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Cyclopalladation of Benzyldiphenylphosphine by Palladium(II) Acetate

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An acetato-bridged binuclear cyclopalladated complex of benzyldiphenylphosphine, [{Pd(C$_6$H$_4$CH$_2$PPh$_2$)(O$_2$CMe)}$_2$], has been obtained by the reaction between the phosphine and palladium(II) acetate. A chloro-bridged analogue, [{Pd(C$_6$H$_4$CH$_2$PPh$_2$)Cl}$_2$], yielded by the metathetical reaction of the acetato-bridged complex with LiCl, undergoes bridge-splitting reactions with 3,5-dimethylpyridine (dmpy) and thallium(I) acetylacetonate (Tl[acac]) to give mononuclear cyclopalladated complexes, [Pd(C$_6$H$_4$CH$_2$PPh$_2$)Cl(dmpy)] and [Pd(C$_6$H$_4$CH$_2$PPh$_2$)(acac)], respectively. These complexes are characterized by means of elemental analysis and IR and NMR spectroscopy.

Introduction

Cyclopalladated complexes have been receiving interest in view of the applications for regiochemically controlled organic syntheses [1–4]. Although bulky benzylphosphines such as P(CH$_2$Ph)$_2$Bu^t [5] and P(CH$_2$Ph)Bu$^t_2$ [5], or an electronically activated benzylphosphine PPh$_2${C$_6$H$_3$(OMe)$_2$-3,4} [6], are readily cyclopalladated, it has been reported that benzyldimethylphosphine [7], benzyldiphenylphosphine (PBzPh$_2$) [8] and dibenzylphenylphosphine (PBz$_2$Ph) [8] are not cyclopalladated. We have revealed that benzyl t-butyl sulphide, which had been reported to give no cyclometallated complex by tetrachloropalladate(II) ion in the presence or absence of sodium acetate [9], is cyclopalladated easily by palladium(II) acetate [10, 11]. As an extension of our investigations concerning the cyclopalladation by palladium(II) acetate [11, 12], we report here the syntheses of cyclopalladated complexes of PBzPh$_2$ by means of palladium(II) acetate and their characterization. Doubly cyclometallated complexes of PBzPh$_2$ were obtained by the reaction of 2-lithiobenzyldiphenylphosphine with [MCl$_2$(SEt$_2$)$_2$] (M = Pd and Pt) [13].

Results and Discussion

Benzyldiphenylphosphine is rather sensitive to air [14] and was obtained as a mixture of PBzPh$_2$ and benzyldiphenylphosphine oxide (BzPh$_2$P=O) in a molar ratio of 4:1. This phosphine reacted with palladium(II) acetate in refluxing methanol to give di-μ-acetato-bis{[2-(diphenylphosphinomethyl)-phenyl-C^1,P]palladium(II)}, [{Pd(C$_6$H$_4$CH$_2$PPh$_2$)(O$_2$CMe)}$_2$] (Ia) in a moderate yield. However, Ia was contaminated with some amounts of BzPh$_2$P=O, even after column chromatographic purification. The impurity, BzPh$_2$P=O, did not affect the reaction of Pd(O$_2$CMe)$_2$ with PBzPh$_2$ itself, because 92% of BzPh$_2$P=O was recovered unchanged after the mixture of BzPh$_2$P=O and Pd(O$_2$CMe)$_2$ in a 1:1 molar ratio had been refluxed in methanol for 2 h. BzPh$_2$P=O was removed when Ia was converted into the chloro-bridged analogue [{Pd(C$_6$H$_4$CH$_2$PPh$_2$)Cl}$_2$]·½Me$_2$C=O (II), by treating with LiCl in an acetone–water solvent. The acetato-bridged cyclopalladated complex was regenerated as a ¼ dichloromethane adduct (Ib) from II by the reaction with silver acetate. The solvated dichloromethane or acetone in Ib or II could not be removed even by heating at 45 °C for 3 h *in vacuo*. It is noteworthy that PBzPh$_2$ is cyclopalladated by palladium(II) acetate, in contrast with the case by tetrachloropalladate(II) ion which gave only an addition complex, *trans*-[PdCl$_2$(PBzPh$_2$)$_2$] [8].

Complex II underwent typical bridge-splitting reactions with 3,5-dimethylpyridine (dmpy) and thallium(I) acetylacetonate (Tl[acac]) to afford the corresponding mononuclear cyclopalladated complexes, [Pd(C$_6$H$_4$CH$_2$PPh$_2$)Cl(dmpy)] (III) and [Pd(C$_6$H$_4$CH$_2$PPh$_2$)(acac)] (IV), respectively (Scheme 1). All the cyclopalladated complexes of PBzPh$_2$ prepared in this study showed IR bands at *ca.* 1435 and 1485 cm^{-1}, characteristic to arylphos-

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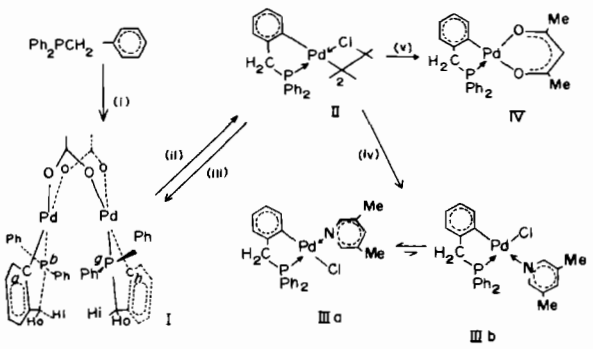
TABLE I. Analytical and ^{1}H NMR Spectral Data.

Complex	M.p.[a] (°C)	Analysis (%)[b]		^{1}H NMR Data[c]				
		C	H	T_m[d] (°C)	CH_2		Me	Others
					δ/ppm	^{2}J(PH)/Hz	δ/ppm	δ/ppm
Ib	186–189	55.85(56.21)	4.32(4.30)	28	2.94(d)[e]	11	1.92(s)	5.24(s)
					2.96(d)[e]	14		(CH_2Cl_2)
II	198	54.92(54.95)	4.15(4.09)	–[f]	–	–	–	–
III	175–177	59.32(59.50)	4.80(4.81)[g]	–41	3.78(d)	12	1.96(s)[e]	8.31(s)
					3.90	–[h]	2.27(s)[e]	(dmpy H^{α})
IV	178–180	59.80(59.95)	4.74(4.82)	28	3.80(d)	12	1.93(s)	5.39(s)
							2.09(s)	(acac CH)

[a]With decomposition. [b]Calculated values are given in parentheses. [c]Recorded in $CDCl_3$. See text for aromatic protons of III. s = Singlet and d = doublet. [d]Measured temperature. [e]See text. [f]Not measured owing to its poor solubility. [g]N, 2.64 (2.68). [h]Coupling constant could not be detected.



Scheme 1. (i) $Pd(O_2CMe)_2$ in refluxing methanol. Ia was contaminated with $BzPh_2P{=}O$. (ii) LiCl in an acetone–H_2O mixture. (iii) $Ag(O_2CMe)$. Ib was obtained as a $\frac{1}{4}CH_2Cl_2$ adduct. (iv) 3,5-Dimethylpyridine. (v) Tl(acac).

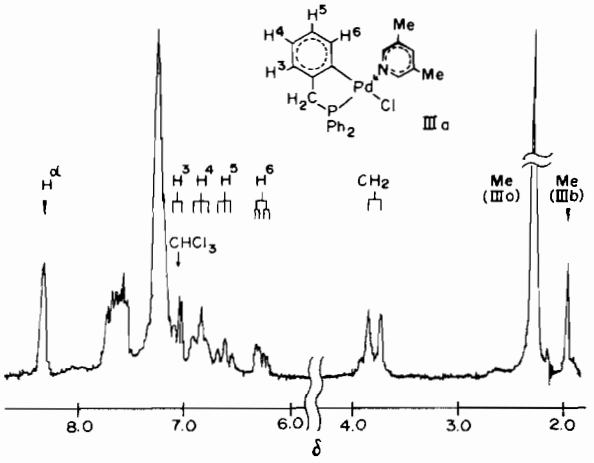


Fig. 1. ^{1}H NMR spectrum of III at –41 °C.

phines. Analytical and ^{1}H NMR spectral data are summarized in Table I.

The IR spectrum of Ib showed two strong absorption bands due to the bridging acetato ligands at 1410 and 1560 cm^{-1} [15]. As for the ^{1}H NMR spectrum, acetato methyl protons were observed at δ 1.92 as only one sharp singlet, indicating that Ib consisted of an ab-hg type isomer alone [12] (Scheme 1). Two benzyl-methylene protons were observed as actually two doublets at δ 2.94 [^{2}J(PH) = 11 Hz] and 2.96 [^{2}J(PH) = 14 Hz] indicating that the methylene protons were non-equivalent. Although they should appear as a double AB quartet owing to the coupling with an adjacent ^{31}P nucleus, two outer bands of the AB quartet were possibly too weak to be detected. These facts imply that Ib has two nearly syn-juxtaposed coordination planes bridged by the two acetato-groups, similar to di-μ-acetato-bis{[2-(2-benzothiazolyl)-5-methylphenyl-C^1,N]palladium(II)} [16]. It is noteworthy that the methylene protons in Ib resonated at the higher fields when compared with methylene signals in the mononuclear cyclopalladated complex III (δ 3.88) and IV (δ 3.80). This fact is probably associated with an anisotropic effect due to the phenylene group of the other cyclopalladated moiety lying actually over the methylene protons.

Complex II could not be characterized by ^{1}H NMR spectroscopy owing to its poor solubility, but was assigned to the chloro-bridged analogue of I in view of its elemental analysis and the characterization of its derivatives, III and IV, as stated above.

As for the mononuclear dmpy complex III, the IR spectrum exhibited a skeletal vibration of the dmpy ring at 1600 cm^{-1}. Complex III showed temperature-dependent ^{1}H NMR spectra. At 28 °C,

methyl proton signal of dmpy resonated at δ 2.33 as a broad singlet, which changed to two very sharp singlets at δ 2.27 (5.1 H) and 1.96 (0.9 H) at −41 °C. At the same temperature the α-protons of dmpy ligand in III resonated as a singlet at δ 8.31 (1.7 H)*. No signal was observed at δ 8.00 corresponding to free dmpy, implying that there are no detectable amounts of free dmpy and II in this system. The two singlets at δ 2.27 and 1.96 were thus ascribed to two geometrical isomers, IIIa and IIIb, respectively (Scheme I). Accordingly, III consists of IIIa and IIIb in a 85:15 ratio at the slow exchange limit, and the exchange between IIIa and IIIb takes place rapidly on the NMR time scale above room temperature. Such rearrangement of the dmpy ligand may arise from the strong *trans* influence of the phosphine group. At −41 °C, *o*-phenylene protons of the isomer IIIa appeared as a refined ABCD pattern, as shown in Fig. 1; a double doublet at δ 6.26 [H^6, $^3J(HH)$ = 7.5 Hz, $^4J(HH)$ = 3 Hz], two triplets at δ 6.60 (H^5) and 6.83 (H^4)**, and a doublet at δ 7.05 (H^3). These assignments were performed in consideration of the anisotropic shielding from the adjacent dmpy ring [17]. These data strongly confirm the cyclopalladated structure of $PBzPh_2$ in III.

The IR spectrum of IV showed two characteristic bands due to O,O′-chelating acac ligand at 1510 and 1570 cm^{-1}. Its mass spectrum gave a parent ion peak at m/e 480, corresponding to ^{106}Pd, and a fragment ion peak at m/e 381 $(P\text{-acac})^+$. These data also suggest that IV has the cyclopalladated structure of $PBzPh_2$.

Experimental

Benzylphosphine $PBzPh_2$ was synthesized according to the literature [14]. General procedures were as described previously [12].

Preparations of $[\{Pd(C_6H_4CH_2PPh_2)(O_2CMe)\}_2]$ (I)

(i) A methanol solution (15 ml) containing palladium(II) acetate (1.11 mmol), $PBzPh_2$ (1.23 mmol), and $BzPh_2P{=}O$ (0.31 mmol) was refluxed for 3 h. The resulting mixture was evaporated to dryness to give a reddish brown oil, which was chromatographed on a silica gel column (200 mesh, 12 × 140 mm). A yellow fraction eluted by dichloromethane/diethyl ether (1/1) was evaporated to dryness. The residue was recrystallized from dichloromethane and hexane to yield Ia as yellow crystals Yield 19%.

(ii) Silver acetate (0.3 mmol) was added to an acetone solution (10 ml) of II, and then the mixture was stirred at room temperature for 1 d. After the mixture was evaporated to dryness, the residue was extracted with dichloromethane. Addition of hexane to the extract gave yellow precipitates, which were filtered and dried *in vacuo* by heating at 45 °C for 3 h to afford Ib as a ¼ dichloromethane adduct. Yield 76%.

Preparation of $[\{Pd(C_6H_4CH_2PPh_2)Cl\}_2]\cdot\frac{1}{2}Me_2C{=}O$ (II)

A mixture of Ia (0.49 mmol) and LiCl (4.01 mmol) in acetone/H_2O (100 ml/5 ml) was stirred for 1d at room temperature. The resulting pale yellow precipitates were collected and washed well with a methanol/water (1/1) mixed solvent to yield II as a ½ acetone adduct. Yield 86%. IR, ν(C=O) 1720 cm^{-1}.

Reaction of II with dmpy

An acetone solution (10 ml) containing II (0.16 mmol) and dmpy (0.35 mmol) was stirred for 20 h at room temperature. Addition of hexane to the resulting mixture gave $[Pd(C_6H_4CH_2PPh_2)Cl(dmpy)]$ (III) as white crystals. Yield 50%.

Reaction of II with Tl(acac)

A dichloromethane suspension (10 ml) containing II (0.19 mmol) and Tl(acac) (0.39 mmol) was stirred for 20 h at room temperature. After centrifuging the reaction mixture the resulting supernatant solution was concentrated and passed through a silica gel column (200 mesh, 12 × 55 mm) with dichloromethane. The yellow fraction was evaporated to dryness to give $[Pd(C_6H_4CH_2PPh_2)(acac)]$ (IV) as yellow-white crystals. Yield 41%.

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*The α-protons of dmpy in the minor component IIIb could not be distinguished owing to overlapping with aromatic protons.

**It seems that the triplet at δ 6.83 overlaps with a signal due to a phenylene proton of IIIb.

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