



Alkoxycarbonylation

Palladium–Bis(carbene) Catalysts for the Bisalkoxycarbonylation of Olefins to Succinic Diesters

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Abstract: A series of Pd-bis(NHC) (NHC = N-heterocyclic carbene) complexes possessing various anions and substituents were used in the bisalkoxycarbonylation of olefins (α -olefins and ethylene) to afford industrially useful succinic diesters in modest to good yields. The influence of different ligands and counteranions of the Pd complexes on their catalytic activity was assessed, and it was found that dimeric Pd–bis(NHC)Br was the best catalyst for the bisalkoxycarbonylation reactions. The structure of dimeric Pd–bis(NHC)Br was confirmed by X-ray crystallographic analysis.

Introduction

Palladium complexes with chelating N-heterocyclic carbene (NHC) ligands are commonly used in Heck and Suzuki reactions. Relative to other ligands, the coordination of chelating NHC ligands to a palladium metal ion improves the stability and activity of the resulting catalysts in such reactions.^[1] Phosphane ligands are commonly used in metal-catalyzed reactions; however, they are sensitive to oxygen, and their synthesis often requires inert reaction conditions and multistep procedures. In contrast, NHC ligands are much less sensitive to oxygen and water, which provides stability to the catalyst, and the introduction of substituents on the nitrogen atom and backbone of bis-NHC systems is relatively easy; this allows convenient modification of the steric and electronic properties of these ligands.^[2]

Pd complexes bearing various ligands have been employed in the coupling of olefins to carbon monoxide (CO) to afford polyketones and mono- and diesters.^[3] Depending on the structure of the ligands and the reaction conditions, two reaction pathways are possible, that is, polymerization and monomer formation (Scheme 1). Pd complexes containing bidentate phosphane and nitrogen ligands favor the formation of polyketones, as demonstrated by Drent and others.^[4] The formation of monomers (monoesters and diesters) occurs in the presence of monodentate phosphane ligands instead.^[5,6] In the case of bidentate phosphane ligands with bulky substituents on the phosphorus atom, monoester formation dominates over polymerization.^[5d,5j] Other than phosphane ligands for Pd-catalyzed coupling reactions of olefins and CO, monodentate NHC ligands have also been used for the Pd-catalyzed alkoxycarbonylation of olefins to afford monoesters.^[5k] Except for Woo's work, carbene ligands have rarely been used in the Pd-catalyzed oxidative carbonylation of olefins owing to facile reductive elimination of



Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201601546. the alkyl-metal NHC complex intermediate formed during the carbonylation of olefins, which is detrimental to catalytic activity.^[5k,7] To avoid this undesirable alkylimidazolium reductive elimination pathway, increasing steric hindrance of the carbene ligand by incorporation of bidentate or tridentate NHC ligands has been proposed.^[1p,2d,7c] Accordingly, in this work, we used palladium complexes with bidentate NHC ligands for the oxidative carbonylation of olefins to afford succinic diesters, which are important building blocks that are used in the synthesis of biodegradable polymers.^[8] The effects of the substituents, tether, and counteranions of the bidentate carbene ligands on the catalytic activity were investigated.



Scheme 1. Pd-catalyzed reactions between olefins and CO.

Results and Discussion

We used six different Pd-bis(NHC) complexes for carbonylation, and their structures are shown in Figure 1. Complexes A,^[10]

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B,^[1b] **D**,^[1b] **E**,^[1b] and **F**^[1o] are known compounds and were prepared according to literature procedures. The synthesis of dimeric complex **C** is shown in Scheme 2. Although a similar procedure was reported to afford monocationic [Pd(NHC)(Br)-(CH₃CN)]PF₆ starting from complex **B**,^[1b] we isolated dimeric monocationic complex **C** instead. The dimeric structure of **C** was confirmed by X-ray structure determination (Figure 2). A single crystal of **C** was obtained by slow evaporation of an acetone solution of **C** at 4 °C to afford an acetone-incorporated dimeric complex. Palladium dimer **C** is assumed to undergo dissociation to form the active catalyst during the catalytic reaction.



Figure 1. Palladium complexes used in the bisalkoxycarbonylation of olefins. Mes = mesityl = 2,4,6-trimethylphenyl.



Scheme 2. Synthesis of complex C.



Figure 2. X-ray structure of C.^[9]

The Pd-catalyzed bisalkoxycarbonylation of 1-decene was performed in the presence of catalyst **A** (0.02 mmol, 4 mol-%), *para*-toluenesulfonic acid (TsOH; 0.05 mmol, 10 mol-%), 1,4-benzoquinone (BQ; 0.5 mmol, 1 equiv.), and methanol (MeOH; 5 mmol, 10 equiv.) in dichloromethane (CH₂Cl₂, 4 mL) at 80 °C under 30 bar of CO. The amounts of additives and solvents, the

temperature, as well as the pressure of CO were examined, and the specified conditions are found to be optimal for this transformation.^[10] Under these oxidative carbonylation conditions, dialkyloxalates could be formed in principle, but our catalytic systems promoted the formation of diesters with 100 % selectivity. Assuming that the catalytic activity was modulated by the nature of the ligands, the anions, the tether length, and the substituents on the nitrogen atom of the complexes were modified (Scheme 3). The catalytic activities of catalysts A and B were compared, and the effect of different halides on the yield of 1b was not substantial. However, selective replacement of a halide ion with a noncoordinating PF_6^- anion led to an improvement in the yield of 1b (catalyst C). Further removal of the halide ion was rather detrimental to the formation of 1b (catalyst **D**). An increase in the steric bulk of the N-bound substituents by replacing the methyl groups with mesityl (2,4,6-trimethylphenyl) groups improved the yield of 1b (catalyst E). An increase in the length of the tether did not lead to an improved yield (catalyst F). Overall, dimeric Pd complex C possessing an N-methyl-substituted bis(carbene) and a halide showed the best catalytic performance.



Scheme 3. Pd-catalyzed bisalkoxycarbonylation of 1a.

Under the optimized conditions shown in Scheme 3, various reactions between ethylene and CO were conducted (Scheme 4). In the presence of methanol, ethanol, and benzyl alcohol, desired succinic diesters were formed with the turnover numbers (TONs) indicated in Scheme 4.



Scheme 4. Pd-catalyzed synthesis of succinic diesters by using ethylene and CO.

In addition to **1b–4b**, various succinic diesters were synthesized from olefins (Table 1). Decene was exposed to the optimized conditions to afford ethyl ester **5b** and benzyl ester **6b**. Hexene participated in the reaction to form **7b** in 78 % yield. The presence of a phenyl substituent distant from the alkene functional group affected the yield, as shown for compounds **8b–10b**. Fluoro-, chloro-, and methyl-substituted styrenes were converted into desired esters **11b**, **12b**, and **13b** in yields of 61, 61, and 50 %, respectively.



Table 1. Examples of succinic diesters.



[a] BnOH (3 equiv.), BQ (1.5 equiv.). [b] BnOH (10 equiv.), BQ (1.0 equiv.).

A plausible catalytic cycle is proposed in Scheme 5. Dimeric complex **C** dissociates in the presence of CO and an alcohol to afford LnBrPd-CO₂R. The empty coordination site of the Pd monomer derived from C is readily occupied by incoming CO and ROH. Migratory insertion of the olefin into the Pd-C bond of LnBrPd–CO₂R provides intermediate I. The addition of CO to I followed by alcoholysis affords a succinic diester along with the generation of LnBrPd-H. Intermediate I might undergo protonolysis to afford the monoester, but in the presence of the bis(NHC)-Pd complex, no monoester formation was observed. Presumably, the formation of γ -chelate complex II is favored for the formation of the diester (succinic diester). In the presence of BQ, Pd-H is converted into Pd-CO2R.[61,69] Accordingly, the Pd-carboalkoxy complex (Pd-CO₂R) re-enters the catalytic cycle to promote the desired bisalkoxycarbonylation of the olefin. The greater catalytic activity of dimeric complex C might be explained by facile insertion of CO into the empty coordination site to afford a Pd-carboalkoxy complex. The role of the halo-



Scheme 5. A plausible catalytic cycle.



gen anion is not clear, but it can be speculated that the decomposition of the Pd catalyst to Pd^0 might be retarded by reoxidative addition of HX (X = Cl and Br).^[61] The addition of TsOH also improves the yield of this transformation, as the oxidizing power of BQ is known to increase in acidic media.^[6g]

Conclusions

We synthesized various Pd–bis(NHC) complexes and employed them in the synthesis of succinic diesters through the bisalkoxycarbonylation of olefins. A dimeric Pd–bis(NHC) complex was synthesized and characterized by X-ray crystallography, and it showed the best catalytic activity owing to the empty coordination site generated upon its dissociation in solution. A variety of olefins participated in the alkoxycarbonylation reaction in the presence of CO and alcohols to afford the corresponding products in modest to good yields.

Experimental Section

Representative Procedure for the Reactions of Olefins: A 50 mL autoclave was charged with a solution of BQ (54.05 mg, 0.5 mmol), TsOH (9.5 mg, 0.05 mmol), catalyst **C** (10.2 mg, 0.02 mmol), 1-decene (**1a**; 95 μ L, 0.5 mmol), and MeOH (202.5 μ L, 5 mmol) in CH₂Cl₂ (4 mL). The autoclave was pressurized with CO (30 bar), and the mixture was stirred at 80 °C for 15 h. The vessel was cooled to room temperature, and the unreacted gas was released. The solvent was removed under vacuum, and the residue was purified by flash column chromatography (silica gel, 1 % EtOAc/hexane) to afford dimethyl 2-octylsuccinate (**1b**; 101.2 mg, 78 %).

Representative Procedure for the Reactions of Ethylene: A 50 mL autoclave was charged with a solution of BQ (54.05 mg, 0.5 mmol), TsOH (9.5 mg, 0.05 mmol), catalyst **C** (10.2 mg, 0.01 mmol), and MeOH (202.5 μ L, 5 mmol) in CH₂Cl₂ (4 mL). The autoclave was pressurized with ethylene gas (5 bar) and subsequently charged with CO gas (10 bar) at room temperature. Then, the contents of the autoclave were stirred at 80 °C for 15 h. The vessel was cooled to room temperature, and the unreacted gas was released. The solvent was removed under vacuum, and the residue was purified by flash column chromatography (silica gel, 5 % Et₂O/ hexane) to afford dimethyl succinate (**2b**; 61.6 mg, TON = 21.1).

Synthesis of Catalyst C: A solution of complex **B** (130 mg, 0.29 mmol) and K[PF₆] (0.973 mg, 5.30 mmol) in acetonitrile (15 mL) and H₂O (10 mL) was stirred at 85 °C for 8 h. The solvent was removed under vacuum and distilled water (10 mL) was added. The resulting mixture was kept at 0 °C for 10 min. The white solid was filtered off, washed with diethyl ether, and dried under vacuum (111.8 mg, 75 %).

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- [10] See the Supporting Information for detailed optimization. The choice of additives was based on ref.^[6m]

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