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Notes

Dichlorobis(tricyclohexylphosphine)palladium(II): Synthesis and Crystal Structure. An Exceptionally Simple and Efficient Preparation of Bis(tricyclohexylphosphine)palladium(0)

Vladimir V. Grushin, Corinne Bensimon, and Howard Alper*

Department of Chemistry, University of Ottawa, 10 Marie Curie, Ottawa, Ontario, Canada K1N 6N5

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Tricyclohexylphosphine (Cy_3P) complexes of palladium have been recently shown to possess unique catalytic activity in the homogeneous carbonylation of chloroarenes under mild conditions.[1,2] The only alternative to commercially available Cy_3P and triisopropylphosphine ligands[1] for this catalytic reaction is 1,3-bis(diisopropylphosphino)propane[3] and some other bidentate phosphines[4] which are not commercially available. The simplest (tricyclohexylphosphine)palladium complex, $[(Cy_3P)_2PdCl_2]$, **1**, is of significant interest due to its demonstrated catalytic properties. For instance, alkoxycarbonylation of iodoarenes in the presence of **1** afforded α-keto esters (double carbonylation products) in high selectivity.[5] We have recently shown that **1** is an excellent catalyst for the hydroxycarbonylation of chloroarenes under exceedingly mild conditions (100 °C, 1 atm CO).[6,7] In addition, **1** can be used for the synthesis of some organometallic compounds (e.g., $[(Cy_3P)_2Pd_2Ph_2(\mu\text{-}OH)_2]$ and $[CpPd(Ph)PCy_3]$) which are not accessible by other means.[7−9]

Surprisingly, no detailed experimental procedure has been described for the synthesis of **1**. In a number of papers[5,10−12] it was mentioned that **1** was synthesized by treatment of $[(PhCN)_2PdCl_2]$ with Cy_3P in benzene. Other articles[7,13,14] refer to old, classical general procedures for the synthesis of $[L_2MCl_2]$ (L = tertiary phosphine; M = Pd, Pt),[15] which are not necessarily appropriate for synthesis of **1** in high yield. In the present paper, we wish to report a detailed procedure for the preparation of **1** in quantitative yield, its special characteristics and X-ray crystal structure, and an exceedingly simple and efficient synthesis of bis(tricyclohexylphosphine)palladium(0) from **1**.

Treatment of sodium tetrachloropalladate with Cy_3P in aqueous ethanol affords **1** in quantitative yield (eq 1). Various

$$2Cy_3P + [PdCl_4]^{2-} \xrightarrow[N_2]{EtOH/H_2O} \underset{\mathbf{1}}{[(Cy_3P)_2PdCl_2]} + 2Cl^- \quad (1)$$

tertiary phosphine complexes of palladium(II) and platinum(II) have been previously synthesized in a similar manner.[16] Reaction **1** should be conducted under nitrogen with oxygen-free solvents, as Cy_3P is air-sensitive. However, complex **1** is air-stable in the solid state and solution, and therefore its isolation can be carried out in air.

It is noteworthy that samples of Cy_3P contaminated with tricyclohexylphosphine oxide can also be successfully used for the synthesis of **1** after the Cy_3P content is estimated by ^{31}P NMR. For example, once we obtained **1** in 98% yield with a sample of Cy_3P containing ca. 40% Cy_3PO due to improper storage. Complex **1** is a pale-yellow crystalline solid which is insoluble in water, hexane, alcohols, acetone, and ether, sparingly soluble in benzene and toluene, and moderately soluble in chloroform and dichloromethane. It can be recrystallized with minor losses from boiling *o*-dichlorobenzene. Four broad multiplets centered at δ 1.25, 1.7, 1.95, and 2.5 are observed in the ^1H NMR spectrum of **1**. Its ^{31}P NMR exhibits a sharp singlet at $\delta = 25.4$ ppm which is close to the values previously reported for **1** in solution[17a] and in the solid state.[17b] As anticipated, the ^{13}C NMR spectrum of **1** consists of four resonances, two of them being singlets and two others being triplets (see Experimental Section) due to the virtual coupling resulting from the *trans*-geometry of the complex in solution. In the solid state, the complex is also *trans*, as revealed by a single crystal X-ray diffraction study.

The X-ray structure of **1** (Figure 1) indicates almost ideal square-planar geometry around the palladium atom. All six cyclohexyl groups are in the chair conformation, with bond lengths and angles within the rings having values similar to those normally observed for this kind of aliphatic ring. Complex **1** is isostructural to *trans*-$[(Cy_3P)_2NiCl_2]$, **1a**,[18] *trans*-$[(Cy_3P)_2PtCl_2]$, **1b**,[19] *trans*-$[(Cy_3P)_2PtI_2]$, **1c**,[20] and *trans*-$[(Ph_3P)_2PdCl_2]$,

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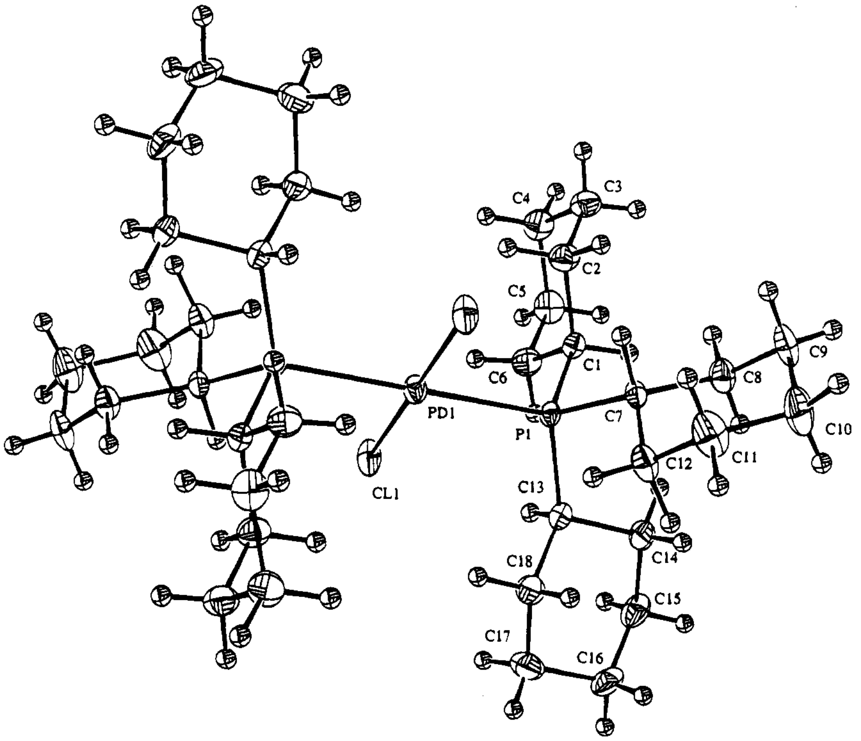

Figure 1. Structure of $[(Cy_3P)_2PdCl_2]$, **1**, showing the atom-labeling scheme. Selected bond distances, Å: Pd—P, 2.3628(9); Pd—Cl, 2.3012(9). Selected bond angles, deg: P—Pd—P, 180; P1—Pd—Cl1, 88.69(3); P1—Pd—Cl1a, 91.31(3); Cl—Pd—Cl, 180.

Table 1. Crystallographic Data for $[(Cy_3P)_2PdCl_2]$, **1**

formula	$C_{36}H_{66}Cl_2P_2Pd$
fw	738.16
cryst shape	cube
cryst dimens, mm	0.2 × 0.2 × 0.2
cryst system	triclinic
lattice params	
a, Å	10.161(4)
b, Å	10.604(4)
c, Å	9.902(4)
α, deg	109.01(3)
β, deg	91.52(3)
γ, deg	112.75(3)
space group	$P\bar{1}$
Z	1
V, Å^3	916.0(6)
d_{calc}, g/cm^3	1.338
T, K	163
radiation (λ, Å)	Mo K_α (0.709 30)
μ, mm^{-1}	1.21
R (R_w), %	2.7 (3.0)

1d,[21] as the same space group ($P\bar{1}$) and very similar lattice parameters have been found for **1** (Table 1) and complexes **1a–d**.[18–21] The Pd—Cl bond length (2.3012(9) Å) in **1** is very close to the Pt—Cl (2.317(2) Å)[19] and Pd—Cl (2.281(1) and 2.296(1) Å;[21a] 2.290(1) Å[21b]) bond distances found for complexes **1b,d**, respectively. At the same time, the Pd—P bond in **1** is longer, by ca. 0.025 Å, when compared with that of $[(Ph_3P)_2PdCl_2]$, **1d**.[21] This elongation is likely due to the difference in effective bulk (cone angle) and basicity between Cy_3P and Ph_3P.

Complex **1** can be used for an exceedingly simple and efficient preparation of bis(tricyclohexylphosphine)palladium(0), **2**, a complex widely used in inorganic and organometallic synthesis.[22] Unlike bis(phosphine) complexes of platinum(0), $[L_2Pt]$, where L = bulky tertiary phosphine such as $t\text{-}Bu_3P$, $i\text{-}Pr_3P$, and Cy_3P, the palladium analogs cannot be obtained by reduction of the corresponding Pd(II) complexes, $[L_2PdCl_2]$.[23] For this reason, multistep procedures have been developed for the preparation of **2** and other bis(phosphine)palladium(0) compounds.[22,24,25] It is noteworthy that some of the steps involve reactions with carbon monoxide and sodium cyclopentadienide in dry solvents and require filtration and/or recrystallization under inert atmosphere. However, **2** can be obtained in a much simpler way by generating the coordinatively-unsaturated Pd(0) species[7,26] from **1** in the presence of Cy_3P (eq 2).

$$[(Cy_3P)_2PdCl_2] + Cy_3P \xrightarrow[-Cy_3PO]{60\%\ KOH/toluene/18\text{-}crown\text{-}6} [(Cy_3P)_2Pd] \qquad (2)$$

Although reaction 2 requires more drastic conditions and longer time than similar transformations of (triphenylphosphine)palladium complexes,[7,26] it furnishes **2** in excellent (85–90%) yield. The isolation of **2** is exceedingly simple and efficient, since it gives the desired complex as colorless crystals which were found spectroscopically pure without recrystallization. A sharp singlet at δ = 39.4 ppm (benzene-d_6, 20 °C) was observed in the ^{31}P NMR spectrum of **2**, indicating that the sample was not contaminated with extra tricyclohexylphosphine.[27] Interestingly, the presence of 18-crown-6 was found necessary for reaction 2, although some similar transformations of $[(Ph_3P)_2PdCl_2]$ were shown to proceed quite readily in the absence of a phase-transfer catalyst.[7,28]

Experimental Section

All chemicals were commercially available and used as received. A Varian XL-300 spectrometer was used for measuring ^1H, ^{13}C, and

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^{31}P NMR spectra. The single crystal diffraction study was carried out with a Rigaku AFC6S diffractometer.

[(Cy$_3$P)$_2$PdCl$_2$], 1. Tricyclohexylphosphine (3.7 g; 13.2 mmol) was dissolved at 50 °C in oxygen-free EtOH (350 mL)—obtained by bubbling N$_2$ for 15–25 min. A degassed solution of Na$_2$[PdCl$_4$] prepared by dissolving PdCl$_2$ (0.89 g; 5.0 mmol) and NaCl (0.65 g; 11.1 mmol) in water (50 mL), followed by bubbling N$_2$ for 15–25 min, was added dropwise to the warm, vigorously stirred ethanol solution of Cy$_3$P, under nitrogen. After all the Na$_2$[PdCl$_4$] solution was added, the mixture was stirred for an additional 1 h under nitrogen. The pale-yellow microcrystalline precipitate of **1** was isolated by filtration in air, thoroughly washed with water, ethanol, and ether, and then dried under vacuum to give 3.5–3.7 g (94–99%) of analytically and spectroscopically pure **1**, mp 297–300 °C dec. Anal. Calcd for C$_{36}$H$_{66}$Cl$_2$P$_2$Pd: C, 58.6; H, 9.0. Found: C, 58.7; H, 9.1. NMR (δ; CDCl$_3$, 20 °C): ^{1}H, 1.0–2.7 (m); ^{31}P, 25.4 (s); ^{13}C, 27.3 (s), 28.3 (virtual triplet, $^2J_{C-P} + {}^4J_{C-P} = 10.7$ Hz), 30.3 (s), 32.5 (virtual triplet, $^1J_{C-P} + {}^3J_{C-P} = 20.0$ Hz).

[(Cy$_3$P)$_2$Pd], 2. Tricyclohexylphosphine (0.20 g; 0.71 mmol) and **1** (0.30 g; 0.41 mmol) were added under nitrogen to an oxygen-free mixture of 60% KOH (5 g), toluene (8 mL), and 18-crown-6 (0.02 g; 0.08 mmol). The mixture was vigorously stirred under reflux (N$_2$) for 20 h. The upper organic layer was transferred via cannula to a Schlenk tube filled with N$_2$, reduced in volume to ca. 2 mL, and treated with oxygen-free MeOH (2 mL). The product, **2**, began precipitating immediately, and three portions of oxygen-free MeOH (2 mL each) were then added after 0.5, 1, and 2 h. After standing for an additional 1 h, the mother liquor was carefully removed by pipet. The colorless, well-shaped crystals of **2** were washed with MeOH (4 × 3 mL) and dried under vacuum. The yield of spectroscopically pure (^{1}H, ^{31}P, ^{13}C NMR)[22,25,27] **2** was 0.230–0.245 g (85–90%).

X-ray Diffraction. A crystal of **1** having approximate dimensions of 0.2 × 0.2 × 0.2 mm was mounted on a glass capillary. The measurements were made at −110 °C with Mo Kα radiation and a graphite monochromator. During the data collection, three standard reflections were measured after every 150 reflections to check the stability of the crystal. No crystal decay was noticed. A total of 2859 reflections were measured. The unique set contained 2682 reflections. Using the criteria $I > 2.5\sigma(I)$, where $\sigma(I)$ is the estimated standard deviation derived from the counting statistics, 2507 out of 2682 reflections were used. The data were corrected for Lorentz and polarization effects.[29] No absorption correction was made.

The structure was solved by direct methods, giving the positions of the Pd, P, and Cl atoms. All the atoms were refined anisotropically except the hydrogens. The hydrogen atoms were found by difference Fourier map. The scattering factors from the *International Tables*[30] were used. The final cycle of full matrix least-squares refinement was based on 2507 observed reflections and 320 parameters. Weights based on counting statistics were used. The maximum and minimum peaks on the final Fourier map corresponded 0.440 and −0.700 e/Å^3, respectively. All the calculations were performed using the NRCVAX crystallographic software package.[31]

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Supplementary Material Available: Full textual and tabular details of the structure solution, additional structural diagrams, and tables of atomic coordinates, bond lengths and angles, and thermal parameters for complex **1** (11 pages). Ordering information is given on any current masthead page.

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