

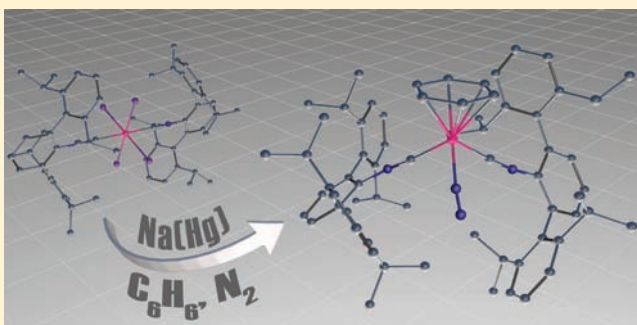
# Oxidative Decarbonylation of *m*-Terphenyl Isocyanide Complexes of Molybdenum and Tungsten: Precursors to Low-Coordinate Isocyanide Complexes

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**S** Supporting Information

**ABSTRACT:** Synthetic studies are presented addressing the oxidative decarbonylation of molybdenum and tungsten complexes supported by the encumbering *m*-terphenyl isocyanide ligand  $\text{CNAr}^{\text{Dipp}^2}$  ( $\text{Ar}^{\text{Dipp}^2} = 2,6-(2,6-(i\text{-Pr})_2\text{C}_6\text{H}_3)_2\text{C}_6\text{H}_3$ ). These studies represent an effort to access halide or pseudohalide  $\text{M}/\text{CNAr}^{\text{Dipp}^2}$  species ( $\text{M} = \text{Mo}, \text{W}$ ) for use as precursors to low-coordinate, low-valent group 6 isocyanide complexes. The synthesis and structural chemistry of the tetra- and tricarbonyl tungsten complexes  $\text{trans-W}(\text{CO})_4(\text{CNAr}^{\text{Dipp}^2})_2$  and  $\text{trans-W}(\text{NCMe})(\text{CO})_3(\text{CNAr}^{\text{Dipp}^2})_2$  are reported. The acetonitrile adducts  $\text{trans-M}(\text{NCMe})(\text{CO})_3(\text{CNAr}^{\text{Dipp}^2})_2$  ( $\text{M} = \text{Mo}, \text{W}$ ) react with  $\text{I}_2$  to form divalent, diiodide complexes in which the extent of decarbonylation differs between Mo and W. In the molybdenum example, the diiodide, dicarbonyl complex  $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}^2})_2$  is generated, which has an  $S = 1$  ground state in solution. Paramagnetic group 6  $\text{MX}_2\text{L}_4$  complexes are rare, and the structure of  $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}^2})_2$  is discussed in relation to other diamagnetic and  $\text{C}_{2v}$ -distorted  $\text{MX}_2\text{L}_4$  complexes. Diiodide  $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}^2})_2$  reacts further with  $\text{I}_2$  to effect complete decarbonylation, producing the paramagnetic tetraiodide complex  $\text{trans-MoI}_4(\text{CNAr}^{\text{Dipp}^2})_2$ . The reactivity of the  $\text{trans-M}(\text{NCMe})(\text{CO})_3(\text{CNAr}^{\text{Dipp}^2})_2$  ( $\text{M} = \text{Mo}, \text{W}$ ) complexes toward benzoyl peroxide is also surveyed, and it is shown that dicarboxylate complexes can be obtained by oxidative or salt-elimination routes. The reduction behavior of the tetraiodide complex  $\text{trans-MoI}_4(\text{CNAr}^{\text{Dipp}^2})_2$  toward Mg metal and sodium amalgam is studied. In benzene solution under  $\text{N}_2$ ,  $\text{trans-MoI}_4(\text{CNAr}^{\text{Dipp}^2})_2$  is reduced by Na/Hg to the  $\eta^6$ -arene-dinitrogen complex,  $(\eta^6\text{-C}_6\text{H}_6)\text{Mo}(\text{N}_2)(\text{CNAr}^{\text{Dipp}^2})_2$ . The diiodide- $\eta^6$ -benzene complex  $(\eta^6\text{-C}_6\text{H}_6)\text{MoI}_2(\text{CNAr}^{\text{Dipp}^2})_2$  is an isolable intermediate in this reduction reaction, and its formation and structure are discussed in context of putative low-coordinate, low-valent molybdenum isocyanide complexes.



## INTRODUCTION

The unsaturated group 6 metal carbonyls, as exemplified by  $[\text{Mo}(\text{CO})_4]$ ,  $[\text{Mo}(\text{CO})_3]$ , and  $[\text{Mo}(\text{CO})_2]$ ,<sup>1,2</sup> serve as the conceptual hallmark for metal-defined coordination geometry.<sup>3–5</sup> Paradoxically, the properties that render these species so intriguing have also prevented systematic surveys of their reactivity patterns. Thus, the high inherent reactivity of the unsaturated group 6 carbonyls, as derived from the juxtaposition of unencumbering ligands, low-coordination numbers, electron-rich metal centers, and a strongly  $\pi$ -acidic ligand field, has required that they be generated and observed by gas phase or matrix isolation techniques. Accordingly, definitive atomic-level detail of their structures and information regarding their reactivity toward substrates is limited.

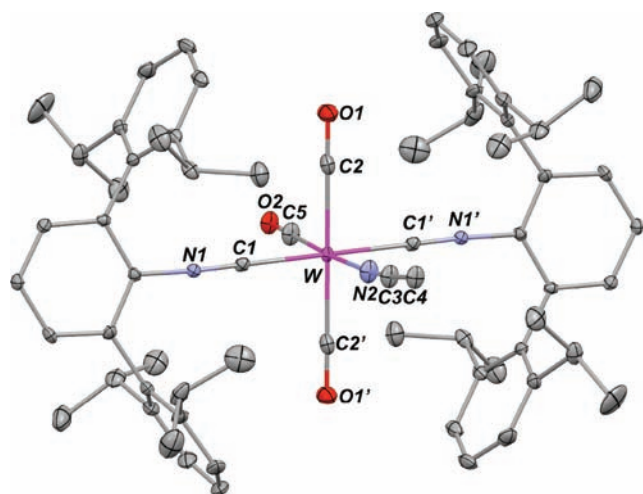
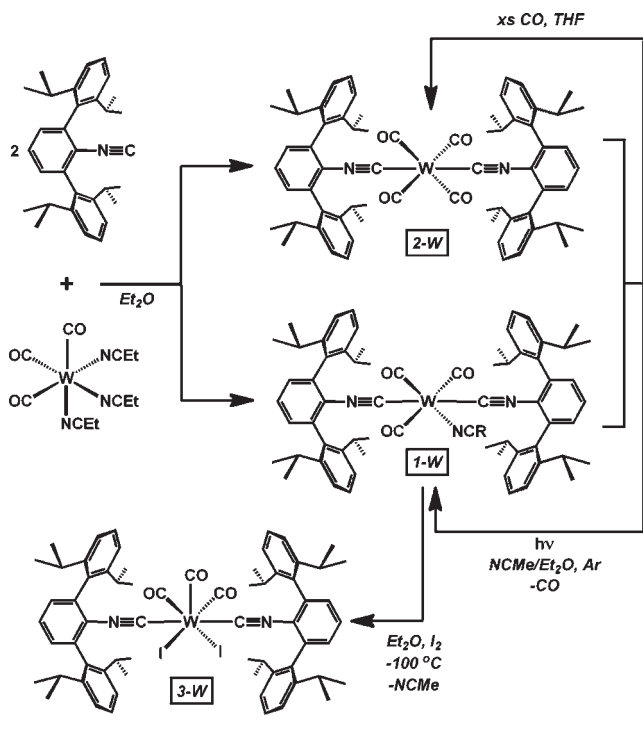
In an effort to construct isolable analogues of the unsaturated transition-metal carbonyls, we have recently introduced the *m*-terphenyl isocyanide ligands  $\text{CNAr}^{\text{Mes}^2}$  and  $\text{CNAr}^{\text{Dipp}^2}$  ( $\text{Ar}^{\text{Mes}^2} = 2,6-(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)_2\text{C}_6\text{H}_3$ ;  $\text{Ar}^{\text{Dipp}^2} = 2,6-(2,6-(i\text{-Pr})_2\text{C}_6\text{H}_3)_2\text{C}_6\text{H}_3$ ).<sup>6,7</sup> These ancillaries were targeted because of (i) the isolobal

relationship between organoisocyanides and  $\text{CO}^8$  and (ii) the established ability of the *m*-terphenyl framework<sup>9</sup> to stabilize low-coordinate transition-metal and main-group complexes.<sup>10</sup> Indeed, when studied in conjunction with zerovalent group 10 metals,  $\text{CNAr}^{\text{Mes}^2}$  and  $\text{CNAr}^{\text{Dipp}^2}$  have been shown to effectively stabilize isocyanide analogues of the binary carbonyls,  $[\text{Ni}(\text{CO})_3]$ <sup>11,12</sup> and  $[\text{Pd}(\text{CO})_2]$ .<sup>13</sup> In addition, the  $\text{CNAr}^{\text{Mes}^2}$  ligand has been used to provide a stable, homoleptic isocyanide analogue of  $\text{Co}(\text{CO})_4$ ,<sup>14</sup> which has been proposed as a reactive intermediate<sup>15</sup> in cobalt carbonyl-catalyzed hydroformylation (oxo catalysis).<sup>16</sup> Accordingly, we reasoned that these encumbering isocyanides could similarly provide a protective shield for group 6 species of the type  $[\text{M}(\text{CNR})_4]$ ,  $[\text{M}(\text{CNR})_3]$ , or  $[\text{M}(\text{CNR})_2]$ , without significantly affecting their preferred coordination geometries (i.e., *cis*-divacant octahedral- $\text{C}_{2v}$ , trigonal pyramidal- $\text{C}_{3v}$ , and bent- $\text{C}_{2v}$ , respectively).<sup>3–5</sup>

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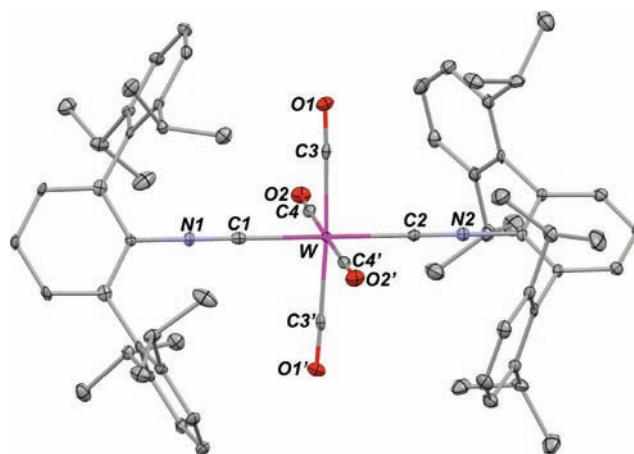
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Scheme 1



**Figure 1.** Molecular structure of *trans*-W(NCMe)(CO)<sub>3</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (1-W) at the 35% probability level. Selected bond distances (Å) and angles (deg): W1–C1 = 2.067(4); W1–C2 = 2.029(6); W1–N2 = 2.262(10); C1–W1–C1' = 180.0(3); C2–W1–C2' = 179.998(1); C5–W1–N2 = 176.5(13); C1–W1–C5 = 90.9(7); C1–W1–N2 = 91.5(4); C1–W1–C2 = 90.5(2).

Our approach toward the synthesis of these low-coordinate, group 6 species has focused on the reduction of suitable mid- to high-valent isocyanide precursor complexes. Herein we present synthetic studies leading to such iodo- and carboxylate-containing precursors supported by the isocyanide CNAr<sup>Dipp2</sup> specifically. Furthermore, we provide evidence that chemical reduction of molybdenum-iodo species, in particular, lead to low-coordinate Mo–CNAr<sup>Dipp2</sup> complexes that can be trapped by arene-solvent molecules.



**Figure 2.** Molecular structure of *trans*-W(CO)<sub>4</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (2-W) at the 35% probability level. Selected bond distances (Å) and angles (deg): W1–C1 = 2.081(10); W1–C2 = 2.084(9); W1–C3 = 2.049(7); W1–C4 = 2.041(7); C1–W1–C2 = 180.000(2); C1–W1–C3 = 91.82(17); C1–W1–C4 = 90.43(18); C2–W1–C3 = 91.82(17); C2–W1–C4 = 89.57(18); C3–W1–C4 = 93.1(2).

We initially hoped that chemical reduction of commercially available group 6 metal halides in the presence of CNAr<sup>Dipp2</sup> would provide a straightforward route to low-valent, low-coordinate [M(CNAr<sup>Dipp2</sup>)<sub>n</sub>] complexes. Such methods have been successful for the synthesis of homoleptic M(CNR)<sub>6</sub> complexes of the low-valent group 6 metals,<sup>17,18</sup> in addition to low-valent isocyanides of other metals such as Fe<sup>19</sup> and Co.<sup>14</sup> In our hands, however, such reduction experiments using CNAr<sup>Dipp2</sup> have led to intractable mixtures. We have also found that addition of CNAr<sup>Dipp2</sup> to common molybdenum starting materials<sup>20</sup> such as MoCl<sub>3</sub>(THF)<sub>3</sub> or MoCl<sub>4</sub>(NCMe)<sub>2</sub> does not result in productive isocyanide binding. Presumably, the presence of chloride ligands renders these Mo centers insufficiently Lewis acidic to tightly bind the encumbering CNAr<sup>Dipp2</sup> isocyanide.<sup>21</sup> Accordingly, we have pursued an alternate synthetic strategy to access precursor compounds. On the basis of our previous findings that CNAr<sup>Dipp2</sup> readily binds to the zerovalent [Mo(CO)<sub>3</sub>(sol)] (sol = solvento) fragment,<sup>7</sup> we focused on an approach involving oxidative decarbonylation of preformed group 6 M(sol)(CO)<sub>3</sub>–(CNAr<sup>Dipp2</sup>)<sub>2</sub> complexes in a manner that preserves metal-isocyanide ligation. This approach was inspired in part from Colton's classic oxidative-decarbonylation studies of the homoleptic group 6 carbonyls with elemental halogens.<sup>22–28</sup>

## RESULTS AND DISCUSSION

### A. Synthesis of W(sol)<sub>n</sub>(CO)<sub>4–n</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> Complexes.

Previously, we reported that treatment of 2.0 equiv of CNAr<sup>Dipp2</sup> with Mo(CO)<sub>3</sub>(NCR)<sub>3</sub> (R = Me or Et) produced a mixture of the tricarbonyl and tetracarbonyl molybdenum complexes *trans*-Mo(NCMe)(CO)<sub>3</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (1-Mo) and *trans*-Mo(CO)<sub>4</sub>–(CNAr<sup>Dipp2</sup>)<sub>2</sub> (2-Mo).<sup>7</sup> As shown in Scheme 1, a similar mixture of tungsten complexes is available by combination of CNAr<sup>Dipp2</sup> and W(CO)<sub>3</sub>(CNEt)<sub>3</sub> in a 2:1 ratio. Extended photolysis of this mixture in 1:1 Et<sub>2</sub>O/MeCN solution with a low-pressure Hg lamp (254 nm) provides *trans*-W(NCMe)(CO)<sub>3</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (1-W) as the exclusive product. Correspondingly, addition of an excess of CO to the mixture is sufficient to fully generate *trans*-W(CO)<sub>4</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (2-W). As expected, single-crystal X-ray

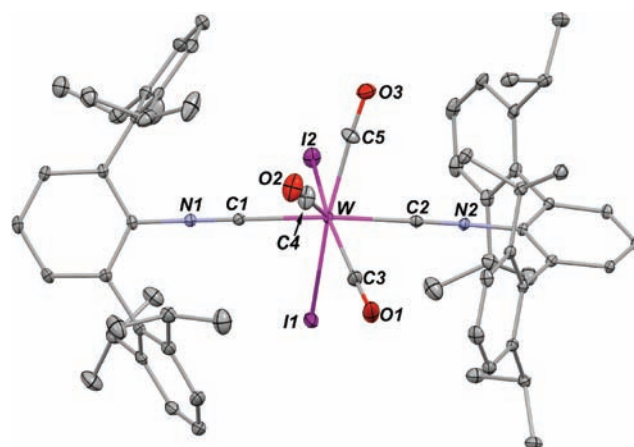
Table 1.  $\nu_{\text{CN}}$  and  $\nu_{\text{CO}}$  Stretching Frequencies

complex	$\nu_{\text{CN}}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{CO}}$ ( $\text{cm}^{-1}$ )
<i>trans</i> -W(NCMe)(CO) <sub>3</sub> (CNAr <sup>Dipp2</sup> ) <sub>2</sub> (1-W) <sup>a</sup>	2026(s)	1886(s)
	1996(s)	1873(s)
<i>trans</i> -Mo(NCMe)(CO) <sub>3</sub> (CNAr <sup>Dipp2</sup> ) <sub>2</sub> (1-Mo) <sup>a,b</sup>	2027(s)	1895(s)
	1998(s)	1873(s)
<i>trans</i> -W(CO) <sub>4</sub> (CNAr <sup>Dipp2</sup> ) <sub>2</sub> (2-W) <sup>a</sup>	2061(s)	1926(vs)
	2009(w)	
<i>trans</i> -Mo(CO) <sub>4</sub> (CNAr <sup>Dipp2</sup> ) <sub>2</sub> (2-Mo) <sup>a,b</sup>	2061(s)	1932(vs)
	2005(w)	
Wl <sub>2</sub> (CO) <sub>3</sub> (CNAr <sup>Dipp2</sup> ) <sub>2</sub> (3-W) <sup>c</sup>	2150(s)	2037(s)
	2099(m)	1982(vs)
<i>trans,trans,trans</i> -MoI <sub>2</sub> (CO) <sub>2</sub> (CNAr <sup>Dipp2</sup> ) <sub>2</sub> (4) <sup>c</sup>	2109(vs)	2004(s)
	1994(s)	
<i>cis,cis,trans</i> -MoI <sub>2</sub> (CO) <sub>2</sub> (CNAr <sup>Dipp2</sup> ) <sub>2</sub> (4) <sup>a,d</sup>	2110(vs)	1982(s)
		1940(w)
<i>trans,trans,trans</i> -MoI <sub>2</sub> (CO) <sub>2</sub> (CNAr <sup>Dipp2</sup> ) <sub>2</sub> (4) <sup>a,d</sup>	2110(vs)	2006(s)
		1997(s)
MoI <sub>2</sub> (THF)(CO) <sub>2</sub> (CNAr <sup>Dipp2</sup> ) <sub>2</sub> (5) <sup>c</sup>	2079(vs)	1969(s)
		1947(w)
<i>trans</i> -MoI <sub>4</sub> (CNAr <sup>Dipp2</sup> ) <sub>2</sub> (6) <sup>c</sup>	2163(s)	
	2135(w)	
W(O <sub>2</sub> CPh) <sub>2</sub> (CO) <sub>2</sub> (CNAr <sup>Dipp2</sup> ) <sub>2</sub> (7) <sup>c</sup>	2135(w)	2002(w)
	2071(vs)	1949(vs)
W(O <sub>2</sub> CMe) <sub>2</sub> (CO) <sub>2</sub> (CNAr <sup>Dipp2</sup> ) <sub>2</sub> (8-W) <sup>c</sup>	2131(w)	2002(w)
	2068(vs)	1943(vs)
Mo(O <sub>2</sub> CMe) <sub>2</sub> (CO)(CNAr <sup>Dipp2</sup> ) <sub>2</sub> (9) <sup>c</sup>	2107(w)	2007(s)
	2032(vs)	1921(m)
<i>trans</i> -MoI <sub>3</sub> (THF)(CNAr <sup>Dipp2</sup> ) <sub>2</sub> (10) <sup>c</sup>	2142(vs)	
	1927(vs)	
$(\eta^6\text{-C}_6\text{H}_6)\text{Mo}(\text{N}_2)(\text{CNAr}^{\text{Dipp2}})_2$ (11) <sup>c</sup>	2086(m)	
	2040(vs)	
$(\eta^6\text{-C}_6\text{H}_6)\text{MoI}_2(\text{CNAr}^{\text{Dipp2}})_2$ (12) <sup>c</sup>	2007(w)	

<sup>a</sup> KBr pellet. <sup>b</sup> Spectrum taken in C<sub>6</sub>D<sub>6</sub> solution in ref 7 and KBr pellet for this work. <sup>c</sup> C<sub>6</sub>D<sub>6</sub> solution. <sup>d</sup> Crystalline mixture of *trans,trans,trans*-MoI<sub>2</sub>(CO)<sub>2</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> and *cis,cis,trans*-MoI<sub>2</sub>(CO)<sub>2</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub>. <sup>e</sup> THF solution.

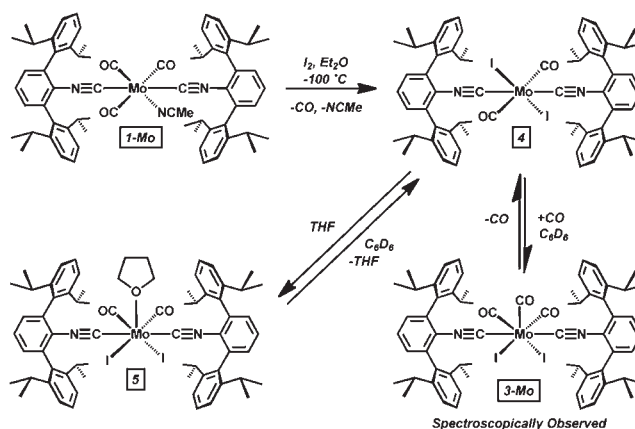
diffraction revealed that both *trans*-W(NCMe)(CO)<sub>3</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (1-W) and *trans*-W(CO)<sub>4</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (2-W) are isostructural with their Mo counterparts (Figures 1 and 2).<sup>7</sup> In addition, the IR spectra of *trans*-W(NCMe)(CO)<sub>3</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (1-W) and *trans*-W(CO)<sub>4</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (2-W) are identical in pattern to their Mo congeners and feature the expected slight shift of the  $\nu_{\text{CO}}$  bands to lower energy (Table 1).<sup>29</sup> This shift is consistent with the increased  $\pi$ -basicity of W relative to Mo. Despite the presence of a labile NCMe ligand, *trans*-W(NCMe)(CO)<sub>3</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (1-W), like its Mo counterpart, resists ligation of another equivalent of CNAr<sup>Dipp2</sup> and does not engage in isocyanide exchange as assayed by <sup>1</sup>H NMR and IR spectroscopy (C<sub>6</sub>D<sub>6</sub>, 20 °C).

**B. Chemical Oxidation of M(NCMe)(CO)<sub>3</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> Complexes with I<sub>2</sub>.** To promote isocyanide retention in higher valent complexes, we targeted group 6 metal centers featuring multiple iodide ligands. This choice stemmed from the successful



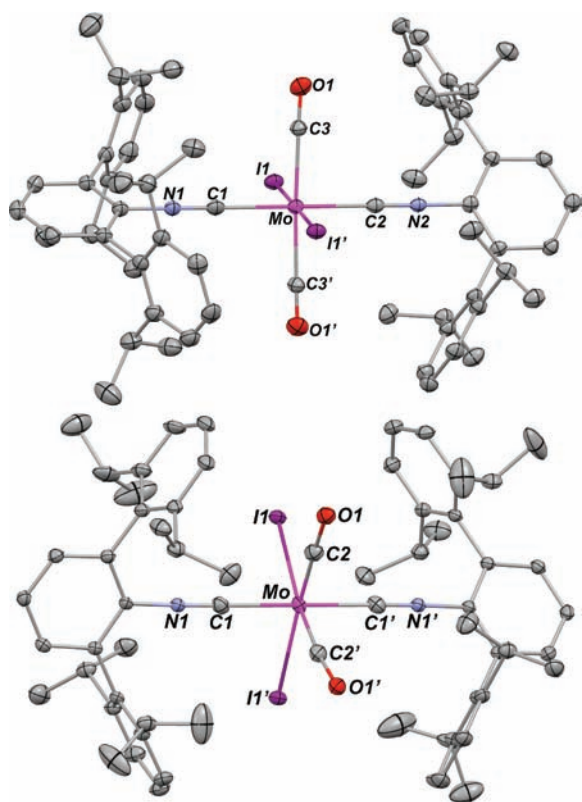
**Figure 3.** Molecular structure of Wl<sub>2</sub>(CO)<sub>3</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (3-W) at the 35% probability level. Selected bond distances (Å) and angles (deg): W1–C1 = 2.113(6); W1–C2 = 2.134(6); W1–C3 = 2.032(7); W1–C4 = 1.980(7); W1–C5 = 2.039(6); W1–I1 = 2.8401(5); W1–I2 = 2.8174(5); C1–W1–C2 = 168.7(2); I1–W1–C5 = 159.5(2); I2–W1–C3 = 159.3(2); C1–W1–I1 = 80.20(15); C1–W1–I2 = 82.08(15); C1–W1–C3 = 108.2(2); C1–W1–C4 = 76.2(3); C1–W1–C5 = 107.2(3); C2–W1–I1 = 90.97(15); C2–W1–I2 = 90.79(15); C2–W1–C3 = 76.0(3); C2–W1–C4 = 115.1(3); C2–W1–C5 = 78.9(3); C2–W1–I1 = 90.97(15); C2–W1–I2 = 90.79(15); I1–W1–I2 = 89.452(18); I1–W1–C3 = 76.2(3); I2–W1–C3 = 76.2(3); C3–W1–C4 = 75.1(2); C4–W1–C5 = 71.7(3); C5–W1–I2 = 73.1(2).

## Scheme 2



isolation of stable *m*-terphenyl-isocyanide-ligated Cu and Co iodo complexes in a range of formal oxidation states.<sup>6,30</sup> Notably, direct treatment of CNAr<sup>Dipp2</sup> with the trivalent molybdenum complex, MoI<sub>3</sub>(THF)<sub>3</sub>,<sup>31</sup> resulted in an array of products and insoluble materials. We believe that aggregation and disproportionation processes of incipiently formed [MoI<sub>3</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub>]<sub>n</sub> complexes may kinetically compete with the binding of a second isocyanide, ultimately leading to undesired products.<sup>32</sup> We reasoned that preligation of two CNAr<sup>Dipp2</sup> units to the metal center may succeed in controlling reaction outcomes by (i) sterically inhibiting multinuclear aggregation and (ii) disfavoring electron transfer reactions by furnishing strong  $\pi$ -back-bonding interactions. Importantly, a cursory survey showed that the tetracarbonyl complexes *trans*-M(CO)<sub>4</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (M = Mo (2-Mo), W (2-W)) did not react with elemental iodine under ambient



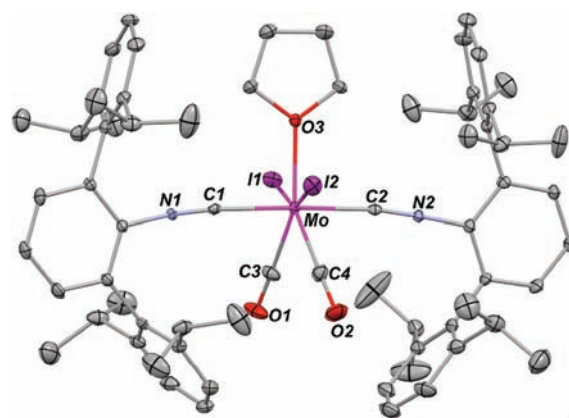


**Figure 4.** Disorder models for the molecular structure of  $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$  (**4**). Top: disorder model for *trans,trans,trans*- $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$ . Bottom: disorder model for *cis,cis,trans*- $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$ . Both isomers are present in crystals of  $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$  (**4**) grown from toluene at  $-35^\circ\text{C}$ .

conditions (THF,  $20^\circ\text{C}$ ). We therefore focused on the reactivity of the acetonitrile adducts *trans*- $\text{M}(\text{NCMe})(\text{CO})_3(\text{CNAr}^{\text{Dipp}2})_2$  ( $\text{M} = \text{Mo}, \text{W}$ ; 1-M) toward  $\text{I}_2$ , in anticipation that dissociation of the labile NCMe ligand would promote inner-sphere oxidation events.

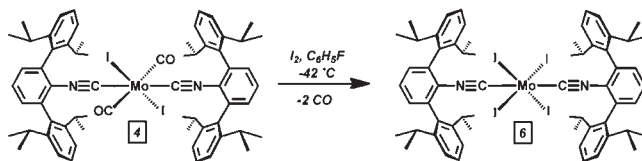
Importantly, this isocyanide retention strategy was successful, but the extent of decarbonylation between the Mo and W congeners differed. Accordingly, treatment of the tungsten derivative *trans*- $\text{W}(\text{NCMe})(\text{CO})_3(\text{CNAr}^{\text{Dipp}2})_2$  (1-W) with 1.0 equiv of  $\text{I}_2$  in  $\text{Et}_2\text{O}$  readily afforded the seven-coordinate complex,  $\text{WI}_2(\text{CO})_3(\text{CNAr}^{\text{Dipp}2})_2$  (3-W), as determined by X-ray diffraction (Scheme 1, Figure 3). The solid-state geometry of  $\text{WI}_2(\text{CO})_3(\text{CNAr}^{\text{Dipp}2})_2$  (3-W) is readily described as capped-octahedral<sup>33</sup> and is similar to other structurally characterized  $\text{MX}_2(\text{CO})_n(\text{L})_m$  ( $m = 5 - n$ ) group 6 complexes.<sup>34</sup> In the solid state,  $\text{WI}_2(\text{CO})_3(\text{CNAr}^{\text{Dipp}2})_2$  (3-W) possesses mirror symmetry and two inequivalent CO sites. However, its  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum in  $\text{C}_6\text{D}_6$  at  $20^\circ\text{C}$  shows only one carbonyl resonance, thus indicating that the encumbering  $\text{CNAr}^{\text{Dipp}2}$  ligands do not impede CO-ligand site exchange in solution at this temperature.

In contrast to its W counterpart, treatment of *trans*- $\text{Mo}(\text{NCMe})(\text{CO})_3(\text{CNAr}^{\text{Dipp}2})_2$  (1-Mo) with 1.0 equiv of  $\text{I}_2$  in  $\text{Et}_2\text{O}$  solution leads to CO loss and formation of the paramagnetic dicarbonyl complex,  $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$  (**4**, Scheme 2). Evans method magnetic moment determination ( $\text{C}_6\text{D}_6/(\text{Me}_3\text{Si})_2\text{O}$ ,  $20^\circ\text{C}$ ) resulted in a  $\mu_{\text{eff}}$  value of  $2.71(3) \mu_{\text{B}}$ , consistent with an  $S = 1$  ground state in solution for the  $d^4$  Mo center in  $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$  (**4**). Importantly, the  $^1\text{H}$  NMR spectrum of  $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$  (**4**) in  $\text{C}_6\text{D}_6$

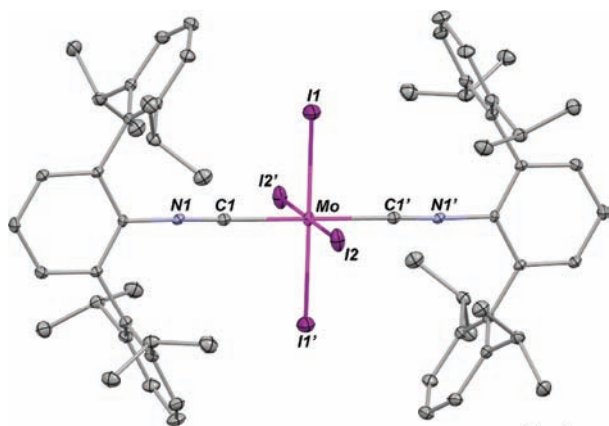


**Figure 5.** Molecular structure of  $\text{MoI}_2(\text{THF})(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$  (**5**) at the 35% probability level. Selected bond distances ( $\text{\AA}$ ) and angles (deg):  $\text{Mo1}-\text{C1} = 2.121(6)$ ;  $\text{Mo1}-\text{C2} = 2.114(6)$ ;  $\text{Mo1}-\text{C3} = 1.977(7)$ ;  $\text{Mo1}-\text{C4} = 1.960(8)$ ;  $\text{Mo1}-\text{I1} = 2.8531(6)$ ;  $\text{Mo1}-\text{I2} = 2.8523(6)$ ;  $\text{Mo1}-\text{O3} = 2.199(4)$ ;  $\text{C1}-\text{Mo1}-\text{C2} = 178.0(2)$ ;  $\text{C3}-\text{Mo1}-\text{I1} = 72.0(2)$ ;  $\text{C3}-\text{Mo1}-\text{C4} = 68.2(3)$ ;  $\text{C4}-\text{Mo1}-\text{I2} = 70.8(2)$ ;  $\text{I1}-\text{Mo1}-\text{I2} = 154.32(2)$ ;  $\text{I1}-\text{Mo1}-\text{O3} = 77.34(10)$ ;  $\text{I2}-\text{Mo1}-\text{O3} = 77.09(10)$ .

### Scheme 3



solution at  $20^\circ\text{C}$  indicates the presence of a single species with resonances ranging from  $+16.18$  to  $-6.33$  ppm (Figure S1). This species is persistent at room temperature for at least 24 h as assayed by  $^1\text{H}$  NMR spectroscopy, and no additional resonances appear in spectra recorded over this time. However, while structural determination on red crystals grown from toluene at  $-35^\circ\text{C}$  revealed a six-coordinate complex with *trans*-disposed isocyanides, refinement indicated a 50/50 mixture of the *cis*- and *trans*-carbonyl orientations in the solid state (Figure 4). In  $\text{C}_6\text{D}_6$  solution and before crystallization from toluene,  $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$  (**4**) features a single  $\nu_{\text{CN}}$  band ( $2109 \text{ cm}^{-1}$ ) and two strong, closely separated  $\nu_{\text{CO}}$  bands ( $2004$  and  $1994 \text{ cm}^{-1}$ ) in its IR spectrum (Table 1). We attribute the close separation of the  $\nu_{\text{CO}}$  bands to splitting of a single band from coupling with other vibronic modes and therefore assign this species as the *trans*-dicarbonyl isomer of  $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$  (**4**). A solid-state IR spectrum (KBr) on the toluene-grown crystals, however, features an additional set of well-separated  $\nu_{\text{CO}}$  bands of unequal intensity ( $1982$  and  $1940 \text{ cm}^{-1}$ ), which we believe indicates the presence of the *cis*-dicarbonyl complex in the solid state (Table 1). Dissolution of these crystals in  $\text{C}_6\text{D}_6$  followed by analysis with both  $^1\text{H}$  NMR and IR spectroscopy within 20 min revealed near-complete regeneration of the spectroscopic signatures for the *trans*-dicarbonyl isomer.<sup>35</sup> Although we have not performed further investigations, these results suggest that a rapid isomerization process is available to  $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$  (**4**) that favors the *trans*-dicarbonyl configuration in solution at room temperature.



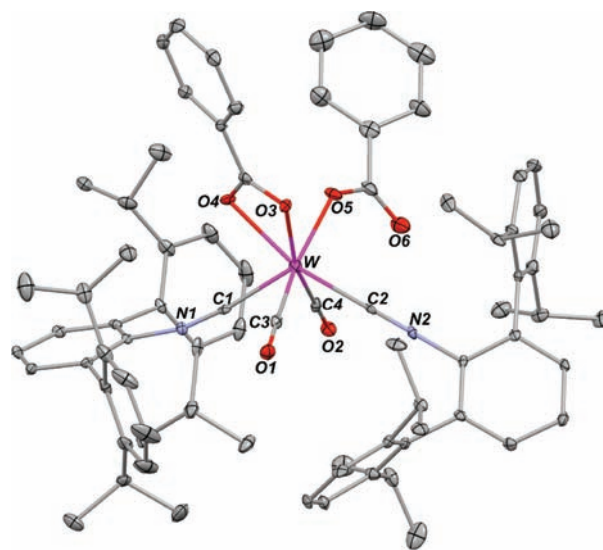
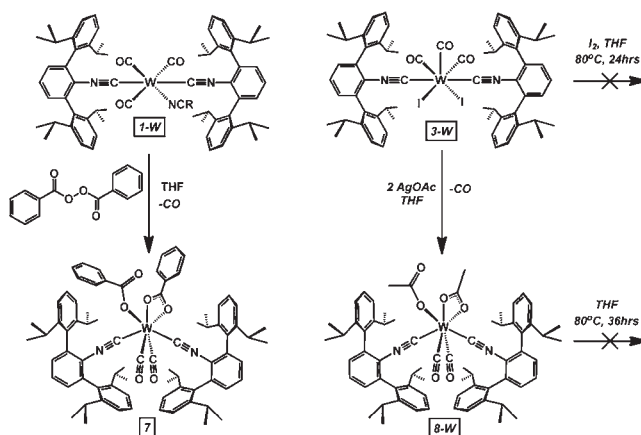
**Figure 6.** Molecular structure of *trans*-Mo<sub>4</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (**6**) at the 35% probability level. Selected bond distances (Å) and angles (deg): Mo1–C1 = 2.148(5); Mo1–I1 = 2.6508(8); Mo1–I2 = 2.7380(7); C1–Mo–I1' = 89.26(13); C1'–Mo–I1' = 90.74(13); I1–Mo1–I2 = 90.0.

Most interestingly, the room-temperature dominant isomer of MoI<sub>2</sub>(CO)<sub>2</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (**4**) represents a very rare paramagnetic group 6 complex with the general formula MX<sub>2</sub>(CO)<sub>2</sub>L<sub>2</sub> (*cis*- or *trans*-(CO)<sub>2</sub>).<sup>25,36</sup> Indeed, the stability of 16e<sup>−</sup>, d<sup>4</sup> MX<sub>2</sub>(CO)<sub>2</sub>L<sub>2</sub> complexes (M = Mo, W) is well-known to arise from a pronounced O<sub>h</sub> → C<sub>2v</sub> electronic distortion that promotes a large HOMO–LUMO gap and, consequently, spin-pairing.<sup>37</sup> However, it has been proposed that strong π-acceptor L ligands, *trans*-oriented as found in *trans*-MoI<sub>2</sub>(CO)<sub>2</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub>, can stabilize an octahedral S = 1 MX<sub>2</sub>(CO)<sub>2</sub>L<sub>2</sub> complex.<sup>37</sup> In this context MoI<sub>2</sub>(CO)<sub>2</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (**4**) is notable, as the complexes [MX<sub>2</sub>(CO)<sub>4</sub>] (M = Mo, W; X = Cl, Br, I), which are the prototypical MX<sub>2</sub>(CO)<sub>2</sub>L<sub>2</sub> examples containing only π-acidic ligands, have been well established as bridging-halide dimers featuring seven-coordinate, diamagnetic metal centers.<sup>22,27,38–40</sup> As shown in Figure 4, the isomers of MoI<sub>2</sub>(CO)<sub>2</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (**4**) possess fairly regular octahedral coordination geometries, with C–Mo–C angles of 178.0(3)° and 180.0(3)° between the two *trans*-CNAr<sup>Dipp2</sup> ligands in the crystallographically independent molecules.

As expected from its electronically unsaturated nature, MoI<sub>2</sub>(CO)<sub>2</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (**4**) can bind additional Lewis basic ligands. Thus, dissolution in THF, followed by crystallization, provides the seven-coordinate, pentagonal bipyramidal complex MoI<sub>2</sub>(THF)(CO)<sub>2</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (**5**) as determined by X-ray diffraction (Scheme 2, Figure 5). The THF ligand in MoI<sub>2</sub>(THF)(CO)<sub>2</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (**5**) is labile, and readily dissociates when the complex is dissolved in C<sub>6</sub>D<sub>6</sub> solution. Furthermore, placement of MoI<sub>2</sub>(CO)<sub>2</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (**4**) under a CO atmosphere (1 atm) results in an equilibrium mixture between it and a diamagnetic species (Scheme 2). We presume that this species is the tricarbonyl complex, MoI<sub>2</sub>(CO)<sub>3</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (**3-Mo**), on the basis of its <sup>1</sup>H NMR spectroscopic similarities to WI<sub>2</sub>(CO)<sub>3</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (**3-W**). However, removal of the CO atmosphere from the reaction mixture readily regenerates MoI<sub>2</sub>(CO)<sub>2</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (**4**). This behavior is similar to that reported for other d<sup>4</sup> MoX<sub>2</sub>(CO)<sub>2</sub>L<sub>2</sub> complexes.<sup>27,41</sup> Notably, the tungsten complex WI<sub>2</sub>(CO)<sub>3</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (**3-W**) shows no tendency to release CO at temperatures up to 80 °C (C<sub>6</sub>D<sub>6</sub>).

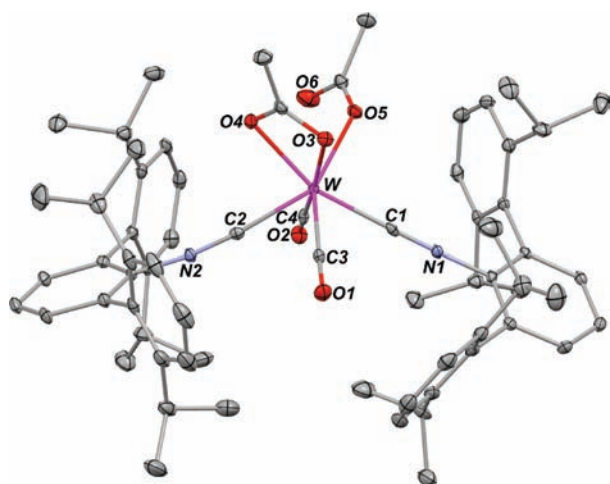
Another contrast between these d<sup>4</sup> Mo- and W-CNAr<sup>Dipp2</sup> systems is that only the Mo complex is reactive toward additional I<sub>2</sub>,

## Scheme 4



**Figure 7.** Molecular structure of W(O<sub>2</sub>CPh)<sub>2</sub>(CO)<sub>2</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (**7**) at the 35% probability level. Selected bond distances (Å) and angles (deg): W1–C1 = 2.038(6); W1–C2 = 2.065(6); W1–C3 = 2.018(7); W–C4 = 2.012(7); W1–O3 = 2.204(4); W1–O4 = 2.222(4); W1–O5 = 2.058(4); C1–W1–C2 = 120.1(2); C1–W1–C3 = 72.4(2); C1–W1–C4 = 73.9(2); C2–W1–C3 = 74.2(2); C2–W1–C4 = 74.2(2); C1–W1–O3 = 117.00(19); C1–W1–O4 = 76.7(2); C2–W1–O5 = 95.9(2); O3–W1–O4 = 58.90(15); O3–W1–O5 = 78.46(17); O4–W1–O5 = 74.19(17).

Thus, treatment of WI<sub>2</sub>(CO)<sub>3</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (**3-W**) with another equivalent of I<sub>2</sub> results in no reaction, whereas MoI<sub>2</sub>(CO)<sub>2</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (**4**) reacts readily in fluorobenzene (C<sub>6</sub>H<sub>5</sub>F) to form the tetraido-complex *trans*-MoI<sub>4</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (**6**, Scheme 3, Figure 6). As expected, *trans*-MoI<sub>4</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (**6**) is paramagnetic and gives rise to solution magnetic moment of μ<sub>eff</sub> = 2.90(3) μ<sub>B</sub>, consistent with an S = 1, d<sup>2</sup> metal center. The IR spectrum of *trans*-MoI<sub>4</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (**6**) in C<sub>6</sub>D<sub>6</sub> solution is also consistent with its formulation and exhibits ν<sub>CN</sub> bands ca. 30–60 cm<sup>−1</sup> higher in energy than the corresponding band in d<sup>4</sup>, MoI<sub>2</sub>(CO)<sub>2</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (**4**). Thus, complete oxidative decarbonylation of Mo(NCMe)(CO)<sub>3</sub>(CNAr<sup>Dipp2</sup>)<sub>2</sub> (**1-Mo**) with isocyanide retention can be achieved for molybdenum in two synthetic steps.



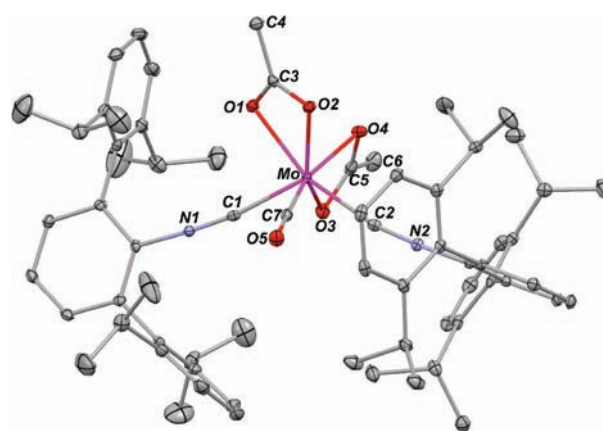
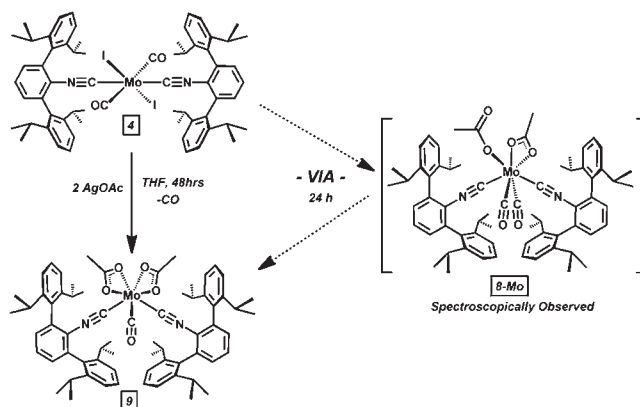
**Figure 8.** Molecular structure of  $W(O_2CMe)_2(CO)_2(CNAr^{Dipp2})_2$  (8-W) at the 35% probability level. Selected bond distances (Å) and angles (deg):  $W1-C1 = 2.077(4)$ ;  $W1-C2 = 2.037(4)$ ;  $W1-C3 = 1.999(4)$ ;  $W1-C4 = 2.022(4)$ ;  $W1-O3 = 2.213(2)$ ;  $W1-O4 = 2.191(3)$ ;  $W1-O5 = 2.083(2)$ ;  $C1-W1-C2 = 121.23(14)$ ;  $C1-W1-C3 = 75.43(14)$ ;  $C1-W1-C4 = 75.04(14)$ ;  $C2-W1-C3 = 70.98(13)$ ;  $C2-W1-C4 = 74.40(14)$ ;  $C1-W1-O3 = 108.77(12)$ ;  $C1-W1-O5 = 85.69(12)$ ;  $C2-W1-O4 = 77.90(12)$ ;  $O3-W1-O4 = 59.01(9)$ ;  $O3-W1-O5 = 75.60(10)$ ;  $O4-W1-O5 = 77.14(10)$ .

Unfortunately, we have found that much lower yields of  $trans-MoI_4(CNAr^{Dipp2})_2$  (6) result from treatment of  $Mo(NCMe)(CO)_3(CNAr^{Dipp2})_2$  (1-Mo) with 2.0 equiv of  $I_2$  (ca. 20%), than are obtained when  $MoI_2(CO)_2(CNAr^{Dipp2})_2$  (4) is isolated and treated with  $I_2$  in a subsequent step (ca. 40–45% overall). Notably,  $trans-MoI_4(CNAr^{Dipp2})_2$  (6) represents, to our knowledge, the first example of a structurally characterized, neutral  $d^5$   $MoI_4L_2$  complex.<sup>42,43</sup>

**C. Acyl Peroxide Oxidation and Coordinatively Induced Decarbonylation.** In addition to iodine, it was of interest to survey if other chemical oxidants could similarly decarbonylate these  $M(sol)(CO)_3(CNAr^{Dipp2})_2$  (1-M) complexes while retaining isocyanide ligation. Particularly appealing were reagents that could deliver oxidizing equivalents while promoting additional decarbonylation events via secondary coordination. In this respect acyl peroxides were intriguing prospects. It was anticipated that the ability of acyl peroxides to effect  $2e^-$  oxidations, coupled with the propensity for  $\kappa^2$ -coordination of the resultant carboxylate ligands, could potentially induce the dissociation of several monodentate CO ligands. Furthermore, carboxylate complexes of medium- and high-valent Mo and W are known,<sup>44–47</sup> and could serve as useful precursors for subsequent reduction reactions.

Addition of benzoyl peroxide to  $trans-W(NCMe)(CO)_3(CNAr^{Dipp2})_2$  (1-W) in THF solution cleanly provided the orange, bis-benzoate dicarbonyl complex,  $W(O_2CPh)_2(CO)_2(CNAr^{Dipp2})_2$  (7, Scheme 4). Crystallographic structure determination revealed both  $\kappa^2$ - and  $\kappa^1$ -coordinated benzoate groups and an overall seven-coordinate geometry best described as a 4:3 piano stool (Figure 7).<sup>48</sup> The  $^1H$  NMR spectrum of  $W(O_2CPh)_2(CO)_2(CNAr^{Dipp2})_2$  (7) at room temperature ( $C_6D_6$ ) exhibits only one benzoate environment, thus indicating interconversion of the  $\kappa^2$ - and  $\kappa^1$ -coordinated ligands. Such coordination behavior has been observed previously for group 6 dicarboxylate complexes<sup>47,49</sup> and, in this system, undoubtedly aids the loss of CO from the

Scheme 5



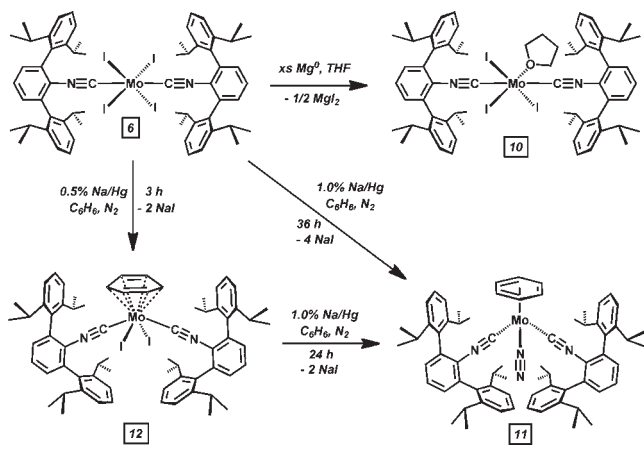
**Figure 9.** Molecular structure of  $Mo(O_2CMe)_2(CO)(CNAr^{Dipp2})_2$  (9) at the 35% probability level. Selected bond distances (Å) and angles (deg):  $Mo1-C1 = 2.017(3)$ ;  $Mo1-C2 = 2.051(2)$ ;  $Mo1-C7 = 1.967(3)$ ;  $Mo1-O1 = 2.2175(16)$ ;  $Mo1-O2 = 2.1435(17)$ ;  $Mo1-O3 = 2.2085(18)$ ;  $Mo1-O4 = 2.2285(17)$ ;  $C1-Mo1-C2 = 118.69(9)$ ;  $C1-Mo1-C7 = 73.20(10)$ ;  $C1-Mo1-O3 = 81.11(8)$ ;  $C1-Mo1-O1 = 79.12(8)$ ;  $C2-Mo1-C7 = 76.58(9)$ ;  $C2-Mo1-O3 = 80.44(8)$ ;  $C2-Mo1-O2 = 107.77(8)$ ;  $C2-Mo1-O4 = 86.96(8)$ ;  $O1-Mo1-O2 = 59.77(6)$ ;  $O1-Mo1-O4 = 80.21(6)$ ;  $O2-Mo1-O4 = 88.02(7)$ .

W center relative to the diiodide complex  $WI_2(CO)_3(CNAr^{Dipp2})_2$  (3-W). To this end, CO loss from  $WI_2(CO)_3(CNAr^{Dipp2})_2$  (3-W) can be induced by addition of external carboxylate ligands. As shown in Scheme 4, treatment of  $WI_2(CO)_3(CNAr^{Dipp2})_2$  (3-W) with 2 equiv of silver acetate ( $AgOAc$ ) results in the diacetate complex  $W(O_2CMe)_2(CO)_2(CNAr^{Dipp2})_2$  (8-W). Crystallographic characterization of  $W(O_2CMe)_2(CO)_2(CNAr^{Dipp2})_2$  (8-W) revealed overall structural features similar to the bis-benzoate derivative  $W(O_2CPh)_2(CO)_2(CNAr^{Dipp2})_2$  (7) including both  $\kappa^2$ - and  $\kappa^1$ -coordinated carboxylate groups (Figure 8).

The molybdenum complex  $trans-Mo(NCMe)(CO)_3(CNAr^{Dipp2})_2$  (1-Mo) did not react cleanly with benzoyl peroxide under a variety of conditions. However, carboxylate ligands can be readily introduced by treatment of the diiodide complex  $MoI_2(CO)_2(CNAr^{Dipp2})_2$  (4) with silver acetate (Scheme 5). Interestingly,  $^1H$  NMR analysis of the reaction mixture after 24 h indicated complete consumption of the starting material and the



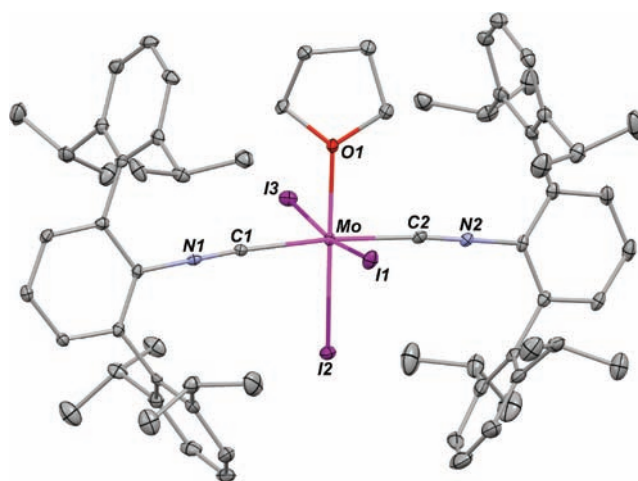
Scheme 6



presence of two new acetate-containing species. After an additional 24 h of stirring only a single product was present, which was identified as the monocarbonyl, diacetate complex  $\text{Mo}(\kappa^2\text{-O}_2\text{CMe})_2(\text{CO})(\text{CNAr}^{\text{Dipp}2})_2$  (9) by X-ray diffraction (Figure 9). While not isolated, we strongly believe that the intermediate in this reaction is the dicarbonyl complex  $\text{Mo}(\text{O}_2\text{CMe})_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$  (8-Mo), as it possesses near-identical  $^1\text{H}$  NMR signatures to the tungsten congener  $\text{W}(\text{O}_2\text{CMe})_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$  (8-W). Notably, despite the presence of two acetate ligands,  $\text{W}(\text{O}_2\text{CMe})_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$  (8-W) does not release an additional CO ligand in solution at temperatures up to  $80^\circ\text{C}$ . Thus, like the Mo and W diiodide complexes discussed above, CO appears to be significantly more labile in the Mo dicarboxylate species relative to its W congener.

Monocarbonyl  $\text{Mo}(\kappa^2\text{-O}_2\text{CMe})_2(\text{CO})(\text{CNAr}^{\text{Dipp}2})_2$  (9) also potentially offers access to unique low-coordinate complexes upon reduction or further elaboration. In this regard it is notable that attempts to convert  $\text{Mo}(\kappa^2\text{-O}_2\text{CMe})_2(\text{CO})(\text{CNAr}^{\text{Dipp}2})_2$  (9) to the five-coordinate diiodide complex  $[\text{MoI}_2(\text{CO})(\text{CNAr}^{\text{Dipp}2})_2]$  via carboxylate esterification<sup>50</sup> with  $\text{Me}_3\text{SiI}$  were unsuccessful. Instead, these reactions resulted in mixtures of the dicarbonyl complex  $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$  (4) along with several other unidentified products ( $^1\text{H}$  NMR), thereby further punctuating the lability of the Mo-CO unit in this isocyanide-supported system. Additional reactivity and reduction studies of these group 6 isocyanide-carboxylate complexes are ongoing.

**D. Chemical Reduction of Iodo-Molybdenum Complexes and Arene-Trapping of Low-Coordinate, Low-Valent Intermediates.** Synthetic access to the di- and tetravalent iodo-molybdenum complexes,  $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$  (4) and  $trans\text{-MoI}_4(\text{CNAr}^{\text{Dipp}2})_2$  (6), allowed us to probe their utility as precursors to low-valent, low-coordinate molybdenum isocyanides. It was hoped that reduction of  $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$  (4) by  $2e^-$  with concomitant iodide loss would generate the four-coordinate complex  $[\text{Mo}(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2]$ . The latter represents a mixed isocyanide/carbonyl analogue of  $[\text{Mo}(\text{CO})_4]$  and should similarly adopt a  $C_{2v}$ , *cis*-divacant octahedral coordination geometry.<sup>1–5</sup> Correspondingly, full reduction of tetrakis(isocyanide)  $trans\text{-MoI}_4(\text{CNAr}^{\text{Dipp}2})_2$  (6) to the zerovalent state could potentially provide a two-coordinate molybdenum isocyanide complex sharing the bent- $C_{2v}$  geometry of  $[\text{Mo}(\text{CO})_2]$ .<sup>1,2,4</sup> Disappointingly, however, treatment of  $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$  (4) with a range of reducing agents resulted in complex and intractable mixtures. The tetracarbonyl complex  $trans\text{-Mo}(\text{CO})_4(\text{CNAr}^{\text{Dipp}2})_2$

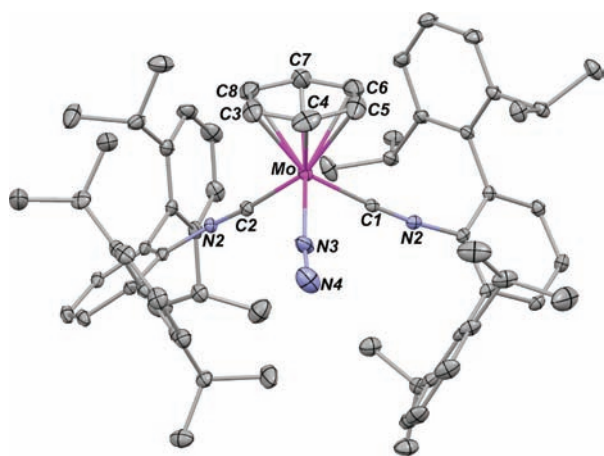


**Figure 10.** Molecular structure of  $trans\text{-Mo}_3(\text{THF})(\text{CNAr}^{\text{Dipp}2})_2$  (10) at the 35% probability level. Selected bond distances (Å) and angles (deg): Mo1–C1 = 2.170(8); Mo1–C2 = 2.173(8); Mo1–I1 = 2.6925(14); Mo1–I2 = 2.7507(12); Mo1–I3 = 2.7497(12); Mo1–O1 = 2.188(5); C1–Mo1–C2 = 175.4(3); C1–Mo1–I1 = 88.77(18); C1–Mo1–I2 = 93.5(2); C1–Mo1–I3 = 88.3(2); C2–Mo1–I1 = 87.09(19); C2–Mo1–I2 = 88.8(2); C2–Mo1–I3 = 90.0(2); I2–Mo1–I1 = 95.34(4); I2–Mo1–I3 = 171.27(3).

(2-Mo) was generated in various quantities in these experiments, which we believe again reflects the lability of the Mo-CO linkage in these isocyanide systems. Accordingly, zerovalent, four-coordinate, isocyanide or mixed carbonyl/isocyanide  $\text{MoL}_4$  complexes remain desired targets.

Despite our difficulties controlling the reduction chemistry of  $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$  (4), fully decarbonylated  $trans\text{-MoI}_4(\text{CNAr}^{\text{Dipp}2})_2$  (6) displayed much cleaner reactivity toward chemical reductants and allowed for a more systematic survey of its reduction behavior. As shown in Scheme 6, treatment of  $trans\text{-MoI}_4(\text{CNAr}^{\text{Dipp}2})_2$  (6) with an excess of Mg metal in THF solution afforded the triiodide complex  $trans\text{-Mo}_3(\text{THF})(\text{CNAr}^{\text{Dipp}2})_2$  (10) as determined by X-ray diffraction (Figure 10). Evans method magnetic moment determination resulted in a  $\mu_{\text{eff}}$  value of  $3.95(1) \mu_{\text{B}}$ , which is consistent with an  $S = 3/2$  ground state for  $trans\text{-Mo}_3(\text{THF})(\text{CNAr}^{\text{Dipp}2})_2$  (10). In addition,  $trans\text{-Mo}_3(\text{THF})(\text{CNAr}^{\text{Dipp}2})_2$  gives rise to a sharp  $\nu_{\text{CN}}$  band at  $2142 \text{ cm}^{-1}$ , which is lower in energy than the corresponding band in the tetraiodide complex  $trans\text{-MoI}_4(\text{CNAr}^{\text{Dipp}2})_2$  (6) and reflects additional electron density on the Mo center (Table 1). Most notably, however, the isolation of  $trans\text{-Mo}_3(\text{THF})(\text{CNAr}^{\text{Dipp}2})_2$  (10) via  $1e^-$  reduction of  $trans\text{-MoI}_4(\text{CNAr}^{\text{Dipp}2})_2$  (6) highlights the success of isocyanide preligation as a synthetic strategy for this system, whereas direct treatment of  $\text{MoI}_3(\text{THF})_3$  with  $\text{CNAr}^{\text{Dipp}2}$  failed to cleanly generate the desired bisisocyanide complex.

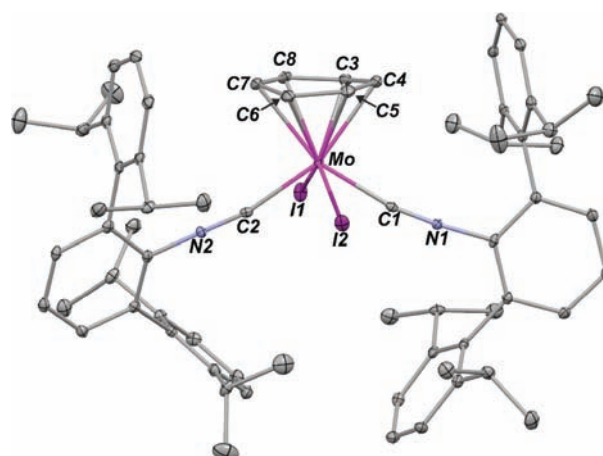
Tetraiodide  $\text{MoI}_4(\text{CNAr}^{\text{Dipp}2})_2$  (6) can also be reduced past the trivalent state when stronger reductants are employed. For example, treatment of  $trans\text{-MoI}_4(\text{CNAr}^{\text{Dipp}2})_2$  (6) with 1% Na/Hg in  $\text{C}_6\text{H}_6$  solution under an  $\text{N}_2$  atmosphere generates the zerovalent,  $\eta^6$ -benzene complex,  $(\eta^6\text{-C}_6\text{H}_6)\text{Mo}(\text{N}_2)(\text{CNAr}^{\text{Dipp}2})_2$  (11), which contains dinitrogen bound in an end-on fashion (Scheme 6, Figure 11). The molecular structure of  $(\eta^6\text{-C}_6\text{H}_6)\text{Mo}(\text{N}_2)(\text{CNAr}^{\text{Dipp}2})_2$  (11) exhibits the three-legged piano stool motif of classical group 6,  $(\eta^6\text{-arene})\text{MoL}_3$  complexes (L = monodentate,  $2e^-$  donor ligand). However, it is noteworthy that dinitrogen-containing variants of this class are relatively rare.<sup>51–54</sup>



**Figure 11.** Molecular structure of  $(\eta^6\text{-C}_6\text{H}_6)\text{Mo}(\text{N}_2)(\text{CNAr}^{\text{Dipp}2})_2$  (**11**) at the 35% probability level. Selected bond distances (Å) and angles (deg): Mo1–C1 = 2.020(3); Mo1–C2 = 2.038(3); Mo1–N3 = 2.075(4); N3–N4 = 1.041(6); Mo1–C3 = 2.264(5); Mo1–C4 = 2.291(5); Mo1–C5 = 2.312(5); Mo1–C6 = 2.265(5); Mo1–C7 = 2.309(5); Mo1–C8 = 2.322(5); C1–Mo1–C2 = 92.63(13); C1–Mo1–N3 = 90.50(15); C2–Mo1–N3 = 91.74(14).

The most intriguing aspect of  $(\eta^6\text{-C}_6\text{H}_6)\text{Mo}(\text{N}_2)(\text{CNAr}^{\text{Dipp}2})_2$  (**11**) concerns its formation upon reduction of *trans*- $\text{MoI}_4(\text{CNAr}^{\text{Dipp}2})_2$  (**6**). While it is interesting to speculate that a zerovalent molybdenum complex of the formulation  $[\text{Mo}(\text{N}_2)_n(\text{CNAr}^{\text{Dipp}2})_2]$  ( $n \leq 4$ ) is present fleetingly in solution, aliquots of the reaction mixture taken before complete formation of  $(\eta^6\text{-C}_6\text{H}_6)\text{Mo}(\text{N}_2)(\text{CNAr}^{\text{Dipp}2})_2$  (**11**) revealed the presence of a diamagnetic intermediate ( $^1\text{H}$  NMR spectroscopy). This intermediate was amenable to isolation by quenching the reduction reaction after 3 h, and X-ray diffraction revealed it to be the  $\eta^6$ -benzene, diiodide complex,  $(\eta^6\text{-C}_6\text{H}_6)\text{MoI}_2(\text{CNAr}^{\text{Dipp}2})_2$  (**12**, Scheme 6, Figure 12).<sup>55</sup> In contrast to zerovalent  $(\eta^6\text{-C}_6\text{H}_6)\text{Mo}(\text{N}_2)(\text{CNAr}^{\text{Dipp}2})_2$  (**11**),  $(\eta^6\text{-C}_6\text{H}_6)\text{MoI}_2(\text{CNAr}^{\text{Dipp}2})_2$  (**12**) possesses an asymmetrically bound benzene ring as indicated by short Mo–C3 and Mo–C6 bond distances (2.255(4) and 2.275(4) Å, respectively) relative to the remaining Mo–C<sub>ring</sub> contacts (2.35(3)<sub>av</sub>). This “folded” or “boat” conformation of the bound benzene is accompanied by a fair degree of dearomatization and is consistent with a 1,4-dienediyl formulation as observed in other  $\eta^6$ -arene complexes (Figure 12).<sup>56–61</sup> Most importantly, however, addition of 1% Na/Hg to isolated  $(\eta^6\text{-C}_6\text{H}_6)\text{MoI}_2(\text{CNAr}^{\text{Dipp}2})_2$  (**12**) in benzene solution under  $\text{N}_2$  generates  $(\eta^6\text{-C}_6\text{H}_6)\text{Mo}(\text{N}_2)(\text{CNAr}^{\text{Dipp}2})_2$  (**11**), thereby showing that the former is indeed a plausible intermediate en route to the zerovalent state.

Several elements of this reduction scheme are noteworthy in the context of generating low-coordinate group 6 isocyanide complexes. At present, we hypothesize that  $2e^-$  reduction of *trans*- $\text{MoI}_4(\text{CNAr}^{\text{Dipp}2})_2$  (**6**) in benzene generates the four-coordinate, divalent complex  $[\text{MoI}_2(\text{CNAr}^{\text{Dipp}2})_2]$ , which is then rapidly intercepted by solvent. Unfortunately, efforts to selectively generate  $[\text{MoI}_2(\text{CNAr}^{\text{Dipp}2})_2]$  in nonaromatic solvents have been unsuccessful thus far, with attempted reductions of *trans*- $\text{MoI}_4(\text{CNAr}^{\text{Dipp}2})_2$  (**6**) in  $\text{Et}_2\text{O}$ , THF, or *n*-pentane in particular leading to intractable mixtures. Importantly, four-coordinate molybdenum  $\text{ML}_2\text{X}_2$  complexes are extremely uncommon, as is expected for a heavier group 6 complex with a formal  $12e^-$  configuration. However, Wolczanski has recently shown that the Mo complex,  $\text{Mo}(\text{silox})_2(\text{PMe}_3)_2$  (silox =  $\text{OSi}(t\text{-Bu})_3$ ),



**Figure 12.** Molecular structure of  $(\eta^6\text{-C}_6\text{H}_6)\text{MoI}_2(\text{CNAr}^{\text{Dipp}2})_2$  (**12**) at the 35% probability level. Selected bond distances (Å) and angles (deg): Mo1–C1 = 2.067(3); Mo1–C2 = 2.068(3); Mo1–I1 = 2.8492(12); Mo1–I2 = 2.8481(19); Mo1–C3 = 2.255(4); Mo1–C4 = 2.361(4); Mo1–C5 = 2.329(4); Mo1–C6 = 2.275(4); Mo1–C7 = 2.385(3); Mo1–C8 = 2.330(4); C3–C4 = 1.404(5); C4–C5 = 1.380(5); C5–C6 = 1.425(5); C6–C7 = 1.402(6); C7–C8 = 1.382(5); C1–Mo1–C2 = 113.98(13); C1–Mo1–I1 = 78.60(9); C1–Mo1–I2 = 75.92(9); C2–Mo1–I1 = 76.88(9); C2–Mo1–I2 = 80.93(9).

can in fact be isolated and that it possesses a pseudotetrahedral  $C_{2v}$  geometry owing to the combined effects of minimizing Mo–O  $\sigma^*$  interactions and maximizing Mo→ $\text{PMe}_3$   $\pi$ -backbonding interactions within the d-orbital manifold.<sup>62</sup> While the coordination spheres of  $\text{Mo}(\text{silox})_2(\text{PMe}_3)_2$  and putative  $[\text{MoI}_2(\text{CNAr}^{\text{Dipp}2})_2]$  are clearly different, they are related in that both possess a  $(\pi\text{-donor})_2(\pi\text{-acceptor})_2$  ligand set. However, the  $\pi$ -donor ability of iodide is clearly marginal relative to silox, and the  $\pi$ -acceptor of an isocyanide is much greater than that of  $\text{PMe}_3$ . How these differences will ultimately affect the chemistry available to the  $[\text{MoI}_2(\text{CNAr}^{\text{Dipp}2})_2]$  fragment is intriguing. To this end, isolation of  $\text{Mo}(\text{silox})_2(\text{PMe}_3)_2$  also reveals that such low-coordinate divalent Mo complexes can be stabilized when the proper steric protection is employed. Accordingly, we speculate that the two-atom linker between the metal center and the *m*-terphenyl unit in  $[\text{MoI}_2(\text{CNAr}^{\text{Dipp}2})_2]$  is insufficient in this regard and evidently does not preclude arene binding. Nevertheless, studies aimed at uncovering the chemistry available to  $[\text{MoI}_2(\text{CNAr}^{\text{Dipp}2})_2]$  by generation and trapping in the presence of other small molecule substrates are continuing.

## EXPERIMENTAL SECTION

**General Considerations.** All manipulations were carried out under an atmosphere of dry dinitrogen using standard Schlenk and glovebox techniques. Solvents were dried and deoxygenated according to standard procedures. Unless otherwise stated, reagent-grade starting materials were purchased from commercial sources and were used as received or purified by standard procedures. The isocyanide ligand  $\text{CNAr}^{\text{Dipp}2}$ ,<sup>7</sup>  $\text{W}(\text{CO})_3(\text{NCEt})_3$ ,<sup>63</sup>  $\text{Mo}(\text{CO})_3(\text{MeCN})_3$ ,<sup>63</sup> and *trans*- $\text{Mo}(\text{NCMe})(\text{CO})_3(\text{CNAr}^{\text{Dipp}2})_2$ <sup>7</sup> were prepared as previously reported. Benzene- $d_6$  (Cambridge Isotope Laboratories) was degassed and stored over 4 Å molecular sieves under  $\text{N}_2$  for 2 days prior to use. THF- $d_8$  was vacuum distilled from Na metal and then stored over 4 Å molecular sieves under  $\text{N}_2$  for 2 days prior to use. Celite 405 (Fisher Scientific) was dried under



vacuum (24 h) at a temperature above 250 °C and stored in the glovebox prior to use.

Solution  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  spectra were recorded on Varian Mercury 300 and 400 spectrometers, a Varian X-Sens500 spectrometer, or a JEOL ECA-500 spectrometer.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  chemical shifts are reported in ppm relative to  $\text{SiMe}_4$  ( $^1\text{H}$  and  $^{13}\text{C}$   $\delta = 0.0$  ppm) with reference to residual solvent resonances of 7.16 ppm ( $^1\text{H}$ ) and 128.06 ppm ( $^{13}\text{C}$ ) for benzene- $d_6$  and 1.72 ppm ( $^1\text{H}$ ) for THF- $d_8$ .<sup>64</sup> FTIR spectra were recorded on a Thermo-Nicolet iS10 FTIR spectrometer. Samples were prepared as  $\text{C}_6\text{D}_6$  solutions injected into a ThermoFisher solution cell equipped with KBr windows or as KBr pellets. For solution FTIR spectra, solvent peaks were digitally subtracted from all spectra by comparison with an authentic spectrum obtained immediately prior to that of the sample. The following abbreviations were used for the intensities and characteristics of important IR absorption bands: vs = very strong, s = strong, m = medium, w = weak, vw = very weak; b = broad, vb = very broad, sh = shoulder. Combustion analyses were performed by Robertson Microлит Laboratories of Madison, NJ.

**Synthesis of  $\text{trans-W}(\text{NCMe})(\text{CO})_3(\text{CNAr}^{\text{Dipp}2})_2$  (1-W).** To an  $\text{Et}_2\text{O}$  slurry of  $\text{W}(\text{CO})_3(\text{NCEt})_3$  (1.000 g, 2.257 mmol, 1 equiv, 30 mL) was added a  $\text{Et}_2\text{O}$  solution of  $\text{CNAr}^{\text{Dipp}2}$  (1.912 g, 4.12 mmol, 2 equiv, 100 mL). The mixture was stirred for 2 h, after which 70 mL of acetonitrile was added. The reaction mixture was then irradiated with a 254 nm Hg lamp while under an Ar purge for 24 h. The reaction mixture was then concentrated to ca.  $1/2$  its original volume under reduced pressure, resulting in the precipitation of an orange solid. This solid was collected via filtration, slurried in cold acetonitrile (20 mL,  $-35$  °C), and then filtered again. Thorough drying of the resulting solid *in vacuo* then afforded  $\text{trans-W}(\text{NCMe})(\text{CO})_3(\text{CNAr}^{\text{Dipp}2})_2$  (1-W). Yield: 1.853 g, 0.160 mmol, 71%.  $^1\text{H}$  NMR (400.1 MHz,  $\text{C}_6\text{D}_6$ , 20 °C):  $\delta = 7.33$  (t, 4H,  $J = 8$  Hz, *p*-Dipp), 7.19 (d, 8H,  $J = 8$  Hz, *m*-Dipp), 6.95 (d, 4H,  $J = 7$  Hz, *m*-Ph), 6.86 (t, 2H,  $J = 7$  Hz, *p*-Ph), 2.78 (sept, 8H,  $J = 7$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.34 (d, 24H,  $J = 7$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.18 (s, 3H,  $\text{NCCH}_3$ ), 1.11 (d, 24H,  $J = 7$  Hz,  $\text{CH}(\text{CH}_3)_2$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ , 20 °C):  $\delta = 205.0$  ( $\text{C}=\text{O}$ ), 199.8 ( $\text{C}\equiv\text{O}$ ), 170.9 ( $\text{C}\equiv\text{N}$ ), 146.7, 138.8, 135.6, 129.9, 129.5, 129.2, 128.6, 125.9, 123.2, 119.0 ( $\text{NCCH}_3$ ), 31.4 ( $\text{CH}(\text{CH}_3)_2$ ), 24.5 ( $\text{CH}(\text{CH}_3)_2$ ), 24.4 ( $\text{CH}(\text{CH}_3)_2$ ), 2.8 ( $\text{NCCH}_3$ ) ppm. FTIR (KBr pellet): ( $\nu_{\text{CN}}$ ) 2026(s) and 1996(s)  $\text{cm}^{-1}$ , ( $\nu_{\text{CO}}$ ) 1886(s), 1873(s) and 1863(m)  $\text{cm}^{-1}$  also 2960, 2925, 2866, 1459, 1415, 1382, 1362, 1046, 803, 755, 584, 521  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{67}\text{H}_{77}\text{N}_3\text{O}_3\text{W}$ : C, 69.60; H, 6.71; N, 3.63. Found: C, 69.05; H, 6.75; N, 3.51.

**Synthesis of  $\text{trans-W}(\text{CO})_4(\text{CNAr}^{\text{Dipp}2})_2$  (2-W).** CO gas (0.043 mL, 1.730 mmol, 10 equiv) was added to a THF solution of  $\text{trans-W}(\text{NCMe})(\text{CO})_3(\text{CNAr}^{\text{Dipp}2})_2$  (1-W, 0.200 g, 0.173 mmol, 20 mL), and the mixture was stirred for 24 h, resulting in the precipitation of a red solid. The reaction mixture was then filtered through a medium porosity frit, and the resulting red powder was washed with THF ( $2 \times 5$  mL), collected, and dried *in vacuo* to afford  $\text{trans-W}(\text{CO})_4(\text{CNAr}^{\text{Dipp}2})_2$  (2-W). Yield: 0.137 g, 0.119 mmol, 68%.  $^1\text{H}$  NMR (400.1 MHz,  $\text{C}_6\text{D}_6$ , 20 °C):  $\delta = 7.36$  (t, 4H,  $J = 8$  Hz, *p*-Dipp), 7.18 (d, 8H,  $J = 8$  Hz, *m*-Dipp), 6.92 (d, 4H,  $J = 8$  Hz, *m*-Ph), 6.85 (t, 2H,  $J = 7$  Hz, *p*-Ph), 2.68 (sept, 8H,  $J = 7$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.32 (d, 24H,  $J = 7$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.06 (d, 24H,  $J = 7$  Hz,  $\text{CH}(\text{CH}_3)_2$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ , 20 °C):  $\delta = 195.5$  ( $\text{C}=\text{O}$ ), 160.8 ( $\text{C}\equiv\text{N}$ ), 146.5, 139.2, 134.9, 129.6, 129.5, 129.2, 127.2, 123.4, 31.4 ( $\text{CH}(\text{CH}_3)_2$ ), 24.5 ( $\text{CH}(\text{CH}_3)_2$ ), 24.3 ( $\text{CH}(\text{CH}_3)_2$ ) ppm. FTIR (KBr pellet): ( $\nu_{\text{CN}}$ ) 2061(s) and 2009(w)  $\text{cm}^{-1}$ , ( $\nu_{\text{CO}}$ ) 1926(vs)  $\text{cm}^{-1}$  also 2961, 2927, 2868, 1459, 1415, 1363, 1055, 803, 755, 596, 570  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{66}\text{H}_{74}\text{N}_2\text{O}_4\text{W}$ : C, 69.34; H, 6.53; N, 2.45. Found: C, 67.95; H, 6.64; N, 2.46.

**Synthesis of  $\text{Wl}_2(\text{CO})_3(\text{CNAr}^{\text{Dipp}2})_2$  (3-W).** To a thawing  $\text{Et}_2\text{O}$  solution of  $\text{trans-W}(\text{NCMe})(\text{CO})_3(\text{CNAr}^{\text{Dipp}2})_2$  (1-W, 1.000 g, 0.864 mmol, 1.00 equiv, 50 mL) was added a thawing  $\text{Et}_2\text{O}$  solution of  $\text{I}_2$

(0.230 g, 0.908 mmol, 1.05 equiv, 20 mL). The resulting mixture was stirred for 1 h resulting in the precipitation of a yellow solid. The reaction mixture was then filtered, and the resulting yellow precipitate was washed with 10 mL of  $\text{Et}_2\text{O}$ , collected, and dried *in vacuo* to afford  $\text{trans-Wl}_2(\text{CO})_3(\text{CNAr}^{\text{Dipp}2})_2$  (3-W). Yield: 0.564 g, 0.412 mmol, 48%.  $^1\text{H}$  NMR (300.1 MHz,  $\text{C}_6\text{D}_6$ , 20 °C):  $\delta = 7.34$  (t, 4H,  $J = 8$  Hz, *p*-Dipp), 7.20 (d, 8H,  $J = 8$  Hz, *m*-Dipp), 6.89 (d, 4H,  $J = 8$  Hz, *m*-Ph), 6.78 (t, 2H,  $J = 7$  Hz, *p*-Ph), 2.61 (sept, 8H,  $J = 7$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.39 (d, 24H,  $J = 7$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.00 (d, 24H,  $J = 7$  Hz,  $\text{CH}(\text{CH}_3)_2$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ , 20 °C):  $\delta = 192.5$  ( $\text{C}=\text{O}$ ), 188.5 ( $\text{C}\equiv\text{N}$ ), 146.4, 140.4, 134.0, 130.7, 130.1, 129.3, 128.6, 126.9, 123.9, 31.4 ( $\text{CH}(\text{CH}_3)_2$ ), 24.8 ( $\text{CH}(\text{CH}_3)_2$ ), 24.4 ( $\text{CH}(\text{CH}_3)_2$ ) ppm. FTIR ( $\text{C}_6\text{D}_6$ , KBr windows): ( $\nu_{\text{CN}}$ ) 2150(s) and 2099(m)  $\text{cm}^{-1}$ , ( $\nu_{\text{CO}}$ ) 2037(s), 1982(vs) and 1944(s)  $\text{cm}^{-1}$  also 2961, 2927, 2868, 1459, 1411, 1384, 1362, 1057, 794, 754  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{65}\text{H}_{74}\text{N}_2\text{O}_3\text{I}_2\text{W}$ : C, 57.03; H, 5.45; N, 2.05. Found: C, 57.12; H, 5.41; N, 1.93.

**Synthesis of  $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$  (4).** To a thawing  $\text{Et}_2\text{O}$  solution of  $\text{trans-Mo}(\text{NCMe})(\text{CO})_3(\text{CNAr}^{\text{Dipp}2})_2$  (1-Mo, 0.100 g, 0.0936 mmol, 1.00 equiv, 40 mL) was added a thawing  $\text{Et}_2\text{O}$  solution of  $\text{I}_2$  (0.024 g, 0.0955 mmol, 1.02 equiv, 20 mL). The reaction mixture was allowed to stir for 6 h, after which the solution was filtered and all volatile materials were removed under reduced pressure. Dissolution of the resulting red residue in a 5:1 toluene/*n*-pentane mixture (6 mL total) followed by filtration and storage at  $-35$  °C for 24 h resulted in red crystals which were collected and dried *in vacuo*. Yield: 0.085 g, 0.0678 mmol, 77%.  $^1\text{H}$  NMR (400.1 MHz,  $\text{C}_6\text{D}_6$ , 20 °C):  $\delta = 16.18$  (d, 4H,  $J = 7$  Hz, *m*-Ph), 9.25 (d, 8H,  $J = 8$  Hz, *m*-Dipp), 8.48 (t, 4H,  $J = 8$  Hz, *p*-Dipp), 6.04 (s, 8H,  $\text{CH}(\text{CH}_3)_2$ ), 3.38 (d, 24H,  $J = 6$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 2.32 (d, 24H,  $J = 7$  Hz,  $\text{CH}(\text{CH}_3)_2$ ),  $-6.33$  (t, 2H,  $J = 8$  Hz, *p*-Ph) ppm.  $\mu_{\text{eff}}$  (Evans method,  $\text{C}_6\text{D}_6$  with  $\text{O}(\text{SiMe}_3)_2$ , 400.1 MHz, 20 °C) =  $2.71$  ( $\pm 0.03$ )  $\mu_{\text{B}}$  (average of 5 independent measurements). FTIR ( $\text{C}_6\text{D}_6$ , KBr windows;  $\text{trans,trans,trans-MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$ ): ( $\nu_{\text{CN}}$ ) 2109- (vs)  $\text{cm}^{-1}$ , ( $\nu_{\text{CO}}$ ) 2004(s) and 1994(s)  $\text{cm}^{-1}$  also 3061, 3020, 2925, 2868, 1577, 1462, 1415, 1386, 1357, 1333, 1252, 1180, 1060, 809, 755  $\text{cm}^{-1}$ . FTIR ( $\text{C}_6\text{D}_6$ , KBr pellet;  $\text{trans,trans,trans-MoI}_2(\text{CO})_2$ - ( $\text{CNAr}^{\text{Dipp}2})_2$  and  $\text{cis,cis,trans-MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$ ): ( $\nu_{\text{CN}}$ ) 2110- (vs)  $\text{cm}^{-1}$ , ( $\nu_{\text{CO}}$ ) 2006(s) and 1997(s)  $\text{cm}^{-1}$  ( $\text{trans-Mo}(\text{CO})_2$ ), ( $\nu_{\text{CO}}$ ) 1982(s) and 1940(w)  $\text{cm}^{-1}$  ( $\text{cis-Mo}(\text{CO})_2$ ). Anal. Calcd for  $\text{C}_{64}\text{H}_{74}\text{N}_2\text{O}_2\text{I}_2\text{Mo}$ : C, 61.35; H, 5.95; N, 2.24. Found: C, 61.16; H, 5.95; N, 2.23.

**Alternative Synthesis of  $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$  (4).** To a thawing acetonitrile solution of  $\text{Mo}(\text{CO})_3(\text{NCMe})_3$  (0.773 g, 2.552 mmol, 1 equiv, 25 mL) was added  $\text{I}_2$  (0.648 g, 2.552 mmol, 1 equiv). The reaction mixture was stirred for 1 h, after which all volatile materials were removed under reduced pressure to afford  $\text{MoI}_2(\text{CO})_3(\text{NCMe})_2$  as a burgundy solid. A 10:1  $\text{Et}_2\text{O}$ /THF (75 mL/7.5 mL) solution was added to  $\text{MoI}_2(\text{CO})_3(\text{NCMe})_2$ , and the reaction mixture was frozen. To the thawing  $\text{Et}_2\text{O}$ /THF solution of  $\text{MoI}_2(\text{CO})_3(\text{NCMe})_2$  was added a thawing  $\text{Et}_2\text{O}$  solution of  $\text{CNAr}^{\text{Dipp}2}$  (2.000 g, 4.721 mmol, 1.85 equiv, 75 mL). The reaction mixture was allowed to stir for 2 h, after which all volatile materials were removed under reduced pressure. Dissolution of the resulting red residue in a 5:1 toluene/*n*-pentane mixture (100 mL total) followed by filtration and storage at  $-35$  °C for 24 h resulted in red crystals, which were collected and dried *in vacuo*. Yield: 2.253 g, 1.798 mmol, 76%.

**Synthesis of  $\text{MoI}_2(\text{THF})(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$  (5).** Solid  $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$  (4, 0.100 g, 0.0798 mmol) was dissolved in 1 mL of THF and stirred for 10 min, gradually changing in color from red to brown. Addition of 0.5 mL of *n*-pentane to the resulting solution followed by filtration and storage at  $-35$  °C for 24 h resulted in brown crystals, which were collected and dried *in vacuo*. Yield: 0.080 g, 0.0604 mmol, 80%.  $^1\text{H}$  NMR (400.1 MHz, THF- $d_8$ , 20 °C):  $\delta = 7.45$  (t, 4H,  $J = 7$  Hz, *p*-Ph), 7.27 (t, 4H,  $J = 8$  Hz, *p*-Dipp), 7.24 (t, 4H,  $J = 8$  Hz, *p*-Dipp), 7.16 (d, 8H,  $J = 8$  Hz, *p*-Ph), 2.54 (sept, 8H,  $J = 7$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.26 (d, 24H,  $J = 7$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.02 (d, 24H,  $J = 7$  Hz,  $\text{CH}(\text{CH}_3)_2$ ) ppm. FTIR (THF, KBr windows): ( $\nu_{\text{CN}}$ ) 2079(vs)  $\text{cm}^{-1}$ , ( $\nu_{\text{CO}}$ ) 1969(s) and

1947(s)  $\text{cm}^{-1}$  also 1594, 1559, 1472, 1465, 1414, 1386, 1364, 872, 823, 809, 793, 158  $\text{cm}^{-1}$ . Satisfactory combustion analysis was not obtained due to repeated and substoichiometric loss of THF. Dissolution of *trans*- $\text{MoI}_2(\text{THF})(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$  (**5**) in  $\text{C}_6\text{D}_6$  returned  $^1\text{H}$  NMR resonances for  $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$  (**4**) and free THF.

**Synthesis of *trans*- $\text{MoI}_4(\text{CNAr}^{\text{Dipp}2})_2$  (**6**).** To a thawing fluorobenzene ( $\text{C}_6\text{H}_5\text{F}$ ) solution of  $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$  (**4**, 0.200 g, 0.160 mmol, 1.00 equiv, 20 mL) was added a thawing fluorobenzene solution of  $\text{I}_2$  (0.043 g, 0.168 mmol, 1.05 equiv, 10 mL). The reaction mixture was allowed to stir for 4 h, after which all volatile materials were removed under reduced pressure. Dissolution of the resulting royal-blue residue in a 2:1 toluene/*n*-pentane mixture (6 mL, total) followed by filtration and storage at  $-35^\circ\text{C}$  for 48 h resulted in royal-blue crystals which were collected and dried *in vacuo*. Yield: 0.125 g, 0.086 mmol, 53%.  $^1\text{H}$  NMR (400.1 MHz,  $\text{C}_6\text{D}_6$ ,  $20^\circ\text{C}$ ):  $\delta = 14.79$  (d, 4H,  $J = 8$  Hz, *m*-Ph), 8.26 (d, 8H,  $J = 8$  Hz, *m*-Dipp), 6.95 (t, 4H,  $J = 8$  Hz, *p*-Dipp), 3.38 (d, 24H,  $J = 7$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.24 (sept, 8H,  $J = 7$  Hz), 1.01 (d, 24H,  $J = 7$  Hz,  $\text{CH}(\text{CH}_3)_2$ ),  $-10.69$  (t, 2H,  $J = 8$  Hz, *p*-Ph) ppm.  $\mu_{\text{eff}}$  (Evans method,  $\text{C}_6\text{D}_6$  with  $\text{O}(\text{SiMe}_3)_2$ , 400.1 MHz,  $20^\circ\text{C}$ ) =  $2.86(\pm 0.03) \mu_{\text{B}}$  (average of 3 independent measurements). FTIR ( $\text{C}_6\text{D}_6$ , KBr windows): ( $\nu_{\text{CN}}$ ) 2163(s) and 2135(w)  $\text{cm}^{-1}$  also 2956, 2926, 2867, 1615, 1587, 1579, 1460, 1407, 1385, 1363, 808, 758, 677  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{62}\text{H}_{74}\text{N}_2\text{I}_4\text{Mo}$ : C, 51.33; H, 5.14; N, 1.93. Found: C, 52.17; H, 5.38; N, 1.82.

**Synthesis of  $\text{W}(\text{O}_2\text{CPh})_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$  (**7**).** To a THF solution of *trans*- $\text{W}(\text{NCMe})(\text{CO})_3(\text{CNAr}^{\text{Dipp}2})_2$  (**1-W**, 0.200 g, 0.173 mmol, 1 equiv, 5 mL) was added a THF solution of benzoyl peroxide (0.084 g, 0.346 mmol, 2 equiv, 5 mL). The reaction mixture was allowed to stir for 24 h, after which all volatile materials were removed under reduced pressure. Dissolution of the resulting orange residue in  $\text{Et}_2\text{O}$  (3 mL) followed by filtration and storage at  $-35^\circ\text{C}$  for 5 days resulted in orange crystals, which were collected and dried *in vacuo*. Yield: 0.050 g, 0.038 mmol, 22%.  $^1\text{H}$  NMR (400.1 MHz,  $\text{C}_6\text{D}_6$ ,  $20^\circ\text{C}$ ):  $\delta = 8.04$  (m, 4H), 7.34 (t, 4H,  $J = 8$  Hz, *p*-Dipp), 7.21 (d, 8H,  $J = 8$  Hz, *m*-Dipp), 7.06 (t, 4H), 7.04 (d, 2H), 6.99 (d, 4H,  $J = 8$  Hz, *m*-Ph), 6.86 (t, 2H,  $J = 8$  Hz, *p*-Ph), 2.71 (sept, 8H,  $J = 7$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.27 (d, 24H,  $J = 7$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.08 (d, 24H,  $J = 7$  Hz,  $\text{CH}(\text{CH}_3)_2$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ ,  $20^\circ\text{C}$ ):  $\delta = 223.1$  ( $\text{C}=\text{O}$ ), 177.3 ( $\text{C}\equiv\text{N}$ ), 175.1 ( $\text{C}=\text{O}$ ), 146.3, 139.1, 135.6, 134.2, 131.4, 130.3, 129.9, 128.6, 127.7, 123.63, 31.4 ( $\text{CH}(\text{CH}_3)_2$ ), 24.9 ( $\text{CH}(\text{CH}_3)_2$ ), 24.1 ( $\text{CH}(\text{CH}_3)_2$ ) ppm. FTIR ( $\text{C}_6\text{D}_6$ , KBr windows): ( $\nu_{\text{CN}}$ ) 2135(w) and 2071(vs)  $\text{cm}^{-1}$ , ( $\nu_{\text{CO}}$ ) 2002(w) and 1949(vs)  $\text{cm}^{-1}$  also 2962, 2926, 2868, 1619 ( $\nu_{\text{C}=\text{O}}$ ), 1505, 1449, 1161, 869, 755, 714  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{78}\text{H}_{84}\text{N}_2\text{O}_6\text{W}$ : C, 70.47; H, 6.37; N, 2.11. Found: C, 70.27; H, 6.40; N, 2.05.

**Synthesis of  $\text{W}(\text{CO})_2(\text{O}_2\text{CMe})_2(\text{CNAr}^{\text{Dipp}2})_2$  (**8-W**).** To a THF solution of  $\text{WI}_2(\text{CO})_3(\text{CNAr}^{\text{Dipp}2})_2$  (**3-W**, 0.100 g, 0.073 mmol, 1 equiv, 3 mL) was added a THF slurry of  $\text{AgOAc}$  (0.037 g, 0.183 mmol, 3 equiv, 5 mL). The reaction mixture was allowed to stir for 12 h, after which the solution was filtered and all volatile materials were removed under reduced pressure. Dissolution of the resulting red residue in a 4:1  $\text{Et}_2\text{O}$ /acetonitrile mixture (5 mL total) followed by filtration and storage at  $-35^\circ\text{C}$  for 24 h resulted in orange crystals, which were collected and dried *in vacuo*. Yield: 0.083 g, 0.069 mmol, 38%.  $^1\text{H}$  NMR (400.1 MHz,  $\text{C}_6\text{D}_6$ ,  $20^\circ\text{C}$ ):  $\delta = 7.36$  (t, 4H,  $J = 8$  Hz, *p*-Dipp), 7.24 (d, 8H,  $J = 8$  Hz, *m*-Dipp), 6.99 (d, 4H,  $J = 7$  Hz, *m*-Ph), 6.86 (t, 2H,  $J = 8$  Hz, *p*-Ph), 2.69 (sept, 8H,  $J = 6$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.72 (s, 6H,  $\text{CH}_3\text{CO}_2$ ), 1.28 (d, 24H,  $J = 6$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.09 (d, 24H,  $J = 6$  Hz,  $\text{CH}(\text{CH}_3)_2$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ ,  $20^\circ\text{C}$ ):  $\delta = 224.5$  ( $\text{C}=\text{O}$ ), 182.0 ( $\text{C}\equiv\text{N}$ ), 175.6 ( $\text{C}=\text{O}$ ), 146.3, 139.0, 134.0, 130.3, 129.8, 128.2, 123.6, 123.4, 31.4 ( $\text{CH}(\text{CH}_3)_2$ ), 25.0 ( $\text{CO}_2\text{CH}_3$ ), 24.9 ( $\text{CH}(\text{CH}_3)_2$ ), 24.0 ( $\text{CH}(\text{CH}_3)_2$ ) ppm. FTIR ( $\text{C}_6\text{D}_6$ , KBr windows): ( $\nu_{\text{CN}}$ ) 2131(w) and 2068(vs)  $\text{cm}^{-1}$ , ( $\nu_{\text{CO}}$ ) 2002(w) and 1943(vs)  $\text{cm}^{-1}$  also 2963, 2925, 2868, 1476, 1413, 1386, 1360, 1302, 761, 691, 664  $\text{cm}^{-1}$  (acetate  $\nu_{\text{C}=\text{O}}$  not conclusively identified). Anal. Calcd for  $\text{C}_{68}\text{H}_{80}\text{N}_2\text{O}_6\text{W}$ : C, 67.77; H, 6.69; N, 2.32. Found: C, 67.69; H, 6.81; N, 2.32.

**Synthesis of  $\text{Mo}(\text{CO})(\text{MeCO}_2)_2(\text{CNAr}^{\text{Dipp}2})_2$  (**9**).** To a THF solution of  $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$  (**4**, 1.000 g, 0.779 mmol, 1 equiv, 30 mL) was added a THF slurry of  $\text{AgOAc}$  (0.280 g, 1.677 mmol, 2.05 equiv, 30 mL). The reaction mixture was allowed to stir for 6 h, filtered, and then stirred for another 48 h. All volatile materials were removed under reduced pressure, and dissolution of the resulting red residue in a 4:1  $\text{Et}_2\text{O}$ /acetonitrile mixture (20 mL total) followed by filtration and storage at  $-35^\circ\text{C}$  for 24 h resulted in orange crystals which were collected and dried *in vacuo*. Yield: 0.350 g, 0.321 mmol, 41%.  $^1\text{H}$  NMR (400.1 MHz,  $\text{C}_6\text{D}_6$ ,  $20^\circ\text{C}$ ):  $\delta = 7.38$  (t, 4H,  $J = 8$  Hz, *p*-Dipp), 7.25 (d, 8H,  $J = 8$  Hz, *m*-Dipp), 6.97 (d, 4H,  $J = 8$  Hz, *m*-Ph), 6.85 (t, 2H,  $J = 7$  Hz, *p*-Ph), 2.72 (sept, 7H,  $J = 7$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.53 (s, 6H,  $\text{CH}_3\text{CO}_2$ ), 1.24 (d, 24H,  $J = 6$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.14 (d, 24H,  $J = 7$  Hz,  $\text{CH}(\text{CH}_3)_2$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ ,  $20^\circ\text{C}$ ):  $\delta = 265.2$  ( $\text{C}\equiv\text{O}$ ), 204.2 ( $\text{C}\equiv\text{N}$ ), 186.3 ( $\text{C}=\text{O}$ ) 146.5, 137.2, 135.0, 130.1, 129.4, 128.7, 127.4, 123.4, 31.5 ( $\text{CH}(\text{CH}_3)_2$ ), 24.7 ( $\text{CO}_2\text{CH}_3$ ), 24.3 ( $\text{CH}(\text{CH}_3)_2$ ), 24.0 ( $\text{CH}(\text{CH}_3)_2$ ) ppm. FTIR ( $\text{C}_6\text{D}_6$ , KBr windows): ( $\nu_{\text{CN}}$ ) 2107(w) and 2032(vs)  $\text{cm}^{-1}$ , ( $\nu_{\text{CO}}$ ) 2007(s) and 1921(m)  $\text{cm}^{-1}$  also 2965, 2925, 2867, 1580, 1466, 1416, 1363, 755  $\text{cm}^{-1}$  (acetate  $\nu_{\text{C}=\text{O}}$  not conclusively identified). Anal. Calcd for  $\text{C}_{67}\text{H}_{80}\text{N}_2\text{O}_5\text{Mo}$ : C, 73.87; H, 7.40; N, 2.57. Found: C, 73.75; H, 7.59; N, 2.61.

**Synthesis of *trans*- $\text{MoI}_3(\text{THF})(\text{CNAr}^{\text{Dipp}2})_2$  (**10**).** To a THF solution of *trans*- $\text{MoI}_4(\text{CNAr}^{\text{Dipp}2})_2$  (**6**, 0.200 g, 0.137 mmol, 50 mL total) was added  $\text{I}_2$ -activated magnesium turnings (0.083 g, 3.446 mmol, 25 equiv). The reaction mixture was allowed to stir for 12 h and gradually changed in color from pale-brown to pale-orange. The resulting solution was decanted off the residual magnesium turnings and then dried under reduced pressure. The residue was then slurried in  $\text{Et}_2\text{O}$  (15 mL), stirred for 20 min, and then dried *in vacuo*. The resulting tan solid was then slurried in  $\text{Et}_2\text{O}$  (20 mL) and filtered through Celite. The solid remaining on the Celite pad was then extracted with THF (5 mL), filtered, layered with *n*-pentane (5 mL), and stored at  $-35^\circ\text{C}$  for 1 day, whereupon tan crystals were obtained. Yield: 0.070 g, 0.050 mmol, 36%.  $^1\text{H}$  NMR (400.1 MHz,  $\text{C}_6\text{D}_6$ ,  $20^\circ\text{C}$ ):  $\delta = 69.65$  (s, 2H, *p*-Ph), 27.72 (s, 4H, *p*-Dipp), 8.35 (s, 8H, *m*-Dipp), 6.26 (s, 4H, THF), 6.04 (s, 4H, THF), 3.55 (s, 24H,  $\text{CH}(\text{CH}_3)_2$ ), 2.48 (s, 24H,  $\text{CH}(\text{CH}_3)_2$ ), 1.37 (s, 8H,  $\text{CH}(\text{CH}_3)_2$ ),  $-17.71$  (s, 4H, *m*-Ph) ppm.  $\mu_{\text{eff}}$  (Evans method,  $\text{C}_6\text{D}_6$  with  $\text{O}(\text{SiMe}_3)_2$ , 400.1 MHz,  $20^\circ\text{C}$ ) =  $3.95(\pm 0.10) \mu_{\text{B}}$  (average of 3 independent measurements). FTIR ( $\text{C}_6\text{D}_6$ , KBr windows): ( $\nu_{\text{CN}}$ ) 2142(vs)  $\text{cm}^{-1}$  also 2962, 2927, 2869, 1461, 1412, 1387, 1364, 1328  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{66}\text{H}_{82}\text{N}_2\text{OI}_3\text{Mo}$ : C, 56.14; H, 5.85; N, 1.89. Found: C, 56.21; H, 6.13; N, 1.94.

**Synthesis of  $\text{Mo}(\text{N}_2)(\eta^6\text{-C}_6\text{H}_6)(\text{CNAr}^{\text{Dipp}2})_2$  (**11**).** To a stirred mixture of 1.0% Na/Hg (Na: 0.633 g, 27.57 mmol; Hg: 63.4 g; 100 equiv Na per Mo) and  $\text{C}_6\text{H}_6$  (50 mL) was added a  $\text{C}_6\text{H}_6$  solution of *trans*- $\text{MoI}_4(\text{CNAr}^{\text{Dipp}2})_2$  (**6**, 0.400 g, 0.276 mmol, 75 mL). The resulting mixture was allowed to stir for 36 h and then filtered through Celite. All volatile materials were then removed under reduced pressure. The resulting red residue was then suspended in  $\text{Et}_2\text{O}$  (10 mL) and filtered through Celite. The filtrate was evaporated to dryness *in vacuo*, and the remaining solid was dissolved in  $\text{Et}_2\text{O}$  (2 mL), filtered, and layered with  $\text{O}(\text{SiMe}_3)_2$  (3 mL) and stored at  $-35^\circ\text{C}$  for 2 days, whereupon red crystals were obtained. Yield: 0.150 g, 0.143 mmol, 52%.  $^1\text{H}$  NMR (400.1 MHz,  $\text{C}_6\text{D}_6$ ,  $20^\circ\text{C}$ ):  $\delta = 7.35$  (t, 4H,  $J = 8$  Hz, *p*-Dipp), 7.21 (dd, 8H,  $J = 8$  Hz, *m*-Dipp), 6.96 (d, 4H,  $J = 8$  Hz, *m*-Ph), 6.87 (t, 2H,  $J = 6$  Hz, *p*-Ph), 3.57 (s, 6H,  $\eta^6\text{-C}_6\text{H}_6$ ), 2.88 (m, 8H,  $J = 7$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.30 (d, 12H,  $J = 7$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.18 (d, 12H,  $J = 7$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.16 (d, 12H,  $J = 7$  Hz,  $\text{CH}(\text{CH}_3)_2$ ), 1.13 (d, 12H,  $J = 7$  Hz,  $\text{CH}(\text{CH}_3)_2$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ ,  $20^\circ\text{C}$ ):  $\delta = 196.2$  ( $\text{C}\equiv\text{N}$ ), 147.1, 146.6, 137.3, 137.1, 131.0, 130.5, 128.9, 124.3, 123.4, 123.2, 84.6 ( $\text{C}_6\text{H}_6$ ), 31.2 ( $\text{CH}(\text{CH}_3)_2$ ), 25.0 ( $\text{CH}(\text{CH}_3)_2$ ), 24.6 ( $\text{CH}(\text{CH}_3)_2$ ), 24.1 ( $\text{CH}(\text{CH}_3)_2$ ), 24.0 ( $\text{CH}(\text{CH}_3)_2$ ) ppm. FTIR ( $\text{C}_6\text{D}_6$ , KBr windows): ( $\nu_{\text{NN}}$ ) 2101(s), ( $\nu_{\text{CN}}$ ) 1979(m) and 1927(vs)  $\text{cm}^{-1}$  also 2965, 2923, 2870, 1618, 1455, 1410, 1155, 758  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{68}\text{H}_{80}\text{N}_4\text{Mo}$ : C, 77.86; H, 7.69; N, 5.34. Found: C, 75.56; H, 7.48; N, 4.27. Repeated



attempts failed to give a more satisfactory combustion analysis. We attribute this to the presence of minor MoI impurities.

**Synthesis of  $\text{MoI}_2(\eta^6\text{-C}_6\text{H}_6)(\text{CNAr}^{\text{Dipp}2})_2$  (12).** To a stirred mixture of 0.5% Na/Hg (Na 0.023 g, 3.43 mmol; Hg 15.8 g; 25 equiv Na per Mo) and  $\text{C}_6\text{H}_6$  (50 mL) was added a  $\text{C}_6\text{H}_6$  solution of  $\text{trans-MoI}_4(\text{CNAr}^{\text{Dipp}2})_2$  (6, 0.200 g, 0.137 mmol, 50 mL). The resulting mixture was allowed to stir for 3 h, and gradually changed from royal blue to red. The reaction mixture was then filtered through Celite and all volatile materials were removed under reduced pressure. The residue was then slurried in *n*-pentane (5 mL), filtered, and washed with *n*-pentane (2 × 5 mL). The remaining solid was dissolved in  $\text{Et}_2\text{O}$  (3 mL), filtered, and layered with  $\text{O}(\text{SiMe}_3)_2$  (3 mL) and stored at  $-35\text{ }^\circ\text{C}$  for 1 d, whereupon brown crystals were obtained. Yield: 0.040 g, 0.031 mmol, 23%.  $^1\text{H NMR}$  (400.1 MHz,  $\text{C}_6\text{D}_6$ ,  $20\text{ }^\circ\text{C}$ ):  $\delta = 7.36$  (t, 4H,  $J = 8\text{ Hz}$ , *p*-Dipp), 7.23 (d, 8H,  $J = 8\text{ Hz}$ , *m*-Dipp), 6.95 (d, 4H,  $J = 7\text{ Hz}$ , *m*-Ph), 6.82 (t, 2H,  $J = 8\text{ Hz}$ , *p*-Ph), 4.35 (s, 6H,  $\eta^6\text{-C}_6\text{H}_6$ ), 2.85 (sept, 8H,  $J = 7\text{ Hz}$ ,  $\text{CH}(\text{CH}_3)_2$ ), 1.43 (d, 24H,  $J = 7\text{ Hz}$ ,  $\text{CH}(\text{CH}_3)_2$ ), 1.09 (d, 24H,  $J = 7\text{ Hz}$ ,  $\text{CH}(\text{CH}_3)_2$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ ,  $20\text{ }^\circ\text{C}$ ):  $\delta = 172.4$  ( $\text{C}\equiv\text{N}$ ), 147.2, 139.1, 136.6, 131.5, 129.5, 129.1, 128.6, 126.9, 123.5, 98.3 ( $\text{C}_6\text{H}_6$ ), 31.3 ( $\text{CH}(\text{CH}_3)_2$ ), 25.1 ( $\text{CH}(\text{CH}_3)_2$ ), 24.9 ( $\text{CH}(\text{CH}_3)_2$ ) ppm. FTIR ( $\text{C}_6\text{D}_6$ , KBr windows): ( $\nu_{\text{CN}}$ ) 2086(m), 2040(vs), 2007(w)  $\text{cm}^{-1}$  also 2959, 2927, 2867, 1614, 1461, 1453, 1416, 1384, 1363, 807, 758  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{68}\text{H}_{80}\text{N}_2\text{I}_2$ . Mo: C, 64.05; H, 6.32; N, 2.20. Found: C, 62.87; H, 6.13; N, 2.22.

**Crystallographic Structure Determinations.** Single crystal X-ray structure determinations were carried out at low temperature on a Bruker P4, Platform or Kappa diffractometer equipped with a Bruker APEX detector. All structures were solved by direct methods with SIR 2004<sup>65</sup> and refined by full-matrix least-squares procedures utilizing SHELXL-97.<sup>66</sup> Crystallographic data-collection and refinement information is listed in Table S1. The crystal structure of 1-W contained positional disorder between one CO ligand and the coordinated acetonitrile molecule. The disorder was modeled such that both the CO and acetonitrile molecules are represented at 50% occupancy in each site. The crystal structure of 4 revealed co-crystallization of a 50/50 mixture of both the *cis*- and *trans*-dicarbonyl isomers. Both *cis*- and *trans*-dicarbonyl isomers contain whole molecule disorder, and consequently, the heavier Mo and I atoms were modeled and refined over several positions. Also, the *cis*-carbonyl isomer contains positional and compositional disorder between the CO ligands and terminal iodides within the equatorial plane of the molecule. The disorder was modeled such that the total of all ligand occupancy equals two CO ligands and two iodide ligands. The crystal structure of 7 contains isopropyl-group positional disorder, which was modeled and refined. The crystal structure of 10 contains positional disorder in one of the bound acetate ligands, which was modeled and refined. The crystal structures of 6 and 11 contain disordered toluene and  $\text{O}(\text{SiMe}_3)_2$  molecules of cocrystallization, respectively. These disordered components were also modeled and refined.

## ■ ASSOCIATED CONTENT

Supporting Information.  $^1\text{H NMR}$  and FTIR spectra for  $\text{MoI}_2(\text{CO})_2(\text{CNAr}^{\text{Dipp}2})_2$  and crystallographic information files (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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