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Complexes of titanium and zirconium containing a tridentate linked amido–cyclopentadienyl ligand with a soft donor group: synthesis, structure, and ethylene polymerization catalysis

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Abstract

Group 4 metal complexes $M(\eta^5{:}\eta^1\text{-}C_5R_4SiMe_2NCH_2CH_2SMe)Cl_2$ ($R = H$, $M = Ti$; $R = Me$, $M = Ti$, Zr) containing the thioether-functionalized linked amido–cyclopentadienyl ligand were synthesized and characterized by ^1H- and ^{13}C-NMR spectroscopy, mass spectrometry, and elemental analysis. The crystal structures of the complexes $Ti(\eta^5{:}\eta^1\text{-}C_5H_4SiMe_2NCH_2CH_2SMe)Cl_2$ and $Zr(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2SMe)Cl_2$ were determined by single-crystal X-ray diffraction studies. The titanium complex is a conventional three-legged piano-stool molecule without an intramolecular interaction between the sulfur donor group and the titanium center, whereas the zirconium complex adopts a trigonal bipyramidal structure, with the five-membered ring and the coordinating methylthio group in the apical positions. Reaction between the titanium dibenzyl $Ti(\eta^5{:}\eta^1\text{-}C_5Me_4ZNCH_2CH_2SMe)(CH_2Ph)_2$ ($Z = SiMe_2$, CH_2SiMe_2) and $B(C_6F_5)_3$ in C_6D_5Br resulted in the clean formation of the solvent-separated ion pair $[Ti(\eta^5{:}\eta^1\text{-}C_5Me_4ZNCH_2CH_2SMe)(\eta^2\text{-}CH_2Ph)]^+[(PhCH_2)B(C_6F_5)_3]^-$. The dichloro complexes $M(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2SMe)Cl_2$, when activated with methylaluminoxane, catalyzed the polymerization of ethylene with moderate activities. The phosphino-functionalized ligand $C_5Me_4SiMe_2NC_6H_4(PPh_2)\text{-}2$ was also coordinated at titanium and zirconium centers; NMR spectroscopic data inferred an intramolecular metal–phosphine interaction for these $M\{\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NC_6H_4(PPh_2)\text{-}2\}Cl_2$ complexes. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Titanium; Zirconium; Linked amido–cyclopentadienyl ligand; Thioether ligand; Benzyl cation; Ethylene polymerization

1. Introduction

In the context of homogeneous olefin polymerization catalysis, complexes of Group 3 and 4 metals containing a linked amido–cyclopentadienyl ligand $C_5R'_4ZNR''$ [1] may be considered as hybrids of the Brintzinger-type ansa-metallocenes [2] and the electronically more unsaturated and sterically more open bis(amido) chelate complexes [3]. (Scheme 1) We recently introduced a potentially tridentate variation of the linked amido–cyclopentadienyl ligand, $C_5R'_4SiMe_2NCH_2CH_2X$, in which the supplementary donor ligand was designed to temporarily protect the highly electrophilic d^0-metal center within this ligand framework [4]. The additional two-electron donor $X = OMe$ and NMe_2 could stabilize alkyl cations of the type $[M(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2X)CH_2Ph]^+$ to make them more amenable to study [5] than those of complexes containing the original bidentate amido–cyclopentadienyl ligand $C_5Me_4SiMe_2NCMe_3$ [6]. Although fluxional on the NMR timescale, the coordination of the third donor group X appeared to be fairly strong, resulting in a decreased activity toward ethylene polymerization. Since soft donor groups are known to stabilize reactive Group 3 and 4 metal centers [7–10], yet remain kinetically labile, we decided to utilize sulfur and phosphorus donor function groups. We report here the synthesis and characterization of Group 4 metal complexes containing tridentate linked amido–cyclopentadienyl ligands with SMe and PPh_2 groups.

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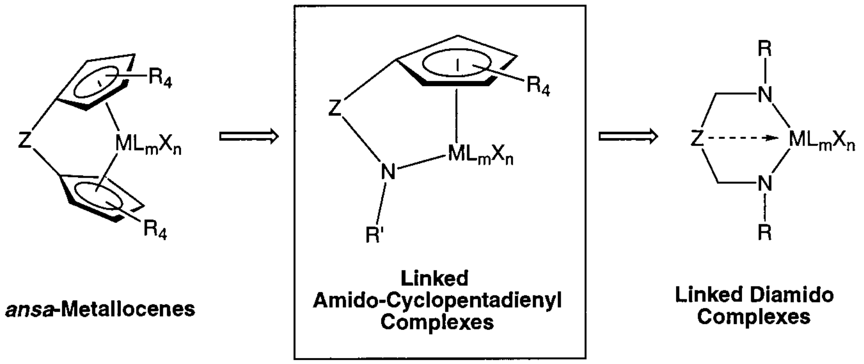


Scheme 1.

2. Results and discussion

2.1. Ligands with a methylthio-functionalized side chain

The synthesis proceeded analogously to the one used to prepare the methoxy- and *N*,*N*-dimethylamino-functionalized complexes of titanium [4a]. Reaction between equimolar amounts of lithium amide Li(NHCH$_2$CH$_2$SMe) and Ti(η^5-C$_5$H$_4$SiMe$_2$Cl)Cl$_3$ in the presence of triethylamine led to the complex Ti(η^5:η^1-C$_5$H$_4$SiMe$_2$NCH$_2$CH$_2$SMe)Cl$_2$ (**1**) in moderate yield as analytically pure, yellow crystals. Because the molecule is C_s-symmetric, as shown by the ^{1}H- and ^{13}C-NMR spectra, it was not possible to decide whether intramolecular coordination of the thioether group was present or not. The methylthio group appears as a resonance at δ 1.86 and 15.0 in the ^{1}H- and ^{13}C-NMR spectra, respectively. Since these values do not differ significantly from those of the free ligand, we suspect that a dynamic situation with the equilibrium shifted towards the from without the thioether coordination is present. The open structure without any intramolecular coordination was found for the crystalline state by X-ray crystal structure analysis. Fig. 1 shows that the methylthioethyl side chain attached to the amido–nitrogen atom is not interacting with the titanium center. The side chain adopts a different conformation to that of the methoxyethyl side chain in Ti(η^5:η^1-C$_5$H$_4$SiMe$_2$NCH$_2$CH$_2$OMe)Cl$_2$, but all metrical parameters pertinent to the titanium coordination are very similar [4b].

The tetramethylcyclopentadienyl analog Ti(η^5:η^1-C$_5$Me$_4$SiMe$_2$N–CH$_2$CH$_2$SMe)Cl$_2$ (**2a**) could also be prepared according to a conventional procedure. It was isolated as yellow crystals, and was fully characterized by elemental analysis, ^{1}H- and ^{13}C-NMR spectroscopy, and mass spectrometry. A molecule with a mirror plane was again observed in solution; its NMR spectrum which did not change in the temperature range + 80 to − 80°C suggests a similar situation as that for **1**, with a preference for the open form [4a,5]. The resonance for the methylthio group was observed at δ 1.94 and 15.1 in the ^{1}H- and ^{13}C-NMR spectrum, respectively. When the ligand (C$_5$Me$_4$)CH$_2$SiMe$_2$NCH$_2$CH$_2$SMe, which is prolonged by a CH$_2$ bridge [4e], was coordinated in an analogous manner, Ti(η^5:η^1-C$_5$Me$_4$CH$_2$SiMe$_2$NCH$_2$CH$_2$SMe)Cl$_2$ (**2b**) was isolated (see Scheme 2).

The homologous zirconium complex Zr(η^5:η^1-C$_5$Me$_4$SiMe$_2$NCH$_2$CH$_2$SMe)Cl$_2$ (**3**) was prepared from the reaction between ZrCl$_4$(THF)$_2$ and Li$_2$(C$_5$Me$_4$SiMe$_2$NCH$_2$CH$_2$SMe) and isolated as hexane-soluble, colorless crystals which could be fully characterized (see Table 1). Analogous to the methoxy and *N*,*N*′-dimethylamino derivatives, Zr(η^5:η^1:η^1-C$_5$Me$_4$SiMe$_2$NCH$_2$-

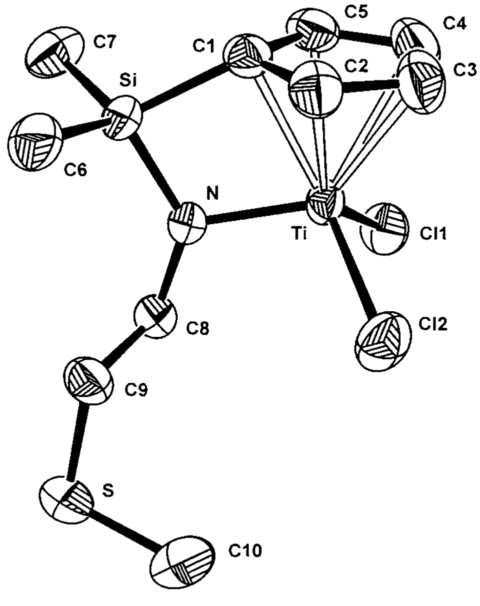
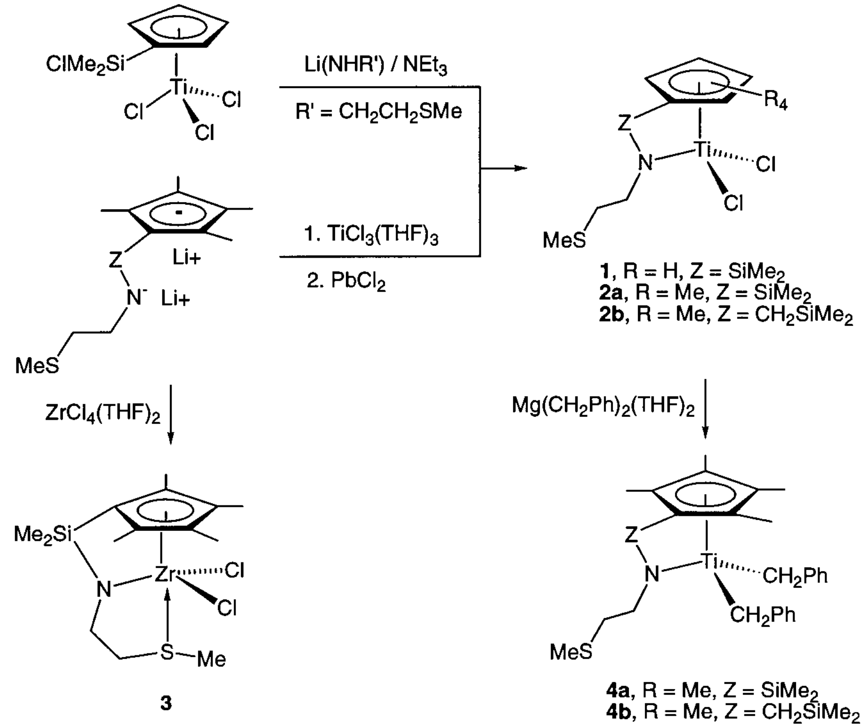


Fig. 1. ORTEP diagram of the molecular structure of Ti(η^5:η^1-C$_5$H$_4$SiMe$_2$NCH$_2$CH$_2$SMe)Cl$_2$ (**1**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for the sake of clarity; selected bond distances (Å) and angles (°): Ti–Cp (centroid) 2.013(3), Ti–N 1.876(3), Si–N 1.748(3), Ti–Cl1 2.264(2), Ti–Cl2 2.266(2), S–C9 1.804(4), S–C10 1.795(6); Si–N–C8 133.5(2), C9–S–C10 100.2(3), N–C8–C9 113.4(3), C8–C9–S 112.5(3), Ti–N–Si 108.5(1), Ti–N–C8 117.9(2).



Scheme 2.

$CH_2X)Cl_2$ ($X = OMe$, NMe_2) (**3**) is a C_s-symmetric molecule, but the resonances for the methylthio group is somewhat low-field shifted compared to those for **2** (δ 1.97 and 16.1). The resonances are invariant in the temperature range of -80 to $+80$°C.

The single-crystal X-ray structure analysis of **3** revealed a trigonal bipyramidal configuration, similar to that found in the structure of $Zr(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2X)Cl_2$ ($X = OMe$, NMe_2), with a zirconium–sulfur distance of 2.791(1) Å (Fig. 2). This value is comparable to that found for $[Zr(\eta^5\text{-}C_5Me_5)_2Me(THT)]^+[BPh_4]^-$ (2.730(4) Å) [8] (THT = tetrahydrothiophene) or $[Zr(\eta^5{:}\eta^1\text{-}C_5Me_4\text{-}CH_2CH_2SMe)Cl_3]_2$ (2.767(2) Å) [11a]. Similar bond lengths between a thioether sulfur and a tetravalent zirconium were reported in chelating bis(amido) complexes: 2.805(1) Å for $Zr\{(2,6\text{-}Me_2C_6H_3NCH_2\text{-}CH_2)_2S\}Me_2$ [9a] and 2.734(1) Å for $Zr\{(^iPrN\text{-}o\text{-}C_6H_4)_2S\}Me_2$ [9b]. The Zr–S bond in **3** is considerably longer than the Zr–O bond of 2.375(2) Å in $Zr(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2OMe)Me_2$ [5], and this results in a significant distortion of the slightly puckered five-membered chelate ring. Although still perfectly planar, the angles around the sp^2-hybridized amido nitrogen are different. Most notably, the Zr–N–C12 angle with 131° is larger than the corresponding angle in $Zr(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4SiMe_2N\text{-}CH_2CH_2OMe)Me_2$ (124.2(2)°) or $Hf(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4\text{-}SiMe_2NCH_2CH_2OMe)Cl_2$ (124.7(5)°). This can be ascribed to the rather distorted chelate ring, which has to accommodate a long Zr–S bond while the other four bonds, including the Zr–N bond of 2.088(2) are relatively short. The sulfur atom is pyramidalized, the angle

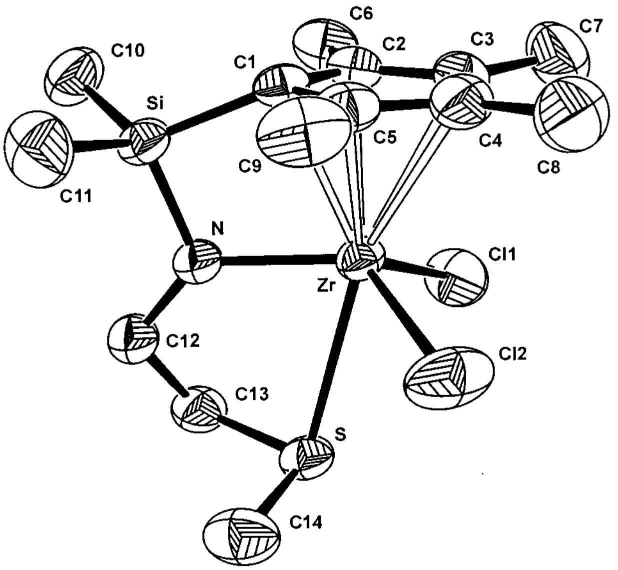


Fig. 2. ORTEP diagram of the molecular structure of $Zr(\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2SMe)Cl_2$ (**3**). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for the sake of clarity; selected bond distances (Å) and angles (°): Zr–S 2.791(1), Zr–Cp (centroid) 2.214(3), Zr–N 2.088(2), Si–N 1.727(2), Zr–Cl1 2.446(1), Zr–Cl2 2.432(1), S–C13 1.799(3), S–C14 1.798(3); Zr–N–Si 107.3(1), Zr–N–C12 131.0(2), Si–N–C12 121.6(2), Cl1–Zr–Cl2 108.27(4), N–C12–C13 111.6(3), C12–C13–S 110.6(2), C13–S–C14 100.6(2), C13–S–Zr 93.7(1), C14–S–Zr 107.8(1).

Table 1
Crystallographic data for $Ti(\eta^5:\eta^1-C_5H_4SiMe_2NCH_2CH_2SMe)Cl_2$ (**1**) and $Zr(\eta^5:\eta^1-C_5Me_4SiMe_2NCH_2CH_2SMe)Cl_2$ (**3**)

Compound	**1**	**3**
Formula	$C_{10}H_{17}Cl_2NSSiTi$	$C_{14}H_{25}Cl_2NSSiZr$
Crystal shape	Prism	Prism
Crystal color	Yellow	White
Crystal size (mm)	0.20 × 0.30 × 0.40	0.45 × 0.65 × 0.70
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$ (no. 2)	*Pbca* (no. 61)
Unit cell dimensions		
a (Å)	8.501(3)	14.954(3)
b (Å)	9.555(5)	9.813(3)
c (Å)	10.902(5)	25.635(9)
α (°)	110.20(4)	
β (°)	111.80(3)	
γ (°)	91.72(4)	
V (Å^3)	758.8(6)	3762(2)
Z	2	8
Wavelength (Å)	0.7107 (Mo–K$_\alpha$)	0.7107 (Mo–K$_\alpha$)
μ_{lin} (mm^{-1})	1.108	1.034
θ Scan range (°)	30	30
Reflections measured	7466	9539
Independent reflections observed	3029	3524
$[I>2\sigma(I)]$	$[R_{int}=0.0313]$	$[R_{int}=0.0460]$
Final R indices R_1, wR_2 (observed data)	0.0563, 0.1260	0.0358, 0.0753
Final R indices R_1, wR_2 (all data)	0.0909, 0.1561	0.0777, 0.0936
Goodness-of-fit	1.149	1.063
Parameters refined	214	204
Residual density: max., min. $\Delta\rho$ (e Å^{-3})	0.626, −1.083	0.563, −0.398

at sulfur C13–S–C14 being 100.6(2)°, similar to the values found for $Zr\{(2,6-Me_2C_6H_3NCH_2CH_2)_2S\}Me_2$ (105.0(2)°) [9a] and $Zr\{(^iPrN-o-C_6H_4)_2S\}-Me_2$-(103.5(1)°) [9b], as well as the titanium complex $[Ti\{(OC_6H_2-4-Me-6-^tBu)_2S\}(O^iPr)_2]_2$ (100.8(2)°) [10f]. This coordination of the sulfur atom (sum of the angles: 302.1°) contrasts to the trigonal planar methoxy oxygen atom that can be regarded as sp^2-hybridized (sum of the angles: 355.9° in $Zr(\eta^5:\eta^1:\eta^1-C_5Me_4-SiMe_2NCH_2CH_2OMe)Me_2$). In conclusion, all the structural features are consistent with a somewhat weaker interaction of the third ligating group.

2.2. Ethylene polymerization and benzyl cation formation

When the dichloro complexes were activated with MAO under standardized conditions, ethylene was polymerized with good activity (Table 2) to high-molecular-weight linear polyethylene. As found previously, it is striking that the zirconium complex **3** is by one order of magnitude less active than the titanium complex **2a**. Furthermore, compared to the prototypical *tert*-butylamido derivative $Ti(\eta^5:\eta^1-C_5Me_4SiMe_2NCMe_3)Cl_2$, the catalyst precursor **2a** is less active, but shows significantly higher activity values than the OMe- and NMe$_2$-functionalized analogs. This can be ascribed to the dissimilar coordination abilities of the various third donor groups, which effectively compete with the incoming ethylene molecule for coordination.

As the analogous methyl cation is very sensitive, we decided to study the solution properties of the titanium benzyl cation, to gain some information about the coordination sphere within the tridentate ligand system. The dibenzyl complexes $Ti(\eta^5:\eta^1-C_5Me_4ZNCH_2CH_2SMe)(CH_2Ph)_2$ ($Z = SiMe_2$ (**4a**), $Z = CH_2SiMe_2$ (**4b**)) were synthesized by alkylating the corresponding dichloro complexes $Ti(\eta^5:\eta^1-C_5Me_4ZNCH_2CH_2SMe)Cl_2$ (**2**) with dibenzylmagnesium. Spectroscopic features of the complexes, isolated as red crystals, indicate a structure similar to that of related dibenzyl complexes of the general type $Ti(\eta^5:\eta^1-C_5R'_4-ZNR'')(CH_2Ph)_2$ [1b,5,12]. When the dibenzyl complexes **4a** and **4b** were treated with one equivalent of $B(C_6F_5)_3$ in C_6D_5Br, NMR spectroscopy indicated clean formation of the benzyl cations $[Ti(\eta^5:\eta^1-C_5Me_4ZNCH_2CH_2SMe)(\eta^2-CH_2Ph)]^+[(PhCH_2)B(C_6F_5)_3]^-$ (**5a** and **5b**). All attempts at isolating the ion pairs on a preparative scale have failed so far, although they appear to be thermally stable as bromobenzene

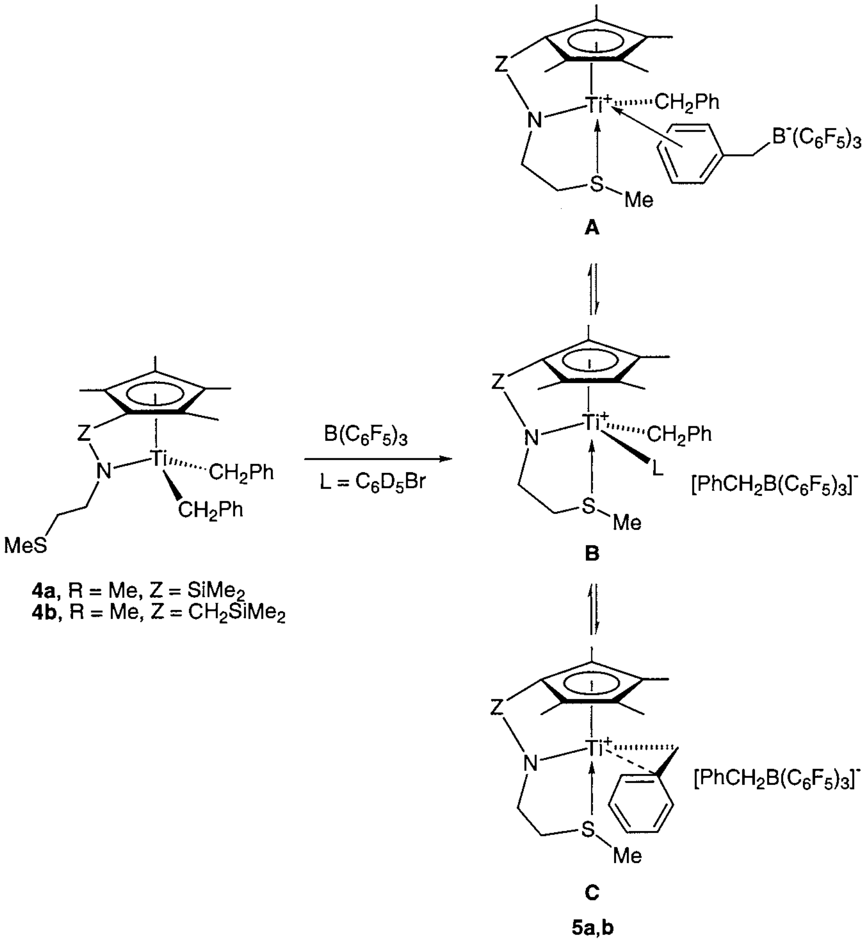
Table 2
Data for ethylene polymerization with methylaluminoxane-activated $Ti(\eta^5:\eta^1-C_5Me_4ZNR')Cl_2$ complexes [a]

Precatalyst	Yield (g)	Activity [b]	T_m (°C) [c]	Ref.
$Ti(\eta^5:\eta^1-C_5Me_4SiMe_2N^tBu)Cl_2$	4.11	950	141.6	[12b]
$Ti(\eta^5:\eta^1-C_5Me_4SiMe_2NCH_2CH_2NMe_2)Cl_2$	0.23	53	135.5	[4e]
$Ti(\eta^5:\eta^1-C_5Me_4SiMe_2NCH_2CH_2OMe)Cl_2$	0.08	12	132.3	[5]
$Zr(\eta^5:\eta^1-C_5Me_4SiMe_2NCH_2CH_2OMe)Me_2$	0.08	13	136.5	[5]
$Ti(\eta^5:\eta^1-C_5Me_4SiMe_2NCH_2CH_2SMe)Cl_2$ (**2a**)	1.15	265	141.0	This work
$Zr(\eta^5:\eta^1-C_5Me_4SiMe_2NCH_2CH_2SMe)Cl_2$ (**3**)	0.15	34	140.3	This work

[a] Polymerization conditions: titanium complex 5 μmol, methylaluminoxane 2500 μmol in 200 ml of toluene at 25°C, constant ethene pressure 3 bar ($c_{ethylene} = 0.432$ mol l^{-1}), reaction time 2 h.

[b] Activity in kg (PE) mol Ti^{-1} × h × $c_{ethylene}$.

[c] Determined by DSC (heating rate, 10 K min^{-1})

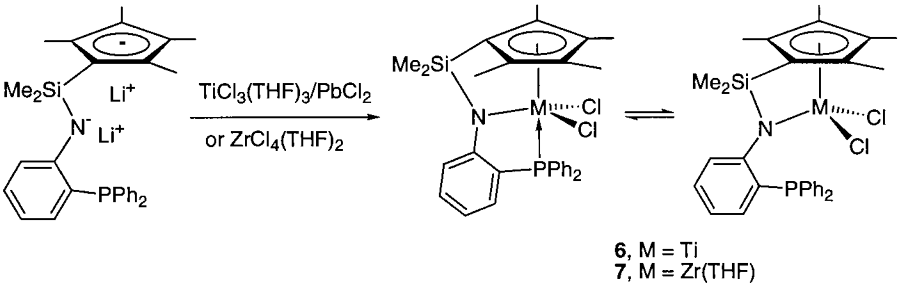


Scheme 3.

solutions. That a solvent-separated ion-pair formed can be concluded from the $\Delta\delta$ (*meta*-, *para*-F) values of 2.8 for the anion $[PhCH_2B(C_6F_5)_3]^-$ in the ^{19}F-NMR spectra of **5a** [13]. The cation contains no mirror plane, and its ^1H-NMR spectrum has two and four signals for the $SiMe_2$- and C_5Me_4-methyl groups, respectively. At 70°C these signals coalesced to one $SiMe_2$ and two C_5Me_4 resonances ($\Delta G^\ddagger = 69$ kJ mol^{-1}), suggesting a rapid symmetrization via a monohapto-bonded benzyl group. At room temperature (r.t.), the benzyl group at $\delta =$ 2.59 and 3.15 has a $^2J_{HH}$ value of 6.3 Hz in the ^1H-NMR spectrum, while the $^1J_{CH}$ value of the ^{13}C resonance at $\delta = 72.3$ is 150 Hz, suggesting a dihapto coordination. As with the methoxy derivative [5], species **C** of the various possible equilibrating species is preferred (Scheme 3). In contrast, the *N*,*N'*-dimethylamino-functionalized analog appears to contain as the main species a monohapto benzyl group of type **B** ($^2J_{HH} = 11.4$ Hz), evidently due to the higher basicity of the amino group [5]. Finally, the longer bridge between the ring and the amido nitrogen does not affect the intramolecular coordination significantly, as can be judged by comparison of the NMR spectroscopic data of **5a** with those of **5b**, which shows resonances for the benzyl group at $\delta = 2.21$ and 3.32, with $^2J_{HH} = 7.4$ Hz, and a ^{13}C resonance at $\delta = 74.2$, with $^1J_{CH} = 144$ Hz. Apparently the less basic OMe and SMe shifts the equilibrium towards the more electrophilic dihapto-bonded benzyl [4e,5,14].

2.3. Ligands with a diphenylphosphino-functionalized side chain

Because the amine $H_2NCH_2CH_2PMe_2$ is difficult to prepare, we turned to the easily accessible *ortho*-diphenylphosphinoaniline [15] as the precursor for the amido side chain. Reaction of $(C_5Me_4H)SiMe_2Cl$ with $Li\{NHC_6H_4(PPh_2)\text{-}2\}$ smoothly produced the cyclopentadiene $(C_5Me_4H)SiMe_2NHC_6H_4(PPh_2)\text{-}2$ (^{31}P-NMR: δ -18.4), which could be deprotonated with two equivalents of *n*-butyllithium. The complexation reaction with $TiCl_3(THF)_3/PbCl_2$ and $ZrCl_4(THF)_2$ gave $M\{\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NC_6H_4(PPh_2)\text{-}2\}Cl_2$ (M = Ti (**6**), Zr = (**7**)) as brown and colorless microcrystals, respectively. Purification proved to be difficult because of their low



6, M = Ti
7, M = Zr(THF)

Scheme 4.

crystallinity, but NMR spectroscopic data suggested the expected structure. While ^{1}H- and ^{13}C-NMR spectra indicate C_s-symmetry for both complexes, the change in the magnitude of the $^1J_{PC}$ and $^2J_{PC}$ values for the *ipso*- and *ortho*-carbon atoms in the ^{13}C-NMR, as well as the significant high-field shift of the ^{31}P-NMR resonance suggests an interaction of the phosphorus atom with the metal center ($\Delta\delta = 34.8$ for **6**; 28.5 for **7**). A similar situation is reported for the half-sandwich complexes $Zr(\eta^5:\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)Cl_3(THF)$ [16a] and $Ti(\eta^5\text{-}C_5H_5)Cl_2(OC_6H_3\text{-}{}^tBu\text{-}6\text{-}PPh_2)$ [16b] in which a metal–phosphorus interaction is present, according to X-ray crystallography and solution studies. In the absence of crystallographic data, we hypothesize that intramolecular coordination of the PPh_2 unit at the metal center is preferred because of the rigid *ortho*-phenylene bridge and the electron-withdrawing anilido group. The zirconium complex **7** retains one molecule of THF, as indicated by NMR spectroscopy. So far all attempts to prepare the dialkyl complexes have failed (see Scheme 4).

3. Conclusions

We have extended the class of tridentate linked amido–cyclopentadienyl ligands to include soft donor groups SMe and PPh_2, which are well suited to form semilabile ligands. We have noted significant differences in the structures, solution dynamics, and reactivities of the resulting titanium and zirconium complexes compared with those containing the OMe- and NMe_2-functionalized systems [4,5]. Although the changes are subtle, the nucleophilicity (donor ability) increases in the order SMe < OMe < NMe_2 and allows more rational modifications to the electrophilicity at the metal center. The role of sulfur donor groups in linked bis(phenoxide) ligands has recently been studied both experimentally [10] and theoretically [17] in view of the commercial interest in olefin polymerization catalysts based on Group 4 metal complexes with non-cyclopentadienyl ligands [3]. The increase in the activity for olefin polymerization in catalysts containing a thioether function is thought to be due to the decrease in the barrier to insertion of ethylene into the growing polymer chain. The thioether ligand and the incoming ethylene substrate [18] are more or less equal donors to the electrophilic alkyl cation, and thus the stability of the π-complex is decreased.

4. Experimental

4.1. General considerations

All experiments were performed under argon using standard Schlenk or glovebox techniques. Diethylether, THF, pentane, and hexane were purified by distillation from sodium–benzophenone ketyl. Toluene was distilled over sodium sand. $H_2NCH_2CH_2SH$ [19], $(C_5Me_4H)SiMe_2Cl$ [7], $(C_5Me_4H)CH_2SiMe_2Cl$ [4e], $Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3$ [20], $TiCl_3(THF)_3$ [21], $ZrCl_4(THF)_2$ [21], and $Mg(CH_2Ph)_2(THF)_2$ [22] were prepared according to literature procedures. All other reagents were commercially available and used as received. NMR spectra were recorded on a Bruker DRX 400 spectrometer (^{1}H, 400 MHz; ^{13}C, 101 MHz; ^{31}P, 162 MHz; ^{19}F, 376 MHz; ^{29}Si, 79.5 MHz) at 298 K, unless otherwise stated. Chemical shifts for ^{1}H and ^{13}C spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane. ^{19}F spectra were referenced externally to $CFCl_3$, ^{31}P spectra to 85% H_3PO_4. Mass spectra were recorded on a Finnigan 8230 spectrometer. Elemental analyses were performed by the microanalytical laboratory of this department.

4.2. (2-Aminoethyl)methylsulfide [23]

At 0°C a suspension of 2-aminoethanethiol (5.40 g, 70.0 mmol) in 40 ml of dry methanol was slowly treated with 13.3 ml (70.0 mmol) of a 30% methanolic solution of NaOMe and 10 ml of additional methanol. The reaction mixture was allowed to warm up to r.t. and concentrated to a volume of 30 ml. After addition of

10.1 g (71.0 mmol) of iodomethane, dissolved in 5 ml of methanol, the mixture was stirred for a further 2 h followed by removal of the solvent in vacuo. After addition of 10 ml of water and 1.5 g of sodium chloride, the aqueous phase was extracted with 3 × 10 ml of CH_2Cl_2 and the combined organic layers were dried over $MgSO_4$. Fractional distillation at 40°C and 12 mbar afforded 1.89 g (30%) of a colorless oil. ^{1}H-NMR ($CDCl_3$): δ 1.37 (s, 2H, NH_2), 1.95 (s, 3H, CH_3), 2.45 (dt, $^2J_{HH} = 6.3$ Hz, 2H, CH_2), 2.74 (dt, $^2J_{HH} = 6.3$ Hz, 2H, CH_2).

4.3. $Ti(\eta^5:\eta^1\text{-}C_5H_4SiMe_2NCH_2CH_2SMe)Cl_2$ (**1**)

To a solution of $Ti(\eta^5\text{-}C_5H_4SiMe_2Cl)Cl_3$ (0.92 g, 2.94 mmol) in 40 ml of THF, was added dropwise a solution of $Li(NHCH_2CH_2SMe)$ (0.29 g, 2.94 mmol) and triethylamine (0.30 g, 2.94 mmol) in 20 ml of THF at − 60°C. The mixture was allowed to warm to r.t. and stirred for 3 h. All volatiles were removed in vacuo and the residue was extracted with 40 ml of a 1:2 hexane–toluene mixture. Filtration and concentration of the extracts, followed by crystallization at − 20°C afforded yellow crystals: yield 0.43 g (44%). ^{1}H-NMR (C_6D_6): δ 0.24 (s, 6H, $SiCH_3$), 1.86 (s, 3H, SCH_3), 2.47 (t, $^3J_{HH} =$ 7.1 Hz, 2H, CH_2S), 4.58 (t, $^3J_{HH} = 7.1$ Hz, 2H, NCH_2), 6.17 ('t', 2H, C_5H_4), 6.57 ('t', 2H, C_5H_4); $^{13}C\{^1H\}$-NMR (C_6D_6): δ 2.4 ($SiCH_3$), 15.0 (SCH_3), 34.8 (SCH_2), 55.8 (NCH_2), 109.2 (ring C at Si), 124.0, 126.0 (C_5H_4). EI MS: m/z (%): 329 (16, M^+), 268 (100, $M^+ - C_2H_5S$), 240 (53, $M^+ - C_3H_7NS$), 205 (27, $M^+ - C_3H_7NS$, − Cl). Anal. Calc. for $C_{10}H_{17}Cl_2NSSiTi$: C, 36.38; H, 5.19; N, 4.24. Found: C, 36.57; H, 5.18; N, 4.195.

4.4. $(C_5Me_4H)SiMe_2NHCH_2CH_2SMe$

$(C_5Me_4H)SiMe_2Cl$ (3.74 g, 17.4 mmol) was added to a suspension of $Li(NHCH_2CH_2SMe)$ (1.69 g, 17.4 mmol) in 60 ml of hexane at − 78°C. The reaction mixture was allowed to warm to r.t. and stirred for 14 h. Filtration of the resulting suspension and removal of all volatiles in vacuo gave crude (C_5Me_4H)-$SiMe_2NHCH_2CH_2SMe$, which was distilled at 100°C and 8×10^{-3} mbar to give a yellow oil: yield 3.33 g (71%). ^{1}H-NMR (C_6D_6) of the 5-isomer: δ 0.10 (s, 6H, $SiCH_3$), 0.78 (s, 1H, NH), 1.82 (s, 3H, SCH_3), 1.96 (s, 6H, $C_5(CH_3)_4$), 2.09 (s, 6H, $C_5(CH_3)_4$), 2.39 ('t', 2H, CH_2S), 2.85 ('t', 2H, NCH_2), 2.89 (s, 1H, C_5Me_4H); $^{13}C\{^1H\}$-NMR (C_6D_6): δ 2.2 ($SiCH_3$), 11.4, 14.6 ($C_5(CH_3)_4$), 15.0 (SCH_3), 39.1 (CH_2S), 40.9 (NCH_2), 56.7 (ring C at Si), 132.7, 135.6 ($C_5(CH_3)_4$); EI MS: m/z (%): 269 (55, M^+), 254 (23, $M^+ - CH_3$), 222 (17, $M^+ - SCH_3$), 208 222 (17, $M^+ - SC_2H_5$). Anal. Calc. for $C_{14}H_{27}NSSi$: C, 62.39; H, 10.10; N, 5.20. Found: C, 61.89; H, 10.29; N, 5.55%.

4.5. $(C_5Me_4H)CH_2SiMe_2NCH_2CH_2SMe$

$(C_5Me_4H)CH_2SiMe_2Cl$ (4.18 g, 18.3 mmol) was added to a suspension of $Li(NHCH_2CH_2SMe)$ (1.78 g, 18.2 mmol) in 70 ml of hexane at − 78°C. The reaction mixture was allowed to warm to r.t. and stirred for 14 h. Filtration of the resulting suspension and removal of all volatiles in vacuo gave crude the product which was distilled at 100–105°C and 8×10^{-3} mbar to give a mixture of isomers as a yellow oil: yield 4.15 g (84%). ^{1}H-NMR (C_6D_6): δ 0.11, 0.15, 0.18 (s, 6H, $SiCH_3$), 0.82 (s, 1H, NH), 1.13, 1.14, 1.17, 1.18 (total 2H, CH_2Si), 1.86, 1.87, 1.90, 1.91, 1.93, 1.96 (s, 15H, $C_5(CH_3)_4$, SCH_3), 2.39 (m, 2H, CH_2S), 2.59, 2.60 (1H, C_5Me_4H), 2.88 (m, 2H, NCH_2); $^{13}C\{^1H\}$-NMR (C_6D_6): δ − 1.1, − 0.9, − 0.8 ($SiCH_3$), 11.4, 11.8, 12.0, 12.6, 14.8, 14.9, 17.0, 17.8 ($C_5(CH_3)_4$, SMe, CH_2Si), 39.2, 40.9, 51.3, 51.7 (CH_2S, NCH_2, ring C at CH_2), 132.1, 134.7, 136.0, 136.6, 138.1, 139.7 ($C_5(CH_3)_4$). Anal. Calc. for $C_{15}H_{29}NSSi$: C, 63.54; H, 10.31; N, 4.94. Found C, 62.49; H, 10.78; N, 5.37%.

4.6. $Ti(\eta^5:\eta^1\text{-}C_5Me_4SiMe_2NCH_2CH_2SMe)Cl_2$ (**2a**)

Crude $Li_2(C_5Me_4SiMe_2NCH_2CH_2SMe)$ (1.86 g, 6.62 mmol), obtained by deprotonation of $(C_5Me_4H)SiMe_2NHCH_2CH_2SMe$ with two equivalents of n-butyllithium in hexane, was dissolved in 40 ml of THF and added dropwise to a suspension of $TiCl_3(THF)_3$ (2.45 g, 6.62 mmol) in 40 ml of toluene at − 60°C. After warming to r.t., the green reaction mixture was stirred for 2 h and treated with solid $PbCl_2$ (1.84 g, 6.62 mmol). After stirring for 12 h, the solvent was removed under vacuum and the residue was extracted with 80 ml of a 2:1 toluene–hexane mixture. Filtration of the extracts, followed by concentrating the filtrate and cooling to − 20°C afforded in several crops of yellow crystals: yield 1.32 g (52%). ^{1}H-NMR (C_6D_6): δ 0.45 (s, 6H, $SiCH_3$), 1.94 (s, 3H, SCH_3), 2.08 (s, 6H, $C_5(CH_3)_4$), 2.09 (s, 6H, $C_5(CH_3)_4$), 2.60 ('t', 2H, CH_2S), 4.50 ('t', 2H, NCH_2); $^{13}C\{^1H\}$ (C_6D_6): δ 6.0 ($SiCH_3$), 12.8 ($C_5(CH_3)_4$), 15.1 (SCH_3), 16.0 ($C_5(CH_3)_4$), 35.4 (CH_2S), 53.8 (NCH_2), 103.2 (ring C at Si), 136.0, 141.0 ($C_5(CH_3)_4$); EI MS: m/z (%): 385 (11, M^+), 370 (8, $M^+ - Me$), 335 (14, $M^+ - Me$, − Cl), 324 (100, $M^+ - C_2H_5S$), 296 (34, $M^+ - C_3H_7NS$). Anal. Calc. for $C_{14}H_{25}Cl_2NSSiTi$: C, 43.53; H, 6.52; N, 3.63. Found: C, 44.06; H, 7.59; N, 3.87%.

4.7. $Ti(\eta^5:\eta^1\text{-}C_5Me_4CH_2SiMe_2NCH_2CH_2SMe)Cl_2$ (**2b**)

Crude $Li_2(C_5Me_4CH_2SiMe_2N\text{–}CH_2CH_2SMe)$ (2.80 g, 9.50 mmol), obtained by double deprotonation of $(C_5Me_4H)CH_2SiMe_2NHCH_2CH_2SMe$ with n-butyllithium in hexane, was dissolved in 120 ml of THF and added dropwise to a suspension of $TiCl_3(THF)_3$ (3.51 g, 9.50 mmol) in 30 ml of THF at − 60°C. After warming up to r.t., the reaction mixture was stirred for 2 h and treated with $PbCl_2$ (2.64 g, 9.50 mmol). After stirring for 12 h, the solvent was removed under vacuum and the residue was extracted with 150 ml of 2:1 toluene–hexane mixture and filtered. Concentrating the filtrate and crystallization at − 20°C afforded yellow crystals: yield 1.48 g (39%). ^1H-NMR (C_6D_6): δ 0.12 (s, 6H, $SiCH_3$), 1.94 (s, 6H, $C_5(CH_3)_4$), 1.96 (s, 2H, CH_2Si), 2.14 (s, 6H, $C_5(CH_3)_4$), 2.16 (s, 3H, SCH_3), 2.74 ('t', 2H, CH_2S), 4.49 ('t', 2H, NCH_2); $^{13}C\{^1H\}$-NMR (C_6D_6): δ 2.2 ($SiCH_3$), 13.3, 13.4 ($C_5(CH_3)_4$), 15.0 (CH_2Si), 15.3 (SCH_3), 33.4 (CH_2S), 51.0 (NCH_2), 128.6, 128.8 ($C_5(CH_3)_4$), 134.4 (ring C at CH_2); EI MS: *m*/*z* (%) 398 (12, M^+), 337 (100, $M^+ - C_2H_5S$), 309 (6, $M^+ - C_3H_7SN$), 302 (9, $M^+ - Cl$, $- C_2H_5S$). Anal. Calc. for $C_{15}H_{27}NCl_2SSiTi$: C, 45.01; H, 6.80; N, 3.50. Found: C, 44.85; H, 6.71; N, 3.71%.

4.8. *Zr(η^5:η^1-$C_5Me_4SiMe_2NCH_2CH_2SMe$)$Cl_2$ (**3**)*

A mixture of $ZrCl_4(THF)_2$ (1.95 g, 5.17 mmol) and $Li_2(C_5Me_4SiMe_2NCH_2CH_2SMe)$ (1.45 g, 5.17 mmol) was treated dropwise with 60 ml of toluene at − 60°C and stirred for 2 days at r.t. All volatiles were removed in vacuo and the residue extracted with hexane. Filtration of the extracts, followed by concentrating the filtrate and cooling to − 50°C afforded colorless crystals: yield 0.93 g (42%). ^1H-NMR (C_6D_6): δ 0.46 (s, 6H, $SiCH_3$), 1.97 (s, 3H, SCH_3), 2.20 (s, 6H, $C_5(CH_3)_4$), 2.25 (s, 6H, $C_5(CH_3)_4$), 2.52 ('t', 2H, CH_2SMe), 3.21 ('t', 2H, NCH_2); $^{13}C\{^1H\}$-NMR (C_6D_6): δ 2.4 ($SiCH_3$), 12.0, 14.7 ($C_5(CH_3)_4$), 16.1 (SCH_3), 38.1 (CH_2S), 49.6 (NCH_2), 101.2 (ring C at Si), 130.8, 131.7 ($C_5(CH_3)_4$); EI MS: *m*/*z* (%) 428 (21, M^+), 413 (62, $M^+ - Me$), 381 (11, $M^+ - SMe$), 368 (39, $M^+ - C_2H_6S$), 339 (21, $M^+ - C_3H_7NS$), 304 (10, $M^+ - C_3H_7NS$, $- Cl$). Anal. Calc. for $C_{14}H_{25}Cl_2NSSiZr$: C, 39.14; H, 5.86; N, 3.26. Found: C, 39.01; H, 5.28; N, 3.43%.

4.9. *Ti(η^5:η^1-$C_5Me_4SiMe_2NCH_2CH_2SMe$)($CH_2Ph$)$_2$ (**4a**)*

A mixture of 0.54 g (1.40 mmol) of Ti(η^5:η^1-$C_5H_4SiMe_2NCH_2CH_2SMe$)Cl_2 and 0.50 g (1.43 mmol) of $Mg(CH_2Ph)_2(THF)_2$ was treated dropwise with 30 ml of hexane at − 60°C and stirred for 20 h at r.t. Evaporation of the solvent and extraction of the residue with 2 × 15 ml of hexane, followed by filtration of the extracts, concentrating the filtrate and cooling to − 50°C afforded red crystals: yield 0.43 g (62%). ^1H-NMR (C_6D_6): δ 0.40 (s, 6H, $SiCH_3$), 1.83 (s, 6H, $C_5(CH_3)_4$), 1.92 (s, 6H, $C_5(CH_3)_4$), 1.94 (s, 3H, SCH_3), 2.20 (d, $^2J_{HH} = 10.2$ Hz, 2H, CH_2Ph), 2.36 (overlap. m, 4H, CH_2Ph, CH_2S), 3.98 (t, $^3J_{HH} = 7.8$ Hz, 2H, NCH_2), 7.01 (m, 6H, C_6H_5), 7.30 (d, $^3J_{HH} = 8.2$ Hz, 4H, *ortho*-C_6H_5); $^{13}C\{^1H\}$-NMR (C_6D_6): δ 3.4 ($SiCH_3$), 11.4, 14.8 ($C_5(CH_3)_4$), 15.3 (SCH_3), 36.8 (CH_2S), 52.2 (NCH_2), 80.5 (CH_2Ph), 97.6 (ring C at Si), 122.2 (*para*-C_6H_5), 126.9 (*ortho*-C_6H_5), 128.6 (*meta*-C_6H_5), 129.6, 135.1 ($C_5(CH_3)_4$), 149.0 (*ipso*-C_6H_5); EI MS: *m*/*z* (%): 496 (25, M^+), 465 (4, $M^+ - C_2H_7$), 301 (3, $M^+ - C_{15}H_{15}$). Anal. Calc. for $C_{28}H_{39}NSSiTi$: C, 67.58; H, 7.90; N, 2.81. Found: C, 65.47; H, 7.86; N, 3.67%.

4.10. *Ti(η^5:η^1-$C_5Me_4CH_2SiMe_2NCH_2CH_2SMe$)-($CH_2Ph$)$_2$ (**4b**)*

Hexane (50 ml) was added to a solid mixture of Ti(η^5:η^1-$C_5Me_4CH_2SiMe_2NCH_2CH_2SMe$)$Cl_2$ (0.39 g, 0.98 mmol) and $Mg(CH_2Ph)_2(THF)_2$ (0.40 g, 1.14 mmol) at − 78°C. The mixture was allowed to warm to r.t. and stirred for 14 h. All volatiles were removed in vacuo and the residue was extracted with 30 ml of hexane. After filtration, the red solution was concentrated and cooled to − 20°C to give red crystals: yield 0.31 g (61%). ^1H-NMR (C_6D_6): δ 0.20 (s, 6H, $SiCH_3$), 1.73 (s, 6H, $C_5(CH_3)_4$), 1.78 (s, 2H, CH_2Si), 1.91 (s, 3H, SCH_3), 1.98 (s, 6H, $C_5(CH_3)_4$), 2.21 (d, $^2J_{HH} = 10.6$ Hz, 2H, CH_2Ph), 2.30 (d, $^2J_{HH} = 10.6$ Hz, 2H, CH_2Ph), 2.49 (m, 2H, CH_2S), 4.26 (m, 2H, NCH_2), 7.03 (m, 6H, C_6H_5), 7.29 (m, 4H, C_6H_5); $^{13}C\{^1H\}$-NMR (C_6D_6): δ 3.0 ($SiCH_3$), 11.9, 12.2 ($C_5(CH_3)_4$), 15.1, 15.3 (CH_2Si, SMe), 35.6 (t, $^1J_{CH} = 140$ Hz, CH_2S), 50.0 (t, $^1J_{CH} = 135.5$ Hz, NCH_2), 78.9 (t, $^1J_{CH} = 121$ Hz, CH_2Ph), 121.6 ($C_5(CH_3)_4$), 122.2 (*para*-C_6H_5), 123.5 ($C_5(CH_3)_4$), 125.4 (ring C at CH_2), 127.0 (*ortho*-C_6H_5), 128.4 (*meta*-C_6H_5), 150.4 (*ipso*-C_6H_5); Anal. Calc. for $C_{29}H_{41}NSSiTi$: C, 68.07; H, 8.08; N, 2.74. Found: C, 67.33; H, 7.36; N, 2.48%.

4.11. *[Ti(η^5:η^1-$C_5Me_4SiMe_2NCH_2CH_2SMe$)-($CH_2Ph$)][B($C_6F_5$)$_3$] (**5a**)*

C_6D_5Br (0.5 ml) was added to a solid mixture of the dibenzyl complex **4a** (18 mg, 36 μmol) and $B(C_6F_5)_3$ (18 mg, 35 μmol) in an NMR tube at − 10°C. The color of the solution turned brown upon warming up to r.t. ^1H-NMR (C_6D_5Br, − 5°C): δ 0.30 (s, 3H, $SiCH_3$), 0.57 (s, 3H, $SiCH_3$), 1.46 (s, 3H, $C_5(CH_3)_4$), 1.67 (s, 3H, $C_5(CH_3)_4$), 2.15 (s, 3H, SMe), 2.16 (s, 3H, $C_5(CH_3)_4$), 2.17 (s, 3H, $C_5(CH_3)_4$), 2.59 (d, $^2J_{HH} = 6.3$ Hz, 1H, $TiCH_2Ph$), 2.71 (m, 1H, CH_2S), 2.95 (m, 1H, CH_2S), 3.15 (d, $^2J_{HH} = 6.3$ Hz, 1H, $TiCH_2Ph$), 3.24 (m, 1H, NCH_2), 3.61 (br s, 2H, BCH_2Ph), 3.95 (m, 1H, NCH_2), 6.28 (br s, 2H, *ortho*-C_6H_5), 7.29 (m, 10H, C_6H_5); $^{13}C\{^1H\}$-NMR (C_6D_5Br, − 5°C): δ 0.5, 2.7 (SiMe), 11.3, 13.3 ($C_5(CH_3)_4$), 16.0, 16.1, 17.8 ($C_5(CH_3)_4$, SMe), 32.9 (BCH_2), 51.3 (CH_2S), 52.3 (NCH_2), 72.3 (t, $^1J_{CH} = 150$ Hz, $TiCH_2$), 110.1 (ring C am Si), 121.3, 122.4, 123.1, 123.3, 127.6, 129.4 (C_6H_5), 132.8, 133.0, 133.3 ($C_5(CH_3)_4$), 135.9 (C_6F_5), 136.6, 136.8, 137.6 (C_6H_5, $C_5(CH_3)_4$), 138.3 (C_6F_5), 139.2 (C_6H_5), 147.7 (C_6F_5), 149.2 (*ipso*-$BCH_2C_6H_5$), 150.1 (C_6F_5); ^{19}F-NMR (C_6D_6Br, − 5°C): δ − 130.1 (d, $^3J_{FF}$ = 22.9 Hz, *ortho*-C_6F_5), − 163.7 (t, $^3J_{FF}$ = 22.9 Hz, *para*-C_6F_5), − 166.6 (t, $^3J_{FF}$ = 20.7 Hz, *meta*-C_6F_5).

4.12. [Ti(η^5:η^1-$C_5Me_4CH_2SiMe_2NCH_2CH_2SMe$)-($CH_2Ph$)][B($C_6F_5$)$_3$] (**5b**)

C_6D_5Br (0.5 ml) was added to an equimolar mixture of dibenzyl **4b** (12 mg, 25 μmol) and B(C_6F_5)$_3$ (13 mg, 25 μmol) in an NMR tube at − 10°C. The color turned brown upon warming up to r.t. ^{1}H-NMR (C_6D_5Br, − 5°C): δ 0.05 (s, 3H, $SiCH_3$), 0.28 (s, 3H, $SiCH_3$), 1.47 (s, 3H, $C_5(CH_3)_4$), 1.74 (s, 3H, $C_5(CH_3)_4$), 1.97 (d, $^2J_{HH}$ = 14.5 Hz, 1H, CH_2Si), 2.10, 2.11 (s, 3H, $C_5(CH_3)_4$; s, 3H, SCH_3), 2.14 (overlap d, 1H, CH_2Si), 2.24 (s, 3H, $C_5(CH_3)_4$), 2.68 (m, 1H, CH_2S), 2.76 (d, $^2J_{HH}$ = 7.4 Hz, 1H, $TiCH_2$), 2.87 (m, 2H, CH_2S, NCH_2), 3.32 (d, $^2J_{HH}$ = 7.4 Hz, 1H, $TiCH_2$), 3.55 (br s, 2H, BCH_2), 3.87 (m, 1H, NCH_2), 6.38 (d, $^3J_{HH}$ = 4.7 Hz, 2H, *ortho*-C_6H_5), 7.07 (m, 2H, C_6H_5), 7.32 (m, 6H, C_6H_5); ^{13}C{^{1}H}-NMR (C_6D_5Br, − 5°C): δ 0.5, 1.8 ($SiCH_3$), 11.2 ($C_5(CH_3)_4$), 13.5, 13.8, 14.3, 16.1, 17.8 ($C_5(CH_3)_4$, SCH_3, CH_2Si), 32.5 (BCH_2), 48.3 (CH_2S), 52.8 (NCH_2), 74.2 (t, $^1J_{CH}$ = 144 Hz, $TiCH_2$), 121.3, 122.4, 123.1, 123.3, 124.4, 124.5, 126.0, 127.6, 128.1, 129.4, 131.4 (C_6H_5, $C_5(CH_3)_4$), 132.8, 133.0, 133.3 ($C_5(CH_3)_4$), 135.4 (C_6H_5), 135.8 (C_6F_5), 137.2 (C_6H_5), 138.4, 139.4, 147.8 (C_6F_5), 149.3 (*ipso*-$BCH_2C_6H_5$), 150.2 (C_6F_5); ^{19}F-NMR (C_6D_5Br, − 5°C): δ − 130.3 (d, $^3J_{FF}$ = 20.8 Hz, *ortho*-C_6F_5), − 163.7 (t, $^3J_{FF}$ = 20.8 Hz, *para*-C_6F_5), − 166.5 (t, $^3J_{FF}$ = 20.8 Hz, *meta*-C_6F_5).

4.13. *Ortho*-diphenylphosphinoaniline [15]

Diphenylphosphine (2.22 g, 11.9 mmol) was added to a solution of 2-iodoaniline (2.61 g, 11.9 mmol) and triethylamine (1.66 ml, 11.9 mmol) in 30 ml of acetonitrile. The reaction mixture was treated with Pd(PPh_3)$_4$ (0.14 g, 0.12 mmol) in 10 ml of acetonitrile and 10 ml of water and stirred under reflux for 40 h. The solvent was removed in vacuo and the residue was extracted with 30 ml of a 1:1 H_2O–CH_2Cl_2 mixture. After removal of the solvent the organic layer afforded a brown solid: yield 2.66 g (81%). ^{1}H-NMR (C_6D_6): δ 3.85 (br s, 2H, NH_2), 6.43 (m, 1H, C_6H_5, C_6H_4), 6.70 ('t', 1H, C_6H_4), 7.13 (m, 8H, C_6H_5, C_6H_4), 7.50 (m, 4H, C_6H_5, C_6H_4); ^{13}C{^{1}H}-NMR (C_6D_6): δ 115.3 (C_6H_4-6), 118.7 (C_6H_4-4), 119.2 (d, $^1J_{PC}$ = 9 Hz, C_6H_4-2), 128.0 (d, $^3J_{PC}$ = 3 Hz, *meta*-C_6H_5), 128.8 (*para*-C_6H_5), 130.7 (C_6H_4-5), 134.1 (d, $^2J_{PC}$ = 19 Hz, *ortho*-C_6H_5), 134.8 (C_6H_4-3), 136.4 (d, $^1J_{PC}$ = 9 Hz, *ipso*-C_6H_5), 150.8 (d, $^2J_{PC}$ = 20 Hz, C_6H_4-1); ^{31}P{^{1}H}-NMR (C_6D_6): δ − 17.0. EI MS: *m*/*z* (%) 277 (100, M^+), 261 (8, $M^+ - NH_2$), 185 (9, $M^+ - C_6H_6N$).

4.14. {(C_5Me_4H)$SiMe_2NHC_6H_4$(PPh_2)-2}

(C_5Me_4H)$SiMe_2Cl$ (1.17 g, 5.46 mmol) was added to a suspension of Li{NHC_6H_4(PPh_2)-2} (1.55 g, 5.46 mmol) in 40 ml of hexane at − 60°C. The reaction mixture was allowed to warm to r.t. and stirred for 14 h. Filtration of the resulting suspension and removal of all volatiles in vacuo gave crude (C_5Me_4H)$SiMe_2$-NHC_6H_4(PPh_2)-2 as a slightly brown, waxy solid: yield 2.14 g (86%). ^{1}H-NMR (C_6D_6): δ 0.24 (s, 6H, $SiCH_3$), 1.38 (s, 1H, NH), 1.90 (s, 6H, $C_5(CH_3)_4$), 1.97 (s, 6H, $C_5(CH_3)_4$), 3.06 (s, 1H, C_5Me_4H), 6.73 ('t', 1H, C_6H_4), 7.02 (m, 1H, C_6H_5, C_6H_4), 7.12 (m, 6H, C_6H_5, C_6H_4), 7.21 (m, 2H, C_6H_5, C_6H_4), 7.47 (m, 4H, C_6H_5, C_6H_4); ^{13}C{^{1}H}-NMR (C_6D_6): δ − 1.9 ($SiCH_3$), 11.5, 14.3 ($C_5(CH_3)_4$), 54.9 (ring C at Si), 115.9 (C_6H_4-6), 118.7 (C_6H_4-4), 122.3 (d, $^1J_{PC}$ = 5 Hz, C_6H_4-2), 128.6 (*meta*-C_6H_5), 128.8 (*para*-C_6H_5), 129.3 ($C_5(CH_3)_4$), 130.8 (C_6H_4-5), 132.4 ($C_5(CH_3)_4$), 134.1 (d, $^2J_{PC}$ = 19 Hz, *ortho*-C_6H_5), 135.5 (C_6H_4-3), 136.5 (d, $^1J_{PC}$ = 8 Hz, *ipso*-C_6H_5), 151.6 (d, $^2J_{PC}$ = 20 Hz, C_6H_4-1);.^{31}P{^{1}H}-NMR (C_6D_6): δ − 18.4. EI MS: *m*/*z* (%) 455 (100, M^+).

4.15. Ti{η^5:η^1-$C_5Me_4SiMe_2NC_6H_4$(PPh_2)-2}Cl_2 (**6**)

A solution of crude Li_2{$C_5Me_4SiMe_2NC_6H_4$(PPh_2)-2}, obtained by double deprotonation of (C_5Me_4H)-$SiMe_2NHC_6H_4$(PPh_2)-2 (2.14 g, 4.70 mmol) with *n*-BuLi in 40 ml of toluene, was added dropwise to a suspension of $TiCl_3(THF)_3$ (1.74 g, 4.70 mmol) in 20 ml of THF at − 60°C. After warming up to r.t. the reaction mixture was stirred for 4 h and treated with $PbCl_2$ (1.31 g, 4.70 mmol). After stirring for 14 h, the solvent was removed under vacuum and the residue was extracted with 60 ml of 2:1 toluene–hexane mixture and filtered. Evaporation of the solvent gave brown microcrystals: yield 1.48 g (55%). ^{1}H-NMR (C_6D_6): δ 0.69 (s, 6H, $SiCH_3$), 2.10 (s, 6H, $C_5(CH_3)_4$), 2.19 (s, 6H, $C_5(CH_3)_4$), 6.79 (m, 1H, C_6H_4), 6.87 (m, 1H, C_6H_4), 7.12 (m, 8H, C_6H_5, C_6H_4), 7.76 (m, 4H, C_6H_5, C_6H_4); ^{13}C{^{1}H}-NMR (C_6D_6): δ 2.7 ($SiCH_3$), 13.0, 15.6 ($C_5(CH_3)_4$), 108.8 (ring C at Si), 116.5 (d, $^3J_{PC}$ = 6 Hz, C_6H_4-6), 123.1 (d, $^3J_{PC}$ = 3 Hz, C_6H_4-4), 124.4 (d, $^1J_{PC}$ = 26 Hz, C_6H_4-2), 127.9 (C_6H_4-5), 128.6 (d, $^2J_{PC}$ = 22 Hz, C_6H_4-3), 128.8 (*meta*-C_6H_5), 129.7 (*para*-C_6H_5), 132.2 ($C_5(CH_3)_4$), 133.8 (d, $^2J_{PC}$ = 19 Hz, *ortho*-C_6H_5), 134.1 (d, $^1J_{PC}$ = 12 Hz, *ipso*-C_6H_5), 135.2 ($C_5(CH_3)_4$), 162.6 (d, $^2J_{PC}$ = 32 Hz, C_6H_4-1); ^{31}P{^{1}H}-NMR (C_6D_6): δ 16.4; EI MS: *m*/*z* (%) = 571 (1, M^+), 275 (73, $NC_6H_4PPh_2^+$), 185 (50, PPh_2^+).

4.16. *$Zr\{\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NC_6H_4(PPh_2)\text{-}2\}Cl_2(THF)$ (7)*

Crude $Li_2\{C_5Me_4SiMe_2NC_6H_4(PPh_2)\text{-}2\}$ (4.11 g, 8.8 mmol), obtained by deprotonation of (C_5Me_4H)-$SiMe_2NHC_6H_4(PPh_2)$-2 with 2 equivalents of *n*-butyllithium in hexane, was dissolved in 45 ml of toluene and added dropwise to a solution of $ZrCl_4(THF)_2$ (3.32 g, 8.8 mmol) in 45 ml of toluene cooled to −78°C. The mixture was allowed to warm up to r.t. and stirred for additional 15 h. The solvent was evaporated and the residue was extracted with 100 ml of a 2:1 toluene–hexane mixture. Filtration of the extracts, followed by concentrating the filtrate afforded a colorless solid: yield 3.71 g (68%). ^{1}H-NMR (C_6D_6): δ 0.70 (s, 6H, $SiCH_3$), 1.43 (m, 4H, β-CH_2 of THF), 2.03 (s, 6H, $C_5(CH_3)_4$), 2.10 (s, 6H, CCH_3), 3.62 (m, 4H, α-CH_2 of THF) 6.64 (m, 1H, C_6H_5, C_6H_4), 6.87 (m, 1H, C_6H_5, C_6H_4), 7.01 (m, 6H, C_6H_5, C_6H_4), 7.42 (m, 2H, C_6H_5, C_6H_4), 7.75 (m, 4H, C_6H_5, C_6H_4); ^{13}C{^{1}H}-NMR (C_6D_6): δ 4.0 (Si*C*H_3), 11.9, 14.3 ($C_5(CH_3)_4$), 25.7 (β-CH_2 of THF), 68.1 (α-CH_2 of THF), 102.2 (ring C at Si), 117.7 (d, $^3J_{PC} = 8$ Hz, C_6H_4-6), 120.5 (d, $^3J_{PC} = 5$ Hz, C_6H_4-4), 122.1 (d, $^1J_{PC} = 36$ Hz, C_6H_4-2), 128.6 (d, $^3J_{PC} = 9$ Hz, *meta*-C_6H_5), 130.0 (*para*-C_6H_5), 131.9 (d, $^2J_{PC} = 29$ Hz, *ortho*-C_6H_5), 132.1 ($C_5(CH_3)_4$), 132.8 (C_6H_4-5), 133.8 ($C_5(CH_3)_4$), 134.0 (d, $^1J_{PC} = 11$ Hz, *ipso*-C_6H_5), 135.3 (C_6H_4-3), 161.9 (d, $^2J_{PC} = 32$ Hz, C_6H_4-1); ^{31}P{^{1}H}-NMR (C_6D_6): δ 10.1; ^{29}Si{^{1}H}-NMR: δ −16.1 (d, $^4J_{PSi} = 5.9$ Hz); EI MS: *m*/*z* (%) 615 (22, M^+), 430 (11, $M^+ - PPh_2$), 318 (4, $M^+ - Cl$, $- C_6H_4PPh_2$), 275 (39, $NC_6H_4PPh_2^+$).

4.17. *X-ray crystal structural analysis and determination of the structures of **1** and **3***

Data sets were obtained with an Enraf–Nonius CAD4 diffractometer in the ω-scan mode. The reflections were corrected for Lp effects using the program system MolEN [24] and for absorption using ψ-scans [25]. All structures were solved by Patterson and Fourier methods using the program SHELXS-86 [26a]. The refinements were carried out using the program SHELXL-93 based on F^2 [26b]. Anisotropic thermal parameters were refined for all non-hydrogen atoms. The hydrogen atoms of the methyl groups in **3** were incorporated into idealized positions of tetrahedral geometry by applying rotating group refinements. All other hydrogen atoms were located and refined with isotropic thermal parameters. Results are given in Table 1.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 126008 for **1**, and 126009 for **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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