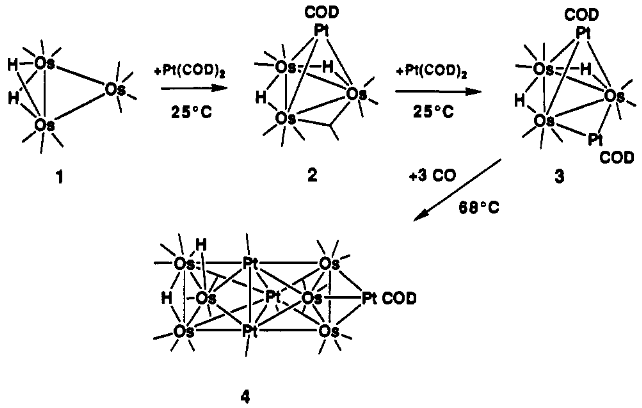
Scheme I



due to the 16-electron configuration of the platinum atom of the bridging Pt(COD) grouping. Compound **3** is also somewhat unstable and its solutions slowly decompose in air in a few hours. Solutions of **3** exposed to CO are rapidly decomposed to yield hydrogen, $PtOs_2(CO)_{10}$,[11] a trace of $Pt_2Os_3(CO)_{14}$,[12] a trace of $Pt_2Os_4(CO)_{18}$,[11] and a small amount of **4**. In the solid state, compound **3** is more stable.

When heated under a nitrogen atmosphere, compound **3** is transformed to the high-nuclearity metal cluster complex **4**, but the yield is relatively low. This can be attributed in part to the fact that the reaction requires the addition of 3 mol of CO. If small amounts of CO are added to the reaction, the yield of **4** is nearly doubled.

Compound **4** exhibits the same selective segregation of the platinum and osmium into triangular groupings of the pure elements as compound **5**. The distance between the Pt_3 and Os_3 layers is significantly smaller in the Pt(COD) capped layer than in the noncapped layer. A similar effect was observed in **5**. An explanation for this is not available at present. It appears that it should be possible to obtain **4** directly from **5** by decarbonylation and addition of hydrogen. Efforts to accomplish this are in progress.

There are relatively few examples of high-nuclearity mixed-metal cluster complexes that contain platinum.[17-19] Several years ago Chini prepared a series of high nuclearity platinum carbonyl cluster complexes $[Pt_3(CO)_6]_n^{2-}$ (n = 2-5) based on triangulated layers of platinum lying in nearly eclipsed conformations.[20] It appears that **4** and **5** may be prototypes for a more extensive series of higher nuclearity metal cluster complexes whose structures are based on alternating triangular layers of platinum and osmium having staggered conformations. Efforts to prepare these are now in progress.

Acknowledgment. These studies were supported by the National Science Foundation under Grant No. CHE-8919786.

Supplementary Material Available: Tables of hydrogen atom positional parameters and anisotropic thermal parameters (5 pages); tables of structure factor amplitudes (34 pages). Ordering information is given on any current masthead page.

---

(17) Fumagalli, A.; Martinengo, S.; Ciani, G. *J. Organomet. Chem.* **1984**, *273*, C46. (b) Fumagalli, A.; Martinengo, S.; Ciani, G. *J. Chem. Soc., Chem. Commun.* **1983**, 1381. (c) Fumagalli, A.; Martinengo, S.; Ciani, G.; Marturano, G. *Inorg. Chem.* **1986**, *25*, 592.

(18) (a) Ceriotti, A.; Demartin, F.; Longoni, G.; Manassero, M.; Marchionna, M.; Piva, G.; Sansoni, M. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 697. (b) Longoni, G.; Manassero, M.; Sansoni, M. *J. Am. Chem. Soc.* **1980**, *102*, 7973. (c) Ceriotti, A.; Demartin, F.; Longoni, G.; Manassero, M.; Piva, G.; Piro, G.; Sansoni, M.; Heaton, B. T. *J. Organomet. Chem.* **1986**, 301, C5.

(19) (a) Couture, C.; Farrar, D. H.; Goudsmit, R. J. *Inorg. Chim. Acta* **1984**, *89*, L29. (b) Couture, C.; Farrar, D. H. *J. Chem. Soc., Chem. Commun.* **1985**, 197. (c) Couture, C.; Farrar, D. H. *J. Chem. Soc., Dalton Trans.* **1987**, 2245. (d) Couture, C.; Farrar, D. H. *J. Chem. Soc., Dalton Trans.* **1987**, 2253. (e) Adams, R. D.; Wu, W. *Organometallics* **1991**, *10*, 35.

(20) (a) Longoni, G.; Chini, P. *J. Am. Chem. Soc.* **1976**, *98*, 7225. (b) Calabrese, J. C.; Dahl, L. F.; Chini, P.; Longoni, G.; Martinengo, S. *J. Am. Chem. Soc.* **1974**, *96*, 2614.

Contribution from the Grupo de Química Organometálica, Departamento de Química Inorgánica, Facultad de Ciencias
Químicas, Universidad de Murcia, 30071 Espinardo, Murcia, Spain, and Departamento de Química Inorgánica,
Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

Platinum-Assisted Addition of Carbonyl-Stabilized Phosphorus Ylides to Benzonitrile To Give Iminophosphorane Complexes of Platinum(II). Crystal and Molecular Structure of *trans*-$[PtCl_2\{E\text{-}N(=PPh_3)C(Ph)=CHCO_2Et\}(NCPh)]\cdot{}^1/_2Me_2CO$

José Vicente,*[,1] María-Teresa Chicote,[1] Juan Fernández-Baeza,[1] Fernando J. Lahoz,*[,2]
and José A. López[2]

Received February 14, 1991

Ylides $Ph_3P=CHCO_2R$ (R = Et, Me) add to *trans*-$[PtCl_2(NCPh)_2]$ to give the first iminophosphorane complexes of platinum $[PtCl_2\{E\text{-}N(=PPh_3)C(Ph)=CHCO_2R\}(NCPh)]$. The complex with R = Et crystallizes with a half-molecule of acetone and is triclinic, space group $P\bar{1}$, with a = 10.753 (1) Å, b = 13.264 (2) Å, c = 14.047 (2) Å, α = 92.25 (1)°, β = 110.65 (1)°, γ = 104.26 (1)°, V = 1799.4 (4) Å^3, and Z = 2. The structure was refined to values of R = 0.025 and R_w = 0.026. The complex has a trans geometry. The P–N [1.641 (4) Å] bond distance is longer than that in free iminophosphoranes. A reaction pathway leading to these complexes is proposed. The E configuration adopted by the iminophosphorane ligand seems to be that minimizing repulsions between PPh_3 and substituents attached to the methine carbon atom.

Introduction

Iminophosphoranes ($R_3P=NR'$) are interesting compounds because of their widespread utility as key intermediates in the synthesis of natural products[3] and other nitrogen–phosphorus compounds.[4] Some of them have been found to possess semiconductor properties,[5] and some have been used as building blocks of backbone polymers.[6] Surprisingly, their use as ligands is very limited,[7] and therefore, the knowledge of how coordination could

---

(1) Universidad de Murcia.

(2) Universidad de Zaragoza.

(3) Zaloom, J.; Calandra, M.; Roberts, D. C. *J. Org. Chem.* **1985**, *50*, 2603. Bachi, M. D.; Vaya, J. *J. Org. Chem.* **1979**, *44*, 4393. Hickey, D. M. B.; Mackenzie, A. R.; Moody, C. J.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1987**, 921.

(4) Barluenga, J.; López, F.; Palacios, F. *Synthesis* **1989**, 298 and references therein.

(5) Bryce, M. R.; Moore, A. J.; Kim, Y. H.; Liu, Z. X.; Nowak, H. J. *Tetrahedron Lett.* **1987**, *28*, 4465.

(6) Allcock, H. R. *Chem. Eng. News* **1985**, *63* (11), 22.

0020-1669/91/1330-3617$02.50/0 © 1991 American Chemical Society

Table I. Crystallographic Data for *trans*-$[\mathrm{PtCl_2}\{E\text{-}\mathrm{N({=}PPh_3)C(Ph){=}CHCO_2Et}\}(\mathrm{NCPh})]\cdot{}^1/_2\mathrm{Me_2CO}$

$\mathrm{C_{36}H_{31}Cl_2N_2O_2PPt}\cdot{}^1/_2\mathrm{C_3H_6O}$	MW = 849.66
a = 10.753 (1) Å	ρ_{calcd} = 1.568 g cm^{-3}
b = 13.264 (2) Å	μ = 41.67 cm^{-1}
c = 14.047 (2) Å	R = 0.025
α = 92.25 (1)°	R_w = 0.026
β = 110.65 (1)°	V = 1799.4 (4) Å^3
γ = 104.26 (1)°	Z = 2
λ - 0.710 69 Å	space group $P\bar{1}$

modify their reactivity is almost unexplored.[8]

Iminophosphoranes are generally prepared by using Staudinger ($\mathrm{R_3P + N_3R' \rightarrow R_3P{=}NR' + N_2}$) and Kirsanov ($\mathrm{R_3PCl_2 + H_2NR' \rightarrow R_3P{=}NR' + 2ClH}$) reactions.[9] Although ylides react with nitriles to give iminophosphoranes (e.g., $\mathrm{Ph_3P{=}CHPh + PhCN \rightarrow Ph_3P{=}NC(Ph){=}CHPh}$), all reported attempts to use resonance-stabilized ylides (e.g., $\mathrm{Ph_3P{=}CHCN}$) have been unsuccessful unless activated nitriles (e.g., $\mathrm{CF_3CN}$) were used.[10] We have also extended this observation to the reaction between $\mathrm{Ph_3P{=}CHCO_2Me}$ and PhCN. We wish to report that carbonyl-stabilized ylides $\mathrm{Ph_3P{=}CHCO_2R}$ (R = Et, Me) add at room temperature to PhCN when it is coordinated to platinum to give the first iminophosphorane complexes of platinum. The limited number of iminophosphorane complexes reported[7] contrasts with the large number of those containing the isoelectronic ylide ligands.[11]

Experimental Section

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer 1430 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured with a Philips PW9501 conductometer. Melting points were determined on a Reichert apparatus and are uncorrected. C, H, and N analyses were carried out with a Perkin-Elmer 240C microanalyzer. Proton NMR spectra were recorded on a Bruker AC-200 spectrometer, and phosphorus NMR spectra were recorded on a Varian FT-80 spectrometer.

Synthesis of *trans*-$[\mathrm{PtCl_2}\{E\text{-}\mathrm{N({=}PPh_3)C(Ph){=}CHCO_2R}\}(\mathrm{NCPh})]$ [R = Et (1a), Me (1b)]. Equimolar amounts (ca. 0.3 mmol) of *trans*-$[\mathrm{PtCl_2(NCPh)_2}]$ and $\mathrm{Ph_3P{=}CHCO_2Et}$ in acetone (20 cm^3) were reacted at room temperature for 14 h, and the reaction mixture was evaporated to dryness. A 100-mg sample of this mixture was washed with 2–4 cm^3 of acetone; complex **1a** remained insoluble (62% yield). Anal. Calcd for $\mathrm{C_{36}H_{31}Cl_2N_2O_2PPt}$: C, 52.69; H, 3.81; N, 3.41. Found: C, 52.53; H, 3.92; N, 3.38. Mp = 162 °C; Λ_M = 2 Ω^{-1} cm^2 mol^{-1} (5 × 10^{-4} mol dm^{-3} in acetone). ^{1}H NMR ($\mathrm{CDCl_3}$, $\mathrm{SiMe_4}$ as reference, 20 °C, 200 MHz): δ 0.79 (t, 3 H, $\mathrm{CH_3}$, $^2J_{\mathrm{HH}}$ = 7 Hz), 3.64 (q, 2 H, $\mathrm{CH_2}$), 5.21 (d, 1 H, CH, $^4J_{\mathrm{PH}}$ = 1 Hz), 7.5 (m, 19 H, Ph), 8.1 ppm (m, 6 H, Ph). ^{31}P{^{1}H} NMR ($\mathrm{CDCl_3}$, $\mathrm{H_3PO_4}$ as reference, 32.20 MHz): δ 36.02 ppm (s with ^{195}Pt satellites, $^2J_{\mathrm{PtP}}$ = 113 Hz). IR: $\nu_{\mathrm{C{=}O}}$ 1710, $\nu_{\mathrm{C{=}C}}$ 1575, 1585, $\nu_{\mathrm{P{=}N}}$ 1270, ν_{PtCl} 330 cm^{-1}.

Table II. Selected Bond Lengths (Å) and Bond Angles (deg) for Complex **1a**

Pt–Cl(1)	2.299 (1)	Pt–Cl(2)	2.316 (1)
Pt–N(1)	2.034 (5)	Pt–N(2)	1.953 (5)
P–N(1)	1.641 (4)	P–C(13)	1.806 (4)
P–C(7)	1.799 (7)	P–C(19)	1.806 (5)
O(1)–C(3)	1.189 (7)	C(1)–C(2)	1.342 (8)
O(2)–C(3)	1.349 (7)	C(1)–C(25)	1.492 (7)
O(2)–C(4)	1.449 (10)	C(2)–C(3)	1.470 (9)
N(1)–C(1)	1.416 (8)	C(4)–C(5)	1.480 (11)
N(2)–C(6)	1.144 (8)	C(6)–C(31)	1.434 (9)
Cl(1)–Pt–Cl(2)	178.8 (1)	Cl(2)–Pt–N(1)	89.3 (1)
Cl(1)–Pt–N(1)	90.4 (1)	Cl(2)–Pt–N(2)	91.8 (1)
Cl(1)–Pt–N(2)	88.6 (2)	N(1)–Pt–N(2)	176.4 (2)
N(1)–P–C(7)	109.3 (3)	C(7)–P–C(13)	104.7 (3)
N(1)–P–C(13)	114.0 (3)	C(7)–P–C(19)	107.6 (3)
N(1)–P–C(19)	109.5 (2)	C(13)–P–C(19)	111.5 (3)
C(3)–O(2)–C(4)	115.8 (4)	C(2)–C(1)–C(25)	122.7 (5)
Pt–N(1)–P	115.1 (2)	C(1)–C(2)–C(3)	124.9 (5)
Pt–N(1)–C(1)	123.1 (3)	O(1)–C(3)–O(2)	122.4 (6)
P–N(1)–C(1)	121.9 (4)	O(1)–C(3)–C(2)	127.7 (5)
Pt–N(2)–C(6)	173.2 (4)	O(2)–C(3)–C(2)	109.8 (4)
N(1)–C(1)–C(2)	123.4 (5)	O(2)–C(4)–C(5)	108.0 (6)
N(1)–C(1)–C(25)	113.8 (5)	N(2)–C(6)–C(31)	177.1 (6)

Prepared by the same method as for **1a**, complex **1b** precipitates from the reaction mixture as a spectroscopically pure compound (47% yield). Anal. Calcd for $\mathrm{C_{35}H_{29}Cl_2N_2O_2PPt}$: C, 52.11; H, 3.62; N, 3.47. Found: C, 52.48; H, 3.86; N, 3.69. Mp = 110 °C; Λ_M = 3 Ω^{-1} cm^2 mol^{-1} (5 × 10^{-4} mol dm^{-3} in acetone). Solvents, references, temperature, and frequencies for ^{1}H and ^{31}P{^{1}H} NMR spectra were the same as those for **1a**. ^{1}H NMR: δ 3.23 (s, 3 H, $\mathrm{CH_3}$), 5.18 (d, 1 H, CH, $^4J_{\mathrm{HP}}$ = 1 Hz), 7.5 (m, 19 H, Ph), 8.1 ppm (m, 6 H, Ph). ^{31}P{^{1}H} NMR: δ 36.19 ppm (s with ^{195}Pt satellites, $^2J_{\mathrm{PtP}}$ = 112 Hz). ^{13}C{^{1}H} NMR: δ 50.24 (s, $\mathrm{CH_3}$), 104.83 (d, CH, $^3J_{\mathrm{PC}}$ = 10 Hz), 124.61 (d, $\mathrm{Ph_3P}$ ipso, $^1J_{\mathrm{PC}}$ = 101 Hz), 135.25 (d, $\mathrm{Ph_3P}$ ortho, $^2J_{\mathrm{PC}}$ = 10 Hz), 128.77 (d, $\mathrm{Ph_3P}$ meta, $^3J_{\mathrm{PC}}$ = 13 Hz), 133.38 (d, $\mathrm{Ph_3P}$ para, $^4J_{\mathrm{PC}}$ = 3 Hz), 166.51 (s, C=O), 165.81 (s, *C*NPh), 140.37 (d, *C*NPPh$_3$(=CHR)Ph, $^2J_{\mathrm{PC}}$ = 12 Hz), 110.44, 115.19 (*Ph*CN ipso and *Ph*C(=CHR)NPPh$_3$ ipso), 126.98, 128.04, 128.91, 130.29, 133.32, 134.01 ppm (*Ph*CN and *Ph*C(=CHR)NPPh$_3$ ortho, meta, and para). IR: $\nu_{\mathrm{C{=}O}}$ 1715, $\nu_{\mathrm{C{=}C}}$ 1580, $\nu_{\mathrm{P{=}N}}$ 1270, ν_{PtCl} 330 cm^{-1}.

Crystal Structure Determination. Crystals of **1a**·$^1/_2$Me$_2$CO, obtained by slow evaporation of an acetone solution of the reaction mixture (see above), are triclinic, space group $P\bar{1}$. A crystal of approximate dimensions 0.21 × 0.16 × 0.14 mm was mounted on a glass fiber and used for the analysis. Crystallographic data are listed in Table I. Diffraction data were collected with a Siemens AED-2 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). Cell parameters were determined from least-squares refinement of 60 centered reflections in the range $20 \leq 2\theta \leq 35°$. Reflections with 2θ in the range $3 \leq 2\theta \leq 45°$ ($+h,\pm k,\pm l$) were measured by using the $\omega/2\theta$ scan technique and corrected for Lorentz and polarization effects. A ψ-scan absorption correction was also applied.[12] Three standard reflections were monitorized every hour to check the stability of the crystal and the experimental conditions: no significant variation was observed. The structure was solved by Patterson and conventional Fourier techniques using the SHELX76 program[13] on a VAX 8300 computer. The non-hydrogen atoms were refined anisotropically, except for those of the disordered solvent. Hydrogen atoms were clearly found from difference Fourier maps and included in the last cycles of refinement, riding on their respective carbon atoms with a common thermal parameter. The refinement converged at R = 0.025, R_w = 0.026 (408 parameters refined) for 4137 observed reflections [$F \leq 4.0\sigma(F)$] of a total of 5004 reflections collected. The weighting scheme used was $w = 0.8939[\sigma^2(F) + 0.000376F^2]^{-1}$. Main bond distances and angles are given in Table II, and atomic positional parameters, in Table III. Tables of the full experimental details of the X-ray analysis, thermal parameters for the non-hydrogen atoms, final atomic coordinates for the hydrogens, complete bond distances and angles, torsion angles, least-squares planes, and observed and calculated structure factors are available as supplementary material.

---

(7) (a) Seidel, W. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 785. (b) Schmidbaur, H.; Wolfsberger, W. *Chem. Ber.* **1967**, *100*, 1000. (c) Kiji, J.; Matsumura, A.; Okazaki, S.; Haishi, T.; Furukawa, J. *J. Chem. Soc., Chem. Commun.* **1975**, 751. (d) Briggs, E. M.; Brown, G. W.; Jiricny, J. *J. Inorg. Nucl. Chem.* **1979**, *41*, 667. (e) Charalambous, J.; Kensett, M. J.; Jenkins, J. M. *J. Chem. Res. Synop.* **1982**, 306. (f) Fenske, D.; Böhm, E.; Dehnicke, K.; Strähle, J. *Z. Naturforsch.* **1988**, *43B*, 1. (g) Maurer, A.; Fenske, D.; Beck, J.; Hiller, W.; Strähle, J.; Böhm, E.; Dehnicke, K. *Z. Naturforsch.* **1988**, *43B*, 5. (h) Wamhoff, H.; Horlemann, N.; Nai-jue, Z.; Fang, G. *Chem.-Ztg.* **1986**, *110*, 315. (i) Dapporto, P.; Denti, G.; Dolcetti, G.; Guedini, M. *J. Chem. Soc., Dalton Trans.* **1983**, 779. (j) Miller, J. S.; Visscher, M. O.; Coulton, K. C. *Inorg. Chem.* **1974**, *13*, 1632. (k) Imhoff, P.; Elsevier, C. J.; Stam, C. H. *Inorg. Chim. Acta* **1990**, *175*, 209. (l) Katti, K. V.; Batchelor, R. J.; Einstein, F. W. B.; Cavell, R. G. *Inorg. Chem.* **1990**, *29*, 808. (m) Katti, K. V.; Cavell, R. G. *Organometallics* **1990**, *8*, 2147. (n) Fernández, M. J.; del Val, J. J.; Oro, L. A.; Palacios, F.; Barluenga, J. *Polyhedron* **1987**, *6*, 1999.

(8) Keim, W.; Behr, A.; Gruber, B.; Hoffmann, B.; Kobaldt, F. H.; Kürschner, U.; Limbäcker, B.; Sistig, F. P. *Organometallics* **1986**, *5*, 2356.

(9) Gololobov, Yu. G.; Zhmurova, I. N.; Kasukhin, L. F. *Tetrahedron* **1981**, *37*, 437.

(10) Ciganek, E. *J. Org. Chem.* **1970**, *35*, 3631.

(11) (a) Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907. (b) Kaska, W. C. *Coord. Chem. Rev.* **1983**, *48*, 1.

(12) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

(13) Sheldrick, G. M. SHELX76: A computer program for crystal structure determination. University of Cambridge, 1976.

Table III. Final Atomic Coordinates ($\times 10^4$) for the Non-Hydrogen Atoms of Complex **1a**[a]

atom	*x*	*y*	*z*
Pt	6700 (2)	14981 (2)	29862 (2)
Cl(1)	2602 (1)	2852 (1)	3898 (1)
Cl(2)	−1293 (1)	136 (1)	2096 (1)
P	−735 (1)	2976 (1)	1586 (1)
O(1)	−2708 (5)	3331 (4)	4570 (3)
O(2)	−3396 (4)	4362 (3)	3395 (3)
N(1)	−509 (4)	2520 (3)	2686 (3)
N(2)	1851 (5)	553 (3)	3213 (3)
C(1)	−1074 (5)	2840 (4)	3378 (4)
C(2)	−2013 (5)	3387 (4)	3129 (4)
C(3)	−2696 (5)	3667 (4)	3800 (4)
C(4)	−4116 (7)	4715 (5)	3983 (5)
C(5)	−4836 (7)	5452 (6)	3414 (6)
C(6)	2650 (6)	87 (4)	3369 (4)
C(7)	305 (6)	2530 (4)	994 (4)
C(8)	1696 (6)	3050 (5)	1295 (5)
C(9)	2484 (7)	2664 (7)	834 (6)
C(10)	1873 (9)	1811 (6)	89 (6)
C(11)	502 (8)	1312 (5)	−223 (5)
C(12)	−291 (7)	1651 (4)	249 (4)
C(13)	−2482 (5)	2503 (4)	652 (4)
C(14)	−2801 (6)	2743 (5)	−346 (4)
C(15)	−4129 (7)	2306 (6)	−1069 (5)
C(16)	−5109 (7)	1632 (6)	−812 (6)
C(17)	−4784 (6)	1382 (5)	161 (6)
C(18)	−3481 (6)	1805 (4)	903 (5)
C(19)	−156 (5)	4394 (4)	1812 (4)
C(20)	−716 (6)	5012 (4)	1104 (4)
C(21)	−199 (7)	6089 (5)	1297 (5)
C(22)	900 (7)	6556 (5)	2203 (5)
C(23)	1451 (6)	5952 (4)	2914 (5)
C(24)	924 (6)	4865 (4)	2727 (4)
C(25)	−461 (5)	2576 (4)	4435 (4)
C(26)	−672 (6)	1551 (4)	4646 (4)
C(27)	−45 (7)	1336 (5)	5629 (5)
C(28)	773 (7)	2155 (6)	6403 (5)
C(29)	1002 (7)	3174 (6)	6202 (5)
C(30)	377 (6)	3389 (4)	5226 (4)
C(31)	3705 (5)	−448 (4)	3574 (4)
C(32)	4788 (6)	−95 (5)	3226 (5)
C(33)	5847 (6)	−580 (6)	3461 (5)
C(34)	5814 (7)	−1393 (5)	4035 (5)
C(35)	4768 (7)	−1734 (5)	4374 (5)
C(36)	3698 (6)	−1270 (4)	4153 (4)
O(3)	−3767 (11)	4953 (8)	−654 (9)
C(37)	−4658 (11)	4784 (8)	−295 (9)
C(38)	−4319 (11)	4982 (8)	852 (9)
C(39)	−6179 (11)	4346 (8)	−964 (9)

[a] Atomic coordinates for the platinum atom are expressed $\times 10^5$. O(3), C(37), C(38), and C(39) belong to the disordered solvent, refined as a rigid model.

Results

$Ph_3P{=}CHCO_2Me$ is recovered unchanged when it is stirred for 64 h at room temperature in benzonitrile. If the mixture of both reagents is refluxed for 5 h, a red solution is obtained from which the ylide (48%) and a mixture also containing it along with other products can be separated. ^1H NMR and mass spectra of this mixture do not show the presence of the iminophosphorane $Ph_3P{=}NC(Ph){=}CHCO_2Et$. However, when equimolar amounts of *trans*-$[PtCl_2(NCPh)_2]$ and $Ph_3P{=}CHCO_2Et$ are reacted (acetone, room temperature, 14 h), a solution is obtained that, after removal of the solvent, gives a mixture containing 70% *trans*-$[PtCl_2\{E\text{-}N({=}PPh_3)C(Ph){=}CHCO_2Et\}(NCPh)]$ (**1a**). Two other unidentified compounds in 20 and 10% yields (by NMR spectroscopy) are also present in the reaction mixture. Complex **1a** can be separated from these byproducts owing to its lower solubility in acetone. Crystals of **1a**·$^1/_2Me_2CO$, suitable for an X-ray study, are obtained by slow evaporation of an acetone solution of the above mentioned mixture.

The reaction of *trans*-$[PtCl_2(NCPh)_2]$ with $Ph_3P{=}CHCO_2Me$ (acetone, 14 h, room temperature) gives *trans*-$[PtCl_2\{E\text{-}N({=}PPh_3)C(Ph){=}CHCO_2Me\}(NCPh)]$ (**1b**), which precipitates in 47% yield from the reaction mixture. From the mother liquor is obtained a mixture of **1b** and several unidentified species.

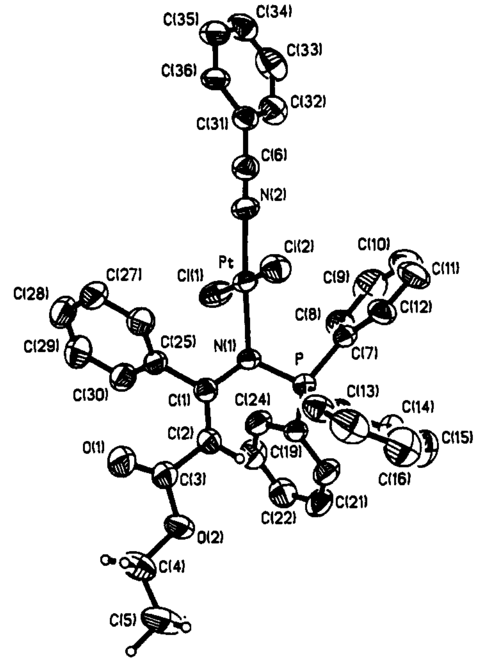
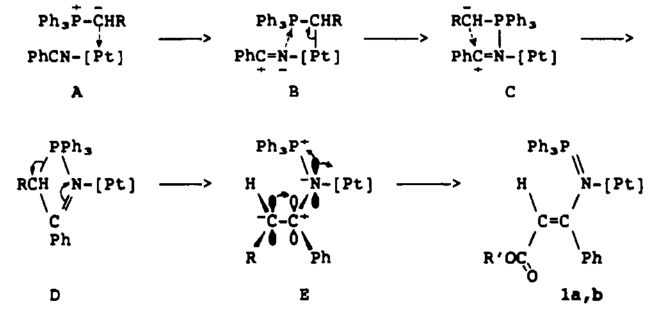


Figure 1. ORTEP drawing of **1a** showing the 50% probability ellipsoids. Hydrogens atoms are omitted for clarity.

Scheme I



[Pt] = $PtCl_2(NCPh)$; R = CO_2R', R'= Me, Et

Reactions between ylides and nitrile complexes have previously been reported to give substitution and orthometalation products,[14,15] but some results[14a] were later corrected.[14b] Our present results show that these reactions can be even more complex than previously assumed.

Iminophosphorane complexes are generally prepared by using the ligand although some Ni(II) complexes and an Ir(I) complex have been obtained by reacting nitroso complexes with PPh_3[7c] and by an intramolecular attack of a coordinated PPh_3 molecule on an imino nitrogen atom,[7i] respectively.

The crystal structure of **1a** (see Figure 1) shows a distorted square-planar coordination for the metal atom with the trans geometry of the starting platinum complex retained. The iminophosphorane ligand adopts an *E* configuration with respect to the C(1)–C(2) bond. Selected bond lengths and angles are listed in Table II.

---

(14) (a) Weleski, E. T., Jr.; Silver, J. L.; Jansson, M. D.; Burmeister, J. L. *J. Organomet. Chem.* **1975**, *102*, 365. (b) Illingsworth, M. L.; Teagle, J. A.; Burmeister, J. L.; Fultz, W. C.; Rheingold, A. L. *Organometallics* **1983**, *2*, 1364.

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

(16) Hewlins, J. E. M. *J. Chem. Soc. B* **1971**, 942. Butterfield, P. J.; Tebby, J. C.; King, T. J. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1237. Molina, P.; Arques, A.; Fresneda, P. M.; Vinader, M. V.; Foces-Foces, C.; Cano, F. H. *Chem. Ber.* **1989**, *122*, 307.

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

Discussion

Scheme I shows our proposal of the reaction pathway leading to complexes **1a,b**. We assume that the ylide first attacks the metal center, to give A, because it is the most electrophilic atom (see also below). A four-membered ring is formed after N→P bonding to give intermediate B. Then the carbon atom of PhCN is much more electrophilic than it is in free PhCN. Therefore, the C–C bond formation, to give C, could compensate the breaking of the Pt–C bond in B. The following steps are as postulated for the reaction between non-resonance-stabilized ylides and nitriles:[10] D → E → **1**.

The initial attack of the ylide could give, as we expected, a substitution product. In fact, we have found that when $[PtCl_2]$ in MeCN reacts with $Ph_3P{=}CHCO_2Me$ at refluxing temperature, the substitution product $[PtCl_2\{CH(PPh_3)CO_2Me\}_2]$ (8%)[18] and its decomposition product, the orthometalated complex $[\overline{Pt\{C_6H_4\{P(Ph_2}CHCO_2Me)_2\}\}(\mu\text{-}Cl)]_2$[14,18] (61%), are obtained. However, at room temperature, this reaction gives adducts similar to **1a,b**.[18]

In addition, when $[PdCl_2(NCPh)_2]$ reacts with $Ph_3P{=}CHCO_2Me$, the substitution product $[PdCl_2\{CH(PPh_3)CO_2Me\}_2]$ is obtained.[15] It is, therefore, reasonable to assume that the first adduct formed (see Scheme I) is a common intermediate in both types of reaction and that at room temperature the addition reaction is preferred to the substitution. It is probable that the latter occurs preferentially at higher temperatures because, under these conditions, the equilibrium is displaced to the formation of the orthometalation reaction product.[14,18] However, a direct attack of the ylide on the carbon atom of the nitrile followed by the formation of the four-membered ring $\overline{C\text{–}C\text{–}P\text{–}N}$ (see D in Scheme I) cannot be discounted.

Only a few of the reported iminophosphorane complexes have been structurally characterized by X-ray methods.[7g–l] The P–N bond distance observed in **1a**, 1.641 (4) Å, is longer than those reported for related free iminophosphoranes,[16] $Ph_3P{=}N(C_6H_4Br\text{-}4)$, $Ph_3P{=}N\{C{=}C(CN)C(CN)_2C(CN)_2C(CN)_2\}$, and $Ph_3P{=}N(R)$ (R being a substituted pyrazolate ring) with values of 1.567 (6), 1.615 (2), and 1.568 (4) Å, respectively. This lengthening of the P–N bond has also been observed[7g–i] in related Cu(I), Zn(II), and Ir(I) complexes containing an iminophosphorane as a terminal ligand (range 1.62–1.64 Å). However, shorter P–N bond distances have been observed in $[RhCl\{N({=}PPh_3)(C_6H_4Me\text{-}4)\}(COD)]$[7k] [1.608 (3) Å] and in $[PdCl_2(NH{=}PPh_2CH_2PPh_2)]$[7l] [1.599 (6) Å].

The P–N bond lengthening in complex **1a** cannot be due to a delocalization of electron density along the P–N(1)–C(1)–C(2)–C(3)–O(1) chain—which could be assumed on the basis of the reasonable planarity of these atoms (no atom deviates more than 0.099 (5) Å from the least-squares plane passing through them)—because C(1)–N(1), C(1)–C(2), C(2)–C(3), and C(3)–O(1) bond distances are as expected[17] for the bond order distribution shown in Scheme I. Probably, the electronic release from the N atom toward the metal upon coordination reduces the electron density available at nitrogen for the P–N double-bond formation.

Interestingly, the least-squares plane defined by atoms involved in the conjugated system P=N(1)—C(1)=C(2)—C(3)=O(1) is nearly perpendicular to the metal coordination plane (dihedral angle of 92.6 (1)°), bringing the C(7)–C(12) and C(25)–C(30) phenyl rings close to the ideal axial coordination sites of the metal (above and below the metal coordination plane) and allowing short intramolecular interatomic distances between the Pt atom and C(26) [3.152 (7) Å] or C(8) [3.495 (7) Å]. This could explain the fact that **1a** does not react with 2,2′-bipyridine (1:1 at room temperature).

The reaction between $[Ni(COD)_2]$ (COD = 1,5-cyclooctadiene), PPh_3, and $Ph_3P{=}NC(O)Ph$ has been reported to take place with migration of a phenyl group to give the oxidative addition reaction product $[\overline{Ni\{P(Ph)_2{=}NC(O}){Ph}\}Ph(PPh_3)]$.[8] An intermediate $[Ni\{N({=}PPh_3)C(O)Ph\}(PPh_3)(COD)]$ with a structure such as that of **1a** could, in our opinion, explain the migration of the phenyl group better than the assumed $[\overline{Ni\{PPh_3{=}NC(O})Ph\}(COD)]$ intermediate.

The *E* configuration adopted by the iminophosphorane ligand minimizes repulsions between PPh_3 and substitutents attached to C(2) (see Figure 1 and intermediate E of Scheme I).

Acknowledgment. We thank the Dirección General de Investigación Científica y Técnica (Spain) (Grant PB89-0430) for financial support; J.F.-B. and J.A.L. are grateful for a grant from the Ministerio de Educacion y Ciencia (Spain).

Supplementary Material Available: For $1a\cdot{}^1/_2Me_2CO$, tables of thermal parameters for non-hydrogen atoms (Table SI), hydrogen atomic coordinates (Table SII), full experimental details of the X-ray analysis (Table SIII), and complete bond distances and angles, torsion angles, and least-squares planes (19 pages); a listing of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

---

[18] Results to be published.