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INSERTION REACTIONS OF DIAZOCYCLOPENTADIENES WITH HALO—TRANSITION METAL COMPLEXES*

KENNETH J. REIMER and ALAN SHAVER

Department of Chemistry, University of Western Ontario, London, Ontario (Canada)

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Summary

The reactivity of diazocyclopentadiene and diazotetraphenylcyclopentadiene, known precursors of interesting carbenes, towards some rhodium, iridium and manganese complexes has been investigated. It was found that reactions of halo-bridged-dirhodium species and manganese pentacarbonyl halides with diazocyclopentadienes at room temperature yielded halo-substituted cyclopentadienyl complexes. This reaction can be considered an insertion of the diazo species into the metal halogen bond accompanied by loss of dinitrogen. The intermediacy of free carbenes is considered unlikely.

A variety of preparative routes are known for the syntheses of carbene complexes [1-6] but it is significant that the most obvious route, the trapping of free carbenes generated from neutral organic carbene precursors has proved "notoriously difficult" [2]. However, two cases in which this appears to have been successfully accomplished using diazoalkane reagents have been described recently [7, 8].

Intrigued by the possibility of designing a suitable system whereby free carbenes could be trapped on a metal complex we have explored the properties of other carbene sources namely diazocyclopentadienes. It has been recently demonstrated [9] that the formation of the triphenylphosphonium tetraphenylcyclopentadienylide (III) by the thermal decomposition of tetraphenyldiazocyclopentadiene (I) in the presence of triphenylphosphine proceeds via the intermediate tetraphenylcyclopentadienylidene (II) as in eqn. 1 ($R = Ph$). Other Lewis bases may be used instead of PPh_3 and the analogous intermediacy

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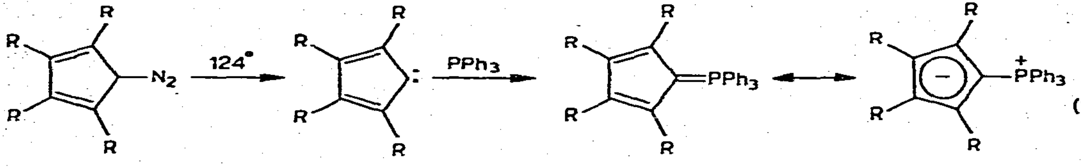
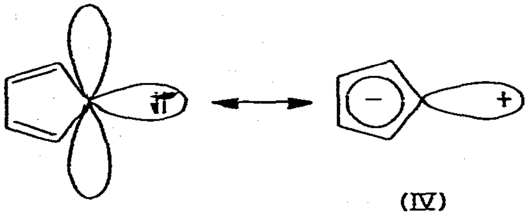


(I) (II) (IIIa) (IIIb) (1)

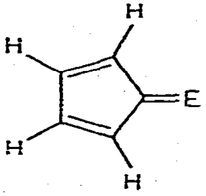
of the free carbene (II) has been suggested in thermal and photolytic reactions of I with pyridine to give pyridinium diazotetraphenylcyclopentadienylide [10,11].

These reactions are not restricted to tetraphenylcyclopentadiene, as diazocyclopentadiene (I, R = H) gives analogous products from photolytic reactions with alkyl sulfides [12]. Quantum mechanical calculations have demonstrated that the singlet state of cyclopentadienylidene is stabilized by interaction of the carbenic electrons with the π-electrons of the ring to form an aromatic system, IV [13]. Thus the formation of the products described above is believed to occur

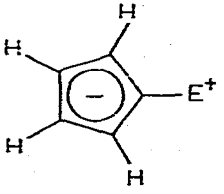


(IV)

by electrophilic attack of the vacant σ orbital of the carbene on the lone pair of electrons of the Lewis base [10-12]. Studies and calculations on compounds of type V have concluded that the ground state may be partitioned into ca. 20% ylene (Va) and 80% ylide (Vb):



(Va)



(Vb)

E = PPh_3[14], SMe_2[15]

In accord with this, V acts as a 6-electron donor in the complexes (η^5-C_5H_4E)-$Mo(CO)_3$ [16, 17].

These observations prompted us to investigate the possibility of trapping cyclopentadienylidene carbenes with nucleophilic transition metal complexes in the anticipation that such products could be considered as examples of novel electrophilic carbene complexes. We have carried out reactions of various diazocyclopentadienes with transition metal complexes. The products can be considered to arise from the insertion of the diazocyclopentadiene into a metal halide bond to give halo-substituted cyclopentadienylmetal compounds. A preliminary account has appeared [18].

Experimental

General

Inert atmosphere techniques were used in the synthesis of all new compounds described in this paper. 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. Accurate determinations of carbonyl stretching frequencies were obtained by methods described previously [19]. ^1H NMR spectra were run by Ms. Heather Schroeder of our department on a Varian Associates HA-100 spectrometer at 100 MHz with tetramethylsilane as an internal reference/lock signal. Molecular weights were determined either in benzene solution using a Hitachi—Perkin—Elmer Model 115 Molecular Weight apparatus, or mass spectrometrically from parent ion peaks. The latter were measured on spectra obtained by Mr. Robert Lazier of our department on 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; Spang Microanalytical Laboratory, Ann Arbor, Michigan; or by Chemalytics Inc., Arizona.

Preparation of starting materials

The following compounds were prepared by published procedures: $[RhCl(COD)]_2$ [20], $[RhBr(COD)]_2$ [20], $[RhCl(CO)_2]_2$ [21], $[RhCl(C_2H_4)_2]_2$ [22], $C_5Ph_4N_2$ [10] and $MnBr(CO)_5$ [23].

Diazocyclopentadiene, $C_5H_4N_2$

The ligand was prepared according to the general method of Weil and Cais [24]. A mixture of cyclopentadiene (7 ml), diethylamine (4.7 ml) and *p*-toluene sulfonyl azide [25] (10.4 g) was allowed to stand at 5°C for 5 d. H_2O (25 ml) was added and the product extracted with pentane (several times, with filtering) from the brown heterogeneous reaction mixture. The extracts were combined and washed with water until a test with litmus paper indicated the absence of amine. After drying over $MgSO_4$ the volume was concentrated to slightly less than 10 ml. (*Caution*: the pure compound is known [26] to be highly explosive and should always be kept in solution [27].) This solution was transferred to a 10 ml volumetric flask and the volume brought to the calibration mark by the addition of pentane. The concentration of the solution was determined by adding a known amount of this solution to an ethereal solution containing excess triphenylphosphine. The concentration could be conveniently calculated from the amount of the adduct, $C_5H_4N_2 \cdot PPh_3$ [24], which crystallized from solution. A typical reaction gave 10 ml of 2.5 *M* solution. (2.3 g, $C_5H_4N_2$, 47% yield based on $CH_3C_6H_4SO_2N_3$ used.) Although the compound decomposed quite rapidly at room temperature, samples stored at —78°C were stable for several months.

Pentacarbonylchloromanganese, $MnCl(CO)_5$

The synthesis of $MnCl(CO)_5$ by the slow passage of chlorine through a cooled carbon tetrachloride solution of $Mn_2(CO)_{10}$ has been reported [28] to give a 65% yield of the required product. However, our attempts to repeat this procedure gave much lower, and variable, yields. Thus, a more reproducible procedure was devised as follows.

The reaction was conducted in a 100 ml two-necked round-bottomed flask fitted with a nitrogen inlet, a magnetic stirrer and an equipressure dropping funnel. Finely ground $Mn_2(CO)_{10}$ (4.0 g, 0.01 mol) was dissolved in a minimum of degassed carbon tetrachloride at 0°C in the nitrogen filled flask. Carbon tetrachloride (25 ml) was saturated with chlorine in the dropping funnel and the yellow solution added dropwise to the cooled, stirred solution of $Mn_2(CO)_{10}$. As the addition proceeded, some $MnCl(CO)_5$ began to precipitate. After complete addition, the reaction mixture was allowed to warm to room temperature and it was then stirred for four hours. The yellow precipitate was filtered in air and washed several times with carbon tetrachloride. The yield of crude product was 4.04 g (86%). The compound was contaminated with only small amounts of $[MnCl(CO)_4]_2$ and white insoluble material. These impurities were negligible and usually no further purification was undertaken. If absolutely pure $MnCl(CO)_5$ was required (as for the kinetic measurements) it was easily obtained by sublimation (40°C/0.1 Torr). Heating always results in some conversion to the involatile $[MnCl(CO)_4]_2$ and only 65% yields (based on $Mn_2(CO)_{10}$ used) were obtained.

Pentacarbonyliodomanganese, $MnI(CO)_5$

Brief details of the preparation of $MnI(CO)_5$ from the direct reaction of $Mn_2(CO)_{10}$ and iodine have been reported [29]. In this work it was found that the best results were obtained from stoichiometric quantities of the reactants heated at 90°C (instead of the suggested 130-140°C) in a sealed Carius tube. Sublimation (40°C/0.1 Torr) separated the product from a non-volatile powder but it was usually contaminated with $Mn_2(CO)_{10}$. Recrystallization from pentane gave an overall 50% yield of ruby-red crystals. The product is best stored at 5°C, since iodine is liberated on prolonged standing at room temperature.

Preparation of pentahapto-halogen-substituted cyclopentadienyl complexes

With the exception of $Rh(\eta^5\text{-}C_5Ph_4Cl)(C_2H_4)_2$ and $Mn(\eta^5\text{-}C_5Ph_4Cl)(CO)_3$, all compounds described in this section were obtained in essentially quantitative yield. Although reactions were often conducted by allowing the reactants to stir overnight, the progress of the reaction may be conveniently monitored by observing the decrease in intensity of the band due to $\nu(NN)$ of the diazocyclopentadiene. This band occurs at ca. 2080 and 2100 cm^{-1} for $C_5Ph_4N_2$ and $C_5H_4N_2$ respectively.

(pentahapto-Chlorotetraphenylcyclopentadienyl)(1,5-cyclooctadiene)rhodium, $Rh(\eta^5\text{-}C_5Ph_4Cl)(COD)$

Benzene (10 ml) was added to a mixture of $[RhCl(COD)]_2$ (0.20 g, 0.40 mmol) and $C_5Ph_4N_2$ (0.320 g, 0.81 mmol) in a nitrogen filled Schlenk tube. Bubbles of gas were evolved and on stirring the red-orange solution lightened in color. The reaction was allowed to proceed overnight and then the solvent was removed in vacuo. The product was recrystallized from pentane.

(pentahapto-Bromotetraphenylcyclopentadienyl)(1,5-cyclooctadiene)rhodium, Rh(η^5-C_5Ph_4Br)(COD) and dicarbonyl(pentahaptochlorotetraphenylcyclopentadienyl)rhodium, Rh(η^5-C_5Ph_4Cl)$(CO)_2$

Both compounds were prepared as above using $[RhBr(COD)]_2$ and $[RhCl(CO)_2]_2$ respectively and the appropriate stoichiometric quantities of $C_5Ph_4N_2$. The latter complex is more soluble than the COD derivative and was recrystallized from hexane.

(pentahapto-Chlorocyclopentadienyl)(1,5-cyclooctadiene)rhodium, Rh(η^5-C_5H_4Cl)COD

To a solution of $[RhCl(COD)]_2$ (0.20 g, 0.40 mmol) in benzene (5 ml) was added a portion of a 2.5 *M* pentane solution of diazocyclopentadiene (0.32 ml, 0.80 mmol). The solution was stirred overnight and stripped down. The product was recrystallized from hexane at —78°C.

(pentahapto-Chlorotetraphenylcyclopentadienyl)diethylenerhodium, Rh(η^5-C_5Ph_4Cl)$(C_2H_4)_2$

Special procedures had to be used for the preparation of this complex. $[RhCl(C_2H_4)_2]_2$ is unstable in solution and if stoichiometric quantities of reactants were used, some $C_5Ph_4N_2$ always remained in the reaction mixture. This made purification of the product very difficult. Therefore, to ensure complete reaction of all ligand, a four-fold excess of $[RhCl(C_2H_4)_2]_2$ was used.

A mixture of $[RhCl(C_2H_4)_2]_2$ (0.5 g, 1.28 mmol) and $C_5Ph_4N_2$ (0.25 g, 0.63 mmol) in benzene (50 ml) was stirred vigorously in a 100 ml round-bottomed flask. At various intervals aliquots were removed from the dark mixture and filtered through glass wool into infrared solution cells. The absorption due to the nitrogen stretching vibration of the ligand was monitored in the infrared spectrum and after nine hours all ligand had been consumed. The mixture was freeze-dried and the residue chromatographed on alumina III, eluting with benzene. The yellow band which preceded a variety of green and blue bands was collected and freeze-dried to a pale yellow powder. Recrystallization from pentane gave 25 mg (7.0%, based on $C_5Ph_4N_2$) of orange crystals.

Tricarbonyl(pentahapto-chlorocyclopentadienyl)manganese, Mn(η^5-C_5H_4Cl)$(CO)_3$

To $MnCl(CO)_5$ (0.2 g, 0.87 mmol) suspended in pentane (10 ml) in a Schlenk tube was added 0.35 ml (0.875 mmol) of a 2.5 *M* pentane solution of diazocyclopentadiene and the mixture stirred overnight. It was then filtered under nitrogen into a 100 ml round-bottomed flask and the volume concentrated to ca. 5 ml by a nitrogen stream. Cooling to —78°C caused the product to crystallize. The remainder of the solvent was removed with a syringe and the product dried by brief evacuation. The flask was then fitted with a sublimation probe and the product sublimed onto the water-cooled finger under static vacuum. The purified product was then transferred quickly (because of its low m.p.) to a nitrogen filled Schlenk tube where it was stored at 5°C.

Tricarbonyl(pentahapto-bromocyclopentadienyl)manganese, Mn(η^5-C_5H_4Br)$(CO)_3$

Diazocyclopentadiene (0.22 ml of a 2.5 *M* pentane solution, 0.55 mmol) was added to a suspension of $MnBr(CO)_5$ (0.150 g, 0.55 mmol) in pentane (20 ml). The mixture was stirred overnight, filtered and concentrated to ca. 5 ml in a nitrogen stream. Cooling to −78°C induced crystallization, the mother liquor was sucked away and the product dried by brief evacuation.

Tricarbonyl(pentahapto-iodocyclopentadienyl)manganese, $Mn(\eta^5\text{-}C_5H_4I)(CO)_3$

This compound was prepared as above using $MnI(CO)_5$, but forty-eight hours were required for complete reaction.

Tricarbonyl(pentahapto-chlorotetraphenylcyclopentadienyl)manganese, $Mn(\eta^5\text{-}C_5Ph_4Cl)(CO)_3$

A different procedure is required for the synthesis of this compound. The reaction is conducted in refluxing benzene under which conditions $MnCl(CO)_5$ decomposes. As the presence of unreacted $C_5Ph_4N_2$ makes purification of the product difficult, excess $MnCl(CO)_5$ is used to ensure complete consumption of the ligand. A mixture of $MnCl(CO)_5$ (0.232 g, 1.0 mmol) and $C_5Ph_4N_2$ (0.200 g, 0.51 mmol) in benzene (50 ml) were refluxed under nitrogen for twenty-eight hours. (After this period the infrared spectrum indicated complete reaction of the ligand.) The reaction mixture was freeze-dried. A sublimation probe was introduced and the brown powder heated at 50°C/0.1 Torr until no additional yellow material collected on the watercooled probe. (Infrared analysis showed this to be $Mn_2(CO)_{10}$). The yellow-brown residue was recrystallized from pentane to give 50 mg (11% based on $C_5Ph_4N_2$) of orange crystals.

Reaction of diazotetraphenylcyclopentadiene with diiron nonacarbonyl

Reaction of the above compounds at room temperature in toluene yields the dimer $[Fe(\eta^5\text{-}C_5Ph_4H)(CO)_2]_2$ as reported [17]. However, in refluxing octane a different product was obtained. $C_5Ph_4N_2$ (0.399 g, 0.001 mol) and $Fe_2(CO)_9$ (0.380 g, 0.001 mol) were combined in 30 ml octane and over a period of 45 min brought to reflux. After 10 min at reflux the solution was cooled, filtered and stripped to dryness. The crude brown product was dissolved in hexane—benzene (4 ml/2 ml) and the solution put on a 25 cm × 2 cm column of Woelm Alumina (activity 3) in hexane. Elution with benzene gave $[Fe(\eta^5\text{-}C_5Ph_4H)(CO)_2]_2$ as a brown band followed by a new compound as a yellow band. Freeze drying the yellow solution gave 0.155 g (29%) which could be recrystallized from CH_2Cl_2—hexane. It gave the following mass spectrum: *m/e* 508 (M^+), 480 (M^+—CO), 452 (M^+—2CO), 424 (M^+—3CO).

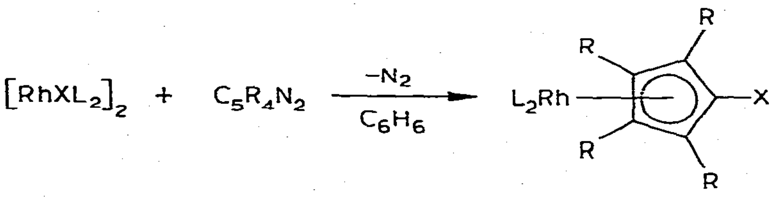
Results

Since the presence of a free carbene species had been demonstrated [9] in the decomposition of tetraphenyldiazocyclopentadiene at 124°C initial experiments consisted of thermal reactions of this diazoalkane with some rhodium and iridium complexes (eqn. 2).

$$C_5Ph_4N_2 + \begin{array}{l} [RhCl(CO)_2]_2 \\ RhCl(PPh_3)_3 \\ RhClCO(PPh_3)_2 \\ IrClCO(PPh_3)_2 \end{array} \xrightarrow[\text{octane or xylene}]{\text{refluxing}} \qquad (2)$$

Vigorous evolution of nitrogen was observed at 124°C but this was followed by the formation of dark, intractable reaction mixtures. Numerous attempts to isolate discrete products by chromatography and/or fractional crystallization proved unsuccessful. Although Vaska's complex, *trans*-carbonylchlorobis(triphenylphosphine)iridium, was recovered quantitatively, in all other instances decomposition of the metal complex had also occurred.

Due to these initial results room temperature reactions were carried out. Thus, both 2,3,4,5-tetraphenyldiazocyclopentadiene and diazocyclopentadiene were found to insert into halogen-bridged dirhodium species to give new halogen-substituted *pentahapto*-cyclopentadienyl complexes, VI (eqn. 3). Except for the case, $L_2 = (C_2H_4)_2$, reaction 3 proceeds quantitatively in benzene under nitrogen atmosphere at room temperature. Most reactions were allowed to proceed for ca. 24 h but each could be conveniently monitored by observing the disappearance of the band (at 2100 cm^{-1} for $C_5H_4N_2$ and 2080 cm^{-1} for $C_5Ph_4N_2$) in the infrared spectrum due to the nitrogen group. The reaction of $C_5Ph_4N_2$ and di-μ-chlorobis(diethylenerhodium) is complicated by the instability of the latter in solution. Consequently, the yield from this reaction is low and an excess of the rhodium complex is required to prevent contamination of the product by excess ligand. Because of the presence of decomposition products in the reaction mixture chromatography is required for isolation of $Rh(\eta^5\text{-}C_5Ph_4Cl)(C_2H_4)_2$, but in all other cases the products were easily purified by recrystallization.

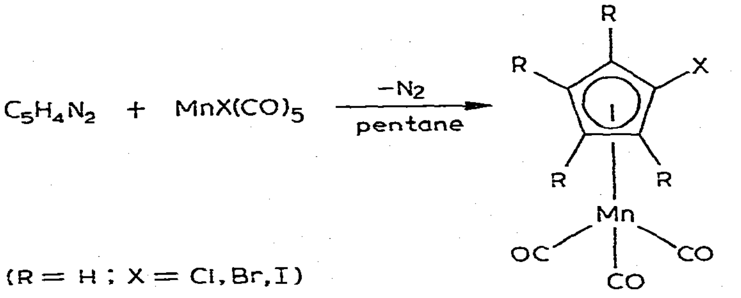


(3)

(VI)

(VI) a : $R = Ph$ $L_2 = COD$ $X = Cl$
b : $R = Ph$ $L_2 = COD$ $X = Br$
c : $R = Ph$ $L_2 = (C_2H_4)_2$ $X = Cl$
d : $R = Ph$ $L_2 = (CO)_2$ $X = Cl$
e : $R = H$ $L_2 = COD$ $X = Cl$

Diazocyclopentadiene was also found to insert into the metal—halogen



(4)

(R = H ; X = Cl, Br, I)

(VII)

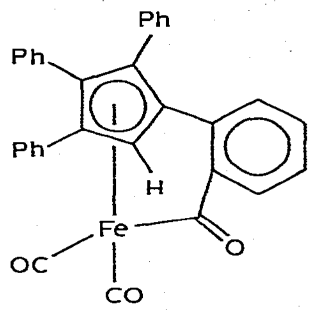
bond of manganese pentacarbonyl halides at room temperature giving the halogen-substituted (*pentahapto*-cyclopentadienyl)tricarbonylmanganese derivatives VII in quantitative yield (eqn. 4). No reaction occurred between tetraphenyldiazocyclopentadiene and pentacarbonylchloromanganese in benzene at room temperature but after several hours at reflux the analogous phenyl-substituted compound VII (R = Ph, X = Cl) was formed. Analytical and physical data for the complexes are presented in Table 1. The manganese complexes VII (R = H; X = Cl, Br, I) have been previously prepared [30,31] by an indirect route.

pentahapto-Cyclopentadienyl complexes may also be obtained from the reaction of diazocyclopentadienes with metal carbonyls. Thus diazocyclopentadiene treated with $Fe_2(CO)_9$ in toluene at room temperature gave $[Fe(\eta^5\text{-}C_5H_5)(CO)_2]_2$ (presumably by means of hydride abstraction from the solvent). The preparation of the tetraphenyl analogue of this dimer by the corresponding reaction with tetraphenyldiazocyclopentadiene has been previously reported [17]. However, it was found that when this reaction was carried out in octane at 124°C a yellow compound analyzing as $Fe(C_5Ph_4H)(CO)_3$ was formed. Molecular weight data were consistent with a monomeric formulation and in the PMR a singlet was found at δ 5.51 ppm. This integrated to be 1 H relative to the multiplet at δ 6.8 to 7.4 for the phenyl resonances. The infrared spectrum showed typical phenyl absorptions as well as three carbonyl bands at 2019, 1979 and 1644 cm^{-1} (cyclohexane solution). Such data are consistent [32] with a *pentahapto*-tetraphenylcyclopentadienyl group having one phenyl group linked to the iron via an acyl group in the *ortho* position, VIII. Confirmation of this structure probably requires X-ray analysis.

TABLE 1

ANALYTICAL AND PHYSICAL DATA FOR SUBSTITUTED CYCLOPENTADIENYL COMPLEXES

Compound	Colour	M.p. (°C)	Analysis found (calcd.) (%)	
			C	H
$Rh(\eta^5\text{-}C_5Ph_4Cl)(COD)$	yellow	208-210	72.08 (72.29)	5.28 (5.21)
$Rh(\eta^5\text{-}C_5Ph_4Br)(COD)$	yellow	202-204 (dec.)	67.56 (67.41)	5.02 (4.85)
$Rh(\eta^5\text{-}C_5Ph_4Cl)(C_2H_4)_2$	orange	154-155 (dec.)	70.36 (70.43)	5.17 (4.98)
$Rh(\eta^5\text{-}C_5Ph_4Cl)(CO)_2$	red	78-81	66.39 (66.17)	3.73 (3.55)
$Rh(\eta^5\text{-}C_5H_4Cl)(COD)$	yellow	63-64	50.14 (50.29)	5.12 (5.15)
$Mn(\eta^5\text{-}C_5H_4Cl)(CO)_3$	yellow	24-25	40.44 (40.30)	1.57 (1.68)
$Mn(\eta^5\text{-}C_5H_4Br)(CO)_3$	yellow	43-45	33.90 (33.96)	1.53 (1.41)
$Mn(\eta^5\text{-}C_5H_4I)(CO)_3$	yellow	29-30	29.13 (29.12)	1.28 (1.22)
$Mn(\eta^5\text{-}C_5Ph_4Cl)(CO)_3$	orange	143-146 (dec.)	71.69 (70.82)	3.99 (3.69)
$Fe(\eta^5\text{-}C_5HPh_3C_6H_4CO)(CO)_2$	yellow	165-166	75.77 (75.63)	3.81 (3.94)



(VIII)

Infrared spectra

In the region 1500 to 400 cm^{-1} (Table 2) the infrared spectra of the halogen-substituted cyclopentadienylmanganese compounds, Mn(η^5-C_5H_4X)$(CO)_3$, are very similar to that of Mn(η^5-C_5H_5)$(CO)_3$ [33] except for new bands at 1180 and 895 cm^{-1} for X = Cl; 1160 and 880 cm^{-1} for X = Br; 1155 and 865 cm^{-1} for X = I. This is consistent with similar X-sensitive bands [34,35] observed for 1,1'-dihaloferrocenes [34]. The similarity in frequencies for the present compounds and the halogen-substituted ferrocenes suggest that such bands may be considered as diagnostic of monohalogen-substituted *pentahapto*-cyclopentadienyl ligands.

The carbonyl stretching frequencies of a number of *pentahapto*-cyclopentadienyl compounds are compared in Table 3. The presence of an electron-withdrawing halogen substituent causes a shift of ν(CO) to higher frequencies reflecting decreased donor and/or increased acceptor properties of the cyclopentadienyl ligand. Phenyl substituents appear to counteract the effect of the halogen and for Mn(η^5-C_5Ph_4Cl)$(CO)_3$ the average value of ν(CO) is slightly lower than that of Mn(η^5-C_5H_5)$(CO)_3$ indicating a relative increase in the electron density on the metal. A similar effect appears to be operative for the analogous rhodium complex although the difference is less significant.

^1H NMR data

Two triplets [37] were found for the ring protons in ^1H NMR spectra of all of the π-C_5H_4X compounds prepared in the study (Table 4). In the case of the rhodium complex, Rh(η^5-C_5H_4Cl)(COD), each of the triplets showed

TABLE 2

INFRARED DATA (cm^{-1}) FOR SOME *pentahapto*-CYCLOPENTADIENYL COMPLEXES OF MANGANESE

Complex	Band positions [a]
Mn(η^5-C_5H_5)$(CO)_3$ [b]	3129w, 1430m, 1332w, 1270vvw, 1203vvw, 1155vvw, 1116w, 1065w(br), 1015m, 943m, 848(sh), 839s, 669s, 635vs, 611(sh), 543s, 500w
Mn(η^5-C_5H_4Cl)$(CO)_3$ [c]	3123w(br), 1436s, 1370w, 1270vvw, 1204vvw, 1180s, 1066vvw, 1025m, 922vvw, 895s, 833s(br), 668vs, 633vvs, 608(sh), 537s, 494w, 479w

[a] Measured as nujol mulls; carbonyl stretching vibrations omitted. [b] Reported spectrum recorded in this laboratory and is in good agreement with literature values [33]. [c] Bromo and iodo derivatives gave essentially identical spectra except for the X-sensitive bands (see text).

TABLE 3

INFRARED CARBONYL STRETCHING FREQUENCIES [a] FOR *pentahapto*-CYCLOPENTADIENYL MANGANESE AND RHODIUM COMPLEXES

Complex	$\nu(C\equiv O)$ (cm^{-1}) [c]	
$Mn(\eta^5\text{-}C_5H_4Me)(CO)_3$	2025	1943
$Mn(\eta^5\text{-}C_5Ph_4Cl)(CO)_3$	2024	1951, 1942
$Mn(\eta^5\text{-}C_5H_5)(CO)_3$	2030	1945
$Mn(\eta^5\text{-}C_5H_4Cl)(CO)_3$	2034	1952
$Mn(\eta^5\text{-}C_5H_4Br)(CO)_3$	2034	1952
$Mn(\eta^5\text{-}C_5H_4I)(CO)_3$	2034	1952
$Rh(\eta^5\text{-}C_5H_5)(CO)_2$ [b]	2051	1987
$Rh(\eta^5\text{-}C_5Ph_4Cl)(CO)_2$	2048	1987

[a] Unless otherwise indicated spectra were measured using cyclohexane solutions in this laboratory. [b] Values taken from ref. 36. [c] Probable error is ±1 cm^{-1}.

additional small coupling to rhodium ($I = 1/2$, 100% abundance). On the basis of previous results [37-39] the chemical shifts of the ring protons of the manganese compounds, $Mn(\eta^5\text{-}C_5H_4X)(CO)_3$, have been assigned [40] as shown in Table 4. By analogy, we have made a similar assignment for the rhodium compound. However, it has been noted [37] that extension of the assignments made for ferrocenes to other cyclopentadienyl complexes may not be possible and thus assignments must be regarded as tentative.

The phenyl resonances appeared as broad complex multiplets in the spectra of $Mn(\eta^5\text{-}C_5Ph_4Cl)(CO)_3$ and $Rh(\eta^5\text{-}C_5Ph_4Cl)(CO)_2$. However, quite an interesting symmetrical pattern appeared in the phenyl region of the spectra of both $Rh(\eta^5\text{-}C_5Ph_4Cl)(COD)$ and $Rh(\eta^5\text{-}C_5Ph_4Cl)(C_2H_4)_2$. The spectrum of the former compound is shown in Fig. 1. The relative intensities of the four distinct multi-

TABLE 4

^1H NMR DATA [a] FOR HALOGEN-SUBSTITUTED CYCLOPENTADIENYL COMPLEXES OF MANGANESE AND RHODIUM

Complex	Ring protons		Phenyl substituents	Other ligand resonances
	$H_{2,5}$	$H_{3,4}$		
(a) *η^5-C_5H_4X derivatives*				
$Mn(\eta^5\text{-}C_5H_4Cl)(CO)_3$ [b]	4.87	4.59		
$Mn(\eta^5\text{-}C_5H_4Br)(CO)_3$ [b]	4.94	4.62		
$Mn(\eta^5\text{-}C_5H_4I)(CO)_3$ [b]	4.94	4.62		
$Rh(\eta^5\text{-}C_5H_4Cl)(COD)$ [b]	5.55 [c]	4.97 [c]		(CH_2) 2.12m, (CH) 3.87 brs
(b) *η^5-C_5Ph_4X derivatives*				
$Rh(\eta^5\text{-}C_5Ph_4Cl)(COD)$ [d]			7.51, 7.19, 6.95, 6.73	(CH_2) 2.26m, (CH) 3.68brs
$Rh(\eta^5\text{-}C_5Ph_4Cl)(C_2H_4)_2$ [d]			7.51, 7.19, 6.95 6.73	(H^i) 1.85m, (H^o) 2.49m
$Rh(\eta^5\text{-}C_5Ph_4Cl)(CO)_2$			7.80-6.96m	
$Mn(\eta^5\text{-}C_5Ph_4Cl)(CO)_3$			7.50-6.90m	

[a] Measured at 100 MHz (30° C) in carbon tetrachloride. Chemical shifts (δ) are given in ppm downfield (positive) from internal TMS. [b] Each of the signals appeared as an apparent triplet, $J = 2.0$ Hz. [c] Each resonance was coupled to rhodium, $J(Rh{-}H) = 1.0$ Hz. [d] Positions of each distinct multiplet (see text).

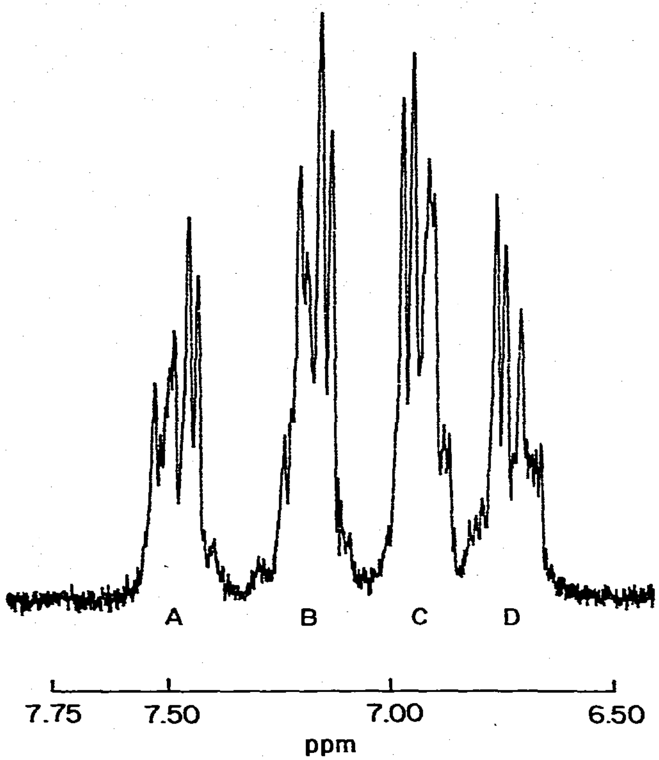


Fig. 1. ^1H NMR spectrum of $Rh(\eta^5\text{-}C_5Ph_4Cl)(COD)$ showing phenyl resonances. Measured at 100 MHz in carbon tetrachloride using a 500 Hz sweep width.

plets A, B, C and D are 2/3/3/2. The separation of these resonances is attributed to chemical shift differences and not fortuitous coupling, by comparison with the 60 MHz spectrum. The pattern is also solvent dependant and for benzene or acetone solutions the chemical shift differences are not as great and an unresolvable multiplet appears. However, in carbon tetrachloride and methylene chloride no temperature dependence was observed in the range -100°C to 80°C. Homonuclear decoupling experiments indicated that resonances A and B are coupled as are C and D.

A possible interpretation is that by some mechanism the protons of each phenyl ring are differentiated into two sets in the ratio 3/2. Since there are two types of phenyl ring, one type on the 2 and 5 positions the other on the 3 and 4 positions of the Cp ring (Cp designates the C_5 ring) the result is four multiplets in the observed ratio. We have considered steric and electronic factors in an attempt to account for the differentiation within the phenyl rings but no ready answer is at hand. The question is complicated by uncertainty as to whether the phenyl rings are static or freely rotating about the phenyl to Cp bonds. The structure of $Rh(\eta^5\text{-}C_5Ph_4Cl)(C_2H_4)_2$ has been determined* (Fig. 2) and consideration of the intramolecular interactions makes free rotation seem unlikely. How-

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* Interesting bonding patterns within the Cp ring involving localizations of carbon—carbon double bonds and other effects were observed (ref. 18). These will form the topics of a full paper by Day and Stults

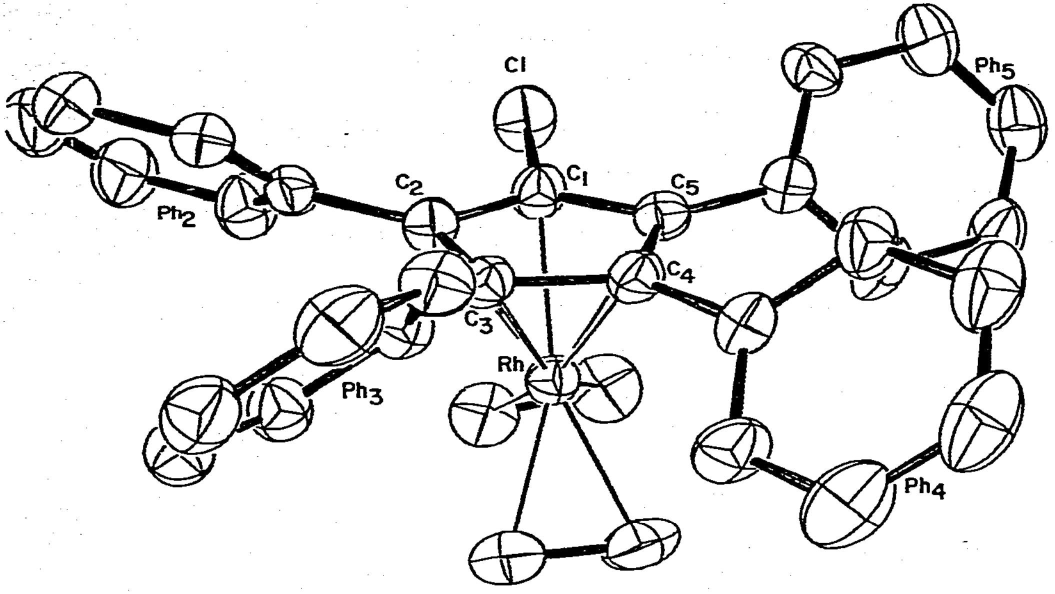

Fig. 2. ORTEP drawing for $Rh(\eta^5\text{-}C_5Ph_4Cl)(C_2H_4)_2$.

ever some synchronous mechanism cannot be ruled out. It may be significant that these patterns are observed only where olefin ligands are present. No such pattern is observed for the compounds containing carbon monoxide ligands.

A variable temperature NMR study in C_6D_6 of $Rh(\eta^5\text{-}C_5Ph_4Cl)(C_2H_4)_2$ revealed that the olefin ligands were undergoing a reorientation, presumably a rotation about the metal—olefin bond axis [41-45]. The free energy of activation for rotation was calculated to be $\Delta F^{\star}_{\mathrm{T}} = 16.4$ kcal mol^{-1}, similar to that observed for $Rh(\eta^5\text{-}C_5H_5)(C_2H_4)_2$ but higher than that for complexes with electron-withdrawing substituents. Although the different solvents employed limit the validity of quantitative comparisons these data are consistent with the interpretation of the infrared data: that the phenyl groups counteract the electron withdrawing effect of the chlorine.

Discussion

The ease with which these reactions produce halogen-substituted *pentahapto*-cyclopentadienyl complexes is in contrast to the usual methods which often require laborious steps [46]. Once formed, the halogenated derivatives are useful intermediates in the synthesis of other substituted compounds. The synthetic utility of the insertion reactions described above may be illustrated by comparison to the previously reported [30] preparation of the halogen-substituted manganese compounds, $Mn(\eta^5\text{-}C_5H_4X)(CO)_3$ (X = Cl, Br, I) from the compound where $X = NH_2$. No yields of purified products were reported. However, from the weights of the crude materials obtained the overall yields must have been less than 20% with respect to $Mn(\eta^5\text{-}C_5H_4NH_2)(CO)_3$. It may also be noted that the synthesis of this starting material requires a number of steps from which it is obtained in only moderate yield. In contrast, the insertion reaction 4 proceeds conveniently in one step and with quantitative yield with respect to $Mn(CO)_5X$. Although neat diazocyclopentadiene is known [26] to be highly explosive in this work it has been found that solutions [27] may be handled conveniently and safely.

Since diazoalkanes are carbene precursors the question arises as to whether carbenes are involved in the insertion reported here. The insertion reaction of $(CF_3)_2CN_2$ with *trans*-$Pt(Cl)(H)(PEt_3)_2$ proceeds only at the temperature at which the diazo compound generates the carbene $(CF_3)_2C$: (i.e. 100°C). On the other hand $IrClCO(PPh_3)_2$ reacts with $(CF_3)_2CN_2$ at room temperature which implies that a free carbene is not involved. Many of the reactions of diazoalkanes with metal complexes are believed to occur via the initial formation of a 1/1 adduct [47-51] which can then undergo further reaction to give a variety of insertion or other products. Only recently, however, were examples of such adducts isolated [51].

It is reasonable to assume that in the room temperature reactions of the diazocyclopentadienes described above free carbenes are not involved. Complexation between the diazo compound and the metal complex probably occurs followed (no order implied) by loss of dinitrogen and transfer of a halide atom from the metal to the ring. The kinetics and mechanism of this reaction are topics requiring additional investigation.

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