Transition Metal Complexes Containing Functionalized Organoimido and Phosphaneiminato Ligands

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Received October 21st, 2002.

Abstract. Two different types of modified imido and phosphaneiminato ligands are investigated, namely chelate ligands and redoxfunctionalised ligands. The first examples of di(organoimido)chromium as well as di(phosphaneiminato)titanium and niobium chelates are described. Furthermore, the first complexes containing redox-functionalised organoimido ligands are presented, together with the first structurally characterised redox-functionalised phosphaneiminato complex. Compounds of the type $[(RN)_2M-(CH_2Ph)_2]$ (M = Cr, Mo) are used as catalysts for the (co-)polymerisation of the polar olefins methyl methacrylate, acrylonitrile and vinyl acetate. A range of X-ray crystal structure determinations provide clear evidence for the quantum-chemical result that, similar to organoimido complexes, the potential energy well for the angle at the nitrogen atom is very shallow for phosphaneiminato complexes.

Keywords: Titanium; Niobium; Chromium; Molybdenum; Iron; Imido complexes; Phosphaneiminato complexes; Chelate complexes; Ferrocenes

Übergangsmetall-Komplexe mit funktionalisierten Organoimido- und Phosphaniminato-Liganden

Inhaltsübersicht. Zwei unterschiedliche Typen modifizierter Imidound Phosphaniminato-Liganden werden untersucht, nämlich Chelatliganden und redoxfunktionalisierte Liganden. Die ersten Beispiele für Di(organoimido)chrom- sowie Di(phosphaniminato)titan- und -niob-Chelate werden beschrieben. Weiterhin werden die ersten Komplexe mit redoxfunktionaliserten Organoimido-Liganden sowie der erste strukturell charakterisierte redoxfunktionalisierte Phosphaniminato-Komplex vorgestellt. Verbindungen des Typs $[(RN)_2M(CH_2Ph)_2]$ (M = Cr, Mo) werden als Katalysatoren für die (Co-)Polymerisation der polaren Olefine Methylmethacrylat, Acrylnitril und Vinylacetat benutzt. Eine Reihe von Röntgenstrukturanalysen liefert klare experimentelle Belege für den quantenchemischen Befund, daß, ähnlich wie bei Imido-Komplexen, die Potentialenergiemulde für den Winkel am Stickstoffatom in Phosphaniminato-Komplexen sehr flach ist.

1 Introduction

Organoimido [1] and phosphaneiminato ligands [2] may be viewed as anionic 6-electron donors of the $1\sigma 2\pi$ type, similar to cyclopentadienyl ligands. This electronic analogy has repercussions on the chemistry of complexes containing such ligands and will provide a leitmotif of this paper.

The chemistry of organoimido [3] and phosphaneiminato complexes [4] has clearly attained a state of maturity now, and the relevance of such compounds for technologically important areas of applied chemistry, such as, for example, olefin polymerisation [5], is beginning to emerge. This devel-

* Prof. Dr. U. Siemeling Universität Kassel Fachbereich 18 (Physik) D-34109 Kassel Fax: +49-(0)561-8044777 E-mail: siemeling@uni-kassel.de opment has spurred our investigations concerning the design of *functionalised* organoimido and phosphaneiminato ligands, which, in comparison to the related functionalised cyclopentadienyl ligands [6], is only at its beginning. We have studied two classes of functionalised ligands in this context, namely (i) chelate ligands (i. e. ligands functionalised with themselves) and (ii) redox-functionalised ligands.

2 Results

2.1 Chelate Complexes

Chelate ligands with two identical metal binding regimes connected by a suitable linker represent the simplest type of functionalised ligands. The chelate effect [7] generally leads to greater complex stability. Furthermore, chelates with a rigid ligand architecture may have special stereochemical properties absent in their unchelated analogues. Finally, the reactivity of chelates may be influenced by the "bite angle" of the chelate ligand. In the chemistry of di(cyclopentadienyl) chelates, these different aspects, and their interplay, have already been put to good use, an excellent example being the stereospecific polymerisation of α -olefins by *ansa*-zirconocene derivatives [8].

2.1.1 Di(organoimido) chelates

There is a well-established isolobal relationship between the metal-ligand fragments $[(C_5R_5)_2M]$ (M = Group 4 metal) and $[(RN)_2M']$ (M' = Group 6 metal) [9], and this has been used to rationalise the finding that, similar to titanocene and zirconocene dichloride, complexes of the type [(RN)₂CrCl₂] and [(RN)₂MoCl₂] polymerise ethylene in the presence of Et₂AlCl, the chromium system being more active than the molybdenum one [10]. $[(tBuN)_2Cr(CH_2Ph)_2]$ has been reported to be an active ethylene polymerisation catalyst in the presence of a suitable activator. The cationic η^2 -benzyl species $[(tBuN)_2Cr(CH_2Ph)]^+$ has been put forward as the catalytically active species [10a, 11]. In this context $[(tBuN)_2Cr(CH_2Ph)]^+$ corresponds to cations of the type $[(C_5R_5)_2Zr(CH_2Ph)]^+$, which have been demonstrated to exhibit excellent polymerisation properties [12]. A recent quantum-chemical study, however, has advocated a species containing a reduced chromium atom as the active catalyst [13].

Our efforts to produce isolobal analogues of *ansa*-titanocene and *ansa*-zirconocene derivatives have resulted in the synthesis of the first di(organoimido)chromium chelates as well as closely related Mo compounds (Scheme 1).

structures The of [(NCMe₂CH₂CH₂CMe₂N)Cr- $(OSiMe_3)_2$] (2), $[(NCMe_2CH_2CH_2CMe_2N)Cr(CH_2Ph)_2]$ (4), [(NCMe₂CH₂CH₂CMe₂N)MoCl₂(DME)] (5) and [(NCMe₂CH₂CH₂CMe₂N)Mo(CH₂Ph)₂] (6) have been determined by X-ray crystallography and are shown in Figures 1 - 4. The coordination of the metal atom of 5 is best described as pseudo-octahedral and closely resembles that of a TADDAMIN-derived molybdenum chelate [(TADDA-MINat)MoCl₂(DME)], which also contains a seven-membered molybdacycle [14]. The coordination of the metal atom of the other complexes is pseudo-tetrahedral. A common feature of all these compounds is the remarkably small N-M-N bite angle (ca. 100°) as well as the strong deviation of the M–N–C angle (< 150°) from linearity. These values are in contrast to those of open-chain analogues such as $[(tBuN)_2Cr(CH_2Ph)_2]$ $[N-Cr-N 116.09(8)^\circ]$, Cr-N-C 166.07(13) and 160.60(13)°] [11], [(tBuN)₂-[N-Mo-N 113.64(7)°, Mo-N-C $Mo(CH_2Ph)_2$] 160.00(12)and 162.83(12)°] [15] and [(2,6 $iPr_2C_6H_3N(tBuN)MoCl_2(DME)$] [N-Mo-N 105.91(9)°, Mo-N-C_{aryl} 174.3(2), Mo-N-C_{alkyl} 157.9(2)°] [16]. Each of the dibenzyl complexes, whether chelate or not, contains one η^1 -coordinated and one η^2 -coordinated CH₂Ph ligand.

We have been able to confirm the results concerning the ethylene polymerisation behaviour of $[(tBuN)_2Cr(CH_2Ph)_2]$ [10a, 11], using this compound in a concentration of



Scheme 1 Synthesis of di(organoimido) chelates of chromium and molybdenum. Reagents and conditions: (i) *n*BuLi (2 equiv.), Me₃SiCl (2 equiv.), diethyl ether; (ii) CrO_2Cl_2 (0.5 equiv.), hexane; (iii) BCl₃ (2 equiv.), dichloromethane; (iv) PhMgCl (2 equiv.), Et₂O; (v) Na₂MoO₄ (1 equiv.), NEt₃ (4 equiv.), Me₃SiCl (8 equiv.), DME; (vi) PhMgCl (2 equiv.), Et₂O.

0.5 mmol/L in toluene or methylcyclohexane with 100 equivalents of *i*Bu₃Al in conjunction with 1 equivalent of $[CPh_3][B(C_6F_5)_4]$ at 30 °C under 4 bar of ethylene. This catalyst formulation produces linear polyethylene. After a polymerisation time of 1 h its activity has been determined as 19.5 g/(mmol·h·bar). Under essentially identical conditions the chelate [(NCMe_2CH_2CH_2CMe_2N)Cr(CH_2Ph)_2] (4) leads to a more active catalyst [47.3 g/(mmol·h·bar)]. This result may be due to both steric and electronic effects, similar to the so-called constrained-geometry olefin polymerisation catalysts [6c].

Owing to their comparatively low Lewis acidity, catalysts based on Group 6 metals may be more tolerant towards



Fig. 1 Molecular structure of $[(NCMe_2CH_2CH_2CMe_2N)Cr-(OSiMe_3)_2]$ (2) in the crystal. Selected bond lengths/pm and angles/°:

 $\begin{array}{l} Cr(1)-N(1) \ 164.5(2), \ Cr(1)-O(1) \ 181.1(2), \ Si(1)-O(1) \ 164.6(2), \ N(1)-C(1) \ 145.6(4); \ O(1)-Cr(1)-O(1A) \ 114.45(14), \ Si(1)-O(1)-Cr(1) \ 136.93(13), \ N(1)-Cr(1)-N(1A) \ 102.83(17), \ Cr(1)-N(1)-C(1) \ 147.8(2). \end{array}$



Fig. 2 Molecular structure of $[(NCMe_2CH_2CH_2CMe_2N)-Cr(CH_2Ph)_2]$ (4) in the crystal. Selected bond lengths/pm and angles/°:

polar, functionalised olefins than Group 4 metal systems. For example, complexes of the type $[(RN)_2CrCl_2]$ have been shown to tolerate ester groups in the cyclopropanation of olefins [17]. We have therefore investigated chromium and molybdenum chelates in the polymerisation of polar olefins, namely methyl methacrylate (MMA), acrylonitrile (AN), and vinyl acetate (VA). Their stereospecific polymerisation



Fig. 3 Molecular structure of $[(NCMe_2CH_2CH_2CMe_2N)MoCl_2-(DME)]$ (5) in the crystal. Selected bond lengths/pm and angles/°: Mo(1)-N(1) 172.8(4), Mo(1)-N(2) 173.6(3), Mo(1)-O(1) 239.3(3), Mo(1)-O(2) 240.5(3), Mo(1)-Cl(1) 242.84(12), Mo(1)-Cl(2) 241.36(12), N(1)-C(1) 145.1(5), N(2)-C(4) 145.5(5); N(1)-Mo(1)-N(2) 99.46(17), Cl(1)-Mo(1)-Cl(2) 158.38(4), O(1)-Mo(1)-O(2) 68.67(10), Mo(1)-N(1)-C(1) 149.8(3), Mo(1)-N(2)-C(4) 147.9(3).



Fig. 4 Molecular structure of $[(NCMe_2CH_2CH_2CMe_2N)Mo-(CH_2Ph)_2]$ (6) in the crystal. Selected bond lengths/pm and angles/°: Mo(1)-N(1) 173.56(8), Mo(1)-N(2) 173.65(8), Mo(1)-C(9) 217.19(10), Mo(1)-C(10) 252.31(9), Mo(1)-C(16) 218.77(11), N(1)-C(1) 145.40(13), N(2)-C(6) 145.59(13); N(1)-Mo(1)-N(2) 102.42(4), Mo(1)-N(1)-C(1) 146.11(7), Mo(1)-N(2)-C(6) 146.38(7), C(9)-Mo(1)-C(10) 35.33(4), Mo(1)-C(16)-C(10) 85.56(6), C(9)-Mo(1)-C(16) 127.68(4), Mo(1)-C(16)-C(17) 112.13(7).

with Ziegler-Natta type Group 4 *ansa*-metallocene catalysts is fraught with many problems [18].

Both the chelate $[(NCMe_2CH_2CMe_2N)Cr(CH_2Ph)_2]$ (4) and the open-chain analogue $[(tBuN)_2Cr(CH_2Ph)_2]$ do not polymerise methyl methacrylate under the conditions used for ethylene polymerisation. However, polymerisation does occur in the absence of any activator. After 24 h ca. 23 % conversion is reached with the chelate 4, whereas only ca. 14 % is observed with $[(tBuN)_2Cr(CH_2Ph)_2]$, since this



Fig. 5 Conversion/time diagram for the polymerisation of MMA with $[(NCMe_2CH_2CH_2CMe_2N)Cr(CH_2Ph)_2]$ (4). Conditions: $[Cr] = 2.0 \cdot 10^{-4}$ M, $T_P = r.t.$



Fig. 6 Conversion/time diagram for the polymerisation of MMA with $[(tBuN)_2Cr(CH_2Ph)_2]$. Conditions: $[Cr] = 2.0 \cdot 10^{-4}$ M, $T_P = r.t.$

ceases to be productive after ca. 6 h (Figs. 5 and 6). So, the conversion/time diagrams prove that the chelate **4** is more stable than the open-chain analogue and therefore remains active for prolonged periods of time. The molybdenum chelate $[(NCMe_2CH_2CH_2CMe_2N)Mo(CH_2Ph)_2]$ (6) also polymerises methyl methacrylate, albeit with much lower efficiency than its chromium analogue (3 % conversion after 6 h).

The enhanced stability of the chromium chelate **4** is also reflected in the temperature dependence. The maximum conversion is reached at ca. 50 °C with **4** (Fig. 7), whereas the less robust open-chain analogue $[(tBuN)_2Cr(CH_2Ph)_2]$ has a slightly lower optimum at ca. 30 °C (Fig. 8). In both cases, a remarkably narrow maximum is followed by a steep decrease caused by thermal deactivation.

The polymer microstructure has been investigated by ${}^{13}C$ NMR spectroscopy. In all cases studied the PMMA contains syndiotactic pentad sequences, with rather similar results being obtained for the three catalysts $[(tBuN)_2 Cr(CH_2Ph)_2]$, $[(NCMe_2CH_2CH_2CMe_2N)Cr(CH_2Ph)_2]$ (4) and $[(NCMe_2CH_2CH_2CMe_2N)Mo(CH_2Ph)_2]$ (6). Figs. 9 and 10 show the temperature dependences of the pentad sequences distribution of the polymers obtained by the polymerisation of MMA with the two chromium catalyst. In both cases the percentage of the syndiotactic rrrr pentad



Fig. 7 Temperature dependence of monomer conversion in the polymerisation of MMA with $[(NCMe_2CH_2CH_2CMe_2N)Cr(CH_2Ph)_2]$ (4). Conditions: $[Cr] = 2.0 \cdot 10^{-4} \text{ M}$, [MMA] = 3.12 M, $t_P = 6 \text{ h}$.



Fig. 8 Temperature dependence of monomer conversion in the polymerisation of MMA with [(tBuN)₂Cr(CH₂Ph)₂]. Conditions: [Cr] = $2.0 \cdot 10^{-4}$ M, [MMA] = 3.12 M, t_P = 6 h.



Fig. 9 Temperature dependence of the pentad sequence distribution in the polymerisation of MMA with $[(NCMe_2CH_2CH_2CMe_2N)-Cr(CH_2Ph)_2]$ (4). Conditions: $[Cr] = 2.0 \cdot 10^{-4} \text{ M}$, [MMA] = 3.12 M, $t_P = 6 \text{ h}$.

decreases from more than 60 % at -45 °C to ca. 40 % at 75 °C, that is with increasing polymerisation temperature the polymer becomes more atactic.

The molecular weights M_n obtained with the chromium chelate 4 range from 148000 to 168000 g/mol with a PDI of



Fig. 10 Temperature dependence of pentad sequence distribution in the polymerisation of MMA with $[(tBuN)_2Cr(CH_2Ph)_2]$. Conditions: $[Cr] = 2.0 \cdot 10^{-4} \text{ M}$, [MMA] = 3.12 M, $t_P = 6 \text{ h}$.

1.5. With the open-chain species $[(tBuN)_2Cr(CH_2Ph)_2]$ even higher molecular weights are obtained (195000 – 220000 g/ mol, PDI 1.6). The molybdenum chelate **6** leads to lower molecular weights (101000 – 162000 g/mol) and considerably higher PDI values (3.0 – 4.9).

The polymerisation of acrylonitrile is also possible with these imido complexes, leading to atactic PAN. $[(tBuN)_2Cr(CH_2Ph)_2]$ affords higher molecular weights $(M_n = 219000 - 254000 \text{ g/mol}, \text{PDI } 2.2 - 2.4)$ than the chromium (154000 - 180000 g/mol, PDI 2.0 - 2.2) and molybdenum chelates (57000 - 84000 g/mol, PDI 2.9). Again, the productivity of the Mo complex is much lower than that of the chromium catalysts. 2 - 5% conversion was reached with $[(NCMe_2CH_2CH_2CMe_2N)Mo(CH_2Ph)_2]$ (6), whereas 12 - 20% was obtained with its chromium analogue 4, and 13 - 26% with $[(tBuN)_2Cr(CH_2Ph)_2]$.

The catalytic efficiency has been determined for both chromium compounds as a function of time (Fig. 11). It is defined as the number of polymer chains generated per catalyst molecule. The number of polymer chains can be calculated by dividing the yield of the obtained polymer by the number average molecular weight of the polymer determined by GPC. Obviously, the amount of catalytically active species increases with time, the efficiency rising gradually from small values to ca. 0.8 after several hours. Even after 6 hours only 80 % of the catalyst is active in polymerising AN. The simplest explanation is a composed reaction in which the formation of the active species is involved.

The three catalysts investigated are also able to polymerise vinyl acetate without any added cocatalyst, leading to rather similar results. Conversions of 5-6% were obtained over the course of 24 h.

The chromium compounds are also effective in the copolymerisation of MMA and AN. The copolymer composition was calculated from the percentage of nitrogen in the copolymers by elemental analyses. A copolymerisation diagram shows the dependence of the copolymer composition F_x on the feed mole fraction f_x (Fig. 12). There is always a slight preference for incorporation of MMA, corresponding to only a small deviation from a true random incorporation



Fig. 11 Catalytic efficiency of $[(NCMe_2CH_2CH_2CMe_2N)-Cr(CH_2Ph)_2]$ (4) and $[(tBuN)_2Cr(CH_2Ph)_2]$ in the polymerisation of AN. Conditions: $[Cr] = 2.0 \cdot 10^{-4}$ M, [AN] = 5 M, $T_P = r.t.$



Fig. 12 Copolymer diagram of the copolymerisation of AN and MMA with $[(tBuN)_2Cr(CH_2Ph)_2]$. Conditions: $[Cr] = 2.0 \cdot 10^{-4}$ M, $T_P = r.t.$, $t_P = 5$ h.

of both monomers into the polymer chain, indicated as a dashed line in Figure 12.

The molecular weight distributions of the resulting polymers have been determined by GPC (Fig. 13). When the feed mole fraction of AN was over 50 %, bimodal behaviour was observed. Solubility tests have shown that the minor peak is most likely due to the homopolymer PAN, which, in contrast to PMMA and the copolymer, is insoluble in chloroform. The main peak corresponds to the copolymer and to over 95 % of the measured sample.

Finally, DSC studies prove that copolymers, rather than blends of homopolymers, have been obtained. The low glass transition temperatures T_g in comparison with those of the respective homopolymers, PAN and PMMA, indicate that the products obtained must be copolymers. T_g is dependent on the feed mole fraction and passes through a minimum for both [(*t*BuN)₂Cr(CH₂Ph)₂] and [(NCMe₂CH₂CH₂-CMe₂N)Cr(CH₂Ph)₂] (4) (Fig. 14).

The mechanism of the polymerisation of the polar olefins with these chromium complexes is not yet understood in detail. A light-induced or spontaneous polymerisation of the monomers can be excluded, since they do not poly-



Fig. 13 Dependence of the average molecular weight of the copolymer on the initial monomer ratio. Conditions: $[Cr] = 2.0 \cdot 10^{-4} \text{ M}$, $T_P = \text{ r.t., } t_P = 5 \text{ h.}$



Fig. 14 Glass transition temperature of the polymers obtained from the copolymerisation of AN and MMA as a function of the feed mole fraction. Conditions: $[Cr] = 2.0 \cdot 10^{-4} \text{ M}$, $T_P = \text{ r.t.}$, $t_P = 5 \text{ h}$.

merise in the absence of the chromium species under the conditions employed.

A redox-chemical initiation of a radical polymerisation seems to be possible with chromium(VI) compounds. However, neither chromates nor dichromates led to the polymerisation of the polar monomers. The fact that polymerisation is also achieved with the molybdenum system provides further evidence against a redox-initiated radical mechanism, since molybdenum(VI) is a much weaker oxidant than chromium(VI). Furthermore, the polymerisation results were unaffected by stoichiometric amounts of the radical scavenger 2,6-di-*tert*-butyl-4-methylphenol (BHT).

An anionic polymerisation, which, in contrast to a cationic mechanism, is possible with the electron-poor olefins MMA and AN, is equally unlikely. The high molecular weights obtained, in conjunction with rather low monomer conversion, are not characteristic for anionic polymerisations. Furthermore, isotactic PMMA is obtained by anionic polymerisation in apolar solvents, whereas in our case a syndiotactic polymer is produced.

An insertion polymerisation with a cationic metal centre, similar to that operative in the polymerisation of ethylene, must be excluded, since the activated complexes do not polymerise the polar olefins used. NMR experiments using equimolar amounts of monomer and catalyst so far have failed to shed light on the mechanism. Further mechanistic work is currently in progress and will be reported in due course.

2.1.2 Di(phosphaneiminato) chelates

Di(phosphaneiminato)titanium(IV) complexes of the type $[(tBu_3PN)_2TiX_2]$ (X = Cl, Me) represent the first noncyclopentadienyl, single-site catalysts competitive with derivatives of metallocenes under commercially relevant polymerisation conditions [5b]. Similar to di(organoimido) complexes of the Group 6 metals, they are isolobal analogues of bent metallocene derivatives of the Group 4 metals.

The number of ansa-di(phosphaneiminato) complexes known to date is very small, and no such compound has been described in the chemistry of the Group 4 metals. A convenient method for the synthesis of phosphaneiminato complexes is the metathesis of silvlated iminophosphoranes with metal halides [4]. For example, the reaction of two equivalents of Ph₃P(NSiMe₃) [19] and tBu₃P(NSiMe₃) [5b], respectively, with TiCl₄ affords [(Ph₃PN)₂TiCl₂] and [(tBu₃PN)₂TiCl₂] in 85 % and 91 % yield, respectively. In contrast, the reaction of (Me₃SiN)Ph₂PCH₂CH₂PPh₂-(NSiMe₃) with TiCl₄ does not lead to a di(phosphaneiminato) chelate. Instead, reaction of a CH₂ group with the strongly Lewis acidic metal halide takes place, and a bis(trimethylsilylphosphoranimino) chelate containing one carbon-titanium bond is obtained [20]. A similar reaction takes place between [VCl₃(THF)₃] and (Me₃SiN)Ph₂PCH₂PPh₂-(NSiMe₃) [21]. Dinuclear complexes containing a bridging di(phosphaneiminato) ligand are formed in the reaction of $(Me_3SiN)Ph_2P(CH_2)_{\mu}PPh_2(NSiMe_3)$ with the comparatively weak Lewis acids Cp^*TiF_3 (n = 2) [22] and Cp^*TiCl_3 (n = 1 [23], 2 [24]).

 $(Me_3SiN)tBu_2P(CH_2)_3PtBu_2(NSiMe_3)$ (7) reacts with TiCl₄ in boiling toluene under dilution conditions, affording the di(phosphaneiminato) chelate $[(NtBu_2P(CH_2)_3PtBu_2N)-TiCl_2]$ (8) (Scheme 2). The hydrocarbyl derivatives $[(NtBu_2P(CH_2)_3PtBu_2N)TiMe_2]$ (9) and $[(NtBu_2P(CH_2)_3-PtBu_2N)Ti(CH_2Ph)_2]$ (10) were obtained from 8 by reaction with methyllithium and benzylmagnesium chloride, respectively (Scheme 2).

A single-crystal X-ray structure analysis was performed for **9** and **10** (Figs. 15 and 16).

The Ti-N [9, 183.5(2) and 181.0(2) pm; 10, 180.7(2) and 182.3(2) pm] and P-N distances [9, 158.9(3) and 156.9(2); 10, 158.7(3) and 158.4(3) pm] are very similar to the respective values found for $[(tBu_3PN)_2TiMe_2]$ [5b] and compatible with bond orders close to two. The N-Ti-N bite angle is 114.81(12)° for 9 and 114.17(12)° for 10, which is only slightly smaller than the value of 117.24(11)° found for $[(tBu_3PN)_2TiMe_2]$. This finding suggests that the eightmembered titanacycle present in 8–10 is essentially unstrained. Two quite different Ti-N-P angles are found for both 9 [140.30(19)° vs. 159.82(19)°] and 10 [140.95(17)° vs. 162.35(17)°], while angles of 171.2(2)° and 175.3(2)° have



Scheme 2 Synthesis of di(phosphaneiminato)titanium chelates. Reagents and conditions: (i) Me_3SiN_3 , toluene; (ii) $TiCl_4$, toluene; (iii) 9: MeLi (> 2 equiv.), diethyl ether; 10: PhCH₂MgCl (> 2 equiv.), diethyl ether.



Fig. 15 Molecular structure of $[(NtBu_2P(CH_2)_3PtBu_2N)TiMe_2]$ (9) in the crystal. Selected bond lengths/pm and angles/°:

 $\begin{array}{l} Ti(1)-C(4) \ 212.4(3), \ Ti(1)-C(5) \ 212.8(3), \ P(1)-C(1) \ 181.3(3), \ P(1)-C(6) \\ 186.9(3), \ P(1)-C(10) \ 186.6(3), \ P(2)-C(3) \ 184.7(3), \ P(2)-C(14) \ 186.7(3), \\ P(2)-C(18) \ 185.9(3), \ C(1)-C(2) \ 155.3(5), \ C(2)-C(3) \ 152.3(4); \\ C(4)-Ti(1)-C(5) \ 107.00(15), \ P(1)-C(1)-C(2) \ 115.8(2), \ C(1)-C(2)-C(3) \\ 110.5(3), \ C(2)-C(3)-P(2) \ 114.1(2). \end{array}$

been reported for $[(tBu_3PN)_2TiMe_2]$ [25]. This lends further credence to the quantum-chemical result that the potential energy well for the angle at the nitrogen atom is very shallow for such compounds [2]. A similar structural feature has previously been observed for a related niobium chelate, exhibiting Nb-N-P angles of 145.3(5)° and 168.6(5)° (vide infra).

The markedly different Ti-N-P angles (ca. 140° vs. ca. 160°) found in the structurally characterized alkyl derivatives **9** and **10** should not be interpreted in terms of linear vs. bent phosphaneiminato ligands, but instead reflect the "softness" of the angle at the nitrogen atom.

There is an isolobal relationship between $[(NtBu_2P-(CH_2)_3PtBu_2N)Ti(CH_2Ph)_2]$ (10) and $[(NCMe_2CH_2CH_2-CMe_2N)Cr(CH_2Ph)_2]$ (4). However, in contrast to the chro-



Fig. 16 Molecular structure of $[(NtBu_2P(CH_2)_3PtBu_2N)Ti-(CH_2Ph)_2]$ (10) in the crystal. Selected bond lengths/pm and angles/°:

 $\begin{array}{l} {\rm Ti}(1)-{\rm C}(4)\ 215.7(5),\ {\rm Ti}(1)-{\rm C}(11)\ 216.5(4),\ {\rm P}(1)-{\rm C}(1)\ 180.5(3),\ {\rm P}(1)-{\rm C}(18)\\ 187.0(3),\ {\rm P}(1)-{\rm C}(22)\ 187.4(3),\ {\rm P}(2)-{\rm C}(3)\ 184.0(3),\ {\rm P}(2)-{\rm C}(26)\ 186.0(3),\\ {\rm P}(2)-{\rm C}(30)\ 186.3(3),\ {\rm C}(1)-{\rm C}(2)\ 153.2(4),\ {\rm C}(2)-{\rm C}(3)\ 154.7(4);\\ {\rm C}(4)-{\rm Ti}(1)-{\rm C}(11)\ 105.47(19),\ {\rm P}(1)-{\rm C}(1)-{\rm C}(2)\ 116.6(2),\ {\rm C}(1)-{\rm C}(2)-{\rm C}(3)\\ 111.8(3),\ {\rm C}(2)-{\rm C}(3)-{\rm P}(2)\ 113.7(2).\\ \end{array}$

mium compound the titanium complex does not polymerise polar olefins.

2.2 Redox-functionalised Complexes

The development of compounds with redox-tunable properties is a challenging field of research and is attracting increased interest [26]. So far the main focus has been on host molecules which bear redox-active substituents and can be utilised for the electrochemical detection of ions in solution. A quite different field, which is still in its infancy, is the development of catalysts carrying a redox switch, since such catalysts offer a scope for new aspects and applications in catalysis [27]. The basic principle of redox-switchable transition metal catalysts is straightforward: The oxidation of a redox-active substituent induces a higher electrophilicity and hence a change in reactivity of the catalytically active transition metal centre. Catalyst activity is a crucial factor in olefin polymerisation processes, which is relevant to such varied aspects as polymer microstructure and process engineering.

2.2.1 Imido complexes

We have chosen imido alkylidene complexes of the type $[(DippN)Mo(CHCMe_2Ph)(OR)_2]$ (Dipp = 2,6-diisopropylphenyl) as study objects. Such compounds are olefin metathesis initiators and polymerise strained cycloolefins [28]. Their catalytic activity and chemical selectivity are known to be governed by the electrophilicity of the metal centre [29]. Owing to the well-behaved redox chemistry of



Scheme 3 Synthesis of the redox-functionalised "*Schrock* type" olefin metathesis initiator 15. Reagents and conditions: (i) $[NH_4]_2Mo_2O_7$ (0.25 equiv.), NEt₃ (4 equiv.), Me₃SiCl (5 equiv), DME; (ii) PhMe₂CCH₂MgCl (2 equiv.), Et₂O; triflic acid (3 equiv.), DME; (iv) KOtBu (2 equiv.), Et₂O.

ferrocene [30], the ferrocenyl group (Fc) was used as redoxactive unit.

The ferrocenyl-substituted aniline $FcdippNH_2$ (11) (Fcdipp = 4-ferrocenyl-2,6-diisopropylphenyl) was used as a precursor for the imido alkylidene complex [(FcdippN)Mo(CHCMe₂Ph)(OtBu)₂] (15) by following a well-established strategy (Scheme 3) [29a, 31]. 15 is the first example of a complex belonging to the family of "*Schrock* type" olefin metathesis initiators which contains a ferrocene unit bound to a spectator ligand.

A single-crystal X-ray structure analysis was performed for **13**. A view of the molecule is shown in Figure 17.

The molybdenum atom is coordinated by two imido and two alkyl ligands in a slightly distorted pseudo-tetrahedral environment. Each C_6 ring plane is almost coplanar to the plane of the cyclopentadienyl ring attached to it (dihedral angles are 9.1° and 21.3°, respectively), indicating a con-



Fig. 17 Molecular structure of $[(FcdippN)_2Mo(CH_2Ph)_2]$ (13) in the crystal. Selected bond lengths/pm and angles/°:

Table 1 Formal electrode potentials (vs. ferrocene/ferrocenium) for the oxidation of the ferrocenyl-funtionalised compounds in dichloromethane solution. Conditions: 298 K; nBu_4NPF_6 (0.1 M) supporting electrolyte; Pt disk working electrode, Ag wire pseudoreference electrode, Pt wire counter electrode; scan rate 0.1V/s; solute concentration: 10^{-3} M; confidence limit 0.01 V; ΔE values referenced to FcdippNH₂ (**11**)

Compound	E^{0}/V	$\Delta E/V$	$\Delta E_{\rm p}/{\rm V}$	
FcdippNH ₂ (11) 12 13	-0.10 0.03 -0.02	0.13 0.08	0.07 0.12 0.09	

siderable degree of π -delocalisation over both rings. Such a delocalisation is beneficial for the interaction between the ferrocenyl units and the molybdenum centre, which was investigated by electrochemical methods (Table 1).

The oxidation of the ferrocenyl substituents gives rise to a single two-electron redox wave in the cyclic voltammogram. The half-wave potential of **13** is shifted significantly by +0.08 V with respect to the potential of FcdippNH₂ (**11**). The ferrocene-centred redox reaction of **13** is cathodically shifted by 0.05 V with respect to the corresponding potential of **12**. These results prove that the potentials are indeed sensitive to the fragment bound to the nitrogen atom of the FcdippN group. Consequently, in **13** and related species the molybdenum centre will be sensitive to the ferrocenyl redox state. The electron-donating effect of a ferrocenyl group has been described to be larger than that of OMe, whereas the electron-withdrawing effect of an oxidised ferrocenyl group resembles that of COOMe [26d].



Fig. 18 Molecular structure of [NbCl₃(NPPh₂Fc)₂] (17) in the crystal. Selected bond lengths/pm and angles/°:

The reaction of 13 with three equivalents of triflic acid proceeds cleanly and swiftly affording [(FcdippN)-Mo(CHCMe₂Ph)(OTf)₂(DME)] (14) in good yield. Reaction of 14 with a slight excess of KO*t*Bu yielded crude [(FcdippN)Mo(CHCMe₂Ph)(O*t*Bu)₂] (15) as a brown solid. Only one alkylidene species was formed, as proven by the occurrence of a single signal for the alkylidene H_{α} proton ($\delta = 11.34$ ppm). Unfortunately, despite many efforts, it has not proved possible to obtain the compound sufficiently pure for further studies.

2.2.2 Phosphaneiminato complexes

Reaction of [Me₃SiNPPh₂Fc] (16) with niobium pentachloride in acetonitrile at 70 °C afforded [NbCl₃(NPPh₂Fc)₂] (17) as a yellow solid in 76 % yield. A single-crystal X-ray structure analysis was performed for this compound. A view of the molecule is shown in Fig. 18. The structure is similar to that of $[NbCl_3(NPiPr_3)_2]$ [32] and [NbCl₃(NPPh₃)₂] [33]. The Nb atom is coordinated by three chloro and two phospaneiminato ligands in a distorted trigonal-bipyramidal arrangement. Two Cl atoms occupy the axial positions forming an angle of 166.17(9)° with the Nb atom, which lies in the plane of the equatorial atoms N(1), N(2) and Cl(3). Both the niobium-nitrogen [Nb(1)-N(1)]184.5(7), Nb(2)-N(2) 183.5(8) pm] and the phosphorus-nitrogen distances [P(1)-N(1) 159.7(8), P(2)-N(2) 159.5(8) pm] are in accord with double bonds.

A striking feature of the structure is the fact that the Nb–N–P bond angles are quite different, namely 145.3(5)° at N(1) and 168.6(5)° at N(2). A similar feature has been observed for the related titanium complexes **9** and **10** (vide supra). The values reported for [NbCl₃(NPPh₃)₂] and [NbCl₃(NP*i*Pr₃)₂] are 156.4(3)/161.9(3)° and 168.5(5)/ 168.2(4)°. The Nb–N and the P–N bond lengths of **17** are identical for both ligands within experimental error and



Fig. 19 Molecular structure of $[NbCl_3{[NPPh_2(C_5H_4)]_2Fe}]$ (18) in the crystal. Selected bond lengths/pm and angles/°:

also compare well with the respective values observed for $[NbCl_3(NPPh_3)_2]$ (Nb-N 182.7(4)/183.0(6) pm, P-N 160.2(5)/159.5(6) pm) and $[NbCl_3(NPiPr_3)_2]$ (Nb-N 183.5(7)/185.3(9) pm, P-N 156.4(9)/159.0(7) pm). As for **9** and **10**, the molecular structure should not be interpreted in terms of linear vs. bent phosphaneiminato ligands, but instead reflects the "softness" of the angle at the nitrogen atom.

The chelate analogue $[NbCl_3{[NPPh_2(C_5H_4)]_2Fe}]$ (18) was obtained by reaction of $[Fe_{(C_5H_4)PPh_2NSiMe_3]}_2$ [34] with niobium pentachloride in acetonitrile at 40 °C as an orange solid in 49 % yield. A single-crystal X-ray structure analysis was performed for this complex. A view of the molecule is shown in Fig. 19. The ferrocene unit is essentially undistorted with eclipsed cyclopentadienyl rings. The Nb atom is coordinated by three chloro and two phosphaneiminato ligands in a distorted trigonal-bipyramidal arrangement. Two Cl atoms occupy the axial positions forming an angle of 165.63(8)° with the Nb atom, which lies in the plane of the equatorial atoms N(1), N(2) and Cl(2). Both the niobium-nitrogen $[Nb(1)-N(1) \quad 184.9(6),$ Nb(1)-N(2) 182.9(6) pm] and the phosphorus-nitrogen distances [P(1)-N(1) 158.8(6), P(2)-N(2) 159.3(6) pm] are in accord with double bonds. In contrast to the unchelated analogue 17, the Nb–N–P bond angles of 18 are very similar [159.1(4)° at N(1) and 153.3(4)° at N(2)].

The redox-functionalised di(phosphaneiminato)niobium complexes polymerise ethylene in the presence of MAO (Nb/Al 1/750, 55 °C, 5 bar ethylene, toluene solvent) with high initial activity. However, the catalytically active species is very short-lived and polymerisation ceases within ca. 1 min.

3 Summary and Outlook

Complexes containing organoimido and phosphaneiminato ligands are prominent examples of compounds containing a nitrido bridge between a main group element (C and P, respectively) and a transition metal. The chemistry of such species has flourished over the past decades and is now being extended to the use of *functionalised* ligands. Such a development is by no means unusual and has been encountered before with, for example, cyclopentadienyl and phosphane ligands [6a].

We have investigated two different types of modified imido and phosphaneiminato ligands, namely chelate ligands and redox-functionalised ligands (including also an example of a redox-functionalised chelate ligand), and have obtained the following main results.

We have synthesised the first di(organoimido)chromium chelates and have further shown that complexes of the type $[(RN)_2M(CH_2Ph)_2]$ (M = Cr, Mo) are active catalysts for the polymerisation of the polar olefins methyl methacrylate, acrylonitrile and vinyl acetate, with copolymerisations being also possible.

We have synthesised the first di(phosphaneiminato)titanium and niobium chelates. The first complexes containing redox-functionalised organoimido ligands have also been prepared as well as the first structurally characterised examples of complexes containing redox-functionalised phosphaneiminato ligands.

We have provided clear experimental evidence for the quantum-chemical result that the potential energy well for the angle at the nitrogen atom is very shallow for phosphaneiminato complexes. Great care should therefore be taken in the interpretation of structural results in terms of linear vs. bent ligands.

It is clear that our investigations have merely scratched the surface and that the chemistry of complexes containing organoimido, phosphaneiminato or related ligands will continue to be a bonanza.

4 Experimental

All manipulations were performed in an inert atmosphere (purified argon or dinitrogen) by using standard Schlenk and cannula techniques or a conventional glovebox. Solvents and reagents used were commercially available and were appropriately dried and purified by using standard procedures. NMR spectra were recorded with a Bruker Avance DRX 500 or a Varian Unity INOVA 500 spectrometer operating at 500.13 MHz for ¹H. Mass spectra were obtained with a VG Autospec instrument. Elemental analyses were performed by the Microanalytical Laboratory of the Universität Bielefeld, the Microanalytical Laboratory Beller (Göttingen) and the Microanalytical Laboratory H. Kolbe (Mülheim an der Ruhr).

The syntheses and properties of the following compounds have already been published: 7-10 [35], 11 [36], 12-15 [37], 16-17 [38], **18** [39].

Me₃Si(H)NCMe₂CH₂CH₂CMe₂N(H)SiMe₃ (1): *n*BuLi (87 mL of a 1.60 M solution in hexane, 139 mmol) was added dropwise to a stirred solution of 2,5-diamino-2,5-dimethylhexane [40] (10.0 g,

69.3 mmol) in diethyl ether (100 mL) cooled to 0 °C. After 3 h at room temperature the mixture was cooled to 0 °C. Chlorotrime-thylsilane (15.1 g, 139 mmol) was added. After 14 h at room temperature the mixture was filtered and the solvent removed in vacuo, leaving the crude product as a light yellow liquid which was purified by distillation. Yield: 15.2 g (76 %), bp (4 mbar) 90 – 93 °C. ¹H NMR (CDCl₃): δ = 0.04 (s, 18 H, SiMe₃), 1.07 (s, 12 H, CMe₂), 1.29 (s, 4 H, CH₂). ¹³C{¹H} NMR (CDCl₃): δ = 2.9 (SiMe₃), 31.4 (*CMe*₂), 41.3 (CH₂), 51.5 (*CMe*₂). ²⁹Si[¹H} NMR (CDCl₃): δ = 2.4. EI-MS (70 eV): mlz = 289 (M⁺, 100 %).

[(NCMe₂CH₂CH₂CMe₂N)Cr(OSiMe₃)₂] (2): A solution of chromyl chloride (4.08 g, 26.3 mmol) in hexane (10 mL) was added dropwise to a stirred solution of **1** (15.2 g, 52.7 mmol) in hexane (100 mL) cooled to -20 °C. The mixture was allowed to warm to room temperature and was subsequently heated to reflux for 4 h. After cooling to room temperature the mixture was filtered and the volume of the filtrate reduced to ca. 40 mL in vacuo. Crystallisation at -60 °C afforded the product as a dark red solid. Yield: 2.90 g (30 %). Elemental analysis: C₁₄H₃₄N₂CrO₂Si₂ (370.6): C 44.50 (calcd. 45.37), H 9.00 (9.25), N 7.85 (7.56) %.

¹H NMR (C₆D₆): $\delta = 0.29$ (s, 18 H, SiMe₃), 0.98 (s, 12 H, CMe₂), 2.18 (s, 4 H, CH₂). ¹³C{¹H} NMR (C₆D₆): $\delta = 2.7$ (SiMe₃), 27.7 (CMe₂), 41.2 (CH₂), 79.4 (CMe₂). ²⁹Si{¹H} NMR (C₆D₆): $\delta = 15.2$. EI-MS (70 eV): m/z = 371 (M⁺, 100 %).

[(NCMe₂CH₂CH₂CMe₂N)CrCl₂] (3): Boron trichloride (15.6 mL of a 1.00 M solution in hexane, 15.6 mmol) was added dropwise to a stirred solution of 2 (2.90 g, 7.82 mmol) in dichloromethane (30 mL) cooled to 0 °C. After 2 h at room temperature volatile components were removed in vacuo. The residue was extracted with hot hexane (5 × 20 mL). The combined extracts were reduced to dryness in vacuo. Sublimation (60 °C, 10^{-3} mbar) of the crude product afforded a reddish black solid. Yield: 1.20 g (58 %). Elemental analysis: C₈H₁₆N₂Cl₂Cr (263.1): C 35.83 (calcd. 36.52), H 5.89 (6.13), N 10.96 (10.65) %.

¹H NMR (C₆D₆): δ = 0.77 (s, 12 H, Me), 1.97 (s, 4 H, CH₂). ¹³C{¹H} NMR (C₆D₆): δ = 25.7 (Me), 40.7 (CH₂), 84.0 (*C*Me₂). EI-MS (70 eV): *m*/*z* = 263 (M⁺, 100 %).

[(NCMe₂CH₂CH₂CMe₂N)Cr(CH₂Ph)₂] (4): Benzylmagnesium chloride (7.14 mL of a 1.00 M solution in diethyl ether, 7.14 mmol) was added dropwise to a stirred solution of **3** (0.94 g, 3.57 mmol) in diethyl ether (100 mL) cooled to -45 °C. The mixture was allowed to warm to room temperature. After 15 h volatile components were removed in vacuo. The residue was extracted with pentane (4 × 30 mL). The volume of the combined extracts was reduced to ca. 40 mL. Crystallisation at -60 °C afforded the product as a red solid. Yield: 0.95 g (71 %). Owing to the high sensitivity of the product towards air and moisture, no reproducible microanalytical data could be obtained.

¹H NMR (C₆D₆): $\delta = 0.99$ (s, 12 H, Me), 1.83 (s, 4 H, CH₂CH₂), 2.53 (s, 4 H, CH₂Ph), 7.00 (m, 10 H, Ph). {¹H} NMR (C₆D₆): $\delta = 27.4$ (Me), 40.6 (CH₂CH₂), 43.7 (CH₂Ph), 74.2 (CMe₂), 124.9 (Ph), 129.0 (Ph), 130.8 (Ph), 141.0 (Ph). EI-MS (70 eV): m/z = 375 (M⁺, 100 %).

[(NCMe₂CH₂CH₂CMe₂N)MoCl₂(DME)] (5): Sodium molybdate (6.00 g, 29.1 mmol) was suspended in DME (150 mL). Triethylamine (11.8 g, 117 mmol), chlorotrimethylsilane (25.5 g, 235 mmol) and a solution of 2,5-diamino-2,5-dimethylhexane [40] (4.20 g, 29.1 mmol) in DME (40 mL) were added. The mixture was heated to reflux for 15 h. After cooling to room temperature the mixture was filtered and the volume of the filtrate reduced to ca. 50 mL in vacuo. Crystallisation at -30 °C afforded the product as a pale green solid. Yield: 6.04 g (52 %). Elemental analysis: C₁₂H₂₆N₂Cl₂MoO₂ (397.2): C 36.29 (calcd. 36.14), H 6.60 (6.44), N 7.14 (7.05) %.

Compound	2	5	6
Chem. formula	C14H34CrN2O2Si2	C ₁₂ H ₂₆ Cl ₂ MoN ₂ O ₂	$C_{22}H_{30}MoN_2$
Formula weight	370.61	397.19	418.42
Crystal size	$0.4 \times 0.4 \times 0.1 \text{ mm}^3$	0.6×0.3×0.2 mm ³	$0.4 \times 0.4 \times 0.3 \text{ mm}^3$
Space group	monoclinic, C2/c	orthorhombic, Pbca	monoclinic, P21/n
aĺÅ	21.031(12)	13.443(4)	8.4600(1)
b/Å	7.631(3)	15.764(4)	16.7250(2)
c/Å	13.578(5)	16.912(6)	14.7170(3)
βl°	100.20(6)	90	99.5490(16)
V/Å ³	2144.7(17)	3583.9(19)	2053.51(5)
Ζ	4	8	4
ρ (calcd.)/g/cm ₃	1.148	1.472	1.353
μ/mm^{-1}	0.650	1.030	0.645
F(000)	800	1632	872
Index ranges	$-27 \le h \le 27, -9 \le k \le 0, -17 \le l \le 17$	$0 \le h \le 18, 0 \le k \le 22, 0 \le l \le 23$	$-13 \le h \le 13, -26 \le k \le 26, -23 \le l \le 23$
θ range/°	2.8-27.5	2.3-30.0	2.7-35.0
Reflections collected	4928	5224	62984
Independent reflections	2469 [R(int.) = 0.0701]	5224	9031 [R(int.) = 0.0400]
Data/restraints/parameters	2469/0/101	5224/0/178	9031/0/346
Goodness-of-fit on F^2	1.003	1.018	1.056
Final $R1^{a}$ [I>2 σ (I)]/wR2 ^b)	0.0479/0.1050	0.0505/0.1279	0.0246/0.0499
Largest diff.peak/hole/e/Å3	0.310/-0.354	0.715/-1.091	0.485/-0.600

Table 2 X-ray crystallographic data

^{a)} $R1 = \Sigma ||F_o| - |F_c|| \Sigma |F_o|;$ ^{b)} $wR2 = \{\Sigma [w(F_o^{2-}F_c^{2})^2] / \Sigma [w(F_o^{2})^2] \}^{0.5}$.

¹H NMR (CDCl₃): δ = 1.25 (s, 12 H, CMe₂), 2.30 (s, 4 H, CH₂CMe₂), 3.66 (s, 6 H, OMe), 3.75 (s, 4 H, OCH₂).

[(NCMe₂CH₂CH₂CMe₂N)Mo(CH₂Ph)₂] (6): Benzylmagnesium chloride (3.52 mL of a 1.00 M solution in diethyl ether, 3.52 mmol) was added dropwise to a stirred solution of **5** (0.70 g, 1.76 mmol) in diethyl ether (70 mL) cooled to -60 °C. The mixture was allowed to warm to room temperature. After 15 h volatile components were removed in vacuo. The residue was extracted with hexane (3 × 20 mL). The volume of the combined extracts was reduced to ca. 30 mL. Crystallisation at -30 °C afforded the product as a light orange solid. Yield: 0.54 g (73 %). Elemental analysis: C₂₂H₃₀N₂Mo (418.4): C 63.13 (calcd. 63.15), H 7.34 (7.23), N 6.65 (6.69) %.

¹H NMR (C₆D₆): $\delta = 1.08$ (s, 12 H, Me), 1.83 (s, 4 H, CH₂CH₂), 2.53 (s, 4 H, CH₂Ph), 7.00 (m, 10 H, Ph). {¹H} NMR (C₆D₆): $\delta = 28.0$ (Me), 41.6 (CH₂CH₂), 43.7 (CH₂Ph), 71.8 (CMe₂), 124.7 (Ph), 128.3 (Ph), 129.6 (Ph), 140.7 (Ph).

Polymerisation Studies: All polymerisations of polar monomers were carried out under argon in a 100 ml flask equipped with a magnetic stirrer and with a cooling jacket for the temperature experiments. Typically, the solution had a total volume of 60 ml and polymerisations were run with 0.012 mmol of catalyst and the appropriate amount of monomer in toluene solution at ambient temperature. The reaction was quenched with methanol at a specific time and the polymer was precipitated in methanol, filtered off and dried in vacuo at 60 °C until a constant weight was achieved. Copolymerisation experiments with acrylonitrile and methyl methacrylate were performed under essentially identical conditions.

The ¹³C NMR spectra were measured in 10 mm NMR tubes with proton broad-band decoupling at 120 °C on a Bruker AMX 300 spectrometer at 75 MHz. The samples of the polymer (200 – 300 mg) were dissolved in 3 mL of a mixture of 1,2,4-trichlorben-zene and 1,1,2,2-tetrachloroethane-d₂ (volume ratio 2.5 : 1). The chemical shifts were calibrated relative to 1,1,2,2-tetrachloroethane-d₂ ($d_c = 74.2$ ppm).

Glass transition temperatures were measured on a Mettler-Toledo DSC 820 calorimeter. The sample was first heated, gradually

cooled and re-heated, typically in a temperature range from 25 °C to 180 °C with a heating rate of 10 $K \cdot min^{-1}$.

Gel permeation chromatographic (GPC) analyses of PMMA, PAN and the AN-MMA copolymer were performed by the Bayer AG Dormagen and by PSS Standards Service GmbH / Mainz, whose support is thankfully acknowledged.

X-ray Crystal Structure Determinations: The crystal structures of **4** [41], **9** [35], **10** [35], **13** [37], **17** [38] and **18** [39] have already been reported. The crystal structures of **2** and **5** were obtained with a Siemens P2₁ four-circle diffractometer at 173 K, that of **6** was obtained with a Nonius Kappa CCD diffractometer at 100 K. Graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) was used in each case. The structures were solved by direct methods. The program package used was SHELXL 97 [42]. Full-matrix least-squares refinement on F^2 was carried out anisotropically for the non-hydrogen atoms. Hydrogen atoms were refined isotropically for **6** and were included at calculated positions using a riding model for **2** and **5**. Further X-ray structure analyses data are given in Table 2.

Full details (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre (2 CCDC 195080, 5 CCDC 195081, 6 CCDC 905082). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code +(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

This work was generously supported by the DFG (Si 429/6) and in part also by the BMBF (03C0276C/3). *O. K.* thanks the DAAD for a travel grant.

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