

# Synthesis, structure and reactivity of Pt<sup>II</sup> complexes containing the [*o*-(di-*o*-tolylphosphino)benzyl] cyclometalated ligand towards $\alpha$ -stabilized phosphorus ylides

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Received 10 November 1997

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## Abstract

The reaction of [Pt(C<sup>^</sup>P)(NCMe)<sub>2</sub>]ClO<sub>4</sub> **2** [C<sup>^</sup>P = *ortho*-(di-*ortho*-tolylphosphino)benzyl], with the  $\alpha$ -stabilized phosphorus ylides Ph<sub>3</sub>P=C(H)R (R = COMe, COPh, COOMe, CN) in a 1:1 molar ratio results in the formation of [Pt(C<sup>^</sup>P){C(H)(R)PPh<sub>3</sub>}(NCMe)]ClO<sub>4</sub> (R = COMe **3**, COPh **4**, COOMe **5**, CN **6**). Complexes **3–6** appear as single isomers in which the ylide is selectively C-coordinated *trans* to the P atom of the C<sup>^</sup>P ligand. The displacement of the remaining coordinated NCMe ligand by adding more ylide was only successfully accomplished with Ph<sub>3</sub>P=C(H)CN, giving [Pt(C<sup>^</sup>P){C(H)(CN)PPh<sub>3</sub>}{NC–C(H)PPh<sub>3</sub>}]ClO<sub>4</sub> **7**, in which one ylide is C-coordinated *trans* to the P atom of the C<sup>^</sup>P ring and the other ylide is N-coordinated *trans* to the C atom, showing the ambidentate character of Ph<sub>3</sub>P=C(H)CN as a ligand. The reaction of [Pt(C<sup>^</sup>P)( $\mu$ -Cl)]<sub>2</sub> **1** with PPh<sub>3</sub> (1:2 molar ratio, CH<sub>2</sub>Cl<sub>2</sub>, r.t.) results in the formation of the two expected isomers *trans*- and *cis*-[Pt(C<sup>^</sup>P)Cl(PPh<sub>3</sub>)] (**8** and **9**, respectively). The *trans* isomer **8** is obtained as a single product by heating the mixture of isomers in toluene or, in one step, by carrying out the reaction of **1** with PPh<sub>3</sub> in refluxing toluene. Treatment of **8** with TiClO<sub>4</sub> in NCMe gives *trans*-[Pt(C<sup>^</sup>P)(PPh<sub>3</sub>)(NCMe)]ClO<sub>4</sub> **10** which can also be obtained by the reaction of **2** with PPh<sub>3</sub>. Complex **10** reacts with Ph<sub>3</sub>P=C(H)R (R = COMe, COOMe, CN) in a 1:1 molar ratio resulting in the displacement of the NCMe ligand and the formation of [Pt(C<sup>^</sup>P){OC(R')=C(H)PPh<sub>3</sub>}]PPh<sub>3</sub>ClO<sub>4</sub> (R' = Me **11**, OMe **12**) or [Pt(C<sup>^</sup>P){NC–C(H)=PPh<sub>3</sub>}]PPh<sub>3</sub>ClO<sub>4</sub> **13** in which the ylide ligand is selectively O- (**11**, **12**) or N-coordinated (**13**). The reaction of [Pt(C<sup>^</sup>P)( $\mu$ -Cl)]<sub>2</sub> **1** with Ph<sub>3</sub>P=C(H)R (R = COMe, COOMe, CN) in a 1:2 molar ratio results in the cleavage of the chlorine-bridge system and the formation of [Pt(C<sup>^</sup>P)Cl{C(H)(R)PPh<sub>3</sub>}] (R = COMe **14**, COOMe **15**, CN **16**) as single isomers in which the ylide is C-coordinated *trans* to the P atom of the C<sup>^</sup>P ligand. Complex **14** reacts with TiClO<sub>4</sub> and Ph<sub>3</sub>P=C(H)COMe (1:1:1 molar ratio) giving [Pt(C<sup>^</sup>P){OC(Me)=C(H)PPh<sub>3</sub>}]<sub>2</sub>ClO<sub>4</sub> **17**. Complex **17** shows two interesting features: the isomerization of the C-linked ylide in **14** to an O-bonded one in **17** and the simultaneous presence of two O-coordinated ylides to the same metal center. The selectivity in the observed coordination modes and the preferred coordination of the ylides *trans* to the P atom of the C<sup>^</sup>P ligand are discussed in terms of electronic and steric factors. © 1998 Elsevier Science S.A. All rights reserved.

**Keywords:** Platinum; C<sup>^</sup>P-cyclometalated; Phosphorus ylides

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## 1. Introduction

Over the last few years our research group has been interested in the coordination chemistry of the  $\alpha$ -stabi-

lized phosphorus ylides Ph<sub>3</sub>P=C(H)R (R = COMe, COPh, COOMe, CN), due to the fact that these ylides can behave as ambidentate ligands [1–4]. The main body of our study comprises the reactivity of the aforementioned ylides Ph<sub>3</sub>P=C(H)R towards C,N-cyclometalated complexes of Pd<sup>II</sup> of stoichiometry [Pd(C<sup>^</sup>N)(L)(L')]ClO<sub>4</sub> or [Pd( $\mu$ -Cl)(C<sup>^</sup>N)]<sub>2</sub>, where

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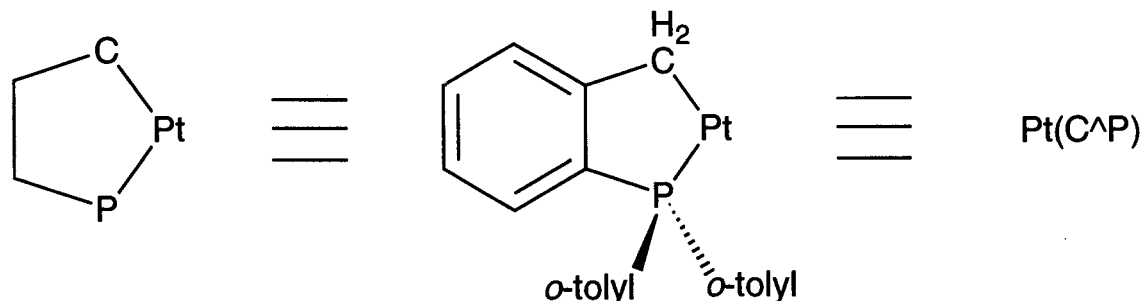


Fig. 1. Schematic representations of the ligand [*o*-(di-*o*-tolylphosphino)benzyl].

$C^{\wedge}N$  = (2-(dimethylamino)methyl)phenyl (or *dm*ba) or *S*- $\alpha$ -(2-(dimethylamino)ethyl)phenyl (or *S*-*dm*phea) and  $L$  = phosphine, phosphite, pyridine,  $L' = NCMe$  or  $L = L' = NCMe$ . In these studies [1–4] we have actually shown the ambidentate character of the  $\alpha$ -stabilized ylides and how it is possible to predict both the coordination site of the ylide (when there are two possibilities) and the donor atom linked to the metal (O- versus C-coordination, N- versus C-coordination) taking into account a simple effect such as the antisymbiotic behaviour of the  $Pd^{II}$  centre [5,6] and the different electronic and steric requirements of the ylides in their different coordination modes.

This previous work has prompted us to extend this kind of chemistry to other metals and cyclometalated systems, with the aim of obtaining new structural situations. We have thus explored the reactivity of the fragment  $[Pt(C^{\wedge}P)]$  [7,8] [ $C^{\wedge}P = ortho$ -(di-*ortho*-tolylphosphino)benzyl] (see Fig. 1) towards  $\alpha$ -stabilized ylides on the grounds that the donor atoms of the cyclometalated  $C^{\wedge}P$  ligand show different electronic and steric properties than those of the ligands  $C^{\wedge}N$  (we now have two soft donor atoms with a high *trans* influence and, in addition, a highly steric-demanding  $P(o\text{-tolyl})_2$  group). Moreover, the platinum atom reveals symbiotic or antisymbiotic behaviour depending on the ligands that are present in the molecule [5], although its behaviour is usually marked by 'orbital-controlled' interactions, i.e. it behaves in an antisymbiotic manner [6]. In this paper we report the results obtained with this kind of chemistry.

## 2. Results and discussion

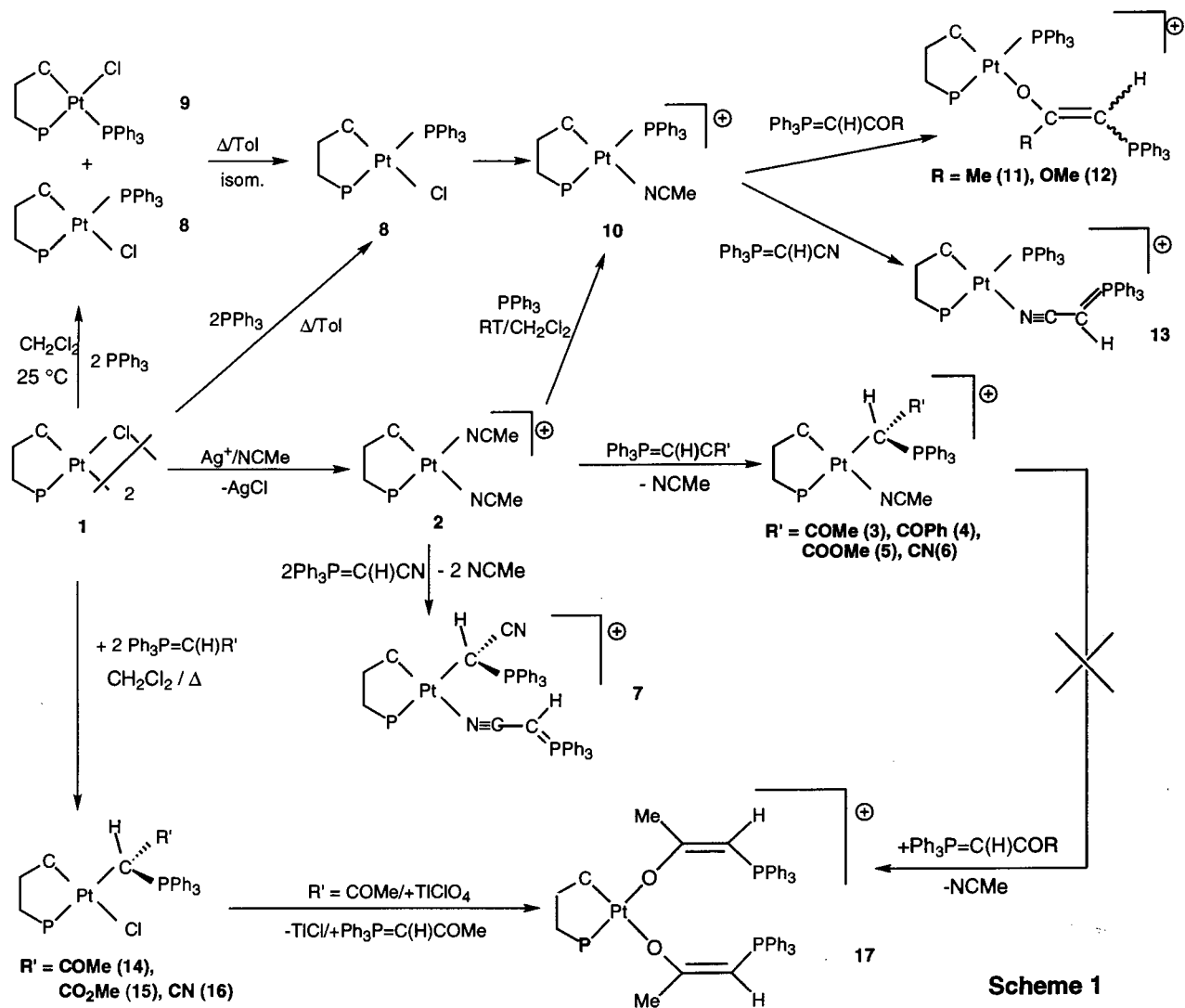
### 2.1. Reactions of $[Pt(C^{\wedge}P)(NCMe)_2]ClO_4$ with ylides

The synthesis of the starting product  $[Pt(C^{\wedge}P)(NCMe)_2]ClO_4$  **2** from  $[Pt(\mu\text{-Cl})(C^{\wedge}P)]_2$  **1** and  $AgClO_4$  (1:2 molar ratio) in  $NCMe$  has been previously described [7]. The reaction of **2** with the stoichiometric amount of the ylides  $Ph_3P=C(H)R$  ( $R = COMe$ ,  $COPh$ ,  $COOMe$ ,  $CN$ ; 1:1 molar ratio) in  $CH_2Cl_2$  at r.t. results

in the formation of the mono-ylide complexes  $[Pt(C^{\wedge}P)(Ph_3PCHR)(NCMe)]ClO_4$  ( $R = COMe$  **3**,  $COPh$  **4**,  $COOMe$  **5**,  $CN$  **6**), according to their elemental analyses of C, H, N and mass spectra (see Section 3).

When reactions between **2** and the keto-stabilized ylides  $Ph_3P=C(H)COR'$  are performed in the same experimental conditions but in a 1:2 molar ratio (Pt:ylide), the formation of the corresponding bis-ylide complexes have not been observed, and only the mixture of the mono-ylide complex and the corresponding free ylide (**3** and  $Ph_3P=C(H)COMe$ , etc) is detected. The same result is observed if the reaction is performed in more drastic conditions ( $CHCl_3$  reflux) and the prolonged treatment of **2** with an excess of ylide in a solvent with a high boiling point (toluene, reflux) leads to the decomposition of the mixture and deposition of black platinum. However, the reaction between **2** and two equivalents of  $Ph_3P=C(H)CN$  ( $CH_2Cl_2$ , r.t.) results in the formation of the bis-ylide complex  $[Pt(C^{\wedge}P)(Ph_3PCHCN)_2]ClO_4$  **7** according to elemental analyses and its mass spectrum (see Section 3). This behaviour is similar to that we have previously observed [2,3] in  $C^{\wedge}N$ -cyclometalated derivatives of palladium (II), except for the synthesis of complex **6** which has no equivalent in palladium chemistry [2].

The elucidation of the coordination mode of the ylide(s) and the stereochemistry of the resulting complexes **3–7** can be inferred from the IR and NMR data. The IR spectra of **3**, **4** and **5** show the presence of absorptions attributed to the coordinated  $NCMe$  ligand (about  $2300\text{--}2200\text{ cm}^{-1}$ ), characteristic absorptions of the  $C^{\wedge}P$  group [7] and a strong absorption in the  $1700\text{--}1600$  region attributed to the carbonyl group of the coordinated ylide. This latter absorption appears to be shifted to higher energies with respect to that in the corresponding free ylide [ $\Delta\nu = \nu_{CO}(\text{complex}) - \nu_{CO}(\text{free ylide}) = 112$  (**3**),  $100$  (**4**),  $65$  (**5**)  $\text{cm}^{-1}$ ] which is indicative of C-coordination [1,3]. The IR spectra of complexes **6** and **7** show a broad absorption in the  $2230\text{--}2170\text{ cm}^{-1}$  region, attributed to the  $CN$  group of the coordinated ylide (although for **6** it also contains the contribution of the  $NCMe$  ligand) and also a shift



to higher energies with respect to that in the free ylide. In this case, as has been discussed [2], this shift could mean that the ylide is either C-bonded (in the usual way) or N-bonded (end-on nitrile).

The NMR spectra of 3–5 show, at r.t., broad, poorly resolved resonances. Measurements at low temperatures ( $\text{CD}_2\text{Cl}_2$ , 188 K) provide more informative spectra. Thus, the  $^1\text{H}$ -NMR spectra of 3–5 show an AB spin system for the diastereotopic  $\text{CH}_2$  protons and two singlet resonances for the methyl groups of the  $\text{C}^{\wedge}\text{P}$  ligand. The ylidic CH proton appears as a doublet for 3 and 4, shifted downfield with respect to that in the corresponding free ylide, and with a value of the coupling constant  $^2J_{\text{P}-\text{H}}$  of about 11 Hz, notably smaller than that found in the free ylide. The ylidic CH resonance in 5 appears as a doublet of doublets, probably by additional coupling with the P atom of the  $\text{C}^{\wedge}\text{P}$  ligand. The disappearance of the molecular plane as a symmetry plane (reflected in the  $\text{C}^{\wedge}\text{P}$  ligand) and the

spectroscopic parameters of the ylidic CH resonance points to C-coordination of the ylide [3]. Moreover, the  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra show the same pattern of resonances for 3–5: a doublet signal (about 27 ppm) with  $^{195}\text{Pt}$  satellites ( $^1J_{\text{Pt}-\text{P}}$  about 3400 Hz) attributed to the P atom of the  $\text{C}^{\wedge}\text{P}$  ligand and another doublet, in the same region, also with  $^{195}\text{Pt}$  satellites in 3 ( $^2J_{\text{Pt}-\text{P}}$  about 78 Hz), attributed to the ylidic phosphorus. The chemical shift of the P-ylidic resonance and the observation of a low but observable value for the coupling constant  $J_{\text{Pt}-\text{P}(\text{ylide})}$  are in line with C-coordination, whilst the shape of the resonances, which are doublets due to the P–P coupling, indicates a relative *trans* location of the C (ylide) and P ( $\text{C}^{\wedge}\text{P}$  ligand) atoms. The structure depicted in Scheme 1 would account for all these facts.

Similar conclusions can be obtained from the NMR spectra of 6. The CH ylidic proton appears in the  $^1\text{H}$ -NMR spectrum as a doublet of doublets at 3.93 ppm and shows  $^{195}\text{Pt}$  satellites, providing proof of the

C-coordination of the ylide *trans* to the P atom of the C $\wedge$ P ligand. The  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **6** shows two doublet resonances, each one with  $^{195}\text{Pt}$  satellites of different magnitude. The structure depicted in Scheme 1 for **6** represents the experimental data obtained. The  $^1\text{H}$ -NMR spectrum of **7** reveals a very similar pattern of resonances to that of **6**, except for the presence of an additional doublet at high field (1.27 ppm,  $^2J_{\text{P-H}} = 4.8$  Hz) which is assigned to the CH ylidic proton of the ylide  $\text{Ph}_3\text{P}=\text{C}(\text{H})\text{CN}$  N-coordinated [2]. Obviously, this N-coordination must be produced *trans* to the C atom of the C $\wedge$ P ligand. Moreover, the  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **7** shows two doublet resonances about 26 ppm with  $^{195}\text{Pt}$  satellites of different magnitudes, attributed to the P atoms of the C $\wedge$ P ligand and the C-coordinated ylide, mutually *trans*, and a singlet signal at 22.7 ppm attributed to the P atom of the N-bonded ylide [2]. Thus, the structure of **7** shown in Scheme 1 accounts for these observations and, once again, clearly shows the ambidentate character (C- versus N-coordination) of the cyano ylide  $\text{Ph}_3\text{P}=\text{C}(\text{H})\text{CN}$ .

The selectivity in the C-coordination *trans* to the P atom of the C $\wedge$ P ligand could be related to steric interactions, given that the voluminous C-bonded ylide would be more stable when coordinated in the less hindered of the two possible positions in the starting compound **2**, that is, *trans* to the P atom.

## 2.2. Synthesis of *trans*- and *cis*-[Pt(C $\wedge$ P)Cl(PPh $_3$ )] (**8**, **9**)

The reaction of the starting dimer  $[\text{Pt}(\mu\text{-Cl})(\text{C}\wedge\text{P})]_2$  **1** with the stoichiometric amount of PPh $_3$  (1:2 molar ratio) in  $\text{CH}_2\text{Cl}_2$  at r.t. produces the gradual dissolution of the dinuclear complex, giving a colorless solution from which a white solid of  $[\text{PtCl}(\text{C}\wedge\text{P})(\text{PPh}_3)]$  stoichiometry can be obtained. Two absorptions are observed in the  $\nu(\text{Pt}-\text{Cl})$  stretching region [9], suggesting the presence of two isomers. This fact is confirmed by the presence in the  $^{31}\text{P}\{^1\text{H}\}$ -NMR of two AB spin systems. The major one (4:1 molar ratio) reveals similar values of the coupling constant  $^1J_{\text{Pt-P}}$  (3126.5, 3047.7 Hz) and a value of  $^2J_{\text{P-P}}$  of 446.6 Hz, both facts indicating the P-*trans*-to-P arrangement [10] (complex **8**). The minor one reveals very different values of  $^1J_{\text{Pt-P}}$  (4370.4, 1834.5 Hz) and a value of  $^2J_{\text{P-P}}$  of 10.3 Hz, clearly showing a *cis* arrangement [10,11] of the P atoms (complex **9**), as depicted in Scheme 1.

The selective synthesis of the *trans* derivative **8** was carried out either by refluxing the mixture of compounds **8** and **9** in toluene or, alternatively, in one step, breaking the chlorine bridge with PPh $_3$  in refluxing toluene (see Section 3). Similar *cis*-*trans* isomerization processes have already been described [12].

## 2.3. Synthesis of *trans*-[Pt(C $\wedge$ P)(PPh $_3$ )(NCMe)](ClO $_4$ ) (**10**) and reactions with ylides

The synthesis of **10** was carried out by two alternative synthetic methods: (a) treatment of *trans*-[PtCl(C $\wedge$ P)(PPh $_3$ )] **8** with  $\text{TIClO}_4$  (1:1 molar ratio) in refluxing NCMe and (b) treatment of  $[\text{Pt}(\text{C}\wedge\text{P})(\text{NCMe})_2]\text{ClO}_4$  **2** with PPh $_3$  (1:1 molar ratio) in  $\text{CH}_2\text{Cl}_2$  at r.t.. In both cases a solid with  $[\text{Pt}(\text{C}\wedge\text{P})(\text{PPh}_3)(\text{NCMe})](\text{ClO}_4)$  (**10**) stoichiometry was obtained, according to their analytical data and mass spectra (see Section 3). The spectral parameters (IR, NMR) were identical, irrespective of the synthetic method.

The IR spectrum confirms the presence of coordinated NCMe (absorptions at 2317 and 2287  $\text{cm}^{-1}$ ) and phosphine ligands. The  $^1\text{H}$ -NMR spectrum shows the presence of all the expected resonances and the  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum shows the presence of an AB spin system with chemical shifts that are very similar to those of the starting compound **8**, as well as coupling constant values in keeping with a *trans* arrangement of the P atoms ( $^1J_{\text{Pt-P}} = 2966.3, 2934.1$  Hz;  $^2J_{\text{P-P}} = 383.7$  Hz) [10] (see Scheme 1).

It is noteworthy to point out the selectivity shown in the displacement of the NCMe ligand *trans* to the P atom of the P(*o*-Tol) $_2$  group. Even if it would seem that the more labilized position would be that which is *trans* to the C atom [7], the steric congestion produced by the bulky *ortho*-tolyl substituents appears to be the reason for the selective coordination *trans* to the P atom, in order to minimize steric repulsions. This fact could also be responsible for the selective C(ylide)-*trans*-P(tol) $_2$  coordination observed in compounds **3**–**7** and for the higher thermodynamic stability of complex **8** with respect to **9**.

The NCMe ligand present in **10** can easily be replaced by other groups and we have tested the reactivity of **10** towards  $\alpha$ -stabilized ylides. The reaction of **10** with the ylides  $\text{Ph}_3\text{P}=\text{C}(\text{H})\text{COR}$  (R = Me, Ph, OMe) and  $\text{Ph}_3\text{P}=\text{C}(\text{H})\text{CN}$  (1:1 molar ratio,  $\text{CH}_2\text{Cl}_2$ , r.t.) results in the formation of the corresponding cationic derivatives with  $[\text{Pt}(\text{C}\wedge\text{P})(\text{PPh}_3)(\text{Ph}_3\text{PCHCOR})](\text{ClO}_4)$  (R = Me **11**, OMe **12**) and  $[\text{Pt}(\text{C}\wedge\text{P})(\text{PPh}_3)(\text{Ph}_3\text{PCHCN})](\text{ClO}_4)$  **13** stoichiometry, according to their elemental analyses and mass spectra (see Section 3). The less basic ylide  $\text{Ph}_3\text{P}=\text{C}(\text{O})\text{Ph}$  did not yield an apparent reaction and the mixture of the starting compounds remained unchanged.

The IR spectra of **11** and **12** show the  $\nu(\text{CO})$  absorption of the ylide ligand shifted to lower energies with respect to that in the free ylide, suggesting an O-coordination [1,3] of this ligand. The IR spectrum of **13** shows the  $\nu(\text{CN})$  absorption shifted to higher energies, which is in keeping with both C- and N-coordination [2].

The NMR spectra of **11** and **12** are in line with the O-coordination inferred from their IR spectra. Thus, the  $^1\text{H-NMR}$  spectrum of **11** shows two sets of resonances with the same pattern but with a different intensity (1.44:1 molar ratio), suggesting the presence of two structural isomers. In both cases the ylidic proton appears as a doublet, with a value of the coupling constant  $^2J_{\text{P-H}}$  of around 20 Hz which is very similar to that observed in the free ylide [13,14], and points to O-coordination [1,3]. The two isomers present are due to the different conformation of the ylide in each complex, cisoid and transoid (see Scheme 1), the transoid isomer being the more abundant one. Similar conclusions can be derived from the  $^1\text{H-NMR}$  spectrum of **12** although in this case the transoid/cisoid molar ratio is 3:1. The  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **11** shows the presence of two AB spin systems, each with similar chemical shifts and coupling constants to those of the starting product **10**, which suggests that the P-*trans*-P arrangement is preserved. In addition, two resonances at 14.01 and 13.38 ppm are attributed to the ylidic P atom, showing high field shifts compared to the corresponding value in the free ylide, this is also in keeping with O-coordination [1,3]. The structures depicted in Scheme 1 are proposed on the basis of these data.

The  $^1\text{H-NMR}$  spectrum of complex **13** shows a single set of resonances in which the doublet of triplets centered at 1.06 ppm ( $^2J_{\text{P-H}} = 5.2$  Hz,  $^5J_{\text{P-H}} = 0.9$  Hz) should be noted. This resonance is attributed to the ylidic CH proton and both the chemical shift and the coupling constant  $^2J_{\text{P-H}}$  are indicative of a N-coordination of the ylide (end-on nitrile form) [2], as depicted in Scheme 1. The observation of an AB spin system in the  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **13**, attributed to the  $\text{PPh}_3$  and the mutually *trans* C $\wedge$ P ligands and a singlet resonance at 21.95 ppm shifted only slightly upfield with respect to the free ylide [15], provide further arguments in favor of N-coordination.

In these cases, the selectivity in the coordination modes of the ylides (always using the heteroatom as the donor atom), seems to be related to steric congestions. In fact, the vacant position in the starting compound **10** is located between two very bulky groups, the  $\text{PPh}_3$  ligand and the  $\text{P}(o\text{-tol})_2$  fragment. Both the O- and the N-coordination modes are less sterically demanding than the C-form and, probably due to this fact, the former two are the preferred coordination modes. This behaviour is closely related to that observed in C,N-cyclometalated ligands [1–3].

#### 2.4. Reactions of $[\text{Pt}(\mu\text{-Cl})(\text{C}\wedge\text{P})_2]$ with ylides

The reaction of the chlorine bridge dimer  $[\text{Pt}(\mu\text{-Cl})(\text{C}\wedge\text{P})_2]$  **1** with the stoichiometric amount of the

ylides  $\text{Ph}_3\text{P}=\text{C}(\text{H})\text{COR}$  (R = Me, Ph, OMe) and  $\text{Ph}_3\text{P}=\text{C}(\text{H})\text{CN}$  (1:2 molar ratio) in refluxing  $\text{CH}_2\text{Cl}_2$  results in the gradual dissolution of the initial suspension. From the resulting colorless solution, white solids of  $[\text{PtCl}(\text{C}\wedge\text{P})(\text{Ph}_3\text{PCHCR}')]_2$  stoichiometry (R' = COMe **14**, COOMe **15**, CN **16**) were obtained after the usual work-up. No reaction was observed for the less basic ylide  $\text{Ph}_3\text{P}=\text{C}(\text{H})\text{COPh}$ , even after prolonged treatment at the reflux temperature.

The IR spectra of **14** and **15** show that the carbonyl absorption is shifted to higher energies, thus indicating the C-coordination of the ylide, as discussed in Section 2.1. The IR spectrum of **16** shows that the  $\nu(\text{CN})$  stretching mode is shifted to higher energies, in keeping with both C- and N-coordination modes. Only one absorption is observed for the  $\nu(\text{Pt-Cl})$  stretching, suggesting that only one isomer is obtained. This  $\nu(\text{Pt-Cl})$  absorption appears at higher wavenumbers than in the starting compound **1**, in line with the change from the bridging mode to the terminal mode for the chlorine ligand.

The NMR spectra confirm C-coordination which, in all cases, is *trans* to the P atom of the  $\text{P}(o\text{-tol})_2$  group. Thus, the  $^1\text{H-NMR}$  spectrum of **14** shows a single set of signals, in keeping with the presence of only one isomer, in which the ylidic CH resonance appears as a doublet of doublets ( $^2J_{\text{P-H}} = 8.5$  Hz,  $^3J_{\text{P-H}} = 3.2$  Hz) flanked by  $^{195}\text{Pt}$  satellites ( $^2J_{\text{Pt-H}} = 60$  Hz). While the value of  $^2J_{\text{P-H}}$  confirms C-coordination, the observation of the coupling constant  $^3J_{\text{P-H}}$  means that C-coordination has taken place *trans* to a second P atom (that of the  $\text{P}(o\text{-tol})_2$  group). The  $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **14**, however, shows two resonances; a broad singlet at about 27 ppm with  $^{195}\text{Pt}$  satellites (3790 Hz) attributed to the P atom of the C $\wedge$ P ring and a doublet at higher field (about 25 ppm,  $^3J_{\text{P-P}} = 10$  Hz) also with  $^{195}\text{Pt}$  satellites (53 Hz) attributed to the P atom of the ylide ligand. All these facts confirm the proposed structure which is depicted in Scheme 1. Similar conclusions can be inferred from the analysis of the NMR spectra of **15** and **16**.

As has been discussed, the selective C-*trans*-to-P-coordination observed seems to be related to steric repulsions. However, this behavior is quite different to that observed with the C,N-cyclometalated complexes [1–3]. In fact, the  $\alpha$ -ketostabilized ylides  $\text{Ph}_3\text{P}=\text{C}(\text{H})\text{COR}$  were not nucleophilic enough to produce the breakage of the bridging chlorine system while in this system **1** reacts slowly giving the corresponding products of the bridge cleavage. Moreover, the cyano-stabilized ylide  $\text{Ph}_3\text{P}=\text{C}(\text{H})\text{CN}$  produces a mixture of C- and N-coordinated ylides after reaction with  $[\text{Pd}(\mu\text{-Cl})(\text{C}\wedge\text{N})_2]$  (C $\wedge$ N = dmbs, *R*-dmphea) while, in this case, the C-coordination mode is observed selectively.

### 2.5. Synthesis of $[Pt(C^{\wedge}P)\{OC(Me)=C(H)PPh_3\}_2](ClO_4)$ (**17**)

Further reactivity of complexes **14–16** have been explored. Treatment of complex **14**  $[Pt-Cl(C^{\wedge}P)\{C(H)PPh_3(COMe)\}]$  with the stoichiometric amounts of  $TiClO_4$  and, following this, the filtration of  $TiCl$ ,  $Ph_3P=C(H)COMe$  (1:1:1 molar ratio, THF, r.t.) results in the formation of a solid of  $[Pt(C^{\wedge}P)(PPh_3CHCOMe)_2](ClO_4)$  stoichiometry (**17**), according to elemental analyses and mass spectrum.

The coordination mode(s) of the ylide is elucidated the analysis of the IR and NMR spectra. The IR spectrum of **17** shows a strong absorption, attributed to the carbonyl groups, at  $1505\text{ cm}^{-1}$ , thus clearly pointing to a shift to lower energies than those in the free ylide and indicating the O-coordination of the ylide. The  $^1H$ -NMR spectrum shows, in addition to the expected resonances for the  $C^{\wedge}P$  ligand, two resonances of relative intensity 1:1 at 4.33 and 3.87 ppm, attributed to the ylidic  $CH$  protons. The signal centered at 4.33 shows a doublet of doublets structure ( $^2J_{P-H} = 24\text{ Hz}$ ,  $^5J_{P-H} = 2.3\text{ Hz}$ ). The value of  $^2J_{P-H}$  clearly shows the O-coordination and the value of  $^5J_{P-H}$  its coordination *trans* to the P atom of the  $C^{\wedge}P$  ring. The signal centered at 3.87 ppm is a doublet with a coupling constant value of  $^2J_{P-H} = 23\text{ Hz}$ , also indicating the O-coordination *trans* to the C atom of the  $C^{\wedge}P$  ligand. Both O-coordinated ylide ligands have a cisoid conformation, as can be inferred from the shape of the *COMe* resonance, doublet due to the coupling with the *trans* ylidic P atom ( $^4J_{P-H}$  around 1–2 Hz). The  $^{31}P\{^1H\}$ -NMR spectrum of **17** shows two resonances in the typical region of O-coordination (14.28 and 13.49 ppm) and the resonance attributed to the  $C^{\wedge}P$  ring at 10.91 ppm ( $^1J_{Pt-P} = 4933.6\text{ Hz}$ ). All these data are in keeping with the structure depicted in Scheme 1.

In our experience, this behaviour does not have any precedent. We have shown the ambidentate character of the ylide  $Ph_3P=CHCN$  in compound **7** allowing the simultaneous coordination of two ylides in different coordination modes. We have also shown that the keto-stabilized ylides can also behave as ambidentates (complexes **3–5** or **14, 15** and complexes **11, 12**), but we have not been successful in synthesizing a similar complex to **7**. In addition, all efforts to synthesize this kind of product starting from **3–5** have led to the obtention of the starting products or to decomposition. Complex **17** contains two ylides, but both are O-coordinated. The question of why a simultaneous C- and O-coordination over the same metal is not possible still remains unanswered, taking into account, in addition, that the synthesis of **17** starting from **14** must occur with an isomerization of one of the ylides, from C- to O-coordinated. Further studies are in progress in order to shed light on this maverick behaviour.

## 3. Experimental section

### 3.1. General comments

Solvents were dried and distilled prior to use by standard methods. Elemental analyses of C, H, N were carried out on a Perkin-Elmer 2400 microanalyser. Infrared spectra ( $4000\text{--}200\text{ cm}^{-1}$ ) were recorded on a Perkin-Elmer 883 infrared spectrophotometer in nujol mulls between polyethylene sheets.  $^1H$  (300.13 MHz) and  $^{31}P\{^1H\}$  (121.49 MHz)-NMR spectra were recorded from  $CDCl_3$ ,  $CD_2Cl_2$  or  $(CD_3)_2CO$  solutions at r.t. (unless otherwise stated) on a Bruker ARX-300 spectrometer;  $^1H$ -NMR spectra were referenced using the solvent signal as an internal standard and  $^{31}P\{^1H\}$ -NMR spectra were externally referenced to  $H_3PO_4$  (85%). Mass spectra (positive ion FAB) were recorded on a V.G. Autospec. spectrometer from  $CH_2Cl_2$  solutions. The starting materials  $[Pt(\mu-Cl)(C^{\wedge}P)]_2$  **1**,  $[Pt(C^{\wedge}P)(NCMe)_2]ClO_4$  **2** [7],  $Ph_3P=C(H)COR$  ( $R = Me, Ph, OMe$ ) [13,14] and  $Ph_3P=C(H)CN$  [15] were prepared according to published methods.

### 3.2. Synthesis of $[Pt(C^{\wedge}P)\{C(H)(COMe)(PPh_3)\}_2](NCMe)ClO_4$ **3**

To a solution of  $[Pt(C^{\wedge}P)(NCMe)_2]ClO_4$  **2** (0.200 g, 0.294 mmol) in 20 ml of  $CH_2Cl_2$  the ylide  $Ph_3P=C(H)COMe$  (0.093 g, 0.294 mmol) was added and the resulting solution was stirred at r.t. for 10 min. The solvent was then evaporated to dryness and the residue was washed with  $Et_2O$  (25 ml) giving **3** as a white solid which was collected and air dried. Obtained: 0.242 g (86% yield). Complex **3** was recrystallized from  $CH_2Cl_2/n$ -hexane, giving poor, colorless, crystals of  $3 \cdot 0.5CH_2Cl_2$ , which were used for analytical and NMR measurements (the amount of  $CH_2Cl_2$  was quoted from the  $^1H$ -NMR of the crystals).

Analysis: Calculated ( $C_{44}H_{42}ClNO_5P_2Pt \cdot 0.5CH_2Cl_2$ ,  $999.76\text{ g mol}^{-1}$ ): C, 53.46; H, 4.33; N, 1.40. Found: C, 53.79; H, 3.98; N, 1.28. IR ( $\nu$ ,  $cm^{-1}$ ): 2326, 2291 ( $\nu_{NCMe}$ ), 1651 ( $\nu_{CO}$ ), 797, 586, 563, 476, 466 ( $\nu_{C^{\wedge}P}$ ). Mass spectrum (FAB<sup>+</sup>) [ $m/z$ , (%): 816 (85%) [(M-NCMe)<sup>+</sup>].  $^1H$ -NMR ( $CD_2Cl_2$ , 188 K):  $\delta$  (ppm), 7.66–6.74 (m, 27H, Ph + *o*-MeC<sub>6</sub>H<sub>4</sub>), 4.39 (d, 1H, *CH* ylide,  $^2J_{P-H} = 8.0\text{ Hz}$ ), 3.26, 3.11 (AB spin system, 2H, *CH*<sub>2</sub>,  $^2J_{H-H} = 16.2\text{ Hz}$ ), 2.66, 2.44, 2.39, 2.08 (4s, 12H, *2o*-MeC<sub>6</sub>H<sub>4</sub> + *COMe* + *NCMe*).  $^{31}P\{^1H\}$ -NMR ( $CD_2Cl_2$ , 188 K):  $\delta$  (ppm), 27.64 (d,  $C^{\wedge}P$ ,  $^1J_{Pt-P} = 3391\text{ Hz}$ ,  $^3J_{P-P} = 8\text{ Hz}$ ), 26.24 (d,  $-P^+Ph_3$ ,  $^2J_{Pt-P} = 78\text{ Hz}$ ).

### 3.3. Synthesis of $[Pt(C^{\wedge}P)\{C(H)(COPh)(PPh_3)\}_2](NCMe)ClO_4$ **4**

Complex **4** was synthesized in the same way as **3**:  $[Pt(C^{\wedge}P)(NCMe)_2]ClO_4$  **2** (0.200 g, 0.294 mmol) was

reacted with  $\text{Ph}_3\text{P}=\text{C}(\text{H})\text{COPh}$  (0.112 g, 0.294 mmol) in  $\text{CH}_2\text{Cl}_2$  at r.t. to give **4** as a white solid. Obtained: 0.236 g (79% yield).

Analysis: Calculated ( $\text{C}_{49}\text{H}_{44}\text{ClNO}_3\text{P}_2\text{Pt}$ , 1019.37 g  $\text{mol}^{-1}$ ): C, 57.73; H, 4.35; N, 1.37. Found: C, 57.76; H, 4.00; N, 1.29. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 2285, 2319 ( $\nu_{\text{NCMe}}$ ), 1629 ( $\nu_{\text{CO}}$ ), 585, 563, 478, 466 ( $\nu_{\text{C}^{\wedge}\text{P}}$ ). Mass spectrum (FAB<sup>+</sup>) [ $m/z$ , (%): 879 (94%) [(M-NCMe)<sup>+</sup>]. <sup>1</sup>H-NMR ( $\text{CD}_2\text{Cl}_2$ , 188 K):  $\delta$  (ppm), 8.15–6.55 (m, 32H, Ph + *o*-MeC<sub>6</sub>H<sub>4</sub>), 5.47 (d, 1H, CH ylide, <sup>2</sup> $J_{\text{P-H}} = 11.5$  Hz), 3.46, 3.15 (AB spin system, 2H, CH<sub>2</sub>, <sup>2</sup> $J_{\text{H-H}} = 16.7$  Hz), 2.30 (s, 3H, *o*-MeC<sub>6</sub>H<sub>4</sub>), 1.97, 1.95 (2s, 6H, *o*-MeC<sub>6</sub>H<sub>4</sub> + NCMe). <sup>31</sup>P{<sup>1</sup>H}-NMR ((CD<sub>3</sub>)<sub>2</sub>CO, 188 K):  $\delta$  (ppm), 27.73 (d, -P<sup>+</sup>Ph<sub>3</sub>, <sup>3</sup> $J_{\text{P-P}} = 10.5$  Hz), 26.97 (d, C<sup>^</sup>P, <sup>1</sup> $J_{\text{Pt-P}} = 3471$  Hz).

#### 3.4. Synthesis of [Pt(C<sup>^</sup>P){C(H)(CO<sub>2</sub>Me)(PPh<sub>3</sub>)}-(NCMe)]ClO<sub>4</sub> **5**

Complex **5** was synthesized in the same way as **3**: [Pt(C<sup>^</sup>P)(NCMe)<sub>2</sub>]ClO<sub>4</sub> **2** (0.200 g, 0.294 mmol) was reacted with  $\text{Ph}_3\text{P}=\text{C}(\text{H})\text{CO}_2\text{Me}$  (0.098 g, 0.294 mmol) in  $\text{CH}_2\text{Cl}_2$  at r.t. to give **5** as a white solid. Obtained: 0.235 g (82% yield).

Analysis: Calculated ( $\text{C}_{44}\text{H}_{42}\text{ClNO}_6\text{P}_2\text{Pt}$ , 973.30 g  $\text{mol}^{-1}$ ): C, 54.29; H, 4.35; N, 1.44. Found: C, 54.83; H, 4.53; N, 1.51. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 2285, 2316 ( $\nu_{\text{NCMe}}$ ), 1686 ( $\nu_{\text{CO}}$ ), 752, 587, 563, 478, 466 ( $\nu_{\text{C}^{\wedge}\text{P}}$ ). Mass spectrum (FAB<sup>+</sup>) [ $m/z$ , (%): 832 (100%) [(M-NCMe)<sup>+</sup>]. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 223K):  $\delta$  (ppm), 7.74–7.16 (m, 27H, Ph + *o*-MeC<sub>6</sub>H<sub>4</sub>), 3.82 (dd, 1H, CH ylide, <sup>2</sup> $J_{\text{P-H}} = 9$  Hz, <sup>3</sup> $J_{\text{P-H}} = 4.1$  Hz), 3.62 (s, 3H, CO<sub>2</sub>Me), 2.40 (s, broad, 6H, *o*-MeC<sub>6</sub>H<sub>4</sub>), 2.44, 2.25 (AB spin system, 2H, CH<sub>2</sub>, <sup>2</sup> $J_{\text{H-H}} = 9.1$  Hz), 1.67 (s, 3H, NCMe). <sup>31</sup>P{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>, 223 K):  $\delta$  (ppm), 27.56 (d, C<sup>^</sup>P, <sup>1</sup> $J_{\text{Pt-P}} = 3378$  Hz, <sup>3</sup> $J_{\text{P-P}} = 9$  Hz), 26.46 (d, -P<sup>+</sup>Ph<sub>3</sub>).

#### 3.5. Synthesis of [Pt(C<sup>^</sup>P){C(H)(CN)(PPh<sub>3</sub>)}-(NCMe)]ClO<sub>4</sub> **6**

Complex **6** was synthesized in the same way as **3**: [Pt(C<sup>^</sup>P)(NCMe)<sub>2</sub>]ClO<sub>4</sub> **2** (0.200 g, 0.294 mmol) was reacted with  $\text{Ph}_3\text{P}=\text{C}(\text{H})\text{CN}$  (0.088 g, 0.294 mmol) in  $\text{CH}_2\text{Cl}_2$  at r.t. to give **6** as a white solid. Obtained: 0.221 g (80% yield).

Analysis: Calculated ( $\text{C}_{43}\text{H}_{39}\text{ClN}_2\text{O}_4\text{P}_2\text{Pt}$ , 940.28 g  $\text{mol}^{-1}$ ): C, 54.93; H, 4.18; N, 2.98. Found: C, 54.65; H, 4.00; N, 2.69. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 2227 (broad,  $\nu_{\text{NCMe}} + \nu_{\text{NC}}$ -ylide), 772, 590, 564, 512, 475, 464 ( $\nu_{\text{C}^{\wedge}\text{P}}$ ). Mass spectrum (FAB<sup>+</sup>) [ $m/z$ , (%): 799 (100%) [(M-NCMe)<sup>+</sup>]. <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (ppm), 7.86–6.61 (m, 27H, Ph + *o*-MeC<sub>6</sub>H<sub>4</sub>), 3.93 (dd, 1H, CH ylide, <sup>2</sup> $J_{\text{P-H}} = 13.8$  Hz, <sup>3</sup> $J_{\text{P-H}} = 8.7$  Hz, <sup>2</sup> $J_{\text{Pt-H}} = 93$  Hz), 3.28, 1.79 (AX spin system, 2H, CH<sub>2</sub>, <sup>2</sup> $J_{\text{H-H}} = 13.8$  Hz, <sup>2</sup> $J_{\text{Pt-H}} = 150$  Hz), 2.39, 1.86 (2s, 6H, *o*-MeC<sub>6</sub>H<sub>4</sub>), 1.64 (s, 3H, NCMe). <sup>31</sup>P{<sup>1</sup>H}-NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (ppm), 27.35 (d, C<sup>^</sup>P, <sup>1</sup> $J_{\text{Pt-P}}$

= 3662 Hz, <sup>3</sup> $J_{\text{P-P}} = 11$  Hz), 25.84 (d, -P<sup>+</sup>Ph<sub>3</sub>, <sup>2</sup> $J_{\text{Pt-P}} = 92$  Hz).

#### 3.6. Synthesis of [Pt(C<sup>^</sup>P){C(H)(CN)(PPh<sub>3</sub>)}-{N≡C-C(H)=PPh<sub>3</sub>}]ClO<sub>4</sub> **7**

Complex **7** was synthesized in the same way as **3**: [Pt(C<sup>^</sup>P)(NCMe)<sub>2</sub>]ClO<sub>4</sub> **2** (0.117 g, 0.172 mmol) was reacted with  $\text{Ph}_3\text{P}=\text{C}(\text{H})\text{CN}$  (0.103 g, 0.344 mmol) in  $\text{CH}_2\text{Cl}_2$  at r.t. to give **7** as a white solid. Obtained: 0.141 g (68% yield).

Analysis: Calculated ( $\text{C}_{61}\text{H}_{52}\text{ClN}_2\text{O}_4\text{P}_3\text{Pt}$ , 1200.55 g  $\text{mol}^{-1}$ ): C, 61.02; H, 4.36; N, 2.33. Found: C, 60.15; H, 4.63; N, 2.19. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 2175 ( $\nu_{\text{CN-ylide}}$ ), 530, 476 ( $\nu_{\text{C}^{\wedge}}$ ). Mass spectrum (FAB<sup>+</sup>) [ $m/z$ , (%): 1101 (31%) [M<sup>+</sup>]. <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  (ppm), 7.67–6.67 (m, 42H, Ph + *o*-MeC<sub>6</sub>H<sub>4</sub>), 3.13 (dd, 1H, CH C-ylide, <sup>2</sup> $J_{\text{P-H}} = 14.3$  Hz, <sup>3</sup> $J_{\text{P-H}} = 8.6$  Hz, <sup>2</sup> $J_{\text{Pt-H}} = 83.3$  Hz), 2.32 (m, broad, 5H, CH<sub>2</sub> + *o*-MeC<sub>6</sub>H<sub>4</sub>), 1.99 (s, 3H, *o*-MeC<sub>6</sub>H<sub>4</sub>), 1.27 (d, 1H, CH N-ylide, <sup>2</sup> $J_{\text{P-H}} = 4.8$  Hz). <sup>31</sup>P{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>, 223 K):  $\delta$  (ppm), 26.67 (d, C<sup>^</sup>P, <sup>1</sup> $J_{\text{Pt-P}} = 3483$  Hz, <sup>3</sup> $J_{\text{P-P}} = 10$  Hz), 25.94 (d, -P<sup>+</sup>Ph<sub>3</sub>, C-ylide, <sup>2</sup> $J_{\text{Pt-P}} = 99$  Hz), 22.77 (s, C=PPh<sub>3</sub>, N-ylide).

#### 3.7. Synthesis of trans-[Pt(C<sup>^</sup>P)Cl(PPh<sub>3</sub>)] **8**

To a suspension of [Pt(C<sup>^</sup>P)(μ-Cl)]<sub>2</sub> **1** (1.000 g, 0.936 mmol) in  $\text{CH}_2\text{Cl}_2$  (40 ml) PPh<sub>3</sub> (0.491 g, 1.872 mmol) was added and the resulting mixture was stirred at r.t.. The initial suspension gradually dissolved (ca. 30 min) giving a colorless solution which was evaporated to dryness. Treatment of the white residue with Et<sub>2</sub>O (30 ml) allows the isolation of a white solid, identified spectroscopically as a mixture of the *trans* (**8**) and *cis* (**9**) isomers (5:1 molar ratio). This solid was dissolved in toluene and the resulting solution refluxed for 12 h, then cooled and evaporated to dryness. Treatment of the residue with Et<sub>2</sub>O (30 ml) allows the isolation of the pure *trans* isomer **8**. Obtained: 1.280 g (86% yield).

Complex **8** can also be obtained in a single step by reacting [Pt(C<sup>^</sup>P)(μ-Cl)]<sub>2</sub> (0.500 g, 0.468 mmol) with PPh<sub>3</sub> (0.246 g, 0.936 mmol) in refluxing toluene (20 ml) for 12 h. The resulting solution was evaporated to dryness and the white residue treated with Et<sub>2</sub>O (25 ml), giving pure **8** as a white solid. Obtained: 0.551 g (74% yield).

Analysis: Calculated ( $\text{C}_{39}\text{H}_{35}\text{ClP}_2\text{Pt}$ , 796.194 g  $\text{mol}^{-1}$ ): C, 58.83; H, 4.43. Found: C, 58.47; H, 3.93. IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 1589, 1567, 806, 749, 584, 561, 534, 480, 469 ( $\nu_{\text{C}^{\wedge}\text{P} + \text{PPh}_3}$ ), 279 ( $\nu_{\text{Pt-Cl}}$ ). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 223 K):  $\delta$  (ppm), 7.66–6.78 (m, 27H, Ph + *o*-MeC<sub>6</sub>H<sub>4</sub>), 2.86 (s, 5H, CH<sub>2</sub> + *o*-MeC<sub>6</sub>H<sub>4</sub>), 2.71 (s, 3H, *o*-MeC<sub>6</sub>H<sub>4</sub>). <sup>31</sup>P{<sup>1</sup>H}-NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  (ppm), 35.87 (d, <sup>1</sup> $J_{\text{Pt-P}} = 3115$  Hz, <sup>2</sup> $J_{\text{P-P}} = 446$  Hz), 28.71 (d, <sup>1</sup> $J_{\text{Pt-P}} = 3027$  Hz).

### 3.8. Synthesis of *trans*-[Pt(C<sup>^</sup>P)(PPh<sub>3</sub>)(NCMe)]ClO<sub>4</sub> **10**

(a) To a solution of **8** (0.200 g, 0.251 mmol) in 25 ml of NCMe (25 ml) TiClO<sub>4</sub> (0.076 g, 0.251 mmol) was added and the resulting suspension was refluxed for 1 h. After cooling, the suspension was filtered and the resulting solution evaporated to dryness, giving an oily residue which was triturated with Et<sub>2</sub>O (25 ml). The resulting white solid (**10**) was filtered and air dried. Obtained: 0.192 g (85% yield). (b) To a solution of [Pt(C<sup>^</sup>P)(NCMe)<sub>2</sub>]ClO<sub>4</sub> **2** (0.360 g, 0.529 mmol) in 40 ml of CH<sub>2</sub>Cl<sub>2</sub> PPh<sub>3</sub> (0.138 g, 0.529 mmol) was added and the resulting solution was stirred for 30 min at r.t.. The solvent was then evaporated to dryness and the residue treated with Et<sub>2</sub>O (35 ml) giving a white solid (**10**), which was collected and air dried. Obtained: 0.432 g (90% yield).

Analysis: Calculated (C<sub>41</sub>H<sub>38</sub>ClNO<sub>4</sub>P<sub>2</sub>Pt, 901.24 g mol<sup>-1</sup>): C, 54.64; H, 4.25; N, 1.55. Found: C, 54.41; H, 4.10; N, 1.42. IR (ν, cm<sup>-1</sup>): 2317, 2287 (ν<sub>NCMe</sub>), 1591, 776, 766, 755, 588, 562, 536, 518, 493, 473, 464 (ν<sub>C<sup>^</sup>P+PPh<sub>3</sub></sub>). Mass spectrum (FAB<sup>+</sup>) [*m/z*, (%): 801 (5%) [M<sup>+</sup>], 760 (100%) [(M-NCMe)<sup>+</sup>]. <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ (ppm), 7.62–7.12 (m, 27H, Ph + *o*-MeC<sub>6</sub>H<sub>4</sub>), 2.64 (s, broad, 8H, CH<sub>2</sub> + *o*-MeC<sub>6</sub>H<sub>4</sub>), 1.57 (s, 3H, NCMe). <sup>31</sup>P{<sup>1</sup>H}-NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ (ppm), 33.19 (d, <sup>2</sup>J<sub>P-P</sub> = 384 Hz, <sup>1</sup>J<sub>Pt-P</sub> = 2966 Hz), 27.81 (d, <sup>1</sup>J<sub>Pt-P</sub> = 2934 Hz).

### 3.9. Synthesis of [Pt(C<sup>^</sup>P){OC(Me)=C(H)(PPh<sub>3</sub>)}(PPh<sub>3</sub>)ClO<sub>4</sub> **11**

To a solution of [Pt(C<sup>^</sup>P)(PPh<sub>3</sub>)(NCMe)]ClO<sub>4</sub> **10** (0.200 g, 0.222 mmol) in 30 ml of CH<sub>2</sub>Cl<sub>2</sub> Ph<sub>3</sub>P=C(H)COMe (0.070 g, 0.222 mmol) was added and the resulting solution was stirred for 30 min at r.t. and then evaporated to dryness. The white residue was treated with Et<sub>2</sub>O (25 ml), giving a white solid which was filtered, washed with additional Et<sub>2</sub>O (25 ml) and air dried. This solid was identified spectroscopically as a mixture of the *transoid* **11a** and *cisoid* **11b** isomers in molar ratio **11a**:**11b** = 1.44:1. Obtained: 0.166 g (64% yield).

Analysis: Calculated (C<sub>60</sub>H<sub>54</sub>ClO<sub>5</sub>P<sub>3</sub>Pt, 1178.5 g mol<sup>-1</sup>): C, 61.15; H, 4.62. Found: C, 60.80; H, 4.72. IR (ν, cm<sup>-1</sup>): 1504 (ν<sub>CO</sub>), 780, 587, 536, 471 (ν<sub>C<sup>^</sup>P</sub>). Mass spectrum (FAB<sup>+</sup>) [*m/z*, (%): 1078 (10%) [M<sup>+</sup>], 816 (6%) [(M-PPh<sub>3</sub>)<sup>+</sup>], 760 (100%) [(M-ylide)<sup>+</sup>]. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ (ppm), 7.53–6.94 (m, Ph + *o*-MeC<sub>6</sub>H<sub>4</sub>), 4.41 (d, CH ylide **11a**, <sup>2</sup>J<sub>P-H</sub> = 18.4 Hz), 3.59 (d, CH ylide **11b**, <sup>2</sup>J<sub>P-H</sub> = 21.2 Hz), 2.91, 2.07 (2 broad s, CH<sub>2</sub> **11a**), 2.72 (s, *o*-MeC<sub>6</sub>H<sub>4</sub> **11b**), 2.61 (s, *o*-MeC<sub>6</sub>H<sub>4</sub> **11a**), 2.38 (s, *o*-MeC<sub>6</sub>H<sub>4</sub> **11a**), 2.16 (s, *o*-MeC<sub>6</sub>H<sub>4</sub> **11b**), 1.83 (s, COMe **11b**), 1.67 (s, COMe **11a**). <sup>31</sup>P{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>): δ (ppm), 36.25 (d, <sup>1</sup>J<sub>Pt-P</sub> = 3198 Hz), 28.25 (d, <sup>1</sup>J<sub>Pt-P</sub> = 3098 Hz) (C<sup>^</sup>P + PPh<sub>3</sub> **11a**, <sup>2</sup>J<sub>P-P</sub> = 414 Hz), 32.97 (d, <sup>1</sup>J<sub>Pt-P</sub> = 2964 Hz), 27.71 (d, <sup>1</sup>J<sub>Pt-P</sub> = 2932 Hz)

(C<sup>^</sup>P + PPh<sub>3</sub> **11b**, <sup>2</sup>J<sub>P-P</sub> = 382 Hz), 14.01 (s, C=PPh<sub>3</sub> **11b**), 13.38 (s, C=PPh<sub>3</sub> **11a**).

### 3.10. Synthesis of [Pt(C<sup>^</sup>P){OC(OMe)=C(H)(PPh<sub>3</sub>)}(PPh<sub>3</sub>)ClO<sub>4</sub> **12**

Complex **12** was synthesized in the same way as **11**: [Pt(C<sup>^</sup>P)(PPh<sub>3</sub>)(NCMe)]ClO<sub>4</sub> **10** (0.138 g, 0.153 mmol) was reacted with Ph<sub>3</sub>P=C(H)CO<sub>2</sub>Me (0.051 g, 0.153 mmol) in CH<sub>2</sub>Cl<sub>2</sub> at r.t. to give **12** as a mixture of the *transoid* **12a** and *cisoid* **12b** isomers in molar ratio of **12a**:**12b** = 3:1. Obtained: 0.125 g (66% yield). Complex **12** was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane, giving colorless crystals of **12**·0.5CH<sub>2</sub>Cl<sub>2</sub>, which were used for analytical and NMR measurements (the amount of CH<sub>2</sub>Cl<sub>2</sub> was quoted from the <sup>1</sup>H-NMR of the crystals).

Analysis: Calculated (C<sub>60</sub>H<sub>54</sub>ClO<sub>6</sub>P<sub>3</sub>Pt·0.5CH<sub>2</sub>Cl<sub>2</sub>, 1237.0 g mol<sup>-1</sup>): C, 58.74; H, 4.48. Found: C, 58.75; H, 4.84. IR (ν, cm<sup>-1</sup>): 1542 (ν<sub>CO</sub>), 586, 471 (ν<sub>C<sup>^</sup>P</sub>). Mass spectrum (FAB<sup>+</sup>) [*m/z*, (%): 1094 (6%) [M<sup>+</sup>], 832 (3%) [(M-PPh<sub>3</sub>)<sup>+</sup>], 760 (100%) [(M-ylide)<sup>+</sup>]. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ (ppm), 7.75–6.82 (m, Ph + *o*-MeC<sub>6</sub>H<sub>4</sub>), 3.12 (d, CH ylide **12a**, <sup>2</sup>J<sub>P-H</sub> = 18.4 Hz), 2.75 (s, CO<sub>2</sub>Me **12a**), 2.61 (s, CO<sub>2</sub>Me **12b**), 2.42 (s, *o*-MeC<sub>6</sub>H<sub>4</sub> **12a**), 2.39 (s, *o*-MeC<sub>6</sub>H<sub>4</sub> **12b**), 1.82 (s, *o*-MeC<sub>6</sub>H<sub>4</sub> **12b**), 1.61 (s, *o*-MeC<sub>6</sub>H<sub>4</sub> **12a**). <sup>31</sup>P{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>): δ (ppm), 36.41 (d, <sup>1</sup>J<sub>Pt-P</sub> = 3173 Hz), 29.88 (d, <sup>1</sup>J<sub>Pt-P</sub> = 3293 Hz) (C<sup>^</sup>P + PPh<sub>3</sub>, **12a**, <sup>2</sup>J<sub>P-P</sub> = 411 Hz), 32.96 (d, <sup>1</sup>J<sub>Pt-P</sub> = 2964 Hz), 27.71 (d, <sup>1</sup>J<sub>Pt-P</sub> = 2931 Hz) (C<sup>^</sup>P + PPh<sub>3</sub>, **12b**, <sup>2</sup>J<sub>P-P</sub> = 386 Hz), 15.76 (s, broad, C = PPh<sub>3</sub> **12a** + **12b**).

### 3.11. Synthesis of [Pt(C<sup>^</sup>P){N≡C-C(H)=PPh<sub>3</sub>}(PPh<sub>3</sub>)ClO<sub>4</sub> **13**

Complex **13** was synthesized in the same way as **11**: [Pt(C<sup>^</sup>P)(PPh<sub>3</sub>)(NCMe)]ClO<sub>4</sub> **10** (0.146 g, 0.162 mmol) was reacted with Ph<sub>3</sub>P=C(H)CN (0.049 g, 0.162 mmol) in CH<sub>2</sub>Cl<sub>2</sub> at r.t. to give **13** as a white solid. Obtained: 0.083 g (44% yield).

Analysis: Calculated (C<sub>59</sub>H<sub>51</sub>ClNO<sub>4</sub>P<sub>3</sub>Pt, 1161.52 g mol<sup>-1</sup>): C, 61.10; H, 4.42; N, 1.20. Found: C, 61.10; H, 4.01; N, 1.03. IR (ν, cm<sup>-1</sup>): 2176 (ν<sub>CN</sub>), 560, 536, 472 (ν<sub>C<sup>^</sup>P</sub>). Mass spectrum (FAB<sup>+</sup>) [*m/z*, (%): 1061 (57%) [M<sup>+</sup>], 799 (12%) [(M-PPh<sub>3</sub>)<sup>+</sup>], 760 (100%) [(M-ylide)<sup>+</sup>]. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ (ppm), 7.46–6.86 (m, 42H, Ph + *o*-MeC<sub>6</sub>H<sub>4</sub>), 3.07 (s, broad, 2H, CH<sub>2</sub>), 2.42 (s, 6H, *o*-MeC<sub>6</sub>H<sub>4</sub>), 1.06 (dt, 1H, CH ylide, <sup>2</sup>J<sub>P-H</sub> = 5.2 Hz, <sup>5</sup>J<sub>P-H</sub> = 0.9 Hz). <sup>31</sup>P{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>): δ (ppm), 32.38 (d, <sup>1</sup>J<sub>Pt-P</sub> = 3022 Hz), 26.98 (d, <sup>1</sup>J<sub>Pt-P</sub> = 2964 Hz) (C<sup>^</sup>P + PPh<sub>3</sub>, <sup>2</sup>J<sub>P-P</sub> = 406 Hz), 21.95 (s, C = PPh<sub>3</sub>).

### 3.12. Synthesis of [Pt(C<sup>^</sup>P)Cl{C(H)(COMe)(PPh<sub>3</sub>)}] **14**

To a suspension of [Pt(C<sup>^</sup>P)(μ-Cl)]<sub>2</sub> **1** (0.100 g, 0.093 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) Ph<sub>3</sub>P=C(H)COMe (0.059 g,



0.187 mmol) was added and the resulting mixture was refluxed for 4 h, resulting in the gradual dissolution of the suspension. After the reaction time, the resulting solution was evaporated to dryness and the residue treated with *n*-hexane (25 ml), giving a white solid which was collected, washed with additional *n*-hexane (20 ml), air dried and identified as **14**. Obtained: 0.126 g (79% yield). This complex was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane giving colorless crystals of **14**·0.5CH<sub>2</sub>Cl<sub>2</sub> which were used for analytical and NMR measurements (the amount of CH<sub>2</sub>Cl<sub>2</sub> was quoted from the <sup>1</sup>H-NMR of the crystals).

Analysis: Calculated (C<sub>42</sub>H<sub>39</sub>ClO<sub>2</sub>Pt·0.5CH<sub>2</sub>Cl<sub>2</sub>, 894.72 g mol<sup>-1</sup>): C, 57.05; H, 4.50. Found: C, 57.36; H, 4.41. IR (ν, cm<sup>-1</sup>): 1648 (ν<sub>CO</sub>), 752, 589, 564, 484, 476, 464 (ν<sub>C^A\_P</sub>), 266 (ν<sub>Pt-Cl</sub>). Mass spectrum (FAB<sup>+</sup>) [*m/z*, (%): 851 (7%) [M<sup>+</sup>], 816 (100%) [(M-Cl)<sup>+</sup>]. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ (ppm), 7.87–6.70 (m, 27H, Ph + *o*-MeC<sub>6</sub>H<sub>4</sub>), 5.53 (dd, 1H, CH ylide, <sup>2</sup>J<sub>P-H</sub> = 8.5 Hz, <sup>3</sup>J<sub>P-H</sub> = 3.2 Hz, <sup>2</sup>J<sub>Pt-H</sub> = 60 Hz), 2.68 (s, broad, 8H, *o*-MeC<sub>6</sub>H<sub>4</sub> + CH<sub>2</sub>), 2.46 (d, 3H, COMe, <sup>4</sup>J<sub>P-H</sub> = 2.3 Hz). <sup>31</sup>P{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>): δ (ppm), 27.32 (s, broad, C^A\_P, <sup>1</sup>J<sub>Pt-P</sub> = 3790 Hz), 24.90 (d, -P<sup>+</sup>Ph<sub>3</sub>, <sup>3</sup>J<sub>P-P</sub> = 10 Hz, <sup>2</sup>J<sub>Pt-P</sub> = 53 Hz).

### 3.13. Synthesis of [Pt(C^A\_P)Cl{C(H)(COOMe)(PPh<sub>3</sub>)}] **15**

Complex **15** was synthesized in the same way as **14**: [Pt(C^A\_P)(μ-Cl)]<sub>2</sub> **1** (0.150 g, 0.140 mmol) was reacted with the ylide Ph<sub>3</sub>P=C(H)CO<sub>2</sub>Me (0.094 g, 0.281 mmol) in refluxing CH<sub>2</sub>Cl<sub>2</sub> to give **15** as a white solid. Obtained: 0.209 g (86% yield).

Analysis: Calculated (C<sub>42</sub>H<sub>39</sub>ClO<sub>2</sub>P<sub>2</sub>Pt, 868.26 g mol<sup>-1</sup>): C, 58.10; H, 4.52. Found: C, 58.26; H, 4.70. IR (ν, cm<sup>-1</sup>): 1688 (ν<sub>CO</sub>), 586, 565, 521, 474, 466 (ν<sub>C^A\_P</sub>), 266 (ν<sub>Pt-Cl</sub>). Mass spectrum (FAB<sup>+</sup>) [*m/z*, (%): 832 (8%) [(M-Cl)<sup>+</sup>]. <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ (ppm), 7.88–6.72 (m, 27H, Ph + *o*-MeC<sub>6</sub>H<sub>4</sub>), 4.96 (d, 1H, CH ylide, <sup>2</sup>J<sub>P-H</sub> = 9 Hz, <sup>2</sup>J<sub>Pt-H</sub> = 62 Hz), 3.57 (s, 3H, CO<sub>2</sub>Me), 3.42, 2.42 (AB spin system, 2H, CH<sub>2</sub>, <sup>2</sup>J<sub>H-H</sub> = 15 Hz), 2.68, 2.64 (2s, 6H, *o*-MeC<sub>6</sub>H<sub>4</sub>). <sup>31</sup>P{<sup>1</sup>H}-NMR (CDCl<sub>3</sub>): δ (ppm), 27.60 (s, broad, C^A\_P, <sup>1</sup>J<sub>Pt-P</sub> = 3726 Hz), 25.2 (d, -P<sup>+</sup>Ph<sub>3</sub>, <sup>2</sup>J<sub>Pt-P</sub> = 67 Hz, <sup>3</sup>J<sub>P-P</sub> = 11 Hz).

### 3.14. Synthesis of [Pt(C^A\_P)Cl{C(H)(CN)(PPh<sub>3</sub>)}] **16**

Complex **16** was synthesized in the same way as **14**, except that the reaction was performed at r.t.: [Pt(C^A\_P)(μ-Cl)]<sub>2</sub> **1** (0.100 g, 0.093 mmol) was reacted with Ph<sub>3</sub>P=C(H)CN (0.056 g, 0.187 mmol) in CH<sub>2</sub>Cl<sub>2</sub> at r.t. to give **16** as a white solid. Obtained: 0.129 g (82% yield). Recrystallization of **16** in CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane gave crystals of **16**·0.5CH<sub>2</sub>Cl<sub>2</sub>, which were used for analytical and NMR purposes (the amount of CH<sub>2</sub>Cl<sub>2</sub> was quoted from the <sup>1</sup>H-NMR of the crystals).

Analysis: Calculated (C<sub>41</sub>H<sub>36</sub>ClNP<sub>2</sub>Pt·0.5CH<sub>2</sub>Cl<sub>2</sub>, 877.69 g mol<sup>-1</sup>): C, 56.79; H, 4.25; N, 1.59. Found: C, 56.59; H, 4.03; N, 1.56. IR (ν, cm<sup>-1</sup>): 2187 (ν<sub>CN</sub>), 747, 588, 560, 529, 476 (ν<sub>C^A\_P</sub>), 266 (ν<sub>Pt-Cl</sub>). Mass spectrum (FAB<sup>+</sup>) [*m/z*, (%): 799 (100%) [(M-Cl)<sup>+</sup>]. <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ (ppm), 7.90–6.78 (m, 27H, Ph + *o*-MeC<sub>6</sub>H<sub>4</sub>), 4.22 (dd, 1H, CH ylide, <sup>2</sup>J<sub>P-H</sub> = 15 Hz, <sup>3</sup>J<sub>P-H</sub> = 8.4 Hz, <sup>2</sup>J<sub>Pt-H</sub> = 79 Hz), 2.80, 2.19 (AB spin system, 2H, CH<sub>2</sub>, <sup>2</sup>J<sub>H-H</sub> = 16 Hz), 2.70, 2.58 (2s, 6H, *o*-MeC<sub>6</sub>H<sub>4</sub>). <sup>31</sup>P{<sup>1</sup>H}-NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ (ppm), 28.59 (s, broad, C^A\_P, <sup>1</sup>J<sub>Pt-P</sub> = 3666 Hz), 26.08 (d, -P<sup>+</sup>Ph<sub>3</sub>, <sup>2</sup>J<sub>Pt-P</sub> = 73 Hz, <sup>3</sup>J<sub>P-P</sub> = 10 Hz).

### 3.15. Synthesis of [Pt(C^A\_P){OC(Me)=C(H)(PPh<sub>3</sub>)}]<sub>2</sub> ClO<sub>4</sub> **17**

To a THF solution (20 ml) of complex [Pt(C^A\_P)Cl{C(H)(COMe)(PPh<sub>3</sub>)}] **14** (0.142 g, 0.166 mmol) TiClO<sub>4</sub> (0.050 g, 0.166 mmol) was added and the resulting suspension was stirred at r.t. for 1 h, then filtered. To the freshly prepared solution of [Pt(C^A\_P)(THF){C(H)(COMe)(PPh<sub>3</sub>)}]ClO<sub>4</sub>, Ph<sub>3</sub>P=C(H)COMe (0.053 g, 0.166 mmol) was added and stirring was continued for 30 min. Subsequent evaporation of the resulting solution and treatment of the white residue with *n*-hexane permitted the isolation of a white solid which was identified as **17**. Obtained: 0.184 g (90% yield).

Analysis: Calculated (C<sub>63</sub>H<sub>58</sub>ClO<sub>6</sub>P<sub>3</sub>Pt, 1234.61 g mol<sup>-1</sup>): C, 61.29; H, 4.73. Found: C, 60.74; H, 4.69. IR (ν, cm<sup>-1</sup>): 1505 (ν<sub>CO</sub>), 750, 593 (ν<sub>C^A\_P</sub>). Mass spectrum (FAB<sup>+</sup>) [*m/z*, (%): 816 (48%) [(M-ylide)<sup>+</sup>]. <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ (ppm), 7.68–6.84 (m, 42H, Ph + *o*-MeC<sub>6</sub>H<sub>4</sub>), 4.33 (dd, 1H, CH ylide *trans* to P, <sup>2</sup>J<sub>P-H</sub> = 24 Hz, <sup>5</sup>J<sub>P-H</sub> = 2.3 Hz), 3.87 (d, 1H, CH ylide *trans* to C, <sup>2</sup>J<sub>P-H</sub> = 23 Hz), 3.05, 2.95 (AB spin system, 2H, CH<sub>2</sub>, <sup>2</sup>J<sub>H-H</sub> = 15 Hz), 2.18 (d, 3H, COMe ylide *trans* to P, <sup>4</sup>J<sub>P-H</sub> = 2 Hz), 2.01 (d, 3H, COMe ylide *trans* to C, <sup>4</sup>J<sub>P-H</sub> = 1.3 Hz), 1.99, 1.81 (2s, 6H, *o*-MeC<sub>6</sub>H<sub>4</sub>). <sup>31</sup>P{<sup>1</sup>H}-NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ (ppm), 14.28 (s, C = PPh<sub>3</sub> ylide *trans* to P), 13.49 (s, C = PPh<sub>3</sub> ylide *trans* to C), 10.91 (s, C^A\_P, <sup>1</sup>J<sub>Pt-P</sub> = 4934 Hz).

### Acknowledgements

We would like to thank the Dirección General de Enseñanza Superior (Spain) for its financial support (Project PB95-0003-C02-01) and Professor J. Forniés for his invaluable logistical support.

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