TABLE III

MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS OF METAL TETRASULFOPHTHALOCYANINES (MSPc) IN THE PRESENCE OF CYANIDE ION, PYRIDINE, AND IMIDAZOLE[a,b]

| System | Diamag. cor. × $10^6$ | $\chi_M \times 10^6$ (complex) | $\mu_{eff}$, B.M. |
|---|---|---|---|
| $Ni^{II}SPc$ | +550 | −441 | 0.50 ± 0.04 |
| $Ni^{II}SPc + 2\ NaCN$[c] | +590 | −510 | 0.43 ± 0.08 |
| $Ni^{II}SPc$ + 2 py | +660 | −555 | 0.50 ± 0.10 |
| $Ni^{II}SPc$ + 2 imid[c] | +600 | −505 | 0.47 ± 0.02 |
| $Cu^{II}SPc$ | +550 | +768 | 1.77 ± 0.05 |
| $Cu^{II}SPc + 2\ NaCN$[c] | +590 | +883 | 1.83 ± 0.07 |
| $Cu^{II}SPc$ + 2 imid[c] | +600 | +703 | 1.76 ± 0.06 |

[a] 0.025 *M* MSPc in water at 20°. [b] py = pyridine, imid = imidazole. [c] $\mu_{eff}$ does not change with 24-hr. aeration.

630 and 334 m$\mu$. Neither the absorption spectra nor the magnetic moments of these compounds are affected by the presence of either cyanide ion or imidazole. Further, extended aeration fails to alter either property.

The fact that the addition of ligands such as pyridine above and below the plane in such complexes as bis(salicylaldoxime)nickel(II) and bis(N-methylsalicylaldimine)nickel(II) converts those planar complexes into spin-free, essentially octahedral derivatives is well known.[11,12] Modern theory has been invoked to explain this effect,[13] in general, in the terms utilized in the discussion of the cobalt(II) case above. In these laboratories[14,15] the nickel(II) atom in other cyclic forced-planar complexes has been found to undergo the transformation from the singlet to the triplet state in the presence of extraplanar ligands weaker than cyanide. Consequently, the fact that nickel(II) tetrasulfophthalocyanine does not exhibit this behavior even in the presence of cyanide ion or imidazole demonstrates that the sulfophthalocyanine ligand exerts an unusually strong ligand field. This conclusion has been reached earlier in conjunction with a study of the magnetic moments of the tetrasulfophthalocyanines of Mn(II), Fe(III), Co(II), Ni(II), and Cu(II).[2] Since spin-paired Mn(II) occurs with only a very few ligands, including $CN^-$, RNC, and tetrasulfophthalocyanine, it was concluded that the ligand field strength of the latter is comparable to that of cyanide. A troublesome consideration follows from this notion. If the two ligands ($CN^-$ and SPc) were of comparable strength, the addition of cyanide above and below the plane might be expected to produce a spin-free pseudooctahedral structure. The difficulty is most probably associated with the failure of such considerations to take into account the very great part the $\pi$-system plays in determining the coordinating ability of th ehighly conjugated cyclic ligand. The $\pi$-bonding molecular orbitals of $e_g$ and $a_{2u}$ symmetry probably play a major role both in determining the stability of the square-planar, spin-paired complex and in preventing its reaction with extraplanar ligands to form spin-free tetragonal complexes.[16]

**Acknowledgment.**—These studies have been made possible by an unrestricted grant from the Research Corporation. The efforts of Mr. Kenneth Long in confirming some of these observations are greatly appreciated.

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[13] C. J. Ballhausen and A. D. Liehr, *J. Am. Chem. Soc.*, **81**, 538 (1959).

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[15] G. Melson and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 4834 (1964).

[16] H. B. Gray and C. J. Ballhausen, *ibid.*, **85**, 260 (1963).

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# Reactions of Alkali Metal Derivatives of Metal Carbonyls. VI. Some Reactions of Anions Prepared from Indenylmolybdenum Tricarbonyl Dimer and Azulenedimolybdenum Hexacarbonyl[1]

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Indenylmolybdenum tricarbonyl dimer, $[C_9H_7Mo(CO)_3]_2$, is reduced by sodium amalgam in tetrahydrofuran to give a brown solution containing the $[C_9H_7Mo(CO)_3]^-$ anion. This solution reacts with methyl iodide to form the expected yellow-orange tricarbonyl $CH_3Mo(CO)_3C_9H_7$. However, allyl chloride and chloromethyl methyl sulfide react with the $[C_9H_7Mo(CO)_3]^-$ anion in tetrahydrofuran solution at room temperature to form the yellow dicarbonyls $\pi$-$C_3H_5Mo(CO)_2C_9H_7$ and $\pi$-$CH_3SCH_2Mo(CO)_2C_9H_7$, respectively, in unusually facile decarbonylation reactions. Treatment of $[C_9H_7Mo(CO)_3]_2$ with iodine in dichloromethane solution gives a brown dicarbonyl iodide $C_9H_7Mo(CO)_2I$ rather than the expected tricarbonyl iodide. Azulenedimolybdenum hexacarbonyl, $C_{10}H_8Mo_2(CO)_6$, reacts with sodium amalgam in tetrahydrofuran to give a yellow-brown solution which gives yellow dimeric $[C_{10}H_8Mo(CO)_3CH_3]_2$ on treatment with methyl iodide.

## A. Indenyl Derivatives

Recently numerous organometallic compounds of interest have been obtained by treatment of various anionic cyclopentadienyl metal carbonyls, especially $[C_5H_5Fe(CO)_2]^-$ and $[C_5H_5M(CO)_3]^-$ (M = Mo or W), with various organic halides.[2] This paper describes

[1] For Part V of this series see R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **2**, 38 (1964).

some reactions of the benzologous indenylmolybdenum tricarbonyl anion, $[C_9H_7Mo(CO)_3]^-$, with certain organic halides as well as an attempt to observe the indenyliron dicarbonyl anion, $[C_9H_7Fe(CO)_2]^-$.

## Experimental

In general infrared spectra (Table II) were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 21 double beam spectrometer with sodium chloride optics. In addition, the metal carbonyl regions were taken in halocarbon oil mulls and recorded on a Beckman IR-9 spectrometer with grating optics. Proton n.m.r. spectra (Table III) were taken in carbon disulfide solution (unless otherwise indicated) on a Varian Associates Model A-60 spectrometer using hexamethyldisiloxane ($\tau$ 9.95), cyclohexane ($\tau$ 8.57), or chloroform ($\tau$ 2.73) as an internal standard. Ultraviolet and visible spectra (Table IV) were taken in spectral grade cyclohexane or reagent grade dioxane solution and recorded on a Cary Model 14 spectrometer. Microanalyses (Table I) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Molecular weight determinations (Mechrolab vapor pressure osmometer in 0.01 to 0.06 *M* benzene solution) were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Melting points were taken in capillaries and are uncorrected.

The reagents used in this work were either commercial samples or prepared by procedures outlined in previous papers from this laboratory.

Tetrahydrofuran was purified by distillation over lithium aluminum hydride. A nitrogen atmosphere was always provided for the following three operations: (a) carrying out reactions, (b) handling all filtered solutions of metal complexes, and (c) admitting to evacuated flasks and sublimers.

**Indenylmolybdenum Tricarbonyl Dimer.**—The procedure given below is far superior to that reported by King and Stone[3] for obtaining quantities of several grams of pure $[C_9H_7Mo(CO)_3]_2$ for preparative purposes.

A mixture of 26.4 g. (100 mmoles) of molybdenum hexacarbonyl, 25 ml. (25 g., 216 mmoles) of indene, and 100 ml. of ethylcyclohexane was heated 16 hr. at the boiling point. The reaction mixture became dark brown. Upon cooling to room temperature, brown crystals separated. These were filtered and washed with several portions of pentane. To ensure absence of any unchanged molybdenum hexacarbonyl, the brown crystals (13.5 g., 64% yield) were heated in a sublimer at 50° (0.1 mm.). In most cases unreacted molybdenum hexacarbonyl was found to be absent from the product. The analyses for a typical product, m.p. 185–188° (lit.[3] m.p. 195–197°) obtained in this manner are given in Table I.

**Reactions between $Na[Mo(CO)_3C_9H_7]$ and Organic Halides.**—A dilute sodium amalgam was prepared under nitrogen from 0.3 g. (13 mg.-atoms) of sodium metal and 3 ml. (40.5 g.) of mercury in a three-neck flask with a stopcock on the bottom for removal of mercury. After the amalgam formation had become complete and the amalgam had cooled to room temperature, 75 to 150 ml. of tetrahydrofuran and 1.48 g. (2.5 mmoles) of indenylmolybdenum tricarbonyl dimer were added. Stirring for 1 hr. at room temperature produced a darker brown solution containing some $[Mo(CO)_3C_9H_7]^-$.

Excess amalgam was removed from this solution through the stopcock at the bottom and excess (1.0 ml.) of the organic halide (methyl iodide, allyl chloride, or chloromethyl methyl sulfide) added. After stirring for ~16 hr. at room temperature, tetrahydrofuran was removed at 25° (30 mm.). The brown residue was extracted with three 50-ml. portions of dichloromethane. Solvent was removed from the filtered dichloromethane extracts at 25° (30 mm.). The residue was extracted with 50 to 100 ml. of pentane in three portions, and the filtered extracts were cooled for several hours in a −78° bath. The yellow crystals of the

Table I

Indenylmolybdenum Compounds

| Compound | Color | M.p., °C. | Preparation | Yield, % | | Analyses, % C | H | O | Mo | S or I | Mol. wt. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| (1) $[C_9H_7Mo(CO)_3]_2$ | Dark brown | 185–188 | $Mo(CO)_6$ + indene | 46 | Calcd. | 48.8 | 2.4 | 16.2 | | ... | |
| | | | | | Found | 48.8 | 2.3 | 16.3 | | ... | |
| (2) $CH_3Mo(CO)_3C_9H_7$ | Yellow-orange | 91–93 dec. | $NaMo(CO)_3C_9H_7 + CH_3I$ | 19[a] | Calcd. | 50.3 | 3.2 | 15.5 | 31.0 | ... | 310 |
| | | | | | Found | 49.8 | 2.9 | 15.8 | 31.5 | ... | 296 |
| (3) $\pi$-$C_3H_5Mo(CO)_2C_9H_7$ | Yellow | 119–121 | $NaMo(CO)_3C_9H_7 + C_3H_5Cl$ | 21[a] | Calcd. | 54.5 | 3.9 | 10.4 | 31.2 | ... | 308 |
| | | | | | Found | 54.9 | 4.0 | 10.3 | 31.2 | ... | 307 |
| (4) $\pi$-$CH_3SCH_2Mo(CO)_2C_9H_7$ | Yellow | 87–89 | $NaMo(CO)_3C_9H_7 + CH_3SCH_2Cl$ | 8[a] | Calcd. | 47.6 | 3.7 | 9.7 | 29.2 | 9.8 | |
| | | | | | Found | 48.4 | 4.0 | 9.6 | 28.8 | 9.5 | |
| (5) $C_9H_7Mo(CO)_2I$ | Brown | 142–145 dec. | $[C_9H_7Mo(CO)_3]_2 + I_2$ | 19 | Calcd. | 33.5 | 1.8 | 8.1 | 24.3 | 32.3 | 394 |
| | | | | | Found | 33.9 | 1.9 | 8.3 | 23.7 | 31.9 | ~450[b] |

[a] Yield based on $[C_9H_7Mo(CO)_3]_2$ rather than on the quantity of sodium salt actually formed. [b] This value may be high due to difficulty in completely dissolving the sample and taking the reading before the onset of decomposition.

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[2] For the earliest report of reactions of this type see T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956).

[3] R. B. King and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 4557 (1960).

TABLE II

INFRARED SPECTRA (CM.$^{-1}$) OF SOME INDENYLMOLYBDENUM CARBONYL COMPOUNDS

| Compound | Metal carbonyl bands$^{a}$ | C–H bands$^{b}$ | Other bands$^{b}$ |
|---|---|---|---|
| (1) $[C_9H_7Mo(CO)_3]_2$ | 1894 sh, 1876 sh, 1862 s | 3060 vvw, 3000 vvw, sh | 1600 vw, 1475 vw, 1440 vw, 1380 vw, 1334 m, 1240 vw, 1208 vw, 1195 vw, 1179 vw, 1149 vw, 1036 w, 1028 sh, 894 vw, 857 vw, 845 vw, 814 m, 805 m, 753 s |
| (2) $CH_3Mo(CO)_3C_9H_7$ | 2024 s, 1945 s, 1911 s | 3050 vw, 2950 vw, 2860 vw | 1605 vw, 1520 vw, 1475 vw, 1445 vw, 1380 vw, 1335 w, 1205 vw, 1150 vw, 1038 vw, 1027 vw, 895 w, 815 m, 750 s |
| (3) $\pi$-$C_3H_5Mo(CO)_2C_9H_7$ | 1937 s, 1867 s, 1855 s | Not clearly obsd. | 1520 vw, 1480 vw, 1332 m, 1247 w, 1220 vw, 1206 vw, 1150 w, 1030 w, 1010 vw, 888 m, 818 s, 743 s |
| (4) $\pi$-$CH_3SCH_2Mo(CO)_2C_9H_7$ | 1940 s, 1858 w, 1817 s | Not clearly obsd. | 1380 w, 1330 w, 1300 w, 1044 vw, 1030 vw, 955 vw, 821 vw, 805 w, 765 vw, 745 m |
| (5) $C_9H_7Mo(CO)_2I$ | 2025 m, 1956 s | 3020 vvw | 1600 vw, 1520 vw, 1477 vw, 1435 w, 1380 w, 1330 w, 1240 vw, 1200 vw, 1040 vw, 1029 vw, 950 vw, 854 w, 845 vw, 820 w, 751 m |

[a] Beckman IR-9 spectrometer; halocarbon oil mull. [b] Perkin-Elmer Model 21 spectrometer; potassium bromide pellets.

TABLE III

PROTON N.M.R. SPECTRA OF $\pi$-INDENYL COMPOUNDS ($\tau$)$^{a,b}$

| Compound | $\pi$-Indenyl protons (see structure I) | | | | | | | Other protons |
|---|---|---|---|---|---|---|---|---|
| | A$^{c}$ | B$^{c}$ | $J_{AB}$$^{e}$ | $J_{A'B}$$^{e}$ | C$^{d}$ | D$^{d}$ | $J_{CD}$$^{e}$ | |
| (1) $CH_3Mo(CO)_3C_9H_7$ | 2.81 (4)$^{f}$ | | ... | ... | 4.31 (2) | 4.65 (1) | 3 | $CH_3$: 10.43 (3)$^{g}$ |
| (2) $CH_3Fe(CO)_2C_9H_7$$^{h}$ | 2.82 (4)$^{f}$ | | ... | ... | 4.77 (2) | 5.21 (1) | 3 | $CH_3$: 10.49 (3)$^{g}$ |
| (3) $\pi$-$C_3H_5Mo(CO)_2C_9H_7$ | 3.01 (4)$^{f}$ | | ... | ... | 4.13 (2) | 4.44 (1) | 2 | $\pi$-$C_3H_5$: 6.70 (1),$^{g}$<br>7.76 (2),$^{i}$<br>9.15 (2)$^{j}$ |
| (4) $\pi$-$CH_3SCH_2Mo(CO)_2C_9H_7$ | 3.11 (4)$^{f}$ | | ... | ... | 4.38 (2) | 4.04 (1) | 2 | $CH_3$$^{k}$: 8.36 (3)$^{g}$ |
| (5) $C_9H_7Mo(CO)_2I$$^{l}$ | 2.36 (2) | 2.68 (2) | 7 | 3 | 3.68 (2) | 4.61 (1) | 2 | |
| (6) $C_5H_5FeC_9H_7$$^{m}$ | 2.59 (2) | 3.22 (2) | 7 | 3 | 5.25 (2) | 6.11 (1) | 2.5 | $\pi$-$C_5H_5$: 6.38 (5)$^{g}$ |
| (7) $(C_9H_7)_2Fe$$^{m}$ | 3.20 (4)$^{f}$ | | ... | ... | 5.54 (2) | 6.08 (1) | 2.5 | |
| (8) $C_9H_7Re(CO)_3$$^{n}$ | 2.57 (2) | 2.90 (2) | Not reported | | 4.3 (3)$^{o}$ | | | |

[a] Relative intensities given in parentheses. [b] $CS_2$ solutions unless otherwise indicated. [c] Six-membered ring protons. [d] Five-membered ring protons. [e] $J$ values are given in c.p.s. [f] All six-membered ring protons (both A and B) have the same chemical shift. [g] Singlet or otherwise unresolved. [h] Only a very weak spectrum obtained of this compound. [i] Doublet, $J = 7$ c.p.s. [j] Doublet, $J = 11$ c.p.s. [k] Location of $CH_2$ resonances in doubt. One proton may be a doublet at $\tau$ 8.17 ($J = 6$ c.p.s.). [l] Acetone solution. [m] Data of R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 796 (1964). [n] Data of E. O. Fischer and W. Fellmann, *J. Organometal. Chem.*, **1**, 191 (1963). [o] Usual $AB_2$ pattern observed but fine structure not reported.

product were filtered and dried. The methyl and $\pi$-allyl derivatives were purified further by sublimation at 70 to 100° at about 0.1 mm.

Yields, analyses, melting points, and spectra of the products thus obtained are given in Tables I–IV.

TABLE IV

ULTRAVIOLET SPECTRA

| Compound | Maxima, m$\mu$$^{a}$ | | |
|---|---|---|---|
| $[C_9H_7Mo(CO)_3]_2$$^{b}$ | 213 (56,000) | | |
| $[C_5H_5Mo(CO)_3]_2$$^{b}$ | 222 (32,350) | | 388 (18,600) |
| $C_9H_7Mo(CO)_2I$$^{b}$ | 213 (55,500) | | |
| $C_5H_5Mo(CO)_3I$$^{b}$ | 213 (25,600) | | 472 (568) |
| $CH_3Mo(CO)_3C_9H_7$$^{c}$ | 222 (43,400) | | |
| $\pi$-$C_3H_5Mo(CO)_2C_9H_7$$^{c}$ | 221 (37,900) | 287 (7520) | |
| $\pi$-$CH_3SCH_2Mo(CO)_2$-$C_9H_7$$^{c}$ | 220 (41,200) | 287 (7960) | |

[a] Extinction coefficient given in parentheses. [b] Dioxane solution. [c] Cyclohexane solution.

**Preparation of $CH_3Fe(CO)_2C_9H_7$.**—A sample of $[C_9H_7Fe(CO)_2]_2$, m.p. 197–199.5° (lit.[4] m.p. 198°) was prepared by boiling iron pentacarbonyl with indene in xylene solution. After removal of xylene, the product was separated from unreacted indene by crystallization from pentane and then recrystallized from a mixture of dichloromethane and hexane.

A 1.13-g. (2.5 mmoles) sample of this $[C_9H_7Fe(CO)_2]_2$ was treated in 100 ml. of tetrahydrofuran with a sodium amalgam prepared from 0.3 g. (13 mg.-atoms) of sodium metal and 3 ml. (40.5 g.) of mercury. After stirring for about 1 hr. at room temperature, the original dark red color of $[C_9H_7Fe(CO)_2]_2$ became dark brown. Excess amalgam was removed and 1.0 ml. (2.28 g., 16 mmoles) of methyl iodide added. After stirring ~16 hr. at room temperature, solvent was removed at 25° (30 mm.). The residue was extracted with three 50-ml. portions of dichloromethane. Solvent was removed from the filtered dichloromethane extracts at 25° (30 mm.) leaving a yellow-brown liquid. A filtered solution of this liquid in ~50 ml. of pentane was chromatographed on a 2 × 30 cm. alumina column. The chromatogram was developed with pentane. A single yellow band was observed which gradually decomposed to a blue substance on the column. The surviving portion of the yellow band was eluted with pentane. Solvent was removed from the filtered eluate at 25° (30 mm.). A yellow-brown liquid remained in quantities too small for further purification or analysis. Examination of the n.m.r. spectrum of a solution of this liquid in carbon disulfide (Table III) indicated it to be reasonably pure $CH_3Fe(CO)_2C_9H_7$.

**Reaction between $[C_9H_7Mo(CO)_3]_2$ and Iodine.**—A mixture of 1.48 g. (2.5 mmoles) of $[C_9H_7Mo(CO)_3]_2$, 1.27 g. (5 mmoles) of iodine, and 50 ml. of dichloromethane was stirred 20 hr. under nitrogen at room temperature. The reaction mixture was then shaken with a solution of 4.0 g. (16.1 mmoles) of sodium thiosulfate 5-hydrate in 120 ml. of water in five portions to assure removal of iodine and polyiodides. The washed dichloromethane

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[4] B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 646 (1958).

layer was dried over anhydrous sodium sulfate. Solvent was removed from the filtered solution at 25° (30 mm.), leaving a brown residue which was washed with three 15-ml. portions of pentane and dried. Brown crystals (0.38 g., 19% yield) of the dicarbonyl iodide $C_9H_7Mo(CO)_2I$ were obtained by recrystallization from a mixture of dichloromethane and hexane followed by further washing with pentane.

A parallel iodination experiment with the $\pi$-cyclopentadienyl derivative $[C_5H_5Mo(CO)_3]_2$ gave the known tricarbonyl iodide, $C_5H_5Mo(CO)_3I$,[2,5] rather than a dicarbonyl iodide, as indicated by elemental analyses and the proton n.m.r. spectrum.

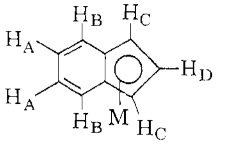
## Discussion

The compound $[C_9H_7Mo(CO)_3]_2$ was first prepared in 1960 by heating molybdenum hexacarbonyl with indene in Soltrol 100, a saturated hydrocarbon petroleum fraction boiling at about 170°, and isolating the product by sublimation from the residue at about 170° (0.1 mm.).[3] However, considerable decomposition occurs during the sublimation of $[C_9H_7Mo(CO)_3]_2$. It has now been found that the reaction between molybdenum hexacarbonyl and indene in the lower-boiling ethylcyclohexane (b.p. $\sim$130°) forms $[C_9H_7Mo(CO)_3]_2$ at a reasonable rate and gives pure brown crystalline material merely by cooling the reaction mixture back to room temperature. The Experimental section describes this improved procedure.

Reduction of $[C_9H_7Mo(CO)_3]_2$ with sodium amalgam in tetrahydrofuran gave a dark brown solution. In order to identify any reactive anionic species in this solution, it was treated with excess methyl iodide. From the resulting reaction mixture a yellow-orange crystalline solid of composition $CH_3Mo(CO)_3C_9H_7$ was isolated. The proton n.m.r. spectrum (Table III) besides indicating the compound to be diamagnetic exhibited a methyl resonance at $\tau$ 10.43 and the characteristic pattern of a $\pi$-indenyl group previously observed in $(C_9H_7)_2Fe$[6] and $C_9H_7Re(CO)_3$.[7] The high chemical shift of the methyl resonance clearly indicates it to be bonded to the molybdenum atom rather than to a carbon atom of the indenyl group. These spectral data confirm the expected structure II for $CH_3Mo(CO)_3C_9H_7$. The isolation of $CH_3Mo(CO)_3C_9H_7$ by methylation of the solution obtained from reduction of $[C_9H_7Mo(CO)_3]_2$ with sodium amalgam in tetrahydrofuran clearly indicates the expected anion $[C_9H_7Mo(CO)_3]^-$ to be present in this solution.

The cyclopentadienylmolybdenum tricarbonyl anion, $[C_5H_5Mo(CO)_3]^-$, is readily obtained by treatment of sodium cyclopentadienide with molybdenum hexacarbonyl in tetrahydrofuran solution at the boiling point.[2] In an attempt to prepare the indenylmolybdenum tricarbonyl anion in an analogous manner, sodium indenide was boiled with molybdenum hexacarbonyl in tetrahydrofuran solution under reflux. However, none of the desired $[C_9H_7Mo(CO)_3]^-$ appeared to be present in the resulting solution since no $CH_3Mo(CO)_3C_9H_7$ was obtained on treatment with methyl iodide at room temperature.

The cyclopentadienyl analog $[C_5H_5Mo(CO)_3]^-$ reacts readily with allyl chloride to form the yellow liquid $\sigma$-allylmolybdenum tricarbonyl cyclopentadienyl derivative $C_3H_5Mo(CO)_3C_5H_5$ which is decarbonylated on ultraviolet irradiation to give the corresponding yellow crystalline $\pi$-allylmolybdenum dicarbonyl cyclopentadienyl derivative $C_3H_5Mo(CO)_2C_5H_5$.[8] In order to prepare the analogous $\pi$-allyl-$\pi$-indenylmolybdenum dicarbonyl, $C_3H_5Mo(CO)_2C_9H_7$ (III), a solution of the $[C_9H_7Mo(CO)_3]^-$ anion was treated will allyl chloride at room temperature expecting to obtain a liquid $\sigma$-allyl derivative, $C_3H_5Mo(CO)_3C_9H_7$, which would then be converted to the desired $\pi$-allyl derivative on ultraviolet irradiation. However, a yellow crystalline product was isolated from the reaction mixture. Analyses and the proton n.m.r. spectrum (Table III) of this material clearly indicated it to be the $\pi$-allyl derivative $C_3H_5Mo(CO)_2C_9H_7$ (III). Apparently the intermediate $\sigma$-allyl-$\pi$-indenyl derivative $C_3H_5Mo(CO)_3$-$C_9H_7$ unlike the analogous $\sigma$-allyl-$\pi$-cyclopentadienyl derivative $C_3H_5Mo(CO)_3C_5H_5$ readily loses carbon monoxide at room temperature in the absence of strong ultraviolet irradiation. This was the first indication that $\pi$-indenyl derivatives of the type $RMo(CO)_3C_9H_7$ lose carbon monoxide more easily than the analogous $\pi$-cyclopentadienyl derivatives $RMo(CO)_3C_5H_5$.



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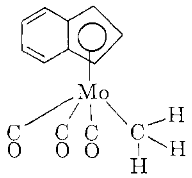

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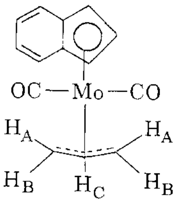

III

The $\pi$-allyl portion of the n.m.r. spectrum of $C_3H_5$-$Mo(CO)_2C_9H_7$ (Table III) corresponds to the spectra of other $\pi$-alyll compounds.[9] The unresolved broad peak (width at half-height $\sim$7 c.p.s.) at $\tau$ 6.70 may be assigned to the single center proton $H_C$ split by $H_A$ and $H_B$ in a manner which was not resolved in the spectrum. The doublet at $\tau$ 7.76 may be assigned to the two *exo*-protons $H_B$ split by the single center proton $H_C$. Similarly the doublet at $\tau$ 9.15 may be assigned to the two *endo*-protons $H_A$ again split by the single center proton $H_C$. The remaining resonances at $\tau$ 3.01, 4.13, and 4.44 clearly arise from the seven protons of the $\pi$-indenyl group.

At this stage investigations were made to determine whether other $\pi$-indenylmolybdenum tricarbonyl derivatives of the type $RMo(CO)_3C_9H_7$ would also lose carbon monoxide more readily than the corresponding $\pi$-cyclopentadienyl derivatives of the type $RMo(CO)_3C_5H_5$.

The compound $\sigma$-$CH_3SCH_2Mo(CO)_3C_5H_5$ is readily formed from $NaMo(CO)_3C_5H_5$ and chloromethyl methyl sulfide at room temperature.[10] Although stable at

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(5) E. W. Abel, A. Singh, and G. Wilkinson, *J. Chem. Soc.*, 1321 (1960).

(6) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 796 (1964).

(7) E. O. Fischer and W. Fellman, *J. Organometal. Chem.*, **1**, 191 (1963).

(8) M. Cousins and M. L. H. Green, *J. Chem. Soc.*, 889 (1963).

(9) See, for example, B. L. Shaw and N. Sheppard, *Chem. Ind.* (London), 517 (1961), and references cited therein.

(10) R. B. King and M. B. Bisnette, *J. Am. Chem. Soc.*, **86**, 1267 (1964); *Inorg. Chem.*, **4**, 486 (1965).

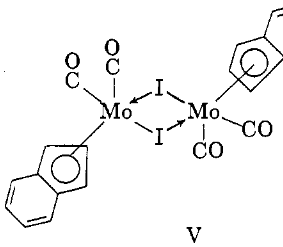
room temperature, it loses carbon monoxide either on ultraviolet irradiation or on sublimation at 70° (0.1 mm.) to form the dicarbonyl $\pi$-$CH_3SCH_2Mo(CO)_2$-$C_5H_5$.[10] However, on treatment with chloromethyl methyl sulfide at room temperature, $NaMo(CO)_3C_9H_7$ formed directly the yellow crystalline dicarbonyl $\pi$-$CH_3SCH_2Mo(CO)_2C_9H_7$ (IV). The intermediate tricarbonyl $\sigma$-$CH_3SCH_2Mo(CO)_3C_9H_7$ was not observed. This reaction is thus the second example of the more facile decarbonylation of $RMo(CO)_3C_9H_7$ compounds as compared with the corresponding $RMo(CO)_3C_5H_5$ compounds.

Attempts were also made to prepare the trifluoroacetyl derivative $CF_3COMo(CO)_3C_9H_7$, which would be expected to decarbonylate readily to form the corresponding trifluoromethyl derivative $CF_3Mo(CO)_3C_9H_7$. However, only $Mo(CO)_6$ in low yield was isolated from the reaction between $NaMo(CO)_3C_9H_7$ and trifluoroacetic anhydride. It is known, however, that acyl $\pi$-cyclopentadienyl derivatives of the type $RCOMo(CO)_3C_5H_5$ are often unstable with respect to decomposition by routes other than decarbonylation to give the corresponding alkyl derivatives[11] and have been isolated only when RCO is a perfluoroacyl group. The corresponding acyl $\pi$-indenyl derivatives $RCOMo(CO)_3C_9H_7$ may be less stable than the corresponding $\pi$-cyclopentadienyl derivatives such that even the perfluoracyl compounds can no longer be prepared.

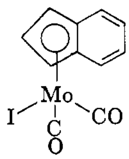
A reaction characteristic of binuclear metal carbonyls and cyclopentadienylmetal carbonyls is cleavage of the metal–metal bond with iodine to give a mononuclear iodide. Examples include reactions of $[Mn(CO)_5]_2$, $[C_5H_5Mo(CO)_3]_2$, $[C_5H_5Cr(NO)_2]_2$, $[C_5H_5Fe(CO)_2]_2$, and $[C_5H_5NiCO]_2$ with iodine to give the mononuclear iodides $Mn(CO)_5I$,[12] $C_5H_5Mo(CO)_3I$,[5] $C_5H_5Cr(NO)_2I$,[13] $C_5H_5Fe(CO)_2I$,[14] and $C_5H_5NiCOI$,[15] respectively. Treatment of $[C_9H_7Mo(CO)_3]_2$ with iodine at room temperature in dichloromethane solution gave a brown crystalline solid. Complete analyses on two independent samples of this material clearly indicated it to be a *di*carbonyl of composition $C_9H_7Mo(CO)_2I$ rather than the expected *tri*carbonyl $C_9H_7Mo(CO)_3I$. In a control experiment $[C_5H_5Mo(CO)_3]_2$ was treated with iodine in dichloromethane solution under exactly the same conditions. This time the product was the known tricarbonyl $C_5H_5Mo(CO)_3I$. This reaction thus represents a third example of the more facile decarbonylation of $RMo(CO)_3C_9H_7$ derivatives as compared with the corresponding $RMo(CO)_3C_5H_5$ derivatives.

The structure of $C_9H_7Mo(CO)_2I$ poses a somewhat perplexing question. The obvious possibility of a dimeric structure (V) with iodine bridges seems to be contraindicated by the molecular weight determinations which on both pure samples suggested a monomeric formulation. The proton n.m.r. spectrum of this diamagnetic compound is very similar to that of the $\pi$-indenyl group in the unambiguous compound $C_5H_5FeC_9H_7$.[6] It therefore seems unlikely that the $\pi$-indenyl ligand is acting as a seven-electron donor in $C_9H_7Mo(CO)_2I$ like the $\pi$-cycloheptatrienyl ligand in $C_7H_7Mo(CO)_2I$.[16] In a $\pi$-indenyl ligand which donates seven electrons to a metal atom at least four of the carbon atoms of the six-membered ring would have to be involved in the bonding to the metal atom. If this occurred the n.m.r. spectrum of the $\pi$-indenyl ligand of $C_9H_7Mo(CO)_2I$ would be expected to be completely different from the n.m.r. spectrum of the $\pi$-indenyl ligand of $C_5H_5FeC_9H_7$ where hydrogenation data clearly indicate four carbon atoms of the six-membered ring not to be involved in the bonding to the metal atom.

On the basis of these considerations the most likely structure for $C_9H_7Mo(CO)_2I$ is VI where the $\pi$-indenyl ring like all of the other presently known $\pi$-indenyl rings donates five electrons to the metal atom, only the five-membered ring being involved in the bonding. This leaves the molybdenum atom with only 16 outer electrons—two less than the favored inert gas configuration. However, many other transition metal compounds with only sixteen outer electrons are known such as tetracoordinate complexes of rhodium(I), palladium(II), and gold(III).



V



VI

The interesting chemistry of the $[C_9H_7Mo(CO)_3]^-$ anion suggested the investigation of other indenylmetal carbonyl anions. In an attempt to prepare the anion $[C_9H_7Fe(CO)_2]^-$ analogous to the well-known $[C_5H_5Fe(CO)_2]^-$ anion,[2,17] $[C_9H_7Fe(CO)_2]_2$ in tetrahydrofuran was reduced with sodium amalgam and the resulting solution treated with methyl iodide hoping to isolate a compound $CH_3Fe(CO)_2C_9H_7$ analogous to $CH_3Fe(CO)_2C_5H_5$.[2] A small quantity of a yellow-brown liquid was obtained from this reaction which failed to crystallize even after chromatography on alumina. The proton n.m.r. spectrum of this material (Table III) was completely analogous to that of $CH_3Mo(CO)_3C_9H_7$, indicating the yellow-brown liquid to be the desired iron compound. The small quantity of material available and the uncertain purity of the noncrystalline product discouraged elemental analyses.

## B. Azulene Derivatives

Several years ago Burton, Pratt, and Wilkinson[18] reported the reaction of molybdenum hexacarbonyl

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[11] J. A. McCleverty and G. Wilkinson, *J. Chem. Soc.*, 4096 (1963).

[12] E. O. Brimm, M. A. Lynch, Jr., and W. J. Sesny, *J. Am. Chem. Soc.*, **76**, 3831 (1954).

[13] R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 791 (1964).

[14] T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 38 (1956).

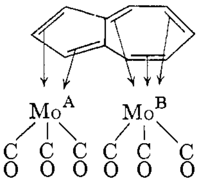
[15] E. O. Fischer and C. Palm, *Ber.*, **91**, 1725 (1958).

[16] D. J. Bertelli, Ph.D. Thesis, University of Washington, 1961 (Prof. H. J. Dauben, Jr., research adviser).

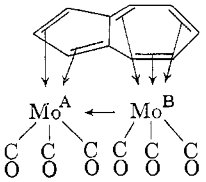
[17] E. O. Fischer and R. Böttcher, *Z. Naturforsch.*, **10b**, 600 (1955).

[18] (a) R. Burton and G. Wilkinson, *Chem. Ind.* (London), 1205 (1958); (b) R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4290 (1960).

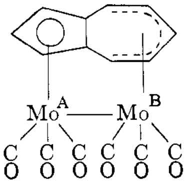
with azulene to give a diamagnetic[19] complex of composition $C_{10}H_8Mo_2(CO)_6$. Two structures (VII and VIII) were suggested for this compound. However, several discoveries since this work of Burton, Pratt, and Wilkinson, notably those of π-allyl and, more particularly, π-cyclohexadienyl and π-cycloheptadienyl metal complexes, suggested a third structure (IX) for $C_{10}H_8Mo_2(CO)_6$ closely related to that of $[C_5H_5Mo(CO)_3]_2$ (X).[20]



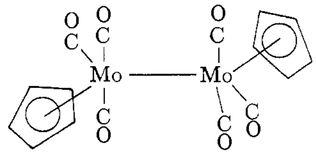
VII



VIII



IX



X

A characteristic reaction[11] of the molybdenum-molybdenum bond in $[C_5H_5Mo(CO)_3]_2$ is its cleavage with sodium in ethereal solvents to form the sodium salt of the mononuclear anion $[C_5H_5Mo(CO)_3]^-$. Methyl iodide reacts with this anion to form the methyl derivative $CH_3Mo(CO)_3C_5H_5$. If the azulene complex had structure IX and behaved analogously, cleavage of the molybdenum–molybdenum bond with sodium should form the binuclear dianion $[C_{10}H_8Mo_2(CO)_6]^{2-}$ which would react with methyl iodide to form a dimethyl derivative $C_{10}H_8Mo_2(CO)_6(CH_3)_2$.

In an attempt to obtain chemical evidence for structure IX for $C_{10}H_8Mo_2(CO)_6$, we therefore investigated its cleavage with sodium amalgam in tetrahydrofuran. A reaction occurred but treatment of the resulting solution with excess methyl iodide gave a methyl derivative of composition $[CH_3Mo(CO)_3C_{10}H_8]_2$ rather than the anticipated composition $C_{10}H_8Mo_2(CO)_6(CH_3)_2$.

## Experimental

The general experimental techniques for part B of this paper were the same as those used in part A. The azulene required for this work was manufactured by Rütgerswerke A.G., and purchased from Henley and Company, Inc., New York, N. Y.

**Azulenedimolybdenum Hexacarbonyl.**—Our procedure for obtaining $C_{10}H_8Mo_2(CO)_6$ differed in some minor respects to that of Burton, Pratt, and Wilkinson.[18] Since our method yields analytically pure material without troublesome recrystallization of this sparingly soluble material, we prefer it at least when quantities of several grams are required.

A mixture of 3.84 g. (30 mmoles) of azulene, 17.4 g. (66 mmoles) of molybdenum hexacarbonyl, and 100 ml. of ethylcyclohexane was boiled under reflux ~16 hr. under nitrogen with magnetic stirring. Cooling to room temperature precipitated the black-red product. This was filtered, washed with several portions of pentane to remove any azulene, and dried. Unreacted molybdenum hexacarbonyl was then sublimed away at 70° (0.1 mm.). The residue was pure azulenedimolybdenum hexacarbonyl. In three such preparations, the yields were 6.4 g. (44%), 10.0 g. (68%), and 13.5 g. (92%).

*Anal.* Calcd. for $C_{16}H_8O_6Mo_2$: C, 39.4; H, 1.6; O, 19.6. Found: C, 39.2; H, 1.6; O, 20.1.

**The Compound $[CH_3Mo(CO)_3C_{10}H_8]_2$.**—A dilute sodium amalgam was prepared by the usual procedure from 0.3 g. (13 mg.-atoms) of sodium and 3 ml. (40.5 g.) of mercury. This amalgam was treated with 1.22 g. (2.5 mmoles) of azulenedimolybdenum hexacarbonyl and about 50 ml. of tetrahydrofuran. After stirring for 1 hr. at room temperature, the original dark red color of $C_{10}H_8Mo_2(CO)_6$ had become the dark yellow color characteristic of the anion. After removal of excess amalgam, the solution was treated with 1.0 ml. (2.28 g., 16 mmoles) of methyl iodide. After stirring for 16 hr. at room temperature, solvent was removed at 25° (30 mm.). The residue was extracted with three 50-ml. portions of dichloromethane. Solvent was removed from the filtered extracts at 25° (30 mm.), leaving a yellow crystalline residue. This was washed with pentane and recrystallized from a mixture of dichloromethane and hexane to give 0.3 to 0.4 g. (37 to 50% yield based on available azulene) of yellow crystalline $[CH_3Mo(CO)_3C_{10}H_8]_2$, m.p. 168–169°.

On heating $[CH_3Mo(CO)_3C_{10}H_8]_2$ above 220° in a capillary, a blue sublimate, apparently azulene, was obtained.

*Anal.* Calcd. for $C_{28}H_{22}O_6Mo_2$: C, 52.0; H, 3.4; O, 14.9; Mo, 29.7; mol. wt., 646. Found (three independent preparations): C, 51.9, 50.3, 50.3; H, 3.4, 3.5, 3.4; O, 15.1, 15.5, 15.7; Mo, 29.4, 30.2, 30.8; mol. wt., 677, 717.

**Infrared Spectrum.**[21]—Carbon-hydrogen bands at 2930 (sh) and 2860 (vw) cm.$^{-1}$; metal carbonyl bands at 2011 (vs) and 1920 (vs) cm.$^{-1}$; other bands at 1144 (vw, br), 1036 (w), 815 (m), 775 (m), 723 (sh), and 715 (w) cm.$^{-1}$.

**Proton N.m.r. Spectrum.**[22]—Resonances at τ 3.72 (double doublet, $J_1$ = 2 c.p.s., $J_2$ = 3 c.p.s.), τ ~4.01 (not resolved), τ 4.87 (doublet, $J$ = 3 c.p.s.), τ 5.62 (triplet, $J$ = 3 c.p.s.), τ 6.76 (broad, width at half-height ~10 c.p.s.), τ 8.59 (broad, not resolved), and τ 9.86 (sharp singlet) of approximate relative intensities 2:1:2:1:1:1:3.

## Discussion

The isolation of a compound $[CH_3Mo(CO)_3C_{10}H_8]_2$ with only one molybdenum atom for each azulene residue by methylation of the solution obtained from sodium amalgam and the compound $C_{10}H_8Mo_2(CO)_6$ with two molybdenum atoms for one azulene residue clearly indicates that the sodium amalgam cleaved one of the molybdenum–azulene bonds. If azulenedimolybdenum hexacarbonyl has structure VII, the bond between the seven-membered ring and the $Mo(CO)_3$ group B would be expected to be more stable than the bond between the five-membered ring and the $Mo(CO)_3$ group A since only the former molybdenum atom (B) has the favored inert gas configuration. A similar argument is probably true for structure VIII, differing from structure VII only by an added (probably rather weak) molybdenum–molybdenum dative bond. However, if azulenedimolybdenum hexacarbonyl has structure IX, the π-cyclopentadienyl type of bond between the five-membered ring and molybdenum atom A would be expected to be more stable than the π-cycloheptadienyl type of bond between the seven-

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[19] The originally found weak paramagnetism of $C_{10}H_8Mo_2(CO)_6$ (ref. 18a) was later found to arise from impurities (ref. 18b). Pure $C_{10}H_8Mo_2(CO)_6$ is diamagnetic (ref. 18b).

[20] F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, **27**, 809 (1957).

[21] The metal carbonyl region of this spectrum was obtained in a halocarbon oil mull and recorded on a Beckman IR-9 spectrometer. The other regions of this spectrum were obtained in potassium bromide pellets and recorded on a Perkin-Elmer Model 21 spectrometer.

[22] This spectrum was taken in both chloroform and acetone-$d_6$ solutions. In both cases, limited solubility made the weakest resonances barely observable.

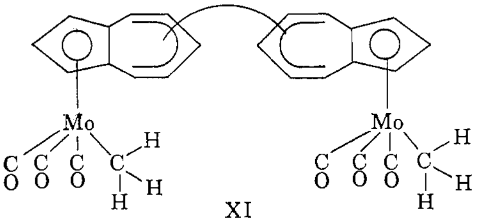
membered ring and molybdenum atom B.[23] Thus the ring to which the molybdenum atom is bonded in $[CH_3Mo(CO)_3C_{10}H_8]_2$ should provide a useful clue to the structure of $C_{10}H_8Mo_2(CO)_6$.

An important feature of the proton n.m.r. spectrum of $[CH_3Mo(CO)_3C_{10}H_8]_2$ is the methyl resonance at $\tau$ 9.86. This chemical shift is in the expected region for a methyl group bonded to a molybdenum atom but too far upfield for a methyl group bonded to a carbon atom. Thus the methyl groups in $[CH_3Mo(CO)_3C_{10}H_8]_2$ appear to be bonded directly to the molybdenum atoms. Structures derived from methylazulenes may thus be eliminated.

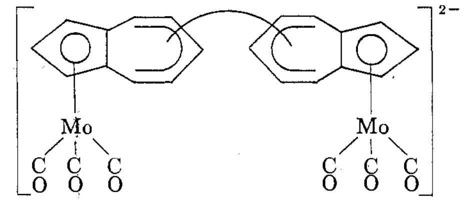
Further characteristic features of the proton n.m.r. spectrum of $[CH_3Mo(CO)_3C_{10}H_8]_2$ are the doublet at $\tau$ 4.87 and the triplet at $\tau$ 5.62 of relative intensities 2:1. Since the splittings of these two resonances are the same, they can reasonably be assumed to be coupled. A comparison with Table III suggests the similarity of these two resonances to those of the five-membered rings of $\pi$-indenyl compounds. Since the five-membered ring in the $\pi$-indenyl compounds is known to be bonded to the metal atom, this resemblance suggests the five-membered ring of the azulene system to be bonded to the metal in $[CH_3Mo(CO)_3C_{10}H_8]_2$.

A further indication of the bonding of the five-membered ring rather than the seven-membered ring of the azulene system to the molybdenum atom is suggested by a comparison of $[CH_3Mo(CO)_3C_{10}H_8]_2$ with the known compounds $[C_{10}H_8Mn(CO)_3]_2$[18] and $[C_{10}H_8V(CO)_4]_2$.[26] All of these dimeric compounds possess similar formulas and colors to the known monomeric $\pi$-cyclopentadienyl compounds, $CH_3Mo(CO)_3C_5H_5$,[2] $C_5H_5Mn(CO)_3$,[27] and $C_5H_5V(CO)_4$.[28] This similarity suggests that the bonding around the metal atoms is similar in the dimeric azulene compounds and the monomeric $\pi$-cyclopentadienyl compounds. This further suggests that the dimerization in these azulene compounds is not due to the formation of a metal–metal bond but instead is due to coupling of the two azulene systems with a carbon–carbon bond. Since all of the five available positions of the five-membered ring are accounted for either by the three observed protons in the n.m.r. spectrum or by the two positions of fusion to the seven-membered ring, this carbon–carbon bond must link the two seven-membered rings.

Unfortunately, the resonances of the protons of the seven-membered ring of $[CH_3Mo(CO)_3C_{10}H_8]_2$ are either too weak or unclearly resolved to be interpreted in detail. It is thus impossible to specify the exact point of linkage of the two seven-membered azulene rings. Thus it is presently impossible to elucidate the structure of $[CH_3Mo(CO)_3C_{10}H_8]_2$ any more exactly than that indicated schematically in structure XI. The anionic precursor, $[C_{10}H_8Mo(CO)_3]_2^{2-}$, may similarly be assigned a partial structure XII.



XI



XII

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[23] Unfortunately, very few $\pi$-cycloheptadienyl compounds (ref. 24) are known, and no direct comparisons of their stabilities with those of the corresponding $\pi$-cyclopentadienyl compounds exist in the literature. However, the work of Fischer, Palm, and Fritz (ref. 25) indicates that the molybdenum tricarbonyl complex of 1,3,5-cyclooctatriene, which like the $\pi$-cycloheptadienyl complexes has two $CH_2$ groups of the ring not involved in the bonding to the metal atom, is much less stable than the corresponding molybdenum tricarbonyl complex of benzene, which like the $\pi$-cyclopentadienyl complexes has all of the ring carbon atoms bonded to the metal atom.

(24) H. J. Dauben, Jr., and D. J. Bertelli, *J. Am. Chem. Soc.*, **83**, 497 (1961).

(25) E. O. Fischer, C. Palm, and H. P. Fritz, *Ber.*, **92**, 2645 (1959).

(26) E. O. Fischer, Abstracts of Papers presented at the Symposium on Current Trends in Organometallic Chemistry, Cincinnati, Ohio, June 1963, p. 66.

(27) E. O. Fischer and R. Jira, *Z. Naturforsch.*, **9b**, 618 (1954).

(28) E. O. Fischer and S. Vigoureux, *Ber.*, **91**, 2205 (1958).