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Alkylaminophosphanyl substituted half-sandwich complexes of vanadium(III) and chromium(III): preparation and reactivity in ethylene polymerisation

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Dedicated to Prof. Dr. Dr. h. c. K. Dehnicke on the occasion of his 70th birthday

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Abstract

[$\mathbf{Cp^R}$(RPNEt$_2$)]M ($\mathbf{Cp^R}$ = t-BuC$_5$H$_3$, C$_5$(CH$_3$)$_4$, indenyl, fluorenyl; M = Li, K) smoothly react with VCl$_3$(Me$_3$P)$_2$ and CrCl$_3$(THF)$_3$ systems giving paramagnetic complexes [$\mathbf{Cp^R}$(R^{1}PNEt$_2$)]MCl$_2$ (M = V(Me$_3$P)$_2$, Cr). After reaction with MAO these complexes are active in the polymerisation of ethylene yielding highly crystalline, high-density products of high molecular weight (M_w ranging from 100 000 to 4.5×10^6 g mol^{-1}, $20 \leq T_p \leq 100$ °C). Polymerisation with chromium complexes leads to the formation of polyethylenes with broad molecular weight distribution. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Homogeneous Ziegler–Natta catalysts; Vanadium; Chromium; Olefin polymerisation

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1. Introduction

Polymers produced by homopolymerisation and/or copolymerisation of small olefins such as ethylene and propene are among the widely used plastics. Apart from the so-called low density polyethylene (LDPE) that is made by a high pressure radical process, polyolefins are mostly produced by using heterogeneous Ziegler–Natta systems [1] and by the Phillips catalyst discovered by Hogan and Banks [2]. The metallocene technology developed during the last 20 years received a great deal of attention largely because of the possibility to design catalysts of well-defined structure and therefore with tailored catalytic properties, stereochemistry and the microstructure of the polymer produced [3]. The sterically less encumbered Constrained Geometry Complexes (CGC) (**I**) as a new class of homogeneous olefin polymerisation catalysts were reported more than 10 years ago [4]. These Group 4 mono-cyclopentadienyl amido derivatives are based on a ligand system, first described by Bercaw [5] for organoscandium complexes, and are distinguished by a sterically accessible catalyst active site, which facilitates incorporation of other olefins into the polyethylene backbone. There are a number of reports in the literature on the copolymerisation of ethylene and linear α-olefins such as propene, 1-butene, 1-hexene, 1-octene [4] and with cyclic monomers such as 5-ethylidene norbornene [6]. Additionally, when compared to bis-cyclopentadienyl metallocenes, the activated CGC catalysts are thermally more stable up to the reaction temperatures of 160 °C and generally produce polymers of higher molar mass [7].

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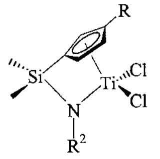
While chemistry and catalytic properties of CGC metal complexes of Group 4 are extensively studied and titanium complexes have been commercialised (INSIGHT-technology) [8], much less is known about the catalytic behaviour of the relative complexes of vanadium and chromium. At the same time vanadium compounds are widely used for the production of synthetic EP(D)M rubbers [9], and a third of the total polyethylene is manufactured with the heterogeneous catalyst of Phillips Petroleum [10]. Cyclopentadienyl vanadium complexes for ethylene and butadiene polymerisation have been reported by Hessen et al. and Ricci et al., respectively [11]. Efforts to develop homogeneous catalytic systems based on chromium cyclopentadienyls (**II**) (Z = silicon or carbon bridge) have been undertaken in the groups of Theopold [10], Jolly [12], Heitz [13] and in some other laboratories [14].



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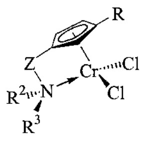

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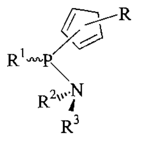
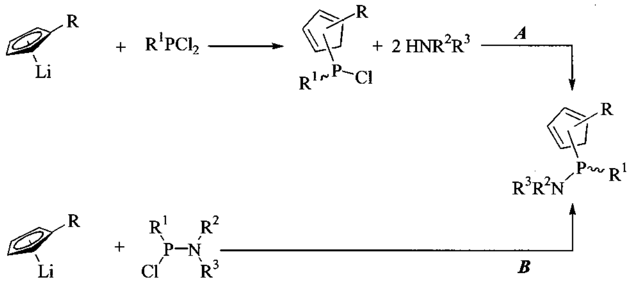
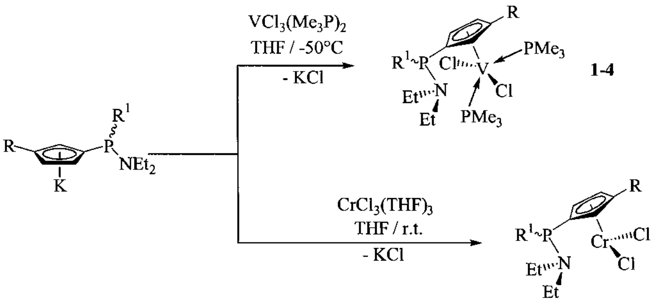


III



Cp^R = Cp, Ind, Flu; R^1 = Alk, Ar; R^2 = H or R^3; R^3 = Alk or Ar.

Scheme 1.



[Cp^R(R^1)PNEt$_2$]MCl$_2$ =
1 [t-BuCp(t-Bu)PNEt$_2$]VCl$_2$(Me$_3$P)$_2$ 77%
2 [Me$_4$C$_5$(t-Bu)PNEt$_2$]VCl$_2$(Me$_3$P)$_2$ 60%
3 [Ind(t-Bu)PNEt$_2$]VCl$_2$(Me$_3$P)$_2$ 84%
4 [Flu(t-Bu)PNEt$_2$]VCl$_2$(Me$_3$P)$_2$ 76%
5 [t-BuCp(t-Bu)PNEt$_2$]CrCl$_2$ 80%
6 [Me$_4$C$_5$(Me)PNEt$_2$]CrCl$_2$ 85%
7 [Me$_4$C$_5$(t-Bu)PNEt$_2$]CrCl$_2$ 63%
8 [Ind(t-Bu)PNEt$_2$]CrCl$_2$ 92%
9 [Flu(t-Bu)PNEt$_2$]CrCl$_2$ 87%

Scheme 2.

We have been exploring the synthesis of new ligands derived from the alkyl(amino)cyclopentadienylphosphanes Cp^{R}P(R^1)NR^{2}R^3 (**III**) (R, R^1, R^2, R^3 = Alk, Ar or H) in an attempt to probe this class of compounds as ligands for the transition metal chemistry [15]. The choice of Cp^{R}P(R^1)NR^{2}R^3 was stimulated by the expectation that the presence of two strong σ-donors connected with the cyclopentadienyl frame could have an impact on the catalytic properties of the target complexes due to electron donating nature of the (R^2)$_2$N(R^1)P-moiety. For instance, in the case of zirconocenes, electron donating ligand substituents stabilise the cationic character of the catalytic active metal centre [16]. On the other hand, the reactive PN(R^2)$_2$ functionality may be used for the derivatisation and/or heterogenisation of the transition metal complexes. Here we report our studies on the synthesis and polymerisation activity of V(III) and Cr(III) complexes with this class of ligands taking ethylene polymerisation as a model reaction.

2. Results and discussion

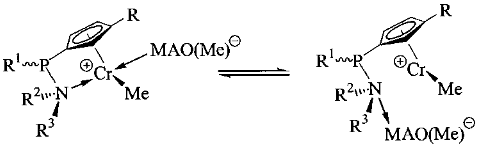
2.1. Preparation of the ligands

There are two main synthetic approaches to the aminophosphanyl cyclopentadienes: (A) a subsequent nucleophilic substitution of the halogen atoms at the phosphorus centre by cyclopentadienyl type carbanios and amines, and (B) the reaction of cyclopentadienyl anions and alkyl(aryl)chloro-*N*,*N*-dialkylaminophosphanes. Both routes have been successfully applied for the preparation of the ligand precursors in our work [15] (Scheme 1).

2.2. Preparation of the complexes

For the preparation of vanadium and chromium complexes we used the same strategy as described in Refs. [12,17]. When lithium or potassium salts of the ligand precursors are reacted with VCl$_3$(Me$_3$P)$_2$ or CrCl$_3$(THF)$_3$ in THF, corresponding half-sandwich complexes are obtained in good yields. In the case of vanadium derivatives, Me$_3$P-adduct was used to stabilise the vanadium(III) centre to prevent a disproportionation to Cp$^R_2$VCl and VCl$_3$ [17] (Scheme 2).

The use of potassium salts of the sterically demanding aminophosphanyl cyclopentadienes, indenes and fluorenes is crucial for the synthesis of vanadium complexes **1**–**4** and these compounds are not accessible from the reaction with lithium salts [17]. Vanadium complexes are moisture- and air-sensitive and have a characteristic blue colour. The vanadium(III) centre is surrounded by two Me$_3$P ligands, which is supported



Scheme 3. Plausible intramolecular interactions in MAO activated complexes.

by electron-spray mass spectrometry and solubility properties. Due to the paramagnetic nature of **1**–**4** (two unpaired electrons, d^2-configuration), informative NMR spectra could not be obtained but the complexes were thoroughly characterised by EI (Electron Impact) and ESI (Electron Spray) mass spectrometry, IR spectroscopy and elemental analyses. Electron impact mass spectra show only ligand fragments, whereas the electron spray technique provides sufficient data for the determination of the chemical composition.

In contrast to the vanadium derivatives, the resulting structure of the chromium complexes described in this work strongly depends on the nature of the cyclopentadienyl ligand. For the synthesis of chromium compounds both lithium and potassium cyclopentadienides are suitable reagents, though the use of potassium salts is favourable for practical reasons, e.g. because of an easier KCl versus LiCl removal from the reaction mixture. The colour of the reaction mixture is blue to sea-blue in all cases and the products formed remain in solution. Once isolated, complexes **6**–**8** are no longer soluble in toluene and can be redissolved only in THF after prolonged stirring at room temperature. ESI MS data show peaks that are heavier than the mass of possible dimeric species. The IR spectra provide evidence for a coordinative $N \rightarrow Cr$ interaction (absorption band at 430–500 cm^{-1}). We speculate, therefore, that compounds **6**–**8** are coordinatively formed polymers. An analogous polymeric composition has been suggested for $[CpCH_2CH_2N\textit{i}\text{-}Pr_2]CrCl_2$ [12]. On the contrary, the isolated complexes **5** and **9** differ from **6**–**8** both in colour and solubility; **5** and **9** are green powders, while **6**–**8** are deep blue materials. The results of an ESI MS investigation of **5** and **9** imply a dimeric structure of these compounds. The absence of the $N \rightarrow Cr$ absorption in the IR spectra at 430–500 cm^{-1} and a new band at 559 cm^{-1} for **5** and 542 cm^{-1} for **9** stemming from the bridging Cr–Cl–Cr fragment support this conclusion [12]. Unfortunately, our efforts to obtain diffraction-quality single crystals of the complexes under discussion have failed so far.

2.3. Ethylene polymerisation studies

The preparative organovanadium and -chromium chemistry described in the preceding section was undertaken in part to provide precursors for an investigation of the catalytic polymerisation of ethylene in the presence of methylalumoxane (MAO), being suitable to roughly estimate the primary catalytic properties. Another reason we decided to take a closer look at complexes with aminophosphanyl moiety at the cyclopentadienyl ring, is the possibility of a CGC-analogous complex geometry: while there is no *intra*molecular coordination between the metal and the diethylamino substituent at the phosphorus group observed in the neutral compounds $[Cp^R(R^1PNEt_2)]MCl_2$ ($M = V(Me_3P)_2$, Cr), an intra- and/or intermolecular interaction in the catalytically active cationic species could however take place (Scheme 3).

The presence of these interactions might create a possibility to control the polymerisation process thermally and in fact to tune the properties of the polymers obtained. The catalytic properties of the left species (Scheme 3) in the equilibrium should be different from those of the species on the right side. A first example of such systems is already reported for zirconocene catalysts [18].

The polymers obtained with catalysts **1**–**9**/MAO are highly linear polyethylene having a melting point (DSC) in a range from 137–140 °C and a high melting enthalpy of 180–250 $J\ g^{-1}$. The molecular weights depend strongly on the polymerisation temperature ranging from 10^5 to $4.5 \times 10^6\ g\ mol^{-1}$. Our main objective, however, was to compare the polymerisation activity of various organovanadium and organochromium compounds and we have not investigated the morphology and molecular weight distributions in detail.

The results of ethylene polymerisation with vanadium complexes/MAO are presented in Table 1.

All studied organovanadium complexes show moderate activity in ethylene polymerisation, the most interesting feature being reciprocal dependence on the polymerisation temperature. Such behaviour might be attributed to the dissociation of the phosphane ligands from vanadium, which leads to a disproportionation of the V(III)-centre and decreases activity. This could account for the fact that our vanadium based catalytic systems quickly deactivate during the polymerisation process.

Although the activity range of the investigated catalysts is quite narrow, one may recognise a tendency that more sterically encumbered and electron rich complexes are more active in the polymerisation of ethylene, the highest activity being observed for the Me_4C_5- and fluorenyl derivatives. Isoelectronic non-substituted vanadium compounds, e.g. $CpVCl_2(Me_3P)_2$, show considerably lower activity under similar polymerisation conditions [19].

Some of the chromium complexes described here show higher catalytic activity than their vanadium analogues. The data obtained for **5**, **7**–**9** are collected in Table 2.

Analogously to the organovanadium catalysts (vide supra) the polymerisation activity shows a dependence (reciprocal) on the polymerisation temperature, Al:Cr ratio and the substitution pattern of the cyclopentadienyl ligand. Again, the highest activities are observed for complexes bearing Me_4C_5- and fluorenyl ligands. This observation is in good agreement with the results reported by Jolly and co-workers [12].

Table 1
Results of ethylene polymerisation with vanadium complexes **1**–**4** [a]

Catalyst	Al:V [b]	$T_{Pol.}$, °C	Activity [c]
[{*t*-BuCp(*t*-Bu)PNEt$_2$}]-VCl$_2$(PMe$_3$)$_2$ (**1**)	500	20	25
1	2000	20	40
1	500	50	25
1	2000	50	27
[{Me$_4$Cp(*t*-Bu)PNEt$_2$}]-VCl$_2$(PMe$_3$)$_2$ (**2**)	500	20	35
2	2000	20	46
2	500	50	24
2	2000	50	33
[{Ind(*t*-Bu)PNEt$_2$}]-VCl$_2$(PMe$_3$)$_2$ (**3**)	500	20	31
3	2000	20	37
3	500	50	13
3	2000	50	15
[{Flu(*t*-Bu)PNEt$_2$}]-VCl$_2$(PMe$_3$)$_2$ (**4**)	500	20	25
4	2000	20	50
4	500	50	25
4	2000	50	44

[a] Toluene (50 ml), ethene (3 bar), $C_{catalyst} = 2 \times 10^{-5}$ mol l^{-1}, $n_{catalyst} = 1$ μmol, $t = 30$ min.
[b] Catalyst preformation 30 min in the absence of monomer.
[c] Activity = kg PE mol [V]$^{-1}$ h^{-1} bar^{-1}.

Table 2
Polymerisation of ethylene with chromium complexes **5**, **7**–**9** [a]

Catalyst	Al:Cr [b]	$T_{Pol.}$ (°C)	Activity [c]
[{(*t*-Bu)Cp(*t*-Bu)PNEt$_2$}]-CrCl$_2$ (**5**)	500	20	30
5	2000	20	62
5	500	50	6.8
5	2000	50	10.8
[{Me$_4$Cp(*t*-Bu)PNEt$_2$}]-CrCl$_2$ (**7**)	500	20	130
7	2000	20	286
7	500	50	50
7	2000	50	95
[{Ind(*t*-Bu)PNEt$_2$}]CrCl$_2$ (**8**)	500	20	3.3
8	2000	20	15.3
8	500	50	1.7
8	2000	50	2.3
[{Flu(*t*-Bu)PNEt$_2$}]CrCl$_2$ (**9**)	500	20	32
9	2000	20	41
9	500	50	24
9	2000	50	35

[a] Toluene (50 ml), ethene (3 bar), $C_{catalyst} = 2 \times 10^{-5}$ mol l^{-1}, $n_{catalyst} = 1$ μmol, $t = 30$ min.
[b] Catalyst preformation 30 min in the absence of monomer.
[c] Activity = kg PE mol [Cr]$^{-1}$·h^{-1} bar^{-1}.

A better catalytic performance of the complexes at room temperature than at elevated temperatures can be explained by taking into consideration the assumption that chromium complexes with a coordinated donor ligand show lower alkene insertion barriers, thus resulting in better activities, than the systems without a donor ligand [20]. It is worth mentioning that most chromium complexes described here are oligomeric and/or polymeric organometallic materials which react with MAO in toluene to give a suspension and not a clear solution, i.e. certain intermolecular interactions between different chromium species remain after reaction with MAO. Moreover, when polymerisation is conducted using the suspension, ethylene consumption is higher than in the case of a clear catalyst solution. Such heterogeneous character of the catalytic system could stem, in our opinion, from an intermolecular coordination of the nitrogen atom of the Et$_2$NP(*t*-Bu)Cp-unit to the chromium cationic centre of a further molecule. The limited stability of such coordinative oligomers would account for the lower catalytic performance at elevated temperatures.

We sought a proof of this hypothesis and investigated the polymerisation behaviour of complex **6** having a methyl group at the phosphorus atom instead of a tertiary butyl one, which should result in less steric demand and, therefore, in a stronger intermolecular coordinative interaction.

Compound **6**, when activated with MAO, produces polyethylene with activities comparable to those observed for metallocenes such as Cp_2ZrCl_2. The data are collected in Table 3. The catalyst **6**/MAO is more active than the others reported here and shows increasing activities in the temperature range from 20 to 50 °C at a constant monomer concentration (0.34 mol l^{-1}) (Table 3; entries 2, 4 and 9) [21]. When polymerisation is conducted at higher temperatures (70 and 100 °C), the catalyst structure changes leading to a decrease of catalytic performance, which is illustrated by entries 8 and 9. The ethylene consumption is thus much higher in the beginning of the polymerisation than in the end of the reaction. The molar mass of the polymer produced under these conditions shows strong dependency on the reaction temperature. At 30 °C (entry 2) ultrahigh molecular weight polymer is obtained, while at 70 °C the molar mass of the polymer is substantially reduced (500 kg mol^{-1}).

When the polymerisation temperature was kept constant (50 °C) and ethene pressure was varied, the activity of **6**/MAO increases with increasing monomer concentration (entries 3, 5 and 6). A clear correlation

Table 3
Polymerisation of ethylene with **6**/MAO [a]

Run	Al:Cr	T_P (°C)	t (min)	$P_{(C2H4)}$ (bar)	Activity [b]	M_w (g mol^{-1})	Remarks
1	500	20	30	2.0	1120	4.1×10^6 [c]	
2	2000	30	30	2.8	846	2.6×10^6 [c]	
3	2000	50	30	3.5	2080	1.1×10^6	
4	2000	50	30	3.5	1320	6.0×10^5	Clear solution
5	2000	50	45	2.8	646	1.5×10^6	
6	2000	50	30	4.5	3793	1.6×10^6	
7	500	50	20	4.5	758	2.4×10^6	
8	2000	70	4	4.5	5178	5.2×10^5	
9	2000	70	30	4.5	576	3.8×10^5	
10	500	100	30	15	73	10^5 [c]	
11	2000 [d]	50	30	4.5	1453	n.d.	

[a] Toluene (50–100 ml), $n_{catalyst} = 1$–5 μmol.

[b] Activity = kg PE mol $[M]^{-1}$ h^{-1} bar^{-1}.

[c] Determined viscosimetrically in *o*-dichlorobenzene at 140 °C.

[d] Polymerisation with Cp_2ZrCl_2.

between the monomer concentration and the molecular weight of the polymer is missing, which indicates the attendance of both β-hydride elimination and β-hydride transfer to the monomer as possible chain termination reactions. The concentration of MAO also has considerable impact on catalyst **6**; significantly higher catalytic activities are recorded with Al:Cr ratio = 2000 than 500 (entries 6 and 7) combined with the reduction in molar mass of the polymer. A chain transfer mechanism to MAO has been detected for chromium boratabenzene complexes [22] and seems to also be present in our system. The molecular weight distributions are remarkably broad ($M_w/M_n \sim 10$–15) and reflect the heterogeneous nature of the catalyst. Noteworthy is the sensitivity of the chromium catalysts towards impurities, which sometimes results in considerable deviations of results from an experiment to another. An interesting addition to the results above is the observation that the polymerisation activity also depends on the ageing time of the catalyst's stock-suspension, best activities being achieved when the suspension is stored for several hours in toluene, which is illustrated in Fig. 1.

In summary, we have synthesised a series of new vanadium and chromium half-sandwich complexes containing aminophosphanyl substituted cyclopentadienyl ligands. The complexes of vanadium show moderate catalytic activities in ethylene polymerisation, while chromium complexes show activity comparable to metallocene and other chromium systems [12,23].

3. Experimental

All manipulations involving air- and moisture-sensitive materials were carried out by standard Schlenk techniques under an atmosphere of dry Ar. Solvents were dried and distilled prior to use and stored under an inert atmosphere. Mass spectra (EIMS) were recorded on a Varian CH-7a device using electron impact with an ionisation energy of 70 eV; all assignments were made with the reference to the most abundant isotopes. Electron spray mass spectra were obtained on a HP 5989B device of Hewlett Packard. C, H and N elemental analyses were carried out by Microanalytical Division of Philipps-University of Marburg and metal and halogen determinations were conducted in the Microanalytical Laboratory of A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences. IR spectra were recorded on a Nicolet 510 FTIR spectrometer. Differential scanning calorimetry (DSC) measurements were made on Pyrus DSC-7 instrument of Perkin–Elmer. Gel permeation chromatography (GPC) was carried out on a Waters GPC apparatus at 160 °C in trichlorobenzene using LLDPE sample for calibration (Dowlex 2045, $M_w = 120\,000$). Ethylene of polymerisation grade was pur-

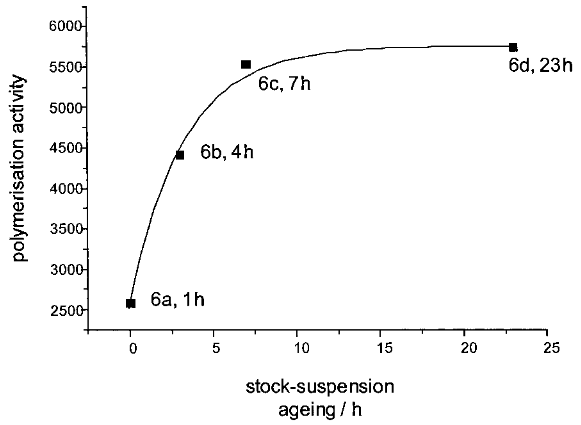


Fig. 1. Polymerisation activity of **6** versus suspension ageing in toluene from a series of tests.

chased from Linde GmbH and was used without further purification. MAO was used as 10%-toluene solution obtained from Witco. Me_3P for in situ preparation of $VCl_3(Me_3P)_2$ [11a] was used as 1 M solution in THF as received from Aldrich. $VCl_3(THF)_3$ [17] and $CrCl_3(THF)_3$ [24] were prepared according to the literature procedures.

*3.1. Preparation of [{t-BuC$_5$H$_3$(t-Bu)PNEt$_2$}VCl$_2$(Me$_3$P)$_2$] (**1**)*

2.0 ml of 1 M Me_3P solution in THF (2 mmol) were added to a suspension of $VCl_3(THF)_3$ (0.73 g, 1.95 mmol) in 30 ml THF and the solution was stirred for 1 h at room temperature (r.t.) [11]. After that the content of the flask was cooled down to − 50 °C and a solution of [*t*-BuC$_5$H$_3$(*t*-Bu)PNEt$_2$]K [15] (0.65 g, 1.95 mmol) in 20 ml THF was added dropwise during 30 min. The colour of the reaction mixture changed from dark-red to blue. Then the reaction mixture was allowed to warm up to r.t. and to stir for 8 h. For work-up, THF was replaced for toluene and KCl was removed by filtration. Volatile components were evaporated in vacuum. The residue was washed with pentane and dried in vacuum. Yield: 0.84 g (77%).

IR (KBr): $\nu = 3054–3000$ [ν(C–H)] s, 2962 [ν(C–CH$_3$)] s, 1461 [ν(C–N)] m, 1415 m, 1364 s, 1299 m, 1203 m, 1160 [ν(C–N–C)$_{as}$] m, 1098 m, 1015 m, 967 vw, 870 [ν(P–N)] m, 808 [ν(P–C)] m, 758 [ν(P–C)] w, 563 [ν(V–Cl)] m. EIMS (70 eV): *m*/*z* (%) = 56 (22) [*t*-Bu], 28 (98) [CH$_2$CH$_2$]. ESIMS: *m*/*z* (%) = 496 (28) [M$^+$ − *t*-Bu], 401 (4) [M$^+$], 168 (78) [C$_3$H$_8$PVCl$_2$]. Anal. Found: C, 49.90; H, 8.79; N, 2.48; V, 9.1; Cl, 12.3. Calc. for $C_{23}H_{49}Cl_2NP_3V$ (533.18): C, 49.83; H, 8.91; N, 2.53; V, 9.2; Cl, 12.8%.

*3.2. Preparation of [{Me$_4$C$_5$(t-Bu)PNEt$_2$}VCl$_2$(Me$_3$P)$_2$] (**2**)*

The product was obtained from 0.93 g (2.92 mmol) of [Me$_4$C$_5$(*t*-Bu)PNEt$_2$]K [15] and 1.09 g (2.92 mmol) of $VCl_3(THF)_3$ in analogy to 3.1. Yield: 0.98 g (60%).

IR (KBr): $\nu = 3095–3000$ [ν(C–H)] s, 2971 [ν(C–CH$_3$)] s, 1301 [ν(C–N)] w, 1206 w, 1105 [ν(C–N–C)$_{as}$] w, 997 w, 877 [ν(P–N)] m, 800 [ν(P–C)] m, 771 [ν(P–C)] w, 583 [ν(V–Cl)] m. EIMS (70 eV): *m*/*z* (%) = 281 (4) [L$^+$], 224 (79) [L$^+$ − *t*-Bu], 160 (43) [*t*-BuPNEt$_2$], 153 (70) [L$^+$ − *t*-Bu-NEt$_2$], 104 (100) [PNEt$_2$]. ESIMS: *m*/*z* (%) = 521 (98) [M$^+$ − 2CH$_4$], 496 (14) [M$^+$ − *t*-Bu], 401 (5) [M$^+$], 318 (100) [M$^+$ − *t*-Bu-PMe$_3$], 168 (78) [C$_3$H$_8$PVCl$_2$]. Anal. Found: C, 49.24; H, 8.77; N, 2.38; V, 9.0; Cl, 12.7. Calc. for $C_{23}H_{49}Cl_2NP_3V$ (533.18): C, 49.83; H, 8.91; N, 2.53; V, 9.2; Cl, 12.8%.

*3.3. Preparation of [{Ind(t-Bu)PNEt$_2$}VCl$_2$(Me$_3$P)$_2$] (**3**)*

The product was obtained from 0.67 g (2.13 mmol) of [Ind(*t*-Bu)PNEt$_2$]K [15] and 0.80 g (2.13 mmol) of $VCl_3(THF)_3$ in analogy to 3.1. Yield: 0.98 g (84%).

IR (KBr): $\nu = 3144–3000$ [ν(C–H)] s, 2967 [ν(C–CH$_3$)] s, 1628 [ν(C = C)$_{Ar}$] m, 1457 [ν(C–N)] m, 1421 m, 1297 m, 1143 [ν(C–N–C)$_{as}$] m, 1017 w, 965 m, 851 [ν(P–N)] w, 808 [ν(P–C)] w, 784 [ν(P–C)] w, 565 [ν(V–Cl)] m. EIMS (70 eV): *m*/*z* (%) = 116 (1) [Ind], 72 (37) [NEt$_2$], 57 (16) [*t*-Bu]. ESIMS: *m*/*z* (%) = 476 (8) [M$^+$ − NEt$_2$], 361 (10) [M$^+$ − Ind], 168 (100) [Cl$_2$VPMe$_2$CH$_2$]. Anal. Found: C, 50.45; H, 7.81; N, 2.44; V, 8.9; Cl, 12.4. Calc. for $C_{23}H_{43}Cl_2NP_3V$ (547.12): C, 50.38; H, 7.90; N, 2.55; V, 9.3; Cl, 12.9%.

*3.4. Preparation of [{Flu(t-Bu)PNEt$_2$}VCl$_2$(Me$_3$P)$_2$] (**4**)*

The product was obtained from 0.50 g (1.75 mmol) of [Flu(*t*-Bu)PNEt$_2$]K [15] and 0.65 g (1.75 mmol) of $VCl_3(THF)_3$ in analogy to 3.1. Yield: 0.79 g (76%).

IR (KBr): $\nu = 3171–3000$ [ν(C–H)] s, 2969 [ν(C–CH$_3$)] s, 1628 [ν(C = C)$_{Ar}$] m, 1447 [ν(C–N)] m, 1299 m, 1106 m, 969 m, 869 [ν(P–N)] w, 785 [ν(P–C)] w, 741[ν(P–C)] w, 551 [ν(V–Cl)] m. EIMS (70 eV): *m*/*z* (%) = 165 (100) [Flu], 56 (52) [C$_4$H$_8$]. ESMS: *m*/*z* (%) = 565 (65) [M$^+$ − 2CH$_4$], 540 (4) [M$^+$ − *t*-Bu], 446 (8) [M$^+$ − 2PMe$_3$], 285 (93) [FluVCl$_2$]. Anal. Found: C, 54.27; H, 7.70; N, 2.21; V, 8.43; Cl, 11.72. Calc. for $C_{27}H_{45}Cl_2NP_3V$ (597.15): C, 54.19; H, 7.58; N, 2.34; V, 8.51; Cl, 11.85%.

*3.5. Preparation of [{t-BuC$_5$H$_3$(t-Bu)PNEt$_2$}CrCl$_2$] (**5**)*

A solution of *n*-BuLi in hexane (1.6 M, 3.35 ml, 5.37 mmol) was added dropwise to a solution of *t*-BuC$_5$H$_4$(*t*-Bu)PNEt$_2$ (1.51 g, 5.37 mmol) in 40 ml THF at − 80 °C. The reaction mixture was stirred for 30 min. After the solution had warmed up to r.t., it was transferred to a drop funnel and slowly added to a suspension of $CrCl_3(THF)_3$ (2.01 g, 5.37 mmol) in 30 ml THF at r.t. The colour of the reaction mixture changed from violet to sea-blue. The reaction mixture was stirred for another 8 h. THF was replaced for toluene and LiCl precipitate was filtered off. Toluene was evaporated in high vacuum and the residual green powder was washed with pentane and dried in vacuum. Yield: 1.73 g (80%).

IR (KBr): $\nu = 3063–3000$ [ν(C–H)] s, 2961 [ν(C–CH$_3$)] s, 1624 vw, 1462 [ν(C–N)] m, 1393 w, 1365 m, 1187 [ν(C–N–C)$_{as}$] m, 1097 m, 1024 m, 939 vw, 813 w, 697 [ν(P–N)] w, 642 [ν(P–C)] m, 559 [ν(Cr–Cl–Cr)] s. EIMS (70 eV): *m*/*z* (%) = 245 (11) [M$^+$ − (*t*-Bu)P(H)NEt$_2$–H], 73 (21) [HNEt$_2$], 57 (100) [*t*-Bu]. ESIMS: *m*/*z* (%) = 789 (7) [M$^+$*2-Me], 762 (9) [(M$^+$*2-Et-Me + 2H) = D*], 702 (14) [D*-4Me], 631 (17) [D*-

$HNEt_2$ = D′], 513 (100) [D′-NEt_2–MeP], 402 (15) [M^+], 370 (20) [$M^+ - 2CH_4$], 315 (98) [M^+ − NEt_2–Me], 297 (100) [$M^+ - H_2PNEt_2$], 281 (7) [L^+]. Anal. Found: C, 50.52; H, 7.83; N, 3.38; Cr, 12.3; Cl, 17.9. Calc. for $C_{17}H_{31}Cl_2CrNP$ (403.31): C, 50.63; H, 7.75; N, 3.47; Cr, 12.9; Cl, 17.6%.

3.6. Preparation of [{Me_4C_5(Me)$PNEt_2$}$CrCl_2$] (**6**)

The product was obtained from 6.28 g (27.66 mmol) of Me_4C_5H(Me)$PNEt_2$, 17.3 ml of 1.6 M *n*-BuLi in hexane (27.66 mmol) and 10.36 g (27.66 mmol) of $CrCl_3(THF)_3$ in analogy to 3.5. Yield: 8.4 g (85%).

IR (KBr): ν = 3023–3000 [ν(C–H)] s, 2968 [ν(C–CH_3)] s, 2407 m, 1623 m, 1453 [ν(C–N)] m, 1384 m, 1298 m, 1207 w, 1105 s, 1063 s, 1022 s, 889 vw, 847 w, 792 [ν(P–N)] m, 744 [ν(P–C)] w, 480 [ν(Cr–Cl)] m, 468 [ν(Cr–N)] m. EIMS (70 eV): *m*/*z* (%) = 330 (10) [M^+ − Et], 243 (20) [M^+ − Me$PNEt_2$], 121 (100) [Me_4Cp], 105 (80) [Me_2CpCH_2]. ESIMS: *m*/*z* (%) = 722 (2) [M*2], 331 (20) [$M^+ - NEt_2$], 238 (100) [Me_4Cp(*t*-Bu)$PNEt_2$ = L], 207 (75) [L − 2Me-H)]. Anal. Found: C, 47.67; H, 7.81; N, 3.83; Cr, 13.5; Cl, 18.4. Calc. for $C_{15}H_{29}Cl_2CrNP$ (377.27): C, 47.75; H, 7.75; N, 3.71; Cr, 13.8; Cl, 18.8%.

3.7. Preparation of [{Me_4C_5(t-Bu)$PNEt_2$}$CrCl_2$] (**7**)

The product was obtained from 2.44 g (9.07 mmol) of [Me_4C_5(*t*-Bu)$PNEt_2$]K in 30 ml THF and 3.44 g (9.07 mmol) of $CrCl_3(THF)_3$ in 50 ml THF in analogy to 3.5. Yield: 2.3 g (63%).

IR (KBr): ν = 3111–3000 [ν(C–H)] m, 2954 [ν(C–CH_3)] m, 2905 [ν(C–H)] m, 2848 [ν(C–H)] m, 1478 m, 1461 [ν(C–N)] m, 1378 m, 1362 m, 1251 s, 1157 [$\nu(C–N–C)_{as}$] m, 1251 s, 1111 s, 1070 m, 959 vw, 734 [ν(P–N)] w, 670 [ν(P–C)] w, 472 [ν(Cr–Cl)] m, 429 [ν(Cr–N)] m. EIMS (70 eV): *m*/*z* (%) = 359 (20) [M^+ − 2Me + H], 274 (28) [Me_4CpP(H)$CrCl_2$], 122 (20) [Me_4Cp], 72 (2) [NEt_2], 57 (100) [*t*-Bu]. ESIMS: *m*/*z* (%) = 928 (1) [M^+*3-L], 806 (3) [M^+*2], 329 (33) [$M^+ - NEt_2$], 160 (32) [*t*-Bu$PNEt_2$]. Anal. Found: C, 50.55; H, 7.83; N, 3.52; Cr, 12.5; Cl, 17.9. Calc. for $C_{17}H_{31}Cl_2CrNP$ (403.31): C, 50.63; H, 7.75; N, 3.47; Cr, 12.9; Cl, 17.6%.

3.8. Preparation of [{Ind(t-Bu)$PNEt_2$}$CrCl_2$] (**8**)

The product was obtained from 3.21 g (10.24 mmol) of [Ind(*t*-Bu)$PNEt_2$]K [15] and 3.83 g (10.24 mmol) of $CrCl_3(THF)_3$ in analogy to 3.7. Yield: 3.7 g (92%).

IR (KBr): ν = 3161–3000 [ν(C–H)] s, 2962 [ν(C–CH_3)] s, 1626 [$\nu(C=C)_{Ar}$] m,1446 [ν(C–N)] m, 1421 m, 1283 m, 1144 [$\nu(C–N–C)_{as}$] s, 1116 m, 1019 m, 958 [$\nu(=C–H)_{Ar}$] m, 743 [ν(P–N)] m, 687 [ν(P–C)] m, 496 [ν(Cr–N)] m. EIMS (70 eV): *m*/*z* (%) = 115 (19) [Ind], 57 (32) [*t*-Bu]. ESIMS: *m*/*z* (%) = 913 (12) [M^+*3-L], 792 (5) [M^+*2], 747 (9) [M^+*2-3Me], 396 (33) [M^+], 369 (30) [M^+ − Et]. Anal. Found: C, 51.51; H, 6.47; N, 3.48; Cr, 13.5; Cl, 18.2. Calc. for $C_{17}H_{25}Cl_2CrNP$ (396.05): C, 51.40; H, 6.34; N, 3.53; Cr, 13.1; Cl, 17.9%.

3.9. Preparation of [{Flu(t-Bu)$PNEt_2$}$CrCl_2$] (**9**)

The product was obtained from 0.50 g (1.75 mmol) of [Flu(*t*-Bu)$PNEt_2$]K [15] and 0.51 g (1.75 mmol) of $CrCl_3(THF)_3$ in analogy to 3.7. Yield: 0.52 g (87%).

IR (KBr), ν (cm^{-1}): 3273–3000 [ν(C–H)] s, 2975 [ν(C–CH_3)] s, 1625 [$\nu(C=C)_{Ar}$] m, 1473 w, 1447 [ν(C–N)] w, 1298 w, 1153 [ν(C–N)] w, 1152 [ν(C–N–C)] w, 1095 w, 1028 w, 740 [ν(P–N)] m, 675 [ν(P–C)] m, 542 [ν(Cr–Cl–Cr)] m. EIMS (70 eV): *m*/*z* (%) = 165 (63) [Flu], 58 (56) [*t*-BuH]. ESIMS: *m*/*z* (%) = 894 (8) [M^+ *2], 822 (13) [M^+*2-NEt_2], 765 (11) [M^+*2-NEt_2-*t*Bu], 447 (30) [M^+], 418 (34) [M^+ − Et], 274 (68) [L]. Anal. Found: C, 56.50; H, 5.93; N, 3.24; Cr, 11.8; Cl, 15.3. Calc. for $C_{21}H_{27}Cl_2CrNP$ (396.05): C, 56.39; H, 6.08; N, 3.13; Cr, 11.6; Cl, 15.8%.

3.10. Polymerisation of ethylene

Polymerisation of ethylene was conducted in all cases in toluene suspension either in a 80 ml glass reactor, or a 300 ml stainless steel autoclave, both equipped with a magnetic stirrer and monomer feed device or a 1 l glass reactor equipped with a propeller-like stirrer (Büchi). Monomer consumption, inside temperature, and pressure were kept constant and controlled by real time monitoring. The stirring speed was 600 rpm and the amount of toluene 200 ml. The reactor was thoroughly dried in vacuum, thereafter charged with toluene, and Ar was replaced for ethylene by feeding ethylene three to four times through the apparatus. Triisobutylalane was optionally used as a scavenger. Then the reactor was charged with an activated catalyst solution or suspension (in case of vanadium catalysts 30 min activation with MAO, for chromium catalysts the activation was performed prior to start the polymerisation). The temperature of the reactor content was brought to the desired value and ethylene feed was maintained during the period of the reaction at a constant pressure. Usually, immediate formation of a polymer precipitate is observed. The polymerisation was stopped by adding 1 ml of methanol. The polymer was filtered of, washed with MeOH, 10% HCl, water, again MeOH, and dried in a vacuum oven at 70 °C to constant weight.

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