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Platinum-Assisted C−C Bond Formation. Synthesis of Platinum Imidoyl Phosphorus Ylide Complexes and the First Crystal Structure of an Imidoyl Phosphorus Ylide Complex

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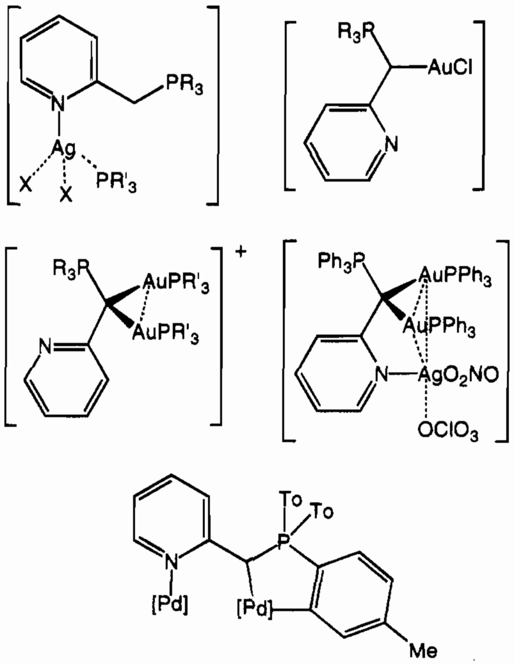
$[To_3PCH_2(Py\text{-}2)]Cl$ ($[1]^+Cl^-$, To = $C_6H_4Me\text{-}4$, Py = pyridine) reacts with $PtCl_2$ (1:1) to give $[PtCl_3\{Py\{CH_2PTo_3\}\text{-}2\}]$ (**2**). This complex reacts with various bases, but complex mixtures, which we were unable to separate, are obtained. However, the reaction between $[1]^+Cl^-$, *trans*-$[PtCl_2(NCPh)_2]$, and Na_2CO_3 after refluxing gives mixtures from which it is possible to isolate and characterize the complex *cis*-$[PtCl_2\{NH{=}C(Ph)C({=}PTo_3)(Py\text{-}2)\text{-}N,N'\}]$ (**3**). Similarly, starting from the *trans*-$[PtCl_2(NCMe)_2]$ complex, *cis*-$[PtCl_2\{NH{=}C(Me)C({=}PTo_3)(Py\text{-}2)\text{-}N,N'\}]$ (**4**) is obtained. These are the first imidoyl phosphorus ylide complexes of platinum. The crystal structures of $\mathbf{3}\cdot CH_2Cl_2$ and $\mathbf{3}\cdot 3CHCl_3$ were determined [$\mathbf{3}\cdot CH_2Cl_2$: $C_{35}H_{33}Cl_4N_2PPt$, triclinic, $P\bar{1}$, 173(2) K, a = 11.367(6) Å, b = 14.252(6) Å, c = 14.532(7) Å, α = 60.87(3)°, β = 74.62(4)°, γ = 73.17(4)°. $\mathbf{3}\cdot 3CHCl_3$: $C_{37}H_{34}Cl_{11}N_2PPt$, triclinic, $P\bar{1}$, 143(2) K, a = 11.257(3) Å, b = 12.132(4) Å, c = 16.921(5) Å, α = 105.90(2)°, β = 105.75(2)°, γ = 90.14(2)°, Z = 2]. These are the first crystal structures of imidoyl phosphorus ylide complexes. The Pt−Cl bond distances are significantly different, showing the greater *trans* influence of imino group compared to the pyridyl group. The double-bond character of the N(1)−C(2) and P−C(1) bonds is reduced *via* conjugation through the C(1)−C(2) bond.

Introduction

We recently reported the synthesis and structure of complexes derived from phosphonium salts $[R_3PCH_2(Py\text{-}2)]X$ [R = Ph, $C_6H_4Me\text{-}4$ (To), Py = pyridine; X = ClO_4, CF_3SO_3].[1] These cationic ligands can coordinate through the nitrogen and also, after single or double deprotonation, through the methylene carbon atom to form ylide complexes or, after orthometalation, to one of the aryl groups attached to the phosphorus atom to give mono-, di-, and tri- homonuclear and heteronuclear Au(I), Ag(I), Cu(I), and Pd(II) complexes (see Chart 1). The initial objective of the present work was to prepare Pt(II) complexes with these cationic ligands and to deprotonate them to form ylide platinum complexes. The differences between Pd(II) and Pt(II) with respect to their tendencies to form ylide complexes are such that interesting differences might be expected. Thus, we have shown that complexes $[MCl_2(NCPh)_2]$ (M = Pd, Pt) react with the ylide $Ph_3P{=}CHCO_2Me$ to give the substitution product $[PdCl_2\{CH(PPh_3)CO_2Me\}_2]$[2] or respectively the iminophosphorane complex $[PtCl_2\{E\text{-}N({=}PPh_3)C(Ph){=}CHCO_2Me\}(NCPh)]$ resulting from the addition of the ylide to one of the coordinated benzonitrile molecules (see Scheme 1).[3] In this paper we report a new difference in reactivity between $[MCl_2(NCPh)_2]$ (M = Pd, Pt) and an ylide. The resulting platinum complexes contain an imidoyl phosphorus ylide ligand. Only a few complexes with such ligands are known,[4] whereas many homologous β-carbonyl phosphorus ylides have been reported.[5]

Chart 1



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(1) (a) Vicente, J.; Chicote, M. T.; Lagunas, M. C.; Jones, P. G.; Bembenek, E. *Organometallics* **1994**, *13*, 1243. (b) Vicente, J.; Chicote, M. T.; Lagunas, M. C. *Inorg. Chem.* **1993**, *32*, 3748. (c) Vicente, J.; Chicote, M. T.; Lagunas, M. C.; Jones, P. G. *J. Chem. Soc., Chem. Commun.* **1991**, 1730.

(2) Vicente, J.; Chicote, M. T.; Fernandez-Baeza, J. *J. Organomet. Chem.* **1989**, *364*, 407.

(3) Vicente, J.; Chicote, M. T.; Fernandez-Baeza, J.; Lahoz, F. J.; López, J. A. *Inorg. Chem.* **1991**, *30*, 3617.

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

(5) Vicente, J.; Chicote, M. T.; Lagunas, M. C.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1991**, 2579 and references therein.

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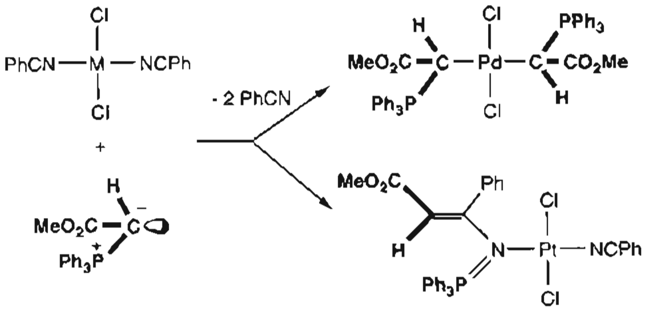
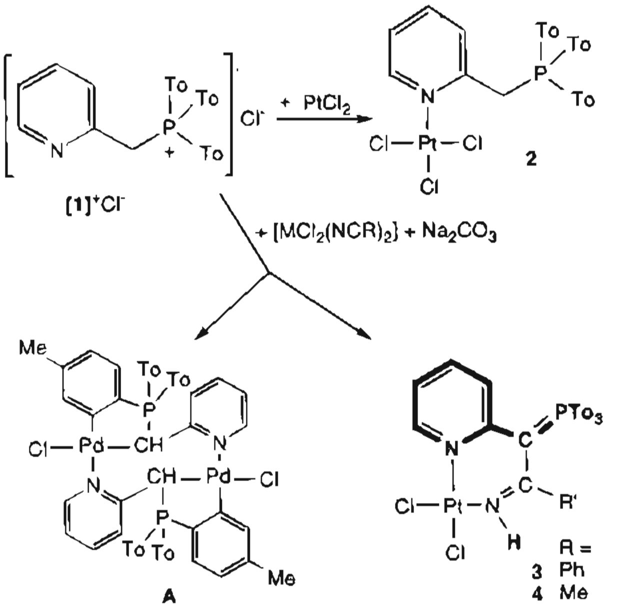
Scheme 1



Scheme 2



Results and Discussion

Both the anion and cation of $[To_3PCH_2(Py\text{-}2)]Cl$ ($[1]^+Cl^-$; To = C_6H_4Me-4, Py = pyridine) coordinate to platinum on refluxing (5.5 h) an acetone suspension of the salt and $PtCl_2$ (1:1). The reaction product, $[PtCl_3\{Py\{CH_2PTo_3\}\text{-}2\}]$ (**2**) (see Scheme 2), precipitates (88% yield) in the reaction medium. However, the reaction between $[PtCl_2(NCPh)_2]$ and $[1]^+Cl^-$ (refluxing 7 h) gives a mixture of **2** (40% yield) and of both reagents. Therefore, the ability for coordination of $[1]^+$ to Pt(II) is similar to that of benzonitrile, probably due to its cationic nature. The coordination of the chloride anion seems to be crucial to the coordination of the cation because the salt $[1]^+ClO_4^-$ does not react with $[PtCl_2(NCPh)_2]$ (1:1, room temperature, 24 h or 2:1, reflux, 8 h). According to these and previous data,[1a] Pt(II) has less affinity for the cationic ligand $[1]^+$ than Pd(II). Thus, $[PdCl_2(NCPh)_2]$ reacts with $[1]^+X^-$ to give $[PdCl_3\{Py\{CH_2PTo_3\}\text{-}2\}]$ (X = Cl; 1:1) or $[PdCl_2\{Py\{CH_2PTo_3\}\text{-}2\}_2](ClO_4)_2$ (X = ClO_4; 1:2).[1a] Depending on molar ratios, some silver salts AgX (X = ClO_4, CF_3SO_3) react with $[1]^+X^-$ to give $[AgX_2\{Py\{CH_2PTo_3\}\text{-}2\}]$ or $[AgX_3\{Py\{CH_2PTo_3\}\text{-}2\}_2]$ whereas others (X = NO_3, $MeCO_2$) do not.[1b]

Complex **2** was reacted with different bases in an attempt to form an ylide complex. However, we obtained the starting material (KOH, room temperature, 8 h) or mixtures that we could not separate [*e.g.*: Tl(acac), 1:1 or 1:2, room temperature, 16 h or 3 h, respectively; Proton Sponge, 1:1, room temperature, 6 h; NaH, 1:1, room temperature, 25 min; $LiBu^n$, 1:1, room temperature, 22 h; Na_2CO_3, 1:2, refluxing in acetone 8 h]. The related palladium complexes $[PdCl_3\{Py\{CH_2PTo_3\}\text{-}2\}]$ or $[PdCl_2\{Py\{CH_2PTo_3\}\text{-}2\}_2](ClO_4)_2$ are doubly deprotonated with some of these bases to give the dinuclear complex **A** (see Scheme 2).[1a] This complex could also be obtained in a one-pot synthesis by reacting $[1]^+Cl^-$, $[PdCl_2(NCPh)_2]$, and Na_2CO_3 (1:1:1). However, reaction of $[1]^+Cl^-$ with *trans*-$[PtCl_2(NCPh)_2]$ and Na_2CO_3 always gives mixtures of three to eight compounds (by ^{31}P NMR), depending on molar ratios, temperature, and reaction time. Nevertheless, from these mixtures it was possible to isolate and characterize the complex *cis*-$[PtCl_2\{NH{=}C(Ph)C({=}PTo_3)(Py\text{-}2)\text{-}N,N'\}]$ (**3**) (see Scheme 2). Similarly, from *trans*-$[PtCl_2(NCMe)_2]$, the complex *cis*-$[PtCl_2\{NH{=}C(Me)C({=}PTo_3)(Py\text{-}2)\text{-}N,N'\}]$ (**4**) could be obtained. From *cis*-$[PtCl_2(NCMe)_2]$, complex **3** could also be isolated, although in lower yield. These complexes result from a C−H addition of the ylide, formed by deprotonation of $[1]^+Cl^-$ with Na_2CO_3, to the C−N bond of one of the coordinated nitrile molecules. A similar process has been reported by Knoll when reacting nitrile complexes of Cr(0) or Mn(I) with phosphorus ylides.[4] As far as we are aware, these are the only precedents for this type of complex. A related reaction is that between $Li(Ph_2PCHY)$ (Y = CN, CO_2Et) and $[PtCl_2(NCPh)_2]$ to give the complex **B** in Scheme 3.[6] However, in this case the attack is by an anionic reagent. It should be emphasized that **3**, and the related Cr(0) or Mn(I) complexes, should be viewed as metalated ylides (see **I** in Chart 2) because ylide complexes [*i.e.*, complexes resulting from coordination of an ylide to a metal center, whether through

Scheme 3

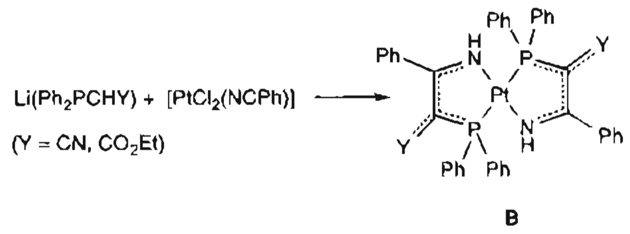
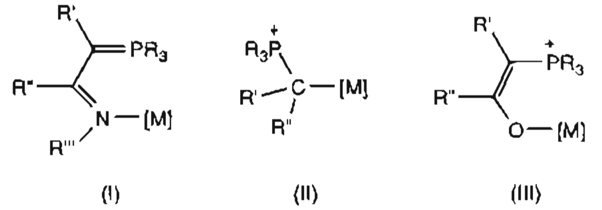
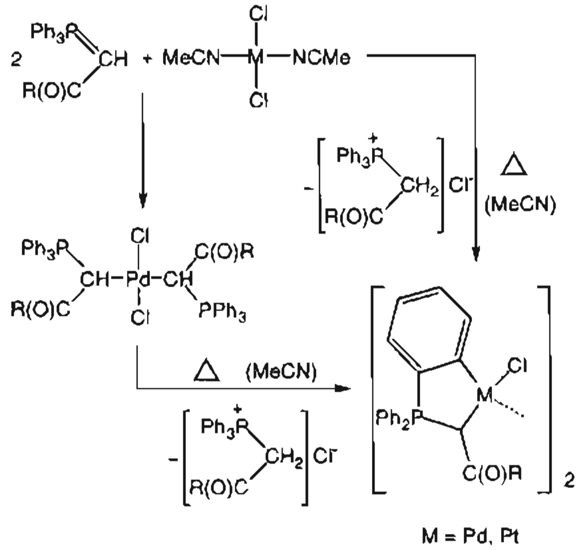


Chart 2



Scheme 4



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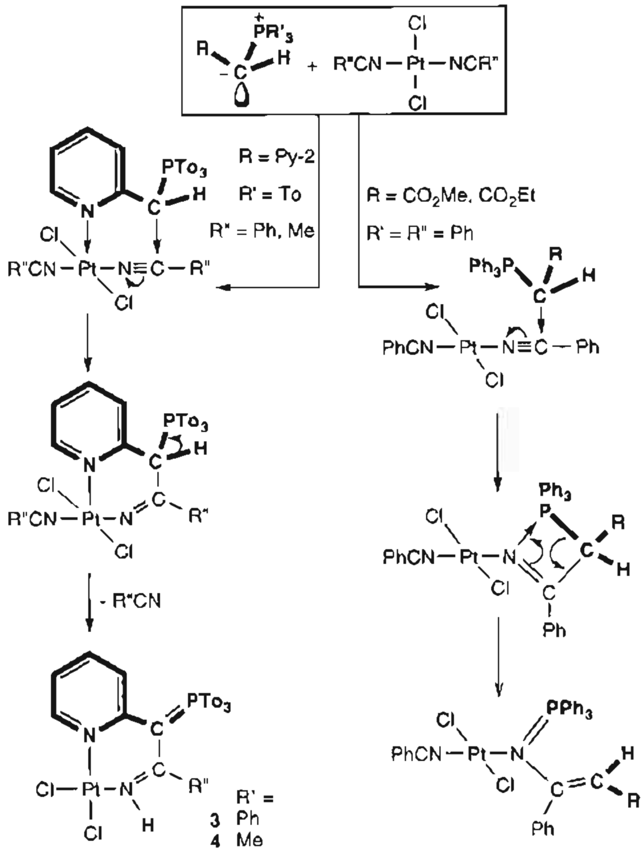
(6) Braunstein, P.; Matt, D.; Dusausoy, Y.; Fischer, J. *Organometallics* **1983**, 2, 1410.

Scheme 5



the carbon (**II** in Chart 2) or a heteroatom, as with carbonyl-stabilized ylides (**III** in Chart 2)] can be seen as metalated phosphonium salts.

Reaction Pathway in the Synthesis of 3 and 4. Reactions between [$MCl_2(NCMe)_2$] (M = Pd and Pt) and various carbonyl-stabilized phosphorus ylides $Ph_3P{=}CHC(O)R$ (Yl) were initially reported to give complexes [$MCl_2(Yl)_2$].[7] However, reinvestigations of some of these reactions showed that results depend on temperature. Thus, when M = Pd at room temperature, [$PdCl_2(Yl)_2$] or [$Pd_2Cl_2(\mu\text{-}Cl)_2(Yl)_2$] is obtained, whereas refluxing in acetonitrile give mixtures of the phosphonium salts [YlH]Cl and orthometalated complexes [Pd{CH{P(2-C_6H_4)Ph_2}-{C(O)R}(μ-Cl)]$_2$.[2,8,9] When M = Pt, refluxing in acetonitrile leads to the above mixture of phosphonium salts and orthometalated complexes (see Scheme 4).[8] We have reinvestigated the room-temperature reactions between [$PtCl_2(NCR)_2$] and some carbonyl-stabilized phosphorus ylides.[3] The products, when R = Ph and Yl = $Ph_3P{=}CHCO_2R'$ (R' = Me, Et), were the first iminophosphorane complexes of Pt(II), *trans*-[$PtCl_2${*E*-N(($=PPh_3$)C(Ph)$=CHCO_2R'$}(NCPh)], *i.e.*, the result of addition of the ylide to one of the coordinated benzonitrile molecules (see Scheme 1). Formation of complexes **3** and **4** can be rationalized in a similar way. Scheme 5 shows our proposals for pathways leading to **3** and **4** or to the iminophosphorane complexes. Nucleophilic attack of the ylide at the carbon atom of the nitrile could be a common first step. However, subsequent coordination of the pyridine ring to the metal center or nucleophilic attack of the nitrile nitrogen on the phosphorus atom, respectively, represents the difference between both processes. In the first case, acid—base migration of the methynic proton to the iminic nitrogen atom or, in the second, P—C bond cleavage lead to the final products. Alternatively, it is also possible that coordination of the pyridinic nitrogen could precede and even guide the subsequent nucleophilic attack in the case of the synthesis of **3** and **4**. An interesting difference between both reaction pathways is that coordination of the pyridine ring imposes a *trans* C—H addition to the nitrile (probably through the solvent or intermolecularly) whereas the P—C addition leads to the formation of a C—N single bond. However, it should be borne in mind that isolation and characterization of one compound of these reactions do not rule out the formation of, *e.g.*, iminophosphorane complexes along with complexes **3** and **4**. Nucleophilic additions of N—H, S—H, or O—H bonds to coordinated nitriles are well-known;[10] however, as far as we are aware, apart from the attack of ylides on coordinated nitriles, only a few C—H additions have previously been reported, although the nucleophiles are carbanionic reagents such as Ph_2PCHY^- (Y = CN, CO_2Et) or acetylacetonate.[6,11]

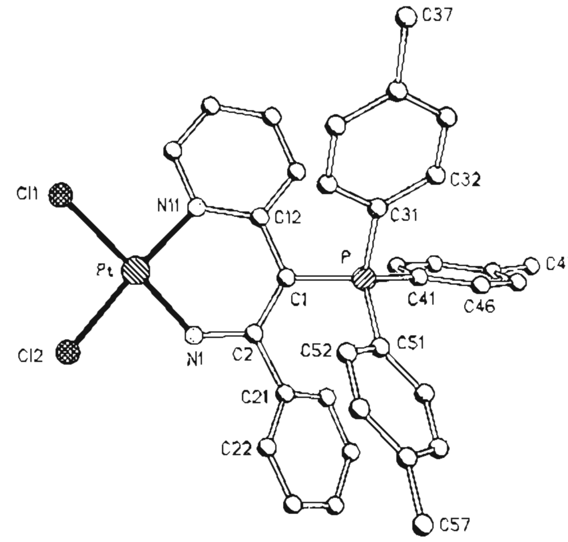


Figure 1. The structure of compound **3'** (or **3"**) in the crystal. Radii are arbitrary. H atoms and solvent of crystallization are omitted for clarity.

Crystal Structure of 3. Complex **3**, isolated as **3**·CH_2Cl_2 (**3'**) and **3**·3$CHCl_3$ (**3"**), is the first imidoyl phosphorus ylide complex characterized by X-ray diffraction (see Figure 1); Tables 1—4 give crystal data, atomic coordinates, and selected bond lengths and angles for **3'** and **3"**. The Pt—Cl bond distances are significantly different, showing the greater *trans* influence of imino group [Pt—Cl(1) **3'**, 2.325(3), **3"** 2.315(2) Å] than that of the pyridyl group [Pt—Cl(2): **3'**, 2.302(3) Å, **3"** 2.296(2) Å]. This observation allows us to assign the ν(ClPd) *trans* to the pyridyl and imino group modes to the observed bands at 311 and 330 cm^{-1}, respectively. For complex **4**, these bands appear at 307 and 321 cm^{-1}, respectively.

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

(8) Illingswoth, M. L.; Teagle, J. A.; Burmeister, J. L.; Fultz, W. C.; Rheingold, A. L. *Organometallics* **1983**, 2, 1364.

(9) Teagle, J. A.; Burmeister, J. L. *Inorg. Chim. Acta* **1986**, *118*, 65. Albanese, J. A.; Rheingold, A. L.; Burmeister, J. L. *Inorg. Chim. Acta* **1988**, *150*, 213. Albanese, J. A.; Staley, D. L.; Rheingold, A. L.; Burmeister, J. L. *J. Organomet. Chem.* **1989**, *375*, 265.

(10) Storhoff, B. N.; Lewis, H. C., Jr. *Coord. Chem. Rev.* **1977**, *23*, 1. Belluco, U.; Michelin, R. A.; Ros, R.; Bertani, R.; Facchin, G.; Mozzon, M.; Zanotto, L. *Inorg. Chim. Acta* **1992**, *198—200*, 883. Pombeiro, A. J. L. *Inorg. Chim. Acta* **1992**, *198—200*, 179. Casas, J. M.; Chisholm, M. H.; Sicilia, M. V.; Streib, W. E. *Polyhedron* **1991**, 1573. Paul, P.; Nag, K. *Inorg. Chem.* **1987**, *26*, 1586. Maresca, L.; Natile, G.; Intini, F. P.; Gasparrini, F.; Tiripicchio, A.; Tiripicchio-Camellini, M. *J. Am. Chem. Soc.* **1986**, *108*, 1180. Thorn, D. L.; Calabrese, J. C. *J. Organomet. Chem.* **1984**, 272, 283. Manzer, L. E. *J. Chem. Soc., Dalton Trans.* **1974**, 1535. Clark, H. C.; Manzer, L. E. *Inorg. Chem.* **1972**, *11*, 2749. Clark, H. C.; Manzer, L. E. *Inorg. Chem.* **1971**, *10*, 2699.

(11) Uchiyama, T.; Toshiyasu, Y.; Nakamura, Y.; Miwa, T.; Matsumoto, K.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 181.

Table 1. Crystallographic Data for **3′** and **3″**

	3′	**3″**		**3′**	**3″**
formula	$C_{35}H_{33}Cl_4$-N_2PPt	$C_{37}H_{34}Cl_{11}$-N_2PPt	M_r	849.49	1122.67
			space group	$P\bar{1}$	$P\bar{1}$
a (Å)	11.367(6)	11.257(3)	*T* (°C)	−100	−130
b (Å)	14.252(6)	12.132(4)	λ (Å)	0.71073	0.71073
c (Å)	14.532(7)	16.921(5)	ρ_{calcd} (g cm^{-3})	1.449	1.749
α (deg)	60.87(3)	105.90(2)	μ (cm^{-1})	3.944	4.049
β (deg)	74.62(4)	105.75(2)	$R(F)^a$	0.069	0.053
γ (deg)	73.17(4)	90.14(2)	$R_w(F^2)^b$	0.203	0.136
V (Å^3)	1947(2)	2131.6(11)	reflns/params	6770/409	8348/359
Z	2	2			

[a] $R(F) = \Sigma|F_o| - |F_c||/\Sigma|F_o|$ for reflections with $F > 4\sigma(F)$. [b] $R_w(F^2) = [\Sigma\{F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{0.5}$ 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. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for Compound **3′**

	x	*y*	*z*	*U*(eq)^a
Pt	6601.5(4)	6433.5(3)	6757.6(3)	30.1(2)
P	2374(2)	6390(2)	6604(2)	27.5(5)
Cl(1)	7428(3)	6442(3)	8054(2)	47.9(7)
Cl(2)	7773(3)	7682(2)	5445(2)	40.4(6)
N(1)	5919(8)	6513(7)	5615(7)	31(2)
C(1)	4008(10)	6001(8)	6588(8)	29(2)
C(2)	4807(10)	6433(8)	5620(8)	29(2)
N(11)	5511(8)	5340(7)	7827(7)	32(2)
C(12)	4455(9)	5277(8)	7622(8)	27(2)
C(13)	3745(11)	4500(8)	8437(9)	35(2)
C(14)	4135(12)	3813(10)	9407(9)	41(2)
C(15)	5233(13)	3864(10)	9587(9)	46(2)
C(16)	5917(12)	4600(10)	8783(9)	42(2)
C(21)	4455(9)	6805(8)	4556(8)	30(2)
C(22)	4704(11)	7803(9)	3715(9)	41(2)
C(23)	4443(14)	8122(10)	2728(9)	54(3)
C(24)	3949(14)	7456(9)	2537(9)	54(3)
C(25)	3705(11)	6468(9)	3364(8)	37(2)
C(26)	3960(10)	6151(8)	4359(8)	32(2)
C(31)	1675(10)	6517(8)	7831(8)	34(2)
C(32)	533(10)	6258(8)	8365(8)	38(2)
C(33)	23(12)	6370(10)	9276(9)	47(2)
C(34)	655(11)	6753(10)	9692(9)	47(2)
C(35)	1797(13)	7035(10)	9138(9)	46(2)
C(36)	2295(10)	6944(10)	8216(9)	38(2)
C(37)	122(18)	6801(13)	10740(10)	71(4)
C(41)	1653(9)	5430(8)	6564(8)	31(2)
C(42)	2349(10)	4414(8)	6684(8)	34(2)
C(43)	1808(11)	3643(8)	6689(8)	35(2)
C(44)	582(9)	3891(9)	6565(8)	37(2)
C(45)	−100(10)	4908(9)	6421(8)	36(2)
C(46)	426(10)	5685(9)	6424(8)	34(2)
C(47)	−31(13)	3046(10)	6604(10)	46(2)
C(51)	1986(9)	7724(8)	5537(8)	30(2)
C(52)	2279(10)	8609(8)	5537(8)	38(2)
C(53)	1954(11)	9657(8)	4754(9)	41(2)
C(54)	1354(11)	9858(9)	3940(9)	42(2)
C(55)	1061(11)	8975(8)	3944(9)	41(2)
C(56)	1388(11)	7917(8)	4724(8)	36(2)
C(57)	1000(13)	11008(10)	3090(12)	56(3)
C(99)	4703(26)	977(19)	2967(15)	124(7)
Cl(3)	5376(28)	1045(24)	1734(15)	200(16)
Cl(4)	5705(14)	48(11)	3906(12)	99(4)
Cl(3′)	4694(24)	1035(12)	1718(13)	132(6)
Cl(4′)	6169(17)	273(19)	3299(17)	147(6)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for Compound **3″**

	x	*y*	*z*	*U*(eq)
Pt	3202.6(3)	5147.1(3)	2361.6(2)	25.2(1)
P	7473(2)	5116(2)	2258.1(12)	22.3(4)
Cl(2)	1784(2)	3581(2)	1906.0(14)	37.0(5)
Cl(1)	2454(2)	5907(2)	3527.2(13)	38.1(5)
C(1)	5897(7)	5350(6)	2008(4)	24.0(14)
C(2)	5017(7)	4482(6)	1384(5)	25.5(15)
N(11)	4436(6)	6524(5)	2659(4)	25.3(13)
C(12)	5544(6)	6435(6)	2498(4)	23.1(14)
C(13)	6352(7)	7430(6)	2778(5)	30(2)
C(14)	6016(8)	8479(7)	3174(5)	35(2)
C(15)	4831(8)	8552(7)	3277(6)	41(2)
C(16)	4088(7)	7581(7)	3023(5)	34(2)
N(1)	3862(6)	4409(5)	1399(4)	28.5(14)
C(21)	5318(6)	3617(6)	663(5)	25.5(14)
C(22)	4926(7)	2473(7)	460(5)	33(2)
C(23)	5156(8)	1673(7)	−229(5)	41(2)
C(24)	5758(8)	2030(7)	−740(5)	40(2)
C(25)	6134(7)	3172(7)	−551(5)	34(2)
C(26)	5918(6)	3965(6)	142(5)	25.8(15)
C(31)	8096(6)	5675(6)	3407(5)	26(2)
C(32)	7369(7)	5514(6)	3926(5)	31(2)
C(33)	7857(8)	5841(7)	4802(5)	37(2)
C(34)	9046(7)	6323(7)	5191(5)	35(2)
C(35)	9783(8)	6460(8)	4687(5)	41(2)
C(36)	9318(7)	6144(7)	3801(5)	34(2)
C(37)	9546(10)	6679(10)	6155(6)	57(3)
C(41)	8335(6)	5778(6)	1731(5)	25.6(15)
C(42)	7738(7)	6464(6)	1224(5)	25.3(15)
C(43)	8360(7)	6955(6)	793(5)	31(2)
C(44)	9601(7)	6781(7)	843(5)	32(2)
C(45)	10184(7)	6104(7)	1351(5)	33(2)
C(46)	9576(7)	5612(7)	1789(5)	28(2)
C(47)	10285(8)	7303(9)	374(6)	45(2)
C(51)	7685(6)	3595(6)	2005(4)	24.9(15)
C(52)	8364(7)	3069(7)	1458(5)	32(2)
C(53)	8531(7)	1916(7)	1318(5)	36(2)
C(54)	8018(7)	1254(7)	1705(5)	35(2)
C(55)	7338(8)	1787(7)	2250(5)	34(2)
C(56)	7168(7)	2941(6)	2409(5)	31(2)
C(57)	8186(10)	−19(8)	1534(6)	51(2)
C(97)	534(16)	−731(14)	3966(11)	106(5)
Cl(91)	393(5)	−1615(4)	2996(3)	120(2)
Cl(92)	−497(9)	360(6)	3889(4)	212(4)
Cl(93)	2002(7)	−114(10)	4485(4)	265(6)
C(98)	5339(9)	2870(9)	4569(6)	50(2)
Cl(94)	4264(3)	1848(3)	4590(2)	79.9(9)
Cl(95)	4628(2)	3683(2)	3897(2)	57.4(6)
Cl(96)	6574(3)	2184(3)	4227(2)	75.9(9)
C(99)	7374(10)	−952(9)	−1824(6)	53(2)
Cl(97)	5769(3)	−966(2)	−2079(2)	66.8(7)
Cl(98)	8017(4)	−488(3)	−714(2)	93.1(12)
Cl(99)	7957(3)	−18(3)	−2289(2)	86.8(10)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The metal atoms display planar coordination (mean deviation of Pt and four donor atoms 0.01 and 0.05 Å for **3′** and **3″**, respectively). The chelate ring is a flattened boat, with Pt and C(1) 0.55 and 0.26 Å out of the plane of N(1), C(2), N(11), C(12) for **3′** and 0.63 and 0.25 Å out of the plane for **3″**. The double bond character of the N(1)−C(2) [**3′**, 1.299(14), **3″**, 1.311(9) Å] and P−C(1) [**3′**, 1.775(11) Å; **3″**, 1.751(7) Å] bonds is reduced *via* conjugation through the C(1)−C(2) bond. Thus, the above-mentioned bonds are longer than those found in compounds containing C(sp^2)=NR [1.279 Å] bonds[12] or in $Ph_3P=CH_2$ [1.697(8), 1.688(3) Å],[13] respectively, whereas the C(1)−C(2) bond distance [**3′**, 1.409(15) Å; **3″**, 1.422(10) Å] is shorter than, for example, C(1)−C(12) [**3′**, 1.473(13) Å; **3″**, 1.471(10) Å] or C(2)−C(21) [**3′**, 1.497(14) Å, **3″**, 1.492(10) Å]. The P−C(1) bond distances are even larger than that found in $Ph_3P=C(C_6F_4CN\text{-}4)CO_2Et$ [1.722(3) Å] in spite of the presence of the two electron-withdrawing substituents, C_6F_4-CN-4 and CO_2Et, attached to the methylene carbon atom.[14]

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

(13) Schmidbaur, H.; Jeong, J.; Schier, A.; Graf, W.; Wilkinson, D. L.; Müller, G.; Krüger, C. *New J. Chem.* **1989**, *13*, 341.

(14) Vicente, J.; Chicote, M. T.; Fernandez-Baeza, J.; Fernandez-Baeza, A. *New J. Chem.* **1994**, *18*, 263.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compounds **3′** and **3″**

bond	**3′**	**3″**		**3′**	**3″**
Pt−N(1)	1.955(9)	1.967(6)	N(1)−C(2)	1.299(14)	1.311(9)
Pt−N(11)	2.029(9)	2.029(6)	C(1)−C(2)	1.409(15)	1.422(10)
Pt−Cl(2)	2.302(3)	2.296(2)	C(1)−C(12)	1.473(13)	1.471(10)
Pt−Cl(1)	2.325(3)	2.315(2)	C(2)−C(21)	1.497(14)	1.492(10)
P−C(1)	1.775(11)	1.751(7)	N(11)−C(12)	1.347(13)	1.347(9)
P−C(51)	1.795(11)	1.808(7)	N(11)−C(16)	1.374(14)	1.371(10)
P−C(41)	1.816(10)	1.800(8)	P−C(31)	1.823(11)	1.807(7)

angle	**3′**	**3″**		**3′**	**3″**
N(1)−Pt−N(11)	88.8(3)	88.6(3)	C(12)−C(1)−P	117.0(8)	117.2(5)
N(1)−Pt−Cl(2)	86.9(3)	87.7(2)	N(1)−C(2)−C(1)	120.6(9)	121.2(7)
N(11)−Pt−Cl(1)	94.1(3)	93.6(2)	N(1)−C(2)−C(21)	116.1(9)	115.3(6)
Cl(2)−Pt−Cl(1)	90.21(11)	90.29(8)	C(1)−C(2)−C(21)	123.3(9)	123.4(6)
C(2)−N(1)−Pt	128.6(7)	126.8(5)	C(12)−N(11)−C(16)	119.2(9)	119.9(7)
C(2)−C(1)−C(12)	123.3(9)	122.9(6)	C(12)−N(11)−Pt	123.3(7)	122.9(5)
C(2)−C(1)−P	119.6(7)	119.9(5)			

Therefore, **3** is an N-metalated imino-stabilized phosphorus ylide. In fact, it does not react with 3,4,5-trimethoxybenzaldehyde (room temperature in dichloromethane or refluxing in toluene). NH protons were located in difference syntheses. IR spectra of complexes **3** and **4** show bands at 3331 and 3268 cm^{-1}, respectively, that must be assigned to the ν(NH) mode.

Conclusions. Our results show that reactions between [$PtCl_2(NCR)_2$] and ylides can even be more complex than previously assumed. Thus, whereas at high temperatures these reactions lead to orthometalated complexes, room-temperature reactions afford iminophosphorane complexes or, as shown here, complexes that can be viewed as N-platinated imino-stabilized phosphorus ylides.

Experimental Section

IR spectroscopy, elemental analyses, conductance measurements, melting point determinations, and NMR spectroscopy were carried out as described elsewhere.[1a] Chemical shifts are referred to TMS (^{1}H) or H_3PO_4 [^{31}P{^{1}H}]. 2-(Chloromethyl)pyridine hydrochloride was purchased from Lancaster.

[To_3PCH_2(Py-2)]Cl ([1]$^+$Cl$^-$). To a suspension of 2-(chloromethyl)pyridine hydrochloride (2.1 g, 12.6 mmol) in chloroform (30 mL) was added To_3P (5.7 g, 18.9 mmol) and the mixture refluxed for 4 h. After cooling, the solution was concentrated to half-volume and diethyl ether added (50 mL) to precipitate [To_3PCH_2(Py-2)]Cl·HCl as an oily product which, after removal of the mother liquors, was stirred vigorously with diethyl ether until a white solid was obtained (4.9 g, 83 %). Anal. Calcd for $C_{27}H_{28}Cl_2NP$: C, 69.23; H, 6.02; N, 2.99. Found: C, 68.58; H, 6.25; N, 3.27. To a solution of this hydrochloride (2.7 g, 5.7 mmol) in dichloromethane (25 mL) was slowly added a suspension of NaH (179 mg, 6.0 mmol) in mineral oil. The resulting suspension was filtered through celite, the solution concentrated to dryness, and the residue washed with diethyl ether, filtered off, and dried under vacuum. Yield: 1.5 g, 61%. Anal. Calcd for $C_{27}H_{27}ClNP$: C, 75.08; H, 6.30; N, 3.24. Found: C, 75.85; H, 6.72; N, 3.08. Mp: 265 °C. Λ_M (in acetone) = 113 Ω^{-1} mol^{-1} cm^2 (5.6 × 10^{-4} mol L^{-1}). NMR: ^{1}H (CDCl$_3$, δ), 2.45 [s, 9H, Me (To)], 5.47 (d, 2H, CH$_2$, $^2J_{PH}$ = 14.7 Hz), 7.11 [m, 1H, py (H5)], 7.4−7.9 (m, 14H, To + py), 8.29 [m, 1H, py (H6)] ppm; ^{31}P{^{1}H} (CDCl$_3$, δ), 22.9 (s) ppm.

[$PtCl_3${Py{CH_2PTo_3}-2}] (2) A suspension of [1]$^+$Cl$^-$ (204.1 mg, 0.472 mmol) and $PtCl_2$ (126 mg, 0.47 mmol) in acetone (20 mL) was refluxed for 5.5 h. The resulting orange suspension was cooled to room temperature and filtered. The orange solid was washed with diethyl ether (2 × 2 mL) and dried in an oven (80 °C) to give **2**. Yield: 292 mg, 89%. Anal. Calcd for $C_{27}H_{27}Cl_3NPPt$: C, 46.46; H, 3.90; N, 2.01. Found: C, 46.18; H, 3.84; N, 2.10 . Mp: 252 °C. Λ_M (in acetone): 5 Ω^{-1} cm^2 mol^{-1} (2 × 10^{-4} mol L^{-1}). IR (cm^{-1}): ν(ClPd) 325. NMR: ^{1}H (CDCl$_3$, δ), 2.44 [s, 9H, Me (To)], 6.11 (d, 2H, CH$_2$, $^2J_{PH}$ = 14.4 Hz), 6.99 ["t", 1H, Py (H5)], 7.11 ["d", 1H, Py (H3)], 7.44 [m, 7H, To + Py (H4)], 7.67 (m, 6H, To), 8.93 ["d", 1H, Py (H6)] ppm; ^{31}P NMR (CDCl$_3$, δ), 20.73 (s) ppm.

***cis*-[$PtCl_2${NH=C(Ph)C(=PTo_3)(Py-2)-*N*,*N*′}] (3).** To a suspension of [1]$^+$Cl$^-$ (243 mg, 0.56 mmol) in acetone (20 mL) were added *trans*-[$PtCl_2(NCPh)_2$] (292 mg, 0.62 mmol) and Na_2CO_3 (119 mg, 1.12 mmol). The pale yellow suspension was heated at reflux to give a darker suspension. After 8.5 h, the resulting orange suspension was cooled to room temperature. The yellow solid obtained was extracted with dichloromethane (*c.a.* 5 mL), the suspension filtered through anhydrous $MgSO_4$, and the filtrate concentrated to *c.a.* 1 mL. Addition of diethyl ether (10 mL) gave complex **3** as a pale yellow solid, which was washed with diethyl ether (2 × 2 mL) and dried in an oven (80 °C). Yield: 173 mg, 40%. Anal. Calcd for $C_{34}H_{31}Cl_2N_2PPt$: C, 53.41; H, 4.09; N, 3.66. Found: C, 52.76; H, 3.94; N, 3.63. Mp: 212 °C. Λ_M (in acetone): 0 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(ClPd) 311, 330; ν(NH) 3331. NMR: ^{1}H (CDCl$_3$, δ), 2.39 [s, 9H, Me (To)], 6.47 ["t", 1H, Py (H5)], 6.70 ["d", 1H, Py (H3)], 6.81 ["t", 2H, Ph], 6.9−7.1 (m, 5H, Py (H4) + Ph + NH), 7.20 (m, 6H, To), 7.51 (m, 6H, To), 9.58 ["d", 1H, Py (H6)] ppm; ^{31}P NMR (CDCl$_3$, δ), 21.18 (s) ppm.

Single crystals of **3′** and **3″** were obtained by slow diffusion of n-hexane into solutions of **3** in dichloromethane and chloroform, respectively. Data were collected at low temperature using Mo Kα radiation (**3′**, Siemens R3, 2θ_{max} 50°; **3″**: Stoe STAD1-4, 2θ_{max} 52°). Absorption corrections were applied using ψ-scans (**3″**) or SHELXA (G. M. Sheldrick, unpublished; **3′**). Cell constants were refined from $\pm\omega$ angles (**3″**) or setting angles (**3′**), of *ca.* 50 reflections in the 2θ range 20−23°. Structures were solved by the heavy-atom method and refined anisotropically on F^2 using SHELXL-93 (G. M. Sheldrick, University of Göttingen). Hydrogen atoms were included using a riding model. The dichloromethane of **3′** is disordered over two sites. Further details are given in Table 1.

***cis*-[$PtCl_2${NH=C(Me)C(=PTo_3)(Py-2)-*N*,*N*′}] (4).** To a suspension of [1]$^+$Cl$^-$ (204.5 mg, 0.562 mmol) in acetone (20 mL) were added *trans*-[$PtCl_2(NCMe)_2$] (181 mg, 0.52 mmol) and Na_2CO_3 (100 mg, 0.95 mmol). The off-white suspension was refluxed. After 9 h, the resulting orange suspension was cooled to room temperature and filtered. The yellow residue obtained was extracted with dichloromethane (*ca.* 5 mL), the suspension filtered through anhydrous $MgSO_4$, and the filtrate concentrated to *ca.* 1 mL. Addition of diethyl ether (*ca.* 10 mL) gave complex **4** as a pale yellow solid, which was washed with diethyl ether (2 × 2 mL) and air-dried. Yield: 68.7 mg, 21%. Anal. Calcd for $C_{29}H_{29}Cl_2N_2PPt$: C, 49.58; H, 4.16; N, 3.99. Found: C, 49.16; H, 4.31; N, 4.08. Mp: 215 °C. Λ_M (in acetone): 0 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): ν(ClPd) 307, 321; ν(NH) 3268. NMR: ^{1}H (CDCl$_3$, δ), 1.53 (s, 3H, Me), 2.44 [s, 9H, Me (To)], 6.38 ["d", 1H, Py (H3)], 6.45 ["t", 1H, Py (H5)], 6.93 ["t", 1H, Py (H4)], 7.03 (br s, 1H, NH), 7.40 (m, 6H, To), 7.79 (dd, 6H, To), 9.53 ["d", 1H, Py (H6)] ppm; ^{31}P (CDCl$_3$, δ), 18.56 (s) ppm.

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Supporting Information Available: Tables giving crystal data and details of the structure determination, atom coordinates, least-squares planes, bond lengths and angles, and anisotropic displacement coefficients for **3′** and **3″** (19 pages). Ordering information is given on any current masthead page.

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