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New Pd–NHC-complexes for the Mizoroki–Heck reaction

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Abstract

The synthesis and structural characterization of novel chelating N-aryl substituted palladium(II)-biscarbene-complexes is reported: 1,1'-bis(4-bromophenyl)-3,3'-methylene-diimidazoline-2,2'-diylidene-palladium(II)-dibromide, 1,1'-bis(4-methoxyphenyl)-3,3'-methylenediimidazoline-2,2'-divlidene-palladium(II)-dibromide and 1,1'-bis(4-n-butoxyphenyl)-3,3'-methylenediimidazoline-2,2'-divlidene-palladium(II)-dibromide have been synthesized in good yields. The catalytic activity of these 1,1'-aryl-3,3'-methylenediimidazoline-2, 2'-divlidene-palladium(II)-dihalogenide complexes was tested for the Mizoroki-Heck reaction in comparison to 1,1'-(bis)methyl-3, 3'-methylenediimidazoline-2,2'-diylidene-palladium(II)-dihalogenide complexes and to 1,1'-bis(phenyl)-3,3'-methylene-diimidazoline-2,2'-dividene-palladium(II)-dibromide. The activity of the aryl substituted catalysts is significantly higher compared to the methyl substituted NHC complexes. They also allow the coupling of arylchlorides with olefins.

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Keywords: Mizoroki-Heck reaction; Palladium; N-heterocyclic carbene; Styrene; Bromoacetophenone; Chloroacetophenone; Bromoanisole; Methylacrylate

1. Introduction

The Mizoroki-Heck reaction has an enormous synthetic potential for generating substituted aryl-olefins [1-6], tolerating a wide range of functional groups [7,8]. During the last decade, important progress has been made in homogeneous Heck catalysis, which is summarized in recent reviews [3,9–15]. Very high turnover numbers (TON) could already be observed for the Heck coupling of iodobenzene with styrene [16–18], while the search for effective catalysts for the coupling of bromo- and especially chloroarenes with olefins is ongoing. The development of catalysts with high TONs for the carbon-carbon coupling of olefins with bromo- and chloroarenes is highly important, since these are interesting substrates for industrial applications [19,20]. Promising approaches for the activation of chloroand bromoarenes have been palladium complexes with Nheterocyclic carbene ligands [21-31], carbocyclic carbene ligands [32], PCP pincer ligands [33,34], CNC pincer ligands [35,36], cyclometallated phosphines [37-40], phosphites [41], phosphonium salts [42–44], bulky Lewis basic phosphines [45,46], phosphinous acid ligands [47,48], aniline ligands [49] as well as cyclometalated sulfur, amine and imine ligands [50-55] as catalysts. The use of immobilized [56] and non immobilized [57] ligand free palladium salts for the Mizoroki-Heck reaction with chloro- and bromoarenes is also discussed in the literature. Recently, Gibson et al. [58] as well as Jones et al. [59] showed that palladium complexes with chiral ligands are well suited as catalysts for the asymmetric Heck reaction. Despite the progress in the design of homogeneous catalysts for the Mizoroki-Heck reaction, the nature of the catalytically active species of this reaction is still not determined [60–66].

Due to the high stability of metal complexes of imidazoline-2-ylidenes towards heat, oxygen and moisture [67],

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they have long been subject of catalytic studies. In addition to the palladium catalyzed Mizoroki–Heck reaction, they have been used for the catalysis of other C–C coupling reactions [68], hydroformylations [69,70], polymerization reactions [71,72], olefin metathesis [73–76], and CH-activation [77–79]. Crucial for this development was the improvement of the synthetic methodology for the preparation of *N*-heterocyclic carbene (NHC) complexes, which has been reported in recent reviews [80,81]. The high synthetic relevance of catalysts for the Heck coupling of bromo- and chloroarenes with olefins makes NHC–palladium complexes promising candidates for these reactions.

2. Results and discussion

2.1. Preparation and structural properties of the Palladium(II)–bis(carbene) complexes

The catalytic activity of Pd-NHC-complexes (Scheme 1) was investigated for the Mizoroki-Heck coupling of arylhalides with olefins and compared to previously published examples. It could be shown that analogous N-aryl substituted Pt-complexes not only show a significantly higher stability than the corresponding N-methyl substituted Ptcomplexes, but that the electronic situation of the metal can be changed depending on the substituent in para-position of the aromatic ring [82]. Therefore, we were especially interested in the catalytic activity of N-aryl substituted Pd-NHC-complexes compared to N-methyl substituted Pd-NHC-complexes, which have been studied previously as it is well known that strongly electron donating ligands improve the activity of Heck catalysts [26,27,83-86]. Compounds 1-4 allow the evaluation of the electronic effect of substituents in the *para*-position of the phenyl ring. Complexes 1, 5 and 6 were prepared following the literature pro-



Scheme 1. Pd-NHC-complexes for the Mizoroki-Heck reaction.

cedures [71,78,85,87], while complexes **2–4** were obtained by conversion of the imidazolium salt with $Pd(OAc)_2$ in DMSO at temperatures up to 130 °C (Scheme 2). Decomposition of the *N*-aryl substituted complexes **1–4** is not observed below 300 °C, demonstrating the high thermal stability of these complexes.

2.2. Spectroscopic properties

The ¹H NMR spectra of the *N*-aryl substituted Pd-complexes 1 and 2 show an AB spin system for the protons of the methylene bridge, while in the ¹H NMR spectra of *N*-alkylsubstituted Pd-complexes (5 and 6) and of the *N*-aryl substituted Pd-complexes (3 and 4) these protons show a singlet [78]. Therefore, the flip of the boat conformation of the central six-membered palladacycle (Scheme 3) is slow on the NMR time-scale at room temperature. This is also observed in the case of sterically demanding alkyl-substituents like *tert*-butyl [71,88].

2.3. Solid state structures

We were able to obtain crystals suitable for X-ray diffraction of complexes 2 and 3 by cooling a hot DMSO solution or condensing THF into DMSO, respectively. Complex 2 crystallizes as a DMSO solvate with two DMSO molecules per Pd-compound, while the DMSO solvate of complex 3 shows only one DMSO molecule per Pd-compound. The ORTEP style plots of 2 and 3 are illustrated in Figs. 1 and 2.

The disparity of the structures at the central bis-NHCunits of compounds 2 and 3 is minimal. The most striking difference is the torsional angle between the plane of the aromatic ring and the plane of the imidazole ring. These torsional angles $(-29.2(5)^{\circ} \text{ and } 40.5(4)^{\circ})$ are slightly smaller for the bromide substituted phenyl ring in complex 2 than in complex 3 $(-54.7(4)^{\circ} \text{ and } 45.6(4)^{\circ})$, which contains the methoxy substituted phenyl ring. It is not possible to distinguish between electronic and packing effects, however, DFT calculations described below and illustrated in Fig. 3, showed only small electronic effects. Comparing the bond lengths and angles of complexes 2 and 3 with the structure of the corresponding methyl substituted compound 5 [89] only negligible differences in the geometry of



Scheme 2. Synthesis of palladium–biscarbene-complexes with aromatic side chains (2: R = Br, 3: R = OMe, 4: R = OBu).



Scheme 3. Illustration of the boat conformation and the flip.



Fig. 1. ORTEP style plot of complex 2 in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are plotted as balls of arbitrary radius. The DMSO molecules are omitted for clarity.



Fig. 2. ORTEP style plot of complex 3 in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are plotted as balls of arbitrary radius. The DMSO molecule is omitted for clarity.



Fig. 3. Superposition of the DFT calculated structures 2 and 3.

the palladium–bis-NHC structure could be observed. This is another evidence that the electronic influence of the side chains does not really affect the structure of the central bis-NHC unit.

To get additional insight concerning the electronic influence of the substituent in *para*-position of the phenyl ring on the geometry of the palladium–bis-NHC structure, we performed DFT geometry optimizations. The calculations were carried out using GAUSSIAN 03 [90]. Details of the DFT calculations are given in Section 4. The results of the geometry optimizations of structures **2** and **3** are illustrated in Fig. 3 as superpositions of the geometries.

The results obtained from the X-ray diffraction study and the DFT calculations are very similar. The computed structures of the palladium-bis-NHC complexes 2 and 3 differ only slightly in the torsion angle between the plane of the aromatic ring and the plane of the imidazole ring (55.79 and -55.79 for 2, 52.01 and -52.01 for 3). These small discrepancies are due to the different electronic properties of the substituents at the phenyl ring. Electron donating substituents like the methoxy group seem to reduce the torsional angle between the aromatic side chain and the NHC ring slightly in comparison to electron withdrawing substituents like bromine.

2.4. Catalysis

For a better comparison of the catalytic activity we used standard conditions with styrene as olefin and sodium acetate as base (Table 1).

Table 1

Influence of the arylhalide on the catalytic reactivity in the Mizoroki-Heck reaction: coupling of different arylhalides with styrene

X DMAc	+ $ X $ $ + $ $ X $ $ +$	+ H>
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Entry	R	Х	Catalyst	mol% Catalyst	<i>t</i> (h)	Conversion (%)	TON	TOF (h^{-1})
1	C(O)CH ₃	Br	1	0.5	8	34	49	6
2	C(O)CH ₃	Br	2	0.5	8	52	74	9
3	C(O)CH ₃	Br	3	0.5	3	99	141	47
4	C(O)CH ₃	Br	4	0.5	8	88 (4% cis)	126	16
5	$C(O)CH_3$	Br	5	0.5	8	56	80	10
6	$C(O)CH_3$	Br	6	0.5	8	80 (5% cis)	114	14
7	$C(O)CH_3$	Br	3	0.01	6	100	7143	1191
8	$C(O)CH_3$	Br	4	0.01	8	94 (2% cis)	6714	839
9	$C(O)CH_3$	Br	6	0.01	8	64 (2% cis)	4571	571
10	$C(O)CH_3$	Br	3	0.001	26	41	29286	1126
11	$C(O)CH_3$	Br	4	0.001	26	93 (3% cis)	66429	2555
12	$C(O)CH_3$	Br	3	0.0001	28	33	235714	8418
13	C(O)CH ₃	Br	4	0.0001	8	48	342857	42857
14	$C(O)CH_3$	Br	4	0.0001	28	100 (4% cis)	714286	25510
15	OCH ₃	Br	1	0.5	8	34	49	6
16	OCH ₃	Br	2	0.5	8	66 (6% cis)	94	12
17	OCH ₃	Br	3	0.5	8	52 (6% cis)	74	9
18	OCH ₃	Br	4	0.5	8	88 (4% cis)	126	16
19	OCH ₃	Br	5	0.5	8	32	46	6
20	OCH ₃	Br	6	0.5	8	30 (7% cis)	43	5
21	OCH ₃	Br	3	0.01	8	21	1500	188
22	OCH ₃	Br	4	0.01	8	26 (2% cis)	1857	232
23	OCH ₃	Br	3	0.001	8	4	2857	357
24	OCH ₃	Br	3	0.001	30	26 (4% cis)	18571	619
25	OCH ₃	Br	4	0.001	8	15 (4% cis)	10714	1339
26	OCH ₃	Br	4	0.001	30	51 (4% cis)	36428	1214
27	C(O)CH ₃	Cl	3	1.0	30	36 (4% cis)	26	0.9
28	$C(O)CH_3$	Cl	4	1.0	30	5	4	0.1
29	C(O)CH ₃	Cl	3	0.5	30	31	44	1.5
30	C(O)CH ₃	Cl	4	0.5	30	34 (4% cis)	49	1.6
31	C(O)CH ₃	Cl	3	0.01	30	16	1143	38
32	C(O)CH ₃	Cl	4	0.01	30	_	_	_

These results confirm that our complexes are highly active catalysts for the Heck-coupling of bromoacetophenone or bromoanisole with styrene. Turnover numbers (TONs) up to 700000 (catalyst 4) could be observed for the coupling of bromoacetophenone without addition of co-catalysts or other additives (Table 1, entry 14). Due to the low solubility of the Pd-complex 4 the conversion of bromoacetophenone with styrene in high concentration is marginally lower compared to the Pd-complex 3 (Table 1, entry 3/4 and entry 7/8). But at lower catalyst concentrations, complex 4 shows a surprising behaviour and a significantly higher TON compared to complex 3 (Table 1, entry 10/11 and entry 12/14). Complexes 1 and 2 are less active and show significantly lower TOFs for the Heck reaction of styrene with bromoacetophenone than the other complexes. Complex 2 was included for comparison although the bromophenyl group of the catalyst itself might react in the Heck reaction leading to catalyst deactivation. In

the NMR spectra of the catalyst after the reaction small alkene signals could be found.

Another reason for the lower activity are obviously the different electronic properties of the substituents, although the activity of complexes 1 and 2 is also hampered by solubility problems. Comparison of the Pd-complexes with aryl substituted ligands to the alkyl complexes 5 and 6 indicate that the aryl substituent stabilizes the catalytically active species. As expected, the +M-effect of the methoxy- and butoxy-substituent stabilizes the catalytically active Pd⁰ species. The influence of the counterion on the TON is only small as can be seen from Table 1, entries 19/20.

Bromoanisole is an example for a haloarene with electron-donating substituents and is well known for smaller reaction rates than what is usually observed for bromoacetophenone. Nevertheless, we could obtain TONs up to 35000 for the Heck coupling of bromoanisole with styrene with our catalysts (Table 1, entry 26). Again, complex **4** is the most active catalyst. The observed differences in the catalytic activity are comparable to the ones obtained for the reactions with bromoacetophenone.

As expected, the TONs for the coupling of chloroarenes with styrene are clearly lower than those for the coupling of bromoarenes (Table 1). However, compared to literature results [54,91,92], catalyst **3** is also a very active catalyst for the Heck coupling of chloroacetophenone (TON > 1000) (Table 1, entry 31). Increasing the amount of catalyst **3** from 0.5 mol% (entry 29) to 1 mol% (entry 27) does not really affect the conversion per reaction time, instead the formation of the *cis*-product is observed.

A great advantage of our catalysts is their high selectivity. Table 1 shows that the amount of *cis*-product formed during the conversion of bromoacetophenone with styrene is very small for catalysts 4 and 6 and below the detection limit for all other catalysts. For the reaction of bromoanisole with styrene the amount of the *cis*-product is slightly higher. In this case it is also formed during the reaction catalyzed with complexes 2 and 3. But when the amount of catalyst 3 was reduced from 0.5 to 0.01 mol% only the *trans*-product was formed. Together with their high catalytic activity this makes our Pd–NHC-complexes interesting Heck catalysts.

We also looked at the effects of different reaction conditions on the catalytic activity of the Pd-NHC-complexes. The screening of several bases showed good results for inexpensive NaOAc (Table 2 and Fig. 4). Stronger bases like KOH lead to quick decomposition of the catalyst and therefore lower conversions. Sodium carbonate is less soluble in DMAc, leading to longer reaction times. To reach 100% conversion it took approximately four times longer for the same reaction conditions with sodium carbonate than for sodium acetate. In addition, the formation of a byproduct (5% of cis-stilbene) was observed in the case of sodium carbonate (Table 2, entry 3). In the presence of $Ca(OH)_2$ the reaction time to reach complete conversion was slightly shorter than with NaOAc, but here even more byproduct was formed (6% cis-isomer) (Table 2, entry 4). Using Cs₂CO₃ partial decomposition of the catalyst was observed and the reaction time was clearly longer than with

Table 2



Fig. 4. Conversion of bromoacetophenone during the Heck-coupling with styrene at $140 \,^{\circ}$ C using different bases in the presence of catalyst **3**.

NaOAc (Table 2, entry 2). Thus, sodium acetate turned out to be the optimal base for our catalysts.

Different olefins do not much affect the reaction rate. Only small differences of the TONs using methylacrylate or styrene were observed (Table 3). Therefore we decided to use styrene as olefin in the standard reaction system for comparison of the catalytic activity of our palladium complexes.

In our case, the use of co-catalysts like NBu₄Br did not improve the catalytic results as it was reported in the literature for the reaction of bromoacetophenone and styrene together with 20 mol% of NBu₄Br [38]. The advantage of our catalysts is their ability to reach full conversion even with concentrations of 0.01 mol%, while very few examples in the literature do reach full conversion. Mostly only with relatively high catalyst concentrations of up to 1% full conversions are observed [93]. The Heck reaction of styrene with bromoanisole often uses higher reaction temperatures, but the results observed with our catalysts are still good in comparison to those reported in the literature. Full conversion for the reaction of bromoanisole with styrene is difficult to achieve, only few examples get close [94].

Summarizing the comparison of our catalysts with literature results, it becomes apparent that our Pd–NHC-complexes are very good catalysts for the Mizoroki–Heck reaction, their biggest advantage being the full conversion at very low concentrations, which leads to TONs and TOFs

.R

) + x	R 140	3 °C, base, DMAc		+ HX	
Entry	R	Х	mol% 3	Base	<i>t</i> (h)	Conversion (%)	TON
1	C(O)CH ₃	Br	0.01	NaOAc	6	100	7143
2	C(O)CH ₃	Br	0.01	Cs ₂ CO ₃	23	51	3643
3	C(O)CH ₃	Br	0.01	Na_2CO_3	22	96 (5% cis)	6857
4	C(O)CH ₃	Br	0.01	Ca(OH) ₂	5	100 (6% cis)	7143

Mizoroki-Heck reaction: coupling of bromoacetophenone with styrene in the presence of different bases

Table 3 Influence of the olefin on the catalytic reactivity	y in the Mizoroki–H	eck reaction	
	R	3	

R' + X + X + HX							
Entry	R	Х	R′	mol% 3	<i>t</i> (h)	Conversion (%)	TON
1	C(O)CH ₃	Br	C(O)OCH ₃	0.01	7	100	7143
2	$C(O)CH_3$	Br	Phenyl	0.01	6	100	7143
3	OCH ₃	Br	C(O)OCH ₃	0.01	22	39	2785
4	OCH ₃	Br	Phenyl	0.01	19	22	1571
5	C(O)CH ₃	Cl	C(O)OCH ₃	0.5	28	28	40
6	$C(O)CH_3$	Cl	Phenyl	0.5	28	30	43

which have not been reported before in the reaction with bromoacetophenone.

3. Conclusion

We present the synthesis and structural characterization of N-aryl substituted palladium biscarbene complexes. The electronic influences of different substituents at the aryl rings on the structure of the Pd-NHC-complex is minimal, but important for their catalytic activity. This allows us to further fine tune the catalysts. We have investigated the performance of N-aryl substituted Pd-NHC complexes (1-4) as catalysts for the Mizoroki-Heck reaction in comparison to N-methyl substituted Pd-NHC complexes (5, 6). We demonstrated that 1,1'-bis(4-methoxyphenyl)-3,3'-methylenediimidazoline-2,2'-diylidene-palladium(II)-dibromide (3) and 1,1'-bis(4-n-butoxyphenyl)-3,3'-methylenediimidazoline-2,2'-diylidene-palladium(II)dibromide (4) are very active and highly selective catalysts in the Heck coupling reaction of haloarenes with styrene and methylacrylate. These results show that bis-NHCpalladium(II)-complexes are useful catalysts in C-C coupling reactions and therefore open new routes for the design of new chelating ligands based on N-heterocyclic carbenes.

4. Computational details

All calculations were carried out using GAUSSIAN 03 [90]. The geometry optimizations of the structures were performed using B3LYP [95] combined with the split valence double- ζ (DZ) basis set 6-31G(d) [96,97] for the non-metal atoms except bromine, the split valence triple- ζ (TZ) basis set 6-311G(d) [98–100] for bromine and the Hay–Wadt-ECP [101] for palladium. No symmetry or internal coordinate constraints were applied during optimizations. Vibrational frequency calculations were carried out for all structures to verify them as true minima by the absence of imaginary eigenvalues. The superposition of the geometries was carried out using the program YASARA [102].

5. Experimental

5.1. General procedure

All reactions were carried out under an atmosphere of dry nitrogen. N,N-dimethylacetamide was distilled prior use and stored over 4 Å molecular sieve under nitrogen. GC–MS spectra were measured on a Hewlett-Packard GC G1800A system. The conversion was measured using diethylene glycol di-*n*-butyl-ether as internal standard. The turnover number (TON) is defined as (mol product)/(mol Pd), while the turnover frequency (TOF) is defined as (mol product)/[(mol Pd) × (reaction time in h)]. The amount of catalyst is defined regarding the amount of the olefin. All catalytic experiments were repeated at least twice, the TON and TOF given is the average value of several GC measurements.

¹H and ¹³C NMR spectra were recorded with a Bruker AC 300 P, Jeol JNM GX-400 or Jeol JNM GX-270 spectrometer. The spectra were referenced internally to the resonances of solvent (¹H, ¹³C). Elemental analyses were performed by the microanalytical laboratory of our institute using an EuroVektor Euro EA-300 Elemental Analyzer. Melting and decomposition points of the complexes **1–4** were determined with a melting point apparatus (Electrothermal 9100) and are uncorrected.

1-*R*-substituted imidazoles (*R*: 4-bromophenyl, 4-methoxyphenyl) [82], 1,1'-*R*-disubstituted-3,3'-methylenediimidazolium-dibromide (*R*: phenyl, 4-bromophenyl, 4-methoxyphenyl) [82,87], 1,1'-bisphenyl-3,3'-methylene-diimidazoline-2,2'-diylidene-palladium(II)-dibromide (1) [87], 1,1'-bismethyl-3,3'-methylene-diimidazoline-2,2'-diylidenepalladium(II)-dibromide (5) [71,85] and 1,1'-bismethyl-3, 3'-methylene-diimidazoline-2,2'-diylidene-palladium(II)dichloride (6) [103] were prepared according to the literature procedures.

5.2. Synthesis of 1-(4-n-butoxyphenyl)-imidazole

The synthesis follows previously published protocols [82,104]. 4-Butoxyaniline (5.96 g, 36 mmol) in methanol

(20 mL) was treated with 30% aq. glyoxal (5.8 mL, 36 mmol) for 16 h at r.t. until a yellowish precipitate was formed. NH₄Cl (3.85 g, 72 mmol) was added, followed by 37% aq. formaldehyde (5.8 mL, 72 mmol). The mixture was diluted with methanol (150 mL) and the resulting mixture refluxed for 1 h. H₃PO₄ (5 mL, 85%) was added over a period of 10 min. The resulting mixture was then stirred at reflux temperature for additional 4 h. After removal of the solvent, the dark residue was poured onto ice (100 g) and treated with aq. 40%KOH solution until pH 9. The resulting mixture was extracted with dichloromethane (three times 250 mL). The organic phases were combined, washed with H₂O, brine and dried over MgSO₄. The solvent was removed and the resulting dark residue was subjected to sublimation in vacuum at 160 °C (Yield: 4.88 g, 63%). ¹H NMR (300 MHz, CDCl₃): δ 7.77 (s, 1H, NCHN), 7.26 (d, J = 9.0 Hz, 2H, Ar), 7.18 (s, 1H, NCH), 7.16 (s, 1H, NCH), 6.94 (d, J = 8.9 Hz, 2H, Ar), 3.96 (t. J = 6.5 Hz, 2H, OCH₂), 1.77 (m, 2H, CH₂), 1.48 (m, ^{13}C 2H, CH_2), 0.96 (t, J = 7.4 Hz, 3H, CH_3) ppm. NMR (75.5 MHz, CDCl₃): δ 158.5 (C-OnBu), 135.7 (NCHN), 130.3 (i-C of Ar), 129.7 (NCH), 123.0 (m-C of Ar), 118.7 (NCH), 115.3 (o-C of Ar), 68.0 (OCH₂), 31.1 (CH₂), 19.1 (CH₂), 13.7 (CH₃) ppm. GC-MS: m/z 160 (M-nBu+H). Anal. 216 (M), Calc. for C₁₃H₁₆N₂O: C, 72.19; H, 7.46; N, 12.95. Found: C, 72.07; H, 7.60; N, 12.96%.

5.3. Synthesis of 1,1'-bis(4-n-butoxyphenyl)-3,3'-methylenediimidazolium-dibromide

In a pressure tube (4-n-butoxyphenyl)-imidazole (4 mmol, 865 mg) and dibromomethane (3 mmol, 521 mg) were heated neat to 130 °C for 48 h. A brown solid forms, which was washed twice with 5 mL of cold THF (Yield: 527 mg, 43%). ¹H NMR (300 MHz, DMSO- d_6): δ 10.28 (s, 2H, NCHN), 8.39 (s, 2H, NCH), 8.32 (s, 2H, NCH), 7.74 (d, J = 9.0 Hz, 4H, Ar), 7.22 (d, J = 9.0 Hz, 4H, Ar), 6.90 (s, 2H, NC H_2 N), 4.07 (t, J = 6.4 Hz, 4H, OCH₂), 1.75 (m, 4H, CH₂), 1.45 (m, 4H, CH₂), 0.94 (t, J = 7.4 Hz, 6H, CH₃) ppm. ¹³C NMR (75.5 MHz, DMSO-d₆): δ 159.6 (C-OnBu), 136.7 (NCN), 127.2 (i-C of Ar), 123.4 (m-C of Ar), 123.4 (NCH), 121.7 (NCH), 115.6 (o-C of Ar), 67.7 (NCH₂N), 58.1 (OCH₂), 30.4 (CH₂), 18.5 (CH₂), 13.5 (CH₃) ppm. Anal. Calc. for C₂₇H₃₄Br₂N₄O₂: C, 53.48; H, 5.65; N, 9.24. Found: C, 53.50; H, 5.69; N, 9.21%.

5.4. Synthesis of 1,1'-bis(4-bromophenyl)-3,3'-methylenediimidazoline-2,2'-diylidene-palladium(II)-dibromide (2)

857 mg 1,1'-bis(4-bromophenyl)-3,3'-methylene-diimidazolium-dibromide (1.38 mmol) and 310 mg palladium(II) acetate (1.38 mmol) were suspended in 10 mL DMSO. The reaction mixture was heated stepwise to 120 °C during 6 h and stirred for 2 h at this temperature. Half of the solvent was removed and a white solid was formed after addition of 15 mL ethanol. The solid was filtrated and washed with 10 mL ethanol. (Yield: 718 mg, 72%), m.p.: 335 °C (decomp.). ¹H NMR (300 MHz, DMSO-*d*₆): δ 7.86–7.83 (m, 6H, NC*H* and Ar), 7.77–7.73 (m, 6H, NC*H* and Ar), 6.52 (d, *J* = 14.0 Hz, 1H, NC*H*₂N), 6.45 (d, *J* = 12.4 Hz, 1H, NC*H*₂N) ppm. ¹³C NMR (75.5 MHz, DMSO-*d*₆): δ 159.5 (NCN), 138.6 (*i*-C of Ar), 131.6 (*m*-C of Ar), 127.1 (*o*-C of Ar), 122.6 (NCH), 122.4 (*C*-Br), 120.9 (NCH), 63.1 (NCH₂N) ppm. Anal. Calc. for C₁₉H₁₄Br₄N₄Pd: C, 31.50; H, 1.95; N, 7.73. Found: C, 31.22; H, 1.99; N, 7.58%.

5.5. Synthesis of 1,1'-bis(4-methoxyphenyl)-3,3'-methylenediimidazoline-2,2'-diylidene-palladium(II)-dibromide (3)

A solution of 430 mg 1,1'-bis(4-methoxyphenyl)-3,3'methylene-diimidazolium-dibromide (0.82 mmol)and 184 mg palladium(II) acetate (0.82 mmol) in 6 mL DMSO was heated stepwise during 6 h to 110 °C and stirred for 2 h at this temperature. After the removal of the solvent. the residue was washed two times with dichloromethane (5 mL) and with acetonitrile (5 mL). The product was obtained as a brown solid (Yield: 316 mg, 61%), m.p.: 328 °C (decomp.). ¹H NMR (300 MHz, DMSO- d_6): δ 7.82 (s, 2H, NCH), 7.68-7.65 (m, 6H, NCH and Ar), 7.14 (d, J = 8.7 Hz, 4H, Ar), 6.46 (s, 2H, NCH₂N), 3.85 (s, 6H, OCH₃) ppm. ¹³C NMR (75.5 MHz, DMSO- d_6): δ 158.7 (C-OCH₃), 144.0 (NCN), 132.3 (i-C of Ar), 126.7 (o-C of Ar), 122.7 (NCH), 121.8 (NCH), 113.7 (m-C of Ar), 63.0 (NCH₂N), 55.3 (OCH₃) ppm. Anal. Calc. for C₂₁H₂₀Br₂N₄O₂Pd: C, 40.25; H, 3.22; N, 8.94. Found: C, 40.34; H, 3.17; N, 9.06%.

5.6. Synthesis of 1,1'-bis(4-n-butoxyphenyl)-3,3'methylenediimidazoline-2,2'-diylidene-palladium(II)dibromide (**4**)

303 mg 1,1'-bis(4-n-butoxyphenyl)-3,3'-methylene-diimidazolium-dibromide (0.5 mmol) and 112 mg palladium(II) acetate (0.5 mmol) dissolved in 8 mL DMSO were stirred at 60 °C for 2 h, at 80 °C for 2 h and finally at 110 °C for 2 h. After removal of the solvent, the residue was washed twice with THF (5 mL) and dichloromethane (5 mL). The product was obtained as a white solid (251 mg; Yield: 71%), m.p.: 326 °C (decomp.). ¹H NMR (500 MHz, DMSO-d₆): δ 7.81 (s, 2H, NCH), 7.68 (s, 2H, NCH), 7.64 (d, J = 8.5 Hz, 4H, o-H of Ar), 7.13 (d, J = 8.7 Hz, 4H, m-H of Ar), 6.45 (s, 2H, NCH₂N), 4.06 (t, J = 6.0 Hz, 4H, OCH₂), 1.75 (m, 4H, CH₂), 1.48 (m, 4H, CH_2), 0.97 (t, J = 7.4 Hz, 6H, CH_3) ppm. ¹³C NMR (162 MHz, DMSO- d_6): δ 158.4 (*C*–O*n*Bu), 144.9 (N*C*N), 132.4 (*i*-C of Ar), 126.1 (*o*-C of Ar), 123.0 (NCH), 122.1 (NCH), 114.4 (*m*-C of Ar), 67.5 (OCH₂), 63.2 (NCH₂N), 30.8 (CH₂), 18.8 (CH₂), 13.8 (CH₃) ppm. Anal. Calc. for C₂₇H₃₂Br₂N₄O₂Pd: C, 45.62; H, 4.54; N, 7.88. Found: C, 45.73; H, 4.56; N, 7.74%.

5.7. General procedure for the Mizoroki-Heck reaction

A 10 mL Schlenk flask equipped with a reflux condenser was degassed and put under an atmosphere of nitrogen. It was charged with aryl halides (1 mmol), styrene or methylacrylate (1.4 mmol), anhydrous sodium acetate (1.1 mmol), diethylene glycol di-*n*-butyl-ether, the denoted amount of catalyst and 5 mL of N,N-dimethylacetamide. After that the flask was placed in a preheated oil bath at 140 °C. Aliquots (0.2 mL) were removed from the reaction mixture after a fixed time period and added to dichloromethane (10 mL) to observe the reaction progress. The organic portion was washed four times with 5 mL of water and dried with anhydrous MgSO₄. The solution was filtered, diluted with 5 mL of dichloromethane and analyzed by gas chromatography.

5.8. Structure determination of compound 2

Crystal data and details on the structure determination are presented in Table 4. Table 5 summarizes selected bond distances and bond angles. Suitable single crystals for the X-ray diffraction study were grown by cooling a saturated, hot solution of 2 in DMSO (see Fig. 1). A clear colorless needle $(0.10 \times 0.13 \times 0.58 \text{ mm})$ was stored under perfluorinated ether, transferred in a Lindemann capillary, fixed and sealed. Preliminary examination and data collection were carried out on an area detection system (NONIUS, kappa-CCD) at the window of a rotating anode (NON-IUS, FR591) and graphite-monochromated Mo K_{α} radiation ($\lambda = 0.71073$ Å). The unit cell parameters were obtained by full-matrix least-squares refinement of 7179 reflections. Data collection were performed at 123 K (OXFORD CRYOSYSTEMS) within a θ -range of $1.45^{\circ} < \theta < 25.34^{\circ}$. Nine data sets were measured in rotation scan modus with $\Delta \varphi / \Delta \omega = 1.0^{\circ}$. A total number of 88284 intensities were integrated. Raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure, for latent decay and absorption effects. After merging, $R_{\text{int}} = 0.046$, a sum of 6963 (all data) and 6232 $[I \ge 2\sigma(I)]$ reflexes remained. The structure was solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. Methyl hydrogen atoms were refined as part of rigid rotating groups, with C-H = 0.98 Å and $U_{iso(H)} = 1.5 U_{eq(C)}$. Other H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C-H distances of 0.99 Å and 0.95 Å, respectively, and $U_{iso(H)} = 1.2 U_{eq(C)}$. Full-matrix least-squares refinements with 329 parameters were carried out by minimizing $\Sigma w (F_o^2 - F_c^2)^2$ with the SHELXL-97 [105] weighting scheme and stopped at shift/ err < 0.001. The final residual electron density maps showed no remarkable features. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography. All calculations were per-

Table 4							
Crystal data	and	crystallographic	details for	· compounds	2	and 3	1

	2	2
	2	3
Measurement	E. Herdtweck	S. Goutal
Formula	$C_{19}H_{14}Br_4N_4Pd$ ·	$C_{21}H_{20}Br_2N_4O_2Pd\cdot$
	$2C_2H_6OS$	C_2H_6OS
Formula weight	880.64	704.77
Color/shape	Colorless/needle	Colorless/block
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$ (No. 14)	<i>P</i> 1 (No. 2)
a(A)	9.6311(1)	9.823(1)
b(A)	21.1983(1)	10.054(1)
<i>c</i> (Å)	18.7303(1)	14.073(1)
α (°)	90	101.29(1)
β (°)	95.2463(2)	106.14(1)
γ (°)	90	96.16(1)
$V(Å^3)$	3808.01(5)	1289.8(2)
Ζ	4	2
$\rho_{\rm calc} ({\rm g/cm^3})$	1.536	1.815
$\mu (\text{mm}^{-1})$	4.816	3.931
Diffractometer	Nonius kappa-CCD	Nonius kappa-CCD
	(area diffraction system);	(area diffraction
	Mo K_{α} ; rotating anode	system); Mo K _α ;
		sealed tube
Temperature (K)	123	198
λ (Å)	0.71073	0.71073
$\theta_{\min/\max}$ (°)	1.45/25.34	3.63/25.00
Reflections	88284	36285
integrated		
Independent	6963	4534
reflections (all		
data)		
Observed reflections	6232	3766
$[I > 2\sigma(I)]$		
Parameter refined	329	311
R_1 (observed/all	0.0284/0.0321	0.0245/0.0378
data)		
wR_2 (observed/all	0.0713/0.0725	0.0458/0.0491
data)		
Goodness-of-fit	1.086/1.086	1.003/1.003
(observed/all		
data)		
Residual electron	-0.93/1.29	-0.43/0.70
density (e Å ⁻³)		

formed on an Intel Pentium II PC, with the STRUX-V system, including the programs SHELXL-97, SIR92, and PLATON [105–110]. In addition, two molecules DMSO become apparent in the final difference Fourier maps but the severe disorder could not modelled properly. This problem was solved by using the PLATON calc squeeze procedure.

5.9. Structure determination of compound 3

Suitable single crystals for the X-ray diffraction study were grown by cooling a saturated, hot solution of **3** in DMSO/THF (see Fig. 2). A clear colorless block $(0.30 \times 0.12 \times 0.10 \text{ mm})$ was stored under perflourinated ether, transferred on a glass capillary and fixed. Preliminary examination and data collection were carried out on an area detecting system (kappa-CCD; Nonius) at the window of a sealed X-ray tube (Nonius, FR590) and graphite monochromated Mo K_{α} radiation ($\lambda = 0.71073$ Å). The

Table 5 Selected bond length (Å) and angles (°) of compound 2 and 3

	2	3
Pd-C1	1.979(3)	1.983(3)
Pd-C5	1.971(3)	1.971(3)
Pd-Br1	2.4828(5)	2.4811(4)
Pd-Br2	2.4690(4)	2.4935(4)
C1-N1	1.358(4)	1.350(4)
C1-N2	1.343(4)	1.351(4)
C5–N3	1.345(4)	1.353(4)
C5-N4	1.358(4)	1.355(4)
C1-Pd-C5	83.42(12)	84.14(13)
C1-Pd-Br1	171.59(9)	171.29(8)
C1–Pd–Br2	92.19(9)	91.48(9)
C5-Pd-Br1	91.04(9)	90.98(9)
C5–Pd–Br2	173.89(9)	173.49(9)
Br1–Pd–Br2	92.84(1)	92.73(2)
N1-C1-N2	105.0(3)	104.6(3)
N3-C5-N4	105.1(3)	104.3(3)
C1-N1-C11-C16	-29.2(5)	-54.7(4)
C5-N4-C21-C26	40.5(4)	45.6(4)

unit cell parameters were obtained by full-matrix leastsquares refinement of 124 reflections. Data collection was performed at 198 K within a θ -range of $3.63^\circ < \theta <$ 25.00°. A total number of 36285 intensities were integrated. Raw data were corrected for Lorentz, polarization, decay and absorption effects. After merging $(R_{int} = 0.053)$ a sum of 4534 independent reflections remained and were used for all calculations. The structure was solved by a combination of direct methods and difference Fourier synthesis. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were calculated in ideal positions riding on the parent carbon atoms. Full-matrix least-squares refinements with 311 parameters were carried out by minimizing $\Sigma w (F_0^2 - F_c^2)^2$ with shelxl-97 weighting scheme and stopped at shift/ err < 0.001. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography [111]. All calculations were performed with the shelxl-97 [105] package and the programs collect [106], DIRAX [112], EVALCCD [113], SIR92 [110], SADABS [114] and PLATON [109].

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Appendix A. supplementary material

CCDC 632784 and 632785 contain the supplementary crystallographic data for **2** and **3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/

conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.11.050.

References

- R.F. Heck, B.M. Trost, I. Fleming, Comprehensive Organic Synthesis, vol. 4, Pergamon, Oxford, UK, 1991, p. 883.
- [2] W.A. Herrmann, B. Cornils, Applied Homogenous Catalysis with Organometallic Compounds, Wiley-VCH, Weinheim, Germany, 2000, p. 712.
- [3] I.P. Beletskaya, A.V. Cheprakov, Chem. Rev. 100 (2000) 3009.
- [4] R.F. Heck, Palladium Reagents in Organic Synthesis, Academic Press, London, UK, 1985.
- [5] J. Tsuji, Palladium Reagents and Catalysts, Wiley, Chichester, UK, 1995.
- [6] A. de Meijere, F. Meyer, Angew. Chem., Int. Ed. Engl. 33 (1994) 2379.
- [7] T. Mizoroki, K. Mori, A. Ozaki, Bull. Chem. Soc. Jpn. 44 (1971) 581.
- [8] R.F. Heck, J.P. Nolly, J. Org. Chem. 37 (1972) 2320.
- [9] R.B. Bedford, Chem. Commun. (2003) 1787.
- [10] R.B. Bedford, C.S.J. Cazin, D. Holder, Coord. Chem. Rev. 248 (2004) 2283.
- [11] T.H. Riermeier, A. Zapf, M. Beller, Top. Catal. 4 (1997) 301.
- [12] E. Peris, R.H. Crabtree, Coord. Chem. Rev. 248 (2004) 2239.
- [13] J. Dupont, R.F. de Souza, P.A.Z. Suarez, Chem. Rev. 102 (2002) 3667.
- [14] N.J. Whitcombe, K.K.M. Hii, S.E. Gibson, Tetrahedron 57 (2001) 7449.
- [15] A.C. Hillier, G.A. Grasa, M.S. Viciu, H.M. Lee, C. Yang, S.P. Nolan, J. Organomet. Chem. 653 (2002) 69.
- [16] B.L. Shaw, S.D. Perera, E.A. Staley, Chem. Commun. (1998) 1361.
- [17] W.A. Herrmann, V.P.W. Boehm, C.-P. Reisinger, J. Organomet. Chem. 576 (1999) 23.
- [18] I.P. Beletskaya, A.V. Chuchuryukin, G. van Koten, H.P. Dijkstra, G.P.M. van Klink, A.N. Kashin, S.E. Nefedov, I.L. Eremenko, Russ. J. Org. Chem. 39 (2003) 1268.
- [19] R.R. Bader, P. Baumeister, H.U. Blaser, Chimia 50 (1996) 99.
- [20] A. Zapf, M. Beller, Top. Catal. 19 (2002) 101.
- [21] K. Selvakumar, A. Zapf, M. Beller, Org. Lett. 4 (2002) 3031.
- [22] D. Kremzow, G. Seidel, C.W. Lehmann, A. Fuerstner, Chem. Eur. J. 11 (2005) 1833.
- [23] A.M. Magill, D.S. McGuinness, K.J. Cavell, G.J.P. Britovsek, V.C. Gibson, A.J.P. White, D.J. Williams, A.H. White, B.W. Skelton, J. Organomet. Chem. 617–618 (2001) 546.
- [24] H.V. Huynh, T.C. Neo, G.K. Tan, Organometallics 25 (2006) 1298.
- [25] H. Lebel, M.K. Janes, A.B. Charette, S.P. Nolan, J. Am. Chem. Soc. 126 (2004) 5046.
- [26] W.A. Herrmann, M. Elison, J. Fischer, C. Köcher, G.R. Artus, Angew. Chem., Int. Ed. Engl. 34 (1995) 2371.
- [27] V.P.W. Boehm, W.A. Herrmann, Chem. Eur. J. 6 (2000) 1017.
- [28] S. Caddick, F.G.N. Cloke, G.K.B. Clentsmith, P.B. Hitchcock, D. McKerrecher, L.R. Titcomb, M.R.V. Williams, J. Organomet. Chem. 617–618 (2001) 635.
- [29] W.A. Herrmann, V.P.W. Boehm, C.W.K. Gstoettmayr, M. Grosche, C.-P. Reisinger, T. Weskamp, J. Organomet. Chem. 617–618 (2001) 616.
- [30] J. Schwarz, V.P.W. Boehm, M.G. Gardiner, M. Grosche, W.A. Herrmann, W. Hieringer, G. Raudaschl-Sieber, Chem. Eur. J. 6 (2000) 1773.
- [31] V. César, S. Bellemin-Laponnaz, L.H. Gade, Organometallics 21 (2002) 5204.

- [32] W.A. Herrmann, K. Oefele, S.K. Schneider, E. Herdtweck, S.D. Hoffmann, Angew. Chem., Int. Ed. Engl. 45 (2006) 3859.
- [33] D. Morales-Morales, R. Redón, C. Yung, C.M. Jensen, Chem. Commun. (2000) 1619.
- [34] C.M. Frech, L.J.W. Shimon, D. Milstein, Angew. Chem., Int. Ed. Engl. 44 (2005) 1709.
- [35] J.A. Loch, M. Albrecht, E. Peris, J. Mata, J.W. Faller, R.H. Crabtree, Organometallics 21 (2002) 700.
- [36] F.E. Hahn, M.C. Jahnke, V. Gomez-Benitez, D. Morales-Morales, T. Pape, Organometallics 24 (2005) 6458.
- [37] A. Schnyder, A.F. Indolese, M. Studer, H.-U. Blaser, Angew. Chem., Int. Ed. Engl. 41 (2002) 3668.
- [38] G.D. Frey, J. Schuetz, E. Herdtweck, W.A. Herrmann, Organometallics 24 (2005) 4416.
- [39] I.D. Kostas, B.R. Steele, A. Terzis, S.V. Amosov, Tetrahedron 59 (2003) 3467.
- [40] M.-H. Huang, L.-C. Liang, Organometallics 23 (2004) 2813.
- [41] M. Beller, A. Zapf, Synlett (1998) 792.
- [42] M.T. Reetz, G. Lohmer, R. Schwickardi, Angew. Chem., Int. Ed. Engl. 37 (1998) 481.
- [43] M.R. Netherton, G.C. Fu, Org. Lett. 3 (2001) 4295.
- [44] A. Datta, K. Ebert, H. Plenio, Organometallics 22 (2003) 4685.
- [45] A.F. Littke, G.C. Fu, Org. Syntheses 81 (2005) 63.
- [46] J.P. Stambuli, S.R. Stauffer, K.H. Shaughnessy, J.F. Hartwig, J. Am. Chem. Soc. 123 (2001) 2677.
- [47] G.Y. Li, G. Zheng, A.F. Noonan, J. Org. Chem. 66 (2001) 8677.
- [48] C. Wolf, R. Lerebours, J. Org. Chem. 68 (2003) 7077.
- [49] O. Baldovino-Pantaleón, J. Barroso-Flores, J.A. Cogordan, S. Hernández-Ortega, R.A. Toscano, D. Morales-Morales, J. Mol. Catal. A: Chem. 247 (2006) 65.
- [50] J. Spencer, D.P. Sharratt, J. Dupont, A.L. Monteiro, V.I. Reis, M.P. Stracke, F. Rominger, I.M. McDonald, Organometallics 24 (2005) 5665.
- [51] M. Ohff, A. Ohff, D. Milstein, Chem. Commun. (1999) 357.
- [52] J. Gil-Moltó, S. Karlstroem, C. Nájera, Tetrahedron 61 (2005) 12168.
- [53] T. Schultz, N. Schmees, A. Pfaltz, Appl. Organometal. Chem. 18 (2004) 595.
- [54] D.A. Alonso, C. Nájera, M.C. Pacheco, Adv. Synth. Catal. 344 (2002) 172.
- [55] C.S. Consorti, M.L. Zanini, S. Leal, G. Ebeling, J. Dupont, Org. Lett. 5 (2003) 983.
- [56] C.M. Crudden, M. Sateesh, R. Lewis, J. Am. Chem. Soc. 127 (2005) 10045.
- [57] A.H.M. de Vries, J.M.C.A. Mulders, J.H.M. Mommers, H.J.W. Henderickx, J.G. de Vries, Org. Lett. 5 (2003) 3285.
- [58] S.E. Gibson, H. Ibrahim, C. Pasquier, V.M. Swamy, Tetrahedron: Asymmetry 15 (2004) 465.
- [59] D.W. Dodd, H.E. Toews, F.d.S. Carneiro, M.C. Jennings, N.D. Jones, Inorg. Chim. Acta 359 (2006) 2850.
- [60] W.A. Herrmann, C. Brossmer, K. Oefele, C.-P. Reisinger, T. Priermeier, M. Beller, H. Fischer, Angew. Chem., Int. Ed. Engl. 34 (1995) 1844.
- [61] J. Louie, J.F. Hartwig, Angew. Chem., Int. Ed. Engl. 35 (1996) 2359.
- [62] C.S. Consorti, F.R. Flores, J. Dupont, J. Am. Chem. Soc. 127 (2005) 12054.
- [63] W.J. Sommer, K. Yu, J.S. Sears, Y. Ji, X. Zheng, R.J. Davis, C.D. Sherrill, C.W. Jones, M. Weck, Organometallics 24 (2005) 4351.
- [64] J.G. de Vries, Dalton Trans. (2006) 421.
- [65] M.B. Thathagar, J.E. ten Elshof, G. Rothenberg, Angew. Chem., Int. Ed. Engl. 45 (2006) 2886.
- [66] M.T. Reetz, E. Westermann, Angew. Chem., Int. Ed. Engl. 39 (2000) 165.
- [67] D. Bourissou, O. Guerret, F.P. Gabbai, G. Bertrand, Chem. Rev. 100 (2000) 39.
- [68] V.P.W. Boehm, T. Weskamp, C.W.K. Gstoettmayr, W.A. Herrmann, Angew. Chem., Int. Ed. Engl. 39 (2000) 1602.

- [69] W.A. Herrmann, J.A. Kulpe, W. Konkol, H. Bahrmann, J. Organomet. Chem. 389 (1990) 85.
- [70] W.A. Herrmann, C.W. Kohlpaintner, Angew. Chem., Int. Ed. Engl. 32 (1993) 1524.
- [71] M.G. Gardiner, W.A. Herrmann, C.-P. Reisinger, J. Schwarz, M. Spiegler, J. Organomet. Chem. 572 (1999) 239.
- [72] J. Schwarz, E. Herdtweck, W.A. Herrmann, M.G. Gardiner, Organometallics 19 (2000) 3154.
- [73] T. Weskamp, W.C. Schattenmann, M. Spiegler, W.A. Herrmann, Angew. Chem., Int. Ed. Engl. 37 (1998) 2490.
- [74] T. Weskamp, F.J. Kohl, W. Hieringer, D. Gleich, W.A. Herrmann, Angew. Chem., Int. Ed. Engl. 38 (1999) 2416.
- [75] M. Scholl, S. Ding, C.W. Lee, R.H. Grubbs, Org. Lett. 1 (1999) 953.
- [76] M.S. Sanford, J.A. Love, R.H. Grubbs, J. Am. Chem. Soc. 123 (2001) 6543.
- [77] M. Muehlhofer, T. Strassner, W.A. Herrmann, Angew. Chem., Int. Ed. Engl. 41 (2002) 1745.
- [78] T. Strassner, M. Muehlhofer, A. Zeller, E. Herdtweck, W.A. Herrmann, J. Organomet. Chem. 689 (2004) 1418.
- [79] S. Ahrens, A. Zeller, M.A. Taige, T. Strassner, Organometallics 25 (2006) 5409.
- [80] T. Weskamp, V.P.W. Boehm, W.A. Herrmann, J. Organomet. Chem. 600 (2000) 12.
- [81] W.A. Herrmann, Angew. Chem., Int. Ed. Engl. 41 (2002) 1290.
- [82] S. Ahrens, E. Herdtweck, S. Goutal, T. Strassner, Eur. J. Inorg. Chem. (2006) 1268.
- [83] H.M. Lee, C.Y. Lu, C.Y. Chen, W.L. Chen, H.C. Lin, P.L. Chiu, P.Y. Cheng, Tetrahedron 60 (2004) 5807.
- [84] C.-J. Jin, B. Twamley, J.M. Shreeve, Organometallics 24 (2005) 3020.
- [85] W.A. Herrmann, C.-P. Reisinger, M. Spiegler, J. Organomet. Chem. 557 (1998) 93.
- [86] M. Mayr, K. Wurst, K.-H. Ongania, M.R. Buchmeiser, Chem. Eur. J. 10 (2004) 1256.
- [87] K.-i. Okuyama, J.-i. Sugiyama, R. Nagahata, M. Asai, M. Ueda, K. Takeuchi, J. Mol. Catal. A: Chem. 203 (2003) 21.
- [88] W.A. Herrmann, J. Schwarz, M.G. Gardiner, Organometallics 18 (1999) 4082.
- [89] E. Herdtweck, M. Muehlhofer, T. Strassner, Acta Crystallogr. Sect. E: Struct. Rep. Online E59 (2003) m970.
- [90] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, GAUSSIAN 03, Gaussian, Inc., Wallingford CT, 2004.
- [91] G.D. Frey, C.-P. Reisinger, E. Herdtweck, W.A. Herrmann, J. Organomet. Chem. 690 (2005) 3193.
- [92] J. Schuetz, E. Herdtweck, W.A. Herrmann, Organometallics 23 (2004) 6084.
- [93] K.-M. Wu, C.-A. Huang, K.-F. Peng, C.-T. Chen, Tetrahedron 61 (2005) 9679.
- [94] H.M. Lee, J.Y. Zeng, C.-H. Hu, M.-T. Lee, Inorg. Chem. 43 (2004) 6822.
- [95] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
- [96] W.J. Hehre, R. Ditchfield, J.A. Pople, J. Chem. Phys. 56 (1972) 2257.

- [97] V.A. Rassolov, J.A. Pople, M.A. Ratner, T.L. Windus, J. Chem. Phys. 109 (1998) 1223.
- [98] R.C. Binning Jr., L.A. Curtiss, J. Comp. Chem. 11 (1990) 1206.
- [99] L.A. Curtiss, M.P. McGrath, J.-P. Blaudeau, N.E. Davis, R.C. Binning Jr., L. Radom, J. Chem. Phys. 103 (1995) 6104.
- [100] M.P. McGrath, L. Radom, J. Chem. Phys. 94 (1991) 511.
- [101] P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 299.
- [102] E. Krieger, www.yasara.org.
- [103] S. Ahrens, T. Strassner, Inorg. Chim. Acta 359 (2006) 4789.
- [104] J. Liu, J. Chen, J. Zhao, Y. Zhao, L. Li, H.A. Zhang, Synthesis 17 (2003) 2661.
- [105] G.M. Sheldrick, SHELXL-97, University of Göttingen, Göttingen, Germany, 1998.
- [106] Data Collection Software for Nonius-kappa CCD Devices, Delft, The Netherlands, 1997–2000.

- [107] Z. Otwinowski, W. Minor, Methods Enzymol. 276 (1997) 307.
- [108] G.R.J. Artus, W. Scherer, T. Priermeier, E. Herdtweck, STRUX-V: A Program System to Handle X-Ray Data, TU Muenchen, Garching, Germany, 1997.
- [109] A.L. Spek, PLATON, Utrecht University, Utrecht, The Netherlands, 2001.
- [110] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, J. Appl. Cryst. 27 (1994) 435.
- [111] A.J.C. Wilson, International Tables for Crystallography, Kluwer Academic Publisher, Dodrecht, The Netherlands, 1992.
- [112] A.J.M. Duisenberg, J. Appl. Cryst. 25 (1992) 92.
- [113] A.J.M. Duisenberg, R.W.W. Hooft, A.M.M. Schreurs, J. Kroon, J. Appl. Cryst. 33 (2000) 893.
- [114] Bruker, SADABS Area Detector Absorption and Other Corrections, 2.03, Delft, Netherlands, 2002.