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Novel Single-Component Palladium(II) Catalysts for the Alternating CO/Propene Copolymerization Reaction

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*Summary: A synthetic route for the preparation of 1,3-bis[diphenylphosphino]propane-1η^2,5η^1-6-ethoxy-exo-5,6-dihydrodicyclopentadienylpalladium(II) hexafluoroantimonate (**3a**) and the tetrafluoroborate derivative (**3b**) is described. **3a** was characterized by single-crystal X-ray structure analysis. Both species are active for the CO/α-olefin copolymerization reaction without any additional activator or cocatalyst. The copolymerization experiments performed with this single-component catalyst (SCC) produced CO/α-olefin copolymers with similar properties compared to those resulting from the well-known di-acetonitrile-1,3-[bis(diphenylphosphino)propane-Pd(II)-bis(tetrafluoroborate) complex activated with methanol. An increase of activity and molecular weight has been achieved through polymerization in liquid propene.*

Introduction

In contrast to metallocene dichlorides, late transition metal polymerization catalysts suffer in most cases from a chemically nonuniform activation reaction. We showed recently that in the case of CO/α-olefin copolymerization reactions alcohols, e.g., methanol or glycols, activate the Pd(II) catalyst precursor by a nucleophilic attack of the coordinated CO monomer.[1] However, this process requires access of the activating species, which also acts as chain transfer agent.[2] We report here on an easy and highly variable synthetic strategy to single-component Pd(II) catalysts (SCC) that are active without addition of further activators or cocatalysts.

Results and Discussion

We started from dicyclopentadiene (Figure 1, **1**) as versatile building block, which gives after treatment with $Na_2[PdCl_4]$ directly the μ^2-chloro-bridged Pd(II) dimer **2** (see Supporting Information for structure information). The addition of RO-H to a coordinated double bond of **1** proceeds spontaneously and in 90% yield (alcoholic solution), in contrast to other nonconjugated dienes, e.g., 1,5-COD,[3] which require a base to induce the reaction.

Complex **2** was subsequently reacted at low temperature with 2 equiv of 1,3-bis[diphenylphosphino]propane (dppp) in the presence of 2 equiv of $AgSbF_6$ or $AgBF_4$ to give directly the desired monocationic complex **3a** or **3b**, respectively, in nearly quantitative yield. The different counterions were introduced to study their influence on the copolymerization reaction. Treatment of **2** with dppp in the absence of any Ag^+ salt leads to decomposition of the complex species probably due to the chloride ion, which might open the dicyclopentadienyl chelate, affording further reactions on the organic fragment.

Chloride abstraction can also be achieved by cheap $NaBF_4$ in CH_2Cl_2 due to the insolubility of NaCl.

Crystals suitable for X-ray structure analysis of **3a** (Figure 2, Table 1) were achieved by slow evaporation of the solvent of a CH_2Cl_2/*n*-pentane solution. The coordination sphere around the Pd center is nearly square planar in both complexes despite the high sterical demand of **1**. The Pd−P distances are slightly enlarged and the corresponding P−Pd−P angle is wider in **3a** compared to those of the symmetrical [1,3-bis(diphenylphosphino)propane]$PdCl_2$ (Pd−P 224.4(1)/224.9(2) pm; P−Pd−P 90.58(5)°).[4]

Copolymerization experiments were performed in CH_2Cl_2 solution and in liquid propylene using **3a**,**b** without any additional cocatalyst and with a conventional cat./co-cat. system ($[dpppPd(NCCH_3)_2](BF_4)_2/CH_3OH$) for comparison. All polymer products show a narrow molecular weight distribution below 1.5 at 20 °C, indicating homogeneous polymerization conditions and a slow, spontaneous chain transfer rate. The polydispersities increase, as expected, at higher temperatures and in liquid propylene. The polymer yield depends clearly on the counterion and are consistently higher for the less coordinating structure (SbF_6^- in **3a**, Table 2, entries 1, 2 and 4, 5). [SCC **3b** (SbF_6^-) shows a higher temperature stability relative to **3a** (BF_4^-). This leads to lower yield (**3a**) at $T_p = 40$ °C and lower M_w, due to the living character of the polymerization reaction.[1]] In addition to a lower activity for the BF_4^- ion in **3b** there is also a trend for reduced molecular weights (Table 2, entries 4, 5).

All polymer products (**3a**,**b** and cat./co-cat.) consist of an identical microstructure (stereo- and regioirregular), as expected for the dpppPd(II) catalytic fragment and independent of the method of activation. There is a slightly lower polymer yield for SCC **3a** in CH_2Cl_2

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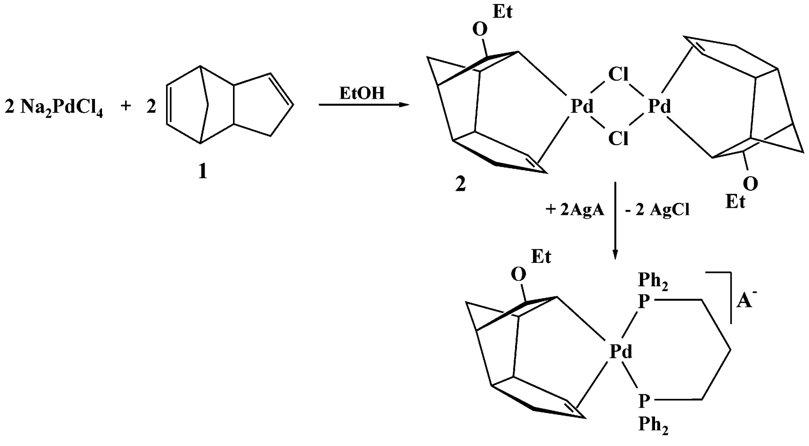

3a (A^-: SbF_6); **3b** (A^-: BF_4)

Figure 1. Two-step preparation of single-component catalysts **3a**,**b**.

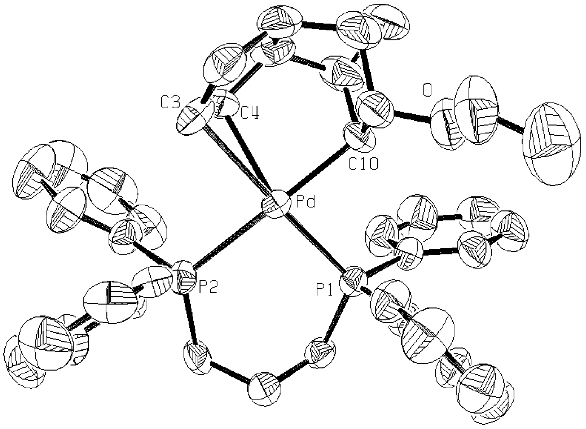

Figure 2. ORTEP plot and atom labeling of **3a**. Thermal ellipsoids are depicted at the 50% probability level. H atoms and the counterion are excluded. Selected bond lengths (Å) and angle (deg): Pd–P1 = 2.272(2); Pd–P2 = 2.389(2); Pd–C3 = 2.479(6); Pd–C4 = 2.325(7); Pd–C10 = 2.115(7); P1–Pd–P2 = 95.41.

Table 1. Crystal Data and Structure Refinement Parameters of 3a

cryst syst	orthorhombic
space group	$Pna2_1$
a, Å	19.735 (4)
b, Å	12.544 (2)
c, Å	15.951 (2)
α, deg	90
β, deg	90
γ, deg	90
vol, Å^3	3948.7(10)
mol wt	931.82
Z	4
ρ(calcd), g/cm^3	1.567
cryst size, mm^3	0.26 × 0.15 × 0.12
recrystallization solvent	CH_2Cl_2/n-pentane
refinement method	full-matrix least-squares on F^2
radiation used μ, cm^{-1}	Mo Kα, 1.28
2θ range, deg	2.06–25.95
no. of collected reflns	30 230
no. of unique reflns	7397
no. of obsd reflns ($I > 2\sigma(I)$)	5483
goodness-of-fit	1.004
final R incides ($I > 2\sigma(I)$)	$R_1 = 0.045$, $wR_2 = 0.100$
R indices (all data)	$R_1 = 0.063$, $wR_2 = 0.105$
Flack param	−0.04 (3)

Table 2. Propene/CO Copolymerization Results in Dichloromethane with 3a,b and the [dpppPd($NCCH_3$)$_2$]/Methanol or Liquid Propene with 3a and the [dpppPd($NCCH_3$)$_2$]/Methanol

entry	SCC^+A^- [a,b]	temp [°C]	yield [g]	activity [kg/mol/h]	M_w [× 10^{-5} g mol^{-1}]	M_w/M_n
1	A^-: SbF_6 (solution)	20	1.15	1.4	1.5	1.3
2	SbF_6 (solution)	40	1.74	2.1	1.3	1.7
3	SbF_6 [c]	40	3.40	4.0	3.2	2.2
4	BF_4	20	0.85	1.0	1.1	1.4
5	BF_4	40	0.41	0.5	0.6	1.9
6	cat./co-cat. [d]	20	1.56	2.2	1.3	1.2
7	cat./co-cat. [e]	40	2.24	3.0	3.2	2.0

[a] [1,3-Bis[diphenylphosphino]propane-1η^2,5η^1-6-ethoxy-exo-5,6-dihydrodicyclopentadi-enepalladium(II)]$^+A^-$. [b] 21 h, 40 μmol of catalyst, 150 mL of dichloromethane, 50 g of propene, 60 bar of CO. [c] 21 h, 100 g of propene (liquid), 60 bar of CO. [d] 18 h, 30 mg of [dpppPd($NCCH_3$)$_2$](BF_4)$_2$, 0.25 mL of methanol (cocatalyst), 150 mL of dichloromethane, 50 g of propene, 60 bar of CO. [e] 19 h, 30 mg of [dpppPd($NCCH_3$)$_2$](BF_4)$_2$ (in 30 mL of CH_2Cl_2), 0.25 mL of methanol (cocatalyst), 100 g of propene (liquid), 60 bar of CO.

solution (Table 2, entry 1) relative to the methanol-activated catalyst. This finding might be attributed to the presence of equimolar amounts of the remaining norbornene double bond, which competes with propene for coordination to the active center. However, this effect becomes negligible in bulk propylene (Table 2, entries 3 and 7), where **3a** gives the highest polymer yield and leads to a product with $M_w = 3.2 \times 10^5$ g/mol.

Experimental Section

Materials. All operations related to catalyst syntheses were carried out under a dry argon atmosphere using standard Schlenk techniques. **1** and the dppp-ligand were purchased from Aldrich, $AgBF_4$ from Merck, and $AgSbF_6$ and CH_2Cl_2 from Fluka. All compounds were analyzed by ^{1}H and ^{13}C NMR and if possible also by ^{31}P NMR on Bruker AMX400 and AMX500 spectrometers at ambient temperature. Elemental analyses were determined in the Microanalytical Laboratory of the University of Ulm. X-ray structure determinations of **3a** was carried out by U. T. (University of Ulm). The data were collected on a STOE IPDS instrument using graphite-monochromatized Mo Kα radiation.

Bis[μ^2-chloro-1η^2,5η^1-6-ethoxy-exo-5,6-dihydrodicyclopentadienepalladium(II)], 2. $Na_2[PdCl_4]$ (31.2 mmol, 8.4 g) was dissolved in 50 mL of ethanol. **1** (31.2 mmol, 4.3 g, Aldrich) is slowly added to the solution, which caused an immediate precipitation of the pale yellow complex. The reaction mixture was stirred for an additional 4 h. Subsequently, the solvent was evaporated and the pale yellow product was filtered off and washed two times each with water and n-hexane. Finally the complex was dried in a vacuum for several hours. $^{51}H^1H$ COSY (400 MHz, DMSO-d_6): δ 6.11 (1H), 5.35 (1H), 3.41 and 3.06 (2H), 3.32 (1H), 3.01−3.00 (1H), 2.61 (1H), 2.54 and 2.30 (2H), 2.27−2.23 (1H), 1.92 (1H), 1.87 (1H), 1.26 and 0.77 (2H), 0.80 (3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 109.2, 108.5, 80.0, 62.5, 57.3, 54.4, 53.5, 43.1, 35.4, 31.1, 15.8. Anal Calcd for $C_{24}H_{34}O_2Cl_2Pd_2$: C 45.16, H 5.37. Found: C 44.59, H 5.25.

1,3-Bis[diphenylphosphino]propane-1η^2,5η^1-6-ethoxy-exo-5,6-dihydrodicyclopentadienepalladium(II) hexafluoroantimonate, 3a (tetrafluoroborate, 3b). Complex **2** (1.56 mmol, 500 mg) and the chelate ligand dppp (1.72 mmol, 710 mg) were dissolved in 50 mL of dichloromethane. The pale yellow mixture was cooled to −10 °C. At this temperature the particular silver salt (1.64 mmol; BF_4 320 mg, SbF_6 560 mg) was added to the reaction mixture. Silver chloride precipitated immediately, and the color of the solution turned to orange. The reaction mixture was stirred for 4 h, AgCl was filtered off, and the solvent was evaporated. The color of both products is yellow to orange.[6] The silver salts can be substituted by the corresponding sodium salts without loss of yield or purity of the product complexes. $^1H^1H$ COSY (400 MHz, $CDCl_3$): δ 7.9−7.4 (20H, phenyl), 7.12 (1H, dcp), 5.81 (1H, dcp), 3.84 (1H, dcp), 3.56 and 3.42 (2H, dcp), 2.99 (1H, dcp), 2.87 (2H, propane bridge), 2.72−2.58 (3H, dcp; 2H, propane bridge), 2.36 (1H, dcp), 2.35−2.17 (1H, dcp; 1H, propane bridge), 1.75 (1H, dcp), 1.25−1.15 (1H, dcp; 1H, propane bridge), 1.09 (1H, dcp), 0.99 (3H, dcp). $^{13}C^1H$ COSY (125 MHz; DMSO-d_6): δ 134−125 (24C), 130.5, 126.1, 80.0, 68.5, 63.5, 58.5, 54.2, 40.6, 30.9 (2C), 26.7, 25.2, 17.9, 15.4. ^{31}P NMR (400 MHz, DMSO-d_6): δ 19.21 (d, 1P, $J_2 = 66.8$ Hz), −0.20 (d, 1P, $J_2 = 66.8$ Hz). Anal. Calcd for $C_{39}H_{43}OF_6P_2PdSb$: C 50.27, H 4.65. Found: C 50.41, H 4.64.

Polymerization Procedure. Solution. The copolymerization experiments were performed in a 250 mL Roth autoclave II equipped with glass inlay and online monitoring of gas flow and pressure. The autoclave was evacuated and flushed with argon several times. The SCC (40 μmol), dissolved in 150 mL of absolute dichloromethane, was added. Subsequently the autoclave was degassed and filled with approximately 50 g of propene and 60 bar of CO. The remaining gases were vented off after 21 h, and the organic solution was washed with water and dried over $CaSO_4$. The polymer was isolated by repeated precipitation in methanol.

Liquid Propylene. 3a or **3b** was added to the glass inlay under argon. Subsequently, the autoclave was closed and evacuated, and approximately 100 g of propylene was condensed into the autoclave, which was subsequently brought to the desired temperature and the CO pressure was set to 60 bar. Polymer isolation and purification was performed as described above.

Conclusion

The reaction of dicyclopentadiene with $PdCl_2$ in alcoholic solution offers an easy way to prepare the stable di-μ^2-dichloro-bridged complex **2** in a one-step reaction and in high yield, which bears a metal−carbon σ- and a π-bond. **2** can be used as educt to prepare a family of single-component catalysts by reaction with phosphine and also other ligands. In our case, stable dppp-mono cations (**3a**,**b**) were prepared by abstraction of the chloride counterion either by silver or even by cheap sodium salts. The corresponding complexes afford CO/propene copolymers without any further cocatalyst. There microstructures are identical to the conventional catalyst/cocatalyst systems. The presented synthetic strategy provides a new route to stable SCCs and was here exclusively applied to prepare these for the CO/propene copolymerization reaction. In addition, the same approach might be useful for the synthesis of catalysts for other processes and should help to avoid reactive and expensive activators, like MAO.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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