43065-08-3; Ph$_4$As[Co(dmgH)$_2$(SCN)(CH$_3$)], 43065-12-9; Ph$_4$As[Co(dmgH)$_2$(NCS)(CHBr$_2$)], 68645-97-6; Ph$_4$As[Co-(dmgH)$_2$(SCN)(CHBr$_2$)], 68645-95-4; Ph$_4$As[Co(dmgH)$_2$(NCS)-(CF$_3$)], 68645-93-2; Ph$_4$As[Co(dmgH)$_2$(SCN)(CF$_3$)], 68645-91-0; Ph$_4$As[Co(dmgH)$_2$(NCSe)(CH$_3$)], 68645-89-6; Ph$_4$As[Co-(dmgH)$_2$(SeCN)(CH$_3$)], 68646-25-3; Ph$_4$As[Co(dmgH)$_2$(NCSe)-(CHBr$_2$)], 68646-23-1; Ph$_4$As[Co(dmgH)$_2$(SeCN)(CHBr$_2$)], 68646-21-9; Ph$_4$As[Co(dmgH)$_2$(NCSe)(CF$_3$)], 68646-19-5; Ph$_4$As[Co(dmgH)$_2$(SeCN)(CF$_3$)], 68646-17-3; Ph$_4$As[Co-(dmgH)$_2$(NCO)(CH$_3$)], 68646-15-1; Ph$_4$As[Co(dmgH)$_2$(NCO)-(CHBr$_2$)], 68646-13-9; Ph$_4$As[Co(dmgH)$_2$(NCO)(CF$_3$)], 68646-11-7; (CH$_3$)Co(dmgH)$_2$(NCS)Co(dmgH)$_2$(py), 68646-09-3; (CH$_3$)Co-(dmgH)$_2$(SCN)Co(dmgH)$_2$(py), 68646-08-2; (CH$_3$)Co(dmgH)$_2$-(NCS)Co(dmgH)$_2$(pip), 68646-07-1; (CH$_3$)Co(dmgH)$_2$(SCN)Co-(dmgH)$_2$(pip), 68646-06-0; (CF$_3$)Co(dmgH)$_2$(NCS)Co(dmgH)$_2$(py), 68646-05-9; (CF$_3$)Co(dmgH)$_2$(SCN)Co(dmgH)$_2$(py), 68646-04-8; (CF$_3$)Co(dmgH)$_2$(NCS)Co(dmgH)$_2$(pip), 68646-03-7; (CF$_3$)Co-(dmgH)$_2$(SCN)Co(dmgH)$_2$(pip), 68646-40-2; (CH$_3$)Co(dmgH)$_2$-(NCSe)Co(dmgH)$_2$(py), 68646-39-9; (CH$_3$)Co(dmgH)$_2$(NCSe)-Co(dmgH)$_2$(pip), 68646-38-8; (CH$_3$)Co(dmgH)$_2$(NCSe)Co-(dmgH)$_2$(py-3-Cl), 68646-37-7; (CH$_3$)Co(dmgH)$_2$(NCSe)Co-(dmgH)$_2$(NH$_3$), 68646-36-6; (CH$_3$)Co(dmgH)$_2$(NCSe)Co-(dmgH)$_2$(NH$_2$-pr), 68646-35-5; (CF$_3$)Co(dmgH)$_2$(NCSe)Co-(dmgH)$_2$(py), 68646-34-4; (CF$_3$)Co(dmgH)$_2$(NCSe)Co(dmgH)$_2$(pip), 68646-33-3; Ph$_4$As[(CH$_3$)Co(dmgH)$_2$(NCS)Co(dmgH)$_2$(CH$_3$)], 43065-20-9; Ph$_4$As[(CF$_3$)Co(dmgH)$_2$(NCS)Co(dmgH)$_2$(CF$_3$)], 68646-32-2; Ph$_4$As[(CH$_3$)Co(dmgH)$_2$(NCSe)Co(dmgH)$_2$(CH$_3$)], 68646-30-0; Ph$_4$As[(CF$_3$)Co(dmgH)$_2$(NCSe)Co(dmgH)$_2$(CF$_3$)], 68715-75-3; Co(dmgH)$_2$(CF$_3$), 68646-28-6; Co(dmgH)$_2$(CF$_3$)(H$_2$O), 59493-04-8; [Co(dmgH)$_2$(CF$_3$)]$_2$, 68646-27-5; Co(dmgH)$_2$(CH$_3$)-(S(CH$_3$)$_2$), 25482-40-0; Co(dmgH)$_2$(CHBr$_2$)(S(CH$_3$)$_2$), 68646-26-4; Co(dmgH)$_2$(CH$_3$), 36609-02-6; Co(dmgH)$_2$(CH$_3$)(py), 23642-14-0.

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Chemistry of Ring-Bridged Bis(η⁵-cyclopentadienyl) Ligands. Derivatives of α,α'-Dicyclopentadienyl-m-xylene

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The synthesis of the ligand α,α'-dicyclopentadienyl-*m*-xylene (**1**) is reported. **1** was found to polymerize readily; however, reaction with sodium hydride, before extensive polymerization had occurred, gave the dianion of disodium (*m*-phenyl-enedimethylene)dicyclopentadienide (**2**). **2** was used to prepare additional derivatives of the type *m*-C$_6$H$_4$(CH$_2$C$_5$H$_4$R)$_2$, where R = CH$_3$ or Si(CH$_3$)$_3$. The thermolysis of Mo(CO)$_6$ and the photolysis of W(CO)$_6$ with dianion **2** in tetrahydrofuran generated *m*-C$_6$H$_4$(CH$_2$C$_5$H$_4$M(CO)$_3$)$_2^{2-}$, where M = Mo (**5**) and W (**6**). These metallo dianions were reacted with alkyl halides to prepare *m*-C$_6$H$_4$(CH$_2$C$_5$H$_4$M(CO)$_3$R)$_2$, where M = Mo and W and R = CH$_3$ and CH$_2$CH$_3$. The chemistry of the bridged molybdenum derivatives was examined in more detail with R = H, I derivatives being prepared. The hydrido derivative was found to reduce 1,3-pentadiene and phenylacetylene with the subsequent formation of complex **14**, *m*-C$_6$H$_4$[CH$_2$C$_5$H$_4$Mo(CO)$_3$]$_2$. A better preparation of **14** involved the reaction of 1,2-dibromoethane with dianion **5** in a 1:1 ratio. Photolysis of the methylmolybdenum derivative in the presence of triphenylphosphine affords *m*-C$_6$H$_4$-[CH$_2$C$_5$H$_4$Mo(CO)$_2$CH$_3$P(C$_6$H$_5$)$_3$]$_2$.

Introduction

We have made a preliminary report[1] of the preparation and chemistry of α,α'-dicyclopentadienyl-*m*-xylene (**1**) *m*-C$_6$H$_4$-(CH$_2$C$_5$H$_5$)$_2$. This ligand belongs to the class of covalently linked bis(cyclopentadiene) ligands Z(C$_5$H$_5$)$_2$ which can be used to prepare linked bimetallic complexes of the type Z-(η⁵-C$_5$H$_4$ML$_n$)$_2$ where L is the extensive group of ligands that binds with metal cyclopentadiene units. Several linked complexes which are derived from the [η⁵-C$_5$H$_5$Fe(CO)$_2$]$_2$ systems have been prepared: [η⁵-C$_5$H$_4$CR$_1$R$_2$CR$_1$R$_2$-η⁵-C$_5$H$_4$]Fe$_2$(CO)$_4$ where R$_1$ = H, R$_2$ = N(CH$_3$)$_2$[2a,c] and R$_1$ = R$_2$ = CH$_3$[2b,c] and (CH$_3$)$_2$Si[η⁵-C$_5$H$_4$Fe(CO)$_2$]$_2$.[1,3] Additionally complexes of the silicon-bridged system which do not contain a metal–metal bond have been reported:[4] (CH$_3$)$_2$Si[η⁵-C$_5$H$_4$M(CO)$_3$]$_2$ where M = Mn or Re and (CH$_3$)$_2$Si[η⁵-C$_5$H$_4$Co(CO)$_2$]$_2$. In this paper the details of the preparation

Table I. ¹H NMR Data for 1 and Its Main-Group Derivatives[a]

compd	C_6H_4	Cp[b] [range]	CH_2	Cp[c]	CH_3	$(CH_3)_3Si$	rel areas
m-$C_6H_4(CH_2C_5H_5)$ (1)	7.0 m	6.12 m [6.3–5.9]	3.63 s	2.78 s			
m-$C_6H_4(CH_2C_5H_4CH_3)_2$ (3)	7.10 m	6.23 m [6.5–5.9]	3.70 br, s	3.0 m	2.13 s[d]		4.0/4.2/4.0/4.0/5.9
m-$C_6H_4[CH_2C_5H_4Si(CH_3)_3]_2$ (4)	7.05 m	6.27 m [6.5–5.9]	3.68 s	2.80 m 3.25 sm, br, s		−0.05 s[e]	4.0/6.3/4.0/1.7/18.0

[a] Chemical shifts in ppm vs. internal Me₄Si in CDCl₃ solvent. Key: s = singlet, d = doublet, m = multiplet, br = broad, sh = shoulder, sm = small, v = very. [b] Cyclopentadienyl vinyl protons (centers of very broad multiplets). [c] Cyclopentadienyl allylic protons. [d] Singlet with very small multiplet on upfield tail. [e] This peak represents 78% (by integration) of the trimethylsilyl isomers present. Additional peaks at 0.12 ppm (closely spaced triplet) and 0.07 ppm (singlet) were 19 and 3% of the total which integrated to 18.0 protons.

Table II. Infrared Carbonyl Stretching Frequencies of the Bridged Bimetallic Derivatives

compd	$\nu(C\equiv O)$,[a] cm^{-1}	solvent
m-$C_6H_4[CH_2C_5H_4Mo(CO)_3]_2^{2-}$ (5)[b]	1898, 1796, 1741	THF
m-$C_6H_4[CH_2C_5H_4W(CO)_3]_2^{2-}$ (6)	1892, 1792, 1736	THF
m-$C_6H_4[CH_2C_5H_4Mo(CO)_3H]_2$ (13)[c]	2025, 1930	C_6H_6
m-$C_6H_4[CH_2C_5H_4Mo(CO)_3CH_3]_2$ (7)	2018, 1926	CH_2Cl_2
m-$C_6H_4[CH_2C_5H_4Mo(CO)_3C_2H_5]_2$ (9)	2013, 1919	CH_2Cl_2
m-$C_6H_4[CH_2C_5H_4Mo(CO)_2P(C_6H_5)_3\text{-}CH_3]_2$ (11)[c]	1960, 1865	CH_2Cl_2
m-$C_6H_4[CH_2C_5H_4Mo(CO)_3I]_2$ (12)[c]	2035, 1960	CH_2Cl_2
m-$C_6H_4[CH_2C_5H_4W(CO)_3CH_3]_2$ (8)	2015, 1916	CH_2Cl_2
m-$C_6H_4[CH_2C_5H_4W(CO)_3C_2H_5]_2$ (10)	2009, 1910	CH_2Cl_2
m-$C_6H_4[CH_2C_5H_4Mo(CO)_3]_2$ (14)[d]	2048, 2011, 1953, 1910, 1867 w, sh	$CH_3C_6H_5$

[a] The absorptions are strong unless otherwise indicated; estimated accuracy is ±2 cm⁻¹. Key: w = weak, sh = shoulder. [b] Reported values for [C₅H₅Mo(CO)₃]⁻ in THF are 1901, 1798, and 1745 cm⁻¹.[32] [c] These carbonyl stretching frequencies were obtained from preparative IR spectra; estimated accuracy is ±5 cm⁻¹. [d] A very weak shoulder attributable to slight decomposition or impurity is sometimes also observed at 1970 cm⁻¹. This peak grows with time in CDCl₃ solvent in the absence of air.

and chemistry of **1** and its dianion m-$C_6H_4(CH_2C_5H_4)_2^{2-}$ (**2**) are reported. Derivatives of **1** and **2** containing both main-group and transition-metal elements have been prepared.

Experimental Section

General Procedures. All manipulations were performed either under a nitrogen atmosphere using standard inert atmosphere techniques or under high vacuum. Tetrahydrofuran (THF) and diethyl ether were distilled under nitrogen over Vitride (sodium bis(2-methoxyethoxy)aluminum hydride, 70% in benzene) that was purchased from Eastman. Other solvents were distilled under nitrogen using appropriate drying agents. The 1,3-bis(bromomethyl)benzene was purchased from Aldrich and recrystallized from hexane. Sodium hydride, as a 50% dispersion in mineral oil (Anal. NaH, 56–58%), was purchased from Alfa-Ventron. Metal carbonyls were sublimed and alkyl halides were distilled prior to use.

Ultraviolet photolyses were performed with a Rayonet RPR-100 photochemical reactor equipped with a magnetic stirrer, utilizing a full set of 16 RPR-2537 Å reactor lamps and round-bottom quartz photolysis vessels. Infrared spectra were recorded with a Perkin-Elmer Model 621 spectrometer using polystyrene for calibration. Preparative infrared spectra were obtained on a Perkin-Elmer Model 137 spectrometer. Proton NMR spectra were recorded on a Varian EM360 (60 MHz) spectrometer in CDCl₃ (99.8%) using Me₄Si as an internal standard. Mass spectra were obtained with a Varian MAT 111 mass spectrometer. The NMR and infrared spectroscopic data are listed in Tables I, II, and III and in a few instances in the experimental directions.

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. All melting points were taken in sealed, evacuated capillaries and are uncorrected.

Synthesis of α,α'-Dicyclopentadienyl-m-xylene (1), m-C₆H₄-(CH₂C₅H₅)₂. Freshly cracked cyclopentadiene (1.33 g, 20.1 mmol) in 10 mL of tetrahydrofuran was added dropwise to 1.05 g (25 mmol) of sodium hydride (56–58% oil dispersion previously washed with 3 × 5 mL of tetrahydrofuran), suspended in 10 mL of tetrahydrofuran with stirring at 0 °C. After the addition was complete (≃15 min), the solution was allowed to warm momentarily and was then filtered under nitrogen into a pressure-equalizing dropping funnel. As the filtered sodium cyclopentadienide solution was added dropwise to 2.64 g (10.0 mmol) of 1,3-bis(bromomethyl)benzene in 5 mL of tetrahydrofuran stirred at 0 °C, the immediate formation of a white precipitate was observed. The mixture was stirred an additional 45 min at 0 °C and then filtered. The sodium bromide was washed with 2 × 7 mL of tetrahydrofuran, and the washings were added to the filtrate. The sodium bromide was dried under vacuum and could be isolated in near-quantitative yields (95–98%). The filtrate and washings were used to prepare dianion **2**.

Prolonged standing or concentration of solutions containing ligand **1** produced yellow oily polymers. Attempts to crack polymerized ligand **1** at elevated temperatures under high vacuum failed, producing instead a hard, clear yellow glass.

Disodium (m-Phenylenedimethylene)dicyclopentadienide (2), m-C₆H₄(CH₂C₅H₄Na)₂. The faint yellow filtrate containing **1** was added, over a 25-min period, directly into a 100-mL round-bottom flask containing 3.37 g (80 mmol, a fourfold excess) of sodium hydride (56–58% oil dispersion) with stirring. The sodium hydride had previously been washed with 3 × 10 mL of tetrahydrofuran and suspended in 5 mL of tetrahydrofuran. After completion of the addition, the mixture was stirred at room temperature until the evolution of hydrogen was no longer apparent (usually 45 min). The mixture was then filtered into a receiving flask and the clear, faint orange filtrate was used in situ for further reactions. Like other cyclopentadienide salts dianion **2** is very air sensitive and solutions may vary from faint orange to reddish brown depending on the care taken in preparation.

α,α'-Bis(methylcyclopentadienyl)-m-xylene (3), m-C₆H₄-(CH₂C₅H₄CH₃)₂, and α,α'-Bis((trimethylsilyl)cyclopentadienyl)-m-xylene (4), m-C₆H₄(CH₂C₅H₄Si(CH₃)₃)₂. A solution of **2**, prepared

Table III. ¹H NMR Data for the Bridged Bimetallic Derivatives[a]

compd	C_6H_4	C_5H_4	CH_2	H	CH_3	C_2H_5	$(C_6H_5)_3$	proton ratios
m-$C_6H_4[CH_2C_5H_4Mo(CO)_3CH_3]_2$ (7)	7.10 m	5.16 s	3.54 s		0.35 s			4:8:4:6
m-$C_6H_4[CH_2C_5H_4Mo(CO)_3C_2H_5]_2$ (9)	7.12 m	5.14 s	3.57 s			1.53 m		4:8:4:10
m-$C_6H_4[CH_2C_5H_4Mo(CO)_3]_2$ (14)	7.08 m	5.13 s	3.65 s					4:8:4
m-$C_6H_4[CH_2C_5H_4Mo(CO)_2P(C_6H_5)_3CH_3]_2$ (11)	7.09 m	4.54 m	3.54 s		0.40 d		7.43 m	4:8:4:6:30
m-$C_6H_4[CH_2C_5H_4Mo(CO)_3I]_2$ (12)	7.18 m	5.46 s	3.83 s					4:8:4
m-$C_6H_4[CH_2C_5H_4W(CO)_3CH_3]_2$ (8)	7.12 m	5.24 s	3.62 s		0.40 s			4:8:4:6
m-$C_6H_4[CH_2C_5H_4W(CO)_3C_2H_5]_2$ (10)	7.14 m	5.23 s	3.66 s			1.52 m		4:8:4:10
m-$C_6H_4[CH_2C_5H_4Mo(CO)_3H]_2$ (13)[b]				−5.45				

[a] Chemical shifts in ppm vs. internal Me₄Si in CDCl₃ solvent. Key: d = doublet, m = multiplet, s = singlet. [b] Chemical shift of hydride in THF.

at half scale (5.0 mmol of **2**), was brought to a volume of 50 mL by addition of tetrahydrofuran. Methyl iodide (2.84 g, 20.0 mmol) was added to the solution by syringe. After 3 h of stirring, the solvent was removed under reduced pressure at room temperature. The residue was extracted with either CDCl₃ or dichloromethane and the solution was then filtered (through a disposable pipet containing 1 cm of silica gel with 1 cm of Celite atop) to obtain spectroscopic samples. The sample was used as such for the ¹H NMR and the solvent was removed from the dichloromethane solution to obtain a sample for the mass spectrum. Mass spectrum (70 eV) *m/e* (relative intensity): 51 (30), 53 (50), 55 (56), 65 (49), 77 (98), 78 (62), 79 (39), 89 (29), 91 (100), 92 (34), 93 (51), 103 (38), 104 (41), 105 (49), 115 (56), 127 (11), 128 (74), 129 (34), 141 (69), 142 (23), 152 (41), 153 (48), 154 (31), 155 (36), 165 (46), 166 (25), 167 (59), 168 (34), 169 (44), 181 (13), 182 (23), 183 (34), 248 (21), *m/e* 262 (41) for the parent ion (M⁺ calcd for C₂₀H₂₂, 262) and a trace peak at M + 14 (peaks below *m/e* 45 not included).

Compound **4**, was prepared in a similar fashion using 2.18 g (20 mmol) of trimethylchlorosilane.

In solution at room temperature compound **3** gradually turns yellow and **4** turns reddish orange. Both **3** and **4** polymerize when stored in solution at room temperature for periods of time, although less readily than **1**.

Disodium [(*m*-Phenylenedimethylene)bis(η⁵-cyclopentadienyl)]-[tricarbonylmolybdate(1–)] (5), *m*-C₆H₄(CH₂C₅H₄Mo(CO)₃Na)₂. A solution of **2** was filtered directly into a 100-mL round-bottom flask containing 5.28 g (20.0 mmol) of Mo(CO)₆. The mixture was refluxed 20 h producing a clear brownish solution (which was clear yellow when diluted 1:10 with tetrahydrofuran). The solvent was removed under reduced pressure leaving a gummy brown solid which was triturated and washed with diethyl ether (8 × 30 mL) affording a light brown powder of **5**. This powder could be stored for short periods of time under inert atmosphere without any appreciable decomposition. However, it was generally redissolved in 40 mL of tetrahydrofuran, filtered through Celite, and used immediately for subsequent reactions. It was also possible to use solutions of **5** without purification. IR (tetrahydrofuran): *ν*(C≡O) 1898, 1796, and 1741 cm⁻¹.

[α,α′-*m*-Xylenebis(η⁵-cyclopentadienyl)]bis[tricarbonyl(methyl)-molybdenum] (7), *m*-C₆H₄(CH₂C₅H₄Mo(CO)₃CH₃)₂. After filtering of a purified 40-mL solution of **5** in tetrahydrofuran through Celite, 2.5 mL (40 mmol) of methyl iodide was added. Although the solution turned a lighter brown and a white precipitate formed shortly after addition of the methyl iodide, the solution was stirred at room temperature for 15 h to ensure complete reaction. The solvent was then stripped off leaving a brown solid which was redissolved in 40 mL of benzene. The benzene solution was filtered through Celite and the solvent removed under reduced pressure leaving a gummy brown solid which was triturated with 5 mL of diethyl ether and then washed with an additional 3 × 5 mL of diethyl ether. This afforded 2.01 g (32%) of **7**, as a very light brown powder. This crude product was found to be sufficiently pure by ¹H NMR and melting point for most purposes. The product was recrystallized from 25% dichloromethane in hexane affording small yellow-orange crystals of **7**, mp 139–140 °C (decomposes with considerable gas evolution to a deep red liquid). IR (CH₂Cl₂) *ν*(C≡O) 2018 and 1926 cm⁻¹. Anal. Calcd for C₂₆H₂₂O₆Mo₂: C, 50.17; H, 3.57; Mo, 30.83. Found: C, 50.05; H, 3.94; Mo, 30.56.

Pure crystalline **7** can be handled in air; however, it was stored under nitrogen. Ethereal solutions of **7** when exposed to air decompose readily, whereas solutions of **7** in other polar solvents are relatively stable to short exposures to air.

[α,α′-*m*-Xylenebis(η⁵-cyclopentadienyl)]bis[tricarbonyl(ethyl)mo-lybdenum] (9), *m*-C₆H₄(CH₂C₅H₄Mo(CO)₃CH₂CH₃)₂. A solution of dianion **5** was used without a prior diethyl ether wash. Ethyl iodide (3.2 mL, 40 mmol) was added to the solution at 0 °C. After stirring of the mixture at 0 °C for 16 h, the solvent was removed from the brown solution under reduced pressure at 0 °C. When the solvent had been removed, the temperature was raised to 36 °C in an attempt to dry the remaining brown oil under vacuum. The residue was dissolved in dichloromethane and the solution was then filtered through Celite. Silica gel was added to the filtrate and the solvent removed under reduced pressure. The solid was placed atop a silica gel chromatography column prepared with hexane. The column was eluted with hexane, separating a yellow band which contained C₅H₅-Mo(CO)₃CH₂CH₃ and Mo(CO)₆, a second small pink band which contained a trace of an unidentified compound, and a third yellow

band, which contained product **9**. The column was then eluted with mixtures of dichloromethane–hexane affording a red band, which was the major component. Product **9** was isolated by concentrating the eluted third band under reduced pressure and then cooling in a dry ice–acetone bath. This yielded 0.420 g (6.5%) of yellow crystalline **9**: mp 89–90 °C (decomposes to a deep brown liquid with gas evolution); IR (CH₂Cl₂) *ν*(C≡O) 2013 and 1919 cm⁻¹.

Removal of the solvent from the red fourth band, in vacuo, afforded 2.65 g of a reddish brown solid. The ¹H NMR of this product exhibited both metal–ethyl and normal ethyl resonances in addition to the resonances characteristic of the *m*-xylyl unit. The product may be similar to **9** but with ethyl groups replacing some hydrogen atoms on the cyclopentadiene rings.

[α,α′-*m*-Xylenebis(η⁵-cyclopentadienyl)]bis[tricarbonyl(hydrido)-molybdenum] (13), *m*-C₆H₄(CH₂C₅H₄Mo(CO)₃H)₂. Trifluoroacetic acid (1.23 g, 10.8 mmol) was added to a 40-mL solution of **5** prepared at half scale and purified by the diethyl ether wash. The reaction mixture was stirred at room temperature for 1 h after which the solvent was stripped off leaving a brown solid. This solid was redissolved in benzene and filtered through Celite. The hydride was either used in the benzene solution or the benzene was removed under reduced pressure and the resultant solid redissolved in tetrahydrofuran. In the ¹H NMR of **13** in tetrahydrofuran the hydride resonance was observed at *τ* 15.45. IR (benzene) *ν*(C≡O) 2025 and 1930 cm⁻¹.

[α,α′-*m*-Xylenebis(η⁵-cyclopentadienyl)]bis[tricarbonylmolybdenum] (14), *m*-C₆H₄(CH₂C₅H₄Mo(CO)₃)₂. A solution of **5** prepared at one-fourth scale (2.5 mmol) was diluted to 50 mL with additional tetrahydrofuran. On slow addition of 0.475 g (2.53 mmol) of 1,2-dibromoethane in 10 mL of tetrahydrofuran, over a 1-h period, the solution darkened and a white precipitate formed. Within 12 h the solution had turned deep red. After stirring of the reaction mixture for 48 h, it was filtered through Celite. The solvent was removed from the filtrate under reduced pressure affording a red solid which was washed repeatedly with diethyl ether and pentane affording 1.27 g (86%) of crude **14**, a brick red powder. Product **14** could be further purified by chromatography on Celite with toluene (or benzene)–hexane mixtures and removal of the solvent under vacuum to afford a brick red powder (crystals of the product have thus far been rather elusive): mp ∼70 °C; IR (CH₃C₆H₅) *ν*(C≡O) 2048, 2011, 1953, 1910, and 1867 cm⁻¹. Anal. Calcd for C₂₄H₁₆O₆Mo₂: C, 48.67; H, 2.72; Mo, 32.40. Found: C, 48.96; H, 3.26; Mo, 32.09.

Compound **14** could also be prepared by stirring hydride **13** in benzene with excess phenylacetylene for periods of a week or longer at room temperature. The reaction time was reduced to less than 10 h when the reaction solution was heated with stirring in a 90 °C oil bath. Similarly, a catalytic amount of trifluoroacetic acid or mixtures of 1,3-pentadiene and phenylacetylene reduced the reaction time to less than 10 h. It was also possible to obtain **14** in low yields by refluxing ligand **1** in tetrahydrofuran with a stoichiometric amount of (CH₃CN)₃Mo(CO)₃ and chromatographing the resultant products.

Disodium [(*m*-Phenylenedimethylene)bis(η⁵-cyclopentadienyl)]-bis[tricarbonyltungstate(1–)] (6), *m*-C₆H₄(CH₂C₅H₄W(CO)₃Na)₂. A solution of **2** was placed into a 150-mL quartz photolysis vessel containing 6.34 g (18.0 mmol) of W(CO)₆. Tetrahydrofuran was added to bring the volume to 150 mL and the solution was then photolyzed with continuous stirring for 2–3 days. During this time the photolysis vessel was cleaned several times. The solution was then transferred from the photolysis vessel and the solvent removed in vacuo. The yellow solid that remained was washed with 5 × 25 mL of diethyl ether affording a yellow powder. The tungsten dianion **6** is storable at this stage, but like the molybdenum dianion (**5**) it is very air sensitive. Generally it was redissolved immediately in 40–50 mL of tetrahydrofuran, and then filtered through Celite, and the reddish orange solution of **6** was used immediately for subsequent reactions. IR (tetrahydrofuran) *ν*(C≡O) 1892, 1792 and 1736 cm⁻¹.

[α,α′-*m*-Xylenebis(η⁵-cyclopentadienyl)]bis[tricarbonyl(methyl)-tungsten] (8), *m*-C₆H₄(CH₂C₅H₄W(CO)₃CH₃)₂. A solution of dianion **6**, which had been ether washed and redissolved in 40 mL of tetrahydrofuran, was stirred at room temperature as 2.5 mL (40 mmol) of methyl iodide was added slowly from a syringe. Gradually the solution became yellow and the reaction was shown to be essentially complete within 15 min as monitored by infrared spectroscopy. However, the reaction mixture was stirred for 15 h before the solvent was removed under reduced pressure to ensure complete reaction. The light brown residue was redissolved in benzene and filtered through Celite. The solvent was removed from the filtrate leaving a yellow
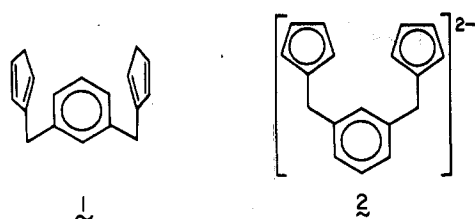
Figure 1. Structures of α,α'-dicyclopentadienyl-*m*-xylene (**1**) and its dianion (**2**).

solid which on washing with 3 × 5 mL of diethyl ether yielded 1.17 g (16% based on W(CO)$_6$) of **8**, a very light brown powder. Traces of W(CO)$_6$ were removed by sublimation at 40 °C. Compound **8** was recrystallized from 15% dichloromethane in hexane. IR (CH$_2$Cl$_2$) ν(C≡O) 2015, 1916 cm^{-1}.

[α,α'-*m*-Xylenebis(η^5-cyclopentadienyl)]bis[tricarbonyl(ethyl)-tungsten] (**10**), *m*-C$_6$H$_4$(CH$_2$C$_5$H$_4$W(CO)$_3$CH$_2$CH$_3$)$_2$. A solution prepared by redissolving ether-washed dianion **6** in 50 mL of tetrahydrofuran was stirred at 0 °C as 3.2 mL (40 mmol) of ethyl iodide was added slowly. The solution was stirred at 0 °C for 12 h during which time a white precipitate formed and the solution turned yellow. The solvent was removed under reduced pressure at 0 °C and the resultant yellow solid was extracted with dichloromethane, and the extracts were filtered through Celite. Silica gel was added to the filtrate and the solvent removed under reduced pressure. The solid was placed atop a silica gel chromatography column prepared with hexane. The first yellow band was eluted off with hexane and contained 0.10 g of C$_5$H$_5$W(CO)$_3$CH$_2$CH$_3$ as well as a small amount of W(CO)$_6$. The second band, also yellow, was eluted with 10% dichloromethane in hexane. After concentration of this band to 10–15 mL, 2.05 g (28%, based on W(CO)$_6$) of powdery yellow **10** was isolated. This was recrystallized from 15% dichloromethane in hexane at –20 °C yielding yellow crystalline **10**: mp 107.0–107.4 °C (slight decomposition); IR (CH$_2$Cl$_2$) ν(C≡O) 2009 and 1910 cm^{-1}. Anal. Calcd for C$_{28}$H$_{26}$O$_6$W$_2$: C, 40.70; H, 3.18; W, 44.50. Found: C, 40.08; H, 3.50; W, 44.43.

[α,α'-*m*-Xylenebis(η^5-cyclopentadienyl)]bis[tricarbonyl(iodo)molybdenum] (**12**), *m*-C$_6$H$_4$(CH$_2$C$_5$H$_4$Mo(CO)$_3$I)$_2$. Iodine, 0.54 g (2.13 mmol) in 5 mL of THF, was added dropwise to a solution of 0.660 g (1.06 mmol) of *m*-C$_6$H$_4$(CH$_2$C$_5$H$_4$Mo(CO)$_3$CH$_3$)$_2$ in 10 mL of THF. The solution was stirred at room temperature for 4 h. The solvent was removed under vacuum leaving a dark brown solid which was washed with 10 mL of diethyl ether and isolated as a brown powder. The product was recrystallized from CH$_2$Cl$_2$/hexane to yield 0.37 g (41%) of dark brown crystals. IR (CH$_2$Cl$_2$) ν(C≡O) 2035 and 1960 cm^{-1}.

[α,α'-*m*-Xylenebis(η^5-cyclopentadienyl)]bis[dicarbonyl(methyl)-(triphenylphosphine)molybdenum] (**11**), *m*-C$_6$H$_4$[CH$_2$C$_5$H$_4$Mo-(CO)$_2$P(C$_6$H$_5$)$_3$CH$_3$]$_2$. *m*-C$_6$H$_4$(CH$_2$C$_5$H$_4$Mo(CO)$_3$CH$_3$)$_2$ (0.622 g, 1.00 mmol) and triphenylphosphine (0.525 g, 2.00 mmol) were dissolved in 50 mL of THF and placed in a 100-mL glass photolysis cell and the solution was irradiated for 48 h. The solution was filtered through Celite and the solvent removed under vacuum yielding a light red solid. The solid was dissolved in 2 mL of CH$_2$Cl$_2$ and placed atop a 2 × 30 cm Florisil column packed with hexane. The column was eluted with hexane and then with CH$_2$Cl$_2$–hexane mixtures. Trace amounts of other materials were obtained in a first yellow band and a second light red band. A third, deep yellow band which eluted with 50:50 CH$_2$Cl$_2$–hexane contained the product. The yield was 0.57 g (52%). The product could be recrystallized from hexane/CH$_2$Cl$_2$ mixtures. IR (CH$_2$Cl$_2$) ν(C≡O) 1960 and 1865 cm^{-1}.

Results and Discussion

The Bridged Dicyclopentadienyl Ligands. The bridged dicyclopentadienyl ligand (**1**) was prepared from 1,3-bis-(bromomethyl)benzene (α,α'-dibromo-*m*-xylene) and the cyclopentadienide anion according to eq 1. A quantitative

$$m\text{-C}_6\text{H}_4(\text{CH}_2\text{Br})_2 + 2\text{NaC}_5\text{H}_5 \xrightarrow[0\,°\text{C}]{\text{THF}}$$
$$m\text{-C}_6\text{H}_4(\text{CH}_2\text{C}_5\text{H}_5)_2 + 2\text{NaBr} \quad (1)$$
$$\mathbf{1}$$
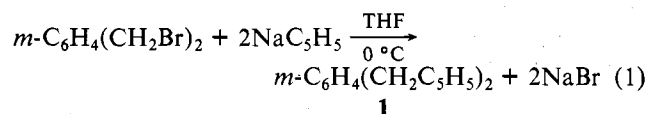
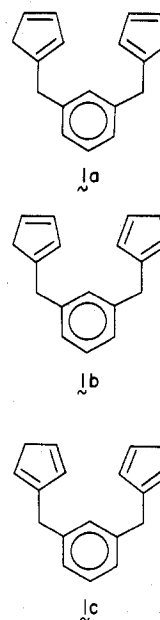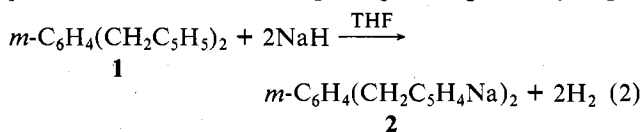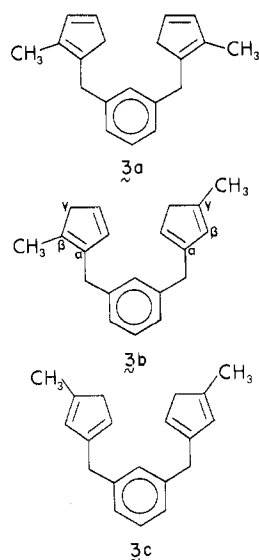isolation of sodium bromide was achieved. The product,

Figure 2. Predominant isomeric structures of α,α'-dicyclopentadienyl-*m*-xylene (**1**): **1a** = α,α'-bis[1,1'-(1,3-cyclopentadienyl)]-*m*-xylene, **1b** = α,α'-bis[1,2'-(1,3-cyclopentadienyl)]-*m*-xylene, **1c** = α,α'-bis[2,2'-(1,3-cyclopentadienyl)]-*m*-xylene.

α,α'-dicyclopentadienyl-*m*-xylene (**1**), did not lend itself well to isolation and characterization. **1** is air sensitive and polymerizes rapidly when neat and at a moderate rate in solution. Attempted thermal cracking at elevated temperatures under vacuum of the yellow oil which results from partially polymerized **1** caused further polymerization to produce a hard yellow glass. The polymerization phenomenon made difficult any consistent spectral, in particular ^{1}H NMR, identification of product **1**. However, the chemical shifts for **1**, as best ascertained, appear in Table I. Although the relative proton ratios obtained for **1** were variable because of the tendency to form polymers, the observed chemical shifts are consistent with the formulation. Since compound **1** can be viewed as containing two monosubstituted cyclopentadienyl units, a comparison of the cyclopentadienyl proton shifts can be made with those of methylcyclopentadiene.[5] The range of the vinylic cyclopentadienyl protons appears approximately 0.1 ppm downfield from those of methylcyclopentadiene. The benzyl protons are shifted 1.3 and 1.7 ppm downfield, as expected, from the methyl protons of toluene and methylcyclopentadiene, respectively.

Methylcyclopentadiene consists of the vinylic isomers 1-methyl-1,3-cyclopentadiene and 2-methyl-1,3-cyclopentadiene in almost equal amounts and a negligible amount of 5-methyl-1,3-cyclopentadiene (ref 5 and references therein). Assuming that substitution of the bromides in α,α'-dibromo-*m*-xylene by cyclopentadienide ion proceeds analogously to substitution at methyl iodide,[6] then of the six possible isomers of **1**, the three isomers shown in Figure 2 should predominate. These three isomers with the rings substituted at the vinylic position result from hydrogen migration.[7]

The problem of the polymerization of compound **1** was overcome by running reaction **1** at a reduced temperature and allowing just sufficient time for completion of the reaction, and immediately thereafter forming a dianion without isolation of **1**. In situ reaction of **1** with excess sodium hydride readily produced dianion **2** according to eq 2. Vigorous hydrogen

$$m\text{-C}_6\text{H}_4(\text{CH}_2\text{C}_5\text{H}_5)_2 + 2\text{NaH} \xrightarrow{\text{THF}}$$
$$\mathbf{1}$$
$$m\text{-C}_6\text{H}_4(\text{CH}_2\text{C}_5\text{H}_4\text{Na})_2 + 2\text{H}_2 \quad (2)$$
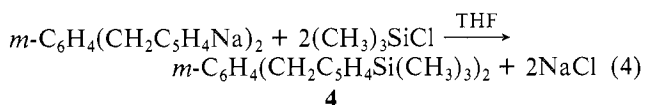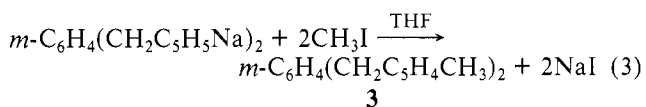$$\mathbf{2}$$

Figure 3. Isomeric structures of **3** indicating the favored positions for methyl substitution.

evolution, although not quantitatively measured, was observed. Each of the six possible isomers of **1** will generate dianion **2**. The dianion produced was generally used in situ without purification or isolation. Solutions of **2** behave similarly to those of the cyclopentadienide anion in that the color may vary from faint yellow-orange to reddish brown depending on the care taken to exclude traces of air from the reaction vessels.

Two main-group derivatives of **1** were prepared from dianion **2** according to eq 3 and 4.   Reactions of single cyclo-

$$m\text{-}C_6H_4(CH_2C_5H_5Na)_2 + 2CH_3I \xrightarrow{\text{THF}}$$
$$m\text{-}C_6H_4(CH_2C_5H_4CH_3)_2 + 2NaI \quad (3)$$
$$\mathbf{3}$$

$$m\text{-}C_6H_4(CH_2C_5H_4Na)_2 + 2(CH_3)_3SiCl \xrightarrow{\text{THF}}$$
$$m\text{-}C_6H_4(CH_2C_5H_4Si(CH_3)_3)_2 + 2NaCl \quad (4)$$
$$\mathbf{4}$$

pentadienide ions analogous to eq 3[6–8] and eq 4[9–12] are well examined. Compounds **3** and **4** are only slightly more stable to polymerization than **1**.

Just considering substitution at any of the α, β, or γ positions of each of the rings (Figure 3) as well as the isomers which arise from well-documented 1,5-hydrogen shifts[5,7,13–15] in substituted cyclopentadiene systems, there are 66 isomers of **3** and **4**. The actual number of isomers obtained is much lower since preferences exist for substitution at certain positions as well as for certain of the isomers arising from 1,5-hydrogen shifts. First, little substitution is expected at the α position of the rings of **2**. This is borne out by data from other disubstituted cyclopentadiene systems. For example, McLean and Haynes[6] observed negligible substitution at the α-carbon atom and a 3.5/1.0 preference for substitution at the β- vs. γ-carbon atom in the methylation of methylcyclopentadiene. Consequently **3** and **4** consist mainly of structures with the substituents in the β and γ positions (Figure 3). Second, the ^{1}H NMR spectra of methylcyclopentadienes[6–8,15] and (trimethylsilyl)cyclopentadienes[12,16–19] have been sufficiently well assigned to use as a guide for evaluating the favored hydrogen shift isomers of **3** and **4** based on NMR data. Table I includes the ^{1}H NMR data for **3** and **4**. The spectrum of **3** contains the resonances due to the benzene ring, benzyl and methyl protons in the expected positions and ratio. Also, the chemical shift values for the vinylic cyclopentadienyl protons are similar to those observed for **1** and the vaious dimethylcyclopentadiene isomers,[6] as are the shifts of the allylic cyclopentadienyl
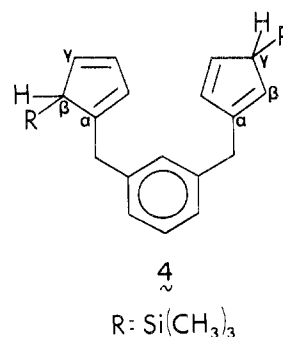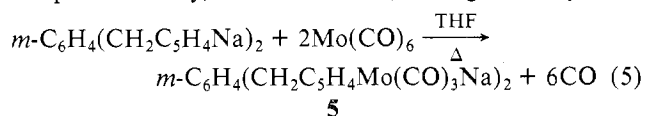

Figure 4. Structure of **4** indicating the favored allylic cyclopentadienyl sites of trimethylsilyl substitution.

protons. The integral ratio indicates the number of vinylic and allylic protons is equivalent. Consequently, those hydrogen shift isomers of **3a,b,c** (a total of 21—six each from **a** and **c** and nine from **b**) which maintain all the substituents at vinylic positions are apparently the principal constituents of **3** (Figure 3).

In the ^{1}H NMR data for **4**, the benzene ring, the benzyl, and the trimethylsilyl protons are present in the expected ratio. The room-temperature spectrum is in the main characteristic of a cyclopentadiene derivative in which the trimethylsilyl group is rapidly migrating about the ring.[17,19] Rapid migration occurs only when the trimethylsilyl groups are substituted at the allylic positions of the cyclopentadiene rings.[17,19] Consequently, the isomers of the structure depicted in Figure 4 arising from migration of the silyl group to all positions in a ring appear to be the principal constituents of **4**. The approximate 4:1 vinylic to allylic cyclopentadienyl proton ratio supports this conclusion. There is some evidence for isomers of **4** with the trimethylsilyl group at vinylic positions of the cyclopentadiene rings. The chemical shift of the trimethylsilyl group at a vinylic position is slightly downfield of tetramethylsilane in (trimethylsilyl)cyclopentadiene and (trimethylsilyl)methylcyclopentadiene while the shift of a trimethylsilyl group on an allylic carbon atom is slightly upfield.[12,17,18] Minor resonances are observed in **4** which are attributable to isomers with the substituent at a vinylic carbon atom. The integral ratio indicates approximately 20% of **4** consists of these isomers.

Bridged Bimetallic Compounds. The investigations were confined to systems prepared from dianion **2** which is derived from the linked ligand, α,α'-dicyclopentadienyl-m-xylene (**1**). Since dianion **2** had been shown to react similarly to the cyclopentadienide anion, the hexacarbonyl derivatives of molybdenum and tungsten were chosen as initial reactants. Cyclopentadienyl carbonyl compounds of these metals can be prepared from cyclopentadienide anions and the respective hexacarbonyl.[20,21]

The dianion **5** was prepared in a fashion similar to the classic preparations used by Wilkinson[22] and Fischer[23] to prepare sodium salts of the type $NaM(CO)_3C_5H_5$ (M = Cr, Mo, or W). Dianion **5** was formed by reacting dianion **2** with molybdenum hexacarbonyl in refluxing tetrahydrofuran according to eq 5. Generally, **5** was used in situ, although a diethyl ether

$$m\text{-}C_6H_4(CH_2C_5H_4Na)_2 + 2Mo(CO)_6 \xrightarrow[\Delta]{\text{THF}}$$
$$m\text{-}C_6H_4(CH_2C_5H_4Mo(CO)_3Na)_2 + 6CO \quad (5)$$
$$\mathbf{5}$$

wash of the solid salt can be used to remove the majority of unreacted metal hexacarbonyl from both **5** and the corresponding tungsten salt **6**. In certain reactions (vide infra), it was found to be advantageous to purify **5** and **6** in this manner.

The tungsten compound, **6**, was prepared by a different method from the conventional preparation of the sodium salt

Scheme I

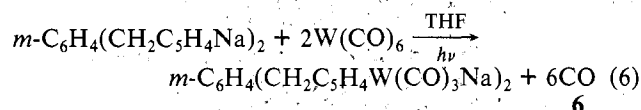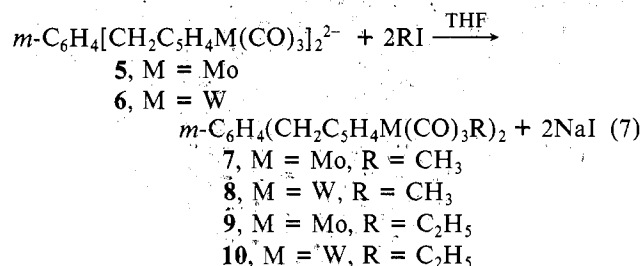**Figure 5.** Infrared spectra in the carbonyl region of (A) m-C_6H_4-$(CH_2C_5H_4Mo(CO)_3Na)_2$ (5) in THF, (B) m-$C_6H_4(CH_2C_5H_4Mo$-$(CO)_3CH_3)_2$ (7) in CH_2Cl_2, and (C) m-$C_6H_4(CH_2C_5H_4Mo(CO)_3)_2$ (14) in $C_6H_5CH_3$.
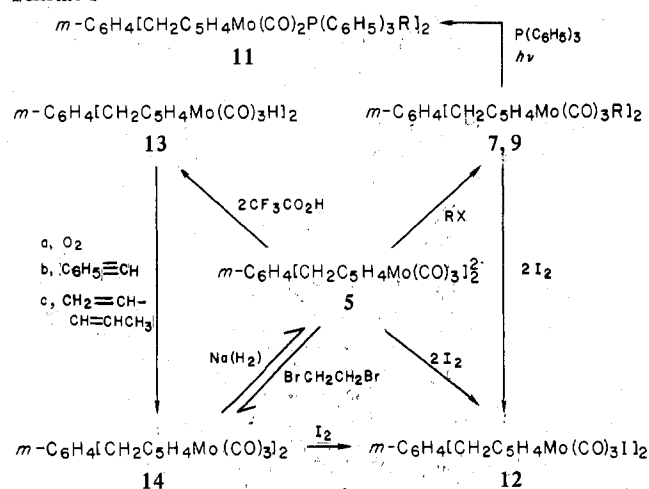
of the cyclopentadienyltungsten tricarbonyl anion.[22,23] 6 was prepared photolytically (eq 6). The photolytic preparation

$$m\text{-}C_6H_4(CH_2C_5H_4Na)_2 + 2W(CO)_6 \xrightarrow[h\nu]{THF}$$
$$m\text{-}C_6H_4(CH_2C_5H_4W(CO)_3Na)_2 + 6CO \quad (6)$$
$$\mathbf{6}$$

of 6 reaches a maximum yield within 2–3 days. Significant loss of 6 is incurred by degradation during prolonged photolysis times. Attempted preparation of 6 in refluxing tetrahydrofuran afforded significantly lower yields for reflux times similar to those used to prepare 5.

These cyclopentadienylmetal carbonyl dianions are useful synthetic intermediates. Metal alkyl derivatives were prepared by reacting alkyl halides with 5 and 6 (eq 7). Both of the

$$m\text{-}C_6H_4[CH_2C_5H_4M(CO)_3]_2^{2-} + 2RI \xrightarrow{THF}$$
$$\mathbf{5}, M = Mo$$
$$\mathbf{6}, M = W$$
$$m\text{-}C_6H_4(CH_2C_5H_4M(CO)_3R)_2 + 2NaI \quad (7)$$
$$\mathbf{7}, M = Mo, R = CH_3$$
$$\mathbf{8}, M = W, R = CH_3$$
$$\mathbf{9}, M = Mo, R = C_2H_5$$
$$\mathbf{10}, M = W, R = C_2H_5$$

methyl derivative preparations utilized dianions that had been previously purified by ether washes. This was necessary because 7 and 8 could not be purified by chromatography. Methyl derivatives isolated chromatographically produced oils or gummy solids because the methyl compounds eluted off with fairly polar solvent mixtures which also bled off polymers and other organic products that were inevitably present in the reaction residue. However, if unreacted metal hexacarbonyls were removed prior to reacting the dianions with methyl iodide, it was then possible to eliminate the organic impurities by washing with small amounts of diethyl ether. Small losses of product were incurred, but fairly pure samples were obtained. Both 7 and 8 were recrystallized from mixtures of dichloromethane in hexane.

Ethyl derivatives were also obtained by similar reactions of 5 and 6 with ethyl iodide but at the lower temperature of 0 °C. The increased solubility of ethyl derivatives 9 and 10 in hexane allowed their chromatographic purification without the problems encountered during purification of the methyl derivatives. Significantly lower yields of 9 were obtained in comparison to 10. The major substance isolated in the preparation of 9 was a red-brown solid which was a mixture of compounds. The mixture exhibited both metal–ethyl and normal ethyl resonances in its ^1H NMR spectrum and did not
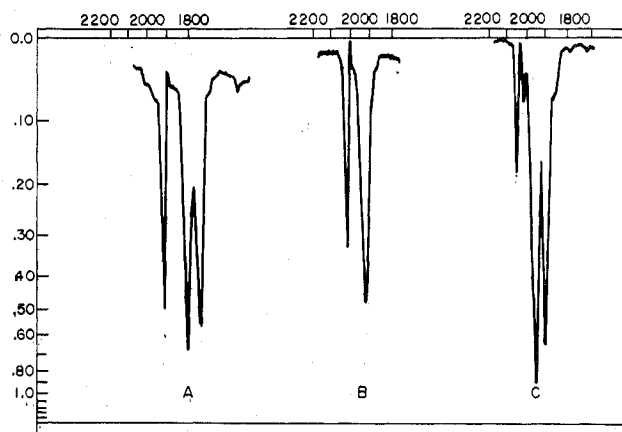
yield distinct compounds upon chromatography. In reactions of $C_5H_5Mo(CO)_3CH_2CH_3$[24] and $C_5H_5M(CO)_3C_6H_5$ (M = Mo, W),[25] mixtures of products result apparently from migration of the ethyl and phenyl groups to replace hydrogen atoms on the cyclopentadienyl rings. The red-brown solid is probably composed of a similar but more complex set of compounds.

The alkyl derivatives are relatively air stable as solids though they were always stored under inert atmosphere. Their melting points range from 12 to 15 °C higher than the analogous unlinked cyclopentadienyl compounds.[22] In comparison, the general tendency of cyclopentadienylmetal carbonyls substituted on the cyclopentadienyl rings is toward lower melting points.[26]

The carbonyl stretching frequencies of compounds 5 through 10 are among those given in Table II, and Figure 5 includes a carbonyl region infrared spectrum of 5 and 7. The dianions (5 and 6) exhibit three strong carbonyl stretching frequencies typical of similar anionic cyclopentadienylmetal carbonyls (see note b, Table II). Compounds of the type $C_5H_5M(CO)_3R$ (R = CH_3, CH_2CH_3; M = Mo, W) exhibit two strong carbonyl stretching bands.[22] The broader of the two characteristic carbonyl absorptions has been shown to resolve into two peaks for $C_5H_5Mo(CO)_3CH_3$ in hexadecane.[27] Ring-substituted compounds of the type $RC_5H_4Mo(CO)_3R'$ (R = CH_3, CH_2CH_3) also have two strong carbonyl stretching modes.[26] The four metal alkyl derivatives of the bridged system (7, 8, 9, and 10) exhibit the same two characteristic stretching modes observed in the analogous unlinked compounds. In order for both the dianions (5 and 6) and the alkyl derivatives (7–10) to approximate the unlinked derivatives, interactions between the two bridged metal centers must be minimal. The m-phenylenedimethylene unit allows the cyclopentadienyl rings to assume an anti conformation with respect to the benzene ring in which the metal centers behave essentially as independent units. This apparently is the preferred conformer of the derivatives in solution.

The ^1H NMR data for the bridged metal alkyl derivatives (7–10) are included in Table III and are consistent with their formulations. The ^1H NMR of 7 is shown in Figure 6. The resonances of the metal methyl protons for both 7 and 8 are sharp singlets and the resonances of the metal ethyl protons for 9 and 10 are unresolved multiplets, all appearing in regions where resonances are obtained for similar unlinked cyclopentadienylmetal alkyl complexes.[22,28,29] The methyl and ethyl proton resonances of such unlinked cyclopentadienyl analogues also appear as singlets and multiplets, respectively.[22,29] The resonances of the cyclopentadienyl and benzyl protons are sharp singlets.
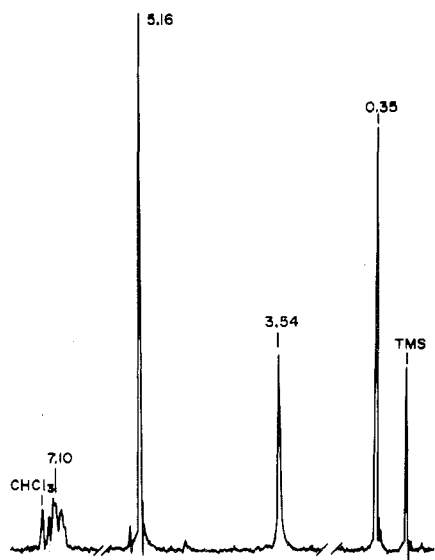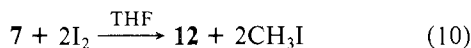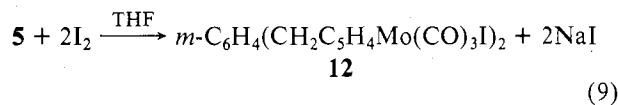
Figure 6. ^{1}H NMR of m-C$_6$H$_4$(CH$_2$C$_5$H$_4$Mo(CO)$_3$CH$_3$)$_2$ (7) in CDCl$_3$; chemical shifts in ppm vs. Me$_4$Si.

The displacement of a carbonyl from each metal in the photolysis of the methylmolybdenum compound (7) in the presence of triphenylphosphine affords derivative **11** according to eq 8. The infrared carbonyl stretching frequencies and ^{1}H

$$7 + 2(C_6H_5)_3P \xrightarrow[h\nu]{THF}$$
$$m\text{-}C_6H_4[CH_2C_5H_4Mo(CO)_2(C_6H_5)_3PCH_3]_2 + 2CO \quad (8)$$
$$\mathbf{11}$$
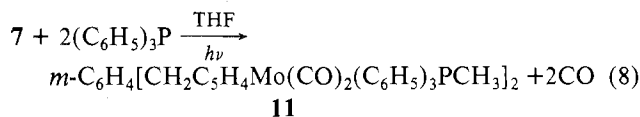
NMR data for **11** appear in Tables II and III, respectively, and are similar to those obtained for the analogous cyclopentadienyl derivative.[30,31] Integration of the triphenylphosphine protons indicates the substitution of two triphenylphosphines. The molybdenum methyl resonance is split into a doublet (J = 3 Hz) implying the substitution of one phosphine on each metal.

The chemistry of the molybdenum system was explored in more detail. An iodide derivative can be prepared from either dianion **5** or methyl derivative **7** according to eq 9 and 10.

$$5 + 2I_2 \xrightarrow{THF} m\text{-}C_6H_4(CH_2C_5H_4Mo(CO)_3I)_2 + 2NaI$$
$$\mathbf{12}$$
$$(9)$$

$$7 + 2I_2 \xrightarrow{THF} 12 + 2CH_3I \quad (10)$$

Since methyl derivative **7** could be obtained in a purer state than dianion **5**, reaction 10 was cleaner and afforded purer product than reaction 9. A reaction analogous to eq 10 has been reported previously for the preparation of π-cyclopentadienylmolybdenum tricarbonyl iodide.[22] The infrared carbonyl stretching frequencies and ^{1}H NMR data for **12** are given in Tables II and III, respectively, and are consistent with its formulation. Complex **12** in dichloromethane does not exhibit the third weak CO stretching mode observed for π-cyclopentadienylmolybdenum tricarbonyl iodide.[22,32,33] However, this additional weak CO stretching mode is not observed for similar iodo compounds with substituted cyclopentadienyl rings.[26]

A hydrido complex was prepared from molybdenum salt **5** and trifluoroacetic acid (eq 11). Glacial acetic acid may be

$$5 + 2CF_3COOH \xrightarrow{THF}$$
$$m\text{-}C_6H_4(CH_2C_5H_4Mo(CO)_3H)_2 + 2CF_3COONa \quad (11)$$
$$\mathbf{13}$$
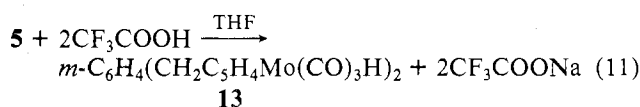
substituted for trifluoroacetic acid in the reaction. The carbonyl stretching frequencies of **13** determined in benzene are given in Table II. The third weak carbonyl stretching band reported for C$_5$H$_5$Mo(CO)$_3$H was not observed for **13** in benzene. The hydride chemical shift determined in tetrahydrofuran is τ 15.45. This is slightly downfield of the reported value of the π-cyclopentadienylmolybdenum tricarbonyl hydride chemical shift, whether determined in tetrahydrofuran[32] or alkane solvents.[29]

A number of reactions were examined to determine the best route to the brick red metal–metal bonded derivative m-C$_6$H$_4$[CH$_2$C$_5$H$_4$Mo(CO)$_3$]$_2$ (**14**). The preparation of **14** was complicated by the difficulty involved in its purification. Crude product **14** could not be recrystallized and chromatographic purification was further complicated by the tendency of **14** to bind irreversibly to most common column chromatography adsorbents such as Florisil silica gel, and alumina. Chromatographic purification of **14** was finally achieved on a chromatography column packed with Celite (diatomaceous earth). Also **14** reacts with halogenated solvents in the absence of oxygen besides being quite sensitive to oxygen when dissolved in any solvent. The best route to **14** involved reaction of 1,2-dibromoethane with dianion **5** because side products were easier to remove (eq 12). The outcome of the reaction

$$5 + BrCH_2CH_2Br \xrightarrow{THF}$$
$$m\text{-}C_6H_4[CH_2C_5H_4Mo(CO)_3]_2 + CH_2{=}CH_2 + 2NaBr$$
$$\mathbf{14}$$
$$(12)$$
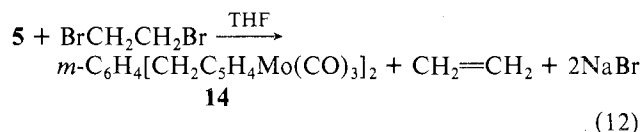
is critically dependent on the reaction conditions. Dilute solutions and slow addition of 1,2-dibromoethane to **5** are essential. Concentrated solutions and rapid addition of 1,2-dibromoethane apparently afford considerable amounts of the bromoethyl derivative, m-C$_6$H$_4$(CH$_2$C$_5$H$_4$Mo(CO)$_3$CH$_2$CH$_2$Br)$_2$. The bromoethyl derivative can be identified by its infrared spectrum. It exhibits the same two strong carbonyl stretching modes characteristic of the metal alkyl derivatives. The bromoethyl product could be anticipated based on the low nucleophilicity of the analogous π-cyclopentadienylmolybdenum tricarbonyl anion.[34] Reactions of the C$_5$H$_5$Mo(CO)$_3$$^-$ anion with α,ω-dibromoalkanes yield π-cyclopentadienylmolybdenum tricarbonyl alkylbromides.[35]

In addition to reaction 12, methods analogous to established routes to [C$_5$H$_5$Mo(CO)$_3$]$_2$ were used in attempts to prepare **14**. The C$_5$H$_5$Mo(CO)$_3$H derivative is known to hydrogenate dienes with formation of a metal–metal bonded dimer.[36] Analogously the reduction of 1,3-pentadiene and phenylacetylene by **13** produced **14** in good yield. The purification of **14** obtained in this manner was more difficult than that obtained by reaction 12. Since air oxidation of C$_5$H$_5$Mo(CO)$_3$H in tetrahydrofuran affords the dimer [C$_5$H$_5$Mo(CO)$_3$]$_2$ in 70% yield,[37] a similar reaction was attempted to prepare **14**; however, exhaustive air oxidation of **13** in tetrahydrofuran resulted in complete decomposition. Controlled limited air oxidation of **13** resulted in a very low yield of **14**. Ligand **1** was found to be inadequate for the preparation of **14** because it has such a great tendency to polymerize. Refluxing ligand **1** in the presence of Mo(CO)$_6$ or (CH$_3$CN)$_3$Mo(CO)$_3$ resulted in very poor yields of **14**.

The ^{1}H NMR and the infrared spectroscopic data for **14** are listed in Tables III and II, respectively, and the infrared spectrum is included in Figure 5. A total of five carbonyl stretching frequencies were observed for **14**. The number of bands in the spectrum can be rationalized based on data from the [C$_5$H$_5$Mo(CO)$_3$]$_2$ system. The cyclopentadienyl rings of [C$_5$H$_5$Mo(CO)$_3$]$_2$ have been shown to be trans (separated by 180°) in the crystal structure.[38,39] Solution infrared studies also have shown this dimer to be trans in cyclohexane.[40]

However, in more polar solvents the cis conformation (0° separation of the cyclopentadienyl rings) predominates with varying amounts of the rotamers observed in which the cyclopentadienyl rings are 60 and 120° apart while two of the three carbonyls are eclipsed.[40]

Although the *m*-phenylenedimethylene bridging unit has considerable rotational flexibility about the benzyl position, the metal–metal bond in **14** constrains such movement. Unlike [C$_5$H$_5$Mo(CO)$_3$]$_2$, the cis conformation of **14** (0° cyclopentadienyl ring separation with respect to the metal centers) is expected both in solution and in the solid. Group theoretical considerations predict the cis conformation of **14**, which has C_{2v} symmetry about the metal centers, should exhibit five infrared-active carbonyl stretching modes, as is observed. The chemistry of **14** is similar to that of [C$_5$H$_5$Mo(CO)$_3$]$_2$. Addition of iodine to **14** cleaved[26] the metal–metal bond with the formation of **12**. Derivative **14** also was reduced with sodium amalgam in tetrahydrofuran as can be done with [C$_5$H$_5$Mo(CO)$_3$]$_2$.[41] The resultant salt had the same characteristics and carbonyl stretching frequencies as **5** prepared from dianion **2**. Reaction of the dianion generated from **14** with methyl iodide yielded **7**. This product gave characterization data identical with those of **7** prepared from dianion **2**.

The chemistry observed for the bridged dimolybdenum complexes is summarized in Scheme I. The chemistry of unlinked cyclopentadienylmolybdenum complexes has been summarized in similar schemes.[42,43] The work on the molybdenum and tungsten complexes of the bridged ligand demonstrates the accessibility of covalently linked η^5-cyclopentadienyl systems, Z(C$_5$H$_4$ML$_n$)$_2$, which contain hydride or alkyl ligands on each metal in addition to carbonyls and phosphines. Consequently the mutual effect of the constrained presence of one metal unit on the reactivity of the other metal unit is open to examination.

Registry No. 1a, 68630-44-4; **1b**, 68630-45-5; **1c**, 68630-46-6; **2**, 68630-47-7; **3a**, 68630-48-8; **3b**, 68630-49-9; **3c**, 68630-50-2; **4**, 68630-51-3; **5**, 68629-68-5; **6**, 68629-69-6; **7**, 68629-70-9; **8**, 68629-71-0; **9**, 68629-72-1; **10**, 68629-56-1; **11**, 68629-57-2; **12**, 68629-58-3; **13**, 68629-59-4; **14**, 68629-60-7; Mo(CO)$_6$, 13939-06-5; W(CO)$_6$, 14040-11-0; cyclopentadiene, 542-92-7; 1,3-bis(bromomethyl)benzene, 626-15-3.

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