On the Use of Non-Symmetrical Mixed PCN and SCN Pincer Palladacycles as Catalyst Precursors for the Heck Reaction

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Abstract: The mixed pincer palladacycles ($Me_2NCH_2(Cl)C{=}CCH_2CH_2Y$-κ*N*,κ*C*,κ*Y*)PdCl (**1**, $Y = PPh_2$; **2**, $OPPh_2$) and (t-$BuSCH_2CH_2C{=}C(Cl)(o$-$NC_5H_4)$-κ*S*,κ*C*,κ*N*)PdCl **3** have been obtained in high yields by chloropalladation of heterosusbstituted alkynes $Me_2NCH_2C{\equiv}CCH_2CH_2PPh_2$, $Me_2NCH_2C{\equiv}CCH_2CH_2OPPh_2$ and t-$BuSCH_2CH_2C{\equiv}C(o$-$NC_5H_4)$, respectively. The molecular structures of **1** and **3** have been ascertained by means of X-ray diffraction analysis. The catalytic properties of these mixed donor group pincer-type palladacycles have been evaluated in the arylation of olefins (Heck reaction). The pincer palladacycle **1** is highly active for the coupling of aryl iodides and aryl bromides with *n*-butyl acrylate. In contrast it is only moderately active for the coupling of aryl chlorides substituted with electron-withdrawing groups and inactive for the coupling of electron neutral and electron deactivated aryl chlorides.

Keywords: arylation; C–C coupling; Heck reaction; palladacycle; palladium

Introduction

Phosphorus-, nitrogen- and sulfur-containing palladacycles typically containing four or six electron monoanionic metallated ligands (Figure 1) are emerging as a new class of efficient and simple catalyst precursors for various reactions.[1] Indeed, pincer palladacycles containing anionic six-electron donor ligands of the type YCY ($Y = NR_2$, SR and PR_2)[2] are among the most effective catalyst precursors for the C–C coupling reactions such as Heck and Suzuki reactions.

The catalytic performances of these pincer palladacycles are strongly dependent upon the nature of the donor group. For example, the phosphinite PCP pincer complex $[PdCl\{C_6H_3(OP$-i-$Pr_2)_2$-$2,6\}]$ effectively promotes the coupling of deactivated aryl chlorides, such as 4-chloroanisole, with styrene under relatively drastic reaction conditions, whereas the $[PdCl\{C_6H_3(CH_2Y)_2$-$2,6\}]$ ($Y = PR_2$, NMe_2 and SR) analogues are only marginally active.[3] Of note is that only symmetrical pincer palladacycles have been tested in C–C coupling reactions so far. On the other hand, the simple dimeric N-containing palladacycle derived from the chloropalladation of *N*,*N*-dimethyl-1-phenylpropargylamine promotes the coupling of aryl iodides and activated aryl bromides (substituted with electron-withdrawing groups) with acrylates and styrene at room temperature.[4] Moreover, it was recently reported that adducts resulting from the association of dimeric nitrogen-containing palladacycles with carbenes[5] or secondary and tertiary phosphines[6] (Figure 1) generate highly active catalyst precursors for C–C and C–N couplings. These catalyst precursors combine the stability induced by the palladated unit with the steric and electronic properties associated with phosphorus and carbene ligands. Structurally, these complexes possess two different donor groups (amine, phos-

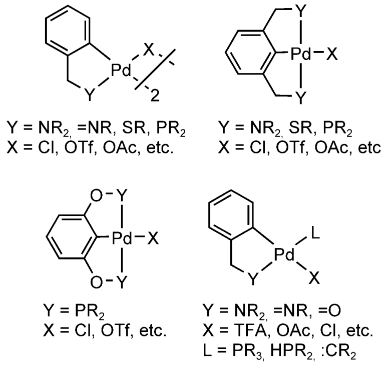

Figure 1. Examples of palladacycles used as catalyst precursors for C–C coupling reactions.

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phine and phosphite) connected only through the metal center. It is therefore of interest to check whether the presence of a covalent connectivity between the two donor groups such as those present in non-symmetrical pincer palladacycles (Figure 2) will improve (or not) their catalytic properties compared to those of the palladacycles adducts.

We have recently reported that various non-symmetrical pincer palladacycles are easily accessible through the chloropalladation of hetero-substituted alkynes. Now we report the structural characterization of compounds **1** and **3**, and a comparison of their catalytic properties in the arylation of *n*-butyl acrylate.[7]

Results and Discussion

Syntheses and X-Ray Structure of Unsymmetrical Palladacycles

The pincer palladacycles **1–3** (Figure 2) have been prepared in high yields by the simple addition of the alkynes 5-*N,N*-dimethylamino-3-pentynyldiphenylphosphine; 5-*N,N*-dimethylamino-3-pentynyldiphenylphosphinite and 4-(*tert*-butylthio)-1-(2-pyridinyl)-1-butyne to a methanolic solution of Li_2PdCl_4 at room temperature (Scheme 1) following the method recently reported.[8]

Compounds **1–3** have been isolated as light yellow powders that are stable to air and moisture, and they start to decompose only above 140 °C. These palladacycles have been fully characterized by means of C,H,N analysis, IR, ^1H, ^{13}C and ^{31}P NMR. Moreover, the molecular structures of **1** and **3** have been ascertained by means of X-ray studies. The drawings of the structures of **1** and **3** are shown in Figures 3 and 4, respectively.

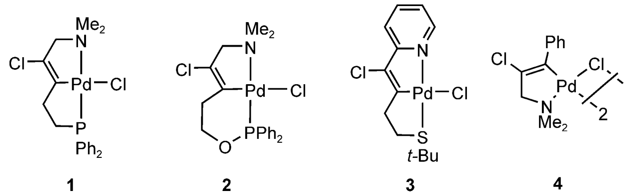
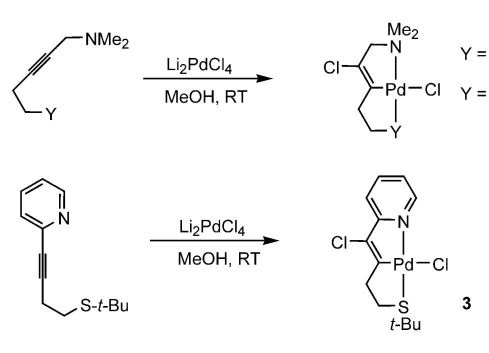


Figure 2. Examples of non-symmetrical pincer and dimeric type palladacycles obtained through the chloropalladation of hetero-substituted alkynes.



Scheme 1. Synthesis of pincer palladacycles **1–3** by chloropalladation.

Crystallographic data and details of the structure determination are presented in Table 1. Selected bond distances and angles are presented in Table 2.

In compound **1** the Pd(II) center is coordinated in a distorted square-planar fashion by the N and the P donor groups, a C(sp^2) vinyl atom of the anionic terdentate ligand system and a Cl atom. The C(vinyl)–Pd–Cl bond

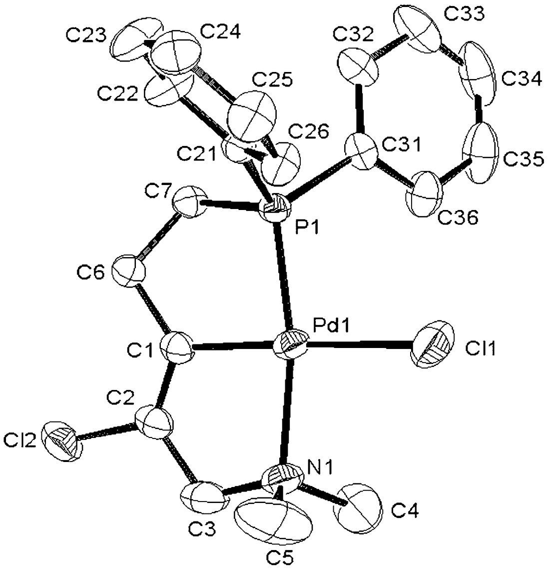


Figure 3. Molecular structure of the complex $[Ph_2PCH_2CH_2C{=}C(Cl)CH_2NMe_2\text{-}\kappa P,\kappa C,\kappa N]PdCl$ (**1**). Hydrogen atoms are omitted for clarity.

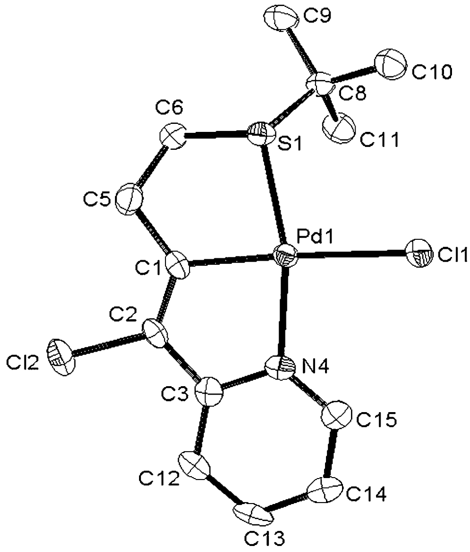


Figure 4. Molecular structure of the complex $[C_6H_4N\text{-}o\text{-}C{=}C(Cl)CH_2CH_2\text{-}t\text{-}BuS\text{-}\kappa N,\kappa C,\kappa S]PdCl$ (**3**).

Table 1. Summary of the crystal data and structure refinement for compounds **1** and **3**.

	Palladacycle **1**	Palladacycle **3**
Empirical formula	$C_{19}H_{22}Cl_2NPPd$	$C_{13}H_{17}Cl_2NPdS$
Formula weight	472.65	396.64
Temperature	200(2) K	200(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Z	4	8
Unit cell dimensions	$a = 11.5325(4)$ Å, $b = 9.8034(3)$ Å, $c = 17.8266(5)$ Å, $\beta = 101.580(1)$ deg.	$a = 25.0655(5)$ Å, $b = 7.3322(2)$ Å, $c = 16.9053(1)$ Å, $\beta = 109.539(1)$ deg
Volume	1974.41(11) Å^3	2928.03(10) Å^3
Density (calculated)	1.59 g/cm^3	1.80 g/cm^3
Absorption coefficient	1.29 mm^{-1}	1.76 mm^{-1}
Crystal shape	polyhedron	polyhedron
Crystal size	0.38 × 0.32 × 0.17 mm	0.36 × 0.34 × 0.30 mm
Theta range for data collect.	1.8 to 27.5 deg.	0.9 to 27.5 deg.
Index ranges	$-14 \leq h \leq 14$, $-12 \leq k \leq 12$, $-23 \leq l \leq 23$	$-32 \leq h \leq 30$, $-7 \leq k \leq 7$, $-3 \leq l \leq 21$
Reflections collected	19918	9999
Independent reflections	4527 (R(int) = 0.0265)	5973 (R(int) = 0.0223)
Observed reflections	4025 ($I > 2\sigma(I)$)	5473 ($I > 2\sigma(I)$)
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4527/0/217	5973/0/332
Goodness-of-fit on F^2	1.05	1.12
Final R indices ($I > 2\sigma(I)$)	R1 = 0.023, wR2 = 0.060	R1 = 0.029, wR2 = 0.076
Largest diff. peak and hole	0.40 and −0.72 eÅ^{-3}	0.86 and −0.57 eÅ^{-3}

angle is 176.6° and the P and N donor groups are also in mutual *trans* positions with a bond angle of 166.6° showing an angular deviation of 13.4° from exact *trans* coordination. This distortion from the ideal square-planar arrangement is the result of the small N–Pd–C(vinyl) and P–Pd–C(vinyl) bite angles in the two five-membered rings of 83.3° and 83.6°, respectively. The σ Pd–C(vinyl) single bond in **1** (1.995 Å) is similar to those observed in analogous compounds, where the distances fall in the range between 1.991 and 2.011 Å.[9]

The crystal structure of **3** consists of two independent molecules found in the asymmetric unit. These structures are quite similar to each other and show a coordination environment around the Pd(II) center similar to the one encountered in the "pincer" palladacycle **1**, and the distances between the Pd(II) center and the coordinated atoms are also rather similar (see Table 1). The Pd(II) center is coordinated in a distorted square-planar fashion by the N and the S donor groups, a C(sp^2) vinyl atom of the anionic terdentate ligand system and a Cl atom. The C(vinyl)–Pd–Cl bond angle is 175.6° and the S and N donor groups are in mutual *trans* positions with an average bond angle of 166.0°. As observed in compound **1**, the distortion from the ideal square-planar arrangement for **3** results from the small N–Pd–C(vinyl) and S–Pd–C(vinyl) bite angles in the two five-membered rings of 81.6° and 84.5°, respectively.

Catalytic Performance of Palladacycles 1–3 in the Heck Reaction

The potential of compounds **1–3** as catalyst precursors was initially probed in the coupling of *n*-butyl acrylate with 4-bromotoluene and 4-bromoanisole using the best reaction conditions [performed at 150 °C using DMA as solvent and NaOAc as the base in the presence of N(*n*-Bu)$_4$Br as salt additive] determined in previous studies with other palladacycles[4] (Table 3).

It is evident from the data presented in Table 3 that, compared with **3**, both **1** and **2** NCP pincer palladacycles are quite superior in the promotion of the Heck coupling of 4-bromoanisole, 4- and 2-bromo-toluene (compare entries 1–3, 4–6 and 8–10 in Table 3) under the same reaction conditions. Notably the phosphine-containing palladacycle **1** is relatively more active than the phosphinite analogue **2**, and a very low catalyst loading can be used in the case of **1** (entry 7, Table 3). This catalytic performance is similar to those obtained using as catalyst precursors the phosphine adducts of N- and P-containing palladacycles, under comparable reaction conditions.

In the case of palladacycle **1** we have also investigated the influence of the base, temperature and catalyst loading in the coupling of *n*-butyl acrylate and other haloarenes (Table 4). It became clear that Na_2CO_3 is a supe-

Table 2. Selected bond distances (A) and angles (°) for compounds **1** and **3**.

Palladacycle **1**		Palladacycle **3a**		Palladacycle **3b**	
Bond distances (Å)					
Pd1–C1	1.995(2)	Pd11–C11	1.971(4)	Pd12–C12	1.974(5)
Pd1–N1	2.1576(17)	Pd11–N41	2.071(4)	Pd12–N42	2.062(4)
Pd1–P1	2.2091(5)	Pd11–S11	2.2899(11)	Pd12–S12	2.2805(12)
Pd1–Cl1	2.3951(6)	Pd11–Cl11	2.3858(12)	Pd12–Cl12	2.3890(12)
Cl2–C2	1.774(2)	Cl21–C21	1.754(4)	Cl22–C22	1.754(5)
P1–C31	1.813(2)	S11–C61	1.818(5)	S12–C62	1.831(5)
P1–C21	1.8152(19)	S11–C81	1.850(5)	S12–C82	1.849(5)
P1–C7	1.8319(19)	C11–C21	1.328(6)	C12–C22	1.327(7)
N1–C5	1.464(3)	C11–C51	1.499(6)	C12–C52	1.507(7)
C1–C2	1.319(3)	C21–C31	1.449(6)	C22–C32	1.439(7)
C1–C6	1.515(3)	C31–N41	1.365(6)	C32–N42	1.355(6)
C2–C3	1.486(3)	C31–C121	1.394(6)	C32–C122	1.399(7)
C6–C7	1.525(3)	N41–C151	1.323(6)	N42–C152	1.336(6)
		C51–C61	1.503(6)	C52–C62	1.505(7)
Bond Angles (°)					
C1–Pd1–N1	83.34(8)	C11–Pd11–N41	81.57(17)	C12–Pd12–N42	81.01(19)
C1–Pd1–P1	83.65(6)	C11–Pd11–S11	84.50(13)	C12–Pd12–S12	84.81(15)
N1–Pd1–P1	166.63(6)	N41–Pd11–S11	166.04(11)	N42–Pd12–S12	165.81(12)
C1–Pd1–Cl1	176.62(6)	C11–Pd11–Cl11	175.58(13)	C12–Pd12–Cl12	174.83(14)
N1–Pd1–Cl1	95.21(6)	N41–Pd11–Cl11	94.42(11)	N42–Pd12–Cl12	94.72(12)
P1–Pd1–Cl1	97.95(2)	S11–Pd11–Cl11	99.48(4)	S12–Pd12–Cl12	99.43(4)
C31–P1–Pd1	118.72(7)	C61–S11–Pd11	98.95(15)	C62–S12–Pd12	98.69(17)
C21–P1–Pd1	114.95(6)	C81–S11–Pd11	113.60(16)	C82–S12–Pd12	113.12(16)
C7–P1–Pd1	103.67(6)	C21–C11–Pd11	113.0(3)	C22–C12–Pd12	113.3(4)
C5–N1–Pd1	108.53(18)	C51–C11–Pd11	119.4(3)	C52–C12–Pd12	119.2(3)
C4–N1–Pd1	109.66(16)	C151–N41–Pd11	127.8(3)	C152–N42–Pd12	127.0(3)
C3–N1–Pd1	108.86(13)	C31–N41–Pd11	112.7(3)	C32–N42–Pd12	113.2(3)
C2–C1–Pd1	112.73(16)	C11–C21–C31	120.3(4)	C12–C22–C32	119.8(4)
C6–C1–Pd1	121.25(13)	C11–C21–Cl21	122.4(4)	C12–C22–Cl22	121.9(4)
C2–C1–C6	126.02(19)	C31–C21–Cl21	117.3(3)	C32–C22–Cl22	118.2(4)
C1–C6–C7	109.42(16)	N41–C31–C21	112.3(4)	N42–C32–C22	112.6(4)
C1–C2–C3	124.4(2)	C11–C51–C61	110.8(4)	C62–C52–C12	110.0(4)
C1–C2–Cl2	122.87(18)	C51–C61–S11	106.9(3)	C52–C62–S12	106.7(4)
C3–C2–Cl2	112.68(16)				
C2–C3–N1	110.00(18)				

Table 3. Heck reaction between *n*-butyl acrylate and aryl bromides catalyzed by pincer complexes **1–3**.[a]

Entry	Palladacycle	ArX	[ArX]/[Pd]	Conv.[x]	Yield[b]	TON[c]
1	**1**	4-MeC$_6$H$_4$Br	10,000	85	85	8,500
2	**2**	4-MeC$_6$H$_4$Br	10,000	51	50	5,000
3	**3**	4-MeC$_6$H$_4$Br	10,000	25	20	2,000
4	**1**	4-MeOC$_6$H$_4$Br	10,000	65	61	6,100
5	**2**	4-MeOC$_6$H$_4$Br	10,000	43	42	4,200
6	**3**	4-MeOC$_6$H$_4$Br	10,000	17	18	1,800
7	**1**	4-MeC$_6$H$_4$Br	100,000	60	67	67,000
8	**1**	2-MeC$_6$H$_4$Br	10,000	48	42	4,200
9	**2**	2-MeC$_6$H$_4$Br	10,000	39	38	3,800
10	**3**	2-MeC$_6$H$_4$Br	10,000	10	9	900

[a] Reaction conditions: DMA (5 mL), NaOAc (1.4 mmol), *n*-butyl acrylate (1.2 mmol) ArX (1 mmol) and N(*n*-Bu)$_4$Br (0.2 mmol), 24 h.

[b] GC Yield (using methyl benzoate as internal standard).

[c] TON [mol of product (*trans*-*n*-butyl cinnamate)/mol of Pd].

[x] Conversion based on the consumption of ArX.

rior base compared to NaOAc, K_3PO_4 and NEt_3 (compare entries 1–6, Table 4) in the absence of the salt additive. However, in the case of NaOAc the addition of $N(n\text{-}Bu)_4Br$ is essential in order to achieve good catalytic activity, in opposition the salt additive has a detrimental effect in the case of sodium carbonate (compare entries 1, 2 and 5, 6 in Table 4). Bromo-arenes substituted with electron-withdrawing groups and iodo-arenes are efficiently coupled with *n*-butyl acrylate using very low catalyst precursor loadings (see entries 16, 17 and 26, 27, Table 4). Although the coupling reaction can be performed using aryl chlorides substituted with electron-withdrawing groups, affording *trans*-cinnamates in modest yields (entries 28–31), the reaction completely fails with non-activated and deactivated chloro-arenes such as 4-chloroanisole.

Although some of these reactions can be carried out at lower temperatures (down to 50 °C), no coupling product was observed when the reaction was performed at room temperature. This latter result is in sharp contrast to the catalytic behavior of the simple dimeric palladacycle **4**, which promotes the coupling of activated bromo- and iodo- arenes with alkenes at room temperature.[4] In this respect, it is now accepted that most of the palladacycles are in fact reservoirs of catalytically active Pd(0) species. The differences observed in the catalytic activities of different palladacycles can be correlated with the rate of the release of the catalytically active Pd(0) species.[10] It is highly probable that in the case of the relatively high thermally robust palladacycle **1** (it starts to decompose only at temperatures above 140 °C) a higher temperature is necessary to start the reaction and to maintain a reasonable rate.[11,12]

To gain some insight into the electronic influence of the *p*-substituent on the aryl halide competitive experiments using seven aryl bromides and five aryl iodides were performed under pseudo-first order conditions with respect to *n*-butyl acrylate (Scheme 2). The reac-

Table 4. Heck reaction between *n*-butyl acrylate and aryl halides using palladacycle **1** as catalyst precursor.[a]

Entry	ArX	Base	Additive	[ArX]/[Pd]	T [°C]	Yield [%][b]	TON[c]
1	4-MeC_6H_4Br	NaOAc		100,000	150	8	8,000
2	4-MeC_6H_4Br	NaOAc	NBu_4Br	100,000	150	67	67,000
3	4-MeC_6H_4Br	K_3PO_4		100,000	150	19	19,000
4	4-MeC_6H_4Br	NEt_3		100,000	150	0	0
5	4-MeC_6H_4Br	Na_2CO_3		100,000	150	100 (97)	100,000
6	4-MeC_6H_4Br	Na_2CO_3	NBu_4Br	100,000	150	64	64,000
7	4-$MeOC_6H_4Br$	NaOAc	NBu_4Br	10,000	150	61	6,100
8	4-$MeOC_6H_4Br$	NaOAc	NBu_4Br	100,000	150	72	72,000
9	4-$MeOC_6H_4Br$	Na_2CO_3		100,000	150	74	74,000
10	4-$MeOC_6H_4Br$	Na_2CO_3		10,000	150	97	9,700
11	4-$NO_2C_6H_4Br$	NaOAc	NBu_4Br	1,000,000	150	37	370,000
12	4-$NO_2C_6H_4Br$	NaOAc	NBu_4Br	100,000	150	100 (93)	100,000
13	4-NCC_6H_4Br	NaOAc	NBu_4Br	10,000	120	92 (90)	10,000
14	4-NCC_6H_4Br	NaOAc	NBu_4Br	10,000	150	85	10,000
15	4-NCC_6H_4Br	NaOAc	NBu_4Br	100,000	150	80	80,000
16	4-NCC_6H_4Br	NaOAc	NBu_4Br	1,000,000	180	45	450,000
17	4-NCC_6H_4Br	NaOAc	NBu_4Br	1,000,000	150	63	630,000
18	4-NCC_6H_4Br	Na_2CO_3		100,000	150	100 (96)	100,000
19	4-$MeCOC_6H_4Br$	NaOAc	NBu_4Br	100,000	150	100 (89)	100,000
20	4-$MeCOC_6H_4Br$	NaOAc	NBu_4Br	1,000,000	150	50	500,000
21	4-$MeCOC_6H_4Br$	NaOAc	NBu_4Br	100,000	120	95	95,000
22	4-$MeCOC_6H_4Br$	Na_2CO_3		100,000	150	68	68,000
23	C_6H_4I[d]	NaOAc	NBu_4Br	100,000	150	100 (95)	100,000
24	C_6H_4I	NaOAc	NBu_4Br	1000	50	6	60
25	C_6H_4I	NaOAc	NBu_4Br	1000	80	100 (98)	1000
26	4-$MeOC_6H_4I$[d]	NaOAc	NBu_4Br	1,000,000	150	95	950,000
27	C_6H_4I	NaOAc	NBu_4Br	1,000,000	150	100	1,000,000
28	4-$MeCOC_6H_4Cl$	NaOAc	NBu_4Br	100	150	40	40
29	4-$MeCOC_6H_4Cl$	Na_2CO_3		100	150	45	45
30	4-NCC_6H_4Cl	NaOAc	NBu_4Br	1000	150	20	200
31	4-NCC_6H_4Cl	Na_2CO_3		1000	150	25	250

[a] Reaction conditions: DMA (5 mL), base (1.4 mmol), *n*-butyl acrylate (1.2 mmol) ArX (1 mmol) and $N(nBu)_4Br$ (0.2 mmol), 24 h.

[b] GC Yield (using methyl benzoate as internal standard), isolated yield in parenthesis.

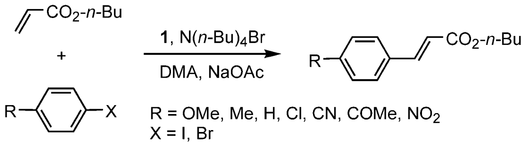
[c] TON (mol product/mol of Pd).

[d] Reaction time: 48 h.

tion rates were determined in the competitive experiments and were corroborated by measuring the relative initial reaction rate in a separate set of experiments (activated from deactivated aryl halides). The resulting Hammett plots are presented in Figures 5 and 6.

The use of σ_p constants results in good fits and correlations yielding a value of $\rho = 2.7$ for aryl bromides and $\rho = 1.44$ for aryl iodides, indicating that in both cases there is an electronic influence. It is clear that these values can be a result of the combination of all elementary steps involved in the catalytic cycle and their absolute values are not of great importance. However, a comparison of these values can give valuable information about the reaction pathways. The ρ values obtained in various reactions involving aryl halides and palladium complexes are summarized in Table 5.

It is clear that for all palladacycles (entries 4–10 and 12–14, Table 5) used in either in Heck or Suzuki couplings a positive slope ρ is observed indicating that, as expected, electron-withdrawing substituents accelerate the reaction. The ρ value observed for aryl iodides is almost identical to that reported for the pincer palladacycle **5** (see entries 11 and 12, Table 5) These values are relatively too low (compared, for example, with those obtained from the oxidative addition of Ar–I with $Pd(PPh_3)_4$, entries 15 and 16, Table 5) to fit the oxidative addition as the rate-determining step. Therefore in case of aryl iodides the rate-determining step (which is sensitive to the electronic influence of aryl iodide) is most probably subsequent to the oxidative addition step. The obtained ρ value of 2.7 is the same observed in the Heck reaction promoted by palladacycle **4** for aryl bromides and these values are relatively lower when compared with that determined for the oxidative addition of aryl chlorides to $Pd(dippp)_2$ (entry 2, Table 5). It is therefore reasonable to assume that for aryl bromides the most probable rate-determining step for the Heck reaction catalyzed by **1** is oxidative addition (the first step in the classical mechanism of the Heck reaction).



Scheme 2. The coupling of *p*-substituted halo-benzenes with *n*-butyl acrylate promoted by palladacycle **1**.

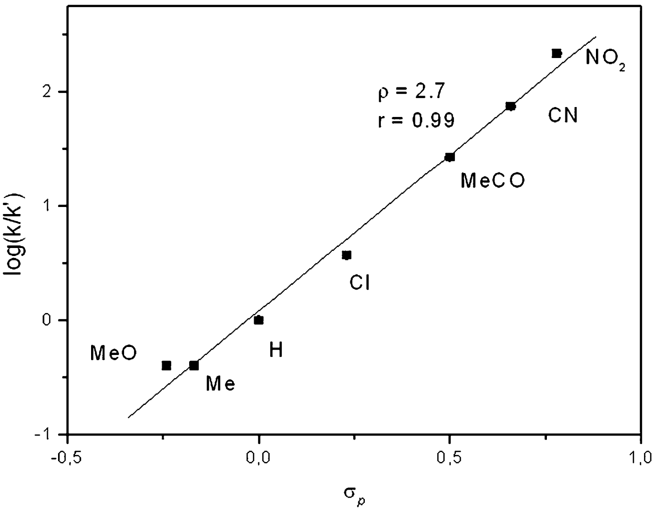


Figure 5. Hammett correlation of competitive reaction of *para*-substituted aryl bromides (0.1 mmol of each) with *n*-butyl acrylate (10 mmol) at 150 °C in DMA promoted by palladacycle **1** using σ_p constants.

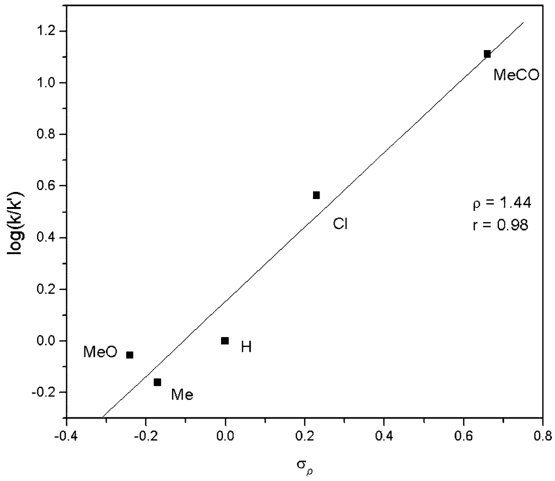
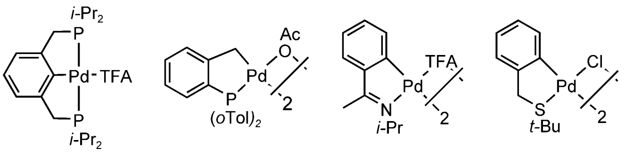


Figure 6. Hammett correlation of competitive reaction of *para*-substituted aryl iodides (0.1 mmol of each) with *n*-butyl acrylate (10 mmol) at 80 °C in DMA promoted by palladacycle **1** using σ_p constants.



5 **6** **7** **8**

Figure 7. Palladacycles reported in Table 5.

Conclusion

In conclusion, we have established new catalysts for the Heck reaction based on non-symmetrical NCP pincer palladacycles. From the standing point of TON values the arylation of *n*-butyl acrylate ranks with the best in the literature for NC, PC, PCP palladacycles and their phosphine adducts. The catalyst precursor **1** probably acts as reservoir of catalytically active Pd(0) species and the Heck reaction follows the classical mechanism

Table 5. Comparison of ρ values obtained for the oxidative addition of aryl halides (Ar–X) to various Pd complexes (Figure 7).

Entry	Pd complex	Reaction	T (°C)	Par.	X	r	ρ	Ref.
1	Pd(dippp)$_2$[a]	Oxid. Add.	60	σ^-	Cl	0.99	5.2 (2.25)[b]	[14]
2	Pd(dippp)$_2$	Oxid. Add	60	σ	Cl	0.74	9.2 (3.99)[b]	[14]
3	Pd[P(*o*-tol)$_3$]$_2$	Heck	130	σ^-	Br	—	1.01 ± 0.03	[15]
4	**6**	Heck	130	σ^-	Br	—	1.58 ± 0.06	[15]
5	**4**	Heck	150	σ	Br	0.99	2.7	[4]
6	**1**	Heck	150	σ	Br	0.99	2.7	This work
7	**7**	Suzuki	130	σ	Br	0.86	1.34	[16]
8	**7**	Suzuki	130	σ^-	Br	0.97	0.99	[16]
9	**8**	Suzuki	80	σ	Br	0.93	2.34	[17]
10	PdCl$_2$(SEt$_2$)$_2$	Suzuki	80	σ	Br	0.98	2.27	[18]
11	**5**	Heck	140	σ	I	—	1.39	[19]
12	**1**	Heck	80	σ	I	0.98	1.44	This work
13	**8**	Suzuki	80	σ	I	0.96	0.65	[17]
14	Pd(PPh$_3$)$_4$	Oxid. Add.	25	σ	I	—	2.3 ± 0.2	[20]
15	Pd(PPh$_3$)$_4$	Oxid. Add.	25	σ	I	0.98	2.0	[21]

[a] dippp = di-isopropylphosphinepropane.

[b] The original ρ values reported were obtained using ***ln*** of k/k′, the values in parentheses have been re-calculated using ***log*** of k/k′ for comparison purposes with all of data presented in the Table.

Pd(0)/Pd(II) as proposed earlier for other palladacycles.[12]

Experimental Section

General Remarks

All reactions involving organometallic compounds were carried out under an argon or nitrogen atmosphere in oven-dried Schlenk tubes. Solvents were dried with suitable drying agents and distilled under argon prior to use. The pincer palladacycles **1–3** have been prepared using the same procedure previously reported.[8] All the other chemicals were purchased from commercial sources (Acros or Aldrich) and used without further purification. Elemental analyses were performed by the Analytical Central Service of IQ-USP (Brazil). NMR spectra were recorded on a Varian Inova 300 spectrometer. Infrared spectra were performed on a Bomem B-102 spectrometer. Gas chromatographic analyses were performed with a Hewlett-Packard-5890 Gas Chromatograph with an FID and 30 meter capillary column with a dimethylpolysiloxane stationary phase. Mass spectra were obtained using a GC/MS Shimadzu QP-5050 (EI, 70 eV).

Typical Experiment for the Heck Reaction

A 10-mL resealable Schlenk flask was evacuated and back-filled with argon and charged with sodium carbonate (1.4 mmol, 150 mg). The flask was evacuated and back-filled with argon and then were added dimethylacetamide (5 mL), 4-bromotoluene (1 mmol, 171 mg), butyl acrylate (1.2 mmol, 172 μL) and methyl benzoate as internal standard (35 mg). After the addition of the palladacycle **1** in dimethylacetamide (42 μL of a 2.4×10^{-4} mol·L^{-1} solution, 10^{-5} mmol) the reaction mixture was stirred at 150 ^{0}C for 24 h. GC analysis indicated 100% yield in butyl *trans*-methylcinnamate. The solution was then allowed to cool to room temperature, taken up in CH$_2$Cl$_2$ (15 mL), washed with 10 wt % aqueous sodium hydroxide (10 mL), and dried over MgSO$_4$. After filtration, the solvent was evaporated to give butyl *trans*-methylcinnamate (yield: 211 mg, 97%) estimated to be > 95% pure by ^{1}H NMR and GC. All the *trans*-cinnamates have been analyzed by CG-MS, ^{1}H and ^{13}C NMR and their spectral data compared to those reported.

Typical Experiment for the Hammet Competition Reaction

The reactions were conducted as described for typical conditions using butyl acrylate (10 mmol, 1.5 mL), methyl benzoate as internal standard (35 mg), 0.2 mmol of C$_6$H$_5$Br and 0.2 mmol of the substrates: 4-MeOC$_6$H$_4$Br, 4-MeC$_6$H$_4$Br, 4-ClC$_6$H$_4$Br or 4-ClC$_6$H$_4$Br, 4-NCC$_6$H$_4$Br, 4-MeCOC$_6$H$_4$Br and 4-NO$_2$C$_6$H$_4$Br. Relative amounts of products were calculated from GC and used to plot the Hammett correlation.

X-Ray Crystallographic Study

Crystals of **1** and **3** were first prepared by slow diffusion of hexane into an acetone solution. However, these crystals suffered from loss of solvent, and were recrystallized from CH$_2$Cl$_2$ by very slow solvent evaporation. A crystal was mounted on a glass fiber with perfluoropolyether. The measurements were made on a Bruker SMART-CCD diffractometer with graphite monochromated Mo-K-alpha radiation. Frames corresponding to a sphere of data (for **1**) or, respectively, more than one asymmetric unit in reciprocal space (for **2**) were collected using the omega-scan technique, 20 s exposures of 0.3 degrees were taken for **1**, 15 s exposures of 0.5 degrees for **2**. An absorption correction was applied in both cases using SADABS[13] based on the Laue symmetry of the reciprocal space, the data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and expanded using Fourier techniques, all non-hydrogen atoms were refined with anisotropic displacement parameters, the hydrogen atoms could be located in the Fourier maps, and all hydrogen atoms were considered at calculated positions. The full-matrix least-squares refinement against F^2 converged. All calculations were performed using the SHELXTL [software package SHELXTL V5.10 for structure solution and refinement, G. M. Sheldrick, Bruker Analytical X-ray-Division, Madison, Wisconsin 1997] crystallographic software package of Bruker. CCDC 226051 (**1**) and CCDC 226052 (**3**) contain the supplementary crystallographic data for these structures. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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