

Isolation and characterization of the acyl complexes
trans-[Pt(PPh₃)₂(COR)Cl] (R = ⁿBu or ^sBu) and their relevance
to the hydroformylation of linear butenes catalyzed
by platinum/tin/triphenylphosphine catalytic systems.
Molecular structure of *cis*-[Pt(PPh₃)₂Cl(SnCl₃)]

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(Received March 30, 1993)

Abstract

The acyl complex *trans*-[Pt(PPh₃)₂(COⁿBu)Cl] (**A**) has been synthesized by reaction of [Pt(PPh₃)₂Cl₂] 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(PPh₃)₂(CO^sBu)Cl] (**B**) was formed. Complexes **A** and **B** do not interconvert. The new acyl complexes **A** and **B** have been characterized by IR and ¹H NMR and ¹³C NMR spectroscopy. The ratio **A**/**B** increases with PPh₃/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 SnCl₂, H₂, HCl and *trans*-[Pt(PPh₃)₂HCl]. From the reaction solutions crystals of *cis*-[Pt(PPh₃)₂Cl(SnCl₃)] 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 SnCl₃ group is confirmed by the lengthening of the *trans* Pt–P distance. The SnCl₃ 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(PPh₃)₂(COR)X] (X = Cl or SnCl₃) 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(PPh₃)₂Cl₂]-SnCl₂ (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 H₂ [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

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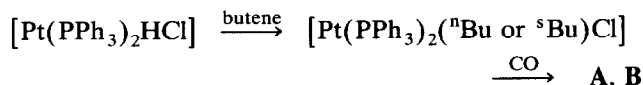
cycle, such as insertion of the olefin into a Pt–H bond and the insertion of CO into the Pt–C bond of the resulting Pt alkyl [12,13].

The present work deals with the synthesis, characterization and reactivity of the new acyl complexes *trans*-[Pt(PPh₃)₂(COⁿBu)Cl] (**A**) and *trans*-[Pt(PPh₃)₂(CO^sBu)Cl] (**B**), and with their role in the hydroformylation of 1-butene and of 2-butene catalyzed by the mixture [Pt(PPh₃)₂Cl₂]/PPh₃/SnCl₂. The molecular structure of *cis*-[Pt(PPh₃)₂Cl(SnCl₃)], 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 PPh₃/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.



Scheme 1.

Ethanol can act as a hydride source for the platinum precursor [14] which is converted into hydride [Pt(PPh₃)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(PPh₃)₂Cl₂] + PPh₃; [Pt] = 0.02 M; [butene]/[Pt] 100; *p*_{CO} = 100 atm; solvent: EtOH (50 ml).

^b Catalyst precursor: [Pt(cod)Cl₂] + PPh₃ + SnCl₂; [Pt] = 0.01 M; Pt/SnCl₂ = 1/5; [butene]/[Pt] = 400; *p* = 140 atm; CO/H₂ = 1/1; solvent: CH₂Cl₂ (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–ⁿBu 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–ⁿBu 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 PPh₃/Pt. When the PPh₃/Pt molar ratio is ≤ 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 [Pt₁₅(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(PPh₃)₃(CO)Cl₂]. Longer reaction times are used only when the stability of the system is sufficiently high, *i.e.* at low temperature and high PPh₃/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 SnCl₂. 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 PPh₃/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
¹ J(Pt–C) (Hz)	975	965
² J(Pt–C) (Hz)	87	87

and 2-methylbutanal). This is probably due to the fact that, on increasing the PPh₃/Pt ratio, the number of the PPh₃ 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–ⁿBu 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)Cl₂]/PPh₃/SnCl₂ 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 ¹H NMR and ¹³C 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(PPh₃)₂(C₂H₄)], following a known procedure [17].

The IR spectrum shows one band for $\nu(\text{C=O})$ 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 ¹³C 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 H₂, HCl and the hydride *trans*-[Pt(PPh₃)₂HCl] in the presence of SnCl₂, which are of relevance to the hydroformylation catalytic cycle. In the absence of SnCl₂ no hydroformylation occurs with any of the platinum reagents.

The reaction of **A** or **B** with SnCl₂ gives mainly decarbonylation with formation of [Pt(PPh₃)₂(CO)Cl][SnCl₃] ($\nu(\text{C=O}) = 2112$ cm⁻¹) and of [Pt(PPh₃)₂-H(CO)(SnCl₃)] ($\nu(\text{C=O}) = 2082, 2061$ 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(PPh₃)₂Cl(SnCl₃)], are present in solution after decarbonylation (see below).

It has been also found that complexes **A** and **B** react with H₂, in the presence of SnCl₂, 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/H₂ = 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(PPh₃)₂H(SnCl₃)] [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(PPh₃)₂HCl] with complexes **A** or **B** in the presence of SnCl₂. 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 SnCl₂ (Pt/HCl/SnCl₂ = 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(PPh₃)₂(CO)Cl][SnCl₃], crystals of *cis*-[Pt(PPh₃)₂-Cl(SnCl₃)] are obtained by layering cyclohexane on the CH₂Cl₂ solution. This complex reacts with molecular

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 C₄₁H₃₉ClOP₂Pt: 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 SnCl₂ and HCl or H₂ or *trans*-[Pt(PPh₃)₂HCl] were performed in

TABLE 3. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^3$)

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 ($\text{\AA}$) and angles ($^\circ$)

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)

a small Schlenk tube, equipped with a magnetic stirring bar, a gas inlet (for H₂) and a rubber septum.

The Schlenk tube with the acyl complex (0.3 g) was purged with N₂ and the solvent (CH₂Cl₂, 15 ml) injected. Anhydrous SnCl₂ (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

C₃₆H₃₀Cl₄P₂PtSn, $M = 980.1$, monoclinic, $P2_1/n$, $a = 12.895(3)$, $b = 16.844(3)$, $c = 16.620(3)$ $\text{\AA}$, $\beta = 102.38(1)^\circ$, $V = 3562$ $\text{\AA}^3$, $Z = 4$, $D_x = 1.846$ $\text{Mg} \cdot \text{m}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.71073$ $\text{\AA}$, $\mu = 5.137$ mm^{-1} , $F(000) = 1888e$, $T = 293$ K.

3.4.2. Data collection and reduction

Single crystal approximately $0.36 \times 0.40 \times 0.09$ mm. Data collection on a Siemens R3m/V diffractometer, graphite-monochromated Mo K α radiation. 25 reflections used ($15 \leq 2\theta \leq 30^\circ$) 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 ($R_{\text{int}} = 0.016$), 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.

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