

Triphenylphosphine-Catalyzed η^1 - η^3 -Allyl Complex Transformation via Carbonyl Insertion into an η^1 -Allyl Complex Including the Structural Analysis of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{PPh}_3)\text{COCH}_2\text{CH}=\text{CHMe}$

Ivan Michelini-Rodriguez, Ana L. Romero, Ramesh N. Kapoor, Francisco Cervantes-Lee, and Keith H. Pannell*

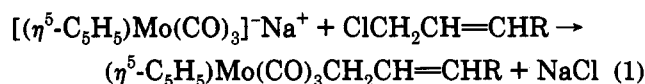
Department of Chemistry, The University of Texas at El Paso, El Paso, Texas 79968-0513

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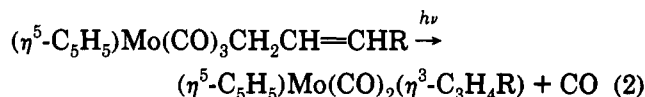
The reaction between $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]\text{-Na}^+$ and allyl bromide, $\text{BrCH}_2\text{CH}=\text{CH}_2$, in the presence of PPh_3 at 0°C led to the formation of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{PPh}_3)\text{COCH}_2\text{CH}=\text{CH}_2$ (Ia) in 45% yield. A similar insertion product Ib was obtained from the reaction between $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]\text{-Na}^+$ and $\text{ClCH}_2\text{CH}=\text{CHMe}$ in the presence of PPh_3 . Related reactions between $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]\text{-Na}^+$, PPh_3 , and propargyl halides did not result in insertion reactions but led to formation of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{CH}_2\text{C}\equiv\text{CR}$. A complete crystal structure analysis of Ib is presented. The complex exhibits a trans configuration about the double bond and also at the square-pyramidal molybdenum center. Complexes Ia and Ib are thermally unstable with respect to formation of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\eta^3\text{-allyl})$ (III), and the direct thermal transformation $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3(\eta^1\text{-C}_3\text{H}_4\text{R}) \rightarrow (\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_4\text{R})$ was readily accomplished by addition of PPh_3 as a catalyst. In the absence of PPh_3 , thermal treatment of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3(\eta^1\text{-allyl})$ led to formation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$. Synthesis of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{L})\text{CH}_2\text{-CH}=\text{CHMe}$, $\text{L} = \text{PPh}_3, \text{P}(\text{OPh})_3$, was accomplished, and thermal treatment led to formation of III.

Introduction

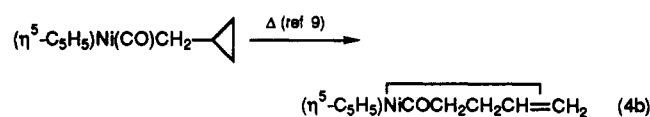
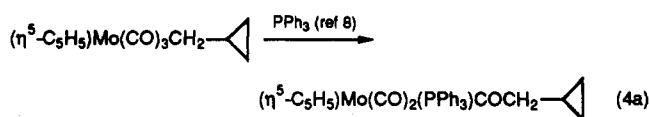
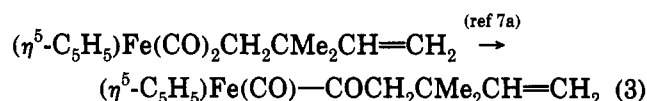
The η^3 -allyl group is one of the most widely studied ligands in transition metal organometallic chemistry.¹ The formation of such complexes often involves the initial formation of η^1 -allyl complexes followed by an η^1 - η^3 transformation, and many examples of η^1 -allyl complexes have long been known and studied.^{2,3} Although carbonyl insertions into η^1 -allyl metal-carbon bonds have been postulated in the carbonylation of allyl bromide by $\text{Ni}(\text{CO})_4$, leading to the formation allyl esters,⁴ only a single report, published recently, describes the formation and characterization of a CO insertion into a η^1 -allyl metal-carbon bond, i.e. *trans*- $(\text{PPh}_3)_2\text{PtCl}(\text{COCH}_2\text{CH}=\text{CH}_2)$.⁵ This study prompts us to report a similar CO insertion reaction in the system $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{CH}_2\text{CH}=\text{CHR}$, $\text{R} = \text{H}, \text{Me}$. Such η^1 complexes are among the most widely studied allyl complexes and are readily synthesized from the reaction of the appropriate transition metal carbonylate and allyl halide, eq 1.^{2,3}



The most characteristic chemical reaction of such η^1 complexes is their photochemical transformation to η^3 complexes, eq 2. This transformation does not occur thermally, due to facile Mo-C bond cleavage that leads to the formation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$; however, a



thermal η^1 - η^3 transformation can be catalyzed by Me_3NO .⁶ No CO insertion reactions have been reported for this type of η^1 -allyl complex, a result that contrasts with those reported for the homoallyl and allene complexes, e.g. $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CH}_2\text{CMe}_2\text{CH}=\text{CH}_2$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3(\text{CH}_2)_2\text{CR}=\text{CHR}$, eq 3, and related cyclopropylmethyl complexes of Ni, W, and Mo that lead to σ and/or σ - π CO insertion complexes, eq 4.



We now report that if the reaction outlined in eq 1 is performed in the presence of PPh_3 , a carbonyl insertion

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product $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{PPh}_3)\text{COCH}_2\text{CH}=\text{CHR}$ is formed. Complete characterization of this new type of complex is reported, including a single-crystal X-ray structure. The thermal chemistry of the new complexes is also reported, resulting in the formation of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_4\text{R})$.

Experimental Section

All reactions were performed in dry, oxygen-free solvents under atmospheres of N_2 or Ar. Analyses were performed by Galbraith Laboratories Inc. $\text{Mo}(\text{CO})_6$ was purchased from Strem Chemicals, silica gel (Grade 950, 60–200 mesh) was from MCB Reagents, and other organics were from Aldrich Chemicals.

Synthesis of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{PPh}_3)\text{COCH}_2\text{CH}=\text{CHMe}$ (Ib). To 70 mL of a THF solution of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]\text{-Na}^+$, prepared by treating 5.28 g (20.0 mmol) of $\text{Mo}(\text{CO})_6$ with 1 equiv of $[\text{C}_5\text{H}_5]^- \text{Na}^+$ in refluxing THF for 24 h, was added 5.2 g (19.8 mmol) of PPh_3 , and the solution was stirred for 1 h. No change was detected by infrared monitoring. To this stirred solution was added a 10% excess of crotyl bromide, $\text{BrCH}_2\text{CH}=\text{CHMe}$, and the mixture was warmed to room temperature and stirred for 24 h. Subsequent to removal of NaBr by filtration, the THF was removed under reduced pressure and the residue was extracted in 100 mL of a 60/40 hexane/methylene chloride solvent mixture. The solvent was removed from this solution to yield approximately 10 g of crude product. A 2.0 g sample was dissolved in the minimum of a 50/50 hexane/methylene chloride solvent mixture, and the solution was placed upon a silica gel column, 2×20 cm, and eluted with hexane. An initial yellow band was formed that, upon collection and solvent removal, yielded 0.05 g (5%) of a yellow wax that was characterized as $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{CH}_2\text{CH}=\text{CHMe}$. IR (hexane): $\nu(\text{CO})$ 2018, 1934 cm^{-1} (lit.³ 2017, 1935 cm^{-1}). Subsequent elution with an 80/20 hexane/methylene chloride solvent mixture led to collection of 1.3 g (60%) of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{PPh}_3)\text{Br}$, identified by comparison of its spectral properties with those published in the literature.¹⁰ Finally, elution with a 50/50 hexane/methylene chloride solvent mixture led to recovery of 0.6 g (27%) of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{PPh}_3)\text{COCH}_2\text{CH}=\text{CHMe}$, mp 125–6 °C dec. IR (CH_2Cl_2): $\nu(\text{CO})$ 1937, 1854, 1611 cm^{-1} . NMR (CDCl_3 , ppm): ^1H 7.38 (m, Ph), 5.48–5.22 (m, $\text{CH}=\text{CH}$), 4.96 (s, C_5H_5), 3.67 (d, $J = 6$ Hz, CH_2), 1.58 (d, $J = 6$ Hz, Me); ^{13}C 239.0, 238.5, 235.4 (CO), 136.3, 135.4, 133.5, 133.3, 130.9, 128.9, 127.3 (Ph, $\text{CH}=\text{CH}$), 97.0 (s, C_5H_5), 68.8 (CH_2), 18.4 (Me). Anal. Calcd (found): C, 64.1 (64.0); H, 4.80 (4.95).

Synthesis of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{PPh}_3)\text{COCH}_2\text{CH}=\text{CH}_2$ (Ia). In a similar reaction we synthesized $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{PPh}_3)\text{COCH}_2\text{CH}=\text{CH}_2$ (Ia) in 45% yield. IR (CH_2Cl_2): $\nu(\text{CO})$, 1938, 1855, 1616 cm^{-1} . NMR (CDCl_3 , ppm): ^1H 7.39 (m, Ph), 5.9, 4.86–5.15 (m, $\text{CH}=\text{CH}_2$), 4.97 (s, C_5H_5), 3.75 (m, CH_2); ^{13}C 239.0, 238.5, 236.1 (CO), 136.2, 135.3, 134.7, 133.5, 133.3, 129.0, 116.5 (Ph, $\text{C}=\text{C}$), 97.0 (C_5H_5), 69.7 (CH_2). Anal. Calcd (found): C, 63.5 (62.9); H, 4.56 (4.60).

Thermal Reaction between PPh_3 and $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{CH}_2\text{CH}=\text{CHMe}$ (III). (a) A refluxing solution of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{CH}_2\text{CH}=\text{CHMe}$ (0.3 g) and PPh_3 (0.3 g) in 20 mL of THF was monitored by infrared spectroscopy. The yellow solution changed color immediately to red, and after 2 h stretching frequencies were observed at 2011 (w), 1968 (m), 1938 (vs, vbd), 1887 (s), 1860 (vs, vb), and 1825 (w) cm^{-1} , indicating the presence of starting material and $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_4\text{Me})$. The bands at 1968, 1887, and 1825 cm^{-1} represent the formation of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_5(\text{PPh}_3)]$ as a byproduct.¹¹ Continued refluxing for 6 h resulted in the disappearance of the starting

Table I. Structure Determination Summary

Crystal Data	
empirical formula	$\text{C}_{30}\text{H}_{27}\text{O}_3\text{PMo}$
color; habit	amber fragment
cryst size (mm)	$0.32 \times 0.28 \times 0.40$
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	
<i>a</i> (Å)	9.046(2)
<i>b</i> (Å)	9.794(2)
<i>c</i> (Å)	16.291(3)
vol (Å ³)	1331.7(4)
<i>Z</i>	2
fw	562.4
density (calc) (Mg/m ³)	1.403
abs coeff (mm ⁻¹)	0.566
<i>F</i> (000)	576
Data Collection	
diffractometer used	Nicolet R3m/V
radiation [λ (Å)]	Mo $K\alpha$ (0.710 73)
temp (K)	298
monochromator	highly oriented graphite crystal
2 θ range (deg)	3.5–45.0
scan type	ω
scan speed (deg/min)	variable; 3.00 to 20.00 in ω
scan range (ω) (deg)	1.20
bckgd measurement	stationary crystal and stationary counter at beginning and end of scan, each for 25.0% of total scan time
no. of std refls	3 measured every 100 refls
index ranges	$-2 \leq h \leq 9, -10 \leq k \leq 10, -17 \leq l \leq 17$
no. of refls colled	3792
no. of indt refls	3408 ($R_{\text{int}} = 1.06\%$)
no. of obsd refls	3167 ($F > 3.0\sigma(F)$)
abs corr	semiempirical
min/max transm	0.6983/0.7758
Solution and Refinement	
system used	Nicolet SHELXTL PLUS (MicroVAX II)
solution	direct methods
refinement method	full-matrix least squares
quantity minimized	$\sum w(F_o - F_c)^2$
absolute config	N/A
extinction corr	$\chi = 0.0016(2)$, where $F^* = F[1 + 0.002\chi F^2/\sin(2\theta)]^{-1/4}$
hydrogen atoms	riding model, fixed isotropic U
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0002F^2$
final <i>R</i> indices (obsd data)	$R = 2.54, R_w = 3.39$
<i>R</i> indices (all data) (%)	$R = 2.82, R_w = 3.53$
goodness-of-fit	1.69
largest and mean Δ/σ	0.437, 0.005
data-to-param ratio	10.0:1
largest diff peak ($e \text{ \AA}^{-3}$)	0.43
largest diff hole ($e \text{ \AA}^{-3}$)	-0.38

material. The solvent was removed, the residue was extracted into 50 mL of hexane, and subsequent to purification via column chromatography (silica gel, eluting with hexane) 0.1 g (34%) of pure $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\eta^3\text{-C}_3\text{H}_4\text{Me})$ was obtained. The residue remaining after hexane extraction contained $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_5(\text{PPh}_3)]$ as a purple powder, identified by IR and NMR analysis.¹¹

Thermal Treatment of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{PPh}_3)\text{COCH}_2\text{CH}=\text{CHMe}$. In 20 mL of THF, 0.1 g of Ia was heated to reflux under Ar and the solution was monitored by IR spectroscopy. Initial rapid formation of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{CH}_2\text{CH}=\text{CHMe}$ was observed, and subsequently, the spectral properties of the solution resembled those reported above for the direct reaction of III with PPh_3 .

Determination of Structure Ib. An irregularly shaped amber crystal was mounted on a glass fiber and covered with epoxy glue. Crystal data were collected at room temperature on an R3m/v Nicolet four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Unit cell parameters and

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Table II. Selected Bond Lengths (Å) and Angles (deg) for Ib

Mo-P	2.465(1)	P-Mo-C(12)	80.7(1)
Mo-C(11)	1.956(3)	P-Mo-C(11)	79.1(1)
Mo-C(12)	1.968(4)	P-Mo-C(6)	134.0(1)
Mo-C(6)	2.249(3)	Mo-C(6)-C(7)	122.0(2)
O(1)-C(11)	1.158(4)	Mo-C(6)-O(3)	121.3(3)
O(2)-C(12)	1.140(4)	O(3)-C(6)-C(7)	116.6(3)
O(3)-C(6)	1.197(4)	C(6)-C(7)-C(8)	113.0(3)
C(6)-C(7)	1.537(5)	C(7)-C(8)-C(9)	123.7(4)
C(7)-C(8)	1.482(7)	C(8)-C(9)-C(10)	129.0(5)

Table III. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³)

	x	y	z	U(eq) ^a
Mo	1599(1)	3948(1)	1738(1)	39(1)
P	2986(1)	6503(1)	2484(1)	38(1)
O(1)	-818(3)	5520(3)	1019(2)	79(1)
O(2)	1484(3)	4034(3)	3644(2)	69(1)
O(3)	-1163(3)	1366(3)	1248(2)	78(1)
C(1)	3927(4)	3669(4)	1333(2)	63(1)
C(2)	2822(4)	3626(4)	585(2)	65(2)
C(3)	1641(4)	2405(4)	408(2)	70(2)
C(4)	2005(4)	1690(3)	1027(3)	69(2)
C(5)	3417(4)	2472(4)	1603(2)	66(2)
C(6)	-741(4)	2623(3)	1669(2)	54(1)
C(7)	-1910(4)	3296(4)	2116(3)	71(2)
C(8)	-2610(5)	2420(4)	2624(3)	81(2)
C(9)	-2497(6)	2900(6)	3453(4)	113(3)
C(10)	-3049(10)	2161(7)	4011(5)	213(7)
C(11)	85(4)	4963(3)	1314(2)	51(1)
C(12)	1509(3)	4038(3)	2948(2)	46(1)
C(13)	3979(3)	7326(3)	1788(2)	42(1)
C(14)	5566(4)	7759(3)	1961(2)	53(1)
C(15)	6266(4)	8370(4)	1411(2)	66(1)
C(16)	5392(5)	8576(3)	693(2)	65(2)
C(17)	3816(5)	8140(4)	499(2)	66(2)
C(18)	3093(4)	7493(3)	1035(2)	57(1)
C(19)	4511(3)	6908(3)	3482(2)	39(1)
C(20)	5078(3)	5821(3)	3739(2)	49(1)
C(21)	6225(4)	6153(3)	4497(2)	58(1)
C(22)	6842(4)	7565(3)	4999(2)	56(1)
C(23)	6309(4)	8665(3)	4755(2)	57(1)
C(24)	5135(3)	8341(3)	4005(2)	50(1)
C(25)	1774(3)	7745(3)	2854(2)	43(1)
C(26)	1704(4)	8988(3)	2618(2)	63(1)
C(27)	735(5)	9849(4)	2890(3)	80(2)
C(28)	-196(5)	9493(5)	3406(3)	85(2)
C(29)	-131(5)	8288(5)	3667(3)	92(2)
C(30)	848(4)	7413(4)	3394(3)	70(2)

^a Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized *U_j* tensor.

standard deviations were obtained by a least squares fit to 25 reflections randomly distributed in reciprocal space and lying in the 2θ range 15–30°. Intensity data were collected in the ω scan mode, with a scan range of 1.2° and a variable speed of 3–20°/min. Background counts were taken with a stationary crystal and a total background time/scan time of 0.5. Three standard reflections were monitored every 100 reflections and showed no significant decay. The data were corrected for Lorentz and polarization effects and a semiempirical absorption correction was also applied, giving a min/max transmission ratio of 0.02/0.044.

The space group was determined to be *P*1̄. The structure was solved by direct methods and refined by full-matrix least squares using the SHELXTL-PLUS crystallographic software package on a Microvax II computer. All crystallographic parameters are recorded in Table I, relevant bond lengths and angles are presented in Table II, and atomic coordinates in Table III.

Results and Discussion

The insertion of CO into the Mo–C bond of η¹-allyl complexes of the (η⁵-C₅H₅)Mo(CO)₃ system is facile if the

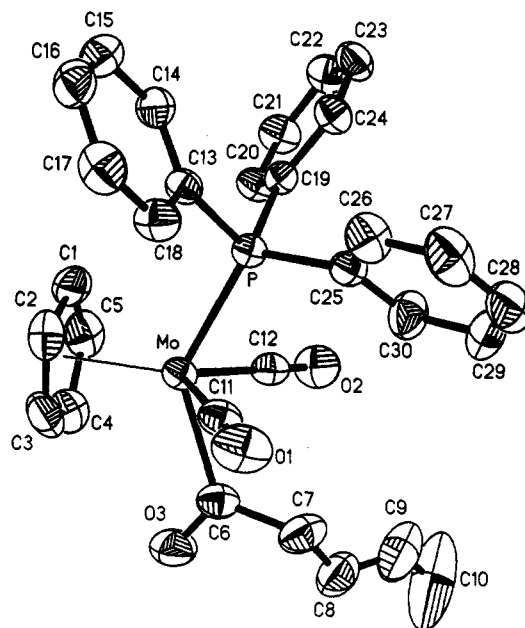
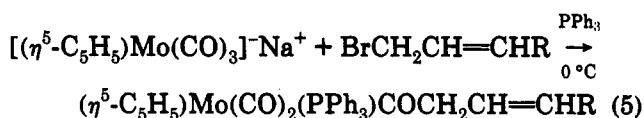


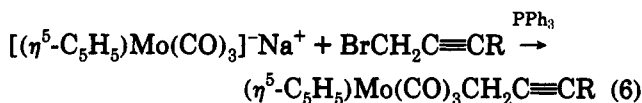
Figure 1. Structure of (η⁵-C₅H₅)Mo(CO)₂(PPh₃)COCH₂CH=CHMe.

initial reaction forming the η¹ complex is performed in the presence of a phosphine ligand, at low temperatures, eq 5.



R = H (Ia), Me (Ib)

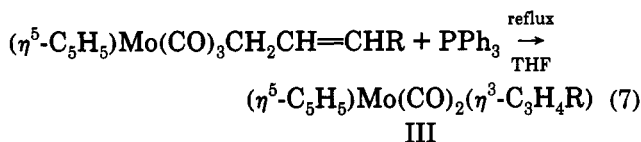
When similar reactions were performed with propargyl bromides in place of the allyl bromides, only "normal" salt elimination chemistry was observed, eq 6, illustrating a distinct difference between the double and triple bond in the organic substrate.



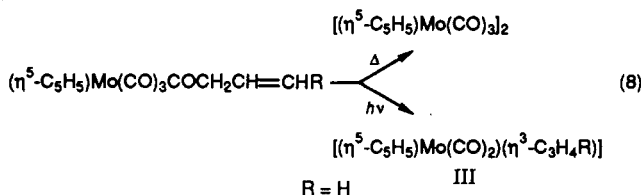
The spectroscopic data for Ib presented in the Experimental Section is in total accord with the structure exhibited in Figure 1, and selected bond lengths and angles are presented in Table II. The structure is in general unremarkable with the expected trans configuration about the olefin double bond and at the square-pyramidal molybdenum atom.

We attempted to perform a CO insertion reaction with the η¹-allyl complex under the conditions reported to cause CO insertion for the related methyl derivative, (η⁵-C₅H₅)Mo(CO)₃Me, i.e. treatment of (η⁵-C₅H₅)Mo(CO)₃-CH₂CH=CHMe (II) with PPh₃ in refluxing THF.^{12a} In our hands this reaction led to the formation of the η³-allyl complex III as the only significant product, eq 7, although intermediate concentrations of I were observed via infrared spectroscopy.

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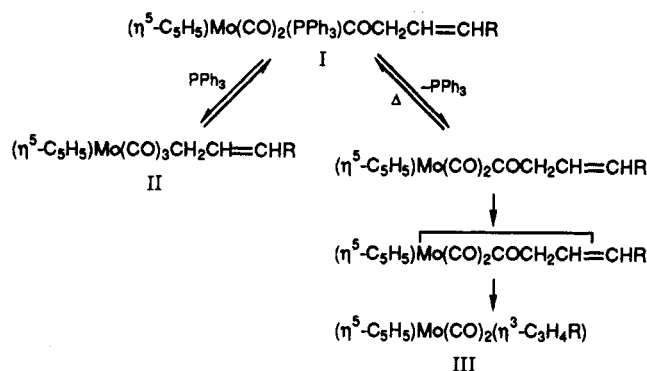
The formation of III in reaction 7 draws attention to the absence of this product from the thermal treatment of $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3(\eta^1\text{-C}_3\text{H}_4\text{R})$ (II) without PPh_3 . Such reactions led to the formation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$ as the only isolated product, a result in agreement with a previous report that only photochemical treatment of IIb led to the formation of IIIb, eq 8.³



These differing results were clarified when we subjected the new CO insertion product Ib to reflux conditions in THF solution. Monitoring of the reaction by infrared spectroscopy permitted observation of the transient formation of IIb and final formation and isolation of IIIb. It is clear that at elevated temperatures the phosphine acts as a catalyst for the transformation II to III, via formation of I. This chemistry is related to the phosphine-catalyzed transformation of cyclopropylmethyl derivatives of Mo to η^3 -allyl complexes.⁸ The proposed mechanism is outlined in Scheme I.

The $\eta^1 \rightarrow \eta^3$ transformation needs the initial formation of a 16-electron intermediate via the loss of either CO or PPh_3 . For the $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_n\text{R}$ complexes expulsion of CO is a process requiring photochemistry, and the thermal treatment of II leads not to CO expulsion but Mo-C cleavage. On the other hand, in $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_{n-1}(\text{PPh}_3)\text{R}$ systems, thermal loss of PPh_3 is relatively facile and in the case of I ultimately leads to the formation of III. We presume that the 16-electron complex formed by loss of PPh_3 from I, i.e. $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{COCH}_2\text{CH}=\text{CHR})$, proceeds to III via coordination of the olefin bond to Mo followed by immediate decarbonylation to form the η^3 -allyl complex. We have found no evidence in the literature for such $\text{LM}-\text{CO}-\text{CH}_2=\text{CHR}$ σ - π complexes probably due to both the small chelate ring size and general stability of the CO expulsion product, the η^3 -allyl system. An early report by Watson and Bergman on the thermal transformation of alkynyl complexes $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3-(\text{CH}_2)_n\text{C}\equiv\text{CMe}$ suggested that nonobservable transients $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2-\text{CO}-(\text{CH}_2)_n\text{C}\equiv\text{CMe}$ were involved in the ultimate production of cyclic products $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2[\text{C}(\text{Me})=\text{C}(\text{O})(\text{CH}_2)_n]$.¹³ Furthermore they noted that the yields of the cyclic product significantly reduced as n became smaller, $3 < 4 < 5$, reflecting the same type of negative entropy associated with intramolecular bonding suggested in the present study. Similar insertion and cyclization reactions have been reported for the cyclo-

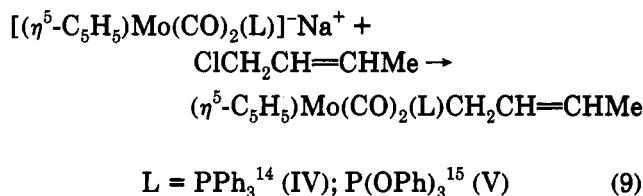
Scheme I



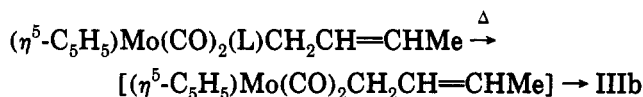
pentadienyl Mo and W allene complexes, $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3(\text{CH}_2)_2\text{CR}=\text{C}=\text{CHR}$.^{7d}

It is interesting to note that the 16-electron intermediate $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2\text{COCH}_2\text{CH}=\text{CHR}$ does not appear to form directly during the thermal treatment of II; otherwise formation of III would be observed. The insertion of CO into metal-carbon bonds has been established to proceed via both associative and dissociative pathways.^{12b,c} In the present system, with respect to the formation of I from II, the former process, involving PPh_3 nucleophilic attack assisting alkyl group migration, must be the preferred pathway.

We have also synthesized the phosphine- and phosphite-substituted complexes of II via the salt elimination reaction (eq 9).



Both complexes are stable crystalline materials, but both may be readily transformed to the π -methallyl complex IIIb via thermal treatment in refluxing hexane.



This result confirms our contention that thermal expulsion of PPh_3 is a facile process for $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{L})\text{R}]$ complexes that leads to a 16-electron system capable of proceeding to the η^3 -allyl systems. We have no evidence for the formation of IV during the treatment of IIa/b with phosphine or during the thermal treatment of Ia/b, but this does not rule out their intermediacy since rapid transformation to III would suggest that equilibrium concentrations could be too small for observation in our experimental setup.

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Supplementary Material Available: Tables of complete bond lengths and bond angles, anisotropic thermal parameters, and H-atom coordinates (4 pages). Ordering information is given on any current masthead page.

OM920715D

(13) Watson, P. L.; Bergman, R. G. *J. Am. Chem. Soc.* 1979, 101, 2055.(14) Formation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{PPh}_3)]^{-}\text{Na}^{+}$ was performed by Na/Hg reduction of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2(\text{PPh}_3)]_2$; Bruce, M. I.; Goodall, B. L.; Sharrocks, D. N.; Stone, F. G. A. *J. Organomet. Chem.* 1972, 39, 139.(15) King, R. B.; Pannell, K. H. *Inorg. Chem.* 1968, 7, 2356.