New Group 4 Metallocene and Niobocene Complexes Containing Phosphane-Functionalized *ansa*-Ligands

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The asymmetric *ansa*-ligand precursors $Me_2Si(C_5Me_4H)(C_5H_4R)$ [R = $CH_2CH_2PPh_2$ (**1**), PPh_2 (**2**)] and their lithium derivatives $Li_2\{Me_2Si(C_5Me_4)(C_5H_3R)\}$ [R = $CH_2CH_2PPh_2$ (**3**), PPh_2 (**4**)] have been prepared. The group 4 metal *ansa* complexes $[M\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R)\}Cl_2]$ [M = Ti, R = $CH_2CH_2PPh_2$ (**5**), PPh_2 (**6**); M = Zr, R = $CH_2CH_2PPh_2$ (**7**), PPh_2 (**8**); M = Hf, R = $CH_2CH_2PPh_2$ (**9**), PPh_2 (**10**)] were obtained by the reaction of $[TiCl_4(THF)_2]$ or MCl_4 (M = Zr or Hf) and the corresponding lithiated *ansa* derivative. The reaction of complexes **7** and **8** with two equivalents of MgMeCl led to the formation of the alkyl complexes $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R)\}Me_2]$ [R = $CH_2CH_2PPh_2$ (**11**), PPh_2 (**12**)]. Methyl abstraction from **11** and **12** with $B(C_5F_6)_3$ gave the cationic species $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R)\}Me]^+$ [R = $CH_2CH_2PPh_2$ (**13**), PPh_2 (**14**)]. The insertion reaction of the isocyanide reagent $CNC_6H_3Me_2\text{-}2,6$ into the Zr–Me bond of complex **12** giving the corresponding η^2-iminoacyl compound $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3PPh_2)\}\{\eta^2\text{-}MeC{=}N(C_6H_3Me_2\text{-}2,6)\}(Me)]$ (**15**) is described. The *ansa*-niobocene imide $[Nb({=}N\mathit{t}Bu)\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3PPh_2)\}Cl]$ (**16**) and the niobocene imide complexes $[Nb({=}N\mathit{t}Bu)(\eta^5\text{-}C_5H_4PPh_2)_2Cl]$ (**17**) were synthesised by the reaction of $[Nb({=}N\mathit{t}Bu)Cl_3(py)_2]$ with $Li_2\{Me_2Si(C_5Me_4)(C_5H_3PPh_2)\}$ (**4**) or two equivalents of $Li(C_5H_4PPh_2)$, respectively. Preliminary results for the catalytic activity of **7** and **8** in the polymerization of ethylene are presented.

Introduction

The use of *ansa*-cyclopentadienyl ligands has received wide attention in the chemistry of group 4 metals,[1] due mainly to their ability to impart to their complexes a selective degree of catalytic activity.[2] Recent studies have demonstrated that the incorporation of an *ansa* bridge may have a profound influence on the chemistry of the metallocene system.[3]

In 1996 we reported the first *ansa*-niobocene complexes, in which both cyclopentadienyl rings are bound only in an η^5 mode to niobium,[4] and since then several complexes of this type have been described.[5]

Furthermore the use of substituted *ansa*-cyclopentadienyl ligands in the synthesis of group 4 metal complexes and their importance in catalysis is receiving special attention,[6] but there are only a few examples for group 5.[3b,5d,6−8] Some examples of asymmetric *ansa*-zirconocene complexes have been described,[8−10] although the vast majority contain indenyl or fluorenyl systems.[11]

Chiral group 4 *ansa*-metallocene complexes are important stereoselective olefin polymerization catalysts, and have also been used as catalysts or reagents in stereoselective olefin and imine hydrogenation, Diels−Alder reactions, and cyclopolymerization.[12] We are investigating the stereoselective synthesis of *ansa*-metallocene complexes and the application of these compounds as catalysts. For example, we recently developed a general synthesis of some $SiMe_2$-bridged asymmetric *ansa*-zirconocene complexes[8,9] and this series of highly active C_1 symmetric olefin polymerization catalysts polymerize propylene with a high level of stereospecificity.[9] Our research in this area is now focused on the elucidation of the mechanism of olefin polymerization as well as on the use of new types of metallocene complexes in stereoselective catalysis.

The role of cyclopentadienyl ligands with attached tertiary phosphane groups in the chemistry of metallocene complexes has been well documented.[13] In the chemistry of group 4 elements several examples of this type of complex have been described. These include $[Ti(\eta\text{-}C_5H_4CH_2CH_2PPh_2)_2Cl_2]$[14] and $[Zr(\eta\text{-}C_5H_4CMe_2\text{-}PPh_2)_2X_2]$ (X = Cl, Me).[15] Special interest in this chemistry has been placed in the ability of the phosphane moiety to join two different metallic centres[16] and to stabilize cat-

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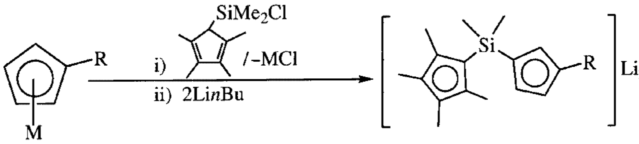
ionic species by intramolecular bonding to the metal centre.[15] However, despite the large number of related complexes reported there has been only one publication on the use of phosphane-substituted cyclopentadienyl ligands in the chemistry of the group 5 elements, in which the synthesis and reactivity of the tantalum complex, $[Ta(\eta\text{-}C_5Me_5)(\eta\text{-}C_5H_4PPh_2)Cl_2]$ is described.[17] To the best of our knowledge the incorporation of such precursors in *ansa*-metallocene systems has not been reported previously.

As an extension of our previous work related to *ansa*-metallocene complexes of zirconium and niobium[4,5d,8,9] we now report the synthesis and characterization of the first phosphane-substituted *ansa*-cyclopentadienyl ligands and their incorporation in new metallocene complexes of the group 4 and 5 elements.

Results and Discussion

We have previously reported the synthesis of asymmetrically substituted cyclopentadienyl *ansa* ligands such as $Me_2Si(C_5Me_4H)(C_5H_4R)$ (R = H, Me, Et, *i*Pr, *t*Bu, $SiMe_3$)[8,9] and using the same methodology the *ansa* ligands $Me_2Si(C_5Me_4H)(C_5H_4CH_2CH_2PPh_2)$ (**1**) and $Me_2Si(C_5Me_4\ H)(C_5H_4PPh_2)$ (**2**) and their lithium derivatives $Li_2\{Me_2Si(C_5Me_4)(C_5H_3CH_2CH_2PPh_2)\}$ (**3**) and $Li_2\{Me_2Si(C_5Me_4)(C_5H_3PPh_2)\}$ (**4**) were prepared [Equation (1)].



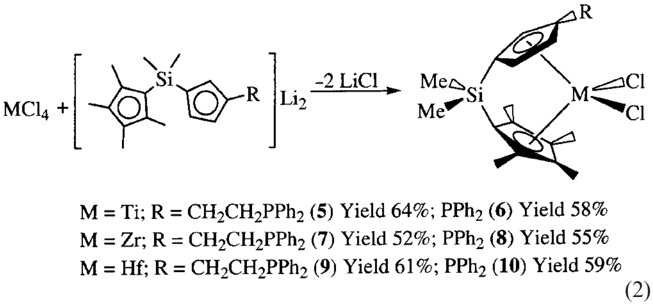
$R = CH_2CH_2PPh_2$ or PPh_2;
M = K or Li

$R = CH_2CH_2PPh_2$ (**3**) Yield 96%
$R = PPh_2$ (**4**) Yield 93%

(1)

The possibility of various isomers for the *ansa* ligands **1** and **2** was confirmed by ^1H NMR spectroscopy. In addition **1** and **2** were characterised by electron impact mass spectrometry (see Exp. Sect.).

The reaction of the di-lithium derivatives of the phosphane-substituted *ansa* ligands **3** and **4** with $[TiCl_4(THF)_2]$ gave the *ansa*-titanocene(IV) complexes $[Ti\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3CH_2CH_2PPh_2)\}Cl_2]$ (**5**) and $[Ti\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3PPh_2)\}Cl_2]$ (**6**) [see Equation (2)].



M = Ti; $R = CH_2CH_2PPh_2$ (**5**) Yield 64%; PPh_2 (**6**) Yield 58%
M = Zr; $R = CH_2CH_2PPh_2$ (**7**) Yield 52%; PPh_2 (**8**) Yield 55%
M = Hf; $R = CH_2CH_2PPh_2$ (**9**) Yield 61%; PPh_2 (**10**) Yield 59%

(2)

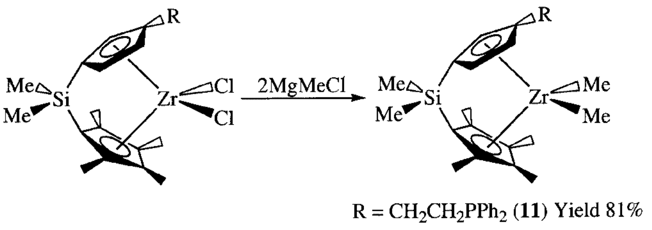
Complexes **5** and **6** were isolated as crystalline solids and characterised spectroscopically. Their ^1H NMR spectra show the lack of symmetry in these chiral C_1 symmetric complexes. Observed signals were assigned to the four inequivalent methyl groups attached to one of the cyclopentadienyl rings, the two distinct methyl groups of the $SiMe_2$ bridge and the three protons of the functionalized cyclopentadienyl moiety (see Exp. Sect.). In addition, in the ^1H NMR spectrum of **5** the expected signals for the alkyl chain and phenyl groups were observed. The ^{31}P NMR spectrum of **5** and **6** gave unique signals at $\delta = -42.8$ and $\delta = -44.0$ ppm, respectively indicating that the phosphorus atom is not interacting directly with the metal centre.[13b]

The *ansa*-metallocene complexes $[M\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R)\}Cl_2]$ [M = Zr, $R = CH_2CH_2PPh_2$ (**7**), PPh_2 (**8**); M = Hf, $R = CH_2CH_2PPh_2$ (**9**), PPh_2 (**10**)] were prepared by the reaction of **3** or **4** with $ZrCl_4$ or $HfCl_4$ [see Equation (2)].

The ^1H NMR spectra for **7**−**10** concurred with those recorded for their titanocene analogues **5** and **6** (see Exp. Sect.). Complexes **5**−**10** represent, to the best of our knowledge, the first examples of group 4 *ansa*-metallocene complexes containing phosphane-substituted cyclopentadienyl moieties.

Compounds **7** and **8** were tested as catalysts in the polymerization of ethylene. The experiments were conducted at 25 °C and 1.5 bar with a zirconocene/MAO ratio of 1:500. Compared with $[Zr(\eta^5\text{-}C_5H_5)_2Cl_2]$ [5000 kg polymer $(mol\ Zr{\cdot}h)^{-1}$], complex **8** has a somewhat lower catalytic activity [3110 kg polymer $(mol\ Zr{\cdot}h)^{-1}$]. Complex **7** was found to be a very poor catalyst [600 kg polymer $(mol\ Zr{\cdot}h)^{-1}$]. The interaction of MAO with the phosphane group and the consequent steric effects exerted by the bulky Ph_2P-MAO unit may be responsible for the low catalytic activities observed.

The alkylzirconocene derivatives $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R)\}Me_2]$ [$R = CH_2CH_2PPh_2$ (**11**), PPh_2 (**12**)] were prepared by the reaction of two equivalents of the Grignard reagent MgMeCl with the corresponding *ansa*-metallocene dichloride complex **5** or **6**, respectively [see Equation (3)].



$R = CH_2CH_2PPh_2$ (**11**) Yield 81%
$R = PPh_2$ (**12**) Yield 80%

(3)

Compounds **11** and **12** were characterised by spectroscopic methods (see Exp. Sect.). ^1H NMR spectroscopy showed the expected signals for the C_1 symmetric complexes **11** and **12**. For the metal-bonded methyl groups two singlets at $\delta = -0.48$ and -0.35 ppm were observed for **11**. In **12** these signals overlap to give one peak at $\delta = -0.49$ ppm. However, the ^{13}C NMR spectrum of **12** gave the expected two distinct signals for the metal-bonded methyl groups. The ^{31}P NMR spectrum of **11** and **12** showed no significant changes with respect to their parent compounds **7** and **8** and therefore it can be proposed that there is no alteration in the coordination mode of the phosphorous atom.

The reaction of **11** and **12** with one molar equivalent of $B(C_6F_5)_3$ gave the cationic species $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3R)\}Me]^+$ [R = $CH_2CH_2PPh_2$ (**13**), PPh_2 (**14**)] with $MeB(C_6F_5)_3$ as the counteranion. The borane reagent reacts preferentially at the more nucleophilic methyl group rather than the phosphane substituent. Complexes **13** and **14** were characterised by ^{1}H, ^{11}B and ^{31}P NMR spectroscopy. The ^{1}H NMR spectra of **13** and **14** revealed the disappearance of one methyl peak and a shifting of the remaining peaks. In addition the Me-B proton resonance was observed as a broad signal at δ = 0.31 ppm.

Initially there exists two possibilities for the methyl abstraction of **11** and **12**. The borane derivative can interact with either the methyl group positioned below or that orientated away from the phosphane substituent of the cyclopentadienyl moiety. ^{1}H NMR spectroscopy revealed in all cases the presence of only one compound and it appears likely on the grounds of steric effects that this corresponds to the product of the alkyl abstraction at the less hindered metal-methyl group. Nevertheless we cannot rule out the rapid exchange of coordination positions between the metal-methyl and boron-coordinated methyl groups; for a similar C_s symmetric *ansa*-system, $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Me]^+$,[9] however, such a phenomenon was not observed. An extensive study into the behaviour of alkyl-zirconocene borate ion pairs has been published recently.[18]

^{31}P NMR spectroscopy revealed that the phosphane groups in **13** and **14** behave in different ways. For **13** a signal at δ = −4.3 ppm (compared with δ = −40.0 ppm for the parent compound **11**) was observed in the ^{31}P NMR spectrum. This is indicative of a change in the coordination mode of the phosphorous atom.[13b] This shift can be explained by the fact that the abstraction of a methyl group by $B(C_6F_5)_3$ creates a vacant coordination site at the metal centre which is occupied by the phosphorous atom of the pendant phosphane ligand (see Figure 1). However, in **14** the geometric restrictions of the phosphane group which is directly attached to the cyclopentadienyl moiety inhibit its coordination to the metal centre in the cationic species and thus ^{31}P NMR spectroscopy gives a signal at δ = −41.4 ppm similar to that observed for the parent complex **12** (see Figure 2).

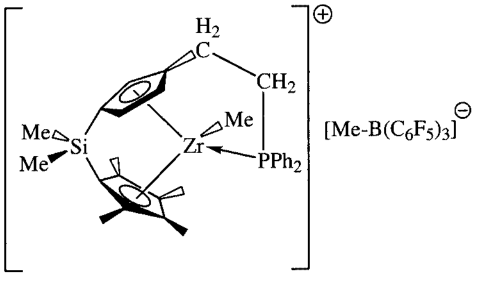


Figure 1. Proposed structure for $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3CH_2CH_2PPh_2)\}Me][MeB(C_6F_5)_3]$ (**13**)

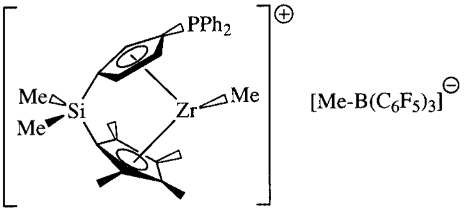
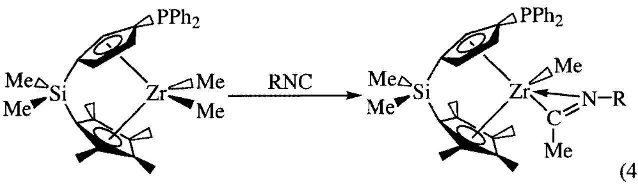


Figure 2. Proposed structure for $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3PPh_2)\}Me][MeB(C_6F_5)_3]$ (**14**)

The reaction of the isocyanide reagent $CNC_6H_3Me_2$-2,6 with **12** has also been studied [Equation (4)]. The product of the insertion reaction $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3PPh_2)\}\{\eta^2\text{-}MeC{=}N(C_6H_3Me_2\text{-}2,6)\}(Me)]$ (**15**) was characterised by ^{1}H, ^{13}C and ^{31}P NMR spectroscopy.



(4)

15
Yield 60%

The migratory insertion of alkyl groups towards isocyanide ligands allows the introduction of iminoacyl groups, which are present in different coordination modes. In fact, for high-valent oxophilic early transition metals, the iminoacyl group typically adopts an η^2-coordination mode through both the nitrogen and carbon atoms.[19] Similarly, an η^2-coordination mode is proposed for the iminoacyl ligand in **15** on the basis of IR and ^{13}C NMR spectroscopy, which show the characteristic ν(C=N) stretching vibration at 1584 cm^{-1} and the iminoacyl quaternary carbon atom signal at δ = 246.8 ppm, respectively.

The ^{1}H NMR spectrum of **15**, in addition to the expected signals for the *ansa*-metallocene protons, gave signals for the metal-bonded methyl group at δ = 0.28 ppm and for the iminoacyl methyl group at δ = 2.19 ppm. The chemical shift observed for the only signal in the ^{31}P NMR spectrum (δ = −43.5 ppm) showed that the chemical properties of the phosphorous atom remained unaltered with respect to the parent complex.

In **12** the two methyl groups are not equivalent and the insertion of the isocyanide probably occurs preferentially into one of the metal-methyl bonds. This was confirmed by NMR spectroscopy, which showed the presence of only one of the possible isomers. For steric reasons we propose that the insertion takes place at the metal-methyl group that is orientated away from the bulky phosphane moiety (Figure 3).

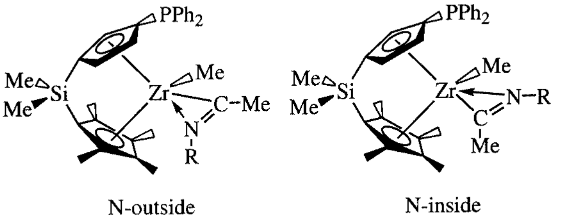


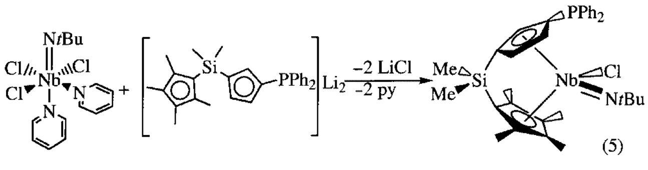
Figure 3. Two possible conformations for the metal-iminoacyl complex **15**

In addition the iminoacyl group can position itself in two distinct conformations, the "proximal" or "N-outside" and the "distal" or "N-inside" configurations (see Figure 3). ^{1}H and ^{13}C NMR spectroscopic data indicated the presence of only one of the two possible conformations. Although it has been demonstrated that the N-outside isomer is the resulting initial kinetic iminoacyl product of the insertion reaction, most group 4 metal derivatives show the structure of the N-inside isomer which results from thermodynamic control.[20] For **15** the isolated product was observed not to evolve over time and, in addition, the NOE experiment showed a negligible effect between the metal-methyl and iminoacyl-methyl groups. Therefore we propose that **15** is the product resulting from thermodynamic control and adopts the N-inside conformation.

A second insertion into the remaining methyl group was not observed even when stoichiometries greater than 1:1 were tested.

The use of phosphane-substituted cyclopentadienyl ligands in the chemistry of group 5 elements has been restricted to one reference concerning the tantalum complex [Ta(η-C_5Me_5)(η-$C_5H_4PPh_2$)Cl_2] and its reactivity.[17] To the best of our knowledge there have been no reports of this type of compounds in the chemistry of niobium.

By the reaction of the lithium derivative Li_2\{$Me_2Si(C_5Me_4)(C_5H_3PPh_2)$\} (**4**) with [Nb(=N*t*Bu)$Cl_3(py)_2$] we have also prepared the *ansa*-phosphane niobocene imido complex [Nb(=N*t*Bu)\{Me_2Si(η^5-C_5Me_4)(η^5-$C_5H_3PPh_2$)\}Cl] (**16**) [Equation (5)]. The complex [Nb(=N*t*Bu)(η^5-$C_5H_4PPh_2$)$_2$Cl] (**17**), was prepared in a similar manner by reaction of two equivalents of Li($C_5H_4PPh_2$) with [Nb(=N*t*Bu)$Cl_3(py)_2$].



(5)

16
Yield 63%

By comparison with our previous work in imidoniobocene chemistry[5d,8,21] we can assume that the imido group acts as a four-electron donor. Complexes **16** and **17** can therefore be considered as "20-electron" complexes. However the two excess electrons are most probably located in a ligand-based orbital as has previously been reported for similar compounds.[22]

Both **16** and **17** were characterised spectroscopically. The ^{1}H NMR spectrum of **16** showed the lack of symmetry in this chiral complex. The four methyl groups attached to the cyclopentadienyl ring are inequivalent as are the methyl groups of the $SiMe_2$ bridge. In addition signals were observed for the alkyl-imido and phenyl groups and the three protons of the phosphane-substituted cyclopentadienyl moiety (see Exp. Sect.). In the case of **17** an ABCD system was observed in the ^{1}H NMR spectrum due to the inequivalency of the cyclopentadienyl ring protons, although a plane of symmetry makes the two cyclopentadienyl rings equivalent, thus giving four multiplets for the eight ring protons. The expected signals for the alkyl-imido and phenyl groups were also observed (see Exp. Sect.).

Complex **16** has the possibility to form two isomers depending on the position of the phosphane group, which can either be orientated towards or away from the imido group (see Figure 4). ^{1}H NMR spectroscopy revealed that only one isomer was present. For other alkyl-substituted *ansa*-niobium complexes this same phenomenon was observed,[8] and all the molecular structures reported for related complexes revealed that the substituent was situated pointing away from the bulky imido group. It is logical to assume the same is true for **16** and therefore the proposed structure (a) is that illustrated in Figure 4.

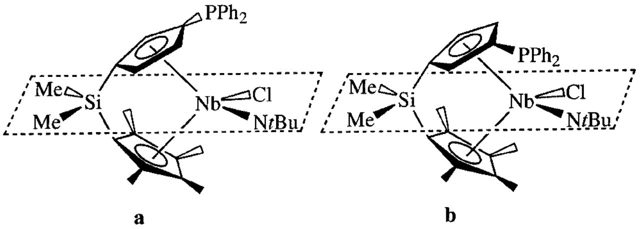


Figure 4. Possible isomers for [Nb(=N*t*Bu)\{Me_2Si(η^5-C_5Me_4)(η^5-$C_5H_3PPh_2$)\}Cl] (**16**)

In conclusion we have reported the synthesis of new phosphane-containing *ansa*-cyclopentadienyl ligands and their lithium derivatives. We have prepared the first phosphane-substituted *ansa*-metallocene complexes with group 4 and group 5 elements. The catalytic activity of the zirconocene complexes has been tested in olefin polymerization and discussed as a function of the phosphane group attached to the cyclopentadienyl ring. The reactivity of some of these compounds has been described.

Experimental Section

General Remarks: All reactions were performed using standard Schlenk-tube techniques under an atmosphere of dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use. K($C_5H_4CH_2CH_2PPh_2$),[23] Li($C_5H_4PPh_2$)[24] and [Nb(=N*t*Bu)$Cl_3(py)_2$][25] were prepared as described earlier. [$TiCl_4(THF)_2$], $ZrCl_4$, $HfCl_4$, $Me_2Si(C_5Me_4H)Cl$, MgMeCl, $B(C_6F_5)_3$ and (2,6-dimethylphenyl)isocyanide were purchased from

Aldrich and used directly. IR spectra were recorded on a Perkin−Elmer PE 883 IR spectrophotometer. ^{1}H and ^{13}C spectra were recorded on Varian FT-300 and Varian Gemini FT-200 spectrometers and referenced to the residual deuterated solvent. Microanalyses were carried out with a Perkin−Elmer 2400 micro analyzer. Mass spectroscopic analyses were performed on a Hewlett−Packard 5988A (*m*/*z* = 50−1000) instrument (electron impact).

Preparation of $Me_2Si(C_5Me_4H)(C_5H_4CH_2CH_2PPh_2)$ (1): $Me_2Si(C_5Me_4H)Cl$ (1.36 g, 6.32 mmol) in THF (50 mL) was added to a solution of $K(C_5H_4CH_2CH_2PPh_2)$ (2.00 g, 6.32 mmol) in THF (50 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for 18 h. Solvent was removed in vacuo and hexane (150 mL) was added to the resulting orange oil. The mixture was filtered and solvent removed from the filtrate under reduced pressure to yield the title compound as a yellow oil (2.78 g, 96%). ^{1}H NMR (200 MHz, C_6D_6, 25 °C) (for the predominant isomer, 60%): δ = 0.10 (s, 6 H, $SiMe_2$), 1.75 and 1.85 (2s, each 6 H, C_5Me_4), 2.20−2.60 and 3.00−3.30 (2m, each 2 H, -CH_2CH_2-), 2.80 and 3.47 (2m, each 1 H, HC_5), 6.35, 6.37 and 6.56 (3m, each 1 H, C_5H_3), 7.00−7.60 (m, 10, PPh_2) ppm. EI-MS: *m*/*z* (%) = 456 (25) [M$^+$], 335 (30) [M$^+$ − C_5Me_4H], 179 (100) [M$^+$ − $C_5H_4CH_2CH_2PPh_2$], 123(65) [M$^+$ − C_5Me_4H − $CH_2CH_2PPh_2$].

Preparation of $Me_2Si(C_5Me_4H)(C_5H_4PPh_2)$ (2): The synthesis of **2** was carried out in an identical manner to **1**. $Me_2Si(C_5Me_4H)Cl$ (1.10 g, 5.12 mmol) and $Li(C_5H_4PPh_2)$ (1.31 g, 5.12 mmol). Yield 2.05 g, 94%. ^{1}H NMR (200 MHz, C_6D_6, 25 °C) (for the predominant isomer, 60%): δ = 0.05 (s, 6 H, $SiMe_2$), 1.70 and 1.80 (2s, each 6 H, C_5Me_4), 3.05 and 3.35 (2m, each 1 H, HC_5), 6.28, 6.32 and 6.52 (3m, each 1 H, C_5H_3), 7.00−7.60 (m, 10, PPh_2) ppm. EI-MS: *m*/*z* (%) = 428 (20) [M$^+$], 307 (25) [M$^+$ − C_5Me_4H], 179 (100) [M$^+$ − $C_5H_4PPh_2$], 123(70) [M$^+$ − C_5Me_4H − PPh_2].

Preparation of $Li_2\{Me_2Si(C_5Me_4)(C_5H_3CH_2CH_2PPh_2)\}$ (3): *n*BuLi (1.6 M in hexane) (7.6 mL, 12.18 mmol) was added via syringe to a solution of **1** (2.78 g, 6.09 mmol) in Et_2O (75 mL) at −78 °C. The mixture was allowed to warm to 10 °C and stirred for 15 h. Solvent was removed in vacuo to give a white solid which was washed with hexane (2 × 50 mL) and dried under vacuum to yield a white solid of the title complex (2.74 g, 96%). $C_{30}H_{35}Li_2PSi$ (468.5): calcd. C 76.90, H 7.53; found C 76.62, H 7.43.

Preparation of $Li_2\{Me_2Si(C_5Me_4)(C_5H_3PPh_2)\}$ (4): The synthesis of **4** was carried out in an identical manner to **3** from **2** (2.19 g, 5.11 mmol) and *n*BuLi (1.6 M in hexane) (6.39 mL, 10.22 mmol). Yield 2.09 g, 93%. $C_{28}H_{31}Li_2PSi$ (440.5): calcd. C 76.35, H 7.09; found C 76.19, H 7.00.

Preparation of $[Ti\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3CH_2CH_2PPh_2)\}Cl_2]$ (5): Compound **3** (1.50 g, 3.20 mmol) in THF (50 mL) was added to a solution of $[TiCl_4(THF)_2]$ (1.07 g, 0.64 mmol) in THF (50 mL). The resulting dark red solution was stirred for 18 h. Solvent was removed in vacuo and toluene (75 mL) was added. The suspension was filtered and the filtrate was concentrated (10 mL) and cooled (−30 °C) to yield the title complex as a red crystalline solid (1.17 g, 64%). ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ = −0.01 and 0.34 (2s, each 3 H, $SiMe_2$), 1.45, 1.60, 2.07 and 2.09 (4s, each 3 H, C_5Me_4), 2.04−2.61 and 2.98−3.35 (2m, each 2 H, -CH_2CH_2-), 4.88, 5.31 and 6.93 (3m, each 1 H, C_5H_3), 7.06−7.12, 7.32−7.55 (m, 10 H, PPh_2) ppm. $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6, 25 °C): δ = −0.7, −0.6 ($SiMe_2$), 12.1, 12.2, 14.5, 14.7 (C_5Me_4), 27.0 (d, $^1J_{C,P}$ = 19.7 Hz), 28.6 (d, $^2J_{C,P}$ = 13.8 Hz) (-CH_2CH_2-), 110.0, 110.7, 112.6 125.0, 126.10 (C_5H_3), 128.0−141.0 (various signals assigned to PPh_2 and C_5Me_4) ppm. $^{31}P\{^1H\}$ NMR (300 MHz, C_6D_6, 25 °C): δ = −42.8 ppm. $C_{30}H_{35}Cl_2PSiTi$ (573.5): calcd. C 62.84, H 6.15; found C 62.56, H 6.09.

The syntheses of **6**−**10** were carried out in an identical manner to **5**.

$[Ti\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3PPh_2)\}Cl_2]$ (6): From $[TiCl_4(THF)_2]$ (1.18 g, 0.89 mmol) and **4** (1.56 g, 3.54 mmol). Yield 1.12 g, 58%. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ = 0.08 and 0.16 (2s, each 3 H, $SiMe_2$), 1.39, 1.54, 1.96 and 2.04 (4s, each 3 H, C_5Me_4), 5.34, 5.45 and 6.32 (3m, each 1 H, C_5H_3), 7.37−7.74 (m, 10 H, PPh_2) ppm. $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6, 25 °C): δ = −1.1, −0.2 ($SiMe_2$), 11.3, 12.9, 13.6, 13.9 (C_5Me_4), 110.4, 112.6, 117.4, 118.4 (d, $^1J_{C,P}$ = 32.4 Hz), 125.6 (C_5H_3), 128.0−138.0 (various signals assigned to PPh_2 and C_5Me_4) ppm. $^{31}P\{^1H\}$ NMR (300 MHz, C_6D_6, 25 °C): δ = −42.2 ppm. $C_{28}H_{31}Cl_2PSiTi$ (545.4): calcd. C 61.66, H 5.73; found C 61.47, H 5.66.

$[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3CH_2CH_2PPh_2)\}Cl_2]$ (7): From $ZrCl_4$ (0.99 g, 4.27 mmol) and **3** (2.00 g, 4.27 mmol). Yield 1.37 g, 52%. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ = 0.33 and 0.37 (2s, each 3 H, $SiMe_2$), 1.58, 1.69, 1.98 and 1.99 (4s, each 3 H, C_5Me_4), 2.28−2.57 and 2.95−3.26 (2m, each 2 H, -CH_2CH_2-), 5.04, 5.37 and 6.72 (3m, each 1 H, C_5H_3), 7.01−7.10, 7.43−7.53 (m, 10 H, PPh_2) ppm. $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6, 25 °C): δ = −0.7, −0.6 ($SiMe_2$), 12.3, 12.4, 14.8, 15.0 (C_5Me_4), 27.0 (d, $^1J_{C,P}$ = 19.8 Hz), 28.6 (d, $^2J_{C,P}$ = 13.5 Hz) (-CH_2CH_2-), 112.3, 113.1, 125.0, 125.1, 126.1 (C_5H_3), 128.0−141.0 (various signals assigned to PPh_2 and C_5Me_4) ppm. $^{31}P\{^1H\}$ NMR (300 MHz, C_6D_6, 25 °C): δ = −39.5 ppm. $C_{30}H_{35}Cl_2PSiZr$ (616.8): calcd. C 58.42, H 5.72; found C 58.33, H 5.68.

$[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3PPh_2)\}Cl_2]$ (8): From $ZrCl_4$ (0.80 g, 3.41 mmol) and **4** (1.50 g, 3.41 mmol). Yield 1.12 g, 55%. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ = 0.18 and 0.30 (2s, each 3 H, $SiMe_2$), 1.56, 1.64, 1.95 and 2.00 (4s, each 3 H, C_5Me_4), 5.54 (2 H), 6.75 (1 H) (m, C_5H_3), 6.97−7.13, 7.38−7.73 (m, 10 H, PPh_2) ppm. $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6, 25 °C): δ = −1.0, −0.7 ($SiMe_2$), 12.4, 12.5, 14.8, 15.0 (C_5Me_4), 110.7, 114.4, 116.5, 120.4, 125.4 (d, $^1J_{C,P}$ = 33.6 Hz) (C_5H_3), 128.0−138.0 (various signals assigned to PPh_2 and C_5Me_4) ppm. $^{31}P\{^1H\}$ NMR (300 MHz, C_6D_6, 25 °C): δ = −43.8 ppm. $C_{28}H_{31}Cl_2PSiZr$ (588.7): calcd. C 57.12, H 5.31; found C 56.99, H 5.25.

$[Hf\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3CH_2CH_2PPh_2)\}Cl_2]$ (9): From $HfCl_4$ (1.08 g, 3.37 mmol) and **3** (1.58 g, 3.37 mmol). Yield 1.45 g, 61%. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ = 0.31 and 0.35 (2s, each 3 H, $SiMe_2$), 1.63, 1.75, 1.99 and 2.00 (4s, each 3 H, C_5Me_4), 2.24−2.59 and 2.98−3.24 (2m, each 2 H, -CH_2CH_2-), 4.98, 5.31 and 6.62 (3m, each 1 H, C_5H_3), 7.01−7.10, 7.40−7.51 (m, 10 H, PPh_2) ppm. $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6, 25 °C): δ = −0.7, −0.6 ($SiMe_2$), 12.1, 12.2, 14.5, 14.7 (C_5Me_4), 27.0 (d, $^1J_{C,P}$ = 19.7 Hz), 28.6 (d, $^2J_{C,P}$ = 13.8 Hz) (−CH_2CH_2-), 110.0, 110.7, 112.61 125.0, 126.1 (C_5H_3), 128.0−141.0 (various signals assigned to PPh_2 and C_5Me_4) ppm. $^{31}P\{^1H\}$ NMR (300 MHz, C_6D_6, 25 °C): δ = −39.8 ppm. $C_{30}H_{35}Cl_2HfPSi$ (704.1): calcd. C 51.18, H 5.01; found C 50.91, H 4.90.

$[Hf\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3PPh_2)\}Cl_2]$ (10): From $HfCl_4$ (1.10 g, 3.43 mmol) and **4** (1.51 g, 3.43 mmol). Yield 1.37 g, 59%. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ = 0.20 and 0.32 (2s, each 3 H, $SiMe_2$), 1.65, 1.73, 1.99, 2.05 (4s, each 3 H, C_5Me_4), 5.52, 5.54 and 6.72 (3m, each 1 H, C_5H_3), 6.99−7.14, 7.37−7.71 (m, 10 H, PPh_2) ppm. $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6, 25 °C): δ = −1.0, −0.7 ($SiMe_2$), 12.2, 12.3, 14.5, 14.7 (C_5Me_4), 112.1, 114.3, 116.5, 120.1, 125.4 (d, $^1J_{C,P}$ = 33.6 Hz) (C_5H_3), 128.0−138.0 (various signals assigned to PPh_2 and C_5Me_4) ppm. $^{31}P\{^1H\}$ NMR (300 MHz,

C_6D_6, 25 °C): δ = −41.0 ppm. $C_{28}H_{31}Cl_2HfPSi$ (676.0): calcd. C 49.75, H 4.62; found C 49.63, H 4.55.

Preparation of $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3CH_2CH_2PPh_2)\}Me_2]$ (11): A 3 M solution of MgMeCl in THF (0.43 mL, 1.30 mmol) was added to a stirred solution of **7** (0.40 g, 0.65 mmol) in THF (50 mL) at −78 °C. The solution was allowed to warm to room temperature and stirred for 4 h. Solvent was removed in vacuo and the remaining solid extracted with hexane (30 mL). A white crystalline solid was obtained by concentrating (5 mL) and cooling (−30 °C) the solution (0.30 g, 81%). ^1H NMR (200 MHz, C_6D_6, 25 °C): δ = −0.48 and −0.35 (2s, each 3 H, Zr-CH_3), 0.34 and 0.37 (2s, each 3 H, $SiMe_2$), 1.54, 1.65, 1.91 and 1.92 (4s, each 3 H, C_5Me_4), 2.38−3.05 (m, 4 H, -CH_2CH_2-), 5.05, 5.28 and 6.58 (3m, each 1 H, C_5H_3), 7.01−7.14, 7.42−7.52 (m, 10 H, PPh_2) ppm. $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6, 25 °C): δ = −0.3, 1.4 ($SiMe_2$), 11.6, 11.7, 14.3, 14.5 (C_5Me_4), 26.9 (d, $^1J_{C,P}$ = 19.6 Hz), 30.5 (d, $^2J_{C,P}$ = 8.6 Hz) (−CH_2CH_2-), 31.4, 35.2 (Zr-CH_3), 111.4, 112.2, 125.0, 125.1, 126.1 (C_5H_3), 128.0−140.0 (various signals assigned to PPh_2 and C_5Me_4) ppm. $^{31}P\{^1H\}$ NMR (300 MHz, C_6D_6, 25 °C): δ = −40.0 ppm. $C_{32}H_{41}PSiZr$ (576.0): calcd. C 66.73, H 7.18; found C 66.51, H 7.12.

Preparation of $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3PPh_2)\}Me_2]$ (12): The synthesis of **12** was carried out in an identical manner to that of **11**, with a 3 M solution of MgMeCl in THF (0.51 mL, 1.52 mmol) and **8** (0.45 g, 0.76 mmol). Yield 0.34 g, 80%. ^1H NMR (200 MHz, C_6D_6): δ = −0.49 (s, 6 H, Zr-CH_3), 0.26 and 0.37 (2s, each 3 H, $SiMe_2$), 1.56, 1.63, 1.89 and 1.97 (4s, each 3 H, C_5Me_4), 5.47, 5.57 and 6.74 (3m, each 1 H, C_5H_3), 7.07−7.17, 7.52−7.74 (m, 10 H, PPh_2) ppm. $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6, 25 °C): δ = −0.7, 0.1 ($SiMe_2$), 11.6, 11.7, 14.4, 14.5 (C_5Me_4), 37.3, 37.7 (Zr-CH_3), 110.4, 115.6, 116.5, 125.5, 127.4 (C_5H_3), 128.0−140.0 (various signals assigned to PPh_2 and C_5Me_4) ppm. $^{31}P\{^1H\}$ NMR (300 MHz, C_6D_6, 25 °C): δ = −44.1 ppm. $C_{30}H_{37}PSiZr$ (547.9): calcd. C 65.76, H 6.81; found C 65.49, H 6.71.

Preparation of $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3CH_2CH_2PPh_2)\}Me][MeB(C_6F_5)]$ (13): A solution of $B(C_6F_5)_3$ (0.25 g, 0.49 mmol) in toluene (25 mL) was added to a stirred solution of **11** (0.28 g, 0.49 mmol) in toluene (25 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred for 30 min. Solvent was removed in vacuo to give the title complex as an orange oil. ^1H NMR (300 MHz, [D$_8$]toluene, 25 °C): δ = −0.11 (s, 3 H, Zr-CH_3), 0.31 (br, 3 H, B-CH_3), 0.50 and 1.17 (2s, each 3 H, $SiMe_2$), 1.29, 1.34, 1.40 and 1.96 (4s, each 3 H, C_5Me_4), 2.20−2.80 (m, 4 H, -CH_2CH_2-), 4.84, 5.01 and 6.58 (3m, each 1 H, C_5H_3), 7.01−7.42 (m, 10 H, PPh_2) ppm. $^{11}B\{^1H\}$ NMR (300 MHz, [D$_8$]toluene, 25 °C): δ = 15 ppm. $^{31}P\{^1H\}$ NMR (300 MHz, [D$_8$]toluene, 25 °C): δ = −4.29 ppm.

Preparation of $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3PPh_2)\}Me][MeB(C_6F_5)]$ (14): The synthesis of **14** was carried out in an identical manner to that of **13**, from $B(C_6F_5)_3$ (0.25 g, 0.49 mmol) and **12** (0.27 g, 0.49 mmol). ^1H NMR (300 MHz, [D$_8$]toluene, 25 °C): δ = −0.49 (s, 3 H, Zr-CH_3), 0.18 and 0.30 (2s, each 3 H, $SiMe_2$), 0.31 (br, 3 H, B-CH_3), 1.56, 1.63, 1.89 and 1.97 (4s, each 3 H, C_5Me_4), 4.98, 5.64 and 6.22 (3m, each 1 H, C_5H_3), 7.01−7.34 (m, 10 H, PPh_2) ppm. $^{11}B\{^1H\}$ NMR (300 MHz, [D$_8$]toluene, 25 °C): δ = 15 ppm. $^{31}P\{^1H\}$ NMR (300 MHz, [D$_8$]toluene, 25 °C): δ = −44.6 ppm.

Preparation of $[Zr\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3PPh_2)\}\{\eta^2\text{-}MeC{=}N(C_6H_3Me_2\text{-}2,6)\}(Me)]$ (15): (2,6-dimethylphenyl)isocyanide (0.12 g, 0.91 mmol) and **12** (0.50 g, 0.91 mmol) were dissolved in THF (100 mL). The resulting orange solution was stirred at room temperature for 18 h. Solvent was removed in vacuo and the remaining solid extracted with toluene (30 mL). An orange solid was obtained by concentrating (5 mL) and cooling (−30 °C) the solution (0.37 g, 60%). IR (Nujol): $\nu_{C=N}$ 1584 cm^{-1}. ^1H NMR (200 MHz, C_6D_6, 25 °C): δ = 0.25 (s, 3 H, Zr-CH_3), 0.36 and 0.58 (2s, each 3 H, $SiMe_2$), 1.28 and 1.50 (2s, each 3 H, $C_6H_3Me_2$), 1.75, 1.82, 1.90 and 1.95 (4s, each 3 H, C_5Me_4), 2.19 (s, 3 H, C-CH_3 iminoacyl) 5.54, 5.65 and 5.88 (3m, each 1 H, C_5H_3), 6.82−7.07, 7.32−7.53 (m, PPh_2 and $C_6H_3Me_2$) ppm. $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6, 25 °C): δ = −0.7, 0.1 ($SiMe_2$), 11.6, 11.7, 14.4, 14.5 (C_5Me_4), 19.8 (CCH_3 iminoacyl), 25.8 (Zr-CH_3), 110.7, 113.4, 120.9, 125.5, 127.4 (C_5H_3), 128.0−140.0 (various signals assigned to PPh_2, $C_6H_3Me_2$, and C_5Me_4), 246.8 (CCH_3 iminoacyl) ppm. $^{31}P\{^1H\}$ NMR (300 MHz, C_6D_6, 25 °C): δ = −43.5 ppm. $C_{39}H_{46}NPSiZr$ (679.1): calcd. C 68.98, H 6.83, N 2.06; found C 68.75, H 6.77, N 2.00.

Preparation of $[Nb(=NtBu)\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3PPh_2)\}Cl]$ (16): THF (50 mL) was added to a solid mixture of $[Nb(=NtBu)Cl_3(py)_2]$ (0.78 g, 1.82 mmol) and **4** (0.80 g, 1.82 mmol). The resulting brown solution was stirred for 12 h. Solvent was removed in vacuo and hexane added (75 mL) to the resulting solid. The mixture was filtered and the filtrate concentrated (10 mL) and cooled to −30 °C. The resulting yellow solid that precipitated from the solution was isolated by filtration (0.67 g, 63%). IR (Nujol): $\nu_{Nb=N}$ = 1255 cm^{-1}. ^1H NMR (200 MHz, C_6D_6, 25 °C): δ = 0.10 and 0.45 (2s, each 3 H, $SiMe_2$), 0.87 (s, 9 H, CMe_3), 1.65, 1.71, 2.03 and 2.25 (4s, each 3 H, C_5Me_4), 5.61, 6.27 and 6.42 (3m, each 1 H, C_5H_3), 6.91−7.80 (m, PPh_2) ppm. $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6, 25 °C): δ = −1.5, −0.8 ($SiMe_2$), 12.6, 13.3, 13.4, 16.4 (C_5Me_4), 31.2 (CMe_3), 71.3 (CMe_3), 102.0, 104.7, 114.5, 114.9, 115.0 (C_5H_3), 128.0−135.0 (various signals assigned to PPh_2 and C_5Me_4) ppm. $^{31}P\{^1H\}$ NMR (300 MHz, C_6D_6, 25 °C): δ = −43.49 ppm. $C_{32}H_{40}ClNNbPSi$ (626.1): calcd. C 61.39, H 6.44, N 2.24; found C 61.17, H 6.36, N 2.25.

Preparation of $[Nb(=NtBu)(\eta^5\text{-}C_5H_4PPh_2)_2Cl]$ (17): The synthesis of **17** was carried out in an identical manner to **16**, from $[Nb(=NtBu)Cl_3(py)_2]$ (0.50 g, 1.16 mmol) and $Li(C_5H_4PPh_2)$ (0.60 g, 2.34 mmol). Yield 0.58 g, 72%. IR (Nujol): $\nu_{Nb=N}$ = 1240 cm^{-1}. ^1H NMR (200 MHz, C_6D_6, 25 °C): δ = 0.96 (s, 9 H, CMe_3), 5.89, 6.05, 6.12 and 6.18 (4m, each 2 H, 2 × C_5H_4), 6.91−7.50 (10 H) (m, PPh_2) ppm. $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6, 25 °C): δ = 29.9 (CMe_3), 70.6 (CMe_3), 111.8, 112.7, 120.6, 120.7 124.7 (C_5H_4), 128.0−134 (various signals assigned to PPh_2) ppm. $^{31}P\{^1H\}$ NMR (300 MHz, C_6D_6, 25 °C). δ = −40.10 ppm. $C_{38}H_{37}ClNNbP_2$ (698.0): calcd. C 65.39, H 5.34, N 2.01; found C 65.17, H 5.23, N 1.99.

Polymerization Experiments: The *ansa*-zirconocene catalyst (**7** or **8**; 6 µmol), MAO (10% in toluene) (3000 µmol) and toluene (150 mL) were mixed together in a Schlenk tube. The N_2 pressure inside the Schlenk tube was reduced by applying vacuum. An ethylene pressure of 1.5 bar was then applied to the Schlenk tube and stirring of the mixture commenced. After exactly 30 min, stirring was halted and the ethylene pressure was released. Excess MAO was then destroyed by adding a mixture of methanol/HCl (90:10) cautiously. The polymer formed was isolated by filtration, washed with ethanol and dried under vacuum at 60 °C for 12 h.

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[1] *Comprehensive Organometallic Chemistry II* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon Press, Oxford, **1995**, vol. 4.

[2] B. Rieger, G. Jany, R. Fawzi, M. Steimann, *Organometallics* **1994**, *13*, 647−653.

[3] [3a] S. L. J. Conway, T. Dijkstra, L. H. Doerrer, J. C. Green, M. L. H. Green, A. H. H. Stephens, *J. Chem. Soc., Dalton Trans.* **1998**, 2689−2695. [3b] J. H. Shin, G. Parkin, *Chem. Commun.* **1999**, 887−888.

[4] A. Antiñolo, M. Martínez-Ripoll, Y. Mugnier, A. Otero, S. Prashar, A. M. Rodriguez, *Organometallics* **1996**, *15*, 3241−3243.

[5] [5a] N. J. Bailey, J. A. Cooper, H. Gailus, M. L. H. Green, J. T. James, M. A. Leech, *J. Chem. Soc., Dalton Trans.* **1997**, 3579−3584. [5b] N. J. Bailey, M. L. H. Green, M. A. Leech, J. F. Saunders, H. M. Tidswell, *J. Organomet. Chem.* **1997**, *538*, 111−118. [5c] W. A. Herrmann, W. Baratta, E. Herdtweck, *J. Organomet. Chem.* **1997**, *541*, 445−460. [5d] A. Antiñolo, A. Otero, S. Prashar, A. M. Rodriguez, *Organometallics* **1998**, *17*, 5454−5459.

[6] M. E. Huttenloch, B. Dorer, U. Rief, M.-H. Prosenc, K. Schmidt, H. H. Brintzinger, *J. Organomet. Chem.* **1997**, *541*, 219−232.

[7] S. L. J. Conway, L. H. Doerrer, M. L. H. Green, M. A. Leech, *Organometallics* **2000**, *19*, 630−637.

[8] A. Antiñolo, I. López-Solera, I. Orive, A. Otero, S. Prashar, A. M. Rodríguez, E. Villaseñor, *Organometallics* **2001**, *20*, 71−78.

[9] A. Antiñolo, I. López-Solera, A. Otero, S. Prashar, A. M. Rodríguez, E. Villaseñor, *Organometallics* **2002**, *21*, 2460−2467.

[10] [10a] Y. Obora, C. L. Stern, T. J. Marks, P. N. Nickias, *Organometallics* **1997**, *16*, 2503−2505. [10b] M. A. Giardello, M. S. Eisen, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1993**, *115*, 3326−3327. [10c] M. A. Giardello, M. S. Eisen, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1995**, *117*, 12114−12129. [10d] H. Schumann, K. Zietzke, R. Weimann, J. Demtschuk, W. Kaminsky, A.-M. Schauwienold, *J. Organomet. Chem.* **1999**, *574*, 228−240. [10e] C. Müller, D. Lilge, M. O. Kristen, P. Jutzi, *Angew. Chem.* **2000**, *112*, 800−803; *Angew. Chem. Int. Ed.* **2000**, *39*, 789−792. [10f] N. Suzuki, T. Mise, Y. Yamaguchi, T. Chihara, Y. Ikegami, H. Ohmori, A. Matsumoto, Y. Wakatsuki, *J. Organomet. Chem.* **1998**, *560*, 47−54. [10g] T. A. Herzog, D. L. Zubris, J. E. Bercaw, *J. Am. Chem. Soc.* **1996**, *118*, 11988−11989.

[11] [11a] R. W. Baker, M. A. Foulkes, P. Turner, *J. Chem. Soc., Dalton Trans.* **2000**, 431−433. [11b] A. Razavi, J. Ferrara, *J. Organomet. Chem.* **1992**, *435*, 299−310. [11c] A. Razavi, J. L. Atwood, *J. Organomet. Chem.* **1993**, *459*, 117−123. [11d] J. A. Ewen, J. L. Jones, A. Razavi, J. Ferrara, *J. Am. Chem. Soc.* **1988**, *110*, 6255−6256. [11e] G. H. Llinas, R. O. Day, M. D. Rausch, J. C. W. Chien, *Organometallics* **1993**, *12*, 1283−1288. [11f] B. Rieger, G. Jany, R. Fawzi, M. Steimann, *Organometallics* **1994**, *13*, 647−653. [11g] M. L. H. Green, N. Ishihara, *J. Chem. Soc., Dalton Trans.* **1994**, 657−665. [11h] A. Razavi, J. L. Atwood, *J. Organomet. Chem.* **1995**, *497*, 105−111. [11i] Y.-X. Chen, M. D. Rausch, J. C. W. Chien, *J. Organomet. Chem.* **1995**, *497*, 1−9. [11j] T. Bürgi, H. Berke, D. Wingbermühle, C. Psiorz, R. Noe, T. Fox, M. Knickmeier, M. Berlekamp, R. Fröhlich, G. Erker, *J. Organomet. Chem.* **1995**, *497*, 149−159. [11k] W. Kaminsky, O. Rabe, A.-M. Schauwienold, G. U. Schupfner, J. Hanss, J. Kopf, D. Veghini, L. M. Henling, T. J. Burkhardt, J. E. Bercaw, *J. Am. Chem. Soc.* **1999**, *121*, 564−573. [11l] J. A. Ewen, R. L. Jones, M. J. Elder, *J. Am. Chem. Soc.* **1998**, *120*, 10786−10787. [11m] K. Patsidis, H. G. Alt, W. Milius, S. J. Palackal, *J. Organomet. Chem.* **1996**, *509*, 63−71. [11n] U. Dietrich, M. Hackmann, B. Rieger, M. Klinga, M. Leskelä, *J. Am. Chem. Soc.* **1999**, *121*, 4348−4355. [11o] E. J. Thomas, J. C. W. Chien, M. D. Rausch, *Organometallics* **1999**, *18*, 1439−1443. [11p] S. C. Yoon, T. K. Han, B. W. Woo, H. Song, S. I. Woo, J. T. Park, *J. Organomet. Chem.* **1997**, *534*, 81−87.

[12] A. H. Hoveyda, J. P. Morken, *Angew. Chem.* **1996**, *108*, 1378−1399; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1262−1284.

[13] [13a] H. Butenschön, *Chem. Rev.* **2000**, *100*, 1527−1564. [13b] R. M. Bellabarba, G. P. Clancy, P. T. Gomes, A. M. Martins, L. H. Rees, M. L. H. Green, *J. Organomet. Chem.* **2001**, *640*, 93−112 and cited references.

[14] J. C. Leblanc, C. Moise, A. Maisonnat, R. Poilblanc, C. Charrier, F. Mathey, *J. Organomet. Chem.* **1982**, *231*, C43−C48.

[15] [15a] B. E. Bosch, G. Erker, R. Fröhlich, O. Meyer, *Organometallics* **1997**, *16*, 5449−5456. [15b] I. Ara, E. Delgado, J. Fornies, E. Hernandez, E. Lalinde, N. Mansilla, M. T. Moreno, *J. Chem. Soc., Dalton Trans.* **1996**, 3201−3207.

[16] [16a] X.-D. He, A. Maisonnat, F. Dahan, R. Poilblanc, *Organometallics* **1989**, *8*, 2618−2626. [16b] W. Tikkanen, Y. Fujita, J. L. Petersen, *Organometallics* **1986**, *5*, 888−894. [16c] R. M. Bullock, C. P. Casey, *Acc. Chem. Res.* **1987**, *20*, 167−173. [16d] F. T. Ladipo, G. K. Anderson, N. P. Rath, *Organometallics* **1994**, *13*, 4741−4745. [16e] J. Szymoniak, M. M. Kubicki, J. Besançon, C. Moïse, *Inorg. Chim. Acta* **1991**, *180*, 153−160.

[17] C. Poulard, G. Boni, P. Richard, C. Moïse, *J. Chem. Soc., Dalton Trans.* **1999**, 2725−2730.

[18] S. Beck, S. Lieber, F. Schaper, A. Geyer, H.-H. Brintzinger, *J. Am. Chem. Soc.* **2001**, *123*, 1483−1489.

[19] L. D. Durfee, I. P. Rothwell, *Chem. Rev.* **1988**, *88*, 1059−1079.

[20] G. Erker, *Acc. Chem. Res.* **1984**, *17*, 103−109.

[21] [21a] A. Antiñolo, M. Fajardo, C. López-Mardomingo, I. López-Solera, A. Otero, Y. Pérez, S. Prashar, *Organometallics* **2001**, *20*, 3132−3138. [21b] A. Antiñolo, M. Fajardo, C. Huertas, A. Otero, S. Prashar, A. M. Rodriguez, *J. Organomet. Chem.* **1999**, *585*, 154−161. [21c] A. Antiñolo, P. Espinosa, M. Fajardo, P. Gómez-Sal, C. López-Mardomingo, A. Martin-Alonso, A. Otero, *J. Chem. Soc., Dalton Trans.* **1995**, 1007−1013. [21d] A. Antiñolo, F. Carrillo-Hermosilla, A. Otero, M. Fajardo, A. Garcés, P. Gómez-Sal, C. López-Mardomingo, A. Martín, C. Miranda, *J. Chem. Soc., Dalton Trans.* **1998**, 59−65.

[22] [22a] A. J. Bridgeman, L. Davis, S. J. Dixon, J. C. Green, I. N. Wright, *J. Chem. Soc., Dalton Trans.* **1995**, 1023−1027. [22b] J. C. Green, M. L. H. Green, J. T. James, P. C. Konidaris, G. H. Maunder, P. Mountford, *J. Chem. Soc., Chem. Commun.* **1992**, 1361−1364. [22c] M. H. Schofield, T. P. Kee, J. T. Anhaus, R. R. Schrock, K. H. Johnson, W. M. Davis, *Inorg. Chem.* **1991**, *30*, 3595−3604. [22d] J. T. Anhaus, T. P. Kee, M. H. Schofield, R. R. Schrock, *J. Am. Chem. Soc.* **1990**, *112*, 1642−1643.

[23] T. W. Graham, A. Llamazares, R. McDonald, M. Cowie, *Organometallics* **1999**, *18*, 3490−3501.

[24] L. P. Casey, R. M. Bullock, W. C. Fultz, A. L. Rheingold, *Organometallics* **1982**, *1*, 1591−1596.

[25] J. Sundermeyer, J. Putterlik, M. Foth, J. S Field, N. Ramesar, *Chem. Ber.* **1994**, *127*, 1201−1212.

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