PREPARATION AND CHARACTERIZATION

OF

$\sigma$-(1-NAPHTHYL)METHYLENYL-$\pi$-CYCLOPENTADIENYLTRICARBONYL-MOLYBDENUM

By

William F. McKenzie
A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science.

Signed: William F. McKenzie

Golden, Colorado
Date: May 1, 1970

Approved: Dean Oosterhout
Thesis Advisor

Golden, Colorado
Date: May 1, 1970
The preparation of \( \sigma-(1\text{-naphthyl})\text{methylenyl-} \pi\text{-cyclopentadienyltricarbonylmolybdenum, } C_{10}H_7CH_2Mo(CO)_3C_5H_5, \) is described. The method involves the reaction of 1-(chloromethyl)-naphthalene with NaMo(CO)_3C_5H_5.

The properties, infrared spectrum, and high-resolution proton magnetic resonance spectra are given.

The structure and stability of \( C_{10}H_7CH_2Mo(CO)_3C_5H_5 \) are discussed.

An attempt to prepare the analogous \( \sigma\text{-trityl derivative, } (C_6H_5)_3CMo(CO)_3C_5H_5 \) was not successful.
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INTRODUCTION

Until early in this century it was generally believed that the transition metals were unable to form organic derivatives. Up to the 1950's the organic chemistry of the transition metals consisted only of some platinum and gold compounds, the not completely understood olefin complexes of platinum and palladium and the enigmatic phenylchromium derivatives (1).

Since the discovery of ferrocene or biscyclopentadienyliron (2, 3) in 1951, concentrated efforts by many chemists have shown that the formation of carbon-metal bonds is a general property of the d-group transition metals. In the past twenty years this property has been demonstrated by the preparation of a wide variety of organometallic compounds. A convenient summary and classification (Tab. 1) of such compounds is based on the number of electrons which are formally considered to arise from the organic ligand and which take part in the metal-ligand bond (1).

The number of organometallic compounds with a metal-carbon \( \sigma \)-bond (one-electron ligand) is comparatively few.
Table 1. A classification of organic groups which act as ligands to transition metals.

With the exception of platinum and gold compounds (4), most derivatives have been made since 1955. Under normal conditions, a $\sigma$-bonded compound is not formed in the reaction of an alkyl or aryl Grignard (or organolithium reagent) with a transition metal halide which is the common preparative route for non-transition metal organometallics. In general such reactions result in organic coupling products with transition metal halides (5).

Fewer still binary aryl and alkyl $\sigma$-bonded compounds are known due to their facile reactivity with respect to air and water. Many binary derivatives have not, in fact, been isolable and only evidence from chemical reac-
tions in solution have been reported. The successful preparations have usually resulted from low temperature reactions and a consideration of electronic conditions for stability. Conversely, if \(\pi\)-bonding ligands such as cyclopentadienyl, carbonyl or nitrosyl are present, very stable compounds with a \(\sigma\)-bonded organic ligand are obtained and many have been isolated (5, 6).

In 1955, Piper and Wilkinson (7, 8, 9) reported in preliminary communications the preparation of several compounds from the \(\pi\)-cyclopentadienylcarbonyl(or nitrosyl) metal halides by the Grignard method, e. g.

\[
\pi\text{-C}_5\text{H}_5\text{Cr(NO)}_2\text{I} + \text{CH}_3\text{MgI} = \pi\text{-C}_5\text{H}_5\text{Cr(NO)}_2\text{CH}_3 + \text{MgI}_2
\]

The method was not uniformly successful. Phenyl magnesium bromide in reaction with \(\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_3\text{I}\) did not produce the corresponding aryl but instead gave a high yield of the binuclear compound \([\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_3]\)_2. They also reported the preparation of the methyl derivative of \(\pi\)-cyclopentadienyltricarbonylmolybdenum by the reaction of the hydride with diazomethane.

\[
\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_3\text{H} + \text{CH}_2\text{N}_2 = \pi\text{-C}_5\text{H}_5\text{Mo(CO)}_3\text{CH}_3 + \text{N}_2
\]

Fisher (10) prepared the analogous methyl and ethyl tungsten derivatives by the diazo method during the same year. The diazo reactions gave very low yields.

In 1956, Piper and Wilkinson (11) prepared the first
extensive series of alkyl and aryl compounds with a sigma bond to transition metals (Cr, Mo, W, and Fe) and with $\pi$-cyclopentadienyl and carbonyl or nitrosyl ligands. The preparative methods were the above discussed Grignard and diazo reactions, and the reaction of alkyl and aryl halides with the sodium salts of $\pi$-cyclopentadienylcarbonyl metals, e. g.

$$\pi\text{-C}_5\text{H}_5\text{Fe(CO)}_2\text{Na} + \text{C}_2\text{H}_5\text{I} = \pi\text{-C}_5\text{H}_5\text{Fe(CO)}_2\text{C}_2\text{H}_5 + \text{NaI}$$

The most general and successful method of preparation was the latter. Among the compounds prepared and characterized by the organic halide reaction were the methyl, ethyl, and iso-propyl derivatives of $\pi$-cyclopentadienyltricarbonylmolybdenum. These molybdenum complexes were found to be stable thermally and somewhat resistant to oxidation.

Although Piper and Wilkinson's work indicated a general preparative method for $\sigma$-bonded organometallics, few additional derivatives have been reported utilizing the $\pi$-cyclopentadienyltricarbonylmolybdenum moiety's unusual stability for studying the nature of the $\sigma$-bond for a variety of alkyls and aryls bonded to a transition metal. $\sigma$-Bonded derivatives of $\pi$-cyclopentadienyltricarbonylmolybdenum since reported include $\text{HCF}_2\text{CF}_2$ (12), $\sigma$-allyl (13), $\sigma$-benzyl (14), $\text{CF}_3\text{CO}$ (15), $\text{C}_3\text{F}_7\text{CO}$ (15, 16), $\text{HOOCCH}_2$ (17), $\text{CH}_3\text{SCH}$ (18), $\text{CF}_3\text{CF}_2\text{CF}_2$ (19), $\text{OCNCH}_2$ (20), $\text{CH}_3\text{OCOCH}_2$ (21), and $\sigma$-cyclopropyl (22).
The $\sigma$-allyl derivative prepared by Cousins and Green (13) was found to be convertible to the $\pi$-allyl compound by ultraviolet irradiation of the $\sigma$-allyl compound in vacuo with the loss of one mole of carbon monoxide. King and Fronzaglia (14) reported an analogous conversion for the $\sigma$-benzyl derivative. This was the first reported example of a $\pi$-benzyl complex in which three carbon atoms of the $\pi$-benzyl ligand, two of which are located in the benzene ring, are complexed with the metal atom.

![Structure of $\pi$-C$_6$H$_5$CH$_2$Mo(CO)$_2$C$_5$H$_5$.](image)

**FIGURE 1.** Structure of $\pi$-C$_6$H$_5$CH$_2$Mo(CO)$_2$C$_5$H$_5$.

An unexpected property of the $\pi$-benzyl compound discovered by King and Fronzaglia was the temperature dependence of its proton magnetic resonance spectrum. It has an nmr spectrum at -30° which is in agreement with figure 1, but at a temperature of +60°, the 2,6- and the 3,5-ring protons coalesce to sharp signals and are equivalent. At
higher temperatures there are two equivalent configurations of the nuclei (Fig. 2), in structure and bonding, and are therefore of equal free energy content. Such molecules have been called fluxional (23).

FIGURE 2. Fluxional nature of $\Pi$-C$_6$H$_5$CH$_2$Mo(CO)$_2$C$_5$H$_5$.

Cotton and LaPrade (24), in 1968, determined the crystal and molecular structure of the p-methyl analog of King and Fronzaglia's compound and also performed a detailed nmr study of the 3,5-diisopropylbenzyl compound (23). They concluded that the rearrangement process is not explained fully by the simple suprafacial jump process shown in figure 2. Their studies indicated that the Mo(CO)$_3$C$_5$H$_5$ moiety "visits" four sites in the rearrangement - the two shown in figure 2 and the two equivalent sites on the obverse of the benzyl ring plane. They also felt that a short-lived $\sigma$-benzyl intermediate was a reasonable mechanistic possibility.
King (25) has speculated that bistritylnickel prepared by Wilke and Schatt (26) should be similar in bonding to the \( \pi \)-benzyl compound due to its relatively high stability for an organonickel complex.

Based upon this previous research, two interesting avenues of extension came to mind and will be discussed here. These avenues have been the basis for the experimental part of this thesis.

Despite King and Fronzaglia's successful preparation of the \( \sigma \)- and \( \pi \)-bonded benzyl derivatives, no report has been found in the literature of the preparation of a \( \sigma \)- or \( \pi \)-bonded polynuclear arylmethylenyl derivative. This is of interest because in the conversion from the \( \sigma \)- to the \( \pi \)-bonded complex, resonance stabilization energy, S. E., is sacrificed. In theory, it should therefore be easier to form the \( \pi \)-bonded derivative if less S. E. is
so sacrificed. In the conversion of $\sigma$- to $\pi$-benzyl (Fig. 3), 38 kcal/mole of S. E. is lost (S. E. values (27)) assuming no S. E. for the diene in conjugation with the $\pi$-bond.

![Chemical structure diagram](attachment:structure.png)

**FIGURE 4.** Conversion of $\sigma$- to $\pi$-(1-naphthyl)methylenyl.

Similarly, in the conversion of the $\sigma$- to $\pi$-(1-naphthyl)methylenyl (Fig. 4), 33 kcal/mole of S. E. is lost. Again the simplifying assumption is made that there is no S. E. for the conjugation in the $\pi$-bonded derivative. It should therefore be approximately 5 kcal/mole easier to form the $\pi$-(1-naphthyl)methylenyl derivative than the $\pi$-benzyl derivative.

The sterically and energetically non-favored $\pi$-(1-naphthyl)methylenyl derivative (Fig. 5) would be 33 kcal/mole more difficult to form than the $\pi$-benzyl compound making the same simplified assumptions.
In a like manner, other systems may be so treated including azulene, phenanthrene, anthracene, quinoline, and acridine.

Although one non-ionic trityl derivative has been reported (26), bistritylnickel, its properties have prevented comparison with the \( \pi \)-benzyl compound. It would therefore be of interest to prepare \( \sigma \)-trityl-\( \pi \)-cyclopentadienyltricarbonylmolybdenum and convert it to the \( \pi \)-bonded trityl derivative which would be a quite fluxional molecule (Fig. 6). In all there should be 6 equivalent configurations of the nuclei in structure and bonding, and all of equal free energy content.

In addition, the preparation and characterization of the \( \pi \)-benzhydryl derivative, which should have 4 equivalent configurations of equal free energy, would be of like interest.
FIGURE 6. Proposed fluxionality of $\pi$-trityl.
EXPERIMENTAL WORK

The experimental work consisted of the preparation and purification of materials, running reactions, and characterization of products.

Reagents and Solvents

Sodium, powdered.

Powdered sodium was prepared from reagent grade sodium metal by the method of Fieser (28) with a slight modification. Approximately 50 ml of dry toluene was poured into a 250-ml round-bottomed, long-necked flask and 2.8 g (0.12 mole) of cleanly cut sodium was quickly weighed and added. To obtain clean sodium powder, any kerosene should be dried off with absorbent paper and the surface oxide should be sliced off with a knife. A stopper was inserted loosely and the flask heated with a heating mantle until the condensation of the boiling toluene rose to the neck of the flask. The flask was then removed and wrapped in a towel, the stopper was inserted fully, and the flask was shaken.
sharply six or seven times in the direction of its length. Some air was admitted to the flask and the mixture was allowed to cool. If the sodium was not finely enough divided, the heating and shaking was repeated. Prior to transferring the sodium to the reaction flask, the toluene was decanted off and the powdered sodium was washed twice with 15 ml portions of dry tetrahydrofuran.

Cyclopentadiene.

Cyclopentadiene was obtained by the thermal cracking of dicyclopentadiene (3a,4,7,7a-tetrahydro-4,7-methano-indene) (Fig. 7), technical grade, inhibited with 1-naphthol, from Eastman Kodak Company. Dicyclopentadiene was

\[
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\end{array}
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2
\begin{array}{c}
\text{\textbullet}
\end{array}
\]

FIGURE 7. Dedimerization of dicyclopentadiene.

was slowly distilled through a 20 cm fractionating column packed with glass helices, collecting that which refluxed below 44°. Cyclopentadiene boils at 42.5°, dicyclopentadiene at 170°. The freshly distilled cyclopentadiene was used within 1 hour because of the slow dimerization that occurs at room temperature (29).
Molybdenum hexacarbonyl.

Molybdenum hexacarbonyl, Mo(CO)$_6$, purchased from Alfa Inorganics, Inc., was used without further purification. **CAUTION!** Molybdenum hexacarbonyl is somewhat volatile and extremely toxic.

1-(Chloromethyl)-naphthalene.

1-(Chloromethyl)-naphthalene, C$_{10}$H$_7$CH$_2$Cl, research grade, $n_D^{20}$ 1.6348 (label), was purchased from Aldrich Chemical Company and used without further purification.

Trityl chloride.

Trityl chloride, (C$_6$H$_5$)$_3$CCl, was used as purchased from Arapahoe Chemicals.

Toluene.

Toluene, reagent grade, from J. T. Baker Chemical Company, was dried over sodium metal before use.

Lithium aluminum hydride.

Lithium aluminum hydride, LiAlH$_4$, research grade, from Alfa Inorganics, Inc., was used as received as a drying agent in the distillation of tetrahydrofuran.

Calcium sulfate, anhydrous.

Anhydrous calcium sulfate, CaSO$_4$, "Drierite," from W. A. Hammond Drierite Company, was used as received to protect the distilled tetrahydrofuran from atmospheric
moisture.

**Tetrahydrofuran.**

Tetrahydrofuran, THF, research grade, boiling range 65.5-66.5° (label), from Matheson Coleman and Bell Company, was dried by refluxing over LiAlH₄ for 1 hour and then distilled using a drying tube packed with "Drierite" connected to the distillation receiver vent. The dryness of the THF was ascertained by the lack of reaction when placed in contact with sodium metal.

**Dichloromethane.**

Dichloromethane, research grade, boiling range 39-40° (label), from Eastman Kodak Company was used as received.

**N,N-Dimethylformamide.**

N,N-Dimethylformamide, DMF, "spectroquality," from Matheson Coleman and Bell Company, was used without further purification.

**Hexane.**

Hexane, technical grade, 95 mole % minimum (label), from Phillips Petroleum Company, was used as received.

**Diethyl ether.**

Anhydrous diethyl ether, reagent grade, from Mallinckrodt Chemical Works, was used as received.
Nitrogen.

Nitrogen, prepurified, manufactured by Linde Division of Union Carbide Corporation was used as received.

Instrumentation

Infrared.

Infrared spectra were run on a Perkin-Elmer 521 Grating Infrared Spectrometer. The spectrum of a solid sample was determined as a KBr pellet. About 1.5 mg of the substance and 300-350 mg of KBr were ground together finely and then pressed in an evacuated (1-2 mm Hg) die under high pressure (at least 20,000 psi) into a small disc that measured about 10 mm in diameter and 1 mm in thickness. A clear pellet was obtained which actually consisted of a solid solution of the substance in potassium bromide. Since potassium bromide does not absorb infrared light in the region 4000-300 cm\(^{-1}\), a complete spectrum of the sample was obtained.

Proton magnetic resonance.

Proton magnetic resonance, pmr, spectra were obtained on a Varian A-60 A instrument. N,N-Dimethylformamide and dichloromethane were used as solvents with tetramethylsilane as an external standard.

Melting point.
Melting points were determined with a Mel-Temp (Lab Devices, Cambridge, Mass.) integrated capillary melting point apparatus.

Chemical Analysis

Carbon and hydrogen determinations were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Synthesis of

\[ \mathcal{O}-(1\text{-Naphthyl})\text{methylene} \text{-}\mathcal{\Pi}\text{-cyclopentadienylnitrilecarbonyl-molybdenum, } C_{10}H_{7}CH_{2}Mo(CO)_{3}C_{5}H_{5}. \]

\( C_{10}H_{7}CH_{2}Mo(CO)_{3}C_{5}H_{5} \) was synthesized by treating sodium cyclopentadienylnitrilecarbonyl-molybdenum, \( \text{NaMo}(CO)_{3}C_{5}H_{5} \), with \( 1\text{-}(\text{chloromethyl})\text{-naphthalene, } C_{10}H_{7}CH_{2}Cl \). Sodium cyclopentadienylnitrilecarbonyl-molybdenum was prepared by treating molybdenum hexacarbonyl, \( \text{Mo}((CO)_{6} \), with sodium cyclopentadienide, \( \text{NaC}_{5}H_{5} \). Sodium cyclopentadienide was prepared from sodium metal and cyclopentadiene.

Procedure.

1. \( \text{Na} + C_{5}H_{6} = \text{NaC}_{5}H_{5} + \text{H}_{2} \)

2. \( \text{Mo}((CO)_{6} + \text{NaC}_{5}H_{5} = \text{NaMo}((CO)_{3}C_{5}H_{5} + 3\text{CO} \)

3. \( C_{10}H_{7}CH_{2}Cl + \text{NaMo}((CO)_{3}C_{5}H_{5} = C_{10}H_{7}CH_{2}Mo((CO)_{3}C_{5}H_{5} + \text{NaI} \)
Preparation of sodium cyclopentadienide.

To a 500-ml three-necked reaction flask equipped with a pressure-equalized dropping funnel, reflux condenser, and nitrogen inlet, was passed a rapid stream of nitrogen for 5 minutes. A teflon-coated magnetic stirring bar, 2.8 g (0.12 mole) of powdered sodium, and 250 ml of dry THF were then added to the flask using the THF to effect the transfer of the sodium. The suspension of sodium in THF was then treated dropwise with freshly distilled cyclopentadiene and stirred with a magnetic stirrer. Approximately 11.5 ml (9.2 g, 0.14 mole) of cyclopentadiene was necessary to dissolve all of the sodium to form a red-violet solution of sodium cyclopentadienide. The reaction was complete after about 2 hours.

Preparation of sodium cyclopentadienyltricarbonylmolybdenum.

The sodium cyclopentadienide solution was treated with 26.4 g (0.1 mole) of molybdenum hexacarbonyl (CAUTION! Mo(CO)₆ is slightly volatile and extremely toxic) and the reaction was refluxed, using a heating mantle, for approximately 15 hours.

Preparation of C₁₀H₇CH₂Mo(CO)₃C₅H₅.

The resulting orange solution of NaMo(CO)₃C₅H₅ was allowed to cool to room temperature and then treated dropwise with 21 ml (0.12 mole) of 1-(chloromethyl)-naphthalene.
The reaction mixture was stirred at room temperature for 26 hours. After transferring the solution to a 500-ml boiling flask, the solvent was removed with a rotary evaporator under reduced pressure (10-15 mm Hg). The residue was extracted with 150 ml of dichloromethane and the extract filtered. The extract was then concentrated by a stream of nitrogen gas blown across the solution surface and following evaporation of about half the solvent, yellow crystals appeared. The yellow product was filtered and washed with several portions (2-4 ml each) of hexane followed by washing with one small portion of cold ether (2 ml). Additional product was recovered from the CH₂Cl₂ solution by further concentration and the total yield was approximately 3 g (7.8 \%).

**Chemical and Physical Properties**

Solid C₁₀H₇CH₂Mo(CO)₃C₅H₅ was quite stable towards oxidation in air. No noticeable alteration occurred after several weeks of unprotected storage. It was insoluble in and unaffected by water. Thermal decomposition occurred above 100° giving a red product, believed to be the binuclear compound, \([\text{Mo(CO)}₃\text{C₅H₅}]₂\) (11), and a tarry material. Acids and bases attack C₁₀H₇CH₂Mo(CO)₃C₅H₅ giving a black organic residue. It was found to be quite soluble in organic solvents (benzene, chloroform, dichloromethane, DMF,
dimethylsulfoxide, and hexane) but, had limited stability towards oxidation in solution. The solutions, red when fresh, turned black after standing for several hours exposed to air.

Attempts to purify or convert the product to the Π-derivative by sublimation were not successful. At the lower temperatures, no change in the product and no sublimation occurred. Higher temperatures resulted in decomposition of the product.

**Melting Point**

In a series of four melting point determinations, \(C_{10}H_7CH_2Mo(CO)_3C_5H_5\) was found to melt at 109.5-110.2° accompanied by decomposition.

**Infrared Spectrum**

The infrared spectrum (Fig. 8) was determined on a KBr pellet, 0.42% \(C_{10}H_7CH_2Mo(CO)_3C_5H_5\). Bands found were: 3100 (w), 3085 (w), 3050 (w), 2990 (vw), 2940 (vw), 1995 (vs), 1931 (vs), 1900 (vs), 1579 (w), 1565 (w), 1560 (sh), 1500 (m), 1420 (sh), 1415 (m), 1386 (m), 1345 (vw), 1335 (vw), 1255 (w), 1229 (vw), 1195 (vw), 1163 (w), 1152 (w), 1100 (vw), 1075 (sh), 1070 (vw), 1039 (w), 1017 (w), 1003 (w), 995 (w), 965 (w), 940 (w), 920 (vw), 890 (vw), 860 (vw), 850 (w), 829 (m), 824 (m), 811 (s), 791 (s), 785 (ms),
FIGURE 8. Infrared spectrum of C$_{10}$H$_7$-CH$_2$Mo(CO)$_3$)$_3$H$_5$. 

WAVELENGTH (MICRONS)

TRANSMITTANCE (PERCENT)
771 (s), 637 (w), 580 (ms), 565 (s), 553 (s), 502 (w), 490 (s), 475 (s), 468 (sh), 445 (s), and 430 (m) cm\(^{-1}\).

The spectrum showed the expected bands for aromatic C-H stretching vibrations, 3100-3050 cm\(^{-1}\); aliphatic C-H stretching vibrations, 2990 and 2940 cm\(^{-1}\), carbonyl absorptions, 1995, 1931, and 1900 cm\(^{-1}\); CH\(_2\) wagging vibrations, 1386 cm\(^{-1}\); and characteristic 1-substituted naphthalene bands at 791 and 771 cm\(^{-1}\). As expected, no C-Cl absorption was observed.

**Proton Magnetic Resonance Spectrum**

The pmr spectra was determined in DMF solution (Figs. 9 and 10), and CH\(_2\)Cl\(_2\) solution. Tetramethylsilane was used as an external standard.

In DMF (temperature, 36°; filter bandwidth, 4 cps; r. f. field, 0.02 mG; sweeptime, 250 sec; sweep width, 500 cps; spectrum amp., 0.5 and 3.2; integral amp., 3.2), the singlet at 3.05 ppm was assigned to the two equivalent methylenyl protons and the sharp singlet at 5.28 ppm was assigned to the five equivalent \(\pi\)-cyclopentadienyl protons. The complex multiplet at 7.10 ppm was due to the naphthyl hydrogens. Integration of the cyclopentadienyl and naphthyl resonances showed the predicted ratio of 5 : 7. Integration including the methylenyl singlet was not possible due to the closely neighboring DMF resonances at 2.43
FIGURE 9. PMR spectrum of C$_{10}$H$_7$CH$_2$Mo(CO)$_3$C$_5$H$_5$, 1.8-4.9 ppm.
FIGURE 10. PMR spectrum of $\text{C}_{10}\text{H}_{7}\text{CH}_2\text{Mo(CO)}_3\text{C}_5\text{H}_5$, 4.9-7.8 ppm.
and 2.55 ppm.

In CH$_2$Cl$_2$ (temperature, 36$^\circ$; filter bandwidth, 4 cps; r. f. field, 0.025 mG; sweep time, 250 sec; sweep width, 500 cps; spectrum amp., 0.5 and 4.0; integral amp. 6.3) resonances were found at 3.32, 5.15, and 7.45 ppm and were assigned to methylenyl, cyclopentadienyl, and naphthyl protons respectively. Integration of the methylenyl and naphthyl proton absorbances showed a ratio of 1.9 : 7 compared to the theoretical 2 : 7 ratio. Integration of the cyclopentadienyl hydrogens was not possible because of the nearby CH$_2$Cl$_2$ absorbance at 5.25 ppm.

### Chemical Analysis

Carbon and hydrogen determinations were performed on a sample of C$_{10}$H$_7$CH$_2$Mo(CO)$_3$C$_5$H$_5$.

Found:  C, 58.96%.  H, 4.03 %.

Calculated:  C, 59.09 %.  H, 3.65 %.

### Attempt to Prepare

$\sigma$-Trityl-$\pi$-cyclopentadienyltricarbonylmolybdenum.

To a previously prepared (in the same manner as previously described) THF solution of sodium cyclopentadienyltricarbonylmolybdenum (0.1 mole) was added 33.5 g (0.12 mole) of tritylchloride. The solution immediately turned dark red accompanied by evolution of carbon monoxide.
After the solution was allowed to react for three days, the THF was stripped off at room temperature under reduced pressure. The residue was then extracted, filtered, and concentrated as before. A light tan non-crystalline solid precipitated from solution. The solid was filtered and washed with several small portions of hexane and then cold ether. Approximately 5 g of tan product was obtained.

The tan product was air stable but decomposed to a black substance in solution (slightly soluble in benzene, DMF, dimethylsulfoxide, and CH₂Cl₂ forming red solutions) on standing and exposed to air.

The tan product did not melt nor immediately decompose up to 300°.

Attempts to sublime the tan product were not successful. At lower temperatures, the tan substance was unchanged and at higher temperatures (up to about 100°), it slowly decomposed to a black tarry substance.

A pmr spectrum was unattainable due to the very limited solubility of the tan product. In dimethylsulfoxide, no resonance signals were observed for the tan product.

The infrared spectrum was run on a KBr pellet, 0.564% tan product (Fig. 11). The spectrum showed the presence of the trityl group. Several carbonyl bands were observed and no C-Cl band was detected.
FIGURE 11. Infrared spectrum of tan product.
Evidence that $\text{C}_{10}\text{H}_7\text{CH}_2\text{Mo(CO)}_3\text{C}_5\text{H}_5$ was prepared was conclusive. The pmr spectra was in agreement with that predicted. Chemical analysis was in accord with the calculated composition. The infrared spectrum showed the expected bands for aromatic and aliphatic C-H stretching vibrations, carbonyl absorptions, $\text{CH}_2$ wagging vibrations, and 1-substituted naphthalene absorptions. No C-Cl absorption was observed.

The molecular geometry predicted (Fig. 12) is that

![Molecular structure diagram](image-url)

**FIGURE 12.** Predicted geometry of $\text{C}_{10}\text{H}_7\text{CH}_2\text{Mo(CO)}_3\text{C}_5\text{H}_5$. 
found by Bennett and Mason (30) for the ethyl derivative. They performed a three dimensional X-ray analysis of CH₂CH₂Mo(CO)₃C₅H₅ and found the molecular stereochemistry to be 7-coordinate (π-C₅H₅ occupying 3 sites) approximating that of the (NbOF₆)⁻³ structure. The six bonding orbitals of the metal to the carbonyl and cyclopentadienyl ligands form a distorted octahedron. The carbon(ethyl)-molybdenum bond lies approximately along a three-fold axis of the octahedron and slightly above the carbonyl-carbon plane. The bond length for the molybdenum-carbon(ethyl) bond, 2.38 Å, was in agreement with the sum of the covalent radius of the sp³ carbon plus one-half of the Mo-Mo distance in [π-C₅H₅Mo(CO)₃]²⁻. This long distance suggests considerable d-electron character in the bond. Because of the bulk of the naphthyl group, the geometry might possibly be somewhat more distorted.

The bonding between the molybdenum atom and the cyclopentadiene ring may be considered as a combination of the molybdenum(II) cation, d⁴, and the cyclopentadienyl anion, C₅H₅⁻. The anion is symmetrical and a planar pentagon in shape. The carbon atoms in the ring each have a p₂ orbital perpendicular to the ring plane which combine into pi molecular orbitals. Three filled molecular orbitals overlap with the empty orbitals on the molybdenum atom to form the π-bond.
In the case of the carbonyl ligands, multiple bonding results from an overlap of the filled sigma orbital with an empty molybdenum sigma orbital combined with a dative overlap of a filled d-pi orbital of the metal with an empty antibonding p-pi orbital of the carbon monoxide. The synergic bonding mechanism and the reported low dipole moment suggests almost electroneutrality for the metal-carbon bond. The difference in bonding between the carbonyl ligands and the aforementioned \(\pi\)-cyclopentadienyl complex is that the cyclopentadienyl donates and back-bonds by invoking pi orbitals whereas the neutral carbonyl ligands form metal bonds by a combination of sigma orbitals and the use of pi orbitals.

The presence of \(\pi\)-cyclopentadienyl and carbonyl ligands on the metal atom so changed the orbitals remaining for bonding purposes that a stable \(\sigma\)-bond was formed. Piper and Wilkinson (11) speculated that in order to obtain a stable metal-carbon \(\sigma\)-bond, the use of a strongly directed orbital of the metal atom is much more necessary than is required for bonding ligands of the type of carbon monoxide. It is not possible to get strongly directed orbitals with only s and d hybrids, since from symmetry considerations, the resulting orbitals must be gerade. The electron density would then be as great in the direction pointing away from the ligand as in the direction towards it. The formation of a stable \(\sigma\)-bonded organometallic
compound may be considered to require considerable p character for the metal-carbon bond in order to achieve the necessary directional property for good overlap with the orbitals of the carbon atom. The energy of the p orbitals relative to the d and s orbitals decreases in going from the first to the third transition metal series and therefore the participation of p orbitals in the bonding should become increasingly easy.

An attempt to form the \( \Pi-C_{10}H_{7}CH_{2}Mo(CO)_{2}C_{5}H_{5} \) compound from the corresponding sigma derivative by heating on a sublimation apparatus was not successful as decomposition occurred.

The trityl derivative was apparently not prepared. The tan product recovered is believed to be a mixture which contains some trityl compound. Piper and Wilkinson (11) thought steric hindrance to be a consideration in their failure to prepare the \( \sigma \)-phenyl and the \( \sigma \)-cyclopentadienyl \( \Pi \)-cyclopentadienyltricarbonylmolybdenum derivatives whereas the analogous iron and chromium compounds were prepared. This might also be the case in the attempted preparation of the trityl derivative.
BIBLIOGRAPHY


