Synthesis and Structure of $[Pd(\mu\text{-}PCy_2)(PCy_2OPh)]_2$: Palladium-Assisted P–O Bond Formation from Secondary Phosphines and the Phenoxide Ion

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Introduction

The high reactivity of P–H bonds of secondary phosphines in Pd(0) complexes was exploited in the synthesis of new polynuclear Pd(I) systems with bridging phosphido ligands;[1] such complexes still contain secondary phosphines as terminal or bridging (through a Pd–H–P agostic interaction) ligands. When bonded to Pd(I) centers, the P–H bonds are less reactive, and a series of substitution reactions were performed on these systems without interference of the secondary phosphines which remain unchanged in the reaction products.[2,3]

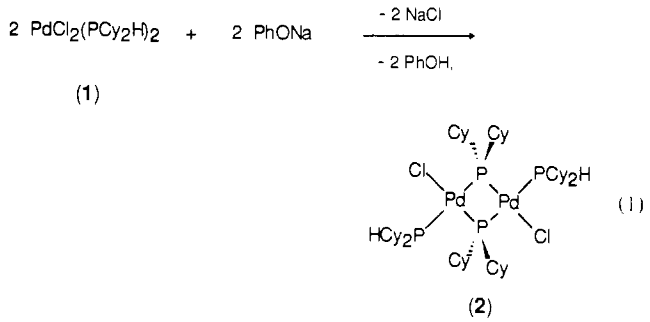
In some case, however, the residual reactivity of the secondary phosphine's P–H bonds on Pd(I) fragments leads to interesting reactions as follows: (a) ethylene insertion giving Pd-bonded tertiary phosphines;[3] (b) proton transfer to an η^3-allyl ligand, allowing the construction of triangulo mixed-valence Pd_3 clusters;[4] (c) secondary-phosphine/bridging-phosphido proton transfer, causing the interchange between these ligands and isomerization, provided one starts from $Pd_2(\mu\text{-}PR_2)(PR'_2H)_n$ fragments with R $\neq$ R′ (n = 3, 4).[5]

We now report the reaction of $PdCl_2(PCy_2H)$ with sodium phenoxide, which, instead of the usual metathesis process, widely employed in the synthesis of metal–aryloxides, gives a reaction constituting, to the best of our knowledge, the first example of P–O bond formation from a metal-bonded secondary phosphine and an aryloxide ion.

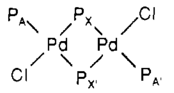
Results and Discussion

Synthesis and Characterization of Complex 2. When equimolar amounts of $PdCl_2(PCy_2H)_2$ (**1**), and PhONa are mixed in thf, a rapid reaction takes place and, after workup, pure $[Pd(\mu\text{-}PCy_2)(Cl)(PCy_2H)]_2$ (**2**) can be isolated in 45% yield (eq 1).

Complex **2** has been characterized by spectroscopic and elemental analyses. Significant absorptions in the IR spectrum (Nujol mull) were observed at 2322 (ν_{PH}) and 275 (ν_{PdCl}) cm^{-1}, while absorptions of the aryl ring were absent. The ^{1}H NMR spectrum exhibits only a double multiplet at 3.67 ppm with the expected large $^1J_{PH}$ (300 Hz, $Cy_2P\text{–}H$) and broad absorptions at 2.5–1.0 ppm due to the cyclohexyl protons.



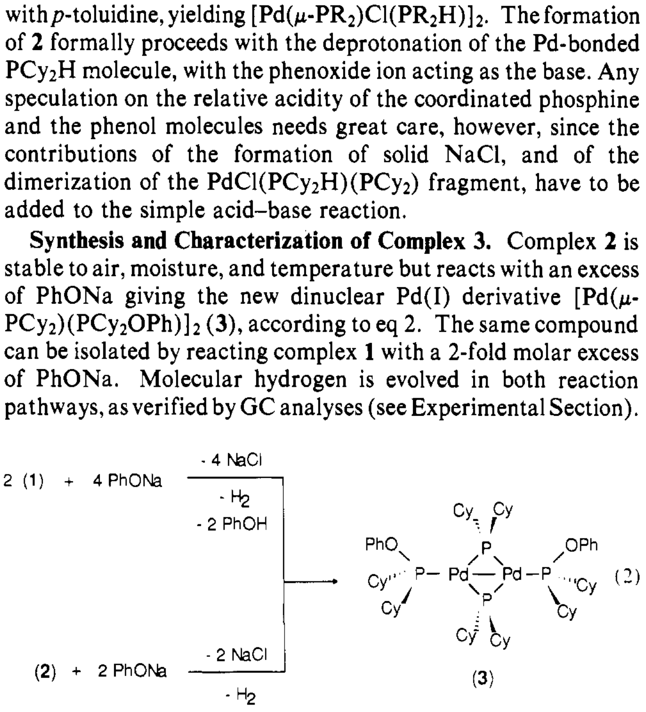
Two signals due to an $[AX]_2$ spin system were observed at 10.1 and –124.1 ppm in the $^{31}P\{^1H\}$ NMR spectrum, the former in the phosphine region and the second at high fields, as usual for bridging phosphido ligands unsupported by metal–metal bonds. $^4J_{AA'}$ = 3, $^2J_{AX}$ = 33, $^2J_{AX'}$ = 371, and $^2J_{XX'}$ = –270 Hz were extracted directly from the spectra, as described in ref 6, simulated spectra with these values of coupling constants were superimposable on the experimental spectra.



The spectrum is very similar to those reported for analogue derivatives of formula $[Pd(\mu\text{-}PR_2)(Cl)(PR'_3)]_2$.[6] The signal at 10.1 ppm is split into a complex multiplet in the proton-coupled ^{31}P NMR spectrum, due to the additional large $^1J_{PH}$.

The reaction of transition metal halides with sodium phenoxide is a general route to metal–phenoxo derivatives; this classical reactivity pattern can be altered when the reactant molecule presents some acidic proton that can be extracted by the phenoxide ion. The formation of compounds structurally related to complex **2**, by the reaction of secondary phosphine palladium(II) halides and a weak base, is not unprecedented; early in 1964 Hayter reported[7] the reaction of $PdCl_2(PR_2H)_2$ (R_2 = Me_2, Et_2, EtPh) with p-toluidine, yielding $[Pd(\mu\text{-}PR_2)Cl(PR_2H)]_2$. The formation of **2** formally proceeds with the deprotonation of the Pd-bonded PCy_2H molecule, with the phenoxide ion acting as the base. Any speculation on the relative acidity of the coordinated phosphine and the phenol molecules needs great care, however, since the contributions of the formation of solid NaCl, and of the dimerization of the $PdCl(PCy_2H)(PCy_2)$ fragment, have to be added to the simple acid–base reaction.

Synthesis and Characterization of Complex 3. Complex **2** is stable to air, moisture, and temperature but reacts with an excess of PhONa giving the new dinuclear Pd(I) derivative $[Pd(\mu\text{-}PCy_2)(PCy_2OPh)]_2$ (**3**), according to eq 2. The same compound can be isolated by reacting complex **1** with a 2-fold molar excess of PhONa. Molecular hydrogen is evolved in both reaction pathways, as verified by GC analyses (see Experimental Section).



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Significant absorptions in the IR spectrum of **3** were observed at 3081vw, 3055 vw ($\nu_{=C-H}$), 1592 s, 1490 s ($\nu_{C=C}$), and 1228 s, 874 s (ν_{P-O}) cm^{-1}. Only signals due to aromatic (7.4–6.9 ppm, m, 10 H) and cyclohexyl protons (2.4–1.0 ppm, broad m, 88 H) were observed in the ^{1}H NMR spectrum, while the region between 2.5 and 6 ppm, where are usually observed the resonances of the P–H functionality, was free. The $^{31}P\{^1H\}$ NMR spectrum of **3** consists of two sharp triplets (238.2 ppm, $^2J_{PP}$ = 53.1 Hz, μ-PCy$_2$; 171.3 ppm, $^2J_{PP}$ = 53.1 Hz, PCy$_2$OPh), only slightly broadened in the corresponding proton-coupled ^{31}P NMR spectrum. All spectra are consistent with a symmetrical structure with two terminally-bonded tertiary phosphorus atoms and two phosphido ligands bridging metal–metal-bonded Pd centers. The downfield shift of the signal at 171.3 ppm with respect to the position where coordinated tertiary phosphine ligands are usually found suggests the formation of a new P–OPh bond on each terminal ligand, in place of the P–H bond which is evidently missing, as tested with certainty by IR and NMR spectra. In fact, $^{31}P\{^1H\}$ NMR absorptions of coordinated dialkylphosphinites have been observed at 140–160 ppm.[8] The structure of complex **3** was confirmed by the X-ray diffraction analysis (see below).

The reaction of **1** with an excess of the phenoxide ion giving **3** is unprecedented. Complex **2** can be supposed to be an intermediate in this reaction; in fact it converts quantitatively to **3** by reaction with 2 equiv of PhONa, and it was observed (by $^{31}P\{^1H\}$ NMR spectroscopy) as a transient species in the early stages of the reaction of **1** with excess PhONa.

The elementary steps leading from **2** to **3** are (not necessarily in the given order) as follows: (a) the cleavage of the Pd–Cl bonds and the formation of NaCl; (b) The cleavage of P–H bonds; (c) the formation of P–O bonds; (d) the elimination of molecular hydrogen, possibly through the formation of Pd–hydride intermediates. Steps b and c and the formation of Pd–H bonds can also occur in an almost concerted way, through a multicenter transition state, as supposed for other σ-bond metathesis reactions.[9]

This is, to our knowledge, the first example of a metal-assisted formation of a dialkylphosphinite from a secondary phosphine and a phenoxide ion. Mention should however be made to a related reaction (at least from the synthetic point of view, e.g. creation of a P–O bond) recently reported by Bergman and coworkers. In this work a dimethylarylphosphinite is supposed to form, after the oxidative addition of a P–C bond of a Ru-bonded PMe$_3$ molecule, by reductive coupling of the resulting dimethyl phosphide ligand and a phenoxide ligand.[8]

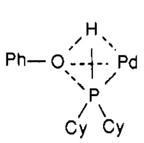

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 3

Pd–Pd′	2.620(2)	C(1)–C(2)	1.29(2)
Pd–P(1)	2.236(2)	C(1)–C(6)	1.41(2)
Pd–P(2)	2.317(3)	C(2)–C(3)	1.38(2)
Pd–P(2)′	2.316(3)	C(3)–C(4)	1.35(2)
P(1)–O	1.688(7)	C(4)–C(5)	1.38(2)
O–C(1)	1.39(1)	C(5)–C(6)	1.40(2)
Pd′–Pd–P(2)	55.59(7)	P(1)–Pd–P(2)′	129.6(1)
Pd–Pd′–P(2)	55.54(6)	P(2)–Pd–P(2)′	111.13(8)
Pd–Pd′–P(1)	173.9(1)	Pd–P(2)–Pd′	68.87(8)
Pd–P(1)–O	124.5(3)	P(1)–O–C(1)	130.7(6)
P(1)–Pd–P(2)	119.2(2)		

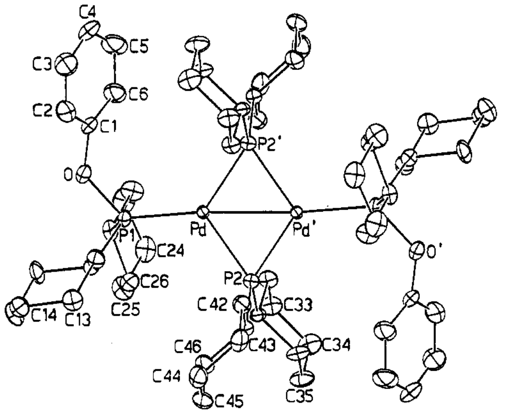

Figure 1. ORTEP view of the molecular structure of complex **3** with the atom numbering.

Table 2. Summary of X-ray Diffraction Data for [Pd(μ-PCy$_2$)(PCy$_2$OPh)]$_2$·C$_6$H$_6$

formula	$C_{66}H_{104}O_2P_4Pd_2$
fw	1266.26
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a, Å	13.092(9)
b, Å	13.162(5)
c, Å	10.730(4)
α, deg	97.93(3)
β, deg	109.22(4)
γ, deg	108.45(5)
V, Å^3	1594(4)
Z	1
ρ_{calcd}, g cm^{-3}	1.319
radiation	Mo Kα (0.7107 Å)
μ, cm^{-1}	6.95
F(000)	668
T, °C	−15
data collcn method	ω
tot. no. of observns, ($3.0 < \theta < 28.0°$)	6824
no. of unique data, $I > 2.5\sigma(I)$	3129
abs corr (min, max, mean)	0.66, 1.18, 0.98
R^a	0.070
$R_w{}^b$ [$w = 1/\sigma^2(F_o)$]	0.082

[a] $R = \sum|\Delta F|/\sum|F_o|$. [b] $R_w = (\sum|\Delta F|^2/\sum w|F_o|^2)^{1/2}$.

Crystal and Molecular Structure of Complex 3. Single crystals of complex **3** were grown by recrystallization from benzene–acetone mixtures, and its crystal and molecular structure was solved. Relevant bond distances and angles are listed in Table 1, and Figure 1 shows an ORTEP projection with the atom numbering. The molecule possesses a center of inversion, in the middle of the Pd–Pd vector, generating a planar, symmetrical, Pd$_2$(μ-P)$_2$ core [torsion angle P(2)–Pd–Pd′–P(2)′ = 180.0°; Pd–P(2) = 2.317(3) and Pd–P(2)′ = 2.316(3) Å]. Each palladium center bears a terminally bonded PCy$_2$OPh molecule, with the P(1)–Pd–Pd′–P(1)′ axis closely approximating to linearity [P(1)–Pd–Pd′ = 173.9(1)°]. The structure of the Pd$_2$(μ-P)$_2$(P$_t$)$_2$ fragment closely resembles that observed in the only two known examples of structurally determined palladium derivatives of formula [M(μ-PR$_2$)(PR$_3$)]$_2$: [Pd(μ-PBu$^t{}_2$)(PBu$^t{}_2$H)]$_2$ (**4**)[1a] and [Pd(μ-PBu$^t{}_2$)(PMe$_3$)]$_2$, (**5**).[10] Structures of this type are also known for M = Ni,[11] and they all present geometric features similar to complex **3**. The Pd–Pd′ distance for **3**, 2.620(2) Å, is significantly longer than in complexes **4** and **5** [2.594(1)[1a] and 2.571(1) [9] Å, respectively] but lies in the range observed in single-bonded Pd^I–Pd^I dimers.[1] The Pd–P(phosphinite) bond length in **3** is 2.236(2) Å, notably shorter than the corresponding distances in complexes **4** and **5** [2.287(2)[1a] and 2.250(5) Å,[10] respectively]. The opposite trend of Pd–Pd and Pd–P(phosphinite) bond lengths, and the closeness to linearity of the P(1)–Pd–Pd′–P(1)′ axis, could suggest that the same metal orbitals are involved in the formation

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Table 3. Positional and Thermal (Å^2) Parameters with Estimated Standard Deviations

atom	x	y	z	U(eq)[a]
Pd	0.00867(8)	0.10086(7)	–0.0066(1)	0.0208(2)
P(1)	0.0352(2)	0.2790(2)	0.0062(3)	0.0313(9)
P(2)	0.1522(2)	0.0594(2)	0.1456(3)	0.0263(9)
O	–0.0509(7)	0.3224(6)	–0.1108(9)	0.044(3)
C(1)	–0.1559(9)	0.2623(9)	–0.224(1)	0.041(4)
C(2)	–0.161(1)	0.275(1)	–0.344(2)	0.092(7)
C(3)	–0.263(2)	0.226(1)	–0.461(2)	0.093(7)
C(4)	–0.364(1)	0.169(1)	–0.448(2)	0.108(7)
C(5)	–0.362(1)	0.155(1)	–0.322(2)	0.081(7)
C(6)	–0.257(1)	0.202(1)	–0.205(2)	0.066(6)
C(11)	0.1741(9)	0.3650(8)	0.002(1)	0.029(3)
C(12)	0.1859(9)	0.3144(9)	–0.127(1)	0.043(4)
C(13)	0.306(1)	0.376(1)	–0.133(1)	0.049(4)
C(14)	0.329(1)	0.500(1)	–0.116(1)	0.054(5)
C(15)	0.317(1)	0.552(1)	0.013(1)	0.052(5)
C(16)	0.197(1)	0.4895(9)	0.013(1)	0.051(5)
C(21)	0.0318(9)	0.3576(8)	0.155(1)	0.031(3)
C(22)	–0.085(1)	0.303(1)	0.172(1)	0.045(4)
C(23)	-0.090(1)	0.362(1)	0.300(2)	0.066(6)
C(24)	0.009(1)	0.366(1)	0.426(1)	0.055(5)
C(25)	0.123(1)	0.423(1)	0.415(1)	0.058(5)
C(26)	0.137(1)	0.370(1)	0.290(2)	0.054(5)
C(31)	0.1984(9)	0.1094(8)	0.330(1)	0.031(4)
C(32)	0.0883(9)	0.0864(9)	0.365(1)	0.036(4)
C(33)	0.123(1)	0.134(1)	0.520(1)	0.046(4)
C(34)	0.203(1)	0.085(1)	0.606(1)	0.054(5)
C(35)	0.310(1)	0.103(1)	0.575(1)	0.052(5)
C(36)	0.2768(9)	0.059(1)	0.422(1)	0.044(4)
C(41)	0.2913(8)	0.0781(8)	0.122(1)	0.027(3)
C(42)	0.264(1)	0.0360(9)	–0.027(1)	0.048(5)
C(43)	0.373(1)	0.043(1)	–0.057(2)	0.055(5)
C(44)	0.467(1)	0.162(1)	0.006(2)	0.060(5)
C(45)	0.493(1)	0.203(1)	0.155(2)	0.060(5)
C(46)	0.3839(9)	0.1967(9)	0.184(1)	0.044(4)
C(51)	0.559(1)	0.442(1)	0.472(2)	0.112(9)
C(52)	0.521(2)	0.425(2)	0.571(2)	0.107(8)
C(53)	0.466(2)	0.487(2)	0.602(2)	0.117(9)

[a] *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as one-third of the trace of the orthogonalized **U** tensor.

of these bonds. It should however be kept in mind that metal–phosphite, –phosphonite and –phosphinite bond lengths are generally shorter than the corresponding metal–phosphine bonds, due to their stronger π-accepting character.[8]

As often observed in related $[M(\mu\text{-}PR_2)(PR_3)]_2$ systems,[1a,10,11] the M–P distance is longer in the bridging than in the terminally bonded ligands [2.317(3) vs 2.236(2) Å]. The oxygen atom of each tertiary phosphine lies close to the $Pd_2(\mu\text{-}P)_2$ core plane [torsion angles P(2)–Pd–P(1)–O = 170.59(0.42)° and P(2)′–Pd–P(1)–O = –13.78(0.48)°], keeping the phosphine ligands in a conformation which reduces the steric repulsion between the cyclohexyl substituents on the phosphine and the phosphido ligands. The P–O distance in the phosphinite molecule [1.688(7) Å] can be compared to only one example of metal coordinated dialkylphosphinite, 1.667(4) Å, in $(Me_3P)_3(\eta^2\text{-}Me_2POC_6H_3)Ru(OC_6H_4Me)$.[8]

Experimental Section

General Data. All manipulations were carried out under a nitrogen atmosphere using standard Schlenck techniques. PCy_2H[12] and $[PdCl_2(PCy_2H)_2]$[7] were prepared according to published procedures. Solvents were dried by conventional methods and distilled prior to use. IR spectra (Nujol mulls, KBr plates) were recorded on a Perkin-Elmer FT-IR 1725X spectrometer. NMR spectra were recorded on a Varian Gemini 200 BB. Frequencies are referred to Me_4Si (^1H) or 85% H_3PO_4 (^{31}P). Gas chromatographic analyses were performed using a DANI 3200 gas chromatograph equipped with a D-SM 5A column.

Preparation of $[Pd(\mu\text{-}PCy_2)Cl(PCy_2H)]_2$, 2. PhONa (58 mg, 0.5 mmol) was added to a suspension of $[PdCl_2(PCy_2H)_2]$ (287 mg, 0.5 mmol) in toluene (30 mL). The colorless suspension turned slowly to yellow and was stirred 3 h at ambient temperature; the solvent was evaporated and the residue extracted with $CHCl_3$. The chloroform solution was concentrated to a small volume, and complex **2** was precipitated by addition of acetone, filtered out, and vacuum dried (171 mg, 64% yield). Anal. Calcd for $C_{48}H_{90}Cl_2P_4Pd_2$: C, 53.6; H, 8.44. Found: C, 53.2; H, 8.46.

Preparation of $\{Pd(\mu\text{-}PCy_2)(PCy_2OPh)\}_2$, 3. Method a. A suspension of $[PdCl_2(PCy_2H)_2]$ (955 mg, 1.66 mmol) and PhONa (385 mg, 3.32 mmol) in toluene (30 mL) was stirred 3 h at 50 °C. The orange suspension was left overnight at ambient temperature and then filtered. The filtered solution was concentrated to *ca.* 5 mL, and acetone (10 mL) was added. An orange solid precipitated and was filtered out and vacuum dried (321 mg, 46% yield). Anal. Calcd for $C_{60}H_{100}O_2P_4Pd_2$: C, 60.5; H, 8.47. Found: C, 59.5; H, 8.34.

Method b. PhONa (37 mg, 0.318 mmol) was added to a yellow solution of complex **2** (150 mg, 0.159 mmol) in toluene (10 mL). The reaction mixture was stirred 3 h at 50 °C, and complex **3** was recovered as above (55% isolated, reaction quantitative by $^{31}P\{^1H\}$ NMR). IR and NMR spectra were identical to those of the samples obtained by method a. The reaction performed by both methods proceeds with hydrogen evolution, as verified by gas-chromatographic analysis.

Molecular Structure Determination. Crystals suitable for X-ray diffraction were obtained as described above. They contain one molecule of benzene per unit cell. A summary of the crystallographic results is presented in Table 2. Data were collected at –15 °C on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation; 6824 reflections ($3.0 < \theta < 28.0°$) were measured, 3129 unique with $I > 2.5\sigma(I)$ were used for further computations.

Data were corrected for anisotropic decay. An absorption correction was carried out using the program DIFABS.[13]

The structure was solved by Patterson and subsequent Fourier difference syntheses. Full-matrix least-squares refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were not refined in their positions but included in structure factors calculations with isotropic thermal parameters of $B(H) = 1.3B(C)$.

Refinement converged with 335 parameters using a statistical weighting scheme $w = 1/[\sigma^2(F_o)]$ at values of $R = 0.070$ and $R_w = 0.082$ with a goodness of fit of 1.577.

A coefficient for secondary extinction was included and refined to 0.559×10^{-7}. Atomic coordinates are given in Table 3. Calculations were performed using the SDP system of programs.

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Supplementary Material Available: Tables of complete positional and thermal parameters, general displacement parameter expressions, and complete bond distances and angles (10 pages). Ordering information is given on any current masthead page.

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