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COMMUNICATION

The first solid phase synthesis of pincer palladium complexes†

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Both dimeric μ-chlorine bridged and monomeric bidentate Pd(II) complexes with *SCN* hybrid pincer-type ligands, bearing thiophosphoryl group and imine moiety of the benzothiazole ring as coordination arms, formed in the reaction with $(PhCN)_2PdCl_2$ under kinetic control (20 °C, dichloromethane solution) were readily converted into the corresponding *SCN* pincer complexes *via* solid phase synthesis (neat, 200 °C, 15 min). The synthesis of pincer complexes can be performed also by heating (200 °C, 5 min) of a homogeneous mixture of the initial reactants, namely, the ligand and $(PhCN)_2PdCl_2$, obtained by manual grinding in a mortar. The efficacy of solid phase approaches is comparable with the analogous synthesis in solutions under severe conditions.

Synthesis and reactivity studies in organometallic chemistry have traditionally been carried out in a solvent (so-called homogeneous solution chemistry), although chemistry in matrices (at low temperature),[1] at interfaces (*e.g.*, heterogeneous catalysis)[2] or reactions in the gas phase[3] have also been described without emphasis on their synthetic potential. From the 1990s, promoted in some respects by interest in the supported heterogeneous catalysts, the development of solid phase synthetic organometallic chemistry can be observed. However, this area has been mostly focused on the advantages of performing organometallic reactions, more precisely, on transition-metal catalyzed reactions encompassing more than cross-couplings, on a solid phase,[4] for example for generation of product libraries on polymer-bound substrates. The reactions *in the solid state* for the direct synthesis of metal complexes in the absence of a solvent has been less mentioned in the literature as the range of organometallic complexes that will react or undergo rearrangement in the solid state is complicated by solid state kinetics and limited by the physical properties of a particular complex which can melt or decompose prior to undergoing any reaction. Nevertheless, this new area of organometallic chemistry has already revealed that high yield syntheses of complexes featuring diverse structures, metal ions, ligand types and dimensionalities are possible in the solid state sometimes exceeding those available by solution routes.[5,6] The syntheses in the solid state are mainly performed under heating (rarely using the microwave assistance[7,8]) or can be promoted by mechanochemistry means,[6,9], *i.e.*, by grinding of solid reactants which often results in the formation of a liquid phase,[10] and the last approach is especially advantageous for the synthesis of polymetallic species.[11]

Cyclometallations, *i.e.*, reactions in which an organic molecule is coordinated to a metal *via* an aromatic or aliphatic carbon that has lost a hydrogen atom and a second donor atom to form a chelate ring, were also performed in a solid state. Indeed, Shaw *et al.* described *O*- and *C*-metallation on heating of platinum(II) dichloride complexes with 2-alkoxyphenylphosphines[12] as well as *C*-platination in the 8- (peri-) position of naphthyl group of $[Pt(X)_2\{PMe_2(1\text{-naphthyl})\}_2]$ (X=Cl, I, Me) complexes and their arsine analogues[13] as early as 1970s. The subsequent examples comprise thermal induced cyclometallations of few other $MCl_2(L)_2$ (M = Pd,Pt)[8,14–16] and $Pd(OAc)_2L_2$[17] complexes as well as solid phase orthometallation of coordinated triphenylphosphine in coordinatively unsaturated iridium[18] and platinum[19] species. Furthermore, in a few cases cyclometallations were carried out on an inert support such as SiO_2 or Al_2O_3 under rather mild conditions.[20–23]

In this communication we report for the first time on the possibility of easy construction of the palladium pincer complexes *via the solid-state* thermal synthesis starting either from their dimeric μ-chlorine or monomeric bidentate precursors or from the homogenous mixture of the ligand and $PdCl_2(PhCN)_2$.

Our group's research has been focused on the elaboration of synthetic approaches to Pd(II) and Pt(II) hybrid pincer systems with *SCY* (*Y* = *S′*, *N*) organothiophosphorus ligands which possess high catalytic activity for the cross-couplings and luminescence properties.[24] In contrast to their symmetric counterparts these novel ligands bearing thiophosphoryl groups with different donor properties (*e.g.*, phosphine sulfide and thiophosphoryloxy) or their combination with other donor functionalities such as thiocarbamide or imino moiety, readily undergo direct cyclopalladation in solutions reacting with $PdCl_2(PhCN)_2$ under very mild conditions[25] (DCM, benzene or MeCN; room temperature, from few minutes to a couple of days) providing the corresponding 5,5- or 5,6-membered pincer products in high (up to 95%) isolated yields. At the same time, if imine functionality was incorporated into the benzothiazole heterocycle,[26] direct cyclopalladation of the

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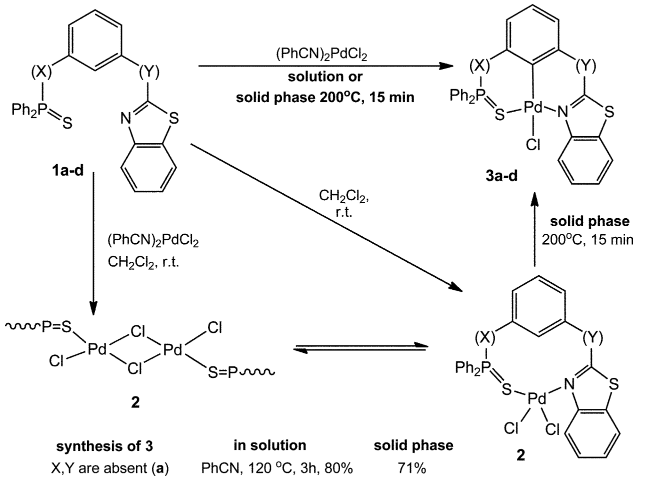
† Electronic supplementary information (ESI) available: A detailed description of the IR and Raman spectral data for ligands **1a–d**, intermediate complexes **2a–d** and the final pincer products **3a–d**, the MALDI mass spectra of complexes **2a–d**, **3a–d**, and X-ray diffraction patterns for **2b**,**3a**,**3c**. See DOI: 10.1039/c1dt10680e

corresponding *SCN* ligands **1a–d** bearing thiophosphoryl group and imine moiety of the benzothiazole ring as coordination arms bound either directly to the central benzene core or attached to the latter one *via* -O- or -NH- linkers, required rather severe conditions, *i.e.*, prolonged reaction times and elevated temperatures (Scheme 1). The structures of the complexes obtained were unambiguously confirmed by multinuclear NMR spectroscopy as well as the single crystal X-ray diffraction study.[26]



synthesis of 3	in solution	solid phase
X,Y are absent (**a**)	PhCN, 120 °C, 3h, 80%	71%
X is absent, Y = O (**b**)	PhCN, 120 °C, 1h, 60%	60%
X=O, Y is absent (**c**)	PhCN, 120 °C, 2h, 75%	70%
X=NH, Y is absent (**d**)	CH_3CN, reflux, 2h, 89%	51%

Scheme 1 Solution and solid phase synthesis of 5,5- and 5,6-membered κ^3-*SCN* hybrid pincer Pd complexes.

Surprisingly, similar reactions of **1a–d** with the same metal precursor performed at room temperature (DCM or MeCN solution) rapidly led to the formation of the other complexes **2a–d**[27] of ML composition (*i.e.*, $LPdCl_2$) according to the C, H, N microanalysis data, which were isolated as dark-beige solids in 86–99% yields. The decomposition of **2a–d** in coordinating solvents such as DMSO or pyridine with deliberation of the corresponding free ligand **1a–d**, easily detected by ^{31}P and ^1H NMR spectroscopy, indicates that no cyclometallation occurred in these cases.

In general, the above reaction could afford either dimeric μ-chlorine complexes or those with a bidentate coordination mode and elemental analysis data fit well both type of the structures. Note that the complex with bidentate coordination may be generated either directly from the reactants or as a result of dynamic transformations of the μ-Cl-bridged complexes in solutions.

The IR and Raman spectra of **2a–d** showing a lower ($\Delta\nu \sim 30$ cm^{-1}) frequency shift of the absorption band corresponding to ν(P=S) vibrations compared to those of the free ligands unambiguously confirm Pd–S=P coordination in all cases (Table S1, Figs.1S–12S†). According to the results of the normal coordinate analysis (NCA) performed for model molecules of **2a**, **3a**, and **3b** (simplified by the substitution of phenyl for methyl group at the phosphorus atom), the bands at ~ 300 and ~330 cm^{-1} correspond to symmetrical and unsymmetrical modes of ν(Pd–S) and ν(Pd–Cl) stretches, respectively. Based on the insignificant changes of the C=N and CH (760–680 cm^{-1} region) vibrations of the benzothiazole moiety in the spectrum of **2a,b** compared to that of the free ligands, these complexes were assigned to a dimeric μ-chlorine structure in which both molecules of the ligand serve as *S*-monodentate ones (coordination *via* P=S group only). The presence of two bands of Pd–Cl vibrations in the IR and Raman spectra of **2a,b** obviously indicates that they have a *trans*-structure.[28] The solid ^{31}P NMR for the complex **2b** has revealed a single signal at 48 ppm confirming the above supposition.

For complexes **2c,d**, in which the phosphorus atom is attached to the central benzene core *via* additional -O- or -NH- linker, the mixed vibrations with significant contribution from ν(C=N) stretch shifted to 1480(IR)/1485(Raman) and 1481(IR)/1491(Raman) cm^{-1} in the spectra for **2c** and **2d**, respectively, indicate the coordination of Pd with the heterocyclic nitrogen atom as well. However, broadening of the lines and the presence of the shoulder bands in the range of the free C=N vibrations allowed suggesting that these complexes present a mixture of complexes belonging to two above mentioned types with domination of a monomeric structure with a bidentate coordination mode. More accurate assignment of the structures is difficult to perform as complexes **2a–c** are insoluble in common solvents (DCM, CH_3CN, CH_3NO_2) and liberate the free ligand in the case of coordinating solvents as mentioned above. In the case of soluble in MeCN complex **2d**, two singlets at *ca.* 65 and 59 ppm in ~2.5 : 1 ratio in the ^{31}P NMR spectrum, where the upfield shifts relative to the signal of the corresponding free ligand **1d** strongly indicate the coordination of NH–P=S group, may serve as evidence of an equilibrium mixture of μ-Cl-bridged and chelate complexes, respectively, existing in solution.

Unfortunately, the matrix-assisted laser desorption/ionization (MALDI-MS) mass spectrometry analysis of **2a–d** did not give an answer about their structure. The spectra have revealed (matrix-free mode) mostly the peaks corresponding to the cationic species of (L-2H)PdCl and (L-H)Pd, detected by MS as isotopomeric clusters of singly charged ions due to the presence of six abundant isotopes of palladium [^{102}Pd (1.02%), ^{104}Pd (11.14%), ^{105}Pd (22.33%), ^{106}Pd (27.33%), ^{108}Pd (26.46%), ^{110}Pd (11.72%)], stable ions $[L\text{-}H]^+$, and low-molecular ions formed due to the heterocycle break. The peaks of low intensity with higher molecular masses containing a number of chlorine atoms and lack of palladium were obviously formed *via* the concomitant ion-molecular reactions (See ESI). Application of an anthracene or dithranol matrix (Fig. 13*S*,14*S*) resulted in the formation of palladium-containing cationic complexes [(L-H)Pd] centered at *m/z* 532 (**2a**), 548 (**2b**, **2c**) and 547 (**2d**) (for ^{106}Pd). In the case of complexes **2c,d**, the spectra additionally demonstrated the formation of bimetallic species $[(L\text{-}H)_2Pd_2Cl]$ (ionic clusters centered at *m/z* 1132 (**2c**) and 1131 (**2d**)). Heavier ions of low intensity in the spectra of **2a,b** bearing one palladium atom and lack of chlorine ones may be tentatively assigned to the products of ion-molecular reactions, *e.g.*, $[(L\text{-}H)_2Pd]$ and $[(L\text{-}H)_2Pd+Ph_2PSO]$. The stable ion with *m/z* 227 in the case of spectra of **2a–d** (dithranol matrix) corresponds perfectly to the moiety $[PhPSOCl_2]^+$ formed due to the rupture of P–C, P–O or P–N bonds in the ligand and chlorination.

It should be noted that the MALDI-mass spectra of the pincer complexes **3a–d** (Fig. 15*S*,16*S*) showed mainly two palladium containing cationic complexes, *i.e.*, lighter ions centered at *m/z* 532 (**3a**), 548 (**3b,3c**) and 547 (**3d**) (for ^{106}Pd) and fit well the isotopic pattern calculated for [(L-H)Pd] which were observed in the MS spectra of complexes **2a–d**, and heavier species (ionic clusters centered at *m/z* 1101(**3a**), 1132 (**3b,3c**) and 1130

(**3d**)) corresponded to the bimetallic ions with Pd–Cl–Pd bond. Furthermore, the spectra of **3d** demonstrated the cluster at *m*/*z* 1097 corresponding to bimetallic ion [(L-H)$_2$Pd$_2$] (Fig. 15S†). The bimetallic complexes apparently were generated as a result of the association of the [M-Cl] cationic species with the corresponding neutral ones similar to the previously reported data.[29,30]

On heating (200 °C, 15 min) in the open test-tubes,[31] the neat samples of **2a–d**, independently from their structure, easily underwent thermally-induced solid-state cyclometallation and transformed to the corresponding pincer complexes **3a–d** with evolution of HCl (the latter was detected by a pH indicator).[32] A simple purification procedure (from the products of thermal decomposition of organic nature) provided the desired products **3a–d** in the isolated yields comparable with those obtained by the synthesis in solution (lower isolated yields in a few cases may be explained by partial solubility of the pincer complexes in the solvents used for recrystallization). According to the ^{31}P NMR data of the crude products (dissolved in DMSO), the cyclometallation in a solid state proceeds in the quantitative yield. Moreover, the IR spectra (KBr) of crude products before the use of any solvent are similar to those of pure pincer complexes **3a–d** excluding some broadening of the corresponding bands.

The solid-state transformations of the intermediate complexes **2a–d** into the corresponding pincer products **3a–d** were investigated by differential scanning calorimetry. The results are summarized in Table 1. In general, all the DSC traces demonstrated similar patterns consisting of two endotherms separated by one exotherm. Thus, the DSC showed a rather sharp endotherm at *ca.*210 °C for **2a,b** with the assumed μ-chlorine bridged structure which may correspond to the rupture of two bridged and one terminal Pd-Cl bonds as well as C–H bond of the central benzene core. In the case of complexes **2c,d** with a putative contribution of chelate bidentate structures, requiring for pincer formation only the rupture of Pd–Cl and C$_{core}$–H bond, the broad endotherm peaks were observed at temperature below 200 °C. Moreover, in the case of compound **2c** the endotherm observed had two maximums at ~175 and ~200 °C. The width of a peak is apparently affected by kinetic of the corresponding processes. The sharp exotherms revealed on further heating apparently correspond to cyclometallation step with generation of the direct Pd–C bond. The enthalpies of this transformation range from 30.5 J g^{-1} to 43.6 J g^{-1}. The last endotherms correspond to melting of the final pincer products and the data obtained fit well the corresponding DSC curves for the authentic complexes **3a,d** used as representative examples, despite the fact that the enthalpies of melting are higher for the pure crystalline pincer products. Furthermore, the DSC of pincer complexes **3a,3d** did not reveal any *endo* or *exo* peaks in the region below *ca.*300 °C and showed only the corresponding melting endotherms (Fig. 1, Table 2, entries 5,6). Thus, DSC proved to be a suitable method to follow the processes that take place on heating of the solid metallocomplexes.

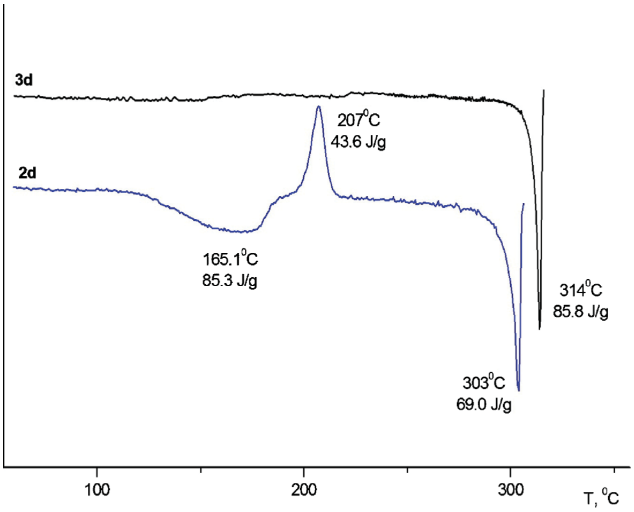


Fig. 1 DSC traces of intermediate mixed complex **2d** and the corresponding pincer product **3d**.

Interestingly, the X-ray powder diffraction patterns of the pincer products **3a,3c** obtained by a solid-phase procedure without additional manipulations correspond, with large sizes of coherently diffracting domains, to those calculated from the single crystal data of the same crystalline products which were obtained in solutions and specially grown up[26] (Fig. 17*S*) while the complex **3b** most likely crystallized in another polymorph modification.

Finally, we succeeded to perform the solid phase synthesis of **3a–d** *via* heating in open test-tube (200 °C, 15 min) of a homogeneous mixture of the initial reactants, namely, the corresponding ligand **1a–d** and (PhCN)$_2$PdCl$_2$, obtained by manual grinding in a mortar. In these cases the products were also formed in the yields close to the quantitative ones. Moreover, the manual grinding for 15 min has already provided the partial (*ca.*10%) transformation of intermediate complexes **2** to pincer products **3** as was demonstrated using the complex **2d** as a representative example. In other words, one may suppose that pincer complexes could be readily generated mechanochemically (*via* high-energy ball-milling) under the conditions as for example recommended for the Wittig reaction.[33] In addition, due to the above mentioned

Table 1 Summary of the DSC results (rate 5 °C min^{-1}, with a hole)

Entry	Complex	T_{max}, °C (–)	Enth. (J g^{-1})	T_{max}, °C (+)	Enth. (J g^{-1})	T_{max}, °C (–)	Enth. melt. (J g^{-1})
1	**2a**	211.0	92.9	228.0	30.5	320.6	20–60[a]
2	**2b**	211,1	123.1	246.5	37.9	301.6	20–60[a]
3	**2c**	171.4, 193.6	83.1	207.3	42.3	281.8	66.2
4	**2d**	165.1 (broad)	85.3	207.0	43.6	303.0	69.0
5	**3a**	—	—	—	—	297.3	67.4
6	**3d**		—	—	—	314.0	85.8

[a] Pincer products **3a,b** produced from **2a,b** in the course of the DCS runs were partially amorphous. The reproducibility of the corresponding enthalpies of melting were poor.

vague similarity of the MALDI mass spectra of **2a–d** and **3a–d** we suggested that the formation of pincer complexes from their precursors might proceed in the gas phase as well.

Therefore, in this communication we report for the first time *the solid-state* reactivity of the coordinated benzothiazole-substituted *SCN*-pincer ligands, namely, the formation of 5,5- or 5,6-membered Pd(II) pincer complexes *via* elimination of HCl upon heating of their solid metal precursors. To conclude the results presented, benzothiazole-substituted *SCN* pincer ligands **1a–d** were shown to form in the reaction with $(PhCN)_2PdCl_2$ in solutions under kinetic control (20 °C) the complexes **2a–d** which were tentatively assigned to the dimeric μ-chlorine bridged species or monomeric complexes with bidentate structure depending on the ligand nature. Similar reaction at elevated temperature and over prolonged time in solution (thermodynamic control of the reaction) resulted in the direct cyclometallation of the benzene core and formation of the corresponding κ^3-*SCN* pincer products **3a–d**. The intermediate complexes **2a–d** or a homogeneous mixture of the initial reactants could be easily transformed into the pincer products using solid-phase synthesis which efficacy is comparable with synthesis in solution in terms of the yields and is advantageous from simplicity, short reaction times and even green chemistry point of view dictating the development of solvent-free processes or application of the alternative ones such as ionic liquids water, and supercritical liquids.

To the best of our knowledge, till now the solid phase synthetic approach has never been applied for the preparation of pincer complexes. Taking into account the above data, this approach obviously is not restricted to the above *SCN*-thiophosphoryl-benzothiazole ligands and may be applied for the synthesis of a range of pincer complexes known to possess high thermal and chemical stability. Quite high reaction temperatures that were needed to complete reactions affording pincer complexes in the solid state apparently may be lowered using an inert support similar to that for monocyclometallations.[20–23] Furthermore, microwave assistance might be useful in optimization the process. The investigations in this area are now in progress.

Acknowledgements

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25 To the best of our knowledge, formation of Pd(II) complex **III** (X = NH) over 5 min in 93% isolated yield is the fastest procedure for the pincer complex preparation known in the literature.

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27 *Synthesis of complexes* ***2a–d*** *(general procedure)*: A solution of $(PhCN)_2PdCl_2$ (65.7 mg, 0.171 mmol) in 4 mL of dichloromethane was slowly dropwise added to a solution of the corresponding ligand **1a–d** (0.171 mmol) in 4 mL of CH_2Cl_2. In 15 min, the resulting precipitate of complex **2a–c** was filtered off, washed with CH_2Cl_2 (10 mL) and Et_2O (15 mL), and dried in *vacuo*. In the case of ligand **1d**, the homogeneous reaction mixture was evaporated to dryness and the resulting residue was washed with ether (15 mL) and dried in *vacuo* to give **2d** as a dark-beige solid. **2a**. Yield: 115.6 mg (98%). Anal. Calc. for $C_{25}H_{18}Cl_2NPPdS_2{\cdot}CH_2Cl_2$: C, 45.27; H, 2.92; N, 2.03. Found: C, 45.51; H, 2.94; N, 2.07%. **2b**. Yield: 101.0 mg (95%). Anal. Calc. for $C_{25}H_{18}Cl_2NOPPdS_2$: C, 48.37; H, 2.92; N, 2.26. Found: C, 48.07; H, 2.74; N, 2.18%. **2c**. Yield: 92.0 mg (86%). Performing of the same reaction in acetonitrile instead of dichloromethane provided complex **2c** in a slightly lower yield of 77%. Anal. Calc. for $C_{25}H_{18}Cl_2NOPPdS_2$: C, 48.37; H, 2.92; N, 2.26. Found: C, 48.04; H, 2.78; N, 2.13%. **2d**. Yield: 103.0 mg (97%). Anal. Calc. for $C_{25}H_{19}Cl_2N_2PPdS_2$: C, 48.44; H, 3.09; N, 4.52. Found: C, 48.64; H, 3.20; N, 4.51%.

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31 *Solid-phase synthesis of pincer complexes* ***3a–d*** *(general procedure):* A charge of complex **2** was heated in an open test tube at 200 °C (oil bath) for 15 min. The resulting residue was dissolved in 30 mL of CH_2Cl_2 (or DMSO-CH_2Cl_2 (1 : 3) mixture in the case of complex **3d**) and filtered through a cotton pad. Addition of diethyl ether (**3a,b**) or pentane (**3c**) to partly evaporated dichloromethane filtrates led to precipitation of the corresponding pincer complexes **3a–c**. Complex **3d** was isolated by precipitation with EtOH from a DMSO solution obtained after removal of dichloromethane from the DMSO-CH_2Cl_2 filtrate. The yields were 71, 60, 70 and 51% for **3a**, **3b**, **3c**, and **3d**, respectively. The physical chemical characteristics (mp, ^{31}P, ^{1}H, and IR spectra) of the complexes were identical to those previously reported for the samples obtained in solutions (see ref. 26).

32 An attempt to perform the transformation at lower temperature (50 °C) was unsuccessful.

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