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SOME REACTIONS OF THE (π-C_5H_5)Rh(CO)L (L=CO, PPh_3) COMPLEXES

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SUMMARY

The reactions of the complexes CpRh(CO)L (Cp=cyclopentadienyl; L=CO, PPh_3) with HCl, $ClCH_2CN$ and $C_6H_5SO_2Cl$ have been investigated. In both cases the reaction with hydrogen chloride gives products which do not contain the cyclopentadienyl ring. Chloroacetonitrile reacts only with CpRh(CO)PPh_3, and gives the cationic complex $[CpRh(CO)(CH_2CN)PPh_3]^+$, which has been isolated and characterized. The sulphonyl chloride $C_6H_5SO_2Cl$ reacts with CpRh(CO)PPh_3 to give a product which had not been fully identified and with $CpRh(CO)_2$ to give CpRh(CO)($C_6H_5SO_2$)Cl.

INTRODUCTION

During recent years[1] there have been numerous studies of oxidative additions to planar tetracoordinate d^8 transition metal complexes to give octahedral coordinate d^6 derivatives. The mechanism of these reactions have been studied[2], and the possibility of isolating the reaction intermediates examined[3]. Only a few studies, however, deal with cyclopentadienyl derivatives of Rh^I and Ir^I.

The complex $CpRh(CO)_2$ react with iodine[4], perfluoroalkyl iodides[5], germanium and tin tetrahalides and halides of triphenyl- and tribenzylsilane[6] to give Rh^{III} complexes. The complex CpRh(CO)($PPhMe_2$) reacts at low temperatures with halogens, CF_3COCl and CH_3COBr to give cationic Rh^{III} complexes, which at higher temperatures lose the carbonyl group to give neutral products[7]. Treatment of CpIr(CO)PPh_3 with halogens and alkyl halides gives stable Ir^{III} cationic complexes[8]. Recently a kinetic study of the mechanism of the oxidative addition of the complexes CpM(CO)L (M=Co, Rh, Ir; L=tertiary phosphines) with CH_3I and C_2H_5I has been reported[9].

We study and discuss in this paper the reactions of the complexes CpRh(CO)L (L=CO, PPh_3) with HCl, $ClCH_2CN$, and $C_6H_5SO_2Cl$.

EXPERIMENTAL

$CpRh(CO)_2$ and $CpRh(CO)PPh_3$ were prepared as previously described[10,11]. The other chemicals used were reagent grade materials. IR spectra were recorded with a Perkin–Elmer mod. 457 spectrometer. Molecular weights were determined on a Knauer vapor pressure osmometer. Melting points (uncorrected) were determined on a Fisher–Jones hot stage apparatus. Elemental analyses were by Alfred Bernhardt, Microanalytisches Laboratorium, Mülheim Germany. All reactions were carried out under nitrogen. Physical properties and characteristic IR data are presented in Table 1.

TABLE 1

PHYSICAL PROPERTIES AND IR DATA (NUJOL MULL)

Compound	Colour	M.p. (°C)	ν(CO) (cm^{-1})	Other bands (cm^{-1})
$[Rh(CO)(PPh_3)Cl]_2$	Yellow-orange	145–160 dec.	1982 vs	ν(Rh–Cl) 296 s
$[Rh(CO)(PPh_3)Br]_2$	Brown	90–112 dec.	1977 vs	
$[Rh(CO)(PPh_3)I]_2$	Brown	113–125 dec.	1972 s	
$[CpRh(CO)(CH_2CN)PPh_3]Cl$	Yellow-orange	98–115 dec.	2076 vs	ν(CN) 2198 m
$[CpRh(CO)(CH_2CN)PPh_3]BPh_4$	Yellow	120–124 dec.	2072 vs	ν(CN) 2204 m
$CpRh(CO)(C_6H_5SO_2)Cl$	Orange	128–130 dec.	2110 vs	ν(Rh–Cl) 316 m

Preparation of $[Rh(CO)(PPh_3)Cl]_2$

When hydrogen chloride was bubbled through a stirred solution of $CpRh(CO)PPh_3$ in pentane, a yellow-orange precipitate formed slowly. After 30 min the precipitate was filtered off, washed several times with pentane, and dried. (Found: C, 53.12; H, 3.74; Cl, 8.50; mol.wt., 846. $C_{19}H_{15}ClOPRh$ calcd.: C, 53.23; H, 3.52; Cl, 8.28%; mol.wt., 858.)

$[Rh(CO)(PPh_3)Br]_2$ and $[Rh(CO)(PPh_3)I]_2$ derivatives were prepared by treatment of the chloro derivative with an excess of the corresponding lithium halide in acetone/methylene chloride (3/1) mixture. (Found: C, 48.08; H, 3.22; Br, 16.64. $C_{19}H_{15}BrOPRh$ calcd.: C, 48.23; H, 3.19; Br, 16.89%.) (Found: C, 43.82; H, 2.98; I, 24.31. $C_{19}H_{15}IOPRh$ calcd.: C, 43.87; H, 2.91; I, 24.40%.)

Preparation of $[CpRh(CO)(CH_2CN)PPh_3]Cl$

$CpRh(CO)PPh_3$ (100 mg; 0.22 mmoles) was dissolved in hexane (150 ml) and an excess chloroacetonitrile (0.4 ml) was added. The solution was vigorously stirred at room temperature until it became colourless (about 5 h). A red oil was obtained on evaporation of the solvent, and addition of ether gave $[CpRh(CO)(CH_2CN)PPh_3]Cl$ as an orange solid. (Found: C, 58.37; H, 4.21; Cl, 6.48; N, 2.76. $C_{26}H_{22}ClNOPRh$ calcd.: C, 58.50; H, 4.15; Cl, 6.64; N, 2.62%.)

Preparation of $[CpRh(CO)(CH_2CN)PPh_3]BPh_4$

The red oil obtained as above described from the reaction of $CpRh(CO)PPh_3$ with $ClCH_2CN$ was dissolved in methyl alcohol and a methanolic solution of sodium tetraphenylboronate was added. The yellow product which formed rapidly was filtered off, washed with methanol and then with pentane, and dried under vacuum. (Found: C, 73.31; H, 5·10; N, 1.86. $C_{50}H_{42}BNOPRh$ calcd.: C, 73.45; H, 5.17; N, 1.71%.)

Preparation of CpRh(CO)($C_6H_5SO_2$)Cl

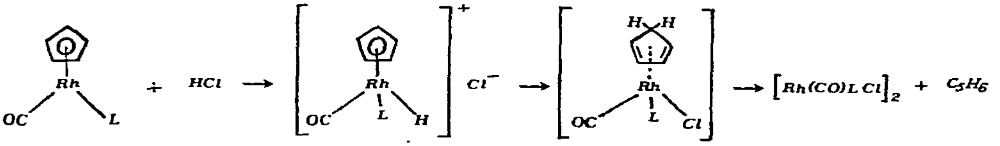
A solution of $CpRh(CO)_2$ in pentane was treated dropwise with benzenesulphonyl chloride in the same solvent. The orange precipitate formed was filtered off, washed several times with pentane, and dried under vacuum. (Found: C, 38.55; H, 2.79; Cl, 9.62. $C_{12}H_{10}ClO_3RhS$ calcd.: C, 38.67; H, 2.70; Cl, 9.51%.)

RESULTS AND DISCUSSION

The reactions of dry hydrogen chloride with the complexes CpRh(CO)L (L=CO, PPh_3) produce compounds which do not contain the cyclopentadienyl ligand. Attack of hydrogen chloride on $CpRh(CO)_2$ gives the known compound $[Rh(CO)_2Cl]_2$, which can be easily identified from its elemental analysis and by comparison of the IR spectrum of the product with that of an authentic sample. The product $[Rh(CO)(PPh_3)Cl]_2$ is new, however, and a dimeric structure has been suggested for it in the light of its molecular weight. The characteristic features of the IR spectrum are a single band at 1982 cm^{-1} due to CO stretching vibration and a band at 296 cm^{-1} due to the Rh–Cl stretch of the bridge chlorines. According to group theory, this compound can be assigned a structure with C_{2h} symmetry, and for such a species a single CO stretch (mode B_u) and single Rh–Cl stretch (mode B_u) are expected in the IR spectrum. The proposed formulation is confirmed by the bridge-splitting reaction on the complex $[Rh(CO)(PPh_3)Cl]_2$, since the only product is *trans*-$[Rh(CO)(PPh_3)Cl]$.

The $[Rh(CO)(PPh_3)Br]_2$ and $[Rh(CO)(PPh_3)I]_2$ derivatives were obtained by exchange of the chloro derivative with excess of the corresponding lithium halide in acetone/methylene chloride (3/1) mixture.

The following mechanistic scheme seems reasonable:



This involves the formation of a labile cationic hydrido complex which undergoes hydrogen ion migration on the cyclopentadienyl ring leading to the formation of the final dimeric complex and free cyclopentadiene. (The presence of the latter in the reaction mixture was confirmed by GLC.) The proposed mechanism can be related to the known protonation reaction of d^8 complexes with strong acids[12], but from our results we cannot rule out a possible direct attack of the proton at the coordinated cyclopentadienyl ring. Further support for the proposed mechanism can be found in the reaction of the analogous Ir^I complex, $CpIr(CO)PPh_3$ with HCl. It is accepted that the electrophilic substitution at metallocenes usually occur through initial coordination of the electrophile to the metal[13], and reaction of $CpIr(CO)PPh_3$ with HCl[6] gives the cationic hydrido complex $[CpIr(CO)(PPh_3)H]^+$ which is consistent with the greater stability of Ir^{III} as compared to Rh^{III} hydrido complexes[14]. The different behaviour of $CpRh(CO)PPh_3$ as compared to the analogous Ir^I compound can be also related to the different strength of the $M-C_5H_5$ bond; in the case of $CpM(CO)PPh_3$ species the $Ir-C_5H_5$ bond can expected to be stronger than the $Rh-C_5H_5$ bond because of the greater importance of back-donation from the iridium atom to the antibonding orbitals of the C_5H_5 ring.

The reaction of $CpRh(CO)PPh_3$ with $ClCH_2CN$ gives the Rh^{III} complex $[CpRh(CO)(CH_2CN)PPh_3]Cl$, which is relatively stable and undergoes only slow decomposition at room temperature. The final product is probably $CpRh(PPh_3)(CH_2CN)Cl$, but we have not sufficient analytical evidence for this at present. The stable tetraphenylboronate salt, $[CpRh(CO)(CH_2CN)PPh_3]BPh_4$ has been isolated. The IR spectra of both these cationic complexes show a band at about 2200 cm^{-1} and a very strong band at 2075 cm^{-1} which can be attributed to $\nu(CN)$ and $\nu(CO)$ respectively. The increase of the $\nu(CO)$ stretching frequency on going from the starting Rh^I materials $CpRh(CO)PPh_3$ to the cationic Rh^{III} product $[CpRh(CO)(CH_2CN)PPh_3]^+$ is in agreement with a diminished π back-donation from the metal to the carbonyl group. This reaction can be discussed in the light of the kinetic studies made by Hart–Davis and Graham[9] on the reaction of $CpRh(CO)PPh_3$ with CH_3I. They show that the rate determining step corresponds to a nucleophilic attack of the metal at the carbon atom of CH_3I, producing an anionic intermediate which undergoes a fast rearrangement, involving migration of the methyl group to the carbon monoxide ligand and coordination of the halogen to the metal, to give $CpRh(COCH_3)LI$. The reaction with $ClCH_2CN$ is probably of the same type. In our case the methylenic carbon atom has a greater positive charge than the carbon atom in CH_3I, and can be expected to undergo more easily nucleophilic attack. The relatively greater stability of the cationic complex $[CpRh(CO)(CH_2CN)PPh_3]^+$ as compared to $[CpRh(CO)L(CH_3)]^+$ can be related to the presence of the electron-withdrawing CN group bonded to the methylenic group, since the stabilizing effect on the metal–carbon σ bond of a highly electronegative group in the organic ligand is well known[3]. The complex $CpRh(CO)_2$ does not react with an excess of $ClCH_2CN$ even under drastic conditions, probably because $CpRh(CO)_2$ has a smaller nucleophilicity than $CpRh(CO)PPh_3$.

The reaction of benzenesulphonyl chloride with the complex $CpRh(CO)_2$ gives the Rh^{III} product, $CpRh(CO)(C_6H_5SO_2)Cl$ which undergoes slow decomposition even in the solid state. Its IR spectrum shows a strong CO stretching frequency at 2110 cm^{-1} and two bands at 1225 and 1050 cm^{-1} which can be assigned respectively to the asymmetric and symmetric stretching modes of the SO_2 group bonded through the sulphur atom to the metal. Following the arguments of Collman and Roper[15], the results can be interpreted as indicating the existence of significant π-bonding between the metal and the sulphonyl group.

The reaction of $CpRh(CO)PPh_3$ with $C_6H_5SO_2Cl$ gives an orange product which has not been unambiguously identified. The presence of a strong band in the IR spectrum at 1967 cm^{-1} corresponding to the $\nu(CO)$ suggests that it is a Rh^I complex, and the absence of a precipitate on treating the product in methanol with either KPF_6 or $NaBPh_4$ suggests that it is not a cationic species. The behaviour may be associated with the π-acceptor ability of the $C_6H_5SO_2$ group, which can stabilize a Rh^I species but not the cationic Rh^{III} complex $[CpRh(CO)(C_6H_5SO_2)PPh_3]^+$.

CONCLUSIONS

(*i*). Oxidation of the rhodium(I) complexes containing the C_5H_5 ligand is not as easy as that of complexes of the type RhL_3X and *trans*-Rh(CO)L_2X.

(*ii*). Oxidation of the CpRh(CO)L complexes always occurs through the formation of cationic intermediates, the stability of which is dependent on the nature of the oxidant.

(*iii*). In attack by carbon centres, the nucleophilicity of the metal is greater in CpRh(CO)PPh_3 than in CpRh$(CO)_2$, because the σ-donor ability of PPh_3 is larger than that of CO.

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