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Platinum Hydride Complexes Containing the Trichlorostannane Ligand: an Unusually Large Tin–Hydrogen Coupling Constant

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The chemistry of hydride complexes of platinum has attracted new interest since the recognition that these derivatives may be intermediates in the hydrogenation of unsaturated organic molecules. In particular, platinum–phosphine complexes in conjunction with tin(II) dichloride have been shown to homogeneously catalyse both the hydrogenation [1] and hydroformylation reactions [2].

We have recently reported synthetic and NMR spectroscopic results demonstrating that the complexes *cis* and *trans*-$[PtCl_2(PR_3)_2]$, R = an alkyl, aryl or alkoxy group, react with tin(II) dichloride to form the complexes $\{PtCl(SnCl_3)Pr_3)_2\}$, I [3]. A similar reaction has been reported for the complexes *trans*-$\{PtHCl(PR_3)_2\}$, R = Et, Ph, to produce *trans*-$\{PtH(SnCl_3)(PR_3)_2\}$, II, although no hydride ^1H NMR data for these molecules have been reported [4]. We find these trichlorostannane hydride complexes give broad or no observable ^{31}P NMR and ^1H hydride signals under normal measuring conditions and that temperatures between −50° and −70 °C are required to obtain satisfactory spectra. The cooled samples afford ^1H and $^{31}P[^1H]$ spectra which contain signals stemming from the coupling of these nuclei to the isotopes ^{117}Sn (I = 1/2, natural abundance, 7.6%) and ^{119}Sn (I = 1/2 natural abundance, 8.6%). The approximately 1700 Hz two-bond tin–hydride couplings in the triphenyl phosphine and dibenzylphenyl phosphine complexes (see Table) are unusual and represent the largest two-bond coupling involving a proton ever to be reported. The ratio of the observed ^{119}Sn to ^{117}Sn couplings is 1.046 and corresponds, within experimental error, to the quotient of their gyromagnetic ratios. Typical values for the coupling of tin to hydrogen through carbon, fall between 50 and 125 Hz [5]. We presume that our extreme values stem partially from the *trans*-orientation of these two atoms [6] and partially from the presence of the three strongly electron withdrawing chlorine atoms on tin $\{(^2J(^{119}Sn{-}C{-}H)$ in $CH_3{-}Sn(CH_3)_3 = 51.5$ Hz; $^2J(^{119}SN{-}C{-}H)$ in $CH_3{-}SnCl_3 = 125.4$ Hz$\}$ [5].

TABLE. NMR Data[a] for the Trichlorostannane Platinum Complexes.

	trans-$[PtH(SnCl_3)(PPh_3)_2]$	*trans*-$[PtH(SnCl_3)(PPh_2Bz)_2]$
δ^1H(hydride)	−8.77	−9.73
^1J(Pt, H)	1294	1308
^2J(Sn, H)	1663, 1740[b]	1650, 1731[b]
^2J(P, H)	9.3	5.1
$\delta^{31}P$	28.5	24.6
^1J(Pt, P)	2650	2713
^2J(Sn, P)	204, 213[b]	197[c]

[a] ^1H and ^{31}P chemical shifts are in ppm relative to TMS and H_3PO_4, respectively, at room temperature. Coupling constants are in Hz. ^1H spectra were measured in CD_2Cl_2 solutions at −70° whereas the ^{31}P spectra were measured in $CDCl_3/CH_2Cl_2$ mixtures at −60°. [b] ^{117}Sn and ^{119}Sn coupling constants, respectively. [c] Average of ^{117}Sn and ^{119}Sn couplings to phosphorus.

The values ^2J(Sn, P) (see Table) are in good agreement with those found for the complexes I [3].

The presence of the tin satellites in the ^1H and ^{31}P spectra confirms that the $SnCl_3^-$ ligand is bound to platinum in solution and not merely present as counterion. The dynamic character of this type of complex on the NMR time scale is in keeping with the observation that the addition of $SnCl_2$ to metal complexes facilitates coordination of unsaturated organic molecules [7]. We find that *trans*-$[PtH(SnCl_3)(PPh_2Bz)_2]$ reacts smoothly with $EtO_2C{-}C{\equiv}CO_2Et$ at room temperature to yield *trans*-$\{Pt(SnCl_3)(EtO_2C{-}C{=}CH(CO_2Et))(PPh_2Bz)_2\}$; $\delta^{31}P$ = 10.1 ppm; ^1J(Pt, P) = 2503 Hz; ^2J(P, Sn) = 259 Hz. A full report on this chemistry will appear later.

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