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Investigation of the Catalytic Activity of a 2-Phenylidenepyridine Palladium(II) Complex Bearing 4,5-Dicyano-1,3-bis(mesityl)imidazol-2-ylidene in the Mizoroki-Heck Reaction

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Keywords: Carbene ligands; Heck reaction; Palladium; Selenium; C–C coupling

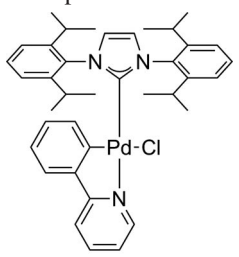
Abstract. The phenylidenepyridine (*ppy*) palladacycles [PdCl(*ppy*)(IMes)] (**4**) [IMes = 1,3-bis(mesityl)imidazol-2-ylidene] and [PdCl(*ppy*){$(CN)_2$IMes}] (**6**) [$(CN)_2$IMes = 4,5-dicyano-1,3-bis(mesityl)imidazol-2-ylidene] were prepared by facile two step syntheses, starting with the reaction of palladium(II) chloride with 2-phenylpyridine followed by subsequent addition of the NHC ligand to the precatalyst precursor $[PdCl(ppy)]_2$. Suitable crystals for the X-ray analysis of the complexes **4** and **6** were obtained. It was shown that **6** has a shorter NHC-palladium bond than the IMes complex **4**. The difference of the palladium carbene bond lengths based on the higher π-acceptor strength of $(CN)_2$IMes in comparison to IMes. Thus, $(CN)_2$IMes should stabilize the catalytically active central palladium atom better than IMes. As a measure for the π-acceptor strength of $(CN)_2$IMes compared to IMes, the selone $(CN)_2$IMes·Se (**7**) was prepared and characterized by ^{77}Se-NMR spectroscopy. The π-acceptor strength of **7** was illuminated by the shift of its ^{77}Se-NMR signal. The ^{77}Se-NMR signal of **7** was shifted to much higher frequencies than the ^{77}Se-NMR signal of IMes·Se. Catalytic experiments using the Mizoroki-Heck reaction of aryl chlorides with *n*-butyl acrylate showed that **6** is the superior performer in comparison to **4**. Using complex **6**, an extensive substrate screening of 26 different aryl bromides with *n*-butyl acrylate was performed. Complex **6** is a suitable precatalyst for *para*-substituted aryl bromides. The catalytically active species was identified by mercury poisoning experiments to be palladium nanoparticles.

Introduction

Since the first mention of the arylation of olefins by *R. F. Heck*[1a] and the benzylation of olefins by *T. Mizoroki*[1a] in the early 1970s, the so called Mizoroki-Heck reaction became one of the most important and most intensively discussed catalytic reactions so far. It is used for the synthesis of pharmaceuticals and natural products.[1c–j] A great advantage of the Mizoroki-Heck reaction is that no organometallic substrate is required for the cross coupling reaction.

One of the greatest challenges for synthetic chemists is the development of new precatalysts. Tertiary phosphines have been the ligands of choice for palladium catalyzed reactions until the middle 1990s. A change of course concerning the development of palladium(II) precatalysts was initiated by the presentation of the first palladium precatalysts bearing *N*-heterocyclic carbenes (NHCs) by *W. A. Herrmann*.[2] In the last two decades, various NHCs for the application in palladium catalyzed reactions were presented. In combination with suitable coligands, a broad scope of effective NHC-palladium(II) precatalysts was prepared.[3] NHCs can easily be modified, sterically as well as electronically, by variation of the nitrogen substituents or the backbone substituents, respectively.[4] Thus, ligands for every special purpose can be generated.

One of the most renowned precatalyst families are the PEPPSI complexes presented by M. Organ (PEPPSI: Pyridine Enhanced Precatalyst Preparation, Stabilization and Initiation).[5] PEPPSI complexes are palladium(II) complexes with a pyridine ligand in *trans* position and two halido ligands in *cis* position to the NHC. In a contribution by *M. Organ* in 2010, the pyridine and one halido ligand were substituted by 2-phenylidenepyridine (*ppy*) to obtain precatalyst [PdCl(*ppy*)(IPr)] (**1**) [IP = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] (Scheme 1).[6] With this complex, the Kumada-Tamao-Currio (KTC) reaction of phenylmagnesium chloride with 4-chloroanisole was performed efficiently.



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Scheme 1. Precatalyst **1** for the Kumada-Tamao-Currio reaction presented by *M. Organ*.[6]

Another modification of the PEPPSI motif was designed by *Navarro* et al., who used diethylamine and triethylamine as so

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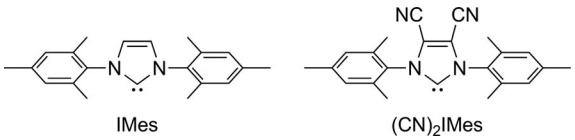
called "throw away ligands" in *trans* position to the NHC-ligand.[6b–f] In combination with sterically demanding NHC ligands, they prepared extremely reactive precatalysts for cross-coupling reactions.[6e]

In the recent years, our group presented a series of palladium(II) precatalysts for the Mizoroki-Heck as well as the Suzuki-Miyaura reaction.[7,8] The precatalysts in these studies were bearing the strong acceptor carbene 4,5-dicyano-1,3-bis(mesityl)imidazol-2-ylidene [$(CN)_2$IMes]. In comparison to analogous complexes bearing the well-known donor NHC 1,3-bis(mesityl)imidazol-2-ylidene (IMes), the precatalysts bearing $(CN)_2$IMes were superior performers in the catalytic reactions used for these studies (Scheme 2).



Scheme 2. NHCs IMes (left) and $(CN)_2$IMes (right) in this study.

As it was shown by *M. Organ* that *ppy* palladium(II) complexes could be used as an efficient precatalysts in cross coupling reactions, we wanted to take a more general look at NHC *ppy* palladium(II) complexes. For this purpose, the NHC moiety of *ppy* palladium(II) complexes should be varied concerning the π-accepting abilities of the NHC ligand and the catalytic activity of the resulting precatalysts should be monitored in reference to the acceptor strength of the used NHC ligand.

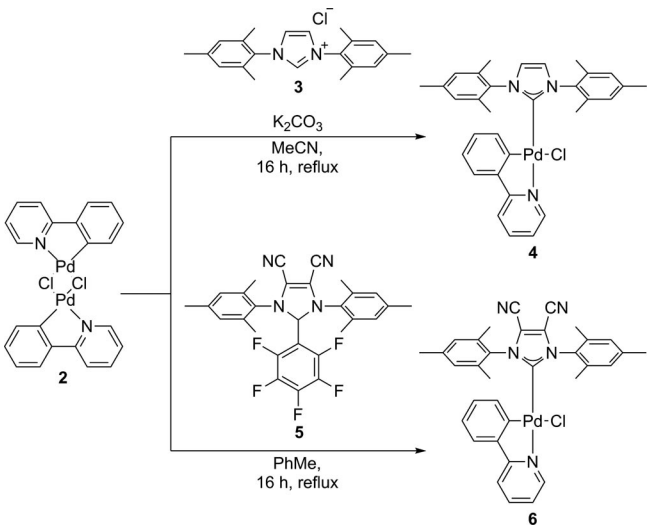
In this contribution, we present the synthesis, the characterization, and the application of the two NHC-phenylidenepyridine palladium(II) complexes [PdCl(*ppy*)(IMes)] (**4**) and [PdCl(*ppy*){$(CN)_2$IMes}] (**6**) in a Mizoroki-Heck reaction of aryl halides and *n*-butyl acrylate. It was evident after the initial catalytic experiments, that **6** performs the Mizoroki-Heck reaction more efficient than **4**. Thus, further experiments were performed exclusively with precatalyst **6**. Poisoning experiments with elemental mercury showed, that the reactions were catalyzed by palladium nanoparticles in the case of **4** as well as of **6**. The results of the poisoning experiments match with the results of our observations in former catalytic studies.[7,8]

The major method for the determination of the acceptor strength of NHC ligands is the determination of Tolman electronic parameters (TEP).[9] But when only information about the π-acceptor strength are needed, other methods are preferable. *C. Ganter* presented a series of NHC selenium adducts, which were characterized by means of ^{77}Se-NMR spectroscopy.[10] The ^{77}Se-NMR signals of the investigated selones are shifted to higher frequencies as the π-acceptor strength of the NHC moieties increase. Thus, the 4,5-dicyano-1,3-bis(mesityl)imidazol-2-selone (**7**) was prepared to take a closer look at the π-acceptor strength of $(CN)_2$IMes. It could be shown that the ^{77}Se-NMR signal of **7** was shifted to much higher frequencies than the signal for the literature known 1,3-bis(mesityl)imidazol-2-selone.[11]

Results and Discussion

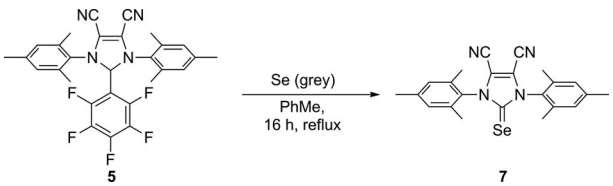
Syntheses

The formation of the palladium(II) precatalysts **4** and **6** was achieved in a straight forward two step synthesis. Stirring palladium(II) chloride and 2-phenylpyridine in methanol for 16 h at room temperature resulted in the already known dinuclear complex [PdCl(*ppy*)]$_2$ (**2**). Complex **2** was refluxed in acetonitrile in the presence of one equivalent 1,3-bis(mesityl)imidazolium chloride (**3**) and four equivalents potassium carbonate to yield **4** in 50 % overall yield after 4 h. Complex **6** was formed in 50 % overall yield by refluxing **2** and two equivalents 4,5-dicyano-1,3-dimesityl-2-(pentafluorophenyl)imidazoline (**5**) in toluene for 16 h. The complexes were purified by liquid chromatography on silica (Scheme 3).



Scheme 3. Synthetic route to the [PdCl(*ppy*)(NHC)] complexes **4** and **6**.

The synthesis of 4,5-dicyano-1,3-bis(mesityl)imidazol-2-selone (**7**) was performed in one step by refluxing **5** for 16 h in toluene in the presence of four equivalents of grey selenium. After subsequent purification of the crude product by liquid chromatography, the pure selenourea derivative **7** was obtained in a yield of 80 % (Scheme 4).



Scheme 4. Synthesis of the selone $(CN)_2$IMes·Se (**7**).

The compounds **4**, **6** and **7** were characterized by means of ^{1}H- and ^{13}C-NMR spectroscopy, FT-IR spectroscopy, elemental analysis (H, C, N) as well as by means of high resolution mass spectroscopy. The selone **7** was additionally characterized by means of ^{77}Se-NMR spectroscopy.

With the ^{77}Se-NMR spectroscopic data of **7**, the π-acceptor strength was measured. The ^{77}Se-NMR signal of **7** was found

at δ = 167 ppm chemical shift relative to dimethylselenide in chloroform. *S. P. Nolan* reported the ^{77}Se-NMR signal for the analogous 1,3-bis(mesityl)imidazol-2-selone to be found at δ = 27 ppm.[11] As ^{77}Se-NMR signals of selones shift to higher frequencies with increasing π-acceptor strength of the substituents, it is clear that $(CN)_2$IMes has to be a much stronger π-acceptor than IMes.

X-ray Diffraction

Single crystals suitable for the X-ray analysis were obtained for the palladium(II) complexes **4** and **6** as well as for the selone **7**. Complex **4** and selone **7** crystallize by slow diffusion of pentane steam into a concentrated dichloromethane solution containing **4** and **7**, respectively. Complex **6** crystallizes by slow solvent evaporation of a saturated acetonitrile solution containing **6**.

The asymmetric unit of **4** contains two independent complex molecules. In the asymmetric unit of **6**, one complex molecule and 1.25 acetonitrile solvent molecules from the crystallization were found. Selected bond lengths, angles, and torsion angles are given in Table 1.

Table 1. Selected bond lengths /Å, angles /°, and torsion angles /° of the [PdCl(*ppy*)(NHC)] complexes **4** and **6**.

	4[a)]	**6**
C1–Pd1	1.992(5)/*1.988(5)*	1.976(4)
C1–N1	1.373(6)/*1.375(6)*	1.372(4)
C1–N2	1.353(6)/*1.350(7)*	1.359(4)
Pd1–C24	1.956(6)/*1.974(5)*	1.994(4)
Pd1–N5	2.092(4)/*2.093(4)*	2.089(3)
Pd1–Cl1	2.4096(15)/*2.4061(15)*	2.3954(9)
N1–C1–N2	104.0(4)/*103.7(4)*	104.9(3)
C4–C2–C3–C5	–	2.2(7)
C1–N1–C15–C16	66.0(7)/105.5(6)	73.4(5)
C1–N2–C6–C7	–102.3(6)/*–66.1(7)*	–95.1(4)

a) Data for the second molecule in the asymmetric unit are given in italic letters.

The molecular structures of **4** and **6** have slightly distorted square-planar coordination arrangements (Figure 1 and Figure 2). In analogous manner to the literature known palladium(II) complex [PdCl(*ppy*)(IPr)] (**1**) (Scheme 1), the *N*-donor of the *ppy* ligand stands in *trans* position and the phenylidene moiety of the *ppy* ligand is coordinated in *cis* position to the NHC ligand. Because $(CN)_2$IMes is a stronger π-acceptor than IMes, the C1–Pd1 bond in complex **6** is shorter than the C1–Pd1 bond in **4**. The bond length difference is about 0.015 Å.

Different torsions for the two mesityl substituents in IMes as well as in $(CN)_2$IMes was observed for complexes **4** and **6**, respectively. In both NHC ligands, one mesityl group is twisted to an almost rectangular position relative to the plane of the carbene ring. The second mesityl group diverged further from perpendicularity. A difference in the twist of the mesityl groups was detected between IMes in **4** and $(CN)_2$IMes in **6**. The two mesityl groups in complex **4** are twisted further away from orthogonality than the corresponding mesityl substituents in complex **6** [torsions in **4**: 66.0(7)/*105.5(6)*° and –102.3(6)/*–66.1(7)*°; torsions in **6**: 73.4(5)° and –95.1(4)°]. Probably, the

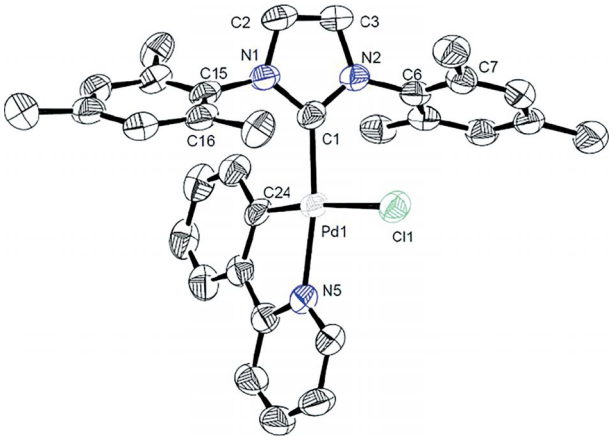


Figure 1. Molecular structure of [PdCl(*ppy*)(IMes)] (**4**). Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms are omitted for clarity.

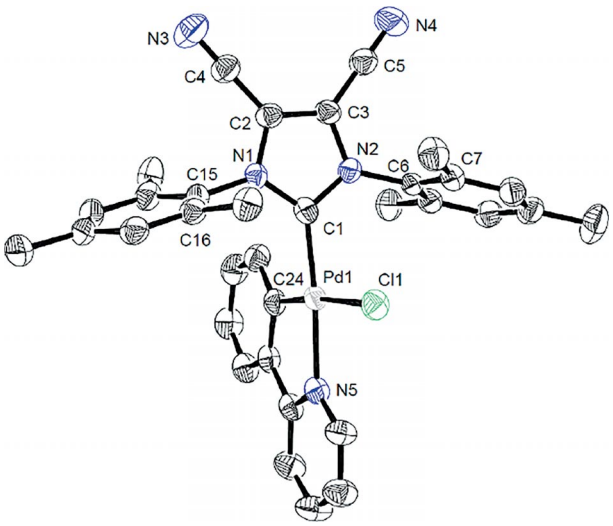


Figure 2. Molecular structure of [PdCl(*ppy*){$(CN)_2$IMes}] (**6**). Thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms are omitted for clarity.

nitrile groups of $(CN)_2$IMes hinder the rotation of the mesityl groups sterically and thus lead to torsion angles, which converge more towards perpendicularity than the mesityl groups in IMes.

The asymmetric unit of C_2 symmetric selone **7** contains half a molecule of the selone. The other half of the molecule was generated corresponding to the C_2 symmetry of the molecule (Figure 3). In analogous manner to the comparison of the C1–Pd1 bond lengths of the palladium(II) complexes **4** and **6**, the C1–Se1 bond of **7** was compared to the C1–Se1 bond of 1,3-bis(mesityl)imidazol-2-selone.[12] The C1–Se1 bond in **7** [1.794(5) Å] is 0.04 Å shorter than the C1–Se1 bond in the selone from IMes. This difference in the C1–Se1 bond lengths confirms, in agreement to the ^{77}Se-NMR experiments, that $(CN)_2$IMes is a strong π-acceptor in comparison to IMes.

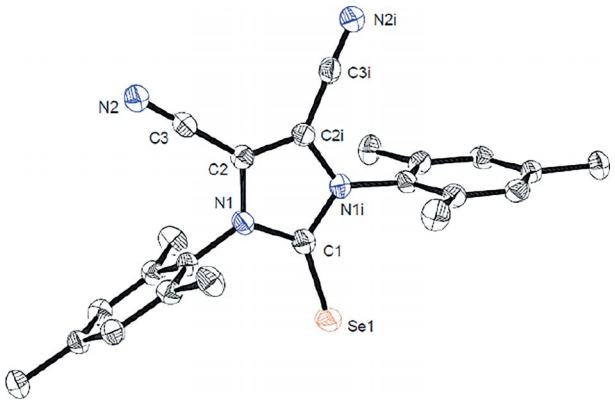
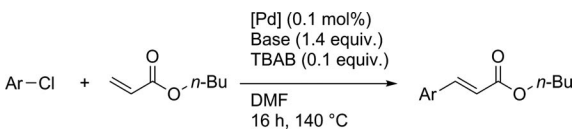


Figure 3. Molecular structure of 4,5-dicyano-1,3-bis(mesityl)imidazol-2-selone (**7**). Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths /Å, angles /° and torsion angles /°: C1–Se1 1.798(5); C1–N1 1.376(5); C1–N1i 1.376(5); N1–C2 1.381(5); N1i–C2i 1.381(5); N1–C1–Ni1 104.8(4); C1–N1–C2 110.6(3); C1–N1i–C2i 110.6(3); C3–C2–C2i–C3i 0.4(7). Hydrogen atoms are omitted for clarity.

Catalytic Studies

Recently, our group used the Mizoroki-Heck reaction as test system for the proof of the catalytic activity of palladium(II) complexes bearing $(CN)_2$IMes.[7] The tested precatalysts unfortunately decomposed in the reaction mixture under the harsh Mizoroki-Heck conditions and formed palladium nanoparticles. Thus, complexes **4** and **6** with the robust *ppy* moiety should be tested in the Mizoroki-Heck reaction with the goal of avoiding the nanoparticle formation.

The catalytic screening was performed, according to our former Mizoroki-Heck study, in *N*,*N*-dimethylformamide (DMF) using one equivalent aryl halide, two equivalents *n*-butyl acrylate, 0.1 mol% precatalyst, 1.4 equivalents sodium carbonate, and 0.1 equivalents tetra-(*n*-butyl)ammonium bromide (TBAB) (Scheme 5). The reaction time was set to 16 h and the reaction temperature to 140 °C (oil bath). Product yields were determined by gas chromatography, using 1,3,5-trimethoxybenzene as the internal standard.[7]



Scheme 5. General reaction conditions for the Mizoroki-Heck reaction of aryl chlorides with *n*-butyl acrylate using the precatalysts **4** and **6**.

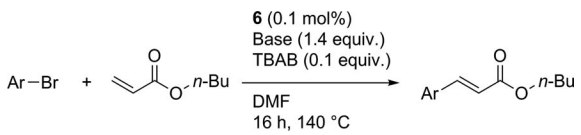
The catalytic activity of precatalysts **4** and **6** was initially determined by the Mizoroki-Heck reaction of aryl chlorides with *n*-butyl acrylate (Table 2). No conversion at all was determined for the reaction of chlorobenzene and 4-chloroanisole using the precatalysts **4** and **6**. For the reaction of 4-chloroacetophenone, the $(CN)_2$IMes complex **6** yielded the desired coupling product in a yield of 31%. A yield of only 10% was obtained using IMes complex **4** (Table 2, entry 3).

Table 2. Yields of the Mizoroki-Heck reaction of aryl chlorides with *n*-butyl acrylate using the [PdCl(*ppy*)(NHC)] complexes **4** and **6**.[a)]

Entry		GC yield[b)] /%	
	Aryl chloride	4	6
1	Chlorobenzene	0	0
2	4-Chloroanisole	0	0
3	4-Chloroacetophenone	10	31

a) Reaction conditions: T = 140 °C (oil bath), t = 16 h, aryl chloride (1.0 equiv.), *n*-butyl acrylate (2.0 equiv.), Na_2CO_3 (1.4 equiv.), TBAB (0.1 equiv.), precatalyst (0.1 mol%) in DMF (0.5 mL). b) Yields were determined from two independent runs by GC-FID using 1,3,5-trimethoxybenzene as internal standard.

Due to the inferior catalytic activity of IMes complex **4**, further catalytic reactions of aryl bromides with *n*-butyl acrylate were performed exclusively with $(CN)_2$IMes complex **6** (Scheme 6). The substrate screening of aryl bromides was conducted for 26 aryl bromides with differing electronic and steric properties.



Scheme 6. General reaction conditions for the Mizoroki-Heck reaction of aryl bromides with *n*-butyl acrylate using the precatalyst **6**.

In general, complex **6** is a suitable precatalyst for aryl bromides. Good to excellent product yields were obtained with *para*-substituted aryl bromides. No general trend between the yields of aryl bromides bearing electron donating *para* substituents or electron withdrawing *para* substituents was identified. The yields for the Mizoroki-Heck reaction of bromoanisoles and bromophenoles decreased with increasing steric stress of the aryl bromides from the *para* to the *meta* and subsequently to the *ortho* derivative (Table 3, entries 3–5 and 16–18). Using sterically stressed and additionally donor substituted aryl bromides lead to yields of 4% for bromomesitylene (Table 3, entry 19) or no yield at all for bromo-2,4,6-triisopropylbenzene (Table 3, entry 23). The reaction of bases like 4-bromoaniline and 3-bromopyridine lead to the desired products in moderate to good yields (Table 3, entries 15 and 22). Also, good yields were achieved for enhanced aromatic systems (Table 3, entries 25 and 26). Even the electronically deactivated 1-bromo-3,4,5-trimethoxybenzene could be converted into the desired cinnamate in good 60% yield (Table 3, entry 24).

It is known from former studies for complexes bearing IMes or $(CN)_2$IMes to form palladium nanoparticles.[7,8] These nanoparticles were the catalytically active species for catalytic processes. Being aware of this fact, poisoning experiments using elemental mercury were performed for the Mizoroki-Heck reaction of bromobenzene with *n*-butyl acrylate and precatalysts **4** and **6**. No product yield was obtained after 8 h when mercury was deployed to the reaction mixture at the start of a reaction. When mercury was added to separate reaction mixtures after 4 h, no further product formation was observed upon the addition of mercury (Figure 4). *Crudden* et al. showed, that palladium black formation is a common problem,

Table 3. Yields of the Mizoroki-Heck reaction of aryl bromides with *n*-butyl acrylate using [PdCl(*ppy*){(CN)$_2$IMes}] (**6**).[a)]

Entry	Aryl bromide	GC-yield[b)] /%
1	Bromobenzene	73
2	4-Bromoacetophenone	60
3	4-Bromoanisole	73
4	3-Bromoanisole	66
5	2-Bromoanisole	53
6	4-Bromobenzaldehyde	77
7	4-Bromotoluene	54
8	4-Bromofluorobenzene	88
9	2-Bromofluorobenzene	85
10	4-Bromo-*N*,*N*-diethylaniline	50
11	4-Bromonitrobenzene	85
12	2-Bromo-5-nitroanisole	46
13	4-Bromo(methylbenzoate)	90
14	4-Bromobenzonitrile	90
15	4-Bromoaniline	74
16	4-Bromophenol	84
17	3-Bromophenol	72
18	2-Bromophenol	48
19	Bromomesitylene	4
20	1,4-Dibromobenzene	82
21	2-Bromobiphenyl	84
22	3-Bromopyridine	41
23	1-Bromo-2,4,6-triisopropylbenzene	0
24	1-Bromo-3,4,5-trimethoxybenzene	60
25	1-Bromonaphtalene	72
26	9-Bromoanthracene	71

a) Reaction conditions: T = 140 °C (oil bath), t = 16 h, aryl bromide (1.0 equiv.), *n*-butyl acrylate (2.0 equiv.), Na_2CO_3 (1.4 equiv.), TBAB (0.1 equiv.), **6** (0.1 mol%) in DMF (0.5 mL). b) Yields were determined from two independent runs by GC-FID using 1,3,5-trimethoxybenzene as internal standard.

when high reaction temperatures are used, even when PEPPSI-type complexes are deployed as precatalysts.[13]

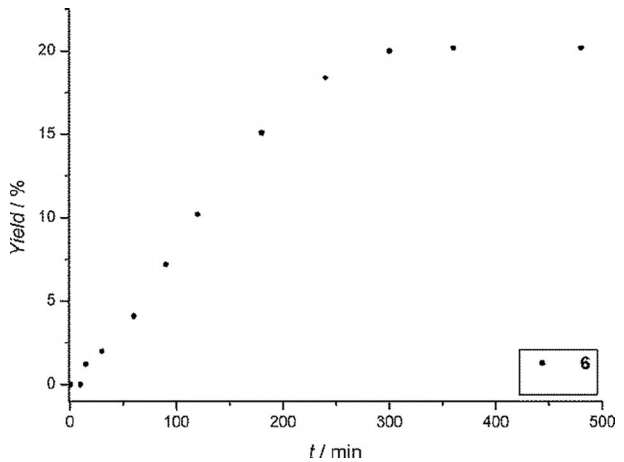


Figure 4. Reaction rate in the Mizoroki-Heck reaction of bromobenzene with *n*-butyl acrylate using **6** as precatalyst and adding mercury after 4 h.

It was also seen that complexes **4** and **6** did not start the reaction immediately. Both complexes needed an initiation phase of approximately ten minutes. No product formation was observed over this time. Such an initiation phase was not determined for other complexes bearing (CN)$_2$IMes. The catalytically active species has to be built from **6** by dissociation of the chelating coligand. Probably, a longer time is required for the phenylidenepyridine moiety to dissociate than for the *dmba* moiety in [PdCl(*dmba*){(CN)$_2$IMes}].[7] The curve for the poisoning experiment of complex **4** is not depicted in Figure 4 as the data points for the first, most important checkpoints match the data determined for **6**.

As the catalytically active species formed from precatalysts **4** and **6** are palladium nanoparticles, differences in the catalytic activity should be caused by differences in the nanoparticle size. Unfortunately, TEM measurements did not provide images fit for the determination of particle size distributions due to massive impurities of the organic bulk. No representative TEM images were found in the data set.

Conclusions

Two palladium(II) complexes, **4** bearing the well known IMes and **6** bearing the maleonitrile based (CN)$_2$IMes, were prepared. X-ray structures of complexes **4** and **6** were obtained and the higher acceptor strength of (CN)$_2$IMes in comparison to IMes, was observed by the shorter palladium-carbene bond in **6**, compared to the palladium-carbene bond in **4**. The π-accepting ability of (CN)$_2$IMes was also shown by ^{77}Se-NMR spectroscopy of the selone **7** derived from (CN)$_2$IMes. The ^{77}Se-NMR signal of **7** was found at δ = 167 ppm and is shifted to much higher frequencies than the signal of the selone derived from IMes. The two complexes **4** and **6** were used as precatalysts in the Mizoroki-Heck reaction of aryl chlorides with *n*-butyl acrylate. Because **6** proved the more effective precatalyst, it was used for a substrate screening in the Mizoroki-Heck reaction using various aryl bromides and *n*-butyl acrylate. It could be shown that sterically unhindered aryl bromides were effectively converted into the desired cinnamates under the use of precatalyst **6**. The product yields massively decreased, when the steric stress of the aryl bromides was increased. Palladium nanoparticles were identified to be the catalytically active species when **4** and **6** are used as precatalysts. The nanoparticles formed from **4** are bigger than the nanoparticles formed from **6**. The size difference illustrates the difference in the reactivity of **4** and **6**, respectively. Also, an initiation phase of approximately ten minutes was determined for **4** and **6**.

Experimental Section

General Information: All manipulations were carried out in an argon atmosphere using standard Schlenk techniques. Dry solvents were used for all manipulations. Solvents were dried after literature procedures.[14] All other chemicals were purchased from commercial sources and used for the reactions as received. Compounds **2**,[15] **3**,[16] and **5**,[17] were synthesized as described in the literature. Elemental analyses (C, H, N) were performed with an Elementar Vario EL elemental analyzer. NMR spectra were recorded with a Bruker Avance 300 or Bruker Avance 500 spectrometer. Resonances for ^{1}H- and ^{13}C-NMR spectra are reported relative to Me_4Si (δ = 0.0 ppm) and calibrated based on the solvent signal for ^{1}H and ^{13}C.[18] Resonances for ^{77}Se-NMR spectra are reported relative to the external standard dimethylselenide (60% in $CDCl_3$). Spectra are reported as follows:

Table 4. Crystallographic data of **4**, **6**, and **7**.

	4	**6**	**7**
Formula	$C_{64}Cl_2H_{64}N_6Pd_2$	$C_{36.5}H_{33.75}ClN_{6.25}Pd$	$C_{23}H_{22}N_4Se$
M_r /g·mol^{-1}	1200.91	701.80	433.40
Crystal size /mm	0.38 × 0.193 × 0.09	0.125 × 0.11 × 0.07	0.2 × 0.1 × 0.09
T /K	210(2)	150(2)	210(2)
Radiation	Mo-K_α	Mo-K_α	Mo-K_α
Crystal system	triclinic	tetragonal	orthorhombic
Space group	$P\bar{1}$	$I4_1/a$	$Fdd2$
a /Å	10.3427(5)	18.3141(5)	10.2554(5)
b /Å	15.7477(7)	18.3141(5)	36.6514(13)
c /Å	17.6547(9)	40.6086(15)	11.3895(4)
α /°	92.394(4)	90.00	90.00
β /°	94.045(4)	90.00	90.00
γ /°	106.530(3)	90.00	90.00
V /Å^3	2744.0(2)	13620.4(9)	4281.0(3)
Z	2	16	8
$\rho_{calcd.}$ /g·cm^{-3}	1.453	1.369	1.345
μ /mm^{-1}	0.800	0.658	1.769
Refl. measured	16884	44174	13521
Unique refl.	8621	6003	1895
R_{int}	0.0403	0.0706	0.0475
2Θ max.	49.106	49.996	49.996
R_1; wR_2 [$I>2\ \sigma(I)$]	0.0435/0.1152	0.0379/0.0858	0.0261/0.0663
R_1; wR_2 (all data)	0.0634/0.1225	0.0640/0.0956	0.0289/0.0678
Difference dens. min./max.	–0.804 / 0.696	–0.470 / 0.478	–0.322 / 0.321
Goodness of fit	1.072	1.011	1.052

chemical shift (δ ppm), multiplicity, integration and coupling constant (Hz). Mass spectra were recorded with a Micromass Q-TOF$_{micro}$ (ESI) or with a Thermo Quest SSQ 710 (70eV) (EI). IR Spectra were recorded with a Thermo Nicolet NEXUS FTIR in a KBr disk between 400 and 4000 cm^{-1} and with a resolution of 4 cm^{-1}. Background measurements were performed before the measuring the samples using a KBr disc or dichloromethane between KBr plates respectively. Single crystal intensity data were collected with a STOE IPDS-2 at 210 K (for **4** and **7**) or 150 K (for **6**) using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Crystal structures were solved by direct methods using SHELXS-2013/1.[19a] Refinements were performed by full-matrix least square methods on F^2 using SHELXS-2014/7.[19b] Non-hydrogen atoms were refined with anisotropic temperature factors. The deposited atom data (CIF) as well as the data in Table 4 reflect only the known cell content.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1416827 (**4**), CCDC-1416828 (**6**), and CCDC-1416829 (**7**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Synthetic Procedures

Synthesis of [PdCl(ppy)(IMes)] (4): In a 50 mL round-bottomed flask equipped with a magnetic stirrer and a reflux condenser, compounds **2** (86.9 mg, 0.15 mmol), **3** (100 mg, 0.29 mmol), and potassium carbonate (162 mg, 1.17 mmol) were suspended in acetonitrile (20 mL). The mixture was heated to reflux for 4 h. After cooling to room temperature, the excess of potassium carbonate was removed by filtration, followed by evaporation of the solvent. The residue was dissolved in dichloromethane (3 mL) and the product was purified by liquid chromatography on silica (height: 25 cm; diameter: 3 cm) with dichloromethane as eluent. Complex **4** was obtained in 55 % yield as a colorless solid. **EA**: C 63.90, H 5.53, N 6.99 %; found: C 63.89, H 5.68, N 7.12 %. **HR-MS** (EI) *m/z*: calcd. for $C_{32}H_{33}ClN_3Pd$: 600.1398 [M]$^+$; found: 600.1404 [M]$^+$. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 9.29 (d, J = 5.7 Hz, 1 H), 7.67 (dt, J = 7.5, 1.8 Hz, 1 H), 6.82 (dd, J = 7.3, 1.5 Hz, 1 H), 7.54 (d, J = 7.8 Hz, 1 H), 7.23 (s, 2 H), 7.09–6.85 (m, 8 H), 6.79 (dd, J = 7.5, 1.2 Hz, 1 H), 2.45 (s, 6 H), 2.29 (s, 6 H), 2.28 (s, 6 H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 164.8, 154.8, 150.1, 146.6, 140.3, 139.0, 138.7, 138.0, 136.6, 134.5, 129.8, 129.3, 128.3, 124.3, 124.1, 123.4, 122.0, 118.1, 21.1, 20.3, 20.0. **FT-IR** (KBr): $\tilde{\nu}$ = 3448, 3156, 3117, 3089, 3004, 2960, 2919, 2857, 2728, 1603, 1581, 1484, 1436, 1401, 1376, 1354, 1327, 1268, 1222, 1165, 1156, 1104, 1065, 1023, 924, 850, 756, 735, 706, 663, 645, 631, 593, 579, 420 cm^{-1}.

[PdCl(ppy){(CN)$_2$IMes}] (6): In a 50 mL round-bottomed flask equipped with a magnetic stirrer and a reflux condenser, compounds **2** (85.0 mg, 0.14 mmol) and **5** (150 mg, 0.28 mmol) were suspended in toluene (20 mL). The reaction mixture was heated to reflux for 16 h. After cooling to room temperature, the solvent was evaporated. The residue was dissolved in dichloromethane (2 mL) and pure **6** was obtained in 55 % yield by liquid chromatography on silica (height: 30 cm; diameter: 2 cm) with dichloromethane as eluent in form of a colorless solid. **EA**: C 62.68, H 4.80, N 10.75 %; found: C 62.83, H 4.72, N 10.92 %. **HR-MS** (EI) *m/z*: calcd. for $C_{34}H_{31}ClN_5Pd$: 650.1303 [M]$^+$; found: 650.1299 [M]$^+$. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 9.23 (d, J = 5.7 Hz, 1 H), 7.73 (dt, J = 7.7, 1.7 Hz, 1 H), 7.57 (d, J = 8.1 Hz, 1 H), 7.43 (dd, J = 7.7, 1.4 Hz, 1 H), 7.13–6.93 (m, 7 H), 6.96 (dd, J = 7.7, 0.9 Hz, 1 H), 2.46 (s, 6 H), 2.33 (s, 6 H), 2.31 (s, 6 H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 190.5, 154.0, 150,1, 146.6, 141.6, 139.7, 137.7, 134.6, 132.7, 130.6, 130.0, 128.7, 124.9, 123.9, 122.3, 118.4, 117.8, 106.8, 21.2, 20.2, 20.1. **FT-IR** (KBr): $\tilde{\nu}$ = 3433, 3045, 3026, 2961, 2921, 2859, 2242, 1605, 1581, 1485, 1457, 1437, 1371, 1325, 1298, 1157, 1067, 1023, 852, 757, 735, 714, 647, 631, 498 cm^{-1}.

4,5-Dicyano-1,3-bis(mesityl)imidazol-2-selone (7): In a 50 mL round bottomed flask equipped with a magnetic stirrer and a reflux con-

denser, **5** (100 mg 0.19 mmol) and grey selenium (60.0 mg, 0.77 mmol) were suspended in toluene (20 mL). The reaction mixture was heated to reflux for 16 h. After cooling to room temperature, the solvent was evaporated and the residue was suspended in dichloromethane (20 mL). To remove the excess of selenium, the suspension was filtered over a pad of celite 500 (height: 1 cm; diameter: 2 cm). The celite was washed with additional 50 mL dichloromethane and the dichloromethane phases were united. The solvent was evaporated. The residue was dissolved in dichloromethane (2 mL). Pure **7** was obtained in 80 % yield by liquid chromatography on silica (height: 25 cm; diameter: 2 cm) with dichloromethane as eluent in form of a shiny yellow crystalline solid. **EA**: C 63.74, H 5.12, N 12.93 %; found: 63.74 H 5.23 N 12.66 %. **HR-MS** (ESI) *m/z*: calcd. for $C_{23}H_{22}N_4Se$: 434.1010 $[M]^+$; found: 435.1074 $[M + H]^+$. **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.10 (s, 4 H), 2.39 (s, 6 H), 2.17 (s, 12 H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 165.3, 141.7, 135.3, 130.6, 130.2, 113.7, 106.3, 21.4, 17.9. **^{77}Se NMR** (75 MHz, $CDCl_3$): δ = 166.6. **FT-IR** (KBr): $\tilde{\nu}$ = 3036, 2984, 2944, 2916, 2857, 2235 (CN), 1744, 1606, 1481, 1456, 1376, 1320, 1289, 1210, 1189, 1078, 1034, 1012, 894, 861, 773, 705, 561, 552, 490 cm^{-1}.

Representative Procedure for the Mizoroki-Heck Reaction: In a 2 mL Schlenk tube with a magnetic stirrer, sodium carbonate (18.7 mg; 176 µmol; 1.4 equiv.) and TBAB (4.1 mg; 12.6 µmol; 0.1 equiv.) were submitted. A solution of the precatalyst (126 nmol; 0.001 equiv.) and 1,3,5-trimethoxybenzene (2.11 mg; 12.6 µmol; 0.1 equiv.) in 0.5 mL *N*,*N*-dimethylformamide was added. The mixture was stirred at room temperature for 5 min. Afterwards, bromobenzene (19.8 mg; 13.2 µL; 126 µmol) and *n*-butyl acrylate (32.3 mg; 35.9 µL; 252 µmol; 2.0 equiv.) were added via syringe and the tube was sealed and secured three times by evacuating and subsequently flushing with argon. The flask was placed in a preheated oil bath at 140 °C and stirred for 16 h. After finishing the reaction, the flask was cooled to 0 °C in an ice bath immediately. The cold mixture was hydrolyzed with hydrochloric acid (2 mL 1 N) and chloroform (2 mL) was added subsequently. The mixture was poured into 20 mL water and the aqueous phase was extracted three times with 2 mL chloroform.

For the substrate screening, the crude product was dissolved in 1.5 mL chloroform (GC grade from MERCK) and the yield was determined using a Perkin-Elmer Clarus 580, equipped with a Perkin-Elmer Elite 5 MS column (length: 30 m, diameter: 0.25 mm). Signals were detected by an FID-detector. The method of internal standard was used to determine GC yields.

For the calibration of the GC setup, the coupling products were isolated once by flash chromatography on silica (height: 460 mm, diameter: 15 mm) with hexane-ethyl acetate mixtures as eluent and characterized by means of ^{1}H and ^{13}C NMR spectroscopy and mass spectrometry. The analytical data of already known products were in agreement with the data already presented in the literature.[7,20]

Supporting Information (see footnote on the first page of this article): ^{1}H-NMR spectra of the new compounds **4**, **6** and **7** and the ^{77}Se-NMR spectrum of selone **7** are provided in the supporting information.

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