Hydride Route for the Palladium-Catalysed Cyclocarbonylation of Monoterpenes

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This paper focuses on the mechanism by which a monoterpene undergoes a cyclocarbonylation reaction catalysed by a palladium complex. Evidence is provided, based on intermediate species observed under pressure or with various ligands, that the catalytic cycle follows a hydride route starting from [Pd(H)($SnCl_3$)L_2]. The [Pd(H)($SnCl_3$)L_2] complexes (L = PPh_3 or PCy_3) have been observed for the first time by multinuclear NMR spectroscopy. Cationic hydride complexes or palladium(0) precursors show either no or poor reactivity. Studies related to model platinum complex chemistry have detected an acylplatinum species. Most of the observations have been done on the cyclocarbonylation of isopulegol, dihydromyrcenol or isolimonene into the corresponding lactones or cyclopentanones. The use of dihydromyrcene allowed us to observe the acylplatinum complex and the corresponding elusive acylpalladium species. The co-catalytic role of $SnCl_2$ is also demonstrated.

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Introduction

Palladium chemistry is currently the workhorse of organic chemistry and is a versatile tool to perform carbon–carbon coupling.[1] When appropriate building blocks are introduced the substrate can follow a multistep functionalisation so that tandem reactions open the way for the preparation of rather sophisticated organic molecules.[2] A number of interesting compounds that show biological activity contain a lactone moiety.[3] During the last few years we have explored the introduction of a CO building block into an unsaturated substrate to obtain such a backbone in a one-pot synthesis.[4] We chose to follow an hemisynthetic way starting from an abundant and cheap raw material like monoterpenes. Thus, we functionalised isopulegol and dihydromyrcenol into the corresponding lactones,[4] and then extended this type of tandem reaction to the cyclocarbonylation of isolimonene, which produces a cyclopentanone.[5] All these reactions are an extension of the classical alkoxycarbonylation reaction by which a terminal alkene is carbonylated in the presence of an alcohol to provide an ester. Generally, this reaction is catalysed by a palladium complex containing a phosphane or a diphosphane ligand, and most often the [$PdCl_2L_2$] precursor is introduced into the medium. These reactions are promoted by the addition of a Lewis acid such as $SnCl_2$. Two catalytic pathways have been considered, and are still proposed in the literature: the first one involves an alkoxycarbonylpalladium intermediate [Pd-COOR] to which the alkene coordinates and finally a *cis*-migration produces an alkylpalladium moiety containing the ester group,[6] whereas the second one starts from an intermediate palladium hydride species [Pd–H] which gives an alkylpalladium intermediate by successive coordination of the alkene and subsequent hydride transfer.[1,7] The copolymerisation of ethylene and carbon monoxide catalysed by the cationic [Pd(diphos)]$^{2+}$ complexes in the presence of methanol perfectly interconnects the two catalytic pathways[8] such that polymers with -CH_2COOCH_3 and -CH_2CH_3 terminal functions are produced in equal proportions. For the alkoxycarbonylation reaction of an alkene, Knifton has reported the [$PdCl_2(PPh_3)_2$]/$SnCl_2$ catalytic system, with which he detected the presence of a ν(Pd–H) stretching frequency.[7] In the literature, several papers deal with evidence that the palladium hydride pathway operates preferentially.[9,10] Particularly, in recent studies Heaton and co-workers have synthesised cationic Pd^{II} hydride complexes containing both a diphosphane ligand and a coordinated solvent molecule, [Pd(H)(dtbpx)(MeOH)]$^+$ [dtbpx = 1,2-(CH_2P*t*Bu_2)$_2C_6H_4$].[10] They demonstrated that this complex is an essential intermediate in the catalytic system for the formation of methyl propanoate by carbonylation of ethene in methanol.

The present study is concerned with spectroscopic evidence obtained for various [Pd(H)(X)L_2] and [Pd(H)L_3]$^+$

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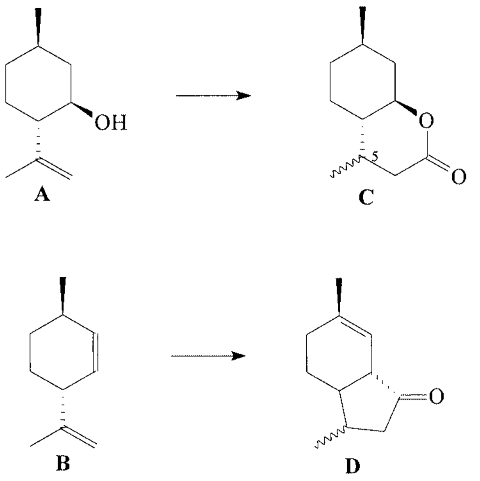
complexes under normal conditions or under CO pressure. We demonstrate that the essential active species in the cyclocarbonylation reaction is $[Pd(H)(SnCl_3)L_2]$.

Results and Discussion

Carbonylation of isopulegol **A** or isolimonene **B**, under a CO pressure of 40 bar, in the presence of $[PdCl_2L_2]/SnCl_2$ provides the lactone **C** or the cyclopentanone **D**, irrespective of whether the medium contains methanol or not (Scheme 1).[4,11,12]



Scheme 1. Cyclocarbonylation of isopulegol **A** and isolimonene **B**.

After catalysis, we never detected any alkoxycarbonylpalladium complex containing the isopulegyl moiety among the organometallic compounds. However, starting from isolimonene, small amounts of dehydro-**D** have previously been identified corresponding to a cyclopentenone resulting from the sacrificial formation of the palladium hydride species.[5,11,13]

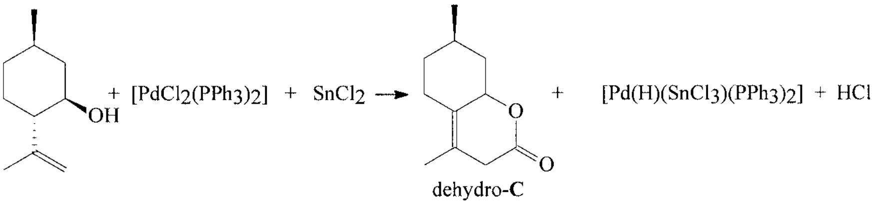
During the present study, we carefully analysed the products resulting from the cyclocarbonylation of isopulegol by GC/MS and we identified small amounts of the unsaturated lactone dehydro-**C**, which leads to Equation (1). In order to gain direct evidence of the involvement of this catalytic hydride route, we prepared a series of neutral and cationic palladium hydride complexes, whose characterisation is described below.

Synthesis of $[Pd(H)(X)L_2]$ and $[Pd(H)(L_3)]^+$ Complexes

Complexes $[PdCl_2L_2]$ were prepared in high yields by addition of PPh_3, PCy_3 or the diphosphane dCypb [dCypb = bis(dicyclohexylphosphanyl)butane] to the complex $[PdCl_2(PhCN)_2]$ according to the published procedures.[12,14,15] Addition of ten equivalents of the silane $HSiPh_3$ to these dichloro-, PPh_3- or PCy_3-containing compounds gave the corresponding hydrido complexes $[Pd(H)(Cl)L_2]$ (L = PPh_3 **1**, PCy_3 **2**) in 40% yields after crystallisation.[16a] For the tricyclohexylphosphane ligand, better yields can be obtained when $[Pd(PCy_3)_2]$ is synthesised by reduction of $[PdCl_2(PCy_3)_2]$. Subsequent addition of one equivalent of anhydrous HCl in diethyl ether affords **2** in 80% yield as a crystalline material.[16b] We did not succeed in preparing [Pd(H)(Cl)(dCypb)] (**3**) by reduction of one chloro ligand in $[PdCl_2(dCypb)]$ by $HSiPh_3$, since in all experiments palladium black precipitated. As our attempts with other diphosphanes also resulted in the precipitation of abundant quantities of black materials, we suspect that this absence of stability is due to the *trans*-position of the incoming hydride ligand to a phosphorus atom. However, starting from $[Pd(PCy_3)_2]$ we succeeded in the exchange of ligand dCypb, and addition in an NMR tube at 183 K of one equivalent of HCl (in Et_2O solution) produced the corresponding hydride [Pd(H)(Cl)(dCypb)] (**3**), which shows a hydride signal at $\delta = -8.0$ ppm (Table 1), a doublet of doublets due to the coupling with a phosphorus in the *trans*-position ($^2J_{^1H,^{31}P_{trans}} = 200$ Hz) and another one in the *cis*-position ($^2J_{^1H,^{31}P_{cis}} = 10$ Hz). However, we could not isolate the hydride in the solid state.

Addition of one equivalent of $SnCl_2$ to $[D_8]$THF solutions of **1** or **2** gives $[Pd(H)(SnCl_3)L_2]$ (L = PPh_3 **4**, PCy_3 **5**). As shown in Table 1, these two derivatives are characterised in their ^1H NMR spectra by a hydride signal at $\delta = -6.90$ and -8.50 ppm, respectively, flanked by two satellites due to $^2J_{^1H,^{119}Sn}$ coupling (944 Hz and 1760 Hz, respectively). The ^1H-^{31}P coupling is too small to be detected. The coupling between ^1H and ^{119}Sn was confirmed by a 2D-HMQC sequence and is shown in Figure 1.

The ^{31}P NMR spectra show a broad singlet at $\delta = 33.80$ ppm for **4** and a singlet at $\delta = 52.26$ ppm for **5** flanked by the two satellites due to the coupling with ^{119}Sn ($^2J_{^{31}P,^{119}Sn} = 138$ Hz). In these compounds, the two phosphane ligands are in mutual *trans* positions and the exchange of a Cl for an $SnCl_3$ ligand results in a decrease of nearly 6 ppm for the chemical shift of the hydride ligand



(1)

Table 1. NMR spectroscopic data for hydridopalladium $[Pd(H)(X)L_2]$ complexes.[a]

Compound	Hydridopalladium complex	^1H NMR δ	$^2J_{^1H,^{31}P}$	^{31}P NMR δ	$^2J_{^{31}P,^{119}Sn}$	^{119}Sn NMR δ	$^2J_{^1H,^{119}Sn}$
1*	*trans*-$[Pd(H)(Cl)(PPh_3)_2]$	–13.12	–	30.75			
2*	*trans*-$[Pd(H)(Cl)(PCy_3)_2]$	–14.32	3	45.63			
3	*cis*-$[Pd(H)(Cl)(dCypb)]$	–8.00	10; 200				
4	*trans*-$[Pd(H)(SnCl_3)(PPh_3)_2]$	–6.90	–	33.80	–	–	944
5	*trans*-$[Pd(H)(SnCl_3)(PCy_3)_2]$	–8.50	–	52.30	138	154	1760

[a] T = 183 K (*: T = 298 K); solvent: $[D_8]THF$; δ in ppm and J in Hz.

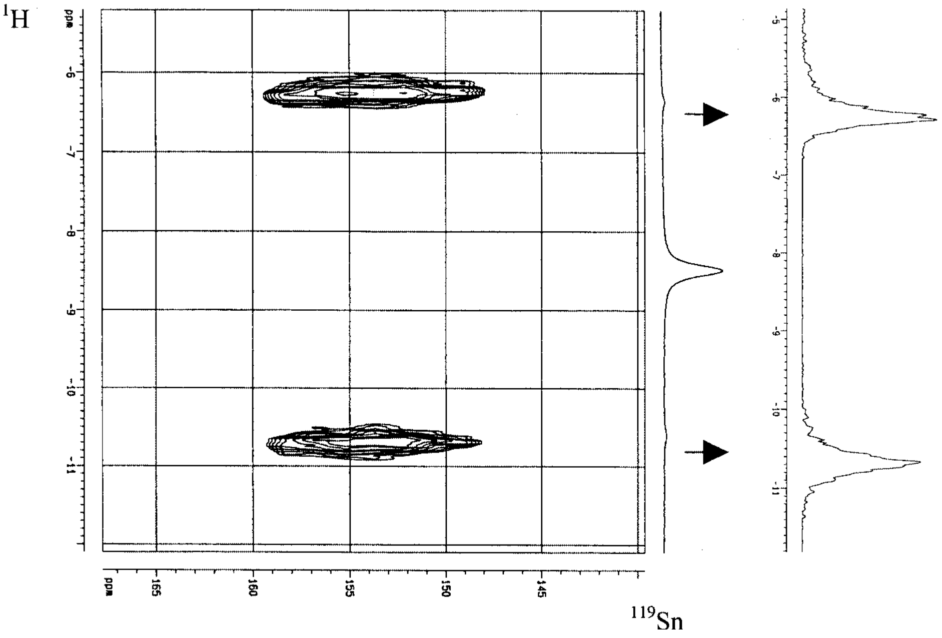


Figure 1. $\{^1H\text{-}^{119}Sn\}$ HMQC spectra of complex **5** with an expansion of the two satellite signals on the right-hand side.

(6.22 ppm between **1** and **4** and 5.82 ppm between **2** and **5**), thus showing that the addition of $SnCl_2$ has a dramatic effect. Such a shift is certainly related to significant changes and decreases in the electron density at the H ligand and thus its hydride character. Recent studies on $[Mo(H)(NO)(dmpe)_2]$ [dmpe = bis(dimethylphosphanyl)ethane] have shown that the hydridic character of the hydride ligand is largely influenced by the nitrosyl ligand in the *trans* position. As a consequence, this complex presents a high propensity to undergo hydride-transfer reactions.[17]

The ^1H NMR spectrum of complex **5** at 183 K shows the additional presence of a small amount of complex **2** (Figure 2). Increasing the temperature to 203 K leads to a large increase in the concentration of **2** due to decoordination of $SnCl_2$, complex **5** becoming the minor species. This observation does not mean that under the catalytic conditions (348–373 K, P_{CO} = 30–100 bar) only the chloro complex is operative. Indeed, the NMR spectra at room temperature (under inert atmosphere) still show the presence of **5** but a fluxional process occurs, as detected by the broadening of its hydride signal, whereas that of **2** remains sharp. We did not observe the possible intermediates, i.e. the *cis*-isomer of **5** or a pentacoordinate species arising from the coordination of $SnCl_2$ to **2**.

It is worth mentioning that addition of $SnCl_2$ to complex **3**, even at 183 K, does not result in the formation of the expected Pd-$SnCl_3$ species. The hydride signal of **3** disappears, and several unassigned signals are detected in the ^{31}P NMR spectrum. Decomposition into an orange material occurs rapidly. Table 1 lists all the NMR spectroscopic data for complexes **1**–**5**.

The synthesis of complexes containing the $Pd(H)(SnBu_3)$ core was attempted in order to introduce another Lewis acid into the coordination sphere of palladium. The synthetic procedure is to add $HSnBu_3$ directly to a palladium(0) species. In fact, $[Pd(PPh_3)_n]$ (n = 2, 3, 4 in solution) reacts sluggishly, and at room temperature gives mainly the complex $[Pd(SnBu_3)_2(PPh_3)_2]$ ($\delta_{^{31}P}$ = 34.30 ppm, $^2J_{^{31}P,^{119}Sn}$ = 113 Hz). Nevertheless, a ν(Pd–H) absorption is detected at 2046 cm^{-1} in the IR spectrum, which belongs presumably to $[Pd(H)(SnBu_3)(PPh_3)_2]$. The reaction proceeds cleanly with $[Pd(PCy_3)_2]$, $[Pd(diphos)(PCy_3)]$ [diphos = 1,2-bis(dicyclohexylphosphanyl)ethane (dCype)], 1,4-bis(dicyclohexylphosphanyl)butane or 1,6-bis(diphenylphosphanyl)hexane

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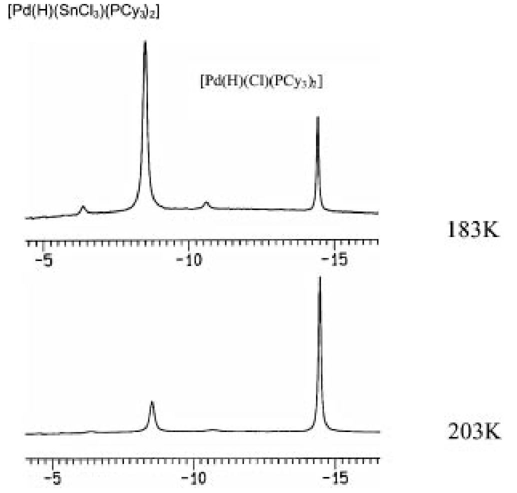

Figure 2. Evidence for a dynamic equilibrium between **2** and **4**.

(dpph) to give, according to ^{1}H and ^{31}P NMR analysis, $[Pd(H)(SnBu_3)(PCy_3)_2]$ (**6**), $[Pd(H)(SnBu_3)(dCype)]$ (**7**), $[Pd(H)(SnBu_3)(dCypb)]$ (**8**) or $[Pd(H)(SnBu_3)(dpph)]$ (**9**), respectively, in which the two hydrido and $SnBu_3$ ligands are in mutual *trans* (**6**) or *cis* (**7**–**9**) positions. Indeed, the hydride signal of **6** is at $\delta = -14.32$ ppm due to the large *trans* influence of the $SnBu_3$ ligand. For **7**–**9**, the hydride signals are at $\delta = -2.67$, -3.84 and -4.06 ppm, respectively. All NMR spectroscopic data are displayed in Table 2. Similarly, the platinum analogue $[Pt(H)(SnBu_3)(PPh_3)_2]$ (**10**) was prepared from $[Pt(PPh_3)_4]$. Here also addition of $HSnBu_3$ provides $[Pt(SnBu_3)_2(PPh_3)_2]$ directly, which was characterised by ^{31}P NMR spectroscopy ($\delta_{^{31}P} = 18.0$ ppm). However, as already described in the literature[18] for the preparation of $[Pt(H)(SnMe_3)(PPh_3)_2]$, bubbling dihydrogen through the solution allows the isolation of **10**.

Comparison between the two $SnCl_3$ and $SnBu_3$ ligands shows immediately that the *trans* influence of the tributyltin ligand is significantly stronger than that of $SnCl_3$ and is rather similar to that of the chloro ligand. The hydridic character decreases significantly when $SnCl_2$ is introduced into the coordination sphere (the chemical shift is $\delta = -8.5$ ppm for **5**, whereas it is $\delta = -14.32$ ppm for **2** and $\delta = -14.53$ ppm for **6**). When we consider complex **8**, in which the hydrido and $SnBu_3$ ligands are in mutual *cis* positions, the situation is more contrasted. Indeed, the hydride signal is found at $\delta = -3.84$ ppm, i.e. roughly 10 ppm to lower field than in **6**. Provided the steric effects are ignored, the phosphorus atom P_A in the *trans* position to $SnBu_3$ [$\delta_{^{31}P} = 27.36$ ppm (t, $J_{^{31}P,^{119}Sn} = 1402$ Hz] receives more electron density from the metal centre than the second phosphorus atom P_B *trans* to the hydride [$\delta_{^{31}P} = 43.96$ ppm (t, $^2J_{^{31}P,^1H} = 166$ Hz], which is not significantly affected by the presence of the $SnBu_3$ in the *trans* position. In the paragraph devoted to catalysis, these electronic effects will be taken into account to explain the various catalytic activities observed.

Variable-temperature ^{1}H and ^{31}P NMR studies of complex **8** (Figure 3) show that a stereochemical non-rigidity phenomenon occurs, and the square-planar complex does not lose the $SnBu_3$ ligand. The ^{1}H NMR signal at room temperature is consistent with a hydride ligand coupled to two equivalent phosphorus atoms and to tin. A fast isomerisation process makes the P_A and P_B phosphorus atoms equivalent. A similar phenomenon has recently been reported for $[Pd(H)(SiR_3)(dCype)]$.[19] In addition, sophisticated ^{1}H-^{119}Sn{^{31}P} 2D-HMQC NMR experiments unambiguously show the ^{119}Sn chemical shift at $\delta = 7.50$ ppm.

Some authors consider that the main role of adding $SnCl_2$ is to provide the $SnCl_3^-$ counterion, but this hypothesis has been essentially confirmed in platinum chemistry.[20] We prepared the cationic hydrido complexes $[Pd(H)L_3]^+$ in the presence of weakly coordinating anions such as CF_3COO^- **a**, BF_4^- **b**, and $TolSO_3^-$ **c**. Table 3 displays all the NMR spectroscopic data related to the complexes that were isolated and characterised by ^{1}H and ^{31}P NMR spectroscopy. They obey the general formula $[Pd(H)(PCy_3)L_2]^+$, except for $[Pd(H)(PCy_3)_2]^+$ (**11**), for which the hydride signal appears at $\delta = -18.8$ ppm as a triplet with a small hydride–phosphorus coupling of 3.5 Hz, consistent with a 14-electron palladium complex having the two PCy_3 ligands in *trans* positions and the hydrogen atom *cis* to each phosphorus atom.[9i–9k,21] For the 16-electron complexes $[Pd(H)(PCy_3)L_2]^+$ {L_2 = dCype **12**, [1,2-bis(diphenylphosphanyl)ethane] (dppe) **13**, [1,3-bis(diphenylphosphanyl)propane] (dppp) **14**, [1,4-bis(diphenylphosphanyl)butane] (dppb) **15**, [1,1′-bis(diphenylphosphanyl)ferrocene] (dppf) **16**}, the nature of the counterion is almost insignificant. For instance, when L_2 = dppp, $\delta_{^1H} = -6.62$ ppm with CF_3COO^- or -6.84 ppm with BF_4^-. Variation of L_2 (**13**–**16**) induces larger effects. For example, for **13a**, **14a**, **15a** and **16a** the shifts are $\delta = -5.58$, -6.62, -6.12 and -7.87 ppm, respectively. The geometry is presumably square planar, with the PCy_3 ligand being *cis* to the hydride ligand. The

Table 2. NMR spectroscopic data for the $[Pd(H)(SnBu_3)L_2]$ complexes.[a]

Compound	Hydridopalladium complex	^{1}H NMR			^{31}P NMR		^{119}Sn NMR
		δ	$^2J_{^1H,^{31}P}$	$^2J_{^1H,^{119}Sn}$	δ	$^2J_{^{31}P,^{119}Sn}$	δ
6	*trans*-$[Pd(H)(SnBu_3)(PCy_3)_2]$	–14.5	5.5	2494	48.30		
7	*cis*-$[Pd(H)(SnBu_3)(dCype)]$	–2.67	177	310	25.10, 45.20		
8*	*cis*-$[Pd(H)(SnBu_3)(dCypb)]$	–3.84	8, 166	200	27.36, 43.96	1402	7.50
9	*cis*-$[Pd(H)(SnBu_3)(dpph)]$	–4.01	200		40.70	–	–

[a] T = 298 K; solvent: C_7D_8; *: a coupling constant is observed between the two phosphorus atoms ($^2J_{^{31}P_A,^{31}P_B} = 20$ Hz).

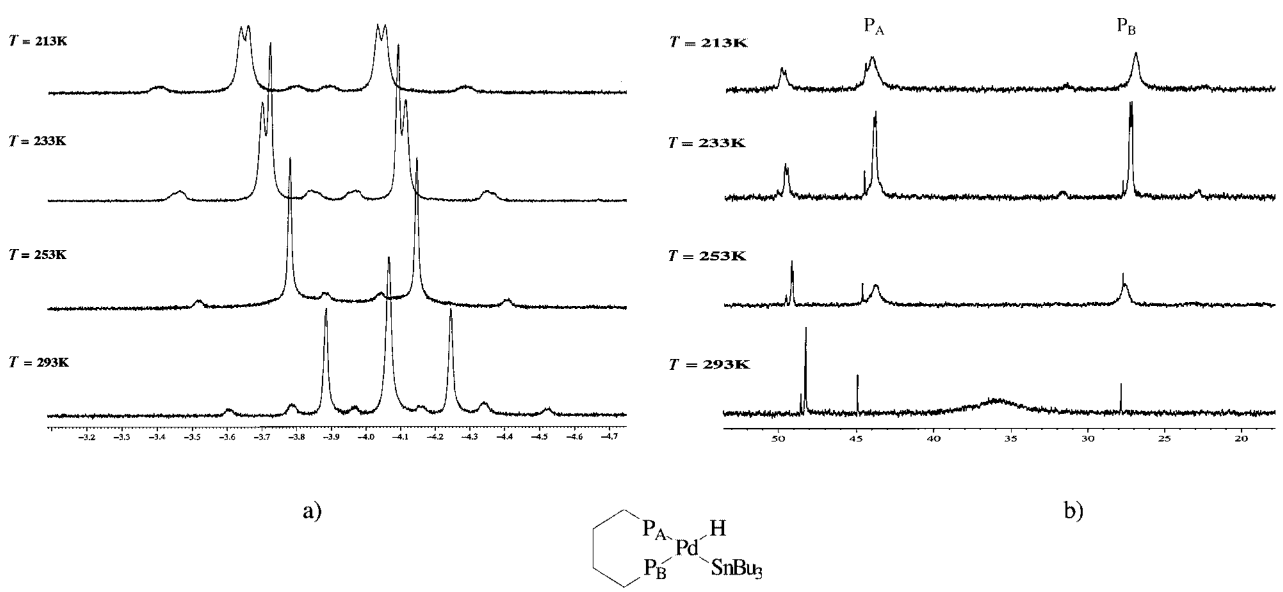

Figure 3. a) Hydride section of the variable temperature ^1H NMR spectra measured for **8**; b) Variable temperature ^{31}P NMR spectra measured for **8**.

Table 3. NMR spectroscopic data of $[Pd(H)(PCy_3)_2]^+(X)^-$ and $[Pd(H)(PCy_3)L_2]^+(X)^-$.

Complexes $[Pd(H)(PCy_3)_2]^+$	δ (^1H) [ppm][a]	$^2J_{^1H,^{31}P}$ [Hz]	δ (^{31}P) [ppm]	$^2J_{^{31}P,^{31}P}$ [Hz]
11a	–18.20	3.5	39.40	–
11b	–18.84	3.7	–	–
11c	–18.71	–	45.7	–
$[Pd(H)(PCy_3)(L_2)]^+(X)^-$				
12a	–6.29	7, 13, 179	86.95, 65.43, 49.68	311, 18, 18
12b	–6.15*	–	–	–
12c	–6.12	9, 12, 177	–	–
13a	–5.58	20, 196	–	–
14a	–6.62	28, 189	51.18, 9.16, 3.58	306, 48, 22
14b	–6.90	12, 75	49.87, 7.66, 3.97	315, 51, 21
15a	–6.12	13, 185	–	–
16a	–7.87	10, 179	52.57, 24.94, 20.15	337, 31, 27

[a] T = 298 K; *: broad signal due to exchange phenomena at room temperature.

diphos ligand shows two phosphorus atoms in different magnetic environments, giving rise to an AMX system (Table 3).

Catalytic Activity in Carbonylation of Isopulegol

The catalytic activity of $[Pd(H)(SnCl_3)(PPh_3)_2]$ {formed from $[Pd(H)(Cl)(PPh_3)_2]$ by addition of an excess of $SnCl_2$ in situ with a P/Pd ratio of 4} was examined in the cyclocarbonylation of isopulegol in toluene, exclusively with CO as a reactant (**A** giving **C** in Scheme 1). Conversion of the substrate is 100% within 16 h at 60 °C (see Table 4, run R1). One more experiment was carried out at the same pressure but at lower temperature (40 °C, run R2): the yield was 62%. The effect of the temperature appears to be prominent, since when the pressure was decreased from 30 bar to 20 bar and even 10 bar the yields were not affected (compare runs R1, R3 and R4 at 60 °C).

Table 4. Catalytic activity for cyclocarbonylation of isopulegol in the presence of $[Pd(H)(Cl)L_2/SnCl_2/L]$.

Test	t [h]	P_{CO} [bar]	T [°C]	Yield [%]	(5*R*)-C [%]	(5*S*)-C [%]	*de*[a] [%]
R1	16	30	60	100	60	40	20
R2	16	30	40	62	35	27	13
R3	40	20	60	100	60	40	20
R4	16	10	60	100	66	44	22
R5	68	10	50	68	45	23	22
R6[b]	16	10	60	100	78	22	56

[a] $de = \{R(\%) - S(\%)\}/\{R(\%) + S(\%)\}$. [b] dppb was used as ligand.

The two diastereomers of lactone **C** were obtained in a nearly 60:40 proportion (runs R1, R3 and R4**)**. In fact, as noted by Knifton in his early studies, the promoting role of the $SnCl_2$ co-catalyst is essentially to increase the regioselectivity of the alkoxycarbonylation of the terminal alkene into the corresponding linear ester.[7] In the present case, the re-

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action with [Pd(H)(Cl)(PPh_3)$_2$] is slower and less diastereoselective.[11] Increasing the electron density on palladium by substituting the PPh_3 ligands with PCy_3 results in the complete absence of reactivity under the same reaction conditions irrespective of whether the complex is prepared and isolated or generated in situ. Formation of [Pd(H)($SnCl_3$)(dppb)] from [Pd(H)(Cl)(PPh_3)$_2$] (**1**), dppb and $SnCl_2$ leads to lower reaction rates but improved diastereomeric ratios (78:22). On the contrary, producing the cationic hydrido precursor **15a** by direct addition of CF_3COOH to [Pd(PCy_3)(dppb)] gives a poor yield of **C** (17%). Similarly, $[Pd(H)(PCy_3)(dppf)]^+[CF_3COO]^-$ (**16a**) leads to a 21% yield. All the other prepared cationic complexes were examined in the carbonylation of isopulegol: the results are similarly deceiving.

Moreover, the effect of the introduction of $SnBu_3$ in the coordination sphere of palladium was analysed. In the presence of [Pd(H)($SnBu_3$)(PPh_3)$_2$], prepared in situ by addition of $HSnBu_3$ to [Pd(PPh_3)$_n$], or *cis*-[Pd(H)($SnBu_3$)(dCypb)], the carbonylation reaction gives only traces of lactone. The important difference in the chemical shift – δ = –14.50 ppm for **6** and δ = –8.50 ppm for **5** – is presumably related to the significant differences in reactivity of the two complexes. Indeed, **6** presents a high hydridic character and its intrasphere nucleophilic attack of the olefin should be easy, this transfer producing the alkyl species, but the coordination of the olefin to the metal centre is presumably retarded. Moreover, we cannot exclude that in the subsequent step the CO migratory insertion could be disfavoured due to the steric hindrance of $SnBu_3$ and/or the electronic effects on palladium.

Mechanistic Proposal

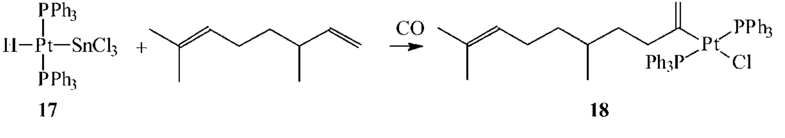
Characterisation of an Acylplatinum Species

Platinum complexes are often used to mimic the reactivity of palladium because they are less labile and they lead to more stable pentacoordinate species. The complex *trans*-[Pt(H)($SnCl_3$)(PPh_3)$_2$] (**17**) was therefore prepared from *cis*-[$PtCl_2$(PPh_3)$_2$][22] and treated with dihydromyrcene at 100 °C under a CO pressure of 40 bar. Microcrystalline material precipitated at the end of the reaction. After separation and dissolution of the solid, analysis by multinuclear NMR showed that its structure corresponds to the square-planar acyl complex *trans*-[PtCl{C(O)$CH_2CH_2CH(CH_3)$-$CH_2CH_2CHC(CH_3)_2$}(PPh_3)$_2$] (**18**), as shown in Equation (2).

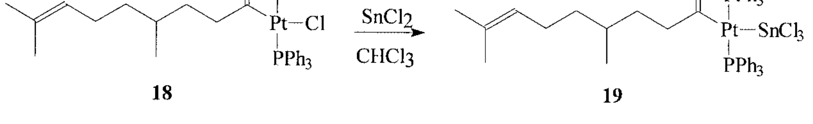
A signal with two satellites is observed in the ^{31}P NMR spectrum at δ = 23.18 ppm due to the coupling with ^{195}Pt ($^1J_{^{31}P,^{195}Pt}$ = 3186 Hz), and a triplet is observed for the ^{195}Pt signal at δ = –3933 ppm due to the coupling with two equivalent phosphorus atoms. Furthermore, in the ^{13}C NMR spectrum the acyl carbon atom appears as a triplet at δ = 219.45 ppm ($^2J_{^{31}P,^{13}C}$ = 6 Hz) flanked by satellites with $^1J_{^{195}Pt,^{13}C}$ = 458 Hz. A similarly high chemical shift value of δ = 243.9 ppm has been found for the C(O)Me carbon in the anionic acylplatinum(II) complex [Li][(η^2-Tp′)Pt(CO-Me)(Me)] [Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate].[23]

Thus, under a CO atmosphere the platinum complex that separates from the medium as a solid contains the acyl moiety *trans* to the chloro atom. We supposed that, in fact, the formation of the $SnCl_3$ ligand is reversible, so we decided to add one equivalent of $SnCl_2$ to the acyl chloro complex. All the analyses show that we unambiguously produced the acylplatinum $SnCl_3$ complex *trans*-[Pt($SnCl_3$){C(O)-$CH_2CH_2CH(CH_3)CH_2CH_2CHC(CH_3)_2$}($PPh_3$)$_2$] (**19**), as given by Equation (3).

The ^{31}P NMR spectrum of this complex shows that the two phosphane ligands are equivalent and give a signal, with two satellites, at δ = 18.95 ppm ($^1J_{^{195}Pt,^{31}P}$ = 3186 Hz). The ^{195}Pt NMR signal at δ = –4466 ppm is a triplet due to the coupling with the two equivalent phosphorus atoms. The ^{119}Sn NMR spectrum contains a signal at δ = 55.61 ppm (t) with a ^{31}P-^{119}Sn coupling constant of 296 Hz that we obtained from ^{31}P-^{119}Sn INEPTND and ^{31}P-^{119}Sn HMQC experiments. Finally, the ^{13}C NMR spectrum presents an acyl signal at δ = 224.80 ppm (t), with $^2J_{^{13}C,^{31}P}$ = 5 Hz, the $^2J_{^{13}C,^{195}Pt}$ coupling constant being difficult to determine due to the low signal-to-noise ratio.

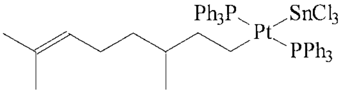


(2)



(3)

Observations by ^{1}H NMR carried out over a period of several days showed that the acyl complex **19** evolves toward the starting complex [Pt(H)(SnCl$_3$)(PPh$_3$)$_2$] (**17**). Dihydromyrcene was also unambiguously detected. Thus, we can deduce that the equilibrium between these two complexes involves the intermediate alkyl species **20** shown in Figure 4. Indeed, decarbonylation of complex **19** would give **20**, which produces the pentacoordinate species [Pt(H)(SnCl$_3$)(dihydromyrcene)(PPh$_3$)$_2$] by β-elimination. This latter complex would give **17** by loss of dihydromyrcene.



20

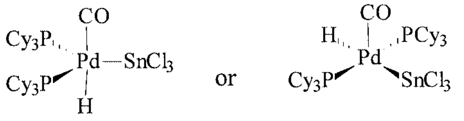
Figure 4. Alkylplatinum species **19** resulting from the addition of dihydromyrcene.

In situ Characterisation of Palladium Species under CO Pressure

Zudin and al.[24] have previously shown that the cationic hydridopalladium complex [Pd(H)(PPh$_3$)$_3$]$^+$[CF$_3$COO]$^-$, prepared in situ, reacts with CO to afford the dinuclear complex [Pd$_2$(μ-H)(μ-CO)(PPh$_3$)$_4$]$^+$[CF$_3$COO]$^-$ in which the hydrido and carbonyl ligands occupy the two bridging positions. A similar monocationic dinuclear complex has been prepared with the diphosphane ligand 1,3-bis[di(isopropyl)-phosphanyl]propane.[25] Moreover, Elsevier and Tóth started from the mononuclear neutral acyl complex [Pd(Cl)(COMe)(bdppp)] [bdppp is (2*S*,4*S*)-2,4-bis(diphenylphosphanyl)pentane] and observed that a methanolysis reaction occurs under a CO atmosphere to provide the elusive intermediate [Pd(H)(Cl)(bdppp)], which leads to a mixture of [PdCl$_2$(bdppp)] and [Pd$_2$(μ-H)(μ-CO)(bdppp)$_2$]$^+$-[Cl]$^-$.[26]

Introduction of SnCl$_2$ into the Palladium Hydride Coordination Sphere

[Pd(H)(SnCl$_3$)(PCy$_3$)$_2$] (**5**), prepared in situ in an NMR tube by addition of one equivalent of SnCl$_2$ to [Pd(H)(Cl)(PCy$_3$)$_2$] (**2**), was pressurised with 3 bar ^{13}CO. The ^{1}H NMR spectra present a broad signal at δ = –8.70 ppm and even at 183 K no ^{1}H-^{31}P nor ^{1}H-^{119}Sn coupling constants could be determined due to an exchange phenomenon. However, the ^{13}C NMR spectra clearly reveal a triplet at δ = 232.4 ppm with a $^2J_{^{13}\mathrm{C},^{31}\mathrm{P}}$ coupling constant of 3.7 Hz, the CO ligand thus being *cis* to two equivalent phosphorus atoms. The same spectra also show two satellites due to ^{13}C-^{119}Sn coupling (^2J = 144.6 Hz), such a value being in agreement with a mutual *cis* arrangement of the CO and SnCl$_3$ ligands. In the ^{31}P NMR spectrum, a signal is detected at δ = 50.80 ppm with two satellites due to a small coupling with ^{119}Sn (^2J = 148 Hz), consistent with the SnCl$_3$ ligand being *cis* with regard to the two equivalent phosphorus atoms. Thus, we can assign to this pentacoordinate species either the trigonal bipyramid geometry **21a** or the square-planar pyramid structure **21b** represented in Figure 5.

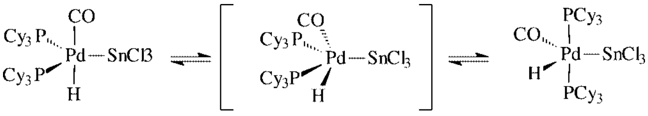


21a **21b**

Figure 5. Two possible geometries for the pentacoordinate species [Pd(H)(SnCl$_3$)(CO)(PCy$_3$)$_2$] (**21a**) and **21b**.

The hydrido and carbonyl ligands in **21a** occupy the axial positions of the tbp geometry. Although such pentacoordinate hydrido species have already been proposed in the literature,[27] no such characterisation has been reported in palladium chemistry. However, it is worth mentioning that a palladium atom with five ligands in tbp or sp environments is known for [Pd(CH$_2$CMe$_2$-*o*-C$_6$H$_4$)-(PMe$_3$)$_2$(SO$_2$)],[28] or for a cationic palladium complex containing a triphosphane ligand and an imine ligand in the *o*-position of an aryl group.[29a]

Although we did not reach the slow exchange limit for complex **21a**, we suggest that a Berry pseudo-rotation mechanism occurs in solution which exchanges the axial and equatorial ligands. In this way the dynamic equilibrium shown in Figure 6 should occur. In this case, the second tbp isomer contains the CO and SnCl$_3$ ligands in mutual *cis* positions with regard to the two PCy$_3$ ligands (Figure 6).



21a **21a'**

Figure 6. Axial–equatorial ligand exchange in [Pd(H)(SnCl$_3$)(CO)(PCy$_3$)$_2$] (**21a**).

In addition to these observations, we detected a weak signal in the ^{1}H NMR spectrum at δ = –14.5 ppm corresponding to a weak signal in the ^{13}C NMR spectrum at δ = 194.6 ppm. Such a value for the hydride ligand recalls the shift of [Pd(H)(Cl)(PCy$_3$)$_2$] (**2**) ($\delta_{^1\mathrm{H}}$ = –14.32 ppm) and we suggest that these signals should correspond to the species [Pd(H)(CO)(Cl)(PCy$_3$)$_2$] (**22**) (**21**/**22** = 65:35). As we previously observed (see above) the equilibrium between [Pd(H)(SnCl$_3$)(PCy$_3$)$_2$] (**5**) and [Pd(H)(Cl)(PCy$_3$)$_2$] (**2**) + SnCl$_2$, and since removing SnCl$_2$ from a pentacoordinate species is rather uncommon, we propose that the complex [Pd(H)(Cl)(CO)(PCy$_3$)$_2$] (**22**) results from the direct coordination of a CO ligand to the square-planar complex [Pd(H)(Cl)(PCy$_3$)$_2$] (**2**).

NMR Monitoring of the Reactivity of the Substrate with [Pd(H)(SnCl$_3$)(PCy$_3$)$_2$] (5)

We carried out the same type of experiments, maintaining the same temperature and concentrations, but now four equivalents of dihydromyrcene were added and the ^{13}CO/^{12}CO pressure was increased to 10 bar. In less than one hour, still at 183 K, the main hydride peak at δ =

–8.7 ppm and the weak signal at δ = –14.5 ppm disappeared, presumably due to the formation of the corresponding alkyl species. In the ^{13}C NMR spectrum two CO signals were detected at δ = 232.6 ppm (complex **23**) and δ = 194.7 ppm (complex **24**) as two triplets with relative intensities of 70:30 and $^2J_{^{13}C,^{31}P}$ coupling constants of 4.5 and 3.2 Hz, respectively; this ratio was found to be 75:25 for the hydride signals of [Pd(H)(SnCl$_3$)(PCy$_3$)$_2$] (**5**) and [Pd(H)(Cl)(PCy$_3$)$_2$] (**2**) in the ^{1}H NMR spectrum. The proximity of the two chemical shifts and the coupling constants for **21a** and **23** led us to propose that we observe the pentacoordinate species in which CO is coordinated as shown in Figure 7. Similarly, we propose that **24**, with the chloro ligand, is characterised by the shift at δ = 194.7 ppm. Pentacoordinated platinum species have previously been described in which the coordination sphere contains the diphosphane dppe, CO, methyl and methoxy ligands.[29b]

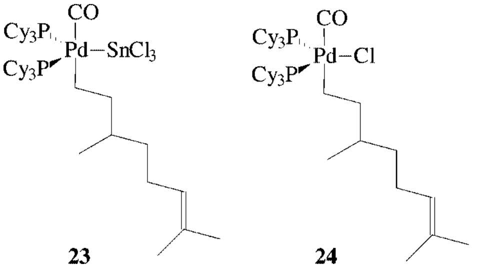


Figure 7. Representation of the two pentacoordinate acyl species **23** and **24** observed under CO pressure in HP/NMR spectroscopy.

The CO migratory insertion is presumably the rate-determining step, since at 183 K the coordination of the alkene followed by the hydride transfer are relatively fast steps. Such an observation parallels the reactivity of [Pd(H)(SnCl$_3$)(PPh$_3$)$_2$] (**4**) in catalytic tests, since at 40 °C and 30 bar the conversion rate is near to 60% in 16 h, whereas at 60 °C and even at 10 bar the reaction reaches completion overnight (see Table 4).

Conclusions

In this paper, the identification of various neutral, cationic, square-planar and pentacoordinate (under CO pressure) hydridopalladium complexes has been described. It appears that the co-catalyst role of SnCl$_2$ is crucial because it produces an active palladium–SnCl$_3$ species. Preparation of [Pd(H)(SnCl$_3$)(PPh$_3$)$_2$], as shown by multinuclear NMR spectroscopy, leads to an active complex which catalyses the alkoxycarbonylation reaction of an alkene efficiently. Thus, we propose a catalytic cycle exclusively based on the hydride route, with the two L phosphorus ligands in *trans* positions (Figure 8).

Recent studies reported by van Leeuwen and Heaton[30] are consistent with the coordination of methanol to explain the last step of the alcoholysis, provided the two phosphane

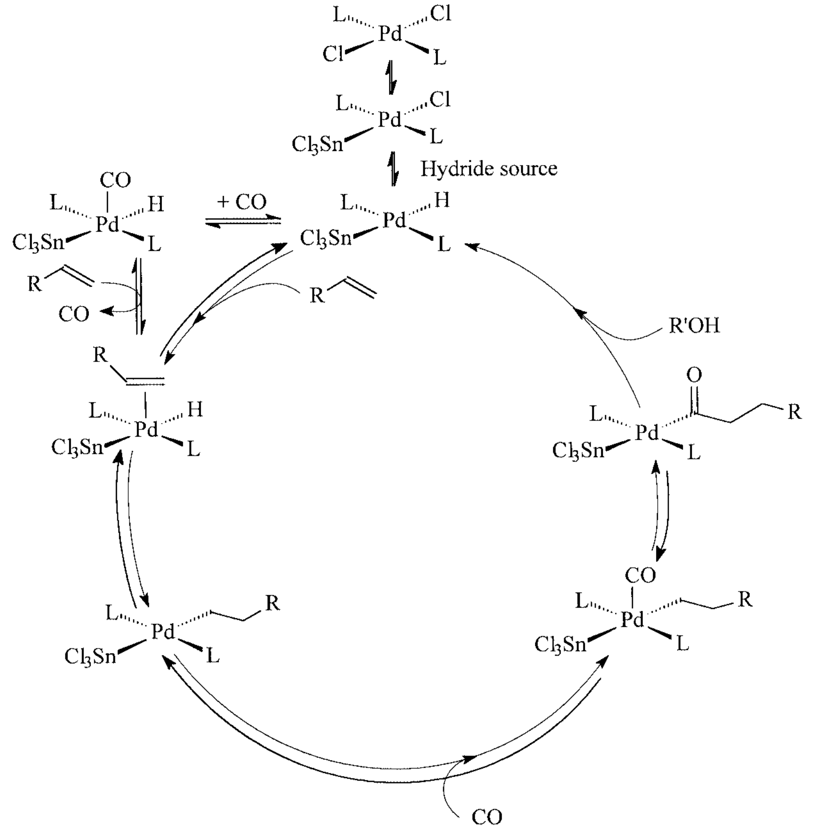


Figure 8. Proposed hydridopalladium route for alkoxycarbonylation reaction.

ligands are mutually *cis*. Our preliminary observations that isomerisation occurs for the monophosphane ligands prompted us to explore and investigate the final step of the catalytic reaction in the present system.

Experimental Section

General Considerations: All reactions and manipulations were carried out in dried and distilled solvents under argon using standard Schlenk techniques. All NMR measurements were performed on Bruker AM250, AMX400 or DRX400 spectrometers using 5-mm triple resonance inverse probes with a dedicated ^{31}P channel. All chemical shifts for ^{1}H and ^{13}C are relative to TMS using ^{1}H (residual) or ^{13}C chemical shifts of the solvent as a secondary standard. The chemical shifts were referenced to external H_3PO_4 (85%) for ^{31}P, $SnMe_4$ for ^{119}Sn and H_2PtCl_6 for ^{195}Pt. High-pressure NMR experiments in situ were carried out in special sapphire tubes with a diameter of 10 mm (for more details concerning the setup and procedure see ref.[31]). IR spectra were recorded on a Perkin–Elmer 1710 FT-IR spectrophotometer. Gas chromatography analyses were performed on a Perkin–Elmer instrument equipped with a DB-5GC column (30 m × 0.25 mm × 0.25 µm) and a flame ionisation detector. Mass spectrometric measurements were performed at the Service de Spectrométrie de Masse de l'Université Paul Sabatier on a NERMAG R 10-10 apparatus for organometallic compounds and on a Perkin–Elmer TURBO MASS instrument equipped with a DB-5MS 30 m × 0.25 mm × 0.25 µm column for organic products. Elemental analysis (C,H,O) was performed at the Ecole Nationale Supérieure des Ingénieurs en Arts Chimiques et Technologiques de Toulouse. Several compounds are unstable, so mass spectrometry or elemental analyses were not always possible.

All the chemical products were purchased from Aldrich Chemical Co., except for the following complexes, which were prepared by the methods reported in the literature: $[PdCl_2(PhCN)_2]$,[15] *cis*-$[PdCl_2(dppb)]$,[12,15] *cis*-$[PdCl_2(dCypb)]$,[12,15] *trans*-$[Pt(H)(SnBu_3)(PPh_3)_2]$ (**6**),[18] *cis*-$[PtCl_2(PPh_3)_2]$,[22] *trans*-$[Pt(H)(SnCl_3)(PPh_3)_2]$ (**17**),[22] *trans*-$[PdCl_2(PPh_3)_2]$,[14] *trans*-$[PdCl_2(PCy_3)_2]$,[12,32] $[Pd(PPh_3)_n]$,[14] $[Pd(PCy_3)_2]$.[32] ^{12}CO and ^{13}CO (99%) were purchased from Air Liquide.

Catalytic Tests: A mixture of triphenylphosphane (0.4 mmol) and tin(II) chloride (0.5 mmol) was introduced into a 150 mL stainless steel autoclave with magnetic stirring. A nitrogen-saturated mixture of palladium complex [chlorobis(triphenylphosphanyl)palladium(II) hydride or dichlorobis(triphenylphosphanyl)palladium (0.2 mmol)] and isopulegol (10 mmol) in toluene (10 mL) was introduced into the evacuated autoclave by aspiration. It was heated (40–60 °C) under pressure (10–30 bar) of carbon monoxide. After 16 h, the autoclave was cooled and then slowly depressurized. The obtained solution was analysed by gas chromatography.

Synthesis of $[Pd(H)(Cl)L_2]$ (L = PPh$_3$ 1; PCy$_3$ 2): A 100 mL benzene solution of $[PdCl_2L_2]$ (0.57 mmol) and $HSiPh_3$ (11.44 mmol) was heated at 70–80 °C for 2 h. The resultant red solution was concentrated to ca. 30 mL, and addition of hexane afforded a powder of *trans*-$[Pd(H)(Cl)L_2]$ which was dissolved in benzene and precipitated with hexane three times; the final product was white and was isolated in 40% yield.

Alternative Method for the Synthesis of 2: A pale-green solution of $[Pd(PCy_3)_2]$ (1 mmol) in 10 mL of toluene was slowly treated with one equivalent of 2 M HCl in diethyl ether solution at room temperature. The resultant pale-yellow solution was evaporated under reduced pressure. The obtained solid was washed three times with diethyl ether; the final product was pale yellow and was isolated in 80% yield.

$[Pd(H)(Cl)(PPh_3)_2]$ (1): IR: ν(Pd–H) = 2050 cm^{-1}. ^{1}H NMR (250 MHz, 293 K, CDCl$_3$): δ = –13.12 ppm. ^{31}P NMR (250 MHz, 293 K, CDCl$_3$): δ = 30.75 ppm.

$[Pd(H)(Cl)(PCy_3)_2]$ (2): IR: ν(Pd–H) = 2046 cm^{-1}. ^{1}H NMR (250 MHz, 293 K, CDCl$_3$): δ = –14.32 ppm. ^{31}P NMR (250 MHz, 293 K, CDCl$_3$): δ = 46.63 ppm.

Preparation of [Pd(H)(Cl)(dCypb)] (3): A solution of $[Pd(PCy_3)_2]$ (0.1 mmol) in 1 mL of [D$_8$]THF was treated with 0.1 mmol of 1,4-bis(dicyclohexylphosphanyl)butane at room temperature. After 1 h, one equivalent of HCl (in Et$_2$O solution) was added and the solution was stirred for 1 h at 183 K. Then, ^{1}H NMR spectra were recorded, and revealed the presence of [Pd(H)(Cl)(dCypb)] (**3**) along with small amounts of $[Pd(H)(Cl)(PCy_3)_2]$ (**2**) and traces of unidentified hydridopalladium complexes. ^{1}H NMR (400.13 MHz, 183 K): δ = –8.0 ppm ($^{2}J_{^{1}H,^{31}P}$ = 10 and 200 Hz). From the integration of the ^{1}H signals, the yield of **3** was estimated to be 40%.

Preparation of $[Pd(H)(SnCl_3)L_2]$ (L = PPh$_3$, 4; PCy$_3$, 5): A solution of $[Pd(H)(Cl)L_2]$ (0.1 mmol) in 1 mL of [D$_8$]THF was treated with one equivalent of anhydrous SnCl$_2$ at 183 K for 2 h, and the ^{1}H, ^{31}P and ^{119}Sn NMR spectra were recorded; the spectra indicated the presence of a mixture of $[Pd(H)(SnCl_3)L_2]$ and $[Pd(H)(Cl)L_2]$ with relative intensities **1**/**4** = 20:80 and **2**/**5** = 75:25.

$[Pd(H)(SnCl_3)(PPh_3)_2]$ (4): ^{1}H NMR (400.13 MHz, 183 K): δ = –6.90 ppm ($^{2}J_{^{1}H,^{119}Sn}$ = 944 Hz). ^{31}P{^{1}H} NMR (161.98 MHz, 183 K): δ = 33.80 ppm.

$[Pd(H)(SnCl_3)(PCy_3)_2]$ (5): ^{1}H NMR (400.13 MHz, 183 K): δ = –8.50 ppm. ^{31}P{^{1}H} NMR (161.98 MHz, 183 K): δ = 52.3 ppm ($^{2}J_{^{31}P,^{119}Sn}$ = 138.1 Hz). ^{1}H-^{119}Sn HMQC NMR (400.13 MHz, 149.21 MHz, 183 K): δ = 154 ppm ($^{2}J_{^{1}H,^{119}Sn}$ = 1760 Hz).

Synthesis of $[Pd(H)(SnBu_3)(dCypb)]$ (8): A solution of $[Pd(PCy_3)_2]$ (0.2 mmol) in 5 mL of toluene was treated with 0.2 mmol of 1,4-bis(dicyclohexylphosphanyl)butane at room temperature. After 1 h, one equivalent of tri(*n*-butyl)tin hydride was added and the solution was stirred for 1 h. Then, the solvent was removed under reduced pressure and the remaining solid with 75% yield was dissolved in C$_7$D$_8$ for characterisation by NMR spectroscopy. ^{1}H NMR (400.13 MHz, 213 K): δ = –3.84 ppm ($^{2}J_{^{1}H,^{31}P_{cis}}$ = 8.4, $^{2}J_{^{1}H,^{31}P_{trans}}$ = 165.9, $^{2}J_{^{1}H,^{119}Sn}$ = 110 Hz). ^{1}H-^{119}Sn {^{31}P} HMQC NMR (400.13 MHz, 149.22 MHz, 253 K): δ = 7.50 ppm. ^{31}P{^{1}H} NMR (161.99 MHz, 233 K): δ = 27.36 ppm ($^{31}P_A$, $^{2}J_{^{31}P_A,^{119}Sn}$ = 1402 Hz), 43.96 ($^{31}P_B$, $^{2}J_{^{31}P_B,^{119}Sn} < 20$ Hz).

Identification of Neutral and Cationic Complexes: A similar procedure to the preceding one was adopted. A solution of $[Pd(PCy_3)_2]$ (0.1 mmol) in 2 mL of [D$_8$]toluene was treated with 0.1 mmol of ligand L (L = dCype, dppe, dppp, dCypb, dppb, dpph, dppf) at room temperature. After 1 h, one equivalent of HX (HX = HSnBu$_3$, CF$_3$COOH, HBF$_4$, TolSO$_3$H) was added and the solution was stirred for 1 h. The solution was filtered and transferred to a 5-mm NMR tube for NMR measurements. Only the most relevant shifts are given below. In addition, after removal of the solvent, the resulting solids were tested in cyclocarbonylation reaction.

$[Pd(H)(SnBu_3)(PCy_3)_2]$ (6): ^{1}H NMR: δ = –14.5 ppm ($^{2}J_{^{1}H,^{31}P}$ = 5.5, ($^{2}J_{^{1}H,^{119}Sn}$ = 2494 Hz). ^{31}P NMR: δ = 48.30 ppm.

$[Pd(H)(SnBu_3)(dCype)]$ (7): ^{1}H NMR: δ = –2.67 ppm ($^{2}J_{^{1}H,^{119}Sn}$ = 310, $^{2}J_{^{1}H,^{31}P_{trans}}$ = 177 Hz). ^{31}P NMR: δ = 25.10 ppm, 45.20 ($^{2}J_{^{1}H,^{31}P_{trans}}$ = 200 Hz), 40.70.

[Pd(H)(SnBu$_3$)(dpph)] (9): ^{1}H NMR: δ = –4.01 ppm (exchange phenomena at room temperature).

[Pd(H)(PCy$_3$)(dCype)]$^+$(CF$_3$COO)$^-$ (12a): ^{1}H NMR: δ = –6.29 ppm ($^2J_{^1\text{H},^{31}\text{P}}$ = 7, 13, 179 Hz). ^{31}P NMR: δ = 86.95, 65.43, 49.68 ppm ($^2J_{^{31}\text{P},^{31}\text{P}}$ = 18, 311 and 18 Hz).

[Pd(H)(PCy$_3$)(dCype)]$^+$(BF$_4$)$^-$ (12b): ^{1}H NMR: δ = –6.15 ppm. (exchange phenomena at room temperature).

[Pd(H)(PCy$_3$)(dCype)]$^+$(TolSO$_3$)$^-$ (12c): ^{1}H NMR: δ = –6.12 ppm ($^2J_{^1\text{H},^{31}\text{P}}$ = 9, 12 and 177 Hz).

[Pd(H)(PCy$_3$)(dppe)]$^+$(CF$_3$COO)$^-$ (13a): ^{1}H NMR: δ = –5.58 ppm ($^2J_{^1\text{H},^{31}\text{P}}$ = 20, 196 Hz.

[Pd(H)(PCy$_3$)(dppp)]$^+$(CF$_3$COO)$^-$ (14a): ^{1}H NMR: δ = –6.62 ppm ($^2J_{^1\text{H},^{31}\text{P}}$ = 28, 189 Hz). ^{31}P NMR: δ = 51.18, 9.16, 3.58 ppm $^2J_{^{31}\text{P},^{31}\text{P}}$ = 306, 48 and 22 Hz).

[Pd(H)(PCy$_3$)(dppp)]$^+$(BF$_4$)$^-$ (14b): ^{1}H NMR: δ = –6.90 ppm ($^2J_{^1\text{H},^{31}\text{P}}$ = 12, 75 Hz). ^{31}P NMR: δ = 49.87, 7.66, 3.97 ppm ($^2J_{^{31}\text{P},^{31}\text{P}}$ = 315, 51 and 21 Hz).

[Pd(H)(PCy$_3$)(dppb)]$^+$(CF$_3$COO)$^-$ (15a): ^{1}H NMR: δ = –6.12 ppm ($^2J_{^1\text{H},^{31}\text{P}}$ = 13, 185 Hz).

[Pd(H)(PCy$_3$)(dppf)]$^+$(CF$_3$COO)$^-$ (16a): ^{1}H NMR: δ = –7.87 ppm ($^2J_{^1\text{H},^{31}\text{P}}$ = 10, 179 Hz). ^{31}P NMR: δ = 52.57, 24.94, 20.15 ppm ($^2J_{^{31}\text{P},^{31}\text{P}}$ = 337, 27, 31 Hz). FAB$^+$/MS: *m*/*z* = 941.3; mode FAB$^-$/MS: *m*/*z* = 113.1.

Synthesis of [(CH$_3$)$_2$C=CH(CH$_2$)$_2$CH(CH$_3$)CH$_2$CH$_2$C(O)-PtCl(PPh$_3$)$_2$] (18): Complexes **18** and **19** were prepared according to the methods previously reported by Gómez et al.[27] A mixture of *trans*-[Pt(H)(Cl)(PPh$_3$)$_2$] (0.473 g, 0.5 mmol), PPh$_3$ (0.118 g, 0.45 mmol), dihydromyrcene (6.90 g, 50.0 mmol) and ethanol (25 mL) was charged in an autoclave. The autoclave was purged of air under reduced pressure and was then pressurised with 50 bar of CO, heated to 100 °C and stirred for 4 h. Then, the reactor was cooled to room temperature and depressurised. The resulting green solution was cooled to –30 °C to give **18** as a white solid, which was washed three times with cool ethanol, diethyl ether and finally dried under vacuo. Yield: 55%.

18: ^{31}P{^{1}H} NMR (161.98 MHz, CDCl$_3$, 298 K): δ = 23.2 ppm ($^2J_{^{31}\text{P},^{195}\text{Pt}}$ = 3510.7 Hz). ^{195}Pt{^{1}H} NMR (85.68 MHz, CDCl$_3$, 298 K): δ = –3933 ppm. ^{13}C{^{1}H}bb+{^{31}P} NMR (100.63 MHz, CDCl$_3$, 298 K): δ = 219.4 ($^2J_{^{13}\text{C},^{31}\text{P}}$ = 6, $^1J_{^{13}\text{C},^{195}\text{Pt}}$ = 457.8 Hz), 135.4, 134.5, 131.3, 131.3, 130.8, 125.4, 57.1, 37.4, 32.1, 31.4, 26.2, 25.9, 19.5, 15.7 ppm.

Synthesis of [(CH$_3$)$_2$C=CH(CH$_2$)$_2$CH(CH$_3$)CH$_2$CH$_2$C(O)-Pt(SnCl$_3$)(PPh$_3$)$_2$] (19): A mixture of complex **18** (0.0922 g, 0.10 mmol), SnCl$_2$ (0.019 g, 0.1 mmol) and CHCl$_3$ (2 mL) was placed in a Schlenk tube and stirred for 15 min at room temperature. The solution was filtered and multinuclear NMR analysis was carried out. After removal of the solvent **19** was obtained as a yellow compound in 50% yield. ^{31}P-^{119}Pt HMQCND {^{1}H}bb NMR (161.98 MHz, 85.63 MHz, CDCl$_3$, 233 K) and ^{31}P{^{1}H} NMR (161.98 MHz, CDCl$_3$, 233 K): δ = 18.9 ppm ($^2J_{^{31}\text{P},^{119}\text{Sn}}$ = 296 Hz). ^{31}P-^{119}Sn INEPTND {^{1}H}bb NMR: δ = 55.6 ppm. ^{31}P-^{195}Pt HMQCND {^{1}H}bb NMR, ^{195}Pt{^{1}H,^{31}P} NMR (85.68 MHz, CDCl$_3$, 233 K) and ^{31}P-^{195}Pt INEPTND {^{1}H}bb NMR: δ = –4466 ppm ($^1J_{^{195}\text{Pt},^{31}\text{P}}$ = 3185.6 Hz). ^{13}C NMR: δ = 224.8, 135.1, 134.2, 132.5, 132.2, 129.9, 125.1, 37.3, 32.0, 30.5, 26.6, 25.7, 18.5, 15.1 ppm.

Observation of Mixtures of [Pd(H)(^{13}CO)(SnCl$_3$)(PCy$_3$)$_2$] (21) and [Pd(H)(^{13}CO)(Cl)(PCy$_3$)$_2$] (22): A solution of [Pd(H)(Cl)L$_2$] (0.1 mmol) in 2 mL of [D$_8$]THF was treated with one equivalent of anhydrous SnCl$_2$ at 183 K. After 2 h, this solution was transferred to a sapphire tube and the solution was charged with 3 bar of ^{13}CO at the same temperature. The ^{1}H, ^{31}P and ^{13}C spectra indicated the presence of [Pd(H)(^{13}CO)(SnCl$_3$)(PCy$_3$)$_2$] (**21**; 65%) and [Pd(H)(^{13}CO)(Cl)(PCy$_3$)$_2$] (**22**; 35%).

[Pd(H)(^{13}CO)(SnCl$_3$)(PCy$_3$)$_2$] (21): ^{1}H NMR: δ = –8.70 ppm. ^{31}P NMR: δ = 50.80 ppm ($^2J_{^{31}\text{P},^{119}\text{Sn}}$ = 148 Hz). ^{13}C NMR: δ = 232.4 ppm (CO; $^2J_{^{13}\text{C},^{31}\text{P}}$ = 3.7, $^2J_{^{13}\text{C},^{119}\text{Sn}}$ = 144.6 Hz).

[Pd(H)(^{13}CO)(Cl)(PCy$_3$)$_2$] (22): ^{1}H NMR: δ = –14.50 ppm. ^{13}C NMR: δ = 194.6 ppm (CO).

Observation of Mixtures of [Pd(Alkyl)(CO)(SnCl$_3$)(PPh$_3$)$_2$] (23) and [Pd(Alkyl)(CO)(Cl)(PPh$_3$)$_2$] (24): A solution of [Pd(H)(Cl)L$_2$] (0.1 mmol) in 2 mL of [D$_8$]THF was treated with one equivalent of anhydrous SnCl$_2$ at 183 K. After 2 h, this solution was transferred to a sapphire tube and the solution was charged with four equivalents of dihydromyrcene and 3 bar of ^{13}CO at the same temperature. Multinuclear NMR analyses indicated the formation of a mixture of **23** and **24**, with a **23**/**24** ratio of 70:30. **23:** ^{13}C NMR: δ = 232.6 ppm ($^2J_{^{13}\text{C},^{31}\text{P}}$ = 4.5 Hz). **24:** ^{13}C NMR: δ = 194.7 ppm ($^2J_{^{13}\text{C},^{31}\text{P}}$ = 3.2 Hz).

Characterisation of Compound (5*R*)-C: MS: *m*/*z* (%) = 95(100), 81 (62), 96(41), 122 (30), 183 (18) [M + 1], 138 (7). ^{1}H NMR (250.13 MHz, CDCl$_3$): δ = 3.75 (ddd, *J* = 4.2, 10.5 and 10.5 Hz, 1 H, H1), 2.55 (dd, *J* = 6.8 and 18 Hz, 1 H, H4$_{ax}$), 1.96 (dd, *J* = 9.4 and 17.8 Hz, 1 H, H4$_{eq}$), 1.8 (m, 1 H, H10$_{eq}$), 1.84 (m, 1 H, H7$_{eq}$), 1.54 (m, 1 H, H8$_{ax}$), 1.45 (m, 1 H, H5), 1.34 (m, 1 H, H9), 1.10 (m, 1 H, H7$_{ax}$), 0.92 (m, 1 H, H8$_{eq}$), 0.82 (d, *J* = 6.2 Hz, 3 H, CH$_3$ 11), 0.80 (m, 1 H, H6), 0.77 (d, *J* = 6.5 Hz, 3 H, CH$_3$ 12) ppm. ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 171.3 (C3), 82.3 (C1), 44.6 (C6), 40.4 (C10), 38.0 (C4), 33.7 (C8), 31.7 (C5), 30.9 (C9), 27.7 (C7), 21.8 (C12), 19.0 (C11) ppm.

Characterisation of Compound (5*S*)-C: MS: *m*/*z* (%) = 96 (100), 81 (85), 122 (31), 183 (12) [M + 1], 138 (6). ^{1}H NMR (250.13 MHz, CDCl$_3$): δ = 4.13 (ddd, *J* = 4.3, 11, and 11 Hz, 1 H, H1), 2.69 (dd, *J* = 6.6 and 17.6 Hz, 1 H, H4$_{ax}$), 2.41 (dd, *J* = 2.8 and 17.6 Hz, 1 H, H4$_{eq}$), 2.13 (ddd, *J* = 1.6, 12, and 12 Hz, 1 H, H10$_{eq}$), 2.07 (m, 1 H, H5), 1.73 (m, 2 H, H8$_{ax}$ and H8$_{eq}$), 1.66 (m, 1 H, H7$_{eq}$), 1.60 (m, 1 H, H6), 1.48 (m, 1 H, H9), 1.27 (ddd, *J* = 3.5, 12.9, and 12.9 Hz, 1 H, H7$_{ax}$), 1.16 (ddd, *J* = 3.0, 12, and 12 Hz, 1 H, H10$_{ax}$), 1.00 (d, *J* = 7.2 Hz, 3 H, CH$_3$ 11), 0.97 (d, *J* = 6.6 Hz, 3 H, CH$_3$ 12). ^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 171.2 (C3), 77.8 (C1), 41.7 (C6), 40.9 (C10), 38.9 (C4), 33.9 (C8), 30.8 (C9), 28.8 (C5), 27.2 (C7), 21.7 (C12), 14.7 (C11) ppm. C$_{11}$H$_{18}$O$_2$ (182.12): calcd. C 71.5, H 10, O 17.6; found C 71.8, H 9.8, O 18.3.

Characterisation of Dehydro-C: MS: *m*/*z* (%) = 181 (14) [M + 1], 138 (12), 123 (40), 109 (13), 95 (66), 81 (100), 67 (69), 55 (30), 41 (55), 29 (13).

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