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# Influence of ancillary ligands in the coordination mode of P and As carbonyl stabilized ylides on Pt(II) systems. X-ray structure of *trans*- $[Pt(PPh_3)_2(CF_3) \{OC(OCH_3)=C(H)(PPh_3)\}][BF_4] \cdot 0.5CH_2Cl_2$

Umberto Belluco<sup>a</sup>, Rino A. Michelin<sup>a</sup>, Roberta Bertani<sup>a</sup>, Giacomo Facchin<sup>a,\*</sup>, Giuseppe Pace<sup>a</sup>, Livio Zanotto<sup>a</sup>, Mirto Mozzon<sup>a</sup>, Michela Furlan<sup>b</sup>, Ennio Zangrando<sup>b</sup>

<sup>a</sup> Istituto di Chimica Industriale e Centro di Studio per la Chimica e Tecnologia dei Composti Metallorganici degli Elementi di Transizione del C.N.R., Facoltà di Ingegneria, Università di Padova, Via F. Marzolo 9, 35131 Padua, Ilay Discrimento di Chimica e Metale Ultri di Università di Padova, Via F. Marzolo 9, 1914 Padua, Ilay

<sup>b</sup> Dipartimento di Scienze Chimiche. Università di Trieste, Via Giorgieri 1, 34127 Trieste, Italy

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### Abstract

The carbonyl stabilized P and As ylides Ph<sub>3</sub>PCHCOR ( $R = CH_3$ , Ph, OCH<sub>3</sub>) and Ph<sub>3</sub>AsCHCOR ( $R = CH_3$ , Ph, OCH<sub>3</sub>) have been reacted with some platinum(II) complexes bearing ancillary ligands with different steric hindrance, in order to determine the factors that influence the C-versus O-coordination mode of the ylides. Thus, the reactions of [(dppe)PtCl<sub>2</sub>] and [(dppv)PtCl<sub>2</sub>] with Ph<sub>3</sub>PCHCOR ( $R = CH_3$ , Ph) give the O-coordinated complexes, while with Ph<sub>3</sub>PCHCOOCH<sub>3</sub> they give the corresponding C-coordinated derivatives. The reactions of *trans*-[(PPh<sub>3</sub>)<sub>2</sub>(CF<sub>3</sub>)Pt(solv)]<sup>+</sup>BF<sub>4</sub><sup>-</sup> yield the O-coordinated compounds and the reactions with [Pt(C<sub>3</sub>H<sub>5</sub>)Cl]<sub>4</sub> give selectively the C-coordinated derivatives as well as the reactions with the dimer [PtCl[P(Bu')<sub>2</sub>C(Me)<sub>2</sub>CH<sub>2</sub>]<sub>2</sub>. The derivative *trans*-[Pt(PPh<sub>3</sub>)<sub>2</sub>(CF<sub>3</sub>)[OC(OCH<sub>3</sub>)=C(H)(PPh<sub>3</sub>)]][BF<sub>4</sub>] crystallizes in the triclinic space group Pī (No. 2), *a* = 10.385(4), *b* = 14.844(5), *c* = 18.511(6) Å, *a*=96.46(2), *β*=97.9(2),  $\gamma$ =97.00(2)°, *V*=2765(1) Å<sup>3</sup>, Z=2. The values of coordination distances and of the Pt–O-C

Keywords: Crystal structures; Platinum complexes; P-ylide complexes; As-ylide complexes; O-coordination complexes

### 1. Introduction

Phosphorus and arsenic ylides form stable complexes with virtually any metal of the Periodic Table upon coordination by various binding modes [1]. In particular, carbonyl stabilized ylides can offer either the ylide methine carbon or the carbonyl oxygen atom as coordination sites according to the following resonance structures:



E = P, As

Carbonyl stabilized ylides have earned renewed interest since (ylide)nickel complexes of the type  $[NiPh(Ph_2PCHCMeO)(L)]$  (L=phosphine, ylide) were

0020-1693/96/\$15.00 © 1996 Elsevier Science S.A. All rights reserved PII \$0020-1693(96)05358-3 found to be active catalysts in olefin oligomerization [2]. Nickel(0) complexes react with carbonyl stabilized ylides of phosphorus and arsenic,  $Ph_3E=ZCOR$  (E=P, As; Z=CH, CR', N) yielding the phenyl migration to the nickel and transformation of the ylide in a PO chelate ligand.

In our laboratory, we have long been interested in the organic [3] and organometallic [4] chemistry of carbonyl stabilized ylides. We reported that Ph<sub>3</sub>PCHCOR (R = CH<sub>3</sub>, Ph) react with [ $(\eta^3-C_3H_3)$ PdCl]<sub>2</sub> to give the corresponding derivatives [ $(\eta^3-C_3H_3)$ PdCl[Ph<sub>3</sub>PC(H)COR]], where the ylides are coordinated to the palladium atom through the methine carbon [4a,b]. Analogously, mono- and bis-ylide C-coordinated complexes are selectively obtained by reacting some P- and As-keto-stabilized ylides with Zeise's salt [4c]. On the contrary, the reaction of [{PtCl(dppe)}]\_2[BF4]2 with carbonyl stabilized As ylides led to novel Pt(II) complexes [PtCl(dppe){OC(R)CH(AsPh\_3)}][BF4] (R = Me, Ph, OMe), in which the ylides are coordinated to the metat to the metat to the metation of [4d]. These latter deriv-

<sup>\*</sup> Corresponding author.

atives are not stable in solution and slowly undergo isomerization to their C-coordinated analogues following a first-order rate law.

Thus, we thought it of interest to study the reactivity of some P- and As-carbonyl stabilized ylides to determine the factors that address the C- versus O-coordination mode and to check whether P or As ylides behave differently toward Pt complexes.

Here we report the r: actions of P and As carbonyl stabilized ylides of different nucleophilicity with a series of platinum(II) complexes bearing different ancillary ligands. Moreover, we report the synthesis and the X-ray structure of trans-[Pt(PPh\_3)\_2(CF\_3){OC(OCH\_3)=C(H)(PPh\_3)}]. [BF<sub>1</sub>], where the P-ylide is O-coordinated to platinum.

#### 2. Experimental

#### 2.1. General procedures

All manipulations were performed under an atmosphere of dry nitrogen. Solvents were dried and freshly distilled under nitrogen from sodium benzophenone ketyl (THF, diethyl ether), calcium hydride (CH<sub>2</sub>Cl<sub>2</sub>) or drierite (acetone) prior to use. All other solvents were reagent grade and used without further purification. <sup>31</sup>P{<sup>1</sup>H} and <sup>19</sup>F NMR spectra were recorded on a Varian FT-80A and <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra on a Bruker AM-400 spectrometer. IR spectra were measured with a Perkin-Elmer 983 spectrophotometer as Nujol mulls or in CH<sub>2</sub>Cl<sub>2</sub> solution. Elemental analyses were carried out by the Department of Analytical Chemistry of the University of Padua.

# 2.2. Starting complexes

The starting complexes  $[PtCl_2(dppe)] [5]$ ,  $[PtCl_2(dppv)] [5]$ , trans- $[Pt(CF_3)Br(PPh_3)_2] [6]$ ,  $[PtCl[P(Bu')_2C(Me)_2CH_2]_2 [7]$ ,  $[Pt(C_3H_5)Cl]_4 [8]$  and the carbonyl-stabilized ylides Ph\_3PCHCOMe (APPY) [9], Ph\_3PCHCOPh (BPPY) [9], Ph\_3PCHCOOMe (CMPPY) [10], Ph\_3ASCHCOMe (APASY) [11], Ph\_3ASCHCOPh (BPASY) [11], Ph\_3ASCHCOOMe (CMPASY) [11] were prepared by literature methods.

#### 2.3. Synthesis of the complexes

# 2.3.1. [(PP)PtCl{Ph3PC(H)COR}][BF4](1-6)

Complexes 1-6 were prepared as described for 1. To a  $CH_2Cl_2$  (50 ml) suspension of [(dppe)PtCl\_1] (0.664 g, 1.00 mmol) was added dropwise at 0°C a 1.025 M acetone solution of AgBF<sub>4</sub> (1.10 ml, 1.12 mmol). After 1 h stirring and upon warming to room temperature the reaction mixture was filtered off to remove solid AgCl. The obtained solution was reacted with a CH<sub>2</sub>Cl<sub>2</sub> solution (15 ml) of Ph<sub>3</sub>PCHCOCH<sub>3</sub> (0.318 g, 1.00 mmol). After 2 h the solution was concentrated to small volume (3, rnl) and by addition of EtoO a white

product of 1 precipitated. It was filtered off, washed with Et<sub>2</sub>O and dried under vacuum. Yield: 0.889 g (86%); m.p. 146–148°C. For complexes **2–6** the yields and m.p. were the following: **2**, 0.953 g (87%) and 154–156°C; **3**, 0.871 g (83%) and 150–152°C; **4**, 0.928 g (90%) and 169–171°C; **5**, 0.975 g (91%) and 142–145°C; **6**, 0.849 g (81%) and 134–136°C.

# 2.3.2. $Trans-[(PPh_3)_2Pt(CF_3){OC(R)C(H)EPh_3}][BF_4]$ (7-10)

Complexes 7-10 were prepared as described for 7. A  $CH_2Cl_2$  (40 ml) suspension of *trans*-[Pt(CF<sub>3</sub>)Br(PPh<sub>3</sub>)<sub>2</sub>] (0.870 g, 1.00 mmol) was treated with a 1.02 M acetone solution of AgBF<sub>4</sub> (0.98 ml, 1.00 mmol). After 30 min stirring at room temperature, AgBr was filtered off and the solution obtained was treated with Ph<sub>3</sub>PCHCOCH<sub>3</sub> (0.318 g, 1.00 mmol). After 30 min the reaction mixture was concentrated to small volume and by addition of n-hexane a white precipitate of 7 formed, which was filtered off, washed with n-hexane and dried under vacuum. Yield: 1.020 g (86%); m.p. 190–192°C. For complexes 8–10 the yields and m.p. were the following: 8, 0.967 g (80%) and 166–168°C; 9, 0.942 g (75%) and 162–164°C; 10, 1.002 g (81%) and 168–170°C.

# 2.3.3. $(u_1^3-C_3H_5)PtCl{Ph_3PC(H)COR}](11-13)$

Complexes 11–13 were prepared as reported for 11. To a CHCl<sub>3</sub> (20 ml) suspension of  $[PtCl(C_3H_3)]_4$  (0.136 g, 0.125 mmol), Ph<sub>3</sub>PCHCOCH<sub>3</sub> (0.139 g, 0.50 mmol) was added. The reaction mixture was stirred at 50°C for 1 h obtaining a clear solution. Then the solution was concentrated to small volume (3 ml) and by addition of n-heptane, a white product of 11 precipitated. It was filtered, washed with n-heptane and dried under vacuum. Yield: 0.280 g (95%); m.p. 162–164°C. For complexes 12 and 13 the yields and m.p. were the following: 12, 0.316 g (97%) and 172–174°C; 13, 0.279 g (92%) and 158–160°C.

# 2.3.4. $[PtCl{P(Bu')_2C(Me)_2CH_2}]{Ph_3EC(H)COR}$ (14–19)

Complexes 14–19 were prepared as reported for 14. A CHCl3 (10 ml) solution of  $[PCI{P(Bu')}_{C}C(Me)_{2}CH_{2}]_{1}$ (0.240 g, 0.28 mmol) was treated at room temperature with Ph\_PCHCOCH<sub>3</sub> (0.180 g, 0.56 mmol). After 30 min stirring the solution was concentrated to small volume (5 ml) and by addition of n-hexane, a white solid of 14 precipitated. It was filtered off, washed with n-hexane and dried under vacuum. Yield: 0.320 g (77%); m.p. 176–178°C. For complexes 15–19 the yields and m.p. were the following: 15, 0.240 g (68%) and 156–158°C; 16, 0.320 g (78%) and 206–208°C; 17, 0.310 g (81%) and i90–192°C; 18, 0.210 g (70%) and 198–200°C; 19, 0.290 g (74%) and 196–198°C.

# 2.4. X-ray structure determination of trans- $[Pt(PPh_3)_2-(CF_3)\{OC(OCH_3)=C(H)(PPh_3)\}][BF_4] \cdot 0.5CH_2Cl_2(8)$

Suitable crystals were grown by the slow diffusion of diethyl ether into a  $CH_2Cl_2$  solution of 8. Crystal data: formula  $C_{58}H_{49}BF_7O_2P_3Pt \cdot 0.5CH_2Cl_2$ , formula weight 1252.25, triclinic, space group  $P\bar{1}$  (No. 2), a = 10.385(4), b = 14.844(5), c = 18.511(6) Å,  $\alpha = 96.46(2)$ ,  $\beta = 99.79(2)$ ,  $\gamma = 97.00(2)^\circ$ , V = 2765(1) Å<sup>3</sup>, Z = 2,  $D_{calc} = 1.504$  g cm<sup>-3</sup>, F(000) = 1250,  $\mu$ (Mo K $\alpha$ ) = 14.9 cm<sup>-1</sup>.

Intensity measurements were carried out on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator and Mo K $\alpha$  radiation,  $\omega$ -2 $\theta$  mode. Unit-cell dimensions were obtained from least-squares treatment of 25 reflections in the range 12-17°. The intensities of three reference reflections monitored during data collections did not show any decay. 12 414 reflections were measured (unique 12033,  $2\theta \max = 54^{\circ}$ ), of which 10 267 having  $I > 3\sigma(I)$ were corrected for Lorentz-polarization factors and used in subsequent refinements. An absorption correction, based on an empirical y scan, was applied. The structure was solved by Patterson and Fourier methods. The analysis of the  $\Delta F$ map revealed the presence of a CH2Cl2 molecule (0.50 occupancy on the basis of the respective electron density peaks in the Fourier map). All non-hydrogen atoms were anisotropically refined by least-squares on  $F_{obs}^2$  with 678 parameters, using the SHELXL 93 package [12]. Hydrogen atoms at calculated positions were introduced in final cycles of refinement as a fixed contribution (riding model, fixed isotropic U). The weighting scheme was  $1/[\sigma^2(F_0^2) + (0.0728P)^2 +$ 4.3075P] with  $P = (F_0^2 + 2F_c^2)/3$ . Final R (= $\Sigma(|F_0| - 1)$  $|F_{\rm c}|/\Sigma|F_{\rm o}|$  and wR ( =  $[\Sigma w (F_{\rm o}^2 - F_{\rm c}^2)^2 / \Sigma w (F_{\rm o}^2)^2]^{1/2}$ ) values were 0.036 and 0.115, respectively,  $\Sigma$  (goodness of fit) = 1.143.

#### 3. Results and discussion

#### 3.1. Synthesis of complexes 1-6

All these compounds were prepared starting from  $[(\dot{P}P)PtCl_2]$  ( $\dot{P}P = bis(diphenylphosphine)ethane (dppe)$  or cis-1,2-bis(diphenylphosphine)ethysme (dppy)) by treatment first with 1 equiv. of AgBF<sub>4</sub> solution in acetone and then, after filtration of the solid AgCl, with 1 equiv. of the appropriate ylide to give the derivatives 1–6 in 81–91% yield, according to Eq. (1):

$$\begin{pmatrix} p^{n} p \end{pmatrix}_{PiCl_{2}} \xrightarrow{+AgBF_{n} - AgCl} \\ + \frac{AgBF_{n} - AgCl}{+Pr_{1}CHCOR} \end{pmatrix} \xrightarrow{P^{n}} p = dppv, R = Me, 1; R = Ph, 2 \\ p^{n} p = dppv, R = Me, 4; R = Ph, 5 \\ p^{n} p = dppv, R = Me, 4; R = Ph, 5 \\ p^{n} p = dppv, R = Me, 4; R = Ph, 5 \\ p^{n} p = dppv, R = Me, 4; R = Ph, 5 \\ p^{n} p = dppv, R = Me, 4; R = Ph, 5 \\ p^{n} p = dppv, R = Me, 4; R = Ph, 5 \\ p^{n} p = dppv, R = Me, 4; R = Ph, 5 \\ p^{n} p = dppv, R = Me, 4; R = Ph, 5 \\ p^{n} p = dppv, R = Me, 4; R = Ph, 5 \\ p^{n} p = dppv, R = Me, 4; R = Ph, 5 \\ p^{n} p = dppv, R = Me, 4; R = Ph, 5 \\ p^{n} p = dppv, R = Me, 4; R = Ph, 5 \\ p^{n} p = dpv, R = Me, 4; R = Me, 4;$$

Table 1 Analytical data and characteristic IR bands for the compounds [(P)-PiCl{Ph<sub>2</sub>PC(H)COR}][BF<sub>a</sub>]

Compound	የቅ	R	Analysis	Þ	IR ° (cm⁻	')
			с	н	v(C=0)	v(Pt-Cl)
1	dppe	СН,	54.47	4.43	1512 s <sup>a</sup>	301
			(54.59)	(4.19)	1514 s °	
2	dppe	C6H5	57.32	4.18	1500 s <sup>d</sup>	307
			(56.97)	(4.14)	1502 s °	
3	dppe	OCH <sub>3</sub>	53.44	4.15	1708 s <sup>a</sup>	319
			(53.75)	(4.13)	1703 s °	
4	dppv	CH,	54.34	3.95	1522 s <sup>d</sup>	301
			(54.69)	(4.01)	1515 s °	
5	dppv	C <sub>4</sub> H <sub>5</sub>	56.63	3.82	1500 s 4	308
			(57.08)	(3.96)	1502 s "	
6	dppv	OCH <sub>1</sub>	53.86	3.87	1688 s <sup>d</sup>	317
		,	(53.86)	(3.94)		

<sup>a</sup> dppe = 1,2-bis(diphenylphosphino)ethane; dppv = 1,2-bis(diphenylphosphino)ethylene.

b Calculated values in parentheses.

<sup>c</sup> s = strong.

d Nujol mull

° Dichloromethane solution.

These compounds are quite stable in the solid state at room temperature and do not show any decomposition or transformation under a nitrogen atmosphere for at least one month in  $CH_2Cl_2$  solution, but they react in either  $CH_2Cl_2$  or  $CHCl_3$ solution with anionic or neutral ligands such as  $Cl^-$  or  $PPh_3$ to give substitution of the coordinated ylide. They were fully characterized by analytical and spectroscopic methods and the data obtained, included in Tables 1–3, suggest a [Pt]-C(ylide) coordination for CMPPY and a [Pt]-O(ylide) coordination for the other ylides on the  $[(PP)Pt-Cl]^+$  fragment according to Eq. (1).

# 3.1.1. [Pt]-C(ylide) complexes

The IR spectra of compounds 3 and 6 (Table 1) show a strong C=O band at 1708 and 1688 cm<sup>-1</sup> (Nuiol mull), respectively, in good agreement with the IR data, reported in the literature, for the carbonyl stretching of M-C(ylide) complexes [4,13]. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra (Table 2) confirm the coordination of the carboxymethylenetriphenylphosphorane to Pt(II) through the ylidic carbon atom on the basis of the phosphonium chemical shift and phosphonium-platinum coupling constant values. The chemical shifts at 28.46 ppm for 3 and 29.42 ppm for 6 (which are at about 11 ppm lower field than that of the free ylide) together with the corresponding <sup>2</sup>J(P<sub>vlide</sub>Pt) values of 92.8 and 102.4 Hz, respectively, closely match those reported for carbonyl-stabilized ylides coordinated to a Pt(II) substrate through the methine carbon atom [4]. The low values of <sup>1</sup>J(P<sub>trans to ylide</sub>Pt) (2603 and 2617 Hz for 3 and 6, respectively) arising from the higher trans influence of a C-coordinated with respect to an Ocoordinated carbonyl stabilized ylide [4d,14], give further support to this coordination mode.

Table 2	
Proton and <sup>31</sup> P{ <sup>1</sup> H} NMR data for the complexes [(PP)PtCl{Ph <sub>3</sub> PC(H)COR}]]	BF4] *

Compound	'H NMR					<sup>31</sup> P NMR					
	δ(H)	²J(HP <sub>yt</sub> :)	<sup>3</sup> J(HP) <sup>b.c</sup>	²J(HPt)	δ(R)	$\delta(\mathbf{P}_{trans})$	<sup>1</sup> J(P <sub>trans</sub> Pt)	$\delta(P_{cit})$	$^{1}J(P_{cis}Pt)$	$^{2}J(P_{trans}P_{cis})$	$\delta(P_{ylide})$
1	4.19 dd	22.5	2.1 °	8.4	2.03 d <sup>d</sup>	32.44 d	3662	41,43 d	3747	6.1	12.89 s
2	4.77 dd	21.5	1.6 °	e		35.18 d	3694	40,96 d	3786	6.0	13.58 s
3	3.96 ddd <sup>f</sup>	9.6	9.6 <sup>b</sup>	87.1	3.46 s	41.00 dd 8	2603	43.54 dd h	3666	3.8	28.46 dd <sup>i</sup>
4	4.24dd	22.3	2.3 °	8.9	1.91 d <sup>1</sup>	37.27 d	3697	48.55 d	3792	5.9	12.91 s
5	4.81 dd	21.4	1.7 °	4.7		38.60 d	3735	48.89 d	3839	5.6	13.85 s
6	4.22 ddd k	11.1	9.5 <sup>b</sup>	85.2	3.57 s	53.14 da 1	2617	49.33 dd "	3733	7.8	29.42 dd "

\* Spectra recorded in CDCl<sub>3</sub> at room temperature;  $\delta$  in ppm, J in Hz; <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR are relative to internal SiMe<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub> (85%), respectively; s=singlet, d=doublet.

b Coupling with the Proof atom.

Coupling with the Peir atom.

<sup>d 4</sup>J(HP<sub>ylide</sub>) 1.1; <sup>3</sup>J(HPt) 5.4.

" Not observed.

<sup>13</sup>J(HP<sub>cu</sub>) 4.8.

F 3J(PronsPylide) 5.9.

<sup>h 3</sup> $J(P_{cn}P_{vlide})$  2.4.

- <sup>i 2</sup>J(P<sub>ylide</sub>Pt) 92.8.
- <sup>j 2</sup>J(HP<sub>vlide</sub>) 1.0; <sup>2</sup>J(HPt) 5.9.
- k 3J(HPers) 5.0.
- <sup>13</sup>J(P<sub>trans</sub>P<sub>ylide</sub>) 7.8.
- <sup>m 3</sup>J(P<sub>cis</sub>P<sub>vlide</sub>) 3.8.
- <sup>n 2</sup>J(PylidePt) 102.4.

Table 3

 $^{13}C{^{1}H} NMR$  data for the complexes [(PP)PtCl{Ph\_3PC(H)COR}][BF\_4] \*

Compound	$\delta(C_{ylide})$	$\delta(C_{carbonyl})$	$\delta(C_R)$	$\delta(C_{diphosphine})$	
1	66.97 dd	190.27 s	b	26.85 dd	29.85 dd
	<sup>1</sup> J(CP) 104.85			'J(CP) 45.30	<sup>1</sup> J(CP) 66.67
	*J(CP) 5.57			<sup>2</sup> J(CP) 16.30	<sup>2</sup> J(CP) 14.05
2	69.34 dd	188.59 d		26.03 dd	28.46 dd
	<sup>1</sup> J(CP) 103.82	<sup>2</sup> J(CP) 7.98		'J(CP) 44.02	'J(CP) 44.27
	<sup>4</sup> J(CP) 5.06			<sup>2</sup> J(CP) 5.60	<sup>2</sup> J(CP) 8.57
3	28.75 ddd	171.03 d	51.63 d	23.83 dd	30.37 dd
	'J(CP) 79.99	<sup>2</sup> J(CP) 5.03	<sup>4</sup> J(CP) 2.00	<sup>1</sup> J(CP) 38.64	<sup>1</sup> J(CP) 42.67
	<sup>2</sup> J(CP <sub>trant</sub> ) 49.75			<sup>2</sup> J(CP) 7.51	2 <sup>J</sup> (CP) 8.69
	$^{2}J(CP_{crr})$ 2.60				
4	67.53 dd	190.37 s	29.41 d	144.92 dd	147.25 dd
	<sup>1</sup> J(CP) 104.44		<sup>3</sup> J(CP) 14.2	<sup>1</sup> J(CP) 59.05	<sup>1</sup> J(CP) 59.20
	<sup>4</sup> J(CP) 6.23			<sup>2</sup> J(CP) 16.26	<sup>2</sup> J(CP) 19.53
5	70.16 dd	188.54 s		144.58 dd	147.40 dd
	<sup>1</sup> J(CP) 104.38			'J(CP) 58,59	'J(CP) 58.49
	<sup>4</sup> J(CP) 5.18			<sup>2</sup> J(CP) 16.48	<sup>2</sup> J(CP) 19.48
6	27.85 ddd	70.53 d	51.30 s	144,29 dd	147.66 dd
	<sup>1</sup> J(CP) 85.45	<sup>2</sup> J(CP) 5.08		<sup>1</sup> J(CP) 52.14	1/(CP) 57.56
	<sup>2</sup> I(CP. ) 47.28			<sup>2</sup> J(CP) 19.08	21(CP) 23 52
	$^{2}J(CP_{cu})$ 3.81				5(01)2002

\* Spectra recorded in CDCl<sub>3</sub> at room temperature; δ in ppm, J in Hz; chemical shifts reported from SiMe<sub>4</sub> by taking the chemical shift of CDCl<sub>3</sub> as + 77.0 ppm.
<sup>b</sup> Masked by diphosphine signals.

In the <sup>1</sup>H NMR spectra (Table 2) of compounds 3 and 6 the ylidic proton gives rise to a doublet of doublets of doublets, flanked by <sup>195</sup>Pt satellites, due to the coupling with the phosphonium group and with both *trans* and *cis* magnetically unequivalent phosphorus atoms of the diphosphine ligand. The multiplicity and the coupling constant values of this proton signal indicate a C-coordinated ylide structure for these complexes [4].

Furthermore, the chemical shifts of the ylidic proton in compounds 3 and 6 at 3.96 and at 4.22 ppm, shifted downfield with respect to the free ylide, and the values of  ${}^{2}J(\text{HP}_{ylide})$  of 9.6 and 11.1 Hz indicate a rehybridization sp<sup>2</sup>  $\rightarrow$  sp<sup>3</sup> of the

met inc carbon atom upon coordination of the ylide to the metal center [13a,15]

Finally, the <sup>13</sup>C{<sup>1</sup>H} NMR spectra show the chemical shifts of the ylide carbon atom at 28.75 and 27.85 ppm, respectively, along with a one-bond coupling constant of 79.99 and 85.45 Hz with the phosphonium moiety [4c] and a  $^{2}J(CP)$  with both *cis* and *trans* phosphorus of the disphosphine ligand (see Table 3) as expected for a C-coordinated ylide on a '(P P) PtCl' moiety [4d].

#### 3.1.2. [Pt]-O(ylide) complexes

Compounds 1, 2, 4 and 5 display IR and NMR spectroscopic data very different from those of complexes 3 and 6 for which a C-coordination of the ylide was inferred.

The IR spectra (Table 1) of these complexes are characterized by a strong  $\nu(C=O)$  stretching in the range 1515– 1500 cm<sup>-1</sup> (CH<sub>2</sub>Cl<sub>2</sub> solution). For compounds 1, 2, 4 and 5, the  $\nu(C=O)$  values are shifted to lower wavenumbers than in the corresponding free ylides according to the data reported for other O-coordinated ylides [4d,16]. The O-coordination mode of ylides in these complexes is confirmed also by NMR spectroscopic data.

The <sup>1</sup>H NMR spectra (Table 2) display some interesting features. The methine resonance of the coordinated APPY or BPPY in complexes 1, 2, 4 and 5 appears as a doublet of doublets in the range 4.19-4.81 ppm with platinum satellites  $(\sim 8 \text{ Hz})$ . The larger coupling constant  $(\sim 20 \text{ Hz})$  is due to the coupling with the phosphorus of the phosphonium group and its value is slightly smaller with respect to the free corresponding ylides (~26 Hz) suggesting a similar hybridization (3) of the ylidic carbon. The lower coupling constant  $(\sim 2 \text{ Hz})$  arises from the coupling of the vlide proton with the trans phosphorus of the disphosphine ligand. This coupling could be due to a long range interaction through the Ocoordinated ylide system or to an agostic interaction of the vlidic proton atom with the metallic fragment. Although the first feature cannot be excluded, the possibility of a real agostic interaction is not acceptable because the <sup>1</sup>H and <sup>13</sup>C NMR spectra of all compounds do not show the characteristic high field proton shift and the reduced  ${}^{1}J({}^{13}C-{}^{1}H)$  value found in the spectra of compounds, for instance of the type  $[C_5R_5LCo(CH_2CHR'-\mu-H)]^+[BF_4]^-$  (L=P(OMe)<sub>3</sub>; R = H, Me; R' = H, Me) [17a] where this kind of two-electron three-center bond takes place [17]. In our derivatives a platinum-proton interaction could exist similar to that previously reported by Pregosin and co-workers in certain Pt(II) complexes, for instance of the type trans-[PtCl<sub>2</sub>(benzoquinoline)(PEt<sub>3</sub>)], where a proton-metal bond weaker than an agostic-type interaction was proposed [18].

The  ${}^{31}P{}^{1}H{}$  NMR spectra (Table 2) of complexes 1, 2, 4 and 5 display only one signal for the phosphonium group indicating the presence of only one isomer. For compounds 1, 4 and 2, 5 containing the APPY and BPPY ligand, respectively, the phosphorus resonance is a singlet, upfield shifted (1.40-3.06 ppm) with respect to the free ligand according to other complexes having O-coordinated ylides [16].

For all the complexes the resonances of the phosphorus atoms of the disphosphine ligand give rise to an AB pattern flanked by <sup>195</sup>Pt satellites, in agreement with a system having two magnetically different phosphorus atoms. The values of <sup>1</sup>J(PPt) for the phosphorus atom *trans* to the ylide ligand are, in these complexes, about 1000 Hz higher than those of the derivatives 3 and 6, where the ylide is C-coordinated, but similar to those reported for compounds having an O-coordination of a carbonyl-stabilized ylide [44].

Finally, a further support of the O-coordination of the ylides in complexes 1, 2, 4 and 5 arises from  $^{13}C(^{1}H)$  NMR spectroscopy. For these compounds the chemical shift of the ylidic carbon atom, ranging between 66.97 and 70.16 ppm, is shifted ~ 40 ppm downfield with respect to that found for the C-coordinated ylide complexes 3 and 6, but again close to that reported for complexes of the Group IV metals, where the ylidic ligand was shown to be O-coordinated [16b]. To the same conclusion leads the analysis of the  $^{1}J(CP)$  coupling constants of ~ 105 Hz, about 20–25 Hz higher than those of C-coordinated ylide complexes (Table 3).

#### 3.2. Synthesis of complexes 7-10

In order to explore the influence of highly sterically demanding *cis* ligands on the coordination mode of carbonyl stabilized ylides on Pt substrates, the complex *trans*- $[(CF_3)PtBr(PPh_3)_2]$  was reacted with APPY, BPPY, CMPPY and APAsY according to Eq. (2):



The spectroscopic data for the derivatives 7–10 suggest an O-coordination of the ylide ligand to the metal center. Their IR spectra (Table 4) display an intense carbonyl band in the range 1500–1520 cm<sup>-1</sup> at lower frequencies with respect to the corresponding free ylides, as usually observed for this type of interaction [4d,16]. The <sup>1</sup>H NMR data of complexes 7 and 9 show the signals of the CH protons as doublets at 5.11 (<sup>2</sup>J(HP) 16.80) and 5.26 (<sup>2</sup>J(HP) 12.52) ppm, respectively, and the <sup>13</sup>C(<sup>1</sup>H) NMR spectra show the signals of the ylidic carbons at 64.14 and 64.77 ppm, respectively (<sup>1</sup>J(CP) ~ 100 Hz), clearly indicating an sp<sup>2</sup> hybridized ylidic carbon atom (see Tables 5 and 6). Analogously the <sup>1</sup>H NMR of 10 shows the ylidic carbon as a singlet at 56.11 spectrum shows the ylidic carbon as a singlet at 66.11

Table 4
Analytical data and characteristic IR bands for the complexes trans-[Pt(CF <sub>3</sub> )(PPh <sub>3</sub> ) <sub>2</sub> {OC(R)C(H)EPh <sub>3</sub> }][BF <sub>4</sub> ]

Compound	E	R	Analysis *		IR <sup>b</sup> (cm <sup>-1</sup> )
			c	Н	ν(C=O)
7	Р	Ме	57.90	4.01	1520 s
			(58.35)	(4.14)	
8	P	OMe	57.10	4.00	1520 s
			(57.58)	(4.08)	
9	Р	Ph	59.85	4.11	1500 s
			(60.25)	(4.09)	
10	As	Me	56.02	3.85	1510 s
			(56.28)	(3.99)	

\* Calculated values in parentheses.

<sup>b</sup> Nujol mull; s = strong.

#### Table 5

 $^{1}H$  and  $^{13}C{^{1}H} NMR$  spectral data for the complexes trans-{Pt(CF<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>{OC(R)C(H)EPh<sub>3</sub>}][BF<sub>4</sub>] <sup>a</sup>

Compound	Ylide resonanc	es						
	δ(Η)	<sup>2</sup> J(HP)	δ(R)	δ(CO)	<sup>2</sup> J(CP)	δ(CH)	'J(CP)	δ(R)
7	5.11 d	16.80	1.63 s	187.84 d	14.14	64.14 d	105.85	26.01 s
8	3.76 d	16.94	3.55 s	173.26 d	8.91	41.46 d	115.85	51.35 s
9	5.26 d	12.52		186.32 d	12.58	64.77 d	106.51	
10	5.05 s		1.68 s	184.05 s		66.11 s		25.71 s

<sup>a</sup> Spectra recorded in CDCl<sub>3</sub> at room temperature; proton chemical shifts are reported from SiMe<sub>4</sub>; carbon chemical shifts reported from SiMe<sub>4</sub> by taking the chemical shift of CDCl<sub>3</sub> as + 77.0 ppm; δ in ppm, J in Hz; s = singlet, d = doublet.

Table 6 <sup>31</sup>P{<sup>1</sup>H} and <sup>10</sup>F{<sup>1</sup>H} NMR spectral data for the complexes *trans*-{ $Pt(CF_3)(PPh_3)_2[OC(R)C(H)EPh_3)][BF_4]$ <sup>\*</sup>

Compound	Yilde resonances	Phosphine reson	ances			
	δ(Ρ)	δ(P)	<sup>1</sup> J(PPt)	δ(F)	<sup>2</sup> J(FPt)	<sup>3</sup> J(PF)
7	12.35 s	24.19 g	3170.0	- 10.27	655.1	17.8
8	13.98 s <sup>b</sup>	24.79 g	3071.9	- 8.81 t	711.5	18.8
9	12.79 s	24.05 g	3112.9	- 10.09 t	659.6	18.2
10		24.11 q	3101.2	-9.70 t	655.1	17.7

<sup>a</sup> Spectra recorded in CDCl<sub>3</sub> at room temperature; <sup>31</sup>P chemical shifts referenced to external H<sub>3</sub>PO<sub>4</sub> (85%); <sup>19</sup>F chemical shifts referenced to internal CFCl<sub>3</sub>; δ in ppm, J in Hz; s = singlet, t = triplet, q = quartet.

 $^{b4}J(PPt) = 12.3.$ 

ppm [4d]. As for complex 8 the chemical shifts of the methinic proton is found at 3.76 ppm, at higher field than in 7, 9 and 10. This shift upfield can be explained by a shielding effect of the metal atom, the ylide moiety in a conformation with the C-H proton being forced towards the metal, as suggested by the X-ray structure in which it is observed that the C-H vector is directed towards the Pt atom with a Pt-H separation of 2.94 Å (see below). This effect results in 8 enhanced with respect to 7, 9 and 10, likely by the stronger interaction of CMPPY with the Pt<sup>+</sup> system due to the higher electron density on the ylide moiety in carbomethoxymethylenetriphenylphosphorane.

The trans geometry of complexes 7-10 is confirmed by their <sup>31</sup>P{<sup>1</sup>H} NMR spectra, which show a quartet due to the

coupling of the magnetically equivalent  $PPh_3$  with the trifluoromethyl group, flanked by <sup>195</sup>Pt satellites.

The  $^{19}$ F NMR spectra show a triplet for the CF<sub>3</sub> group due to the coupling with the equivalent P atoms, flanked by  $^{195}$ Pt satellites.

# 3.3. Synthesis of complexes 11-13

The reactions between  $[(C_3H_5)PtCl]_4$  and the carbonyl stabilized ylides APPY, BPPY and CMPPY lead to the formation of complexes 11–13 according to Eq. (3). The compounds, differently from the analogous Pd(II) derivatives, are stable in the common organic solvents and do not undergo ligand dissociation [4a,b].

Compound -	R	Analysis <sup>a</sup>		IR <sup>b</sup> (cm <sup>-1</sup> )		<sup>31</sup> P{ <sup>1</sup> H} NM	IR <sup>c.d</sup>
		c	н	ν(C=O)	v(Pt-Cl)	δ(Ρ)	²J(PPt)
11	Me	46.83	3.98	1643 s	281 m	27.09 \$	92.8
		(47.41) °	(3.98)			22.75 s	57.7
12	Ph	52.21	4.00	1616 s	275 m	26.72 s	118.2
		(53.42)	(4.02)			23.00 s	84.6
13	OMe	47.12	4.00	1682 s	281 m	28.74 s	118.2
		(47.57)	(3.99)			24.77 s	78.6

table 7 Analytical data, characteristic IR bands and <sup>31</sup>Pt<sup>1</sup>H} NMR data for the complexes [PtCl( $\pi^3$ -C,H<sub>5</sub>)(Ph-PCHCOR)]

a Calculated values in parentheses.

<sup>b</sup> Nujcl mull; s = strong, m = medium

<sup>c</sup> Phosphorus chemical shifts referenced to external H<sub>3</sub>PO<sub>4</sub> (85%); δ in ppm, J in Hz, s = singlet.

<sup>d</sup> Ylide resonances.

" The values have been calculated for C24H24ClOPPt+H2O.

$$\frac{1}{4} [(C_3H_3)PiCl]_4 + Ph_3PCHCOR \longrightarrow \langle P_1 \\ P_2 \\ H \\ COR \\ R = Me, 11 \\ R = Ph, 12 \\ R = 0Me, 13 \\ R = 0Me,$$

The IR spectra (Table 7) of 11–13 show intense C=O absorptions in the range 1616–1682 cm<sup>-1</sup> indicating that the ylides are coordinated through the methine carbon. The <sup>1</sup>H NMR spectra (Table 8) show that each derivative is present in two diastereoisomeric forms (about 2:3) due to the presence of the asymmetric coordinated ylide carbon and of the prochiral allyl ligand on the metal center [4a,b]. The C-coordination is confirmed by the <sup>1</sup>H NMR spectra, which show the ylidic protons as doublets in the range 5.54–4.44 ppm with the values of <sup>2</sup>*J*(HP) and <sup>2</sup>*J*(HPt) similar to those observed for 3 and 6. In Fig. 1 is reported the <sup>1</sup>H NMR spectrum for [( $\eta^3$ -C<sub>3</sub>H<sub>3</sub>)PtCl{Ph<sub>3</sub>PCHCOOMe}] (13). The <sup>31</sup>P{<sup>1</sup>H} MR spectra show two singlets for each compound flanked by <sup>195</sup>Pt satellites.

The spectroscopic data indicate that in these complexes, having a low sterically demanding metallic framework, the C-coordination of the entering ylide ligand is favored with respect to the O-coordination: although the methine carbon atom is more sterically hindered than the carbonyl oxygen coordinating site, it is also the atom with the highest electronic density of the whole ligand molecule.

#### 3.4. Synthesis of complexes 14-19

The above results suggest that the coordination mode of these carbonyl stabilized ylides can be drastically influenced by the hindrance of the ancillary ligands on the Pt atom. The low sterically demanding allyl system allows the ylide to coordinate through the methine carbon carrying a bulky onium group, while the highly sterically demanding triphenylphosphine ligands in the 'trans-Pt(CF<sub>3</sub>) (PPh<sub>3</sub>)<sub>2</sub>' substrate force the ylides to coordinate through the less hindered carbonyl oxygen atom. With the aim to have a deeper insight, we reacted the carbonyl stabilized ylides with the dimer  $[PtCl{P(Bu')_2C(Me)_2CH_2}]_2$ , bearing either a hindered phosphorus atom  $-P(Bu')_2$  and a less hindered  $-CH_2$  moiety directly bonded to the platinum. The bridge splitting of the dimer  $[PtCl{P(Bu')_2C(Me)_2CH_2}]_2$  with carbonyl stabilized ylides could give four different isomers: (i) C-coordinated ylide *cis* to  $-CH_2$ ; (ii) C-coordinated ylide *cis* to -P(Bu')\_2; (iii) O-coordinated ylide *cis* to  $-CH_2$ ; (iv) O-coordinated ylide *cis* to  $-P(Bu')_2$ .

It is noteworthy that in all the reactions we carried out, either with P and As ylides, the only isolated product was the C-coordinated derivative bearing the ylide in *cis* position to the less hindered  $-CH_2$  moiety, according to Eq. (4):



All the IR and NMR spectroscopic data (Tables 9 and 10) agree with a C-coordinated ylide cis to the  $-CH_2$  group of the cyclometallated phosphine without any other signals due to different isomeric forms.

The IR spectra show the CO absorption in the range 1609– 1677  $\text{cm}^{-1}$  in agreement with the proposed coordination mode.

The <sup>1</sup>H NMR spectra show the ylidic proton as a doublet of doublets in the range 4.35–5.74 ppm due to the coupling with the P<sub>ylide</sub> and the P<sub>phosphine</sub> flanked by <sup>195</sup>Pt satellites and the values of the <sup>2</sup>/(HP<sub>ylide</sub>) (see Table 10) clearly indicate the C-coordination.

It should be noted that in all the derivatives 14-19 the proton in  $-CH_2$ , the methyls in  $-C(Me)_2$  and the tert-butyl

Table 8 <sup>1</sup> H and <sup>31</sup> P( <sup>1</sup> H	I) NMR spec	ctral data for th	he complexes [	PiCI( $\eta^3$ -C <sub>3</sub> F	Is) (Ph3PCHC	OR)] ª					
Compound	Ylide rest	onances					Allyl resonances <sup>b</sup>				
	8(H)	(dH)/ <sub>2</sub>	(J4H)/2	δ(R)	<sup>4</sup> <i>J</i> (HP)	4J(HPt)	δ(H <sub>1</sub> )	ô(H2)	ô(H3)	ð(H4)	δ(H <sub>c</sub> )
=	4.96 d 4.92 d	5.3 4.1	80.30 80.30	2.44 d 2.28 d	2.4 2.1	9.0 13.2	0.51 dd <sup>3</sup> /(H <sub>1</sub> H <sub>c</sub> ) 10.6 <sup>2</sup> /(H <sub>1</sub> H <sub>2</sub> ) 2.8 <sup>2</sup> /(H <sub>1</sub> Pt) 84.1	E	2.23 d <sup>3</sup> J(H <sub>3</sub> H <sub>c</sub> ) 12.7 <sup>2</sup> J(H <sub>3</sub> Pt) 52.8	3.92 d <sup>3</sup> J(HH) 7.6 <sup>2</sup> J(HPt) 17.3	4.25 m ²J(HPt) 75.58
							1.24 dd <sup>3</sup> /(Hi <sub>1</sub> H <sub>C</sub> ) 12.7 <sup>2</sup> /(Hi <sub>1</sub> H <sub>2</sub> ) 2.1 <sup>2</sup> /(Hi <sub>1</sub> Pt) 86.9	1.51 ddd <sup>3</sup> /(H <sup>2</sup> /H <sub>c</sub> )6.0 <sup>2</sup> /(H <sup>3</sup> /H <sup>1</sup> ) 4.0 <sup>4</sup> /(H <sup>3</sup> /H <sup>1</sup> ) 2.0 <sup>2</sup> /(HPt) 40.0			
12	5.54 d 5.45 d	3.9 2.5	88.00 82.50				0.43 dd <sup>3</sup> J(H <sub>2</sub> H <sub>C</sub> ) 10.5 <sup>2</sup> J(H <sub>1</sub> H <sub>2</sub> ) 1.81 <sup>2</sup> J(H <sub>1</sub> Pt) 84.4	2.25 ddd <sup>3</sup> /(H <sub>2</sub> H <sub>5</sub> ) 6.2 <sup>4</sup> /(H <sub>2</sub> H <sub>3</sub> ) 2.1 <sup>7</sup> /(H <sub>2</sub> H <sub>1</sub> ) 4.2 <sup>7</sup> /(HPt) 34.3	2.01 m	3.83 d <sup>2</sup> J(HPt) 19.8 <sup>3</sup> J(H <sub>3</sub> H <sub>C</sub> ) 7.9	4.17 m ²J(HPt) 75.5
							1.16 d <sup>3</sup> /(H <sub>1</sub> H <sub>C</sub> ) 10.28 <sup>2</sup> /(HPt) 73.10	1.57 ddd <sup>3</sup> /(H <sup>2</sup> <sub>2</sub> H <sub>2</sub> ) 5.9 <sup>4</sup> /(H <sup>2</sup> <sub>2</sub> H <sub>1</sub> ) 2.0 <sup>2</sup> /(H <sup>2</sup> <sub>2</sub> H <sub>1</sub> ) 4.1 <sup>2</sup> /(HPt) 29.7			
13	4.53 s 4.44 s	0.50 2.64	94.39 89.84	3.52 s 3.59 s			0.57 dd <sup>3</sup> /(H <sub>1</sub> H <sub>C</sub> ) 10.87 <sup>2</sup> /(H <sub>1</sub> H <sub>2</sub> ) 2.4 <sup>2</sup> /(H <sub>1</sub> Pt) 82.5	2.43 ddd <sup>3</sup> /(H <sub>2</sub> H <sub>2</sub> ) 6.2 <sup>4</sup> /(H <sub>2</sub> H <sub>1</sub> ) 2.5 <sup>2</sup> /(H <sub>2</sub> H <sub>1</sub> ) 4.4 <sup>2</sup> /(HPt) 33.3	2.11 dd <sup>3</sup> 7(H <sub>5.3</sub> H <sub>C</sub> ) 10.6 <sup>2</sup> 7(HPt) 39.5	3.85 d <sup>2</sup> J(HPt) 24.5 <sup>3</sup> J(H <sub>4</sub> H <sub>c</sub> ) 6.9	4.22 m ²J(HPt) 73.5
							1.24 d <sup>3</sup> /(H <sub>i</sub> H <sub>c</sub> ) 12.7 <sup>2</sup> /(H <sub>i</sub> Pt) 86.9	1.65 ddd <sup>3</sup> /(H2Hc) 5.8 <sup>4</sup> /(H2H5) 2.0 <sup>2</sup> /(H2H1) 5.3 <sup>2</sup> /(HPt) 33.6			
<ul> <li>Spectra recol ms = masked.</li> <li>Proton labeli</li> </ul>	rded in CDC ng: H, and H	$I_3$ at room ten $I_1 = syn$ , <i>cis</i> to	nperature; prott ylide; H <sub>2</sub> and ]	on chemical s $H'_2 = anti, cis$	shifts are repor to ylide; H <sub>3</sub> ar	ted from SiMe nd H' <sub>5</sub> = anti, tr	24: phosphorus chemical ans to ylide; H <sub>4</sub> = syn, n	shifts referenced to example to example to $d_{c} = a d l y$	ternal H <sub>3</sub> PO4 (85%); 8 ii lic central proton.	n ppm, <i>J</i> in Hz; s = s	inglet, d = doublet,

362



Fig. 1. 'H NMR spectrum for [PtCl( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>){Ph<sub>3</sub>PCHCOOMe}] (13).

groups of the chelated phosphine ligand are not magnetically equivalent giving rise in the <sup>1</sup>H NMR spectra to a couple of proton, methyl and butyl signals as reported in Table 10.

The <sup>31</sup>P{<sup>1</sup>H} NMR spectra for compounds **14–16** show the  $P_{\text{yhde}}$  as a doublet in the range 24.37–26.78 ppm due to the coupling with the phosphine P atom flanked by satellites due to <sup>195</sup>Pt. The P atoms of the phosphine appear for compounds **14–16** as doublets in the range – 13.37 to – 10.45 ppm with the <sup>195</sup>Pt satellites and for **17–19** as singlets in the range – 10.45 to – 8.00 ppm. The values are in agreement with those observed for complexes of the type [Pt(PC)LX] previously reported [7].

In the case of the phosphonium ylide derivatives the spectra show always small signals corresponding to the starting Pt dimer and free ylide indicating that Eq. (4) is an equilibrium strongly shifted to the right.

# 3.5. X-ray structure of trans-[Pt(PPh\_3)\_2(CF\_3){OC(OCH\_3)=C(H)(PPh\_3)}][BF\_4](8)

The crystal structure contains Pt complex cations,  $BF_4^$ anions and a  $CH_2Cl_2$  molecule of crystallization with partial occupancy (see Section 2).

The Pt(II) complex of the O-coordinated stabilized phosphonium ylide is depicted in Fig. 2. Final atomic parameters are reported in Table 11 and a selection of bond lengths and angles in Table 12.

The coordination geometry around Pt(II) is essentially square planar with C(1)-Pt-O(1) and P(1)-Pt-P(2) angles showing slight deviations from linearity (Table 12). The donor atoms are coplanar ( $\pm 0.005$ Å) with the metal slightly displaced from the mean coordination plane by 0.031(2) Å. The Pt-O(1) distance of 2.093(3) Å is longer than that observed in *trans*-(PPh<sub>3</sub>)<sub>2</sub>Pt(Ph)(OO-Bu') [19]. The Pt-P distances of 2.347(1) and 2.333(1) Å are longer than the values usually found for triphenylphosphines in *trans* position bonded to Pt(II) (ranging from 2.274(2) to 2.320(2) Å) [19,20]. Both features may be explained by steric requirements likely originating from the bulky PPh<sub>3</sub> group of the ylide moiety.

In fact, the arrangement of the latter with a torsion angle O(1)-C(3)-C(2)-P(3) of  $166.5(4)^\circ$ , brings the phospho-

Table 9

Analytical data, characteristic IR bands and <sup>31</sup>P{'H} NMR spectra for the complexes [PiCl{P(Bu')\_2C(Me)\_2CH\_2}(Ph\_2ECHCOR)]

Compound	E	R	Analysis *		IR <sup>b</sup> (cm <sup>-1</sup> )		<sup>31</sup> P{ <sup>1</sup> H} NMR <sup>c</sup>	
			c	н	ν(C=O)	ν(Pt-Cl)	δ(P <sub>ylide</sub> )	<b>δ(PC)</b>
14	Р	Ме	52.78 (52.83)	6.06 (6.05)	1624 ª 1621 °	246 m	24.37 d <sup>3</sup> J(PP) 10.0 <sup>2</sup> J(PPt) 41.6	- 11.52 d <sup>3</sup> J(PP) 10.0 <sup>1</sup> J(PPt) 2912.9
15	Р	ОМе	50.98 (51.73)	5.80 (5.92)	1677 ª 1615 °	249 m	24.89 d <sup>3</sup> J(PP) 11.4 <sup>2</sup> J(PPt) 64.2	10.45 d <sup>3</sup> J(PP) 11.4 <sup>1</sup> J(PPt) 2868.5
16	P	Ph	56.00 (56.19)	5.25 (5.83)	1611 ª 1605 °	248 m	26.78 d <sup>3</sup> J(PP) 10.9 <sup>2</sup> J(PPt) 53.4	- 13.33 d <sup>3</sup> J(PP) 10.9 <sup>1</sup> J(PPt) 2954.6
17	As	Ме	49.19 (49.99)	5.65 (5.71)	1618 ª 1618 °	252 m		– 9.25 s <sup>1</sup> J(PPt) 2752.7
18	As	OMe	48.85 (48.92)	5.55 (5.60)	1670 ª 1662 °	252 m		– 8.00 s <sup>1</sup> J(PPt) 2693.8
19	As	Ph	53.20 (53.31)	5.48 (5.53)	1609 <sup>4</sup> 1604 °	253 m		– 10.45 s <sup>1</sup> J(PPt) 2776.5

a Calculated values in parentheses.

b s = strong.

<sup>c</sup> Spectra recorded in CDCl<sub>3</sub> at room temperature; δ in ppm; J in Hz; s = singlet, d = doublet; phosphorus chemical shifts referenced to external H<sub>3</sub>PO<sub>4</sub> (85%); δ in ppm, J in Hz, d = doublet.

<sup>d</sup> Nujol mull.

" CH2Cl2 solution.

Compound	Ylide reso.	nances											
	ð(CH)	(dH)/;	(dH)/ <sub>i</sub>	<sup>2</sup> J(HPt)	ð(R)	ð(t-Bu)	3J(HP)	ð(Me)	3J(HP)	8(H)	(HH)/ <sub>2</sub>	(HP)/s	(14H)/2
14	A. 93 dd	7.13	6.17	51.19	2.47 d <sup>b</sup>	1.48 đ 1.43 đ	13.15	1.30 d 0 88 d	13.70 13.06	0.37 dd - 0 53 dd	9.21 9.21	13.36 4 86	121.07
15	4.35 dd	77.7	0.59	61.65	3.61 s	1.47 d	13.01	1.28 d	13.37	0.53 dd	9.36	12.14	114.74
16	5.48 dd	1.36	5.04	52.53		140 d	12.89	0.94 d	13.48	0.19 dd	06.8 00 °	11.06	94.40 117.33
17	5.16 d		8.20	61.61	2.40 s °	0 c7 1	13.11	1.29 d	13.53	0.44 dd	9.23	12.60	114.18
	1 64 4		8 35	70.80	3.61 s	1.42 d 1.48 d	12.84 12.86	0.87 d 1.28 d	12.96 13.23	-0.20 dd 0.62 dd	9.23 9.29	6.75 11.13	97.65 112.08
81	n +C.+			001		1.40 d	12.64	0.93 d 0.05 d	12.88	0.06 dd	9.29 0.40	7.70	98.07
61	5.74 d		8.17	06.10		1.29 d	13.01	0.84 d	13.17	-0.14 t	9.40	9.02	105.15



Fig. 2. Perspective view of the cation of 8 The phenyl carbon atoms are omitted for the sake of clarity.

nium group away from the Pt(PPh<sub>3</sub>)<sub>2</sub> system and forces the C(2)H proton to point towards the metal with a I't...H nonbonding interaction of 2.94 Å.

The carbomethoxymethylene system makes a dihedral angle of 86.9(2)° with the coordination mean plane and the Pt-O(1)-C(3)-C(2) adopts a cisoid conformation (torsion angle of  $0.4(8)^\circ$ ).

The arrangement of the vlide in the present compound differs from that found in TiCl<sub>4</sub>(APPY-O)(THF) [16b] and in trans-[Sn(CH<sub>3</sub>)<sub>3</sub>Cl(APPY-O)] [21] complexes (APPY = acetylmethylenetriphenylphosphorane) where the calculated torsion angles M-O-C-C and O-C-C-P indicate a transoid and cisoid conformation, respectively. However, the O(1)-C(3) and C(2)-C(3) bond lengths of 1.271(6) and 1.393(8) Å are comparable with the values observed in the cited Ti and Sn complexes, indicating for the latter a double-bond character.

Finally, the Pt-CF<sub>3</sub> distance of 1.994(5) Å is similar, within experimental error, to that found in the hydrido trifluoromethyl complex trans- $[Pt(H)(CF_1)(PPh_2)_2]$ (2.009(8) Å) [22]. It is noteworthy that 8 is the first Obound Pt-ylide complex whose structure has been confirmed by a single crystal X-ray diffraction study.

# 4. Conclusions

The carbonyl stabilized ylides present two possible coordination sites towards metal centers: the methine carbon and the oxygen atom. Since the higher electron density is located on the methine carbon, this is the most nucleophilic site [1], and thus the preferential metal coordination mode involves the vlidic C atom. However, a high steric hindrance around the metal appears to influence significantly the ylide coordination mode. In fact, for the low sterically demanding 'Pt( $n^3$ allyl)Cl' fragment the reactions with Ph<sub>3</sub>PCHCOR  $(R = CH_3, Ph, OCH_3)$  yield selectively the C-bonded derivatives, while for the larger 'trans-(PPh3)2Pt(CF3)' fragment only the O-coordination occurs.

In the case of the '(PP)PtCl' moiety, where the diphenylphosphine ligand exhibits a steric hindrance higher than the

2 **Table** 

Table 11 Fractional atomic parameters and isotropic thermal parameters U for trans- $[Pt(PPh_3)_2(CF_3)]OC(OCH_3)=C(H)(PPh_3)]BF_4] \cdot 0.5CH_2Cl_2(8)$ 

Atom	x	y	z	U <sub>eq</sub> <sup>a</sup>
Pt	0.16302(2)	0.213211(12)	0.143720(10)	0.03108(8)
P(1)	0.09737(13)	0.07783(9)	0.19045(7)	0.0333(3)
P(2)	0.23837(13)	0.34325(9)	0.09440(8)	0.0344(3)
P(3)	0.53833(14)	0.25954(11)	0.36233(8)	0.0427(3)
F(1)	-0.0287(3)	0.3362(2)	0.1309(3)	0.0615(10)
F(2)	-0.0916(4)	0.2196(3)	0.1806(3)	0.0665(11)
F(3)	-0.0979(4)	0.2085(3)	0.0637(3)	0.0708(12)
0(1)	0.3556(3)	0.1813(2)	0.1553(2)	0.0354(7)
O(2)	0.5610(4)	0.1765(3)	0.2123(2)	0.0494(10)
C(1)	-0.0198(5)	0.2450(4)	0.1291(4)	0.0439(12)
C(2)	0.4293(5)	0.2516(4)	0.2801(3)	0.0430(12)
C(3)	0.4432(5)	0.2029(4)	0.2137(3)	0.0371(11)
C(4)	0.5830(6)	0.1287(5)	0.1445(4)	0.058(2)
C(5)	-0.0648(5)	0.0155(3)	0.1466(3)	0.0403(11)
C(6)	-0.1056(6)	0.0119(4)	0.0708(4)	0.0502(14)
C(7)	-0.2243(7)	-0.0380(5)	0.0350(4)	0.059(2)
C(8)	-0.3026(7)	-0.0845(5)	0.0744(5)	0.067(2)
C(9)	-0.2642(7)	-0.0827(5)	0.1486(5)	0.072(2)
C(10)	0 1455(6)	-0.0323(5)	0.1847(4)	0.059(2)
C(11)	0.2077(5)	-0.0067(3)	0.1772(3)	0.0347(10)
C(12)	0.1790(6)	-0.0762(4)	0.1176(4)	0.0518(14)
C(13)	0.2687(7)	-0.1374(5)	0.1099(4)	0.065(2)
C(14)	0.3828(6)	-0.1300(4)	0.1589(4)	0.054(2)
C(15)	0.4127(6)	-0.0623(4)	0.2180(4)	0.0520(14)
C(16)	0.3254(6)	-0.0002(4)	0.2266(3)	0.0458(13)
C(17)	0.0985(5)	0.0918(4)	0.2895(3)	0.0411(11)
C(18)	0.1057(6)	0.0189(4)	0.3300(3)	0.0490(13)
C(19)	0.1027(7)	0.0298(5)	0.4045(4)	0.061(2)
C(20)	0.0954(9)	0.1152(6)	0.4398(4)	9.074(2)
C(21)	0.0914(9)	0.1890(6)	0.4016(4)	0.071(2)
C(22)	0.0929(7)	0.1787(4)	0.3269(4)	0.0531(14)
C(23)	0.5703(6)	0.1495(5)	0.3868(3)	0.0496(14)
C(24)	0.6909(7)	0.1184(5)	0.3835(4)	0.064(2)
C(25)	0.7048(9)	0.0300(6)	0.3971(5)	0.079(2)
C(26)	0.6020(10)	-0.02/2(6)	0.4118(5)	0.079(2)
C(27)	0.4622(9)	0.0010(0)	0.4139(4)	0.071(2)
C(20)	0.4046(7)	0.0902(3)	0.4016(4)	0.050(2)
C(29)	0.4013(0)	0.3107(3)	0.4310(3)	0.0312(14)
C(30)	0.4621(6)	0.2900(0)	0.5550(5)	0.072(2)
C(31)	0.4265(11)	0.3434(7)	0.5359(5)	0.091(3)
C(33)	0.3376(9)	0.4350(6)	0.4680(5)	0.093(3)
C(34)	0.3900(7)	0.3867(5)	04147(4)	0.064(2)
C(35)	0.6971(6)	0.3272(4)	0.3683(3)	0.0481(13)
C(36)	0.0971(0)	0.3272(4)	0.3003(3) 0.4352(4)	0.061(2)
C(37)	0.9057(7)	0.3948(6)	0.4427(4)	0.068(2)
C(38)	0.9379(8)	0.4350(7)	0.3840(5)	0.087(3)
C(39)	0.8500(10)	0.4211(8)	0.3173(6)	0.100(3)
C(40)	0.7315(8)	0.3662(7)	0.3097(4)	0.081(3)
C(41)	0.1386(5)	0.3541(4)	0.0063(3)	0.0407(11)
C(42)	0.1235(7)	0.4387(5)	-0.0174(4)	0.056(2)
C(43)	0.0605(8)	0.4412(6)	-0.0896(4)	0.070(2)
C(44)	0.0137(8)	0.3629(6)	-0.1380(4)	0.068(2)
C(45)	0.0294(7	0.2795(5)	-0.1146(4)	0.065(2)
C(46)	0.0895(7)	0.2751(5)	-0.0424(4)	0.056(2)
C(47)	0.4018(5)	0.3451(4)	0.0720(3)	0.0397(11)
C(48)	0.5145(6)	0.3743(5)	0.1256(4)	0.056(2)
C(49)	0.6393(7)	0.3744(6)	0.1092(4)	0.065(2)
C(50)	0.6557(7)	0.3476(5)	0.0378(4)	0.060(2)
C(51)	0.5458(7)	0.3210(5)	-0.0164(4)	0.062(2)
				(continued)

Atom	x	у	z	U <sub>eq</sub> *
C(52)	0.4197(7)	0.3184(5)	-0.0005(4)	0.057(2)
C(53)	0.2564(5)	0.4489(4)	0.1573(3)	0.0403(11)
C(54)	0.2095(6)	0.4492(4)	0.2238(4)	0.0485(13)
C(55)	0.2259(7)	0.5284(5)	0.2734(4)	0.060(2)
C(56)	0.2902(8)	0.6089(5)	0.2573(5)	0.067(2)
C(57)	0.3390(8)	0.6090(5)	0.1931(5)	0.066(2)
C(58)	0.3238(7)	0.5295(4)	0.1433(4)	0.057(2)
В	0.1237(14)	0.7585(9)	0.3816(7)	0.090(3)
F(4)	0.0965(8)	0.7806(5)	0.3127(4)	0.130(2)
F(5)	0.1009(11)	0.6689(5)	0.3790(5)	0.162(4)
F(6)	0.0644(13)	0.8006(8)	0.4272(6)	0.212(5)
F(7)	0.2515(10)	0.7868(9)	0.4082(6)	0.198(5)
C(59)	0.2156(16)	0.2949(12)	0.7179(10)	0.074(4) <sup>b</sup>
Cl(1)	0.3024(8)	0.2097(4)	0.6968(3)	0.125(3) <sup>b</sup>
Cl(2)	0.3111(5)	0.3846(5)	0.7749(5)	0.133(3) <sup>b</sup>

\*  $U_{eq} = 1/3$  of the trace of the orthogonalized U.

<sup>b</sup> Occupancy 0.5.

Table 11 (continued)

Table 12 Selected bond lengths (Å) and angles (°) for trans- $[Pt(PPh_3)_2(CF_3)- {OC(OCH_3)=C(H)(PPh_3)}][BF_4] \cdot 0.5CH_2Cl_2 (8)$ 

Pt-C(1)	1.994(5)	P(3)-C(2)	1.719(6)
Pt-O(1)	2.093(3)	P(3)-C(23)	1.798(7)
Pt-P(1)	2.347(1)	P(3)-C(29)	1.810(7)
Pt-P(2)	2.333(1)	P(3)-C(35)	1.802(6)
P(1)-C(5)	1.827(5)	F(1)-C(1)	1.365(6)
P(1)-C(11)	1.824(5)	F(2)-C(1)	1.365(7)
P(1)-C(17)	1.819(6)	F(3)-C(1)	1.351(7)
P(2)-C(41)	1.812(6)	O(1)-C(3)	1.271(6)
P(2)-C(47)	1.812(6)	O(2)-C(3)	1.333(6)
P(2)-C(53)	1.815(6)	O(2)-C(4)	1.438(8)
		C(2)-C(3)	1.393(8)
P(1)-PtP(2)	176.43(4)	Pt-P(2)-C(47)	114.7(2)
P(1)-Pt-O(1)	89.4(1)	Pt-P(2)-C(53)	113.7(2)
P(1)-Pt-C(1)	92.1(2)	C(2)-P(3)-C(23)	112.8(3)
P(2)-Pt-O(1)	87.5(1)	C(2)-P(3)-C(29)	105.7(3)
P(2)-Pt-C(1)	91.0(2)	C(2)-P(3)-C(35)	116.2(3)
O(1)-Pt-C(1)	177.9(2)	Pt-O(1)-C(3)	124.9(3)
Pt-P(1)-C(5)	116.0(2)	C(3)-O(2)-C(4)	118.4(5)
Pi-P(1)-C(17)	114.7(2)	C(3)-C(2)-P(3)	124.5(4)
Pt-P(1)-C(11)	111.6(2)	O(1)-C(3)-O(2)	117.5(5)
Pt-P(2)-C(41)	112.9(2)	O(1)-C(3)-C(2)	126.8(5)
		O(2)-C(3)-C(2)	115.7(5)

allyl but lower than two mutually *trans* PPh<sub>3</sub> ligands, the most nucleophilic ylide Ph<sub>3</sub>PCHCOOMe coordinates via C to the Pt center, while the less nucleophilic Ph<sub>3</sub>PCHCOR (R = Me, Ph) are forced to coordinate through the less hindered carbonyl oxygen atom.

Finally, for the complexes containing the  $P(Bu^{i})_{2}$ -C(Me)<sub>2</sub>CH<sub>2</sub> ligand having a bulky  $-P(Bu^{i})_{2}$  moiety and a -CH<sub>2</sub> group bonded to platinum., the complexes obtained present only the C-coordination mode of the ylide in *cis* position to the less hindered -CH<sub>2</sub> group.

# 5. Supplementary material

Complete list of bond angles and distances, atomic coordinates of H atoms and anisotropic thermal parameters for compound 8 are available from author E.Z. on request.

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#### References

- A.W. Johnson, Ylides and Imines of Phosphorous, Wiley, New York, 1993.
- [2] (a) W. Keim, F.H. Howaldi, R. Goddard and C. Krüger, Angew. Chem., Int. Ed. Engl., 17 (1978) 466; (b) W. Keim, A. Behr, B. Gruber, B. Hoffmann, F.H. Howaldt, U. Kürschner, B. Limbacker and F.P. Sistig, Organometallics, 5 (1986) 2356; (c) K.A.O. Starzewski and L. Born, Organometallics, 11 (1992) 2701.
- [3] (a) L. Pandolfo, G. Facchin, R. Bertani, G. Valle and P. Ganis, Angew. Chem., Int. Ed. Engl., 33 (1994) 576; (b) L. Pandolfo, R. Bertani, G. Facchin, L. Zanotto, P. Ganis, G. Valle and R. Seraglia, Inorg. Chim. Acta, 237 (1995) 27.
- [4] (a) G. Facchin, R. Bertani, M. Calligaris, G. Nardin and M. Mari, J. Chem. Soc., Dalton Trans., (1987) 1381; (b) G. Facchin, R. Bertani, L. Zanotto, M. Calligaris and G. Nardini, J. Organomet. Chem., 366 (1989) 409; (c) G. Facchin, L. Zanotto, R. Bertani and G. Nardin, Inorg. Chim. Acta, 245 (1996) 157; (d) G. Facchin, L. Zanotto, R. Bertani, L. Canovese and P. Uguagliati, J. Chem. Soc., Dalton Trans., (1993) 2871.
- [5] G. Booth and J. Chatt, J. Chem. Soc. A, (1966) 636.
- [6] R.A. Michelin, M. Napoli and R. Ros, J. Organomet. Chem., 175 (1979) 239.
- [7] H.C. Clark, A.B. Goel, R.G. Goel and S. Goel, *Inorg. Chem.*, 19 (1980) 3220.
- [8] B.E. Mann, B.L. Shaw and G. Shaw, J. Chem. Soc. A, (1971) 3536.

- [9] F. Ramirez and S. Dershowitz, J. Org. Chem., 22 (1957) 41.
- [10] O. von Isler, H. Gutmann, M. Montavon, R. Rüegg, G. Ryser and P. Zeller, *Helv. Chim. Acta*, 50 (1957) 1242.
- [11] J.B. Hendrichson, R.E. Spenger and J.J. Sims, *Tetrahedron*, 19 (1963) 707; N.A. Nesmeyanov, V.V. Pravdina and O.A. Reutov, *Proc. Acad. Sci. USSR*, 155 (1964) 424; A.W. Johnson and H. Shubert, J. Org. *Chem.*, 35 (1970) 2678.
- [12] G.M. Sheldrick, SHELXL 93, program for the refinement of crystal structures, University of Göttingen, Germany, 1993.
- [13] (a) H. Koezuka, G. Matsubayashi and T. Taneka, Inorg. Chem., 15 (1976) 417; (b) E.T. Waleski, Jr., J.L. Silver, M.D. Jansson and J.L. Burmeister, J. Organomet. Chem., 102 (1975) 365; (c) H. Takahashi, Y. Oosawa, A. Kobayashi, T. Saito and Y. Sasuki, Bull. Chem. Soc. Jpn., 50 (1977) 1771.
- [14] (a) T.G. Appleton, H.C. Clark and L.E. Manzer, Coord. Chem. Rev., 10 (1973) 335; (b) K. Ito, M. Fukui and Y. Ishii, J. Organomet. Chem., 129 (1977) 259.
- [15] P.S. Progosin and R.W. Kunz, <sup>31</sup>P and <sup>13</sup>C NMR of Transition Metal Phospline Complexes, Springer, New York, 1979.
- [16] (a) R. Uson, J. Fornies, R. Navarro, P. Espinet and C. Mendevil, J. Organomet. Chem., 290 (1985) 125; (b) J.A. Albanese, D.L. Staley, A.L. Rheingold and J.L. Burmeister, *Inorg. Chem.*, 29 (1990) 2209, and Refs. therein.
- [17] (a) M. Brookhar, D.M. Lincoln, A.F. Volpe, Jr. and G.F. Schmidt, Organometallics, 8 (1989) 1212; (b) M. Brookhart and M.L.H. Green, J. Organomet. Chem., 250 (1983) 395; (c) M. Brookhart, M.L.H. Green and L.L. Wong, Prog. Inorg. Chem., 36 (1988) 1; (d) N. Carr, B.J. Dunne, A.G. Orpen and J.L. Spencer, J. Chem. Soc., Chem. Commun., (1988) 926.
- [18] (a) A. Albinati, C.G. Anklin, F. Ganazzoli, H. Rüegg and P.S. Pregosin, *Inorg. Chem.*, 26 (1987) 503; (b) A. Albinati, C. Arz and P.S. Pregosin, *Inorg. Chem.*, 26 (1987) 508; (c) A. Albinati, P.S. Pregosin and F. Wombacher, *Inorg. Chem.*, 29 (1990) 1812.
- [19] G. Strukul, R.A. Michelin, J.D. Orbell and L. Randaccio, *Inorg. Chem.*, 22 (1983) 3706.
- [20] M.A. Bennett, H.-K. Chee and G.B. Robertson, Inorg. Chem., 18 (1979) 1061.
- [21] J. Buckle, P.G. Harrison, T.J. King and J.A. Richards, J. Chem. Soc., Chem. Commun., (1972) 1104.
- [22] R.A. Michelin, R. Ros, G. Guadalupi, G. Bombieri, F. Benetollo and G. Chapuis, *Inorg. Chem.*, 28 (1989) 840.