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Pentamethylocyclopentadienylrhodium and -iridium Halides. I. Synthesis and Properties

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Abstract: Details of the reactions of hexamethyl(Dewar benzene), HMDB (hexamethylbicyclo[2.2.0]hexadiene) (1), and of 1-(1-chloroethyl)pentamethylocyclopentadiene (4a) with RhCl3·3H2O and IrCl3·5H2O to give the pentamethylocyclopentadienyl complexes, (C5Me5MCl)2 (5), and proposals for the mechanisms of these reactions are presented. The pentamethylocyclopentadienyl-metal bonds in 5 is very strong, but reactions readily proceed at the halogens. Adducts of the type C5Me5M(L)Cl (L = p-toluidine, pyridine, triphenylphosphate) are described as well as their reactions to form C5Me5MMePPPh3 and C5Me5Me3LPPPh3. The synthesis of C5Me5Ir(CO)5 is also reported.

In 1967 one of us, in connection with some work on the complexes derived from 2-butyne and palladium chloride, began an investigation of the reactions of hexamethyl(Dewar benzene) (HMDB, hexamethylbicyclo[2.2.0]hexadiene) (1) toward transition metal halides. This led, in the first instance, to the preparation of hexamethyl(Dewar benzene) palladium chloride, \( \text{PdCl}_2 \), and later to that of the platinum analog, \( \text{PtCl}_2 \). At the same time, a number of other authors reported the synthesis of other HMDB complexes, notably of the group VIb metals \( \text{Mo(CO)}_4 \), \( \text{W(CO)}_4 \), and \( \text{IrCl}_3 \), and of rhodium(I) \( \text{RhCl}_3 \), \( \text{RhCl}_3 \). The X-ray crystal structure determination of \( \text{C}_5\text{Me}_5\text{RhCl}_2 \) (L = p-toluidine, pyridine, triphenylphosphine) is in agreement with the proposed structure.

Our interest in these complexes, especially as possible intermediates in the metal-catalyzed trimerization of 2-butyne, led us to explore the reactions of HMDB toward rhodium and iridium trichloride hydrates.

Results and Discussion

Formation of Dichloro(pentamethylocyclopentadienyl)-rhodium and -iridium Complexes from HMDB and Related Compounds. The Dewar benzene (1) reacted readily with \( \text{RhCl}_3 \) in methanol at 65 °C under nitrogen to give a nearly quantitative yield (based on \( \text{RhCl}_3 \)) of red crystals, together with a substantial amount of hexamethylenylbenzene (HMB). HMDB is normally quite stable to isomerization under these conditions in the absence of the metal halide; even in the presence of acid only a small degree of isomerization was observed by Criegee and Gruner. The metal must therefore play an important role in this isomerization.

The red crystals were finally identified as dichloro(pentamethylocyclopentadienyl)rhodium dimer (3). The methanol and other volatile products were distilled off and analyzed by a combination of vpc and mass spectrometry, and found to contain, apart from methanol, one major component and two minor ones. The major component was isolated and shown to be dimethylacetal (MeCH(OMe)2), and the minor ones were identified as methyl chloride and dimethyl ether. The two latter compounds do not appear to be significant as far as the general ring-contraction reaction is concerned since they were also observed to occur in reactions in which rhodium trichloride was heated in methanol containing sodium carbonate in the absence of HMDB.

(2) Fellow of the Alfred P. Sloan Foundation and author to whom any correspondence should be addressed.
(4) P. V. Balakrishnan and P. M. Maitlis, ibid., 1303 (1968).
(9) The structures of these materials are unknown and are certainly not as simple as the formulas, \( \text{RhCl}_3 \cdot 3\text{H}_2\text{O} \) and \( \text{IrCl}_3 \cdot 5\text{H}_2\text{O} \), might imply. Furthermore, materials from different sources have somewhat different properties.
(11) R. Criegee and H. Gruner, ibid., 6, 467 (1968).
(12) This complex was simultaneously prepared by Booth, Haszeldine, and Hill, who reported it as a hexamethylenbenzenerhodium(III) complex \( \text{C}_5\text{Me}_5\text{RhCl}_3 \). As reported earlier by Kang and Maitlis, this formulation is incorrect; Booth, et al., now concur with our proposed structure.
(15) Personal communication by Professor R. N. Haszeldine.
Quantitative vpc analysis showed that the amount of dimethylacetal present was approximately correct for a stoichiometric reaction.

\[
\begin{align*}
2 & \rightarrow \ + 2\text{RhCl}_3\cdot 3\text{H}_2\text{O} + 4\text{MeOH} \rightarrow \\
2\text{MeCH(OMe)}_3 + 4\text{HCl} + 8\text{H}_2\text{O} \\
\end{align*}
\]

Although the yield of 3 was much lower (25%) under heterogeneous conditions, in water the reaction still proceeded and acetaldehyde was detected as the by-product.

\[
2(\text{I}) + 2\text{RhCl}_3\cdot 3\text{H}_2\text{O} \xrightarrow{\text{H}_2\text{O}, 60^\circ} 3 + 2\text{CH}_2\text{CHO} + 4\text{HCl} + 4\text{H}_2\text{O}
\]

The reaction in methanol was also attempted with iridium trichloride hydrate but with erratic and disappointing results. At best, a 9% yield of the iridium analog of 3 was obtained. The reason why these remarkable ring-contraction reactions occurred remained obscure until, in connection with some work on the formation of dichloropentamethylcyclopentadienylplatinum, we realized that the presence of acid was essential for the preparation of 3. Although the details of the mechanism still require a careful kinetic study for elucidation, the gross overall reaction path now seems clear.

The reaction of HMDB with acid (e.g., HCl in methylene chloride) was already reported by Schiffer and Hellmann in 1967. Reinvestigation of the products of this reaction (at 30–60°C) by Paquette and Krow and by Criegee and Grüner showed the major products to be the 1-(1-substituted ethyl)pentamethylcyclopentadienes (4).17

\[
1 + H^+X^- \rightarrow \begin{array}{c}
\text{CHXMe} \\
4, X = \text{Cl, Br, MeO}
\end{array}
\]

Reaction of the chloro compound (4, X = Cl) with either the rhodium or the iridium chloride hydrates in methanol at 65°C gave 5 (M = Rh or Ir) in 92 and 85% yields, respectively. The methoxy compound (4, X = OMe) was also allowed to react with RhCl3·3H2O to give 5 (M = Rh) in 55% yield. In both cases the only significant by-product was dimethylacetal.

\[
\begin{align*}
\text{MCl}_3 \cdot x\text{H}_2\text{O} & \rightleftharpoons [\text{MCl}(x-1)\text{H}_2\text{O}]^{+} + \text{H}^+ \\
1 + H^+ + X^- & \rightarrow 4 \\
4 (X = \text{Cl}) & + \text{OMe}^- \xrightarrow{\text{M}^{11+}} 4 (X = \text{OMe}) + \text{Cl}^- \\
4 (X = \text{OMe}) & + \text{MCl}_3S_2 \rightarrow \begin{array}{c}
\text{MeCH(OMe)}, \\
4, X = \text{Cl, Br, MeO}
\end{array}
\]

Since the iridium complex (5, M = Ir) was obtained in better than 85% yield from this last reaction, by comparison with the 9% from HMDB, it is reasonable to suppose that 4 (X = Cl or OMe or OH) is an intermediate in both the reactions. This arises by addition of acid to HMDB in the first reaction, probably catalyzed by the metal trihalide. A reaction mechanism as shown in Scheme I can explain these results. A suggestion that pentamethylcyclopentadiene (C5Me5H) itself is an intermediate in this reaction seems unlikely since it is formed only in very low yield by prolonged action of dilute methanolic acid on 4 (X = OMe) while the reactions described here give very high yields.

Scheme I

\[
\begin{align*}
\text{MCl}_3 \cdot x\text{H}_2\text{O} & \rightleftharpoons [\text{MCl}(x-1)\text{H}_2\text{O}]^{+} + \text{H}^+ \\
1 + H^+ + X^- & \rightarrow 4 \\
4 (X = \text{Cl}) & + \text{OMe}^- \xrightarrow{\text{M}^{11+}} 4 (X = \text{OMe}) + \text{Cl}^- \\
4 (X = \text{OMe}) & + \text{MCl}_3S_2 \rightarrow \begin{array}{c}
\text{MeCH(OMe)}, \\
4, X = \text{Cl, Br, MeO}
\end{array}
\]

The acid necessary for the conversion of HMDB to 4 is present in the reaction mixture. It was found that 0.01 M aqueous solutions of the rhodium and iridium chlorides had pH's of 2.7 and 2.9, respectively. The protons presumably arise by ionization of coordinated water molecules.

The driving force for the reaction, i.e., for cleavage of the C–C bond, is the great stability of the pentamethylcyclopentadienyl–metal complexes. The acetal arises from the intermediate ion (MeCH=OMe)+ by reaction with methanol. Intermediates involving M(I) or M–H species do not appear likely since we were able to show that the reaction also proceeds under aqueous conditions. A very similar scheme can be written to account for this latter reaction and the formation of acetaldehyde.

Shortly before we elucidated this reaction, Kasahara, et al., briefly reported the reaction

\[
\begin{align*}
\text{C}_6\text{Me}_6\text{Cl}_2 \rightarrow \text{MeCH(OMe)}_3 \quad & \rightarrow \text{MCl}_3 \cdot x\text{H}_2\text{O} \\
\text{MCl}_3 \cdot x\text{H}_2\text{O} & \rightarrow [\text{MCl}(x-1)\text{H}_2\text{O}]^{+} + \text{H}^+ \\
1 + H^+ + X^- & \rightarrow 4 \\
4 (X = \text{Cl}) & + \text{OMe}^- \xrightarrow{\text{M}^{11+}} 4 (X = \text{OMe}) + \text{Cl}^- \\
4 (X = \text{OMe}) & + \text{MCl}_3S_2 \rightarrow \begin{array}{c}
\text{MeCH(OMe)}, \\
4, X = \text{Cl, Br, MeO}
\end{array}
\]


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which appeared to involve a remarkable ring contraction. Subsequent attempts both by Kasahara and ourselves to repeat this have not been successful, and only inorganic materials were isolated. The original report should therefore be treated with considerable caution.

I-(1-Chloroethyl)pentamethylcyclopentadiene (4, X = Cl) in excess also reacted with [Rh(CO)2Cl]2 in methanol to give a product (6) in which a pentamethylcyclopentadienyl ring is present. This material was an orange-yellow solid, which decomposed readily to rhodium metal and 3, particularly in solution. It showed the presence of two bands due to terminal chlorines. The pmr spectra of both complexes in CDCl3 solution showed only one singlet nearly quantitatively to give the known products 7, 10b and 8, 10c, respectively.

\[ 4 \ (X = Cl) + [Rh(CO)2Cl]_2 \rightarrow \text{Metal} \]

\[ 6 + \text{p-toluidine} \rightarrow \text{C}_5\text{Me}_5\text{RhCl}_2(\text{p-toluidine}) + \text{Cl} \]

The path by which 6 is formed is rather obscure and no information is available at the moment. The complex 6 could not be obtained from (C5Me5RhCl)2 and [Rh(CO)2Cl]2 under a variety of conditions.

A number of attempts have been made to form other pentamethylcyclopentadienyl complexes by reaction of 4 with other metal complexes, particularly those in low oxidation states (e.g., Fe(CO)5, Co(CO)4−, Cr(CO)6), but so far with success. The usual product here was HMB which was also observed by Hellmann and Schäfer to result from reaction of 4 (X = Cl) with zinc. The chloro compound (4, X = Cl) was also dehydrochlorinated slowly to HMB on prolonged refluxing with 3 in methanol.

Properties of the Dichloropentamethylcyclopentadienylrhodium- and -iridium Complexes. The rhodium and iridium complexes (5) were obtained as dark red and orange crystals, respectively. Their structures were deduced on the basis of their analyses (Table I) and further reactions. From their osmometrically determined molecular weights in chloroform, the molecules appear to be largely dimeric, but some higher oligomeric species may also be present in the rhodium complex.

The pmr spectra of both complexes in CDCl3 solution showed only one singlet (Table II) due to the 15 equivalent methyl protons; the infrared spectra were rather featureless but showed close similarities to those of other pentamethylcyclopentadienylmetal complexes reported by King and Bisnette; three \( \nu_{\text{Rh-Cl}} \) bands were observed in the far-infrared of 3 in agreement with the presence of bridging and terminal chlorines.

The lack of volatility of the complexes precluded our obtaining much mass spectroscopic data on 5; however, the rhodium complex at an inlet temperature of 210°C did give peaks at m/z 237 (C5Me5CH2RhCl2−), corresponding to loss of HCl from C5Me5RhCl2− and 134 (C5Me5CH+). The lack of volatility of the complexes precluded our obtaining much mass spectroscopic data on 5; however, the rhodium complex at an inlet temperature of 210°C did give peaks at m/z 237 (C5Me5CH2RhCl2−), corresponding to loss of HCl from C5Me5RhCl2− and 134 (C5Me5CH+), and confirmed that a hexamethylbenzene complex was not present.

The complexes are characterized by low reactivity toward many reagents; for example, the C5Me5−Rh bond could not be cleaved by base, cyanide, or, apparently,

Table I. Analyses of Pentamethylcyclopentadienylrhodium- and -iridium Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>C</th>
<th>H</th>
<th>Cl</th>
<th>Other</th>
<th>Analyses, %</th>
<th>Found, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C5Me5RhCl]2 (3)</td>
<td>38.62</td>
<td>4.89</td>
<td>22.94</td>
<td>Rh, 33.30 mol wt 618</td>
<td>Cl, 5.15</td>
<td>22.87</td>
</tr>
<tr>
<td>[C5Me5IrCl]2 (5)</td>
<td>30.15</td>
<td>3.80</td>
<td>17.80</td>
<td>mol wt 796</td>
<td>Cl, 3.95</td>
<td>17.20</td>
</tr>
<tr>
<td>[C5Me5RhCl2] (11)</td>
<td>24.42</td>
<td>3.09</td>
<td></td>
<td>mol wt 984</td>
<td>Cl, 3.55</td>
<td></td>
</tr>
<tr>
<td>[C5Me5Rh(OCOCH3)2H2O] (12)</td>
<td>44.92</td>
<td>6.15</td>
<td></td>
<td>mol wt 571</td>
<td>Cl, 6.13</td>
<td></td>
</tr>
<tr>
<td>[C5Me5RhCl(C2H4N)2] (10a)</td>
<td>46.41</td>
<td>5.19</td>
<td>18.27</td>
<td>N, 3.61</td>
<td>mol wt 642</td>
<td>17.37</td>
</tr>
<tr>
<td>[C5Me5IrCl(C2H4N)2] (10b)</td>
<td>49.06</td>
<td>5.81</td>
<td>17.04</td>
<td>N, 3.36</td>
<td>mol wt 531</td>
<td>17.24</td>
</tr>
<tr>
<td>[C5Me5RhCl(PPh3)] (10c)</td>
<td>58.86</td>
<td>5.29</td>
<td>12.41</td>
<td>P, 5.42</td>
<td>mol wt 629</td>
<td>12.21</td>
</tr>
<tr>
<td>[C5Me5RhCl(PPh3)] (13)</td>
<td>44.57</td>
<td>3.98</td>
<td></td>
<td>mol wt 571</td>
<td>Cl, 3.95</td>
<td></td>
</tr>
<tr>
<td>[C5Me5RhCl(C2H4N)2] (17)</td>
<td>50.99</td>
<td>4.55</td>
<td>10.76</td>
<td>N, 4.10</td>
<td>mol wt 642</td>
<td>11.01</td>
</tr>
<tr>
<td>[C5Me5RhCl(diphos)]1PF6− (19)</td>
<td>54.35</td>
<td>5.35</td>
<td>13.95</td>
<td>P, 5.09</td>
<td>mol wt 699</td>
<td>13.95</td>
</tr>
<tr>
<td>[C5Me5RhCl(diphos)] (18)</td>
<td>52.86</td>
<td>4.77</td>
<td></td>
<td>mol wt 707</td>
<td>P, 5.96</td>
<td></td>
</tr>
<tr>
<td>[C5Me5RhMe(PPh3)] (15)</td>
<td>60.10</td>
<td>5.52</td>
<td>10.04</td>
<td>mol wt 197</td>
<td>6.85</td>
<td></td>
</tr>
<tr>
<td>[C5Me5RhMe(PPh3)] (14)</td>
<td>54.22</td>
<td>5.18</td>
<td></td>
<td>mol wt 642</td>
<td>3.78</td>
<td></td>
</tr>
<tr>
<td>[C5Me5RhCl(C2H4N)2] (6)</td>
<td>67.79</td>
<td>6.85</td>
<td></td>
<td>mol wt 531</td>
<td>6.91</td>
<td></td>
</tr>
<tr>
<td>[C5Me5IrCl(C2H4N)2] (20)</td>
<td>28.68</td>
<td>2.99</td>
<td>21.07</td>
<td>mol wt 383</td>
<td>3.01</td>
<td></td>
</tr>
<tr>
<td>[C5Me5IrCl(C2H4N)2] (20)</td>
<td>37.59</td>
<td>3.92</td>
<td></td>
<td>mol wt 370</td>
<td>4.04</td>
<td></td>
</tr>
</tbody>
</table>


(22) Personal communication by Professor Kasahara.

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The reactivity of the complexes with sodium iodide in acetone to give (1963). Complexes are also quite stable to air both in the solid and in solution, however, still await full characterization. The properties described for these compounds agree well with those of the pentamethylcyclopentadienyl complexes. We have also developed a simple route to the unsubstituted complex 9. This was obtained in 75–80% yield by refluxing a suspension of RhCl₃·3H₂O with freshly cracked cyclopentadiene in methanol.

The reaction with chloro(1,5-cyclooctadiene)rhodium dimer proceeded analogously but in higher yield in the presence of sodium carbonate.

The reactivity of the complexes 5 and 9 lies in the M–Cl bonds which undergo displacement reactions very readily. Chloride in 5 was exchanged for iodide by reaction with sodium iodide in acetone to give 11, and for acetate by reaction with silver acetate to give 12. The halogen bridges were cleaved by a variety of ligands, L. These reactions are summarized in Scheme II; analytical and nmr data are given in Tables I and II, respectively.

The adducts 10 varied considerably in stability; 10b and especially 10a reverted readily back to 3, particularly in solution in the absence of free ligand. The phosphine complex 10c, however, did not appear to dissociate. Its pmr spectrum showed multiplets due to the phenyl resonances at 2.2 and 2.65 and a doublet at 8.64 (J = 4.0 cps) due to long-range coupling of the 15 equivalent methyl protons with 31P. The intensity ratio was 1:1 as expected.

The iodo complex 11 underwent similar reactions, to give 13, for example, and also reacted with carbon monoxide to give the very unstable deep violet carbonyl 16, characterized by a carbonyl stretching frequency at 2035 cm⁻¹. Elemental analysis was not possible as it decomposed very readily both in solution and in the solid to regenerate 11. No carbonyl complex could be isolated from 3.

Both the triphenylphosphine complexes 10c and 13 reacted with an excess of methylmagnesium iodide. The reaction of 10c gave largely the iodomethyl complex 15 (halogen exchange occurring) and some of the dimeric methyl complex 14. The latter was the only product from the reaction with 13.

An interesting dinuclear complex 17 was obtained from reaction of 1 mole of bis(1,2-diphenylphosphino)ethane (diphos) with 3 in ethanol. The pmr spectrum was as expected for the phenyl and CH₂ protons; however, the methyl protons showed an unusual pattern, believed to be caused by the magnetic inequivalence of the two 31P atoms to which the methyls are coupled (Figure 1).

Complex 3 reacted with an excess of diphos to give complex 18, which had a normal molecular weight in chloroform. If the C₅Me₅ ring is assumed, as usual, to be equivalent to a tridentate ligand, then this complex

Table II. Pmr Spectra

<table>
<thead>
<tr>
<th>Complex</th>
<th>Complex</th>
<th>Resonances (ρ)</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>[C₅Me₅RhCl₂] (3)</td>
<td>8.40 (s)</td>
<td>2.80 (d, aromatic), 5.13 (b, NH₃), 7.65 (s, Me)</td>
<td></td>
</tr>
<tr>
<td>[C₅Me₅RhL₆] (11)</td>
<td>8.10 (s)</td>
<td>2.2, 2.65 (m, aromatic)</td>
<td></td>
</tr>
<tr>
<td>C₅Me₅RhCl₂(C₂H₅N) (10b)</td>
<td>8.64 (s)</td>
<td>7.3 (b, CH₃), 2.10; 2.75 (m, aromatic)</td>
<td></td>
</tr>
<tr>
<td>C₅Me₅RhCl₂(PPh₃) (10c)</td>
<td>8.64 (d, J₆₅₋₆₂ = 4 cps)</td>
<td>7.5 (b, CH₃), 2.40; 2.87 (m, aromatic)</td>
<td></td>
</tr>
<tr>
<td>C₅Me₅RhCl₃(diphos) (17)</td>
<td>8.62 (t, see Figure 1)</td>
<td>7.20 (b, CH₃), 2.42; 2.90 (m, aromatic)</td>
<td></td>
</tr>
<tr>
<td>C₅Me₅RhCl₃(diphos) (18)</td>
<td>8.47 (t, J₆₅₋₆₂ = 3 cps)</td>
<td>2.65 (m, aromatic), 10.18 (dd, Me, J₆₅₋₆₂ = 5.0, J₆₅₋₁₆ = 2.5 cps)</td>
<td></td>
</tr>
<tr>
<td>C₅Me₅RhCl₂(dipos) (PF₆) (19)</td>
<td>8.51 (t, J₆₅₋₆₂ = 3 cps)</td>
<td>2.32, 2.62 (m, aromatic), 9.10 (dd, Me, J₆₅₋₁₆ = 6.4, J₆₅₋₁₆ = 2.4 cps)</td>
<td></td>
</tr>
<tr>
<td>C₅Me₅Rh(Me)PPh₃ (14)</td>
<td>8.60 (dd, J₆₅₋₆₂ = 2.2, J₆₅₋₁₆ = 0.4 cps)</td>
<td>5.02 (s, H₂O), 7.99 (s, OAc)</td>
<td></td>
</tr>
<tr>
<td>C₅Me₅RhCl₂(PPh₃) (15)</td>
<td>8.50 (dd, J₆₅₋₆₂ = 2.6, J₆₅₋₁₆ = 0.4 cps)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₅Me₅RhCl₃(PPh₃) (13)</td>
<td>8.23 (d, J₆₅₋₁₆ = 4.2 cps)</td>
<td></td>
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</tr>
<tr>
<td>C₅Me₅RhCl₃(PPh₃) (12)</td>
<td>8.36 (s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₅Me₅RhCl₃Rh(CO)₂ (6)</td>
<td>8.27 (s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₅Me₅RhCl₂RhCl₃ (5, M = Ir)</td>
<td>8.41 (s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₅Me₅IrCl₂PPh₃ (11c)</td>
<td>8.66 (d, J₆₅₋₁₆ = 2.0 cps)</td>
<td>2.25, 2.65 (m, aromatic)</td>
<td></td>
</tr>
<tr>
<td>C₅Me₅Ir(CO)₂ (20)</td>
<td>7.81 (s)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
is formally seven-coordinate rhodium(II1). In the presence of ammonium hexafluorophosphate in ethanol, the ionic complex 19 was obtained. The pmr spectra of both 18 and 19 were normal, the C₅Me₅ protons appearing as triplets owing to coupling to two equivalent phosphorus nuclei.

The iridium complex, [C₅Me₅IrCl₂]₂, has not as yet been investigated in as much detail, but some very similar reactions have been observed; for example, it reacted with triphenylphosphine to give C₅Me₅IrCl₃PPh₃. The complex also reacted with Fe₃(CO)₁₂ (or Fe₂(CO)₉) in benzene at 80° to give a 90% yield of the dicarbonyl 20 (νCO 1925, 2000 cm⁻¹).²⁹ This dicarbonyl is a volatile yellow solid, which is stable for a few days. No transfer of the C₅Me₅ ligand to the iron was observed, in agreement with our other observations of the low reactivity of the C₅Me₅-Rh and -Ir bonds.

Complex 20 was also obtained from reaction of the dichloride and carbon monoxide in ethanol containing sodium carbonate, but in rather lower yield (67%).

Attempts to make the rhodium analog, C₅Me₅-Rh(CO)₂, by these and other routes were unsuccessful; only very unstable materials were obtained.

These rhodium and iridium complexes are of considerable interest since they are easily converted to Rh(I) and Ir(I) complexes without loss of the C₅Me₅ ligand and many catalytic reactions of these elements in these oxidation states can be studied conveniently. Many of

[29] These values compare with 1957 and 2037 cm⁻¹ for CsH₃Ir(CO)₂ found by Fischer and Brenner.²⁹ The decrease in νCO observed is presumably caused by stronger back-bonding of the C₅Me₅ group to the iridium.

the other Rh(I) and Ir(I) complexes which are catalytically active have also contained tertiary phosphines or arsines, which for some purposes are undesirable. This objection does not apply to these complexes and they also have the property of having a very simple stereochemistry by virtue of the presence of the C₅Me₅ ring. Some studies of these reactions will be reported shortly.

Experimental Section

All melting points were determined on a capillary melting point apparatus (Thomas Hoover) and are uncorrected. Infrared spectra were measured on a Perkin-Elmer 357G or a Beckman IR 5 spectrometer.

Pmr spectra were measured in CDCl₃ or benzene solution on a Varian A-60 or HA-100 spectrometer using tetramethylsilane as internal reference. Molecular weights were determined in chloroform or benzene on a Mechrolab osmometer. Analyses by vapor phase chromatography (vpc) were performed with Varian Aerograph 204 or A90-P3 instruments using Carbowax columns. Mass spectra were measured on a Hitachi Perkin-Elmer RMU-6A spectrometer.

Formaldehyde and benzene spectra were measured on a Hitachi Perkin-Elmer RMU-6A spectrometer.

Graph 204 or A90-P3 instruments using Carbowax columns. Mass analyzer were performed as described by Paquette and Krow. They are as follows:

- 1-(1-Chloroethyl)- and 1-(1-methoxyethyl)pentamethylcyclpentadienylidene were prepared as described by Paquette and Krow and by Criegee and Gruner. The identity of these materials was established by their nmr spectra and high-resolution mass spectrometry. Our nmr spectra agree well with the values reported by Criegee and Gruner but not with those of Paquette and Krow. They are as follows: 5.87 (1 H, q, J₆-7 = 6.5 cps), 8.12 (3 H, s, bd), 8.26 (6 H, m), 5.31 (3 H, bd), 6.90 (3 H, s), and 8.97 (3 H, d, J₆-7 = 6.5 cps) for 4 (X = Cl), and 6.67 (3 H, s), 6.80 (1 H, t, J₆-7 = 6.5 cps), 8.27 (12 H, s), 9.83 (3 H, s), and 9.38 (3 H, d, J₆-7 = 6.5 CPS) for 4 (X = OMe).

Dichloropentamethylcyclopentadienylrhodium Dimer (3). Reaction of Hexamethyl(Dewar benzene) with RhCl₃·3H₂O in Methanol. A mixture of RhCl₃·3H₂O (1 g) and hexamethyl Dewar benzene (HMBD, 2.0 g) in 30 ml of methanol was stirred at 65° under nitrogen for 15 hr. The reaction mixture was allowed to cool to room temperature and the solvent was removed under vacuum. The residue was washed with ether to remove excess hexamethylbenzene and left oily red crystals which were extracted with chloroform. The solution was dried over anhydrous sodium sulfate, the red solubles were distilled off into a liquid nitrogen trap at the end of the reaction. The distillate was then analyzed by vpc, and the volatile products were chromatographed on Florisil with benzene as eluent to give 750 mg of hexamethylbenzene which was identical with an authentic sample.

This experiment was repeated many times on different scales to determine the volatile products. In these, the reactions were run under a solid CO₂-acetone condenser, and the methanol and other volatile materials were distilled off into a liquid nitrogen trap at the end of the reaction. The distillate was then analyzed by vpc, and the various constituents were identified by mass spectrometry and by comparison of their retention times with authentic specimens. The largest component was identified as dimethylacetal; the others were methyl chloride and dimethyl ether. The dimethylacetal was also isolated by preparative vpc, and its nmr spectrum was shown to be identical with that of an authentic sample.

The distillate from a reaction in which 2.03 g of RhCl₃·3H₂O, 3 g of HMBD, and 20 ml of methanol were added to react for 24 hr was washed with ether to remove excess hexamethylbenzene. The distillate was found to contain between 40 and 50 µl of dimethylacetal/ml compared to an expected value of 40 µl/ml.

Reaction of RhCl₃·3H₂O with Hexamethyl(Dewar benzene) in Water. To a solution of RhCl₃·3H₂O (200 mg) in 5 ml of distilled water at 90° was added HMBD (400 mg) with magnetic stirring under nitrogen. After the reaction mixture had been stirred at 90° for 20 hr, the solvent was removed under reduced pressure. The oily residue was extracted with chloroform and the chloroform extracts were dried over anhydrous sodium sulfate. The solvent was distilled in vacuo into a liquid nitrogen trap, and the residue was washed with ether to remove hexamethylbenzene. Recrystallization of the residue from chloroform–benzene afforded 58 mg (25%) of [C₅Me₅RhCl₂] as dark red crystals.

Vapor phase chromatography of the methanol distilled acetal showed that dimethylacetal was the other volatile product of the reaction.

Dichloropentamethylcyclopentadienyliridium Dimer (5, M = Ir). Reaction of IrCl₃·5H₂O with HMBD. A mixture of IrCl₃·5H₂O (500 mg) and HMBD (1 g) in 80 ml of methanol was stirred at 65° under nitrogen for 20 hr. The reaction mixture was worked up as described above to give 87 mg (9%) of [C₅Me₅IrCl₂] as orange crystals, mp >230° dec, and 800 mg of HMBD. The properties of the complex are very similar to those of [C₅Me₅RhCl₂].

Dichloropentamethylcyclopentadienyliridium. Method A. A solution of IrCl₃·5H₂O (1 g) and 1-(1-chloroethyl)pentamethylcyclopentadiene (1 g) in 30 ml of methanol was stirred at 65° under nitrogen for 20 hr. The reaction mixture was allowed to stand at room temperature overnight. The orange crystalline solid which was precipitated was collected on a filter, washed with a small amount of methanol and ether, and then dried in air to give 690 mg of crude [C₅Me₅IrCl₂]. The filtrate was evaporated under reduced pressure and the residue was washed with ether to give another 160 mg of crude [C₅Me₅IrCl₂], total yield 850 mg (85%). It was recrystallized from chloroform–benzene to give the pure product as orange crystals, mp >230° dec. Dimethylacetal was detected in the methanol distillate.

Dichloropentamethylcyclopentadienyliridium. Method B. Hydrogen chloride gas was bubbled into the solution of HMBD (3 g) in 25 ml of methylene chloride at room temperature with stirring for 1 hr. After the deep purple solution was stirred for 5 hr, the solvent was removed under reduced pressure to give the crude 1-(1-chloroethyl)pentamethylcyclopentadiene. This was added to a suspension of IrCl₃·5H₂O (2 g) in 30 ml of methanol and the reaction was carried out in the manner outlined in method A to give 1.92 g (89%) of [C₅Me₅IrCl₂].

Dichloropentamethylcyclopentadienylidinyliridium (10a). A suspension of [C₅Me₅RhCl₂] (300 mg, 0.48 mmole) in 20 ml of chloroform was added 0.5 ml of pyridine with stirring at 25° under nitrogen. The reaction mixture was stirred for 30 min, then allowed to stand at room temperature overnight, the orange-yellow crystals which deposited were collected on a filter, washed with ether, and dried in air to yield 260 mg (82%) of analytically pure pyridine adduct. It is slightly soluble in chloroform and methylene chloride, but readily reverses back to [C₅Me₅RhCl₂] in these solvents.

Dichloro(p-toluidine)pentamethylcyclopentadienyliridium (10b). A solution of [C₅Me₅RhCl₂] (300 mg, 0.48 mmole) and p-toluidine (600 mg, 5.6 mmole) in 20 ml of chloroform was stirred at 25° under nitrogen for 3 hr. The red solution was filtered and allowed to stand at 0° overnight. The red crystals were collected on a filter, washed with ether, and dried in air to yield 340 mg (85%) of pure p-toluidine adduct. Although the p-toluidine adduct in the solid state is stable, it is unstable in solution and a starting material.

Dichloro(triphenylphosphine)pentamethylcyclopentadienyliridium (10c). A suspension of [C₅Me₅RhCl₂] (300 mg, 0.48 mmole) and triphenylphosphine (300 mg, 1.14 mmole) in 20 ml of ethanol was refluxed under nitrogen for 5 hr, then allowed to cool; the red brown crystals which deposited were collected on a filter and washed with ethanol and ether to yield 450 mg (89%) of the pure product, mp >320°.
The petroleum ether solution was evaporated under reduced pressure; the residue was dissolved in benzene and chromatographed on Florisil with benzene as eluent to give 71 mg (8% of C₂₅H₁₉R₁₂)₂P₈h as yellow crystals.

Diaceto(pentamethylenecyclopentadienyl)rhodium Hydrate [C₅Me₅Rh(OAc)₂H₂O]. (12). A suspension of [C₅Me₅RhCl]₂ (200 mg, 0.31 mmole) and silver acetate (265 mg) in 30 ml of benzene was refluxed under nitrogen with stirring for 3 hr. The mixture was filtered and the residue washed with benzene. The combined filtrates were evaporated to dryness on a rotary evaporator and the residue extracted with ether. On removal of the ether a red-orange solid remained which was crystallized from ether-hexane to give 190 mg (93% of pure [C₅Me₅Rh(OAc)₂H₂O], mp 143-145°C.

The presence of coordinated water was confirmed by the pmr spectrum which showed singlets at 5.02 (H₂O), 7.99 (acetate), and 8.36 (methyls) in the ratio of 2:6:12.

Preparation of C₅Me₅RhCl[Rh(CO)₅]. (6). A mixture of [RhCl(CO)₅] (300 mg) and 1,1-di(chloromethyl)pentamethylenecyclopentadiene (1 g) in 20 ml of methanol was stirred at 25°C for 3 hr. After cooling to room temperature, the solvent was removed under pressure. The residue was washed with ether and then the insoluble red-orange crystals were collected on a filter and dried in vacuo to give 350 mg (90%) of the analytically pure product which had no sharp melting point. It was unstable in air and easily decomposed in solution to give [Me₅CrRhCl]Cl and rhodium metal.

Reaction of C₅Me₅RhCl[Rh(CO)₅] with PPh₃. A suspension of C₅Me₅RhCl[Rh(CO)₅] (100 mg, 0.19 mmole) in 20 ml of benzene containing 5 ml of anhydrous methanol was refluxed under nitrogen with stirring for 15 hr. The reaction mixture was then cooled and filtered and the solvent evaporated to dryness on a rotary evaporator. The residue was then dissolved in 10 ml of hot methanol and the solution was refluxed under nitrogen with stirring for a few minutes and 300 ml of hot hexane was added. The solution was filtered, the solvent removed and the residue extracted with ether. On removal of the ether a solid residue remained which was crystallized from ether-hexane to give 140 mg (97%) pure of [C₅Me₅RhCl[Rh(CO)₅][PPh₃] (10b), identical with an authentic sample.

The filtrate was evaporated under reduced pressure to give a yellow solid. Recrystallization of the yellow solid from benzene-hexane afforded 120 mg (90%), based on C₅Me₅RhCl[Rh(CO)₅][PPh₃] (10b) of (P₃Ph)₃RhOCOCl. These complexes were identified by comparison of their pmr and infrared spectra with those of authentic specimens.

Reaction of C₅Me₅RhCl[Rh(CO)₅] with p-Toluidine. p-Toluidine (340 mg) was added to a suspension of C₅Me₅RhCl[Rh(CO)₅] (100 mg) in 10 ml of benzene and stirred at 25°C for 3 hr. The red solid was then collected on a filter, washed with ether, and dried to give 80 mg (100%) of C₅Me₅RhCl[p-toluidine] (10b), identical with an authentic sample. The combined filtrates were concentrated to 10 ml and hexane was added to precipitate the orange crystalline RhCl[CO]₅[p-toluidine] (7). This was filtered, washed with hexane, and dried to yield 65 mg (100%). The complex was identical with an authentic sample.

Dichloro(triphenylphosphine)pentamethylenecyclopentadienyliridium. A suspension of [C₅Me₅IrCl₃] (300 mg, 0.4 mmole) and triphenylphosphine (300 mg, 1.14 mmole) in 20 ml of ethanol was refluxed under nitrogen with stirring for 15 hr. After cooling, the brick-red solid was collected on a filter, washed with methanol and ether, and dried to yield 480 mg (100%) of C₅Me₅IrCl[p-toluidine] (20b), identical with an authentic sample.

The petroleum ether solution was evaporated under reduced pressure; the residue was dissolved in benzene and chromatographed on Florisil with benzene as eluent to give 71 mg (8% of C₂₅H₁₉R₁₂)₂P₈h as yellow crystals.

The petroleum ether solution was evaporated under reduced pressure; the residue was dissolved in benzene and chromatographed on Florisil with benzene as eluent to give 71 mg (8% of C₂₅H₁₉R₁₂)₂P₈h as yellow crystals.
benzene was refluxed with stirring under nitrogen for 24 hr. After cooling, the orange-yellow solution was filtered and the residue washed with a small amount of ether. The combined filtrate was evaporated on a rotary evaporator; the residue was dissolved in benzene and chromatographed on Florisil with benzene as eluent to give 240 mg (89%) of yellow crystals of \( \text{C}_5\text{Me}_5\text{Ir}(\text{CO})_2 \), mp 145-148\(^\circ\) dec. This compound is very soluble in organic solvents and could also be sublimed at 50\(^\circ\) (10\(^{-2}\) mm). It is air stable for a few days. The infrared spectrum shows strong \( \nu_{\text{CO}} \) at 1925 and 2000 cm\(^{-1}\).

It could also be prepared from \( [\text{C}_5\text{Me}_5\text{IrCl}_2]^+ \) and \( \text{Fe}(\text{CO})_5 \), and as follows. Carbon monoxide was bubbled into the suspension of \( [\text{C}_5\text{Me}_5\text{IrCl}_2] \) (100 mg) and anhydrous sodium carbonate (50 mg) in 30 ml of ethanol with stirring at 70\(^\circ\) for 3 hr. The orange-yellow solution was filtered and the solvent was evaporated under reduced pressure. The residue was extracted with benzene, the solvent removed, and the residue purified by sublimation at 50\(^\circ\) (10\(^{-2}\) mm); yield 65 mg (62\%) of \( \text{C}_5\text{Me}_5\text{Ir}(\text{CO})_2 \).

Attempts to prepare \( \text{C}_5\text{Me}_5\text{Rh}(\text{CO})_2 \) by any of these routes led only to very unstable materials which showed complex absorptions in the carbonyl stretching region of the infrared but were not otherwise characterized.

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**The Circular Dichroism of Square-Planar, Tetradeionate Schiff Base Chelates of Copper(II)**

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**Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received February 13, 1969**

**Abstract:** The circular dichroism (CD) and electronic absorption spectra of a series of nine copper(II) complexes with tetradeionate Schiff bases derived from \( (-)-\)-propane-1,2-diamine and \( (R,R)-\)-cyclohexane-1,2-diamine have been measured in chloroform and in pyridine. The signs of the Cotton effects of d-d and ligand transitions for this series of complexes can be correlated with the absolute configuration of a proposed flattened tetrahedral array of donor atoms about the copper ion. This configuration is produced stereospecifically by the conformational preference of the central \( \text{gauche} \) chelate ring which results from the steric requirements of the ligands. The circular dichroism spectra of these complexes reveal more detailed band splittings in the d-d transition region than do the corresponding electronic spectra. By comparison of these CD bands with published polarized crystal spectra, tentative assignments of the metal ion transitions are proposed. Solvent effects, when they are not precluded by steric interactions, assist in the assignment of the metal ion transitions.

The circular dichroism (CD) spectra of transition metal complexes have been extensively studied in recent years, as their interpretation can yield valuable information concerning the origin of absorption bands in the electronic spectra of the complexes.\(^2\) In addition, the sensitivity of circular dichroism to molecular structure makes the technique valuable for investigating the conformations and configurations of chelate molecules.\(^3\)

The majority of previous investigations of optically active complexes have dealt with the inert, dihedral chelates of \( d^3 \) and \( d^4 \) metal ions.\(^2\) The study of complexes in which the optical activity is induced by means of active ligands, however, is also of great interest.\(^3\)

Several important studies of this type have appeared,\(^4-7\) but no extensive study of a series of related compounds has been carried out to provide generalizations regarding the effect of the extra-chromophoric portion of the molecule on the optical activity of the metal ion transitions. Such correlations, involving the 3000-Å absorption of the carbonyl chromophore, are very familiar.\(^8\)

Since the \( n \rightarrow \pi^* \) transition of the carbonyl chromophore, like metal ion d-d transitions, is an example of a magnetic-dipole-allowed transition which is formally parity forbidden but acquires electric-dipole intensity by means of a noncentrosymmetric perturbation,\(^9\) it is of interest to compare structure-activity relationships in the two systems. For the copper(II) ion, attempts have been made to see to what extent the optical activity of the d-d transitions is governed by symmetry rules,\(^10-12\) similar to the octant rule\(^8\) for the carbonyl group.

Since the initial study\(^13\) of the optical rotatory dispersion (ORD) of chelates of the type described here,

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(1) Presented in part at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Abstract INOR-76.


(11) M. Parris and A. E. Hodes, ibid., 90, 1999 (1968).
