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Three-centre Rh—H—Sn bonds: an NMR study of the effects of varying the electron density on rhodium†

Laurence Carlton*
Centre for Molecular Design, Department of Chemistry, University of the Witwatersrand, Johannesburg, Republic of South Africa

The complexes [Rh(X)(H)(SnPh$_3$)(PPh$_3$)(L)] (X = NCBPh$_3$ (a), N(CN)$_2$ (b), NCS (c), NCO (d), N$_3$ (e); L = 1-methylimidazole) (1) show systematic changes in δ(^{119}Sn), δ(^{103}Rh), J(^{119}Sn–^{1}H) and J(^{119}Sn–^{103}Rh) that are related to the electron-donating properties of X. As X becomes more electron-rich, δ(^{103}Rh), J(^{119}Sn–^{1}H) and J(^{119}Sn–^{103}Rh) increase and δ^{119}Sn) decreases. The related complexes *trans*-[Rh(X)(H)(SnPh$_3$)(PPh$_3$)$_2$(L)] (X = N(CN)$_2$, NCO; L = 4-carboxymethylpyridine (x), pyridine (y) and 4-dimethylaminopyridine (z)) (2), show a continuation of the trends in δ(^{119}Sn) and J(^{119}Sn–^{1}H), but not δ(^{103}Rh) or J(^{119}Sn–^{103}Rh). Data for 1 and 2 show that within certain limits of type of ligand varied (X = N-donor, L = a pyridine) and coordination geometry, the response of δ(^{119}Sn) and J(^{119}Sn–^{1}H) to changes in electron density on rhodium is largely independent of the means by which the change is effected. Copyright © 2001 John Wiley & Sons, Ltd.

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INTRODUCTION

Three-centre bonded complexes serve as models for the transition state in the oxidative addition of an alkane to a *d*-block metal.[1] By using tin instead of carbon a much wider range of such complexes becomes accessible and the higher natural abundance of spin 1/2 isotopes (^{119}Sn 8.6%, ^{117}Sn 7.6%) facilitates the measurement of NMR parameters. The tin–hydrogen spin-coupling constant J(Sn–H) [for values $\lesssim 200$ Hz $J(^{119}\text{Sn–}^1\text{H}) \approx J(^{117}\text{Sn–}^1\text{H})$] in a three-centre bonded Ph$_3$SnH complex has a value in the range ≈90–350 Hz,[2] significantly higher than for the full oxidative addition product (≈20–40 Hz) but much lower than for free Ph$_3$SnH [J(^{19}Sn–^{1}H) = 1950 Hz], making it a useful indicator of the presence of a three-centre bond.

The three-centre-bonded complexes on which this study is based form part of a series that is described more fully elsewhere.[3]

EXPERIMENTAL

Complexes **1** and **2** (Fig. 1) are readily prepared *in situ* at 0 °C (**1**) and −50 °C (**2**) from [Rh(X)(PPh$_3$)$_3$],[4] a nucleophile and Ph$_3$SnH. For a typical measurement the sample was prepared by dissolving [Rh(X)(PPh$_3$)$_3$] (20 mg) in 0.5 ml of 10% pyridine–dichloromethane (5% CD$_2$Cl$_2$) in an NMR tube under argon. The tube was cooled to −50 °C in a xylene slurry, Ph$_3$SnH (≈10 mg) was added, and the tube sealed and transferred quickly to the spectrometer at −60 °C. Spectra were recorded on a Bruker DRX 400 spectrometer equipped with a 5 mm triple resonance inverse probe with extended decoupler range and dedicated ^{31}P channel. ^{103}Rh spectra were obtained by indirect detection using phosphorus by means of the pulse sequence $\{\pi/2(^{31}\text{P})–1/[2J(^{103}\text{Rh}–^{31}\text{P})]–\pi/2(^{103}\text{Rh})–\tau\text{-}\pi/2(^{103}\text{rh}(–\text{Aq}(^{31}\text{P})\}$.[5]

RESULTS AND DISCUSSION

When J(^{119}Sn–^{1}H) for complex **1** (L = 1-methylimidazole) is plotted as a function of δ(^{119}Sn) (Fig.

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* Correspondence to: Laurence Carlton, Centre for Molecular Design, Department of Chemistry, University of the Witwatersrand, Johannesburg, Republic of South Africa.

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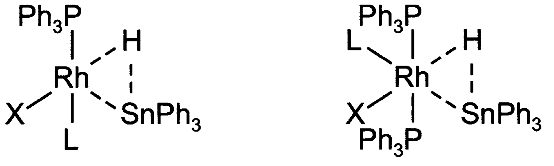

1 **2**

Figure 1 Complexes studied. X = NCBPh$_3$ (a), N(CN)$_2$ (b), NCS (c), NCO (d), N$_3$ (e); L = 1-methylimidazole (**1** only), 4-MeO$_2$Cpy (x), py (y), 4-Me$_2$Npy (z).

2a and Table 1) an approximately linear relationship is found with $^2J(^{119}Sn–^1H)$ (positive sign) increasing and $\delta(^{119}Sn)$ decreasing as ligand X becomes more strongly electron donating. A similar result is found for $^2J(^{119}Sn–^1H)/\delta(^{103}Rh)$ (Fig. 2b) and $^2J(^{119}Sn–^1H)/^1J(^{119}Sn–^{103}Rh)$ (Fig. 2c) with both $\delta(^{103}Rh)$ and $^1J(^{103}Rh–^{119}Sn)$ (positive sign) increasing as X becomes more electron rich.

In Fig. 3 a plot of $J(^{119}Sn–^1H)$ against $\delta(^{119}Sn)$ is shown for **1** and **2** with X = N(CN)$_2$ and NCO and with L varied. The effect on the $J(^{119}Sn–^1H)$/

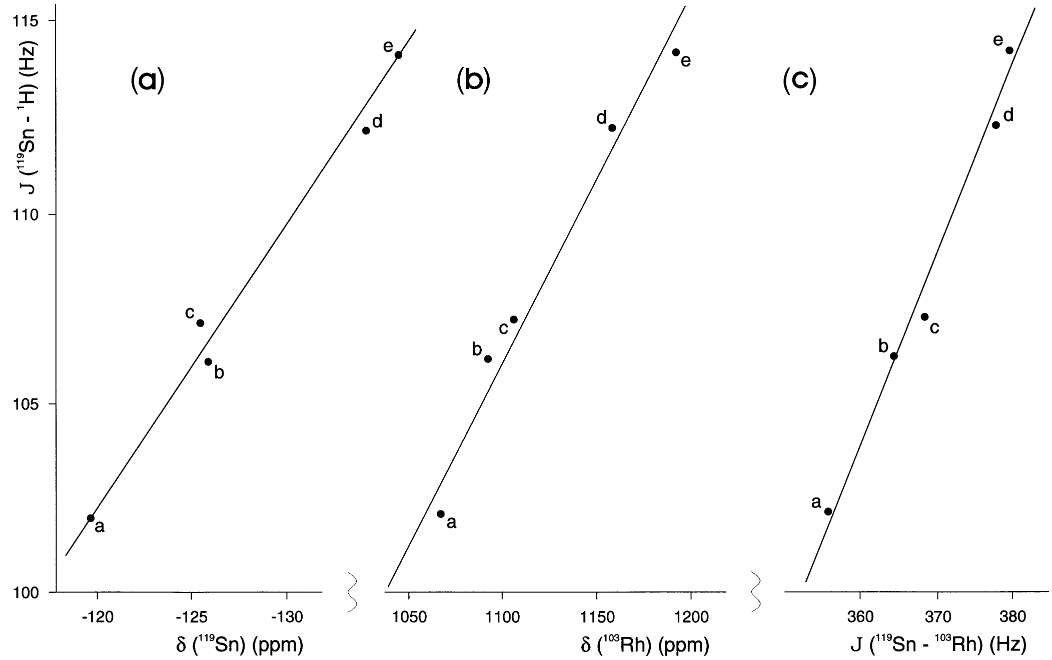

Figure 2 Plots of $J(^{119}Sn–^1H)$ against $\delta(^{119}Sn)$ (a), $\delta(^{103}Rh)$ (b) and $J(^{119}Sn–^{103}Rh)$ (c) for **1** (L = 1-methylimidazole, X varied) in dichloromethane at −25 °C.

Table 1 Spectral data for [Rh(X)(H)(SnPh$_3$)(PPh$_3$)(L)][a] (**1**) (L = 1-methylimidazole)

X	$\delta(^{103}Rh)$[b]	$\delta(^{119}Sn)$[c]	$J(^{119}Sn–^1H)$[d]	$J(^{119}Sn–^{103}Rh)$[d]
NCBPh$_3$	1067	−119.7	102	356
N(CN)$_2$	1094	−126.0	106	365
NCS	1108	−125.7	107	369
NCO	1162	−134.6	112	379
N$_3$	1196	−136.3	114	381

[a] Solvent dichloromethane, temperature −25 °C.
[b] δ relative to 3.16 MHz (Ref. 6).
[c] δ relative to SnMe$_4$, external standard.
[d] Coupling constants in hertz. The sign of each is most probably positive.

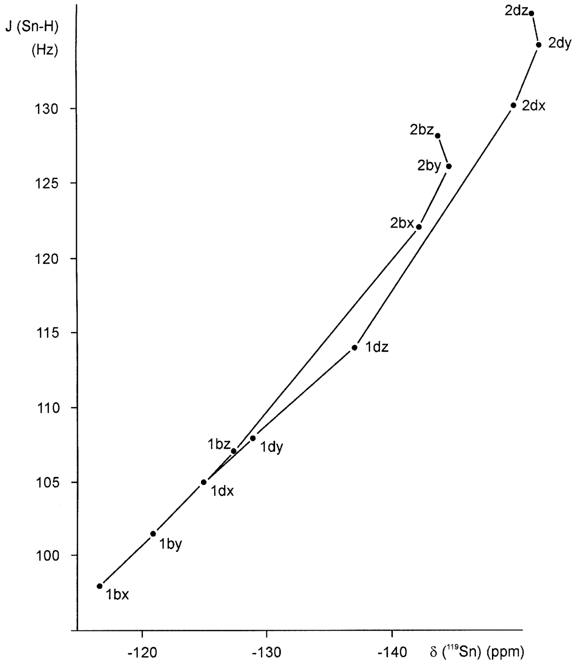

Figure 3 Plot of J(^{119}Sn–^{1}H) against δ(^{119}Sn) for **1** and **2** [X = N(CN)$_2$ (b), NCO (d); L = MeO$_2$Cpy (x), py (y), Me$_2$Npy (z)] in dichloromethane at −60 °C.

δ(^{119}Sn) gradient of varying X and L and of the change in coordination geometry from **1** to the more electron-rich **2**, is relatively slight. For **1** the effects of change of X and change of L are indistinguishable. This correlation between J(^{119}Sn–^{1}H) and δ(^{119}Sn) is most clearly seen for X = N-donor and L = a pyridine, becoming less clear for X = chloride (not shown) and does not hold for an isomeric form of **2** with a phosphine positioned *trans* to tin. The values of δ(^{103}Rh) and J(^{119}Sn–^{103}Rh) do not show continuity from **1** to **2** [δ(^{103}Rh) decreases to ≈500 ppm].

The rhodium and tin chemical shifts are a function of both ΔE^{-1} (where ΔE is an average electronic excitation energy) and $<r^{-3}>$ (where r is the average d orbital radius),[7,8] terms that exert opposing influences on δ in response to changes in electron density on the metal. ΔE^{-1} is also a major contributor to J(^{119}Sn–^{1}H) and J(^{119}Sn–^{103}Rh). The change in δ(^{103}Rh) can be accounted for in terms of a decrease in ΔE that might be expected to accompany the presence of increasingly electron-donating ligands, and similarly for J(^{119}Sn–^{1}H) and J(^{119}Sn–^{103}Rh). The decrease in δ(^{119}Sn) is likely to reflect a dominant role for $<r^{-3}>$ and also a progressive change in coordination number from four to five.[8]

Complexes **2** with X = N(CN)$_2$, NCO and L = 4-Me$_2$Npy, show a departure from the trend to lower δ(^{119}Sn) (Fig. 3) as L becomes more nucleophilic. Here an *increase* in δ(^{119}Sn) is observed together with a quite small increase in J(^{119}Sn–^{1}H). These findings can be rationalized in terms of a change in tin geometry, now in the direction of four-coordinate, that might be expected to accompany a weakening of the Ph$_3$SnH–Rh interaction. As a consequence of the complementary increase in the Sn–H interaction, an increased contribution from ^{1}J(^{119}Sn–^{1}H) (which has negative sign) would be expected to diminish the observed change in J(^{119}Sn–^{1}H).

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Table 2 Spectral data for [Rh(X)(H)(SnPh$_3$)(PPh$_3$)(L)] (**1**) and [Rh(X)(H)(SnPh$_3$)(PPh$_3$)$_2$(L)] (**2**)[a]

		Complex **1**		Complex **2**	
X	L	δ(^{119}Sn)[b]	J(^{119}Sn–^{1}H)[c]	δ(^{119}Sn)[b]	J(^{119}Sn–^{1}H)[c]
N(CN)$_2$	4-MeO$_2$Cpy	−116.6	98	−142.5	122
N(CN)$_2$	py	−120.9	101.5	−144.8	126
N(CN)$_2$	4-Me$_2$Npy	−127.4	107	−144.0	128
NCO	4-MeO$_2$Cpy	−125.0	105	−150.0	130
NCO	py	−129.0	108.5	−152.1	134
NCO	4-Me$_2$Npy	−137.2	115.5	−151.7	136

[a] Solvent dichloromethane, temperature −60 °C.
[b] δ relative to SnMe$_4$ (frequency of external standard at −25 °C).
[c] Coupling constants in hertz, sign positive.

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