THE NATURE OF $Pt/SnCl_3^-$ SALTS IN SOLUTION BY MULTINUCLEAR NMR.

UNUSUALLY LARGE SPIN-SPIN COUPLING, CLUSTER SIZE, FLUXIONALITY, AND A CAVEAT.

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It was recently shown that even when tin envirnoments are averaged by intra-molecular rearrangement, the number of tin atoms in the molecule can be deduced from the ^{119}Sn NMR because of the fortuitous presence of $^{119}Sn-^{117}Sn$ coupling (1). We recently have extended these principles to an investigation of the platinum trichlorostannates which are effective homogeneous catalysts for a variety of reactions (2,3). A few examples are noteworthy at this time.

RESULTS AND DISCUSSION

The red, trigonal bipyramidal (3) $Pt(SnCl_3)_5^{3-}$ was found to have invariant ^{119}Sn and ^{195}Pt NMR spectra from 183 to 363K. Hence, $Pt(SnCl_3)_5^{3-}$ appears to be stereochemically nonrigid. The NMR data are (acetone-d_6): $\delta(^{119}Sn)$, -387 ppm (4) from external $SnMe_4$; $^1J(^{195}Pt,\ ^{119}Sn) = 16,024$ Hz; $^2J(^{119}Sn,\ ^{117}Sn) = 6,230$ Hz; $\delta(^{195}Pt)$ -6415 ppm (4) from external 0.1$\underline{M}$ Na_2PtCl_6; $^1J(^{195}Pt,\ ^{119}Sn) = 16,030$ Hz; $^1J(^{195}Pt,\ ^{117}Sn) = 15,312$ Hz.

The observation of spin coupling leads to two important conclusions, a) the dynamic process is intramolecular, and b) the relative intensities establish the $PtSn_5$ stoichiometry in solution. There is no NMR evidence for appreciable concentrations of $Pt(SnCl_3)_4^{2-}$, a possible catalytic intermediate (5).

Authentic samples of yellow (6) $[PtCl_2(SnCl_3)_2]^{2-}$ give yellow solutions with one pattern of the expected relative intensities for the $PtSn_2$ stoichiometry. The NMR data are (acetone-d_6): $\delta(^{119}Sn)$, -142 ppm (4) from external $SnMe_4$; $^1J(^{195}Pt,^{119}Sn) = 27,640$ Hz; $^2J(^{119}Sn,^{117}Sn) = 2485$ Hz; $\delta(^{195}Pt)$, -4701 from external 0.1$\underline{M}$ Na_2PtCl_6; $^1J(^{195}Pt,^{119}Sn)=27,635$ Hz; $^1J(^{195}Pt,^{117}Sn) = 26,400$ Hz. Red solutions of the supposed red isomer (6) of $[PtCl_2(SnCl_3)_2]^{2-}$ isolated from 3M HCl appear to be a mixture of red $[Pt(SnCl_3)_5]^{3-}$ and the yellow $[PtCl_2(SnCl_3)_2]^{2-}$

We find no other species of significant concentration in solution. Previous investigators (7) have suggested that the red solid $[PtCl_2(SnCl_3)_2]^{2-}$ is actually a mixture of yellow $[PtCl_2(SnCl_3)_2]^{2-}$ and red $[Pt(SnCl_3)_5]^{3-}$.

The magnitude of $J(^{195}Pt,\ ^{119}Sn)$ is unusually large in these anions. In

fact, square planar complexes involving Pt^{II} and SnCl$_3^-$ apparently afford the largest spin coupling constants known (8). The reduced coupling constant $[K_{AX} = J_{AX} \cdot (4\pi^2/\gamma_A\gamma_X h)]$ avoids any dependence on individual nuclear properties (9) and provides a more meaningful comparison of spin-spin interactions involving different atom pairs. In our case, $|K_{PtSn}| = 2,869$ nm^{-3}. Other large couplings have been observed previously, but nothing of this magnitude, even when given as a reduced constant. Some examples are [J(Hz) followed by K(nm^{-3})]

$^1J(^{199}Hg, {}^{31}P) = 12,970$, $|K| = 1492$ in HgOAc[PO(OEt)$_2$] (10);

$^1J(^{195}Pt, {}^{31}P) = 9,150$, $|K| = 875$ in Pt(triphos)P(OPh)$_3$ (11);

$^1J(^{107}Ag, {}^{31}P) = 756$, $|K| = 384$ in Ag[P(OEt)$_3$]$_2$ClO$_4$ (12);

$^1J(^{199}Hg, {}^{183}W) = 706$, $|K| = 798$ in [W(CO)$_3$(C$_5$H$_5$)]HgCl (13).

The usually accepted Fermi contact expression for spin-spin coupling (14) suggests that this coupling is large because of a high mutual polarisability of the s-orbitals on Pt and Sn, a high s-character in the bond, and the relatively large gyromagnetic constants of Sn and Pt.

The observation of a full spectrum when such large spin couplings are present can afford some difficulty and a caveat is appropriate. For instance, if the center of the ^{195}Pt signal (15) is placed at the mid-point of a 20 KHz window on a FT instrument with quadrature detection, the ^{119}Sn and ^{117}Sn satellites for J(Pt,Sn) > 20 KHz are outside the spectral window but can appear as foldover depending on the cutoff of the filter and the magnitude of J. In the case of such a ^{195}Pt spectrum, a check of the ratio J(^{117}Sn,^{195}Pt)/ J(^{119}Sn,^{195}Pt) against the ratio of the respective gyromagnetic constants (.956) reveals the error. However, the corresponding ^{119}Sn spectrum (15) has only one set of satellites which would give a false J(^{195}Pt, ^{119}Sn) for J's > 20 KHz. Therefore, in cases where there is no check on the basis of gyromagnetic constants, the center of the signal should be offset from the center of the spectral window to see if peak separations within the apparent multiplet remain invariant.

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