An NMR study of *trans* ligand influence in rhodium η^2 triphenyltin hydride complexes

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Edited by Jay A. Labinger, California Institute of Technology, Pasadena, CA, and accepted by the Editorial Board January 24, 2007 (received for review November 6, 2006)

The complex $[\text{Rh}(\text{O}_2\text{Cisoq})(\text{H})(\text{SnPh}_3)(\text{PPh}_3)_2]$ (O_2Cisoq = isoquinoline-1-carboxylate), characterized by x-ray crystallography, was used as a precursor to three-center bonded complexes $[\text{Rh}(\text{O}_2\text{Cisoq})(\eta^2\text{-HSnPh}_3)(\text{PPh}_3)(4\text{-Rpy})]$ (R = carbomethoxy, acyl, bromo, aldehyde, hydrogen, methoxy, dimethylamino), which were prepared *in situ* from the bis(phosphine) complex in dichloromethane by addition of the pyridine. Of two isomeric forms of $[\text{Rh}(\text{O}_2\text{Cisoq})(\eta^2\text{-HSnPh}_3)(\text{PPh}_3)(4\text{-Rpy})]$, one, with 4-Rpy positioned *trans* to tin, is formed at 0°C; the other, with isoquinoline positioned *trans* to tin, is formed by partial (25–50%) conversion of the first isomer (in solution) upon warming to 30–35°C for a few minutes. The relative coordination geometries of the two isomers were established by using a ^{15}N -enriched pyridine. NMR parameters (^1H , ^{31}P , ^{103}Rh , and ^{119}Sn) for the pyridine-containing complexes show trends consistent with a significantly greater SnH interaction in complexes having isoquinoline lying *trans* to tin and a threshold of σ donor strength for the pyridine below which the influence on Rh(SnH) bonding is minimal and above which the influence is to enhance the SnH interaction. Possible reasons for these effects are discussed.

^{103}Rh NMR | ^{119}Sn NMR | three-center bond | *trans* influence

Three-center bonds between a transition metal, hydrogen, and a group 4 element [i.e., $\text{M}(\text{EH})$, where E carries substituents] are of interest as intermediates in numerous metal-catalyzed reactions and also in their own right as examples of how, with a suitable combination of ligands, a transition metal can bind to a σ bond, an interaction historically considered to be most unlikely. A transition metal σ complex, or three-center bonded complex, reflects a finely balanced electronic state of the metal such that a relatively small change in electron density can lead to an oxidative addition product (where permitted by the coordination geometry and oxidation state of the metal) or to the dissociation of the σ bond (EH) from the metal. Numerous examples of transition metal $-\text{R}_3\text{CH}$, $-\text{R}_3\text{SiH}$, $-\text{R}_3\text{GeH}$ (1, 2), and $-\text{R}_3\text{SnH}$ (3–11) complexes [among a wider range of types, including $\text{M}(\text{H}_2)$] are known, and the relevant literature for $-\text{R}_3\text{CH}$ (12–24) complexes (almost all of which are agostic, i.e., supported) and $-\text{R}_3\text{SiH}$ (25–29) complexes has been extensively reviewed.

The characterization of three-center bonds has relied heavily on x-ray diffraction, which suffers from the drawback that a hydrogen in close proximity to a heavy atom is often difficult to locate with accuracy. For the purpose of locating such hydrogens, neutron diffraction is a superior method. A further problem associated with solid samples is that packing forces within a crystal can modify or distort a three-center bond, changing it from the form in which it exists in solution. The most commonly used means of characterizing three-center bonds in solution is NMR spectroscopy, aided by the fact that ^1H , ^{13}C , ^{29}Si , ^{119}Sn , and in some cases the transition metal (e.g., ^{103}Rh), are all NMR-active nuclei with nuclear spin quantum number $I = \frac{1}{2}$, giving narrow lines in the NMR spectrum and readily showing spin–spin coupling, which is the means for discerning the presence of a three-center bond. $\text{M}(\text{CH})$ three-center bonds are now reported on the basis of NMR evidence alone (30). Although the magnitude of $J(\text{E,H})$, the spin–spin coupling constant

between ^1H and nucleus E (^{13}C , ^{29}Si , etc.), can be used to identify a three-center bond, a correlation between $J(\text{E,H})$ and the strength of the three-center bond may hold good over only a fairly narrow range of complexes.

A method of characterizing three-center bonds that is not readily susceptible to misinterpretation is measurement of the activation energy for the dissociation of EH from M. The requirement (not always easily fulfilled) is that the $\text{M}(\text{EH})$ complex, in a suitable solvent, should dissociate cleanly, without side reactions or solvent effects, within an acceptable temperature range and must be amenable to monitoring by a suitable spectroscopic technique (e.g., NMR or IR). From rate constants measured at various temperatures, thermodynamic parameters can be obtained (31). The existence of a three-center bond can be inferred from values of $J(\text{E,H})$ (absolute magnitudes) that lie in the range ≈ 50 –100 Hz ($\text{E} = ^{13}\text{C}$) (13), ≈ 20 –90 Hz ($\text{E} = ^{29}\text{Si}$) (26, 27, 32–34), and ≈ 90 –350 Hz ($\text{E} = ^{119}\text{Sn}$) (3–11). The relationship between coupling constant and three-center bond has been validated, at least in part, by neutron diffraction studies that include $[\text{Ta}(\eta^2\text{-CHCMe}_3)(\text{PMe}_3)_2\text{Cl}_3]$ (35), for which the C–H distance is unusually long (1.131 (3) Å) and $J(^{13}\text{C}-^1\text{H})$ is 101 Hz and by kinetic studies of $[\text{Mn}(\text{Cp})(\eta^2\text{-HSiPh}_3)(\text{CO})_2]$ (36) and $[\text{Rh}(\text{NCBPh}_3)(\eta^2\text{-HSnPh}_3)(\text{PPh}_3)(4\text{-Me}_2\text{Npy})]$ (10) for which $J(\text{E,H})$ and enthalpies of dissociation of R_3EH are ≈ 65 Hz (32), 122 $\text{kJ}\cdot\text{mol}^{-1}$ and 106 Hz, 97 $\text{kJ}\cdot\text{mol}^{-1}$, respectively.

The present study examines the influence on the magnitude of $J(\text{E,H})$ and other NMR parameters of changes in the σ donor strength of a neutral ligand (pyridine) and of the number of points of attachment (the denticity) of the ligand positioned *trans* to tin in two series of isomeric rhodium η^2 -triphenyltin hydride complexes.

Results and Discussion

The complex $[\text{Rh}(\text{O}_2\text{Cisoq})(\text{H})(\text{SnPh}_3)(\text{PPh}_3)_2]$ (1) is chiral and crystallizes in the space group *Cc*, where each enantiomer is related to its mirror image by a *c* glide plane. The geometry about rhodium (Fig. 1) is distorted octahedral with the two phosphines orientated mutually *cis*, one phosphine lying *trans* to tin and the other *trans* to the isoquinoline nitrogen. In the remaining position, the hydride (which was not located in the electron density map but instead was geometrically inserted) lies *trans* to the carboxylate oxygen. The geometry about tin is distorted tetrahedral, with the greatest distortion ($\text{Rh}-\text{Sn}-\text{C}$ (11) = 131.26°) occurring with respect to the phenyl group facing the

Author contributions: L.C. designed research; L.C., M.A.F., and E.S. performed research; L.C. contributed new reagents/analytic tools; L.C. and M.A.F. analyzed data; and L.C. wrote the paper.

The authors declare no conflict of interest.

This article is a PNAS Direct Submission. J.A.L. is a guest editor invited by the Editorial Board.

Data deposition: Atomic coordinates for compound 1 have been deposited in the Cambridge Structural Database, Cambridge Crystallographic Database Centre, Cambridge CB2 1EZ, United Kingdom (CSD reference no. 633409).

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Fig. 1. Thermal ellipsoid plot of $[\text{Rh}(\text{O}_2\text{Cisoq})(\text{H})(\text{SnPh}_3)(\text{PPh}_3)_2]$ (**1**) with ellipsoids drawn at the 30% probability level. Hydride is inserted geometrically. Cocrystallized CH_2Cl_2 is omitted.

phosphine, indicating steric repulsion from a phosphine phenyl group. No significant distortion can be attributed to an interaction between tin and the hydride. Selected bond lengths and angles are given in Table 1.

NMR data for **1** (Table 2) are fully in agreement with this geometry: one phosphorus shows $J(\text{Sn},\text{P})$ of 1,901 Hz and the other shows $J(\text{Sn},\text{P})$ of 196 Hz, consistent with the general rule that a *trans* coupling constant is approximately an order of magnitude larger than a *cis* coupling constant. The chemical shift of the hydride lies in the range encountered for complexes in which the *trans* ligand is an O donor, and the magnitude of $J(\text{P},\text{H})$ confirms that both phosphorus atoms are positioned *cis* to the hydride. The magnitude of $J(\text{Sn},\text{H})$ (66 Hz) indicates that the coordination of Ph_3SnH in the complex (in solution) lies not far from the borderline between an oxidative addition product and a three-center bond.

When a solution of **1** in dichloromethane at 0°C is treated with a pyridine (Scheme 1), a product (**a**) is obtained in which one triphenylphosphine of **1** has been replaced by pyridine. The ^1H and $^{31}\text{P}\{^1\text{H}\}$ spectra (Fig. 2) show that the phosphine that remains is positioned *cis* to tin [$J(\text{Sn},\text{P}) = 220\text{--}230$ Hz] and also *cis* to the hydride [$J(\text{P},\text{H}) \approx 30$ Hz]. The hydride, as in **1**, lies *trans* to oxygen. What remains unclear at this stage is the identity of the ligand positioned *trans* to tin: the incoming pyridine or the isoquinoline of the bidentate isoquinolinecarboxylate. The magnitude of $J(\text{Sn},\text{H})$ (which represents largely 2J Sn–Rh–H coupling rather than 1J Sn–H coupling) indicates a three-center bond.

Table 1. Selected bond lengths and angles for complex **1**

Bond	Length, Å	Angle	°
Rh–N	2.148(4)	N–Rh–O(1)	76.66(19)
Rh–O(1)	2.157(5)	N–Rh–P(1)	169.71(14)
Rh–P(1)	2.271(2)	O(1)–Rh–P(1)	95.42(14)
Rh–P(2)	2.4038(18)	N–Rh–P(2)	89.84(4)
Rh–Sn	2.6361(8)	O(1)–Rh–P(2)	98.43(14)
		P(1)–Rh–P(2)	97.91(7)
		N–Rh–Sn	82.27(14)
		O(1)–Rh–Sn	96.79(13)
		P(1)–Rh–Sn	92.29(5)
		P(2)–Rh–Sn	160.75(5)
		C(11)–Sn–Rh	131.3(2)
		C(21)–Sn–Rh	111.23(18)
		C(31)–Sn–Rh	107.65(19)

When the pyridine-containing solution is warmed for a few minutes, a second product (**b**) appears with NMR parameters that are very similar to those obtained from **a** [except for $J(\text{Sn},\text{H})$, which is much larger for **b** than for **a**]. The coordination geometry of **b** must therefore differ from that of **a** with respect to the relative positions of pyridine and isoquinoline, which, being chemically similar, cannot readily be distinguished on the basis of their influence on the tin chemical shift $\delta(^{119}\text{Sn})$. This difficulty of assignment can be resolved by the use of an ^{15}N 99% enriched pyridine (Scheme 1) which, when bound to rhodium in **a** and **b**, allows the isomers to be distinguished on the basis of the phosphorus–nitrogen coupling constant. $J(\text{P},\text{N})$ is found to have a magnitude of 44.9 Hz for isomer **b**, confirming that ^{15}N is positioned *trans* to phosphorus and is undetectable (apart from a slight broadening of the ^{31}P lines) in **a**. Isomers **a** and **b**, therefore, have the respective coordination geometries given in Scheme 1. Spectra are shown in Fig. 2.

The most notable difference between the two isomers with regard to the NMR data is in the magnitude of $J(\text{Sn},\text{H})$ which increases by ≈ 40 Hz upon going from **a** to **b**. This increase can be accounted for as follows. The two isomers differ in coordination geometry only in the relative positions of the pyridine and the isoquinoline. Pyridine and isoquinoline have similar σ donor properties, and it is highly unlikely that the large changes in $J(\text{Sn},\text{H})$ can be attributed to these small differences in the electron-donating ability of the ligand lying *trans* to tin (pyridine in **a** and isoquinoline in **b**). However, the fact that isoquinoline is part of a bidentate ligand ensures that its bond to rhodium is much more stable than the bond of a similar but monodentate ligand (the well known chelate effect). The large *trans* influence (37) of tin will then cause the bond to pyridine (in **a**) to be weakened to a greater extent than the bond to isoquinoline (in **b**), diminishing the pyridine's contribution of electron density to rhodium and hence its influence on the Rh(SnH) bond strength and on $J(\text{Sn},\text{H})$. In the electron-rich complexes **3–9**, the SnH and the ligand lying *trans* to tin can be viewed as competing to donate electron density (or rather, in the case of SnH, to resist pressures to accept more) to rhodium, which then attempts to redistribute electron density among the ligands. In isomer **a**, this redistribution occurs by a weakening of the bond to pyridine; in isomer **b** it occurs by a weakening of the bond to SnH. Evidence for a weakened bond to pyridine in **a** can be seen in the spectra in Fig. 2 *A* and *B*, recorded at 248 and 300 K, respectively, which show the hydride signals of both **8a** and **8b** ($\text{R} = \text{OMe}$). At 300 K, the signal from **8a** is broadened, consistent with the reversible dissociation of a ligand.

To examine the effect on the NMR parameters of the three-center bond of small incremental changes in electron density on rhodium, the σ donor properties of the pyridine (in the complexes $[\text{Rh}(\text{O}_2\text{Cisoq})(\eta^2\text{-HSnPh}_3)(\text{PPh}_3)(4\text{-Rpy})]$; **3–9** in Scheme 1) were modified. Substituents on the pyridine, located in the 4-position to minimize steric interactions with neighboring ligands, were varied from strongly electron-withdrawing (MeO_2C) to strongly electron-donating (Me_2N), a range of influence that has been quantified in the form of the Hammett σ function (38). The NMR parameters most responsive to changes occurring at the three-center bond are $\delta(^{119}\text{Sn})$ and $J(\text{Sn},\text{H})$; values of these, measured for complexes **3–9**, are shown in Fig. 3 plotted against values of Hammett σ for the substituent on pyridine.

The most significant features of the data in Fig. 3 are (i) the large increase in $J(\text{Sn},\text{H})$ (noted above) upon going from isomer **a** to isomer **b**, (ii) the increase in $J(\text{Sn},\text{H})$ and decrease in $\delta(^{119}\text{Sn})$ that accompany an increase in the electron-donating ability of substituent R, and (iii) the close correlation that exists between $J(\text{Sn},\text{H})$ and $\delta(^{119}\text{Sn})$. This correlation extends to an apparent discontinuity in the otherwise fairly smooth trend of the data, arising from the complexes having electron-withdrawing substituents on the pyridine. Here, a change of R from MeO_2C and

Table 2. NMR spectral data

Complex*	$\delta(^1\text{H})^\dagger$	$\delta(^{31}\text{P})^\ddagger$	$\delta(^{103}\text{Rh})^\S$	$\delta(^{119}\text{Sn})^\parallel$	$J(\text{P},\text{H})^\parallel$	$J(\text{Rh},\text{H})^\parallel$	$J(\text{Sn},\text{H})^{\parallel**}$	$J(\text{Rh},\text{P})^\parallel$	$J(\text{Sn},\text{P})^\parallel$	$J(\text{Sn},\text{Rh})^\parallel$
1 ^{††}	−17.52	45.25 27.21	798	−79.8	29.6 5.1	16.5	66	128 93	196 1901	313
2a py ^{−15} N ^{§§}	−18.52	53.47	1,159	—	32.5	20.3	—	133	—	—
3a MeO ₂ Cpy	−18.55	52.88	1,182	−112.2	32.9	20.2	109	133	223	391
4a MeCOpy	−18.54	52.84	1,181	−112.2	33.0	20.3	109	133	222	389
5a Brpy	−18.64	52.96	1,179	−111.8	32.9	20.3	109	133	224	390
6a HCOpy	−18.54	52.80	1,181	−111.9	32.9	20.3	108.5	133	223	392
7a py	−18.59	53.11	1,192	−114.3	33.3	20.4	110.5	133	223	390
8a MeOpy	−18.63	53.22	1,194	−114.8	33.3	20.4	111.5	133	227	389
9a Me ₂ Npy	−18.70	53.31	1,210	−116.2	33.7	20.5	113.5	133	230	383
2b py ^{−15} N ^{§§}	−18.68	52.06	1,119	—	24.7	19.2	149	141	—	—
3b MeO ₂ Cpy	−18.80	51.84	1,128	−117.4	24.5	19.5	152.5	139	224	341
4b MeCOpy	−18.77	51.68	1,130	−117.2	24.5	19.7	152	139	227	343
5b Brpy	−18.88	52.19	1,123	−118.6	24.6	19.5	152	140	226	344
6b HCOpy	−18.77	51.69	1,133	−116.8	24.5	19.5	152	139	224	343
7b py	−18.79	51.96	1,125	−118.7	24.3	19.5	154	138	229	349
8b MeOpy	−18.84	52.22	1,125	−121.0	24.2	19.6	156	139	229	353
9b Me ₂ Npy	−18.90	52.09	1,128	−124.5	24.0	19.9	158.5	137	229	364

*Complex 1: *cis*-[Rh(O₂Cisoq)(H)(SnPh₃)(PPh₃)₂]; complexes 2–9: [Rh(O₂Cisoq)(H)(SnPh₃)(PPh₃)(4-Rpy)] (isomers **a** and **b**). Rpy indicated. Solution (0.005–0.015 M) in CD₂Cl₂/CH₂Cl₂ (5%) at 248 K.

[†]Chemical shifts in ppm from TMS (internal standard).

[‡]Chemical shifts in ppm from a frequency defined by H₃PO₄ (external standard) at 300 K.

[§]Chemical shifts in ppm from $\Xi(^{103}\text{Rh}) = 3.16$ MHz.

^{||}Chemical shifts in ppm from a frequency defined by SnMe₄ (external standard) at 248 K.

^{||}Coupling constants (absolute magnitude) in hertz. Signs are probably as follows: ²J(Sn,H_{cis}), ²J(Sn,P_{cis}), and ¹J(Sn,Rh) positive; ¹J(Rh,H), ¹J(Rh,P), and ²J(P,H_{cis}) negative (see ref. 20).

^{**}J(¹¹⁹Sn,¹H) ≈ J(¹¹⁷Sn,¹H). J(Sn,H) is accurate to approximately ±0.5 Hz.

^{††}|J(P,P)| = 16.1 Hz.

^{§§}The Sn satellites to the ¹H signal were obscured by signals from side products, preventing the measurement of J(Sn,H). The concentration of **2a** (and **2b**) was too low to permit the recording of a ¹¹⁹Sn spectrum.

^{§§}|J(P,N_{trans})| = 44.9 Hz; |J(Rh,N)| = 13 Hz.

MeCO to the less electron-withdrawing HCO and Br causes insignificant changes [with the exception of $\delta(^{119}\text{Sn})$ for isomer **b** with R = Br]. Only upon going to data points for R = H do changes in $\delta(^{119}\text{Sn})$ and J(Sn,H) become apparent, with a steady, almost linear increase in J(Sn,H) and decrease in $\delta(^{119}\text{Sn})$ to more negative values, upon going from R = H to MeO to Me₂N. Complexes of 4-MeO₂Cpy and 4-Brpy were included in the study to establish more firmly that initial results obtained with 4-MeCOpy and 4-HCOpy reflected a real effect. Other NMR parameters (Table 2) for complexes of the less electron-rich pyridines (**3a–6a** and **3b–6b**) are similarly insensitive to a change in R from MeO₂C or MeCO to Br or HCO.

Another noteworthy feature of the NMR data is that, for isomer **a**, there is a significant increase in $\delta(^{103}\text{Rh})$ upon going from R = Br (**5a**) or HCO (**6a**) to R = H (**7a**) and to complexes of the more electron-rich pyridines (**8a** and **9a**), but for isomer

b there is very little change across the full range of pyridines [$\delta(^{103}\text{Rh})$ for **3b–9b** lies between 1,123 and 1,133 ppm]. Findings similar to those for **b** are reported elsewhere for three-center Rh(SnH) bonds believed to be close to the dissociation limit (11).

The diminished response of NMR parameters to changes in the more electron-withdrawing substituents of pyridine in **3b–9b** can be rationalized in terms of a threshold of σ donor strength that must be exceeded before the pyridine can influence bonding elsewhere in the complex. This threshold can be viewed as arising from the fact that the complexes [Rh(O₂Cisoq)(η^2 -HSnPh₃)(PPh₃)(4-Rpy)] are electron-rich (the isoquinoline carboxylate combines a strong σ donor and strong π donor) and any additional electron density that is brought to the rhodium must be relocated among the ligands, which compete to resist this change. A neutral ligand that is not a strong σ donor will consequently bind more weakly than might otherwise be expected. A stronger σ donor can overcome the resistance of, in this case, the SnH ligand, which can be regarded as a reluctant acceptor of electron density. In an environment of high electron density, changes can be regarded as occurring at tin that favor its more ready acceptance of electron density, namely a closer approach to a five-coordinate geometry and a stronger interaction with the hydride. A change from four-coordinate to five-coordinate bonding at tin has been shown to be accompanied by a change in $\delta(^{119}\text{Sn})$ to lower values, consistent with the data in Fig. 3 (39).

Conclusions

Insofar as an increase in J(SnH) and a decrease in $\delta(^{119}\text{Sn})$ are indicative of an increase in the strength of the SnH interaction in an Rh(SnH) complex, the following conclusions can be drawn. If a pyridine or related group is located in the position *trans* to tin, its influence on the strength of the SnH interaction is much greater if it (the pyridine) is part of a bidentate chelating ligand rather than

MeCO (4), Br (5), HCO (6), H (7), MeO (8), Me₂N (9).

Scheme 1.

Fig. 2. NMR spectra of the two three-center bonded isomers. ^1H (A and B), $^{31}\text{P}\{^1\text{H}\}$ (C), $^{119}\text{Sn}\{^1\text{H}\}$ (D and E), $^{119}\text{Sn}\{^1\text{H}\}$ (F) spectra; A–D and F (A, C, D, and F at 248 K; B at 300 K) were recorded from $[\text{Rh}(\text{O}_2\text{Cisoq})(\eta^2\text{-H}_2\text{SnPh}_3)(4\text{-MeOpy})]$ (**8a** and **8b**). The signal from isomer **a** appears to the left and from isomer **b** to the right in each spectrum. Spectrum E (248 K) was recorded from **2a** and **2b**, containing py^{-15}N .

a simple monodentate ligand. The influence of small increases in the electron-donating ability of a coordinated pyridine on the SnH interaction only becomes significant after a certain threshold of σ donor power has been reached. Beyond this point, an increase in the strength of the SnH interaction occurs regardless of whether the pyridine is positioned *cis* or *trans* to tin.

Materials and Methods

The compounds $[\text{Rh}(\text{Cl})(\text{PPh}_3)_3]$ (**40**) and 3,5-dicarbomethoxy-4-phenylpyridine- ^{15}N (**41**) were prepared in accordance with published methods. Dichloromethane was distilled from P_2O_5 , and diethyl ether, hexane, and pyridine were dried over calcium hydride. Other reagents were of the highest available purity and were used without further treatment. All operations were performed under an argon atmosphere.

$[\text{Rh}(\text{O}_2\text{Cisoq})(\text{H})(\text{SnPh}_3)(\text{PPh}_3)_2]$ (CH_2Cl_2 , **1.** KO_2Cisoq (0.082 mmol) in 1 ml of H_2O , from a solution prepared from isoquinoline carboxylic acid and KOH) was added to $[\text{Rh}(\text{Cl})(\text{PPh}_3)_3]$ (0.076 g, 0.082 mmol) in dichloromethane (3 ml), and the mixture was stirred vigorously at room temperature for 40 min. The dark-red dichloromethane solution was separated from the aqueous layer, dried over magne-

Fig. 3. Influence of the pyridine substituent on NMR parameters related to the three-center bond. Plots of $J(\text{Sn},\text{H})$ (A) and $\delta(^{119}\text{Sn})$ (B), both against Hammett σ for complexes **3a–9a** and **3b–9b**. The isomer **a** or **b** is identified, together with the pyridine substituent R.

sium sulfate, and then treated with Ph_3SnH (0.03 g, 0.086 mmol). A color change to yellow-orange was immediately observed. The solution was concentrated, $\text{Et}_2\text{O}/\text{hexane}$ (2:1) was added, and the mixture was allowed to stand at -20°C for 1 day to give orange crystals. The product was washed with hexane and dried under vacuum. Yield 0.066 g (65%). Anal. Calcd. for $\text{C}_{65}\text{H}_{54}\text{Cl}_2\text{NO}_2\text{P}_2\text{RhSn}$: C, 63.19; H, 4.41; N, 1.13. Found: C, 63.07; H, 4.56; N, 1.07.

Pyridine-Containing Complexes. Pyridine-containing derivatives of **1** were prepared *in situ* in an NMR tube. Complex **1** (10 mg, 0.008 mmol) in 5% $\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$ (0.6 ml) was cooled to $\approx 0^\circ\text{C}$, the pyridine (10% by volume or 40 mg if solid) was added, and the tube was sealed and then quickly shaken to mix the contents before transferring to the spectrometer at -25°C . With the more electron-

rich pyridines, conversion of **1** to a pyridine-containing product (isomer **a**) was quantitative; with the less electron-rich pyridines, incomplete conversion was observed (by ^{31}P NMR). On warming the above solutions to 30–35°C for 5–10 min, isomer **b** was formed to an extent of 25–50% (of total **a** + **b**).

X-Ray Crystallography. The crystal structure was solved by direct methods using *SHELXTL* (42). Nonhydrogen atoms were first refined isotropically, followed by anisotropic refinement by full-matrix least-squares calculations based on F^2 using *SHELXTL*. With the exception of the hydride, all hydrogen atoms were first located in the difference map, then positioned geometrically and allowed to ride on their respective parent atoms. The hydride atom was placed geometrically, equidistant from the P1, P2, Sn, and N atoms and 1.45 Å from the rhodium atom. The structure contains a disordered dichloromethane molecule. Attempts to resolve the disorder were unsuccessful. The structure was therefore processed with *SQUEEZE* (43, 44), which accounted for 48 electrons, close to the 42 required for a dichloromethane molecule. In the final refinements, the contri-

bution of the dichloromethane molecule to the structure was added to the $F000$ crystal density and unit cell content values.

NMR Spectroscopy. Spectra were recorded at 248 K on a Bruker (Reinstetten, Germany) DRX 400 spectrometer equipped with a 5-mm triple-resonance inverse probe with a dedicated ^{31}P channel and extended decoupler range, operating at 400.13 MHz (^1H), 161.98 MHz (^{31}P), 12.65 MHz (^{103}Rh), and 149.21 MHz (^{119}Sn). Two-dimensional ^{103}Rh - ^{31}P spectra were obtained by using the heteronuclear multiple quantum correlation (HMQC) pulse sequence of Bax *et al.* (45). Further details are given in ref. 11. Chemical shifts were referenced to the generally accepted standards of tetramethylsilane (TMS), H_3PO_4 , Ξ (^{103}Rh) = 3.16 MHz, and SnMe_4 , with negative values indicating shielding. The chemical shifts of H_3PO_4 (85%, 300 K) and SnMe_4 (neat liquid, 248 K) with a CD_2Cl_2 external lock correspond to frequencies of 161.975500 and 149.210995 MHz, respectively, in a field (9.398 T) in which the protons of TMS (in CD_2Cl_2 at 300 K) resonate at 400.130020 MHz.

We thank the University of the Witwatersrand for financial support and Deutscher Akademischer Austauschdienst for a scholarship (to E.S.).

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