



Tandem Suzuki–Miyaura/transfer hydrogenation reaction catalyzed by a Pd–Ru complex bearing an anionic dicarbene



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ABSTRACT

A hetero-bimetallic Pd–Ru *N*-Heterocyclic Dicarbene (NHDC) complex was synthesized from a Ag–Ru complex by transmetalation. The Pd–Ru system displays high catalytic activity in tandem Suzuki–Miyaura cross-coupling/transfer hydrogenation reaction of bromoaryl ketones with boronic acids in toluene and 2-propanol in the presence of KOH.

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1. Introduction

The combination of two catalytic transformations to a single tandem process appears to be particularly appealing in organic synthesis since this protocol reduces the number of synthetic steps toward the target compound, with concomitant reduction of solvent amounts and increase in overall yield [1,2]. Bimetallic systems have become the subject of current research as they are expected to induce cooperative effects among the involved metals [3–9]. For the Suzuki–Miyaura/transfer hydrogenation transformation entailing C–C and C–H bond forming reactions, catalysts are mainly based on heterogeneous systems [4,10] and enzymes [11–15]. By contrast, homogeneous bimetallic catalysts for this tandem reaction are less common [3,5,16,17], and some of them display higher activity compared to the combination of the single monometallic species [5,17]. Therefore, the design of novel heterobimetallic complexes based on suitable ligands is crucial to achieve more efficient catalysts for tandem reactions.

In the last two decades, *N*-heterocyclic carbenes (NHC) have been extensively employed as ligands for the preparation of efficient homogeneous catalysts [18–23]. In particular, our groups described several NHC Ru catalysts for the transfer hydrogenation (TH) of ketones in 2-propanol [24–26]. Current advances in car-

bene chemistry focus on the development of unusual coordination geometries of the carbene ligand, and apart from abnormal carbenes [27,28], imidazolyl-derived anionic dicarbenes (*N*-heterocyclic dicarbenes, NHDCs) have recently attracted significant interest [24,29–32]. These compounds inherently allow the synthesis of bimetallic structures bearing two main-group elements [29,30,32–36] or one main-group element and one transition metal [37–41], and examples featuring two transition metal centers are almost exclusively homobimetallic [42–48]. Although their ditopic character renders these compounds highly promising for homogeneous catalysis, only one example of a catalytic application has been reported to date comprising an Au–B system applied in the skeletal rearrangement of enynes [41]. We describe here the isolation of a rare example of a heterobimetallic Pd–Ru NHDC complex that was found active as catalyst in tandem Suzuki–Miyaura cross-coupling/transfer hydrogenation reaction of bromoaryl ketones with boronic acids in toluene and 2-propanol.

2. Experimental

All reactions were performed under oxygen free, dry conditions in an argon atmosphere using standard Schlenk and glovebox techniques. The solvents used were purified, degassed, and dried according to standard purification techniques [49] or obtained from an MBraun solvent purification system. Complexes **1**, **2** [24] and [PdCl₂(IMes)₂] (IMes = 1,3-bis(mesityl)-imidazol-2-ylidene)

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[50] were obtained according to literature procedures. All further chemicals were purchased from commercial sources and used as received. NMR spectra were acquired on a Bruker Avance Ultra-shield 400 MHz, a Bruker DPX 400 MHz spectrometer, and a Bruker AC 200 spectrometer. All ^1H and ^{13}C chemical shifts are reported in parts per million (ppm) relative to TMS, with the residual solvent peak serving as internal reference [51]. ^{31}P NMR spectra are referenced to 85% H_3PO_4 as external standard. ESI mass spectra were acquired on a Thermo Scientific LCG Fleet. GC analysis was done with an Agilent 7890b GC system using an Agilent HP-5 column (30 m \times 25 μm \times 0.32 mm) and a Varian CP3380 GC system using a MEGA-DEX DETTBSBETA column (25.0 m \times 25 μm \times 0.25 mm). Elemental analyses were carried out in the microanalytical laboratory at Technische Universität München.

2.1. Synthesis of complex **3**

Complex **2** (109 mg, 0.05 mmol), $[\text{PdCl}_2(\text{cod})]$ (15.5 mg, 0.055 mmol, 1.10 equiv.) and Ag_2O (13.7 mg, 0.06 mmol) were suspended in 10 mL of toluene and stirred at room temperature for 60 min under protection of light. The formed gray precipitate was filtered off with a filter cannula and the volatiles of the filtrate were removed under reduced pressure. The crude product was washed with *n*-pentane (2 \times 2 mL) and dried *in vacuo*. Complex **3** was obtained as brown-yellow powder in 80% yield (81.0 mg, 0.040 mmol). ^1H NMR (400 MHz, CD_2Cl_2 , RT): δ = 7.91–7.87 (m, 4H, Ar–H), 7.46–7.31 (m, 16H, Ar–H), 7.16–7.09 (m, 14H, Ar–H), 6.98–6.92 (m, 6H, Ar–H), 6.85–6.82 (m, 6H, Ar–H), 6.64 (s, 2H, Ar–H), 6.39–6.26 (m, 4H, Ar–H), 5.93 (t, $^2J_{\text{HH}} = 12.5$ Hz, 2H, CHHP), 5.43 (s, 2H, Ar–H), 4.70 (m, 2H, CHHP), 4.05 (m, 2H, CHHP), 2.81 (d, $^2J_{\text{HH}} = 13.8$ Hz, 2H, CHHP), 2.46 (s, 6H, CH_3), 2.38 (s, 6H, CH_3), 2.19 (s, 6H, CH_3), 2.04 (s, 6H, CH_3), 1.94 (s, 6H, CH_3), 1.84 (s, 6H, CH_3), 0.66 (s, 6H, CH_3). ^{13}C $\{^1\text{H}\}$ NMR (101 MHz, CD_2Cl_2 , RT): δ = 194.0 (dd, $^2J_{\text{CPcis}} = 11.2$ Hz, $^2J_{\text{CPtrans}} = 101.0$ Hz, NCN), 183.8 (s, OAc), 168.4 (d, $^3J_{\text{CP}} = 12.0$ Hz, NCN) 150.7 (dd, $^2J_{\text{CPcis}} = 9.8$ Hz, $^2J_{\text{CPcis}} = 19.4$ Hz, NCHN), 138.6, 138.0, 137.8, 137.7, 137.2, 136.7, 136.6, 136.3, 135.9, 135.2, 135.1, 134.9, 134.8, 134.7, 134.2, 134.1, 134.0, 131.7, 131.2, 130.6, 130.2, 129.3–128.0, 124.7, 123.8, 120.4 (aromatic carbon atoms), 53.4 (NCH₂P), 48.1 (d, $^1J_{\text{CP}} = 39.1$ Hz, NCH₂P), 23.7 (CH_3), 21.5 (CH_3), 21.1 (CH_3), 20.2 (CH_3), 19.3 (CH_3), 19.2 (CH_3), 17.5 (CH_3). ^{31}P $\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2 , RT): δ = 81.6 (d, $^2J_{\text{PP}} = 25.0$ Hz, major and minor isomers), 81.5 (d, $^2J_{\text{PP}} = 24.7$ Hz, minor isomer), 57.5 (d, $^2J_{\text{PP}} = 24.7$ Hz, minor isomer), 57.0 (d, $^2J_{\text{PP}} = 25.0$ Hz, major isomer), 56.5 (d, $^2J_{\text{PP}} = 24.7$ Hz, minor isomer). Elemental analysis calcd (%) for $\text{C}_{104}\text{H}_{104}\text{Cl}_2\text{N}_8\text{O}_4\text{PdRu}_2 \times \text{CH}_2\text{Cl}_2$: C, 59.53; H, 5.05 N, 5.29. Found: C, 59.27; H 5.20; N, 5.26. MS (ESI): m/z (%) = 1016.9 (30) [M^{2+}], 998.6 (100) [$\text{M}^{2+}-\text{Cl}$], 667.8 (55) [$\text{M}^{3+}-\text{Cl}$].

2.2. Transfer hydrogenation reactions

In a typical experiment, the reactor was charged with 2-propanol (9.8 ml), the ketone (1 mmol), anisole (50 mg) and the catalyst (0.05–0.1 mol%). The mixture was heated to 100 °C for 1 min and a 0.1 M solution of NaOiPr in 2-propanol (200 μl , 0.05 mmol, 5 mol%) was added to the stirred mixture. 1 mL aliquots of the reaction mixture were taken at the required reaction times, cooled with an ice bath and filtered over a short pad of silica. The sample was diluted with toluene to a volume of 1 mL and characterized by gas chromatography.

2.3. Tandem reactions in toluene/2-propanol mixture

In a typical run, a Schlenk tube was charged with 4-bromoacetophenone (0.1 mmol), phenylboronic acid (0.125–0.175 mmol), anisole (25 mg) and the base (0.2–0.3 mmol). To this

mixture, 1 mL of a stock solution of catalyst **3** (1 mg/mL in toluene) and 1 mL of 2-propanol were added (**3**: 0.5 mol%). The Schlenk tube was sealed and heated to 100 °C. After 1 h, the reaction was terminated by cooling with an ice bath and a 1 mL aliquot of the reaction mixture was taken and filtered over a pad of silica. The sample was diluted with toluene to a volume of 1 mL and characterized by gas chromatography.

2.4. Tandem catalytic reactions using toluene followed by addition of 2-propanol

In a typical run, a Schlenk tube was charged with the ketone (0.1 mmol), phenylboronic acid (0.175 mmol), anisole (25 mg) and potassium hydroxide (0.3 mmol). This mixture was suspended in the required amount of a toluene stock solution of the catalyst(s), and the tube was sealed with a septum and heated to 100 °C for 15 min ([Pd]: 0.5 mol%, [Ru]: 1.0 mol%). 1 mL of 2-propanol was added and after further 15 min at 100 °C the reaction was terminated by cooling with an ice bath. A 1 mL aliquot of the reaction mixture was taken and filtered over a pad of silica. The sample was diluted with toluene to a volume of 1 mL and characterized by gas chromatography.

3. Results and discussion

Recently, we described novel hetero-bimetallic NHDC complexes based on Ag–Ru and Au–Ru metals [20], whose syntheses entail the reaction of the abnormal carbene ruthenium complex **1** with Ag_2O leading to formation of the Ag–Ru derivative **2** (Scheme 1).

Treatment of the cationic Ag–Ru complex **2** with $[\text{PdCl}_2(\text{cod})]$ in toluene for 60 min affords the neutral Pd–Ru complex **3** by transmetalation (80% yield) [52,53]. The ^1H NMR spectrum of **3** in CD_2Cl_2 shows six different signals for the mesityl methyl groups and one signal for the acetate group. The $^{13}\text{C}\{^1\text{H}\}$ NMR of the normal Ru carbene appears as a doublet of doublets at δ = 194.0 ppm with a $^2J_{\text{CP}} = 101.0$ and 11.2 Hz, due to the *trans* and *cis* P atoms; whereas the abnormal Ru carbene signal is at δ = 150.7 ppm ($^2J_{\text{CP}} = 9.8$ and 19.4 Hz), in agreement with the data of **1** and **2** [24]. The formation of the Pd normal carbene is confirmed by the doublet at 168.4 ppm, displaying a $^3J_{\text{CP}} = 12.0$ Hz. In addition, the peaks at δ = 53.4 and 48.1 ppm ($^1J_{\text{CP}} = 39.1$ Hz) are for the CH_2P moieties. Variable temperature $^{31}\text{P}\{^1\text{H}\}$ NMR studies in toluene-*d*₈ show that at 90 °C **3** displays two main doublets at δ = 81.6 and 57.0 ppm with $^2J_{\text{PP}} = 20.7$ Hz. At 22 °C the complex exhibits a *pseudo*-triplet at δ = 81.8 ppm and four doublets in the range 58.3–56.8 ppm with $^2J_{\text{PP}} = 22$ –25 Hz, consistent with the presence of four species, which is likely due to the different conformation of the four five-membered P–NHC metallacycles of **3** [54]. The Pd–Ru complex **3** is a novel example of a hetero-bimetallic NHDC complex that can be easily prepared from the abnormal carbene **1**, showing the potential of this route for the synthesis of multinuclear carbene complexes.

Complex **3** was found active in the catalytic transfer hydrogenation (TH) of ketones using 2-propanol as hydrogen source. Acetophenone and 4-phenylacetophenone are easily reduced to the corresponding alcohols with **3** as catalyst (0.05 mol%) in 120 min at 100 °C in the presence of 5 mol% of NaOiPr (Table 1).

Remarkably, with Pd–Ru complex **3** under these catalytic conditions, 4-bromoacetophenone is poorly converted to 1-(4-bromophenyl)ethanol (9% yield) and no dehalogenation products (i.e. acetophenone or 1-phenylethanol) are observed in the reaction mixture. Conversely, with Ru complex **1** (0.1 mol%) quantitative reduction to 4-bromophenylethanol is attained in 20 min (Table 1).

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