Article

Syntheses and ^{31}P NMR Studies of Transition Metal Complexes Containing Derivatives of Dioxaphospholane and Dioxaphosphorinane

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A síntese de vários complexos de Pt(II), Pt(0) e Pd(II) com 2-cloro-1,3,2-dioxafosfolana, 2-fluoro-1,3,2-dioxafosfolana, 2-cloro-4,5-benzo-1,3,2-dioxafosfolana, 2-fluoro-4,5-benzo-1,3,2-dioxafosfolana, 2-cloro-1,3,2-dioxafosforinana e 2-fluoro-1,3,2-dioxafosforinana é descrita. Estudos de RMN de ^{31}P{^{1}H} destes complexos revelam alguns aspectos inexplorados em relação às constantes de acoplamento ^{1}J(PtP), os quais chamam a atenção para o conceito de ácidos e bases duros e macios. Este trabalho mostra também as diferenças espectroscópicas de RMN de ^{31}P{^{1}H} entre isômeros *cis* e *trans*.

The syntheses of various complexes of Pt(II), Pt(0) and Pd(II) with 2-chloro-1,3,2-dioxaphospholane, 2-fluoro-1,3,2-dioxaphospholane, 2-chloro-4,5-benzo-1,3,2-dioxaphospholane, 2-fluoro-4,5-benzo-1,3,2-dioxaphospholane, 2-chloro-1,3,2-dioxaphosphorinane, 2-fluoro-1,3,2-dioxaphosphorinane are reported. ^{31}P{^{1}H} NMR studies of these complexes reveals some aspects still unexplored in terms of the magnitude of the coupling constants ^{1}J(PtP), which brings light to the soft and hard acid-base concept. This work also shows the ^{31}P{^{1}H} nmr spectroscopic differences between *cis* and *trans* isomers.

Keywords: ^{31}P NMR spectroscopy, acid-base hard and soft concept, dioxaphospholane and dioxaphosphorinane

Introduction

A variety of complexes containing phosphorus ligands have been reported over the past years and the interest on their chemistry is growing due to their possible catalytic activity. Our main interests have been to prepare new complexes containing unusual phosphorus ligands and investigate their chemical properties by the use of NMR spectroscopy.

The reactivity of dioxaphospholane and related compounds towards several organic compounds is well documented[1]. As a result of those studies several applications for this class of compound have been found. Some examples are the use of dioxaphospholanes in the development of specific imunoassays for the detection of pesticides[2], polymerisation reactions[3,4], syntheses of naturally ocuring lipids[5] and to analyse labile hydrogens functional on coal materials[6]. However few publications dealing with complexation of dioxaphospholanes have appeared in the literature.

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Recent reports of the new facile preparation methods of dioxaphospholane derivatives[7] and their ruthenium (II) complexes[8] prompted us to report some new platinum and palladium complexes.

The ligands $C_2H_4O_2PCl$ **1**, $C_2H_4O_2PF$ **2**, $C_6H_4O_2PCl$ **3**, $C_6H_4O_2PF$ **4**, $C_3H_6O_2PCl$ **5** and $C_3H_6O_2PF$ **6** used to prepare the platinum(0), platinum(II) and palladium(II) complexes, herein reported, are as follow.

X = Cl **1**   X = Cl **3**   X = Cl **5**
X = F **2**   X = F **4**   X = F **6**
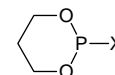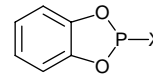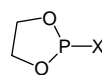
Results and Discussion

Syntheses and characterisation of platinum(0) complexes

Complexes [Pt(PPh$_3$)$_2$(C$_6$H$_4$O$_2$PCl)] **7**, [Pt(PPh$_3$)$_2$(C$_3$H$_6$O$_2$PCl)] **8** and [Pt(PPh$_3$)$_2$(C$_3$H$_6$O$_2$PF)] **9** have been obtained by treatment of [Pt(PPh$_3$)$_2$(C$_2$H$_4$)], in toluene, with ligands **3**, **5** and **6** respectively, at 0°C.

7

8 X = Cl
9 X = F

[PtCl$_2$(PEt$_3$)(C$_6$H$_4$O$_2$PCl)] **12**, [PtCl$_2$(PEt$_3$)(C$_6$H$_4$O$_2$PF)] **13** and [PtCl$_2$(PEt$_3$)(C$_3$H$_6$O$_2$PCl)] **14**, respectively.

X = Cl **10**
X = F **11**

X = Cl **12**
X = F **13**

14
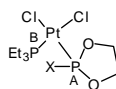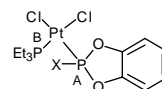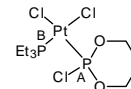
The ^{31}P{^{1}H} NMR spectra of the three complexes show a similar pattern of lines, which consists of an AB$_2$X spin system (A,B = ^{31}P, 100%; X = ^{195}Pt, 33.8%) for the two first compounds and of an AB$_2$XY spin system (A,B = ^{31}P, 100%; X = ^{195}Pt, 33.8%; Y = ^{19}F, 100%;) for the latter. Complexes **7** and **8** show a triplet with the platinum satellites at δ 60 and δ 38, respectively, relative to P$_A$ whereas P$_B$ is seen as a doublet with the platinum satellites at δ 22 and δ 27. A doublet of triplet at δ 113 and a doublet of doublets at δ 16 with the platinum satellites are observed in the ^{31}P{^{1}H} NMR spectrum of **9**. These results suggest a trigonal planar geometry around the platinum centre and due to the fact that both PPh$_3$ ligands are equivalent in the ^{31}P{^{1}H} NMR spectra it can be said that either the chloro atom at the dioxaphospholane ligand lies on a perpendicular plane to the one containing the Pt atom and the two PPh$_3$ or there is a rapid rotation around the Pt-dioxaphospholane bond. Identical conclusion has been reached about a similar platinum(0) complex, [Pt(PPh$_3$)$_2$(R$_2$C=P-N(R)-PR)][9]. The ^{31}P{^{1}H} NMR data are shown in Table 1.

It is interesting to compare the coupling constants ^1J(PtP$_A$) for complexes **8** and **9**. As would be expected, the PtP$_A$ coupling constant in **9** is larger than in **8**, reflecting the increase of s character on the Pt-P bond, caused by the presence of the more electronegative fluorine, bonded through the P$_A$, in the first complex[10]. The ^{31}P{^{1}H} NMR studies also suggest an increase in the magnitude of ^1J(PtP$_A$) on changing the group bonded to the oxygen atom in the phosphorus from -CH$_2$CH$_2$CH$_2$- to 1,2-benzo. A very small change is observed in the ^1JP$_A$F coupling constant of the ligand **6** (1304 Hz) upon coordination to platinum(0) to form complex **9** (*vide* Table 1). A long range ^3J(P$_B$F) coupling constant is also observed in the ^{31}P{^{1}H} NMR spectrum of **9**.

The ^{31}P{^{1}H} NMR studies of complexes **10 – 14** showed that they posses a *cis* arrangement around the platinum centre since the values for the ^2J(P$_A$P$_B$) coupling constants lie between 23 and 41 Hz and those for the ^1J(PtP) are typical for this kind of complexes[10].

Some of these complexes – **10**, **11** and **13** – have been obtained as a mixture of two conformers, **a** and **b**, as confirmed by the ^{31}P{^{1}H} NMR spectra, which consist of two sub spectra with the pattern of lines corresponding to an ABX spin system (A, B = ^{31}P, 100%; X = ^{195}Pt, 33,8%). In most of the spectra some lines, corresponding to one of the conformers, are superimposed to the ones of the other conformer. This is exemplified by the ^{31}P{^{1}H} NMR spectrum of **10** in which the signal corresponding to P$_A$ appears as a "false triplet" instead of two doublets. However, two doublets, in the P$_B$ region of the spectrum, are easily assigned. As little difference is seen in the ^{31}P{^{1}H} NMR data for both conformers **a** and **b** of **10**, **11** and **12**, their formation can be understood as a result of the coexistence of two conformers for the free ligands[11,12], as depicted in Scheme 1. In this case, the metal fragment [PtCl$_2$(PEt$_3$)] can be bonded through the phosphorus lone pair in an axial or equatorial position (Scheme 2).

Syntheses and characterisation of platinum(II) complexes

Treatment of [Pt$_2$Cl$_4$(PEt$_3$)$_2$], in CH$_2$Cl$_2$ at room temperature, with the ligands **1 – 5** yields the square planar complexes [PtCl$_2$(PEt$_3$)(C$_2$H$_4$O$_2$PCl)] **10**, [PtCl$_2$(PEt$_3$)(C$_2$H$_4$O$_2$PF)] **11**,

axial

equatorial

n = 0 or 1

Scheme 1.

axial

equatorial

n = 0 or 1

Scheme 2.

Table 1. ^{31}P{^{1}H} NMR data for complexes **7 – 9** (*J* in Hz)

Complexes	δ_{PA}	δ_{PB}	^1J(PtP$_A$)	^1J(PtP$_B$)	^2J(P$_A$P$_B$)	^1J(P$_A$F)	^3J(P$_B$F)
7	61	22	5420	2584	24	—	—
8	38	27	4856	2831	21	—	—
9	113	16	6603	3487	68	1194	68

Table 2. ^{31}P{^{1}H} NMR data for the platinum(II) complexes (J in Hz)

| Complexes	δ_{PA}	δ_{PB}	$^1J(PtP_A)$	$^1J(PtP_B)$	$^2J(P_AP_B)$	$^1J(P_AF)$	$^3J(P_BF)$
10 a	83	21	5789	2184	27	—	—
b	84	22	5789	2250	27	—	—
11 a	110	58	3860	5600	41	556	27
b	110	51	3860	5600	41	556	27
12	61	22	5420	2584	24	—	—
13 a	125	73	4000	5490	35	590	26
b	110	73	3680	5490	35	590	26
14	125	73	5750	3330	23	—	—

The ^{31}P{^{1}H} NMR spectra of complexes **11** and **13** show a decrease in the $^1J(PF)$ coupling constants (556 and 590 Hz, respectively) compared to those found for the free ligands (1302 and 1171 Hz, respectively). This large decrease in the $^1J(PF)$ coupling constants, upon complexation, suggests a fluxional behaviour involving a change between the fluorine bonded through the phosphorus atom with the chlorine bonded through the platinum atom. It is interesting to note that an additional long range $^3J(PF)$ coupling constant has also been observed for both complexes and its value is ~26 Hz. Due to the small $^2J(PP)$ coupling constants measured in the ^{31}P{^{1}H} NMR spectra, a *cis* arrangement around the platinum centre can be suggested for both complexes. The ^{31}P{^{1}H} NMR data for all the Pt(II) complexes, herein reported, have been compiled in Table 2.

Unlike for platinum(0) complexes, a change of chlorine for fluorine on the phosphorus of the dioxaphospholane does not produce an increase in the $^1J(PtP_A)$ coupling constant. The $^1J(PtP_A)$ observed for the chlorodioxaphospholane complexes **11** and **13** are in fact considerably larger than those found for their analogues with the fluorodioxaphospholanes **10** and **12** (*vide* Table 2). Similar results, though with smaller differences between the coupling constants, have been obtained by Nixon and co-workers[13] for complexes of the type [RhCl(P$_B$Ph$_3$)(η^1-XP$_A$=CR$_2$)], *i.e.* $^1J(RhP_A)$ = 264 Hz when X = Cl and 258 Hz when X = F. These results can be understood in terms of the hard and soft acid-base concept[14]. It seems that the fluoro ligands **2** and **4** are a lot softer than platinum(II). Then, complexes **11** and **13** can be regarded as a pair of hard acid-soft base, and in this case they will be less stable than their analogues with the chloro ligands, complexes **10** and **12**. One would therefore expect the Pt-P$_A$ bond length to be longer in complexes **11** and **13** than in the analogues **10** and **12**. Longer bond lengths in a soft acid-hard base pair than in soft acid-not so hard base pair have been evidenced, very recently, by Durig and co-workers[15]. The B-P bond length in the H$_3$BPF$_3$ pair is 1.836Å, whereas in H$_3$BPH$_3$ it is 1.943Å. So, if the bond lengths are longer, the $^1J(MP)$ must be smaller because of the smaller contact between the bonding orbitals of the metal and phosphorus nuclei, even if the s character in the phosphorus lone pair is increased. In fact, a less soft metal might simply not react with a ligand in which the s character of the phosphorus lone pair has been increased.

Syntheses and characterisation of palladium(II) complexes

Treatment of the dimeric complex [Pd$_2$Cl$_4$(PEt$_3$)$_2$], in CH$_2$Cl$_2$ at room temperature, with ligands **1**, **3** and **4** affords the square planar complexes [PdCl$_2$(PEt$_3$)(C$_2$H$_4$O$_2$PCl)] **15**, [PdCl$_2$(PEt$_3$)(C$_6$H$_4$O$_2$PCl)] **16** and [PdCl$_2$(PEt$_3$)(C$_6$H$_4$O$_2$PF)] **17**, respectively, as depicted bellow.
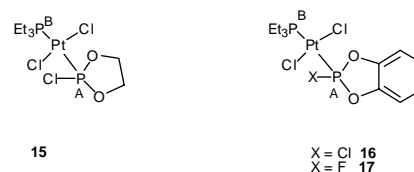
Very simple ^{31}P{^{1}H} NMR spectra have been obtained for complexes **15 – 17**. Patterns of lines corresponding to AB or ABX spin systems (A, B = ^{31}P, 100%; X = ^{19}F, 100%) are observed for complexes derived from chloro ligands **15** and **16**, and for that derived from the fluoro ligand, **17**, respectively. Similarly to the platinum(II) complexes, palladium(II) complexes are also formed as a mixture of two conformers **a** and **b** (*vide* Table 3), with the exception to the fluoro derivative, which might be due to the small size of fluorine, compared to chlorine.

Table 3. ^{31}P{^{1}H} NMR data for the palladium(II) complexes (J in Hz).

Complexes	δ_{PA}	δ_{PB}	$^2J(P_AP_B)$	$^3J(P_AF)$
15 a	108	45	216	—
b	107	44	216	—
16 a	117	30	614	—
b	98	30	614	—
17	118	50	20	1377

It is interesting that the chloro derivative ligands **1** and **3** yield *trans* complexes **15** and **16**, as shown by the

$^2J(P_A P_B)$ coupling constants measured in the $^{31}P\{^1H\}$ NMR spectra (Table 3), whereas ligand **4** affords complex **17** with *cis* configuration around the metallic centre[10]. Again, an explanation in terms of the combined sizes of palladium atom and the halogen bonded through the phosphorus can be given. Since platinum is bigger than palladium, it allows a *cis* configuration of the phosphorus ligand, showing a better *trans* influence of the chlorine ligand. In the palladium complexes **15** and **16** it seems that the major role is played by the steric hindrance of the chlorine in the dioxaphospholane. On the other hand, the *trans* influence of the chlorine is evidenced by the formation of a *cis* complex **17** because fluorine is smaller. The $^2J(P_A P_B)$ coupling constants (Table 3) are in accordance with the data found in the literature[9,10].

Conclusions

The $^{31}P\{^1H\}$ NMR results for the platinum(0) complexes show that changing the dioxaphospholane P bonded chlorine for fluorine leads to an increase in the s character of the phosphorus lone-pair and, as a consequence, to a increase in the Pt-P coupling constant. On the other hand, $^1J(PtP)$ coupling constants of platinum(II) complexes tend to decrease upon changing the chlorine for fluorine, thus revealing a relationship between the Pearson soft and hard acid-base concept and Pt-P coupling constants. Although a larger number of systems would need to be studied, the present work is a good starting point and dioxaphospholane and dioxaphosphorinane derivatives are good systems for the study of this relationship.

Experimental

All reactions were carried out either under dry dinitrogen in Schlenk tubes or by use of high-vacuum techniques. Glassware was flame-dried in vacuum and solvents were dried, freshly distilled under dinitrogen, and degassed prior to use. The NMR spectra were recorded on a Bruker DRX400 spectrometer at 400.13 MHz for ^1H and 161.98 MHz for ^{31}P. All chemical shift data were recorded at 25°C and are quoted in ppm, with positive values to high frequency of the indicated reference (external 85% H_3PO_4 for ^{31}P and $SiMe_4$ for ^1H) and corrected with respect to the appropriate deuterium frequency. Coupling constants are quoted in Hertz.

2-chloro-1,3,2-dioxaphospholane **1**, 2-chloro-4,5-benzo-1,3,2-dioxaphospholane **3** and 2-chloro-1,3,2-dioxaphosphorinane **5** have been prepared from the corresponding diol with PCl_3, following methods described in the literature[7]. The corresponding fluoro derivatives, 2-fluoro-1,3,2-dioxaphospholane **2**, 2-fluoro-4,5-benzo-1,3,2-dioxaphospholane **4** and 2-fluoro-1,3,2-dioxaphosphorinane **6**, have been prepared by treatment of **1**, **3** and **5** with SbF_3, respectively[16]. The $[Pt(PPh_3)_2(C_2H_4)]$; $[Pt_2Cl_4(PEt_3)_2]$ and $[PdCl_4(PEt_3)_2]$ were prepared by the published methods[17,18].

*Synthesis of (2-chloro-4,5-benzo-1,3,2-dioxaphospholane)bis(triphenylphosphane)platinum(0) **7***

To a solution of **3** (0.15 g, 0.84 mmol), in dichloromethane (10 mL), a solution of $[Pt(PPh_3)_2(C_2H_4)]$ (0.63 g, 0.84 mmol), also in dichloromethane (20 mL), was added at room temperature. The mixture was keept under stirring for 24 h and the solvent was pumped till dry and the oil obtained was washed with toluene (8 x 10 mL) to yield a cream powder (0.27 g, 37%). Found: C, 56.00; H, 3.65. Calc. for $C_{42}H_{34}P_3O_2ClPt$: C, 56.28; H, 3.80%.

*Synthesis of (2-chloro-1,3,2-dioxaphosphorinane)bis(triphenylphosphane)platinum(0) **8***

A solution of **5** (0.03 g, 0.20 mmol) in toluene (20 mL) was added dropwise, at ice temperature, to a solution of $[Pt(C_2H_4)(PPh_3)_2]$ (0.09 g, 0.20 mmol) in toluene (15 mL). After stirring for 24 h, the solvent was pumped off till dry to yield a yellow powder (0.07 g, 41%). Found: C, 55.31; H, 4.38. Calc. for $C_{39}H_{36}P_3O_2ClPt$: C, 54.45; H, 4.20%.

*Synthesis of (2-fluoro-1,3,2-dioxaphosphorinane)bis(triphenylphosphane)platinum(0) **9***

To a solution of $[Pt(PPh_3)_2(C_2H_4)]$ (0.15 g, 0.35 mmol) in toluene (10 mL), at ice temperature, was added a solution of **6** (0.04 g, 0.35 mmol), also in toluene (10 mL). The mixture was kept under stirring, at ice temperature, for 2 h and for further 22 h at room temperature. After complete evaporation of the solvent, a green solid was obtained (0.12 g, 45%). Found: C, 56.00; H, 4.25. Calc. for $C_{39}H_{36}P_3O_2FPt$: C, 56.18; H, 4.32%.

*Synthesis of cis-dichloro(2-chloro-1,3,2-dioxaphospholane)platinum(II) **10***

To a solution of **1** (0.07 g, 0.56 mmol) in dichloromethane (10 mL) a solution of $[Pt_2Cl_4(PEt_3)_2]$ (0.22 g, 0.28 mmol) in dichloromethane (20 mL), at ice temperature. The mixture was stirred for 2 h at ice temperature and for 46 h at room temperature. The oil obtained was washed with n-hexane (8 x 10 mL) to yield a yellow powder. (0.25 g, 89%). Found: C, 19.02; H, 3.90. Calc. for $C_8H_{19}P_2O_2Cl_3Pt$: C, 18.80; H, 3.72%; ^1H NMR ($CDCl_3$): δ 1.15- 1.19 (m, 9H; $3CH_3$) δ 2.16- 2.18 (m, 6H, $3CH_2$) δ 3.73 – 3.75 (m, 4H, $2CH_2$).

Synthesis of cis-dichloro(2-fluoro-1,3,2-dioxaphospholane) platinum(II) **11**

To a toluene solution of **2** (0.04 g, 0.35 mmol), $[Pt_2Cl_4(PEt_3)_2]$ (0.13 g, 0.17 mmol), in toluene (5 mL), was added and the mixture was stirred for 24 h to yield a yellow powder which was filtered and washed with n-hexane (8 x 10 mL). (0.09 g, 48%). Found: C, 19.35; H, 3.88. Calc. for $C_8H_{19}P_2O_2Cl_2FPt$: C, 19.38; H, 3.92%.

Synthesis of cis-dichloro(2-chloro-4,5-benzo-1,3,2-dioxaphospholane)platinum(II) **12**

To a solution of **3** (0.07 g, 0.42 mmol) in dichloromethane (10 mL) a solution of $[Pt_2Cl_4(PEt_3)_2]$ (0.16g, 0.21mmol), also in dichloromethane (20 mL), was added, at ice temperature. The mixture was kept under stirring for 2 h at ice temperature and for further 46 h at room temperature. After this time the solvent was pumped off till dryness and the oil obtained was washed with hexane (8 x 6 mL) to yield a yellow powder. (0.2 g, 91%). Found: C, 20.95; H, 2.80. Calc. for $C_{12}H_{19}P_2O_2Cl_3Pt$: C, 21.65; H, 2.86%; ^{1}H NMR (CDCl$_3$): δ 1.06 – 1.18 (m, 9H, 3CH$_3$) δ 1.84 – 1.97 (m, 6H, 3CH$_2$) δ 7.00 – 7.18 (m, 4H, 4CH).

Synthesis of cis-dichloro(2-fluoro-4,5-benzo-1,3,2-dioxaphospholane)platinum(II) **13**

A solution of $[Pt_2Cl_4(PEt_3)_2]$ (0.33 g, 0.43 mmol) in toluene (40 mL) was added dropwise to a toluene solution of **4** (0.14 g, 0.86 mmol). The mixture was stirred for 24 h and the product was obtained as a yellow powder after filtration. (0.27 g, 57%). Found: C, 23.01; H, 2.78. Calc. for $C_{12}H_{19}P_2O_2Cl_2FPt$: C, 22.55; H, 2.98%.

Synthesis of cis-dichloro(2-chloro-1,3,2-dioxaphosphorinane) platinum(II) **14**

To a solution of $[Pt_2Cl_4(PEt_3)_2]$ (0.09 g, 0.12 mmol) in toluene (10 mL) was added to a solution of **5** (0.03 g, 0.24 mmol) in toluene (10 mL), at ice temperature. The mixture was stirred for 2 h at ice temperature and for further 48 h at room temperature. After this period the yellow solid obtained was filtered and washed with toluene. (0.05 g, 42%). Found: C, 20.31; H, 3.92. Calc. for $C_9H_{21}P_2O_2Cl_3Pt$: C, 20.59; H, 4.00%.

Synthesis of trans-dichloro(2-chloro-1,3,2-dioxaphospholane) palladium(II) **15**

To a solution of **1** (0.14 g, 1.12 mmol) in dichloromethane (10 mL) a solution of $[Pd_2Cl_4(PEt_3)_2]$ (0.33 g, 0.56 mmol), also in dichloromethane (20 mL), was added dropwise, at ice temperature. The mixture was stirred for 2h at ice temperature and for further 22 h at room temperature. Upon evaporation of the solvent, an oil was obtained and washed with hexane (8 x 6 mL) to yield a yellow solid. (0.30 g, 64%). Found: C, 22.00; H, 4.3. Calc. for $C_8H_{19}P_2O_2Cl_3Pd$: C, 22.75; H, 4.5%.

Synthesis of trans-dichloro(2-chloro-4,5-benzo-1,3,2-dioxaphospholane)palladium(II) **16**

To a solution of **3** (0.07 g, 0.42 mmol) in dichloromethane (10 mL) a solution of $[Pd_2Cl_4(PEt_3)_2]$ (0.12 g, 0.21 mmol), also in dichloromethane (20 mL), was added dropwise, at ice temperature. The mixture was stirred for 2 h at ice temperature and for further 22 h at room temperature. Upon evaporation of the solvent, an oil was obtained and washed with hexane (8x6mL) to yield a yellow solid. (0.16 g, 84%). Found: C, 27.98; H, 3.20. Calc. for $C_{12}H_{19}P_2O_2Cl_3Pd$: C, 28.19; H, 3.46%.

Synthesis of cis-dichloro(2-fluoro-4,5-benzo-1,3,2-dioxaphospholane)palladium(II) **17**

To a solution of **4** (0.06 g, 0.40 mmol) in dichloromethane (10 mL) a solution of $[Pd_2Cl_4(PEt_3)_2]$ (0.12 g, 0.20 mmol), also in dichloromethane (20 mL), was added dropwise, at ice temperature. The mixture was stirred for 2 h at ice temperature and for further 22 h at room temperature. Upon evaporation of the solvent, an oil was obtained and washed with hexane (8 x 6 mL) to yield a yellow solid. (0.10g, 60%). Found: C, 26.98; H, 3.02. Calc. for $C_{12}H_{19}P_2O_2Cl_3Pd$: C, 27.51; H, 3.27%.

Acknowledgements

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