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Acetoxime coordinates to palladium(II) and is catalytically hydrolysed to acetone †

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Several new palladium(II) complexes containing acetoxime as a unidentate ligand were synthesized from *cis*-$[Pd(en)(solv)_2]^{2+}$ **1a** and *cis*-$[Pd(dtod)(solv)_2]^{2+}$ **1b**, in which the displaceable ligand solv is water or acetone, en is ethane-1,2-diamine, and dtod is 3,6-dithia-1,8-octanediol. The acetoxime complexes are characterized by UV-visible spectrophotometry and ^{1}H and ^{13}C NMR spectroscopy in solution. Acetoxime in the mono-oxime complexes *cis*-$[Pd(en)\{N(OH)C(CH_3)_2\}(solv)]^{2+}$ **2a** and *cis*-$[Pd(dtod)\{N(OH)C(CH_3)_2\}(solv)]^{2+}$ **2b** undergoes hydrolysis to acetone and hydroxylamine. The proposed mechanism involves internal attack of a Pd^{II}-bound hydroxo ligand at the coordinated acetoxime. This palladium(II)-catalysed hydrolysis is at least 10^4 times faster than hydrolysis in the absence of a catalyst. The rate enhancement arises from polarization of acetoxime upon coordination to palladium(II), the availability of the nucleophilic hydroxo ligand, and close proximity of these two species. The complex $[Pd(dien)\{N(OH)C(CH_3)_2\}]^{2+}$, which contains the tridentate diethylenetriamine ligand, is almost unreactive toward hydrolysis because it lacks a Pd^{II}-bound aqua or hydroxo ligand, so that the reaction occurs *via* the less-favorable external attack of solvent water. Acetoxime in the bis-acetoxime complex *cis*-$[Pd(dtod)\{N(OH)C(CH_3)_2\}_2]^{2+}$ **3b** hydrolyses very slowly because this complex also lacks aqua or hydroxo ligands. Therefore, this complex was crystallized and its structure determined by X-ray crystallography.

Introduction

Palladium complexes are well known reagents and catalysts in organic synthesis.[1] We recently reported the use of various palladium(II) aqua complexes as catalysts for the hydration and alcoholysis of nitriles,[2,3] hydrolytic cleavage of peptides,[4] decomposition of urea to carbon dioxide and ammonia,[5] and alcoholysis of urea to ammonia and various carbamate esters.[6] Clearly, palladium(II) aqua complexes are versatile catalysts for various reactions. They contain labile aqua or other solvent ligands that can be displaced by a substrate. In many cases, the coordinated substrate thus becomes activated toward nucleophilic addition of water or alcohols. Relatively little is known about oximes as ligands. They predominantly coordinate to transition metals *via* the nitrogen atom.[7] Only several reactions of coordinated oximes have been reported, namely dehydration, ester hydrolysis, and reduction.[8–10] To our knowledge, hydrolysis of oximes catalysed by transition-metal complexes has not been studied. Here we report kinetics of hydrolysis of acetoxime to acetone catalysed by two palladium(II) complexes, identify active species in the hydrolysis reaction, propose a reaction mechanism, and fully characterize a bis(acetoxime) complex that is relatively stable toward hydrolysis.

Experimental

Chemicals

The deuterium-containing compounds D_2O and $DClO_4$, the salts $K_2[PdCl_4]$, $PdCl_2$, and $AgClO_4{\cdot}H_2O$, the hydrolysis substrate $C(CH_3)_2N(OH)$, and the complex *cis*-$[Pt(en)Cl_2]$ were obtained from Sigma Chemical Co. and Aldrich Chemical Co., anhydrous $AgBF_4$ and $AgClO_4$ (**CAUTION**: strong oxidant!) from G. Frederich Smith Chemical Co., ligands ethane-1,2-diamine (en) and 3,6-dithia-1,8-octanediol (dtod) from Aldrich Chemical Co. and acetone-d_6, methanol-d_4, and dimethylformamide-d_7 from Cambridge Isotope Laboratories. These and all other chemicals were of reagent grade.

Proton and carbon-13 NMR spectra

These spectra were recorded with Varian VXR-300 and Bruker DRX-400 spectrometers. The ^{1}H and ^{13}C chemical shifts (δ) are given in ppm downfield relative to tetramethylsilane, using the methyl resonance of the solvent, acetone-d_6, as a secondary reference. The internal reference in ^{1}H NMR kinetic experiments was tetramethylsilane. That in ^{13}C NMR kinetic experiments done in acetone-d_6 was the carbonyl resonance of this solvent because its chemical shift is similar to that of oximes. The quality of the ^{13}C NMR spectra was improved by their acquisition in narrow windows. The ^{1}H and ^{13}C NMR resonances were integrated with respective estimated errors of ±5 and 10%. Concentrations of the compounds were determined on the basis of these integrals and the known initial concentrations of the reagents. Equilibrium constants, rates, and rate constants were calculated from the known concentrations of the reactants and products, with estimated errors of 10–20%.

Palladium(II) complexes

The palladium(II) complexes *cis*-$[Pd(en)Cl_2]$, $[Pd(dien)Cl]Cl$, and *cis*-$[Pd(dtod)Cl_2]$ were prepared by published procedures.[6,11] The chloro ligands were displaced by the solvent ligands (solv) as solutions of these complexes were stirred with two equivalents of $AgBF_4$, $AgClO_4$, or $AgClO_4{\cdot}H_2O$ in acetone-d_6, for 1 h at 25 °C, in the dark. The solid AgCl was filtered off in the dark, and a fresh solution of the solvent complex was used in further experiments. The salt *cis*-$[Pd(en)(solv)_2][ClO_4]_2$ **1a**$(ClO_4)_2$ had the absorption maximum at 360 nm, as reported

† Electronic supplementary information (ESI) available: diagrams of the palladium(II) and platinum(II) catalysts. See http://www.rsc.org/suppdata/dt/b0/b008753j/

before.[11] The complex *trans*-[Pd(PhCN)$_2$Cl$_2$] was prepared by the published procedure.[12] The complex *cis*-[Pd(dtod)Cl$_2$] is soluble in *N*,*N*-dimethylformamide and acetone. Calc. for *cis*-[Pd(dtod)Cl$_2$]: C, 20.04; H, 3.92. Found: C 20.53; H 3.91%. ^{13}C NMR at 293 K in DMF-d_6: δ 60.5, 2CH$_2$; 41.0, CH$_2$; 40.6, CH$_2$; 39.3, CH$_2$ and 39.0, CH$_2$. ^{13}C NMR in DMF-d_6 at 313 K: δ 60.5, 2CH$_2$; 40.8, 2CH$_2$ and 39.15, 2CH$_2$. ^{13}C NMR of *cis*-[Pd(dtod)(solv)$_2$]$^{2+}$ **1b** in acetone-d_6 at 313 K: δ 59.5, 2CH$_2$; 41.6, 2CH$_2$ and 39.2, 2CH$_2$.[3,6] The coordinated solvent (solv) is acetone-d_6 or H$_2$O. Investigated solvent complexes are shown in Chart 1 in the Supporting Information.† The mono(acetoxime) complexes *cis*-[Pd(en){N(OH)C(CH$_3$)$_2$}(solv)][BF$_4$]$_2$ **2a**(BF$_4$)$_2$ and *cis*-[Pd(dtod){N(OH)C(CH$_3$)$_2$}(solv)][BF$_4$]$_2$ **2b**(BF$_4$)$_2$ were prepared from *cis*-[Pd(en)(solv)$_2$][BF$_4$]$_2$ **1a**(BF$_4$)$_2$ and *cis*-[Pd(dtod)(solv)$_2$][BF$_4$]$_2$ **1b**(BF$_4$)$_2$, respectively, and 1 equivalent of C(CH$_3$)$_2$N(OH) in acetone at room temperature. The product was formed within 2 minutes and detected by ^{1}H NMR spectroscopy. The ^{1}H and ^{13}C NMR chemical shifts for the cationic palladium(II) complexes are independent of the counter ion. ^{1}H NMR for acetoxime ligand in acetone-d_6 at 313 K: in **2a**, δ 2.64 s and 2.08 s, 2CH$_3$; N(OH) not detected; in **2b**, δ 2.6 br and 2.2 br, 2CH$_3$; N(OH) not detected. ^{13}C NMR for acetoxime ligand in acetone-d_6 at 313 K: in **2a**, δ 172.8, C=N; 24.3 and 18.4, 2CH$_3$; in **2b**, δ 172.3, C=N; 24.3 and 18.4, 2CH$_3$. The bis(acetoxime) complex *cis*-[Pd(dtod){N(OH)C(CH$_3$)$_2$}$_2$][BF$_4$]$_2$ **3b**(BF$_4$)$_2$ was prepared from 10 ml of a 0.1 M solution of **1b**(BF$_4$)$_2$ and a more than 100-fold molar excess of C(CH$_3$)$_2$N(OH) in acetone at room temperature. The mixture was stirred overnight and the yellow precipitate filtered off. The clear solution contained unspent C(CH$_3$)$_2$N(OH). The solid is soluble in acetone. Isolated yield, 0.30 g or 50%. ^{1}H NMR for acetoxime ligand in **3b** in acetone-d_6 at 313 K: δ 2.6 br and 2.18 br, 2CH$_3$; N(OH) not detected. ^{13}C NMR for acetoxime ligand in **3b** in acetone-d_6 at 313 K: δ 171.4, C=N; 24.7 and 18.6, 2CH$_3$. Calc. for C$_{12}$H$_{28}$B$_2$F$_8$N$_2$O$_4$PdS$_2$: C 23.68; H 4.64. Found: C 23.25; H 4.70%. A crystal of X-ray quality was grown from a saturated solution of **3b** in acetone at room temperature. The bis(acetoxime) complex *cis*-[Pd(en){N(OH)C(CH$_3$)$_2$}$_2$]$^{2+}$ **3a** was prepared similarly and characterized by ^{1}H and ^{13}C NMR spectroscopy. Isolated yield, 60%. Calc. for C$_8$H$_{22}$B$_2$F$_8$N$_4$O$_2$Pd: C 19.76; H 4.56. Found: C 19.51; H 4.61%. ^{1}H NMR for acetoxime ligand in **3a** in acetone-d_6 at 313 K: δ 2.71 s and 2.08 s, 2CH$_3$; N(OH) not detected. ^{13}C NMR for acetoxime ligand in **3a** in acetone-d_6 at 313 K: δ 171.3, C=N; 24.7 and 18.6, 2CH$_3$.

Crystal and molecular structure of *cis*-[Pd(dtod){N(OH)C(CH$_3$)$_2$}$_2$][BF$_4$]$_2$ 3b(BF$_4$)$_2$

Crystallographic details are given in Table 2 and Fig. 1,[13] The systematic absences in the diffraction data were consistent with the space groups *Cc* and *C*2/*c*.[14] The *E* statistics suggested the centrosymmetric space group *C*2/*c*, consistent with the *Z* value and location of the molecule on a twofold axis. The correctness of this was confirmed by the results of refinement which were chemically reasonable and computationally stable. All hydrogen atoms were included in the structure factor calculation at idealized positions and allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. The cationic palladium complex occupies a twofold crystallographic axis. The tetrafluoroborate anion is located in a general position.

CCDC reference number 153204.

See http://www.rsc.org/suppdata/dt/b0/b008753j/ for crystallographic data in CIF or other electronic format.

Binding of acetoxime to the metal complexes

The coordination was followed by UV-visible spectrophotometry and by ^{1}H and ^{13}C NMR spectroscopy. The solvent was neat acetone and acetone that was made 0.300 or 1.50 M in water and the temperature was 313 ± 0.5 K. The concentrations of a solvent complex and acetoxime were varied in the ranges 0.001–0.010 and 0.003–0.030 M, respectively, in spectrophotometric experiments, and in the ranges 0.010–0.100 and 0.030–0.300 M, respectively, in NMR spectroscopic experiments. The binding constants were quantitatively determined by ^{1}H NMR spectroscopy. They were independent within the experimental error of the initial concentrations of each complex and acetoxime. The reported values for each complex in Table 1 are the average results of several experiments.

Kinetics of reactions

The solvent in experiments concerning kinetics of hydrolysis was always acetone-d_6 that was made 0.300 M in water. The temperature was always 313 ± 0.5 K. In the experiments concerning "background" hydrolysis the acetone solution was always made 0.0010 M in DClO$_4$; the initial concentrations of acetoxime were 0.100 and 0.300 M. An average value from these two experiments was taken as the observed rate constant of the "background" hydrolysis. In experiments concerning catalytic hydrolysis the initial concentrations of palladium(II) solvent complex and acetoxime were 0.100 and 0.300 M, respectively, unless stated otherwise. Hydrolysis of acetoxime was followed by ^{1}H NMR spectroscopy. In a typical experiment, to a solution of a freshly prepared solvent complex was added solid C(CH$_3$)$_2$N(OH) to start the reaction, and the acquisition began within less than a minute. The initial rates were determined in experiments in which only the first 3–5% of the reaction were followed. The observed rate constants were determined from the initial rates and the known concentration of the reactive mono(acetoxime) complex. The latter was determined directly from ^{1}H NMR spectra. In experiments concerning turnover numbers the initial concentrations of the catalyst, *cis*-[Pd(dtod)(solv)$_2$]$^{2+}$, and acetoxime were 0.100 and 0.400 M or 0.100 and 0.800 M, respectively. The solvent was acetone-d_6 that was made 1.50 M in D$_2$O.

Composition of the reaction mixtures

The reactant was acetoxime and the products were acetone and hydroxylamine. These three compounds were detected by ^{1}H or ^{13}C NMR spectroscopy. ^{1}H NMR data: for C(CH$_3$)$_2$N(OH), δ 1.79 and 1.78, 2CH$_3$; 9.7 br, OH; for (CH$_3$)$_2$CO, 2.06; for NH$_2$OH: 3.9 br; for hydroxylamine ligand in *cis*-[Pd(dtod)(NH$_2$OH)(solv)]$^{2+}$, 2.1 br. ^{13}C NMR data: for C(CH$_3$)$_2$N(OH), δ 22.5 and 14.5, 2CH$_3$; 154.2, C=N; for (CH$_3$)$_2$CO, 30.0, 2CH$_3$; 207.0 CO. Assignments of resonances were confirmed by spiking the reaction mixture with the pure chemical of interest, if this chemical was commercially available. The chemical shifts could deviate from the stated values by 0.10 ppm or less, depending on the composition of the reaction mixture and other conditions.

Results and discussion

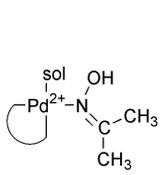
Binding of acetoxime to palladium(II)

Acetoxime replaces relatively labile solvent ligands in *cis*-[Pd(en)(solv)$_2$]$^{2+}$ **1a** and *cis*-[Pd(dtod)(solv)$_2$]$^{2+}$ **1b** and coordinates to palladium(II) *via* the nitrogen atom, forming mono- and bis-(oxime) complexes **2** and **3**. The observed blue shift of the d–d absorption bands of palladium(II) complexes upon oxime coordination is consistent with the relative strengths of the ligand fields of the oxime and solv (acetone and aqua) ligands.[15] Both types of complexes (**2** and **3**) were characterized by ^{1}H and ^{13}C NMR spectroscopy (see above). The methyl ^{1}H resonances of acetoxime move 0.30 and 0.80 ppm downfield upon coordination. Similar shifts were observed for the N-coordinated acetoxime ligands in [PtCl$_3${N(OH)C(CH$_3$)$_2$}]$^-$ and orthopalladated aryl oximes.[9,16,17] The imino ^{13}C resonance of acetoxime also shifts downfield upon coordin-

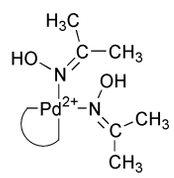
Table 1 Equilibrium constants (unitless numbers)[a] for coordination of acetoxime to palladium(II) and platinum(II)[b]

Solvent complex	K_1	K_2	$K = K_1K_2$
cis-$[Pd(en)(solv)_2]^{2+}$	325	33	1.1×10^4
cis-$[Pd(en)(solv)_2]^{2+}$ [c]	320	30	1.0×10^4
cis-$[Pd(dtod)(solv)_2]^{2+}$	39	3	1.2×10^2
cis-$[Pt(en)(solv)_2]^{2+}$	35	3	1.1×10^2
$[Pd(dien)(solv)]^{2+}$	2	—	—

[a] Defined in eqns. (1) and (2). [b] The solvent was a 0.300 M solution of D_2O in acetone-d_6, so that ligand solv was either of these compounds; the temperature was 313 K. The solvent complexes are shown in Chart 1 in the Supporting Information.† [c] The solvent was a 1.50 M solution of D_2O in acetone-d_6, so that the ligand solv was either of these compounds; the temperature was 313 K.



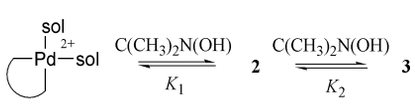
2a
2b



3a
3b

ation, in agreement with the report for O-bound acetamide in $[Pt(dien)\{O{=}C(NH_2)(CH_3)\}]^{2+}$.[18]

The ratio between the concentrations of complexes **2** and **3** depends on the relative concentrations of the starting materials. If a high excess (>100 equivalents) of acetoxime over **1** is added to a 0.100 M solution of **1**, complex **3** is the predominant species in solution. The equilibrium constants K_1, K_2, and K, defined in eqns. (1) and (2), are given in Table 1. Their relatively



(1)

$$K = K_1K_2 \quad (2)$$

high values reflect favorable binding of acetoxime to the palladium(II) complexes.

The presence of 1.5 M water in an acetone solution does not affect oxime binding significantly, as Table 1 shows. Indeed, water is a weaker ligand than acetoxime and does not compete for binding to palladium(II).[19] Thus, a small concentration of water added to the reaction mixture permits catalytic hydrolysis of the coordinated acetoxime without displacing it from the palladium(II) coordination sphere.

Molecular structure and hydrogen bonding in *cis*-[Pd(dtod)-{N(OH)C(CH$_3$)$_2$}$_2$][BF$_4$]$_2$ 3b(BF$_4$)$_2$

A search of the Cambridge Structural Database[20] revealed that compound **3b** is the first crystallographically characterized palladium(II) complex with one bidentate sulfur ligand and two unidentate nitrogen ligands. As expected, the nitrogen ligands occupy *cis* positions. Complex **3b** sits on a crystallographic two-fold axis that contains the palladium atom and bisects the C(1)–C(1A) bond. The tetrafluoroborate anions sit in general positions. As Fig. 1 shows, the coordination around the palladium atom is square planar with typical palladium–sulfur and –nitrogen distances. The dihedral angle between the planar acetoxime ligands is 60.2(2)°. The torsion angle S(1)–C(1)–C(1A)–S(1A) is 52.0(2)°. In the intramolecular hydrogen bond O(2)–H(2)···O(1) the oxygen–oxygen distance is 2.612(5) Å and the O–H–O angle 129.2(4)°. There is also an intermolecular bond between the cation and the anion, O(1)–H(1)···F(2) [$-x$, y, $\frac{1}{2} - z$]; the O–F distance is 2.732(5) Å and the O–H–F angle 163.7(4)°.

Table 2 Crystallographic data for the compound **3b**(BF$_4$)$_2$

Formula	$C_{12}H_{28}B_2F_8N_2O_4PdS_2$
Formula weight	608.50
Crystal system	Monoclinic
Space group	*C*2/*c*
a/Å	17.1864(8)
b/Å	13.0928(6)
c/Å	11.1356(5)
β/°	113.952(1)
V/Å^3	2289.93(18)
Z	4
μ(MoKα)/cm^{-1}	1.078
T/K	173(2)
Reflections collected	13519
Independent reflections	2338 (R(int) = 0.021)
$R(F)$ (%)	2.25
$R(wF^2)$ (%)	6.17

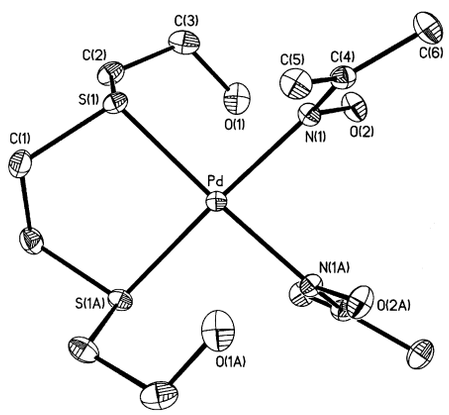
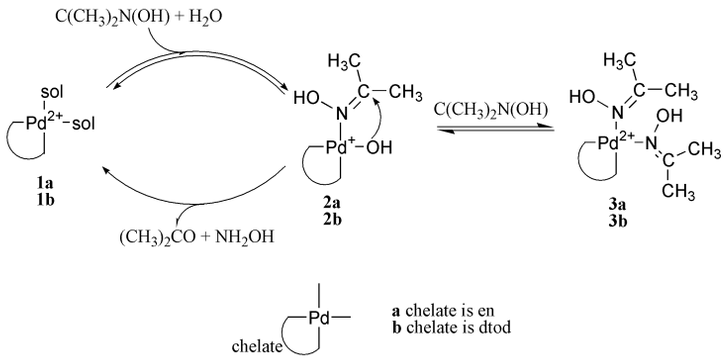


Fig. 1 ORTEP[21] drawing of *cis*-$[Pd(dtod)\{N(OH)C(CH_3)_2\}_2][BF_4]_2$ **3b**$(BF_4)_2$. The thermal ellipsoids of the non-hydrogen atoms are drawn at 30% probability level. The tetrafluoroborate anions and hydrogen atoms were omitted for clarity. The Pd–S(1) and Pd–N(1) distances are 2.2888(5) and 2.0573(17), respectively. Selected angles are N(1)–Pd–S(1), 92.54(5); S(1)–Pd–S(1A), 90.13(3); N(1)–Pd–N(1A), 84.80(10); and N(1)–Pd–S(1A), 177.19(5)°.

Hydrolysis of acetoxime to acetone catalysed by palladium(II) solvent complexes

The appearance of product, acetone-h_6, was monitored by following its methyl resonance at δ 2.06 in ^{1}H NMR spectra. In the absence of palladium(II) complexes free acetoxime is stable toward hydrolysis, as Table 3 shows. Acetoxime coordination to palladium(II) enhances the electrophilicity of the imine carbon and activates the ligand toward addition of water and cleavage of the C=N bond. Similar activation occurs upon coordination of urea derivatives,[5,6] nitriles,[2,3] and peptides.[4] As Table 3 shows, solvent palladium(II) complexes accelerate hydrolysis of acetoxime by a factor greater than 10^4. All the complexes containing bidentate ligands are similarly effective as catalysts.[22] Acetoxime hydrolysis is first order with respect to the catalyst concentration: increasing the concentration of *cis*-$[Pd(dtod)(solv)_2]^{2+}$ from 0.100 to 0.200 M results in doubling the rate from 8.6 ± 1.0 to 16.0 ± 2.0 M h^{-1}.

Since the reactive species, complex **2**, is structurally similar to the reactive species that we found in the study of urea hydrolysis, the proposed mechanism in Scheme 1 is analogous to the mechanism for urea hydrolysis, which we examined in great detail.[5] Initial coordination of acetoxime to palladium(II) is followed by internal attack of a Pd^{II}-bound hydroxo ligand at the imine carbon of the acetoxime activated by coordination.[17] The aqua ligand is a poorer nucleophile than a hydroxo ligand and free water and therefore sluggishly attacks coordinated substrates.[5] The internal-attack mechanism is supported by the very low reactivity of $[Pd(dien)(solv)]^{2+}$ complex, as Table 3 shows. Complex $[Pd(dien)\{N(OH)C(CH_3)_2\}]^{2+}$ contains activated acetoxime but lacks a hydroxo ligand, so that hydrolysis



Scheme 1 Mechanism of acetoxime hydrolysis.

Table 3 Initial concentrations of the reactive complexes **2**, initial rates for the appearance of acetone, and microscopic rate constants for hydrolysis of coordinated acetoxime in palladium(II) and platinum(II) complexes[a]

Solvent complex[b]	[**2**]/M	$10^3 v_i$/M h^{-1}	$10^3 k$/h^{-1}
None	—	$<1.5 \times 10^{-4}$ [c]	$<5 \times 10^{-4}$ [c]
cis-[Pd(en)(solv)$_2$]$^{2+}$	0.020	1.5 ± 0.3	75.0 ± 15.0
cis-[Pd(dtod)(solv)$_2$]$^{2+}$	0.060	8.6 ± 1.0	143.3 ± 16.7
cis-[Pt(en)(solv)$_2$]$^{2+}$	0.060	1.9 ± 0.4	31.7 ± 6.7
[Pd(dien)(solv)]$^{2+}$	0.035	<0.03	<0.9

[a] The solvent was a 0.300 M solution of D_2O in acetone-d_6, and the temperature was 313 K. The initial concentrations of the solvent complex (catalyst) and $C(CH_3)_2N(OH)$ were 0.100 and 0.300 M, respectively. Reactive complexes **2** were formed *in situ* from the respective solvent complex and acetoxime. The concentrations of complexes **2** are given. [b] The solvent complexes are shown in Chart 1 in ESI Supporting Information. [c] Estimated on the basis of the sensitivity of ^{1}H NMR spectroscopy (usually 1% of the predominant resonance). No reaction was observed after 833 days at 313 K. The solvent was a 0.300 M solution of D_2O in acetone-d_6.

can occur only by external attack of water, which is less favorable. The most efficient catalyst *cis*-[Pd(dtod)(solv)$_2$]$^{2+}$ contains *trans*-labilizing sulfur atoms, as the low values of the binding constants in Table 1 show. The aqua ligand in this complex is less acidic than those in less reactive catalysts *cis*-[Pd(en)(solv)$_2$]$^{2+}$ and *cis*-[Pt(en)(solv)$_2$]$^{2+}$.[5] Clearly, dissociation of product, hydroxylamine, is required to achieve more rapid hydrolysis. Acetoxime in [Pd(dtod){N(OH)C(CH$_3$)$_2$}$_2$]$^{2+}$ **3b** undergoes very slow hydrolysis ($k < 1 \times 10^{-4}$ h^{-1}) because the aqua or hydroxo ligand is absent and therefore the internal-attack mechanism cannot operate. This stability allowed the crystallization of this unprecedented complex, as its BF_4^- salt.

The products of hydrolysis are acetone and free and Pd(II)-bound hydroxylamine. They were detected by ^{1}H and ^{13}C NMR spectroscopy. Coordination of hydroxylamine to palladium(II) lowers the concentration of the catalytically active palladium(II) complex.[23] Owing to this product inhibition, the turnover number is only 2–4. When the molar ratio acetoxime to catalyst is increased further to 5 : 1 and 10 : 1, the turnover number remains 2–4 and the overall reaction is not complete.

Conclusion

Simple palladium(II) complexes catalyse hydrolysis of acetoxime to acetone under mild conditions in contrast to the uncatalysed hydrolysis of acetoxime, which requires extremely high temperatures (>100 °C) and high concentrations of acid (>1.0 M).[24] The present study is yet another example of the versatility of palladium(II) complexes as catalysts for organic transformations.

Acknowledgements

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