Synthesis by Ligand Exchange, Structural Characterization, and Aqueous Chemistry of Ortho-Palladated Oximes

Alexander D. Ryabov,*[1a] Gregory M. Kazankov,[1b] Anatoly K. Yatsimirsky,[1b] Ludmila G. Kuz'mina,[1c] Ol'ga Yu. Burtseva,[1c] Natalia V. Dvortsova,[1c] and Vladimir A. Polyakov[1d]

Division of Chemistry, G. V. Plekhanov Russian Economic Academy, Stremyanny per. 28, 113054, Moscow, Russia, Department of Chemistry, Moscow State University, 119899, Moscow, Russia, N. S. Kurnakov Institute of General and Inorganic Chemistry, Leninsky pr. 31, 117907, Moscow, Russia, and Mendeleev Institute of Chemical Technology, Miusskaya pl. 9, 125190, Moscow, Russia

Received January 29, 1992

Dimeric chloro-bridged ortho-palladated complexes of general formula $[PdCl\{C_6H_4(CR{=}NOH)\text{-}2\}]_2$, where R = H, Me, Et, and Ph, were prepared via the ligand-exchange reaction starting from aryl oximes and cyclopalladated complexes of *N*,*N*-dimethylbenzylamine, ((dimethylamino)methyl)ferrocene, or benzophenone oxime. By reaction with various pyridines (Zpy), the dimers were converted into the corresponding monomers $[PdCl\{C_6H_4(CR{=}NOH)\text{-}2\}(Zpy)]$ (**4**). Four acetophenone oxime (R = Me) derivatives with Z = H (**4b**), 4-Me_2N (**4c**), 2-Me (**4d**), and 2,4,6-Me_3 (**4e**) were characterized by X-ray crystallography. Compound **4b**: $C_{13}H_{13}N_2OPdCl$, orthorhombic, space group *Pcab*, a = 15.385 (4) Å, b = 20.980 (1) Å, c = 8.140 (1) Å, Z = 8. Compound **4c**: $C_{15}H_{18}N_3OPdCl$, triclinic, space group $P\bar{1}$, a = 8.307 (5) Å, b = 8.772 (6) Å, c = 11.949 (8) Å, α = 82.15 (5)°, β = 77.36 (5)°, γ = 68.00 (5)°, Z = 2. Compound **4d**: $C_{14}H_{15}N_2OPdCl\cdot{}^1/_2C_6H_6$, monoclinic, space group $C2/c$, a = 21.978 (8) Å, b = 9.702 (2) Å, c = 21.728 (8) Å, β = 132.99 (2)°, Z = 8. Compound **4e**: $C_{16}H_{19}N_2OPdCl$, monoclinic, space group $P2_1/n$, a = 9.488 (2) Å, b = 15.664 (4) Å, c = 11.221 (3) Å, β = 91.12 (1)°, Z = 4. All have a square planar coordination at palladium with a slight tetrahedral distortion and trans nitrogens. The pyridine and palladium planes are practically perpendicular only in the case of **4d,e**; an interaction of the pyridine 2- and 2,6-methyl C–H bonds with the palladium axial sites is proposed. The Pd–Cl bond length is large in all four complexes, of ca. 2.4 Å, and the chloro ligand is readily hydrolyzed in aqueous solution to afford the aqua/hydroxo species $[Pd\{C_6H_4(CR{=}NOH)\text{-}2\}(Zpy)OH_n]^{(n-1)+}$ (n = 1, 2). In the pH range 3–9 the complexes are involved in two acid–base equilibria with the values of pK_{a1} and pK_{a2} of ca. 7 and <5 ascribed to deprotonation of the oxime hydroxyl and the aqua ligand, respectively. The very low values of pK_{a2} were confirmed by the study of several related monomeric palladacycles lacking the oxime group.

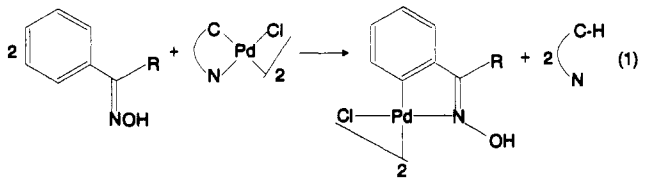
Introduction

When Cope and Siekman first reported on the cyclopalladation of azobenzene,[2] one could hardly predict how rapid the growth of the chemistry of cyclometalated compounds would be.[3-12] The interest in palladacycles was initially encouraged by obvious perspectives of using the compounds in organic synthesis,[13] but very soon palladacycles began to be involved with other branches of chemistry including, in particular, such diverse areas as catalysis,[14] photochemistry,[15] and liquid-crystal materials.[16] This work precedes a report on a novel, rather unexpected utilization of monomeric cyclopalladated aryl oximes as mimetics of hydrolytic metalloenzymes.[17] The key palladium compounds have been derived from oxime ligands, whose metallacyclic chemistry is well-known.[18-24] However, the reported synthesis of ortho-palladated aromatic oximes,[18] the particular object of our research, suffers from the presence of byproducts if tetrachlo-

(1) (a) G. V. Plekhanov Academy. Alexander von Humboldt Fellow (1991–1992) in the Institut für Anorganische Chemie, Universität Witten/Herdecke, Stockumer Str. 10, 5810 Witten-Annen, FRG. (b) Moscow State University. (c) N. S. Kurnakov Institute. (d) Mendeleev Institute.
(2) Cope, A. C.; Siekman, R. W. *J. Am. Chem. Soc.* **1965**, *87*, 3272.
(3) Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 327.
(4) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73.
(5) Omae, I. *Chem. Rev.* **1979**, *79*, 287; *Coord. Chem. Rev.* **1979**, *28*, 97; **1980**, *32*, 235; **1982**, *42*, 245; **1988**, *83*, 137; *Organometallic Intramolecular-coordination Compounds*; Elsevier Science Publishers: Amsterdam, New York, 1986.
(6) Abicht, H.-P.; Issleib, P. *Z. Chem.* **1977**, *17*, 1.
(7) Constable, E. C. *Polyhedron* **1984**, *3*, 1037.
(8) Rothwell, I. P. *Polyhedron* **1985**, *4*, 177; *Acc. Chem. Res.* **1988**, *21*, 153.
(9) Newkome, G. R.; Puckett, W. E.; Gupta, V. K.; Kiefer, G. *Chem. Rev.* **1986**, *86*, 451. Evans, D. W.; Baker, G. R.; Newkome, G. R. *Coord. Chem. Rev.* **1989**, *93*, 155.
(10) Dunina, V. V.; Zalevskaya, O. A.; Potapov, V. M. *Usp. Khim.* **1988**, *57*, 434.
(11) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91.
(12) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403.
(13) For reviews, see: Ryabov, A. D. *Synthesis* **1985**, 233. Pfeffer, M. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 567.
(14) Karpeiskaya, E. I.; Godunova, L. F.; Levitina, E. S.; Lyubeznova, M. R.; Klabunovsky, E. I.; Lubuzh, E. D.; Lutsenko, A. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, 85. Santra, P. K.; Saha, C. H. *J. Mol. Catal.* **1987**, *39*, 279. Bose, A.; Saha, C. H. *J. Mol. Catal.* **1989**, *49*, 271.
(15) Wakatsuki, Y.; Yamazaki, H.; Grutsch, P. A.; Southanam, M.; Kutal, C. *J. Am. Chem. Soc.* **1985**, *107*, 8153. Cornioley-Deuschel, C.; Ward, T.; von Zelewsky, A. *Helv. Chim. Acta* **1988**, *71*, 130. Maestri, M.; Sandrini, D.; Balzani, V.; von Zelewsky, A.; Jolliet, P. *Helv. Chim. Acta* **1988**, *71*, 134. Schwartz, R.; Gliemann, G.; Jolliet, P.; von Zelewsky, A. *Inorg. Chem.* **1989**, *28*, 742. Craig, C. A.; Watts, R. J. *Inorg. Chem.* **1989**, *28*, 309.
(16) Lanfredi, A. M. M.; Ugozzoli, F.; Ghedini, M.; Licoccia, S. *Inorg. Chim. Acta* **1984**, *86*, 165. Ghedini, M.; Armentano, S.; Neve, F. *Inorg. Chim. Acta* **1987**, *134*, 23. Espinet, P.; Lalinde, E.; Markos, M.; Perez, J.; Serrano, J. L. *Organometallics* **1990**, *9*, 555. Ghedini, M.; Pucci, D. *J. Organomet. Chem.* **1990**, *395*, 105. Ghedini, M.; Morrone, S.; De Munno, G.; Grispini, A. *J. Organomet. Chem.* **1991**, *415*, 281.
(17) Yatsimirsky, A. K.; Kazankov, G. M.; Ryabov, A. D. *J. Chem. Soc., Perkin Trans. 2*, in press.
(18) Onoue, H.; Minami, K.; Nakagava, K. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3480.
(19) Grigor, B. A.; Nielson, A. J. *J. Organomet. Chem.* **1977**, *132*, 439.
(20) Constable, A. G.; McDonald, W. S.; Sawkins, L. S.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1978**, 1061; *J. Chem. Soc., Dalton Trans.* **1980**, 1992.
(21) Baldwin, J. E.; Najera, C.; Yus, M. *J. Chem. Soc., Chem. Commun.* **1985**, 126. Baldwin, J. E.; Jones, R. H.; Najera, C.; Yus, M. *Tetrahedron* **1985**, *41*, 699.
(22) Nielson, A. J. *J. Chem. Soc., Dalton Trans.* **1981**, 205.
(23) Carr, K.; Sutherland, J. K. *J. Chem. Soc., Chem. Commun.* **1984**, 1227. Nishiyama, H.; Matsumoto, M.; Matsumoto, T.; Miura, R.; Itoh, K. *Organometallics* **1984**, *4*, 1911.
(24) Phillips, I. G.; Steel, P. J. *J. Organomet. Chem.* **1991**, *410*, 247.

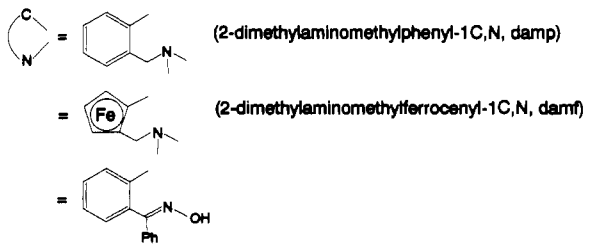
0020-1669/92/1331-3083$03.00/0

Chart I



1 2

R = H (a); Me (b); Et (c); Ph (d)



(2-dimethylaminomethylphenyl-1C,N, damp)

(2-dimethylaminomethylferrocenyl-1C,N, damf)

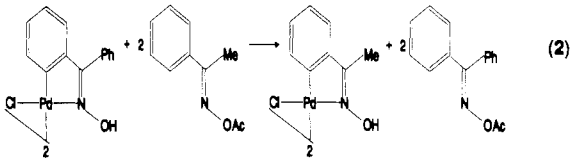
ropalladate(II) is a metalating agent. Hence, in this work we report on a convenient synthesis of ortho-palladated aryl oximes based on the ligand-exchange procedure[25] and on their properties in the solid state and in solution.[26]

Results

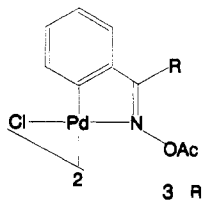
Synthesis of Ortho-Palladated Aryl Oximes via Ligand Exchange. Originally proposed in 1984,[25] the exchange of cyclopalladated ligands has transformed into a versatile procedure for preparation of various pallada-[27-30] and platinacycles.[31] Here, we applied it for the synthesis of aryl oxime complexes (eq 1 in Chart I). Starting from either *N,N*-dimethylbenzylamine or ((dimethylamino)methyl)ferrocene chloro-bridged dimers, cyclopalladated aryl oximes **2a–d** were obtained under usual conditions for this reaction (Table I). The procedure is advantageous compared to that previously reported[18] in terms of slightly higher yields and the lack of byproducts containing N-coordinated nonpalladated ligands. The soluble ortho-palladated benzophenone oxime dimer **2d** can also be used as a starting palladium complex (Table I, entries 8–10). Neither the benzaldehyde oxime complex **2a** nor the acetophenone oxime complex **2b** displays similar behavior.

Although we were unaware of a true *Z*/*E* composition of the starting aryl oximes, the corresponding palladacycles, where the ligands are in the *E*-form, were obtained in high yields. This probably means that aryl oximes may undergo $Z \rightarrow E$ isomerization in the course of the reaction. The isomerization would be favored by initial N-coordination of oximes with the metal, as has been recently proposed in a similar case.[32]

An attempt was made to obtain the *O*-acetyl oxime chloro-bridged dimers **3** starting, for example, from acetophenone *O*-acetyloxime and the corresponding ortho-palladated chloro-bridged dimers. No reaction was observed in the case of the *N,N*-dimethylbenzylamine and ((dimethylamino)methyl)ferrocene complexes. With complex **2d** as a palladating agent, the exchange reaction does occur (eq 2), but the products are complex



2d **2b**



3 R = Me (a); Et (b); Ph (c)

2b and benzophenone *O*-acetyloxime, the latter detected by GLC (72%). The reaction is formally the exchange of phenyl and methyl groups, but it surely does not involve C–C bond metathesis. The mechanism[17] probably involves ligand exchange to produce ortho-palladated acetophenone *O*-acetyloxime and free benzophenone oxime. The latter, a powerful nucleophile, deacylates the ortho-palladated product to afford complex **2b** and free O-acylated benzophenone oxime. Equation 2 accounts for the unsuccessful attempts to prepare ortho-palladated *O*-acetyloximes by reacting them with Na_2PdCl_4 in MeOH as solvent:[18] after the formation, the product, as a result of the nucleophilic attack by methanol, loses the acyl function.

The preparation of O-acylated complexes **3** was accomplished by acylation of the corresponding chloro-bridged dimers **2** in refluxing acetic anhydride by using the procedure of Shaw et al.[20] The dimeric species obtained were then converted into neutral or cationic monomeric complexes **4** or **5** by reacting with substituted pyridines or 2,2′-dipyridyl, respectively, the latter in the presence of $NaPF_6$. All the compounds reported, including the dimeric and monomeric species, were characterized by analytical and ^1H NMR spectral data, but a few monomeric pyridine complexes **4b–e** were characterized by X-ray crystallography (Chart II).

^1H NMR Data for Monomeric Complexes 4. The spectral features of the compounds are typical of the palladacycles of this type[33-36] (Table II). As could be anticipated, there is an upfield shift of the proton H^6 of the ortho-palladated ring in all complexes **4**. It shows that the phenyl ring is metalated and located in the palladium plane and both nitrogens are mutually trans. Discussed in detail elsewhere,[33,34] the effect is due to a pyridine ligand which is not in the palladium plane (and the X-ray data obtained support this; see below). Other resonances of oxime ligands including the hydroxy proton show minor changes on cyclopalladation (Table II). The only exception is the observed drift of the azamethyne proton of benzaldehyde oxime, which is seen at δ 8.47 and 7.33 in the free ligand and complex **4a**, respectively.

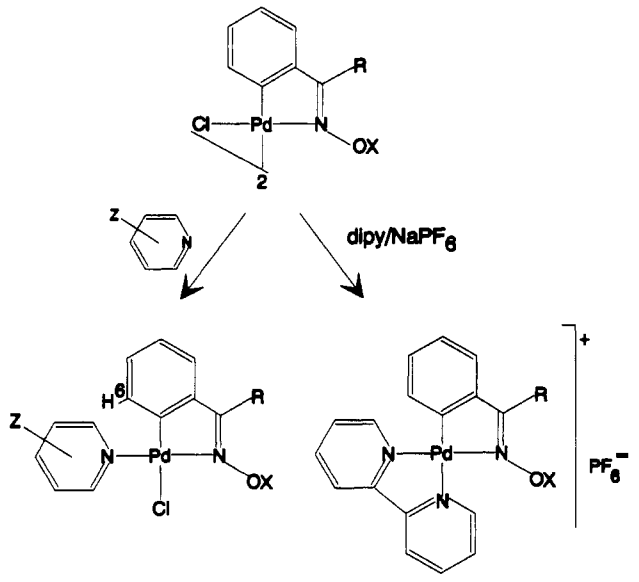
X-ray Structural Data for Monomers 4b–e. General views of complexes **4b–e** are shown in Figures 1–4, while the most important bond lengths and bond angles are summarized in Tables III and IV, respectively. All the complexes have a square planar coordination at palladium with a slight tetrahedral distortion.

(25) Ryabov, A. D.; Yatsimirsky, A. K. *Inorg. Chem.* **1984**, *23*, 789.
(26) A preliminary communication has appeared: Kazankov, G. M.; Polyakov, V. A.; Ryabov, A. D.; Yatsimirsky, A. K. *Metalloorganich. Khim.* **1990**, *3*, 644.
(27) Ryabov, A. D.; Kazankov, G. M. *J. Organomet. Chem.* **1984**, *268*, 85. Ryabov, A. D. *Koord. Khim.* **1985**, *11*, 1532.
(28) Ryabov, A. D. *Inorg. Chem.* **1987**, *26*, 1252. Ryabov, A. D.; Eliseev, A. V.; Sergeyenko, E. S.; Usatov, A. V.; Zakharkin, L. I.; Kalinin, V. N. *Polyhedron* **1989**, *8*, 1485.
(29) Granell, J.; Sainz, D.; Sales, J.; Solans, X.; Font-Altaba, M. *J. Chem. Soc., Dalton Trans.* **1986**, 1785. Ceder, R. M.; Gomez, M.; Sales, J. *J. Organomet. Chem.* **1989**, *361*, 391.
(30) Dupont, J.; Beydoun, N.; Pfeffer, M. *J. Chem. Soc., Dalton Trans.* **1989**, 1715.
(31) Pregosin, P. S.; Wombacher, F.; Albinati, A.; Lianza, F. *J. Organomet. Chem.* **1991**, *418*, 249.
(32) Albert, J.; Gomez, N.; Granell, J.; Sales, J.; Solans, X. *Organometallics* **1990**, *9*, 1375.
(33) Deeming, A. J.; Rothwell, I. P.; Hursthouse, M. B.; New, L. *J. Chem. Soc., Dalton Trans.* **1978**, 1490.
(34) (a) Ryabov, A. D.; Polyakov, V. A.; Yatsimirsky, A. K. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1503; *Inorg. Chim. Acta* **1984**, *91*, 59.
(35) Hiraki, K.; Fuchita, Y.; Uchiyama, T., *Inorg. Chim. Acta* **1983**, *69*, 187.
(36) Albinati, A.; Affolter, S.; Pregosin, P. S. *Organometallics* **1990**, *9*, 379.

Table I. Synthesis of Ortho-Palladated Oximes via Ligand-Exchange Reactions

entry	starting complex	incoming ligand	product	solv (°C)	reacn time, h	yield, %
1	$[Pd(damp)Cl]_2$	benzaldehyde oxime	**2a**	$HOAc/CHCl_3$ (50)	20	81
2		acetophenone oxime	**2b**		8	92
3		propiophenone oxime	**2c**		12	95
4		benzophenone oxime	**2d**		24	86
5		acetophenone *O*-acetyloxime			30	0
6	$[Pd(damf)Cl]_2$	acetophenone oxime	**2b**	HOAc (25)	10	84
7		propiophenone oxime	**2c**		10	76
8	**2d**	acetophenone oxime	**2b**	HOAc (50)	24	92
9	**2d**	propiophenone oxime	**2c**		24	86
10	**2d**	acetophenone *O*-acetyloxime	**2b**		24	82

Chart II



4

	R	Z	X
a	H	H	H
b	Me	H	H
c	Me	4-Me_2N	H
d	Me	2-Me	H
e	Me	2,4,6-Me_3	H
f	Et	H	H
g	Et	H	Ac
h	Ph	H	H
i	Ph	2,4,6-Me_3	H
j	Ph	4-MeOOC	H
k	Ph	H	Ac

5

	R	X
a	Me	H
b	Ph	H
c	Ph	Ac

The pyridine and oxime nitrogens are positioned trans, confirming the structural conclusions from the ^1H NMR data. The imine Pd–N(1) bonds are shorter than the pyridine Pd–N(2) bonds evidently due to the back-bonding involving the imine π^*-system and the d_{zx} palladium orbital, since the palladium and imine nitrogen planes are practically coplanar.

The five-membered chelate rings are slightly strained, since the N(1)PdC(1) bond angles are acute in all cases (79.6–80.6°). Similar decrease in the bond angles is observed at all atoms of the five-membered chelate ring. The Pd–C bond length (1.980–2.004 Å) is typical of the Pd–C(sp^2) bonds with the aryl function coplanar with the palladium atom.[37] Back-donation from d_{yz} palladium to antibonding π^* phenyl orbitals is the obvious reason for this bond shortening. The Pd–Cl bonds are very similar in all four complexes, 2.412–2.430 Å, and close to the upper limit of the range typical of Pd–Cl bonds (2.37–2.45 Å).[38] The lengthening of the Pd–X bond trans to the phenyl ring is not, of course, unusual and is well documented in the literature.[39–41] In our case however there is an additional reason for the stretch of the Pd–Cl bond, i.e. the intramolecular O(1)–H···Cl hydrogen bond. Accordingly, some "flow off" of the electron density from chloride to the hydroxy hydrogen would weaken the Pd–Cl bond. As a result, the chloro ligand becomes weakly bound and is readily hydrolyzed in aqueous solutions (see below).

The palladium and pyridine planes are practically perpendicular in complexes **4d** and **4e**. The corresponding dihedral angles (α_D) between the planes are equal to 84.1 and 81.4°, respectively, and should be compared with α_D of 52.1 and 62.6° obtained for **4b** and **4c**, respectively. Manipulations with molecular models suggest that such an orientation is not due to steric interactions between one (in **4d**) or two (in **4e**) ortho methyls of the coordinated pyridines with cyclopalladated phenyl ring. The methyl groups do preclude the free rotation of the pyridines around the Pd–N bond because of the interaction with the atoms of the C–H^6 bond, but they can easily attain various orientations with the values of α_D in the range 40–90°. We assume that the perpendicular orientation is more likely brought about by the agostic C–H···Pd contacts, well documented by now in many transition metal complexes.[42,43] In fact, the C–H distance in the "agostic fragment" of **4d** is somewhat lengthened (ca. 1.13 Å), while the CCH bond angle is noticeably decreased (87.3°). The geometrical correction of this H atom using the standard C–H distances and HCC/HCH angles (0.96 Å and 105.5°, respectively) changes the Pd···H distance insignificantly, and this value remains short enough in all cases. Therefore, one can argue that complex **4d** has a rather strong agostic contact. Interestingly, the agostic Pd···H contact is shorter (2.27 Å) in the case of **4d**, where only one methyl group is involved. In the case of **4e** where two methyl groups donate C–H bonds, the corresponding distances are equal to 2.64 and 2.79 Å, showing a sort of "saturation effect". Similar geometrical correction in the case of **4e** changes the Pd···H distance insignificantly also. This value is always close to the sum of the van der waals radii, suggesting weak agostic bonds in the case of **4e**. We have previously postulated[44] that agostic interactions of this type should stabilize the perpendicular orientation of pyridines in related palladium complexes, and this has found an experimental support here.

To this end, complexes **4d,e** possess hydrogen bonds of two types, i.e. agostic and normal, where C–H···Pd and O–H···Cl fragments are involved. Intramolecular hydrogen bonding in transition metal chloro complexes is known in the literature,[45,46]

(37) Struchkov, Yu. T.; Batsanov, A. S.; Slovokhotov, Yu. L. *Sov. Sci. Rev. B Chem.* **1987**, *10*, 386.
(38) Zir-Lebed', L. N.; Kuz'mina, L. G.; Struchkov, Yu. T.; Tiomkin, O. N.; Golodov, V. A. *Koord. Khim.* **1978**, *4*, 1046.
(39) Barr, N.; Dyke, S. F.; Smith, G.; Kennard, C. H. L.; McKee, V. *J. Organomet. Chem.* **1985**, *288*, 109.
(40) Musaev, A. A.; Usubaliev, B. T.; Guliev, A. A.; Bashilov, V. V.; Sokolov, V. I. *Zh. Strukt. Khim.* **1985**, *26*, 166.
(41) Kuz'mina, L. G.; Burtseva, O. Yu.; Porai-Koshits, M. A.; Dunina, V. V.; Zalevskaya, O. A.; Potapov, V. M. *Zh. Obshch. Khim.* **1989**, *59*, 2525.
(42) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1.
(43) Ginzburg, A. G. *Usp. Khim.* **1988**, *57*, 2046.
(44) Polyakov, V. A.; Ryabov, A. D. *J. Chem. Soc., Dalton Trans.* **1986**, 589.
(45) Nakazawa, H.; Sakaguchi, U.; Yoneda, H.; Morimoto, Y. *Inorg. Chem.* **1981**, *20*, 973. Sosa, M.; Tobe, M. *J. Chem. Soc., Dalton Trans.* **1985**, 475.

Table II. ^{1}H NMR Spectral Data for Ortho-Palladated Complexes **4**

complex (R, X, X)	chem shifts, ppm
4a (H, H, H)	6.20 (dd, H^6)
	6.70–7.13 (m, H^3–H^5)
	7.42 (td, $H^{3'}$, $H^{6'}$)
	7.33 (s, N=CH)
	7.88 (td, $H^{6'}$)
	8.82 (dd, $H^{2'}$, $H^{6'}$)
	ca. 10 (bs, NOH)
4b (Me, H, H)	2.24 (s, CH_3)
	6.19 (d, J = 7, H^6)[a]
	6.75–7.09 (m, $H^{3'}$–$H^{5'}$)
	7.43 (td, $H^{3'}$, $H^{6'}$)
	7.85 (td, $H^{4'}$)
	8.80 (dd, $H^{2'}$, $H^{6'}$)
	10.3 (s, NOH)
4c (Me, 4-Me_2N, H)	2.20 (s, CCH_3)
	3.05 (s, NCH_3)
	6.37 (dd, J = 6, 1, H^6)
	6.47 (dd, $H^{3'}$, $H^{5'}$)
	6.70–7.10 (m, H^3–H^5)
	8.23 (dd, $H^{2'}$, $H^{6'}$)
	9.89 (s, NOH)[b]
4d (Me, 2-Me, H)	2.19 (s, CCH_3)
	2.98 (s, $pyCH_3$)
	5.85 (dd, J = 6, 1, H^6)
	6.65–7.01 (m, H^3–H^5)
	7.21 (td, $H^{5'}$)
	7.37 (dd, $H^{3'}$)
	7.71 (dd, $H^{4'}$)
	8.87 (dd, $H^{6'}$)
	10.11 (s, NOH)
4e (Me, 2,4,6-Me_3, H)	2.23 (s, CCH_3)
	2.35 (s, 4′-CH_3)
	2.97 (s, 2′,6′-CH_3)
	5.77 (d, H^6)
	6.60–7.20 (m, H^3–H^5)
	7.10 (s, $H^{3'}$, $H^{5'}$)
	10.14 (s, NOH)
4f (Et, H, H)[c]	1.18 (t, CH_3)
	2.56 (q, CH_2)
	6.22 (dd, H^6)
	6.77–7.13 (m, H^3–H^5)
4g (Et, H, $OCCH_3$)[c]	1.16 (t, CH_2CH_3)
	2.23 (s, $COCH_3$)
	2.68 (q, CH_2CH_3)
	6.50 (dd, H^6)
	6.95–7.37 (m, H^3–H^5)
4h (Ph, H, H)	5.25 (dd, H^6)
	6.75–7.05 (m, H^3–H^5)
	7.26–7.55 (m, Ph, $H^{3'}$, $H^{5'}$)
	7.81 (td, H^4)
	8.90 (d, $H^{2'}$, $H^{6'}$)
	10.25 (s, NOH)
4i (Ph, 2,4,6-Me_3, H)	2.36 (s, 4′-CH_3)
	3.03 (s, 2′,6′-CH_3)
	5.88 (d, H^6)
	6.80–7.50 (m, Ar)
	10.27 (s, NOH)
4j (Ph, 4-H_3COOC, H)	3.95 (s, CH_3)
	6.19 (dd, H^6)
	6.60–7.00 (m, H^3–H^5)
	7.99 (dd, $H^{3'}$, $H^{5'}$)
	9.04 (dd, $H^{2'}$, $H^{6'}$)
	10.13 (s, NOH)
4k (Ph, H, $OCCH_3$)	2.25 (s, $COCH_3$)
	5.26 (dd, H^6)
	6.76–7.04 (m, H^3–H^5)
	7.26–7.55 (m, Ph, $H^{3'}$, $H^{5'}$)
	7.79 (td, H^4)
	8.90 (d, $H^{2'}$, $H^{6'}$)
	10.25 (s, NOH)

[a] J values in Hz. [b] Signal observed at −80 °C in CD_2Cl_2. [c] Obtained by addition of py-d_5 to the corresponding dimer.

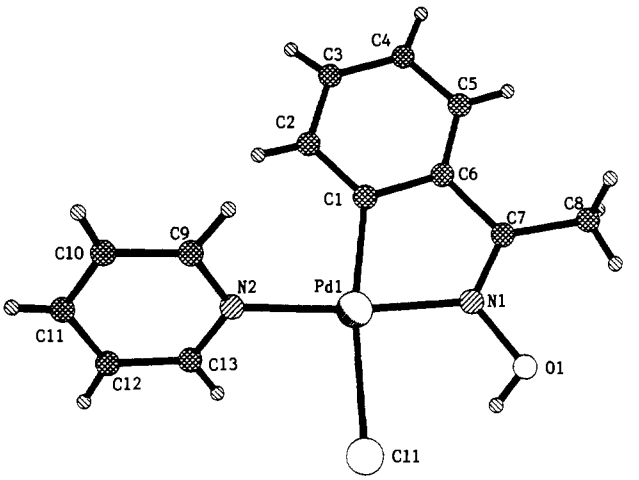


Figure 1. View of complex **4b**.

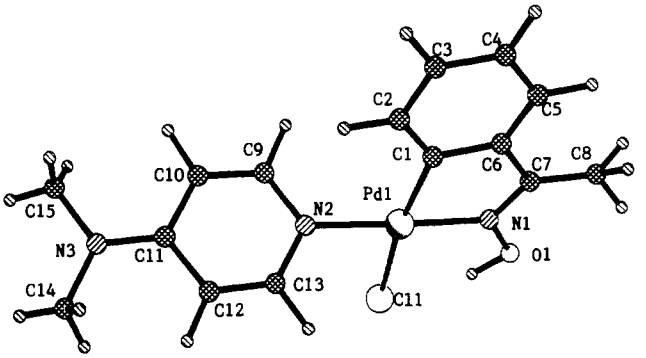


Figure 2. View of complex **4c**.

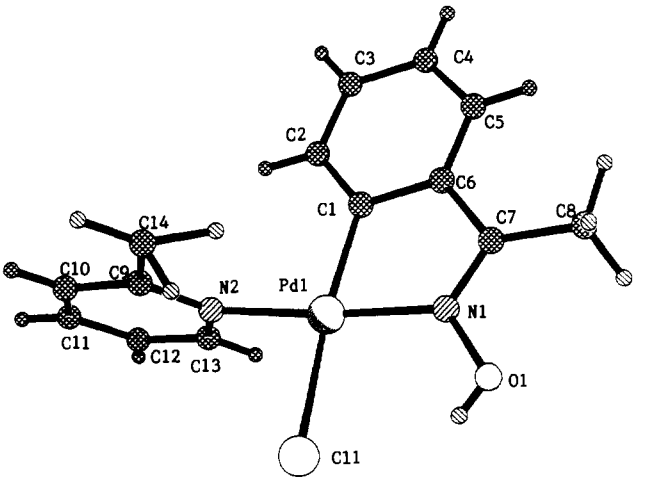


Figure 3. View of complex **4d**.

but to our knowledge, **4d** and **4e** are rare examples where two different hydrogen bonds coexist.

NMR versus X-ray Data. The agostic interactions in complexes **4d,e** may also be detected in solution.[47] The resonances from the 2- and 6-methyls of the pyridine ligand are in fact shifted upfield by ca. 0.4 ppm. However, all the methyl protons of **4d** remain equivalent and a sharp singlet at δ 2.97 is observed even at −80 °C in a CD_2Cl_2 solution. Therefore, it is very likely that a particular C–H···Pd contact develops only on going from solution to the solid state.

The value of dihedral angle α_D between the palladium and pyridine planes may be related to the chemical shift of the proton H^6 of the ortho-palladated oxime. The highest upfield drift will

(46) Imakoshi, K.; Ichimura, A.; Kinoshita, I.; Ooi, S. *Inorg. Chem.* **1990**, *29*, 4005. Winter, C. H.; Sheridan, P. H.; Heeg, M. J. *Inorg. Chem.* **1991**, *30*, 1962.

(47) Pregosin, P. S.; Wombacher, F. *Magn. Reson. Chem.* **1991**, *29*, S106.

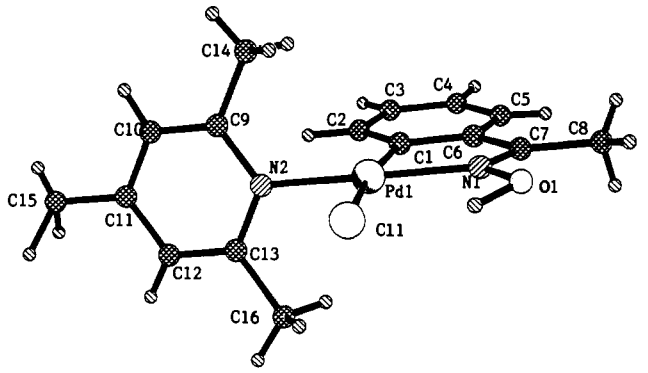


Figure 4. View of complex **4e**.

Table III. Selected Bond Lengths (Å) in Complexes **4b–e**

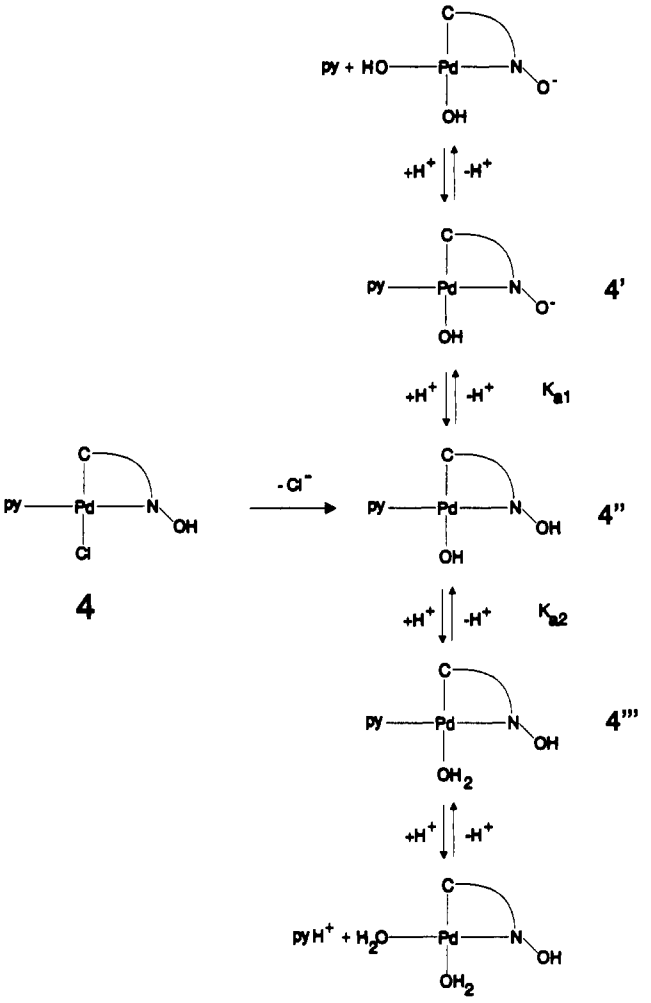
bond	4b	4c	4d	4e
Pd–C(1)	1.983 (5)	1.890 (5)	1.978 (7)	2.004 (5)
Pd–N(1)	1.993 (5)	1.997 (5)	1.988 (6)	1.981 (4)
Pd–N(2)	2.040 (4)	2.030 (5)	2.041 (6)	2.043 (4)
Pd–Cl	2.413 (2)	2.412 (2)	2.421 (2)	2.430 (1)
C(1)–C(2)	1.390 (7)	1.375 (7)	1.39 (1)	1.375 (7)
C(2)–C(3)	1.391 (7)	1.411 (8)	1.38 (1)	1.400 (8)
C(3)–C(4)	1.364 (8)	1.372 (9)	1.37 (1)	1.36 (1)
C(4)–C(5)	1.393 (9)	1.378 (8)	1.38 (1)	1.38 (1)
C(5)–C(6)	1.387 (8)	1.392 (8)	1.39 (1)	1.388 (8)
C(1)–C(6)	1.408 (7)	1.432 (6)	1.42 (3)	1.395 (7)
C(6)–C(7)	1.468 (8)	1.450 (7)	1.47 (1)	1.466 (7)
C(7)–C(8)	1.486 (8)	1.483 (9)	1.48 (4)	1.482 (8)
O–N(1)	1.390 (6)	1.384 (6)	1.390 (8)	1.393 (6)
N(1)–C(7)	1.271 (7)	1.293 (7)	1.279 (9)	1.302 (8)
N(2)–C(9)	1.341 (7)	1.349 (7)	1.33 (1)	1.350 (6)
C(9)–C(10)	1.376 (9)	1.365 (9)	1.39 (4)	1.381 (8)
C(10)–C(11)	1.375 (9)	1.418 (8)	1.35 (1)	1.368 (9)
C(11)–C(12)	1.367 (9)	1.412 (8)	1.39 (6)	1.37 (1)
C(12)–C(13)	1.372 (9)	1.351 (9)	1.39 (1)	1.378 (9)
N(3)–C(11)		1.345 (7)		
C(9)–C(14)			1.48 (4)	1.480 (9)
C(13)–C(16)				1.500 (9)
O–H(1)	0.80	0.99	0.73	1.00

Table IV. Selected Bond Angles (deg) in Complexes **4b–e**

angle	4b	4c	4d	4e
Cl–Pd–C(1)	169.5 (1)	170.7 (2)	171.1 (2)	171.1 (1)
Cl–Pd–N(1)	90.9 (1)	90.1 (2)	91.9 (2)	91.1 (1)
Cl–Pd–N(2)	93.4 (1)	92.9 (1)	93.2 (2)	95.3 (2)
N(1)–Pd–N(2)	174.7 (2)	177.0 (2)	175.0 (3)	173.3 (2)
N(1)–Pd–C(1)	79.6 (2)	80.6 (2)	79.7 (3)	80.0 (2)
N(2)–Pd–C(1)	96.3 (2)	96.4 (2)	95.2 (3)	93.6 (2)
Pd–C(1)–C(2)	129.7 (4)	129.7 (4)	128.7.6	128.1 (4)
C(1)–C(2)–C(3)	120.1 (5)	120.5 (5)	120.4 (8)	119.0 (5)
C(2)–C(3)–C(4)	122.4 (5)	120.7 (6)	120.8 (9)	121.2 (6)
C(3)–C(4)–C(5)	118.2 (6)	119.9 (6)	119.9 (9)	120.1 (6)
C(4)–C(5)–C(6)	119.9 (5)	120.3 (5)	120.0 (9)	119.8 (6)
C(1)–C(6)–C(5)	121.6 (5)	120.3 (5)	120.6 (9)	120.2 (5)
Pd–N(1)–C(7)	120.3 (4)	118.9 (4)	120.1 (6)	120.0 (4)
N(1)–C(7)–C(6)	111.6 (4)	112.4 (5)	111.7 (6)	110.9 (5)
N(1)–C(7)–C(8)	125.1 (5)	122.3 (5)	123.2 (8)	124.3 (5)
Pd–N(2)–C(9)	121.8 (4)	123.6 (4)	122.0 (5)	121.0 (3)
N(2)–C(9)–C(10)	121.5 (6)	124.1 (5)	120.0 (8)	120.8 (5)
C(9)–C(10)–C(11)	119.6 (6)	120.3 (5)	119.7 (9)	121.2 (6)
C(10)–C(11)–C(12)	119.2 (6)	115.0 (5)	120.0 (9)	117.0 (6)
C(11)–C(12)–C(13)	118.6 (6)	120.2 (6)	119.4 (9)	121.4 (6)
N(2)–C(13)–C(12)	122.9 (6)	124.9 (6)	120.4 (8)	120.6 (5)
N(3)–C(11)–C(12)		122.7 (5)		
N(2)–C(9)–C(14)			118.9 (8)	118.5 (5)
N(2)–C(13)–C(16)				117.9 (5)
Pd–N(1)–O	122.7 (3)	123.9 (4)	123.4 (5)	123.3 (3)
N(1)–O–H(1)	103.2	96.2	104.8	97.8

be when the planes are perpendicular ($\alpha_D = 90°$), and the smallest, when coplanar ($\alpha_D = 0°$). The structural data reveal the largest α_D = 84.1 and 81.4° for **4d,e** because of the agostic anchoring, and the H^6 resonance is seen in the highest field at δ 5.83 and 5.77, respectively. The values of α_D are equal to 52.1 and 67.2° for **4b,c**, and the signals from H^6 are seen at δ 6.19 and 6.37, respectively.

Scheme I



Behavior of Monomers 4 in Aqueous Solution. Although complexes **4** are uncharged, they are sufficiently soluble in water for a systematic spectrophotometric study. We were interested in the acidity of oxime hydroxyl and the resistance of the coordinated chloride to hydrolysis. The experiments were carried out with many complexes **4**, and the main conclusions are the following. The chloro ligand undergoes ready aquation in the pH range 3–10 to produce the corresponding aqua/hydroxo species **4'–4'''** (Scheme I; charges of complexes have been omitted for clarity). The electronic spectrum of native complex **4b** in a buffered solution is identical to that of the complex pretreated with ca. 150% excess $Ag[ClO_4]$. Both spectra are identical at pH 7.0. Consequently, monomeric complexes of type **4** undergo spontaneous hydrolysis to afford aqua/hydroxo species without interference from silver(I). Thus, the "aqueous" behavior of chloro complexes **4** is very similar to that of dien (1,7-diamino-4-azaheptane) complexes $[Pd(1,1,4,7,7\text{-}R^5dien)Cl]^+$, where R = H, Me, or Et,[48,49] which also transform readily into the aqua/hydroxo species.

The hydrolyzed species exist in aqueous solution in a monomeric form, since for **4** at pH = 3.5–9.0 and 25 °C the Beer law holds in the concentration range (1–8) × 10^{-5} mol dm^{-3}. At extreme pHs, i.e. below 3 and higher 10, we found a reversible departure of the coordinated pyridine, as concluded from the observation of the fine pyridine structure at 240–270 nm hidden

(48) Baddley, W. H.; Basolo, F. *J. Am. Chem. Soc.* **1966**, *88*, 2944.
(49) Kotowski, M.; van Eldik, R. *Inorg. Chem.* **1984**, *23*, 3310.

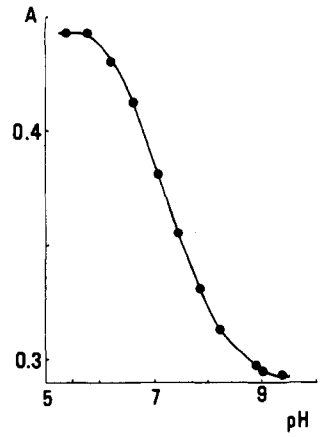


Figure 5. Change of absorption of an aqueous solution of complex **4b** at 260 nm and 45 °C as a function of pH ([**4b**] = 7.3 × 10^{-5} mol dm^{-3}).

Table V. Deprotonation Constants of Complexes **4** and **6b–10b** at 45 °C and Ionic Strength 0.1 M ($NaClO_4$)

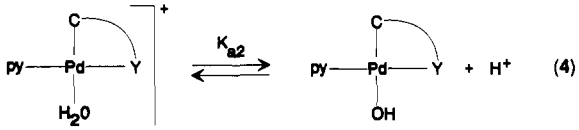
complex	pK_{a1}	pK_{a2}	complex	pK_{a1}	pK_{a2}
4a	6.89 ± 0.06		**7**		4.14 ± 0.06
4b	7.12 ± 0.05		**8**		4.46 ± 0.02
4c	7.27 ± 0.08		**9**		4.84 ± 0.07
4h	7.02 ± 0.03		**10**		4.91 ± 0.06
6		4.18 ± 0.01			

when the ligand is coordinated. On the change to neutral solutions from both extremes, these bands disappear suggesting recoordination. Again very similar pyridine dissociation was very recently reported for the cationic complex (1,5-diamino-3-azapentane)(pyridine)palladium(II).[50]

The spectra of complexes **4** are pH dependent in the range 6–8. The corresponding data for **4b** are shown in Figure 5. A computer fitting of the data according to eq 3 provided the value of pK_{a1}

$$A = [4]_t(\epsilon_{HA}[H^+] + \epsilon_A K_a)/([H^+] + K_a) \qquad (3)$$

of 7.12 ± 0.5, where A is the absorption, $[4]_t$ is the total concentration of **4b** in solution, and ϵ_{HA} and ϵ_A are the extinction coefficients of the protonated and deprotonated forms, respectively. Data for other complexes **4** were analyzed in the same way, and the values of pK_{a1} are summarized in Table V. As shown in Scheme I, one could anticipate two values of K_a in the pH range 3–9, arising from deprotonation of the oxime hydroxy group and the palladium-bound aqua ligand. Unfortunately, only one pK_a could be extracted from the pH spectrophotometric titration, on one hand, and there is no straightforward evidence for ascribing the K_{a1} values to either of the groups, on the other. Therefore, for a correct assignment, we undertook a similar spectrophotometric study of closely related complexes **6a–10a**, which have no oxime functionality, and hence, the products of their hydrolysis, complexes **6b–10b** (Chart III), have coordinated water as the only dissociating group. The spectra of hydrolyzed species **6b–10b** depend on pH in the range 3–6. The corresponding plot for complex **6b** is shown in Figure 6. A well-defined isosbestic point at 265 nm shows that only two species, aqua and hydroxo, are present in solution (eq 4). Analysis of the spectral data in



(4)

terms of eq 3 allows one to calculate the equilibrium constants K_{a2}, and the values of pK_{a2} are also summarized in Table V.

(50) Cannovese, L.; Cattalini, L.; Uguagliati, P.; Tobe, M. L. *J. Chem. Soc., Dalton Trans.* **1990**, 867, 3271.

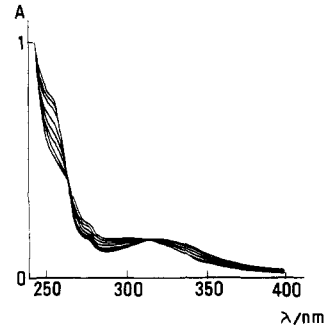
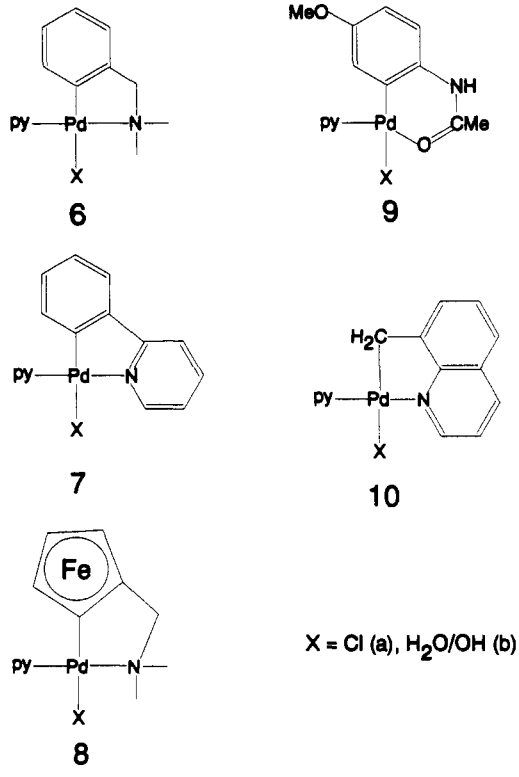


Figure 6. Electronic spectra of complex **6b** at different pH values in the range 2–6 and 45 °C ([**6b**] = 5 × 10^{-5} mol dm^{-3}).

Chart III



Obtained for **6b–10b**, these are noticeably lower than those evaluated for oxime complexes **4**. Therefore, the values of pK_{a1} and pK_{a2} should be referred to different ionizable groups. Hence, the pK_{a1} values of ca. 7 evaluated for oxime complexes **4** should be ascribed to the hydroxy group rather than to the coordinated aqua ligand.

Discussion

The acidity of aryl oximes increases by ca. 4 orders of magnitude as a result of ortho-palladation. For example, the pK_a values of free aceto- and benzophenone oximes measured at 45 °C are equal to 11.47 and 11.18, respectively. The corresponding values for the ortho-palladated ligands in complexes **4b** and **4h** drop to 7.12 and 7.02, respectively. This effect is normal and quite expected taking into consideration the values of ΔpK_a for coordinated with Zn(2+) pyridyl-2-aldoxime (3.54[51] and 3.80[52]) and pyridyl-2-methylketoxime (3.50[52]). Much more surprising is a great decrease in the pK_{a2} of coordinated water in aqua complexes **6b–10b** and, probably, **4'''**, since the values of pK_a of palladium(II) cationic complexes even of charge 2+ are generally close to 7.[53-55] The charge of a complex has the greatest affect

(51) Breslow, R.; Chipmon, D. *J. Am. Chem. Soc.* **1965**, *87*, 4165.
(52) Suh, J.; Cheong, M.; Han, H. *Bioorg. Chem.* **1984**, *12*, 188.
(53) Breet, E. J. L.; van Eldik, R.; Kelm, H. *Polyhedron* **1983**, *2*, 1181.

Table VI. Crystallographic Data for Compounds **4b–e**

compd	4b	4c	4d	4e
chem formula	$C_{13}H_{13}N_2OPdCl$	$C_{15}H_{18}N_3OPdCl$	$C_{14}H_{15}N_2OPdCl \cdot {}^1/_2C_6H_6$	$C_{16}H_{19}N_2OPdCl$
fw	355.10	398.16	408.18	397.18
lattice	orthorhombic	triclinic	monoclinic	monoclinic
space group	*Pcab* (No. 61)	$P\bar{1}$ (No. 2)	*C*2/*c* (No. 15)	$P2_1/n$ (No. 14)
a, Å	15.385 (4)	8.307 (5)	21.978 (8)	9.488 (2)
b, Å	20.980 (1)	8.772 (6)	9.702 (2)	15.664 (4)
c, Å	8.140 (1)	11.949 (8)	21.728 (8)	11.221 (3)
α, deg	90	82.15 (5)	90	90
β, deg	90	77.36 (5)	132.99 (2)	91.12 (1)
γ, deg	90	68.00 (5)	90	90
V, Å^3	2627.4	786.3	3389.0	1667.3
Z	8	2	8	4
T, °C	20	20	20	20
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73
ρ_{calcd}, g cm^{-3}	1.78	1.68	1.60	1.58
μ(Mo Kα), cm^{-1}	8.1	6.9	6.4	6.5
R^a	0.0251	0.0355	0.0338	0.0346
$R_w{}^a$	0.0251	0.0355	0.0338	0.0346

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$. Weighting scheme: $w = [\sigma^2(F_o) + nF_o^2]^{-1}$.

on the acidity of coordinated water.[56] In our case, the charge is only 1+, but the acidity is even higher. We believe that the major reasons are the presence of the phenyl ring trans to the aqua ligand, and its location in the palladium plane. The latter is extremely favorable for the back-donation from the metal to the phenyl ring, which could increase a formal positive charge at palladium. A support for this idea may be found by comparing the values of pK_{a2} in the series of complexes **6b–10b**. The highest value is in the case of 8-methylquinoline complex **10b**, where the direct electron transfer from palladium to the antibonding π^* orbitals of the quinoline ring is restricted because of the methylene bridge. Another possible reason for such high acidity is the presence of coordinated py. In fact, there is an indication that the pK_a of water might be even less than 1.5 in the complex $[Pd(terpy)OH_2]^{2+}$.[57] The nature of the chelate arm of palladacycles has little effect on the acidity of coordinated water.

To this end, in aqueous solution, ortho-palladated oximes **4** generate two adjacent nucleophilic centers, the oximato oxygen and the coordinated hydroxide. These centers are governed by the pK_{a1} and pK_{a2} of ca. 7 and ca. 4–5, respectively. In a subsequent paper,[17] we will describe the activity of these species with respect to nitrophenyl esters.

Conclusion. The present study has demonstrated that the cyclopalladated oxime ligands in complexes **4** are inert to substitution and bear their own nucleophilic centers, i.e. deprotonated oxime hydroxyls. The chloro ligand in the position trans to the palladium–carbon σ-bond is readily hydrolyzed in aqueous solution, and the complexes attain the very acidic aqua ligand as an additional nucleophile. The coordination sphere of palladium thus gives rise to a multifunctional catalyst with two proximate, oximato and hydroxo, nucleophilic centers. The principles of organization of the complexes described have much in common with what is realized in hydrolytic metalloenzymes, and hence, cyclopalladated oximates can be used as mimetics of these biocatalysts.

Experimental Section

General Methods. All spectrophotometric determinations were performed on a Hitachi 150-20 spectrophotometer. ^{1}H NMR spectra were recorded at ambient temperature in $CDCl_3$ unless otherwise stated with tetramethylsilane (TMS) or hexamethyldisiloxane as internal standards on Tesla BS-467 or BS-497 instruments. Chemical shifts are given in a δ scale versus TMS throughout; *J* values are in Hertz. GLC analyses were made on a Chrom-5 chromatograph using a 100-mm column (1-mm diameter) with a graphitized carbon "Sterling MT" (0.2–0.6 mm).

Materials. Aryl oximes, PhC(R)=NOH (R = H, Me, Et, Ph), were prepared from the precursor aldehydes or ketones by reacting them with hydroxylamine as described elsewhere.[58] 2-Methylpyridine was purchased from Reakhim; the sources of other substituted pyridines were as in the previous work.[44] 2,2′-Dipyridyl was a Reanal reagent. Silver(I) hexafluorophosphate was a kind gift from Dr. D. Muratov. Cyclopalladated dimeric chloro-bridged derivatives of *N*,*N*-dimethylbenzylamine, $[PdCl(damp)]_2$,[34a] ((dimethylamino)methyl)ferrocene, $[PdCl(damf)]_2$,[59] 4-methoxyacetanilide, $[PdCl(MeO\text{-}aa)]_2$,[60] and 8-methylquinoline, $[PdCl(mq)]_2$,[25] were prepared as described. The 2-phenylpyridine dimer $[PdCl(pp)]_2$ was obtained in 89% yield according to the ligand-exchange procedure identical to that for 2-benzylpyridine.[27] Pyridine-containing monomeric species **6a–10a** were obtained from the chloro-bridged dimers $[PdCl(damp)]_2$, $[PdCl(pp)]_2$, $[PdCl(damf)]_2$, $[PdCl(MeO\text{-}aa)]_2$, and $[PdCl(mg)]_2$, respectively, according to the general procedure described in detail elsewhere.[34]

General Procedure for Preparation of Chloro-Bridged Dimers Bis(μ-chloro)bis[(2-(1-(hydroxyimino)alkyl)phenyl-*C*^{1},*N*)palladium(II)] (2a–d) (Alkyl = Methyl, Ethyl, *n*-Propyl, Benzyl) via Ligand Exchange. To a solution of 0.25 mmol of starting ortho-palladated chloro-bridged dimer ($[PdCl(damp)]_2$, $[PdCl(damf)]_2$, **2d**) in 10 mL of a 1:1 mixture of chloroform–acetic acid (chloroform was pretreated with water to remove reducing alcohols and then dried) was added 10 mL of solution of the corresponding oxime (0.5 mmol), and the resulting mixture was thermostated at 50 °C for ca. 24 h. If the product precipitated (as in the case of **2a–c**), it was separated by filtration, washed with *n*-hexane, and recrystallized from benzene–hexane (1:1). If the product remained in solution (**2d**), the mixture was diluted with 50 mL of chloroform, washed with 80 mL of 5% Na_2CO_3, and dried over Na_2SO_4. The solution was then concentrated to 5 mL, and the product was precipitated by addition of excess *n*-hexane and finally recrystallized from benzene–hexane. Yields are summarized in Table I. All the compounds showed satisfactory C (±0.25), H (±0.15), and N (±0.30%) analyses.

Preparation of Monomeric Pyridine Adducts Chloro[2-(1-(hydroxyimino)alkyl)phenyl-*C*^{1},*N*](Z-pyridine)palladium(II) (4) (Alkyl = Methyl, Ethyl, *n*-Propyl, Benzyl). Preparation was carried out by mixing the corresponding chloro-bridged dimer **2** with substituted pyridine. This procedure is described in detail elsewhere.[34,44] Yields were usually higher than 90%. Again, satisfactory C, H, and N analyses were obtained for all the complexes. The complexes are sufficiently soluble for ^{1}H NMR; these data are summarized in Table II.

Preparation of Monomeric 2,2′-Dipyridyl Adducts (2-(1-(Hydroxyimino)phenyl-*C*^{1},*N*)(2,2′-dipyridyl)palladium(II) Hexafluorophosphate (5) (Alkyl = Ethyl, Benzyl). A parent chloro-bridged dimer (0.1 mmol) suspended in a 1:5 chloroform–acetone mixture (20 mL) was mixed with 2,2′-dipyridyl (62.4 mg, 0.4 mmol) and $AgPF_6$ (75.8 mg, 0.3 mmol), and

(54) Breet, E. J. L.; van Eldik, R.; Kelm, H. *Inorg. Chim. Acta* **1985**, *85*, 151. Hohmann, H.; van Eldik, R. *Inorg. Chim. Acta* **1990**, *174*, 87.
(55) Hay, R. W.; Basak, A. K. *J. Chem. Soc., Dalton Trans.* **1982**, 1819.
(56) Bertini, I.; Luchinat, C.; Rosi, M.; Sgamellotti, A.; Tarantelli, F. *Inorg. Chem.* **1990**, *29*, 1460.
(57) Castan, P.; Dahan, F.; Wimmer, S.; Wimmer, F. L. *J. Chem. Soc., Dalton Trans.* **1990**, 2679.
(58) Beckman, E. *Chem. Ber.* **1890**, *23*, 1680; *Ann. Chem.* **1909**, *365*, 200.
(59) Gaunt, J. C.; Shaw, B. L. *J. Organomet. Chem.* **1975**, *102*, 511.
(60) Horino, H.; Inoue, N. *J. Org. Chem.* **1981**, *46*, 4416.

the mixture was stirred for 3 h by magnetic bar at ambient temperature. Precipitated silver(I) chloride was filtered off, and the solvent was allowed to evaporate slowly to produce the final material. The latter was filtered out, washed with hexane, and dried in air. Yields were 70–73%. Satisfactory C, H, and N analyses were obtained. The ^{1}H NMR spectra were poorly resolved at 100 MHz, and only broad signals were observed in the aromatic region.

Preparation of O-Acylated Chloro-Bridged Dimers Bis(μ-chloro)bis[(2-(1-(acetoxylimino)alkyl)phenyl-C^1,N)palladium(II)] (3) (Alkyl = Ethyl, *n*-Propyl, Benzyl). This was done according to a slightly modified procedure developed by Shaw et al.[20] Complex **2c** (76.3 mg, 0.3 mmol) was dissolved in 5 mL of refluxing acetic anhydride. After 2–3 min, a yellow precipitate was formed which was filtered out, washed with hexane, and air dried to yield 65.6 mg of **3b**. Related complexes **3a,c** were obtained similarly in 70 and 74% yield, respectively. C, H, and N analyses were as above. Representative ^{1}H NMR data are given in Table II.

Spectrophotometric Study of the Behavior of Complexes 4 and 6–10 in Aqueous Solution. Stock solutions of cyclopalladated monomeric complexes **4** and **6a–10a** ((1–5) × 10^{-3} mol dm^{-3}) were prepared in dimethyl sulfoxide. Aliquots were added to a corresponding buffer solution with the ionic strength of 0.1 mol dm^{-3} ($NaClO_4$). Acetate (pH 3.0–6.0), maleate (5.5–7.5), and 5,5′-diethylbarbiturate (7.0–9.0) buffer solutions (0.01 mol dm^{-3}) were employed. Final concentrations of palladium complexes were 10^{-5}–10^{-4} mol dm^{-3}. The solutions were placed into a 1-cm spectrophotometric cell and thermostated by circulating water in the cell compartment of the spectrophotometer before the spectra were recorded.

X-ray Structural Determinations. Crystal data and details of the data-collection procedure, structure solution, and refinement are given in Table VI. All X-ray crystallographic measurements were made with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) at 293 K. All structures were solved by the Patterson method and subsequently by Fourier difference maps. The hydrogen atoms were located in the difference maps. The refinement of structures was performed by the full-matrix least-squares method with anisotropic thermal parameters for all non-hydrogen atoms excluding isotropic parameters for carbon atoms of the C_6H_6 solvate molecule in structure **4d**. All hydrogen atoms in all structures were included in the refinement with fixed positional and isotropic thermal parameters (B = 6 Å^2). Special attention has been paid to the localization of the H-atoms of the 2- and 6-methyl groups of the pyridine ligands in structures **4d,e**. Their positions were located from the difference synthesis of the electronic density. The corresponding peaks were all the highest remaining peaks. All calculations were performed on a IBM PC-ET computer with the SHELX system of programs.

Supplementary Material Available: Listings of crystallographic details, positional and thermal parameters, and complete bond lengths and angles (7 pages). Ordering information is given on any current masthead page.