Short Communication

A new mixed alkoxo aryloxo palladium complex with a bidentate nitrogen donor system

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(Received October 2, 1992; revised December 10, 1992)

Abstract

The reaction of [Pd(OPh)$_2$(bpy)] with 1,1,1,3,3,3-hexafluoro-2-propanol affords a 'mixed' aryloxo alkoxo palladium complex, [Pd(OCH(CF$_3$)$_2$)(OPh)(HOPh)(bpy)] (4). A single crystal X-ray diffraction study of 4 shows the presence of an intermolecular O–H$\cdots$O hydrogen bond and an intramolecular C–H$\cdots$O interaction, which could represent the initial stage of a base-assisted β-hydride elimination.

Introduction

Information concerning the nature and properties of palladium alkoxide and aryloxide complexes is timely in view of the interest in a number of important palladium-catalyzed synthetic organic reactions which involve such complexes as intermediates [1]. Recent examples include the lactonization of unsaturated alcohols, the oxidation of catecholates and the acetalization of ketones [2–4]. Unfortunately, the synthesis and reactivity of palladium alkoxide and aryloxide complexes have been little explored, probably because it was thought that the Pd–O bond would be weak, due to a mismatch of the hard, basic RO$^-$ ligands with a soft Group VIII metal center, and therefore difficult to study [5]. However, Bäckvall et al. showed, using theoretical calculations, that the palladium–oxygen bond is of comparable strength or stronger than the palla-

dium–carbon bond [6]. Recently, in our research concerning the oxygenation of aromatic compounds [7], a new class of nitrogen ligated palladium(II) compounds containing aryloxide ligands have been prepared. In this paper the first example of a late transition metal complex with both an alkoxide and an aryloxide ligand, [Pd(OCH(CF$_3$)$_2$)(OPh)(HOPh)(bpy)] (4), is reported.

Experimental

General

Reactions were performed in an atmosphere of nitrogen using standard Schlenk techniques. Solvents were dried and stored under nitrogen. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 200 spectrometer at 298 K. IR spectra (KBr discs) were recorded on a Perkin-Elmer 283 instrument. Elemental analyses were carried out by the Institute of Applied Chemistry (TNO) Zeist or by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. The complex [Pd(OPh)$_2$(bpy)] was made according to literature procedures [8].

[Pd(OCH(CF$_3$)$_2$)(OPh)(HOPh)(bpy)] (4)

To a suspension of [Pd(OPh)$_2$(bpy)] (1) (0.20 g; 0.45 mmol) in CH$_2$Cl$_2$ (15 ml) was added 1,1,1,3,3,3-hexafluoro-2-propanol (0.38 g; 2.25 mmol). After 1 h stirring the yellow solution was filtered off over celite and evaporated to a small volume (c. 5 ml). The pure product was obtained by diffusion of pentane into this solution. The resulting long, needle-shaped yellow crystals (suitable for X-ray diffraction) were washed with pentane (3×10 ml) and dried *in vacuo*. Yield 0.22 g (81%). ^{1}H NMR (CD$_2$Cl$_2$): 8.83 (dd, 1H, ^3J(H, H) = 6 Hz, ^4J(H, H) = 1 Hz, H$_6$), 8.47 (dd, 1H, ^3J(H, H) = 6 Hz, ^4J(H, H) = 1 Hz, H$'_6$), 8.15–8.03 (m, 2H, H$_4$, H$'_4$), 7.98 (d, 2H, ^3J(H, H) = 8 Hz, H$_3$, H$'_3$), 7.65 (td, 1H, ^3J(H, H) = 6 Hz, ^4J(H, H) = 1 Hz, H$'_5$), 7.46 (td, 1H, ^3J(H, H) = 6 Hz, ^4J(H, H) = 1 Hz, H$_5$), 7.32 (d, 2H, ^3J(H, H) = 7 Hz, o-ArH), 7.07 (td, 2H, ^3J(H, H) = 7 Hz, ^4J(H, H) = 1 Hz, m-ArH), 6.57 (td, 1H, ^3J(H, H) = 7 Hz, ^4J(H, H) = 1 Hz, p-ArH), 4.26 (septet, 1H, ^3J(F, H) = 7 Hz). ^{13}C NMR (CD$_2$Cl$_2$): 168.33 (ipso-CAr), 157.44, 157.35 (C$_2$), 152.30, 150.12 (C$_6$), 142.02, 141.58 (C$_5$), 130.73 (ortho-CAr), 128.83, 128.57, 123.96, 123.76 (C$_3$, C$_4$), 121.51 (meta-CAr), 117.21 (para-CAr), 75.30 (OCH, ^2J(C, F) = 30.5 Hz).

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X-ray data collection and structure refinement

Complex 4, $C_{25}H_{20}F_6N_2O_3Pd$, $M_r = 616.85$, yellow block-shaped crystal ($0.60 \times 0.37 \times 0.25$ mm), space group $P2_1/c$, with $a = 8.3241(14)$, $b = 11.0316(17)$, $c = 26.376(3)$ Å, $\beta = 93.01(1)°$, $V = 2418.7(6)$ Å^3, $Z = 4$, $D_{calc} = 1.694$ g cm^{-3}, $F(000) = 1232$, μ(Mo Kα) = 8.3 cm^{-1}; 5091 independent reflections ($0.77 < \theta < 26.5°$; ω/2θ scan; $T = 160$ K) were measured on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å; 50 kV, 200 mA). The crystal was of rather poor quality, as indicated by broad reflection profiles. Data were corrected for Lorentz–polarization effects, for a small linear decay (2.3%) of the intensity control reflections and for absorption (DIFABS; correction range 0.873–1.282). The structure was solved by Patterson (SHELXS86) and difference Fourier techniques and refined with full-matrix least-squares (SHELX76). The O(3) H atom was located from a difference Fourier map, all other hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms. All non-H atoms were refined with anisotropic thermal parameters, hydrogen atoms with one common isotropic thermal parameter. Convergence was reached at $R = 0.0694$, $R_w = 0.0663$, $w = 1/[\sigma^2(F)]$ for 3328 reflections with $I > 3.0$ $\sigma(I)$ and 338 parameters. See also 'Supplementary material'.

Results and discussion

Existing methods for preparing palladium alkoxide complexes with donor ligands [1] are not very successful for the preparation of palladium alkoxide complexes containing N-donor ligands. A new and convenient synthetic method for the synthesis of such complexes comprises the 2:1 molar reaction of sodium phenoxide (NaOPh) with $Pd(OAc)_2$ in the presence of bpy (2,2'-bipyridine), tmeda (N,N,N',N'-tetramethylethylene-diamine), dpe (1,2-dipiperidinoethane) or dmap (2-N,N-(dimethylamino)methylpyridine). This reaction affords new, air-stable, solid, orange complexes $[Pd(OPh)_2(bpy)]$ (1a), $[Pd(OPh)_2(tmeda)]$ (1b), $[Pd(OPh)_2(dpe)]$ (1c) and $[Pd(OPh)_2(dmpa)]$ (1d) (ν(C–O) = 1280 1a, 1b and 1d; 1275 cm^{-1} 1c) (see Scheme 1). In reactions with pentafluorophenol ($pK_a = 5.52$), complexes 1 undergo quantitative substitution of the phenoxide anion for $C_6F_5O^-$ to afford $[Pd(OC_6F_5)_2(bpy)]$ (2a), $[Pd(OC_6F_5)_2(tmeda)]$ (2b), $[Pd(OC_6F_5)_2(dpe)]$ (2c) and $Pd(OC_6F_5)_2(dmap)]$ (2d) (ν(C–O) = 1310 2a, 2b and 2d; 1305 cm^{-1} 2c) (see Scheme 1). Satisfactory microanalysis results have been obtained for the new compounds 1a, 1b, 1d, 2a, 2b and 3. The tmeda complexes 1b and 2b both react with an excess of pentafluorothiophenol ($pK_a = 2.68$) to afford
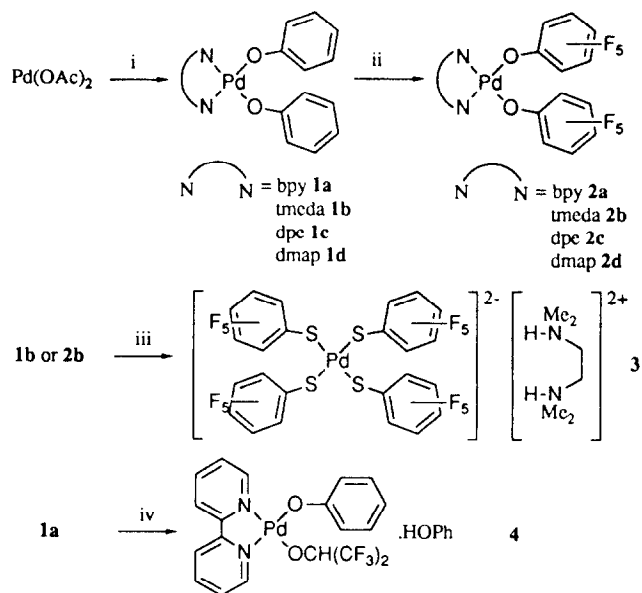
Scheme 1. Reagents: i: bpy, tmeda, dpe or dmap, NaOPh, CH_2Cl_2; ii: HOC_6F_5, CH_2Cl_2; iii: HSC_6F_5, CH_2Cl_2; iv: $HOCH(CF_3)_2$, CH_2Cl_2.

the crystalline complex $[Pd(SC_6F_5)_4][H(Me)_2NCH_2-CH_2N(Me)_2H]$ (3) containing two N–H$\cdots$S hydrogen bonds [8].

An interesting reactivity of 1a is found in its reaction with an excess of 1,1,1,3,3,3-hexafluoro-2-propanol ($pK_a = 9.3$), that affords an unusual palladium complex $[Pd(OCH(CF_3)_2)(OPh)(HOPh)(bpy)]$ (4) (ν(C–O) = 1275; 1260 cm^{-1}) with an alkoxide and an aryloxide ligand (Scheme 1). To the best of our knowledge this is the first isolated 'mixed' alkoxide aryloxide metal complex. A single crystal X-ray diffraction study of 4 shows this complex to have the same geometry as found in the crystal structures of the bis-aryloxo palladium complexes 1a and 2a [8]. Complex 4 possesses a square planar coordination sphere containing two different anionic ligands, $-OC_6H_5$ and $-OCH(CF_3)_2$, and this is, therefore, the first structure report of a 'mixed' alkoxo aryloxo palladium complex (Fig. 1).

The C–O distance of the phenoxide unit in 4 is slightly longer than those found in $[Pd(OPh)_2(bpy)]$ (1a) and $[Pd(OC_6F_5)_2(bpy)]$ (2a) (4: 1.359(10), 1a: 1.332(13), 2a: 1.308(7) Å). An explanation for this difference, although small, is to be found in the association of phenol to the O atom of the phenoxide ligand through strong O–H$\cdots$O hydrogen bonding (O(1)$\cdots$O(3) 2.642(8) Å). Lengthening of a C–O bond in an aryloxide unit was also reported for the association of phenol to $[Pd(Me)(OPh)(PMe_3)_2]$ [9]. Another factor that can contribute to a lengthening of the C–O distance of the phenoxide unit in 4 is found in the position of the acidic proton of the $OCH(CF_3)_2$ group close to the oxygen atom of the phenoxide fragment, which can be seen as a C–H$\cdots$O interaction (O(1)$\cdots$C(17) 2.95(1)

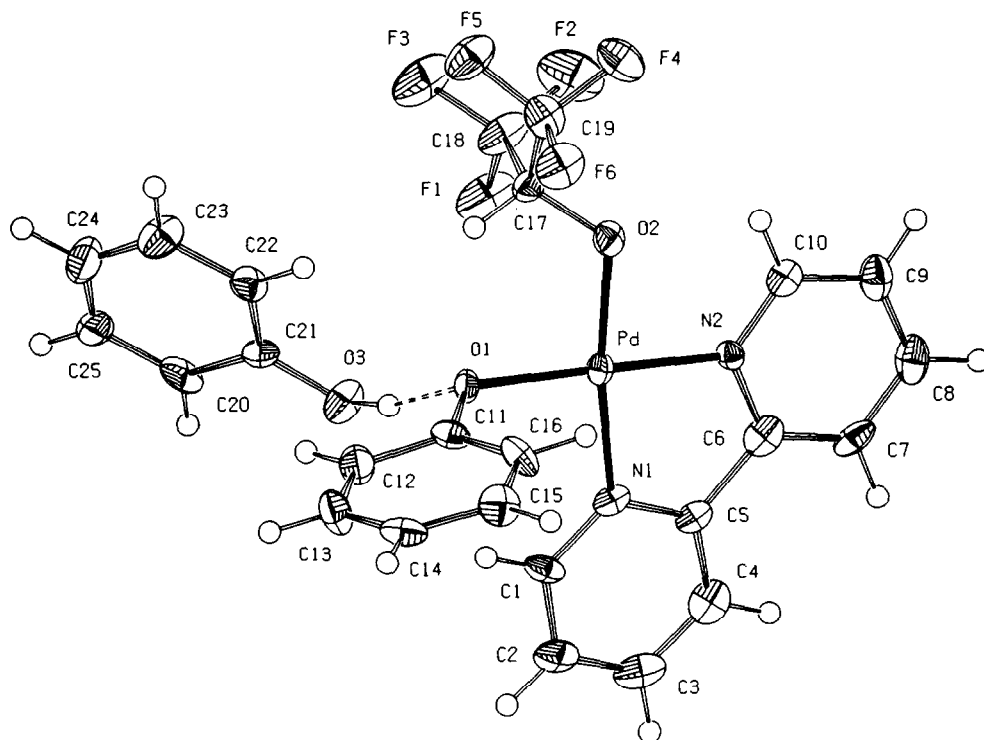Fig. 1. Thermal ellipsoid plot (at 50% probability) of [Pd(OCH(CF$_3$)$_2$)(OPh)(HOPh)(bpy)] (4). Selected bond distances (Å) and angles (°) for 4: Pd–O(1) 1.997(5); Pd–O(2) 1.984(6); Pd–N(1) 1.999(7); Pd–N(2) 1.996(8); O(1)–C(11) 1.359(10); O(2)–C(17) 1.363(10); O(1)···O(3) 2.642(8); O(1)···C(17) 2.95(1); O(1)–Pd–O(2) 92.1(2); O(1)–Pd–N(1) 95.9(3); O(1)–Pd–N(2) 175.2(3); O(2)–Pd–N(1) 171.8(3); O(2)–Pd–N(2) 90.8(2); N(1)–Pd–N(2) 81.2(3); Pd–O(1)–C(11) 119.9(5); Pd–O(2)–C(17) 120.2(5).

Å). The C–H bond is polarized and forms an electrostatic interaction with the O atom of the phenoxide group. C–H···O contacts may be termed steering interactions which, though small in energy (1–2 kcal mol^{-1}), are sufficient to select a preferred molecular conformation [10]. This intramolecular interaction could represent the initial stage of a base-assisted β-hydride elimination, involving transfer of the proton from OCH(CF$_3$)$_2$ to the oxygen atom of the phenoxide anion, that would result in a ketone and a phenol coordinated to a palladium atom (see Scheme 2).

Such complexes have recently been proposed as intermediates in palladium-catalyzed acetalization reactions [4]. The next step is the loss of hexafluoroacetone and the formation of palladium aryloxide hydride species, which will decompose further. However, few stable hydride alkoxide or aryloxide palladium(II) complexes are known in the literature [11]. The possibility of promoting a base-assisted elimination reaction with

complex 4, to provide a potentially stable palladium(II) aryloxide hydride with N-donor ligands is now being further investigated.
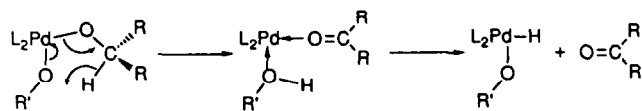
Supplementary material

Further crystallographic details can be obtained on request from the Director of the Cambridge Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB21EW, UK.

Acknowledgements

Scheme 2. Base-assisted elimination reaction (L$_2$ = bidentate donor ligand).

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