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help of Professor M. Rettig on the section of the Discussion dealing with pseudocontact shifts is acknowledged.

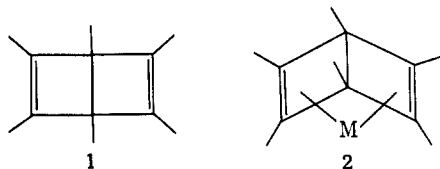
## Pentamethylcyclopentadienylrhodium and -iridium Halides. I. Synthesis and Properties<sup>1</sup>

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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)pentamethylcyclopentadiene (4a) with  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{IrCl}_3 \cdot 5\text{H}_2\text{O}$  to give the pentamethylcyclopentadienyl complexes,  $(\text{C}_5\text{Me}_5\text{MCl}_2)_2$  (5), and proposals for the mechanisms of these reactions are presented. The pentamethylcyclopentadienyl-metal bond in 5 is very strong, but reactions readily proceed at the halogens. Adducts of the type  $\text{C}_5\text{Me}_5\text{RhCl}_2\text{L}$  ( $\text{L} = p$ -toluidine, pyridine, triphenylphosphine) are described as well as their reactions to form  $\text{C}_5\text{Me}_5\text{RhMe}_2\text{PPh}_3$  and  $\text{C}_5\text{Me}_5\text{RhMeIPPh}_3$ . The synthesis of  $\text{C}_5\text{Me}_5\text{Ir}(\text{CO})_2$  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 (2,  $\text{M} = \text{PdCl}_2$ ),<sup>3</sup> and later to that of the platinum analog (2,  $\text{M}$



=  $\text{PtCl}_2$ ).<sup>4</sup> At the same time, a number of other authors reported the synthesis of other HMDB complexes, notably of the group VIb metals (2,  $\text{M} = \text{Cr}(\text{CO})_4$ ,  $\text{Mo}(\text{CO})_4$ , and  $\text{W}(\text{CO})_4$ )<sup>5</sup> and of rhodium(I) (2,  $\text{M} = \text{RhCl}$ , dimer).<sup>6</sup> The X-ray crystal structure determination of 2 ( $\text{M} = \text{Cr}(\text{CO})_4$ ) is in agreement with the proposed structure.<sup>7</sup>

Our interest in these complexes, especially as possible intermediates in the metal-catalyzed trimerization of 2-butyne,<sup>8</sup> led us to explore the reactions of HMDB toward rhodium and iridium trichloride hydrates.<sup>9</sup>

(1) Parts of this work have appeared as communications: J. W. Kang and P. M. Maitlis, *J. Am. Chem. Soc.*, **90**, 3259 (1968); J. W. Kang, K. Moseley, and P. M. Maitlis, *Chem. Commun.*, 1304 (1968).

(2) Fellow of the Alfred P. Sloan Foundation and author to whom any correspondence should be addressed.

(3) H. Dietl and P. M. Maitlis, *Chem. Commun.*, 759 (1967).

(4) P. V. Balakrishnan and P. M. Maitlis, *ibid.*, 1303 (1968).

(5) E. O. Fischer, W. Berngruber, and C. G. Kreiter, *Chem. Ber.*, **101**, 825 (1968); *cf.*, E. O. Fischer, C. G. Kreiter, and W. Berngruber, *Angew. Chem. Intern. Ed. Engl.*, **6**, 634 (1967).

(6) H. C. Volger and H. Hogeveen, *Rec. Trav. Chim.*, **86**, 830 (1967).

(7) G. Huttner and O. S. Mills, *Chem. Commun.*, 344 (1968).

(8) H. Reinheimer, H. Dietl, J. Moffat, D. Wolff, and P. M. Maitlis, *J. Am. Chem. Soc.*, **90**, 5321 (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.

### Results and Discussion

**Formation of Dichloro(pentamethylcyclopentadienyl)rhodium and -iridium Complexes from HMDB and Related Compounds.** The Dewar benzene (1) reacted readily with  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  in methanol at  $65^\circ$  under nitrogen to give a nearly quantitative yield (based on  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ ) of red crystals, together with a substantial amount of hexamethylbenzene (HMB). HMDB is normally quite stable to isomerization under these conditions in the absence of the metal halide;<sup>10</sup> even in the presence of acid only a small degree of isomerization was observed by Criegee and Grüner.<sup>11</sup> The metal must therefore play an important role in this isomerization.

The red crystals were finally identified as dichloro(pentamethylcyclopentadienyl)rhodium dimer (3).<sup>12</sup> 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 ( $\text{MeCH}(\text{OMe})_2$ ), 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.

(10) W. Schäfer and H. Hellmann, *Angew. Chem. Intern. Ed. Engl.*, **5**, 518 (1967).

(11) R. Criegee and H. Grüner, *ibid.*, **6**, 467 (1968).

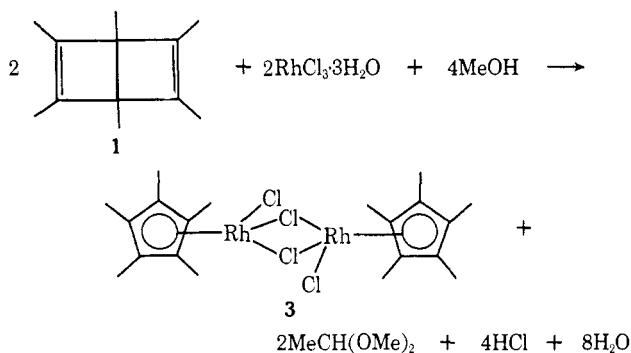
(12) This complex was simultaneously prepared by Booth, Haszeldine, and Hill, who reported it as a hexamethylbenzenerhodium(III) complex  $[(\text{C}_6\text{Me}_6\text{RhCl})_2\text{Cl}]_2$ .<sup>13</sup> As reported earlier by Kang and Maitlis,<sup>14</sup> this formulation is incorrect; Booth, *et al.*, now concur with our proposed structure.<sup>15</sup>

(13) B. L. Booth, R. N. Haszeldine, and M. Hill, *Chem. Commun.*, 1118 (1967).

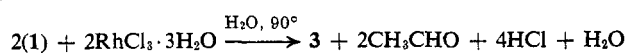
(14) J. W. Kang and P. M. Maitlis, *J. Am. Chem. Soc.*, **90**, 3259 (1968).

(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

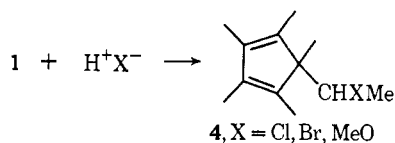


Although the yield of **3** was much lower (25%) under heterogeneous conditions, in water the reaction still proceeded and acetaldehyde was detected as the by-product.



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 dichloro(pentamethylcyclopentadiene)platinum,<sup>4</sup> 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 over-all reaction path now seems clear.

The reaction of HMDB with acid (e.g., HCl in methylene chloride) was already reported by Schäfer and Hellmann in 1967.<sup>10</sup> Reinvestigation of the products of this reaction (at 30–60°) by Paquette and Krow<sup>16</sup> and by Criegee and Grüner<sup>11</sup> showed the major products to be the 1-(1-substituted ethyl)pentamethylcyclopentadienes (**4**).<sup>17</sup>



Reaction of the chloro compound (**4**, X = Cl) with either the rhodium or the iridium chloride hydrates in methanol at 65° gave **5** (M = Rh or Ir) in 92 and 85% yield, respectively. The methoxy compound **4** (X = OMe) was also allowed to react with  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  to give **5** (M = Rh) in 55% yield. In both cases the only significant by-product was dimethylacetal.

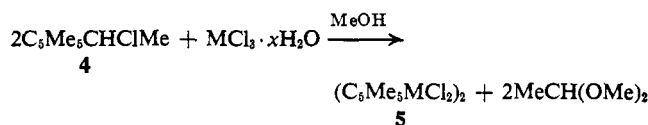
(16) L. A. Paquette and G. R. Krow, *Tetrahedron Letters*, 2139 (1968).

(17) Compounds of type **4** arise from **1** via a complex series of rearrangements, involving bicyclo[3.1.0]hexenyl and bicyclo[2.1.1]hexenyl cations as intermediates, as has been shown by the very elegant low-temperature nmr studies of Hogeveen and Volger,<sup>18</sup> Paquette, Krow, Bollinger, and Olah,<sup>19</sup> and Childs and Winstein.<sup>20</sup>

(18) H. Hogeveen and H. C. Volger, *Rec. Trav. Chim.*, **87**, 1042 (1968).

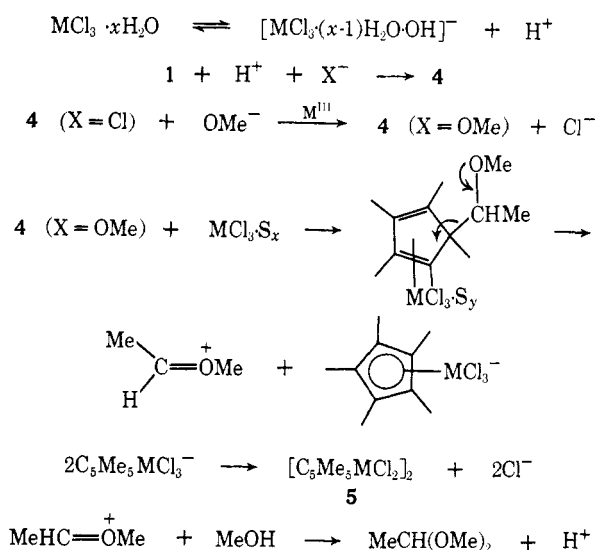
(19) L. A. Paquette, G. R. Krow, J. M. Bollinger, and G. A. Olah, *J. Am. Chem. Soc.*, **90**, 7147 (1968).

(20) R. F. Childs and S. Winstein, *ibid.*, **90**, 7146 (1968).



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 ( $\text{C}_5\text{Me}_5\text{H}$ ) itself is an intermediate in this reaction<sup>15</sup> seems unlikely since it is formed only in very low yield by prolonged action of dilute methanolic acid on **4** (X = OMe)<sup>16,11</sup> while the reactions described here give very high yields.

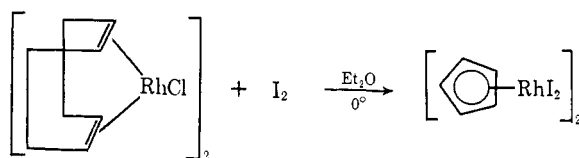
#### Scheme I



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  $(\text{MeCH}=\text{OMe})^+$  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.*,<sup>21</sup> briefly reported the reaction



(21) A. Kasahara, T. Izumi, and K. Tanaka, *Bull. Chem. Soc. Japan*, **40**, 699 (1967).

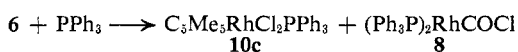
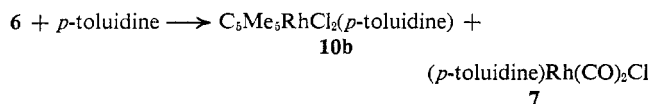
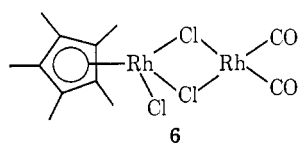
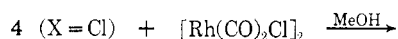
Table I. Analyses of Pentamethylcyclopentadienylrhodium and -iridium Complexes

Complex	Calcd				Analyses, %			
	C	H	Cl	Other	C	H	Cl	Other
$[\text{C}_5\text{Me}_5\text{RhCl}_2]_2$ ( <b>3</b> )	38.62	4.89	22.94	Rh, 33.30 mol wt 618	38.75	5.15	22.87	Rh, 32.91 mol wt 740 <sup>a</sup>
$[\text{C}_5\text{Me}_5\text{IrCl}_2]_2$ ( <b>5</b> , M = Ir)	30.15	3.80	17.80	mol wt 796	30.30	3.95	17.20	mol wt 780 <sup>a</sup>
$[\text{C}_5\text{Me}_5\text{RhI}_2]_2$ ( <b>11</b> )	24.42	3.09		I, 51.59 Rh, 20.29 mol wt 984	24.36	3.55		I, 51.48 Rh, 21.43 mol wt 943 <sup>a</sup>
$[\text{C}_5\text{Me}_5\text{Rh}(\text{OCOCH}_3)_2 \cdot \text{H}_2\text{O}]$ ( <b>12</b> )	44.92	6.15			45.56	6.13		
$\text{C}_5\text{Me}_5\text{RhCl}_2(\text{C}_6\text{H}_5\text{N})$ ( <b>10a</b> )	46.41	5.19	18.27	N, 3.61	46.41	5.17	18.37	N, 3.50
$\text{C}_5\text{Me}_5\text{RhCl}_2(\text{C}_7\text{H}_9\text{N})$ ( <b>10b</b> )	49.06	5.81	17.04	N, 3.36	49.02	5.87	17.24	N, 3.44
$\text{C}_5\text{Me}_5\text{RhCl}_2(\text{PPh}_3)$ ( <b>10c</b> )	58.86	5.29	12.41	P, 5.42 mol wt 571	58.49	5.27	12.21	P, 5.96 mol wt 530 <sup>a</sup>
$\text{C}_5\text{Me}_5\text{RhI}_2(\text{PPh}_3)$ ( <b>13</b> )	44.57	3.98		I, 33.69	44.54	3.95		I, 33.48
$\text{C}_5\text{Me}_5\text{IrCl}_2(\text{PPh}_3)$	50.99	4.55	10.76		50.66	4.26	11.01	
$[(\text{C}_5\text{Me}_5\text{RhCl}_2)_2(\text{diphos})]$ ( <b>17</b> )	54.35	5.35	13.95	P, 6.09	53.85	5.58	13.95	P, 6.79
$[\text{C}_5\text{Me}_5\text{RhCl}(\text{diphos})]^+\text{PF}_6^-$ ( <b>19</b> )	52.86	4.77			52.25	4.80		
$\text{C}_5\text{Me}_5\text{RhCl}_2(\text{diphos})$ ( <b>18</b> )	60.10	5.52	10.04	mol wt 707	60.71	5.52	10.23	mol wt 699 <sup>a</sup>
$\text{C}_5\text{Me}_5\text{RhI}(\text{Me})(\text{PPh}_3)$ ( <b>15</b> )	54.22	5.18		I, 19.76 mol wt 642	54.06	5.18		I, 19.80 mol wt 629 <sup>b</sup>
$\text{C}_5\text{Me}_5\text{RhMe}_2(\text{PPh}_3)$ ( <b>14</b> )	67.79	6.85		P, 5.84 mol wt 531	68.02	6.91		P, 5.84 mol wt 525 <sup>b</sup>
$\text{C}_5\text{Me}_5\text{RhCl}_3\text{Rh}(\text{CO})_2$ ( <b>6</b> )	28.68	2.99	21.07		28.23	3.01	21.51	
$\text{C}_5\text{Me}_5\text{Ir}(\text{CO})_2$ ( <b>20</b> )	37.59	3.92		mol wt 383	38.04	4.04		mol wt 370 <sup>b</sup>

<sup>a</sup> Molecular weight determined osmotically in  $\text{CHCl}_3$ . <sup>b</sup> Molecular weight determined osmotically in  $\text{C}_6\text{H}_6$ .

which appeared to involve a remarkable ring contraction. Subsequent attempts both by Kasahara<sup>22</sup> 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.

1-(1-Chloroethyl)pentamethylcyclopentadiene (**4**, X = Cl) in excess also reacted with  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  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 carbonyls (1975 and 2050  $\text{cm}^{-1}$ ) in the infrared and a singlet at  $\tau$  8.27 due to the methyl protons. The monomeric structure **6** shown is suggested but the molecular size is not known. The formula was also established by the following reactions with *p*-toluidine and triphenylphosphine which proceeded nearly quantitatively to give the known products **7**, **10b** and **8**, **10c**, respectively.



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  $(\text{C}_5\text{Me}_5\text{RhCl}_2)_2$  and  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  under a variety of conditions.

(22) Personal communication by Professor Kasahara.

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.*,  $\text{Fe}(\text{CO})_5$ ,  $\text{Co}(\text{CO})_4^-$ ,  $\text{Cr}(\text{CO})_6$ ), but so far without 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 osmotically 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  $\text{CDCl}_3$  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;<sup>23</sup> 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° did give peaks at *m/e* 237 ( $\text{C}_5\text{Me}_4\text{CH}_2\text{Rh}^+$ , corresponding to loss of HCl from  $\text{C}_5\text{Me}_5\text{RhCl}^+$ ) and 134 ( $\text{C}_5\text{Me}_4\text{CH}_2^+$ ), and confirmed that a hexamethylbenzene complex was not present.

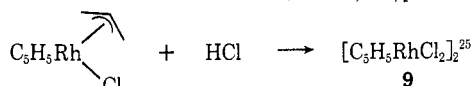
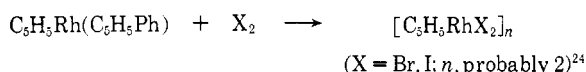
The complexes are characterized by low reactivity toward many reagents; for example, the  $\text{C}_5\text{Me}_5\text{-Rh}$  bond could not be cleaved by base, cyanide, or, apparently,

(23) R. B. King and M. B. Bisnette, *J. Organometal. Chem.*, **8**, 287 (1967).

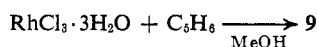
Table II. Pmr Spectra

Complex	Resonances ( $\tau$ )	
	$C_5Me_5$	Others
$[C_5Me_5RhCl_2]_2$ ( <b>3</b> )	8.40 (s)	
$[C_5Me_5RhI_2]_2$ ( <b>11</b> )	8.10 (s)	
$C_5Me_5RhCl_2(C_6H_5N)$ ( <b>10b</b> )	8.64 (s)	2.80 (d, aromatic), 5.13 (b, $NH_2$ ), 7.68 (s, Me)
$C_5Me_5RhCl_2(PPh_3)$ ( <b>10c</b> )	8.64 (d, $J_{Me-P} = 4$ cps)	2.2, 2.65 (m, aromatic)
$[(C_5Me_5RhCl_2)_2(diphos)]$ ( <b>17</b> )	8.62 (t, see Figure 1)	7.3 (b, $CH_2$ ), 2.10; 2.75 (m, aromatic)
$C_5Me_5RhCl_2(diphos)$ ( <b>18</b> )	8.47 (t, $J_{Me-P} = 3$ cps)	7.5 (b, $CH_2$ ), 2.40; 2.87 (m, aromatic)
$[C_5Me_5RhCl(diphos)]PF_6$ ( <b>19</b> )	8.51 (t, $J_{Me-P} = 3$ cps)	7.20 (b, $CH_2$ ), 2.42; 2.90 (m, aromatic)
$C_5Me_5RhMe_2PPh_3$ ( <b>14</b> )	8.60 (dd, $J_{Me-P} = 2.2$ , $J_{Me-Rh} = 0.4$ cps)	2.65 (m, aromatic), 10.18 (dd, Me, $J_{Me-P} 5.0$ , $J_{Me-Rh} = 2.5$ cps)
$C_5Me_5RhI(Me)PPh_3$ ( <b>15</b> )	8.50 (dd, $J_{Me-P} = 2.6$ , $J_{Me-Rh} = 0.4$ cps)	2.32, 2.62 (m, aromatic), 9.10 (dd, Me, $J_{Me-P} = 6.4$ , $J_{Me-Rh} = 2.4$ cps)
$C_5Me_5RhI_2PPh_3$ ( <b>13</b> )	8.23 (d, $J_{Me-P} = 4.2$ cps)	
$[C_5Me_5Rh(OAc)_2H_2O]_n$ ( <b>12</b> )	8.36 (s)	5.02 (s, $H_2O$ ), 7.99 (s, OAc)
$C_5Me_5RhCl_3Rh(CO)_2$ ( <b>6</b> )	8.27 (s)	
$[C_5Me_5IrCl_2]_2$ ( <b>5</b> , M = Ir)	8.41 (s)	
$C_5Me_5IrCl_2PPh_3$	8.66 (d, $J_{Me-P} = 2.0$ cps)	2.25, 2.65 (m, aromatic)
$C_5Me_5Ir(CO)_2$ ( <b>20</b> )	7.81 (s)	

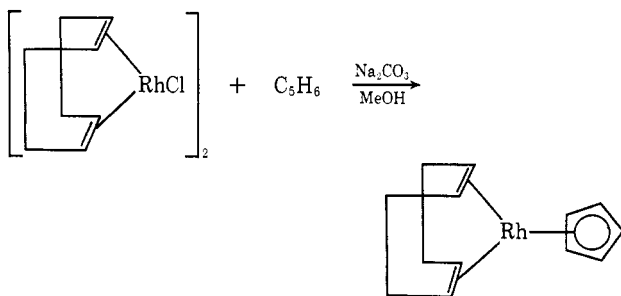
hydridic reducing agents. The products of these reactions, however, still await full characterization. The complexes are also quite stable to air both in the solid and in solution. Although the complexes described here are new, the unsubstituted cyclopentadienylrhodium halides  $[C_5H_5RhX_2]_n$  and some derivatives thereof have been mentioned by Angelici and Fischer,<sup>24</sup> Powell and Shaw,<sup>25</sup> as well as by Kasahara, *et al.*<sup>21</sup> They were made by the following routes.



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 55–60% yield by refluxing a suspension of  $RhCl_3 \cdot 3H_2O$  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 **3** was exchanged for iodide by reaction with sodium iodide in acetone to give **11**, and for acetate

(24) R. J. Angelici and E. O. Fischer, *J. Am. Chem. Soc.*, **85**, 3733 (1963).

(25) J. Powell and B. L. Shaw, *J. Chem. Soc., A*, 583 (1968).

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  $\tau$  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  $^{31}P$ .<sup>26</sup> 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  $2035\text{ cm}^{-1}$ . 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 dimethyl complex **14**. The latter was the only product from the reaction with **13**.

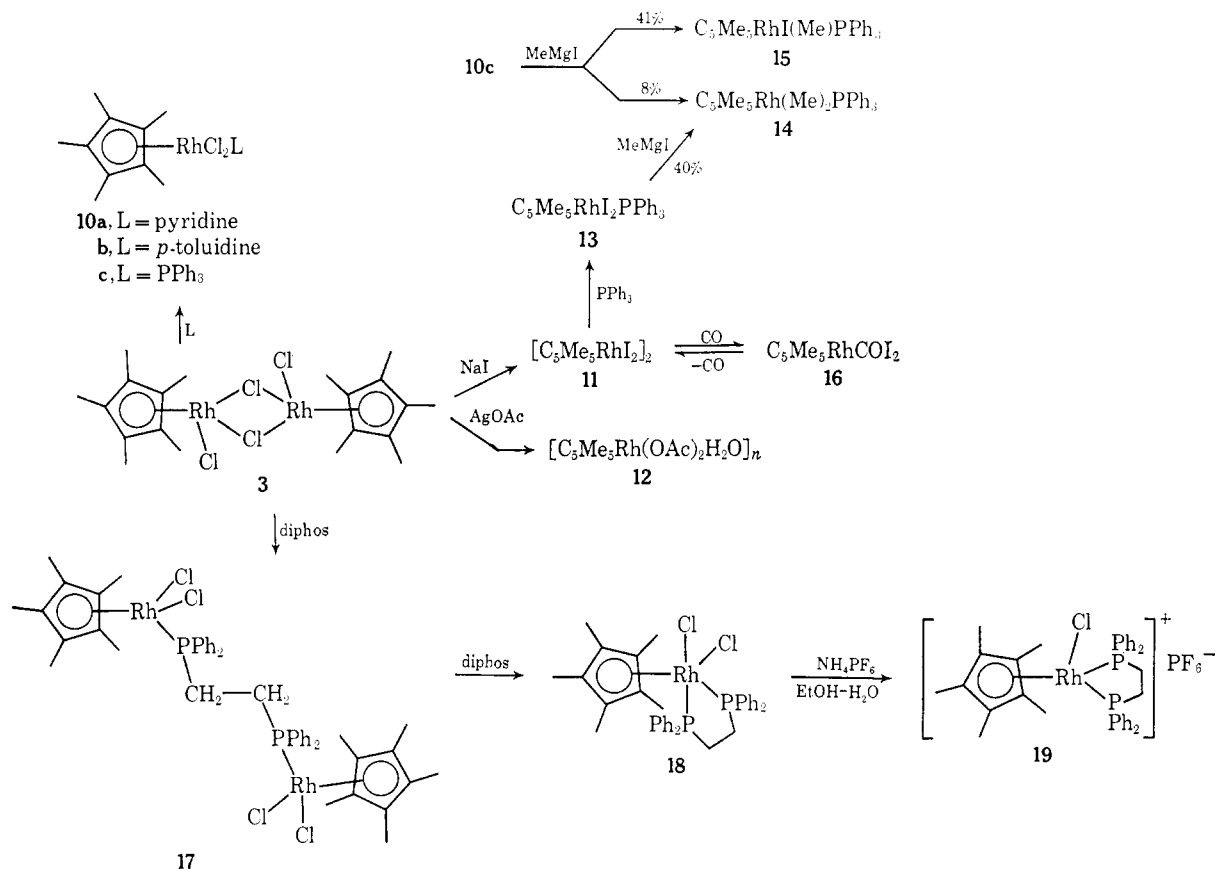
An interesting dinuclear complex **17** was obtained from reaction of 1 mole of bis(1,2-diphenylphosphino)ethane (diphos) with **3** in ethanol. The pmr spectrum was as expected for the phenyl and  $CH_2$  protons; however, the methyl protons showed an unusual pattern, believed to be caused by the magnetic inequivalence of the two  $^{31}P$  atoms to which the methyls are coupled (Figure 1).<sup>27</sup>

Complex **3** reacted with an excess of diphos to give complex **18**, which had a normal molecular weight in chloroform. If the  $C_5Me_5$  ring is assumed, as usual, to be equivalent to a tridentate ligand, then this complex

(26) Coupling of the pentamethylcyclopentadienyl protons to  $^{103}Rh$  was not observed, even at 100 Mcps, except for **9** and **10**, where it was 0.4 cps.

(27) A somewhat similar spectrum has been observed for the methyl protons of the phosphine ligand in  $[(\pi\text{-2-methylallyl})Pd(PMe_2Ph)_2]BPh_4$ .<sup>28</sup>

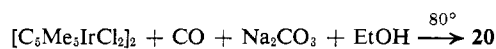
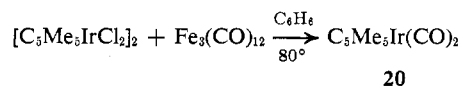
(28) J. Powell and B. L. Shaw, *J. Chem. Soc., A*, 774 (1968).



is formally seven-coordinate rhodium(III). 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 C<sub>5</sub>Me<sub>5</sub> protons appear-

ing as triplets owing to coupling to two equivalent phosphorus nuclei.

The iridium complex, [C<sub>5</sub>Me<sub>5</sub>IrCl<sub>2</sub>]<sub>2</sub>, 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 C<sub>5</sub>Me<sub>5</sub>IrCl<sub>2</sub>PPh<sub>3</sub>. The complex also reacted with Fe<sub>3</sub>(CO)<sub>12</sub> (or Fe<sub>2</sub>(CO)<sub>9</sub>) in benzene at 80° to give a 90% yield of the dicarbonyl **20** (ν<sub>CO</sub> 1925, 2000 cm<sup>-1</sup>).<sup>29</sup> This dicarbonyl is a volatile yellow solid, which is stable for a few days. No transfer of the C<sub>5</sub>Me<sub>5</sub> ligand to the iron was observed, in agreement with our other observations of the low reactivity of the C<sub>5</sub>Me<sub>5</sub>-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, C<sub>5</sub>Me<sub>5</sub>Rh(CO)<sub>2</sub>, 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 C<sub>5</sub>Me<sub>5</sub> 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<sup>-1</sup> for C<sub>5</sub>H<sub>5</sub>Ir(CO)<sub>2</sub> found by Fischer and Brenner.<sup>30</sup> The decrease in ν<sub>CO</sub> observed is presumably caused by stronger back-bonding of the C<sub>5</sub>Me<sub>5</sub> group to the iridium.

(30) E. O. Fischer and K. S. Brenner, *Z. Naturforsch.*, **17b**, 774 (1962).

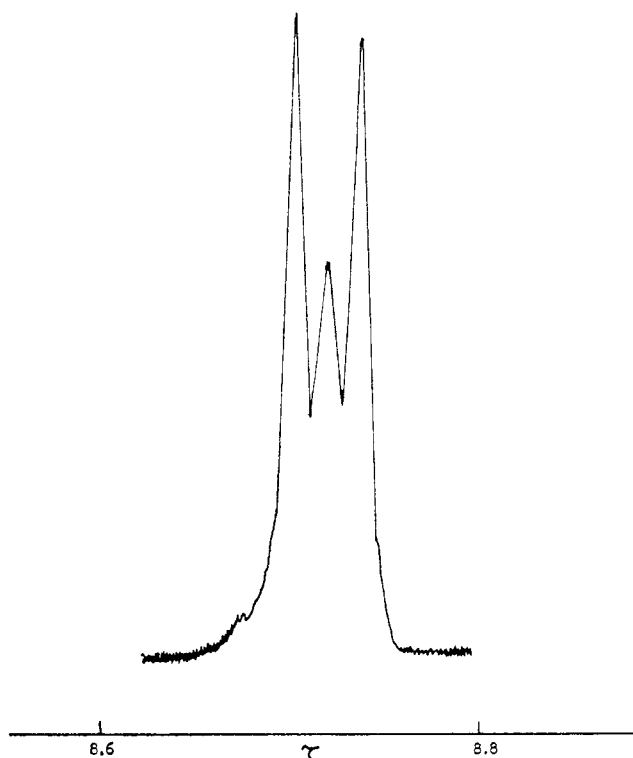


Figure 1. Pmr spectrum of [C<sub>5</sub>Me<sub>5</sub>RhCl<sub>2</sub>]<sub>2</sub>(diphos) in CDCl<sub>3</sub> in the methyl region.

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  $C_5Me_5$  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 337G or a Beckman IR 5 spectrometer.

Pmr spectra were measured in  $CDCl_3$  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-P<sub>3</sub> instruments using Carbowax columns. Mass spectra were measured on a Hitachi Perkin-Elmer RMU-6A spectrometer.

1-(1-Chloroethyl)- and 1-(1-methoxyethyl)-pentamethylcyclopentadiene were prepared as described by Paquette and Krow<sup>16</sup> and by Criegee and Grüner.<sup>11</sup> 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 Grüner but not with those of Paquette and Krow. They are as follows:  $\tau$  5.87 (1 H, q,  $J_{H-Me} = 6.5$  cps), 8.12 (3 H, s, bd), 8.26 (6 H, m), 8.31 (3 H, bd), 8.90 (3 H, s), and 8.97 (3 H, d,  $J_{Me-H} = 6.5$  cps) for **4** (X = Cl), and  $\tau$  6.67 (3 H, s), 6.80 (1 H, q,  $J_{H-Me} = 6.5$  cps), 8.27 (12 H, m), 8.98 (3 H, s), and 9.38 (3 H, d,  $J_{Me-H} = 6.5$  cps) for **4** (X = OMe).

$RhCl_3 \cdot 3H_2O$  and  $IrCl_3 \cdot 5H_2O$  were commercial samples supplied by Johnson, Matthey, and Mallory.

**Dichloropentamethylcyclopentadienylrhodium Dimer (3). Reaction of Hexamethyl(Dewar benzene) with  $RhCl_3 \cdot 3H_2O$  in Methanol.** A mixture of  $RhCl_3 \cdot 3H_2O$  (1 g) and hexamethyl(Dewar benzene) (HMDB, 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 and evaporated under reduced pressure, and the residue was recrystallized from chloroform-benzene to give 1.10 g (93%, based on  $RhCl_3 \cdot 3H_2O$ ) of  $[C_5Me_5RhCl_2]_2$  as dark red crystals, mp >230°.

The complex was soluble in chloroform, moderately soluble in methanol, ethanol, methylene chloride, and tetrahydrofuran, but insoluble in carbon tetrachloride and hydrocarbons. The complex showed bands at 243, 281, and 456  $cm^{-1}$ , consistent with the presence of bridging and terminal chlorines.<sup>21</sup>

The ethereal solution was evaporated under reduced pressure and the residue was 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  $CO_2$ -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  $RhCl_3 \cdot 3H_2O$ , 3 g of HMDB, and 20 ml of methanol were allowed to react for 24 hr was analyzed quantitatively for the acetal by vpc. The distillate was found to contain between 40 and 50  $\mu l$  of dimethylacetal/ml compared to an expected value of 40  $\mu l$ /ml.

**Reaction of  $RhCl_3 \cdot 3H_2O$  with Hexamethyl(Dewar benzene) in Water.** To a solution of  $RhCl_3 \cdot 3H_2O$  (200 mg) in 5 ml of distilled water at 90° was added HMDB (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  $[C_5Me_5RhCl_2]_2$  as dark red crystals.

The pmr spectrum of this material was identical with that of a sample as prepared above.

Vpc analysis of the aqueous distillate on a Carbowax column showed the presence only of acetaldehyde. This was confirmed by measurement of the pmr and mass spectra of the material.

**Reaction of  $RhCl_3 \cdot 3H_2O$  with 1-(1-Chloroethyl)pentamethylcyclopentadiene (4, X = Cl).** A solution of  $RhCl_3 \cdot 3H_2O$  (2 g) and 1-(1-chloroethyl)pentamethylcyclopentadiene (2 g) in 30 ml of methanol was stirred under nitrogen at 65° for 5 hr. The reaction mixture was worked up as described above to give 2.10 g (92%) of  $[C_5Me_5RhCl_2]_2$ .

Vapor phase chromatography of the methanol distillate again showed that dimethylacetal was the other volatile product of the reaction.

**Reaction of  $RhCl_3 \cdot 3H_2O$  with 1-(1-Methoxyethyl)pentamethylcyclopentadiene (4, X = OMe).** The reaction of  $RhCl_3 \cdot 3H_2O$  (2 g) and 1-(1-methoxyethyl)pentamethylcyclopentadiene (2 g) was performed in the same way as described above. It yielded 1.25 g (55%) of  $[C_5Me_5RhCl_2]_2$  and dimethylacetal was again the volatile product.

**Dichloropentamethylcyclopentadienyliridium Dimer (5, M = Ir). Reaction of  $IrCl_3 \cdot 5H_2O$  with HMDB.** A mixture of  $IrCl_3 \cdot 5H_2O$  (500 mg) and HMDB (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  $[C_5Me_5IrCl_2]_2$  as orange crystals, mp >230° dec, and 800 mg of HMB. The properties of the complex are very similar to those of  $[C_5Me_5RhCl_2]_2$ .

**Reaction of  $IrCl_3 \cdot 5H_2O$  with 1-(1-Chloroethyl)pentamethylcyclopentadiene. Method A.** A solution of  $IrCl_3 \cdot 5H_2O$  (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 cool to room temperature. The orange 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  $[C_5Me_5IrCl_2]_2$ . The filtrate was evaporated under reduced pressure and the residue was washed with ether to give another 160 mg of crude  $[C_5Me_5IrCl_2]_2$ , 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.

**Method B.** Hydrogen chloride gas was bubbled into the solution of HMDB (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  $IrCl_3 \cdot 5H_2O$  (2 g) in 30 ml of methanol and the reaction was carried out in the manner outlined in method A to give 1.82 g (89%) of  $[C_5Me_5IrCl_2]_2$ .

**Dichloro(pyridine)pentamethylcyclopentadienylrhodium (10a).** To a suspension of  $[C_5Me_5RhCl_2]_2$  (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 reverts back to  $[C_5Me_5RhCl_2]_2$  in these solvents.

**Dichloro(*p*-toluidine)pentamethylcyclopentadienylrhodium (10b).** A solution of  $[C_5Me_5RhCl_2]_2$  (300 mg, 0.48 mmole) and *p*-toluidine (600 mg, 5.6 mmoles) 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 (86%) of pure *p*-toluidine adduct. Although the *p*-toluidine adduct in the solid state is stable, it is unstable in solution and affords starting material.

**Dichloro(triphenylphosphine)pentamethylcyclopentadienylrhodium (10c).** A suspension of  $[C_5Me_5RhCl_2]_2$  (300 mg, 0.48 mmole) and triphenylphosphine (300 mg, 1.14 mmoles) in 20 ml of ethanol was refluxed under nitrogen for 5 hr, then allowed to cool; the reddish 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 >230°.

(31) M. A. Bennett, R. J. H. Clark, and D. L. Milner, *Inorg. Chem.*, **6**, 1647 (1967).

**Bis(1,2-diphenylphosphino)ethanebis(dichloropentamethylcyclopentadienylrhodium) (17).** A suspension of  $[\text{C}_5\text{Me}_5\text{RhCl}_2]_2$  (300 mg, 0.48 mmole) and bis(1,2-diphenylphosphino)ethane (200 mg, 0.50 mmole) in 50 ml of ethanol was refluxed with stirring under nitrogen for 2 hr. The red solution was filtered, concentrated to ca. 10 ml under vacuum, and allowed to stand at room temperature overnight. The red crystals were collected on a filter and dried *in vacuo* to yield 400 mg of the pure adduct 17, mp 235–238° dec.

The filtrate was evaporated under vacuum and the residue was washed with hot hexane to afford 75 mg of the crude product; the total yield of 17 was 475 mg (95%).

**Dichloro[bis(1,2-diphenylphosphino)ethane]pentamethylcyclopentadienylrhodium (18).** A suspension of  $[\text{C}_5\text{Me}_5\text{RhCl}_2]_2$  (300 mg, 0.48 mmole) and bis(1,2-diphenylphosphino)ethane (1 g, 2.50 mmoles) in 50 ml of ethanol was refluxed with stirring under nitrogen for 5 hr. The orange-red solution was filtered, the solvent removed *in vacuo*, and the residue washed with warm benzene and dried in air. Recrystallization of the crude product from chloroform–benzene afforded 640 mg (93%) of the pure product as orange-yellow crystals, mp 213–215° dec.

A solution of ammonium hexafluorophosphate (200 mg) in 10 ml of water was added to  $\text{C}_5\text{Me}_5\text{Rh}(\text{diphos})\text{Cl}_2$  (200 mg) in 10 ml of ethanol. Immediate precipitation of the yellow  $[\text{C}_5\text{Me}_5\text{Rh}(\text{diphos})\text{Cl}]\text{PF}_6$  salt (19) occurred; this was filtered off, washed with water, and dried *in vacuo*; yield 210 mg (95%) of analytically pure material, mp >250°.

**Diiodopentamethylcyclopentadienylrhodium Dimer (11).** A suspension of  $[\text{C}_5\text{Me}_5\text{RhCl}_2]_2$  (200 mg, 0.32 mmole) and sodium iodide (500 mg, 3.3 mmoles) in 30 ml of acetone was refluxed with stirring under nitrogen for 3 hr. After the reaction mixture was cooled, the dark purple crystals were collected on a filter, washed with water, a small amount of acetone, and ether, and dried in air to yield 260 mg (81%) of the iodo complex. Recrystallization of the iodo complex from chloroform–methanol afforded 245 mg of pure product, mp >230°. It is moderately soluble in chloroform and methylene chloride and slightly soluble in acetone and benzene.

**Diiodo(triphenylphosphine)pentamethylcyclopentadienylrhodium (13).** A mixture of  $[\text{C}_5\text{Me}_5\text{RhI}_2]_2$  (500 mg, 0.52 mmole) and triphenylphosphine (1 g, 3.81 mmoles) in 30 ml of acetone was refluxed with stirring under nitrogen for 5 hr. The reaction mixture was cooled and the crystalline product which had precipitated was filtered, washed with acetone, and dried to give 720 mg (94%) of pure  $\text{C}_5\text{Me}_5\text{RhI}_2\text{PPh}_3$  as dark violet crystals, mp >230°.

**Reaction of  $[\text{C}_5\text{Me}_5\text{RhI}_2]_2$  with Carbon Monoxide.** Carbon monoxide was bubbled into a well-stirred suspension of  $[\text{C}_5\text{Me}_5\text{RhI}_2]_2$  (300 mg) in 25 ml of benzene at 80° for 3 hr. The dark violet solution was filtered and the solvent was removed under reduced pressure. Recrystallization of the residue from benzene afforded 300 mg of  $\text{C}_5\text{Me}_5\text{Rh}(\text{CO})\text{I}_2$  (16) as dark violet crystals.

The complex was unstable in the solid state, but even more so in solution and decomposed rapidly to give  $[\text{C}_5\text{Me}_5\text{RhI}_2]_2$ . The infrared spectrum of the complex (16) showed an absorption at 2035  $\text{cm}^{-1}$  which is assigned to a terminal carbonyl group.

**Dimethyl(triphenylphosphine)pentamethylcyclopentadienylrhodium (14).** To a solution of methylmagnesium iodide (from methyl iodide (2 g) and magnesium (340 mg)) in 50 ml of dry ether was added  $\text{C}_5\text{Me}_5\text{RhI}_2\text{PPh}_3$  (500 mg) with stirring at 0° under nitrogen. The reaction mixture was stirred at 0° for 2 hr. The excess Grignard reagent was hydrolyzed with aqueous ammonium chloride and the mixture was filtered. The ethereal solution was washed with water and dried over anhydrous sodium sulfate. After the solvent was removed *in vacuo*, the residue was dissolved in benzene and chromatographed on Florisil with benzene as eluent. The yellow fraction was collected and the solvent was evaporated under vacuum. Recrystallization of the residue from ether at –20° afforded 142 mg (40%) of the pure product as yellow crystals, mp 184–186° dec.

**Iodo(methyl)(triphenylphosphine)pentamethylcyclopentadienylrhodium (15).** To a solution of methylmagnesium iodide (from methyl iodide (2 g) and magnesium (340 mg)) in 50 ml of dry ether at 0° under nitrogen was added  $\text{C}_5\text{Me}_5\text{RhCl}_2\text{PPh}_3$  (500 mg) with stirring. The reaction mixture was stirred at 0° for 2 hr. The excess Grignard reagent was hydrolyzed with aqueous ammonium chloride and the mixture was filtered. The ethereal solution was washed with water and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue extracted with petroleum ether. Recrystallization of the crude product from the excess ether afforded 595 mg (41%) of the pure complex 15 as reddish brown crystals, mp 110–115° dec.

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  $\text{C}_5\text{Me}_5\text{Rh}(\text{CH}_3)_2\text{PPh}_3$  as yellow crystals.

**Diacetato(pentamethylcyclopentadienyl)rhodium Hydrate  $[\text{C}_5\text{Me}_5\text{Rh}(\text{OAc})_2\text{H}_2\text{O}]_n$  (12).** A suspension of  $[\text{C}_5\text{Me}_5\text{RhCl}_2]_2$  (200 mg) and silver acetate (2.16 g) in 30 ml of benzene was refluxed under nitrogen with stirring for 3 hr. The mixture was cooled and 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 (79%) of pure  $[\text{C}_5\text{Me}_5\text{Rh}(\text{OAc})_2\cdot\text{H}_2\text{O}]_n$ , mp 143–145° dec.

The presence of coordinated water was confirmed by the pmr spectrum which showed singlets at  $\tau$  5.02 ( $\text{H}_2\text{O}$ ), 7.99 (acetate), and 8.36 (methyls) in the ratio of 2.1:6.2:1.8.

**Preparation of  $\text{C}_5\text{Me}_5\text{RhCl}_2\text{Rh}(\text{CO})_2$  (6).** A mixture of  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  (300 mg) and 1-(1-chloroethyl)pentamethylcyclopentadiene (1 g) in 20 ml of methanol was stirred at 65° under nitrogen for 2 hr. After cooling to room temperature, the solvent was removed under pressure. The residue was washed with ether and then the insoluble reddish 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  $[\text{Me}_5\text{C}_5\text{RhCl}_2]_2$  and rhodium metal.

**Reaction of  $\text{C}_5\text{Me}_5\text{RhCl}_2\text{Rh}(\text{CO})_2$  with  $\text{PPh}_3$ .** A suspension of  $\text{C}_5\text{Me}_5\text{Rh}_2\text{Cl}_2(\text{CO})_2$  (100 mg, 0.19 mmole) in 20 ml of benzene containing triphenylphosphine (300 mg, 1.10 mmoles) was stirred at room temperature for 1 hr. Reaction immediately occurred with the evolution of gas ( $\text{CO}$ ) and a brick-red solid precipitated. The reaction mixture was then heated at 80° for a few minutes and cooled; the brick-red crystals were collected on a filter, washed with benzene and ether, and then dried in air to give 95 mg (90%, based on  $\text{C}_5\text{Me}_5\text{RhCl}_2\text{Rh}(\text{CO})_2$ ) of  $\text{C}_5\text{Me}_5\text{RhCl}_2\text{PPh}_3$  (10c).

The filtrate was evaporated under reduced pressure to give a yellow solid. Recrystallization of the yellow solid from benzene–methanol afforded 120 mg (90%, based on  $\text{C}_5\text{Me}_5\text{RhCl}_2\text{Rh}(\text{CO})_2$ ) of  $(\text{Ph}_3\text{P})_2\text{RhCOCl}$ . These complexes were identified by comparison of their pmr and infrared spectra with those of authentic specimens.

**Reaction of  $\text{C}_5\text{Me}_5\text{RhCl}_2\text{Rh}(\text{CO})_2$  with *p*-Toluidine.** *p*-Toluidine (340 mg) was added to a suspension of  $\text{C}_5\text{Me}_5\text{RhCl}_2\text{Rh}(\text{CO})_2$  (100 mg) in 10 ml of benzene and stirred at 25° for 3 hr. The red solid was then collected on a filter, washed with ether, and dried to give 80 mg (100%) of  $\text{C}_5\text{Me}_5\text{RhCl}_2(p\text{-toluidine})$  (10b), identical with an authentic sample. The combined filtrates were concentrated to 10 ml and hexane was added to precipitate the orange crystalline  $\text{Rh}(\text{CO})_2\text{Cl}(p\text{-toluidine})$  (7). This was filtered, washed with hexane, and dried to yield 65 mg (100%). The complex was identical with an authentic sample.

**Dichloro(triphenylphosphine)pentamethylcyclopentadienyliridium.** A suspension of  $[\text{C}_5\text{Me}_5\text{IrCl}_2]_2$  (300 mg, 0.4 mmole) and triphenylphosphine (300 mg, 1.14 mmoles) in 20 ml of ethanol was refluxed under nitrogen for 2 hr. After cooling to the room temperature, the orange crystals deposited were collected on a filter and washed with ethanol and ether to yield 410 mg (82%) of the analytically pure product, mp >230°.

**Dichloro(cyclopentadienyl)rhodium Dimer (9).** A mixture of  $\text{RhCl}_3\cdot 3\text{H}_2\text{O}$  (1 g) and freshly distilled cyclopentadiene (1 g) in 30 ml of methanol was refluxed under nitrogen with stirring for 15 hr. After cooling, the brick solid was collected on a filter, washed with methanol and ether, and air dried to give 540 mg of  $[\text{C}_5\text{Rh}_2\text{Cl}_2]_2$  (60% based on  $\text{RhCl}_3\cdot 3\text{H}_2\text{O}$ ). This complex could not be recrystallized because of its total insolubility in common organic solvents and water.

**(1,5-Cyclooctadiene)(cyclopentadienyl)rhodium.** A mixture of chloro(1,5-cyclooctadiene)rhodium dimer (200 mg), anhydrous sodium carbonate (200 mg), and freshly distilled cyclopentadiene (500 mg) in 20 ml of methanol was stirred at 60° for 5 hr. The reaction mixture was then cooled and filtered and the solvent removed *in vacuo*. The residue was extracted with ether, the ether removed, and the yellow product sublimed at 60° ( $10^{-2}$  mm) to give 400 mg (88%) of (1,5-cyclooctadiene)(cyclopentadienyl)rhodium, mp 107–108° dec (lit.<sup>32</sup> mp 108–108.5°). The pmr spectrum showed resonances at  $\tau$  4.83 (5 H, s), 6.03 (4 H, bd), and 7.92 (8 H, bd).

**Dicarbonyl(pentamethylcyclopentadienyl)iridium (20).** A suspension of  $[\text{C}_5\text{Me}_5\text{IrCl}_2]_2$  (300 mg) and  $\text{Fe}_3(\text{CO})_{12}$  (300 mg) in 100 ml of

(32) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).

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  $C_5Me_5Ir(CO)_2$ , mp 145–148° dec. This compound is very soluble in organic solvents and could also be sublimed at 50° (10<sup>-2</sup> mm). It is air stable for a few days. The infrared spectrum shows strong  $\nu_{CO}$  at 1925 and 2000 cm<sup>-1</sup>.

It could also be prepared from  $[C_5Me_5IrCl_2]_2$  and  $Fe_2(CO)_9$ , and as follows. Carbon monoxide was bubbled into the suspension of  $[C_5Me_5IrCl_2]_2$  (100 mg) and anhydrous sodium carbonate (50 mg) in 30 ml of ethanol with stirring at 70° 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° (10<sup>-2</sup> mm); yield 65 mg (62%) of  $C_5Me_5Ir(CO)_2$ .

Attempts to prepare  $C_5Me_5Rh(CO)_2$  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, Tetradentate Schiff Base Chelates of Copper (II)<sup>1</sup>

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**Abstract:** The circular dichroism (CD) and electronic absorption spectra of a series of nine copper(II) complexes with tetradentate Schiff bases derived from (*R*)-(-)-propane-1,2-diamine and (*RR*)-(-)-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 (*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.<sup>2</sup> In addition, the sensitivity of circular dichroism to molecular structure makes the technique valuable for investigating the conformations and configurations of chelate molecules.<sup>3</sup>

The majority of previous investigations of optically active complexes have dealt with the inert, dihedral chelates of d<sup>3</sup> and d<sup>6</sup> metal ions.<sup>2</sup> The study of complexes in which the optical activity is induced by means of active ligands, however, is also of great interest.<sup>3</sup> Several important studies of this type have appeared,<sup>4-7</sup> 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.<sup>8</sup> 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,<sup>9</sup> 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,<sup>10-12</sup> similar to the octant rule<sup>8</sup> for the carbonyl group.

Since the initial study<sup>13</sup> of the optical rotatory dispersion (ORD) of chelates of the type described here,

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