Unusual Dinuclear Hydridorhodium(III) Complexes Containing Bulky Phosphanyl(stibanyl)methanes as Chelating Ligands☆

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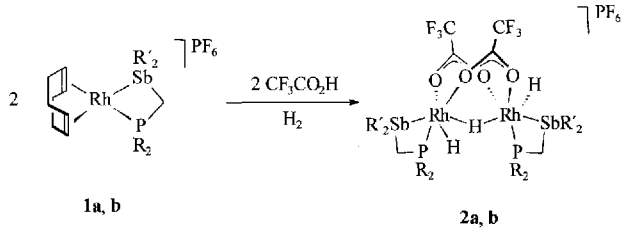
The mononuclear starting materials $[Rh(\eta^4\text{-}C_8H_{12})(\kappa^2\text{-}P,Sb\text{-}i Pr_2PCH_2SbR_2)]PF_6$ (**1a**, **b**) react with CF_3CO_2H in the presence of H_2 to give the dinuclear hydridorhodium(III) complexes $[\{RhH(\kappa^2\text{-}P,Sb\text{-}i Pr_2PCH_2SbR_2)\}_2(\mu\text{-}H)(\mu\text{-}O_2CCF_3)_2]PF_6$ (**2a**, **b**) in almost quantitative yield. The X-ray crystal structural analysis of **2b** (R = *t*Bu) reveals a distorted octahedral geometry around the two metal centers with the two phosphanyl(stibanyl)methanes in a chelating and the two trifluoracetate ligands in a bridging coordination mode.

In our quest for new unsymmetrical (possibly hemilabile) chelating ligands, we recently reported the synthesis of phosphanyl(stibanyl)methanes $R_2PCH_2SbR'_2$ with bulky alkyl or cycloalkyl groups R and R'.[1] Depending on the reaction conditions, these ligands react with $[C_8H_{12}RhCl]_2$ to give either neutral compounds $[RhCl(\eta^4\text{-}C_8H_{12})(\kappa\text{-}P\text{-}R_2PCH_2SbR'_2)]$ or related cationic derivatives $[Rh(\eta^4\text{-}C_8H_{12})(\kappa^2\text{-}P,Sb\text{-}R_2PCH_2SbR'_2)]X$. For $X = BPh_4$, the latter affords, in the presence of H_2, the half-sandwich type complexes $[(\eta^6\text{-}C_6H_5BPh_3)Rh(\kappa^2\text{-}P,Sb\text{-}R_2PCH_2SbR'_2)]$, in which the tetraphenyloborate is coordinated like a substituted arene to the metal center.[1][2]

In order to broaden the chemistry of rhodium compounds with phosphanyl(stibanyl)methanes as ligands, we also attempted to prepare carboxylato complexes $[Rh(\eta^2\text{-}O_2CR)(\kappa^2\text{-}P,Sb\text{-}R_2PCH_2SbR'_2)]$ or the corresponding dimers from the cationic species $[Rh(\eta^4\text{-}C_8H_{12})(\kappa^2\text{-}P,Sb\text{-}R_2PCH_2SbR'_2)]X$ and RCO_2H. We anticipated that under H_2 the diolefin would be hydrogenated and finally displaced by the carboxylato anion.

However, the reaction of **1a**, **b** (Scheme 1) with CF_3CO_2H proceeds in a somewhat different way. Both substrates react quite rapidly, in the presence of H_2 and in the molar ratio 1:3, to give yellow air-stable products **2a**, **b** in nearly quantitative yield. Both compounds are thermally unstable (**2a** less than **2b**) and also slowly decompose in solution (THF, CH_2Cl_2). While the IR and ^{19}F-NMR spectra of **2a**, **b** confirm that in agreement with the assumed composition one (or two) CF_3CO_2 unit(s) are coordinated to the rhodium center, the ^1H-NMR spectra unexpectedly reveal the presence of two types of metal-bonded hydrido ligands. The signal at $\delta = -18.45$ (for **2a**) or -18.41 (for **2b**) is split into a doublet of doublets due to coupling with one ^{31}P and one ^{103}Rh nucleus, and is assigned to a terminal RhH unit. The second resonance (with half the intensity of the first one) at $\delta = -17.00$ (for **2a**) and -16.55 (for **2b**) appears as a triplet of triplets with a rather large Rh-H coupling of ca. 27 Hz. The latter is typical for a bridging RhHRh moiety.[3] The CH_3 protons of the isopropyl groups at the phosphorus atom display four doublets of equal intensity (6:6:6:6) in the $^1H\{^{31}P\}$-NMR spectrum while those of the isopropyl groups at the antimony atom (in **2a**) give rise to three doublets in the ratio 6:6:12. For the protons of the *tert*-butyl groups of **2b** two singlets of equal intensity are observed. The chemical shift of the CH_3 resonances as well as that of the signal assigned to the PCH_2Sb protons is almost identical to that of the starting materials **1a**, **b** indicating that the coordination mode of the phosphanyl(stibanyl)methanes is unchanged.

Scheme 1. R = R' = *i*Pr: **a**; R = *i*Pr, R' = *t*Bu: **b**



The result of the X-ray crystal structure analysis of **2b** is shown in Figure 1. The geometry around both metal centers is distorted octahedral with two oxygen atoms of the bridging trifluoracetates, the phosphorus and the antimony atoms, the terminal and the bridging hydride occupying the six coordination sites. On each rhodium center, one oxygen atom is *trans*-disposed to the phosphorus atom and the other to the terminal hydride. The dinuclear cation possesses C_2 symmetry, the rotational axis lying between the [O,C,O] planes and passing through the hydrogen atom H(3). The Sb–Rh–Rh–Sb unit is nearly linear with Sb–Rh distances that are almost identical to the Sb–Rh bond length of **1b** [2.5876(5) Å].[1] The distance Rh(1)–Rh(2) [2.955(2) Å] is significantly larger than in the structurally related dinuclear hydridorhodium cations

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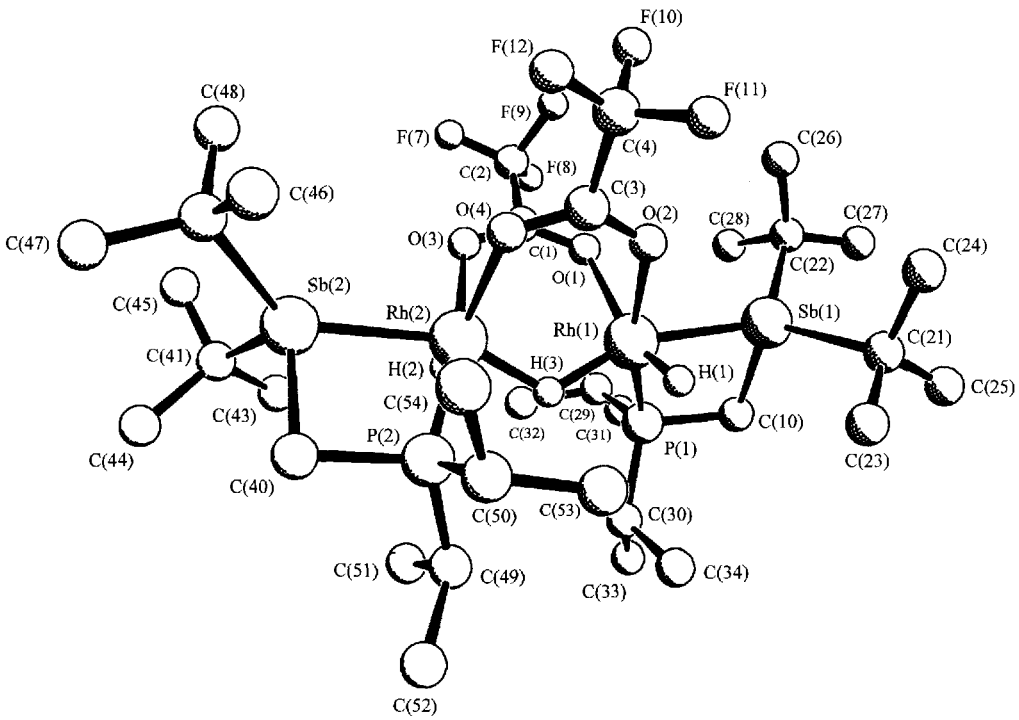
Figure 1. Molecular structure of **2b**[a]



[a] Selected bond lengths [Å] and angles [°]: Rh(1)–Rh(2) 2.955(2), Rh(1)–P(1) 2.244(4), Rh(1)–Sb(1) 2.533(2), Rh(2)–P(2) 2.229(4), Rh(2)–Sb(2) 2.583(2), P(1)–C(10) 1.83(2), Sb(1)–C(10) 2.16(2), P(2)–C(40) 1.84(2), Sb(2)–C(40) 2.17(2), Rh(1)–O(1) 2.21(1), Rh(1)–O(2) 2.16(1), Rh(2)–O(3) 2.17(1), Rh(2)–O(4) 2.218(9), O(1)–O(3) 2.2372(5), O(2)–O(4) 2.2224(5); P(1)–Rh(1)–Sb(1) 75.7(1), P(2)–Rh(2)–Sb(2) 75.9(1), P(1)–C(10)–Sb(1) 94.5(6), P(2)–C(40)–Sb(2) 95.4(7), P(1)–Rh(1)–O(1) 98.5(3), P(1)–Rh(1)–O(2) 168.0(3), P(2)–Rh(2)–O(3) 171.0(3), P(2)–Rh(2)–O(4) 100.6(3), Sb(1)–Rh(1)–O(1) 95.2(2), Sb(1)–Rh(1)–O(2) 92.7(3), Sb(2)–Rh(2)–O(3) 96.0(3), Sb(2)–Rh(2)–O(4) 96.5(2), Sb(1)–Rh(1)–Rh(2) 171.52(5), Sb(2)–Rh(2)–Rh(1) 175.82(5), O(1)–Rh(1)–O(2) 85.3(4), O(3)–Rh(2)–O(4) 83.9(4).

$[\{RhH(\kappa^2\text{-}P,P\text{-}i Pr_2P(CH_2)_3P i Pr_2)\}_2(\mu\text{-}H)_2(\mu\text{-}O,O\text{-}ClO_4)]^+$ [2.617(1) Å][4] and $[Rh_2(CO)_2(\mu\text{-}P,P\text{-}Ph_2PCH_2PPh_2)_2(\mu\text{-}H)(\mu\text{-}CO)]^+$ [2.731(2) Å],[5] where a rhodium–rhodium single bond is assumed. However, in these cations the oxidation number of Rh is +2 instead of +3 as in **2b**. With regard to the Rh(1)–H(3)–Rh(2) three-center two-electron bond, a similar situation is found in the neutral dinuclear complex $[\{(\eta^5\text{-}C_5Me_5)RhCl\}_2(\mu\text{-}Cl)(\mu\text{-}H)]$ where the Rh–Rh distance is 2.906(1) Å.[6] In this case, a weak metal-metal interaction has been discussed.[6] The bond angles in the RhPCSb chelates and in the bridging RhOCORh systems are almost the same as in the mononuclear compound **1b** or in dinuclear $Rh_2(\mu\text{-}O_2CCH_3)_2$ complexes[7] and need no further comments.

The problem of why the anticipated carboxylato complexes $[Rh(\eta^2\text{-}O_2CCF_3)(\kappa^2\text{-}P,Sb\text{-}R_2PCH_2SbR'_2)]$ or $[\{Rh(\kappa^2\text{-}P,Sb\text{-}R_2PCH_2SbR'_2)\}_2(\mu\text{-}O_2CCF_3)_2]$ are not obtained from **1a**, **b**, CF_3CO_2H, and H_2 is not clear. We assume that in the initial step of the reaction, the cyclooctadiene ligand of **1a**, **b** is hydrogenated and a mononuclear, probably solvated dihydridorhodium(III) cation $[RhH_2(\kappa^2\text{-}P,Sb\text{-}R_2PCH_2SbR'_2)]^+$ is generated. Upon attack of the carboxylic acid, another cationic intermediate $[RhH(\eta^2\text{-}O_2CCF_3)(\kappa^2\text{-}P,Sb\text{-}R_2PCH_2SbR'_2)]^+$ could be formed which by dimerization, addition of H_2 and deprotonation should yield the final product. It is worth mentioning that on treatment of **1a**, **b** with acetic acid in the presence of H_2 complete decomposition occurs and no hydridorhodium complex containing $iPr_2PCH_2SbR_2$ as ligand can be isolated.

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Experimental Section

All operations were carried out under argon using Schlenk techniques. The starting materials **1a** and **1b** were prepared as described in the literature.[1] – IR: Perkin-Elmer 1420. – NMR: Bruker AMX 400.

1. *Preparation of* $[\{RhH(\kappa^2\text{-}P,Sb\text{-}iPr_2PCH_2SbiPr_2)\}_2(\mu\text{-}H)(\mu\text{-}O_2CCF_3)_2]PF_6$ (**2a**): A solution of 89 mg (0.13 mmol) of **1a** in 6 ml of CH_2Cl_2 was treated with 30 µl (0.39 mmol) of CF_3CO_2H and then stirred under H_2 (1.0 bar) for 10 min at room temp. A change of color from orange-red to yellow occurred. After removal of the solvent in vacuo, an oily residue was obtained which upon treatment with 10 ml of ether (twice) and 5 ml of pentane (twice) gave a yellow, almost air-stable solid; yield 71 mg (88%); dec. temp. 52°C. – IR (CH_2Cl_2): $\tilde{\nu}$ = 2100 cm^{-1} [ν(RhH)], 1670 [$\nu(OCO)_{asym}$], 1460 [$\nu(OCO)_{sym}$], 1200, 1150 [ν(CF)]. – ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 2.99, 2.80 [2 sept, J(HH) = 7.2 Hz, 2 H each, $SbCHCH_3$], 2.68 [br. d, J(PH) = 9.2 Hz, 4 H, PCH_2Sb], 2.19, 1.94 (2 m, 4 H each, $PCHCH_3$), 1.56, 1.55 [2 d, J(HH) = 7.2 Hz,

6 H each, $SbCHC\mathit{H}_3$], 1.48 [d, J(HH) = 7.2 Hz, 12 H, $SbCHC\mathit{H}_3$], 1.37–1.13 (br. m, 24 H, $PCHC\mathit{H}_3$), −17.00 [tt, J(RhH) = 26.5, J(PH) = 10.7 Hz, 1 H, Rh–H–Rh], −18.45 [dd, J(RhH) = 13.7, J(PH) = 24.4 Hz, 2 H, RhH]. – ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 169.1 [q, J(FC) = 37.6 Hz, $O_2\mathit{C}CF_3$], 115.9 [q, J(FC) = 281.8 Hz, CF_3], 28.9 [d, J(PC) = 26.8 Hz, $PCHCH_3$], 26.4 [d, J(PC) = 24.2 Hz, $PCHCH_3$], 25.6, 23.2 (2 s, $SbCHCH_3$), 22.2, 21.8, 21.4 (3 s, $SbCHCH_3$), 20.1, 17.2, 17.1 (3 s, $PCHCH_3$), 16.8 [d, J(PC) = 5.0 Hz, $PCHCH_3$], 14.9 [dd, J(RhC) = 1.9, J(PC) = 19.1 Hz, PCH_2Sb]. – ^{19}F NMR (188.3 MHz, CD_2Cl_2): δ = −73.4 [d, J(PF) = 710.6 Hz, PF_6^-], −75.4 (s, CF_3). – ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ = 46.1 [d, J(RhP) = 110.8 Hz, $i\mathrm{Pr}_2\mathrm{P}$], −144.0 [sept, J(FP) = 710.6 Hz, PF_6^-]. – $C_{30}H_{63}F_{12}P_3Rh_2Sb_2$ (1258.0): calcd. C 28.64, H 5.05; found C 29.01, H 5.18.

2. *Preparation of* $[\{RhH(\kappa^2\text{-}P,Sb\text{-}i\mathrm{Pr}_2PCH_2SbtBu_2)\}_2(\mu\text{-}H)(\mu\text{-}O_2CCF_3)_2]PF_6$ (**2b**): Analogously as described for **2a**, from 127 mg (0.17 mmol) of **1b** and 43 µl (0.56 mmol) of CF_3CO_2H. The yellow solid was recrystallized from 3 ml of methanol (40°C to −78°C); yield 96 mg (84%); dec. temp. 69°C. – IR (CH_2Cl_2): $\tilde{\nu}$ = 2125 cm^{-1} [ν(RhH)], 1665 [$\nu(OCO)_{asym}$], 1465 [$\nu(OCO)_{sym}$], 1205, 1150 [ν(CF)]. – ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 2.69 [d, J(PH) = 9.6 Hz, 4 H, PCH_2Sb], 2.46, 2.02 (2 m, 2 H each, $PC\mathit{H}CH_3$), 1.59, 1.55 (2 s, 18 H each, $SbCCH_3$), 1.33, 1.27 [2 m, in ^{1}H{^{31}P} 2 d, J(HH) = 7.1 Hz, 6 H each, $PCHC\mathit{H}_3$], 1.24 [m, in ^{1}H{^{31}P} d, J(HH) = 7.3 Hz, 6 H, $PCHC\mathit{H}_3$], 1.20 [m, in ^{1}H{^{31}P} d, J(HH) = 6.8 Hz, 6 H, $PCHC\mathit{H}_3$], −16.55 [tt, J(RhH) = 27.0, J(PH) = 10.7 Hz, 1 H, Rh–H–Rh], −18.41 [dd, J(RhH) = 13.7, J(PH) = 24.4 Hz, 2 H, RhH]. – ^{13}C NMR (100.6 Mhz, CD_2Cl_2): δ = 169.3 [q, J(FC) = 38.2 Hz, $O_2\mathit{C}CF_3$], 116.0 [q, J(FC) = 288.9 Hz, CF_3], 43.7, 40.2 (2 s, $SbCCH_3$), 31.4, 31.3 (2 s, $SbCCH_3$), 29.9 [d, J(PC) = 24.8 Hz, $PCHCH_3$], 26.1 [d, J(PC) = 23.1 Hz, $PCHCH_3$], 20.7 (s, $PCH\mathit{C}H_3$), 17.8 [d, J(PC) = 5.1 Hz, $PCH\mathit{C}H_3$], 17.2 [d, J(PC) = 4.7 Hz, $PCH\mathit{C}H_3$], 17.1 [d, J(PC) = 1.5 Hz, $PCH\mathit{C}H_3$], 15.6 [dd, J(RhC) = 1.9, J(PC) = 17.2 Hz, PCH_2Sb]. – ^{19}F NMR (376.6 MHz, CD_2Cl_2): δ = −73.7 [d, J(PF) = 711.6 Hz, PF_6^-], – 75.5 (s, CF_3). – ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ = 43.8 [d, J(RhP) = 111.6 Hz, $i\mathrm{Pr}_2\mathrm{P}$], −143.7 [sept, J(FP) = 711.6 Hz, PF_6^-]. – $C_{34}H_{71}F_{12}P_3Rh_2Sb_2$ (1314.2): calcd. C 31.07, H 5.44, Rh 15.66; found C 30.70, H 5.49, Rh 15.69.

3. *Determination of the X-ray Crystal Structure of* **2b**[8]: Single crystals were grown upon slow cooling of a saturated solution of **2b** in methanol from 25°C to −78°C. Crystal data (from 25 reflections, 10° < Θ < 16°): triclinic; space group $P\bar{1}$ (No. 2); a = 9.462(7), b = 15.88(1), c = 17.93(1) Å, α = 89.22(5), β = 86.44(5), γ = 76.11(6)°; V = 2609(3) Å^3, Z = 2; $d_{calcd.}$ = 1.673 gcm^{-3}; μ(Mo-K_α) = 1.812 mm^{-1}; crystal size 0.25 × 0.35 × 0.45 mm; Enraf-Nonius CAD-4 diffractometer, Mo-K_α radiation (0.70930 Å), graphite monochromator, zirconium filter (factor 15.41); T = 293(2)K; ω-Θ scan, max. 2θ = 50°; 7439 reflections measured, 6832 independent, 4576 with $I > 2\sigma(I)$. Intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction (Ψ-scan method) was applied (min. transmission 70.68%). The structure was solved by direct methods (SHELXS-86). Atomic coordinates and the anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least squares on F_o (SHELXL-93). The positions of all hydrogen atoms except H(1), H(2), and H(3) were calculated according to ideal geometry (C–H 0.95 Å) and were refined by using the riding method. The positions of H(1), H(2), and H(3) could be located in a final difference Fourier synthesis and refined isotropically [with fixed distances Rh(1)–H(1) and Rh(2)–H(2) of 1.3 Å and a "same distance" restraint for Rh(1)–H(3) and Rh(2)–H(3)]. Since there is a disorder of the PF_6 anion, only the fluorine atoms F(3) and F(6) could be refined anisotropically. Conventional R = 0.0700 [for 4576 reflections with $I > 2\sigma(I)$], and weighted $wR2$ = 0.2315 for all 6832 located reflections; reflex/parameter ratio 11.8; residual electron density +0.874/−1.269 eÅ^{-3}.

☆ Dedicated to Professor *Luigi Venanzi* on the occasion of his 70th birthday.

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[8] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100461. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: internat. +44(0)1223/336-033; e-mail: deposit@chemcrys.cam.ac.uk).

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