14b**) and the tungsten alkynyls [W(C≡CPh)(η^3-allyl)(CO)$_2$-(phen)] (**12**), [W(C≡CSiMe$_3$)(η^3-allyl)(CO)$_2$(phen)] (**13**), and [W(C≡CH)(η^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[27] program. The structure was solved by direct methods with SHELXTL.[28] A semiempirical absorption correction was applied with SADABS.[29] 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.[30] 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.[31] Isotropic least-squares refinement on F^2 was performed using SHELXL97.[32] An empirical absorption correction was applied at this stage, using XABS2.[33] All the H atoms were located by Fourier synthesis. During the final 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.[34] Geometrical calculations were made with PARST.[35]

Synthesis of [W(CH$_3$)(η^3-C$_3$H$_5$)(CO)$_2$(phen)] (6). To a solution of **2**[36] (0.10 g, 0.20 mmol) in THF (20 mL) was added MgMe$_2$ (0.20 mmol, 0.7 mL of a 0.29 M solution in Et$_2$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$_2$Cl$_2$): 1914, 1820 (ν_{CO}). ^{1}H NMR (CD$_2$-Cl$_2$): 9.08, 8.48, 8.01 and 7.75 [m, 2H each, phen], 2.70 [d (5.9), 2H, H$_{syn}$], 2.04 [m, 1H, CH of η^3-C$_3$H$_5$], 1.64 [d (8.3), 2H, H$_{anti}$], −0.83 [s, 3H W-*C*H$_3$]. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 227.97 [CO], 150.97, 144.66, 135.33, 130.22, 127.00 and 124.36 [phen], 65.84 [C^2 of η^3-C$_3$H$_5$], 43.30 [C^1 and C^3 of η^3-C$_3$H$_5$], 14.90 [W-*C*H$_3$]. Anal. Calcd for C$_{18}$H$_{16}$N$_2$O$_2$W: C, 62.08; H, 4.34; N, 6.06. Found: C, 61.78; H, 4.29; N, 6.13.

Synthesis of [W(CH$_2$CH$_3$)(η^3-C$_3$H$_5$)(CO)$_2$(phen)] (7). 7 was obtained from **2** (0.10 g, 0.20 mmol) and MgEt$_2$ (1.14 mL of a 0.21 M solution in Et$_2$O, 0.24 mmol). Yield: 0.057 g, 65% (dark blue solid). IR (CH$_2$Cl$_2$): 1917, 1826 (ν_{CO}). ^{1}H NMR (CD$_2$-Cl$_2$): 9.02, 8.44, 7.97 and 7.74 [m, 2H each, phen], 2.71 [d (6.2), 2H, H$_{syn}$], 2.66 [m, 1H, CH of η^3-C$_3$H$_5$], 1.47 [t (7.8), 3H, W-CH$_2$*C*H$_3$], 1.35 [d (8.2), 2H, H$_{anti}$], −0.34 [q (7.8), 2H, Mo-*C*H$_2$CH$_3$]. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 227.87 [CO], 150.92, 143.36, 136.34, 127.06, 124.97 and 124.01 [phen], 67.63 [C^2 of η^3-C$_3$H$_5$], 45.01 [C^1 and C^3 of η^3-C$_3$H$_5$], 24.41 [Mo-CH$_2$*C*H$_3$], 14.17 [Mo-*C*H$_2$CH$_3$]. Anal. Calcd for C$_{19}$H$_{18}$N$_2$O$_2$W: C, 46.55; H, 3.70; N, 5.71. Found: C, 46.48; H, 3.59; N, 5.81.

Synthesis of [W(CH$_2$C$_6$H$_5$)(η^3-C$_3$H$_5$)(CO)$_2$(phen)] (8). 8 was obtained from **2** (0.10 g, 0.20 mmol) and MgBz$_2$ (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$_2$Cl$_2$): 1917, 1827 (ν_{CO}). ^{1}H NMR (CD$_2$Cl$_2$): 8.96, 8.34, 7.85 and 7.65 [m, 2H each, phen], 6.26 [m, 3H, C$_6$H$_5$], 6.19 [m, 2H, C$_6$H$_5$], 2.72 [d (6.1), 2H, H$_{syn}$], 1.95 [s, 2H, W-C*H*$_2$C$_6$H$_5$], 1.87 [m, 1H, CH of η^3-C$_3$H$_5$], 1.66 [d (8.4), 2H, H$_{anti}$]. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 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$_6$H$_5$], 65.67 [C^2 of η^3-C$_3$H$_5$], 45.10 [C^1 and C^3 of η^3-C$_3$H$_5$], 38.24 [W-*C*H$_2$C$_6$H$_5$]. Anal. Calcd for C$_{24}$H$_{20}$N$_2$O$_2$W: C, 52.19; H, 3.65; N, 5.07. Found: C, 51.93; H, 3.72; N, 5.05.

Synthesis of [Mo(CH$_3$)(η^3-methallyl)(CO)$_2$(phen)] (9). 9 was obtained from **1c**[37] (0.10 g, 0.24 mmol) and MgMe$_2$ (0.9 mL of a 0.29 M solution in Et$_2$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$_2$Cl$_2$): 1921, 1831 (ν_{CO}). ^{1}H NMR (CD$_2$Cl$_2$): 8.91, 8.39, 7.97 and 7.71 [m, 2H each, phen], 2.55 [s, 2H, H$_{syn}$], 1.56 [s, 2H, H$_{anti}$], 0.59 [s, 3H, C*H*$_3$ of methallyl], −0.72 [s, 3H, Mo-C*H*$_3$]. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 235.80 [CO], 151.24, 144.20, 135.48, 130.57, 127.48 and 124.16 [phen], 83.32 [C^2 of methallyl], 53.48 [C^1 and C^3 of methallyl], 18.86 [*C*H$_3$ of methallyl], 11.15. [Mo-*C*H$_3$]. Anal. Calcd for C$_{19}$H$_{18}$MoN$_2$O$_2$: C, 56.73; H, 4.51; N, 6.96. Found: C, 56.81; H, 4.49; N, 6.73.

Synthesis of [Mo(C≡CPh)(η^3-C$_3$H$_5$)(CO)$_2$(bipy)] (10). To a solution of phenylacetylene (51 μL, 0.46 mmol) in THF (10 mL) cooled to 195 K was added ^{n}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

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resulting dark red solution was evaporated in vacuo, and the residue was extracted with CH_2Cl_2 (30 mL) and filtered through diatomaceous earth. Pure **10** was obtained by slow diffusion of hexane into a CH_2Cl_2 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_2Cl_2): 2077 ($\nu_{C\equiv C}$); 1939, 1852 (ν_{CO}). ^{1}H NMR (CD_2Cl_2): 8.72, 8.01, 7.95 and 7.44 [m, 2H each, bipy], 6.97 [m, 3H, C_6H_5], 6.77 [m, 2H, C_6H_5], 3.30 [m, 1H, CH of η^3-C_3H_5], 3.15 [d (6.6), 2H, H_{syn}], 1.69 [d (9.7), 2H, H_{anti}]. ^{13}C{^{1}H} NMR (CD_2Cl_2): 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_6H_5], 78.22 [C^2 of η^3-C_3H_5], 56.76 [C^1 and C^3 of η^3-C_3H_5]. Anal. Calcd for $C_{23}H_{18}MoN_2O_2$: C, 61.34; H, 4.03; N, 6.22. Found: C, 61.47; H, 3.92; N, 5.98.

Synthesis of [Mo(C≡CSiMe$_3$)(η^3-C$_3$H$_5$)(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$_3$ solution prepared in situ by reaction of HC≡CSiMe$_3$ (74 μL, 0.52 mmol) and ^{n}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_2Cl_2): 2015 ($\nu_{C\equiv C}$); 1937, 1850 (ν_{CO}). ^{1}H NMR (CD_2Cl_2): 8.64, 8.13, 7.98 and 7.42 [m, 2H each, bipy], 3.42 [m, 1H, CH of η^3-C_3H_5], 3.15 [d (6.6), 2H, H_{syn}], 1.64 [d (9.9), 2H, H_{anti}], −0.38 [s, 9H, Mo-C≡CSi(CH_3)$_3$]. ^{13}C{^{1}H} NMR (CD_2Cl_2): 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 of η^3-C_3H_5], 56.71 [C^1 and C^3 of η^3-C_3H_5], 1.13 [Mo-C≡CSi-(*C*H$_3$)$_3$]. Anal. Calcd for $C_{20}H_{22}MoN_2O_2Si$: C, 53.81; H, 4.97; N, 6.27. Found: C, 54.02; H, 4.95; N, 6.31.

[W(C≡CPh)(η^3-C$_3$H$_5$)(CO)$_2$(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_2Cl_2): 2082 ($\nu_{C\equiv C}$); 1929, 1838 (ν_{CO}). ^{1}H NMR (CD_2Cl_2): 9.18, 8.53, 8.00 and 7.81 [m, 2H each, phen], 6.87 [m, 3H, C_6H_5], 6.48 [m, 2H, C_6H_5], 3.19 [d (6.4), 2H, H_{syn}], 2.34 [m, 1H, CH of η^3-C_3H_5], 1.94 [d (9.4), 2H, H_{anti}]. ^{13}C{^{1}H} NMR (CD_2Cl_2): 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_6H_5], 139.59 [W-*C*≡C], 116.32 [W-C≡*C*], 70.60 [C^2 of η^3-C_3H_5], 40.81 [C^1 and C^3 of η^3-C_3H_5]. Anal. Calcd for $C_{23}H_{18}N_2O_2W$: C, 53.40; H, 3.23; N, 4.98. Found: C, 53.16; H, 3.19; N, 5.04.

[W(C≡CSiMe$_3$)(η^3-C$_3$H$_5$)(CO)$_2$(phen)] (13). Compound **13** was prepared analogously from **2** (0.10 g, 0.20 mmol) and LiC≡CSiMe$_3$ (0.40 mmol). Yield: 0.100 g, 85% (red-brown solid). IR (CH_2Cl_2): 2027 ($\nu_{C\equiv C}$); 1934, 1850 (ν_{CO}). ^{1}H NMR (CD_2Cl_2): 9.08, 8.50, 7.97 and 7.74 [m, 2H each, phen], 3.18 [d (6.6), 2H, H_{syn}], 2.43 [m, 1H, CH of η^3-C_3H_5], 1.87 [d (9.7), 2H, H_{anti}], −0.27 [s, 9H, W-C≡CSi(CH_3)$_3$]. ^{13}C{^{1}H} NMR (CD_2Cl_2): 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^2 of η^3-C_3H_5], 48.67 [C^1 and C^3 of η^3-C_3H_5], 1.18 [W-C≡CSi(*C*H$_3$)$_3$]. Anal. Calcd for $C_{22}H_{22}N_2O_2SiW$: C, 47.32; H, 3.97; N, 5.02. Found: C, 47.61; H, 4.07; N, 4.96.

[Mo(C≡CH)(η^3-C$_3$H$_5$)(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(η^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_2Cl_2 (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_2Cl_2): 1933 ($\nu_{C\equiv C}$); 1947, 1855 (ν_{CO}). ^{1}H NMR (CD_2Cl_2): 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 η^3-C_3H_5], 2.12 [s, 1H, Mo-C≡C*H*], 1.64 [d (9.6), 2H, H_{anti}]. ^{13}C-{^{1}H} NMR (CD_2Cl_2): 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^2 of η^3-C_3H_5], 56.45 [C^1 and C^3 of η^3-C_3H_5]. Anal. Calcd for $C_{17}H_{14}MoN_2O_2$: 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)(η^3-C$_3$H$_5$)(CO)$_2$(phen)] (15). 15 was prepared from [WCl(η^3-C_3H_5)(CO)$_2$(phen)] (**2**) (0.10 g, 0.20 mmol) and NaC≡CH. Yield: 0.08 g, 86% (dark red solid). IR (CH_2Cl_2): 1929 ($\nu_{C\equiv C}$); 1950, 1841 (ν_{CO}). ^{1}H NMR (CD_2Cl_2): 9.12, 8.52, 7.99 and 7.79 [m, 2H each, phen], 3.10 [d (6.3), 2H, H_{syn}], 2.12 [s, 1H, W-C≡C*H*], 2.02 [m, 1H, CH of η^3-C_3H_5], 1.88 [d (9.1), 2H, H_{anti}]. ^{13}C{^{1}H} NMR (CD_2Cl_2): 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^2 of η^3-C_3H_5], 40.47 [C^1 and C^3 of η^3-C_3H_5]. Anal. Calcd for $C_{19}H_{14}N_2O_2W$: C, 46.94; H, 2.90; N, 5.76. Found: C, 46.96; H, 2.97; N, 5.68.

Acknowledgment. We thank Ministerio de Ciencia y Tecnología (Projects MCT-00-BQU-0220, PB97-0470-C02-01, and CICYT BQU2000-0219) and FICYT (PR-01-GE-7) for financial support and for a predoctoral fellowship (to L.R.). Anonymous reviewers are thanked for criticism.

Supporting Information Available: Complete details for the synthesis of alkylating reagents, complexes **1**−**5**, [MoI(η^3-C_3H_5)(CO)$_2$(phen)], and [Mo(C≡CH)(η^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.

OM0107800

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Published on March 16, 2002 on http://pubs.acs.org | doi: 10.1021/om0107800