

Self-Assembly of *p*-Nitro NCN-Pincer Palladium Complexes into Dimers through Electron Donor–Acceptor Interactions

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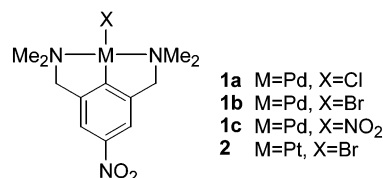
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Summary: *p*-Nitro-substituted NCN–palladium complexes self-assemble into dimers in the solid state. A NO₂-to-Pd(II) electron donor–acceptor (EDA) interaction is proposed to account for this observation. Similar behavior is not observed for their platinum analogues.

Ligand functionalization offers an important tool for electronic fine-tuning of organometallic complexes. The anionic terdentate ECE ligating “pincer” complexes, in particular, have attracted attention, since both variations in the trans-coordinating donor atoms (E) and the introduction of substituents on the phenyl ring para to the C_{ipso}–metal bond allow the manipulation of the properties and reactivities of the resulting complexes.^{1,2} The square-planar d⁸-metal pincer complexes [MX(ECE)] with M = Pd, Pt offer a variety of interesting structural possibilities, acting either in the monocationic [M(ECE)]⁺ forms as Lewis acids or in their neutral forms as Lewis bases.^{1a} In this communication we report the unexpected dimerization of the *p*-nitro-substituted NCN-pincer palladium(II) complexes [PdX(NCN-NO₂)] with X = Cl (**1a**), Br (**1b**)³ (Chart 1) through electron donor–acceptor (EDA) interactions. A related interaction is observed for the pincer palladium(II) complex [Pd(NO₂)(NCN-NO₂)] (**1c**). However, it is not observed for the analogous platinum(II) complex [PtBr(NCN-NO₂)] (**2**) or for other para-substituted pincer palladium complexes. The noncovalent EDA interaction between palladium and the nitro substituent described here is a new structural motif in supramolecular organometallic chemistry.

Crystals of **1a** were grown by slow vapor diffusion of diethyl ether into a concentrated dichloromethane solution, while suitable crystals of **1b** were obtained by slow concentration of a dichloromethane solution.⁴ Both complexes are isostructural and have approximate,

Chart 1. *p*-Nitro-Substituted NCN-Pincer Complexes 1a–c and 2



noncrystallographic *C_s* symmetry in the solid state. The palladium(II) metal centers have distorted-square-planar geometries comparable with those found for *C₂*-symmetric NCN-pincer palladium complexes.⁵ In the crystal state **1a** and **1b** form closely packed dimeric structures (see Figure 1).

As a consequence of the *C_s* symmetry, both five-membered metallacycles are puckered in the same direction, with Pd1–N1–C7–C2 and Pd1–N2–C10–C6 torsion angles of 23.75(18) and –17.72(17)°, respectively, for compound **1a**. The dimeric structure is centrosymmetric; consequently, both participating aryl rings are parallel and are positioned directly on top of one another (Table 1). The face-to-face center-to-center arrangement of the aryl rings in the dimer could be typical for π -stacked donor–acceptor pairs.⁶ The disposition of the amino methyl groups C8 and C11 leaves enough space to accommodate the nitro substituent of the other molecule in the dimer. The dimer is additionally stabilized by weak hydrogen bonds between aromatic, benzylic, and aliphatic C–H hydrogens as donors and halogenide and nitro groups as acceptors. However, the presence of these weak hydrogen bonds cannot solely account for the dimeric structure encountered.

Interestingly, the short intermolecular contacts between the palladium atoms and the nitro substituents

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(2) (a) Slagt, M. Q.; Klein Gebbink, R. J. M.; Lutz, M.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Dalton Trans.* **2002**, 2591–2593. (b) Grimm, J. C.; Nachtigal, C.; Mack, H.-G.; Kaska, W. C.; Mayer, H. A. *Inorg. Chem. Commun.* **2001**, *3*, 511–514. (c) Gossage, R. A.; van de Kuil, L. A.; van Koten, G. *Acc. Chem. Res.* **1998**, *31*, 423–431.

(3) The synthesis of complexes **1a**, **1b**, and **2** is reported in ref 2a. **1c** was obtained from **1a** or **1b**, upon halide abstraction with AgBF₄ in acetone, followed by treatment with an excess of NaNO₂.

(4) Selected bond lengths (Å), angles (deg), and dihedral angles (deg) for **1a**: Pd1–C1 = 1.9131(18), Pd1–N1 = 2.1018(15), Pd1–N2 = 2.1007(15), Pd1–C11 = 2.4277(5); C1–Pd1–N1 = 82.48(7), C1–Pd1–N2 = 82.49(7), C1–Pd1–C11 = 172.81(5), N1–Pd1–N2 = 163.56(6); Pd1–N1–C7–C2 = 23.75(18), Pd1–N2–C10–C6 = –17.72(17). Selected bond lengths (Å), angles (deg), and dihedral angles (deg) for **1b**: Pd1–C1 = 1.913(2), Pd1–N1 = 2.107(2), Pd1–N2 = 2.105(2), Pd1–Br1 = 2.5516(3); C1–Pd1–N1 = 82.41(9), C1–Pd1–N2 = 82.33(9), C1–Pd1–Br1 = 172.10(7), N1–Pd1–N2 = 163.58(8); Pd1–N1–C7–C2 = –25.0(2), Pd1–N2–C10–C6 = 17.4(2).

(5) For example: (a) Albrecht, M.; Lutz, M.; Schreurs, A. M. M.; Lutz, E. T. H.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Dalton Trans.* **2000**, 3797–3804. (b) Lagunas, M.-C.; Gossage, R. A.; Spek, A. L.; van Koten, G. *Organometallics* **1998**, *17*, 731.

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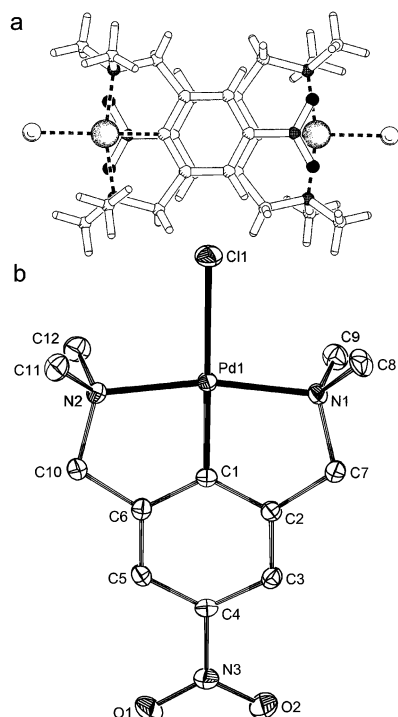


Figure 1. (a) Packing diagram of $[\text{PdCl}(\text{NCN-NO}_2)]$ (**1a**) showing the dimeric substructure. (b) Displacement ellipsoid plot (50% probability level) of **1a**. Hydrogen atoms have been omitted for clarity.

Table 1. Relative Orientation of the Participating Aryl Rings in the Dimeric Structures of 1a, 1b, and 1c (Residues 1 and 2)

	1a	1b	1c_1 ^a	1c_2 ^b
interplane distance (Å) ^c	3.516	3.503	3.540/3.397	3.557
distortion (deg) ^d	8.62	10.63	17.29/23.64	24.20
interplane dihedral angle (deg)	0.00	0.00	8.22	0.00

^a For the dimer between residues 1 and 2. ^b For the dimer between residues 3 and 3ⁱ ($1-x, 1-y, 1-z$). ^c Perpendicular distance from the ring centroid to the plane of the other ring. ^d Angle between the plane normal and the vector connecting the two ring centroids.

Table 2. Short Intramolecular Contacts (Å) between the Pd Atom and the NO₂ Substituent in the Dimeric Structures of 1a, 1b, and 1c

	1a	1b	1c_1 ^a	1c_2 (Å) ^b	sum of van der Waals radii ^c
Pd...N3 ⁱ	3.818(2)	3.851(3)	3.724(2)/ 4.051(2)	4.0301(19)	3.85
Pd...O1 ⁱ	3.8753(19)	3.863(3)	3.5853(16)/ 4.2149(19)	4.0006(16)	3.82
Pd...O2 ⁱ	3.8759(19)	3.973(3)	3.6930(18)/ 3.8208(16)	3.9847(18)	3.82

^a For the palladium atoms of residues 1 and 2, respectively. ^b For the palladium atoms of residues 3 and 3ⁱ ($1-x, 1-y, 1-z$), respectively. ^c See ref 7. Symmetry operations i: (**1a**) $1-x, -y, -z$, (**1b**) $1-x, -y, -z$, (**1c_1**) x, y, z , (**1c_2**) $1-x, 1-y, 1-z$.

indicate the presence of an additional interaction. The distance between the palladium atoms and the NO₂-nitrogens is slightly shorter ($\text{Pd1}\cdots\text{N3}^i = 3.818(2)$ Å) for **1a** than the sum of the van der Waals radii (3.85 Å) (Table 2).⁷ While the coordination of positively charged metals to nitro substituents is generally considered to involve mainly the negatively charged oxygen atoms,

the palladium atoms in **1a** and **1b** are clearly in closer contact with the nitrogen atom than the NO₂ oxygen atoms.

In fact, we propose the presence of an electron donor–acceptor (EDA) interaction to be responsible for this close contact between the two $[\text{PdX}(\text{NCN-NO}_2)]$ units in the dimer. This type of EDA interaction can be rationalized using the qualitative orbital model, proposed by Alvarez et al. for the description of $\text{M}\cdots\text{M}$ interactions in dimers and stacks of square-planar $d^8\text{-ML}_4$ complexes.⁸ Both the filled d_z^2 and the empty p_z frontier orbitals of the metal center possess the correct symmetry for binding along the z axis. The relative energies of these orbitals can be tuned by choosing appropriate ligands (L) in the xy plane. The use of better σ -donor ligands stabilizes the filled d_z^2 orbital and enlarges its size. The presence of π -acceptor ligands stabilizes the empty p_z orbital by making this orbital less contracted, while π -donor ligands do the opposite.^{8a,b} Colorful examples of the bonding of Lewis basic NCN-pincer platinum(II) complexes to Lewis acidic SO₂ and I₂ ligands have been reported previously.^{1a} On the basis of the qualitative orbital description (vide supra) and the observation that NCN-pincer palladium complexes do not bind to Lewis acids such as their platinum analogues,⁹ we propose that the palladium(II) atom acts as a Lewis acid in the formation of the dimeric structures observed for **1a** and **1b**. The *p*-nitro substituent on the NCN-pincer ligand withdraws electron density, rendering the pincer ligand a poorer σ -donor, resulting in a destabilized and more contracted filled palladium d_z^2 orbital. Simultaneously, the aryl ligand becomes a better π -acceptor, thereby stabilizing the empty p_z orbital. These combined effects make the metal less prone to act as a Lewis base but, instead, improve its Lewis acidic properties. These Lewis acidic palladium(II) atoms can have attractive interactions with the filled π orbitals of the nitro substituent of the neighboring complex. Comparison of **1a** and **1b** indicates that the influence of the halide on the dimeric structure is only marginal, since the intermolecular distances are similar (Table 2). The somewhat longer Pd \cdots N3 contacts in **1b** compared to those in **1a** might be ascribed to destabilization of the p_z orbital by the more π -basic bromide ligand. Replacement of the halide by the π -acidic nitrite anion (NO₂[−]), to afford complex **1c**, was expected to influence the dimerization behavior. Interestingly, the crystal structure of **1c** contains three independent molecules. Residues 1 and 2 form a dimer with one another, while residue 3 assembles into a dimer with a symmetry-generated molecule of itself (see Figure 2).¹⁰ The pincer complex of residue 3 has approximate C_2 symmetry, with the chelate rings puckered in opposite directions. The metal complexes of residues 1 and 2 have their chelate rings puckered in the same direction (approximate C_s symmetry), as in **1a** and **1b**. The nitrite anion coordinates to the metal via its

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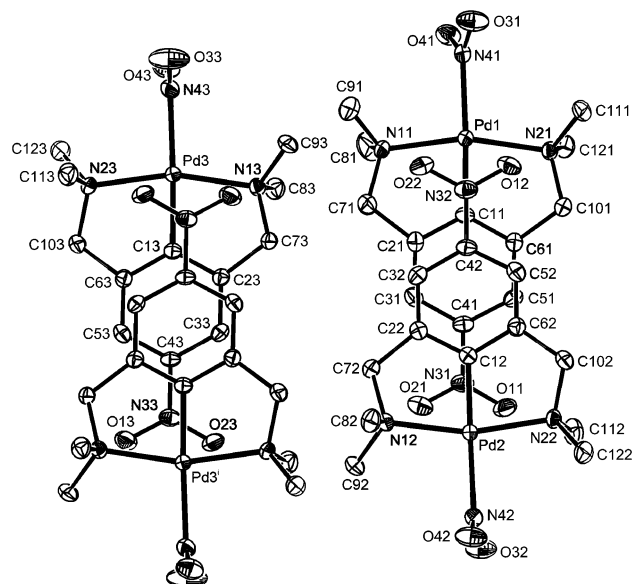


Figure 2. Displacement ellipsoid plot (50% probability level) of $[\text{Pd}(\text{NO}_2)(\text{NCN-NO}_2)]$ (**1c**), showing both dimeric units as they exist next to each other in the solid state. Hydrogen atoms have been omitted for clarity. Symmetry operation $i: 1 - x, 1 - y, 1 - z$.

nitrogen atom and is oriented such that the NO_2 plane is nearly orthogonal with respect to the coordination plane of the palladium atom. The relative arrangement of the interacting complexes in the dimers differs markedly from that in **1a** and **1b**. The aryl rings are shifted sideways (Table 1), and here, the oxygen atoms of the nitro substituent are in close contact with the palladium atom of the neighboring complex (Table 2).

As a result of the nearly orthogonal orientation of the nitrite ligand, the effect of its π system on the relative energies of the metal d_z^2 or p_z orbitals is small.¹¹ Hence, these orbitals are mainly influenced by the σ -donating properties of the ligand. We therefore ascribe the differences in the geometry of the dimers in **1c** compared to **1a** and **1b** mainly to steric factors imposed by the nitrite ligand.

The nitro-substituted NCN-pincer platinum(II) complex **2** was crystallized by vapor diffusion of diethyl ether in a concentrated dichloromethane solution.¹² The crystal structure of **2** contains two independent molecules of comparable geometry. Interestingly, no dimers are formed here; rather, the molecules display monomeric structures as normally encountered in d^8 -metal pincer complexes (Figure 3).¹³ The molecules have approximate C_2 symmetry, with both five-membered metallacycles puckered in opposite directions.

(10) Selected bond lengths (\AA), angles (deg), and dihedral angles (deg) for **1c** are as follows. Residue 1: Pd1–C11 = 1.919(2), Pd1–N11 = 2.0908(17), Pd1–N21 = 2.1054(17), Pd1–N41 = 2.1184(19); C11–Pd1–N11 = 82.45(8), C11–Pd1–N21 = 82.06(8), C11–Pd1–N41 = 177.50(8), N11–Pd1–N21 = 162.79(7); Pd1–N11–C71–C21 = –23.6(2), Pd1–N21–C101–C61 = 21.6(2), N11–Pd1–N41–O41 = –67.11(17). Residue 2: N12–Pd2–N42–O42 = –83.13(17). Residue 3: Pd3–C13 = 1.917(2), Pd3–N13 = 2.1052(16), Pd3–N23 = 2.0968(17), Pd3–N43 = 2.1250(19); C13–Pd3–N13 = 81.49(8), C13–Pd3–N23 = 82.09(8), C13–Pd3–N43 = 177.43(8), N13–Pd3–N23 = 163.45(7); Pd3–N13–C73–C23 = 25.61(19), Pd3–N23–C103–C63 = 27.9(2), N13–Pd3–N43–O43 = 94.42(17).

(11) The π -system of the orthogonally oriented nitrite ligand has the correct symmetry for constructive overlap with the $d_{x^2-y^2}$ orbital on the palladium atom.

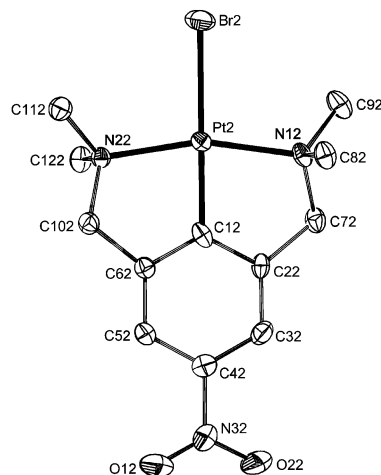


Figure 3. Displacement ellipsoid plot (50% probability level) of one of the independent molecules of $[\text{PtBr}(\text{NCN-NO}_2)]$ (**2**). Hydrogen atoms have been omitted for clarity.

Obviously, the attractive $\text{NO}_2 \cdots \text{Pd}$ binding interactions that lead to dimers in the solid-state structures of **1a** and **1b** are less pronounced for the platinum complex **2**. Most likely, the Lewis acidity of the p_z orbital is to a greater extent countered by the filled d_z^2 orbital on platinum, leading to an overall repulsive interaction with the filled π orbitals of the nitro substituent. It should be noted that the d_z^2 orbital of the platinum(II) center in **2** is still able to act as a Lewis base for reversible $\eta^1\text{-Pt-SO}_2$ binding, as was confirmed by ^1H and ^{195}Pt NMR and IR spectroscopy.¹⁴ As is also the case for other NCN-pincer palladium complexes,⁹ neither **1a** nor **1b** forms such an adduct with SO_2 . Dilution experiments using ^1H NMR (5–100 mM) and UV–vis (10^{-6} – 10^{-4} M) afforded no conclusive evidence for either the formation or breakup of dimers in solution. We are currently studying the supramolecular structure of other para-substituted NCN-pincer metal complexes both in solution and in the solid state.

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Supporting Information Available: Text and tables giving crystallographic data for **1a**, **1b**, **1c**, and **2** and text giving characterization data for **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(12) Selected bond lengths (\AA), angles (deg), and dihedral angles (deg) for **2** (residue 2): Pt2–C12 = 1.937(4), Pt2–N12 = 2.105(3), Pt2–N22 = 2.099(2), Pt2–Br12 = 2.5211(4); C12–Pt2–N12 = 81.78(11), C12–Pt2–N22 = 81.46(11), C12–Pt2–Br12 = 175.56(8), N12–Pt2–N22 = 163.20(11); Pt2–N12–C72–C22 = –31.5(3), Pt2–N22–C102–C62 = –34.0(3).

(13) The monomeric structure found for complex **2** is general for NCN-pincer platinum complexes. This further attenuates the finding that p -nitro-functionalized NCN-pincer palladium complexes form dimers in the solid state.

(14) In contrast with other NCN-pincer platinum complexes, complexation of **2** with SO_2 does not lead to significant spectroscopic changes in the UV/vis absorbance region. The characteristic orange color of the $[\text{PtX}(\text{NCN})\text{SO}_2]$ adducts originates from two Pt–S metal to ligand charge transfer bands located at approximately 350–370 and 400–420 nm. The orange sulfur dioxide free complex **2** has a broad absorbance located at 384 nm. Addition of SO_2 results in a small shift of this band to 379 nm, combined with a small decrease in intensity.