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Formation of Platinum–Tin Bond by Tin(II)Chloride Insertion[1]

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The first ^{119}Sn NMR evidence for the presence of direct platinum–tin bond in solution has been obtained for $PtCl(SnCl_3)(bdpp)$ complex (bdpp = (2*S*,4*S*)-2,4-*bis*(diphenylphosphino)pentane). Various $PtCl_2(L_2)$ complexes (L_2 = heterobidentate P–P, P–O, P–N, P–S chelating ligands) have been reacted with tin(II)chloride resulting in the formation of the corresponding $PtCl(SnCl_3)(L_2)$ derivatives. Tin(II)chloride has been inserted into the Pt–Cl bond *trans* to the harder donor atom of the L_2 ligand.

KEY WORDS: NMR; tin(II)chloride; insertion; platinum; platinum–tin bond.

INTRODUCTION

The importance of tin(II)halide additives in various homogeneous platinum-catalyzed reactions is well known. Tin(II)chloride has been used for a long time in hydrogenation reactions carried out in the presence of chloroplatinic acid [1].

The hydroformylation of various functionalized and unfunctionalized alkenes with platinum–phosphine–tin(II)chloride "preformed" and "*in situ*" systems is also well documented [2–6]. The most often used systems contain $PtCl_2$(diphosphine) and $PtCl(SnCl_3)$(diphosphine) precursors.

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[1] This paper is dedicated to the 70th birthday anniversary of Prof. László Markó, in recognition of his contribution to cluster chemistry, coordination chemistry, and homogeneous catalysis.

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Although the investigation of "tin chloride-free" ionic systems [7–10] are of increasing importance, the application of the platinum–tin systems of the above type is still overhelming.

In spite of the wide application of platinum catalysts in hydroformylation in the past two decades, the reaction mechanism has still some open questions. The details of the reaction mechanism, especially the role of tin(II)halides in various steps of the reaction mechanism, have been discussed on the basis of NMR investigations using suitable model compounds [11–13] and HP NMR under "real oxo-conditions" [14, 15].

The NMR has proven to be extremely useful in determining the geometry of platinum–tin complexes in solutions [16]. Tin has three different isotopes with $I = 1/2$ that are observable by NMR spectroscopy. Two of these, ^{119}Sn and ^{117}Sn, have reasonable natural abondances (8.6% and 7.6%, respectively). For determination of NMR patterns either by direct detection or their coupling to other NMR active nuclei can be considered. Due to its slightly higher receptivity, ^{119}Sn is usually the isotope that is observed. Since tin chemical shifts are notoriously solvent and temperature dependent, especially the coupling constants give important information on the relative geometry of NMR active nuclei.

Although the existence of a direct platinum–tin bond in $PtX(SnCl_3)(L_2)$ complexes (where $X = I$, Cl; L_2 = mono or bidentate neutral ligand) has been shown by the presence of tin satellites in ^{31}P NMR ($J(^{117,119}Sn, ^{31}P)$ coupling constant) [17] and by X-ray structural determination [18], to the best of our knowledge, direct ^{119}Sn NMR-based proof for these catalytically important species containing chelating diphosphine has not been obtained yet.

The insertion of $SnCl_2$ into metal–halide bonds which is one of the fundamental reactions in coordination chemistry has been reviewed [19]. It is known for a long time, that both *cis*- and *trans*-$PtCl_2(L_2)$ (L = monodentate phosphine) complexes react with tin(II)chloride yielding exclusively *trans*-$PtCl(SnCl_3)L_2$ [20]. Due to the applicability of platinum–diphosphine–tin(II)chloride systems as homogeneous catalysts, the structure of the corresponding $PtCl(SnCl_3)$(diphosphine) precursors has been studied in detail by ^{31}P NMR spectroscopy. The $PtCl_2(L_2)$ complexes contain mainly bidentate ligands of C_2 symmetry (L_2), like the chiral *diop* [21–23], *chiraphos* [24], *bdpp* [25], etc. or achiral $PPh_2(CH_2)_nPPh_2$-type diphosphines [26]. There are also some applications for diphosphines possessing two different diphenylphosphino groups like *prophos* [27], *bppm* [28]. The successful application of a heterobidentate phosphine–phosphite ligand with binaphtyl skeleton in rhodium-catalyzed asymmetric hydroformylation [29, 30] focused attention to the importance of heterobidentate ligands [5].

In the present paper, we report on the first ^{119}Sn NMR of a PtCl($SnCl_3$)(diphosphine) complex and the selectivity of tin(II)chloride insertion into $PtCl_2(L_2)$ complexes containing heterobidentate ligands.

EXPERIMENTAL

Chemicals

The diphosphine ligand, *bdpp* were purchased from Strem and has been used without further purification. Anhydrous tin(II)chloride was prepared from $SnCl_2 \cdot 2H_2O$ by reacting it with acetic anhydride and washing with ether. The heterobidentate ligands, **1**–**4** were prepared as described previously [31–34]. All $PtCl_2(L_2)$ complexes were prepared according to the literature using $PtCl_2(PhCN)_2$ as starting complex [35]. All complexes gave satisfactory elemental analysis.

Instrumentation

^{1}H and ^{31}P NMR spectra were recorded in $CDCl_3$ on a Varian Unity 300 spectrometer at 300 and 121.4 MHz, respectively. Chemical shifts are reported in δ ppm, referred to TMS (tetramethylsilane) as internal standard and to orthophosphoric acid (85%, higher fields refer to lower chemical shifts) as external standard. ^{119}Sn NMR were recorded in CD_2Cl_2/CH_2Cl_2 on a JEOL GSX-270 spectrometer at 100.6 MHz. ^{119}Sn chemical shifts are reported in ppm relative to tetramethylstannane.

RESULTS AND DISCUSSION

^{119}Sn NMR of PtCl($SnCl_3$)(bdpp) (bdpp = (2*S*,4*S*)-2,4-*bis*(diphenylphosphino)pentane)

The above complex containing a diphosphine ligand of C_2 symmetry (Fig. 1) has been used succesfully in enantioselective hydroformylation and its structure was determined by usual analytical methods [18]. The characteristic $^2J_{cis}(^{117,119}Sn, ^{31}P)$ and $^2J_{trans}(^{117}Sn, ^{31}P)$, $^2J_{trans}(^{119}Sn, ^{31}P)$ coupling constants of 180 Hz and 3933 Hz, 4115 Hz, respectively, obtained from ^{31}P NMR spectrum, refer to the presence of a direct platinum–tin bond. The two-bond coupling of tin to the *trans* phosphorus atom is more than an order of magnitude larger than that to a *cis* phosphorus, as it is expected. It is worth noting, that the determination of a ^2J(Sn, P) coupling

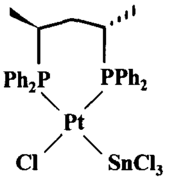


Fig. 1. The structure of $PtCl(SnCl_3)$(bdpp) complex.

constants from a ^{31}P NMR requires a very high signal to noise ratio, because of the low intensity of the tin satellites. (They are as small as ca. 4% of the intensity of the main peak (central line) of the multiplet.)

Unfortunately, the ^{195}Pt NMR measurements did not result in a spectrum of satisfactory quality giving the exact coupling information.

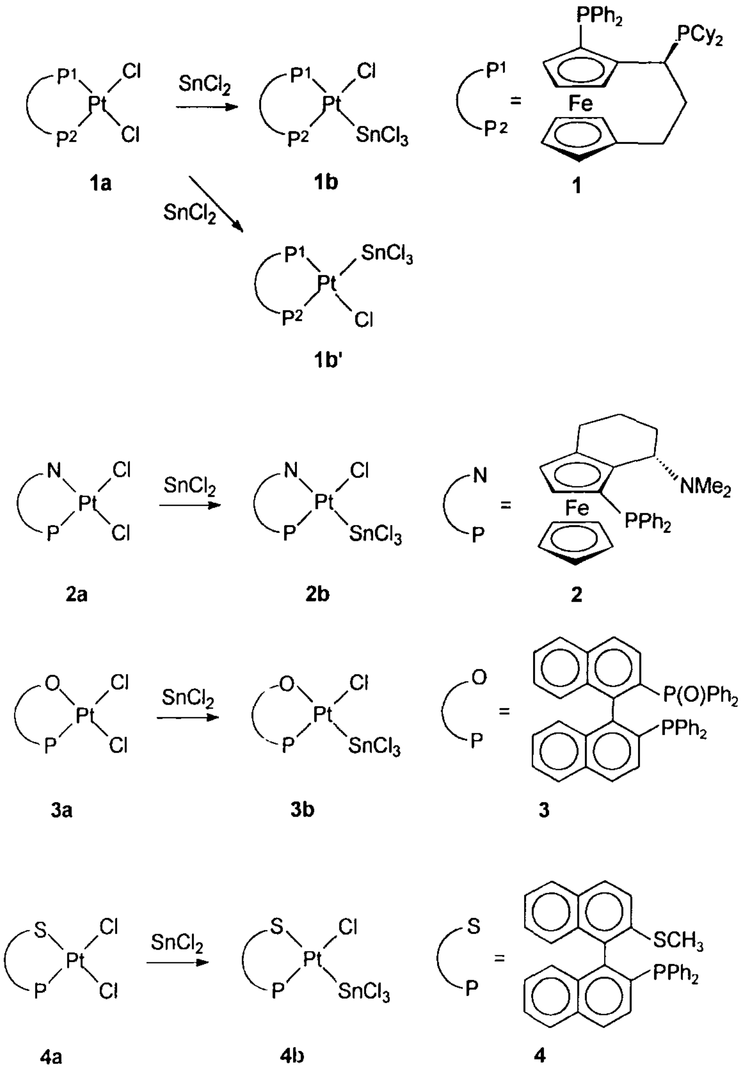
However, the ^{119}Sn NMR obtained in CD_2Cl_2/CH_2Cl_2 displays a characteristic multiplet at -21.95 ppm. The central dd pattern, due to the coupling of ^{119}Sn nuclei to two chemically nonequivalent phosphorus of *bdpp*, is flanked by platinum satellites of ca. 17% intensity as a consequence of the 33.8% natural abundance of ^{195}Pt ($I = 1/2$). Both $^2J_{cis}(^{119}Sn, ^{31}P) = 187.1$ Hz and $^2J_{trans}(^{119}Sn, ^{31}P) = 4090$ Hz coupling constants can easily be determined. The difference between $^2J_{cis}(Sn, P)$ coupling constants obtained in ^{31}P (*vide supra*) and ^{119}Sn NMR measurements are due to the overlapping of ^{117}Sn and ^{119}Sn satellites in ^{31}P NMR resulting in a much broader satellite than usual.

The $^1J(^{195}Pt, ^{119}Sn)$ coupling constant (16945 Hz) is an unquestionable proof for the direct platinum–tin bond. For the above square planar complex, the magnitude of the tin–platinum coupling constant is in agreement with the presence of a phosphine *trans* to the tin atom.

NMR Investigation of the $SnCl_2$ Insertion into the Pt–Cl Bond of $PtCl_2$(Heterobidentate Ligand)-Type Complexes

Although the $PtCl(SnCl_3)(c_2$-diphoshine) complexes have been characterized carefully and their formation as a function of electronic and steric parameters of the phosphine has been usually discussed together with their catalytic investigation, a little is known about $Pt–SnCl_3$ complexes containing various heterobidentate ligands. Therefore, $PtCl_2(L_2)$ complexes (where L_2 stands for 2-diphenylphosphino-1,1′-(1-dicyclohexylphosphino-1,3-propanediyl)ferrocene (**1**), 1-diphenylphosphino-α-N,N-dimethylamino

[2,3]tetramethyleneferrocene (**2**), 2-diphenylphosphino-2′-diphenylphosphinyl-1,1′-binaphthyl (**3**), and S-methyl 2-diphenylphosphino-1,1′-binaphthyl-2′-thiol (**4**)) were reacted with a stoichiometric amount of tin(II)chloride in chloroform or dichloromethane (Scheme 1). (All ligands were used in racemic form.) The formation of the corresponding $PtCl(SnCl_3)(L_2)$ has



Scheme 1. The reaction of $SnCl_2$ with $PtCl_2(L)$ complexes containing heterobidentate P–P, P–N, P–O, P–S chelating ligands (L) (in complexes **1a**, **1b**, and **1b′**: $P^1 = PCy_2$, $P^2 = PPh_2$).

Table I. ^{31}P NMR Data of Pt Complexes Containing Heterobidentate Ligands

Complexes[a]	δP ppm	$^1J(^{195}Pt, ^{31}P)$ Hz	$J(P^1, P^2)$ Hz	$^2J(^{31}P, ^{117}Sn)$ Hz	$^2J(^{31}P, ^{119}Sn)$ Hz
$PtCl(SnCl_3)$(**1**) (**1b**)[b]	0.2	3446	15	205[d]	—[d]
	53.7	2921		3630	3812
$PtCl(SnCl_3)$(**1**) (**1b'**)[c]	8.5	2931	16	4220	4408
	59.4	3426		193[d]	—[d]
$PtCl(SnCl_3)$(**2**) (**2b**)	2.0	3933	—	186	195
$PtCl(SnCl_3)$(**3**) (**3b**)	16.7	3812	—	185[d]	—[d]
	48.3	—			
$PtCl(SnCl_3)$(**4**) (**4b**)	11.6	3753	—	200[d]	—[d]

[a] For structures of **1b**–**4b** see Scheme 1.

[b] $SnCl_3$ moiety *trans* to PCy_2.

[c] $SnCl_3$ moiety *trans* to PPh_2.

[d] ^{117}Sn and ^{119}Sn satellites ($^2J_{cis}(^{117,119}Sn, ^{31}P)$) coincide.

been observed in all cases. The presence of trichlorostannato moiety in the complex has been proved by NMR. Both the changes of the ^{31}P chemical shifts in $PtCl_2(L_2)$ complexes and the presence of the tin satellites in ^{31}P NMR indicate it (Table 1).

Two isomers, **1b** and **1b'** have been formed in a ratio of ca. 60/40, when diphosphine (**1**) possessing two different donor phosphorus has been used as bidentate ligand. The signal of the phosphorus possessing $^1J(^{195}Pt, ^{31}P)$ less than 3000 Hz can be assigned to phosphorus *trans* to the trichlorostannato ligand. The structure can also be verified considering the presence of the corresponding tin satellites on the phosphorus signals. In the prevailing trichlorostannato complex (**1b**) the tin(II)chloride insertion takes place *trans* to the more basic dicyclohexylphosphino moiety. It is worth noting that similar selectivity was obtained with $PtCl_2$(prophos) (prophos = 1,2-bis(diphenylphosphino)propane), where tin(II)chloride insertion took place *trans* to the slightly more basic phosphorus adjacent to $CH(CH_3)$ moiety of the phosphine backbone [27].

Surprisingly high selectivity has been obtained for the reaction of $PtCl_2$(**2**) (**2a**), $PtCl_2$(**3**) (**3a**), $PtCl_2$(**4**) (**4a**), with tin(II)chloride resulting in the formation of **2b**, **3b**, and **4b**, respectively. In these cases, where the basicity of the two donor functionality is substantially different, tin(II)chloride insertion into Pt–Cl bond takes place selectively *trans* to the harder donor ligand.

In case of **2b** the *cis* position of the phosphorus and the trichlorostannato ligand has been proved by the characteristic ${}^2J_{cis}({}^{117,119}Sn, {}^{31}P)$ coupling constant in ${}^{31}P$ NMR. The coordination of nitrogen was proved by the Pt satellites of the proton signals (${}^3J({}^{195}Pt, {}^1H) = 26$ Hz, ${}^3J({}^{195}Pt, {}^1H) = 30$ Hz) of the diastereotopic NMe_2 methyl groups.

In complex **3b** the tin satellites are in similar position indicating the *cis* arrangement of P and Sn. The absence of both platinum and tin satellites on phosphinyl phosphorus is due to the coordination $P=O$ moiety to platinum through oxygen [36].

The bidentate coordination of the phosphino-thioether ligand, **4** in **4b** is proved both by ${}^{31}P$ and ${}^1H$ NMR. While the typical ${}^2J_{cis}({}^{117,119}Sn, {}^{31}P)$ refers to the phosphorus *cis* to trichlorostannato moiety, the ${}^3J({}^{195}Pt, {}^1H) = 39$ Hz coupling on SCH_3 clearly shows the sulfur coordination, and additionally, the ${}^4J({}^{117,119}Sn, {}^1H) =$ ca. 51 Hz appearing as week satellites, is an indication for the Sn-Pt-SCH_3 *trans* arrangement.

CONCLUSIONS

We have shown that the insertion of tin(II)chloride into platinum–chlorine bond in $PtCl_2$(heterobidentate ligand) complexes takes place selectively. The selectivity is substantially determined by the electronic properties of the donor ligands: tin(II)chloride inserts into the Pt–Cl bond *trans* to the harder donor ligand. This fact could be explained by the labilization of the appropriate chloro ligand. It is in accordance with earlier findings, which propose the coordination of tin(II)chloride to the halogen of the Pt–Cl bond [37, 38]. The Pt–Cl–$SnCl_2$ intermediate is probably rearranged to Pt–$SnCl_3$ through a triangular intermediate with a platinum–tin bridging halide.

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REFERENCES

1. G. W. Parshall and S. D. Ittel, *Homogeneous Catalysis*, 2nd Ed. (J. Wiley & Sons, New York, 1992).
2. C. Botteghi, S. Paganelli, A. Schionato, and M. Marchetti (1991). *Chirality* 3, 355.
3. G. Consiglio, *in* I. Ojima (ed.), *Catalysis Asymmetyric Synthesis* (VCH Publishers, New York, 1993), 273.

4. R. Noyori, *Asymmetric Catalysis in Organic Synthesis* (J. Wiley & Sons, New York, 1994).
5. S. Gladiali, J. C. Bayón, and C. Claver (1995). *Tetrahedron: Asymmetry* **6**, 1453.
6. F. Agbossou, J.-F. Carpentier, and A. Mortreux (1995). *Chem. Rev.* **95**, 2485.
7. P. W. N. M. van Leeuwen, C. F. Roobek, R. L. Wife, and J. H. G. J. Frijns (1986). *J. Chem. Soc. Chem. Commun.* 31.
8. P. W. N. M. van Leeuwen, C. F. Roobek, and J. H. G. J. Frijns (1990). *Organometallics* **9**, 1211.
9. C. Botteghi, S. Paganelli, U. Matteoli, A. Scrivanti, R. Ciorciaro, and L. M. Venanzi (1990). *Helv. Chim. Acta* **73**, 284.
10. C. Botteghi, S. Paganelli, A. Perosa, R. Lazzaroni, and G. Uccello-Barretta (1993). *J. Organomet. Chem.* **447**, 153.
11. A. Scrivanti, A. Berton, L. Toniolo, and C. Botteghi (1986). *J. Organomet. Chem.* **314**, 369.
12. H. J. Ruegg, P. S. Pregosin, A. Scrivanti, L. Toniolo, and C. Botteghi (1986). *J. Organomet. Chem.* **316**, 233.
13. M. Gomez, G. Muller, D. Sainz, J. Sales, and X. Solans (1991). *Organometallics* **10**, 4036.
14. I. Tóth, T. Kégl, C. J. Elsevier, and L. Kollár (1994). *Inorg. Chem.* **33**, 5708.
15. T. Kégl, L. Kollár, and L. Radics (1977). *Inorg. Chim. Acta* **265**, 249.
16. P. S. Pregosin, *in* J. G. Verkade and D. L. Quin (eds.), *Phosphorus-31 NMR Spectroscopy* (VCH Publishers, Deerfield Beach, Florida, 1987), pp. 465–530.
17. P. S. Pregosin and R. W. Kunz, *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes* (Springer Verlag, Heidelberg, 1979).
18. E. Farkas, L. Kollár, M. Moret, and A. Sironi (1996). *Organometallics* **15**, 1345.
19. M. S. Holt, W. L. Wilson, and J. H. Nelson (1989). *Chem. Rev.* **89**, 11.
20. L. Y. Al't, E. N. Yurchenko, and A. P. Chernyshev (1980). *Koord. Khim.* **6**, 1085.
21. C. U. Pittman, Y. Kawabata, and L. I. Flowers (1982). *J. Chem. Soc., Chem. Commun.* 473.
22. P. Haelg, G. Consiglio, and P. Pino (1985). *J. Organomet. Chem.* **296**, 281.
23. L. Kollár, G. Consiglio, and P. Pino (1987). *J. Organomet. Chem.* **330**, 305.
24. G. Consiglio, F. Morandini, M. Scalone, and P. Pino (1985). *J. Organomet. Chem.* **279**, 193.
25. L. Kollár, J. Bakos, I. Tóth, and B. Heil (1988). *J. Organomet. Chem.* **350**, 277.
26. Y. Kawabata, T. Hayashi, and I. Ogata (1979). *J. Chem. Soc., Chem. Commun.* 462.
27. M. Scalone, PhD thesis, ETH-Zurich, 1983.
28. G. Parrinello and J. K. Stille (1987). *J. Am. Chem. Soc.* **109**, 7122.
29. N. Sakai, S. Mano, K. Nozaki, and H. Takaya (1993). *J. Am. Chem. Soc.* **115**, 7033.
30. N. Sakai, K. Nozaki, and H. Takaya (1994). *J. Chem. Soc., Chem. Commun.* 395.
31. G. Kutschera, C. Kratky, W. Weissensteiner, and M. Widhalm (1996). *J. Organomet. Chem.* **508**, 195.
32. B. Jedlicka, C. Kratky, W. Weissensteiner, and M. Widhalm (1993). *J. Chem. Soc., Chem. Commun.* 1329.
33. F. Ozawa, A. Kubo, and T. Hayashi (1992). *Chem. Lett.* 2177.
34. S. Gladiali, A. Dore, and D. Fabbri (1994). *Tetrahedron: Asymmetry* **5**, 1143.
35. F. R. Hartley (1970). *Organomet. Chem. Rev. A* **6**, 119.
36. R. Wegman, A. G. Abatjoglu, and A. M. Harrison (1987). *J. Chem. Soc., Chem. Commun.* 1891.
37. M. Elder and D. Hall (1969). *Inorg. Chem.* **8**, 1273.
38. B. R. James (1979). *Adv. Organomet. Chem.* **17**, 319.