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Dedicated to Professor Alexandru T. BALABAN on the occasion of his 90th anniversary

{2,6-BIS[(DIMETHYLAMINO)METHYL]PHENYL}MERCURY(II) ACETATE, [2,6-$(Me_2NCH_2)_2C_6H_3$]Hg(OAc) – A USEFUL INTERMEDIATE FOR SELECTIVE PALLADATION OF 1,3-$(Me_2NCH_2)_2C_6H_4$

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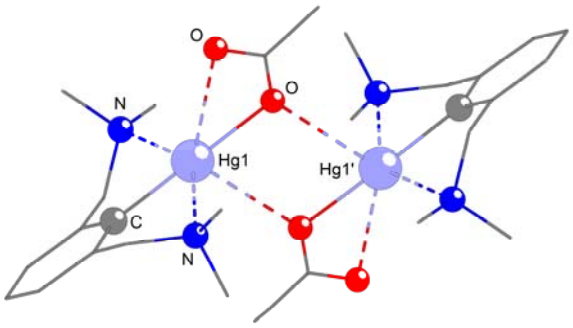
The compound [2,6-$(Me_2NCH_2)_2C_6H_3$]Hg(OAc) (**1**) was prepared by direct mercuration of 1,3-$(Me_2NCH_2)_2C_6H_4$ with $Hg(OAc)_2$. Treatment of **1** with excess of LiCl resulted in isolation of the chloride [2,6-$(Me_2NCH_2)_2C_6H_3$]HgCl (**2**) in a good yield. The IR spectroscopy confirms the presence of the acetate group in **1**. Both compounds **1** and **2** were characterized by solution multinuclear (^{1}H, ^{13}C and ^{199}Hg) NMR spectroscopy and mass spectrometry. Their crystal and molecular structures were established by single-crystal X-ray diffraction. Different intermolecular interactions, *i.e.* Hg···Hg, O···Hg and C–H···π ($Ar_{centroid}$), were found for both compounds in solid state resulting in dimer or chain polymer associations.



INTRODUCTION

The chemistry of organopalladium(II) compounds containing a *N,C,N*-pincer ligand (abbreviated in the subsequent discussion as generic "*NCN*" ligand) as those depicted in Chart 1 raised a tremendous interest and such compounds were often investigated in relation to their catalytic activity for a wide variety of reactions,[1] *e.g.* Michael addition of *α*-cyano carboxylates to alkyl vinyl ketone,[2] cyclopropanation of ethyl cinnamate with diazomethane,[3] Heck-type reaction of aryl iodides and acrylates,[2f,4] or functionalized alkenes,[5] aldol-type condensation of isocyanoacetate and aldehydes,[6] regioselective transfer of the triorganostannyl or -silyl groups to propargylic substrates,[7] Suzuki–Miyaura,[8] Sonogashira,[9] and Hiyama[10] cross-coupling reactions, as well as cross-coupling reaction between *trans*-phenylvinylboronic acid and vinyl epoxide,[11] selective *α*-monoarylation of ketones with aryl bromides,[12] reaction of benzyl nitriles with sulfonimines,[13] aza-Morita–Baylis–Hillman reaction of acrylonitrile with sulfonimines,[14] allylation of isatin-derived ketimines,[15] stereoselective 1,4

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addition of alkylphenylphosphines to *α,β*-unsaturated carbonyl compounds,[16] C–H functionalization of benzyl nitriles with *N*-tosylaldimines to form *β*-aminonitriles,[17] oxidative borylation of allylic C–H bonds in alkenes,[18] etc.

Depending on the nature of the organic proligand the creation of a *σ*-Pd–C_{aryl} bond and thus the synthesis of such organopalladium(II) species can be usually achieved through one of the following methods:[1a,2f] (*i*) direct cyclopalladation by C–MR_3 (M = Si,[19] Sn[6c,19b,20]) activation using $[PdCl_2(NCPh)_2]$ or $Pd(OAc)_2$; (*ii*) oxidative addition to C–halogen bond using $[Pd(dba)_2]$[6b,21] or $[Pd_2(dba)_3]$[2d,2g,9,10,12,17] (dba = dibenzylideneacetone); (*iii*) transmetallation, using (*NCN*)Li compounds [obtained from lithiation of either *NC(H)N*[2a,b,d,5a,6a,11] or *NC(X)N* (X = halide)[5a,19e,22] precursors] and palladium(II) salts, *e.g.* $[PdX_2(COD)]$ (X = Cl, Br; COD = 1,5-cyclooctadiene), $[PdCl_2(SR_2)_2]$ (R = Me, Et).

When the direct C2 palladation of *NC(H)N* pincer proligands *via* C–H activation was attempted, the regioselectivity of metalation could not be generally controlled[1a,2f] or was not achieved at all.[2b] Thus, reactions carried out to obtain the targeted *ortho,ortho*-biscyclo palladated species from 1,3-$(R_2NCH_2)_2C_6H_4$ (**A**, R = Me, Et),[19c,23] 1,3-$(RN{=}CH)_2C_6H_4$ (**B**)[19b,24] or 1,3-(2′-Py)$_2C_6H_4$ (**C**)[6d,25] resulted instead in doubly metallation of 4,6-positions (Scheme 1). It is worthwhile however to mention here that using more severe reaction conditions, *i.e.* $Na_2[PdCl_4]$ in refluxing glacial acetic acid for 18 h, the proligand 1,3-(2′-Py)$_2C_6H_4$ and related chiral species could be directly palladated at the carbon in position 2.[6d]

The direct lithiation of a *NC(H)N* pincer proligand with *n*-BuLi also lacks selectivity and resulted in inseparable mixtures of isomers, *e.g.* [2,6-$(Me_2NCH_2)_2C_6H_3$]Li and [2,4-$(Me_2NCH_2)_2C_6H_3$]Li in the case of 1,3-$(Me_2NCH_2)_2C_6H_4$,[26] and therefore prefunctionalization of the pincer proligand, *e.g.* as 1-Br-2,6-$(Me_2NCH_2)_2C_6H_3$, is required before its use in preparative methods (*i*)-(*iii*) listed above.

The [{2,6-$(Me_2NCH_2)_2C_6H_3$}PdX] (X = Cl, Br, OAc) species are of particular interest since they were reported to catalyze triorganostannyl or -silyl transfer to propargylic substrates,[7] and oxidative borylation of allylic C–H bonds in alkenes.[18] In addition to the methods (*i*)-(*iii*), transmetallation of this particular pincer ligand by reacting [{2,6-$(Me_2NCH_2)_2C_6H_3$}Rh(COD)] with $[PdCl_2(NCPh)_2]$ or [{2,6-$(Me_2NCH_2)_2C_6H_3$}Au(PPh_3)] with $[PdCl_2(SEt_2)_2]$ were also reported;[27] however, these procedures are expensive and require [2,6-$(Me_2NCH_2)_2C_6H_3$]Li as a precursor for the preparation of Rh(I) or Au(I) complexes.[27a,28] Much more convenient seems to be the use of organomercury(II) compounds as transmetallation agents to palladium,[4,6d,29] since (*NCN*)HgX species can easily be obtained from direct metalation of the pincer proligand, *NC(H)N*, with $Hg(OAc)_2$.[4,6d,29b,c,30]

We report here on the mercuration of 1,3-$(Me_2NCH_2)_2C_6H_4$ to [2,6-$(Me_2NCH_2)_2C_6H_3$] Hg(OAc) (**1**) and its conversion to the corresponding chloride, [2,6-$(Me_2NCH_2)_2C_6H_3$] HgCl (**2**), as well as the spectroscopic characterization in solution and the solid state molecular structure of both these two organomercury(II) compounds, useful intermediates for selective palladation of this aromatic *NC(H)N* pincer proligand.

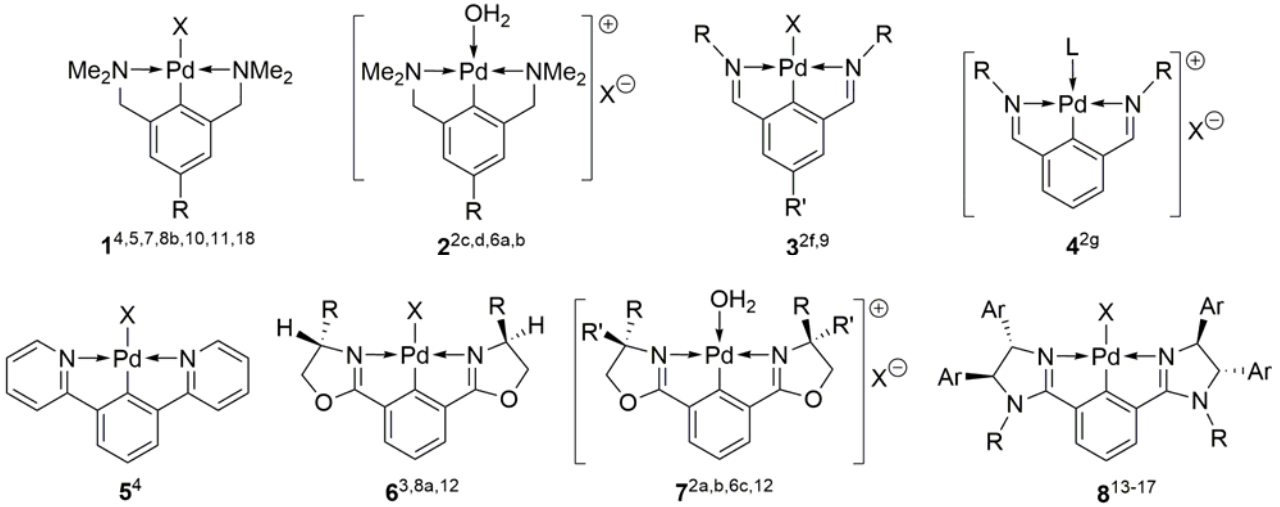
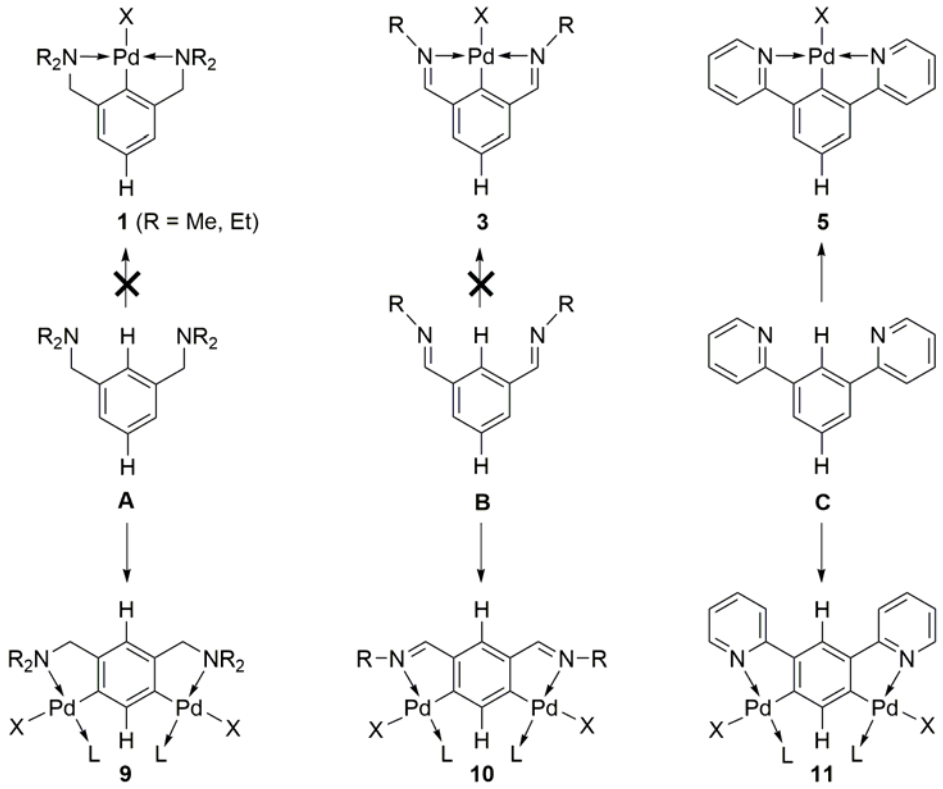


Chart 1 – Organopalladium(II) complexes containing a *N,C,N*-pincer ligand.



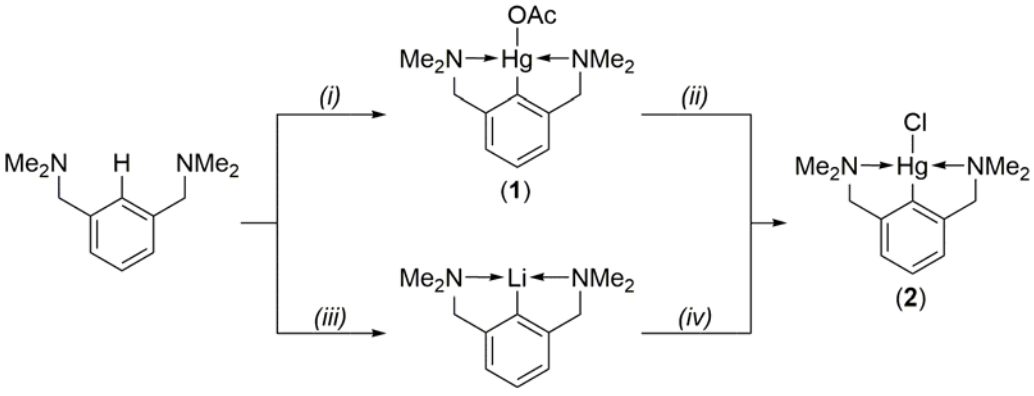
Scheme 1 – Palladation of *NC(H)N* pincer proligands.

RESULTS

The acetate [2,6-$(Me_2NCH_2)_2C_6H_3$]Hg(OAc) (**1**) was obtained using the direct mercuration method, *i.e.* by reacting 1,3-$(Me_2NCH_2)_2C_6H_4$ with $Hg(OAc)_2$ in absolute ethanol, at room temperature, under argon. Halogen exchange reaction between **1** and an excess of LiCl, carried out in methanol, afforded the isolation of the corresponding chloride [2,6-$(Me_2NCH_2)_2C_6H_3$] HgCl (**2**) (Scheme 2).

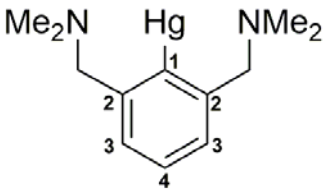
After workup procedures carried out in open atmosphere both compounds were isolated as white (the acetate **1**) or pale yellow (the chloride **2**) crystalline solids with a good solubility in common organic solvents (alcohols, chlorinated solvents as CH_2Cl_2 or $CHCl_3$); the acetate **1** is even soluble in pentane. Details of the preparations are given in the Experimental section.

Elemental analysis and the HRMS data confirmed the purity and identity of the organomercury(II) compounds. The APCI+ mass spectra showed the $[M+2MeOH-H]^+$ and $[M+H]^+$ ions as base peaks for **1** and **2**, respectively. The IR spectrum of the acetate **1** showed very strong bands at 1630 and 1298 cm^{-1} which were assigned to ν_{as}(COO) and ν_s(COO) stretching vibrations.



Scheme 2 – Synthesis of compounds **1** and **2**: *(i)* $Hg(OAc)_2$/EtOH; *(ii)* LiCl/MeOH; *(iii)* *n*-BuLi/hexane; *(iv)* $HgCl_2$/THF.

Both compounds were characterized in solution by ^{1}H, $^{13}C\{^{1}H\}$ and $^{199}Hg\{^{1}H\}$ NMR spectroscopy. The NMR spectra were recorded in $CDCl_3$ at room temperature. The assignment of the observed ^{1}H and ^{13}C resonances for the pincer ligand was made using 2D experiments, according to the numbering scheme shown in Scheme 3.



Scheme 3 – Numbering scheme for NMR assignments.

The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra for compounds **1** and **2** exhibited the expected resonances for the organic substituent on mercury both in the aromatic and aliphatic regions. For the two pendant arms of the pincer ligand only one set of resonances was observed. Aditionally to the number of resonances observed in the spectrum of **2** for compound **1** one singlet ^{1}H resonance and two ^{13}C resonances, respectively, were observed for the acetate group.

Single crystals of good quality were obtained for both compounds by slow evaporation of the solvent from solutions of acetate **1** in pentane and chloride **2** in Et_2O, in open atmosphere. The crystal and molecular structures were established by X-ray diffraction studies. The ORTEP-like representations of the molecular structure of compounds **1** and **2**, with the atom numbering scheme, are depicted in Fig. 1. Selected interatomic distances and bond angles are listed in Table 1. The unit cell of compound **2** contains four independent molecules (designated as **2A**, **2B**, **2C** and **2D**), with quite similar molecular parameters (see Table 1) which fit in two groups, *i.e.* **2A**/**2D** and **2B**/**2C**, and therefore only data for molecules **2A** and **2B** will be mentioned in the subsequent discussion.

Table 1

Selected interatomic distances (Å) and angles (deg) for RHg(OAc) (**1**) and RHgCl (**2**)[a] [R = 2,6-$(Me_2NCH_2)_2C_6H_3$]

	1[b]		**2A**	**2B**	**2C**	**2D**
Hg(1)–C(1)	2.066(6)	Hg(1)–C(1)	2.067(18)	2.08(2)	2.048(18)	2.073(17)
Hg(1)–O(1)	2.072(4)	Hg(1)–Cl(1)	2.319(5)	2.319(6)	2.330(6)	2.320(6)
Hg(1)–O(2)	2.828(5)					
Hg(1)–N(1)	2.949(6)	Hg(1)–N(1)	2.896(15)	2.830(15)	2.832(16)	2.862(18)
Hg(1)–N(2)	2.759(6)	Hg(1)–N(2)	2.733(17)	2.902(15)	2.973(14)	2.777(16)
Hg(1)–O(1′)	2.884(5)					
C(13)–O(1)	1.254(9)					
C(13)–O(2)	1.220(10)					
C(1)–Hg(1)–O(1)	178.3(2)	C(1)–Hg(1)–Cl(1)	179.4(6)	176.7(5)	177.3(5)	178.8(5)
C(1)–Hg(1)–O(2)	131.6(2)					
C(1)–Hg(1)–N(1)	71.4(2)	C(1)–Hg(1)–N(1)	71.2(6)	72.4(6)	72.2(6)	71.3(6)
C(1)–Hg(1)–N(2)	74.0(2)	C(1)–Hg(1)–N(2)	75.0(6)	69.9(6)	70.6(6)	73.7(6)
N(1)–Hg(1)–N(2)	145.31(16)	N(1)–Hg(1)–N(2)	132.6(5)	121.4(5)	123.6(5)	131.6(5)
N(1)–Hg(1)–O(1)	107.54(19)	N(1)–Hg(1)–Cl(1)	109.3(3)	109.9(3)	108.8(3)	109.5(4)
N(1)–Hg(1)–O(2)	110.99(17)					
N(2)–Hg(1)–O(1)	107.12(19)	N(2)–Hg(1)–Cl(1)	104.4(4)	110.3(3)	110.4(3)	106.2(4)
N(2)–Hg(1)–O(2)	90.58(17)					
O(1)–Hg(1)–O(2)	49.85(18)					
Hg(1)–O(1)–C(13)	111.5(5)					
Hg(1)–O(2)–C(13)	75.6(4)					
O(1)–C(13)–O(2)	123.1(7)					

[a] All atoms are designated as E(xA), E(xB), E(xC) and E(xD) for independent molecules **2A**, **2B**, **2C** and **2D**, respectively;
[b] Symmetry equivalent atoms (*1–x, 2–y, –z*) are given by "prime".

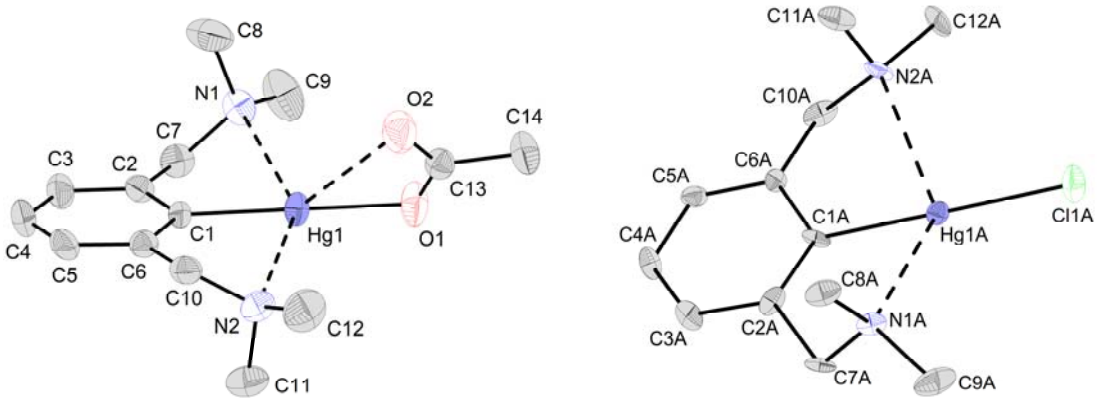


Fig. 1 – ORTEP representation at 30% probability and atom numbering scheme for the isomer $pR_{N(1)}$-$pR_{N(2)}$ in the crystal of [2,6-$(Me_2NCH_2)_2C_6H_3$]Hg(OAc) (**1**) (*left*), and of isomer $pS_{N(1)}$, $pR_{N(2)}$ in the crystal of [2,6-$(Me_2NCH_2)_2C_6H_3$]HgCl (**2**) (*right*). Hydrogen atoms are omitted for clarity.

DISCUSSION

The main disadvantage of the direct mercuration of an aromatic substrate is the potential result of polymercurated species in addition to the desired monomercurated compound.[31] The problem can be usually controlled by using the appropriate mercurating agent, the solvent, the temperature,[31c] or by using appropriate directing substituents grafted on the aromatic ring as are the pendant arms with potential donor atoms. The two-step method of synthesis of the chloride **2** *via* direct mercuration of the 1,3-$(Me_2NCH_2)_2C_6H_4$ proligand and acetate / chloride exchange is a valuable alternative for the preparation of this organomercury(II) compound. A similar procedure was reported previously for the synthesis of related (*NCN*)HgCl.[30] The alternative reported method for the synthesis of **2** required the reaction of $HgCl_2$ with an *in situ* prepared organolithium intermediate, [2,6-$(Me_2NCH_2)_2C_6H_3$]Li, from *n*-BuLi and either 1,3-$(Me_2NCH_2)_2C_6H_4$,[32] or 1-Br-2,6-$(Me_2NCH_2)_2C_6H_3$.[29a] In both these last strategies difficulties can arise in controlling the lithiation of the *NC(H)N* pincer proligand due to lithiated side-products,[26] or impurification with the related bromide, [2,6-$(Me_2NCH_2)_2C_6H_3$]HgBr, due to halogen exchange promoted by the residual LiBr available in the reaction mixture.[33] A proof that such halogen exchange reaction can take place is the reported single-crystal X-ray structure of the mixed-halide species [2,6-$(Me_2NCH_2)_2C_6H_3$]HgX (X = Cl/Br).[33]

Solution behaviour

The $^{199}Hg\{^1H\}$ NMR spectra for compounds **1** and **2** show one singlet resonance (δ_{Hg} –1229.5 and –934.1 ppm, in $CDCl_3$, respectively) thus indicating the presence of only one organomercury(II) species in solution, at room temperature. The magnitude of the chemical ^{199}Hg chemical shifts for acetate **1** and chloride **2** are similar to those observed for the related *N,C,N*-pincer ligand-containing compounds [2,6-$\{O(CH_2CH_2)_2NCH_2\}_2C_6H_3$]HgX: δ_{Hg} –1200 ppm for X = OAc, and δ_{Hg} –912 ppm for X = Cl, in $CDCl_3$, respectively.[30a]

The ^1H and $^{13}C\{^1H\}$ NMR spectra of compounds **1** and **2** are very similar. In the aliphatic region one set of singlet resonances are present for proton and carbon nuclei of the CH_2 and NMe_2 of both pendant arms of the pincer ligand attached to mercury atom, *i.e.* δ_H 2.25 and 3.36 ppm, and δ_C 44.98 and 66.15 ppm for acetate **1** *vs* δ_H 2.26 and 3.98 ppm, and δ_C 44.83 and 65.97 ppm for chloride **2**. This is consistent with equivalence of the two pendant arms per pincer ligand unit and suggests either the absence of intramolecular N→Hg coordination of both nitrogen to the metal center or with a fast conformational change of the chelate five-membered HgC_3N rings [assuming a planar (*N,C,N*)HgX core] in solution, thus yielding averaged NMR resonances. The $^{13}C\{^1H\}$ NMR spectra show in the aromatic region the expected resonances for all six carbon atoms of the aromatic ring; for **1** an additional signal was observed at δ_C 176.87 ppm for the carboxylic carbon atom.

Solid state structure

Common features for both compounds **1** and **2** are (*i*) the almost co-linear arrangement of the covalent bonds at the mercury atom [bond angles:

C–Hg–O 178.3(2)° for **1**, and C–Hg–Cl 179.4(6) / 176.7(5)° for molecules **2A** / **2B**], and (*ii*) the fact that the 2,6-$(Me_2NCH_2)_2C_6H_3$ substituent acts as an *N*,*C*,*N*-pincer ligand, *i.e.* the metal center is strongly intramolecular coordinated by both nitrogen atoms from the pendant arms [c.f. the sum of the covalent and van der Waals radii of the corresponding atoms: Σr_{cov}(Hg,N) 2.14 Å;[34] Σr_{vdW}(Hg,N) 4.11 Å[35]]. The N–Hg interactions per metal atom are of different lengths, *i.e.* Hg(1)–N(1) / Hg(1)–N(2) 2.949(6) / 2.759(6) Å in **1**, 2.896(15) / 2.733(17) Å in **2A**, and 2.830(15) / 2.902(15) Å in **2B**. These values are in the range reported for other related compounds containing sp^3 hybridized nitrogen as donor atom for mercury, *i.e.* the mixed-halide species [2,6-$(Me_2NCH_2)_2C_6H_3$]HgX (X = Cl/Br) [Hg–N 2.764(7) / 2.867(6) Å] or [2,6-$\{O(CH_2CH_2)_2NCH_2\}_2C_6H_3$]HgX [Hg–N 2.787(6) / 2.858(6) for X = OAc, and 2.840(6) / 2.877(5) Å for X = Cl].[30a] However, there is also a major difference between the molecules of compounds **1** and **2** regarding the positions of the nitrogens coordinated to mercury atom: while in **1** the two nitrogen atoms of the pincer ligand are placed on opposite sides of the planar ArHgX system (defined subsequently as C_6HgX, X = O, Cl) [atom deviations from best C_6HgX plane: N(1) –0.84 Å, N(2) 0.72 Å], for all independent molecules of **2** they are placed on the same side of the planar ArHgX system [atom deviations from best C_6HgX plane: N(1) / N(2) 0.82 / 0.72 Å for **2A**, 0.95 / 1.10 Å for **2B**, –0.88 / –1.11 Å for **2C**, –0.79 / –0.75 Å for **2D**]. The resulted N_2CHgX coordination cores are thus different, *i.e.* square planar for the molecule of **1**, with a distortion mainly due to the constraints imposed by the coordinated amine arms [N(1)–Hg(1)–N(2) 145.31(16)°], and distorted "see-saw" for the molecules of **2** [N(1)–Hg(1)–N(2) 132.6(5), 121.4(5), 123.6(5) and 131.6(5)° for **2A** to **2D**, respectively, and C(1)−Hg(1)−N angles in the range 69.9(6)-75.0(6)°].

The acetate ligand exhibits a strong anisobidentate, chelate pattern in the molecule of **1** [Hg(1)–O(1) 2.072(4) Å, Hg(1)–O(2) 2.828(5) Å; c.f. the sum of the covalent and van der Waals radii of the corresponding atoms: Σr_{cov}(Hg,O) 2.10 Å;[34] Σr_{vdW}(Hg,O) 3.95 Å[35]], with an acute O(1)–Hg(1)–O(2) angle of 49.85(18)°. This is, at the limit, consistent with monodentate pattern of the acetate ligand suggested by the solid state infrared data.[36]

The five-membered HgC_3N rings are non-planar, with the nitrogen atom displaced out of the best plane defined by the HgC_3 system; this induces planar chirality (with the aromatic ring and the nitrogen atom as chiral plane and pilot atom, respectively).[37] As result both compounds crystallize as racemates, *i.e.* 1:1 mixtures of $pR_{N(1)}$, $pR_{N(2)}$ / $pS_{N(1)}$, $pS_{N(2)}$ isomers for **1**, and pairs of $pR_{N(1)}$, $pS_{N(2)}$ / $pS_{N(1)}$, $pR_{N(2)}$ isomers for each of the independent molecules of **2**, respectively (with respect to the two chelate rings in a molecular unit).

In the crystal of **1** dimer associations between pairs of isomers $pR_{N(1)}$, $pR_{N(2)}$ and $pS_{N(1)}$, $pS_{N(2)}$ are formed through acetate groups acting as bimetallic triconnective ligands (Fig. 2), the oxygen atom in *trans* to the carbon in the linear C–Hg–O unit within a molecule being involved in a strongly asymmetric intermolecular Hg–O···Hg bridge [Hg(1)–O(1) 2.072(4) Å, Hg(1′)···O(1) 2.884(5) Å]. Continuous shape measures (CShM) analysis of **2**, carried out with SHAPE, indicate a coordination geometry around the mercury atom of distorted trigonal prism (CShM = 12.65; for an ideal TPR-6, CShM = 0).[38]

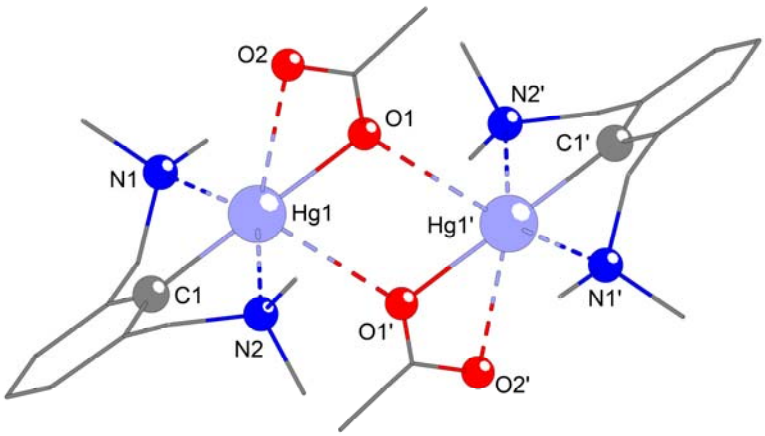


Fig. 2 – View of the dimer associations between isomers $pR_{N(1)}$-$pR_{N(2)}$ and $pS_{N(1a)}$-$pS_{N(2a)}$ in the crystal of **1**, built through intermolecular Hg···O interactions [symmetry equivalent atoms (*1–x, 2–y, –z*) are given by "prime"]. Hydrogen atoms are omitted for clarity.

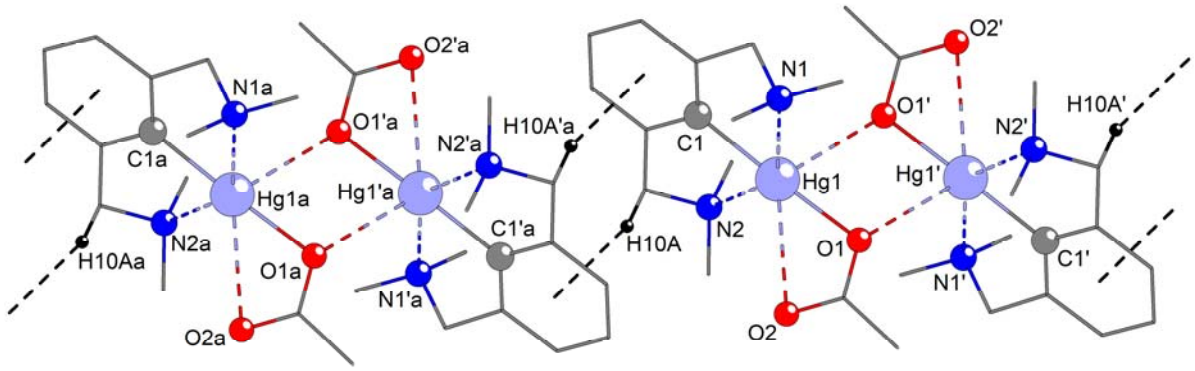


Fig. 3 – View along *b* axis of a fragment of the chain polymer association of dimers based on intermolecular C–$H_{methylene}$···π ($Ar_{centroid}$) interactions in the crystal of **1** (only hydrogens involved in intermolecular contacts are shown) [symmetry equivalent atoms (*1–x, 2–y, –z*), (*–1+x, y, z*) and (*–x, 2–y, –z*) are given by "prime", "a" and "prime a", respectively].

Further inter-dimer C–$H_{methylene}$···π ($Ar_{centroid}$) interactions [C(10)–H(10A)···Ar{C(1′a)-C(6′a)} 2.74 Å; γ = 7.4º; *i.e.* H···$Ar_{centroid}$ contacts shorter than 3.1 Å, with an angle γ between the normal to the aromatic ring and the line defined by the H atom and $Ar_{centroid}$ smaller than 30°][39] connect in a "*head-to-tail*" fashion the dimers of **1** into a supramolecular polymer chain (Fig. 3).

A closer check of the crystal of the chloride **2** reveals the fact that two types of dimers are formed between different independent molecules. Thus, isomers $pS_{N(1)}$, $pR_{N(2)}$-**2A** and $pR_{N(1)}$, $pS_{N(2)}$-**2D** (as well as isomers $pR_{N(1)}$, $pS_{N(2)}$-**2A** and $pS_{N(1)}$, $pR_{N(2)}$-**2D**) are connected through two C–$H_{methylene}$···π ($Ar_{centroid}$) interactions [C(7A)–H(7AB)···Ar{C(1D)-C(6D)} 2.85 Å and γ = 24.0º; C(10D)–H(10DA)···Ar{C(1A)-C(6D)} 2.97 Å and γ = 27.1º]. In addition, a metalophilic Hg···Hg interaction[40] supports this supramolecular dimer association (Figure 4, left) [Hg(1A)···Hg(1D) 3.5007(11) Å; c.f. the sum of the van der Waals radii for two mercury atoms, Σr_{vdW}(Hg,Hg) 4.90 Å[35]]. A similar intermolecular d^{10}···d^{10} metal interaction was previously reported to be present in the crystal of the mixed-halide species [2,6-(Me_2NCH_2)$_2C_6H_3$]HgX (X = Cl/Br) [Hg···Hg 3.6153(3) Å].[33] The other type of dimer is established between isomers $pR_{N(1)}$-$pS_{N(2)}$-**2B** and $pR_{N(1)}$, $pS_{N(2)}$-**2C** (as well as between $pS_{N(1)}$, $pR_{N(2)}$-**2B** and $pS_{N(1)}$, $pR_{N(2)}$-**2C**, respectively) through only one intermolecular C–H_{methyl}···π ($Ar_{centroid}$) interaction [C(8B)–H(8BC)···Ar{C(1C)-C(6C)} 3.04 Å, γ = 2.2º] (Figure 4, right). Except the above mentioned mercurophilic interaction between molecules **2A** and **2D**, no other intermolecular distances shorter than the sum of the van der Waals radii of the corresponding heavy atoms are present in the crystal of **2**.

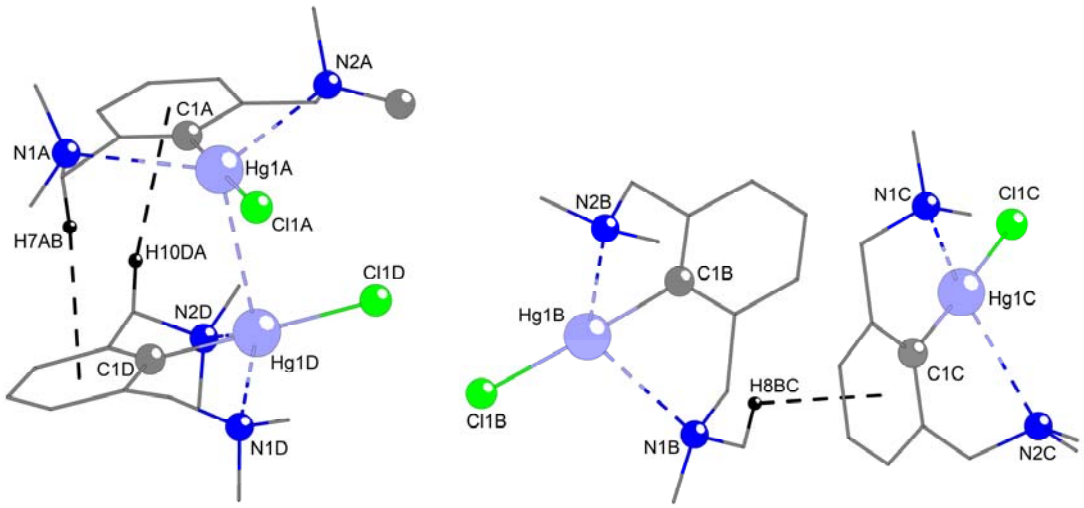


Fig. 4 – View of associations in the crystal of **2**, *i.e.* dimer built from isomers $pS_{N(1)}$, $pR_{N(2)}$-**2A** and $pR_{N(1)}$, $pS_{N(2)}$-**2D** through intermolecular metalophilic Hg···Hg and C–$H_{methylene}$···π ($Ar_{centroid}$) interactions (*left*), and dimer built from isomers $pR_{N(1)}$, $pS_{N(2)}$-**2B** and $pR_{N(1)}$, $pS_{N(2)}$-**2C** through intermolecular C–H_{methyl}···π ($Ar_{centroid}$) interactions (*right*) (only hydrogens involved in intermolecular contacts are shown).

The chloride **2** was previously reported as a transmetallating agent when stirred with $Pd(OAc)_2$ in CH_2Cl_2, for 24 h, to produce in 55% yield the organopalladium(II) species, [{2,6-$(Me_2NCH_2)_2C_6H_3$}Pd(OAc)], which was characterized by NMR in $CDCl_3$.[29a] The synthesis of the same compound was achieved by reacting the corresponding organopalladium(II) bromide with AgOAc.[41] In an experiment carried out at NMR level, $Pd(OAc)_2$ and **2** were mixed in a 1:1 molar ratio, in $CDCl_3$, in open atmosphere. Sonication of the reaction mixture for 5 min produced a bright yellow solution, thus suggesting an instant reaction. The ^{1}H NMR spectrum recorded immediately indicated a conversion of cca. 80% (based on ^{1}H NMR integrals). The ^{1}H and $^{13}C\{^1H\}$ NMR spectra obtained after 5 hr using this crude solution indicated the quantitative formation of the expected [{2,6-$(Me_2NCH_2)_2C_6H_3$}Pd(OAc)]. The formation of ClHg(OAc) as transmetallation reaction product was confirmed by extra peaks observed in both ^{1}H (δ_H 2.25 ppm for methyl protons) and $^{13}C\{^1H\}$ [δ_C 22.51 and 179.55 ppm for methyl and carboxylate carbons, respectively] NMR spectra of this crude solution.

EXPERIMENTAL

The reactions were performed under argon, while the work-up of the crude reaction mixtures were carried out in open atmosphere, using freshly distilled solvents. Starting materials such as $Hg(OAc)_2$, $Pd(OAc)_2$ and anhydrous LiCl were purchased from commercial sources (Alfa Aesar or Fluorochem LTD) and used as supplied. The diamine 1,3-$(Me_2NCH_2)_2C_6H_4$ was obtained according to a published method.[42] Multinuclear NMR (^{1}H, ^{13}C, ^{199}Hg) spectra as well as 2D NMR spectra were recorded at room temperature on a BRUKER Avance III 400 instrument, using solutions in $CDCl_3$. The ^{1}H chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent ($CHCl_3$, 7.26 ppm), while the ^{13}C chemical shifts are reported in δ units (ppm) relative to the peak of the deuterated solvent ($CDCl_3$, 77.16 ppm).[43] The ^{1}H and ^{13}C resonances were assigned using 2D NMR experiments (COSY, HSQC, HMBC). The ^{199}Hg chemical shifts are reported in δ units (ppm) relative to Me_2Hg (0 ppm). The NMR spectra were processed using the *MestReNova* software.[44] The MS/HRMS APCI(+) spectra were recorded on a Thermo Scientific Orbitrap XL mass spectrometer equipped with a standard ESI/APCI source. Data analysis and calculations of the theoretical isotopic patterns were carried out with the *Xcalibur* software package.[45] ATR-FTIR spectra were recorded on a Jasco FTIR-610 spectrometer, equipped with ATR module with a horizontal ZnSe crystal (Jasco PRO400S). The resolution of the spectra was 4 cm^{-1} and scans were repeated 100 times. The melting points were measured with an Electrothermal 9200 apparatus and are not corrected.

Synthesis of [2,6-$(Me_2NCH_2)_2C_6H_3$]Hg(OAc) (**1**)

A mixture of $Hg(OAc)_2$ (0.478 g, 1.5 mmol) and 1,3-$(Me_2NCH_2)_2C_6H_4$ (0.288 g, 1.5 mmol) was introduced in a 50 mL flask. After evacuating and refilling with argon (3 times) the reaction flask, 30 mL EtOH were added and the obtained solution was stirred for 30 min, at room temperature. Then the reaction mixture was filtered off and the solvent was removed under vacuum. The remaining product was extracted with 2 × 10 mL CH_2Cl_2, the unified organic phase was washed with 3 × 15 mL H_2O, then dried over anhydrous Na_2SO_4. The oily solid remaining after the chlorinated solvent evaporation was extracted with small portions of pentane (5 × 5 mL). After removal of the solvent under vacuum, the title compound **1** was obtained as a white solid. Yield: 0.34 (50%). M.p. = 86-87 °C. IR (ATR, υ, cm^{-1}): 3041 (w), 2974 (w), 2943 (w), 2856 (w), 2819 (m), 2773 (m), 1630 (vs), 1446 (m), 1358 (s), 1298 (vs), 1205 (w), 1176 (w), 1151 (w), 1099 (w), 1028 (vs), 949 (w), 922 (w), 852 (vs), 777 (vs), 719 (w), 687 (vs), 619 (w), 540 (w). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.11 [s, 3H, OC(O)CH_3], 2.25 [s, 12H, N(CH_3)$_2$], 3.36 (s, 4H, –CH_2–), 7.05 (d, 2H, H-3, C_6H_3, $^3J_{HH}$ = 7.3 Hz), 7.14 (m, 1H, H-4, C_6H_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.62 MHz): δ 23.49 [s, OC(O)CH_3], 44.98 [s, N(CH_3)$_2$], 66.15 (s, –CH_2–, $^3J_{HgC}$ = 120.9 Hz), 128.04 (s, C-3, $^3J_{HgC}$ = 185.5 Hz), 128.26 (s, C-4), 144.76 (s, C-2), 145.79 (s, C-1), 176.87 [s, OC(O)CH_3]. $^{199}Hg\{^1H\}$ NMR ($CDCl_3$, 71.61 MHz): δ –1229.5 (s). MS (APCI+, MeCN), *m/z* (relative intensity, %): 189.14 (27) $[M-HgOAc-2H]^+$, 191.15 (38) $[M-HgOAc]^+$, 451.13 (26) $[M-H]^+$, 515.21 (100) $[M+2MeOH-H]^+$. HRMS (APCI+, MeCN), *m/z*: $[M-H]^+$ calcd. for $C_{14}H_{21}HgN_2O_2$ 451.13038. Found, 451.13262.

Synthesis of [2,6-$(Me_2NCH_2)_2C_6H_3$)HgCl (**2**)

In a 25 mL flask a solution of an excess of anhydrous LiCl (0.042 g, 1 mmol) in 10 mL MeOH was added to **1** (0.217 g, 0.48 mmol), under argon. After stirring overnight, at room temperature, the solvent was removed under vacuum. The solid was extracted with 3 × 5 mL CH_2Cl_2, the unified organic phase was filtered on glassfiber, then the solvent was evaporated and the resulting slightly yellow solid was dried in vacuum to give **2**. Yield: 0.176 (86%). M.p. = 89-90 °C. IR (ATR, υ, cm^{-1}): 2979 (w), 2943 (m), 2856 (m), 2816 (s), 2771 (s), 1448 (s), 1360 (s), 1259 (m), 1209 (w), 1174 (s), 1147 (m), 1093 (m), 1024 (vs), 951 (w), 904 (w), 845 (vs), 798 (s), 764 (s), 714 (w), 640 (w), 530 (w). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.26 [s, 12H, N(CH_3)$_2$], 3.98 (s, 4H, –CH_2–), 7.07 (d, 2H, H-3, C_6H_3, $^3J_{HH}$ = 7.3 Hz), 7.15 (t, 1H, H-4, C_6H_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.62 MHz): δ 44.83 [s, N(CH_3)$_2$], 65.97 (s, –CH_2–, $^3J_{HgC}$ = 116.0 Hz), 128.06 (s, C-3, $^3J_{HgC}$ = 177.8 Hz), 128.33 (s, C-4), 144.89 (s, C-2), 151.06 (s, C-1). $^{199}Hg\{^1H\}$ NMR ($CDCl_3$, 71.61 MHz): δ –934.1 (s). MS (APCI+, MeCN), *m/z* (relative intensity, %): 191.15 (100) $[M-HgCl]^+$, 429.10 (100) $[M+H]^+$. HRMS (APCI+, MeCN), *m/z*: $[M-H]^+$ calcd. for $C_{12}H_{20}ClHgN_2$ 429.10158. Found, 429.10278.

*Reaction of [2,6-$(Me_2NCH_2)_2C_6H_3$)HgCl (**2**) with $Pd(OAc)_2$ (NMR tube experiment)*

A 5 mm NMR tube was charged with chloride **2** (9.5 mg, 0.0222 mmol), $Pd(OAc)_2$ (5 mg, 0.0222 mmol) and 0.5 mL $CDCl_3$, in open atmosphere. The obtained reaction mixture was sonicated for 5 min, when a bright yellow solution was obtained. The NMR analysis was performed on this solution

without further processing and provided evidences for the quantitative formation of [{2,6-$(Me_2NCH_2)_2C_6H_3$}Pd(OAc)]. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.17 [s, 3H, OC(O)CH_3], 2.88 [s, 12H, N(CH_3)$_2$], 4.00 (s, 4H, –CH_2–), 6.79 (d, 2H, H-3, C_6H_3, $^3J_{HH}$ = 7.5 Hz), 7.00 (t, 1H, H-4, C_6H_3, $^3J_{HH}$ = 7.5 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.62 MHz): δ 23.25 [s, OC(O)CH_3], 52.52 [s, N(CH_3)$_2$], 73.99 (s, –CH_2–), 120.03 (s, C-3), 125.12 (s, C-4), 144.94 (s, C-2), 153.39 (s, C-1), 177.82 [s, OC(O)CH_3].

Crystal structure determination

Single crystals of **1** and **2** were obtained by slow evaporation of the solvent from solutions of **1** in pentane and **2** in Et_2O, in open atmosphere. The details of the crystal structure determination and refinement are given in Table 2. Crystallographic measurements were carried out with Rigaku Oxford-Diffraction XCALIBUR E CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The unit cell determination and data integration were carried out using the CrysAlis package of Oxford Diffraction[46] and the structures were solved by direct methods using Olex2 software[47] with the SHELXT structure solution program and refined by full-matrix least-squares on F^2 with SHELXL-2015.[48] Atomic displacements for non-hydrogen atoms were refined using an anisotropic model. Hydrogen atoms have been placed in fixed, idealized positions accounting for the hybridization of the supporting atoms. The drawings were created with the Diamond program.[49]

CONCLUSIONS

The new acetate [2,6-$(Me_2NCH_2)_2C_6H_3$]Hg(OAc) (**1**) was obtained by direct mercuration of the aromatic proligand. This *N,C,N*-pincer ligand-containing organomercury(II) species proved to be a valuable intermediate in the preparation of the corresponding chloride **2** which can be used as transmetallation agent to achieve the palladation of 1,3-$(Me_2NCH_2)_2C_6H_4$ at C2 position. Both compounds **1** and **2** were characterized by solution multinuclear (^{1}H, ^{13}C and ^{199}Hg) NMR spectroscopy and their molecular structures were established by single-crystal X-ray diffraction. Dimeric associations based on bridging acetate ligand or intermolecular C–$H_{aliphatic}$···π ($Ar_{centroid}$) and metalophilic Hg···Hg interactions were evidenced in their crystals. Preliminary data obtained at NMR experiment level indicated that using sonication of the reaction mixture of **2** and $Pd(OAc)_2$ (1:1 molar ratio) a quantitative transmetallation of the *N,C,N*-pincer ligand from chloride **2** to palladium was achieved with formation of [{2,6-$(Me_2NCH_2)_2C_6H_3$}Pd(OAc)].

Table 2

Crystallographic data for RHg(OAc) (**1**) and RHgCl (**2**) [R = 2,6-$(Me_2NCH_2)_2C_6H_3$]

	1	**2**
Molecular formula	$C_{14}H_{22}HgN_2O_2$	$C_{12}H_{19}ClHgN_2$
M	450.92	427.33
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$Pca2_1$
Temperature (K)	293(2)	293(2)
a/Å	11.1848(6)	17.9910(8)
b/Å	12.8525(9)	9.4033(5)
c/ Å	11.4776(10)	34.5569(17)
α/°	90	90
β/°	92.533(6)	90
γ/°	90	90
V/Å^3	1648.3(2)	5846.2(5)
Z	4	16
D_{calc}/gcm^{-3}	1.817	1.942
F(000)	864	3232
μ(Mo-Kα)/mm^{-1}	9.338	10.692
Crystal size (mm^3)	0.35 × 0.20 × 0.20	0.35 × 0.35 × 0.25
θ range for data collection (°)	2.415 to 28.277	2.166 to 25.027
Reflections collected	8996	23141
Independent reflections	4078 [R_{int} = 0.0435]	10195 [R_{int} = 0.0726]
Absorption correction	Multi-Scan[50]	Multi-Scan[50]
Data / restraints / parameters	4078 / 0 / 177	10195 / 43 / 593
Goodness-of-fit on F^2	1.022	0.962
Final *R* indices [I>2σ(I)]	R_1 = 0.0479	R_1 = 0.0502
	wR_2 = 0.0662	wR_2 = 0.0690
R indices (all data)	R_1 = 0.0858	R_1 = 0.0672
	wR_2 = 0.0780	wR_2 = 0.0737
Largest difference peak and hole (e Å^{-3})	1.071 and –1.215	1.325 and –1.982
Flack parameter		–0.003(9)

Supplementary material

Crystallographic data for the structural analysis of compounds **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre [CCDC no. 2045104 (**1**) and 2045103 (**2**)]. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http:// www.ccdc.cam.ac.uk).

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