Synthesis of Molybdenum Dicarbonyl Complexes Bearing Tethered Homoallylic Amines and Sulfides

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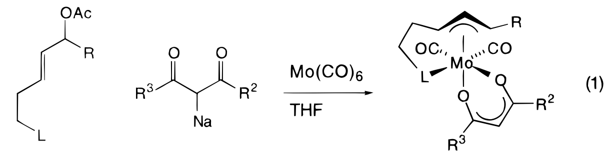
Summary: A series of organomolybdenum complexes, ***8*−*14****, bearing a π-allyl ligand tethered to a chelating heteroatom, have been synthesized from the reaction of allylic acetates* ***1*−*4*** *with the sodium salt of β-dicarbonyl compounds* ***5*−*7*** *and Mo(CO)$_6$ in THF. X-ray structural analysis established the relative configuration at the metal center.*

Allylmetal complexes, as organic reagents or reaction intermediates, are of significant utility in organic chemistry. Among the most noteworthy and commonly used are allylpalladium(+2) complexes,[1] which react with nucleophiles and allylstannanes and allylboranes,[2] which react with electrophiles.[3] π-Allylmolybdenum complexes[4−8] are particularly versatile reagents since they have been shown to react with both electrophiles and nucleophiles, depending on the nature of the other ligands on the complex. As part of our continuing effort to develop new heteroatom-directed organic reactions,[9,10] we now report the synthesis of new organomolybdenum complexes bearing a π-allyl ligand tethered to a chelating heteroatom. It is anticipated that these allylic metal complexes will undergo reactions with electrophiles and/or nucleophiles selectively due to the influence of the chelating heteroatom.

The π-allyl molybdenum complexes **8**−**14** were easily prepared by heating allylic acetates **1**−**4** in the presence of the sodium salt of β-dicarbonyl compounds **5**−**7** and Mo(CO)$_6$ in THF (eq 1 and Table 1).[11] Generally, prolonged heating was found to cause decomposition of the complexes. However, complex **8** was particularly stable and could be heated to 150 °C in a sealed tube in toluene for 48 h without decomposition. The π-allyl complexes could be purified using silica gel column chromatography or by crystallization from hexane at −20 °C. During an investigation into the synthesis of π-allyl complexes with thioether ligands, we found that the analogous molybdenum complexes derived from reaction of allylic acetates **3** or **4** with the sodium salt of diethyl malonate were found to be relatively unstable. The molybdenum complexes could be observed in the crude reaction mixtures using ^{1}H NMR spectroscopy, but decomposed during attempted isolation. The stabil-



(1)

1 L=NMe$_2$ R=H
2 L=NMe$_2$ R=Me
3 L=SMe R=H
4 L=SMe R=Me

5 $R^2 = R^3 = OEt$
6 $R^2 = R^3 = CH_3$
7 $R^2 = CH_3$, $R^3 = CF_3$

	L	R	R_2	R_3
8	NMe$_2$	H	OEt	OEt
9	NMe$_2$	H	CH$_3$	CF$_3$
10	NMe$_2$	Me	OEt	OEt
11	NMe$_2$	Me	CH$_3$	CH$_3$
12	NMe$_2$	Me	CH$_3$	CF$_3$
13	SMe	H	CH$_3$	CH$_3$
14	SMe	Me	CH$_3$	CH$_3$

Table 1

allylic acetate	nucleophile	molybdenum complex	% yield[a]
1	**5**	**8**	88
1	**7**	**9**	75 (1:1)
2	**5**	**10**	75 (1:1)
2	**6**	**11**	81 (6:1)
2	**7**	**12**	69 (*b*)
3	**6**	**13**	84
4	**6**	**14**	73

[a] Isolated yield. [b] See text.

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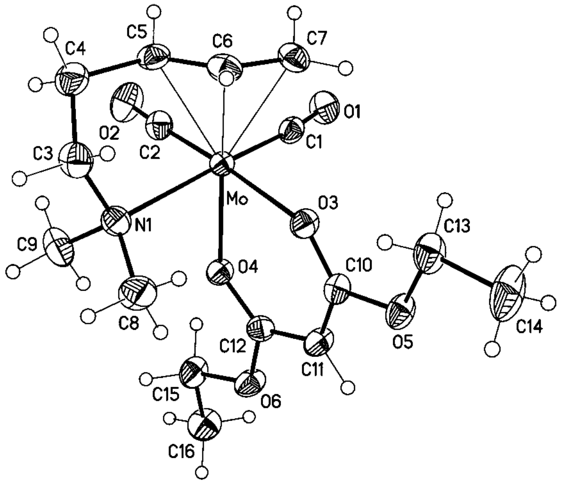

Figure 1. Molecular structure of **8**, with 50% probability ellipsoids, showing the atom-numbering scheme.

ity of the thioether complexes could be increased by exchanging the bidentate ligand, and the corresponding 2,4-pentanedionate complexes **13** and **14** were easily synthesized and purified.

The X-ray structures obtained for complexes **8** (Figure 1) and **14** (Figure 2), which both contain a coordinating heteroatom moiety as part of the tridentate π-allyl ligand, show identical arrangements of ligands around the molybdenum atom as the related (π-allyl)dicarbonylmolybdenum complexes bearing a bidentate ligand reported by Miguel.[12,13] The open face of the allyl moiety is directed toward the two carbonyls, as has been found in other (π-allyl)dicarbonylmolybdenum complexes.[14] Both structures were solved by direct methods in SHELXTL[15] and refined using full-matrix least-squares on F^2. The non-H atoms were refined with anisotropic thermal parameters. All of the H atoms were calculated in idealized positions and were refined riding on their parent atoms except those of C13, C14, C13′, and C14′. These methyl H atoms were found in a difference Fourier map to occupy positions different from their ideal positions and were refined without constraints. Compound **14** has two complexes in the asymmetric unit for a $Z = 8$ in space group $P2_1/c$. Attempts were made to search for possible higher crystallographic symmetry, but none were found. For compound **8**, 218 parameters were refined in the final cycle of refinement using 3475 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 2.38% and 5.74%, respectively. For compound **14**, 410 parameters were refined in the final cycle of refinement using 5211 reflections with $I > 2\sigma(I)$ to yield R_1 and wR_2 of 2.91% and 5.21%, respectively (Table 2). Selected bond lengths and angles for **8** and **14** are listed in the Supporting Information.

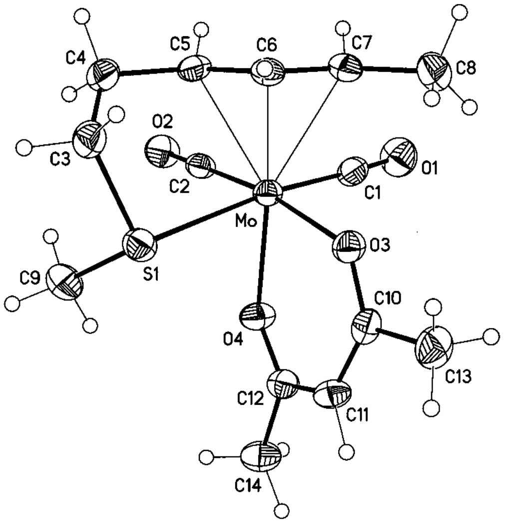

Figure 2. Molecular structure of one molecule of **14**, with 50% probability ellipsoids, showing the atom-numbering scheme.

Table 2. Crystallographic Data

	8	14
A. Crystal Data (173 K)		
a, Å	7.4178(3)	6.6680(1)
b, Å	9.3707(3)	16.3818(4)
c, Å	13.5155(5)	29.3201(6)
β, deg	92.000(1)	91.161(1)
V, Å^3	938.89(6)	3202.1(1)
d_{calc}, g cm^{-3} (173 K)	1.497	1.578
empirical formula	$C_{16}H_{25}MoNO_6$	$C_{13}H_{20}MoO_4S$
fw	423.31	380.30
cryst syst	monoclinic	monoclinic
space group	Pn	$P2_1/c$
Z	2	8
$F(000)$, electrons	436	1552
B. Structure Refinement		
refinement method	full-matrix least-squares on F^2	
S, goodness-of-fit[c]	1.038	1.017
R_1/reflections[a]	2.38/3475 > $2\sigma(I)$	2.91/5211 > $2\sigma(I)$
wR_2/reflections[b]	5.74/3547	5.21/7354
R_{int} (%)	2.34	4.22

[a] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [c] $S = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (0.0370p)^2 + 0.31p]$, $p = [\max(F_o^2,0) + 2F_c^2]/3$.

Interestingly, complexes **8**, **13**, and **14** were obtained as single stereoisomers, but complex **10** was obtained as an inseparable 1:1 mixture of isomers. The ^1H NMR spectrum of this mixture indicated that the isomers are of very similar structure due to the similar chemical shifts and splitting patterns observed for all of the signals. The coupling constant for the triplet assigned

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(11) Typical experimental procedure: Complex 8. A mixture of Mo(CO)$_6$ (308 mg, 1.17 mmol), amine **1** (200 mg, 1.17 mmol), and 0.1 M sodium diethylmalonate (11.7 mL, 1.17 mmol) was refluxed in THF under N_2 for 16 h. After cooling, the mixture was filtered through Celite using EtOAc. The yellow solution was concentrated in vacuo, and the resulting yellow solid was recrystallized from hexane to yield complex **8** as yellow crystals (436 mg, 88%). Mp = 93−94 °C. ^1H NMR (500 MHz, $CDCl_3$): δ 0.99 (d, 1H, J = 9.1 Hz, CHCHC*H*H), 1.20 (t, 3H, J = 7.1 Hz, OCH_2CH_3), 1.37 (t, 3H, J = 7.1 Hz, OCH_2CH_3), 1.77 (s, 3H, $N(CH_3)CH_3$), 2.22 (dd, 1H, J = 3.3, 8.7 Hz, CH_2C*H*CHCH), 2.45 (dd, 1H, J = 4.7, 11.2 Hz, NCH_2CH*H*CH), 2.47 (s, 3H, $N(CH_3)CH_3$), 2.65−2.74 (m, 1H, NCH_2C*H*HCH), 2.80−2.85 (1H, m, NCH*H*), 2.88 (dd, 1H, J = 4.5, 13.6 Hz, NC*H*H), 3.00 (d, 1H, J = 6.6 Hz, CHCHCH*H*), 3.24 (dd, 1H, J = 8.8, 9.0 Hz, CHC*H*CH_2), 3.92 (qd, 1H, J = 7.1, 10.7 Hz, OCH*H*CH_3), 3.97 (qd, 1H, J = 7.1, 10.7 Hz, OCH*H*CH_3), 4.17 (qd, 1H, J = 7.1, 10.7 Hz, OC*H*HCH_3), 4.23 (s, 1H, malonate C−H), 4.40 (qd, 1H, J = 7.1, 10.7 Hz, OC*H*HCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.6, 14.7, 27.4, 47.9, 48.7, 52.7, 59.4, 60.2 (2C), 66.0, 68.9, 77.2, 173.4, 174.5, 226.0, 227.8. IR (soln. in CCl_4): 1950, 1850 cm^{-1}. LRMS (CI, +ve): m/e = 426.4 [M(^{98}Mo) + H$^+$, 100], with associated isotope patterns. Anal. Calcd for $C_{16}H_{25}NO_6Mo$: C, 45.40; H, 5.95. Found: C, 45.34; H, 6.01.

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as the central proton on the π-allyl system is the same in both isomers, suggesting that the complexes both contain the *syn*−*syn*-1,3-disubstituted π-allyl ligand. If the steric bulk of the bidentate ligand is reduced from diethyl malonate to 2,4-pentanedione, a 6:1 mixture of isomeric complexes **11** was obtained instead, which indicates that an unfavorable steric interaction in complex **10** may be caused by the β-dicarbonyl compound. Inspection of molecular models and the related X-ray structure of complex **8** suggests that the likely steric interaction in **10** would be between one of the ethyl esters of the diethyl malonate ligand and the methyl substituent of the 1,3-disubstituted π-allyl ligand. Reaction of allylic acetate **1** with the sodium salt of 1,1,1-trifluoropentanedione and Mo(CO)$_6$ yields **9** as a 1:1 mixture of complexes, since the bidentate ligand can be coordinated in two different orientations. The situation is slightly more complicated with complex **12** prepared from the reaction of the sodium salt of 1,1,1-trifluoropentanedione with allylic acetate **2** and Mo(CO)$_6$. The two major isomers are present in a 1:1 mixture, again due to the two possible orientations of the bidentate ligand as observed in complex **9**, but two other minor isomers are also observed, which is in accordance with the results observed for complex **11**.

New molybdenum dicarbonyl complexes bearing tridentate ligands have been synthesized. The reactivity of these novel complexes is currently under investigation and will be reported in due course.

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Supporting Information Available: Experimental data—including spectral information and analyses—for all compounds, X-ray acquisition information, and associated tables of crystallographic information. This material is available free of charge via the Internet at http://pubs.acs.org.

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