Cyclometalated Complexes with Triphosphine Ligands: A Novel Route for Promoting Pentacoordination in Palladium(II)

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The palladium(II) compound [Pd{3,4-$(MeO)_2C_6H_2C(H){=}NCy$}{$(Ph_2PCH_2CH_2)_2PPh$-P,P,P}]-[PF_6] was synthesized and characterized by elemental analysis (C, H, N) and by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy in $CDCl_3$ and $^{31}P\{^1H\}$ solid-state NMR spectroscopy. The molecular structure was determined by X-ray crystallography, showing it to be the first pentacoordinated cyclometalated palladium(II) complex.

Introduction

The stereochemistry of divalent palladium is characterized by the square-planar arrangement in the majority of its coordination and organometallic compounds. Coordination number six has been reported for a few unusual complexes whose structures have been investigated, generally showing two weaker interactions on the metal atom.[1] Five-coordinate Pd(II) complexes have been more extensively investigated, probably due to the interest in clarifying the kinetic properties for substitution and exchange reactions for palladium complexes in solution and in biological systems.[2] When we reacted cyclometalated halide-bridged palladium(II) dimer complexes with tertiary mono- and diphosphines, we obtained only four-coordinate compounds with a square-planar environment for the palladium atom,[3] and as part of our studies on reactions of the mentioned halide-bridged complexes with phosphines we are currently interested in reactions with tri- and tetradentate phosphines, a strategy that we reasoned would modify the geometry and coordination number at the metal center. In addition, polyphosphine ligands offer a number of special characteristics, among which are the formation of stable complexes in many metals with different oxidation states and coordination numbers and the stereoselective occupation of centers of the cooordination polyhedron.[4] In the past few years, there has been a growing interest in the synthesis of transition metal complexes containing polydentate phosphine ligands, mainly due to their applications as homogeneous and heterogeneous catalysts.[5] Here, we wish to present the results of the reaction between bis(2-diphenylphosphinoethyl)phenylphosphine (triphos) and the cyclometalated palladium(II) dimer complex **1**.[6]

Reuslts and Discussion

The reaction of **1** with 2 equiv of $(Ph_2PCH_2CH_2)_2PPh$ and ammonium hexafluorophosphate in acetone at room temperature for 6 h afforded complex **2** (Figure 1) as a yellow solid in 91% yield.

The elemental analyses are consistent with the empirical formula $[C_{49}H_{53}NO_2P_3Pd][PF_6]$ (**2**), which indicates a mononuclear structure and suggests that the chlorine ligands are absent. This was confirmed by the IR spectrum, which revealed the absence of bands due to Pd−Cl bonds. The $^{31}P\{^1H\}$ spectrum shows a triplet ($\delta = 85.3$, 1P) and a doublet ($\delta = 42.6$, 2P). This suggests two mutually trans phosphorus atoms, with the third

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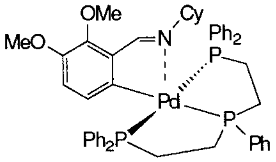

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Figure 1. $C_{49}H_{53}NO_2P_3Pd$ cation.

phosphorus nearly trans to the metalated carbon. The ^{31}P resonance of the central phosphorus nucleus appears at higher frequency due to the smaller trans influence of the carbon atom.[7] Interaction of the metal to the C=N nitrogen atom is shown by the shift of the ν(C=N) stretching vibration to lower wavenumbers[8] and by the upfield shift to the HC=N proton resonance in the ^1H NMR spectrum;[9] the spectroscopic evidence points to a square-pyramidal geometry in solution, with the nitrogen atom at the apical position; low-temperature NMR (213 K) did not show any significant changes. The proton in the ortho position to the Pd−C bond appears as a doublet by coupling to one ^{31}P atom. The value of the conductivity data (135 Ω^{-1} cm^2 mol^{-1} in dry acetonitrile) shows the compound to be a 1:1 electrolyte.[10] The ^{31}P solid-state NMR spectrum exhibits a different pattern with respect to the solution spectrum: a singlet (δ = 75.1, 1P) and a doublet of doublets (δ = 44.6, 2P) were observed. We thought this could be consistent with a trigonal-bipiramidal geometry for the palladium atom, with the resonances assigned to the phosphorus nucleus at the apical position, trans to the phenyl carbon atom, and to the other two phosphorus nuclei in the equatorial plane, respectively. The ^2J(PP) value in solution is 27 Hz, while in the solid state ^2J(P1P2) is 300 Hz. So, not only the appearance of the spectrum changes from a triplet and a doublet (in solution) to a singlet and a doublet of doublets (in the solid) but also the coupling constant undergoes a remarkably large variation. This we think is due to the structural changes mentioned above. We reasoned that if no changes took place, both spectra should be fairly alike, so we looked at the PF_6 signals (for which no changes are to be expected) and we observed that there are five lines in each spectrum (the two outermost lines are not observed) centered at −143 ppm in both spectra, and with the same J(PP) value in solution and in the solid, i.e., 710 Hz.

Table 1. Crystal Data and Structure Refinement for 2

identification code	hard12
empirical formula	$C_{50}H_{54}Cl_3F_6NO_2P_4Pd$
fw	1151.57
temperature	293(2) K
wavelength	0.71073 Å
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	a = 11.569(3) Å, α = 96.030(7)° b = 12.105(4) Å, β = 106.59(2)° c = 20.001(5) Å, γ = 92.44(4)°
volume	2661.8(13) Å^3
Z	2
density (calcd)	1.437 Mg/m^3
abs coeff	0.679 mm^{-1}
F(000)	1176
cryst size	0.7 × 0.4 × 0.25 mm
θ range for data collection	1.84−22.50°
index ranges	$-1 \le h \le 11$, $-12 \le k \le 12$, $-21 \le l \le 21$
no. of reflns collected	8324
no. of indep reflns	6829 (R_{int} = 0.0182)
abs corr	semiempirical
max. and min. transmn	0.678 and 0.457
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	6829/0/594
goodness-of-fit on F^2	1.050
final R indices [$I > 2\sigma(I)$]	R1 = 0.538, wR2 = 0.1471
R indices (all data)	R1 = 0.0637, wR2 = 0.1545
largest diff peak and hole	0.807 and −0.657 e Å^{-3}

Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound 2

	Bond Distances		
Pd(1)−C(6)	2.072(5)	Pd(1)−P(1)	2.293(2)
Pd(1)−P(3)	2.306(2)	Pd(1)−P(2)	2.321(2)
Pd(1)−N(1)	2.359(4)	N(1)−C(5)	1.269(7)
C(5)−C(11)	1.461(7)	C(6)−C(11)	1.407(7)
	Bond Angles		
C(6)−Pd(1)−P(1)	94.5(2)	C(6)−Pd(1)−P(3)	174.24(14)
P(1)−Pd(1)−P(3)	83.69(6)	C(6)−Pd(1)−P(2)	92.41(14)
P(1)−Pd(1)−P(2)	140.28(6)	P(3)−Pd(1)−P(2)	85.55(6)
C(6)−Pd(1)−N(1)	77.3(2)	P(1)−Pd(1)−N(1)	116.07(11)
P(3)−Pd(1)−N(1)	108.41(11)	P(2)−Pd(1)−N(1)	103.61(11)
C(5)−N(1)−Pd(1)	109.5(3)	C(6)−C(11)−C(5)	118.8(5)
N(1)−C(5)−C(11)	120.0(5)	C(11)−C(6)−Pd(1)	114.4(4)

The five-coordinate structural geometry of **2**, which crystallizes as yellow prisms from chloroform, has been definitively ascertained by an X-ray structure analysis (Experimental Details and Tables 1 and 2). A view of the molecular structure is shown in Figure 2. In the case of palladium(II) cyclometalated compounds the presence of five-coordinate species has been suggested assuming weak Pd···N interactions on the basis of Pd−N bond distances in the range 2.710(6)−2.805(5) Å;[11] a value of 2.576(4) Å has been recently given.[12] To the best of our knowledge, the Pd−N bond length reported here for **2**, 2.359(4) Å, is thus far the shortest distance known for these types of compounds and very close to the Pd−N bond length of 2.23(2) Å in an authentic trigonal-bipyramidal Pd(II) complex.[13] The molecular structure of **2** consists of discrete [Pd(C−N)(triphos)]$^+$ cations and PF_6^- anions. The palladium(II) atom is bonded to five atoms: three phosphorus atoms from a tridentate bis(2-diphenylphosphinoethyl)phenylphosphine, one nitrogen atom, and the adjacent ortho carbon of a N-(3,4-dimethoxybenzylidene)cyclohexylamine ligand in a distorted trigonal-bipyramidal coordination. The equatorial plane is formed by palladium, nitrogen, and the terminal phosphorus atoms of the phosphine ligand (maximum deviation from the Pd(1)−N(1)−P(1)−P(2) mean plane is 0.074 Å for P(1)). Carbon, C(6), and central phosphorus, P(3), complete the coordination sphere at the apical positions. The P(1)−Pd(1)−P(2)

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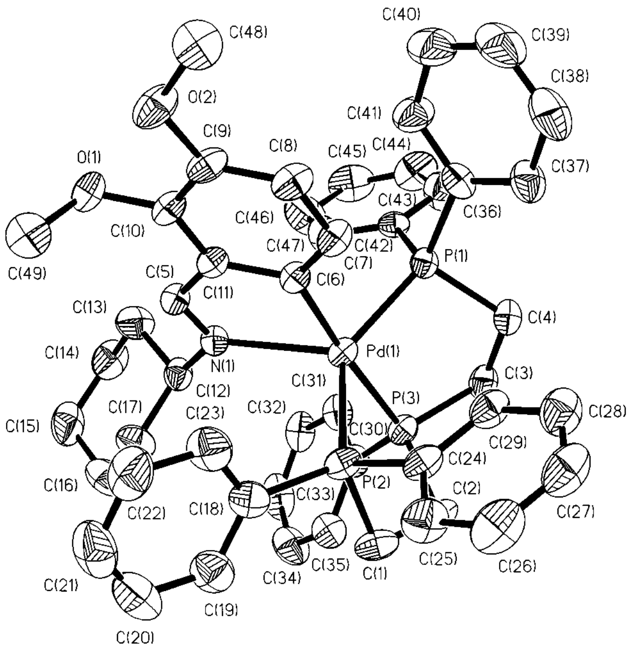

Figure 2. Structure of the cation for compound **2** showing the atom-numbering scheme. Hydrogen atoms were omitted for clarity.

angle between terminal phosphorus atoms is enlarged, 140°, so that the polyhedron may be viewed as distorted toward square-based pyramidal, although the P(3)−Pd(1)−C(6) angle remains at 174°. The cation has very approximate mirror symmetry through the unique phosphorus, the palladium, and the mean plane of the tridentate ligand. The donor atoms of the chelating Schiff base ligand occupy cis sites with a somewhat reduced bond angle (C(6)−Pd(1)−N(1) 77.3(2)°) consequent upon chelation. The sum of angles on palladium in the equatorial plane is 359.96°. The Pd(1)−C(6) bond length, 2.072(5) Å, is longer than those found in related complexes where partial multiple-bond character of the Pd−C bond was assumed,[14] supporting a phosphine ligand in the trans position. The Pd−P bond lengths [Pd(1)−P(1), 2.293(2) Å; Pd(1)−P(2), 2.321(2) Å; Pd(1)−P(3), 2.306(2) Å] suggest that a slightly partial double bond between the palladium and phosphorus atoms may exist.[15] The shortest Pd···F contact with the PF$_6$ counterion is 6.0237(0.0094) Å, and the shortest Pd···Cl contact with the solvent is 6.9895(0.0054) Å.[16]

Conclusions

We have shown that five-coordinate cyclometalated palladium(II) compounds may be synthesized with ligands such as tridentate phosphines that control the geometry and coordination number at the metal center. This is the first example of a “true” five-coordinate example of its kind, by formation of three five-membered rings at palladium: two comprising the triphos ligand and the palladacycle from the C,N-bonded organic ligand. This together with recent results obtained by us portrays a new and systematic route to produce five-coordinate cyclometalated palladium(II) complexes. Our efforts are now focused on the preparation of similar complexes with other polyphosphine ligands and metals.

Experimental Details

Solvents were purified by standard methods.[17] Chemicals were reagent grade. Palladium(II) acetate was purchased from Alfa Products. The phosphine bis(2-diphenylphosphinoethyl)-phenylphosphine (triphos) was purchased from Aldrich-Chemie. Microanalyses were carried out at the Servicio de Análisis Elemental at the University of Santiago using a Carlo Erba elemental analyzer, model 1108. NMR spectra were obtained as CDCl$_3$ or DMSO-d_6 solutions and referenced to SiMe$_4$ (^{1}H, ^{13}C) or 85% H$_3$PO$_4$ (^{31}P{^{1}H}) and were recorded on Bruker WM250 and AMX-300 spectrometers. All chemical shifts were reported downfield from standards. Coumpound [Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=NCy}(μ-Cl)]$_2$ (**1**) has been synthesized by us before.[6]

Synthesis of Compound 2. To a suspension of the chloro-bridged dimer complex [Pd{3,4-(MeO)$_2$C$_6$H$_2$C(H)=NCy}(μ-Cl)]$_2$ (**1**) (120.0 mg, 0.154 mmol) in acetone (10 cm^3) was added (Ph$_2$PCH$_2$CH$_2$)$_2$PPh (105.0 mg, 0.308 mmol). The mixture was stirred at room temperature for 1 h, then NH$_4$PF$_6$ (0.051 mg, 0.312 mmol) was added, and the resulting solid was filtered off and dried in vacuo. Recrystallization from dichloromethane/hexane gave the final compound as a pale yellow solid. Yield: 95%. Anal. (%) Found: C 57.08, H 5.21, N 1.42. Calcd for C$_{49}$H$_{53}$F$_6$NO$_2$P$_4$Pd: C 57.01, H 5.18, N 1.36. IR: ν(C=N) = 1603 cm^{-1}; Λ_M = 135 Ω^{-1} cm^2 mol^{-1}. ^{31}P NMR (CDCl$_3$): δ = 85.3 (t, 1P), δ = 42.6 (d, 2P). ^{31}P NMR (solid): δ = 75.1 (s, 1P), δ = 44.6 (dd, 2P). ^{1}H NMR (CDCl$_3$): δ = 8.45 (s, 1H, HC=N), δ = 6.17 (d, 1H, H4, ^3J(H4,H5) = 7.50 Hz), δ = 5.50 (t, 1H, H5 ^4J(P,H5) = 7.50 Hz).

Crystal data for 2: C$_{49}$H$_{53}$F$_6$NO$_2$P$_4$Pd·CHCl$_3$, yellow oblong crystals, M_r = 1151.57, crystal dimensions 0.7 × 0.4 × 0.25 mm^3, a = 11.569(3) Å, b = 12.105(4) Å, c = 20.001 (5) Å, α = 96.030(7)°, β = 106.59(2)°, γ = 92.44(4)°. V = 2661.8(13) Å^3, ρ_{calc} = 1.437 g/cm^3, μ = 0.679 mm^{-1}, Z = 2, triclinic, space group $P\bar{1}$ (no. 2). Crystal structure determination: Three-dimensional, room-temperature X-ray data were collected in the range 4°< 2θ < 45° on a Siemens P4 diffractometer by the omega scan method using graphite-monochromated Mo Kα radiation (λ = 0.7107 Å). Of the 8324 reflections measured, all of which were corrected for Lorentz and polarization effects, and for absorption by analysis of 10 psi scans (max./min. transmision 0.678, 0.457), 6829 independent reflections exceeded the significance level $|F|/\sigma(|F|) > 4.0$. The structure was solved by direct methods (SHELXS-86) and refined (SHELXS-

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[16] To ascertain that the 3-MeO group is not a steric trap that prevents the imine function from being anywhere else but in the proximity of the palladium atom, thus forcing the complex to be five-coordinate, we have synthesized a related complex with no substituents at the 3 or 5 positions, [Pd{4-(CHO)C$_6$H$_3$C(H)=NCy}{(Ph$_2$PCH$_2$CH$_2$)$_2$PPhP,P,P}][PF$_6$], and the results are similar to the ones reported here. Thus, the IR and ^{1}H NMR data show there is interaction of the palladium atom with the C=N nitrogen atom; in the ^{31}P{^{1}H} NMR spectrum in CDCl$_3$ a triplet and a doublet were observed, as for complex **2**. The molecular structure of this compound was determined by X-ray crystallography; the Pd−N distance of 2.438 Å is, with the exception of compound **2**, the shortest distance so far reported for these compounds (see text), pointing toward a close-to-pentacoordinated complex, as well.

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93) by full matrix blocked least squares on F^2 with allowance for the thermal anisotropy of all non-hydrogen atoms. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final $R = 0.0538$, $R_w = 0.1471$ (for 594 refined parameters). Max./min. residual electron density are 0.807/−0.657 e Å^{-3}. Crystallogrphic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 112251. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: (+44)1223−336−033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates, and isotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 112251.

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