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Rice University, 1987
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THE SYNTHESIS OF CATIONIC BIS(η⁶-ARENEMANGANESE SANDWICH COMPLEXES

BY

A. W. MOOREHEAD

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

MASTER OF ARTS

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April 1987
The Synthesis of Cationic Bis(η⁶-arene)manganese
Sandwich Complexes

by

A. W. Moorehead

Abstract

The use of elemental iodine as an in situ oxidant allows the metal vapor synthesis of bis(η⁶-arene)manganese cationic sandwich complexes from alkyl substituted arenes. These stable 18 electron species are isolated as hexafluorophosphate salts. ¹H NMR, ¹³C NMR, and FABMS spectra were secured for each compound.
To John Payne Bell
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Introduction

1. Properties

The bis-$\eta^6$-arene metal complexes generally exist as colored, air-sensitive, crystalline solids. These compounds may be sublimed in vacuo at $\sim$100°C and are at least partially soluble in most organic solvents. The thermal stability of these complexes is conducive to manipulations, and some of the bis-$\eta^6$-arene complexes are stable to 300°C.\textsuperscript{1,2}

Studies on the thermodynamic properties of the bis-arene metal complexes have produced data\textsuperscript{3} from which mean bond dissociation energies of the metal-ring bonds have been derived.\textsuperscript{1} From the data presented in Table I one can conclude that alkyl substituents make very little difference in the bond-strengths of bis($\eta^6$-arene)Cr complexes. Also, the bond strength of bis($\eta^6$-benzene)V is much greater than that of its chromium analogue. Green has suggested that the energy of the molecular orbitals of vanadium closely approximates the energy of those of benzene, resulting in a strong bonding interaction. Bond strengths in the bis-arene complexes seem to follow the order V $\gg$ Mo $>$ Cr.

Most bis($\eta^6$-arene) metal complexes are air-oxidized to bis-arene cations, which are more resilient to oxidative decomposition than the neutral bis-arene complexes. In weak alkaline solutions [bis($\eta^6$-benzene)$_2$Cr]$^+$ can be kept for extended periods of time. Bis($\eta^6$-benzene)chromium readily forms a charge transfer complex with tetracyanoethylene in methanol/benzene solution, and many of the bis-arene metal complexes show an ability to act as electron donors.\textsuperscript{4,5,6} The $^1$H NMR spectra of the bis-arene complexes show the expected general upfield shift of the arene protons relative to the protons of the free arene. This
partial shielding arises from removal of deshielding \( \pi \)-electron density from the ligated arene rings.\(^7\)

Table I.

Some Thermodynamic Data on Bis-\( \eta^6 \)-arene Complexes

<table>
<thead>
<tr>
<th>Metal-ring bond in the complex</th>
<th>( \ddot{D}^{(a)} ) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\eta^6-C_6H_6)_2Cr)</td>
<td>40.5 ± 8</td>
</tr>
<tr>
<td>((\eta^6\text{-cumene})_2)</td>
<td>41.0 ± 2</td>
</tr>
<tr>
<td>((\eta^6\text{-mesitylene})_2\text{Cr})</td>
<td>41.5 ± 2</td>
</tr>
<tr>
<td>((\eta^6-C_6H_6)_2\text{Mo})</td>
<td>50.7 ± 2</td>
</tr>
<tr>
<td>((\eta^5-C_5H_5)_2\text{Ni})</td>
<td>56.6 ± 10</td>
</tr>
<tr>
<td>((\eta^5-C_5H_5)_2\text{Fe})</td>
<td>69.5 ± 10</td>
</tr>
<tr>
<td>((\eta^6-C_6H_6)_2\text{V})</td>
<td>70.0 ± 2</td>
</tr>
</tbody>
</table>

\(^{(a)}\ddot{D}\) is the mean bond dissociation energy of \( MR_n \); \( \ddot{D}(\text{M-R}) = \Delta H^*/n. \) The heat of the dissociation process, \( MR_n(g) \rightarrow M(g) + nR(g) \) in which all metal-carbon bonds are broken, is given by \( \Delta H^\circ \). The units of \( \Delta H^\circ \) are kcal/mol.

2. Methods of Preparation

A. Classical Methods

1. Grignard reaction with transition metal halides

Bis-arene metal complexes can be prepared by the reaction of an aryl Grignard reagent with a transition metal halide below 0 °C. The mixed sandwich compound \((\eta C_5H_5)\text{Mn}(\eta^6C_6H_6)\) 1 can be prepared in this manner.\(^{9a-c}\)

\[
\text{MnCl}_2 + C_5H_6 + C_6H_5MgBr \rightarrow \begin{array}{c}
\text{Mn} \\
\text{1}
\end{array}
\]
With subsequent modifications of the above procedure, one can obtain, among other products, bis(\(\eta^6\)-benzene)chromium(0) 13 in 10-12% yield (Scheme I).\(^{10,11}\)

Scheme I.

\[\text{CrCl}_3 + 3\text{C}_6\text{H}_5\text{MgBr} \rightarrow (\text{C}_6\text{H}_5)_3\text{Cr} \cdot 3\text{THF} + 3\text{MgBrCl}\]

\[\begin{align*}
\text{a} & \quad \text{CrCl}_3 + 3\text{C}_6\text{H}_5\text{MgBr} \rightarrow (\text{C}_6\text{H}_5)_3\text{Cr} \cdot 3\text{THF} + 3\text{MgBrCl} \\
\text{b} & \quad (\text{C}_6\text{H}_5)_3\text{Cr} \cdot 3\text{THF} \xrightarrow{\text{Diethyl Ether}} \text{an intermediate} \\
\text{c} & \quad \text{an intermediate} \xrightarrow{\text{N}_2, \text{H}_2\text{O}} \text{13}
\end{align*}\]

Reaction \textbf{a} of Scheme I results in the formation of a chromium-arene sigma-bound complex which is coordinated with three equivalents of THF. Reaction \textbf{b} shows the subsequent stripping of the THF ligands by washing the complex with ether. Hydrolysis under \(\text{N}_2\) (reaction \textbf{c}, Scheme I) results in the evolution of hydrogen and the liberation of zero valent bis(\(\eta^6\)-arene) chromium complexes.

Other bis-arene metal complexes have been made using this synthetic method; however, this synthesis, when using other metal halides, is often tedious in that the intermediates formed (reaction \textbf{b}, Scheme I) are much harder to handle.

2. The Fischer-Hafner method

This synthetic method was first employed by Fischer and Hafner\(^{12}\) in their synthesis of bis(\(\eta^6\)-benzene)chromium 13. This reaction consists of
reduction of a suitable metal salt with powdered aluminum followed by
addition of an arene ligand to the reduced metal (Scheme II).

Scheme II.

\[ \text{a} \quad 3\text{CrCl}_3 + 2\text{Al} + \text{AlCl}_3 + 6\text{C}_6\text{H}_6 \rightarrow 3[(\eta^6-\text{C}_6\text{H}_6)_2\text{Cr}]^+\text{[AlCl}_4]^- \]

\[ \text{b} \quad [(\eta^6-\text{C}_6\text{H}_6)_2\text{Cr}]^+ + \text{S}_2\text{O}_4^{2-} + 4\text{OH}^- \rightarrow (\eta^6-\text{C}_6\text{H}_6)_2\text{Cr} + 2\text{H}_2\text{O} + 2\text{SO}_3^{2-} \]

\[ \text{c} \quad 2[(\eta^6-\text{C}_6\text{H}_6)_2\text{Cr}]^+ + \text{H}_2\text{O} \rightarrow 13 + 2\text{C}_6\text{H}_6 + \text{Cr}^{2+} \]

The production of the cation (Scheme II, part a) is catalyzed by \text{AlCl}_3 and
a trace of mesitylene,\textsuperscript{13} and is achieved in nearly quantitative yield. The
cation is then reduced (Scheme II, part b) to bis(\eta^6-benzene)chromium(0) by
addition of aqueous sodium dithionite. Alternatively, the sandwich
compound can be obtained by disproportionation of the cation in aqueous
alkaline solution\textsuperscript{1,4} (Scheme II, part c). By use of the Fischer-Hafner
method, many arene sandwich complexes of the d-block transition metals have
been prepared.\textsuperscript{1,2}

When halo-arenes are employed as substrates, dehalogenation affords
the hydrocarbon bis(\eta^6-arene)-metal complexes.\textsuperscript{15,16} The most versatile of
the "wet" synthetic methods for the production of bis-arene complexes is
quite limited as to what substituents can be tolerated on the aromatic
ring.\textsuperscript{17} The Fischer-Hafner method fails when the arene ligand contains
functional groups possessing lone pairs of electrons. This occurs because
of the required use of the Lewis acid \text{AlCl}_3 which complexes with the lone
pair electrons, thus ending the reaction sequence.\textsuperscript{18} Only parent and alkyl
substituted bis-arene complexes can be synthesized by this route.
3. Preparation from the polymerization of disubstituted acetylenes

Treatment of triphenyl chromium complexes with disubstituted acetylenes results frequently in the cyclic polymerization of the acetylene and the formation of bis(η⁶-arene) chromium complexes and substituted benzenes.¹⁹,²⁰ Bis(η⁶-arene) metal complexes of cobalt and manganese have been prepared in a similar manner.²¹,²²,²³

A mixture of metal halide and trialkyl aluminum²⁴ may be substituted for the metal alkyl complex, and with this route the arene may be employed directly instead of starting from an acetylene.²⁵ Methods of preparation 1, 2, and 3 are the most important of the classical routes to the bis(η⁶-arene) metal complexes, and by 1966 the synthesis of many of these complexes had been accomplished; however, only parent and alkyl-substituted bis-arene complexes could be synthesized due to the reasons mentioned previously. To synthesize bis-arene complexes containing halogens or other groups with lone-pair electrons, a new approach was required.

B. Metal Vapor Synthesis

Cocondensation of metal vapors with organic substrates was first reported by P. L. Timms in 1969.²⁶ Since that time many reports have been published in the field of metal vapor synthesis and many reviews have been written on the subject.¹⁷,¹⁸,²⁷-³⁷

Probably the most notable aspect of the chemistry of the early transition metals is their reaction with arene substrates to form bis(η⁶-arene) metal complexes.³³ Metal vapor synthesis provided a direct route to the bis-arene metal complexes, an approach which was immune to the limitations of the classical Fischer-Hafner synthesis.¹,² The synthesis of bis(η⁶-halo-arene) metal complexes was to be the first of several
breakthroughs precipitated by the advent of metal vapor synthesis.\textsuperscript{33,5} Because the chemistry of the alkyl-substituted and parent bis(\(\eta^6\)-arene)-metal complexes was limited, Zeiss\textsuperscript{2} in a 1966 publication, had stated that, "...It may be hoped of course that this situation will be changed by original effort. Meanwhile, the bis-arene complexes must be viewed as 'dead end' compounds." This "original effort" crystallized as the metal vapor synthesis and in the decade following Timms' 1969 communication the synthesis of many new sandwich compounds was achieved.\textsuperscript{1,35} The synthesis of these new metal complexes proved to be a revolution in the field of early transition metal chemistry\textsuperscript{33,34} in that the field had been greatly expanded: new reactions were discovered,\textsuperscript{35} factors contributing to stability were disclosed,\textsuperscript{17,31,37} and new and exciting technical applications were revealed.\textsuperscript{35}

Of the advances afforded by metal vapor synthesis, the most apparent are the bis(\(\eta^6\)-halo-arene) metal complexes. Although several reviews cover their synthesis and chemistry,\textsuperscript{17,31,32,33} a few points of interest will be recounted here.

From the data covered in Table II one can readily see the effect of halo substitution on the stability of the bis-arene complexes. The remarkable air stability of these complexes has been attributed to a kinetic effect.\textsuperscript{38} The first step in the oxidative decomposition of bis(\(\eta^6\)-arene)chromium complexes and analogous complexes possessing electron-donating substituents is the one electron oxidation of chromium producing a Cr\textsuperscript{+} complex.\textsuperscript{43,44} This process would be impaired should the complexed arene contain electron withdrawing substituents. From these
<table>
<thead>
<tr>
<th>Metal</th>
<th>Arene</th>
<th>Yield</th>
<th>Observations</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>C₆H₅Cl</td>
<td>47%</td>
<td>Air-stable, olive-green plates</td>
<td>39, 40</td>
</tr>
<tr>
<td>Cr</td>
<td>C₆H₅F</td>
<td>32%</td>
<td>Air-stable yellow solid</td>
<td>39,40,41</td>
</tr>
<tr>
<td>Cr</td>
<td>m-C₆H₄Cl₂</td>
<td>10%</td>
<td>Olive-green air-stable solid</td>
<td>35</td>
</tr>
<tr>
<td>Cr</td>
<td>p-C₆H₄F₂</td>
<td>12%</td>
<td>Bright yellow air-stable solid</td>
<td>39</td>
</tr>
<tr>
<td>Cr</td>
<td>C₆H₅CF₃</td>
<td>26%</td>
<td>Slightly air-sensitive yellow solid</td>
<td>31</td>
</tr>
<tr>
<td>Cr</td>
<td>m-(CF₃)₂C₆H₄</td>
<td>17%</td>
<td>Air-stable yellow-green solid</td>
<td>&quot;</td>
</tr>
<tr>
<td>Cr</td>
<td>p-(CF₃)₂C₆H₄</td>
<td>38%</td>
<td>Air-stable amber solid</td>
<td>&quot;</td>
</tr>
<tr>
<td>Cr</td>
<td>o-ClC₆H₄CF₃</td>
<td>33%</td>
<td>Air-stable yellow-green solid</td>
<td>&quot;</td>
</tr>
<tr>
<td>V</td>
<td>C₆H₅F</td>
<td>13%</td>
<td>Air-sensitive solid</td>
<td>&quot;</td>
</tr>
<tr>
<td>V</td>
<td>C₆H₅Cl</td>
<td>7%</td>
<td>Orange-red air-sensitive solid</td>
<td>&quot;</td>
</tr>
<tr>
<td>Metal</td>
<td>Arene</td>
<td>Yield</td>
<td>Observations</td>
<td>Reference</td>
</tr>
<tr>
<td>-------</td>
<td>-----------</td>
<td>-------</td>
<td>-------------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>V</td>
<td>p-C₆H₄F₂</td>
<td>1%</td>
<td>Red air-sensitive solid</td>
<td>&quot;</td>
</tr>
<tr>
<td>V</td>
<td>C₆H₅CF₃</td>
<td>2%</td>
<td>Orange mod. air-sensitive solid</td>
<td>&quot;</td>
</tr>
<tr>
<td>Mo</td>
<td>C₆H₅F</td>
<td>30-50%</td>
<td>Green, air-sensitive solid</td>
<td>42</td>
</tr>
<tr>
<td>Mo</td>
<td>C₆H₅Cl</td>
<td>30-50%</td>
<td>Green, air-sensitive solid</td>
<td>&quot;</td>
</tr>
<tr>
<td>W</td>
<td>C₆H₅F</td>
<td>30-50%</td>
<td>Green air-sensitive solid</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

Considerations, one might be tempted to postulate that stability incurred in the halo-substituted bis-arene complexes should increase with increasing halogen substitution of the complexed arene rings. This notion has been shown to be untrue. In the case of fluoro-substituted bis-arene complexes, explosive character has been encountered and, in the case of chromium, ligands with more than two fluorine groups attached cannot be tolerated due to the extreme lability imparted to the product. This lability coupled with the large amounts of energy released upon the formation of metal-halogen bonds should convince investigators to proceed with caution when attempting the synthesis of polyhalogenated-bis-arene complexes.
The strength of the metal arene bonds of the bis(\(\eta^6\)-halo arene)Cr complexes appears to be weaker than their parent and alkyl-substituted analogues.\(^{38}\) Evidence supporting this statement can be garnered from an experiment\(^{41}\) in which the \(^{19}\)F chemical shifts of a series of substituted bis(\(\eta^6\)-fluorobenzene)chromium complexes were analyzed. These \(^{19}\)F chemical shifts matched those of the corresponding \(C_6F_5X\) system (\(X = H, F, Cl, CH_3,\) or \(CF_3\)) suggesting that the overall electron withdrawing effect of a \(\pi\)-bonded chromium atom on each ring is similar to the effect of four ring fluorine substituents. From the above statements one can readily construe the nature of the bonding in these halo-substituted systems: the "tug of war", fomented by the electron withdrawing nature of the metal atom as opposed to the electron withdrawing nature of the complexed arene ring's halo substituents, should account for the extreme lability mentioned previously.

Suffice it to say the scope of reactivity demonstrated by the bis(\(\eta^6\)-arene)metal complexes has been broadened by the introduction of the new sandwich compounds synthesized by using the metal vapor technique.\(^{34,35,36,37}\)

An interesting application of the metal vapor technique\(^{46,47}\) was demonstrated when Timms reported the reaction of various metal vapors (Ti, Cr, V, and Mo) with DC 510 (Dow Corning 510 silicone diffusion pump oil-a phenylmethyl siloxane polymer). Metal atoms coordinated to at least 50% of the "pendant" arene rings of the siloxane chain.\(^{2,48,49}\) Liquid polyphenyl ethers gave stable bis(\(\eta^6\)-arene)metal complexes with V or Cr atoms\(^{47}\) and polystyrene in solution with diethylene glycol dibutyl ether reacted with Cr atoms\(^{47,50}\) to yield a complex in which 55% of the available phenyl groups are coordinated to the metal.
Few alternative methods of making metal complexes with polymers are known and the metal vapor technique has been shown to be a useful tool in the pursuit of these new materials.

1. Synthesis machines

Progress in the field of metal vapor synthesis has proceeded concurrently with changes in the design of the metal vapor synthesis machines. Methods of producing a metal flux have been changed as the use of resistively heated furnaces$^{42,27}$ and metal wires has been superceded by the employment of electron gun furnaces.$^{53}$ Reactors have been redesigned to facilitate work-up procedures and sophisticated vacuum systems are being used.$^{33}$

The synthesis machines used initially were the static reactors, (Timms' reactors) depicted in the literature in the pioneering work of Timms$^{51}$ and in the works of others (Klabunde,$^{37}$ Green,$^{33}$ Skell$^{36}$). Shown in Figure 1$^{52}$ is the static metal vapor reactor which is an approximation of the design developed by Timms.$^{51}$ Two component reactions, involving a metal and an organic substrate, can be carried out using the static reactor. Indeed, most of the transition metal bis-arene complexes were made using reactors similar to the one shown in Figure 1. However, the relatively small size of the reaction vessel$^{52}$ limits the amount of product that can be made. A large scale modification of the static reactor, similar to that reported by Green,$^{33}$ was recently constructed in our
laboratory. In regard to reaction scale and ease of use, the reactor depicted in Figure II proved to be advantageous to our interests.

The basic components of all synthesis machines are: a reaction vessel, a metal vapor production unit (a furnace), a ligand inlet system, a pumping system and a cryogenic cooling system. We constructed a metal vapor reactor (Figure III) in which ultraviolet light could be used in cocondensation reactions.\textsuperscript{52,54} This photochemical reactor was employed in several projects, one of which is the topic of the appended Communication.\textsuperscript{55}

The original research, to be described in the text of this thesis, was performed using the large scale static reactor (Figure II). Therefore, a general experimental procedure follows.

Metal powder (1 to 7 grams)\textsuperscript{56} is added to a Sylvania (resistively heated) furnace mantle. The weight of the mantle plus metal is recorded. The filled mantle is then attached to the furnace electrodes and the bell-jar is secured in place. To the bottom inlet port, one might attach a pre-weighed ampule containing a sublimable solid if so desired. Similarly, an ampule containing a liquid ligand might be attached to the liquid ligand inlet system. The bell-jar cooling jacket is affixed and the system is evacuated to ~50 microns using a rough pump. After four hours the rough pump is isolated and the diffusion pump is brought in line with the reactor. When the reactor pressure is below one micron, furnace outgassing is commenced. The furnace mantle is maintained at red heat for at least twenty minutes. The diffusion pump cold trap is then filled with liquid nitrogen, the flange heating tape is turned on as is the liquid ligand inlet heating tape. The bell-jar cooling jacket is then filled with liquid nitrogen.
The liquid ligand dropping funnel is filled with ligand and the rate of ligand addition is adjusted. The sublimable-solid ampule is opened to the reactor and as soon as the liquid ligand has condensed on the walls of the bell jar, the furnace temperature is brought to the metal vaporization temperature range to begin the reaction.

For our purposes, cocondensations in the large scale reactor are continued for periods of up to five hours. The furnace is then slowly cooled, the solid ligand ampule is closed and traces of liquid ligand are allowed to evaporate into the reactor. The diffusion pump is isolated from the reactor and the liquid nitrogen in the diffusion pump cold trap is removed. The liquid ligand inlet heating tape is turned off as soon as liquid ligand is seen to be absent from the inlet expansion chamber. The liquid nitrogen in the bell-jar cooling jacket is removed. The reactor is now filled with argon gas until greater than atmospheric pressure has been achieved. The reactor is left in line with the argon source. The bell-jar dome cap is replaced with a septum and the cocondensates are allowed to melt. After the cocondensates have melted, the flange heating tape is turned off.

Dry, deoxygenated solvents can be introduced through the septum and the reaction products may be removed via double-ended needles.

2. Parent and alkyl substituted bis-arene metal complexes

Presented here is a discussion of some of the parent and alkyl substituted bis-arene metal complexes that have been made by the metal vapor synthesis method. This discussion is in no way comprehensive as the purpose of this section is not to provide the reader with a review, but to provide a background - especially concerning physical characteristics
Figure 1

DIAGRAM OF A STATIC METAL VAPOR REACTOR

A) Reactor
B) Reactor top flange
C) Furnace
D) Furnace leads
E) Substrate inlet tube and flange fitting
F) Furnace lead flange fittings
G) Flange fitting for thermocouple gauge tube and inert gas inlet valve
H) Thermocouple gauge tube
I) Inert gas inlet valve
J) Substrate reservoir connecting tube
K) Accessory connection manifold
L) Stabilizing ligand reservoir and/or cryotrap for removing volatiles
M) Main LN₂ vacuum trap
N) Rough pump connection manifold
O) Valve to diffusion pump
Figure II

DIAGRAM OF A LARGE SCALE, STATIC METAL VAPOR REACTOR

A) Dome cap
B) Coolant bath holder
C) 6" Diameter glass beli-jar
D) Furnace mantle
E) LN₂ trap
F) Inlet port (for sublimable solids)
G) Furnace electrodes
H) Inlet port (adjoining liquid inlet system)
I) Product collection gutter
J) Liquid ligand inlet ring
Figure III

DIAGRAM OF THE PHOTOCHEMICAL METAL VAPOR REACTOR

A) Reaction drum
B) Metal furnace and cooling shield
C) Substrate inlets
D) Mercury lamp, photolysis well and reflecting shield
E) Collection funnel
F) Collection flask
G) Motor drive pulley
H) Mechanical vacuum gauge
Figure III.
and spectral data - with which the author's original research might be compared.

Cocondensation at -196°C of titanium metal vapor with toluene, mesitylene, and benzene led to compounds 3-5 respectively. Compounds 3-5 are diamagnetic, burgundy-red, very air-sensitive substances which have been characterized as zerovalent titanium species.\(^5^7\)

\[ \text{Ti} \]
\[ \text{3} \]

\[ \text{Ti} \]
\[ \text{4} \]

\[ \text{Ti} \]
\[ \text{5} \]

Compound 5 is slightly soluble in light petroleum ether and acetone but more soluble in benzene.\(^5^8\) These solutions appear to be thermally unstable at room temperature and there is evidence that decomposition is catalyzed by the presence of titanium clusters.\(^5^7,5^8\) Yields of 3-5 were reported as being low. Cocondensation of hafnium metal vapors with toluene and trimethyl phosphine (in 20:1 ratio) yielded at -196°C compound 6 in 30% yield. If one substitutes benzene for toluene, the parent compound 7 can be made in a likewise fashion.\(^5^9\) Similarly, cocondensation with zirconium led to compound 8 in 40% yield.

\[ \text{PMe}_3 \text{Hf} \]
\[ \text{6} \]

\[ \text{PMe}_3 \text{Hf} \]
\[ \text{7} \]

\[ \text{PMe}_3 \text{Zr} \]
\[ \text{8} \]

Compounds 6-8 are air and water-sensitive non-sublimable dark-green crystalline compounds. They are readily soluble in benzene and toluene and
partially soluble in light petroleum ether.\textsuperscript{59}

\textit{Bis(\eta^6-benzene)vanadium} 9 was produced in 2% yield by the cocondensation of vanadium vapor with a greater than 15-fold excess of benzene at -196°C. Compound 9 is an air-sensitive, dark red, paramagnetic, sublimable compound which decomposes above 300°C.\textsuperscript{38}

\begin{center}
\includegraphics[width=0.2\textwidth]{image}
\end{center}

No NMR data are available due to the paramagnetic nature of 9. Higher yields of \textit{bis(\eta^6-arene)vanadium} sandwich compounds were obtained when vanadium vapors were cocondensed with arenes bearing electron withdrawing groups\textsuperscript{38,16}

Cocondensation of niobium metal vapors with benzene, toluene, or mesitylene gives the \textit{bis-arenes} 10, 11 and 12, respectively.\textsuperscript{60}

\begin{center}
\includegraphics[width=0.6\textwidth]{image}
\end{center}

Compound 12 was formed in 40% yield and is representative of compounds made using niobium vapors and alkyl substituted arenes. These niobium compounds are deep red-purple, extremely air-sensitive, paramagnetic, and 12 is sublimable.

The metal vapor synthesis of \textit{bis(\eta^6-benzene)chromium} 13 was reported in the first publication describing the reaction of metal vapors with organic substrates.\textsuperscript{26} Since then a great body of work has been published
featuring the reaction of chromium vapors with organic substrates, and a few bis(η\textsuperscript{6}-arene)chromium compounds will be discussed here.

Compounds 13-18 are black to olive-green, air-sensitive solids which are volatile above ambient temperature and at low pressure (ca. 60°C, 10\textsuperscript{-3} torr for 13). Yields range from 30-60%.

The cocondensation of molybdenum metal atoms with benzene, toluene, or mesitylene gives the compounds 19-21, respectively. Yields range from 10-20%.

Compounds 19-21 are green, air-sensitive, sublimable solids. Similarly, cocondensation at -196°C of tungsten atoms with benzene, toluene, or mesitylene gives the corresponding bis-arene tungsten compounds 22, 23, and 24, respectively.

Compounds 22-24 are green, air-sensitive solids which can be recrystallized...
from light petroleum ether. Yields of these compounds average 30%.

Of relevance to the original research to be presented in this thesis are the spectral data of the bis(η⁶-arene)metal complexes. The most telling spectral evidence to be given here are the proton NMR data of these complexes. For a detailed discussion of the effects of metal complexation on the peak positions of an arene's proton and carbon-13 NMR spectra, one is referred to the works of Lagowski et al.⁷,⁴⁰ and to several reviews.²⁷-³⁷ Table III is a compilation of some of the spectral data of parent and alkyl-substituted bis(η⁶-arene)metal complexes.

The Synthesis of Manganese Sandwich Cations

1. Discussion

In the mid-sixties, E. O. Fischer and his co-workers reported the synthesis of the novel bis(η⁶-arene)manganese sandwich cation 25 in 2% yield. Compound 25 was a pinkish-white, air-sensitive solid which was soluble in methyl ethyl ketone, acetone, and other polar organic solvents. The purification of 25 was accomplished by recrystallization from acetone at -80°C. Prior to 1986 the mixed sandwich cation 25 was the only known bis(η⁶-arene)manganese sandwich cation.
Table III. 
\(^1H\) nmr data of parent and alkyl substituted bis-arene metal complexes

<table>
<thead>
<tr>
<th>Compound number</th>
<th>(^1H) Nmr</th>
<th>Mass Spectra</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>(\delta 4.89, 10H^s,) complex ((2C_6H_5)) &lt;br&gt; (\delta 2.15, 6H^s,) singlet, ((CH_3)^s)</td>
<td>232(66), ([H_{16}C_{14}Ti]^+) &lt;br&gt; 140, (100); ([H_8C_6]Ti]^+;) &lt;br&gt; 138(40), ([CH_5C_7]Ti]^+;) &lt;br&gt; 116(15), ([H_{16}C_{14}Ti]^2+;) to (3), ([H_8C_7]Ti]^2+; 48 (29), Ti(^+)</td>
<td>57, 58</td>
</tr>
<tr>
<td>4</td>
<td>(\delta 4.69, 6H^s,) ((2\text{-symmetrical} C_3H_5^s)); (\delta 1.96, 18H^s,) ((2\text{-symmetrical} (CH_3)_3^Ar))</td>
<td></td>
<td>57, 58</td>
</tr>
<tr>
<td>5</td>
<td>(\delta 5.04,) singlet. ((2C_6H_5), (C_8D_6);) (\delta 5.13,) singlet. ((2C_6H_5)) in (d^8) acetone</td>
<td>204(20), ([H_{12}D_{15}]Ti]^+;) 126(43), ([CH_5C_6]Ti]^+;) 48(100), Ti(^+)</td>
<td>57, 58</td>
</tr>
<tr>
<td>6</td>
<td>(\delta 5.30,) ((2H,) multi., ArH); (\delta 4.00,) ((8H,) multi., ArH); (\delta 2.00,) ((6H,) singlet, Me); 0.90 ((9H,) doublet, J_{PH} 5Hz, PMe_)</td>
<td></td>
<td>59</td>
</tr>
<tr>
<td>7</td>
<td>(\delta 4.5) ((12H,) doublet, J_{PH} 0.8H_, ArH); (\delta 0.95) ((9H, J_{PH} 4H_, PMe_)</td>
<td></td>
<td>59</td>
</tr>
<tr>
<td>8</td>
<td>(\delta 5.55) ((2H, m_H, ArH);) (\delta 4.13) ((8H, m_H, ArH);) (\delta 2.20) ((6H,) multi. Me); (\delta 0.85) ((9H,) doublet, J_{PH} 4Hz, PMe_)</td>
<td></td>
<td>59</td>
</tr>
</tbody>
</table>
Table III Cont'd

$^1$H nmr data of parent and alkyl substituted bis-arene metal complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^1$H Nmr</th>
<th>Mass Spectra</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>$\delta$ 4.12, 6H$^3$</td>
<td>208.0337 (high res.)</td>
<td>7, 40</td>
</tr>
<tr>
<td>14</td>
<td>$\delta$ 4.16, 5H$^3$; $\delta$ 1.98, 3H$^3$</td>
<td>236.0664 (high res.)</td>
<td>7, 40</td>
</tr>
<tr>
<td>15</td>
<td>$\delta$ 4.06, 4H$^3$; $\delta$ 2.02, 6H$^s$</td>
<td>264.0970 (high res.)</td>
<td>7, 40</td>
</tr>
<tr>
<td>16</td>
<td>$\delta$ 4.06, 4H$^3$; $\delta$ 2.02, 6H$^s$</td>
<td>264.0969 (high res.)</td>
<td>7, 40</td>
</tr>
<tr>
<td>17</td>
<td>$\delta$ 4.12, 4H$^3$; $\delta$ 2.06, 6H$^s$</td>
<td>264.0970 (high res.)</td>
<td>7, 40</td>
</tr>
<tr>
<td>18</td>
<td>$\delta$ 3.94, 3H$^3$; $\delta$ 2.05, 9H$^s$</td>
<td>292.1273</td>
<td>7, 40</td>
</tr>
<tr>
<td>19</td>
<td>$\delta$ 4.60, sing.</td>
<td></td>
<td>58</td>
</tr>
<tr>
<td>20</td>
<td>$\delta$ 4.60, mult. (5H$^3$); $\delta$ 1.89, singlet (8H$^s$</td>
<td></td>
<td>58</td>
</tr>
<tr>
<td>22</td>
<td>$\delta$ 5.00 (S, 6H$^s$</td>
<td></td>
<td>61</td>
</tr>
<tr>
<td>23</td>
<td>$\delta$ 4.90 (s, 5H$^3$); $\delta$ 1.97 (s, 3H$^3$)</td>
<td></td>
<td>61</td>
</tr>
<tr>
<td>24</td>
<td>$\delta$ 4.75 (6H$^s$, s, ArH); $\delta$ 2.03 (18H$^s$, s, Me)</td>
<td></td>
<td>61</td>
</tr>
</tbody>
</table>
The synthesis of the mixed sandwich compound 1 provides an example for comparison of yields obtained when using different types of synthetic pathways. The synthesis of 1 by the metal vapor route was reported in 1975. Though yields of the manganese sandwich compounds are low relative to those for sandwich compounds of other metals (95% for bis-benzene chromium, 13), the yields reported for the metal vapor synthesis of 1 are comparable to yields obtained by the "wet synthetic routes" (see Table IV).

<table>
<thead>
<tr>
<th>Synthetic Method</th>
<th>R,R¹ Substitution</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal vapor synthesis⁴⁰</td>
<td>R=R¹=H</td>
<td>0.4%</td>
</tr>
<tr>
<td>Metal vapor synthesis⁴⁰</td>
<td>R=CH₃R¹=H</td>
<td>0.7%</td>
</tr>
<tr>
<td>Metal vapor synthesis⁴⁰</td>
<td>R=R¹=CH₃</td>
<td>Trace</td>
</tr>
<tr>
<td>Wet synthesis⁶²</td>
<td>R=R¹=H</td>
<td>2-3%</td>
</tr>
<tr>
<td>Wet synthesis⁶²</td>
<td>R=R¹=H</td>
<td>0.4%</td>
</tr>
</tbody>
</table>

Taking into account the labor involved in the different syntheses of 1, it can readily be seen that the metal vapor synthetic route to 1 is the better, more economical route.

In a preliminary note published by Klabunde,⁴⁵ the cocondensation of various transition metal vapors with hexafluorobenzene or benzene were reported. When manganese vapors were cocondensed with either of the arene substrates, either no complex formed or decomposition occurred at very low temperatures (above -80°C).⁴⁵ This result can be rationalized in terms of the effective atomic number rule - a zerovalent bis(η⁶-arene)manganese sandwich complex would be an unstable 19 electron system.⁶⁴
2. Results

We have produced, by the cocondensation of manganese vapor with arenes in the presence of an oxidant (elemental iodine), the bis(η⁶-arene)manganese sandwich cations 26-30. Compounds 26-30 are pinkish-white, air-sensitive, diamagnetic compounds which were isolated as hexafluorophosphate salts.

Cocondensation of manganese vapor with the arene and elemental iodine (approximate ratios were 3:45:1) using the reactor depicted in Figure II resulted in the formation of the cationic sandwich compounds in 0.2 to 0.3% yield. The low yields of these compounds, relative to the yields of other sandwich compounds made by metal vapor synthesis, might be partially accounted for by the fact that iodine is the limiting reagent which may be considered only a scavenger of the initially formed neutral complex. We propose that a 19 electron neutral sandwich compound is first formed, and that this species then reacts rapidly with iodine to form the cationic sandwich compound (Scheme III).
In support of the proposed mechanism, studies using matrix isolation have shown that neutral bis-arene metal complexes of the later first row transition metals can be formed at low temperatures.65

---

**Table V.**

$^1$H NMR Data for the Known Bis-arene Manganese Sandwich Cations

<table>
<thead>
<tr>
<th>Compound Number</th>
<th>Chemical Shift, ppm</th>
<th>Relative Area</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>25$^{23}$</td>
<td>δ 5.16</td>
<td>1</td>
<td>s, benzene ring</td>
</tr>
<tr>
<td>25$^{23}$</td>
<td>δ 2.23</td>
<td>3</td>
<td>s, methyl</td>
</tr>
<tr>
<td>26$^{66}$</td>
<td>δ 5.74</td>
<td>5</td>
<td>br s, aromatic</td>
</tr>
<tr>
<td>26$^{66}$</td>
<td>δ 2.39</td>
<td>3</td>
<td>s, methyl</td>
</tr>
<tr>
<td>27$^{66}$</td>
<td>δ 5.42</td>
<td>3</td>
<td>s, aromatic</td>
</tr>
<tr>
<td>27$^{66}$</td>
<td>δ 2.47</td>
<td>9</td>
<td>s, methyl</td>
</tr>
<tr>
<td>28$^{66}$</td>
<td>δ 5.68</td>
<td>4</td>
<td>d, aromatic</td>
</tr>
<tr>
<td>28$^{66}$</td>
<td>δ 2.42</td>
<td>6</td>
<td>s, methyl</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Substance</th>
<th>δ</th>
<th>Int.</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2966</td>
<td>5.63</td>
<td>4</td>
<td>s, aromatic</td>
</tr>
<tr>
<td>2966</td>
<td>2.42</td>
<td>6</td>
<td>s, methyl</td>
</tr>
<tr>
<td>3066</td>
<td>5.62</td>
<td>4</td>
<td>s, aromatic</td>
</tr>
<tr>
<td>3066</td>
<td>2.42</td>
<td>6</td>
<td>s, methyl</td>
</tr>
</tbody>
</table>

A Discussion of the Spectral Data

One outstanding feature of the NMR spectra of the bis-arene metal sandwich complexes is the large upfield shift of the ring hydrogen atoms. The ring hydrogen atoms of bis(\(\eta^6\)-benzene)chromium 13 resonate as 3.12 ppm upfield from the uncomplexed benzene resonance.\(^7\) The complexes in Table III show comparable upfield shifts. This large shielding effect in the complexed arene has been observed in the \(13\text{C}\) spectra\(^4\) and also in the \(19\text{F}\) spectra.\(^1\) It appears to be a general phenomenon in the NMR spectrum for any classical, cyclic, aromatic system in which all ring carbons are involved in \(\pi\)-bonding to a metal.\(^7\)

The source of this large shielding increase has been attributed to quenching of the ring current effect, changes in the hydridization of the ring carbon atoms, or electron density changes. A host of hypotheses concerning this effect can be found in the literature as this characteristic shielding increase is still the topic of much speculation. The phenomenon is empirically quite useful for characterizing these compounds.

For alkyl benzene sandwich complexes the resonance for the ring hydrogen atoms is generally a singlet, in some cases quite broad.\(^7\) With regard to this the proton NMR spectra of 26-30 are typical. The ring hydrogens show the characteristic upfield shifts in resonance position;
however, this upfield shift is not as great as that found for bis-benzene chromium (3.12 ppm upfield relative to uncomplexed benzene) due to the cationic nature of the manganese sandwich compounds. On the average, the ring proton resonances of these complexes appear 1.4-1.5 ppm upfield relative to the uncomplexed arene. As expected, the exocyclic protons show little if any difference in resonance positions relative to those found for the uncomplexed arenes.

Resonance positions in the carbon-13 NMR show on average 40-45 ppm upfield shifts relative to uncomplexed arenes.

The FABMS data obtained for 16 - 30 shows fragmentation patterns reminiscent of those obtained for the complexes listed in Table III. In most cases the base peak is that corresponding to the molecular ion and subsequent fragmentations corresponding to loss of one, and both rings are evident. Evidence pertaining to the existence of the metal ion Mn is also present. Based on this evidence, and on similarities in the physical characteristics of 26-30 to 25, we have made our structural assignments.

3. Conclusion

The synthesis of bis(η⁵-arene)manganese sandwich cation complexes can be accomplished by metal vapor synthesis using alkyl substituted arenes, elemental iodine and manganese. Attempts to synthesize the parent, bis(benzene)manganese hexafluorophosphate, have failed.

4. Experimental Section

Reagents

Manganese metal (powdered, 99.5% purity) obtained from the Fairmont Co. was used without purification. The alkyl substituted arenes were
obtained from Aldrich (>98% purity) and were used with no further purification. The iodine used was Mallinckrodt "Analytical Reagent" grade. All reagents were partially degassed prior to use. THF was distilled under nitrogen from a sodium/potassium alloy and was subjected to further degassing immediately before work-up. Deionized water was obtained from the department and was partially degassed prior to use. Ammonium hexafluorophosphate was obtained from Aldrich in 98% purity.

Identification of Compounds

Nuclear magnetic spectroscopic data were obtained in acetone-d₆ solvent using a JEOL FX 90 Q FT-NMR Spectrometer. FABMS spectra were obtained on a KRATOS MS-50 high resolution mass spectrometer (courtesy of the University of Texas Medical Center, Houston, Texas) with an Ion Tech Saddlefield fast atom gun using xenon atoms. The samples were run using a thioglycerine matrix. Only the cationic portion of the samples was observed.

Typical Preparation of a Bis(η⁶-arene)Manganese Cation

Manganese was vaporized from a resistively heated furnace mantle at 6.8A and 5.25V, and at a pressure below 10⁻⁴ torr. Iodine vapor and an alkyl substituted arene vapor were codeposited with manganese vapor onto the liquid nitrogen cooled walls of the glass reactor. Codeposition was maintained for 3 to 5 hours over which molar ratios of 1:45:3 (iodine/arene/metal) were codeposited. After completion of the deposition, the cold matrix was dark red-brown in color. The reactor was pressurized with argon and then warmed to ambient temperature. The reaction mixture was dissolved in THF, the solution was removed by double-ended needle, and filtered through Celite. The excess ligand and THF were slowly pumped off and the complex was dissolved in partially degassed water. This water solution was filtered through Celite. The complex was precipitated as a
hexafluorophosphate salt by the addition of a partially degassed aqueous solution of ammonium hexafluorophosphate.

Modifications of the above procedure were employed in unsuccessful attempts to improve yields. For example, the ammonium hexafluorophosphate was dissolved in THF in an attempt to achieve exchange with the iodide counter-ion inside the reactor in the first stages of the work-up.

**Yields and Spectra of Compounds 25-29**

Bis(toluene)manganese hexafluorophosphate [25] (0.2-0.3% yield) \(^1\text{H}\) NMR: \(\delta\) 5.74 (5H, br, aromatic H), 2.39 (3H, s, \(\text{CH}_3\)); \(^{13}\text{C}\) NMR: \(\delta\) 98.1 (C-1), 84.2 (C-2 and C-6), 83.2 (C-3 and C-5), 82.3 (C-4), 19.4 (CH\(_3\)); FABMS: \(m/e\) 240 (17%, [M + H]\(^+\)), 239 (100%, [M\(^+\)]), 147 (15%, [M-C\(_7\)H\(_8\)]\(^+\)).

Bis(mesitylene)manganese hexafluorophosphate [26] (0.28% yield) \(^1\text{H}\) NMR: \(\delta\) 5.42 (3H, s, aromatic H), 2.47 (9H, s, \(\text{CH}_3\)); \(^{13}\text{C}\) NMR: \(\delta\) 99.1 (C-1, C-3, and C-5), 85.3 (C-2, C-4, and C-6), 19.5 (CH\(_3\)); FABMS: \(m/e\) 296 (100%, [M + H]\(^+\)), 178 (29%, [M-C\(_9\)H\(_{10}\)]\(^+\)), 175 (133%, [M-C\(_9\)H\(_{12}\)]\(^+\)).

Bis(o-xylene)manganese hexafluorophosphate [27] (trace) \(^1\text{H}\) NMR: \(\delta\) 5.68 (4H, d, aromatic H), 2.42 (6H, s, \(\text{CH}_3\)); \(^{13}\text{C}\) NMR: \(\delta\) 97.9 (C-1 and C-2), 85.7 (C-3 and C-6), 83.9 (C-4 and C-5), 18.1 (CH\(_3\)); FABMS: \(m/e\) 267 (100%, [M\(^+\)].

Bis(p-xylene)manganese hexafluorophosphate (0.2% yield) \(^1\text{H}\) NMR \(\delta\) 5.62 (4H, s, aromatic H), 2.42 (6H, s, \(\text{CH}_3\)); \(^{13}\text{C}\) NMR: \(\delta\) 97.9 (C-1 and C-4), 85.1 (C-2, C-3, C-5, and C-6), 19.3 (CH\(_3\)); FABMS: \(m/e\) 267 (100%, [M\(^+\)].
Bis($η^6$-p-xylene)manganese hexafluorophosphate (30)
Bis(η⁶-o-xylene)manganese hexafluorophosphate (28)
Bis(η₆-mesitylene)manganese hexafluorophosphate (27)

FABMS data

R.T.
Bis(η⁶-toluene)manganese hexafluorophosphate (26)

FABMS data
Bis(η⁶-p-xylene)manganese hexafluorophosphate (30)

\(^1\)H nmr data
Bis(η⁶-o-xylene)manganese hexafluorophosphate (28)

\(^1\text{H nmr data}\)

Bis(η⁶-m-xylene)manganese hexafluorophosphate (29)

\(^1\text{H nmr data}\)
Bis(\(\eta^6\)-toluene)manganese hexafluorophosphate (26)

\(^1\text{H} \text{ nmr data}\)

Bis(\(\eta^6\)-mesitylene)manganese hexafluorophosphate (27)

\(^1\text{H} \text{ nmr data}\)
Bis(η⁶-toluene)manganese hexafluorophosphate (26)

^{13}\text{C} \ nmr \ data

Bis(η⁶-mesitylene)manganese hexafluorophosphate (27)

^{13}\text{C} \ nmr \ data
Bis($\eta^6$-o-xylene)manganese hexafluorophosphate (28)

$^{13}$C nmr data

ppm ($\delta$) 200 180 160 140 120 100 80 60 40 20 0

Bis($\eta^6$-m-xylene)manganese hexafluorophosphate (29)

$^{13}$C nmr data

ppm ($\delta$) 160 140 120 100 80 60 40 20 0
Bis(η⁶-p-xylene)manganese hexafluorophosphate (30)

$^{13}$C nmr data

ppm ($\delta$) 220 200 180 160 140 120 100 80 60 40 20 0
References and Notes


22. Only one bis-arene sandwich cation of manganese has been reported. An earlier report has been shown to be incorrect.


32. Timms, P. L. *Faraday Symposium* 1973, 8-1B.


56. The amount of metal used in a given reaction depends upon the size of the furnace mantle. We used an average of three grams of metal per reaction. Also, yields were based on the amount of metal vaporized.


66. This work.
Photoactivation of Methyl Acetate by Chromium Atoms

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Received November 19, 1985

Summary: Photolysis of the cocondensate of methyl acetate and chromium vapor yields a complex that decomposes to acetaldehyde and formaldehyde.

The advent of metal vapor synthesis during the past decade provides an important new method for the preparation of certain organometallic species that are difficult to synthesize by more traditional routes. Metal atoms are in a state of "ultimate coordinative unsaturation" and are highly reactive. However, in any metal vapor reaction there is always a major competing reaction—metal atom recombination to form metal clusters and particles. If the desired metal atom/substrate reaction has a significant activation barrier, then clustering may become the dominant reaction at the low temperatures required by the technique unless the substrate has a significant ability to adduct with the metal atoms. Even then, there has been no convenient method of imparting the addition energy into the system needed to make the reaction proceed.

Photolysis has often been used in matrix isolation spectroscopy as a way of introducing additional energy into the systems studied. Photoexcitation of macroscale metal vapor reactions promises to be a similarly useful method of producing new chemistry. We report here the results of a study on the photoactivation of methyl acetate by chromium atoms using a metal vapor reactor.
Figure 1. Photochemical metal vapor reactor.

Scheme I

\[
\text{CH}_3\text{C}^\text{OCH}_3 + \text{Cr} \rightarrow \text{CH}_3\text{C}-\text{Cr}-\text{C}-\text{CH}_3 \\
\text{hv} \rightarrow \text{CH}_3\text{C}-\text{Cr}-\text{OCH}_3
\]

\[
\text{CH}_3\text{C}^\text{H} \rightarrow \text{Cr} \rightarrow \text{CH}_2\text{C}-\text{Cr}-\text{H} + \text{CH}_2\text{O}
\]

The reactor used in this study is illustrated in Figure 1. This apparatus may be used to cocondense metal vapor with any sufficiently volatile organic compound onto a stainless-steel drum at 77 K. The drum is rotated during the cocondensation to assure that the cocondensate is uniformly deposited. Photolysis is carried out during the cocondensation using a 450-W medium-pressure Hg arc lamp. All reactions are carried out at 10^4 torr. Products may be readily collected in the receiving flask as the matrix is allowed to warm.

When the cocondensate of methyl acetate and chromium vapor is photolyzed, the major organic product is acetaldehyde. Under the most favorable conditions (700/1 molar ratio of ester to metal) acetaldehyde is produced in a 60% yield (based on metal deposited). Several other
minor products are isolated from the reaction including methanol, methyl formate, and formaldehyde. Cocondensation of the ester with chromium vapor in the absence of photolysis yields only trace amounts of methanol and methyl formate. A thermal reaction of excess methyl acetate with the metal clusters and particles formed upon warmup would account for the formation of methanol and methyl formate; this appears to be a minor reaction pathway in both cases.

An attractive rationalization of the photoformation of acetaldehyde and formaldehyde in this system is illustrated in Scheme 1. The formation of adduct I has been demonstrated at 15 K by using matrix isolation spectroscopy where cocondensation of chromium and methyl acetate produced clearly discernible shifts in the carbonyl and C=O stretching frequencies.10 The existence of a stable ligated metal species at 77 K can be shown by the fact that the same products are produced if the reactants are first cocondensed and then the matrix is photolyzed. The extremely high organic to metal ratio required for this reaction clearly indicates that a metal atom reaction is occurring. Photolysis of the chromium atom into the C=OCH₃ bond of the adducted ester would form intermediate 2. Decomposition of 2 by β-hydride transfer11 and reductive elimination12 would then yield acetaldehyde and formaldehyde in equimolar quantities; the low observed yield of formaldehyde may be accounted for by its difficulty of isolation. Photolytic cocondensation of chromium and methyl acetate-d₅ yields acetaldehyde-d₅ as predicted by this mechanism.

Other acetate esters also react with chromium vapor to yield acetaldehyde, but the efficiency of the reaction drops dramatically as the size of the alkyl group is increased.

We are continuing to investigate the photolytic reactions of metal atoms with other organic compounds, and the results of these studies will be reported later.

Acknowledgment. We gratefully acknowledge the 3M Co. for support of this work.


(6) Howard and Miles have used a similar device in their ESR studies.12 Ours is a true preparative device, while theirs is a microscale matrix isolation device.
(9) Over a 3-h period 0.36 mmol of chromium was condensed with 256 mmol of methyl acetate. Volatile products were identified by GC and GC/MS using a Porapak QS column. Toluene yield of acetaldehyde was determined by using benzene as an internal standard.
(10) Methyl acetate and chromium vapor were codeposited with excess argon onto a copper surface. Stretching frequencies were determined by using a Beckman IR-9 infrared spectrometer. The carbonyl and C-O stretching frequencies of adduct 1 were measured as 1837 and 1110 cm⁻¹, respectively, compared to 1799 and 1252 cm⁻¹ for free methyl acetate.