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# Charge-Tagged Acetate Ligands As Mass Spectrometry Probes for Metal Complexes Investigations: Applications in Suzuki and Heck Phosphine-Free Reactions

Felipe F. D. Oliveira,[†] Marcelo R. dos Santos,[†] Priscila M. Lalli,[‡] Eduardo M. Schmidt,[‡] Peter Bakuzis,[†] Alexandre A. M. Lapis,[§] Adriano L. Monteiro,[⊥] Marcos N. Eberlin,*[,‡] and Brenno A. D. Neto*[,†]

[†]Laboratory of Medicinal and Technological Chemistry, Chemistry Institute, University of Brasília (UnB), Campus Universitário Darcy Ribeiro, CEP 70904-970, P.O. Box 4478, Brasília-DF, Brazil

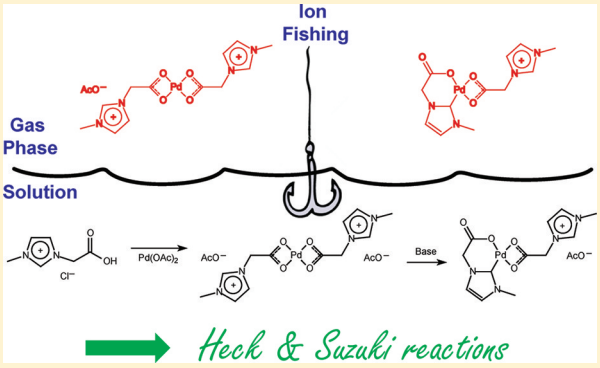
[‡]ThoMSon Mass Spectrometry Laboratory, University of Campinas-UNICAMP, Campinas, SP, Brazil

[§]Universidade Federal da Fronteira Sul, Chapecó, SC, Brazil

[⊥]Laboratory of Molecular Catalysis, Institute of Chemistry, UFRGS, 91501-970, Porto Alegre, RS, Brazil

Supporting Information

**ABSTRACT:** An acetate anion bearing an imidazolium cation as its charge tag was reacted with $M(OAc)_2$ complexes (where M = Ni, Cu, and Pd; *in situ* reaction) to form members of a new class of charge-tagged metal complexes. The formation of these unprecedented precatalysts with potential for cross-coupling reactions was confirmed by electrospray ionization (and tandem) mass spectrometry. The catalytic performance of the palladium complex was tested in Heck and Suzuki cross-coupling reactions, often with superior activity and yields as compared with $Pd(OAc)_2$.




## INTRODUCTION

The task of elucidating the mechanism of ligand exchange and aggregate formation, the type of coordination, and the metal oxidation states during reactions in which organometallic complexes function as catalysts has been challenging. Metal centers may switch coordination states (or aggregate states) in the presence of different ligands throughout the reaction, forming complexes of distinctive geometries and catalytic activities.[1] The understanding of such dynamic equilibria is therefore of fundamental importance to control organometallic reactions and catalysis.[2] This knowledge is also crucial for designing better (pre)catalysts. NMR, IR, and UV−vis may provide valuable data related to the structure and reactivity of such complexes in dynamic equilibria, but they are often too slow or display overlapping peaks; thus, these techniques may fail to follow fast subtle changes in coordination and aggregation, the number of attached ligands, or the oxidation states of the metals.

Electrospray ionization mass spectrometry (ESI-MS) has been widely used for the online monitoring of reactions.[3] ESI[4] is soft, samples both cations and anions, displays high sensitivity, and allows the immediate transfer to the gas phase, in undisturbed forms, of most ionic species present in the reaction solution. Working in both positive and negative ion modes, ESI(±)-MS monitoring provides, therefore, continuous snapshots of the changing ionic composition of reaction solutions, facilitating the detection of key intermediates.[5] ESI(±)-MS is, however, blind to neutrals, but neutral organometallic species are common reagents and intermediates. Protonation has been the major solution to permit ESI monitoring of neutrals,[6] yet pH adjustments may disturb reaction equilibria or change the reaction pathway. Following a strategy originally developed in the gas phase,[7] charge tags for reactants have been used in solution[8] to facilitate ESI(±) monitoring with little disturbance in reactivity. For organometallic catalysis, this strategy would also be beneficial, and Pd catalysts with $[R_3NR^+]$[9] and $[ArSO_3^-]$[10] tags have been recently prepared and characterized.

Nickel, copper, and palladium are among the most used transition metals in catalysis, and $Ni(OAc)_2$, $Cu(OAc)_2$, and $Pd(OAc)_2$ are commonly used in a plethora of cross-coupling reactions.[11] The acetate anion ($OAc^-$) is one of the most common ligands in catalysts. For instance, $Pd(OAc)_2$ and palladium derivatives have been used in Heck, Suzuki, and Negishi reactions.[12] Ni and Cu are also used as alternative metals in these reactions.[11b,13] These metal complexes are also

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used in many different reactions, such as hydrogenation and hydroamination.[14]

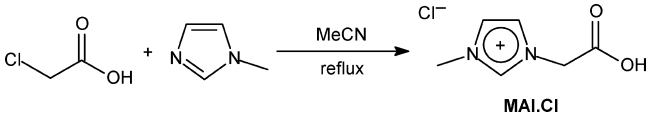
Of special interest is palladium chemistry. It has been suggested that $AcO^-$ anions are coordinated in the Pd center during the neutral Heck mechanism to stabilize the metal in the time of the catalytic cycle.[11d] Moreover, bidentate ligands such as those with carboxylate groups may act as efficient stabilizers for the Pd intermediates in the Heck and Suzuki cross-coupling reactions.[11e]

On the basis of our interest in catalysis[15] and the use of ESI-MS(/MS) to investigate the mechanisms of organic[16] and organometallic[17] reactions, we have envisaged that imidazolium ions would serve as efficient charge tags for acetate anions. In addition, the presence of an imidazolium moiety could generate a bidentate carbene-carboxylate ligand via proton abstraction. Moreover, the new palladium complex could act as an efficient catalyst for palladium-catalyzed cross-coupling reactions.

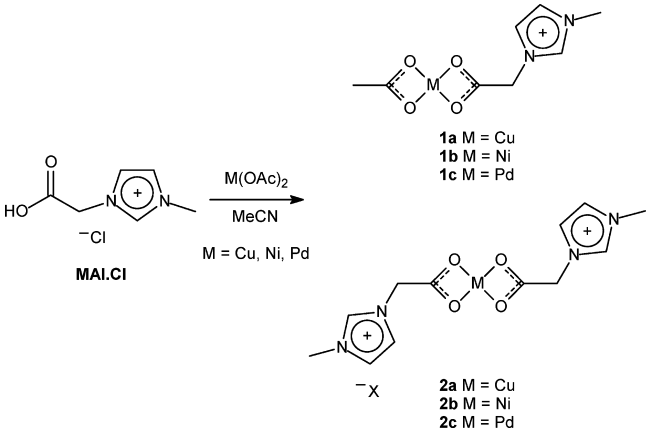
## RESULTS AND DISCUSSION

A charge tag comprised of a 1,3-dialkylimidazolium ion (Scheme 1) was thought to be ideal due to the high thermal stability of ionic liquid derivatives[18] based on 1,3-imidazolium

**Scheme 1. Synthesis of the Charge-Tagged Acetate Ligand**




**Scheme 2. Charge-Tagged Complexes Generated *in Situ* via Reactions of MAI·Cl with Neutral $M(OAc)_2$ Complexes (M = Cu, Ni, Pd)**



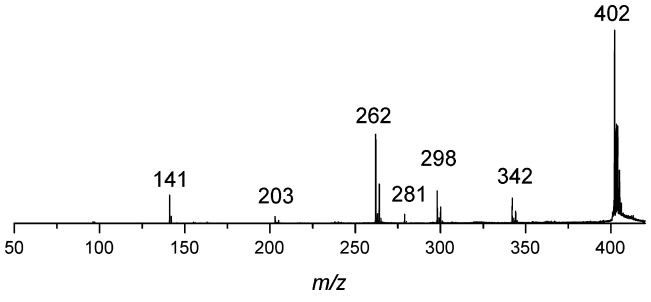




**Figure 1.** ESI(+)-MS of the reaction solution of **MAI·Cl** and $Cu(OAc)_2$.

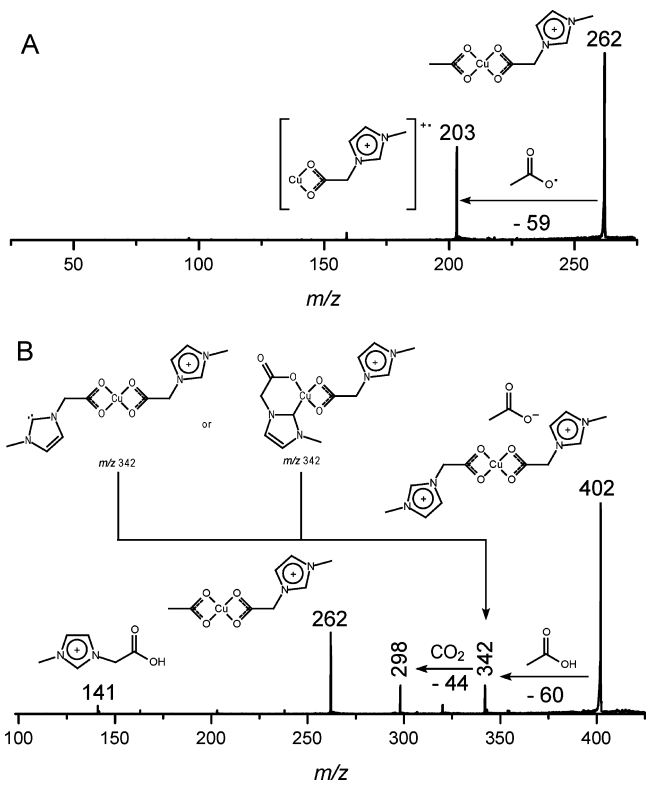
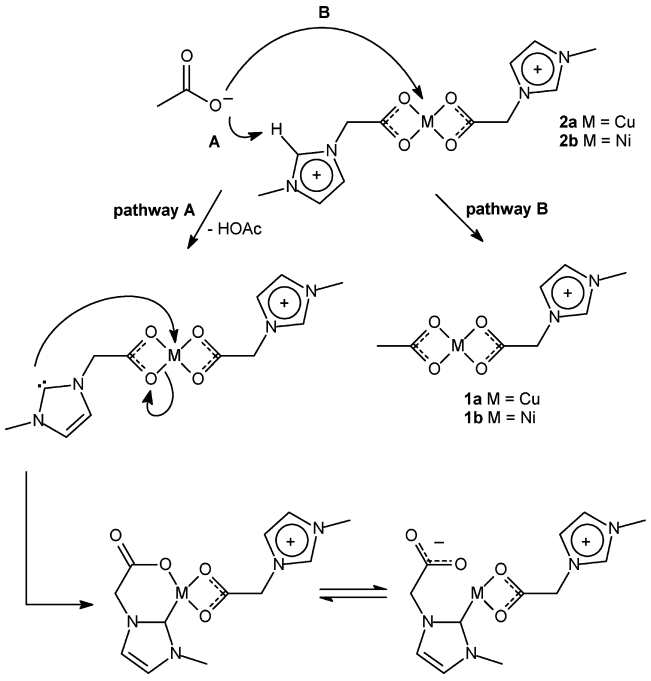



**Figure 2.** (A) ESI(+)-MS/MS of **1a** of $m/z$ 262 and (B) $[\mathbf{2a{\cdot}OAc}]^+$ of $m/z$ 402.

**Scheme 3. Gas-Phase CID-Induced Reactions[a]**




[a]Pathway A leads to the organometallic formation. Pathway B is a ligand exchange.

ions and their nearly universal solubility,[19] as well as highly efficient ESI-MS detection.[20]

The precursor 1-methyl-3-carboxymethylimidazolium (**MAI**) chloride (**MAI·Cl**) was obtained in 95% yield upon treating chloroacetic acid with methylimidazole. With **MAI·Cl** in hand,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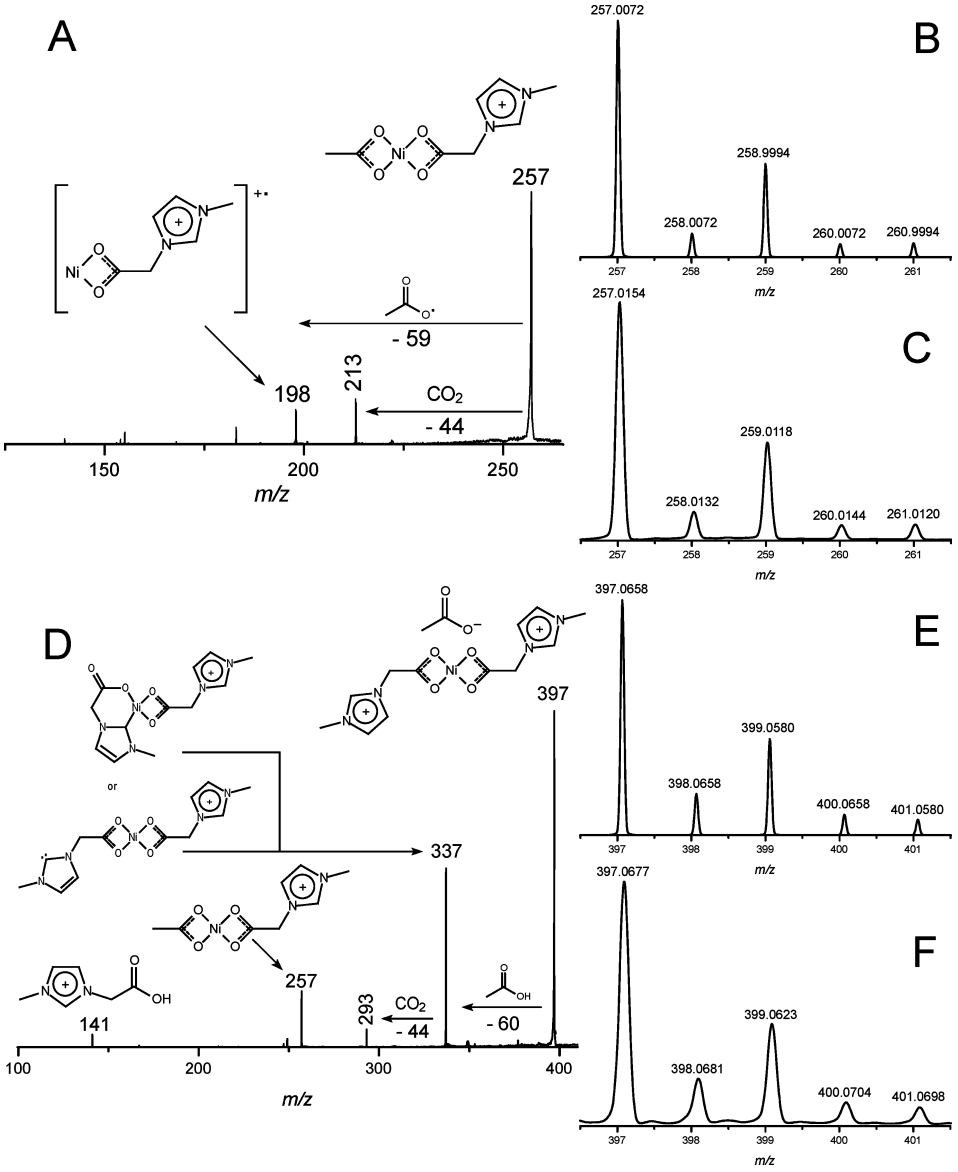


**Figure 3.** ESI(+)-MS/MS of (A) **1b** of *m*/*z* 257 and (D) [**2b·OAc**]$^+$ of *m*/*z* 397. (B and E) Simulated and (C and F) experimental isotopic patterns of **1b** and **2b**.

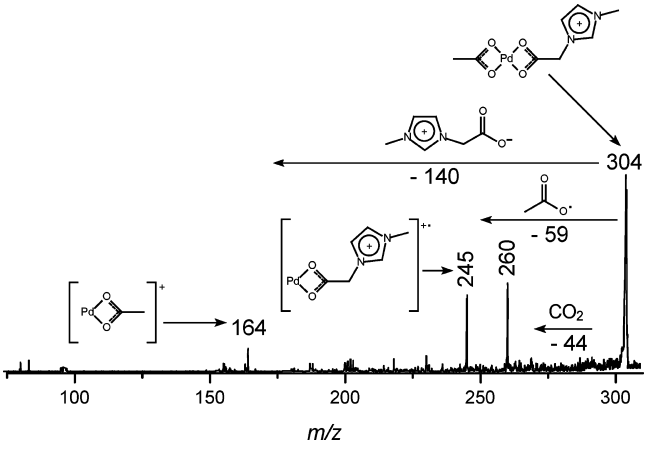


**Figure 4.** ESI(+)-MS/MS of **1c** of *m*/*z* 304.

we treated it with the corresponding neutral complexes $M(OAc)_2$ (M = Cu, Ni, Pd; *in situ* reaction) in acetonitrile and followed the ligand exchange reactions via ESI(+)-MS (Scheme 2).

First, **MAI·Cl** was characterized by high-resolution ESI(+)-MS (see Supporting Information, Figure S1) in a 50 $\mu$M acetonitrile solution. The cationic ligand **MAI·Cl** (two equivalents) was then added to form 50 $\mu$M acetonitrile solutions of $M(OAc)_2$ (M = Ni, Cu, Pd). When the Cu reaction was monitored online by ESI(+)-MS (Figure 1), two pairs of abundant isotopologue ions were rapidly observed: that of *m*/*z* 262 for $^{63}$Cu and *m*/*z* 264 for $^{65}$Cu, corresponding to **1a**, and a second pair of *m*/*z* 402/404 corresponding to [**2a·OAc**]$^+$.

The agreement between the simulated and experimental isotopologue patterns and exact masses (Figure S2) corroborates the proposed structures and elemental compositions of **1a** and [**2a·OAc**]$^+$. These ions were then characterized by ESI(+)-MS/MS (Figure 2).

Upon dissociation, **1a** loses an acetate radical (OAc·) of 59 Da (Figure 2A), whereas **2a** of *m*/*z* 402 shows a much richer dissociation chemistry. Loss of HOAc, which forms the ion of *m*/*z* 342, likely involves the C2−H acid hydrogen of the 1,3-


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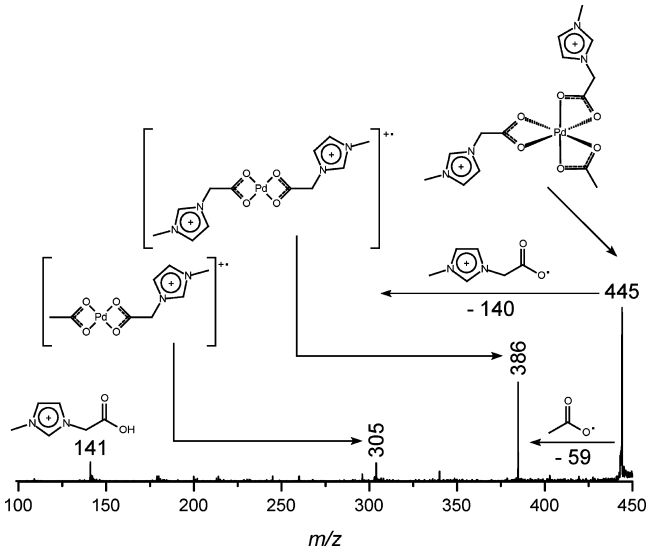



**Figure 5.** ESI(+)-MS/MS of $[\mathbf{2c}\cdot\mathbf{OAc}]^+$ of $m/z$ 445.

imidazolium moiety, forming therefore an unprecedented cationic Cu-organometallic complex with both a charge-tagged acetate anion ligand and a second acetate anion ligand bearing a neutral 1,3-imidazolic carbene substituent (Figure 2, Scheme 3, Pathway A). Most likely, the 1,3-imidazolic carbene (Arduengo-type carbene[21]) replaces the carboxylate, thus coordinating with the Cu center (Scheme 3, Pathway A), in analogy to a nickel complex recently described.[22] This "intramolecular" exchange of ligands seems to explain the subsequent loss of $CO_2$, forming the ion of $m/z$ 298. Exchange by $OAc^-$ of the **MAI** ligand anion would lead to the ion of $m/z$ 262 (Scheme 3, Pathway B).

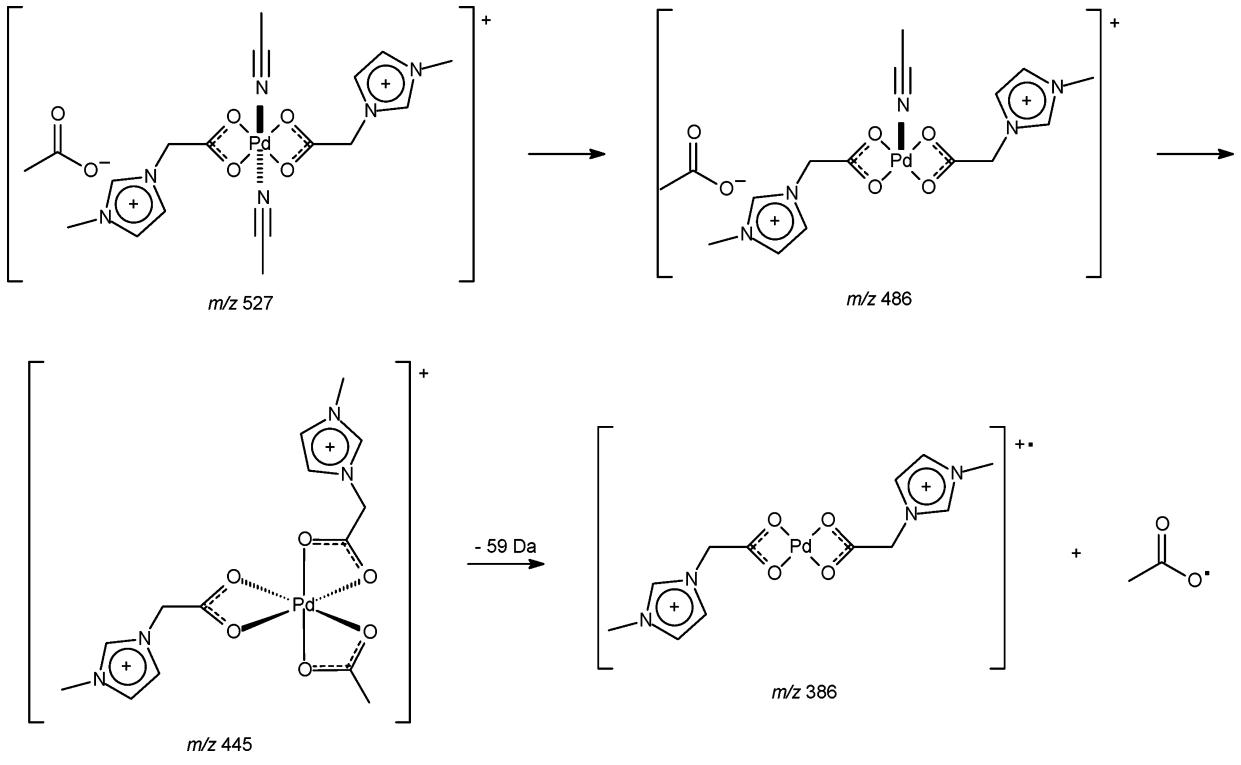
Similar reaction monitoring was performed using $Ni(OAc)_2$, and similar reactivity leading to the desirable singly and doubly charge-tagged complexes was also observed (Figure 3). Dissociation of the ion of $m/z$ 257 (**1b**) again showed the preferential loss of the acetate radical (Figure 3A). The ESI(+)-MS/MS of $[\mathbf{2b}\cdot\mathbf{OAc}]^+$ of $m/z$ 397 shows neutral loss of acetic acid (Figure 3D), as observed earlier for the copper complex, as well as the ligand exchange process (Scheme 3).

Again, ESI(+)-MS(/MS) monitoring of the reaction of **MAI·Cl** with $Pd(OAc)_2$ formed the singly and doubly charge-tagged Pd complexes **1c** and **2c** (Figures S3 and S4, respectively). ESI(+)-MS(/MS) of **1c** (Figure 4) is interesting, because it shows loss of both the charge-tagged acetate ligand ($m/z$ 245) and the radical form of **MAI** ($m/z$ 164). The loss of the OAC radical is therefore preferred. This is an important finding, indicating favored binding of the charge-tagged acetate anion.

A unique gas phase chemistry was also observed with palladium for $[\mathbf{2c}\cdot\mathbf{OAc}]^+$. Whereas the corresponding Cu (Figure 2B) and Ni (Figure 3D) complexes lose AcOH (60 Da), the Pd analogue $[\mathbf{2c}\cdot\mathbf{OAc}]^+$ loses preferentially an AcO radical (59 Da) to form the ion of $m/z$ 386 (Figure 5).

This chemistry seems therefore to indicate that the acetate counteranion is not only attached to the imidazolium ring, as expected for imidazolium-based compounds,[23] but also directly coordinated to the metal center (Figure 5 and Scheme 4), thus, in perfect accordance with the proposition of some intermediates in the neutral Heck reaction with a negative palladium center, as previously discussed by Amatore and Jutand.[11f–j] Note that $[\mathbf{2c}\cdot\mathbf{OAc}]^+$ also loses the charge-tagged ligand to form the ion of $m/z$ 305. Pd complexes may be less sensitive to steric hindrance, thus more prone to coordinate

**Scheme 4. Proposed Route for Dissociation of $[\mathbf{2c}\cdot\mathbf{OAc}]^+$ and MeCN-Coordinated Adducts**[a]




[a]Note that, formally, the Pd center is negative.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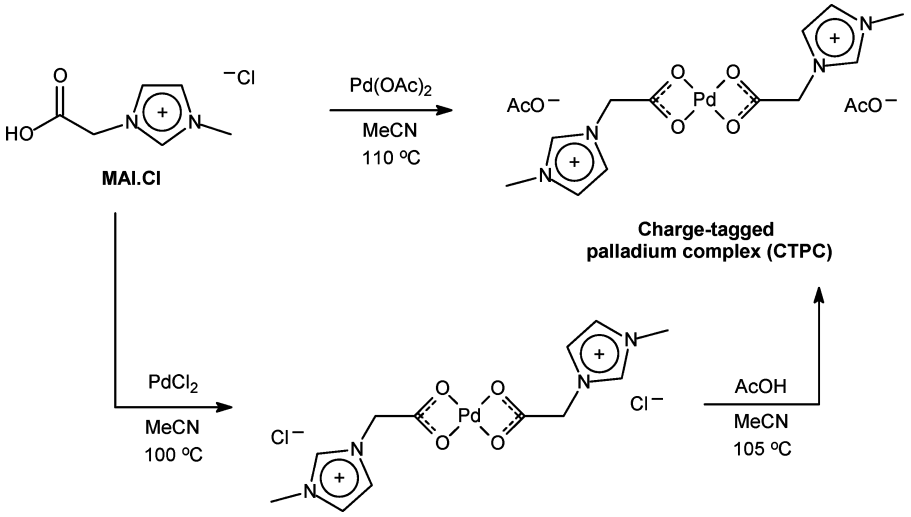
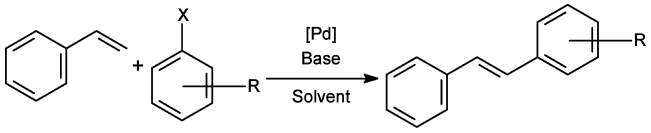
**Scheme 5. Synthesis of the Charge-Tagged Palladium Complex (CTPC) by Two Different Routes**




**Scheme 6. Heck Reaction (phosphine-free condition) Catalyzed by the Charge-Tagged Palladium Complex (CTPC)**




with the solvent (acetonitrile); hence $CH_3CN$ adducts $[\mathbf{2c(MeCN)_2{\cdot}OAc}]^+$ (*m*/*z* 527) and $[\mathbf{2c(MeCN){\cdot}OAc}]^+$ (*m*/*z* 486) were also detected and characterized (Scheme 4). ESI-MSMS analyses show that the ion of *m*/*z* 527 was dissociated, giving the ion of *m*/*z* 486, and the ion of *m*/*z* 486 was dissociated, giving the ion of *m*/*z* 445. This loss indicates that the acetate anion can substitute the solvent molecule in the metal center (Scheme 4).

The *in situ* formation of a bidentate imidazolic carbene-carboxylate ligand from the charge-tagged complexes **2** (Scheme 3) could increase the stabilization of the metal center and make them promising *phosphine-free* catalysts for the cross-coupling reactions. Therefore, an initial screening was performed to determine the best conditions for the Heck and Suzuki cross-coupling reactions. First, we synthesized the charge-tagged palladium complex (**CTPC**, Scheme 5) and used it as the catalyst for the cross-coupling reactions.

For the Heck reaction we chose the coupling of bromobenzene with styrene as model reaction (Scheme 6). And Table 1 summarizes the results.

Among the solvents (DMF, $H_2O$, MeCN, MeOH) and bases ($NEt_3$, NaOAc, $K_2CO_3$, $K_3PO_4$, KOtBu) examined, the best results were obtained using $K_2CO_3$ as the base in MeOH (Table 1, entry 12). Quantitative yields were obtained for bromo- and iodobenzene. The less reactive chlorobenzene gave only traces of coupling product. Note that the catalyst was effective in water for the reaction with iodobenzene (100% yield) and bromobenzene (50%).

To test the catalyst (**CTPC**) for the Suzuki reaction, we chose the coupling of bromobenzene with 4-methoxyphenylboronic acid as the model reaction (Scheme 7, Table 2).

The same bases and solvents were evaluated, and again the best results were obtained using $K_2CO_3$ as the base and MeOH as the solvent (Table 2, entry 12). Quantitative yields were

**Table 1. Results of the Heck Reaction (phosphine-free) Mediated by the Imidazolium-Tagged Palladium Complex (CTPC)[a]**

| entry | X | R | base | solvent | yield (%)[b] |
|---|---|---|---|---|---|
| 1 | Br | H | AcONa | DMF | 19 |
| 2 | Br | H | AcONa | MeCN | 3 |
| 3 | Br | H | AcONa | MeOH | 80 |
| 4 | Br | H | $K_3PO_4$ | DMF | 37 |
| 5 | Br | H | $K_3PO_4$ | MeCN | 2 |
| 6 | Br | H | $K_3PO_4$ | MeOH | 100 |
| 7 | Br | H | KO*t*Bu | DMF | 50 |
| 8 | Br | H | KO*t*Bu | MeCN | traces |
| 9 | Br | H | KO*t*Bu | MeOH | ≈100 |
| 10 | Br | H | $K_2CO_3$ | DMF | 88 |
| 11 | Br | H | $K_2CO_3$ | MeCN | 2 |
| 12 | Br | H | $K_2CO_3$ | MeOH | ≈100 |
| 13 | Br | H | $Et_3N$ | DMF | 28 |
| 14 | Br | H | $Et_3N$ | MeCN | 12 |
| 15 | Br | H | $Et_3N$ | MeOH | 13 |
| 16 | Br | H | $K_2CO_3$ | $H_2O$ | 50 |
| 17 | Cl | H | $K_2CO_3$ | $H_2O$ | traces |
| 18 | I | H | $K_2CO_3$ | $H_2O$ | ≈100 |
| 19 | I | H | $K_2CO_3$ | MeOH | ≈100 |
| 20 | Cl | H | $K_2CO_3$ | MeOH | traces |
| 21 | Br | 4-OMe | $K_2CO_3$ | MeOH | ≈100 |
| 22 | I | 4-OMe | $K_2CO_3$ | MeOH | ≈100 |
| 23 | I | 4-Me | $K_2CO_3$ | MeOH | ≈100 |
| 24 | Br | 4-Me | $K_2CO_3$ | MeOH | ≈100 |
| 25[b] | Cl | H | $K_2CO_3$ | MeOH | traces |

[a]Aryl halide (0.5 mmol), styrene (0.7 mmol), base (1.5 mmol), **CTPC** catalyst (1 mol %), solvent (3 mL), 24 h at 110 °C. [b]Excess of Ph−Cl (2.00 equiv). [c]Yields determined by GC analyses. Isolated yields were slightly lower (≈5−7% of loss).

obtained for bromo- and iodobenzene in the presence of MeOH or water as the solvent. The less reactive chlorobenzene gave only 5% of coupling product.

To confirm the beneficial role of the imidazolium tag, we compared the doubly charged Pd complex with $Pd(OAc)_2$ under the same reaction conditions. We were delighted to see that after one hour of reaction at 110 °C the Heck reaction of bromobenzene with styrene using the charge-tagged complex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**Scheme 7. Suzuki Reaction (phosphine-free condition) Catalyzed by the Charge-Tagged Palladium Complex (CTPC)**

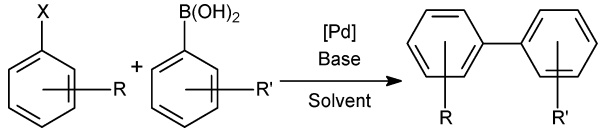


**Table 2. Results of the Suzuki Reaction (phosphine-free condition) Mediated by the Imidazolium-Tagged Palladium Complex (CTPC)[a]**

| entry | X | R | R′ | base | solvent | yield (%)[c] |
|---|---|---|---|---|---|---|
| 1 | Br | H | 4-OMe | AcONa | DMF | 95 |
| 2 | Br | H | 4-OMe | AcONa | MeCN | 90 |
| 3 | Br | H | 4-OMe | AcONa | MeOH | 95 |
| 4 | Br | H | 4-OMe | $K_3PO_4$ | DMF | 25 |
| 5 | Br | H | 4-OMe | $K_3PO_4$ | MeCN | 93 |
| 6 | Br | H | 4-OMe | $K_3PO_4$ | MeOH | ≈100 |
| 7 | Br | H | 4-OMe | KO*t*Bu | DMF | 20 |
| 8 | Br | H | 4-OMe | KO*t*Bu | MeCN | traces |
| 9 | Br | H | 4-OMe | KO*t*Bu | MeOH | ≈100 |
| 10 | Br | H | 4-OMe | $K_2CO_3$ | DMF | 94 |
| 11 | Br | H | 4-OMe | $K_2CO_3$ | MeCN | 90 |
| 12 | Br | H | 4-OMe | $K_2CO_3$ | MeOH | ≈100 |
| 13 | Br | H | 4-OMe | $Et_3N$ | DMF | 50 |
| 14 | Br | H | 4-OMe | $Et_3N$ | MeCN | 80 |
| 15 | Br | H | 4-OMe | $Et_3N$ | MeOH | 80 |
| 16 | I | H | 4-OMe | $K_2CO_3$ | $H_2O$ | ≈100 |
| 17 | Br | H | 4-OMe | $K_2CO_3$ | $H_2O$ | ≈100 |
| 18 | Cl | H | 4-OMe | $K_2CO_3$ | $H_2O$ | 6 |
| 19 | I | H | 4-OMe | $K_2CO_3$ | MeOH | ≈100 |
| 20 | Cl | H | 4-OMe | $K_2CO_3$ | MeOH | 1 |
| 21 | I | 4-OMe | H | $K_2CO_3$ | MeOH | ≈100 |
| 22 | Br | 4-OMe | H | $K_2CO_3$ | MeOH | ≈100 |
| 23 | I | 4-Me | H | $K_2CO_3$ | MeOH | ≈100 |
| 24 | Br | 4-Me | H | $K_2CO_3$ | MeOH | ≈100 |
| 25[b] | Cl | H | 4-OMe | $K_2CO_3$ | MeOH | 5 |

[a]Aryl halide (0.5 mmol), aryl boronic acid (0.7 mmol), base (1.5 mmol), solvent (3 mL), **CTPC** catalyst (1 mol %), 4 h at 130 °C. [b]Aryl halide (1.4 mmol). [c]Yields determined by GC analyses. Isolated yields were slightly lower (≈5−7% of loss).

gave the coupling product in 85% yield, whereas with $Pd(OAc)_2$ the yield was much lower, ca. 6%. This indicates that the novel catalyst **CTPC** is significantly more active than $Pd(OAc)_2$ as the promoter of the Heck reaction.

For the Suzuki reaction of bromobenzene with 4-methoxyphenylboronic acid at 130 °C, quantitative yields were obtained after one hour using both complexes as catalyst. However, when the complexes were compared at room temperature and one hour of reaction time, the Suzuki coupling product was obtained in 95% yield using the charge-tagged complex as compared to 75% using $Pd(OAc)_2$. Once more, the new palladium catalyst showed promising and better activity, despite the fact that the yield for one hour is only slightly higher.

The improved catalytic activity of the charge-tagged acetate Pd complex may arise from base abstraction of the acidic hydrogen of the imidazolium ring (C2−H), thus forming a neutral carbene Pd complex that undergoes cyclization to form

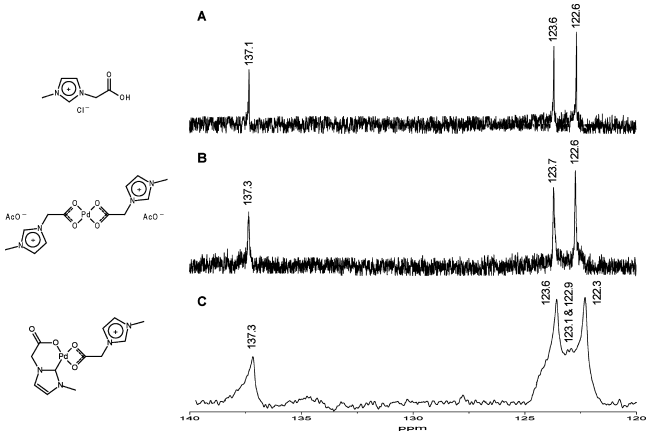


**Figure 6.** Expansion of the imidazolium carbon regions of $^{13}C\{^1H\}$ NMR data (DMSO-$d_6$). (A) For the ligand **MAI**. (B) For the palladium complex (**CTPC**). (C) For the palladium complex after KO*t*Bu addition.

a cyclic organometallic palladium species (Scheme 3). To verify this hypothesis, which is slightly different form the gas phase,[24] we performed $^{13}C\{^1H\}$ NMR experiments with the aim to prove the *in situ* formation of the cyclic organometallic species under the reaction conditions (Figure 6 and Figures S5−S8). Remember that the unsuccessful detection of this palladium organometallic species via MS does not mean the species is not formed, only that it may have a too low intensity or may be in the presence of isobars or near many ions with close $m/z$ values, thus preventing its MSMS characterization.

Fortunately, changes in ion signal occur after the base addition for the imidazolium carbon signals, pointing firmly to the *in situ* formation of the new Pd−C bond likely from the carbene cyclization process depicted in Scheme 3. Interestingly, in the presence of the base (which turns the system biphasic: the solid base and the DMSO-$d_6$ solution with other components), the C4 and C5 positions of the imidazolium ring split into four signals (Figure 6C), while just one signal related to the C2 position is noted, clearly showing the loss of symmetry in the structure of the **CTPC** (Figure 6B). Very low intensity signals at ($\delta$) 174.7, 169.0, and 168.7 ppm are also noted. One signal is related to an acetate anion, the second is related to a MAI anion, and the last is probably the carbene signal. However, because more than 130 000 scans were necessary to see these signals and because they are of low intensity, an exact assignment is not possible. But it points firmly to the interception of the organometallic species.

## ■ CONCLUSION

Novel singly and doubly charge-tagged acetate complexes of Cu, Ni, and Pd have been synthesized *in situ* from reactions of their corresponding neutral complexes $M(OAc)_2$ with a charge-tagged acetate anion. The preferential binding to the metal center of the charge-tagged acetate ligand favors ligand exchange, and highly abundant singly (**1**) and doubly charged complexes (**2**) were promptly formed. Owing to the charge tags, these species were gently and efficiently transferred from the solution to the gas phase and properly characterized by ESI(+)-MS(/MS). These charge-tagged metal catalysts open new avenues for studying, via continuous ESI(+)-MS(/MS) monitoring, the mechanism of catalysis in organometallic reactions and their fast dynamic equilibria in a variety of cross-coupling reactions. Catalytic evaluation of the *phosphine-free*


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doubly charge-tagged complex of Pd demonstrated its superior performance compared with the corresponding neutral Pd(OAc)$_2$. The *in situ* formation of a bidentate imidazolic carbene-carboxylate ligand upon proton abstraction from a charged-tagged Pd complex after base addition, as indicated by the experiments performed, is possibly responsible for the superior catalytic activity of the charge-tagged catalyst. We are currently testing via ESI-MS(/MS) monitoring the use of these charge-tagged complexes of Ni, Cu, and Pd and evaluating their efficiency as catalysts in a variety of cross-coupling reactions.

## EXPERIMENTAL SECTION

**General Methods and Materials.** Styrene was freshly distilled prior to its use, while other reagents and solvents were used as commercially available. The nuclear magnetic resonance spectra of hydrogen ($^1$H NMR) and carbon ($^{13}$C NMR) were obtained with a 300 MHz NMR instrument. Chemical shifts were expressed in parts per million (ppm) and referenced by the signals of TMS or of the residual hydrogen atoms of the deuterated solvents ($CDCl_3$, DMSO-$d_6$, $CD_3OD$, or $D_2O$) depending on the case, as indicated in the figure legends. Gas chromatography analyses were performed using a Shimpack semicapillary column (5% PhMe silicone, 30 m × 0.25 mm × 0.25 μm). GC analyses were performed using the following standard condition: $T$(injector) = 250 °C; $T$(detector) = 250 °C; $T$(column) = 100 °C for 1 min and then a heating rate of 20 °C min$^{-1}$ to 250 °C and remaining at this temperature for 7 min; nitrogen was used as the carrier gas with a standard FID detector. ESI-MS and ESI-MS/MS measurements were performed in the positive ion mode ($m/z$ 50−2000 range) on a Synapt HDMS (high-definition mass spectrometer) instrument. This instrument has a hybrid quadrupole/ion mobility/orthogonal acceleration time-of-flight (oa-TOF) geometry and was used in the TOF mode, with the mobility cell switched off and working only as an ion guide. All samples were dissolved in acetonitrile to form 50 μM solutions and were infused directly into the ESI source at a flow rate of 5 μL/min. ESI source conditions were as follows: capillary voltage 3.0 kV, sample cone 30 V, extraction cone 3 V.

**General Procedure for the Heck Reactions.** A sealed Schlenk tube containing 3 mL of methanol (or the other solvent), 1.5 mmol of $K_2CO_3$ (or other base), 5 μmol of the catalyst (1 mol %), 0.5 mmol of the aryl halide, and 0.7 mmol of styrene was allowed to react at 110 °C. The solvent was removed at reduced pressure, and the pure product was obtained by column chromatography purification.

**General Procedure for the Suzuki Reactions.** A sealed Schlenk tube containing 3 mL of methanol (or the other solvent), 1.5 mmol of $K_2CO_3$ (or other base), 0.7 mmol of the boronic acid, 5 μmol of the catalyst (1 mol %), and 0.5 mmol of the aryl halide was allowed to react at 130 °C. The solvent was removed at reduced pressure, and the pure product was obtained by column chromatography purification.

**Synthesis of the Known Charge-Tagged Imidazolium-Based Ligand (MAI·Cl, 1-methyl-3-carboxymethylimidazolium chloride).** The procedure is adapted from a previous report.[25] A 1.00 mmol amount of chloroacetic acid and 1.10 mmol of methylimidazole were added to anhydrous acetonitrile (2 mL), and the solution was heated at 100 °C for 6 h in a sealed Schlenk tube. After cooling, the mixture was filtered and the resulting solid was washed with ethyl acetate to remove any unreacted methylimidazole. The desired product was obtained as a white solid in 95% yield. $^1$H NMR (300 MHz, $D_2O$): $\delta$ (ppm) 8.83 (s, 1H), 7.52 (t, $J$ = 2.34 Hz, 2H), 5.15 (s, 2H), 3.95 (s, 3H). $^{13}$C NMR (75 MHz, $D_2O$ tube charged with $C_6D_6$ in a sealed capillary tube to set the scale): $\delta$ (ppm) 170.9, 138.1, 125.2, 124.2, 50.7, 36.7. $^1$H NMR ($CD_3OD$, 300 MHz): $\delta$ ppm 8.73 (s, 1H), 7.43 (s, 1H), 7.42 (s 1H), 5.02 (s, 2H), 3.85 (s, 3H). $^{13}$C NMR ($CD_3OD$, 75 MHz): $\delta$ ppm 170.8, 138.6, 124.6, 124.5, 51.0, 36.9. $^{13}$C NMR (DMSO-$d_6$, 75 MHz): $\delta$ ppm 172.0, 137.3, 123.7, 122.5, 35.7, 21.2. IR (KBr, cm$^{-1}$): 3111, 3090, 2984, 2880, 1734, 1580, 1398, 1193, 675, 620. Anal. Calcd for $C_6H_9N_2O_2Cl$: C, 40.81; H, 5.14; N, 15.86. Found: C, 40.90; H, 5.22; N, 15.72.

**Synthesis of the Charge-Tagged Palladium Complex with Chloride Anions.** A 1.00 mmol amount of MAI.Cl, 0.50 mmol of $PdCl_2$, and 2 mL of acetonitrile were mixed in a Shelenk tube. The mixure was refluxed for 15 h to guarantee HCl elimination. The solvent was removed, and the solid washed with ethyl acetate, resulting in the palladium complex in 98% yield. $^1$H NMR ($CD_3OD$, 300 MHz): $\delta$ ppm 8.92 (s, 1H), 7.54 (s, 1H), 7.53 (s, 1H), 5.12 (s,2H), 3.95 (s, 3H). $^{13}$C NMR ($CD_3OD$, 75 MHz): $\delta$ ppm 170.8, 138.4, 124.6, 124.6, 51.0, 36.9. IR (KBr, cm$^{-1}$): 3218, 3177, 3139, 3080, 2969, 1760, 1627, 1568, 1175, 676, 614.

**Synthesis of the Charge-Tagged Palladium Compex with Acetate Anions (CTPC).** (a) A 1.00 mmol amount of **MAI·Cl**, 0.50 mmol of Pd(OAc)$_2$, and 2 mL of acetonitrile were mixed in a Shelenk tube. The mixure was heated at 110 °C for 18 h to guarantee HOAc elimination. The solvent and HOAc were removed under high vacuum, and the solid washed with ethyl acetate, resulting in the palladium complex with acetate anions in 99% yield. (b) A 0.50 mmol amount of the palladium complex with chloride anions and HOAc (2 mL) were heated at 105 °C for 2 h. Excess HOAc was removed under vacuum, and the solid washed with ethyl acetate, resulting in the new complex in 95% yield. $^{13}$C NMR (DMSO-$d_6$, 75 MHz): $\delta$ ppm 175.6, 172.2, 137.3, 123.6, 122.7, 35.7, 30.8, 21.2.

## ASSOCIATED CONTENT

### Supporting Information

Mass and NMR spectra related with this article. These materials are available free of charge via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION

### Corresponding Author

*E-mail: brenno.ipi@gmail.com; eberlin@iqm.unicamp.br.

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