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Synthesis and Reactivity of Molybdenum Complexes Containing Functionalized Alkynyl Ligands: A Photochemically Activated CO-Releasing Molecule (PhotoCO-RM)

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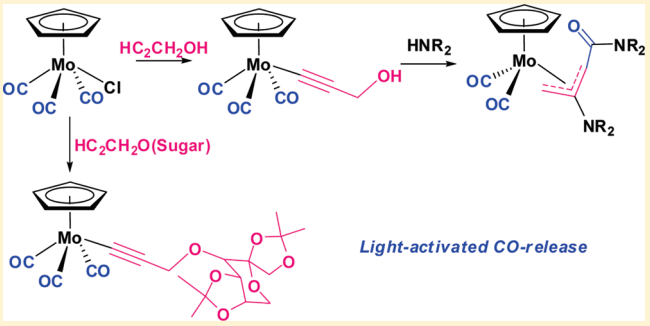
Supporting Information

ABSTRACT: Reaction of $[MoCl(\eta^5\text{-}C_5H_5)(CO)_3]$ with propargyl alcohols $HC{\equiv}CCR^1R^2OH$ in the presence of catalytic amounts of CuI and using NEt_2H as solvent results in the formation of alkynyl complexes $[Mo(C{\equiv}CR^1R^2OH)(\eta^5\text{-}C_5H_5)(CO)_3]$. The structure of the complexes where $R^1 = R^2 = Me$ and $R^1 = Me$, $R^2 = Ph$ were confirmed by single-crystal X-ray diffraction. The method could be extended to a range of propargyl ethers and propargyl esters, which allowed for the preparation of molybdenum complexes containing pendant salicylate and β-D-fructopyranose groups. The alkynyl complex $[Mo(C{\equiv}CCH_2OH)(\eta^5\text{-}C_5H_5)(CO)_3]$ undergoes a further reaction with NEt_2H to give the substituted allyl complex $[Mo(\eta^3\text{-}H_2CC\{NEt_2\}CHC\{O\}NEt_2)(\eta^5\text{-}C_5H_5)(CO)_3]$. Similar products could be obtained from the reaction of $[MoCl(\eta^5\text{-}C_5H_5)(CO)_3]$ with $HC{\equiv}CCH_2OH$ in the presence of CuI using pyrrolidine or piperidine as solvent. In the case of the reaction with piperidine a further product could be isolated that has arisen from the coupling of two propargyl alcohol molecules to afford a butadienyl ligand. The CO-releasing properties of a number of these novel complexes have been investigated. In the case of the water-soluble alkynyl complex containing a β-D-fructopyranose group CO release was shown to be promoted by exposure to UV light, revealing a new class of photochemically activated CO-releasing molecules (PhotoCO-RMs).



INTRODUCTION

Transition metal alkynyl complexes (M-C≡CR) have proven to be versatile and robust synthons for a range of applications.[1] From a frontier molecular orbital perspective, the alkynyl anion is isoelectronic with carbon monoxide; however in the case of the alkynyl group the nature of the metal−ligand interaction may be influenced by the effect of the different substituents on the β-carbon.[2] The synthetic routes available to these species using terminal alkynes as precursors have ensured that a library of metal alkynyl complexes based on different metals with a host of different substituents is now known.[3] Given this ability to tune the nature of the metal−ligand interaction, it is unsurprising that metal−alkynyl complexes have been exploited, among other applications, as materials for nonlinear optics[3] and colorimetric sensors.[4]

A number of synthetic methods have been developed to prepare metal−alkynyl complexes. These include the transmetalation of metal halide complexes with alkynyl nucleophiles such as organo-tin, organo-lithium,[5] and organo-copper[6] and, more recently, the use of alkynyl-substituted gold complexes as effective reagents for transmetalation.[7] In the majority of cases the alkynyl nucleophiles are prepared by deprotonation of an appropriate terminal alkyne. The copper(I)-catalyzed coupling of metal halides to terminal alkynes using amines as solvents is also an attractive method for the preparation of metal alkynyl complexes, as it does not require the preformation of the transmetalating agent.[8] This method has found a number of applications, for example, in the synthesis of carbon-rich metal diynyl complexes,[9] half-sandwich iron,[10] ruthenium, and tungsten alkynyl complexes.[8] The deprotonation of vinylidene ligands (M═C═CHR), traditionally formed by a metal-mediated tautomerization of terminal alkynes,[11] provides an important complementary method to the transmetalation approach to alkynyl complexes.

Given that metal−alkynyl complexes typically possess strong metal−carbon bonds and their properties may be easily modulated by the substituent on the alkynyl ligands, complexes containing carbonyl co-ligands might find application as potential therapeutic carbon monoxide-releasing molecules (CO-RMs).[12] A number of different structural motifs have been explored as CO-RMs (Figure 1). For example, simple metal carbonyl compounds $[MX(CO)_5]^-$ (M = Cr, Mo, W) have been investigated,[13] as have the rhenium(II) complexes $[ReBr_2(CO)_2L_2]$,[14] tetrachlorocarbonyliridates,[15] manganese thiocarboxylates,[16] and tricarbonyl group 7 compounds with imidazole-based phosphines.[17]

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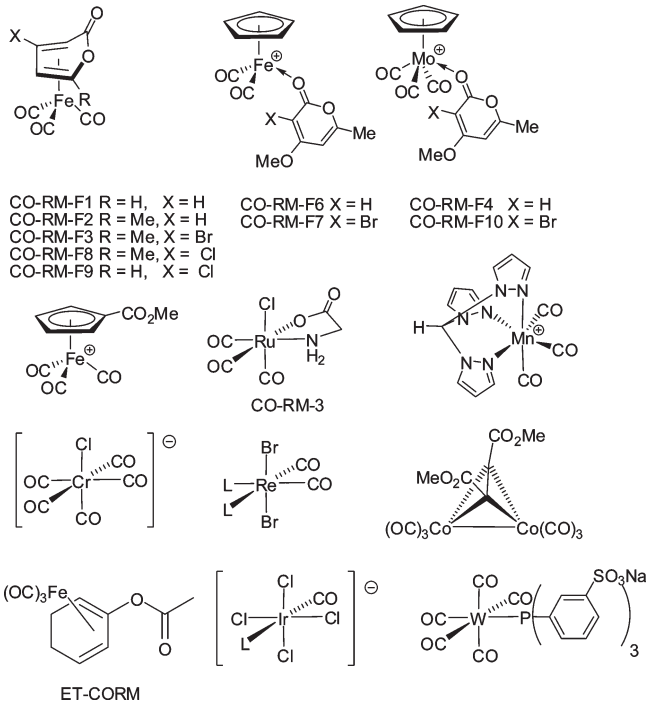


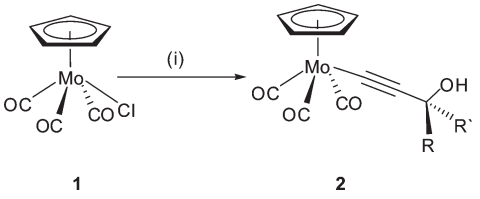
Figure 1. Structures of selected CO-RMs.

More elaborate structures based on iron[18] as well as dicobalt alkyne complexes[19] and photochemically activated systems (PhotoCORMs) have also been reported.[18d,20,21] Very recently, oxobutadiene iron tricarbonyl compounds have been shown to act as enzyme-triggered CO-releasing molecules (ET-CORMs).[22]

One particular focus of the development of CO-RMs has been to incorporate biologically compatible ligands into the coordination sphere of the metal. For example, complexes containing amino acid derivatives have been investigated such as the extensively studied ruthenium glycinate complex, CO-RM-3,[23] and the series of compounds $M(NH_2CHRCO_2R')(CO)_5$ (M = Cr, Mo, W), where dissociation of the amino acid esters is crucial to CO release.[24] We have shown that iron tricarbonyl, cyclopentadienyl iron, and molybdenum complexes containing the 2-pyrone motif may form an effective class of CO-RMs.[25] Notably, complex CO-RM-F10 (Figure 1) was shown to release CO and act as an effective vasorelaxing agent at a concentration where the complex exhibited little toxicity.

With these factors in mind, complexes based on the $[Mo(C{\equiv}CR)(\eta^5\text{-}C_5H_5)(CO)_3]$ framework were considered to have potential as an effective class of CO-RM, where the substituent on the alkynyl ligand may be selected to alter solubility and potential uptake of the complex. Given the ease with which substituted propargyl compounds $HC{\equiv}CCH_2OR$ may be prepared from the reaction of $HC{\equiv}CCH_2Br$ with appropriate nucleophiles, the development of a synthetic route to complexes $[Mo(C{\equiv}CCH_2OR)(\eta^5\text{-}C_5H_5)(CO)_3]$ was sought. The methodology to prepare these complexes is herein described, along with the observation of an unusual condensation reaction between an alkynyl group, a carbonyl ligand, and the amine solvent. In addition, the CO-releasing properties of a number of selected compounds are described, which demonstrate that a sugar-substituted complex is an effective photochemically activated CO-RM.

Scheme 1[a]



[a] (i) + $HC{\equiv}CCR^1R^2(OH)$, CuI, NH_2Me 1 M solution in THF (**2a**) or $NHEt_2$ (**2b**−**e**), 20 min.

RESULTS AND DISCUSSION

Synthesis of Propargyl Alcohol Complexes. Reaction of $[MoCl(\eta^5\text{-}C_5H_5)(CO)_3]$, **1**, with propargyl alcohols $HC{\equiv}CC(OH)R^1R^2$ in the presence of CuI for ca. 20 min results in the formation of alkynyl-substituted complexes $[Mo(C{\equiv}CC\{OH\}R^1R^2)(\eta^5\text{-}C_5H_5)(CO)_3]$ (**2a**, $R^1 = R^2 = H$; **2b**, $R^1 = R^2 = Ph$; **2c**, $R^1 = R^2 = Me$; **2d**, $R^1 = Ph$, $R^2 = Me$; **2e**, $R^1 = Ph$, $R^2 = H$), Scheme 1. In the case of complex **2a**, the reaction was performed in a 1 M solution of NH_2Me in THF in order to minimize the subsequent formation of η^3-allyl complexes (see text): in the other instances the reaction was performed using $NHEt_2$ as solvent. The complexes proved to be photosensitive and decomposed on exposure to ambient light.[26]

Complex **2a** exhibited a number of spectroscopic features that are typical for this series of compounds. For example, a band was observed at 2114 cm^{-1} in the IR spectrum, which was assigned to the C≡C stretch of the alkynyl ligand, as were the expected two bands at 2044 and 1963 cm^{-1} in the terminal metal carbonyl region. In addition to the resonances of the cyclopentadienyl and carbonyl ligands, the $^{13}C\{^1H\}$ NMR spectrum displayed resonances at δ 127.4, δ 82.4, and δ 53.4 for the α-, β-, and γ-carbon of the alkynyl ligand, respectively. The structures of complexes **2c** and **2d** were confirmed by single-crystal X-ray diffraction studies. Selected bond angles and lengths for complexes **2c** and **2d** are presented in Table 1, details of the data collection and structure refinement for all complexes are reported in Table 2, and the molecular structures of **2c** and **2d** are illustrated in Figures 2 and 3, respectively. The structural determinations demonstrated that the features predicted on the basis of the spectroscopic data were indeed present. The complexes adopt four-legged piano-stool geometries with Mo−C and C≡C bond lengths of 2.1494(16) and 1.203(2) Å, respectively, for complex **2c**; in **2d** the corresponding distances were 2.1536(12) and 1.2096(17) Å. In both cases the alkynyl ligands are essentially linear. (For **2c** Mo(1)−C(9)−C(10) 178.44(15)°, C(9)−C(10)−C(11A) 172.0(4)°, C(9)−C(10)−C(11B) 174.2(3)°; for **2d** Mo(1)−C(9)−C(10) 177.67(10)°, C(9)−C(10)−C(11) 178.88(13)°.) These metrical parameters are typical for molybdenum alkynyl complexes.[27]

The structural determination of **2d** also demonstrated that, in the solid state, an OH-π hydrogen bond is present between the OH group on the alkynyl ligand and the C≡C on a neighbor (Figure 3b). The bond lengths (C(9)−O(4) 3.214(2) Å; C(10)−O(4) 3.234(2) Å; C(9)−H(4) 2.46(2) Å; C(10)−H(4) 2.46(2) Å; π-C≡C centroid−H(4) 2.39(3) Å, π-C≡C centroid−O(4) 3.167(3) Å) indicate that this a relatively strong interaction of this type.[28] The hydrogen-bonding network within the structure of **2c** proved to be somewhat more complex. The CMe_2OH group was disordered over two positions. In one position the OH

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Table 1. Selected Bond Lengths (Å) for Complexes 2c, 2d, 5a, 5b, 5c, and 6

	2c	2d	5a	5b	5c	6[b]
Mo−C(1)	2.3455(16)	2.3390(13)	2.3229(17)	2.3790(14)	2.387(3)	2.321(3)
Mo−C(2)	2.3048(16)	2.3655(13)	2.3204(17)	2.3890(14)	2.357(3)	2.377(3)
Mo−C(3)	2.3005(16)	2.3484(13)	2.3577(16)	2.3490(14)	2.311(3)	2.374(3)
Mo−C(4)	2.3439(16)	2.3105(13)	2.3890(16)	2.3201(14)	2.310(3)	2.316(3)
Mo−C(5)	2.3724(16)	2.3079(13)	2.3677(17)	2.3311(14)	2.347(3)	2.296(3)
Mo−C(6)	2.0050(16)	2.0062(14)	1.9501(16)	1.9546(14)	1.956(3)	1.953(3)
Mo−C(7)	1.9998(16)	2.0121(14)	1.9501(17)	1.9534(14)	1.950(4)	2.003(3)
Mo−C(8)	2.0085(16)	2.0024(15)	2.3065(15)	2.3162(14)	2.315(3)	
Mo−C(9)	2.1494(16)	2.1536(12)	2.4851(15)	2.4602(13)	2.411(3)	
Mo−C(10)			2.3195(15)	2.3330(13)	2.318(3)	2.181(3)
C(6)−O(1)	1.138(2)	1.1412(17)	1.159(2)	1.1595(18)	1.156(4)	1.169(3)
C(7)−O(2)	1.1459(19)	1.1408(17)	1.162(2)	1.1596(18)	1.158(4)	1.145(4)
C(8)−O(3)	1.137(2)	1.1471(18)				1.438(4)
C(8)−C(9)			1.423(2)	1.4227(19)	1.407(4)	1.493(4)
C(9)−C(10)	1.203(2)	1.2096(17)	1.447(2)	1.4446(18)	1.446(4)	1.337(4)
C(10)−C(11)	1.557(15)[a] 1.469(6)	1.4855(16)	1.493(2)	1.4946(18)	1.501(4)	1.407(4)
C(11)−C(13)						1.418(4)

[a] Data for both positions. [b] Data of one of the two independent molecules in the asymmetric unit.

group is engaged in hydrogen bonding with the C≡C π-system of a neighbor, although the interaction is not as strong as in **2d** (C(9)−O(4B) 3.3224(1) Å, C(10)−O(4B) 3.3672(2) Å). In the second position, the OH group acts as a hydrogen bond donor to the oxygen atom of the OH group (intermolecular contact H(4A)···O(4B) 2.4045(1) Å), which is in close proximity to the C≡C π-system. These two interactions are shown in Figure 2b.

The corresponding reactions between **1** and alkynes HC≡C-$(CH_2)_n$OH (n = 2, 3, 4) resulted in the formation of complexes $[Mo(C{\equiv}C\{CH_2\}_nOH)(\eta^5\text{-}C_5H_5)(CO)_3]$ (n = 2, **3a**; n = 3, **3b**; n = 4, **3c**). In this context, it should be noted that Liu and coworkers have described the synthesis of related complexes $[W(C{\equiv}CCH_2\{CR_2\}_nOH)(\eta^5\text{-}C_5H_5)(CO)_3]$ (n = 1, 2) via a similar route.[29] Reaction of **1** with a range of substituted propargyl ethers HC≡CCH$_2$OR (R = OAc, CH$_2$Ph, salicylate, asprin, and fructopyranose) afforded the corresponding complexes $[Mo(C{\equiv}CCH_2OR)(\eta^5\text{-}C_5H_5)(CO)_3]$ (R = OAc, **4a**; R = CH$_2$Ph, **4b**; R = salicylate, **4c**; R = asprin, **4d**; and R = fructopyranose, **4e**) (Scheme 2). In each case, the products could be isolated following chromatography on silica gel and were characterized by both NMR and IR spectroscopy as well as high-resolution mass spectrometry. These results demonstrated that the coupling method was tolerant to a range of different functional groups on the alkyne and represents the desired method to prepare potential CO-RMs based on the $[Mo(\eta^5\text{-}C_5H_5)(CO)_3]$ fragment from terminal alkynes.

Formation of Allyl Complexes. Performing the reaction of **1** with HC≡CCH$_2$OH in the presence of CuI in NEt$_2$H for 20 min did not allow for the alkynyl complex **2a** to be isolated. In this case a new product, which was shown to be the substituted-allyl complex **5a** (Scheme 3), was isolated. The IR spectrum of **5a** recorded in CH$_2$Cl$_2$ solution exhibited two sharp bands in the metal−carbonyl stretching region at 1931 and 1843 cm^{-1}, consistent with the presence of two mutually *cis* carbonyl ligands. In addition a further band in the spectrum was observed at 1602 cm^{-1}, which was assigned to the amide group. The ^{1}H NMR spectrum of **5a** displayed a resonance for an η^5-cyclopentadienyl group at δ 5.12 and also showed evidence for the two NEt$_2$ groups. In one instance the ethyl groups were equivalent (one resonance observed for the methyl group and two for the diasterotopic methylene protons); in the other case, the ethyl groups were found to be nonequivalent (two resonances for the methyl groups were observed and four signals for the methylene protons). In addition to these peaks, three further resonances were observed for the allyl group at δ 2.99 (apparent t, 1H, $^4J_{HH}$ = 3.0 Hz), 3.50 (d, 1H, $^4J_{HH}$ = 3.5 Hz), and 4.09 (d, 1H, $^4J_{HH}$ = 2.5 Hz). A COSY experiment demonstrated that the resonance at δ 2.99 was coupled to those at δ 3.50 and 4.09, but the latter two peaks did not exhibit a mutual coupling. A HMQC experiment demonstrated that the resonance at δ 4.09 was coupled to a CH resonance in the $^{13}C\{^1H\}$ NMR spectrum at δ 37.7, whereas the two other proton resonances for the allyl group showed a coupling to a CH$_2$ resonance at δ 23.4. The $^{13}C\{^1H\}$ NMR spectrum of **5a** also exhibited a resonance at δ 140.9, which was assigned to the central carbon atom of the allyl ligand. Two resonances for the carbonyl groups attached to the metal were observed at δ 250.9 and 246.4, and a peak at δ 175.0 was assigned to the carbon atom of the amide group.

In a similar manner, prolonged reaction of **1** with HC≡CCH$_2$-(OH) in the presence of CuI in pyrrolidine and piperidine as solvents afforded complexes **5b** and **5c**, respectively. In the case of the reaction with piperidine an additional product, **6**, was isolated (see text). Complexes **5a**−**c** exhibited a similar series of spectroscopic features, and, in addition, their structures were confirmed by single-crystal X-ray diffraction experiments. The molecular structures of the complexes are shown in Figure 4, with selected bond lengths in Table 1. The structural determinations demonstrated that, as predicted on the basis of the spectroscopic data, the complexes all possessed analogous structures. The molybdenum is coordinated by an η^5-cyclopentadienyl and two carbonyl ligands, and the bond lengths within these groups are essentially as expected. The remaining coordination sites at the metal are occupied by a single ligand formed by the condensation of the propargyl alcohol with two equivalents of the

Table 2. Data Collection and Structural Refinements Details for Single-Crystal X-ray Diffraction Studies of Complexes 2c, 2d, 5a, 5b, 5c, and 6

	2c	2d	5a·CH_2Cl_2	5b	5c	6
empirical formula	$C_{13}H_{12}MoO_4$	$C_{18}H_{14}MoO_4$	$C_{19.50}H_{29}ClMoN_2O_3$	$C_{19}H_{24}MoN_2O_3$	$C_{21}H_{28}MoN_2O_3$	$C_{19}H_{23}MoNO_5$
fw	328.17	390.23	470.84	424.34	452.39	441.32
temperature/K	110.0	110(2)	110(2)	110(2)	110(2)	110(2)
wavelength/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	monoclinic	monoclinic	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2(1)/n$	$C2/c$	$P\bar{1}$	$C2/c$	$Pna2(1)$
a/Å	6.5791(4)	9.4514(16)	30.691(3)	8.2474(11)	22.297(11)	17.023(3)
b/Å	8.2078(5)	12.599(2)	9.9703(10)	10.4284(14)	7.938(4)	8.5476(13)
c/Å	12.1346(8)	13.711(2)	15.1389(15)	10.9979(15)	23.925(12)	25.323(4)
α/deg	90.3600(10)	90	90	75.001(2)	90	90
β/deg	95.5800(10)	90.867(3)	111.134(2)	74.407(2)	108.277(11)	90
γ/deg	92.2120(10)	90	90	83.552(2)	90	90
volume/Å^3	651.64(7)	1632.6(5)	4321.0(7)	879.1(2)	4021(3)	3684.7(10)
Z	2	4	8	2	8	8
density (calculated)/ Mg m^{-3}	1.672	1.588	1.448	1.603	1.495	1.591
absorp coeff/mm^{-1}	1.009	0.820	0.751	0.767	0.676	0.741
F(000)	328	784	1944	436	1872	1808
cryst size/mm^3	0.37 × 0.11 × 0.10	0.20 × 0.20 × 0.08	0.35 × 0.19 × 0.19	0.35 × 0.22 × 0.16	0.22 × 0.21 × 0.18	0.26 × 0.06 × 0.04
ϕ range for data collection/deg	1.69 to 28.25	2.20 to 30.04	2.16 to 28.30	1.98 to 28.38	1.79 to 28.42	1.61 to 28.30
index ranges	$-8 \le h \le 8$	$-13 \le h \le 13$	$-40 \le h \le 40$,	$-11 \le h \le 11$	$-29 \le h \le 29$	$-22 \le h \le 22$
	$-10 \le k \le 10$	$-17 \le k \le 17$	$-13 \le k \le 13$,	$-13 \le k \le 13$	$-10 \le k \le 10$	$-11 \le k \le 11$
	$-16 \le l \le 16$	$-19 \le l \le 19$	$-20 \le l \le 20$	$-14 \le l \le 14$	$-31 \le l \le 31$	$-33 \le l \le 33$
reflns collected	6723	18 156	29 065	9054	19 781	36 194
indep reflns	3181[R(int) = 0.0157]	4706 [R(int) = 0.0156]	5374 [R(int) = 0.0218]	4322 [R(int) = 0.0119]	4968 [R(int) = 0.0753]	9139 [R(int) = 0.0387]
completeness to θ	98.7% (to 28.25)	98.4% (to 30.04)	100% (to 28.30)	98.2% (to 28.38)	98.2% (to 28.42)	99.9% (28.30)
absorp correction	semiempirical from equivalents					
max. and min. transmn	1.000 and 0.830	0.937 and 0.836	0.867 and 0.782	0.885 and 0.791	0.885 and 0.062	0.971 and 0.844
refinement method	full-matrix least-squares on F^2					
data/restraints/params	3181/6/200	4706/0/213	5374/0/260	4322/0/238	4968/0/253	9139/13/500
goodness-of-fit on F^2	1.054	1.044	1.046	1.065	1.031	1.009
final R indices	R1 = 0.0187	R1 = 0.0195	R1 = 0.0243	R1 = 0.0189	R1 = 0.0431	R1 = 0.0291
[$I > 2\sigma(I)$]	wR2 = 0.0464	wR2 = 0.0511	wR2 = 0.0598	wR2 = 0.0473	wR2 = 0.0897	wR2 = 0.0628
R indices (all data)	R1 = 0.0194	R1 = 0.0215	R1 = 0.0266	R1 = 0.0197	R1 = 0.0600	R1 = 0.0375
	wR2 = 0.0469	wR2 = 0.0525	wR2 = 0.0612	wR2 = 0.0478	wR2 = 0.0983	wR2 = 0.0663
largest diff. peak and hole/e Å^{-3}	0.495 and −0.548	0.574 and −0.478	1.025 and −0.757	0.650 and −0.371	1.194 and −0.629	0.905 and −0.357

amine solvent and a further carbonyl group that was presumably initially coordinated to the metal. This has resulted in the generation of an amide group attached to one terminus of the allyl ligand, whereas the second NEt_2 group is attached to the central atom: the allyl group adopts an *endo* configuration. An examination of the bond lengths between the C_3 framework and the molybdenum indicates that the allyl ligand is asymmetrically coordinated to the metal. In all cases, the Mo−C bonds between the two terminal carbon atoms are within the range typically observed for this type of complex (e.g., for **5a** Mo−C(8) 2.3065(15) Å, Mo−C(10) 2.3195(15) Å); however the distance to the central carbon atom is considerably longer (for **5a** Mo−C(9) 2.4851(15) Å). This suggests that the metal has an extremely weak interaction with this carbon atom and the C−C bonds within the allyl ligand are also somewhat longer than expected (for **5a** C(8)−C(9) 1.423(2) Å and C(9)−C(10) 1.447(2) Å). Furthermore, the carbon−nitrogen distance to the central carbon atom suggests the presence of some C−N multiple-bonding character (for **5a**, C(9)−N(2) 1.356(2) Å), and the sum of the bond angles around the nitrogen atom are 359.82° (**5a**), 357.95° (**5b**), and 349.59° (**5c**), suggesting a lack of pyramidalization. One possible interpretation of these data is that the lone pair of the nitrogen atom is involved in significant π-bonding with the allyl group and that the bonding within complexes **5** is best described by a combination of two resonances forms, **A** and **B** (Figure 5). The allyl ligand in structure **A** may simply be viewed as acting in a classical η^3-fashion. In structure **B** the C_3 ligand may be considered to be acting as a metallocyclopropane with no interaction between the central carbon atom and the metal. Here, a formal double bond between the central carbon atom and

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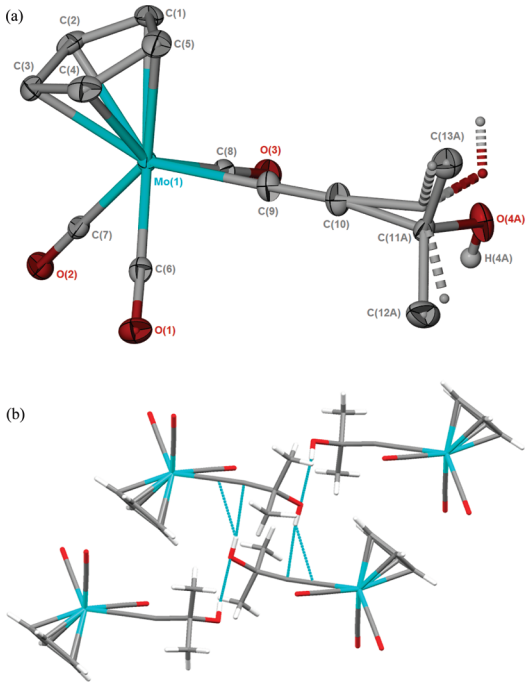


Figure 2. (a) Molecular structure of **2c**. Thermal ellipsoids are shown at the 50% probability level, and hydrogen atoms (except for H(4A)) omitted for clarity. The second disordered conformer of the CMe_2OH group is shown with dashed bonds. (b) Hydrogen-bonding arrangements in the solid state.

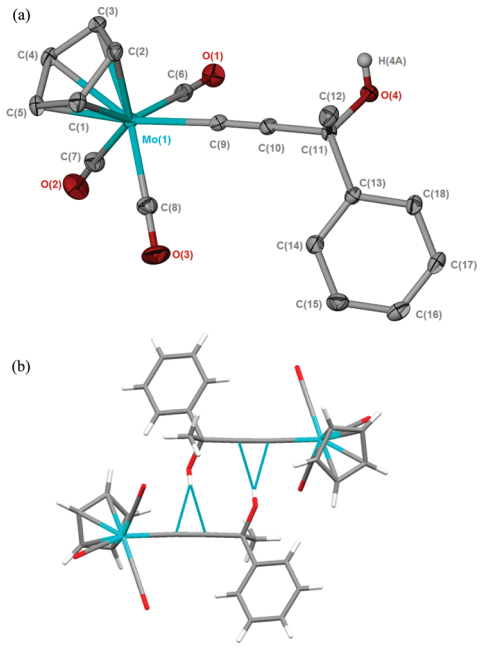
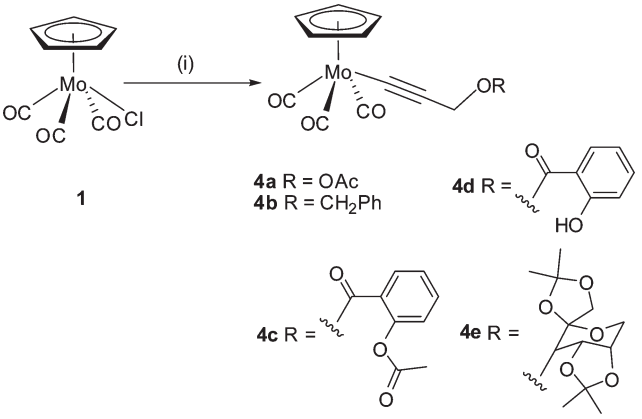


Figure 3. (a) Molecular structure of **2d**. Thermal ellipsoids are shown at the 50% probability level, and hydrogen atoms (except for H(4A)) omitted for clarity. (b) Packing diagram showing OH-π hydrogen-bonding motif.

the metal is present with a formal negative charge being placed on the molybdenum. Resonance form **B** not only provides a convenient explanation for the unusually long Mo−C bond lengths observed in the structures of **5** but also provides a rationale for

Scheme 2[a]



[a] (i) + $HC{\equiv}CCH_2OR$, CuI, $NHEt_2$ (**2b**−**e**), 20 min.

the remarkably low stretching frequency for the metal carbonyl bands in the IR spectrum. For comparisons, the *endo* isomer of $[Mo(\eta^3\text{-}C_3H_5)(\eta^5\text{-}C_5H_5)(CO)_2]$ exhibits bands at 1970 and 1903 cm^{-1} in cyclohexane solution,[30] whereas the analogous bands in **5a** occur at 1931 and 1843 cm^{-1}, consistent with the metal center being far more electron rich. This type of asymmetry in the binding of the allyl ligand may be contrasted with, for example, complexes based on the $[M(\eta^3\text{-allyl})(L)(CO)(NO)]$ ($L = \eta^5\text{-}C_5H_5$ or Tp), in which a shift from $\eta^3-\eta^2$ type binding is observed due to the different π-acidities of the NO^+ and CO ligands.[31]

As indicated above, the reaction of **1** with $HC{\equiv}CCH_2(OH)$ in the presence of CuI employing piperidine as solvent gave, in addition to **5c**, a further product, **6**, which could be isolated following column chromatography on silica gel. The IR spectrum of **6** exhibited two bands in the metal carbonyl stretching region at 1990 and 1931 cm^{-1}, which would appear to indicate that the metal in **6** is somewhat less electron rich than in **5c**. A further C−O stretching band was observed at 1596 cm^{-1}, which was assigned to the presence of an amide group. A high-resolution mass spectrum of **6** indicated that the product had arisen from the condensation of two molecules of $HC{\equiv}CCH_2(OH)$ with a molecule of the amine solvent. The structure of **6** was determined by a single-crystal X-ray diffraction study, which demonstrated that **6** crystallized in the orthorhombic space group $Pna2_1$ and that the asymmetric unit contained both enantiomers of **6** (Figure 6). The structural determination showed that the molybdenum atom in **6** was coordinated by a η^5-bound cyclopentadienyl ring and two metal carbonyl groups. The remaining coordination sites at the metal were shown to be occupied by a single ligand, formed (as expected on the basis of the data from mass spectrometry) from two molecules of $HC{\equiv}CCH_2(OH)$ and a piperidine group as part of an amide group. As in the case of complexes **5**, the CO group of this amide is assumed to have arisen from coupling of a metal carbonyl with the amine solvent. The alkynes have coupled in such a manner to create an η^3-butadienyl ligand, and the bond lengths within this group demonstrate that the ligand is asymmetrically bound to the metal with Mo(1)−C(10) (2.181(3) Å) being shorter that the remaining molybdenum carbon bonds (Mo(1)−C(11) 2.300(3) Å; Mo(1)−C(13) 2.352(3) Å). This has been observed in other molybdenum butadienyl ligands,[32,33] although in some other examples of Group 6 metals the binding is more symmetric.[34]

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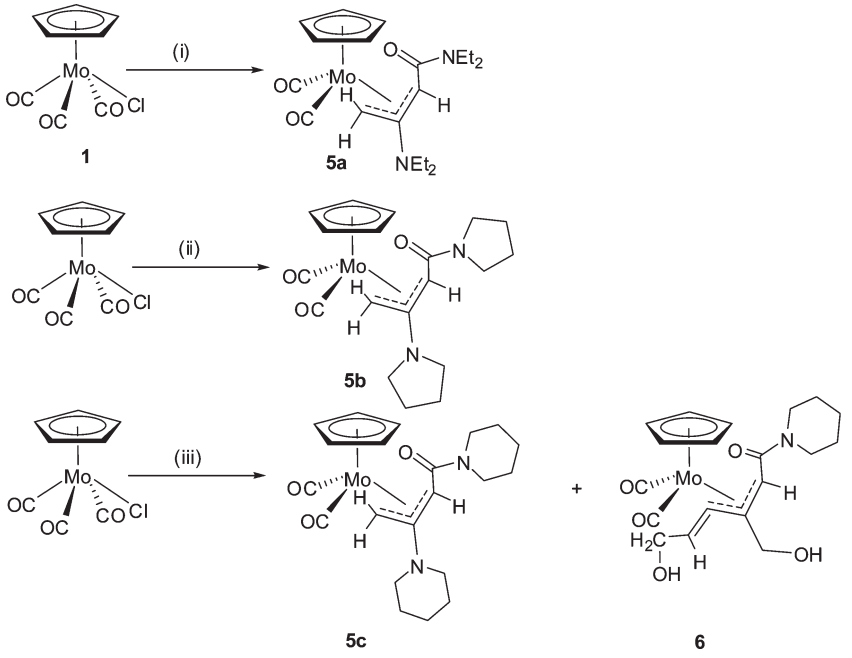
Scheme 3[a]



[a] (i) + $HC{\equiv}CCH_2(OH)$, CuI, $NHEt_2$; (ii) + $HC{\equiv}CCH_2(OH)$, CuI, pyrrolidine; (iii) + $HC{\equiv}CCH_2(OH)$, CuI, piperidine.

The NMR spectra of **6** exhibit a number of pertinent features that would be expected on the basis of the structure determined by X-ray crystallography. For example in the ^1H NMR spectrum a resonance at 6.71 (dd, J = 6.0 Hz, 8.0 Hz, 1H) for the proton attached to the C-terminus of the alkene ligand was observed. Furthermore the $^{13}C\{^1H\}$ NMR spectrum exhibited diagnostic resonances at δ 170.1, 92.0, and 86.9 for the three molybdenum-bound atoms of the butadienyl ligand:[33] a resonance for the uncoordinated carbon atom of this ligand was observed at δ 116.0.

A number of further experiments were undertaken in order to gain insight into the mechanism by which complexes **5** and **6** were formed. In the first instance, a sample of **2a** was simply dissolved in $NHEt_2$. This resulted in the rapid (ca. 20 min) formation of **5a** as the only product from the reaction, indicating that CuI was required only for the formation of the alkynyl complexes and was not necessary for the subsequent generation of the allyl complexes. In addition, it was observed that dissolution of **4a**, $[Mo(C{\equiv}CCH_2OAc)(\eta^5\text{-}C_5H_5)(CO)_3]$, in $NHEt_2$ also resulted in the formation of **5a**.

These results demonstrated that, at least in the case of the unsubstituted alkynes, coupling between the alkynyl ligand, a carbonyl ligand, and the amine solvent may occur. Similar coupling reactions between carbonyl ligands and amines have also been observed in the case of Group 6 tricrabonyl complexes containing η^1-propargyl ligands[35] and related species with an η^2-bound tritylallene.[36] In the latter case, as in the chemistry reported here, an allyl ligand with a terminal amido group was prepared. However, in contrast to the chemistry reported by Lin, the reaction of complexes **2** with the amine is a condensation reaction and also leads in the incorporation of an additional amino group in the backbone of the resulting allyl ligand. This additional amino group does appear to be responsible for the asymmetric binding of the allyl ligand.

CO-Release Tests. The ability of selected complexes to release CO (as potential CO-RMs) was assessed using an assay based on the conversion of deoxymyoglobin (deoxy-Mb) to carbon monoxymyoglobin (MbCO).[37−39] Here a solution of deoxy-Mb of known concentration is treated with the appropriate metal carbonyl compound, and any CO released from the coordination sphere of the metal is subsequently captured by the protein to form MbCO. This conversion is monitored effectively by observing the changes in the Q-bands of the protein between 500 and 600 nm, thus allowing the rate and extent of CO to be quantified.

The abilities of complexes **1**, **4b**, and **4e** were all evaluated in this fashion, as was $[Mo(C{\equiv}CPh)(\eta^5\text{-}C_5H_5)(CO)_3]$, **7**, prepared by the method of Bruce.[8] Complex **1** exhibited fast and controlled CO release. A typical series of spectra for the conversion of deoxy-Mb to MbCO by this complex are shown in Figure 7. Solutions of **1** with concentrations of 60, 40, and 20 μM were evaluated, which exhibited half-lives for CO release of 644, 615, and 863 s, respectively. Complexes **4b** and **7** proved to be insoluble in the aqueous medium used for the assay, and an upshift in the baseline was immediately observed: no CO release was subsequently detected. In contrast **4e** proved to be soluble in the assay medium and released CO very slowly. An experiment with a 60 μM solution of **4e** resulted, after two hours, in the generation of an MbCO solution with a concentration of 2.2 μM.

The potential for the photochemical promotion of CO release from transition metal complexes has been reported.[40] Dimeric $[Mn_2(CO)_{10}]$ was the first compound where photochemically induced CO release was observed,[37] and this has found application in a number of animal studies.[41] Also, $Mn(CO)_3$ complexes supported by tris(pyrazolyl)methane[20] and imidazole-based phosphine ligands[17] release CO only on exposure to UV light, as does $[W(CO)_5(TPPTS)]^{3-}$ ($TPPTS^{3-}$ = tris(sulfonatophenyl)phosphine trianion).[21] Similarly the CO release from **4e** could also be promoted by exposure to UV light. Solutions of **4e** with concentrations of 60, 40, and 20 μM were prepared and exposed to light of wavelength 325 nm from a 6 W hand-held lamp. This resulted in a far more rapid release of CO when compared to the thermal reaction, with the 60, 40, and 20 μM

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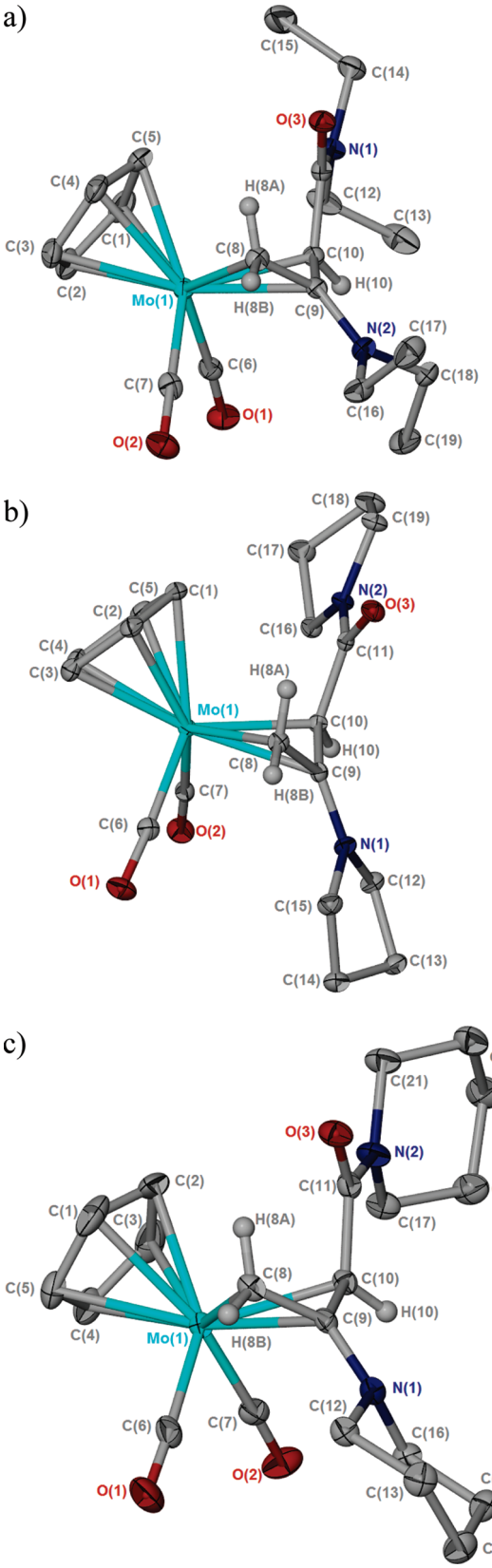

Figure 4. Molecular structure of complex **5a** (top), **5b** (middle), and **5c** (bottom). Thermal ellipsoids are shown at the 50% probability level, and hydrogen atoms (except for those attached to the allyl group) omitted for clarity. A CH_2Cl_2 of crystallization is also omitted from the structural representation of **5a**.

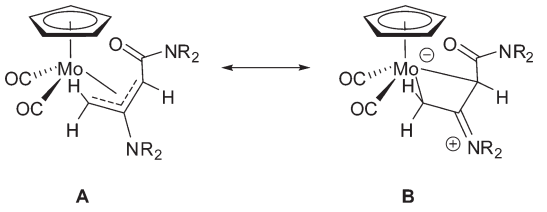

Figure 5. Proposed resonance forms for the bonding between the allyl ligand and the molybdenum in complexes **5**.

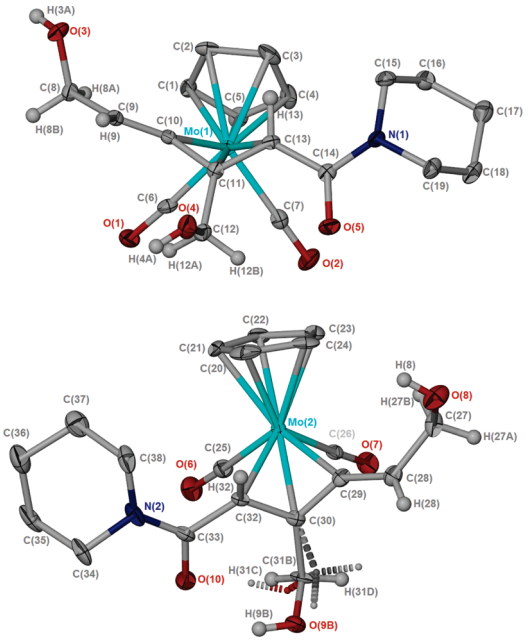

Figure 6. Structure of the two independent molecules in the asymmetric unit of complex **6**. Thermal ellipsoids are shown at the 50% probability level, and hydrogen atoms (except for those attached to the butadienyl ligand and OH groups) omitted for clarity. The bond lengths and angles within the two independent molecules are generally statistically identical: disorder in one CH_2OH group is shown with dotted lines.

solutions exhibiting half-lives of 962, 966, and 778 s, respectively. Furthermore, the solution of **4e** with a concentration of 20 μM resulted in the formation of an MbCO concentration of 44.8 μM over the course of 2.5 h, indicating that each complex was releasing ca. 2.2 molecules of CO. These data show that complex **4e** has the potential to act as a light-activated water-soluble CO-RM, capable of releasing multiple molecules of CO.

In conclusion, we have shown that the copper-promoted coupling of propargyl-substituted alkynes, $HC{\equiv}CCR^1R^2(OR^3)$, to $[Mo(\eta^5\text{-}C_5H_5)Cl(CO)_3]$ is a versatile method for the incorporation of a range of different functional groups into the coordination sphere of the metal. In the case of the parent propargyl alcohol, the resulting alkynyl complex $[Mo(C{\equiv}CC\text{-}H_2\{OH\})(\eta^5\text{-}C_5H_5)(CO)_3]$ undergoes a rapid reaction with the secondary amine solvent to give substituted allyl complexes. The fructopyranose-substitued alkynyl complex is a water-soluble CO-release molecule where release may be stimulated by exposure to UV light.

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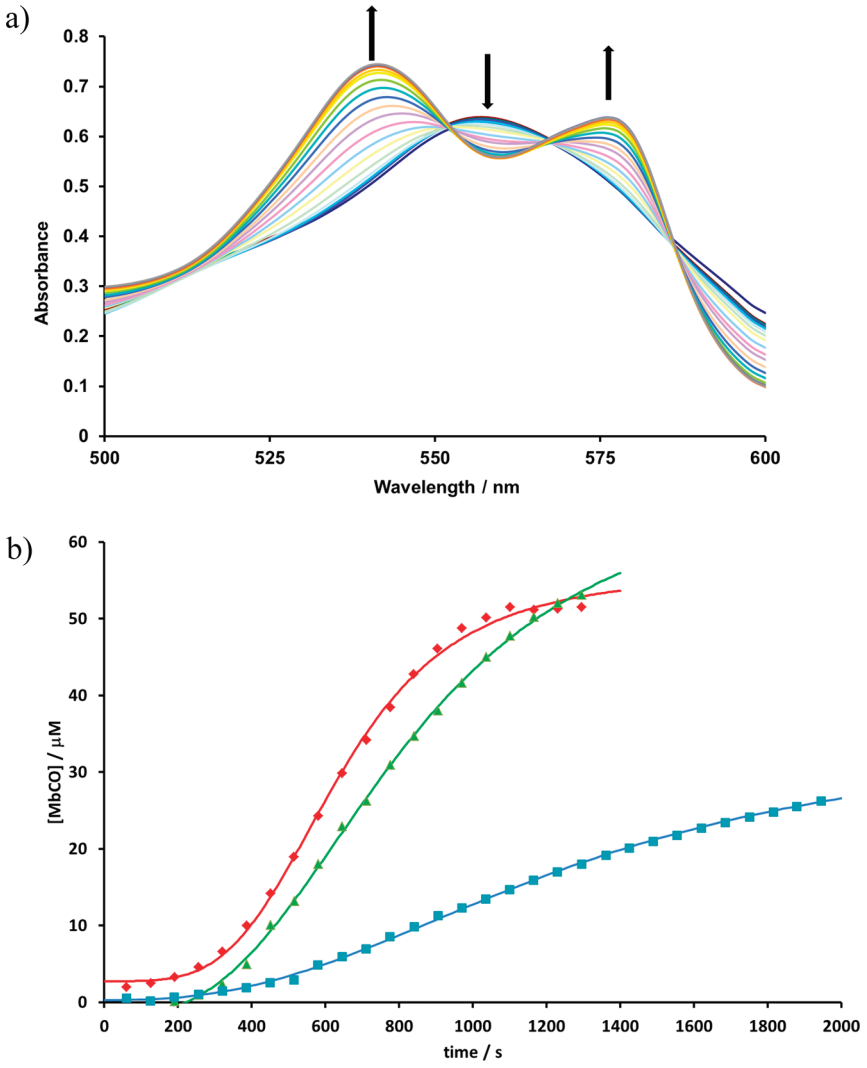

Figure 7. CO release profile for **1**. (a) UV−vis spectrum showing the Q-bands during the conversion of deoxy-Mb to MbCO with time for a 60 μM solution. (b) Plot of [Mb-CO] against time: (red ◆) [**1**] = 60 μM, (green ▲) [**1**] = 40 μM, and (blue ■) [**1**] = 20 μM.

EXPERIMENTAL SECTION

All manipulations were conveniently accomplished by using standard Schlenk line and glovebox apparatus. [Mo(η^5-C_5H_5)Cl(CO)$_3$], **1**, was prepared according to a modified literature procedure.[42] Mo(CO)$_6$ was purchased from Strem Chemicals Inc. and propargylic alcohols were obtained from Aldrich. 2-Propinyl salicylate,[43] (2-propinyl)-2-acetyl salicylate,[43] and 1,2:4,5-di-*O*-isopropylidene-3-*O*-(2-propinyl)-β-D-fructopyranose[44] were prepared according to the literature methods. IR spectra were acquired on a Mattson Research Series FT-IR spectrometer using CsCl solution cells. NMR spectra were recorded using $CDCl_3$ as solvent on either a Bruker AMX300 (operating frequencies ^{1}H 300.13 MHz, ^{13}C 76.98 MHz), Bruker AV500 (operating frequencies ^{1}H 500.13 MHz, ^{13}C 125.77 MHz), Bruker AV700 (operating frequencies ^{1}H 700.13 MHz, ^{13}C 176.05 MHz), or JEOL EX400 (operating frequencies ^{1}H 400.13 MHz, ^{13}C spectroscopic 100.60 MHz) spectrometer. For ^{13}C NMR data, "*cis*" and "*trans*" carbonyl resonances refer to orientation relative to the alkynyl ligand. Mass spectra were obtained using the ESI technique on a Bruker microTOF instrument. CO-release tests were performed as described previously.[13,19,24,39]

Preparation of [Mo(C≡CCH$_2$OH)(η^5-C$_5$H$_5$)(CO)$_3$], 2a. A Schlenk tube was charged with 281 mg (1.0 mmol) of [MoCl(η^5-C_5H_5)(CO)$_3$], and 5 mL of a 1 M solution of NH_2Me in THF was added. HC≡CCH$_2$(OH) (69 μL, 1.2 mmol) was added, and the reaction stirred for 15 min. The solvent was removed under vacuum, and the product isolated by column chromatography. Yield: 180 mg (59%) of an orange-red solid. IR ν (cm^{-1}): 2114 (w) (C≡C), 2044 (s) (C≡O), 1963 (vs) (C≡O). ^{1}H NMR: δ 1.63 (br, 1H, O*H*), 4.28 (s, 2H, C*H*$_2$), 5.50 (s, 5H, η^5-C$_5$*H*$_5$). ^{13}C{^{1}H} NMR: δ 53.4 (CH_2OH), 82.4 (Mo-C≡C), 92.9 (η^5-C_5H_5), 127.4 (Mo-C≡C), 222.8 (*cis*-C≡O), 238.5 (*trans*-C≡O). HRMS: [M + Na]$^+$ 324.9364 (324.9371 expected for $C_{11}H_8MoNaO_4$).

Preparation of Complexes 2b−e, 3a−c, and 4a−e. These species were all prepared according to a general procedure. A Schlenk tube was charged with 281 mg (1.0 mmol) of [MoCl(η^5-C_5H_5)(CO)$_3$], and the appropriate amine (3 mL) was added followed by the propargyl alcohol (1.2 equivalents) and a catalytic amount of CuI. The reaction mixture was stirred for 15−20 min, during which time a color change from red to yellow occurred. After this time, the volatile materials were removed under vacuum. Column chromatography on silica gel with a mixture of CH_2Cl_2 and hexane afforded photosensitive yellow products.

[Mo(C≡CCPh$_2${OH})(η^5-C$_5$H$_5$)(CO)$_3$], 2b. Yield: 280 mg (61%) of a yellow solid. IR ν (cm^{-1}): 2114 (w) (C≡C), 2040 (s) (C≡O), 1963 (vs) (C≡O). ^{1}H NMR: δ 2.68 (s, 1H, O*H*), 5.44 (s, 5H, η^5-C$_5$*H*$_5$), 7.22 (5H, C$_6$*H*$_5$), 7.61 (5H, C$_6$*H*$_5$). ^{13}C{^{1}H} NMR: δ 75.6 (CPh_2OH),

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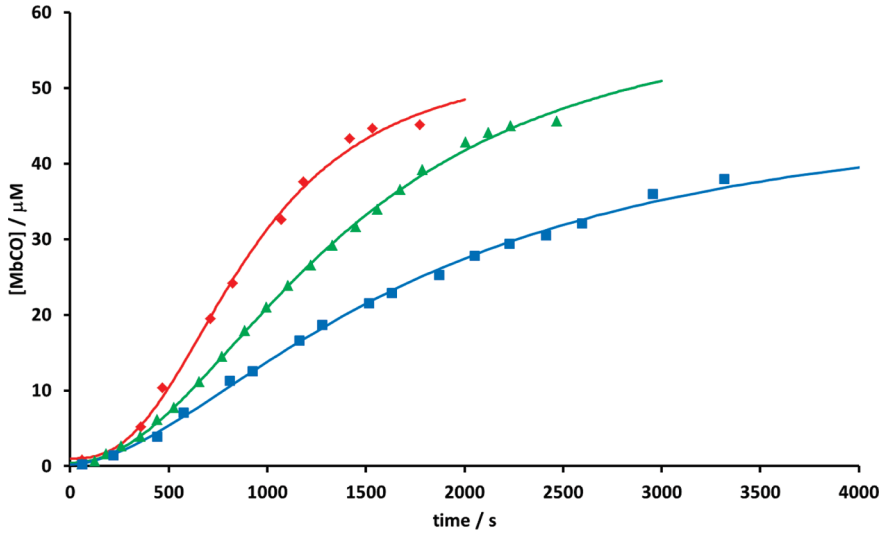

Figure 8. CO release profile for **4e**. Plot of [Mb-CO] against time under exposure to UV light: (red ◆) [**1**] = 60 μM, (green ▲) [**1**] = 40 μM, and (blue ■) [**1**] = 20 μM.

84.1 (Mo-C≡*C*), 92.9 (η^5-*C*$_5$H$_5$), 126.1 (*C*$_6$H$_5$), 127.0 (*C*$_6$H$_5$), 128.0 (*C*$_6$H$_5$), 147.0 (*C*$_6$H$_5$), 131.8 (Mo-*C*≡C), 222.6 (*cis*-*C*≡O), 238.6 (*trans*-*C*≡O). HRMS: [M − OH]$^+$ 437.0 (437.0 expected for $C_{23}H_{16}MoO_4$).

[Mo(C≡CCMe$_2${OH})(η^5-C$_5$H$_5$)(CO)$_3$], 2c. Yield: 150 mg (45%) of an orange solid. IR ν (cm^{-1}): 2113 (w) (C≡C), 2044 (s) (C≡O), 1961 (vs) (C≡O). ^{1}H NMR: δ 1.45 (s, 6H, C*H*$_3$), 1.94 (br, 1H, O*H*), 5.47 (s, 5H, η^5-C$_5$*H*$_5$). ^{13}C{^{1}H} NMR: δ 32.3 (*C*H$_3$), 66.7 (*C*Me$_2${OH}), 75.9 (Mo-C≡*C*), 92.8 (η^5-*C*$_5$H$_5$), 134.4 (Mo-*C*≡C), 222.8 (*cis*-*C*≡O), 239.2 (*trans*-*C*≡O). Anal. Found (expected)/%: C 47.60 (47.58), H 3.66 (3.69). HRMS: [M + Na]$^+$ 352.9675 (352.9687 expected for $C_{13}H_{12}MoO_4Na$).

[Mo(C≡CCPhMe{OH})(η^5-C$_5$H$_5$)(CO)$_3$], 2d. Yield: 250 mg (63%) of a yellow solid. IR ν (cm^{-1}): 2110 (w) (C≡C), 2044 (s) (C≡O), 1963 (vs) (C≡O). ^{1}H NMR: δ 1.70 (s, 3H, C*H*$_3$), 2.30 (br, 1H, O*H*), 5.49 (s, 5H, η^5-C$_5$*H*$_5$), 7.29 (3H, C$_6$*H*$_5$), 7.69 (m, 2H, C$_6$*H*$_5$). ^{13}C{^{1}H} NMR: δ 34.3 (*C*H$_3$), 71.3 (*C*(Ph)MeOH), 80.4 (Mo-C≡*C*), 92.8 (η^5-*C*$_5$H$_5$), 125.3 (*C*$_6$H$_5$), 127.9 (*C*$_6$H$_5$), 128.7 (Mo-C≡*C*), 132.0 (*C*$_6$H$_5$), 147.7 (*C*$_6$H$_5$), 222.7 (*cis*-*C*≡O), 238.8 (*trans*-*C*≡O). Anal. Found (expected)/%: C 55.40 (55.35), H 3.62 (3.62). HRMS: [M + Na]$^+$ 414.9822 (414.9842 expected for $C_{18}H_{14}MoNaO_4$).

[Mo(C≡CCHPh{OH})(η^5-C$_5$H$_5$)(CO)$_3$], 2e. Yield: 87 mg (26%) of an orange solid. IR ν (cm^{-1}): 2114 (w) (C≡C), 2043 (s) (C≡O), 1962 (vs) (C≡O). ^{1}H NMR δ 2.15 (s, 1H, O*H*), 2.72 (s, C*H*), 5.48 (s, 5H, η^5-C$_5$*H*$_5$), 7.07−7.13 (5H, C$_6$*H*$_5$). ^{13}C NMR: δ 66.4 (*C*H), 83.9 (Mo-C≡*C*), 92.9 (η^5-*C*$_5$H$_5$), 126.9 (*C*$_6$H$_5$), 127.7 (*C*$_6$H$_5$), 128.3 (*C*$_6$H$_5$), 128.7 (*C*$_6$H$_5$), 142.6 (Mo-C≡*C*), 222.7 (*cis*-*C*≡O), 238.6 (*trans*-*C*≡O). HRMS: [M + Na]$^+$ 400.9678 (400.9685 expected for $C_{17}H_{12}MoO_4Na$).

[Mo(C≡CC$_2$H$_4${OH})(η^5-C$_5$H$_5$)(CO)$_3$], 3a. Yield: 168 mg (44%) of a yellow solid. IR ν (cm^{-1}): 2116(w) (C≡C), 2040 (s) (C≡O), 1964 (vs) (C≡O). ^{1}H NMR: δ 2.00 (br, 1H, O*H*), 2.55 (t, $^3J_{HH}$ = 8.0 Hz, ≡CC*H*$_2$), 3.58 (br, 2H, C*H*$_2$OH), 5.46 (s, 5H, η^5-C$_5$*H*$_5$). ^{13}C NMR: δ 26.9 (≡C*C*H$_2$), 61.8 (*C*H$_2$OH), 75.1 (Mo-C≡*C*), 93.0 (η^5-*C*$_5$H$_5$), 124.8 (Mo-*C*≡C), 223.1 (cis-*C*≡O), 239.2 (trans-*C*≡O). HRMS: [M + H]$^+$ 316.9707 (316.9708 expected for $C_{12}H_{11}MoO_4$).

[Mo(C≡CC$_3$H$_6${OH})(η^5-C$_5$H$_5$)(CO)$_3$], 3b. Yield: 107 mg (32%) of an orange oil. IR ν (cm^{-1}): 2110 (w) (C≡C), 2042 (s) (C≡O), 1960 (vs) (C≡O). ^{1}H NMR: δ 1.71 (apparent sextet, $^3J_{HH}$ = 6.0 Hz, 2H, C*H*$_2$), 2.43 (t, $^3J_{HH}$ = 6.6 Hz, ≡CC*H*$_2$), 2.54 (br, 1H, OH), 3.78 (t, $^3J_{HH}$ = 5.6 Hz, 2H, C*H*$_2$OH), 5.47 (s, 5H, η^5-C$_5$*H*$_5$). ^{13}C NMR: δ 19.9 (*C*H$_2$), 32.0 (≡C*C*H$_2$), 63.5 (*C*H$_2$OH), 72.6 (Mo-C≡*C*), 92.8 (η^5-*C*$_5$H$_5$), 129.3 (Mo-*C*≡C), 222.8 (*cis*-*C*≡O), 239.4 (*trans*-*C*≡O). HRMS: [M + H]$^+$ 330.9875 (330.9865 expected for $C_{13}H_{13}MoO_4$).

[Mo(C≡CC$_4$H$_8$OH)(η^5-C$_5$H$_5$)(CO)$_3$], 3c. Yield: 190 mg (55%) of an orange solid. IR ν (cm^{-1}): 2115 (w) (C≡C), 2044 (s) (C≡O), 1964 (vs) (C≡O). ^{1}H NMR: δ 1.55 (m, 2H, C*H*$_2$), 1.65 (m, 2H, C*H*$_2$), 1.87 (br, 1H, O*H*), 2.34 (t, 2H, $^3J_{HH}$ = 6.6 Hz, C*H*$_2$), 3.65 (t, 2H, $^3J_{HH}$ = 6.4 Hz, C*H*$_2$OH), 5.47 (s, 5H, η^5-C$_5$*H*$_5$). ^{13}C NMR: δ 14.2 (*C*H$_2$), 22.2 (*C*H$_2$), 32.1 (C*C*H$_2$), 62.5 (*C*H$_2$OH), 70.5 (Mo-C≡*C*), 92.9 (η^5-*C*$_5$H$_5$), 129.8 (Mo-*C*≡C), 222.8 (*cis*-*C*≡O), 239.8 (*trans*-*C*≡O). HRMS: [M + H]$^+$ 330.9875 (343.9946 expected for $C_{13}H_{15}MoO_4$).

[Mo(C≡CCH$_2$OAc)(η^5-C$_5$H$_5$)(CO)$_3$], 4a. Yield: 170 mg (49%) of a yellow solid. IR ν (cm^{-1}): 2125(w) (C≡C), 2045 (s), 1965 (vs) (C≡O), 1732 (m) (C═O). ^{1}H NMR: δ 2.06 (s, 3H, C*H*$_3$), 4.71 (s, 2H, C*H*$_2$), 5.50 (s, 5H, η^5-C$_5$*H*$_5$). ^{13}C{^{1}H} NMR: δ 21.1 (*C*H$_3$), 55.0 (*C*H$_2$OAc), 85.4 (C≡*C*CH$_2$), 92.9 (η^5-*C*$_5$H$_5$), 121.7 (Mo-*C*≡C), 170.7 (*C*═O), 222.8 (*cis*-*C*≡O), 238.5 (*trans*-*C*≡O). HRMS: [M + Na]$^+$ 366.9467 (366.9477 expected for $C_{13}H_{10}MoNaO_5$).

[Mo(C≡CCH$_2$OCH$_2$Ph)(η^5-C$_5$H$_5$)(CO)$_3$], 4b. Yield: 205 mg (49%) of an orange solid. IR ν (cm^{-1}): 2125 (w) (C≡C), 2044 (s) (C≡O), 1963 (vs) (C≡O). ^{1}H NMR: δ 4.23 (s, 2H, ≡CC*H*$_2$), 4.62 (s, 2H, OC*H*$_2$), 5.52 (s, 5H, η^5-C$_5$*H*$_5$), 7.33−7.36 (5H, C$_6$*H*$_5$). ^{13}C{^{1}H} NMR: δ 59.7 (≡*C*CH$_2$), 70.7 (*C*H$_2$), 82.7 (Mo-C≡*C*), 92.9 (η^5-*C*$_5$H$_5$), 124.9 (Mo-*C*≡C), 127.5 (*C*$_6$H$_5$), 128.2 (*C*$_6$H$_5$), 128.3 (*C*$_6$H$_5$), 128.5 (*C*$_6$H$_5$), 222.8 (*cis*-*C*≡O), 238.8 (*trans*-*C*≡O). HRMS: [M + Na]$^+$ 414.9835 (414.9842 expected for $C_{18}H_{14}MoNaO_4$).

[Mo(C≡CCH$_2$OC(O){C$_6$H$_4$-2-OCOMe})(η^5-C$_5$H$_5$)(CO)$_3$], 4c. Yield: 80 mg (17%) of an orange oil. IR ν (cm^{-1}): 2124 (w) (C≡C), 2045 (s) (C≡O), 1965 (vs) (C≡O). ^{1}H NMR: δ 2.39 (s, 3H, C*H*$_3$), 4.92 (s, 2H, C*H*$_2$), 5.52 (s, 5H, η^5-C$_5$*H*$_5$), 7.09−8.05 (4H, C$_6$*H*$_4$). ^{13}C NMR: δ 21.2 (*C*H$_3$),55.8 (*C*H$_2$), 86.3 (C≡*C*), 93.1 (η^5-*C*$_5$H$_5$), 121.5 (Mo-*C*≡C), 123.6 (*C*$_6$H$_5$), 123.7 (*C*$_6$H$_5$), 132.1 (*C*$_6$H$_5$), 123.6 (*C*$_6$H$_5$), 133.8 (*C*$_6$H$_5$), 150.6 (*C*$_6$H$_5$), 164.3 (*C*═O), 170.0 (*C*═O), 222.8 (*cis*-*C*≡O), 238.4 (*trans*-*C*≡O). HRMS: [M + H]$^+$ 464.9863 (464.9871 expected for $C_{20}H_{15}MoO_7$).

[Mo(C≡CCH$_2$OC(O){C$_6$H$_4$-2-OH})(η^5-C$_5$H$_5$)(CO)$_3$], 4d, . Yield: 38 mg (9%) of a yellow solid. IR ν (cm^{-1}): 2123 (w) (C≡C), 2046 (s) (C≡O), 1965 (vs) (C≡O). ^{1}H NMR: δ 4.99 (s, 2H, C*H*$_2$), 5.52 (s, 5H, η^5-C$_5$*H*$_5$), 6.88−7.90 (4H, C$_6$*H*$_4$), 10.7 (s, 1H, O*H*). ^{13}C NMR: δ 55.8 (*C*H$_2$), 87.5 (Mo-C≡*C*), 93.1 (η^5-*C*$_5$H$_5$), 112.7 (*C*$_6$H$_4$), 117.6 (*C*$_6$H$_4$), 119.4 (*C*$_6$H$_4$), 121.1 (Mo-C≡*C*), 130.3 (*C*$_6$H$_4$), 136.1 (*C*$_6$H$_4$),

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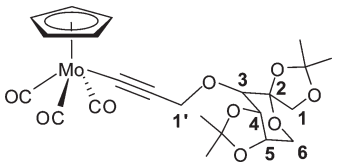
161.6 (C_6H_4), 169.8 (C═O), 222.7 (*cis*-C≡O), 238.3 (*trans*-C≡O). HRMS: $[M + H]^+$ 422.9761 (422.9764 expected for $C_{18}H_{13}MoO_6$).

[Mo(C≡CCH$_2$O-β-D-fructopyranose)(η^5-C$_5$H$_5$)(CO)$_3$], 4e.



Yield: 170 mg (40%) of a yellow powder. IR ν (cm^{-1}): 2113 (w) (C≡C), 2044 (s) (C≡O), 1964 (vs) (C≡O). ^{1}H NMR: δ 1.24 (3H CH_3), 1.34 (3H CH_3), 1.46 (3H CH_3), 1.58 (3H CH_3), 3.91 (m, 2H, CH_2), 4.10 (m, 3H, CH), 4.30 (dd, 1H, J = 5.6 Hz, 8.8 Hz, H^1), 4.36 (d, 1H, J = 8.8 Hz, H^1), 4.46 (d, 1H, J = 15.6 Hz, $H^{1\prime}$), 4.57 (d, 1H, J = 15.6 Hz, $H^{1\prime}$), 5.40 (s, 5H, η^5-C$_5H_5$). ^{13}C NMR: δ 26.2 (CH$_3$), 26.6 (CH$_3$), 27.0 (CH$_3$), 28.3 (CH$_3$), 60.2 (C^6), 61.2 (C^1), 72.1 ($C^{1\prime}$), 72.8 (C^5), 74.1 (C^4), 78.1 (C^3), 83.0 (Mo-C≡C), 92.9 (η^5-C_5H_5), 104.8 (C^2), 109.1 ($C\{CH_3\}_2$), 112.0 ($C\{CH_3\}_2$), 125.0 (Mo-C≡C), 222.7 (*cis*-C≡O), 238.5 (*trans*-C≡O). HRMS: $[M + H]^+$ 545.0714 (545.0709 expected for $C_{23}H_{27}MoO_9$).

General Procedure for the Preparation of Complexes 5. [(η^5-C$_5$H$_5$)Mo(CO)$_3$Cl] (281 mg, 1 mmol) was dissolved in the appropriate amine (3 mL), and HC≡CCH$_2$OH (125 μL, 1.2 mmol) was added followed by a catalytic amount of CuI. The reaction was stirred at 25 °C for 10 to 15 min, and the solvent was then removed under reduced pressure. The residue was purified by column chromatography by elution with hexane and acetone. Crystals were obtained by slow evaporation of a saturated hexane solution of complex with a trace of dry CH_2Cl_2 at −30 or 25 °C.

[Mo(η^3-H$_2$CCN{C$_2$H$_5$}$_2$CHC{═O}N{C$_2$H$_5$}$_2$)(η^5-C$_5$H$_5$)(CO)$_2$], 5a. Yield: 130 mg (41%) of an orange solid. IR ν (cm^{-1}): 1931 (s) (C≡O), 1843 (s) (C≡O), 1602 (m) (C═O). ^{1}H NMR: δ 1.11 (t, 6H, 7.2 Hz, 2CH$_3$), 1.14 (t, 3H, 7.2 Hz, CH$_3$), 1.36 (t, 3H, 7.2 Hz, CH$_3$), 2.93 (m, 2H, CH$_2$), 2.99 (apparent t, 1H, J_{HH} = 3.0 Hz, C═C-CH$_2$), 3.13 (m, 2H, CH$_2$), 3.21 (apparent sextet, 1H, 7.5 Hz), 3.50 (d, 1H, $^2J_{HH}$ = 3.5 Hz, HC═C-CH$_2$), 3.56 (apparent sextet, 1H, 7.0 Hz), 4.01 (apparent sextet, 1H, 7.0 Hz), 4.09 (d, 1H, $^4J_{HH}$ = 2.5 Hz, HC═C-C), 5.12 (s, 5H). ^{13}C{^{1}H} NMR: δ 12.89 (2 × CH$_3$), 13.9 (CH$_3$), 14.0 (CH$_3$), 23.4 (CH-C═CH$_2$), 37.7 (CH-C═CH$_2$), 40.1 (CH$_2$), 41.8 (CH$_2$), 42.9 (2 × CH$_2$), 93.5 (η^5-C$_5$H$_5$), 140.9 (CH-C═CH$_2$), 175.0 (O═C), 246.4 (C≡O), 250.9 (C≡O). Anal. Found (expected)/%: C 53.01 (53.27), H 6.53 (6.59), N 6.39 (6.54). HRMS: $[M + H]^+$ 431.1235 (431.1231 expected for $C_{19}H_{29}MoN_2O_3$).

[Mo(η^3-CH$_2$CN{C$_4$H$_8$}CHC{═O}N{C$_4$H$_8$})(η^5-C$_5$H$_5$)(CO)$_2$], 5b. Yield: 81 mg (19%). IR ν (cm^{-1}): 1932 (s) (C≡O), 1845 (s) (C≡O), 1600 (m) (C═O). ^{1}H NMR: δ 1.60 (br, 4H, CH$_2$), 1.73 (m, 4H, CH$_2$), 2.16 (br, 2H, CH$_2$), 2.62 (br, 2H, CH$_2$), 3.05 (apparent t, J_{HH} = 2.6 Hz, 1H, HC═C-CH$_2$), 3.10 (br, 2H, NCH$_2$), 3.35 (d, $^2J_{HH}$ = 2.8 Hz, HC═C-CH$_2$), 3.72 (br, 2H, NCH$_2$), 3.98 (d, $^4J_{HH}$ = 2.4 Hz, HC═C-CH$_2$), 5.07(s, 5H, η^5-C$_5$H$_5$). ^{13}C{^{1}H} NMR: δ 24.6 (CH$_2$), 24.8 (CH$_2$), 26.4 (CH$_2$), 26.6 (CH$_2$), 29.3 (CH$_2$), 31.8 (H$_2$C═C-CH), 45.7 (CH$_2$), 46.5 (CH$_2$), 93.3 (η^5-C$_5$H$_5$), 135.8 (H$_2$C═C-CH), 174.0 (C═O), 245.9 (C≡O), 250.5 (C≡O). Anal. Found (expected)/%: C 55.72 (55.75), H 6.20 (6.21), N 6.09 (6.19). HRMS: $[M + H]^+$ 427.0910 (427.0918 expected for $C_{19}H_{25}MoN_2O_3$).

[Mo(η^3-CH$_2$CN{C$_5$H$_{10}$}CHC{═O}N{C$_5$H$_{10}$})(η^5-C$_5$H$_5$)(CO)$_2$], 5c. Yield: 70 mg (15%). IR ν (cm^{-1}): 1936 (s), 1851 (s) (C≡O), 1603 (w) (C═O). ^{1}H NMR: δ 1.42 (m, 2H, CH$_2$), 1.50 (m, 6H, 3CH$_2$), 1.63 (m, 4H, 2CH$_2$), 2.88 (m, 4H, 2CH$_2$), 3.21 (apparent t, 1H, J_{HH} = 2.4 Hz, HC═C-CH$_2$), 3.25 (m, 1H, O═C-NCH$_2$), 3.41 (m, 1H, (O═C-NCH$_2$), 3.48 (d, 1H, $^2J_{HH}$ = 2.8 Hz, HC═C-CH$_2$), 3.64 (m, 1H, O═C-NCH$_2$), 3.75 (m, 1H, O═C-NCH$_2$), 4.20 (d, 1H, $^4J_{HH}$ = 2.8 Hz, HC═C-CH$_2$), 5.07 (s, 5H, η^5-C$_5$H$_5$). ^{13}C{^{1}H} NMR: 23.6 (CH$_2$), 24.8 (CH$_2$), 25.4 (CH$_2$), 25.9 (CH$_2$), 26.0 (CH$_2$), 26.6 (CH$_2$), 36.3 (HC-C═CH$_2$), 42.5 (CH$_2$), 46.5 (CH$_2$), 93.2 (η^5-C$_5$H$_5$), 137.1 (HC-C═CH$_2$), 174.8 (C═O), 245.7 (C≡O), 249.3 (C≡O). Anal. Found (expected)/%: C 55.75 (55.21), H 6.24 (5.95), N 6.19 (5.84). HRMS: $[M + H]^+$ 455.1231 (455.1231 expected for $C_{21}H_{29}MoN_2O_3$).

[Mo(η^3-C{═CHCH$_2$OH}C═CHC{═O}NC$_5$H$_{10}$)(η^5-C$_5$H$_5$)(CO)$_2$], 6. Yield: 141 mg (31%). IR ν (cm^{-1}): 1990 (s) (C≡O), 1931 (s) (C≡O), 1596 (m) (C═O). ^{1}H NMR: δ 1.59 (br, 10H, CH$_2$), 3.45 (br, 2H, OCH$_2$), 3.77 (br, 1H, OH), 3.90 (dd, $^4J_{HH}$ = 3.8 Hz, $^3J_{HH}$ = 10.6 Hz, 2H, OCH$_2$), 4.30 (dd, $^4J_{HH}$ = 6.0 Hz, $^3J_{HH}$ = 13.2 Hz, 1H, CH), 4.41 (d, $^3J_{HH}$ = 12.4 Hz, 1H, CH), 5.38 (s, 5H, η^5-C$_5H_5$), 5.67 (br, 1H, OH), 6.71 (dd, $^4J_{HH}$ = 6.0 Hz, 8.0 Hz, 1H, CH). ^{13}C{^{1}H} NMR: δ 24.6 (CH$_2$), 25.8 (CH$_2$), 26.8 (CH$_2$), 43.4 (CH$_2$), 47.4 (CH$_2$), 31.8 (HC═), 64.9 (OCH$_2$), 65.2 (OCH$_2$), 86.9 (Cq), 90.6 (η^5-C$_5$H$_5$), 92.0 (CH), 116.0 (═CH), 170.1 (Cq), 172.4 (NC═O), 232.0 (C≡O), 232.1 (C≡O). Anal. Found (calculated)/%: C 51.71 (50.75), H 5.25 (5.21), N 3.17 (3.01). HRMS: $[M + H]^+$ 444.0688 (444.0707 expected for $C_{19}H_{24}MoNO_5$).

Details of X-ray Diffraction Experiments. Details of the collection and refinement are presented in Table 2. Diffraction data were collected at 110 K on a Bruker Smart Apex diffractometer with Mo Kα radiation (λ = 0.71073 Å) using a SMART CCD camera. Diffractometer control, data collection, and initial unit cell determination were performed using SMART.[45] Frame integration and unit-cell refinement were carried out with SAINT+.[46] Absorption corrections were applied by SADABS (v2.03, Sheldrick).[47] Structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares using SHELXL-97.[48] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using a "riding model" and included in the refinement at calculated positions. CCDC 827195 (**2c**), 827196 (**2d**), 827197 (**5a**), 827198 (**5b**), 827199 (**5c**), and 827200 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Supporting Information. Details of the X-ray structure determination of compounds **2c**, **2d**, **5a**, **5b**, **5c**, and **6** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(26) In addition, complex **2d** undergoes a further reaction in $CDCl_3$ solution over a period of 12 h to give a product, which appears to result from the elimination of water. On the basis of the available data we have tentatively assigned this product as $[Mo(C{\equiv}CC\{Ph\}{=}CH_2)(\eta^5\text{-}C_5H_5)(CO)_3]$. The corresponding elimination of water from methyl-substituted hydroxyvinylidene complexes to give vinylvinylidene ligands has been reported. See: (a) Bustelo, E.; Tenorio, M. J.; Puerta, M. C.; Valerga, P. *Organometallics* **1999**, *18*, 4563. (b) Cadierno, V.; Conejero, S.; Gamasa, M. P.; Gimeno, J.; Rodríguez, M. A. *Organometallics* **2001**, *21*, 203.

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