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# The reaction in acetonitrile between $PdCl_2$ and the carbonyl-stabilized ylide $Ph_3P{=}CHCO_2Me$. Synthesis of $[Pd\{CH\{P(2\text{-}C_6H_4)Ph_2\}(CO_2Me)\}(\mu\text{-}Cl)]_2$ and some of its derivatives and of $[PdCl_2\{CH(PPh_3)CO_2Me\}_2]$

**Jose Vicente *, Maria T. Chicote, and Juan Fernandez-Baeza**
*Departamento de Quimica Inorganica, Universidad de Murcia, 30171 Espinardo-Murcia (Spain)*

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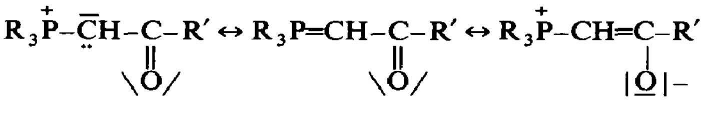
## Abstract

Upon reaction of $PdCl_2$ with the ylide $Ph_3P{=}CHCO_2Me$ in acetonitrile (1/2) at room temperature the complex $[PdCl_2\{CH(PPh_3)CO_2Me\}_2]$ (**1**) separates. The same reaction at the reflux temperature gives the dinuclear complex $[Pd\{CH\{P(2\text{-}C_6H_4)Ph_2\}(CO_2Me)\}(\mu\text{-}Cl)]_2$ (**2**) along with the phosphonium salt $[Ph_3PCH_2CO_2Me]Cl$. Complex **1** is better obtained by reaction (1/2) of $[PdCl_2(NCC_6H_5)_2]$ with the ylide at room temperature. Complex **2** reacts with $PPh_3$ (1/2) or pyridine (py) (excess) to give the products of bridge-splitting $[Pd\{CH\{P(2\text{-}C_6H_4)Ph_2\}(CO_2Me)\}Cl(L)]$ ($L = PPh_3$ (**3**), L = py (**4**)). Complex **3** is also obtained when a 1/4 molar ratio of the reactants is used but, in the presence of $NaClO_4$ the complex $[Pd\{CH\{P(2\text{-}C_6H_4)Ph_2\}(CO_2Me)\}(PPh_3)_2]ClO_4$ (**5**) is obtained; complex **2** reacts with bidentate ligands LL in the presence of $NaClO_4$ (1/2/3) to give $[Pd\{CH\{P(2\text{-}C_6H_4)Ph_2\}(CO_2Me)\}(LL)]ClO_4$ [LL = 2,2′-bipyridine (bipy) (**6**), 1,10-phenanthroline (phen) (**7**), and with Tlacac (1/2) (acacH = acetylacetone) to give $[Pd\{CH\{P(2\text{-}C_6H_4)Ph_2\}(CO_2Me)\}(acac)]$ (**8**).

## Introduction

Carbonyl-stabilized phosphorus ylides are interesting ligands because they can behave as C- and/or O-donor ligands owing to the delocalization of the ylidic electron pair:



$$R_3\overset{+}{P}-\overset{-}{\underset{\cdot\cdot}{C}}H-\underset{\underset{\backslash O/}{\|}}{C}-R' \leftrightarrow R_3P{=}CH-\underset{\underset{\backslash O/}{\|}}{C}-R' \leftrightarrow R_3\overset{+}{P}-CH{=}\underset{\underset{|\underline{O}|^-}{|}}{C}-R'$$

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This delocalization also makes these ligands weak nucleophiles, but this does not reduce their interest as ligands, and surprisingly, it was their weak donor ability that allowed us to prepare new types of ylide complexes [1].

When we became interested in the chemistry of these ligands we decided initially to prepare only their halide-gold(I) and -gold(III) complexes because this field was almost unexplored, and because the corresponding palladium and platinum complexes (in the organometallic chemistry of which we are also interested) had been extensively studied by Burmeister [2], who had described about 15 complexes of the type $[MX_2L_2]$ (M = Pd, Pt; X = Cl, SCN; L = several $R_3P{=}CHC(O)R'$ ligands). However, in 1984 we became aware of a paper by this author in which he proved that one of the complexes previously formulated as $[PtCl_2\{CH(PPh_3)C(O)Me\}_2]$, was actually a mixture (2/1) of the phosphonium salt $[Ph_3PCH_2C(O)Me]Cl$ and the *ortho*-metallated complex $[\overline{Pt\{CH\{P(2\text{-}C}_6H_4)Ph_2\}\{C(O)Me\}\}(\mu\text{-}Cl)]_2$ [3]. Although neither *ortho*-metallation reactions are unusual in the chemistry of platinum, and this was not the first example of *ortho*-metallation of an ylide [4], we thought it of interest to study this type of reaction. Our reasoning was that we believed that the research [3] had mainly been focused on the study of the nature of the *ortho*-metallated complex, i.e. on the final complex, and that certain questions had not been addressed, namely could the complexes $[MX_2L_2]$ be intermediates in the *ortho*-metallation reaction? and if they were, could they be isolated? If not, could they be made by any other alternative route? Finally, were all the previously-described complexes mixtures?

In this paper we present the results of work aimed at answering some of these questions involving study of the reaction between $PdCl_2$ and $Ph_3P{=}CHCO_2Me$. We also describe the synthesis of some derivatives of the corresponding Burmeister's *ortho*-metallated ylide complex $[\overline{Pd\{CH\{P(2\text{-}C}_6H_4)Ph_2\}(CO_2Me)\}(\mu\text{-}Cl)]_2$.

While this research was in progress another paper appeared from Burmeister's group [5] in which three other complexes initially assumed to be $[MX_2L_2]$ species (M = Pd, Pt; X = Cl; L = $R_3P{=}CHC(O)R'$) were shown actually to be *ortho*-metallated complexes. In the report the authors implied that were still interested only in the *ortho*-metallation reaction. In 1985 another group [6] reported two complexes $[PdCl_2\{CH(Ph_3P)CO_2R\}_2]$ (R = Pr, Bu).

## Results and discussion

### *The reaction $Cl_2Pd + Ph_3P{=}CHCO_2Me$ (1/2) in acetonitrile*

Addition of $Ph_3P{=}CHCO_2Me$ to a saturated solution of $PdCl_2$ in acetonitrile (and so containing $[PdCl_2(NCCH_3)_2]$) at room temperature gave, after 15 min of stirring, a precipitate of $[PdCl_2\{CH(PPh_3)CO_2Me\}_2]$ (**1**) in high yield (82%).

When the ylide was added to a refluxing solution of $PdCl_2$ in acetonitrile and after 3 min of stirring the suspension was quickly cooled to room temperature and filtered, and isolated solid was complex **1** (65% yield). From the solution further **1** (12%) and a mixture of $[\overline{Pd\{CH\{P(2\text{-}C}_6H_4)Ph_2\}(CO_2Me)\}(\mu\text{-}Cl)]_2$ (**2**) and $[Ph_3PCH_2CO_2Me]Cl$ (10% of the total reactants weight) were obtained.

When the last reaction is continued, the initial precipitate slowly dissolves and a greenish-yellow one appears, and after 1 h the precipitate is the *ortho*-metallated complex **2** (62% yield). If the solution is evaporated to dryness the residue is soluble in acetone; addition of diethyl ether to the acetone solution gave an oily orange product that could not be characterized. However, upon refluxing (8 h) a suspension of $PdCl_2$ and the ylide (1/2) in acetonitrile complex **2** separated (71% yield); when the solution was concentrated and diethyl ether added, a mixture of the by-product $[Ph_3PCH_2CO_2Me]Cl$ with complex **2** was obtained. Complex **2** was also obtained (60% yield) by refluxing complex **1** in acetonitrile for 1.5 h.

In our hands the reaction between $PdCl_2$ and $Ph_3P{=}CHCO_2Me$, under conditions described by Burmeister (addition of the ylide to a hot acetonitrile solution of $PdCl_2$, and the mixture allowed to cool to room temperature then stirred for 1 h) gave a precipitate of complex **1**, as reported [2], although in much lower yield (ca. 10%; reported: 64%). From the mother liquor we isolated a mixture containing mainly the phosphonium salt along with complex **2** (ca. 45%). Thus at least one of the phosphorus ylide complexes reported in [2] was correctly formulated, although it is not the main product of the reaction. However, the lower yield that we observed could be due to an error in the reported reaction time (1 h) or to the imprecision of the statement "the reaction mixture was stirred and very slowly allowed to cool to room temperature".

Our results show that: (i) the reaction gives initially complex **1** and then the *ortho*-metalated complex **2** in refluxing acetonitrile; (ii) complex **1** is a precursor of complex **2**; (iii) both complexes can be isolated independently; and (iv) the complex described in [2] as $[PdCl_2\{CH(PPh_3)CO_2Me\}_2]$ was correctly formulated.

Complex **1** was also obtained (86% yield) by treating $[PdCl_2(NCC_6H_5)_2]$ with the ylide (1/2) in acetone at room temperature.

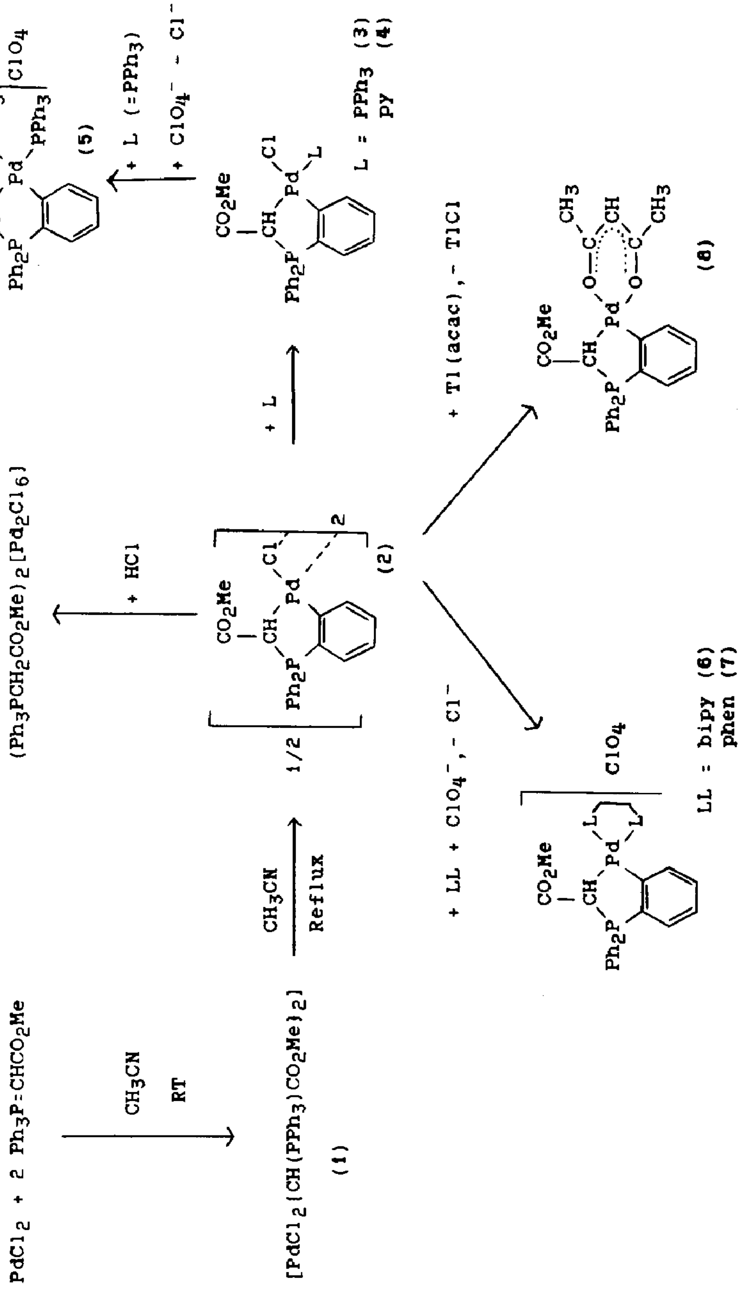
*Synthesis of derivatives of complex 2*

The addition of $PPh_3$ (1/2) to a suspension of complex **2** in dichloromethane gives a solution from which the product of bridge-splitting $[\overline{Pd\{CH\{P(2\text{-}C}_6H_4)Ph_2\}(CO_2Me)Cl(PPh_3)]$ (**3**) can be isolated. Under the same conditions, pyridine reacts with **2** also to give a solution, but concentration (3 $cm^3$) and addition of diethyl ether (25 $cm^3$) led to precipitation of complex **2**. However, when an excess (8/1) of pyridine was used $[\overline{Pd\{CH\{P(2\text{-}C}_6H_4)Ph_2\}(CO_2Me)\}Cl(py)]$ (**4**) was isolated. The equilibrium between **2** and **4** can be used to purify complex **2**, which is a yellow complex. It is possible that the greenish-yellow colour of the initially-obtained product was due to some adsorbed colloidal palladium metal.

The reaction of **2** with an excess of $PPh_3$ (1/4) also gives complex **3**. However, when this reaction is carried out in the presence of $NaClO_4$ (1/4/3) in acetone the complex $[\overline{Pd\{CH\{P(2\text{-}C}_6H_4)Ph_2\}(CO_2Me)\}(PPh_3)_2]ClO_4$ (**5**) is obtained; the reaction is fast at room temperature. However, no reaction took place between **2**, $NaClO_4$, and the bidentate ligand 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) (1/3/2) in acetone at room temperature (during 5 or 3 h, respectively) but refluxing the suspensions for 1 h gave solutions from which the complexes $[\overline{Pd\{CH\{P(2\text{-}C}_6H_4)Ph_2\}(CO_2Me)\}(LL)]ClO_4$ (LL = 2,2′-bipyridine (bipy) (**6**), 1,10-phenanthroline (phen) (**7**)) were isolated.

The synthesis of complexes **3**–**7** demonstrates the high stability of the five-membered metallacycle ring. However, this ring is broken when an excess of aqueous hydrochloric acid is added to a suspension of **2** in dichloromethane, the salt $(Ph_3PCH_2CO_2Me)_2[Pd_2Cl_6]$ being formed.

Complex **2** reacts with Tl(acac) (acacH = acetylacetone) (1/2) at room temperature in $CH_2Cl_2$, to give $[\overline{Pd\{CH\{P(2\text{-}C}_6H_4)Ph_2\}(CO_2Me)\}(acac)]$ (**8**).


PdCl2 + 2 Ph3P=CHCO2Me
CH3CN
RT
[PdCl2(CH(PPh3)CO2Me)2]
(1)
CH3CN
Reflux
1/2
(2)
+ HCl
(Ph3PCH2CO2Me)2[Pd2Cl6]
+ L
L = PPh3 (3)
py (4)
+ L (=PPh3)
+ ClO4− − Cl−
(5)
+ LL + ClO4−, − Cl−
LL : bipy (6)
phen (7)
+ Tl(acac), − TlCl
(8)

Scheme 1

### *Spectral data and structure of complexes*

As complexes **1** and **2** are very insoluble in most common solvents neither NMR nor conductivity studies could be performed. However, their analytical data, IR spectra, and the synthesis of the derivatives **3**–**8** from complex **2** adequately establish their identities. There are sufficient differences in the IR spectra of **1** and **2** to enable us to distinguished when a sample is a mixture of both. The most important ones are the bands at 805(m), 420(w) and 325(w) $cm^{-1}$ for **1**, and those at 1560(m), 1268(m, sh), 1240(w), 830(m), 485(m) and 320(w) $cm^{-1}$ for **2**. The other bands in both complexes show only small frequency differences or have less diagnostic value.

The band corresponding to $\nu$(CO) for both complexes appears at ca. 1680 $cm^{-1}$, which means that the ylides are C-coordinated [1]. The $\nu$(CO) band for complexes **3**–**8** appears also in the narrow range 1680–1690 $cm^{-1}$.

The 350–200 $cm^{-1}$ region of the IR spectra of the chloro-complexes **1**–**4** shows bands that can be tentatively assigned to $\nu$(PdCl): **1**, 325(m); **2**, 270(w), 255(w); **3**, 272(m); **4**, 340(w), 290(w), 275(w) $cm^{-1}$. As $\nu$(PdCl) *trans* to any of the carbon donor atoms in **3** appears at much lower frequency than the corresponding band for **1**, it is reasonable to assume a *trans* geometry for **1**, and this is in accord with the greater *trans* influence of an ylide (or aryl) than of a chloro ligand. We observed a similar difference between $\nu$(AuCl) *trans* to chloro (360 $m^{-1}$) and that *trans* to the ylide (315 $cm^{-1}$) in $[AuCl_3\{CH(PPh_3)CO_2Me\}]$ [1]. The low values of $\nu$(PdCl) for complex **2** are in accord with its assumed dinuclear structure involving chloro bridges. Of the three bands appearing in this region for complex **4**, the 340 $cm^{-1}$ one seems to be of too high a frequency for $\nu$(PdCl) *trans* to the ylide or the aryl ligand. The other two could arise from the presence of both isomers, as observed for solutions (see below).

Table 1 contains the significant $^1H$ and $^{31}P\{^1H\}$ NMR data. Methyl and methine resonances appear in the same regions as for some gold complexes containing the non-metallated ylide $Ph_3PCHCO_2Me$ [1]. Because coupling between the methine proton and the phosphorus of the metallacycle is usually very small or not observed,

Table 1

Proton and 31-phosphorus NMR data [a]

| Compound | $^1H$ NMR | | $^{31}P\{^1H\}$ NMR |
|---|---|---|---|
| | $\delta(CH_3)$ | $\delta$(CH) | |
| $[\overline{Pd\{CH\{P(2\text{-}C}_6H_4)Ph_2\}(CO_2Me)\}Cl(PPh_3)]$ (**3**) | 3.6 | 4.0(d)<br>*J*(PH) 9 | 16.6(d); 19.7(d)<br>*J*(PP) 19 |
| $[\overline{Pd\{CH\{P(2\text{-}C}_6H_4)Ph_2\}(CO_2Me)\}Cl(py)]$ (**4**) [b] | 3.1 | 3.6 | 16.9 |
| | 3.6 | 3.9 | 22.0 |
| $[\overline{Pd\{CH\{P(2\text{-}C}_6H_4)Ph_2\}(CO_2Me)\}(bipy)ClO_4$ (**6**) | 3.4 | 3.8(d)<br>*J*(PH) 1.8 | 22.7 |
| $[\overline{Pd\{CH\{P(2\text{-}C}_6H_4)Ph_2\}(CO_2Me)\}(phen)]ClO_4$ (**7**) | 3.5 | 4.2(d)<br>*J*(PH) 1.5 | 23.3 |
| $[\overline{Pd\{CH\{P(2\text{-}C}_6H_4)Ph_2\}(CO_2Me)\}(acac)]$ (**8**) [c] | 3.5 | 3.7 | 21.4 |
| | 1.9; 2.0 | 5.2 | |

[a] Recorded in $CDCl_3$; $\delta$ $^1H$ and $^{31}P$ NMR data in ppm relative to TMS and $H_3PO_4$, respectively; *J* in Hz. When not stated signals are singlet. [b] See text. [c] The signals of the second row correspond to the acac ligand.

it is possible that the coupling of the methine proton in **3** was with the phosphorus of $PPh_3$. In this case the complex must have both groups in *trans*. Both the $^1H$ and $^{31}P$ NMR spectra of complex **4** show duplicate signals that must arise from the presence of both possible isomers in a 3/2 ratio. Data in the first row correspond to the most abundant isomer.

Complexes **3–8** show molar conductivities in acetone, and **3** and **8** molecular weights in chloroform, which are in accord with their formulations. Table 2 gives analytical and other data for all the reported complexes. Scheme 1 summarizes the reactions reported, and shows the proposed structure of the new complexes.

## Experimental

The recording of infrared and NMR spectra, the C, H and N analyses, the conductance measurements, and the melting point determinations were carried out as described previously [1]. Molecular weights of **3** and **8** (see Table 2) were determined with a Knauer vapour pressure osmometer. Reactions were carried out at room temperature with magnetic stirring, and without special precautions against light or atmospheric moisture unless otherwise stated.

Table 2

Analytical and other data for complexes **1–8**

| Compound | M.p. (°C) | $\Lambda_M$ [a] | Analytical data (found (calc.)(%)) C | H | N | Cl | Yield (%) |
|---|---|---|---|---|---|---|---|
| $[PdCl_2\{CH(PPh_3)CO_2Me\}_2]$ (**1**) | 203 [b] | – | 58.84 | 4.65 | | 8.32 | 86 |
| | | | (59.63) | (4.53) | | (8.38) | |
| $[\overline{Pd\{CH\{P(2\text{-}C}_6H_4)Ph_2\}(CO_2Me)\}(\mu\text{-}Cl)]_2$ (**2**) | 273 [c] | – | 53.14 | 4.13 | | 7.46 | 70 |
| | | | (53.08) | (3.82) | | (7.35) | |
| $[\overline{Pd\{CH\{P(2\text{-}C}_6H_4)Ph_2\}(CO_2Me)\}Cl(PPh_3)]$ (**3**) [d] | 251 [c] | 0 | 63.74 | 4.85 | | | 75 |
| | | | (63.52) | (4.51) | | | |
| $[\overline{Pd\{CH\{P(2\text{-}C}_6H_4)Ph_2\}(CO_2Me)\}Cl(py)]$ (**4**) | 179 | 0 | 57.21 | 4.75 | 2.45 | | 61 |
| | | | (56.34) | (4.18) | (2.53) | | |
| $[\overline{Pd\{CH\{P(2\text{-}C}_6H_4)Ph_2\}(CO_2Me)\}(PPh_3)_2]ClO_4$ (**5**) | 212 | 106 | 63.73 | 5.03 | | | 81 |
| | | | (64.35) | (4.55) | | | |
| $[\overline{Pd\{CH\{P(2\text{-}C}_6H_4)Ph_2\}(CO_2Me)\}(bipy)]ClO_4$ (**6**) | 160 | 125 | 53.11 | 3.89 | 4.29 | | 71 |
| | | | (53.54) | (3.77) | (4.03) | | |
| $[\overline{Pd\{CH\{P(2\text{-}C}_6H_4)Ph_2\}(CO_2Me)\}(phen)]ClO_4$ (**7**) | 198 | 117 | 54.65 | 3.95 | 4.25 | | 62 |
| | | | (55.09) | (3.64) | (3.90) | | |
| $[\overline{Pd\{CH\{P(2\text{-}C}_6H_4)Ph_2\}(CO_2Me)\}(acac)]$ (**8**) [d] | 214 | 0 | 58.33 | 4.91 | | | 81 |
| | | | (57.97) | (4.68) | | | |

[a] In $\approx 10^{-4}$ *M* solutions in acetone ($\Omega^{-1}$ $cm^2$ $mol^{-1}$). [b] Reported 192–194°C [2]. [c] With decomposition. [d] Mol. wt. found (calc.): **3**, 734 (737); **8**, 549 (539).

*The reaction $Cl_2Pd + Ph_3P{=}CHCO_2Me$ (1/2) in acetonitrile*

*Room temperature reaction.* $Ph_3P{=}CHCO_2CH_3$ (185 mg, 0.55 mmol) was added to a saturated solution of $PdCl_2$ (49 mg, 0.28 mmol) in $CH_3CN$ (10 $cm^3$) and the suspension stirred for 15 min, then filtered. The solid washed with diethyl ether to give **1** in 82% yield.

*Reflux temperature reactions.* $PdCl_2$ (60 mg, 0.34 mmol) was refluxed with $CH_3CN$ (10 $cm^3$) and when dissolution was complete $Ph_3P{=}CHCO_2CH_3$ (226.3 mg, 0.68 mmol) was added. A green-yellow precipitate immediately appeared. After 3 min refluxing the suspension was rapidly cooled to room temperature (by immersing the flask into a water bath at room temperature), the suspension filtered, and the solid washed with diethyl ether (20 $cm^3$) to give **1** (185 mg, 65% yield). The mother liquor was evaporated to dryness and the solid extracted with acetone (30 $cm^3$). The extract was filtered to yield a second crop of **1** (35 mg, 12%). The filtrate was concentrated and diethyl ether added, to give a mixture of **2** and $(Ph_3PCH_2CO_2Me)Cl$ (30 mg).

When a similar mixture of reactants and solvent was kept at the reflux temperature for 1 h, then rapidly cooled to room temperature, complex **2** (100 mg, 0.10 mmol, 62% yield) separated.

A suspension of **1** (130 m, 0.15 mmol) in $CH_3CN$ (15 $cm^3$) was refluxed for 90 min, then allowed to cool to room temperature and filtered. Complex **2** (43 mg, 0.04 mmol) was obtained in 60% yield.

The following are the best methods for making complexes **1** and **2**. The yields in Table 2 refer to these procedures.

*$[PdCl_2\{CH(PPh_3)CO_2Me\}_2]$ (1).* To a solution of $[PdCl_2(NCC_6H_5)_2]$ (50 mg, 0.13 mmol) in acetone (20 $cm^3$) was added solid $Ph_3P{=}CHCO_2Me$ (87.2 mg, 0.26 mmol). The mixture stirred for 24 h, the resulting suspension filtered, and the yellow solid washed with diethyl ether (20 $cm^3$) to give **1**.

*$[\overline{Pd\{CH\{P(2\text{-}C}_6H_4)Ph_2\}(CO_2Me)\}(\mu\text{-}Cl)]_2$ (2).* To a suspension of $PdCl_2$ (90 mg, 0.51 mmol) in acetonitrile (20 $cm^3$) was added solid $Ph_3P{=}CHCO_2Me$ (340 mg, 1.02 mmol). The mixture was refluxed for 8 h and then allowed to cool to room temperature. The suspension was filtered and the solid washed with diethyl ether (10 $cm^3$) to give **2** as a greenish-yellow solid. **2** can be recrystallized by treating a solution in dichloromethane with pyridine (1/1), filtering the solution through $MgSO_4$, then concentrating it. When pure, **2** is yellow.

*Reaction of complex 2 and aqueous HCl.* To a suspension of **2** (27 mg, 0.03 mmol) in dichloromethane (20 $cm^3$) was added aqueous HCl (0.06 $cm^3$, ca. 5 mmol). After 1 h the resulting orange solution was concentrated (3 $cm^3$) and diethyl ether (30 $cm^3$) added to precipitate an orange solid, which was recrystallized from dichloromethane/diethyl ether to give $[Ph_3PCH_2CO_2Me]_2[Pd_2Cl_4(\mu\text{-}Cl)_2]$ (23 mg, 74% yield). M.p. 175 °C, $\Lambda_M$ 100 $\Omega^{-1}$ $cm^2$ $mol^{-1}$. Elemental analysis: Found (calc.): C, 46.82 (46.02); H, 3.86 (3.68); IR: $\nu_{asym}$ ($CO_2$) 1725 $cm^{-1}$, $\nu$(PdCl) 330 $cm^{-1}$.

*$[\overline{Pd\{CH\{P(2\text{-}C}_6H_4)Ph_2\}(CO_2Me)\}Cl(PPh_3)]$ (3).* To a suspension of **2** (60 mg, 0.06 mmol) in dichloromethane (20 $cm^3$) was added solid $PPh_3$ (33 mg, 0.13 mmol). The mixture was stirred for 30 min, the resulting colourless solution was concentrated (2 $cm^3$), and diethyl ether (30 $cm^3$) added to precipitate a white solid, which was recrystallized from dichloromethane/diethyl ether to give **3**.

$[\overline{Pd\{CH\{P(2\text{-}C}_6H_4)Ph_2\}(CO_2Me)\}Cl(py)]$ *(4)*. To a suspension of **2** (30 mg, 0.03 mmol) in acetone (2 cm$^3$) was added pyridine (0.04 cm$^3$, 0.5 mmol). After 30 min n-hexane (30 cm$^3$) was added to the resulting solution to precipitate **4** as a white solid.

$[\overline{Pd\{CH\{P(2\text{-}C}_6H_4)Ph_2\}(CO_2Me)\}(PPh_3)_2]ClO_4$ *(5)*. To a suspension of **3** (60 mg, 0.08 mmol) in acetone (25 cm$^3$) was added $PPh_3$ (21.3 mg, 0.08 mmol). The mixture was stirred for 5 h, the solvent was evaporated, the residue stirred with dichloromethane (30 cm$^3$), the suspension filtered through $MgSO_4$, and the filtrate concentrated (3 cm$^3$). Addition of diethyl ether (30 cm$^3$) then gave **5** as a white solid.

$[\overline{Pd\{CH\{P(2\text{-}C}_6H_4)Ph_2\}(CO_2Me)\}(LL)]ClO_4$ *(LL = bipy (6), LL = phen (7))*. To a suspension of **2** (60 mg, 0.06 mmol) in acetone (25 cm$^3$) were added the appropriate bidentate ligand and $NaClO_4 \cdot H_2O$ in the molar ratio 1/2/3. After 5 h (for complex **6**) or 3 h (for complex **7**) stirring at room temperature no change was observed, and so the suspension was refluxed for 1 h. The solvent was evaporated, the residue stirred with dichloromethane (30 cm$^3$), the suspensions filtered through $MgSO_4$, and the filtrate concentrated (3 cm$^3$). Addition of diethyl ether (30 cm$^3$) then gave **6** or **7** as a white solid.

$[\overline{Pd\{CH\{P(2\text{-}C}_6H_4)Ph_2\}(CO_2Me)\}(acac)]$ *(8)*. To a suspension of **2** (60 mg, 0.06 mmol) in dichloromethane (25 cm$^3$) was added solid Tl(acac) (38.3 mg, 0.13 mmol). The mixture was stirred for 3 h and the resulting suspension then filtered. The filtrate was concentrated (3 cm$^3$) and n-hexane (20 cm$^3$) added, to precipitate a white solid, which was recrystallized from dichloromethane/n-hexane to give **8**.

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## References

1 (a) J. Vicente, M.T. Chicote, J.A. Cayuelas, J. Fernandez-Baeza, P.G. Jones, G.M. Sheldrick and P. Espinet, J. Chem. Soc. Dalton, (1985) 1; (b) J. Vicente, M.T. Chicote, I. Saura-Llamas, J. Turpin and J. Fernandez-Baeza, J. Organomet. Chem., 333 (1987) 129; (c) J. Vicente, M.T. Chicote, J. Fernandez-Baeza, J. Martin, I. Saura-Llamas and J. Turpin, ibid., 331 (1987) 4; (d) J. Vicente, M.T. Chicote, I. Saura-Llamas, P.G. Jones, K. Meyer-Bäse and C.F. Erdbrügger, Organometallics, 7 (1988) 997.

2 E.T. Weleski, Jr., J.L. Silver, M.D. Jansson and J.L. Burmeister, J. Organomet. Chem., 102 (1975) 365.

3 M.L. Illingsworth, J.A. Teagle, J.L. Burmeister, W.C. Fultz, and A.L. Rheingold, Organometallics, 2 (1983) 1364.

4 J.C. Baldwin and W.C. Kaska, Inorg. Chem., 18 (1979) 686.

5 J.A. Teagle and J.L. Burmeister, Inorg. Chim. Acta, 118 (1986) 65.

6 R. Sanehi, R.N. Bansal and R.C. Mehrotra. Indian J. Chem. Sect. A, 24 (1985) 1031; Chem. Abstr., 106 (1987) 18786c.