

Short Communication

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

G. Marc Kapteijn, David M. Grove, Gerard van Koten*

Debye Research Institute, Department of Metal-Mediated Synthesis, University of Utrecht, Padualaan 8, 3584 CH Utrecht (Netherlands)

Wilberth J. J. Smeets and Anthony L. Spek

Bijvoet Research Institute, Vakgroep Kristal- en Structuurchemie, University of Utrecht, Padualaan 8, 3584 CH Utrecht (Netherlands)

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

Abstract

The reaction of $[\text{Pd}(\text{OPh})_2(\text{bpy})]$ with 1,1,1,3,3,3-hexafluoro-2-propanol affords a 'mixed' aryloxo alkoxo palladium complex, $[\text{Pd}(\text{OCH}(\text{CF}_3)_2)(\text{OPh})(\text{HOPh})(\text{bpy})]$ (**4**). A single crystal X-ray diffraction study of **4** shows the presence of an intermolecular O–H···O hydrogen bond and an intramolecular C–H···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 aryloxo 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 aryloxo 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 aryloxo ligands have been prepared. In this paper the first example of a late transition metal complex with both an alkoxide and an aryloxo ligand, $[\text{Pd}(\text{OCH}(\text{CF}_3)_2)(\text{OPh})(\text{HOPh})(\text{bpy})]$ (**4**), is reported.

Experimental

General

Reactions were performed in an atmosphere of nitrogen using standard Schlenk techniques. Solvents were dried and stored under nitrogen. ^1H 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 $[\text{Pd}(\text{OPh})_2(\text{bpy})]$ was made according to literature procedures [8].

$[\text{Pd}(\text{OCH}(\text{CF}_3)_2)(\text{OPh})(\text{HOPh})(\text{bpy})]$ (**4**)

To a suspension of $[\text{Pd}(\text{OPh})_2(\text{bpy})]$ (**1**) (0.20 g; 0.45 mmol) in CH_2Cl_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%). ^1H NMR (CD_2Cl_2): 8.83 (dd, 1H, $^3J(\text{H}, \text{H})=6$ Hz, $^4J(\text{H}, \text{H})=1$ Hz, H_6), 8.47 (dd, 1H, $^3J(\text{H}, \text{H})=6$ Hz, $^4J(\text{H}, \text{H})=1$ Hz, H'_6), 8.15–8.03 (m, 2H, H_4 , H'_4), 7.98 (d, 2H, $^3J(\text{H}, \text{H})=8$ Hz, H_3 , H'_3), 7.65 (td, 1H, $^3J(\text{H}, \text{H})=6$ Hz, $^4J(\text{H}, \text{H})=1$ Hz, H'_5), 7.46 (td, 1H, $^3J(\text{H}, \text{H})=6$ Hz, $^4J(\text{H}, \text{H})=1$ Hz, H_5), 7.32 (d, 2H, $^3J(\text{H}, \text{H})=7$ Hz, *o*-ArH), 7.07 (td, 2H, $^3J(\text{H}, \text{H})=7$ Hz, $^4J(\text{H}, \text{H})=1$ Hz, *m*-ArH), 6.57 (td, 1H, $^3J(\text{H}, \text{H})=7$ Hz, $^4J(\text{H}, \text{H})=1$ Hz, *p*-ArH), 4.26 (septet, 1H, $^3J(\text{F}, \text{H})=7$ Hz). ^{13}C NMR (CD_2Cl_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, $^2J(\text{C}, \text{F})=30.5$ Hz).

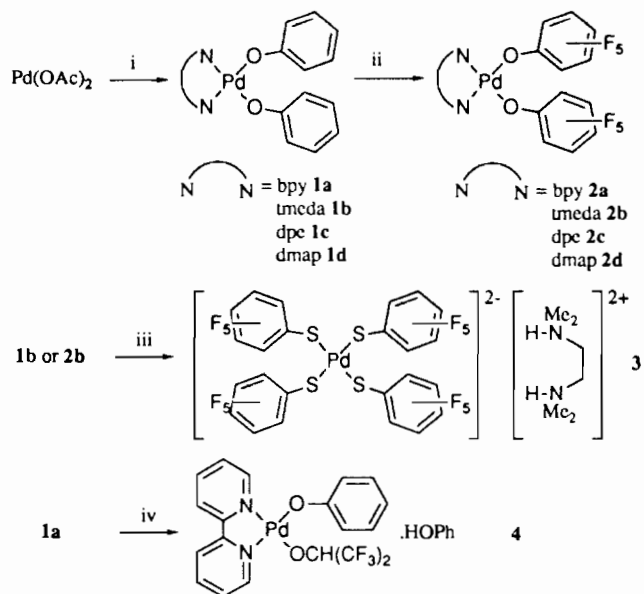
*Author to whom correspondence should be addressed.

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, $\beta = 93.01(1)^\circ$, $V = 2418.7(6)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.694$ g cm⁻³, $F(000) = 1232$, $\mu(\text{Mo K}\alpha) = 8.3$ cm⁻¹; 5091 independent reflections ($0.77 < \theta < 26.5^\circ$; $\omega/2\theta$ scan; $T = 160$ K) were measured on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated Mo K α 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'*-tetramethylethylenediamine), 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(dmap)] (**1d**) ($\nu(\text{C-O}) = 1280$ **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 C₆F₅O⁻ to afford [Pd(OC₆F₅)₂(bpy)] (**2a**), [Pd(OC₆F₅)₂(tmeda)] (**2b**), [Pd(OC₆F₅)₂(dpe)] (**2c**) and Pd(OC₆F₅)₂(dmap)] (**2d**) ($\nu(\text{C-O}) = 1310$ **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, CH₂Cl₂; ii: HOC₆F₅, CH₂Cl₂; iii: HSC₆F₅, CH₂Cl₂; iv: HOCH(CF₃)₂, CH₂Cl₂.

the crystalline complex [Pd(SC₆F₅)₄][H(Me)₂NCH₂-CH₂N(Me)₂H] (**3**) containing two N-H···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(CF₃)₂)(OPh)(HOPh)(bpy)] (**4**) ($\nu(\text{C-O}) = 1275$; 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, -OC₆H₅ and -OCH(CF₃)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(OC₆F₅)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···O hydrogen bonding (O(1)···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)(PMe₃)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(CF₃)₂ group close to the oxygen atom of the phenoxide fragment, which can be seen as a C–H···O interaction (O(1)···C(17) 2.95(1)

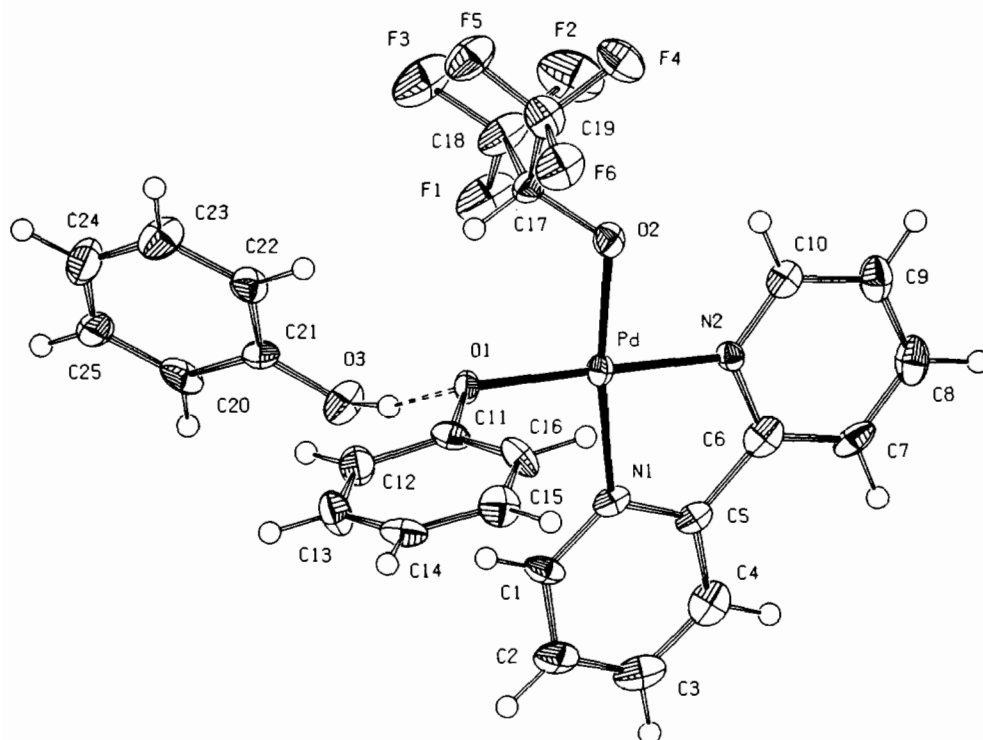


Fig. 1. Thermal ellipsoid plot (at 50% probability) of $[\text{Pd}(\text{OCH}(\text{CF}_3)_2)(\text{OPh})(\text{HOPh})(\text{bpy})]$ (**4**). Selected bond distances (Å) and angles (°) for **4**: Pd–O(1) 1.997(5); Pd–O(2) 1.984(6); Pd–N(1) 1.999(7); Pd–N(2) 1.996(8); O(1)–C(11) 1.359(10); O(2)–C(17) 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 $\text{OCH}(\text{CF}_3)_2$ 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 aryloxy hydride species, which will decompose further. However, few stable hydride alkoxide or aryloxy 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) aryloxy hydride with N-donor ligands is now being further investigated.

Supplementary material

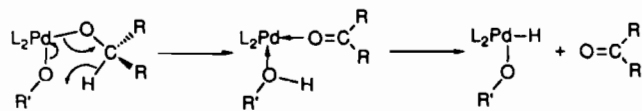
Further crystallographic details can be obtained on request from the Director of the Cambridge Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB21EW, UK.

Acknowledgements

Shell Research B.V. (G.M.K.) is gratefully thanked for financial support. The investigations were supported in part (A.L.S.) by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organization for Scientific Research (N.W.O.).

References

- 1 H. E. Bryndza and W. Tam, *Chem. Rev.*, **88** (1988) 1163.



Scheme 2. Base-assisted elimination reaction (L_2 = bidentate donor ligand).

- 2 B. E. Ali and H. Alper, *J. Org. Chem.*, *56* (1991) 5357.
- 3 P. Barbaro, C. Bianchini, P. Frediani, A. Meli and F. Vizza, *Inorg. Chem.*, *31* (1992) 1523.
- 4 J. Ott, B. Schmid, L. M. Venanzi, G. Wang and T. R. Ward, *New J. Chem.*, *14* (1990) 495.
- 5 (a) R. G. Pearson, *J. Am. Chem. Soc.*, *85* (1963) 3533; (b) F. R. Hartley, *The Chemistry of Platinum and Palladium*, Wiley, New York, 1973, p. 169.
- 6 (a) J. E. Bäckvall, E. E. Bjorkman, L. Petterson and R. J. Siegbahn, *J. Am. Chem. Soc.*, *106* (1984) 4369; (b) *107* (1985) 7265.
- 7 (a) P. L. Alsters, H. T. Theunissen, J. Boersma and G. van Koten, *Recl. Trav. Chim. Pays-Bas*, *109* (1990) 487; P. L. Alsters, J. Boersma and G. van Koten, *Tetrahedron Lett.*, *32* (1991) 675.
- 8 G. M. Kapteijn, D. M. Grove, A. L. Spek and G. van Koten, paper in preparation.
- 9 Y.-J. Kim, K. Osakada, A. Takenaka and A. Yamamoto, *J. Am. Chem. Soc.*, *112* (1990) 1096.
- 10 G. R. Desiraju, *Acc. Chem. Res.*, *24* (1991) 290.
- 11 J. Forbies, M. Green, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, (1977) 1006.