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FIVE COORDINATE RHODIUM(I) COMPLEXES CONTAINING THE THIHALOGENOTIN GROUP

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Summary

The preparation and properties of five coordinate rhodium complexes with mono- or bidentate phosphorus donor ligands of the general formulae $[Rh(SnCl_3)(diolefin)L_2]$, $[Rh(SnClX_2)(diolefin)(L—L)]$ or $[Rh(dppe)_2]SnClX_2$ (X = Cl or Br) are described. The temperature dependence of the ^{31}P NMR spectra and the $^1J(Rh, P)$ and $^2J(Sn, P)$ values are discussed.

Introduction

A large number of transition metal compounds containing covalently-bonded SnX_3^- ligands have been reported [1,2]. In particular five coordinate rhodium(I) complexes of the type $[Rh(SnX_3)(diolefin)_2]$ (X = Cl, diolefin = 2,5-norbornadiene (NBD) or 1,3-butadiene; X = Br, diolefin = NBD) and $[Rh(SnX_3)(NBD)L_2]$ (X = Cl or Br, L = tertiary phosphine ligand) have been described [3—5]. Previous attempts to obtain complexes with 1,5-cyclooctadiene (COD) have failed [3—5]. It has been suggested that the unknown $[Rh(SnCl_3)(COD)_2]$ is unstable with respect to $[RhCl(COD)]_2$ and $SnCl_2$ [4]; however, in keeping with the tendency of iridium to stabilize five coordinate complexes, the preparation [3,6] and single crystal X-ray [6] structure determination of the $[Ir(SnCl_3)(COD)_2]$ have been reported.

We describe below the preparation and properties of complexes of the type $[Rh(SnCl_3)(diolefin)L_2]$ (diolefin = COD or NBD and L = PPh_xEt_{3-x}) and $[Rh(SnCl_3)(diolefin)(L—L)]$ (Y_2 = COD or NBD and L—L = bis(1,2-diphenylphosphino)ethane (dppe), bis(1,3-diphenylphosphino)propane (dppp), bis(1,4-diphenylphosphino)butane (dppb), *cis*-bis(1,2-diphenylphosphino)ethylene (dppen) and (—)-2,3-isopropylidene-2,3-dihydroxybis(1,4-diphenylphosphino)-butane (diop) and other related complexes).

Results and discussion

(a) Preparation and properties of the complexes

We find that five coordinate complexes containing tin—rhodium bonds may be obtained by the action of $SnCl_3^-$ on cationic species according to eq. 1.

$$[Rh(diolefin)L_2]^+ + SnCl_3^- \rightarrow [Rh(SnCl_3)(diolefin)L_2] \quad (1)$$

The preparation of the compounds $[Rh(SnCl_3)(diolefin)L_2]$ and $[Rh(SnCl_3)(diolefin)(L—L)]$ may be achieved without the isolation of the cationic [7] species $[Rh(diolefin)L_2]^+$. Addition of $SnCl_2$ to the solution defined by eq. 2 leads to the desired product. The same method is effective for the synthesis of the complexes $[Rh(SnCl_3)(diolefin)(L—L)]$.

$$[RhCl(diolefin)L] + L \overset{MeOH}{\rightleftharpoons} [Rh(diolefin)L_2]^+ + Cl^- \quad (2)$$

When $SnBr_2$ was used the new derivative $[Rh(SnClBr_2)(COD)(dppe)]$ was isolated (eq. 3).

$$1/2[RhCl(COD)]_2 + dppe + SnBr_2 \rightarrow [Rh(SnClBr_2)(COD)(dppe)] \quad (3)$$

Table 1 lists the analytical data for the isolated complexes. These are yellow solids, and show conductivities in solution much smaller than those expected for 1/1 electrolytes.

$[Rh(SnCl_3)(COD)(PPh_3)_2]$ is inactive towards the hydroformylation of 1-heptene (100°C; total pressure, 50 atm; H_2/CO molar ratio 1/1), but it is a moderately good catalyst for the hydrogenation of olefins. Addition of $SnCl_2$ or $SnBr_2$ to solutions of $[Rh(dppe)_2]Cl$ [8] prepared "in situ" from $[RhCl(CO)_2]_2$ or $[RhCl(COD)]_2$ permit the isolation of the $[Rh(dppe)_2]SnClX_2$ (X = Cl or Br) complexes. These yellow compounds melt with decomposition and behave as completely dissociated 1/1 electrolytes in acetone.

The bubbling of carbon monoxide at ordinary pressure through chloroform solutions of $[Rh(SnCl_3)(NBD)(PPh_xEt_{3-x})_2]$ results in the displacement of NBD (eq. 4). The new dicarbonyl complexes were isolated as yellow crystalline solids except where L = $PPhEt_2$ and PEt_3, when only yellow oils were obtained. In these latter cases the characterisation of the products is based on the close analogy between their IR spectra and those of the isolated complexes.

$$[Rh(SnCl_3)(NBD)(PPh_xEt_{3-x})_2] + CO \rightarrow [Rh(SnCl_3)(CO)_2(PPh_xEt_{3-x})_2] + (NBD) \quad (4)$$

(b) IR spectra

Table 2 shows the characteristic tin—chlorine stretching vibrations. Coordination of the $SnCl_3^-$ ligand in the $[Rh(SnCl_3)(diolefin)L_2]$ complexes is evident from the considerable increase in the tin—chlorine stretching frequencies upon coordination. The cationic $[Rh(dppe)_2]SnCl_3$ complex shows two ν(Sn—Cl) stretching frequencies at 287 and 252 cm^{-1}, characteristic of the free $SnCl_3^-$ ion [9].

Some of the complexes contain three tin—chlorine stretching frequencies instead of the expected two. This has been observed previously [4,9] and is due

TABLE 1

ANALYTICAL RESULTS, MELTING POINTS, YIELD AND MOLAR, CONDUCTIVITIES OF FIVE COORDINATE RHODIUM (I) COMPLEXES

Complex		Analyses (Found (calcd.)(%))		M.p. or dec. p. (°C)	Yield (%)	Λ_M (ohm^{-1} cm^2 mol^{-1})
		C	H			
$[Rh(SnCl_3)(COD)(dppe)]$	(I)	47.70 (48.93)	4.07 (4.35)	167—169	85	1
$[Rh(SnCl_3)(COD)(dppp)]$	(II)	49.47 (49.54)	4.44 (4.48)	145—148	54	6
$[Rh(SnClBr_2)(COD)(dppe)]$	(III)	45.17 (44.22)	4.15 (3.92)	151—155	88	2
$[Rh(SnCl_3)(COD)(dppb)]$	(IV)	49.33 (50.13)	4.52 (4.67)	132—134	66	6
$[Rh(SnCl_3)(COD)(dppen)]$	(V)	48.72 (49.05)	4.21 (4.11)	175—177	65	8
$[Rh(SnCl_3)(COD)(PPhEt_2)_2]$	(VI)	42.61 (43.74)	5.45 (5.73)	117—118	59	16
$[Rh(SnCl_3)(COD)(PPh_2Et)_2]$	(VII)	49.56 (49.99)	5.16 (4.86)	110—112	31	15
$[Rh(SnCl_3)(NBD)(dppe)]$	(VIII)	48.01 (48.42)	3.95 (3.94)	175—177	76	4
$[Rh(SnClBr_2)(NBD)(dppe)]$	(IX)	44.23 (43.68)	3.69 (3.58)	157—159	41	2
$[Rh(SnCl_3)(NBD)(dppp)]$	(X)	48.53 (49.05)	4.04 (4.12)	155—158	64	5
$[Rh(SnCl_3)(NBD)(dppb)]$	(XI)	49.23 (49.66)	4.04 (4.29)	170—172	82	2
$[Rh(SnCl_3)(NBD)(dppen)]$	(XII)	48.03 (48.44)	3.72 (3.70)	165—169	60	2
$[Rh(SnClBr_2)(NBD)(dppen)]$	(XIII)	44.02 (43.78)	3.46 (3.34)	153—158	63	3
$[Rh(SnCl_3)(NBD)(diop)]$	(XIV)	50.14 (49.68)	4.77 (4.39)	157—159	33	3
$[Rh(SnCl_3)(NBD)(PEt_3)_2]$	(XV)	34.59 (34.75)	5.43 (5.79)	126—128	53	4
$[Rh(SnCl_3)(NBD)(PPhEt_2)_2]$	(XVI)	44.49 (43.07)	5.35 (5.18)	132—135	52	2
$[Rh(SnCl_3)(NBD)(PPh_2Et)_2]$	(XVII)	49.06 (49.52)	4.33 (4.48)	158—159	63	3
$[Rh(SnCl_3)(NBD)(PPh_3)_2]$	(XVIII)	54.64 (53.38)	4.24 (4.02)	140—142	70	14
$[Rh(SnCl_3)(CO)_2(PPh_2Et)_2]$	(XIX)	43.34 (44.32)	3.65 (3.69)	140—142	59	11
$[Rh(SnCl_3)(CO)_2(PPh_3)_2]$	(XX)	49.89 (50.21)	3.62 (3.30)	176—178	45	3
$[Rh(dppe)_2]SnCl_3$	(XXI)	55.07 (55.53)	4.22 (4.30)	190—194	60	96
$[Rh(dppe)_2]SnClBr_2$	(XXII)	49.72 (51.39)	4.01 (3.98)	196—198	57	96

to removal of the degeneracy of the asymmetric stretching vibration by the influence of the site symmetry in the crystal. Nevertheless there is some controversy in the literature over the assignment of the tin—chlorine stretching frequencies and some authors assign the peak at higher wavenumber to asymmetric stretch [1].

TABLE 2

IR DATA FOR THE COMPLEXES CONTAINING THE TRICHLOROTIN GROUP [a]

Complex	diolefin: NBD		diolefin: COD	
	ν_{sym}(Sn—Cl)	ν_{asym}(Sn—Cl)	ν_{sym}(Sn—Cl)	ν_{asym}(Sn—Cl)
[Rh($SnCl_3$)(diolefin)(dppe)]	300	280	295	272
[Rh($SnCl_3$)(diolefin)(dppp)]	308, 302	286, 277	300	272
[Rh($SnCl_3$)(diolefin)(dppb)]	308	280	300	285, 275
[Rh($SnCl_3$)(diolefin)(dppen)]	300	285	295	272
[Rh($SnCl_3$)(diolefin)(PEt_3)$_2$]	290	270	—	—
[Rh($SnCl_3$)(diolefin)($PPhEt_2$)$_2$]	302	285, 275	290	275
[Rh($SnCl_3$)(diolefin)(PPh_2Et)$_2$]	305	280, 267	301	279
[Rh($SnCl_3$)(diolefin)(PPh_3)$_2$]	305	280 [b]	—	—
[Rh($SnCl_3$)(diolefin)($AsPh_3$)$_2$]	307	284 [b]	—	—
[Rh($SnCl_3$)(diolefin)($SbPh_3$)$_2$]	311	296 [b]	—	—
[Rh(dppe)$_2$]$SnCl_3$	287	252	287	252

[a] Nujol mulls. [b] Ref. 4.

Inspection of the higher Sn—Cl stretching frequencies for the [Rh($SnCl_3$)(NBD)L_2] complexes reveals that they are slightly shifted towards higher energies in the sequence: $PEt_3 < PPhEt_2 < PPh_2Et < PPh_3 < AsPh_3 < SbPh_3$; i.e. the order of decreasing σ-donor strength of the monodentate ligand L. On an electroneutrality basis, as L becomes a poorer donor, a stronger Sn—Rh interaction (higher Sn—Cl stretching frequencies) is required, as supported by Mössbauer measurements [10].

The IR data for [Rh($SnCl_3$)(diolefin)(L—L)] (diolefin = NBD or COD) complexes show higher values of ν(Sn—Cl) for the norbornadiene derivatives, indicating that because of the higher π-acidity of norbornadiene [11], the rhodium becomes a better acceptor, the $SnCl_3^-$ ligand donates more charge, and the Sn—Cl bonds are strengthened.

The IR spectra of complexes of the type [Rh($SnCl_3$)(CO)$_2$$L_2$] show typical bands of the coordinated $SnCl_3^-$ ligand and two ν(CO) bands characteristic for terminal carbonyls in the 2040—1980 cm^{-1} region, in chloroform solution, while in Nujol mulls three bands are observed.

(c) ^{31}P NMR

The ^{31}P chemical shifts and coupling constants for the complexes [Rh($SnCl_3$)(NBD)L_2] (L = PEt_3, PEt_2Ph, $PEtPh_2$, PPh_3) and [Rh($SnCl_3$)(NBD)(L—L)], (L—L = dppe, dppp, dppb, dppen) are shown in Table 3 and are consistent with the proposed molecular composition. At normal probe temperature (~30°C) phosphorus coupling to the two NMR active tin isotopes, ^{117}Sn (I = 1/2, natural abundance 7.6%) and ^{119}Sn (I = 1/2, natural abundance 8.6%), is not observable, although coupling to rhodium is clearly present. Since the infrared data point to coordination of the trichlorostannyl group, the samples were cooled in order to look for some form of dynamic behaviour on the NMR time scale. The temperature dependence of the ^{31}P spectra suggest that two processes are occurring. One of these involves ligand exchange and is slow for all the L and L—L at —20°C. At this temperature the ^{31}P spectra are doublets (due

TABLE 3

^{31}P MNR PARAMETERS [a] FOR THE TRICHLOROSTANNANE COMPLEXES

Compound	Chemical Shift	^1J(Rh, P)	^2J(Sn, P) [b]
$[Rh(SnCl_3)(NBD)(PEt_3)_2]$	18.7	129	184, 176
$[Rh(SnCl_3)(NBD)(PEt_2Ph)_2]$	24.9	130	187, 178
$[Rh(SnCl_3)(NBD)(PEtPh_2)_2]$	29.8	131	152, 144
$[Rh(SnCl_3)(NBD)(PPh_3)_2]$	35.5	132	190, 182
$[Rh(SnCl_3)(NBD)(dppe)]$	60.1	133	119, 113
$[Rh(SnCl_3)(NBD)(dppen)]$	57.3	132	102, 98
$[Rh(SnCl_3)(NBD)(dppp)]$	20.4	128	115, 109
$[Rh(SnCl_3)(NBD)(dppb)]$	30.9	131	129, 122

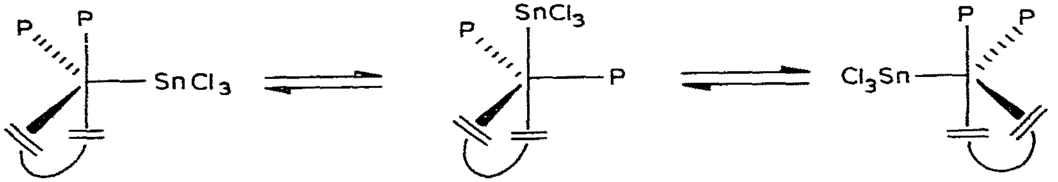
[a] Chemical shift are in ppm relative to H_3PO_4 at room temperature. Coupling constants are in Hz and are estimated to be ±3 Hz. The data are for solutions at —20°C. [b] ^{119}Sn and ^{117}Sn coupling constants, respectively.

to rhodium coupling) flanked by the satellites. For the series L = PEt_3, PEt_2Ph, $PEtPh_2$, PPh_3, the activation energy for exchange decreases with increasing phenyl substitution. This, combined with the previously discussed conductivity data, suggests that phosphine dissociation may be responsible for the exchange and for the failure to observe tin—phosphorus coupling at ~30°C.

The second process, which is still rapid at —90°C, probably involves an intramolecular process. Five coordinate rhodium d^8 complexes are known to be stereochemically non-rigid on the NMR time scale and to undergo Berry pseudorotation with activation energies of the order of 7.5—12 kcal/mol [12]. For L = PPh_3 at —110°C we have observed a ^{31}P spectrum containing at least six relatively sharp resonances. Assuming that the norbornadiene ligand will only span chelating sites which are 90° apart, several isomers are possible. Since the spectrum quality is not sufficient to permit a definite structural assignment, we can only suggest that a number of these isomers must be present in solution. Shapley and Osborn [13] have suggested that the complexes $[Ir(SnCl_3)(COD)L_2]$ exist as distorted trigonal bipyramidal structures having the trichlorostannane ligand in an equatorial position. Churchill and Lin [14] find that the overall coordination geometry for $[Ir(SnCl_3)(COD)(PMe_2Ph)_2]$ lies almost midway between a trigonal bipyramid and a square pyramid. It, therefore seems likely that there will not be a high energy barrier separating the various isomers in our complexes, and that very low temperatures will be required to slow these processes. We return to the question of an equatorial as opposed to an axial $SnCl_3$ below.

At —20°C the rhodium—phosphorus one-bond coupling constants for all of our complexes fall in the narrow range 128—133 Hz, and do not appear to be sensitive to the nature of the phosphine. Given that the molecules are stereochemically non-rigid at this temperature, it is possible that our ^1J(Rh, P) values represent a relatively constant average comprised of $^1J(Rh, P_{ax})$ and $^1J(Rh, P_{eq})$ components. Significant differences in these two types of one-bond coupling constant are known, e.g. in $[Rh(P(OMe)_3)_5]BPh_4$: $^1J(Rh, P_{ax})$ 143 Hz; $^1J(Rh, P_{eq})$ 206 Hz [12], but the absolute difference will be smaller for phosphorus ligands not containing three electron-withdrawing substituents. Therefore, the values ^1J(Rh, P) may not have much meaning without a more exact knowledge of the limiting structure(s).

The values ^2J(Sn, P) at —20° C are more revealing and can be seen to vary from ~102 to 190 Hz (for the ^{119}Sn coupling). The values are all relatively large for the monodentate phosphine ligands but much smaller for the bidentate systems. Further, the ^2J(Sn, P) values within our four bidentate complexes decrease as the flexibility of the bidentate decreases. Shapley and Osborn [13] have predicted that the $SnCl_3^-$ ligand should occupy an equatorial position in the complexes [$Ir(SnCl_3)(COD)L_2$] and that the interconversion from one isomer to another would have a higher energy of activation when L_2 = bidentate phosphine. This is based on the expectation that since the bidentate ligand "bite" angle is restricted, chelating strain destabilization will occur in the transition state B, thus increasing the energy barrier to intramolecular rearrangement. We believe that this tendency is reflected in our ^2J(Sn, P) data, and that the equilibrium composition at —20° C contains a larger proportion of structures similar to A and C *, whereas the monodentate phosphine complexes may give an equilibrium mixture containing more "B" type components.



(A) (B) (C)

As expected [15] the ^{31}P chemical shifts move progressively downfield as phenyl is substituted for ethyl on phosphorus. The bidentate phosphines, dppe and dppen, show the large low field shift associated with five membered chelate rings.

Further studies involving the ^{119}Sn NMR properties of these complexes are in progress.

Experimental

The C, H and N analyses were carried out with a Perkin—Elmer 240 microanalyzer. Conductivities were measured in ca. 5×10^{-4} *M*, acetone solution with a Philips 9501/01 conductimeter. The IR spectra were recorded on a Perkin—Elmer 577 spectrophotometer (over the range 4000—200 cm^{-1}) using Nujol mulls between polyethylene sheets or potassium bromide disks. ^{31}P NMR spectra were measured as CD_2Cl_2 solutions using a Bruker HX-90 NMR Spectrometer operating at 36.43 MHz in Fourier transform mode. The data were acquired from 1000 transients using spectral widths of 6024 Hz and 8 K data

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* We do not suggest that the structure of our chelate complex is a trigonal bipyramid. This would be inconsistent with the ^{31}P spectrum of [$Rh(SnCl_3)(NBD)(dppe)$] at —100° C, which shows equivalent phosphorous atoms and little change from the doublet with tin satellites found at —20° C, but rather that the distorted structures differ for the chelating and monodentate phosphine complexes.

points in the free induction decay. Typically, the pulse width was 7 microseconds (50 degree flip angle). ^{31}P chemical shifts are relative to external H_3PO_4 with a positive sign indicating a shift to lower field.

Complexes of the type [Rh(SnCl$_3$)(diolefin)L$_2$] or [Rh(SnClX$_2$)(diolefin)-(L—L)]

To a stirred methanol suspension of the dimeric complex $[RhCl(COD)]_2$ or $[RhCl(NBD)]_2$ was added a stoichiometric amount of the corresponding phosphine or diphosphine, and stirring was continued until a clear orange-coloured solution was obtained. Addition of $SnCl_2 \cdot 2\ H_2O$ or $SnBr_2$ (stoichiometric ratio) generally led to the precipitation of the corresponding complex, which was recrystallized from dichloromethane/ether.

Complexes of the type [Rh(dppe)$_2$]SnClX$_2$ (X = Cl or Br)

The addition of equimolar amount of $SnCl_2 \cdot 2\ H_2O$ or $SnBr_2$ to methanol solutions of $[Rh(dppe)_2]Cl$ [8] gave a yellow precipitate, which was filtered off and washed with ether.

Complexes of the type [Rh(SnCl$_3$)(CO)$_2$L$_2$]

Bubbling of CO at normal pressure and room temperature through chloroform solutions of complexes of the type $[Rh(SnCl_3)(NBD)L_2]$ caused fading of the solution and formation of complexes $[Rh(SnCl_3)(CO)_2L_2]$. After addition of ether these were isolated as solids in the case of L being PPh_3 and PPh_2Et; but for L = $PPhEt_2$ and PEt_3 non-crystallizable oils were obtained.

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