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Ligand-Cyclometallation on Rh(I) Complexes Initiated by Cyclic Organotin Compounds Leads Oxidatively to Rh(III) Analogues

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Reactions of[$RhClL_3$], where L = PEt_3, PBu^n_3, PPh_3, with $(R_2Sn)_n$ (in slight excess), where R = Me or Ph, n = 6 and R = Et, n = 9, were carried out in the hope of obtaining rhodium(I) complexes formed by insertion of R_2Sn moieties into Rh—Cl bonds. The ^{31}P NMR spectral data of the reaction mixtures showed that no Rh—Sn species could be detected in the products, but rather an interesting new complex, formed by cyclometallation involving a β-hydrogen transfer from the ligands PEt_3 or PBu^n_3, or from the ortho-carbanato of the phenyl group of PPh_3 in the complexes [$RhClL_3$], to form the Rh(III) complexes. Explanations of such results are given and discussed.

INTRODUCTION

There is considerable interest in coordination chemistry about the tertiary phosphine ligands, partially due to their relevance in catalysis. Thus, it has been reported that rhodium complexes of tertiary phosphine (R_3P) and related ligands show catalytic activity for alkene hydroformulation and methanol carbonylation[1–7]. As part of our interest in coordination chemistry for such ligands, the type of interaction between organotin compounds and transition metal ions, and in continuation with our continuous work[8–10], we report here the reaction of [$RhClL_3$], L = PEt_3, PBu^n_3, PPh_3 with cyclic organotin compounds $(R_2Sn)_n$, R = Me or Ph, n = 6; R = Et, n = 9, which results in the formation of cyclometallated Rh(III) complexes (Scheme-1); as containing no Rh–Sn bonds expected to be formed from the insertion of R_2Sn moieties into Rh—Cl bonds.

EXPERIMENTAL

All the solvents were dry and oxygen-free, and reactions were carried out under dry nitrogen or argon. The ^{31}P NMR spectra were recorded at 40.48 MHz on a Jeol PFT100 instrument using trimethylphosphine (TMP) as an external reference.

$RhCl_3$, $SnMe_2Cl_2$, $SnEt_2Cl_2$ and $SnPh_2Cl_2$ were commrcial products. The cyclic organotin compounds $(R_2Sn)_n$, R = Me or Ph, n = 6 and R = Et, n = 9 were prepared according to a literature method using R_2SnCl_2 (R = Me, Et, Ph) as starting materials[11]. The rhodium(I) complexes [$RhClL_3$], L = PEt_3, PBu^t_3, PPh_3

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were prepared by treating 1 : 6 molar quantities of the famous Wilkinson complex $[RhCl(COD)]_2$ and the corresponding phosphine (L) in toluene. Wilkinson complex was prepared from $RhCl_3$ and COD (COD is 1,5-cyclooctadiene).

Reaction between $[RhClL_3]$ and $(R_2Sn)_n$

A stock solution of the complex, *e.g.*, $[RhCl(PBu^n_3)_3$ in toluene (0.52 M) {prepared by treating the complex $[RhCl(COD)]_2$ (2.0 g, 3.0 mmol) in toluene (10 mL) with PBu^n_3 (3.5 g, 18 mmol)} was prepared and appropriate quantities used as indicated below.

The solution of $[RhCl(PBu^n_3)_3]$ (2 mL, 1.04 mmol) was added to a suspension of $(Me_2Sn)_6$ (0.1 g, 0.29 mmol) in toluene (10 mL). The mixture was stirred under argon for *ca.* 48 h; then the solution was concentrated and the ^{31}P NMR spectrum recorded. Similar procedures were used for $(Ph_2Sn)_6$ and $(Et_2Sn)_9$, and for the complex containing the PEt_3 ligand.

Only one UV light reaction between $[RhCl(PPh_3)_3]$ and $(Ph_2Sn)_6$ was carried out, and this involved irradiation of a toulene solution for *ca.* 1 h.

In situ reaction between $[RhCl(PBu^n_3)_3]$ and HCl gas

The complex $[RhCl(PBu^n_3)_3]$ (0.5 mL, 0.26 mmol) in toluene was placed in an (8 mm) ^{31}P NMR tube under argon and dry HCl gas was bubbled through for *ca.* 30 sec. The ^{31}P NMR spectrum was recorded.

RESULTS AND DISCUSSION

The reaction of $[RhClL_3]$, L = PEt_3, PBu^n_3, PPh_3 with $(R_2Sn)_n$ (in slight excess) were carried out in toluene under argon or nitrogen with exclusion of air and moisture, in the hope of obtaining complexes containg Rh—Sn bonds.

Reaction of $[RhClL_3]$ with $(R_2Sn)_n$

The ^{31}P NMR spectrum of a mixture obtained after *ca.* 48 h from the reaction between $[RhCl(PEt_3)_3]$ with $(Me_2Sn)_6$ in toluene at room temperature, revealed, in addition to the unreacted rhodium starting material, another complex (12% proportion). The spectrum of which comprised a doublet of doublets {δ 125.0 ppm; $^1J(RhP)$ 94.6 Hz; $^2J(PP)$ 27.0 Hz} and a doublet of doublets to higher frequency {δ 115.6 ppm; $^1J(RhP)$ 149.5 Hz; $^2J(PP)$ 27.0 Hz} representing the A part of an AB_2 spectrum with addition coupling to Rh (Fig. 1); no tin satellites were present. An identical ^{31}P NMR spectrum was obtained for the product formed after *ca.* 120 h from the reaction between $[RhCl(PEt_3)_3]$ and $(Ph_2Sn)_6$ in toluene.

Similar results were obtained when the complex $[RhCl(PBu^n_3)_3]$ was used with $(R_2Sn)_n$ in toluene (Table-1).

For the reaction between $[RhCl(PPh_3)_3]$ and $(Ph_2Sn)_6$ in toluene at room temperature, the ^{31}P NMR spectrum of the mixture after *ca.* 120 h revealed only the unchanged rhodium starting material. When the system was irradiated with

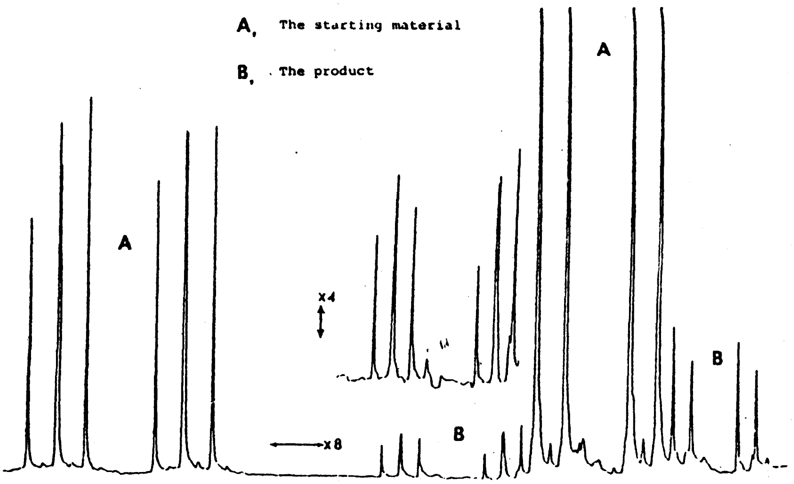


Fig. 1 The ^{31}P-{^1H} NMR spectrum of the proposed reaction between $[RhCl(PEt_3)_3]$ and $(R_2Sn)_n$.

UV light for *ca.* 1 h, the spectrum revealed, in addition to the unchanged rhodium starting material (31% proportion), a second complex (26% proportion) as well as some free phosphine (probably came from decomposition of the complexes). The new complex had a ^{31}P NMR spectrum similar in form to those of the complexes above (Table-1).

TABLE-1

^{31}P-{^1H} NMR DATA FOR Rh(I) AND Rh(III) COMPLEXES[a]

Complex	Parameters for P *trans*- to Cl		Parameters for P *trans*- to P		
	-δ ppm	$^1J(RhP)$ Hz	-δ ppm	$^1J(RhP)$ Hz	$^2J(PP)$ Hz
$[RhCl(PEt_3)_3]$	103.3	184.3	120.7	135.5	41.5
$[RhCl(PBu^n_3)_3]$	112.4	185.6	128.3	134.2	40.3
$[RhCl(PPh_3)_3]$	93.2	190.4	109.6	144	37.8
	93.0[b]	189.0[b]	109.5[b]	142[b]	38.0[b]
mer-$[RhHCl_2(PBu^n_3)_3$	110.4	132.1	129.5	94.0	27.9
mer-$[RhHCl(C_2H_4PEt_2)(PEt_3)_2$	115.5	149.0	125.0	95.2	27.0
mer-$[RhHCl(C_4H_8PBu^n_2)(PBu^n_3)_2$	123.0	149.5	129.4	95.0	26.8
mer-$[RhHCl(C_6H_4PPh_2)(PPh_3)_2$	112.8	153.3	126,0	99.0	25.6

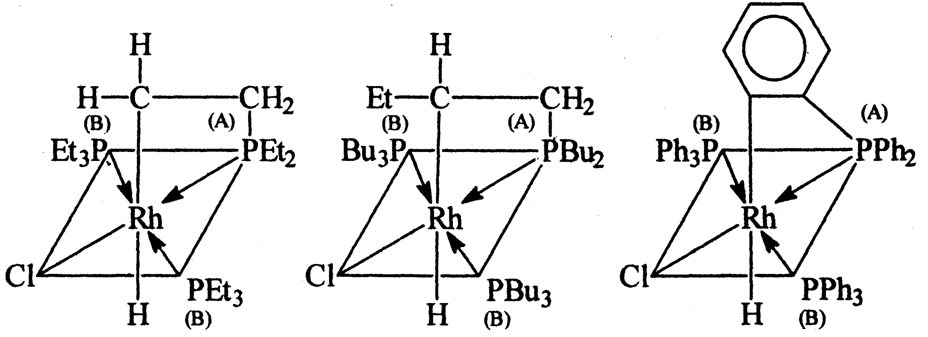
[a]Spectra recorded in toluene, using TMP as an external reference.

[b]Data obtained from reference 15.

Since the ^{31}P NMR parameters of the products obtained above arise from Rh(III) complexes, and there are no tin satellites, it was thought that the product might be of the HCl adduct formed from HCl produced somehow by hydrolysis of the tin compound in the presence of Rh-Cl species. Thus, the complex *mer*-[$RhHCl_2(PBu_3^n)_3$] was prepared by passing HCl gas through a toluene solution[12] of [$RhClL_3$]. The values of $^1J(RhP)$ for the *mer*-[$RhHCl_2(PBu_3^n)_3$] were closely similar to those for the products discussed above but the chemical shifts were different (Table-1). The only suggestion we can make to explain these results is that cyclometallation occurred as a result of either leaving the reaction mixture for a long period, in the presence of the tin compounds, or heating it. To test this possibility, a toluene solution of [$RhCl(PBu_3^n)_3$] was heated at 100°C for *ca.* 3 h under dry argon and then put aside for *ca.* 48 h, the ^{31}P NMR spectrum of which revealed the presence of the same complex obtained earlier from the proposed reaction between [$RhCl(PBu_3^n)_3$] and $(R_2Sn)_n$, in almost similar proportion.

Identification of the products

The ^{31}P NMR spectrum of the starting material [$RhClL_3$] comprised a doublet of doublets at lower frequency for P *trans*- to P with $^1J(RhP)$ of *ca.* 135 Hz, and a doublet of doublets at a higher frequency for P *trans*- to chlorine with $^1J(RhP)$ of *ca.* 185 Hz and $^2J(PP)$ of *ca.* 41 Hz. Such coupling constants are lower by about 30% for Rh(III) complexes[13]. Since the products we obtained have ^{31}P NMR spectra similar in form to that of Rh(I) starting material [doublet of doublets at higher field and doublet of doublets at lower field (Fig. 1)], it must contain three phosphorus atoms, two of them in *trans*- relationship to each other, and the third one in *trans*- relationship to some other species, tentatively identified as to be chlorine (Scheme-1).



(1) (2) (3)

Scheme-1. The suggested structures of the new cyclometallated Rh(III) complexes.

The values of $^1J(RhP)$ and $^2J(PP)$ (Table-1) are consistent with those for Rh(III) complexes having the *meridional* and not *facial* configuration. The products, however, could well be formed by cyclometallation involving a β-hydrogen transfer either from PEt_3 or PBu_3^n to Rh(I) to form the Rh(III) complex (1) or (2), or hydrogen transfer from the ortho-carbanato of the phenyl group of PPh_3 to Rh(I) to form complex (3) (Scheme-1). Support for this suggestion comes from the fact that the chemical shifts for phosphorus (A) of the suggested structures are downfield by *ca.* 11 ppm (L = PEt_3, PBu^n_3) and *ca.* 20 ppm (L = PPh_3) from those of the starting material [$RhClL_3$] (Table-1) and such downfield shifts would be normal for cyclometallation, *e.g.*, the values of δ for metallated Fe or Os complexes are shifted by 20 to 50 ppm downfield from that for the non-metallated complexes[14].

It should be noted that an attempt was made to obtain a good yield of the product in order to observe the Rh-H resonance in the ^1H NMR and IR spectroscopy, involving heating the reaction mixture of [$RhClL_3$] and $(R_2Sn)_n$ or leaving it for a longer time, it was found that the yield slightly decreased, and we deduce from these observations that the cyclometallation was reversible:

$$[RhCl(PBu^n_3)_3] \rightleftharpoons mer\text{-}[RhHCl(C_4H_8PBu^n_2)(PBu^n_3)_2]$$

Unfortunately because the yields of these products were small, the hydride resonance could not be detected by ^1H NMR spectroscopy. These was a small peak in the IR spectrum at 1930 cm^{-1}, which could be due to ν(R—H).

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