

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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Received 27 January 2005; revised 25 February 2005; accepted 28 February 2005
Available online 13 April 2005

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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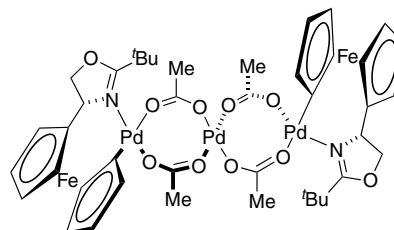
Keywords: Catalysis; Ferrocenes; Heck reaction; Metallacycles; Oxazolines; Palladium

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.

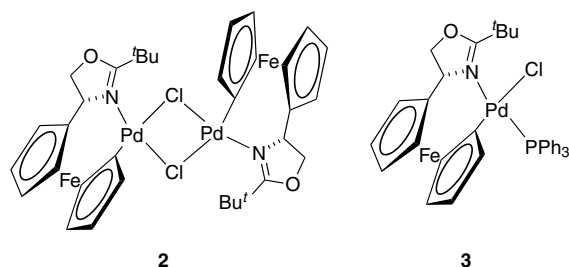
We have recently found that the cyclopalladation of 4-ferrocenyl-1,3-oxazolines takes place in an

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 pentametallic 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.

Table 2

Heck reactions of iodo- and bromoarenes with monosubstituted olefins in DMA, catalysed by complex **2**

| Entry | Ar-X | R | Conditions ^a | Time | Yield (%) ^b |
|-------|--------------------|--------------------|-------------------------|--------|------------------------|
| 1 | Ph-I | CO ₂ Me | A | 20 min | 100 |
| 2 | Ph-I | Ph | A | 3 h | 80 |
| 3 | <i>p</i> -MeOPh-I | CO ₂ Me | A | 72 h | 100 |
| 4 | <i>p</i> -MeOPh-I | Ph | A | 7 h | 67 |
| 5 | Ph-Br | CO ₂ Et | B | 48 h | 64 |
| 6 | Ph-Br | Ph | B | 72 h | 44 |
| 7 | <i>p</i> -HOPh-Br | CO ₂ Et | B | 48 h | 55 |
| 8 | <i>p</i> -HOPh-Br | Ph | B | 72 h | 40 |
| 9 | 1-Bromonaphthalene | CO ₂ Et | B | 48 h | 51 |
| 10 | 1-Bromonaphthalene | Ph | B | 72 h | 53 |

^a Reaction conditions A: 1 mmol aryl iodide, 1.2 mmol olefin, 1.4 mmol triethylamine, 0.005 mmol **2**, 2 mL DMA, 80 °C. Reaction conditions B: 1 mmol aryl bromide, 1.2 mmol olefin, 1.4 mmol K₃PO₄, 0.005 mmol **2**, 2 mL DMA, 140 °C.

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

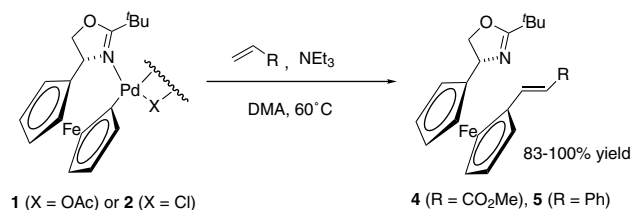
obtained when the reactions were performed at 140 °C and using potassium phosphate as the base (both triethylamine and sodium acetate gave inferior results). It is worth noting however that at the same temperature cyclopalladated complexes derived from (*N,N*-dimethylaminomethyl)ferrocene failed to give any Heck product from bromobenzene [7]. On the other hand, the 1'-carbopalladated ferrocene **2** appears to be much less sensitive to the presence of electron-donating substituents in the aryl bromide than *ortho*-palladated acetylferrocenyl oxime [6a], since 4-bromophenol (entries 7 and 8) gave yields very similar to those obtained either with bromobenzene (entries 5 and 6) or with 1-bromonaphthalene (entries 9 and 10). In conclusion, 1'-carbopalladated ferrocene complexes such as **2** appear to be much more active catalysts for the Heck reaction, especially with iodoarenes, than previously known NC-palladacycles derived from ferrocene.

The introduction of palladacycles as catalysts in Heck reactions was accompanied by a stimulating controversy on the mechanism of this process [10], since several authors suggested the possibility of a non-conventional pathway via Pd(II)/Pd(IV) intermediates [3,4a,4c,4g,11]. On the other hand, recent investigations tend to indicate that palladacycles are not the true catalysts but instead some sort of soluble Pd(0) particles or under-ligated species [4h,5,12]. The matter is however still open to debate, and in particular the problem of how Pd(0) is generated from the palladacycle pre-catalyst is an unresolved question, due to the lack of direct experimental evidence.

During the TLC monitoring of the Heck arylation of methyl acrylate with iodobenzene, we observed that in the first stages of the reaction the starting palladium com-

plex had disappeared, giving rise to a new ferrocene derivative that could be isolated after chromatographic purification of the reaction crude. Based on spectral data, this compound was identified as the (*S*)-2-*tert*-butyl-4-[1'-((*E*)-2-methoxycarbonylethenyl)ferrocenyl]-1,3-oxazoline **4**. This assignment was later confirmed when we obtained quantitatively the same compound **4** (along with a black palladium precipitate) by reaction of **2** with an excess of methyl acrylate in the presence of triethylamine (Scheme 1). In the Heck reactions using styrene as the olefin, a similar behaviour was observed, the starting 1'-carbopalladated complex **2** being quickly replaced by the 1'-olefinated 4-ferrocenyl-1,3-oxazoline **5**. As before, this compound was quantitatively obtained from **2** by treatment with styrene in the presence of base. When the acetate-bridged complex **1** was used as the starting material, the reaction was somewhat slower and the acrylate-substituted ferrocene **4** was obtained in 83% yield after 3 h.

It is thus readily apparent that the facile, non-catalytic Heck reaction between the olefin and the 1'-carbopalladated complex [13] is the source of the actual Pd(0) catalyst. Beletskaya [4h] had already suggested the possibility of a similar pathway in the promotion of Heck reactions by NC-palladacycles, but no direct



Scheme 1.

experimental evidence was provided in support of this hypothesis. Since the generation of **4** or **5** in the reaction medium was not accompanied by the formation of any black palladium precipitate, we believe that either soluble palladium nanoparticles or “homeopathic” ligand-free palladium [1h,12c] are the responsible of the catalytic activity in our case. In order to validate this hypothesis, we performed a mercury drop test [14], that turned out to be positive: when to the reaction between iodobenzene and methyl acrylate, performed under the conditions of entry 5 of Table 1, were added after 15 min 300 molar equiv. (with respect to Pd) of metallic mercury, the yield of methyl cinnamate after 4 h dropped from 100% to 25%.

Further evidence favouring the involvement of a Pd(0)/Pd(II) catalytic cycle was gathered when 2,3-dihydrofuran was employed in a Heck reaction with iodobenzene (Table 3).

The reaction turned out to be regioselective [15], 2-phenyl-2,3-dihydrofuran **6** being obtained preferentially (entry 1) or exclusively (entry 4) when potassium phosphate was used as a base; on the other hand, 2-phenyl-2,5-dihydrofuran **7** was the sole product formed when silver oxide (entry 2) or silver carbonate (entries 3 and 5) were employed. It can also be seen that the dimeric complex **2** led to somewhat better yields than the monomer **3**. In all instances, **6** and **7** were obtained in racemic form, a result which is again compatible with the initial formation of a Pd(0) species as the actual catalyst. The reaction did not take place when phenyl triflate was used instead of iodobenzene.

In summary, we have found that 1'-carbopalladated-4-ferrocenyl-1,3-oxazolines behave as active promoters of the Heck olefination, allowing the reaction to be performed at lower temperatures than in the case of previously known NC-palladacycle pre-catalysts derived from ferrocene. In the reaction medium, the olefin partner couples with the 1'-position of the ferrocene, leading to the formation of soluble palladium(0) catalytic species. For the first time, the ligand-olefin adduct has been

isolated and unequivocally characterised. Further investigations on the catalytic activity of this new structural class of palladacycles are underway in our laboratory.

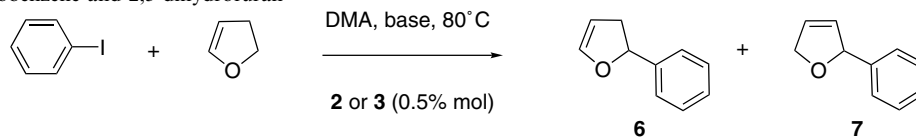
3. Experimental

General and analytical methods. Melting points were determined in an open capillary tube and are uncorrected. Optical rotations were measured at room temperature (r.t.) (23 °C) on a Perkin–Elmer 241 MC polarimeter. Concentrations are given in g 100 ml⁻¹. Infrared spectra were recorded in a Fourier transform mode, using NaCl film or KBr pellet techniques. The ¹H-NMR spectra were recorded at 200 MHz (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), and the ¹³C NMR spectra were recorded at 50.3 MHz. Chemical shifts are given in ppm and referenced to Me₄Si (¹H) or CHCl₃ (¹³C). *J* values are given in Hz. Carbon multiplicities were established by DEPT experiments. Mass spectra (MS) were run on a Hewlett–Packard HP-5988 A spectrometer, using FAB or MALDI ionisation techniques. Exact mass measurements (HRMS) were performed by the “Unidade de Espectrometria de Masas de la Universidad de Santiago de Compostela”. All reactions were run in flame or oven-dried glassware. Reaction progress was followed by TLC (Merck DC-Alufolien KIESELGEL 60 F254). Silica gel (70–230 mesh) was used for column chromatography. Triethylamine was distilled from calcium hydride. Olefins and aryl halides used in the Heck reactions were obtained from commercial sources and used as received. Compounds **1–3** were prepared as previously described by us [8].

3.1. Typical experimental procedure for heck coupling of aryl iodides with terminal olefins (conditions A, Table 2)

A 10-mL, heavy-wall borosilicate glass tube was charged with iodobenzene (112 μL, 1 mmol), methyl

Table 3
Heck reactions of iodobenzene and 2,3-dihydrofuran^a



| Entry | Palladacycle | Base | Time (h) | 6 (% yield) ^b | 7 (% yield) ^b |
|-------|--------------|---------------------------------|----------|---------------------------------|---------------------------------|
| 1 | 2 | K ₃ PO ₄ | 3 | 89 | 8 |
| 2 | 2 | Ag ₂ O | 10 | 0 | 45 |
| 3 | 2 | Ag ₂ CO ₃ | 16 | 0 | 68 |
| 4 | 3 | K ₃ PO ₄ | 3 | 58 | 0 |
| 5 | 3 | Ag ₂ CO ₃ | 16 | 0 | 55 |

^a All reactions were performed with 1 mmol of iodobenzene, 5 mmol of 2,3-dihydrofuran, 2 mmol of base and 0.005 mmol of palladacycle in 2 mL of DMA under argon at 80 °C.

^b Yields refer to product isolated after chromatographic purification.

acrylate (108 μL , 1.2 mmol), triethylamine (195 μL , 1.4 mmol), palladacycle **2** (4.5 mg, 0.005 mmol) and *N,N*-dimethylacetamide (DMA, 2 mL). The tube was closed and the mixture was stirred at 80 °C for 20 min. After cooling to room temperature, the crude reaction mixture was poured into water (10 mL) and extracted with diethyl ether (3×10 mL). The organic phases were washed with brine (10 mL), dried over anhydrous magnesium sulphate, evaporated under reduced pressure and the resulting crude product was purified by flash chromatography on silica gel (hexane–ethyl acetate) to afford 164 mg (quantitative yield) of (*E*)-methyl cinnamate.

3.2. Typical experimental procedure for heck coupling of aryl bromides with terminal olefins (conditions B, Table 2)

A 10-mL, heavy-wall borosilicate glass tube was charged with bromobenzene (100 μL , 1 mmol), ethyl acrylate (130 μL , 1.2 mmol), potassium phosphate (0.297 g, 1.4 mmol), palladacycle **2** (4.5 mg, 0.005 mmol) and DMA (2 mL). The tube was closed and the mixture was stirred at 80 °C for 48 h. After cooling to room temperature, the crude reaction mixture was poured into water (10 mL) and extracted with diethyl ether (3×10 mL). The organic phases were washed with brine (10 mL), dried over anhydrous magnesium sulphate, evaporated under reduced pressure and the resulting crude product was purified by flash chromatography on silica gel (hexane–ethyl acetate) to afford 112 mg (64% yield) of (*E*)-ethyl cinnamate.

3.3. (*S*)-2-*tert*-Butyl-4-[1'-((*E*)-2-methoxycarbonyl-ethenyl)ferrocenyl]-1,3-oxazoline, **4**

In a 10-mL round-bottomed flask, a solution of the cyclopalladated complex **2** (40 mg, 0.045 mmol) triethylamine (610 μL , 4.5 mmol) and methyl acrylate (400 μL , 4.5 mmol) in DMA (2 mL) was stirred at 60 °C for 1 h. After being cooled to room temperature, the reaction mixture was poured into water (10 mL) and extracted with diethyl ether (3×10 mL). The combined extracts were washed with brine (5 mL), dried over anhydrous magnesium sulphate and purified by column chromatography on silica gel (hexane–ethyl acetate), to give 35 mg (100% yield) of the 1'-substituted 4-ferrocenyl-1,3-oxazoline **4**. M.p. 160 °C (dec.). $[\alpha]_{\text{D}} = -10$ ($c = 0.45$, CHCl_3). IR (KBr): $\nu = 2925$, 1717, 1653, 1634, 1456, 1306, 1196, 1161, 804 cm^{-1} . ^1H NMR (200 MHz, CDCl_3): δ (ppm) 1.26 (s, 9H, $3 \times \text{CH}_3$), 3.76 (s, 3H, O- CH_3), 4.04 (m, 2H, $\text{CH}_2\text{-O}$), 4.14 (m, 4H, CH-Fc), 4.40 (m, 2H, CH-Fc), 4.47 (m, 2H, CH-Fc), 4.80 (m, 1H, CH-N), 6.03 (d, $J = 15.8$ Hz, CH=), 7.56 (d, $J = 15.8$ Hz, CH=). ^{13}C NMR (50.3 MHz, CDCl_3): δ (ppm) 27.9 (CH_3), 33.2 (Cq), 51.4 (CH_3), 64.2 (CH),

67.4 (CH), 68.6 (CH), 68.9 (CH), 69.0 (CH), 69.7 (CH), 69.8 (CH), 71.2 (CH), 73.2 (CH), 78.9 (CH_2), 90.3 (Cq), 91.8 (Cq), 114.6 (CH), 145.4 (CH), 167.3 (Cq), 173.7 (Cq). MS (MALDI-Dith/THF) $m/e = 396.0$ ($\text{M} + 1^+$, 100%). HRMS Calcd. for $\text{C}_{21}\text{H}_{25}\text{FeNO}_3$: 395.1177. Found: 395.1183.

3.4. (*S*)-2-*tert*-Butyl-4-[1'-((*E*)-2-phenylethenyl)ferrocenyl]-1,3-oxazoline, **5**

In a 10-mL round-bottomed flask, a solution of the cyclopalladated complex **2** (40 mg, 0.045 mmol) triethylamine (610 μL , 4.5 mmol) and styrene (300 μL , 4.5 mmol) in DMA (2 mL) was stirred at 60 °C for 1 h. After being cooled to room temperature, the reaction mixture was poured into water (10 mL) and extracted with diethyl ether (3×10 mL). The combined extracts were washed with brine (5 mL), dried over anhydrous magnesium sulphate and purified by column chromatography on silica gel (hexane–ethyl acetate), to give 36 mg (100% yield) of the 1'-substituted 4-ferrocenyl-1,3-oxazoline **5**. M.p. 160 °C (dec.). $[\alpha]_{\text{D}} = -57$ ($c = 0.50$, CHCl_3). IR (KBr): $\nu = 2969$, 1731, 1655, 1458, 1137, 1029, 819 cm^{-1} . ^1H NMR (200 MHz, CDCl_3): δ (ppm) 1.25 (s, 9H, $3 \times \text{CH}_3$), 4.11 (br s, 2H, $\text{CH}_2\text{-O}$), 4.14 (m, 4H, CH-Fc), 4.27 (m, 2H, CH-Fc), 4.45 (m, 2H, CH-Fc), 4.81 (m, 1H, CH-N), 6.59 (d, $J = 16.0$ Hz, CH=), 6.86 (d, $J = 16.1$ Hz, CH=), 7.32 (m, 5H, CH_{Ph}). ^{13}C NMR (50.3 MHz, CDCl_3): δ (ppm) 27.9 ($3 \times \text{CH}_3$), 33.2 (Cq), 64.5 (CH), 66.4 (CH), 66.9 (CH), 67.0 (CH), 67.4 (CH), 67.8 (CH), 67.9 (CH), 68.6 (CH), 69.4 (CH), 73.2 (CH_2), 90.6 (Cq), 91.1 (Cq), 125.7 (CH), 126.2 (CH), 126.4 (CH), 126.7 (CH), 128.5 (CH), 137.6 (Cq), 173.4 (Cq). MS (FAB $^+$) $m/e = 413.1$ (M^+ , 100%). HRMS Calcd. for $\text{C}_{25}\text{H}_{28}\text{FeNO}$: 413.1523. Found: 413.1523.

3.5. General experimental procedure for the Heck reaction of phenyl iodide with 2,3-dihydrofuran

A 20-mL Schlenk tube was charged under argon with iodobenzene (112 μL , 1 mmol), 2,3-dihydrofuran (108 μL , 5 mmol), potassium phosphate, silver oxide or silver carbonate (2 mmol), palladacycle **2** (4.5 mg, 0.005 mmol) and dry DMA (2 mL). The tube was closed and the mixture was stirred at 80 °C until TLC monitoring revealed that iodobenzene had disappeared (3–16 h). After cooling to room temperature, the crude reaction mixture was diluted with diethyl ether (30 mL) and filtered through a short Celite[®] pad. The solvent was evaporated under reduced pressure and the resulting crude product was purified by flash chromatography on silica gel (hexane–dichloromethane) to give the phenyl-substituted dihydrofurans **6** or **7**, whose spectral data coincided with those described in the literature [16].

Acknowledgements

We gratefully acknowledge financial support from DGI (Grant BQU2003-03426) and from DURSI (Grant 2001SGR-00050). M.R. is grateful to the Generalitat de Catalunya (DURSI) for a predoctoral fellowship.

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