Journal of Organometallic Chemistry, 333 (1987) C53–C56
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Hydrochalcogenide and hydride-hydrochalcogenide complexes of rhodium with the tripodal tetraphosphine pp_3

Massimo Di Vaira, Piero Stoppioni

Dipartimento di Chimica, Università die Firenze, Via Maragliano 77, 50144 Firenze (Italy)

and Maurizio Peruzzini

Istituto ISSECC, CNR, Via J. Nardi 39, 50132 Firenze (Italy)

(Received July 20th, 1987)

Abstract

The stable hydrochalcogenide $[(pp_3)Rh(XH)]$ complexes (pp_3 = tris(2-diphenylphosphinoethyl)phosphine; X = S (**1**), Se (**2**)) have been prepared by treatment of $[RhCl(cod)]_2$ with hydrochalcogenide solutions in the presence of pp_3. The two compounds react with CF_3SO_3H to yield the rare *cis*-hydride-hydrochalcogenide $[(pp_3)Rh(H)(XH)]CF_3SO_3$ compounds (X = S (**3**), Se (**4**)), which appear to be formed through an internal oxidative addition.

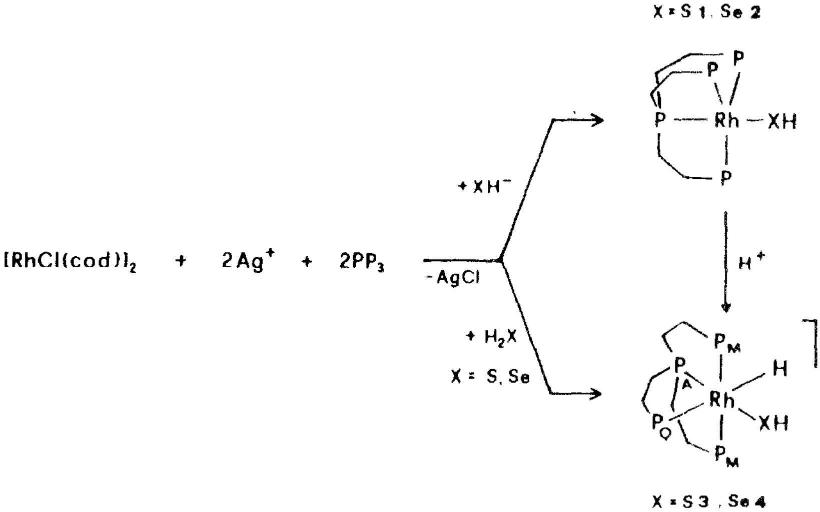
Much activity is currently devoted to the chemistry of H_2S and HS^- containing complexes [1], which form a class of compounds structurally related to metal sulphide hydrodesulfurization catalysts as well as to important biological systems [2]. Considerably less attention has been addressed to analogous compounds containing heavier chalcogens [3].

We describe here hydrochalcogenide rhodium complexes containing the tripodal polyphosphine tris(2-diphenylphosphinoethyl)phosphine, $P(CH_2CH_2PPh_2)_3$ (pp_3), as coligand and report on their reactions with some electrophilic reagents.

A THF solution of $[RhCl(cod)]_2$ (cod = 1,5-cyclooctadiene) was treated with the stoichiometric amount of $AgBF_4$ then filtered; a solution of pp_3 in dichloromethane and a clear ethanol solution obtained by reduction of the chalcogen (sulfur or selenium) with sodium tetrahydroborate were then added (Scheme 1). From the resulting solution the $[(pp_3)Rh(XH)]$ complexes (X = S (**1**), Se (**2**)) were obtained in good yields (ca. 75%) by reducing the volume of solvent under nitrogen.

The compounds, which gave satisfactory C, H, P, Rh and S or Se elemental analyses, were characterized by ^1H, ^{31}P NMR (Table 1) and infrared spectroscopy. The XH stretch occurs at 2540w (X = S) and 2360w cm^{-1} (X = Se). The ^1H hydrosulfide resonance is broad even at low temperature (ca. $-50\,^\circ C$); the corre-

0022-328X/87/$03.50



Scheme 1

Table 1

^1H [a] and $^{31}P\{^1H\}$ [b] NMR spectral data

Compound	^1H		^{31}P		
	δ	J	pattern	δ	J
1 [c]	−3.11 m (SH)		AM_3X	δ(A) 156.57 δ(M) 44.18	P_AP_M 17.2 P_ARh 110.3 P_MRh 148.8
2	−6.29 dq (SeH)	HP_A 5.0 HP_M 10.1	AM_3X	δ(A) 156.54 δ(M) 44.61	P_AP_M 17.6 P_ARh 114.6 P_MRh 148.1
3	−2.52 q (SH) −8.90 ddq(RhH)	HP 5.7 HP_Q 162.5 HP_M 10.0 HP_A 13.8 HRh 10.0	AM_2QX	δ(A) 140.51 δ(M) 42.59 δ(Q) 29.52	P_AP_M 5.8 P_AP_Q 5.8 P_MP_Q 17.2 P_ARh 88.7 P_MRh 100.0 P_QRh 84.5
4	−5.27 q (SeH) −9.25 ddq(RhH)	HP 6.2 HP_Q 156.6 HP_M 9.7 HP_A 14.2 HRh 9.7	AM_2QX	δ(A) 141.93 δ(M) 30.85 Δ(Q) 44.17	P_AP_M 5.4 P_AP_Q 5.4 P_MP_Q 16.9 P_ARh 91.3 P_MRh 99.0 P_QRh 85.3
5	1.94 s (SMe) −9.12 dm(RhH)	HP_{trans} 151.0	AM_2QX	δ(A) 137.54 δ(M) 43.00 δ(Q) 29.05	P_AP_M 6.8 P_AP_Q 6.8 P_MP_Q 17.3 P_ARh 87.6 P_MRh 99.1 P_QRh 85.0

[a] 80 MHz at room temperature. In ppm from external TMS. The signals from the hydrogen atoms of the pp_3 ligand are not reported. Coupling constants in Hz. Key: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. [b] 32.19 MHz at room temperature. In ppm from external H_3PO_4 85%; downfield values are assumed to be positive. Coupling constants in Hz. [c] At 220 K.

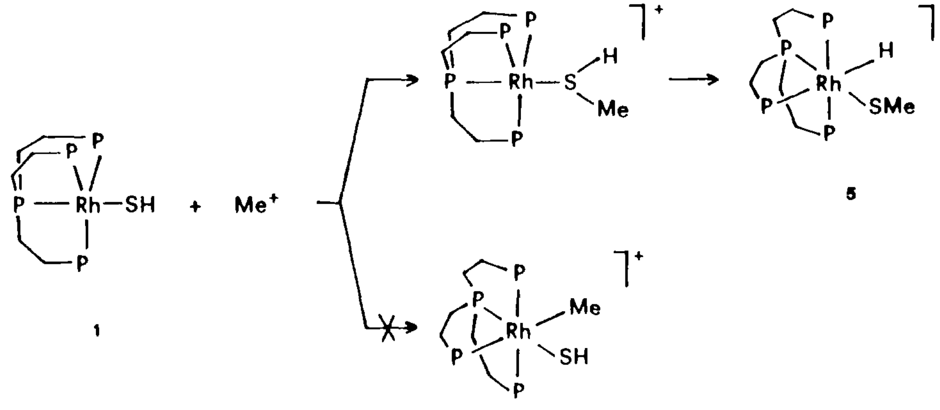
sponding signal for the selenium derivative exhibits fine structure due to coupling with the P atoms of the ligand. The $^{31}P\{^1H\}$ spectra of the two compounds are typical of an AM_3X system (A = apical phosphorus, M = peripheral phosphorus atoms of the pp_3 ligand; X = rhodium). The hydrochalcogenide compounds are accordingly assigned a trigonal bipyramidal geometry, with the three peripheral phosphorus atoms of the ligand in the equatorial plane, and the apical P donor and the chalcogen atom of the XH group in the axial positions.

Compounds **1** and **2** react in anhydrous THF at 0 °C with CF_3SO_3H to yield microcristalline compounds of formula $[(pp_3)Rh(H)(XH)]CF_3SO_3$ (X = S (**3**), Se (**4**)) (satisfactory C, H, P, Rh and S or Se elemental analyses); these were isolated in good yield (ca. 85%) after addition of benzene.

The RhH and XH stretching frequencies (**3**: RhH 2060m, SH 2560w cm^{-1}, **4**: RhH 2060m, SeH 2390w cm^{-1}) match the expected values. The ^{31}P data for **3** and **4** suggest an AM_2QX spin system (the labels are as in scheme 1). Such a system, which is also consistent with the ^1H data, points to a six-coordinate geometry for compounds **3** and **4**, the hydride and hydrochalcogenide being in *cis* positions (Scheme 1) [4 *].

The hydride-hydrochalcogenide derivatives **3** and **4** may also be obtained, although in lower yield (ca. 50%), through oxidative addition of the H_2X (X = S, Se) molecule to the $[(pp_3)Rh]^+$ fragment generated as described for the synthesis of compounds **1** and **2** (Scheme 1). In the light of this alternative synthesis, the electrophilic attack on **1** and **2** is considered to occur at the chalcogen atom of the XH group, yielding a pentacoordinate intermediate $[(pp_3)Rh(XH_2)]^+$, which is transformed into the final products apparently by internal oxidative addition involving splitting of the coordinated H_2X ligand.

The hydrosulfide derivative **1** in THF reacts with neat CF_3SO_3Me (Scheme 2) to yield the *cis* hydride-methylchalcogenide complex $[(pp_3)Rh(H)(SMe))]CF_3SO_5$ (**5**) as indicated by NMR data. This reaction provides further evidence for the intramolecular rearrangement to compounds **3** and **4**.



Scheme 2.

A reference number marked with an asterisk indicates a note in the list of references.

References

1 H. Vahrenkamp in A. Müller and B. Krebs (Eds.), Sulfur its Significance for Chemistry, for the Geo-, Bio- and Cosmosphere and Technology, Studies in Inorganic Chemistry, Vol. 5, p. 121–139, Elsevier, Amsterdam, 1984.

2 T.G. Spiro, Iron-Sulfur Proteins, Wiley, New York, 1982, p. 177; C. Verger and W.E. Newton (Eds.), Advances in Nitrogen Fixation Research, M. Nijhoff and W. Junk, The Hague, 1984.

3 H.J. Gysling, in S. Patai and Z. Rappoport (Eds.), The Chemistry of Organic Selenium and Tellurium Compounds, Vol. I, p. 679–855, John Wiley, New York, 1986.

4 ^{31}P NMR spectra without proton decoupling provide unequivocal information about the nature of the P atom lying *trans* to the hydride ligand in **4** and **5**.