



# Synthesis and reaction chemistry of 4-nitrile-substituted NCN-pincer palladium(II) and platinum(II) complexes (NCN = [N≡C-4-C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6]<sup>−</sup>)

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## ABSTRACT

Nitrile-functionalized NCN-pincer complexes of type [MBr(N≡C-4-C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6)] (**6a**, M = Pd; **6b**, M = Pt) (NCN = [C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6]<sup>−</sup>) are accessible by the reaction of Br-1-N≡C-4-C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6 (**2b**) with [Pd<sub>2</sub>(dba)<sub>3</sub> · CHCl<sub>3</sub>] (**5a**) (dba = dibenzylidene acetone) and [Pt(tol-4)<sub>2</sub>(SEt<sub>2</sub>)<sub>2</sub>] (**5b**) (tol = tolyl), respectively. Complex **6b** could successfully be converted to the linear coordination polymer {[Pt(N≡C-4-C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6)](ClO<sub>4</sub>)<sub>n</sub> (**8**) upon its reaction with the organometallic hetero-bimetallic π-tweezer compound {[Ti](μ-σ,π-C≡CSiMe<sub>3</sub>)<sub>2</sub>}AgOCIO<sub>3</sub> (**7**) ([Ti] = (η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>Ti). The structures of **6a** (M = Pd) and **6b** (M = Pt) in the solid state are reported. In both complexes the d<sup>8</sup>-configured transition metal ions palladium(II) and platinum(II) possess a somewhat distorted square-planar coordination sphere. Coordination number 4 at the group-10 metal atoms M is reached by the coordination of two *ortho*-substituents Me<sub>2</sub>NCH<sub>2</sub>, the NCN *ipso*-carbon atom and the bromide ligand. The N≡C group is *para*-positioned with respect to M.

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## 1. Introduction

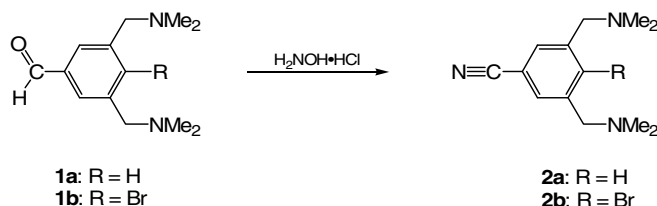
Organometallic complexes can successfully be used in the synthesis of new materials with novel properties [1]. In this respect, much interest exists in the use of transition metal systems with coordinatively unsaturated metal ions, because they allow the synthesis of linear [2], square [3], cubic [4], helical [5] or even more complex geometric architectures [6] *via* self-assembly in the presence of suitable ligands by following, for example, the molecular “Tinkertoy” approach [7]. Another possibility to prepare such assemblies relies upon the use of transition metal complexes featuring donor and acceptor groups in the same molecule. As ligating site(s), either organic or inorganic σ- and π-donors and as acceptor component(s) transition metal atoms are present in these complexes.

We report here on the synthesis and reaction chemistry of nitrile-functionalized NCN-pincer metal complexes of type [MBr(N≡C-4-C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6)] (M = Pd, Pt; NCN = [C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6]<sup>−</sup>). The properties of the linear coordination polymer {[Pt(N≡C-4-C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6)](ClO<sub>4</sub>)<sub>n</sub> will be discussed as well.

## 2. Results and discussion

### 2.1. Synthesis and spectroscopy

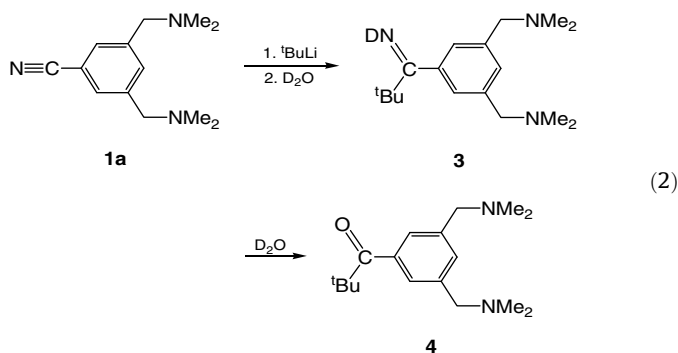
For the synthesis of the NCN-pincer molecules N≡C-4-C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-3,5 (**2a**) and 1-Br-N≡C-4-C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6 (**2b**) various synthetic methodologies are available [8]. Following the procedure reported by Olah et al. [8a] the benzaldehydes HC(O)-4-C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-3,5 (**1a**) and Br-1-HC(O)-4-C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6 (**1b**) were converted to **2a** and **2b** upon their reaction with hydroxylamine in formic acid at reflux temperatures (see equation below). After appropriate work-up, **2a** and **2b** could be isolated as yellow oils in ca. 55% yield.



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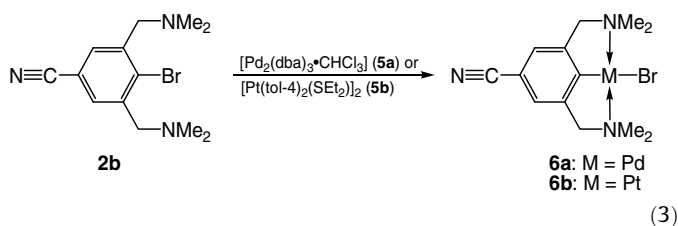
Compound **2b** is also accessible by treatment of **1b** with ammonia in the presence of iodine as oxidizing agent (Section 4). This synthetic procedure was recently published by Fang and coworkers for the preparation of benzonitrile and Br-1-N≡C-4-C<sub>6</sub>H<sub>4</sub> from benzaldehyde and 4-BrC<sub>6</sub>H<sub>4</sub>CHO, respectively [8c]. This approach was successfully transferred to the synthesis of **1b**. By doing so, the yield of **2b** could be increased from 55% to 70%. Nevertheless, this reaction is limited, because small quantities of iodine and **1b** (typical run: 0.25 mmol) have to be used. **Caution** is advisable, since highly explosive [N<sub>3</sub> · NH<sub>3</sub>] can be formed as a side product during the course of the reaction [8c].

In general, a two-step metallation–*trans* metallation synthesis procedure can be used in the preparation of transition metal pincer complexes [9,10]. Lithiation of C<sub>6</sub>H<sub>4</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-1,3 with <sup>t</sup>BuLi or <sup>t</sup>BuLi gives the corresponding metallated aryl Li(C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6) which further reacts with [PtCl<sub>2</sub>(SEt<sub>2</sub>)<sub>2</sub>] to produce the respective transition metal complex [10]. However, this procedure is not applicable for the synthesis of nitrile-functionalized NCN-pincer complexes since by the reaction of **2a** with <sup>t</sup>BuLi the <sup>t</sup>Bu anion undergoes nucleophilic attack at the nitrile carbon atom [11]. This was shown by the reaction of the *in situ* formed lithium ketiminate with D<sub>2</sub>O which gave DN=C(<sup>t</sup>Bu)-1-C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-3,5 (**3**) (Eq. (2)). With an excess of D<sub>2</sub>O, the ketone O=C(<sup>t</sup>Bu)-1-C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-3,5 (**4**) was formed (see equation below).

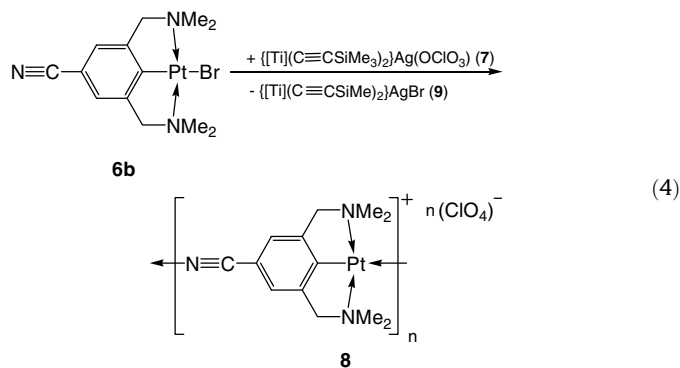


Compounds **3** and **4** were characterized by GC–MS analysis of a sample taken from the crude reaction mixture. The molecular ion peak M<sup>+</sup> could be detected at *m/z* 275 (**3**) and 276 (**4**), respectively. Further typical fragments that were observed for **3** and **4** were M<sup>+</sup>–NMe<sub>2</sub>, M<sup>+</sup>–Bu and M<sup>+</sup>–2NMe<sub>2</sub> (Section 4).

Another possibility to introduce transition metal atoms in NCN-pincer chemistry is given by the oxidative addition of carbon–halide bonds to transition metals in low oxidation states, i.e. [Pd<sub>2</sub>(dba)<sub>3</sub> · CHCl<sub>3</sub>] (**5a**) (dba = dibenzylidene acetone) [12]. Thus, the reaction of **2b** with **5a** in benzene or toluene as solvent at 25 °C afforded [PdBr(N≡C-4-C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6)] (**6a**). After appropriate work-up, **6a** could be isolated as a pale yellow solid in 69% yield (Eq. (3)). For the preparation of the iso-structural platinum NCN-pincer complex [PtBr(N≡C-4-C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6)] (**6b**) the platinum(0) source [Pt(tol-4)<sub>2</sub>(SEt<sub>2</sub>)<sub>2</sub>] (**5b**) (tol = tolyl) was used. After heating **2b** and **5b** in an aromatic solvent such as benzene or toluene, yellow **6b** could be isolated from the reaction solution in 85% yield (see equation below) (see Section 4).



Complexes **6a** and **6b** possess a potentially σ-coordinating *para*-N≡C group. To study the consequences of the presence of this group during halide abstraction, compounds **6a** and **6b** were reacted with the silver salts [AgX] (X = BF<sub>4</sub>, PF<sub>6</sub>, ClO<sub>4</sub>, OTf). An immediate pale yellow solid precipitated which appeared to be the cationic pincer complex [M(N≡C-4-C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6)]<sup>+</sup> (M = Pd, Pt) along with [AgBr]. Due to the low solubility of both species no separation was possible, neither by chromatography nor by crystallization. This problem could be solved by using soluble halide abstracting reagents such as the organometallic heterobimetallic π-tweezer complex {[Ti](μ-σ,π-C≡CSiMe<sub>3</sub>)<sub>2</sub>}AgOCIO<sub>3</sub> (**7**) [13]. This reaction resulted in the formation of {[Pt(N≡C-4-C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6)](ClO<sub>4</sub>)<sub>n</sub> (**8**) along with {[Ti](μ-σ,π-C≡CSiMe<sub>3</sub>)<sub>2</sub>}-AgBr (**9**) (Eq. (4)). The alternate formation of heterotrimeric {[Ti](μ-σ,π-C≡CSiMe<sub>3</sub>)<sub>2</sub>}Ag(N≡C-4-C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6)PtBr (**10**), however, was not observed. The formation of **8** and **9** from **6b** and **7** is most likely due to the high affinity of the silver(I) ion in **7** for bromide as well as due to the low solubility of **8** which immediately precipitated from the reaction solution.



The  $\nu_{\text{C}\equiv\text{N}}$  of **2**, **6** and **8** are distinctly different and for this reason allow the monitoring of the reaction progress. If **2a** and **2b** are reacted with **5a** and **5b**, respectively, the  $\nu_{\text{C}\equiv\text{N}}$  absorptions typical for **2a** (2230 cm<sup>-1</sup>) and **2b** (2231 cm<sup>-1</sup>) shift to lower wavenumbers (**6a** and **6b**: 2219 cm<sup>-1</sup>), which are typical for substituted benzonitriles, *cf.* the substitution of benzonitrile with an electron donating *p*-methoxy group leads to a shift of the  $\nu_{\text{C}\equiv\text{N}}$  from 2230 (benzonitrile) to 2216 cm<sup>-1</sup> (anisonitrile) [14]. Most likely the structure of **8** is a polymeric one as is indicated by a shift of  $\nu_{\text{C}\equiv\text{N}}$  to higher wavenumbers (2247 cm<sup>-1</sup>). When compared to **6**, this  $\nu_{\text{C}\equiv\text{N}}$  value points to a dative-binding of the C≡N group to a Pt(II) ion. This observation is consistent with the data reported for other cyanide transition metal complexes, e.g., {(dppp)Pd(C<sub>6</sub>H<sub>4</sub>(C≡N)<sub>2</sub>-1,4)<sub>2</sub>-(OTf)<sub>2</sub>)}<sub>4</sub> (2280 cm<sup>-1</sup>) (dppp = 1,3-bis(diphenylphosphino)propane) [3a] and [(FcC≡CC<sub>6</sub>H<sub>4</sub>C≡N-1,4)<sub>2</sub>Pd(PPh<sub>3</sub>)<sub>2</sub>](OTf)<sub>2</sub> (2276 cm<sup>-1</sup>) [15]. The *non*-coordinating nature of the ClO<sub>4</sub><sup>-</sup> anion could nicely be confirmed by IR spectroscopy. Only one band was found at 1091 cm<sup>-1</sup> ( $\nu_{\text{Cl-O}}$ ) indicating a *T<sub>d</sub>* symmetry of the ClO<sub>4</sub><sup>-</sup> counterion [16]. On the basis of these data we propose for **8** a linear polymeric structure in the solid state as shown in Fig. 1, which is a commonly found structural motive in cyano transition metal chemistry [3a,17,18]. Structures of coordination polymers with linear M ← N≡C arrangements have been reported, *cf. mer*, *trans*-[RuCl<sub>2</sub>(η<sup>3</sup>-NN'N)(N≡CPh)] (NN'N = 2,6-bis[(dimethylamino)methyl]pyridine) [18].

The <sup>1</sup>H NMR spectra of **2a** and **2b** show the resonance signals typical for NCN-pincer metal complexes [10,12,19]. The NMe<sub>2</sub> and CH<sub>2</sub> protons of the NCN-pincer appear as singlets at 2.18 and 3.37 ppm for **2a** and at 2.30 and 3.53 ppm for **2b**. Coordination of the *ortho*-substituents CH<sub>2</sub>NMe<sub>2</sub> to palladium (**6a**) or platinum (**6b**, **8**) results in a significant shift of the NMe<sub>2</sub> and CH<sub>2</sub> resonance signals to lower field (NMe<sub>2</sub>: 2.95 (**6a**), 3.02 (**6b**) and 3.01 (**8**); CH<sub>2</sub>:

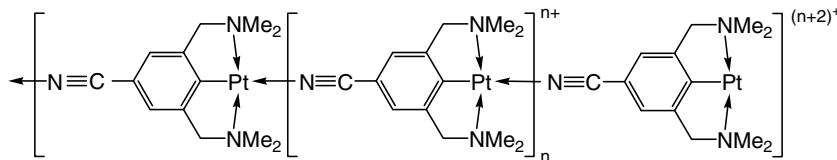


Fig. 1. Proposed polymeric structure of **8** in the solid state.

4.17 (**6a**), 4.07 (**6b**), and 4.17 ppm (**8**)). The presence of the Pt(II) ion in **6b** and **8** is supported by the observation of  $^3J_{\text{PtH}}$  coupling constants of 38–40 Hz for the NMe<sub>2</sub> entities and 45–49 Hz for the CH<sub>2</sub> units (see Section 4).

Characteristic downfield shifts for the NMe<sub>2</sub> and CH<sub>2</sub> carbon atoms have also been found in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra going in the series from **2a** and **2b**, **6a** and **6b** to **8** (see Section 4). All other resonance signals appear as well-resolved signals in the expected regions.

## 2.2. Structures of **6a** and **6b** in the solid state

Single crystals of **6a** and **6b** suitable for X-ray structure analysis could be grown by cooling a 1:1 (v/v) mixture of dichloromethane/acetone containing **6a** or **6b** to  $-30^\circ\text{C}$ . The molecular structures of **6a** and **6b** are shown in Fig. 2. Geometrical details are listed in Table 1, while the crystal and intensity collection data are summarized in Table 2 (see Section 4).

Complexes **6a** and **6b** are *iso*-structural, but crystallize in different monoclinic space groups (**6a**:  $P2_1/c$ , **6b**:  $C2/c$ ). The main geometric features of **6a** and **6b** resemble the structural data characteristic for other NCN-pincer palladium and platinum complexes [10,12,18]. The metal atoms Pd1 (**6a**) and Pt1 (**6b**) adopt a somewhat distorted square-planar geometry set-up by C4, N1, N2 and Br1 (**6a**) and C1, N1, N2 and Br1 (**6b**), respectively (Fig. 2). The latter coordination planes are almost coplanar with the benzene ring C1–C6 (**6a**:  $11.7(2)^\circ$ , **6b**:  $12.1(2)^\circ$ ) of the NCN-pincer ligand. As expected, the *para* nitrile group is linear (**6a**: N3–C13–C1,  $178.4(6)^\circ$ ; **6b**: N3–C13–C4,  $178.8(5)^\circ$ ).

Interestingly, comparison of the structure of **6a** with that of the *para*-nitro substituted NCN-pincer palladium complex, which forms a dimer in the solid state *via* self-assembly as result of electron-donor–acceptor interactions between Pd(II) and the nitrogen atom of the NO<sub>2</sub> group, shows that in the solid state **6a** exists as discrete monomers [20]. This indicates that the nitrile entity in **6a** is not strong enough to withdraw electron density at the palladium atom to make it sufficient Lewis-acidic.

## 3. Conclusion

The synthesis of the nitrile-functionalized palladium and platinum NCN-pincer transition metal complexes  $[\text{MBr}(\text{N}\equiv\text{C}-4-\text{C}_6\text{H}_2(\text{CH}_2\text{NMe}_2)_2-2,6)]$  (M = Pd, Pt) by treatment of Br-1-N $\equiv$ C-4-C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6 with  $[\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3]$  (dba = dibenzylidene acetone) and  $[\text{Pt}(\text{tol}-4)_2(\text{SEt}_2)_2]$  (tol = tolyl), respectively, is reported. Within these reactions an oxidative addition of the NCN-pincer C–Br bond to Pd and Pt occurs (NCN =  $[\text{C}_6\text{H}_2(\text{CH}_2\text{NMe}_2)_2-2,6]^-$ ). The corresponding platinum complex could successfully be converted to the coordination polymer  $\{[\text{Pt}(\text{N}\equiv\text{C}-4-\text{C}_6\text{H}_2(\text{CH}_2\text{NMe}_2)_2-2,6)](\text{ClO}_4)\}_n$  upon its reaction with the halide abstracting reagent  $\{[\text{Ti}](\mu-\sigma,\pi-\text{C}\equiv\text{CSiMe}_3)_2\}\text{AgOClO}_3$  ( $[\text{Ti}] = (\eta^5-\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}$ ). The structure of this coordination polymer is proposed to contain in the solid state linear C $\equiv$ N $\rightarrow$ Pt arrangements which is a commonly structural motive in cyano transition metal chemistry, *e.g.* *mer,trans*- $[\text{RuCl}_2(\eta^3-\text{NN}'\text{N})(\text{N}\equiv\text{CPh})]$  (N–N'/N = 2,6-bis[(dimethylamino)methyl]pyridine).

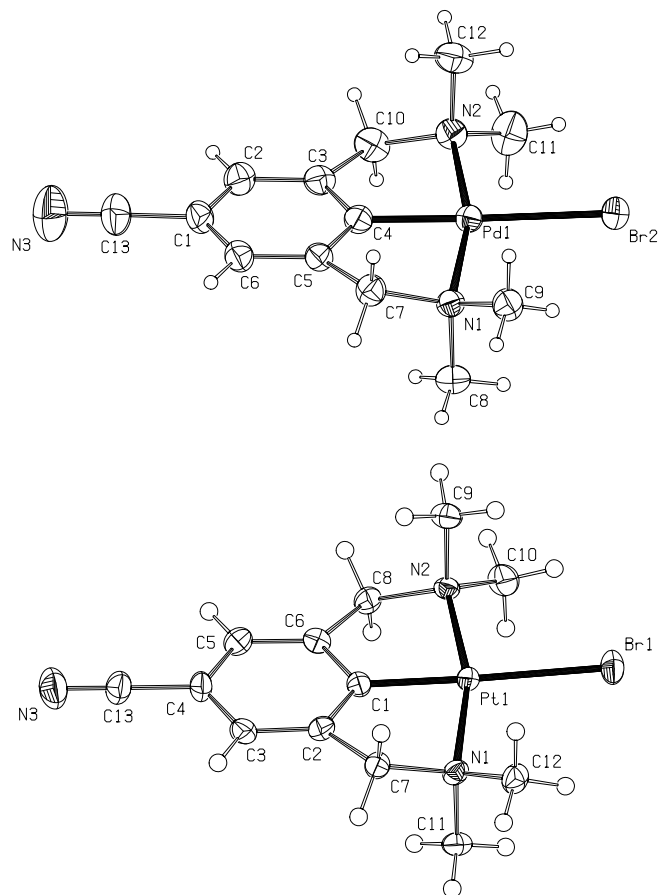


Fig. 2. ORTEP diagram of the molecular structure of **6a** (top, 30% probability level) and **6b** (bottom, 50% probability level) with the atom numbering scheme.

## 4. Experimental

**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 were recorded with a Perkin Elmer FT-IR 1000 spectrometer. NMR spectra were recorded with a Bruker Avance 250 spectrometer ( $^1\text{H}$  NMR at 250.12 MHz and  $^{13}\text{C}\{^1\text{H}\}$  NMR at 62.86 MHz) or with a Varian Inova 300 spectrometer ( $^1\text{H}$  NMR at 300.10 MHz and  $^{13}\text{C}\{^1\text{H}\}$  NMR at 75.47 MHz) in the Fourier transform mode. Chemical shifts are reported in  $\delta$  units (parts per million) downfield from tetramethylsilane ( $\delta = 0.00$  ppm) with the solvent as the reference signal (CDCl<sub>3</sub>:  $^1\text{H}$  NMR,  $\delta = 7.26$ ;  $^{13}\text{C}\{^1\text{H}\}$  NMR,  $\delta = 77.0$ ; *d*<sub>6</sub>-acetone:  $^1\text{H}$  NMR,  $\delta = 2.06$ ;  $^{13}\text{C}\{^1\text{H}\}$  NMR,  $\delta = 29.8$  and 206.1; CD<sub>3</sub>CN:  $^1\text{H}$  NMR,  $\delta = 1.94$ ;  $^{13}\text{C}\{^1\text{H}\}$  NMR,  $\delta = 1.3$  and 118.7). Melting points were determined using sealed nitrogen purged capillaries with a Gallenkamp (type MFB 595 010 M) melting point apparatus. Microanalyses were performed by the Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim a. d. Ruhr and by the

**Table 1**  
Selected bond distances (Å), bond angles and torsion angles (°) for **6a** and **6b**<sup>a</sup>

Bond distances (Å)		Bond angles (°)		Torsion angles (°)	
<b>Complex 6a</b>					
Pd1–Br1	2.5239(5)	Br1–Pd1–C4	178.27(9)	C4–C5–C7–N1	–23.0(4)
Pd1–C4	1.906(4)	N1–Pd1–N2	163.07(10)	C4–C3–C10–N2	–22.0(4)
Pd1–N1	2.105(2)	Br1–Pd1–N1	99.40(7)	Pd1–N1–C7–C5	30.9(3)
Pd1–N2	2.108(3)	Br1–Pd1–N2	97.52(7)	Pd1–N2–C10–C3	28.5(4)
C13–N3	1.129(6)	C1–C13–N3	178.39(56)		
<b>Complex 6b</b>					
Pt1–Br1	2.5246(5)	Br1–Pt1–C1	177.14(13)	C1–C2–C7–N1	–23.6(6)
Pt1–C1	1.909(5)	N1–Pt1–N2	163.76(16)	C1–C6–C8–N2	–25.2(5)
Pt1–N1	2.104(4)	Br1–Pt1–N1	98.23(13)	Pt1–N1–C7–C2	32.2(4)
Pt1–N2	2.095(4)	Br1–Pt1–N2	98.01(9)	Pt1–N2–C8–C6	31.0(4)
C13–N3	1.140(7)	C4–C13–N3	178.8(5)		

<sup>a</sup> Standard deviation(s) are given as the last significant figures in parenthesis.

**Table 2**  
Crystal and intensity collection data for **6a** and **6b**

	Complex <b>6a</b>	Complex <b>6b</b>
Chemical formula	C <sub>13</sub> H <sub>18</sub> BrN <sub>3</sub> Pd	C <sub>13</sub> H <sub>18</sub> BrN <sub>3</sub> Pt
Formula weight	402.61	491.30
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	13.7496(18)	20.8422(6)
<i>b</i> (Å)	9.2511(12)	15.9393(5)
<i>c</i> (Å)	12.0041(15)	8.9024(3)
<i>V</i> (Å <sup>3</sup> )	1484.3(3)	2863.42(16)
$\beta$ (°)	103.560(3)	104.4882(12)
$\delta_{\text{calc}}$ (g cm <sup>-3</sup> )	1.802	2.279
<i>F</i> (000)	792	1840
<i>Z</i>	4	8
Crystal dimensions (mm)	0.3 × 0.2 × 0.2	0.30 × 0.18 × 0.09
Radiation ( $\lambda$ , Å)	Mo K $\alpha$ (0.71073)	Mo K $\alpha$ (0.71073)
Maximum and minimum transmission	0.99999, 0.71662	0.327, 0.129
Absorption coefficient (mm <sup>-1</sup> )	3.929	12.578
Temperature (K)	298(2)	150
Scan range (°)	2.68 ≤ $\theta$ ≤ 26.39	1.6 ≤ $\theta$ ≤ 27.4
Index ranges	–17 ≤ <i>h</i> ≤ 16, 0 ≤ <i>k</i> ≤ 11, 0 ≤ <i>l</i> ≤ 14	–26 ≤ <i>h</i> ≤ 26, –20 ≤ <i>k</i> ≤ 20, –11 ≤ <i>l</i> ≤ 11
Total reflections	9017	15832
Unique reflections	3196	3249
Observed reflections [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	3001	2727
Refined parameters	235	167
Completeness to $\theta_{\text{max}}$ (%)	98.7	99.3
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	0.0267, 0.0645 <sup>a</sup>	0.0285, 0.0702 <sup>b</sup>
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.0386, 0.0694 <sup>a</sup>	0.0396, 0.0702 <sup>b</sup>
<i>R</i> <sub>int</sub> , <i>S</i>	0.0291, 0.978	0.071, 1.03
Maximum and minimum peaks in final Fourier map (e Å <sup>-3</sup> )	0.368, –0.581	1.33, –1.68

<sup>a</sup>  $w = 1/[\sigma^2(F_o^2) + (0.0348P)^2 + 3.3232P]$ , where  $P = [F_o^2 + 2F_c^2]/3$ .

<sup>b</sup>  $w = 1/[\sigma^2(F_o^2) + (0.0348P)^2 + 3.3232P]$ , where  $P = [F_o^2 + 2F_c^2]/3$ .

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**General remarks.** HC(O)-1-C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-3,5 (**1a**) [19], Br-1-HC(O)-4-C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6 (**1b**) [12], [Pd<sub>2</sub>(dba)<sub>3</sub> · CHCl<sub>3</sub>] (**5a**) [21], [Pt(tol-4)<sub>2</sub>(SEt<sub>2</sub>)<sub>2</sub>] (**5b**) [22] and [Ti(μ-σ,π-C≡CSiMe<sub>3</sub>)<sub>2</sub>]AgOClO<sub>3</sub> (**7**) [13] were prepared following published procedures. All other chemicals were purchased from commercial suppliers and were used as received.

#### 4.1. Synthesis of N≡C-1-C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-3,5 (**2a**)

Compound **1a** (1.10 g, 4.99 mmol) was dissolved in 10 mL of concentrated formic acid and 450 mg (6.48 mmol) of H<sub>2</sub>NOH · HCl

were added in a single portion. After heating the reaction mixture to reflux for 90 min it was cooled to 25 °C and afterwards carefully poured on 50 mL of crushed ice. The pH value of the solution was adjusted to 8 with 4 M NaOH. The aqueous phase was extracted twice with 100 mL of diethyl ether. The combined organic phases were dried over MgSO<sub>4</sub>, filtered through a pad of Celite and all volatiles were removed in *oil-pump vacuum* to gave **2a** (600 mg, 2.76 mmol, 55% based on **1a**) as a yellow oil.

IR (NaCl): [cm<sup>-1</sup>] 2230 (s) [ $\nu_{\text{C}\equiv\text{N}}$ ]. <sup>1</sup>H NMR (CDCl<sub>3</sub>): [δ] 2.18 (s, 12H, NMe<sub>2</sub>), 3.37 (s, 4H, CH<sub>2</sub>N), 7.46 (bs, 3H, C<sub>6</sub>H<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): [δ] 45.2 (NCH<sub>3</sub>), 63.2 (NCH<sub>2</sub>), 112.1 (C–C≡N), 118.8 (C≡N), 131.0 (CH/C<sub>6</sub>H<sub>3</sub>), 133.7 (CH/C<sub>6</sub>H<sub>3</sub>), 140.4 (<sup>i</sup>C/C<sub>6</sub>H<sub>3</sub>). EI-MS [*m/z* (rel. int.)] 217 (5) [M<sup>+</sup>], 174 (100) [M<sup>+</sup>–NC<sub>2</sub>H<sub>5</sub>], 129 (50) [M<sup>+</sup>–2NMe<sub>2</sub>], 103 (40) [M<sup>+</sup>–(NMe<sub>2</sub>)<sub>2</sub>CN]. Anal. Calc. for C<sub>13</sub>H<sub>19</sub>N<sub>3</sub> (217.30): C, 71.85; H, 8.81; N, 19.34. Found: C, 71.75; H, 8.96; N, 18.62%.

#### 4.2. Synthesis of Br-1-N≡C-4-C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6 (**2b**)

**Method 1.** Molecule **2b** was prepared according to the procedure described for **2a** using 1.00 g (3.34 mmol) of Br-1-HC(O)-4-C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6 (**1b**) and 302 mg (4.35 mmol) of H<sub>2</sub>NOH · HCl. After appropriate work-up, 550 mg (1.89 mmol, 56% based on **1b**) of **2b** could be isolated as a yellow oil.

**Method 2.** Compound **1b** (73 mg, 0.24 mmol) was dissolved in 10 mL of conc. aqueous NH<sub>3</sub> and 2 mL of tetrahydrofuran and I<sub>2</sub> (68 mg, 0.27 mmol) were added in a single portion. The reaction mixture was stirred for 1 h at 25 °C. Afterwards it was quenched with 10 mL of acetone and extracted twice with 50 mL of diethyl ether. The combined organic phases were dried over MgSO<sub>4</sub>, filtered through a pad of Celite and all volatiles were evaporated in *oil-pump vacuum* to gave **2b** (50 mg, 0.17 mmol, 70% based on **1b**) as a yellow oil.

IR (NaCl): [cm<sup>-1</sup>] 2231 (s) [ $\nu_{\text{C}\equiv\text{N}}$ ]. <sup>1</sup>H NMR (CDCl<sub>3</sub>): [δ] 2.30 (s, 12H, NMe<sub>2</sub>), 3.53 (s, 4H, CH<sub>2</sub>N), 7.67 (s, 2 H, C<sub>6</sub>H<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): [δ] 45.6 (NCH<sub>3</sub>), 63.3 (NCH<sub>2</sub>), 111.0 (C–C≡N), 118.5 (C≡N), 131.4 (<sup>i</sup>CBr/C<sub>6</sub>H<sub>2</sub>), 131.8 (CH/C<sub>6</sub>H<sub>2</sub>), 140.6 (<sup>i</sup>C/C<sub>6</sub>H<sub>2</sub>). Anal. Calc. for C<sub>13</sub>H<sub>18</sub>BrN<sub>3</sub> (296.20): C, 52.71; H, 6.13; N, 14.19. Found: C, 52.65; H, 6.58; N, 13.77%.

#### 4.3. Synthesis of [PdBr(N≡C-4-C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6)] (**6a**)

Molecule **2b** (76 mg, 0.26 mmol) and 130 mg (0.13 mmol) of [Pd<sub>2</sub>(dba)<sub>3</sub> · CHCl<sub>3</sub>] (**5a**) were dissolved in 20 mL of benzene and the reaction solution 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 evaporated in *oil-pump vacuum* and the greenish-black residue was dissolved in 20 mL of chloroform. The solution was filtered through a pad of Celite and the eluate was



concentrated in *oil-pump vacuum* to 5 mL. On addition of *n*-hexane (50 mL) a yellow solid precipitated, which was washed three times with *n*-hexane (10 mL) and diethyl ether (10 mL) to give **6a** as a pale yellow solid in 70 mg yield (0.17 mmol, 69 % based on **5a**).

M.p.: [°C] > 200. IR (KBr): [cm<sup>-1</sup>] 2219 (m) [ν<sub>C≡N</sub>]. <sup>1</sup>H NMR (d<sub>6</sub>-acetone): [δ] 2.95 (s, 12H, NMe<sub>2</sub>), 4.17 (s, 4H, CH<sub>2</sub>N), 7.17 (s, 2H, C<sub>6</sub>H<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (d<sub>6</sub>-acetone): [δ] 53.9 (NCH<sub>3</sub>), 74.7 (NCH<sub>2</sub>), 108.1 (C–C≡N), 120.3 (C≡N), 123.8 (CH/C<sub>6</sub>H<sub>2</sub>), 129.8 (<sup>i</sup>C/C<sub>6</sub>H<sub>2</sub>), 147.9 (<sup>i</sup>Cpdt/C<sub>6</sub>H<sub>2</sub>). Anal. Calc. for C<sub>13</sub>H<sub>18</sub>BrN<sub>3</sub>Pd (402.63): C, 38.78; H, 4.51; N, 10.44. Found: C, 38.58; H, 4.42; N, 10.47%.

#### 4.4. Synthesis of [PtBr(N≡C-4-C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6)] (**6b**)

Compound **2b** (198 mg, 0.63 mmol) and 290 mg (0.31 mmol) of [Pt(tol-4)<sub>2</sub>(SEt<sub>2</sub>)<sub>2</sub>] (**5b**) were dissolved in 30 mL of benzene and were heated to reflux for 5 min. The yellow solution was then cooled to 25 °C and concentrated in *oil-pump vacuum* to 10 mL. Upon addition of 20 mL of *n*-hexane to the reaction solution 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*. Yield: 130 mg (0.26 mmol, 85% based on **5b**) of **6b**.

M.p.: [°C] > 200. IR (KBr): [cm<sup>-1</sup>] 2219 (m) [ν<sub>C≡N</sub>]. <sup>1</sup>H NMR (CDCl<sub>3</sub>): [δ] 3.16 (s, <sup>3</sup>J<sub>PTIH</sub> = 38.4 Hz, 12H, NMe<sub>2</sub>), 4.02 (s, <sup>3</sup>J<sub>PTIH</sub> = 46.8 Hz, 4H, CH<sub>2</sub>N), 7.07 (s, <sup>4</sup>J<sub>PTIH</sub> = 8.0 Hz, 2H, C<sub>6</sub>H<sub>2</sub>). (CD<sub>3</sub>CN): [δ] 3.02 (s, <sup>3</sup>J<sub>PTIH</sub> = 38.5 Hz, 12H, NMe<sub>2</sub>), 4.07 (s, <sup>3</sup>J<sub>PTIH</sub> = 45.4 Hz, 4H, CH<sub>2</sub>N), 7.12 (s, 2H, C<sub>6</sub>H<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): [δ] 55.0 (NCH<sub>3</sub>), 76.7 (NCH<sub>2</sub>), 106.0 (C–C≡N), 118.1 (C≡N), 123.0 (CH/C<sub>6</sub>H<sub>2</sub>), 144.2 (<sup>i</sup>C/C<sub>6</sub>H<sub>2</sub>), 151.3 (<sup>i</sup>Cpdt/C<sub>6</sub>H<sub>2</sub>). Anal. Calc. for C<sub>13</sub>H<sub>18</sub>BrN<sub>3</sub>Pt (491.29): C, 31.78; H, 3.69; N, 8.55. Found: C, 32.13; H, 3.95; N, 8.38%.

### 5. X-ray structure determinations of **6a** and **6b**

**6a**: X-ray structure analysis was performed with a BRUKER SMART CCD equipment. Reflections were collected in the ω-scan mode in 0.3° steps and an exposure time of 45 seconds per frame. All data were corrected for absorption using SADABS [23]. The structure was solved by direct methods using SHELXS-97 [24] and refined by full-matrix least-square procedures on F<sup>2</sup> using SHELXL-97 [25]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms have been taken from the difference Fourier map and refined freely.

**6b**: Intensity data were collected on a Nonius Kappa CCD diffractometer. A multi-scan based absorption correction was applied using the program PLATON/MULABS [26,27]. The structure was solved by direct methods using SHELXS-97 [24] and refined by full-matrix least-squares procedures on F<sup>2</sup> using SHELXS-97 [25]. All non-hydrogen atoms were refined anisotropically. All hydrogen atom positions were constrained to idealized geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter values related to the equivalent displacement parameter value of their carrier atoms. Structure validation was done with PLATON/CHECKIF [26].

The structure plots were performed with Platon [26].

### 6. Synthesis of {[Pt(N≡C-4-C<sub>6</sub>H<sub>2</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-2,6)](ClO<sub>4</sub>)<sub>n</sub>} (**8**)

{[Ti](μ-σ,π-C≡CSiMe<sub>3</sub>)<sub>2</sub>}AgOClO<sub>3</sub> (**7**) (52 mg, 0.072 mmol) was dissolved in 20 mL of tetrahydrofuran and 35 mg (0.071 mmol) of **6b** in 20 mL of tetrahydrofuran were added dropwise at 25 °C. After the reaction mixture was stirred for 10 min at this temperature the pale yellow precipitate was filtered off, washed twice with tetrahydrofuran (5 mL) and dried in *oil-pump vacuum* to give 35 mg (0.069 mmol, 96% based on **6b**) of **8**.

M.p.: [°C] 173 (dec.). IR (NaCl): [cm<sup>-1</sup>] 2247 (m) [ν<sub>C≡N</sub>], 1091 (s) [ν<sub>Cl-O</sub>]. <sup>1</sup>H NMR (CD<sub>3</sub>CN): [δ] 1.83 (m, 2H, 1/2 thf), 3.01 (s, <sup>3</sup>J<sub>PTIH</sub> = 39.5 Hz, 12H, NMe<sub>2</sub>), 3.66 (m, 2H, 1/2 thf), 4.17 (s, <sup>3</sup>J<sub>PTIH</sub> = 48.7 Hz, 4H, CH<sub>2</sub>N), 7.19 (s, 2H, C<sub>6</sub>H<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN): [δ] 26.1 (thf), 53.0 (NCH<sub>3</sub>), 68.1 (thf), 74.8 (NCH<sub>2</sub>), 106.7 (C–C≡N), 119.0 (C≡N), 122.4 (CH/C<sub>6</sub>H<sub>2</sub>), 145.7 (<sup>i</sup>C/C<sub>6</sub>H<sub>2</sub>), 149.5 (<sup>i</sup>Cpdt/C<sub>6</sub>H<sub>2</sub>). Anal. Calc. for C<sub>13</sub>H<sub>18</sub>ClN<sub>3</sub>O<sub>4</sub>Pt · 1/2Thf (510.83): C, 32.94; H, 4.05; N, 7.68. Found: C, 33.13; H, 4.23; N, 7.89%.

### 7. Reaction of N≡C-1-C<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>-3,5 (**2a**) with <sup>t</sup>BuLi and D<sub>2</sub>O

Compound **2a** (50 mg, 0.23 mmol) was dissolved in 20 mL of diethyl ether and 0.16 mL (0.24 mmol) of <sup>t</sup>BuLi (1.5 M in *n*-hexane) were added dropwise at –80 °C or 25 °C. After stirring at these temperatures for 30 min, 0.5 mL of D<sub>2</sub>O were added in one single portion. Stirring was continued for 30 min and the reaction solution was allowed to warm to 25 °C. All volatiles were removed in *oil-pump vacuum* to give a mixture of DN=C(<sup>t</sup>Bu)-1-C<sub>6</sub>H<sub>3</sub>-(CH<sub>2</sub>NMe<sub>2</sub>-3,5)<sub>2</sub> (**3**) and O=C(<sup>t</sup>Bu)-1-C<sub>6</sub>H<sub>3</sub>-(CH<sub>2</sub>NMe<sub>2</sub>-3,5)<sub>2</sub> (**4**), respectively, as yellow oil.

**3**: As C<sub>17</sub>H<sub>29</sub>N<sub>3</sub>: EI MS [m/z (rel. int.)] 275 (40) [M<sup>+</sup>], 260 (125) [M<sup>+</sup>-Me], 231 (75) [M<sup>+</sup>-NMe<sub>2</sub>], 218 (50) [M<sup>+</sup>-<sup>t</sup>Bu], 187 (90) [M<sup>+</sup>-2 NMe<sub>2</sub>], 173 (100) [M<sup>+</sup>-CH<sub>2</sub>(NMe<sub>2</sub>)<sub>2</sub>].

**4**: EI MS [m/z (rel. int.)] 276 (10) [M<sup>+</sup>], 232 (100) [M<sup>+</sup>-NMe<sub>2</sub>], 219 (20) [M<sup>+</sup>-<sup>t</sup>Bu], 188 (75) [M<sup>+</sup>-2 NMe<sub>2</sub>], 103 (55) [M<sup>+</sup>-<sup>t</sup>Bu-(CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>].

### Supplementary material

CCDC 240801 and 673470 contain the supplementary crystallographic data for compound **6a** and **6b**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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