

Supplementary data

New diphosphine ligands based on diphenyl ether for the Pd-catalyzed CO/ethene copolymerization

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Experimental section

General Considerations: All manipulations were carried out under an argon atmosphere, using modified Schlenk techniques or in a Braun glovebox unless otherwise stated. All glassware was dried by heating under vacuum. *p*-tolylether, acrylonitrile and solvents were commercially available and purchased from Aldrich. The solvents and TMEDA (N,N,N',N'-tetramethylethylenediamine) were refluxed over CaH₂ and distilled prior to use. Acrylonitrile was degassed prior to use. Reacting gases, carbon monoxide and ethylene were used without purification. Purity: CO: 99.97%, ethene: 99.95%. Pd(acac)₂ was obtained from Degussa (Germany).

The elemental analyses were obtained from H. Kolbe, Mikroanalytisches Laboratorium, Mülheim (Germany). ¹H and ¹³C{¹H} were recorded on a Varian Mercury 400 spectrometer and all chemical shifts are reported relative to the residual proton resonance

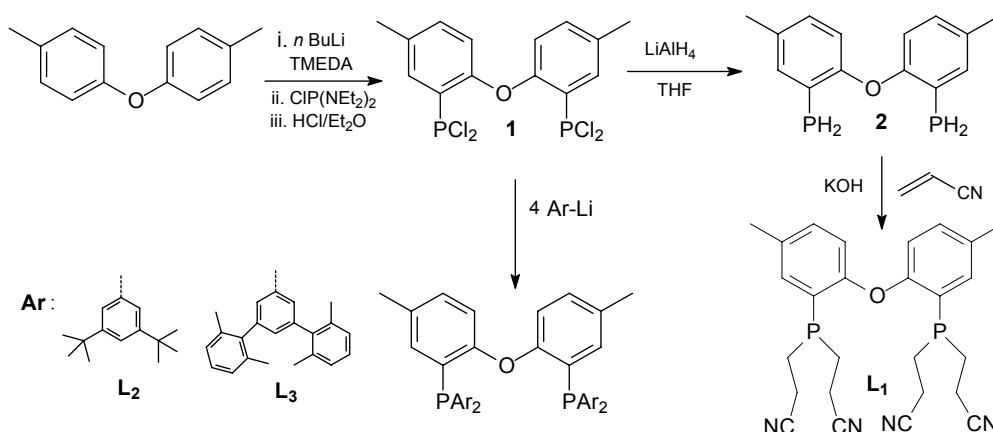
in the deuterated solvents, $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Varian Mercury 200 spectrometer and all $^{31}\text{P}\{^1\text{H}\}$ chemical shifts are referred to an 85% aqueous solution of H_3PO_4 . High pressure reactions were carried out in a home-made stainless steel autoclave (100 mL), equipped with a magnetic stirrer. GC measurements were performed on a Shimadzu 17A chromatograph (split/splitless injector, equipped with a 50 m ULTRA column and with a F.I.D.). GC-MS measurements (E.I. detection) were performed on a HP 5890/5971 apparatus, equipped with a ZB-5 column (5% cross-linked phenyl polysiloxane) with an internal diameter of 0.25 mm and film thickness of 0.25 μm . The mass characterization of palladium complexes has been performed by externally calibrated positive mode reflection MALDI-TOF using a Micromass TofSpec 2E-C equipped with a 2 GHz digitizer. The sample were diluted in ethylacetate, mixed with a concentrated solution of DHB in ethylacetate, and spotted directly on the stainless steel MALDI target. IR spectra were recorded on a Shimadzu 7300 FT-IR spectrometer.

The characterization of the CO/ethene copolymer was performed on a Voyager-DE-STR (Applied Biosystems, Framingham, MA) instrument equipped with a 337 nm nitrogen laser. All spectra were acquired in the positive ion reflector mode. Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) was used as matrix. Sodium trifluoroacetate (Aldrich, 98%) was added as the cationic ionization agent. The matrix was dissolved in THF at a concentration of 40 mg/mL. The polymer was dissolved in HFIP (1 mg/ml) and was deposit (0.5 μL) prior to the matrix on the target. For each spectrum 1000 laser shots were accumulated. In a typical MALDI experiment, the matrix and the salt solutions were premixed in the ratio: 5 μL matrix: 0.5 μL salt. Approximately 0.5 μL of the obtained mixture was hand spotted on the target plate.

General procedure for the copolymerization of ethene and carbon monoxide

In a typical experiment, a solution of the desired palladium complex (0.02 mmol) dissolved in 10 mL of anhydrous MeOH was injected into a 75 mL stainless steel autoclave. The autoclave was flushed three times with 3 bar of ethene, then pressurized with 25 bar of ethene and 25 bar of carbon monoxide at room temperature and then heated up to 60°C. After the desired time, the reaction was stopped by cooling the autoclave to room temperature by means of an ice bath. After the unreacted gases were released, the solution was analysed by GC and GC-MS.

a) Preparation of the Ligands



Scheme 1

Synthesis of 2,2'-bis(dichlorophosphino)-4,4'-dimethyl-diphenylether (**1**)

Starting from di-*p*-tolylether, compound **1** was synthesized following a similar procedure reported for 1,2-bis(dichlorophosphino) benzene [1]. Overall yield: 58%.

δ_{H} (400 MHz, CDCl₃) 7.8 (br s, 2H ar), 7.28 (dd, $J_{\text{HH}} = 1.6, 8.4$ Hz, 2H ar), 6.78 (dd, $J_{\text{HH}} = 2.8, 8.4$ Hz, 2H ar), 2.4 (s, 6H, CH₃).

δ_C (100.6 MHz, $CDCl_3$) 155.8 (d, $J_{CP} = 26$ Hz, Car), 134.8 (br s, Car), 131.3 (br s, Car), 131 (s, Car), 130.3 (s, Car), 117.9 (s, Car), 20.8 (s, CH_3).

δ_P (80.9 MHz, $CDCl_3$) 158.0 (s).

Synthesis of 2,2'-bis(diphenyl)phosphino-4,4'-dimethyl-diphenylether (2)

The reaction was carried out following a similar procedure reported for 2,6-diisopropylphenylphosphane [2].

A suspension of $LiAlH_4$ (167 mg, 4.4 mmol) in 9 mL of dry THF was cooled down with an ice-salt bath at $-5^\circ C$. A solution of 2,2'-bis(dichlorophosphino)-4,4'-dimethyl-diphenylether (400 mg, 1 mmol) was dissolved in 5 mL of dry THF and was added dropwise via teflon cannula to the suspension of $LiAlH_4$. After the addition, the reaction mixture was allowed to warm up to room temperature and then was stirred for one hour.

The solvent was removed under reduced pressure, then toluene was added and the slurry was filtered under argon.

The collected solution was evaporated and a white crystalline solid was obtained. Yield: 80%.

δ_H (400 MHz, $CDCl_3$) 7.38 (br d, $J_{HH} = 5.2$ Hz, 2H ar), 7.07 (br d, $J_{HH} = 8.0$ Hz, 2H ar), 6.69 (dd, $J_{HH} = 8.0, 2.80$ Hz, 2H ar), 4.17 (d, $^1J_{PH} = 205.7$ Hz, 2H), 3.66 (d, $^1J_{PH} = 205.7$ Hz, 2H), 2.34 (s, CH_3 , 6H).

δ_C ($CDCl_3$, 100.63 MHz) 156 (d, $J_{CP} = 8.3$ Hz, Car), 136.6 (d, $J_{CP} = 13.8$ Hz, Car), 132.9 (d, $J_{CP} = 3.8$ Hz, Car), 130.6 (s, Car), 120.5 (d, $J_{CP} = 11.5$ Hz, Car), 117.5 (s, Car), 20.6 (s, CH_3).

δ_P (80.9 MHz, $CDCl_3$) -140.7 (s).

$\nu_{max}(KBr)/cm^{-1}$ 2962, 2910, 1643, 940.

Synthesis of 2,2'-bis(di-(2-cyanoethyl)phenyl)phosphino-4,4'-dimethyl-diphenylether (L₁)

Compound L₁ was synthesized in similar way to a procedure described for bis-2-cyanoethylphenylphosphine [3].

2,2'-bis(diphenyl)phosphino-4,4'-dimethyl-diphenylether (1.71 g, 6.52 mmol) was dissolved in a mixture of dry CH₃CN (10 mL) and dry THF (18 mL) and was cooled down to 0°C. Subsequently 2.6 mL of a KOH solution (10M), was added dropwise and the ice bath was removed. Freshly distilled acrylonitrile (2.06 mL, 31.3 mmol, 4.8 eq) was added slowly, controlling that the temperature was between 5°C and 30°C. The reaction mixture was kept in the darkness and stirred for one hour at room temperature, then the mixture was filtrated under argon to remove the white precipitate formed during the reaction. The solvent was evaporated and the residue was purified by column chromatography (neutral Al₂O₃, eluent: CH₂Cl₂) giving a pale yellow oil. Yield: 50%.

δ_{H} (CDCl₃, 400 MHz) 7.27 (br dd, 2H ar), 7.16 (dd, $J_{\text{HH}} = 8.2, 1.6$ Hz, 2H ar), 6.65 (dd, $J_{\text{HH}} = 8.2, 3.6$ Hz, 2H ar), 2.45 (m, 8H, NCC_H2), 2.34 (s, 6H, CH₃), 2.3 (m, 4H, PCH₂), 2.12 (m, 4H, PCH₂), δ_{C} (CDCl₃, 75.46 MHz) 156.7 (d, $J_{\text{CP}} = 13.2$ Hz, Car), 133.9 (br s, Car), 133.6 (s, Car), 132.5 (s, Car), 123.2 (d, $J_{\text{CP}} = 13.2$ Hz, Car), 118.9 (d, $J_{\text{CP}} = 12.4$ Hz, CN), 117.7 (s, Car), 22.1 (d, $J_{\text{CP}} = 16$ Hz, P-CH₂), 20.4 (s, CH₃), 14.1 (d, $J_{\text{CP}} = 23.2$ Hz, NC-CH₂), δ_{P} (CDCl₃, 80.9 MHz) -30.5 (s).

ν_{max} (KBr)/cm⁻¹ 3014, 2919, 2246, 1592, 1466, 1232, 1168, 821, 733.

MS (maldi-tof) m/z 475.4 (M⁺)

Synthesis of 2,2'-bis(di-(3,5-di-*tert*-butyl)phenyl)phosphino-4,4'-dimethyl-diphenylether (L₂)

1-bromo-3,5-di-*tert*-butylbenzene was prepared according to the procedure reported in lit. [4]

A solution of 1-bromo-3,5-di-*tert*-butylbenzene (1.6 g, 6 mmol) in 15 mL of dry hexane and distilled TMEDA (0.9 mL, 6 mmol, 1eq) was cooled down to -30°C and *n*BuLi (2.5 M in hexanes, 3 mL, 7.5 mmol, 1.2 eq) was added dropwise. The reaction mixture was stirred for two hours at -30°C, then a solution of 2,2'-bis(dichlorophosphino)-4,4'-dimethyl-diphenylether (350 mg, 0.875 mmol) in 10 mL of dry THF was cooled down to

0°C and added slowly via Teflon cannula. After stirring overnight at room temperature, the reaction mixture was filtered through a short pad of neutral Al₂O₃ under argon and then the solvent was evaporated. The pale sticky solid obtained was purified via crystallization from dichloromethane and methanol and a white crystalline product was obtained.

Yield: 69%. M.p. 85°C. δ_{H} (CDCl₃, 400 MHz) 7.31 (br s, 4H ar), 7.22 (m, 8H ar), 6.7 (br, 2H ar), 6.63 (br, 2 H ar), 6.0 (dd, $J_{\text{HH}} = 4.4, 8$ Hz, 2H ar), 2.1 (s, 6H, CH₃), 1.23 (s, 72H, *t*Bu).

δ_{C} (100.6 MHz, CDCl₃) 157.7 (d, $J_{\text{CP}} = 17.5$ Hz, C ar), 149.9 (s, C ar), 136 (br s, C ar), 133.7 (s, C ar), 131.8 (s, C ar), 130 (br s, C ar), 128.5 (d, $J_{\text{PC}} = 21.4$ Hz, C ar), 122.2 (s, C ar), 117.7 (s, C ar), 34.8 (s, C), 31.4 (s, CH₃), 20.9 (s, CH₃), δ_{P} (CDCl₃, 80.9 MHz) -15.5 (s).

ν_{max} (KBr)/cm⁻¹ 2958, 2899, 2859, 1592, 1465, 1362, 1251, 1133, 705.

MS (maldi-tof) *m/z* 1015.71 (M⁺). Anal. Calcd. for C₇₀H₉₆OP₂: C 82.80, H 9.53. Found: C 82.68, H 9.58.

Synthesis of 2,2'-bis(di-(2,6,2'',6''-tetramethyl-1,1':3',1'',-terphenyl)phosphino-4,4'-dimethyl-diphenylether (L₃)

1-iodo-2,4,6-tribromobenzene was prepared from 2,4,6-tribromoaniline following the procedure reported in lit. [5]. Yield: 68%.

5'-bromo-2,6,2'',6''-tetramethyl-1,1':3',1'',-terphenyl was obtained from 1-iodo-2,4,6-tribromobenzene as described in literature [6]. Yield: 30%

A solution of 5'-bromo-2,6,2'',6''-tetramethyl-1,1':3',1'',-terphenyl (1g, 2.74 mmol) in 16 mL of dry THF was cooled down to -78°C and *n*BuLi (2.5 M in hexanes, 1.096 mL, 2.74 mmol, 1.0 eq) was added slowly.

The reaction mixture was stirred for one hour at -78°C, then a solution of 2,2'-bis(dichlorophosphino)-4,4'-dimethyl-diphenylether (274 mg, 0.685 mmol) in 10 mL of dry THF was added dropwise via teflon cannula and the reaction was left to stir for overnight at room temperature. The solvent was removed under reduced pressure, the residue was dissolved in dry toluene and the snow-white solid was filtered off.

The crude product was purified by crystallization from CH₂Cl₂ and MeOH. Yield: 39%.

M.p. 192°C. δ_{H} (CDCl₃, 400 MHz) 7.1 (m, 36H ar), 6.82 (br dd, 2H ar), 6.69 (br, 2H ar), 6.38 (br dd, 2H ar), 2.13 (s, 6H, CH₃), 2.0 (s, CH₃, 24H), 1.91 (s, CH₃, 24H).

δ_{C} (CDCl₃, 100.6 MHz) 157.8 (d, $J_{\text{CP}} = 17.6$ Hz, C ar), 141.8 (s, C ar), 141.6 (d, $J_{\text{CP}} = 6.8$ Hz, C ar), 137.9 (d, $J_{\text{CP}} = 14.5$ Hz, C ar), 136.1 (d, $J_{\text{CP}} = 9.1$ Hz, C ar), 134.7 (s, C ar), 133.2 (d, $J_{\text{CP}} = 19.8$ Hz, C ar), 132.8 (s, C ar), 131.1 (s, C ar), 130.3 (s, C ar), 127.5 (br s, C ar), 127.3 (s, C ar), 117.9 (s, C ar), 21.2 (br s, CH₃), 21.1 (br s, CH₃).

δ_{P} (CDCl₃, 80.9 MHz) -17.5 (s).

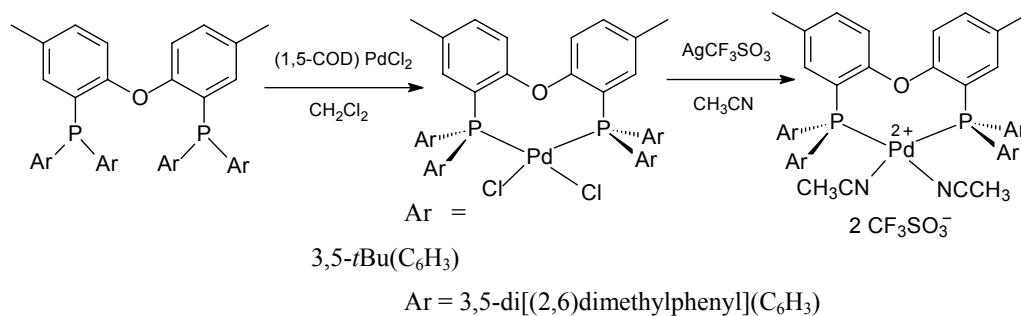
ν_{max} (KBr)/cm⁻¹ 3057, 3018, 2958, 2912, 2851, 1592, 1465, 1263, 1232, 1105, 1030, 770.

MS (maldi-tof): m/z 1400.61 (M⁺). Anal.Calcd. for C₁₀₂H₉₆OP₂: C 87.52, H 6.91. Found: C 87.33, H 6.94.

b) Preparation of the Pd-complexes

The synthesis of palladium complexes suitable for the catalysis, has been performed in two steps:

- 1) synthesis of the palladium dichloride complex.
- 2) transformation of the palladium dichloride complex into the triflate complex



Scheme 2

Synthesis of cis-[(L₂)PdCl₂] (**6**)

A solution of the ligand L₂ (1.25 g, 1.23 mmol) in 15 mL of dry dichloromethane was added to a stirred solution of (COD)PdCl₂ (0.352 g, 1.23 mmol, prepared as in lit. [7]) in

10 mL of dry dichloromethane at room temperature. The reaction mixture was stirred for one hour at room temperature and then diethyl ether was added to allow the formation of a yellow precipitate which was isolated by filtration, washed with diethyl ether and dried in vacuo. Yield: 80%.

δ_{H} (CDCl₃, 400 MHz) 7.8 (br s, 4H ar), 7.46 (br s, 3H ar), 7.18 (br s, 5H ar), 7.02 (m, 6H ar), 2.05 (s, 6H, CH₃), 1.27 (br s, 36H, *t*Bu), 1.03 (br s, 36H, *t*Bu).

δ_{C} (CDCl₃, 100.6 MHz) 157 (d, $J_{\text{CP}} = 6.9$ Hz, C ar), 149.4 (d, $J_{\text{CP}} = 10.7$ Hz, C ar), 149.1 (d, $J_{\text{CP}} = 10$ Hz, C ar), 134.5 (s, C ar), 133 (s, C ar), 132.8 (br s, C ar), 131.9 (s, C ar), 131.4 (s, C ar), 127.7 (d, $J_{\text{PC}} = 9.7$ Hz, C ar), 127 (br s, C ar), 124.8 (br s, C ar), 124.2 (d, $J_{\text{PC}} = 3$ Hz, C ar), 123.7 (br s, C ar), 121.7 (br s, C ar), 117.1 (s, C ar), 34.9 (s, C), 34.7 (s, C), 31.3 (s, CH₃), 31.1 (s, CH₃), 20.6 (s, CH₃).

δ_{P} (CDCl₃, 80.9 MHz) 25.5 (s).

ν_{max} (KBr)/cm⁻¹ 2958, 2899, 2867, 1592, 1465, 1263, 1101, 800.

MS (maldi-tof) *m/z* 1157 (M⁺-Cl).

Synthesis of *cis*-[(L₂)Pd(NCCH₃)₂]²⁺[CF₃SO₃]⁻₂ (7)

The reaction was carried out following a similar procedure reported in lit. [8].

A solution of Ag(CF₃SO₃) (528 mg, 2.05 mmol, 2.5 eq) in 8 mL of dry acetonitrile, was added dropwise to a solution of complex **6** (980 mg, 0.822 mmol, 1eq) in 8 mL of dry dichloromethane. Immediately the white precipitate of AgCl was formed, the mixture was stirred at room temperature for 15 minutes, then the solvent was removed under vacuum and dichloromethane was added to the residue. The suspension was filtered under argon and diethyl ether was added to allow the formation of a yellow precipitate which was isolated by filtration, washed with diethyl ether and dried in vacuo. Yield: 90%.

δ_{H} (CDCl₃, 400 MHz) 7.74 (br s, 6H ar), 7.38 (d, $J_{\text{HH}} = 2.4$ Hz, 6H ar), 6.92 (d, $J_{\text{HH}} = 11.4$ Hz, 6H ar), 2.1 (s, 6H, CH₃), 2.06 (s, 6H, CH₃CN), 1.32 (br s, 36H, *t*Bu), 1.05 (br s, 36H, *t*Bu).

δ_{C} (CDCl₃, 100.6 MHz) 156.4 (d, $J_{\text{CP}} = 5.3$ Hz, C ar), 152.3 (br s, C ar), 151.5 (br s, C ar), 135.9 (s, C ar), 135.6 (d, $J_{\text{CP}} = 8.45$ Hz, C ar), 133.5 (s, C ar), 131.3 (br s, C ar), 127.9 (br

s, C ar), 126.8 (br s, C ar), 122.7 (d, $J_{PC} = 4.6$ Hz, C ar), 120.8 (br s, C ar), 120 (q, $J_{CF} = 319.7$ Hz, CF_3), 119.7 (s, CN), 119.1 (s, C ar), 35.1 (br s, C), 31 (br s, CH_3), 20.6 (s, CH_3), 2.53 (s, CH_3CN).

$\delta_P(CDCl_3, 80.9$ MHz) 32.3 (s).

$\nu_{max}(KBr)/cm^{-1}$ 2966, 2903, 2867, 2325, 2285, 1592, 1465, 1220, 1168, 1026, 709, 634.

MS(maldi-tof) m/z 1269.5 ($M^+ - 2CH_3CN - CF_3SO_3$).

Synthesis of cis- $[(L_3)PdCl_2]$ (9)

The reaction was carried out following the procedure explained above for complex 6. Yield: 82%.

$\delta_H(CDCl_3, 400$ MHz) 7.1 (m, 38H ar), 6.82 (br d, 2H ar), 6.75 (br dd, 2H ar), 2.15 (s, 6H, CH_3), 2.0 (m, CH_3 , 48H).

$\delta_C(CDCl_3, 100.6$ MHz) 157 (d, $J_{CP} = 6.1$ Hz, C ar), 140.6 (br t, C ar), 136.9 (s, C ar), 136.1 (br s, C ar), 135.7 (m, Car), 133.8 (s, C ar), 133.6 (br s, C ar), 131.9 (s, C ar), 128.7 (s, C ar), 127.4 (m, C ar), 123.5 (d, $J_{CP} = 3.8$ Hz, C ar), 123.1 (d, $J_{CP} = 3.8$ Hz, C ar), 120.1 (br s, C ar), 116.9 (s, C ar), 21.1 (br s, CH_3), 20.8 (s, CH_3). $\delta_P(80.9$ MHz, $CDCl_3$) 18.6 (s).

$\nu_{max}(KBr)/cm^{-1}$ 3057, 3022, 2958, 2915, 2847, 1588, 1465, 1263, 1034, 770.

MS (maldi-tof) m/z 1540 ($M^+ - Cl$)

Synthesis of cis- $[(L_3)Pd(NCCH_3)_2]^{2+}[CF_3SO_3]_2^-$ (10)

The reaction was carried out in a similar procedure as described for complex 7. Yield: 85%.

$\delta_H(400$ MHz, $CDCl_3$) 7.15 (m, 34H ar), 6.9 (dd, 4H ar), 6.5 (br d, 4H ar), 2.1 (s, 6H), 2 (s, 6H, CH_3CN), 1.9 (m, 48 H).

$\delta_C(CDCl_3, 100.6$ MHz) 156.3 (br s, C ar), 142.4 (d, $J_{CP} = 9.2$ Hz, Car), 142.2 (d, $J_{CP} = 9.2$ Hz, Car), 139.7 (br s, C ar), 136.1 (m, C ar), 134.5 (s, C ar), 132.8 (br s, C ar), 127 (m, Car), 121.1 (s, CH_3CN), 120.1 (q, $J_{CF} = 319$ Hz, CF_3), 118.4 (s, C ar), 21.2 (s), 20.8 (s). 20.7 (s), 2.7 (s, CH_3CN).

$\delta_P(80.9$ MHz, $CDCl_3$) 28.5 (s).

$\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3062, 3022, 2959, 2919, 2856, 2316, 2290, 1593, 1474, 1264, 1026, 805, 773, 635.

MS(maldi-tof) m/z 1504.37 ($\text{M}^+ - 2\text{CH}_3\text{CN} - 2\text{CF}_3\text{SO}_3$).

Synthesis of *cis*-[(DPEphos)PdCl₂] (11)

The complex has been prepared as reported in lit. [9].

Synthesis of *cis*-[(DPEphos)Pd(NCCH₃)₂]²⁺[CF₃SO₃]₂⁻ (12)

The procedure is the same as described for complex 7 and 10. Yield: 92%.

$\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 7.6-7.46 (m, 20H ar), 7.1 (dd, $J_{\text{HH}} = 4.4, 8 \text{ Hz}$), 6.99 (t, $J_{\text{HH}} = 8 \text{ Hz}$), 6.73 (dd, $J_{\text{HH}} = 1.6, 8 \text{ Hz}$), 2 (s, 6H, CH₃CN).

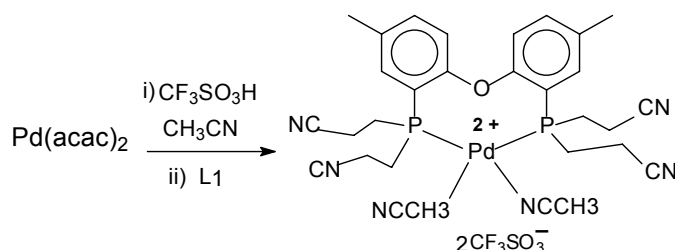
$\delta_{\text{C}}(\text{CDCl}_3, 100.63 \text{ MHz})$ 158.7 (br s, C ar), 135.6 (br s, C ar), 134.2 (d, $J_{\text{PC}} = 11.5 \text{ Hz}$, C ar), 132.8 (s, C ar), 129.3 (d, $J_{\text{PC}} = 12.2 \text{ Hz}$, C ar), 126 (d, $J_{\text{PC}} = 9.2 \text{ Hz}$, C ar), 125.1 (s, C ar), 124.4 (s, CH ar), 122 (br s, C ar), 120.2 (q, $J_{\text{CF}} = 319.7 \text{ Hz}$, CF₃), 118.5 (s, CH₃CN), 117.4 (s, C ar), 2.7 (s, CH₃CN). $\delta_{\text{P}}(\text{CDCl}_3, 80.9 \text{ MHz})$ 24.5 (s).

$\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3061, 2922, 2329, 2293, 1596, 1564, 1438, 1255, 1164, 1030, 744, 693, 634.

MS(maldi-tof) m/z 835.03 ($\text{M}^+ - \text{CH}_3\text{CN} - \text{CF}_3\text{SO}_3$).

Synthesis of *cis*-[(L₁)Pd(NCCH₃)₂]²⁺[CF₃SO₃]₂⁻ (13)

The complex suitable for the copolymerization was prepared following the route shown below (Scheme3):



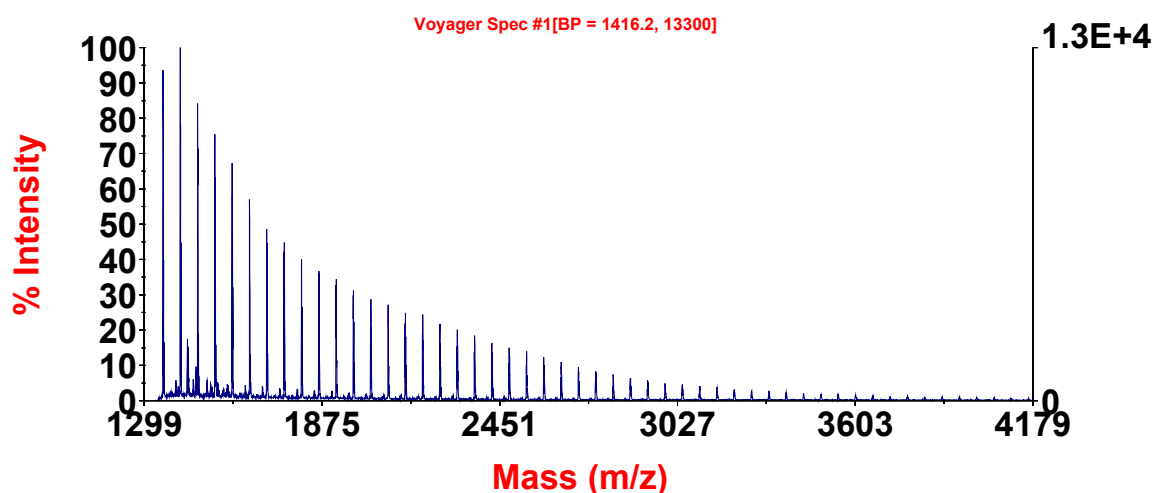
A solution of **L**₁ (332 mg, 0.697 mmol) in 8 mL of dry acetonitrile was added dropwise to a solution of [Pd(NCCH₃)₄][CF₃SO₃]₂ (396 mg, 0.697 mmol) in 10 mL of dry dichloromethane. The mixture was stirred at room temperature for one hour, then the solvent was evaporated and the residue was recrystallized from diethyl ether. Yield: 65%
 δ_{H} (400 MHz, CDCl₃) 7.5 (d, $J_{\text{HH}} = 9$ Hz, 2H ar), 7.26 (br dd, 2H ar), 7.18 (br dd, 2H ar), 2.8 (br s, 8H, NCCH₂), 2.5 (s, 6H, NCCH₂), 2.35 (s, 6H, CH₃), 2.15 (s, 8H, m, PCH₂), 2.1 (s, 6H, CH₃CN), δ_{C} (CD₃CN, 100.63 MHz) 157 (br s, Car), 137.2 (d, $J_{\text{CP}} = 7.6$ Hz, Car), 136.2 (s, Car), 133.1 (s, Car), 128.9 (s, Car), 125.3 (s, Car), 121.9 (br s, CH₃CN), 121 (q, $J_{\text{CF}} = 320$ Hz, CF₃), 118.6 (d, $J_{\text{CP}} = 12.4$ Hz, CN), 26.4 (d, $J_{\text{CP}} = 9.9$ Hz, P-CH₂), 19.8 (s, CH₃), 12.6 (br s, NC-CH₂), δ_{P} (80.9 MHz, CD₃CN) 14.3 (br s).

ν_{max} (KBr)/cm⁻¹ 2958, 2927, 2312, 2249, 1664, 1469, 1251, 1168, 1030, 642.

MS: m/z 812.2 (M⁺-CF₃SO₃)

Maldi-Tof-MS analysis of the CO/ethane copolymer

Figure: Maldi-Tof-MS of CO/ethene copolymer prepared in methanol in the presence of complex [(L₂)Pd(NCCH₃)₂(CF₃SO₃)₂], see manuscript, entry 4, table 1.



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