$(CO)_3]^+[FeCl_4]^-$. The measured gram-susceptibility of the material was 34.8 cgsu; the spin-only value calculated for five unpaired electrons of the tetrachloroferrate(III) anion is 35.4 cgsu.[20]

Acknowledgment.—We thank the National Research Council of Canada and the University of Alberta for financial support. We are grateful to Dr. M. G. Hogben for assistance in the measurement and interpretation of the nmr spectra of $(Cl_3Si)_2FeH(CO)_2C_5H_5$.

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[20] We are indebted to Mr. E. D. Day, of this department, who determined the susceptibility for us using a Faraday apparatus.

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Cyclopentadienyl(triphenylphosphine)ethylenerhodium and Related Compounds

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Received August 13, 1970

Sodium cyclopentadienide reacts with $(CH_3COCHCOCH_3)RhP(C_6H_5)_3(C_2H_4)$ to form $C_5H_5RhP(C_6H_5)_3(C_2H_4)$ and with $[As(C_6H_5)_3]_2Rh(C_2H_4)Cl$ to yield $C_5H_5RhAs(C_6H_5)_3(C_2H_4)$. Some oxidative addition reactions of halogens and alkyl halides have been carried out on these cyclopentadienylrhodium compounds and are consistent with the formation of ionic intermediates. The tetrafluoroethylene compound $C_5H_5RhP(C_6H_5)_3(C_2F_4)$ has been prepared by abstraction of bromine from $C_5H_5RhP(C_6H_5)_3(C_2F_4Br)Br$ using metallic zinc.

Introduction

It has been shown in earlier work of this laboratory[1,2] that the compounds C_5H_5MLY (M = Rh or Ir, L = a phosphine, and Y = CO) can undergo oxidation (i) with retention of Y to give an ionic compound, (ii) with insertion of Y into a newly formed bond, and (iii) with complete elimination of Y. Ligands other than CO might behave similarly but in order that the three modes of reaction can remain, Y must be capable of acting as an insertion reagent.[3,4] The other possibilities for Y are then almost limited to isocyanides,[5] sulfur dioxide,[6] or olefins.[7-10]

The compounds chosen for study were C_5H_5RhL-(olefin) since reactions of one olefin derivative have implications for a large number of others. Such compounds might also have applications in the field of catalysis.[11]

Results and Discussion

By analogy with the preparation of $C_5H_5Rh(CO)P(CH_3)_2C_6H_5$ from $C_5H_5Rh(CO)_2$,[1,12] it might be considered that a ligand could displace ethylene from the known $C_5H_5Rh(C_2H_4)_2$ to afford the prototype of the required olefin compounds, $C_5H_5RhL(C_2H_4)$. However, as Cramer has shown,[13] this reaction only takes place if L has some Lewis acid character, presumably because there is no mechanism for attack if L is a base such as triphenylphosphine. In a 16-electron rather than an 18-electron system there is a means of attack, for an 18-electron complex could form as an intermediate. Thus displacement of ethylene by triphenylphosphine was attempted in acetylacetonatobisethylenerhodium. Substitution of one ethylene ligand was achieved in similar fashion to the substitution of carbon monoxide in acetylacetonatodicarbonylrhodium.[14] Subsequent reaction of $(CH_3COCHCOCH_3)Rh(C_2H_4)P(C_6H_5)_3$ with sodium cyclopentadienide gave the required compound $C_5H_5RhP(C_6H_5)_3(C_2H_4)$ (**1**) in moderate yield.

$$(CH_3COCHCOCH_3)Rh(C_2H_4)_2 \xrightarrow{P(C_6H_5)_3} (CH_3COCHCOCH_3)RhP(C_6H_5)_3(C_2H_4) \xrightarrow{C_5H_5Na} \underset{\mathbf{1}}{C_5H_5RhP(C_6H_5)_3(C_2H_4)}$$

Attempts to prepare the analogous triphenylarsine complex by this method were without success; this seems to be attributable to incomplete replacement of a single ethylene ligand from $(CH_3COCHCOCH_3)Rh(C_2H_4)_2$ at temperatures where general decomposition was minimal.

Another possible method of obtaining the compound $C_5H_5RhP(C_6H_5)_3(C_2H_4)$ is by a route found applicable to $C_5H_5RhP(C_6H_5)_3(CO)$.[2] Displacement of triphenylphosphine from Wilkinson's compound, $[(C_6H_5)_3P]_3RhCl$, gives $[(C_6H_5)_3P]_2Rh(C_2H_4)Cl$ (**2**), which might react with sodium cyclopentadienide. The ethylene in **2** is very labile[15a] and appears to be lost so easily that it is not retained in the latter reaction.[15b] In the arsine complex analogous to **2**[16] the ethylene is not as labile and we have found that the corresponding reaction

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[15] (a) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *ibid.*, *A*, 1711 (1966). (b) A reviewer has suggested that loss of ethylene from the phosphine complex might have been circumvented by use of an ethylene atmosphere, and that the ionic compound **4** might have been recrystallized in an ethylene atmosphere.

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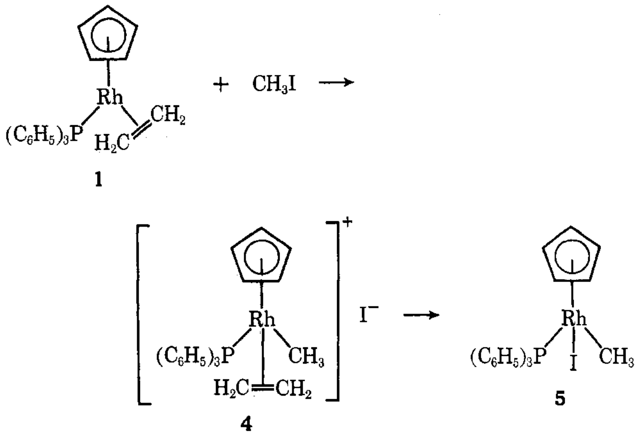
under similar conditions affords a reasonable yield of $C_5H_5RhAs(C_6H_5)_3(C_2H_4)$ (**3**).

$$[(C_6H_5)_3As]_2Rh(C_2H_4)Cl \xrightarrow{C_5H_5Na} C_5H_5RhAs(C_6H_5)_3(C_2H_4)$$

Reactions of halogens with **1** can be anticipated to give compounds of the type $C_5H_5RhP(C_6H_5)_3X_2$[17] and this was confirmed by the reactions with bromine and iodine. This reaction presumably takes place *via* an ionic intermediate,[1] but no evidence for this was actually observed.

In the reaction of methyl iodide with **1**, an almost colorless solid was formed initially, presumably $[C_5H_5RhP(C_6H_5)_3(C_2H_4)CH_3]^+I^-$ (**4**). A light color appears from previous work[1,2] to be typical of ionic compounds of this type. The intermediate **4** is rapidly transformed in dichloromethane with elimination of ethylene to form $C_5H_5RhP(C_6H_5)_3CH_3I$ (**5**). Although the ionic derivative **4** was not obtained in a pure state[15b] (strenuous efforts were not made, but an attempt to precipitate the tetraphenylboron salt from a methanol solution of **4** did not yield a stable product), it was possible to isolate the arsine analog by reaction of **3** with methyl iodide. This is consistent with the known tendency of $[(C_6H_5)_3P]_2Rh(C_2H_4)Cl$ to lose ethylene more readily than $[(C_6H_5)_3As]_2Rh(C_2H_4)Cl$.[15,16]



For both phosphine and arsine reactions there was evidence for small yields of diiodides, $C_5H_5RhLI_2$. Since the methyl iodide was free of iodine initially, either iodine was produced by a mechanism which may or may not involve the transition metal, or the compound $C_5H_5RhLCH_3I$ undergoes a further reaction. More work is necessary to clarify this feature.

Similar reactions occurred on treatment of **1** with methyl bromide, benzyl bromide, perfluoropropyl iodide, 1,2-dibromotetrafluoroethane, and *p*-toluenesulfonyl chloride, but no ionic intermediates were observed. Stannic bromide yields the compound $C_5H_5RhP(C_6H_5)_3(SnBr_3)Br$ although it did not seem possible to prepare this compound by the reaction of triphenylphosphine with $C_5H_5CORh(SnBr_3)Br$.[18] All such reactions are classified as oxidative addition reactions to a d^8 complex.[19]

The compound $C_5H_5RhP(C_6H_5)_3(C_2F_4Br)Br$ formed from 1,2-dibromotetrafluoroethane was reduced by zinc to give the tetrafluoroethylene derivative, $C_5H_5RhP(C_6H_5)_3(C_2F_4)$ (**7**). This compound could not be prepared by the methods used for **1** and **3**, probably because the tetrafluoroethyl moiety does not survive treatment with sodium cyclopentadienide. Zinc reduction of 1,2-dibromotetrafluoroethylene is of course used for the preparation of tetrafluoroethylene. Here, the synthesis of a tetrafluoroethylene derivative (**7**) is achieved by reduction, after an oxidative addition reaction, and the hazard associated with gaseous tetrafluoroethylene is avoided.

$$C_5H_5RhP(C_6H_5)_3(C_2H_4) \xrightarrow{BrCF_2CF_2Br}$$

$$\underset{\mathbf{6}}{C_5H_5RhP(C_6H_5)_3(CF_2CF_2Br)Br} \xrightarrow{Zn\text{-}DMF}$$

$$\underset{\mathbf{7}}{C_5H_5RhP(C_6H_5)_3(C_2F_4)} \xrightarrow{HI} \underset{\mathbf{8}}{C_5H_5RhP(C_6H_5)_3(C_2F_4H)I}$$

Although this type of reaction might appear to have great potential, our preliminary investigations suggest that it is rather limited in application. The common d^8 complexes, $Fe(CO)_5$ and $C_5H_5Co(CO)_2$, react with 1,2-dibromotetrafluoroethane only at temperatures where there is general decomposition. Some related dibromides, namely, CF_2Br_2, $CF_3CFBrCF_2Br$, and $BrCF_2CH_2Br$, have reacted with **1**, but in each case only $C_5H_5RhP(C_6H_5)_3Br_2$ was isolated (in high yield). Changing the conditions of these reactions by varying the temperature or polarity of the solvent appears to cause no change in the final product. The isolation of solely dihalides is not unusual in such oxidative addition reactions. The activated iodides CF_3I, CF_3CFICF_3, and CH_2CHCH_2I give only $C_5H_5RhP(C_6H_5)_3I_2$ in good yields.

Reaction of **7** with aqueous hydriodic acid gives the tetrafluoroethyliodo compound $C_5H_5RhP(C_6H_5)_3(C_2F_4H)I$ (**8**). Protonation likely takes place at rhodium initially since it is clear from reactions of the related compounds **1** and **3** that a high electron density is present on the metal. Subsequent insertion would then occur by a further reaction of type (ii) mentioned in the Introduction. Treatment of **1** with hydriodic acid appears to give only $C_5H_5RhP(C_6H_5)_3I_2$ although $C_5H_5Rh(C_2H_4)_2$ has been reported to react with hydrogen chloride at low temperature to yield $C_5H_5Rh(C_2H_4)(C_2H_5)Cl$.[20]

Nmr Spectra.—At least two sets of resonances were observed in each proton nmr spectrum (Table I), and these can be attributed to the cyclopentadienyl protons and the phenyl protons of the phosphorus or arsenic ligand. The phenyl resonances show typical complex structures and thus for each compound only the chemical shift of the most intense line is listed in Table I. The cyclopentadienyl resonances are expected to be split by rhodium (^{103}Rh, 100% abundance, spin $^1/_2$) and by phosphorus when the latter is present. This feature was observed, but in some cases the rhodium coupling (~0.4 cps) seemed beyond the resolution of the spectrometer; in other cases, where a fluorocarbon moiety was attached to rhodium, coupling to fluorine broadened the resonances.

The ^1H nmr spectrum of $C_5H_5Rh(C_2H_4)_2$ has been discussed in detail by Cramer,[21] and in particular the

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TABLE I

^{1}H NMR SPECTRAL DATA AT 60 MC AND 40°

Compound	Solvent	$\tau_{C_6H_5}$[a]	$\tau_{C_5H_5}$	τ_R[b]	$J_{C_5H_5-P}$[c]	$J_{C_5H_5-Rh}$	J_{R-P}[b]	J_{R-Rh}[b]
$C_5H_5RhP(C_6H_5)_3(C_2H_4)$	$(CD_3)_2CO$	2.59	4.91	7.48, 9.08[d]	1.1	0.6	...	...
$C_5H_5RhAs(C_6H_5)_3(C_2H_4)$	$(CD_3)_2CO$	2.57	4.87	7.58, 8.93[d]	...	0.8	...	...
$C_5H_5RhP(C_6H_5)_3Br_2$	$CDCl_3$	2.52	4.59	...	2.2	...	...	...
$C_5H_5RhP(C_6H_5)_3I_2$	$CDCl_3$	2.55	4.55	...	2.1	...	...	...
$C_5H_5RhP(C_6H_5)_3CH_3I$	$CDCl_3$	2.59	4.87	8.61	1.8	0.5	6.2	2.5
$C_5H_5RhAs(C_6H_5)_3CH_3I$	$CDCl_3$	2.55	4.80	8.49	...	0.5	...	2.6
$C_5H_5RhP(C_6H_5)_3CH_3Br$	$CDCl_3$	2.57	4.92	8.57	1.7	0.5	6.4	2.4
$C_5H_5RhP(C_6H_5)_3(CH_2C_6H_5)Br$	$CDCl_3$	2.57	5.30	6.52[e]	1.7	0.5	3.8 (A)[e] 12.0 (B)[e]	3.8 (A)[e] 2.3 (B)[e]
$C_5H_5RhP(C_6H_5)_3C_3F_7I$[f]	$CDCl_3$	2.57	4.60	...	1.8	...	...	...
$C_5H_5RhP(C_6H_5)_3(C_2F_4Br)Br$	$CDCl_3$	2.59	4.71	...	1.8	...	...	...
$C_5H_5RhP(C_6H_5)_3(C_2F_4)$[g]	$CDCl_3$	2.62	4.96	...	...	...	...	...
$C_5H_5RhP(C_6H_5)_3(C_2F_4H)I$	$CDCl_3$	2.57	4.72	...	...	...	...	...
$C_5H_5RhP(C_6H_5)_3(SO_2C_6H_4CH_3)$-$Cl \cdot 0.5CH_2Cl_2$[h]	$CDCl_3$	2.52	4.85	7.63	1.8	0.5	...	...
$C_5H_5RhP(C_6H_5)_3(SnBr_3)Br$	$CDCl_3$	2.52	4.57	...	1.7	...	...	...

[a] τ values are in ppm. [b] R refers to methyl or methylene protons. [c] Coupling constants are reported in cps. [d] The τ values reported refer to the centers of each part of a complex doublet. [e] The AB part of an ABMX pattern was observed; separation between A (lower field) and B (higher field) resonances is 0.38 ppm, $J_{AB} = 8.1$ cps. [f] In the ^{19}F nmr spectrum using C_6F_6 as reference (163.0 ppm upfield from $CFCl_3$) the resonances, relative to $CFCl_3$, were at 57.8 ppm (broad), 79.4 ppm (triplet, $J = 11.7$ cps), and 112.8 ppm (broad). [g] In the ^{19}F nmr spectrum measured as footnote *f*, resonances were at 103.1 ppm (broad) and 111.2 ppm (broad). [h] Also shows resonance at τ 4.71 ppm, integrating to one proton.

energy associated with rotation of the ethylene ligands was determined. At the temperature of 40° employed for the work reported here, the ethylene resonances for compounds **1** and **3** are little changed from those observed for the parent bis-ethylene compound.[21] Deuterioacetone was used as solvent for the ethylene derivatives reported here since they seem to be unstable in chlorinated solvents.

The spectra of the compounds $C_5H_5RhP(C_6H_5)_3CH_3I$ and $C_5H_5RhAs(C_6H_5)_3CH_3I$ were useful in confirming the assignment of rhodium and phosphorus coupling to both methyl and cyclopentadienyl protons.[2] It can be seen (Table I) that phosphorus has the larger coupling to both of these sets of protons.

The asymmetry of the compound $C_5H_5RhP(C_6H_5)_3(CH_2C_6H_5)Br$ was confirmed by a chemical shift separation between the resonances of the two methylene protons. The difference between this chemical shift and coupling constants was determined by measurement of the spectra at 100 Mc as well as 60 Mc. The expected AB pattern was further split by coupling to rhodium and phosphorus. Very different couplings were observed from phosphorus to the individual methylene protons, as has been found for the related compounds $C_5H_5COFeP(C_6H_5)_3CH_2Si(CH_3)_3$ ($J_{A-P} = 2$ cps, $J_{B-P} = 13$ cps).[22] It is interesting to note that, in contrast to the gem protons mentioned here, gem methyl groups in, for example, $C_5H_5RhP(CH_3)_2C_6H_5(COCH_3)Br$, appear to couple equally to both rhodium and phosphorus.[1]

The ^{1}H nmr spectrum was useful in showing the presence of dichloromethane in the crystals of the compound $C_5H_5RhP(C_6H_5)_3(SO_2C_6H_4CH_3)Cl \cdot 0.5CH_2Cl_2$ although the exact molar ratio of *p*-tolylsulfinate to dichloromethane seemed best determined by analytical results. The same ratio has already been found for some related iridium compounds.[2] All ^{1}H nmr resonances were found to integrate correctly for the formulas proposed.

Great difficulty was experienced in obtaining ^{19}F nmr spectra for the fluorocarbon derivatives. The coupling of fluorines to each other (asymmetry at rhodium), to rhodium, to phosphorus, and even to the cyclopentadienyl ring would be expected to result in broad resonances. In fact for the two compounds $C_5H_5RhP(C_6H_5)_3(C_2F_4Br)Br$ and $C_5H_5RhP(C_6H_5)_3(C_2F_4H)Br$, no resonances could be found. Three resonances, consistent with literature results,[23] were found for $C_5H_5RhP(C_6H_5)_3(C_3F_7)I$, and for the remote CF_3 group a coupling was resolved, presumably due to the α fluorines.[23]

The compound $C_5H_5RhP(C_6H_5)_3(C_2F_4)$ (**7**) exhibited two broad resonances separated by 8 ppm and so, according to Parshall,[24] the tetrafluoroethylene is predominantly σ bonded. Further, the infrared spectrum of **7** in a Nujol mull showed strong C–F peaks at 802, 1028, 1093, and 1101 cm^{-1}, also consistent with a σ-bonded ligand.[24]

Experimental Section

The starting materials $(CH_3COCHCOCH_3)Rh(C_2H_4)_2$[21] and $[(C_6H_5)_3As]_2Rh(C_2H_4)Cl$[16] were prepared by literature methods. Alkyl iodides were purified before use by distillation from sodium thiosulfate. Other reagents were used as obtained from commercial sources.

Microanalyses (Table II) were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach über Engelskirchen, Germany, and by the microanalytical laboratory of this department. Infrared spectra were measured with a Perkin-Elmer 337 grating spectrometer using a polystyrene film for calibration purposes. A Varian A-56/60-A spectrometer was used to obtain both ^{1}H and ^{19}F nmr spectra. Physical properties are listed in Table III.

Preparation of $(CH_3COCHCOCH_3)Rh(C_2H_4)P(C_6H_5)_3$.—A solution of freshly crystallized triphenylphosphine (1.25 g, 4.8 mmol) in dichloromethane (5 ml) was added slowly to $(CH_3COCHCOCH_3)Rh(C_2H_4)_2$ (1.2 g, 4.8 mmol) also dissolved in dichloromethane (5 ml). Evolution of gas took place, and after stirring the mixture for 1 hr and concentrating to 5 ml, hexane (20 ml) was added. Orange crystals of product (1.26 g, 2.56 mmol, 53%) were obtained on cooling to 0°.

Preparation of $C_5H_5RhP(C_6H_5)_3(C_2H_4)$ (1).—A solution of 1 *M* sodium cyclopentadienide (10 ml, 10 mmol) in tetrahydrofuran was evaporated to dryness and to this was added $(CH_3COCHCOCH_3)Rh(C_2H_4)P(C_6H_5)_3$ (1.26 g, 2.56 mmol) dissolved in benzene (30 ml). The mixture was stirred for 24 hr and filtered through a short column of Florisil. The resulting orange solution was concentrated to 5 ml and hexane (20 ml) added. Cooling to −15° afforded orange crystals of the required compound (0.61 g, 1.33 mmol, 52%).

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TABLE II

ANALYTICAL DATA

Compound	% calcd C	H	X	P or As	% found C	H	X	P or As
$(CH_3COCHCOCH_3)RhP(C_6H_5)_3(C_2H_4)$	60.99	5.32	...	6.29	61.15	5.28	...	6.59
$C_5H_5RhP(C_6H_5)_3(C_2H_4)$	65.51	5.28	...	6.76	65.99	5.03	...	6.98
$C_5H_5RhAs(C_6H_5)_3(C_2H_4)$	59.78	4.83	...	14.92	59.76	4.77	...	14.79
$C_5H_5RhP(C_6H_5)_3Br_2$	46.81	3.42	...	...	46.13	3.55	...	...
$C_5H_5RhP(C_6H_5)_3I_2$	40.38	2.95	37.10	4.53	40.51	2.91	37.33	4.58
$C_5H_5RhAs(C_6H_5)_3I_2$	37.94	2.76	...	...	37.94	2.76	...	...
$C_5H_5RhP(C_6H_5)_3CH_3I$	50.37	4.05	22.18	5.41	50.20	4.13	22.37	5.28
$[C_5H_5RhAs(C_6H_5)_3CH_3(C_2H_4)]^+I^-$	48.47	4.22	...	...	47.92	4.02	...	...
$C_5H_5RhAs(C_6H_5)_3CH_3I$	46.78	3.76	...	...	46.63	3.67	...	...
$C_5H_5RhP(C_6H_5)_3CH_3Br$	54.88	4.41	...	...	54.78	4.30	...	...
$C_5H_5RhP(C_6H_5)_3(CH_2C_6H_5)Br$	59.92	4.53	...	...	59.44	4.50	...	...
$C_5H_5RhP(C_6H_5)_3C_3F_7I$	43.00	2.78	...	...	42.89	2.96	...	...
$C_5H_5RhP(C_6H_5)_3(C_2F_4Br)Br$	43.51	2.92	...	...	43.62	2.94	...	...
$C_5H_5RhP(C_6H_5)_3(C_2F_4)$	56.62	3.80	14.33	5.84	56.61	3.69	14.30	5.83
$C_5H_5RhP(C_6H_5)_3(C_2F_4H)I$	45.62	3.22	...	...	45.55	3.24	...	...
$C_5H_5RhP(C_6H_5)_3(SO_2C_6H_4CH_3)Cl \cdot 0.5CH_2Cl_2$	55.22	4.25	10.69	4.67	55.01	4.73	11.33	4.83
$C_5H_5RhP(C_6H_5)_3(SnBr_3)Br$	31.80	2.32	...	...	31.74	1.95	...	...

TABLE III

PHYSICAL PROPERTIES

Compond	Mp,[a] °C	Color	% yield
$(CH_3COCHCOCH_3)RhP(C_6H_5)_3(C_2H_4)$	135	Yellow	53
$C_5H_5RhP(C_6H_5)_3(C_2H_4)$	150	Orange-red	52
$C_5H_5RhAs(C_6H_5)_3(C_2H_4)$	143	Orange-red	38
$C_5H_5RhP(C_6H_5)_3Br_2$	260	Red	88
$C_5H_5RhP(C_6H_5)_3I_2$	260	Black	88
$C_5H_5RhAs(C_6H_5)_3I_2$	275	Black	2[b]
$C_5H_5RhP(C_6H_5)_3CH_3I$	174	Orange-brown	68
$[C_5H_5RhAs(C_6H_5)_3(C_2H_4)CH_3]^+I^-$	60	Pale yellow	32[b]
$C_5H_5RhAs(C_6H_5)_3CH_3I$	190	Orange-brown	25[b]
$C_5H_5RhP(C_6H_5)_3CH_3Br$	193	Orange-red	61
$C_5H_5RhP(C_6H_5)_3(CH_2C_6H_5)Br$	145	Red	40
$C_5H_5RhP(C_6H_5)_3C_3F_7I$	190	Red	68
$C_5H_5RhP(C_6H_5)_3(C_2F_4Br)Br$	200	Orange	52
$C_5H_5RhP(C_6H_5)_3(C_2F_4)$	183	Pale yellow	46
$C_5H_5RhP(C_6H_5)_3(C_2F_4H)I$	230	Red	86
$C_5H_5RhP(C_6H_5)_3(SO_2C_6H_4CH_3)Cl \cdot 0.5CH_2Cl_2$	120	Orange	82
$C_5H_5RhP(C_6H_5)_3(SnBr_3)Br$	120	Red	48

[a] All compounds decompose with melting over a 5–10° range.

[b] These compounds were produced in the same reaction: therefore, overall percentage yield is 59%.

Preparation of $C_5H_5RhAs(C_6H_5)_3(C_2H_4)$ (3).—Benzene (30 ml) was used to dissolve $[(C_6H_5)_3As]_2Rh(C_2H_4)Cl$ (3.88 g, 4.98 mmol) and the solution was added to dry solid sodium cyclopentadienide formed by evaporation of a 1 *M* solution in tetrahydrofuran (25 ml). The mixture was stirred for 2 days, filtered through a short column of Florisil, and concentrated to 5 ml. Addition of hexane (20 ml) and cooling to −15° produced orange-red crystals of the required compound (0.96 g, 1.91 mmol, 38%).

Preparation of $C_5H_5RhP(C_6H_5)_3I_2$.—The compound $C_5H_5RhP(C_6H_5)_3(C_2H_4)$ (0.23 g, 0.50 mmol) was dissolved in dichloromethane (10 ml) and iodine (0.13 g, 0.50 mmol) was added. After stirring for 30 min, hexane (10 ml) was added and the mixture was cooled to 0°. Fine black needles of product (0.30 g, 0.44 mmol, 88%) were isolated.

In an analogous procedure using bromine in place of iodine, the compound $C_5H_5RhP(C_6H_5)_3Br_2$ was formed, also in 88% yield.

Preparation of $C_5H_5RhP(C_6H_5)_3CH_3I$ (5).—Methyl iodide (3.0 ml, 6.8 g, 48 mmol) was added to $C_5H_5RhP(C_6H_5)_3(C_2H_4)$ (0.40 g, 0.87 mmol). Complete solution took place and then a very pale solid rapidly precipitated out. This precipitate dissolved in dichloromethane to give a very dark solution which was chromatographed on a column of Florisil using dichloromethane as eluent. First collected was an orange-red band and then a very deep red band. The solutions containing the two bands were individually concentrated to a small volume and hexane was added to give crystalline products on cooling. The first product was found to be pure $C_5H_5RhP(C_6H_5)_3CH_3I$ (0.34 g, 0.59 mmol, 68%). The second (0.05 g) was found spectroscopically to be predominantly the diiodide with some of the methyliodo derivative.

Reaction of $C_5H_5RhAs(C_6H_5)_3C_2H_4$ with CH_3I.—The compound $C_5H_5RhAs(C_6H_5)_3(C_2H_4)$ (0.29 g, 0.58 mmol) was dissolved in methyl iodide (0.50 ml, 1.14 g, 8.0 mmol) and after stirring for about 1 min a light precipitate formed. Diethyl ether (20 ml) was added and the solid was collected. This was recrystallized from methanol–diethyl ether to afford pale yellow needles of $[C_5H_5RhAs(C_6H_5)_3(C_2H_4)CH_3]^+I^-$ (0.12 g, 0.19 mmol, 32%). The remaining methyl iodide–diethyl ether and methanol–diethyl ether solutions were evaporated to dryness and the combined solid residues were dissolved in dichloromethane (10 ml). After stirring for 12 hr the solution was subjected to chromatography on a column of Florisil with dichloromethane as eluent. A red-orange band was collected first and was followed by a red-brown band. The solutions containing the two bands were separately evaporated down to 5 ml and pentane (20 ml) was added. The first product, which formed as orange-brown crystals, was shown to be $C_5H_5RhAs(C_6H_5)_3CH_3I$ (0.09 g, 0.15 mmol, 25%). The second solution afforded black crystals of $C_5H_5RhAs(C_6H_5)_3I_2$ (0.01 g, 0.01 mmol, 2%).

Preparation of $C_5H_5RhP(C_6H_5)_3CH_3Br$.—The compound $C_5H_5RhP(C_6H_5)_3(C_2H_4)$ (0.40 g, 0.87 mmol) was placed in a Carius tube and methyl bromide (3.5 g, 37 mmol) was added by distillation. After sealing, the mixture was allowed to stand at room temperature for 3 days and excess methyl bromide was then removed under reduced pressure. The resulting solid was chromatographed on a Florisil column using dichloromethane as solvent. The required compound appeared as an orange band and was first to be eluted. A small red band remained on the column but this could not be removed by dichloromethane. The solution of $C_5H_5RhP(C_6H_5)_3CH_3Br$ was concentrated to 3 ml and hexane (10 ml) was added to afford bright orange crystals (0.28 g, 0.53 mmol, 61%).

Preparation of $C_5H_5RhP(C_6H_5)_3(CH_2C_6H_5)Br$.—Benzyl bromide (1.0 ml, 1.44 g, 8.4 mmol) was added to a solution of $C_5H_5RhP(C_6H_5)_3(C_2H_4)$ (0.46 g, 1.0 mmol) in dichloromethane (5 ml). After stirring for 12 hr the mixture was subjected to chromatography on a Florisil column using dichloromethane as eluent. The first dark red band was collected, the solution was concentrated to 5 ml, and hexane was added. A small amount of a compound presumed to be $C_5H_5RhP(C_6H_5)_3Br_2$ crystallized first, but addition of more hexane gave the required compound (0.24 g, 0.40 mmol, 40%).

Perfluoropropyl iodide was allowed to react similarly for a period of 24 hr. The product, $C_5H_5RhP(C_6H_5)_3(n\text{-}C_3F_7)I$, was collected as the first band from a Florisil column and isolated as dark red crystals in 68% yield.

Preparation of $C_5H_5RhP(C_6H_5)_3(C_2F_4Br)Br$ (6).—The compound $C_5H_5RhP(C_6H_5)_3(C_2H_4)$ (0.23 g, 0.5 mmol) was dissolved in dichloromethane (5 ml) and 1,2-dibromotetrafluoroethane (1.0 g, 3.8 mmol) was added. After 12 hr the mixture was evaporated to dryness and the residue was chromatographed on a column of Florisil using dichloromethane as eluent. A bright orange band was collected first and a dark red band was then eluted using a 1:1 dichloromethane–acetone mixture. The solutions containing these two bands were separately concentrated to 10 ml and hexane (30 ml) was added to each. Cooling to

−15° gave $C_5H_5RhP(C_6H_5)_3(C_2F_4Br)Br$ (0.180 g, 0.26 mmol, 52%) from the first band and $C_5H_5RhP(C_6H_5)_3Br_2$ (0.094 g, 0.16 mmol, 32%) from the second.

Preparation of $C_5H_5RhP(C_6H_5)_3(C_2F_4)$ (7).—Finely powdered zinc dust (2.0 g, 15.3 mg-atoms) was added to a solution of $C_5H_6RhP(C_6H_5)_3(C_2F_4Br)Br$ (0.180 g, 0.26 mmol) in *N*,*N*-dimethylformamide (20 ml). After stirring for 16 hr at 60°, the solvent was removed under reduced pressure. Chromatography of the resulting mixture using Florisil and benzene as eluent first produced a pale yellow band from the column. The solution containing this band was concentrated to 5 ml and hexane (30 ml) was added. Pale yellow crystals of product (0.065 g, 0.12 mmol, 46%) were formed on cooling to −15°.

Preparation of $C_5H_5RhP(C_6H_5)_3(C_2F_4H)I$ (8).—The compound $C_5H_5RhP(C_6H_5)_3(C_2F_4)$ (0.050 g, 0.094 mmol) was dissolved in dichloromethane (10 ml) and 55% aqueous hydriodic acid (0.4 mmol) was added. After stirring for 1 hr and evaporating to dryness, the residue was recrystallized from dichloromethane–hexane. Reddish crystals (0.053 g, 0.081 mmol) were obtained in 86% yield.

Preparation of $C_5H_5RhP(C_6H_5)_3(SnBr_3)Br$.—Stannic bromide (0.22 g, 0.50 mmol) was added to a stirred solution of $C_5H_5RhP(C_6H_5)_3(C_2H_4)$ (0.23 g, 0.50 mmol) in dichloromethane (15 ml). After 1 hr, hexane (30 ml) was added to give red crystals, which were recrystallized twice from dichloromethane–hexane. Thus a sample of pure product (0.21 g, 0.24 mmol, 48%) was isolated.

In an analogous procedure *p*-toluenesulfonyl chloride gave pure $C_5H_5RhP(C_6H_5)_3(SO_2C_6H_4CH_3)Cl \cdot 0.5CH_2Cl_2$ from the first crystallization (82% yield). The infrared spectrum of this compound in a Nujol mull showed typical stretching modes for an SO_2 group[19] at 1224, 1204, 1093, and 1045 cm^{-1}.

Acknowledgment.—We thank the National Research Council of Canada for financial support and for a scholarship to A. J. O.

CONTRIBUTION FROM THE GENERAL ELECTRIC COMPANY,
RESEARCH AND DEVELOPMENT CENTER, SCHENECTADY, NEW YORK 12301

Studies of Intermolecular Interactions in Square-Planar d^8 Metal Complexes. I. The Physical Properties of Magnus' Green Salt and Some Related Complexes at High Pressures[1]

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Received October 13, 1970

The intermolecular interactions in Magnus' green salt $[Pt(NH_3)_4PtCl_4]$, dicarbonylacetylacetonatoiridium(I), and some related platinum and palladium complexes are investigated by means of electrical, spectral, and X-ray powder diffraction measurements carried out at pressures up to *ca.* 170,000 atm. The marked changes in spectral and electrical properties observed as a function of pressure are interpreted in terms of the internuclear distance changes occurring in the solid, leading to new information regarding the structure–property relationships in this type of compound.

Introduction

In Magnus' green salt (MGS) $[Pt(NH_3)_4PtCl_4]$, dicarbonylacetylacetonatoiridium(I) $[Ir(CO)_2(acac)]$, and a number of other d^8 metal complexes, the planar complex units stack in columns in the crystal with the metal atoms aligned along the columnar axis, forming continuous chains. The unusual solid-state properties associated with many of these compounds point to the existence of a direct interaction between the metal atoms in these chains. For example, in several cases, highly anisotropic conduction and photoconduction have been observed with room-temperature conductivities as high as 10^{-4} ohm^{-1} cm^{-1} in the direction of highest conductivity, which is coincident with the metal–metal chain direction in the crystal.[2] Moreover, studies of homologous series of complexes such as $M(A)_4MCl_4$ (M = Pd, Pt; A = NH_3, CH_3NH_2, $C_2H_5NH_2$)[3] and $M'(CO)_2(acac)$ (M' = Ir, Rh)[2a,b] have revealed a dependence of the conductivity upon both the distance between the metal atoms and the principal quantum number of the metal valence orbitals. Similarly, the electronic spectra of the compounds of this type are often markedly different from that of the constituent complex units in solution but tend to approach the solution spectra as the separation between the metal atoms is increased or the principal quantum number of the metal valence orbitals is decreased through structural modifications such as those indicated above.[4]

An intrinsic band model has been proposed which accounts, in a qualitative way, for many of these observations;[2,4] however, further experimental and theoretical studies are clearly needed before any firm conclusions about the electronic structure of these solids can be made. In particular, more detailed information regarding the dependence of the physical properties of such materials upon the structural parameters in the solid would be useful, both for the purpose of testing theoretical hypotheses and as a guide to future synthetic work. The use of high-pressure techniques to obtain structure–property information of this type is well established.[5] With the aid of such techniques, changes in the internuclear distances in solids can be

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