Inorg. Chem. **2000,** *39,* 2957−2960 **2957**

Reactivity of Pd(0) Complexes with the Phosphino Ylide $[Ph_2PCH_2PPh_2{=}C(H)C(O)Me]$. Molecular Structure of $[Pd(\mathit{P}Ph_2CHPPh_2\mathit{C}(H)C(O)Me)_2]$

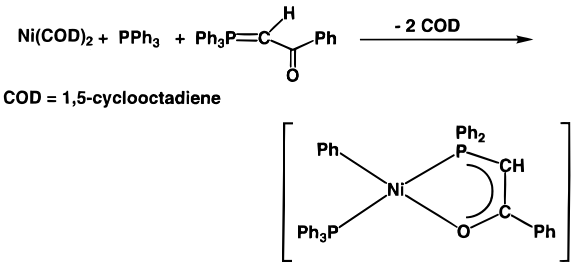
Larry R. Falvello, Susana Fernández, Rafael Navarro,* and Esteban P. Urriolabeitia

Departamento de Química Inorgánica, Instituto de Ciencia de
Materiales de Aragón, Universidad de Zaragoza, CSIC,
E-50009 Zaragoza, Spain

Received August 2, 1999

Introduction

The reactivity of zerovalent metal complexes toward phosphorus ylides has attracted the interest of chemists due to the versatility of its reaction pathways and the variety of the resulting products and their different applications.[1] One of the most impacting results was the discovery that Ni(0) complexes reacted with α-stabilized ylides $Ph_3P{=}C(H)COR$, yielding phosphino−enolato complexes of Ni(II) (see eq 1), which are very active catalysts for the linear oligomerization of ethylene.[2,3] This reaction proceeds through formal Ni insertion into one ylide P−C(Ph) bond, and this process has been studied from both the synthetic and catalytic points of view.[4−14] However, to the best of our knowledge, no reports have appeared concerning the reactivity of Pd(0) toward ylides, despite the catalytic importance of Pd complexes.[15,16] In this paper we report the reactivity of Pd(0) complexes toward α-keto-stabilized ylides such as $Ph_3P{=}C(H)COR$ (R = Me, Ph, OMe) and $PPh_2CH_2PPh_2{=}C(H)C(O)Me$. While Pd(0) complexes do not react with ylides such as $Ph_3P{=}C(H)COR$ to give identifiable products, the reaction with $PPh_2CH_2PPh_2{=}C(H)C(O)Me$ results in a Pd(II) complex containing the anion $[PPh_2CHPPh_2C(H)C(O)Me]^-$. The structure of $[Pd(\mathit{P}Ph_2CHPPh_2\mathit{C}(H)C(O)Me)_2]$ (**1**) is also reported.



(1)

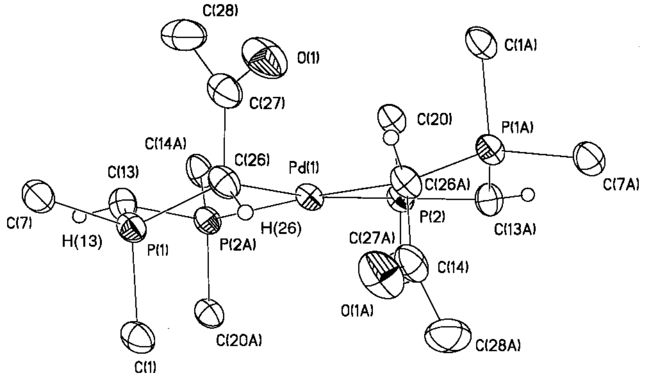


Figure 1. Thermal ellipsoid plot of $[Pd(\mathit{P}Ph_2CHPPh_2\mathit{C}(H)C(O)Me)_2]$ (**1**). H atoms and Ph groups have been omitted for clarity. Atoms are drawn at the 50% probability level.

Results and Discussion

When deep violet suspensions of $Pd_2(dba)_3{\cdot}CHCl_3$ (dba = *trans*,*trans*-dibenzylideneacetone) in CH_2Cl_2 or $CHCl_3$ were treated with different molar ratios of the ylides $Ph_3P{=}C(H)COR$ (1:4 or 1:8), very complex mixtures of unidentified products were obtained, which were not analyzed further. We then explored the reactivity of $PPh_2CH_2PPh_2{=}C(H)C(O)Me$ (dppm-Y_{Me}) toward $Pd_2(dba)_3{\cdot}CHCl_3$, aiming to obtain $[Pd^0(dppm\text{-}Y_{Me})_4]$ by analogy with the reaction with PPh_3, which affords $[Pd^0(PPh_3)_4]$. However, the reaction of $Pd_2(dba)_3{\cdot}CHCl_3$ with $PPh_2CH_2PPh_2{=}C(H)C(O)Me$ (1:8 molar ratio) in CH_2Cl_2 at room temperature gives, in minutes, an orange solution from which $[Pd^{II}(\mathit{P}Ph_2CHPPh_2\mathit{C}(H)C(O)Me)_2]$ (**1**) (see Scheme 1) is isolated (66% yield) after evaporation of the solvent and treatment of the residue with Et_2O. The analysis of the ethereal solution revealed the presence of dba and free dppm-Y_{Me}, together with a small quantity of the oxide $O{=}PPh_2CH_2PPh_2{=}C(H)C(O)Me$.[17] During the reaction, evolution of H_2 was detected by gas chromatography. In the same way, the treatment of $Pd(PPh_3)_4$ with the phosphino ylide (1:2 molar ratio) in CH_2Cl_2 gives **1** (67% yield). Crystals of **1** of adequate quality for X-ray measurements were obtained by vapor condensation of Et_2O into a saturated solution of **1** in CH_2Cl_2.

A drawing of complex **1** is shown in Figure 1, relevant crystallographic parameters are given in Table 1, and selected bond distances and angles are collected in Table 2. The Pd atom is located in a distorted square-planar environment, surrounded

---

(1) Johnson, A. W.; Kaska, W. C.; Starzewski, K. A. O.; Dixon, D. A. *Ylides and Imines of Phosphorus*; John Wiley & Sons: New York, 1993; Chapter 14 and references given therein.

(2) Keim, W.; Kowaldt, F. H.; Goddard, R.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 466.

(3) Starzewski, K. A. O.; Born, L. *Organometallics* **1992**, *11*, 2701 and references therein.

(4) Keim, W.; Behr, A.; Limbacker, B.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 503.

(5) Peukert, M.; Keim, W. *J. Mol. Catal.* **1984**, *22*, 289.

(6) Keim, W.; Appel, R.; Storeck, A.; Krüger, C.; Goddard, R. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 116.

(7) Fink, G.; Mohring, V. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1001.

(8) Starzewski, K. A. O.; Witte, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 599.

(9) Starzewski, K. A. O.; Witte, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 63.

(10) Behr, A.; Keim, W.; Thelen, G. *J. Organomet. Chem.* **1983**, *249*, C38.

(11) Klabunde, U.; Ittel, S. D. *J. Mol. Catal.* **1987**, *41*, 123.

(12) Klabunde, U.; Tulip, T. H.; Roe, D. C.; Ittel, S. D. *J. Organomet. Chem.* **1987**, *334*, 141.

(13) Starzewski, K. A. O.; Witte, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 839.

(14) Starzewski, K. A. O.; Bayer, G. M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 961.

(15) Heck, R. F. *Palladium Reagents in Organic Syntheses*; Academic Press: New York, 1985.

(16) Tsuji, J. *Palladium Reagents and Catalysts*, John Wiley & Sons: Chichester, England, 1995.

(17) This oxide was characterized by comparison of its spectral properties (MS, IR, and NMR) with those of $O{=}PPh_2CH_2PPh_2{=}C(H)C(O)OMe$: Gimeno, M. C.; Jones, P. G.; Laguna, A.; Villacampa, M. D. *J. Chem. Soc., Dalton Trans.* **1995**, 805.

10.1021/ic990923z CCC: $19.00

Scheme 1

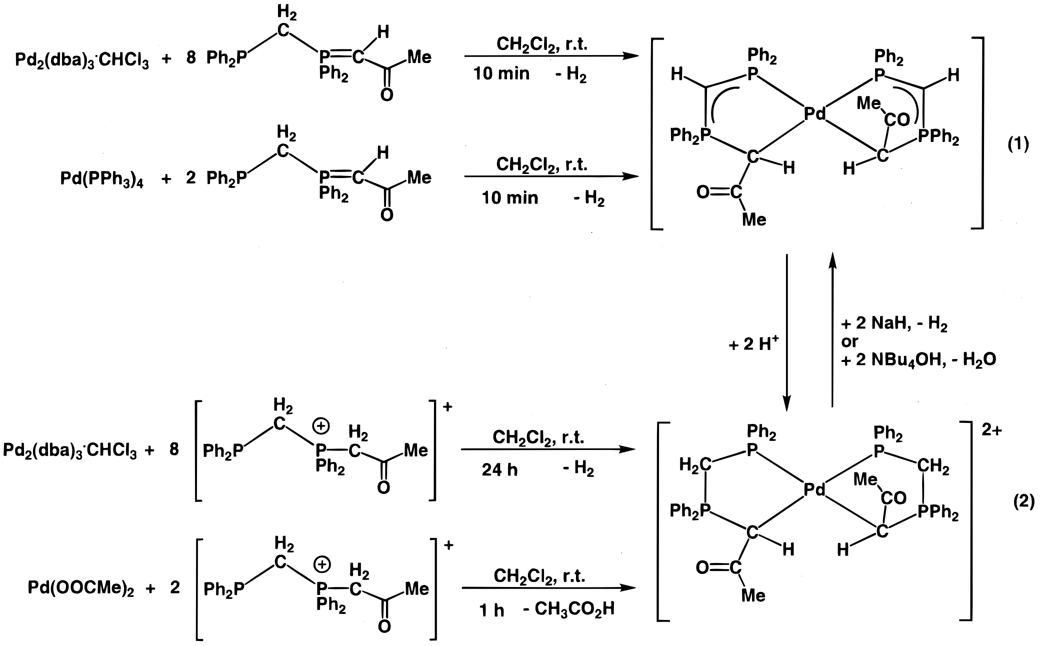


Table 1. Crystallographic Data for **1**

empirical formula	$C_{56}H_{50}O_2P_4Pd$	β (deg)	108.236(17)
fw	985.24	V (Å^3)	4669.0(13)
T (°C)	−50	Z	4
λ (Å)	0.710 73	ρ_{calcd} (g cm^{-3})	1.402
space group	$C2/c$ (no. 15)	μ (mm^{-1})	0.577
a (Å)	16.443(3)	final R indices[a] $[I > 2\sigma(I)]$	R1 = 0.0350, wR2 = 0.0840
b (Å)	17.7206(17)		
c (Å)	16.871(3)		

[a] $R1= \Sigma\,(|F_o| - |F_c|)/\Sigma\,|F_o|$. $wR2= [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

Pd1−C26	2.171(2)	Pd1−P2	2.3301(6)	P1−C13	1.699(3)
P1−C26	1.780(2)	P1−C7	1.812(2)	P1−C1	1.830(3)
P2−C13[a]	1.744(2)	P2−C14	1.821(3)	P2−C20	1.825(2)
C13−H13	0.91(3)	C26−C27	1.485(3)	C27−O1	1.225(3)
C28−C28	1.505(4)				

C26[a]−Pd1−C26	84.85(12)	C26−Pd1−P2	171.64(6)
C26[a]−Pd1−P2	88.45(6)	P2[a]−Pd1−P2	98.64(3)
C13−P1−C26	108.87(11)	C13−P1−C7	111.92(12)
C26−P1−C7	111.66(11)	C13−P1−C1	114.96(12)
C26−P1−C1	106.64(12)	C7−P1−C1	102.63(11)
C13[a]−P2−C14	105.58(12)	C13[a]−P2−C20	109.15(11)
C14−P2−C20	104.27(12)	C13[a]−P2−Pd1	106.81(8)
C14−P2−Pd1	120.60(8)	C20−P2−Pd1	110.02(8)
P1−C13−P2[a]	108.89(13)	P1−C13−H13	119.0(17)
P2[a]−C13−H13	119.1(17)	C27−C26−P1	118.08(18)
C27−C26−Pd1	104.43(14)	P1−C26−Pd1	108.02(11)
O1−C27−C26	120.3(3)	O1−C27−C28	118.2(2)
C26−C27−C28	121.5(2)		

[a] Symmetry transformations used to generate equivalent atoms: $-x + 1, y, -z + 3/2$.

by the P atoms of the PPh_2 units and the two ylidic C atoms. The ligand $[PPh_2CHPPh_2C(H)C(O)Me]^-$ acts as a P,C-chelate. The relative arrangement of the metallacycles is P-*trans*-to-C, and the two chiral ylidic C atoms in a given molecule show the same absolute configuration [*S* in Figure 1 for C26]. The axial disposition of the two C(O)Me groups on opposite sides of the molecular plane may result from minimization of intramolecular repulsions.

The Pd−C(ylide) bond distance [Pd1−C26 = 2.171(2) Å] is similar to that found in $[Pd\{(CH_2)_2S(O)Me\}\{PPh_2CH_2PPh_2C(H)COPh\}]I{\cdot}CH_2Cl_2{\cdot}H_2O$[18] [2.183(5) Å], while the Pd−P bond distance is slightly longer in **1** [Pd1−P2 = 2.3301(6) Å] than that in the aforementioned complex [2.301(1) Å].[18] The bond distance P1−C13 [1.699(3) Å] is quite short, and falls in the range of distances found for the **P**−**C** bond in free ylides: for instance, those found in $Ph_3\mathbf{P}{=}\mathbf{C}(H)COCH_2PPh_2$ (1.708(5) and 1.723(6) Å)[19] and that found in $[Pd(dmba)\{P(OMe)_3\}[NC{-}\mathbf{C}(H){=}\mathbf{P}Ph_3]]^+$ (1.710(4) Å).[20] The P2−C13 bond distance is 1.744(2) Å. These bond distances P1−C13 and P2−C13 clearly reflect the presence of additional charge density—and thus, some double bond character—which arises from the deprotonation of the methylene unit PCH_2P and its transformation into the methanide unit $[PC(H)P]^-$. These values also show the delocalization of the charge density through the system P2−C13−P1. After deprotonation, the methanide carbon C13 is rehybridized from sp^3 to sp^2, and this fact is clearly seen in the bond angles P1−C13−H13 [119.0(17)°] and P2−C13−H13 [119.1(17)°]. The P1−C26 bond distance [1.780(2) Å] is the same, within experimental error, as those found in related compounds. For instance, the **C**(ylide)−**P**Ph_3 bond distance in $[Pd(dmba)(py)\{\mathbf{C}(H)COOMe(\mathbf{P}Ph_3)]^+$ is 1.782(3) Å,[21] and that found in $[Pd(dmba)(OH_2)\{\mathbf{C}(H)CONMe_2(\mathbf{P}Ph_3)]^+$ is 1.788(7) Å.[22]

Complex **1** shows, in the IR spectrum, the ν(CO) absorption at 1623 cm^{-1}, in a region typical for the P,C-bonded phosphino ylides.[23] Moreover, the IR spectrum shows two bands of medium intensity at 874 and 825 cm^{-1}, which are indicative of the presence of the deprotonated unit P−C(H)−P.[24] The ^{1}H NMR

---

(18) Lin, I. J. B.; Shy, H. C.; Liu, C. W.; Liu, L.-K.; Yeh, S.-K. *J. Chem. Soc., Dalton Trans.* **1990**, 2509.

(19) Soulivong, D.; Wieser, C.; Marcellin, M.; Matt, D.; Harriman, A.; Toupet, L. *J. Chem. Soc., Dalton Trans.* **1997**, 2257.

(20) Falvello, L. R.; Fernández, S.; Navarro, R.; Urriolabeitia, E. P. *Inorg. Chem.* **1997**, *36*, 1136.

(21) Falvello, L. R.; Fernández, S.; Navarro, R.; Pascual, I.; Urriolabeitia, E. P. *J. Chem. Soc., Dalton Trans.* **1997**, 763.

(22) Barco, I. C.; Falvello, L. R.; Fernández, S.; Navarro, R.; Urriolabeitia, E. P. *J. Chem. Soc., Dalton Trans.* **1998**, 1699.

(23) Falvello, L. R.; Fernández, S.; Navarro, R.; Urriolabeitia, E. P. *New J. Chem.* **1997**, *21*, 909.

(24) Forniés, J.; Navarro, R.; Urriolabeitia, E. P. *J. Organomet. Chem.* **1990**, *390*, 257.

spectrum shows, in addition to the expected aromatic resonances, three broad peaks centered at 4.33 ppm, 1.95 and 1.83 ppm, with relative intensities 1:3:1, which are attributable to the ylidic C(Pd)*H* proton, the methyl group, and the methanide PC(*H*)P proton, respectively.[25] The $^{31}P\{^1H\}$ NMR spectrum of **1** shows a broad multiplet centered at 29.49 ppm, which resembles a poorly resolved AB spin system. The broad shape of the resonances could not be resolved by a change of solvent ($CDCl_3$, C_6D_6, or $(CD_3)_2CO$), nor by cooling the solutions.

Complex **1** can be protonated by addition of the stoichiometric amount of $HClO_4$. The reaction was performed at room temperature in CH_2Cl_2, and the resulting dicationic complex $[Pd(\mathit{P}Ph_2CH_2PPh_2\mathit{C}(H)C(O)Me)_2](ClO_4)_2$ (**2**) was obtained as a white solid. Complex **2** has been characterized on the basis of its analytical and spectroscopic data (see the Experimental Section). The ^1H NMR spectrum shows three complex multiplets attributed to the $PC\mathit{H_2}PC\mathit{H}$ protons, and the $^{31}P\{^1H\}$ NMR spectrum shows an AA′XX′ spin system with coupling constants typical for a cis arrangement of the coordinated P atoms. It is worth noting that **2** can also be obtained by reaction of $Pd_2(dba)_3{\cdot}CHCl_3$ with $[Ph_2PCH_2PPh_2CH_2C(O)Me]ClO_4$ (1:8 molar ratio), although this reaction is slower (24 h) than that described for **1** (10 min; see Scheme 1). Complex **2** can also be obtained in better yields by direct deprotonation of $[Ph_2PCH_2PPh_2CH_2C(O)Me]ClO_4$ by $Pd(OAc)_2$. In turn, complex **2** reacts with NaH (THF) or NBu_4OH (acetone), resulting in the deprotonation of the CH_2 group and formation of **1**. Nickel(II) complexes containing P,C-bonded nonstabilized methanides related to **1** have been reported,[26,27] and Ni(II) and Pt(II)[28] complexes with nonstabilized ylides related to **2** have also appeared in the literature.

The synthesis of **1** and **2** starting from a Pd(0) complex is rather unexpected, since it implies two C−H activations of two different types of C−H bonds. Moreover, one of the “activated” carbon atoms in **1** is not coordinated to the metal center in the final product. A number of questions rise now. For instance, at which stage of the reaction are the C−H activations promoted, at which stage of the reaction is the oxidation of Pd^0 to Pd^{II} produced, or which is the true “activator” of the C−H bonds, the metal center or other species? Although both C−H bonds are activated, why does the Pd atom bond only to the carbon adjacent to the acetyl group? Due to the intrinsic importance of the C−H activation processes promoted by palladium complexes, we are now focusing our efforts to answer all these questions and to elucidate the intimate mechanism of this type of reaction.

Experimental Section

Safety Note: Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared and they should be handled with great caution. See: *J. Chem. Educ.* **1973**, *50*, A335.

General Procedures. Solvents were dried and distilled by standard methods before use. Elemental analyses and IR, NMR, and mass spectra were obtained as described elsewhere.[20] The compounds $Pd_2(dba)_3{\cdot}CHCl_3$,[29] $[Pd(PPh_3)_4]$,[30] $[Pd(OAc)_2]$,[31] $[PPh_2CH_2PPh_2CH_2C(O)Me]ClO_4$,[23] and $PPh_2CH_2PPh_2{=}C(H)C(O)Me$[23] were obtained as previously reported.

$[Pd(\mathit{P}Ph_2CHPPh_2\mathit{C}HCOMe)_2]$ (1). (a) To a suspension of $Pd_2dba_3{\cdot}CHCl_3$ (0.085 g, 0.093 mmol) in 20 mL of CH_2Cl_2 was added the ylide $PPh_2CH_2PPh_2CHCOMe$ (0.328 g, 0.744 mmol), and the mixture was stirred at room temperature for 10 min. During this time a gradual change of color from deep violet to orange was observed. The resulting solution was evaporated to dryness. The orange residue was treated with Et_2O (30 mL) and filtered. The resulting deep yellow solid (**1**) was washed with Et_2O (3 × 10 mL) and air-dried. Yield: 0.120 g (66%). (b) To a yellow solution of $Pd(PPh_3)_4$ (0.133 g, 0.115 mmol) in 15 mL of CH_2Cl_2 was added the ylide $PPh_2CH_2PPh_2CHCOMe$ (0.101 g, 0.230 mmol), and the mixture was stirred at room temperature for 10 min. The resulting solution was evaporated to dryness. The orange residue was treated with Et_2O (30 mL), filtered, and air-dried. Yield: 0.076 g (67%). (c) To a suspension of **2** (0.196 g, 0.165 mmol) in THF (20 mL) was added NaH (0.097 g, 4.0 mmol). The resulting orange suspension was stirred for 2 h and then filtered, and the resulting solution was evaporated to dryness. The residue was treated with Et_2O (30 mL), giving **1** as a yellow solid which was filtered, washed with Et_2O (20 mL), and air-dried. (d) A 5 mm NMR tube was charged with **2** and suspended in 0.5 mL of acetone-*d*.[6] To this suspension, was added NBu_4OH (40 wt % H_2O solution) (1 drop). The white suspension evolved in a matter of seconds to give an orange solution, in which only resonances attributable to **1** were detected in the $^{31}P\{^1H\}$ NMR spectrum.

Anal. Calcd for $C_{56}H_{50}O_2P_4Pd$ (985.24 g/mol): C, 68.26; H, 5.11. Found: C, 67.70; H, 4.83. MS [*m/z*, %]: 985 [M^+, 55%]. IR (ν, cm^{-1}): 1623 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 7.78−6.66 (m, 20H, Ph), 4.33 (s, 1H, br, PC(*H*)Pd), 1.95 (s, br, 3H, CO*Me*), 1.83 (s, br, 1H, PC(*H*)P). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 29.49 (br m).

$[Pd(\mathit{P}Ph_2CH_2PPh_2\mathit{C}HCOMe)_2](ClO_4)_2$ (2). (a) To a solution of $Pd(OAc)_2$ (0.097 g, 0.43 mmol) in CH_2Cl_2 (20 mL) was added $[Ph_2PCH_2PPh_2CH_2COMe](ClO_4)$ (0.468 g, 0.865 mmol), and the resulting orange solution was stirred for 2 h at room temperature and then evaporated to dryness. Through addition of $CHCl_3$ (15 mL) to the oily residue and continuous stirring, **2** was obtained as a white solid. Yield: 0.374 g (73%). (b) To a suspension of $Pd_2dba_3{\cdot}CHCl_3$ (0.064 g, 0.07 mmol) in CH_2Cl_2 (20 mL) was added $[Ph_2PCH_2PPh_2CH_2COMe](ClO_4)$ (0.303 g, 0.560 mmol). The resulting yellow solution was stirred for 24 h and then evaporated to dryness. Through addition of $CHCl_3$ (15 mL) to the residue and continuous stirring, **2** was obtained as a white solid. Yield: 0.075 g (53% yield). (c) To a solution of (**1**) (0.084 g, 0.085 mmol) in CH_2Cl_2 (25 mL) was added $HClO_4$ (60 wt % in water) (18 μL, 0.17 mmol), and the resulting solution was stirred for 1 h at room temperature and then concentrated to a volume of 5 mL. The white solid (**2**) was filtered and washed with Et_2O (10 mL). Yield: 0.043 g (43%).

Anal. Calcd for $C_{56}H_{52}Cl_2O_{10}P_4Pd{\cdot}CH_2Cl_2$ (1271.122 g/mol): C, 53.85; H, 4.28. Found: C, 54.27; H, 4.01. MS [*m/z*, %]: 1087 [$(M\text{-}ClO_4)^+$, 6%]. IR (ν, cm^{-1}): 1637 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 7.84−7.11 (m, 20H, Ph), 5.75 (m, 1H, C(*H*)Pd), 4.66 (ddd, 1H, $PC\mathit{H_2}P$, $^2J_{H-H} = 15.6$ Hz, $^2J_{P-H} = 18$ Hz, $^2J_{P-H} = 11.1$ Hz), 4.32 (m, br, $PC\mathit{H_2}P$, 1H), 2.14 (d, 3H, −C(O)*Me*, $^4J_{P-H} = 0.9$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 41.17, 32.05 (AA′XX′ spin system, $^2J_{A-X} = 55$ Hz, $^3J_{A-X'} = -12$ Hz, $^2J_{A-A'} = 29.64$ Hz, $^4J_{X-X'} = 0$ Hz).

Crystal Structure Determination of 1. A yellow crystal of **1** was mounted at the end of a quartz fiber and covered with epoxy. Geometric and intensity data were measured using normal procedures on an automated Enraf Nonius CAD-4 four-circle diffractometer. After preliminary indexing and transformation of the cell to a conventional setting, axial photographs were taken of the *a*-, *b*- and *c*-axes to verify the Laue symmetry and cell dimensions. The scan parameters for intensity data collection were chosen on the basis of two-dimensional $\omega-\theta$ plots of 25 reflections. Three monitor reflections were measured after every 3 h of beam time, and the orientation of the crystal was checked after every 400 intensity measurements. Absorption correc-

---

[25] Usón, R.; Laguna, A.; Laguna, M.; Lázaro, I. *Organometallics* **1987**, *6*, 2326.

[26] Schmidbaur, H.; Deschler, U.; Milewski-Mahrla, B. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 586.

[27] Gong, J. K.; Peters, T. B.; Fanwick, P. E.; Kubiak, C. P. *Organometallics* **1992**, *11*, 1392.

[28] Alcock, N. W.; Pringle, P. G.; Bergamini, P.; Sostero, S.; Traverso, O. *J. Chem. Soc., Dalton Trans.* **1990**, 1553.

[29] Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organomet. Chem.* **1974**, *65*, 253.

[30] Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.

[31] Stephenson, T. A.; Morehouse, S. M.; Powell, A. R.; Heffer, J. P.; Wilkinson, G. *J. Chem. Soc.* **1965**, 3632.

tions[32] were based on azimuthal scans of 11 reflections which had Eulerian angle χ spread between 90° and 30° when in their bisecting positions. Accurate unit cell dimensions were determined from 25 centered reflections in the 2θ range $27.12 \leq 2\theta \leq 32.03°$, each centered at four distinct goniometer positions. The structure was solved and developed by Patterson and Fourier methods.[33] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms of the aromatic moieties were constrained to idealized geometries, except H13, which was located in a difference Fourier map and refined as an independent atom without constraints or restraints. The isotropic displacement parameter of each of these hydrogen atoms, except H13, was set to a value of 1.2 times the equivalent isotropic displacement parameter of its parent carbon atom. The structure was refined to F_o^2, and all reflections were used in the least-squares calculation.[34] Crystallographic calculations were done on a Local Area VAXCluster (VAX/VMS V5.5-2). Data reduction was done by the program XCAD4B.[35]

Acknowledgment. We thank the Dirección General de Investigación Científica y Técnica (Spain) for financial support (Projects PB95-0003-C02-1 and PB95-0792) and Prof. J. Forniés for invaluable logistical support.

Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of [Pd(*P*Ph$_2$CH-PPh$_2$*C*HCOMe)$_2$] (**1**). This material is available free of charge via the Internet at http://pubs.acs.org.

IC990923Z

---

(32) Absorption corrections and molecular graphics were done using the commercial package SHELXTL-PLUS, Release 4.21/V, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1990.

(33) Sheldrick, G. M. SHELXS-86. *Acta Crystallogr.* **1990**, *A46*, 467.

(34) Sheldrick, G. M. SHELXL-93: FORTRAN program for the refinement of crystal structures from diffraction data, University of Göttingen, Göttingen, Germany, 1993.

(35) Harms, K. Private communication, 1995.

Additions and Corrections

2000, Volume 39

Ulrich Bierbach, Michal Sabat, and Nicholas Farrell*: Inversion of the Cis Geometry Requirement for Cytotoxicity in Structurally Novel Platinum(II) Complexes Containing the Bidentate N,O-Donor Pyridin-2-yl-acetate.

Page 1887. There is an error in the caption of Figure 2. In the last two sentences, the terms “syn” and “anti” were inadvertently interchanged. Those sentences should read as follows.

Anti refers to a conformation with H8$_{\text{purine}}$ or H6$_{\text{pyrimidine}}$ situated above the sugar moiety ($\chi = 180 \pm 90°$). In the syn conformation, these protons point away from the sugar and produce a short H8/H1′ and H6/H1′ contact, respectively ($\chi = 0 \pm 90°$).

IC0004840

10.1021/ic0004840