SYNTHESIS, ^{119}Sn, ^{13}C AND ^{195}Pt NMR STUDIES OF FIVE-COORDINATE RHODIUM(I), IRIDIUM(I) AND PLATINUM(II) COMPLEXES CONTAINING THREE TRICHLOROSTANNATE LIGANDS

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Summary

The synthesis and ^{119}Sn NMR characteristics of new five-coordinate tris(trichlorostannato) complexes of Rh^I, Ir^I and Pt^{II} are reported. The Rh^I and Ir^I complexes are complex dianions of the form $(PPN)_2[M(SnCl_3)_3L_2]$ where L can be CO, $C≡N$(cyclohexyl) or L_2, a diolefin such as 1,5-COD or NBD (norbornadiene). The anionic platinum complexes $(PPN)[Pt(SnCl_3)_3L_2]$ contain similar L ligands. A number of neutral monotrichlorostannato complexes of type $[M(SnCl_3)L_4]$ including $[Ir(SnCl_3)(NBD)(1,5-COD)]$ have been prepared and characterized. Their $\delta(^{119}$Sn$)$, $\delta(^{13}$C$)$, $\delta(^{195}$Pt$)$ as well as $^1J(^{103}$Rh, ^{119}Sn$)$, $^1J(^{195}$Pt, ^{119}Sn$)$, $^2J(^{119}$Sn, ^{117}Sn$)$ and $^2J(^{119}$Sn, ^{13}C$)$ data are given. A *trans* influence series, based on $^1J(^{195}$Pt, ^{119}Sn$)$, reveals the following sequence: $H^- > PR_3 > AsR_3 > SnCl_3^- > $ olefin $> Cl^-$.

Introduction

There is a continuing interest in the chemistry of trichlorostannate complexes of palladium(II) and platinum(II) because of their participation in homogeneous hydrogenation [1] and hydroformylation [2] reactions. There are many well characterized monoSnCl$_3$ complexes of these metals [3], and recent NMR [4–7] and X-ray diffraction studies [4,8] have demonstrated the stability of anionic poly SnCl$_3$ complexes such as $[Pt(SnCl_3)_3(AsMe_3)_2]^-$ [4]. This latter complex contains three platinum–tin bonds in the equatorial plane of a trigonal bipyramid. Indeed, anions of the general type $[Pt(SnCl_3)_3L_2]^-$, L = PEt_3, PPr_3^n, $AsEt_3$, $P(OEt)_3$ are readily synthesized [5]. There are fewer examples of bis SnCl$_3$ compounds, i.e. $[Pt(SnCl_3)_2L_2]$, although we recently determined the solution [5] and solid state [9] structure of L = $P(OPh)_3$.

The trichlorostannate chemistry of Rh^I and Ir^I has received less attention. In earlier studies Young et al. [10] reported the dimeric anionic complexes $[Rh_2Cl_2(SnCl_3)_4]^{4-}$ as well as $[Rh(SnCl_3)(PPh_3)_3]$, the SnCl$_3$ analog of Wilkinson's

catalyst. Kingston and Scollary [11] have described a series of rhodium carbonyl complexes containing two and three $SnCl_3$ groups, e.g. $(NMe_4)_2[RhCl(SnCl_3)_2(CO)]$ and $(AsPh_4)_2[Rh(SnCl_3)_3(CO)]$, while Yurchenko et al. [12] have described the syntheses of $[Ir(SnCl_3)_3(PPh_3)_3]$ and $[IrCl(SnCl_3)_2(CO)(P(C_6H_{13})_3)_2]$. Several groups have used Ir or Rh $SnCl_2$ mixtures as homogeneous catalysts. For example: mixtures of $RhCl_3 \cdot 3H_2O$ and $SnCl_2 \cdot 2H_2O$ dehydrogenate propanol to give acetone [13]; $[Ir(SnX_3)(COD)L_2]$ complexes are precursors of hydrogenation and isomerization catalysts [14], and Kaspar et al. [1] find that Rh^{III} and Ir^{III}-Sn^{II} systems catalyse hydrogen transfer from isopropanol to cyclohexanones.

In many of these studies the characterization rests primarily on microanalytical and IR data. Although these are often sufficient, it seemed to us that ^{119}Sn NMR spectroscopy ($I = 1/2$, natural abundance 8.6%) could contribute significantly in this branch of tin chemistry. Recently, we used this tool to establish the presence of the various chloro and bromo complexes $[Rh(SnCl_nBr_{(3-n)}NBD)(PEtPh_2)_2]$, and correlated $^1J(^{103}Rh, ^{119}Sn)$ with the sum of the Pauling electronegativities for the halogens [15]. Further, Moriyama et al. [16] described the ^{119}Sn NMR parameters of the compounds $[Rh(SnCl_3)_nCl_{(6-n)}]^{3-}$, $n = 1-5$, and found a correlation between $^1J(^{103}Rh, ^{119}Sn)$ and $\delta^{119}Sn$. Consequently, we considered it useful to further investigate the chemistry and ^{119}Sn NMR spectroscopy of the $SnCl_3$ ligand, and we describe below some results for new tristrichlorostannate complexes of Rh^I, Ir^I, Pd^{II} and Pt^{II}.

Results and discussion

1. Preparation of the complexes

a. $ML_2(SnCl)_3^{n-}$ anions

The new five-coordinate Rh^I, Ir^I, Pd^{II} and Pt^{II} complexes are listed in Table 1, along with pertinent IR and microanalytical data. All the Rh^I complexes were conveniently prepared by the addition of $SnCl_2$ and (PPN)Cl to the dimers $[MCl(diolefin)]_2$, as shown in equation 1.

$$[MCl(diolefin)]_2 + 6SnCl_2 + 4(PPN)Cl \rightarrow 2(PPN)_2[M(SnCl_3)_3(diolefin)] \qquad (1)$$
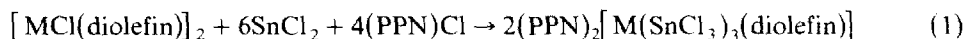
(Ia, diolefin = 1,5-COD;

Ib, diolefin = NBD;

Ic, diolefin = DCP)

Compound Ib served as a convenient starting material for the anions $[Rh(CO)_2(SnCl_3)_3]^{2-}$ and $[Rh(C\equiv N\text{-cy})_2(SnCl_3)_3]^{2-}$, cy = cyclohexyl as indicated in eq. 2. $(PPN)_2[Ir(SnCl_3)_3(1,5\text{-COD})]$ (IIIa) was prepared in a manner analogous to Ia, whereas the $[Ir(SnCl_3)_3(NBD)]^{2-}$ anion (IIIb) was prepared by the slow (several days) reaction of $[Ir(SnCl_3)(NBD)(COD)]$ with $SnCl_2$ and (PPN)Cl (see Experimental).

$$\text{Ib} + 2CO \rightarrow (PPN)_2[Rh(SnCl_3)_3(CO)_2] + NBD$$
$$(\text{IIa})$$

$$\text{Ib} + 2(C\equiv N\text{-cy}) \rightarrow (PPN)_2[Rh(SnCl_3)_3(C\equiv N\text{-}(cy)_2] + NBD \qquad (2)$$
$$(\text{IIb})$$
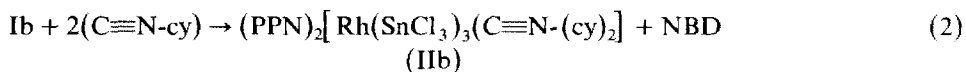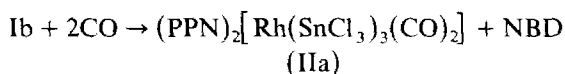
TABLE 1

MICROANALYTICAL AND IR [a] DATA FOR THE COMPLEXES

Compound	Analysis found (calcd.) (%)			$\nu(SnCl)$ (cm^{-1})	$\nu(CO)$ [b] (cm^{-1})
	C	H	Cl		
(PPN)$_2$[Rh(SnCl$_3$)$_3$(NBD)]	48.65 (48.72)	3.68 (3.52)	16.29 (16.38)	335, 300	
(PPN)$_2$[Rh(SnCl$_3$)$_3$(1,5-COD)]	48.93 (48.92)	3.59 (3.66)	16.29 (16.28)	335, 300	
(PPN)$_2$[Rh(SnCl$_3$)$_3$(DCP)]	49.19 (49.55)	3.78 (3.65)	16.43 (16.06)	340, 305	
(PPN)$_2$[Rh(SnCl$_3$)$_3$(CN(Cy))$_2$]·0.5 CH$_2$Cl$_2$	48.65 (49.09)	3.91 (3.95)	16.23 (16.75)	~ 300	2210, 2155
(PPN)$_2$[Rh(SnCl$_3$)$_3$(CO)$_2$]	46.59 (46.53)	3.28 (3.17)	16.93 (16.70)	~ 300	2060, 2010
(PPN)$_2$[Ir(SnCl$_3$)$_3$(1,5-COD)]	46.49 (46.81)	3.40 (3.53)	15.83 (15.54)	338, 300	
(PPN)$_2$[Ir(SnCl$_3$)$_3$(NBD)]	46.17 (46.59)	3.58 (3.37)	17.10 (15.67)	340, 300	
[Rh(SnCl$_3$)(NBD)$_2$]	32.89 (32.83)	3.06 (3.15)	20.97 (20.76)	310	
[Ir(SnCl$_3$)(NBD)$_2$]	27.99 (27.95)	2.62 (2.68)	17.49 (17.68)	323	
[Ir(SnCl$_3$)(1,5-COD)$_2$]	30.31 (30.33)	3.79 (3.82)	16.77 (16.70)	315	
[Ir(SnCl$_3$)(NBD)(1,5-COD)]	29.38 (29.17)	3.20 (3.26)	17.35 (17.22)	320	
(Et$_4$N)[Pt(SnCl$_3$)$_3$(1,5-COD)]	16.71 (17.33)	2.72 (2.91)	28.96 (28.78)		

[a] As KBr pellets. [b] resp. $\nu(C\equiv N)$.

$$\left[PtCl_2(\text{diolefin}) \right] + 3SnCl_2 + (PPN)Cl \rightarrow$$

$$(PPN)\left[Pt(SnCl_3)_3(\text{diolefin}) \right] \qquad (3)$$
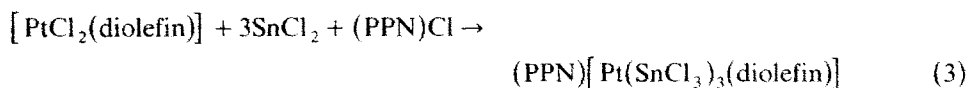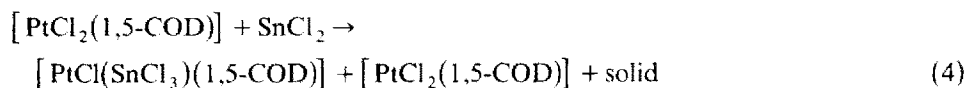
(IVa, diolefin = 1,5-COD; IVb, diolefin = NBD)

Five-coordinate Pd^{II} and Pt^{II} complexes can be obtained from the monomeric $[MCl_2(\text{diolefin})]$ compounds (eq. 3) by the method used for the Rh^I and Ir^I complexes; however, the $[Pd(SnCl_3)_3(1,5\text{-COD})]$-anion proved difficult to isolate and was identified via its ^{119}Sn NMR and ^{13}C characteristics. Solutions of this material were found to be unstable, and to slowly precipitate palladium metal. The complex $(PPN)[Pt(SnCl_3)_3(CO)_2]$ was prepared by passing a CO stream through a solution of IVa. All of the isolable anionic complexes are air-stable solids, moderately soluble in CH_2Cl_2 and $CHCl_3$. The number of coordinated tin atoms was determined by the ratio of ^{119}Sn to ^{117}Sn satellites in their ^{119}Sn and ^{195}Pt and ^{13}C NMR spectra (see below) [17]. Interestingly, the presence of the π-acceptors CO, $C\equiv N(\text{cyclohexyl})$ and diolefin is not incompatible with that of several coordinated $SnCl_3$ ligands.

The reaction of $[RhCl(\text{diolefin})]_2$ with $SnCl_2$ and $(PPN)Cl$ (eq. 1) presumably leads to bridge splitting, during (or after) which the tin ligand coordinates to rhodium. In the hope of intercepting mono- and/or bis-trichlorostannato intermediates we studied this reaction with less than the stoichiometric amounts of $SnCl_2$, but for neither Rh^I nor Ir^I were we successful in characterizing such complexes. The ^{119}Sn NMR spectra of a mixture of $[RhCl(1,5\text{-COD})]_2$ and one equivalent of $SnCl_2$ per rhodium show resonances for the $[Rh(SnCl_3)_3(1,5\text{-COD})]^{2-}$ anion and a broad, poorly defined signal, $\delta(^{119}Sn) = 5$ ppm. Obviously the various equilibria favor the formation of the tris $SnCl_3$ complex, in keeping with the recognized tendency of this ligand to stabilize five-coordination [3a,b,18,19,20].

Reaction of $[PtCl_2(1,5\text{-COD})]$ with one equivalent of $SnCl_2$ in CH_2Cl_2, on the other hand (eq. 4), affords a suspension, whose filtrate clearly shows resonances attributable to the mono $SnCl_3$ complex $[PtCl(SnCl_3)(1,5\text{-COD})]$ (V) $\delta(^{119}Sn) = -115.8$ ppm, $^1J(^{195}Pt, ^{119}Sn) = 25,964$ Hz, $\delta(^{195}Pt) = -3758$, $\delta(^{13}C) = 122.2$, 90.1 ppm, together with signals derived from the unreacted starting material $[PtCl_2(1,5\text{-COD})]$. This reaction is not straightforward in that in acetone solution the diolefin is set free. Further studies on olefin complexes are in progress.

$$\left[PtCl_2(1,5\text{-COD}) \right] + SnCl_2 \rightarrow$$

$$\left[PtCl(SnCl_3)(1,5\text{-COD}) \right] + \left[PtCl_2(1,5\text{-COD}) \right] + \text{solid} \qquad (4)$$

b. MonoSnCl$_3$ five-coordinate complexes

Given our interest in the tris $SnCl_3$ compounds, we sought additional related complexes for the purposes of comparison. Complexes of the form $[M(SnCl_3)(\text{di-olefin})_2]$, $M = Rh$, Ir, are well known; indeed the solid state structure for $[Ir(SnCl_3)(1,5\text{-COD})_2]$ (VIa) was reported in 1967 [3a]. We find this type of compound is readily obtained through reaction of the corresponding dimeric complex with $SnCl_2$ and excess olefin (e.g. eq. 5).

$$\left[IrCl(1,5\text{-COD}) \right]_2 + 2SnCl_2 + \text{xs } 1,5\text{-COD} \rightarrow 2\left[Ir(SnCl_3)(1,5\text{-COD})_2 \right] \qquad (5)$$

This complex can also be prepared by treating the tris $SnCl_3$ complex Ia with excess diolefin.

Of some interest is the mixed olefin complex [Ir(SnCl$_3$)(NBD)(1,5-COD)], which can be prepared by reaction of the 1,5-COD dimer with SnCl$_2$ and excess NBD. The presence of two different chelating diolefins is shown by the microanalytical, ^{1}H and ^{13}C spectroscopic data. It is certain that only the norbornadiene molecule is coordinated. These mono SnCl$_3$ are useful models in the discussion of the spectroscopy which follows.

2. NMR spectroscopy

a. ^{119}Sn NMR spectroscopy

^{119}Sn NMR spectroscopy is a most valuable aid in this chemistry. Of the three isotopes with $I = 1/2$, ^{119}Sn, ^{117}Sn and ^{115}Sn, only the first two are sufficiently abundant, 8.6% and 7.6% respectively, to be readily observable. For our "M(SnCl$_3$)$_3$," complexes we can expect compounds in which there are significant quantities of both ^{119}Sn and ^{117}Sn and these isotopomers reveal signals due to tin–tin spin-spin coupling in the spectra of both of these nuclei. The relative intensities of these lines are important. Rudolph et al. [17] have considered the relevant statistics, which reveal that the ^{117}Sn satellites will be 4.1 and 8.2% of the main ^{119}Sn signal for complexes with two and three coordinated Sn atoms, respectively. Consequently, with good signal-to-noise ratios, the distinction between bis- and tris-SnCl$_3$ complexes is readily made, and allows us to be certain of the complex composition with respect to tin. Naturally, the mono SnCl$_3$ complexes show no satellites in their ^{119}Sn spectra.

The ^{119}Sn NMR characteristics for our complexes are listed in Table 2. The tin resonances span the range from $\delta = +156.7$ to -292.9 ppm with the iridium complexes appearing at higher field than the rhodium analogs. This dependence on the central metal is a common observation for many ligating nuclei, including ^{31}P and ^{13}C [21], and it has also been found for the ^{119}Sn resonances of Pd^{II} and Pt^{II} SnCl$_3$ complexes [5] and a variety of SnMe$_3$ complexes [22].

We do not find any general obvious connection between $\delta(^{119}$Sn) and the remaining coordinated ligands. Specifically, we note that substitution of CO or C≡N(cy) for a diolefin in the rhodium complexes, is associated with a downfield shift, but this is not the case for the Pt^{II} complexes. Despite the lack of generality there are a few interesting variations in $\delta(^{119}$Sn); e.g. the nature of the olefin plays a role and thus $\delta(^{119}$Sn) for [Ir(SnCl$_3$)(NBD)$_2$] is -226.6 ppm and successive replacement of NBD by 1,5-COD induces upfield shifts of 39.6 and 26.7 ppm. Moreover, whereas $\delta(^{119}$Sn) does not vary very much with the olefin (< 17 ppm) for the complexes [Rh(Sn(Cl$_3$)$_3$(diolefin)]$^{2-}$, for the [Pt(SnCl$_3$)$_3$(diolefin)]$^-$ compounds $\Delta\delta$ is > 77 ppm. Despite these observations, it is probably too soon to assess the utility of this NMR parameter.

The various coupling constants to ^{119}Sn, however, are somewhat more revealing. The values $^1J(^{103}$Rh, ^{119}Sn) vary from 513 to 983 Hz, and while we find no correlation between these and either $\delta(^{119}$Sn) or another easily recognizable ligand characteristic, we note: a) in the series [Rh(SnCl$_3$)$_3$(diolefin)]$^{2-}$, the value $^1J(^{103}$Rh, ^{119}Sn) increases in the order DCP (597 Hz) < COD (651 Hz) < NBD (758 Hz) and b) that substitution of the diolefin by either CO (864 Hz) or cyclohexyl isonitrile (983 Hz) also results in an increase in this parameter. The difference of 107 Hz in $^1J(^{103}$Rh, ^{119}Sn) between the 1,5-COD and NBD complexes is noteworthy in that for

TABLE 2

METAL NMR DATA [a] FOR THE COMPLEXES

Compound	$\delta(^{119}Sn)$	$^2J(^{119}Sn, ^{117}Sn)$	$^1J(^{103}Rh, ^{119}Sn)$	$^1J(^{195}Pt, ^{119}Sn)(\delta(^{195}Pt))$
(PPN)₂[Rh(SnCl₃)₃(NBD)][b]	38.8	2,411	758	
(PPN)₂[Rh(SnCl₃)₃(1,5-COD)][b]	25.7	1,681	651	
(PPN)₂[Rh(SnCl₃)₃(DCP)][c]	22.3	1,685	597	
(PPN)₂[Rh(SnCl₃)₃(CN(cy))₂]	50.2	13,513	986	
(PPN)₂[Rh(SnCl₃)₃(CO)₂][b]	89.1	9,341	864	
(PPN)₂[Ir(SnCl₃)₃(1,5-COD)][b]	−216.5	1,513		
(PPN)₂[Ir(SnCl₃)₃(NBD)]	−268.7	1,502		
[Rh(SnCl₃)(NBD)₂][b]	156.7		845	
[Ir(SnCl₃)(NBD)₂][b]	−226.6			
[Ir(SnCl₃)(1,5-COD)₂][b]	−292.9			
[Ir(SnCl₃)(NBD)(1,5-COD)][b]	−266.2			
(PPN)[Pt(SnCl₃)₃(NBD)][e]	−209.8	697		16,453 (−5408)
(PPN)[Pt(SnCl₃)₃(1,5-COD)][c]	−132.5	619		13,840 (−5402)
(PPN)[Pt(SnCl₃)₃(CO)₂][e]	−144.8	5,736		14,678 (−5687)
[PtCl(SnCl₃)(1,5-COD)][c]	−115.8			25,964 (−3758)
[PtCl₂(1,5-COD)][b]				(−3336)
(PPN)[Pd(SnCl₃)₃(1,5-COD)][c]	33.2	1,092		

[a] Chemical shifts in ppm, relative to Me₄Sn and Na₂PtCl₆ (negative sign indicates a high field shift with respect to reference). Coupling constants in Hz. [b] CDCl₃, RT. [c] CH₂Cl₂/CDCl₃, RT. [d] Acetone-d₆, 233 K. [e] CDCl₃, 223 K. ¹⁹⁵Pt chemical shifts relative to Na₂PtCl₆(ap). A negative sign signifies an upfield shift.

the complexes $[Pt(SnCl_3)_3(diolefin)]^-$ a similar effect on $^1J(^{195}Pt, ^{119}Sn)$ is observed. For 1,5-COD $^1J(^{195}Pt, ^{119}Sn)$ is 13,840 Hz, whereas in NBD the value is increased to 16,453 Hz. The ratios of these numbers (0.84 in the Rh case, 0.86 in the Pt example) are similar, suggesting that each olefin binds to the transition metal in a characteristic way.

The magnitudes of both of these one-bond metal–tin coupling constants are reasonable when compared with the literature values; e.g. 547–864 Hz for $^1J(^{103}Rh, ^{119}Sn)$ [15,16], 2,500–35,000 Hz for $^1J(^{195}Pt, ^{119}Sn)$ [4,5,7,23,24,25,26]. Interestingly, $^1J(^{195}Pt, ^{119}Sn)$ for $[PtCl(SnCl_3)(1,5\text{-}COD)]$ at 25,964 Hz lies between the values for *trans*-$[PtCl(SnCl_3)(PEt_3)_2]$, 29,077 Hz [5], and *trans*-$[Pt(SnCl_3)_2(PEt_3)_2]$, 23,517 Hz [5]. Combining the new data with earlier results [5,25], we can now derive a *trans* influence series, based on $^1J(^{195}Pt, ^{119}Sn)$ in which H > P > As > SnCl$_3$ > 1,5-COD > Cl. Thus, the SnCl$_3$ ligand, appears as a moderate σ-donor using this spin-spin interaction as probe although it is thought to exercise a sizeable *trans* effect [27,28].

The most interesting coupling constant is certainly $^2J(^{119}Sn, ^{117}Sn)$. This homonuclear spin-spin interaction derives from isotopomers in which one molecule has both ^{117}Sn and ^{119}Sn nuclei, and is readily measured in the ^{119}Sn spectrum. In our anions this parameter varies between 619 Hz to 13,513 Hz, although much larger values are known [5,8]. We have no theoretical explanation for these values at present, but we note once again that the changes within a group of compounds are informative. For the Rh^I complexes I and II, the values go from 1681 Hz to 13,513 Hz; with IIb > IIa and both of these ≫ Ia–Ic.

Given that the values $^1J(^{103}Rh, ^{119}Sn)$ and $^1J(^{195}Pt, ^{119}Sn)$ do not vary as much, it seems unlikely that an individual Rh–Sn bond, as characterized by the *s*-coefficients of the atomic orbitals which comprise the complex molecular orbitals, are responsible for this ≃ 9-fold change. (We assume that accepted theory is relevant for $^2J(^{119}Sn, ^{117}Sn)$ [21]). Moreover, since we observe only one ^{119}Sn resonance for our trisSnCl$_3$ complexes, we can exclude structures (and therefore reasoning based on them) associated with having two tin atoms *trans* to one another ($^2J(^{119}Sn, ^{117}Sn)_{trans}$ is ≫ $^2J(^{119}Sn, ^{117}Sn)_{cis}$ [5]). It seems plausible that both differing electronic and geometric effects may be responsible for the observed differences. Specifically, the relatively large value for $(PPN)_2[Rh(SnCl_3)_3(C\equiv Ncy)_2]$ suggests a different geometry for this molecule, relative to the olefin complexes. The two isonitrile ligands, as somewhat stronger σ-donors, might well occupy the apical positions of a trigonal bipyramid [29] thus placing the Sn atoms in the equatorial plane (as is known for the $[Pt(SnCl_3)_3(AsMe_3)_3]^-$ ion [4]. Preference of SnCl$_3$ for the equatorial position is in keeping with its characteristics as a weak σ-donor and a π-acceptor [29].
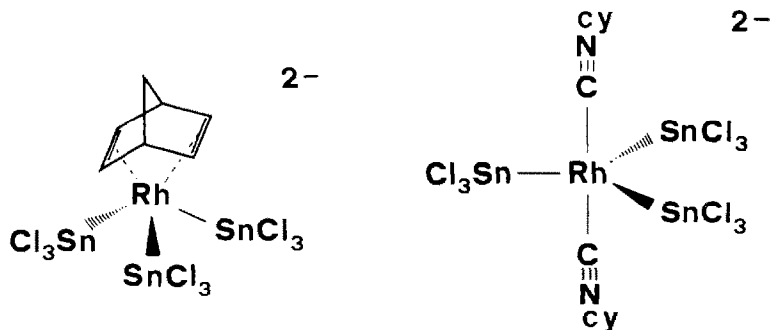
TABLE 3

^{13}C NMR DATA[a] FOR THE COMPLEXES[b]

Compound	$\delta(^{13}C)$	$^{1}J(^{103}Rh, {}^{13}C)$	$^{1}J(^{195}Pt, {}^{13}C)$	$^{2}J(^{119,117}Sn, {}^{13}C)$
(PPN)$_2$[Rh(SnCl$_3$)$_3$(NBD)][c]	61.13	4.7		50.1
(PPN)$_2$[Rh(SnCl$_3$)$_3$(1,5-COD)][c]	78.29	8.3		30.3
(PPN)$_2$[Rh(SnCl$_3$)$_3$(DCP)][d]	90.65; 78.87; 73.71; 61.15	7.4; 9.2		33.3; 22.2
(PPN)$_2$[Rh(SnCl$_3$)$_3$(CO$_2$)][c]	194.8	48.8		131.8
(PPN)$_2$[Ir(SnCl$_3$)$_3$(1,5-COD)][c]	61.27			34.6
(PPN)$_2$[Ir(SnCl$_3$)$_3$(NBD)][c]	64.03			29.6
[Rh(SnCl$_3$)(NBD)$_2$][c]	61.81; 51.56	5.54; 7.40		
[Ir(SnCl$_3$)(NBD)$_2$][c]	64.63; 48.59			
[Ir(SnCl$_3$)(1,5-COD)$_2$][c]	83.82; 73.04			
[Ir(SnCl$_3$)(NBD)(1,5-COD)][c]	80.70; 68.98; 64.86; 47.94			
(PPN)[Pt(SnCl$_3$)$_3$(NBD)][a]	56.2		58	58
(PPN)[Pt(SnCl$_3$)$_3$(1,5-COD)][c]	92.6		91	33
[PtCl(SnCl$_3$)(1,5-COD)]	122.2; 90.1			
(PPN)[Pd(SnCl$_3$)$_3$(1,5-COD)]	113.7			

[a] Chemical shifts in ppm, relative to TMS. Coupling constants in Hz. [b] Only for olefinic or carbonyl carbon atoms. [c] CDCl$_3$, RT. [d] CD$_2$Cl$_2$/CDCl$_3$, RT. [e] CDCl$_3$, 223 K.

For the olefin complexes we have already noted differences in $^1J(^{103}Rh, ^{119}Sn)$, and $^1J(^{195}Pt, ^{119}Sn)$ between NBD and the other olefins, and our tin–tin J data confirm this. Given that two-bond tin–tin couplings can be $> 35,000$ Hz, the value of 619 Hz in (PPN)[Pt(SnCl$_3$)$_3$(COD)] is interesting in that it is the smallest of its kind observed to date.

b. ^{13}C and ^{195}Pt NMR spectroscopy

^{13}C chemical shift data and coupling constants are listed in Table 3, and inspection reveals that:

a) The ^{13}C positions of the two olefin resonances in [PtCl(SnCl$_3$)(COD)] (V) differ by 32.1 ppm.

b) There are a total of 5 NBD and 4 COD ^{13}C signals in the room temperature spectra of [Ir(SnCl$_3$)(NBD)$_2$] and [Ir(SnCl$_3$)(1,5-COD)$_2$], respectively.

c) The five-coordinate tris SnCl$_3$ complexes show ^{13}C coordination chemical shifts which are similar in magnitude to those of the starting chloro complexes; however, the monoSnCl$_3$ complexes show smaller $\Delta\delta$ values.

d) The ^{195}Pt coordination chemical shifts ($\delta(^{195}$Pt)chloro-complex) – ($\delta(^{195}$Pt)-trichlorostannato complex) are in keeping with the literature [7,25], i.e. there is an upfield shift of several hundred ppm on going from Pt–Cl to Pt–SnCl$_3$.

Point a) may be related to the geometry of the complex. Presumably, in the square planar complex the usual *trans* influence operates with the result that the double bond *trans* to SnCl$_3$ does not coordinate as strongly as that *trans* to Cl. The ^{13}C coordination chemical shifts (δ ligand – δ complex) for V are 6.3 and 38.4 ppm, respectively, with the former in marked contrast to what is found for a complex such as [PtMe$_2$(COD)], $\Delta\delta = 29.5$ ppm [30]. This small $\Delta\delta$ value of 6.3 suggests that the SnCl$_3$ labilizes the olefin. A weakening of the olefin–platinum bond is consistent with the absence of reports of planar complexes of platinum containing SnCl$_3$ *trans* to a monodentate olefin. Indeed, we have already mentioned that V was not observed in acetone solution, suggesting that only minor modification of the reaction conditions can lead to olefin substitution. It is interesting that this ^{13}C NMR information is complemented by the relatively large $^1J(^{195}Pt, ^{119}Sn)$ value, showing that the SnCl$_3$ is firmly attached to the metal.

Point b) is related to the apparent lower symmetry of VIa (and VIb and its rhodium analog).
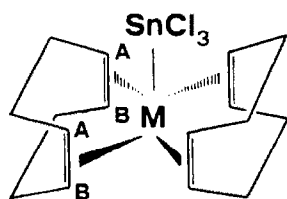
(a)
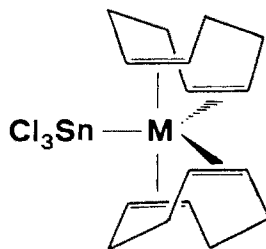
(b)

This could result, in part, from a trigonal bipyramidal structure such as shown for (b) * and thus Venanzi and co-workers [3a] have observed different Ir–C distances for the axial and equatorial coordinated olefins. However, given the low activation energy for Berry and "turnstile" rearrangements, in five-coordinate complexes [31] we feel it unlikely that our data represent a static situation on the NMR time scale. Rather, we feel that an "average" structure, such as (a) in which the sites A and B differ by virtue of their proximity to $SnCl_3$, is more appropriate. Alternatively, structure (b) in which there is an axial–equatorial fluxionality at room temperature, but in which the A and B sites maintain their position relative to $SnCl_3$, is also acceptable. In any case, the lower symmetry is observable at room temperature, no matter what its source.

Experimental

The olefins and solvents were obtained from Fluka AG, Buchs, Switzerland, and were "pro analysi". All reactions were carried out under N_2. The complexes [MCl(diolefin)]$_2$, M = Rh, Ir, diolefin = COD, (1,5-cyclooctadiene), NBD (norbornadiene) and DCP (dicyclopentadiene) were prepared according to the literature [32], as were the compounds [PtCl$_2$(diolefin)] [33] and [Ir(SnCl$_3$)(NBD)$_2$] [10]. NMR spectra were measured in 10 mm tubes (5 mm for ^{1}H NMR) using a Bruker WM-250 operating at 101.3 MHz for ^{31}P, 93.3 MHz for ^{119}Sn, 62.9 MHz for ^{13}C and 53.77 MHz for ^{195}Pt. Solvents, temperatures and experimental errors are given in the Tables. IR spectra were measured as KBr pellets using a Beckmann IR 4250 instrument. Microanalytical data are from the E.T.H. Zentrum, Zürich. Bis-triphenylphosphineimine [(PPh$_3$)$_2$N]Cl=(PPN)Cl was prepared according to the literature [34].

Preparation of (PPN)$_2$[Rh(SnCl$_3$)$_3$(COD)]
Solid anhydrous tin(II) chloride (0.683 g, 3.60 mmol) was added to a suspension of [RhCl(COD)]$_2$ (0.296 g, 0.600 mmol) in 20 ml acetone. Stirring for 10 minutes was followed by the addition of (PPN)Cl (1.380 g, 2.40 mmol) in a mixture of 20 ml acetone and 5 ml methylene chloride. The resulting red solution was concentrated to approximately half its volume by passing N_2 over the solution, then treated with 10 ml MeOH and cooled to ~ 0°C with an ice bath. The deep red crystalline solid which precipitated was filtered and dried in vacuum (2.195 g, 93.2%).
The following were prepared in an identical manner:
(PPN)$_2$[Rh(SnCl$_3$)$_3$(NBD)], from 0.277 g complex we obtain 2.299 g (98.4%) of product.
(PPN)$_2$[Rh(SnCl$_3$)$_3$(DCP)], from 0.054 g complex we obtain 0.359 g (90.3%) of product.
(PPN)$_2$[Ir(SnCl$_3$)$_3$(COD)], from 0.134 g complex we obtain 0.793 g (96.5%) of product.

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* If (b) is the correct static structure we expect four olefinic resonances, arising from non-equivalent olefins and SnCl$_3$ proximity effects.

Preparation of (PPN)₂[Rh(SnCl₃)₃(C≡N(cyclohexyl))₂]

A solution of (PPN)₂[Rh(SnCl₃)₃(NBD)] (0.195 g, 0.100 mmol) in 2 ml CH₂Cl₂ was treated with 2 ml of a 0.10 *M* solution of C≡N(cyclohexyl) in acetone. Concentration to ≃ 2 ml in a nitrogen stream was followed by the slow addition of 10 ml of an acetone/ether (40/60) solution such that the layers mixed slowly. After standing for two days at −20°C the red-brown solid was filtered off and dried in vacuum (0.148 g, 71%).

Preparation of [Rh(SnCl₃)(NBD)₂]

A suspension of [RhCl(NBD)]₂ (0.046 g, 0.100 mmol) in 4 ml EtOH was treated first with solid tin(II) chloride (0.070 g, 0.37 mmol) and then 2 ml neat NBD. A yellow crystalline solid separated immediately. This was filtered off, washed with EtOH to remove excess tin(II) chloride and then dried in vacuum (0.082 mg, 80%).

The complex [Ir(SnCl₃)(COD)₂] was prepared in a similar way. From 0.067 g of dimer 0.118 g (93%) of product was obtained.

The complex [Ir(SnCl₃)(COD)(NBD)] was prepared from [IrCl(COD)]₂ as described above, except that an excess of NBD was added after the tin(II) chloride. From [IrCl(COD)]₂ (0.067 g, 0.100 mmol) with 0.37 mmol tin(II) chloride and 2 ml neat NBD, 0.106 g (86%) of product was obtained.

Preparation of (PPN)₂[Ir(SnCl₃)₃(NBD)]

A solution of [Ir(SnCl₃)(NBD)(COD)] (0.062 g, 0.100 mmol) in 4 ml CH₂Cl₂ was treated with solid tin(II) chloride (0.038 g, 0.200 mmol) and (PPN)Cl (0.115 g, 0.200 mmol). After stirring for 10 days the resulting yellow solution was concentrated to approximately half its volume and treated with 10 ml of an acetone/ether (40/60) solution. The resulting yellow solid was filtered off and dried in vacuum (0.140 g, 69%).

Preparation of (PPN)₂[Rh(SnCl₃)₃(CO)₂]

A solution of (PPN)₂[Rh(SnCl₃)₃(COD)] (0.196 g, 0.10 mmol) in 5 ml CH₂Cl₂ was treated with gaseous CO for 20 min after which the solution was evaporated and the product dried in vacuum (0.125 g, 91.6%).

Preparation of [Ph₄As][Pt(SnCl₃)₃(COD)]

Anhydrous tin(II) chloride (57 mg, 0.30 mmol) was added to a solution of [PtCl₂(COD)] (38 mg, 0.70 mmol) and [Ph₄As]Cl (42 mg, 0.10 mmol) in 4 ml CH₂Cl₂. Stirring for one hour was followed by filtration. To the clear red filtrate was carefully added a 1 : 2 mixture of benzene and petroleum ether (30–60°C) such that the two phases remained immiscible. Storage at −20°C for one week led to slow precipitation of the product (118 mg, 87%). The following were prepared in the same way:

[PPN][Pt(SnCl₃)₃(COD)],   115 mg   (76%)

[Et₄N][Pt(SnCl₃)₃(COD)],   104 mg   (94%)

[Ph₄As][Pt(SnCl₃)₃(NBD)],   116 mg   (86%)

[PPN][Pt(SnCl₃)₃(NBD)],   109 mg   (73%).

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