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Synthesis, Nujol matrix and solution photochemistry of $M(CO)_2[\eta^5,\eta^3\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_6]$ (where M = Cr or Mo): molecular structures of $Cr(CO)_2[\eta^5,\eta^3\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_6]$, $Mo(CO)_2[\eta^5,\eta^3\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_6]$, and $Mo(CO)[P(C_6H_5)_3][\eta^5,\eta^3\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_6]$[☆]

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Abstract

Reaction of chromium or molybdenum carbonyl with 2,2-bis(cyclopentadienyl)propane yields mixtures of products including $M_2(CO)_6[\eta^5,\eta^5\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_4]$, $M_2(CO)_6[\eta^5\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_4]_2$, and the title compounds, $M(CO)_2[\eta^5,\eta^3\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_6]$, in which an η^3-pentenyl group is tethered to the η^5-cyclopentadienyl (Cp) group by a 2,2-propyl linkage. Although several isomers are possible for the cyclopentenyl groups, chromium and molybdenum appear to form only single, but unique isomers. Photolysis of $M(CO)_2[\eta^5,\eta^3\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_6]$, M = Cr or Mo, in Nujol glass at ca. 77 K has been found to be wavelength-dependent with low energy photolyses resulting in $\eta^3 \rightarrow \eta^1$ transformations while higher energy photolyses result in loss of carbon monoxide. Solution photolysis of the molybdenum derivative with triphenylphosphine yields as a first product $Mo(CO)_2[P(C_6H_5)_3][\eta^5,\eta^1\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_6]$, which undergoes decomposition upon work-up to yield both starting material, and $Mo(CO)[P(C_6H_5)_3][\eta^5,\eta^3\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_6]$. The molecular structures of three compounds have been determined: $Mo(CO)_2[\eta^5,\eta^3\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_6]$: monoclinic, $P2_1/c$, $a = 8.2767(4)$, $b = 19.875(1)$, $c = 7.960(1)$ Å, $\beta = 96.720(6)°$, $V = 1300.4(1)$ Å^3, $Z = 4$, $R(F) = 2.82$; $Cr(CO)_2[\eta^5,\eta^3\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_6]$: monoclinic, $P2_1/c$, $a = 9.960(1)$, $b = 9.1015(6)$, $c = 13.997(1)$ Å, $\beta = 92.460(9)°$, $V = 1267.7(2)$ Å^3, $Z = 4$, $R(F) = 4.67$; $Mo(CO)[P(C_6H_5)_3][\eta^5,\eta^3\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_6]$: monoclinic, $P2_1/c$, $a = 7.939(1)$, $b = 22.381(3)$, $c = 15.050(2)$ Å, $\beta = 103.55(1)°$, $V = 2599.8(5)$ Å^3, $Z = 4$, $R(F) = 4.01$. © 1999 Published by Elsevier Science S.A. All rights reserved.

Keywords: Organometallic photochemistry; Matrix photochemistry; Chromium allyl; Molybdenum allyl; Haptotropic rearrangement

We have recently reported the synthesis of $Ru(CO)_2(\eta^5,\eta^1\text{-}C_5H_4\text{–}CR_2\text{–}C_5H_5)$ [1] and have found it to be a versatile reagent for the synthesis of heterobimetallic compounds of ruthenium with the Group VI metals, iron, nickel, manganese, and rhodium [2]. Green [3] has reported the synthesis of $ZrCl(\eta^5\text{-}C_5H_5)[\eta^5,\eta^2\text{-}C_5H_4C(CH_3)_2C_9H_6]$ which has been shown to react with $ClM(CO)_n$, where M = Mn ($n = 5$) and Rh ($n = 2$) to yield heterobimetallic compounds. In these

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[☆] Dedicated to our dear friend and colleague, Professor Alberto Ceccon, on the occasion of his 65th birthday.

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cases a Cp or indenyl ring is loosely bound in the monometallic compound making it available for reaction with a second metal. Building upon this idea we sought to prepare $M(CO)_3(\eta^5,\eta^1\text{-}C_5H_4{-}CR_2{-}C_5H_5)$, where M is a Group VI metal and R = H or CH_3. While these target molecules remain elusive, we have isolated chromium and molybdenum derivatives of the form $M(CO)_2(\eta^5,\eta^3\text{-}C_5H_4{-}CR_2{-}C_5H_6)$ in which one diene has been reduced to a trihapto allyl. In this paper we describe the synthesis, characterization, and molecular structures of these new compounds, and examine their photochemistry both in solution and in Nujol matrices at ca. 77 K.

1. Results and discussion

1.1. Synthesis of $M(CO)_3(\eta^5,\eta^3\text{-}C_5H_4{-}CR_2{-}C_5H_6)$

By analogy with the previously reported synthesis of $Ru(CO)_2(\eta^5,\eta^1\text{-}C_5H_4{-}CR_2{-}C_5H_5)$ [1], $Br_2Mo(CO)_4$ was reacted with one equivalent of $C(CH_3)_2(C_5H_4Na)_2$ in THF. Work-up of the reaction followed by chromatography yielded only the previously reported $Mo_2(CO)_6[\eta^5,\eta^5\text{-}C_5H_4{-}C(CH_3)_2{-}C_5H_4]$ [4] and $[Mo(CO)_3Br]_2[\eta^5,\eta^5\text{-}C_5H_4{-}C(CH_3)_2{-}C_5H_4]$. Repeating this reaction with $C(CH_3)_2(C_5H_4Tl)_2$ yielded similar results.

Reaction of the neutral ligand 2,2-bis(Cp)propane (mixture of isomers) with $Mo(CO)_6$ or $Mo(CO)_3(CH_3CN)_3$ in refluxing xylene followed by work up and chromatography yielded three bands, a clear yellow band that gave a yellow crystalline solid **I**, a broad red band that was shown by HPLC to consist of a number of components, and $Mo_2(CO)_6[\eta^5,\eta^5\text{-}C_5H_4{-}C(CH_3)_2{-}C_5H_4]$.

The mixture of components making up the broad red band had an IR spectrum consistent with the presence of $(C_5H_4R)_2Mo_2(CO)_6$ units. ^1H- and ^{13}C-NMR spectra of this mixture were complex, but clearly indicated C_5H_4R units and cyclopentadiene or cyclopentene rings. No parent mass was observed in MS, but those fragments observed were consistent with the proposed formulation.

Reaction of the red mixture with K-Selectride yielded a solution in which the $(C_5H_4R)Mo(CO)_3$ anion was identified by IR bands at 1895, 1790, 1746, and 1700 cm^{-1}. Subsequent reaction of this anion mixture with methyl iodide yielded a mixture whose IR bands at 2012 and 1924 cm^{-1} were consistent with the expected $(C_5H_4R)Mo(CO)_3CH_3$ species, but whose NMR was uninterpretable beyond the presence of a substituted metal bound Cp group and a metal bound methyl group.

Photolysis of the red mixture in chloroform resulted in a color change from red to yellow–orange. The IR spectrum of the isolated material showed two terminal carbonyl bands at 2052 and 1972 cm^{-1} virtually identical to those of $(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$. The ^1H-NMR spectrum contained resonances for a metal bound Cp ring and a complex set of resonances consistent with an unbound cyclopentadiene ring. Unfortunately it was not possible to separate the isomers of this mixture even through the use of medium pressure chromatography on silica gel.

The available evidence suggests that a mixture of isomers of $Mo_2(CO)_6[\eta^5\text{-}C_5H_4{-}C(CH_3)_2{-}C_5H_5]$ are formed in the initial reaction. We are currently exploring the possibility of deprotonating the cyclopentadiene ring of these compounds or their methyl and chloride derivatives to permit a second metal to be introduced.

The yellow solid **I**, was found to have two IR bands in the terminal carbonyl region at 1956 and 1879 cm^{-1} (CH_2Cl_2) and 1967 and 1898 cm^{-1} (Nujol) in the carbonyl stretching region. $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-}C_5H_7)$ has been reported to have carbonyl stretching bands at 1950 and 1880 cm^{-1} in alkanes [5]. ^1H- and ^{13}C-NMR spectra were consistent with the formulation of the compound as $Mo(CO)_2[\eta^5,\eta^3\text{-}C_5H_4{-}C(CH_3)_2{-}C_5H_6]$ in which the pendant cyclopentenyl group is asymmetrically bound to the metal. 2-D COSY, NOESY and H–C correlation spectra permitted assignment of all resonances except for the *ipso*-carbons. The numbering diagram for resonance assignments in **I** is presented in Fig. 1.

The molecular structure of **I** was determined from crystals grown by vapor diffusion methods and the resultant structure is presented in Fig. 2. Crystallographic data are summarized in Table 1, while bond length and bond angle data for **I** are presented in Table 2. All bond lengths and angles are within normal ranges and there does not appear to be any significant strain within the ring formed by the metal, η^5-Cp and η^3-cyclopentenyl groups. The bridge atom, C(11) is drawn about 7.9° below the plane of the Cp ring.

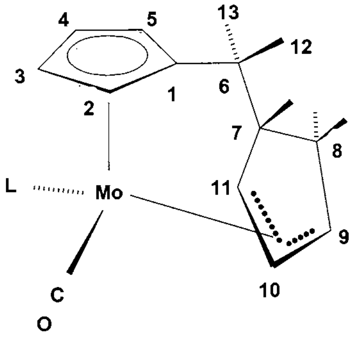


Fig. 1. NMR numbering scheme for **I**, L = CO, and **III**, L = $P(C_6H_5)_3$.

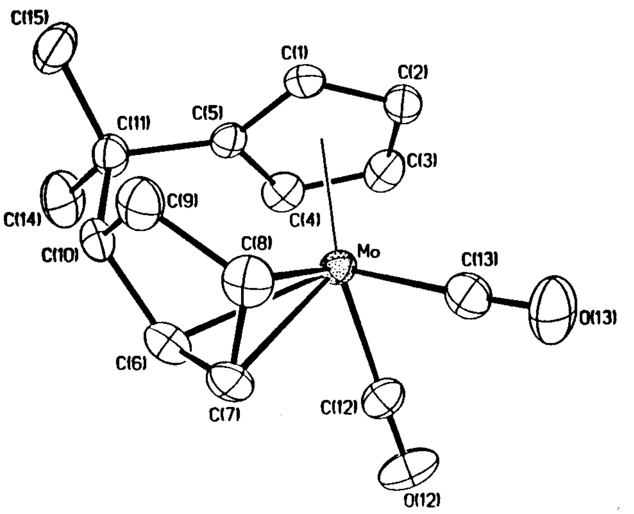


Fig. 2. Molecular structure of **I**.

Reaction of 2,2-bis(Cp)propane with $Cr(CO)_6$ in refluxing 10:1 butyl ether:THF for 48 h yielded, after work-up and chromatography, a single yellow band from which **II** was recovered as a crystalline solid. IR spectra of the reaction mixture after 24 h provided spectral evidence for the presence of $(\eta^5\text{-}C_5H_4R)Cr(CO)_3H$ species. Compound **II** was found to have a pair of IR bands at 1929 and 1856 cm^{-1} (CH_2Cl_2) or 1940 and 1876 cm^{-1} (Nujol) in the terminal carbonyl region. The compound $(\eta^5\text{-}C_5H_5)Cr(CO)_2(\eta^3\text{-}C_5H_7)$ is reported to have IR stretching bands at 1942 and 1880 cm^{-1} in alkane solvents [5]. The ^1H- and ^{13}C-NMR spectra required that the molecule have approximate C_s symmetry and 2-D spectra permitted most resonances to be assigned. Neither the *ipso*-carbon, C-1, nor the allyl carbon, C-7, could be assigned with confidence. The numbering scheme for this molecule is presented in Fig. 3. It is interesting to note that there is no spectral or chromatographic evidence of other isomers of **II**, thus the reactions of molybdenum and chromium yield isomerically pure, but different products.

Crystals of **II** were grown by vapor diffusion and the molecular structure was determined (see Fig. 4). As anticipated, the molecule exhibits approximate C_s symmetry in which the allyl group is centered on the carbon connecting the cyclopentenyl ring to the bridge. Bond lengths and angles for **II** are presented in Table 3. Although most bond lengths and angles in this molecule are within normal ranges, the bond angle of the bridge carbon, C(11)–C(6)–C(5) is compressed to 97.0(3)° compared to an angle of 108.0(4)° for the comparable angle in **I**, indicating considerable strain at this position in **II**. Additionally, C(6) is drawn about 23.2° below the plane of the Cp ring in order to accommodate the bonding of the cyclopentenyl ring. Strain is further reflected in the distortion of the cyclopentenyl ring, C(7)–C(11), from planarity by bending C(8) and C(9) away from the metal. The torsional angle about the C(8)–C(9) bond is 1.3°. C(6) is folded about 34.4° from the plane formed by C(7)–C(10).

Repeated attempts to prepare the tungsten analog of **I** and **II** using both $W(CO)_6$ and $W(CO)_3(CH_3CN)_3$ were unsuccessful.

Table 1
Crystallographic data for $Mo(CO)_2[\eta^5,\eta^3\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_6]$ (**I**) $Cr(CO)_2[\eta^5,\eta^3\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_6]$ (**II**) and $Mo(CO)[P(C_6H_5)_3][\eta^5,\eta^3\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_6]$ (**III**)

	I	II	III
Empirical formula	$C_{15}H_{16}MoO_2$	$C_{15}H_{16}CrO_2$	$C_{32}H_{31}MoOP$
Formula weight	324.22	280.28	558.48
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	8.2767(4)	9.960(1)	7.939(1)
b (Å)	19.875(1)	9.1015(6)	22.381(3)
c (Å)	7.960(1)	13.997(1)	15.050(2)
α (°)	90	90	90
β (°)	96.720(6)	92.460(9)	103.55(1)
γ (°)	90	90	90
V (Å^3)	1300.4(1)	1267.7(2)	2599.8(5)
Z	4	4	4
Crystal color	Yellow block	Yellow block	Yellow block
$D_{calc.}$ (g cm^{-3})	1.656	1.469	1.427
μ(Mo–K_α) (cm^{-1})	9.99	8.92	5.89
Temperature (K)	298(2)	298(2)	298(2)
Radiation	Mo–K_α ($\lambda = 0.71073$ Å)	Mo–K_α ($\lambda = 0.71073$ Å)	Mo–K_α ($\lambda = 0.71073$ Å)
$R(F)$ [a] (%)	2.82	4.67	4.01
$R(wF^2)$ [a] (%)	6.97	13.08	7.29

[a] Quantity minimized $= R(wF^2) = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[(wF_o^2)^2]^{0.5}$; $R = \Sigma\Delta/\Sigma(F_o)$, $\Delta = |(F_o - F_c)|$.

Table 2
Bond lengths (Å) and bond angles (°) for $Mo(CO)_2[\eta^5,\eta^3\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_6]$ (**I**) and $Mo(CO)[P(C_6H_5)_3][\eta^5,\eta^3\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_6]$ (**III**)

Atoms	I	Atoms	III
Bond lengths			
C_1–C_2	1.410(6)	C_{11}–C_{12}	1.407(7)
C_2–C_3	1.391(7)	C_{12}–C_{13}	1.402(8)
C_3–C_4	1.405(6)	C_{13}–C_{14}	1.424(8)
C_4–C_5	1.425(5)	C_{14}–C_{15}	1.424(7)
C_1–C_5	1.412(5)	C_{11}–C_{15}	1.427(7)
C_5–C_{11}	1.536(6)	C_{15}–C_{16}	1.516(7)
C_{11}–C_{10}	1.534(5)	C_5–C_{16}	1.543(7)
C_9–C_{10}	1.562(6)	C_1–C_5	1.546(7)
C_8–C_9	1.493(6)	C_1–C_2	1.511(7)
C_7–C_8	1.408(6)	C_2–C_3	1.410(7)
C_6–C_7	1.399(6)	C_3–C_4	1.400(7)
C_6–C_{10}	1.543(6)	C_4–C_5	1.532(7)
Mo–C_8	2.324(4)	Mo–C_2	2.307(5)
Mo–C_7	2.257(4)	Mo–C_3	2.236(5)
Mo–C_6	2.290(4)	Mo–C_4	2.256(5)
Mo–C_{12}	1.966(5)		
Mo–C_{13}	1.990(5)	Mo–C_{51}	1.926(6)
C_{12}–O_{12}	1.154(5)		
C_{13}–O_{13}	1.153(5)	C_{51}–O_{51}	1.172(6)
		Mo–P	2.467(2)
Bond angles			
C_5–C_{11}–C_{10}	106.8(3)	C_{15}–C_{16}–C_5	105.8(4)
C_{10}–C_9–C_8	104.7(4)	C_5–C_1–C_2	104.2(4)
C_9–C_8–C_7	198.3(4)	C_1–C_2–C_3	108.0(5)
C_8–C_7–C_6	105.7(4)	C_2–C_3–C_4	105.6(5)
C_7–C_6–C_{10}	111.1(4)	C_3–C_4–C_5	110.8(4)
C_6–C_9–C_{10}	100.5(3)	C_4–C_5–C_1	101.7(4)
C_{12}–Mo–C_{13}	83.2(2)	C_{51}–Mo–P	82.6(2)
C_8–Mo–C_{13}	77.1(2)	C_2–Mo–P	80.77(14)
C_6–Mo–C_{12}	88.8(2)	C_4–Mo–C_{51}	88.4(2)

It is likely that all compounds isolated from the reaction of 2,2-bis(Cp)propane and chromium and molybdenum carbonyls proceed through the intermediacy of a set of isomers of the form $M(CO)_3H[\eta^5\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_5]$ as illustrated in Scheme 1. Reaction with a second molecule of molybdenum carbonyl yields $[M(CO)_3H]_2[\eta^5,\eta^5\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_4]$ which loses H_2 to give $M_2(CO)_6[\eta^5,\eta^5\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_4]$. Reaction of two molecules of $M(CO)_3H[\eta^5,\eta^5\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_4]$ resulting in loss of H_2 yields $M_2(CO)_6[\eta^5\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_5]_2$, while a combination of hydride transfer and loss of CO results in the formation of **I** and **II**. Wrighton has reported the formation of $(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_7)M(CO)_2$, where M = Cr and Mo, by photolysis of the respective metal carbonyl with an excess of cyclopentadiene [5]. A metal hydride was assumed to be an intermediate in this process. The mechanism of the hydride transfer to the cyclopentadiene ring in the formation of compounds **I** and **II** is not known at this time and may involve radical intermediates. It is interesting to note that although several isomers of **I** and **II** are possible, we have found no spectral or chromatographic evidence to sug-

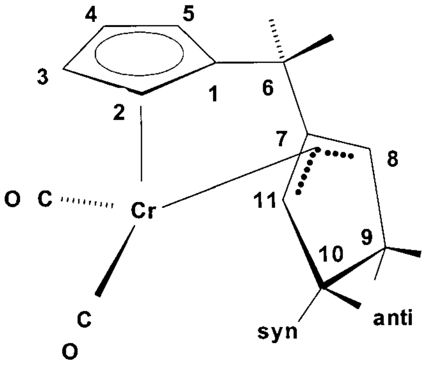


Fig. 3. NMR numbering scheme for **II**.

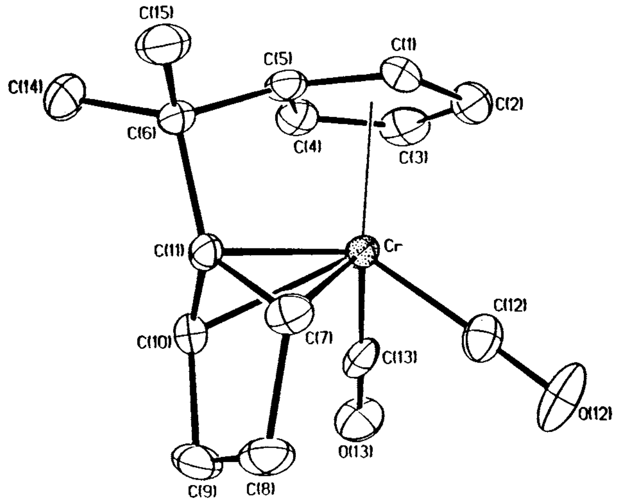
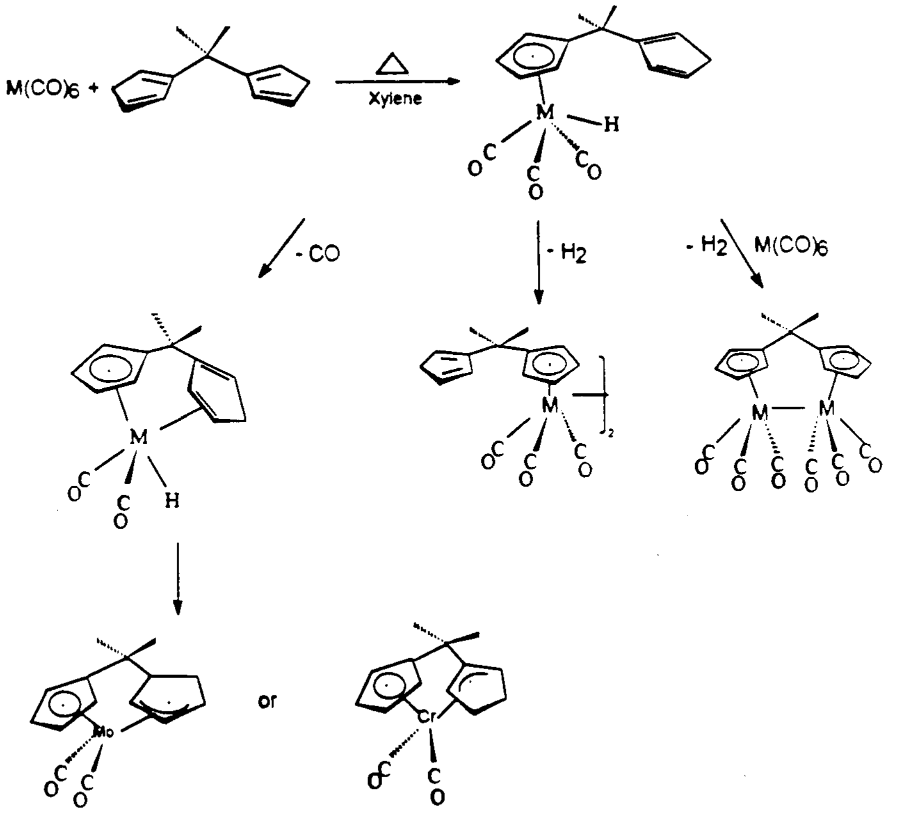


Fig. 4. Molecular structure of **II**.

Table 3
Bond lengths (Å) and bond angles (°) for $Cr(CO)_2[\eta^5,\eta^3\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_6]$ (**II**)

Atoms	II	Atoms	II
Bond lengths			
C_1–C_2	1.422(6)	C_9–C_{10}	1.522(6)
C_2–C_3	1.395(7)	C_{10}–C_{11}	1.422(6)
C_3–C_4	1.404(6)	Cr–C_7	2.259(4)
C_4–C_5	1.433(6)	Cr–C_{10}	2.238(4)
C_1–C_5	1.417(6)	Cr–C_{11}	2.104(4)
C_5–C_6	1.523(6)	Cr–C_{12}	1.826(5)
C_6–C_{11}	1.520(6)	Cr–C_{13}	1.821(5)
C_7–C_{11}	1.434(5)	C_{12}–O_{12}	1.156(5)
C_7–C_8	1.513(6)	C_{13}–O_{13}	1.155(5)
C_8–C_9	1.534(7)		
Bond angles			
C_5–C_6–C_{11}	97.0(3)	C_7–C_{11}–C_{10}	104.3(3)
C_{11}–C_7–C_8	108.8(4)	C_7–Cr–C_{12}	75.1(2)
C_7–C_8–C_9	104.4(3)	C_{10}–Cr–C_{13}	74.4(2)
C_8–C_9–C_{10}	103.1(3)	C_{12}–Cr–C_{13}	84.3(2)
C_9–C_{10}–C_{11}	109.2(4)		



Scheme 1.

gest that any other isomers are formed in these reactions. The stereospecificity of these reactions may arise from optimization of the stability of the final species.

1.2. Nujol matrix photochemistry of $M(CO)_3(\eta^5,\eta^3$-C_5H_4–CR_2–$C_5H_6)$, where $M = Cr$ or Mo

Apparatus and procedures for Nujol matrix photochemistry have been previously described [6].

The electronic spectrum of **I** isolated in Nujol at ca. 77 K showed a strong absorption at 355 and a weaker feature at 420 nm. Photolysis at 500 ± 70 nm bleached the band at 355 nm, while a new band appeared at ca. 310 nm. Subsequent photolysis at $350 < \lambda < 370$ nm resulted in the formation of a new band at 340 nm.

The IR spectrum of **I** in a Nujol solution at ca. 77 K (Fig. 5(a)) has bands at 1967 and 1898 cm^{-1} similar in position to those of other compounds in the $(\eta^5$-$C_5H_5)Mo(CO)_2(\eta^3$-allyl) series. Photolysis at 500 ± 70 nm resulted in the growth of two new bands at 1940 and 1874 cm^{-1} and a decrease in the bands of **I**. It should be noted that no bands for 'free' CO could be observed in the spectrum of this sample. Annealing the sample to 133 K resulted in a simple reversal of the photolysis reaction. Photolysis of a second sample at 500 ± 70 nm as above, followed by an additional photolysis at $350 < \lambda < 370$ nm (Fig. 5(c)) resulted in the growth of bands at 2132 ('free' CO), 1954, 1940, 1917, 1871, and 1608 cm^{-1}. The band at 1608 cm^{-1} was detected only in concentrated solutions. Continued photolysis at $350 < \lambda < 370$ nm resulted in further decreases in bands of **I**, and decreases in the band at 1940 cm^{-1}. Annealing this sample to 133 K (Fig. 5(d)) resulted in bands for 'free' CO and those at 1954 and 1871 cm^{-1} to decrease while bands of **I** and new bands at 2024, 2017, and 1928 cm^{-1} appeared. In concentrated samples a band at 1603 cm^{-1} was also found to grow in.

It appears that at least three photoproducts are generated during the photolysis of **I** and at least two new species form upon annealing of the photoproducts. Scheme 2 summarizes these observations and our analysis of the photochemical and thermal processes. Photolysis in the visible spectrum at 500 ± 70 nm results in the formation of species **IA** with carbonyl bands at 1940 and 1874 cm^{-1} with no apparent loss of CO. Opening of the η^3-allyl ligand to an η^1-allyl is the most probable low energy process. The asymmetric substitution of the cyclopentenyl ring creates two unique hinge points, C(6) and C(8), for the η^1-allyl opening, although an opening at C(6) would appear to yield the least sterically hindered intermediate. An intermediate opening at C(6) would also most easily account for the conformation of the triphenylphosphine derivative, **III**, to be described below.

Photolysis at $350 < \lambda < 370$ nm results in the appearance of a new band at 1954 cm^{-1} and equivalent growth of the band at 1871 cm^{-1} (which overlaps with the lower energy band of the 1940 and 1874 cm^{-1} pair). We propose that these bands arise from the second η^1-allyl species **IB**, with a hinge opening at the C(8) carbon.

The unique band at 1917 cm^{-1} is assigned to the carbonyl-loss species, **IC**, which forms only at high energy. We cannot distinguish between a simple carbonyl-loss species and one in which a concurrent hydride shift might form $Mo(CO)H[\eta^5,\eta^4-C_5H_4-C(CH_3)_2-C_5H_5]$, although the fact that this species does not appear to reverse upon annealing argues for the formation of a stable, 18-electron species.

Annealing the photolyzed sample to 173 K results in the decrease in bands associated with **IA** and **IB**, and the growth of new bands at 2024, 2017, and 1928 cm^{-1} as well as those of starting material. These new bands only arise when 'free' CO is present in the matrix, and are very similar in position to those of $(\eta^5-C_5H_5)Mo(CO)_3CH_3$ in frozen Nujol (2023 and 1935 cm^{-1}). We propose that the two sets of bands arise from a pair of $Mo(CO)_3[\eta^5,\eta^1-C_5H_4-C(CH_3)_2-C_5H_5]$ species, **ID** and **IE**, resulting from capture of CO by either **IA** or **IB**.

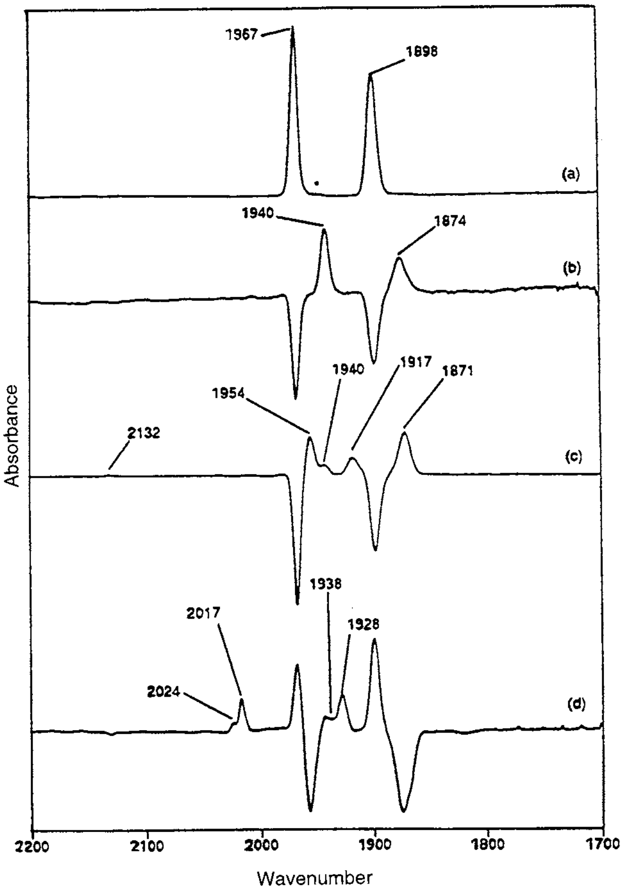


Fig. 5. IR spectra of $Mo(CO)_2[\eta^5,\eta^3-C_5H_4-C(CH_3)_2-C_5H_6]$ (**I**). (a) Starting material. (b) Subtraction spectrum, 120 min irradiation $\lambda = 500 \pm 70$ nm minus (a). (c) Subtraction spectrum, 30 min irradiation at $350 < \lambda < 370$ nm minus (a). (d) Subtraction spectrum, anneal to 173 K minus 120 min photolysis at $350 < \lambda < 370$ nm. * This band arises from a natural abundance of ^{13}CO.

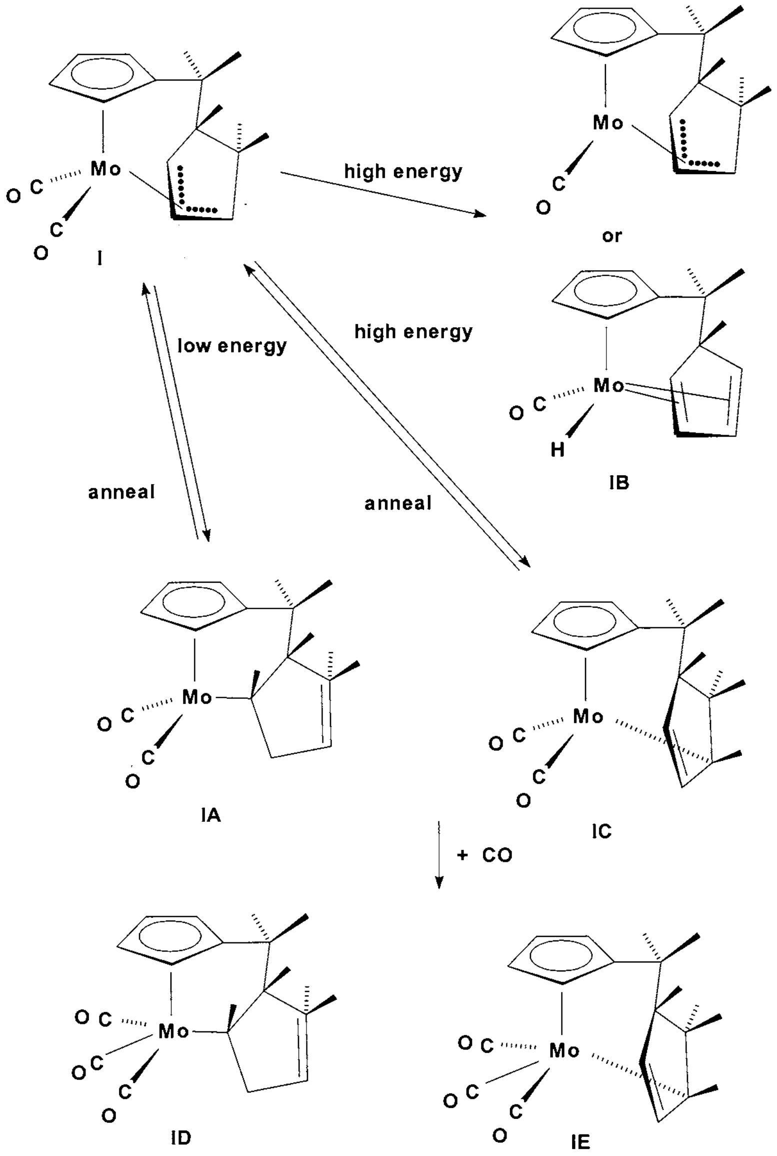
The electronic spectrum for **II** isolated in a Nujol matrix at ca. 77 K showed two weak absorption bands at 340 and 430 nm in addition to the continuum cutoff at about 280 nm. The IR spectrum of **II** in a Nujol matrix at ca. 77 K (Fig. 6(a)) consists of two carbonyl stretching bands at 1940 and 1876 cm^{-1}.

Irradiation of **II** in the Nujol matrix at low energies, $470 < \lambda < 640$ nm, corresponding to the bottom edge of the 430 nm absorption feature resulted in a small decrease in the bands of the starting material and growth of two new bands at 1941 and 1878 cm^{-1}. Annealing this sample to ca. 133 K resulted in complete reversal with no new products being formed. Sequential photolysis of a sample at $470 < \lambda < 640$ nm followed by photolysis at $340 < \lambda < 420$ nm resulted in additional growth of the bands at 1941 and 1878 cm^{-1} and the appearance of small bands at 2132 and 1917 cm^{-1} (Fig. 6(b)). High energy photolysis, $260 < \lambda < 420$ nm, of a second sample containing both **II** and the low energy photoproduct resulted in a decrease of bands of both sets of bands and growth of new bands at 2132, 1957, 1917, and 1883 cm^{-1} (Fig. 6(b)). The band at 2132 cm^{-1} is associated with 'free' carbon monoxide in the matrix. In all experiments the band at 1917 cm^{-1} was substantially more intense than those at 1957 and 1883 cm^{-1}. Annealing these samples to ca. 133 K resulted in only the first photoproduct reforming **II**.

The results of the several photochemical experiments on **II** and our proposed assignments of the resultant species are summarized in Scheme 3. Photolysis into the two low lying absorption bands of **II** results in an opening of the η^3-allyl to an η^1-allyl species, **IIA**, similar to the transformation observed for **I**. Higher energy photolysis gives rise to CO-loss to give the species with a band at 1917 cm^{-1}, **IIB**, that does not reverse upon annealing, suggesting that CO-loss is accompanied by a hydride shift to the metal from the cyclopentenyl ring to form an η^4-cyclopentadiene ring analogous to that proposed for **I**. **IIC** appears to be a minor product forming simultaneously with **IIB**, and may be a carbene/hydride arising from rearrangement of the η^1-allyl.

1.3. Solution photochemistry of $Mo(CO)_2[\eta^5,\eta^3-C_5H_4-C(CH_3)_2-C_5H_6]$

The observation of η^1-allyl species in the matrix photolysis of **I**, and their subsequent capture of CO to



Scheme 2.

form a product assigned as $Mo(CO)_3[\eta^5,\eta^1-C_5H_4-C(CH_3)_2-C_5H_6]$, suggested that it might be possible to generate these photointermediates in solution and capture them with a phosphine ligand. The photolysis of **I** in benzene solution with triphenylphosphine was followed by IR. During the photolysis the bands due to the starting material (1957 and 1876 cm^{-1}) decreased over a 50 min period while new bands at 1933 and 1852 cm^{-1} grew in. Bands at 1947 and 1871 cm^{-1} have been reported for $CH_3Mo(CO)_2(PPh_3)(\eta^5-C_5H_5)$ in cyclohexane and indicated that the expected $Mo(CO)_2(PPh_3)[\eta^5,\eta^1-C_5H_4-C(CH_3)_2-C_5H_6]$ product had been formed [7]. Toward the end of the photolysis period a low energy shoulder emerged at 1830 cm^{-1}. After removal of benzene by rotary evaporation from a warm water bath, chromatographic purification of the reaction mixture recovered starting material and a single product, **III**, whose IR band at 1829 cm^{-1} suggested that it was the material produced toward the end of the photolysis. None of the initially formed phosphine addition product was isolated. Repeating the experiment with HPLC monitoring confirmed that the major photolysis product disappeared during work-up with formation of starting material and **III**.

^1H- and ^{13}C-NMR spectra of **III** confirmed the presence of a triphenylphosphine ligand as well as a single, metal-bound carbonyl group. The proton and carbon resonances of the Cp/allyl ligand were almost identical in position and pattern to those of **I** requiring that **III** be assigned the formula $Mo(CO)(PPh_3)[\eta^5,\eta^3-C_5H_4-C(CH_3)_2-C_5H_6]$. The numbering scheme for proton and carbon resonances is identical to that for **I**.

Crystals grown by vapor diffusion were used to determine the molecular structure of **III**, shown in Fig.

7. Bond length and bond angle data are presented in Table 2. As anticipated, the structure of **III** retains the ring geometries of **I** with the triphenylphosphine group adding to the metal on the side opposite to the allyl. Introduction of a triphenylphosphine ligand into the coordination sphere of the molybdenum has remarkably little effect on the geometry of the metal–Cp–cyclopentenyl unit. The reduced π-acid character of the phosphine relative to CO is reflected in a slight reduction (ca. 0.02 Å) of the Mo–C bond lengths for the allyl unit, and a shortening of the Mo–CO bond length (1.990(5) in **I** and 1.926(6) in **III**) and concomitant lengthening of the C–O bond (1.153(5) in **I** and 1.172(6) in **III**). The bridge atom, C(16) is drawn about 6.8° below the plane of the Cp ring.

The spectral and chromatographic evidence requires that photolysis initially forms the expected phosphine addition product, $Mo(CO)_2(PPh_3)[\eta^5,\eta^1\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_6]$, in which the allyl group has undergone an $\eta^3 \rightarrow \eta^1$ hinge opening, and that this material decomposes during work-up by loss of either the CO or PPh_3 to give $Mo(CO)(PPh_3)[\eta^5,\eta^3\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_6]$ or the starting material, respectively. Although we cannot completely rule out the possibility that some quantity of **III** is formed directly by CO loss, we believe it is diagnostic that **III** is not observed until the later stages of the photolysis or upon work-up.

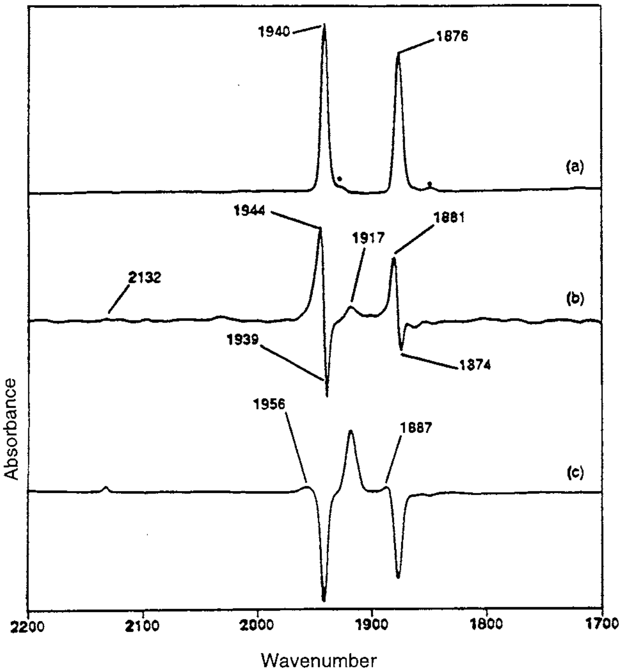


Fig. 6. IR spectra of $Cr(CO)_2[\eta^5,\eta^3\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_6]$, **II**. (a) Starting material. (b) Subtraction spectrum, 30 min irradiation at $340 < \lambda < 420$ nm following 30 min irradiation at $\lambda = 500 \pm 70$ nm minus (a). (c) Subtraction spectrum, 15 min irradiation at $225 < \lambda < 415$ nm minus 60 min total irradiation at $340 < \lambda < 570$ nm. Note: * Bands arise from a natural abundance of ^{13}CO.

We have carried out the analogous photolysis of $Mo(CO)_2(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)$ in the presence of triphenylphosphine under similar conditions to those described above and found no evidence for formation of a phosphine containing product. This is consistent with observations to be reported separately that $Mo(CO)_2(\eta^5\text{-}C_5H_5)(\eta^1\text{-}C_3H_5)$ is only rarely observed even at 77 K in a Nujol matrix. We believe that the thermal relaxation $\eta^1 \rightarrow \eta^3$ is fast under solution conditions precluding simple substitution by a ligand such as triphenylphosphine.

2. Experimental

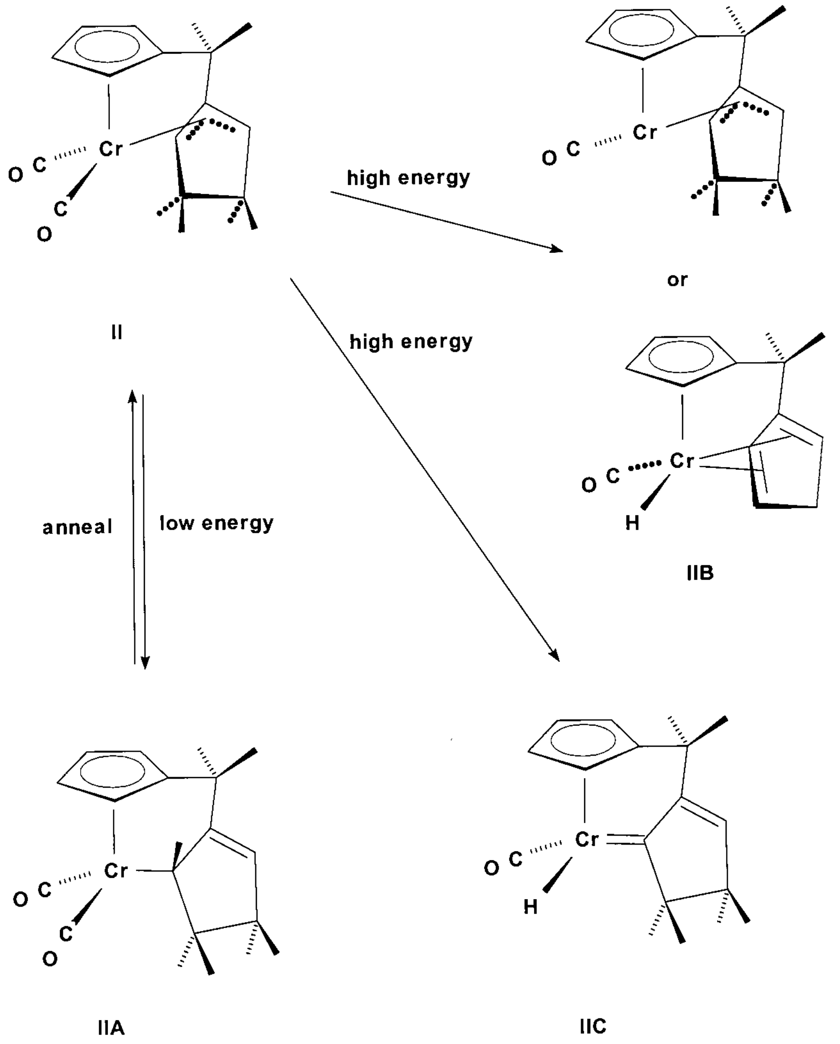
All synthesis were carried out under an atmosphere of dinitrogen using standard Schlenk techniques. All purification chromatography was performed using reagent grade solvents and neutral alumina provided by CAMAG Inc. or silica gel (Fisher Scientific). All preparative solvents were dried and distilled under nitrogen.

^1H-, ^{13}C-, and ^{13}P-NMR spectra were recorded on an Bruker NR-300 spectrometer (University of Idaho) or a QE300 NMR Spectrometer (US Naval Academy). Chemical shifts were reported relative to TMS using appropriate solvent resonances as internal standards. IR spectra were obtained using a Perkin–Elmer Spectrum 1000 FT-IR spectrometer. Elemental analysis was performed by Desert Analysis of Tucson, Arizona.

Metal carbonyls were purchased from Strem Chemicals, Inc. and used as received. Bis(Cp)methane [8] and 2,2-bis(Cp)propane [9] were prepared by literature methods.

2.1. *Synthesis of* $Mo(CO)_2[\mu\text{-}\eta^5,\eta^3\text{:}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_6]$, ***I***

2,2-Bis(Cp)propane (2.0 g, 11.5 mmol), and $Mo(CO)_6$ (3.0 g, 11.5 mmol) were placed in a 500 ml Schlenk flask under nitrogen. Air-free xylene, 250 ml, was added to the flask and the reaction mixture was refluxed for 48 h. The red reaction mixture was stripped under vacuum and the resulting dark red solid was chromatographed on alumina with petroleum ether as an eluent. An initial elution gave a yellow band which, after removal of solvent, gave **I** as an orange–yellow solid: 0.99 g, 27% yield. m.p. (dec.) 104–107°C. IR (CH_2Cl_2) 1956 and 1879 cm^{-1}. ^1H-NMR: (δ, $CDCl_3$) 5.96 (m, 1H, Cp H-5), 5.47 (m, 1H, Cp H-2), 5.04 (m, 2H, Cp H-3, H-4), 4.62 (m, 1H, allyl H-11), 4.09 (1H, m, allyl H-9), 3.68 (m, 1H, allyl H-10), 2.57 (d of d, 1H, $J_{7a-8a} = 9.0$, $J_{7a-11} = 2.9$ Hz, H-7a) 2.44 (ddd, 1H, $J_{8a-7a} = 9.0$, $J_{8a-8s} = 13.6$, $J_{8a-9} = 2.27$ Hz, H-8a), 2.06 (d, 1H, Cp, $J_{8a-8s} = 13.6$ Hz, H-8s), 1.34 (s, 3H, CH_3-12), 0.94 (s, 3H, CH_3-13). ^{13}C-NMR: (δ, $CDCl_3$) 239.8 and 239.2



Scheme 3.

(2CO, Mo–CO), 129.1 (s, *ipso*-Cp, C-1), 99.7 (C-3), 92.0 (C-2), and 84.6 (C-5), 83.1 (C-10), 81.0 (C-4), 68.1 (C-11), 64.9 (C-7), 56.2 (C-9), 40.2 (C-6), 34.1 (C-8), 26.4 (CH_3, C-12), 25.9 (CH_3, C-13). Anal. Calc. $C_{15}H_{16}O_2Mo$: C, 55.57; H, 4.94. Found: C, 55.80; H, 4.67%.

2.2. Synthesis of $Cr(CO)_2[\mu\text{-}\eta^5,\eta^3\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_6]$ (**II**)

2,2′-Bis-(Cp)propane (2.45 g, 14 mmol) and $Cr(CO)_6$ (3 g, 14 mmol) were placed in a 500 ml Schlenk flask under nitrogen. Air free solvent mixture of 10:1 butyl ether:THF (250 ml) was added to the flask and the reaction mixture was gently refluxed for 48 h. The green–yellow reaction mixture was stripped under vacuum and the resulting dark green–yellow solid was chromatographed under nitrogen atmosphere on alumina with degassed petroleum ether as an eluent. A yellow band was isolated which, after solvent removal, produced **II** as an orange–yellow solid: 0.38 g, 10% yield. M.p. (dec.) 208–210°C. IR (cm^{-1}, CH_2Cl_2) 1928 and 1855.5. ^{1}H-NMR: (δ, $CDCl_3$) 5.07 (t, 2H, Cp), 4.00 (t, 2H, Cp), 3.78 (br m, 2H, H-8, H-11), 2.11 (d of m, 2H, $J = 11.9$ Hz, H-9a, H-10a), 1.45 (d of m, 2H,

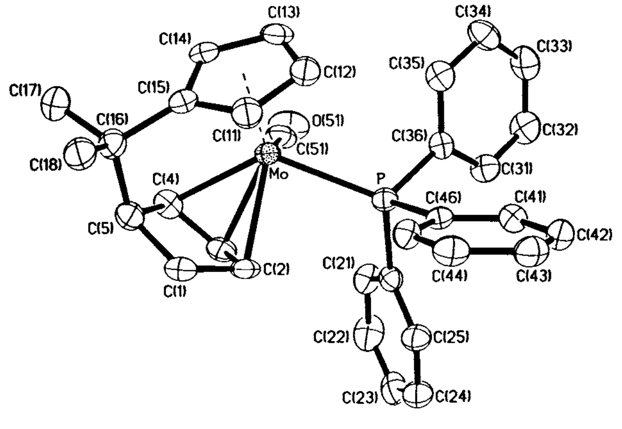


Fig. 7. Molecular structure of **III**.

$J = 11.9$ Hz, H-9s, H-10s), 1.10 (s, CH$_3$). ^{13}C-NMR: (δ, CDCl$_3$) 245.7 (2CO, Cr–CO), 91.8 (Cp), 81.3 (Cp), 68.4 (C-8, C-11), 29.7 (C-6), 28.7 (C-9, C-10), 23.5 (CH$_3$). C-1 and C-7 could not be assigned with confidence. Anal. Calc. $C_{15}H_{16}O_2Cr$: C, 64.28; H, 5.77. Found: C, 64.06; H, 5.47%.

2.3. *Synthesis of* $Mo(CO)PPh_3[\mu\text{-}\eta^5,\eta^3\text{-}C_5H_4\text{–}C(CH_3)_2\text{–}C_5H_6]$ **(III)**

Compound **I** (0.68 g, 2.0 mmol) and triphenylphosphine (0.53 g, 2.0 mmol) were placed in a 400 ml quartz irradiation vessel. Air-free redistilled benzene was added and the solution was stirred under nitrogen. The reaction cell was cooled by water and nitrogen was bubbled through the cell. A medium pressure mercury lamp was used for irradiation of the reactants. After 90 min of irradiation the color of the solution changed from yellow to dark yellow. The photolysis was stopped when IR spectra showed the absence of starting material and the present of a stretching band at 1833 cm^{-1}. The resultant mixture was stripped of benzene with a rotary evaporator and the resulting solid was chromatographed on alumina. Initial elution with petroleum ether removed unreacted phosphine. The main product band was then chromatographed with a 90:10 mixture of petroleum ether:methylene chloride. Upon elution two yellow bands were collected. The first showed a single IR stretching band at 1829 cm^{-1}: 0.25 g, 22% yield. The second band had IR bands of **I** and two new stretching bands at 1928 and 1848 cm^{-1} which are consistent with the second band being a mixture of starting material and a species with two carbonyl groups and a triphenylphosphine ligand. The solid from the second band was taken up and rechromatographed on silica gel with petroleum ether as an eluent. Two yellow bands were isolated that were found to be **I** and **III**. Repeated purification attempts failed to isolate the simple addition product as a pure material. It appears that this species decomposes into either **I** or **III** during purification. **III** was isolated as yellow crystals, yield 22%. M.p. (dec.) 205–207°C. IR (cm^{-1}, CH$_2$Cl$_2$) 1829. ^{1}H-NMR: (δ, CDCl$_3$) 7.32 (br, 15H, triphenylphosphine H), 5.79 (s, 1H, Cp H-5), 5.02 (s, 1H, Cp H-2), 4.95 (s, 1H, Cp H-3), 4.74 (s, 1H, Cp H-4), 4.19 (s, 1H, allylic H-11), 3.05 (d, allylic H-9, $J_{H-P} = 11.6$ Hz), 3.00 (s, 1H, allylic H-10), 2.8 (d, 1H,, $J_{7a-8a} = 10.1$ Hz, H-7a), 2.36 (dd, 1H, $J_{8a-7a} = 10.1$ Hz, $J_{8a-8s} = 13.5$ Hz, H-8a), 1.30 (s, 3H, CH$_3$ H-12), 0.98 (s, 3H, CH$_3$ H-13) ^{13}C-NMR: (δ, CDCl$_3$) 250.4 (d, $J_{C-P} = 16.3$ Hz, Mo–CO), 137 (d, $J_{C-P} = 35.9$ Hz, *ipso*-Ph), 133 (d, $J_{C-P} =$ 10.7 Hz, *o*-Ph), 129.2 (s, *p*-Ph) 127.8 (d, $J_{C-P} = 7$ Hz, *m*-Ph), 127 (*ipso*-Cp, C-1) 98.3 (Cp C-3), 95.3 (Cp C-2), 84.0 (Cp C-5) 83.1 (C-10), 81.7 (Cp C-4), 66.6 (C-11), 64.4 (C-7), 58.4 (d, $J_{C-P} = 5.0$ Hz, C-9), 35.5 (C-6), 30.3 (C-8), 26.8 (C, CH$_3$, C-12), 25.7 (C, CH$_3$, C-13). ^{31}P-NMR: (δ, CDCl$_3$) 73.6 (Mo–PPh$_3$). Anal. Calc. $C_{32}H_{31}OMoP$: C, 68.81; H, 5.61; P, 5.54. Found: C, 68.54; H, 5.42; P, 5.79%.

Acknowledgements

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