Platinum-Assisted Addition of Carbonyl-Stabilized Phosphorus Ylides to Pentafluorobenzonitrile and Acetonitrile To Give Platinum(II) Complexes Containing Iminophosphorane and/or N-Bonded β-Imino Phosphorus Ylide Ligands. Crystal and Molecular Structures of *trans*-[PtCl$_2${*E*-NH=C(C$_6$F$_5$)C(=PPh$_3$)C(O)Me}$_2$] and *trans*-[PtCl$_2${*E*-N(=PPh$_3$)C(C$_6$F$_5$)=CHCO$_2$Et}{*E*-NH=C(C$_6$F$_5$)C(=PPh$_3$)CO$_2$Et}][†]

José Vicente,*,[‡] María Teresa Chicote,* and Michael A. Beswick

Grupo de Química Organometálica,[§] Departamento de Química Inorgánica, Facultad de Química,
Universidad de Murcia, Apartado 4021, Murcia, 30071 Spain

M. Carmen Ramirez de Arellano

University Chemical Laboratory, Lensfield Road, CB2 1EW Cambridge, U.K.

Received December 28, 1995[⊗]

PtCl$_2$ reacts with C$_6$F$_5$CN to give *trans*-[PtCl$_2$(NCC$_6$F$_5$)$_2$] (**1**) which, in turn, reacts with carbonyl-stabilized phosphorus ylides Ph$_3$P=CHR [R = C(O)Me, CO$_2$Et] to give *trans*-[PtCl$_2${NH=C(C$_6$F$_5$)C(=PPh$_3$)CO$_2$Et}{NCC$_6$F$_5$}] (**2a**), *trans*-[PtCl$_2${NH=C(C$_6$F$_5$)C(=PPh$_3$)CO$_2$Et}$_2$] (**3a**), *trans*-[PtCl$_2${*E*-NH=C(C$_6$F$_5$)C(=PPh$_3$)C(O)Me}$_2$] (**3b**) or *trans*-[PtCl$_2${*E*-N(=PPh$_3$)C(C$_6$F$_5$)=CHCO$_2$Et}{*E*-NH=C(C$_6$F$_5$)C(=PPh$_3$)CO$_2$Et}] (**4**), depending on the reaction conditions. Similarly, Ph$_3$P=CHCO$_2$Me reacts with *trans*-[PtCl$_2$(NCMe)$_2$] to give *trans*-[PtCl$_2${NH=CMeC(=PPh$_3$)CO$_2$Me}(NCMe)] (**2b**). Complex **3b**·CH$_2$Cl$_2$ crystallizes in the triclinic system, space group $P\bar{1}$, with a = 7.596(2) Å, b = 12.694(3) Å, c = 16.962(3) Å, α = 104.28(3)°, β = 102.73(3)°, γ = 104.43(3)°, V = 1464.2(6) Å^3, and Z = 1. The structure was refined to values of R1 = 0.0411 and wR2 = 0.1172 [$I > 2\sigma(I)$] and shows two chloro and two N-bonded β-imino phosphorus ylide ligands in a *trans* geometry. Complex **4** crystallizes in the monoclinic system, space group $P2_1/c$, with a = 16.400(8) Å, b = 14.354(7) Å, c = 23.221(12) Å, α = 90(3)°, β = 92.42(2)°, γ = 90°, V = 5462(5) Å^3, and Z = 4. The structure was refined to values of R1 = 0.0246 and wR2 = 0.0557 [$I > 2\sigma(I)$]. This complex has also a *trans*-geometry and shows that while the attack of the ylide on one of the nitrile ligands produces a β-imino-phosphorus ylide ligand the addition on the second nitrile leads to an iminophosphorane ligand.

Introduction

[PtCl$_2$(NCMe)$_2$] was reported to react with carbonyl-stabilized phosphorus ylides at the refluxing temperature of MeCN to give complexes [PtCl$_2${CH(PPh$_3$)C(O)R}$_2$] (R = alkyl, aryl, alkoxy, aryloxy; see Scheme 1).[1] However, the same authors proved later that some of these products were really mixtures of phosphonium salts and orthometalated complexes $[\overline{\mathrm{Pt}\{\mathrm{CH}\{\mathrm{P}(\mathrm{C}}_6\mathrm{H}_4\text{-}2)\mathrm{Ph}_2\}\{\mathrm{C(O)R}\}(\mu\text{-Cl})]_2$ (see Scheme 1).[2] We became interested in these reactions first because we were preparing a series of carbonyl-stabilized phosphorus ylido complexes of gold(I),[3,4] -(II),[4] and -(III),[3b] Pd(II),[5] Ag(I),[6] and heteronuclear AuAg, AuCu[7] and second because nobody had reexamined such reactions to see if the complexes [PtCl$_2$(ylide)$_2$] can be prepared from [PtCl$_2$(NCR)$_2$] using different nitriles and the same or other experimental conditions (*e.g.*, at room temperature). We started these studies by reacting [PtCl$_2$(NCPh)$_2$] with Ph$_3$P=CHCO$_2$R (R = Me, Et) and, to our surprise, we obtained the first iminophosphorano complexes of platinum which involves C−P bond cleavage and C=C bond formation (see **B** in Scheme 2).[8] Recently, we have reacted [PtCl$_2$(NCR)$_2$] (R = Me, Ph) and To$_3$P=CH(py-2) (To = 4-MeC$_6$H$_4$; py-2 = 2-pyridyl) in an attempt to force the coordination of the ylide assisted by the pyridine substituent (see **A** in Scheme 2). However, from the mixture obtained, we isolated the first complexes containing a N-bonded β-imino-phosphorus ylide ligand of platinum after a C−H addition of the ylide to the C≡N bond of the nitrile.[9]

In this paper we report reactions of carbonyl stabilized phosphorus ylides Ph$_3$P=CHC(O)R (R = Me, OEt) with *trans*-[PtCl$_2$(NCR)$_2$] (R = C$_6$F$_5$, Me) that again do not lead to [PtCl$_2$(ylide)$_2$] but to complexes containing N-bonded β-iminophosphorus ylide (we will call these ylideimino complexes; see **a** in

---

[†] Dedicated to Professor Rafael Usón on the occasion of his 70th birthday.

[‡] E-mail: jvs@fcu.um.es

[§] http://www.scc.um.es/gi/gqo

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1996.

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

(2) Illingsworth, M. L.; Teagle, J. A.; Burmeister, J. L.; Fultz, W. C.; Rheingold, A. L. *Organometallics* **1983**, *2*, 1364. Teagle J. A.; Burmeister, J. L. *Inorg. Chim. Acta* **1986**, *118*, 65.

(3) (a) Vicente, J.; Chicote, M. T.; Saura-Llamas, I.; Lagunas, M. C. *J. Chem. Soc., Chem. Commun.* **1992**, 915. (b) Vicente, J.; Chicote, M. T.; Lagunas, M. C.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1991**, 2579 and references therein.

(4) Vicente, J.; Chicote, M. T.; Saura-Llamas, I. *J. Chem. Soc., Dalton Trans.* **1990**, 1941 and references therein.

(5) (a) Vicente, J.; Chicote, M. T.; Lagunas, M. C.; Jones, P. G.; Bembenek, E. *Organometallics* **1994**, *13*, 1243. (b) Vicente, J.; Chicote, M. T.; Saura-Llamas, I.; López-Muñoz, M. J.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1990**, 3683. (c) Vicente, J.; Chicote, M. T.; Fernandez-Baeza, J. *J. Organomet. Chem.* **1989**, *364*, 407.

(6) Vicente, J.; Chicote, M. T.; Saura-Llamas, I. *J. Chem. Educ.* **1993**, *70*, 163 and references therein.

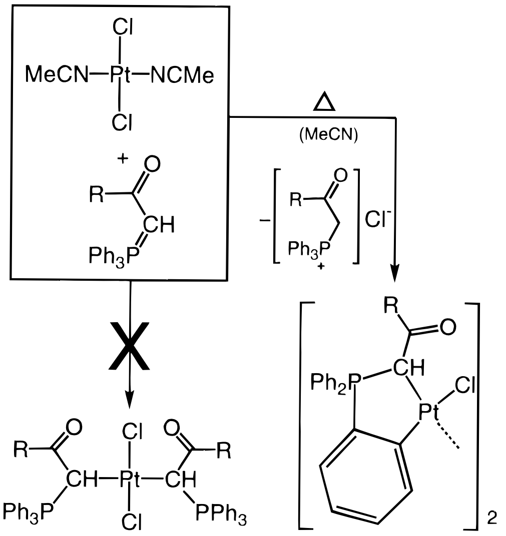
(7) Vicente, J.; Chicote, M. T.; Lagunas, M. C. *Inorg. Chem.* **1993**, *32*, 3748 and references therein.

(8) Vicente, J.; Chicote, M. T.; Fernández-Baeza, J.; Lahoz, F. *Inorg. Chem.* **1991**, *30*, 3617

(9) Vicente, J.; Chicote, M. T.; Lagunas, M. C.; Jones, P. G. *Inorg. Chem.* **1995**, *34*, 5441.

S0020-1669(95)01666-1 CCC: \$12.00

Scheme 1



Scheme 2. Synthesis of Complexes **2**−**4** and Previous Results

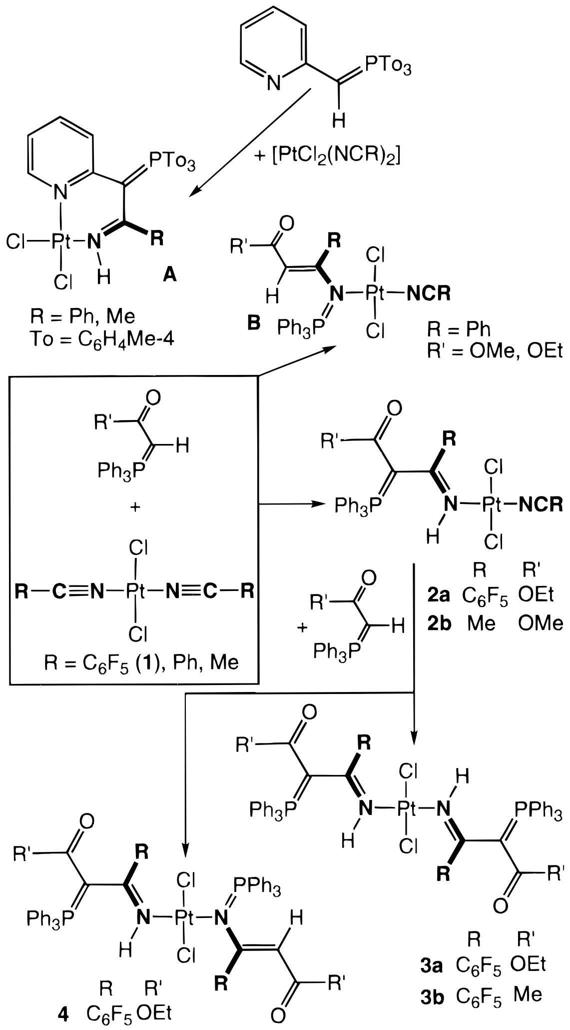
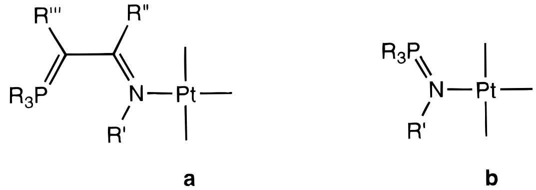


Chart 1) or this and iminophosphorane (see **b** in Chart 1) ligands depending on the nature of the ylide and of R and on the reaction conditions. These reactions involving nucleophilic attack towards coordinated nitriles have attracted interest since the pionering works of Clark and Manzer[10] to the present.[11] The polarizing action of the metal renders the ligands more susceptible to the attack of alcohols, amines, carbanions, or methylidenetriarylphosphoranes, to form imino ether, amidino,[11] and ylideimino complexes.[12] Some examples of the reverse reaction, namely the attack of C_6F_5CN to cationic complexes of Pt containing methanol as a ligand, $[\{M\}-MeOH]^+$ have been reported to yield the corresponding imino ether derivatives $[\{M\}-NH{=}C(OMe)C_6F_5]^+$.[10] It has also been reported that the formation of some hydrido Re(III) complexes occurs through methyleneamido intermediates resulting from the protonation of a nitrile ligand.[13] The only reported platinum complexes containing ylideimine or iminophosphorane ligands are four ylideimino complexes prepared by us[8,9] and a family of iminophosphorano complexes recently reported.[14]

Chart 1



Experimental Section

All the reactions were carried out in normal laboratory conditions. Technical grade solvents were purified by standard procedures. The IR, elemental analyses, melting point determinations, and NMR spectra recording were carried out as described elsewhere.[5a] Chemical shifts are referred to TMS (^1H) or H_3PO_4 [$^{31}P\{^1H\}$] or $CFCl_3$ (^{19}F).

***trans*-[PtCl₂(NCC₆F₅)₂] (1).** $PtCl_2$ (720 mg, 2.70 mmol) was refluxed in C_6F_5CN (15 mL) for 4 h. The solution was filtered while hot through $MgSO_4$, allowed to cool to room temperature, and left overnight at which point a yellow precipitate formed from the brown solution. The brown liquid was decanted off and the precipitate recrystallized from dichloromethane and diethyl ether, giving the yellow compound **1**. Yield: 1306 mg, 74%. Anal. Calcd for $C_{14}Cl_2F_{10}N_2Pt$: C, 25.78; N, 4.30. Found: C, 25.96; N, 4.30. Mp: >320 °C. $^{19}F\{^1H\}$-NMR ($CDCl_3$, δ): −155.22 (m), −134.66 (m), −126.46 (m) ppm. IR (Nujol): $\nu_{C\equiv N}$ 2314, ν_{PtCl} 362, 329, 299 cm^{-1}.

***trans*-[PtCl₂{NH=C(C₆F₅)C(=PPh₃)CO₂Et}(NCC₆F₅)] (2a).** **1** (200 mg, 0.30 mmol) and $Ph_3P{=}CHCO_2Et$ (107 mg, 0.30 mmol) were stirred for 24 h in acetone (20 mL). The resulting yellow solution was concentrated to near dryness, and on the addition of diethyl ether (20 mL) the yellow compound **2a** precipitated. It was recrystallized from dichloromethane/diethyl ether. Yield: 230 mg, 75%. Anal. Calcd for $C_{36}H_{21}Cl_2F_{10}N_2O_2PPt$: C, 43.22; H, 2.12; N, 2.80. Found C, 43.33; H, 2.07; N, 2.70. Mp: 180 °C. ^1H NMR ($CDCl_3$, δ): 0.46 (t, 3H, Me), 3.68 (q, 2H, CH_2), 7.48−7.62 (m, 15H, PPh_3), 10.69 (s, 1H, NH) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 18.19 (s) ppm. ^{19}F NMR ($CDCl_3$ δ): −162.19 (m, 2F, C_6F_5), −156.64 (m, 2F, C_6F_5), −153.24 (t, 1F, C_6F_5), −138.01 (m, 1F, C_6F_5), −134.09 (m, 2F, C_6F_5), −127.57 (m, 2F, C_6F_5), ppm. IR (Nujol): ν_{NH} 3195, $\nu_{C\equiv N}$ 2350, ν_{PtCl} 329 cm^{-1}.

---

(10) (a) Clark, H. C.; Manzer, L. E. *Inorg. Chem.* **1971**, *10*, 2699. (b) Clark, H. C.; Manzer, L. E. *Inorg. Chem.* **1972**, *11*, 2749. (c) Manzer, L. E. *J. Chem. Soc., Dalton Trans.* **1974**, 1535. (d) Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1973**, *47*, C17.

(11) (a) Cini, R.; Caputo, P. A.; Intini, F. P.; Natile, G. *Inorg. Chem.* **1995**, *34*, 1130 and references therein. (b) Bertani, R.; Gotti, M.; Michelin, R. A.; Mozzon, M.; Bandoli, G.; Angelici, R. J. *Organometallics*, **1996**, *15*, 1236 and references therein.

(12) Knoll, L. *J. Organomet. Chem.* **1978**, *155*, C63. Knoll, L.; Wolff, H. *Chem. Ber.* **1979**, *112*, 2709. Knoll, L. *J. Organomet. Chem.* **1980**, *186*, C42

(13) Fraústo da Silva, J. R.; Guedes da Silva, M. F. C.; Henderson, R. A.; Pombeiro, A. J. L.; Richards,R. L. *J. Organomet. Chem.* **1993**, *461*, 141.

(14) Avis, M. W.; Vrieze, K.; Kooijman, H.; Veldman, N.; Speck, A. L.; Elsevier, C. J. *Inorg. Chem.* **1995**, *34*, 4092. Avis, M. W.; Vrieze, K.; Ernsting, J. M.; Elsevier, C. J.; Veldman, N.; Speck, A. L.; Katti, K. V.; Barnes, C. L. *Organometallics* **1996**, *15*, 2376. Avis, M. W.; Elsevier, C. J.; Veldman, N.; Kooijman, H.; Speck, A. L. *Inorg. Chem.* **1996**, *35*, 1518.

***trans*-[$PtCl_2${NH=C(Me)C(=PPh_3)CO_2Me}(NCMe)] (2b).** *trans*-[$PtCl_2(NCMe)_2$] (237 mg, 0.68 mmol) and Ph_3P=$CHCO_2Me$ (455 mg, 1.36 mmol) were stirred in acetone (10 mL) for 48 h. The resulting suspension was filtered off and the yellow solid washed twice with acetone (2 mL) and air dried to give **2b**, which was recrystallized from dichloromethane/diethyl ether. Yield: 280 mg, 60%. Anal. Calcd for $C_{25}H_{25}Cl_2N_2O_2PPt$: C, 44.00; H, 3.69; N, 4.10. Found: C, 43.90; H, 3.46; N, 3.96. Mp: 199 °C. ^1H NMR (CD_2Cl_2, δ): 1.87 (s, 3 H, Me), 2.41 (s, 3 H, MeCN), 2.99 (s, 3H, CO_2Me), 7.56−7.83 (m, 15 H, PPh_3), 9.50 (s, br, 1H, NH) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ): 17.87 (s) ppm. IR (Nujol): ν_{NH} 3259, $\nu_{C\equiv N}$ 2329, ν_{PtCl} 345, 327 cm^{-1}.

***trans*-[$PtCl_2${NH=C(C_6F_5)C(=PPh_3)CO_2Et}$_2$] (3a).** **1** (150 mg, 0.23 mmol) and Ph_3P=$CHCO_2Et$ (176 mg, 0.51 mmol) were stirred in acetone (20 mL) in an ice bath for 30 min. The resulting orange solution was concentrated to near dryness and on the addition of diethyl ether (20 mL) an orange precipitate formed (220 mg) containing (by NMR) a mixture of **4** and **3a** (in approximately a 3:2 ratio). When the crude product was dissolved in the minimum of dichloromethane and layered with methanol, a first set of orange crystals formed, which proved to be compound **4** (30 mg); the crystals were removed and the solution allowed to slowly evaporate over 24 h, yielding yellow crystals which proved to be compound **3a**. Yield: 38%. Anal. Calcd for $C_{58}H_{42}Cl_2F_{10}N_2O_4P_2Pt$: C, 51.64; H, 3.14; N, 2.08. Found: C, 51.49; H, 3.15; N, 1.86. Mp: 184 °C. ^1H NMR ($CDCl_3$, δ): 0.49 (t, 3 H, Me), 3.60 (q, 2H, CH_2), 7.4−7.57 (m, 15 H, PPh_3), 10.53 (s, 1H, NH) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 17.68 (s) ppm. ^{19}F NMR ($CDCl_3$, δ): −164.93 (s, 2F, CF), −156.52 (t, 2F, CF), −136.57 (m, 1F, CF) ppm. IR (Nujol): ν_{NH} 3190, ν_{PtCl} 336 cm^{-1}.

***trans*-[$PtCl_2${NH=C(C_6F_5)C(=PPh_3)C(O)Me}$_2$] (3b).** **1** (94 mg, 0.14 mmol) and Ph_3P=CHCOMe (100 mg, 0.31 mmol) were refluxed in acetone (20 mL) for 1 h, the resulting yellow solution was concentrated to near dryness, and on addition of diethyl ether (30 mL) the yellow compound **3b** precipitated. Yield: 152 mg, 82%. Anal. Calcd for $C_{56}H_{38}Cl_2F_{10}N_2O_2P_2Pt$: C, 52.19; H, 2.97; N, 2.17. Found: C, 51.81; H, 3.06; N, 2.07. Mp: 243 °C. ^1H NMR (CD_2Cl_2, δ): 2.02 (s, 3 H, Me), 7.4−7.6 (m, 15 H, PPh_3), 8.05 (s, br, 1H, NH) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, δ): 14.52 (s) ppm. $^{19}F\{^1H\}$ NMR (CD_2Cl_2, δ): −162.13 (s, 2F), −152.07 (s, 1F), −133.22 (s, 2F) ppm. IR (Nujol): ν_{NH} 3293, ν_{PtCl} 331, 321 cm^{-1}.

A yellow prism 0.45 × 0.35 × 0.28 mm of **3b**·CH_2Cl_2, obtained by vapor diffusion of diethyl ether into a solution of **3b** in dichloromethane, was used to collect 3888 reflections on a Siemens R3mV diffractometer ($2\theta_{max}$ 45°, 3715 unique, R_{int} 0.023). Data were collected using Mo Kα radiation. The orientation matrix was refined from setting angles of 32 reflections in the 2θ range 20−25°. An absorption correction based on ψ-scans was applied, with transmission factors 0.334−0.484. The structure was solved by direct methods and refined anisotropically on all F^2 data using SHELXL-93 (G. M. Sheldrick, University of Göttingen). Hydrogen atoms were included using a riding model. The final wR2 for 386 parameters was 0.117 [R1 = 0.041 for $I > 2\sigma(I)$]. The dichloromethane molecule is disordered over two sites. Tables 1 and 2 give crystallographic data and selected bond lengths and angles, respectively.

***trans*-[$PtCl_2${N(=PPh_3)C(C_6F_5)=$CHCO_2Et$}{*E*-NH=C(C_6F_5)C(=PPh_3)CO_2Et}] (4).** **1** (150 mg, 0.23 mmol) and Ph_3P=$CHCO_2Et$ (176 mg, 0.51 mmol) were refluxed in acetone (20 mL) for 2 h, the resulting orange solution was concentrated to near dryness, and on the addition of diethyl ether (20 mL) the orange compound **4** precipitated. Yield: 225 mg, 73%. Anal. Calcd for $C_{58}H_{42}Cl_2F_{10}N_2O_4P_2Pt$: C, 51.64; H, 3.14; N, 2.08. Found: C, 51.74; H, 3.28; N, 2.12. Mp: 178 °C. ^1H NMR ($CDCl_3$, δ): 0.43 (t, 3 H, Me), 0.89 (t, 3 H, Me), 3.58 (q, 2H, CH_2), 3.69 (q, 2H, Me), 5.04 (s, 1H, CH), 7.38−7.70 (m, 24 H, PPh_3), 8.07 (m, 6 H, PPh_3), 10.18 (s, 1H, NH) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, δ): 18.07 (s, P=C), 36.85 (s, P=N) ppm. ^{19}F NMR ($CDCl_3$, δ): −164.89 (t, 2F), −162.82 (t, 2F), −156.53 (t, 1F), −154.59 (t, 1F), −135.94(m, 4F) ppm. IR (Nujol): ν_{NH} 3195, $\nu_{P=N}$ 1274, ν_{PtCl} 331 cm^{-1}.

An orange block 0.41 × 0.38 × 0.35 mm, obtained by slow diffusion of methanol into a solution of **4** in dichloromethane, was used to collect 7330 reflections at 153 K on a Stoe STADI-4 diffractometer ($2\theta_{max}$ 45°, 7118 unique, R_{int} 0.015). Data were collected at low temperature using Mo Kα radiation. The orientation matrix was refined from setting angles of 42 reflections in the 2θ range 20−25°. An absorption correction based on ψ-scans was applied, with transmission factors 0.953−0.732. The structure was solved by direct methods and refined anisotropically on all F^2 data using SHELXL-93 (G. M. Sheldrick, University of Göttingen). Hydrogen atoms for the methyl group were refined using a rigid model and the others riding. The final wR2 for 714 parameters was 0.056 [R1 = 0.025 for $I > 2\sigma(I)$]. Tables 1 and 3 give crystallographic data and selected bond lengths and angles, respectively.

Table 1. Crystallographic Data for **3b** and **4**

	3b	**4**
formula	$C_{57}H_{40}Cl_4F_{10}N_2O_2P_2Pt$	$C_{58}H_{42}Cl_2F_{10}N_2O_4P_2Pt$
M	1373.74	1348.87
space group	$P\bar{1}$	$P2_1/c$
a (Å)	7.596(2)	16.400(8)
b (Å)	12.694(3)	14.354(7)
c (Å)	16.962(3)	23.221(12)
α (deg)	104.28(3)	
β (deg)	102.73(3)	92.42(2)
γ (deg)	104.43(3)	
V(Å^3)	1464(2)	5462(1)
Z	1	4
T (K)	293	153
λ (Å)	0.710 73	0.710 73
ρ_{calcd} (g cm^{-3})	1.558	1.640
F(000)	678	2672
μ (mm^{-1})	2.7	2.8
no. of reflns/ Params	3888/386	7330/714
$R(F)$[a]	0.041	0.025
$R_w(F^2)$[b]	0.117	0.056

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for reflections with $F > 4\sigma(F)$. [b] $R_w(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and a and b are constants set by the program.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compound **3a**

Pt−N	1.997(6)	Pt−Cl	2.302(2)
N−C(1)	1.294(9)	C(1)−C(2)	1.443(10)
C(2)−C(3)	1.434(10)	C(2)−P	1.767(7)
N−Pt−Cl	94.8(2)	N−Pt−Cl[a]	85.2(2)
C(1)−N−Pt	136.2(5)	N−C(1)−C(2)	125.1(6)
N−C(1)−C(41)	117.0(6)	C(2)−C(1)−C(41)	117.9(6)
C(3)−C(2)−C(1)	127.6(7)	C(3)−C(2)−P	109.7(5)
C(1)−C(2)−P	122.6(5)		

[a] Symmetry operator: −*x*, −*y*, −*z*.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound **4**

Pt−N(1)	2.005(3)	Pt−N(2)	2.086(3)
Pt−Cl(2)	2.3022(13)	Pt−Cl(1)	2.3066(12)
N(1)−C(1)	1.303(5)	C(1)−C(2)	1.435(5)
C(2)−C(3)	1.454(6)	N(2)−C(6)	1.399(5)
C(6)−C(7)	1.349(5)	C(7)−C(8)	1.463(6)
C(2)−P(1)	1.770(4)	N(2)−P(2)	1.643(3)
N(1)−Pt−Cl(2)	84.99(10)	N(2)−Pt−Cl(2)	88.80(9)
N(1)−Pt−Cl(1)	95.91(10)	N(2)−Pt−Cl(1)	90.19(9)
C(1)−N(1)−Pt	139.2(3)	N(1)−C(1)−C(2)	123.7(4)
N(1)−C(1)−C(11)	116.5(3)	C(2)−C(1)−C(11)	119.8(3)
C(1)−C(2)−C(3)	118.8(3)	C(1)−C(2)−P(1)	128.3(3)
C(3)−C(2)−P(1)	112.9(3)	C(6)−N(2)−P(2)	121.2(3)
C(6)−N(2)−Pt	120.8(2)	P(2)−N(2)−Pt	116.9(2)
C(7)−C(6)−N(2)	126.5(3)	C(7)−C(6)−C(51)	120.8(3)
N(2)−C(6)−C(51)	112.7(3)		

Results

When $PtCl_2$ is refluxed in C_6F_5CN a solution is obtained from which *trans*-[$PtCl_2(NCC_6F_5)_2$] (**1**) is obtained on cooling. The reaction of **1** with Ph_3P=$CHCO_2Et$ gives three different products depending on the reaction conditions. Thus, when an equimolecular mixture of **1** and the ylide is stirred in acetone for 24 h at room temperature, the complex containing one N-bonded β-iminophosphorus ylide ligand (we will call it ylideimine ligand), *trans*-[$PtCl_2${NH=C(C_6F_5)C(=PPh_3)CO_2Et}{NCC_6F_5}] (**2a**), is obtained in high yield (see Scheme 2). A related complex, *trans*-[$PtCl_2${NH=CMeC(=PPh_3)CO_2Me}{NCMe}] (**2b**), is obtained by reacting [$PtCl_2(NCMe)_2$] with Ph_3P=$CHCO_2$Me (1:2, acetone, 48 h).

When a mixture of **1** and Ph_3P=$CHCO_2$Et (1:2.2 molar ratio) is stirred in acetone in an ice bath for 30 min, a mixture containing *trans*-[$PtCl_2${NH=C(C_6F_5)C(=PPh_3)CO_2Et}$_2$] (**3a**) and *trans*-[$PtCl_2${*E*-N(=PPh_3)C(C_6F_5)=$CHCO_2$Et}{*E*-NH=C-(C_6F_5)C(=PPh_3)CO_2Et}] (**4**) in a 2:3 molar ratio (according to NMR data) is obtained (see Scheme 2). When the same reaction mixture is stirred at room temperature for 24 h, a mixture of **3a** and **4** is also obtained but in this case the molar ratio is 1:3. If the same reaction mixture is refluxed in acetone for 2 h, an orange solution is obtained from which **4** is isolated. The yield (73%) does not increase if the reflux is maintained for 2 days.

Complex **1** reacts with Ph_3P=CHC(O)Me (1:2) in acetone at room temperature for 1 h to give a solution from which, upon concentration and addition of diethyl ether, *trans*-[$PtCl_2${*E*-NH=C(C_6F_5)C(=PPh_3)C(O)Me}$_2$] (**3b**) is obtained in high yield. **3b** is also obtained in similar yield when the reaction time is 24 h or when the reaction mixture is refluxed for 1 h. This complex is recovered unchanged after refluxing it in ethanol for 2 h.

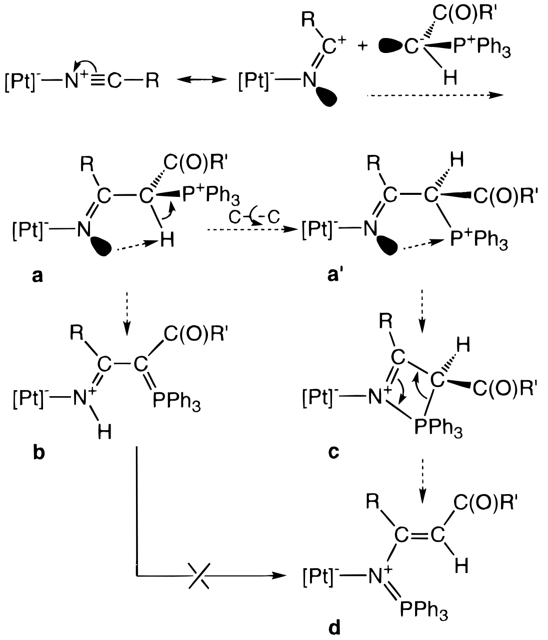
When **1** is reacted with Ph_3P=CHC(O)R (R = OMe, Ph) (1:2) in acetone at room temperature for 24 h, the solutions concentrated and diethyl ether added, solid compounds are obtained which elemental analyses correspond to 2:1 adducts. However their ^{1}H, ^{19}F, and ^{31}P{^{1}H} NMR spectra show complex mixtures which we could not resolve.

Discussion

From the above and previous results,[8,9] it can be inferred that the attack of the ylides to the platinum-coordinated nitrile ligands is dependent on the nature of the nitrile and of the ylide and on reaction conditions. Remarkable differences are found between different nitriles. Thus, Ph_3P=$CHCO_2$Me reacts (2:1) with *trans*-[$PtCl_2(NCMe)_2$] to give the product of the addition of the ylide to only one nitrile ligand (see **2b** in Scheme 2), whereas the analogous Ph_3P=$CHCO_2$Et reacts with **1** giving products of addition of the ylide to both nitrile ligands (see **3a** and **4** in Scheme 2). Moreover, ylides Ph_3P=$CHCO_2$R (R = Me, Et) react (1:1) with *trans*-[$PtCl_2(NCPh)_2$] to give iminophosphorane complexes (**B** in Scheme 2)[8] whereas with **1** Ph_3P=$CHCO_2$Et gives an ylideimino complex (**2a**).

The nature of the ylide and the reaction conditions also have influence on the result. Thus, **1** reacts with Ph_3P=CHC(O)Me (*ca.* 1:2) to give only the bis(ylideimino) complex **3b** whereas with Ph_3P=$CHCO_2$Et (*ca.* 1:2) it gives **4** or mixtures of **4** and **3a** depending on reaction conditions (Scheme 2).

Scheme 3. Proposed Reaction Pathway for the Formation of Complexes **2**−**4**



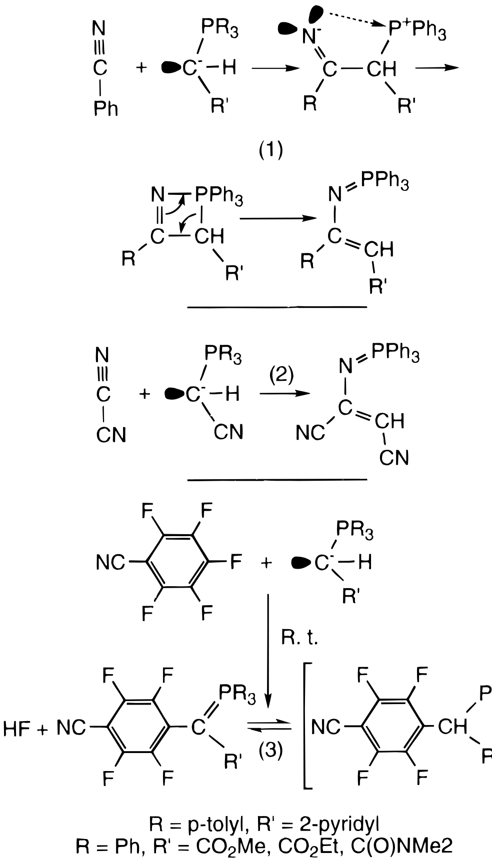
Scheme 3 is our proposal to rationalize the above results. We assume, as is usual,[11] that the nitrile carbon atom suffers a nucleophilic attack by the ylide to give an intermediate that we represent in Scheme 3 in two different conformations, **a** and **a′**. Formation of the ylideimine ligand in **b** or the iminophosphorane ligand in **d** only requires migration of the ylidic hydrogen atom or, respectively, the PPh_3 group to the nitrile nitrogen. In the first case, the final *trans* positions of the R group and the H atom (*E*-isomer), as observed in the X-ray crystal structure of **3b** (see below), suggest that the attack of the ylide is *trans* to the more congested group, *i.e.*, the platinum moiety. Although the *trans* nucleophilic addition of alcohols on nitrile−Pt complexes leading to the *Z*-isomers has been reported to be favored, isomerization to the more stable *E*-isomers takes place readily unless the substituent in the nitrile is very bulky.[11] Similarly, the rehybridization of the C(sp^3) to C(sp^2) from **c** to **d** seems to occur to minimize repulsions between PPh_3 and the substituents attached to such carbon atom because a final *cis* positions of the H atom and the N=PPh_3 moiety is obtained, as observed in the X-ray crystal structure of **4** (see below). This geometry was also that of the complex obtained by reacting [$PtCl_2(NCPh)_2$] and Ph_3P=$CHCO_2$Et.[8]

The complex [$PtCl_2(PhCN)_2$] is the only one giving an iminophosphorane ligand in the first attack of the ylide Ph_3P=$CHCO_2$R to the nitrile (see **B** in Scheme 2) while the analogous MeCN and C_6F_5CN complexes give an ylideimine ligand (**2a**,**b**). However, due to the complex nature of the mixture obtained in the reactions with [$PtCl_2(PhCN)_2$], it is difficult to explain this different behavior.[8] The isolation of the ylideimino complex **2a** in the 1:1 reaction and the presence of the same ligand in the 2:1 reaction products **3a** and **4** suggests that a *cis* C−H addition of the ylide to the nitrile (intermediate **b**) is the first step in all reactions between Ph_3P=$CHCO_2$Et and **1**. The *trans* C−H addition observed in the reaction between [$PtCl_2(NCR)_2$] (R = Me, Ph) and To_3P=CH(py-2) (To = 4-MeC_6H_4; py-2 = 2-pyridyl, see **A** in Scheme 2)[9] is imposed by the coordination of the pyridinic nitrogen.

The different behavior of [$PtCl_2(C_6F_5CN)_2$] and [$PtCl_2(MeCN)_2$] against ylides Ph_3P=$CHCO_2$R (R = Me or Et) can be interpreted having in mind that, after formation of the monoadducts **2a** and **2b**, respectively, the better donor ability of the resulting ylideimine ligand when R = Me than C_6F_5 should induce a decrease of the electrophilic character of the nitrile carbon atom of the remaining nitrile ligand. This decrease would be enough as to impede, or severely reduce, formation of a diadduct such as **3** or **4** when [$PtCl_2(MeCN)_2$] reacts with Ph_3P=$CHCO_2$Me in 1:2 molar ratio. Although formation of some amount of a diadduct can not be discarded, the mother liquor resulting after removing the first crop of **2b** contains a complex mixture in which the main component is **2b**.

The results obtained in the 1:2 reactions between **1** and Ph_3P=$CHCO_2$Et show that attack of the ylide to the remaining

Scheme 4



coordinated nitrile occurs in two different ways to give complexes **3a** and **4**. The isolation of this mixture and the fact that the amount of **4** increases when the reaction temperature raises could be interpreted assuming that complex **3a** is first formed and then one ylideimine ligand isomerizes to an iminophosphorane ligand to give **4** (see **b** → **d** in Scheme 3). Fortunately, it is quite ease to verify this assumption simply by refluxing an acetone solution of **3a**. The recovering of **3a** from this experiment, after 2h refluxing, proves that syntheses of both complexes follow two independent ways as shown in Scheme 3. The **a′** → **c** → **d** reaction way leading to an iminophosphorane ligand has a noticeable temperature dependence likely due to the steric hindrance of the PPh_3 group. Thus, when the temperature is lowered, the reactions rates leading to **b** and **c** are comparable and at 0° a 2:3 mixture of **3a** and **4** is obtained. However, the process **a′** → **c** → **d** is clearly favored when the temperature is raised because at acetone refluxing only **4** is obtained.

The different behavior of ylides $Ph_3P{=}CHCO_2Et$ and $Ph_3P{=}CHCOMe$ against complex **1** can be explained using our proposed reaction pathway. The greater electron-withdrawing character of the C(O)Me group with respect to that of CO_2Et confers a greater acidic character of the CH proton, increasing the rate of the reaction **a** → **b**. This and the high activation energy due to the steric hindrance of the PPh_3 group can be the reasons for obtaining the bis(ylideimino) complex **3b** and not a mixture of **3b** and a complex similar to **4** when $R' = Me$.

Non-resonance-stabilized ylides react with aliphatic and aromatic nitriles to give iminophosphoranes. In these processes formation of intermediates similar to **a′** and **c** have also been postulated (see eq 1 in Scheme 4).[15a] However, resonance-stabilized ylides, like those here studied, only react with nitriles carrying strong electron-withdrawing groups, such as NCCN or CF_3CN (see eq 2 in Scheme 4).[15b] C_6F_5CN is an exception because it reacts with stabilized and nonstabilized ylides $R_3P{=}CHR'$ (R = *p*-tolyl, R′ = 2-pyridyl; R = Ph, R′ = CO_2Me, CO_2Et, $C(O)NMe_2$) giving rise to the substitution of the *p*-F atom (see eq 3 in Scheme 4).[16] Therefore, coordination of C_6F_5CN to platinum not only changes the atom to which the ylide attacks but also allows an iminophosphorane to form in spite of the electron-withdrawing nature of the C_6F_5 group.

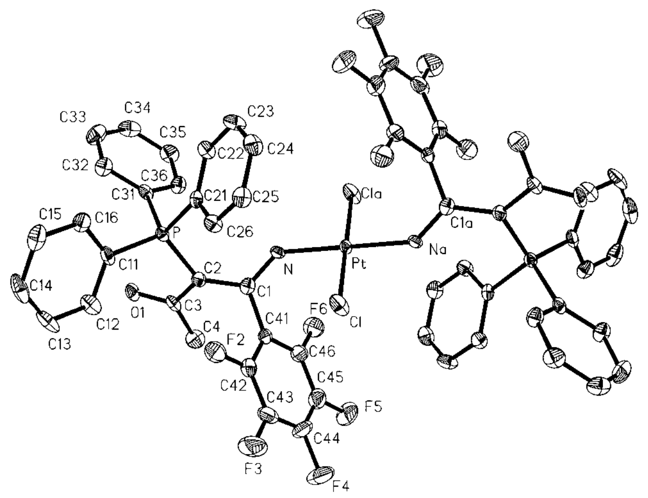


Figure 1. Structure of compound **3b**. H atoms and CH_2Cl_2 of crystallization are omitted for clarity.

Scheme 2 resumes all the different products that can be obtained by reacting *trans*-$[PtCl_2(NCR)_2]$ with ylides: *Z*-(complexes **A**)[9] and *E*-ylideimino (**2a**, **2b**), *E*-iminophosphorano (complexes **B**),[8] bis(*E*-ylideimino) (**3a**, **3b**), and mixed *E*-ylideimino, *E*-iminophosphorano (**4**) complexes.

Structure of Complexes. The crystal structure of complex **3b**·CH_2Cl_2 has been solved (see Figure 1); Tables 1 and 2 give crystal data and selected bond lengths and angles. It displays a crystallographic symmetry center. The coordination around platinum is planar with NPtN and ClPtCl angles of 180° and ClPtN angles of 94.8 and 85.2°. The Pt−Cl [2.302(2) Å] and Pt−N [1.997(5) Å] distances are normal for a Pt(II) complex and very similar to those found in *cis*-$[PtCl_2\{E\text{-}HN{=}C(OMe)Me\}_2]$ [Pt−Cl 2.298(2) and 2.301(2) Å and Pt−N 1.989(7) and 2.009(8) Å][11] indicating that Cl and both imino ligands have similar *trans* influence. The atoms O(1), C(3), C(2), P, and C(1) are in a plane (mean deviation 0.0094 Å) while the N atom is out of this plane (N−C(1)−C(2)−P 39°). In favor of a delocalization of electron density over the O(1), C(3), C(2), P, and C(1) atoms is the P−C(2) distance [1.767(7) Å] which is intermediate between that corresponding to a $P(4){-}C_{sp^2}$ single bond (mean value 1.793 Å)[17] and that found in the related ylide $Ph_3P{=}C(C_6F_4CN\text{-}4)CO_2Et$ [1.722(3) Å].[16b] The C(1)−N [1.294(9) Å] bond length is similar to those found in *cis*-$[PtCl_2\{E\text{-}HN{=}C(OMe)Me\}_2]$ [1.307(11) and 1.294(12) Å].[11] Only marginal deviations of the bond distances C(2)−C(3) [1.434(10) Å *vs* the mean value of 1.471 Å for the single bond in a C=C−C(O)−C arrangement], and C(3)=O [1.240(9) Å *vs* the mean value of 1.210 Å for the C−C(=O)−C arrangement] are observed. The C(1)−C(2) bond length is normal for a single

---

(15) (a) Johnson, A. W. *Ylides and Imines of Phosphorous*; J. Wiley & Sons: New York, 1993; p 201. (b) Ciganek, E. *J. Org. Chem.* **1970**, *11*, 3631.

(16) (a) Vicente, J.; Chicote, M. T.; Fernández-Baeza, J.; Fernández-Baeza, A.; Jones, P. G. *J. Am. Chem. Soc.* **1993**, *115*, 794. (b) Vicente, J.; Chicote, M. T.; Fernandez-Baeza, J.; Fernandez-Baeza, A. *New J. Chem.* **1994**, *18*, 263.

(17) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2*, **1987**, S1.

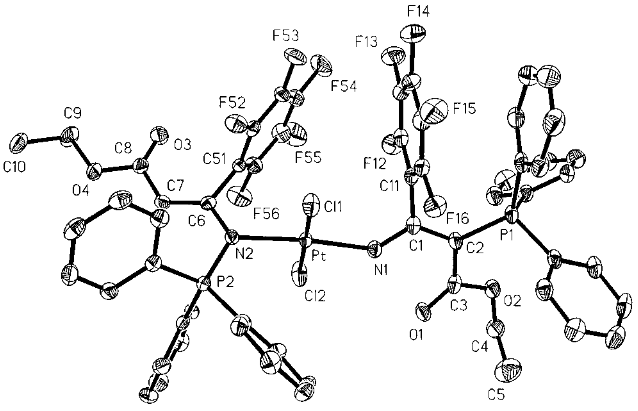


Figure 2. Structure of compound **4**. H atoms are omitted for clarity.

bond [1.443(10) Å *vs* the mean value of 1.460 Å in a C=C−C(O)R arrangement].

The crystal structure of **4** shows the platinum atom in a distorted square planar environment and the same *trans* geometry of the starting complex (see Figure 2). Tables 1 and 3 give crystal data and selected bond lengths and angles. In the ylideimine ligand the significant bond distances and angles as well as the Pt−N(1) bond length are almost identical with those found in complex **3b** while those in the iminophosphorane ligand and the Pt−N(2) bond length are almost the same as those found in the iminophosphorano complex *trans*-$[PtCl_2\{E\text{-}N(=PPh_3)C(Ph)=CHCO_2Et\}(NCPh)]$ (see **B** in Scheme 2, R′ = OEt) reported by us.[8] The *E* geometry of the iminophosphorane ligand is also a common feature of both complexes.

When both crystal structures are compared, the most striking feature is the difference in the relative positions of the two C_6F_5 groups they contain. While in **3b** both C_6F_5 groups lie on opposite sides with respect to the N−Pt−N axis, in **4** they lie on the same side which can be interpreted as a consequence of the larger steric hindrance caused by the PPh_3 when it is bonded to the nitrogen atom.

The ^{19}F NMR of complex **1** shows three intense resonances corresponding to one the two possible isomers for a $[PtCl_2(NCC_6F_5)_2]$ stoichiometry while only a trace amount of the other isomer is present. We assume complex **1** to be the *trans* isomer based on its preparation procedure because it has been reported that although the *cis*-$[PtCl_2(NCR)_2]$ complexes are kinetically favored they isomerize to the *trans* species on heating or on prolonged stirring at room temperature.[18] If the ^{19}F NMR spectra of complexes **1**−**4** are compared, the resonances due to the ligand C_6F_5CN appear in the ranges −155.22 to −156.64, −134.66 to −138.01, and −126.46 to −127.57 ppm, those corresponding to the ylideimine ligand in the ranges −162.13 to −163.4, −152.07 to −155.08, and −133.22 to −134.94 ppm, and those due to the iminophosphorane ligand at −164.89, −156.53, and −135.94 ppm. Similarly, from the ^{31}P NMR spectra of **2a**, **2b**, **3a**, **3b**, and **4** the two resonances corresponding to PPh_3 appearing in **4** at 18.07 and 36.85 ppm can be assigned to the ylideimine and the iminophosphorane ligands, respectively. The ^{31}P resonance corresponding to the iminophosphorane ligand is in the same region as those observed in the previously reported iminophosphorano complexes *trans*-$[PtCl_2\{E\text{-}N(=PPh_3)C(Ph)=CHCO_2R\}(NCPh)]$ (R = Me (36.19 ppm), Et (36.02 ppm)).[8] The δ(NH) in the ^1H NMR of complexes **2a**, **2b**, **3a**, **3b**, and **4** is observed as a broad singlet in the 8.05−10.69 ppm range.

The IR spectra of **1**, **2a**, and **2b** show the ν(CN) stretching mode as a weak band in the 2310−2350 cm^{-1} range while in the spectra of complexes **2a**−**4** the ν(NH) stretching mode appears as a weak broad band (sharp in **3b**) in the 3190−3300 cm^{-1} range. Although *trans*-$[PtCl_2L_2]$ complexes have only one IR-active ν(PtCl) mode, two or even three bands are observed to appear in the 300−370 cm^{-1} region in complexes with L = nitrile and imidoester.[18b] Because the *cis* isomer should give two bands, the number of bands in this region does not have diagnostic utility. In our complexes one (**2a**, **3a**, **4**), two (**2b**, **3b**), or three (**1**) bands are observed in this region. In the Experimental Section, we have indicated these bands as ν(PtCl) although some of them could not be due to such modes. The *cis* or *trans* geometry of products of addition of different nucleophiles to $[PtCl_2(NCR)_2]$ have been shown to be the same as the starting complexes[11a] unless the nucleophile induces a change of geometry as occurs in the synthesis of complex **A** (see Scheme 2).[9] Therefore the *trans* geometry of complexes **3b** and **4** points to a *trans* geometry for **1**, and consequently, the other complexes (**2** and **3a**) should have the same geometry. The X-ray crystal structure of complex **B** (see Scheme 2) also agrees with this rule.[8] In addition, the method of synthesis and isolation of **1** are those established for the synthesis of *trans*-$[PtCl_2(NCR)_2]$ complexes.[18b]

The IR spectrum of **4** shows the ν(P=N) at 1274 cm^{-1}, very close to those observed in other iminophosphorano-Pt(II) complexes reported by us (at 1270 cm^{-1}).[8] Given that ν(C=O), ν(C=N) and ν(C=C) bands should appear in the same region, unequivocal assignment is precluded in some cases. These bands are observed in the 1705−1570 cm^{-1} region. However, of the two bands at 1646 and 1575 cm^{-1} in complex **3b**, the first can be assigned to ν(C=N).[10a,c] Therefore, ν(CO) (at 1571 cm^{-1}) is shifted 31 cm^{-1} to a higher wavenumber with respect to the same band in the parent ylide $Ph_3P=CHC(O)Me$, which means that the ylene form $[Ph_3P=C(R)C(O)Me]$ [R = $C(C_6F_5)=NH\{Pt\}$] is in **3b** more important than that in the parent ylide (R = H). Hence, the nitrogen ligand in **3b** must be viewed as a β-imino-stabilized phosphorus ylide, according to the name we have given to it and to its representation in Scheme 2.

Conclusions. The reactivity of $[PtCl_2(NCR)_2]$ with carbonyl stabilized phosphorus ylides $Ph_3P=CHC(O)R'$ is even more complex than previously assumed. We have shown that ylideimine and iminophosphorane ligands can be generated as a result of the nucleophilic attack of an ylide to a coordinated nitrile. The results depend on the nature of R and R′. When R = Me, only one nitrile is attacked, giving an monoylideimino complex. When R = C_6F_5, the result depends on the basic character of the ylide. The ylide with R′ = Me gives a bis(ylideimino) complex while the more basic ylide with R′ = OEt gives preferentially a mixed ylideimino−iminophosphorano complex although a bis(ylideimino) complex can also be isolated if the reaction is carried out at low temperature.

In this paper we have shown several facts for the first time: (i) ylides can attack two nitrile ligands of a complex; (ii) this double attack can give two different types of complexes, bis(ylideimino) (**3a,b**) or mixed ylideimino−iminophosphorano (**4**) complexes; (iii) these two types of complexes are obtained because the second nucleophilic attack can occur through two independent reaction ways depending on reaction conditions; (iv) complexes containing two ylideimine ligands can be synthesized (**3a,b**); (v) one complex containing ylideimine and iminophosphorane ligands was synthesized (**4**); (vi) the *cis* addition of an ylide to a nitrile ligand in a platinum complex

---

(18) (a) Fanizzi, F. P.; Intini, F. P.; Maresca, L.; Natile, G. *J. Chem. Soc., Dalton Trans.* **1990**, 199. (b) Fraccarollo, D.; Bertani, R.; Mozzon, M.; Belluco, U.; Michelin, R. A. *Inorg. Chim. Acta* **1992**, *201*, 15.

took place (vii) X-ray crystal structures of complexes containing a cis-ylideimine ligand were obtained (**3b**, **4**).

Acknowledgment. We thank Dirección General de Investigación Científica y Técnica (Grant PB92-0982-C) for financial support and the University of Cambridge for data collection facilities. M.C.R.A. thanks the Commission of the European Communities for a research training fellowship from the Human Capital and Mobility Research Program. M.A.B gratefully acknowledges The Royal Society for a European Science Exchange fellowship.

Supporting Information Available: Tables giving crystal data and details of the structure determination, atom coordinates, bond lengths and angles, and anisotropic displacement coefficients for **3b** and **4** (11 pages). Ordering information is given on any current masthead page.

IC951666A