

On the identification of ionic species of neutral halogen dimers, monomers and pincer type palladacycles in solution by electrospray mass and tandem mass spectrometry

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Abstract

Electrospray (ESI) mass spectra analysis of acetonitrile solutions of a series of neutral chloro dimers, pincer type, and monomeric palladacycles has enabled the detection of several of their derived ionic species. The monometallic cationic complexes $\text{Pd}[\kappa^1\text{-C}, \kappa^1\text{-N}, \kappa^1\text{-S-C}=(\text{CH}_3\text{S-2-C}_6\text{H}_4)\text{C}(\text{Cl})\text{CH}_2\text{N}(\text{CH}_3)_2]^+$ (**1a**) and $[\text{Pd}[\kappa^1\text{-C}, \kappa^1\text{-N}, \kappa^1\text{-S-C}=(\text{CH}_3\text{S-2-C}_6\text{H}_4)\text{C}(\text{Cl})\text{CH}_2\text{N}(\text{CH}_3)_2](\text{CH}_3\text{CN})]^+$ (**1b**) and the bimetallic cationic complex $[\kappa^1\text{-C}, \kappa^1\text{-N}, \kappa^1\text{-S-C}=(\text{CH}_3\text{S-2-C}_6\text{H}_4)\text{C}(\text{Cl})\text{CH}_2\text{N}(\text{CH}_3)_2]\text{Pd-Cl-Pd}[\kappa^1\text{-C}, \kappa^1\text{-N}, \kappa^1\text{-S-C}=(\text{CH}_3\text{S-2-C}_6\text{H}_4)\text{C}(\text{Cl})\text{CH}_2\text{N}(\text{CH}_3)_2]^+$ (**1c**) were detected from an acetonitrile solution of the pincer palladacycles $\text{Pd}[\kappa^1\text{-C}, \kappa^1\text{-N}, \kappa^1\text{-S-C}=(\text{CH}_3\text{S-2-C}_6\text{H}_4)\text{C}(\text{Cl})\text{CH}_2\text{N}(\text{CH}_3)_2](\text{Cl})$ **1**. For the dimeric compounds $\{\text{Pd}[\kappa^1\text{-C}, \kappa^1\text{-N-C}=(\text{Y-2-C}_6\text{H}_4)\text{C}(\text{Cl})\text{CH}_2\text{N}(\text{CH}_3)_2](\mu\text{-Cl})\}_2$ (**2**, Y = H and **3**, CF₃), highly electronically unsaturated palladacycles $[\text{Pd}[\kappa^1\text{-C}, \kappa^1\text{-N-C}=(\text{Y-2-C}_6\text{H}_4)\text{C}(\text{Cl})\text{CH}_2\text{N}(\text{CH}_3)_2]^+$ (**2d**, **3d**) and their mono and di-acetonitrile adducts, namely, $[\text{Pd}[\kappa^1\text{-C}, \kappa^1\text{-N-C}=(\text{Y-2-C}_6\text{H}_4)\text{C}(\text{Cl})\text{CH}_2\text{N}(\text{CH}_3)_2](\text{CH}_3\text{CN})]^+$ (**2e**, **3e**) and $[\text{Pd}[\kappa^1\text{-C}, \kappa^1\text{-N-C}=(\text{Y-2-C}_6\text{H}_4)\text{C}(\text{Cl})\text{CH}_2\text{N}(\text{CH}_3)_2](\text{CH}_3\text{CN})_2]^+$ (**2f** and **3f**) were detected together with the bimetallic complex $[\text{Pd}[\kappa^1\text{-C}, \kappa^1\text{-N-C}=(\text{Y-2-C}_6\text{H}_4)\text{C}(\text{Cl})\text{CH}_2\text{N}(\text{CH}_3)_2]\text{-Cl-Pd}[\kappa^1\text{-C}, \kappa^1\text{-N-C}=(\text{Y-2-C}_6\text{H}_4)\text{C}(\text{Cl})\text{CH}_2\text{N}(\text{CH}_3)_2]^+$ (**2a**, **3a**) and its acetonitrile adducts $[\kappa^1\text{-C}, \kappa^1\text{-N-C}=(\text{Y-2-C}_6\text{H}_4)\text{C}(\text{Cl})\text{CH}_2\text{N}(\text{CH}_3)_2](\text{CH}_3\text{CN})\text{Pd-Cl-Pd}[\kappa^1\text{-C}, \kappa^1\text{-N-C}=(\text{Y-2-C}_6\text{H}_4)\text{C}(\text{Cl})\text{CH}_2\text{N}(\text{CH}_3)_2]^+$ (**2b**, **3b**) and $[\kappa^1\text{-C}, \kappa^1\text{-N-C}=(\text{Y-2-C}_6\text{H}_4)\text{C}(\text{Cl})\text{CH}_2\text{N}(\text{CH}_3)_2](\text{CH}_3\text{CN})\text{Pd-Cl-Pd}[\kappa^1\text{-C}, \kappa^1\text{-N-C}=(\text{Y-2-C}_6\text{H}_4)\text{C}(\text{Cl})\text{CH}_2\text{N}(\text{CH}_3)_2](\text{CH}_3\text{CN})]^+$ (**2c**, **3c**). The dimeric palladacycle $\{\text{Pd}[\kappa^1\text{-C}, \kappa^1\text{-N-C}=(\text{CH}_3\text{O-2-C}_6\text{H}_4)\text{C}(\text{Cl})\text{CH}_2\text{N}(\text{CH}_3)_2](\mu\text{-Cl})\}_2$ (**4**) is unique as it behaves as a pincer type compound with the OCH₃ substituent acting as an intramolecular coordinating group which prevents acetonitrile full coordination, thus forming the cationic complexes $[(\text{C}_6\text{H}_4(o\text{-CH}_3\text{O})\text{C}=\text{C}(\text{Cl})\text{CH}_2\text{N}(\text{CH}_3)_2\text{-}\kappa\text{O}, \kappa\text{C}, \kappa\text{N})\text{Pd}]^+$ (**4b**), $[(\text{C}_6\text{H}_4(o\text{-CH}_3\text{O})\text{C}=\text{C}(\text{Cl})\text{CH}_2\text{N}(\text{CH}_3)_2\text{-}\kappa\text{O}, \kappa\text{C}, \kappa\text{N})\text{Pd}(\text{CH}_3\text{CN})]^+$ (**4c**) and $[(\text{C}_6\text{H}_4(o\text{-MeO})\text{C}=\text{C}(\text{Cl})\text{CH}_2\text{N}(\text{CH}_3)_2\text{-}\kappa\text{O}, \kappa\text{C}, \kappa\text{N})\text{Pd-Cl-Pd}(\text{C}_6\text{H}_4(o\text{-CH}_3\text{O})\text{C}=\text{C}(\text{Cl})\text{CH}_2\text{N}(\text{CH}_3)_2\text{-}\kappa\text{O}, \kappa\text{C}, \kappa\text{N})]^+$ (**4a**). ESI-MS spectra analysis of acetonitrile solutions of the monomeric palladacycles $\text{Pd}[\kappa^1\text{-C}, \kappa^1\text{-N-C}=(\text{Y-2-C}_6\text{H}_4)\text{C}(\text{Cl})\text{CH}_2\text{N}(\text{CH}_3)_2](\text{Cl})(\text{Py})$ (**5**, Y = H and **6**, Y = CF₃) allows the detection of some of the same species observed in the spectra of the dimeric palladacycles, i.e., monometallic cationic **2d-3d**, **2e-3e** and $\{\text{Pd}[\kappa^1\text{-C}, \kappa^1\text{-N-C}=(\text{Y-2-C}_6\text{H}_4)\text{C}(\text{Cl})\text{CH}_2\text{N}(\text{CH}_3)_2](\text{Py})\}^+$ (**5a**, **6a**) and $\{\text{Pd}[\kappa^1\text{-C}, \kappa^1\text{-N-C}=(\text{Y-2-C}_6\text{H}_4)\text{C}(\text{Cl})\text{CH}_2\text{N}(\text{CH}_3)_2](\text{CH}_3\text{CN})(\text{Py})\}^+$ (**5b**, **6b**) and the bimetallic **2a**, **3a**, **2b**, **3b**, **2c** and **3c**. In all cationic complexes detected by ESI-MS, the cyclometallated moiety was intact indicating the high stability of the four or six electron anionic chelate ligands. The anionic (chloride) or neutral (pyridine) ligands are, however, easily replaced by the acetonitrile solvent.

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1. Introduction

Palladacycles containing a Pd–C bond, intramolecularly stabilized by at least one Pd–hetero-atom bond (Fig. 1), are easily accessible through various methods

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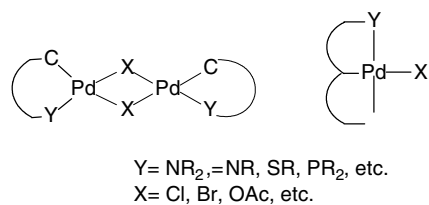


Fig. 1. Typical skeleton of dimeric and pincer type palladacycles.

such as C–H bond activation, oxidative addition of aryl halides to Pd(0) precursors, transmetalation using organo-alkali reagents, transcyclopalladation and chloropalladation (for reviews see [1]).

Palladacycles are usually present both in solution and the solid state as neutral halogen dimers or are of the monomeric pincer type (Fig. 1). The possibility of modulating their steric and electronic properties by changing the nature of the metallated carbon (sp³ or sp²), donor atom (N, P, S, etc.), size of the ring (3-, 4-, 5-, 6-, 7-, 8- and 9-membered), and type of the X ligand (i.e. rendering the complex neutral or ionic) infers to this class of compounds various important applications such as catalyst precursors, intermediates for organic syntheses, liquid crystals, photo and electro-luminescent devices, and drugs (cytotoxic agents), see for example [2]. Most of these applications involve the use of palladacycles dissolved in organic solvents in which it is often assumed that the neutral nature of the halogen dimers or pincer type structures is usually maintained [1,2]. Indeed, classical spectroscopic data such as NMR experiments confirm this assumption for the majority of palladacycles. It has been proposed, however, in particular for C–C bond-forming reactions promoted by palladium catalyst precursors, that ionic species (either cationic or anionic) are formed in solution (see for example [3]), but so far no such ionic species have been unambiguously detected in solutions of neutral halogen dimers or pincer palladacycles (see Fig. 1) even in solvents of relatively high coordinating ability such as acetonitrile (compared to other classical organic solvents).

We have recently reported that palladacycles derived from the chloropalladation of hetero-substituted alkynes [4] are among the most simple and effective catalyst precursors for the Heck coupling reaction [5], whereas some of them possess interesting photo-luminescent properties in solution [6]. It is, therefore, of great interest to investigate whether these neutral complexes can generate ionic species when dissolved in organic solvents.

Electrospray (ESI) is a soft and wide-ranging ionization technique that has revolutionized the way molecules are ionized and transferred to mass spectrometers for mass and property measurements, and structural characterization [7]. Although electrospray mass (and tandem mass) spectrometry has been mainly and most

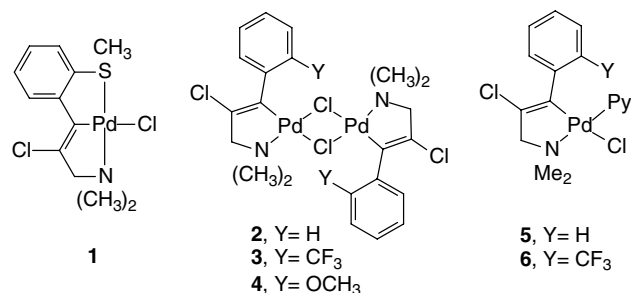


Fig. 2. Structures of palladacycles 1–6.

successfully applied to the analysis of biomolecules [8], it has been increasingly used as a powerful structural characterization technique for organometallic and coordination compounds [9], transient intermediates [10], as well as for the study of intrinsic coordination catalysis [11]. In these cases, the data obtained by ESI experiments can be used as a model for the reactivity of complexes in *solution* in terms of selectivity, stability, ligand exchange processes and represent a method to observe “intermediates” in catalytic reactions [12].

The possibility of the formation of ionic palladacyclic species when dissolved in organic solvents, even in very low concentrations, points to electrospray mass spectrometry (ESI-MS) in both positive and negative modes as an appropriate detection technique. We report herein the first ESI-MS detection and ESI-MS/MS characterization of gaseous ionic and highly electronic unsaturated palladacycle species formed when neutral chloro bridged dimers and pincer type palladacycle complexes (Fig. 2) are dissolved in acetonitrile.

2. Results and discussion

Compounds 1–7 (Fig. 2) were chosen for they are quite representative of the palladacycle family and have been already fully characterized [4,13] both in solid state and solution, which facilitates the comparison of their structural solution NMR patterns with those observed herein by ESI-MS and ESI-MS/MS.

Fig. 3 shows the ESI(+) mass spectrum of an acetonitrile solution of palladacycle 1. Through ESI, three cationic palladacycles (**1a–1c**) are transferred from the solution to the gas phase (Scheme 1), and are therefore detected by mass spectrometry. It is likely that the solution contains mainly **1**, but neutral **1** is in equilibrium with **1a** and Cl[−]. Because palladium displays six abundant isotopes, [¹⁰²Pd (1.02%), ¹⁰⁴Pd (11.14%), ¹⁰⁵Pd (22.33%), ¹⁰⁶Pd (27.33%), ¹⁰⁸Pd (26.46%), ¹¹⁰Pd (11.72%)], the cationic complex **1a** is detected by MS as an isotopomeric cluster of singly charged ions centered at *m/z* 348 (for ¹⁰⁶Pd), and with an isotopic pattern that matches perfectly that calculated for C₁₂H₁₅ClNPdS (Fig. 3).

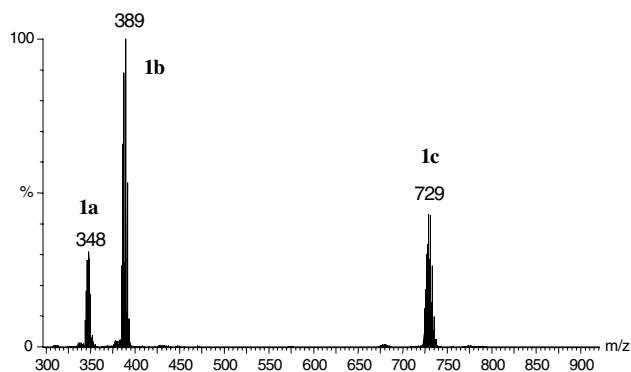


Fig. 3. ESI(+)-MS spectrum of the acetonitrile solution of the palladacycle **1**. For the structures of the marked ionic palladacycles, see Scheme 1.

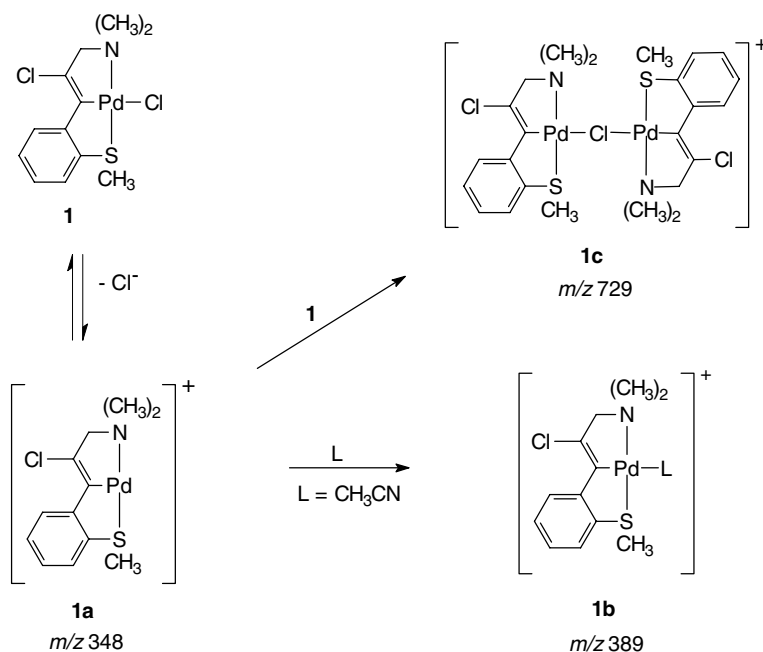
In solution, **1a** associates with the acetonitrile solvent (L) forming **1b**, which is transferred to the gas phase by ESI and detected by MS as an ionic cluster centered at m/z 389 (**1b**). Additionally, **1a** associates also with the neutral palladacycle molecule **1** forming the bimetallic ionic specie **1c**, which is seen in the ESI-MS spectrum as an ionic cluster centered at m/z 729. The isotopic pattern for **1c** is also consistent with that calculated for a Pd_2 -species. Fig. 4(a) shows now the ESI-MS/MS tandem mass spectrum of gaseous **1c**, that is, of the entire ionic cluster centered at m/z 729. The precursor ion **1c** loses, upon collision activation and Pd–Cl bond cleavage, a neutral fragment of 381 Da to form the ionic cluster centered at m/z 348 (**1a**). The ESI-MS/MS spectrum of gaseous **1b** (m/z 389) also shows major dissociation to **1a** owing to the loss of the acetonitrile ligand and breaking

of the weakest Pd–NCCH₃ bond (Fig. 4(b)). The ESI-MS/MS spectrum of gaseous **1a** (m/z 348) is rather interesting: it shows a major dissociation route involving HCl loss to form the cluster of a Pd-containing isotomeric fragment ions centered at m/z 312 followed by the loss of a “sole” Pd atom to form the fragment ion of m/z 204 (Fig. 4(c)). Note the great simplification of the isotope pattern of the m/z 204 ion owing to its zero Pd composition. One probable pathway for this fragmentation is shown in Scheme 2.

Under the same experimental ESI(+)-MS conditions, the spectra of the chloro dimer compounds **2** and **3** (Fig. 5) display two classes of cationic palladacycles (Scheme 3). The first class is composed of the bimetallic cationic palladacycles **2a** and **3a** formed, likely, by ionization of **2** and **3** in the acetonitrile solution (in equilibrium with chloride) and their corresponding mono **2b** and **3b** and di-acetonitrile adducts **2c** and **3c**, all of them displaying matching isotopic patterns. The second class is composed of monometallic highly electronically unsaturated (12 electron) species **2d** and **3d** and their corresponding mono (**2e**, **3e**) and di-acetonitrile adducts (**2f**, **3f**). Species **2d** and **3d** are formed by the cleavage of the Pd–Cl bond of **2a** and **3a**, respectively (Scheme 3).

In order to get some insight on the relative energy of the mono-palladium cationic species observed in the ES-MS, the energy of **2d**, **2e** and **2f** (Fig. 6) was calculated by means of full geometry optimization without any constraint.

The calculations were performed with the GAUSSIAN 98’5 program at a HF/B3LYP level of theory, using a Dunning–Huzinaga DZ95 basis set complemented with



Scheme 1.

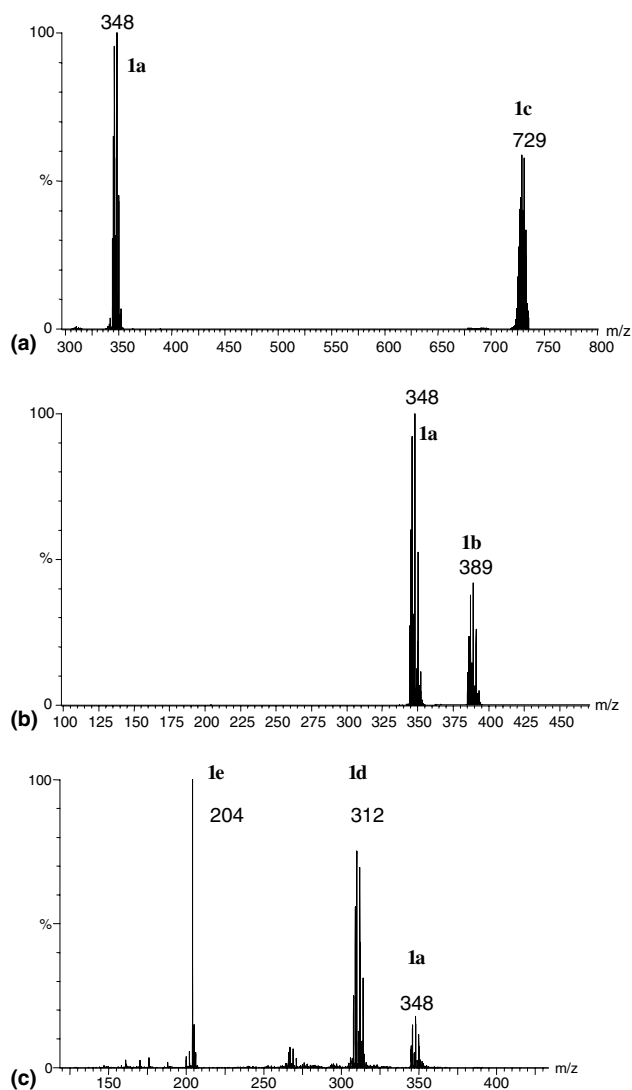


Fig. 4. ESI(+)-MS/MS spectra of (a) **1c** (ionic cluster centered at m/z 729), (b) **1b** (m/z 389), and (c) **1a** (m/z 348).

polarization functions for the non-metal atoms and a DZ valence basis set plus an effective core potential for the palladium. The relative energies were obtained by addition of one and two acetonitrile molecules to the

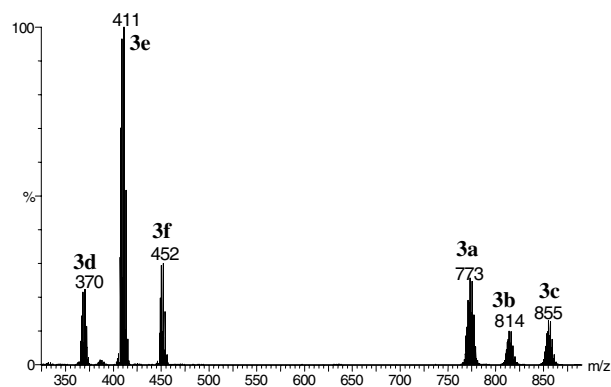
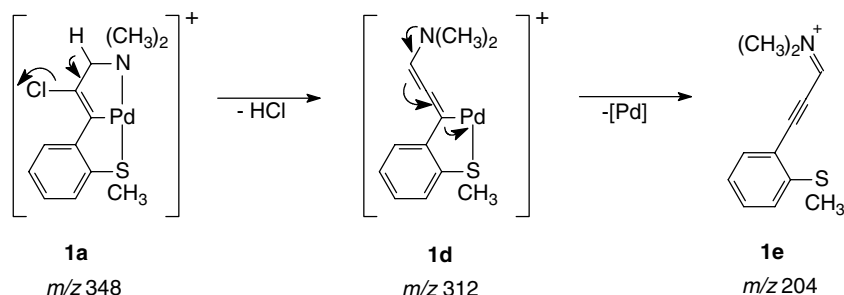


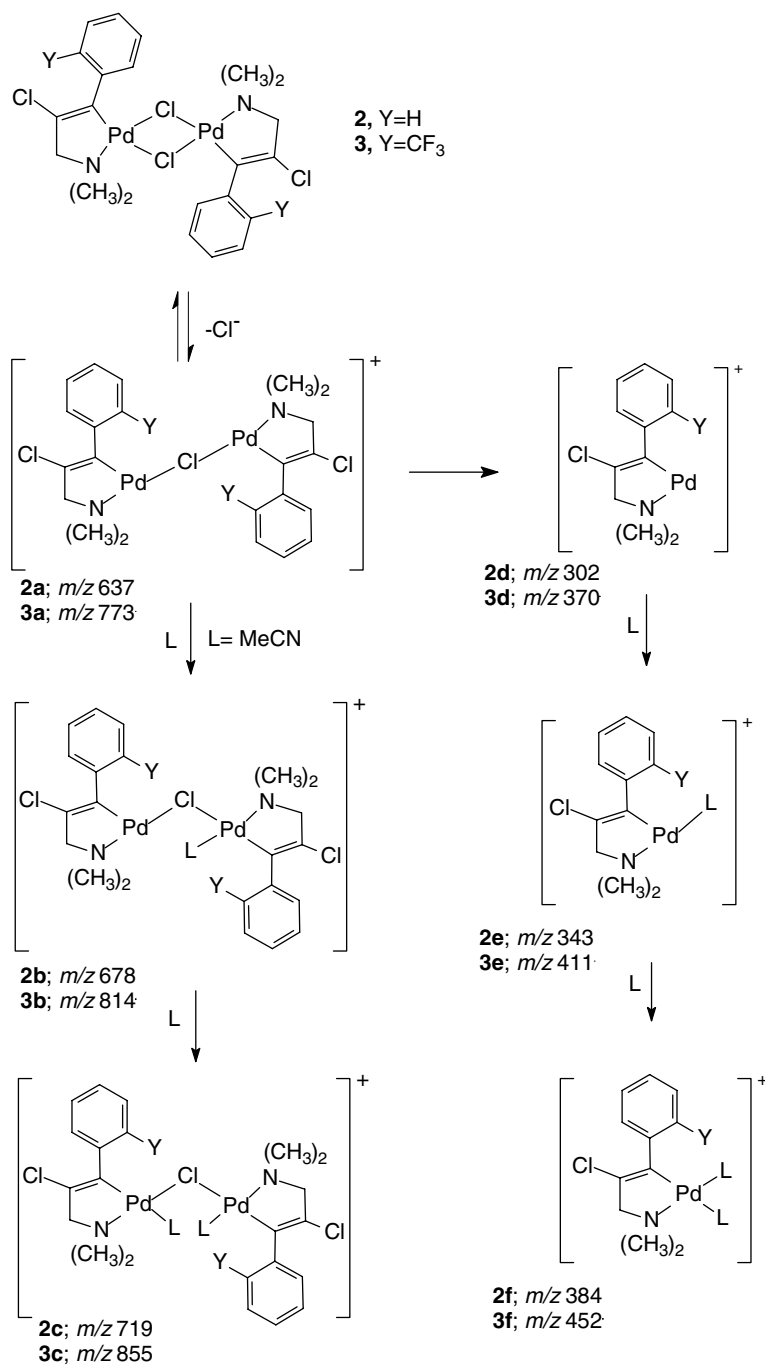
Fig. 5. ESI(+)-MS spectrum of the acetonitrile solution of the palladacycle **3**. For the structures of the marked ionic palladacycles, see Scheme 2.

optimized geometry of **2d** and they are summarized in Fig. 7.

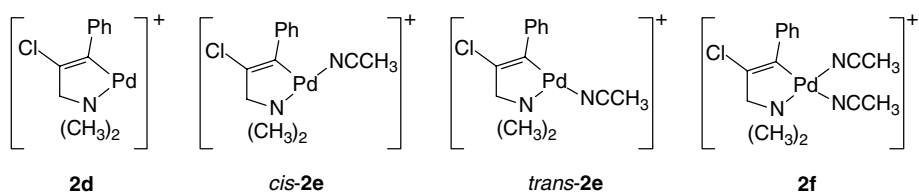
As expected the most stable compound is the 16-electron cationic **2f** and the most energetically unstable is the 12-electron **2d**. Of note, the 14 electron *cis*-**2e** (acetonitrile–Pd–C bond) geometry is 2.3 kcal/mol more stable than its *trans*-**2e** counterpart. This is most probably a result of the larger *trans* influence of the C ligand as compared to the dimethyl amino group. Indeed, the Pd–NCCH₃ bond in *trans*-**2e** is 0.113 Å longer than in its *cis*-**2e** isomer. This bond difference is similar to that found in the bis acetonitrile adduct **2f** (*trans*-C–Pd–NCCH₃ = 2.234 Å and *trans*-Me₂N–P–NCCH₃ = 2.081 Å). Moreover, this bond distance difference is in the same order of magnitude to those encountered in the vast majority of monomeric palladacycles [14]. The formation of compound **2e** is formally resulting from the addition of one acetonitrile molecule to the **2d** compound. It is expected that the acetonitrile addition should occur preferentially *cis* to the Pd–C bond, since the soft Pd(II) center will place the incoming acetonitrile ligand *cis* to the Pd–C bond (antisymbiotic effect) [15]. Of note, the vast majority of addition/substitution reactions involving halogen dimer palladacycles with 2 electron donor ligands occurs preferentially *cis* to the Pd–C bond [16].



Scheme 2.



Scheme 3.

Fig. 6. Monometallic palladacycles observed by ES-MS of **2** in acetonitrile.

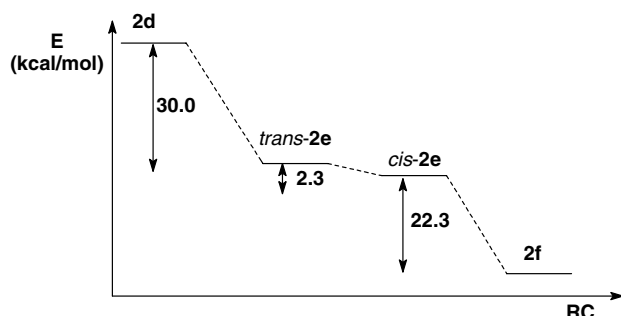


Fig. 7. Calculated relative energy of the compounds **2e** and **2f** obtained by addition of one and two acetonitrile molecules to **2d**.

The ESI(+) mass spectrum (Fig. 8) of the dimeric palladacycle **4** ($Y = \text{OCH}_3$, Fig. 2) is unique, since only three cationic species are detected: **4a–4c** (Scheme 4).

Note that **4a–4c** have likely structural skeleton analogous to those of **1a–1c** from **1** (Scheme 1). Similarly, species **4a** (m/z 699) is formed by ionization of neutral **4** in the acetonitrile solution, whereas **4b** (m/z 332) is formed from **4a** by the breaking of the labile Pd–Cl–Pd bond. In great contrast with the analogues **2a** and **3a**, which undergo both mono and di-acetonitrile addition to a great extent, no acetonitrile addition at all is observed for **4a**, whereas just one molecule of acetonitrile adds to **4b** to form **4c** (m/z 373). This restricted acetonitrile coordination, herein easily perceived from the ESI-MS spectrum, results very likely from intramolecular Pd-coordination of the ortho methoxy group, which prevents further acetonitrile coordination (Scheme 3). Note that the dimeric nature of **4** has been unambiguously established by an X-ray study and that the formation of the pincer type compound with Pd-coordinated methoxy groups, similar to those described in Scheme 3, has already been speculated in solution from NMR studies [13a]. Moreover, theoretical calculations indicated that the most stable geometries for compounds **4b** and **4c** are that those containing the methoxy moiety coordinated to the palladium cen-

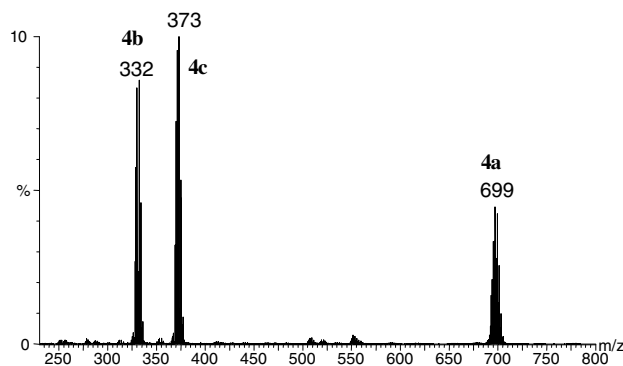


Fig. 8. Positive ESI-MS of an acetonitrile solution of palladacycle **4**. For the structures of the marked ionic palladacycles, see Scheme 3.

ter. The calculated Pd–OCH₃ distances for **4b** and **4c** were 2.131 and 2.151 Å, respectively. These bond distances are slightly shorter than those observed by X-ray studies in other palladacycles for Pd–O=C (2.163 Å) [17] and for Pd–O(R)CH₃ (2.236 Å) [18] bonds.

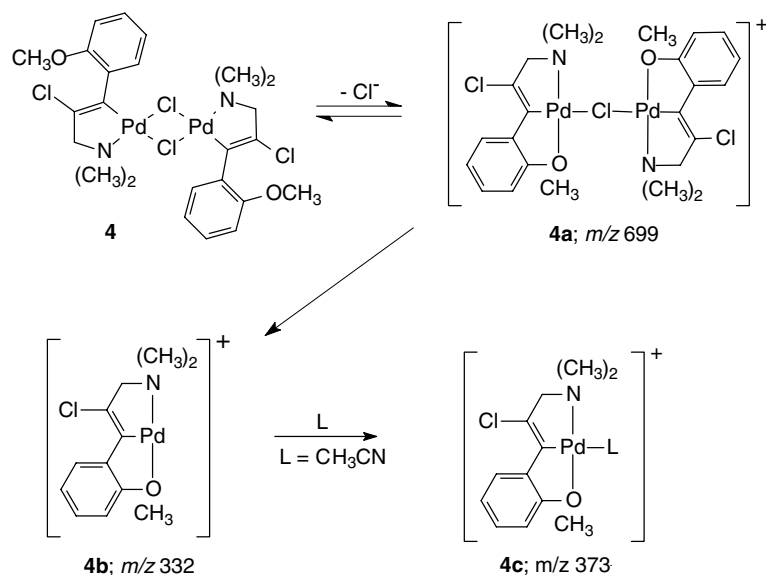
The ESI-MS/MS spectrum of Fig. 9(a) shows **4a** dissociating mainly to **4b** (m/z 332), whereas that of Fig. 9(b) shows **4c** (m/z 373) dissociating, as expected, also to **4b** (m/z 332) by acetonitrile loss.

The ESI(+) mass spectra of the monomeric monometallic palladacycles **5** and **6** (Fig. 10) display a total of seven classes of cationic palladacycles. The first class is constituted of the cationic species **5a** and **6a** formed by direct ionization of **5** and **6** in the acetonitrile solution; the second class, **5b** and **6b**, is formed by further acetonitrile coordination. The third class is composed of the bimetallic cationic palladacycle **5c** and **6c** formed by dimerization with the release of the two pyridine ligands. Two other classes are formed by mono and di addition of acetonitrile to **5c** and **6c**, that is, species **5d–6d** and **5e–6e**, respectively. The last two classes are composed of species **5f** and **6f** formed by the cleavage of the Pd–Py bond from **5a/6a** and their acetonitrile mono adducts **5g–6g** (Scheme 5). Note that formation of **5f** and **6f** can also be assumed to occur via Pd–Cl bond cleavage of **5c** and **6c**.

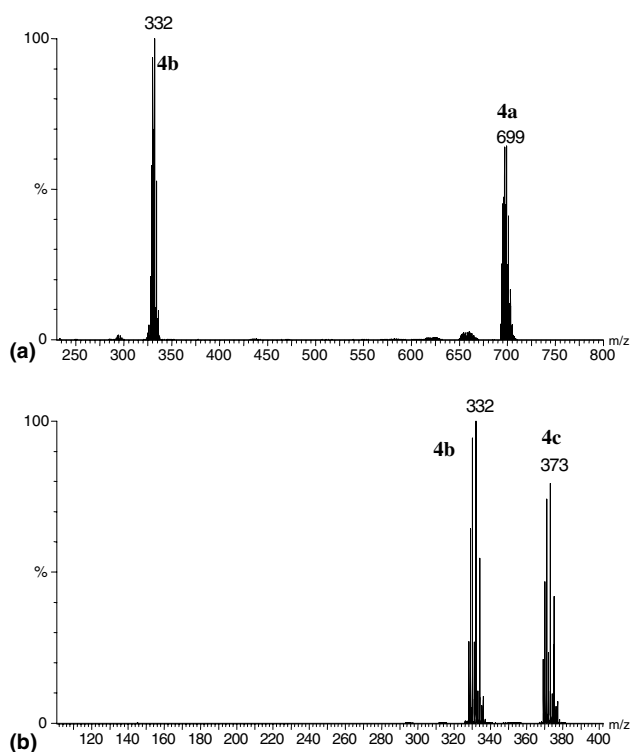
Bimetallic complexes where one of the chloro bridged ligands is substituted by a two-electron ligand such as acetonitrile (see Schemes 3–5) have been proposed, but never detected, as intermediates in the chloro-bridged splitting reaction of halogen dimer palladacycles [16]. Moreover, the ¹H NMR spectra of compounds **1–6** in deuterated acetonitrile show the presence in solution of the classical *cisoid* and *transoid* isomers in the case of the dimers **2–4** and a single component for the other palladacycles. It is clear from the present ESI-MS data that the cyclopalladated moiety remains intact during de ESI process, whatever the precursors (pincer **1**, chloro dimer **2** and **3** or monomeric **5** and **6**). The other ligands (chloro and pyridine) are, however easily released in, or replaced by, acetonitrile (a weakly coordinating ligand).

It is important to note that in order to obtain by ESI a gas phase composition of ions that most closely reflect that in solution, the cone voltage was set to minimize both gas phase association and dissociation processes. The ideal ESI cone voltage for such systems was found to be near 10 V for the palladacycles investigated herein.

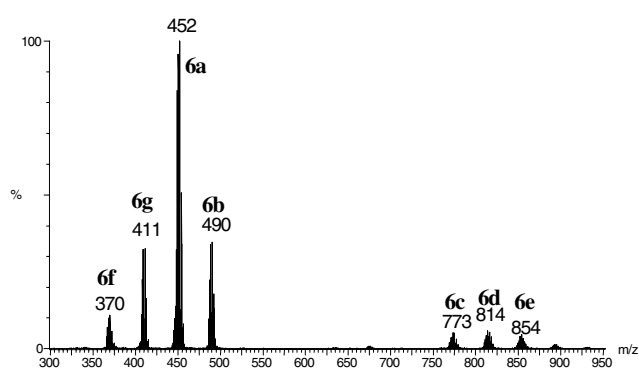
ESI is proving to be a suitable technique for the investigation of ionic palladium species containing weakly coordinating groups such as **4a–c**, in which the benzene ring methoxy substituent is coordinated intramolecularly to the central Pd atom. Note that such fine structural detail would be hard to detect by other



Scheme 4.

Fig. 9. ESI-MS/MS spectra of (a) **4a** of *m/z* 699 and (b) **4c** at *m/z* 373.

classic spectroscopic techniques. The ESI-MS data presented herein show that the formation of cationic complexes in solution is likely to be a much more general trend of palladacycles, and their formation should be considered when analyzing the solution properties and behavior, and catalytic activity of palladacycles. Finally, as already proposed, due to the intrinsic soft ionization pattern of ESI mass spec-

Fig. 10. Positive ESI-MS of palladacycle **6**. For the structures of the marked ionic palladacycles, see Scheme 5.

trometry can constitute an efficient method for the characterization of metal complexes in solution [12].

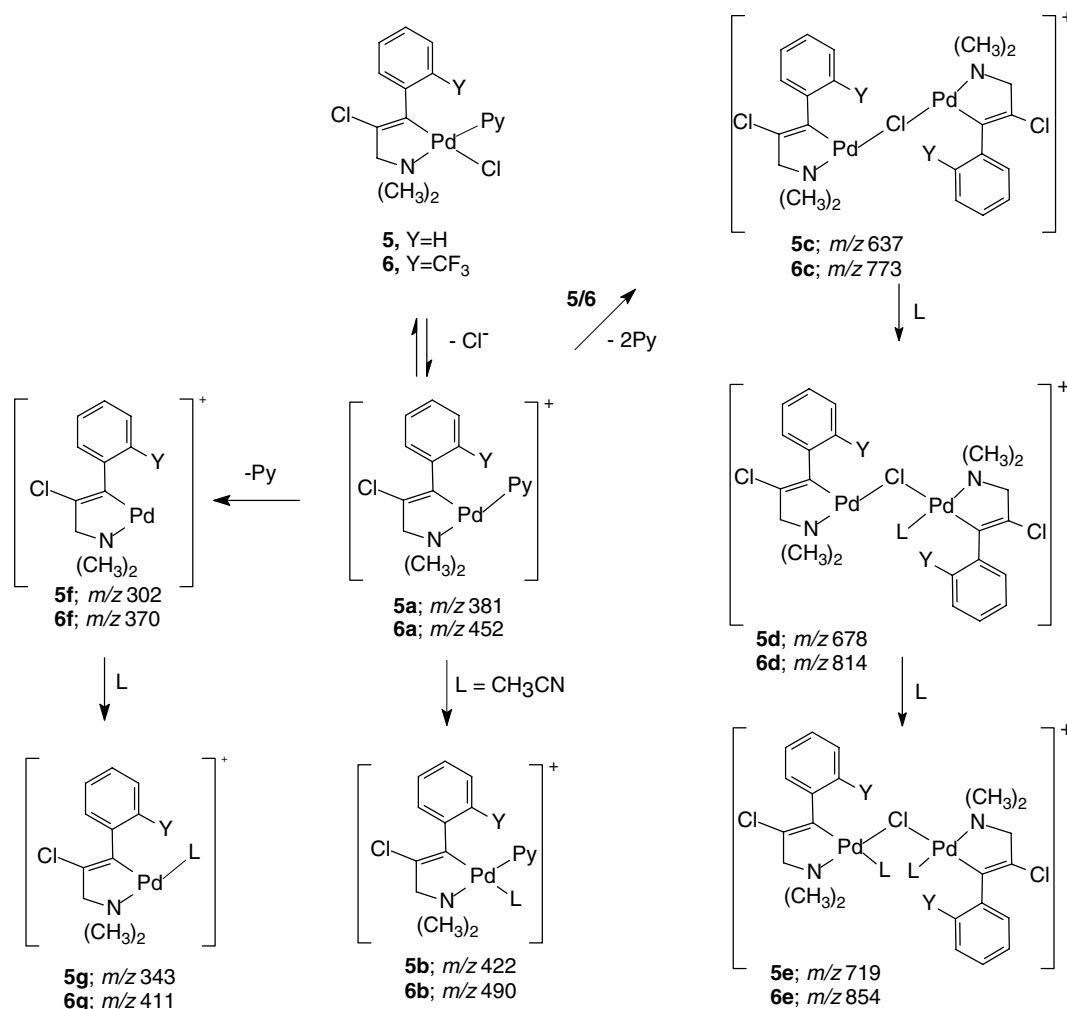
3. Experimental

3.1. General methods

All reactions involving organometallic compounds were carried out under argon or nitrogen atmosphere in oven dried Schlenk tubes. The palladacycles were prepared according to known procedures [13], and their purity was checked by 1H and ^{13}C NMR, IR and CHN analysis. Solvents were dried with suitable drying agents and distilled under argon prior to use.

3.2. ES-MS experiments

Electrospray mass and tandem mass spectra were recorded on a Q-ToF (Micromass) mass spectrometer with



Scheme 5.

a scanning quadrupole (Q), a collision-cell “rf-only” quadrupole (q) and a high-resolution orthogonal time of flight (o-TOF) configuration. The sample introduction was performed using a syringe pump (Harvard Apparatus, Pump 11) set to 10 $\mu\text{l}/\text{min}$ pumped through an uncoated fused-silica capillary. All samples were dissolved in acetonitrile. The ESI-MS mass spectra were acquired using an ESI capillary voltage of 3 kV and a cone voltage of 10 V. Isotopic patterns were calculated using the MassLynx software.

3.3. Theoretical calculations

The energy of all calculated species was obtained by full geometry optimization without any constraint. The calculations were performed with the GAUSSIAN 98' [19] Program at a HF/B3LYP level of theory, using a Dunning–Huzinaga DZ95 [20] basis set complemented with polarization functions for the non-metal atoms and a DZ valence basis set plus an effective core potential for the palladium [21].

Acknowledgements

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