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[Pd(H)($SnCl_3$)L_2]: The key active species in the catalyzed alkoxycarbonylation reaction of terminal alkenes

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Abstract

The four complexes [Pd(H)(Cl)L_2] and [Pd(H)($SnCl_3$)L_2], L = PPh_3, PCy_3, have been synthesized and fully characterized by multinuclear NMR. They represent the active species of the hydride palladium-catalyzed alkoxycarbonylation of terminal alkenes. Isolation of the model acylplatinum complex, resulting from the carbonylation of dihydromyrcene, clearly shows that $SnCl_2$ as co-catalyst produces a $SnCl_3$ ligand which modulates the metal center electron density.

Keywords: Hydridopalladium; Alkoxycarbonylation; ^{119}Sn and Multinuclear NMR; Palladium chemistry

1. Introduction

Palladium complexes of the type [$PdCl_2L_2$] are efficient precursors that catalyze the alkoxycarbonylation of alkenes producing the corresponding esters or lactones [1]. Knifton [2] discovered in 1976 that the system [$PdCl_2(PPh_3)_2$] in the presence of $SnCl_2$ catalyzed more efficiently the alkoxycarbonylation of terminal alkenes, and proposed on the basis of infrared observations the involvement of the [Pd(H)($SnCl_3$)(PPh_3)$_2$] active species. Further studies carried out by Toniolo and his group [3] have shown that could be considered the competitive pathway involving the isolated alkoxycarbonyl active species [Pd(Cl)(COOR)L_2] arising from the attack of the ROH alcohol onto a coordinated carbonyl ligand but that this Pd–COOR species leads in fact to deactivation. Using a diphosphine ligand leads to good conversion rates of ethylene into methylpropanoate [4]. However, substitution of the two chloro ligands by non-coordinating anions gives a related catalytic process for the copolymerization of ethylene and carbon monoxide catalyzed by $[Pd(diphos)]^{2+}$ precursors in methanol. Two interconnected catalytic cycles arise from the $[Pd(H)(diphos)]^{+}$ and $[Pd(COOMe)(diphos)]^{+}$ active species [4]. Recent studies on [$Pd(OTs)_2(PPh_3)_2$] by Toniolo and coworkers [5] demonstrate that the presence of water in the medium leads to the hydrolysis of an inactive [Pd–COOMe] species to a [Pd–COOH] species which provides the hydride species by loss of CO_2. This hydride route is the most efficient one to produce the methoxycarbonylation of ethene into methylpropanoate [6]. Nevertheless, all the studies devoted to the demonstration that a hydridopalladium complex is the effective active species have gained indirect proofs only because it has always been difficult to prove their presence under catalytic conditions. The reason is that hydridopalladium complexes are usually quite reactive and unstable species [6,7]. Very recently, in a paper reporting on cleavage of allylic alcohols catalyzed by hydridopalladium complexes mentioned the authors gave up isolating these complexes which are too unstable and they

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preferred to synthesize the platinum analogues [8]. Heaton and his group [6] described two years ago an interesting study on the synthesis and characterization by NMR of cationic Pd(II) hydride complexes containing the diphosphine d′bpx ligand (d′bpx = 1,2-$(CH_2PBu^t_2)_2C_6H_4$) and a neutral or an anionic ligand. They demonstrated that this diphosphine used in their study can stabilize the hydride even in the presence of weakly coordinating ligands. In order to gain further evidences for such a route in the catalytic system $[PdCl_2(PPh_3)_2/SnCl_2]$ we have prepared four hydrido complexes $[Pd(H)(Cl)L_2]$ (L = PPh_3 (**1**); L = PCy_3 (**3**)), and $[Pd(H)(SnCl_3)L_2]$ (L = PPh_3 (**2**); L = PCy_3 (**4**)), which contain either the Cl^- or $SnCl_3^-$ ligand, the latter resulting from addition of the long-studied $SnCl_2$ promoter. Complexes **1** and **3** have previously been observed in solution [9]. NMR studies provide evidence that an equilibrium exists in solution between **3** and **4**/free $SnCl_2$. Finally, we have succeeded in isolating the acyl complex *trans*-$[(CH_3)_2C{=}CH(CH_2)_2CH(CH_3)CH_2CH_2C(O)Pt(SnCl_3)(PPh_3)_2]$ (**8**) and followed the reversible process of decarbonylation, and β-elimination restoring the substrate and $[Pt(H)(SnCl_3)(PPh_3)_2]$. Therefore we can validate the involvement of a hydrido metal active species in the catalytic cycle of the alkoxycarbonylation of dihydromyrcene, and generally speaking of a terminal alkene.

2. Results and discussion

2.1. Characterization of the hydride complexes

The hydridopalladium(II) complex *trans*-$[Pd(H)(Cl)(PPh_3)_2]$ (**1**) is conveniently prepared by heating a mixture of *trans*-$[PdCl_2(PPh_3)_2]$ and an excess of $HSiPh_3$ at 80 °C for 2 h in benzene. Concentration of the solution and addition of *n*-heptane lead to precipitation of a red complex, from which the removal of $ClSiPh_3$ is tedious because it requires various successive precipitations. The solid material shows an IR active Pd–H band at 2050 cm^{-1} and, dissolved in $CDCl_3$, a hydride signal at −13.12 ppm (s) in ^1H NMR, and a singlet at 30.75 ppm in ^{31}P similar to those reported in the literature [9]. Further addition of one equivalent of $SnCl_2$ to **1** in THF at −90 °C affords *trans*-$[Pd(H)(SnCl_3)(PPh_3)_2]$ (**2**) showing a ^1H NMR signal at −6.90 ppm flanked by two satellites due to the coupling ^1H–^{119}Sn (^2J = 944 Hz) and a ^{31}P NMR signal at 33.80 ppm, the small coupling ^1H–^{31}P constant enlarging somewhat the signal. Small quantities of $[Pd(H)(SiPh_3)(PPh_3)_2]$ are also detected with a signal at −10.30 ppm and two satellites with a coupling constant $^2J(^{29}Si,^1H)$ = 64 Hz. Similar experiments starting from *cis*-$[PdCl_2(dppb)]$, which contains the bis(diphenylphosphino)butane bidentate ligand, show that addition of $HSiPh_3$ results in the rapid precipitation of palladium black; the instability of the complex being presumably due to the large *trans*-effect of a phosphorus atom in *trans* position with respect to the hydride ligand. We observed that the most convenient method to prepare $[Pd(H)(Cl)(PCy_3)_2]$ (**3**) is to slowly adding one equivalent of HCl 2M in diethylether solution to $[Pd(PCy_3)_2]$, even at room temperature. The yellow solid, that is almost quantitatively isolated, is characterized by a hydride signal at −14.32 ppm (s) and a phosphorus signal at 46.63 ppm (s) [9d]. Addition of one equivalent of $SnCl_2$ at −90 °C gives $[Pd(H)(SnCl_3)(PCy_3)_2]$ (**4**), for which the corresponding signals are −8.50 ppm (t) and 52.3 ppm (t, $^2J(^{119}Sn,^{31}P)$ = 138.1 Hz), in ^1H and ^{31}P NMR respectively. Moreover, ^1H–^{119}Sn HMQC NMR spectra allow the assignment of the doublet centered at 154 ppm with a $^2J(^{119}Sn,^1H)$ coupling constant of 1760 Hz (see Fig. 1).

Thus, the basicity of the tricyclohexylphosphine ligand displays a more hydridic character of the H-Pd bond as evidenced by ^1H NMR: resonance is observed at −8.50 ppm instead of −6.90 ppm for its analogue **2** in triphenylphosphine. The bulkiness of the ligand can also explain the stability of the complex. Analysis of **4** at the room temperature is not informative due to a fast fluxional process. Increasing the temperature from −90 to −70 °C shows that there is an equilibrium between **4** and the neutral complex **3** and free $SnCl_2$, as shown by the two ^1H spectra in Fig. 2. Previous observations in platinum chemistry have been reported on the reversible insertion of $SnCl_2$ into a Pt–Cl bond [10].

Our observations reveal the dramatic effect exerted by $SnCl_2$: indeed, for the two complexes **2** and **4**, a great deal of electron density is released from the Pd atom as shown by the shift of ca 6 ppm (difference of 6.22 between **1** and **2**, 5.82 between **3** and **4**) for the hydride

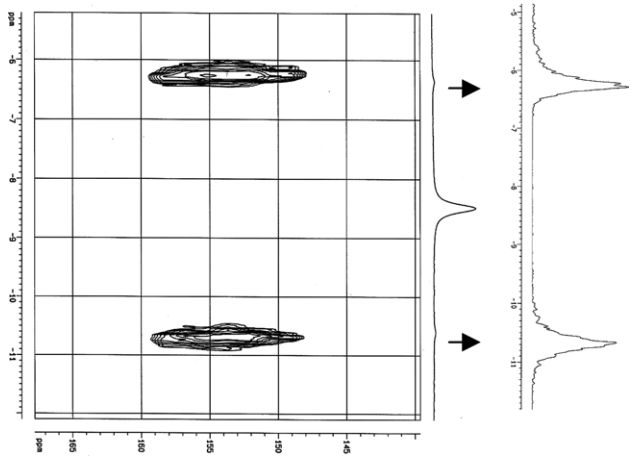


Fig. 1. ^1H–^{119}Sn HMQC NMR spectrum of **4**.

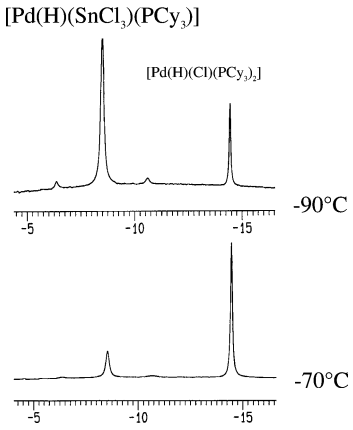


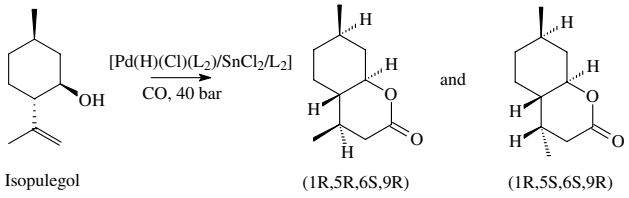
Fig. 2. Two ^{1}H spectra at −90 and −70 °C of **3** and **4**.

signal when moving from a Pd–Cl to a Pd–$SnCl_3$ bond. This effect should explain the co-catalytic behavior of $SnCl_2$ which promotes the coordination of the C=C double bond of the substrate in the palladium-catalyzed alkoxycarbonylation reaction [11].

After a hydride transfer step to the alkene, which originates the alkyl species, a migratory insertion of the CO ligand would afford the corresponding acyl species. Many efforts were made to isolate such a species relevant to palladium catalytic chemistry, but with no success yet. However, platinum complexes parallel the reaction pathway of their palladium congeners, and several $[Pt(H)(SnCl_3)L_2]$ complexes as well as their corresponding acyl species $[Pt(COR)(SnCl_3)L_2]$ were isolated and identified [12]. For out part, we have succeeded in identifying this step by reacting *trans*-$[Pt(H)(SnCl_3)(PPh_3)_2]$ (**5**) with dihydromyrcene under a CO pressure of 40 bar at 100 °C in ethanol, for 4 h. Releasing the pressure in the autoclave and slowly decreasing the temperature permit the formation of white micro-crystals of the acyl-chloro complex $[(CH_3)_2C{=}CH(CH_2)_2CH(CH_3)CH_2CH_2C(O)Pt(Cl)(PPh_3)_2]$ (**7**) by loss of $SnCl_2$. Relevant NMR data are a triplet for the ^{31}P signal at 23.2 ppm, $^{1}J(^{195}Pt,^{31}P) = 3526$ Hz; a triplet for the ^{195}Pt signal at −3933 ppm; a main triplet for the ^{13}CO signal at 219.5 ppm, $^{2}J(^{31}P,^{13}C) = 6$ Hz accompanied by Pt satellites ($^{1}J(^{195}Pt,^{13}C) = 458$ Hz). Further addition of one equiv of $SnCl_2$ to a previously concentrated $CDCl_3$ solution gives the analogous of **7** containing a Pt–$SnCl_3$ moiety. This complex **8** has been also characterized and displays the corresponding series of signals in ^{31}P, ^{195}Pt and ^{13}C NMR at 18.9 ppm, $^{1}J(^{195}Pt,^{31}P) = 3186$ Hz; −4466 ppm; 224.8 ppm, $^{2}J(^{31}P,^{13}C) = 5$ Hz respectively, and moreover a ^{119}Sn signal at 55.6 ppm (t), $^{1}J(^{119}Sn,^{31}P) = 296$ Hz by ^{31}P–^{119}Sn HMQC. Eq. (1) summarizes the reactions observed when using platinum model analogues (Scheme 1).

Presumably the loss of $SnCl_2$ that leads to the formation of **7** is due to an equilibrium between the two Pt–$SnCl_3$ and Pt–Cl species as observed for the analogous Pd complexes **3** and **4**. Crystallization of **7** causes the shift of this equilibrium. We can deduce that the attack of the alcohol followed by ester elimination restoring the platinum hydride complex requires higher activation energy than for palladium. Similar observations have been reported by Gómez et al. [12b] when reacting pentene with $[Pt(H)(SnCl_3)(PPh_3)_2]$ under CO pressure, except the authors reported that $SnCl_2$ was bonded to the acyl-oxygen atom. For our part, we found that **7** is unambiguously transformed into **8** by addition of $SnCl_2$ which displays a Pt–$SnCl_3$ bond. Moreover, NMR observations of **8** over long periods (until 6 days) show that decarbonylation occurs slowly and reversibly to give complex **6**, and then by β-H elimination restores the hydride **5** and dihydromyrcene, which mimics the active species in the palladium catalysis.

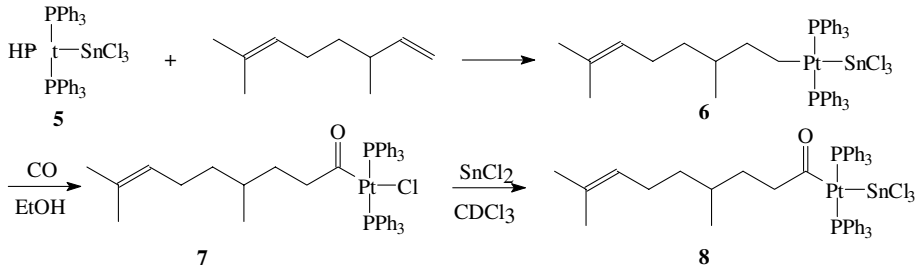
2.2. Catalytic experiments



Cyclocarbonylation of isopulégol

(1)

In routine catalytic experiments for the carbonylation of isopulegol into the corresponding lactones, $[PdCl_2(PPh_3)_2]$ was introduced in the presence of 2.5 equivalents $SnCl_2$ and 2 of PPh_3 (Sn/Pd = 2.5 and P/Pd = 4). In 16 h, at 30 bar of CO, the conversion was complete giving selectively the couple of the two diastereomers (Table 1, run 1). Starting from $[Pd(H)(Cl)(PPh_3)_2]$ and adding the same quantities of $SnCl_2$ and PPh_3 allowed to transform completely isopulegol at 30 bar (run 2). We explored lower pressures for this carbonylation reaction. At 10 bar the hydride palladium complex $[Pd(H)(SnCl_3)(PPh_3)_2]$, which is rapidly produced from the chloro complex (see above), still fully converted the substrate (run 3). We noted a dramatic effect of the temperature since at 40 °C the hydride gave rise to a yield of 62% in lactones (run 4). We can note that opening the autoclave at the end of theses reactions, under ambient conditions, gave yellow solutions. In run 1, the color was more pronounced and often orange crystals of $[PdCl_2(PPh_3)_2]$ appeared due to the presence of HCl formed during preformation in the medium. In the other cases a yellow, lightly green, solution produced rapidly decomposition and palladium



Scheme 1. Reactivity of $[Pt(H)(SnCl_3)(PPh_3)_2]$ with dihydromyrcene.

Table 1
Cyclocarbonylation of isopulegol catalyzed by a palladium hydride either formed in situ (run 1) and preformed (runs 2, 3 and 4)

Run	Starting complex	T (°C)	P_{CO} (bar)	Yield (%)	(1R,5R,6S,9R) (%)	(1R,5S,6S,9R) (%)
1	$[PdCl_2(PPh_3)_2]$	60	30	100	62	38
2	$[Pd(H)(Cl)(PPh_3)_2]$	60	30	100	60	40
3	$[Pd(H)(Cl)(PPh_3)_2]$	60	10	100	61	39
4	$[Pd(H)(Cl)(PPh_3)_2]$	40	30	62	35	27

Experimental conditions: Sn/Pd = 2.5; P/Pd = 4.

black precipitates, consistently with the low stability of $[Pd(H)(Cl)(PPh_3)_2]$ as soon as few quantities of air are admitted.

Thus, all of the reactions described in this paper are consistent with a hydridopalladium route for the catalyzed alkoxycarbonylation reaction of a terminal alkene to produce the corresponding ester. We also show that the promoting effect of $SnCl_2$ is due to the formation of a Pd–$SnCl_3$ species.

3. Experimental

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 and AMX400 spectrometers using 5 mm triple resonance inverse probes with 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. IR spectra were obtained on a Perkin–Elmer 1710 spectrometer, absorption are reported in cm^{-1}. Analytical GC was carried out on a Perkin–Elmer chromatography with DB-5GC (30 m–0.25 mm–0.25 μm) column and a flame ionization detector.

3.1. Preparation of complexes

The following complexes were prepared by the methods reported: *trans*-$[PdCl_2(PPh_3)_2]$ [13], *cis*-$[PdCl_2$-(dppb)] [14], *trans*-$[PdCl_2(PCy_3)_2]$ [14,15], $[Pd(PCy_3)_2]$ [15], *cis*-$[PtCl_2(PPh_3)_2]$ [16], *trans*-$[Pt(H)$-$(SnCl_3)(PPh_3)_2]$ [16].

3.2. Preparation of trans-[Pd(H)Cl(PPh$_3$)$_2$] (1)

A 100 mL benzene solution of $[PdCl_2(PPh_3)_2]$ (400 mg, 0.57 mmol) and $HSiPh_3$ (2.98 g, 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 powder of *trans*-$[Pd(H)Cl(PPh_3)_2]$ which was dissolved in benzene and precipitated with hexane 3 times; the final product is white with 40% isolated yield.

3.3. Preparation of [Pd(H)(SnCl$_3$)(L$_2$)] (L = PPh$_3$ (2) or PCy$_3$, (4))

A solution of $[Pd(H)(Cl)(L_2)]$ (0.1 mmol) in 1 mL of [D8]THF was treated with one equivalent of anhydrous $SnCl_2$ within 2 h at 183 K, and the ^{1}H, ^{31}P, ^{119}Sn NMR spectra were recorded; the spectra revealing the presence of $[Pd(H)(SnCl_3)(L_2)]$:

$[HPd(SnCl_3)(PPh_3)_2]$ (**2**): ^{1}H NMR (400.13 MHz, 183 K): $\delta = -6.90$ ppm ($^{2}J(^{1}H,^{119}Sn) = 944$ Hz), $^{31}P\{^{1}H\}$-NMR (161.98 MHz, 183 K): $\delta = 33.80$ ppm; $[Pd(H)$-$(SnCl_3)(PCy_3)_2]$ (**4**) in ^{1}H NMR (400.13 MHz, 183 K): $\delta = -8.50$ ppm, $^{31}P\{^{1}H\}$NMR (161.98 MHz, 183 K): $\delta = 52.3$ ppm ($^{2}J(^{31}P,^{119}Sn) = 138.1$ Hz), ^{1}H–^{119}Sn HMQC NMR (400.13 MHz, 149.21 MHz), 183 K: $\delta(^{119}Sn) = 154$ ppm ($^{2}J(^{1}H,^{119}Sn) = 1760$ Hz).

3.4. NMR data for [(CH$_3$)$_2$C=CH(CH$_2$)$_2$CH(CH$_3$)CH$_2$CH$_2$C(O)PtCl(PPh$_3$)$_2$] (7)

$^{31}P\{^{1}H\}$ NMR (161.98 MHz, $CDCl_3$, 298 K): $\delta = 23.2$ ppm ($^{2}J(^{31}P,^{195}Pt) = 3526$ Hz), $^{195}Pt\{^{1}H\}$ NMR (85.68 MHz, $CDCl_3$, 298 K): $\delta = -3933$ ppm; ^{13}C–$\{^{1}H\}$bb + $\{^{31}P\}$ NMR (100.63 MHz, $CDCl_3$, 298 K): ^{13}C NMR; $\delta(^{13}CO) = 219.4$ ppm, ($^{2}J(^{13}C,^{31}P) = 6$

Hz, $^{1}J(^{13}C,^{195}Pt)$ = 458 Hz), 135.4, 134.5, 131.3, 131.4, 130.8, 125.4, 57.1, 37.4, 32.1, 31.4, 26.2, 25.9, 19.5, 15.7.

3.5. NMR data for $[(CH_3)_2C{=}CH(CH_2)_2CH(CH_3)CH_2CH_2C(O)Pt(SnCl_3)(PPh_3)_2]$ (**8**)

^{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): $\delta(^{31}P)$ = 18.9 ppm, ($^{2}J(^{31}P,^{119}Sn)$ = 296 Hz); ^{31}P–^{119}Sn INEPTND$\{^{1}H\}$bb NMR: $\delta(^{119}Sn)$=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: $\delta(^{195}Pt)$ = −4466 ppm ($^{1}J(^{195}Pt,^{31}P)$ = 3185.6 Hz). ^{13}C NMR: $\delta(^{13}CO)$ = 224.8 ppm, $^{2}J(^{31}P,^{13}C)$ = 5 Hz, 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.

3.6. Catalytic tests

A mixture of triphenylphosphine (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 (hydrurochlorobis(triphenylphosphino)palladium(II) or dichlorobis(triphenylphosphino)palladium, 0.2 mmol), isopulegol (10 mmol) in toluene (10 mL) was introduced into the evacuated autoclave by aspiration. It was heated under pressure of carbon monoxide. After 16 h, the autoclave was cooled and then slowly depressurized. The obtained solution was analyzed by gas chromatography.

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