

NEW SUPRAMOLECULAR METALLOGELS DERIVED FROM ORTHO-PALLADATED BENZYLAMINE AND EXO-DENTATE DIIMINES

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Abstract. This Communication describes the serendipitous discovery of the new class of supramolecular metallogels. The target materials were obtained during the attempts to synthesize the binuclear palladium complexes by the reaction of *ortho*-palladated *N,N*-dimethylbenzylamine with *exo*-dentate *N*-donor ligands – 4,4'-bipyridyl and (*E,E*)-1,2-bis(4-pyridyl)ethylene – in benzene. Gel drying was made by simple solvent evaporation and by supercritical CO₂ drying. The morphology of corresponding xerogels and aerogels as revealed by SEM study showed that the methods of solvent removal is crucial for the solid-state structure of the final materials. The tentative scheme of the gel formation is suggested.

Keywords: *ortho*-palladated benzylamines, supramolecular metallogels, supercritical fluids.

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1. Introduction

ortho-Metallated primary, secondary, and tertiary benzylamines belong to the very important family of organometallic compounds due to their wide-explored catalytic properties (Dupont *et al.*, 2005; Roy & Uozumi, 2018). For example, they are used as C-C cross-coupling catalysts (Buxaderas *et al.*, 2013; Ghorpade *et al.*, 2018; Gómez-Martínez, *et al.*, 2017; Lucio-Martínez *et al.*, 2016; Sable *et al.*, 2017).

In the frames of our work on stereo- and enantioselective catalysts (Medved'ko *et al.*, 2017), we found that chiral of *N*-isopropyl- α -methylbenzylamine could form unusual trimeric palladium complexes of type [LPdCl]₃ which exist in solution in equilibrium with more typical dimeric form [LPdCl]₂ (Vatsadze *et al.*, 2009). Both forms could be monomerized by the action of tertiary amine like pyridine to give rise to a catalytically active species of type [LCIPdPy]. We were interested whether it is possible to get two palladium atoms in one complex molecule upon action of *exo*-bidentate ligands of bipy-type. In this Communication we report on successful attempts to synthesize such kind of complexes and serendipitous discovery that the monomerization process with use of bipy and its congeners proceeds with formation of supramolecular metallogel.

2. Experimental

The solution of 0.1 mmol of 4,4'-bipyridine in 6 ml of benzene was added to the solution of 0.1 mmol of di- μ -chlorobis[(*N,N*-dimethylbenzylamino-2C,N)palladium(II)] in 11 ml of benzene under stirring. The reaction mixture was

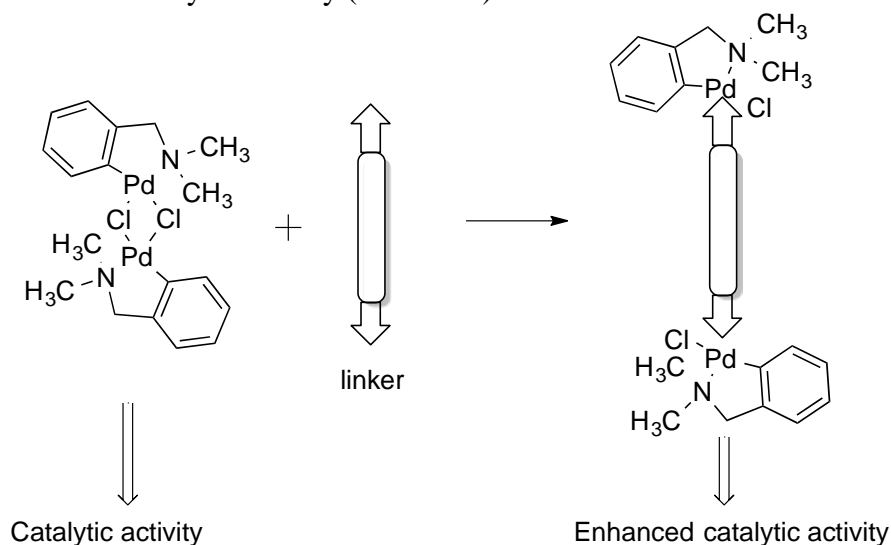
quickly decolorized and gelled. To characterize obtained gel the reaction mixture was refluxed for several minutes and precipitated solid was filtered, washed with chloroform, acetone and diethyl ether and dried. Yield: 59.3 mg of white solid (82%). M.p. 235-240°C (dec.).

$^1\text{H-NMR}$ (400 MHz, CDCl_3 , ppm): 2.95 (s, 12H, CH_3); 4.01 (s, 4H, CH_2); 6.08 (d, 2H, CH(6)); 6.78-6.82 (m, 2H, CH(3)); 6.99-7.01 (m, 4H, CH(4,5)); 7.62 (m, 4H, CH(3,5)-bipy), 9.05 (m, 4H, CH(2,6)-bipy).

SEM study. Before measurements the samples were mounted on a 25 mm aluminum specimen stub and fixed by conductive graphite paint. Metal coating with a thin film (10 nm) of platinum/palladium alloy (80/20) was performed using magnetron sputtering method as described earlier (Kashin & Ananikov, 2011). The observations were carried out using Hitachi SU8000 field-emission scanning electron microscope (FE-SEM). Images were acquired in secondary electron mode at 10 kV accelerating voltage and at working distance 8-10 mm. Morphology of the samples was studied taking into account possible influence of metal coating on the surface.

3. Results and discussion

As we mentioned in the Introduction, the main idea of this study was to synthesize a complex, which would comprise two palladium atoms in one molecule in order to enhance its known catalytic activity (Scheme 1).



Scheme 1. A general approach to synthesizing binuclear Pd complexes

To achieve such a goal, we chose the di- μ -chlorobis[*N,N*-dimethylbenzylamino-2C,N]palladium(II)] and 4,4'-bipyridyl as model starting compounds and benzene as a solvent since both substrates are soluble in it.

To our surprise, the mixing of two solutions (that one containing Pd precursor was of light yellow color) with continuous stirring led to immediate formation of thick gel-like mass (Fig. 1), decolorizing of reaction mixture and complete stop of magnetic bar stirring. Prolongation of stirring for several hours led to decomposition of gel and formation of white precipitate. The same result was observed upon heating the reaction mass to boiling point of benzene. Prolonged shaking or using of spatula to disturb the

reaction mass also led to gel decomposition.



Figure 1. Photographs of gel-like reaction mixtures after 25 (left) and 50 (right) seconds of the reaction

Since our main goal was to synthesize the BPC, we attempted to isolate the final compound. To do this, the gel was heated up to boiling, then cooled down; the white precipitate formed was filtered off, washed with chloroform, acetone and ether. The final white powder was studied by NMR spectroscopy (Fig. 2).

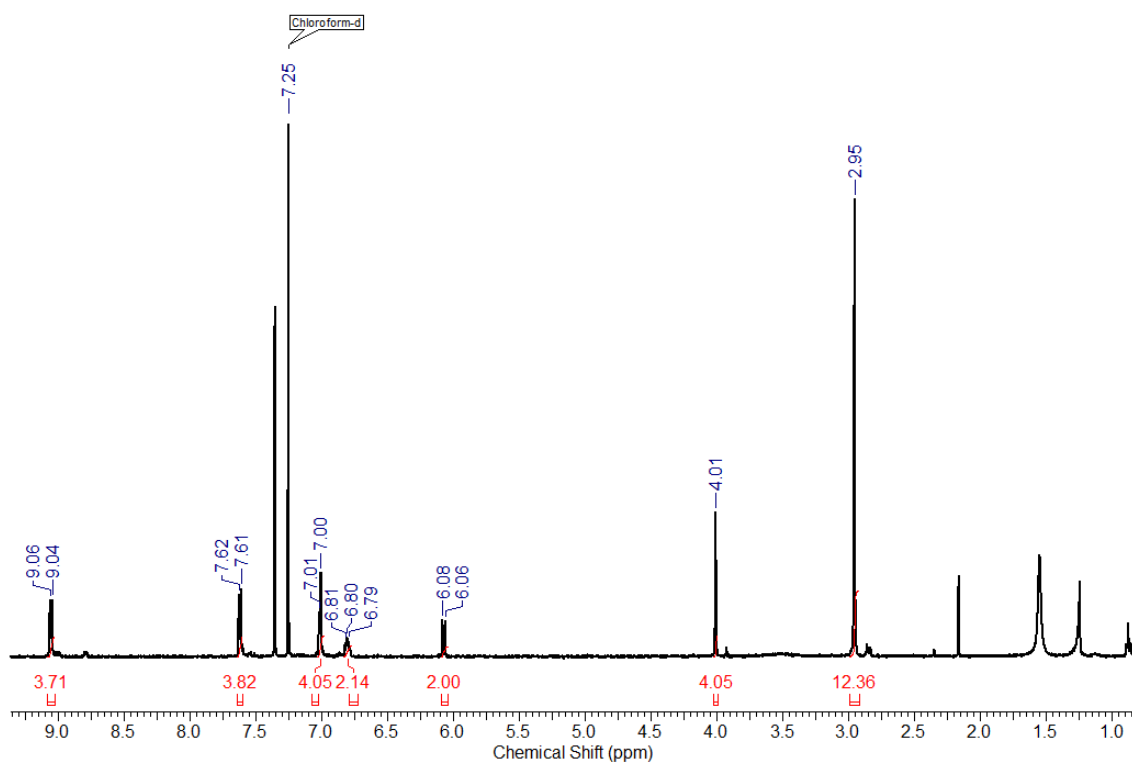
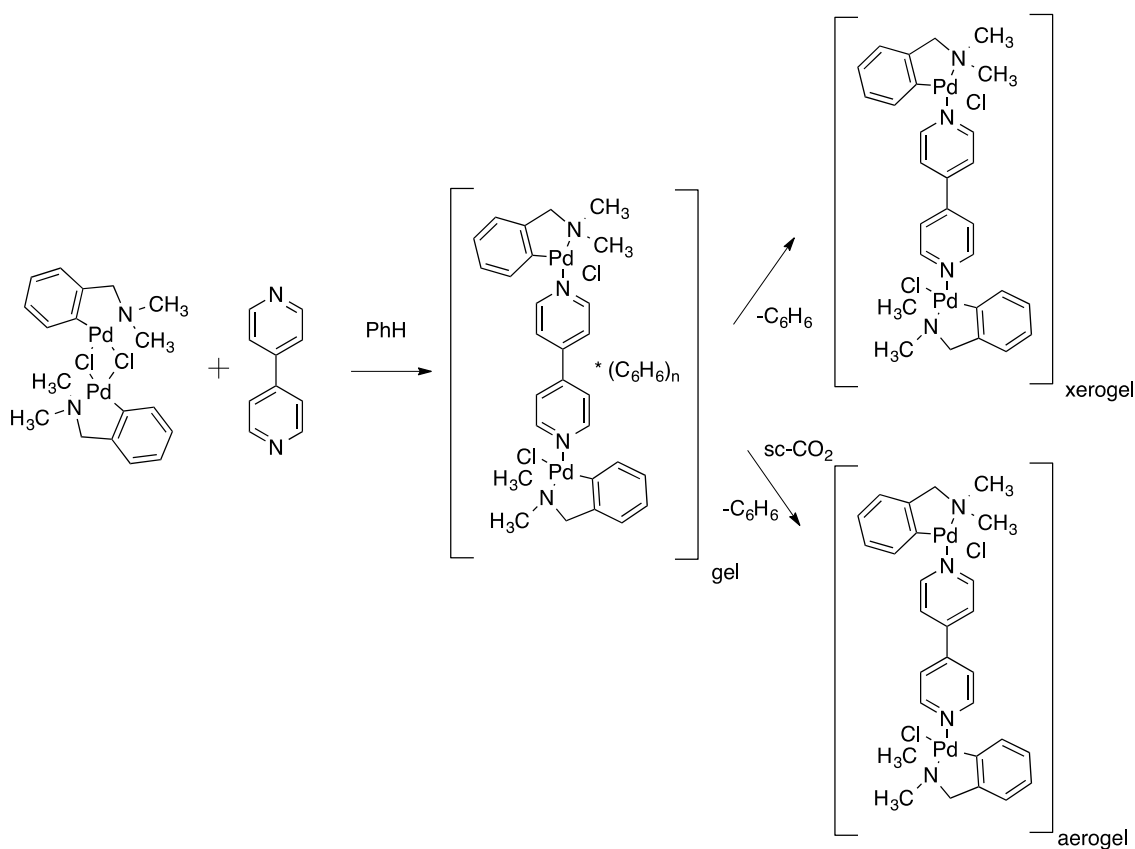


Figure 2. Proton NMR spectrum of the product of interaction of di- μ -chlorobis[(*N,N*-dimethylbenzylamino)-2C,N]palladium(II)] and 4,4'-bipyridine

The main result of this investigation was the conclusion that the ratio between palladium part of complex and linker molecule was 2:1, as it was designed at the beginning.

It is clearly seen from the spectrum, that bipy molecule is symmetrically coordinated to two equivalent palladium centers (signals at 9.05 and 7.61 ppm, both 4 protons). The integrity of *ortho*-palladated part of the product is confirmed by the signals of *N*-methyl groups (singlet at 2.95 ppm, 12 protons), methylene protons (singlet at 4.01 ppm, 4 protons) and characteristic group of aromatic protons of unsymmetrically *ortho*-disubstituted benzene ring at 6.08 (doublet, 2 protons), 6.78-6.82 (multiplet, 2 protons) and 6.99-7.01 (multiplet, 4 protons) ppm. The most characteristic signal confirming the substitution of chlorine atom at Pd center for aromatic pyridine moiety is the signal at 6.08 ppm, which moved upfield compared to the starting complex (Vatsadze *et al.*, 2017). Some signals of low intensity are due to solvent impurities, to possible formation of 1:1 complex and to the non-removed benzene molecules. The later would confirm the strong binding between complex molecules and benzene solvent during the gel formation.

Having in hand a new class of supramolecular gel, it was tempting to study some of its structural features. To do this, we attempted to remove solvent from benzenogel using two techniques, i.e., evaporation of solvent at room temperature to get xerogel and supercritical carbon dioxide washing to obtain aerogel (Scheme 2).



Scheme 2. Two ways to remove solvent from benzenogel

The first way was just simple: the vessel with gel was left open for several days. The resulting powder was studied by SEM (Fig. 3a, c, e). The second technique included the use of supercritical carbon dioxide washing with subsequent fast removal of the fluid at elevated temperature (ca. 50 °C) and pressure (ca. 80 bar). The resulting powder was also studied by SEM (Fig. 3b, d, f).

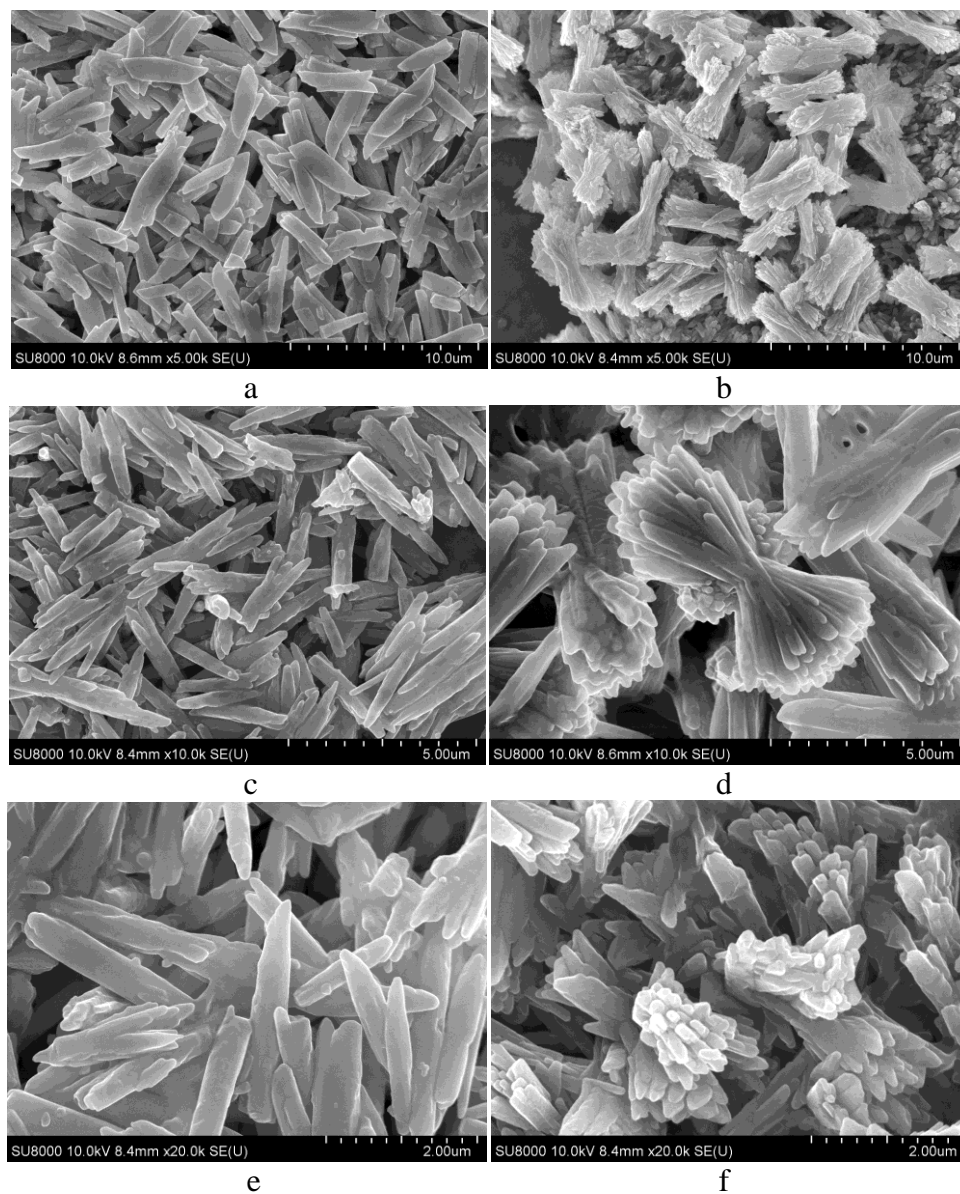


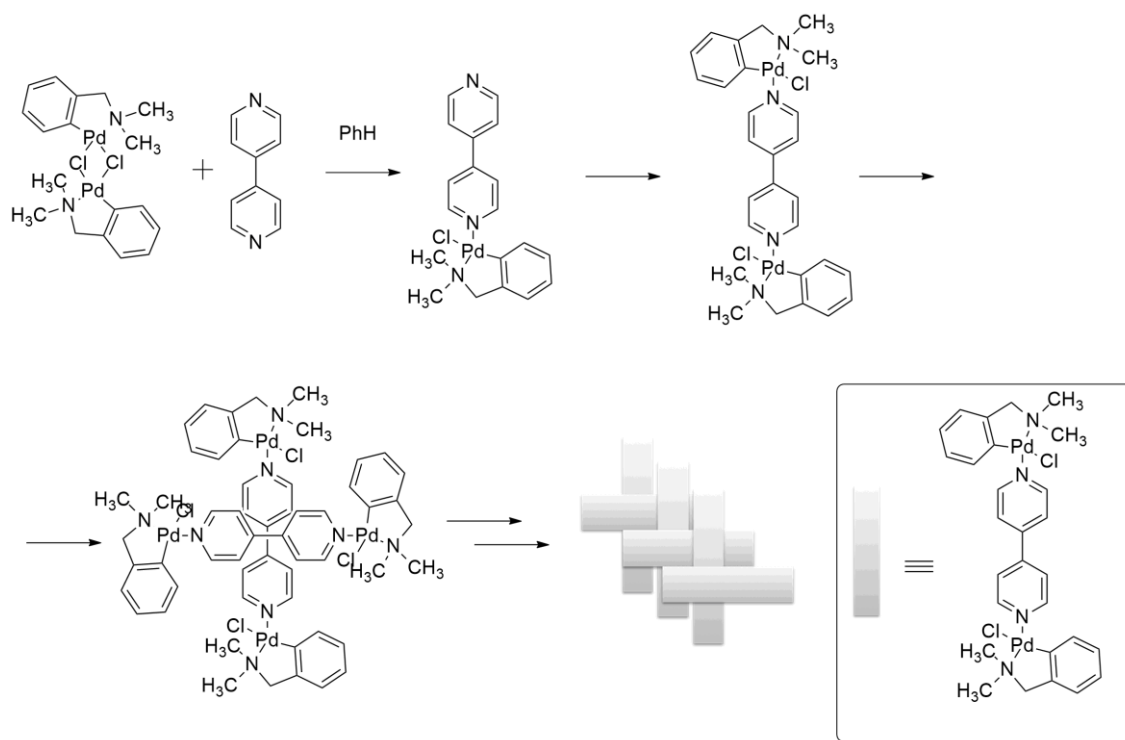
Figure 3. SEM micrographs for xerogel (a, c, e) and aerogel (b, d, f). The scale bar is 10 microns (a and b), 5 microns (c and d) and 2 microns (e and f)

The images in Fig. 3 clearly show the difference in morphology of the powder surface and particle shapes: while those for simple benzene removal are characterized by smooth uniform rods, those from sc-CO₂ washing look like tufts of more tiny rods. This difference might play a role in catalytic activity of complexes obtained by different routes. To our regret, the solubility of all powders was too small to study the catalytic activity in homogenous catalysis in typical experiments used in our lab.

We also tried to involve other starting compounds in interaction. While reaction of di- μ -chlorobis[*N,N*-dimethylbenzylamino-2C,N]palladium(II)] and (*E,E*)-1,2-bis(4-pyridyl)ethylene (bpe) led to the formation of novel gel-like material, the other bipy-type molecules (pyrazine) and different starting *ortho*-palladated benzylamines did not lead to formation of gels.

These findings led us to the tentative conclusion about the requirement for the gel formation and the explanation of its structure. First, one needs a long-conjugated system for the linker molecule (bipy, bpe, but not pyrazine). Second, the presence of two methyl radicals at nitrogen atoms of benzylamine is crucial for gel formation. Also, it should be taken in account that introduction of α -alkyl group at benzylamine ligand also do not allow to get gel.

Scheme 3 shows our tentative explanation of formation of gels during the reaction of di- μ -chlorobis[*N,N*-dimethylbenzylamino-2C,N]palladium(II)] with bipy/dpe. To our opinion, the main driving force for supramolecular polymerization is the π - π -stacking interactions between conjugated *N*-donor type linkers.



Scheme 3. The schematic explanation of gel formation

It should be noted here that this route to make supramolecular metallogels was mentioned in our recent review as “Approach 2” (Fig. 35, (Ananikov *et al.*, 2014)). In general, the emerging area of supramolecular metallogels is already covered by several excellent review papers ((Hirst *et al.*, 2008; Amabilino *et al.*, 2017; (Jones & Steed, 2016; Piepenbrock *et al.*, 2010; Steed, 2010), which unambiguously confirm that this branch of material chemistry is nowadays extremely rapidly growing in last decade due to many exciting applications exhibited by supramolecular gels (Draper & Adams, 2017).

4. Conclusion

In this report we showed that the interaction of dimeric form of *ortho*-palladated complex [LPdCl]₂ with bipy-type molecules lead to formation of complexes [LCIPd-bipy-PdCIL] in which two palladium atoms are present in one molecule. During the synthesis of such complexes the formation of supramolecular benzenogels was observed. The new metallogels were formed presumably via a set of weak intermolecular secondary bonds that's why they found to be not stable upon heating, shaking and even staying. The removal of solvent by supercritical CO₂ washing lead to the substantial change in final morphology of solid material compared to that formed by direct evaporation of benzene. The study of catalytic properties of new complexes is on our agenda.

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