in compounds that have hexacoordinated tin atoms. Thus, the number of tin atoms found in these structures ranges from two to six, excluding five. In a somewhat analogous sense, four-coordinated aluminum–nitrogen compounds[12,13] form oligomers with the number of aluminum atoms ranging from two to eight excluding five. It is to be expected that additional structural forms of organostannoxane derivatives will most likely be uncovered in the near future.

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Supplementary Material Available: Atomic coordinates (Table S1) and anisotropic thermal parameters (Table S2) for non-hydrogen atoms and atomic coordinates and isotropic thermal parameters for hydrogen atoms (Table S3) (3 pages). Ordering information given on any current masthead page.

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Evidence for a Molecular Hydrogen Complex of Rhodium. Some Factors Affecting *cis*-Dihydride ↔ η^2-Dihydrogen Exchange

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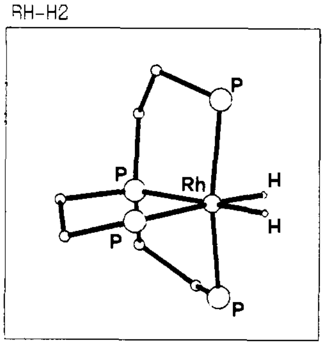
Evidence for *cis*-dihydride ↔ η^2-dihydrogen exchange has been provided for few transition-metal species,[1] and no data are reported for rhodium, which is one of the most active metals for catalytic homogeneous hydrogenations.[2] We now show that rhodium can arrest the oxidative addition of dihydrogen to give an η^2-adduct.

By treatment of the monohydride [(PP$_3$)RhH] (**1**)[3] in tetrahydrofuran (THF) with an equimolar amount of $HBF_4{\cdot}OEt_2$, colorless crystals of $[(PP_3)RhH_2](BF_4){\cdot}C_2H_5OH$ (**2**) are obtained in 60% yield after addition of ethanol [PP$_3$ = $P(CH_2CH_2PPh_2)_3$].[4] The yield increases up to 95% if the reaction mixture is kept under H_2 atmosphere during the addition of ethanol. Compound **2** is air stable and soluble in common organic solvents. The cation $[(PP_3)RhH_2]^+$ has a pseudooctahedral structure (see I) with the PP$_3$Rh fragment arranged in the fashion of a L_4M system with C_{2v} symmetry. Two *cis*-hydride ligands lie in the equatorial plane[5] together with the central P atom and one terminal P atom of the PP$_3$ ligand. The remaining phosphorus atoms complete the octahedron lying trans to each other in axial positions. These results are derived from an X-ray study of **2** which is not to be reported in detail in the present communication.[6] The octahedral structure is maintained in solution below 183 K, whereas at higher temperatures the compound rearranges to a different geometry. This is evidenced by $^{31}P\{^1H\}$ NMR spectroscopy[7] in the temperature range 183–303 K which is consistent with the equivalence of the three terminal phosphorus atoms and an overall C_{3v} symmetry of the (PP$_3$)Rh fragment (at 303 K in THF, δ P$_A$ 140.14, δ P$_B$ 60.78, $J_{P_AP_B}$ = 5.7 Hz, J_{P_ARh} = 71.0 Hz, J_{P_BRh} = 101.1 Hz). Below 103 K, the AB$_3$X spin system transforms into an AB$_2$CX one (at 173 K, δ P$_A$ 139.79, δ P$_B$ 62.70, δ P$_C$ 59.30, $J_{P_AP_B} < 2$ Hz, $J_{P_AP_C}$ 2.5 Hz, $J_{P_BP_C}$ = 10.2 Hz, J_{P_ARh} = 69.6 Hz, J_{P_BRh} = 75.0 Hz, J_{P_CRh} = 70.3 Hz) (Figure 1).



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Analogously, the ^{1}H NMR spectrum in the temperature range 183–303 K is characterized by the equivalence of the two hydrogen ligands (C_4D_8O δ −7.39, J_{HP_A} = 67.0 Hz, J_{HP_B} = 13.7 Hz, J_{HRh} = 13.7 Hz). Below 183 K, the resonances of the two hydrogens are well-separated giving rise to two unresolved multiplets, each of which split into a doublet by the strong coupling with the trans phosphorus atoms (δ −5.10, J_{HP_C} = 135 Hz, δ −10.15, J_{HP_A} = 130 Hz) (Figure 2).

Whereas NMR spectroscopy only suggests that **2** in ambient temperature solution contains H_2 rather than hydride ligands, evidence for direct H–H bonding is provided by H/D exchange experiments as well as by the chemistry of **2**. The monohydride [(PP$_3$)RhH] in C_4D_8O (TDF) oxidatively adds D$^+$ from CF_3CO_2D to give $[(PP_3)Rh(HD)](O_2CCF_3)$ (**3**) whose ^{1}H NMR spectrum (303 K) permits the measurement of J_{HD} (18 Hz) indicating H–D bonding. In fact, this value, although smaller than those reported for other η^2-HD complexes (28.6–34 Hz),[1a–d,8] is much larger than would be expected for a classical M(H)(D) complex (<1Hz).[9] As a matter of fact, an approximate value of 2 Hz has been found for the complex $[(np_3)Rh(H)(D)](O_2CCF_3)$ (**4**) obtained by treatment of [(np$_3$)RhH][3] with CF_3CO_2D [np$_3$ = $N(CH_2CH_2PPh_2)_3$]. The dihydrogen nature of **2** is supported also by the T_1 value of 170 ms (TDF, 303 K, 80 MHz, inversion-recovery method). The small H–D coupling constant and the relatively short T_1 are strongly indicative of a H–H bond distance in **2** significatively longer than those found for authenticated η^2-H$_2$ complexes.[1a,8b] In nice agreement with the η^2-H$_2$ formulation, **2** reacts with an excess of D_2 to generate the isotopomer $[(PP_3)Rh(D_2)](SO_3CF_3)$ (**5**). No trace of coordinated (HD) was observed within 6 h. Similarly, the ^{1}H NMR spectrum of a 1:1

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(3) The compound [(PP$_3$)RhH] has been obtained as yellow crystalline material following the procedure used to synthesize the np$_3$ analogue [(np$_3$)RhH] as reported in the following: Di Vaira, M.; Peruzzini, M.; Zanobini, F.; Stoppioni, P. *Inorg. Chim. Acta* **1983**, *69*, 37. IR 1740 cm^{-1} (s), ν (Rh–H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K) AB$_3$X system, δ P$_A$ 158.88 ($J_{P_AP_B}$ = 19.2 Hz, J_{P_ARh} = 88.5 Hz), δ P$_B$ 63.99 (J_{P_BRh} = 162.0 Hz); ^{1}H NMR (CD_2Cl_2, 298 K) δ −6.56 (d of quintet, $J_{HP_{trans}}$ = 130.0 Hz, $J_{HP_{cis}}$ = 17.0 Hz, J_{HRh} = 17.0 Hz, P–Rh–H, 1 H).

(4) IR 2035 cm^{-1} (m), 1840 cm^{-1} (m), ν (Rh–H).

(5) The Rh–H distances of 1.64 (3) and 1.63 (3) Å, respectively, are in line with those reported for other Rh(III) hydrides. See, for example: Ott, J.; Venanzi, L. M.; Ghilardi, C. A.; Midollini, S.; Orlandini, A. *J. Organomet. Chem.* **1985**, *291*, 89 and references quoted therein.

(6) Crystal data: $C_{42}H_{44}BF_4P_4Rh{\cdot}0.5CH_3CH_2OH$; triclinic, $P1$; δ = 13.470 (7) Å, b = 13.179 (7) Å, c = 14.812 (7) Å, α = 115.98 (8)°, β = 118.01 (8)°, γ = 84.84 (7)°; $Z = 2$; D_{calcd} = 1.42 g cm^{-3}. At the present moment the structure is satisfactorily refined to an R value of 0.062.

(7) The $^{31}P\{^1H\}$ (32.2 MHz) and ^{1}H NMR (80 MHz) spectra were recorded on a Varian CFT-20 spectrometer and then checked with a Varian VXR 300 instrument.

(8) (a) Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1986**, 506. (b) Morris, R. H.; Sawyer, J. F.; Shiralian, M.; Zubkowsky, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 5581. (c) Kubas, G. J.; Ryan, R. R.; Wrobleski, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 1339.

(9) Moore, D. S.; Robinson, S. D. *Chem. Soc. Rev.* **1983**, *12*, 415.

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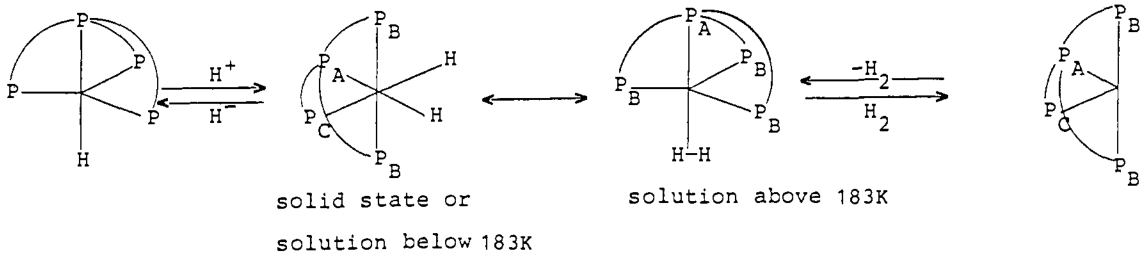

Figure 1. Evolution of the $(PP_3)Rh$ fragment on going from $(PP_3)RhH$ to $(PP_3)Rh^+$.

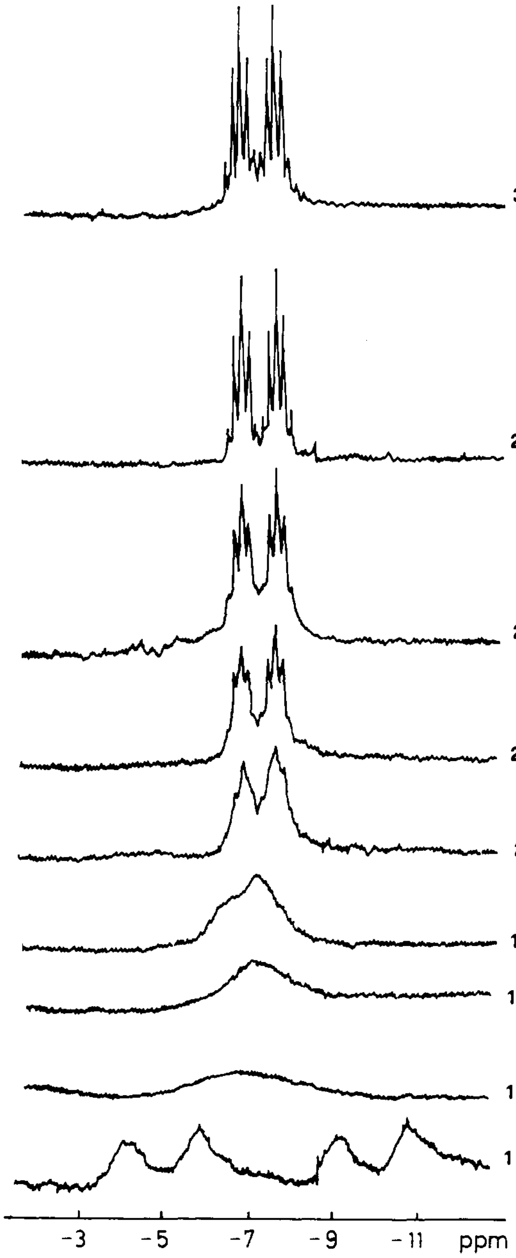

Figure 2. Variable temperature ^1H NMR (TDF, 80 MHz) of $[(PP_3)RhH_2]^+$; Me_4Si reference.

mixture of **2** and **5** in TDF did not provide evidence for crossover products. These results are consistent with previous considerations according to which the simultaneous coordination to two dihydrogen molecules to the same metal center is a condition for the H/D exchange.[1a] Such a process is certainly hampered by the presence of tripodal ligands.

Compound **2** in THF spontaneously loses H_2 at room temperature to give red solutions from which crystals of $[(PP_3)Rh(SO_3CF_3)]$ (**6**) are obtained in 90% yield following the addition of $SO_3CF_3^-$ anion.[10] The conversion of **2** into **6** is completed within 2 h. The compound **6** in turn adds H_2 (1 atm) to reform **2**. Finally, **2** quickly exchanges H_2 with C_2H_4 to give $[(PP_3)Rh(C_2H_4)](SO_3CF_3)$[11] (**7**) whose ^{31}P NMR spectrum with an AB_3X spin system closely resembles that of **2**. This result is reasonable because of the analogy between the binding of H_2 and olefins to metals.

It has been previously argued that both steric and electronic factors must be finely "tuned" on a metal fragment to permit the formation of an η^2-H_2 adduct.[1a] The geometric change of the $(PP_3)Rh$ fragment from C_{2v} to C_{3v} symmetry (Figure 1) is accompanied by a certain variation of the fragmental frontier orbitals. Likely the key to understand the mechanism of the present *cis*-dihydride ↔ η^2-dihydrogen interconversion may be found in the orbital control operated by the $(PP_3)Rh$ fragment.

Supplementary Material Available: Analytical data and experimental (80 MHz) and computed ^1H NMR spectrum of $[(PP_3)Rh(HD)](O_2CCF_3)$ (2 pages). Ordering information is given on any current masthead page.

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(10) The compound, which is a nonconductor in CH_3CN and $C_2H_5NO_2$, exists in solution as a 1:1 mixture of two isomers most likely due to the triflate ligand (IR 1310 cm^{-1} (s), ν (SO) of coordinated triflate). $^{31}P\{^1H\}$ NMR (CD_3COCD_3, 298 K) AB_2CX system, isomer 1: δ P_A 112.33, δ P_B 52.06, δ P_C 24.70; isomer 2: δ P_A 104.15, δ P_B 52.06, δ P_A 112.33, δ P_B 52.06, δ P_C 24.70; isomer 2: δ P_A 104.15, δ P_B 52.06, δ P_C 16.52 ($J_{P_AP_B}$ = 27.0 Hz, $J_{P_AP_C}$ = 14.2 Hz, $J_{P_BP_C}$ = 34.3 Hz, J_{P_ARh} = 119.7 Hz, J_{P_BRh} = 132.1 Hz, J_{P_CRh} =140.9 Hz). The colorless tetraphenylborate or tetrafluoroborate salts of $[(PP_3)RhH_2]^+$ are indefinitely stable under a dihydrogen atmosphere but, analogously to **2**, lose H_2 under nitrogen to give red solutions which still exhibit, although poorly resolved, ^{31}P NMR AB_2CX spin systems.

(11) $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K) AB_3X system δ P_A 150.28 ($J_{P_AP_B}$ = 22.2 Hz, J_{P_ARh} = 102.0 Hz), δ P_B 55.25 (J_{P_BRh} = 129.4 Hz); ^1H NMR (CD_2Cl_2, 298 K) δ 3.29 (s, C_2H_4, 4 H).

Organoselenium Chemistry.[1] Redox Chemistry of Selenocysteine Model Systems

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Glutathione peroxidase is a mammalian selenoenzyme that catalyzes the reduction of hydroperoxides by glutathione[2] and which represents the principal role played by the essential trace element selenium.[3] Isolation studies have shown that its active

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