

Cyclopalladated Complexes with Functionalized Diphosphines via Activation of Chelated 1,1-Bis(diphenylphosphino)ethene

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Summary: The reaction of **1** with 1,1-bis(diphenylphosphino)ethene (vdpp) gave the mononuclear cyclometalated compound **2**. The withdrawing effect of the cyclopalladated moiety suffices to polarize the C=CH₂ double bond to afford the addition products **3–8**, by treatment of complex **2** with primary aliphatic and aromatic amines. The molecular structures of **2**, **4**, and **8** have been determined by X-ray crystallography, showing that the C–C distance in **4** and **8** has the expected single-bond length upon addition.

Introduction

Tertiary mono- and polydentate phosphine ligands play an important role in coordination and in organometallic chemistry, owing to their ability to stabilize a great variety of metal complexes in different oxidation states as well as to their application in homogeneous catalysis.^{1,2}

The design and availability of new types of phosphines may be accomplished in the absence of a metal, and the new phosphine may then be integrated into the metal coordination sphere, but it may also be convenient to develop new ligands once the phosphine precursor has been coordinated to the metal center(s). Typical examples of the latter case are the C–H acidity of the CH₂ bridge in bis(diphenylphosphino)methane (dppm)^{3–5} or the activated C=C group of 1,1-bis(diphenylphosphino)ethene (vdpp).

It has been reported that, although the vinylidene double bond in uncoordinated vdpp is not susceptible to nucleophilic attack,⁶ complexation to different metal fragments, e.g. M(CO)₄ (M = Cr, Mo, W),^{7,8} MX₂ (M =

Pd, Pt; X = Me, AcO, Cl, I),^{9,10} and RuCl₂,¹¹ or even complexes with an A-frame structure,¹² activates the double bond toward conjugate or Michael addition, due to the additional polarizing effect of the metal center, of a variety of nucleophiles (amines, hydrazines, acetylides anions, among others). To the best of our knowledge, only one example of previous work on the attempted activation of vdpp bonded to a cyclopalladated moiety, in an 8-methylquinoline derivative, has been reported.¹³ In this paper we report that in complexes of the type [(C–M)Pd(vdpp-*P,P'*)]⁺X[–] nucleophilic addition to the vinylidene double bond was made possible, and the present work constitutes the synthesis and isolation of the first pure addition products of cyclometalated complexes with functionalized phosphines, which is difficult to achieve through other procedures.

Experimental Section

General Comments. Solvents were dried prior to use according to the standard methods.¹⁴ Ph₂PC(=CH₂)PPh₂ (vdpp) was prepared following to procedures described elsewhere.⁶ Chemicals were used as supplied from commercial sources. Elemental analyses were carried out by the Servicios Generales de la Universidad de A Coruña using a Carlo-Erba elemental analyzer (Model 1108). IR spectra were recorded as Nujol mulls or polythene disks on a Perkin-Elmer 1330 spectrophotometer. NMR spectra were obtained as CDCl₃ solutions and referenced to SiMe₄ (¹H) or 85% H₃PO₄ (³¹P{¹H}) and were recorded on a Bruker AC 20005 spectrometer (200 MHz for ¹H, 81 MHz for ³¹P{¹H}). Conductivity measurements were made on a CRISON GLP 32 conductivimeter using 10^{–3} mol dm^{–3} solutions in dry acetonitrile. The synthesis of [Pd{3,4-[O(CH₂)₂O]C₆H₂C(H)=N(C₆H₁₁)-C₆N}(μ-CH₃CO₂)₂}]₂ was reported in a recent paper from this laboratory.¹⁵

[Pd{3,4-[O(CH₂)₂O]C₆H₂C(H)=N(C₆H₁₁)-C₆N}(Ph₂P)₂-CHCH₂(4-MeNC₅H₉)-*P,P'*)](PF₆) (**3**). To a solution of **2** (100

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(1) Cotton, F. A.; Hong, B. *Prog. Inorg. Chem.* **1992**, 40, 179.

(2) Pignolet, L. H. *Homogeneous Catalysis with Metal Phosphine Complexes*; Plenum Press: New York, 1983.

(3) Al-Jibori, S.; Shaw, B. L. *Inorg. Chim. Acta* **1982**, 65, L123.

(4) Al-Jibori, S.; Hall, M.; Hutton, A. T.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1984**, 863.

(5) (a) Ruiz, J.; Riera, V.; Vivanco, M.; Lanfranchi, M.; Tiripicchio, A. *Organometallics* **1998**, 17, 3835. (b) Ruiz, J.; Riera, V.; Vivanco, M.; García-Granda, S.; Díaz, M. R. *Organometallics* **1998**, 17, 4562.

(6) Colquhoun, I. J.; McFarlane, W. J. *J. Chem. Soc., Dalton Trans.* **1982**, 1915.

(7) (a) Herring, A. M.; Koskimies, S. H.; Shaw, B. L. *J. Organomet. Chem.* **1988**, 338, 13. (b) Hassan, F. S. M.; Shaw, B. L.; Thornton-Pett, M. J. *J. Chem. Soc., Dalton Trans.* **1988**, 89.

(8) Bookham, J. L.; McFarlane, W.; Colquhoun, I. J. *J. Chem. Soc., Dalton Trans.* **1988**, 503.

(9) Higgins, S. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1989**, 1527 and references therein.

(10) (a) King, G.; Higgins, S. J.; Hopton, A. J. *J. Chem. Soc., Dalton Trans.* **1992**, 3403. (b) Keiter, R. L.; Benson, J. W.; Keiter, E. A.; Lin, W.; Jia, Z.; Olson, D. M.; Brandt, D. E.; Wheeler, J. L. *Organometallics* **1998**, 17, 4291.

(11) Barkley, J. V.; Higgins, S. J.; McCart, M. K.; Pounds, T. J. *Inorg. Chem.* **1997**, 36, 6188.

(12) Schmidbaur, H.; Herr, R.; Müller, G.; Riede, J. *Organometallics* **1985**, 4, 1208.

(13) Herring, A. M.; Higgins, S. J.; Jacobsen, G. B.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1986**, 882.

(14) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. L. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon: London, 1988.

(15) Tejjido, B.; Fernández, A.; López-Torres, M.; Castro-Juiz, S.; Ortigueira, J. M.; Vila, J. M.; Fernández, J. J. *J. Organomet. Chem.* **2000**, 598, 71.

mg, 0.112 mmol) in benzene (5 mL) was added 4-methylpiperidine (12 mg, 0.120 mmol). After the mixture was stirred for 2 h under argon, the solid formed was filtered off, washed with cold benzene, and dried in vacuo. The final product was isolated as pale yellow needles by recrystallization from dichloromethane/*n*-hexane (89.1%). Anal. Found: C, 57.0; H, 5.4; N, 2.8. Calcd for $C_{47}H_{53}O_2PdN_2P_3F_6$: C, 56.8; H, 5.6; N, 2.9. IR: $\nu(C=N)$ 1610 cm^{-1} . NMR: δ_H (CDCl_3) 8.06 (1H, d, $J(\text{PH}) = 7.8$ Hz, Hi), 6.94 (1H, d, $J(\text{PH}) = 3.9$ Hz, H2), 6.00 (1H, dd, $J(\text{PH}) = 9.8, 7.4$ Hz, H5), 4.95 (1H, m, PCHP), 4.11 (4H, br, $\text{OCH}_2\text{CH}_2\text{O}$), 0.80 (3H, d, $J(\text{HH}) = 6.4$ Hz, Me); δ_P (CDCl_3) 11.84 (1P, d, $J(\text{PP}) = 54.0$ Hz, $P_{\text{trans-N}}$), -9.16 (1P, d, $P_{\text{trans-C}}$), -146.9 (1P, h, $J(\text{PF}) = 713.0$ Hz, PF_6^-). Specific molar conductivity, Λ_m : $131.5 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$.

A similar method was used for the addition products **4–8**.

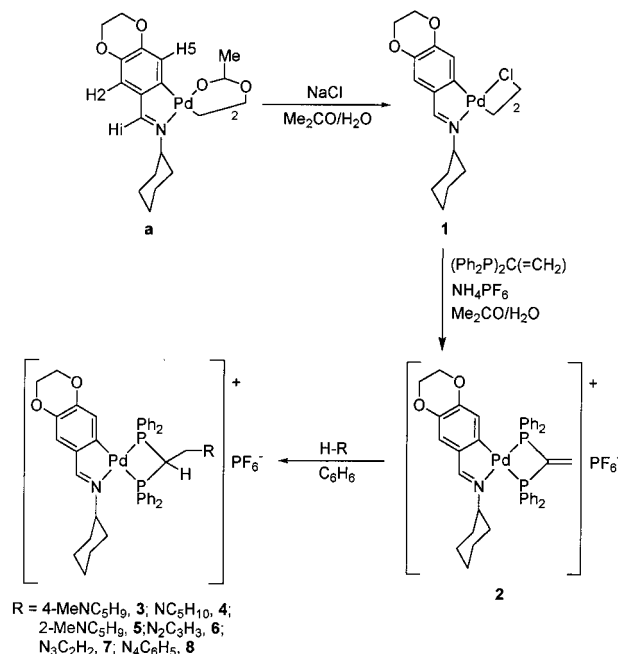
Crystal Structure Determination. For complexes **2**, **4**, and **8** three-dimensional X-ray data were collected on a Siemens Smart CCD diffractometer by the ω -scan method (at room temperature for **2** and **4** and at 173 K for **8**). All the reflections measured were corrected for Lorentz and polarization effects (and for absorption by semiempirical methods based on symmetry-equivalent and repeated reflections). The structures were solved by direct methods and refined by full-matrix least squares on F^2 with allowance for thermal anisotropy of all non-hydrogen atoms. Hydrogen atoms were included in calculated positions and refined in the riding mode. In complex **4** the PF_6^- ion was found to be disordered, occupying two positions with one of the components showing less than ideal geometry and large U_{ij} values. The occupancies of each component were approximately 50%. In complex **8** the disordered C(9), C(10), and C(11) atoms were refined by taking into account the minor components with approximately 65% and 35% occupancies. The largest residual peaks were adjacent to the palladium atoms, except for complex **4**, which showed a large peak ($1.571 \text{ e}/\text{\AA}^3$) in the vicinity of the disordered PF_6^- ion. The structure solution and refinement were carried out using the program package SHELX-97.¹⁶

Crystal Data and Details on Data Collection and Refinement. (a) **Compound 2:** $C_{41}H_{40}F_6NO_2P_3Pd$, fw = 892.05, monoclinic, $C2/c$, $a = 25.507(3) \text{ \AA}$, $b = 12.977(1) \text{ \AA}$, $c = 24.061(4) \text{ \AA}$, $\beta = 95.59(1)^\circ$, $V = 7926.4(17) \text{ \AA}^3$, $Z = 8$; 21 598 reflections measured; 9777 unique reflections ($R_{\text{int}} = 0.021$). The θ range was 1.60 – 28.30° with hkl indices -33 to $+33$, -17 to $+12$, and -32 to $+31$. An absorption correction was applied ($\mu = 0.654 \text{ mm}^{-1}$, 0.76 – 0.96 transmission). R values ($I > 2\sigma(I)$): $R_1 = 0.0388$, $wR_2 = 0.0997$. R values (all reflections): $R_1 = 0.0520$, $wR_2 = 0.1083$, $GOF = 1.039$. The residual electron density is between -0.607 and $1.018 \text{ e}/\text{\AA}^3$.

Compound 4: $C_{46}H_{51}F_6N_2O_2P_3Pd$, fw = 977.20, triclinic, $P\bar{1}$, $a = 11.239(1) \text{ \AA}$, $b = 14.599(1) \text{ \AA}$, $c = 17.885(1) \text{ \AA}$, $\alpha = 74.885(1)^\circ$, $\beta = 83.533(1)^\circ$, $\gamma = 82.472(1)^\circ$, $V = 2799.2(1) \text{ \AA}^3$, $Z = 2$, $\rho = 1.159 \text{ Mg/m}^3$; 16 333 reflections measured; 9702 unique reflections ($R_{\text{int}} = 0.034$). The θ range was 1.18 – 25.00° with hkl indices -13 to $+13$, -17 to $+17$, and -21 to $+15$. An absorption correction was applied ($\mu = 0.469 \text{ mm}^{-1}$, 0.77 – 0.82 transmission). R values ($I > 2\sigma(I)$): $R_1 = 0.0778$, $wR_2 = 0.2239$. R values (all reflections): $R_1 = 0.1059$, $wR_2 = 0.2508$, $GOF = 0.994$. The residual electron density is between -1.052 and $1.571 \text{ e}/\text{\AA}^3$.

Compound 8: $C_{48}H_{50}Cl_2F_6N_5O_3P_3Pd$, fw = 1129.14, monoclinic, $C2/c$, $a = 12.042(2) \text{ \AA}$, $b = 17.688(1) \text{ \AA}$, $c = 23.011(1) \text{ \AA}$, $\beta = 91.699(1)^\circ$, $V = 4898.9(1) \text{ \AA}^3$, $Z = 4$, $\rho = 1.531 \text{ Mg/m}^3$; 35 801 reflections measured; 12 110 unique reflections ($R_{\text{int}} = 0.049$). The θ range was 1.45 – 28.32° with hkl indices -15 to $+16$, -20 to $+23$, and -20 to $+30$. An absorption correction was applied ($\mu = 0.656 \text{ mm}^{-1}$, 0.73 – 0.88 transmission). R values ($I > 2\sigma(I)$): $R_1 = 0.0603$, $wR_2 = 0.1418$. R values (all

Scheme 1



reflections): $R_1 = 0.1037$, $wR_2 = 0.1659$, $GOF = 1.043$. The residual electron density is between -0.946 and $1.061 \text{ e}/\text{\AA}^3$.

Results and Discussion

For the convenience of the reader the compounds and reactions are shown in Scheme 1. We have reported the synthesis of the dinuclear acetate-bridged complex **a**,¹⁵ which when treated with an aqueous solution of sodium chloride gave the chloride-bridged complex **1**. Coordination of the metal to the imine nitrogen atom was evidenced by the shift of the $\nu(C=N)$ stretching vibration toward lower wavenumbers by ca. 30 cm^{-1} in the IR spectrum and by the upfield shift of the $HC=N$ proton signal in the ^1H NMR spectrum by ca. 0.4 ppm .^{17,18} The IR spectra showed two $\nu(\text{Pd}-\text{Cl})$ bands, consistent with an asymmetric Pd_2Cl_2 bridging unit.¹⁹

Reaction of **1** with vdpp in a 1:2 molar ratio and of ammonium hexafluorophosphate in acetone at room temperature gave the mononuclear cyclometalated palladium(II) complex **2**. The molecular structure of **2** is depicted in Figure 1, and selected bond lengths and angles are given in the figure caption.

Treatment of a benzene solution of **2** at room temperature under argon with ca. 1 mol equiv of 4-methylpiperidine for 2 h afforded in high yield ($>80\%$) the addition derivative **3**, as an air-stable solid (Scheme 1). The ^1H NMR spectrum showed the absence of the vinylidene proton resonance of **2** and a multiplet ca. 4.80 ppm assignable to the P_2CH proton. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed two doublets assigned to the two inequivalent phosphorus atoms with a coupling constant very different from that observed for the starting material. Surprisingly, the $^2J(\text{PP})$ value in **2** is smaller than in **3** (14.8 vs 54 Hz), despite the fact that the $\text{P}-\text{C}-\text{P}$ carbon atom in **2** shows sp^2 hybridization, as

(17) Onoue, H.; Moritani, I. *J. Organomet. Chem.* **1972**, *43*, 431.

(18) Ustynyuk, Y.; Chertov, V. A.; Barinov, J. V. *J. Organomet. Chem.* **1971**, *29*, C53.

(19) Pereira, M. T.; Vila, J. M.; Gayoso, E.; Gayoso, M.; Hiller, W.; Strähle, J. *J. Coord. Chem.* **1988**, *18*, 245.

(16) Sheldrick, G. M. SHELX-97: An Integrated System for Solving and Refining Crystal Structures from Diffraction Data; University of Gottingen, Gottingen, Germany, 1997.

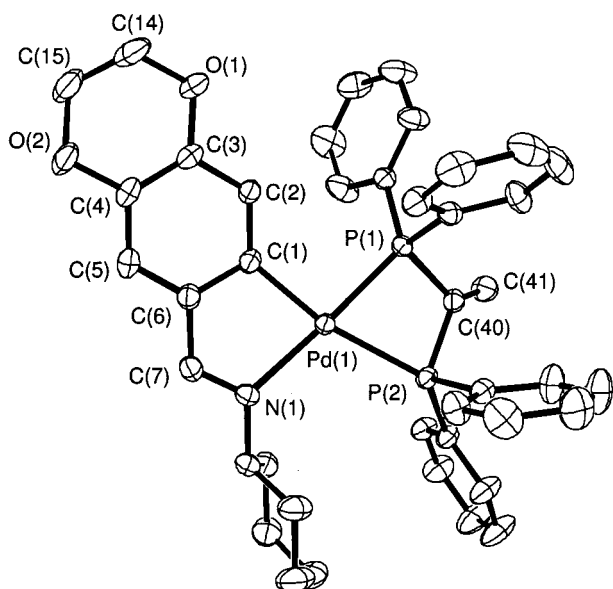


Figure 1. ORTEP view of the cation for complex **2** with thermal ellipsoids at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)–C(1), 2.035(3); Pd(1)–N(1), 2.121(2); C(7)–N(1), 1.280(4); Pd(1)–P(1), 2.2492(7); Pd(1)–P(2), 2.4182(7); C(40)–C(41), 1.315(4); C(1)–Pd(1)–N(1), 81.02(10); C(1)–Pd(1)–P(1), 96.56(8); N(1)–Pd(1)–P(2), 110.40(7); P(1)–Pd(1)–P(2), 72.25(3); P(1)–C(40)–P(2), 98.03(13).

opposed to the sp^3 hybridization of the same carbon in **3**. We believe this may be due to the greater contribution of $^2J(PP)$ across the metal center (normally of negative sign) in the addition products than in **2**, thus lowering the absolute value of the coupling constant; the reverse trend has been observed in complexes of the group 6 metals.^{20,21} Reaction of **2** with piperidine and 2-methylpiperidine gave the adducts **4** and **5**, respectively, as air-stable solids (Scheme 1). The conductivity data for complexes **2–5** ($125\text{--}150\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$ in $10^{-3}\text{ mol dm}^{-3}$ solutions in dry acetonitrile) show they are 1:1 electrolytes.²² In complexes **2–5**, the ^1H NMR spectra showed that the $\text{HC}=\text{N}$ resonance (doublet) was only coupled to the trans phosphorus nucleus ($^4J(\text{PHi}) = \text{ca. } 7.8\text{ Hz}$). The H5 resonance appeared as a doublet of doublets due to coupling to both phosphorus nuclei ($^4J(\text{P}_{\text{trans}}-\text{NH5}) = \text{ca. } 9.8\text{ Hz}$, $^4J(\text{P}_{\text{trans}}-\text{CH5}) = \text{ca. } 7.4\text{ Hz}$), while the signal assigned to the H2 nucleus appeared as a doublet ($^5J(\text{PH2}) = \text{ca. } 3.4\text{ Hz}$) by coupling to only the phosphorus atom trans to carbon. These data support the presence of the cyclometalated ring.²³ Of particular interest is the addition compound **5**, the 2-methylpiperidine derivative, in which the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed two pairs of doublets, suggesting the presence of isomers probably due to the presence of two chiral carbon atoms, the C_α atom with respect to both phosphorus atoms and the $C\text{--Me}$ atom of the piperidine ring. The molecular structure of **4** is depicted

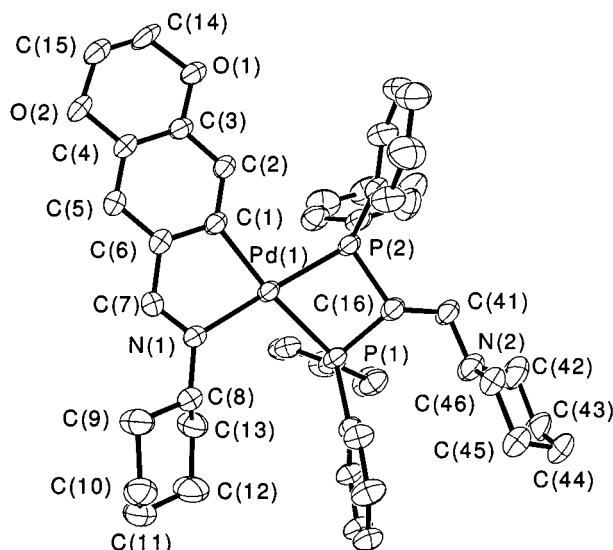


Figure 2. ORTEP view of the cation for complex **4** with thermal ellipsoids at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)–C(1), 2.052(6); Pd(1)–N(1), 2.112(5); C(7)–N(1), 1.259(9); Pd(1)–P(2), 2.2726(18); Pd(1)–P(1), 2.3622(16); C(16)–C(41), 1.509(9); C(1)–Pd(1)–N(1), 81.8(2); C(1)–Pd(1)–P(2), 99.4(2); N(1)–Pd(1)–P(1), 106.52(15); P(2)–Pd(1)–P(1), 72.93(6); P(1)–C(16)–P(2), 95.2(3).

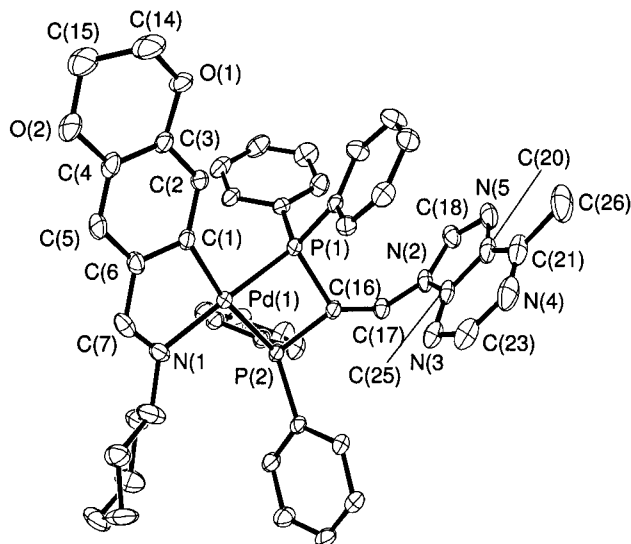


Figure 3. ORTEP view of the cation for complex **8** with thermal ellipsoids at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd(1)–C(1), 2.036(4); Pd(1)–N(1), 2.091(4); C(7)–N(1), 1.271(6); Pd(1)–P(1), 2.2432(11); Pd(1)–P(2), 2.3965(11); C(16)–C(17), 1.516(6); C(1)–Pd(1)–N(1), 81.38(16); C(1)–Pd(1)–P(1), 97.49(12); N(1)–Pd(1)–P(2), 108.95(12); P(1)–Pd(1)–P(2), 72.25(4); P(1)–C(16)–P(2), 95.08(19).

in Figure 2, and selected bond lengths and angles are given in the figure caption.

The addition products **6–8** could be obtained by stirring the reaction mixture in benzene for 6 h and conveniently isolated and characterized. The molecular structure of **8** is depicted in Figure 3, and selected bond lengths and angles are given in the figure caption. Thus, under the mild conditions used here the withdrawing effect of the cyclopalladated moiety suffices to polarize

(20) Vila, J. M.; Shaw, B. L. Unpublished results.

(21) Vila, J. M.; Gayoso, M.; Fernández, A.; Fernández, J. J.; Suárez, A. 29th International Conference on Coordination Chemistry: Lausanne, Switzerland, July 1992.

(22) Geary, W. J. *Coord. Chem. Rev.* **1971**, 7, 81.

(23) Vila, J. M.; Gayoso, M.; López-Torres, M.; Fernández, J. J.; Fernández, A.; Ortigueira, J. M.; Bailey, N. A.; Adams, H. *J. Organomet. Chem.* **1996**, 511, 129.

the C=CH₂ double bond and to afford the addition product.

Treatment of **2** with 2,2,6,6-tetramethylpiperidine did not give the addition product, and no change in the starting complex was observed, regardless of the reaction conditions used, even when a large excess of the amine was added. This suggests that the presence of the two methyl substituents in the α -position of the piperidine ring does not allow addition to the C=CH₂ double bond of the coordinated diphosphine, presumably due to steric hindrance by the phenyl rings of the diphosphine ligand, as opposed to less sterically demanding 2-methylpiperidine.

Molecular Structures of Complexes **2**, **4**, and **8**.

Suitable crystals were grown by slowly evaporating dichloromethane solutions of complexes **2**, **4**, and **8**. The labeling schemes for the complexes are shown in Figures 1–3. The crystals consist of discrete molecules, separated by normal van der Waals distances. Crystallographic data are given in the Experimental Section and the Supporting Information, and selected interatomic distances and angles are listed in the figure captions.

Each palladium atom is in a slightly distorted square-planar environment. The coordination sphere around each palladium atom consists of a nitrogen atom of the imine group, an ortho carbon of the phenyl ring, and two phosphorus atoms from a chelating diphosphine ligand (see Figures 1–3). The sums of angles about palladium are 360.23° (**2**), 360.25° (**4**), and 360.07° (**8**), with the more noticeable distortions in the somewhat reduced “bite” angles consequent upon chelation, which are C(1)–Pd(1)–N(1) = 81.02(10)° (**2**), 81.8(2)° (**4**), and 81.38(16)° (**8**) and P(1)–Pd(1)–P(2) = 72.25(3)° (**2**), 72.93(6)° (**4**), and 72.25(4)° (**8**), respectively. The requirements of the four-membered chelate rings force the bond angles P(1)–C(40)_{sp}²–P(2) to 98.03(13)° (**2**), P(1)–C(16)_{sp}³–P(2) to 95.2(3)° (**4**), and P(1)–C(16)_{sp}³–P(2) to 95.08(19)° (**8**), which are smaller than the value in free vdpp, 118.4°,²⁴ and rather low values for sp² and sp³ bond angles, although some four-membered chelate rings involving coordinated phosphines with a even smaller P–C–P angle have been reported.²⁵

(24) Schmidbaur, H.; Herr, R.; Riede, J. *Chem. Ber.* **1984**, *117*, 2372.

The palladium–nitrogen bond lengths, 2.121(2) Å (**2**), 2.112(5) Å (**4**), and 2.091(4) Å (**8**), are shorter than expected, reflecting the trans influence of the phosphorus atom.²³ In contrast with this, the palladium–carbon bond lengths, 2.035(3) Å (**2**), 2.052(6) Å (**4**), and 2.036(4) Å (**8**), are shorter than the theoretical value, in agreement with the proposed partial multiple-bond character of the Pd–C bond.^{26,27}

The differing trans influences of the phenyl carbon and imine nitrogen atoms is reflected in the palladium–phosphorus distance trans to carbon, relative to that trans to nitrogen. Thus, we have Pd(1)–P(1) = 2.2492(7) Å vs Pd(1)–P(2) = 2.4182(7) Å in complex **2**, Pd(1)–P(2) = 2.2726(18) Å vs Pd(1)–P(1) = 2.3622(16) Å in complex **4**, and Pd(1)–P(1) = 2.2432(11) Å vs Pd(1)–P(2) = 2.3965(11) Å in complex **8**.^{23,28}

The C(40)–C(41) bond length in complex **2**, 1.315(4) Å, is shorter than in compounds **4** and **8**, 1.509(9) and 1.516(6) Å, respectively, consequent upon addition. For complex **8** the purine moiety is essentially planar, and it is tilted with respect to the cyclometalated ring at ca. 108°, but the packing arrangement shows that it is parallel to a phenyl ring of the phosphorus atom trans to nitrogen (the angle between these planes is 9.3°, and the mean distance is 3.50 Å).

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Supporting Information Available: Experimental details for the synthesis and characterization of **1**, **2**, and **4–8** and tables giving atomic coordinates, displacement parameters, and bond distances and angles for **2**, **4**, and **8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(25) (a) Steffen, W. L.; Palenik, G. J. *Inorg. Chem.* **1976**, *15*, 2432. (b) Lee, C. L.; Yang, Y. P.; Rettig, S.; James, B. R.; Nelson, D. A.; Lilga, M. A. *Organometallics* **1986**, *5*, 2220.

(26) Suarez, A.; Vila, J. M.; Gayoso, E.; Gayoso, M.; Hiller, W.; Castiñeiras, A.; Strähle, J. Z. *Inorg. Allg. Chem.* **1986**, *535*, 213.

(27) Lousame, M.; Fernández, A.; López-Torres, M.; Vázquez-García, D.; Vila, J. M.; Suárez, A.; Ortigueira, J. M.; Fernández, J. J. *Eur. J. Inorg. Chem.* **2000**, 2055.

(28) Bosque, R.; López, C.; Solans, X.; Font-Bardiá, M. *Organometallics* **1999**, *18*, 1267.