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Reactivity of [MCl(η^3-allyl)(1,10-phenanthroline)(CO)$_2$] (M = Mo, W) Complexes toward Enolate Anions

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The reactions of the complexes [MCl(η^3-C_3H_4-R)(CO)$_2$(phen)] (**1a**−**c**; M = Mo, W) with $KCH_2C(O)Ar$ afford the O-bound enolato complexes [M(η^3-C_3H_4-R){OC(=CH_2)Ar}(CO)$_2$(phen)] (**2a**−**d**). On the other hand, the reactions of molybdenum chloro complexes with KCH_2CN yield the complexes [Mo(η^3-C_3H_4-R)(CH_2CN)(CO)$_2$(phen)] (**3a**,**b**), in which the nitrile enolate ligand is C-bound. In addition to the spectroscopic characterization by means of IR and NMR, the structures of [Mo(η^3-C_3H_5){OC(=CH_2)(naphthyl}(CO)$_2$(phen)] (**2c**) and [Mo(η^3-C_3H_4-Me-2)(CH_2CN)(CO)$_2$(phen)] (**3a**) were determined by X-ray diffraction.

Introduction

Transition-metal enolates are intermediates in several catalytic reactions;[1] hence, the synthesis of well-defined examples of this class of complexes and the study of their reactivity has attracted much interest. A growing number of such complexes have been characterized, some of them by X-ray crystallography, and different coordination modes of the enolato ligand have been established, the most common of these being η^1-C or η^1-O.[2−4] With regard to molybdenum(II) and tungsten(II) complexes, which are the ones pertinent to the work described here, Bergman and Heathcock reported the synthesis of enolato complexes containing the {CpM(CO)$_3$} fragment and carried out an extensive study of their reactivity.[5] Gibson reported the structural characterization of the unexpected coordination modes adopted by enolate groups in high-oxidation-state molybdenum complexes.[6] We have recently found that [MoCl(η^3-allyl)(CO)$_2$(N−N)] (N−N = 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen)) complexes react with dialkylmagnesium reagents or with sodium alkoxides to afford the alkyl and alkoxo complexes [Mo(R)(η^3-allyl)(CO)$_2$(N−N)][7] and [Mo(OR)(η^3-allyl)(CO)$_2$(N−N)],[8] respectively; these complexes display interesting reactivity.[8,9] As an extension of this work, we set out to explore the reactivity of enolate anions with [MoCl(η^3-allyl)(CO)$_2$(N−N)] complexes, and we report our findings here.

Results and Discussion

The complex [MoCl(η^3-C_3H_4-Me-2)(CO)$_2$(phen)][10] (**1a**) reacted with a stoichiometric amount of a freshly

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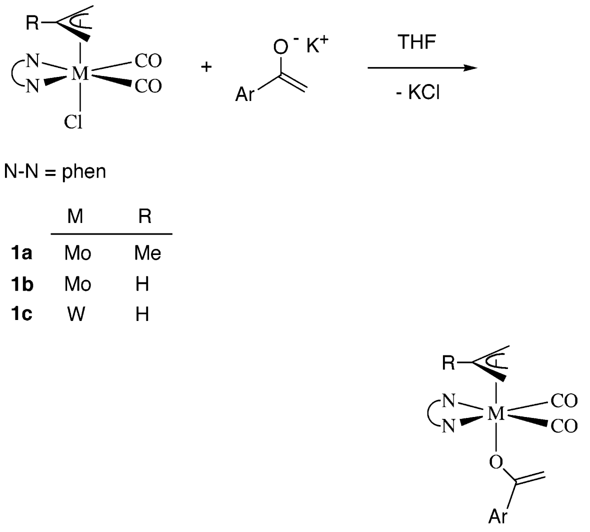
Scheme 1



N-N = phen

	M	R
1a	Mo	Me
1b	Mo	H
1c	W	H

	M	R	Ar
2a	Mo	Me	Ph
2b	Mo	Me	naphthyl
2c	Mo	H	naphthyl
2d	W	H	Ph

prepared solution of the enolate $KCH_2C(O)Ph$ in tetrahydrofuran (THF) to afford the new compound **2a** (see Scheme 1). The reaction was instantaneous, as shown by a change in color (from red to red-brown) and in the IR spectrum, the two similarly intense bands of **1a** at 1950 and 1872 cm^{-1} being replaced by new ones at 1940 and 1857 cm^{-1}, indicating the persistence of a *cis*-Mo$(CO)_2$ unit. The spectroscopic and analytical data of **2a** (which was isolated in good yield as a brick red microcrystalline solid by means of a simple workup procedure, as detailed in the Experimental Section) were consistent with a composition of $[Mo(\eta^3\text{-}C_3H_4\text{-Me-2})\{OC({=}CH_2)Ph\}(CO)_2(phen)]$. The phen and methallyl ^{1}H NMR patterns indicated the presence of a molecular mirror plane and, therefore, the geometry shown in Scheme 1. The fact that **2a** features an intact η^3-methallyl group, in line with our previous findings in the reactions of $[MoCl(\eta^3\text{-allyl})(CO)_2(phen)]$ compounds with MgR_2,[7] NaOR,[8] KN(H)Ar,[11] and NaCN[12] reagents, was not anticipated, since resonance-stabilized carbanions, including enolates, are known to attack the allyl ligand of related pseudooctahedral molybdenum complexes.[13] The coordination of the enolato ligand through its oxygen atom was deduced by the occurrence of two singlets at 4.40 and 4.30 ppm, characteristic of the uncoordinated $H_2C{=}C$ moiety. Coordination of the carbon atoms of the enolato ligand in addition to the oxygen atom, found in several molybdenum complexes,[6,14] is precluded here by the saturated (18 electrons) character of the metal atoms in the products displayed in Scheme 1. The limited solubility of **2a** precluded the acquisition of a significant ^{13}C NMR spectrum. However, H−C coupling constants of 151 and 166 Hz could be measured from the ^{13}C satellites in the ^{1}H NMR spectrum. These values are indicative of sp^2 hybridization for the involved carbon, further confirming the O-bound coordination mode of the enolato ligand.[15] The naphthyl derivative $[Mo(\eta^3\text{-}C_3H_4\text{-Me-2})\{OC({=}CH_2)(naphthyl)\}(CO)_2(phen)]$ (**2b**; its preparation and characterization were similar to those of **2a**) showed an enhanced solubility, and its ^{13}C NMR, which confirms the presence of a molecular mirror plane (a single Mo−CO signal and symmetric phen and methallyl sets of signals), featured singlets at 83.0 and 170.2 ppm, attributed to the $H_2C{=}C$ and C−O−Mo groups, respectively.

To investigate whether the enolate nucleophile did not attack the allyl group because of the presence of the methyl substituent on the allyl central carbon,[16] the reaction of $[MoCl(\eta^3\text{-}C_3H_5)(CO)_2(phen)]$[17] (**1b**) with $KCH_2C(O)(naphthyl)$ was studied. The product was the complex $[Mo(\eta^3\text{-}C_3H_5)\{OC({=}CH_2)(naphthyl)\}(CO)_2(phen)]$ (**2c**), found to be isostructural with **2a**,**b**. The structure of **2c** in the solid state was determined by single-crystal X-ray diffraction, and the result (Figure 1a and Tables 1 and 3) agrees with the solution spectroscopic data and, in particular, confirms the presence of the O-bound enolate. Thus, the distances O(3)−C(6) (1.314(10) Å) and C(6)−C(7) (1.346(12) Å) are consistent with single and double bonds, respectively.[18] The Mo−O distance in **2c** (2.079(6) Å) is slightly longer than in the hydroxo complex $[Mo(OH)(\eta^3\text{-}C_3H_4\text{-Me-2})(CO)_2(phen)]$[19] (2.055(5) Å); the difference can be attributed to the better donor properties of the OH ligand (evidenced by the lower ν(CO) wavenumber values, 1929 and 1843 cm^{-1} in THF, of the hydroxo complex) and its smaller size. For both the $\eta^3\text{-}C_3H_5$ and $\eta^3\text{-}C_3H_4\text{-Me-2}$ ligands, we have failed to detect by ^{1}H NMR the olefins resulting from enolate attack to the allyl group. We have recently observed such products from the coupling between η^3-allyl and alkyl, alkynyl, or enolato (R) ligands in the reaction of $[MoCl(\eta^3\text{-allyl})(CO)_2(dmpm)]$ (dmpm = bis(dimethylphosphino)methane).[20] The difference in reactivity can be attributed to the relative positions of the allyl and R groups: cis in the dmpm complexes and trans, precluding the possibility of coupling, in the phen complexes.

The tungsten complex $[W(\eta^3\text{-}C_3H_5)\{OC({=}CH_2)Ph\}(CO)_2(phen)]$ (**2d**) was synthesized as described above for the molybdenum counterparts by starting from the known precursor $[WCl(\eta^3\text{-}C_3H_5)(CO)_2(phen)]$,[21] and its characterization (see Experimental Section) indicated a similar structure.

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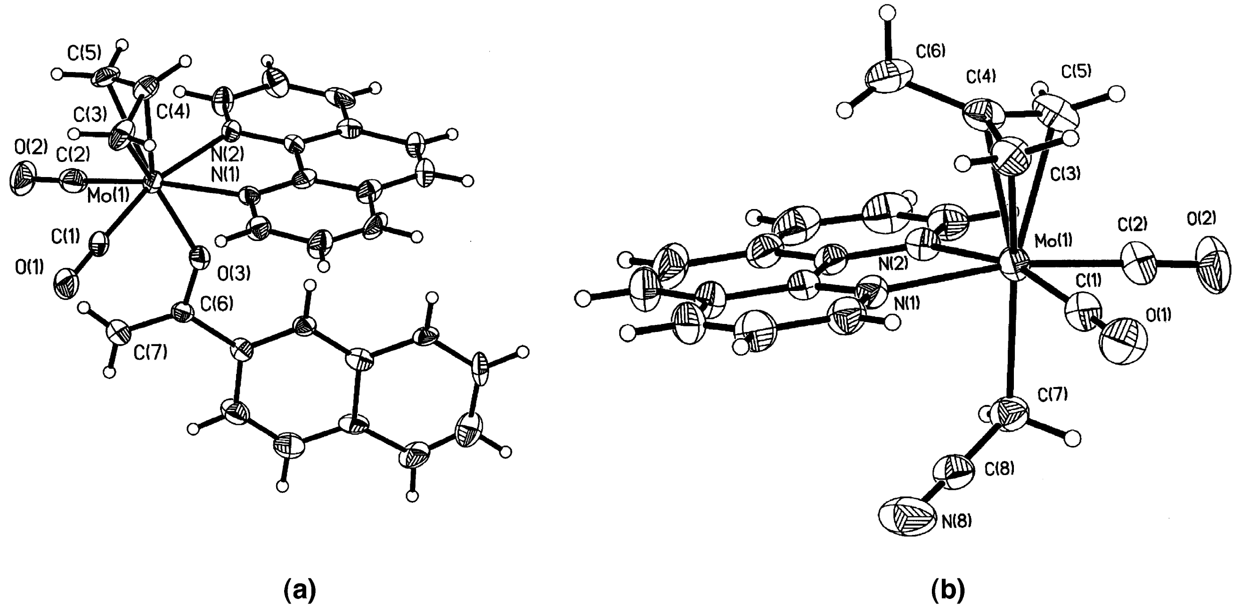

Figure 1. (a) Thermal ellipsoid (30% probability) plots of (a) **2c** and (b) **3a**.

Table 1. Selected Bond Distances and Angles for Complex 2c

Bond Distances (Å)			
Mo(1)−O(3)	2.079(6)	C(6)−C(7)	1.346(12)
O(3)−C(6)	1.314(10)	C(6)−C(31)	1.498(12)
Mo(1)−C(1)	1.924(11)	Mo(1)−C(2)	1.937(13)
Mo(1)−C(4)	2.227(9)	Mo(1)−C(5)	2.333(9)
Mo(1)−N(1)	2.234(7)	Mo(1)−N(2)	2.260(8)
Mo(1)−C(3)	2.326(10)		
Bond Angles (deg)			
C(6)−O(3)−Mo(1)	137.9(6)	C(7)−C(6)−C(31)	124.4(8)
O(3)−C(6)−C(7)	123.9(9)	O(3)−C(6)−C(31)	111.8(7)
C(1)−Mo(1)−O(3)	91.4(3)	C(2)−Mo(1)−O(3)	95.2(4)

There are two important differences between the enolates **2a**−**d** and the previously isolated molybdenum(II) and tungsten(II) enolato complexes: **2a**−**d** can be easily obtained by the reaction of the potassium enolates and the appropriate chloro precursors; in contrast, alkaline enolates were found to be unreactive toward [CpMCl(CO)$_3$] (M = Mo, W) complexes, and enolates of the {CpM(CO)$_3$} fragments were prepared by reaction of 2-chloro ketones with Na[CpM(CO)$_3$] reagents.[5] On the other hand, the enolato ligands in the complexes of the aforementioned cyclopentadienylmetal fragments are C-bound, whereas **2a**−**d** are the only molybdenum(II) and tungsten(II) O-bound enolates.[22] Heating THF solutions of **2a**−**d** at 50 °C for 7 h periods did not cause any changes in the IR spectra, and higher temperatures (65 °C) in THF led only to decomposition. Therefore, the observed O-bound products seem to be the thermodynamically preferred isomers. The preference for the O-bound coordination mode suggests a somewhat hard character of the {Mo(η^3-allyl)(CO)$_2$(phen)} fragment. Indeed, the NCS ligand (a textbook example of an ambident ligand that binds soft metal centers through S and hard metal centers through N) is N-bound in the crystallographically characterized [Mo(η^3-C$_3$H$_4$-Me-2)(NCS)(CO)$_2$(phen)] complexes.[23]

Table 2. Selected Bond Distances and Angles for Complex 3a

Bond Distances (Å)			
Mo(1)−C(7)	2.310(3)	N(8)−C(8)	1.135(4)
C(7)−C(8)	1.394(4)	Mo(1)−C(1)	1.953(3)
Mo(1)−C(2)	1.949(3)	Mo(1)−N(1)	2.225(2)
Mo(1)−N(2)	2.231(2)	Mo(1)−C(4)	2.259(3)
Mo(1)−C(3)	2.308(3)	Mo(1)−C(5)	2.320(3)
Bond Angles (deg)			
C(8)−C(7)−Mo(1)	114.7(2)	N(8)−C(8)−C(7)	177.2(4)
C(1)−Mo(1)−C(7)	86.49(12)	C(2)−Mo(1)−C(7)	84.71(12)

Complex **1a** reacted with a stoichiometric amount of KCH$_2$CN in THF. Within 1 h at room temperature, the IR spectrum of the reaction mixture was found to consist of two strong bands at 1938 and 1857 cm^{-1}, attributed to a new cis-dicarbonyl species, and a weak band at 2187 cm^{-1}, due to the presence of a CN group. Unlike the reactions with ketone enolates described above, it was now possible to observe during the IR monitoring of the reaction the presence of an intermediate displaying two strong ν_{CO} bands at 1912 and 1825 cm^{-1} and a weak band at 2178 cm^{-1} assigned to the keteniminate ligand. The reaction of the allyl complex **1b** with KCH$_2$CN followed an identical course. The final products of these reactions, **3a**,**b**, were isolated as crystalline purple solids and characterized by IR and NMR (^{1}H and ^{13}C) and, in the case of **3a**, also by single-crystal X-ray diffraction (Figure 1b and Tables 2 and 3). The presence of the Mo−CH$_2$CN grouping was indicated by ^{1}H (singlets at 0.62 (**3a**) and 0.71 (**3b**) ppm) and ^{13}C NMR (CH$_2$ and CN carbons at 0.41 and 150.5 ppm, respectively, for **3b**). The X-ray structure confirmed the [Mo(η^3-C$_3$H$_4$-Me-2)(CH$_2$CN)(CO)$_2$(phen)] (**3a**) composition and, in particular, the C-bound coordination of the enolato ligand. The structure of **3a** was found to be similar to that of the

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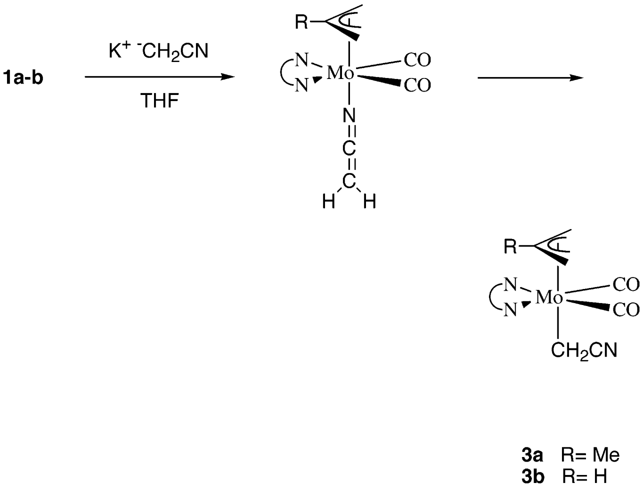
Table 3. Crystal Data and Refinement Details for Complexes 2c and 3a

	2c	**3a**
formula	$C_{30}H_{23}Cl_3MoN_2O_3$	$C_{20}H_{17}MoN_3O_2$
fw	661.79	427.31
cryst syst	orthorhombic	tetragonal
space group	$P2_12_12_1$	$I4_1/2$
a, Å	19.693(4)	21.663(2)
b, Å	10.350(2)	21.663(2)
c, Å	13.524(3)	15.609(2)
V, Å^3	2756(9)	7325.1(15)
Z	4	16
T, K	299(2)	299(2)
D_c, g cm^{-3}	1.595	1.550
$F(000)$	1330	3456
λ(Mo Kα), Å	0.710 73	0.710 73
cryst size, mm	0.10 × 0.13 × 0.21	0.14 × 0.21 × 0.3
μ, mm^{-1}	0.802	0.735
scan range, deg	$1.83 \leq \theta \leq 23.28$	$1.61 \leq \theta \leq 23.30$
no. of rflns measd	12 541	16 193
no. of indep rflns	3957	2642
no. of data/restraints/ params	3957/0/346	2642/0/236
goodness of fit on F^2	1.049	1.022
R1/wR2 ($I > 2\sigma(I)$)	0.0557/0.1541	0.0252/0.0633
R1/wR2 (all data)	0.0777/0.1667	0.0337/0.0673

Scheme 2



complex [Mo(η^3-C_3H_4-Me-2)(CH_3)(CO)$_2$(phen)],[7b] including very similar Mo−C(alkyl) distances (2.310(3) Å (**3a**) and 2.339(3) Å). Given the structures of **3a**,**b**, we propose that the intermediates observed in the reactions leading to their preparation are the N-bound tautomers depicted in Scheme 2.[24] The N-bound coordination mode would account for the relatively low IR ν_{CO} values; thus, the amido complex [Mo(η^3-C_3H_4-Me-2){N(H)(p-tol)}(CO)$_2$(phen)][11] features IR bands at 1926 and 1839 cm^{-1}.

Experimental Section

General conditions were reported elsewhere.[19]

Synthesis of [Mo(η^3-C_3H_4-Me-2){OC(=CH_2)Ph}(CO)$_2$(phen)] (2a). $KN(SiMe_3)_2$ (1 mL of a 0.5 M solution in toluene, 0.50 mmol) was added to a cooled (−78 °C) solution of acetophenone (58 μL, 0.5 mmol) in THF (10 mL). The mixture was stirred for 15 min and then added via cannula onto a solution of **1a** (0.200 g, 0.46 mmol) in THF (10 mL). The mixture was stirred for 30 min. The solvent was evaporated under vacuum, the residue was extracted with CH_2Cl_2 (20 mL), and the solution was filtered through a short column of diatomaceous earth. In vacuo concentration and addition of hexanes (20 mL) caused the precipitation of a brick red microcrystalline solid, which was washed with hexane and dried under vacuum. Yield: 0.180, 75%. Anal. Calcd for $C_{26}H_{22}MoN_2O_3$: C, 61.66; H, 3.37; N, 5.53. Found: C, 61.40; H, 3.54; N, 5.62. IR (THF; cm^{-1}): 1940, 1857 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 9.19 (dd ($J_{H2,3}$ = 3.5 Hz, $J_{H2,4}$ = 1.6 Hz), 2H, $H_{2,9}$), 8.51 (dd ($J_{H4,3}$ = 6.7 Hz, $J_{H4,5}$ = 1.3 Hz), 2H, $H_{4,7}$), 7.99 [s, 2H, $H_{5,6}$), 7.81 (dd, 2H, $H_{3,8}$), 6.71 (m, 5H, Ph), 4.40 (s ($^1J_{CH}$ = 151 Hz), 1H, =CH_2), 4.30 (s ($^1J_{CH}$ = 166 Hz), 1H, =CH_2), 3.13 (s, 2H, H_s), 1.33 (s, 2H, H_a), 0.95 (s, 3H, η^3-C_3H_4(CH_3)-2).

Synthesis of [Mo(η^3-C_3H_4-Me-2){OC(=CH_2)(naphthyl)}(CO)$_2$(phen)] (2b). This compound was prepared as described for **2a**, from **1a** (0.200 g, 0.47 mmol), 2′-acetonaphthone (0.083 g, 0.49 mmol), and $KN(SiMe_3)_2$ (1 mL of a 0.5 M solution in toluene, 0.50 mmol). Yield: 0.170 g, 65%. Anal. Calcd for $C_{30}H_{24}MoN_2O_3$: C, 64.75; H, 4.35; N, 5.03. Found: C, 64.54; H, 4.52; N, 4.92. IR (CH_2Cl_2; cm^{-1}): 1936, 1847 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 9.13 (dd ($J_{H2,3}$ = 3.5 Hz, $J_{H2,4}$ = 1.6 Hz), 2H, $H_{2,9}$), 8.43 (dd ($J_{H4,3}$ = 6.7 Hz, $J_{H4,5}$ = 1.3 Hz), 2H, $H_{4,7}$), 7.93 (s, 2H, $H_{5,6}$), 7.71 (dd, 2H, $H_{3,8}$), 7.39 (m, 6H, naphthyl), 6.55 (s, 1H, naphthyl), 4.63 (s ($^1J_{CH}$ = 160 Hz), 1H, =CH_2), 4.49 (s ($^1J_{CH}$ = 154 Hz), 1H, =CH_2), 3.08 (s, 2H, H_s), 1.29 (s, 2H, H_a), 0.91 (s, 3H, η^3-C_3H_4(CH_3)-2). ^{13}C NMR (CD_2Cl_2): δ 228.75 (s, CO), 170.2 (Mo−OC(CH_2)R), 151.5, 145.7, 138.0, 133.4, 130.5, 130.0, 128.8, 128.7, 128.1, 127.63, 126.9, 126.5, 125.2, 124.9, 124.2, 123.2 (s, phen and naphthyl), 83.2 (s, C^2 of η^3-C_3H_4-CH_3-2), 83.0 (s, =CH$_2$), 54.7 (s, C^1 and C^3 of η^3-C_3H_4-CH_3-2), 20.0 (s, η^3-C_3H_4-CH$_3$-2).

Synthesis of [Mo(η^3-C_3H_5){OC(=CH_2)(naphthyl)}(CO)$_2$(phen)] (2c). This compound was prepared as described for **2a**, from **1b** (0.100 g, 0.24 mmol), acetonaphthone (0.043 g, 0.25 mmol), and $KN(SiMe_3)_2$ (0.25 mmol). By slow diffusion of hexane into a concentrated solution of **2c** in CH_2Cl_2 at −20 °C red crystals were obtained, one of which was used for an X-ray analysis. Yield: 0.09 g, 70%. Anal. Calcd for $C_{29}H_{22}MoN_2O_3$: C, 64.21; H, 4.08; N, 5.16. Found: C, 64.32; H, 4.21; N, 5.31. IR (CH_2Cl_2; cm^{-1}): 1935, 1848 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 9.20 (dd ($J_{H2,3}$ = 3.5 Hz, $J_{H2,4}$ = 1.6 Hz), 2H, $H_{2,9}$), 8.53 (dd ($J_{H4,3}$ = 6.7 Hz, $J_{H4,5}$ = 1.3 Hz), 2H, $H_{4,7}$), 8.02 (s, 2H, $H_{5,6}$), 7.96−7.30 (m, 8H, $H_{3,8}$ of phen and naphthyl), 6.69 (s, 1H, naphthyl), 4.73 (s ($^1J_{CH}$ = 153 Hz), 1H, =CH_2), 4.56 (s ($^1J_{CH}$ = 142 Hz), 1H, =CH_2), 3.34 (d (J_{HH} = 6.3 Hz), 2H, H_s), 3.20 (m, 1H, H_c), 1.33 (d (J_{HH} = 9.1 Hz), 2H, H_a).

Synthesis of [W(η^3-C_3H_5){OC(=CH_2)Ph}(CO)$_2$(phen)] (2d). This compound was prepared as described for **2a**, from **1c** (0.075 g, 0.15 mmol), acetophenone (17 μL, 0.15 mmol), and $KN(SiMe_3)_2$ (0.3 mL of a 0.5 M solution in toluene, 0.15 mmol). Yield: 0.075 mg, 86%. Anal. Calcd for $C_{25}H_{20}N_2O_3W$: C, 51.74; H, 3.47; N, 4.82. Found: C, 51.47; H, 3.21; N, 5.01. IR (CH_2Cl_2; cm^{-1}): 1925, 1831 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 9.22 (m, 2H, $H_{2,9}$), 8.54 (m, 2H, $H_{4,7}$), 7.99 (s, 2H, $H_{5,6}$), 7.95 (m, 2H, $H_{3,8}$), 6.79 (m, 5H, Ph), 4.47 (s ($^1J_{CH}$ = 155 Hz), 1H, =CH_2), 4.32 (s ($^1J_{CH}$ = 157 Hz), 1H, =CH_2), 3.09 (d (J_{HH} = 6.2 Hz), 2H, H_s), 2.28 (m, 1H, H_c), 1.50 (d (J_{HH} = 9.1 Hz), 2H, H_a).

Synthesis of [Mo(η^3-C_3H_4-Me-2)(CH_2CN)(CO)$_2$(phen)] (3a). $KN(SiMe_3)_2$ (0.98 mL of a 0.5 M solution in toluene, 0.49 mmol) was added to a cooled (−78 °C) solution of MeCN (26 μL, 0.49 mmol) in THF (10 mL); the mixture was stirred for 15 min and then added via cannula onto a solution of **1a** (0.200 g, 0.46 mmol) in THF (10 mL). After 1 h of stirring, the purple solution was evaporated to dryness, the residue was extracted with CH_2Cl_2 (15 mL), and the extract was filtered through diatomaceous earth and evaporated. By slow diffusion of hexane into a concentrated solution of **3a** in THF purple crystals were obtained, one of which was used for X-ray diffraction. Yield: 0.145 g, 70%. Anal. Calcd for $C_{20}H_{17}MoN_3O_2$: C, 56.21; H, 4.01; N, 9.83. Found: C, 56.02; H, 4.31;

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[24] For recent leading references on C- or N-bound nitrile enolates, see: (a) Naota, T.; Tannna, A.; Kamuro, S.; Murahashi, S.-I. *J. Am. Chem. Soc.* **2002**, *124*, 6842. (b) Culkin, D. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 9330.

N, 9.64. IR (THF; cm^{-1}): 1938, 1857 (ν_{CO}), 2187 (ν_{CN}). ^{1}H NMR (CD_2Cl_2): δ 8.96 (dd ($J_{H2,3} = 3.5$ Hz, $J_{H2,4} = 1.6$ Hz), 2H, $H_{2,9}$), 8.46 (dd ($J_{H4,3} = 6.7$ Hz, $J_{H4,5} = 1.3$ Hz), 2H, $H_{4,7}$), 8.00 (s, 2H, $H_{5,6}$), 7.83 (m, 8H, $H_{3,8}$), 2.76 (s, 2H, H_s), 1.58 (s, 2H, H_a), 0.62 (s, 2H, CH_2CN), 0.57 (s, 3H, η^3-C_3H_4(CH_3)-2). ^{13}C NMR (C_6D_6): δ 230.2 (s, CO), 151.4, 144.8, 135.6, 129.8, 124.2 (s, phen), 81.2 (s, C^2 of η^3-C_3H_4-CH_3-2), 52.4 (s, C^1 and C^3 of η^3-C_3H_4-CH_3-2), 18.49 (s, η^3-C_3H_4-CH$_3$-2), 0.01 (s, CH$_2$CN).

Synthesis of [Mo(η^3-C_3H_5)(CH_2CN)$(CO)_2$(phen)] (3b). This compound was prepared as described for **3a**, from **1b** (0.05 g, 0.12 mmol), MeCN (10 μL, 0.17 mmol), and KN$(SiMe_3)_2$ (0.35 mL, 0.17 mmol). By diffusion of hexane into a concentrated solution of **3b** in THF at −20 °C a purple microcrystalline solid was obtained. Yield: 0.040 g, 80%. Anal. Calcd for $C_{19}H_{15}MoN_3O_2$: C, 55.22; H, 3.66; N, 10.16. Found: C, 55.45; H, 3.51; N, 9.92. IR (THF; cm^{-1}): 1936, 1849 (ν_{CO}), 2183 (ν_{CN}). ^{1}H NMR (CD_2Cl_2): δ 9.02 (dd ($J_{H2,3} = 3.5$ Hz, $J_{H2,4} = 1.6$ Hz), 2H, $H_{2,9}$), 8.50 (dd ($J_{H4,3} = 6.7$ Hz, $J_{H4,5} = 1.3$ Hz), 2H, $H_{4,7}$), 8.01 (s, 2H, $H_{5,6}$), 7.61 (m, 2H, $H_{3,8}$), 3.34 (s br, 2H, H_s), 2.94 (m, 1H, H_c), 1.57 (d ($J_{HH} = 8.4$ Hz), 2H, H_a), 0.71 (s, 2H, CH_2CN). ^{13}C NMR (CD_2Cl_2): δ 230.2 (s, CO), 152.4, 144.7, 137.33, 130.5, 127.6, 125.1 (s, phen), 150.5 (s, CN), 73.1 (s, C^2 of η^3-C_3H_4-CH_3-2), 54.8 (s, C^1 and C^3 of η^3-C_3H_4-CH_3-2), 0.41 (s, CH$_2$CN).

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Supporting Information Available: Text giving a general description of crystal structure determination for compounds **2c** and **3a** and tables giving positional and thermal parameters, bond distances, and bond angles for **2c** and **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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