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Preliminary communication

CATIONIC THIOCARBONYL COMPLEXES OF RHODIUM(I)

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Summary

The syntheses are described of a range of cationic rhodium(I) thiocarbonyl complexes containing tertiary phosphine, phosphinite, phosphonite and phosphite ligands.

The first reported transition metal thiocarbonyl complexes were of rhodium, *trans*-$RhX(CS)(PPh_3)_2$ ($X = Cl, Br$) [1]. Although numerous thiocarbonyl complexes of other metals have now been reported [2] little progress has been made in extending the range of rhodium thiocarbonyl compounds. Only six other examples of such complexes are known [3—5]. We report here the synthesis of a new series of cationic rhodium(I) thiocarbonyl complexes with tertiary phosphines, phosphinites, phosphonites, and phosphites as ligands (Table 1). The complexes are of three types: $[Rh(CS)L_3]^+$ ($L = PMePh_2, PEt_2Ph, PPh(OPh)_2$), $[Rh(CS)L_4]^+$ ($L = PMe_2Ph, PPh_2(OMe), PPh(OMe)_2, PPh(OEt)_2, P(OMe)_3, P(OEt)_3$), and $[Rh(CS)L_2]^+$ ($L = Ph_2PCH_2CH_2PPh_2$). Satisfactory analyses (C, H, P and S) were obtained for all compounds and conductivity measurements in acetonitrile confirm their formulation as 1/1 electrolytes.

The complexes were prepared under an inert atmosphere by adding an excess of L to a suspension of *trans*-$RhCl(CS)(PPh_3)_2$ in methanol or diethyl ether and stirring until a clear solution was obtained. A slight excess of the required counterion ($NaBPh_4$ or NH_4PF_6) in methanol or acetone was added and the products precipitated after further stirring. Recrystallization from dichloromethane/diethyl ether mixtures gave pure compounds in good yields (40—80%). The phosphine complexes and $[Rh(CS)(PPh(OPh)_2)_3]PF_6$ are air stable but the remaining complexes decompose rapidly on exposure to the atmosphere. Dichloromethane and acetonitrile solutions of all the complexes decompose rapidly in the air.

Cationic rhodium(I) carbonyl complexes of the types $[Rh(CO)_nL_{5-n}]^+$ (n = 1—3) and $[Rh(CO)L_3]^+$ (L = phosphorus donor ligand) are well known [6—8] and in particular the analogous carbonyl complexes $[Rh(CO)L_3]^+$ (L = $PMePh_2$, PEt_2Ph) and $[Rh(CO)L_4]^+$ (L = PMe_2Ph, $P(OMe)_3$) have been isolated [6,8]. The routes to the carbonyl analogues involve preliminary synthesis of $RhCl(CO)L_2$ (L = $PMePh_2$, PEt_2Ph, PMe_2Ph) or $[Rh(P(OMe)_3)_4]^+$ [6,8] and by comparison are less direct than the syntheses of the thiocarbonyl complexes from the same rhodium(I) precursor, $RhCl(CS)(PPh_3)_2$. It is noteworthy that 1,2-bis(diphenylphosphino)ethane fails to eliminate the thiocarbonyl group from $RhCl(CS)(PPh_3)_2$ whereas displacement of CO from $RhCl(CO)(PPh_3)_2$ and other rhodium(I) carbonyl complexes by this phosphine is facile, allowing the reaction to be used for determination of the CO content of these complexes [7]. Previous attempts to prepare $[Rh(CO)(Ph_2PCH_2CH_2PPh_2)_2]^+$ have been unsuccessful [9,10]. Both the carbonyl and thiocarbonyl iridium(I) analogues are stable [11,12], however, and can be prepared by methods similar to that reported here [9,12].

Preliminary results of crystal structure determinations [13] on representative four- and five-coordinate cations confirm their formulation. The coordination environment around rhodium is essentially square planar in $[Rh(CS)(PMePh_2)_3]PF_6$, and consists of a distorted trigonal bipyramid in $[Rh(CS)(PMe_2Ph)_4]BPh_4$. In the latter complex the thiocarbonyl group is in the equatorial plane. The structure of $[Rh(CS)(Ph_2PCH_2CH_2PPh_2)_2]^+$ is expected to be similar to that found for $[Ir(CO)(Ph_2PCH_2CH_2PPh_2)_2]Cl$ [11], with the CS group occupying an equatorial position in a distorted trigonal bipyramid.

As noted previously for complexes of the types $[ML_4]^+$, $[ML_5]^+$ [14] and $[M(CO)L_3]^+$, $[M(CO)L_4]^+$ [6] (M = Rh, Ir; L = phosphorus donor ligand), it seems likely that the steric requirements of the P donor ligand are primarily responsible for determining the stereochemistry of the thiocarbonyl cations. Using ligand cone angles [15] as estimates of ligand size, the most bulky of the ligands studied are the phosphines $PMePh_2$ and PEt_2Ph, and these give four coordinate complexes. Distinction between the steric requirements of $PPh(OPh)_2$, which also allows only four coordination, and certain other ligands favouring five-coordinate structures (e.g. $PPh_2(OMe)$) is less obvious. Electronic effects, originating in the phenoxide groups, may be particularly important here.

Each complex exhibits a very strong, single IR band assigned to ν(CS) (Table 1) within the range previously observed (1381—1193 cm^{-1}) [2] for metal thiocarbonyl complexes. Absorptions for the four-coordinate complexes occur at higher wave numbers (1281—1333 cm^{-1}) than those for the five-coordinate complexes (1232—1278 cm^{-1}). Noting the importance of π-back-bonding to CS in metal—CS bonds [2,16], it is possible that the higher values of ν(CS) for the four-coordinate complexes result from more efficient overlap of ligand—phosphorus d_π-orbitals with rhodium d_π-orbitals (compared to the five-coordinate case), thereby reducing back-donation to π-antibonding orbitals on CS. In support of this, ν(CS) for $[Rh(CS)(PPh(OPh)_2)_3]^+$ is signifi-

TABLE 1

CATIONIC THIOCARBONYL COMPLEXES OF RHODIUM(I) AND THEIR CARBON—SULPHUR ABSORPTIONS (cm^{-1})

Compound	Colour	ν(CS)[a]
$[Rh(CS)(PMePh_2)_3]PF_6$	red	1300
$[Rh(CS)(PEt_2Ph)_3]PF_6$	red	1281
$[Rh(CS)(PPh(OPh)_2)_3]PF_6$	red	1333
$[Rh(CS)(PMe_2Ph)_4]BPh_4$	orange brown	1232
$[Rh(CS)(PPh_2(OMe))_4]PF_6$	yellow	1278
$[Rh(CS)(PPh(OMe)_2)_4]PF_6$	yellow	1261
$[Rh(CS)(PPh(OEt_2)_4]PF_6$	yellow	1260
$[Rh(CS)(P(OMe)_3)_4]BPh_4$	yellow	1274
$[Rh(CS)(P(OEt)_3)_4]PF_6$	yellow	1269
$[Rh(CS)(Ph_2PCH_2CH_2PPh_2)_2]PF_6$	yellow	1257
$[Rh(CS)(Ph_2PCH_2CH_2PPh_2)_2]BPh_4$	yellow	1258

[a] Nujol mull.

cantly higher than that for the other four-coordinate complexes, in agreement with the greater π-acidity of phosphonite compared to phosphine ligands.

Other physical measurements (^{13}C and ^{31}P NMR) on these thiocarbonyl complexes and their carbonyl analogues are in progress.

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