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Chromium imine and amine complexes as homogeneous catalysts for the trimerisation and polymerisation of ethylene

Martin E. Bluhm *, Olaf Walter, Manfred Döring

Forschungszentrum Karlsruhe, Institute for Technical Chemistry (ITC-CPV), P.O. Box 3640, 76021 Karlsruhe, Germany

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Abstract

Cr(III) complexes of tridendate imine and amine ligands with N, P, O, S donor atoms **1** and **2** have been prepared and tested as catalysts in the oligomerisation and polymerisation of ethylene giving excellent selectivity towards 1-hexene and polymerisation to polyethylene when activated with cocatalysts. X-ray structure analyses of the precatalysts **1a–c**, **1i**, and **2b** are investigated. The metal–ligand binding in **1a** and **1b** is nearly the same, which leads to similar catalytic activities of these precatalysts.

Keywords: Trimerisation; Polymerisation; Single-site catalysts; Ethylene; Chromium

1. Introduction

Catalytic oligomerisations are used in the SHOP process to produce a variety of linear α-olefins (C_6-C_{20}-LAO) [1]. The increasing demand especially of 1-hexene as comonomer for the production of linear low density polyethylene (LLDPE) recommends selective methods in the production of 1-hexene [2]. The technically used Phillips catalyst contains a Cr(III) compound, pyrrole, and is partially used together with alkyl aluminum [3]. Neutral phosphorous containing ligands [4–6] are used as well as 1,3,5-triazacyclohexanes [7,8] as ligands for Cr(III) catalyst precursors. Recently, Cr(III) coordination compounds with symmetrical PNP- or SNS-ligands derived from bis(chloroethyl)amine were described as highly active catalysts for the trimerisation of ethylene with methylaluminoxane (MAO) [9–12]. Other substituted PNP chromium(III) precatalysts have recently been described as suitable compounds for the trimerisation of ethylene after activation with $H(Et_2O)_2B[C_6H_3(CF_3)_2]_4$ [13]. ONN imine Cr(III) complexes have also been described as polymerisation catalysts [14].

Here, we report new complexes of Cr(III) with symmetrical and asymmetrical N, P, O, S ligands that produce in combination with methylaluminoxane either selectively 1-hexene or polyethylene.

2. Experimental

All handlings were carried out under an atmosphere of argon using standard Schlenk techniques. NMR spectra were recorded on a Bruker spectrometer 250 MHz (^1H) and 62.9 MHz (^{13}C) at 293 K. Mass spectra were obtained using electron ionisation (EI), electron spray ionisation (ESI) or field ionisation (FI). Oligomer products were analysed by GC with a flame ionisation detector, using a 50-m DB1 column, injector temperature 300 °C and the following temperature program: 40 °C/5 min, 40–300 and 5 °C/10 min. The products were quantified, using *n*-tridecane as internal standard.

* Corresponding author. Tel.: +49 7247 82 2383; fax: +49 7247 82 2244.
E-mail address: martin.bluhm@itc-cpv.fzk.de (M.E. Bluhm).

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2.1. Materials

Methylaluminumoxide MAO (10 mol% solution in toluene) and ethyl aluminum sesquichloride were purchased commercially and used as received.

2.2. Synthesis of ligands

2.2.1. Ligand **Ia**

To a solution of 2-(diphenylphosphino)benzaldehyde (560 mg, 1.9 mmol) in 50 mL of CH_2Cl_2 is added 2-(diphenylphosphino)ethylamine (442 mg, 1.9 mmol). The reaction mixture is stirred for 12 h. The solvent is removed in vacuo and the residue is recrystallized from hot *n*-hexane. Yield: 505 mg, 1 mmol (53%). ^{1}H NMR (C_6D_6) δ 8.94 (d, 1H), 8.11–8.16 (m, 1H), 7.31–7.41 (m, 8H), 6.93–7.15 (m, 16H), 3.51–3.61 (m, 2H), 2.16–2.22 (m, 2H); ^{1}H{^{31}P} NMR (C_6D_6) δ 8.94 (s), 8.11–8.16 (m), 7.31–7.41 (m), 6.93–7.15 (m), 3.51 (t), 2.22 (t); ^{13}C{^{31}P} NMR (C_6D_6) δ 159.2, 139.5, 138.0, 137.8, 134.4, 133.8, 133.2, 130.3, 128.9, 128.6, 127.6, 58.3, 30.4; ^{31}P NMR (C_6D_6) δ 1.8, −4.8; EI$^+$-MS *m*/*z* = 501 (M$^+$).

2.2.2. Ligand **Ib**

To a solution of 2-(diphenylphosphino)benzaldehyde (500 mg, 1.7 mmol) in 30 mL of CH_2Cl_2 is added 2-(ethylthio)ethylamine hydrochloride (244 mg, 1.7 mmol) and 0.25 mL of triethylamine. The reaction mixture is stirred for 4 h. The CH_2Cl_2 is removed in vacuo and the residue is suspended in *n*-hexane. Insoluable solids are filtered and the hexane is removed in vacuo. The residue is recrystallized from hot *n*-hexane. Yield: 213 mg, 0.6 mmol (33%). ^{1}H NMR ($CDCl_3$) δ 8.81 (d, 1H), 7.87–7.92 (m, 1H), 7.18–7.28 (m, 12H), 6.78–6.82 (m, 1H), 3.59–3.62 (m, 2H), 2.48–2.54 (m, 2H), 2.36–2.45 (m, 2H), 1.10–1.16 (m, 3H); ^{1}H{^{31}P} NMR ($CDCl_3$) δ 8.81 (s), 7.87–7.92 (m), 7.18–7.28 (m), 6.78–6.82 (m), 3.59 (t), 2.51 (t), 2.41 (q), 1.12 (t); ^{13}C{^{31}P} NMR ($CDCl_3$) δ 160.3, 138.9, 137.1, 136.2, 133.6, 133.5, 133.0, 131.6, 130.0, 128.8, 128.6, 128.5, 128.3, 127.4, 60.5, 31.8, 25.7, 14.5; ^{31}P NMR ($CDCl_3$) δ −12.3; EI$^+$-MS *m*/*z* = 361 (M$^+$).

2.2.3. Ligand **Ic**

To a solution of 2-(diphenylphosphino)benzaldehyde (500 mg, 1.7 mmol) in 40 mL of CH_2Cl_2 is added 3-(diphenylphosphino)-1-propylamine (419 mg, 1.7 mmol). The reaction mixture is stirred for 4 h. The solvent is removed in vacuo and the residue is recrystallized from hot *n*-hexane. Yield: 545 mg, 1 mmol (62%). ^{1}H NMR ($CDCl_3$) δ 8.88 (d, 1H), 7.96–8.00 (m, 1H), 7.21–7.45 (m, 6H), 6.90–6.94 (m, 17H), 6.82–6.91 (m, 1H), 3.53–3.59 (m, 2H), 1.96–2.02 (m, 2H), 1.64–1.74 (m, 2H); ^{1}H{^{31}P} NMR ($CDCl_3$) δ 8.88 (s), 7.96–8.00 (m), 7.21–7.45 (m), 6.90–6.94 (m), 6.82–6.91 (m), 3.53–3.59 (m), 1.96–2.02 (m), 1.64–1.74 (m); ^{13}C{^{31}P} NMR ($CDCl_3$) δ 159.6, 139.3, 138.6, 137.2, 136.6, 133.7, 133.2, 132.5, 129.9, 128.6, 128.4, 128.2, 128.1, 127.7, 62.0, 27.0, 25.3; ^{31}P NMR ($CDCl_3$) δ −12.0, −14.8; EI$^+$-MS *m*/*z* = 516 (M$^+$).

2.2.4. Ligand **Id**

See Refs. [15,16].

2.2.5. Ligand **Ie**

See Ref. [17]. To a solution of 2-(diphenylphosphino)benzaldehyde (500 mg, 1.7 mmol) in 40 mL of benzene is added 2-(dimethylamino)ethylamine (150 mg, 1.7 mmol). The reaction mixture is heated under reflux for 2 h. The solvent is removed in vacuo and the residue is recrystallized from hot *n*-hexane. Yield: 448 mg, 1.2 mmol (73%). ^{1}H NMR ($CDCl_3$) δ 8.82 (d, 1H), 7.87–7.92 (m, 1H), 7.15–7.32 (m, 12H), 6.75–6.81 (m, 1H), 3.49–3.55 (m, 2H), 2.27–2.32 (m, 2H), 2.11 (s, 6H); ^{1}H{^{31}P} NMR ($CDCl_3$) δ 8.82 (s), 7.87–7.92 (m), 7.15–7.32 (m), 6.75–6.81 (m), 3.52 (t), 2.30 (t), 2.11 (s); ^{13}C{^{31}P} NMR ($CDCl_3$) δ 160.4, 139.4, 137.3, 136.5, 134.0, 133.8, 133.2, 132.0, 130.1, 129.0, 128.8, 128.7, 128.6, 127.6, 59.8, 59.4, 45.6; ^{31}P NMR ($CDCl_3$) δ −12.2; EI$^+$-MS *m*/*z* = 516 (M$^+$).

2.2.6. Ligand **If**

To a solution of 2-(methylthio)benzaldehyde (250 mg, 1.6 mmol) in 40 mL of CH_2Cl_2 is added 2-(diphenylphosphino)ethylamine (377 mg, 1.6 mmol). The reaction mixture is stirred for 22 h. The solvent is removed in vacuo and the residue is recrystallized first from hot *n*-hexane and then from methanol. Yield: 246 mg, 0.7 mmol (42 %). ^{1}H NMR ($CDCl_3$) δ 8.60 (m, 1H), 7.69 (m, 1H), 7.35–7.66 (m, 4H), 7.15–7.24 (m, 8H), 7.04–7.10 (m, 1H), 3.64–3.73 (m, 2H), 2.40–2.43 (m, 2H), 2.33 (s, 3H); ^{31}P NMR ($CDCl_3$) δ −17.7; FI$^+$-MS *m*/*z* = 363 (M$^+$).

2.2.7. Ligand **Ig**

To a solution of 2-(methylthio)benzaldehyde (500 mg, 3.3 mmol) in 40 mL of CH_2Cl_2 is added 2-methoxy-ethylamine (246 mg, 3.3 mmol). The reaction mixture is stirred for 12 h. The solvent is removed in vacuo. For purification, the major part of the product is dissolved in hot *n*-hexane and filtered from insoluable byproducts. After cooling, the *n*-hexane is removed in vacuo to give a yellow oil. Yield: 552 mg, 2.6 mmol (80%). ^{1}H NMR ($CDCl_3$) δ 8.68 (s, 1H), 7.78 (m, 1H), 7.12–7.23 (m, 3H), 3.73 (m, 2H), 3.62 (m, 2H), 3.29 (s, 3H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 160.6, 139.1, 134.1, 133.0, 130.6, 128.4, 128.2, 127.9, 127.5, 127.3, 125.1, 124.9, 122.2, 72.0, 60.9, 58.7, 16.8; EI$^+$-MS *m*/*z* = 210 (M + H$^+$).

2.2.8. Ligand ***Ih***

See Ref. [18]. To a solution of 2-methoxybenzaldehyde (1.5 g, 0.01 mol) in 40 mL of CH_2Cl_2 is added 2-(methylthio)anilin (1.5 g, 0.01 mol). The reaction mixture is stirred for 12 h. The solvent is removed in vacuo giving a yellow residue. Yield: 2.2 g, 8.7 mmol (79%). ^1H NMR ($CDCl_3$) 8.92 (s, 1H), 8.24 (d, 1H), 7.35–7.41 (m, 1H), 6.85–7.15 (m, 6H), 3.82 (s, 3H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$) 159.7, 133.6, 130.4, 128.5, 126.5, 125.9, 125.1, 121.0, 118.3, 111.6, 111.0, 108.3, 103.5, 102.4, 100.8, 55.6, 15.2.

2.2.9. Ligand ***Ii***

To a solution of 2-(methylthio)benzaldehyde (358 mg, 2.4 mmol) in 30 mL of CH_2Cl_2 is added 2-(ethylthio)ethylamine hydrochloride (500 mg, 3.5 mmol, 1.5 eq.) and 0.5 mL of triethylamine. The reaction mixture is stirred for 5 h. The CH_2Cl_2 is removed in vacuo and the residue is suspended in *n*-hexane. Insoluable solids are filtered and the hexane is removed in vacuo giving a colourless oil. Yield: 212 mg, 0.9 mmol (37%). ^1H NMR ($CDCl_3$) δ 8.69 (s, 1H), 7.78 (d, 1H), 7.13–7.25 (m, 3H), 3.78 (t, 2H), 2.80 (t, 2H), 2.53 (q, 2H), 2.39 (s, 3H), 1.19 (t, 3H); ^{13}C NMR ($CDCl_3$) δ 160.6, 139.7, 134.5, 131.2, 128.7, 128.5, 128.2, 127.8, 125.9, 61.4, 32.9, 26.7, 17.3, 15.3.

2.2.10. Ligand ***Ij***

To a solution of 2-(methylthio)benzaldehyde (500 mg, 3.3 mmol) in 50 mL of CH_2Cl_2 is added to 2-(dimethylamino)ethylamine hydrochloride (290 mg, 3.3 mmol). The reaction mixture is stirred for 16 h. The CH_2Cl_2 is removed in vacuo. For purification, the major part of the product is dissolved in hot *n*-hexane and filtered from insoluable byproducts. After cooling, the *n*-hexane is removed in vacuo giving a colourless oil. Yield: 364 mg, 1.6 mmol (49%). ^1H NMR ($CDCl_3$) δ 8.68 (s, 1H), 7.77 (d, 1H), 7.10–7.26 (m, 3H), 3.70 (t, 2H), 2.58 (t, 2H), 2.36 (s, 3H), 2.24 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 159.7, 138.9, 134.1, 130.4, 128.1, 127.0, 125.3, 59.9, 59.7, 45.6, 16.6; EI^+-MS $m/z = 223$ ($M + H^+$)

2.2.11. Ligand ***Ik***

To a solution of 2-(diphenylphosphino)benzaldehyde (300 mg, 1 mmol) in 30 mL of CH_2Cl_2 is added 2-methoxy-ethylamine (78 mg, 1 mmol). The reaction mixture is stirred for 16 h. The solvent is removed in vacuo and the residue is recrystallized from *n*-hexane. Yield: 134 mg, 0.38 mmol (39%). ^1H NMR ($CDCl_3$) δ 8.86 (d, 1H), 7.98 (m, 1H), 7.15–7.34 (m, 12H), 6.78–6.81 (m, 1H), 3.60 (m, 2H), 3.39 (m, 2H), 3.14 (s, 3H); $^1H\{^{31}P\}$ NMR ($CDCl_3$) δ 8.86 (s), 7.98 (d), 7.15–7.34 (m), 6.78–6.81 (m), 3.60 (t), 3.39 (t), 3.14 (s); $^{13}C\{^{31}P\}$ NMR ($CDCl_3$) δ 161.5, 136.4, 134.0, 133.9, 133.7, 133.4, 133.1, 132.2, 131.9, 130.5, 129.0, 128.9, 128.7, 128.6, 128.0, 71.8, 61.3, 58.6; ^{31}P NMR ($CDCl_3$) δ −12.6; EI^+-MS $m/z = 348$ ($M + H^+$).

2.2.12. Ligand ***IIa***

To a suspension of **Ia** (505 mg, 1 mmol) in 30 mL of methanol is added under argon $NaBH_4$ (113 mg, 3 mmol). The reaction mixture is stirred for 12 h. The methanol is removed in vacuo and the residue is taken up in water. Extraction with CH_2Cl_2 (three times) gives a colourless organic phase. After seperation, the organic phase is dried over Na_2SO_4. Solids are filtered from the solution and the CH_2Cl_2 is removed in vacuo giving a colourless solid, which is recrystallized from hot *n*-hexane. Yield: 160 mg, 0.3 mmol (30%). ^1H NMR ($CDCl_3$) δ 7.05–7.51 (m, 23H), 6.77–6.81 (m, 1H), 3.98 (s, 2H), 2.65 (m, 2H), 2.18 (m, 2H); $^1H\{^{31}P\}$ NMR ($CDCl_3$) δ 7.05–7.51 (m), 6.77–6.81 (d), 3.98 (s), 2.65 (t), 2.18 (t); $^{13}C\{^{31}P\}$ NMR ($CDCl_3$) δ 135.8, 134.0, 133.8, 132.7, 132.0, 131.9, 131.8, 130.1, 129.4, 129.0, 128.7, 128.5, 128.4, 128.3, 49.9, 44.9, 26.7; ^{31}P NMR ($CDCl_3$) δ −15.1, −19.5; EI^+-MS $m/z = 504$ ($M + H^+$).

2.2.13. Ligand ***IIb***

To a suspension of **Ib** (270 mg, 0.7 mmol) in 40 mL of methanol is added under argon $NaBH_4$ (81 mg, 2 mmol). The reaction mixture is stirred for 12 h. The methanol is removed in vacuo and the residue is taken up in water. Extraction with CH_2Cl_2 (three times) gives a colourless organic phase. After seperation, the organic phase is dried over Na_2SO_4. Solids are filtered from the solution and the CH_2Cl_2 is removed in vacuo giving a colourless solid, which is recrystallized from *n*-hexane. Yield: 194 mg, 0.5 mmol (70%). ^1H NMR ($CDCl_3$) δ 7.04–7.46 (m, 13H), 6.77–6.81 (m, 1H), 3.97 (s, 2H), 2.66 (m, 2H), 2.44–2.49 (m, 2H), 2.33–2.41 (q, 2H), 1.12 (t, 3H); $^{13}C\{^{31}P\}$ NMR ($CDCl_3$) δ 142.9, 136.4, 135.9, 133.8, 133.7, 131.9, 131.8, 129.4, 129.1, 129.0, 128.7, 128.6, 128.5 127.6, 51.4, 47.6, 31.1, 25.7, 14.8; ^{31}P NMR ($CDCl_3$) δ −14.9; EI^+-MS $m/z = 380$ ($M + H^+$).

2.2.14. Ligand ***IIc***

To a suspension of **Ih** (1 g, 3.9 mmol) in 90 mL of methanol is added under argon $NaBH_4$ (0.44 g, 11 mmol). The reaction mixture is stirred for 3 h. The methanol is removed in vacuo and the residue is taken up in water. Extraction with CH_2Cl_2 (three times) gives a yellow organic phase. After seperation, the organic phase is dried over Na_2SO_4. Solids are filtered from the solution and the CH_2Cl_2 is removed in vacuo giving a yellow oil. Yield: 668 mg, 2.6 mmol (66%). ^1H NMR ($CDCl_3$) δ 7.32 (d, 1H), 7.07–7.20 (m, 3H), 6.79–6.85 (m, 2H), 6.60–6.63 (m, 2H), 4.34 (s, 2H), 3.81 (s, 3H), 2.27 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 157.8, 134.5, 129.9, 129.1, 128.9, 120.9, 111.9, 110.6, 55.7, 44.2, 18.7.

2.2.15. Preparation of 1 and 2

The synthesis of the complexes **1** and **2** is illustrated by the procedure applied for **1a**. A solution of ligand **Ia** (218 mg, 0.43 mmol) in 20 mL of dry THF was added under argon to a solution/suspension of $CrCl_3(thf)_3$ (151 mg, 0.43 mmol) [19] in 20 mL of dry THF. The reaction mixture is stirred for 15 h at r.t. The THF is removed in vacuo and the solid is washed with diethylether/CH_2Cl_2. The solid is then dried in vacuo. Yield: 269 mg, 0.41 mmol (95%). All complexes **1** and **2** were prepared in an identical fashion with yields of over 80% in each case.

1a: FI^+-MS: *m/z* 658.0246 (calcd.), found 658.0151 for $^{12}C^{331}H_{29}{}^{14}N^{31}P_2{}^{35}Cl_3{}^{52}Cr$, $\delta = 9.5$ mDa; $C_{33}H_{29}NP_2Cl_3Cr \cdot 2THF \cdot CH_2Cl_2$: Calcd. (Found) C 56.74 (57.36), H 5.33 (4.98), N 1.58 (1.58).

1b: FI^+-MS: *m/z* 533.9838 (calcd.), found 533.9846 for $^{12}C_{23}{}^{1}H_{24}{}^{14}N^{31}P^{32}S^{35}Cl_3{}^{52}Cr$, $\delta = 0.8$ mDa; $C_{23}H_{24}NPSCl_3Cr \cdot 2THF \cdot CH_2Cl_2$: Calcd. (Found) C 50.24 (49.97), H 5.53 (5.54), N 1.83 (1.60), S 4.19 (4.54).

1c: FI^+-MS: *m/z* 674.0470 (calcd.), found 674.0451 for $^{12}C_{32}{}^{13}C_2{}^{1}H_{31}{}^{14}N^{31}P_2{}^{35}Cl_3{}^{52}Cr$, $\delta = 9.5$ mDa; $C_{34}H_{31}NP_2Cl_3Cr \cdot 2THF \cdot CH_2Cl_2$: Calcd. (Found) C 57.19 (57.43), H 5.47 (5.67), N 1.55 (1.45).

1d: FI^+-MS: *m/z* 551.0070 (calcd.), found 551.0108 for $^{12}C_{26}{}^{1}H_{23}{}^{14}N_2{}^{31}P^{35}Cl_3{}^{52}Cr$, $\delta = 3.8$ mDa; $C_{26}H_{23}N_2PCl_3Cr \cdot 2THF \cdot CH_2Cl_2$: Calcd. (Found) C 53.76 (54.16), H 5.28 (5.14), N 3.58 (4.08).

1e: FI^+-MS: *m/z* 517.0226 (calcd.), found 517.0156 for $^{12}C_{23}{}^{1}H_{25}{}^{14}N_2{}^{31}P^{35}Cl_3{}^{52}Cr$, $\delta = 7.0$ mDa; $C_{23}H_{25}N_2PCl_3Cr \cdot 2THF \cdot CH_2Cl_2$: Calcd. (Found) C 51.39 (51.68), H 5.79 (6.12), N 3.75 (4.11).

1f: FI^+-MS: *m/z* 521.9748 (calcd.), found 521.9847 for $^{12}C_{20}{}^{13}C_2{}^{1}H_{22}{}^{14}N^{31}P^{32}S^{35}Cl_3{}^{52}Cr$, $\delta = 9.9$ mDa; $C_{22}H_{22}NPSCl_3Cr$: Calcd. (Found) C 50.64 (50.16), H 4.25 (4.51), N 2.68 (2.41), S 6.14 (5.96).

1g: FI^+-MS: *m/z* 365.9345 (calcd.), found 365.9342 for $^{12}C_{11}{}^{1}H_{15}{}^{14}N^{16}O^{32}S^{35}Cl_3{}^{52}Cr$, $\delta = 0.3$ mDa; $C_{11}H_{15}NOSCl_3Cr \cdot THF \cdot CH_2Cl_2$: Calcd. (Found) C 36.63 (36.30), H 4.80 (5.10), N 2.67 (2.43), S 6.11 (6.24).

1h: $C_{15}H_{15}NOSCl_3Cr \cdot THF \cdot CH_2Cl_2$: Calcd. (Found) C 41.94 (41.55), H 4.40 (4.75), N 2.45 (2.19), S 5.60 (5.58).

1i: ESI^+-MS: *m/z* 361 $[M - Cl]^+$; $C_{12}H_{17}NS_2Cl_3Cr$: Calcd. (Found) C 36.24 (36.18), H 4.31 (4.52), N 3.52 (3.43), S 16.12 (16.02).

1j: ESI^+-MS: *m/z* 343 $[M - Cl]^+$; $C_{12}H_{18}N_2SCl_3Cr$: Calcd. (Found) C 37.86 (38.01), H 4.77 (5.00), N 7.36 (7.51), S 8.42 (8.44).

1k: $C_{22}H_{22}NOPCl_3Cr \cdot 2THF \cdot CH_2Cl_2$: Calcd. (Found) C 50.67 (50.44), H 5.49 (5.22), N 1.91 (1.68).

2a: ESI^+-MS: *m/z* 625 $[M - Cl]^+$; $C_{33}H_{31}NP_2Cl_3Cr \cdot 2THF \cdot CH_2Cl_2$: Calcd. (Found) C 56.61 (56.88), H 5.54 (5.28), N 1.57 (1.41).

2b: ESI^+-MS: *m/z* 556 $[M + NH_4]^+$; $C_{23}H_{26}NPSCl_3Cr$: Calcd. (Found) C 51.36 (51.19), H 4.87 (5.00), N 2.60 (2.56), S 5.96 (5.91).

2c: ESI^+-MS: *m/z* 436 $[M + NH_4]^+$; $C_{15}H_{17}NOSCl_3$-$Cr \cdot THF \cdot CH_2Cl_2$: Calcd. (Found) C 41.79 (42.13), H 4.73 (4.79), N 2.44 (2.23), S 5.58 (5.38).

(a) Low-pressure tests. The precatalyst was dissolved in 30 mL of toluene in a Schlenk flask under argon. A complete solution was obtained by leaving the flask in an ultrasonic bath for several minutes. A 150 mL glass reactor was evacuated and then filled with argon. The precatalyst solution was added under argon into the reactor vessel. Under stirring the cocatalyst MAO (0.6 mL, approx. 100 eq. of a 10 mol% MAO solution in toluene) and *n*-tridecane standard solution were added under argon. For several minutes ethylene was bubbled through the reactor to displace the argon. Then the reactor was closed and pressurized to 3 bar with ethylene. The reactor pressure was maintained constant throughout the oligomerisation run by manually controlled addition of ethylene. Runs were terminated by venting off volatiles and extracting the solution with dilute hydrochloric acid and water. Quantitative GC analysis of the organic layer was performed immediately after the extraction.

(b) High-pressure tests. The same procedure as described for low-pressure tests was applied. Instead of a glass reactor was used a 150 mL stainless steel reactor with cooling mantle. After the reactor was closed it was pressurized to 30 bar with ethylene.

3. Results and discussion

The tridentate imine ligands **I** and the amine ligands **II** were prepared via literature procedures or via adaptation of these [20–22]. When reacted with $CrCl_3(thf)_3$ [19] the complexes **1** and **2** are formed and isolated after workup as green or blue-green powders in 80–100% yield (Fig. 1 and Table 1) [23].

The imine complexes **1a** and **1b** were tested as most active for ethylene trimerisation with excellent selectivity

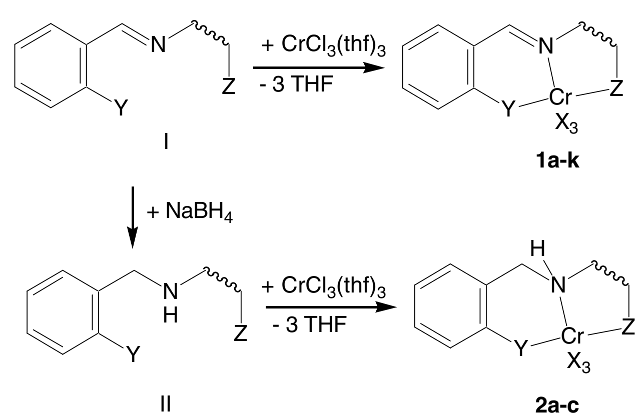

Fig. 1. Synthesis of the Cr(III) precatalysts **1** and **2**.

Table 1
Precatalysts **1** and **2** (X = Cl)

	Y	Z	Bridge
1a	PPh_2	PPh_2	$(CH_2)_2$
1b	PPh_2	SEt	$(CH_2)_2$
1c	PPh_2	PPh_2	$(CH_2)_3$
1d	PPh_2	C_5H_4N	$(CH_2)_2$
1e	PPh_2	NMe_2	$(CH_2)_2$
1f	SMe	PPh_2	$(CH_2)_2$
1g	SMe	OMe	$(CH_2)_2$
1h	OMe	SMe	C_6H_4
1i	SMe	SEt	$(CH_2)_2$
1j	SMe	NMe_2	$(CH_2)_2$
1k	PPh_2	OMe	$(CH_2)_2$
2a	PPh_2	PPh_2	$(CH_2)_2$
2b	PPh_2	SEt	$(CH_2)_2$
2c	OMe	SMe	C_6H_4

towards 1-hexene when activated with 100 eq. MAO (Table 2, entries 1–4) [23].

In **1b**, one phosphorous donor is replaced by a sulfur containing donor group. Both complexes **1a** and **1b** react similarly under catalytic conditions. This is in line with earlier observations in PNP and SNS chromium(III) complexes [9–12]. Almost the same effect is also observed for the amine complexes **2a** and **2b** which both have the same backbone, but **2b** contains a methylmercapto instead of a diphenylphosphane substituent. Both complexes react under the same reaction conditions mainly to polyethylene besides hexene. Here, SNS and other substituents like nitrogen or oxygen containing groups led to a dramatic decrease in the rate for trimerisation but increased rate in the formation of polyethylene (Table 2, entries 7–18). Reaction temperature and ethylene pressure have both a big influence on the product distribution. At reaction temperatures between 70 and 85 °C, and 30 bar of ethylene pressure the formation of polymer increases (Table 2, entry 3). At room temperature and 3 bar of ethylene pressure the rate of trimerisation was increased (Table 2, entry 2). The activity of all complexes **1** and **2** decreases with low ethylene pressure. When a higher amount of MAO

Table 2
Ethylene trimerisation/polymerisation with complexes **1** and **2**[a]

Number	Catalyst (μmol)	*T* (°C)	Run time (h)	PE (wt%)	Hexenes (wt%)	α-Selectivity of oligomers	Productivity (h^{-1})[b]
1	**1a** (10)	24–30	1	17	83	98	5742
2	**1a** (10)	24	2	2	98	99	470
3	**1a** (10)	85	1	98	2	98	2294
4	**1a** (10)[c]	24–30	1	14	86	99	4308
5	**1a** (10)[d]	24–30	1	100	–	–	2966
6	**1b** (10)	24–30	1	18	82	99	2268
7	**1c** (10)	24–30	1	73	27	99	3054
8	**1d** (10)	24–27	1	80	20	99	943
9	**1e** (10)	24–31	1	100	–	–	660
10	**1f** (10)	24–30	1	81	10[e]	97	8381
11	**1g** (10)	24–30	1	88	12	99	525
12	**1h** (10)	24–30	1	100	–	–	867
13	**1i** (10)	24–30	1	100	–	–	8280
14	**1j** (10)	24–30	1	98	2	98	3283
15	**1k** (10)	24–30	1	97	3	98	549
16	**2a** (10)	24–30	1	67	33	99	2483
17	**2b** (10)	25–31	1	56	44	99	1204
18	**2c** (10)	25–31	1	100	–	–	3858

[a] The precatalysts in entries 1–3, 6–18 were first dissolved in 30 mL of toluene in an ultrasonic bath and then activated with approx. 100 eq. MAO (0.6 mL of a 10 mol% MAO solution in toluene), 30 bar ethylene (entries 1, 3–18) or 3 bar ethylene (entry 2). The yield and the α-olefin content were determined by GC with a flame ionisation detector using calibration curves with standard solutions.
[b] Average turnover frequency of ethylene conversion.
[c] 500 eq. MAO (0.6 mL of a 10 mol% MAO solution in toluene) used.
[d] 100 eq. $Et_2AlCl \cdot Cl_2AlEt$ used as co-catalyst.
[e] Formation of 9 wt% octenes.

was used, the product distribution was not changed to the formation of higher olefins and polymer with no increase of the activity of the complexes (Table 2, entry 4). On the other hand, ethyl aluminum chlorides used as cocatalyst increase the formation of polymer with the precatalyst **1a** (Table 2, entry 5). The use of ethyl aluminum chlorides as cocatalyst together with diimine-nickel(II) catalysts was observed earlier to increase the formation of higher olefins [24].

Single crystals of **1a**–**c**, **1i**, and **2b** suitable for X-ray diffraction studies were grown from a dichloromethane solution, layered with THF and pentane. The molecular structures of **1a**–**c**, **1i** along with selected bond distances and angles, are shown in Figs. 2–4. All three complexes display a slightly distorted octahedral geometry. The chelate bite angles of the PNP and the PNS ligands in the complexes are similar [82.01(7)°, 85.17(7)° (**1a**); 85.02(6)°, 88.47(6)° (**1b**); 87.22(4)°, 89.04(4)° (**1c**), 84.55(7)°, 89.79(7)° (**2b**)], while the difference of the bite angles is larger in **1i** [84.94(4)°, 91.50(4)°]. Accordingly, the Cr–P [2.441(1)–2.474(1) Å] and the Cr–S distances [2.454(1)–2.456(1) Å] are similar in the structures of **1a**–**c** and **2b**. In **1i** (Fig. 5), the Cr–S bond lengths are shorter [2.403(1)–2.418(1)] compared with the other sulfur coordinated chromium complexes **1b** and **2b**. The Cr–N distances in each complex [2.118(3) Å (**1a**), 2.092(2) Å (**1b**), 2.103(1) Å (**1c**), 2.069(1) (**1i**), 2.123(2) (**2b**)] are similar and within the range of Cr(III) amine bond lengths (2.05–2.19 Å) [9–12,25,26]. The metal–ligand binding in **1a** and **1b** is nearly the same, which is confirmed with the similar catalytic activities of the complexes **1a** and **1b** (Table 2, entries 1 and 4). Obviously, the addition of one bridging methylene group in **1c** leads to a decrease in trimerisation activity (Table 2, entry 7 and Table 3).

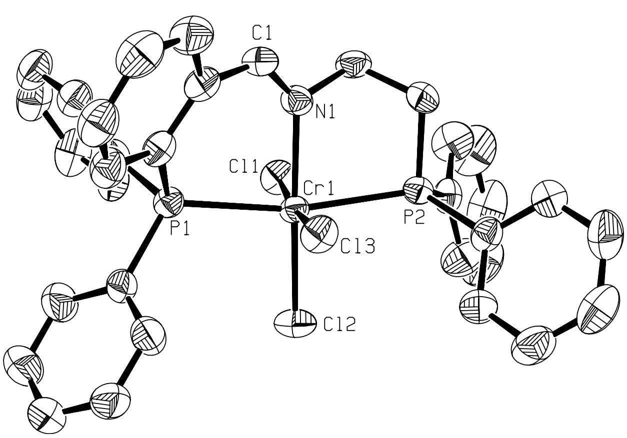

Fig. 2. Molecular structure of **1a**. Crystallized thf and CH_2Cl_2 molecules are not reported in this figure. Selected bond distances (Å) and angles (°): Cr–P1 2.469(3), Cr–P2 2.464(1), Cr–N1 2.118(3), Cr–Cl1 2.311(1), C1–N1 1.281(4), P1–Cr–N1 85.17(7), P2–Cr–N1 85.01(7), P1–Cr–P2 166.76(3), N1–Cr–Cl2 177.83(7).

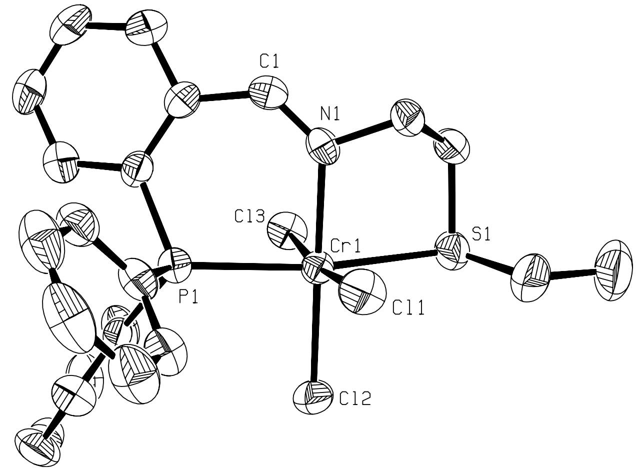

Fig. 3. Molecular structure of **1b**. Selected bond distances (Å) and angles (°): Cr–P1 2.441(1), Cr–S1 2.456(1), Cr–N1 2.092(2), Cr–Cl1 2.298(1), C1–N1 1.280(3), P1–Cr–N1 88.47(6), S1–Cr–N1 85.02(6), P1–Cr–S1 170.67(3), N1–Cr–Cl2 179.38(6).

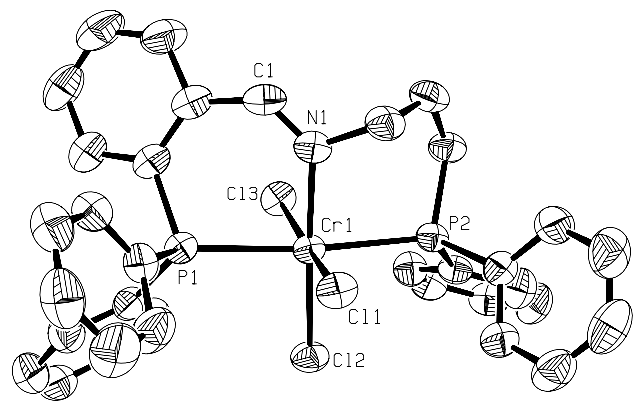

Fig. 4. Molecular structure of **1c**. Selected bond distances (Å) and angles (°): Cr–P1 2.474(1), Cr–P2 2.503(1), Cr–N1 2.103(1), Cr–Cl1 2.311(1), C1–N1 1.279(2), P1–Cr–N1 87.22(4), P2–Cr–N1 89.04(4), P1–Cr–P2 172.70(1), N1–Cr–Cl2 177.40(4).

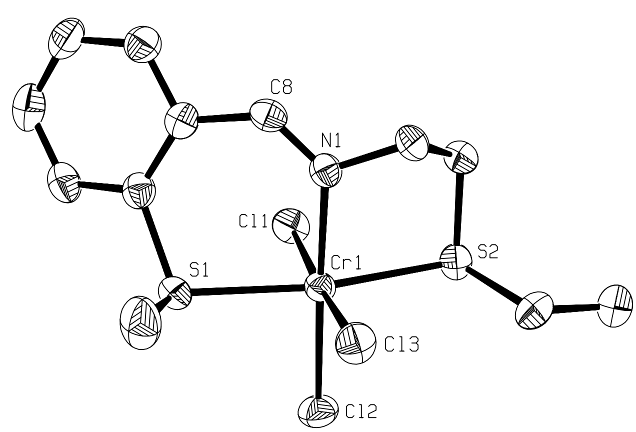

Fig. 5. Molecular structure of **1i**. Selected bond distances (Å) and angles (°): Cr–S1 2.403(1), Cr–S2 2.418(1), Cr–N1 2.069(1), Cr–Cl1 2.311(1), C8–N1 1.284(2), S1–Cr–N1 91.50(4), S2–Cr–N1 84.94(4), S1–Cr–S2 168.89(2), N1–Cr–Cl2 177.84(4).

Table 3
Crystallographic data

	1a	**1b**	**1c**	**1i**	**2b**
Empirical formula	$C_{66}H_{58}Cl_6Cr_2N_2P_4 \cdot 0.9CH_2Cl_2 \cdot 0.5thf$	$C_{23}H_{24}Cl_3CrNPS$	$C_{34}H_{31}Cl_3CrNP_2$	$C_{12}H_{17}Cl_3CrNS_2$	$C_{23}H_{26}Cl_3CrNPS$
CCDC-Nr.	234622	234623	239777	239778	239779
Formula weight (g mol^{-1})	1431.91	535.81	673.89	397.74	537.83
Temperature (K)	200(2)	200(2)	200(2)	200(2)	200(2)
Wavelength, λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	*Pbca* (No. 61)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
Unit cell dimensions					
a (Å)	23.556(2)	9.761(1) Å	10.440(1)	8.375(1)	10.558
b (Å)	14.765(1)	10.981(1)	12.480(1)	10.913	10.927
c (Å)	39.613(3)	12.576(9)	12.950(1)	17.711	12.085
α (°)	90	109.984(1)	72.156(1)	90	107.118(2)
β (°)	90	94.841	77.064(1)	95.409	99.450(2)
γ (°)	90	105.346(1)	83.763(1)	90	108.058(2)
V (Å^3)	13777.5(2)	1198.7(2)	1563.7(2) 1611.6(2)	1206.0(2)	
Z	8	2	2	4	2
$\rho_{calcd.}$ (g cm^{-3})	1.381	1.485	1.431	1.639	1.481
μ (mm^{-1})	0.753	0.977	0.750	1.451	0.971
$F(0\,0\,0)$	5884	550	694	812	554
Crystal size (mm^3)	$0.5 \times 0.4 \times 0.2$	$0.3 \times 0.2 \times 0.1$	$1.0 \times 0.6 \times 0.5$	$0.2 \times 0.2 \times 0.1$	$0.4 \times 0.15 \times 0.1$
θ Range for data collection (°)	1.34–28.31	1.76–28.30	1.69–28.28	2.19–28.29	1.84–28.32
Index ranges	$-31 \leqslant h \leqslant 31$, $-19 \leqslant k \leqslant 9$, $-52 \leqslant l \leqslant 52$	$-13 \leqslant h \leqslant 12$, $-14 \leqslant k \leqslant 14$, $-16 \leqslant l \leqslant 16$	$-13 \leqslant h \leqslant 13$, $-16 \leqslant k \leqslant 16$, $-16 \leqslant l \leqslant 16$	$-11 \leqslant h \leqslant 11$, $-14 \leqslant k \leqslant 14$, $-23 \leqslant l \leqslant 23$	$-14 \leqslant h \leqslant 14$, $-14 \leqslant k \leqslant 14$, $-16 \leqslant l \leqslant 16$
Reflections collected	137,175	12,584	16,405	18,808	14,664
Independent reflections	16,998 [R_{int} = 0.0528]	5717 [R_{int} = 0.0376]	7313 [R_{int} = 0.0136]	3960 [R_{int} = 0.0389]	5809 [R_{int} = 0.0478]
Data/restraints/parameters	16,998/6/839	5717/0/278	7313/0/375	3960/0/180	5809/0/279
Goodness-of-fit on F^2	1.057	0.885	1.053	1.022	0.886
Final R indices [$I > 2\sigma(I)$][a]	R_1 = 0.0518, wR_2 = 0.1681	R_1 = 0.0398, wR_2 = 0.0749	R_1 = 0.0269, wR_2 = 0.0755	R_1 = 0.0256, wR_2 = 0.0607	R_1 = 0.0428, wR_2 = 0.0824
R indices (all data)[a]	R_1 = 0.0752, wR_2 = 0.1794	R_1 = 0.0756, wR_2 = 0.0806	R_1 = 0.0317, wR_2 = 0.0779	R_1 = 0.0369, wR_2 = 0.0624	R_1 = 0.0855, wR_2 = 0.0914

[a] $R_1 = [\sum |F_o| - |F_c|]/\sum |F_o|, wR_2 = [[\sum w(|F_o^2 - F_c^2|)^2]/[\sum w(F_o^2)]]^{1/2}, w = 1/[(\sigma F_o)^2 + (aP)^2]$. The value of aP was obtained from structure refinement.

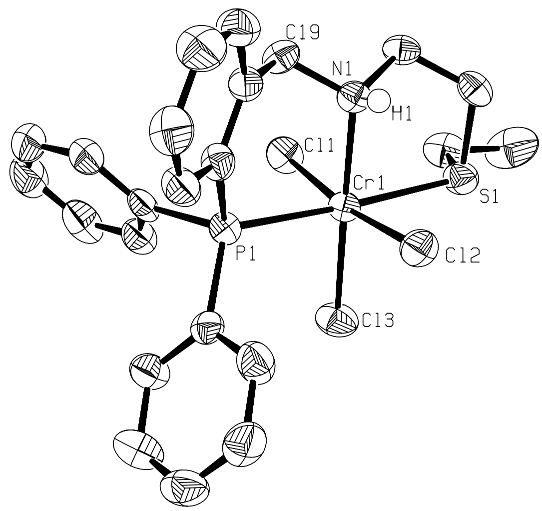

Fig. 6. Molecular structure of **2b**. Selected bond distances (Å) and angles (°): Cr–P1 2.473(1), Cr–S1 2.454(1), Cr–N1 2.123(2), Cr–Cl1 2.290(1), C19–N1 1.502(3), P1–Cr–N1 89.79(7), S1–Cr–N1 84.55(7), P1–Cr–S1 173.23(3), N1–Cr–Cl3 178.68(8).

1i only produces polyethylene (Table 2, entry 13). Although the coordination sphere in the PNS amine complex **2b** (Fig. 6) is similar to the respective imine complex **1b**, the behaviour in the catalysis with ethylene and MAO as cocatalyst is different under the same reaction conditions. The electronic properties of **2b** seem to be one reason for this different catalytic activity. The precursor complex **2b** produces a mixture of polyethylene and hexenes as well as the PNP amine chromium(III) complex **2a**. The other ONS amine chromium(III) precursor **2c** leads to the formation of polyethylene (Table 2, entries 16–18).

Investigations about the polymer properties are in progress, but differential scanning calorimetry already showed melting ranges between 126 and 142 °C with energies between 180 and 220 J/g. These values are in line with values given for HDPE [27]. Investigations about the possible inclusion of hexene as comonomer into the polymer chain have to be accomplished.

4. Conclusions

In summary, the described chromium(III) complexes **1** and **2** reveal differences in their behaviour as precatalysts for the trimerisation or polymerisation of ethylene. Depending on the ethylene pressure and the nature of the ligand, both catalysts **1a** and **1b** show good activities and selectivities with ethylene in presence of MAO as cocatalyst for producing 1-hexene. Other precatalysts mainly produce polyethylene (**1e**, **1h**–**k**, **2c**). X-ray structure analyses of **1a** and **1b** show similar Cr–heteroatom bond lengths and coordination spheres around the chromium(III) metal ions. Similar catalytic activity and product distributions are as well obtained with **1a** and **1b** as for the corresponding amine chromium(III) complexes **2a** and **2b**. The amine precatalysts **2a**, **b** react differently in the catalysis with ethylene compared to their imine based analogues **1a, 1b**. **2a**, **b** mainly form polyethylene besides hexene.

4.1. Crystal structure determination

The intensity data for the compounds were collected by a a Siemens Smart 1000 CCD diffractometer using graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz and polarisation effects, but not for absorption [28,29].

The structures were resolved by direct methods (SHELXS [30]) and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97 [31]). The hydrogen atoms were localized by difference Fourier synthesis and refined isotropically. The data are deposited in the Cambridge Crystallographic Data Centre [32].

All non-hydrogen atoms were refined anisotropically [31]. XP (SIEMENS Analytical X-ray Instruments, Inc.) and Ortep [33] were used for structure representations.

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