

**Multinuclear NMR Investigations of Bis- $\mu$ -[bis-(diphenylphosphino)methane] bis(trichlorostannio)-diplatinum(Pt–Pt) and Bis- $\mu$ -[bis(diphenylphosphino)methane] chloro(trichlorostannio)diplatinum(Pt–Pt); Observation of the Largest Recorded  $^3J$  Coupling Constant**

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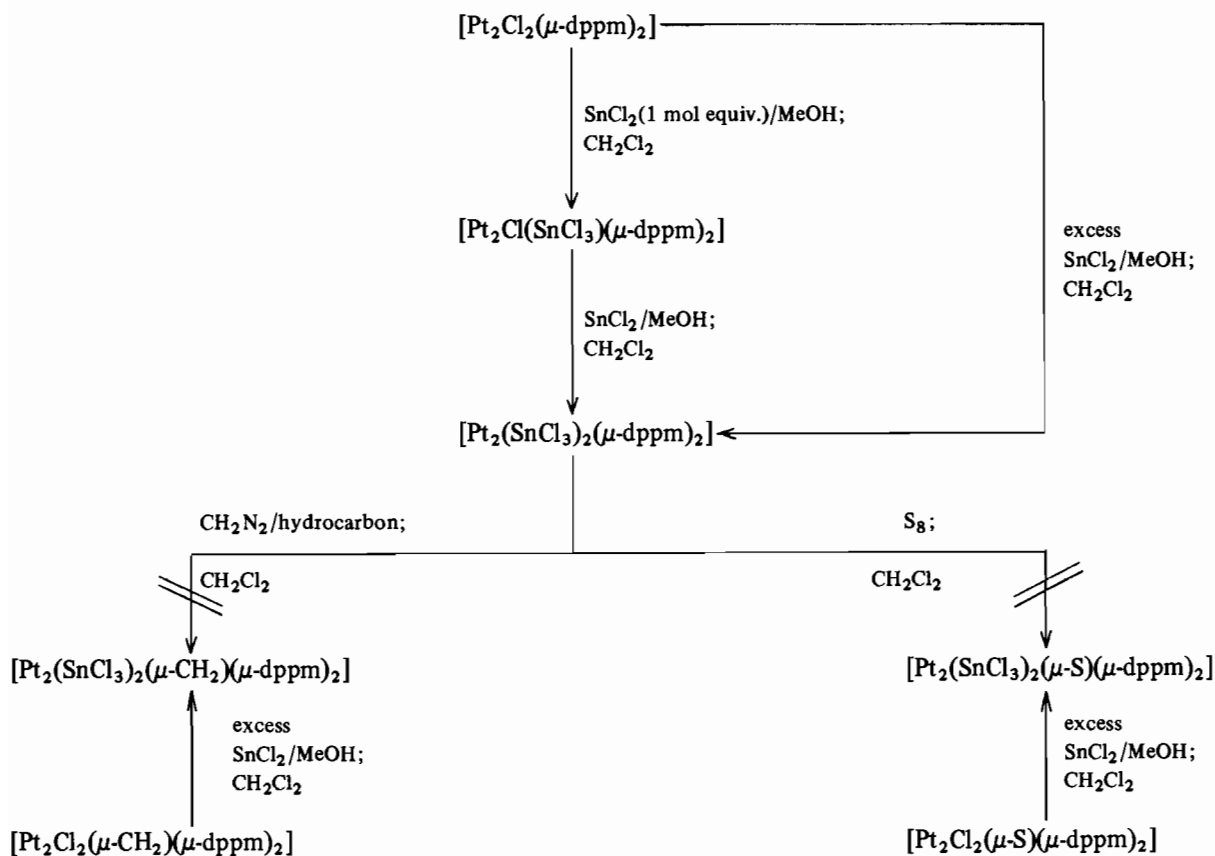
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A number of trichlorostannio derivatives of platinum(II) are known, and have been shown to be highly selective hydroformylation catalysts [1], and also to

be active in the water gas shift reaction [2]. No trichlorostannio derivatives of platinum(I) have as yet been prepared. The palladium(I) complex  $[\text{Pd}_2\text{Cl}(\text{SnCl}_3)(\mu\text{-dppm})_2]$  (ddpm = bis(diphenylphosphino)methane) has been reported and characterised crystallographically, but attempts to isolate  $[\text{Pd}_2(\text{SnCl}_3)_2(\mu\text{-dppm})_2]$  were unsuccessful [3]. We report here the successful preparation isolation and characterisation of the complexes  $[\text{Pt}_2(\text{SnCl}_3)_2(\mu\text{-dppm})_2]$ ,  $[\text{Pt}_2\text{Cl}(\text{SnCl}_3)(\mu\text{-dppm})_2]$  and  $[\text{Pt}_2(\text{SnCl}_3)_2(\mu\text{-X})(\mu\text{-dppm})_2]$  (X = CH<sub>2</sub> or S), and comment on some intriguing features of their chemistry and spectroscopic behaviour.

The preparations of the complexes  $[\text{Pt}_2(\text{SnCl}_3)_2(\mu\text{-dppm})_2]$  and  $(\text{Pt}_2\text{Cl}(\text{SnCl}_3)(\mu\text{-dppm})_2)$  are detailed in the Scheme. In contrast to the palladium system, no difficulty was experienced in the isolation of the bis(trichlorostannio) derivative, and the major experimental problem proved to be the isolation of the mono(trichlorostannio) derivative free from either  $[\text{Pt}_2\text{Cl}_2(\mu\text{-dppm})_2]$  or  $[\text{Pt}_2(\text{SnCl}_3)_2(\mu\text{-dppm})_2]$ . As indicated in the Scheme,  $[\text{Pt}_2(\text{SnCl}_3)_2(\mu\text{-dppm})_2]$  shows very little reactivity towards such reagents as sulphur or diazomethane in comparison with  $[\text{Pt}_2\text{Cl}_2$

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Scheme. The syntheses of some trichlorostannio derivatives of platinum.

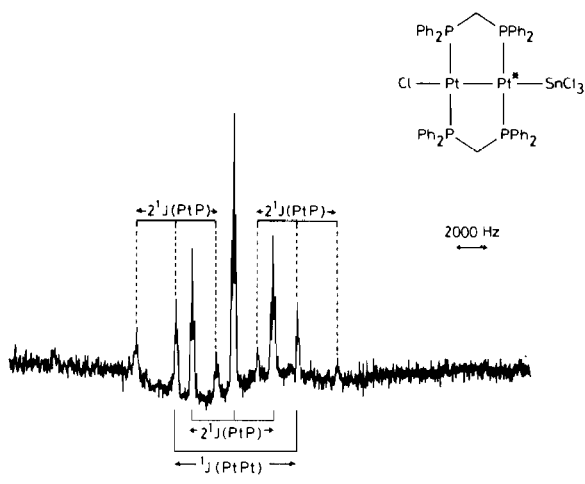


Fig. 1.  $^{195}\text{Pt}$   $\{^1\text{H}\}$  NMR spectrum (53.5 MHz) of  $[\text{Pt}_2\text{Cl}(\text{SnCl}_3)(\mu\text{-dppm})_2]$  in  $\text{CD}_2\text{Cl}_2$  solution at ambient probe temperature, showing the high field signal due to the platinum (marked by an asterisk) which is directly bonded to the trichlorostannio group. Each major peak appears as a triplet due to  $^2J(\text{PtP})$  coupling.

$(\mu\text{-dppm})_2$  [4]. This lack of reactivity, however, cannot be attributed to product instability, as the complexes  $[\text{Pt}_2(\text{SnCl}_3)_2(\mu\text{-X})(\mu\text{-dppm})_2]$  ( $\text{X} = \text{CH}_2$  or  $\text{S}$ ) are readily prepared by treatment of  $[\text{Pt}_2\text{Cl}_2(\mu\text{-X})(\mu\text{-dppm})_2]$  in dichloromethane with anhydrous  $\text{SnCl}_2$  in methanol. Rather, the lack of reactivity of  $[\text{Pt}_2(\text{SnCl}_3)_2(\mu\text{-dppm})_2]$  may be attributed to steric hindrance created by the distortion of the bridging ligands by the bulky  $\text{SnCl}_3$  groups, thus restricting access of even small molecules to the metal-metal bond.

The complexes  $[\text{Pt}_2(\text{SnCl}_3)_2(\mu\text{-dppm})_2]$  and  $[\text{Pt}_2(\text{SnCl}_3)_2(\mu\text{-dppm})_2]$  have been investigated by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ ,  $^{117}\text{Sn}$ ,  $^{119}\text{Sn}$  and  $^{195}\text{Pt}$  NMR spectroscopy using JEOL FX90Q, Bruker WH-400 and Bruker WM-250 spectrometers. The analyses of such spectra and the isotopomer distributions in such molecules are complicated, but routine, and details of such analyses are available elsewhere [5]. However, some features of the spectroscopic study are worthy of special comment. The  $^{195}\text{Pt}$  spectrum of  $[\text{Pt}_2\text{Cl}(\text{SnCl}_3)(\mu\text{-dppm})_2]$  (see Fig. 1) represents one of the first [6, 7] direct observations of  $^1J(\text{PtPt})$  in an unsymmetrical dimeric complex. It is perhaps surprising, at first sight, that with a chemical shift difference of 1043 ppm (*ca.* 56000 Hz) and a  $^1J(\text{PtPt})$  value of 8200 Hz this system is AB and not AX. Moreover, the  $^{119}\text{Sn}$  NMR spectrum for this complex yielded values of  $^1J(\text{PtSn})$  and  $^2J(\text{PtSn})$  of 11750 and 9670 Hz. As has been found previously [5] for  $[\text{Pt}_2\text{L}_2(\mu\text{-dppm})_2]^{2+}$  ( $\text{L} =$  various phosphine ligands), the linear  $\text{L}-\text{Pt}-\text{Pt}-\text{L}$  skeleton is ideally arranged for the transmission of large coupling across a metal-metal bond. This is more than amply demonstrated by the  $^{117}\text{Sn}$  and

$^{119}\text{Sn}$  NMR spectra (see Fig. 2) of  $[\text{Pt}_2(\text{SnCl}_3)_2(\mu\text{-dppm})_2]$ . A value of  $^3J(^{117}\text{Sn}, ^{119}\text{Sn})$  of 24300 Hz was observed, which was the only coupling constant to yield the same value in both the  $^{117}\text{Sn}$  and  $^{119}\text{Sn}$  NMR spectra. The assignment of the satellites as  $^3J(^{117}\text{Sn}, ^{119}\text{Sn})$  is further supported by the observation that in the  $^{119}\text{Sn}$  NMR spectrum of  $[\text{Pt}_2\text{Cl}(\text{SnCl}_3)(\mu\text{-dppm})_2]$ , no such satellites are observed, although the satellites due to the sum of  $^1J(\text{PtSn})$  and  $^2J(\text{PtSn})$  are still apparent. The reduced coupling constant  $^3K(^{117}\text{Sn}^{119}\text{Sn}) = 1522 \times 10^{20} \text{N A}^{-2} \text{m}^{-3}$  is remarkably large, and of the order of magnitude of the largest  $^1K$  values so far reported [8]. This is, we believe, not only the largest three-bond coupling constant yet observed, but is also larger than the two-bond coupling constant yet reported  $\{^2J(^{117}\text{Sn}^{119}\text{Sn}) = 21254 \text{ Hz} (^2K = 1332 \times 10^{20} \text{N A}^{-2} \text{m}^{-3})\}$  for the complex  $[\text{RuCl}(\text{SnCl}_3)_5]^{4-}$  [9]. The value of  $^1J(\text{PtPt})$  for  $[\text{Pt}_2\text{Cl}(\text{SnCl}_3)(\mu\text{-dppm})_2]$  of 8200 Hz falls very close to the values for  $[\text{Pt}_2\text{Cl}_2(\mu\text{-dppm})_2]$  ( $8180 \pm 17 \text{ Hz}$ ) [10, 11] and  $[\text{Pt}_2(\text{SnCl}_3)_2(\mu\text{-dppm})_2]$  (7628 Hz), which were not directly observed but were calculated from second-order features in both the  $^{31}\text{P}$  and  $^{195}\text{Pt}$  NMR spectra. Introduction of the trichlorostannio group onto the  $\{\text{Pt}_2(\mu\text{-dppm})_2\}$  skeleton provides a very sensitive probe for all the couplings within the molecule and particularly those couplings associated with the Pt-Pt interaction. Work in progress will establish the sensitivity of these parameters to such features as the *trans* influence and the Pt-Pt bond strength, as the extremely large values associated with Pt-Sn coupling constants allow the detection of even small phenomenological changes.

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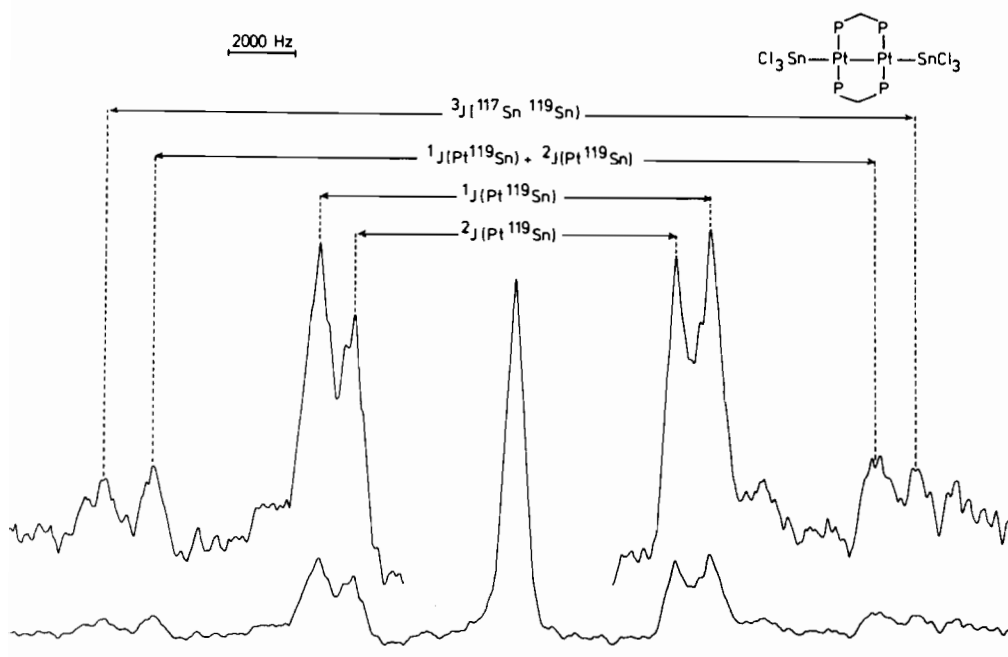


Fig. 2.  $^{119}\text{Sn}$  NMR spectrum (149.5 MHz) of  $[\text{Pt}_2(\text{SnCl}_3)_2(\mu\text{-dppm})_2]$  in  $\text{CD}_2\text{Cl}_2$  at ambient probe temperature.

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