

ALKYL AND ARYL DERIVATIVES OF  
 $\pi$ -CYCLOPENTADIENYL COMPOUNDS OF CHROMIUM,  
 MOLYBDENUM, TUNGSTEN, AND IRON

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**Abstract**—The preparation of alkyl and aryl  $\pi$ -cyclopentadienyl carbon monoxide or nitric oxide compounds of Cr, Mo, W, and Fe is described. The methods involve the reaction of halides such as  $\pi$ -C<sub>5</sub>H<sub>5</sub>Cr(NO)I with Grignard reagents, the reaction of  $\pi$ -C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>3</sub>H with diazomethane, and the reaction of sodium salts such as  $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>Na with alkyl or aryl halides.

The properties and infra-red spectra of the compounds, and high-resolution nuclear magnetic resonance spectra of some of these and other cyclopentadienyl compounds are given.

The structure, stabilities, and some reactions of the alkyl, aryl, and  $\sigma$ -cyclopentadienyl derivatives and of the  $\pi$ -cyclopentadienyl-tricarbon monoxide hydrides of Cr, Mo, and W are discussed.

The compound  $\pi$ -C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>2</sub>NO, the halides  $\pi$ -C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>3</sub>X, and the methyl compound ( $\pi$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ti(CH<sub>3</sub>)<sub>2</sub> are also described.

1. INTRODUCTION

THE number of well characterized organometallic compounds, that is to say compounds with a metal-to carbon  $\sigma$ -bond, of the transitional metals, is few.<sup>(1a)</sup> Methyl platinum derivatives are firmly established, and the work of HERMAN and NELSON<sup>(1b)</sup> conclusively showed the existence of aryl titanium compounds. Naphthyl derivatives of cobalt have been reported, but require further characterization. The existence of numerous "polyphenyl" chromium compounds, originally studied by HEIN, is certain, but it is not proved that there is a metal-to-carbon  $\sigma$ -bond present in these compounds; indeed, a new type of structure recently proposed for these chromium derivatives by ZEISS and TSUTSUI<sup>(1c)</sup> involves the direct bonding of a benzene nucleus to the metal atom in a manner analogous to that of the cyclopentadienyl ring in the now well-known  $\pi$ -cyclopentadienyl metal compounds of which ferrocene is the prototype, and would require the use of two  $\pi$ -electrons of the ring in metal-ring bonding.†

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† Note added in proof—

ZEISS and TSUTSUI's proposal concerning the structures of HEIN's compounds has been given strong support by the recent preparation of di(benzene) chromium, (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>Cr, by E. O. FISCHER and W. HAFNER (*Z. Naturforsch.* **10b**, 665, 1955). This compound, which can be regarded as the parent compound from which HEIN's compounds can in principle be derived, may be considered as electronically analogous to ferrocene, with two  $\pi$  electrons from each ring being involved in the primary metal to ring bond. Two members of the isoelectronic series C<sub>4</sub>H<sub>4</sub><sup>2-</sup>, C<sub>5</sub>H<sub>5</sub><sup>-</sup>, C<sub>6</sub>H<sub>6</sub>, C<sub>7</sub>H<sub>7</sub><sup>+</sup> have thus now been shown to form "sandwich" type compounds with transitional metals; the possibility that the first member can form metal compounds has been discussed by H. C. LONGUET-HIGGINS and L. E. ORGEL (Chemical Society Discussion, London, December 1955, see *Chemistry and Industry*, 153, 1956), whilst the possibility that the last member, the tropylium ion, can form sandwich-type compounds where a transition metal can be obtained in a system with a formal negative charge, e.g., as in C<sub>7</sub>H<sub>7</sub>Re(CO)<sub>2</sub>, is currently being investigated.

See now: E. O. FISCHER, S. HAFNER, and H. O. STAHL *Z. anorg. Chem.* **282**, 47 (1956).

It would seem that the compound  $\pi$ -C<sub>5</sub>H<sub>5</sub>Cr(NO)<sub>2</sub>C<sub>6</sub>H<sub>5</sub> described in this paper is the only chromium phenyl derivative known at the present time.

<sup>(1)</sup> (a) For complete references to the literature: see F. A. COTTON *Chem. Reviews* **55**, 551 (1955). (b) D. F. HERMAN and W. K. NELSON *J. Amer. Chem. Soc.* **75**, 3877, 3882 (1953). (c) H. H. ZEISS and M. TSUTSUI Abstracts of Papers presented at the 126th meeting of the American Chemical Society, New York, September 1954, p. 29-O; cf. also ref. (1a), p. 569.

Recently, the preparations of mononuclear  $\pi$ -cyclopentadienyl carbon monoxide and nitric oxide metal halides,<sup>(2, 3)</sup> e.g.  $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>Cl,  $\pi$ -C<sub>5</sub>H<sub>5</sub>Cr(NO)<sub>2</sub>Cl, and of the related hydrides and the salts,<sup>(4, 5)</sup> e.g.  $\pi$ -C<sub>5</sub>H<sub>5</sub>Cr(CO)<sub>3</sub>H,  $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>Na, have been described.

From compounds of these types, by the preparative methods outlined below, we have been able to prepare a number of compounds with a transitional metal-to-carbon  $\sigma$ -bond, e.g.  $\pi$ -C<sub>5</sub>H<sub>5</sub>W(CO)<sub>3</sub>CH<sub>3</sub>,  $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>, of considerable stability. In addition to the alkyl and aryl compounds, derivatives in which a cyclopentadienyl group is bound to the metal atom by a  $\sigma$ -bond to a carbon atom have been characterized, e.g.  $\pi$ -C<sub>5</sub>H<sub>5</sub>Cr(NO)<sub>2</sub> $\sigma$ -C<sub>5</sub>H<sub>5</sub>.

1.1. The Grignard Method

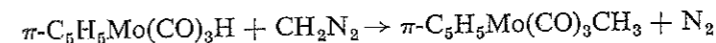
The preparation of several compounds from the  $\pi$ -cyclopentadienyl carbon monoxide or nitric oxide metal halides by this classical method has been noted in preliminary communications,<sup>(6, 7, 8)</sup> e.g.  $\pi$ -C<sub>5</sub>H<sub>5</sub>Cr(NO)<sub>2</sub>I + CH<sub>3</sub>MgI  $\rightarrow$   $\pi$ -C<sub>5</sub>H<sub>5</sub>-Cr(NO)<sub>2</sub>CH<sub>3</sub> + MgI<sub>2</sub>. The method is not uniformly successful, and the yields of the products depend very much on the natures of the reactants; thus, the action of phenyl magnesium bromide on  $\pi$ -C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>3</sub>I does not produce the corresponding aryl, but instead gives a high yield of the binuclear compound  $\pi$ -C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>6</sub>-Mo $\pi$ -C<sub>5</sub>H<sub>5</sub>. The yields of the Grignard reactions of  $\pi$ -cyclopentadienyl metal halides are generally somewhat erratic and the values recorded subsequently are only approximate.

The use of sodium cyclopentadienide in tetrahydrofuran as a reagent for the preparation of derivatives with a cyclopentadienyl ring  $\sigma$ -bonded to a metal atom falls, of course, in this class. The first reported use of this procedure, with  $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>Br, was by HALLAM and PAUSON,<sup>(9)</sup> but the nature of the product,  $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub> $\sigma$ -C<sub>5</sub>H<sub>5</sub>, was not appreciated by these authors.

The Grignard procedure has also been used to prepare ( $\pi$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ti(CH<sub>3</sub>)<sub>2</sub> from ( $\pi$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>TiCl<sub>2</sub>.

1.2. Reaction of Diazo Compounds with Hydrides

The discovery of the  $\pi$ -cyclopentadienyl carbon monoxide hydrides of Cr, Mo, and W<sup>4</sup>, suggested that alkyl derivatives could be made by a reaction with diazomethane or similar compounds, according to the equation, e.g.



The preparation of  $\pi$ -C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>3</sub>CH<sub>3</sub> by this method was reported in a preliminary note,<sup>(7)</sup> while in a review article, E. O. FISCHER<sup>(5)</sup> independently reported the similar preparation of tungsten methyl and ethyl compounds; details of his work

<sup>(1a)</sup> T. S. PIPER, F. A. COTTON, and G. WILKINSON *J. Inorg. Nucl. Chem.* **1**, 165 (1955).

<sup>(1b)</sup> T. S. PIPER and G. WILKINSON *ibid.* **2**, 38 (1956).

<sup>(1c)</sup> E. O. FISCHER and W. HAFNER *Z. Naturforsch.* **10b**, 140 (1955).

<sup>(2)</sup> E. O. FISCHER *Angew. Chem.* **67**, 475 (1955).

<sup>(3)</sup> T. S. PIPER and G. WILKINSON *Chem. and Ind.* **41**, 1296 (1955).

<sup>(4)</sup> T. S. PIPER and G. WILKINSON *Naturwiss.* **42**, 625 (1955).

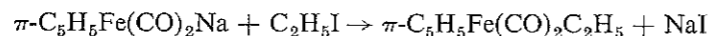
<sup>(5)</sup> T. S. PIPER and G. WILKINSON *ibid.* **43**, 15 (1956).

<sup>(6)</sup> B. F. HALLAM and P. L. PAUSON *Chem. and Ind.* **23**, 653 (1955).

are not yet available.\* Since we were unable to obtain high yields with molybdenum, this method of preparation of alkyls was abandoned in favour of Method 3.

### 1.3. Reaction of Alkyl and Aryl Halides with Sodium Salts of $\pi$ -Cyclopentadienyl Compounds

By the reaction of alkyl or aryl halides with the sodium salt of the  $\pi$ -cyclopentadienyl metal derivative we have been able to prepare numerous alkyl and aryl compounds of Cr, Mo, W, and Fe. The reactions, which are of the type:



in some cases give almost quantitative yields of the desired products. This procedure is potentially applicable for the preparation of compounds with  $\sigma$ -bonds between a transitional element and elements other than carbon by use of suitable halides.\*

The alkyl and aryl compounds described in this paper are listed in Table 1 together with the preparative method and the yield, the colours, and the melting-point of the compounds.

Whilst derivatives of chromium, molybdenum, tungsten, and iron have, so far, been prepared, there now seems to be no reason why similar derivatives of other transitional metals cannot be made. In fact, since all the alkyls and aryl compounds obey the structural principles for mononuclear  $\pi$ -cyclopentadienyl compounds discussed previously,<sup>(2)</sup> one can indeed expect that, provided the starting materials suitable for use in the preparative procedures outlined above become available, as yet unmade compounds, e.g.  $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{NO})(\text{CO})\text{CH}_3$ , should be reasonably stable.

Some other  $\pi$ -cyclopentadienyl compounds prepared during the course of these studies, e.g.  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{NO}$ ,  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Cl}$ , and some of the reactions of  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{H}$ , are described in the experimental section.

## 2. EXPERIMENTAL

### Preparations

(\*) All the preparations described below were carried out in a nitrogen atmosphere. Tetrahydrofuran was purified before use by distillation in nitrogen over lithium aluminium hydride. We are deeply indebted to Dr. E. O. BRIMM and the Linde Air Products Company, Tonawanda, N.Y., for several gifts of chromium, molybdenum, and tungsten hexacarbonyls, and to the Climax Molybdenum Company, New York, N.Y., for the welcome gift of several pounds of molybdenum hexacarbonyl.

#### 2.1. Alkyl and Aryl Compounds by the Grignard Procedure (Method I)

The halides  $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Br}$  and  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$  in dilute ether solution (0.02 to 0.1 molar) were treated with the appropriate Grignard reagent in ether or with sodium cyclopentadienide in tetrahydrofuran. Stoichiometric quantities of the reactants were used in all cases, and the Grignard or sodium cyclopentadienide solution was added to the halide solution dropwise with brisk stirring. The mixtures were then stirred rapidly for two to three hours at 25° and the solvent was then removed.

From the residue, methyl compounds,  $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{CH}_3$  and  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$ , were isolated by vacuum sublimation to an ice-cooled probe; the ethyl compounds were also isolated directly by sublimation, and it was necessary to cool the probe with dry ice.

The phenyl and  $\sigma$ -cyclopentadienyl derivatives were isolated by chromatography; the compounds were extracted from the reaction residue with petroleum ether (30–60°) and were transferred in this

\* Note added in proof—

The compound  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Si}(\text{CH}_3)_3$  has now been prepared by the reaction of  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Na}$  with trimethylchlorosilane (T. S. PIPER, D. LEMAL, and G. WILKINSON *Naturwiss.* 43, 129, 1956). See now: E. O. FISCHER, S. HAFNER, and H. O. STAHL *Z. anorg. Chem.* 282, 47 (1956).

TABLE I.—ALKYL AND ARYL DERIVATIVES OF  $\pi$ -CYCLOPENTADIENYL METAL COMPOUNDS

Compound	Preparation*	Purification†	Yield %	Colour	m.p. °C
$\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{CH}_3$	I	A	60	dark green	82.8–83.2
$\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{CH}_2\text{Cl}$	II (on chloride)	B	3	green	71
$\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{C}_2\text{H}_5$	I	A	5	green	oil
$\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{C}_6\text{H}_5$	I	BA	0.5	green	oil
$\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\sigma\text{-C}_2\text{H}_5$	Ia	BA	20	brown	66.5–67.2
$\pi\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_2\text{CH}_3$	III	A	1–3	yellow	—
$\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{CH}_3$	II	A	4	yellow	124 (d)
	III	A	85		
$\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{C}_2\text{H}_5$	III	A	78	yellow	77.5–78.5 (d)
$\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{iso-C}_3\text{H}_7$	III	A	5	yellow	29–30
$\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$	III	A	80	lemon yellow	144.7–145.3
$\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{C}_2\text{H}_5$	III	A	75	yellow	93.0–93.5 (slight d)
					78–82
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$	I	A	50	caramel	oil
	III	A	70	(waxy)	
$\pi\text{-C}_5\text{H}_5(\text{CO})_2\text{C}_2\text{H}_5$	III	A	60	caramel	oil
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\sigma\text{-C}_2\text{H}_5$	Ia	BA	15	orange	46
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_6\text{H}_5$	I	BA	5	caramel	26–30
	III	BA	2		
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CH}_3)_2$	I	A	1	orange-yellow (waxy)	decomp. ~100

\* I = Grignard reagent in ether on the bromide or iodide compounds.

Ia = Sodium cyclopentadienide in tetrahydrofuran on the bromide or iodide compounds.

II = Diazomethane reaction.

III = Alkyl or aryl iodide on the sodium salt  $\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_2\text{Na}$ .

† Isolation from the evaporated reaction mixture: A by direct sublimation in vacuum; B by extraction with petroleum ether (30–60°) and chromatographic separation on alumina using benzene-petroleum ether mixtures.

‡ Compound identified by infra-red spectrum only.

solvent to an alumina column. The products were eluted with petroleum ether-benzene mixtures. The preparation of  $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\sigma\text{-C}_2\text{H}_5$  from 2.6 g (0.1 mole) of  $\text{C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Br}$  may be taken as an example. The residue from the reaction with sodium cyclopentadienide after removal of solvent was extracted with 200 ml petroleum ether and the filtered extract passed through 30 g alumina in a small column. Using 50-ml portions, the column was washed with petroleum ether containing first 10%, then 20% of benzene. Subsequently the desired product was eluted from the column with a 2:1 mixture of petroleum ether and benzene. The progress of the separation was checked by measurement of the infra-red spectrum of the various fractions obtained.

After chromatographic separation, the products were sublimed at ~50°C at 10<sup>-3</sup> mm Hg, and collected on an ice-cooled probe. The  $\pi$ -cyclopentadienyl metal bromide compounds can be used in these preparations, and give yields comparable to those using the iodides. For the chlorides, however, the yield of the alkyl and aryl compounds is often greatly reduced and in some cases no product can be isolated. A summary of the preparations of the alkyl and aryl derivatives by the Grignard method is presented in Table 2. The reaction conditions are as stated above, except where noted. Standardized Grignard reagents were used throughout. Column 4, labelled addition, gives the yield of the alkyl or aryl derivative. Column 5, labelled reduction, gives the yield of the appropriate binuclear carbon-monoxide compound. In the case of the chromium derivatives, no evidence for the existence of a binuclear nitric-oxide derivative was obtained. Studies of reaction products other than the ones noted here have not been made at the present time.

TABLE 2.—YIELDS AND PRODUCTS IN GRIGNARD REACTIONS

Metal derivative	Grignard Reagent	Solvent	Addition	Reduction	Biphenyl	Number of Experiments
$\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Cl}$	$\text{CH}_3\text{MgI}$	$(\text{C}_2\text{H}_5)_2\text{O}$	40%	—	—	2
$\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Br}$	$\text{CH}_3\text{MgI}$	$(\text{C}_2\text{H}_5)_2\text{O}$	60	—	—	3
$\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Br}$	$\text{CH}_3\text{MgI}$	$\text{C}_6\text{H}_6\text{O}$	trace	—	—	2
$\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Br}$	$\text{CH}_3\text{MgI}^*$	$\text{C}_6\text{H}_6\text{O}$	1	—	—	1
$\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{I}$	$\text{CH}_3\text{MgI}$	$(\text{C}_2\text{H}_5)_2\text{O}$	55	—	—	1
$\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Cl}$	$\text{C}_2\text{H}_5\text{MgBr}$	$(\text{C}_2\text{H}_5)_2\text{O}$	0.2	—	—	1
$\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Br}$	$\text{C}_2\text{H}_5\text{MgBr}$	$(\text{C}_2\text{H}_5)_2\text{O}$	5	—	—	2
$\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Cl}$	$\text{C}_6\text{H}_5\text{MgBr}$	$(\text{C}_2\text{H}_5)_2\text{O}$	0.1	—	—	1
$\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Br}$	$\text{C}_6\text{H}_5\text{MgBr}$	$(\text{C}_2\text{H}_5)_2\text{O}$	0.5	—	53%	2
$\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Br}$	$\text{C}_6\text{H}_5\text{Na}$	$(\text{C}_2\text{H}_5)_2\text{O}$	20	—	—	2
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$	$\text{CH}_3\text{MgI}$	$\text{C}_6\text{H}_6\text{O}$	0	—	—	1
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$	$\text{CH}_3\text{MgI}^\dagger$	$(\text{C}_2\text{H}_5)_2\text{O}$	50	0	—	3
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$	$\text{CH}_3\text{MgI}^\ddagger$	$(\text{C}_2\text{H}_5)_2\text{O}$	46	0	—	1
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$	$\text{C}_2\text{H}_5\text{MgBr}$	$(\text{C}_2\text{H}_5)_2\text{O}$	0	17%	—	1
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$	$\text{C}_6\text{H}_5\text{MgBr}^\S$	$(\text{C}_2\text{H}_5)_2\text{O}$	4.7	60	68	1
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$	$\text{C}_6\text{H}_5\text{MgBr}$	$(\text{C}_2\text{H}_5)_2\text{O}$	3	60	70	2
$\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{I}$	$\text{CH}_3\text{MgI}$	$(\text{C}_2\text{H}_5)_2\text{O}$	0	—	—	2
$\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{I}$	$\text{CH}_3\text{MgI}^\S$	$(\text{C}_2\text{H}_5)_2\text{O}$	0	—	—	1
$\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{I}$	$\text{C}_6\text{H}_5\text{MgI}$	$(\text{C}_2\text{H}_5)_2\text{O}$	0	59	72	2
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$	$\text{C}_6\text{H}_5\text{Na}$	$(\text{C}_2\text{H}_5)_2\text{O}$	15	15	—	2
$\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{I}$	$\text{C}_6\text{H}_5\text{Na}$	$(\text{C}_2\text{H}_5)_2\text{O}$	0	—	—	1

\* Allowed to stand 15 hours, using a 50% excess of  $\text{CH}_3\text{MgI}$ .

† 27% of the starting material  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$  was recovered.

‡ 7 mole % anhydrous cobaltous chloride was added to the reaction mixture.

§ 5 mole % magnesium iodide added.

## 2.2. Di( $\pi$ -cyclopentadienyl)-dimethyl-titanium, $(\pi\text{-C}_5\text{H}_5)_2(\text{CH}_3)_2\text{Ti}$

Various aryl compounds, e.g.  $(\text{C}_6\text{H}_5)_2\text{Ti}(\pi\text{-C}_5\text{H}_5)_2$ , have been prepared<sup>(10)</sup> by the reaction of lithium aryls with di( $\pi$ -cyclopentadienyl) titanium halides. In view of the stability of the methyl compounds described in this paper, we attempted the preparation of a methyl titanium derivative by the Grignard method.

To di( $\pi$ -cyclopentadienyl) titanium dichloride<sup>(11)</sup> (2 g) in tetrahydrofuran (150 ml) the stoichiometric quantity methyl magnesium iodide was added slowly with stirring at 25°C. The solution darkened initially, but then became orange-yellow. After stirring for two hours, a few millilitres of methanol were added, the solvent was rapidly removed in vacuum, and the residue extracted with petroleum ether. The product was obtained by cooling the filtered petroleum solution to -80°C; it was then purified by sublimation at 40°C at 10<sup>-4</sup> mm Hg. The yield was 30 mg, about 1%; other products of the reaction have not been studied. The compound is an orange-yellow waxy solid, decomposing spontaneously above 100°C. During the sublimation in several preparations, the residue and the sublimate spontaneously decomposed to a black solid. This decomposition is apparently autocatalytic. Careful and rapid separation is therefore necessary.

## 2.3. $\pi$ -Cyclopentadienyl-tricarbon monoxide-methyl-molybdenum, $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{CH}_3$ by the Diazomethane Procedure (Method II)

7.0 g of the hydride,  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{H}$ , in 200 ml ether, were treated with about a twofold excess of diazomethane in ether at 0°C for 24 hours. The diazomethane was prepared from N-methyl-N-nitrosourea by the usual procedure. The solvent was removed and the crude product sublimed from

(10) L. SUMMERS, R. H. ULOTH, and A. HOLMES *J. Amer. Chem. Soc.* **77**, 3604 (1955).

(11) G. WILKINSON and J. M. BIRMINGHAM *J. Amer. Chem. Soc.* **76**, 4281 (1954).

the residue in vacuum. It was separated from a red oily material (unidentified) which also sublimed by chromatography on alumina, using benzene-petroleum mixtures. The yield of  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{CH}_3$  was only 0.22 g (3% based on the hydride), and this preparative method was abandoned in favour of the Method III.

## 2.4. $\pi$ -Cyclopentadienyl-dinitric oxide-chloromethyl-chromium

To 0.21 g  $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Cl}$  in 200 ml ether containing 3 millimoles diazomethane at 25°C was added 5–10 g copper powder. The mixture was stirred vigorously for 15 hours. The solvent was removed and the product was extracted with petroleum ether; it was then purified by chromatography on alumina. Yield ~5 mg (~3% based on the chloride). Due to small and erratic yields and the difficulties in purification on account of the moderately rapid decomposition of the compound by air, characterization of this compound was based on its infra-red spectrum, taken in  $\text{CS}_2$  and  $\text{CCl}_4$  solution, which shows two C-H stretching frequencies of the methylene group and a C-Cl stretching frequency at 670  $\text{cm}^{-1}$  (vs) in addition to bands characteristic for the ring.

## 2.5. Alkyl and Aryl Compounds from the Reaction of Alkyl Halides with Sodium Salts (Method III)

To the tetrahydrofuran solution of  $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{CO})_3\text{Na}$ ,  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Na}$ ,  $\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{Na}$ , or  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Na}$  (Preps. 6 and 7), was added the alkyl or aryl iodide in an excess sufficient to react with the total amount of sodium used in the preparations. A rapid reaction occurred with the alkyl iodides, but the mixtures were stirred for a few hours at ~40°C to ensure complete reaction. The reaction of iodobenzene with  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Na}$  is much slower than with the alkyl iodides, and is incomplete; here, the mixtures were stirred at 25°C for about 4 days. There appears to be no reaction of iodobenzene with  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Na}$  or with  $\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{Na}$ .

After the reaction period, the solvent was removed. The alkyl compounds were recovered by direct sublimation in vacuum at ~50°C from the reaction flask to a cooling probe inserted into a neck of the flask. The phenyl iron compound was extracted from the reaction mixture with petroleum ether and was adsorbed from this solution on an alumina column; biphenyl was eluted with petroleum ether + 10% benzene, and the product subsequently eluted with petroleum ether + 30–40% benzene.

In all cases the products were purified by sublimation in vacuum at 25–50°C.

## 2.6. The Sodium Salts, $\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_3\text{Na}$ of Cr, Mo, and W

To a solution of sodium cyclopentadienide (0.12 mole) in tetrahydrofuran (200 ml) was added the solid hexacarbonyl (0.1 mole). The solution was refluxed for 12 hours and the solvent removed in vacuum. A test was made for unreacted carbonyl at this point; the stirrer was replaced by a water-cooled probe fitted by a ground joint into the neck of the flask, and the evacuated flask was warmed to ~60°C. Using  $\text{Mo}(\text{CO})_6$  and  $\text{W}(\text{CO})_6$ , the reaction is essentially complete in 12 hours and little or no carbonyl is recovered; with  $\text{Cr}(\text{CO})_6$ , one-third of the carbonyl is recovered. No attempt has been made to isolate the pure sodium salts, and the products were utilized *in situ* for further reactions.

## 2.7. The Sodium Salt $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Na}$

To 0.5 mole of sodium as 6% sodium amalgam in tetrahydrofuran (100 ml) was added a solution of  $(\pi\text{-C}_5\text{H}_5)_2\text{Fe}(\text{CO})_2$  (0.1 mole) in tetrahydrofuran (100 ml). The mixture was stirred rapidly for 12 hours, and the product, containing an excess of the amalgam, was used directly in subsequent reactions.

## 2.8. The $\pi$ -cyclopentadienyl-tricarbon monoxide-hydrides of Cr, Mo, and W

Only a statement of the method of preparation of these compounds has been previously provided.<sup>(4)\*</sup>

To the dry sodium salts prepared as above (Prep. 6) the theoretical amount (0.12 mole) of glacial acetic acid in tetrahydrofuran (150 ml) was added. The mixture was stirred briefly and the solvent removed in vacuum. The product was then sublimed to a probe cooled to 0°C in vacuum. The

\* Note added in proof—

See now: E. O. FISCHER, W. HAFNER, and H. O. STAHL *Z. anorg. Chem.* **282**, 47 (1956).

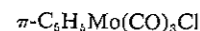
chromium hydride sublimates at  $10^{-3}$  mm Hg at room temperature, while the tungsten and molybdenum compounds require warming to  $50^{\circ}\text{C}$ .

The yields of  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{H}$  and  $\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{H}$  were about 90% for the overall preparation from the hexacarbonyls.

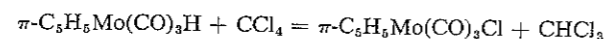
### 2.9. $\pi$ -Cyclopentadienyl-dinitric oxide-chromium Halides

The following preparation of  $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Cl}$  (or Br) is superior to that given previously.<sup>(12)</sup> By the reaction of sodium cyclopentadienide with anhydrous chromic chloride, 50 g of  $(\pi\text{-C}_5\text{H}_5)_2\text{Cr}$ <sup>(12)</sup> was prepared. The crude product was dissolved in ether (700 ml) and a stream of hydrogen halide passed through the solution, with stirring, until the solution, which contains a blue-green suspension of the binuclear  $\pi$ -cyclopentadienyl chromium bridging halide,<sup>(13)</sup> was green in colour. A large excess of nitric oxide was then bubbled through the mixture, which was stirred vigorously at  $25^{\circ}\text{C}$ . The solvent was then removed and the product crystallized from dichloromethane. For the bromide, 52 g of  $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Br}$  was isolated (yield 65% based on  $\text{CrCl}_3$ ); the compound forms very dark-brown crystals, m.p.  $140\text{--}141^{\circ}\text{C}$ . The iodide was prepared by treating the bromide with the theoretical quantity of aqueous silver nitrate. An excess of concentrated hydriodic acid was added and the iodide was extracted from the aqueous suspension by chloroform. Crystallization from dichloromethane gave a high yield of  $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{I}$ , m.p.  $149\text{--}151^{\circ}\text{C}$ .

### 2.10. $\pi$ -Cyclopentadienyl-tricarbon monoxide-molybdenum Halides,



The hydride was dissolved in an excess of carbon tetrachloride. The reaction



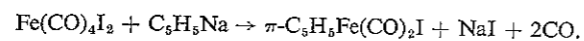
was complete in  $\sim 20$  min at  $25^{\circ}\text{C}$ . The chloride was precipitated quantitatively. It was isolated by filtering the carbon tetrachloride solution as orange-red crystals which decompose at  $145^{\circ}\text{C}$  without melting. (Analysis—Required: C 34.25, H 1.8, Cl 12.64, Mo 34.2; found: C 34.8, H 2.0, Cl 12.77, Mo 34.1.) The formation of chloroform in the above reaction was shown by infra-red analysis. The compound  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Cl}$  is insoluble in water and is decomposed by silver-nitrate solution. Unlike the case of the iron halides, e.g.  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Cl}$ ,<sup>(12)</sup> there is thus no evidence for the formation of cationic species in aqueous solution. The compound is only slightly soluble in petroleum, but is soluble in polar organic solvents without decomposition.

$\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{Br}$ . This compound was prepared by the reaction of  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{H}$  with *N*-bromosuccinimide in ether solution. The product was crystallized from dichloromethane as red crystals, m.p.,  $150\text{--}151^{\circ}\text{C}$ . There is no reaction between  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{H}$  and ethyl bromide even on refluxing the mixture for several days.

$\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{I}$ . The hydride was refluxed with an excess of methyl iodide in benzene for 24 hours. Crystallization of the solid residue from dichloromethane-petroleum ether mixtures by cooling gave a quantitative yield of  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{I}$  as red crystals, m.p.  $134\text{--}134.5^{\circ}\text{C}$ . (Analysis—Required: C 25.8, H 1.35, I 34.1, Mo 25.8; found: C 25.74, H 1.5, I 34.5, Mo 25.7. Molecular weight by the isopiestic method in dichloromethane: found 375, required 372.) This iodide can also be obtained in  $\sim 60\%$  yield by refluxing the mercury salt  $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2\text{Hg}$ <sup>(14)</sup> with iodine in benzene for a few hours.

### 2.11. $\pi$ -Cyclopentadienyl-dicarbon monoxide-iodo-iron.

This compound was originally prepared<sup>(12)</sup> by treating  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_4\text{Fe}\pi\text{-C}_5\text{H}_5$  with iodine. We have attempted to prepare it by the simpler route



The iron carbonyl iodide was prepared by the addition of iodine to a slight excess of  $\text{Fe}(\text{CO})_5$  in ether, and the mixture stirred for 2 hours. One equivalent of sodium cyclopentadienide in tetrahydrofuran was then added, and the mixture stirred for 2 hours. The solvent was removed, and the residue

<sup>(12)</sup> G. WILKINSON, F. A. COTTON, and J. M. BIRMINGHAM *J. Inorg. Nucl. Chem.* **2**, 95 (1956).

<sup>(13)</sup> A. K. FISCHER and G. WILKINSON unpublished work.

extracted with 30% benzene in petroleum ether. The product was adsorbed from this solution on an alumina column, and was eluted by a 1 : 1 benzene-petroleum ether mixture. Yield  $\sim 10\%$ .

### 2.12. $\pi$ -Cyclopentadienyl-dicarbon monoxide-nitric oxide-molybdenum

2.5 g of  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{H}$  in 100 ml ether was treated with an excess of *N*-methyl-*N* nitroso-*p*-toluene sulphonamide in ether. The solvent was removed and the product sublimed in vacuum at  $50^{\circ}\text{C}$  to an ice-cooled probe. Yield 1.4 g (55%). The compound forms stable orange crystals, m.p.  $85\text{--}85.7^{\circ}\text{C}$ . It is readily soluble in organic solvents without decomposition. (Analysis—Required for  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{NO}$ : C 34.0, H 2.0, N 5.67, Mo 38.85; found: C 34.2, H 2.2, N 5.67, Mo 38.66.)

The compound can also be made by the direct action of nitric oxide on  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{H}$ , in an organic solvent.

#### B. Properties

### 2.14. General Properties of the Alkyl and Aryl Compounds

Analytical data are presented in Table 3. Whilst only  $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{CH}_3$  has been shown to be diamagnetic by direct measurement by the Gouy method, the fact that high-resolution nuclear magnetic-resonance spectra of the compounds can be obtained (*vide infra*) shows that all these compounds are diamagnetic.

All the compounds are readily soluble in petroleum ether ( $30\text{--}60^{\circ}$ ) and indeed in all common organic solvents; they sublime easily in high vacuum at temperatures from  $25\text{--}50^{\circ}\text{C}$  and they have a noticeable camphoraceous odour. In organic solvents, all the compounds are slowly decomposed by air, some more rapidly than others, but the solutions can be preserved in vacuum or in an inert atmosphere.

TABLE 3.—ANALYTICAL DATA\*

Compound	Required				Found			
	C	H	N	Metal	C	H	N	Metal
$\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{CH}_3$ †	37.5	4.2	14.6	27.1	37.4	4.3	14.5	27.0
$\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{C}_6\text{H}_5$	49.6	4.2	11.6	21.5	49.7	4.4	11.7	21.3
$\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{CH}_3$	41.6	3.4		36.9	41.1	3.2		37.1
$\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{C}_2\text{H}_5$	43.8	3.7		35.0	43.8	3.76		35.4
$\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{iso-C}_3\text{H}_7$	45.8	4.2			45.8	4.3		
$\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{CH}_3$	31.1	2.3		52.85	31.1	2.5		52.85
$\pi\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{C}_2\text{H}_5$	33.2	2.8		50.5	33.3	2.8		50.8
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$	50.0	4.2		29.1	49.0	4.2		29.2
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_2\text{H}_5$				27.1				26.8
$\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_6\text{H}_5$	61.4	4.0		22.0	62.4	4.2		21.8
$(\pi\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CH}_3)_2$	69.3	7.8			68.2	7.8		

\* Microanalyses by S. NAGY, Massachusetts Institute of Technology and Schwartzkopf Laboratories, Woodside, New York.

† Molecular weight by isopiestic method in dichloromethane; found 188, required 192.

The iron compounds have the lowest stability, both thermally and towards air. The compound  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_3$ , as the solid shows decomposition in air within a few hours; the ethyl compound begins to decompose within 15 min, whilst the phenyl is somewhat more resistant to air than is the methyl compound.

The chromium-nitric oxide derivatives show the same order of stabilities as the iron carbon monoxide derivatives, viz. phenyl > methyl > ethyl, but are more stable; the methyl compound, for example, begins to decompose in air only after a day or two.

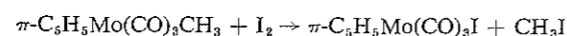
The compounds  $\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})_3\text{R}$  of the Group VI elements show great differences in stability,

both thermally and towards air. The chromium compound,  $\pi$ -C<sub>5</sub>H<sub>5</sub>Cr(CO)<sub>3</sub>CH<sub>3</sub>, is rather unstable and is quite readily oxidized by air, and is indeed very difficult, if not impossible, to obtain in a pure state. The molybdenum methyl compound begins to decompose in air after a few days and upon heating in vacuum at 110°C. The tungsten analogue, however, appears to be stable indefinitely in air and melts at 145°C without decomposition; its solutions in organic solvents are quite stable for at least several days.

The ethyl compounds are generally noticeably less stable than the methyl compounds, and the molybdenum isopropyl compound is less stable than the ethyl.

Thermal decomposition of  $\pi$ -C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>3</sub>CH<sub>3</sub> and  $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>CH<sub>3</sub> at 110°C has been found to produce the binuclear carbon-monoxide compounds in addition to tarry material.

All the compounds are insoluble in and are unaffected by water, with the exception of  $\pi$ -C<sub>5</sub>H<sub>5</sub>Cr(NO)<sub>2</sub>CH<sub>3</sub>, which is slightly soluble in water, giving a faint-yellow solution. Acids and bases attack both the alkyls and aryls. With acids, both the  $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>R and  $\pi$ -C<sub>5</sub>H<sub>5</sub>Cr(NO)<sub>2</sub>R groups of compounds give the cations [ $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>]<sup>+</sup> and [ $\pi$ -C<sub>5</sub>H<sub>5</sub>Cr(NO)<sub>2</sub>]<sup>+</sup>; these cations (which may well have one firmly co-ordinated water molecule) give precipitates with silicotungstic acid and REINECKE'S salt, similar to those given by ions such as [( $\pi$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe]<sup>+</sup>. The molybdenum and tungsten compounds slowly decompose with acids and bases, and there is no evidence for the formation of cations. All the alkyl and aryl compounds are attacked by halogens; with iodine, for example, the iodide and the alkyl or aryl halide is formed quantitatively—thus



None of these compounds react with ferrous chloride in tetrahydrofuran. With the exception of  $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>σ-C<sub>5</sub>H<sub>5</sub> and  $\pi$ -C<sub>5</sub>H<sub>5</sub>Cr(NO)<sub>2</sub>σ-C<sub>5</sub>H<sub>5</sub>, none react with maleic anhydride in benzene solution; for these two compounds, the addition of maleic anhydride causes a rapid change in colour and the compounds cannot be subsequently recovered; the maleic anhydride adducts were not sufficiently stable to allow isolation and characterization.

### 2.15. Some Properties of the $\pi$ -Cyclopentadienyl-tricarbon monoxide Hydrides of Cr, Mo, and W

These three compounds form yellow crystals; the increase in stability with increasing atomic number is noteworthy. The chromium compound,<sup>(14)</sup>  $\pi$ -C<sub>5</sub>H<sub>5</sub>Cr(CO)<sub>3</sub>H is instantaneously oxidized by air both as the solid or in solution and also decomposes at its melting-point 57–58°C. Solutions of  $\pi$ -C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>3</sub>H are also instantaneously decomposed by air, but the crystals require several minutes for complete decomposition; the compound melts at 54–55°C, and thermal decomposition in vacuum begins at about 110°C. The stability of  $\pi$ -C<sub>5</sub>H<sub>5</sub>W(CO)<sub>3</sub>H (m.p. 68.5–69.5°C) is considerable; complete oxidation of the solid in air requires several days, and decomposition of the solutions by air is noticeable only after 15 min or so. The solid is stable in vacuum up to 180°C. In all three cases, thermal decomposition gives the binuclear compounds  $\pi$ -C<sub>5</sub>H<sub>5</sub>M(CO)<sub>6</sub>Mπ-C<sub>5</sub>H<sub>5</sub>.

It is interesting to note that in nonpolar solvents such as petroleum ether, the compounds  $\pi$ -C<sub>5</sub>H<sub>5</sub>M(CO)<sub>3</sub>H are decomposed to a black mass by air. In polar solvents, however, particularly in tetrahydrofuran, smooth oxidation to  $\pi$ -C<sub>5</sub>H<sub>5</sub>M(CO)<sub>6</sub>Mπ-C<sub>5</sub>H<sub>5</sub> occurs; studies on the mechanism of these oxidations are in progress. In this way, we prepared the molybdenum compound<sup>(15)</sup> in 70% yield; this compound has properties essentially identical with those reported for the compound C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>5</sub>MoC<sub>5</sub>H<sub>5</sub>.<sup>(14)</sup> As noted earlier,<sup>(7)</sup> it must be presumed that the only binuclear molybdenum compound is  $\pi$ -C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>6</sub>Moπ-C<sub>5</sub>H<sub>5</sub>. The reason for the different stoichiometry found previously is not clear, and it may be noted that the infra-red spectrum of the original sample in the solid state showed a definite splitting in the C-O stretching region which was not found in C<sub>5</sub>H<sub>5</sub>W(CO)<sub>5</sub>WC<sub>5</sub>H<sub>5</sub>.<sup>(15)</sup> The present failure to repeat the original work and the formation of only  $\pi$ -C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>6</sub>Moπ-C<sub>5</sub>H<sub>5</sub> by the high-temperature reaction of cyclopentadiene with molybdenum carbonyl with properties and infra-red spectrum identical to those of the product formed by air oxidation of  $\pi$ -C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>3</sub>H, strongly suggests that the original stoichiometry was incorrect.

The infra-red spectrum of  $\pi$ -C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>6</sub>Moπ-C<sub>5</sub>H<sub>5</sub> is almost identical with that of its tungsten analogue both in solution and in the solid state; in the C-O stretching region it has strong bands at 1960 and 1916 cm<sup>-1</sup> in solution and at 1951, 1920, and 1892 cm<sup>-1</sup> in the solid state.

<sup>(14)</sup> G. WILKINSON *J. Amer. Chem. Soc.* 76, 209 (1954).

<sup>(15)</sup> F. A. COTTON, A. D. LIEHR, and G. WILKINSON *J. Inorg. Nucl. Chem.* 1, 175 (1955).

TABLE 4.—INFRA-RED SPECTRA\*

Compound	Column	Compound	Column
$\pi$ -C <sub>5</sub> H <sub>5</sub> Cr(NO) <sub>2</sub> CH <sub>3</sub>	1	$\pi$ -C <sub>5</sub> H <sub>5</sub> Mo(CO) <sub>3</sub> C <sub>2</sub> H <sub>5</sub>	12
$\pi$ -C <sub>5</sub> H <sub>5</sub> Cr(NO) <sub>2</sub> C <sub>3</sub> H <sub>7</sub>	2	$\pi$ -C <sub>5</sub> H <sub>5</sub> Mo(CO) <sub>3</sub> iso-C <sub>3</sub> H <sub>7</sub>	13
$\pi$ -C <sub>5</sub> H <sub>5</sub> Cr(NO) <sub>2</sub> CH <sub>2</sub> Cl	3	$\pi$ -C <sub>5</sub> H <sub>5</sub> W(CO) <sub>3</sub> CH <sub>3</sub>	14
$\pi$ -C <sub>5</sub> H <sub>5</sub> Cr(NO) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	4	$\pi$ -C <sub>5</sub> H <sub>5</sub> W(CO) <sub>3</sub> C <sub>2</sub> H <sub>5</sub>	15
$\pi$ -C <sub>5</sub> H <sub>5</sub> Cr(NO) <sub>2</sub> σ-C <sub>5</sub> H <sub>5</sub>	5	( $\pi$ -C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Ti(CH <sub>3</sub> ) <sub>2</sub>	16
$\pi$ -C <sub>5</sub> H <sub>5</sub> Cr(CO) <sub>3</sub> CH <sub>3</sub>	6	$\pi$ -C <sub>5</sub> H <sub>5</sub> Mo(CO) <sub>3</sub> H	17
$\pi$ -C <sub>5</sub> H <sub>5</sub> Fe(CO) <sub>2</sub> CH <sub>3</sub>	7	$\pi$ -C <sub>5</sub> H <sub>5</sub> W(CO) <sub>3</sub> H	18
$\pi$ -C <sub>5</sub> H <sub>5</sub> Fe(CO) <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	8	$\pi$ -C <sub>5</sub> H <sub>5</sub> Mo(CO) <sub>2</sub> NO	19
$\pi$ -C <sub>5</sub> H <sub>5</sub> Fe(CO) <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	9	$\pi$ -C <sub>5</sub> H <sub>5</sub> Mo(CO) <sub>3</sub> Cl	20
$\pi$ -C <sub>5</sub> H <sub>5</sub> Fe(CO) <sub>2</sub> σ-C <sub>5</sub> H <sub>5</sub>	10	$\pi$ -C <sub>5</sub> H <sub>5</sub> Mo(CO) <sub>3</sub> Br	21
$\pi$ -C <sub>5</sub> H <sub>5</sub> Mo(CO) <sub>3</sub> CH <sub>3</sub>	11	$\pi$ -C <sub>5</sub> H <sub>5</sub> Mo(CO) <sub>3</sub> I	22

\* The spectra were measured in solution in CCl<sub>4</sub>, 4000–1350 cm<sup>-1</sup>, and in CS<sub>2</sub>, 1350–450 cm<sup>-1</sup>, except for the compounds 6, 16, 17, 18, and 19, which were measured in CS<sub>2</sub> solution only.

TABLE 4 (continued)

	1	2	3	4	5	6	7
C-O, N-O overtone	3530 w 3410 m 3330 w	3530 w 3410 m 3330 w	3550 w 3430 m 3330 w	3530 w 3430 m 3330 w	3530 vw 3410 w 3330 vw		3900 w
C-H stretch	3105 w 2958 m 2889 m	3105 w 2920 ms 2840 m	3100 w 2960 sh 2910 m 2270 w	3100 w 3030 m	3080 m 2952 w	3085 w 2950 m 2870 m	3105 w 2960 m 2900 m 2810 w
C-O, N-O stretch	1779 vs 1670 vs	1777 vs 1673 vs	1797 vs 1704 vs	1820 sh 1790 vs 1718 sh 1685 vs	1787 vs 1685 vs	2010 vs 1930 vs	2120 w 2010 vs 1955 vs 1920 w
				1560 m 1485 w 1470 ms 1450 w 1425 ms	1610 w 1445 m 1430 m 1375 m 1360 w		1840 w 1760 w 1680 w 1520 w 1430 m 1420 m 1360 w
	1430 m 1360 w	1450 m 1430 m 1370 m	1430 sh 1425 m 1360 w 1300 w 1115 vs	1150 w	1085 w 1080 m 1060 w 1020 ms 1005 m 965 m 930 w 920 sh 885 m 840 s	1160 m 1010 m	1170 s 1110 m 1060 w 1015 m 1000 m
	1130 ms 1060 w 1015 m 1010 m	1125 ms 1013 sh 1006 m	1085 w 1060 w 1015 m 1005 m	1055 m 1065 w 1010 ms	995 m 920 sh 885 m 840 s 825 vs 805 w 740 vs 735 sh 707 w	848 sh 832 s 650 s	840 sh 825 vs 790 m 760 vw 634 s 592 s 570 s 560 s 466 w
	915 w 820 vs 744 w 730 sh 646 m 604 vs 579 m 534 w	815 vs	825 vs 760 w 700 w 670 vs	820 vs 772 m 726 vs 695 s 688 m			



TABLE 5.—NUCLEAR MAGNETIC RESONANCE SPECTRA

Compound	Chemical shift in p.p.m. vs. C <sub>6</sub> H <sub>6</sub> protons in toluene					
	σ-C <sub>5</sub> H <sub>5</sub>	π-C <sub>5</sub> H <sub>5</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	H	Misc.
(π-C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Fe	—	3.1	—	—	—	—
(π-C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Ru	—	2.7	—	—	—	—
(π-C <sub>5</sub> H <sub>4</sub> CH <sub>3</sub> ) <sub>2</sub> Fe <sup>(a)</sup>	—	3.2	5.4	—	—	—
π-C <sub>5</sub> H <sub>5</sub> Mn(CO) <sub>3</sub>	—	3.1	—	—	—	—
π-C <sub>5</sub> H <sub>5</sub> NiNO	—	2.2	—	—	—	—
π-C <sub>5</sub> H <sub>5</sub> Cr(NO) <sub>2</sub> CH <sub>3</sub>	—	2.6	6.9	—	—	—
π-C <sub>5</sub> H <sub>5</sub> Mo(CO) <sub>3</sub> CH <sub>3</sub>	—	2.6	6.9	—	—	—
π-C <sub>5</sub> H <sub>5</sub> Mo(CO) <sub>3</sub> C <sub>2</sub> H <sub>5</sub>	—	2.5	—	6.0 <sup>(b)</sup>	—	—
π-C <sub>5</sub> H <sub>5</sub> Mo(CO) <sub>3</sub> iso-C <sub>2</sub> H <sub>7</sub>	—	2.5	5.5	—	—	—
π-C <sub>5</sub> H <sub>5</sub> W(CO) <sub>3</sub> CH <sub>3</sub>	—	—	6.0 <sup>(c)</sup>	—	—	—
π-C <sub>5</sub> H <sub>5</sub> W(CO) <sub>3</sub> C <sub>2</sub> H <sub>5</sub>	—	2.5	—	5.8 <sup>(b)</sup>	—	—
π-C <sub>5</sub> H <sub>5</sub> Fe(CO) <sub>2</sub> CH <sub>3</sub>	—	3.0	7.2	—	—	—
(π-C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Ti(CH <sub>3</sub> ) <sub>2</sub>	—	1.5	7.6	—	—	—
π-C <sub>5</sub> H <sub>5</sub> Fe(CO) <sub>2</sub> σ-C <sub>5</sub> H <sub>5</sub> <sup>(d)</sup>	0.6	2.1	—	—	—	—
π-C <sub>5</sub> H <sub>5</sub> Cr(NO) <sub>2</sub> σ-C <sub>5</sub> H <sub>5</sub> <sup>(d)</sup>	0.5	1.8	—	—	—	—
σ-C <sub>5</sub> H <sub>5</sub> CuP(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	1.0	—	—	6.6 <sup>(b)</sup>	—	—
P(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	—	—	—	6.4 <sup>(b)</sup>	—	—
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Mg <sup>(e)</sup>	—	—	—	—	—	0.3
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Mg <sup>(f)</sup>	—	—	—	—	—	1.3
(σ-C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> Hg	1.5 <sup>(g)</sup>	—	—	—	—	—
(CH <sub>3</sub> ) <sub>6</sub> Si <sub>2</sub> O	—	—	7.4	—	—	—
C <sub>5</sub> H <sub>0</sub>	—	—	—	—	—	0.8 <sup>(h)</sup> 4.2 <sup>(i)</sup>
π-C <sub>5</sub> H <sub>5</sub> Cr(CO) <sub>3</sub> H	—	3.1	—	—	13.1	—
π-C <sub>5</sub> H <sub>5</sub> Mo(CO) <sub>3</sub> H	—	2.5	—	—	12.8	—
π-C <sub>5</sub> H <sub>5</sub> W(CO) <sub>3</sub> H	—	2.4	—	—	14.7	—
(π-C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub> ReH	—	3.1	—	—	20.5	—
(C <sub>5</sub> H <sub>5</sub> ) <sub>3</sub> SiH <sup>(j)</sup>	—	—	—	6.2 <sup>(b)</sup>	3.2	—
H <sub>2</sub> Fe(CO) <sub>4</sub> <sup>(k)</sup>	—	—	—	—	17.4	—
HCo(CO) <sub>4</sub> <sup>(l)</sup>	—	—	—	—	17.3±2	—

<sup>(a)</sup> L. T. REYNOLDS and G. WILKINSON, unpublished work.<sup>(b)</sup> Methylene and methyl group resonances not resolved.<sup>(c)</sup> Methyl peak split by methylene hydrogen; methylene peak was not resolved.<sup>(d)</sup> In CS<sub>2</sub> solutions (by sample replacement): area ratio 4.9(σ): 5.0(π).<sup>(e)</sup> Probably ionic (cf. reference 12).<sup>(f)</sup> In tetrahydrofuran solution.<sup>(g)</sup> Broad shoulder at about 1.8 p.p.m.<sup>(h)</sup> Olefinic protons.<sup>(i)</sup> Methylenic protons.<sup>(j)</sup> A. LOUIS ALLRED, private communication.<sup>(k)</sup> G. WILKINSON and F. A. COTTON, unpublished work; no solvent used.<sup>(l)</sup> Calculated from data of H. S. GUTOWSKY.<sup>(18)</sup><sup>(18)</sup> H. S. GUTOWSKY, quoted by R. A. FRIEDEL, I. WENDER, S. L. SHUPLER, and HEINZ W. STERNBERG, *J. Amer. Chem. Soc.* 77, 3951 (1955).

TABLE 6.—ULTRA-VIOLET ABSORPTION SPECTRA

Compound	λ (Å)	ε <sub>max</sub>
π-C <sub>5</sub> H <sub>5</sub> Mn(CO) <sub>3</sub>	3,320	1,010
π-C <sub>5</sub> H <sub>5</sub> Cr(NO) <sub>2</sub> CH <sub>3</sub>	4,600	1,520
π-C <sub>5</sub> H <sub>5</sub> Cr(NO) <sub>2</sub> σ-C <sub>5</sub> H <sub>5</sub>	3,000	2,750
π-C <sub>5</sub> H <sub>5</sub> Cr(NO) <sub>2</sub> σ-C <sub>5</sub> H <sub>5</sub>	4,500	1,360 (shoulder)
π-C <sub>5</sub> H <sub>5</sub> Mo(CO) <sub>3</sub> CH <sub>3</sub>	3,040	11,300
π-C <sub>5</sub> H <sub>5</sub> Mo(CO) <sub>3</sub> C <sub>2</sub> H <sub>5</sub>	3,150	1,960
π-C <sub>5</sub> H <sub>5</sub> Mo(CO) <sub>3</sub> C <sub>2</sub> H <sub>5</sub>	3,130	2,120
π-C <sub>5</sub> H <sub>5</sub> W(CO) <sub>3</sub> CH <sub>3</sub>	3,130	2,430
π-C <sub>5</sub> H <sub>5</sub> W(CO) <sub>3</sub> C <sub>2</sub> H <sub>5</sub>	3,130	2,390
π-C <sub>5</sub> H <sub>5</sub> Fe(CO) <sub>2</sub> CH <sub>3</sub>	3,530	730
π-C <sub>5</sub> H <sub>5</sub> Fe(CO) <sub>2</sub> σ-C <sub>5</sub> H <sub>5</sub>	3,180	8,040
(C <sub>5</sub> H <sub>5</sub> ) <sub>3</sub> Mn <sub>2</sub> (NO) <sub>3</sub>	2,930	24,000

## 2.18. Infra-red Spectra

Infra-red spectra were measured on a Perkin-Elmer double-beam recording spectrophotometer, Model 21, using sodium-chloride optics. In the potassium-bromide region, a Perkin-Elmer single-beam spectrometer, Model 12c, was used.

Most of the compounds were studied in carbon-tetrachloride solution from 4000 cm<sup>-1</sup> to 1350 cm<sup>-1</sup> and in carbon disulphide from 1350 cm<sup>-1</sup> to 450 cm<sup>-1</sup>. The data are presented in Table 4. In addition, the spectrum of the vapour of C<sub>5</sub>H<sub>5</sub>Mo(CO)<sub>3</sub>CH<sub>3</sub> was obtained at about 100°C: in this case, the bands in the C-O stretching region occurred at 2030 cm<sup>-1</sup> (s), 1957 cm<sup>-1</sup> (vs), and 1920 cm<sup>-1</sup> (w). The methyl group is identified by its two C-H stretching frequencies at ~2960 cm<sup>-1</sup> and 2890 cm<sup>-1</sup>, and by symmetrical metal-methyl deformation frequency at ~1150 cm<sup>-1</sup>. The ethyl group is identified by its C-CH<sub>2</sub> asymmetric deformation at ~1450 cm<sup>-1</sup> and by its C-CH<sub>3</sub> symmetric deformation at ~1370 cm<sup>-1</sup>. For phenyl compounds, C-C stretching frequencies are found at ~1570 cm<sup>-1</sup> and ~1470 cm<sup>-1</sup> (the C-C stretching frequency for the π-cyclopentadienyl ring lies in the region 1430–1420 cm<sup>-1</sup>); the C-H out-of-plane bending vibrations characteristic of monosubstituted benzenes are found at 728 and 695 cm<sup>-1</sup>.

## 3. DISCUSSION

## 3.1. The Structure of the Alkyl and Aryl Derivatives

In all the compounds π-C<sub>5</sub>H<sub>5</sub>M(CO)<sub>x</sub>(NO)<sub>y</sub>R, the cyclopentadienyl ring is unquestionably bound to the metal atom by a bond similar to that in ferrocene and other bis(π-cyclopentadienyl) metal compounds.<sup>(19, 20)</sup> For mononuclear π-cyclopentadienyl compounds this point has been previously discussed,<sup>(2)</sup> and a comparison of the infra-red absorption data in Table 4 with those given in previous papers<sup>(2)</sup> shows many common features attributable to the π-cyclopentadienyl ring-metal system. Additional proof of the π-cyclopentadienyl nature of the rings is the failure, e.g. of π-C<sub>5</sub>H<sub>5</sub>Cr(NO)<sub>2</sub>CH<sub>3</sub> or π-C<sub>5</sub>H<sub>5</sub>W(CO)<sub>3</sub>C<sub>2</sub>H<sub>5</sub>, to react with maleic anhydride in benzene solution, with water, or with ferrous chloride in tetrahydrofuran. For the compound (π-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Ti(CH<sub>3</sub>)<sub>2</sub>, the same arguments concerning the bonding of the rings hold. In the compounds such as π-C<sub>5</sub>H<sub>5</sub>Cr(NO)<sub>2</sub>σ-C<sub>5</sub>H<sub>5</sub>, there is unequivocal evidence, which is discussed in detail below, that there is only one π-cyclopentadienyl

<sup>(19)</sup> W. MOFFETT *J. Amer. Chem. Soc.* 76, 3386 (1954).<sup>(20)</sup> J. D. DUNITZ and L. E. ORGEL *J. Chem. Phys.* 23, 954 (1955).

ring bonded to the metal atom. At first sight, it might appear certain from the methods of preparation of the alkyl and aryl compounds, and from the diamagnetism of the molecules (which is to be expected since these are structurally similar to other mononuclear  $\pi$ -cyclopentadienyl metal compounds<sup>(21)</sup>), that the alkyl and aryl groups in  $\pi$ -C<sub>5</sub>H<sub>5</sub>M(CO)<sub>x</sub>(NO)<sub>y</sub>R are indeed bound directly to the transition-metal atom. It is conceivable, however, although unlikely (since feasible electronic structures would be difficult to write), that the alkyl or aryl groups could be attached to nitrogen, carbon, or oxygen atoms, e.g. as an ether grouping M—C—O—R. There is strong evidence that this is not the case. (a) In the compounds  $\pi$ -C<sub>5</sub>H<sub>5</sub>Cr(NO)<sub>2</sub>R and  $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>R, two intense N-O or C-O stretching frequencies are observed in essentially the same regions and with essentially the same separations, e.g. for the N-O bands,  $\sim 100$  cm<sup>-1</sup>, as when alkyl or aryl groups are absent; thus the bands in  $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>CH<sub>3</sub> are at 2010 and 1955 cm<sup>-1</sup>, whereas in  $\pi$ -C<sub>5</sub>H<sub>5</sub>Co(CO)<sub>2</sub> they are at 2028 and 1967 cm<sup>-1</sup> and in  $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>Cl at 2050 and 2010 cm<sup>-1</sup>. (b) Catalytic hydrogenation of  $\pi$ -C<sub>5</sub>H<sub>5</sub>Cr(NO)<sub>2</sub>CH<sub>3</sub> in ethanol solution at 25°C, using ADAMS'S catalyst, gave methane, which was identified by its infra-red spectrum. No methylamine, which would have been expected from an N-methyl compound, could be detected; an O-methyl compound would not be reduced to methane under these conditions. (c) In the  $\pi$ -C<sub>5</sub>H<sub>5</sub>M(CO)<sub>3</sub>R alkyl compounds, the existence of only two strong bands in the 1900–2000 cm<sup>-1</sup> region (*vide infra*) and the occurrence of a medium to strong band in the region 1110–1190 cm<sup>-1</sup>, might be construed as indicating two M-C-O groups and one M-C-O-R group in the molecule. Analogies to carbon compounds, where in ethers, for example, O-CH<sub>3</sub> stretches occur at 1150–1060 cm<sup>-1</sup> (s) and an O-CH<sub>3</sub> deformation in CH<sub>3</sub>COCH<sub>3</sub> at 1466 cm<sup>-1</sup>, may well be invalid, and there seem to be too few bands to fit this possibility. The medium-strong band in the 1110–1190 cm<sup>-1</sup> region occurs also in  $\pi$ -C<sub>5</sub>H<sub>5</sub>Cr(NO)<sub>2</sub>R<sub>alkyl</sub> and  $\pi$ -C<sub>5</sub>H<sub>5</sub>Fe(CO)<sub>2</sub>R<sub>alkyl</sub> e.g. in  $\pi$ -C<sub>5</sub>H<sub>5</sub>Cr(NO)<sub>2</sub>CH<sub>3</sub> at 1130 cm<sup>-1</sup>, and is hence probably attributable to metal-alkyl group interaction; it may be noted that in dimethylzinc<sup>(21)</sup> the symmetrical metal-methyl deformation frequency occurs in this region. (d) In the methyl compounds  $\pi$ -C<sub>5</sub>H<sub>5</sub>M(CO)<sub>x</sub>(NO)<sub>y</sub>CH<sub>3</sub>, the methyl-group proton resonances (Table 5) all occur at a similarly large shift relative to methyl groups in benzene derivatives or in 1,1'-dimethylferrocene, and resemble in this respect methyl groups in methyl silicon compounds (Table 5 and ref. 22); furthermore, in the ethyl compounds in no case are the methyl and methylene proton resonances resolved. The similarity of the chemical shifts in the  $\pi$ -C<sub>5</sub>H<sub>5</sub>M(CO)<sub>2</sub>R compounds, where any possibility of bonding of the alkyl group other than directly to the metal atom is clearly ruled out as above, to those in the  $\pi$ -C<sub>5</sub>H<sub>5</sub>M(CO)<sub>3</sub>R compounds indicates similar bonding for the alkyl groups in all cases.

In view of the above, we take it that in the  $\pi$ -C<sub>5</sub>H<sub>5</sub>M(CO)<sub>x</sub>(NO)<sub>2</sub>R compounds there is a metal-to-carbon  $\sigma$ -bond. Whilst it is clear that metal-to-carbon  $\sigma$ -bonds, as in simple alkyls and aryls, are unstable for most of the transitional metals (cf. ref. 1a), it now seems that the presence on the metal atom of a  $\pi$ -cyclopentadienyl ring, together with other suitable ligands, so changes the orbitals remaining for bonding purposes that stable  $\sigma$ -bonds can be formed between a transitional metal atom and an alkyl or aryl group.

<sup>(21)</sup> Cf. H. S. GUTOWSKY *J. Chem. Phys.* 17, 129 (1949).

<sup>(22)</sup> Cf. Table 5 and also *Radiofrequency Spectroscopy* 1, No. 2, Varian Associates, Palo Alto, Calif.

JAFFÉ<sup>(23)</sup> has made calculations concerning the stability of transition metal-to-carbon  $\sigma$ -bonds in simple alkyls or aryls, i.e. with no other groups present on the metal atom, based on  $sd^n$  hybrids of the metal atom; he concluded that the bonds would have low stability and that the strength should be greatest for elements of the first transitional series. Aside from considerations of bond strength in cases such as those JAFFÉ considered, the failure to isolate simple alkyls and aryls may be attributed in part to the fact that partially occupied  $d$  orbitals would be present which would be expected to lead to increased lability and reactivity. The compounds noted in the present work are all diamagnetic, and the chemical reactivity would be expected to be lower for this reason alone, quite apart from other factors.

In the previous discussion of the fact that the mononuclear  $\pi$ -cyclopentadienyl carbon-monoxide or nitric-oxide metal derivatives follow a "fourteen-electron rule",<sup>(2)</sup> it was suggested that in considering the bonding of the ligands to the metal atom it was not necessary to invoke the use of more than one  $p$  orbital, on the average, together with  $s$  and  $d$  orbitals; in the first transitional series, the  $p$  orbitals lie considerably above those of the  $s$  and  $d$  orbitals, and thus on energetic grounds alone their use in bonding would be disfavoured.

In the bonding of an alkyl group to the metal atom, there is small possibility of multiple bonding between the metal and the carbon atoms. This is in contrast to the case where carbon monoxide is bound to a metal atom, since here, where there are orbitals available on the ligand, multiple bonds to the metal are well known to occur. Thus, in order to obtain a stable metal-to-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 using only  $s$  and  $d$  hybrids, since from symmetry arguments the resulting orbitals must be gerade, i.e. the electron density will be as great in the direction pointing away from the ligand as in the direction towards it. Hence the formation of stable metal-to-carbon  $\sigma$ -bonds may be considered to require considerable  $p$  character in order to achieve the necessary directional property for good overlap with the orbitals of the carbon atom. Since the energy of the  $p$  orbitals relative to the  $d$  and  $s$  orbitals falls in going from the first to the third transitional-series elements, the participation of  $p$  orbitals in the bonding of the groups other than the  $\pi$ -cyclopentadienyl ring should become increasingly easy.

Although other factors may contribute to the chemical stabilities, the stability order does suggest that the strength of the metal-to-carbon  $\sigma$  bond increases with increasing atomic weight of the metal, as would be expected on the above view.

The structures of the molecules  $\pi$ -C<sub>5</sub>H<sub>5</sub>M(CO)<sub>x</sub>(NO)<sub>y</sub>R must be similar to those of the other mononuclear  $\pi$ -cyclopentadienyl metal compounds.<sup>(2)</sup> For three groups, as in  $\pi$ -C<sub>5</sub>H<sub>5</sub>Cr(NO)<sub>2</sub>CH<sub>3</sub>, the NO and CH<sub>3</sub> groups will be directed towards the corners of a trigonal, not necessarily regular, pyramid with the metal at its apex. For the Group VI metal compounds,  $\pi$ -C<sub>5</sub>H<sub>5</sub>M(CO)<sub>3</sub>R, the infra-red data concerning the C-O stretching frequencies suggest that there are two sets of compounds which normally would be expected to have a similar configuration, i.e. one with the CO and R groups directed to the corners of a tetragonal, not necessarily regular, pyramid. For the compounds where R = H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, and *iso*-C<sub>3</sub>H<sub>7</sub>, two strong absorptions occur in

<sup>(23)</sup> (a) H. H. JAFFÉ and G. O. DOAK *J. Chem. Phys.* 21, 19b (1953).

(b) H. H. JAFFÉ *ibid.* 22, 1462 (1954).



the C-O stretching region. It would be tempting to assume that the CO groups have local symmetry  $C_{3v}$ , with the R groups lying along the principal axis of the molecule; in the case of the hydrides this may well be so (*vide infra*). When R = Cl, Br, and I, three bands are found, one of these appearing as a shoulder in the iodide, with the splitting increasing in the order  $I < Br < Cl$ . In the vapour-phase spectrum of  $\pi$ - $C_5H_5Mo(CO)_3CH_3$ , and often in the solution spectra of the first group of compounds, a third band does occur in the C-O stretching region, but of intensity so low that it is not certain that it is a fundamental. The existence of only two strong bands in the first group may hence be due to accidental cancellation of dipole moments, or to the coincidence of two bands; the latter explanation gains support from the decreasing splitting in the halides with decreasing electro-negativity of the R group.

### 3.2. $\sigma$ -Bonded Cyclopentadienyl Derivatives

The chemical properties of cyclopentadienyltrimethylsilane<sup>(24)</sup> indicated that the cyclopentadienyl ring was bonded to the silicon atom by a localized silicon-to-carbon bond. The first evidence that similar bonds could be formed between the  $C_5H_5$  ring and a transitional metal came from a study of the compounds  $(C_5H_5)_3Mn_2(NO)_3$ <sup>(24)</sup> and  $C_5H_5CuP(C_2H_5)_3$ <sup>(25)</sup> in which the compound  $(C_5H_5)_2Hg$ <sup>(25)</sup> was prepared for comparison. It was subsequently suggested<sup>(6)</sup> that in the compounds of empirical formula,  $(C_5H_5)_2Cr(NO)_2$  and  $(C_5H_5)_2Fe(CO)_2$ , one ring was  $\sigma$ -bonded to the metal atom.

The evidence that in these various compounds, one  $C_5H_5$  ring (in the case of  $(C_5H_5)_2Hg$ , two rings) is bound to the metal atom by a localized bond is as follows. (a) All the compounds react with maleic anhydride, although the adducts have been characterized only in the cases of the silicon and mercury compounds. (b) Where the C-H stretching region could be investigated, the infra-red spectrum of the compounds showed a band at  $3080\text{ cm}^{-1}$  (m) and one or two weaker absorptions. Cyclopentadiene itself shows C-H stretching frequencies in the infra-red at  $3100\text{ cm}^{-1}$  and  $2900\text{ cm}^{-1}$ ; a  $\pi$ -cyclopentadienyl ring, on the other hand, has but one frequency in this region at  $3100\text{--}3085\text{ cm}^{-1}$  (w). It may be noted that one of the bands from a  $\sigma$ -cyclopentadienyl ring may overlap the C-H frequency due to a  $\pi$ -cyclopentadienyl ring, so that in a compound with both types of ring present, more than two C-H stretching frequencies may not be found. In addition, the spectra of these compounds showed an absorption at  $1610\text{--}1640\text{ cm}^{-1}$  (w), possibly attributable to a C=C stretching frequency, and at least one absorption at  $720\text{--}760\text{ cm}^{-1}$  (vs). These bands are not observed in the spectra of  $\pi$ -cyclopentadienyl compounds (cf. ref. 2 and Table 4), but, as previously pointed out,<sup>(25)</sup> the spectra of the  $\sigma$ -cyclopentadienyl compounds of copper, mercury, and silicon otherwise bear little resemblance to one another. The compounds  $(C_5H_5)_2Cr(NO)_2$ ,  $(C_5H_5)_2Fe(CO)_2$ , and  $(C_5H_5)_3Mn_2(NO)_3$  have in common bands at  $1445$  (m),  $1375$  (m),  $1085$  (m),  $885$  (m), and  $840$  (s)  $\text{cm}^{-1}$ , none of which are due to the  $\pi$ -cyclopentadienyl ring. (c) In the ultra-violet absorption spectra of the compounds, intense end-absorption obscures the region where a diene system might be expected to absorb ( $\epsilon = 3000$  at  $2400\text{ \AA}$ ); however, as discussed previously,<sup>(25)</sup> the mercury and copper compounds have intense absorptions which are probably due to the metal-carbon

<sup>(24)</sup> K. C. FRISCH *J. Amer. Chem. Soc.* **75**, 6050 (1953).

<sup>(25)</sup> T. S. PIPER and G. WILKINSON *J. Inorg. Nucl. Chem.* **2**, 32 (1956).

$\sigma$ -bond. (d) The high-resolution nuclear magnetic-resonance spectra of  $(C_5H_5)_2Cr(NO)_2$  and  $(C_5H_5)_2Fe(CO)_2$  show two peaks whose chemical shifts are appropriate for a  $\sigma$ -bonded and a  $\pi$ -bonded ring, respectively, and provide unequivocal evidence for the existence of two types of cyclopentadienyl rings in the compounds. For  $(C_5H_5)_2Hg$  and  $C_5H_5CuP(C_2H_5)_3$ , peaks characteristic of  $\sigma$ -cyclopentadienyl rings are also observed. These points are discussed in detail below.

### 3.3. High-resolution Nuclear Magnetic Resonance (n.m.r.) Studies

Table 5 records the n.m.r. spectra of several of the compounds prepared in this work. Some general features are apparent. All of the compounds which, from other physical and chemical evidence, are known to have a  $\pi$ -cyclopentadienyl ring bonded to the transition-metal atom, have a single proton resonance between 2.5 and 3.1 p.p.m. relative to benzene; for magnesium cyclopentadienide, the shift is very solvent-dependent, but both here and in the  $\sigma$ -cyclopentadienides the proton shift is considerably smaller than for  $\pi$ -cyclopentadienyl compounds. For all of the compounds with a metal-methyl bond, the methyl-group protons show a peak  $\sim 7$  p.p.m.; in the ethyl compounds, the methylene and methyl resonances were not resolved.

The large chemical shifts of the "hydridic" hydrogen atoms in the chromium, molybdenum, and tungsten compounds  $\pi$ - $C_5H_5M(CO)_3H$  are similar to those observed for the compound  $(\pi$ - $C_5H_5)_2ReH$ ,<sup>(17)</sup> cobalt hydrocarbonyl,<sup>(18)</sup> and iron hydrocarbonyl. For these transitional metal "hydrides," which are certainly not hydrides in the sense of furnishing hydride ions, there is no obvious connection between acidity and the chemical shift. Thus,  $(\pi$ - $C_5H_5)_2ReH$  is a weak base, reacting with acids to form the cation  $[(\pi$ - $C_5H_5)_2ReH_2]^+$ , the Group VI compounds are acids weaker than acetic acid, whilst the iron and cobalt hydrocarbonyls are well known to behave as strong acids in aqueous solution. The chemical shift of the "hydridic" protons falls in the order  $ReH > Co, FeH > Cr, Mo, or W$ . Although the shift in the Cr, Mo, and W compounds is essentially the same, indicating the similar nature of the proton shielding, there is a very pronounced increase in chemical and thermal stability with increasing atomic weight—thus the tungsten compound is stable to about  $180^\circ\text{C}$ . A similar increase in stability with atomic weight might well occur with the simple hydrocarbonyls, but those of second or third series transitional elements can hardly be said to have been characterized at the present time. In these transitional metal "hydrides," the protons are extremely well shielded from the effects of the applied field; the chemical shifts, of 12–21 p.p.m. relative to benzene, are the largest recorded for protons, and are in striking contrast to the shifts for protons in normal hydrides, e.g. 3.2 p.p.m. for  $(C_2H_5)_3SiH$ . It would appear that the shifts cannot be attributed primarily to  $s$  electrons about the hydrogen nucleus, and the proton must be buried in the electron density surrounding the metal atom. The hydrogen atom may perhaps best be regarded as bound to  $d$  orbitals, nonbonding as far as other ligands are concerned. For the hydrocarbonyls the proton may be located between the ligands at about the same distance from the metal atom as the centroid of maximum charge for the metal-carbon bond of the ligands. For the  $\pi$ -cyclopentadienyl compounds the proton could also be located between the ring and the metal atom, e.g. in  $(\pi$ - $C_5H_5)_2ReH$  in the  $d(a_{1g})$  orbital; in the compounds with one  $\pi$ -cyclopentadienyl ring, location between the CO ligands and the ring are both possible positions.

In the various compounds where the methyl group is bound to the metal atom, absorptions are found at  $\sim 7$  p.p.m. relative to benzene; these shifts for the methyl group are greater than is found for methyls attached to carbon atoms, e.g. as in toluene or 1,1'-dimethylferrocene, but comparable to those observed for methyl silicon compounds, and may be due to the lower electronegativity of the atom to which carbon is bound. The nonresolution of the methyl and methylene proton resonances in both transition metal, silicon, and phosphorous ethyl compounds may have a similar explanation. DAILEY and SHOOLERY<sup>(16)</sup> have studied the electron withdrawal power of substituent groups in ethyl derivatives. Although in these cases the substituents formed bonds with the methylene group using primarily a *p* orbital, and hence analogy to the present cases where the involvement of *d* orbitals is possible may not necessarily be close, it would appear that where the electronegativity of the atom to which the methylene group is bound has an electronegativity value below  $\sim 1.7$ , the methyl and methylene resonances might be expected to coalesce. Whilst the different electronegativities of atoms to which a group is bound may be responsible for part of the chemical shifts, i.e. these results in part from variation in ionic character of the bonds, other factors are involved. Not only are the shifts, say for the methyl-group protons, larger when the group is bound to silicon or a transitional metal than when it is bonded to carbon, but in the  $\pi$ -cyclopentadienyl compounds the ring protons are considerably more diamagnetically shielded than those in benzene in spite of the well known chemical similarity of the  $\pi$ -cyclopentadienyl rings in ferrocene to that of benzene. Such a large diamagnetic shift could arise if the external field induces within these magnetically anisotropic molecules, a local secondary magnetic field which acts against the applied field at the proton positions. Electrons in *d* orbitals or in hybrid orbitals with *d* components may be involved, and directional effects due to the applied field might occur. In an analysis of the chemical shifts in fluorine compounds, SAIKA and SLICHTER<sup>(26)</sup> have concluded that paramagnetic terms for the atom were principally responsible for the chemical shifts; here, however, these led to a paramagnetic shift. In the present compounds, paramagnetic terms of atoms other than the one whose resonances are being studied may be important and their direction may be dependent on the geometry of the molecules. It seems safe to conclude that the unusually large diamagnetic shifts observed, e.g. for protons in the  $\pi$ -cyclopentadienyl or methyl groups, are due to the association with the metal atom.

Although it is not possible to say with any certainty, the greater stability of the methyl derivatives, compared to the ethyls, may be due to some double-bond character in the metal-to-carbon bond, since in organic chemistry it has been postulated that methyl groups can release electron density.<sup>(27)</sup> This might have been expected to decrease the electron density at the methyl-group protons; the shielding for the methyls is consistently greater than for the methyl + methylene protons in the ethyls, however, although if the metal-carbon distance were shorter in the methyl derivatives, increased shielding of the protons by electron density from other ligands or the metal atom might be expected.

For a  $\sigma$ -cyclopentadienyl ring,  $M-\langle \square \rangle$ , we expected to observe two absorptions with areas in the ratio of 4 : 1 at chemical shifts of about +0.8 and +4.2 relative to

<sup>(26)</sup> A. SAIKA and C. P. SLICHTER *J. Chem. Phys.* **22**, 26 (1954).

<sup>(27)</sup> Cf. C. A. COULSON *Quarterly Reviews* **1**, 144 (1947).

benzene, characteristic of olefinic and methylenic hydrogens respectively. Cyclopentadiene itself shows such absorptions.

For the compounds noted above, for which other evidence indicates a  $\sigma$ -bonded cyclopentadienyl ring, only *one* peak could be attributed to this ring. For example, in the spectrum of  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\sigma\text{-C}_5\text{H}_5$ , only two peaks were observed, at chemical shifts of +0.6 and +2.1 relative to benzene, with the area ratios of 1 : 1. The latter peak must be attributed to a  $\pi$ -cyclopentadienyl ring. One explanation of the fact that all the protons in  $\sigma$ -rings have the same chemical shift would be the dissociation of the compounds into ions, e.g.  $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2^+$ ,  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2^+$ , and  $\text{C}_5\text{H}_5^-$ ; the failure of the compounds to react with water and ferrous chloride in tetrahydrofuran suggests that dissociation is unlikely; however, the compounds do react with acids and the possibility of a very slow reaction with water is not eliminated, since if the half time of the dissociated state is very short, reaction may occur only slowly. An alternative explanation is to postulate that the metal atom is executing a 1,2-rearrangement at a rate greater than the expected chemical shift of 200–300 cycles per second; the  $\sigma$ -cyclopentadienyl ring may thus be regarded as rotating, and in respect to n.m.r. measurements all of the protons thus become equivalent. Since mercury and some transition metals are known to form co-ordination complexes with unsaturated hydrocarbons, it is possible that the ring rotation occurs through an intramolecular complex of the metal atom with the  $\pi$ -electron system of the cyclopentadienyl ring as a transition state. Such a postulate is of course not inconsistent with infra-red and chemical evidence for a metal-carbon localized  $\sigma$ -bond, since the rotation undoubtedly would occur at a rate such that the metal atom is bound to a single carbon atom most of the time.

#### 3.4. Grignard Reactions

The products and the yields obtained in the synthesis of the metal alkyl and aryl derivatives by the Grignard method are given in Table 2. "Addition" refers to the formation of a metal-to-carbon bond and "reduction" to the formation of the known binuclear compounds,  $(\pi\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$  and  $(\pi\text{-C}_5\text{H}_5)_2\text{Mo}_2(\text{CO})_6$ . A careful search among the products formed by action of Grignard reagents on  $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Br}$  gave no evidence of a binuclear compound, although it might well be prepared by other methods. It should be noted that in each case considerable decomposition occurs with the formation of tars. The reactions leading to decomposition probably proceed similarly to the attack of Grignard reagents on the carbon-monoxide groups of metal carbonyls.<sup>(28)</sup>

From the table it may be seen that yields of addition are higher with diethyl ether than with tetrahydrofuran, with bromides and iodides than with chlorides, and with the methyl Grignard reagent than with ethyl or phenyl Grignard reagents. The yield of addition product may be explained in terms of the action of one mole of the Grignard reagent on a complex comprising one mole of the Grignard reagent with the cyclopentadienylmetal-halogen derivative, analogous to the mechanism postulated for the reaction of nitriles with Grignard reagents.<sup>(29)</sup> In agreement with this view, complex formation is decreased by a more polar solvent and by the more

<sup>(28)</sup> Cf. F. L. BENTON, M. C. NOSS, and P. A. MCCUSKER *J. Amer. Chem. Soc.* **67**, 82 (1945).

<sup>(29)</sup> C. G. SWAIN *J. Amer. Chem. Soc.* **69**, 2306 (1947).

electronegative chloride ion leading to reduced yields of addition relative to reduction and decomposition. In the addition reaction, steric hindrance of the Grignard reagent in the case of ethyl or phenyl as compared to methyl, or of the metal atom in the case of  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{I}$  as compared to  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$ , may account for the observed yields. However, yield studies alone are hardly sufficient to determine the mechanism or mechanisms involved, and complex formation is suggested only as a convenient generalization. The reaction of sodium cyclopentadienide with  $\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2\text{Br}$  and  $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{I}$  produced the respective  $\sigma$ -cyclopentadienyl derivatives in 15–20% yield, but with  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{I}$  no derivative was obtained; no evidence for a molybdenum phenyl compound was obtained either. These results are perhaps related to the greater steric hindrance at the molybdenum atom and also to electronegativity differences, since while cations  $[\pi\text{-C}_5\text{H}_5\text{Cr}(\text{NO})_2]^+$  and  $[\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]^+$  have been characterized, a cationic species  $[\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3]^+$  does not appear to exist.