Coordination Modes

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σ–π Continuum in Indole–Palladium(II) Complexes

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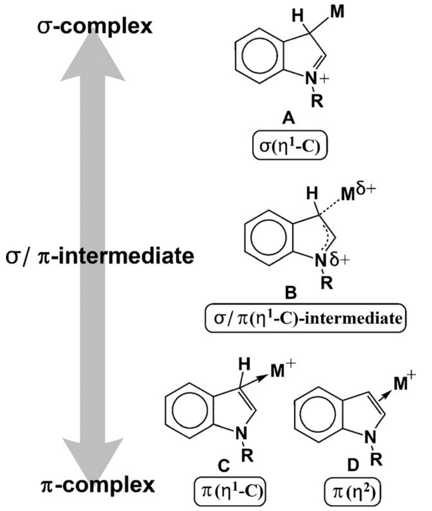
Abstract: *The intrinsic features of (hetero-arene)–metal interactions have been elusive mainly because the systematic structure analysis of non-anchored hetero-arene–metal complexes has been hampered by their labile nature. We report successful isolation and systematic structure analysis of a series of non-anchored indole–palladium(II) complexes. It was revealed that there is a σ–π continuum for the indole–metal interaction, while it has been thought that the dominant coordination mode of indole to a metal center is the Wheland-intermediate-type σ-mode in light of the seemingly strong electron-donating ability of indole. Several factors which affect the σ- or π-character of indole–metal interactions are discussed.*

The coordination behavior of hetero-arenes to a transition metal center has attracted considerable attention since their coordination through low-hapticity modes have been thought to be involved in metal-mediated or metal-catalyzed transformations of hetero-arenes.[1,2] However, it has been difficult to address the intrinsic features of (hetero-arene)–metal interactions, mainly owing to the labile nature of non-anchored hetero-arene–metal complexes. In fact, it is quite rare for non-anchored hetero-arene transition metal complexes to be isolated, and their structures has not been characterized by X-ray crystallography.[3] Nevertheless, it has been assumed that Wheland-intermediate-type σ-complexes are preferentially formed upon coordination of hetero-arenes to a metal center, in view of the seemingly greater electron-donating ability of hetero-arenes. Furthermore, synthetically useful palladium-catalyzed direct transformations of indoles have been proposed to be initiated by the formation of a σ-indole–palladium(II) complex, in which a metal center is σ(η^1-C)-bonded to the nucleophilic C3 atom of the indole ring, giving an indolium-type structure (**A**; Scheme 1).[1] However, the dominance of σ-mode has not been verified by systematic structure analysis of non-anchored indole–metal complexes. We considered the possibility that the pure σ-complexes are not always formed in (hetero-arene)–metal complexes; that is, for the indole complexes, σ/π-intermediate- (**B**) and π-modes (**C** or **D**) (Scheme 1)[4] may be taken into consideration, when the electron-donating property of a hetero-arene, or the electron-accepting property of a metal center is insufficient to induce strong intramolecular charge transfer. Herein, we confirmed the existence of a σ–π continuum in (hetero-arene)–metal complexes through isolation and systematic structure analysis of non-anchored indole–metal complexes.



Scheme 1. σ–π Continuum for mononuclear indole complexes.

To examine the (hetero-arene)–metal interaction, we chose non-anchored indole–Pd^{II} complexes as model compounds because of their relevance to catalysis. In our study, the anchored indole complexes, of which the isolation is much easier than that of non-anchored ones,[5] were not used because the chelating structures give rise to geometric constraints, which could affect the coordination modes of indole.[6] We successfully isolated a series of dicationic Pd^{II} complexes (**3** or **4**), bearing indole, *N*-methylindole, or *N*-benzylindole, by treatment of the dicationic Pd^{II} precursor $[Pd(CH_3CN)_4][BF_4]_2$ (**1**)[7] or $[Pd(CH_3CN)_2(dppe)][BF_4]_2$ (**2**)[8] with indoles in nitromethane or 1,2-dichloroethane (Scheme 2). The indole–palladium adduct $[Pd(indole)(CH_3CN)_3][BF_4]_2$ (**3-H**), $[Pd(N\text{-methylindole})(CH_3CN)_3][BF_4]_2$ (**3-Me**), or $[Pd(N\text{-benzylindole})(CH_3CN)_3][BF_4]_2$ (**3-Bn**) was formed almost quantitatively by treatment of **1** with the corresponding indole (1 equiv) in CD_3NO_2 at room temperature. On the other hand, the bisphosphine-ligated Pd^{II} complex $[Pd(N\text{-methylindole})(CH_3CN)(dppe)][BF_4]_2$ (**4-Me**) was not observed as the major product by a similar

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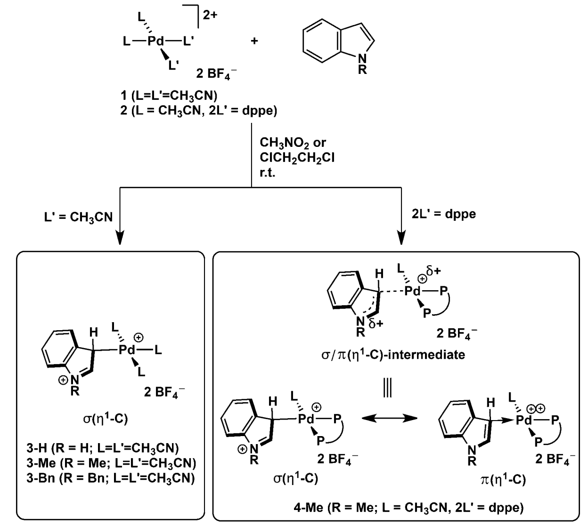
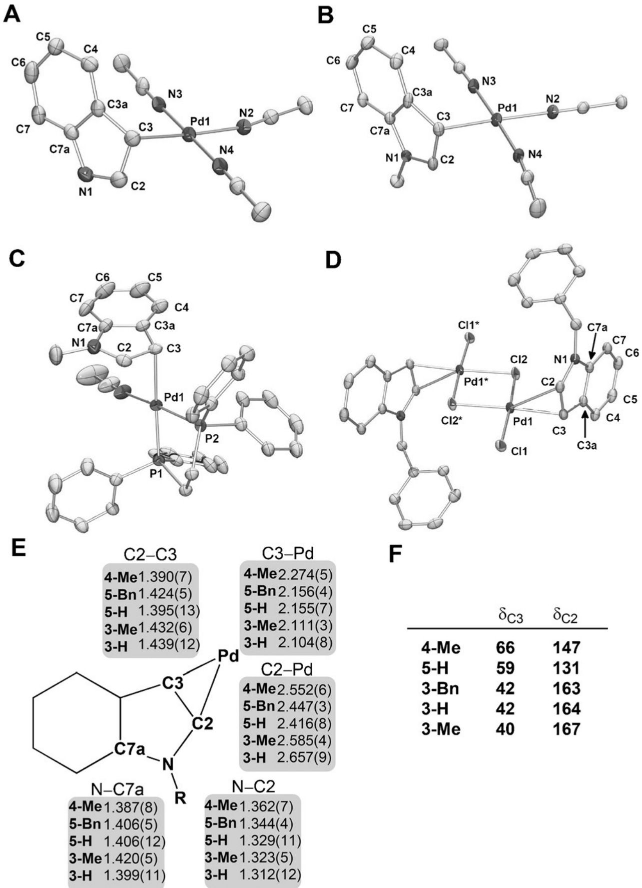


Scheme 2. Synthesis of dicationic indole–Pd^{II} adducts. The σ(η^1-C)-mode of **3-H**, **3-Me**, and **3-Bn**, and the σ/π(η^1-C)-mode for **4-Me** were assigned.

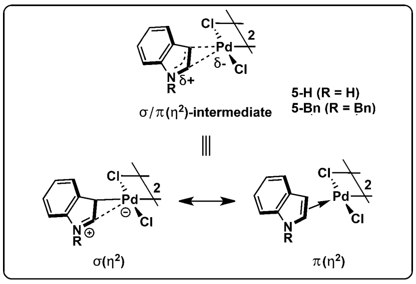


	δ_{C3}	δ_{C2}
4-Me	**66**	**147**
5-H	**59**	**131**
3-Bn	**42**	**163**
3-H	**42**	**164**
3-Me	**40**	**167**

Figure 1. A–D) The ORTEPs of **3-H**, **3-Me**, **4-Me**, and **5-Bn**, respectively. E) Selected bond lengths (Å). F) Selected ^{13}C NMR chemical shifts (ppm).

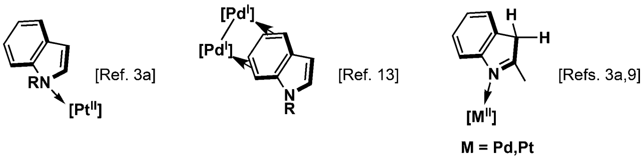
treatment in CD_3NO_2, because the equilibrium lies almost to the starting materials. However, repeated evaporation from 1,2-dichloroethane resulted in the shift of equilibrium to the indole–palladium adduct **4-Me** by removal of free CH_3CN, yielding **4-Me**. The neutral Zeise-dimer-type complex of indole $[Pd(indole)Cl_2]_2$ (**5-H**)[3c] or of *N*-benzylindole $[Pd(N\text{-}benzylindole)Cl_2]_2$ (**5-Bn**) was isolated by treatment of $PdCl_2(CH_3CN)_2$ with the corresponding indole in CH_2Cl_2.[9]

The structure analyses of **3-H**, **3-Me**, **4-Me**, **5-H**, and **5-Bn** were carried out by X-ray crystallographic analysis (Figure 1). The molecular structures of **3-H** and **3-Me** (**A** and **B**; Figure 1) exhibited the σ(η^1-C)-mode (**A**): for example, for **3-Me**, the η^1-C mode was assigned by the short Pd–C3 length ($d_{Pd-C3} = 2.111(3)$ Å) and the long Pd–C2 length ($d_{Pd-C2} = 2.585(4)$ Å), where the latter is out of the range of the Pd–C coordination bonds; the strong indolium character was assigned by the shortened N1–C2 lengths ($d_{N-C2} = 1.323(5)$ Å) and elongated C2–C3 lengths ($d_{C2-C3} = 1.432(6)$ Å) compared to free *N*-methylindole (d_{N-C2}(calcd) $= 1.379$ Å; d_{C2-C3}(calcd) $= 1.380$ Å)[10] (**E**; Figure 1). Similar structural trends were found for the known anchored σ(η^1-C)–indole complex; for example, in bis[μ-2-(3*H*-indol-3-yl-1κ*C*^{3}:2κ*N*)ethyl(4-oxo-1κ*O*-pent-2-en-2-yl)amido-1κ*N*]dipalladium, $d_{N-C2} = 1.320(7)$ Å, and $d_{C2-C3} = 1.442(8)$ Å.[5e,11] In contrast, the molecular structure of **4-Me** (**C**; Figure 1) showed the σ/π(η^1-C)-intermediate-mode, where d_{N-C2} (1.362(7) Å) and d_{C2-C3} (1.390(7) Å) in **4-Me** resembled that of the free *N*-methylindole than to that of the free *N*-methylindolium,[10] reflecting the decrease of σ-character and increase of π-character. Against the previous assumption that σ(η^1-C)-mode is involved in a neutral indole–palladium complex,[3c] the coordination of indole or *N*-benzylindole in the neutral complex **5-H** or **5-Bn** was in the η^2-mode (**F**; Figure 1); that is, $d_{Pd-C2} = 2.416(8)$ Å, $d_{Pd-C3} = 2.155(7)$ Å for **5-H**; $d_{Pd-C2} = 2.447(3)$ Å, $d_{Pd-C3} = 2.156(4)$ Å for **5-Bn**. Within the η^2-mode, the indole ligands showed the σ/π-intermediate-character, where d_{N-C2} (1.344(4) Å) for **5-Bn** is longer than that in **3-Me** and shorter than that in **4-Me** (Scheme 3).[12]



Scheme 3. Neutral indole–Pd^{II} dichloride dimers **5-H** and **5-Bn**.

The $^{13}C\{^1H\}$ NMR analyses in solution supported the structural trend observed in the crystalline state (**F**; Figure 1). The large down-field shift of the C2 resonances by ≈ 41 ppm, and the large up-field shift of the C3 resonances by ≈ 63 ppm compared to those of free indole ($\delta_{C2} = 126$ ppm, $\delta_{C3} = 103$ ppm) of the dicationic tris-nitrile complexes **3-H**, **3-Me**, and **3-Bn** represent their indolium character. On the other hand, smaller down-field shift of the C2 resonance ($\Delta\delta = 21$ ppm) and smaller up-field shift of the C3 resonance ($\Delta\delta = 37$ ppm) of **4-Me** from those in free *N*-methylindole are consistent with their σ/π-intermediate-mode. For the neutral indole–palladium(II) complexes, the C3 chemical shift of **5-H** was similar to that of **4-Me**, while the C2 chemical shift ($\delta_{C2} = 131$ ppm) of **5-H** was less down-field shifted from that of free indole, probably owing to the involvement of C2 in the π(η^2)-coordination. In our study, we did not observe the formation of N-bound indole–Pd^{II} complexes, nor six-membered-ring-bound indole–Pd^{II} complexes, while indole–Pt^{II} complexes thermodynamically favor the N-bound mode,[3a] and the μ-indole Pd^{I}–Pd^{I} complexes adopt coordination through the [C4,C5,C6,C7] position (Scheme 4).[13,14] It was reported that a 3*H*-tautomer complex was formed when Na_2PdCl_4 was treated with 2-methylindole in a protic solvent (MeOH).[9] In our study, we used aprotic solvents, such as CH_3NO_2 and CH_2Cl_2, to retard the tautomerization of indoles to 3*H*-indoles. In fact, tautomerization of the indole ligand in **5-H** to a 3*H*-indole ligand was observed when an excess amount of MeOH was added to a CD_2Cl_2 solution of **5-H** (Supporting Information).



Scheme 4. The N-bound Pt^{II} complex,[3a] [C4,C5,C6,C7]-bound Pd–Pd complex,[13] and N-bound 3*H*-indole tautomer complex.[3a, 9]

Table 2: Mayer bond indices (BIs) and n_σ values in parenthesis.

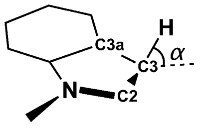
	N−C2	C2−C3	N−C7a
N-methylindole	1.14 (0%)	1.67 (0%)	1.04 (0%)
$PdCl_2$(*N*-methylindole)(HCN) (**5-Me′**)	1.16 (4%)	1.38 (40%)	0.99 (22%)
[Pd(*N*-methylindole)(dppe)(Ph)]$^+$ (**6-Me**)	1.24 (18%)	1.40 (38%)	0.99 (22%)
[Pd(*N*-methylindole)(dppe)(HCN)]$^{2+}$ (**4-Me′**)	1.30 (29%)	1.32 (49%)	0.96 (35%)
$GaCl_3$(*N*-methylindole)	1.33 (34%)	1.29 (53%)	0.95 (39%)
$AlCl_3$(*N*-methylindole)	1.34 (36%)	1.31 (50%)	0.96 (35%)
[Pd(*N*-methylindole)(HCN)$_3$]$^{2+}$ (**3-Me′**)	1.57 (77%)	1.07 (83%)	0.85 (83%)
[*N*-methylindolium]$^+$	1.70 (100%)	0.95 (100%)	0.81 (100%)
ΔBI	−0.56	0.72	0.23

Theoretical calculations supported the σ–π continuum of the indole–Pd^{II} complexes. Geometry optimization of the model compounds [Pd(*N*-methylindole)(HCN)$_3$]$^{2+}$ (**3-Me′**), [Pd(*N*-methylindole)(dppe)(HCN)]$^{2+}$ (**4-Me′**), $PdCl_2$(*N*-methylindole)(HCN) (**5-Me′**), [Pd(*N*-methylindole)(dppe)(Ph)]$^+$ (**6-Me**), as well as free *N*-methylindole, free *N*-methylindolium, and Lewis-acid adducts, $GaCl_3$(*N*-methylindole) and $AlCl_3$(*N*-methylindole),[15] were carried out at the MP2 level. As shown in Table 1, N−C2, C2−C3, and N−C7a lengths varied largely between indole and indolium ($\Delta d_{N-C2} = 0.075$ Å; $\Delta d_{C2-C3} = -0.105$ Å; $\Delta d_{N-C7a} = -0.054$ Å). Therefore, we chose these three bonds as the indicators to quantitatively evaluate the σ- and π-character. The Mayer bond indices (BIs) for these three bonds were used to estimate the σ-character (n_σ), according to the following equation, n_σ-(complex)[%] = [BI(*N*-methylindole)−BI(complex)]/$\Delta BI_0 \times 100$, where ΔBI_0 = BI(*N*-methylindole)−BI (*N*-methylindolium) (Table 2). In our consideration, we assume that the σ- and π-modes are the major resonance structures as shown in Scheme 1, although this does not mean the nonexistence of other minor resonance structures. The n_σ values derived from each bond of dicationic tris-nitrile complex **3-Me′** are 77–83%, indicating the strong σ(η^1-C) character. The dicationic diphosphine complex **4-Me′** showed considerably lower σ-character (n_σ = 29–49%). The Lewis-acid adducts $AlCl_3$(*N*-methylindole) and $GaCl_3$(*N*-methylindole) also showed lower n_σ values (35–50% and 34–53%, respectively). For the neutral palladium dichloride complex **5-Me′**, the n_σ values for N−C2 (4%) and *N*−C7a (22%) suggested small σ-character, although n_σ(C2−C3) (40%) deviated from the trend of N−C2 and N−C7a, probably because of the η^2-coordination mode. In fact, the optimized structure for **5-Me′** showed a less-distorted η^2-mode ($d_{Pd-C2} = 2.276$ Å, $d_{Pd-C3} = 2.213$ Å; see below). Thus, theoretical calculations showed that **3-Me′** is the σ-complex, while **4-Me′**, $AlCl_3$(*N*-methylindole), and $GaCl_3$(*N*-methylindole) are the σ/π-intermediate-complexes, and **5-Me′** with a symmetric η^2-mode is the π-complex. It is also noted that the cationic indole phenyl complex [Pd(*N*-methylindole)(dppe)(Ph)]$^+$ (**6-Me**), which may be related to a catalytic intermediate of indole arylation reactions, showed the π(η^2)-mode (n_σ = 18–38%). It should also be mentioned that the extent of pyramidalization at the C3 carbon reflects the covalent σ-character about the Pd−C3 bond. The angle (α) between the C2-C3-C3a plane and C3−H bond (Scheme 5) decreased in the following order: *N*-methylindolium (53°) > **3-Me′** (42°) > **4-Me′** (23°), $AlCl_3$(*N*-methylindole) (21°), $GaCl_3$(*N*-methylindole) (20°), **6-Me** (19°), **5-Me′** (18°) > *N*-methylindole (0°).

Table 1: Optimized structural parameters (Å) at the MP2 level.

	N−C2	C2−C3	N−C7a	Pd−C2	Pd−C3
N-methylindole	1.379	1.380	1.378	–	–
$PdCl_2$(*N*-methylindole)(HCN) (**5-Me′**)	1.374	1.423	1.384	2.276	2.213
[Pd(*N*-methylindole)(dppe)(Ph)]$^+$ (**6-Me**)	1.365	1.424	1.381	2.424	2.271
[Pd(*N*-methylindole)(dppe)(HCN)]$^{2+}$ (**4-Me′**)	1.353	1.427	1.390	2.522	2.247
$GaCl_3$(*N*-methylindole)	1.347	1.413	1.389	–	–
$AlCl_3$(*N*-methylindole)	1.346	1.412	1.388	–	–
[Pd(*N*-methylindole)(HCN)$_3$]$^{2+}$ (**3-Me′**)	1.311	1.472	1.421	2.752	2.063
[*N*-methylindolium]$^+$	1.304	1.485	1.432	–	–
Δ*d*	0.075	−0.105	−0.054		

The correlation between the σ–π continuum and intramolecular charge transfer was examined by the natural atomic orbital (NAO)

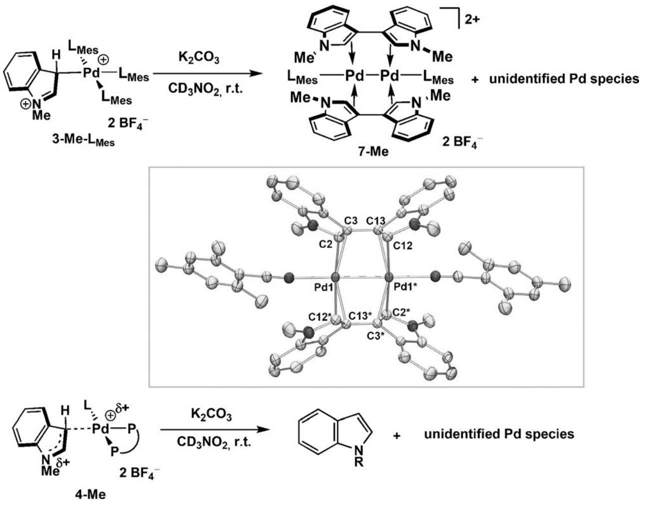


Scheme 5. The deviation angle (α) in the indole ligand.

population analysis. Positive charge on the *N*-methylindole moiety in η^1-indole complexes decreased in the following order: *N*-methylindolium (+1) > **3-Me′** (+0.80) > **4-Me′** (+0.37) > $GaCl_3$(*N*-methylindole) (+0.23), $AlCl_3$(*N*-methylindole) (+0.19) > *N*-methylindole (0). This trend clearly showed that the strong charge transfer between the indole ligand and a metal center leads to an increase of the σ-character. The phosphine ligands are capable of delocalizing cationic charge of a complex,[16] which weakens the electron-accepting ability of a metal center.[17] Thus, the auxiliary ligands largely affect the σ–π state of indole complexes. It should be noted that the positive charge of the indole ligand in the $\pi(\eta^2)$ complex **5-Me′** (+0.25) or **6-Me** (+0.28) is in the range of those found for η^1-σ/π-intermediate-complexes. This may suggest that a subtle change of the charge transfer ability, as well as of any other factors, causes a shift between the σ/π-intermediate- and π-modes in the region of weak charge transfer.

Thus, our experimental and theoretical results showed that there is the σ–π continuum in indole–Pd^{II} complexes. The σ–π continuum has been previously observed in the η^1-arene–metal complexes,[18,19] although the pure σ-complexes of arenes (Wheland-intermediate-type) have been rarely identified due to the insufficient charge transfer between the arene ligand and a metal center.[18c] The present observation of the nearly pure σ-complex of indole might reflect the more efficient electron donating ability of indole than of arenes. However, our results suggested that the pure σ-complex of indole is formed only when the metal center is highly electrophilic; that is, a dicationic $[Pd(CH_3CN)_3]^{2+}$ moiety. When a Pd^{II} center is ligated by phosphine or chloride ligands, the electron-accepting property of a metal center is insufficient, leading to the σ/π-intermediate-complexes or π-complexes of indole.

As indicated in the synthesis (Scheme 1), the indole ligand in the σ/π-intermediate-mode is replaced with coordinative substrates more easily than in the $\sigma(\eta^1\text{-C})$-mode; for example, the σ/π-intermediate-complex **4-Me** released the *N*-methylindole ligand in the presence of 1 equiv of CH_3CN, or acetone in CD_2Cl_2 at ambient temperature, while the $\sigma(\eta^1\text{-C})$-complex **3-Me** remained intact even in the presence of 5 equiv of CH_3CN or acetone in CD_3NO_2 at ambient temperature.[20] We also observed the quantitative release of the *N*-methylindole ligand when **4-Me** was treated with K_2CO_3. On the other hand, treatment of the σ-complex **3-Me** with K_2CO_3 gave a complicated mixture, where free *N*-methylindole was not detected. Similar treatment of a σ-complex containing bulkier nitrile ligands $[Pd(N\text{-methylindole})(L_{Mes})_3][BF_4]_2$ (L_{Mes} = 2,4,6-trimethylbenzonitrile; **3-Me-L$_{Mes}$**)[21] afforded a bi-*N*-methylindolyl Pd^I–Pd^I complex $[Pd_2(\text{bi-}N\text{-methylindolyl})_2(L_{Mes})_2][BF_4]_2$ (**7-Me**) as the major product (Scheme 6). Complex **7-Me** was characterized by NMR analysis and X-ray structure analysis (Scheme 6). The ^1H NMR monitoring experiments showed a single species, with diagnostic ^1H signals at δ 9.04, 8.55, 8.02, and 7.90 ppm in CD_3NO_2, was formed immediately, and then **7-Me** was generated gradually.



Scheme 6. Reaction of σ- and σ/π-intermediate-complexes of *N*-methylindole with K_2CO_3. In a gray box is the ORTEP of **7-Me**.

Although isolation and structural characterization of the initial product has not been attained, it is reasonably assumed that the deprotonated product $[Pd(N\text{-methylindolyl})(L_{Mes})_3]^+$ was formed initially, and then disproportionation and reductive coupling could afford **7-Me**. We note that the relatively labile nature of σ/π-intermediate-complexes in solution does not rule out the possibility that the σ/π-intermediate-mode is involved in the palladium-catalyzed transformation of indoles.[22]

In summary, we have shown that there is a σ–π continuum in (hetero-arene)–metal complexes through isolation and systematic structural analysis of σ- and π-modes in indole–Pd^{II} complexes, while the σ-mode had been assumed as the dominant mode for (hetero-arene)–metal interactions. The $\sigma(\eta^1\text{-C})$-mode was observed only for the complexes in the relatively strong charge transfer region, while the σ/π-intermediate- or π-mode in either η^1-C or η^2-fashion was adopted by the complexes in the relatively weak charge transfer region. Several factors, such as the nature of the auxiliary ligands and total charge of the complex, affect the σ–π state. The insights into the (hetero-arene)–metal interaction reported here will provide a structural perspective on the key catalytic intermediates of metal-catalyzed hetero-arene transformations; for example, the σ-mode may be related with the deprotonative metalation pathway,[22] while the π-mode may be related with the carbo-metallation pathway.[23] Further studies to verify the reactivity of σ-, σ/π-intermediate-, and π-complexes of indole and other hetero-arenes are now underway in our laboratory.

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Keywords: indoles · palladium · π-complexes · σ-complexes · σ–π continuum

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