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Aryl–Pd covalently bonded palladacycles, novel amino and oxime catalysts {di-μ-chlorobis(benzaldehydeoxime-6-*C*,*N*)dipalladium(II), di-μ-chlorobis(dimethylbenzylamine-6-*C*,*N*)dipalladium(II)} for the Heck reaction[†]

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Abstract

Amine and oxime palladacycles with an aryl–Pd covalent bond were found to be robust catalysts for the Heck reaction of aryl iodides, bromides and even chlorides. High TONs and TOFs were obtained with these palladacycles. © 2000 Elsevier Science Ltd. All rights reserved.

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We and others have reported several novel catalysts for the Heck reaction.[1] Palladium complexes have been the most commonly used catalysts with various phosphines as ligands.[2] Some of the more recent examples of efficient catalysts are novel cyclopalladated tris-*o*-tolylphosphine, *N*-heterocyclic carbene palladium, tridentate aryl bisphosphine Pd(II) (PCP), and *ortho*-palladated triaryl phosphites, all of which give very high TONs.[3–6] The palladacycle formed from $Pd(OAc)_2$ and $P(o\text{-tol})_3$ was a better catalyst than the conventional 'in situ catalyst' produced from $Pd(OAc)_2$ and $P(o\text{-tol})_3$. A major drawback of the use of phosphine ligands in such catalytic reactions is the oxidation of the phosphine to a phosphine oxide as well as cleavage of the P–C bond, causing degradation of the ligand, reduction of the metal and termination of the catalytic cycle. The palladacycles reportedly show extraordinary thermal stability (140–180°C) and the PCP, triarylphosphite and carbene Pd complexes can be used in air with slightly reduced efficiency.

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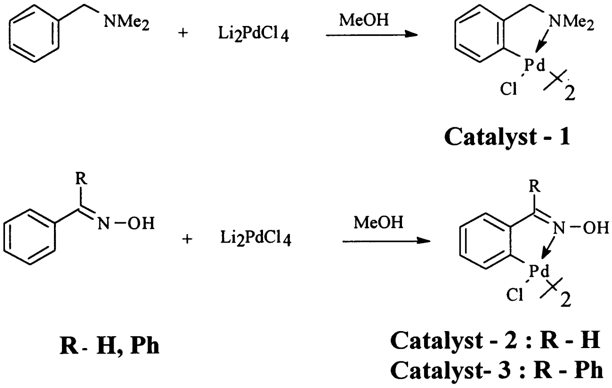
In our study for novel catalysts for the Heck reaction, we decided to investigate the non phosphino palladacycles from *N*,*N*-dimethylbenzylamine, benzaldoxime and benzophenone oxime. These complexes have been previously reported and easily synthesized from readily available *N*,*N*-dimethylbenzylamine, benzaldehyde oxime, benzophenone oxime and Li_2PdCl_4.[7] Such ligands are not as readily oxidizable as phosphines and the metal complexes with a covalently bonded Pd to the aromatic ring, could be more stable and efficient catalysts (Scheme 1).



Scheme 1. Preparation of palladacycle

Aryl iodides, bromides and electron deficient chlorides react with ethyl acrylate and styrene in the presence of these Pd complexes as catalysts to give high yields of the substituted products (*E*-cinnamate and stilbene) with excellent turn over numbers. Table 1 shows the results of our experiments with the various aryl halides and olefins in presence of these three palladacyles. High TONs (72, 000–1, 45, 454) as well as high TOFs (1, 625–20, 780) can be obtained with aryl iodides and bromides. The bromides and chlorides take longer reaction times for completion. Electron withdrawing groups activate aryl chlorides. The use of a Lewis acid as a cocatalyst ($ZnCl_2$), which would help labilize the halide, increased the reaction rate and the yield of the reaction. The palladacycle **3** was an excellent catalyst and the reaction of bromobenzene with ethyl acrylate and styrene gave 90 and 96% yields (TON 450) in 1 h (shorter reaction time compared to the other catalysts). The TON for bromobenzene with the catalyst **1** (87, 000–89, 000) was higher than with the catalyst **2** (72, 000–78, 000).

In a typical experiment, 4-iodoanisole (11.7 g, 50 mmol), ethyl acrylate (10 g, 100 mmol), K_2CO_3 (8.28 g, 60 mmol) and 50 mL 1-methylpyrrolidinone, were taken in a round bottomed flask and the Pd complex **1** (0.00027 g, 0.0005 mmol) was added as catalyst. The reaction mixture was heated in an oil bath maintained at 150°C for 8 h followed by the usual extractive work up and column chromatography over silica gel to give (*E*)-ethyl-4-methoxycinnamate (9.223 g, 88.3%, 44.77 mmol, TON 89, 540 (mol product per mol **1**), TOF 11, 192 mol product per mol **1** per hour).

When aluminium chloride was used as a cocatalyst, the reaction of 4-chlorotoluene, with styrene, gave the substituted product (as *E*-isomer) in low yields. Bu_4NI was also used as cocatalyst for the reaction of 4-chlorotoluene and 2-chloropyridine with ethyl acrylate and styrene in the presence of palladacycle **3**. The normal substitution products were obtained in moderate yields.

Table 1
Heck vinylation of aryl halides catalyzed by amine and oxime palladacycles

S. No.	Reactant (mmol)	Olefin (mmol)	Catalyst	Product	Time (h)	Yield	TON	TOF
1	4-MeOPhI (50)	Ethylacrylate (100)	**1**	Ethyl-4-methoxy-cinnamate	8	88	89, 540	11, 190
			3		2	90	453	226
2	4-MeOPhI (50)	Styrene (60)	**1**	4-Methoxy-stilbene	48	76	76, 000	1, 740
			2		48	92	1, 38, 666	2, 888
			3		6	97	485	90
3	PhI (50)	Ethylacrylate (100)	**2**	Ethyl cinnamate	7	96	1, 45, 454	20, 778
4	PhBr (50)	Ethylacrylate (100)	**1**	Ethyl cinnamate	34	90	90, 000	2, 647
			2		37	52	72, 000	1, 946
			3		1	89.8	437	437
5	PhBr (50)	Styrene (60)	**1**	Stilbene	29	86.6	86, 666	2, 988
			2		48	52	78, 000	240
			3		1	96	483	483
6	4-ClPhNO$_2$ (5)	Ethylacrylate (10)	**1**	Ethyl-4-nitro-cinnamate	31	51	287	
			2		30	60	300	
7	4-ClPhNO$_2$ (50)	Styrene (60)	**1**	4-Nitro-stilbene	42	71	70, 000	1, 666
			2		40	69	350	
8	4-ClPhCN (5)	Styrene (6)	**2**	4-Cyano-stilbene	24	78.5	350	
9	2-BrPy (5)	Ethylacrylate (10)	**2**	Ethyl-3-(2-pyridyl) acrylate	48	68	4, 090	
10	4-ClPhCH$_3$ (2)	Styrene (4)	**3**[a]	4-Methylstilbene	12	18		
			3[b]		24	28		

[a] Cocatalyst: AlCl$_3$; temperature 130°C.
[b] Cocatalyst: Bu$_4$NI; temperature 130°C.

We have thus described three novel non phosphino palladacycles as efficient catalysts for the activation of aryl halides for reaction with olefins.

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