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Hydrogen Bridging Rhodium and Tin: An NMR Study of $[Rh(H)\{(\mu\text{-}H)SnR_3\}_2(PPh_3)_2]$ (R = ^{n}Bu, Ph)

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The activation of C–H bonds by binding to transition metals is of considerable current interest in the search for catalysts that can usefully derivatize hydrocarbons.[1] Complexes have been characterized with "agostic" C–H bonds in varying degrees of approach to a metal[2] and have served as models for the intermediate stages in oxidative addition.[3] Recently these studies have been extended to include Si–H,[4–8] Ge–H,[7] and Sn–H[9] bonds where it has been shown by Schubert *et al.* (using X-ray and neutron diffraction) that in the complexes $[MeCp(CO)_2Mn(H)ER_3]$ (E = Si,[6,8] Sn[9]) the E–H fragment is also bound in an η^2 fashion. Binding is accompanied by changes in the ^{1}H NMR spectrum of E–H, where the signal from H is found in the low-frequency region ($\delta \sim -10$ ppm) and the magnitude of the E–H (E = ^{29}Si, ^{119}Sn, ^{117}Sn) coupling constant is greatly reduced compared with that of free R_3EH.[4,6,9] Where a transition metal–R_3EH adduct cannot be isolated in a form suitable for diffraction studies evidence for its structure must be provided largely by NMR spectroscopy. We report complexes of rhodium characterized in this way where two R_3SnH molecules occupy positions as ligands binding via hydride bridges.

The $^{31}P\{^1H\}$ spectra recorded from mixtures of $[RhH(PPh_3)_4]$[10] and excess (~3-fold) R_3SnH (R = ^{n}Bu, **1**, or Ph, **2**) in toluene at room temperature each show a doublet (coupling of ^{31}P to ^{103}Rh), the signal from **2** having satellites and the signal from **1** having no satellites that can be detected.[11] In the low-frequency region of the ^{1}H spectrum of both **1** and **2** a multiplet (Figure 1a, dt, hydride coupling to Rh and two equivalent phosphines) is observed with satellites integrating for 30% of the signal; i.e., hydride is coupling to two tin atoms per molecule of complex, $J(^{119}Sn\text{–}^1H)$ = 126 Hz (**1**) and 170 Hz (**2**). These values are much smaller than those of free R_3SnH[12] but in turn are considerably larger than values measured from compounds in which the oxidative addition is considered to be complete, viz. $[Rh(H)_2(Sn^nBu_3)(PPh_3)_3]$ (*vide infra*), products obtained from the reaction of R_3SnH with $[RhX(PPh_3)_3]$ (X = Cl, OCN),[13] and $[Rh(C_5Me_5)(H)(SnR_3)(CO)]$ and related complexes described by Maitlis,[14] where $J(^{119}Sn\text{–}^1H) \sim 40$ Hz. ^{31}P spectra obtained with decoupling of all protons except those resonating at low frequency consist of a doublet of quartets (Figure 1b); i.e., three apparently equivalent hydrides are bound to the metal. At reduced temperature (Figure 1c) three signals are observed in the ^{1}H spectrum of **2** (only two in the spectrum of **1**), consistent with the "freezing out" of a process by which a rapid exchange of R_3Sn among the hydrides occurs, and two broad signals are found in the $^{119}Sn\{^1H\}$ spectrum (Figure 1d), indicating nonequivalence of the two tin atoms [one signal is observed at 22 °C[11] (Figure 1e)]. The $^{31}P\{^1H\}$ signal is not significantly changed at −50 °C. Products **1** and **2** are therefore formulated as $[RhH\{(\mu\text{-}H)SnR_3\}_2(PPh_3)_2]$, where rapid relocation of R_3Sn among the hydrides at ambient temperature causes all three hydrides and both tins to appear equivalent on the NMR time scale (Scheme I). A similar process, in which one SnR_3 ligand participates, has been proposed by Schubert *et al.* for the complex $[FeH_3(SnPh_3)(PPh_2{}^nBu)_3]$.[15]

In other complexes where strong evidence exists for an M-H-Sn bridge[9,16] $J(^{119}Sn\text{–}^1H)$ is found in the range 148–328 Hz, complexes showing the lower values having electron-donating substituents on both the transition metal and Sn and those with

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(11) ^{1}H NMR (toluene-d_8, 22 °C): **1**, δ −8.85 [dt, J(Rh–H) = 14.1, J(P–H) = 27.3, $J(^{119}$Sn–H) = 126, $J(^{117}$Sn–H) = 122 Hz]; **2**, δ −7.60 [dt, J(Rh–H) = 11.9, J(P–H) = 26.1, $J(^{119}$Sn–H) = 170, $J(^{117}$Sn–H) = 166 Hz]. ^{31}P NMR (toluene/toluene-d_8, 22 °C): **1**, δ 42.9 [d, J(Rh–P) = 103.2 Hz]; **2**, 37.6 [d, J(Rh–P) = 99.6 Hz, $J(^{119}$Sn–P) ≈ $J(^{117}$Sn–P) = 17 Hz] (H_3PO_4 external standard). ^{119}Sn NMR (toluene/toluene-d_8, 22 °C) **1**, δ −11.7 [d, J(Sn–Rh) = 102.9 Hz]; **2**, δ −58.4 [dt, J(Sn–Rh) = 148.5, J(Sn–P) = 17.5 Hz] ($SnMe_4$ external standard).

(12) ^{1}H NMR (C_6D_6, 22 °C): ^{n}Bu$_3$SnH, δ 5.06 [$J(^{119}$Sn–H) = 1578, $J(^{117}$Sn–H) = 1508 Hz]; Ph_3SnH, δ 6.80 [$J(^{119}$Sn–H) = 1950, $J(^{117}$Sn–H) = 1864 Hz]. ^{119}Sn NMR (0.1 M in toluene/toluene-d_8, 22 °C): ^{n}Bu$_3$SnH, δ −88.4; Ph_3SnH, δ −162.1 ($SnMe_4$ external standard).

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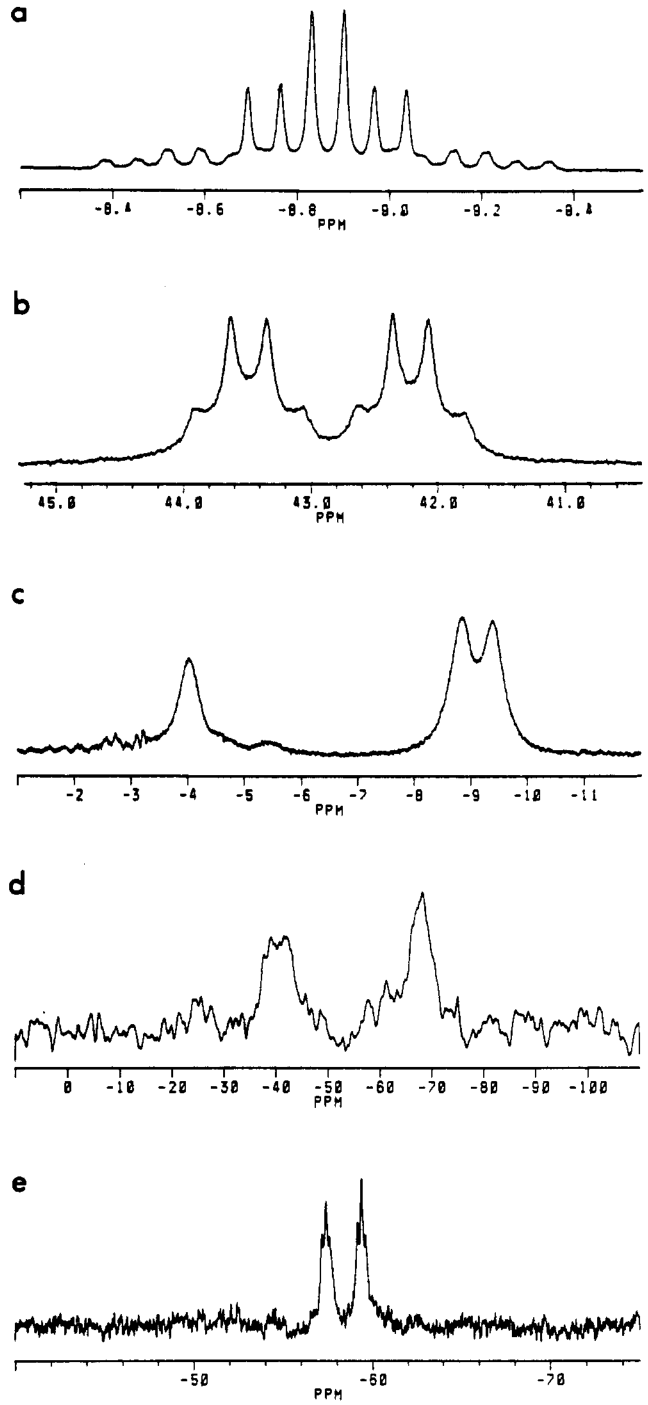
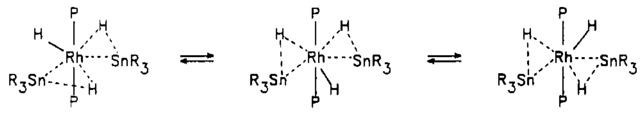


Figure 1. (a) ^{1}H signal (hydride) from 1 at 22 °C. (b) ^{31}P signal from 1 with partial decoupling (coupling to hydrides still effective) (22 °C). (c) ^{1}H signals (hydride) from 2 at −75 °C. (d) ^{119}Sn{^{1}H} signals from 2 at −70 °C. (e) ^{119}Sn{^{1}H} signal from 2 at 22 °C (the resolution is better at 50 °C). The solvent is toluene.

higher values having electron-withdrawing substituents. The value of *J*(Sn–H) is particularly sensitive to the substituents bound to tin: in a series of complexes [Mo(Cp)$_2${(μ-H)SnR$_3$}] reported by Bulychev *et al.*[16b] *J*(^{119}Sn–^{1}H) varies from 148 Hz (R = Me) to 318 Hz (R = Cl). Similar effects are observed in complexes where there is good reason for believing that there is no bond between hydrogen and tin.[17]

Theoretical studies of the binding of R$_3$EH (E = C, Si, Sn) to a 14- or 16-electron metal fragment[1b,18] have identified the major electronic interactions as being (i) donation of electron density from the E–H σ orbital to a vacant orbital of σ symmetry on the metal, (ii) a flow of electron density in the reverse direction from a filled metal orbital of π symmetry to the E–H σ^* orbital and (iii), because of the geometry of interaction, dictated by the steric properties of the substituents on E, a repulsion between the filled metal orbital and the E–H σ orbital. In the absence of the last of these interactions the encounter between a suitable coordinatively unsaturated metal complex and E–H might in most cases be expected to lead smoothly to an oxidative addition product. The extent to which a favorable conjunction of E–H and metal M proceeds toward oxidative addition is influenced by the properties of the substituents on E and the ligands on M[6] and can involve largely σ or largely σ^* activation of the E–H bond,[18b] the latter favored by electron-donating substituents on M and electron-withdrawing substituents on E. In the case of **1** and **2** the hydrogens clearly have hydridic character and the extent to which electron density on the metal becomes involved in bonding is reflected by the magnitude of *J*(Rh–P),[11] which is characteristic of an Rh$^{\text{III}}$ complex.[19]

Scheme I



R = Bu, Ph; P = PPh$_3$

The difference between the values of *J*(Sn–P) for **1** (too small to detect) and **2** (17 Hz) can be rationalized in terms of a greater repulsion between Rh and Sn in **1** than in **2** arising from interaction iii (above), which is larger in **1** as a result of the increased electron density in the E–H bond when E has butyl substituents. With the electron-withdrawing phenyl groups in **2** the Rh-Sn interaction is stronger and the system closer to the oxidative addition limit. On the basis of this interpretation, the bonding in **1** is perhaps better described as "open"[20] compared with the bonding in **2** where the evidence suggests that it is "closed".

Product **2** can be isolated as yellow crystals[21] from a variety of solvents, the best yield (72%) being obtained using toluene, and is unaffected by 1–2 h of exposure to air. Unfortunately all crystals were found to be multiply twinned and the few potentially suitable fragments decomposed rapidly on exposure to X-rays. Efforts to overcome these problems are in progress. Attempts to isolate **1** give instead [*fac*-Rh(H)$_2$(Sn^{n}Bu$_3$)(PPh$_3$)$_3$]: from the high value of *J*(Sn–P$_{trans}$) and the low value of *J*(Sn–H)[22] it would appear that here ^{n}Bu$_3$SnH has undergone full oxidative addition. This compound is also stereochemically nonrigid in solution and was characterized using spectra recorded at −50 °C.

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(21) Anal. Found: C, 64.87%; H, 4.61%. Calcd for **2**: C, 64.99; H, 4.77.

(22) ^{1}H NMR (toluene-*d*$_8$, −50 °C): δ −10.60 [dmult, *J*(P–H *trans*) ~120 Hz]. ^{1}H (22 °C): δ −10.78 [dq, *J*(Rh–H) = 10.3, *J*(P–H) = 29.5, *J*(^{119}Sn–^{1}H) ~ *J*(^{117}Sn–^{1}H) = 39.5 Hz]. ^{31}P NMR (toluene/toluene-*d*$_8$, −50 °C): δ 40.5 [dd (broadened), *J*(Rh–P) = 110.6 Hz], 30.9 [dt (broadened), *J*(Rh–P) = 108.8, *J*(Sn–P$_{trans}$) ~1140 Hz] (δ relative to PPh$_3$ at −4.70). ^{119}Sn NMR (toluene/toluene-*d*$_8$, −50 °C): δ −4.2 [ddt, *J*(Sn–Rh) = 232, *J*(Sn–P *trans*) = 1161, *J*(Sn–P$_{cis}$) = 78 Hz] (SnMe$_4$, external standard).