Novel C–C Bond Formation Reactions Mediated by (Oxaallyl)molybdenum Complexes

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Treatment of $Mo(CO)_3(NCMe)_3$ with α-chloroacetophenone yields intermediate aldol condensation products that can be trapped as stable cyclopentadienyl complexes. The reactions are highly stereoselective and give predominantly one isomer of each product. $CpMo(CO)_2$-[η^3-$CH_2C(Ph)$=$CH(COPh)$] and $CpMo(CO)_2$[η^3-$CH_2C(Ph)CHC(Ph)$=$CH(COPh)$] were isolated and characterized by X-ray crystallography.

Allyl transition-metal complexes have been studied extensively owing to their potential for controlling regio- and stereoselectivity in their reactions. Many of these investigations have led to the discovery of useful and effective reactions for stereoselective formation of carbon–carbon bonds.[1] The analogous "oxaallyl" compounds have received less attention owing largely to difficulties encountered in their isolation and characterization. These oxaallyls, which are sometimes described in the literature as η^3-transition-metal enolates, have been assumed to be reactive intermediates in various C–C bond-forming reactions.[2] As part of our efforts to expand the scope of transition-metal-mediated stereoselective carbon–carbon bond formation reactions, we have investigated the potential of α-halo ketones as precursors for oxaallyl complexes in transition-metal-mediated aldol condensation reactions. Low-valent organometallic complexes have been known to effect aldol condensation reactions by activating α-halo ketones.[3] An example of such a transformation is

$$RCOCH_2X + Mo(CO)_6 \xrightarrow[\text{then } H_2O]{DME} RCOCH_3 + RCOCH{=}C\begin{matrix}R\\ \diagup\\ \diagdown\\ CH_3\end{matrix}$$

Many mechanistic questions about the reaction remain to be answered, and the factors determining the partitioning between methyl ketone and aldol product are uncertain.

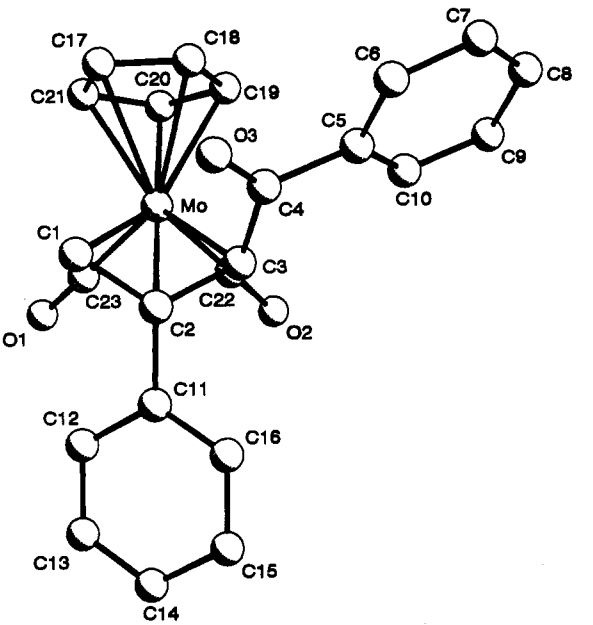

Figure 1. PLUTO drawing of 1.

For the case of $Mo(CO)_6$ in 1,2-dimethoxyethane, α-halo ketones generally afforded the methyl ketone as the major or only product. We anticipated that intermediates might be trapped and greater selectivity in the reactions could be observed by using a different molybdenum reagent and by controlling reaction conditions. We chose to examine the interaction of 2-chloroacetophenone with the more electron rich complex $Mo(CO)_3(NCMe)_3$, expecting that it would be more susceptible to oxidative addition of 2-halo ketones than $Mo(CO)_6$. We found that the reactions could be carried out with less forcing conditions than those where the hexacarbonyl was used, e.g., 0 °C rather than the reflux temperature of 1,2-dimethoxyethane (~85 °C). The products were precursors to aldols rather than methyl ketones.

Results

Treatment of $Mo(CO)_3(NCMe)_3$ with 1 equiv of 2-chloroacetophenone at 0 °C followed by trapping and stabilization of the product by subsequent introduction of LiCp, yielded **1** and **2**. These compounds effectively result from the condensation of two and three acetophenone units, respectively.

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(2) (a) Heathcock, C. H. In *Asymmetric Synthesis*; Morrison, J. D., Ed. Academic Press: New York, 1984; Vol. 3, Part B. (b) Evans, D. A.; Vogel, E.; Nelson, J. V. *J. Am. Chem. Soc.* **1979,** *101,* 6120. (c) Hirama, H.; Garvey, D. S.; Lu, L. D. L.; Masamune, S. *Tetrahedron Lett.* **1970,** *20,* 3937. (d) Inone, T.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1980,** *53,* 174. (e) Heathcock, C. H.; Buse, C. T.; Kleschick, W. A.; Pirrung, M. C.; Sohn, J. E.; Lampe, J. *J. Org. Chem.* **1980,** *45,* 1066. (f) Pirrung, M. C.; Heathcock, C. H. *Ibid.* **1980,** *45,* 1727. (g) Schwartz, J.; Loots, M. J.; Kosugi, H. *J. Am. Chem. Soc.* **1980,** *102,* 1333. (h) Evans, D. A.; McGee, L. R. *Tetrahedron Lett.* **1980,** *21,* 3975. (i) Yamamoto, Y.; Maruyama, K. *Tetrahedron Lett.* **1980,** *21,* 4607. (j) Ito, Y.; Nakatsuka, M.; Kise, N.; Saegusa, T. *Tetrahedron Lett.* **1980,** *21,* 2873.

(3) (a) Alper, H.; Des Roches, D. *J. Org. Chem.* **1976,** *41,* 806. (b) Alper, H.; Keung, E. C. H. *J. Org. Chem.* **1976,** *41,* 806. (c) Yishisato, E.; Tsutsumi, S. *J. Am. Chem. Soc.* **1968,** *90,* 4488.

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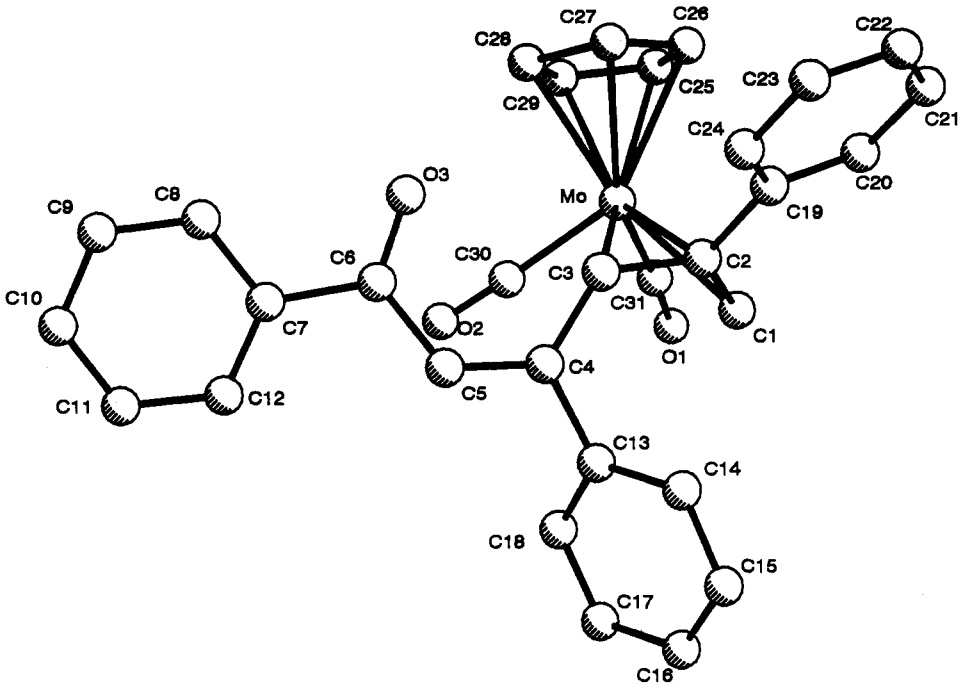
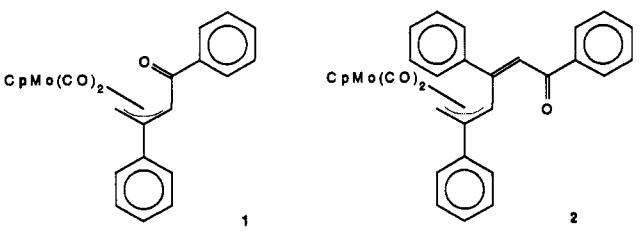


Figure 2. PLUTO drawing of **2**.



Compounds **1** and **2** in the solid state were stable to air and moisture at ambient temperature and were readily isolated with conventional chromatographic techniques. X-ray crystallographic analysis of **1** showed that the solid-state conformation of the allyl relative to the Cp is endo and it contains an anti benzoyl group, as illustrated in Figure 1. However, the crystallographic analysis of compound **2** has revealed that the allyl portion of the ligand has an exo conformation.

Proton NMR and IR spectra are consistent with a single conformer, suggesting that predominantly one conformer (>98%) exists in solution for both **1** and **2**. However, we have previously shown that rapid interconversion of exo and endo conformers occurs in $CpMo(CO)_2(\eta^3$-allyl) complexes.[4] One might not expect large differences in stability in solution because the unfavorable steric interactions of the phenyl group on the allyl in the exo conformation with the Cp ring might be compensated by those of the anti substituent in the endo conformation. The C1–C3 vector in **1** is nearly parallel to the Cp plane, whereas, in **2** there is a significant rotation. This presumably relieves some of the steric strain between the phenyl and the Cp ring. Although one might assume the same conformers are present in solution as in the solid, at this point it is not absolutely clear which conformers predominate in solution. A larger geminal coupling is usually observed in the exo isomer.[4] This indicates that **2** with $|J(H_a-H_s)| = 3.4$ Hz is exo and that **1** with $|J(H_a-H_s)| < 0.5$ is endo; hence this parameter indicates that the stable conformers are the same in the solids as in solution. The high-field shift of the anti proton in **2**, however, is usually associated with an endo conformer, but this might arise from a ring current effect from the phenyl.

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Discussion

Further studies would be needed to elucidate the mechanistic aspects of this reaction; however, a reasonable proposition is that a reactive η^3-oxaallyl complex, such as $(\eta^3$-O=CPhCH$_2$)Mo(CO)$_2$(NCMe)$_2$X, **3′**, is formed initially. This formulation is based on analogous reactions of η^3-allyl complexes that are isolated from reactions between $Mo(CO)_3(NCMe)_3$ and allyl halides.[5] Transition-metal oxaallyl complexes or π-bound enolates have long been proposed as short-lived intermediates in various organic transformations mediated by transition metals.[2] Only recently, however, were such complexes observed by spectroscopic means and, in rare cases, isolated and characterized structurally.[6]

$Mo[\eta^3$-CH$_2$C(Ph)CH(COPh)](CO)$_2$(NCMe)$_2$Cl, **1′**, is presumably the precursor that reacts with CpLi to yield **1**. A plausible mechanism would start by an aldol type reaction of the initially formed oxaallyl complex, **3′**, or more likely, its η^1 counterpart. It appears that reaction of **3′** is facile and self-condensation with another **3′** would yield a species with a Mo–O bond, as shown in Scheme I. The sequence of events in the formation of the olefin double bond is unclear. Nevertheless, the intermediate would eventually yield **1′** on elimination of OH. It is possible that the double bond is not formed until after LiCp is added. We feel, however, that a pathway for formation of **1′** via the condensation of **3′** with free 2-chloroacetophenone is less likely because an experiment using 2 equiv of 2-chloroacetophenone did not alter the yield of **1** significantly.

Subsequent condensation of **1′** or its precursor with **3′** would lead to **2′**, which would be converted to **2** upon

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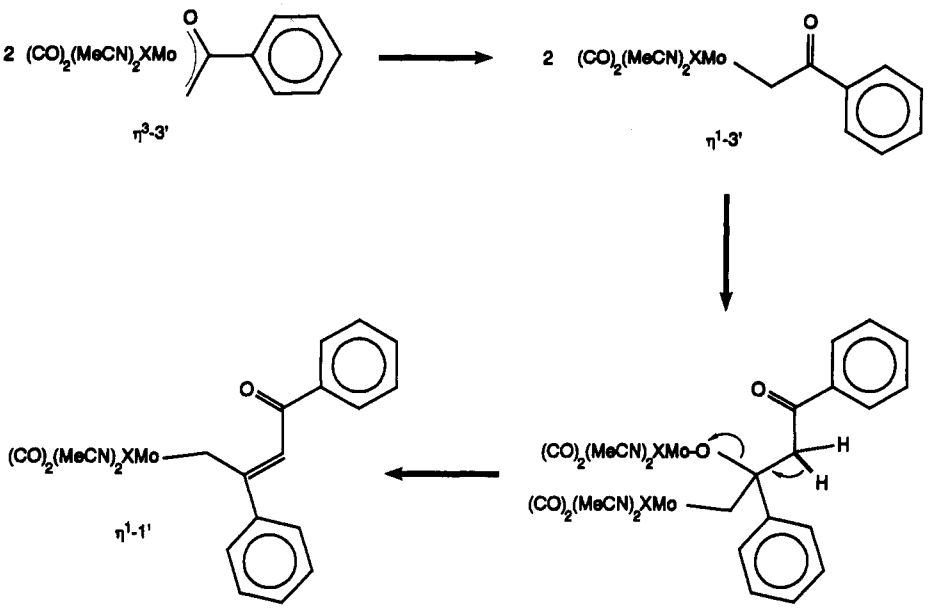
Scheme I



addition of CpLi. This indicates that the oxaallyl species have a fairly rapid reaction rate with themselves but that other ketones, such as complex 1′, can be intercepted by 3′. This suggested that conditions might be developed which would allow reactions with other ketones or aldehydes to give crossed aldol type products.

Preliminary experiments with mixtures of chloroacetophenone, benzaldehyde, and $Mo(CO)_3(NCMe)_3$ did not allow trapping of a stable organometallic compound but yielded a complex mixture of organic products. The GC/MS of the major products suggested that the primary path involved reactions of the benzaldehyde with 1′ and not with 3′. We also did not detect any significant formation of Ph(C=O)CH=CHPh, as a result of crossed aldol condensation between the oxaallyl and benzaldehyde. A similar reaction carried out using acetophenone in place of benzaldehyde did not generate condensation products from acetophenone and 3′ but did yield the organometallic 1. Therefore, it appears that the tendency 3′ has to couple another molecule of 3′ may be too strong for significant cross coupling with unactivated ketones. We are currently investigating conditions to gain better control of the course of the reactions. It appears, however, that there is substantial regiocontrol and stereocontrol in the products having a given formula, and this has potential for synthetic applications.

Liu has reported that a molybdenum ketoallyl similar to 1 yields the alcohol upon treatment with $NaBH_4$ at ambient temperature.[8] This reaction shows a high degree of diastereoselectivity owing to the hindrance of one enantioface of the ketone by the bulky molybdenum moiety. To our surprise, there was little reactivity of 1 toward $NaBH_4$ under similar conditions. Complex 1 does react with DIBAL, however, but unfortunately gives complicated mixtures of products even when carried out at −77 °C.

We[7,9] and others[8,10,11] have developed substantial chemistry that allows the elaboration of molybdenum allyls.

Table I. Crystallographic Data for $CpMo(CO)_2$(1-benzoyl-2-phenylallyl), 1, and $CpMo(CO)_2$(1-benzoylstyryl-2-phenylallyl), 2

1	2
$MoO_3C_{23}H_{18}$	$MoO_3C_{31}H_{24}$
a = 10.043(7) Å	a = 9.948(3) Å
b = 8.593(1) Å	b = 14.828(3) Å
c = 22.158(4) Å	c = 17.380(2) Å
β = 101.27(4)°	β = 106.32(1)°
V = 1876(1) Å^3	V = 2460.2(9) Å^3
Z = 4	Z = 4
fw 438.33	fw 540.47
space group $P2_1/c$ (No. 14)	space group $P2_1/c$ (No. 14)
T = 23 °C	T = 23 °C
ρ = 1.552 g/cm^3	ρ = 1.459 g/cm^3
μ = 59.81 cm^{-1}	μ = 46.70 cm^{-1}
R = 0.041	R = 0.035
R_w = 0.046	R_w = 0.040

The stereochemical control in this system, as shown in the formation of 1 and 2, may prove useful in broader synthetic schemes. We are continuing to explore the potential uses of these novel reactions in stereocontrolled syntheses.

Experimental Section

All manipulations were performed using standard Schlenk conditions. Deuterated solvents were purchased from CID Isotopes and were dried with 4-Å molecular sieves. Acetonitrile was purified by distillation from CaH_2 under nitrogen before use. THF was purified by distillation from potassium benzophenone under nitrogen before use. All other solvents were of analytical grade and were used without further purification. Adsorption alumina (100–200 mesh) was purchased from Fisher.

Preparation of $CpMo(CO)_2[\eta^3$-$CH_2C(Ph)CH(COPh)]$, 1. $Mo(CO)_6$ (6.00 g, 22.7 mmol) was added to 100 mL of acetonitrile and the mixture heated under reflux for 12 h. After the solvent was removed from the resulting yellow solution, 100 mL of freshly distilled THF was added to the residue. The suspension was treated with 4.20 g (27.0 mmol) of 2-chloroacetophenone at 0 °C, and the mixture was allowed to stir as it warmed to room temperature. After 12 h of stirring at room temperature, 1.66 g (23.0 mmol) of CpLi was added and the dark brown mixture was stirred at room temperature for 6 h. The volatiles were removed

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(8) Vong, W.-J.; Peng, S.-M.; Liu, R.-S. *Organometallics* **1990**, *9*, 2187.

(9) Faller, J. W.; Linebarrier, D. L. *Organometallics* **1990**, *9*, 3182–3184.

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(11) Hansson, S.; Miller, J. F.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1990**, *112*, 9660.

Table II. Positional Parameters and *B*(eq) for CpMo(CO)$_2$(1-benzoyl-2-phenylallyl), 1

atom	*x*	*y*	*z*	*B*(eq), Å^2
Mo	0.23355(6)	0.11224(6)	0.20005(3)	2.35(2)
O(1)	0.2895(6)	−0.0983(6)	0.3170(2)	5.0(3)
O(2)	0.5325(6)	0.1902(7)	0.2581(3)	4.9(3)
O(3)	0.0084(5)	0.4339(6)	0.1347(2)	4.1(3)
C(1)	0.0481(7)	0.2021(8)	0.2378(3)	3.0(3)
C(2)	0.1545(7)	0.3098(7)	0.2554(3)	2.4(3)
C(3)	0.2118(6)	0.3806(8)	0.2074(3)	2.3(3)
C(4)	0.1331(7)	0.4350(7)	0.1476(3)	2.7(3)
C(5)	0.2131(8)	0.5014(7)	0.1034(3)	2.6(3)
C(6)	0.1421(8)	0.5794(8)	0.0520(3)	3.6(3)
C(7)	0.210(1)	0.645(1)	0.0097(4)	5.4(5)
C(8)	0.349(1)	0.637(1)	0.0198(4)	5.0(4)
C(9)	0.4207(8)	0.560(1)	0.0698(4)	4.4(4)
C(10)	0.3513(8)	0.4914(8)	0.1111(3)	3.2(3)
C(11)	0.2139(6)	0.3474(7)	0.3214(3)	2.5(3)
C(12)	0.2044(8)	0.2463(8)	0.3702(3)	3.3(3)
C(13)	0.2551(8)	0.292(1)	0.4299(4)	4.0(4)
C(14)	0.3137(9)	0.432(1)	0.4426(3)	4.6(4)
C(15)	0.3236(8)	0.536(1)	0.3953(3)	4.0(4)
C(16)	0.2741(7)	0.4921(8)	0.3348(3)	3.0(3)
C(17)	0.073(1)	0.007(1)	0.1154(4)	5.1(5)
C(18)	0.1520(8)	0.1151(9)	0.0922(3)	3.9(3)
C(19)	0.2885(8)	0.067(1)	0.1057(3)	4.3(4)
C(20)	0.294(1)	−0.074(1)	0.1369(4)	5.4(5)
C(21)	0.161(1)	−0.110(1)	0.1440(4)	6.2(5)
C(22)	0.4170(7)	0.1646(8)	0.2360(3)	2.8(3)
C(23)	0.2652(8)	−0.0176(8)	0.2750(4)	3.4(3)

under vacuum. The residue was dissolved in a minimum amount of methylene chloride and loaded on a 3- × 40-cm alumina column. A red band was eluted with a 1:10 mixture of methylene chloride and hexane, and it was set aside for subsequent workup (vide infra). An orange band was eluted with a 1:1 mixture of methylene chloride and hexane. Removal of the solvent from the orange eluate and recrystallization from a 1:3 mixture of methylene chloride and hexane at −20 °C yielded X-ray quality red-orange crystals of **1** (1.28 g, 2.92 mmol, 12.8%): IR (CH_2Cl_2) ν(CO) 1972 (s), 1901 (s), ν(C=O) 1635 cm^{-1} (m); ^{1}H NMR ($CDCl_3$, 25 °C, 300 MHz) δ 3.87 (d, 1 H, CHH_s, J = 1.9 Hz), 4.19 (s, 1 H, CH_aH), 5.04 (s, 5 H, *H*Cp), 5.47 (d, 1 H, $CH_2C(Ph)CH_{s'}$, J = 1.9), 7.20–8.02 (m, 10 H, 2 C_6H_5). Anal. Calcd for $C_{23}H_{18}O_3Mo$: C, 63.02; H, 4.14. Found: C, 62.4; H, 4.10.

Preparation of CpMo(CO)$_2$[η^3-CH$_2$C(Ph)CHC(Ph)=CH-(COPh)], 2. The first eluate from the chromatographic separation above was allowed to stand 12 h, during which time some red $[CpMo(CO)_3]_2$ dimer precipitated. Removal of the solvent and purification by preparative TLC on silica gel to remove dimer yielded an orange microcrystalline compound. Recrystallization from a mixture of 1:4 methylene chloride and hexane at −20 °C yielded **2** (0.25 g, 0.46 mmol, 2.0%) as red-orange, air-stable crystals: IR (CH_2Cl_2) ν(CO) 1955 (s), 1878 (s), ν(C=O) 1630 cm^{-1} (m); ^{1}H NMR ($CDCl_3$, 25 °C, 300 MHz) δ 1.16 (d, 1 H, CHH_a, J = 3.4 Hz), 3.71 (dd, 1 H, CH_sH, J = 3.4, 1.8 Hz), 5.05 (s, 5 H, *H*Cp), 6.58 (d, 1 H, C$H_{s'}$R, J = 1.8 Hz), 6.65 [s, 1 H, −C(Ph)=C*H*(COPh)], 7.15–7.92 (m, 15 H, $3C_6H_5$). The ^{1}H NMR showed no indication of solvent incorporation, and the formulation was confirmed by X-ray crystallographic analysis.

Crystallographic Studies. Crystals of **1** and **2** measuring approximately 0.27 × 0.29 × 0.31 and 0.27 × 0.24 × 0.14 mm, respectively, were used for X-ray analyses. The crystals were mounted in capillaries and data collected on a Rigaku AFC5S

Table III. Positional Parameters and *B*(eq) for CpMo(CO)$_2$(Benzoylstyryl-2-phenylallyl), 2

atom	*x*	*y*	*z*	*B*(eq), Å^2
Mo	0.05674(4)	0.23152(3)	0.02524(3)	3.64(2)
O(1)	0.1204(6)	0.0305(4)	0.0706(3)	9.6(3)
O(2)	0.3549(4)	0.2358(3)	0.1401(2)	5.8(2)
O(3)	0.2692(4)	0.4475(2)	0.0456(2)	4.6(2)
C(1)	0.0729(6)	0.1510(4)	−0.0880(3)	4.0(3)
C(2)	0.0619(5)	0.2440(3)	−0.1033(3)	3.0(2)
C(3)	0.1718(5)	0.3017(3)	−0.0595(3)	2.9(2)
C(4)	0.3216(5)	0.2882(3)	−0.0420(3)	2.9(2)
C(5)	0.4169(5)	0.3456(3)	0.0044(3)	3.1(2)
C(6)	0.3874(5)	0.4212(3)	0.0505(3)	3.1(2)
C(7)	0.5081(5)	0.4656(3)	0.1100(3)	3.1(2)
C(8)	0.4790(6)	0.5417(4)	0.1486(3)	4.0(3)
C(9)	0.5854(7)	0.5856(4)	0.2052(4)	5.0(3)
C(10)	0.7193(7)	0.5540(4)	0.2230(3)	4.8(3)
C(11)	0.7488(6)	0.4794(4)	0.1861(4)	5.2(3)
C(12)	0.6442(6)	0.4347(4)	0.1288(3)	4.2(3)
C(13)	0.3790(5)	0.2105(3)	−0.0784(3)	3.2(2)
C(14)	0.3356(6)	0.1937(4)	−0.1606(3)	4.4(3)
C(15)	0.3975(8)	0.1266(5)	−0.1938(4)	5.9(4)
C(16)	0.4994(8)	0.0754(5)	−0.1461(6)	6.9(4)
C(17)	0.5427(7)	0.0887(5)	−0.0645(5)	6.3(4)
C(18)	0.4821(6)	0.1569(4)	−0.0312(4)	4.7(3)
C(19)	−0.0642(5)	0.2825(4)	−0.1632(3)	3.3(2)
C(20)	−0.1878(6)	0.2342(4)	−0.1937(3)	4.6(3)
C(21)	−0.2994(6)	0.2709(6)	−0.2510(4)	5.6(3)
C(22)	−0.2911(7)	0.3562(6)	−0.2787(4)	5.7(3)
C(23)	−0.1720(7)	0.4050(5)	−0.2498(4)	5.5(3)
C(24)	−0.0599(6)	0.3685(4)	−0.1927(3)	4.2(3)
C(25)	−0.1483(7)	0.2287(6)	0.0662(5)	7.7(4)
C(26)	−0.1800(7)]	0.2798(7)	−0.0014(4)	7.3(4)
C(27)	−0.0982(9)	0.3552(6)	0.0121(5)	6.8(4)
C(28)	−0.0103(7)	0.3520(6)	0.0916(5)	6.8(4)
C(29)	−0.0437(8)	0.2708(7)	0.1242(4)	7.2(4)
C(30)	0.2455(6)	0.2341(4)	0.0951(3)	3.9(2)
C(31)	0.0901(8)	0.1051(5)	0.0527(4)	6.3(4)

diffractometer using graphite-monochromated Cu Kα radiation. Systematic absences consistent with $P2_1/c$ and monoclinic cells were found for both crystals. The positions of the molybdenum atoms were determined from Patterson maps, and the remaining non-hydrogen atoms were found in subsequent difference Fourier maps using the TEXSAN structure determination package. All hydrogen atoms were included in calculated positions. Anisotropic refinement and absorption corrections were carried out following procedures outlined elsewhere.[9] The results are given in full in the supplementary material but are summarized in Tables I–III.

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Supplementary Material Available: Table S1, giving crystallographic data for X-ray diffraction studies of **1**, Table S2, listing intramolecular bond distances for **1**, Table S3, listing intramolecular bond angles for **1**, Table S4, showing U values for **1**, Table S5, giving crystallographic data for X-ray diffraction studies of **2**, Table S6, listing intramolecular bond distances for **2**, Table S7, listing intramolecular bond angles for **2**, and Table S8, showing U values for **2** (10 pages). Ordering information is given on any current masthead page.

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