Synthesis of a New Pd(II) Complex with One hfac-*O, O'* and One hfac-Monoxime-*C, N* as Ligands; Unexpected C-O Bond Formation between C^3-Bonded hfac and *N*-Bonded Monoxime

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Reaction of [Pd(hfac)$_2$] with monoximes gave new Pd complexes with one hfac-*O,O'*-chelate and one hfac-oxime-*C,N*-chelate, [Pd(hfac){N(=CRR')OC(OH)(CF$_3$)CHCOCF$_3$}], in which a C-O bond was formed between the C^3-bonded hfac and the *N*-bonded monoxime.

Monoximes coordinate to a metal as neutral molecules through their N or O donor atoms. They also form a η^2–*N,O*– chelate or a bridge between two metals as monoanions through their N-O unit.[1] Coordinated monoximes show some interesting reactivities.[2] Kukushkin *et al* reported that monoximes *N*-coordinated to Pt reacted with each other or with acetone to afford a new *N,N*-chelate or *N,O*-chelate with C-O bond formation respectively.[2] These reactions proceed only under oxidative reaction conditions, accompanying change of the metal oxidation state (Pt(IV) to Pt(II)) or requiring the presence of *p*-chloroperoxybenzoic acid because dehydrogenation of the oximes is required. Here we report the preparation of a new *N,C*-chelated Pd(II) complex under mild reaction conditions without oxidizing agents.

Acetaldoxime was treated with one molar equivalent of bis(hexafluoroacetylacetonato)palladium(II), [Pd(hfac)$_2$], in CH$_2$Cl$_2$ at room temperature for 1 day. A large quantity of n-pentane was added to the solution and the resulting mixture was left to stand in a refrigerator overnight to give yellow needles of [Pd(hfac){N(=CH(Me))OC(OH)(CF$_3$)CHCOCF$_3$] **2a**[3] in a 77% yield. The structure of **2a** was determined by an X-ray diffraction study (Figure 1).[4] The coordination geometry around the palladium atom was square-planar with C_1, N_1, O_2 donor atoms. N(1) in oxime and C(10) in hfac coordinate to Pd(1). The length of the newly formed O(3)-C(8) bond is 1.421(16) Å. C(8) and C(10) have sp^3 characteristics as suggested from the bond lengths and bond angles around them. The absolute configurations at C(8) and C(10) are both *R* in Figure 1. A hydrogen bond seems to exist between O(4)-H and O(5), judging from the short O(4)--O(5) distance(2.671(15) Å).

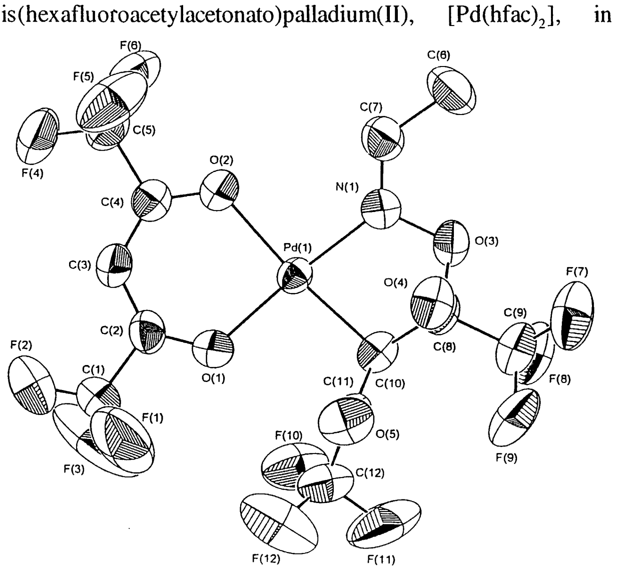


Figure 1. ORTEP drawing of **2a**. The selected bond distances (Å) and angles (°) are as follows; Pd(1)-O(1) = 2.006(9), Pd(1)-O(2) = 2.080(9), Pd(1)-N(1) = 1.973(10), Pd(1)-C(10) = 2.048(12), O(3)-N(1) = 1.412(13), O(3)-C(8) = 1.421(16), C(8)-C(10) = 1.516(17), O(1)-Pd(1)-O(2) = 91.1(4), O(1)-Pd(1)-C(10) = 94.0(5), O(2)-Pd(1)-N(1) = 92.7(4), N(1)-Pd(1)-C(10) = 81.9(5), N(1)-O(3)-C(8) = 107.0(8), O(3)-C(8)-C(10) = 110.2(10), C(8)-C(10)-C(11) = 114.9(10).

The ^{19}F NMR spectrum of **2a** is shown in Figure 2. The pair of low field signals is assigned to the CF$_3$ in a *O,O'*-chelated hfac ligand on the basis of accumulated data.[5,6] One of the CF$_3$ groups in the hfac chelate and the dangling CF$_3$ group in the *C,N*-chelate exhibit F-F coupling with each other through space because the C(1)--C(12) distance is rather short (4.410 Å) in the X-ray structure. Similar through-space F-F coupling has been reported for a trinuclear Pd(II) complex bridged by urea(2-) and methoxide.[6] The NMR data of **2a** are simple, showing that only one set of configurations (*R, R / S, S* or *R, S / S, R*) exists in solution. The configuration in crystal will probabely persist in solution because of the higher stability of *R, R / S, S* owing to the intramolecular hydrogen bond. ^{19}F NMR demonstrated that other monoximes such as acetoxime also reacted with [Pd(hfac)$_2$] to afford the complexes **2**. These complexes were not isolated as solids. When [Pd(hfac)$_2$] and

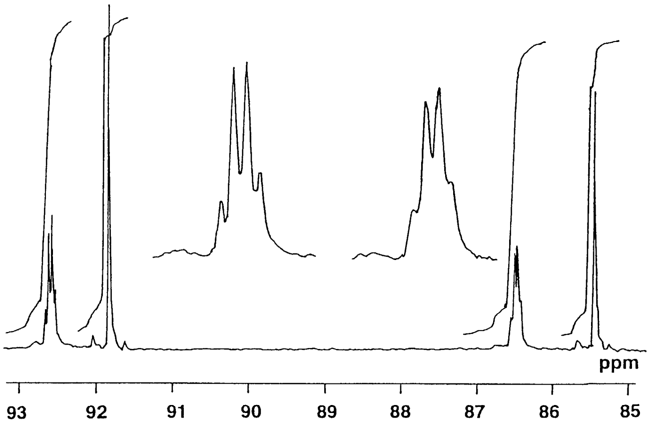
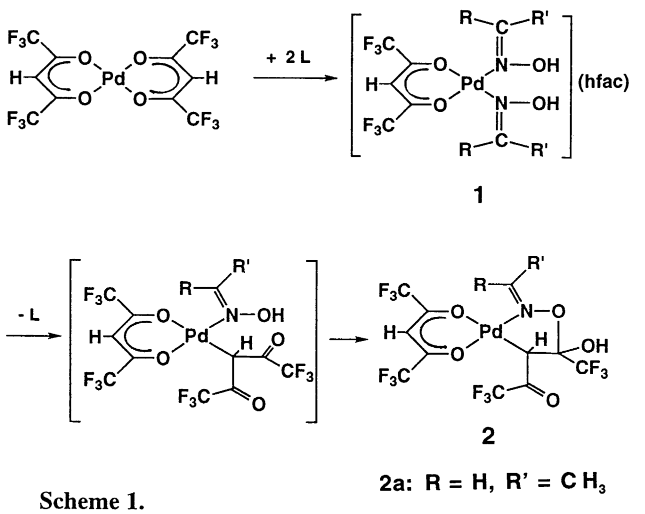


Figure 2. ^{19}F NMR spectrum of **2a** in CDCl$_3$ (ext. C$_6$F$_6$).



Scheme 1.

one molar equivalents of monoxime (L) were reacted at -30 °C in chloroform, the formation of [Pd(hfac)L_2](hfac) **1** and [PdL_4](hfac)$_2$ **3** could be confirmed by NMR spectroscopy.[7] At room temperature the signals of **1** and **3** diminished in intensity and the signals of **2** appeared. Complexes of type **1** have been reported to be the intermediate in the formation of [Pd(β-dik)(β-dik-C^3)L] (β-dik = β-diketonate) in the reaction of [Pd(β-dik)$_2$] and a Lewis base (L).[8] From these facts the reaction is suggested to proceed as shown in Scheme 1; in which includes a nucleophilic attack of the OH group in the *N*-bonded oxime on one of the carbonyl carbons in the C^3-bonded hfac followed by a proton transfer to form the C-O bond. Reaction of monoximes with [Pt(hfac)$_2$] under the same conditions afforded only [Pt(hfac)L_2](hfac) and [PtL_4](hfac)$_2$.

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References and Notes

1 "Comprehensive Coordination Chemistry," ed by G. Wilkinson, Vol. 2, Pergamon Press(1987), pp 269-270.

2 V. Y. Kukushkin, D. Tudela, Y. A. Izotova, V. K. Belsky, and A. I. Stash, *Inorg. Chem.*, **35**, 4926(1996) and references cited therein.

3 Selected data for **2a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.28 (d, 3H, *J*(H-H) = 6 Hz, CH_3), 4.50 (s, 1H, Pd-CH), 6.23 (s, 1H, hfac-CH), 6.86 (br, 1H, OH), 7.38 (q, 1H, *J*(H-H) = 6 Hz, =CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2 (s, CH_3), 37.1 (s, Pd-CH), 92.1 (s, hfac-CH), 103.5 (q, *J*(F-H) = 36 Hz, C-OH), 115.6 (q, *J*(F-C) = 287 Hz, *C*F_3-C(OH)), 116.5 (q, *J*(F-C) = 284 Hz, hfac-CF_3), 117.0 (q, *J*(F-C) = 285 Hz), hfac-CF_3), 119.9 (q, *J*(F-C) = 287 Hz, *C*F_3C(=O)), 159.4 (s, C=N), 175.2 (q, *J*(F-C) = 36 Hz, hfac-CO), 175.9 (q, *J*(F-C) = 36 Hz, hfac-CO), 198.1 (q, *J*(F-C) = 37 Hz, *C*(=O)CF_3). ^{19}F NMR (84 MHz, $CDCl_3$, ext. C_6F_6) δ 85.4 (s, CF_3-C(OH)), 86.5 (q, through-space-J(F-F) = 4 Hz, C(=O)CF_3), 91.8 (s, hfac-CF_3), 92.6 (q, through-space-J(F-F) = 4 Hz, hfac-CF_3). FAB MS. *m/z* 579 (M^+). Anal. Found: C, 24.79; H, 1.35; N, 2.06%. Calcd for $C_{12}H_7O_5NF_{12}Pd$: C, 24.87; H, 1.22; N, 2.42%.

4 Crystal data for **2a**: formula $C_{12}H_7F_{12}N_1O_5Pd_1$, fw 579.6, triclinic, space group $P\bar{1}$, a = 8.731(3) Å, b = 10.066(3) Å, c = 11.403(3) Å, α = 108.97(2)°, β = 89.99(2)°, γ = 96.14(2)°, V = 941.6(5) Å^3, Z = 2, D_{calc} = 2.040 g cm^{-3}, Mo-Kα (λ = 0.7107 Å) radiation, room temperature. All crystallographic measurements were made using a MAC science MXC3 diffractometer. Lattice parameters were determined by application of the automatic diffractometer indexing routine to the positions of 22 reflections. Data were measured in the range $3 \le 2\theta \le 50°$ in the ω-2θ scan with three check reflections being measured every 100 data. The structure was solved by direct methods (SIR92) and refined by full-matrix least squares analysis using 4740 unique reflections resulting in final R factor = 0.062, Rw = 0.077. Refinement was anisotropic for all non-hydrogen atoms.

5 For Example, A. R. Siedle, R. A. Newmark, and L. H. Pignolet, *Inorg. Chem.*, **22**, 2281(1983); S. Okeya, T. Miyamoto, S. Ooi, Y. Nakamura, and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **57**, 395(1984).

6 S. Okeya, S. Koshino, M. Namie, I. Nagasawa, and Y. Kushi, *J. Chem. Soc., Chem. Commun.*, **1995,** 2123.

7 Selected data for **1a** (L = acetaldoxime): ^{19}F NMR (84 MHz, $CDCl_3$, -30 °C, ext. C_6F_6) δ 90.5 (s, hfac$^-$-CF_3), 92.6 (s, hfac-CF_3).

8 S. Okeya, H. Sazaki, M. Ogita, T. Takemoto, Y. Onuki, Y. Nakamura, B. K. Mohapatra, and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **54**, 1978(1981); S. Matsumoto and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, **53**, 1577(1980).