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Palladium(II)-Promoted Cyclization Reaction of 4-Hydroxybutyronitrile to 2-Iminotetrahydrofuran. X-ray Structure of *cis*-$[PdCl_2\{N(H){=}\overline{CCH_2CH_2CH_2O}\}(PPh_3)]\cdot{}^1/_2CH_2Cl_2$

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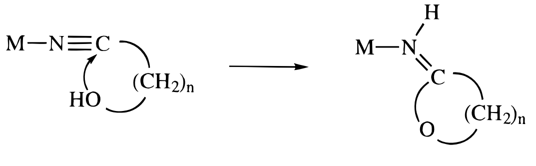
Reaction of 3-bromo-1-propanol with $Et_4N(CN)$ in CH_2Cl_2 at room temperature gives in high yield 4-hydroxybutyronitrile, $HO(CH_2)_3CN$ (**1**), which upon reaction with Na_2PdCl_4 affords $[PdCl_2\{N(H){=}\overline{CCH_2CH_2CH_2O}\}_2]$ (**2**), containing two 2-iminotetrahydrofuran ligands derived from intramolecular cyclization of **1**. Substitution of one imino ligand for an entering nucleophile L leads to the complexes $[PdCl_2\{N(H){=}\overline{CCH_2CH_2CH_2O}\}(L)]$ (L = PPh_3 (**3**), py (**4**), DMF (**5**)) . Similarly, the reaction of **2** with 1 equiv of *cis*-$Ph_2PCH{=}CHPPh_2$ results in the displacement of the two iminolactone ligands and formation of $[PdCl_2(Ph_2PCH{=}CHPPh_2)]$. The ligand **1** and the complexes **2**−**5** were characterized by analytical and spectroscopic techniques. IR data suggest that **2** and **3** are present as a mixture of *cis* and *trans* isomers, while **4** and **5** have a *trans* stereochemistry. Complex **3** gave crystals of the *cis* form, as evidenced by an X-ray structural determination.

Introduction

Coordination of a nitrile, RCN, to an electron-withdrawing transition-metal ion results in an enhanced electrophilicity of the nitrile carbon, thus making it susceptible to nucleophilic attack. Reactions of metal nitriles with protic nucleophiles such as water, alcohols, and amines to generate the corresponding amidates, imido esters, and amidines, respectively, have been extensively reviewed.[1]

We have been recently concerned with the conversion of Pt(II)-coordinated nitriles to N-heterocycles such as 2-oxazoline and 1,3-oxazine, which are formed upon reaction of RCN ligands with $HOCH_2CH_2Cl$/base[2a,b] or $\overline{OCH_2C}H_2/Cl^-$ [2c] and $HOCH_2CH_2CH_2Cl$/base[2d] systems, respectively. An extension of this reaction chemistry would take advantage of the incorporation in the nitrile alkyl chain of a nucleophilic group capable of attacking intramolecularly the metal-coordinated nitrile, thus providing a new route to heterocyclic compounds. Hydroxyalkyl nitriles of the type $HO(CH_2)_nCN$ having a suitable chain length (n = 3, 4) would likely fulfill these requirements, since they are expected, upon coordination to late transition-metal ions, to give iminolactones by intramolecular nucleophilic attack of the −OH functionality on the nitrile carbon atom as illustrated in eq 1.



(1)

Here we report the synthesis of 4-hydroxybutyronitrile, $HO(CH_2)_3CN$, and its conversion to 2-iminotetrahydrofuran promoted by Pd(II).

Experimental Section

General Procedures. All reactions were carried out under an N_2 atmosphere. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium/benzophenone, and CH_2Cl_2 was distilled from CaH_2; all the other solvents were of reagent grade and were used without further purification. IR spectra were taken on a Perkin-Elmer 983 spectrophotometer (abbreviations: s = strong, m = medium, w = weak). Proton and

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carbon-13 NMR spectra were obtained on a Bruker AC-200 spectrometer. ^{1}H NMR shifts were recorded relative to the residual ^{1}H resonances in the deuterated solvents: $CDCl_3$, δ 7.23; CD_3SOCD_3, δ 2.50. The $^{13}C\{^1H\}$ NMR shifts are given relative to the solvent resonance: $CDCl_3$, δ 77.0; CD_2Cl_2, δ 53.8. $^{31}P\{^1H\}$ NMR spectra were run on a Varian FT 80-A spectrometer; chemical shifts are referenced to external 85% H_3PO_4, with downfield values taken as positive. In all the NMR spectra *J* values are in Hz (abbreviations used: s = singlet, t = triplet, m = multiplet, br = broad). The fast atom bombardment (FAB) mass spectra were obtained on a VG ZAB 2F instrument operating with a Xe atom beam energy of 8 keV using *m*-nitrobenzyl alcohol as a matrix. The GC−MS analyses were performed on a Carlo Erba QMD 1000 instrument using a PS 264 capillary column (30 m × 3 μm) from 100 to 250 °C at 10 °C/min with a He flow of 1 mL/min. Elemental analyses were performed by the Department of Analytical, Inorganic and Organometallic Chemistry of the University of Padova. The melting points were taken on a hot plate apparatus and are uncorrected.

Synthesis of $HO(CH_2)_3CN$ (1). To a solution of $Et_4N(CN)$ (4 g, 0.026 mol) in CH_2Cl_2 (20 mL) was added $HO(CH_2)_3Br$ (2.5 mL, 0.027 mol) at room temperature to give a pale yellow solution. The reaction course was followed by IR spectroscopy, which showed the disappearance with time of the $\nu(C{\equiv}N)$ band at 2065 cm^{-1} due to $Et_4N(CN)$ and an increase of the corresponding absorption at 2249 cm^{-1} due to the final product. After it was stirred for 22 h, the reaction mixture was taken to dryness under reduced pressure and the solid residue was washed five times (5 × 20 mL) with an Et_2O/CH_2Cl_2 (4:1 v/v) mixture to remove Et_4NBr. The washes were combined, and after filtration, the solution was taken to dryness to give an oily residue. Yield: 8.04 g (79%). IR (liquid film): $\nu(C{\equiv}N)$ 2249 cm^{-1} (s); $\nu(OH)$ 3441 cm^{-1} (s). ^{1}H NMR (δ, $CDCl_3$): 3.43 [t, $^3J_{HH}$ 5.90, 2H, CH_2OH]; 2.26 [t, $^3J_{HH}$ 7.03, 2H, CH_2CN]; 1.61 (m, 2H, CH_2); 3.59 (s-br, 1H, OH). $^{13}C\{^1H$-undecoupled$\}$ NMR (δ, $CDCl_3$): 119.55 (m, CN); 59.26 [tt, $^1J_{CH}$ 142.9, $^2J_{CH}$ 3.67, CH_2OH]; 27.38 [t, $^1J_{CH}$ 130.34, $-CH_2-$); 13.045 [t, $^1J_{CH}$ 135.92, CH_2CN].

Synthesis of $[PdCl_2\{N(H){=}\overline{CCH_2CH_2CH_2O}\}_2]$ (2). To a stirred suspension of $PdCl_2$ (0.22 g, 1.00 mmol) in H_2O (40 mL) at room temperature was added an excess of NaCl (0.15 g, 2.6 mmol) to give, after 2 h, a clear yellow-brown solution, which was then treated with an excess of **1** (0.3 mL, $d = 1.0473$ g/cm^3, 4.0 mmol). After the mixture was stirred at room temperature for 3 days, a brown precipitate formed, which was filtered off, washed with H_2O (3 × 3 mL) and Et_2O (5 × 3 mL), and dried under vacuum. Yield: 0.26 g (75%). Mp: 208−211 °C dec. Anal. Calcd for $C_8H_{14}N_2O_2Cl_2Pd$: C, 26.7; H, 4.0; N, 8.0. Found: C, 25.22; H, 3.87; N, 8.03. IR (Nujol mull): $\nu(NH)$ 3213 cm^{-1} (vs); $\nu(C{=}N)$ 1684 cm^{-1} (s); $\nu(PdCl)$ 353 (m), 300, and 281 (w-m) cm^{-1} . ^{1}H NMR (δ, CD_3SOCD_3): 7.5−8.3 (br, NH); 4.04 (m, 2H, OCH_2); 3.15 [m, 1H, $CH_2(C{=}N)$]; 2.71 [m, 1H, $CH_2(C{=}N)$]; 2.23 (m, 2H, $-CH_2-$).

Synthesis of $[PdCl_2\{N(H){=}\overline{CCH_2CH_2CH_2O}\}(L)$. L = PPh_3 (3). To a suspension of **2** (0.12 g, 0.322 mmol) in CH_2Cl_2 (20 mL) was added PPh_3 (0.08 g, 0.320 mmol), and the reaction mixture was stirred at room temperature until complete dissolution of the starting complex. After 1 h a yellow-brown solution was obtained, which was concentrated under reduced pressure to a small volume (3 mL). Then, upon addition of Et_2O (30 mL), a yellow solid formed, which was filtered off, washed with Et_2O (2 × 10 mL), and dried under vacuum. Yield: 0.16 g (94%). Mp: 260 °C dec. Anal. Calcd for $C_{22}H_{22}NOPCl_2Pd$: C, 50.35; H, 4.23; N, 2.67. Found: C, 49.85; H, 4.13; N, 2.58. IR (Nujol mull): $\nu(NH)$ 3156 cm^{-1} (s); $\nu(C{=}N)$ 1676 cm^{-1} (s); $\nu(PdCl)$ 337, 292, and 262 cm^{-1} (m). ^{1}H NMR (δ, $CDCl_3$): 6.53 (br, 1H, NH); 4.29 (t, $^3J_{HH}$ 7.05, 2H, OCH_2); 3.17 [t, $^3J_{HH}$ 7.03, 2H, $CH_2(C{=}N)$]; 2.17 (m, 2H, $-CH_2-$). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 28.03 (s) and 25.56 (s). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2): 179.1 (C=N); 66.0 (OCH_2); 23.8 [$CH_2(C{=}N)$]; 15.5 ($-CH_2-$). FAB MS (*m*-nitrobenzyl alcohol; *m/z* (relative abundance %)): 489 ($[(PPh_3)Pd(HN\overline{CCH_2CH_2CH_2O})Cl]^+$, 40%); 453 ($[(PPh_3)Pd(HN\overline{CCH_2CH_2CH_2O})]^+$, 10%); 369 ($[Pd\text{-}PPh_3]^+$, 35%); 404 ($[ClPd(PPh_3)H]^{\bullet+}$, 30%).

L = py (4). To a suspension of **2** (0.15 g, 0.43 mol) in CH_2Cl_2 (20 mL) an excess of pyridine (0.15 mL, 1.8 mol) was added and the reaction mixture was stirred at room temperature until complete dissolution of the starting complex. After 4 h the yellow solution was concentrated under reduced pressure to a small volume (3 mL) and treated with Et_2O (20 mL). A yellow solid formed, which was filtered off, washed with Et_2O (2 × 10 mL), and dried under vacuum. Yield: 0.11 g (78%). Mp: 201 °C dec. Anal. Calcd for $C_9H_{12}N_2Cl_2Pd$: C, 31.66; H, 3.54; N, 8.20. Found: 32.14; H, 3.74; N, 8.64. IR (Nujol mull): $\nu(NH)$ 3198 cm^{-1} (s); $\nu(C{=}N)$ 1679 cm^{-1} (s); $\nu(PdCl)$ 354 cm^{-1} (m). ^{1}H NMR (δ, $CDCl_3$): 5.70 (br, 1H, NH); 4.41 (m, 2H, OCH_2); 3.33 (m, 1H, $NCCH_2$); 2.91 (m, 1H, $NCCH_2$); 2.24 (m, 2H, CH_2).

L = DMF (5). A suspension of **2** (0.2 g, 0.57 mmol) in DMF (20 mL) was stirred at room temperature. After 48 h a light yellow solution was obtained. Workup as for **4** gave **5**. Yield: 0.16 g (83%). Mp: 222 °C dec. Anal. Calcd for $C_7H_{14}N_2O_2Cl_2Pd$: C, 25.06; H, 4.21; N, 8.35. Found: C, 25.12; H, 4.12; N, 7.93. IR (Nujol mull): $\nu(NH)$ 3212 cm^{-1} (s); $\nu(C{=}N)$ 1684 cm^{-1} (s); $\nu(PdCl)$ 354 cm^{-1} (m). ^{1}H NMR (δ, $CDCl_3$): 5.70 (br, 1H, NH); 4.55 (m, 2H, OCH_2); 3.29 (m, 1H, $NCCH_2$); 2.75 (m, 1H, $NCCH_2$); 2.21 (m, 2H, CH_2).

Reaction of 2 with *cis*-1,2-Bis(diphenylphosphino)ethylene. A suspension of **2** (0.1 g, 0.28 mmol) in CH_2Cl_2 (20 mL) was treated with *cis*-$Ph_2PCH{=}CHPPh_2$[3] (0.114 g, 0.28 mmol) at room temperature. The slow dissolution of the starting compound **2** was accompanied by the formation of a white precipitate, which, after 20 h, was filtered off, washed with Et_2O, and dried under vacuum. It was identified as $[PdCl_2(Ph_2PCH{=}CHPPh_2)]$ by comparison with a sample independently prepared.[4] Yield: 0.155 g (96%). IR (Nujol mull): $\nu(PdCl)$ 286 (m), 309 (s) cm^{-1}. $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 48.36 ppm (s, $^1J_{PtP}$ 3682).

The mother liquors were taken to dryness to give an oily residue. IR (liquid film): $\nu(NH)$ 3385 cm^{-1}; $\nu(C{=}N)$ 1662 cm^{-1}. ^{1}H NMR (δ, $CDCl_3$): 3.52 (m, 2H, OCH_2); 2.77 (m, 2H, $NCCH_2$); 1.85 (m, 2H, CH_2). A CH_2Cl_2 solution of the oil was analyzed by GC−MS. Only one compound, apart from the solvent, was present with the retention time 6.03 min: *m/z* 86 (MH^+, relative intensity 40%); 56 ($[MH - H_2CO]^+$, 35%); 42 ($[CH_2CH_2CH_2]^+$, 98%); 28 ($[CH_2CH_2]^+$, 100%).

Single-Crystal X-ray Diffraction Analysis of *cis*-3. Crystals suitable for X-ray data collection were obtained from a mixed solvent (CH_2Cl_2/Et_2O); eventually a small crystal was directly transferred, with mother liquor, to a glass capillary and then mounted on the diffractometer. All crystallographic measurements were carried out at 294 K on a Nicolet Siemens R3m/V diffractometer, using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The unit-cell parameters and their associated estimated standard deviations were obtained from a least-squares fit of the setting angles of 50 reflections in the range $18 > 2\theta > 26°$ (see Table 1 for crystal data). Although the data collection was fast, a significant decrease (up to 30%) in intensity was observed by two standard reflections measured after each 100 reflections throughout collection (4 days). A correction for crystal decay was applied to the measured counts, but an empirical absorption correction based on the azimuthal ψ-scan method was impossible to apply. The structure was determined *via* the standard heavy-atom method and Fourier difference technique, and it was refined by full-matrix least squares using the SHELXTL-Plus program system.[5] All non-hydrogen atoms were refined with anisotro-

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Table 1. Crystallographic Data for cis-[PdCl$_2${N(H)=CCH$_2$CH$_2$CH$_2$O}(PPh$_3$)] (*cis*-3)

formula	$C_{22}H_{22}Cl_2NOPPd\cdot{}^1/_2CH_2Cl_2$
fw	567.1
cryst syst	triclinic
space group	$P\bar{1}$
a	9.113(2) Å
b	16.110(4) Å
c	18.192(4) Å
α	109.21(2)°
β	91.78(2)°
γ	93.34(2)°
V	2517(1) Å^3
Z	4
diffractometer	Siemens R3m/V
T	21 °C
λ	0.7107 Å
μ	11.3 cm^{-1}
ρ(calcd)	1.499 g cm^{-3}
no. of observns ($F_o \geq 4\sigma(F_o)$)	4674 (up to $2\theta = 45°$)
anisotropy for non-H atoms	
R	0.069
weighting scheme	$w^{-1} = \sigma(F) + 0.0041F^2$
R_w	0.081

pic thermal parameters, except for the carbon and chlorine atoms of the disordered CH_2Cl_2 molecule, which were refined isotropically. The solvent molecule was disordered essentially over two positions with site occupation factors of $^2/_3$ and $^1/_3$. No attempts were made to locate the hydrogen atoms. The deterioration of the crystal during the data collection and probably the inadequate description of the disorder of the CH_2Cl_2 molecule explain the relatively high R value; however, the model establishes the binding/stereochemistry around the metal atom. The final atomic fractional coordinates are reported in Table 2, while selected bond distances and angles are given in Table 3.

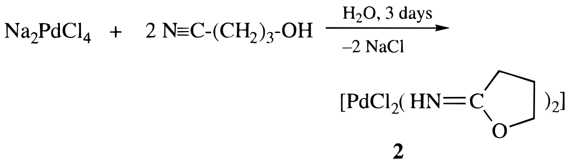
Results and Discussion

4-Hydroxybutyronitrile (**1**) was readily prepared via a substitution reaction between 1 equiv of $Et_4N(CN)$ and $HO(CH_2)_3Br$ in CH_2Cl_2 at room temperature (eq 2). The

$$HO\text{-}(CH_2)_3\text{-}Br + NEt_4(CN) \xrightarrow[\text{RT, 22 h}]{CH_2Cl_2} \underset{\mathbf{1}}{HO\text{-}(CH_2)_3\text{-}CN} + NEt_4Br \qquad (2)$$

reaction occurs in the homogeneous phase under mild conditions; workup of the reaction mixture gave **1** in ca. 80% yield as the only reaction product. This method proved to be more efficient than that previously reported involving heating $EtOH/H_2O$ solutions of KCN and 3-chloro-1-propanol.[6] Compound **1** is thermally stable, and we had no spectroscopic evidence for spontaneous ring closure, as previously reported.[7] The hydroxyalkanenitrile **1** was characterized by spectroscopic data. Characteristic IR (liquid film) features are the C≡N and O−H stretching absorptions, which appear as strong bands at 2249 and 3441 cm^{-1}, respectively. In the ^{1}H NMR spectrum the CH_2OH and CH_2CN protons appear as triplets at 3.43 and 2.26 ppm, respectively, by coupling with the adjacent methylene protons, which appear as a multiplet at 1.61 ppm. The OH proton resonates at 3.59 ppm, giving rise to a broad signal. In the ^{13}C NMR spectrum the nitrile carbon appears at 119.55 ppm.

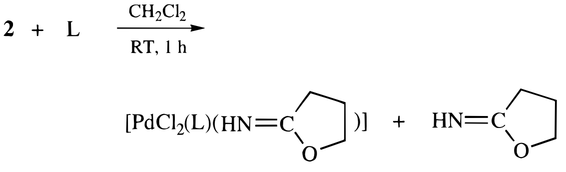
The reaction of Na_2PdCl_4, obtained in situ on treatment of an aqueous suspension of $PdCl_2$ with NaCl,[8] with a slight excess of **1** at room temperature affords a poorly soluble brown product, which was identified as compound **2** (eq 3) on the basis of analytical and ^{1}H NMR data. The formation of **2** can be explained by



2 (3)

initial coordination of the nitrile moiety to the Pd(II) center, which activates the nitrile carbon toward intramolecular nucleophilic attack of the dangling −OH group; proton transfer to the imino nitrogen atom then gives the observed product **2**. The intermediate Pd(II)−nitrile complex could not be detected by IR or ^{1}H NMR spectroscopy. The IR spectrum of **2** shows strong absorptions at 3197 cm^{-1} and at 1681 cm^{-1} due to N−H and C=N stretching bands, respectively. Three absorptions in the Pd−Cl region (350−280 cm^{-1}) suggest the presence of a mixture of *trans* (one band) and *cis* (two bands) isomers, with the absorption at higher wavenumbers corresponding to the *trans* species.[9] The ^{1}H NMR spectrum shows complex multiplets for the $-CH_2$ ring protons, as also found in other C- or N-coordinated ring systems such as *cis*-[MCl$_2${CN(R)CH$_2$CH$_2$NH}(L)] (M = Pd, Pt; R = alkyl, aryl; L = tertiary phosphine, isocyanide)[10] and *cis*- and *trans*-[PtCl$_2${N=C(R)OCH$_2$CH$_2$CH$_2$}$_2$].[2d] The chemical shift assignments were made by comparison with those of Pt(II)-coordinated *N*-oxazoline complexes.[2b,c,11]

Substitution of one imino ligand in **2** by an entering nucleophile L leads to complexes **3**−**5** (eq 4). The



(4)

L = PPh$_3$ (**3**), Py (**4**), DMF (**5**)

presence of the free iminolactone in solution was confirmed by GC−MS analysis of the reaction mixtures. As for **2**, compound **3** was likely formed as a mixture of *cis* and *trans* isomers (although crystals of **3** were obtained only for the *cis* form, see the molecular structure below), as indicated by the presence of three bands in the Pd−Cl region; this is also supported by

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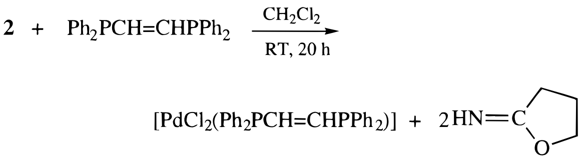
Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) of *cis*-3

	x	y	z	U_{eq}[c]		x	y	z	U_{eq}[c]
Pd(1)	616(1)	3561(1)	4199(1)	39(1)	P(1B)	4802(4)	7515(2)	624(2)	40(1)
Cl(1A)	2076(4)	4698(2)	3953(2)	52(1)	O(1B)	8333(10)	6137(7)	−587(5)	61(4)
Cl(2A)	126(4)	2853(2)	2883(2)	62(1)	N(1B)	6014(12)	5776(7)	−376(6)	47(4)
P(1A)	−813(4)	2494(2)	4420(2)	44(1)	C(1B)	7017(13)	5718(7)	−833(7)	39(4)
O(1A)	3132(10)	3976(6)	5627(5)	58(4)	C(2B)	9311(18)	5968(12)	−1240(10)	74(7)
N(1A)	813(12)	4261(7)	5353(6)	45(4)	C(3B)	8588(21)	5244(12)	−1880(10)	87(8)
C(1A)	1892(15)	4356(8)	5843(8)	47(5)	C(4B)	6986(16)	5211(9)	−1676(8)	57(6)
C(2A)	4143(18)	4151(12)	6312(11)	78(8)	C(5B)	5649(14)	8632(8)	1083(8)	47(5)
C(3A)	3543(19)	4882(12)	6929(9)	75(7)	C(6B)	5159(18)	9308(9)	828(9)	66(6)
C(4A)	1966(16)	4875(9)	6689(7)	53(5)	C(7B)	5780(19)	10149(9)	1155(9)	69(7)
C(5A)	−278(15)	1376(8)	4014(7)	46(5)	C(8B)	6837(19)	10351(10)	1737(10)	69(7)
C(6A)	−923(19)	728(9)	4287(9)	67(6)	C(9B)	7347(18)	9697(10)	1997(10)	67(6)
C(7A)	−507(21)	−125(10)	4024(10)	75(7)	C(10B)	6717(15)	8829(8)	1657(8)	50(5)
C(8A)	561(23)	−334(10)	3487(12)	90(9)	C(11B)	4511(14)	7437(8)	−393(7)	43(5)
C(9A)	1205(18)	277(9)	3201(12)	83(8)	C(12B)	3137(17)	7262(10)	−774(8)	59(6)
C(10A)	800(15)	1165(9)	3492(10)	61(6)	C(13B)	2962(21)	7190(12)	−1536(10)	78(8)
C(11A)	−917(18)	2637(8)	5447(8)	59(6)	C(14B)	4143(23)	7282(10)	−1962(9)	73(7)
C(12A)	378(21)	2515(10)	5843(10)	80(8)	C(15B)	5522(21)	7456(10)	−1590(9)	68(7)
C(13A)	326(29)	2640(12)	6633(11)	99(10)	C(16B)	5721(17)	7544(9)	−804(9)	61(6)
C(14A)	−890(41)	2890(12)	7031(13)	130(14)	C(17B)	2935(14)	7493(8)	953(7)	43(5)
C(15A)	−2133(30)	3026(14)	6642(11)	106(11)	C(18B)	2191(16)	6707(9)	769(8)	54(6)
C(16A)	−2142(21)	2901(10)	5869(9)	71(7)	C(19B)	678(15)	6618(10)	859(8)	55(6)
C(17A)	−2700(15)	2538(9)	4102(7)	49(5)	C(20B)	−14(17)	7361(11)	1174(10)	68(7)
C(18A)	−3612(15)	1783(10)	3714(8)	59(6)	C(21B)	729(17)	8150(10)	1374(9)	67(7)
C(19A)	−5037(17)	1862(11)	3534(10)	74(7)	C(22B)	2193(15)	8232(9)	1284(8)	55(6)
C(20A)	−5629(17)	2657(13)	3744(11)	75(8)	Cl(1)[a]	266(9)	1422(6)	338(5)	105(2)
C(21A)	−4711(16)	3429(12)	4148(9)	66(7)	Cl(2)[a]	1960(9)	554(6)	1190(5)	102(2)
C(22A)	−3319(16)	3341(9)	4292(7)	52(5)	C(23)[a]	292(27)	967(18)	1069(16)	78(7)
Pd(2)	5998(1)	6408(1)	798(1)	39(1)	Cl(1′)[b]	5881(14)	8449(9)	4496(8)	78(3)
Cl(1B)	7252(4)	5244(2)	1000(2)	52(1)	Cl(2′)[b]	4973(22)	9594(15)	3615(13)	127(6)
Cl(2B)	5706(4)	7014(2)	2116(2)	60(1)	C(23′)[b]	4830(101)	8776(62)	3717(55)	193(33)

[a] Site occupancy $^2/_3$. [b] Site occupancy $^1/_3$. [c] Equivalent isotropic U, defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

the presence of two resonances of the PPh$_3$ ligand in the ^{31}P NMR spectrum. On the other hand, complexes **4** and **5** show only one Pd−Cl band at ca. 350 cm^{-1}, indicating a *trans* geometry. Other IR and ^{1}H NMR data (see Experimental Section) are similar to those described for **2**. The higher solubility of complexes **3**−**5** compared to that of **2** allowed us to grow crystals of **3** suitable for X-ray analysis, which showed that **3** consisted of only the *cis* isomer (see below).

Similarly, the reaction of **2** with 1 equiv of *cis*-1,2-bis(diphenylphosphino)ethylene results in the complete displacement of the two iminolactone ligands, as shown in eq 5.



(5)

X-ray Structure Analysis of *cis*-3. The molecular structure of *cis*-[PdCl$_2${N(H)=$\overline{\text{CCH}_2\text{CH}_2\text{CH}_2\text{O}}$}(PPh$_3$)] (*cis*-**3**) is shown in Figure 1, together with the atom labeling.[12] The crystal contains two crystallographically independent, monomeric, neutral and well-separated moieties (*A* and *B*) and a disordered CH$_2$Cl$_2$ molecule. The two moieties are superimposable; in fact, the weighted root-mean-square deviation, derived from the BMFIT program,[13] is only 0.043 Å, when the fitting is performed using the coordination geometry and the five-membered-ring atoms. Nevertheless, no bond distances and angles differ by more than 2 standard deviations.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for *cis*-3

	molecule *A*	molecule *B*
Pd−Cl(1)	2.371(4)	2.374(4)
Pd−Cl(2)	2.304(3)	2.302(3)
Pd−P(1)	2.245(4)	2.246(4)
Pd−N(7)	2.026(9)	2.042(10)
N(1)−C(1)	1.27(2)	1.24(2)
C(1)−O(1)	1.32(2)	1.33(1)
O(1)−C(2)	1.46(2)	1.47(2)
C(2)−C(3)	1.48(2)	1.46(2)
C(3)−C(4)	1.49(2)	1.52(2)
C(4)−C(1)	1.49(2)	1.48(2)
Pd−C(mean)	1.81(1)	1.82(1)
Cl(1)−Pd−Cl(2)	91.1(1)	90.7(1)
Cl(1)−Pd−P(1)	178.6(1)	179.2(1)
Cl(1)−Pd−N(1)	89.1(3)	88.9(3)
Cl(2)−Pd−P(1)	88.3(1)	88.5(1)
Cl(2)−Pd−N(1)	172.8(3)	172.7(3)
P(1)−Pd−N(1)	91.3(3)	91.8(3)
Pd−N(1)−C(1)	129.7(9)	130.8(8)
N(1)−C(1)−O(1)	121(1)	121(1)
C(1)−O(1)−C(2)	109(1)	110(1)
O(1)−C(2)−C(3)	105(1)	107(1)
C(2)−C(3)−C(4)	106(1)	105(1)
C(3)−C(4)−C(1)	103(1)	104(1)
C(4)−C(1)−O(1)	112(1)	111(1)
C(4)−C(1)−N(1)	127(1)	128(1)

The palladium atom is surrounded, as expected, by a *cis* square-planar Cl$_2$PN donor set and the distances/angles around the metal agree well with the values in several other monomeric *cis*-Cl$_2$PdPN complexes (see Table 4). In particular, the greater *trans* influence of the phosphine,[14] compared to a nitrogen donor, can be seen in the lengthening of Pd−Cl(1) by 0.069 Å relative to Pd−Cl(2), the average being 0.085 Å for the other

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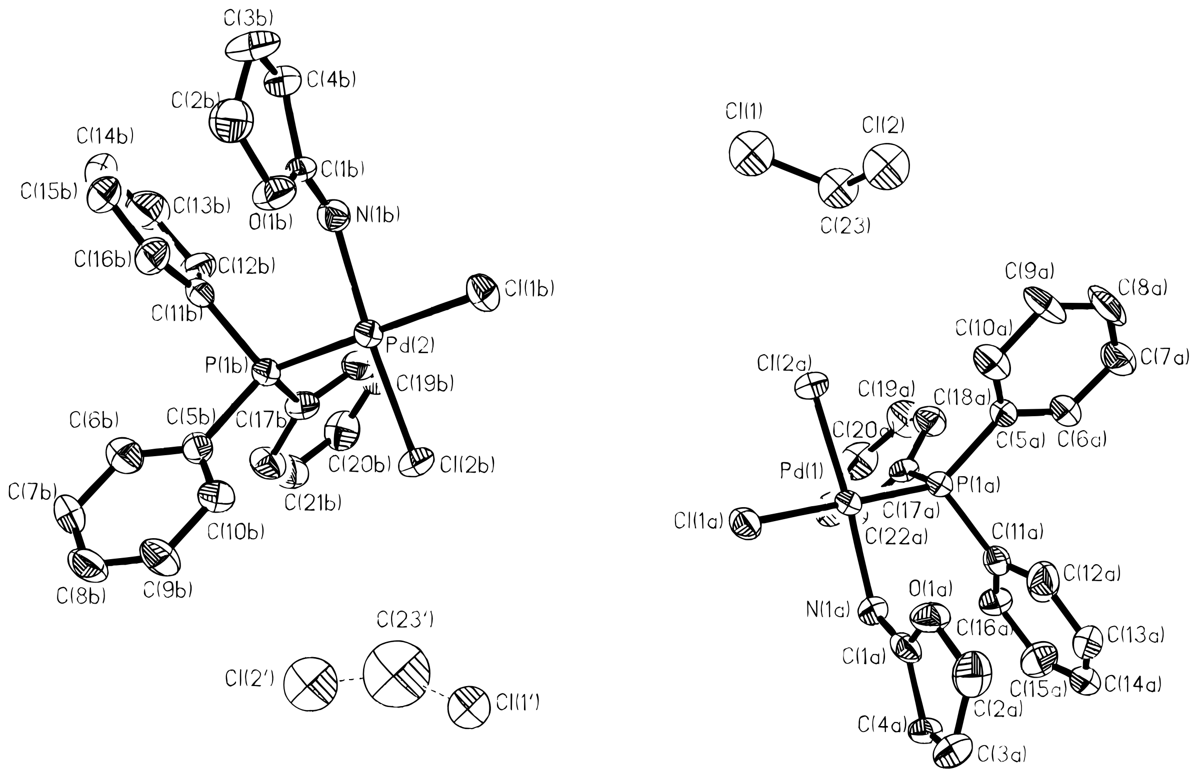

Figure 1. ORTEP diagram of the two molecules *A* and *B* of *cis*-**3**, showing the-atom labeling scheme. Thermal ellipsoids are drawn at the 40% probability level. The two sites of the disordered CH_2Cl_2 molecule are also shown.

Table 4. Comparison of Bond Distances (Å), Angles (deg), and Tetrahedral Distortion (Δ, Å) in Neutral Monomeric Palladium(II) Complexes Containing the *cis*-Cl_2PdPN Core, with two Unidentate PN ligands for the First Two Complexes and a Bidentate Ligand for the Others

	Pd−Cl										
complex	trans to P	trans to N	Pd−P	Pd−N	$Cl_{trans\ to\ P}$− Pd−P	$Cl_{trans\ to\ N}$− Pd−N	Cl− Pd−Cl	P− Pd−N	Δ	Δ	ref
$\mathbf{Cl_2Pd}(\mathbf{P}\mathrm{Ph_3})[\mathbf{N}\mathrm{H{=}\overline{CO(CH_2)_2C}H_2}]$	2.372(4)	2.303(3)	2.245(4)	2.036(9)	179.0(1)	172.8(4)	91.0(1)	91.6(3)	0.07	±0.06	present work
$\mathbf{Cl_2Pd}(\mathbf{P}\mathrm{Ph_3})[\mathrm{Me_2SN}\mathbf{R}]$[a]	2.374(2)	2.289(2)	2.246(2)	2.022(5)	176.0(1)	175.9(2)	92.2(1)	96.4(2)	0.01	±0.06	*e*
$\mathbf{Cl_2Pd}[\mathrm{PhBu}\mathbf{P}\mathrm{C_6H_4CH(Me)}\mathbf{N}\mathrm{Me_2}]$	2.386(1)	2.285(1)	2.241(1)	2.134(4)	176.3(1)	168.1(1)	88.1(1)	94.0(1)	0.07	±0.14	*f*
$\mathbf{Cl_2Pd}[\mathrm{Bu_2}\mathbf{P}\mathrm{CH_2\text{-}2\text{-}}\mathbf{R}]$[b]	2.393(1)	2.294(1)	2.229(1)	2.078(4)	164.9(1)	176.0(1)	90.8(1)	82.3(1)	0.12	±0.17	*g*
$\mathbf{Cl_2Pd}[\mathrm{Ph_2}\mathbf{P}\mathrm{CH_2CH_2\{(CH_2)_2SMe\}}\mathbf{N}\mathrm{Me_2}]$	2.370(2)	2.293(3)	2.214(2)	2.158(7)	177.9(1)	176.7(2)	91.1(1)	86.5(2)	0.03	±0.01	*h*
$\mathbf{Cl_2Pd}[\mathrm{Ph_2}\mathbf{P}\mathrm{CH_2CH\{(CH_2)_3SMe\}}\mathbf{N}\mathrm{Me_2}]$	2.374(3)	2.289(5)	2.194(3)	2.12(1)	173.9(2)	175.5(3)	91.3(2)	86.9(3)	0.04	±0.08	*h*
$\mathbf{Cl_2Pd}[\mathrm{Ph_2}\mathbf{P}\mathrm{CH_2PPh_2}\mathbf{N}\mathrm{H}]$	2.375(2)	2.319(2)	2.224(2)	2.021(6)	175.4(1)	177.0(2)	94.6(7)	87.1(2)	0.01	±0.01	*i*
$\mathbf{Cl_2Pd}[\mathrm{Ph_2}\mathbf{P}\mathrm{C_{10}H_{15}N}\mathbf{N}\mathrm{Me_2}]$	2.396(4)	2.297(4)	2.205(3)	2.108(7)	164.4(1)	171.2(2)	89.6(2)	96.1(2)	0.07	±0.22	*j*
$\mathbf{Cl_2Pd}[\mathrm{Ph_2}\mathbf{P}\mathrm{C_6H_2(3,6\text{-}OMe)\text{-}2\text{-}}\mathbf{R}]$[c]	2.378(2)	2.277(3)	2.232(2)	2.049(6)	171.6(1)	168.6(2)	91.4(2)	84.7(2)	0.04	±0.18	*k*
$\mathbf{Cl_2Pd}[(p\text{-}\mathrm{MeC_6H_4})_2\mathbf{PR}]$[d]	2.38(1)	2.30(1)	2.18(1)	2.14(3)	177.6(4)	174.0(8)	91.4(5)	85.1(8)	0.02	±0.05	*l*
$\mathbf{Cl_2Pd}[\mathrm{Ph_2}\mathbf{P}\mathrm{C_6H_4CH_2OCH_2C_5H_4}\mathbf{N}]$	2.351(1)	2.282(2)	2.254(1)	2.044(4)	177.5(1)	176.0(1)	91.6(1)	93.3(1)	0.05	±0.00	*m*

[a] R = 2-pyrimidinyl. [b] R = 8-methylquinoline. [c] R = isoquinoline. [d] R = $CH_2CH(i\text{-}Pr)NHCH_2(p\text{-}OMeC_6H_4)$. [e] Davidson, J. L.; Preston, P. N.; Spankie, S. A. R.; Douglas, G.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1989**, 497. [f] Takenaka, A.; Sasada, Y.; Yamamoto, K., Tsuji, J. *Bull Chem. Soc. Jpn.* **1977**, *50*, 3177. [g] Deeming, A. J.; Rothwell, I. P.; Hursthouse, M. B.; Abdul Malik, K. M. *J. Chem. Soc., Dalton Trans.* **1980**, 1974. [h] Cross, G.; Vriesema, B. K.; Boven, G.; Kellogg, R. M.; van Bolhuis, F. *J. Organomet. Chem.* **1989**, *370*, 357. [i] Katti, K. V.; Batchelor, R. J.; Einstein, F. W. B.; Cavell, R. G. *Inorg. Chem.* **1990**, *29*, 808. [j] Perera, S. D.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1992**, 999. [k] Alcock, N. W.; Brown, J. M.; Pearson, M.; Woodward, S. *Tetrahedron: Asymmetry* **1992**, *3*, 17. [l] Albinati, A.; Lianza, F.; Berger, H.; Pregosin, P. S.; Rüegger, H.; Kunz, R. W. *Inorg. Chem.* **1993**, *32*, 478. [m] Tani, K.; Yabuta, M.; Nakamura, S.; Yamagata, T. *J. Chem. Soc., Dalton Trans.* **1993**, 2781.

complexes. The Pd−N distance of 2.036(9) Å represents the first distance determination of a Pd−N(imine) type bond, and it lies at the end of the wide range of values (2.02−2.16 Å) observed in the complexes (Table 4). The complex molecules are packed according to van der Waals interactions (Figure 2); only the N−H···Cl contacts may be unusual. Assuming a planar geometry around N, the intermolecular NH···Cl (at *x*, 1 − *y*, 1 − *z*) separation is 2.37 Å with an N−H···Cl angle of 179° (N···Cl = 3.27 Å) in moiety *A*; the corresponding values in *B* (2.40 Å, 172°, and 3.29 Å) pertain to the chlorine atom at 1 − *x*, 1 − *y*, *z*. On the other hand, the N···Cl distances are just the sum of the van der Waals radii (1.55 + 1.75 Å),[15] and these may be regarded as interactions between these atoms.

Conclusions

In summary, the hydroxyalkanenitrile $HO(CH_2)_3$-CN is readily converted to the iminolactone $HN{=}\overline{CCH_2CH_2CH_2O}$ by intramolecular ring closure promoted by Pd(II). Although this reaction chemistry is unprecedented for transition-metal-coordinated nitriles, it can be related to that reported for the hydroxy-

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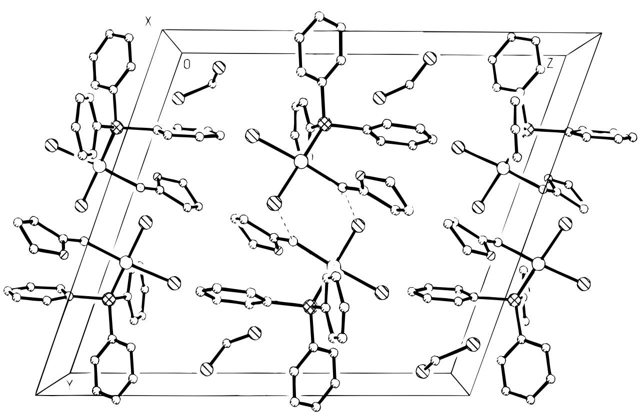

Figure 2. Packing diagram of *cis*-**3**; dotted lines show the relevant N(1)−H···Cl(1) contacts.

alkyl isocyanide $HO(CH_2)_3NC$,[16a,b] which is unreactive as the free ligand or when coordinated to transition metals in low oxidation states toward intramolecular nucleophilic attack at the isocyanide carbon by the hydroxyl oxygen, but it is spontaneously converted to the oxazolidin-2-ylidene ligand when coordinated to Pd(II).[16c] Furthermore, the synthetic procedure described above represents a new suitable method for the preparation of the imino tetrahydrofuran $HN{=}CCH_2CH_2CH_2O$, which is alternatively prepared by organic methods via cyclization reactions of amides[17] under stronger conditions or by ring expansion of epoxides.[18]

Further development of the chemistry of hydroxyalkanenitriles $HO(CH_2)_nCN$ as well as of other functionalized nitriles is under study.

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Supporting Information Available: Anisotropic thermal parameters (Table S1), remaining bond lengths (Table S2), and angles (Table S3), and a diagram showing the superimposition of molecules A and B (Figure 3) (6 pages). Ordering information is given on any current masthead page.

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