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Hydrochalcogenide and Hydride Hydrochalcogenide Derivatives of Rhodium

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By the reaction of hydrochalcogenide solutions with the $(pp_3)Rh$ cationic species [pp_3 = tris(2-(diphenylphosphino)ethyl)phosphine, $P(CH_2CH_2PPh_2)_3$] the hydrochalcogenide compounds $[(pp_3)RhXH]$ [X = S (**1**), Se (**2**), Te (**3**)] have been obtained. The crystal structures of **1**–**3** were elucidated through complete X-ray analyses. The isomorphous compounds **1**–**3** crystallize in the hexagonal $P6_3$ space group with $Z = 2$ and the following lattice constants. **1**: $a = 13.524$ (6), $c = 12.119$ (8) Å. **2**: $a = 13.542$ (6), $c = 12.188$ (7) Å. **3**: $a = 13.573$ (6), $c = 12.346$ (6) Å. In all complexes the metal atom exhibits a trigonal-bipyramidal coordination geometry with the three terminal phosphorus atoms of the ligand in the equatorial plane and the apical phosphorus atom of the same ligand and the chalcogen atom of the XH group in the axial positions. Complexes **1**–**3** react with CF_3SO_3H, yielding the rare hydride hydrochalcogenide compounds $[(pp_3)Rh(H)(XH)]CF_3SO_3$ [X = S (**5**), Se (**6**), Te (**7**)]. On the basis of their IR and NMR data, these are assigned an octahedral geometry with the hydride and hydrochalcogenide ligands in cis positions, the four P atoms of the pp_3 ligand occupying the remaining coordination sites. Compounds **5** and **6** are also obtained by reacting the $(pp_3)Rh$ cationic species with H_2X (X = S, Se). Complexes **1** and **2** react with $CF_3SO_3CH_3$, yielding the cis hydride methylchalcogenide derivatives $[(pp_3)Rh(H)(XCH_3)]CF_3SO_3$ [X = S (**8**), Se (**9**)]. The reactions prove that the electrophilic attack on hydrochalcogenide compounds **1**–**3** occurs on a lone pair of the chalcogen atom rather than on the sterically hindered metal center so that the final products are obtained through an "internal" oxidative addition.

Introduction

Metallothiols, the organometallic counterpart of mercaptans, are an expanding class of compounds characterized by the presence of the M–SH functional group.[1-27] There has been much interest in such derivatives, not only because they are structurally related to metal sulfide hydrodesulfurization catalysts[28] but also because they provide model compounds for biological systems[29] involved inter alia in nitrogen fixation and hydrogenation processes. Considerably less attention has been given to analogous compounds containing selenium[30] or, particularly, tellurium,[31] although increasing interest in their organometallic chemistry is to be expected in view of their potential use as sources of organoselenium and organotellurium compounds.[32] Further interest is provided by the opportunity to investigate possible changes in the reactivity of the M–XH functional group on changing the nature of the X chalcogen atom.

In the present paper we report on the synthesis and characterization of a family of hydrochalcogenide rhodium derivatives formed by the tripodal polyphosphine tris(2-(diphenylphosphino)ethyl)phosphine, pp_3, and describe their reactivity toward electrophiles. To the best of our knowledge, only few rhodium compounds containing the coordinating SH group have been described,[9-11a,33] while no SeH or TeH rhodium complexes have been reported so far. A preliminary account of part of this work has already been published.[34]

Experimental Section

General Data. All solvents were reagent grade and were appropriately dried and freed of molecular oxygen prior to use. The infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer using samples mulled in Nujol between KBr plates. NMR spectra were collected on Varian CFT20 and Varian VXR300 spectrometers operating at 80 and 300 MHz (^1H) and at 32.2 and 121.4 MHz (^{31}P). Phosphorus-31 positive chemical shifts are to high frequency relative to an 85% H_3PO_4 external standard at 0.0 ppm. Conductivity measurements were carried out with a WTW Model CBR/B conductivity bridge. The data were obtained at ca. 10^{-3} M sample concentrations in 1,2-dichloroethane solutions. Analytical data for carbon and hydrogen were obtained in the Microanalytical Laboratory of the Chemistry Department of the University of Florence with a Carlo Erba (Model 1106) elemental analyzer; rhodium, phosphorus, sulfur, selenium, and tellurium elemental analyses were performed by Mikroanalytisches Labor Pascher, Remagen, FRG. The ligand tris(2-(diphenylphosphino)ethyl)phosphine, pp_3 (Pressure), and the reagents H_2S (Matheson, CP grade), $NaBH_4$, $AgCF_3SO_3$, $(Bu_4N)BH_4$ (Fluka), sulfur, gray selenium, tellurium (Merck), CF_3SO_3H, $CF_3SO_3CH_3$ (Aldrich), and $Na_2S{\cdot}9H_2O$ (Carlo Erba) were used as received. H_2Se was generated from Al_2Se_3 (Strem). The complex $[RhCl(cod)]_2$ (cod = cycloocta-1,5-diene) was prepared according to the published procedure.[35]

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Synthesis of the Compounds. All manipulations were carried out under a purified nitrogen atmosphere with the use of standard Schlenk line techniques. All the complexes were collected on a sintered-glass frit, in a closed system, and washed with absolute ethanol (**1**–**3**) or benzene (**5**–**9**) and then petroleum ether (bp 40–70 °C) before being dried in a stream of nitrogen.

[(pp$_3$)RhSH] (1). A tetrahydrofuran solution (10 mL) of $AgCF_3SO_3$ (0.26 g, 1 mmol) was added to $[RhCl(cod)]_2$ (0.25 g, 0.5 mmol) in the same solvent (30 mL). The resulting mixture was stirred at 40–45 °C for 1 h and filtered to eliminate AgCl; pp$_3$ (0.67 g, 1 mmol) dissolved in tetrahydrofuran (20 mL) was added to the yellow filtrate to give a light red solution of [(pp$_3$)Rh(cod)]CF_3SO_3 (**4**), which was added of $Na_2S\cdot 9H_2O$ (0.24 g, 1 mmol) dissolved in ethanol (30 mL). Red crystals of **1** were obtained by adding ethanol and slowly concentrating the resulting solution. Yield: 85%. The same product was obtained by adding to **4** in tetrahydrofuran a hydrosulfide solution, which was prepared by reducing S_8 (0.03 g, 0.125 mmol) with $(NBu_4)BH_4$ (0.51 g, 2 mmol) in ethanol at room temperature. Anal. Calcd for [(pp$_3$)RhSH] (**1**), $C_{42}H_{43}P_4RhS$: C, 62.54; H, 5.37; P, 15.36; Rh, 12.76; S, 3.97. Found: C, 62.47; H, 5.41; P, 15.24; Rh, 12.68; S, 3.76.

Table I. Crystallographic Data for [(pp$_3$)RhSH] (**1**), [(pp$_3$)RhSeH] (**2**), and [(pp$_3$)RhTeH] (**3**)

	1	**2**	**3**
formula	$C_{42}H_{43}P_4RhS$	$C_{42}H_{43}P_4RhSe$	$C_{42}H_{43}P_4RhTe$
fw	806.67	853.57	902.21
cryst syst	hexagonal	hexagonal	hexagonal
space group	$P6_3$	$P6_3$	$P6_3$
a, Å	13.524 (6)	13.542 (6)	13.573 (6)
b, Å	13.524 (6)	13.542 (6)	13.573 (6)
c, Å	12.119 (8)	12.188 (7)	12.346 (6)
α, deg	90	90	90
β, deg	90	90	90
γ, deg	120	120	120
V, Å^3	1920 (2)	1936 (2)	1970 (2)
Z	2	2	2
d(calcd), g cm^{-3}	1.395	1.464	1.521
μ(Mo Kα), cm^{-1}	6.82	15.55	13.42
R^a	0.030	0.051	0.053
$R_w{}^b$	0.037	0.062	0.059

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

[(pp$_3$)RhSeH] (2). A clear hydroselenide solution, obtained by reducing at 45–50 °C a suspension of gray selenium (0.08 g, 1 mmol) in ethanol (30 mL) with $(NBu_4)BH_4$ (0.51 g, 2 mmol), was added to a solution of **4** (1 mmol) prepared as described above. Orange crystals of **2** were obtained after addition of ethanol (20 mL). Yield: 80%. Anal. Calcd for [(pp$_3$)RhSeH] (**2**), $C_{42}H_{43}P_4RhSe$: C, 59.10; H, 5.08; Rh, 12.06; Se, 9.25. Found: C, 59.00; H, 5.15; Rh, 11.87; Se, 9.12.

[(pp$_3$)RhTeH] (3). A hydrotelluride solution was prepared by addition of solid $NaBH_4$ (0.08 g, 2 mmol) to a suspension of tellurium (0.13 g, 1 mmol) in ethanol (30 mL). The resulting slurry was stirred at 60 °C for 1 h, this being necessary in order to consume the Te powder. The clear solution was added, while still hot, to **4** (1 mmol) in tetrahydrofuran (see above). Quick concentration in the dark yielded cherry red crystals of **3**. Yield: 60%. This compound slowly decomposes in the light even under an inert atmosphere; however, it can be stored for several months without apparent decomposition in the dark at −20 °C. Anal. Calcd for [(pp$_3$)RhTeH] (**3**), $C_{42}H_{43}P_4RhTe$: C, 55.91; H, 4.80; Rh, 11.41; Te, 14.14. Found: C, 55.84; H, 4.90; Rh, 11.35; Te, 14.03.

[(pp$_3$)Rh(H)(XH)]CF_3SO_3 [X = S (5), Se (6), Te (7)]. Neat CF_3SO_3H (0.6 mmol) was added to a suspension of [(pp$_3$)RhXH] (X = S, Se, Te) (0.5 mmol) in tetrahydrofuran (30 mL) at 0 °C with stirring. The parent complex dissolved within few minutes to yield a clear solution. The microcrystalline compounds **5**–**7** were obtained by adding a large excess of benzene (60 mL). The yields were typically ca. 80%. The tellurium derivative (**7**) decomposes in a few days even when it is stored in the dark at low temperature. Anal. Calcd for [(pp$_3$)Rh(H)(SH)]CF_3SO_3 (**5**), $C_{43}H_{44}F_3O_3P_4RhS_2$: C, 53.98; H, 4.64; Rh, 10.76; S, 6.70. Found: C, 53.86; H, 4.70; Rh, 10.65; S, 6.62. Calcd for [(pp$_3$)Rh(H)(SeH)]CF_3SO_3 (**6**), $C_{43}H_{44}F_3O_3P_4RhSSe$: C, 51.46; H, 4.42; P, 12.34; Se, 7.87. Found: C, 51.23; H, 4.47; P, 12.29; Se, 7.80. Calcd for [(pp$_3$)Rh(H)(TeH)]CF_3SO_3 (**7**), $C_{43}H_{44}F_3O_3P_4RhSTe$: C, 49.08; H, 4.21; P, 11.77; Te, 12.13. Found: C, 48.32; H, 4.15; P, 11.36; Te, 11.64.

Reactions of 4 with H_2X (X = S, Se). Gaseous hydrogen sulfide or selenide was bubbled into a cooled (0 °C) tetrahydrofuran solution (30 mL) of **4** (0.5 mmol) prepared as described above. The red color disappeared immediately to produce a colorless solution. After 5 min benzene was added and the solution was concentrated under a brisk current of nitrogen to yield pale green (**5**) or pale yellow (**6**) crystals. Yield: 60% (**5**), 50% (**6**).

[(pp$_3$)Rh(H)(XCH$_3$)]CF_3SO_3 [X = S (8), Se (9)]. Neat $CF_3SO_3CH_3$ (0.5 mmol) was added to a suspension of [(pp$_3$)RhXH] (0.5 mmol) in tetrahydrofuran (30 mL) at 0 °C. The parent compound dissolved in 30 min, and complexes **8** and **9** were obtained as light yellow crystals by addition of benzene (50 mL). Typical yield: 55%. Anal. Calcd for [(pp$_3$)Rh(H)(SCH$_3$)]CF_3SO_3 (**8**), $C_{44}H_{46}F_3O_3P_4RhS_2$: C, 54.44; H, 4.78; Rh, 10.60; S, 6.61. Found: C, 54.40; H, 4.81; Rh, 10.52; S, 6.45. Calcd for [(pp$_3$)Rh(H)(SeCH$_3$)]CF_3SO_3 (**9**), $C_{44}H_{46}F_3O_3P_4RhSSe$: C, 51.93; H, 4.56; Se, 7.76. Found: C, 51.84; H, 4.70; Se, 7.68.

X-ray Structural Determinations. Crystals of the isomorphous compounds **1**–**3** were in form of hexagonal prisms, those of **3** being however

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Table II. Positional Parameters and Equivalent Isotropic Thermal Parameters for [$(pp_3)RhSH$] (**1**)[a,b]

atom	x	y	z	U_{eq}, Å^2
Rh[c,d]	6667	3333	3000	33 (1)
S[c]	6667	3333	979 (3)	53 (1)
P(1)	6323 (1)	1478 (1)	3201 (1)	38 (1)
P(2)[c]	6667	3333	4814 (2)	44 (1)
C(1)	6623 (5)	1314 (5)	4665 (5)	59 (4)
C(2)	6148 (5)	1913 (5)	5381 (5)	59 (3)
C(11)	4842 (3)	289 (3)	3032 (6)	38 (2)
C(12)	4086 (4)	474 (4)	2419 (4)	44 (3)
C(13)	2964 (5)	−399 (5)	2282 (5)	53 (3)
C(14)	2586 (4)	−1430 (4)	2778 (5)	52 (3)
C(15)	3322 (4)	−1623 (4)	3405 (5)	53 (3)
C(16)	4450 (4)	−777 (4)	3529 (5)	47 (3)
C(21)	7064 (4)	878 (4)	2425 (5)	47 (3)
C(22)	7848 (4)	619 (4)	2903 (9)	67 (4)
C(23)	8419 (5)	203 (6)	2235 (10)	85 (6)
C(24)	8190 (6)	23 (6)	1139 (9)	86 (6)
C(25)	7419 (7)	275 (6)	656 (8)	82 (5)
C(26)	6868 (6)	695 (5)	1306 (6)	65 (4)

[a] In this and following tables of atomic parameters, coordinates are multiplied by 10^4 and temperature factors by 10^3; standard deviations on the least significant digit(s) are in parentheses. [b] The equivalent isotropic thermal parameter is defined as $(1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$. [c] Atom in special position, on a 3-fold axis. [d] z coordinate of Rh fixed during refinement (see text).

Table III. Positional Parameters and Isotropic Thermal Parameters for [$(pp_3)RhSeH$] (**2**)[a]

atom	x	y	z	U_{eq} or U, Å^2
Rh[b,c]	6667	3333	3000	41 (1)
Se[b]	6667	3333	916 (3)	64 (2)
P(1)	6311 (3)	1479 (3)	3185 (4)	48 (2)
P(2)[b]	6667	3333	4794 (5)	50 (3)
C(1)	6608 (13)	1337 (13)	4647 (13)	61 (4)
C(2)	6144 (12)	1928 (12)	5359 (14)	72 (5)
C(11)	4830 (7)	294 (5)	3008 (7)	45 (3)
C(12)	4084 (7)	495 (5)	2385 (7)	52 (4)
C(13)	2954 (7)	−367 (5)	2250 (7)	58 (4)
C(14)	2569 (7)	−1430 (5)	2737 (7)	57 (4)
C(15)	3315 (7)	−1631 (5)	3359 (7)	65 (4)
C(16)	4446 (7)	−769 (5)	3495 (7)	50 (3)
C(21)	7051 (7)	863 (8)	2416 (6)	48 (4)
C(22)	7842 (7)	623 (8)	2896 (6)	66 (4)
C(23)	8413 (7)	213 (8)	2255 (6)	63 (4)
C(24)	8192 (7)	43 (8)	1132 (6)	81 (5)
C(25)	7400 (7)	283 (8)	651 (6)	86 (5)
C(26)	6830 (7)	693 (8)	1293 (6)	69 (5)

[a] The isotropic temperature factor is of the form $\exp[-8\pi^2U(\sin^2\theta)/\lambda^2]$, and the equivalent isotropic thermal parameter is defined as $(1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$. [b] Atom in special position, on a 3-fold axis. [c] z coordinate of Rh fixed during refinement (see text).

Table IV. Positional Parameters and Isotropic Thermal Parameters for [$(pp_3)RhTeH$] (**3**)[a]

atom	x	y	z	U_{eq} or U, Å^2
Rh[b,c]	3333	6667	5000	35 (1)
Te[b]	3333	6667	7169 (2)	56 (2)
P(1)	4805 (4)	6281 (4)	4813 (4)	42 (3)
P(2)[b]	3333	6667	3223 (7)	55 (5)
C(1)	5227 (17)	6536 (17)	3390 (15)	60 (6)
C(2)	4183 (16)	6123 (16)	2658 (16)	63 (5)
C(11)	4491 (8)	4806 (9)	5048 (9)	41 (4)
C(12)	3541 (8)	4062 (9)	5658 (9)	49 (5)
C(13)	3278 (8)	2937 (9)	5804 (9)	53 (5)
C(14)	3965 (8)	2556 (9)	5341 (9)	52 (5)
C(15)	4915 (8)	3300 (9)	4731 (9)	60 (6)
C(16)	5177 (8)	4424 (9)	4585 (9)	49 (5)
C(21)	6166 (10)	7013 (10)	5610 (8)	46 (5)
C(22)	7180 (10)	7825 (10)	5129 (8)	53 (5)
C(23)	8164 (10)	8408 (10)	5753 (8)	54 (5)
C(24)	8143 (10)	8179 (10)	6858 (8)	65 (6)
C(25)	7119 (10)	7367 (10)	7339 (8)	81 (7)
C(26)	6135 (10)	6784 (10)	6715 (8)	59 (6)

[a] The isotropic temperature factor is of the form $\exp[-8\pi^2U(\sin^2\theta)/\lambda^2]$, and the equivalent isotropic thermal parameter is defined as $(1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$. [b] Atom in special position, on a 3-fold axis. [c] z coordinate of Rh fixed during refinement (see text).

Table V. Selected Bond Distances (Å) and Angles (deg) for [$(pp_3)RhSH$] (**1**), [$(pp_3)RhSeH$] (**2**), and [$(pp_3)RhTeH$] (**3**)[a–c]

	1	**2**	**3**
Rh–X	2.450 (3)	2.540 (3)	2.678 (3)
Rh–P(1)	2.326 (2)	2.320 (4)	2.316 (5)
Rh–P(2)	2.198 (3)	2.187 (7)	2.194 (8)
X–Rh–P(1)	96.0 (1)	95.6 (1)	95.7 (1)
P(1)–Rh–P(2)	84.0 (1)	84.4 (2)	84.3 (2)
P(1)–Rh–P(1)′	118.9 (1)	119.1 (2)	119.0 (2)

[a] X = S (**1**), Se (**2**), or Te (**3**). [b] The X–Rh–P(2) angle is constrained to 180° by symmetry; the X–Rh–P(1) and P(1)–Rh–P(2) angles are complementary to that value. [c] P(1)′ is related to P(1) through a 3-fold axis.

rather ill-formed. The crystals provided increasingly worse material for X-ray diffraction going from **1** to **3**; moreover that of **3** had to be coated with paraffin in order to prevent decomposition. Crystal data for the three compounds are given in Table I. A Philips PW 1100 diffractometer and graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) were used for all operations. Unit cell parameters were determined by least-squares refinement of the angular settings of 24 reflections in each case, having θ in the ranges 15–17° (**1**), 12–13° (**2**), and 12–13° (**3**). For **1** the $\pm h,\pm k,+l$ reflections (four forms, internal R = 0.027) were collected, whereas for **2** and **3** only the $+h,+k,+l$ form of the $6/m$ Laue class was collected. The intensities of three standard reflections, monitored periodically throughout the data collections, did not reveal any significant trends. Corrections for absorption were applied by a numerical procedure[36] for **1** and **2** [transmission coefficients 0.80–0.85 (**1**) and 0.52–0.61 (**2**)] and by an empirical procedure[37] for **3** (correction factor 0.80–1.20) in view of the ill-defined shape of the latter crystal. The principal computer programs used in the crystallographic calculations are given in refs 36–38.

The structure of compound **1** was solved by heavy-atom methods and refined by full-matrix least squares in which the function $\sum w(|F_o| - |F_c|)^2$ was minimized, with the weighting scheme $w = [\sigma^2(F_o) + gF_o^2]^{-1}$ [g = 0.0004 (**1**), 0.0007 (**2**), and 0.0005 (**3**)]. The structures of the isomorphous compounds **2** and **3** were refined by using as initial values for the atomic coordinates those from the structure of **1**. The asymmetric unit content corresponded to one-third of the chemical formula, with the Rh, chalcogen, and the central P atom of the phosphine ligand lying in special positions on a 3-fold axis. In each case the z coordinate of Rh was not allowed to refine, due to the polar nature of the space group. The correct enantiomorph was assigned for each structure on the basis of Hamilton's test[39] applied to the final model. The alternative choice of enantiomorph could be rejected in each case at the 0.005 level. The chirality of the crystal of compound **3** was found to be opposite to that of **1** and **2**. In the final refinement cycles on **1** all non-hydrogen atoms were assigned anisotropic temperature factors. Hydrogen atoms were introduced in calculated positions (C–H = 1.00 Å), each with a temperature factor ca. 20% larger than the equivalent isotropic temperature factor of the corresponding carbon atom. In the refinements on **2** and **3** only the Rh, Se (or Te), and P atoms were assigned anisotropic temperature factors, due to the worse quality and smaller number of data with respect to **1**; carbon atoms were refined isotropically, and phenyl groups were refined as rigid bodies. The H atom contributions were calculated as for **1**. The position of the XH hydrogen atom, which is probably affected by 3-fold disorder due to the location of the X atom on a 3 axis, could not be safely detected in any case from ΔF maps. The final R values were 0.030 (**1**), 0.051 (**2**), and 0.053 (**3**).

Scattering factors for the neutral atoms and the anomalous dispersion corrections for Rh, Se, and Te were taken from ref 40 Tables II–IV contain lists of atomic positional parameters and isotropic or equivalent

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(38) Johnson, C. K. *Oak Ridge Natl. Lab.* [*Rep.*] *ORNL* (*U.S.*) **1965**, *ORNL 3794*.

(39) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.

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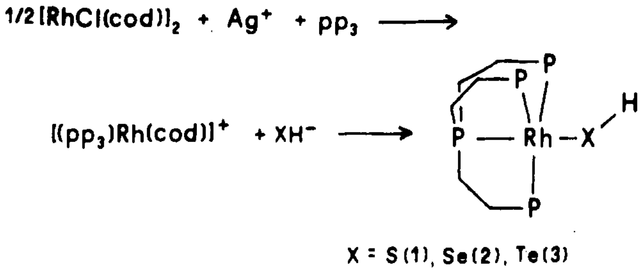
Scheme I



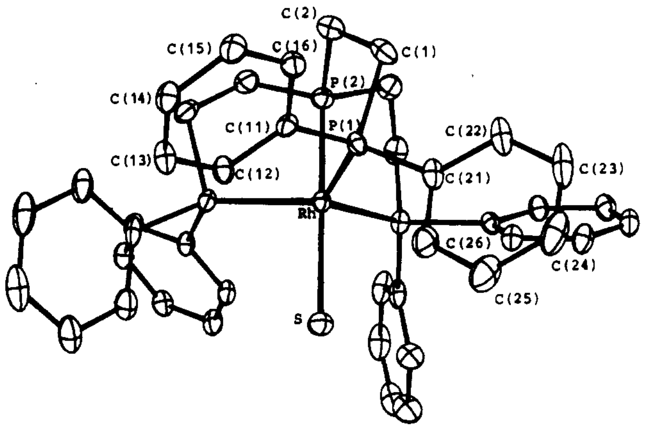


Figure 1. Perspective view of the [(pp$_3$)RhSH] molecule in **1**, with 20% probability ellipsoids. A 3-fold axis passes through the atoms S, Rh, and P(2). Only symmetry-independent atoms are labeled.

isotropic thermal parameters for **1**–**3**. Values of selected bond distances and angles for the three compounds appear in Table V. Available as supplementary material are details on data collections and structure refinements, lists of anisotropic thermal parameters for the three compounds, extended tables of bond distances and angles, lists of hydrogen atom coordinates, and tables of observed and calculated structure factors. (See paragraph at end of paper regarding supplementary material.)

Results

The transformations observed in this work are summarized in Schemes I and II. A structural study was undertaken for **1**–**3**, whose results are presented in Tables I–V and in Figure 1. The results are discussed in the appropriate sections that follow.

Discussion

Synthesis and Characterization of [(pp$_3$)RhXH][X = S (1), Se (2), Te (3)]. The hydrochalcogenide complexes **1**–**3** have been synthesized by reacting a tetrahydrofuran solution of [(pp$_3$)Rh(cod)]CF$_3$SO$_3$[41] (**4**) with different sources of hydrochalcogenides (Scheme I). Compounds **1** and **2** are obtained as air stable red-orange crystals, whereas **3** slowly decomposes, releasing tellurium, even under inert atmosphere when exposed to light. This behavior closely parallels that recently reported for (PPh$_4$)TeH, the only other well-characterized solid containing the TeH group, which instantly turns black on exposure to the air and darkens upon storage under nitrogen over several weeks.[42] The compounds **1**–**3**, which behave as nonelectrolytes in 1,2-dichloroethane, are obtained as analytically pure, diamagnetic crystals. They are sparingly soluble in chlorinated solvents, where they slowly decompose to form the known [(pp$_3$)RhCl] derivative.[43] The formation of the [(pp$_3$)RhXH] compounds from **4** is likely to occur via ligand (cod) replacement (Scheme I) by the hydrochalcogenide ligands. Complexes **1**–**3** have been fully characterized by means of IR and ^{1}H and ^{31}P NMR spectroscopies, as well as by X-ray structural determinations. Their infrared spectra (Table VI) show bands at 2540, 2260, and 1925 cm^{-1} for **1**, **2**, and **3**, respectively, which may be safely attributed to the stretching vibration of the XH group. Noticeably, while the SH and SeH absorptions have the expected low intensities,[44] the TeH stretching is characterized by a strong intensity. To the best of our knowledge, no TeH stretching vibration has been reported for the few hydrotelluride compounds described up to now;[31,45] in such complexes, containing carbon monoxide as coligand, the TeH band is probably masked by the strong carbonyl stretching vibrations. Highly diagnostic for the solution stereochemistry of the compounds are the ^{31}P{^{1}H} NMR spectra (Table VII), which consist of first-order AM$_3$X spin systems, in agreement with a trigonal-bipyramidal geometry around the metal. They exhibit two well-resolved resonances, each doubled by coupling to ^{103}Rh ($I = {}^1/_2$), having a 1:3 intensity ratio. The less intense signal, occurring at lower field and consisting of a doublet of quartets, is attributed to the apical phosphorus atom, P$_A$, of the tripodal tetraphosphine. The high-field signal, consisting of a doublet of doublets, is assigned to the resonance of the three equivalent terminal phosphorus atoms, P$_M$, lying in the equatorial plane of the trigonal bipyramid. Both the coupling constants and the chemical shifts are in the expected ranges for trigonal-bipyramidal compounds of Rh(I) with tripodal polyphosphines.[43,46] The proton spectra of compounds **1**–**3** exhibit in the high-field region resonances (Table VII) whose intensities, multiplicities, and chemical shifts are consistent with those expected for the SH, SeH, and TeH signals. The SH group yields a broad resonance at room temperature, which on lowering the temperature to −50 °C resolves into a quartet of doublets. The same multiplicity is exhibited at room temperature by the resonances of the hydroselenide and hydrotelluride groups, which occur at lower frequencies than that of the SH group. The observed multiplicity arises from coupling to the three equivalent phosphorus atoms of the pp$_3$ ligand and by additional coupling to the apical phosphorus atom of the polyphosphine. The residual coupling to rhodium is not observed; it is actually expected to be less than 1–2 Hz.[9] Within the series of the hydrochalcogenide complexes **1**–**3**, a high-field shift is observed on going from the hydrosulfide to the hydrotelluride derivative, in agreement with previous results.[19c,31a,d,47]

Table VI. Important Infrared Spectral Data (cm^{-1}) for the Complexes^a

no.	compd	ν(XH)	ν(RhH)
1	[(pp$_3$)RhSH]	2540 w	
2	[(pp$_3$)RhSeH]	2260 w	
3	[(pp$_3$)RhTeH]	1925 s	
5	[(pp$_3$)Rh(H)(SH)]CF$_3$SO$_3$	2560 w	2060 s, b
6	[(pp$_3$)Rh(H)(SeH)]CF$_3$SO$_3$	2295 s	2055 s, b
7	[(pp$_3$)Rh(H)(TeH)]CF$_3$SO$_3$	1930 w	2060 w, b
8	[(pp$_3$)Rh(H)(SCH$_3$)]CF$_3$SO$_3$		2030 s, b
9	[(pp$_3$)Rh(H)(SeCH$_3$)]CF$_3$SO$_3$		2040 w, b

^{a}Nujol mull. Key: w, weak; s, strong; b, broad.

The structures of the isomorphous compounds **1**–**3** consist of isolated [(pp$_3$)RhXH] molecules (Figure 1) that occupy sites of 3 symmetry, with the chalcogen, rhodium, and the central phosphorus atom of the pp$_3$ ligand lying on the 3-fold axis. The metal atom is in a trigonal-bipyramidal environment with the peripheral P atoms of the polydentate ligand in the equatorial plane

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[45] A broad absorbance centered near 1975 cm^{-1} has been assigned to the Te–H stretching mode in (PPh$_4$)TeH; see ref 41.

[46] (a) Di Vaira, M.; Peruzzini, M.; Zanobini, F.; Stoppioni, P. *Inorg. Chim. Acta* **1983**, *69*, 37. (b) Bianchini, C.; Meli, A.; Peruzzini, M.; Ramirez, J. A.; Vacca, A.; Vizza, F.; Zanobini, F. *Organometallics* **1989**, *8*, 337. (c) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Ramirez, J. A.; Vacca, A.; Zanobini, F. *Organometallics* **1989**, *8*, 2179. (d) Bianchini, C.; Meli, A.; Peruzzini, M.; Zanobini, F.; Zanello, P. *Organometallics* **1990**, *9*, 241. (e) Gambaro, J. J.; Hohman, W. H.; Meek, D. W. *Inorg. Chem.* **1989**, *28*, 4154.

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Scheme II

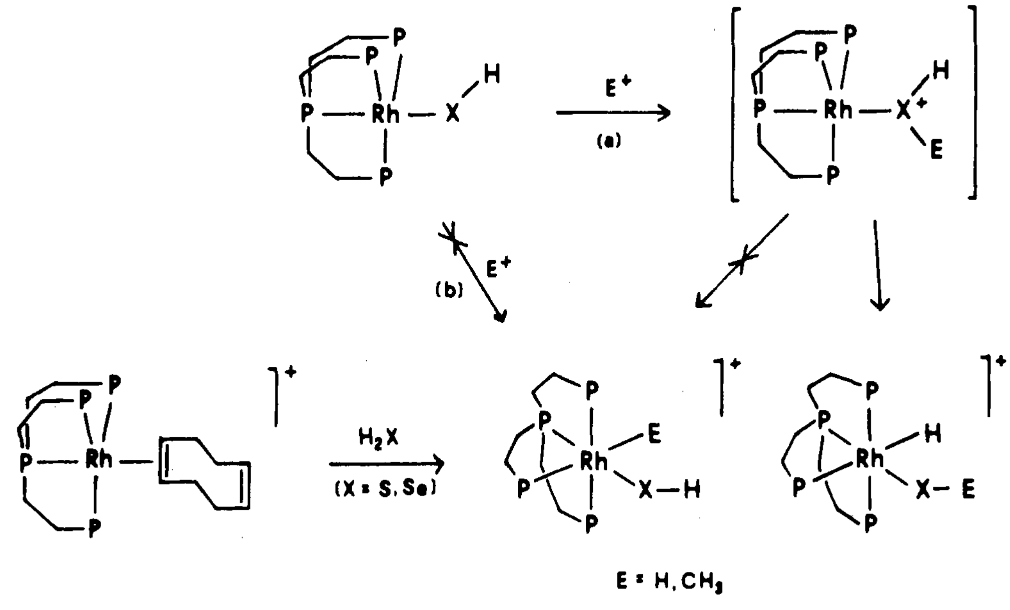

Table VII. NMR Spectral Data for the Complexes

		^{1}H^{a}			^{31}P{^{1}H}^{b}				
								coupling const^{d}	
compd	solvnt	chem shift (multiplicity)^{c}	assgnt	coupling const^{d}	pattern^{e}	chem shift^{f}	assgnt	J(PP)	J(PRh)
1^{g}	$CDCl_3$	−3.11 (dq)	SH	4.9, $^{3}J(HP_A)$	AM_3X	156.57	P_A	17.2	110.3 (P_ARh)
				10.8, $^{3}J(HP_M)$		44.18	P_M		148.8 (P_MRh)
2	CD_2Cl_2	−6.29 (dq)	SeH	5.0, $^{3}J(HP_A)$	AM_3X	156.54	P_A	17.6	114.6 (P_ARh)
				10.1, $^{3}J(HP_M)$		44.61	P_M		148.1 (P_MRh)
3	CD_2Cl_2	−13.13 (dq)	TeH	5.0, $^{3}J(HP_A)$	AM_3X	146.12	P_A	16.9	126.5 (P_ARh)
				12.9, $^{3}J(HP_M)$		39.78	P_M		147.5 (P_MRh)
5	$(CD_3)_2CO$	−2.52 (qu)	SH	5.7, $^{3}J(HP)$	AM_2QX	140.51	P_A	5.8 (P_AP_M)	88.7 (P_ARh)
		−8.90 (ddq)	RhH	162.5, $^{2}J(HP_Q)$		42.59	P_M	5.8 (P_AP_Q)	100.0 (P_MRh)
				10.0, $^{2}J(HP_M)$		29.52	P_Q	17.2 (P_MP_Q)	84.5 (P_QRh)
				13.8, $^{2}J(HP_A)$					
				10.0, $^{1}J(HRh)$					
6	$(CD_3)_2CO$	−5.27 (qu)	SeH	6.2, $^{3}J(HP)$	AM_2QX	141.93	P_A	5.1 (P_AP_M)	91.3 (P_ARh)
		−9.25 (ddq)	RhH	156.6, $^{2}J(HP_Q)$		44.17	P_M	5.6 (P_AP_Q)	99.0 (P_MRh)
				9.7, $^{2}J(HP_M)$		30.85	P_Q	16.9 (P_MP_Q)	85.3 (P_QRh)
				14.2, $^{2}J(HP_A)$					
				9.7, $^{1}J(HRh)$					
7^{h}	CD_2Cl_2	−9.12 (m)	TeH						
		−9.43 (dm)	RhH	≈145, $^{2}J(HP_Q)$					
8	$(CD_3)_2CO$	1.94 (s)	SMe		AM_2QX	137.54	P_A	6.8 (P_AP_M)	87.6 (P_ARh)
		−9.12 (ddq)	RhH	151.8, $^{2}J(HP_Q)$		43.00	P_M	6.8 (P_AP_Q)	99.1 (P_MRh)
				10.8, $^{2}J(HP_M)$		29.05	P_Q	17.3 (P_MP_Q)	85.0 (P_QRh)
				12.7, $^{2}J(HP_A)$					
				10.8, $^{1}J(HRh)$					
9	$CDCl_3$	1.19 (s)	SeMe		AM_2QX	136.38	P_A	5.7 (P_AP_M)	88.8 (P_ARh)
		−9.57 (ddq)	RhH	152.1, $^{2}J(HP_Q)$		43.89	P_M	7.8 (P_AP_Q)	100.9 (P_MRh)
				10.3, $^{2}J(HP_M)$		32.83	P_Q	16.8 (P_MP_Q)	85.3 (P_QRh)
				12.2, $^{2}J(HP_A)$					
				10.3, $^{1}J(HRh)$					

[a] All ^{1}H NMR spectra were recorded at 80 or 300 MHz at room temperature. The resonances due to the hydrogen atoms of the pp_3 ligand are not reported. [b] All the proton-decoupled ^{31}P NMR spectra were recorded at 32.19 or 121.42 MHz at room temperature, unless otherwise stated. [c] In ppm from external TMS. Key: s, singlet; d, doublet; q, quartet; qu, quintet; m, multiplet. [d] Coupling constants (J) are in Hz. [e] The letters A, M, and Q refer to the apical and terminal phosphorus atoms of the pp_3 ligand, respectively. X denotes the ^{103}Rh nucleus. [f] In ppm from external H_3PO_4 (85%); downfield values are assumed to be positive. [g] At 220 K. [h] The fast decomposition of **7** in solution (see text) with release of tellurium and formation of some paramagnetic impurities is responsible for the low-quality ^{1}H NMR spectra and has so far precluded satisfactory recording of ^{31}P NMR spectra.

and the central pp_3 phosphorus atom and the chalcogen atom in the axial positions. The metal is displaced by 0.24 (**1**), 0.22 (**2**), and 0.23 (**3**) Å from the equatorial plane toward the chalcogen atom. The corresponding Rh–P distances for the three compounds agree with each other and are in the range of values found for other rhodium compounds with phosphine ligands.[9,11a,48] The Rh–S distance in **1**, 2.450 (3) Å (Table V), is only slightly longer than that, 2.418 (3) Å, found for the compound [(CO)$(PPh_3)_2$RhSH].[9] The Rh–Se distance in **2**, 2.540 (3) Å, is close to those found for other compounds presenting Rh–Se interactions,[48,49] although the significance of comparisons is limited in this case by the absence of structures containing the SeH group

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as a ligand. The Rh–Te distance in **3**, 2.678 (3) Å, is in the range of those (2.56–2.72 Å) found for rhodium derivatives containing the Te_2 bridging unit.[50] It should be noted that the present Rh–Te distance is shorter, by 0.05 Å, than would be expected on consideration of the Rh–Se value and of the difference between the covalent radii of the Se and Te atoms,[51] a similar shortening being estimated by the same criterion for the present Rh–Se bond with respect to the Rh–S one.

Reactions of [(pp_3)RhXH] (X = S, Se, Te) Complexes with Electrophiles. (a) Synthesis and Characterization of Hydride Hydrochalcogenide Compounds. The chemical properties of the hydrochalcogenide group, XH, bonded to a metal–ligand moiety are markedly different from those of thiols, selenols, and tellurols, RXH, which contain the XH functional group bound to an organic fragment. In particular, an electron rich d^8-ML_4 metal fragment, like that employed in this work, is anticipated to increase the electron density on the chalcogen atom, which is expected to acquire distinct reactivity.[52] The reactions of hydrochalcogenides **1**–**3** with electrophilic organic reagents may accordingly provide excellent routes to the rare chalcogenol (RXH) and dihydrochalcogenide (H_2X) complexes. However, such reactions have not been widely documented and have been so far described only for the anionic $[W(CO)_5SH]^-$ and $[Fe(CO)_4SR]^-$ species,[16b,14] which upon electrophilic attack dimerize with loss of neutral ligand molecules. The present Rh(I) derivatives may yield alternative reactions with respect to those undergone by the above tungsten and iron anionic species. Indeed, the presence of the tripodal polyphosphine pp_3 favors smoother reactions at the metal center, as the ML_4 fragment may bring about, with a small conformational rearrangement, the interconversion from the C_{3v} to the C_{2v} geometry required for an overall octahedral arrangement about the metal atom.[43,46] The trigonal-bipyramidal hydrochalcogenide compounds [(pp_3)RhXH] contain two nucleophilic sites on their framework, namely the electron-rich Rh(I) center and the chalcogen atom of the XH group. Thus, at least in principle, two different sorts of reactions may occur with electrophiles. The first one would produce a cis octahedral Rh(III) complex through the addition of the electrophile (E^+) to the Rh(I) atom [(Scheme II(b)]. By contrast, the other route [Scheme II(a)] would give an intermediate trigonal bipyramidal species through direct attack on the chalcogen atom. Such a complex may be stable enough to be isolated, or it may transform through the oxidative-addition reaction of the XHE ligand, yielding octahedral Rh(III) species. Noticeably, if the E^+ electrophile is not H^+, the two final products of the oxidative-addition reaction (Scheme II) should be well recognizable from spectroscopic (IR, ^1H NMR) data.

With the aim of shedding some light on the factors governing these aspects of reactivity, we have investigated the reactions of hydrochalcogenide compounds **1**–**3** with the strong electrophilic reagents CF_3SO_3H and $CF_3SO_3CH_3$. The reaction of CF_3SO_3H with [(pp_3)RhXH] suspended in tetrahydrofuran or dissolved in dichloromethane produces a rapid fading of color from red-orange to pale yellow. Addition of benzene and concentration of the solution in a brisk stream of nitrogen yield microcrystalline products of formula [(pp_3)Rh(H)(XH)]CF_3SO_3 [X = S (**5**), Se (**6**), Te (**7**)] in good yield. Compounds **5** and **6** are stable under nitrogen and behave as 1:1 electrolytes in dichloroethane solution. They are soluble in polar organic solvents, where they quickly decompose when exposed to the air. The hydride hydrotelluride compound **7** quickly releases elemental tellurium in solution; such behavior greatly interferes with its characterization. Moreover, solid samples of **7** darken in a few days, even in a Schlenk tube at low temperature, yielding an intractable material. The formulation of these compounds as cis hydride hydrochalcogenide octahedral complexes is based on their infrared and NMR spectra (see Tables VI and VII) as well as on the elemental analyses (see the Experimental Section). The IR spectra of compounds **5**–**7** present a highly diagnostic RhH stretching vibration as well as the typical stretching frequencies for the uncoordinated $CF_3SO_3^-$ anion.[53] The XH stretching vibrations, although weak, are present at 2560, 2295, and 1930 cm^{-1} in the spectra of **5**–**7**, respectively. The $^{31}P\{^1H\}$ NMR spectra (Table VII), showing an AM_2QX spin system, are consistent with an approximate octahedral geometry for the complexes, with the hydride and the hydrochalcogenide groups in cis positions. The spectra consist of three groups of resonances (each signal is doubled by coupling to ^{103}Rh) whose intensity ratio is 1:2:1. The low-field resonance, consisting of a doublet of quartets, is assigned to the central P atom to the pp_3 ligand, P_A, that equally couples to the three cis phosphorus atoms (P_M and P_Q) of the tetradentate polyphosphine. The more intense high-field signal, assigned to the two phosphorus atoms, P_M, mutually trans in the octahedron, appears as two well-separated doublets of doublets due to coupling to the apical P atom, P_A, and to the residual terminal phosphorus atom, P_Q. The coupling constant to the latter nucleus, i.e. $J(P_M–P_Q)$, is assumed to be the larger one, as it results from interaction between P atoms belonging to different chelate rings.[54] The remaining high-field signal, attributed to the P_Q atom, appears as a doublet of triplets of doublets. Such a spin system originates from the coupling to the two mutually trans P_M atoms and to the apical P_A phosphorus atom. All of the $^{31}P\{^1H\}$ NMR parameters, which are listed in Table VII, are in good agreement with the literature data for transition-metal compounds containing the polyphosphine pp_3.[43,46,54a] The ^1H NMR spectra provide the conclusive evidence for the identity of the products. The spectra of the complexes are exceedingly similar, each consisting of the usual uninformative pattern due to the protons of the pp_3 ligand in both the aromatic and aliphatic regions and of two well-separated resonances in the high-field region. The lower frequency resonance in each spectrum may be assigned to the hydride ligand, as suggested both by the value of the chemical shift and by the large coupling constant [$J(H–P_{trans}) > 145$ Hz], which halves each signal into a well-separated doublet. Such couplings are typical of hydrogen atoms lying trans to a phosphine ligand.[43,55] The higher frequency signal is assigned to the hydrogen atom bound to the sulfur or selenium atom. It consists of a quintet, proving that the hydrogen of the XH group is equally coupled to the four phosphorus atoms of the pp_3 ligand, irrespective of their nature and position in the coordination polyhedron. The hydride hydrotelluride compound **7** does not yield good-quality spectra due to decomposition. However, the presence of three unresolved multiplets in the high-field region of the proton spectrum, two of which are separated by ca. 145 Hz, is consistent with its formulation as the tellurium analogue of **5** and **6**. The hydrochalcogenide resonance exhibits a significant downfield shift, which increases on going from compound **1**, **2**, or **3**, respectively, to **5**, **6**, or **7**. Such a trend is in agreement with the change in the oxidation number of the metal between the two sets of compounds and with the decrease in electronegativity of the chalcogen atom on going from S to Te.

Compounds **5** and **6** are also obtained, although in a lower yield, by bubbling H_2S or H_2Se into an ice-cooled tetrahydrofuran solution of **4**. In such reactions the displacement of the cycloocta-1,5-diene ligand by H_2X (X = S, Se) is thought to generate the highly reactive [$(pp_3)Rh(XH_2)$]$^+$ cations, which promote the oxidative addition of the acidic X–H bond to yield the hydride hydrochalcogenide derivatives **5** and **6**. These reactions provide indirect confirmatory evidence for the nature of compounds **5** and **6** and agree with the well-established tendency of d^8-ML_4 fragments (M = Rh, Ir) to promote oxidative additions with organic and inorganic molecules, including thiols and hydrogen sulfide.[10–12,33] Interestingly, the electrophilic addition of H^+ to the

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trigonal-bipyramidal complexes [(pp$_3$)RhXH] is highly stereospecific. In fact, the hydride ligand is located trans to a terminal phosphorus atom, P_Q, rather than to the bridgehead phosphorus atom P_A. In the absence of X-ray structure determinations, this is nevertheless unequivocally demonstrated by ^{31}P proton-coupled NMR spectra.[43,46] Indeed, whereas the P_A resonance is only broadened by coupling to the proton nuclei, the P_Q signal is resolved into two distinct broad resonances. The large coupling constant between these two signals closely approaches the $J(H-P_{trans})$ value found for the hydride resonance in ^1H NMR spectra.

(b) Reactions of 1 and 2 with $CF_3SO_3CH_3$. As mentioned above, compounds **5**–**7** might form either by direct protonation of the rhodium atom [Scheme II(b)] or through a cationic intermediate [Scheme II(a)], which evolves to the final product, via "internal" oxidative addition. Unfortunately, deuterium-labeled experiments with CF_3COOD failed to elucidate the mechanism because the added deuterium atom equilibrates between the two sites, at the rhodium or at the chalcogen atom. Such behavior has already been observed for cis hydride sulfide complexes of ruthenium and platinum.[4b,30a] In order to understand the mechanism of protonation, the reactions of the hydrosulfide and hydroselenide derivatives **1** and **2** with the methyl ester of the triflic acid were studied. The reactions of [(pp$_3$)RhXH] (X = S, Se) with the stoichiometric amount of $CF_3SO_3CH_3$ in dichloromethane solution yielded, after addition of benzene, pale yellow microcrystalline products. Elemental analyses and chemical–physical measurements support their formulation as hydride methylchalcogenide compounds of formula [(pp$_3$)Rh(H)(XCH$_3$)]CF$_3$SO$_3$ [X = S (**8**), Se (**9**)]. The IR and ^1H NMR data clearly indicate that they contain the hydride and the methylchalcogenide groups. In particular, the IR spectra do not show any absorbance in the XH region, whereas they show an RhH stretching vibration at ca. 2000 cm^{-1} (Table VI). The proton NMR spectra of the two derivatives are similar and exhibit resonances that can be attributed, according to their intensities and chemical shifts, to hydride hydrogen atoms [$\delta = -9.12$ (**8**), $\delta = -9.57$ (**9**); $J(H-P_{trans}) = 152.0$ Hz], while no signal ascribable to hydrochalcogenide protons is observed. Resonances at 1.94 and 1.19 ppm in the spectra of **8** and **9**, respectively, may be assigned to the CH_3 bound to the S or Se atom. These results rule out a direct attack of CH_3^+ at the sterically hindered rhodium, which would preserve the hydrosulfide group. On the other hand, they provide evidence for the initial attack of CH_3^+ at the more nucleophilic chalcogen atom to form the trigonal-bipyramidal [(pp$_3$)Rh(HXCH$_3$)]$^+$ cation, which converts to the cis hydride methylsulfide or methylselenide complex by X–H internal oxidative addition of the CH_3XH ligand. Occurrence of the oxidative addition for the X–H rather than the X–CH_3 bond is in accordance with the smaller X–H bond energy, compared to the X–CH_3 one.[56]

In conclusion, on the basis of our present data and in consistency with other recent results,[14] we propose that the electrophilic attack on hydrochalcogenide complexes occurs on a lone pair of the chalcogen atom rather than on the less electronegative and sterically hindered metal center.

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Supplementary Material Available: Full details of the crystal data and crystallographic data collections (Table SI), thermal parameters for **1**–**3** (Table SII), bond distances and angles for compound **1** (Table SIII) and for compounds **2** and **3** (Table SIV), and hydrogen atom coordinates (Table SV) for the three compounds (7 pages); listings of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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Cluster Synthesis. 30. New Platinum–Osmium Carbonyl Cluster Complexes from the Reaction of $Os_3(CO)_{10}(NCMe)_2$ with $Pt(COD)_2$

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Two new platinum–osmium carbonyl cluster complexes, $Pt_2Os_3(CO)_{10}(COD)_2$ (**1**) and $PtOs_3(CO)_8(COD)(\mu\text{-}C_8H_{11})(\mu\text{-}H)$ (**2**), were obtained in yields of 18% and 4%, respectively, from the reaction of $Os_3(CO)_{10}(NCMe)_2$ with $Pt(COD)_2$ at 25 °C. Both products were characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. Compound **1** contains a tetrahedral Pt_2Os_2 cluster with an $Os(CO)_4$ group bridging the Os–Os edge. Compound **2** contains a tetrahedral $PtOs_3$ cluster with a COD ligand activated at one of the olefin C–H bonds bridging an Os–Os edge of the cluster. Compound **1** is formally electron deficient and readily reacts with CO at 25 °C/1 atm to yield a series of two products, $Pt_2Os_3(CO)_{14}$ (**3**) and the known complex $PtOs_2(CO)_{10}$ (**4**). **3** and **4** were both characterized by single-crystal X-ray diffraction analyses. Compound **3** contains two structurally similar but symmetry-independent molecules in the crystal. Both molecules contain planar clusters of five metal atoms, with a "truncated raft" structure. Compound **4** contains a triangle of one platinum and two osmium atoms. Compound **3** reacts with $Os(CO)_5$ to form the known compound $Pt_2Os_4(CO)_{18}$ (**5**) in 92% yield. Crystal data: for **1**, space group *Pnma*, $a = 11.559$ (2) Å, $b = 14.984$ (2) Å, $c = 17.222$ (4) Å, $R = 0.037$ for 1891 reflections; for **2**, space group $P2_1/c$, $a = 10.433$ (2) Å, $b = 10.066$ (2) Å, c = 24.976 (3) Å, $\beta = 92.52$ (1)°, $R = 0.028$ for 2825 reflections; for **3**, space group $P2_1/c$, $a = 14.895$ (3) Å, $b = 12.060$ (2) Å, $c = 25.615$ (3) Å, $\beta = 92.87$ (1)°, $R = 0.040$ for 2740 reflections; for **4**, space group $P\bar{1}$, $a = 8.997$ (3) Å, $b = 12.888$ (3) Å, $c = 7.082$ (2) Å, $\alpha = 98.52$ (2)°, $\beta = 105.61$ (2)°, $\gamma = 81.51$ (2)°, $R = 0.034$ for 2051 reflections.

Introduction

The superior properties of platinum alloy re-forming catalysts have led to their widespread utilization by the petroleum industry.[1] Hopes of learning more about the bifunctional reactivity of these catalysts have generated a great interest in the chemistry of heteronuclear cluster complexes containing platinum.[2] We have recently found that interesting new heteronuclear cluster complexes containing platinum are readily obtained from the reactions of $Pt(COD)_2$ (COD = 1,5-cyclooctadiene) with the pentacarbonyl

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