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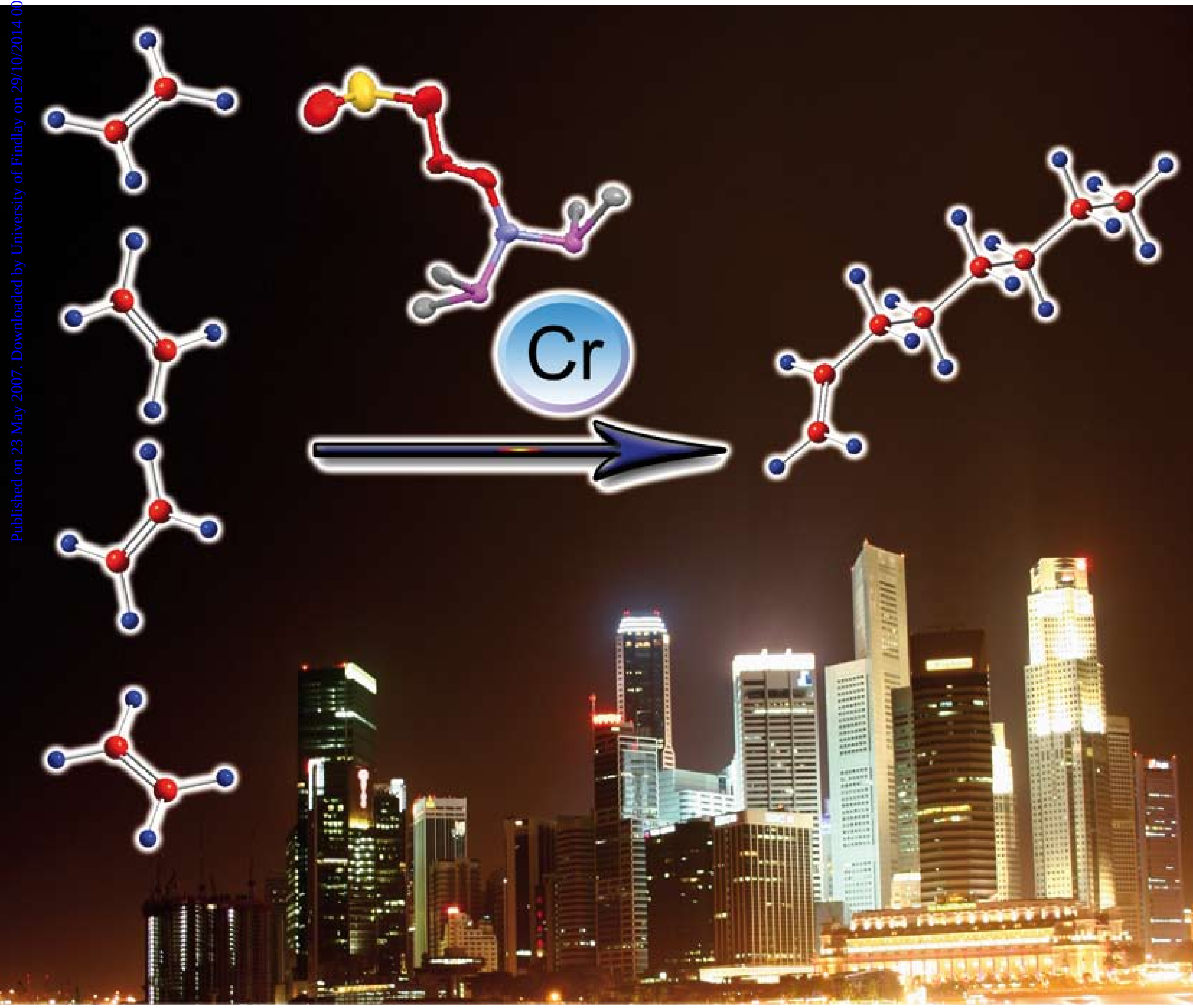

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Chromium(III) catalysed ethylene tetramerization promoted by bis(phosphino)amines with an N-functionalized pendant†‡

Zhiqiang Weng,* Shihui Teo and T. S. Andy Hor*

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Several *N*-functionalized bis(phosphino)amine ligands with ether, thioether and pyridyl tethers $[(R'')_2PN(R')P(R'')_2 = PNP]$ (**1a–1g**) have been synthesized. They react with $CrCl_3(THF)_3$ in CH_2Cl_2 to give dinuclear chloro bridged $Cr_2(\mu\text{-}Cl)_2Cl_4(PNP)_2$ (**2**) which converts to the corresponding mononuclear solvento complexes *fac*-$CrCl_3(PNP)(NCR)$ (**3**). The structures of the ligand **1d** with $R' = \text{-}(CH_2)_3SCH_3$ and $R'' = Ph$, and the complexes with $R = CH_3$ (**3a**) and C_2H_5 (**3b**), $R' = \text{-}(CH_2)_3SCH_3$ and $R'' = Ph$) have been established by single-crystal X-ray crystallography. All ligands are active towards ethylene tetramerization in the presence of Cr(III) and excess MAO at 80 °C in toluene. The ligand with thioether pendant $Et_2PN(CH_2CH_2CH_2SCH_3)PEt_2$ (**1c**) shows the highest selectivity (55% weight in liquid product distribution) towards 1-octene. Complexes **3a** and **3b** are active towards ethylene polymerization under thermal conditions.

Introduction

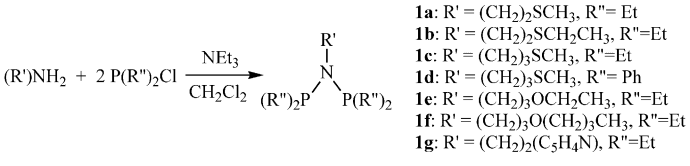
Driven by the high technological value and economic demand for linear α-olefins, especially the C_4–C_8 range, research into selective ethylene oligomerization is gathering pace.[1] Much development has been witnessed in the trimerization technology.[2–6] Selective tetramerization, which was once thought to be improbable,[7] has also been recently realized.[8] The latest mechanistic studies pointed to a metallacycloalkane pathway.[9] For example, favorable formation of 1-octene would be promoted by the stability of metallacycloheptane and instability of the metallacyclononane.[10] Although the factors behind their relative stabilities are still poorly understood, the importance of the ligand and its electronic and coordinative effects on the metal is unquestionable.[11] The next phase of development thus demands better ligand and catalyst design and better understanding of the interactions among the catalyst, co-catalyst, substrate and perhaps even the medium. It would also be desirable to design thermally stable catalysts that can withstand the harsh conditions used in ethylene oligomerization.

Among the catalysts known, the most effective catalysts for ethylene tetramerization are Cr(III) supported by nitrogen linked diphosphine ligands.[8,10] In this paper, we modify the ligand framework by introducing a functionalized and hemilabile side chain to the *N*-donor of bis(phosphino)amine ligands, and examine its effect on oligomerization activities. Notable success has been experienced by the use of suitable side-arms in olefin oligomerization/polymerization.[12] Our earlier results suggested that a combinative use of a hemilabile ligand and an unsaturated metal would promote efficient catalysis.[13] We herein examine if such a combination could benefit ethylene oligomerization and the thermal stability of the catalyst.

Results and discussion

Ligand design

Bis(phosphino)amines are the ligands of choice because of their good stability and donor characteristics to Cr(III). The addition of a functional side-arm at the N-site would raise the denticity and coordinative flexibility of these ligands. This potential of tethering prompted us to prepare new *N*-donor-functionalized ligands (**1a–1g**), in one-step (65–97% yield), from the acid condensation reaction of stoichiometric quantities of a functionalized primary amine and R_2PCl.[14] (Scheme 1) The donor functionality is represented by ether (**1e** and **1f**), thioether (**1a–1d**) and pyridyl (**1g**), ranging from weak to moderate basicity. This side-arm is designed for its potential ability to undergo reversible coordination to metal *viz.* Cr during the catalytic cycle. These ligands are best represented as [2 + 2] multidentate ligands with two strong donors (*viz.* P, P) supplemented by two weak donor sites (*viz.* N, X). In conjunction with a weakly coordinative solvent, such as CH_3CN, they would provide the best support for a metal that undergoes a series of coordinative, oxidative and geometric changes during the catalytic cycle. During the preparation of this manuscript, Bercaw *et al.* published a similar approach to ethylene tri- and tetramerisation using chromium dinuclear complexes with a similar ether tether to support the $\text{-}PPh_2$ donors.[15] Our work focuses on both ether and thioether "side-arms" to support mainly the $\text{-}PEt_2$. It is also



Scheme 1

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† Dedicated to Dr Lai Yoong Goh on the occasion of her retirement

‡ Electronic supplementary information (ESI) available: ORTEP diagrams and tables of crystallographic data for compounds **1d**, **3a** and **3b**. See DOI: 10.1039/b702636f

notable that Bercaw's syntheses in CH_2Cl_2 resulted in dinuclear complexes whereas our preparations in CH_3CN resulted in the isolation of the solvento mononuclear complexes.

All ligands have been spectroscopically characterized. X-Ray single-crystal crystallographic analysis was carried out on a representative ligand *viz.* **1d**. (Fig. 1) It shows the PNP skeleton with a methyl propyl thioether side-chain extended from the N-site. The P–N–P angle (110.7(3)°) reflects a higher sp^3 than sp^2 character although the short P–N bond (average 1.718(6) Å) [compared to other typical N–P single bonds (1.70–1.95 Å)][16] could suggest some π character.

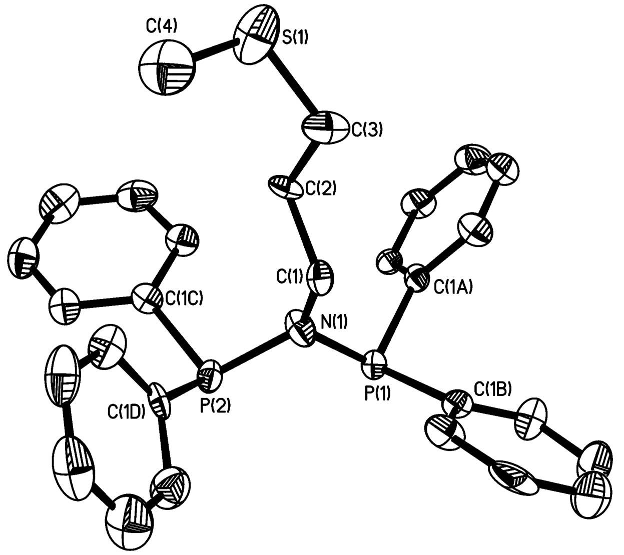
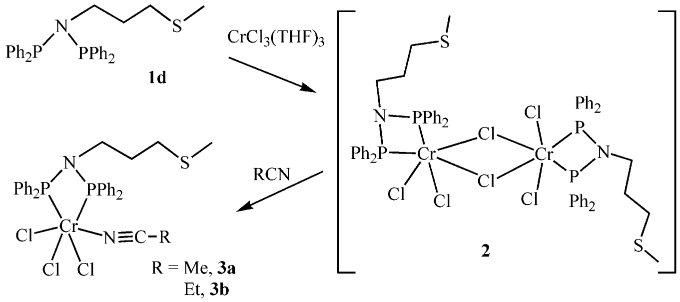


Fig. 1 Molecular structure of **1d** (H atoms and the minor disorder components are omitted for clarity). Thermal ellipsoids are drawn at the 40% probability level.

Complex synthesis

Complexation occurs readily at rt between the Lewis acidic $CrCl_3(THF)_3$ and the basic ligand **1**. In CH_2Cl_2, dinuclear adducts with doubly-bridging chlorides are formed (Scheme 2). This is best represented by the formation of $\{[Ph_2PN(CH_2CH_2CH_2SCH_3)PPh_2]CrCl_2(\mu_2\text{-}Cl)]\}_2$ (**2**) from **1d**. The metal prefers to form the chloride-bridged dinuclear complex with the stronger donors (4Cl, 2P) over the mononuclear analogue coordinated by the much weaker thioether and amine donors. A related structure of $\{[Ph_2PN(CH_2CH_2OCH_3)PPh_2]CrCl_2(\mu_2\text{-}Cl)]\}_2$ has been reported.[15]



Scheme 2

The significance of **2** is exemplified by its ready conversion to a potentially unsaturated Cr(III) that is catalytically active. Indeed, in a donor-solvent such as CH_3CN or CH_3CH_2CN, it readily undergoes bridge-cleavage to yield the corresponding mononuclear solvento complexes (represented by **3a** and **3b**). Single-crystal X-ray diffraction studies of **3a** and **3b** revealed a mononuclear octahedral *fac*-$[Cr^{III}Cl_3]$ supported by a PP-chelate and nitrile (Fig. 2, Table 1) Not surprisingly, the metal chooses the nitrile over the thio function, which remains a pendant side-arm. The strained 4-membered ring forces an acute P–Cr–P chelate angle 66.37(9)° (**3a**) and 66.01(5)° (**3b**) whereas the P–N–P contracts from 110.7(3)° in the ligand to 106.7(4)° (**3a**) and 105.7(2)° (**3b**) in the complexed state. The chelate angles are smaller than those

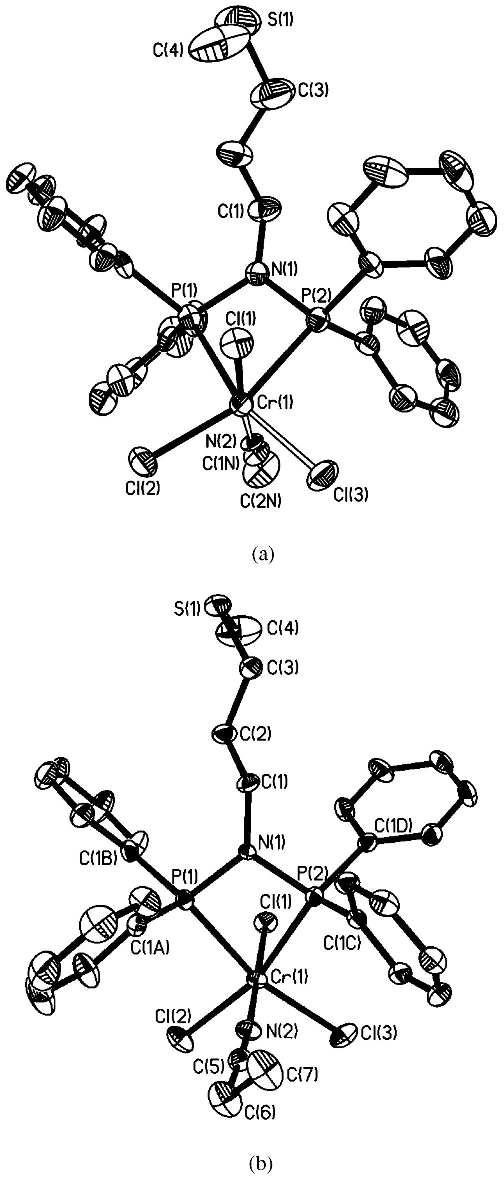


Fig. 2 Molecular structure of **3a** and **3b** (H atoms and the minor disorder components in **3a** are omitted). Thermal ellipsoids are drawn at the 40% probability level.

Table 1 Selected bond lengths (Å) and angles (°) of **1d**, **3a**, and **3b**

	Compound		
	1d	**3a**	**3b**
Bond lengths (Å)			
Cr(1)–N(2)		2.044(17)	2.038(4)
Cr(1)–Cl(1)		2.244(5)	2.2600(15)
Cr(1)–Cl(2)		2.293(3)	2.3186(16)
Cr(1)–Cl(3)		2.298(3)	2.2979(16)
Cr(1)–P(1)		2.478(3)	2.5102(15)
Cr(1)–P(2)		2.482(3)	2.4609(15)
N(1)–C(1)	1.483(8)	1.506(12)	1.487(6)
N(1)–P(1)	1.715(6)	1.693(8)	1.698(4)
N(1)–P(2)	1.721(5)	1.691(8)	1.700(4)
S(1)–C(3)	1.743(8)	1.767(13)	1.806(5)
S(1)–C(4)	1.779(9)	1.805(17)	1.780(8)
Bond angles (°)			
P(1)–Cr(1)–P(2)		66.37(9)	66.01(5)
Cl(1)–Cr(1)–Cl(3)		93.27(12)	92.97(6)
Cl(2)–Cr(1)–Cl(3)		103.5(2)	102.21(6)
N(2)–Cr(1)–Cl(1)		171.9(5)	175.93(13)
Cl(2)–Cr(1)–P(1)		94.90(10)	96.56(6)
Cl(3)–Cr(1)–P(2)		95.3(2)	94.90(5)
P(1)–N(1)–P(2)	110.7(3)	106.7(4)	105.7(2)
C(3)–S(1)–C(4)	101.5(5)	102.5(7)	102.3(3)
C(1)–N(1)–P(1)	121.9(6)	127.8(7)	130.6(3)
C(1)–N(1)–P(2)	124.9(6)	125.5(7)	123.7(3)

found in the dinuclear complexes $\{[Ph_2PN(R')PPh_2]CrCl_2(\mu_2\text{-}Cl)]\}_2$ [R′ = $CH_2CH_2OCH_3$ (66.837(18)°),[15] Ph (66.62(7)°)[8]]. The pendant thioether is located away from the metal to avoid interference with the coordination sphere. In both complexes, the Cr–Cl bond *trans* to the nitrile is distinctly shorter, and presumably stronger, compared to the other two.

Catalytic ethylene tetramerization

A catalytic mixture containing $Cr(acac)_3/CrCl_3(THF)_3$: ligand (**1a–1g**) : methylaluminoxane (MAO) (1 : 2 : 440) is mixed under 30 bar pressure of ethylene at 80 °C in toluene in the commercial Endeavor Parallel Reactor. The results are summarized in Table 2. All the mixtures are active, showing good turnovers of ~32000–61000 g g^{-1} in 3 h. The isomeric distributions however are sensitive to the nature of the functionalized side-chain at N. The thioether ligands show higher selectivity than their ether counterparts with respect to octene formation (33–55% in Entries 1–4 *vs.* 35–38% in Entries 5–6). Both series perform significantly better than the pyridyl derivative (19%) (Entry 7). When compared to the dinuclear complexes reported by Bercaw *et al.*,[15] the ether-functionalized ligands (**1e** and **1f**) together with $Cr(acac)_3$ appear to be less selective towards trimerization but more so towards tetramerization and higher oligomer formation. In all cases under study, the selectivity of 1-octene over other octenes is excellent (96–99%). The length of the side chain influences the selectivity. Use of a methyl propyl thioether residue in conjunction with an electron-donating and less hindered ethyl substituent at the phosphine gives 1-octene in excess of 55 mass% (Entry 3).[17] This is comparable to the high performance catalysts in the Sasol process with selectivities up to 70%,[8,10] both of which exceed the conventional one-step ethylene oligomerization or tetramerization technology that generally gives 1-octene in yields <26 mass%.[18–20] Preliminary data also suggested that the system comprising Cr(III) with **1c** can maintain its activity, without visible loss, for 8 h at 80 °C under 30 bar ethylene pressure in the presence of methylaluminoxane (MAO). This stability is higher than those observed in many other ligands system such as those with *o*-methoxyphenyl substituents.[4,15] Its productivity (14659 g g^{-1} Cr h^{-1}) is also much higher than that of the PNP ligand with no tethering donor groups, *e.g.* $Et_2PN(CH_3)PEt_2$ (4400 g g^{-1} Cr h^{-1}).[8] These data, together with the differences observed for different N-bonded tethers, provided indirect evidence that the pendant group would affect the tetramerization outcome.

The higher homologues of α-C_{11}-olefins are formed as by-products. Current research is directed at their elimination through other ligand and metal designs. Preliminary data suggested that direct use of **3a** or **3b** as catalyst at 80 °C and 30 bar of ethylene pressure in the presence of MAO gives no oligomerization product but polymers up to TOF of 24 310 h^{-1} and 29 170 h^{-1} respectively. It demonstrates the potential of using thermally a stable catalyst to promote ethylene polymerization under pressured and thermal conditions.

Conclusions

Although it is clear that the nature of the N-pendant influences the catalytic outcome, we have no strong evidence, at least in this system, that this is realized in the form of the expected protection and deprotection of the metal in the course of the catalytic cycle. Recent reports suggested possible involvement of a cationic MAO-stabilized species and the Cr(II)/(IV) couple.[9c] There is also a question of the possibility of disproportionation of Cr(II) to re-generate the catalytically active Cr(III) [and Cr(0)], thus reviving a

Table 2 Key ethylene oligomerization data using Cr(III) and ligand **1** as catalyst[a]

					Liquid product distribution (%)				
Run (ligand)	Activity[b]	Total product/mg	Solids (%)	Liquids (%)	C_6	C_8	C_{10}	C_{11+}	1-C_8 (%)
1 (**1a**)	41500	772	11.1	88.9	25.9	49.3	1.3	24.5	97.7
2 (**1b**)	53600	997	24.3	75.7	18.0	36.8	1.6	43.3	98.5
3 (**1c**)	43980	818	4.9	95.1	26.7	55.5	1.2	16.2	98.5
4 (**1d**)[d]	18600	346	62.4	37.6	9.2	33.3	1.9	54.8	97.0
5 (**1e**)	61020	1135	26.9	73.1	17.3	35.3	1.8	45.4	97.8
6 (**1f**)	48870	909	26.4	73.6	17.9	37.8	1.8	42.2	97.5
7 (**1g**)	30540	569	23.4	77.6	11.7	19.3	2.3	66.2	96.2

[a] Standard reaction conditions: 0.36 μmol $Cr(acac)_3$, 2 equiv. of ligand, 440 equiv. of MAO, 4 ml toluene, 30 bar ethylene, 3 h, 80 °C. (run 7; $CrCl_3\cdot(THF)_3$). [b] Activity = g prod. per g Cr. [c] % = weight%. [d] 1 h.

catalytic process.[21] Future research in our laboratory will include the examination of the interaction of our pendant with aluminate anion and the compatibility of our ligands with Cr(II) and Cr(IV).

Experimental

General

All reactions were carried out using conventional Schlenk techniques under an inert atmosphere of nitrogen or argon with an M. Braun Labmaster 130 Inert Gas System. NMR spectra were measured on Bruker ACF300 300 MHz FT NMR spectrometers (^1H at 300.14 MHz, ^{13}C at 75.43 MHz and ^{31}P at 121.49 MHz). Mass spectra were obtained on a Finnigan Mat 95XL-T spectrometer. Elemental analyses were performed by the microanalytical laboratory in-house. All chemicals were obtained from Sigma-Aldrich or Stem Chemicals unless stated otherwise. In all the examples, the molar mass of methylaluminoxane (MAO) (10 wt% in toluene solution) was taken to be 58.016 g mol^{-1}, corresponding to the (CH_3-Al-O) unit, in order to calculate the molar quantities of MAO used in the preparation of the catalysts described below. Ligands (**1a–1g**) are prepared with modifications on literature procedures.[14]

Preparation of $Et_2PN(CH_2CH_2SCH_3)PEt_2$ (1a)

To a mixture of 2-(methylthio)ethylamine (101 mg, 1.11 mmol) and triethylamine (0.6 ml) in dichloromethane (5 ml) at rt was added a solution of chlorodiethylphosphine (277 mg, 2.22 mmol) in CH_2Cl_2 (4 ml). The resulting solution was stirred for 20 h, after which the solvent was evaporated to dryness and toluene (5 ml) added. The suspension was filtered through a layer of Celite to remove the triethylammonium salt formed. The product $Et_2PN(CH_2CH_2SCH_3)PEt_2$ (**1a**) (192 mg, 0.72 mmol, 65% yield) was isolated as a colorless oil after solvent removal. ^1H NMR ($CDCl_3$): δ 3.15–3.02 (q, $J = 9.18$, 2H, N-CH_2-C), 2.58–2.52 (m, 2H, C-CH_2-S), 2.10 (s, 3H, S-CH_3), 1.68–1.56 (m, 8H, -PCH_2-), 1.06–0.96 (m, 12H, P-C-CH_3). ^{13}C NMR ($CDCl_3$): δ 48.49, 22.61, 15.56, 9.68, 9.44. ^{31}P NMR ($CDCl_3$): δ 58.52. MS (FAB^+): m/z 252 $[M + H]^+$.

Preparation of $Et_2PN(CH_2CH_2SCH_2CH_3)PEt_2$ (1b)

By using a similar method as above, a mixture of 2-(ethylthio)-ethylamine (42 mg, 0.4 mmol) and triethylamine (0.2 ml) with chlorodiethylphosphine (99 mg, 0.8 mmol) gave $Et_2PN(CH_2CH_2SCH_2CH_3)PEt_2$ (**1b**) (84 mg, 0.299 mmol, 75% yield) as an colorless oil. ^1H NMR ($CDCl_3$): δ 3.13–3.08 (m, 2H, N-CH_2-C), 2.60–2.52 (m, 4H, -CH_2-S-CH_2-), 1.88–1.62 (m, 8H, -PCH_2), 1.31–1.00 (m, 15H, C-CH_3, P-CH_2CH_3). ^{31}P NMR ($CDCl_3$): δ 58.36. MS (FAB^+): m/z 282 $[M + H]^+$.

Preparation of $Et_2PN(CH_2CH_2CH_2SCH_3)PEt_2$ (1c)

By using a similar method as adopted above, a mixture of 3-(methylthio)propylamine (29 mg, 0.276 mmol), triethylamine (0.2 ml) and chlorodiethylphosphine (70 mg, 0.56 mmol) gave $Et_2PN(CH_2CH_2CH_2SCH_3)PEt_2$ (**1c**) (64 mg, 0.228 mmol, 84% yield) as an colorless oil. ^1H NMR ($CDCl_3$): δ 3.09–2.97 (m, 2H, N-CH_2-C), 2.57–2.45. (m, 2H, C-CH_2-S), 2.10 (s, 3H, S-CH_3), 1.88–1.56 (m, 8H, -PCH_2-), 1.26–0.96 (m, 14H, C-CH_2-C, P-C-CH_3). ^{13}C NMR ($CDCl_3$): δ 48.00, 31.84, 22.61, 15.56, 9.77, 9.53. ^{31}P NMR ($CDCl_3$): δ 58.55. MS (FAB^+): m/z 282 $[M + H]^+$.

Preparation of $Ph_2PN(CH_2CH_2CH_2SCH_3)PPh_2$ (1d)

By using a similar method as above, a mixture of 3-(methylthio)propylamine (60 mg, 0.571 mmol), triethylamine (0.6 ml) and chlorodiphenylphosphine (251 mg, 1.14 mmol) gave $Ph_2PN(CH_2CH_2CH_2SCH_3)PPh_2$ (**1d**) (261 mg, 0.552 mmol, 97% yield) as a white solid. ^1H NMR ($CDCl_3$): δ 7.44–7.34 (m, 20H, Ph), 3.47–3.35 (m, 2H, N-CH_2-C), 2.15–2.10 (t, 2H, $J = 7.02$ Hz, C-CH_2-S), 1.86 (s, 3H, S-CH_3), 1.44–1.36 (m, 2H, C-CH_2-C). ^{31}P NMR ($CDCl_3$): δ 63.49. MS (FAB^+): m/z 474 $[M + H]^+$. Elemental analysis (%) calcd for $C_{28}H_{29}NP_2S$: C 70.89, H 6.19, N 2.95; found: C 70.48, H 6.28, N 2.85.

Preparation of $Et_2PN(CH_2CH_2CH_2OCH_2CH_3)PEt_2$ (1e)

By using a similar method, a mixture of 3-ethoxypropylamine (37 mg, 0.359 mmol), triethylamine (0.2 ml) and chlorodiethylphosphine (90 mg, 0.722 mmol) gave $Et_2PN(CH_2CH_2CH_2OCH_2CH_3)PEt_2$ (**1e**) (92 mg, 0.33 mmol, 91% yield) as a colorless oil. ^{31}P NMR ($CDCl_3$): δ 58.55. ^1H NMR ($CDCl_3$): δ 3.38–3.30 (m, 4H, CH_2–OCH_2), 3.09–2.92 (m, 2H, N–CH_2–), 1.70–1.04 (m, 25H, –CH_2–, –CH_3, PCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 68.58, 67.91, 30.13, 27.32, 20.74, 19.86, 14.90. MS (FAB^+): m/z 280 $[M + H]^+$.

Preparation of $Et_2PN(CH_2CH_2CH_2OCH_2CH_2CH_2CH_3)PEt_2$ (1f)

By using a similar method, a mixture of 3-butoxypropylamine (47 mg, 0.359 mmol), triethylamine (0.2 ml) and chlorodiethylphosphine (90 mg, 0.722 mmol) gave $Et_2PN(CH_2CH_2CH_2OCH_2CH_2CH_2CH_3)PEt_2$ (**1f**) (97 mg, 0.316 mmol, 87% yield) as a colorless oil. ^1H NMR ($CDCl_3$): δ 3.38–3.34 (m, 4H, CH_2-O-CH_2), 2.58–2.52 (m, 2H, N-CH_2-), 1.86–0.87 (m, 49H, -CH_2-, -CH_3, PCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 70.50, 68.58, 45.88, 31.70, 22.52, 19.24, 13.79, 9.73, 9.48. ^{31}P NMR ($CDCl_3$): δ 58.61. MS (FAB^+): m/z 308 $[M + H]^+$, 250 $[M - CH_2CH_2CH_2CH_3]^+$.

Preparation of $Et_2PN(CH_2CH_2(C_5H_4N))PEt_2$ (1g)

By using a similar method, a mixture of 2-(2-aminoethyl)pyridine (141 mg, 1.157 mmol), triethylamine (0.8 ml) and chlorodiethylphosphine (288 mg, 2.313 mmol) gave $Et_2PN(CH_2CH_2(C_5H_4N))PEt_2$ (**1g**) (336 mg, 1.128 mmol, 97% yield) as a colorless oil. ^1H NMR ($CDCl_3$): δ 8.49–8.47 (t, 1H, $J = 4.77$ Hz, C-H), 7.56–7.55 (m, 1H, C-H), 7.13–7.09 (m, 2H, C-H_2), 3.35–3.28 (q, 2H, N-CH_2-), 2.99–2.95 (t, $J = 6.42$, 2H, =C-CH-), 1.86–0.99 (m, 20H, PCH_2CH_3). ^{31}P NMR ($CDCl_3$): δ 58.41.

Synthesis of $\{[Ph_2PN(CH_2CH_2CH_2SCH_3)PPh_2]CrCl_2(\mu_2\text{-}Cl)]\}_2$ (2)

To a solution of $Ph_2PN(CH_2CH_2CH_2SCH_3)PPh_2$ (**1d**) (141 mg, 0.298 mmol) in CH_2Cl_2 (5 ml) was added $CrCl_3(THF)_3$ (112 mg, 0.298 mmol) and stirred at rt for 30 min to give a green solution. The mixture was concentrated under vacuum, after which excess hexane was added to precipitate the dark green solid, which was collected by filtration and washed with hexane. Yield 183 mg (97%). IR [KBr, cm^{-1}] 3056 (m), 2954 (m), 2917 (m), 1482 (m), 1434 (s), 1279 (w), 1314 (w), 1188 (w), 1095 (s), 1027 (w), 998 (w), 961 (w), 880 (m), 746 (s), 694 (s), 504 (s). MS (FAB$^+$): *m/z* 632 [1/2(M)]$^+$, 595 [1/2(M) − Cl]$^+$, 560 [1/2(M) − 2Cl]$^+$, 508 [1/2(M) − 2Cl − Cr]$^+$, 474 [L]$^+$, 185 [PPh$_2$]$^+$. Elemental analysis (%) calcd for $C_{56}H_{61}N_2O_{1.5}P_4S_2Cr_2Cl_6$: (as 1.5 hydrate) C 51.04, H 4.89, N 2.13; found: C 51.16, H 5.00, N 2.08.

Synthesis of [$Ph_2PN(CH_2CH_2CH_2SCH_3)PPh_2$]$CrCl_3(CH_3CN)$ (3a)

CH_3CN (1 ml) was introduced to a test tube containing solid **2** (48 mg, 0.076 mmol), after which blue microcrystals readily precipitated. The mixture was kept at −30 °C for 1 day to give more crystals. The mother liquor was removed and the crystals were washed with hexane, and then dried under vacuum to give of **3a**. Yield 37 mg (73%). IR [KBr, cm^{-1}] 3055 (m), 2984 (w), 2920 (w), 1482 (m), 1435 (s), 1313 (w), 1188 (w), 1094 (s), 1027 (w), 999 (w), 942 (w), 883 (m), 800 (w), 749 (s), 697 (s), 508 (m). MS (FAB$^+$): *m/z* 595 [M − Cl − CH_3CN]$^+$, 560 [M − 2Cl − CH_3CN]$^+$, 508 [M − 2Cl − CH_3CN − Cr]$^+$, 474 [L]$^+$, 185 [PPh$_2$]$^+$. Elemental analysis (%) calcd for $C_{30}H_{32}N_2P_2SCrCl_3$: C 53.54, H 4.79, N 4.16; found: C 53.51, H 5.04, N 4.13.

Synthesis of [$Ph_2PN(CH_2CH_2CH_2SCH_3)PPh_2$]$CrCl_3$-($CH_3CH_2CN$) (3b)

By following a procedure similar to that for **3a**, solid **2** in CH_3CH_2CN gave blue crystals of **3b**. Yield 43 mg (82.70%). IR [KBr, cm^{-1}] 3060 (m), 2958 (w), 2920 (w), 1482 (w), 1435 (s), 1312 (w), 1187 (w), 1093 (s), 1027 (w), 999 (w), 942 (w), 888 (m), 797 (w), 749 (s), 695 (s), 541 (w), 505 (m), 489 (w). MS (FAB$^+$): *m/z* 595 [M − Cl − CH_3CH_2CN]$^+$, 560 [M − 2Cl − CH_3CH_2CN]$^+$, 508 [M − 2Cl − CH_3CH_2CN − Cr]$^+$, 474 [L]$^+$, 185 [PPh$_2$]$^+$. Elemental analysis (%) calcd for $C_{31}H_{34}N_2P_2SCrCl_3$: C 54.20, H 4.99, N 4.08; found: C 54.07, H 5.22, N 3.98.

Oligomerization of ethylene

The catalytic activities were screened by Endeavor Parallel Pressure Reactor, following recommended procedures. At the end of each experiment, the vessel was cooled to ambient temperature and depressurized. The reaction mixture was cooled to 0 °C and terminated by addition of 10% aq. HCl. A small sample of the upper-layer solution was filtered through a layer of Celite and analysed by GC. The individual products of oligomerization were identified by GC-MS. The remainder of the upper-layer solution was filtered to isolate the solid polymeric products. The solid products were suspended in 10% aq. HCl and stirred for 24 h, dried under reduced pressure and weighed.

Crystal structure analyses

Diffraction-quality single crystals were obtained at −30 °C as follows: **1d** as light yellow diamond-like crystals after 4 days from a toluene solution; **3a** and **3b** as blue needles after 2 days from solutions in CH_3CN and CH_3CH_2CN, respectively. These crystals were mounted on quartz fibers and X-ray data collected on a Bruker AXS APEX diffractometer, equipped with a CCD detector, using Mo-Kα radiation (λ 0.71073 Å). The data was corrected for Lorentz and polarisation effect with the SMART suite of programs[22] and for absorption effects with SADABS.[23] Structure solution and refinement were carried out with the

Table 3 Selected crystal data, data collection and refinement parameters of compounds **1d**, **3a** and **3b**

	Compound		
	1d	**3a**	**3b**
Formula	$C_{28}H_{29}NP_2S$	$C_{30}H_{32}Cl_3CrN_2P_2S$	$C_{31}H_{34}Cl_3CrN_2P_2S$
Formula weight	473.52	672.93	686.95
Crystal size/mm	0.26 × 0.10 × 0.06	0.10 × 0.08 × 0.02	0.18 × 0.06 × 0.02
Temperature/K	223(2)	223(2)	223(2)
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	*P*2(1)2(1)2(1)	*P*2(1)/*n*	*Pbca*
a/Å	9.2813(10)	11.3331(13)	11.213(2)
b/Å	9.8308(8)	16.3009(19)	16.453(3)
c/Å	27.659(3)	17.286(2)	34.766(7)
α/°	90	90	90
β/°	90	99.248(4)	90
γ/°	90	90	90
V/Å^3	2523.6(4)	3151.8(6)	6414(2)
Z	4	4	8
D_c/g cm^{-3}	1.246	1.418	1.423
Radiation used	Mo-Kα	Mo-Kα	Mo-Kα
μ/mm^{-1}	0.271	0.808	0.796
θ range/°	1.47 to 25.00	1.73 to 25.00	2.16 to 25.00
No. of unique reflections measured	6731	18076	35350
Max., min. transmission	0.9839 and 0.9328	0.9840 and 0.9235	0.9843 and 0.8700
Final R indices [$I > 2\sigma(I)$]^{a,b}	$R_1 = 0.0838$, w$R_2 = 0.1564$	$R_1 = 0.1172$, w$R_2 = 0.1964$	$R_1 = 0.0713$, w$R_2 = 0.1314$
R indices (all data)	$R_1 = 0.1113$, w$R_2 = 0.1758$	$R_1 = 0.1918$, w$R_2 = 0.2264$	$R_1 = 0.1024$, w$R_2 = 0.1432$
Goodness-of-fit on F^{2c}	1.077	1.095	1.112
Large diff. peak and hole/e Å^{-3}	0.447 and −0.382	0.610 and −0.498	0.401 and −0.445

[a] $R = (\Sigma|F_o| - |F_c|)\Sigma|F_o|$. [b] $wR_2 = [(\Sigma\omega|F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$. [c] $\mathrm{GoF} = [(\Sigma\omega|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{1/2}$.

SHELXTL suite of programs.[24] The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. In **1d**, The C1–C2 of the C_3H_6 chain is disordered into two positions with 66 : 34 ratio. The disordered parts C1–C2 and C1x–C2x were refined with the ratio as free-variable to give the final ratio of 65/35. The bond lengths involving these disordered atoms were also restrained to avoid excessive deviations of the bond lengths and thermal parameters from normal values. There is also a disorder in **3a** involving the switching of one Cl and the acetonitrile at 61 to 39 occupancies. The Cl/acetonitrile disordered pair occupancy ratio was refined as a free variable. Restraints were also applied to the bond lengths and thermal parameters of the acetonitrile to keep them in the usual range as these did not behave well during refinement. The data collection and processing parameters are given in Table 3.

CCDC reference numbers 637514 (**1d**), 637515 (**3a**) and 637516 (**3b**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b702636f.

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