Organometallics **1996,** *15,* 1345−1350 1345

Halogen Exchange in Platinum−Phosphine−Tin(II) Halide Systems. Characterization of the Novel PtI($SnCl_3$)[(2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane] Complex

Edit Farkas and László Kollár*

Department of Organic Chemistry, University of Veszprém, P.O. Box 158,
H-8201 Veszprém, Hungary

Massimo Moret and Angelo Sironi*

Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università di Milano,
Via G. Venezian 21, I-20133 Milano, Italy

Received December 8, 1995[⊗]

The investigation of the $PtCl_2$(diphosphine) + SnI_2 and PtI_2(diphosphine) + $SnCl_2$ systems of catalytic importance (where diphosphines are 2,3-bis(diphenylphosphino)butane and 2,4-bis(diphenylphosphino)pentane) by NMR in solution has been carried out. Novel PtI($SnCl_3$)(diphosphine) and PtI($SnCl_2I$)(diphosphine) complexes were formed as a consequence of the halide exchange reaction. The selective formation of PtI($SnCl_3$)[2,4-bis(diphenylphosphino)pentane] was observed in the reaction of $PtCl_2$[2,4-bis(diphenylphosphino)pentane] and 0.5 $SnCl_2$ and 0.5 SnI_2. PtI($SnCl_3$)[2,4-bis(diphenylphosphino)pentane], the first platinum complex which contains a chiral chelating diphosphine and $SnCl_3$ ligand, was structurally characterized by X-ray diffraction.

Introduction

Platinum−phosphine compounds in the presence of tin(II) chloride and PtCl($SnCl_3$)(diphosphine) "preformed" catalysts show excellent activity in hydroformylation.[1] The role of tin(II) chloride in the platinum-catalyzed hydroformylation reaction is contradictory.[2] It has been the subject of many studies but not yet fully understood. $SnCl_2$ can act as a Lewis acid, as a counterion ($SnCl_3^-$), and as a ligand directly bonded to platinum.

Although some IVB and VB halides have been tested as additives with $PtCl_2(PPh_3)_2$ *in situ* catalysts at the very beginning of this research,[3] the use of $SnCl_2$ as cocatalyst remained prevailing in homogeneous hydroformylation. Very few publications have dealt with the possible role of the additives.[4] From the work of Schwager and Knifton Sn(II) halides (especially $SnCl_2$) proved to be superior to other cocatalysts. The effect of $SnCl_2$ on the hydroformylation of various substrates by using platinum(II) *in situ* catalysts which are formed from a $PtCl_2(P_2)$ precursor (P_2 = two monophosphines or chelating diphosphine) is the subject of a number of publications.[5] The carbene-like insertion of $SnCl_2$ into the Pt−Cl bond resulted in the formation of a trichlorostannato ligand yielding a PtCl($SnCl_3$)P_2 type complex.[6] In the presence of a third phosphine ligand the Pt−Sn bond was split and the $[PtCl(P)(P_2)]^+SnCl_3^-$ ionic complex was formed.[7] Although the $PtCl_2P_2$−$SnCl_2$ system seemed to be the most promising combination, $SnBr_2$ and SnI_2 as cocatalysts also showed some catalytic activity.[3] The activity of the catalyst formed with SnF_2 is rather low using $PtCl_2$(diphosphine) complexes as catalytic precursors.[8]

There are no publications available, according to the best of our knowledge, on the structure of the Pt−Sn complexes containing two different halides at the same time. Additionally, no crystal structural determinations of a platinum complex bearing a chelating diphosphine and a $SnCl_3$ ligand have ever been described in any literature. Due to the importance of these systems in asymmetric hydroformylation, the investigation of the structure of Pt−optically active ditertiary phosphine complexes could give a deeper insight into the stereochemical outcome of the reaction.

[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1996.

(1) Botteghi, C.; Paganelli, S.; Schionato, A.; Marchetti, M. *Chirality* **1991**, *3*, 355. Colquhoun, H. M.; Thompson, D. J.; Twigg, M. V. *Carbonylation. Direct Synthesis of Carbonyl Compounds;* Plenum Press: New York and London, 1991.

(2) (a) Scrivanti, A.; Berton, A; Toniolo, L; Botteghi, C. *J. Organomet. Chem*. **1986**, *314*, 369. (b) Gomez, M.; Muller, G.; Sainz, D.; Sales, J.; Solans, X. *Organometallics* **1991**, *10*, 4036.

(3) Hsu, C. Y.; Orchin, M. *J. Am. Chem. Soc.* **1975**, *97*, 3553. Schwager, J.; Knifton, J. F. *J. Catal.* **1976**, *45*, 256.

(4) Kollár, L.; Sándor, P.; Szalontai, G.; Heil, B. *J. Organomet. Chem*. **1990**, *393*, 153.

(5) (a) Clark, H. C.; Davies, J. A. *J. Organomet. Chem*. **1981**, *213*, 503. (b) Hayashi, T.; Kawabata, Y.; Isoyama, T.; Ogata, I. *Bull. Chem. Soc. Jpn*. **1981**, *54*, 3438. (c) Bardi, R.; Piazessi, A. M.; Del Pra, A.; Cavinato, G.; Toniolo, L. *J. Organomet. Chem*. **1982**, *234*, 107. (d) Moretti, G.; Botteghi, C.; Toniolo, L. *J. Mol. Catal*. **1987**, *39*, 177. (e) Graziani, R.; Cavinato, G.; Casellato, U.; Toniolo, L. *J. Organomet. Chem*. **1988**, *353*, 125. (f) Consiglio, G.; Pino, P.; Flowers, L. I.; Pittmann, C. U., Jr. *J. Chem. Soc., Chem. Commun*. **1983**, 612. (g) Stille, J. K.; Parrinello, G. *J. Mol. Catal*. **1983**, *21*, 203. (h) Haelg, P.; Consiglio, G.; Pino, P. *J. Organomet. Chem*. **1985**, *296*, 281. (i) Consiglio, G.; Morandini, F.; Scalone, M.; Pino, P. *J. Organomet. Chem*. **1985**, *279*, 193. (j) Kollár, L.; Consiglio, G.; Pino, P. *J. Organomet. Chem*. **1987**, *330*, 305. (k) Parrinello, G.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 7122. (l) Kollár, L.; Bakos, J.; Tóth, I.; Heil, B. *J. Organomet. Chem*. **1988**, *350*, 277. (m) Kollár, L.; Bakos, J.; Tóth, I.; Heil, B. *J. Organomet. Chem*. **1989**, *370*, 257. (n) Consiglio, G.; Nefkens, S. C. A.; Borer, A. *Organometallics* **1991**, *10*, 2046. (o) Tóth, I.; Guo, I.; Hanson, B. *Organometallics* **1993**, *12*, 848.

(6) Pregosin, P. S.; Sze, S. N. *Helv. Chim. Acta* **1978**, *61*, 1848.

(7) Kollár, L.; Szalontai, G. *J. Organomet. Chem*. **1991**, *421*, 341.

(8) Kollár, L.; Kégl, T.; Bakos, J. *J. Organomet. Chem*. **1993**, *453*, 155.

0276-7333/96/2315-1345$12.00/0

Table 1. Reaction of $PtCl_2$(bdpp) (and $PtCl_2$(chiraphos)) with $SnCl_2$ and SnI_2 at Different Ratios of the Reagents

Pt:$SnCl_2$:SnI_2	compn of the reacn mixture
1:0.5:0	55% **8**; 45% $PtCl_2$(bdpp)[a]
1:0.5:0.5	25% **8**; 64% **7**; 11% $PtCl_2$(bdpp)[a]
1:0.75:0	57% **8**; 43% $PtCl_2$(bdpp)[a]
1:0.75:0.25	35% **8**; 58% **7**; 7% $PtCl_2$(bdpp)[b]
1:0.875:0	61% **8**; 39% $PtCl_2$(bdpp)[b]
	64% **8**; 36% $PtCl_2$(bdpp)[c]
1:0.875:0.175	50% **8**; 20% **7**; 30% $PtCl_2$(bdpp)[b]
	40% **8**; 29% **7**; 31% $PtCl_2$(bdpp)[c]
1:0.5:0.5	51% **10**; 16% **9**; 33% $PtCl_2$(chiraphos)[b]
	56% **10**; 12% **9**; 32% $PtCl_2$(chiraphos)[c]

[a] Reaction time 30 min. [b] Reaction time 5 min. [c] Reaction time 24 h.

In the present paper, the reactions of $PtCl_2P_2$ and SnI_2 and ($SnCl_2$) as well as PtI_2P_2 and $SnCl_2$ and (SnI_2) are described. Furthermore, the structural characterization of the formed complexes, by NMR spectroscopy and X-ray diffraction, are also reported.

Results and Discussion

(i) Reactions of $PtX_2(P_2)$ and SnX_2. With the reaction of *cis*-$PtCl_2(PPh_3)_2$ and SnI_2 in $CDCl_3$ the mixture of *cis*- and *trans*-$PtI_2(PPh_3)_2$ (**1** and **2**) complexes were formed. The ratio of **1** and **2** in the final reaction mixture is practically the same as that obtained by reacting $PtI_2(PhCN)_2$ and PPh_3. When the reaction was followed by ^{31}P NMR, no traces of $SnCl_2$ and SnI_2 insertion products like $PtI(SnICl_2)(PPh_3)_2$ or $PtCl(SnClI_2)(PPh_3)_2$ were observed.

In addition to $PtCl_2$(diphosphine) complexes of known NMR characteristics some novel PtI_2(diphosphine) derivatives such as PtI_2(bdpp) (bdpp = (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane) (**3**), PtI_2(chiraphos) (chiraphos = (2*S*,3*S*)-2,3-bis(diphenylphosphino)butane) (**4**), PtI_2(dppb) (dppb = 1,4-bis(diphenylphosphino)butane) (**5**), and PtI_2(prophos) (prophos= (*R*)-1,2-bis(diphenylphosphino)propane) (**6**) were synthesized in order to make a comparison with the chlorine analogs (Table 3; Experimental Section) and to use them as starting materials for further reactions.

The reaction of dichloroplatinum compounds with SnI_2 has also been tested by using diphosphines instead of PPh_3 as a ligand. In case of bdpp, in addition to PtI_2(bdpp) (**3**), two further complexes were observed: $PtI(SnCl_3)$(bdpp) (**7**) and maybe $PtI(SnCl_2I)$(bdpp) (**7a**) (present in a small amount) (Table 1). (The insertion of SnI_2 was not found to take place into Pt−I bonds in a detectable amount.)

A systematic study was carried out in order to clear up the mechanism of the formation of **7**. As expected, the reaction of $PtCl_2$(bdpp) and 0.5 equiv of $SnCl_2$ resulted in the formation of the well-known $PtCl(SnCl_3)$(bdpp) (**8**)[5l] (Figure 1). After addition of 0.5 equiv of SnI_2 to this mixture, the exclusive formation of **7** was observed. Approximately a 1/1 mixture of **7** and **8** was formed by using a ratio of $SnCl_2/SnI_2$ = 0.75/0.25.

The Cl−I exchange was influenced by the size of the Pt−diphosphine chelate ring, and this was observed by using chiraphos (five-membered ring) instead of bdpp (six-membered ring). Surprisingly, the reaction of $PtCl_2$(chiraphos) with 0.5 $SnCl_2$ and 0.5 SnI_2 gave $PtI(SnCl_3)$(chiraphos) (**9**) in low yield, $PtCl(SnCl_3)$(chiraphos) (**10**) predominating (Table 1).

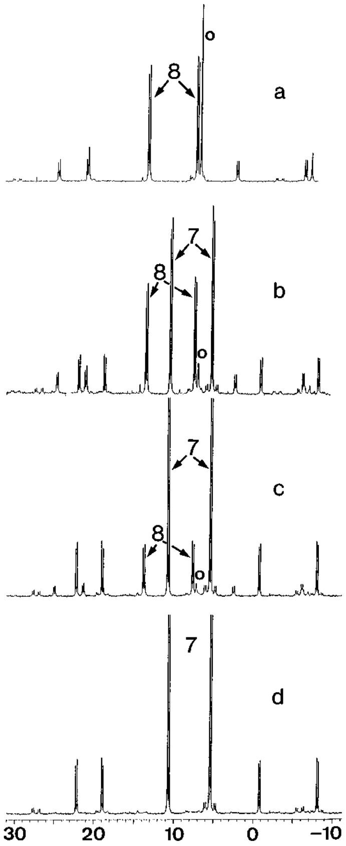

Figure 1. ^{31}P NMR spectra of the $PtCl_2$(bdpp) + 0.5 $SnCl_2$ + 0.5 SnI_2 systems. Key: spectrum **a**, Pt/$SnCl_2$/SnI_2 = 1/0.5/0; spectrum **b**, Pt/$SnCl_2$/SnI_2 = 1/0.75/0.25; spectrum **c**, Pt/$SnCl_2$/SnI_2 = 1/0.5/0.5, after 0.5 h; spectrum **d**, Pt/$SnCl_2$/SnI_2 = 1/0.5/0.5, after 5 h. **o** stands for $PtCl_2$(bdpp) (starting material); arrows indicate the central lines (phosphorus bonded to Pt other than ^{195}Pt ($I = {}^1/_2$)).

There are two possible explanations for the formation of the “mixed halide” complex **7** which are as follows: (i) The SnI_2 insertion is followed by the dissociation of SnClI, and in a similar sequence of reactions a mutual exchange of Cl and I between platinum and tin takes place. (ii) The exchange of the halides resulting in the formation of the proposed key-intermediate SnClI could also take place between free SnI_2 and $SnCl_2$ (formed by dissociation of $PtCl(SnCl_3)$(diphosphine) to a low extent).

Using PtI_2(P-P) (**3** and **4**) as starting complexes, the reaction mixtures are more complex; however, at different $SnCl_2/SnI_2$ ratios, **7** and **9** were formed as main products, respectively. While the reaction of **3** with the equimolar amount of $SnCl_2$ resulted in the formation of **7** in 55% in 0.5 h, the same reaction using **4** yields **9** in 33% yield. Carrying out the reaction with Pt/$SnCl_2$/SnI_2 = 1/1/1 ratio, the amounts of $PtCl(SnCl_2I)$(P-P) and $PtI(SnCl_2I)$(P-P) type complexes are comparable to $PtI(SnCl_3)$(P-P) complexes. The formation of some I_2 can be observed in all cases.

(ii) Characterization of 7. The formation of a Pt−I bond with the reaction of Pt−Cl bond and SnI_2 has been proved by various analytical methods. $PtI(SnCl_3)$(bdpp) (**7**) which gave satisfactory elemental analysis was investigated by far-IR spectroscopy. The Pt−I vibration frequency was shifted to lower values as expected.[9] Due to the fact that Pt−I bonding and stretching modes occur at lower frequencies than Sn−Cl bonding frequences and the resolution is quite poor, the resonances are not easy to assign.[10] The Raman spectra of **7** clearly show the presence of a Pt−I bond at 175 cm^{-1} and the Pt−SnCl$_3$ moiety at 336 cm^{-1}.

The ^{31}P NMR spectrum of **7** shows a characteristic pattern of two chemically different phosphorus atoms analogous to those of PtCl(SnCl$_3$)(diphosphine). The central lines are flanked by the platinum and tin satellites (Figure 1, Table 4). While the J_{trans}(P−^{117}Sn) and J_{trans}(P−^{119}Sn) couplings give separated satellites, the cis satellites of ^{117}Sn and ^{119}Sn coincide.

(iii) Reaction of 7 with PPh$_3$. It has been shown that the addition of monodentate phosphine to PtCl(SnCl$_3$)(diphosphine) yields the complex cation [PtCl(monophosphine)(diphosphine)]$^+$, and SnCl$_3^-$ acts as counterion.[7]

Reacting PPh$_3$ with the "preformed" PtI(SnCl$_3$)(bdpp) (**7**) and PtCl(SnCl$_3$)(bdpp) (**8**), different complex cations containing three coordinated phosphorus atoms were formed, which indicate the presence of Pt−Cl and Pt−I bonds, respectively.

$$\mathrm{PtX(SnCl_3)(bdpp)} + \mathrm{PPh_3} \rightarrow [\mathrm{PtX(PPh_3)(bdpp)}]^+\mathrm{SnCl_3}^-$$
$$\mathbf{7}, \mathrm{X} = \mathrm{I}$$
$$\mathbf{8}, \mathrm{X} = \mathrm{Cl}$$

On the basis of the ^{31}P NMR spectra of the cations the phosphorus atoms are easy to assign. The J(Pt−P) coupling constants are about 2400 Hz when P is in the *trans* position (22.1 ppm, 2368 Hz (P of the bdpp *trans* to PPh$_3$); 14.6 ppm, 2309 Hz (PPh$_3$) for **7**; 14.55 ppm, 2386 Hz (P of the bdpp *trans* to PPh$_3$); 10.07 ppm, 2307 Hz (PPh$_3$) for **8**) and in the range 3300−3500 Hz when the phosphorus atoms are in the *cis* position showing the *trans* influence of a halide (12.1 ppm, 3454 Hz for **8**; 9.62 ppm, 3298 Hz for **7**). The J_{cis}(P−P) and J_{trans}(P−P) coupling constants also correspond to a square planar geometry of the complex cation possessing three different phosphorus atoms (20.0, 25.4, 392 Hz for **8**; 17.9, 26.1, 397 Hz for **7**).

(iv) Description of the Crystal Structure of PtI(SnCl$_3$)[(2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane]·CHCl$_3$. The crystal structure of the title compound consists of a packing of PtI(SnCl$_3$)(bdpp) and clathrate CHCl$_3$ molecules separated by normal van der Waals contacts. There are two independent PtI(SnCl$_3$)(bdpp) (and two CHCl$_3$) molecules (**A** and **B**) in the asymmetric unit. Since molecule **A** is slightly disordered (the central carbon atom of the metallacycle and the methyl substituents have two possible locations; see Experimental Section), three different conformations of the metallacycle are present in the same crystal. Figure 2a−c shows ORTEP[19] drawings of the three conformations (**A**, **A′**, and **B**) in their absolute configuration. Relevant selected bond parameters are reported in Table 2. The coordination around the Pt atom is square planar; however, in molecule **B** there is a small tetrahedral distortion, the PtP$_2$ plane being rotated at an angle of 10.2(1)° with respect to that of PtSnI.

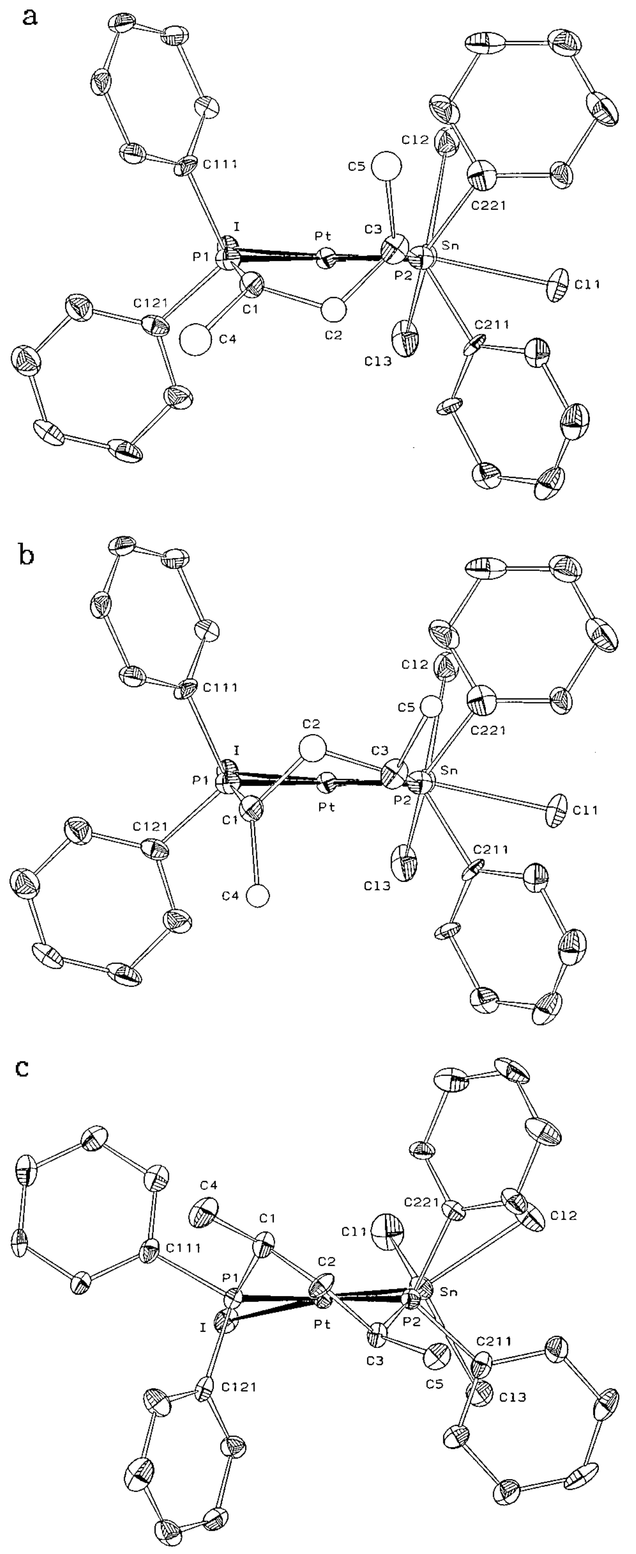

Figure 2. ORTEP[19] drawings of different conformers found in the solid states of PtI(SnCl$_3$)[(2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane]·CHCl$_3$. The view is along the P−Pt−P bisector: (a) molecule **A**; (b) molecule **A′**; (c) molecule **B**. Thermal ellipsoids were drawn at the 30% probability level. Hydrogen atoms were omitted for clarity.

The Pt−Sn bond (average 2.614 Å) distance is at the top of the range of 2.487−2.634 Å observed for such interactions[11] and is close to the value of 2.598 Å found in the related PtCl(SnCl$_3$)(diop).[12] The Pt−I (mean

---

[9] Nakamoto, N. In *Infrared Spectroscopy in Spectroscopy and Structure of Metal Chelate Compounds*; Nakamoto, K., McCarthy, P. J., Eds.; John Wiley and Sons, Inc.: New York, London, Sydney, 1968; p 216.

[10] Holt, M. S.; Wilson, W. L.; Nelson, J. H. *Chem. Rev.* **1989**, *89*, 11.

[11] Grassi, M.; Meile, S. V.; Musco, A.; Pontellini, R.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1990**, 251.

Table 2. Selected Bond Lengths [Å] and Bond Angles (deg) for 7

	A	**A′**	**B**
	Bond Lengths		
Pt−P(2)	2.248(4)		2.253(4)
Pt−P(1)	2.303(5)		2.297(4)
Pt−Sn	2.6113(13)		2.6154(14)
Pt−I	2.6565(13)		2.6415(13)
P(1)−C(1)	1.840(5)		1.830(5)
P(2)−C(3)	1.833(5)		1.829(5)
C(1)−C(2)	1.560(12)	1.541(13)	1.544(11)
C(1)−C(4)	1.543(12)	1.543(13)	1.539(11)
C(2)−C(3)	1.540(12)	1.550(13)	1.534(11)
C(3)−C(5)	1.536(12)	1.542(13)	1.538(11)
	Bond Angles		
P(2)−Pt−P(1)	95.7(2)		91.0(2)
P(2)−Pt−Sn	90.64(12)		91.95(12)
P(1)−Pt−Sn	173.66(13)		174.67(13)
P(2)−Pt−I	172.48(13)		170.84(14)
P(1)−Pt−I	90.71(13)		91.00(11)
Sn−Pt−I	82.96(4)		86.73(4)
C(1)−P(1)−Pt	117.3(6)		109.7(5)
C(211)−P(2)−Pt	112.9(4)		108.7(4)
C(221)−P(2)−Pt	107.5(6)		114.6(4)
C(3)−P(2)−Pt	118.4(6)		112.6(4)
C(4)−C(1)−C(2)	108(2)	128(3)	110.6(13)
C(4)−C(1)−P(1)	116(2)	110(2)	117.5(10)
C(2)−C(1)−P(1)	119.8(13)	101(2)	112.4(9)
C(3)−C(2)−C(1)	113(2)	114(2)	119.9(11)
C(5)−C(3)−C(2)	122(2)	94(3)	108.9(11)
C(5)−C(3)−P(2)	113(2)	115(2)	115.8(9)
C(2)−C(3)−P(2)	108.3(13)	117(2)	114.1(9)

Table 3. NMR Data for $\mathrm{PtX_2P_2}$ Complexes[a]

$\mathrm{PtX_2P_2}$	*J*(Pt−P) (Hz)	δ (ppm)
cis-$\mathrm{PtCl_2(PPh_3)_2}$	3673	14.92
trans-$\mathrm{PtCl_2(PPh_3)_2}$	2636	20.20
$\mathrm{PtCl_2}$(bdpp)	3417	7.62
$\mathrm{PtCl_2}$(chiraphos)	3530	41.4
$\mathrm{PtCl_2}$(dppb)	3538	9.9
$\mathrm{PtCl_2}$(prophos)	3610[b]	48.0
	3567[c]	31.4
cis-$\mathrm{PtI_2(PPh_3)_2}$ (**1**)	3455	11.92
trans-$\mathrm{PtI_2(PPh_3)_2}$ (**2**)	2496	12.65
$\mathrm{PtI_2}$(bdpp) (**3**)	3252	5.76
$\mathrm{PtI_2}$(chiraphos) (**4**)	3291	40.36
$\mathrm{PtI_2}$(dppb) (**5**)	3333	5.43
$\mathrm{PtI_2}$(prophos) (**6**)	3361	48.04[b]
	3312	29.76[c]

[a] $\mathrm{CDCl_3}$, room temperature. [b] P adjacent to $\mathrm{CH(CH_3)}$. [c] P adjacent to $\mathrm{CH_2}$.

2.650 Å) bond length is slightly larger than the average Pt(II)−I bond distance found in the literature in tetracoordinated Pt complexes (2.622 Å).[13] The Pt−P bond lengths fall in the normal range found for that interactions; however, internal comparison between the Pt−P bond distances trans to the $\mathrm{SnCl_3}$ ligand (mean 2.300 Å) and those trans to the I atom (mean 2.250 Å) clearly shows that the $\mathrm{SnCl_3}$ ligand has a stronger *trans* influence than iodine.

In order to fully describe the conformation of the bdpp ligand, one can use the torsional angles within the metallacycle together with the P−Pt−P−C_{ipso} and the Pt−P−C_{ipso}−C_{ortho} ones, which describe the ring conformation, the axial/equatorial character of the phenyl rings with respect to the P−Pt−P plane, and the face/edge exposure of the phenyls, respectively. A close analysis of these data shows that the two independent molecules in the asymmetric unit have markedly different geometries: the Pt(bdpp) metallacycle conformation being closer to skew-boat in **A** and to δ-skew in **B**. The disorder present in molecule **A** evidences the conformational flexibility of six-membered metallacycles, and it can be rationalized by assuming the superposition of two different conformations **A** and **A′** which share the phenyl disposition but differ in the methyl arrangement (equatorial/axial *vs* axial/equatorial) and in the location of the central $\mathrm{CH_2}$ moiety (above *vs* below the P−Pt−P plane).

When the metallacycle conformation changes substantially, as in the **A**/**B** interconversion, there are correspondingly large variations in the axial/equatorial character and in the face/edge exposure of the phenyl rings. The bond angles at the Pt atom are also sensitive to the conformation of the bdpp ligand since the skew-boat conformation requires a larger P−Pt−P “bite” angle [95.7(2)° in **A**] than the δ-skew one [91.0(2)° in **B**].[14] As a matter of fact the shrinkage of the “bite” angle is associated with a corresponding widening of the I−Pt−Sn angle (and to a different rotameric disposition of the $\mathrm{SnCl_3}$ ligand) which ranges from 82.96(4)° in **A** to 86.73(4)° in **B**.

The following considerations emerge from the present crystallographic study: (i) Six-membered metallacycles are rather flexible, and the tendency of methyl groups to occupy equatorial positions is not enough to reduce their conformational variability even if, according to experimental and theoretical data,[15] the skew conformation is slightly preferred. (ii) Different conformations of the metallacycle can share the same phenyl disposition. (iii) Large variations of the ring conformations can significantly affect the stereochemistry at the Pt atom.

It is worth noting that the lack of a close correspondence between the phenyl and the metallacycle conformations does not necessarily imply a “weak” transfer of the “chiral inprinting” from one side to the other of the metal complex since the average molecular conformation induced by (*S*,*S*)-bdpp will be in any case enantiomeric with respect to that induced by (*R*,*R*)-bdpp.

Experimental Section

General Comments. The compounds described in this report are sensitive to oxygen and moisture and so need to be handled in a standard vacuum line or under purified argon atmosphere. The $\mathrm{PtCl_2}$(diphosphine)-type starting compounds were prepared and purified by literature methods.[5i,l] Solvents were dried by conventional procedures.

The ^{31}P NMR spectra were recorded at 121.4 MHz on a Varian Unity 300 spectrometer at room temperature under argon. The chemical shifts were reported relative to $\mathrm{H_3PO_4}$. Infrared spectra of Nujol mulls were recorded on a Bio-Rad FTS-40. The elemental analyses were performed on a 1108 Carloerba apparatus.

---

[12] Consiglio, G.; Pino, P.; Scalone, M. ETH-Zurich, unpublished results.

[13] Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

[14] The fact that δ-skew conformations have a smaller “bite” angle than the other ones can be also verified in the crystal structure determinations of $\mathrm{[Rh(BDPP)(NBD)]^+}$ (chair; P−Rh−P 95.1(3)°) and $\mathrm{[Rh(BDPP)(COD)]^+}$ (δ-skew; P−Rh−P 88.6(1)°): Bakos, J.; Tóth, I.; Szalontai, G.; Párkányi, L. *J. Organomet. Chem.* **1989**, *370*, 263.

[15] Boucher, H.; Bosnich, B. *Inorg. Chem.* **1976**, *15*, 1471. Kojima, M.; Fujita, M.; Fujita, F. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 898. Kojima, M.; Fujita, J. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3237. Goto, M.; Nakayabu, N.; Ito, H.; Tsubamato, H.; Nabayashi, K.; Kuroda, Y.; Sakai, T. *Inorg. Chem.* **1986**, *25*, 1684. DeHayes, L. J.; Bush, D. H. *Inorg. Chem.* **1973**, *12*, 1505. Niketic, S. R.; Woldbye, F. *Acta Chem. Scand.* **1973**, *27*, 621.

Table 4. NMR Data for the Platinum Complexes Obtained in the PtX_2(diphosphine) + $SnCl_2$ + SnI_2 System (X = Cl, I)

	P^A (*trans* to $SnCl_3^-$)				P^B (*cis* to $SnCl_3^-$)		
$PtX(SnCl_3)(PP)$	δ (ppm)	*J*(Pt−P) (Hz)	*J*(Sn−P)[a] (Hz)	*J*(P−P) (Hz)	δ (ppm)	*J*(Pt−P) (Hz)	*J*(Sn−P)[b] (Hz)
7	10.6	2786	4105; 3937	24.2	5.4	3278	157
8	13.7	2729	4115; 3933	24.7	7.5	3337	180
9	48.1	2844	*c*	13.9	39.7	3177	151
10	46.9	2841	3812; 3975	13.7	38.4	3180	178

[a] $J_{trans}(^{119}Sn-^{31}P)$; $J_{trans}(^{117}Sn-^{31}P)$. [b] $J_{cis}(^{119}Sn-^{31}P)$ and $J_{cis}(^{117}Sn-^{31}P)$ coincide. [c] Because of the low intensity of the tin satellites, *J*(Sn−P) values were not determined.

Synthesis of $PtI_2(PhCN)_2$ and PtI_2(diphosphine) Complexes. A solution of 0.25 g (0.55 mmol) of PtI_2 in 10 mL of benzonitrile was reacted at 100 °C for 1 h. The hot solution was filtered and cooled to room temperature. Dark yellow crystals were obtained which were used for experiments without further purification. (Yield: 80%. Anal. Calcd for $C_{14}H_{10}I_2N_2Pt$: C, 25.67; H, 1.54. Found: C, 25.84; H, 1.71. IR (Nujol, cm^{-1}): 198, 157 (ν(Pt−I); 103 (δ(Pt−I).)

A 0.25 mmol amount of $PtI_2(PhCN)_2$ was dissolved in refluxing benzene, and a solution of 0.26 mmol of diphosphine in 3.5 mL of benzene was added. The experiment was conducted for 2 h. A powderlike yellow solid was formed, which was filtered off after the mixture was cooled to room temperature. The product was washed with cold benzene. The yields were only slightly dependent on the type of diphosphine used and were in the range of 85−92%. All products gave satisfactory analysis. The products were characterized by ^{31}P NMR (Table 3).

Synthesis of $PtI(SnCl_3)$(bdpp) (7). A solution of 105.9 mg (0.15 mmol) of $PtCl_2$(bdpp) and 14.2 mg (0.075 mmol) of $SnCl_2$ in 6 mL of chloroform was stirred under argon until the solution became completely homogeneous. A 27.9 mg (0.075 mmol) amount of SnI_2 was added, and the reaction was carried out for 2 h. After the solution was allowed to stand, some pale yellow crystals separated, and these were filtered out and dried. Then 1 mL of hexane was added to the mother liquid to obtain an additional amount of the product. Yield: 70%. Anal. Calcd for $C_{29}H_{30}Cl_3IPtSn$: C, 35.27; H, 3.06; Found: C, 35.44; H, 3.21. IR (Nujol, cm^{-1}): 163, 154 (ν(Pt−I); 339, 316, 296 (ν(Sn−Cl); 85−140 (br) (ν(Sn-Pt); bond angle bending mode frequencies δ(Pt−I) and δ(Sn−Cl) are not resolved. ^{31}P NMR: Table 4

Structure Determination and Refinements. A transparent yellow crystal of dimensions 0.15 × 0.10 × 0.07 mm was mounted on an Enraf-Nonius CAD-4 diffractometer, and 25 intense reflections having a θ value in the range 10.0−14.0° were centered using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Least-squares refinement of their setting angles resulted in the unit-cell parameters reported in Table 5, together with an orientation matrix relating the crystal axes to the diffractometer axes. A total of 6804 diffracted intensities [4256 with $I > 3\sigma(I)$] were collected at room temperature with variable scan speed (maximum scan time for each reflection: 70 s), and by exploring the quadrant of the reciprocal lattice with $-17 \le h \le 17$, $0 \le k \le 17$, and $0 \le l \le 19$, out to a maximum 2θ angle of 50°.

Intensity was checked by monitoring three standard reflections every 60 min, and no decay was observed. The diffracted intensities were corrected for Lorentz, polarization, and background effects. An empirical absorption correction was applied according to the method developed by North *et al.* based on Ψ scans [Ψ 0−360°, every 10°] of three reflections having χ values near 90°.[16] The position of the two independent platinum atoms was determined from a three-dimensional Patterson function. The coordinates of the remaining non-hydrogen atoms were located by successive least-squares refinements and Fourier difference maps.

Table 5. Summary of Crystal Data and Data-Collection/Analysis Parameters for 7·$CHCl_3$

formula	$C_{30}H_{31}Cl_6IP_2PtSn$
M	1106.87
cryst system	monoclinic
space group	$P2_1$ (No. 4)
a/Å	15.488(2)
b/Å	14.999(2)
c/Å	16.303(2)
β/deg	98.67(1)
V/Å^3	3744.0(8)
Z	4
D_c/g cm^{-3}	1.964
F(000)	2096
cryst dimens/ mm	0.15 × 0.10 × 0.07
μ(Mo Kα)/mm^{-1}	5.76
min relative transm factor	0.92
no. of reflcns for Ψ-scan	3
θ range/deg	3−25
scan mode	ω
scan range/deg	0.7 + 0.35 tan θ
required σ(*I*)/*I*	0.01
max scan time/s	70
octants of recipr space collcd	±*h*,*k*,*l*
cryst decay	no
no. of collcd reflcns (at RT)	6804
no. of unique obsd reflns [$I > 3\sigma(I)$]	4256
no. of refined params	644
weights	$1.0/(\sigma^2(F_o^2) + (0.0298P)^2 + 8.5733P)$[a]
max shift/error	<0.01
*R*1[b]	0.0327
w*R*2[c]	0.0686
goodness of fit[d] (on F_o^2)	1.115
max peak diff Fourier map/e Å^{-3}	0.56

[a] $P = (F_o^2 + 2F_c^2)/3$. [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$. [d] $GoF = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where *n* is the number of reflections and *p* is the number of refined parameters.

Full-matrix least squares were based on F^2. Anisotropic thermal parameters were assigned to all non-hydrogen atoms but those of the disordered metallacycle in molecule **A** which were refined with isotropic thermal parameters and were found to have similar P−C and C−C bond distances; the final occupancy factors were 0.66 and 0.34 for the **A** and **A′** atoms, respectively. The phenyl groups were treated as rigid bodies of D_{6h} symmetry (C−C 1.39 Å). Hydrogen atoms were placed in idealized positions (C−H 0.93−0.98 Å) and refined, riding on their parent atom with a common refinable isotropic thermal parameters ($U = 0.082(8)$ Å^2).

The crystal structure is pseudosymmetric (the pseudo center being at ca. 0.244, −0.247, −0.261); however, (i) the chiral nature of the molecule, (ii) the presence of plenty of intense *h*01 reflections with *l* or *h* + *l* odd (which should be absent in the case of the centrosymmetric $P2_1/c$ or $P2_1/n$ space group), (iii) the marked different conformation of molecules **A** and **B**, and (iv) the impossibility of refining a sensible molecular model in the centrosymmetric $P2_1/c$ or $P2_1/n$ space groups definitely confirm the correctness of the $P2_1$ space group even in the presence of two independent pseudosymmetric molecules.

---

(16) North, A. C. T.; Philips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

The absolute configuration was determined by internal comparison and subsequently confirmed by refining the Flack parameter. The final values of the agreement indices, $R1$ and $wR2$, for the correct (and uncorrect) enantiomeric choice were 0.0327 (0.0374) and 0.0686 (0.0813), respectively. Maximum residual in the final difference Fourier synthesis: 0.56 e/Å^3. Scattering factors for neutral non-hydrogen atoms and hydrogen atoms and anomalous dispersion corrections for scattering factors were taken from ref 17.

All the calculations were performed on a Personal IRIS 35 using SHELXL-93.[18]

Acknowledgment. L.K. thank G. Szalontai and S. Iglewski for NMR measurements. The financial support of the Hungarian National Science Foundation (OTKA T4292) and that of the Commission of the European Communities (COST PL927474) is acknowledged.

Supporting Information Available: Listings of bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and thermal parameters, atomic coordinates of non-hydrogen atoms and thermal parameters, and torsional angles (Tables S1−S5) (6 pages). Ordering information is given on any current masthead page.

OM9509406

---

(17) *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C, Tables 4.2.6.8 and 6.1.1.4.

(18) Sheldrick, G. M. SHELXL-93: program for structure refinement. University of Goettingen, 1994.

(19) Johnson, C. K. ORTEP: a FORTRAN thermal-ellipsoid-plot program for crystal structure illustrations. Oak Ridge National Laboratory, Oak Ridge, TN, 1971.