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CATIONIC RHODIUM(I) THIOCARBONYL COMPLEXES WITH TRIPHENYLPHOSPHINE AND N-DONOR LIGANDS

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Summary

The preparation of cationic rhodium(I) thiocarbonyl complexes of the general formula $[Rh(CS)(PPh_3)_2L]ClO_4$ (L being mono- or bi-dentate N-donor ligands or triphenylphosphine) is described. The carbonylation of these compounds and the catalytic activity of $[Rh(CS)(PPh_3)_3]ClO_4$ and its carbonyl homologue have been studied along with oxidative addition reactions of $[Rh(CS)(PPh_3)_2(py)]ClO_4$ with halogens. The formation of an acid-base adduct $[Rh(CS)(PPh_3)_2Cl]HgCl_2$ is discussed.

The recent publication [1] of the synthesis of the first cationic rhodium(I) thiocarbonyl compounds with a series of P-donor ligands has prompted us to describe our work in this field.

The reaction of *trans*-$RhCl(CS)(PPh_3)_2$ (I) with $AgClO_4$ (1/1) in acetone/dichloromethane (3/1) solution, followed by filtration of the precipitated AgCl and addition of the appropriate ligand L (L being C_5H_5N (py), 2-$C_2H_5C_5H_4N$ (2-Etpy), 4-$C_2H_5C_5H_4N$ (4-Etpy), $C_{10}H_8N_2$ (bipy), $C_{12}H_8N_2$ (phen), *o*-$C_6H_4(CN)_2$ (dnf) or $P(C_6H_5)_3$ (PPh_3)) to the filtrate gave solutions from which complexes of the general formula $[Rh(CS)(PPh_3)_2L]ClO_4$ were isolated. They are yellow or orange-red microcrystalline solids which behave as 1/1 electrolytes in acetone solution. They were characterized by elemental analyses (C, H and N) and by their IR and NMR spectra (Table 1).

When L is a monodentate ligand the absorption due to $\nu(CS)$ is located as a single band in the 1330—1310 cm^{-1} region, whilst when L is a bidentate ligand (bipy, phen) the absorption assignable to $\nu(CS)$ is clearly shifted towards lower energies (1290, 1285 cm^{-1}), which would be consistent with pentacoordination in these compounds [1].

TABLE 1

ANALYTICAL RESULTS, MOLAR CONDUCTIVITIES, IR DATA, YIELDS AND COLOUR OF CATIONIC THIOCARBONYL COMPLEXES OF RHODIUM(I)

Complex	Found (calcd.) (%)			Λ_M (ohm^{-1} cm^2 mol^{-1})	ν(C≡S) (cm^{-1})	$\nu(ClO_4^-)$ (cm^{-1})	Yield (%)	Colour
	C	H	N					
$[Rh(CS)(PPh_3)(tmed)]ClO_4$ (II) [a]	46.87 (48.04)	4.90 (4.96)	4.46 (4.48)	143	1313s	1090vs 625m	60	red
$[Rh(CS)(PPh_3)_2(py)]ClO_4$ (III) [a]	60.13 (59.33)	4.14 (4.12)	1.86 (1.65)	136	1320s	1095s 623m	84	orange-yellow
$[Rh(CS)(PPh_3)_2(2\text{-}Etpy)]ClO_4$ (IV) [a]	59.59 (60.17)	4.43 (4.44)	1.58 (1.59)	134	1315s	1098s 623m	96	orange-yellow
$[Rh(CS)(PPh_3)_2(4\text{-}Etpy)]ClO_4$ (V) [a]	58.74 (60.17)	4.56 (4.44)	1.56 (1.59)	140	1310s	1095s 620m	88	orange-yellow
$[Rh(CS)(PPh_3)_2(bipy)]ClO_4$ (VI) [a]	61.56 (60.88)	4.22 (4.10)	3.20 (3.02)	130	1290s	1090s 622m	86	yellow
$[Rh(CS)(PPh_3)_2(phen)]ClO_4$ (VII) [a]	62.61 (62.80)	4.43 (3.89)	3.04 (2.87)	116	1285s	1093s 622m	75	yellow
$[Rh(CS)(PPh_3)_2(dnf)]ClO_4$ (VIII) [a]	59.41 (60.10)	4.10 (3.78)	3.28 (3.11)	138	1327s	1095s 625m	80	orange-yellow
$[Rh(CS)(PPh_3)_3]ClO_4$ (IX) [b]	64.25 (63.93)	5.37 (4.35)	— —	140	1312s	1095s 622m	82	yellow

[a] Nujol mulls. [b] KBr discs.

When L = *N,N,N′,N′*-tetramethylethylenediamine (tmed) the addition of the ligand gives rise to the displacement of one mol of PPh_3 to give $[Rh(CS)(PPh_3)(tmed)]ClO_4$. In this case the band due to ν(CS) appears at 1315 cm^{-1}, as in the afore-described tetracoordinated complexes, which probably have a square-planar geometry.

When carbon monoxide at ordinary pressure is bubbled through chloroform solutions of the complexes several patterns of behavior are observed; When L = 4-Etpy, 2-Etpy, bipy of phen no reaction takes place during 2 h; when L = tmed, py or PPh_3 reactions do occur as is evident from the progressive change in the spectra in the 2000 cm^{-1} region, but decomposition occurred at the same time and no characterizable compound can be isolated, Finally, when L = dnf a reversible carbonylation takes place (ν(CO): 2080m and 2045s cm^{-1}); the bands due to ν(CO) disappear if the solution is evaporated under vacuum or if argon is bubbled through [2].

Our studies of the catalytic behavior of cationic rhodium(I) complexes show that both $[Rh(CS)(PPh_3)_3]ClO_4$ (IX) and $[Rh(CO)(PPh_3)_3]ClO_4$ (X) [3], act as catalysts for the hydrogenation of cyclic and terminal olefins (1 atm H_2, room temperature), the thiocarbonyl complex being less active.

$[Rh(CS)(PPh_3)_2(py)]ClO_4$ (III) reacts with the halogens Cl_2, Br_2 and I_2 by oxidative addition. This can be clearly seen from the marked shift of the vibration due to ν(CS) and from the values of the coupling constant ^1J(Rh—P): these do not change as the halogen is varied (see Table 2), but the chemical shifts do vary. Only the iodine derivative, which is only slightly soluble, could be isolated $[RhI_2(CS)(PPh_3)_2(Py)]ClO_4$ (Found: C, 44.72; H, 3.48; N, 1.63; $C_{42}H_{35}I_2ClNO_4SP_2Rh$ calcd.: C, 45.68; H, 3.17; N, 1.26%).

The relation ^1J(Rh—P) hexacoordinated/^1J(Rh—P) tetracoordinated for these cationic organic complexes was found to be 0.57, a value very close to that (0.58) observed [4] for the complexes *trans*-$Rh(CO)(PR_3)_2Cl_3$ and *trans*-$Rh(CO)(PR_3)_2Cl$.

The reaction of $Rh(CS)(PPh_3)_2Cl$ (I) with $HgCl_2$ (1/1) in dichloromethane gives a red product of the formula $Rh(CS)(PPh_3)_2Cl \cdot HgCl_2$ (XI). (Found: C, 44.79; H, 3.05. $C_{37}H_{30}Cl_3SP_2HgRh$ calcd.: C, 45.45; H, 3.08%) (Λ_M(acetone): 5 ohm^{-1} cm^2 mol^{-1}). The value of the coupling constant ^1J(Rh—P) (see Table 2) excludes an oxidative addition reaction, such as that described for $(Ph_2MeAs)_3Cl_2Rh/HgCl$

TABLE 2

IR, ^{31}P NMR DATA AND COLOUR OF THIOCARBONYL COMPLEXES OF RHODIUM

Complex	ν(C≡S) (cm^{-1}) [a]	$\|^1J(Rh—P)\|$ (Hz)	δ (ppm) [b]	$\delta_{complex} - \delta_{ligand}$ [e]	Colour
III	1320	143	34.56 [c]	41.2	orange-yellow
III + Cl_2	1365, 1375	82	16.06 [d]	22.7	light yellow
III + Br_2	1360, 1370	82	9.37 [d]	16.0	yellow
III + I_2	1360	82	—0.68 [d]	5.9	violet
XI	1310	136.7	30.85 [c]	37.45	dark red
I	1310	144	32.44 [c]	39.04	orange-yellow

[a] Nujol. [b] Measured with reference to 85% H_3PO_4 in D_2O as external standard; positive values mean downfield from H_3PO_4, δ values (± 0.03). [c] Room temperature. [d] —40°C. [e] δ_{PPh_3} = —6.6 ppm.

[5]. On the other hand, the existence of an acid—base interaction of the type Rh—C≡S→$HgCl_2$, (as previously proposed for similar species of tungsten(0) [6]) can be ruled out since the band to be assigned to ν(CS) in $Rh(CS)(PPh_3)_2Cl$ (see Table 2) is not changed by the reaction with $HgCl_2$. We therefore propose the formation of an adduct of the Rh→$HgCl_2$ type, some examples of which have been reported for neutral rhodium(I) complexes [7].

The ^{31}P spectra of our complexes in CD_2Cl_2 show doublets of 1/1 intensity due to Rh—P coupling. This means that the PPh_3 ligands must be mutually *trans* in all cases.

Experimental

C, H and N analyses were carried out with a Perkin—Elmer 240 microanalyzer. Conductivities were measured in approx. 5×10^{-4} *M* acetone solutions with a Philips 9501/01 conductimeter. IR spectra were recorded on a Perkin—Elmer 577 spectrophotometer (over the range 4000—200 cm^{-1}) using either Nujol mulls between polyethylene sheets or KBr pellets. ^1H NMR spectra were obtained on a Perkin—Elmer R-12B instrument. ^{31}P-$\{^1H\}$ noise decoupled spectra were recorded on a Bruker WH-90FT NMR spectrometer at 36.43 MHz, using the deuterium resonance of the solvent (CD_2Cl_2) as an internal lock; 5000 accumulations at a 30° pulse angle and 2 sec pulse sequence were needed for a spectrum. The saturated solutions of III + Cl_2, Br_2 or I_2 in 5 mm test-tubes were measured at —70°C in order to increase the signal to noise ratio. There was no evidence of exchange processes between —70 and 0°C. The chemical shifts were measured relative to external 85% H_3PO_4 in D_2O.

A conventional hydrogenation apparatus with septum was used; the order of addition was catalyst solution (0.03 mmol in 10 ml of absolute ethanol), hydrogen (10 minutes prehydrogenation time), and substrate (3 mmol in 5 ml of absolute ethanol).

All the solvents were distilled and degassed. Ethanol was distilled from calcium hydride. All reactions were carried out under argon.

Preparation of cationic rhodium(I) thiocarbonyl complexes

The compound $RhCl(CS)(PPh_3)_2$ was prepared according to Baird and Wilkinson [8], and identified by elemental analyses and IR spectroscopy.

A stoichiometric amount of $AgClO_4$ was added to an approx. 4×10^{-2} *M* acetone/dichloromethane (3/1) solution of I. The formed AgCl was filtered off and the filtrate was added to a stoichiometric amount of the appropriate ligand. The resulting solution was stirred for 10 min and evaporated to dryness. The residue was extracted with the minimal amount of dichloromethane. Addition of ethyl ether caused precipitation of the complex which was recrystallized from dichloromethane/ether.

Complex VII crystallized with 2 mol of dichloromethane (Found: C, 54.67; H, 4.02; N, 2.59. $C_{49}H_{38}ClN_2O_4SP_2Rh$ calcd.: C, 54.62; H, 3.74; N, 2.49%) which can be removed by vacuum-treatment at 60°C for 2 h.

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