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GROUP V COMPLEXES OF THE TRICARBONYL(η-CYCLOHEPTATRIENYLIUM)MOLYBDENUM CATION AND THEIR REDUCTION TO MONOSUBSTITUTED DERIVATIVES OF TRICARBONYL(1-6-η-CYCLOHEPTATRIENE)MOLYBDENUM

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Summary

Reaction of $[(\eta\text{-}C_7H_7)Mo(CO)_3][PF_6]$ with certain Group V donor ligands afforded monosubstituted complexes $[(\eta\text{-}C_7H_7)Mo(CO)_2L][PF_6]$ (L = $P(OPh)_3$, PPh_3, PPh_2Me, $PPhMe_2$, $AsPh_3$, $SbPh_3$). These were reduced by $NaBH_4$ to the corresponding cycloheptatriene complexes $(1\text{-}6\text{-}\eta\text{-}C_7H_8)Mo(CO)_2L$. In addition, the preparation of alkylcycloheptatriene complexes $(1\text{-}6\text{-}\eta\text{-}C_7H_7R)Mo(CO)_2L$ (R = Me, L = $P(OPh)_3$, PPh_3, PPh_2Me; R = t-Bu, L = PPh_3) is described. Spectroscopic properties, including ^{13}C NMR, are reported.

Introduction

Facile ring displacement by phosphines and other Lewis bases has made $(1\text{-}6\text{-}\eta\text{-}C_7H_8)Mo(CO)_3$ a useful intermediate in the preparation of tris-substituted complexes of molybdenum carbonyl [1]. As a consequence derivatives of the type $(1\text{-}6\text{-}\eta\text{-}C_7H_8)Mo(CO)_2L$ are not accessible by the direct route, and it was the objective of the present work to prepare such carbonyl substituted products by alternative means. The well known borohydride reduction of $[(\eta\text{-}C_7H_7)Cr(CO)_3]^+$ [2] suggested that the reduction of substituted molybdenum cations would lead to the desired neutral complexes, and this was found to be the case. This route has very recently been used by other workers for the preparation of one of the complexes reported here, $(1\text{-}6\text{-}\eta\text{-}C_7H_8)Mo(CO)_2PPh_3$ [3].

Experimental

Melting points were determined using a Kofler hotstage microscope. Analytical results (Table 1) were obtained by the Microanalytical Laboratory of this department, except as noted. Table 1 lists as footnotes molar conductivities of selected ionic derivatives.

TABLE 1

YIELDS, COLORS, MELTING POINTS, MICROANALYTICAL DATA AND CONDUCTIVITY [a]

Compound	Yield (%)	Color	M.p. (°C)	Analysis found (calcd.) (%)	
				C	H
$[C_7H_7Mo(CO)_2P(OPh)_3][PF_6]$	45	orange	131	46.42 (46.44)	3.22 (3.19)
$[C_7H_7Mo(CO)_2PPh_3][PF_6]$ [b]	77	orange-red	206 dec.	49.76 (49.86)	3.20 (3.41)
$[C_7H_7Mo(CO)_2PPh_2Me][AsF_6]$	44	wine	185 dec.	41.79 (41.80)	3.27 (3.19)
$[C_7H_7Mo(CO)_2PPhMe_2][PF_6]$ [c]	30	red-brown	170 dec.	38.41 (38.80)	3.19 (3.42)
$[C_7H_7Mo(CO)_2AsPh_3][PF_6]$ [d]	67	red	218-219 dec.	46.55 (46.71)	3.13 (3.19)
$[C_7H_7Mo(CO)_2SbPh_3][PF_6]$ [e]	41	red	209-211 dec.	43.65 (43.76)	2.89 (2.99)
$C_7H_8Mo(CO)_2P(OPh)_3$ [f]	71	orange-red	190	58.91 (58.50)	3.63 (4.18)
$(C_7H_7Me)Mo(CO)_2P(OPh)_3 \cdot CH_2Cl_2$	82	red	72-73	53.13 (53.31)	3.95 (4.16)
$C_7H_8Mo(CO)_2PPh_3$	70	red	177-178	64.59 (64.04)	4.96 (4.58)
$(C_7H_7Me)Mo(CO)_2PPh_3$	85	brown-red	175-178	63.62 (64.62)	4.38 (4.84)
$(C_7H_7\text{-}t\text{-}Bu)Mo(CO)_2PPh_3$	48	orange-red	155-157	66.06 (66.19)	5.42 (5.55)
$C_7H_8Mo(CO)_2PPh_2Me$	65	deep red	116-120	58.79 (59.60)	4.86 (4.55)
$(C_7H_7Me)Mo(CO)_2PPh_2Me$	68	red	120	59.58 (60.27)	5.21 (5.06)
$C_7H_8Mo(CO)_2PPhMe_2$	64	red-orange	117	53.04 (53.42)	4.79 (4.90)
$C_7H_8Mo(CO)_2AsPh_3$	72	orange	172 dec.	58.40 (58.93)	4.10 (4.21)
$C_7H_8Mo(CO)_2SbPh_3$	74	deep red	150-151 dec.	54.21 (54.31)	3.81 (3.88)

[a] Conductivity measurements quoted in footnotes *b-e* were performed on ca. 10^{-3} *M* solutions in nitromethane at 25° using a Philips conductivity bridge, model PR 9500. [b] 76.9 cm^2 ohm^{-1} mol^{-1}. [c] 63.2 cm^2 ohm^{-1} mol^{-1}. [d] 80.0 cm^2 ohm^{-1} mol^{-1}. [e] 80.7 cm^2 ohm^{-1} mol^{-1}. [f] Found: Mo, 17.58; O, 14.34; P, 5.48; mol. wt. = 562. Calcd.: Mo, 17.30; O, 14.43; P, 5.59; Mol. wt. = 554. (Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach über Engelskirchen, West Germany).

Infrared spectra of the carbonyl stretching region were measured by means of a Perkin—Elmer Model 337 spectrometer at a scanning rate of 39 cm^{-1} min^{-1}, and recorded in expanded form (1 cm of chart ≈ 10 cm^{-1}) on an external recorder. Spectra were calibrated with bands of gaseous CO and DBr, and are considered accurate to ± 1 cm^{-1}. Band positions quoted in Table 2 refer to the midpoint at half-height.

Proton NMR spectra were measured on Varian A56/60 and A56/60a instruments using tetramethylsilane as an internal standard. Selected NMR data for the cationic cycloheptatrienylium derivatives are listed as footnotes to Table 2. The NMR data for the neutral cycloheptatriene derivatives are given separately in Table 3.

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TABLE 2

CARBONYL STRETCHING FREQUENCIES[a] AND NMR DATA[b] FOR THE CYCLOHEPTATRIENYLIUM RESONANCE

Compound	Frequencies (cm^{-1})	
$[C_7H_7Mo(CO)_2P(OPh)_3][PF_6]$[c]	2040(10.0)	2000(8.2)
$[C_7H_7Mo(CO)_2PPh_3][PF_6]$[d]	2027(10.0)	1985(8.5)
$[C_7H_7Mo(CO)_2PPh_2Me][PF_6]$[e]	2023(10.0)	1981(8.4)
$[C_7H_7Mo(CO)_2PPhMe_2][PF_6]$[f]	2020(10.0)	1976(8.0)
$[C_7H_7Mo(CO)_2AsPh_3][PF_6]$[g]	2031(10.0)	1987(8.4)
$[C_7H_7Mo(CO)_2SbPh_3][PF_6]$[h]	2027(10.0)	1986(8.3)
$C_7H_8Mo(CO)_2P(OPh)_3$	1948.5(10.0)	1892(4.3, sh)
	1885(6.6)	1876(6.1)
$(C_7H_7Me)Mo(CO)_2P(OPh)_3$	1947.5(10.0)	1894(5.5)
	1885(7.9)	1876(7.1, sh)
$C_7H_8Mo(CO)_2PPh_3$	1931(10.0)	1857(8.5)
$(C_7H_7Me)Mo(CO)_2PPh_3$[i]	1905(10.0)	1826(8.0)
$(C_7H_7\text{-t-Bu})Mo(CO)_2PPh_3$	1932(10.0)	1855(8.4)
$C_7H_8Mo(CO'_2PPh_2Me$	1926(10.0)	1854(8.4)
$(C_7H_7Me)Mo(CO)_2PPh_2Me$	1926(10.0)	1854(8.4)
$C_7H_8Mo(CO)_2PPhMe_2$	1925.5(10.0)	1851(8.3)
$C_7H_8Mo(CO)_2AsPh_3$	1931(10.0)	1858(8.1)
$C_7H_8Mo(CO)_2SbPh_3$	1932.5(10.0)	1862(8.5)

[a] Dichloromethane and n-hexane solutions were used for the cationic and neutral derivatives respectively, except where noted. Figures in parentheses are relative band intensities. [b] The τ value quoted in footnotes *c-h* refers to the cycloheptatrienyl group of the compound in question. [c] τ 4.5 in $CDCl_3$; $J(P—C_7H_7)$ = 2.8 Hz. [d] τ 4.0 in CD_3CN; $J(P—C_7H_7)$ = 2.1 Hz. [e] τ 4.2 in $CDCl_3$; $J(P—C_7H_7)$ = 2.4 Hz. [f] τ 4.2 in $CDCl_3$; $J(P—C_7H_7)$ = 2.5 Hz. [g] τ 3.9 in acetone-d_6. [h] τ 3.8 in acetone-d_6. [i] Measured in CH_2Cl_2.

TABLE 3

^{1}H NMR SPECTRAL DATA AND ASSIGNMENTS[a] FOR THE CYCLOHEPTATRIENE COMPOUNDS

	Chemical shift (τ value)[b]				
Compound	H(3,4)	H(2,5)	H(1,6)	H(7)	Other
$C_7H_8Mo(CO)_3$[c]	4.0 dd	5.1 q	6.4 dt	≈7.2 c	
$C_7H_8Mo(CO)_2P(OPh)_3$[d]	4.7 t	5.6 m(br)	7.2 m	≈7.5 c	
$(C_7H_7Me)Mo(CO)_2P(OPh)_3 \cdot CH_2Cl_2$[d]	4.6	5.5	6.8 dt	≈7.2 qu	$C_7—CH_3$ = 9.92(6.5) $^*CH_2Cl_2$ = 4.6
$C_7H_8Mo(CO)_2PPh_3$[c]	4.4 dd	5.2 (br)	7.0 (br)	≈7.7 c	
$(C_7H_7\text{-t-Bu})Mo(CO)_2PPh_3$[d]	4.7 dd	5.3 (br)	6.8 dt	≈9.1 c	$C_7—C(CH_3)_3$ = 9.75
$C_7H_8Mo(CO)_2PPh_2Me$[c]	4.3 (br)	5.3 (br)	7.0 (br)	≈7.7 (br)	$P—CH_3$ = 7.82(7.0)
$(C_7H_7Me)Mo(CO)_2PPh_2Me$[d]	4.5 dd	5.3 q	6.7 dt	≈7.8	$P—CH_3$ = 7.81(7.0) $C_7—CH_3$ = 9.92(6.8)
$C_7H_8Mo(CO)_2PPhMe_2$[c]	4.4 dd	5.2 (br)	7.0 m	≈7.7	$P—CH_3$ = 8.00(7.5)
$C_7H_8Mo(CO)_2AsPh_3$[c]	4.4 (br)	5.3 (br)	7.0 m	≈8.0 m	
$C_7H_8Mo(CO)_2SbPh_3$[c]	4.2 dt	5.3 (br)	6.7 m	≈8.1 m	

[a] H(1,6), H(2,5) and H(3,4) refer to the ring protons bonded to the carbon atoms respectively adjacent, once and twice removed from the methylene carbon C(7). [b] Relative to TMS. $P—C_6H_5$ τ values not given. Figures in parentheses are *J* values in Hz. Key: (br) = broad, m = multiplet, c = complex, dd = double doublet, t = triplet, dt = double triplet, q = quintet, qu = quartet. [c] In $CDCl_3$. [d] In CD_2Cl_2.

TABLE 4

^{13}C NMR DATA FOR $C_7H_8Mo(CO)_2L$ (L = CO, $P(OPh)_3$, PPh_3, PPh_2Me AND $PPhMe_2$) [a]

Compound	δ(3,4)	δ(2,5)	δ(1,6)	δ(7)	δ(CO)	T(K)	δ(α)	δ(β)	or δ(γ)	δ(δ)	δ(CH$_3$)
$C_7H_8Mo(CO)_3$ [b]	104.00	98.82	61.88	27.47	220.79 [c]	300					
$C_7H_8Mo(CO)_2P(OPh)_3$ [c]	101.90	94.89	58.15	27.19	[f]	273	152.22(4)	121.81(4)	129.80	124.07	
	102.98	92.46	61.01	26.60	213.4(17)	203	151.62(4)	121.70	129.85		
$C_7H_8Mo(CO)_2PPh_3$ [c]	105.37	87.46	65.00	25.53	224.14(11)	228	139.37(38)	128.62(17)	133.70	129.78	
$C_7H_8Mo(CO)_2PPh_2Me$ [b]	105.42	88.58	62.04	27.62	224.78(10)	203	140.91(36)	129.05(11)	132.40(11)	129.26	21.86(24)
	104.6	89.5	61.6	27.2	224.45(10)	300	141.9(35)	129.8	132.4	129.0	21.6(25)
$C_7H_8Mo(CO)_2PPhMe_2$ [b]	104.97	88.20	61.63	26.83	224.25(12)	233	[f]	[f]	[f]	[f]	21.27(28)

[a] Chemical shifts in ppm relative to TMS. J(P—C) values in brackets (Hz). Methylene carbon atom numbered C7. α, β, γ and δ refer to the carbon atoms of the phosphorus phenyl group(s). [b] Acetone-d_6; (ketonic ^{13}C = 207.69). [c] CD_2Cl_2. [e] Reference [17]; 217.93 and 229.17 ppm (2/1) at 222 K. [f] Not measured.

Proton-decoupled Fourier transform ^{13}C NMR spectra of some cycloheptatriene complexes were recorded on Bruker HFX-10 or Varian HLFT instruments operating at 22.6 MHz and 22.15 MHz respectively. In general, 4000 scans produced adequate spectra. Results are given in Table 4.

Mass spectra of the cycloheptatriene derivatives were obtained using an A.E.I. MS-12 instrument (70 eV, direct introduction of sample at lowest temperature necessary to produce the molecular ion). Table 5 assigns the common fragments in the mass spectra of some representative compounds.

Tricarbonyl(η-cycloheptatrienylium)molybdenum(I) hexafluorophosphate was prepared by an established method [4]. Group V ligands were purchased from Strem Chemicals Inc., and those which were solids were recrystallized from n-pentane before use. Sodium borohydride was purchased from the American Drug and Chemical Co. and Fisher Scientific Co. Alkyllithium reagents were purchased from Ventron Corp. Aluminium oxide (Baker Chemical Co.) and Florisil (Fisher Scientific Co.) were used for column chromatography.

All reactions were performed under a nitrogen atmosphere, and details of

TABLE 5

RELATIVE INTENSITIES OF FRAGMENTS IN THE MASS SPECTRA

$C_7H_8Mo(CO)_2L$

Fragment	L = CO	L = P(OPh)$_3$	L = PPh$_3$	L = PPhMe$_2$	L = AsPh$_3$
$C_7H_8Mo(CO)_2L^+$	40	14	5	23	2
$C_7H_8Mo(CO)L^+$	18	7	2	7	0.5
$C_7H_8MoL^+$	15		3	7	5
$C_7H_6MoL^+$		68	35	100	2
$C_7H_4MoL^+$			3		
$C_7H_8Mo^+$	100	3			
$C_7H_6Mo^+$	45				
$C_7H_8^+$	24	3	1	22	12
$C_7H_7^+$	39	24	5	43	29
$C_7H_6^+$		67	11	2	
L^+		45	100	21	35
$(L{-}Ph)^+$			12		100
$(L{-}OPh)^+$		100			
$(L{-}Me)^+$				16	

$(C_7H_7$-t-$Bu)Mo(CO)_2PPh_3$

Fragment	Rel. int.
$(C_7H_7$-t-$Bu)Mo(CO)_2PPh_3^+$	6
$(C_7H_7$-t-$Bu)Mo(CO)PPh_3^+$	≈0
$(C_7H_7$-t-$Bu)MoPPh_3^+$	≈0
$C_7H_7Mo(CO)_2PPh_3^+$	22
$(C_7H_5$-t-$Bu)MoPPh_3^+$	20
$C_7H_7Mo(CO)PPh_3^+$	8
$C_7H_7MoPPh_3^+$	100
$C_7H_7^+$	55
PPh_3^+	65
$P(C_6H_4)_2^+$	30

$(C_7H_7Me)Mo(CO)_2PPh_2Me$

Fragment	Rel. int.
$(C_7H_7Me)Mo(CO)_2PPh_2Me^+$	16
$(C_7H_7Me)Mo(CO)PPh_2Me^+$	5
$(C_7H_7Me)MoPPh_2Me^+$	4
$(C_7H_5Me)MoPPh_2Me^+$	100
$C_7H_8^+$	≈0
$C_7H_7^+$	37
$C_7H_6^+$	≈0
PPh_2Me^+	48
PPh_2^+	19

representative preparations are given below. Ethanol used as reaction solvent was "95%" grade (see Results and discussion).

Preparation of $[(\eta\text{-}C_7H_7)Mo(CO)_2PPh_3][PF_6]$

Triphenylphosphine (2.7 g, 10.7 mmol) and $[(\eta\text{-}C_7H_7)Mo(CO)_3][PF_6]$ (4.2 g, 10.1 mmol) in 120 ml of ethanol were heated at reflux for 1 h. The red reaction mixture was allowed to cool to room temperature, affording a massive precipitate. This was filtered, washed with ethanol, air dried and collected (5.1 g, 78% yield). The red solid was used as obtained for further reaction. The analytical sample was recrystallized from dichloromethane/ethanol.

The PPh_2Me, $AsPh_3$ and $SbPh_3$ derivatives were prepared similarly.

Preparation of $[(\eta\text{-}C_7H_7)Mo(CO)_2P(OPh)_3][PF_6]$

Triphenylphosphite (3.3 g, 10.7 mmol) and $[(\eta\text{-}C_7H_7)Mo(CO)_3][PF_6]$ (4.2 g, 10.1 mmol) in 60 ml of ethanol were heated at reflux for 0.5 h. Some $Mo(CO)_6$ was formed and sublimed onto the water-cooled condenser. The orange-red reaction mixture was filtered while hot and the solution was cooled overnight at −20°. The orange solid formed was filtered and washed with ether. Recrystallization from dichloromethane/ether afforded the analytical sample (3.2 g, 45% yield).

Preparation of $[(\eta\text{-}C_7H_7)Mo(CO)_2PPhMe_2][PF_6]$

To a suspension of $[(\eta\text{-}C_7H_7)Mo(CO)_3][PF_6]$ (6.0 g, 14.4 mmol) in 60 ml of ethanol at reflux, phenyldimethylphosphine (3-4 ml) in 20 ml of ethanol was added through a dropping funnel over the course of 1.5 h. The reaction was monitored by the dissolution of the orange starting material and addition was stopped when the solution became clear. The hot solution was filtered and cooled to 0°, affording a brown precipitate. This was filtered, washed with ether, dried and purified by chromatography over an alumina column. It eluted as a single red band with dichloromethane. Recrystallization from dichloromethane/ethanol afforded the analytical sample (2.4 g, 30% yield).

To the filtrate from the reaction mixture, 30 ml of ether was added. On cooling overnight 0.4 g of white crystals were obtained. This compound was characterized as the known *fac*-$(CO)_3Mo(PPhMe_2)_3$ [5]. A large excess of ligand resulted in a greater yield of this substance.

Preparation of $(1\text{-}6\text{-}\eta\text{-}C_7H_8)Mo(CO)_2PPh_3$

Method A. The compound $[(\eta\text{-}C_7H_7)Mo(CO)_2PPh_3][PF_6]$ (2.2 g, 3.4 mmol) was placed in a benzene/water (300/100 ml) mixture, containing a few drops of acetone to promote better mixing between the phases. Excess sodium borohydride (5-8 g) was added in small portions and the mixture was stirred vigorously for 3 h. The benzene layer acquired a deep red coloration as the product was formed. The reaction mixture was then transferred to a separatory funnel and the water layer discarded. The benzene layer was washed with several portions of water and then placed over anhydrous magnesium sulphate to dry overnight. The solution was filtered and the solvent removed on a rotary evaporator using water aspiration. Recrystallization from dichloromethane/pentane afforded the red crystalline product (1.1 g, 63% yield).

The $P(OPh)_3$, PPh_2Me, and $PPhMe_2$ derivatives were prepared similarly with the exception that they were recrystallized from hot petroleum ether (60-80°).

Method B. To a magnetically stirred THF solution of $[(\eta\text{-}C_7H_7)Mo(CO)_2\text{-}PPh_3][PF_6]$ (1.1 g, 1.7 mmol) excess sodium borohydride was added in small portions over a period of 1 h. The solution was filtered and the solvent removed on a rotary evaporator. Chromatography on Florisil, using dichloromethane as solvent and eluant, was followed by recrystallization from dichloromethane/heptane to give the product (0.6 g, 70% yield).

The $AsPh_3$ and $SbPh_3$ derivatives were prepared similarly with the exception that they were recrystallized from hot petroleum ether (60-80°).

Preparation of $(1\text{-}6\text{-}\eta\text{-}C_7H_7Me)Mo(CO)_2P(OPh)_3$

To a suspension of $[(\eta\text{-}C_7H_7)Mo(CO)_2P(OPh)_3][PF_6]$ (0.75 g, 1.1 mmol) in 60 ml of ether, 1.5 *M* methyllithium in ether (0.9 ml, 1.3 mmol) was added. After stirring for 1 h the deep-red reaction mixture was filtered and the ether solvent removed on a rotary evaporator. The product was extracted with 50 ml hot petroleum ether (60-80°) and crystallized on cooling to −20°. Recrystallization from dichloromethane afforded red plate-like crystals (0.5 g, 82% yield).

Preparation of $(1\text{-}6\text{-}\eta\text{-}C_7H_7Me)Mo(CO)_2PPh_2Me$

To a solution of $[(\eta\text{-}C_7H_7)Mo(CO)_2PPh_2Me][PF_6]$ (1.7 g, 2.9 mmol) in 20 ml tetrahydrofuran, 2 ml of 1.5 *M* methyllithium in ether was added slowly and the solution stirred for 1 h. The solvent was removed under reduced pressure and the residue extracted with dichloromethane and filtered. The solution was concentrated and chromatographed on Florisil, eluting as a single red band in dichloromethane. Recrystallization from hot petroleum ether (60-80°) afforded the product (0.9 g, 68% yield).

The compounds $(1\text{-}6\text{-}\eta\text{-}C_7H_7\text{-t-Bu})Mo(CO)_2PPh_3$ and $(1\text{-}6\text{-}\eta\text{-}C_7H_7Me)Mo(CO)_2\text{-}PPh_3$ were prepared similarly. The latter was only slightly soluble in dichloromethane and was purified by washing with dichloromethane and tetrahydrofuran.

Results and discussion

It has been found that substituted cycloheptatrienylium cations may be reduced using sodium borohydride to the neutral 1-6-η-cycloheptatriene complexes. Thus, provided that the appropriate substituted cation can be prepared, the following route leads to the desired neutral complexes:

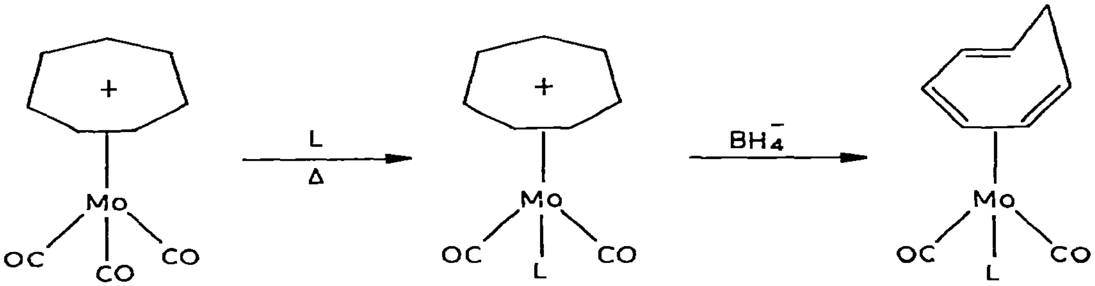

Table 1 lists the six phosphine, phosphite, arsine, and stibine cations which were prepared in this work, and their hydride reduction products. In addition, alkyl-substituted cycloheptatriene complexes were formed in the analogous reaction of organolithium reagents.

The ligands $P(OPh)_3$, PPh_3, PPh_2Me, $AsPh_3$ and $SbPh_3$ reacted with $[(\eta\text{-}C_7H_7)Mo(CO)_3][PF_6]$ in refluxing ethanol with displacement of a single carbonyl group. Yields ranged from 41-77% and the reaction was accompanied by the formation of unidentified byproducts not containing metal carbonyl groups. Reactions with $P(OMe)_3$, $P(OEt)_3$, $P(n\text{-}Bu)_3$, and PEt_3, resulted largely in ring displacement, with formation of the *fac*-$L_3Mo(CO)_3$ product.

These results are consistent with the initial formation of a *pentahapto* intermediate $[(1\text{-}5\text{-}\eta\text{-}C_7H_7)Mo(CO)_3L]^+$ as postulated in a kinetic study of the reaction with acetonitrile as ligand [6]. Loss of a carbonyl from this intermediate would presumably be favored when less basic and bulkier aryl-substituted ligands were involved, while more nucleophilic and less hindered ligands would attack the molybdenum, with eventual displacement of the ring. Both pathways were observed when the reaction was carried out with $PPhMe_2$; with a large excess of this ligand $(OC)_3Mo(PPhMe_2)_3$ was formed almost exclusively, whereas with slow addition of ligand, $[(\eta\text{-}C_7H_7)Mo(CO)_2PPhMe_2]^+$ was predominant.

It is worth noting that the solvent plays a critical role in these reactions. When "98% ethanol" (ca. 2% benzene) was used, yields were curtailed in some reactions, and no carbonyl-containing product was obtained in others. The presence of ca. 5% water ("95% ethanol") is necessary for most of these reactions, an observation we are unable to rationalize.

The compounds of type $[(\eta\text{-}C_7H_7)Mo(CO)_2L][PF_6]$ range in color from orange to wine-red. They are insoluble in water and hydrocarbon solvents but readily soluble in dichloromethane, acetone, and acetonitrile. In solution they undergo slow decomposition, even under nitrogen, but solid samples are air stable for long periods of time.

The addition of sodium borohydride to the cationic complexes afforded the corresponding cycloheptatriene derivatives in yields ranging from 65-74%. The reductions were carried out using either a two-layer water/benzene system or more conveniently in tetrahydrofuran. The recently reported triphenylphosphine derivative [3] was prepared using water/tetrahydrofuran as solvent.

Addition of alkyllithium reagents to selected cationic complexes in tetrahydrofuran or ether resulted in the formation of alkylcycloheptatriene complexes of general formula $(1\text{-}6\text{-}\eta\text{-}C_7H_7R)Mo(CO)_2L$ ($R = Me$, $L = P(OPh)_3$, PPh_3, PPh_2Me; $R = t\text{-}Bu$, $L = PPh_3$). Similar additions to cationic complexes of this type have been shown to occur from the less sterically hindered *exo* side [7-9] and NMR studies (see below) are consistent with this stereochemistry in the present derivatives. In contrast, when $[(\eta\text{-}C_7H_7)Mo(CO)_3]^+$ was treated with methyllithium, complete decomposition resulted; its instability to nucleophilic attack has already been noted [9].

The $(1\text{-}6\text{-}\eta\text{-}C_7H_8)Mo(CO)_2\text{-}PPh_3$ and $\text{-}AsPh_3$ complexes failed to react with additional PPh_3 and $AsPh_3$ even in refluxing benzene. As noted earlier $(1\text{-}6\text{-}\eta\text{-}C_7H_8)Mo(CO)_3$ reacts with donor molecules at room temperature with loss of the ring. No doubt this difference is due to a combination of electronic and steric factors.

The cycloheptatriene compounds prepared form red crystals which are air stable for long periods. The stability of these derivatives is in marked contrast to that reported for (1-6-η-C_7H_8)Cr(CO)$_2$-P(OPh)$_3$ and -PPh$_3$ [10]. The derivatives prepared in the present work are sufficiently soluble in hydrocarbon solvents for infrared measurements. In donor solvents such as acetonitrile and acetone, they begin to oxidize after a few hours.

Spectroscopic properties

Carbonyl stretching bands observed in the infrared spectrum of all the complexes are reported in Table 2. The expected two bands are observed except in the cases of (1-6-η-C_7H_8)Mo(CO)$_2$P(OPh)$_3$ and its 7-methyl analogue, which show a symmetrical, high frequency band and a lower frequency band split into two peaks and a shoulder. Repeated recrystallizations and chromatography did not change the spectra of these triphenylphosphite complexes. A complete elemental analysis of (1-6-η-C_7H_8)Mo(CO)$_2$P(OPh)$_3$ supported the formula, while osmometric molecular weight and mass spectral measurements confirmed the monomeric character. Moreover, the ^{1}H and ^{13}C NMR spectra displayed no unusual features.

Conformational isomerism has been invoked in other phosphite complexes [11, 12] and is probably also the source of the supernumerary carbonyl stretching bands in the present cases. However, the observed spectra are not typical, showing splitting of only the lower frequency band. To our knowledge, a similar splitting has been observed in only one other system [13].

The ^{1}H NMR spectra of η-C_7H_7 derivatives show a sharp signal (a doublet in the phosphorus derivatives) near τ 4 confirming the presence of the symmetrical seven-membered ring. Details are given as footnotes to Table 2. Table 3 presents details of ^{1}H NMR spectra of the 1-6-η-C_7H_7R complexes, which closely resemble those of the parent tricarbonyls [10, 14, 15].

A distinction between *exo* and *endo* isomers in substituted cycloheptatriene derivatives may be made on the basis of ^{1}H NMR spectra of chromium derivatives [15]. It was found that *exo* alkyl groups were shifted to higher field and *endo* to lower field by comparison with the uncoordinated hydrocarbon. In the present work the methyl resonance of (1-6-η-C_7H_7Me)Mo(CO)$_2$L (L = P(OPh)$_3$ and PPh$_2$Me) occurred at τ 9.9, shifted from τ 9.06 in C_7H_7Me, indicative of *exo* geometry.

The ^{13}C NMR spectra of (1-6-η-C_7H_8)Mo(CO)$_2$L (L = P(OPh)$_3$, PPh$_2$Me, PPhMe$_2$) compounds at various temperatures are listed in Table 4. Four signals due to ring carbon atoms were observed at all temperatures; these closely resembled the spectrum of the parent tricarbonyl [16, 17] and were similarly assigned. Only one ^{13}CO signal (with ^2J(P—C) ranging from 10 to 17 Hz) was observed down to the lowest temperature at which a satisfactory spectrum could be obtained (—70° in the most favorable cases). The latter point is particularly interesting with respect to the behavior of the parent tricarbonyl, which exhibits two ^{13}CO signals in 2/1 intensity ratio at —50° (as expected for the C_s molecule) and a single averaged signal at room temperature [17]. In the monosubstituted complexes, C_s and C_1 conformers are possible, and the barrier to their interconversion would be expected to be at least as high as that of the tricarbonyl. Thus, the observed single ^{13}CO peak at low temperature for the monosubstituted compounds implies the existence of a single conformer having C_s symmetry. A C_1 conformer would give rise to two ^{13}CO signals as well as a more complex spectrum for the ring.

Major fragments in the mass spectra of representative cycloheptatriene compounds are listed in Table 5. Peaks for $[P]^+$ and $[P - CO]^+$ were observed for all compounds, but at lower relative intensities than in the tricarbonyl. Loss of the last CO was accompanied by elimination of H_2. In most cases the $[P - 2CO - 2H]^+$ peak was the most intense peak containing molybdenum, and in some cases the base peak. The ion $[C_7H_8Mo]^+$ was either not observed or of weak intensity, whereas $[C_7H_8Mo]^+$ forms the base peak in the spectrum of $C_7H_8Mo(CO)_3$.

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