A Hypervalent Phosphorane–Palladium Cation Complex Bearing Benzaldehyde†

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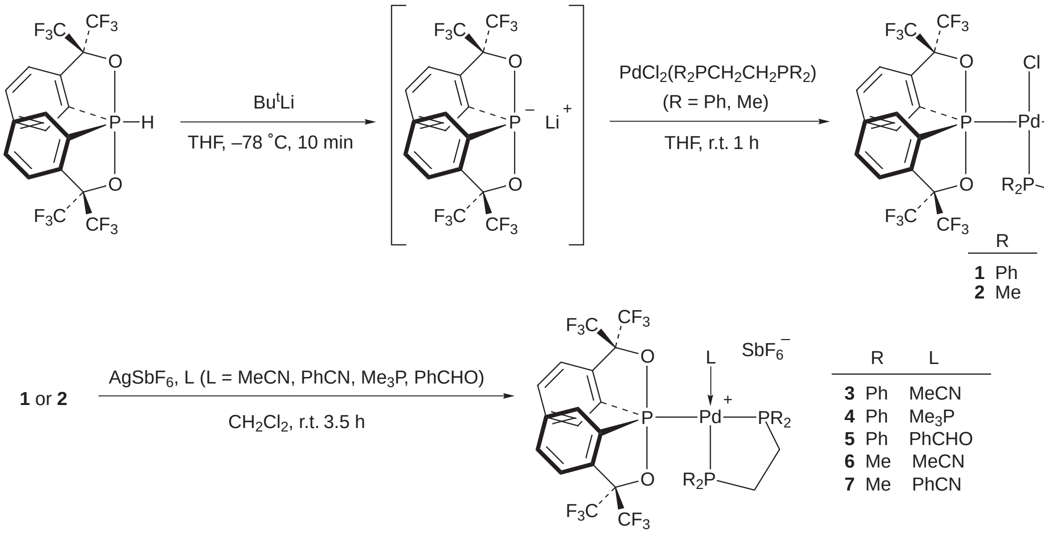
$[Rf_2PPd(PhCHO)(Ph_2PCH_2CH_2PPh_2)] + SbF_6^-[Rf = o\text{-}C_6H_4C(CF_3)_2O]$ **5** is prepared by the reaction of $Rf_2PPdCl(Ph_2PCH_2CH_2PPh_2)$ **1** with $AgSbF_6$ in the presence of benzaldehyde in 92% yield, and the structure determined by X-ray diffraction analysis.

Palladium cations have attracted interest recently in organic synthesis as chiral Lewis acids[1] and in polymerization catalysts.[2] Although the isolation and structural characterization of several palladium(II) cations[3] have been reported and intermediacy of some carbonyl and imine complexes postulated,[4] there has been no report on the crystal structure of those bearing an aldehyde. During the course of our investigation on compounds bearing a hypervalent Group 15 element–transition metal bond;[5] we isolated several five-coordinate antimony(V) compounds bearing an Sb–Fe bond. Here we report the synthesis, structures and some reactions of five-coordinate phosphorus(V) compounds bearing palladium(II) cations. Especially the stable palladium(II) cation **5** with benzaldehyde, which is the first example of a fully structurally characterized palladium cation–aldehyde complex, is interesting not only in relation to the structure, but also as to the possibility that novel chiral catalysts bearing a hypervalent Group 15 element–palladium bond can be prepared based on our recent isolation of chiral hypervalent phosphoranes with a chiral center only at the phosphorus atom.[6]

First we tried to synthesize $Rf_2PPdCl(PR_3)_2$ [$Rf = o\text{-}C_6H_4C(CF_3)_2O$, R = Ph or Me] by the reaction of lithium phosphoranide $Rf_2P^-Li^+$, generated *in situ* from the reaction of Rf_2PH with Bu^tLi at −78 °C, with $PdCl_2(PR_3)_2$. However, these complexes were too unstable to isolate. Fortunately, when we used $PdCl_2(R_2PCH_2CH_2PR_2)$ (R = Ph or Me) as a starting material, stable $Rf_2PPdCl(R_2PCH_2CH_2PR_2)$ (R = Ph, 82% **1**; R = Me, 73% **2**) were obtained in good yields (Scheme 1).

Suitable crystals of these complexes for X-ray diffraction analysis were obtained by recrystallization from CH_2Cl_2/n-hexane at low temperatures. The results showed a square planar structure at the palladium atom and a trigonal bipyramidal structure at the hypervalent phosphorus atom in both cases, and the ORTEP drawing of $Rf_2PPdCl(Ph_2PCH_2CH_2PPh_2)$ **1** and crystal data are omitted by shortening.

The reaction of complexes **1** and **2** with $AgSbF_6$ in the presence of Lewis bases gave stable palladium cation complexes $[Rf_2PPd(L)(R_2PCH_2CH_2PR_2)]^+SbF_6^-$(R = Ph, L = MeCN, 96% **3**; R = Ph, L = Me_3P, 93% **4**, R = Ph, L = PhCHO, 92%; **5** R = Me, L = MeCN, 89% **6**; R = Me, L = PhCN, 83% **7**) in high yields (Scheme 1). Although we were able to isolate **5**, $[Rf_2PPd(PhCHO)(Me_2PCH_2CH_2PMe_2)]^+SbF_6^-$ could not be isolated from the reaction of $Rf_2PPdCl(Me_2PCH_2CH_2PMe_2)$ **2** with $AgSbF_6$ in the presence of benzaldehyde, probably because of the strong electron-donating property of 1,2-bis(dimethylphosphino)ethane and the weak coordinating ability of the aldehyde (see below). The IR spectrum of **5** showed the C=O stretching frequency at 1629 cm^{-1} (KBr) which is lowered by 72 cm^{-1} than that for free benzaldehyde (1701 cm^{-1}, KBr). In the ^{13}C NMR (CD_2Cl_2) the signal of the C=O carbon was observed at δ 202, at lower field than that of free benzaldehyde δ 192. These results are consistent with the Lewis acidity of the palladium cation



Scheme 1

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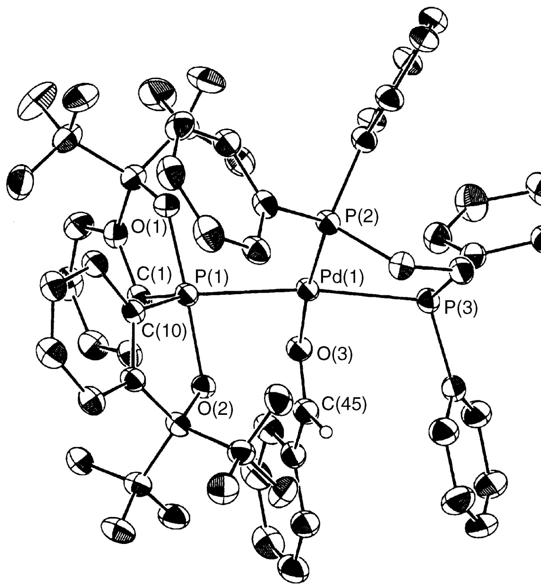

Fig. 1 Molecular structure of complex **5**. Selected bond lengths (Å) and angles (°): Pd1–O3 2.170(3), Pd1–P1 2.371(1), Pd1–P2 2.249(1), Pd1–P3 2.352(1), P1–O1 1.780(3), P1–O2 1.851(3), P1–C1 1.831(3), P1-C10 1.845(3); O3–Pd1-P1 88.2(1), O3–Pd1–P2 173.1(1), O3–Pd1–P3 90.9(1), P1–Pd1–P2 98.0(1), P1–Pd1–P3 171.1(1), P2–Pd1-P3 83.3(1), O1–P1–O2 177.3(2)

$[Rf_2PPd(dppe)]^+$ and the data for other Lewis acid–aldehyde complexes such as $B(C_6F_5)_3 \cdot PhCHO$, $[CpFe(CO)_2(PhCHO)]^+PF_6^-$, and $Ti(OPr^i)Cl_3(PhCHO)(OEt_2)$.[7] Suitable crystals of complex **5** for structural analysis were obtained by recrystallization from $CH_2Cl_2/CHCl_3$ in a freezer. The ORTEP drawing for complex **5** is shown in Fig. 1. The geometry around the palladium atom is square planar and that of the hypervalent phosphorus atom is trigonal bipyramidal. Thus, the structures of **1** and **5** are essentially the same. The benzaldehyde is coordinated to the palladium atom in σ (η^1) fashion, and the plane of the aldehyde is perpendicular to the plane of the palladium which is defined by P(1)–P(2)–P(3)–O(3). The Pd1–O3 bond length [2.170(3) Å] in **5** is longer than that in palladium alkoxide [2.046(2)–2.106(3) Å][8] or palladium cation–ketone complexes [2.101(5)–2.116(5) Å],[3] indicating that the interaction between the palladium cation and the oxygen of the benzaldehyde is not so strong as that of ketones. This weak coordination may be a reason why **5** did not react with excess of acetophenone silyl enol ether at room temperature for 1 d. However, **5** did react with MeLi at −94 °C to give 1-phenylethanol quantitatively.

Synthesis of a chiral complex, which corresponds to **5**, and the asymmetric induction by chiral **5** are currently under investigation.

Experimental

Preparation of complexes **1** *and* **2**.—$[Rf_2P]^-Li^+$ was generated *in situ* by treatment of Rf_2PH (504 mg, 0.98 mmol) with Bu^tLi (1.64 M in *n*-pentane, 0.60 mL, 0.98 mmol) in THF (15 mL) at −78°C for 10 min and $PdCl_2(dppe)$ (564 mg, 0.98 mmol) was added. The mixture was stirred for 1 h at room temperature and was filtered. Complex **1** (848 mg, 0.80 mmol) was obtained in 82% yield in a pure form after chromatography [SiO_2, benzene] and **2** was obtained by similar procedures; **1** [mp *ca.* 245 °C (decomp.) and **2** [mp *ca.* 250 °C (decomp.] gave satisfactory elemental analyses for C, H and N. Complex **1**: ^{19}F NMR ($CDCl_3$) δ − 74.3 (q, 3 F, $J = 10$), −74.2 (q, 3 F, $J = 10$), −73.4 (q, 3 F, $J = 10$), −72.9 (q, 3 F, $J = 10$); ^{31}P NMR ($CDCl_3$) δ 4.6 (dd, 1 P, $J = 12$, 750), 47.8 (dd, 1 P, $J = 24$, 750), 52.4 (dd, 1 P, $J = 12$, 24). Complex **2**: ^{19}F NMR ($CDCl_3$) δ −75.1 (q, 3 F, $J = 9$), −74.6 (q, 3 F, $J = 9$), −73.9 (q, 3 F, $J = 9$), −73.1 (q, 3 F, $J = 9$); ^{31}P NMR ($CDCl_3$) δ 4.1 (dd,1 P, $J = 17$, 745), 44.7 (dd, 1 P, $J = 17$, 22), 51.9 (dd, 1 P, $J = 17, 745$).

Preparation of Complex **5**.—Complex **1** (420 mg, 0.40 mmol) was added to a solution of $AgSbF_6$ (137 mg, 0.40 mmol) in CH_2Cl_2 (10 mL) at room temperature. After 20 min, benzaldehyde (0.20 mL, 2.00 mmol) was added and the mixture was stirred for 3.5 h. Filtration of the reaction mixture after addition of Et_2O gave analytically pure cation complex **5** [494 mg, 0.36 mmol, 92%, mp *ca.* 130 °C (decomp.] as yellow precipitates. Other cation complexes **3**, **4**, **6**, and **7** were obtained by similar procedures and will be reported later in detail. All cation complexes gave satisfactory elemental analyses for C, H and N. Complex **5**: ^1H NMR (CD_2Cl_2) δ 9.12 (br s, 1 H, PhC*H*O); ^{19}F NMR (CD_2Cl_2) δ −77.0 (br q, 6 F), −75.9 (br q, 6 F); ^{31}P NMR (CD_2Cl_2) δ 1.0 (br dd, 1 P), 50.6 (dd, 1 P, $J = 20$, 613 Hz), 55.7 (br dd, 1 P); ^{13}C NMR (CD_2Cl_2) δ 202 (m, 1 C, Ph*C*HO); IR (KBr, νC=O) 1629 cm^{-1}.

Crystal Data for Complex $\mathbf{5}\cdot 3CHCl_3$.— $C_{54}H_{41}F_{18}O_3Cl_9P_3PdSb$, $M = 1720.07$, triclinic, space group $P\bar{1}$, $a = 11.614(1)$, $b = 15.0900(9)$, $c = 20.965(2)$ Å, $\alpha = 99.037(5)$, $\beta = 98.537(4)$, $\gamma = 110.692(5)°$, $U = 3310.8$ Å^3, $Z = 2$, $D_c = 1.53$ g cm^{-3}, $T = 200$ K. Crystal data were collected on a Mac Science DIP2030 imaging plate equipped with graphite-monochromated Mo–Kα radiation ($\lambda = 0.71073$ Å). Unit cell parameters were determined by autoindexing several images in each data set separately with the program DENZO.[9] For each data set, rotation images were collected in 3° increments with a total rotation of 180° about ϕ. Data were processed by using SCALEPACK.[9] The structures were solved by a direct method with the program Crystan-GM (Mac Science) and by refined full-matrix least squares. Final $R1 = 0.063$ ($Rw = 0.076$) for 8944 observed reflections (1002 parameters) with $I > 3\sigma(I)$. Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Research (S)*, 1999, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 423/21.

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