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Reactivity of carbonyl stabilized ylides with Zeise's salt. Synthesis, characterization of mono- and bis-ylidic Pt(II) derivatives and X-ray crystal structure of the $\{\overline{PtCl_2[C(H)COCH_3(PPh_2\text{-}o\text{-}C}_6H_4)]\}[PPh_3CH_2COCH_3]$ complex

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Abstract

Phosphorus and arsenic keto-stabilized ylides (APPY, CMPPY, BPPY, BCyPY-OMe, APAsY, CMPAsY, BPAsY) react with Zeise's salt to give the corresponding monosubstituted Pt(II) complexes *trans*-$[PtCl_2(\eta^2\text{-}C_2H_4)(\text{ylide})]$ (**1–7**). The bis-ylide complexes *trans*-$[PtCl_2(\text{ylide})_2]$ (**8–12**) and *trans*-$[PtCl_2(\text{ylide})(\text{ylide}')]$ (**13–17**) can be prepared by reaction of **1–7** with the corresponding ylides. Upon heating complex **8** *trans*-$\{PtCl_2[C(H)(PPh_3)COCH_3]_2\}$ in THF a cyclization reaction occurred to give $\{PtCl_2[C(H)COCH_3(PPh_2\text{-}o\text{-}C_6H_4)]\}[Ph_3PCH_2COCH_3]$ (**18**). The molecular structure of compound **18** was determined by X-ray diffraction. The molecule consists of a metallic anion and a phosphonium counterion. Compound **18** crystallizes in the monoclinic space group *P*2$_1$/*c* with unit cell parameters $a = 13.855(3)$, $b = 14.242(3)$, $c = 20.173(4)$ Å, $\beta = 109.31(5)°$, $Z = 4$.

Keywords: Crystal structures; Platinum complexes; Ylide complexes; Ketostabilized ylides; Phosphorus; Arsenic

1. Introduction

Although the coordination chemistry of carbonyl stabilized ylides towards transition metal substrates is well investigated [1,2] and a variety of structurally different coordination modes have been reported [3], relatively little is published about the synthesis and reactivity of transition metal derivatives having two carbonyl stabilized ylides coordinated to the same metal center [4]. Many of these complexes have been often prepared, under drastic experimental conditions, by reaction of an appropriate metallic substrate with two equivalents of ylide. However, this synthetic methodology presents several disadvantages such as: (i) formation of mixtures of products, (ii) low yield of the bis-ylide derivative, (iii) possibility to synthesize only bis-ylide complexes containing two identical ylide ligands.

In this paper we report an easier and general method for the preparation, in high yields, of bis-ylide Pt(II) complexes, under mild experimental conditions, containing either two identical or different ylides by introduction, step by step, of the two ligands starting from Zeise's salt. We also report a cyclization reaction of the *trans*-$PtCl_2[CH(PPh_3)COCH_3]_2$ derivative, leading to the formation of an ionic complex in which a ylidic ligand is cyclometallated to the metal through the methinic carbon and an *ortho*-carbon atom of one of the phosphorus substituted phenyl groups. Other examples of similar cyclometallation reactions of carbonyl stabilized ylides have been reported [2].

2. Experimental

2.1. General

Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled over sodium/benzophenone ketyl and CH_2Cl_2 over CaH_2 just before use. All other solvents were reagent grade and used without further purifications. All reactions were performed under an N_2 atmosphere using standard Schlenk techniques. ^1H and $^{13}C\{^1H\}$NMR spectra were recorded on a Bruker AC 200 MHz spectrometer and $^{31}P\{^1H\}$NMR on a Varian FT-80A spectrometer. IR spectra were taken on a Perkin-Elmer 983 spectrophotometer. Melting points were determined on a hot plate apparatus and are uncorrected.

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Table 1
IR and NMR spectroscopic data for free ylides [a]

Ylide	IR (cm^{-1})	NMR								
		^{1}H			^{13}C					^{31}P{^{1}H}
	ν(CO)	δ(CH)	^2J(HP)	δ(R)	δ(CH)	^1J(CH)	^1J(CP)	δ(CO)	δ(R)	δ(P)
APPY	1533 vs	4 20 br	26 29	2 59 d [b]	51 34 dd	164 51	107 79	190 41 d [c]	28 21 qd [d]	14 31 s
CMPPY	1615 vs	2 88 br		3 49 s	29 86 br			171 47 d [c]	49 57 q [f]	17 69 s
BPPY	1513 vs	4 42 br	23 78		50 29 dd	163 69	112 40	184 18 s		16 64 s
((B-*p*-OMe)CyPY)	1523 vs	3 39 br		3 75 s	44 00 dd	151 55	96 93	183 38 s	55 13 q [g]	28 44 s
APAsY	1511 vs	3 95 br		2 06 s	57 12 d	175 23		187 03 d [h]	26 20 q [i]	
CMPAsY	1604 vs	2 46 br		2 54 br	32 84 br			171 71 [j]	50 08 q [k]	
BPAsY	1501 vs	4 71 s			57 32 d	174 07		181 59 d [l]		

[a] IR spectra recorded in Nujol mull, vs = very strong NMR spectra recorded in CDCl$_3$, δ in ppm, J in Hz, ^{1}H and ^{31}P{^{1}H} NMR chemical shifts were referenced to internal SiMe$_4$ and H$_3$PO$_4$ (85%), respectively, and ^{13}C NMR chemical shifts reported from SiMe$_4$ by taking the chemical shift of CDCl$_3$ as + 77 0 ppm, s = singlet, d = doublet, q = quartet, br = broad

[b] ^4J(HP) = 1 80

[c] ^2J(CP) = 4 88

[d] ^1J(CH) = 125 65, ^3J(CP) = 15 93

[e] ^2J(CP) = 10 87

[f] ^1J(CH) = 144 28

[g] ^1J(CH) = 143 62

[h] ^2J(CH) = 4 53

[i] ^1J(CH) = 125 81

[j] ^2J(CH) = 8 62

[k] ^1J(CH) = 138 30

[l] ^2J(CH) = 3 07

Elemental analyses were performed by the Department of Inorganic, Metallorganic and Analytical Chemistry of Padua

2 2. *Starting materials*

The complexes K[PtCl$_3$(η^2-C$_2$H$_4$)] H$_2$O [5] and [PtCl$_2$(η^2-C$_2$H$_4$)]$_2$ [6] and the ylides Ph$_3$PCHCOMe [7] (APPY), Ph$_3$PCHCOOMe [8] (CMPPY), Ph$_3$PCHCOPh [7] (BPPY), Ph$_3$AsCHCOMe [9] (APAsY), Ph$_3$AsCHCOOMe [9] (CMPAsY) and Ph$_3$AsCHCOPh [9] (BPAsY) were obtained according to the literature procedures Cy$_3$PCHCOC$_6$H$_4$-*p*-OMe ((B-*p*-OMe)CyPY) was prepared by modifying the original method reported for the parent ylides [10] A suspension of [Cy$_3$PCH$_2$COC$_6$H$_4$-*p*-OMe]Br (2 55 g, 5 0 mmol) in THF (60 ml) was treated with NEt$_3$ (2 8 ml, 20 0 mmol) for 3 h The reaction mixture was filtered, washed with THF (2 × 10 ml) and the resulting solution reduced to a small volume (5 ml) under vacuum Addition of Et$_2$O (50 ml) gave a white solid Yield 0 204 g (95%) Selected spectroscopic data for the free ylides used in this work are summarized in Table 1

2 3 *Synthesis of [R'$_3$PCH$_2$COR][PtCl$_3$(η^2-C$_2$H$_4$)] (R' = Ph, R = Me (S1), OMe (S2), Ph (S3) R' = Cy, R = C$_6$H$_4$-p-OMe (S4))*

The salts **S1–S4** were prepared by the same general method reported below for **S1** To a solution of Zeise's salt (0 116 g, 0.30 mmol) in CHCl$_3$ (20 ml), solid [Ph$_3$PCH$_2$COMe]Cl (0 106 g, 0 30 mmol) was added in one portion After filtration of the KCl, the clear solution was reduced to a small volume Addition of Et$_2$O afforded **S1** in almost quantitative yield The spectroscopic data for **S1–S4** are reported in Table 2

2 4 *Synthesis of trans-[PtCl$_2$(η^2-C$_2$H$_4$)(ylide)] (ylide = APPY (1), CMPPY (2), BPPY (3), ((B-p-OMe)CyPY) (4), APAsY (5), CMPAsY (6), BPAsY (7))*

All these complexes were prepared by the same standard procedure that is described below for **1** To a solution of Zeise's salt (0.116 g, 0 30 mmol) in MeOH (5 ml) a solution of APPY (0 095 g, 0 30 mmol) in the same solvent (5 ml) was added and the reaction mixture stirred for 10 min The yellow solid formed was filtered off, washed with H$_2$O (3 × 5 ml) to remove KCl, and Et$_2$O (3 × 5 ml) and dried under vacuum Yield 0 170 g (92%), m p 126–128 °C (dec.) *Anal* Found C, 45.54, H, 3 80 Calc for C$_{23}$H$_{23}$Cl$_2$OPPt. C, 45 11, H, 3 79% IR (nujol) (cm^{-1}) ν(CO) 1671vs, ν(Pt–Cl) 326m The same product was also obtained by treating a methanolic solution of [PtCl$_2$(η^2-C$_2$H$_4$)]$_2$ with two equivalents of APPY

Complex **2**: yield 87%, m p 134–136 °C (dec). *Anal* Found. C, 43 96, H, 3 87 Calc for C$_{23}$H$_{23}$Cl$_2$O$_2$PPt C, 43 96, H, 3.69% IR (nujol) (cm^{-1}). ν(CO) 1699vs, ν(Pt–Cl) 330m

Table 2
Spectroscopic data for complexes [R′$_3$PCH$_2$COR][PtCl$_3$(η^2-C_2H_4)] [a]

R	R′	IR (cm^{-1})	NMR							
			^{1}H			^{13}C{^{1}H}				^{31}P{^{1}H}
		ν(CO)	δ(CH_2)	δ(C_2H_4)	δ(R)	δ(CH_2)	δ(C_2H_4)	δ(CO)	δ(R)	δ(P)
Me	Ph	1715 s	5 30 d (11 59)	4 23 s (64 73)	2 48 d (2 09)	40 06 d (59 23)	67 93 s (191 98)	200 20 d (5 23)	32 68 d (5 18)	19 63 s
OMe	Ph	1743 s	4 97 d (13 53)	4 26 s (64 64)	3 55 s	32 92 d (57 42)	67 62 s (193 19)	164 72 d (2 97)	53 46 s	20 49 s
Ph	Ph	1672 s	6 23 d (12 34)	4 74 s (64 78)		37 33 d (61 80)	67 62 s (191 38)	191 40 d (3 59)		21 65 s
C_6H_4-*p*-OMe	Cy	1661 s	4 37 d (11 21)	4 46 s (64 78)	3 86 s		68 19 s (182 48)	191 45 d (5 33)	55 67 s	35 71 s

[a] IR spectra recorded in Nujol mull, s = strong NMR spectra recorded in $CDCl_3$ δ in ppm J in Hz, ^{1}H and ^{31}P{^{1}H} NMR chemical shifts were referenced to internal $SiMe_4$ and H_3PO_4 (85%), respectively, and ^{13}C NMR chemical shifts reported from $SiMe_4$ by taking the chemical shift of $CDCl_3$ as + 77 0 ppm, s = singlet, d = doublet

Complex **3** yield 95%, m p 129–131 °C (dec) *Anal* Found C, 49 94, H, 3 78 Calc for $C_{28}H_{25}Cl_2OPPt$ C, 49 86, H, 3 74% IR (nujol) (cm^{-1}) ν(CO) 1650vs, ν(Pt–Cl) 335m

Complex **4**: yield 86%, m p 212–214 °C (dec) *Anal* Found. C, 48 71, H, 6 30 Calc for $C_{29}H_{45}Cl_2O_2PPt$ C, 48 20, H, 6 28% IR (nujol) (cm^{-1}) ν(CO) 1639vs, ν(Pt–Cl) 333m

Complex **5** yield 87%, m p 133–135 °C (dec) *Anal* Found C, 42 08, H, 3 61 Calc for $C_{23}H_{23}AsCl_2OPt$ C, 42 09, H, 3.53% IR (nujol) (cm^{-1}) ν(CO) 1669vs, ν(Pt–Cl) 344m

Complex **6** yield 85%, m p 134–136 °C (dec) *Anal* Found C, 40 39, H, 3 55. Calc for $C_{23}H_{23}AsCl_2O_2Pt$ C, 41 09, H, 3 45% IR (nujol) (cm^{-1}) ν(CO) 1696vs, ν(Pt–Cl) 320m

Complex **7**. yield 84%, m p 149–151 °C (dec) *Anal* Found. C, 46 90, H, 3 53 Calc for $C_{28}H_{25}AsCl_2OPt$ C, 46 81, H, 3.51% IR (nujol) (cm^{-1}) ν(CO) 1645vs, ν(Pt–Cl) 336m

The ^{1}H ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra for compounds **1–7** are reported in Tables 3 and 4

*2 5 Synthesis of trans-[PtCl$_2$(ylide)$_2$] (ylide = APPY (**8**), CMPPY (**9**), BPPY (**10**), ((B-p-OMe)CyPY) (**11**), APAsY (**12**))*

Complexes **8–12** were prepared by the same procedure reported below for **8** To a solution of **1** (0.184 g, 0 30 mmol) in THF (25 ml), solid APPY (0 095 g, 0 30 mmol) was added in one portion The reaction mixture was stirred for 12 h at room temperature and the solid formed filtered off, washed with fresh THF (3 × 5 ml) and dried under vacuum Yield 0 190 g (70%), m p 180–183 °C (dec) *Anal* Found C, 55 44, H, 4 20 Calc for $C_{42}H_{38}Cl_2O_2P_2Pt$ C. 55.88; H, 4 24% IR (nujol) (cm^{-1}) ν(CO) 1651vs.

Complex **9** yield 67%, m p 213–214 °C (dec.). *Anal* Found C, 54 04; H, 4 24 Calc for $C_{42}H_{38}Cl_2O_4P_2Pt$ C, 53 97, H, 4 10% IR (nujol) (cm^{-1}) ν(CO) 1686vs

Table 3
^{1}H and ^{31}P{^{1}H} NMR data for the complexes *trans*-[PtCl$_2$(η^2-C_2H_4)(ylide)] [a]

Compound	^{1}H NMR						^{31}P{^{1}H} NMR	
	δ(CH)	^2J(HP)	^2J(HPt)	δ(C_2H_4)	^2J(HPt)	δ(R)	δ(P)	^2J(HPt)
1	6 08 d	3 73	113 88	4 74 s	50 62	2 46 d [b]	27 52 s	65 1
2	5 51 d	7 16	112 85	4 65 s	50 63	3 63 s	27 21 s	76 9
3	6 62 d	4 75	113 73	4 66 s	50 97		29 11 s	78 7
4	5 48 d	6 76	111 81	4 67 m	63 28	3 86 s	39 62 s	66 8
5	6 25 s		115 83	4 75 m	47 21	2 44 s [c]		
6	5 57 s		111 53	4 67 s	48 33	3 63 s		
7	6 82 s		116 66	4 71 s	49 39			

[a] Spectra recorded in $CDCl_3$, δ in ppm, J in Hz, ^{1}H and ^{31}P{^{1}H} NMR chemical shifts were referenced to internal $SiMe_4$ and H_3PO_4 (85%), respectively, s = singlet, d = doublet, m = multiplet

[b] ^4J(HP) = 2 5, ^4J(HPt) = 5 2

[c] ^4J(HPt) = 4 44

Table 4
$^{13}C\{^1H\}$ NMR data for the complexes *trans*-[$PtCl_2(\eta^2-C_2H_4)$(ylide)] [a]

Compound	δ(CH)	^1J(CP)	^1J(CPt)	δ(CO)	^2J(CP)	δ(C_2H_4)	^2J(CPt)	δ(R)
1	37.83 d	46.25	599.98	203.13 d	5.79	84.31 s	103.65	32.01 d [b]
2	25.03 d	50.32	612.86	173.06 s	n.o.	83.87 s	106.48	52.12 s
3	34.84 d	48.86	582.62	196.03 d	5.23	84.11 s	106.58	
4	32.53 d	41.19	n.o.	195.72 s	n.o.	83.14 s	100.53	55.35 s
5	46.25 s		658.82	205.42 s		82.26 s	94.76	30.66 s
6	31.27 s		682.73	174.39 s		85.49 s	96.87	52.35 s
7	42.98 s		644.46	197.39		85.78 s	96.08	

[a] Spectra recorded in $CDCl_3$, δ in ppm, *J* in Hz. chemical shifts reported from $SiMe_4$ by taking the chemical shift of $CDCl_3$ as +77.0 ppm, s = singlet, d = doublet, n.o. = not observed.
[b] ^3J(CP) = 10.52.

Complex **10**: yield 64%, m.p. 216–218 °C (dec.). *Anal.* Found: C, 60.30; H, 4.01. Calc. for $C_{52}H_{42}Cl_2O_2P_2Pt$: C, 60.82; H, 4.12%. IR (nujol) (cm^{-1}): ν(CO) 1634vs.

Complex **11**: yield 93%, m.p. 252–254 °C (dec.). *Anal.* Found: C, 57.58; H, 7.45. Calc. for $C_{54}H_{82}Cl_2O_4P_2Pt$: C, 57.75; H, 7.36%. IR (nujol) (cm^{-1}): ν(CO) 1624vs.

Complex **12**: yield 71%, m.p. 191–192 °C (dec.). *Anal.* Found: C, 50.63; H, 3.71. Calc. for $C_{42}H_{38}As_2Cl_2O_2Pt$: C, 50.92; H, 3.87%. IR (nujol) (cm^{-1}): ν(CO) 1641vs.

An alternative method to prepare complexes **8–12** involves the reaction between K[$PtCl_3(\eta^2-C_2H_4)$]·H_2O in THF solution and two equivalents of the ylide under the same experimental conditions reported above. The ^1H NMR spectra for derivatives **8–12** are reported in Table 5.

2.6. Synthesis of *trans-[PtCl₂(ylide)(ylide′)] (ylide = APPY, ylide′ = CMPPY (13); ylide = APPY, ylide′ = BPPY (14), ylide = CMPPY, ylide′ = BPPY (15), ylide = ((B-p-OMe)CyPY), ylide′ = CMPPY (16), ylide = CMAsPY, ylide′ = APPY (17))*

Complexes **13–17** were obtained by the same procedure described for **8** by reacting compounds **1**, **2**, **4** and **6** with one equivalent of the appropriate ylide.

Complex **13**: yield 58%, m.p. 192–193 °C (dec.). *Anal.* Found: C, 54.47; H, 4.10. Calc. for $C_{42}H_{38}Cl_2O_3P_2Pt$: C, 54.91; H, 4.17%. IR (nujol) (cm^{-1}): $\nu(CO)_{APPY}$ 1651vs, $\nu(CO)_{CMPPY}$ 1685.

Complex **14**: yield 43%, m.p. 194–196 °C (dec.). *Anal.* Found: C, 58.22; H, 4.08. Calc. for $C_{47}H_{40}Cl_2O_2P_2Pt$: C, 58.51; H, 4.18%. IR (nujol) (cm^{-1}): $\nu(CO)_{APPY}$ 1656vs, $\nu(CO)_{BPPY}$ 1630vs.

Complex **15**: yield 51%, m.p. 184–185 °C (dec.). *Anal.* Found: C, 57.28; H, 3.97. Calc. for $C_{47}H_{40}Cl_2O_3P_2Pt$: C, 57.56; H, 4.11%. IR (nujol) (cm^{-1}): $\nu(CO)_{CMPPY}$ 1685vs, $\nu(CO)_{BPPY}$ 1632vs.

Complex **16**: yield 80%, m.p. 235–237 °C (dec.). *Anal.* Found: C, 55.83; H, 5.70. Calc. for $C_{48}H_{60}Cl_2O_4P_2Pt$: C, 56.03; H, 5.88%. IR (nujol) (cm^{-1}): $\nu(CO)_{((B\text{-}p\text{-}OMe)CyPY)}$ 1630vs; $\nu(CO)_{CMPPY}$ 1639vs.

Complex **17**: yield 91%, m.p. 176–178 °C (dec.). *Anal.* Found: C, 52.18; H, 4.10. Calc. for $C_{42}H_{38}AsCl_2O_3PPt$: C, 52.40; H, 3.98%. IR (nujol) (cm^{-1}): $\nu(CO)_{CMAsPY}$ 1682vs, $\nu(CO)_{APPY}$ 1650vs.

The ^1H NMR spectra for complexes **13–17** are reported in Table 5.

2.7. Cyclization reaction of complex 8. Synthesis of *{PtCl₂[CH(COCH₃)PPh₂(o-C₆H₄)][Ph₃PCH₂COCH₃]} (18)*

A suspension of complex **8** (0.301 g, 0.33 mmol) in THF (30 ml) was refluxed for 12 h under N_2 atmosphere. The color of the solid changed from pale yellow to white. The final reaction mixture was filtered off, the residue washed several times with water (5×30 ml) and Et_2O (3×10 ml) and dried under vacuum. Yield 0.269 g (89%), m.p. 237–239 °C (dec.). *Anal.* Found: C, 55.62; H, 4.19; Cl, 8.01. Calc. for $C_{42}H_{38}Cl_2O_2P_2Pt$: C, 55.88; H, 4.24; Cl, 7.85%. IR (nujol) (cm^{-1}): ν(CO) 1707vs, 1640vs, ν(Pt–Cl) 284m, 250m. The same product **18** was also obtained by refluxing derivative **8** in CH_3CN for 44 h.

2.8. X-ray structure of *{PtCl₂[CH(COCH₃)PPh₂(o-C₆H₄)][Ph₃PCH₂COCH₃]}*

A summary of the crystallographic data is given in Table 6. Crystals for X-ray intensity measurements were obtained by recrystallization from a dichloromethane/ether solution. A small, colorless crystal, of approximate dimension 0.3×0.2×0.2 mm was mounted on a glass fiber. Cell parameters were determined from Weissenberg photographs and refined by a least-squares fit of the 2θ, X, Φ setting angles of the Enraf-Nonius CAD-4 diffractometer for 25 accurately centered reflections in the range 26 < 2θ < 34°. Intensity data were collected by the Ω–2θ scan mode with graphite-monochromatized Mo Kα radiation in the range 4 ≤ 2θ ≤ 58°. Scans were made with a maximum time of 60 s for reflection. Three standard reflections monitored every 300 showed no appreciable change in intensity throughout the data collection. Data were corrected for Lorentz and polarization effects and for absorption based on additional azimuthal scan data. After averaging, 5142 independent reflections with $I_o > 3\sigma(I_o)$ were used in the following calculations. The

Table 5
^{1}H NMR data for the complexes *trans*-[PtCl$_2$(ylide)(ylide′)] [a]

Compound	ylide	δ(CH)	^2J(HP)	δ(R)	ylide′	δ(CH)	^2J(HP)	δ(R)
8 [b]	APPY	5 60 d	1 70	2 58 d [c]	APPY			
		5 28 d	0 65	2 50 d [d]				
9	CMPPY	5 09 d	4 35	3 66 s	CMPPY			
		5 00 d	4 19	3 61 s				
10	BPPY	6 17 d	1 08		BPPY			
		6 09 d	1 62					
11 [e]	(B-*p*-OMe)CyPY	5 25 d	3 40	3 77 s	(B-*p*-OMe)CyPY			
		5 10 d	4 66					
12	APAsY	5 84 s [f]			APAsY			
		5 80 s [g]						
13	APPY	5 59 s, br		2 50 d [h]	CMPPY	5 10 d	3 93	3 66 s
		5 49 s, br		2 48 d [i]		5 00 d	4 14	
14 [j]	APPY	5 54 s, br		2 44 s br	BPPY	6 17 s, br		
				2 43 s br		6 09 s, br		
15	BPPY	6 09 d	1 79		CMPPY	5 04 d	4 42	3 68 s
		6 07 d	1 34			5 01 d	4 24	3 66 s
16	CMPPY [k]	4 98 d	4 40	3 58 s	(B-*p*-OMe)CyPY [l]	5 07 d	3 94	3 79 s
		4 97 d	3 89	3 51 s		5 01 d	3 54	3 77 s
17 [m]	APPY	5 40 d	0 50	2 46 d [n]	CMAsPY	5 46 s		3 68 s
		5 34 d	0 50	2 40 d [o]		5 41s		3 63 s

[a] Spectra recorded in CDCl$_3$, δ in ppm, J in Hz. ^{1}H NMR chemical shifts were referenced to internal SiMe$_4$, s = singlet, d = doublet br = broad
[b] ^{31}P{^{1}H} NMR δ(P) = 25 48s, ^2J(PPt) = 66 7, δ(P) = 24 75s, ^2J(PPt) = 66 9
[c] ^4J(HP) = 2 13
[d] ^4J(HP) = 2 22
[e] ^{31}P{^{1}H} NMR δ(P) = 35 28s, ^2J(PPt) = 31 2, δ(P) = 35 17s, ^2J(PPt) = 31 3
[f] ^2J(HPt) = 96 84
[g] ^2J(HPt) = 94 67
[h] ^4J(HP) = 2 37
[i] ^4J(HP) = 2 37
[j] ^{31}P{^{1}H} NMR δ(P) = 26 35s ^2J(PPt) = 73 9, δ(P) = 24 33s, ^2J(PPt) = 69 0
[k] ^{31}P{^{1}H} NMR δ(P) = 23 85s, ^2J(PPt) = 79 6
[l] ^{31}P{^{1}H} NMR δ(P) = 35 35s, ^2J(PPt) = 66 6
[m] ^{31}P{^{1}H} NMR δ(P) = 25 61s, ^2J(PPt) = 69 0, δ(P) = 25 20s, ^2J(PPt) = 69 0
[n] ^4J(HP) = 2 33
[o] ^4J(HP) = 2 35

structure was solved by conventional Patterson and Fourier methods After the anisotropic refinement, a three-dimensional difference Fourier synthesis was calculated to locate the H atoms Calculated positions of all the latter occurred in positive regions of the electron-density map. The final anisotropic full-matrix least-squares refinement, including the fixed contribution of the hydrogen atoms, gave a conventional R value of 0 043 The final weighting scheme was $w = 1/[\sigma(F) + (pF)^2 = 1]$ with $p = 0\ 04$ Neutral atom scattering factors were taken from Ref [11] Real and imaginary contributions of all non-hydrogen atoms were included in the calculations All calculations were carried out using the MOLEN program package [12] on a VAX 2000 computer Positional parameters are listed in Table 7, intermolecular bond distances and angles are given in Tables 8 and 9, respectively

Table 6
Crystallographic data for **18**

Formula	PtC$_{42}$H$_{35}$Cl$_2$O$_2$P$_2$
Space group	$P2_1/c$
Molecular weight	902 7
Z	4
a (Å)	13 855(3)
b (Å)	14 242(3)
c (Å)	20 173(4)
β (°)	109 31(5)
D_c (g cm^{-3})	1 60
D_o (g cm^{-3})	1 58
μ(Mo Kα) (cm^{-1})	40 3
$R(F_o)$	0 043
$R(F_w)$	0 053

3. Results and discussion

3 1 Synthesis and characterization of trans-[PtCl$_2$(η^2-C$_2$H$_4$)(C-ylide)] complexes

Zeise's salt reacts with one equivalent of carbonyl stabilized ylides Ph$_3$ECHCOR (E = P, As) in methanol to form microcrystalline yellow precipitates **1–7** (Eq. (1)) which immediately separate from the solution in high yield.

Table 7
Positional parameters and their e.s.d.s

Atom	x	y	z	B (Å)
Pt	0.23717(3)	0.15127(2)	0.42670(2)	2.641(5)
Cl1	0.3509(2)	0.0315(2)	0.4207(1)	3.89(5)
Cl2	0.2260(2)	0.0844(2)	0.5342(1)	4.53(6)
P1	0.0578(2)	0.2623(2)	0.3405(1)	2.90(5)
P2	0.3642(2)	0.7604(2)	0.5048(1)	2.99(5)
O1	0.1981(6)	0.4050(6)	0.4237(4)	5.1(2)
O2	0.3404(7)	0.8114(6)	0.6387(4)	5.6(2)
C1	0.2384(7)	0.2080(7)	0.3376(4)	3.1(2)
C2	0.3182(7)	0.2035(9)	0.3099(5)	4.1(2)
C3	0.3098(8)	0.2435(9)	0.2467(5)	4.4(2)
C4	0.2239(8)	0.2913(8)	0.2073(5)	4.0(2)
C5	0.1432(8)	0.3000(8)	0.2332(5)	3.8(2)
C6	0.1517(6)	0.2599(7)	0.2970(4)	2.8(2)
C7	−0.0245(6)	0.1615(7)	0.3145(5)	3.0(2)
C8	−0.0480(9)	0.1291(8)	0.2462(6)	4.3(3)
C9	−0.122(1)	0.0595(9)	0.2214(7)	5.7(3)
C10	−0.1747(9)	0.0276(9)	0.2639(8)	5.8(3)
C11	−0.1518(9)	0.059(1)	0.3307(7)	6.2(3)
C12	−0.0774(9)	0.1287(8)	0.3565(6)	4.7(3)
C13	−0.0294(7)	0.3598(7)	0.3201(5)	3.7(2)
C14	−0.082(1)	0.384(1)	0.2518(7)	6.2(4)
C15	−0.155(1)	0.457(1)	0.2400(9)	8.8(4)
C16	−0.178(1)	0.498(1)	0.294(1)	9.5(5)
C17	−0.126(1)	0.471(1)	0.361(1)	8.6(5)
C18	−0.0523(9)	0.4023(9)	0.3745(8)	5.9(3)
C19	0.3951(7)	0.7691(7)	0.4257(4)	2.8(2)
C20	0.4887(7)	0.8030(9)	0.4260(5)	4.0(2)
C21	0.5110(8)	0.8074(8)	0.3643(5)	4.3(2)
C22	0.4400(8)	0.7777(9)	0.3017(5)	4.5(3)
C23	0.3467(8)	0.748(1)	0.3006(5)	4.7(3)
C24	0.3239(8)	0.7409(9)	0.3626(5)	4.1(2)
C25	0.4271(7)	0.6605(8)	0.5547(5)	3.5(2)
C26	0.5186(9)	0.630(1)	0.5499(6)	5.4(3)
C27	0.5700(9)	0.555(1)	0.5885(7)	6.2(3)
C28	0.529(1)	0.509(1)	0.6325(7)	5.9(3)
C29	0.438(1)	0.5381(9)	0.6383(6)	5.6(3)
C30	0.3862(9)	0.6152(8)	0.6004(6)	4.5(3)
C31	0.2282(7)	0.7517(9)	0.4814(5)	3.9(2)
C32	0.1832(8)	0.662(1)	0.4661(6)	5.5(3)
C33	0.077(1)	0.657(1)	0.4438(7)	8.0(4)
C34	0.0206(9)	0.736(2)	0.4366(7)	9.8(5)
C35	0.0621(9)	0.820(1)	0.4492(6)	7.5(4)
C36	0.1697(8)	0.833(1)	0.4734(6)	5.5(3)
C37	0.1311(7)	0.2532(6)	0.4311(5)	2.8(2)
C38	0.1813(7)	0.3402(7)	0.4591(5)	3.4(2)
C39	0.2458(9)	0.343(1)	0.5377(5)	4.9(3)
C40	0.4085(7)	0.8663(7)	0.5530(4)	3.1(2)
C42	0.437(1)	0.951(1)	0.6682(7)	6.2(4)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$

$$K[PtCl_3(\eta^2\text{-}C_2H_4)] + \text{ylide} \xrightarrow[\text{MeOH r.t.}]{-KCl} \underline{\text{trans}}\text{-}[PtCl_2(\eta^2\text{-}C_2H_4)(\text{ylide})] \qquad (1)$$

ylide = APPY (1) CMPPY (2) BPPY (3) BCyPY-OMe (4) APAsY (5) CMPAsY (6) BPAsY (7)

The compounds are stable in the solid state but derivatives **1–4** begin to decompose in chlorinated solvents within a few hours to give a mixture of products in which the salts $[R'_3PCH_2COR][PtCl_3(\eta^2\text{-}C_2H_4)]$ were identified by comparison of their spectroscopic data with those of authentic samples prepared independently (see Section 2.3 and Table 2). In the IR spectra of complexes **1–7** the ν(CO) stretching band of the coordinated carbonyl stabilized ylides falls in the range 1639–1699 cm^{-1}, at about 100 cm^{-1} higher than those of the corresponding ylides (see Table 1), indicating that in all the complexes coordination of the ylide ligand involves the methine carbon atom [13]. IR spectra of these derivatives show also two vibrations between 300 and 350 cm^{-1} in the region of Pt–Cl stretchings. For these complexes we suggest a *trans* geometry around the Pt atom considering that for compounds *cis*-$[PtCl_2L(\text{ylide})]$ (L = PMe_2Ph, ylide = $Me_2SCHCOPh$, L = Me_2S, ylide = $Me(Ph)SCHCOC_6H_4$-*p*-Cl) the ν(Pt–Cl) *trans* to the ylide ligand falls below 300 cm^{-1} [13a,14] and on the basis of the data reported for complexes of the type *trans*-$[PtCl_2(NCR)_2]$ [15] also for which two bands were observed in the Pt–Cl region. In addition this assignment is also supported by the high *trans* effect of the coordinated olefin ligand [16]. The ^1H NMR spectra exhibit the ylide methine proton resonances as doublets for complexes **1–4** and as singlets for derivatives **5–7** in the range 5.48–6.82 ppm. The resonance of the methine proton is always flanked by the ^{195}Pt satellites with ^2J(HPt) of 112–117 Hz which are in agreement with analogous coupling constants found for other Pt(II) C-coordinated carbonyl stabilized ylide complexes [13,14,17]. The $^{31}P\{^1H\}$ NMR spectra of derivatives **1–3** and **4** display a sharp resonance in the

Table 8
Bond distances (Å)

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Pt	Cl1	2.353(3)	C13	C18	1.38(2)
Pt	Cl2	2.420(3)	C14	C15	1.41(2)
Pt	C1	1.98(1)	C15	C16	1.36(3)
Pt	C37	2.088(9)	C16	C17	1.36(3)
P1	C6	1.79(1)	C17	C18	1.38(2)
P1	C7	1.800(9)	C19	C20	1.38(1)
P1	C13	1.80(1)	C19	C24	1.39(1)
P1	C37	1.777(8)	C20	C21	1.38(2)
P2	C19	1.79(1)	C21	C22	1.39(1)
P2	C25	1.79(1)	C22	C23	1.36(2)
P2	C31	1.79(1)	C23	C24	1.39(2)
P2	C40	1.790(9)	C25	C26	1.37(2)
O1	C38	1.19(1)	C25	C30	1.39(2)
O2	C41	1.20(1)	C26	C27	1.37(2)
C1	C2	1.39(2)	C27	C28	1.37(2)
C1	C6	1.42(1)	C28	C29	1.37(2)
C2	C3	1.37(2)	C29	C30	1.39(2)
C3	C4	1.37(1)	C31	C32	1.40(2)
C4	C5	1.39(2)	C31	C36	1.39(2)
C5	C6	1.38(1)	C32	C33	1.39(2)
C7	C8	1.39(1)	C33	C34	1.35(3)
C7	C12	1.37(2)	C34	C35	1.32(3)
C8	C9	1.40(2)	C35	C36	1.42(2)
C9	C10	1.37(2)	C37	C38	1.50(1)
C10	C11	1.35(2)	C38	C39	1.51(1)
C11	C12	1.40(2)	C40	C41	1.50(1)
C13	C14	1.37(2)	C41	C42	1.48(2)

Numbers in parentheses are e.s.d.s in the least significant digits

Table 9
Bond angles (°)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Cl1	Pt	Cl2	90.2(1)	C14	C15	C16	121(1)
Cl1	Pt	C1	92.4(3)	C15	C16	C17	120(1)
Cl1	Pt	C37	177.5(3)	C16	C17	C18	120(2)
Cl2	Pt	C1	176.9(3)	C13	C18	C17	121(1)
Cl2	Pt	C37	88.9(3)	P2	C19	C20	121.4(6)
C1	Pt	C37	88.4(4)	P2	C19	C24	119.4(8)
C6	P1	C7	109.6(5)	C20	C19	C24	119(1)
C6	P1	C13	116.4(5)	C19	C20	C21	120.1(8)
C6	P1	C37	104.0(4)	C19	C20	C21	120.1(8)
C7	P1	C13	103.6(4)	C20	C21	C22	120(1)
C7	P1	C37	109.4(4)	C21	C22	C23	120(1)
C13	P1	C37	113.8(5)	C22	C23	C24	120.6(9)
C19	P2	C25	109.9(5)	C19	C24	C23	120(1)
C19	P2	C31	108.1(4)	P2	C25	C26	119.8(9)
C19	P2	C40	106.6(5)	P2	C25	C30	120.7(8)
C25	P2	C31	111.6(5)	C26	C25	C30	119(1)
C25	P2	C40	110.4(4)	C25	C26	C27	121(1)
C31	P2	C40	110.1(5)	C26	C27	C28	119(1)
Pt	C1	C6	118.5(7)	C27	C28	C29	121(1)
C2	C1	C6	115.2(9)	C28	C29	C30	121(1)
C1	C2	C3	121.3(9)	C25	C30	C29	119(1)
C2	C3	C4	123(1)	P2	C31	C32	118.2(9
C3	C4	C5	119(1)	P2	C31	C36	119.7(9)
C4	C5	C6	119.0(9)	C32	C31	C36	122(1)
P1	C6	C1	109.9(7)	C31	C32	C33	118(1)
P1	C6	C5	126.7(7)	C32	C33	C34	120(2)
C1	C6	C5	123(1)	C33	C34	C35	123(1)
P1	C7	C8	118.2(8)	C34	C35	C36	122(1)
P1	C7	C12	120.6(8)	C31	C36	C35	116(1)
C8	C7	C12	120.1(9)	Pt	C37	P1	100.3(5)
C7	C8	C9	120(1)	Pt	C37	C38	106.2(6)
C8	C9	C10	119(1)	P1	C37	C38	112.7(6)
C9	C10	C11	121(1)	O1	C38	C37	124.1(8)
C10	C11	C12	120(1)	O1	C38	C39	119.8(9)
C7	C12	C11	119(1)	C37	C38	C39	116.1(9)
P1	C13	C14	121(1)	P2	C40	C41	115.9(7)
P1	C13	C18	118.1(8)	O2	C41	C40	121.3(9)
C14	C13	C18	120(1)	O2	C41	C42	123(1)
C13	C14	C15	118(1)	C40	C41	C42	116(1)

Numbers in parentheses are e.s.d.s in the least significant digits

range 27.21–29.11 and 39.62 ppm, respectively, which are consistent, as well as the magnitude of the corresponding ^{195}Pt–^{31}P coupling constant (Table 3), with the values reported for several Pt(II)-coordinated phosphonium ylide systems [18]. The olefinic protons of compounds **1**–**7** give rise, in the ^{1}H NMR spectra, to a single resonance in the range 4.65–4.75 ppm with relative ^{195}Pt satellites (^{2}J(HPt) = 48.3–51.0 Hz) while the IR spectra show a weak band ranging between 1520 and 1527 cm^{-1}, characteristic for Pt(II)-coordinated ethylene complexes [19], due to coupled ν(CC) + δ_s(CH$_2$) modes of the olefinic systems [20]. The ^{13}C{^{1}H} NMR spectra (see Table 4) give some interesting information about the ylide ligand which are worthy of comment. It was shown that the values of $^{1}J(\text{Pt–C})_{\text{olefin}}$ in complexes *trans*-[PtX$_2$(olefin)L], in which the ligand L does not show π-acid properties, can be correlated to the relative *trans*-influence of the ligand L [19b,21]. In complexes **1**–**3** the carbonyl stabilized C-coordinated phosphonium ylides display values of $^{1}J(\text{Pt–C})_{\text{C}_2\text{H}_4}$ between 103.65 and 106.58 Hz while the corresponding arsonium ylides, in complexes **5**–**7**, show $^{1}J(\text{Pt–C})_{\text{C}_2\text{H}_4}$ values about 9 Hz smaller. Since higher values of $^{1}J(\text{Pt–C})_{\text{C}_2\text{H}_4}$ indicate a lower *trans*-influence [21b] of the corresponding *trans* ligand, these $^{1}J(\text{Pt–C})_{\text{C}_2\text{H}_4}$ data suggest that arsonium ylides have a larger *trans*-influence than the corresponding phosphonium ones. Comparing these values with those reported for other L ligands in compounds of the type *trans*-[PtCl$_2$(η^2-C$_2$H$_4$)L] [22] it is possible to insert the carbonyl stabilized ylides in a series of ligands ordered in function of increasing *trans*-influence: NCMe < Cl < py ≤ NH$_2$R ≤ NHR$_2$ ≪ carbonyl stabilized phosphonium ylides < carbonyl stabilized arsonium ylides ≪ Me. Further, in the ^{13}C{^{1}H} NMR spectra of complexes **1**–**3** the $^{1}J(\text{Pt–C})_{\text{ylide}}$, varying between 582.62 Hz for Ph$_3$PCHCOPh to 612.86 for Ph$_3$PCHCOOMe, appears to parallel the ylide basicity as reflected by the pK_a values of the conjugate phosphonium acids [Ph$_3$PCH$_2$COR]Cl [23] The same trend is observed in the ^1J(Pt–C)$_{ylide}$ values for the arsonium ylide derivatives on going from complexes **5** to **7**. However, the pK_a values of the arsonium salts [Ph$_3$AsCH$_2$COMe]$^+$ and [Ph$_3$AsCH$_2$COOMe]$^+$ are not reported and their determination by potentiometric titration is complicated by slow keto–enol equilibria [24] However, likewise with the corresponding phosphonium ylides, it is reasonable to assume that the basicity of the Ph$_3$AsCHCOR systems increases in the order. R = Ph < Me < OMe, so that the ^1J(Pt–C)$_{ylide}$ values could be taken as an indirect measurement of the basicity of ylides for which the usual titration methods are unsuccessful

3.2 Reaction of trans-[PtCl$_2$(η^2-C$_2$H$_4$)(C-ylide)] with ylides

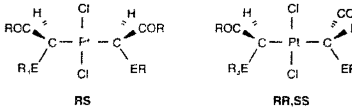
Transition metal complexes having coordinated olefins can react with ylides in two different ways. (i) by nucleophilic attack of the ylidic carbon atom to the coordinated unsaturated double bond with the formation of metal–alkyl derivatives [25] or (ii) by attack of the ylide to the metal center with substitution of the olefinic ligand and formation of a metal–C(ylide) σ-bond [1] By addition to *trans*-[PtCl$_2$(η^2-C$_2$H$_4$)(C-ylide)] complexes of an equimolar amount of ylide, only the substitution of the ethylene occurs and the bis-ylide Pt(II) derivatives **8–17** are obtained (Eq (2))

$$\underline{trans}\text{-}[PtCl_2(\eta^2\text{-}C_2H_4)(ylide)] + ylide \longrightarrow \underline{trans}\text{-}[PtCl_2(ylide)(ylide')] \qquad (2)$$

ylide = ylide = APPY (8) CMPPY (9) BPPY (10) BCyPY-OMe (11) APAsY (12)

ylide = APPY ylide' = CMPPY (13)
" = APPY " = BPPY (14)
" = CMPPY " = BPPY (15)
" = CMPPY " = BCyPY OMe (16)
" = APPY " = CMPAsY (17)

Up to now, only one example of a bis-carbonyl stabilized ylide Pt(II) complex is known, obtained by reaction of PtCl$_2$ and two equivalents of Ph$_3$AsCHCOPh in refluxing CH$_3$CN [26] All the compounds prepared following Eq (2) are very stable in the solid state as well as in solution but only the complexes **8**, **11**, **14**, **16** and **17** show a good solubility in the common organic solvents In the IR spectra the bands corresponding to the ν(CO) vibrations appear in the range 1624–1693 cm^{-1} indicating that both ylides in all these complexes are C-coordinated to the platinum atom [13]. The NMR spectra (Table 5) of complexes **8–11** display some interesting features Each of these compounds can exist as two diastereoisomeric forms, as previously shown for similar Pd complexes [4a,d], owing to the simultaneous presence on the metal center of two asymmetric methine carbon atoms. In the ^{1}H NMR spectra the ylidic proton resonances appear as two close but distinct doublets (having slightly different ^2J(HP)) in the range 5.00–6.17 ppm, shifted ~0.3–0.8 ppm upfield with respect to the corresponding signals in the starting compounds **1–4** Complexes **8** and **9** show also two proton resonances, which can be assigned to –Me and –OMe groups, respectively, arising from the *RS* and *RR,SS* diastereoisomeric structures (Scheme 1)



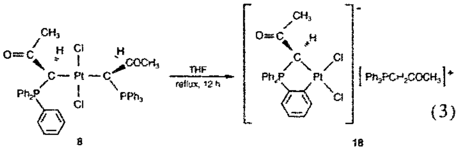
Scheme 1

Consistently, the ^{31}P{^{1}H} NMR spectra of derivatives **8** and **11** display two singlets for each compound, with associated ^{195}Pt satellites For complexes **9** and **10**, unsatisfactory ^{31}P{^{1}H} NMR data were obtained because of their very low solubility in all solvents Unlike the parent palladium bis-ylide complexes [4a,d], the Pt(II) derivatives **8–12** did not show dissociation in solution of the ylide ligand as shown by the absence of signals relative to the free ylide in the ^{1}H NMR spectra and in the ^{31}P{^{1}H} NMR for the more soluble complexes **8** and **11** In addition, by reacting **8**, with five equivalents of the more nucleophilic ylide CMPPY, in CH$_2$Cl$_2$ solution, the unreacted starting bis-ylide complex was recovered in high yield after several days at room temperature in contrast to what was previously observed for Pd(II) bis-ylide systems [4d] This feature is in agreement with the general higher stability of a Pt(II)–C(sp^3) versus Pd(II)–C(sp^3) σ-bond [27] and, in the case of ylidic complexes, in analogous Pd(II)– and Pt(II)–C(ylide) allyl derivatives [13b,28]. In complexes **13–17**, prepared following Eq (2), the platinum atom is bonded to two different carbonyl stabilized ylides They are almost insoluble compounds, and the ^{31}P{^{1}H} NMR spectrum was obtained only for **14**, **16** (both showing only a slightly broad signal for each ylide ligand) and **17** IR and ^{1}H NMR data, reported in Section 2 and Table 5, show that in all complexes both ylide ligands are C-bonded to the platinum in a *trans*-configuration and no spectral evidence of equilibrium with the free ylide in solution is shown

For complexes **13** and **14** some data are worth mentioning In the ^{1}H NMR of **13** while the methinic resonance of the coordinated CMPPY show the expected two doublets, the ylidic signals of APPY appear as two slightly broad singlets due to the value of ^2J(HP) = 0 Hz as previously noted in similar derivatives [4d] The same consideration can be applied to the broad signals of the BPPY ligand in **14**, while APPY displays only one broad resonance probably arising from very close chemical shifts of the methinic proton of the two diastereoisomers

3.3 Cyclization reaction of trans-[PtCl$_2$[C(H)(PPh$_3$)COCH$_3$]$_2$]

When a THF suspension of complex **8** was refluxed overnight, a color change from yellow to white of the insoluble material was observed. After filtration, the product showed in the IR spectrum two strong bands at 1707 and 1640 cm^{-1} and in the Pt–Cl region two vibrations at very low frequencies (282 and 250 cm^{-1}). The ^{31}P{^{1}H} NMR spectrum exhibited a singlet at 25.01 ppm, associated with ^{195}Pt satellites, and a second resonance at 19.76 ppm very close to that of the phosphonium salt [$Ph_3PCH_2COCH_3$]Cl (19.81 ppm in $CDCl_3$). In the ^{1}H NMR spectrum the ylide proton resonance was observed as a doublet at 4.57 ppm with a ^2J(HPt) of 122 Hz, thus suggesting a direct bond of the methine carbon with the platinum atom [13,14,17]. Further, the ^{13}C{^{1}H} NMR spectrum, in agreement with the ^{1}H and ^{31}P{^{1}H} NMR data, showed resonances corresponding to the phosphonium moiety ($\delta = 39.98$ d, J(CP) = 58.6 Hz) and to a Pt(II) coordinated ylide ligand ($\delta = 32.00$ d, ^1J(CP) = 56.7 Hz). These data match closely with those reported by Burmeister and co-workers for the cyclometallated dimer [Pt(μ-Cl)$CH_3COCHP(C_6H_4)(C_6H_5)_2$]$_2$ obtained by refluxing $PtCl_2$ with two equivalents of APPY in CH_3CN [3f]. We can reasonably suppose that a similar cyclometallation reaction happens on refluxing complex **8** in THF. However, in our case, after prolonged and successive treatments of the product **18** with water, in an attempt to wash the phosphonium salt, the corresponding signals remain still present in all the IR and NMR spectra. As a consequence, on the basis of those spectral data, we formulated for derivative **18** an ionic structure (see Eq. (3)) which was confirmed by an X-ray crystal structure determination.



(3)

ORTEP [29] plots of complex **18** are reported in Fig. 1(a) and (b). The molecule consists of a metallic anion (Fig. 1(a)) and a phosphonium counterion (Fig. 1(b)). In the metallic anion the Pt atom has a geometry virtually planar and is part of a five-membered cycle. The structural data, angles and distances, of the cyclometallated ylide ligand are very similar to those reported by Burmeister and co-workers for the dimeric derivative [Pt(μ-Cl)$CH_3COCHP(C_6H_4)$-$(C_6H_5)_2$]$_2$ which contains the same cyclometallated ylide framework [3f]. Also the Pt–Cl lengths (2.420 and 2.353 Å), that in our case are relative to two terminal chloride atoms, are not much different from those reported for the above chloride bridged dimer (2.438 and 2.384 Å).

The associate phosphonium cation shows the structural data characteristic for these types of salts. The phosphorus atom is approximately tetrahedral with a P–C(40) (Fig. 1(b)) distance of 1.79 Å which is in agreement with accepted values for P–C(sp^3) bond lengths in phosphonium ions [30] and the spatial arrangement of the system suggests a weakly dipolar interaction between the positive phosphorus and the carbonyl oxygen atom.

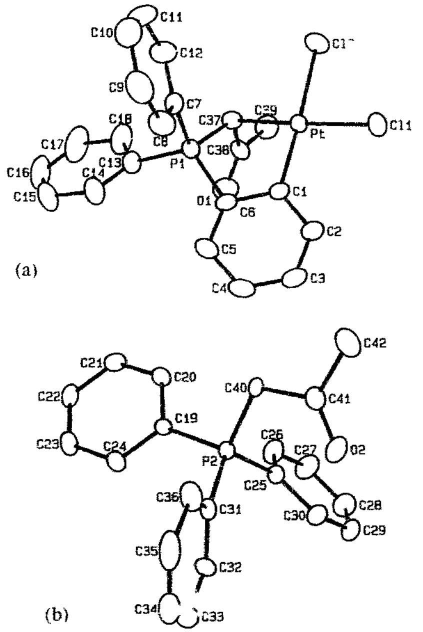


Fig. 1. (a) ORTEP plot of the metallic anion. (b) ORTEP plot of the phosphonium counterion.

An alternative method for the synthesis of derivative **18** was found during the characterization of complex **8**. A CH_2Cl_2 solution of this complex remained for several days at room temperature. The IR spectrum of the resulting white solution revealed the disappearance of the ν(CO) band at 1651 cm^{-1}, characteristic of compound **8**, and the formation of two new carbonyl bands at 1707 and 1640 cm^{-1}. Spectroscopic and analytical characterizations of the product recovered from the solution showed that its data were identical to those of complex **18** obtained in refluxing THF or CH_3CN. The transformation of complex **8** into derivative **18**, in CH_2Cl_2 solution at room temperature, could involve a mechanism in which in a first step the highly negatively charged Pt center can be protonated by traces of HCl present in the CH_2Cl_2 solvent. A successive transfer of the proton from the metal to a coordinated ylide ligand with elimination of a phosphonium cation followed by an internal oxidative addition reaction of the remaining coordinated ylide ligand and subsequent reductive elimination of HCl from a Pt(IV) intermediate [31] could account for the formation of the final cyclometallated product **18**. The catalytical function of HCl to promote the rearrangement of complex **8** is evidenced by a separate experiment in which K_2CO_3 was added to the solvent to eliminate traces of HCl. Under these conditions the reaction does not proceed and complex **8** can be recovered unaltered after two weeks. Some evidence indicates that similar rearrangements happen also for the derivatives **10** and **13**, and more detailed investigations regarding these processes are underway.

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