Mixed N-heterocyclic carbene and phosphine palladium complexes for telomerization of butadiene with methanol

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ABSTRACT

A series of hydrophilic palladium-NHC complexes have been prepared and evaluated in the telomerization of butadiene with methanol under mild conditions (50 °C) in the presence or absence of water. Palladium complexes bearing mixed NHC-phosphine or zwitterionic imidazolinium ligands exhibited high efficiency in pure methanol (TON up to 59,000). Unfortunately, they could not be used for the télomérisation of butadiene with hydrosoluble substrate as they are inactive in the presence of water. On the other hand, catalyst prepared *in situ* from Pd(OAc)$_2$ and IMes.Cl was active in biphasic conditions and TON up to 10,200 was then achieved.

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1. Introduction

The palladium-catalyzed telomerization of 1,3-dienes with different alcohols is well documented. Many studies reported the formation of octadienyl ethers starting from simple alcohols, but also from polyols such as ethylene glycol, glycerol, mono and polysaccharides [1–10]. An industrial application concerned the hydrodimerization of butadiene to produce 2,7-octadien-1-ol, precursor of polymer plasticizer [11]. Moreover, the telomerization of butadiene with methanol is also of large importance as the octadienyl methyl ether is precursor of 1-octene after selective hydrogenation and methanol elimination.

Recently, the group of Beller described the preparation of palladium–carbene complexes which were very efficient for the telomerization of butadiene with methanol, diols, aminoalcohols, amines, but also for the telomerization and dimerization of the much less reactive isoprene [12–17]. Isolated complexes or *in situ* prepared catalysts were reported for this reaction. Such N-heterocyclic carbene-based catalysts exhibited higher activities towards telomerization compared to the corresponding phosphine-based complexes. Moreover, high chimioselectivity (>98%) and regioselectivity (up to 99/1) were reported with these

catalysts. These carbene-based complexes were successfully applied to the telomerization of butadiene with primary and secondary alcohols [14]. Very high turnover number (TON up to 94,000) was observed at 90 °C. The structure of the ligand influenced dramatically the selectivity of the reaction. Telomerization of isoprene with methanol using these ligands yielded mainly head-to-head isomer in contrast to palladium/phosphine catalysts [16]. In the presence of sterically hindered 1,3-bis-(2,6-diisopropylphenyl)imidazolidene ligand, the dimerization was favoured while main of the carbene ligands yielded generally the telomerization product [16–18].

Behr reported the palladium-catalyzed telomerization of butadiene with ethylene glycol in biphasic systems using carbene ligand [9,10,19]. With the complexes prepared *in situ* from Pd(acac)$_2$ and N-heterocyclic carbene (1,3-dimesityl-imidazolin-2-ylidene) ligands, the catalysts did not decompose, while slight lower reactivity was achieved in comparison to water-free conditions [10].

Following our aim to carry out the telomerization of starch, we wish to develop catalytic systems able to perform this reaction in aqueous media [20,21]. Giving the success of NHC-metal complexes in a wide range of catalytic reactions together with the potentially improved stability of these catalysts compared to phosphine-metal species, hydrophylic NHC-ligands would be expected to give efficient aqueous phase catalytic system. Considering the fact that complexes prepared with N-heterocylic

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carbenes exhibited very efficient telomerization of butadiene with alcohols, we aimed to prepare hydrosoluble carbene and to use them as ligand in palladium-catalyzed telomerization of butadiene with methanol.

To our knowledge, very few reports are dealing with the use of carbene-based complexes in aqueous medium. Rhodium and ruthenium complexes bearing hydrophylic carbene were described by Ozdemir et al. in the synthesis of 2,3-dimethyl furanne via enynol intramolecular cyclization [22]. Recently, Grubbs reported olefin metathesis in water using imidazol-2-ylidene ligand substituted by polyethylene glycol chain [23,24]. NHC ligands were also involved in Suzuki-type reaction in water [25]. In this paper, we will describe the preparation and the use of different NHC-palladium based complexes more specifically using hydrosoluble palladium complexes: first hydrosoluble imidazolinium-chelated palladium catalyst is reported, and then palladium complexes bearing one hydrosoluble phosphine ligand and one classical carbene ligand are described. In parallel, bis(NHC)-complexes of palladium(II) described by Nolan were investigated for this study [26]. All these complexes are evaluated in the telomerization of butadiene with methanol, focussing on the influence of the presence of water on their reactivity.

2. Experimental section

All the complexes were prepared under nitrogen using standard Schlenck techniques. The solvents were degassed prior to use. Proton, carbon and phosphorous NMR were recorded on a Bruker A 250 MHz.

2.1. Synthesis of di-μ-iodobis(2,4,6-trimethylphenylimidazolin-2-ylidene)-diiododipalladium. [(IMes)PdI$_2$]$_2$ 2

337 mg Pd(OAc)$_2$ (1.5 mmol), 899 mg NaI (6 mmol), 185 mg t-BuOK (1.65 mmol) and 511 mg Imes.HCl (1.5 mmol) were dissolved in 100 mL anhydrous THF. The solution was stirred under N_2 at 30 °C for 24 h. After filtration of the solid, the solvent was evaporated to yield a red solid that was chromatographied on silica. After purification, 701 mg orange solid was obtained (71%). ^{1}H NMR (CDCl$_3$): δ, 2.21 [6H, s]; 2.35 [6H, s]; 2.39 [6H, s]; 6.97 [2H, s]; 7.00 [4H, s] ^{1}H NMR (DMSO) δ 2.30 [12 H, s]; 2.32 [6H, s]; 7.03 [4H, s]; 7.62 [2H, s]. ^{13}C NMR (CDCl$_3$): δ 20.77; 21.20; 21.39; 124.72; 129.32; 129.68; 135.16; 135.51; 135.68; 139.07; 166.41. ESI-MS: m/z: 1329.3 [M]$^+$; 1202.6 [M−I+Na]$^+$.

2.2. Synthesis of diiodo-(2,4,6-trimethylphenylimidazolin-2-ylidene)(triphenylphosphino) palladium. PdI$_2$(Imes)(PPh$_3$) 3

In a Schlenk under nitrogen, 150 mg di-μ-iodobis(2,4,6-tri-methylphenylimidazolin-2-ylidene)-diiododipalladium **2** (0.113 mmol) were dissolved in 5 mL anhydrous THF. A solution of 60 mg PPh$_3$ (0.226 mmol) in 3 mL anhydrous THF was added dropwise and the solution turned from red to orange. The mixture was stirred at room temperature for 30 min. After evaporation of the solvent, the solid was washed with hexane and dried to yield orange solid (132 mg, 82%). Single crystals were obtained by slow evaporation of chloroform solution. ^{1}H NMR (CDCl$_3$): δ 2.43 [12H, s], 2.45 [6H, s], 7.04 [4H, s], 7.08 [2H, s], 7.19–7.42 [15H, M]; ^{13}C NMR (CDCl$_3$) δ 21.18; 21.93; 124.30 [d, J = 9 Hz]; 127.08 [d, J = 16 Hz]; 129.24; 129.59; 133.77; 134.52; 135.37 [d, J = 17 Hz]; 136.08; 136.22; 138.59; 166.58. ^{31}P NMR (CDCl$_3$) δ 14.54; Anal. Calcd: C, 49.24 (50.53); H, 4.09 (4.24); I, 27.43 (27.38); N, 3.18 (3.02); P, 2.95 (3.34); Pd, 11.77 (11.48). ESI-MS: m/z: 799 [M−I]$^+$; 303.4 [imidazolium]$^+$.

2.3. Synthesis of diiodo-(2,4,6-trimethylphenylimidazolin-2-ylidene)((3-sulfonatophenyl) diphenylphosphino) palladium. PdI$_2$(Imes)(TPPMS) 4

In a Schlenk under nitrogen, 100 mg di-μ-iodobis(2,4,6-tri-methylphenylimidazolin-2-ylidene)-diiododipalladium **2** (0.075 mmol) and 54.7 mg TPPMS (diphenyl(3-sulfonatophenyl)pho-sphine) (0.150 mmol) were dissolved in 10 mL degassed THF. The mixture was stirred at room temperature for 30 min. After evaporation of the solvent, the solid was washed with hexane and dried to yield yellow solid (142 mg, 92%). ^{1}H NMR (δ, DMSO): 2.33 (12H, s), 2.38 (6H, s), 7.07 (4H, s), 7.24–7.43 (12H, M), 7.45 (1H, d, ^{3}J$_{H-H}$ = 75 Hz), 7.55 (1H, d, ^{3}J$_{H-H}$ = 7.5 Hz), 7.65 (2H, s). ^{1}H NMR (δ, MeOD): 2.38 (12H, s), 2.41 (6H, s), 7.03 (4H, s), 7.19–7.51 (14H, M), 7.72 (2H, d, J$_{H-H}$ = 7.5 Hz). ^{13}C NMR (δ, DMSO) 20.68, 21.31, 125.36 (d, J_{CP} = 9 Hz), 126.50 (d, J_{CP} = 20 Hz), 127.14 (d, J_{CP} = 16 Hz), 128.87, 129.89, 133.18, 133.91, 134.08 (d, J_{CP} = 17 Hz), 135.40, 135.92, 135.76 (d, J_{CP} = 27 Hz), 137.98, 147.08 (d, J_{CP} = 11 Hz), 163.04; ^{31}P NMR (δ, DMSO) 14.72; ^{31}P NMR (δ, MeOD) 14.89; Anal. Calcd: C, 44.20 (45.52); H, 3.87 (3.72); I, 23.46 (24.67); N, 2.62 (2.72); Na, 2.39 (2.23); P, 2.83 (3.01); Pd, 9.95 (10.34); S, 2.83 (3.12), ESI-MS: m/z: 1004.7 [M−Na]$^−$.

2.4. Synthesis of diiodo-(2,4,6-trimethylphenylimidazolin-2-ylidene)(tri(3-sulfonatophenyl) phosphino) palladium. PdI$_2$(Imes)(TPPTS) 5

In a Schlenk under nitrogen, 200 mg di-μ-iodobis(2,4,6-tri-methylphenylimidazolin-2-ylidene)-diiododipalladium **2** (0.15 mmol) and 220.0 mg TPPTS (tri-(sulfonatophenyl)phosphine) (0.30 mmol, 85% purity) were dissolved a THF/H$_2$O solution (10/1). The mixture was stirred at room temperature for 30 min. After evaporation of the solvent, an orange solid was obtained (388 mg, 92%). ^{1}H NMR (δ, DMSO): 2.33 (12H, s), 2.36 (6H, s), 7.08 (4H, s), 7.22–7.35 (6H, M), 7.57 (6H, d, ^{3}J$_{H-H}$ = 7.5 Hz), 7.64 (2H, s); ^{13}C NMR (δ, DMSO) 20.71, 21.26, 125.40 (d, J_{CP} = 9 Hz), 126.70 (d, J_{CP} = 18 Hz), 127.22, 128.98, 129.28 (d, J_{CP} = 3 Hz), 132.82, 133.54, 135.40, 135.89, 137.72 (d, J_{CP} = 28 Hz), 138.04, 146.49 (d, J_{CP} = 14 Hz); ^{31}P NMR (δ, DMSO) 13.43 (5%), 14.96 (79%), 25,92 (16%; OTPPTS present in the initial TPPTS); ESI-MS: m/z: 1208.8 [M−Na]$^−$.

2.5. Telomerization of butadiene with methanol

All the catalytic reactions were performed in a stainless steel autoclave equipped with a mechanical stirrer and a heating jacket.

2.6. In organic media

In a typical reaction, degassed methanol (22.4 mL, 0.55 mol) and NaOH (222 mg, 5.5 mmol) were introduced in the autoclave. The preformed complex PdI$_2$(Imes)(PPh$_3$) (13 mg, 0.005 mol%) was then added under nitrogen. The autoclave was cooled to −30 °C, and the desired volume of butadiene was introduced from a graduated burette (typically 23.5 mL, 0.28 mol). The reactor was then slowly heated to the desired temperature (50 °C), the pressure increased up to 6 bar. After 24 h, the autoclave was cooled to room temperature, the excess butadiene was eliminated and the autoclave was purged with argon. An aliquot (50 mg) was diluted in THF (1 mL) and 20 mg of n-dodecane was added as external standard for GC analysis according to literature procedure [15]. The conversion attained 90%.

2.7. In the presence of water

In a typical reaction, degassed methanol (22.5 mL, 0.55 mol), H$_2$O (22.5 mL) and NaOH (222 mg, 5.5 mmol) were introduced in