Organometallics **1991**, *10*, 4036-4045

Stoichiometric Model Reactions in Olefin Hydroformylation by Platinum–Tin Systems

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Received April 9, 1991

The three independent steps involved in the hydroformylation process, insertion of the olefin, insertion of carbon monoxide, and hydrogenolysis, have been investigated with use of platinum–tin catalysts and 1-pentene as olefin at low pressure and temperature in CH_2Cl_2. In the temperature range 198–308 K, the three reactions can be studied consecutively. All the intermediates observed were prepared and characterized separately. The complex *trans*-$[PtH(SnCl_3)(PPh_3)_2]$ was used as the initial compound for this sequence. The hydrido complex crystallized in the monoclinic space group $C2/c$, with a = 31.345 (5) Å, b = 12.716 (3) Å, c = 18.135 (3) Å, β = 96.5 (2)°, Z = 8, and R (R_w) = 0.056 (0.060) for 3235 independent reflections having $I > 2.56\sigma(I)$. The large Pt–Sn bond (2.601 (1) Å) distance correlates satisfactorily with the low ^1J(Pt–Sn) value. The Pt–Sn bond is necessary for the insertion of 1-pentene in the hydrido–platinum complex and for the hydrogenolysis of the acyl compounds under these mild conditions. The insertion of 1-pentene was observed at 198 K, giving the cis-alkyl complex; CO insertion took place after isomerization to the trans-alkyl complex. The instability of Pt–Sn and Pt–C bonds in the trans-acyl complex favors easy decarbonylation or loss of $SnCl_2$, so any other platinum complex without tin accepts $SnCl_2$ from the acyl complex. The hydrogenolysis of *trans*-$[Pt(SnCl_3)(COC_5H_{11})(PPh_3)_2]$ under 1.5 bar of H_2–CO (1:1) did not yield n-hexanal quantitatively; only 12% of n-hexanal was formed. Thus, decarbonylation was the main process observed. From the reactions studied, it is possible to propose the following order of Pt–Sn bond stability: *trans*-$[Pt(SnCl_3)(COC_5H_{11})(PPh_3)_2]$ < $[Pt(SnCl_3)(C_5H_{11})(PPh_3)_2]$ < *trans*-$[PtH(SnCl_3)(PPh_3)_2]$ < $[PtH(SnCl_3)(CO)(PPh_3)_2]$ < $[Pt(\mu\text{-}Cl)(SnCl_3)(PPh_3)]_2$ < $[PtCl(SnCl_3)(PPh_3)]^-$ < $[PtCl_2(SnCl_3)_2]^{2-}$. The insertion reactions studied with *cis*-$[PtCl_2(olefin)(PR_3)]$ as an olefin carrier and the hydrido–platinum complexes *trans*-$[PtHCl(PPh_3)_2]$, *trans*-$[PtH(SnCl_3)(PPh_3)_2]$, and $[PtH(SnCl_3)(CO)(PPh_3)_2]$ as hydrogen carriers exclude the participation of intermolecular steps by reaction of two different platinum complexes under the experimental conditions described.

Introduction

The hydroformylation of olefins is a homogeneously catalyzed process of major industrial importance. This reaction is catalyzed by a wide range of transition-metal complexes, those of cobalt and especially rhodium being the only ones used in industrial processes.[1]

Extending the scope to new olefins, in order to obtain more selective processes and more selective catalysts, has promoted the study of new mono- and bimetallic complexes as catalysts. Among them, systems based on the platinum complexes $[PtCl_2(PR_3)_2]$ and $SnCl_2$ have been the most useful in the hydroformylation of terminal alkenes, giving highly linear aldehydes as the product. The catalytic activity of these systems has been known since 1975,[2] and they have been used and studied in the hydroformylation of different kinds of alkenes, such as linear olefins, cyclic olefins, styrene, etc.[3-5] It is in the field of asymmetric hydroformylation that the Pt–Sn system is most efficient.[6]

By analogy with the cobalt- and rhodium-based catalysts, a tentative catalytic cycle has been proposed,[3] in which the active catalytic species is thought to be $[PtH(SnCl_3)(CO)(PPh_3)]$. Insertion of the olefin into a Pt–H bond, carbonylation of the Pt–alkyl intermediate formed, and hydrogenolysis of the resulting acyl intermediate, which leads to the aldehyde and regeneration of the starting Pt–H species, have been proposed. These systems are very suitable for mechanistic studies, because it is possible to isolate the intermediates at low temperature and study the stoichiometric reactions corresponding to the different steps of the cycle.

The role of $SnCl_2$ has been the subject of many studies, but it is not yet fully understood. It can act (a) as a Lewis acid, (b) as a counterion like $SnCl_3^-$, and (c) as a ligand directly bonded to platinum, favoring the insertion, carbonylation, and hydrogenolysis processes indicated before[7] either by stabilizing the pentacoordinated intermediates and/or labilizing the trans position. However, it has been questioned whether indeed it functions as a ligand, since cationic platinum complexes are active catalysts in the absence of $SnCl_3^-$,[8] lending support to its role as a noncoordinating anion rather than as a ligand. Different splitting reactions of Pt–acyl complexes giving the aldehydes have been proposed. Besides direct hydrogenolysis with H_2, the actions of $HSnCl_3$[9] and more recently of HCl have been considered.[10,11] Recently, catalytic systems of

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[1] Cornils, B. In *New Synthesis with Carbon Monoxide*; Falbe, J. Ed.; Springer-Verlag: New York, 1980; pp 1-225.

[2] Hsu, C. Y.; Orchin, M. *J. Am. Chem. Soc.* **1975**, *97*, 3553.

[3] Schwager, J.; Knifton, J. F. *J. Catal.* **1976**, *45*, 256.

[4] (a) Bardi, R.; Piazzesi, A. M.; Del Pra, A.; Cavinato, G.; Toniolo, L. *J. Organomet. Chem.* **1982**, *234*, 107. (b) Moretti, G.; Botteghi, C.; Toniolo, L. *J. Mol. Catal.* **1987**, *39*, 177. (c) Graziani, R.; Cavinato, G.; Casellato, U.; Toniolo, L. *J. Organomet. Chem.* **1988**, *353*, 125. (d) Clark, H. C.; Davies, J. A. *J. Organomet. Chem.* **1981**, *213*, 503. (e) Hayashi, T.; Kawabata, Y.; Isoyama, T.; Ogata, I. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3438.

[5] Muller, G.; Sainz, D.; Sales, J. *J. Mol. Catal.* **1990**, *63*, 173.

[6] (a) Parrinello, G.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 7122. (b) Stille, J. K.; Parrinello, G. *J. Mol. Catal.* **1983**, *21*, 203. (c) Kollár, L.; Consiglio, G.; Pino, P. *J. Organomet. Chem.* **1987**, *330*, 305. (d) Kollár, L.; Bakos, J.; Tóth, I.; Heil, B. *J. Organomet. Chem.* **1988**, *350*, 277.

[7] Scrivanti, A.; Berton, A.; Toniolo, L.; Botteghi, C. *J. Organomet. Chem.* **1986**, *314*, 369.

[8] (a) Tang, S. C.; Kim, L. *J. Mol. Catal.* **1982**, *14*, 231. (b) Paumard, E.; Mortreux, A.; Petit, F. *J. Chem. Soc., Chem. Commun.* **1989**, 1380.

[9] Pino, P. *Ann. N.Y. Acad. Sci.* **1983**, *415*, 111.

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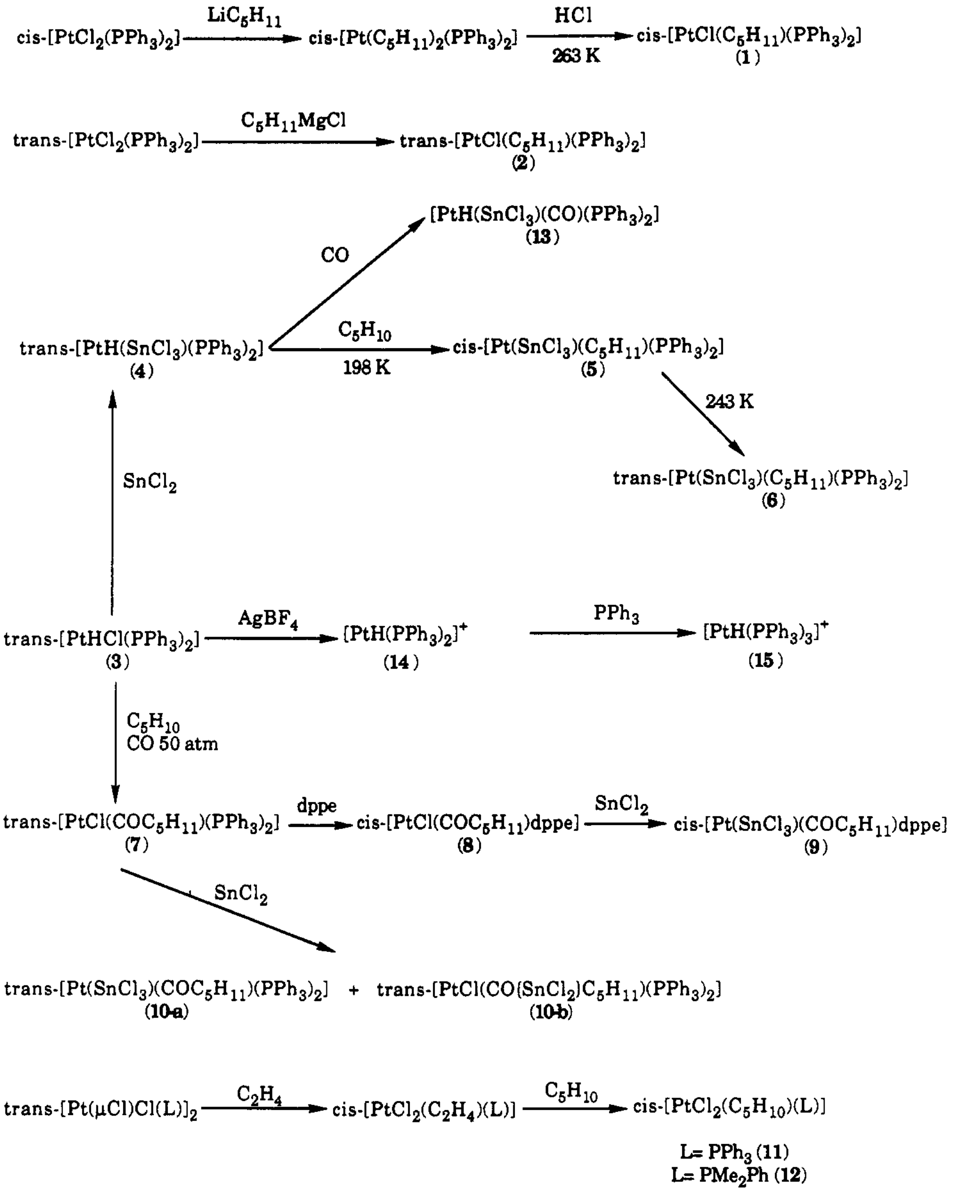
Scheme I



platinum without $SnCl_2$ have also been described.[12]

In order to shed more light on the hydroformylation process of olefins by Pt–Sn-based catalysts, especially on the role of $SnCl_2$, different complexes of platinum have been prepared and studied. Thus, Pt–hydrido, Pt–alkyl, and Pt–acyl complexes containing or not containing the $SnCl_3^-$ ligand have been obtained, and (a) the 1-pentene insertion reaction and (b) hydrogenolysis of the corresponding Pt–acyl complexes have been studied. In contrast to previously reported results from similar studies, mainly with ethylene,[13] it has been observed that the decarbonylation of acyl complexes *trans*-$[Pt(SnCl_3)(COR)(PPh_3)_2]$ is more favored than the formation of aldehydes.

In order to determine whether any step of the process is binuclear, analogous to cobalt- or rhodium-based catalysts,[14] the reactions mentioned have been studied with use of *cis*-$[PtCl_2(olefin)(PR_3)]$ as an olefin carrier and the hydrido–platinum complexes *trans*-$[PtHCl(PPh_3)_2]$, *trans*-$[PtH(SnCl_3)(PPh_3)_2]$, and $[PtH(SnCl_3)(CO)(PPh_3)_2]$ as hydrogen carriers.

Results

Preparation and Characterization of Platinum Complexes. Scheme I shows the preparation methods of the different platinum complexes obtained. The alkyl–platinum complexes *cis*- and *trans*-$[PtCl(C_5H_{11})(PPh_3)_2]$ (**1**, **2**) and *cis*-$[Pt(C_5H_{11})_2(PPh_3)_2]$ were obtained from *cis*- or *trans*-$[PtCl_2(PPh_3)_2]$ and Grignard or lithium reagents by published methods.[15] The complexes containing the $SnCl_3^-$ ligand, *cis*- and *trans*-$[Pt(SnCl_3)(C_5H_{11})(PPh_3)_2]$ (**5**, **6**) can only be prepared in solution, and it was not possible to isolate them as solids because they undergo β-elimination and loss of $SnCl_2$ at room temperature. The complex *cis*-$[Pt(SnCl_3)(C_5H_{11})(PPh_3)_2]$ (**5**) was obtained by the in-

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(10) Scrivanti, A.; Paganelli, S.; Matteoli, U.; Botteghi, C. *J. Organomet. Chem.* **1990**, *385*, 439.

(11) (a) Ancillotti, F.; Lami, M.; Marchionna, M. *J. Mol. Catal.* **1990**, *58*, 331. (b) Ancellotti, F.; Lami, M.; Marchionna, M. *J. Mol. Catal.* **1990**, *58*, 345.

(12) Van Leeuwen, P. W. N. M.; Roobeek, C. F.; Frijns, J. H. G. *Organometallics* **1990**, *9*, 1211.

(13) Ruegg, H. J.; Pregosin, P. S.; Scrivanti, A.; Toniolo, L.;Botteghi, C. *J. Organomet. Chem.* **1986**, *316*, 233.

(14) (a) Hoff, C. D.; Ungváry, F.; King, R. B.; Markó, L. *J. Am. Chem. Soc.* **1985**, *107*, 666. (b) Collman, J. P.; Belmont, J. A.; Brauman, J. I. *J. Am. Chem. Soc.* **1983**, *105*, 7288.

(15) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1959**, 705.

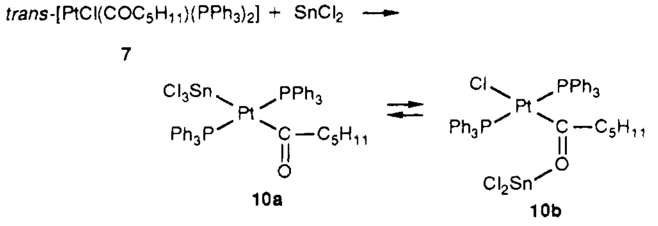
Table I. $^{31}P\{^1H\}$ NMR Data[a]

compd	$\delta(^{31}P)$	$^1J(^{195}Pt-^{31}P)$	other J
cis-[PtCl$_2$(PPh$_3$)$_2$]	14.7	3679	
	13.9[b]	3681	
trans-[PtCl$_2$(PPh$_3$)$_2$]	22.0	2605	
cis-[PtCl$_2$(PMe$_2$Ph)$_2$]	−15.3	3545	
cis-[PtCl$_2$dppe]	43.8[b]	3600	
trans-[Pt(μ-Cl)Cl(PPh$_3$)]$_2$	4.8[c]	4116	^4J(P–P) 7.9
trans-[Pt(μ-Cl)Cl(PMe$_2$Ph)]$_2$	−18.1[b]	3897	
cis-[PtCl(SnCl$_3$)(PPh$_3$)$_2$][d]	29.1 (d)	3102[e]	^2J(P–P) 14.4
	10.8 (d)	3629[f]	
trans-[Pt(μ-Cl)(SnCl$_3$)(PPh$_3$)]$_2$	8.1	3718	^2J(Sn–P) 210,[g] 199[h] ^4J(P–P) 3.3
cis-[PtCl(C$_5$H$_{11}$)(PPh$_3$)$_2$] (**1**)	23.1 (d)	4749[f]	^2J(P–P) 12.5
	25.3 (d)	1518[i]	
trans-[PtCl(C$_5$H$_{11}$)(PPh$_3$)$_2$] (**2**)	30.8	3328	
trans-[PtHCl(PPh$_3$)$_2$] (**3**)	29.7	2966	
	28.4[c]	3023	
trans-[PtH(SnCl$_3$)(PPh$_3$)$_2$] (**4**)	29.1	2647	^2J(Sn–P) 210
cis-[Pt(SnCl$_3$)(C$_5$H$_{11}$)(PPh$_3$)$_2$] (**5**)	31.4 (d)	3965[e]	^2J(Sn–P) 3744,[g] 3566[h]
	18.5 (d)[d]	1861[i]	^2J(P–P) 17.7
trans-[Pt(SnCl$_3$)(C$_5$H$_{11}$)(PPh$_3$)$_2$] (**6**)[d]	26.2	3013	
trans-[PtCl(COC$_5$H$_{11}$)(PPh$_3$)$_2$] (**7**)	22.3	3454	
	20.5[c]	3525	
cis-[PtCl(COC$_5$H$_{11}$)dppe] (**8**)	29.5 (d)	4484[f]	^2J(P–P) 2.4
	31.7 (d)	1382[i]	
cis-[Pt(SnCl$_3$)(COC$_5$H$_{11}$)dppe] (**9**)[d]	42.1 (d)	3756[e]	^2J(P–P) 9.4
	40.8 (d)	1511[i]	
trans-[Pt(SnCl$_3$)(COC$_5$H$_{11}$)(PPh$_3$)$_2$] (**10a**)	16.4	3205	^2J(Sn–P) 287
trans-[PtCl(CO{SnCl$_2$}C$_5$H$_{11}$)(PPh$_3$)$_2$] (**10b**)	17.7	2926	
cis-[PtCl$_2$(C$_5$H$_{10}$)(PPh$_3$)] (**11**)	14.6	3314	
	13.4[c]	3318	
cis-[PtCl$_2$(C$_5$H$_{10}$)(PMe$_2$Ph)] (**12**)	−7.1	3135	
	−11.1[c]	3149	
[PtH(SnCl$_3$)(CO)(PPh$_3$)$_2$] (**13**)[d]	15.0	2872	
[PtH(PPh$_3$)$_3$]$^+$ (**14**)	23.9 (m)	2829	^2J(P–P) 18.8
	23.4 (m)	2220	
[PtH(PPh$_3$)$_2$]$^+$ (**15**)	30.4	3024	

[a] δ in ppm, J in Hz; T = 198 K, solvent CH$_2$Cl$_2$; d = doublet, m = multiplet. [b] CH$_2$Cl$_2$, 308 K. [c] CHCl$_3$, 308 K. [d] $^2J(Sn-^{31}P)$ not observed. [e] P trans to SnCl$_3^-$. [f] P trans to Cl$^-$. [g] $^2J(^{117}Sn-^{31}P)$. [h] $^2J(^{119}Sn-^{31}P)$. [i] P trans to the organic group (alkyl or acyl).

sertion reaction of 1-pentene with *trans*-[PtH(SnCl$_3$)(PPh$_3$)$_2$] (**4**) at 198 K; when the mixture was warmed to 243 K, the isomerization to *trans*-[Pt(SnCl$_3$)(C$_5$H$_{11}$)(PPh$_3$)$_2$] (**6**) was achieved. Similar reactions have been reported for other olefins.[7,16]

The acyl complex *trans*-[PtCl(COC$_5$H$_{11}$)(PPh$_3$)$_2$] (**7**) was obtained from *trans*-[PtHCl(PPh$_3$)$_2$] (**3**), 1-pentene, and CO (50 atm). Posterior addition of an excess of dppe gave *cis*-[PtCl(COC$_5$H$_{11}$)dppe] (**8**). The action of SnCl$_2$ on the acyl complex **8** gave *cis*-[Pt(SnCl$_3$)(COC$_5$H$_{11}$)dppe] (**9**), but in the same reaction with **7**, two species, in relative quantities of 1:1, were observed: one was the *trans*-[Pt(SnCl$_3$)(COC$_5$H$_{11}$)(PPh$_3$)$_2$] (**10a**) complex, containing a Pt–Sn bond, and the other was *trans*-[PtCl(CO{SnCl$_2$}C$_5$H$_{11}$)(PPh$_3$)$_2$] (**10b**), with a tin–oxygen bond.



The structure of **10b** is proposed from NMR data (see Table I) in analogy with compounds described previously by Scrivanti and Pregosin.[13] In the solid state it is possible to obtain mainly **10a** or **10b** depending on the experimental conditions. Thus, after 10 min at 283 K a solid is obtained; the IR spectrum of this solid shows a strong ν(CO) band at 1500 cm^{-1} from compound **10b** and a weak ν(CO) band at 1670 cm^{-1} from compound **10a**. If the reaction time is 3 h at room temperature, the solid obtained shows in the IR spectrum practically only a ν(CO) band at 1670 cm^{-1}

Table II. Crystallographic Data Collection for *trans*-[PtH(SnCl$_3$)(PPh$_3$)$_2$] (4)

formula	C$_{36}$H$_{31}$P$_2$Cl$_3$SnPt
mol wt	945.7
a, Å	31.345 (5)
b, Å	12.716 (3)
c, Å	18.135 (3)
β, deg	96.5 (2)
Z	8
V, Å^3	7182 (4)
d_{calc}, g/cm^3	1.749
T, K	298
radiation	Mo Kα (graphite monochromated)
λ, Å	0.71069
F(000)	3648.0
cryst syst	monoclinic
space group	$C2/c$
meas rflns	hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$
cryst dimens, mm	0.07 × 0.07 × 0.07
μ(Mo Kα), cm^{-1}	51.26
diffractometer	Philips PW-1100
data collcn range, deg	2–25
scan method	ω–2θ
max scan speed, deg s^{-1}	0.03
scan width, deg	0.8
no. of rflns collcd	4722
no. of rflns obsd ($I \geq 2.5\sigma(I)$)	3235
final R	0.056
final R_w	0.060

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(16) Petrosyan, V. S.; Permin, A. B.; Bogdashkina, V. I.; Krut'ko, D. P. *J. Organomet. Chem.* **1985**, *292*, 303.

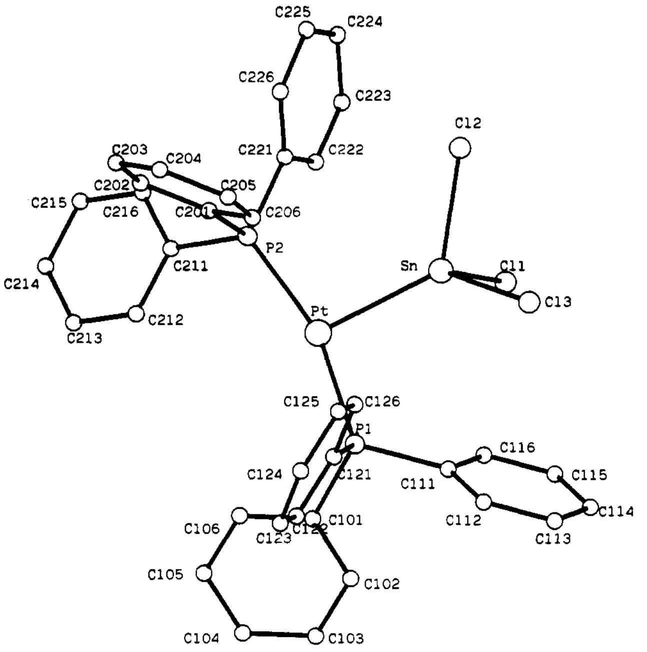

Figure 1. Crystal structure of *trans*-[PtH(SnCl$_3$)(PPh$_3$)$_2$] (4).

Table III. Selected Bond Lengths (Å) for *trans*-[PtH(SnCl$_3$)(PPh$_3$)$_2$] (4)

Sn–Pt	2.601 (1)	C(101)–P(1)	1.820 (10)
P(1)–Pt	2.303 (4)	C(111)–P(1)	1.820 (11)
P(2)–Pt	2.299 (4)	C(121)–P(1)	1.789 (10)
Cl(1)–Sn	2.373 (5)	C(201)–P(2)	1.833 (12)
Cl(2)–Sn	2.283 (5)	C(211)–P(2)	1.814 (12)
Cl(3)–Sn	2.367 (6)	C(221)–P(2)	1.816 (12)

(**10a**). The magnitude of the ν(CO) band in compound **10b** was that expected for the proposed "carbenoid" structure.[13]

The π-olefinic compounds *cis*-[PtCl$_2$(C$_5$H$_{10}$)(PPh$_3$)] (**11**) and *cis*-[PtCl$_2$(C$_5$H$_{10}$)(PMe$_2$Ph)] (**12**) were obtained by olefin substitution from the complexes *cis*-[PtCl$_2$(C$_2$H$_4$)(PPh$_3$)] and *cis*-[PtCl$_2$(C$_2$H$_4$)(PMe$_2$Ph)], respectively. It was not possible to obtain the compound [PtCl(SnCl$_3$)(C$_5$H$_{10}$)(PPh$_3$)] from the dimer *trans*-[Pt(μ-Cl)(SnCl$_3$)(PPh$_3$)] and 1-pentene, from **11** and SnCl$_2$, or from [Pt(μ-Cl)Cl(C$_5$H$_{10}$)]$_2$, PPh$_3$, and SnCl$_2$, suggesting that the coordination of SnCl$_2$ to the platinum produces a remarkable increase in the lability of the π-bonded olefin to the metal. The pentacoordinated complex [PtH(SnCl$_3$)(CO)(PPh$_3$)$_2$] (**13**) was obtained by slow evaporation, under a CO atmosphere, of a solution of *trans*-[PtH(SnCl$_3$)(PPh$_3$)$_2$] (**4**).[7]

Solutions of the cationic species [PtH(PPh$_3$)$_2$]$^+$ (**14**) were obtained from *trans*-[PtHCl(PPh$_3$)$_2$] (**3**) and AgBF$_4$ in CH$_2$Cl$_2$ at 198 K. The action of PPh$_3$ on the complex **14** yielded the species [PtH(PPh$_3$)$_3$)]$^+$ (**15**).

Table I shows the ^{31}P{^{1}H} NMR data for the platinum complexes prepared, which were used to characterize the species formed in the reactions studied.

The molecular and crystal structures of *trans*-[PtH(SnCl$_3$)(PPh$_3$)$_2$] (**4**) were determined by X-ray diffraction. The crystal structure is composed of discrete molecules separated by van der Waals distances (Figure 1). Selected bond lengths and angles are listed in Tables III and IV and atomic coordinates in Table V. The compound exhibits the typical square-planar coordination of Pt, but it is somewhat distorted by the reduced steric requirements of the hydrido ligand. The two P atoms of the phosphine ligands are approximately trans to each other; the angle P(1)–Pt–P(2) of 161.6 (1)° is smaller than that observed in other platinum hydride compounds with two triphenylphosphine ligands.[17] Although the position of the hydride ligand was not determined, its presence was unambiguously verified by IR and ^{1}H NMR spectroscopy. The Pt–P distances (2.303 (4) and 2.299 (4) Å) are longer than those found in analogous hydride compounds such as *trans*-[PtH(C$_6$H$_4$F-*p*)(PPh$_3$)$_2$][17] (2.256 (6) and 2.264 (5)

Table IV. Selected Angles (deg) for *trans*-[PtH(SnCl$_3$)(PPh$_3$)$_2$] (4)

P(1)–Pt–Sn	99.2 (1)	C(211)–P(2)–Pt	117.0 (4)
P(2)–Pt–Sn	98.5 (1)	C(211)–P(2)–C(201)	103.9 (5)
P(2)–Pt–P(1)	161.3 (1)	C(221)–P(2)–Pt	120.0 (4)
Cl(1)–Sn–Pt	117.1 (1)	C(221)–P(2)–C(201)	105.9 (5)
Cl(2)–Sn–Pt	125.3 (1)	C(221)–P(2)–C(211)	101.1 (5)
Cl(2)–Sn–Cl(1)	95.1 (2)	C(102)–C(101)–P(1)	117.9 (7)
Cl(3)–Sn–Pt	118.7 (1)	C(106)–C(101)–P(1)	122.0 (9)
Cl(3)–Sn–Cl(1)	100.6 (2)	C(112)–C(111)–P(1)	122.3 (7)
Cl(3)–Sn–Cl(2)	94.7 (2)	C(116)–C(11)–P(1)	117.7 (8)
C(101)–P(1)–Pt	116.7 (4)	C(122)–C(121)–P(1)	122.0 (8)
C(111)–P(1)–Pt	120.7 (4)	C(126)–C(121)–P(1)	118.0 (7)
C(111)–P(1)–C(101)	101.4 (5)	C(202)–C(201)–P(2)	123.6 (9)
C(121)–P(1)–Pt	108.5 (4)	C(206)–C(201)–P(2)	116.4 (9)
C(121)–P(1)–C(101)	104.3 (5)	C(212)–C(211)–P(2)	119.2 (8)
C(121)–P(1)–C(111)	103.5 (5)	C(222)–C(221)–P(2)	122.6 (8)
C(201)–P(2)–Pt	107.6 (4)	C(226)–C(221)–P(2)	117.3 (9)

Table V. Final Atomic Coordinates for *trans*-[PtH(SnCl$_3$)(PPh$_3$)$_2$] (4)

atom	x/a	y/b	z/c	B_{eq},[a] Å^2
Pt	0.1187 (0)	0.0858 (1)	0.4686 (0)	3.12 (3)
Sn	0.1283 (0)	0.1702 (1)	0.3410 (1)	3.72 (6)
P(1)	0.1658 (1)	−0.0529 (3)	0.4663 (2)	3.30 (19)
P(2)	0.0746 (1)	0.2109 (3)	0.5113 (2)	3.33 (19)
Cl(1)	0.0865 (2)	0.0998 (5)	0.2352 (3)	6.81 (30)
Cl(2)	0.1139 (2)	0.3493 (4)	0.3084 (3)	5.61 (26)
Cl(3)	0.1973 (2)	0.1691 (4)	0.2999 (3)	6.11 (28)
C(101)	0.1477 (4)	−0.1795 (7)	0.4978 (6)	3.50 (75)
C(102)	0.1264 (4)	−0.1812 (7)	0.5613 (6)	6.04 (114)
C(103)	0.1135 (4)	−0.2768 (7)	0.5893 (6)	6.68 (123)
C(104)	0.1219 (4)	−0.3707 (7)	0.5538 (6)	5.48 (102)
C(105)	0.1431 (4)	−0.3690 (7)	0.4903 (6)	7.05 (131)
C(106)	0.1560 (4)	−0.2734 (7)	0.4623 (6)	5.70 (109)
C(111)	0.1870 (4)	−0.0898 (9)	0.3805 (5)	3.94 (81)
C(112)	0.2307 (4)	−0.1071 (9)	0.3771 (5)	4.22 (86)
C(113)	0.2452 (4)	−0.1369 (9)	0.3102 (5)	6.13 (113)
C(114)	0.2160 (4)	−0.1493 (9)	0.2468 (5)	5.76 (109)
C(115)	0.1723 (4)	−0.1319 (9)	0.2502 (5)	5.78 (109)
C(116)	0.1578 (4)	−0.1022 (9)	0.3171 (5)	5.08 (99)
C(121)	0.2129 (3)	−0.0244 (8)	0.5283 (5)	3.38 (72)
C(122)	0.2294 (3)	−0.0952 (8)	0.5829 (5)	5.19 (92)
C(123)	0.2658 (3)	−0.0687 (8)	0.6309 (5)	6.92 (133)
C(124)	0.2856 (3)	0.0286 (8)	0.6243 (5)	6.05 (114)
C(125)	0.2690 (3)	0.0994 (8)	0.5697 (5)	6.41 (122)
C(126)	0.2326 (3)	0.0729 (8)	0.5217 (5)	5.33 (96)
C(201)	0.1072 (4)	0.2902 (9)	0.5808 (6)	3.94 (83)
C(202)	0.0917 (4)	0.3323 (9)	0.6435 (6)	6.40 (118)
C(203)	0.1182 (4)	0.3949 (9)	0.6925 (6)	7.40 (138)
C(204)	0.1603 (4)	0.4153 (9)	0.6786 (6)	7.51 (137)
C(205)	0.1759 (4)	0.3731 (9)	0.6159 (6)	7.30 (134)
C(206)	0.1493 (4)	0.3106 (9)	0.5669 (6)	5.83 (108)
C(211)	0.0308 (3)	0.1641 (8)	0.5600 (6)	5.83 (108)
C(212)	0.0364 (3)	0.0725 (8)	0.6024 (6)	5.50 (104)
C(213)	0.0045 (3)	0.0402 (8)	0.6452 (6)	6.92 (128)
C(214)	−0.0329 (3)	0.0994 (8)	0.6458 (6)	7.18 (133)
C(215)	−0.0385 (3)	0.1910 (8)	0.6034 (6)	6.63 (126)
C(216)	−0.0066 (3)	0.2233 (8)	0.5606 (6)	6.00 (113)
C(221)	0.0467 (4)	0.3041 (9)	0.4470 (6)	4.02 (89)
C(222)	0.0508 (4)	0.4127 (9)	0.4559 (6)	6.88 (122)
C(223)	0.0264 (4)	0.4803 (9)	0.4074 (6)	10.05 (170)
C(224)	−0.0021 (4)	0.4394 (9)	0.3499 (6)	11.77 (226)
C(225)	−0.0062 (4)	0.3308 (9)	0.3409 (6)	7.98 (143)
C(226)	0.0182 (4)	0.2631 (9)	0.3895 (6)	4.83 (99)

[a] $B_{eq} = {}^8/_3\pi^2\sum_{ij}U_{ij}(a_i{\cdot}a_j)a_ia_j$.

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[17] Crespo, M.; Sales, J.; Solans, X.; Font-Altaba, M. *J. Chem. Soc., Dalton Trans.* **1988**, 1617.

Table VI. Pt–Sn Bond Distances and $^1J(^{195}Pt–^{119}Sn)$ Values

compd	d(Pt–Sn), Å	$J(^{195}Pt–^{119}Sn)$, Hz	ref
$[Pt(\mu-Cl)(SnCl_3)(PEt_3)]_2$	2.487 (3)	35 309	21
$[PtCl(SnCl_3)(PEt_3)(PhC(NH_2)=NOH)]$	2.501 (1)	32 760	24, 21
$[PtCl(SnCl_3)(PEt_3)(NH_2C_6H_4-p-Cl)]$	2.514 (1)	31 348	25
$[Pt(\eta^3-C_4H_7)(SnCl_3)(CH_2=CHPh)]$	2.539 (1)	28 496	26
$[Pt(\eta^3-C_4H_7)(SnCl_3)(CO)]$	2.550 (1)	29 287	27
trans-$[Pt(SnCl_3)_2(P(OPh)_3)_2]$	2.599 (2)	19 043	28
trans-$[PtH(SnCl_3)(PCy_3)_2]$	2.600 (2)	11 242	19
trans-$[PtH(SnCl_3)(PPh_3)_2]$ (4)	2.601 (1)	11 512	this work, 23
trans-$[Pt(SnCl_3)(COPh)(PEt_3)_2]$	2.634 (1)	2 376	20

Å) or *trans*-$[PtH(CH_2CN)(PPh_3)_2]$[18] (2.276 (4) and 2.272 (4) Å), indicating that there is an important steric repulsion between the ligand $SnCl_3^-$ and PPh_3.

The most interesting feature is the relatively large Pt–Sn bond length (2.601 (1) Å) since this represents one of the longest Pt–Sn distances observed in square-planar platinum complexes, similar to that observed in the compound *trans*-$[PtH(SnCl_3)(PCy_3)_2]$[19] (2.600 (2) Å; see Table VI). Only the complex *trans*-$[Pt(SnCl_3)(COPh)(PEt_3)_2]$[20] has a longer Pt–Sn bond. Pregosin[21] proposed an inverse relationship between the $^1J(^{195}Pt,^{119}Sn)$ value and Pt–Sn bond length, in accordance with the hypothesis that coupling constants and bond lengths are relatable concepts.[22] The long Pt–Sn bond separation in *trans*-$[PtH(SnCl_3)(PPh_3)_2]$ (4) correlates satisfactorily with the low ^1J(Pt,Sn) value[23] (see Table VI).

Stability in Solution of the Platinum Complexes. In order to determine the stability of the platinum complexes prepared, their behavior in solution was studied. In some cases the effect of the addition of $SnCl_2$ to the solutions was also studied. A solution of the platinum complex (0.1 mmol) in CH_2Cl_2 in a 10-mm NMR tube under N_2 was prepared and the $^{31}P\{^1H\}$ NMR spectrum recorded periodically at different temperatures and times, depending on the results observed.

(a) Hydrido Complexes. The complex *trans*-$[PtHCl(PPh_3)_2]$ (3) was stable under the conditions used, and after 24 h at 293 K it was recovered unaltered. Longer times and especially the action of light produced slow decomposition, and the formation of *cis*-$[PtCl_2(PPh_3)_2]$ was observed. The $SnCl_3^-$-containing complex *trans*-$[PtH(SnCl_3)(PPh_3)_2]$ (4) was less stable, although it did not decompose at 198 K for 12 h; at 253 K, it slowly lost $SnCl_2$, giving the complex *trans*-$[PtHCl(PPh_3)_2]$ (3). The pentacoordinated complex $[PtH(SnCl_3)(CO)(PPh_3)_2]$ (13) was also stable at a low temperature (198 K), but at 293 K it lost CO, leading to 4; under a CO atmosphere 13 was stable.

(b) σ-Alkyl Complexes. The σ-alkyl complexes *cis*- and *trans*-$[PtCl(C_5H_{11})(PPh_3)_2]$ (1, 2) were stable at room temperature.[29] However, the compounds containing $SnCl_3^-$ *cis*- and *trans*-$[Pt(SnCl_3)(C_5H_{11})(PPh_3)_2]$ (5, 6) were less stable; at 198 K the compound *cis*-$[Pt(SnCl_3)(C_5H_{11})(PPh_3)_2]$ (5) remained unchanged for 12 h or more, but when the temperature was increased to 243 K, complete isomerization to *trans*-$[Pt(SnCl_3)(C_5H_{11})(PPh_3)_2]$ (6) took place and the β-elimination process started simultaneously, giving *trans*-$[PtH(SnCl_3)(PPh_3)_2]$ (4) and pentenes.

(c) σ-Acyl Complexes. The acyl complex *trans*-$[PtCl(COC_5H_{11})(PPh_3)_2]$ (7) was stable for several weeks at room temperature. However, the $SnCl_3^-$-containing compound *trans*-$[Pt(SnCl_3)(COC_5H_{11})(PPh_3)_2]$ (10a) was only stable at 198 K; at 293 K slow decarbonylation and β-elimination were observed, giving CO, pentene, and *trans*-$[PtH(SnCl_3)(PPh_3)_2]$ (4). After ca. 24 h the decomposition was complete.

(d) π-Olefin Complexes. The π-olefin-coordinated complex *cis*-$[PtCl_2(C_5H_{10})(PPh_3)]$ (11) was stable at 198 K, but at 293 K slow loss of 1-pentene took place to give the dimer complex *trans*-$[Pt(\mu-Cl)Cl(PPh_3)]_2$ and *cis*- and *trans*-$[PtCl_2(PPh_3)_2]$. The addition of $SnCl_2$ on 11 at 198 K immediately gives the dimer compound *trans*-$[Pt(\mu-Cl)(SnCl_3)(PPh_3)]_2$. After 1 h at 198 K this complex completely decomposed, and only insoluble residues, nondetectable by ^{31}P NMR spectroscopy, were observed.

In general, compounds containing the $SnCl_3^-$ ligand are very reactive; loss of $SnCl_2$ or labilization of the trans ligand is observed, due to the strong trans effect of the $SnCl_3^-$ ligand.

Insertion Reactions of 1-Pentene and Carbon Monoxide. The insertion reactions were carried out in a 10-mm NMR tube, with solutions of platinum complex (~0.3 mmol) in CH_2Cl_2 (2 mL) under nitrogen or carbon monoxide.

The complex *trans*-$[PtHCl(PPh_3)_2]$ (3) does not undergo the insertion of 1-pentene as expected. The analogous complex *trans*-$[PtHCl(PEt_3)_2]$ undergoes insertion of ethylene at 40 atm and 363 K,[30] but the insertion of 1-propene requires 220 atm, and the insertion of 1-octene does not take place.[31] The complex *trans*-$[PtH(SnCl_3)(PPh_3)_2]$ (4) quantitatively undergoes insertion of 1-pentene at 198 K. The reaction is complicated, and several species are detected. Initially the formation of *cis*-$[Pt(SnCl_3)(C_5H_{11})(PPh_3)_2]$ (5) is observed; after 40 min at 198 K, all the complex 4 has disappeared and the signals corresponding to the decomposition products, *cis*-$[PtCl_2(PPh_3)_2]$ and $[PtH(PPh_3)_3]^+$ (15), together with the complex 5 can be observed. Thus, no substantial change was observed over 2 h. When the temperature was increased gradually, the isomerization of *cis*-$[Pt(SnCl_3(C_5H_{11})(PPh_3)_2]$ (5) to *trans*-$[Pt(SnCl_3)(C_5H_{11})(PPh_3)_2]$ (6) takes place at 243 K and at 263 K is complete. The signals corresponding to the species *cis*-$[PtCl_2(PPh_3)_2]$ and $[PtH(PPh_3)_3]^+$ (15) increase, and new signals corresponding to *trans*-$[PtHCl(PPh_3)_2]$ (3), formed by β-elimination and loss of $SnCl_2$, are observed. After 12 h at 263 K, only the

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[18] Del Pra, A.; Forsellini, E.; Bombieri, G.; Michelin, R. A.; Ros, R. *J. Chem. Soc., Dalton Trans.* **1979**, 1862.

[19] Clark, H. C.; Ferguson, G.; Hampden-Smith, M. J.; Rüegger, H.; Ruhl, B. L. *Can. J. Chem.* **1988**, *66*, 3120.

[20] Albinati, A.; Gunten, U. V.; Pregosin, P. S.; Ruegg, H. J. *J. Organomet. Chem.* **1985**, *295*, 239.

[21] Albinati, A.; Naegeli, R.; Ostoja Starzewski, K. H. A.; Pregosin, P. S.; Rüegger, H. *Inorg. Chim. Acta* **1983**, *76*, L231.

[22] Buergi, H. B.; Fischer, E.; Kunz, R. W.; Parvez, M.; Pregosin, P. S. *Inorg. Chem.* **1982**, *21*, 1246.

[23] Ostoja Starzewski, K. H. A.; Pregosin, P. S.; Rüegger, H. *Helv. Chim. Acta* **1982**, *65*, 785.

[24] Goel, A. B.; Goel, S.; Vanderveer, D. *Inorg. Chim. Acta* **1981**, *54*, L5.

[25] Albinati, A.; Moriyama, H.; Rüegger, H.; Pregosin, P. S. *Inorg. Chem.* **1985**, *24*, 4430.

[26] Musco, A.; Pontellini, R.; Grassi, M.; Sironi, A.; Meille, S. V.; Rüegger, H.; Ammann, C.; Pregosin, P. S. *Organometallics* **1988**, *7*, 2130.

[27] Grassi, M.; Meille, S. V.; Musco, A.; Pontellini, R.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1989**, 615.

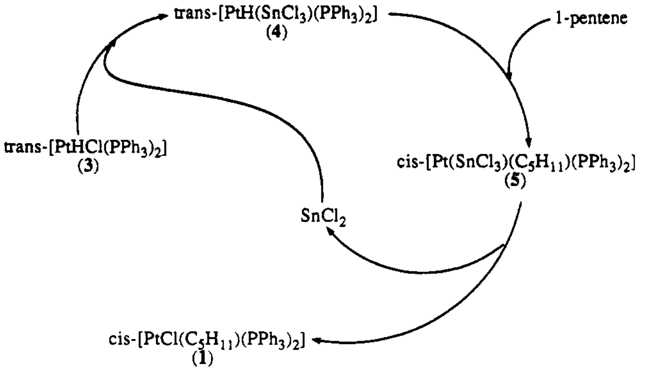
[28] Albinati, A.; Pregosin, P. S.; Rüegger, H. *Inorg. Chem.* **1984**, *23*, 3223.

[29] Brainard, R. L.; Whitesides, G. M. *Organometallics* **1985**, *4*, 1550.

[30] Chatt, J.; Shaw, B. L. *J. Chem. Soc. A* **1962**, 5075.

[31] Chatt, J.; Coffey, R. S.; Gough, A.; Thompson, D. T. *J. Chem. Soc. A* **1968**, 190.

Scheme II



signals corresponding to the *cis*-$[PtCl_2(PPh_3)_2]$, *trans*-$[PtHCl(PPh_3)_2]$ (**3**), and *trans*-$[PtCl(C_5H_{11})(PPh_3)_2]$ (**2**) complexes are observed, together with insoluble residues containing $SnCl_2$. The formation of the complex **2** is in accordance with the easy loss of $SnCl_2$ in this kind of compound.

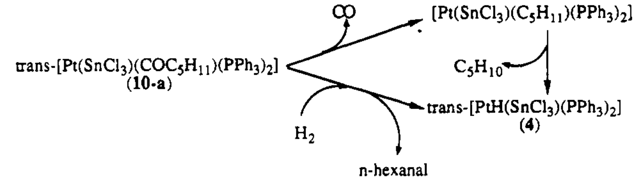
If 1-pentene is added to a solution of **3** and **4** (1:1) at 198 K, in addition to *cis*-$[Pt(SnCl_3)(C_5H_{11})(PPh_3)_2]$ (**5**), *cis*-$[PtCl_2(PPh_3)_2]$, and $[PtH(PPh_3)_3]^+$ (**15**) the new signals of *cis*-$[PtCl(C_5H_{11})(PPh_3)_2]$ (**1**) are detected after 15 min. These data suggest that the complex *trans*-$[PtHCl(PPh_3)_2]$ (**3**) acts as an acceptor of $SnCl_2$ from the complex **5**, generating the complexes **1** and **4**, since the complex **5** is stable under these conditions (see Scheme II). At 243 K the isomerization reaction from cis (**1** and **5**) to trans (**2** and **6**) is observed. The quantitative isomerization of *cis*-$[Pt(SnCl_3)(C_5H_{11})(PPh_3)_2]$ (**5**) and *cis*-$[PtCl(C_5H_{11})(PPh_3)_2]$ (**1**) to the corresponding *trans*-$[Pt(SnCl_3)(C_5H_{11})(PPh_3)_2]$ (**6**) and *trans*-$[PtCl(C_5H_{11})(PPh_3)_2]$ (**2**) is observed at 223 K, after 15 min, when an excess of CO is added. This result is in accordance with the known catalytic activity of carbon monoxide to produce cis–trans isomerization.[7] Also, a small amount of $[PtH(SnCl_3)(CO)(PPh_3)_2]$ (**13**) is observed, produced by the coordination of CO to *trans*-$[PtH(SnCl_3)(PPh_3)_2]$ (**4**) originated by the β-elimination of **6**.

When the temperature is increased to 308 K, the insertion of CO takes place, the ^{31}P spectra show only the signals due to *trans*-$[PtCl(COC_5H_{11})(PPh_3)_2]$ (**7**), *trans*-$[Pt(SnCl_3)(COC_5H_{11})(PPh_3)_2]$ (**10a**), and *trans*-$[PtCl(CO\{SnCl_2\}C_5H_{11})(PPh_3)_2]$ (**10b**), and insoluble compounds containing $SnCl_3^-$ are formed. As expected, at 198 K no reaction of the pentacoordinated complex $[PtH(SnCl_3)(CO)(PPh_3)_2]$ (**13**) and 1-pentene is observed, due to the saturated coordination sphere of this platinum complex. Analogously, a mixture of *trans*-$[PtHCl(PPh_3)_2]$ (**3**) and $[PtH(SnCl_3)(CO)(PPh_3)_2]$ (**13**) at 198 K does not undergo any reaction, showing that the Pt–$SnCl_3$ bond in complex **13** is strong, since the complex **3** accepts $SnCl_2$ easily, giving **4**.

The action of CO on the hydrido complexes **3** and **4** has also been studied. The complex *trans*-$[PtHCl(PPh_3)_2]$ (**3**) is recovered unaltered when treated with CO even at 100 atm and room temperature. However, the complex *trans*-$[PtH(SnCl_3)(PPh_3)_2]$ (**4**) easily coordinates CO at 1 atm and 198 K, giving the pentacoordinated complex $[PtH(SnCl_3)(CO)(PPh_3)_2]$ (**13**). Under these conditions, the species $[PtH(CO)(PPh_3)_2]^+$ is not observed, suggesting that the equilibrium proposed by Scrivanti[7] is completely on the left in CH_2Cl_2, showing the high capacity of the $SnCl_3^-$ ligand to stabilize pentacoordinated compounds:

$$\underset{\mathbf{13}}{[PtH(SnCl_3)(CO)(PPh_3)_2]} \rightleftarrows [PtH(CO)(PPh_3)_2]^+ + SnCl_3^-$$

Scheme III



Hydrogenolysis. The acyl complex *trans*-$[PtCl(COC_5H_{11})(PPh_3)_2]$ (**7**) does not react with H_2 at 1.5 atm and room temperature over a period of 24 h. The analogous complex *cis*-$[PtCl(COC_5H_{11})dppe]$ (**8**) also does not react with H_2. The action of H_2 on the acyl complex **10** at 1.5 atm and 308 K, for 24 h, gives *trans*-$[PtH(SnCl_3)(PPh_3)_2]$ (**4**) and a low amount of **15**. By GC and GC/MS, 1-pentene (12%), *cis*-2-pentene (22%), *trans*-2-pentene (34%), pentane (10%), *n*-hexanal (4%), and CO are detected (yields based on the amount of acyl complex used). At high H_2 pressure (50 atm) and 373 K, the same organic gaseous compounds, in different proportions, are detected, but the amount of hexanal rises only to 10%. These results suggest that the trichlorostannate–acyl complex undergoes decarbonylation and β-elimination reactions simultaneously with hydrogenolysis. Thus, if the acyl complex is treated with H_2 and CO (1.5 atm, 1:1), the decarbonylation reaction is partially inhibited and the gaseous mixture contains more hexanal (12%), 1-pentene (80%), and 2-pentene (4%), but no pentane is observed and the complex $[PtH(SnCl_3)(CO)(PPh_3)_2]$ (**13**) is recovered.

A detailed study of the action of H_2 (1 atm) on several acyl complexes $[PtCl(COR)(PPh_3)_2]$ (R = CH_3, Et, Pr, Bu^t, Hex, CH_2CH_2Ph) with $SnCl_2$ (1:1) in CH_2Cl_2 at room temperature was made.[13] After 24 h, the quantitative formation of aldehyde is observed. The formation of aldehyde (RCHO) depends on the quantity of the acyl form, *trans*-$[Pt(SnCl_3)(COR)(PPh_3)_2]$, present in relation to that of *trans*-$[PtCl(CO\{SnCl_2\}R)(PPh_3)_2]$. The complex with the largest amount of acyl form reacts fastest; thus, when all the complex is in the acyl form, hydrogenolysis is completed in 7 h. However, if the solution contains a 1:1 mixture of both species, hydrogenolysis takes 24 h.

In solution, the complex *trans*-$[Pt(SnCl_3)(COC_5H_{11})(PPh_3)_2]$ (**10a**) is in the same proportion as the other acyl complex without the Pt–Sn bond $[PtCl(CO\{SnCl_2\}C_5H_{11})(PPh_3)_2]$ (**10b**) (1:1). The low amount of aldehyde formed suggests that the decarbonylation reaction is very important under the experimental conditions; this evidence is supported by the results of Clark[32] concerning the capacity of $SnCl_2$ to promote the decarbonylation of acyl-Pt complexes.

It is not possible to exclude the activity of the "carbenoid" form, but the suggestion of Scrivanti and Pregosin,[13] that the reactivity is only related to the Pt–Sn acyl complex, seems reasonable. Accordingly, the complex *cis*-$[Pt(SnCl_3)(COC_5H_{11})dppe]$ (**9**), which in solution only exists in the Pt–Sn form, reacts with H_2 (1.5 atm), yielding 1-pentene, 2-pentene (cis–trans), pentane, and hexanal (8%). Finally, only the complex *cis*-$[PtCl_2dppe]$ is observed because the hydrido complex is very unstable; thus, the formation of aldehyde via hydrogenolysis of the acyl complex is only possible if the process involves a Pt–Sn bond (**9**, **10a**), but high CO pressure is necessary to stop the decarbonylation reaction.

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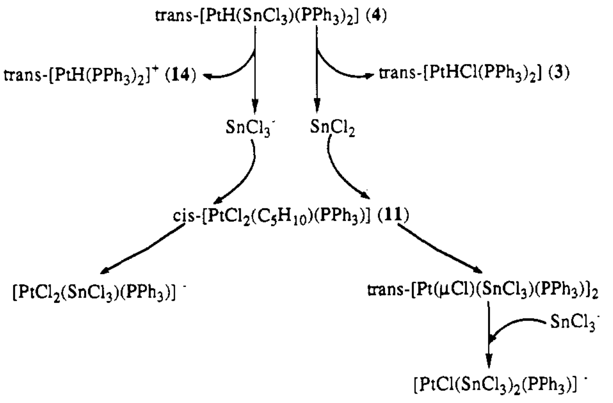
(32) Anderson, G. K.; Clark, H. C.; Davies, J. A. *Organometallics* **1982**, *1*, 64.

Scheme IV



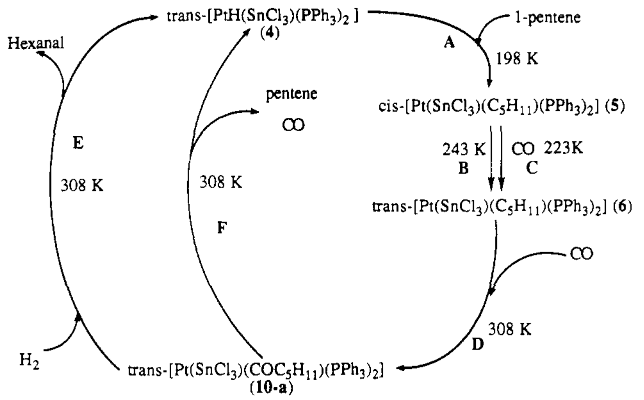
The participation in the catalytic process of HCl, produced in the activation phase of the catalyst precursor, has recently been proposed, since 2-chlorobutane is produced as a typical byproduct in the hydroformylation of 2-butenes.[11] Scrivanti et al.[10] observe the formation of a substantial amount of *n*-heptanal (~20%), studying the action of dry HCl on the acyl complex *trans*-[PtCl(CO-hexyl)(PPh$_3$)$_2$] in the presence of an excess of SnCl$_2$ after 3 days. We have studied the action of dry HCl on the complex *trans*-[Pt(SnCl$_3$)(COC$_5$H$_{11}$)(PPh$_3$)$_2$] (**10a**) in CH$_2$Cl$_2$, and after 2 days only 10% of *n*-hexanal was detected and *cis*-[PtCl(SnCl$_3$)(PPh$_3$)$_2$] recovered. 1-Pentene (50%) and 2-pentene (cis–trans) (12%) and other organic compounds heavier than *n*-hexanal were also detected, suggesting that under the conditions studied decarbonylation of the acyl complex is still the favored reaction. If the action of dry HCl on the complex **10a** is studied in the simultaneous presence of H$_2$ or H$_2$ and CO, the results obtained are practically identical with those obtained without HCl (see above).

Intermolecular Reactions. In order to determine whether any step of the process is bimolecular, the reactions with the participation of platinum complexes containing coordinated pentene or hydrido–platinum compounds were studied.

(a) Olefin Insertion Reactions. The complex *cis*-[PtCl$_2$(C$_5$H$_{10}$)(PPh$_3$)] (**11**) was used as an olefin carrier. The complex *trans*-[PtHCl(PPh$_3$)$_2$] (**3**) does not react with *cis*-[PtCl$_2$(C$_5$H$_{10}$)(PPh$_3$)] (**11**) at room temperature; only the decomposition of **11** is observed. However, *trans*-[PtH(SnCl$_3$)(PPh$_3$)$_2$] (**4**) and **11** react immediately at 198 K, giving *trans*-[PtHCl(PPh$_3$)$_2$] (**3**), 1-pentene, and [PtH(PPh$_3$)$_2$]$^+$ (**14**). At 308 K, only *cis*-[PtCl$_2$(PPh$_3$)$_2$] is observed. The study of the reaction of *trans*-[PtH(SnCl$_3$)(PPh$_3$)$_2$] (**4**) and *cis*-[PtCl$_2$(C$_5$H$_{10}$)(PMe$_2$Ph)] (**12**) confirms the formation of **14** and suggests that complexes **3** and **14** are formed from **4**. These results show that complex **11** acts as an SnCl$_2$ acceptor, as has been proved in its reaction with the acyl complex **10a**, where *trans*-[PtCl(COC$_5$H$_{11}$)(PPh$_3$)$_2$] (**7**) and insoluble residues were formed, due to the tendency of π-coordinated olefin complexes to accept SnCl$_2$.

These data suggest that *trans*-[PtH(SnCl$_3$)(PPh$_3$)$_2$] (**4**) at 198 K loses SnCl$_2$ or SnCl$_3^-$, yielding *trans*-[PtHCl(PPh$_3$)$_2$] (**3**) or [PtH(PPh$_3$)$_2$]$^+$ (**14**), respectively; **11** reacts with SnCl$_2$, giving 1-pentene and *trans*-[Pt(μ-Cl)(SnCl$_3$)(PPh$_3$)]$_2$. This complex reacts[33] with SnCl$_3^-$, generating insoluble species such as [PtCl(SnCl$_3$)$_2$(PPh$_3$)]$^-$ (Scheme IV).

Scheme V. Proposed Cycle for Hydroformylation of 1-Pentene at P = 1–1.5 atm and T = 198–308 K



(b) Hydrogenolysis. As hydrogen donors the following complexes were used in reactions with acyl–platinum complexes: *trans*-[PtHCl(PPh$_3$)$_2$] (**3**), *trans*-[PtH(SnCl$_3$)(PPh$_3$)$_2$] (**4**), and [PtH(SnCl$_3$)(CO)(PPh$_3$)$_2$] (**13**). As expected, the complex *trans*-[PtCl(COC$_5$H$_{11}$)(PPh$_3$)$_2$] (**7**) does not react at 308 K with the hydrido complex **3**. However, the reaction of *trans*-[PtHCl(PPh$_3$)$_2$] (**3**) with the acyl complex **10** containing SnCl$_2$ at 198 K immediately gives *trans*-[PtH(SnCl$_3$)(PPh$_3$)$_2$] (**4**) and *trans*-[PtCl(COC$_5$H$_{11}$)(PPh$_3$)$_2$] (**7**), formed by the transference of SnCl$_2$ to **3**. This was the only interchange reaction of SnCl$_2$ observed. The complex *trans*-[PtH(SnCl$_3$)(PPh$_3$)$_2$] (**4**) does not react at 198 K, with **7** or with **10**. As, in any case, the formation of aldehyde is not observed, we can say that the hydroformylation of olefins with the Pt–Sn system studied is not a binuclear process.

The pentacoordinated complex [PtH(SnCl$_3$)(CO)(PPh$_3$)$_2$] (**13**) also does not react with the acyl–platinum complexes **7** and **10**. In no case is interchange of SnCl$_2$ observed, since the complex **13** is really a pentacoordinated complex with a strong Pt–Sn bond.

Discussion

The reactions studied allow us to propose the complex *trans*-[PtH(SnCl$_3$)(PPh$_3$)$_2$] (**4**) as the starting species in a cycle of stoichiometric reactions. The successive addition of the reagents olefins, CO, and hydrogen yield aldehydes under these experimental conditions (Scheme V).

At 198 K, complex **4** undergoes the insertion of 1-pentene, giving **5** (step A). The insertion of 1-pentene at 198 K in the hydrido complex **4** is highly regioselective, and only the linear alkyl complex **5** is formed. This complex isomerizes to the trans species **6**, by warming to 243 K (step B) or by the action of CO at 223 K (step C). At room temperature, the insertion of CO takes place with formation of acyl complex **10a** (step D); this complex reacts with H$_2$, yielding hexanal and regenerating the initial complex **4** (step E). As stated before, hydrogenolysis does not give hexanal quantitatively under these conditions, since complex **10a** also undergoes decarbonylation and β-elimination, yielding **4** (step F). The acyl complex **10a** exists in solution in equilibrium (1:1) with the carbenoid form *trans*-[PtCl(CO{SnCl$_2$}C$_5$H$_{11}$)(PPh$_3$)$_2$] (**10b**) without the Pt–Sn bond. The hydrogenolysis reactions without SnCl$_2$, and the results obtained with the complex *cis*-[Pt(SnCl$_3$)(COC$_5$H$_{11}$)(dppe)] (**9**) (which in solution only exists in the Pt–Sn acyl form), suggest that all the aldehyde formed results from this Pt–Sn acyl form. As hydrogenolysis requires the highest temperature, step E will determine the turnover of the hydroformylation cycle.

Hydrogenation and isomerization of olefins, at low pressure and temperature, can be produced by the par-

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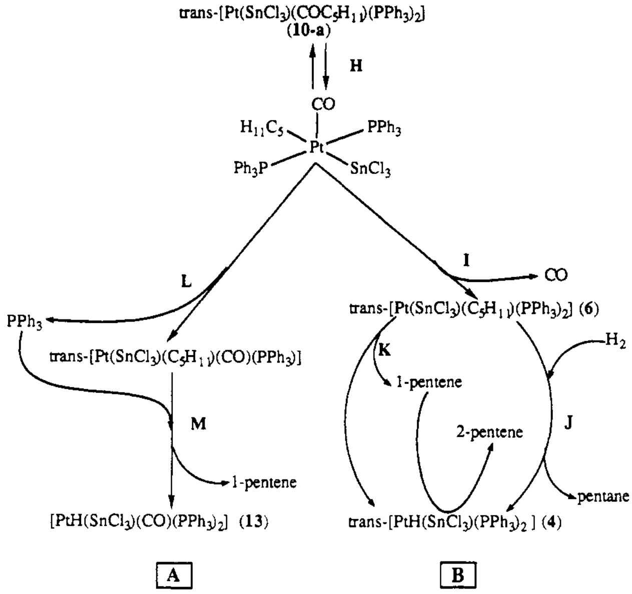
[33] Anderson, G. K.; Clark, H. C.; Davies, J. A. *Inorg. Chem.* **1983**, *22*, 434.

Scheme VI. Isomerization and Hydrogenation of the Olefin in the Presence (A) or in the Absence (B) of CO



ticipation of alkyl (**5** and **6**) and acyl (**10**) complexes (Scheme VI). Clark[32] proposed that the decarbonylation of the acyl complexes occurs by means of the pentacoordinated complex $[Pt(SnCl_3)R(CO)(PPh_3)_2]$ (step H). If no CO is present, the acyl complex loses CO, giving **6** (step I), which reacts with hydrogen,[16] giving pentane (step J) and **4**. β-Elimination at room temperature of **6** gives 1-pentene and also **4** (step K). The high amount of 2-pentene (cis and trans) observed (56%) was formed by reaction of 1-pentene and **4**. If CO is present, the acyl complex has to eliminate PPh_3 (step L), and the complex formed, $[Pt(SnCl_3)(C_5H_{11})(CO)(PPh_3)]$, undergoes β-elimination, giving 1-pentene and **13** (step M). No pentane was observed, and the isomerization of 1-pentene to 2-pentene is very low.

Concluding Remarks

The three processes involved in the hydroformylation of olefins, insertion of the olefin and carbon monoxide and hydrogenolysis, can be studied consecutively with the Pt/Sn system, taking advantage of the increasing activation energies of the successive independent steps. This gradation of the activation energies is a characteristic feature of this system, since other platinum compounds without tin show the lowest activation energies of activation for the insertion process of carbon monoxide.[12]

The presence of $SnCl_2$ decreases the activation energies of the insertion of olefin and hydrogenolysis reactions. The known capacity of $SnCl_2$ to improve the reactivity of platinum complexes with hydroformylation substrates (CO, H_2, and olefins) was proved in the reactions discussed. Thus, *trans*-$[PtHCl(PPh_3)_2]$ (**3**) and *trans*-$[PtCl(COC_5H_{11})(PPh_3)_2]$ (**7**) do not react with either 1-pentene or CO or H_2. The acyl compound with H_2 (1.5 bar) at room temperature gives mainly decarbonylation products (at least 65% of the initial complex) and only 4% of hexanal. In the presence of CO hydrogenolysis to *n*-hexanal increases to 12%. Thus, under in these mild conditions decarbonylation is the main process of the acyl complexes containing the $SnCl_3^-$ ligand.

Formation of pentane from the acyl complexes is completely inhibited in the presence of CO. This fact shows that the hydrogenation of the olefins under oxo conditions is produced by the hydrogenolysis of the alkyl complexes.

The participation of free HCl in the hydrogenolysis of the acyl complexes under oxo conditions can be discounted, since with large amounts of HCl results similar to those obtained with free H_2 reactions are observed. In any case we have not observed the formation of chloropentane either in stoichiometric reactions or in the catalytic tests.[5] Chloroalkyls could be formed by an independent process, since $[PtCl_2(CO)olefin]$ catalyzes the hydrochlorination of olefins as reported by Calderazzo.[34]

In the trans complexes, the lability of the $Pt-SnCl_3$ bond increases from the hydride to the acyl intermediates, so the $SnCl_3^-$ ligand in the acyl complex is easily removed by any other platinum species without tin. This lability is one potential way of deactivating the catalytic species. Thus, the Pt:Sn ratio of 1:(3–5) used under oxo conditions probably reflects the amount of free $SnCl_3^-$ necessary to retain the Pt–Sn bond.

From the reactions studied, it is possible to propose the following order of the Pt–Sn bond stability:

$$\mathit{trans}\text{-}[Pt(SnCl_3)(COC_5H_{11})(PPh_3)_2] < [Pt(SnCl_3)(C_5H_{11})(PPh_3)_2] < \mathit{trans}\text{-}[PtH(SnCl_3)(PPh_3)_2] < [PtH(SnCl_3)(CO)(PPh_3)_2] < [Pt(\mu\text{-}Cl)(SnCl_3)(PPh_3)]_2 < [PtCl(SnCl_3)(PPh_3)]^- < [PtCl_2(SnCl_3)_2]^{2-}$$

In the process catalyzed by cobalt or rhodium systems, in addition to the direct reaction of H_2 with the acyl complexes, a dinuclear reductive elimination with another hydride complex has been proposed.[14] Pino also suggested that aldehyde splitting can occur via interaction of $HSnCl_3$ with an acyl–platinum complex.[9]

Our results exclude the participation of intermolecular steps by the reaction of two different Pt complexes under the experimental conditions described; thus, only the transference of $SnCl_2$ was observed.

However, it should be noted that under the conditions studied it is not possible to attain a catalytic cycle, since the formation of the pentacoordinated complex $[PtH(SnCl_3)(CO)(PPh_3)_2]$ (**13**) prevents any other subsequent reaction.

Experimental Section

^1H NMR spectra were obtained on a Bruker FT-80 SY (80 MHz) or Varian XL-200 (200 MHz) instrument. Spectra were recorded for $CDCl_3$ solutions. $^{31}P\{^1H\}$ (32.4 MHz) spectra were obtained on a Bruker FT-80 SY instrument. Spectra were recorded for CH_2Cl_2 or $CHCl_3$ solutions. Chemical shifts were measured in ppm relative to the internal standard Me_4Si or to the external standard 85% H_3PO_4. A positive sign indicates a shift to lower field. Coupling constants (*J*) are in Hz. The sample temperature was controlled with a BVT-1000 instrument by passing a stream of cooled N_2 over the sample tube and was estimated to be accurate to ±1 K. IR spectra were measured as KBr pellets with a Perkin-Elmer IR 1330 instrument over the range 4000–200 cm^{-1}. Chemical analyses were carried out at the Institut de Química Bio-Orgànica de Barcelona (CSIC). Gas chromatography analyses were performed on a Hewlett-Packard HP-5890 A instrument equipped with a HP Ultra-2 capillary column 25 m long and a flame ionization detector; helium was used as the carrier gas. The analyses were performed with an internal standard (cyclohexene), the overall error being less than 2–5%. The identification of the reaction products was checked by GC–MS measured on a HP CG/MS 5988 A instrument equipped with a HP-5890 A gas chromatograph using a HP Ultra-2 capillary column 25 m long, by electronic impact and chemical ionization (CH_4).

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(34) Alper, H.; Huang, Y.; Dell'Amico, D. B.; Calderazzo, F.; Pasqualetti, N.; Veracini, C. A. *Organometallics* 1991, *10*, 1665.

Crystallographic Studies. An equidimensional crystal (0.07 × 0.07 × 0.07 mm) was selected and mounted on a Philips PW-1100 four-circle diffractometer. Unit-cell parameters were determined from automatic centering of 25 reflections ($4 \leq \theta \leq 12°$) and refined by the least-squares method. Intensities were collected with graphite-monochromatized Mo Kα radiation, by the ω-scan technique, with a scan width of 0.8° and a scan speed of 0.03° s^{-1}. A total of 4722 reflections were measured in the range $2 \leq \theta \leq 25°$, 3235 of which were assumed as observed by applying the condition $I \geq 2.5\sigma(I)$. Three reflections were measured every 2 h as a control of orientation and intensity; significant intensity decay was not observed. Lorentz–polarization was observed, but no absorption corrections were made.

The Pt atom was located by a Patterson synthesis, and the remaining non-hydrogen atoms were found by the DIRDIF method[35] and refined by the full-matrix least-squares method, with use of the SHELX76 computer program.[36] The function minimized was $\sum w[|F_o| - |F_c|]^2$, where $w = [\sigma^2(F_o) + 0.0042(F_0)^2]^{-1}$, f, f', and f'' were taken from ref 37. Phenyl ring atoms were refined with constrained planarity and bond lengths and angles. H atoms were not located. The final R factor was 0.056 ($R_w = 0.060$) for all observed reflections. The maximum shift/esd was 0.3 in U_{22} of C(126); maximum and minimum peaks in the final difference synthesis were 0.3 and −0.3 e Å^{-3}, respectively. Crystal parameters, data collection details, and results of the refinements are summarized in Table II.

Materials and Syntheses. Anhydrous SnCl$_2$ was prepared by the method reported,[38] and 1-pentene was purchased from Fluka. The solvents were dried and freshly distilled under N$_2$, prior to use.

The following complexes were prepared by the methods reported: *cis*-[PtCl$_2$(PPh$_3$)$_2$],[39] *trans*-[PtCl$_2$(PPh$_3$)$_2$],[39] *cis*-[PtCl$_2$(dppe)],[40] *trans*-[Pt(μ-Cl)Cl(PPh$_3$)]$_2$,[41,42] *cis*-[PtCl(SnCl$_3$)(PPh$_3$)$_2$],[43] *trans*-[Pt(μ-Cl)(SnCl$_3$)(PPh$_3$)]$_2$,[44] *trans*-[PtHCl(PPh$_3$)$_2$] (**3**),[39,45] *cis*-[PtCl$_2$(C$_2$H$_4$)(PPh$_3$)],[46] *cis*-[PtCl$_2$(C$_2$H$_4$)(PMe$_2$Ph)] was prepared by the method reported for *cis*-[PtCl$_2$(C$_2$H$_4$)(PPh$_3$)], *trans*-[PtH(SnCl$_3$)(PPh$_3$)$_2$] (**4**),[2] [PtH(SnCl$_3$)(CO)(PPh$_3$)$_2$] (**13**).[7]

***cis*-[PtCl(C$_5$H$_{11}$)(PPh$_3$)$_2$] (1).** At 203 K, 1.5 g (10 mmol) of C$_5$H$_{11}$Br was added dropwise to a mixture of 0.2 g (29 mmol) of Li in 20 mL of ether, under nitrogen. After all the C$_5$H$_{11}$Br had been added, the mixture was heated at room temperature and stirred for 2 h. After this time 10 mL of this solution was added dropwise to a mixture of *cis*-[PtCl$_2$(PPh$_3$)$_2$] (0.6 g, 0.76 mmol) and 30 mL of ether at 273 K. The mixture was heated to room temperature and stirred for 1 h. The solution was hydrolyzed with methanol and the solvent removed. When pentane was added to the residue, a white solid of *cis*-[Pt(C$_5$H$_{11}$)$_2$(PPh$_3$)$_2$] was formed. The product was recrystallized from CHCl$_3$ and pentane. A solution of 0.47 g (0.54 mmol) of *cis*-[Pt(C$_5$H$_{11}$)$_2$(PPh$_3$)$_2$] in CHCl$_3$ at 263 K was treated for 10 s with a stream of dry HCl. The solvent was removed. The residue was composed of *cis*-[PtCl$_2$(PPh$_3$)$_2$] and *cis*-[PtCl(C$_5$H$_{11}$)(PPh$_3$)$_2$] (1). This mixture was stirred at 273 K with CHCl$_3$ and filtered. The solvent was removed, and compound 1 was obtained. The product was recrystallized from CH$_2$Cl$_2$ and pentane; yield 0.28 g (63%). Anal. Calcd for C$_{41}$H$_{41}$ClPt: C, 64.80; H, 5.40. Found: C, 63.8; H, 5.0.

***trans*-[PtCl(C$_5$H$_{11}$)(PPh$_3$)$_2$] (2).** At 273 K, 3.0 g (20 mmol) of C$_5$H$_{11}$Br, under N$_2$, was added dropwise to a mixture of 0.48 g (20 mmol) of Mg in 50 mL of ether with an I$_2$ crystal. After all the C$_5$H$_{11}$Br was added, the mixture was stirred for 2 h until no Mg remained. Then *trans*-[PtCl$_2$(PPh$_3$)$_2$] (0.8 g, 1 mmol) was added to this solution and the mixture was stirred for 1 h. The solution was hydrolyzed with ice and an HCl solution of 2%. The organic layer was separated and dried and the solvent removed, giving a white solid. The product was recrystallized from CHCl$_3$/pentane mixture; yield 0.56 g (68%). Anal. Calcd for C$_{41}$H$_{41}$ClPt: C, 64.80; H, 5.40. Found: C, 64.0; H, 5.1.

Solutions of *cis*-[Pt(SnCl$_3$)(C$_5$H$_{11}$)(PPh$_3$)$_2$] (5) and *trans*-[Pt(SnCl$_3$)(C$_5$H$_{11}$)(PPh$_3$)$_2$] (6). The complex *trans*-[PtH(SnCl$_3$)(PPh$_3$)$_2$] (**4**; 0.056 g, 0.059 mmol) was weighed in an NMR tube (10-mm diameter) and the solvent CH$_2$Cl$_2$ (2 mL) added. After the mixture was cooled to 198 K, 1-pentene (0.6 mL) was added and the reaction was monitored by ^{31}P NMR spectroscopy. After a period of 40 min, the main product was *cis*-[Pt(SnCl$_3$)(C$_5$H$_{11}$)(PPh$_3$)$_2$] (**5**). At 243 K the isomerization of **5** to *trans*-[Pt(SnCl$_3$)(C$_5$H$_{11}$)(PPh$_3$)$_2$] (**6**) was complete in 15 min.

***trans*-[PtCl(COC$_5$H$_{11}$)(PPh$_3$)$_2$] (7).** A mixture of *trans*-[PtHCl(PPh$_3$)$_2$] (**3**; 1.5 g, 2.0 mmol), PPh$_3$ 0.34 g (1.3 mmol), 1-pentene (14.0 g, 200 mmol), and ethanol (100 mL) was placed in a pressure reactor. The reactor was cooled and purged with CO and, after being pressurized with 50 atm of CO, heated to 100 °C and stirred for 4 h. After this time the reactor was cooled and slowly depressurized, giving a white solid of *trans*-[PtCl(COC$_5$H$_{11}$)(PPh$_3$)$_2$] (**7**), which was washed with cool ethanol and ether. The solid was recrystallized from CH$_2$Cl$_2$; yield 1.48 g (87%). IR data: ν(C=O) 1645 (s) cm^{-1}. ^{1}H NMR (200 MHz, in CDCl$_3$ at 308 K): δ 1.45 (m, COCH_2R), 0.8 (m, COCH$_3$CH_2R), 0.3–0.5 (bm, COCH$_2$CH$_2$CH_2CH_2CH$_3$), 0.6 (t, RCH_3). Anal. Calcd for C$_{42}$H$_{41}$ClOP$_2$Pt: C, 59.05; H, 4.80. Found: C, 58.5; H, 4.8.

***cis*-[PtCl(COC$_5$H$_{11}$)(dppe)] (8).** dppe (0.25 g, 0.64 mmol) was added to a solution of *cis*-[PtCl(COC$_5$H$_{11}$)(PPh$_3$)$_2$] (**7**; 0.5 g, 0.58 mmol) in 10 mL of toluene under N$_2$, and the mixture was stirred at room temperature for 4 h. The solvent was removed and the residue was treated with hexane, giving a white precipitate. The product was recrystallized from CHCl$_3$/hexane; yield 0.35 g (85%). IR data: ν(C=O) 1625 (s) cm^{-1}. Anal. Calcd for C$_{32}$H$_{35}$ClOP$_2$Pt: C, 52.78; H, 4.81. Found: C, 51.8; H, 4.8.

***cis*-[Pt(SnCl$_3$)(COC$_5$H$_{11}$)(dppe)] (9).** A mixture of *cis*-[PtCl(COC$_5$H$_{11}$)(dppe)] (**8**; 0.43 g; 0.59 mmol), SnCl$_2$ (0.22 g, 1.2 mmol), and CHCl$_3$ (15 mL), under N$_2$, was stirred for 10 min at room temperature. The mixture was filtered and the solvent removed, giving an orange compound, which was washed with ether; yield 0.47 g (87%). IR data: ν(C=O) 1630 (s) cm^{-1}; ν(Sn—Cl) 310 (s), 330 (s) cm^{-1}. Anal. Calcd for C$_{32}$H$_{35}$Cl$_3$OP$_2$PtSn: C, 41.87; H, 3.82. Found: C, 40.2; H, 3.6.

***trans*-[Pt(SnCl$_3$)(COC$_5$H$_{11}$)(PPh$_3$)$_2$] (10a) and *trans*-[PtCl(CO{SnCl$_2$}C$_5$H$_{11}$)(PPh$_3$)$_2$] (10b).** The method of preparation of these compounds gives a solution of **10a** and **10b**, but in the solid state it is possible to obtain mainly **10a** or **10b**, depending on the experimental conditions (methods A and B, respectively).

A. A mixture of *trans*-[PtCl(COC$_5$H$_{11}$)(PPh$_3$)$_2$] (**7**; 0.5 g, 0.59 mmol), SnCl$_2$ (0.22 g, 1.2 mmol), and CHCl$_3$ (15 mL), under N$_2$, was stirred for 4 h. The mixture was filtered and the solvent removed. The orange solid was washed with ether. The IR data (ν(C=O) 1665 cm^{-1}) shows that the solid is mainly the compound *trans*-[Pt(SnCl$_3$)(COC$_5$H$_{11}$)(PPh$_3$)$_2$] (**10a**) together with a small amount of [PtCl(CO{SnCl$_2$}C$_5$H$_{11}$)(PPh$_3$)$_2$] (**10b**), overall yield 0.45 g (73%). IR data: ν(C=O) 1665 (s) cm^{-1} (**10a**), 1500 (w) cm^{-1} (**10b**); ν(Sn—Cl) 305 (s) cm^{-1} (**10a**).

B. A mixture of *trans*-[PtCl(COC$_5$H$_{11}$)(PPh$_3$)$_2$] (**7**; 0.5 g, 0.59 mmol), SnCl$_2$ (0.22 g, 1.2 mmol), and CHCl$_3$ (15 mL), under N$_2$, was stirred for only 10 min. The mixture was rapidly filtered and the solvent removed. The orange solid was washed with ether. The IR data (ν(C=O) 1500 cm^{-1}) shows that the solid is mainly the compound [PtCl(CO{SnCl$_2$}C$_5$H$_{11}$)(PPh$_3$)$_2$] (**10b**) together with a small amount of *trans*-[Pt(SnCl$_3$)(COC$_5$H$_{11}$)(PPh$_3$)$_2$] (**10a**), overall yield 0.4 g (65%). IR data: δ(C=O) 1665 (w) cm^{-1} (**10a**), 1500 (s) cm^{-1} (**10b**); ν(Sn—Cl) 300 (s), 275 (s) cm^{-1} (**10b**). ^{1}H NMR

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(35) Beurskens, P. T.; Bosman, W. P.; Doesburg, H. N.; Gould, R. D.; Van der Hark, T. E.; Prick, P. A. J.; Nordik, J. H.; Beurskens, G.; Parthasarati, V. DIRDIF, an automatic procedure for phase extension and refinement of difference structure factors; Technical Report 1981/2, Crystallography Laboratory Toernooiveld: Nijmegen, The Netherlands, 1981.

(36) Sheldrick, G. M. SHELX, a computer program for crystal structure determination; University of Cambridge, Cambridge, England, 1976.

(37) *International Tables of X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99–100, 149.

(38) Baudler, M. In *Handbook of Preparative Inorganic Chemistry*, 2nd ed.; Brauer, G. Ed.; Academic Press: New York, 1963; Vol. 1, pp 728–729.

(39) Cavinato, G.; Toniolo, L. *Inorg. Chim. Acta* **1981**, *52*, 39.

(40) Appleton, T. G.; Bennett, M. A.; Tomkins, I. B. *J. Chem. Soc., Dalton Trans.* **1976**, 439.

(41) Hartley, F. R.; Searle, G. W. *Inorg. Chem.* **1973**, *12*, 1949.

(42) Smithies, A. C.; Schmidt, P.; Orchin, M. *Inorg. Synth.* **1970**, *12*, 240.

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

(44) Pregosin, P. S.; Rüegger, H. *Inorg. Chim. Acta* **1984**, *86*, 55.

(45) Bailar, J. C.; Itatani, H. *Inorg. Chem.* **1965**, *4*, 1618.

(46) De Renzi, A.; Paiaro, G.; Panunzi, A. *Gazz. Chim. Ital.* **1972**, *102*, 413.

(200 MHz, in $CDCl_3$ at 308 K): for **10a** and **10b** δ 1.6 (m, $COCH_2R$), 0.8 (m, $COCH_2CH_2R$), 0.4 (m, $COCH_2CH_2CH_2CH_2CH_3$); δ 0.65 (t, RCH_3 (**10a**); δ 0.07 (s, $COCH_2R$ (**10b**). Anal. Calcd for $C_{42}H_{41}Cl_3OP_2PtSn$: C, 48.30; H, 3.93. Found: C, 47.0; H, 3.8.

***cis*-[PtCl$_2$(C$_5$H$_{10}$)(L)] (L = PPh$_3$ (11), PMe$_2$Ph (12)).** An excess of 1-pentene (0.4 g, 10 mmol) was stirred with *cis*-[$PtCl_2(C_2H_4)(L)$] (L = PPh_3 or L = PMe_2Ph; 0.9 mmol) in $CHCl_3$ at room temperature for 1 h (L = PPh_3) or 6 h (L = PMe_2Ph). The mixture was filtered and the solvent removed, and a white precipitate was formed. The products were recrystallized from a CH_2Cl_2/pentane mixture. For L = PPh_3 the yield was 0.43 g (80%). Anal. Calcd for $C_{23}H_{25}Cl_2PPt$: C, 46.16; H, 4.18. Found: C, 45.9; H, 4.1. For L = PMe_3Ph, the yield was 0.13 g (30%). Anal. Calcd for $C_{13}H_{21}Cl_2PPt$: C, 32.90; H, 4.43. Found: C, 32.5; H, 4.2.

Solutions of [PtH(PPh$_3$)$_2$]$^+$ (14) and [PtH(PPh$_3$)$_3$)]$^+$ (15). $AgBF_4$ (0.07 g, 0.35 mmol) was added by stirring to a solution of *trans*-[$PtHCl(PPh_3)_2$] (**3**; 0.25 g, 0.33 mmol) in CH_2Cl_2 (10 mL) at 198 K. After 20 min the mixture was filtered and the solution analyzed by ^{31}P NMR spectroscopy, showing only the signal of the species [$PtH(PPh_3)_2$]$^+$ (**14**).

To the solution of [$PtH(PPh_3)_2$]$^+$ (**14**) was added PPh_3 (0.17 g, 0.66 mmol) at 198 K. After 5 min the solution was analyzed by ^{31}P NMR spectroscopy, showing only the signals assigned to the cation [$PtH(PPh_3)_3$)]$^+$ (**15**).

Reactions. The stability test was performed in a Schlenk tube equipped with a magnetic stirring bar, a gas inlet, and a rubber septum. The Schlenk tube with the compound was purged with N_2, and the progress of the reaction was periodically checked by ^{31}P NMR spectroscopy.

The reactions of **3** and/or **4** and 1-pentene and/or CO were performed in an NMR tube by the same general method: as an example, we give the reaction of *trans*-[$PtH(SnCl_3)(PPh_3)_2$] (**4**) and 1-pentene. The complex *trans*-[$PtH(SnCl_3)(PPh_3)_2$] (**4**) was weighed in an NMR tube (10-mm diameter) and the solvent CH_2Cl_2 (2 mL) added. After the mixture was cooled to 198 K, 1-pentene (0.6 mL) was added and the reaction was monitored by ^{31}P NMR spectroscopy. After each 5-min period ^{31}P NMR spectrum was carried out. When there was no change, the temperature was raised by intervals of 5 K until 308 K, and after stabilization of each temperature, spectra were recorded until no change was observed. In the case of the reaction with CO, the tube was sealed with a rubber septum and allowed to reach the reaction temperature in the NMR probe. The gas (ca. 1 mL) was injected through the septum into the solution.

The reactions of the acyl complexes **7**–**9** and **10a**,**b** and H_2 or H_2/CO were performed in a small Schlenk tube, equipped with a magnetic stirring bar, a gas inlet, and a rubber septum. The Schlenk tube with the acyl complex (0.3 mmol) was purged with N_2 and the solvent CH_2Cl_2 injected (5 mL). Then the N_2 atmosphere was replaced by hydrogen or H_2/CO (1.5 atm) at room temperature. After 24 h the solution was examined by ^{31}P NMR spectroscopy and analyzed by GC and GC/MS methods.

The reactions of **3**, **4**, or **13** and **11** or acyl complexes **7** and **10a**,**b** were performed in NMR tubes. As an example, a stoichiometric amount of *trans*-[$PtH(SnCl_3)(PPh_3)_2$] (**4**; 0.12 mmol) in 1.5 mL of CH_2Cl_2 and *cis*-[$PtCl_2(C_5H_{10})(PPh_3)$] (**11**; 0.13 mmol) in 1.5 mL of CH_2Cl_2 were placed in different 10-mm NMR tubes. After the solutions were cooled to 198 K, the spectrum of each one was recorded, the solutions were mixed, and the reaction was monitored by ^{31}P NMR spectroscopy. After each 5-min period a spectrum was measured. When there was no change, the temperature was raised by intervals of 5 K until 308 K, and after stabilization of each temperature spectra were recorded until no change was observed.

Acknowledgment. We thank the DGICYT (Grant No. PB 85-0013) for financial support and Johnson Matthey for the geneous loan of platinum salts.

Registry No. **1**, 136764-70-0; **2**, 136844-93-4; **3**, 16841-99-9; **4**, 18117-31-2; **5**, 133451-47-5; **6**, 136844-94-5; **7**, 136764-71-1; **8**, 136764-72-2; **9**, 136764-73-3; **10a**, 136764-74-4; **10b**, 136764-78-8; **11**, 136764-75-5; **12**, 136764-76-6; **13**, 72794-37-7; **14**, 115777-43-0; **15**, 47899-53-6; *cis*-[$Pt(C_5H_{11})_2(PPh_3)_2$], 136764-77-7; *cis*-[$PtCl_2(PPh_3)_2$], 15604-36-1; *trans*-[$PtCl_2(PPh_3)_2$], 14056-88-3; *cis*-[$PtCl_2(C_2H_4)(PPh_3)$], 38095-87-3; *cis*-[$PtCl_2(C_2H_4)(PMe_2Ph)$], 38498-20-3; 1-pentene, 109-67-1.

Supplementary Material Available: Listings of all bond distances and angles and anisotropic thermal parameters for **4** (2 pages); a listing of observed and calculated structure factors for **4** (14 pages). Ordering information is given on any current masthead page.