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Oxime-substituted NCN-pincer palladium and platinum halide polymers through *non*-covalent hydrogen bonding (NCN = $[C_6H_2(CH_2NMe_2)_2\text{-}2,6]^-$)

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ABSTRACT

The oxime-substituted NCN-pincer molecules HON═CH-1-$C_6H_3(CH_2NMe_2)_2$-3,5 (**2a**) and HON═CH-4-$C_6H_2(CH_2NMe_2)_2$-2,6-Br-1 (**2b**) were accessible by treatment of the benzaldehydes H(O)C-4-$C_6H_3(CH_2NMe_2)_2$-3,5 (**1a**) and H(O)C-4-$C_6H_2(CH_2NMe_2)_2$-2,6-Br-1 (**1b**) with an excess of hydroxylamine. In the solid state both compounds are forming polymers with intermolecular O–H···N connectivities between the Me_2NCH_2 substituents and the oxime entity of further molecules of **2a** and **2b**, respectively. Characteristic for **2a** and **2b** is a helically arrangement involving a crystallographic 2_1 screw axis of the HON═CH-1-$C_6H_3(CH_2NMe_2)_2$-3,5 and HON═CH-4-$C_6H_2(CH_2NMe_2)_2$-2,6-Br-1 building blocks.

The reaction of **2b** with equimolar amounts of $[Pd_2(dba)_3 \cdot CHCl_3]$ (**3**) (dba = dibenzylidene acetone) or $[Pt(tol)_2(SEt_2)]_2$ (**4**) (tol = 4-tolyl) gave by an oxidative addition of the C–Br unit to M coordination polymers with a [(HON═CH-4-$C_6H_2(CH_2NMe_2)_2$-2,6)MBr] repeating unit (**5**: M = Pd, **6**: M = Pt). Complexes **5** and **6** are in the solid state linear hydrogen-bridged polymers with O–H···Br contacts between the oxime entities and the metal-bonded bromide.

1. Introduction

Since the pioneering work of Hantzch and Werner in the late 19th century and of Chugaev in 1905 on oximes and transition metal complexes thereof this class of compounds has been intensively studied [1,2]. Molecular recognition by the formation of intermolecular hydrogen bonds in oximes, is widely used for the construction of supramolecular aggregates in the solid state [3]. Oximes have an O–H group as hydrogen bond donor; the N and O atoms are potential hydrogen bond acceptors, whereby in most cases bonding to the N atom is preferred [4]. Most of all oximes form hydrogen-bonded dimers in the solid state (graph set $R_2^2(6)$), but also trimers [5], tetramers [6] and linear chains [7] are relatively common. Additional flexibility is achieved by the possible *E*/*Z* isomerism of the oxime group. Furthermore, diverse coordination modes including nitrogen- and/or oxygen-coordination to different transition metal atoms are known for oximato-metal species [2–8].

Other versatile ligand systems for the stabilization of low-valent transition metal centers are monoanionic, (potentially) terdentate bisphosphino-, bissulfido- and bisaminoaryl anions of general type $[C_6H_3(CH_2ER_n)_2\text{-}2,6]^-$ (n = 1, 2; E = P, S, N; R = organic group) abbreviated as PCP-, SCS- or NCN-pincers [9,10]. In the corresponding PCP, SCS or NCN transition metal complexes stable carbon–metal σ-bonds are present, due to the *ortho*-chelating effect of the pincer ligands.

A combination of both, the oxime and the pincer ligating groups in a single molecule opens the possibility to prepare multimetallic species with interesting coordination modes and properties. The formation of larger molecules *via* self assembly should be possible.

We report here on the synthesis and reaction chemistry of oxime-functionalized NCN-pincer molecules. Depending on the nature of the 4-oxime-substituted NCN-pincer part different structural motifs are observed in the solid state.

2. Results and discussion

2.1. Synthesis and spectroscopy

Several methods for the preparation of oximes exist including the reduction of nitro compounds [11], oxidation of amines [12], addition of NOCl to alkenes [13] and addition of hydroxylamine to aldehydes or ketones [14]. In the synthesis of the title compounds the benzaldehydes H(O)C-1-$C_6H_3(CH_2NMe_2)_2$-3,5 (**1a**) and H(O)C-4-$C_6H_2(CH_2NMe_2)_2$-2,6-Br-1 (**1b**) were heated to reflux with an excess of hydroxylamine in ethanol solutions for 1 h

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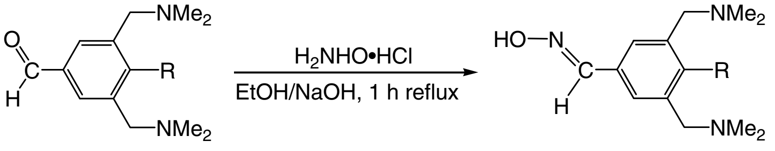
(Eq. (1)). After appropriate work-up, HON=CH-1-$C_6H_3(CH_2NMe_2)_2$-3,5 (**2a**) and HON=CH-4-$C_6H_2(CH_2NMe_2)_2$-2,6-Br-1 (**2b**) could be isolated as colorless solids in 74% (**2a**) and 79% (**2b**) yield, respectively.



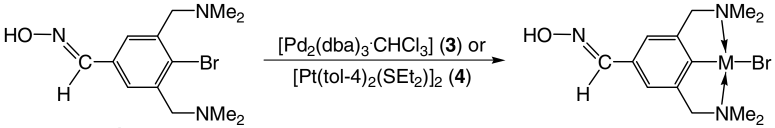
1a, R = H
1b, R = Br

2a, R = H
2b, R = Br

(1)

Single X-ray structure analysis shows the exclusive formation of the *E*-isomer (see below).

Carbon-halide oxidative addition to transition metals in low oxidation states has been successfully used to prepare organometallic C–M–X species (X = halide) [15]. Thus, **2b** was reacted with $[Pd_2(dba)_3 \cdot CHCl_3]$ (**3**) (dba = dibenzylidene acetone) in benzene at 25 °C (Eq. (2)). An irreversible chemo-selective oxidative addition of **2b** to Pd took place and the insertion product [(HON=CH-4-$C_6H_2(CH_2NMe_2)_2$-2,6)PdBr] (**5**) was formed, which, after appropriate work-up, could be isolated as a pale yellow solid in 86% yield. When instead of **3** the platinum(0) source $[Pt(tol)_2(SEt_2)]_2$ (**4**) (tol = 4- tolyl) is used, then the iso-structural platinum pincer complex [(HON=CH-4-$C_6H_2(CH_2NMe_2)_2$-2,6)PtBr] (**6**) is formed. Yellow **6** could be isolated in 98% yield (Eq. (2)).



2b

5, M = Pd
6, M = Pt

(2)

The ^1H and $^{13}C\{^1H\}$ NMR spectra of **2a**, **2b**, **5** and **6** show resonance signals typical for NCN-pincer complexes [10,15]. The Me_2N and CH_2 protons for the *non*-metallated pincers **2a** and **2b** appear as singlets at 2.22 and 3.43 ppm for **2a** and at 2.33 and 3.60 ppm for **2b**. A small downfield shift of these resonance signals is noticed for **2b**, when compared to **2a**, explainable by the electron withdrawing properties of the bromine atom. Upon coordination of the Me_2NCH_2 *ortho*-substituents to palladium (**5**) or platinum (**6**) a significant shift of these resonance signals to lower field is observed (**5**: NMe_2, 2.94; CH_2, 4.10; **6**: NMe_2, 3.07; CH_2, 4.10 ppm). A similar tendency can be recognized in the $^{13}C\{^1H\}$ NMR spectra for these building blocks ($N(CH_3)_2$: 44.9 (**2a**), 45.3 (**2b**), 53.7 (**5**), and 55.2 (**6**); CH_2: 63.7 (**2a**), 63.4 (**2b**), 74.2 (**5**), and 77.7 ppm (**6**)). For **6** typical ^{195}Pt satellites are found with coupling constants of 38.5 Hz ($^3J_{PtH(Me)}$) and 45.6 Hz ($^3J_{PtH(CH2)}$), respectively.

NMR spectroscopy also unequivocally allows to determine the oxime moiety in **2a**, **2b**, **5** and **6**. The N=C*H* methine proton can be detected at ca. 8 ppm in the ^1H NMR, while the sp^2-hybridized carbon atom of this unit is found at ca. 149 ppm in the $^{13}C\{^1H\}$ NMR spectrum [16].

IR spectroscopy is also suitable to determine the oxime moiety present in **2a**, **2b**, **5** and **6**. The stretching vibration for the C=N entity is found at 1655 (**2a**) or 1654 cm^{-1} (**2b**, **5**, **6**) having both weak intensity [17]. In addition, a broad intense vibration is observed between 3150 and 3300 cm^{-1} which is characteristic for intra- or intermolecular hydrogen bond formations [17]. For **2a** and **2b** this ν_{OH} absorption is found at 3165 and 3162 cm^{-1}, respectively, when measured in Nujol. The existence of O–H···N bridges could be proven by single crystal X-ray structure analysis (Figs. 1 and 2). For complexes **5** and **6** the ν_{OH} vibrations are found at 3176 and 3174 cm^{-1} (Nujol). The slight shift to higher wavenumbers, when compared to **2a** and **2b**, indicates a somewhat stronger O–H and thereof a weaker hydrogen acceptor bond in **5** and **6**. This can be explained by the fact that the Me_2NCH_2 substituents are datively-bonded to M (M = Pd, Pt) and hence, cannot anymore act as hydrogen acceptors. As result thereof, a different structural bonding motif with the weaker acceptor bromine (O–H···Br) is found which preserves in the solid state (**5**). Based on the IR data of **5** and **6** it can be concluded that also for **6** a polymeric structure is a dominant structural feature in the solid state (Section 4).

2.2. Solid state structures of *2a*, *2b* and *5*

Single crystals of **2a** and **2b** suitable for X-ray structure analysis were obtained by slow evaporation of diethyl ether solutions containing either **2a** or **2b** at −30 °C. The molecular structures of **2a** and **2b** are shown in Figs. 1 and 2. Geometric details are listed in Table 1 and the experimental crystal data are summarized in Table 3 (Section 4).

The main geometric features of **2a** and **2b** resemble to those which are characteristic for aldoximes and *non*-metallated NCN-pincer molecules in the solid state [2a,15,18]. The X-ray crystal structure analyses clearly show that only the *E*-isomer of oximes **2a** and **2b** with torsion angles of 179.73(13) (C1–C7–N1–O1 for **2a**) and 178.0(2) ° (C4–C13–N3–O1 for **2b**) were formed (Figs. 1 and 2).

The Me_2NCH_2 substituents point away from the C–R entity (**2a**: R = H, **2b**: R = Br) in *ortho*-position towards the amino-methyl substituents. For both compounds one Me_2N group is located above the benzene ring (**2a**: N2, C9 and C10, distance $C_{6,plane}$–N2 = 1.3691(13) Å; **2b**: N2, C11 and C12, $d(C_{6,plane}–N2)$ = 1.290(2) Å), while the second Me_2N entity is positioned below the aromatic ring (**2a**: N3, C12 and C13, $d(C_{6,plane}–N3)$ = 0.9247(12) Å; **2b**: N1, C8 and C9, $d(C_{6,plane}–N1)$ = 0.357(2) Å).

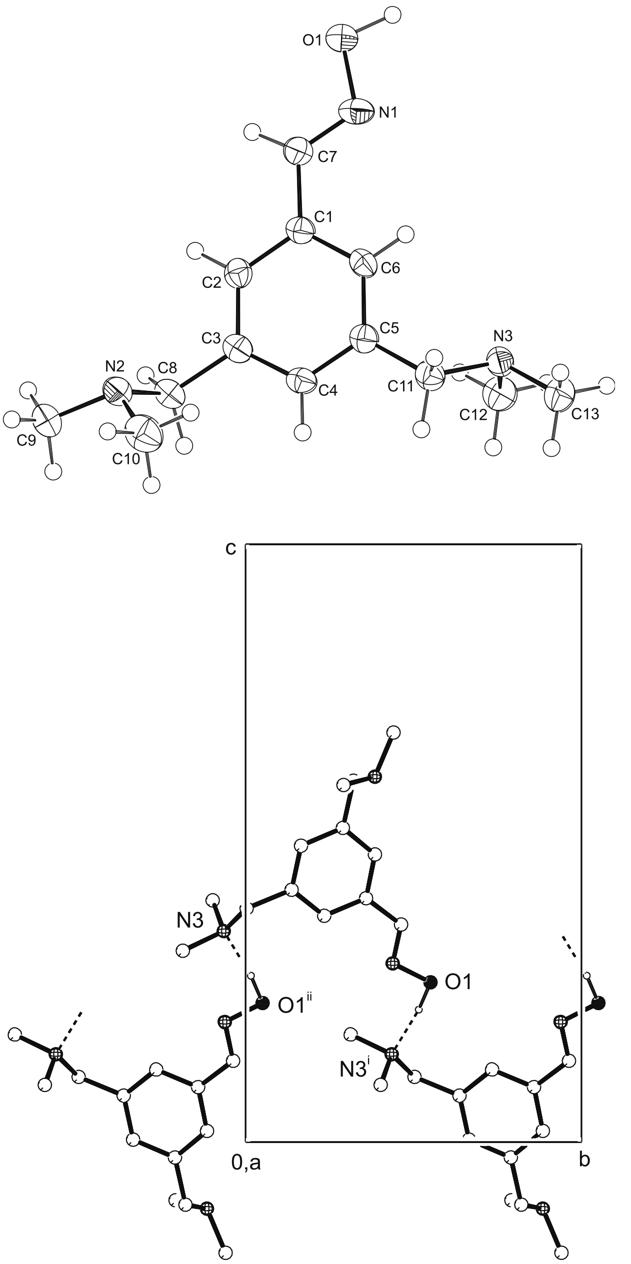


Fig. 1. Displacement ellipsoid plot (50% probability level) of the molecular structure of **2a** in the crystal and atom numbering scheme (top). Hydrogen-bonded one-dimensional chain of **2a** in the direction of the crystallographic *b*-axis. C–H hydrogen atoms are omitted for clarity. Symmetry operations: (i) −*x*, *y* + 0.5, 0.5 − *z*; (ii) −*x*, *y* − 0.5, 0.5 − *z* (bottom).

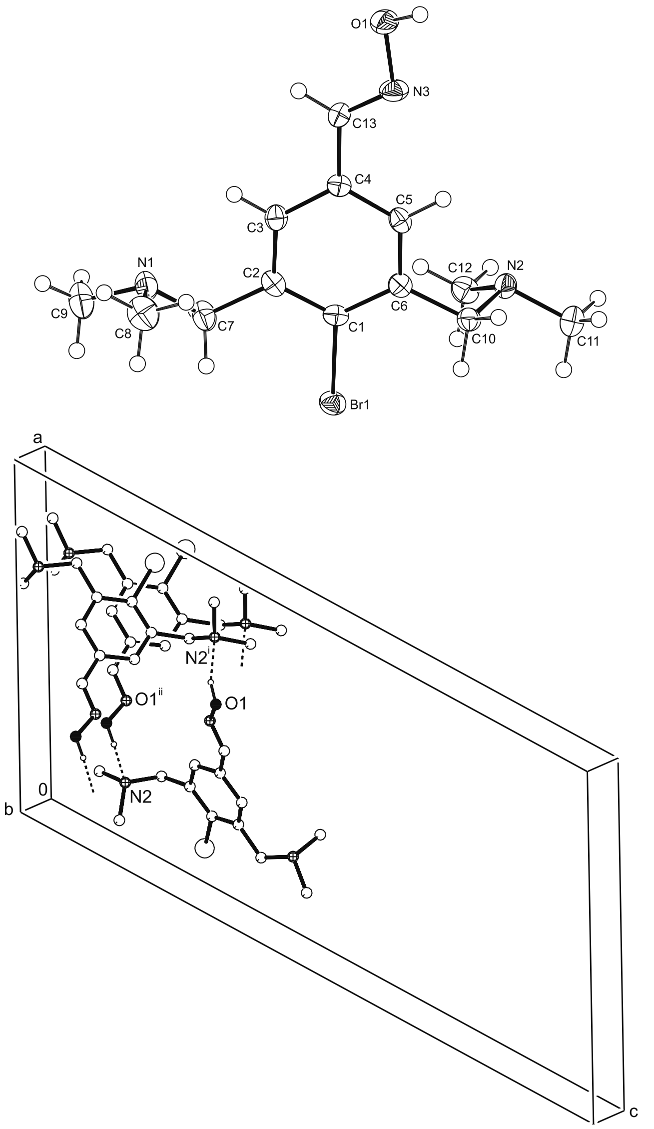


Fig. 2. Displacement ellipsoid plot (50% probability level) of the molecular structure of **2b** in the crystal and atom numbering scheme (top). Hydrogen-bonded one-dimensional chain of **2b** in the direction of the crystallographic *b*-axis. C–H hydrogen atoms are omitted for clarity. Symmetry operations: (i) 1 − *x*, *y* + 0.5, 0.5 − *z*; (ii) 1 − *x*, *y* − 0.5, 0.5 − *z* (bottom).

Oximes are known to form aggregates in the solid state, for example, benzaldehyde oxim crystallizes as a tetramer by forming intermolecular O–H···N bonds with the nitrogen atom of the oxime group as hydrogen acceptor [16]. In **2a** and **2b** four potential hydrogen bond acceptors are present: the O and N atoms of the oxime moiety and two tertiary Me_2NCH_2 amine groups. In both cases one Me_2NCH_2 amine is chosen as hydrogen bond acceptor (**2a**: N3; **2b**: N2) (Figs. 1 and 2; Table 2). Whereas, the other three potential acceptors do not participate in the hydrogen bonding. As a consequence in **2a** and **2b**, one-dimensional hydrogen-bonded chains are formed. In both cases these chains have a helical form involving a crystallographic 2_1 screw axis. The major difference between **2a** and **2b** is that in **2a** the phenyl plane has an angle of 17.94(5)° with respect to the screw axis, while in **2b** this angle is 44.61(8)°. This leads to a longer repeating unit in **2a** (length of *b*-axis = 10.1344(1) Å) than in **2b** (length of *b*-axis = 4.8213(1) Å).

Single crystals of **5** could be obtained by slow evaporation of a dichloromethane–acetone solution (ratio 20:1) containing **5** at −30 °C. The molecular structure of **5** is shown in Fig. 3. Selected bond distances, angles, and torsion angles are listed in Table 1 and experimental crystal data are presented in Table 3 (Section 4).

The Pd1 atom adopts a distorted square-planar geometry, setup by C4, N1, N2 and Br1 (Fig. 3). The C4–Pd1–Br1 bond angle is with 178.3(2)° linear, while the N1–Pd1–N2 angle is with 162.6(2)° deformed from linearity. The coordination plane around Pd1 is with 11.1(3)° almost coplanar to the benzene ring C1–C6. As for **2a** and **2b**, the oxime functionality in **5** has a *E*-configuration (torsion angle (C1–C13–N3–O1) = −178.2(8)°) and is coplanar with the plane build-up by the benzene ring (angle $\text{plane}_{C1,C13,N3,O1}$–$\text{plane}_{C1-C6}$ = 4.8(12)°).

Table 1
Selected bond lengths (Å), angles (°), and torsion angles (°) for **2a**, **2b** and **5**[a]

Bond lengths		Bond angles		Torsion angles	
*Compound **2a***					
C7–N1	1.286(2)	C1–C7–N1	120.62(14)	C4–C3–C8–N2	95.95(16)
N1–O1	1.3986(15)	C7–N1–O1	111.09(12)	C4–C5–C11–N3	129.49(14)
				C1–C7–N1–O1	179.73(13)
*Compound **2b***					
C13–N3	1.260(3)	C4–C13–N3	120.1(2)	C1–C2–C7–N1	163.7(2)
N3–O1	1.416(3)	C13–N3–O1	111.7(2)	C1–C6–C10–N2	108.4(2)
C1–Br1	1.923(2)			C4–C13–N3–O1	178.0(2)
*Complex **5***					
Pd1–Br1	2.5498(17)	Br1–Pd1–C4	178.3(2)	C4–C3–C7–N1	−20.4(8)
Pd1–C4	1.923(8)	N1–Pd1–N2	162.6(2)	C4–C5–C10–N2	−19.6(11)
Pd1–N1	2.131(6)	Br1–Pd1–N1	97.41(17)	Pd1–N1–C7–C3	28.4(7)
Pd1–N2	2.152(7)	Br1–Pd1–N2	99.48(18)	Pd1–N2-C10–C5	25.7(9)
C13–N3	1.265(12)	C1–C13–N3	122.4(8)	C1–C13–N3–O1	−178.2(8)
N3–O1	1.425(10)	C13–N3–O1	110.6(7)		

[a] Standard uncertainties are given in the last significant figure(s) in parenthesis.

Table 2
Hydrogen bonding interactions for **2a**, **2b** and **5**[a]

Compd.	D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
2a	O1–H1O···N3[i]	1.02	1.72	2.7315(16)	171.2
2b	O1–H1···N2[ii]	0.88(3)	1.98(3)	2.791(3)	152(3)
5	O1–H1···Br1[iii]	0.96(14)	2.38(15)	3.266(9)	154(12)

Symmetry operations: (i) $-x$, $y + 0.5$, $0.5 - z$; (ii) $1 - x$, $y + 0.5$, $0.5 - z$; (iii) $1 + x$, y, $z - 1$.

[a] Standard uncertainties are given in the last significant figure(s) in parenthesis.

The two Me_2NCH_2 *ortho*-substituents are datively-bonded to Pd1 (Pd1–N1 = 2.131(6), Pd1–N2 = 2.152(7) Å) and hence, cannot act as hydrogen acceptor as in **2a** and **2b**, respectively. But in contrast to **2b**, where the C–Br group cannot be considered as hydrogen bond acceptor, the metal-bound Br atom of **5** is a potential hydrogen bond acceptor like other metal-bound halides [19,22]. Interestingly enough, as in **2a** and in **2b**, the oxime group does not accept hydrogen bonds, but the Br atom does. The oxime group is also not involved in metal coordination, which would certainly be possible [2–8]. The "donor–acceptor distance" of the hydrogen bond is with 3.266(9) Å relatively long (sum of contact radii: 3.37 Å [20]). Similar interactions were found in other transition metal complexes, *i.e.* [*trans*-$FeBr_4(H_2O)_2$], $(Ph_3AsOH)_2[CuBr_4]$, or [1-(5,6-dimethylbenzimidazolyl)-3-benzimidazolyl-2-thiapropane]$HgBr_2 \cdot MeOH$ [21]. Complex **5** forms in the solid state an almost linear polymeric chain through *non*-covalent hydrogen bonding (Fig. 3), whereby the planes of the benzene rings are in a perfect coplanar arrangement due to crystallographic symmetry. Such structural arrangements have also been found for other *para*-H-donor substituted NCN-pincer complexes, such as $[PtCl(C_6H_2)(CH_2NMe_2)_2\text{-}2,6\text{-}C{\equiv}CH\text{-}4]$ and $[PtCl(C_6H_2)(CH_2NMe_2)_2\text{-}2,6\text{-}OH\text{-}4]$, respectively [22]. In the case of the latter compound evidence was provided that these polymers are also present in solution [22].

3. Conclusion

The synthesis and characterization of oxime-substituted NCN-pincer molecules $HON{=}CH\text{-}1\text{-}C_6H_3(CH_2NMe_2)_2\text{-}3,5$ (**2a**), $HON{=}CH\text{-}4\text{-}C_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}Br\text{-}1$ (**2b**) and $[(HON{=}CH\text{-}4\text{-}C_6H_2(CH_2NMe_2)_2\text{-}2,6)MBr]$ (M = Pd (**5**), Pt (**6**)) by applying different synthesis methodologies is described. For the preparation of **2a** and **2b** the appropriate benzaldehydes $H(O)C\text{-}1\text{-}C_6H_3(CH_2NMe_2)_2\text{-}3,5$ and $H(O)C\text{-}4\text{-}C_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}Br\text{-}1$ were reacted with hydroxylamine, while complexes **5** and **6** are accessible in a straightforward manner upon treatment with $[Pd_2(dba)_3]$ and $[Pt(tol\text{-}4)_2(SEt_2)]_2$, respectively. In the solid state polymeric structures are formed through *non*-covalent hydrogen bonding. Compounds **2a** and **2b** form infinite, one-dimensional hydrogen-bonded helical chains with only one Me_2NCH_2 amine as hydrogen bond acceptor, while **5** forms linear polymeric chains build-up by NO–H···Br hydrogen bonds.

4. Experimental

4.1. General methods

All reactions were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. Tetrahydrofuran, diethyl ether, benzene and *n*-hexane were purified by distillation from sodium/benzophenone ketyl. Infrared spectra (KBr) were recorded with a Perkin Elmer FT-IR 1000 spectrometer. NMR spectra were recorded with a Bruker Avance 250 spectrometer (^1H NMR at 250.12, $^{13}C\{^1H\}$ NMR at 62.86 MHz) or with a Varian Inova 300 spectrometer (^1H NMR at 300.10, $^{13}C\{^1H\}$ NMR at 75.47 MHz) in the Fourier transform mode. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane ($\delta = 0.00$ ppm) with the solvent as the reference signal ($CDCl_3$: ^1H NMR, $\delta = 7.26$; $^{13}C\{^1H\}$ NMR, $\delta = 77.0$; acetone-d_6: ^1H NMR, $\delta = 2.06$; $^{13}C\{^1H\}$ NMR, $\delta = 29.8$). Melting points were determined using sealed nitrogen purged capillaries with a Gallenkamp MFB 595 010 M melting point apparatus. Microanalyses were performed by the Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim an der Ruhr and partly by the Department of Organic Chemistry at Chemnitz, Technical University.

4.2. General remarks

$H(O)C\text{-}1\text{-}C_6H_3(CH_2NMe_2)_2\text{-}3,5$ (**1a**) [23], $H(O)C\text{-}4\text{-}C_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}Br\text{-}1$ (**1b**) [15], $[Pd_2(dba)_3 \cdot CHCl_3]$ (**3**) [24] and $[Pt(4\text{-}tol)_2(SEt_2)]_2$ (**4**) [25] were prepared following published procedures. All other chemicals were purchased from commercial sources and were used without any further purification.

5. Synthesis of $HON{=}CH\text{-}1\text{-}C_6H_3(CH_2NMe_2)_2\text{-}3,5$ (2a)

To 660 mg (3.00 mmol) of **1a** and 1.0 g (14.4 mmol) of $H_2NOH \cdot HCl$ dissolved in 50 mL of ethanol were added 15 mL (15.0 mmol) of 1 M NaOH. After the reaction mixture was heated for 1 h to reflux, 100 mL of water were added and the reaction solution was allowed to cool to 25 °C. The aqueous phase was extracted three times with 100 mL of diethyl ether and the combined

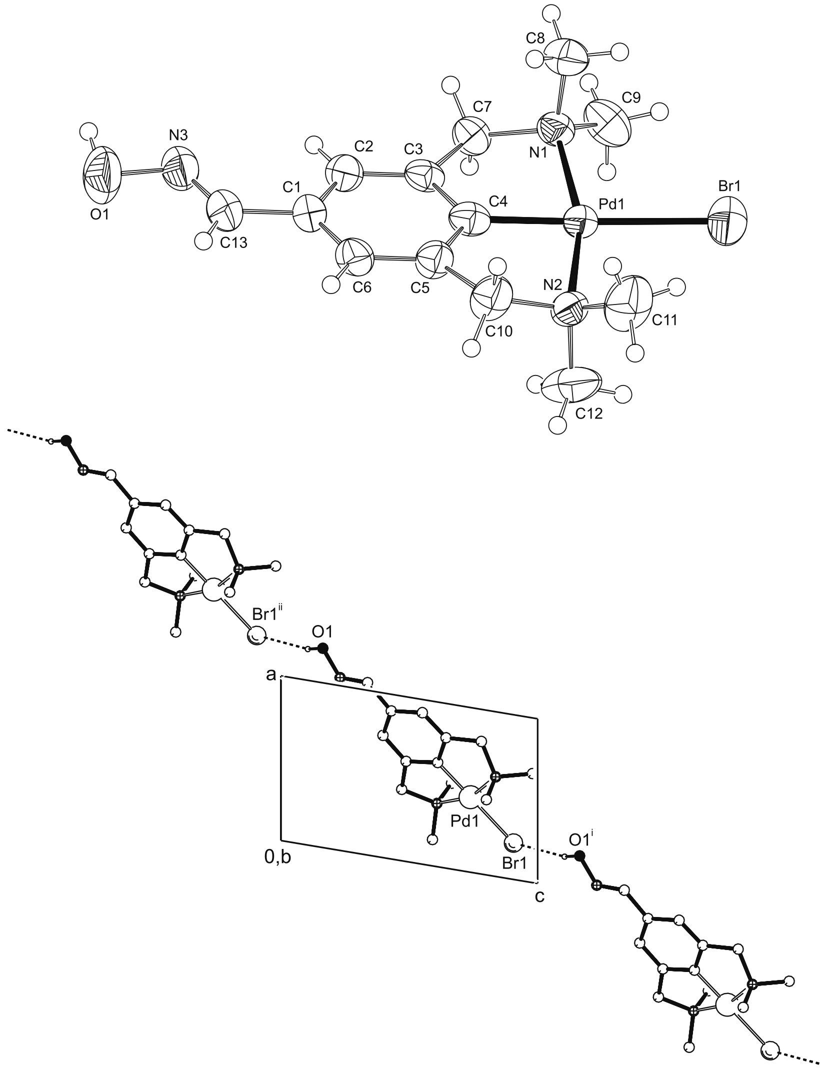


Fig. 3. Displacement ellipsoid plot (50% probability level) of the molecular structure of **5** in the crystal and atom numbering scheme (top). Hydrogen-bonded one-dimensional chain of **5** in the direction of the crystallographic $[1, 0, \bar{1}]$ diagonal. C–H hydrogen atoms are omitted for clarity. Symmetry operations: (i) $x - 1, y, z + 1$; (ii) $x + 1, y, z - 1$ (bottom).

organic phases were dried over $MgSO_4$, filtered and evaporated in *oil-pump vacuum* to gave a yellow oil. Upon addition of 3 mL of cold diethyl ether a colorless solid precipitated which was collected and dried in *oil-pump vacuum* to afford 520 mg (2.21 mmol, 74% based on **1a**) of **2a**.

M.p.: (°C) 112. IR (KBr): (cm^{-1}) 3169 (s) [ν_{OH}], 1655 (m) [$\nu_{C=N}$]; (Nujol): (cm^{-1}) 3165 [ν_{OH}]. ^{1}H NMR ($CDCl_3$): [δ] 2.22 (s, 12H, N*Me*$_2$), 3.43 (s, 4H, C*H*$_2$N), 7.21 (s, 1H, C_6H_3), 7.58 (s, 2H, C_6H_3), 8.07 (s, 1H, N=C*H*), 10.75 (br s, 1 H, O*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): [δ] 44.9 (N*C*H$_3$), 63.7 (N*C*H$_2$), 126.1 (*C*H/C_6H_3), 131.4 (*C*H/C_6H_3), 133.3 (^{i}C/C_6H_3), 138.3 (^{i}C/C_6H_3), 148.9 (N=*C*H). EI-MS [*m*/*z* (rel. int.)] 235 (10) [M$^+$], 217 (5) [M$^+$–H_2O], 192 (100) [M$^+$–NC_2H_5], 174 (70) [M$^+$–NMe_2OH], 147 (80) [M$^+$–2NMe_2], 130 (45) [M$^+$–$(NMe_2)_2OH$], 103 (30) [C_8H_8]. Anal. Calc. for $C_{13}H_{21}N_3O$ (235.32): C, 66.35; H, 8.99; N, 17.86. Found: C, 66.44; H, 9.11; N, 17.74%.

6. Synthesis of HON=CH-4-$C_6H_2(CH_2NMe_2)_2$-2,6-Br-1 (2b)

Compound **2b** was prepared according to the procedure described above by using 1.0 g (3.34 mmol) of **1b**, 1.16 g (16.7 mmol) of $H_2NOH \cdot HCl$ and 17 mL (17.0 mmol) of 1 M NaOH. Yield: 830 mg (2.64 mmol, 79% based on **1b**).

M.p.: (°C) 94. IR (KBr): (cm^{-1}) 3166 (s) [ν_{OH}], 1654 (m) [$\nu_{C=N}$]; (Nujol): (cm^{-1}) 3162 [ν_{OH}]. ^{1}H NMR ($CDCl_3$): [δ] 2.33 (s, 12H, N*Me*$_2$), 3.60 (s, 4H, C*H*$_2$N), 7.62 (s, 2H, C_6H_2), 8.09 (s, 1H, N=C*H*), 11.35 (br s, 1 H, O*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): [δ] 45.3 (N*C*H$_3$), 63.4 (N*C*H$_2$), 127.9 (^{i}*C*Br/C_6H_2), 128.2 (*C*H/C_6H_2), 132.2 (^{i}*C*/C_6H_2), 138.4 (^{i}*C*/C_6H_2), 148.2 (N=*C*H). Anal. Calc. for $C_{13}H_{20}BrN_3O$ (314.21): C, 49.69; H, 6.42; N, 13.27. Found: C, 49.84; H, 6.40; N, 13.39%.

7. Synthesis of [(HON=CH-4-$C_6H_2(CH_2NMe_2)_2$-2,6)PdBr] (5)

100 mg (0.32 mmol) of **2b** and 160 mg (0.15 mmol) of **3** were dissolved in 15 mL of benzene and the reaction mixture was stirred for 18 h at 25 °C. Afterwards, 20 mL of tetrahydrofuran were added and stirring was continued for 2 h. All volatiles were removed in *oil-pump vacuum* and the residual greenish-black solid was dissolved in 20 mL of chloroform. The solution was filtered through Celite and concentrated in *oil-pump vacuum* to 5 mL. *n*-Hexane (50 mL) was added, whereby a yellow solid precipitated, which was collected and washed twice with *n*-hexane (10 mL) and

Table 3
Summary of crystallographic data for **2a**, **2b** and **5**

Compd.	**2a**	**2b**	**5**
Formula	$C_{13}H_{21}N_3O$	$C_{13}H_{20}BrN_3O$	$C_{13}H_{20}BrN_3OPd$
Fw	235.33	314.23	420.63
Crystal color	Colorless	Colorless	Colorless
Crystal size (mm^3)	0.36 × 0.36 × 0.15	0.36 × 0.09 × 0.03	0.4 × 0.3 × 0.1
Temperature (K)	150	150	298
λ (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pbca* (no. 61)	$P2_1/c$ (no. 14)	*Cc* (no. 9)
a (Å)	14.5429(1)	13.3626(3)	6.461(5)
b (Å)	10.1344(1)	4.8213(1)	24.635(18)
c (Å)	18.1260(2)	24.9384(5)	10.212(7)
β (°)		117.8142(11)	99.476(12)
V (Å^3)	2671.47(4)	1421.03(5)	1603(2)
Z	8	4	4
D_x (g/cm^3)	1.170	1.469	1.743
μ (mm^{-1})	0.076	2.886	3.646
Abs. Corr.	None	Multi-scan	Multi-scan
Abs. Corr. range		0.83–0.92	0.34–1.00
Refl. collected/unique	30740/2408	21386/3262	10865/3179
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.60	0.65	0.63
Parameters/restraints	158/0	175/0	182/2
R_1/wR_2 [$I > 2\sigma(I)$]	0.0402/0.1086	0.0309/0.0700	0.0466/0.1286
R_1/wR_2 [all refl.]	0.0557/0.1179	0.0537/0.0779	0.0502/0.1340
S	1.076	1.070	1.070
Flack × parameter [504]			0.10(2)
$\rho_{min/max}$ (e/Å^3)	−0.20/0.29	−0.42/0.69	−0.83/0.68

diethyl ether (10 mL) to gave **5** as a pale yellow solid (95 mg, 0.23 mmol, 68% based on **3**).

M.p.: (°C) 94. IR (KBr): (cm^{-1}) 3279 (vs) [ν_{OH}], 1654 (m) [$\nu_{C=N}$]; (Nujol): (cm^{-1}) 3176 [ν_{OH}]. ^{1}H NMR (acetone-d_6): [δ] 2.94 (s, 12H, N*Me*$_2$), 4.10 (s, 4H, C*H*$_2$N), 7.05 (s, 2H, C_6H_2), 8.00 (s, 1H, N=C*H*), 10.21 (br s, 1H, O*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): [δ] 53.7 (N*C*H$_3$), 74.2 (N*C*H$_2$), 118.4 (*C*H/C_6H_2), 128.9 (^{i}*C*/C_6H_2), 145.5 (^{i}*C*/C_6H_2), 150.5 (N=*C*H), 160.9 (^{i}*C*Pd/C_6H_2). Anal. Calc. for $C_{13}H_{20}BrN_3OPd$ (420.64): C, 37.12; H, 4.79; N, 9.99. Found: C, 37.27; H, 4.87; N, 9.75%.

8. Synthesis of [(HON=CH-4-$C_6H_2(CH_2NMe_2)_2$-2,6)PtBr] (6)

165 mg (0.53 mmol) of **2b** and 234 mg (0.25 mmol) of **4** were dissolved in 20 mL of benzene and the reaction mixture was refluxed for 5 min. The yellow solution was cooled to 25 °C and concentrated in *oil-pump vacuum* to 5 mL. Upon addition of 20 mL of *n*-hexane a yellow precipitate formed which was collected, washed twice with *n*-hexane (10 mL) and diethyl ether (10 mL) and dried in *oil-pump vacuum* to afford **6** as a yellow solid (125 mg, 0.25 mmol, 98% based on **4**).

M.p.: (°C) 94. IR (KBr): (cm^{-1}) 3292 (vs) [ν_{OH}], 1654 (m) [$\nu_{C=N}$]; (Nujol): (cm^{-1}) 3174 [ν_{OH}]. ^{1}H NMR (acetone-d_6): [δ] 3.07 (s, $^3J_{PtH}$ = 38.48 Hz, 12H, N*Me*$_2$), 4.10 (s, $^3J_{PtH}$ = 45.62 Hz, 4 H, C*H*$_2$N), 7.05 (s, 2H, C_6H_2), 7.97 (s, 1 H, N=C*H*), 9.92 (br s, 1 H, O*H*). ^{13}C{^{1}H} NMR (acetone-d_6): [δ] 55.2 (N*C*H$_3$), 77.7 (N*C*H$_2$), 118.5 (*C*H/C_6H_2), 129.2 (^{i}*C*/C_6H_2), 145.1 (^{i}*C*/C_6H_2), 148.7 (N=*C*H), 150.7 (^{i}*C*Pt/C_6H_2). Anal. Calc. for $C_{13}H_{20}BrN_3OPt \cdot 1/3C_6H_6$ (509.30): C, 33.65; H, 4.14; N, 7.95. Found: C, 33.16; H, 4.18; N, 7.95%.

9. X-ray crystal structure determinations of 2a, 2b and 5

X-ray intensities were measured on a Nonius Kappa CCD diffractometer with rotating anode (compounds **2a** and **2b**) or on a Bruker Smart 1k CCD diffractometer (compound **5**). The structures were solved with Direct Methods [26] (**2a** and **5**) or with automated Patterson methods [27] (**2b**). Structure refinement was performed with SHELXL-97 [28] on F^2 of all reflections. *Non*-hydrogen atoms were refined freely with anisotropic displacement parameters. In **2a** and **2b** all hydrogen atoms were located in the difference Fourier map. In **5** the O–H hydrogen atom was located in the difference Fourier map and all other hydrogen atoms were introduced in geometrically optimized positions. All C–H hydrogen atoms were refined with a riding model. The O–H hydrogen atom of **2a** was kept fixed in the located position. In **2b** and **5** the O–H hydrogen atoms were refined freely with isotropic displacement parameters. Drawings, geometry calculations and checking for higher symmetry was performed with the PLATON program [29]. Further crystallographic details are given in Table 3.

10. Supplementary material

CCDC 604434, 604435 and 604436 contain the supplementary crystallographic data for **2a**, **2b** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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References

[1] (a) A. Hantzch, A. Werner, Chem. Ber. 23 (1890) 1;
(b) L. Tschugaeff, Chem. Ber. 38 (1905) 2520.
[2] (a) For example see: A. Chakravorty, Coord. Chem. Rev. 13 (1974) 1;
(b) V.Y. Kukushkin, D. Tudela, A.J.L. Pombeiro, Coord. Chem. Rev. 156 (1996) 333;
(c) V.Y. Kukushkin, A.J.L. Pombeiro, Coord. Chem. Rev. 181 (1999) 147;
(d) T.C. Stamatatos, A. Bell, P. Cooper, A. Terzis, C.P. Raptopoulou, S.L. Heath, R.E.P. Winpenny, S.P. Perlepes, Inorg. Chem. Commun. 8 (2005) 533.
[3] (a) S. Kawata, S. Kitagawa, H. Machida, T. Nakamoto, M. Kondo, M. Katada, K. Kikuchi, I. Ikemoto, Inorg. Chim. Acta 229 (1995) 211;
(b) A.G. Smith, P.A. Tasker, D.J. White, Coord. Chem. Rev. 241 (2003) 61;
(c) A.M. Beatty, Coord. Chem. Rev. 246 (2003) 131;
(d) D. Robertson, J.F. Cannon, N. Gerasimchuk, Inorg. Chem. 44 (2005) 8326;
(e) C.J. Milios, T.C. Stamatatos, S.P. Perlepes, Polyhedron 25 (2006) 134.

[4] (a) V. Bertolasi, G. Gilli, A.C. Veronese, Acta Crystallogr., Sect. B 38 (1982) 502;
(b) L. Chertanova, C. Pacard, A. Sheremetev, Acta Crystallogr., Sect. B 50 (1994) 708.

[5] M. Lutz, A.L. Spek, R. Dabirian, C.A. van Walree, L.W. Jenneskens, Acta Crystallogr., Sect. C 60 (2004) o127.

[6] B. Jerslev, Acta Crystallogr., Sect. C 39 (1983) 1447.

[7] E.A. Bruton, L. Brammer, C.F. Pigge, C.B. Aakeröy, D.S. Leinen, New J. Chem. 27 (2003) 1084.

[8] (a) For example see: M. Carcelli, P. Cozzini, R. Marroni, P. Pelagatti, C. Pelizzi, P. Sgarabotto, Inorg. Chim. Acta 285 (1999) 138;
(b) T.H. Lu, Y.J. Lin, H. Luh, F.L. Liao, C.S. Chung, Acta Crystallogr., Sect. C 57 (2001) 1398.

[9] (a) For example see: J.M. Longmire, X. Zhang, M. Shang, Organometallics 17 (1998) 4374;
(b) P. Dani, M. Albrecht, G.P.M. van Klink, G. van Koten, Organometallics 19 (2000) 4468;
(c) D.E. Bergbreiter, P.L. Osburn, Y. Liu, J. Am. Chem. Soc. 121 (1999) 9531;
(d) H.P. Dijkstra, P. Steenwinkel, D.M. Grove, M. Lutz, A.L. Spek, G. van Koten, Angew. Chem., Int. Ed. Engl. 38 (1999) 2186.

[10] (a) For example see: P. Steenwinkel, R.A. Gossage, G. van Koten, Chem. Eur. J. 4 (1998) 759;
(b) R.A. Gossage, L.A. van de Kuil, G. van Koten, Acc. Chem. Res. 31 (1998) 423;
(c) M. Albrecht, G. van Koten, Angew. Chem., Int. Ed. Engl. 40 (2001) 3750.

[11] K. Johnson, E.F. Degering, J. Am. Chem. Soc. 61 (1939) 3194.

[12] K. Kahr, C. Berther, Chem. Ber. 93 (1960) 132.

[13] P.P. Kadzyauskas, N.S. Zefirov, Russ. Chem. Rev. 37 (1968) 543.

[14] (a) For example see: W.P. Jencks, J. Am. Chem. Soc. 81 (1959) 475;
(b) W.H. Jones, E.W. Tristram, W.F. Benning, J. Am. Chem. Soc. 81 (1959) 2151;
(c) P.B. Bandgar, S.V. Sadavarte, L.S. Uppalla, R. Govande, Monatsh. Chem. 132 (2001) 403;
(d) M. Blackwell, P.J. Dunn, A.B. Graham, R. Grigg, P. Higginson, I.S. Saba, M. Thornton-Pett, Tetrahedron 58 (2002) 7715.

[15] For example: G. Rodriguez, M. Albrecht, J. Schoenmaker, A. Ford, M. Lutz, A.L. Spek, G. van Koten, J. Am. Chem. Soc. 124 (2002) 5127.

[16] (a) W. Funcke, C. von Sonntag, Carbohydr. Res. 69 (1979) 247;
(b) R. Gawinecki, E. Kohlehmainen, R. Kauppinen, J. Chem. Soc., Perkin Trans. 2 (1998) 25.

[17] (a) D.G. O'Sullivan, P.W. Sadler, J. Org. Chem. 22 (1957) 283;
(b) G.E. Philbrook, T.C. Getten, J. Org. Chem. 24 (1959) 568;
(c) J.D. Martin, K.A. Abboud, K.H. Dahmen, Inorg. Chem. 37 (1998) 5811.

[18] (a) S.L. James, N. Veldman, A.L. Spek, G. van Koten, Chem. Commun. (1996) 253;
(b) S. Back, M. Lutz, A.L. Spek, H. Lang, G. van Koten, J. Organomet. Chem. 620 (2001) 227;
(c) S. Back, M. Albrecht, A.L. Spek, G. Rheinwald, H. Lang, G. van Koten, Organometallics 20 (2001) 1024.

[19] G. Aullón, D. Bellamy, L. Brammer, E.A. Bruton, A.G. Orpen, Chem. Commun. (1998) 653.

[20] A. Bondi, J. Phys. Chem. 68 (1964) 441.

[21] (a) R.E. Greeney, C.P. Landee, J.H. Zhang, W.M. Reiff, Inorg. Chem. 29 (1990) 3119;
(b) A.C. Massabni, O.R. Nascimento, K. Halvorson, R.D. Willet, Inorg. Chem. 31 (1992) 1779;
(c) C.J. Matthews, W. Clegg, S.L. Heath, N.C. Martin, M.N.S. Hill, J.C. Lockhart, Inorg. Chem. 37 (1998) 199.

[22] (a) S.I. James, G. Verspui, A.L. Spek, G. van Koten, Chem. Commun. (1996) 1309;
(b) P.J. Davies, N. Veldman, D.M. Grove, A.L. Spek, B.T.G. Lutz, G. van Koten, Angew. Chem., Int. Ed. Engl. 35 (1996) 1959;
(c) M. Albrecht, M. Lutz, A.L. Spek, G. van Koten, Nature 406 (2000) 970;
(d) M. Albrecht, M. Lutz, A.M.M. Scheurs, E.T.H. Lutz, A.L. Spek, G. van Koten, J. Chem. Soc., Dalton Trans. (2000) 3797.

[23] M.D. Meijer, M. Rump, R.A. Gossage, J.H.T.B. Jastrzebski, G. van Koten, Tetrahedron Lett. 39 (1998) 6773.

[24] S. Komiya, Synthesis of Organometallic Compounds, Wiley, Winchester, 1997.

[25] (a) B.R. Steele, K. Vrize, Transition Met. Chem. 2 (1977) 140;
(b) A.J. Canty, J. Patel, B.W. Skelton, A.J. White, J. Organomet. Chem. 599 (2000) 195.

[26] G.M. Sheldrick, SHELXS-97. Program for Crystal Structure Solution, University of Göttingen, Germany, 1997.

[27] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. Garcia-Granda, R.O. Gould, J.M.M. Smits, C. Smykalla, The DIRDIF99 Program System. Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1999.

[28] G.M. Sheldrick, SHELXL-97. Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.

[29] A.L. Spek, J. Appl. Crystallogr. 36 (2003) 7.