

1'-Carbopalladated-4-ferrocenyl-1,3-oxazolines as catalysts for Heck reactions: Further evidence in support of the Pd(0)/Pd(II) mechanism

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Abstract

1'-Carbopalladated complexes derived from 4-ferrocenyl-1,3-oxazolines are reported in this paper as efficient catalysts for the Heck coupling of iodo- and bromoarenes with alkenes. Experimental evidence points out strongly towards the involvement of a Pd(0)/Pd(II) catalytic cycle in the mechanism of the reaction. For the first time, the disassembly of the carbopalladated complex via coupling with the olefin in a non-catalytic Heck reaction has been demonstrated to be the origin of the release of Pd(0) from the palladacycle carrier.

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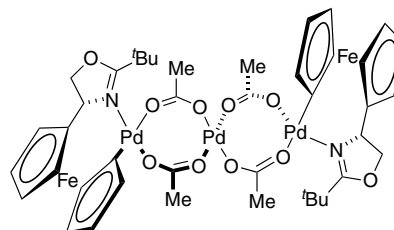
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1. Introduction

The palladium-catalysed vinylation of aryl or alkenyl halides or triflates in the presence of base, known as the Heck (or Heck-Mizoroki) reaction [1], is one of the most useful synthetic methods for the formation of carbon–carbon bonds. It is therefore not surprising that the interest in the uncovering of new substrates and catalytic systems for this process continues unabated [2]. Among the new generations of catalysts, palladacycles have been shown to be extremely active in the promotion of Heck reactions [3]. Although cyclopalladated aromatic compounds are the choice systems for these catalysts [4,5], a couple of *ortho*-palladated ferrocene derivatives [6,7] have been shown to catalyse the arylation of acrylate esters and of styrene.

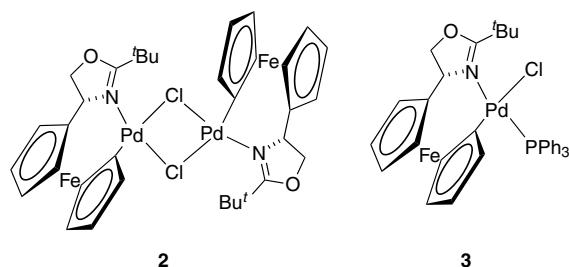
We have recently found that the cyclopalladation of 4-ferrocenyl-1,3-oxazolines takes place in an

unprecedented interannular fashion, leading to the formation of 1'-carbopalladated complexes [8]. Thus, starting from highly enantiopure (>98% ee) (*S*)-2-*tert*-butyl-4-ferrocenyl-1,3-oxazoline [9], and depending upon the source of palladium (II), the cyclopalladated dimers **1** and **2** can be obtained in good yields. The dimeric complex **2** can be easily converted to the monomer **3** upon treatment with triphenylphosphine. These complexes are not only thermally stable, but insensitive to oxygen and moisture.



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The unusual structure of these compounds has prompted us to study their behaviour as catalysts in a variety of carbon–carbon and carbon–heteroatom bond-forming processes [8]. This paper reports a study of the catalytic activity of complexes 1–3 in the Heck reaction of iodo- and bromoarenes, that has also provided compelling evidence for the involvement of the “textbook” Pd(0)/Pd(II) catalytic cycle in the mechanism of the processes under investigation.

2. Results and discussion

The arylation of methyl acrylate by iodobenzene in *N,N*-dimethylacetamide (DMA) and using triethylamine as a base was initially selected as the benchmark reaction in order to assess the ability of the 1'-carbopalladated 4-ferrocenyl-1,3-oxazoline derivatives 1–3 to promote the Heck reaction (Table 1).

The initial experiments showed that all three complexes readily catalysed the Heck reaction at 80 °C under aerobic conditions (entries 1–3), although the acetate-bridged pentametallal complex 1 was somewhat less active than 2 or 3. It is worth noting here that in the two previous reports on the use of *ortho*-palladated ferrocene derivatives as catalysts for the Heck reaction

[6a,7], not only the reaction temperatures were much higher (140–150 °C), but several hours were required in order to achieve quantitative conversions. Taking into account the similar activities of complexes 2 and 3, and the fact that 2 is both phosphine-free and more readily available than 3, in all of the subsequent experiments the former compound was selected as the catalyst. The amount of 2 could be reduced to 0.5% mol without compromising the efficiency of the process (entry 4). With a 0.01% molar amount of 2, the time necessary for total conversion increased to 4 h (entry 5). Even with 0.001% mol of the catalyst, a 90% yield of methyl cinnamate was isolated after 30 h (entry 6), implying that turnover numbers of at least 45,000 per palladium atom can be easily achieved at 80 °C with complex 2. It is also noticeable that with this catalyst the reaction can be performed at temperatures lower than 80 °C. At 60 °C, a 64% yield of methyl cinnamate was obtained after only 1 h (entry 7). The reaction also takes place at room temperature, although at a very slow rate (entry 8). This is a remarkable result, since with the sole exception of a chloropalladated propargyl amine [5], all palladacycles reported to date require temperatures higher than 80 °C in order to promote the Heck olefination of aryl iodides.

We proceeded next to perform more Heck reactions with different substrates (Table 2).

The reaction of iodobenzene with styrene (entry 2) was somewhat slower than with methyl acrylate (entry 1), affording pure (*E*)-stilbene in 80% yield after 3 h at 80 °C. Compared with iodobenzene, *p*-iodoanisole required, not unexpectedly, longer reaction times, but both methyl (*E*)-4-methylcinnamate (entry 3) and (*E*)-4-methylstilbene (entry 4) were isolated in good yields. Complex 2 showed a diminished catalytic efficiency in the Heck couplings of the relatively inactive bromoarenes (entries 5–10), and best results were

Table 1
Heck coupling of iodobenzene with methyl acrylate in the presence of palladacycles 1–3^a

Entry	Palladacycle (% mol)	<i>T</i> (°C)	Time	Yield (%) ^b
1	1 (4.6)	80	15 min	63
2	2 (4.8)	80	15 min	100
3	3 (4.9)	80	15 min	100
4	2 (0.5)	80	20 min	100
5 ^c	2 (0.01)	80	4 h	100
6 ^c	2 (0.001)	80	30 h	90
7	2 (0.5)	60	1 h	64
8	2 (0.5)	r.t.	6 days	9

^a Until otherwise specified, reactions were carried out with 1 mmol of iodobenzene, 1.2 mmol of methyl acrylate and 1.4 mmol of triethylamine in air.

^b Isolated yield of (*E*)-methyl cinnamate after chromatographic purification.

^c These reactions were run on a 50-mmol scale.

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