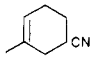
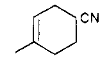
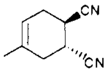
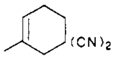
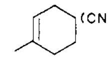
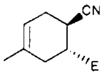
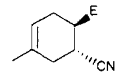
Table I. Secondary Deuterium KIEs in Isoprene 4 + 2 Cycloadditions[f]

acrylonitrile +				maximum[c]
$d_0/4,4\text{-}d_2$	at 100 °C[a]	1/1.105 (0.007)	1/0.99 (0.002)	1/1.22
$d_0/1,1\text{-}d_2$[e]	at 100 °C[a]	1/1.020 (0.030)	1/1.13 (0.04)	1/1.22
fumaronitrile +				maximum[c]
$d_0/4,4\text{-}d_2$	at 100 °C[a]	1/1.05 (0.022)		1/1.22
$d_0/1,1\text{-}d_2$[e]	at 100 °C[a]	1/1.05 (0.03)		1/1.22
vinylidene cyanide +				maximum[c]
$d_0/4,4\text{-}d_2$	at 25 °C[a]	1/1.26 (0.07)	1/0.98 (0.06)	1/1.35
$d_0/1,1\text{-}d_2$[e]	at 25 °C[b]	1/1.02 (0.10)	1/1.28 (0.07)	1/1.35
methyl *trans*-β-cyanoacrylate +		 regioisomer 1[d]	 regioisomer 2[d]	maximum[c]
$d_0/4,4\text{-}d_2$	at 25 °C[b]	1/1.14 (0.04)	1/1.125 (0.025)	1/1.35
$d_0/1,1\text{-}d_2$[e]	at 25 °C[b]	1/1.09 (0.05)	1/1.11 (0.04)	1/1.35

[a] Analyses by GCMS in CI mode—see footnote 5. [b] Analyses by capillary GC—see footnote 6. [c] Calculated for two deuteriums at the reaction temperature—see footnote 7. [d] The regiochemistry could not be assigned due to the inseparability of the diastereomers on a preparative scale. [e] Determined from KIE for $1,1,4,4\text{-}d_4$/KIE for $4,4\text{-}d_2$. [f] Standard deviations are in parentheses.

All reactions in Table I reveal either no KIE or an inverse KIE which is expected if the site in transition state becomes tetravalent. The "meta" adduct from reaction of $4,4\text{-}d_2$ with acrylonitrile has a KIE which must be related to the extent of bond making at the β site of acrylonitrile; the "para" adduct has but a very small KIE suggesting little bond making to the α site of acrylonitrile (the gross para/meta ratio is 7:3). The effects with $1,1\text{-}d_2$ reveal the same unsymmetrical transition state. Significant is the fact that the inverse KIE observed at the β site of acrylonitrile in both experiments is only half of the maximum value expected indicating an early, unsymmetrical transition state—not one with a single bond fully formed. If the reaction involved biradicals, the obvious cyano-bearing diradical species leading to each of the regioisomers would dominate, and the maximum value for the KIE should have been observed at the site of bonding to the β carbon of acrylonitrile in both experiments. With the more unsymmetrical dienophile, vinylidene cyanide, a more unsymmetrical transition state is observed since the para/meta ratio is 7:1 and the KIE at the bond forming to the β site of the dienophile is half to three-quarters of the maximum value and there is little if any KIE in bond making to the α site.[5,8]

The reaction of fumaronitrile provides only one adduct, but it is significant that the KIEs at C1 and C4 of the diene are roughly equal and one-quarter of the maximum value. If biradicals were involved, the one with a bond to C-1 of isoprene should dominate by at least a factor of 7 over the one with a bond to C-4 judging by the regiochemistry with highly unsymmetrical dienophiles.[8] This would require the KIE at C-1 to be near the maximum value and that at C-4 to be very small.[9] In the reaction of $4,4\text{-}d_2$ (and $1,1\text{-}d_2$) with methyl *trans*-β-cyanoacrylate,[10] both regioisomers[11] show the same inverse KIE (within experimental error) at each site, and it is roughly one-third of the maximum value. If the reaction were stepwise, then the two biradicals giving each regioisomer should be involved in a ratio of ca. 7:1, assuming that α cyano radical stabilization is equivalent to α carbomethoxy radical stabilization (since the regiopreference is unity, the assumption must be true). Under this circumstance, the KIE for $4,4\text{-}d_2$ should be roughly $^1/_8$ the maximum value, and the KIE for $1,1\text{-}d_2$ should be roughly $^7/_8$ the maximum value in each regioisomer. Thus, the KIEs with fumaronitrile and the nearly symmetrical–unsymmetrical dienophile are consistent with a nearly synchronous, concerted pathway with an early transition state.

Acknowledgment. We thank the National Science Foundation for support, and we thank Professor Ronald A. Hites and Dr. William Simonsick for providing the GCMS-CI instrument and help in its use, respectively.

A New Structural Form of Tin in a Cubic Cluster

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We have reported new forms of tin comprised of oligomeric oxotin carboxylates that are based on the compositions $[\mathrm{R'Sn(O)O_2CR}]_6$[1-5] and $[(\mathrm{R'Sn(O)O_2CR})_2\mathrm{R'Sn(O_2CR)_3}]_2$.[2-5] These have "drum" and "ladder" structures, respectively. We also reported the oxygen-capped cluster, $[(n\text{-}\mathrm{BuSn(OH)O_2PPh_2})_3\mathrm{O}][\mathrm{Ph_2PO_2}]$,[6] which has tin in a partial cubic array surrounded by chelating phosphinate groups. In all of these forms, tin generally is octahedrally coordinated. One useful synthetic route for their formation employs the interaction of an alkyl or aryl stannoic acid with either a carboxylic acid or a phosphorus-containing acid.

The number of tin atoms in these oligomers is either three or six. We now have obtained an additional form containing four tin atoms. The present report concerns the synthesis and structural

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(8) The Diels–Alder reaction of 1,1-dichloro-2,2-difluoroethylene with isoprene gives almost an identical regiopreference: Bartlett, P. D.; Wallibillich, E. H.; Wingrove, A. S.; Swenton, J. S.; Montgomery, L. K.; Kramer, B. D. *J. Am. Chem. Soc.* **1968**, *90*, 2049. In a 2 + 2 and in a 4 + 4 cycloaddition which probably proceed via biradicals, the KIEs at the obvious bond-forming site are near the maximum values of Holder et al. (Holder, R. W.; Graf, N. A.; Duesler, E.; Moss, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 2926) and Chou et al. (Chou, C. H.; Trahanovsky, W. S. *J. Am. Chem. Soc.* **1986**, *108*, 4138.), respectively; in the 2 + 2 cycloaddition, the SDKIE at a radical site is unity.

(9) the same analysis can be applied to Seltzer's results.[4b]

(10) Sauers, C. K.; Cotter, R. J. *J. Org. Chem.* **1961**, *26*, 6.

(11) The ratio of regioisomers from methyl *trans*-β-cyanoacrylate is 1:1. PMR of the mixture (360 MHz, $\mathrm{CDCl_3}$): δ 5.45 (s, 1 H); 5.36 (s, 1 H); 3.75 (s, 6 H); 3.05 (m, 2 H); 2.85 (m, 2 H); 2.4 (m, 8 H); 1.65 (s, 6 H).

(1) Chandrasekhar, V.; Day, R.O.; Holmes, R. R. *Inorg. Chem.* **1985**, *24*, 1970–1971.

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(4) Chandrasekhar, V.; Schmid, C. G.; Burton, S. D.; Holmes, J. M.; Day, R. O.; Holmes, R. R. *Inorg. Chem.* **1987**, *26*, 1050–1056.

(5) Chandrasekhar, V.; Schmid, C. G.; Shafeizad, S.; Johnson, S. E.; Holmes, J. M.; Day, R. O.; Holmes, R. R. *Abstracts of Papers*, 191st National Meeting of the American Chemical Society, New York, NY; American Chemical Society: Washington, DC, 1986; INOR 179.

(6) Day, R. O.; Holmes, J. M.; Chandrasekhar, V.; Holmes, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 940–941.

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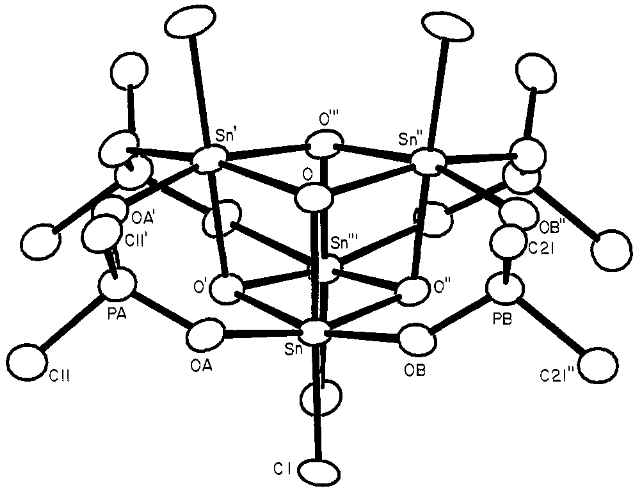

Figure 1. ORTEP plot of $[n\text{-BuSn(O)O}_2\text{P(C}_6\text{H}_{11})_2]_4$ with all pendant carbon atoms of the cyclohexyl and *n*-Bu groups omitted for purposes of clarity. Symmetry operators: $' = {}^1/_4 - x, y, {}^1/_4 - z$; $'' = {}^1/_4 - x, {}^1/_4 - y, z$; $''' = x, {}^1/_4 - y, {}^1/_4 - z$.

Table I. Selected Distances (Å) and Angles (deg) for $[n\text{-BuSn(O)O}_2\text{P(C}_6\text{H}_{11})_2]_4$[a]

Sn–O	2.046 (6)	Sn–OA	2.136 (7)
Sn–O′	2.129 (6)	Sn–OB	2.148 (6)
Sn–O″	2.148 (6)	Sn–Cl	2.13 (1)
PA–OA	1.518 (7)	PB–OB	1.519 (7)
Sn–Sn′	3.179 (1)	O–O′	2.686 (8)
Sn–Sn″	3.181 (1)	O–O″	2.710 (8)
Sn–Sn‴	3.253 (1)	O–O‴	2.757 (8)
O–Sn–O′	80.1 (2)	Sn–O–Sn′	99.2 (2)
O–Sn–O″	80.5 (2)	Sn–O–Sn″	98.6 (2)
O′–Sn–O″	80.3 (2)	Sn′–O–Sn″	99.0 (2)
avg	80.3 (2)	avg	98.9 (2)
O–Sn–Cl	178.2 (4)	O–Sn–OA	84.7 (2)
O′–Sn–OB	164.7 (2)	O–Sn–OB	86.1 (2)
O″–Sn–OA	163.8 (2)	O′–Sn–OA	90.8 (2)
O′–Sn–Cl	101.6 (4)	O″–Sn–OB	91.0 (2)
O″–Sn–Cl	99.1 (4)		
OA–Sn–OB	94.4 (2)	Sn–OA–PA	130.7 (4)
OA–Sn–Cl	95.9 (4)	Sn–OB–PB	129.7 (4)
OB–Sn–Cl	92.2 (4)		

[a] esd's are in parentheses. The atom labeling scheme is shown in Figure 1.

characterization of this novel substance.

The reaction of *n*-butylstannoic acid with dicyclohexylphosphinic acid proceeds according to eq 1 to give a 20% yield of the oxotin

$$4n\text{-BuSn(O)OH} + 4(\text{C}_6\text{H}_{11})_2\text{P(O)OH} \rightarrow [n\text{-BuSn(O)O}_2\text{P(C}_6\text{H}_{11})_2]_4 + 4\text{H}_2\text{O} \quad (1)$$

composition, mp 263–265 °C.[7] Colorless arrowhead-shaped crystals for X-ray diffraction analysis[8] were grown from a

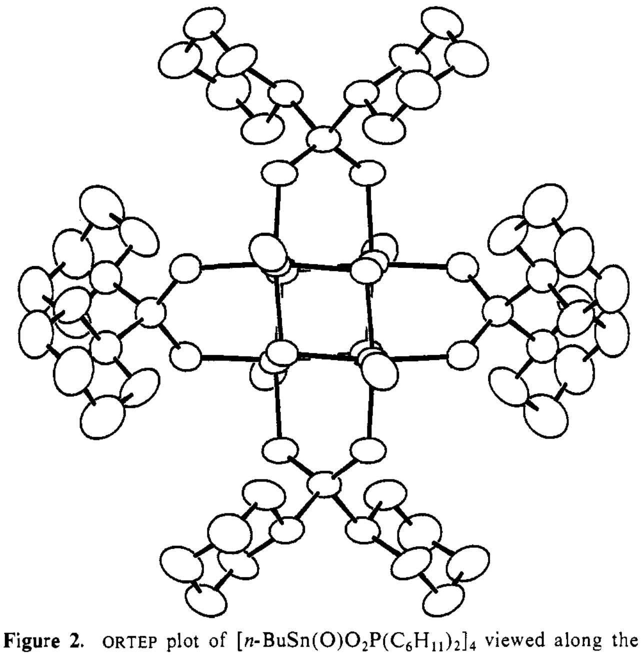

Figure 2. ORTEP plot of $[n\text{-BuSn(O)O}_2\text{P(C}_6\text{H}_{11})_2]_4$ viewed along the twofold axis parallel to *x*, with thermal ellipsoids at the 30% probability level. The pendant atoms of the *n*-Bu groups have been omitted for purposes of clarity.

CH_2Cl_2/hexane solution. Anal. Calcd for $\text{C}_{64}\text{H}_{124}\text{O}_{12}\text{P}_4\text{Sn}_4$: C, 45.64; H, 7.37. Found: C, 45.68; H, 7.28.

As shown in Figure 1, the core of the molecule is defined by tin atoms and trivalent oxygen atoms which occupy the corners of a distorted cube, each face of which is defined by a four-membered $(\text{–Sn–O–})_2$ stannoxane ring. The top and bottom faces of the cube are open, while each of its four sides is spanned diagonally by a phosphinate bridge between two tin atoms. The phosphinate bridges are required by symmetry to be symmetrical. The sides of the cube are not planar but, as in the "drum" class,[1-5] are folded along the Sn–Sn vectors so that the oxygen atoms are directed toward the interior of the cube. This is apparent in Figure 2. The geometry about the tin atoms is distorted octahedral (Table I), where the distortions are occasioned by the constraints of stannoxane rings and the bridging phosphinate groups.

The formation of the cube arrangement instead of the drum structure of the same empirical composition is most likely aided by the presence of the bulky cyclohexane units attached to the phosphinate ligands (Figure 2). The hydrogen atoms of adjacent cyclohexyl groups are already in van der Waals contact, 2.326 Å for the closest such distance in the cube compared to 2.4 Å for the van der Waal's sum. In the cube, the interligand phosphinate O–Sn–O angles (OA–Sn–OB) are 94.4 (2)°, whereas this angle in the related drum compound $[n\text{-BuSn(O)O}_2\text{P(OPh)}_2]_6$[10] is 79.9 (2)°. Thus, steric crowding would be encountered if the drum formed instead of the cube since the expected decrease in this angle, close to 15°, could force the dicyclohexyl phosphinate groups into even closer proximity.

The tetramer has crystallographic D_2 symmetry in which each of the two crystallographically independent phosphorus atoms is constrained to lie on a twofold axis. However, the idealized molecular symmetry, D_{2d}, indicates that the phosphorus atoms as well as the tin atoms should be chemically equivalent. The latter is consistent with solution ^{119}Sn NMR data which shows a single resonance in CDCl_3 with triplet character centered at −462.8 ppm (^2J $^{119}\text{Sn–O–}^{31}\text{P}$ = 116 Hz).

The common structural unit in all of the oligomeric forms described so far is the four-membered dimeric distannoxane ring, Sn_2O_2. Related work[11] shows that this unit is present by itself

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[7] A mixture of *n*-butylstannoic acid (2.08 g, 10 mmol) and dicyclohexyl phosphinic acid (2.30 g, 10 mmol) were heated together in toluene (85 mL) for 3 h with the azeotropic removal of water by using a Dean Stark apparatus. Toluene was removed from the homogeneous solution, and diethyl ether (30 mL) was added. A crystalline precipitate was obtained.

[8] The tetrameric stannoxane $[n\text{-BuSn(O)O}_2\text{P(C}_6\text{H}_{11})_2]_4$ crystallizes in the orthorhombic space group *Fddd* (origin taken at $\bar{1}$)[9] with $a = 20.200$ (2) Å, $b = 46.656$ (6) Å, $c = 15.969$ (2) Å, $Z = 8$, and $\mu_{\text{Mo K}\bar{\alpha}} = 1.45$ mm^{-1}. The crystal used in the X-ray study had maximum dimensions of approximately 0.15 mm × 0.20 mm × 0.40 mm. A total of 2373 independent reflections $(+h,+k,+l)$ were measured at room temperature with use of the θ–2θ scan mode and graphite monochromated Mo K$\bar{\alpha}$ radiation ($\lambda = 0.71073$ Å), for $3° \leq 2\theta_{\text{Mo K}\bar{\alpha}} \leq 43°$, on an Enraf-Nonius CAD4 diffractometer. No corrections were made for absorption. Full-matrix least-squares refinement (nonhydrogen atoms anisotropic, cyclohexyl group hydrogen atoms riding isotropic, butyl hydrogen atoms omitted, function minimized $\sum w(|F_o| - |F_c|)^2$, $w^{1/2} = 2F_oL_p/\sigma_I$) led to $R = 0.043$ and $R_w = 0.052$ for the 1411 reflections having $I \geq 2\sigma_I$. Mean atomic scattering factors were taken from ref 9, 1974; Vol. IV, pp 72–98. Real and imaginary dispersion corrections for Sn, O, and P were taken from the same source, pp 149–150. All calculations were performed on a Microvax II computer by using the Enraf-Nonius CAD4 SDP system of programs.

[9] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1969; Vol. I, p 75.

[10] Chandrasekhar, V.; Holmes, J. M.; Day, R. O.; Holmes, R. R., unpublished work.

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.

Acknowledgment. The support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation (Grant No. CHE8504737) is gratefully acknowledged.

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 $\leftrightarrow$ η^2-Dihydrogen Exchange

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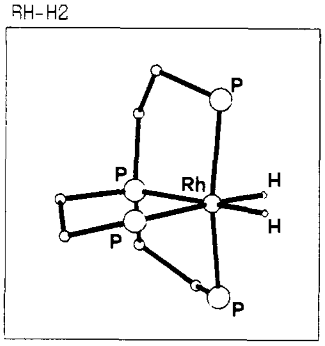
Evidence for *cis*-dihydride $\leftrightarrow$ η^2-dihydrogen exchange has been provided for few transition-metal species,[1] and no data are reported for rhodium, which is one of the most active metals for catalytic homogeneous hydrogenations.[2] We now show that rhodium can arrest the oxidative addition 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$_2$H$_5$OH (**2**) are obtained in 60% yield after addition of ethanol [PP$_3$ = P(CH$_2$CH$_2$PPh$_2$)$_3$].[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$_4$M 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{^{1}H} 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$_4$D$_8$O 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$_4$D$_8$O (TDF) oxidatively adds D$^+$ from CF$_3$CO$_2$D to give [(PP$_3$)Rh(HD)](O$_2$CCF$_3$) (**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$_2$CCF$_3$) (**4**) obtained by treatment of [(np$_3$)RhH][3] with CF$_3$CO$_2$D [np$_3$ = N(CH$_2$CH$_2$PPh$_2$)$_3$]. 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$_3$CF$_3$) (**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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(2) (a) Halpern, J. *Adv. Catal.* **1959**, *11*, 301. (b) James, B. R. *Homogeneous Hydrogenation*; Wiley: New York, 1973.
(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{^{1}H} NMR (CD$_2$Cl$_2$, 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$_2$Cl$_2$, 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$_4$P$_4$Rh$\cdot$0.5CH$_3$CH$_2$OH; triclinic, $P\bar{1}$; 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{^{1}H} (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.
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