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Mono- and Dinuclear Five-coordinate Cyclometalated Palladium(II) Compounds

**Margarita López-Torres,[†] Alberto Fernández,[†] Jesús J. Fernández,[†] Antonio Suárez,[†]
Mª Teresa Pereira,[‡] Juan M. Ortigueira,[‡] José M. Vila,*,[‡] and H. Adams[§]**

Departamento de Química Fundamental, Universidad de La Coruña, E−15071 La Coruña, Spain,
Departamento de Química Inorgánica, Universidad de Santiago de Compostela, E−15782 Santiago de
Compostela, Spain, and Department of Chemistry, The University, Sheffield S3 7HF, U.K.

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Reaction of cyclometalated halide-bridged Pd(II) complexes **1**−**4** with the tertiary triphosphine ligand $(Ph_2PCH_2CH_2)_2PPh$ (triphos) yielded complexes $[\{(Ph_2PCH_2CH_2)_2PPh\text{-}P,P,P\}Pd\{N(Cy){=}(H)C\}C_6H_2\{C(H){=}N(Cy)\}Pd\{(Ph_2PCH_2CH_2)_2PPh\text{-}P,P,P\}][ClO_4]_2$**5**, $[Pd\{C_6H_4\text{-}N{=}NC_6H_5\}\{(Ph_2PCH_2CH_2)_2PPh\text{-}P,P,P\}][ClO_4]$ **6**, and $[Pd\{R\text{-}C_6H_3C(H){=}NCy\}\{(Ph_2PCH_2CH_2)_2PPh\text{-}P,P,P\}][ClO_4]$ (**7**; R = 4-CHO, **8**; 3-CHO). Spectroscopic and analytic data suggest five-coordination on the palladium atom, which, for complexes **5**, **6**, and **7**, was confirmed by X-ray crystallography. The geometry around palladium may be view as a distorted trigonal bipyramid, with the palladium, nitrogen, and terminal phosphorus atoms in the equatorial plane. Compound **5** is the first doubly cyclometalated palladium(II) compound with two pentacoordinated metal centers. The structure of **6** comprises two discrete cations with slightly different geometries, showing the importance of crystal packing forces in order to determine the coordination arrangement.

Introduction

Palladium(II) coordination and organometallic compounds usually show square planar environments at the metal center; five- and six-coordinate species being less common.[1] In the past few years we have studied the reactivity of cyclometalated palladium(II) complexes with nucleophiles such as tertiary mono- and diphosphine ligands; the reactions invariably yielded square planar complexes.[2] We then became interested in tri- and tetradentate polyphosphine ligands which are known to promote the formation of stable complexes of transition metals with uncommon coordination numbers and geometries.[3] Consequently, we have reported the synthesis of the first pentacoordinated cyclometalated palladium(II) complex by reaction of a monodentate Schiff base cyclometalated derivative and the triphosphine bis(2-diphenylphosphinoethyl)phenylphosphine (triphos),[4] in which the coordination geometry of the palladium atom is a distorted trigonal pyramid with a Pd−N bond slightly longer than the value expected for a true Pd−N bond (2.359(4) versus 2.23(2) Å). To ascertain that polyphosphine ligands, and in particular triphos, are prone to induce a close to five-coordination environment in palladium(II) cyclometalated compounds, with very short Pd−N distances, we have extended our previous studies to ligands with different steric and electronic requirements, such as bidentate Schiff bases derived form terephthalaldehyde or isophthalaldehyde, and azobenzene. We are also aware of the importance of a systematic route to synthesize five-coordinate palladium(II) species, regardless of the specific characteristics of the ligands, in order to study the accessibility of the fifth position at the palladium center and to clarify the kinetic properties for substitution and exchange reactions in solution and in biological systems.[5] In addition, the synthesis of transition metal complexes with polydentate phosphine ligands is potentially interesting due to their applications in homogeneous and heterogeneous catalysis.[6]

In the present communication, we report the reaction of the cyclometalated complexes $[(Cl)PdN(Cy){=}C(H)C_6H_2C(H){=}N(Cy)Pd(Cl)]_n$ **1**, $[Pd\{C_6H_4N{=}NC_6H_5\}(\mu\text{-}Cl)]_2$ **2**, $[\{Pd[4\text{-}(CHO)\text{-}C_6H_3C(H){=}NCy](Cl)\}_2]$ **3**, and $[\{Pd[3\text{-}(CHO)C_6H_3C(H){=}NCy]\text{-}(Cl)\}_2]$ **4** with triphos to give the new pentacoordinated species **5**, **6**, **7**, and **8**, respectively, which have been fully characterized by elemental analysis (C, H, N), conductivity measurements, IR, ^1H, and $^{31}P-\{^1H\}$ NMR spectroscopy, and, in part (complexes **5**, **6,** and **7**), by X-ray crystallography.

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 handled with great caution.

Solvents were purified by standard methods.[7] Chemicals were reagent grade. The triphosphine $(Ph_2PCH_2CH_2)_2PPh$ (triphos) was purchased

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* To whom correspondence should be addressed. E-mail: qideport@usc.es.

[†] Departamento de Química Fundamental, Universidad de La Coruña.

[‡] Departamento de Química Inorgánica, Universidad de Santiago de Compostela.

[§] Department of Chemistry, The University.

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from Aldrich-Chemie. The synthesis of the cyclometalated complexes **1**,[8] **2**,[9] **3**,[10] and **4**[11] has been reported previously. Microanalyses were carried out using a Carlo-Erba Elemental Analyzer, Model 1108. IR spectra were recorded as Nujol mulls or KBr disks. NMR spectra were obtained as $CDCl_3$ solutions, referenced to $SiMe_4$ (^{1}H and ^{13}C) or 85% H_3PO_4 ($^{31}P-\{^{1}H\}$), and recorded on a Bruker AC-2005 spectrometer (200 MHz for ^{1}H, 81.0 MHz for ^{31}P). All chemical shifts are reported downfield from standards.

Syntheses. [{(Ph$_2$PCH$_2$CH$_2$)$_2$PPh-*P,P,P*}Pd{N(Cy)=(H)C}C$_6$H$_2$-{C(H)=N(Cy)}Pd{(Ph$_2$PCH$_2$CH$_2$)$_2$-PPh-*P,P,P*}][ClO$_4$]$_2$ 5. To a suspension of **1** (0.026 g, 0.045 mmol) in acetone (ca. 15 cm^3), $(Ph_2PCH_2CH_2)_2PPh$ (0.048 g, 0.090 mmol) was added. The resulting mixture was stirred at room temperature for 24 h, after which an excess of sodium perchlorate was added, and the mixture was stirred for a further 2 h. The complex was then precipitated out by addition of water, filtered off, dried in vacuo, and recrystallized from dichloromethane/*n*-hexane. (Yield: 0.07 g, 88%.) Anal. Calcd for $C_{88}H_{92}N_2O_8P_6Cl_2Pd_2$: C, 59.5; N, 1.6; H, 5.2%. Found: C, 59.0; N, 1.5; H, 5.3%. ; ν_{max}/cm^{-1} (C=N) 1621 m. δ_H 5.65 [d, 2H, J(PH) = 6.4 Hz, $H_{2,5}$]. δ_p 80.9 [t, 1P, J(PP) = 26.3 Hz], 41.9 [d, 2P]. Specific molar conductivity, Λ_m 310 ohm^{-1} cm^2 mol^{-1} (in dry acetonitrile).

Complexes **6**, **7**, and **8** were synthesized similarly.

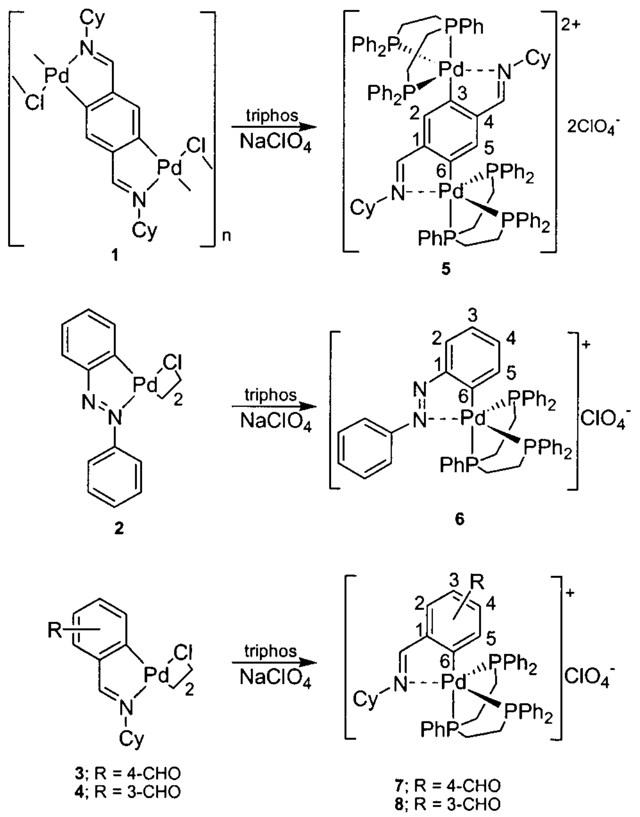
[Pd{C$_6$H$_4$N=NC$_6$H$_5$}{(Ph$_2$PCH$_2$CH$_2$)$_2$PPh-*P,P,P*}][ClO$_4$] 6: (Yield: 0.07 g, 82%.) Anal. Calcd for $C_{46}H_{42}N_2O_4P_3ClPd$: C, 59.9; N, 3.0; H, 4.6%. Found: C, 59.7; N; 3.1; H 4.5%. δ_H 8.04 [dd, 1H, J(HH) = 7.6 and 2.6 Hz, H_2], 6.47 [t, 1H, J(HH) = 7.3 Hz, H_4], 5.85 [t, 1H, J(PH) = 7.3 Hz, J(HH) = 7.3 Hz, H_5]. δ_p 84.2 [t, 1P, J(PP) = 25.0 Hz], 42.7 [d, 2P]. Specific molar conductivity, Λ_m 104 ohm^{-1} cm^2 mol^{-1} (in dry acetonitrile).

[Pd{4-(CHO)C$_6$H$_3$C(H)=NCy}{(Ph$_2$PCH$_2$CH$_2$)$_2$PPh-*P,P,P*}]-[ClO$_4$] 7: (Yield: 0.05 g, 80%.) Anal. Calcd for $C_{48}H_{49}NO_5P_3ClPd$: C, 60.4; N, 1.5; H, 5.2%. Found: C, 60.0; N; 1.7; H 4.9%. ν_{max}/cm^{-1} (C=N) 1609 m, (C=O) 1690 s. δ_H 8.89 [s, 1H, HC=O], 8.22 [s, 1H, HC=N], 6.02 [d, 1H, J(HP) 7.8 = Hz, H_5]. δ_p 83.5 [t, 2P, J(PP)= 25.4 Hz], 42.6 [d, 2P]. Specific molar conductivity, Λ_m 170 ohm^{-1} cm^2 mol^{-1} (in dry acetonitrile).

[Pd{3-(CHO)C$_6$H$_3$C(H)=NCy}{(Ph$_2$PCH$_2$CH$_2$)$_2$PPh-*P,P,P*}]-[ClO$_4$] 8: (Yield: 0.05 g, 80%.) Anal. Calcd for $C_{48}H_{49}NO_5P_3ClPd$: C, 60.4; N, 1.5; H, 5.2%. Found: C, 60.1; N; 1.5; H 4.9%. ν_{max}/cm^{-1} (C=N) 1615 m, (C=O) 1690 s. δ_H 9.78 [s, 1H, HC=O], 8.19 [s, 1H, HC=N], 6.84 [d, 1H, J(HH) = 7.8 Hz, H_4], 6.07 [t, 1H, J(PH) = 7.8 Hz, H_5]. δ_p 84.2 [t, 2P, J(PP) = 25.4 Hz], 42.4 [d, 1P]. Specific molar conductivity, Λ_m 165 ohm^{-1} cm^2 mol^{-1} (in dry acetonitrile).

Crystal Structure Determination. For complexes **5**, **6**, and **7**, three-dimensional, room-temperature X-ray data were collected (on a Siemens Smart CCD diffractometer for **5** and a Siemens P4 diffractometer for **6** and **7**) by the omega scan method. All the reflections measured were corrected for Lorentz and polarization effects. A semi-empirical absorption correction based on symmetry-equivalent and repeated reflections was performed for complex **5** only. 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 riding mode. For complex **5**, the perchlorate anion was found to be disordered, with the pairs Cl1/Cl1′ and O3/O3′ having 64/35% occupancies. The structure solution and refinement were carried out using the program package SHELX-97.[12]

Scheme 1



Results and Discussion

Reaction of the cyclometalated complexes **1**, **2**, **3**, and **4** with triphos followed by treatment with sodium perchlorate in a water/acetone mixture yielded the dinuclear and mononuclear cyclometalated complexes [{(Ph$_2$PCH$_2$CH$_2$)$_2$PPh-*P,P,P*}Pd-{N(Cy)=(H)-C}C$_6$H$_2${C(H)=N(Cy)}Pd{(Ph$_2$PCH$_2$CH$_2$)$_2$PPh-*P,P,P*}]-[ClO$_4$]$_2$(**5**), [Pd{C$_6$H$_4$N=NC$_6$H$_5$}{(Ph$_2$P-CH$_2$CH$_2$)$_2$PPh-*P,P,P*}]-[ClO$_4$] (**6**), [Pd{4-(CHO)C$_6$H$_3$C(H)=NCy}{(Ph$_2$PCH$_2$CH$_2$)$_2$-PPh-*P,P,P*}][ClO$_4$] (**7**), and [Pd{3-(CHO)C$_6$H$_3$C(H)=NCy}{(Ph$_2$-PCH$_2$CH$_2$)$_2$PPh-*P,P,P*}][ClO$_4$] (**8**), respectively, as pure and air-stable solids (see Scheme 1) which were fully characterized (see Experimental section).

The phosphorus resonances in the $^{31}P-\{^{1}H\}$ NMR spectra of the complexes were downfield shifted from their values in the free phosphine, suggesting coordination of all the phosphorus atoms to the metal center. A triplet resonance at ca. δ 82 was assigned to the central ^{31}P nucleus, which was trans to the phenyl carbon atom, and a doublet signal at ca. δ 42 was assigned to the two equivalent, mutually trans phosphorus nuclei. The latter signal appeared at lower frequency in accordance with the high trans influence of the phosphine ligand.[13] The resonance of the protons in the ortho position to the metalated carbon appeared as a doublet (for complexes **5** and **7**) or a triplet (for complexes **6** and **8**), showing coupling to the central ^{31}P atom [J(PH) = 6.4, 7.3, 7.8, and 7.8 Hz for **5**, **6**, **7**, and **8**, respectively]; no coupling was observed to the terminal phosphorus nuclei. These data are in accordance with a disposition in which the metalated ring is nearly perpendicular to the plane defined by the three phosphorus atoms; these observations were confirmed by selective decoupling experiments. The absence of the ν(Pd−

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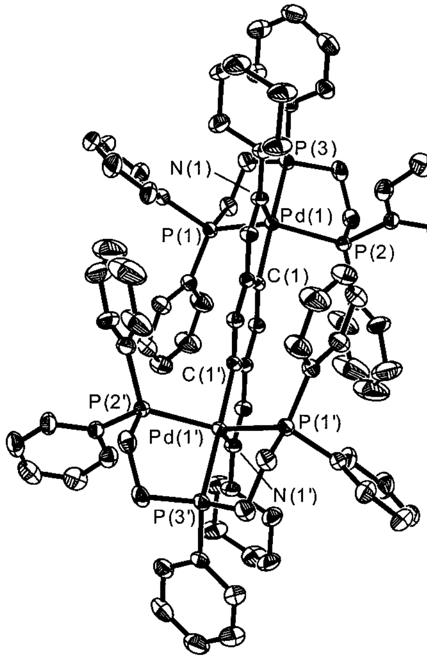

Figure 1. Perspective view (ORTEP) of the cation of complex **5**.

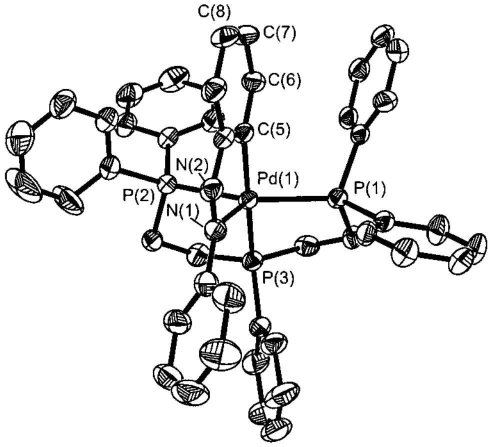

Figure 2. Perspective view (ORTEP) of the cation of complex **6**.

Cl) band in the IR spectrum confirms Pd−Cl bond cleavage upon coordination of the palladium atom to the three phosphorus atoms. For complexes **5**, **7**, and **8,** the shift of the ν(C=N) stretching vibration to lower wavenumbers[14] and the upfield shift of the HC=N proton resonance in the ^{1}H NMR spectra[15] indicate the existence of a palladium−nitrogen interaction in solution. Conductivity measurements show the expected values for 1:2 (**5**) and 1:1 electrolytes (**6**−**8**).

Crystal Structures of Complexes 5, 6, and 7. Complexes **5**, **6**, and **7** have been characterized crystallographically. A view of the molecular structures is shown in Figures 1 , 2, and 3. Crystal data are given in the Table 1 , and selected bond distances and angles with estimated standard deviations are shown in Tables 2 , 3, and 4. Selected geometric parameters are summarized in Table 5.

The molecular structure of **5** contains a discrete centosymmetric dinuclear cation of $[\{(Ph_2PCH_2CH_2)_2PPh\text{-}P,P,P\}Pd\{N(Cy){=}(H)C\}C_6H_2\{C(H){=}N(Cy)\}Pd\{(Ph_2PCH_2CH_2)_2PPh\text{-}P,P,P\}]^{2+}$ (half of the cation per asymmetric unit) and two perchlorate anions. The structure of **6** comprises two discrete $[Pd\{C_6H_4N{=}NC_6H_5\}\{(Ph_2PCH_2CH_2)_2PPh\text{-}P,P,P\}]^+$ cations (which are slightly different and will be labeled as **6a** and **6b**), two perchlorate anions, and a chloroform and a methanol solvent molecule per asymmetric unit. The asymmetric unit of **7** contains a $[Pd\{4\text{-}(CHO)C_6H_3C(H){=}NCy\}\{(Ph_2PCH_2CH_2)_2PPh\text{-}P,P,P\}]^+$ cation and a perchlorate counterion.

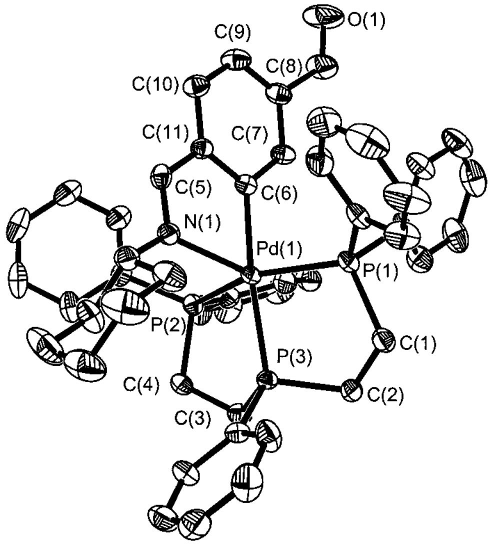

Figure 3. Perspective view (ORTEP) of the cation of complex **7**.

In each structure, the palladium atom is bonded to the adjacent ortho carbon of the phenyl ring, to one nitrogen atom, and to the three phosphorus atoms of the tridentate phosphine ligand.

Coordination around the palladium atom may be view as a distorted trigonal bipyramid, with the palladium, nitrogen, and terminal phosphorus atoms in the equatorial plane (rms for the mean planes; 0.0282, 0.0189, 0.0169, and 0.0138 Å for **5**, **6a**, **6b**, and **7**, respectively); the maximum deviation of palladium from this plane is −0.056, **5**, 0.0339, **6a**, 0.0378, **6b**, and −0.0276 Å, **7**. The metalated carbon atom and the central phosphorus atom are at the apical positions.

Pd(II) five-coordinate complexes, with trimethyl-, triethyl-, and triphenylphosphine, as well as with bis(diphenylphosphino)-methane (dppm), have been reported showing Pd···N weak interactions in the range 2.576(4)−2.805(5).[16] D. Weaver was the first to report the crystal structure of a palladated azobenzene compound with two triethylphosphine ligands where the closest Pd−N distance was 3.12 Å, therefore, the nitrogen atoms were not bonded to the palladium atom.[17] More recently, in a related structure by J. Dehand, the Pd−N distance was reported to be greater, 4 Å.[18] The present results show that the triphosphine ligand used here has an altogether different effect on the coordination of the metal atom in all cases, regardless of the metalated organic moiety. We have recently reported an even shorter distance of 2.359(4) Å.[4] However, in the case of complex

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Table 1. Crystallographic Data for Complexes **5**, **6**, and **7**

	5	**6**	**7**
chemical formula	$C_{88}H_{92}N_2Cl_2O_8P_6Pd_2$	$C_{47}H_{44.5}N_2O_{4.5}Cl_{2.5}P_3Pd$	$C_{49}H_{50}NO_5Cl_4P_3Pd$
fw	1775.16	997.28	1074.01
T	293(2) °C	293(2) °C	293(2) °C
λ	0.71073 Å	0.71073 Å	0.71073 Å
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	P1-bar	$P2_1/c$
a	11.529(1) Å	13.527(6) Å	18.058(6) Å
b	22.359(1) Å	17.542(5) Å	12.896(6) Å
c	16.071(1) Å	20.100(6) Å	21.464(5) Å
α		98.71(1)°	
β	97.996(1)°	97.73(3)°	98.47(2)°
γ		100.22(2)°	
V	4102.5(1) Å^3	4575(3) Å^3	4944(3) Å^3
Z	2	4	4
μ	6.78 cm^{-1}	7.03 cm^{-1}	7.35 cm^{-1}
$\rho_{calc.}$	1.473 g cm^{-3}	1.448 g cm^{-3}	1.443 g cm^{-3}
R_1[a]	0.0473	0.0677	0.0576
wR_2[b]	0.1173	0.1987	0.1443

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $[F > 4\sigma(F)]$. [b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, all data.

Table 2. Selected Bond Distances (Å) and Angles (Deg) for Complex **5**

Pd(1)−C(1)	2.049(3)	N(1)−C(4)	1.281(4)
Pd(1)−N(1)	2.338(3)	N(1)−C(5)	1.480(4)
Pd(1)−P(1)	2.318(1)	C(1)−C(3)	1.411(4)
Pd(1)−P(2)	2.312(1)	C(3)−C(4)	1.447(4)
Pd(1)−P(3)	2.338(3)		
P(2)−Pd(1)−P(1)	128.35(3)	P(2)−Pd(1)−P(3)	84.75(3)
C(1)−Pd(1)−N(1)	78.3(1)	P(1)−Pd(1)−P(3)	84.63(3)
P(2)−Pd(1)−N(1)	115.12(7)	N(1)−Pd(1)−P(3)	108.40(7)
C(1)−Pd(1)−P(3)	173.26(9)	P(1)−Pd(1)−N(1)	116.21(7)
C(1)−Pd(1)−P(2)	93.20(9)	C(1)−Pd(1)−P(1)	91.66(9)

Table 3. Selected Bond Distances (Å) and Angles (Deg) for Complex **6**

6a		**6b**	
Pd(1a)−C(5a)	2.052(6)	Pd(1b)−C(5b)	2.062(7)
Pd(1a)−P(2a)	2.341(2)	Pd(1b)−P(2b)	2.324(2)
Pd(1a)−P(3a)	2.312(2)	Pd(1b)−P(1b)	2.305(2)
Pd(1a)−P(1a)	2.303(2)	Pd(1b)−P(3b)	2.285(6)
Pd(1a)−N(1a)	2.366(5)	Pd(1b)−N(1b)	2.560(6)
N(1a)−C(11a)	1.437(8)	N(1b)−C(11b)	1.433(9)
N(1a)−N(2a)	1.261(7)	N(1b)−N(2b)	1.251(8)
C(5a)−C(10a)	1.39(1)	C(5a)−C(10a)	1.40(1)
C(10a)−N(2a)	1.412(9)	C(10a)−N(2a)	1.410(9)
P(2a)−Pd(1a)−P(1a)	139.02(7)	P(2b)−Pd(1b)−P(1b)	151.06(7)
C(5a)−Pd(1a)−N(1a)	74.4(2)	C(5b)−Pd(1b)−N(1b)	71.7(2)
P(2a)−Pd(1a)−N(1a)	103.6(2)	P(2b)−Pd(1b)−N(1b)	95.5(1)
P(1a)−Pd(1a)−N(1a)	117.3(2)	P(1b)−Pd(1b)−N(1b)	113.2(1)
C(5a)−Pd(1a)−P(3a)	176.1(2)	C(5b)−Pd(1b)−P(3b)	171.3(2)
P(2a)−Pd(1a)−P(3a)	85.70(7)	P(2b)−Pd(1b)−P(3b)	85.30(7)
P(1a)−Pd(1a)−P(3a)	84.10(7)	P(1b)−Pd(1b)−P(3b)	84.43(8)
N(1a)−Pd(1a)−P(3a)	109.5(1)	N(1b)−Pd(1b)−P(3b)	116.4(2)
C(5a)−Pd(1a)−P(2a)	93.4(2)	C(5b)−Pd(1b)−P(2b)	91.0(2)
C(5a)−Pd(1a)−P(1)	94.2(2)	C(5b)−Pd(1b)−P(1b)	95.2(2)

Table 4. Selected Bond Distances (Å) and Angles (Deg) for Complex **7**

Pd(1)−C(5)	2.075(6)	N(1)−C(11)	1.263(7)
Pd(1)−N(1)	2.437(5)	N(1)−C(12)	1.479(7)
Pd(1)−P(1)	2.304(1)	C(5)−C(10)	1.410(8)
Pd(1)−P(2)	2.331(1)	C(3)−C(4)	1.483(8)
Pd(1)−P(3)	2.348(1)		
P(2)−Pd(1)−P(1)	149.51(6)	P(2)−Pd(1)−P(3)	85.49(6)
C(5)−Pd(1)−N(1)	76.9(2)	P(1)−Pd(1)−P(3)	85.64(6)
P(2)−Pd(1)−N(1)	99.2(1)	N(1)−Pd(1)−P(3)	111.4(1)
C(5)−Pd(1)−P(3)	171.7(1)	P(1)−Pd(1)−N(1)	111.2(1)
C(5)−Pd(1)−P(2)	93.0(1)	C(5)−Pd(1)−P(1)	91.7(1)

Table 5. Selected Geometric Parameters for Complexes **5**, **6**, and **7**

	5	**6a**	**6b**	**7**
Pd−N	2.338(3)	2.366(5)	2.560(6)	2.437(5)
Pd−C	2.049(3)	2.052(6)	2.062(7)	2.075(6)
N−Pd−$P_{term.}$	116.21(7)	117.3(2)	113.2(1)	111.2(1)
	115.12(7)	103.6(2)	95.5(1)	99.2(1)
P_{term}−Pd−$P_{term.}$	128.35(3)	139.02(7)	151.06(7)	149.51(6)
C−Pd−$P_{centr.}$	173.26(9)	176.1(2)	171.3(2)	171.7(1)

5, the Pd−N bond length, 2.338(3) Å, is yet, to the best of our knowledge, the shortest distance known for these type of compounds, and it is very close to the Pd−N bond length of 2.23(2) Å found in an authentic pentacoordinated palladium(II) complex,[19] making compound **5** first doubly cyclometalated palladium(II) compound with two pentacoordinated metal centers. The Pd−N bond length, 2.366(5) Å, in complex **6b** is close to the value reported by us, whereas in complex **6a** a rather longer Pd−N distance of 2.560(5) Å was observed. The differing Pd−N bond lengths in **6a** and **6b** may be rationalized in terms of packing forces within the crystal lattice. The relative disposition of the phenyl rings attached to the central phosphorus, P(3), and to the N(1) atom could explain the different bond lengths (Figure 4 shows the different coordination geometry of **6a** and **6b**). While in **6b** these are almost parallel, the crystal structure of **6a** shows the P(3) phenyl ring to be twisted toward the N(1) phenyl ring. As a consequence of this, the minimum distance between phenyl carbon atoms is 3.5 Å for **6b** and 3.3 Å for **6a**. Therefore, the steric repulsion "pushes" the N(1a) ring, and thus the N(1a) nitrogen atom, enlarging the Pd−N bond distance. The Pd(1)−N(1) bond distance of 2.437(5) Å for **7** is intermediate between those for **5** and **6**.

The differing Pd−N bond lengths may move coordination at palladium from trigonal bypiramidal to distorted square-base pyramidal. This is evident from the variation of the bond angles at the metal center on going from **5** to **6a**, **7** and **6b**. In **5**, the P(1)−Pd(1)−N(1), P(2)−Pd(1)−N(1), and P(1)−Pd(1)−P(2) bond angles are in the proximity of the ideal value of 120° expected for planar trigonal geometry, with values of 116.21(7), 115.12(7), and 128.35(3)°, respectively. However, in **6b**, opening of the P(1)−Pd(1)−P(2) bond angle brings the bond angles at palladium to P(1b)−Pd(1b)−N(1b) 113.2(1), P(2b)−Pd(1b)−N(1b) 95.5(1), and P(1b)−Pd(1b)−P(2b) 151.06(7)°, the latter is more in accordance with a distorted square pyramidal geometry. This puts the nitrogen atom at the apical position with subsequent lengthening of the Pd−N

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[19] Cecconi, F.; Ghilardi, C. A.; Midollini, S.; Moneti, S.; Orlandini, A.; Scapacci, G. *J. Chem. Soc., Dalton Trans.* **1989**, 211.

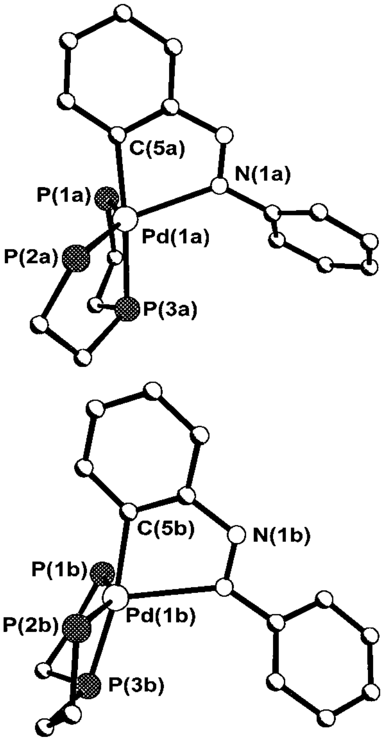

Figure 4. Comparative view of the cations of **6a** and **6b**. Phosphine phenyl rings have been omitted for clarity.

distance to 2.560(6) Å, a value still below those reported of 2.576−2.805 Å. The distortion is not so noticeable in **6a**, with bond angles of P(1a)−Pd(1a)−N(1a) 117.3(2), P(2a)−Pd(1a)−N(1a) 103.6(2), and P(1a)−Pd(1a)−P(2a) 139.02(7)°, thus bringing the Pd−N bond length to 2.366 Å. Bond angle values for **7** are intermediate between those for **6b** and **6a** (P(1)−Pd(1)−N(1) 111.2(1), P(2)−Pd(1)−N(1) 99.2(1), and P(1)−Pd(1)−P(2) 149.51(6)°) in agreement with the Pd(1)−N(1) bond length of 2.437(5)°. The C−Pd−P(3) bond angle is in all cases close to the value of 180°, as would be expected for the metalated carbon and P(3) atoms in the axial positions of a trigonal bymiramid or situated at opposite positions of the base in the square pyramid.

The mean deviation from the CPdP$_3$ least squares plane (which could be regarded as the basal plane for a square pyramid) shows the magnitude of the distortion toward square-base pyramidal geometry. The mean deviation is larger in the complexes with the shortest Pd−N bond length (mean deviation 0.4368, 0.3564, 0.2341, and 0.2139 for complexes **5**, **6a**, **7**, and **6b**, respectively).

The Pd−C bond lengths of 2.049(3), 2.052(6), 2.062(7), and 2.075(6) Å for **5**, **6a**, **6b**, and **7** are similar to those found in related cyclometalated complexes[20,4] with C trans to phosphorus but longer than Pd−C distances found in cyclometalated complexes with carbon trans to nitrogen or chlorine, supporting a phosphine ligand in the trans position. The Pd−P bond lengths are similar to those found in related Pd(II) complexes[4,20,21]and suggest that slightly partial double bond between the palladium and phosphorus atoms may exist.[22]

In summary, the reaction of cyclometalated complexes with the triphosphine ligand, triphos, constitutes a systematic route for promoting pentacoordination in palladium(II) complexes in the solid state regardless of the nature of the ligand and of the specific properties of the starting complex. This is shown by the X-ray crystal structures, one of which constitutes the first example of a doubly five-coordinate cyclometalated palladium(II) complex with trigonal bipyramidal geometry at each metal center.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **5**, **6**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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