

# ESI-MS and DFT Study of Solvent Bonding in Dicyclopalladated 4-Phenylaminoazobenzene

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RECEIVED: February 29, 2024 ★ REVISED: June 12, 2024 ★ ACCEPTED: June 12, 2024

THIS PAPER IS DEDICATED TO THE LATE PROFESSOR TOMISLAV CVITAŠ

**Abstract:** A study of solvent bonding and release in the dicyclopalladated 4-phenylaminoazobenzene chloride complex is reported. An ESI mass spectrometric study in the positive-ion mode has confirmed the rapid exchange of labile solvent ligands. A qualitative order of binding ability to palladium centers was established: MeCN < H<sub>2</sub>O < DMSO (*O*-bonded) < NH<sub>3</sub>. DFT calculations of isomeric dicyclopalladated complexes and their cationic species containing various combinations of coordinated solvents have revealed that solvent binding differs in mono- or disolvated cations as well as in neutral complexes, while their structural features are governed by the transphobic effect.

**Keywords:** mass spectrometry, palladated complex, azobenzene, DFT calculations, solvent bonding.

## INTRODUCTION

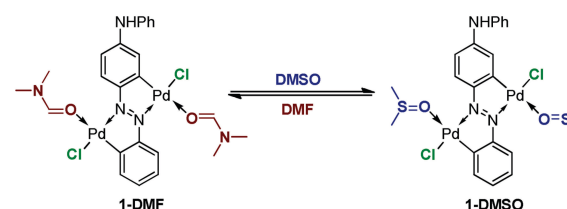
CYCLOPALLADATED compounds have been extensively studied due to their wide application in organic synthesis and catalysis, and recently as birefringents in liquid crystalline materials, as active units in antitumor drugs, and in the design of photosensitizers that can be used as biomolecular labels or for organic light-emitting diodes (OLEDs).<sup>[1–3]</sup>

We have focused our research on cyclopalladated compounds with azobenzenes due to their photochromic properties.<sup>[4–8]</sup> Convenient and simple routes to dicyclopalladated chloride<sup>[5]</sup> and acetate<sup>[6]</sup> complexes in solution and in the solid state were reported. Dicyclopalladated azobenzenes are characterized by the planarity of the whole Pd-core, which consists of four fused rings, two phenyl rings and two five-membered palladacycles (Scheme 1).<sup>[5,6]</sup> The ligand arrangement follows the *trans* choice concept and may be related to the transphobic effect.<sup>[9,10]</sup> Two weak *O*-donor ligands are bonded *trans* to phenyl carbon, which makes these complexes attractive as versatile organometallic precursors<sup>[7,8]</sup> and catalysts.<sup>[10]</sup> Moreover, dicyclopalladated complexes with electron-donating substituents on the azobenzene and their

complexes with *N*-ligands<sup>[7]</sup> and phosphines<sup>[8]</sup> proved as rare examples of Pd-emitters at room temperature both in solution and the solid state.<sup>[5,7,8]</sup> The low excitation energy (550–700 nm) makes these compounds excellent candidates for non-invasive luminescent (bio)probes or cellular dyes.<sup>[11]</sup>

Electrospray ionization mass spectrometry (ESI-MS) allows a study of inorganic and organometallic compounds in solution as a complementary technique to NMR spectroscopy and electrochemistry.<sup>[12,13]</sup>

Although NMR spectroscopy is frequently used for monitoring the reactions in solution, results are often limited by solubility, high reaction rates, or paramagnetism.<sup>[12,13]</sup> ESI is a soft ionization technique that gently transfers pre-existing ions with minimum fragmentation from the solution to the gas phase.<sup>[12,13]</sup> The ability to



Scheme 1.

detect and characterize species and reaction intermediates in solution, often at very low concentrations, makes ESI-MS a convenient technique for investigating diverse scientific areas ranging from catalytic reaction mechanisms<sup>[14]</sup> to studies of metallodrugs in complex biological samples and characterization of their interactions with biomolecules.<sup>[15]</sup>

Herein, we report the solvent-exchange processes in dipalladated systems studied by positive-ion ESI mass spectrometry and complemented by quantum-chemical (density functional theory, DFT) calculations used to rationalize the experimental data. ESI-MS proved to be an informative and convenient method for the solvent-exchange study on dicyclopalladated compounds due to the solubility and sensitivity limitations of NMR spectroscopy. The focus was on the identification, release, and exchange of solvent molecules bound to the dicyclopalladated core, as this essential structural feature controls the reactivity of the dipalladated halide complexes. This study is an integral part of the structural, chemical, and physical characterization of the title compounds, including an insight into their stability, reactivity, and behaviour in chemically and biologically relevant organic solvents.

## RESULTS AND DISCUSSION

### ESI-MS Study

Our<sup>[5]</sup> and literature<sup>[16]</sup> data describing the behaviour of dicyclopalladated complexes in solution confirmed that palladium centres in these compounds could bind *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), water, pyridine derivatives, and amino acids. Although Pd(II) generally prefers *N*- and *S*-donors and has a relatively small affinity for *O*-donors, crystallographic experiments showed that DMF and DMSO molecules in these complexes were coordinated through oxygen atoms.<sup>[5]</sup> Similar behaviour was observed for monocyclopalladated azobenzene complexes with *O*-ligands (H<sub>2</sub>O, triflate, perchlorate anions, phosphine oxides) coordinated with oxygen atoms *trans* to aryl carbon.<sup>[9]</sup> The coordinated solvents are removed by washing the complexes with H<sub>2</sub>O, alcohols, or common organic solvents (CH<sub>2</sub>Cl<sub>2</sub> or acetone), which demonstrates the lability of Pd-O(DMF) or Pd-O(DMSO) bonds.<sup>[5a]</sup>

To overcome the solubility and sensitivity issues of other methods, the ESI-MS technique, recently employed on palladium(II) halide complexes,<sup>[4,17]</sup> was selected as a suitable method for analysis of ionic palladium species containing weakly bound solvents since it previously provided a valuable and fast method for studying ligand lability.<sup>[12,13,18]</sup>

The dicyclopalladated complex **1** ([Pd<sub>2</sub>(L-2H)Cl<sub>2</sub>], where L is 4-phenylaminoazobenzene) was selected as the

representative compound for the solvent-exchange studies due to its better solubility in organic solvents compared to other dicyclopalladated complexes.

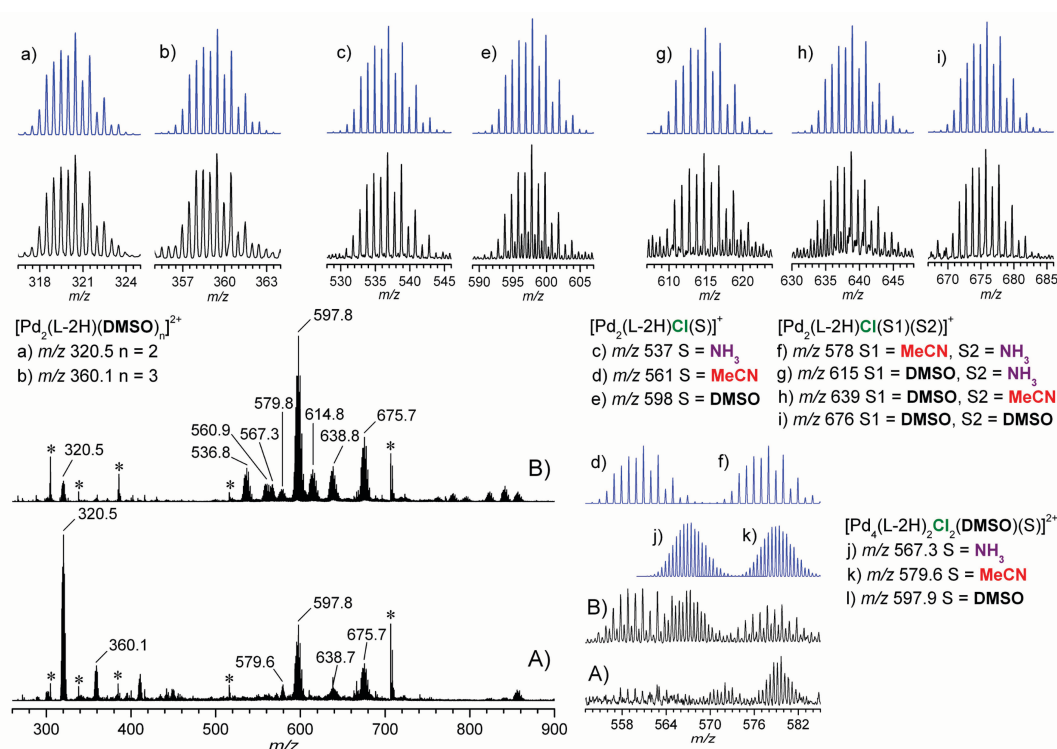
After rapid sample preparation using **1**-DMF, recorded positive-ion spectra did not detect any DMF species. These results indicated that the first exchange process was rapid and complete, in which two coordinated DMF molecules were replaced in solution with DMSO, forming **1**-DMSO (Scheme 1).

„Mixed“ solvent cations [Pd<sub>2</sub>(L-2H)Cl(S<sub>1</sub>)(S<sub>2</sub>)]<sup>+</sup> (S<sub>1</sub> ≠ S<sub>2</sub>) observed in the first order spectra of DMSO/MeCN samples, Figure 1, indicated the second exchange of solvents occurring after mixing the stock DMSO solution with MeCN. This process could have occurred in solution or in the mass spectrometer since the formation of solvent (*e.g.*, water, MeCN) adducts inside the ion trap is relatively common for metalloorganics.<sup>[12,13,18–21]</sup> It is important to note that ions without coordinated solvents, [Pd<sub>2</sub>(L-2H)Cl]<sup>+</sup> (*m/z* 520), were not observed in the first order (+)ESI mass spectra.

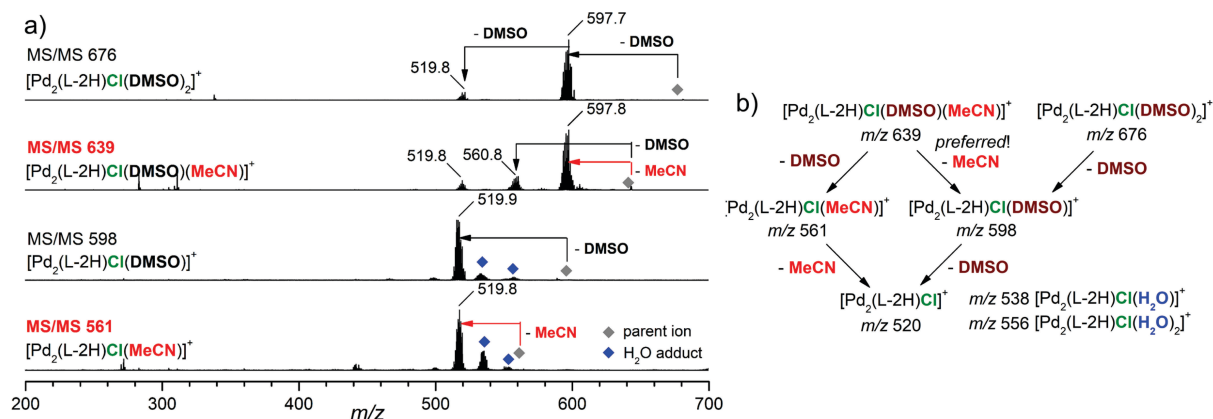
The complex **1** in DMSO/MeCN produced a rich (+)ESI mass spectrum with different types of DMSO cations, Figure 1. The adducts, [Pd<sub>2</sub>(L-2H)Cl(DMSO)(S)]<sup>+</sup> (S = DMSO or MeCN; *m/z* 676 or 639), [Pd<sub>2</sub>(L-2H)Cl(DMSO)]<sup>+</sup> (*m/z* 598) and dications [Pd<sub>2</sub>(L-2H)(DMSO)<sub>n</sub>]<sup>2+</sup> (*n* = 2 or 3; *m/z* 320.5 or 360.1) gave the most intensive signals. In MeCN containing small amounts of ammonia as an impurity,<sup>[13c,22]</sup> the spectrum showed additional signals of NH<sub>3</sub> adducts, [Pd<sub>2</sub>(L-2H)Cl(S)(NH<sub>3</sub>)]<sup>+</sup> (S = DMSO or MeCN, *m/z* 615 or 578), [Pd<sub>2</sub>(L-2H)Cl(NH<sub>3</sub>)]<sup>+</sup> (*m/z* 537) and [Pd<sub>4</sub>(L-2H)<sub>2</sub>Cl<sub>2</sub>(DMSO)(NH<sub>3</sub>)]<sup>2+</sup> (*m/z* 567.3), Figure 1. The observation of NH<sub>3</sub> associates indicated the increased sensitivity of dicyclopalladated complexes toward ammonia, which agrees with our previous study of rapid bonding of ammonia by dicyclopalladated azobenzenes in solution and in the solid state.<sup>[7a]</sup>

Tandem mass spectra of the ions observed in the first order spectra confirmed their identification (Figure 2). Collisional activation of mono- or disolvent species induced preferential loss of only one solvent ligand (DMSO or MeCN) from the isolated cations, indicating the tendency of these species to preserve ligands and, if possible, avoid formation of sub-coordinated metal centre [Pd<sub>2</sub>(L-2H)Cl]<sup>+</sup> (*m/z* 520).

Tandem experiments with varying activation amplitude showed that cations [Pd<sub>2</sub>(L-2H)Cl(S<sub>1</sub>)(S<sub>2</sub>)]<sup>+</sup> were losing the coordinated solvents even at low amplitude, Figure 3. Loss was occurring stepwise and produced the common core cation [Pd<sub>2</sub>(L-2H)Cl]<sup>+</sup> (*m/z* 520), Figure 2. Ligand bonding strength could be qualitatively determined from MS<sup>*n*</sup> spectra of „mixed“ cation [Pd<sub>2</sub>(L-2H)Cl(DMSO)(MeCN)]<sup>+</sup> (*m/z* 639, Figures 2 and 3). The experiment produced a strong signal of



**Figure 1.** (+)ESI mass spectra of **1** in DMSO/MeCN solution using A) fresh and B) MeCN containing ammonia. Insets: calculated (blue) and experimental (black) isotopic distributions for selected signals: a)  $m/z$  320.5,  $C_{22}H_{25}N_3O_2Pd_2S_2$ ; b)  $m/z$  360.1,  $C_{24}H_{31}N_3O_3Pd_2S_3$ ; c)  $m/z$  537,  $C_{18}H_{16}ClN_4Pd_2$ ; d)  $m/z$  561,  $C_{20}H_{16}ClN_4Pd_2$ ; e)  $m/z$  598,  $C_{20}H_{19}ClN_3OPd_2S_2$ ; f)  $m/z$  578,  $C_{20}H_{19}ClN_5Pd_2$ ; g)  $m/z$  615,  $C_{20}H_{22}ClN_4OPd_2S_2$ ; h)  $m/z$  639,  $C_{22}H_{22}ClN_4OPd_2S_2$ ; i)  $m/z$  676,  $C_{22}H_{25}ClN_3O_2Pd_2S_2$ ; j)  $m/z$  567.3,  $C_{22}H_{25}ClN_3O_2Pd_2S_2$ ; k)  $m/z$  579.6,  $C_{40}H_{35}Cl_2N_7OPd_4S$  and l)  $m/z$  597.9,  $C_{40}H_{38}Cl_2N_6O_2Pd_4S_2$ . Signals of the impurities in the solvents are denoted with an asterisk (\*). L = 4-phenylaminoazobenzene.

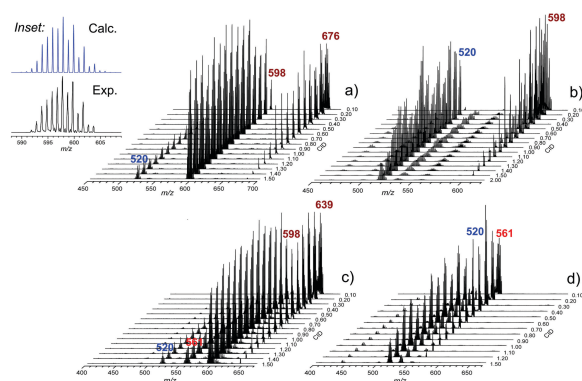


**Figure 2.** a) Tandem MS/MS experiments showing solvent release in **1** under (+)ESI-MS conditions and b) fragmentation of solvent adduct cations of **1** leading to the core cation  $[Pd_2(L-2H)Cl]^+$  ( $m/z$  520). L = 4-phenylaminoazobenzene.

$[Pd_2(L-2H)Cl(DMSO)]^+$  ions ( $m/z$  598) and only a weak signal of  $[Pd_2(L-2H)Cl(MeCN)]^+$  ions ( $m/z$  561), which showed that the most labile ligand in this species, *i.e.*, MeCN, was ejected more readily than DMSO.

ESI-MS experiments confirmed that sub-coordinated metal centres, formed by the ionization process, tend to

overcome destabilization due to ligand loss by coordinating other available ligands. The dicyclopalladated core  $[Pd_2(L-2H)Cl]^+$  cation, an electronically unsaturated  $14e^-/12e^-$  species, filled vacant coordination positions by bonding water molecules, which were according to tandem experiments preferred to MeCN as ligands, creating the



**Figure 3.** The effect of collision energy on CID in the ion trap of a)  $[\text{Pd}_2(\text{L-2H})\text{Cl}(\text{DMSO})_2]^+$  ( $m/z$  676), b)  $[\text{Pd}_2(\text{L-2H})\text{Cl}(\text{DMSO})]^+$  ( $m/z$  598), c)  $[\text{Pd}_2(\text{L-2H})\text{Cl}(\text{DMSO})(\text{MeCN})]^+$  ( $m/z$  639), and d)  $[\text{Pd}_2(\text{L-2H})\text{Cl}(\text{MeCN})]^+$  ( $m/z$  561) of complex **1**. L = 4-phenylaminoazobenzene. Inset shows the experimental MS/MS spectrum of the cation  $m/z$  598 at CID amplitude 0.1 (black) and the isotopic distribution calculated for  $m/z$  598,  $\text{C}_{20}\text{H}_{19}\text{ClN}_3\text{OPd}_2\text{S}$  (blue).

mono- and diaqua adducts, Figures 2 and 3. Moreover, if the signals of dipalladated ions  $[\text{Pd}_2(\text{L-2H})\text{Cl}]^+$  were isolated with no collisional energy input, two associates (with one or two  $\text{H}_2\text{O}$  molecules) were present. Similar aqua species formed in the mass spectrometer by gas-phase association reactions with  $\text{H}_2\text{O}$  from the solution were reported for palladium-alanine complexes.<sup>[19]</sup> Ions  $[\text{Pd}_2(\text{L-2H})\text{Cl}(\text{H}_2\text{O})_n]^+$  ( $n = 1, 2$ ) readily produced  $[\text{Pd}_2(\text{L-2H})\text{Cl}]^+$  ions under collisional activation.

The data suggested that *O*-bonded DMF was readily exchanged with *O*-bonded DMSO. Aqua adducts were preferred to MeCN adducts. Low-intensity signals assigned to MeCN species were observed only in DMSO samples, whereas traces of ammonia were bonded and detected in the spectra, Figure 1. Thus, ESI-MS easily differentiated (de)coordination of different solvents and could provide the following qualitative binding ability order:  $\text{MeCN} < \text{H}_2\text{O} < \text{DMSO}$  (*O*-bonded)  $< \text{NH}_3$ . These results also agree with our crystallographic experiments<sup>[5]</sup> and the ligand binding order reported for cationic  $[\text{Pd}(\text{dppe})(\text{solvent})_2]^{2+}$  complexes.<sup>[23]</sup>

### Quantum-Chemical Study

In order to gain some insight into the relative stabilities of the palladium species relevant for the solvent exchange, the energies of dicyclopalladated complexes with different types of coordinated solvent molecules  $[\text{Pd}_2(\text{L-2H})\text{Cl}_2(\text{S}_1)(\text{S}_2)]$  ( $\text{S}_1, \text{S}_2 = \text{DMSO}, \text{H}_2\text{O}, \text{NH}_3$ , and MeCN) and their daughter cationic species were calculated for the complex **1**. According to our previous studies, two geometries for dipalladated complexes are possible: the

dicyclopalladated core with four planar rings typical for the title complexes<sup>[5]</sup> and the bridged geometry with two palladium centres on the same side of the azobenzene ligand and only one five-membered cyclopalladated ring observed with bipyridine and phosphine complexes.<sup>[7,8]</sup> As the change in the coordinated solvents could induce structural change from planar to bridged molecule, we have examined the stabilities of both possible structures and their solvent-bonding isomers. We mention that energetically more favourable bridged species are those in which the five-membered palladacycle with the phenyl ring bearing the more electron-donating substituent is preserved.<sup>[5]</sup> Furthermore, since DMSO ligand could be coordinated through sulphur or oxygen atoms, both possibilities were tested. Previous<sup>[5]</sup> and here reported calculations showed that *O*-bonded DMSO species were more stable than analogous *S*-bonded species in these complexes.

**Stabilities of Neutral Complexes.** In calculated planar geometries for  $[\text{Pd}_2(\text{L-2H})\text{Cl}_2(\text{S}_1)(\text{S}_2)]$  species in MeCN and  $\text{NH}_3$  ligands are in a *trans* position to the azo-nitrogen, whereas the chlorine ligand is pushed into the *trans* position to the phenyl ring carbon. Simultaneously, the Pd-Cl bond is elongated if compared to the Pd-Cl bond *trans* to the azo-nitrogen. This geometry is analogous to the molecular structure of pyridine complexes  $[\text{Pd}_2(\text{L-2H})\text{Cl}_2(\text{py})_2]$ .<sup>[5]</sup> *O*-donor solvents, DMSO, DMF, and  $\text{H}_2\text{O}$ , are in *trans* position to the phenyl ring carbon and thus leave the chloride in *trans* position to the azonitrogen, corresponding to molecular structures of **1-DMF** and **1-DMSO** (Scheme 1).<sup>[5]</sup> The MeCN ligand behaves analogous to the *O*-donor ligands. The most stable bridged species have solvents on Pd<sub>2</sub> atom bonded *trans* to the phenyl carbon. These geometric features agree with the *trans* choice concept, where the ligand with the hardest donor atom chooses the ligand with the softest donor atom as an ancillary ligand in the *trans* position.<sup>[9]</sup> Calculations also indicated that planar neutral complexes are about 20–50 kJ/mol more stable in MeCN than the bridged structures, Table 1. Thus, studied complexes are not expected to isomerize into bridged species in solution. Presented computational results support the coordination of labile *O*-donor ligands in *trans* position to the phenyl carbon, which, with a known ability of these compounds to coordinate phosphines,<sup>[8]</sup> makes the title complexes strong candidates for catalytic trials.

Stabilities of the calculated species relevant for the DMSO/MeCN sample are collected in Table 1 relative to the planar adduct  $[\text{Pd}_2(\text{L-2H})\text{Cl}_2(\text{DMSO})_2]$ . If the exchange of only one solvent molecule *S* from  $[\text{Pd}_2(\text{L-2H})\text{Cl}_2(\text{S})_2]$  species (*S* = DMSO,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  or MeCN) with DMSO,  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  or MeCN was taken into consideration, computational results



show that DMSO and water adducts,  $[\text{Pd}_2(\text{L-2H})\text{Cl}_2(\text{DMSO})(\text{S})]$  and  $[\text{Pd}_2(\text{L-2H})\text{Cl}_2(\text{H}_2\text{O})(\text{S})]$ , which are close in energy, are ca. 30 kJ/mol less stable than  $\text{NH}_3$  species  $[\text{Pd}_2(\text{L-2H})\text{Cl}_2(\text{NH}_3)(\text{S})]$  and ca. 20 kJ/mol more stable than MeCN species  $[\text{Pd}_2(\text{L-2H})\text{Cl}_2(\text{MeCN})(\text{S})]$ . Thus, stability order concerning coordinated solvents,  $\text{MeCN} < \text{O-DMSO} \approx \text{H}_2\text{O} < \text{NH}_3$ , suggested that MeCN adducts could not be expected in DMSO/MeCN, whereas both aqua and DMSO complexes could be present in DMSO/MeCN solution. This order corresponds reasonably well to the experimentally obtained qualitative solvent binding ability order. It should be noted that energy differences between isomers with two different solvent molecules bonding to two different palladium centres in the mixed  $[\text{Pd}_2(\text{L-2H})\text{Cl}_2(\text{S1})(\text{S2})]$  species ( $\text{S1} \neq \text{S2}$ ) are less than 3 kJ/mol (Table 1) and thus could not be distinguished experimentally.

**Stabilities of Cations.** Three observed types of cations,  $[\text{Pd}_2(\text{L-2H})\text{Cl}(\text{S1})(\text{S2})]^+$ ,  $[\text{Pd}_2(\text{L-2H})\text{Cl}(\text{S})]^+$  and  $[\text{Pd}_2(\text{L-2H})(\text{S1})(\text{S2})]^{2+}$  ( $\text{S}, \text{S1}, \text{S2} = \text{DMSO}, \text{H}_2\text{O}, \text{NH}_3$ , and MeCN), were selected for the computational analysis in the gas phase. Calculations supported the experimental data and indicated that metal centres tend to avoid sub-coordination. The most stable were  $16e^-/14e^-$  cationic species  $[\text{Pd}_2(\text{L-2H})\text{Cl}(\text{S1})(\text{S2})]^+$ . Ions  $[\text{Pd}_2(\text{L-2H})\text{Cl}(\text{S})]^+$   $14e^-/14e^-$  were about 120 kJ/mol less stable, whereas the most energetically unstable were the  $14e^-/12e^-$  ions  $[\text{Pd}_2(\text{L-2H})\text{Cl}]^+$ . These species were, as expected, extremely

**Table 1.** Energies of planar isomers of  $[\text{Pd}_2(\text{L-2H})\text{Cl}_2(\text{S1})(\text{S2})]$  relative to planar  $[\text{Pd}_2(\text{L-2H})\text{Cl}_2(\text{O-DMSO})_2]$  in IEF-PCM MeCN. L = 4-phenylaminoazobenzene. Relative energies of Cl-bridged species are given in parentheses.

S2 \ S1	O-DMSO	H <sub>2</sub> O	MeCN	iso-NH <sub>3</sub>
O-DMSO	0.0 (51.3)	-3.6	18.9	-29.9
H <sub>2</sub> O	-4.6	-8.3 (41.6)	15.9	-36.3
MeCN	18.4	14.4	37.4 (63.3)	-11.4
iso-NH <sub>3</sub>	-32.9	-37.4	-13.7	-63.1 (-37.3)

unstable and about 330 kJ/mol higher in energy than  $16e^-/14e^-$  ions.  $[\text{Pd}_2(\text{L-2H})\text{Cl}(\text{S1})(\text{S2})]^+$  with both added solvent molecules bonded to the same palladium centre, making the  $16e^-/12e^-$ , were less stable than isomeric  $14e^-/14e^-$  species. A similar trend was observed for solvent adducts of monocyclopalladated alkynes.<sup>[24]</sup>

Dications  $[\text{Pd}_2(\text{L-2H})(\text{S1})(\text{S2})]^{2+}$  with one solvent *per* metal bonded in *trans* position to the azo-nitrogen were the most stable isomers, in agreement with the transphobic effect.  $[\text{Pd}_2(\text{L-2H})(\text{DMSO})_2]^{2+}$  was at least 16 kJ/mol more stable than any other dicationic species (Table 2). Calculated stabilities corresponded nicely with the experimental results that showed DMSO dications giving strong signals and  $[\text{Pd}_2(\text{L-2H})(\text{DMSO})(\text{NH}_3)]^{2+}$  ions detected as low-intensity signals in the DMSO/MeCN spectrum. Other species were not observed and, according to calculations, would be 30 kJ/mol less stable than the di-DMSO dication, Table 2. It should be noted that bridged dications were at least 120 kJ/mol destabilized if compared to the planar isomers, and thus, they could not be expected even under mass spectrometric conditions.

Ions  $[\text{Pd}_2(\text{L-2H})\text{Cl}(\text{S})]^+$  prefer Cl bonded to Pd1 and solvent *cis* to the Pd2-C bond (P1, Table 3). Their stabilities follow the solvent order: S-DMSO  $\ll$  MeCN  $<$  H<sub>2</sub>O  $<$  O-DMSO  $\approx$  NH<sub>3</sub>. The planar species  $[\text{Pd}_2(\text{L-2H})\text{Cl}]^+$ , which has not been observed in the first order (+)ESI spectra, is expectedly 205 kJ/mol less stable than  $[\text{Pd}_2(\text{L-2H})\text{Cl}(\text{O-DMSO})]^+$ . Planar isomers of  $[\text{Pd}_2(\text{L-2H})\text{Cl}(\text{S})]^+$  and also  $[\text{Pd}_2(\text{L-2H})(\text{S1})(\text{S2})]^{2+}$  with ligands bonded *trans* to the carbon atom were found only for NH<sub>3</sub>, yet due to the transphobic effect were significantly less stable than their isomers with solvent ligands *trans* to azonitrogen. Bridged

**Table 2.** Energies of planar  $[\text{Pd}_2(\text{L-2H})(\text{S1})(\text{S2})]^{2+}$  isomers relative to planar  $[\text{Pd}_2(\text{L-2H})(\text{O-DMSO})_2]^{2+}$  in the gas phase. L = 4-phenylaminoazobenzene.

S2 \ S1	O-DMSO	H <sub>2</sub> O	MeCN	NH <sub>3</sub>	S-DMSO
O-DMSO	0.0	72.9	31.0	16.2	60.1
H <sub>2</sub> O	70.2	147.2	106.3	93.2	134.0
MeCN	31.1	103.7	63.6	50.0	91.8
NH <sub>3</sub>	16.8	89.6	49.1	35.9	76.9
S-DMSO	70.6	143.5	103.3	89.9	134.4

**Table 3.** Energies of  $[\text{Pd}_2(\text{L}-2\text{H})\text{Cl}(\text{S})]^+$  isomers relative to planar  $[\text{Pd}_2(\text{L}-2\text{H})\text{Cl}(\text{O}-\text{DMSO})]^+$  in the gas phase. L = 4-phenylaminoazobenzene.

S =	O-DMSO	H <sub>2</sub> O	MeCN	NH <sub>3</sub>	S-DMSO
<b>P1</b>	0.0	12.7	21.3	−0.5	56.0
<b>P2</b>	9.5	64.4	33.6	12.6	64.2
<b>B-cis</b>	56.6	90.1	65.2	35.9	80.6
<b>B-trans</b>	79.1	108.6	98.5	72.8	128.8

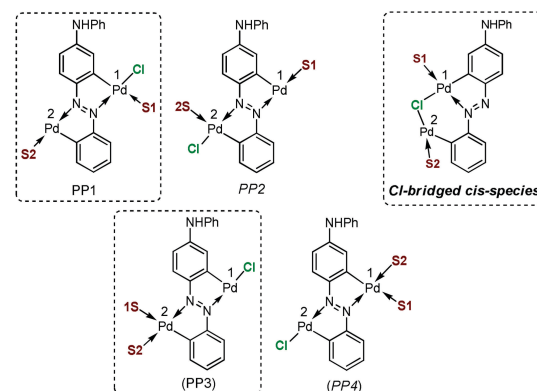
cations  $[\text{Pd}_2(\text{L}-2\text{H})\text{Cl}(\text{S})]^+$  (**B-cis**, Table 3) are 10–45 kJ/mol less stable than planar ions. Isomerization from **B-cis** to **B-trans** species is energetically unfavourable by 20–50 kJ/mol.

In the case of the „mixed“ disolvent cations  $[\text{Pd}_2(\text{L}-2\text{H})\text{Cl}(\text{S}_1)(\text{S}_2)]^+$ , the situation is not so simple. The position, combination, and interaction between the coordinated solvents become essential factors in cation stabilization. Species  $[\text{Pd}_2(\text{L}-2\text{H})\text{Cl}(\text{S}_1)(\text{S}_2)]^+$  keep Cl bonded to the Pd1 atom *trans* to azo-nitrogen and one solvent ligand on each palladium centre (PP1, Table 4). Isomers with the Pd1–Cl bond are calculated as 2–14 kJ/mol more stable than those with Pd2–Cl. In general, according to the most stable species for the definite solvent combination (marked blue in Table 4), O-donors, O-DMSO, and H<sub>2</sub>O, prefer bonding to the Pd1 centre, whereas N-donors, MeCN and NH<sub>3</sub>, favour Pd2 centre. If only one solvent ligand is varied in  $[\text{Pd}_2(\text{L}-2\text{H})\text{Cl}(\text{S}_1)(\text{S}_2)]^+$ , cations containing NH<sub>3</sub> or O-DMSO are close in energy and are at least 18 kJ/mol more stable than MeCN or H<sub>2</sub>O cations, Table 4. Cations with two solvents bonded to the same metal centre are, in general, less stable than those with one solvent ligand *per* metal.

The most stable bridged isomers for all combinations of solvents have solvents coordinated *cis* to the Pd2–Cl bond. Only in the case of cations  $[\text{Pd}_2(\text{L}-2\text{H})\text{Cl}(\text{S}_1)(\text{S}_2)]^+$  with N-donor ligands, NH<sub>3</sub> and MeCN, several *cis*-bridged isomers are close in stability to the planar isomers, Table 4. Other conceivable bridged isomers, *i.e.*, ones with terminal Pd2–Cl and bridging solvent or with Cl-bridge and two solvents on Pd1, are less stable than *cis*-bridged species.

Presented computational results rationalize experimental findings for DMSO/MeCN samples. ESI-MS detected mainly DMSO associated with water and NH<sub>3</sub>, whereas the unstable MeCN adducts gave only lower-intensity signals and quickly released the coordinated MeCN. It should be noted that the detection of signals

**Table 4.** Energies of  $[\text{Pd}_2(\text{L}-2\text{H})\text{Cl}(\text{S}_1)(\text{S}_2)]^+$  isomers relative to planar  $[\text{Pd}_2(\text{L}-2\text{H})\text{Cl}(\text{O}-\text{DMSO})_2]^+$  in the gas phase. Energies of the planar isomers with Cl bonded to Pd1 (PP1 and PP3) or Pd2 (PP2 and PP4) are given in normal or *italic*, respectively, whereas energies of *cis*-bridged species are given in **bold**. Energies of PP1/PP2 and PP3/PP4 species are given without and in parentheses, respectively. The most stable species for distinct solvent combinations is given in **blue**. L = 4-phenylaminoazobenzene.



S2 \ S1	O-DMSO	H <sub>2</sub> O	MeCN	NH <sub>3</sub>
O-DMSO	0.0 (16.4)	17.7 (37.2)	33.6 (44.7)	1.6 (19.8)
H <sub>2</sub> O	32.4 (47.3)	57.5 (81.6)	44.7 (76.9)	9.4 (55.7)
MeCN	17.9 (32.7)	37.2 (64.1)	56.4 (56.2)	20.6 (33.5)
NH <sub>3</sub>	44.7 (−1.8)	67.5 (31.0)	54.0 (23.5)	18.8 (11.0)
	14.5	38.1	24.0	−10.8

(a) S2 = NH<sub>3</sub> bonded *cis* to Pd2–Cl bond.

assigned to NH<sub>3</sub> species in (+)ESI spectra indicated significant stability of NH<sub>3</sub> associates, which is in accordance with calculations.

## CONCLUSION

ESI-MS study of the exchange of solvent molecules coordinated to palladium centres was complemented by NMR spectroscopy and DFT calculations. Experimental and computational analysis showed that labile solvent ligands exchanged rapidly in solution and were readily released under collisional activation. The qualitative order of solvent binding ability to palladium centres has been established as follows: MeCN < H<sub>2</sub>O < DMSO (O-bonded) < NH<sub>3</sub>. DFT calculations of stabilities of dicyclopalladated complexes

containing various combinations of coordinated solvents revealed that solvent binding energies differ in mono- or disolvated cations and neutral complexes, whereas structural features of species are governed by transphobic effect. According to calculations, bridged species are generally less stable than planar dicyclopalladated structures.

Dicyclopalladated complexes showed versatile reactivity during the ESI process. Both dissociation and association reactions were observed, identified, and analysed by tandem mass experiments. Coordinated solvent ligands were released stepwise before the decomposition of the stable dimetallated core cations  $[\text{Pd}_2(\text{L-2H})\text{Cl}]^+$  or anions  $[\text{Pd}_2(\text{L-2H})\text{Cl}_3]^-$  started.

This study is the first comprehensive analysis of ESI-MS behaviour and solvent exchange of cyclopalladated systems. The reported data will allow a more straightforward interpretation of mass spectra for metallacycles and will, in the future, serve as a valuable data source for the studies of dicyclopalladated compounds. This work validated DFT calculations as a complementary method to ESI mass spectrometry which can be utilized to identify reaction products in solution and in the gas phase, as well as a powerful tool for unravelling the mass spectrometric behaviour of compounds.

## EXPERIMENTAL SECTION

**General.** All chemicals and solvents were used as supplied, and the reactions were carried out under aerobic conditions. Solvents were not dried before use. Dicyclopalladated 4-phenylaminoazobenzene chloride complex  $\{(\text{DMF})\text{PdCl}(\mu - \text{C}_6\text{H}_5\text{NHC}_6\text{H}_3\text{N}=\text{NC}_6\text{H}_3\text{NHC}_6\text{H}_5)\text{PdCl}(\text{DMF})\}$  was prepared in DMF according to the previously reported procedure.<sup>[5]</sup>

**ESI Mass Spectrometry.** ESI mass spectra were recorded on an amaZon ETD ion trap mass spectrometer (Bruker Daltonik, Bremen, Germany) in positive-ion mode. Helium was used as a collision gas. The compounds were dissolved in DMSO to obtain a concentration of approximately  $10^{-4}$  mol/dm<sup>3</sup>. The stock solution was diluted with MeCN to approximately  $10^{-5}$  mol/dm<sup>3</sup> and injected directly into the ESI source. The whole preparation process lasted up to 5 minutes. Solutions of lower concentrations gave too low signals with even the most intensive signals in the spectra hardly distinguishable from the noise. The expected natural abundance isotope patterns were calculated using ICR-2LS program.<sup>[25]</sup>

Tandem mass spectra ( $\text{MS}_n$ ,  $n = 2$  and  $3$ ) and calculated expected natural abundance isotope patterns for ion clusters provided the given fragment assignment and revealed the charge of the ion by the  $m/z$  separation

between adjacent peaks. Pd and Cl isotopic abundances allowed straightforward determination of the elemental composition of most fragment ion structures. The stated  $m/z$  values throughout this work correspond to the most intensive peak in the observed isotope pattern.

**Computational Details.** All calculations were carried out using the B3LYP functional implemented in Gaussian09.<sup>[26]</sup> Full geometry optimizations were accompanied by vibrational frequency calculations that identified all calculated geometries as minima. The standard 6-31G(d,p) basis set was used for C, H, N, O, and Cl atoms, whereas Pd atoms were modelled by the Stuttgart-Dresden (SDD) pseudopotential and the accompanying SDD basis set.<sup>[27]</sup> Cationic species were modelled in the gas phase, whereas the bulk solvent (MeCN) was modelled for neutral dicyclopalladated complexes  $[\text{Pd}_2(\text{L-2H})\text{Cl}_2(\text{S1})(\text{S2})]$  using the polarizable continuum model (IEF-PCM).<sup>[28]</sup>

**Conflict of interest.** The authors declare no competing financial interests.

**Acknowledgment.** Financial support was provided by the Croatian Science Foundation (grant IP-2019-04-9951). Computations were done on the Isabella cluster at SRCE, Zagreb. Authors thank Hasan Muharemović and Tomislav Mrla for the help with the data processing. PNNL and the omics.pnl.gov website are kindly acknowledged for the ICR-2LS software.

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