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Preliminary communication

Formation of a dithiophosphinate rhodium(III) complex from the unstable three-membered ring species $[(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}PSPh_2)\overline{RhPh_2PS}]$. Crystal structure of $[(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}PSPh_2)\overline{RhPh_2SPS}]$

M.T. Pinillos, M.P. Jarauta, D. Carmona, L.A. Oro *

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-Consejo Superior de Investigaciones Cientificas, 5009 Zaragoza (Spain).

M.C. Apreda, C. Foces-Foces and F.H. Cano

Departamento de Rayos-X, Instituto Rocasolano, Consejo Superior de Investigaciones Cientificas, Serrano 119, 23006 Madrid (Spain).

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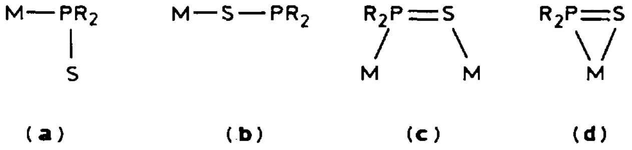
Abstract

The complex $[(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}PSPh_2)\overline{RhPh_2PS}]$ (**1**) has been prepared. The highly reactive three-membered ring $\overline{Rh\text{-}Ph_2PS}$ in **1** undergoes sulphur insertion to give the derivative $[(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}PSPh_2)\overline{RhPh_2SPS}]$ (**2**) containing the stable four-membered $\overline{RhPh_2SPS}$ ring. The structure of complex **2** has been determined by X-ray crystallography.

Deprotonated secondary phosphine sulfide (thiophosphinito) ligands R_2PS^- may coordinate end-on through phosphorus [1] or sulphur atom [2] (**a**,**b**), or bridge between two metal centres via the phosphorus and sulphur atoms [3,4] (**c**). Thewissen reported the first examples of side-on bonded Ph_2PS^- ligand for rhodium and iridium complexes [5] (**d**). The highly reactive three-membered ring $\overline{MPh_2PS}$ formed by this last mode of coordination (η^2-Ph_2PS) undergoes insertion reactions with activated alkynes [6]. This behaviour is analogous to that of η^2-hetero-allene complexes of rhodium. Such complexes with side-on coordinated isothiocyanates



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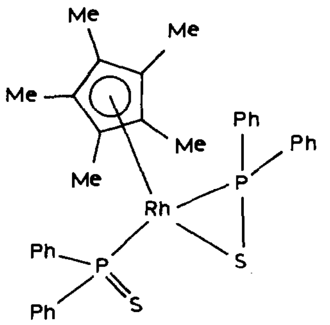

Fig. 1. Proposed structure for complex **1**.

(η^2-RNCS), easily obtained for the C=S fragment, undergo insertion reactions by attack of the carbon atom of a second RNCS molecule at the endocyclic nucleophile, and subsequent elimination of CNR, to give isocyanide-dithiocarbonimidato derivatives [7].

We describe here the synthesis of a mononuclear compound $[(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}PSPh_2)\overline{RhPh_2PS}]$ (**1**), that involves both a side-on and an end-on coordinated Ph_2PS^- ligand. This complex is converted into the rhodium(III) dithiophosphinate complex $[(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}PSPh_2)\overline{RhPh_2SPS}]$ (**2**) by sulphur insertion into the Rh–P bond of the unstable thiaphosphametallacyclopropene.

Addition of KOH in methanol to a methanolic solution of complex $[(\eta^5\text{-}C_5Me_5)RhCl(\mu\text{-}Cl)]_2$ a 2 molar proportion of $Ph_2P(S)H$, at room temperature resulted in precipitation of the orange crystalline complex **1** in 40% yield. The elemental analysis was consistent with the empirical formula $[RhC_{34}H_{35}S_2P_2]$, and the complex was monomeric in chloroform. The suggested formulation and coordination modes are strongly supported by the following spectroscopic observations; (i) a ^1H NMR pseudotriplet δ 1.42 ppm for the hydrogen atoms of the C_5Me_5 group [15 H, J(PH) 3.2 Hz]; (ii) two doublets of doublets in the ^{31}P NMR centered at $\delta(P_1)$ 54.8 ppm and $\delta(P_2)$ 49.88 ppm [$^1J(RhP_1)$ 142 Hz, $^1J(RhP_2)$ 120 Hz, $^2J(P_1P_2)$ 35 Hz]. The small value $^1J(RhP_2)$ of 120 Hz and the requirement of six coordination for the rhodium(III) center indicate the incorporation of P_2 into a three-membered ring system [5] (Fig. 1).

Interestingly, when a solution of **1** in methanol was left to stand for 24 h the complex was slowly converted into the dithiophosphinate complex **2**. The IR spectrum of **2** contains a medium band at ca. 590 cm^{-1} and a strong one at ca. 575 cm^{-1} characteristic of the bidentate $Ph_2PS_2^-$ ligand. The P=S stretching frequency of the unidentate group appears at ca. 630 cm^{-1}. In the ^1H NMR spectrum, coupling between the hydrogen atoms of the C_5Me_5 ring and only one phosphorus nucleus was detected [d, δ 1.42 ppm, J(PH) 3.2 Hz]. The ^{31}P NMR spectrum showed a doublet of doublets at ca. δ(P(1)) 63.2 ppm [^1J(RhP(1)) 128 Hz, ^3J(P(2)P(1)) 11 Hz]; and a pseudotriplet at δ(P(2)) 83 ppm [$^2J(RhP_2) = {}^3J(P(1)P(2)) = 11$ Hz]. These data are in accord with those found by Stephenson [8] for a rhodium(III) complex containing the (η^2-Ph_2PS_2) ligand.

These studies indicate that **1** is converted into **2** by an intermolecular process, and it may be seen as a nucleophilic attack on the endocyclic electrophile of the η^2-coordinated Ph_2PS^-, by a sulphur atom of the second molecule, as a result of

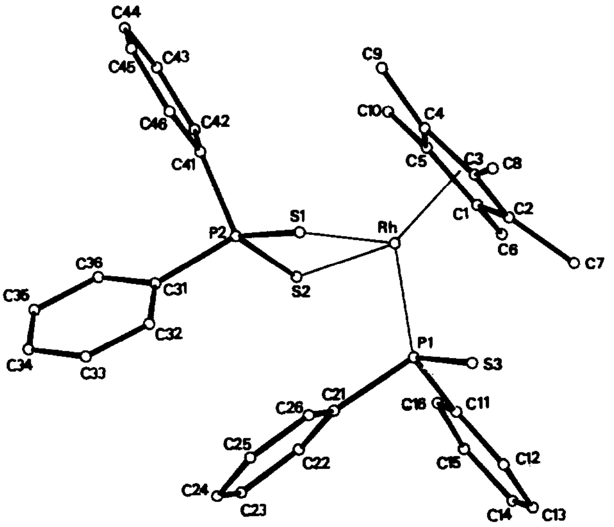

Fig. 2. The molecular structure of $[(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}PSPh_2)\overline{RhPh_2SPS}]$ (2). Bond lengths: Rh–P(1), 2.335(2); Rh–S(1), 2.421(1); Rh–S(2), 2.453(1); Rh–CT *, 1.852(3); P(1)–S(3), 1.993(2); P(1)–C(11), 1.838(6); P(1)–C(21), 1.841(6); P(2)–S(1), 2.006(2); P(2)–S(2), 2.011(2); P(2)–C(31), 1.807(5); P(2)–C(41), 1.808(5) Å; bond angles: C(31)–P(2)–C(41), 100.2(2); S(1)–P(2)–S(2), 105.3(1)°. (CT * is the centroid of the pentamethylcyclopentadienyl).

which the stable four-membered $\overline{RhPh_2SPS}$ ring structure is formed. The overall reaction can be regarded as a sulphur abstraction, in which the sulphur is transferred from one Ph_2PS molecule to another, yielding the dithiophosphinate ligand.

The structure * of the complex **2** was confirmed by X-ray diffraction with a crystal grown from methanol (Fig. 2). The coordination sphere of the rhodium atom consists of one pentamethylcyclopentadienyl group, one phosphorus atom of the bound thiophosphinito ligand, and two sulphur atoms of the bound diphenyldithiophosphinate group. The geometry about the rhodium atom is octahedral, with the centroid of the pentamethylcyclopentadienyl ring occupying the center of three octahedral sites.

The Rh–S distances are longer than those in other complexes containing Rh–S bonds [9]. The P(2)–S(i) ($i = 1,2$) distances of 2.006(2) and 2.011(2) Å differ by only 0.013 Å from that for the formally double bond P(1)–S(3) 1.993(2) Å. This is consistent with the delocalized P–S multiple-bond character expected in the dithiophosphinate ligand.

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* *Crystal Structure.* Data for $[(\eta^5\text{-}C_5Me_5)(\eta^1\text{-}PSPh_2)\overline{RhPh_2SPS}]$. $P2_1/c$, a 12.9530(3), b 12.6832(2), c 19.7813(7) Å, β 95.369(2)°, V 3235.5(2)Å^3, D_{cal} 1.447 g cm^{-3}, $Z = 4$, μ(Cu-K_α) 72.67 cm^{-1}. 4949 independent reflexions, 3890 were observed [$3\sigma(I)$ criterion], Philips PW1100 diffractometer up to 60° in θ. Patterson and direct methods. Refinement was carried out on F_0 with 2 blocks and anisotropic thermal parameters for the non-hydrogen atoms. The H atoms were kept isotropic. Empirical absorption was applied. Agreement factors: $R = 0.039$ and $R_w = 0.039$. A list of atomic coordinates and a complete table of bond angles and distances have been deposited with the the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lendsfield Road, Cambridge CB2 1EW.

The angles around the P atom reflect tetrahedral geometry, and it is noteworthy that the C(31)–P(2)–C(41) is smaller than the S(1)–P(2)–S(2) angle.

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