

# Reactivity of $[\text{MCl}(\eta^3\text{-allyl})(1,10\text{-phenanthroline})(\text{CO})_2]$ ( $\text{M} = \text{Mo}, \text{W}$ ) Complexes toward Enolate Anions

Dolores Morales, M. Elena Navarro Clemente,<sup>†</sup> Julio Pérez,<sup>\*</sup> Lucía Riera, and Víctor Riera

Departamento de Química Orgánica e Inorgánica-IUQOEM, Universidad de Oviedo-CSIC, 33071 Oviedo, Spain

Daniel Miguel

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47071 Valladolid, Spain

Received April 15, 2003

The reactions of the complexes  $[\text{MCl}(\eta^3\text{-C}_3\text{H}_4\text{-R})(\text{CO})_2(\text{phen})]$  (**1a–c**;  $\text{M} = \text{Mo}, \text{W}$ ) with  $\text{KCH}_2\text{C}(\text{O})\text{Ar}$  afford the O-bound enolato complexes  $[\text{M}(\eta^3\text{-C}_3\text{H}_4\text{-R})\{\text{OC}(=\text{CH}_2)\text{Ar}\}(\text{CO})_2(\text{phen})]$  (**2a–d**). On the other hand, the reactions of molybdenum chloro complexes with  $\text{KCH}_2\text{CN}$  yield the complexes  $[\text{Mo}(\eta^3\text{-C}_3\text{H}_4\text{-R})(\text{CH}_2\text{CN})(\text{CO})_2(\text{phen})]$  (**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  $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\{\text{OC}(=\text{CH}_2)(\text{naphthyl})\}(\text{CO})_2(\text{phen})]$  (**2c**) and  $[\text{Mo}(\eta^3\text{-C}_3\text{H}_4\text{-Me-2})(\text{CH}_2\text{CN})(\text{CO})_2(\text{phen})]$  (**3a**) were determined by X-ray diffraction.

## Introduction

Transition-metal enolates are intermediates in several catalytic reactions;<sup>1</sup> 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  $\eta^1\text{-C}$  or  $\eta^1\text{-O}$ .<sup>2–4</sup> 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  $\{\text{CpM-}$

$(\text{CO})_3\}$  fragment and carried out an extensive study of their reactivity.<sup>5</sup> Gibson reported the structural characterization of the unexpected coordination modes adopted by enolate groups in high-oxidation-state molybdenum complexes.<sup>6</sup> We have recently found that  $[\text{MoCl}(\eta^3\text{-allyl})(\text{CO})_2(\text{N-N})]$  ( $\text{N-N} = 2,2'\text{-bipyridine}$  (bipy), 1,10-phenanthroline (phen)) complexes react with dialkylmagnesium reagents or with sodium alkoxides to afford the alkyl and alkoxo complexes  $[\text{Mo}(\text{R})(\eta^3\text{-allyl})(\text{CO})_2(\text{N-N})]$ <sup>7</sup> and  $[\text{Mo}(\text{OR})(\eta^3\text{-allyl})(\text{CO})_2(\text{N-N})]$ ,<sup>8</sup> respectively; these complexes display interesting reactivity.<sup>8,9</sup> As an extension of this work, we set out to explore the reactivity of enolate anions with  $[\text{MoCl}(\eta^3\text{-allyl})(\text{CO})_2(\text{N-N})]$  complexes, and we report our findings here.

## Results and Discussion

The complex  $[\text{MoCl}(\eta^3\text{-C}_3\text{H}_4\text{-Me-2})(\text{CO})_2(\text{phen})]$ <sup>10</sup> (**1a**) reacted with a stoichiometric amount of a freshly

<sup>\*</sup> To whom correspondence should be addressed. E-mail: japm@saaron.quimica.uniovi.es.

<sup>†</sup> Permanent address: ESIQIE-IPN, Edificio 6, 6217 UPALM, Mexico D.F., Mexico.

(1) (a) Trost, B. M.; Verhoeven, T. R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 8, p 838. (b) Tsuji, J. *J. Org. Chem.* **1987**, *52*, 2988. (c) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1624. (d) Hamann, B. C.; Hartwig, J. F. *J. Am. Chem. Soc.* **1997**, *119*, 12382. (e) Krüger, J.; Carreira, E. M. *J. Am. Chem. Soc.* **1998**, *120*, 837. (f) Sim, W.-S.; Li, T.-C.; Yang, P.-X.; Yeo, B.-S. *J. Am. Chem. Soc.* **2002**, *124*, 4970.

(2) For leading examples of a O-bound enolates see the following. Ru: (a) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *Organometallics* **1991**, *10*, 3326. (b) Hartwig, J. F.; Bergman, R. G.; Andersen, R. A. *Organometallics* **1991**, *10*, 3344. (c) Pd: Andrieu, J.; Braunstein, P.; Naud, F.; Adams, R. D. *J. Organomet. Chem.* **2000**, *601*, 43. (d) Ti(IV): Agapie, T.; Diaconescu, P. L.; Mindiola, D. J.; Cummins, C. C. *Organometallics* **2002**, *21*, 1329. (e) Ni: Cámpora, J.; Maya, C. M.; Palma, P.; Carmona, E.; Gutiérrez-Puebla, E.; Ruiz, C. *J. Am. Chem. Soc.* **2003**, *125*, 1482. (f) Cámpora, J.; Maya, C. M.; Palma, P.; Carmona, E.; Graiff, C.; Tiripicchio, A. *Chem. Commun.* **2003**, 1742.

(3) For examples of C-bound enolates see ref 2a,b,e and the following. (a) Ni compounds: Burkhardt, E. R.; Bergman, R. G.; Heathcock, C. H. *Organometallics* **1990**, *9*, 30. Pd compounds: ref 3a and (b) Veya, P.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1993**, *12*, 4899. (c) Vicente, J.; Abad, J. A.; Chicote, M.-T.; Abrisqueta, M.-D.; Lorca, J.-A.; Ramírez de Arellano, M. C. *Organometallics* **1998**, *17*, 1564. (d) Bouchra, E. M.; Hani, E.; Vaissermann, J.; Jaouen, G. *Organometallics* **1995**, *14*, 3296. Pt compounds: (e) Matsumoto, K.; Ochiai, M. *Coord. Chem. Rev.* **2002**, *231*, 229.

(4) For transition-metal complexes with enolato ligands in other coordination modes see: (a) Murahashi, T.; Kurosawa, H. *J. Organomet. Chem.* **1999**, *574*, 142. (b) Ruiz, J.; Rodríguez, V.; Cutillas, N.; Pardo, M.; Pérez, J.; López, G.; Chaloner, P.; Hitchcock, P. B. *Organometallics* **2001**, *20*, 1973. (c) Vicente, J.; Arcas, A.; Fernández-Hernández, J. M.; Bautista, D. *Organometallics* **2001**, *20*, 2767.

(5) (a) Doney, J. J.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1985**, *107*, 3724. (b) Burkhardt, E. R.; Doney, J. J.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1987**, *109*, 2022.

(6) Cameron, P. A.; Britovsek, G. J. P.; Gibson, V. C.; Williams, D. J.; White, A. J. P. *Chem. Commun.* **1998**, 737.

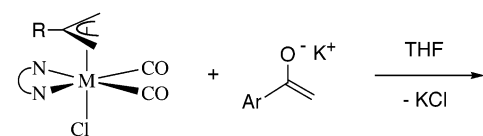
(7) (a) Pérez, J.; Riera, L.; Riera, V.; García-Granda, S.; García-Rodríguez, E. *J. Am. Chem. Soc.* **2001**, *123*, 7469. (b) Pérez, J.; Riera, L.; Riera, V.; García-Granda, S.; García-Rodríguez, E.; Miguel, D. *Organometallics* **2002**, *21*, 1622.

(8) Hevia, E.; Pérez, J.; Riera, L.; Riera, V.; Miguel, D. *Organometallics* **2002**, *21*, 1750.

(9) (a) Reactivity of alkyl complexes: Pérez, J.; Riera, L.; Riera, V.; García-Granda, S.; García-Rodríguez, E.; Miguel, D. *Chem. Commun.* **2002**, 384. (b) Reactivity of alkoxo complexes: Hevia, E.; Pérez, J.; Riera, L.; Riera, V.; del Río, I.; García-Granda, S.; Miguel, D. *Chem. Eur. J.* **2002**, *8*, 4510.

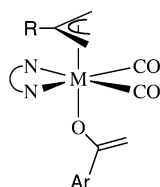
(10) Powell, P. J. *J. Organomet. Chem.* **1977**, *129*, 175.

Scheme 1



N-N = phen

	M	R
<b>1a</b>	Mo	Me
<b>1b</b>	Mo	H
<b>1c</b>	W	H



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

prepared solution of the enolate  $\text{KCH}_2\text{C}(\text{O})\text{Ph}$  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  $1872\text{ cm}^{-1}$  being replaced by new ones at 1940 and  $1857\text{ cm}^{-1}$ , indicating the persistence of a *cis*-Mo(CO)<sub>2</sub> 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  $[\text{Mo}(\eta^3\text{-C}_3\text{H}_4\text{-Me-2})\{\text{OC}(\text{=CH}_2)\text{-Ph}\}(\text{CO})_2(\text{phen})]$ . The phen and methallyl  $^1\text{H}$  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  $\eta^3$ -methallyl group, in line with our previous findings in the reactions of  $[\text{MoCl}(\eta^3\text{-allyl})(\text{CO})_2(\text{phen})]$  compounds with  $\text{MgR}_2$ ,<sup>7</sup>  $\text{NaOR}$ ,<sup>8</sup>  $\text{KN}(\text{H})\text{Ar}$ ,<sup>11</sup> and  $\text{NaCN}$ <sup>12</sup> reagents, was not anticipated, since resonance-stabilized carbanions, including enolates, are known to attack the allyl ligand of related pseudooctahedral molybdenum complexes.<sup>13</sup> 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  $\text{H}_2\text{C}=\text{C}$  moiety. Coordination of the carbon atoms of the enolato ligand in addition to the oxygen atom, found in several molybdenum complexes,<sup>6,14</sup> 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  $^{13}\text{C}$  NMR spectrum. However, H–C coupling constants of 151 and 166 Hz could be measured from the  $^{13}\text{C}$  satellites in the  $^1\text{H}$  NMR spectrum. These values are indicative of  $\text{sp}^2$  hybridization for the involved carbon, further confirming the O-bound coordination mode of the enolato ligand.<sup>15</sup> The naphthyl derivative  $[\text{Mo}(\eta^3\text{-C}_3\text{H}_4\text{-Me-2})\{\text{OC}(\text{=CH}_2)\text{-(naphthyl)}\}(\text{CO})_2(\text{phen})]$  (**2b**; its preparation and characterization were similar to those of **2a**) showed an enhanced solubility, and its  $^{13}\text{C}$  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  $\text{H}_2\text{C}=\text{C}$  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,<sup>16</sup> the reaction of  $[\text{MoCl}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{phen})]$ <sup>17</sup> (**1b**) with  $\text{KCH}_2\text{C}(\text{O})(\text{naphthyl})$  was studied. The product was the complex  $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)\{\text{OC}(\text{=CH}_2)(\text{naphthyl})\}(\text{CO})_2(\text{phen})]$  (**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) ( $1.314(10)\text{ \AA}$ ) and C(6)–C(7) ( $1.346(12)\text{ \AA}$ ) are consistent with single and double bonds, respectively.<sup>18</sup> The Mo–O distance in **2c** ( $2.079(6)\text{ \AA}$ ) is slightly longer than in the hydroxo complex  $[\text{Mo}(\text{OH})(\eta^3\text{-C}_3\text{H}_4\text{-Me-2})(\text{CO})_2(\text{phen})]$ <sup>19</sup> ( $2.055(5)\text{ \AA}$ ); the difference can be attributed to the better donor properties of the OH ligand (evidenced by the lower  $\nu(\text{CO})$  wavenumber values, 1929 and  $1843\text{ cm}^{-1}$  in THF, of the hydroxo complex) and its smaller size. For both the  $\eta^3\text{-C}_3\text{H}_5$  and  $\eta^3\text{-C}_3\text{H}_4\text{-Me-2}$  ligands, we have failed to detect by  $^1\text{H}$  NMR the olefins resulting from enolate attack to the allyl group. We have recently observed such products from the coupling between  $\eta^3$ -allyl and alkyl, alkynyl, or enolato (R) ligands in the reaction of  $[\text{MoCl}(\eta^3\text{-allyl})(\text{CO})_2(\text{dmpm})]$  (dmpm = bis(dimethylphosphino)methane).<sup>20</sup> 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  $[\text{W}(\eta^3\text{-C}_3\text{H}_5)\{\text{OC}(\text{=CH}_2)\text{Ph}\}(\text{CO})_2(\text{phen})]$  (**2d**) was synthesized as described above for the molybdenum counterparts by starting from the known precursor  $[\text{WCl}(\eta^3\text{-C}_3\text{H}_5)(\text{CO})_2(\text{phen})]$ ,<sup>21</sup> and its characterization (see Experimental Section) indicated a similar structure.

(14)  $\eta^2(\text{C},\text{O})$ -enolate molybdenum complexes have been obtained by Templeton by deprotonation of  $\eta^2$ -acyls: Rusik, C. A.; Collins, M. A.; Gamble, A. S.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 2550.

(15) An anonymous reviewer is thanked for this suggestion.

(16) Borgmann, C.; Limberg, C.; Kaifer, E.; Pritzkow, H.; Zsolnai, L. *J. Organomet. Chem.* **1999**, *580*, 214.

(17) tom Dieck, H.; Friedel, H. *J. Organomet. Chem.* **1968**, *14*, 375.

(18) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Robin, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1–S19.

(19) Morales, D.; Navarro Clemente, M. E.; Pérez, J.; Riera, L.; Riera, V.; Miguel, D. *Organometallics* **2002**, *21*, 4934.

(20) Pérez, J.; Riera, V.; Rodríguez, A.; García-Granda, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1427.

(21) Brisdon, B. J.; Griffin, G. F. *J. Chem. Soc., Dalton Trans.* **1975**, 1999.

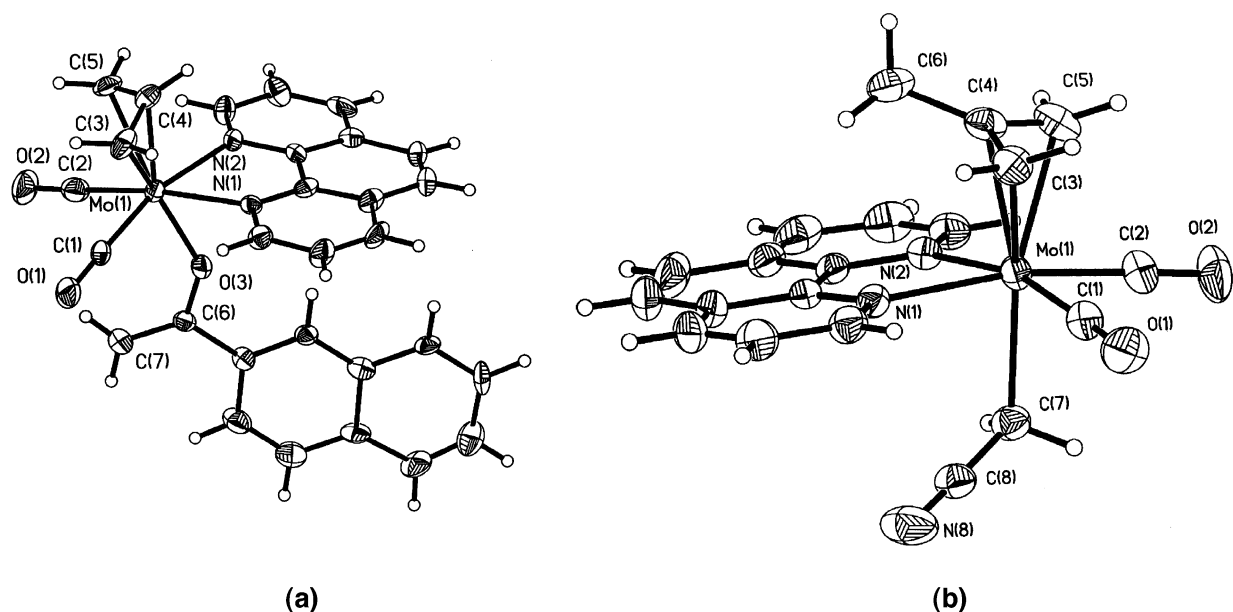
(11) Morales, D.; Pérez, J.; Riera, L.; Riera, V.; Miguel, D. *Inorg. Chem.* **2002**, *41*, 4111.

(12) Hevia, E.; Pérez, J.; Riera, L.; Riera, V.; García-Granda, S.; García-Rodríguez, E.; Miguel, D. *Eur. J. Inorg. Chem.* **2003**, 1113.

(13) (a) Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1982**, *104*, 5543.

(b) Trost, B. M.; Merlic, C. A. *J. Am. Chem. Soc.* **1990**, *112*, 9590.

(c) For enolate attack at the  $\eta^3$ -allyl ligand of other Mo(II) compounds see: VanArsdale, W. E.; Winter, R. E. K.; Kochi, J. K. *Organometallics* **1986**, *5*, 645.

**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  $[\text{CpM}(\text{CO})_3]$  ( $\text{M} = \text{Mo}, \text{W}$ ) complexes, and enolates of the  $\{\text{CpM}(\text{CO})_3\}$  fragments were prepared by reaction of 2-chloro ketones with  $\text{Na}[\text{CpM}(\text{CO})_3]$  reagents.<sup>5</sup> 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.<sup>22</sup> 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  $\{\text{Mo}(\eta^3\text{-allyl})(\text{CO})_2(\text{phen})\}$  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  $[\text{Mo}(\eta^3\text{-C}_3\text{H}_4\text{-Me-2})\text{-(NCS)}(\text{CO})_2(\text{phen})]$  complexes.<sup>23</sup>

Complex **1a** reacted with a stoichiometric amount of  $\text{KCH}_2\text{CN}$  in THF. Within 1 h at room temperature, the IR spectrum of the reaction mixture was found to consist

**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)

of two strong bands at 1938 and 1857  $\text{cm}^{-1}$ , attributed to a new cis-dicarbonyl species, and a weak band at 2187  $\text{cm}^{-1}$ , 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  $\nu_{\text{CO}}$  bands at 1912 and 1825  $\text{cm}^{-1}$  and a weak band at 2178  $\text{cm}^{-1}$  assigned to the ketenimine ligand. The reaction of the allyl complex **1b** with  $\text{KCH}_2\text{CN}$  followed an identical course. The final products of these reactions, **3a,b**, were isolated as crystalline purple solids and characterized by IR and NMR ( $^1\text{H}$  and  $^{13}\text{C}$ ) and, in the case of **3a**, also by single-crystal X-ray diffraction (Figure 1b and Tables 2 and 3). The presence of the  $\text{Mo}-\text{CH}_2\text{CN}$  grouping was indicated by  $^1\text{H}$  (singlets at 0.62 (**3a**) and 0.71 (**3b**) ppm) and  $^{13}\text{C}$  NMR ( $\text{CH}_2$  and CN carbons at 0.41 and 150.5 ppm, respectively, for **3b**). The X-ray structure confirmed the  $[\text{Mo}(\eta^3\text{-C}_3\text{H}_4\text{-Me-2})\text{-(CH}_2\text{CN)}(\text{CO})_2(\text{phen})]$  (**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

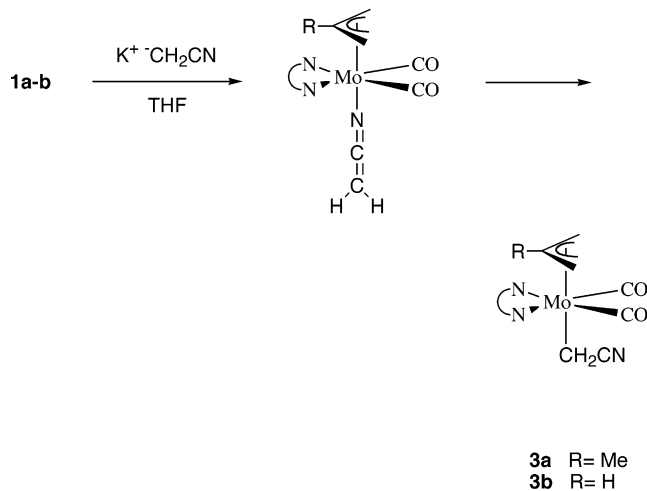
(22) See ref 14 and the following. (a) An O-bound enolate has been recently found as part of a chelate ligand in a molybdenum complex: Andrews, C. D.; Burrows, A. D.; Jeffery, J. C.; Lynam, J. M.; Mahon, M. F. *J. Organomet. Chem.* **2003**, 665, 15. (b) A nondetected molybdenum(II) O-bound enolato complex has been proposed to occur as an intermediate: Hirao, T.; Fujihara, Y.; Tsuno, S.; Ohshiro, Y.; Agawa, T. *Chem. Lett.* **1984**, 367.

(23) Graham, A. J.; Fenn, R. H. *J. Organomet. Chem.* **1970**, 25, 173. The bipy analogue is isostructural: Graham, A. J.; Fenn, R. H. *J. Organomet. Chem.* **1969**, 17, 405.



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

	2c	3a
formula	C <sub>30</sub> H <sub>23</sub> Cl <sub>3</sub> MoN <sub>2</sub> O <sub>3</sub>	C <sub>20</sub> H <sub>17</sub> MoN <sub>3</sub> O <sub>2</sub>
fw	661.79	427.31
cryst syst	orthorhombic	tetragonal
space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>I</i> 4 <sub>1</sub> /2
<i>a</i> , Å	19.693(4)	21.663(2)
<i>b</i> , Å	10.350(2)	21.663(2)
<i>c</i> , Å	13.524(3)	15.609(2)
<i>V</i> , Å <sup>3</sup>	2756(9)	7325.1(15)
<i>Z</i>	4	16
<i>T</i> , K	299(2)	299(2)
<i>D<sub>c</sub></i> , g cm <sup>-3</sup>	1.595	1.550
<i>F</i> (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 <sup>-1</sup>	0.802	0.735
scan range, deg	1.83 ≤ θ ≤ 23.28	1.61 ≤ θ ≤ 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 <i>F</i> <sup>2</sup>	1.049	1.022
R1/wR2 ( <i>I</i> > 2σ( <i>I</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( $\eta^3$ -C<sub>3</sub>H<sub>4</sub>-Me-2)(CH<sub>3</sub>)(CO)<sub>2</sub>(phen)],<sup>7b</sup> 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.<sup>24</sup> The N-bound coordination mode would account for the relatively low IR  $\nu_{\text{CO}}$  values; thus, the amido complex [Mo( $\eta^3$ -C<sub>3</sub>H<sub>4</sub>-Me-2){N(H)(*p*-tol)}-(CO)<sub>2</sub>(phen)]<sup>11</sup> features IR bands at 1926 and 1839 cm<sup>-1</sup>.

## Experimental Section

General conditions were reported elsewhere.<sup>19</sup>

**Synthesis of [Mo( $\eta^3$ -C<sub>3</sub>H<sub>4</sub>-Me-2){OC(=CH<sub>2</sub>)Ph}(CO)<sub>2</sub>(phen)] (**2a**).** KN(SiMe<sub>3</sub>)<sub>2</sub> (1 mL of a 0.5 M solution in toluene, 0.50 mmol) was added to a cooled (–78 °C) solution of acetophenone (58  $\mu$ L, 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<sub>2</sub>Cl<sub>2</sub> (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<sub>26</sub>H<sub>22</sub>MoN<sub>2</sub>O<sub>3</sub>: C, 61.66; H, 3.37; N, 5.53. Found: C, 61.40; H, 3.54; N, 5.62. IR (THF; cm<sup>-1</sup>): 1940, 1857 ( $\nu_{\text{CO}}$ ). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  9.19 (dd ( $J_{\text{H}2,3}$  = 3.5 Hz,  $J_{\text{H}2,4}$  = 1.6 Hz), 2H, H<sub>2,9</sub>), 8.51 (dd ( $J_{\text{H}4,3}$  = 6.7 Hz,  $J_{\text{H}4,5}$  = 1.3 Hz), 2H, H<sub>4,7</sub>), 7.99 [s, 2H, H<sub>5,6</sub>), 7.81 (dd, 2H, H<sub>3,8</sub>), 6.71 (m, 5H, Ph), 4.40 (s ( $^1J_{\text{CH}}$  = 151 Hz), 1H, =CH<sub>2</sub>), 4.30 (s ( $^1J_{\text{CH}}$  = 166 Hz), 1H, =CH<sub>2</sub>), 3.13 (s, 2H, H<sub>s</sub>), 1.33 (s, 2H, H<sub>a</sub>), 0.95 (s, 3H,  $\eta^3$ -C<sub>3</sub>H<sub>4</sub>(CH<sub>3</sub>)-2).

**Synthesis of [Mo( $\eta^3$ -C<sub>3</sub>H<sub>4</sub>-Me-2){OC(=CH<sub>2</sub>)(naphthyl)}-(CO)<sub>2</sub>(phen)] (**2b**).** This compound was prepared as described for **2a**, from **1a** (0.200 g, 0.47 mmol), 2'-acetophenone (0.083 g, 0.49 mmol), and KN(SiMe<sub>3</sub>)<sub>2</sub> (1 mL of a 0.5 M solution in toluene, 0.50 mmol). Yield: 0.170 g, 65%. Anal. Calcd for C<sub>30</sub>H<sub>24</sub>MoN<sub>2</sub>O<sub>3</sub>: C, 64.75; H, 4.35; N, 5.03. Found: C, 64.54; H, 4.52; N, 4.92. IR (CH<sub>2</sub>Cl<sub>2</sub>; cm<sup>-1</sup>): 1936, 1847 ( $\nu_{\text{CO}}$ ). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  9.13 (dd ( $J_{\text{H}2,3}$  = 3.5 Hz,  $J_{\text{H}2,4}$  = 1.6 Hz), 2H, H<sub>2,9</sub>), 8.43 (dd ( $J_{\text{H}4,3}$  = 6.7 Hz,  $J_{\text{H}4,5}$  = 1.3 Hz), 2H, H<sub>4,7</sub>), 7.93 (s, 2H, H<sub>5,6</sub>), 7.71 (dd, 2H, H<sub>3,8</sub>), 7.39 (m, 6H, naphthyl), 6.55 (s, 1H, naphthyl), 4.63 (s ( $^1J_{\text{CH}}$  = 160 Hz), 1H, =CH<sub>2</sub>), 4.49 (s ( $^1J_{\text{CH}}$  = 154 Hz), 1H, =CH<sub>2</sub>), 3.08 (s, 2H, H<sub>s</sub>), 1.29 (s, 2H, H<sub>a</sub>), 0.91 (s, 3H,  $\eta^3$ -C<sub>3</sub>H<sub>4</sub>(CH<sub>3</sub>)-2). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  228.75 (s, CO), 170.2 (Mo–OC(CH<sub>2</sub>)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<sup>2</sup> of  $\eta^3$ -C<sub>3</sub>H<sub>4</sub>-CH<sub>3</sub>-2), 83.0 (s, =CH<sub>2</sub>), 54.7 (s, C<sup>1</sup> and C<sup>3</sup> of  $\eta^3$ -C<sub>3</sub>H<sub>4</sub>-CH<sub>3</sub>-2), 20.0 (s,  $\eta^3$ -C<sub>3</sub>H<sub>4</sub>-CH<sub>3</sub>-2).

**Synthesis of [Mo( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>){OC(=CH<sub>2</sub>)(naphthyl)}-(CO)<sub>2</sub>(phen)] (**2c**).** This compound was prepared as described for **2a**, from **1b** (0.100 g, 0.24 mmol), acetophenone (0.043 g, 0.25 mmol), and KN(SiMe<sub>3</sub>)<sub>2</sub> (0.25 mmol). By slow diffusion of hexane into a concentrated solution of **2c** in CH<sub>2</sub>Cl<sub>2</sub> 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<sub>29</sub>H<sub>22</sub>MoN<sub>2</sub>O<sub>3</sub>: C, 64.21; H, 4.08; N, 5.16. Found: C, 64.32; H, 4.21; N, 5.31. IR (CH<sub>2</sub>Cl<sub>2</sub>; cm<sup>-1</sup>): 1935, 1848 ( $\nu_{\text{CO}}$ ). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  9.20 (dd ( $J_{\text{H}2,3}$  = 3.5 Hz,  $J_{\text{H}2,4}$  = 1.6 Hz), 2H, H<sub>2,9</sub>), 8.53 (dd ( $J_{\text{H}4,3}$  = 6.7 Hz,  $J_{\text{H}4,5}$  = 1.3 Hz), 2H, H<sub>4,7</sub>), 8.02 (s, 2H, H<sub>5,6</sub>), 7.96–7.30 (m, 8H, H<sub>3,8</sub> of phen and naphthyl), 6.69 (s, 1H, naphthyl), 4.73 (s ( $^1J_{\text{CH}}$  = 153 Hz), 1H, =CH<sub>2</sub>), 4.56 (s ( $^1J_{\text{CH}}$  = 142 Hz), 1H, =CH<sub>2</sub>), 3.34 (d ( $J_{\text{HH}}$  = 6.3 Hz), 2H, H<sub>s</sub>), 3.20 (m, 1H, H<sub>d</sub>), 1.33 (d ( $J_{\text{HH}}$  = 9.1 Hz), 2H, H<sub>a</sub>).

**Synthesis of [W( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>){OC(=CH<sub>2</sub>)Ph}(CO)<sub>2</sub>(phen)] (**2d**).** This compound was prepared as described for **2a**, from **1c** (0.075 g, 0.15 mmol), acetophenone (17  $\mu$ L, 0.15 mmol), and KN(SiMe<sub>3</sub>)<sub>2</sub> (0.3 mL of a 0.5 M solution in toluene, 0.15 mmol). Yield: 0.075 mg, 86%. Anal. Calcd for C<sub>25</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>W: C, 51.74; H, 3.47; N, 4.82. Found: C, 51.47; H, 3.21; N, 5.01. IR (CH<sub>2</sub>Cl<sub>2</sub>; cm<sup>-1</sup>): 1925, 1831 ( $\nu_{\text{CO}}$ ). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  9.22 (m, 2H, H<sub>2,9</sub>), 8.54 (m, 2H, H<sub>4,7</sub>), 7.99 (s, 2H, H<sub>5,6</sub>), 7.95 (m, 2H, H<sub>3,8</sub>), 6.79 (m, 5H, Ph), 4.47 (s ( $^1J_{\text{CH}}$  = 155 Hz), 1H, =CH<sub>2</sub>), 4.32 (s ( $^1J_{\text{CH}}$  = 157 Hz), 1H, =CH<sub>2</sub>), 3.09 (d ( $J_{\text{HH}}$  = 6.2 Hz), 2H, H<sub>s</sub>), 2.28 (m, 1H, H<sub>c</sub>), 1.50 (d ( $J_{\text{HH}}$  = 9.1 Hz), 2H, H<sub>a</sub>).

**Synthesis of [Mo( $\eta^3$ -C<sub>3</sub>H<sub>4</sub>-Me-2)(CH<sub>2</sub>CN)(CO)<sub>2</sub>(phen)] (**3a**).** KN(SiMe<sub>3</sub>)<sub>2</sub> (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  $\mu$ L, 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<sub>2</sub>Cl<sub>2</sub> (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<sub>20</sub>H<sub>17</sub>MoN<sub>3</sub>O<sub>2</sub>: C, 56.21; H, 4.01; N, 9.83. Found: C, 56.02; H, 4.31;

(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;  $\text{cm}^{-1}$ ): 1938, 1857 ( $\nu_{\text{CO}}$ ), 2187 ( $\nu_{\text{CN}}$ ).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.96 (dd ( $J_{\text{H}2,3} = 3.5$  Hz,  $J_{\text{H}2,4} = 1.6$  Hz), 2H,  $\text{H}_{2,9}$ ), 8.46 (dd ( $J_{\text{H}4,3} = 6.7$  Hz,  $J_{\text{H}4,5} = 1.3$  Hz), 2H,  $\text{H}_{4,7}$ ), 8.00 (s, 2H,  $\text{H}_{5,6}$ ), 7.83 (m, 8H,  $\text{H}_{3,8}$ ), 2.76 (s, 2H,  $\text{H}_3$ ), 1.58 (s, 2H,  $\text{H}_a$ ), 0.62 (s, 2H,  $\text{CH}_2\text{CN}$ ), 0.57 (s, 3H,  $\eta^3\text{-C}_3\text{H}_4(\text{CH}_3)_2$ ).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  230.2 (s, CO), 151.4, 144.8, 135.6, 129.8, 124.2 (s, phen), 81.2 (s,  $\text{C}^2$  of  $\eta^3\text{-C}_3\text{H}_4\text{-CH}_3\text{-2}$ ), 52.4 (s,  $\text{C}^1$  and  $\text{C}^3$  of  $\eta^3\text{-C}_3\text{H}_4\text{-CH}_3\text{-2}$ ), 18.49 (s,  $\eta^3\text{-C}_3\text{H}_4\text{-CH}_3\text{-2}$ ), 0.01 (s,  $\text{CH}_2\text{CN}$ ).

**Synthesis of  $[\text{Mo}(\eta^3\text{-C}_3\text{H}_5)(\text{CH}_2\text{CN})(\text{CO})_2(\text{phen})]$  (**3b**).** This compound was prepared as described for **3a**, from **1b** (0.05 g, 0.12 mmol), MeCN (10  $\mu\text{L}$ , 0.17 mmol), and  $\text{KN}(\text{SiMe}_3)_2$  (0.35 mL, 0.17 mmol). By diffusion of hexane into a concentrated solution of **3b** in THF at  $-20^\circ\text{C}$  a purple microcrystalline solid was obtained. Yield: 0.040 g, 80%. Anal. Calcd for  $\text{C}_{19}\text{H}_{15}\text{MoN}_3\text{O}_2$ : C, 55.22; H, 3.66; N, 10.16. Found: C, 55.45; H, 3.51; N, 9.92. IR (THF;  $\text{cm}^{-1}$ ): 1936, 1849 ( $\nu_{\text{CO}}$ ), 2183 ( $\nu_{\text{CN}}$ ).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  9.02 (dd ( $J_{\text{H}2,3} = 3.5$  Hz,  $J_{\text{H}2,4} = 1.6$  Hz), 2H,  $\text{H}_{2,9}$ ), 8.50 (dd ( $J_{\text{H}4,3} = 6.7$  Hz,  $J_{\text{H}4,5} = 1.3$  Hz), 2H,  $\text{H}_{4,7}$ ), 8.01 (s, 2H,  $\text{H}_{5,6}$ ), 7.61 (m, 2H,  $\text{H}_{3,8}$ ), 3.34 (s br, 2H,  $\text{H}_3$ ), 2.94 (m, 1H,  $\text{H}_c$ ), 1.57 (d ( $J_{\text{HH}} = 8.4$  Hz), 2H,  $\text{H}_a$ ), 0.71 (s, 2H,  $\text{CH}_2\text{CN}$ ).  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  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,  $\text{C}^2$  of  $\eta^3\text{-C}_3\text{H}_4\text{-CH}_3\text{-2}$ ), 54.8 (s,  $\text{C}^1$  and  $\text{C}^3$  of  $\eta^3\text{-C}_3\text{H}_4\text{-CH}_3\text{-2}$ ), 0.41 (s,  $\text{CH}_2\text{CN}$ ).

**Acknowledgment.** We thank the Ministerio de Ciencia y Tecnología (Grants MCT-00-BQU2000-0220 and BQU2002-03414) and the Principado de Asturias (PR-01-GE-7) for support and predoctoral (L.R.) and postdoctoral (D.M.) scholarships. M.E.N.C. thanks the PCI-AL.E-2002, AECI (Spain) and IPN (Mexico) for a visiting professorship. Dr. A. D. Hopkins (University of Cambridge) is thanked for proofreading the final version of the paper.

**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>.

OM030275Y