

- (7) F. A. Cotton and F. Zingales, *Chem. Ind. (London)*, 1219 (1960).
- (8) E. W. Abel and B. C. Crosse, *Organomet. Chem. Rev.*, **2**, 443 (1967).
- (9) G. C. Farber and G. R. Dobson, *J. Chem. Soc. A*, 317 (1966).
- (10) G. R. Dobson and L. W. Houk, *Inorg. Chim. Acta*, **1**, 287 (1967).
- (11) W. Strohmeier and J. F. Guttenberger, *Chem. Ber.*, **97**, 1871 (1964).
- (12) Repeated attempts to isolate pure  $\eta^5\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2(\text{SPh}_2)$  were unsuccessful, as Strohmeier and Guttenberger<sup>11</sup> also found. However, when the reaction mixture from  $\eta^5\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3$  and  $\text{SPh}_2$  was concentrated and cooled to  $-78^\circ$ , a dark red-brown oil separated at the bottom of the Schlenk tube. This oil was redissolved in methylcyclohexane and the resulting solution was used in the subsequent kinetic studies.
- (13) W. Strohmeier and C. Barbeau, *Z. Naturforsch., Teil B*, **17**, 848 (1962).
- (14) W. Strohmeier and F.-J. Muller, *Chem. Ber.*, **100**, 2812 (1967).
- (15) R. J. Angelici and W. Loewen, *Inorg. Chem.*, **6**, 682 (1967).
- (16) Owing to the extremely fast reaction of  $\eta^5\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2(\text{SPh}_2)$  with  $\text{P}(\text{O}-n\text{-Bu})_3$ , the rates for this reaction were determined at  $75.0\text{--}85.0^\circ$  rather than  $85.0\text{--}95.0^\circ$  as was the case for the other reactions studied.
- (17) P. S. Braterman and J. D. Black, *J. Organomet. Chem.*, **39**, C3 (1972).
- (18) I. S. Butler and T. Sawai, unpublished results.
- (19) A. Garcia-Rodriguez, M.Sc. Thesis, McGill University, 1974.

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## Pentachlorocyclopentadienyl Derivatives of Manganese and Rhodium

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Reaction of diazotetrachlorocyclopentadiene, I, with di- $\mu$ -chloro-bis(1,5-cyclooctadienylrhodium),  $[\text{RhCl}(1,5\text{-C}_8\text{H}_{12})_2]_2$ , gives high yields of ( $\eta^5$ -pentachlorocyclopentadienyl)(1,5-cyclooctadiene)rhodium,  $\text{Rh}(\eta^5\text{-C}_5\text{Cl}_5)(\text{COD})$ , II. A similar reaction between I and pentacarbonylchloromanganese,  $\text{MnCl}(\text{CO})_5$ , gave two products: pentacarbonyl( $\eta^1$ -pentachlorocyclopentadienyl)manganese,  $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5$ , III, and tricarbonyl( $\eta^5$ -pentachlorocyclopentadienyl)manganese,  $\text{Mn}(\eta^5\text{-C}_5\text{Cl}_5)(\text{CO})_3$ , IV. III is the first transition metal complex containing a  $\eta^1\text{-C}_5\text{Cl}_5$  ring and for which there is no analog in  $\text{C}_5\text{H}_5\text{-Mn}$  chemistry. These compounds and other polychloro-substituted cyclopentadienyl complexes have been characterized by infrared, Raman,  $^{13}\text{C}$  nuclear magnetic resonance, and  $^{35}\text{Cl}$  nuclear quadrupole resonance spectroscopy. Qualitative results from investigations into the mechanism of the insertion reactions of diazocyclopentadienes into manganese-halogen bonds are discussed.

The vast and rapid development of the chemistry of cyclopentadienylmetal compounds was aided by their convenient preparation using a variety of methods. However, the synthesis of pentasubstituted-cyclopentadienyl complexes, no less potentially interesting, has presented problems. In the past few years some of these problems have been solved and sound preparative routes to pentamethylcyclopentadienyl derivatives, for example, have been found. These efforts have been rewarded by new structures and reactivity imparted to the complexes by pentamethyl substitution. Recently pentachlorocyclopentadienyl complexes have attracted attention; the presence of five electronegative groups would be expected to modify the bonding and chemistry of the complexes in new and exciting ways.

The first of such compounds, decachloroferrocene and decachlororuthenocene were obtained by repetitive metalation exchange-halogenation reactions.<sup>2,3</sup> These showed a very high resistance to oxidation and also some interesting structural features.<sup>4</sup> Unsubstituted cyclopentadienyl complexes are conveniently prepared by the reactions of alkali metal, Grignard, or thallium derivatives of  $\text{C}_5\text{H}_5^-$  with transition metal compounds.<sup>5</sup> Although  $\text{LiC}_5\text{Cl}_5$ <sup>6</sup> and the corresponding Grignard reagent have been known for some time, attempts to use them as reagents for the preparation of transition metal-pentachlorocyclopentadienyl complexes have been unsuccessful.<sup>3,7</sup> More recently salts of the  $\text{C}_5\text{Cl}_5^-$  anion with large cations such as  $\text{Tl}^+$ ,  $(\text{C}_4\text{H}_9)_4\text{P}^+$ , and  $(\text{C}_2\text{H}_5)_3\text{NH}^+$  were isolated.<sup>8,9</sup> These were found to be thermally unstable, decomposing in the solid above  $-15^\circ$  and in solution at  $-30^\circ$ . For example,  $\text{TlC}_5\text{Cl}_5$  "ignites spontaneously at  $-15^\circ$  in air or in nitrogen atmosphere with emission of orange light but without violence".<sup>8</sup> All attempts to effect reaction of these compounds with transition metal halides to give perchlorocyclopentadienyl complexes failed. However, thallium pentachlorocyclopentadienide proved to be a useful reagent in the synthesis of a series of  $\sigma$ -bonded mercurial derivatives of the type  $\text{Hg}(\eta^1\text{-C}_5\text{Cl}_5)_2$  and  $\text{Hg}(\eta^1\text{-C}_5\text{Cl}_5)\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{Ph}$ ).<sup>9,10</sup>

We have reported that reactions of diazocyclopentadiene with dihalo-bridged rhodium dimers such as  $[\text{RhCl}(1,5\text{-C}_8\text{H}_{12})_2]_2$  or with manganese pentacarbonyl halides give halo-substituted cyclopentadienyl complexes.<sup>11</sup> Since 2,3,4,5-tetrachlorodiazocyclopentadiene, I, is known, a logical extension of these insertion reactions was to investigate the suitability of this compound as a reagent for the preparation of pentachlorocyclopentadienyl complexes. This has been carried out with some success. We report here the facile high-yield syntheses of some derivatives of  $\text{C}_5\text{Cl}_5^-$  including  $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5$ , the first transition metal complex in which the  $\text{C}_5\text{Cl}_5^-$  ligand is  $\sigma$  bonded. A preliminary communication has appeared.<sup>12</sup>

**Experimental Section**

Inert-atmosphere techniques were used in the synthesis of all new compounds described. Nitrogen gas (Liquid Carbonic, "Hi pure") was used without further purification. All solvents although of "spectroquality", were dried over molecular sieves (BDH, Type 5A) and were vacuum degassed or purged with nitrogen before use.

Infrared spectra were recorded on a Perkin-Elmer Model 621 grating spectrophotometer. For typical spectra, calibration was accomplished using the  $1602\text{-cm}^{-1}$  peak of polystyrene. For accurate determination of carbonyl stretching frequencies the instrument was run on expanded scale (ca.  $1\text{ cm}^{-1}/\text{mm}$  of chart paper). Each spectrum was calibrated by recording the spectrum of indene<sup>13</sup> in the region  $2300\text{--}1900\text{ cm}^{-1}$  before the sample was run. Reported values of  $\nu(\text{C}=\text{O})$  are probably accurate to  $\pm 1\text{ cm}^{-1}$ .

Raman spectra were obtained from crystalline samples using a Spex Model 1400 spectrometer. The  $5146\text{-\AA}$  line of the argon laser was employed, and a cooled, spinning-cell technique was required to avoid thermal decomposition of the compounds. Nuclear quadrupole resonance spectra were recorded on a Decca Radar NQR spectrometer at  $77^\circ\text{K}$ .

$^1\text{H}$  NMR spectra were run on a Varian Associates HA-100 spectrometer at  $100\text{ MHz}$  with tetramethylsilane as an internal reference-lock signal. The  $^{13}\text{C}$  NMR spectra were obtained using a Varian XL-100-15 spectrometer operating in the pulsed Fourier transform mode at  $25.2\text{ MHz}$ . Chemical shifts were measured in dichloromethane solution relative to the internal  $\text{CD}_2\text{Cl}_2$  solvent resonance and are reported in ppm downfield (positive) from TMS using the conversion  $\delta_{\text{TMS}} = \delta_{\text{CD}_2\text{Cl}_2} + 53.61\text{ ppm}$ .

The authors wish to express their gratitude to the following people for their generous assistance in performing several of the spectroscopic

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Molecular weights were determined either in benzene solution using a Hitachi Perkin-Elmer Model 115 molecular weight apparatus or by mass spectrometry from parent ion peaks. The latter were measured on spectra obtained from a Varian M-66 mass spectrometer.

Melting points were obtained in air using a Thomas-Hoover "unimelt" capillary melting point apparatus and are uncorrected.

Analyses were performed by Alfred Bernhardt, Elbach über Engelskirchen, West Germany, or Spang Microanalytical Laboratory, Ann Arbor, Mich.

The following chemicals were obtained commercially and were sufficiently pure for immediate use:  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  from Alfa Inorganics and Johnson, Matthey and Mallory, and hexachlorocyclopentadiene from K & K Laboratories Inc. The following compounds were prepared by published procedures:  $[\text{RhCl}(\text{COD})]_2$ ,<sup>14</sup>  $[\text{RhBr}(\text{COD})]_2$ ,<sup>14</sup>  $[\text{RhCl}(\text{CO})_2]_2$ ,<sup>15</sup>  $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ ,<sup>16</sup>  $\text{MnH}(\text{CO})_5$ ,<sup>17</sup> and  $\text{MnX}(\text{CO})_5$  where  $\text{X} = \text{Cl}$ ,<sup>11b</sup>  $\text{Br}$ ,<sup>17</sup> and  $^{11b}$  and  $[\text{MnCl}(\text{CO})_4]_2$ .<sup>18</sup>

The synthesis of  $\text{C}_5\text{Cl}_4\text{N}_2$  follows the series of reactions



The preparation of 2,3,4,5-tetrachlorodiazocyclopentadiene hydrazone has been reported in the patent literature<sup>19</sup> and elsewhere.<sup>20,21</sup> The synthesis presented here represents a considerable modification of previous methods and provides a convenient route to reasonable yields of this compound in a high degree of purity. A variety of reagents, such as mercury(II) oxide,<sup>20</sup> sodium hypochlorite,<sup>21</sup> and silver oxide<sup>22</sup> have been used for the oxidation of the hydrazone, but only the latter was used in this work. This preparation of  $\text{C}_5\text{Cl}_4\text{N}_2$  was used with some minor alterations.

**2,3,4,5-Tetrachlorodiazocyclopentadiene Hydrazone,  $\text{C}_5\text{Cl}_4\text{NNH}_2$ .** Hydrazine hydrate (29.4 ml, 30.32 g, 0.61 mol) was added slowly to a cooled ( $0^\circ$ ) solution of hexachlorocyclopentadiene (16 ml, 27.3 g, 0.10 mol) in 200 ml of methanol. The solution immediately turned dark red. The mixture was stirred for 5 days at  $5^\circ$  during which time a red solid collected on the walls of the flask. The mixture was poured onto 5 l. of water and filtered. The solid was air-dried, dissolved in ether, and filtered. The filtrate was evaporated to dryness and the residue was extracted with cyclohexane on a Soxhlet extractor. The solution was concentrated and cooled, and the red-brown crystals were filtered off. Additional product could be obtained by washing the material remaining in the thimble with water and extracting again with cyclohexane; total yield 15 g (65%).

**2,3,4,5-Tetrachlorodiazocyclopentadiene,  $\text{C}_5\text{Cl}_4\text{N}_2$ .** Silver oxide (28.3 g, 0.122 mol),<sup>23</sup>  $\text{C}_5\text{Cl}_4\text{NNH}_2$  (11.32 g, 0.049 mol), and anhydrous magnesium sulfate (2–3 g) were placed in a 500-ml erlenmeyer flask and 125 ml of ether was added. The stopper was secured with an elastic band and the flask wrapped with a wet towel to counteract the heat evolved in the early stages of the reaction. The mixture was then agitated on a mechanical shaker for 20 hr (stirring with a magnetic stir bar proved inadequate). The mixture was filtered and the filtrate evaporated to dryness. The residue was recrystallized from boiling methanol to give 8.8 g (78%) of orange needles. Recrystallization from methanol rather than the reported chromatography was found to be a more convenient purification step. If kept in the dark and under nitrogen,  $\text{C}_5\text{Cl}_4\text{N}_2$  may be stored at room temperature unchanged<sup>23</sup> for several months.

**Pentacarbonyl( $\eta^1$ -pentachlorocyclopentadienyl)manganese,  $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5$ .** Eighty milliliters of degassed pentane was added to a mixture of  $\text{MnCl}(\text{CO})_5$  (1.0 g, 4.35 mmol) and  $\text{C}_5\text{Cl}_4\text{N}_2$  (1.0 g, 4.35 mmol) in a nitrogen-filled 100-ml two-necked flask. The flask was closed and the mixture was stirred for 24 hr at room temperature. The mixture was then filtered and cooled to  $-78^\circ$  overnight. During this time large cubic yellow crystals were formed. The solution was removed by means of a syringe and the crystals (0.99 g) were dried first in a nitrogen stream and then briefly in vacuo. Infrared analysis indicated that this crop contained mainly  $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5$  but it was contaminated with a small amount of  $\text{Mn}(\eta^5\text{-C}_5\text{Cl}_5)(\text{CO})_3$ . Recrystallization from pentane by slow cooling of a saturated solution to  $-20^\circ$  gave 0.91 g (48% yield) of pure  $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5$ .

The mother liquor was concentrated to  $\sim 50\%$  of its volume and cooled to  $-78^\circ$  to give an additional 0.44 g of gummy yellow needles. The second crop (ir data indicated only the  $\eta^5$  compound) was purified by sublimation ( $40^\circ$  (0.1 mm)), yielding 0.43 g (27%) of  $\text{Mn}(\eta^5\text{-C}_5\text{Cl}_5)(\text{CO})_3$ .

The overall yield of the two products was 75%.

The relative amounts of the two compounds depend greatly on the reaction time. In order to optimize the yield of the  $\sigma$  compound the reaction should be monitored by observing the infrared spectrum ( $\nu(\text{NN})$  for  $\text{C}_5\text{Cl}_4\text{N}_2$  is  $2110\text{ cm}^{-1}$ ) and worked up as soon as the reaction is completed. Depending on the amount of  $\eta^5$  compound present in the reaction mixture the purity of the initial crop of crystals is highly variable. However, the less soluble  $\eta^1$  product is easily isolated by fractional recrystallization at  $-20^\circ$ . These mother liquors may be stripped and combined with the second crop of crystals which are always mainly  $\text{Mn}(\eta^5\text{-C}_5\text{Cl}_5)(\text{CO})_3$  and sublimed to obtain the  $\eta^5$  product. Any remaining traces of  $\sigma$  complex are converted to the  $\pi$  compound during sublimation.

**Pentacarbonyl( $\eta^1$ -bromotetrachlorocyclopentadienyl)manganese,  $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_4\text{Br})(\text{CO})_5$ .** This compound was prepared in a manner identical with that for  $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5$ . A reaction employing  $\text{MnBr}(\text{CO})_5$  (0.4 g, 1.46 mmol) and  $\text{C}_5\text{Cl}_4\text{N}_2$  (0.336 g, 1.46 mmol) in 20 ml of pentane gave, after 2 days, 0.22 g (35%) of  $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_4\text{Br})(\text{CO})_5$  and 0.25 g (41%) of  $\text{Mn}(\eta^5\text{-C}_5\text{Cl}_4\text{Br})(\text{CO})_3$ . The overall yield was 76%.

**Pentacarbonyl( $\eta^1$ -tetrachlorocyclopentadienyl)manganese,  $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_4\text{H})(\text{CO})_5$ .**  $\text{MnH}(\text{CO})_5$  (0.196 g, 1 mmol) was condensed into a Carius tube containing  $\text{C}_5\text{Cl}_4\text{N}_2$  (0.230 g, 1 mmol) in pentane (8 ml). The tube was sealed and, after warming to room temperature, was agitated on a mechanical shaker for 14 hr. During this time yellow crystals of  $\text{MnCl}(\text{CO})_5$  formed on the walls of the tube. The tube was opened, and the crystals were filtered off and air-dried. Yields of  $\text{MnCl}(\text{CO})_5$  varied from 30 to 100 mg under identical reaction conditions.

The mother liquor was transferred to a nitrogen-filled Schlenk tube and cooled to  $-20^\circ$ . Yellow crystals slowly formed. They were filtered and dried in a nitrogen stream. Recrystallization from pentane usually gave  $\sim 60$  mg (15%) of  $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_4\text{H})(\text{CO})_5$ . Further cooling of the mother liquor gave additional product but it was always contaminated with a green-blue tar.

**Reaction of Pentacarbonylironmanganese and 2,3,4,5-Tetrachlorodiazocyclopentadiene.** A solution containing  $\text{MnI}(\text{CO})_5$  (0.2 g, 0.621 mmol) and  $\text{C}_5\text{Cl}_4\text{N}_2$  (0.143 g, 0.621 mmol) in pentane (25 ml) was stirred for 48 hr at room temperature. After this period a yellow precipitate had formed on the walls of the flask and an infrared spectrum of the solution showed the absence of free ligand. The mixture was filtered and cooled to  $-78^\circ$ . A small number of gummy yellow crystals formed, the mother liquor was removed, and the crystals were dried in a nitrogen stream. The infrared spectrum of the yellow precipitate suggested that it was a mixture of  $\text{MnI}(\text{CO})_5$  and  $[\text{MnI}(\text{CO})_4]_2$ . The crystals obtained at  $-78^\circ$  were also a mixture, possibly of  $\eta^1$  and  $\eta^5$  derivatives. Recrystallization was unsuccessful at accomplishing separation but bands ( $\nu(\text{CO})$  2048 (s), 1979 (vs)  $\text{cm}^{-1}$ ; cyclohexane) attributable to a  $\pi$  derivative increased in intensity suggesting decomposition of a  $\sigma$  compound. The solids obtained were always contaminated with organic tars and because of the small quantities isolated no further identification was attempted. Although this reaction was repeated several times and on different scales, identical results were obtained.

**( $\eta^5$ -Pentachlorocyclopentadienyl)(1,5-cyclooctadiene)rhodium,  $\text{Rh}(\eta^5\text{-C}_5\text{Cl}_5)(\text{COD})$ .** A benzene solution (50 ml) containing  $[(\text{RhCl}(\text{COD}))_2]$  (1.06 g, 2.15 mmol) and  $\text{C}_5\text{Cl}_4\text{N}_2$  (0.99 g, 4.30 mmol) was stirred for 10 hr at room temperature. The orange solution was stripped of solvent and the product was recrystallized from hexane to give 1.80 g (94%) of large orange crystals.

**Tricarbonyl( $\eta^5$ -pentachlorocyclopentadienyl)manganese,  $\text{Mn}(\eta^5\text{-C}_5\text{Cl}_5)(\text{CO})_3$ .** Sixty milliliters of octane was added to 1.62 g (7.04 mmol) each of  $\text{MnCl}(\text{CO})_5$  and  $\text{C}_5\text{Cl}_4\text{N}_2$  in a 100-ml round-bottomed flask. The flask was closed and the mixture stirred vigorously for 36 hr. The solution was filtered, the flask fitted with a reflux condenser, and the orange solution heated to  $80^\circ$  for ca. 15 min. (Some darkening of the solution occurs but this represents an insignificant amount of decomposition.) The solution was cooled to room temperature and the octane removed in vacuo. During this procedure the solution was kept at room temperature, but not heated to prevent loss of product. The flask was then fitted with a sublimation probe and the product was sublimed onto the water-cooled finger ( $40^\circ$  (1.0 mm)). Because of the presence of residual octane the sublimate was often oily. This was easily corrected by recrystallization from pentane to give 2.20 g (83%) of yellow crystals.

**Tricarbonyl( $\eta^5$ -bromotetrachlorocyclopentadienyl)manganese,**

Table I. Analytical and Physical Data for Perhalocyclopentadienyl Complexes

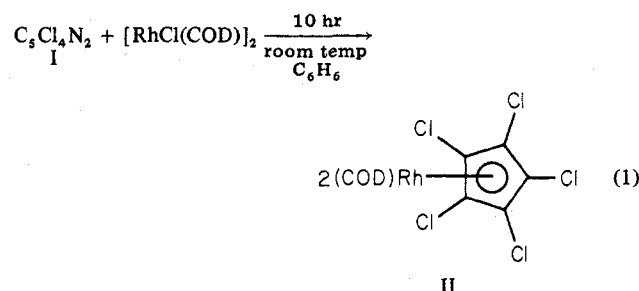
| Compd <sup>a</sup>                                                | Mp, °C | % C              |       | % H   |       | % halogen |                |
|-------------------------------------------------------------------|--------|------------------|-------|-------|-------|-----------|----------------|
|                                                                   |        | Calcd            | Found | Calcd | Found | Calcd     | Found          |
| Rh( $\eta^5$ -C <sub>5</sub> Cl <sub>5</sub> )(COD) <sup>b</sup>  | II     | 92-94 dec        | 38.43 | 38.43 | 2.68  | 3.03      |                |
| Mn( $\eta^5$ -C <sub>5</sub> Cl <sub>5</sub> )(CO) <sub>3</sub>   | IV     | 83-85            | 25.54 | 25.49 | <0.1  |           | Cl 47.14 47.12 |
| Mn( $\eta^5$ -C <sub>5</sub> Cl <sub>4</sub> Br)(CO) <sub>3</sub> | VI     | 81-82            | 22.84 | 22.87 | <0.1  |           | Cl 33.71 33.66 |
|                                                                   |        |                  |       |       |       |           | Br 19.00 18.88 |
| Mn( $\eta^1$ -C <sub>5</sub> Cl <sub>5</sub> )(CO) <sub>5</sub>   | III    | 110 <sup>c</sup> | 27.79 | 27.94 | <0.1  |           | Cl 41.01 41.23 |
| Mn( $\eta^1$ -C <sub>5</sub> Cl <sub>4</sub> Br)(CO) <sub>5</sub> | V      | 103 <sup>c</sup> | 25.20 | 25.16 | <0.1  |           | Cl 29.75 29.78 |
|                                                                   |        |                  |       |       |       |           | Br 16.76 16.75 |
| Mn( $\eta^1$ -C <sub>5</sub> Cl <sub>4</sub> H)(CO) <sub>5</sub>  | VII    | 92 dec           | 30.19 | 30.12 | 0.25  | 0.50      | Cl 35.65 35.36 |

<sup>a</sup> All compounds are yellow unless indicated otherwise. <sup>b</sup> Orange. <sup>c</sup> Compound melts with effervescence to give the  $\eta^5$  analog.

Mn( $\eta^5$ -C<sub>5</sub>Cl<sub>4</sub>Br)(CO)<sub>3</sub>. As above, MnBr(CO)<sub>5</sub> (0.30 g, 1.1 mmol) and C<sub>5</sub>Cl<sub>4</sub>N<sub>2</sub> (0.252 g, 1.1 mmol) in 35 ml of octane gave 0.39 g (95%) of product.

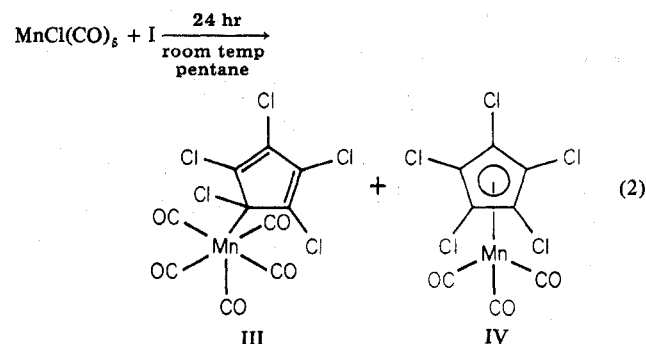
## Results and Discussion

**Preparation.** When I was allowed to react with di- $\mu$ -chloro-bis(1,5-cyclooctadienylrhodium) in benzene at room temperature, slow evolution of nitrogen ensued and II was produced in high yield. Reaction 1 proceeds smoothly and like



other reactions of diazocyclopentadienes<sup>11</sup> may be conveniently monitored in the infrared spectrum by observing the disappearance of the band at 2110 cm<sup>-1</sup> due to the diazo group. Compound II is somewhat thermally unstable and at room temperature turns black after several days. The amount of decomposition is small as most of the sample can be recovered by recrystallization. At -15° it may be stored unchanged for several months.

The reaction of pentacarbonylchloromanganese and I was also successful but in a remarkable and unanticipated manner. Two yellow crystalline products Mn( $\eta^1$ -C<sub>5</sub>Cl<sub>5</sub>)(CO)<sub>5</sub>, III, and Mn( $\eta^5$ -C<sub>5</sub>Cl<sub>5</sub>)(CO)<sub>3</sub>, IV, were obtained as in (2). Both



compounds are formed in the reaction and the relative amounts of each are highly dependent on the reaction conditions. This will be discussed in greater detail below but a typical reaction gave an overall yield of 75%, consisting of 48% III and 27% IV. Compound III being less soluble, they are conveniently separated by fractional crystallization from the filtered reaction mixture.

An analogous reaction occurred between MnBr(CO)<sub>5</sub> and

C<sub>5</sub>Cl<sub>4</sub>N<sub>2</sub> giving Mn( $\eta^1$ -C<sub>5</sub>Cl<sub>4</sub>Br)(CO)<sub>5</sub>, V, and Mn( $\eta^5$ -C<sub>5</sub>Cl<sub>4</sub>Br)(CO)<sub>3</sub>, VI, but a slightly longer reaction time was required (36 hr instead of 24 hr for reactions employing identical concentrations of reactants). Separation of the products was accomplished in an identical manner.

Both of the  $\sigma$ -bonded compounds are stable in the solid state. Samples exposed to light and air show no visible signs of deterioration and their infrared spectra and melting points were unchanged over a period of at least 6 months. Compounds III and V melt at 110 and 103°, respectively, with effervescence, to give quantitative yields of the  $\pi$ -bonded analogs. This conversion also takes place slowly in solution at room temperature.

When the  $\eta^5$  compounds were the sole products desired, the appropriate reaction was carried out in octane. After all of the diazo compound had been consumed, the reaction solution was warmed to ~80° for a few minutes (until the evolution of carbon monoxide subsided), cooled, and stripped to dryness. Sublimation of the residue gave high yields (>80%) of the desired product uncontaminated by any  $\sigma$  compound.

The reaction of C<sub>5</sub>Cl<sub>4</sub>N<sub>2</sub> and MnI(CO)<sub>5</sub> was somewhat less successful. Although the infrared spectrum of the reaction mixture indicated the slow consumption of the ligand and the appearance of bands suggestive of  $\sigma$ - and  $\pi$ -bonded C<sub>5</sub>Cl<sub>4</sub>I- compounds, no products of this type could be isolated. A precipitate which formed after 48 hr appeared to be a mixture of MnI(CO)<sub>5</sub> and [MnI(CO)<sub>4</sub>]<sub>2</sub>. Some further crystals were obtained from the reaction solution, but although they appeared to be a  $\eta^1$  derivative, this could not be established with certainty. Contamination with a greenish blue tar precluded further purification and identification.

When C<sub>5</sub>Cl<sub>4</sub>N<sub>2</sub> was allowed to react with MnH(CO)<sub>5</sub> in pentane at room temperature the major product was MnCl(CO)<sub>5</sub>. However, by careful fractional crystallization a small amount of Mn( $\eta^1$ -C<sub>5</sub>Cl<sub>4</sub>H)(CO)<sub>5</sub>, VII, was obtained. All of the diazo compound had been consumed and although there was evidence in the infrared spectrum for a  $\eta^5$  complex, it could not be isolated from the greenish blue residue. At 92° VII melts with effervescence but the residue appears to decompose rather than convert to a stable  $\pi$ -bonded analog. Such a product may be initially formed but it is evidently unstable at this temperature. There was evidence for Mn( $\eta^5$ -C<sub>5</sub>Cl<sub>4</sub>H)(CO)<sub>3</sub> in the mass spectrum of VII.

The analytical and physical data for the complexes obtained from the insertion reactions of I are presented in Table I. These data are in excellent agreement with the proposed formulations. Parent ion peaks of the appropriate relative intensities<sup>6</sup> were observed in the mass spectra for all of the compounds except the  $\eta^1$  derivatives. These compounds showed fragmentation patterns characteristic of the  $\eta^5$  analogs. Evidently loss of CO occurs before or upon electron impact.

**Bonding Patterns in Halogen-Substituted Cyclopentadienylmetal Complexes.** The structures of the compounds Mn( $\eta^1$ -C<sub>5</sub>Cl<sub>5</sub>)(CO)<sub>5</sub>, III, and Rh( $\eta^5$ -C<sub>5</sub>Cl<sub>5</sub>)(COD), II, have been reported in preliminary communications<sup>12,24</sup> and provide

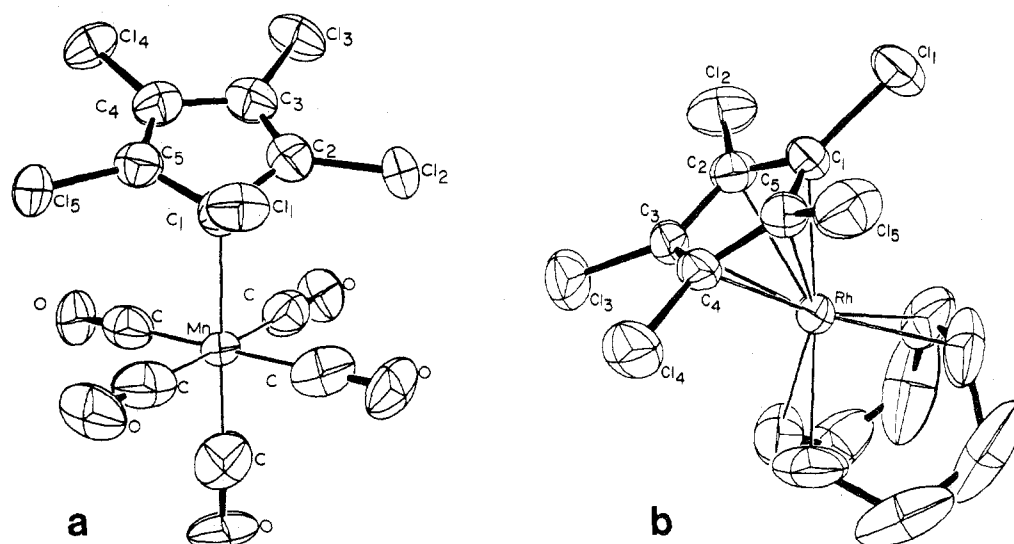


Figure 1. ORTEP drawings of (a)  $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5$  and (b)  $\text{Rh}(\eta^5\text{-C}_5\text{Cl}_5)(\text{COD})$ .

Table II. Characteristic Infrared Absorptions ( $\text{cm}^{-1}$ ) for Ionic and  $\pi$ -Bonded  $\text{C}_5\text{Cl}_4\text{X}$  Groups ( $\text{X} = \text{Cl}, \text{Br}$ )<sup>a</sup>

| Type of absorption | Ionic $\text{C}_5\text{Cl}_5^-$ <sup>b</sup> | $\text{Fe}(\text{C}_5\text{Cl}_5)_2$ <sup>c</sup> | $\text{Mn}(\text{C}_5\text{Cl}_5)(\text{CO})_3$ <sup>d</sup> | $\text{Mn}(\text{C}_5\text{Cl}_4\text{Br})(\text{CO})_3$ <sup>d</sup> | $\text{Rh}(\text{C}_5\text{Cl}_5)(\text{COD})$ <sup>d</sup> |
|--------------------|----------------------------------------------|---------------------------------------------------|--------------------------------------------------------------|-----------------------------------------------------------------------|-------------------------------------------------------------|
| Ring modes         | 1410–1415 s                                  | 1350 s<br>1307 m                                  | 1383 s<br>1365 sh<br>1340 m<br>1315 sh                       | 1381 s<br>1363 sh<br>1343 m<br>1328 sh                                | 1403 s<br>1343 m                                            |
| C–Cl str           | 657–681 m–s                                  | 702 s                                             | 709 vs                                                       | 700 vs                                                                | 693 vs                                                      |

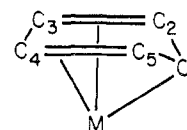
<sup>a</sup> 4000–650  $\text{cm}^{-1}$ ; bands due to other ligand vibrations are omitted. <sup>b</sup> Reference 8. <sup>c</sup> Reference 2. <sup>d</sup> Measured as KBr pellets.

excellent references for the spectroscopic identification of other complexes. A full discussion of these structures is not within the scope of this paper but will be the topic of future papers by Professor V. W. Day. The discussion will be restricted to the macro arrangement of the atoms and some interesting features of the pentachlorocyclopentadienyl rings will be mentioned. ORTEP drawings for the molecules are shown in Figure 1.

The data for  $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5$  are notable as this is the first structure determination of an  $\eta^1$ -pentachlorocyclopentadienyl complex. In this complex the manganese is octahedrally coordinated to five carbonyl groups and a  $\sigma$ -bonded perchlorocyclopentadienyl ligand. The  $\text{C}_5\text{Cl}_5^-$  group is bonded to the manganese through a single carbon atom at a distance of 2.204 (6) Å and possesses the normal characteristics of a  $\sigma$ -bonded cyclopentadienyl group, namely, two short, 1.351 (8, 6, 6)<sup>25</sup> Å, and three long, 1.487 (8, 12, 13) Å, carbon-carbon bonds. The four carbon atoms of the cyclopentadienyl ring involved in the two double bonds are bonded to chlorine atoms at an average distance of 1.693 (6, 4, 5) Å while the fifth carbon atom is bonded to a chlorine atom at a distance of 1.798 (6) Å—observations also consistent with a  $\sigma$ -bonded cyclopentadienyl ring.

The structural analysis of II shows that the crystal contains discrete  $\text{Rh}(\eta^5\text{-C}_5\text{Cl}_5)(\text{COD})$  molecules in which the Rh is  $\eta^5$  bonded to the substituted cyclopentadienyl ring and  $\pi$  bonded to the two double bonds of the cyclooctadiene ligand. In addition the following observations were made about the bond parameters within the  $\text{RhC}_5\text{Cl}_5$  moiety: (i) the presence of two short and three long C–C bonds within the ring, (ii) four short and one long carbon-to-chlorine bond lengths, and (iii) three classes of metal-to-cyclopentadienyl carbon bond lengths produced by a folding of the cyclopentadienyl ligand by 4.6° such that one carbon is brought closer to the rhodium (i.e., C<sub>1</sub> below). This was interpreted as being a reflection of considerable contribution of the bonding model shown where the ring is bonded to metal via two  $\pi$  bonds and one  $\sigma$  bond.

This type of localization had never been observed before and



was attributed to the low symmetry of the complex and the chloro substituents.

**Infrared Spectra.** In principle, the nature of bonding between a cyclopentadienyl ring and a metal may be deduced by means of infrared spectra. This is due to a change in the number of vibrational bands as the symmetry of the ligand is altered by interaction with the metal.  $\pi$ - and  $\sigma$ -bonded cyclopentadienyl ligands are often distinguished because of the more complex spectra associated with the latter. West et al.<sup>10</sup> have previously compiled the infrared spectroscopic data for known pentachlorocyclopentadienyl compounds and this list has now been extended to include the present derivatives (Tables II and III). The greater complexity of the spectra of the  $\eta^1$  complexes is evident from a comparison of the two tables. Since the structure of  $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5$  has been determined, its infrared spectrum can be used as a model to compare with that of other molecules that may contain a  $\sigma$ -bonded  $\text{C}_5\text{Cl}_5^-$ . Such a comparison with the infrared spectra of the  $\text{C}_5\text{Cl}_5$  derivatives of mercury provides additional confirmation of presence of  $\sigma\text{-C}_5\text{Cl}_5^-$  groups as had been proposed by West.

A distinguishing feature of the spectra of the  $\sigma$ -bonded compounds is the presence of bands at ca. 1560  $\text{cm}^{-1}$  due to  $\nu(\text{C}=\text{C})$ .  $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5$  and  $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_4\text{Br})(\text{CO})_5$  gave virtually identical infrared spectra, except for the absence of an allylic C–Cl stretching band in the spectrum of the latter. It would be anticipated that the C–Br stretch would fall in the region 650–500  $\text{cm}^{-1}$  but identification of such a band was precluded by the presence of strong absorptions due to Mn–C stretching and Mn–C–O bending modes.

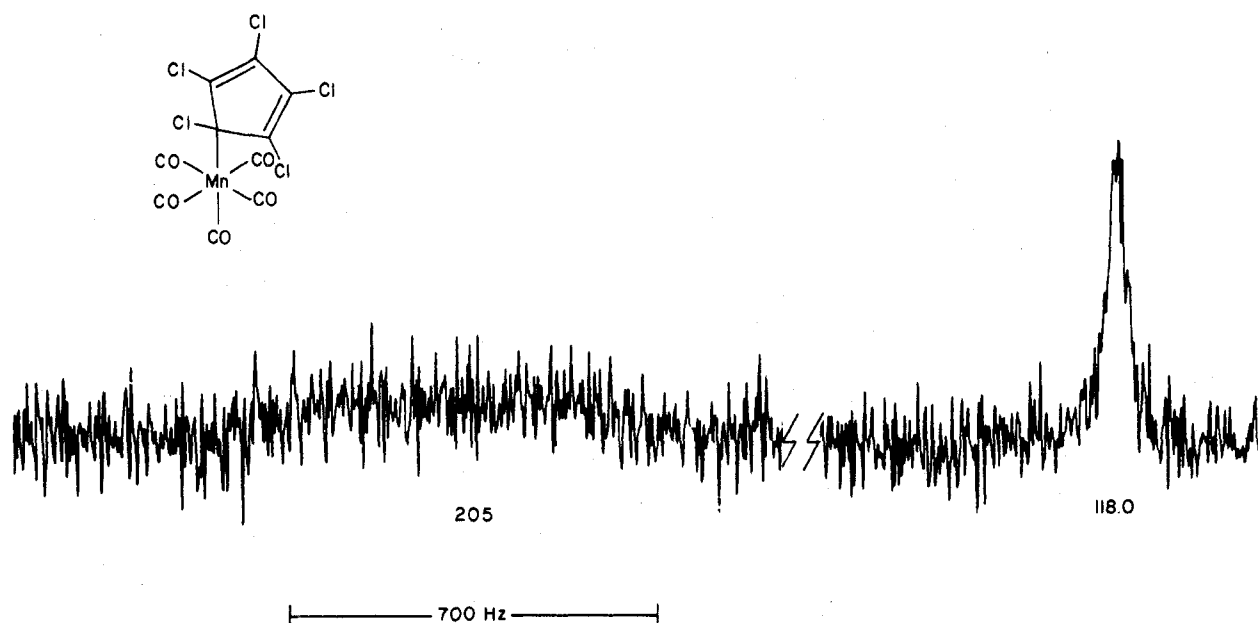


Figure 2.  $^{13}\text{C}$  NMR spectrum of  $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5$  in  $\text{CD}_2\text{Cl}_2$  solution at  $30^\circ\text{C}$ .

Table III. Characteristic Infrared Absorptions ( $\text{cm}^{-1}$ ) for  $\sigma$ -Bonded  $\text{C}_5\text{Cl}_4\text{X}$  Groups ( $\text{X} = \text{Cl}, \text{Br}$ )<sup>a</sup>

| Type of absorption           | $\text{C}_5\text{Cl}_4\text{HgX}^b$ | $\text{Mn}(\text{C}_5\text{Cl}_5\text{-(CO)})_5$ | $\text{Mn}(\text{C}_5\text{-(Cl}_4\text{Br)-CO})_5$ | $\text{Mn}(\text{C}_5\text{-(Cl}_4\text{H)-CO})_5^c$ |
|------------------------------|-------------------------------------|--------------------------------------------------|-----------------------------------------------------|------------------------------------------------------|
| Ring modes                   | 1536–1586 s-vs                      | 1565 s                                           | 1566 m                                              | 1557 sh                                              |
|                              | 1558–1566 w, sh                     | 1561 sh                                          | 1543 sh                                             | 1542 m                                               |
|                              | 1243–1259 vs                        | 1264 s                                           | 1263 s                                              | 1283 s                                               |
|                              | 1187–1204 m-s                       | 1191 w                                           | 1183 w                                              | 1262 sh                                              |
|                              | 1127–1138 m-vs                      | 1122 m                                           | 1115 m                                              | 1253 sh                                              |
|                              | 970–979 w-m                         | 969 vw                                           | 970 vw                                              | 1148 m                                               |
|                              | 946–954 m                           | 943 vw                                           | 929 vw                                              | 1092 w                                               |
|                              | 647–655 m-s                         | d                                                | d                                                   | 981 vw                                               |
|                              | 508–519 vvw-w                       | d                                                | d                                                   | 948 w                                                |
|                              | 339–365 vvw-w                       | d                                                | d                                                   | 887 s                                                |
| Allylic C-Cl str (multiplet) | 720–766 w-vs                        | 706 m, sh                                        |                                                     |                                                      |
| Vinylic C-Cl str             | 689–697 s-vs                        | 694 vs                                           | 689 vs                                              | 682 s                                                |

<sup>a</sup> Measured as Nujol mulls for the manganese compounds and unchanged as KBr pellets. <sup>b</sup> Reference 10. <sup>c</sup> Except for C-Cl stretch other bands are not assigned. <sup>d</sup> Could not be detected with certainty due to presence of other ligand bands.

The spectrum of  $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_4\text{H})(\text{CO})_5$  was very different from that of the other  $\eta^1$  compounds as would be anticipated for the substitution of a halogen with hydrogen. The vinylic C-Cl stretch was assigned by comparison with the other spectra but no assignments of the other bands were attempted. Consistent with the proposed formulation is the presence of a band at  $1557\text{ cm}^{-1}$  due to  $\nu(\text{C}=\text{C})$  of the  $\sigma$ -bonded ring.

Four carbonyl stretching bands were observed in the solution infrared spectrum of  $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5$  (Table IV). The assignments are based on the arguments presented previously by several authors.<sup>26–28</sup> Although theory predicts three infrared bands for local  $\text{C}_{4v}$  symmetry, the infrared-forbidden  $\text{B}_1$  mode is sometimes observed in the infrared spectra of  $\text{MnL}(\text{CO})_5$  complexes and is often accompanied by splitting of the E mode. This has been attributed<sup>29–31</sup> to a lowering of the symmetry by the ligand, L, but other mechanisms have also been considered.<sup>32,33</sup> All four modes are Raman active and four bands were observed in the Raman spectrum of  $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5$ .

The infrared spectrum of  $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_4\text{Br})(\text{CO})_5$  is identical in the carbonyl region with that of  $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5$ . The substitution of a halogen by hydrogen as in  $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_4\text{H})(\text{CO})_5$  causes a shift in frequencies. In addition, the  $\text{B}_1$  band is absent in the infrared spectrum. However, four bands were found in the Raman spectrum giving additional confirmation for the proposed formulation.

Table IV. Carbonyl Stretching Frequencies ( $\text{cm}^{-1}$ ) for  $\text{C}_5\text{Cl}_4\text{X-Mn}$  Complexes ( $\text{X} = \text{Cl}, \text{Br}, \text{H}$ )<sup>a</sup>

| Compd                                                           | $\nu(\text{CO})$   |                     |                     |                    |
|-----------------------------------------------------------------|--------------------|---------------------|---------------------|--------------------|
|                                                                 | $\text{A}_1$       | $\text{B}_1$        | E                   | $\text{A}_1^{(1)}$ |
| $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5$          | 2048 s             |                     | 1982 vs             |                    |
| $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_4\text{Br})(\text{CO})_5$ | 2047 s             |                     | 1980 vs             |                    |
| $\nu(\text{CO})$                                                |                    |                     |                     |                    |
| Compd                                                           | $\text{A}_1^{(2)}$ | $\text{B}_1$        | E                   | $\text{A}_1^{(1)}$ |
| $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5$          | 2126 m<br>(2125 s) | 2076 w<br>(2083 vs) | 2043 vs<br>(2029 w) | 2012 s<br>(2004 m) |
| $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_4\text{Br})(\text{CO})_5$ | 2127 m             | 2076 w              | 2043 vs             | 2012 s             |
| $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_4\text{H})(\text{CO})_5$  | 2125 m<br>(2118 s) |                     | 2041 vs<br>(2035 w) | 2006 s<br>(1992 m) |

<sup>a</sup> Infrared measurements using cyclohexane solutions except for those in parentheses which are from solid-state Raman spectra.

$\text{C}_5\text{Cl}_4\text{H})(\text{CO})_5$  causes a shift in frequencies. In addition, the  $\text{B}_1$  band is absent in the infrared spectrum. However, four bands were found in the Raman spectrum giving additional confirmation for the proposed formulation.

The infrared spectra in the carbonyl region of the  $\eta^5\text{-C}_5\text{Cl}_5^-$  and  $\eta^5\text{-C}_5\text{Cl}_4\text{Br}^-$  compounds showed two bands consistent with local  $\text{C}_{3v}$  symmetry. For the former compound these were shifted an average of  $28\text{ cm}^{-1}$  to higher wave numbers than those observed for  $\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3$ . This suggests that the  $\eta^5\text{-C}_5\text{Cl}_5$  ring is a poorer electron donor and/or a better electron acceptor than the  $\eta^5\text{-C}_5\text{H}_5$  moiety.

<sup>13</sup>C NMR. For these compounds  $^{13}\text{C}$  NMR provides a useful tool for their characterization. The spectra presented here are the first such for perhalocyclopentadienyl complexes. Attempts<sup>10</sup> to measure the  $^{13}\text{C}$  spectra of the pentachlorocyclopentadienylmercurials were precluded by solubility and stability problems and there have been no reports of such spectra for the perchlorometalocenenes.

The spectrum obtained for III is shown in Figure 2 and the data for the rest are summarized in Table V which also contains chemical shift data reported for analogous unsubstituted cyclopentadienyl complexes.

The signals due to the cyclopentadienyl ring carbons of the  $\eta^5\text{-C}_5\text{Cl}_5^-$  and  $\eta^5\text{-C}_5\text{Cl}_4\text{Br}^-$  complexes are sharp in contrast to the slightly broadened resonances (width at half-height  $\Delta\nu_{1/2} = \sim 15\text{ Hz}$ ) observed for the carbonyl carbons. Similar effects have been noted in the spectra of  $\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3$ <sup>34</sup> and

Table V.  $^{13}\text{C}$  NMR Data<sup>a</sup> for Cyclopentadienylmanganese and -rhodium Complexes

| Complex                                                         | $\delta(\text{C})$                 |                    |                                                         |
|-----------------------------------------------------------------|------------------------------------|--------------------|---------------------------------------------------------|
|                                                                 | Cyclopentadienyl carbons           | Carbonyl carbons   | Other resonances                                        |
| $\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3$           | 75 <sup>d</sup>                    | 225.1 <sup>e</sup> |                                                         |
| $\text{Mn}(\eta^5\text{-C}_5\text{Cl}_5)(\text{CO})_3$          | 94.6                               | 219.8 <sup>b</sup> |                                                         |
| $\text{Mn}(\eta^5\text{-C}_5\text{Cl}_4\text{Br})(\text{CO})_3$ | 79.8, 95.6, 97.8                   | 220.8 <sup>c</sup> |                                                         |
| $\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{COD})$            | 86.5 <sup>f</sup>                  |                    | $\delta(\text{CH})$ 62.4; $J(\text{Rh-C}) = 14$         |
| $\text{Rh}(\eta^5\text{-C}_5\text{Cl}_5)(\text{COD})$           | 94.1; $J(\text{Rh-C}) = 4 (\pm 1)$ |                    | $\delta(\text{CH})$ 80.4; $J(\text{Rh-C}) = 13 (\pm 1)$ |
|                                                                 |                                    |                    | $\delta(\text{CH}_2)$ 32.1                              |
| $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5$          | 118                                | $\sim 205$         |                                                         |

<sup>a</sup> Chemical shifts are given in ppm from TMS (downfield positive) and coupling constants are in Hz. For the halogenated compounds spectra were obtained using  $\text{CD}_2\text{Cl}_2$  as a solvent. <sup>b</sup>  $\Delta\nu_{1/2} = 13$  Hz. <sup>c</sup>  $\Delta\nu_{1/2} = 15$  Hz. <sup>d</sup> Reference 38. <sup>e</sup> Reference 34. <sup>f</sup> Reference 41.

$\text{Mn}(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})_3$ .<sup>35</sup> The broadening of the carbonyl signals is attributed<sup>34-37</sup> to coupling with the manganese nucleus ( $I = 5/2$ , 100% abundance) which is undergoing a moderately rapid quadrupole-induced relaxation. Difficulties are often encountered in detecting the signals of metal carbonyls due to the long relaxation times of carbonyl carbon nuclei which allow them to be easily saturated.<sup>36,37</sup> This problem can often be circumvented by the use of a shiftless relaxation reagent (e.g.,  $\text{Cr}(\text{acac})_3$ <sup>35-37</sup>) but this was not required for measuring the spectra reported here.

The resonances due to the pentachlorocyclopentadienyl carbons appear to lower field than those reported for analogous  $\text{C}_5\text{H}_5^-$  derivatives. This may be anticipated as chlorine is known to act as a deshielder in organic compounds.<sup>39,40</sup> Relative to chlorine, bromine is a shielding substituent and consequently in the spectrum of  $\text{Mn}(\eta^5\text{-C}_5\text{Cl}_4\text{Br})(\text{CO})_3$  the line at highest field (79.8 ppm) is assigned to C-Br. For  $\text{Rh}(\eta^5\text{-C}_5\text{Cl}_5)(\text{COD})$  coupling of the rhodium nucleus ( $I = 1/2$ , 100% abundance) to the olefinic carbons of the 1,5-cyclooctadiene ligand was observed ( $J(^{103}\text{Rh}-^{13}\text{C}) = 13$  Hz). This is identical with that reported<sup>41</sup> for  $\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{COD})$ . For the latter compound this was interpreted in terms of 60% contribution from a bonding model involving  $\sigma$ -bond formation of an  $\text{sp}^3$  rehybridized olefin carbon and a  $\text{dsp}^2$  metal orbital. It is interesting that coupling is observed to the pentachlorocyclopentadienyl carbon atoms in the spectrum of  $\text{Rh}(\eta^5\text{-C}_5\text{Cl}_5)(\text{COD})$ . No  $^{103}\text{Rh}-^{13}\text{C}$  coupling has been reported for any  $\eta^5\text{-C}_5\text{H}_5\text{-Rh}$  complexes. This absence of coupling could be due to a number of factors but it has been suggested<sup>41</sup> that it is a reflection of predominantly  $\pi$  character in the metal-cyclopentadienyl bond whereas metal-olefin bonds have substantial  $\sigma$ -bond character. If this explanation is correct, it implies that the bonding of the  $\text{Rh}-\eta^5\text{-C}_5\text{Cl}_5$  moiety differs from that of the  $\text{Rh}-\eta^5\text{-C}_5\text{H}_5$  group. This is consistent with the interpretation of the type of bond localization observed in the  $\text{C}_5\text{Cl}_5\text{-Rh}$  moiety in II.

The spectrum of  $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5$ , III, was of particular interest because of the possibility of fluxionality.<sup>42</sup> Little is known of the effect of ring substitution on the fluxionality of  $\sigma$ -bonded cyclopentadienyl complexes probably because of the small number of such complexes known. However, cyclopentadienylmercurials show fluxional behavior<sup>43</sup> while pentamethylcyclopentadienyls of mercury reportedly do not.<sup>44</sup>

The only resonance that could be detected for the ring carbons of III appeared (at  $30^\circ$ ) as a broad signal ( $\Delta\nu_{1/2} = 50$  Hz) shifted to lower field relative to those observed for the  $\eta^5$  complexes. An extremely broad signal at  $\sim 200$  ppm was observed for the carbonyl carbons and this was not affected by the addition of  $\text{Cr}(\text{acac})_3$ . A resonance of comparable intensity and line width has been assigned to the carbonyl carbons in the spectrum of  $\text{Mn}(\text{CH}_3)(\text{CO})_5$ .<sup>35</sup> Little else can be determined from this resonance and the following discussion will address itself primarily to the interpretation of the ring carbon signal at 118 ppm.

For  $\sigma$ -cyclopentadienyl compounds undergoing fast migration the signal of the ring carbons should have the value

of  $\delta(\text{C})_{\text{av}}$  corresponding to all of the states being averaged out

$$\delta(\text{C})_{\text{av}} = 1/5 [\delta(\text{C}_1) + \delta(\text{C}_2) + \delta(\text{C}_3) + \delta(\text{C}_4) + \delta(\text{C}_5)]$$

On this basis it has been suggested that the  $^{13}\text{C}$  chemical shifts can be used to differentiate between  $\sigma$ - and  $\pi$ -bonded  $\text{C}_5\text{H}_5$  derivatives with  $\delta(\text{C})_{\text{av}}$  at 113 to 118 ppm for the former and at 70 to 93 ppm for the latter.<sup>45</sup> The position to lower field for  $\eta^1$  compounds is due to the large contribution to  $\delta(\text{C})_{\text{av}}$  from vinylic carbons which are more deshielded than  $\text{sp}^3$  carbons. For the present compounds  $\delta(\text{C})_{\text{av}}$  for  $\pi$ -bonded  $\text{C}_5\text{Cl}_5^-$  compounds is 94 ppm, i.e., the low-field end of the range reported for  $\pi$ -bonded  $\text{C}_5\text{H}_5^-$  complexes. It is not known what the chemical shifts of the vinylic carbons of a  $\eta^1\text{-C}_5\text{Cl}_5^-$  complex would be. It has been found that the  $^{13}\text{C}$  shieldings of the  $\text{sp}^2$  carbons in  $\text{C}_5\text{Cl}_6$ ,  $\text{C}_5\text{Br}_6$ ,<sup>46</sup> and  $\text{C}_5\text{H}_6$ <sup>39</sup> are very similar. Consequently it is possible that the chemical shifts of  $\text{C}_{2,5}$  and  $\text{C}_{3,4}$  of a  $\sigma$ -bonded  $\text{C}_5\text{Cl}_5^-$  complex might be comparable to those found for  $\sigma$ -bonded  $\text{C}_5\text{H}_5^-$  compounds. Similarly the signal due to the allylic carbon would be expected to appear upfield from the vinylic resonances (for  $\text{Fe}(\eta^1\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$ ,  $\delta(\text{C}_1) = 28.2$ ,  $\delta(\text{C}_{2,5}) = 145$ , and  $\delta(\text{C}_{3,4}) = 122$  ppm<sup>47</sup>) but the exact positions of such peaks are impossible to predict. The  $^{13}\text{C}$  spectrum of a perchloro- $\sigma$ -allylic derivative would provide useful information in this regard but none has been reported. An additional complication is the absence of data regarding the magnitude of manganese-carbon coupling.

The limitations imposed by the lack of available  $^{13}\text{C}$  NMR data for chlorocarbon-metal complexes allows the spectrum illustrated in Figure 2 to be interpreted in two ways.

First, the molecule could be considered to be static at this temperature. The signal at 118 ppm may be assigned to the two resonances of the vinylic carbons which are closely spaced and broadened by coupling to the manganese nucleus. The inability to detect another signal to higher field (for  $\text{C}_1$ ) could also be due to broadening resulting from coupling.

Alternatively, the ring could be undergoing rearrangement rapidly on the  $^{13}\text{C}$  NMR time scale such that the resonances have coalesced. Some broadening of the average signal might be anticipated due to manganese coupling but the magnitude of such coupling is unknown. Assuming the effect of the chlorine substituents (on all the chemical shifts) is a slight deshielding, the peak position is consistent with  $\delta(\text{C})_{\text{av}}$ , i.e., the lower part of the range reported for  $\sigma$ -bonded  $\text{C}_5\text{H}_5^-$  compounds.

The usual method<sup>42,47</sup> of ascertaining fluxionality is to perform a variable-temperature experiment. Unfortunately for the present compound solubility and stability problems narrowed the temperature range which could be examined. As previously discussed, at higher temperatures particularly in solution, III converts to the  $\eta^5$  analog by loss of two carbonyl ligands. This limited the "high" temperature experiment to  $50^\circ$  where, in a closed NMR tube, the conversion took several hours. At this temperature the signal at 118 ppm was essentially identical with that at  $30^\circ$  but no signal due to the carbonyl carbons could be detected (experiments using  $\text{Cr}$ -

Table VI.  $^{35}\text{Cl}$  NQR Frequencies of Perhalocyclopentadienyl Complexes

| Compd                                                           | Freq, <sup>a</sup> MHz                                                                                      |                                 |
|-----------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------|---------------------------------|
| $\text{Mn}(\eta^5\text{-C}_5\text{Cl}_5)(\text{CO})_3$          | 38.742 (8), 38.932 (9), 38.967 (7), 39.016 (8), 39.063 (8), 39.082 (18), 39.201 (8)                         |                                 |
| $\text{Rh}(\eta^5\text{-C}_5\text{Cl}_5)(\text{COD})$           | 37.769 (4), 37.778 (4), 37.941 (5), 38.056 (4), 38.063 (5), 38.185 (5), 38.277 (10), 38.363 (5), 38.446 (5) |                                 |
| $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5$          | Vinyl chloride resonances<br>36.617 (8), 36.560 (8), 36.237 (8), 36.144 (8)                                 | Allylic resonance<br>37.257 (8) |
| $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_4\text{Br})(\text{CO})_5$ | 36.15 (2), 36.22 (2), 36.56 (1.5), 36.63 (2)                                                                |                                 |

<sup>a</sup> Numbers in parentheses indicate signal-to-noise ratios; resonant frequencies are accurate to  $\pm 0.005$  MHz except for last compound where accuracy is  $\pm 0.015$  MHz.

(acac)<sub>3</sub> gave identical results). At higher temperatures relaxation of quadrupole nuclei becomes slower and thus the carbonyl resonance might be harder to detect. The line width of the signal at 118 ppm was not significantly affected. Solubility problems limited low-temperature experiments to  $-50^\circ$  and dilute samples were required to prevent the compound from crystallizing. No signal was detected for either the carbonyl carbons or the pentachlorocyclopentadienyl carbons at  $-50$ ,  $-20$ , or  $0^\circ$ . Since relaxation of quadrupole nuclei becomes faster at lower temperatures, it would be anticipated that the signals would *sharpen* if coupling to manganese was the major factor affecting the line widths. It is tempting to interpret the absence of a ring carbon signal at lower temperature as evidence of fluxionality. However, because of the large number of unknown variables this question must be considered open. Unfortunately, we were unable to obtain spectra for  $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_4\text{X})(\text{CO})_5$  where  $\text{X} = \text{Br}$  and  $\text{H}$ .

**$^{35}\text{Cl}$  Nuclear Quadrupole Resonance Spectra.** In Table VI are given the NQR spectra of four of the compounds prepared in this study. NQR spectra are obtained in the solid state. Consequently multiple lines in the spectrum can arise from chemically equivalent atoms occupying nonequivalent positions in the crystal lattice as well as from chemically inequivalent atoms in the molecule.<sup>48</sup> Crystallographic splitting however is usually smaller than that due to chemically different atoms and for compounds of this type it has been found that the former is limited to ca. 2% of the frequency.<sup>8,10</sup>

The spectrum of  $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5$  shows five lines similar to the spectra reported for the pentachlorocyclopentadienylmercurials.<sup>10</sup> The frequencies are similar to the values found in the spectrum of  $\text{Hg}(\eta^1\text{-C}_5\text{Cl}_5)(\text{Ph})$  where it has been shown<sup>49</sup> that the spectrum has not been affected by intermolecular coordination of the chlorines. The assignments of the allylic and vinylic chlorines follow those previously proposed. Studies<sup>49</sup> of a large number of pentachlorocyclopentadienes have shown that the values of  $\nu$  for the chlorines in the 3 and 4 positions fall close to 37.0 MHz. Accordingly, for  $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5$  the two highest vinylic frequencies are assigned to  $\text{Cl}_{3,4}$  and the others to  $\text{Cl}_{2,5}$ .

The spectrum of  $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_4\text{Br})(\text{CO})_5$ , V, was of interest with regard to the position of the Br on the ring. Four lines were observed with frequencies very similar to those of the  $\eta^1\text{-C}_5\text{Cl}_5^-$  compound. The signals were weak and broad in comparison to those for II and the resonance for the allylic chlorine could not be measured. This suggests the possibility that the bromine occupies the allylic position in at least 80% of the molecules but not in all of them. This is consistent with the failure to observe a band corresponding to an allylic C-Cl stretch in the infrared spectrum of V. Taken together these two observations suggest that the  $\eta^1$  ring in V is static. However, care must be used in drawing conclusions based on the absence of spectroscopic features. It is also possible that the weak intensities are due to disorder in the crystals.

The spectrum of  $\text{Mn}(\eta^5\text{-C}_5\text{Cl}_5)(\text{CO})_3$  is very complex suggesting the presence of two crystallographically inequivalent

molecules in the unit cell. This would give rise to a 10-line pattern but because of the narrowness of the range only seven could be distinguished. However, the relative intensities suggest that one of the lines is probably due to accidental coincidence of three signals. The splitting involved is small (0.459 MHz) indicating the chemical equivalence of all of the chlorines.

Similarly,  $\text{Rh}(\eta^5\text{-C}_5\text{Cl}_5)(\text{COD})$  gives a complex spectrum suggesting the possibility of more than one inequivalent molecule per unit cell. However, this is not anticipated for the space group (*Pnma*) which was found in the structure determination of this compound indicating the possibility of a crystalline phase change at lower temperature. Such changes are well known and for the pentachlorocyclopentadienylmercurials several of the compounds exhibited different crystalline modifications and NQR spectra at  $77^\circ\text{K}$ . The splitting is larger in this spectrum (0.677 MHz) approaching the limit expected for crystallographic effects but is probably consistent with the chemical equivalence of the chlorines (at least within the sensitivity of the NQR experiment).

**Reactions of the Perchlorocyclopentadienyl Complexes.** Tricarbonyl( $\eta^5$ -cyclopentadienyl)manganese reacts with a variety of ligands to produce complexes of the type  $\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{L})$  or  $\text{Mn}(\eta^5\text{-C}_5\text{H}_5)\text{CO}(\text{L})_2$ .<sup>50,51</sup> Under normal conditions it is inert to substitution but under strong uv irradiation the reaction occurs smoothly. Reaction may also be induced thermally but this has been found to give less satisfactory results.

The analogous pentachlorocyclopentadienyl complex,  $\text{Mn}(\eta^5\text{-C}_5\text{Cl}_5)(\text{CO})_3$ , IV, is unreactive at room temperature and there was no evidence of reaction with a variety of ligands including carbon monoxide. The irradiation of solutions of IV in either the presence or the absence of an additional ligand resulted in rapid and extensive decomposition. The formation of green and blue tars suggests the scission of the  $\text{Mn-C}_5\text{Cl}_5$  bond giving  $\text{C}_5\text{Cl}_5^-$ . Previous work<sup>8</sup> has shown that such colored materials are characteristic of the decomposing anion. Thermal reactions could be induced but only with great difficulty. Thus, when a benzene solution of IV and triethylphosphine was refluxed for 12 hr, new bands appeared in the infrared spectrum and a small amount of crystalline product contaminated with excess  $\text{Et}_3\text{P}$  was isolated. The infrared spectrum of this material gave two bands in the carbonyl stretching region at 1942 and  $1895\text{ cm}^{-1}$  consistent with a dicarbonyl species,  $\text{Mn}(\eta^5\text{-C}_5\text{Cl}_5)(\text{CO})_2(\text{PEt}_3)$ . On standing overnight the crystals decomposed to a green tar. Attempts to reproduce this reaction or to obtain other substituted products were unsuccessful.

When  $\text{Mn}(\eta^1\text{-C}_5\text{Cl}_5)(\text{CO})_5$  was allowed to react with triphenylphosphine in pentane, a mixture of starting material and an unidentifiable precipitate was obtained. Similarly, the addition of triethylphosphine to a pentane solution of  $\text{Rh}(\eta^5\text{-C}_5\text{Cl}_5)(\text{COD})$  resulted in the immediate formation of a yellow-green precipitate which then rapidly decomposed to a blue-green tar. These results are analogous to those reported for the reactions of the pentachlorocyclopentadienyl-

Other factors are also clearly important for the successful insertion of a diazocyclopentadiene. Thus tetraphenyl-diazocyclopentadiene only reacts with pentacarbonylchloromanganese at 80°. <sup>11</sup> The nature of these factors is unknown at the present time. A large number of reactions were at-

Table VII. Attempted Insertion Reactions

| Metal complex                                              | C <sub>5</sub> H <sub>4</sub> N <sub>2</sub> | C <sub>5</sub> Cl <sub>4</sub> N <sub>2</sub> |
|------------------------------------------------------------|----------------------------------------------|-----------------------------------------------|
| Halogen-Bridged Complexes                                  |                                              |                                               |
| RhCl(C <sub>5</sub> H <sub>14</sub> ) <sub>2</sub>         | A, pentane                                   | A, pentane                                    |
| [RhCl(CO) <sub>2</sub> ] <sub>2</sub>                      | A, pentane                                   | A, pentane                                    |
| [PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]      |                                              | B, C <sub>6</sub> H <sub>6</sub>              |
| [RhClCO(PEt <sub>3</sub> ) <sub>2</sub> ]                  | A, pentane                                   | A, pentane                                    |
| [IrCl(COD)] <sub>2</sub>                                   | A, C <sub>6</sub> H <sub>6</sub>             | A, C <sub>6</sub> H <sub>6</sub>              |
| [RhCl(C <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> ]       | A, pentane                                   | A, pentane                                    |
| Complexes with Terminal Metal-Halogen Bonds                |                                              |                                               |
| Mn(CO) <sub>5</sub> [P(OPh) <sub>3</sub> ] <sub>2</sub> Br |                                              | C, C <sub>6</sub> H <sub>6</sub>              |
| FeBr(CO) <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> )     | C, C <sub>6</sub> H <sub>6</sub>             | C, C <sub>6</sub> H <sub>6</sub>              |
| PtCl(Me)(diars)                                            | C, C <sub>6</sub> H <sub>6</sub>             |                                               |
| PtCl(Me)(COD)                                              | B, C <sub>6</sub> H <sub>6</sub>             | B, C <sub>6</sub> H <sub>6</sub>              |
| RhCl(PPh <sub>3</sub> ) <sub>3</sub>                       | B, CH <sub>2</sub> Cl <sub>2</sub>           |                                               |
| RhCl(COD)(PPh <sub>3</sub> )                               |                                              | B, C <sub>6</sub> H <sub>6</sub>              |
| [Ph <sub>4</sub> As][RhCl <sub>2</sub> (CO) <sub>2</sub> ] | B, CH <sub>2</sub> Cl <sub>2</sub>           |                                               |
| Attempted Preparation of Perchlorometallobenes             |                                              |                                               |
| "Activated" FeCl <sub>2</sub>                              |                                              | D, THF                                        |
| MoCl <sub>2</sub> (CO) <sub>4</sub>                        |                                              | B, CH <sub>2</sub> Cl <sub>2</sub>            |
| [RuCl <sub>2</sub> (CO) <sub>2</sub> ] <sub>n</sub>        |                                              | B, acetone                                    |
| FeCl <sub>2</sub> ·4H <sub>2</sub> O                       |                                              | D, THF                                        |
| CuCl <sub>2</sub> ·2H <sub>2</sub> O                       |                                              | B, THF                                        |
| CoCl <sub>2</sub>                                          |                                              | C, THF                                        |

tempted with a variety of metal complexes. The results of several of these reactions are listed in the Appendix. In several instances vigorous reaction occurred on the addition of the diazocyclopentadiene resulting in extensive decomposition. For many of these cases the additional ligands on the metal were quite labile, and although alternative reaction pathways cannot be precluded, it is anticipated that in several instances insertion did occur but the products were unstable.

One such example is the reaction of [RhCl(CO)<sub>2</sub>]<sub>2</sub> with C<sub>5</sub>H<sub>4</sub>N<sub>2</sub>. Under CO atmosphere at 0° extensive decomposition occurred on the addition of the ligand. The infrared spectrum of the reaction solution showed two bands at 2061 and 1987 cm<sup>-1</sup> consistent with the formation of Rh(η<sup>1</sup>-C<sub>5</sub>H<sub>4</sub>Cl)(CO)<sub>2</sub> (cf. ν(CO) 2051 and 1987 cm<sup>-1</sup> for Rh(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub><sup>62</sup>). However, this compound was present in low concentration and on warming vigorous evolution of CO occurred.

Other compounds showed no evidence of reaction even at 80°, or catalyzed the slow decomposition of the ligand. Notably, copper and palladium complexes reacted in the latter manner consistent with the well-known<sup>59,63</sup> catalytic properties of such metals in the reactions of other diazoalkanes.

To date, there are five pentachlorocyclopentadienyl complexes of the transition metals and some complexes of mercury. The synthesis of those reported here using the insertion reaction of C<sub>5</sub>Cl<sub>4</sub>N<sub>2</sub> into metal-chlorine bonds proceeds smoothly and in high yield. Unfortunately, the generality of this reaction is not great. However, the compounds obtained are of great interest; Mn(η<sup>1</sup>-C<sub>5</sub>Cl<sub>5</sub>)(CO)<sub>5</sub> has no analog in C<sub>5</sub>H<sub>5</sub>-Mn chemistry and the bond localizations observed for Rh(η<sup>5</sup>-C<sub>5</sub>Cl<sub>5</sub>)(COD) are unique. We expect such discoveries will continue to reward efforts on the synthesis of organometallic derivatives of C<sub>5</sub>Cl<sub>5</sub><sup>-</sup>.

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#### Appendix. Attempted Insertion Reactions

In addition to the results that have been described, an extensive series of reactions was carried out to try to determine

the factors influencing the insertion reactions of diazocyclopentadienes. Also, it was hoped that a general route to perchlorometallobenes could be devised. Unfortunately, the majority of reactions were unsuccessful.

Stoichiometric quantities of reactants were employed except in attempts to prepare perchlorometallobenes where a ratio of 2:1 (C<sub>5</sub>Cl<sub>4</sub>N<sub>2</sub>:metal complex) was used. The infrared absorption due to the nitrogen stretching vibration of the ligand was monitored, and if no change had occurred after 24 hr, the reaction mixture was refluxed. In a few instances when reflux conditions failed, photolysis was attempted by irradiation with a General Electric 100-W Hg lamp.

In those cases where there was a significant change in ν(NN) the reaction was continued under those conditions until all ligand was consumed. The reaction mixture was usually worked up and the material examined for evidence of complex formation. However, if the concentration of the reactant metal complex could be monitored in the infrared spectrum and no change had occurred, the mixture was discarded without workup. Table VII is divided according to the type of metal complex used, or in the case of perchlorometallobenes, the product desired. The solvent is indicated and the outcome of the reaction may be determined from the following code: A, vigorous reaction with extensive visible decomposition of the reactants at room temperature; B, decrease in ν(NN) but no evidence of desired complex formation at room temperature; C, no reaction at room temperature, slow or no decrease in ν(NN) at reflux; D, decrease of ν(NN) under reflux conditions but no complex isolated.

Other results indicated C<sub>5</sub>H<sub>4</sub>N<sub>2</sub> and C<sub>5</sub>Cl<sub>4</sub>N<sub>2</sub> to be more reactive than C<sub>5</sub>Ph<sub>4</sub>N<sub>2</sub> and most exploratory work concentrated on these ligands. When MnH(CO)<sub>5</sub> was allowed to react with C<sub>5</sub>H<sub>4</sub>N<sub>2</sub> the major product was a brown tar. Attempts to insert C<sub>5</sub>H<sub>4</sub>N<sub>2</sub> or C<sub>5</sub>Cl<sub>4</sub>N<sub>2</sub> into the manganese-carbon bonds of Mn(CF<sub>3</sub>)(CO)<sub>5</sub> and Mn(CH<sub>3</sub>)(CO)<sub>5</sub> were also unsuccessful.

**Registry No.** C<sub>5</sub>Cl<sub>4</sub>N<sub>2</sub>, 21572-61-2; MnCl(CO)<sub>5</sub>, 14100-30-2; MnBr(CO)<sub>5</sub>, 14516-54-2; MnH(CO)<sub>5</sub>, 16972-33-1; [RhCl(COD)]<sub>2</sub>, 12092-47-6; MnI(CO)<sub>5</sub>, 14879-42-6; Mn(η<sup>1</sup>-C<sub>5</sub>Cl<sub>5</sub>)(CO)<sub>5</sub>, 53158-67-1; Mn(η<sup>1</sup>-C<sub>5</sub>Cl<sub>4</sub>Br)(CO)<sub>5</sub>, 56282-18-9; Mn(η<sup>1</sup>-C<sub>5</sub>Cl<sub>4</sub>H)(CO)<sub>5</sub>, 56282-19-0; Rh(η<sup>5</sup>-C<sub>5</sub>Cl<sub>5</sub>)(COD), 56282-20-3; Mn(η<sup>5</sup>-C<sub>5</sub>Cl<sub>5</sub>)(CO)<sub>3</sub>, 56282-21-4; Mn(η<sup>5</sup>-C<sub>5</sub>Cl<sub>4</sub>Br)(CO)<sub>3</sub>, 56282-22-5; [MnI(CO)<sub>4</sub>]<sub>2</sub>, 16973-20-9; C<sub>5</sub>Cl<sub>4</sub>NNH<sub>2</sub>, 17581-52-1.

#### References and Notes

- (1) (a) This work is part of the material submitted by K.J.R. in partial fulfillment of the requirements for the Ph.D. degree in chemistry, University of Western Ontario. Present address: Department of Chemistry, University of British Columbia, Vancouver, B.C., Canada. (b) Present address: Department of Chemistry, McGill University, Montreal, Quebec, Canada.
- (2) F. L. Hedberg and H. Rosenberg, *J. Am. Chem. Soc.*, **92**, 3239 (1970).
- (3) F. L. Hedberg and H. Rosenberg, *J. Am. Chem. Soc.*, **95**, 870 (1973).
- (4) G. M. Brown, F. L. Hedberg, and H. Rosenberg, *J. Chem. Soc., Chem. Commun.*, 5 (1972), and references therein.
- (5) J. M. Birmingham, *Adv. Organomet. Chem.*, **2**, 365 (1964).
- (6) T. Chivers "Chemistry of the Carbon-Halogen Bond", S. Patai, Ed., Wiley, New York, N.Y., 1973, and references therein.
- (7) R. L. Schaaf, P. T. Kan, and K. L. Rinehart, Jr., Wright Air Development Center Technical Report 58-187, Part II, May 1960, AD243566L; footnote 9 in ref. 3.
- (8) G. Wulfsberg and R. West, *J. Am. Chem. Soc.*, **94**, 6069 (1972).
- (9) G. Wulfsberg and R. West, *J. Am. Chem. Soc.*, **93**, 4085 (1971).
- (10) G. Wulfsberg, R. West, and V. N. Mallikarjuna Rao, *J. Am. Chem. Soc.*, **95**, 8658 (1973).
- (11) (a) V. W. Day, B. R. Stults, K. J. Reimer, and A. Shaver, *J. Am. Chem. Soc.*, **96**, 1227 (1974); (b) K. J. Reimer and A. Shaver, *J. Organomet. Chem.*, **93**, 239 (1975).
- (12) V. W. Day, B. R. Stults, K. J. Reimer, and A. Shaver, *J. Am. Chem. Soc.*, **96**, 4008 (1974).
- (13) P. N. Jones and A. Nadeau, *Spectrochim. Acta*, **20**, 1175 (1964).
- (14) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).
- (15) J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, **8**, 211 (1966).
- (16) R. Cramer, *Inorg. Chem.*, **1**, 722 (1962).
- (17) R. B. King "Organometallic Synthesis", Vol. 1, J. J. Eisch and R. B. King, Ed., Academic Press, New York, N.Y., 1965.
- (18) F. Zingales and U. Sartorelli, *Inorg. Chem.*, **6**, 1243 (1967).

- (19) E. T. McBee, U.S. Patent 3,141,043 (July 14, 1964; Appl. Mar 24, 1961); *Chem. Abstr.*, **61**, 8205f (1964).
- (20) F. Klages and K. Bott, *Chem. Ber.*, **97**, 735 (1964).
- (21) H. Disselkottter, *Angew. Chem., Int. Ed. Engl.*, **3**, 379 (1964).
- (22) E. T. McBee, J. A. Bosoms, and C. J. Morton, *J. Org. Chem.*, **31**, 768 (1966).
- (23) The original paper<sup>22</sup> incorrectly reported 0.125 mol of Ag<sub>2</sub>O as being 15.5 g. The correct amount, used here, is required for the reaction to be completed in a reasonable length of time. CsCl<sub>4</sub>N<sub>2</sub> is said to be very stable<sup>22</sup> and we experienced no difficulty. However it is advisable to use care when subjecting the compound to extreme reaction conditions.
- (24) V. W. Day, K. J. Reimer, and A. Shaver, *J. Chem. Soc., Chem. Commun.*, 403 (1975).
- (25) The first number in parentheses is the rms estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the average value, respectively.
- (26) L. M. Haines and M. H. B. Stiddard, *Adv. Inorg. Chem. Radiochem.*, **12**, 53 (1969), and references therein.
- (27) A. Davidson and J. W. Faller, *Inorg. Chem.*, **6**, 845 (1967).
- (28) F. A. Cotton, *Inorg. Chem.*, **3**, 702 (1964).
- (29) M. Bigorgne, R. Poilblanc, and M. Pankowski, *Spectrochim. Acta, Part A*, **26**, 1217 (1970).
- (30) J. B. Wilford and F. G. A. Stone, *J. Organomet. Chem.*, **2**, 371 (1964).
- (31) J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, **4**, 389 (1965).
- (32) S. F. A. Kettle and I. Paul, *Inorg. Chim. Acta*, **2**, 15 (1968).
- (33) J. R. Miller, *Inorg. Chim. Acta*, **2**, 421 (1968).
- (34) G. M. Bodner and L. J. Todd, *Inorg. Chem.*, **13**, 1335 (1974).
- (35) O. A. Gansow, A. R. Burke, and G. N. La Mar, *J. Chem. Soc., Chem. Commun.*, 456 (1972).
- (36) L. J. Todd and J. R. Wilkinson, *J. Organomet. Chem.*, **77**, 1 (1974), and references therein.
- (37) B. E. Mann, *Adv. Organomet. Chem.*, **12**, 135 (1974), and references therein.
- (38) P. C. Lauterbur and R. B. King, *J. Am. Chem. Soc.*, **87**, 3266 (1965).
- (39) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, N.Y., 1972.
- (40) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley, New York, N.Y., 1972.
- (41) G. M. Bodner, B. N. Storhoff, D. Doddrell, and L. J. Todd, *J. Chem. Soc. D*, 1530 (1970).
- (42) F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968).
- (43) P. West, M. C. Woodville, and M. D. Rausch, *J. Am. Chem. Soc.*, **91**, 5649 (1969).
- (44) B. Floris, G. Illuminati, and G. Ortaggi, *J. Chem. Soc. D*, 492 (1969).
- (45) Yu. K. Grishin, N. M. Sergoyev, and Yu. A. Ustynyuk, *Org. Magn. Reson.*, **4**, 377 (1972).
- (46) G. E. Hawkes, R. A. Smith, and J. D. Roberts, *J. Org. Chem.*, **39**, 1276 (1974).
- (47) D. J. Ciappenelli, F. A. Cotton, and L. Kruczynski, *J. Organomet. Chem.*, **42**, 159 (1972).
- (48) M. Kubo and D. Nakamura, *Adv. Inorg. Radiochem.*, **8**, 257 (1966).
- (49) G. Wulfsberg and R. West, private communication.
- (50) E. O. Fischer and M. Heberhold, "Essays in Coordination Chemistry", W. Schneider, G. Anderegg, and R. Gut, Ed., Birkhauser, Basel and Stuttgart, 1964.
- (51) M. L. H. Green, "Organometallic Compounds", Vol. II, G. E. Coates, M. L. H. Green, and K. Wade, Ed., Methuen, London, 1968, and references therein.
- (52) C. H. Bamford, J. W. Burley, and M. Coldbeck, *J. Chem. Soc., Dalton Trans.*, 1846 (1972).
- (53) R. J. Angelici and F. Basolo, *J. Am. Chem. Soc.*, **84**, 2495 (1962).
- (54) J. C. Hileman, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, **1**, 933 (1962).
- (55) M. A. El-Sayed and H. D. Kaesz, *Inorg. Chem.*, **2**, 158 (1963).
- (56) J. Cooke, W. R. Cullen, and F. G. A. Stone, *J. Chem. Soc. A*, 1872 (1969).
- (57) J. Clemens, M. Green, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1620 (1973).
- (58) J. Clemens, M. Green, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 93 (1974).
- (59) M. F. Lappert and J. S. Poland, *Adv. Organomet. Chem.*, **9**, 397 (1970).
- (60) S. Otsuka, A. Nakamura, T. Koyama, and Y. Tatsuno, *J. Chem. Soc., Chem. Commun.*, 1105 (1972).
- (61) R. West, *Accounts Chem. Res.*, **3**, 130 (1970).
- (62) E. O. Fischer and K. Bittler, *Z. Naturforsch., Teil B*, **16**, 225 (1961).
- (63) D. A. Cardin, B. Cetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, **2**, 99 (1973).

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## Iron-57 Mössbauer Study of Iron(II)-Carbene Compounds. Bonding Characteristics of Carbenes

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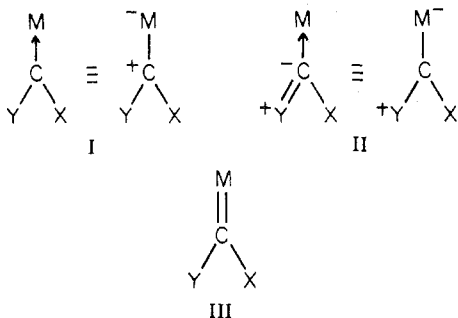
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<sup>57</sup>Fe Mössbauer spectra are reported for a number of six-coordinate iron(II) isocyanide-carbene complexes of the type [Fe(CNMe)<sub>5</sub>(carbene)](PF<sub>6</sub>)<sub>2</sub> and [Fe(CNMe)<sub>4</sub>(carbene)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>. The signs of the <sup>57</sup>Fe QS for [Fe(CNMe)<sub>5</sub>(C(NH<sub>2</sub>)NHMe)](PF<sub>6</sub>)<sub>2</sub> and [Fe(CNMe)<sub>4</sub>[(CNHMe)<sub>2</sub>N<sub>2</sub>HPh]](PF<sub>6</sub>)<sub>2</sub> are negative and positive, respectively. The derived partial center shift (pcs) and partial quadrupole splittings (pqs) for carbenes indicate that they are very good σ donors relative to all neutral ligands and poor π acceptors. In particular, our carbenes are better σ donors and worse π acceptors than MeNC. Using the point charge model including distortions, we attempt to explain the larger quadrupole splittings for the compounds containing chelating carbenes, and the unusual quadrupole splittings for "trans"- and cis-Fe(o-phen)<sub>2</sub>(CN)<sub>2</sub> and K<sub>2</sub>[Fe(o-phen)(CN)<sub>4</sub>].

### Introduction

Many recent papers and reviews have discussed the structure and bonding of metal-carbene compounds. The bonding in these compounds is considered to be a hybrid of the structures I-III<sup>1</sup> (where X and Y are heteroatoms such as O or N with



nonbonding electrons).

Cardin et al.<sup>2</sup> and Cotton et al.<sup>1</sup> have discussed X-ray structural and other data which indicate that the carbene is a hybrid mainly of structures I and II; i.e., there is little π back-bonding from the metal to the carbene as in III.

A number of spectroscopic techniques have been used to compare the bonding of carbenes with other neutral ligands—with a wide variety of conclusions. Thus, Darensbourg and Darensbourg<sup>3</sup> in an infrared study of Cr(CO)<sub>5</sub>L compounds suggested that carbenes were comparable to phosphines as donors and were strong π acceptors. The very recent photoelectron study of Jolly et al.<sup>4</sup> supported this view by suggesting that structure III contributed 45% to the overall hybrid. In striking contrast, <sup>13</sup>C NMR studies<sup>5,6</sup> suggest that there is electron deficiency on the carbene carbon. These workers have characterized such compounds as transition metal stabilized carbonium ions. More specifically, Clark and Manzer<sup>7</sup> suggested that carbenes are stronger σ donors and/or