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Palladium(II) Complexes of Unsymmetrical *CNN* Pincer Ligands

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Unsymmetrical 1-(arylimino)-3-(2-hetarylimino)isoindolines have been prepared from 1,3-diiminoisoindoline, an arylamine (aniline, 2-methylaniline, 2-iodoaniline), and a heteroaromatic amine (2-amino-6-methylpyridine, 2-amino-4-methylthiazole) in a stepwise manner by two consecutive condensations. The metalation reactions of these compounds with palladium(II) acetate proceed upon cyclopalladation of the carbocyclic aryl moieties and yield unsymmetrical *C,N,N* pincer complexes in all cases. X-ray crystallographic analysis were performed on single crystals of hydrogen{acetato[1-phenylimino-3-(6-methylpyridylimino)isoindolinato]palladate(II)} H[(phpi)Pd(OAc)] and pyridine[1-(2-tolylimino)-3-(4-methylthiazolylimino)isoindolinato]palladium(II) [(2-tolti)Pd(py)] by which the coordination mode, the conformation, the protonation site, and the trans influence of the carbon donor were established. For one more *C,N,N* pincer complex, hydrogen{acetato[1-(2-iodophenylimino)-3-(6-methylpyridylimino)isoindolinato]palladate(II)} H[(2-Iphpi)Pd(OAc)], a similar mononuclear coordination mode was confirmed by ^{1}H NMR spectroscopy, whereas for the product of an oxidative addition reaction of a palladium(0) precursor to the iodoaryl derivative a product with exo coordination was found. First experiments showed the effectivity of one of these complexes as a precatalyst in CC coupling reactions (Heck and Stille coupling).

Introduction

Pincer complexes are coordination compounds of metal ions carrying one meridonal-tridentate ligand.[1] Two types of pincer complexes, both named after the donor atoms of the chelate ligand, have become of particular importance in the field, the *PCP* pincers,[2] and the *NCN* pincers.[3] Members of both types have been demonstrated in the recent past to be excellent precatalysts for CC coupling reactions, aldol condensations, and other transformations. In addition, *PCP* and *NCN* pincer complexes have advantageously been used in studies of bond activation processes (C−H and C−C activation etc.),[4] and reports about their application as sensoric material, photosensitizer, and in biohybrids have appeared in the literature.[5] Besides these pincer ligands other ligand systems with similar donor sets have been designed and investigated, including those with NHC carbene donors,[6]

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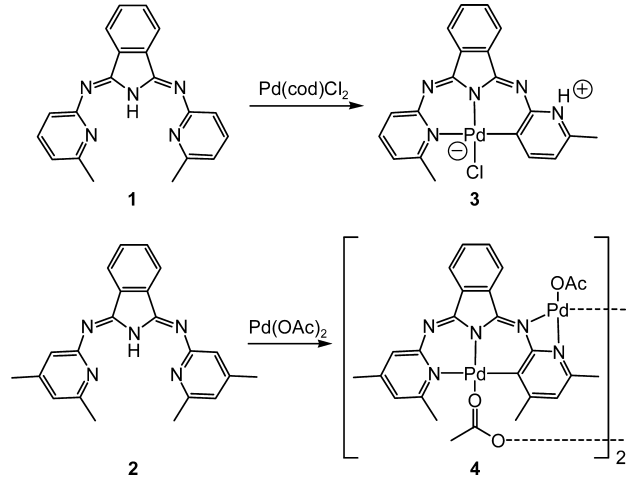
S donors,[7] or others.[8] However, reports concerning the preparation and use of unsymmetric donor pincer ligands are rare.[9]

New examples of *CNN* pincer complexes have recently been found with the sterically congested 1,3-bis(6-methylpyridylimino)isoindoline ligands 6-Me-bpi **1**[10] and 4,6-Me_2-bpi **2**[11] (Scheme 1). In the course of reactions of **1** and **2** with [Pd(cod)Cl_2] and palladium(II)acetate, respectively, the spontaneous, strain triggered rotation of one of the 6-methylpyridyl rings, followed by cyclopalladation in the respective 3-positions of these rings, has been observed. The anionic [(6-Me-bpi*)Pd(X)]$^-$ species (X = Cl, OAc; the asterisk indicates a C−H activated, dianionic ligand) that are initially formed in this process then bind to a proton or, with dimerization, to a second equiv of palladium(II) acetate, and have been isolated as neutral *CNN* pincer **3** and **4**, respectively (Scheme 1). X-ray crystallographic work performed on these complexes provided detailed insight into a strong trans influence of the carbon donor.

Scheme 1. Formation of Cyclopalladated (bpi*)Pd Complexes **3** and **4**



It can be expected that the trans influence of the carbon donor of *CNN* pincer complexes like **3** and **4** increases the lability of the bound terminal heterocycle (i.e., the pyridyl moiety in these cases). This increase may gain additional support by a well-positioned steric constraint so that the terminal heterocycle of sterically constrained (bai*)-based *CNN* pincer complexes becomes hemilabile (bai* = C−H activated dianion of a bis(arylimino)isoindoline). This hemilability leaves the option of two reactive sites at the palladium ion in the cis position and thus the promise for catalytic activity in CC coupling reactions.[8] Unsymmetric 1-(arylimino)-3-(hetarylimino)isoindolines should be ideal candidates for the selective preparation of such *CNN* pincer complexes. However, literature mentions members of this class of ligands only as components in complex mixtures.[12] We have now studied preparation strategies for sterically hindered 1-(arylimino)-3-(hetarylimino)isoindolines and cyclopalladation reactions[13] of the products and report here the successful syntheses and first applications of such pincer compounds.

Experimental Section

All reagents were purchased from commercial sources and used as received. Solvents were dried prior to use by standard procedures and stored under Argon in the dark. Reactions were performed in Schlenk equipment under an atmosphere of purified argon. NMR spectra were obtained on a Bruker DRX 400, DRX 300, or ARX 200 spectrometer. Chemical shifts (δ) are given in ppm relative to residual protio solvent resonances (^{1}H spectra), deuterio solvent (^{13}C), or phosphoric acid (^{31}P). Mass spectra were recorded on a VB Tribid or a Varian CH7 (EI, 70 eV), an IonSpec Ultima (ESI), or a QStarPulsar i (ESI and APCI). *m*/*z* values are given for the most abundant isotopes only. UV−vis data was collected on a Shimadzu UV-1601 PC spectrophotometer. GC measurements were

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undertaken on a Agilent 6850 Network GC using helium as carrier gas, a Agilent HP-1 column, and a FID for quantitative detection.

Preparation of 1-Arylimino-3-iminoisoindolines 9−11: General Procedure. 1,3-Diiminoisoindoline **5** (0.72 g, 4.95 mmol) and the aniline derivative **6**, **7**, or **8** (1 equiv) are suspended in ethanol (10 mL) and heated to reflux for 6 (**9**) or 18 h (**10**, **11**), respectively. The solvent is then removed in vacuo, and the residue is subjected to silica chromatography. In a first fraction, unreacted aniline derivative is eluted with dichloromethane. After changing the solvent to ethyl acetate the product is obtained in the second, yellowish fraction.

1-Phenylimino-3-iminoisoindoline (9). Obtained (227 mg, 21%) as a yellow solid; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 4.61 (s br, 2 H, NH_2), 7.00−7.03 (m, 2 H, 2-CH_{Ph}), 7.15−7.21 (m, 1 H, 4-CH_{Ph}), 7.35−7.41 (m, 2 H, 3-CH_{Ph}), 7.48−7.52 (m, 1 H, α-CH), 7.55−7.66 (m, 2 H, β'-CH, β-CH), 7.90−7.96 (m, 1 H, α′-CH); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 120.2, 121.9, 122.4, 123.5, 129.0, 130.9, 131.9, 132.5, 133.2, 137.4, 150.9, 157.1; MS (EI, 70 eV): m/z = 221 ($M^{+\bullet}$); HRMS (EI): Calcd for $C_{14}H_{11}N_3$: 221.0953; found: 221.0955.

1-(2-Tolylimino)-3-iminoisoindoline (10). Obtained (218 mg, 19%) as a yellow solid; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 2.11 (s, 3 H, CH_3), 6.86−6.90 (m, 1 H, CH_{Ph}), 7.13−7.30 (m, 3 H, CH_{Ph}), 7.37−7.40 (m, 1 H, α-CH), 7.54−7.66 (m, 2 H, β-CH), 7.95−7.99 (m, 1 H, α-CH), no signal for NH protons observed; ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 17.7, 119.8, 121.2, 122.4, 122.9, 126.3, 129.5, 130.2, 130.6, 131.7, 133.8, 137.8, 151.0, 160.1, 168.2; MS (EI, 70 eV): m/z = 235 ($M^{+\bullet}$); HRMS (EI): Calcd for $C_{15}H_{13}N_3$: 235.1109; found: 235.1116.

1-(1-Iodophenylimino)-3-iminoisoindoline (11). Obtained (610 mg, 36%) as a yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.75 (br.s, 2 H, NH_2), 6.92 (dt, J = 7.8 Hz, J = 1.3 Hz, 1 H, CH_{Ph}), 7.01 (dd, J = 7.9 Hz, J = 1.6 Hz, 1 H, CH_{Ph}), 7.33−7.40 (m, 2 H, α-CH, CH_{Ph}), 7.53−7.68 (m, 2 H, β'-CH, β-CH), 7.91 (dd, J = 7.9 Hz, J = 1.3 Hz, 1 H, CH_{Ph}), 8.02 (d, 1 H, α′-CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 121.7, 122.6, 123.2, 124.3, 128.4, 130.7, 131.7, 132.2, 132.8, 136.6, 138.6, 152.6; MS (EI, 70 eV): m/z = 347 ($M^{+\bullet}$); HRMS (EI): Calcd for $C_{14}H_{11}IN_3$: 346.9919; found: 346.9914.

Preparation of 1-Hetarylimino-3-aryliminoisoindolines 14−16: General Procedure. 1-Arylimino-3-iminoisoindoline **9**, **10**, or **11** (1 equiv, 1.0 mmol) and heterocycle **12** or **13** (1 equiv, 1.0 mmol) are suspended in *n*-butanol (10 mL) and heated to reflux for 7 h. After removal of all volatiles, the residue is purified by column chromatography as indicated below.

1-(6-Methylpyridylimino)-3-phenyliminoisoindoline (14). Obtained (194 mg, 88%) after chromatography on silica with pentane/ethyl acetate (3:1) as a yellow solid; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 2.16 (s, 3 H, Me), 6.85 (d, J = 7.3 Hz, 1 H, 5-CH_{Py}), 7.15−7.24 (m, 4 H, 4 × CH_{Ph}), 7.41−7.48 (m, 2 H, 3-CH_{Ph}), 7.56−7.63 (m, 1 H, 4-CH_{Py}), 7.64−7.78 (m, 2 H, β-CH, β'-CH), 7.95−8.05 (m, 2 H, α-CH, α′-CH), 12.28 (br.s, 1 H, NH); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 120.2, 121.9, 122.4, 123.5, 129.0, 130.9, 131.9, 132.5, 133.2, 137.4, 150.9, 157.1; MS (EI, 70 eV): m/z = 221 ($M^{+\bullet}$); HRMS (EI): Calcd for $C_{14}H_{11}N_3$: 221.0953; found: 221.0955.

1-(4-Methylthiazolylimino)-3-(2-tolylimino)isoindoline (15). Obtained (120 mg, 36%) after chromatography on silica with pentane/ethyl acetate (6:1) as a yellow solid; ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 2.15 (s, 3 H, Me), 2.26 (s, 3 H, Me), 6.60 (s, 1H, CH_{Th}), 7.01−7.07 (m, 1 H, CH_{Ph}), 7.09−7.18 (m, 1 H, CH_{Ph}), 7.25−7.33 (m, 2 H, CH_{Ph}), 7.61−7.72 (m, 2 H, β-CH), 7.94−7.96 (m, 1 H, α-CH), 8.05−8.08 (m, 1 H, α-CH), 11.65 (br.s, 1 H, NH); ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 16.2, 16.8, 110.1, 118.9, 121.8, 123.8, 125.9, 129.6, 130.1, 130.9, 131.2, 133.7, 134.7, 146.7, 149.3, 149.5, 153.1, 170.9; MS (EI, 70 eV): m/z = 332 ($M^{+\bullet}$); HRMS (EI): Calcd for $C_{19}H_{16}N_4S$: 332.1096; found: 332.1089.

1-(6-Methylpyridylimino)-3-(1-iodophenylimino)isoindoline (16). Obtained (175 mg, 40%) after chromatography on silica with pentane/ethyl acetate (5:1) as a yellow solid; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.18 (s, 3 H, Me), 6.84−6.95 (m, 2 H, 5-CH_{Ph}, 5-CH_{Py}), 7.15−7.26 (m, 2 H, 3-CH_{Ph}, 3-CH_{Py}), 6.44 (td, J = 7.9 Hz, J = 1.5 Hz, 1 H, 4-CH_{Ph}), 7.61 (t, J = 7.7, 1 H, 4-CH_{Py}), 7.67−7.74 (m, 2 H, β-CH, β'-CH), 7.98 (dd, J = 6.6 Hz, J = 1.3 Hz, 1 H, 6-CH_{Ph}), 8.02−8.21 (m, 2 H, α-CH, α′-CH), 12.31 (br.s, 1 H, NH); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.3, 92.5, 119.8, 120.5, 120.8, 122.7, 122.9, 125.8, 129.5, 132.0, 133.9, 136.7, 138.6, 139.7, 151.0, 152.5, 153.9, 156.1, 160.1; UV−vis (CH_2Cl_2): λ_{max} = 231, 273, 349 nm; MS (EI, 70 eV): m/z = 438 ($M^{+\bullet}$); HRMS (EI): Calcd for $C_{20}H_{15}IN_4$: 438.0341; found: 438.0349.

Preparation of Palladium(II) Complexes of 1-Hetarylimino-3-aryliminoisoindolines 17−19: General procedure. 1-Hetarylimino-3-aryliminoisoindoline **14**, **15**, or **16** (1 equiv, 0.4 mmol) and $Pd(OAc)_2$ (1 equiv, 0.4 mmol) are suspended in methanol (8 mL) at ambient temperature and stirred for 16 h. After removal of all volatiles the residue is purified as indicated below.

Hydrogen{acetato-[1-(6-methylpyridylimino)-3-phenyliminoisoindolinato]palladate(II)} H[(phpi)Pd(OAc)] (17). Obtained from **14** (19 mg, 10%) after fractionating recrystallization from *n*-hexane/chloroform (1:1) as a bright red solid; ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 1.90 (s, 3 H, OAc), 2.93 (s, 3 H, $-CH_3$), 6.95−6.99 (m, 1 H, CH_{Ph}), 7.14−7.19 (m, 2 H, CH_{Py}, CH_{Ph}), 7.29−7.34 (m, 2 H, CH_{Py}, CH_{Ph}), 7.58−7.62 (m, 2 H, β,β'-CH), 7.66 (d, J = 7.2 Hz, 1 H, CH_{Ph}), 7.87 (t, J = 7.7 Hz, 1 H, 4-CH_{Py}), 7.92−7.99 (m, 2 H, α′-CH), 11.93 (br.s, 1 H, NH); ^{13}C NMR (HMQC, 400 MHz, [D_6]DMSO): δ = 20.4, 26.0, 120.5, 120.8, 121.5, 123.5, 125.0, 128.6, 129.6, 131.0, 132.8, 138.6 (no quarternary carbon centers were observed); UV−vis (CH_2Cl_2): λ_{max} = 232, 337, 448 nm; MS (APCI): m/z = 416 ([M−HOAc]$^-$); HRMS (APCI): Calcd for $C_{20}H_{14}N_4Pd$: 416.0248; found: 416.0248. CHN determinations did not result in reproducible data due to varying amounts of cocrystallized **17′**.

Pyridin-[1-(4-methylthiazolylimino)-3-(2-tolylimino)isoindolinato]-palladium(II) [(2-tolti)Pd(py)] (18). Obtained from cyclopalladated **15** by recrystallization from pyridine/*n*-hexane as a reddish-brown solid (91%); ^{1}H NMR (400 MHz, CD_2Cl_2/C_5D_5N): δ = 1.09 (s, 3 H, Me), 2.79 (s, 3H, Me), 5.81 (d, 1 H, J = 7.8 Hz, CH_{Ph}), 6.40 (s, 1 H, CH_{Th}), 6.60 (t, 1 H, J = 7.5 Hz, CH_{Ph}), 7.06 (d, 1 H, J = 7.0 Hz, CH_{Ph}), 7.35−7.41 (m, 1 H, β-CH), 7.40−7.50 (m, 1 H, β-CH), 7.97 (d, 1 H, J = 7.5 Hz, α-CH), 8.11 (d, 1 H, J = 7.3 H, α-CH); ^{13}C NMR (100 MHz, CD_2Cl_2/C_5D_5N): δ = 17.0, 19.7, 20.8, 110.1, 121.1, 121.4, 124.0, 126.6, 128.9, 130.0, 133.1, 135.7, 138.6, 139.0, 141.6, 146.3, 149.0, 155.8, 171.4, 172.8; UV−vis (CH_2Cl_2): λ_{max} = 237, 440 nm; MS (ESI, CH_3CN): m/z = 478 ([M - py + CH_3CN + H]$^+$); HRMS (ESI): Calcd for $C_{21}H_{18}N_5PdS$ ([M - py + CH_3CN + H]$^+$): 478.0312; found: 478.0319; CHN analysis: Calcd for $C_{24}H_{19}N_5PdS$ C 55.87, H 3.71, N 13.57; found C 55.74, H 3.55, N 13.27.

Hydrogen{acetato-[1-(6-methylpyridylimino)-3-(1-iodophenylimino)isoindolinato]palladate(II)} H[(2-Iphpi)Pd(OAc)] (19). Obtained from **16** (99 mg, 41%) after extraction in toluene, evaporation of the solvent and recrystallization from dichloromethane/*n*-hexane as a bright red solid; ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 1.88 (s, 3 H, OAc), 2.73 (s, 3 H, $-CH_3$), 6.69 (t, J = 7.6 Hz, 1 H, 4-CH_{Ph}), 7.21 (d, J = 7.3 Hz, 1 H, 3-CH_{Py}), 7.36 (d, J = 7.8 Hz, 1 H, 5-CH_{Py}), 7.60−7.67 (m, 2 H, β'-CH, β-CH), 7.67−7.71 (m, 1 H, CH_{Ph}), 7.80 (d, J = 7.3 Hz, 1 H, CH_{Ph}), 7.90 (t, J = 7.6 Hz,

Table 1. Crystallographic Data for the Complexes **17**, **18**, and **20**

compound	**17**	**18**	**20**
formula	$C_{22.925}H_{18.925}Cl_{2.77}N_4O_2Pd_{1.02}$	$C_{24}H_{19}N_5Pd\ S$	$C_{57}H_{47}Cl_2IN_4P_2Pd$
molecular mass	589.34	515.90	1154.13
a/Å	23.2418(17)	12.737(4)	12.0384(13)
b/Å	11.5637(11)	12.633(7)	13.2267(15)
c/Å	17.9680(12)	17.184(6)	15.940(2)
α/°	90	90	83.055(14)
β/°	104.537(5)	130.34(2)	86.798(14)
γ/°	90	90	82.664(13)
Z	8	4	2
d/g·cm^{-3}	1.675	1.626	1.535
cryst syst	monoclinic	monoclinic	triclinic
space group	*C*2/*c*	$P2_1/c$	$P\bar{1}$
diffractometer	IPDS 1	IPDS 1	IPDS 1
radiation	Mo Kα	Mo Kα	Mo Kα
monochromator	graphite	graphite	graphite
cryst size/mm	0.36 × 0.24 × 0.14	0.26 × 0.08 × 0.07	0.24 × 0.23 × 0.07
temperature/K	193(2)	193(2)	193(2)
data collection	*σ* scan	*σ* scan	*σ* scan
Θ range/°	1.98−25.87	2.24−25.99	1.91−26.07
h range	$-28 \le h \le 28$	$-15 \le h \le 15$	$-14 \le h \le 14$
k range	$-14 \le k \le 14$	$-15 \le k \le 15$	$-16 \le k \le 16$
l range	$-21 \le l \le 21$	$-21 \le l \le 20$	$-19 \le l \le 19$
measured reflns	22 437	16 023	24 990
indep. reflns[a]	3370	2192	7374
abs. coefficient	1.151	1.002	1.204
struct. solution[b]	direct	direct	Patterson
final R_1 value	0.0434	0.0281	0.0303
final wR_2 value	0.1053	0.0544	0.0758

[a] $I < 2\sigma(I)$; [b] All structures were solved using *SHELXS, Program for Crystal Structure Determination*[14] and refined with *SHELXL*, Program for Crystal Structure Refinement.[15]

1 H, 4-CH_{Py}), 7.94 (d, $J = 7.1$ Hz, 1 H, α′-CH), 7.99 (d, $J = 7.1$ Hz, 1 H, α-CH), 11.8 (br.s, 1 H, NH); ^{13}C NMR (100 MHz, CD_2Cl_2): $\delta = 21.0, 25.8, 104.4, 120.8, 120.9, 121.0, 121.6, 124.6, 129.5, 129.9, 130.7, 133.5, 135.5, 137.5, 138.9, 154.9, 158.8, 179.4, 201.9$; UV−vis ($CH_2Cl_2$): $\lambda_{max} = 236, 334, 443$ nm; MS (ESI): $m/z = 543$ ([M−OAc]$^+$); HRMS (ESI): Calcd for $C_{20}H_{14}IN_4Pd$ ([M−OAc]$^+$): 542.92980; found: 542.92168; CHN analysis: Calcd for $C_{22}H_{17}IN_4PdO_2 \times CH_2Cl_2$ C 43.84, H 2.84, N 9.30; found C 43.94, H 3.11, N 9.05.

Synthesis of 20. H(1-Iphpi) **16** (30 mg, 0.07 mmol) and $Pd(PPh_3)_4$ (79 mg, 0.07 mmol) are dissolved in absolute THF (2 mL) in the dark and are stirred at ambient temperature for 16 h. The product crystallizes directly from the reaction mixture and can be filtered off as a bright yellow material.

Yield: 47 mg, 64%; ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 2.41$ (s, 3 H, CH_3), 6.34−6.38 (m, 2 H, CH_{Ph}), 6.58 (t, $J = 7.6$ Hz, 1 H, CH_{Ph}), 6.92 (d, $J = 7.3$ Hz, 1 H, CH_{Py}), 7.10−7.18 (m, 21 H, CH_{Ph}, CH_{PPh3}), 7.48−7.64 (m, 11 H, CH_{Py}, CH_{PPh3}), 7.75 (t, $J = 6.6$ Hz, 1 H, CH_{Py}), 7.77−7.97 (m, 2 H, *β*,*β*′-CH), 8.01 (d, $J = 7.6$ Hz, 1 H, α′-CH), 8.44 (d, $J = 7.6$ Hz, 1 H, α-CH), 11.2 (s, 1 H, NH); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta = 24.5, 119.1, 119.8, 120.3, 122.3, 124.1, 127.4 - 127.5$ (m, PPh_3), 130.0, 131.1, 131.6, 132.5, 132.8, 133.1, 134.9−135.1 (m, PPh_3), 135.6, 136.0, 136.8, 138.4, 146.9, 150.0, 153.8, 156.2, 160.2, 205.5; ^{31}P NMR (81 MHz, CD_2Cl_2): $\delta = 25.0$; UV−vis (CH_2Cl_2): $\lambda_{max} = 224, 342$ nm; MS (ESI): $m/z = 416$ ([**20** − I − 2 PPh_3]$^+$); several attempted combustion analyses gave *C* values deviating from theory by ≥20% for unclear reasons.

X-ray Analyses. X-ray quality crystals of **17**/**17′** and **20** were grown by slow evaporation from chloroform or dichloromethane solutions, respectively, at ambient temperature. A crystal of **18** grew from a pyridine solution layered with *n*-hexane. Crystallographic data for all three compounds is given in Table 1.

Results and Discussions

Preparation of Unsymmetrical H(bai) Species. Whereas several protocols for the preparation of symmetrical H(bai) species (bai = anion of a bis(arylimino)isoindoline) are known,[16] unsymmetrical H(bai) ligands have only been prepared as mixtures so far.[12] On the base of known preparations of symmetrical H(bai)s, four different two-step strategies can be proposed for the synthesis of unsymmetric H(bai)s with one terminal phenyl and one terminal hetaryl functionality. The introduction of the first arylimino group can be attempted by condensation of either the aniline or the hetarylamine with either phthalodinitrile or 1,3-diiminoisoindoline, followed by the introduction of the respective other terminal aromatic unit in a second condensation step.

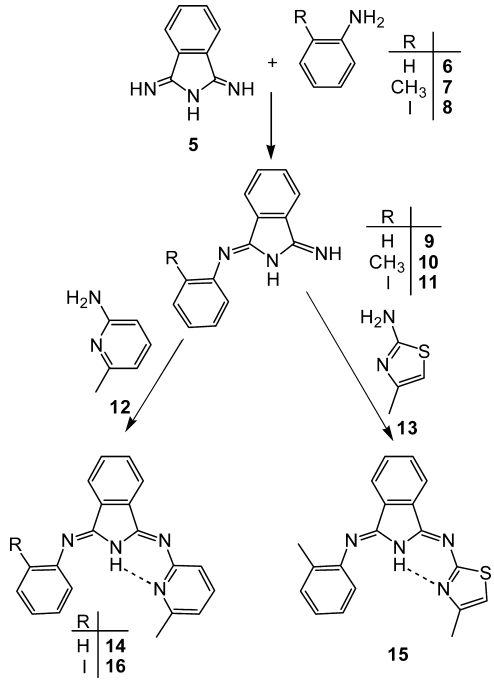
To effectively perform the first step, that is, the preparation of 1-(arylimino)-3-iminoisoindolines, in an acceptable yield and purity the possible double condensation to the symmetrical H(bai) has to be controlled. This can be done if the starting material is more reactive than the product of monocondensation, which is usually the case for 1,3-diiminoisoindoline **5**.[12a,16a] Two issues deserve consideration to choose the appropriate amino component for the first condensation. On the one hand, the monocondensation product should be as unreactive as possible, and on the other hand the possible scrambling during the second condensation

(14) Sheldrick, G. M. *SHELXS-97, A Program for Automatic Solution of Crystal Structure*; Universität Göttingen: Göttingen, Germany, 1997.

(15) G. M. Sheldrick *SHELXL-97, A Program for Crystal Structure Refinement*; Universität Göttingen: Göttingen, Germany, 1997.

(16) (a) Elvidge, J. A.; Linstead, R. P. *J. Chem. Soc.* **1952**, 5000–5007. (b) Siegl, W. O. *J. Org. Chem.* **1977**, *42*, 1872–1878. (c) Siegl, W. O. *J. Heterocyclic Chem.* **1981**, *18*, 1613–1618.

Scheme 2. Two-Step Preparation of Unsymmetric H(bai) **14**−**16**

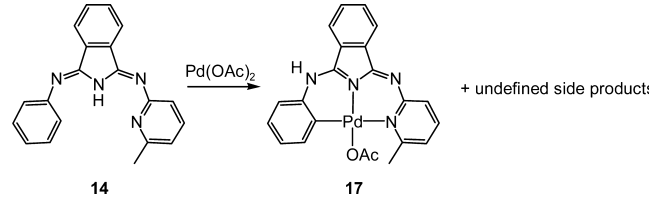


step is required to be kept to a minimum. Because of the well-known influence of the electronic properties of the arylimino moiety and its ability to act as hydrogen bond acceptor on the tautomeric amino−imino equilibrium[12a,b,17] of substituted 1,3-diiminoisoindolines, the first point clearly favors the more electron-rich aniline derivative as a precursor for the first condensation step. The second criterium also favors the initial introduction of the more electron-rich arylamine because this moiety is supposed to act sluggishly as a leaving group for the undesired ipso substitution. These general considerations about the optimum synthetic scheme were confirmed by the successful syntheses of **14**, **15**, and **16** (Scheme 2).

9 has been described before[18] so that only supplementary spectroscopic data are reported for this compound in the Experimental section. For **10**, **11** and **14**-**16** the composition was proven by high resolution mass spectra. The NMR spectra of the new 1,3-diiminoisoindolines are composed from the subspectra of the different aromatic moieties. The unsymmetric molecular structures, however, lead to very congested aromatic regions in the ^{1}H NMR spectra, which require 2D methods for interpretation. Characteristic and easily detectable are the singlets for the different methyl groups that appear in the ^{1}H NMR spectra at 2.11 (**10**), 2.16 (**14**), 2.15/2.26 (**15**) and 2.18 ppm (**16**). These signals are well suited to serve as spectroscopic probes for reaction control during the metalation experiments. The broad signals at 4.61 and 5.75 ppm for nitrogen bound protons of **9** and **11**, respectively, indicate that the less-reactive amino tautomers prevail for the monocondensation products (for **10**, no NH signal could be detected). The NH-derived signals

(17) Anderson, O. P.; Cour, A. I.; Berg, A.; Garrett, A. D.; Wicholas, M. *Inorg. Chem.* **2003**, *42*, 4513–4515.
(18) Clark, P. F.; Elvidge, J. A.; Linstead, R. P. *J. Chem. Soc.* **1953**, 3593–3601.

Scheme 3. Cyclometalation of H(phpi) **14** with Palladium(II) Acetate



shift dramatically to 12.28, 11.65, and 12.31 ppm after condensation with the hetarylamine, indicating the presence of the imino form with an intramolecular NH···N bridge for the new unsymmetric H(bai)s **14**, **15**, and **16**, respectively.

Metalation of New H(bai) Species. The treatment of phenylimino-6-methylpyridyliminoisoindoline [H(phpi)] **14** with 1 equiv of palladium(II)acetate results in the formation of the desired cyclopalladated complex H[(phpi)Pd(OAc)] **17**, accompanied by large amounts of many unassigned byproduct (Scheme 3). **17** can be purified by a tedious fractionating crystallization protocol with loss of most of the material and was obtained in 10% yield only. The protonation of an exocyclic nitrogen site appears to occur as a consequence of charge balance and had been observed before in palladium(II) and cadmium(II) chelates of bai ligands.[10a,17]

^{1}H NMR and H,H COSY spectra confirm the 2-position of the phenyl ring as the site of CH activation by the observation of four adjacent CH groups with multiplet signals at 7.66, 7.32, 7.16, and 6.97 ppm. In addition, the multiplet signals for a second ABCD spin system at the isoindoline subunit and those for the three CH groups of the pyridyl moiety are present in the aromatic region of the spectrum. In the aliphatic region, two singlets are observed for the acetato ligand (1.90 ppm) and for the pyridyl methyl group, which is markedly shifted by about 0.8 ppm with respect to the free ligand **14** to 2.93 ppm. A broad absorption at 11.9 ppm indicates the presence of an acidic N-bonded proton. A well-resolved ^{13}C NMR spectrum of **17** could not be recorded because of the insufficient solubility of the complex in common solvents. Resonance data for all nonquarternary carbon atoms, however, was obtained indirectly from the CH HMQC spectrum of the compound.

A single crystal suitable for an X-ray diffraction study was obtained from a chloroform solution of unpurified **17** and was investigated crystallographically. **17** crystallizes in the monoclinic system, space group *C*2/*c*, with $Z = 8$. Two crystallographically identical molecules are found in the asymmetric unit as chloroform solvates of a doubly hydrogen-bonded dimer. About two percent of the lattice sites of each of these dimers are statistically occupied by a tetranuclear dimer of **17′**. Because of the small amount of this side product only the sites for the additional palladium atoms Pd2 can be found, whereas no changes for the light atom sites are apparent. The molecular structures of the dimers of **17** and of **17′** are presented in Figures 1 and 2, respectively. Table 1 gives crystallographic details. Selected bond lengths and angles are summarized in Table 2.

The results from the X-ray crystallographic structure determination of **17** confirms the connectivities derived from the NMR study. The palladium(II) ion is bound in a distorted

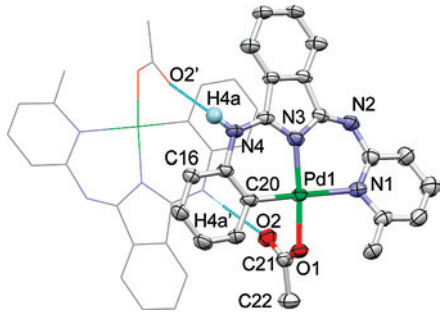


Figure 1. Doubly H-bonded dimer of **17**. Ellipsoids are set at the 50% probability level. Hydrogen atoms and solvent molecules removed for clarity.

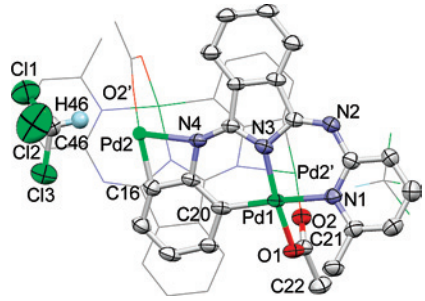


Figure 2. Assumed molecular structure of the tetranuclear dimer **17′**. Localization of Pd2/Pd2′ and of the solvated chloroform molecules in the main structure (hydrogen atoms omitted, ellipsoids set at 50% probability).

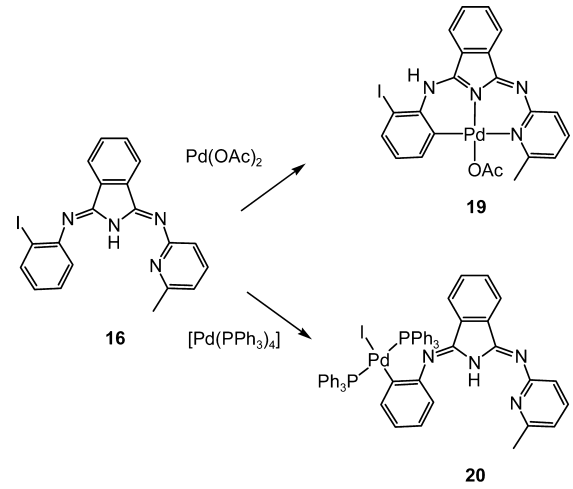
Table 2. Selected Bond Lengths (Angstroms) and Angles (Degrees) for **17** and **18**[a]

compound	**17/17′**	**18**
Pd1−C20	1.980(5)	2.013(4)
Pd1−N1	2.163(4)	2.147(3)
Pd1−N3	1.972(3)	1.972(3)
Pd1−O1/N5	2.065(3)	2.049(3)
Pd2−C16	1.903(15)	
Pd2−N4	2.087(16)	
Pd2−O2′	1.509(14)	
C20−Pd1−N1	170.16(14)	176.72(14)
C20−Pd1−N3	90.67(15)	89.16(13)
C20−Pd1−O1/N5	91.04(14)	91.24(14)
N1−Pd1−N3	89.41(13)	87.57(12)
N1−Pd1−O1/N5	90.96(12)	92.04(12)
N3−Pd1−O1/N5	167.76(12)	176.72(14)
C16−Pd2−N4	72.6(5)	
C16−Pd2−O2′	166.9(11)	
N4−Pd2−O2′	105.0(8)	
N4−H4a	0.81(4)	
O2′···H4a	2.07(5)	
N4−H4a−O2′	175(4)	

[a] Unified numbering scheme used for **17/17′** and for **18** to indicate equivalent positions.

square-planar fashion to two nitrogen (N1,N3), one carbon (C20) and one oxygen donor (O1) in distances of 2.163(4), 1.972(3), 1.980(5), and 2.065(3) Å, respectively. The trans influence of the carbon donor C20 onto the juxtaposed Pd1−N1 bond is clearly visible and of similar strength as reported for **3** (Pd−N 2.152 Å)[10a] and **4** (Pd−N 2.174 Å).[10b] For comparison, the Pd−N bonds to the terminal pyridins in *NNN* bonded (bpi)PdX species are typically in the range of 2.027−2.090 Å.[10b,11,19] The steric interaction between the pyridine bound methyl group and O1 induces a distortion of the coordination sphere toward a tetrahedron. In addition,

Scheme 4. Preparation of the Iodophenyl Derivative **19** and of the Exo Complex **20**



the conformation of the bai* ligand of **17** is also distorted from planarity mainly by the displacement of the pyridylimino moiety.

The protonated (bai*)PdOAc units dimerize via two identical H bridges N4−H4a···O2′ and N4′−H4a′···O2, with NH and OH distances of 0.81 and 2.07 Å, respectively, and with an almost linear NHO angle of 175°. The presence of the hydrogen bridges in the solid state allows the localization of the acidic protons at the N4, N4′ position. The (bai*)PdOAc fragments of **17** are situated in an antiperiplanar fashion atop of each other in a distance of 3.172 Å. In solution, however, this dimerization does not seem to occur to a detectable amount because no special high-field shift for those protons above the aromatic ring current of the other half-have been found for any investigated concentration between 10^{-4} and 10^{-6} mol/L.

A second palladium complex, the tetranuclear dimer **17′**, is present in the crystal and occupies statistically about 2% of the sites of the dimeric units of **17**. Figure 2 shows the putative molecular structure of **17′** on the basis of the crystallographic data. From a chemical point of view, the assumed structure also appears reasonable due to the similarity with that of the known tetranuclear dimer **4**. In the structure of the main molecule **17**, the space segment needed to host a fourth, neutral ligand on the external Pd2 atom of the minor **17′** is occupied by a molecule of chloroform. The identity of the fourth ligand could not be unraveled.

Obviously, **17′** derives from a double cyclopalladation taking place on the same aryl moiety of a bai ligand, and the question arises, how the second metalation step occurs. **17** might be attacked by palladium(II) directly at the peripheral N4 position and subsequently undergoes a σ metathesis under formation of a four-membered ring. Alternatively palladium(II) may attack at the hemilabile N1 site of the pyridylimino moiety and cleave the original

(19) (a) Meder, M.; Galka, C. H.; Gade, L. H. *Monatsh. Chem.* **2005**, *136*, 1693–1706. (b) Siggelkow, B. A.; Gade, L. H. *Z. Anorg. Allg. Chem.* **2005**, *631*, 2575–2584. (c) Meder, M. B.; Haller, I.; Gade, L. H. *Dalton Trans.* **2005**, 1403–1415. (d) Siggelkow, B. A.; Meder, M. B.; Galka, C. H.; Gade, L. H. *Eur. J. Inorg. Chem.* **2004**, 3424–3435. (e) Bröring, M.; Kleeberg, C. *Inorg. Chim. Acta* **2007**, *360*, 2905–2910.

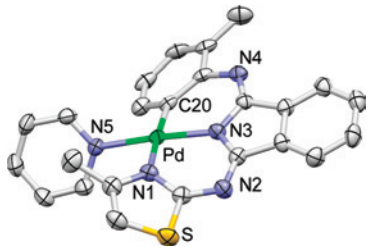


Figure 3. Molecular structure of **18**. Ellipsoids are set at the 50% probability level. Hydrogen atoms were removed for clarity. The numbering scheme is adapted to that of **17**/**17′** for better comparison.

Pd−N3 bond. This would leave one palladium ion bonded to C16 and the other palladium ion bonded to N1,N3. With respect to the strain of the four-membered ring, the second scenario appears more probable. All attempts to prepare **17′** selectively failed for the formation of complex product mixtures. The lesson learned from these experiments is that there is a general but unselective reactivity of the mononuclear **17** with excess palladium(II) acetate.

To reduce the number of side products and to ease the workup and purification of the desired *CNN* bonded complexes, the reactive 2-position of the phenylimino subunit was substituted in further experiments with a methyl or an iodo substituent. The treatment of 2-tolyl-4-methylthiazolylisoindoline [H(2-tolti)] **15** with palladium acetate indeed yields the desired complex H(2-tolti)Pd(OAc), which was recrystallized from pyridine/*n*-hexane to give [(2-tolti)Pd(py)] **18** as the only isolated product in 80% yield. The assumed constitution of **18** was proven by elemental analysis and mass spectra.

18 was characterized spectroscopically by 1D and 2D NMR techniques in a pyridine-d_5/dichloromethane-d_2 mixture. Because of the reduced number of CH groups in **18**-d_5, the aromatic region of the ^{1}H NMR spectrum is less congested and more easily interpreted than in the case of **17**. The three aromatic subunits of the 2-tolti ligand display one singlet at 6.40 ppm for the thiazole, an ABC spin system at 5.81, 6.60, and 7.06 ppm for the 2-tolyl moiety, and the typical ABCD system of the central isoindoline unit at 7.38, 7.45, 7.97, and 8.11 ppm. In addition, singlets for methyl groups at the 2-tolyl group and the thiazole unit are present at 1.09 and 2.79 ppm, with the latter one showing the typical low-field shift of the palladated ligand already observed for **17**.

A single-crystal X-ray diffraction study could be undertaken on a small red crystal of **18** (Tables 1 and 2) and revealed an unexpected helical twist of the 2-tolti ligand. Figure 3 illustrates the solid-state molecular structure of **18**. As expected, the palladium ion is coordinated to N1, N3, N5, and C20 in distances similar to those found for **17**/**17′**. The PdN_3C coordination unit is, however, almost planar, and the strain induced by the presence of the pyridine ligand is mainly compensated for by an elongation of the Pd−C bond to 2.013 Å and by a helical distortion of the bai* ligand. This distortion mode is new for (bai)Pd species but has been seen occasionally for tripyrrin complexes of palladium(II).[20] **18** is obviously racemic in the solid state. In solution, however, the helix seems to invert rapidly so that the process can not be visualized by proton NMR techniques.

In analogy to **18**, the complex carrying the iodo-substituted ligand 2-iodophenyl-4-methylthiazolylisoindoline [H2-Iphpi)] H(2-Iphpi)Pd(OAc) **19** forms upon treatment of **16** with palladium acetate and can easily be isolated in a pure form in 41% yield. Deiodination and formation of **17** was not observed during the transformation. The composition $C_{22}H_{17}IN_4O_2Pd$ was confirmed by CHN analysis and mass spectra. The site of CH activation can be demonstrated by ^{1}H NMR and H,H COSY spectroscopy. Besides the ABCD system of the isoindoline unit, two different ABC spin systems are detected in the H,H COSY at 6.69, 7.69, and 7.80 ppm, and at 7.21, 7.36, and 7.90 ppm for the iodophenyl and the methylpyridyl ring, respectively. As before, two singlets for the methyl groups are present at 1.88 and 2.73 ppm for the acetate and the methylpyridine unit, with the latter one displaying the expected low-field shift, and the acidic proton produces a broad signal at 11.8 ppm.

A complex analogous to **17** but with an anionic iodido ligand should be available simply by treatment of H(2-Iphpi) **16** with zerovalent palladium and oxidative addition of the carbon−iodine bond. If equimolar amounts of **16** and $Pd(PPh_3)_4$ are mixed in THF solution, however, the new species **20** with an exobonded palladium ion forms instead (scheme 4).

The presence of two equivalent phosphine ligands and thus of a trans-configured palladium(II) complex is apparent from ^{31}P NMR spectroscopy, which shows only one singlet at 25.02 ppm. The aromatic region of the ^{1}H NMR spectrum of **20** is governed by the strong absorptions of the PPh_3 phenyl groups at 7.14 and 7.56 ppm. Therefore only the singlet for the methyl group at 2.41 ppm and the broad signal at 11.2 ppm for the acidic NH proton are of diagnostic value. The connectivities within **20** were established by a single crystal X-ray diffraction study. **20** crystallizes in the triclinic system, space group $P\bar{1}$, with $Z = 2$ and one molecule of disordered dichloromethane per formula unit. The molecular structure and selected parameters of **20** are given in Figure 4. For crystallographic details, see Table 1.

The molecular structure of **20** shows a trans configured palladium(II) complex bound only to the C20 atom of the bai′ ligand. As expected, the palladium atom is coordinated in a distorted square-planar geometry, and the bond lengths within the $PdIP_2C$ coordination unit are in agreement with values found for many similar compounds.[21] It is interesting to note that **20** is not transformed into a *CNN* chelate complex

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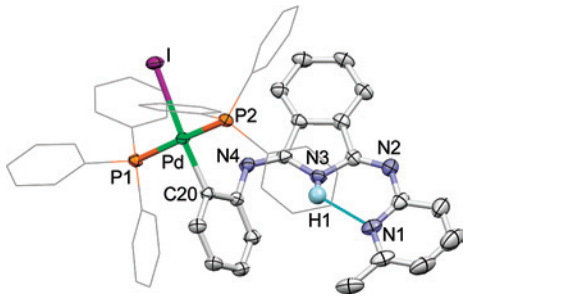
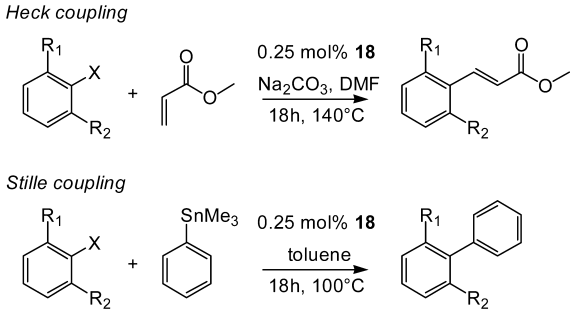


Figure 4. Molecular structure of the exo complex **20**. Selected bond lengths (Angstroms) and angles (Degrees): Pd−I 2.6926(4), Pd−P1 2.3345(7), Pd−P2 2.3255(7), Pd−C20 2.021(3); I−Pd−P1 91.06(2), I−Pd−P2 90.96(2), I−Pd−C20 172.92(8), P1−Pd−P2 1.73.77(3), P1−Pd−C20 87.73(7), P2−Pd−C20 90.98(7). Ellipsoids are set at the 50% probability level. Hydrogen atoms and solvent molecules removed for clarity.

Scheme 5. CC Coupling Reactions Catalyzed by (2-tolti)Pd(py) **18**



21 (R_1=R_2=H, X=I)
22 (R_1=R_2=H, X=Br)
23 (R_1=R_2=H, X=Cl)
24 (R_1=Me, R_2=H, X=I)
25 (R_1=R_2=Me, X=I)

even under prolonged heating. The unstrained complex with the strong Pd−P bonds is obviously favored over the strained chelate species with the weak Pd−N bonds and does not convert.

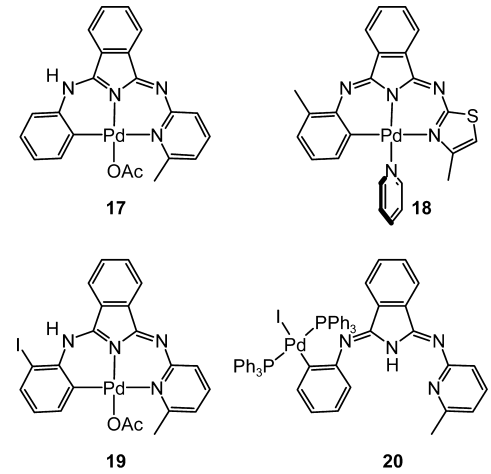
CC Coupling Catalyzes with 18. Pincer complexes of palladium(II) are of general interest in the context of catalytic CC coupling reactions.[1,22] We have attempted to use the easily accessible **18** as a precatalyst for Heck- and Stille-type coupling reactions as depicted in Scheme 5. The catalytic performance was studied as a function of electronic and steric factors of the substrate. For comparison, palladium(II) acetate was used as standard. The results are given in Table 3.

In the Heck reaction, the reactivity decreases as expected in the order X = I > X = Br > X = Cl,[23] whereas the

Table 3. Results from the Catalytic CC Coupling Study

catalyst	substrate	yield (%)	TON	TOF (min^{-1})
		Heck reaction		
$Pd(OAc)_2$	**21**	73	297	0.27
18	**21**	96	385	0.36
18	**22**	33	133	0.12
18	**23**	1	4	0.003
18	**24**	98	392	0.36
18	**25**	78	315	0.29
		Stille reaction		
$Pd(OAc)_2$	**21**	23	89	0.09
18	**21**	40	154	0.16
18	**22**	39	153	0.15
18	**24**	35	135	0.14
18	**25**	20	78	0.08

Chart 1. Overview of Palladium(II) Chelates in This Work **17**−**20**



increase in steric repulsion from **21** over **24** to **25** has only a minor effect on the outcome of the reaction. The activity of **18** as a precatalyst is higher compared to palladium acetate, but does not reach the performance of some other palladium complexes that have been studied earlier.[2c,23,24] A similar picture is provided by the attempts to catalyze Stille coupling reactions. In this case, however, the influence of steric bulk is much more pronounced than for the Heck reaction. In all cases, the reaction mixtures turned dark upon heating, and the addition of mercury stopped the transformations immediately, indicating that the active species is elemental palladium throughout.[25]

Conclusions

In summary, we have presented a strategy for the preparation of unsymmetric *CNN* pincer complexes by a stepwise condensation to bis(arylimino)isoindolines and successive cyclopalladation. Several new species from this class could be prepared, characterized, and visualized by X-ray crystallographic analyses. The simple phenylimino substituted bai ligand H(phpi) reacts with palladium(II) acetate upon cyclopalladation to yield the expected complex [(phpi)Pd(OAc)] but tends to side reactions. As a product from one such side

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reaction, a dimetalated product could be detected crystallographically. If the coordination site for a second palladium atom, that is, the 2-position of the phenyl group, is substituted by methyl or even by iodine, the respective ligands H(2-tolti) and H(2-Iphti) react cleanly and produce the desired mononuclear products in acceptable yields. In this system, the iodophenyl group is not attacked by palladium(II) acetate but can easily be used for oxidative addition to the zerovalent palladium precursor $[Pd(PPh_3)_4]$ to yield an exo complex. The performance of one of the new compounds as precatalysts in CC coupling reactions has been proven for Heck- and Stille-type reactions with a number of substrates differing in sterics and electronics, and it could be shown that the active catalyst is elemental palladium rather than the complex itself. These first results open new possibilities for a ligand design based on bai-type molecules and show promise for further studies.

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Supporting Information Available: 2D-NMR spectra (COSY, NOESY) for **17**−**20**, and crystallographic information files (CIF) for **17**, **18**, and **20**. This material is available free of charge via the Internet at http://pubs.acs.org.

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