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Chromium (III)-bis(iminophosphoranyl)methanido complexes: synthesis, X-ray crystal structures and catalytic ethylene oligomerization†

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Bis(aminophoshonium) salts derived from bis(diphenylphosphino)methane were prepared and triply deprotonated with potassium hexamethyldisilazane to yield the corresponding bis(iminophosphoranyl)methanides, which were then subjected to coordination with $Cr^{III}Cl_3(THF)_3$. Binuclear complexes of type $[(HC(PPh_2NR)_2Cr(\mu\text{-}Cl)(Cl))_2]$ (R = *i*Pr, *t*Bu) with an octahedral coordination geometry and a long C–Cr bond were obtained and structurally characterized. In the case of R = *o*-MeO-C_6H_4, a monomeric species featuring no C–Cr bond is observed. Preliminary evaluation of catalytic activities of these complexes in ethylene oligomerization and polymerization is reported.

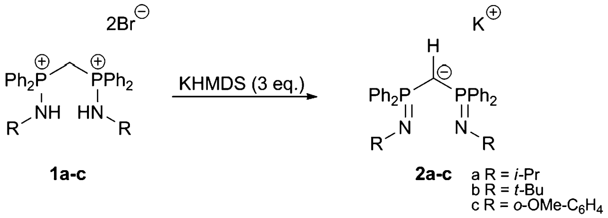
Introduction

The development of transition metal catalysts for ethylene oligomerization and polymerization is still a growing area of research, since α-olefins are widely used in a variety of industrial processes, ranging from co-monomers in the synthesis of low density polyethylene to intermediates for synthetic lubricants, plasticizers and surfactants.[1] In this context, chromium-based catalysts have attracted much attention due to their potential in selective oligomerization processes, in which the nature of the obtained olefinic oligomers can be easily modified by fine tuning the metal coordination sphere. Thus, chromium complexes bearing bidentate P∼P,[2] tridentate S∼P∼S,[3] S∼N∼S, P∼N∼P,[4] N∼N∼N,[5] and P∼P∼O[6] ligands were found to give mainly trimers. Not only is the nature of the coordinating atoms determining for the selectivity of the oligomerization process, but also the nature of their substituents and the link between these coordination sites. Indeed, diphosphinoamine (P∼N∼P) chromium complexes catalyze ethylene tri- and tetramerization if the nitrogen atom bears ether groups[7] whereas with other substituents on this atom, the same type of ligand induces a higher selectivity towards tetramerization.[8] As we recently demonstrated the potential of iminophosphorane-based ligands in ethylene oligomerization,[9] we pursue a research program dedicated to the use of iminophosphorane ligands in homogeneous catalysis. Comparatively, these ligands have received very little attention compared to imines, their carbon analogs, and have been rarely exploited in catalysis.[10,11] However, since these ligands exhibit different electronic and steric properties with regard to imines, namely the absence of a real π-system and a positively charged phosphorus center making the nitrogen atom a harder donor, iminophosphorane complexes deserve much interest. Thus, having developed a straightforward route to bis(iminophosphoranes) and their anionic derivatives starting from bis(aminophosphonium) derivatives,[12] we were interested in evaluating the potential of such ligands in oligomerization reactions. Thus we report here on the synthesis and complete characterization of three bis(iminophosphorane)-methanido chromium(III) complexes and discuss the preliminary results of their activity in ethylene oligomerization.

Results and discussion

Deprotonation of bis(aminophosphonium) salts, and coordination to $CrCl_3(THF)_3$

Monoanionic derivatives of bis(iminophosphorane) were conveniently obtained by triple deprotonation of the corresponding bis(aminophosphonium) salts **1a–c** (Scheme 1), the latter being prepared in a two-step synthesis starting from bis(diphenylphosphino)methane, bromine, and the corresponding primary amine RNH_2, as described earlier.[12] KHMDS



Scheme 1 Synthesis of bis(iminophosphoranyl)methanides **2**.

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† Electronic supplementary information (ESI) available: ORTEP plot of the X-ray structure and important structural data of **3a** as well as crystal data for structures **3a–c**, details of GC trace, DSC and polymer melting points. CCDC reference numbers 651318–651320. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b904619d

(KHMDS = potassium hexamethyldisilazane) was preferred to *n*BuLi to achieve the proton abstraction, because of better precipitation properties of the potassium bromide salt in THF, which facilitates its removal. The deprotonation reaction proceeded rapidly and its completeness was checked by ^{31}P{^{1}H} NMR, the singlet at 33.5; 29.5; 36.9 corresponding to **1a–c** being replaced by a singlet at 16.0; 3.9; 11.5 ppm for **2a–c**. The potassium bis(iminophosphoranyl)methanides **2a–c** were thus obtained as pale yellow powders in high yields and fully characterized by ^{1}H, ^{13}C and ^{31}P NMR. However, they were found to be too moisture sensitive to furnish satisfactory elemental analyses. Addition of $CrCl_3(THF)_3$ to THF solutions of **2a–c** afforded blue (**3a** and **b**) or brown (**3c**) complexes, respectively. Due to the strong paramagnetic nature of the octahedral d^{3}-Cr(III) center, no signals could be observed for any of these complexes in ^{1}H, ^{13}C and ^{31}P NMR. However, the complete disappearance of the ligand signals is a sign of the completeness of the reaction.

Structural characterization of the complexes 3a–c

Single X-ray quality crystals of all complexes **3a–c** could be grown (see Experimental section for details). Views of one molecule of **3b** and **3c** are shown in Fig. 1 and Fig. 2 along with some important structural parameters (see ESI† for details on the structure of **3a**). **3a** and **b** both present a dimeric structure similar to the one reported by Wei and Stephan[13] for the chromium(II) complex [((HC(PPh$_2$NSiMe$_3$)$_2$Cr(μ-Cl))$_2$].

The anionic nature of the bis(iminophosphoranyl)methanide ligand was confirmed by the location and subsequent refinement of the single proton in the X-ray structures. Furthermore, both structures show coordination of the central carbon atom to the chromium center with Cr1–C1 bond lengths of 2.2311(14) Å (**3a**) and 2.185(3) Å (**3b**), respectively. This length is intermediate between the short Cr1–C1 distance of 2.148(5) Å found in the [C(PPh$_2$NSiMe$_3$)$_2$Cr]$_2$ bridging carbene complex[14] and the one of 2.264(3) Å observed for [(HC(PPh$_2$NSiMe$_3$)$_2$)Cr(μ-Cl)]$_2$.[13] The Cr···Cr separation measured at 3.6360(5) Å for **3a** and 3.7231(8) Å for **3b** is slightly greater than that reported by Stephan and Wei for the TMS-substituted dimer.[13] The distortion from an octahedral geometry around each of the chromium central atoms is evidenced by a Cl1–Cr1–C1 angle of 171.13(4)° in **3a** and 171.02(7)° for **3b**. As expected from their inherent similarity, both structures present essentially identical structural features. The potential tetradentate coordination of **2c**, owing to the presence of two methoxy groups, is confirmed in the structure **3c**. Complex **3c** is indeed a monomeric species in the solid state with a distorted octahedral geometry around the chromium center. The methoxy groups occupy two equatorial coordination sites with a very short average Cr1–O bond length of 2.091(4) Å, and thus complete the coordination sphere. The Cr–N distances are 2.013(4) Å and 1.999(5) Å long, respectively. Both nitrogen and oxygen atoms form an equatorial coordination plane with a mean deviation of only 0.41°. No Cr1···C1 bond was observed in this structure. Moreover, the Cr1–N1–P1–C1–P2–N2 ring system exhibits boat-like geometry which strongly differs from the structures recorded for **3a** and **b** (Fig. 3). Such a structural element was observed by Stephan and Wei for the second isomer in the solid state structure of [(HC(PPh$_2$NSiMe$_3$)$_2$)Cr(μ-Cl)]$_2$.[13] Nevertheless, there the Cr1···C1 distance of 2.921(3) Å is much shorter than that of 3.366(6) Å measured for **3c**.

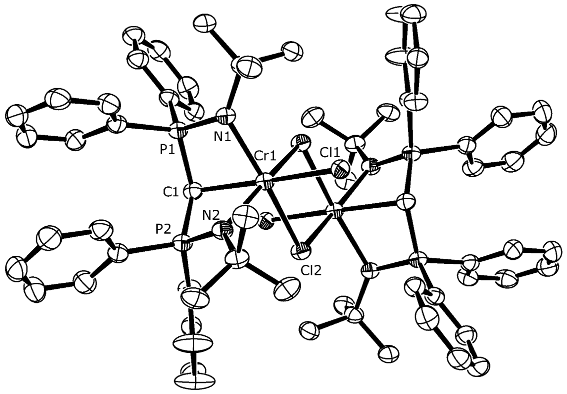

Fig. 1 X-Ray solid state structure of **3b** which lies about an inversion center. Hydrogen atoms have been omitted for clarity. Ellipsoids are drawn at the 50% probability level. Ellipsoids are drawn at the 50% probability level. Bond distances (Å) and angles (°): Cr1–N1 = 2.100(2), Cr1–Cl1 = 2.4211(7), Cr1–Cl2 = 2.3971(7), Cr1–C1 = 2.185(3), N1–P1 = 1.604(2), N2–P2 = 1.603(2), P2–C1 = 1.764(2), P1–C1 = 1.750(3), Cl1–Cr1–Cl2 = 90.90(2), N1–Cr1–Cl1 = 90.06(6), C1–Cr1–Cl2 = 171.02(7), P1–C1–P2 = 122.92(15), N1–Cr1–N2 = 96.97(8).

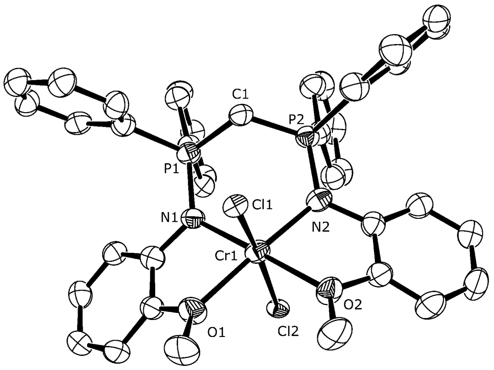

Fig. 2 X-Ray solid state structure of **3c**. Hydrogen atoms have been omitted for clarity. Ellipsoids are drawn at the 50% probability level. Bond distances (Å) and angles (°): Cr1–N1 = 2.013(4), Cr1–Cl1 = 2.3742(15), Cr1–Cl2 = 2.3641(15), Cr1–C1 = 3.366(6), N1–P1 = 1.636(5), P2–N2 = 1.628(5), P2–C1 = 1.726(6), P1–C1 = 1.702(6), Cr1–O1 = 2.087(4), Cl1–Cr1–Cl2 = 168.55(6), N1–Cr1–Cl1 = 95.64(14), C1–Cr1–Cl2 = 118.0(11), P1–C1–P2 = 118.5(4), N1–Cr1–N2 = 101.55(19), O1–Cr1–O2 = 101.14(16).

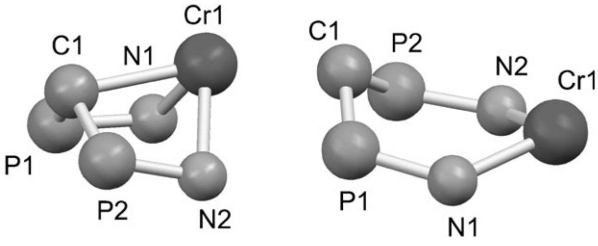

Fig. 3 Diagram of the bis(iminophosphoranyl)methanide geometry on the Cr(III) center of **3b** (left) and **3c** (right).

Ethylene oligomerization

The catalytic activities of the complexes **3a–c** in ethylene oligomerization and polymerization were investigated. Experiments were carried at both 45 °C as well as 20 °C in the presence of MAO (MAO = methylaluminoxane) with a MAO/Cr ratio of 300 (or 600, run 3), and toluene as solvent. The ethylene pressure was kept constant at 30 bar throughout the catalytic run (0.5 h). The products of the catalytic conversions were oligomers, mainly linear α-olefins (Table 1), as detected by GC. Two important common features of all catalyst precursors **3a–c** were observed. First, the productivity increased significantly when the oligomerization reactions were carried out at lower temperatures. This effect was most pronounced for **3a**, for which the productivity increased from 18 421 to 19 789 mol(C_2H_4) per mol(Cr). Secondly, all catalysts exhibited two distinct product distributions in the liquid phase with one maximum production of 1-hexene and a second tight distribution in the C_{14}–C_{24} range. This bimodal product distribution might be due to two competing oligomerization mechanisms. The C_4–C_8 fraction would be produced by a metallacycle mechanism[15] whereas the higher C_{14}–C_{24} fraction would be formed by a degenerative polymerization mechanism.[16] Further analysis of this fraction reveals that neither a classic Schultz–Flory nor Poisson distribution is present and only linear α-olefins with even and uneven carbon number were formed as major products. To further understand the origin of the olefins with uneven carbon number, which might stem either from chain transfer to an Al–Me species[17,18] or from a metathesis mechanism involving a bimetallic chromium species,[19] a catalytic test employing 600 eq. of MAO was carried out (run 3). However, no significant change in the quantity of α-olefins with uneven carbon number was observed. The relatively rapid enclosure of the catalyst with polymeric material and thus deactivation of the catalytic species under the chosen experimental conditions is probably at the origin of the insensitivity towards a changing MAO/Cr ratio and precludes further analysis in this direction. Complex **3c** shows the highest C_6-productivity along with an α-selectivity of 95%, a result which may be ascribed to the monomeric nature of the catalyst precursor, as observed with other chromium-based catalytic systems for ethylene oligomerization.[8] Each of the catalytic runs produced a polymeric fraction accounting for 15–23% of the total production, whose quantity did not change significantly with the reaction temperature.

Conclusions

In conclusion, three bis(diphenylphosphino)methanido chromium(III) complexes **3a–c** were synthesized and fully characterized. Depending on the nature of the nitrogen substituent, two different structure types were obtained: a dimeric complex containing a Cr–C1 bond and a monomeric species where the chromium coordination is completed by two pendant oxygen donors. **3a–c** proved to be active catalysts for ethylene oligomerization and polymerization with activities up to 19 789 mol(C_2H_4) per mol(Cr). Future work will focus on rationalizing the observed product distribution using theoretical studies.

Experimental

General considerations

All manipulations were carried out under argon or nitrogen using standard Schlenk or glove box techniques. Solvents were dried according to standard procedures and distilled prior to use. **1a**, **2a**,[12] and $CrCl_3(THF)_3$[20] were prepared as described before. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker Avance 300 spectrometer at 20 °C. Coupling constants *J* are reported in Hz, chemical shifts in ppm. Elemental analyses were performed at the Service d'analyse du CNRS, Gif-sur-Yvette, France. MAO was obtained from Sigma-Aldrich (10 wt% in toluene), ethylene from Air Liquide (N25 grade). GC analyses were carried out using a Perichrom PR2100 gas chromatograph equipped with a HP PONA column (0.2 mm × 50 m × 0.5 μm).

General procedure for the preparation of bis(iminophosphonium) bromides 1b and c

In analogy to the procedure previously described,[12] a solution of bis(diphenyphosphino)methane (150 mg, 0.39 mmol) in dichloromethane (10 mL) was cooled to −78 °C and bromine (125 mg, 0.8 mmol, 40 μL) was added dropwise from a syringe. The cold bath was removed and the reaction mixture was allowed to warm to ambient temperature. A yellow-white precipitate was observed. At −78 °C, the corresponding primary amine (1.56 mmol) was added dropwise and the reaction mixture was allowed to warm to ambient temperature, upon which a white precipitate of ammonium bromide formed. The salt was filtered off, and the filtrate dried *in vacuo*. The solid residue was washed with THF (2 × 25 mL) to yield a white powder after drying *in vacuo*.

Table 1 Ethylene oligomerization with complexes **3a–c** (conditions: 30 bar C_2H_4, 8 μmol of Cr, 20 mL toluene, 0.5 h, MAO/Cr = 300)

Run	Complex	*T*/°C	C_4 [1-C_4] (%)	C_6 [1-C_6] (%)	C_8 [1-C_8] (%)	C_{14}–C_{24} (%)	Polymer (%)	TON/mol (C_2H_4) per mol (Cr)
1	**3a**	45	2 [91]	8 [98]	3 [99]	69	18	18 421
2	**3a**	20	3 [95]	11 [98]	5 [99]	65	16	19 789
3[a]	**3a**	20	2 [93]	10 [98]	5 [99]	66	17	19 258
4	**3b**	45	2 [90]	5 [97]	2 [99]	69	19	16 841
5	**3b**	20	2 [90]	6 [98]	3 [99]	66	23	17 892
6	**3c**	45	6 [95]	13 [98]	3 [99]	63	15	18 266
7	**3c**	20	6 [95]	14 [98]	3 [99]	61	16	18 973

[a] MAO/Cr = 600.

Compound 1b. Yield: 166 mg (0.24 mmol, 62%) (Found: C 57.75, H 6.08, N 3.99%. $C_{33}H_{42}Br_2N_2P_2$ requires C 57.57, H 6.15, N 4.07%); $\delta_{P\{1H\}}$ (121.5 MHz, $CDCl_3$) 29.5 (s, P); δ_H (300 MHz, $CDCl_3$) 0.96 (18H, s, $C(CH_3)_3$), 6.60 (2H, t, $^2J_{PH}$ 16.5, N-*H*), 6.96 (2H, s, PCH_2P), 7.60 (8H, m, *o*-C*H*(PPh_2)), 7.73 (4H, t, $^3J_{HH}$ 7.0, *p*-C*H*(PPh_2)), 8.07 (8H, dd, $^4J_{HP}$ 11.5, $^3J_{HH}$ 8.0, 8H, *m*-C*H*(PPh_2)); δ_C (75.5 MHz, $CDCl_3$) 25.6 (t, $^1J_{CP}$ 64.5, PCH_2P), 31.1 (s, $C(CH_3)_3$), 56.4 (s, $C(CH_3)_3$), 121.6 (d, $^1J_{CP}$ 102.0, *ipso*-*C*(PPh_2)), 129.2 (dd, $^2J_{CP}$ 6.7, *o*-*C*H(PPh_2)), 134.4 (dd, $^3J_{CP}$ 6.5, *m*-*C*H(PPh_2)), 134.8 (s, *p*-*C*H(PPh_2)).

Compound 1c. Yield: 159 mg (0.28 mmol, 72%) (Found C 59.36, H 4.92, N 3.37%. $C_{39}H_{38}Br_2N_2O_2P_2$ requires C 59.41, H 4.86, N 3.55%); $\delta_{P\{1H\}}$ (121.5 MHz, $CDCl_3$) 36.9 (s, P); δ_H (300 MHz, $CDCl_3$) 3.11 (6H, s, OCH_3), 5.78 (2H, t, $^2J_{HP}$ 14.5, PCH_2P), 6.31 (2H, d, $^3J_{HH}$ 7.0, N-CC*H*), 6.86 (4H, m, N-CCHC*H*C*H*), 7.36–7.48 (12H, m, *o*, *p*-C*H*(PPh_2)), 7.57 (2H, d, $^3J_{HH}$ 7.0, C(OCH_3)C*H*), 8.29 (8H, dd, $^3J_{HH}$ 9.0, $^3J_{HH}$ 7.5, *m*-C*H*(PPh_2)), 9.55 (2H, d, $^2J_{PH}$ 9.4, N*H*); δ_C (75.5 MHz, $CDCl_3$) 30.5 (t, $^1J_{CP}$ 60.9, PCH_2P), 54.4 (s, OCH_3), 111.0 (s, N-C*C*H), 121.8 (s, N-CCHCH), 122.4 (s, *ipso*-*C*(PPh_2)), 124.5 (s, N-CC(OCH_3)*C*H), 125.6 (s, C(OCH_3)CH*C*H), 125.8 (s, N-*C*), 129.5 (d, $^2J_{CP}$ 8.0, *o*-*C*H(PPh_2)), 132.2 (d, $^3J_{CP}$ 7.0, *m*-*C*H(PPh_2)), 148.5 (s, *C*(OCH_3)).

General procedure for the preparation of the bis(iminophosphoranyl)methanides 2b and c

KHMDS (38 mg, 0.19 mmol) was added to a suspension of 0.063 mmol of the corresponding bis(iminophosphonium) bromide **1** in THF (5 mL). The reaction mixture immediately became clear taking a pale yellow color. Precipitating potassium bromide was removed by centrifugation and the supernatant solution dried *in vacuo* to yield a pale yellow powder.

Compound 2b. Yield: 34 mg (0.061 mmol, 98%). $\delta_{P\{1H\}}$ (121.5 MHz, [D_8]-THF) 3.9 (s, P); δ_H (300 MHz, [D_8]-THF) 0.89 (18H, s, $C(CH_3)_3$), 1.05 (1H, t, $^2J_{HP}$ 3.0, PC*H*P), 7.12 (16H, m, *o*-C*H*, *m*-C*H*(PPh_2)), 7.79 (8H, m, *p*-C*H*(PPh_2)); δ_C (75.5 MHz, [D_8]-THF) 35.8 (dd, $^3J_{CP}$ 5.5, $C(CH_3)_3$), 52.1 (s, $C(CH_3)_3$), 127.5 (dd, $^2J_{CP}$ 5.5, *o*-*C*H(PPh_2)), 128.5 (s, *p*-*C*H(PPh_2)), 133.2 (dd, $^3J_{CP}$ 4.5, *m*-*C*H(PPh_2)), 146.2 (d, $^1J_{CP}$ 87.5, *ipso*-*C*(PPh_2)).

Compound 2c. Yield: 41 mg (0.062 mmol, 99%); $\delta_{P\{1H\}}$ (121.5 MHz, [D_8]-THF) 11.5 (s, P); δ_H (300 MHz, [D_8]-THF) 2.07 (1H, s, PC*H*P), 3.48 (6H, s, OCH_3), 6.12–6.45 (8H, m, C(OCH_3)C*H*C*H*C*H*C*H*), 6.94 (12H, m, *o*, *p*-C*H*(PPh_2)), 7.78 (8H, m, *m*-C*H*(PPh_2)); δ_C (75.5 MHz, [D_8]-THF) 11.6 (t, $^1J_{CP}$ 120.0, P*C*HP), 55.9 (s, OCH_3), 112.5 (s, C(OCH_3)CH*C*H), 114.3 (s, N-CCH*C*H), 121.9 (s, C(OCH_3)*C*H), 122.6 (dd, $^3J_{CP}$ 7.0, N-C*C*H), 128.1 (dd, $^2J_{CP}$ 5.5, *o*-*C*H(PPh_2)), 129.3 (s, *p*-*C*H(PPh_2)), 132.2 (dd, $^3J_{CP}$ 4.0, *m*-*C*H(PPh_2)), 140.5 (d, $^1J_{CP}$ 101.0, *ipso*-*C*(PPh_2)), 145.6 (s, N-*C*), 153.6 (dd, $^3J_{CP}$ 11.0, N-C*C*(OCH_3)).

X-Ray crystallography

In each case a suitable single crystal was selected and coated with an inert perfluoro polyether oil, then mounted in a cold nitrogen stream. Data were collected at 150.0(1) K on a Nonius Kappa CCD diffractometer using a Mo-Kα (λ = 0.71073 Å) X-ray source and a graphite monochromator. All data were measured using phi and omega scans. The crystal structures were solved using SIR97[21] and SHELXL-97.[22] Molecular drawings were made using ORTEP-III.[23]

General procedure for the preparation of the complexes 3a–c

In THF (5 mL), $CrCl_3(THF)_3$ (24 mg, 0.063 mmol) was added to a solution of the corresponding bis(iminophosphoranyl)-methanide **2** (0.063 mmol) resulting in an immediate color change of the reaction mixture. After 1 h of stirring, the reaction mixture was centrifuged and the supernatant solution was dried *in vacuo*. The solid residue was finally washed with petroleum ether 40/65 (2 × 5 mL).

Compound 3a. Yield: 38 mg (0.029 mmol, 92%) of a dark blue powder. X-Ray quality crystals were obtained by overnight standing of a concentrated dichloromethane solution of **3a**. $C_{62}H_{70}Cl_4Cr_2N_4P_4$: calcd. C 60.01, H 5.69, N 4.51%; found C 60.14, H 5.42, N 4.27%.

Compound 3b. Yield: 36 mg (0.026 mmol, 84%) of a blue powder. X-Ray quality crystals were obtained by overnight standing of a concentrated THF solution of **3b**. $C_{66}H_{78}Cl_4Cr_2N_4P_4$: calcd. C 61.12, H, 6.06, N 4.32%; found C 60.97, H 6.22, N 4.19%.

Compound 3c. Yield: 43 mg (0.055 mmol, 87%) of a brown powder. X-Ray quality crystals were obtained by overnight standing of a concentrated THF solution of **3c**. $C_{39}H_{35}Cl_2CrN_2O_2P_2$: calcd. C 62.58, H 4.71, N 3.74%; found C 62.41, H 4.88, N 3.59%.

General oligomerization procedure

All catalytic reactions were carried out in a magnetically stirred stainless steel autoclave (120 mL) equipped with a pressure gauge and needle valves for injection of chemicals. The interior of the autoclave was protected from corrosion by a Teflon/protective coating and a glass liner. A typical reaction was performed by introducing into the reactor under nitrogen atmosphere the complex (4 μmol in the case of the dimeric complexes **3a** and **b**, 8 μmol in the case of **3c**) and toluene (20 mL). After injection of the MAO solution (300 eq.), the reactor was immediately brought to the desired working pressure, and continuously fed by ethylene using a reserve bottle. The reaction was stopped by shutting off the ethylene supply and cooling down the system to −70 °C. After the pressure in the reactor has decreased to atmospheric pressure, the reaction was quenched by adding 1 mL of methanol. *n*-Heptane used as internal standard was also introduced and the mixture was analyzed by quantitative GC, first calibrated with authentic samples (except in the case of butenes for which the calibration was based on the response factor of *n*-pentane).

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