Journal of Organometallic Chemistry, 466 (1994) 277–282

Isolation and characterization of the acyl complexes *trans*-[Pt(PPh$_3$)$_2$(COR)Cl] (R = ^{n}Bu or ^{s}Bu) and their relevance to the hydroformylation of linear butenes catalyzed by platinum/tin/triphenylphosphine catalytic systems. Molecular structure of *cis*-[Pt(PPh$_3$)$_2$Cl(SnCl$_3$)]

G. Cavinato [a], G. De Munno [b], M. Lami [c], M. Marchionna [c], L. Toniolo [d] and D. Viterbo [e]

[a] *Dipartimento di Chimica Inorganica, Via Loredan, 4, Università di Padova, 35131 Padova (Italy)*
[b] *Dipartimento di Chimica, Università della Calabria, 87030 Arcavacata di Rende (Italy)*
[c] *SNAMPROGETTI S.p.A., Research Division, Via Maritano 26, 20097 (Italy)*
[d] *Dipartimento di Chimica, Università di Venezia, Calle Larga S. Marta 2137, 30123 Venezia (Italy)*
[e] *Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Università di Torino, Via P. Giuria 7, 10125 Torino (Italy)*

(Received March 30, 1993)

Abstract

The acyl complex *trans*-[Pt(PPh$_3$)$_2$(CO^{n}Bu)Cl] (**A**) has been synthesized by reaction of [Pt(PPh$_3$)$_2$Cl$_2$] with 1-butene under 100 atm of CO at 80–100°C, in ethanol. With 2-butene rather than 1-butene under the same conditions, a mixture of the above acyl complex and of *trans*-[Pt(PPh$_3$)$_2$(CO^{s}Bu)Cl] (**B**) was formed. Complexes **A** and **B** do not interconvert. The new acyl complexes **A** and **B** have been characterized by IR and ^{1}H NMR and ^{13}C NMR spectroscopy. The ratio **A**/**B** increases with PPh$_3$/Pt ratio and with temperature. The formation of two isomers when 2-butene is used involves an isomerization process which is likely to be limited to the alkyl precursor complexes. The reactivity of complexes **A** and **B** has been tested in reactions with SnCl$_2$, H$_2$, HCl and *trans*-[Pt(PPh$_3$)$_2$HCl]. From the reaction solutions crystals of *cis*-[Pt(PPh$_3$)$_2$Cl(SnCl$_3$)] have been obtained. Its molecular structure has been determined by X-ray diffraction. The Pt atom has *cis* square planar coordination, with angular distortions due to steric factors. The strong *trans* influence of the SnCl$_3$ group is confirmed by the lengthening of the *trans* Pt–P distance. The SnCl$_3$ group has the pyramidal geometry found in all related compounds.

Key words: Acyl; Butenes; Hydroformylation; Platinum; Tin

1. Introduction

Hydroformylation of olefins catalyzed by platinum/tin/phosphine systems is of much current interest because of the usually high activity and selectivity. Triphenylphosphine is most usually employed [1–4], although chelating phosphines also have been extensively studied [5,6] especially for asymmetric hydroformylation [7,8]. Most of the studies deal with the hydroformylation of 1-olefins, which are more reactive than internal olefins.

It has been reported that platinum acyl complexes *trans*-[Pt(PPh$_3$)$_2$(COR)X] (X = Cl or SnCl$_3$) with linear chains R, have been isolated during the course of hydrocarboalkoxylation or hydroformylation of 1-olefins, such as for example propene or 1-hexene, catalyzed by [Pt(PPh$_3$)$_2$Cl$_2$]-SnCl$_2$ (Pt/Sn = 1/5; p_{CO} = 20–50 atm; 70°C; ethanol or a ketone as solvent; possibly in the presence of 20–50 atm of H$_2$ [9–11]). These acyl complexes are catalytic intermediates or precursors of active catalytic species in these reactions. A Pt–Sn bond plays a key role in catalytic activity and is essential in promoting the hydrogenolysis of the Pt–acyl bond, leading to the aldehyde. This step is likely to be slower than the other steps of the catalytic

---

Correspondence to: Professor L. Toniolo.

0022-328X/94/$7.00
SSDI 0022-328X(93)23958-Z

cycle, such as insertion of the olefin into a Pt–H bond and the insertion of CO into the Pt–C bond of the resulting Pt alkyl [12,13].

The present work deals with the synthesis, characterization and reactivity of the new acyl complexes *trans*-$[Pt(PPh_3)_2(CO^nBu)Cl]$ (**A**) and *trans*-$[Pt(PPh_3)_2(CO^sBu)Cl]$ (**B**), and with their role in the hydroformylation of 1-butene and of 2-butene catalyzed by the mixture $[Pt(PPh_3)_2Cl_2]/PPh_3/SnCl_2$. The molecular structure of *cis*-$[Pt(PPh_3)_2Cl(SnCl_3)]$, which was isolated after reaction of complex **B** with HCl, is also reported.

2. Results and discussion

The syntheses reported in Table 1 refer to the syntheses of acyl complexes **A** and **B**. Experiments have been carried out in ethanol, in the absence of dihydrogen, using the procedure already reported [9–11], but varying the temperature and the PPh_3/Pt molar ratio, under slightly different conditions that have also allowed the isolation of the branched-chain complex **B** together with complex **A**.

The formation of the acyl complexes can be schematized as below.

$$[Pt(PPh_3)_2HCl] \xrightarrow{\text{butene}} [Pt(PPh_3)_2({}^nBu \text{ or } {}^sBu)Cl] \xrightarrow{CO} \mathbf{A}, \mathbf{B}$$

Scheme 1.

Ethanol can act as a hydride source for the platinum precursor [14] which is converted into hydride $[Pt(PPh_3)_2HCl]$. The olefin inserts into the Pt–H bond with formation of a linear or branched butyl derivative, into which CO inserts yielding the observed acyl complexes **A** and **B**.

TABLE 1. Regioselectivity in synthesis and catalysis

Run	Olefin	PPh_3/Pt	T (°C)	N/B	
				Synthesis [a]	Catalysis [b]
1	1-butene	5	100	100/0 [c]	99/1
2	2-butene	5	120	92/8 [d]	68/32
3	2-butene	5	80	69/31 [d]	55/45
4	2-butene	2	120	82/18 [e]	52/48
5	2-butene	2	80	49/51 [f]	16/84

[a] Platinum precursor: $[Pt(PPh_3)_2Cl_2] + PPh_3$; $[Pt] = 0.02$ M; [butene/Pt] 100; $p_{CO} = 100$ atm; solvent: EtOH (50 ml).

[b] Catalyst precursor: $[Pt(cod)Cl_2] + PPh_3 + SnCl_2$; $[Pt] = 0.01$ M; $Pt/SnCl_2 = 1/5$; $[butene/Pt] = 400$; $p = 140$ atm; $CO/H_2 = 1/1$; solvent: CH_2Cl_2 (30 ml); reaction time (t): 1.5 h for 1-butene, 2 h for *cis*-2-butene. Runs 1, 2, 4, and 5 ref. [15]; run 3 this work.

[c] $t = 7$ h.

[d] $t = 64$ h.

[e] $t = 16$ h.

[f] $t = 30$ h.

When 1-butene is used, only the linear acyl complex **A** is obtained (70% yield). When 2-butene is used both complexes **A** and the branched isomer **B** are obtained (50% total yield). It is worth noting that this is the first branched-chain isomer that has been isolated during the course of hydroformylation or related experiments.

Under the synthesis conditions reported in Table 1, complexes **A** and **B** do not interconvert. A reasonable explanation of these results is as follows. The insertion of 1-butene into the Pt–H bond gives mainly a species having a Pt–^{n}Bu moiety, which quickly reacts with CO yielding complex **A**. However 2-butene yields two isomers, with linear or branched alkyls, through an isomerization process. The Pt–^{n}Bu isomer appears to be the more favoured because 1-butene yields complex **A** with practically 100% regioselectivity. It appears also that the insertion of CO occurs at a rate close to that of the isomerization process, and that it is practically irreversible, preventing the equilibration of complexes **A** and **B**. If both the insertion of the olefin and of CO were reversible, or the isomerization were fast in comparison to the CO insertion, 1-butene and 2-butene should yield the same product.

The selectivity towards the linear isomer **A** increases with temperature and with the molar ratio PPh_3/Pt. When the PPh_3/Pt molar ratio is $\leqslant 2$ the system is unstable, particularly at high temperature and during long reaction times. Formation of Pt metal, together with traces of anionic platinum clusters of the type $[Pt_{15}(CO)_{30}]^{2-}$ [15], is observed. As a result the yield in acyl complexes is lower. No acyl complex was isolated or detected in solution when employing the catalytic system in the ratio $Pt/P = 1/1$, for example when using $[Pt(PPh_3)(CO)Cl_2]$. Longer reaction times are used only when the stability of the system is sufficiently high, *i.e.* at low temperature and high PPh_3/Pt ratio. These observations show that for internal olefins, optimization of an established procedure of synthesis is much more complicated than with terminal olefins.

The catalytic hydroformylation of the butenes has been carried out under conditions close to those employed for the synthesis of the acyl complexes, but also in the presence of molecular hydrogen and of $SnCl_2$. The results obtained in the catalytic experiments (Table 1) parallel those just described for the synthesis of acyl complexes **A** and **B**. Thus, 1-butene yields the linear pentanal with nearly total regioselectivity, whereas 2-butene also gives the branched isomer.

The internal olefin is less reactive, as commonly found in hydroformylation reactions [2]. As already mentioned, on increasing either the PPh_3/Pt molar ratio or the temperature, the N/B ratio of the acyl complexes **A** and **B** increases (N/B refers also to the ratio between normal and branched aldehyde, pentanal

TABLE 2. IR and NMR data for the acyl complexes

	[Pt(PPh$_3$)$_2$(CO^{n}Bu)Cl]	[Pt(PPh$_3$)$_2$(CO^{s}Bu)Cl]
ν_{CO} (cm^{-1}) (CH$_2$Cl$_2$)	1641	1630
^{1}H NMR (δ, ppm) (CDCl$_3$)	1.5 (t, 2H) (J = 7.0 Hz) 0.6–0.25 (m, 7H)	1.73 (m, 2H) 0.48 (d, 3H) (J = 7.0 Hz) 0.40 (t, 3H); 0.15 (m, 2H)
^{13}C NMR (δ, ppm) (CDCl$_3$)	218.5 (t); 58.3 (t) 25.9; 21.7; 13.5	220.7 (t); 60.4 (t) 25.4; 14.0; 12.6
^1J(Pt–C) (Hz)	975	965
^2J(Pt–C) (Hz)	87	87

and 2-methylbutanal). This is probably due to the fact that, on increasing the PPh$_3$/Pt ratio, the number of the PPh$_3$ molecules coordinated to platinum increases, increasing the steric hindrance on the metal. Under these conditions the formation of the less sterically hindered intermediate having a Pt–^{n}Bu moiety is likely to be favoured compared to the isomer having a branched butyl chain. These results are consistent with those observed for the hydroformylation of butenes promoted by [Pt(cod)Cl$_2$]/PPh$_3$/SnCl$_2$ under similar conditions [4,16].

For the synthesis of the acyl complexes, the N/B ratio is higher than that observed for catalytic hydroformylation, probably because in the former case the reaction is stoichiometric and much slower than the catalytic one: a longer lifetime of the alkyl complex in the synthesis might allow the isomerization to proceed to a marked extent. The ratio is very close only for run 3. However, in this case the catalytic run is very slow (turnover frequency = 0.2 h^{-1}). The different N/B ratio may reflect also the influence on the regioselectivity steps of the Pt–Sn bonds, present only in the hydroformylation catalytic system.

The new acyl complexes **A** and **B** have been characterized by IR and ^{1}H NMR and ^{13}C NMR spectroscopies (Table 2). Pure complex **A** has been prepared by run 1 (Table 1), whereas pure complex **B** has been prepared by adding the chloride of 2-methylbutanoic acid to [Pt(PPh$_3$)$_2$(C$_2$H$_4$)], following a known procedure [17].

The IR spectrum shows one band for ν(C=O) at *ca.* 1630–1640 cm^{-1}, as found in related acyl complexes of Pt^{II} [9–11]. The proportion of the two acyl complexes was measured by the relative intensities of the ^{13}C NMR signal at δ 13.5 of the normal acyl species and the signal at δ 12.6 of the branched one.

The reactivity of complexes **A** and **B** has been tested in reactions with H$_2$, HCl and the hydride *trans*-[Pt(PPh$_3$)$_2$HCl] in the presence of SnCl$_2$, which are of relevance to the hydroformylation catalytic cycle. In the absence of SnCl$_2$ no hydroformylation occurs with any of the platinum reagents.

The reaction of **A** or **B** with SnCl$_2$ gives mainly decarbonylation with formation of [Pt(PPh$_3$)$_2$(CO)Cl] [SnCl$_3$] (ν(C≡O) = 2112 cm^{-1}) and of [Pt(PPh$_3$)$_2$-H(CO)(SnCl$_3$)] (ν(C≡O) = 2082, 2061 cm^{-1}) [18], butenes and butane. It is likely that the first step of the reaction is the reverse of CO insertion into a Pt–C σ-bond of an alkyl species. The resultant Pt-alkyl intermediate is unstable and gives the observed products. Thus the decomposition of complexes **A** and **B** basically reverses the reaction of their formation in Scheme 1. This behaviour has already been described for related acyl complexes with a linear R group [19]. Probably, other species such as for example [Pt(PPh$_3$)$_2$Cl(SnCl$_3$)], are present in solution after decarbonylation (see below).

It has been also found that complexes **A** and **B** react with H$_2$, in the presence of SnCl$_2$, to give the corresponding aldehyde, although in small yield (*ca.* 10%). When employing a mixture of the two acyl complexes, the N/B ratio of these species is maintained in the final aldehyde products, suggesting that complexes **A** and **B** have similar reactivity, and also that under hydroformylation conditions (80–120°C; p = 140 atm, CO/H$_2$ = 1/1; Pt/Sn = 1/5) they probably do not interconvert as found for example in related Pd complexes [20]. It is known that 1-pentene isomerizes to 2-pentene (*cis* and *trans*) under ambient conditions, in the presence of the hydride *trans*-[Pt(PPh$_3$)$_2$H(SnCl$_3$)] [19]. Thus also under hydroformylation conditions the CO insertion is likely to be fast and irreversible, preventing the isomerization process through Pt–Bu intermediates.

In addition, it has been observed that the reaction time for the completion of the hydrogenation of complex **B** (t = 30 h) is intermediate between that for R = Et (t = 72 h) and that for R = 1-hexyl (t = 24 h) [21].

As the aldehyde may also form via interaction of the acyl complex with a hydride, we checked the reaction of *trans*-[Pt(PPh$_3$)$_2$HCl] with complexes **A** or **B** in the presence of SnCl$_2$. However no aldehyde is observed, decarbonylation products being the only species detected.

Since traces of acid affect the hydroformylation of linear butene with the platinum/tin systems [4,16], the reaction of the acyl complexes with HCl has been checked. Complex **B** reacts with HCl, in the presence of SnCl$_2$ (Pt/HCl/SnCl$_2$ = 1/1), yielding only 6% 2-methylbutanal, and mainly decarbonylation products. The reactivity of complex **A** is similar. From the resulting solution, which also contains the species [Pt(PPh$_3$)$_2$(CO)Cl][SnCl$_3$], crystals of *cis*-[Pt(PPh$_3$)$_2$-Cl(SnCl$_3$)] are obtained by layering cyclohexane on the CH$_2$Cl$_2$ solution. This complex reacts with molecular

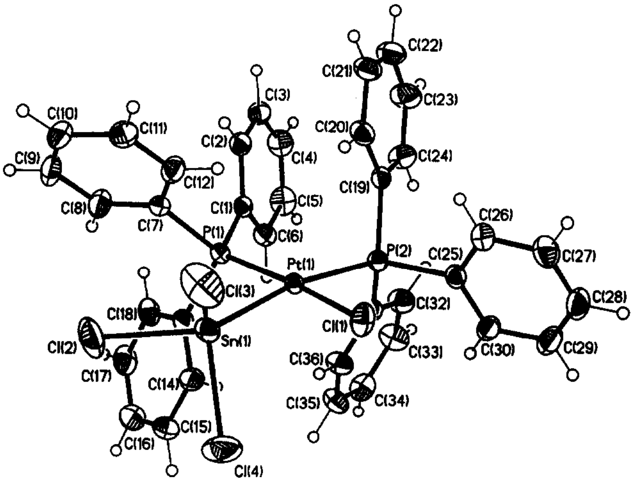

Fig. 1. Molecular structure of *cis*-[Pt(PPh$_3$)$_2$Cl(SnCl$_3$)].

hydrogen yielding the hydride *trans*-[Pt(PPh$_3$)$_2$-H(SnCl$_3$)], which is one of the hydrides that starts the catalytic cycle [12,19]. The structure of *cis*-[Pt(PPh$_3$)$_2$-Cl(SnCl$_3$)] is described below.

The comparison here reported between branched and linear acyl species sheds some more light on the isomerizing behaviour of the system. Catalysis experiments have previously suggested that the isomerizing effects of temperature [4,16,22], of the particular kind of phosphorus ligand L [23], and of the L/Pt molar ratio [4,22] were all related to the different stabilities of alkyl complexes. All the evidence obtained in the present work further confirms that isomerization is confined to alkyl complexes, and does not involve acyl species.

2.1. Structure of cis-[Pt(PPh$_3$)$_2$Cl(SnCl$_3$)

The molecular structure and atom-numbering scheme are shown in Fig. 1. The structure consists of discrete square planar *cis* molecules. A considerable widening of the P(1)–Pt(1)–P(2) angle and narrowing of the opposite Sn(1)–Pt(1)–Cl(1) angle are observed, ascribed to the steric repulsion of the two triphenylphosphines. Similar angular distortions are found in *cis*-[Pt(PPh$_3$)$_2$Cl$_2$] [24]. The Pt(1)–Sn(1) distance falls within the range of values reported in the literature (*cf*. Table 6 of ref. [19]) and is very close to the values of 2.601(1) and 2.600(2) Å reported for *trans*-[Pt-(PPh$_3$)$_2$H(SnCl$_3$)] (19) and *trans*-[Pt(PCy$_3$)$_2$H(SnCl$_3$)] [26].

The significant difference between the two Pt(1)–P bond lengths is consistent with the strong *trans* effect of the SnCl$_3$ group associated with the opposite *cis* effect [26].

Indeed while the *trans* Pt(1)–P(2) bond is longer than the reported mean Pt–P distance of 2.294 Å [27], the *cis* Pt(1)–P(1) bond is shorter, consistent with the ^{31}P-NMR results [28]. The Pt(1)–Cl(1) distance is similar to the values in *cis*-[Pt(PPh$_3$)$_2$Cl$_2$] [24].

As in related compounds, the SnCl$_3$ group has a pyramidal geometry with an average Pt–Sn–Cl angle of 119.4° and an average Cl–Sn–Cl angle of 97.9°.

3. Experimental section

All the reactions were carried out under strict anaerobic conditions. Solvents were distilled prior to use.

1-Butene, *cis*-2-butene and *trans*-2-butene (all 99.5% pure) (Matheson) and anhydrous SnCl$_2$, SOCl$_2$, CH$_3$CH$_2$CH(CH$_3$)COOH and PPh$_3$ (Fluka) were used as purchased.

[Pt(cod)Cl$_2$] [29], [Pt(PPh$_3$)$_2$Cl$_2$] [30], [Pt(PPh$_3$)$_2$-HCl] [31], [Pt(PPh$_3$)(CO)Cl$_2$] [32], [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] [33], and CH$_3$CH$_2$CH(CH$_3$)COCl [34] were prepared as described in the literature.

GC/MS measurements were performed on a Finnegan 4500 instrument, NMR experiments on a Bruker AC200 (200 MHz) instrument. Gas chromatographic analyses and catalytic runs were performed as described elsewhere [16].

3.1. Preparation of the acyl complexes

trans-[Pt(PPh$_3$)$_2$(CO^{n}Bu)Cl] and mixtures with *trans*-[Pt(PPh$_3$)$_2$(CO^{s}Bu)Cl] were obtained by modifying a known procedure [9–11].

In a typical experiment, 0.80 g of *cis*-[Pt(PPh$_3$)$_2$Cl$_2$] together with 0.26 g of PPh$_3$ and 50 ml of ethanol (isopropanol can also be used) were introduced into an autoclave. The autoclave was cooled, loaded with 2.0 g of butene and then pressurized with 100 atm of CO. It was placed in a thermostatted oil bath and finally the temperature was raised to the desired value. At the end of the reaction time (Table 1) the autoclave was cooled and, after a few hours, depressurized.

White crystals of the acyl complexes were filtered off, washed with EtOH and dried under vacuum.

The yield was nearly 70% for *trans*-[Pt(PPh$_3$)$_2$-(CO^{n}Bu)Cl] when using 1-butene and 50% of a mixture containing both *trans*-[Pt(PPh$_3$)$_2$(CO^{n}Bu)Cl] and *trans*-[Pt(PPh$_3$)$_2$(CO^{s}Bu)Cl] when employing 2-butenes.

Anal. Calcd. for C$_{41}$H$_{39}$ClOP$_2$Pt: C 58.57; H 4.68. Found: C 58.82; H 4.85%.

3.2. Preparation of trans-[Pt(PPh$_3$)$_2$(CO^{s}Bu)Cl]

The literature procedure was followed [11]. s-Butanoyl chloride (1 ml) was added dropwise to a solution of [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] (1.50 g) in 20 ml of toluene. Gas evolution began immediately and a pale yellow-green solution was formed. This was kept at room temperature for 1 h, during which time pale yellow crystals separated. Hexane (*ca.* 30 ml) was added to precipitate further solid. The solid was filtered off, dried (1.43 g, 85%) and recrystallized from toluene/hexane. Anal. Calcd. for $C_{41}H_{39}ClOP_2Pt$: C 58.57; H 4.68. Found: C 58.82; H 4.85%.

3.3. Reactivity of the acyl complexes

The reactions of the acyl complexes with $SnCl_2$ and HCl or H_2 or *trans*-[Pt(PPh$_3$)$_2$HCl] were performed in a small Schlenk tube, equipped with a magnetic stirring bar, a gas inlet (for H_2) and a rubber septum.

TABLE 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

Atom	*x*	*y*	*z*	U_{eq} [a]
Pt(1)	516(1)	1645(1)	1756(1)	28(1)
Sn(1)	1726(1)	1680(1)	697(1)	41(1)
P(1)	−592(1)	2577(1)	1075(1)	30(1)
P(2)	−253(1)	1539(1)	2890(1)	31(1)
Cl(1)	1769(2)	669(1)	2266(1)	51(1)
Cl(2)	1594(2)	2545(2)	−436(2)	93(1)
Cl(3)	1992(3)	501(2)	22(2)	95(1)
Cl(4)	3492(2)	2018(2)	1309(2)	89(1)
C(1)	−1852(5)	2765(3)	1366(4)	33(2)
C(2)	−2763(5)	2368(4)	981(4)	43(2)
C(3)	−3704(6)	2482(5)	1232(5)	54(3)
C(4)	−3731(6)	2998(5)	1877(5)	59(3)
C(5)	−2846(7)	3392(5)	2260(6)	58(3)
C(6)	−1889(6)	3289(4)	2010(5)	42(2)
C(7)	−964(5)	2301(4)	−10(4)	35(2)
C(8)	−1243(7)	2861(5)	−626(4)	54(3)
C(9)	−1446(7)	2648(5)	−1443(5)	63(3)
C(10)	−1397(7)	1872(6)	−1666(5)	61(3)
C(11)	−1152(6)	1295(5)	−1047(5)	56(3)
C(12)	−947(6)	1506(4)	−233(4)	48(3)
C(13)	40(5)	3554(4)	1140(4)	37(2)
C(14)	1116(6)	3618(4)	1449(5)	47(2)
C(15)	1603(7)	4351(5)	1521(5)	63(3)
C(16)	1014(7)	5028(5)	1283(5)	66(3)
C(17)	−59(8)	4971(4)	978(5)	62(3)
C(18)	−550(7)	4230(4)	900(5)	49(3)
C(19)	−1626(5)	1193(3)	2595(4)	34(2)
C(20)	−1872(6)	673(4)	1937(4)	48(3)
C(21)	−2876(6)	338(5)	1711(5)	55(3)
C(22)	−3632(7)	530(5)	2144(5)	61(3)
C(23)	−3423(7)	1054(6)	2754(6)	70(4)
C(24)	−2427(6)	1384(5)	3000(5)	54(3)
C(25)	368(5)	817(4)	3658(4)	39(2)
C(26)	255(6)	13(5)	3494(5)	52(3)
C(27)	766(7)	−525(5)	4091(6)	66(3)
C(28)	1349(7)	−274(6)	4817(6)	65(3)
C(29)	1460(7)	504(6)	4983(5)	63(3)
C(30)	989(6)	1069(5)	4405(4)	48(2)
C(31)	−103(5)	2480(4)	3446(3)	33(2)
C(32)	−673(6)	2721(5)	4030(5)	56(3)
C(33)	−503(7)	3438(5)	4406(6)	60(3)
C(34)	295(7)	3934(5)	4261(5)	56(3)
C(35)	893(7)	3697(5)	3716(5)	58(3)
C(36)	696(6)	2981(4)	3306(5)	48(3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 4. Selected bond lengths (Å) and angles (°)

Pt(1)–Sn(1)	2.590(1)	Pt(1)–P(1)	2.256(2)
Pt(1)–P(2)	2.317(2)	Pt(1)–Cl(1)	2.333(2)
Sn(1)–Cl(2)	2.359(3)	Sn(1)–Cl(3)	2.341(3)
Sn(1)–Cl(4)	2.356(2)	P(1)–C(1)	1.821(7)
P(1)–C(7)	1.824(6)	P(1)–C(13)	1.829(7)
P(2)–C(19)	1.828(7)	P(2)–C(25)	1.819(6)
P(2)–C(31)	1.824(6)		
Sn(1)–Pt(1)–P(1)	93.0(1)	Sn(1)–Pt(1)–P(2)	168.3(1)
P(1)–Pt(1)–P(2)	97.2(1)	Sn(1)–Pt(1)–Cl(1)	78.0(1)
P(1)–Pt(1)–Cl(1)	170.7(1)	P(2)–Pt(1)–Cl(1)	91.9(1)
Pt(1)–Sn(1)–Cl(2)	127.2(1)	Pt(1)–Sn(1)–Cl(3)	118.5(1)
Cl(2)–Sn(1)–Cl(3)	97.7(1)	Pt(1)–Sn(1)–Cl(4)	112.3(1)
Cl(2)–Sn(1)–Cl(4)	95.3(1)	Cl(3)–Sn(1)–Cl(4)	100.7(1)
Pt(1)–P(1)–C(1)	119.6(2)	Pt(1)–P(1)–C(7)	108.8(2)
C(1)–P(1)–C(7)	104.2(3)	Pt(1)–P(1)–C(13)	111.7(2)
C(1)–P(1)–C(13)	103.8(3)	C(7)–P(1)–C(13)	107.9(3)
Pt(1)–P(2)–C(19)	111.5(2)	Pt(1)–P(2)–C(25)	115.0(2)
C(19)–P(2)–C(25)	103.3(3)	Pt(1)–P(2)–C(31)	109.1(2)
C(19)–P(2)–C(31)	113.8(3)	C(25)–P(2)–C(31)	104.0(3)

The Schlenk tube with the acyl complex (0.3 g) was purged with N_2 and the solvent (CH_2Cl_2, 15 ml) injected. Anhydrous $SnCl_2$ (Pt/Sn = 1/1) and the desired reagent were then added. After 24 h the solution was examined by IR spectroscopy and analyzed by GC methods.

3.4. X-ray crystal data and structure solution and refinement

3.4.1. Crystal data

$C_{36}H_{30}Cl_4P_2PtSn$, M = 980.1, monoclinic, $P2_1/n$, $a = 12.895(3)$, $b = 16.844(3)$, $c = 16.620(3)$ Å, $\beta = 102.38(1)°$, $V = 3562$ Å^3, $Z = 4$, $D_x = 1.846$ Mg·m^{-3}, λ(Mo Kα) = 0.71073 Å, $\mu = 5.137$ mm^{-1}, $F(000) =$ 1888e, $T = 293$ K.

3.4.2. Data collection and reduction

Single crystal approximately 0.36 × 0.40 × 0.09 mm. Data collection on a Siemens R3m/V diffractometer, graphite-monochromated Mo Kα radiation. 25 reflections used ($15 \leq 2\theta \leq 30°$) to measure lattice parameters. *hkl* ranges 0–16, 0–21, −21–20; 2θ up to 54°; ω-scan. Two standard reflections measured every 150 reflections, no decline in intensity during data collection. 8489 reflections collected. Lorentz and polarization, but not absorption, corrections were applied. Of 7745 unique reflections ($R_{int} = 0.016$), 5536 with $F > 6\sigma(F)$ were used in the refinement.

3.4.3. Structure solution and refinement

Structure solution by direct methods and refinement by full-matrix least squares on $|F|$, using the SHELXTL

PLUS [25] system of programs. Hydrogen atoms located in calculated positions and refined as riding atoms with fixed isotropic U. Final $R = 0.037$ and $wR = 0.050$ for 397 parameters, with $w = [\sigma^2(F) + 0.0017F^2]^{-1}$; $S = 0.97$; largest Δ/σ in final cycle 0.006; $\Delta\rho$ for the final model between -0.98 and 2.36 e Å^{-3}. Atomic coordinates for non-hydrogen atoms are listed in Table 3 and some selected bond distances and angles appear in Table 4. Further details of the structure determination with a full list of bond lengths and angles, H coordinates, anisotropic temperature factors and structure factors, are available from the authors or the Cambridge Crystallographic Data Centre.

Acknowledgments

The authors thank SNAMPROGETTI S.p.A. for its kind permission to publish this material and the Consiglio Nazionale delle Ricerche (CNR) for partial financial support.

References

1 C.Y. Hsu and M. Orchin, *J. Am. Chem. Soc., 97* (1975) 3553.
2 I. Schwager and J.F. Knifton, *J. Catal., 45* (1976) 256.
3 G. Cavinato and L. Toniolo, *J. Organomet. Chem., 241* (1983) 275.
4 F. Ancillotti, M. Lami and M. Marchionna, *J. Mol. Catal., 58* (1990) 345.
5 T. Hayashi, Y. Kawabata, T. Isoyama and I. Ogata, *Bull. Chem. Soc. Jpn., 54* (1981) 3438.
6 A. Scrivanti, C. Botteghi, L. Toniolo and A. Berton, *J. Organomet. Chem., 344* (1988) 261.
7 L. Kollar, G. Consiglio and P. Pino, *J. Organomet. Chem., 330* (1987) 305.
8 G. Parrinello and J.K. Stille, *J. Am. Chem. Soc., 109* (1987) 7122.
9 R. Bardi, A.M. Piazzesi, G. Cavinato, P. Cavoli and L. Toniolo, *J. Organomet. Chem., 224* (1982) 407.
10 R. Bardi, A.M. Piazzesi, A. Del Prà, G. Cavinato and L. Toniolo, *J. Organomet. Chem., 234* (1982) 107.
11 G. Cavinato and L. Toniolo, *J. Organomet. Chem., 241* (1983) 275.
12 A. Scrivanti, G. Cavinato, L. Toniolo and C. Botteghi, *J. Organomet. Chem., 286* (1985) 115.
13 A. Scrivanti, A. Berton, L. Toniolo and C. Botteghi, *J. Organomet. Chem., 314* (1986) 369.
14 J. Chatt and B.L. Shaw, *J. Chem. Soc.*, (1962) 5075.
15 G. Longoni and P. Chini, *J. Am. Chem. Soc., 98* (1976) 7225.
16 F. Ancillotti, M. Lami and M. Marchionna, *J. Mol. Catal., 58* (1990) 331.
17 S.P. Dent, C. Eaborn and A. Pidcock, *J. Organomet. Chem., 97* (1975) 307.
18 M. Kubota, D.A. Phillips and J.E. Jacobsen, *J. Coord. Chem., 10* (1980) 125.
19 M. Gomez, G. Muller, D. Sainz, J. Sales and X. Solans, *Organometallics, 10* (1991) 4036.
20 J.S. Brumbaugh and A. Sen, *J. Am. Chem. Soc., 110* (1988) 803.
21 H.J. Ruegg, P.S. Pregosin, A. Scrivanti, L. Toniolo and C. Botteghi, *J. Organomet. Chem., 316* (1986) 233.
22 F. Ancillotti, M. Lami and M. Marchionna, *J. Mol. Catal., 66* (1991) 37.
23 F. Ancillotti, M. Lami and M. Marchionna, *J. Mol. Catal., 63* (1990) 15.
24 G.K. Anderson, H.C. Clark, J.A. Davies, G. Ferguson and M. Parvez, *J. Cryst. Spectrosc. Res., 12* (1982) 449.
25 A. Albinati, U. von Gunten, P.S. Pregosin and H.J. Ruegg, *J. Organomet. Chem., 295* (1985) 239.
26 H.C. Clark, G. Ferguson, M.J. Hampden-Smith, H. Ruegger and B.L. Ruhl, *Can. J. Chem., 66* (1988) 3120.
27 A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, (1989) S1.
28 R.K. Harris, I.J. McNaught, P. Reams and K.J. Parker, *Mag. Reson. Chem., 39* (1991) S60.
29 D. Drew, J.R. Doyle and A.G. Shaver, *Inorg. Synth., 13* (1972) 47.
30 G. Cavinato and L. Toniolo, *Inorg. Chim. Acta, 52* (1981) 39.
31 J.C. Bailar and H. Itatani, *Inorg. Chem., 4* (1965) 1618.
32 G.K. Anderson, H.C. Clark and J.A. Davies, *Inorg. Chem., 20* (1981) 1636.
33 U. Nagel, *Chem. Ber., 115* (1982) 1998.
34 A.I. Vogel, *Practical Organic Chemistry*, 4th Ed., Longmans, London, 1978.
35 SHELXTL PLUS Version 3.4, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, 1989.