

# Mixed Dicarboxylato–Bis(carbene) Complexes of Palladium(II): Synthesis, Structures, Trans–Cis Isomerism, and Catalytic Activity

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Mixed dicarboxylato–bis(carbene) complexes of palladium(II) have been prepared by reacting *cis*-diiodo-bis(*N,N'*-dimethylbenzimidazolin-2-ylidene)palladium(II) (*cis*-A) with AgO<sub>2</sub>CR, where R = CH<sub>3</sub>, CF<sub>3</sub>, and CF<sub>2</sub>CF<sub>3</sub>. In this manner, *cis*-diacetato-bis(*N,N'*-dimethylbenzimidazolin-2-ylidene)palladium(II) (**1**), *cis*-di(trifluoroacetato)-bis(*N,N'*-dimethylbenzimidazolin-2-ylidene)palladium(II) (**2**), and *cis*-di(pentafluoropropionato)-bis(*N,N'*-dimethylbenzimidazolin-2-ylidene)palladium(II) (**3**) were obtained. Complexes **1–3** were fully characterized by multinuclear NMR spectroscopies as well as ESI mass spectrometry. X-ray crystal structure analyses of the first mixed carboxylato/benzimidazolin-2-ylidene complexes reveal mononuclear species with a square-planar palladium(II) center coordinated by two monodentate carbene and two monodentate carboxylato ligands in a *cis* arrangement. The *cis* configuration was found to be thermodynamically favored in this type of complexes. The results also show that the introduction of N-heterocyclic carbene ligands stabilizes the palladium–carboxylate moiety effectively, thus preventing both reductive decomposition and autoionization processes. A preliminary catalytic study revealed that complexes **1–3** are highly active in the Mizoroki–Heck coupling of aryl bromides and activated aryl chlorides.

## Introduction

C–C coupling reactions of the Heck type are among the most powerful organic transformations<sup>1</sup> used in synthetic chemistry, and many catalysts including Pd/phosphine and Pd/NHC<sup>2</sup> (NHC = N-heterocyclic carbene) systems have been developed. However, the most commonly used catalyst mixture in research laboratories simply contains Pd(OAc)<sub>2</sub> with excess phosphines such as PPh<sub>3</sub> as stabilizing ligands. The formation of Pd(II) phosphine–carboxylates as key intermediates has been proposed, which decompose reductively to form catalytically active Pd<sup>0</sup> species.<sup>3</sup> Other typical side reactions of Pd(II) phosphine–carboxylates leading to catalyst deactivation include phosphine oxidation and the autoionization processes.<sup>4</sup> A stabilization of the Pd carboxylate moiety, which allows a more detailed structural characterization, can be achieved by introducing chelating diphosphines.<sup>5</sup> However, the use of environmentally

unfriendly phosphines, which experience dissociative problems, remains a major disadvantage of such systems.

More recent research has shown that the replacement of phosphines by one bulky monodentate<sup>6</sup> or *cis*-chelating dicarbene<sup>7</sup> ligands not only is feasible but also leads to even more stable Pd–carboxylates, which are catalyst precursors for C–H activation,<sup>7b</sup> aerobic oxidation of alcohols,<sup>6a,b</sup> hydroarylation of alkynes,<sup>6d</sup> and Suzuki–Miyaura couplings.<sup>6c</sup> All these examples contain carbene ligands that are derived from imidazolium precursors, and despite these few reports, mixed carboxylato–carbene complexes in general and their potential application as phosphine-free catalysts remain relatively unexplored. Less attention has also been paid to complexes with benzannulated carbenes, although these may exhibit interesting properties due to their intermediate position between saturated and unsaturated NHCs.<sup>8</sup> We herein present the first palladium–carboxylates supported by benzannulated NHC ligands, their *trans*–*cis*

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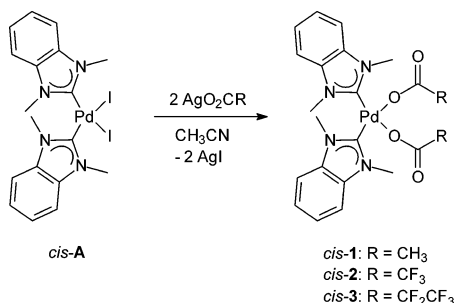
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## Scheme 1. Synthesis of the Carbene Complexes 1–3

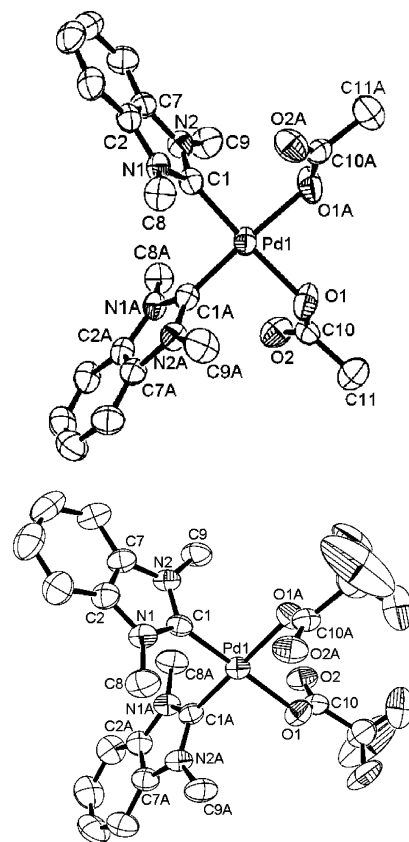


isomerization, and their application as catalyst precursors in Mizoroki–Heck couplings.

## Results and Discussion

**Synthesis and Characterization.** Mixed dicarboxylato–bis(carbene) complexes of palladium(II) can be prepared by reacting free carbenes with Pd(OAc)<sub>2</sub>.<sup>9</sup> However, this method requires the isolation of the free carbenes, which are air- and moisture-sensitive. In addition, it is impracticable for benzimidazolin-2-ylidenes, since these readily undergo dimerization, forming electron-rich enetetramines.<sup>8b,10</sup> A more convenient route, which does not require an inert atmosphere, is the metathesis reaction of easily available and air-stable dihalo–bis(carbene) palladium(II) complexes with Ag–carboxylates.<sup>7</sup> Hence, the mixed carboxylato–carbene complexes **1–3** were prepared by reacting precursor complex *cis-A*<sup>11</sup> with AgO<sub>2</sub>CCH<sub>3</sub>, AgO<sub>2</sub>CCF<sub>3</sub>, and AgO<sub>2</sub>CCF<sub>2</sub>CF<sub>3</sub>, respectively, as depicted in Scheme 1. The complexes were isolated as white and air-stable solids. Even in solution, the complexes are unusually stable, and no palladium black was observed upon prolonged standing, even in polar solvents such as DMSO. In general, the substitution of both iodo ligands in *cis-A* by carboxylates leads to an improved solubility. All novel complexes are soluble in halogenated solvents, acetone, CH<sub>3</sub>CN, DMSO, and DMF and insoluble in nonpolar solvents such as diethyl ether, hexane, and toluene. In addition, the fluorocarboxylato complexes **2** and **3** are also soluble in THF.

The <sup>1</sup>H NMR resonances of the benzimidazolin-2-ylidene ligands in **1–3** remain largely unaffected upon coordination of the carboxylato ligands to the carbene complex fragment. On the other hand, the influence of the various anions is reflected in the <sup>13</sup>C chemical shift of the carbene carbon. The coordination of the acetate anion leads to a slight upfield shift from 175.1 ppm in *cis-A* to 172.4 ppm in **1**. This shielding effect is even greater when fluorocarboxylato ligands are employed, where upfield shifts of the carbene carbon signal to 159.3 and 159.6 ppm for **2** and **3**, respectively, are observed. We have observed a similar but much more pronounced upfield shift in methylene-bridged imidazolin-2-ylidene analogues recently.<sup>7b</sup> The <sup>13</sup>C NMR signals for the CF<sub>2/3</sub> groups of the fluorocarboxylato ligands in **2** (116 ppm, q) and **3** (118.5 ppm, qt, and 106.3 ppm, tq) show the expected splitting pattern due to <sup>13</sup>C–<sup>19</sup>F heteronuclear couplings, which fall in the range of <sup>1</sup>J(C,F) = 264–290 Hz and <sup>2</sup>J(C,F) = 35–37 Hz. In the <sup>19</sup>F NMR spectra, only broad singlets are observed for the CF<sub>2/3</sub> groups, indicating that homonuclear <sup>19</sup>F–<sup>19</sup>F couplings in **3** were not resolved under



**Figure 1.** Molecular structures of the complexes **1** (upper) and **2** (lower).

the given conditions. More importantly, even in the polar solvent DMSO-*d*<sub>6</sub> we did not find any NMR evidence for a possible autoionization process as observed for diphosphine analogues.<sup>4</sup> <sup>1</sup>H NMR spectroscopy showed also no indication for a bridging coordination mode of the carboxylato ligands.

The formation of complexes **1–3** was further confirmed by ESI mass spectrometry. The mass spectra of all complexes in the positive mode are dominated by the fragment peaks [M – O<sub>2</sub>CR]<sup>+</sup> arising from loss of one carboxylato ligand.

Single crystals of complexes **1–3** suitable for X-ray diffraction studies were obtained as solvates by slow evaporation of concentrated CH<sub>2</sub>Cl<sub>2</sub>/toluene (**1**·CH<sub>2</sub>Cl<sub>2</sub>), acetone/toluene (**2**·(CH<sub>3</sub>)<sub>2</sub>CO), and acetonitrile/toluene (**3**·0.5C<sub>7</sub>H<sub>8</sub>) solutions at ambient temperature. The molecular structures of complexes **1** and **2** are depicted as representatives in Figure 1, selected bond parameters are summarized in Table 1, and crystallographic data are listed in Table 2. All three complexes crystallized as mononuclear complexes, in which the palladium center is coordinated by two carbene and two carboxylato ligands in a nearly perfect square-planar geometry (sum of angles around Pd is 360.36° for **1**, 360.22° for **2**, and 360.26° and 360.35° for the two independent molecules of **3**). To the best of our knowledge, **1–3** are the first examples of dicarboxylato–bis(carbene) complexes<sup>6c,9</sup> that show a cis arrangement of their monodentate ligands. The carbene ring planes of all complexes are orientated almost perpendicular to the PdC<sub>2</sub>O<sub>2</sub> coordination plane with dihedral angles ranging from 63° to 75°, which is a common feature for bis(carbene) complexes. More importantly, the Pd–C bonds in **1–3** (1.955–1.969 Å) are significantly shorter than those found in trans-configured analogues (~2.04 Å),<sup>6c,9</sup> reflecting a strong trans influence of the carbene ligands and a preference for the cis arrangement (vide infra). The Pd–C bonds are also shortened when compared to the precursor

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**Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1–3**

|  | 1          | 2          | 3          |            |             |            |
|--|------------|------------|------------|------------|-------------|------------|
|  |            |            | molecule A |            | molecule B  |            |
| Pd1–C1   | 1.964(4)   | 1.964(3)   | Pd1–C1     | 1.955(7)   | Pd2–C25     | 1.965(6)   |
| Pd1–O1   | 2.076(4)   | 2.073(2)   | Pd1–C10    | 1.970(7)   | Pd2–C34     | 1.965(7)   |
| N1–C1  | 1.354(6)   | 1.345(4)   | Pd1–O1     | 2.058(4)   | Pd2–O5      | 2.074(5)   |
| N1–C2  | 1.392(5)   | 1.385(3)   | Pd1–O3     | 2.089(4)   | Pd2–O7      | 2.086(4)   |
| N1–C8  | 1.451(5)   | 1.462(4)   | N1–C1      | 1.351(9)   | N5–C25      | 1.345(9)   |
| N2–C1  | 1.355(5)   | 1.346(3)   | N1–C2      | 1.395(8)   | N5–C31      | 1.388(9)   |
| N2–C7  | 1.389(5)   | 1.391(4)   | N1–C8      | 1.474(9)   | N5–C33      | 1.475(8)   |
| N2–C9  | 1.454(5)   | 1.456(4)   | N2–C1      | 1.349(8)   | N6–C25      | 1.353(8)   |
| C1–Pd1–C1A   | 91.94(16)  | 89.61(11)  | N2–C7      | 1.395(8)   | N6–C26      | 1.392(9)   |
| C1–Pd1–O1  | 174.65(15) | 176.34(10) | N2–C9      | 1.471(9)   | N6–C32      | 1.453(9)   |
| C1–Pd1–O1A   | 91.19(15)  | 91.58(10)  | N3–C10     | 1.347(8)   | N7–C34      | 1.339(7)   |
| O1–Pd1–O1A   | 86.03(13)  | 87.43(8)   | N3–C11     | 1.383(9)   | N7–C35      | 1.383(9)   |
| C1–N1–C2   | 110.07(32) | 110.59(23) | N3–C17     | 1.461(10)  | N7–C41      | 1.463(10)  |
| C1–N2–C7   | 110.44(32) | 110.12(21) | N4–C10     | 1.351(9)   | N8–C34      | 1.354(8)   |
| N1–C1–N2   | 106.38(33) | 106.83(22) | N4–C16     | 1.403(9)   | N8–C40      | 1.388(8)   |
|  |            |            | N4–C18     | 1.455(9)   | N8–C42      | 1.457(9)   |
|  |            |            | C1–Pd1–C10 | 88.60(28)  | C34–Pd2–C25 | 93.46(25)  |
|  |            |            | C1–Pd1–O1  | 95.81(24)  | C25–Pd2–O5  | 91.77(23)  |
|  |            |            | C10–Pd1–O1 | 171.42(23) | C34–Pd2–O5  | 172.9(2)   |
|  |            |            | C1–Pd1–O3  | 178.62(24) | C25–Pd2–O7  | 175.32(23) |
|  |            |            | C10–Pd1–O3 | 90.97(24)  | C34–Pd2–O7  | 88.58(20)  |
|  |            |            | O1–Pd1–O3  | 84.78(17)  | O5–Pd2–O7   | 86.56(17)  |
|  |            |            | C1–N1–C2   | 110.26(54) | C25–N5–C31  | 110.92(56) |
|  |            |            | C1–N2–C7   | 110.62(52) | C25–N6–C26  | 110.29(54) |
|  |            |            | N2–C1–N1   | 106.50(51) | N5–C25–N6   | 106.19(52) |
|  |            |            | C10–N3–C11 | 110.39(55) | C34–N7–C35  | 110.76(53) |
|  |            |            | C10–N4–C16 | 110.03(57) | C34–N8–C40  | 110.41(47) |
|  |            |            | N3–C10–N4  | 106.88(54) | N7–C34–N8   | 106.77(50) |
| PdC <sub>2</sub> O <sub>2</sub> /carbene<br>dihedral angle | 70.27°     | 70.75°     |            | 62.60°     |             | 68.83°     |
|  |            |            |            | 64.75°     |             | 74.48°     |

**Table 2. Selected Crystal Data, Data Collection, and Refinement Parameters for Complexes 1–3**

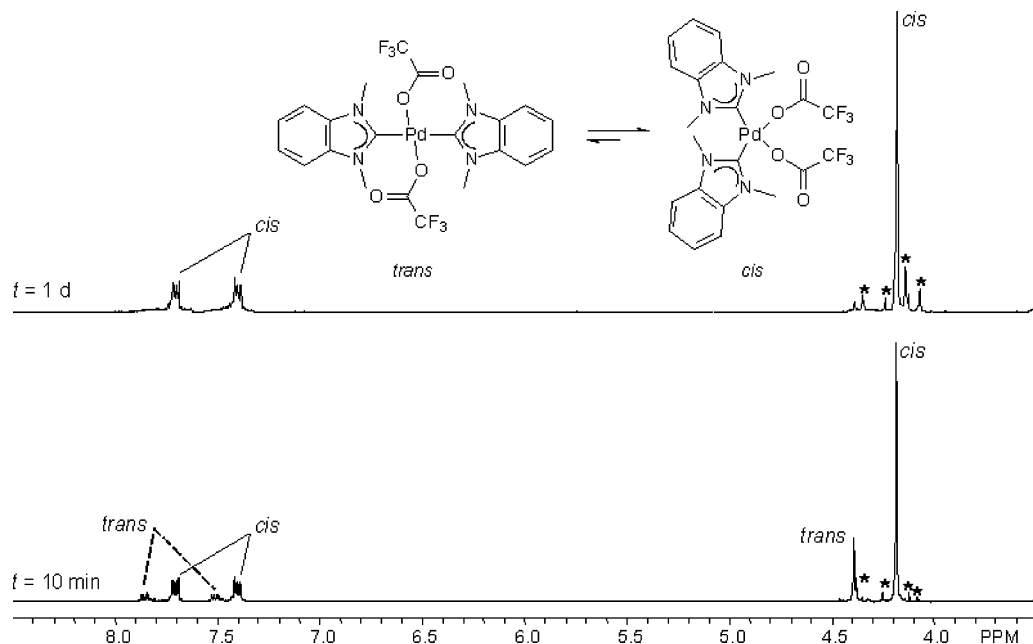
|   | 1·CH <sub>2</sub> Cl <sub>2</sub>  | 2·(CH <sub>3</sub> ) <sub>2</sub> CO  | 3·0.5(C <sub>7</sub> H <sub>8</sub> )  |
|---|--|---|--|
| formula   | C <sub>23</sub> H <sub>28</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>4</sub> Pd | C <sub>25</sub> H <sub>26</sub> F <sub>6</sub> N <sub>4</sub> O <sub>5</sub> Pd | C <sub>24</sub> H <sub>20</sub> F <sub>10</sub> N <sub>4</sub> O <sub>4</sub> Pd·0.5(C <sub>7</sub> H <sub>8</sub> ) |
| fw  | 601.79   | 682.90  | 770.91   |
| color, habit                                    | colorless block  | colorless block   | colorless long rod   |
| cryst size (mm)                                 | 0.40 × 0.36 × 0.28   | 0.40 × 0.40 × 0.32  | 0.38 × 0.26 × 0.10   |
| temperature (K)                                 | 223(2)   | 223(2)  | 223(2)   |
| cryst syst                                      | monoclinic   | monoclinic  | monoclinic   |
| space group                                     | C2/c   | C2/c  | P2(1)/c  |
| a (Å)   | 19.699(2)  | 17.7749(10)   | 12.1440(5)   |
| b (Å)   | 10.4716(12)  | 13.2977(7)  | 24.1984(10)  |
| c (Å)   | 12.4761(15)  | 12.9440(7)  | 21.5159(13)  |
| α (deg)   | 90   | 90  | 90   |
| β (deg)   | 101.167(3)   | 106.5660(10)  | 97.893(10)   |
| γ (deg)   | 90   | 90  | 90   |
| V (Å <sup>3</sup> )                             | 2520.4(5)  | 2932.5(3)   | 6262.9(6)  |
| Z   | 4  | 4   | 8  |
| D <sub>c</sub> (g cm <sup>-3</sup> )            | 1.586  | 1.547   | 1.635  |
| radiation used                                  | Mo Kα  | Mo Kα   | Mo Kα  |
| μ (mm <sup>-1</sup> )                           | 0.985  | 0.711   | 0.692  |
| θ range (deg)                                   | 2.11 to 27.50  | 1.94 to 27.50   | 1.68 to 25.00  |
| no. of unique reflns measd                      | 8641   | 10 608  | 36 187   |
| max., min. transmn                              | 0.7700 and 0.6940  | 0.8044 and 0.7640   | 0.9341 and 0.7790  |
| final R indices [I > 2σ(I)]                     | R <sub>1</sub> = 0.0553, wR <sub>2</sub> = 0.1254                                | R <sub>1</sub> = 0.0361, wR <sub>2</sub> = 0.0987                               | R <sub>1</sub> = 0.0631, wR <sub>2</sub> = 0.1599  |
| R indices (all data)                            | R <sub>1</sub> = 0.0673, wR <sub>2</sub> = 0.1309                                | R <sub>1</sub> = 0.0394, wR <sub>2</sub> = 0.1015                               | R <sub>1</sub> = 0.0887, wR <sub>2</sub> = 0.1739  |
| goodness-of-fit on F <sup>2</sup>               | 1.098  | 1.062   | 1.031  |
| largest diff peak and hole (e Å <sup>-3</sup> ) | 1.287 and -0.558   | 0.712 and -0.707  | 1.304 and -0.916   |

complex *cis-A* (1.987 and 1.989 Å). Presumably, the electron-withdrawing nature of the carboxylato ligands induces a higher Lewis acidity of the palladium(II) center, which in turn leads to a higher electron donation of the carbene ligands to the metal center.

The two carboxylato ligands are coordinated in a monodentate fashion with their pendant oxygen atoms found in syn (**1**, **2**, or **3**) or anti conformation (**3**, molecule B). There is no indication for the preference of either conformation, since both were found in the two independent molecules of **3**. Further structural parameters are unexceptional and do not require further comments.

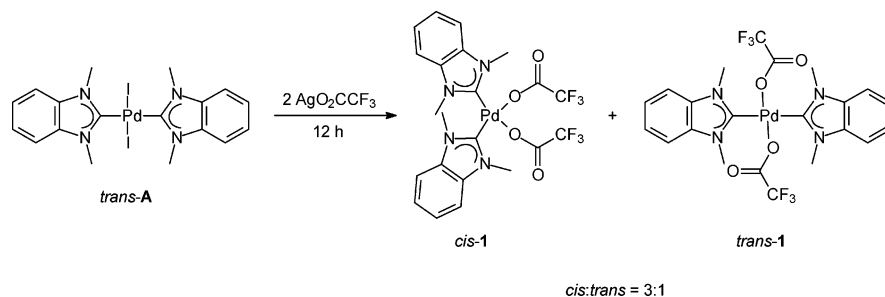
We have also attempted to selectively isolate the corresponding trans-configured dicarboxylate–bis(carbene) complexes. However, the reaction of pure *trans-A*<sup>12</sup> with 2 equiv of AgO<sub>2</sub>-CCF<sub>3</sub> in acetonitrile at ambient temperature afforded a mixture of **2** and its trans isomer in a 3:1 ratio as detected by <sup>1</sup>H NMR spectroscopy in DMSO-*d*<sub>6</sub> (Scheme 2). After 1 day the <sup>1</sup>H NMR spectrum of the same sample indicated an almost complete conversion into **2** (Figure 2). Apparently, the breaking of the Pd–I bond and the subsequent coordination of the weaker

(12) Huynh, H. V.; Ho, H. H. J.; Neo, T. C.; Koh, L. L. *J. Organomet. Chem.* **2005**, *690*, 3854.



**Figure 2.** Trans–cis isomerism monitored by  $^1\text{H}$  NMR spectroscopy. Signals arising from impurities are indicated with an asterisk.

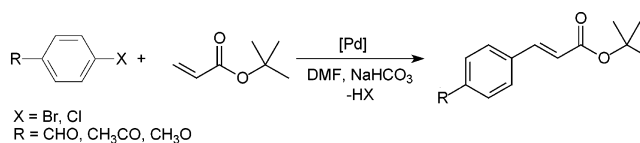
**Scheme 2. Attempted Synthesis of a *trans*-Dicarboxylato–Bis-carbene Complex**



carboxylato ligand favor a *cis* arrangement due to the strong *trans* influence of the benzimidazolin-2-ylidene ligand. On the basis of this observation we believe that such a halo/carboxylato ligand exchange can be used to generate thermodynamically favored *cis*-bis(benzimidazolin-2-ylidene) complexes of palladium(II).<sup>13</sup>

**Mizoroki–Heck Catalysis.** In a preliminary study, the *cis*-bis(benzimidazolin-2-ylidene) palladium(II) complexes **1–3** were tested for their catalytic activity in the Mizoroki–Heck reaction. The coupling of aryl bromides and chlorides with *tert*-butyl acrylate in DMF with 1 mol % catalyst loading and a reaction time of 24 h was chosen as a standard test reaction. To prevent carboxylate scrambling, we avoided the use of NaOAc and opted for  $\text{NaHCO}_3$  as a base instead. The results summarized in Table 3 indicate a high catalytic activity of these complexes. All three complexes can couple 4-bromobenzaldehyde at 120 °C in quantitative yield, giving selectively the corresponding *E*-cinnamate (entries 1–3). The coupling of electron-rich and deactivated 4-bromoanisole is more difficult, but proceeds cleanly with the addition of  $\text{NBu}_4\text{Br}$  and at a higher temperature of 140 °C affording the coupled product in a very good yield of 94% in all three cases (entries 4–6). Using the same conditions, activated 4-chloroacetophenone gives a quantitative conversion (entries 10–12). The superiority in the coupling of 4-chloroacetophenone over 4-bromoanisole clearly reflects the importance of aryl substituents. To this point, it is

**Table 3. Mizoroki–Heck Coupling Reactions<sup>a</sup> Catalyzed by Complexes 1–3**



| entry           | catalyst | aryl halide          | temp [°C] | yield <sup>b</sup> [%] |
|-----------------|----------|----------------------|-----------|------------------------|
| 1               | <b>1</b> | 4-bromobenzaldehyde  | 120       | >99                    |
| 2               | <b>2</b> | 4-bromobenzaldehyde  | 120       | >99                    |
| 3               | <b>3</b> | 4-bromobenzaldehyde  | 120       | >99                    |
| 4 <sup>c</sup>  | <b>1</b> | 4-bromoanisole       | 140       | 94                     |
| 5 <sup>c</sup>  | <b>2</b> | 4-bromoanisole       | 140       | 94                     |
| 6 <sup>c</sup>  | <b>3</b> | 4-bromoanisole       | 140       | 94                     |
| 7 <sup>c</sup>  | <b>1</b> | 4-chlorobenzaldehyde | 140       | >99                    |
| 8 <sup>c</sup>  | <b>2</b> | 4-chlorobenzaldehyde | 140       | 77                     |
| 9 <sup>c</sup>  | <b>3</b> | 4-chlorobenzaldehyde | 140       | 85                     |
| 10 <sup>c</sup> | <b>1</b> | 4-chloroacetophenone | 140       | >99                    |
| 11 <sup>c</sup> | <b>2</b> | 4-chloroacetophenone | 140       | >99                    |
| 12 <sup>c</sup> | <b>3</b> | 4-chloroacetophenone | 140       | >99                    |

<sup>a</sup> Reaction conditions generally not optimized. <sup>b</sup> Yields were determined by  $^1\text{H}$  NMR spectroscopy and are an average of two runs. <sup>c</sup> With addition of 1.5 equiv of  $[\text{N}(n\text{-C}_4\text{H}_9)_4]\text{Br}$ .

worth mentioning that all complexes show the same catalytic activity. It seems that the labile carboxylato ligand has no or only very little influence on the catalytic activity. This is expected when the anionic ligand does not participate in the catalytic cycle, which is in line with the standard model of the Heck reaction with  $[\text{Pd}^0\text{L}_2]$  ( $\text{L} = \text{PR}_3$  or here NHC) as the key intermediate. Interestingly, when 4-chlorobenzaldehyde was

(13) Research in our laboratories is currently underway to strengthen this proposal. Results will be published in a forthcoming paper.

employed in the reaction, the three complexes show different catalytic activities. Complex **1** was most effective and gave quantitative yield, whereas **2** and **3** activated the aryl chloride slightly less efficiently with good yields of 77% and 85%, respectively (entries 7–9). These surprising results and the superiority of the acetato complex **1** may be explained using the Amatore–Jutand model, which proposes the  $16e^-$  species  $[\text{Pd}^0\text{L}_2(\text{OAc})]^-$  as a key intermediate.<sup>3d–g</sup> This model emphasizes the important ability of the acetato ligand in stabilizing active  $\text{Pd}^0$  species and explains indirectly the advantage of NaOAc as a base in the Mizoroki–Heck reaction. This ability is probably less pronounced for the fluorocarboxylato ligands in **2** and **3** due to their weaker donor strength. However, it is unclear why this effect was observed only in the coupling of 4-chlorobenzaldehyde. Investigations are currently underway to gain a better understanding of such a counteranion effect and to expand the scope of benzimidazolin-2-ylidene complexes in catalysis.

### Conclusion

We have reported a facile synthesis and full characterization of the first dicarboxylato–bis(benzimidazolin-2-ylidene) complexes of palladium(II), **1–3**. The identity of **1–3** as cis complexes has been confirmed by X-ray diffraction studies. To the best of our knowledge **1–3** are the first examples of cis-configured dicarboxylato–bis(carbene) Pd(II) complexes with monodentate ligands.  $^1\text{H}$  NMR studies indicate that the cis arrangement is the more favorable conformation for this type of complexes. A preliminary catalytic study shows that all three novel complexes are highly active in the Mizoroki–Heck reaction. Further studies are underway to investigate a possible counteranion effect.

### Experimental Section

**General Considerations.** Unless otherwise stated, all manipulations, including the catalytic runs, were performed without taking precautions to exclude air and moisture. *N,N*-Dimethylformamide used for the Mizoroki–Heck reaction was purchased from J.T. Baker (“Baker analyzed” ACS reagent). All solvents were used as received.  $\text{Pd}(\text{OAc})_2$  and silver carboxylates were purchased from Sigma–Aldrich and used as received. *cis*-Diiodo-bis(*N,N'*-dimethylbenzimidazolin-2-ylidene)palladium(II) (*cis*-**A**) was prepared according to a literature procedure.<sup>11</sup>  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR spectra were recorded on a Bruker ACF 300 spectrometer using  $\text{Me}_4\text{Si}$  as internal and  $\text{CF}_3\text{CO}_2\text{H}$  as an external standard. ESI mass spectra were obtained using a Finnigan MAT LCQ spectrometer. Elemental analyses were performed on a Perkin–Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore.

***cis*-Diacetato-bis(*N,N'*-dimethylbenzimidazolin-2-ylidene)palladium(II) (**1**).** A mixture of *cis*-diiodo-bis(*N,N'*-dimethylbenzimidazolin-2-ylidene)palladium(II) (*cis*-**A**) (200 mg, 0.31 mmol) and  $\text{AgO}_2\text{CCH}_3$  (114 mg, 0.62 mmol) was suspended in acetonitrile (40 mL) and stirred at 80 °C overnight shielded from light. The resulting light green suspension was filtered from the precipitated AgI over Celite and the solvent removed in vacuo to give the crude product as a white powder. Slow evaporation at ambient temperature of a concentrated dichloromethane/toluene solution yielded trans-

parent prisms suitable for X-ray diffraction studies. Yield: 140 mg (0.27 mmol, 87%). Anal. Calcd for  $\text{C}_{22}\text{H}_{26}\text{N}_4\text{O}_4\text{Pd}$ : C, 51.12; H, 5.07; N, 10.84. Found: C, 51.41; H, 5.28; N, 10.90.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.32–7.23 (m, 8 H, Ar–H), 4.21 (s, 12 H,  $\text{NCH}_3$ ), 1.86 (s, 6 H,  $\text{O}_2\text{CCH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.48 MHz,  $\text{CDCl}_3$ ):  $\delta$  177.3 (s, COO), 172.4 (s, N–C–N), 134.2, 123.4, 110.1 (s, Ar–C), 34.6 (s,  $\text{NCH}_3$ ), 23.3 (s,  $\text{O}_2\text{CCH}_3$ ). MS (ESI, positive ions)  $m/z$  (%): 457 (100)  $[\text{M} - \text{O}_2\text{CCH}_3]^+$ .

***cis*-Di(trifluoroacetato)-bis(*N,N'*-dimethylbenzimidazolin-2-ylidene)palladium(II) (**2**).** Complex **2** was prepared in analogy to **1** from *cis*-**A** (275 mg, 0.420 mmol) and  $\text{AgO}_2\text{CCF}_3$  (180 mg, 0.815 mmol). Slow evaporation at ambient temperature of a concentrated acetonitrile/toluene solution yielded transparent needles suitable for X-ray diffraction studies. Yield: 205 mg, 0.328 mmol, 78%. Anal. Calcd for  $\text{C}_{22}\text{H}_{20}\text{F}_6\text{N}_4\text{O}_4\text{Pd}$ : C, 42.29; H, 3.23; N, 8.97. Found: C, 41.81; H, 3.58; N, 8.90.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  7.70 (dd,  $^3J(\text{H,H}) = 6$  Hz,  $^4J(\text{H,H}) = 3$  Hz, 4 H, Ar–H), 7.39 (dd,  $^3J(\text{H,H}) = 6$  Hz,  $^4J(\text{H,H}) = 3$  Hz, 4 H, Ar–H), 4.19 (s, 12 H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.48 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  163.9 (s, br, COO), 159.3 (s, br, N–C–N), 134.0, 123.7 (s, Ar–C), 116.0 (q,  $^1J(\text{C,F}) = 289.7$  Hz,  $\text{CF}_3$ ), 111.3 (s, Ar–C), 34.8 (s,  $\text{CH}_3$ ).  $^{19}\text{F}$  NMR (282.38 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  2.69 (s, br, 6 F,  $\text{CF}_3$ ). MS (ESI, positive ions)  $m/z$  (%): 511 (46)  $[\text{M} - \text{O}_2\text{CCF}_3]^+$ .

***cis*-Di(pentafluoropropionato)-bis(*N,N'*-dimethylbenzimidazolin-2-ylidene)palladium(II) (**3**).** Complex **3** was prepared in analogy to **1** from **A** (275 mg, 0.420 mmol) and  $\text{AgO}_2\text{CCF}_2\text{CF}_3$  (230 mg, 0.849 mmol). Recrystallization from an acetonitrile/toluene solution yielded transparent needles suitable for X-ray diffraction studies. Yield: 284 mg, 0.376 mmol, 94%. Anal. Calcd for  $\text{C}_{24}\text{H}_{20}\text{F}_{10}\text{N}_4\text{O}_4\text{Pd}$ : C, 39.77; H, 2.78; N, 7.73. Found: C, 39.81; H, 2.87; N, 7.79.  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  7.70 (dd,  $^3J(\text{H,H}) = 6.2$  Hz,  $^4J(\text{H,H}) = 3$  Hz, 4 H, Ar–H), 7.38 (dd,  $^3J(\text{H,H}) = 6.2$  Hz,  $^4J(\text{H,H}) = 3$  Hz, 4 H, Ar–H), 4.20 (s, 12 H,  $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.48 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  164.0 (s, br, COO), 159.6 (s, br, N–C–N), 134.0, 123.7, 111.2 (s, Ar–C), 118.5 (qt,  $^1J(\text{C,F}) = 285.5$  Hz,  $^2J(\text{C,F}) = 35.0$  Hz,  $\text{CF}_3$ ), 106.3 (tq,  $^1J(\text{C,F}) = 264.2$  Hz,  $^2J(\text{C,F}) = 36.5$  Hz,  $\text{CF}_2$ ).  $^{19}\text{F}$  NMR (282.38 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  –6.33 (s, br, 4 F,  $\text{CF}_2$ ), –42.67 (s, br, 6 F,  $\text{CF}_3$ ). MS (ESI, positive ions)  $m/z$  (%): 561 (84)  $[\text{M} - \text{O}_2\text{CCF}_2\text{CF}_3]^+$ .

**X-ray Diffraction Studies.** Diffraction data for **1–3** were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 223(2) K using graphite-monochromated Mo  $\text{K}\alpha$  radiation ( $\lambda = 0.71073$  Å). Data were collected over the full sphere and were corrected for absorption. Structure solutions were found by the Patterson method. Structure refinement was carried out by full-matrix least squares on  $F^2$  using SHELXL-97<sup>14</sup> with first isotropic and later anisotropic displacement parameters for all non-hydrogen atoms.

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**Supporting Information Available:** Crystallographic data for **1–3** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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