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PH-functionalised phosphanylalkyl(silyl)cyclopentadienyl ligands: Synthesis and catalytic properties of $[\{(\eta^5\text{-}C_5H_4)CMe_2PH^tBu\}MCl_3]$ ($M = Ti$, Zr) and $[\{(\eta^5\text{-}C_5H_4)SiMe_2PHR\}ZrCl_3]$ ($R = Ph$, Cy)

Thomas Koch [a], Evamarie Hey-Hawkins [a,*], Mercedes Galan-Fereres [b], Moris S. Eisen [b]

[a] *Institut für Anorganische Chemie der Universität, Johannisallee 29, D-04103 Leipzig, Germany*
[b] *Department of Chemistry and Institute of Catalysis Science and Technology, Technion-Israel Institute of Technology, Haifa 32000, Israel*

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Dedicated to Professor Dr Rüdiger Mews on the occasion of his 60th birthday

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Abstract

The silylated phosphanylsilylcyclopentadienes 1- and 3-$SiMe_3$–1-$SiMe_2PHRC_5H_4$ [$R = Ph$ (**1**), Cy (**2**)] and phosphanylalkylcyclopentadienes 1-, 2- and 3-CMe_2PH^tBu–1-$SiMe_3C_5H_4$ (**3**) were prepared from LiPHR and 1-$SiMe_3$–1-$SiMe_2ClC_5H_4$ and $Li[1\text{-}PH^tBuCMe_2C_5H_4]$ and $SiMe_3Cl$, respectively. Complexes **1** and **2** react with $ZrCl_4$ to give $[\{(\eta^5\text{-}C_5H_4)SiMe_2PHR\}ZrCl_3]$ [$R = Ph$ (**4**), Cy (**5**)], and **3** reacts with MCl_4 with formation of $[\{(\eta^5\text{-}C_5H_4)CMe_2PH^tBu\}MCl_3]$ [$M = Ti$ (**6**), Zr (**7**)]. Complexes **1**–**7** were characterised by NMR and IR spectroscopy and mass spectrometry. Complexes **4**–**7** were studied in the catalytic polymerisation of ethene and propene with activation by methylalumoxane (MAO) as cocatalyst.

Keywords: PH-functionalised phosphanylalkyl(silyl)cyclopentadienyl ligands; Zirconium complexes; Titanium complexes; Polymerisation studies

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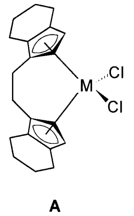
1. Introduction

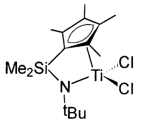
After the discovery of α-olefin polymerisation [1], numerous metallocene and monocyclopentadienyl derivatives with different steric and electronic properties were synthesised and employed as catalysts in polymerisation reactions.

Ansa-metallocene dichlorides **A** of Ti, Zr, and Hf, especially chiral ones, are important catalysts for isotactic polymerisation of olefins with promotion by methylalumoxane (MAO). Therefore, intensive research is being carried out towards the synthesis of improved catalysts [2–5].

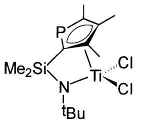
Recently, monocyclopentadienyl derivatives **B** in which the cyclopentadienyl ring has a heteroatom-functionalised side-chain were prepared and employed in the polymerisation and copolymerisation of olefins [6]. These studies were also extended to phospholyl ligands (**C**) [7].



A
(M = Ti, Zr, Hf)



B



C

While numerous cyclopentadienyl ligands with *O*- and *N*-functionalised side-chains are known, the number of cyclopentadienes with a *P*-functionalised alkyl or silyl side-chain is still small [8], and we have only recently reported on the first compounds in which the P atom bears a reactive substituent (e.g. PH) [9,10].The lithium salts $[Li(tmeda)]_2[PhPCMe_2(C_5H_4)]$ [11] and $[Li(tmeda)][R_2PCMe_2(C_5H_4)]$ ($R = Ph$, Me) [12], 1-$SiMe_2PHMes^*C_5Me_4H$ and its dipotassium salt, $[K_2(THF)_4(1\text{-}SiMe_2PMes^*C_5Me_4)]_2$ ($Mes^* = 2,4,6\text{-}^tBu_3$-

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* Corresponding author. Tel.: +49-341-9736-151; fax: 49-341-9739-319

E-mail addresses: hey@rz.uni-leipzig.de (E. Hey-Hawkins), chmoris@techunix.technion.ac.il (M.S. Eisen).

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C_6H_2) [13] have been structurally characterised. Such compounds should be useful precursors for dianionic bifunctional ligands in transition metal chemistry. In addition, the presence of a P-containing group is advantageous for reactivity studies by ^{31}P NMR spectroscopy.

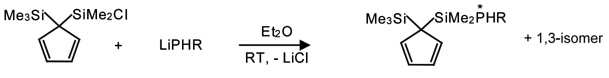
We have previously reported the synthesis of the PH-functionalised ferrocene derivatives *rac*-[Fe$\{(\eta^5$-$C_5H_4)CMe_2PHR\}_2$] (R = Ph, Mes) [14] and the metallocene derivatives [$\{(\eta^5$-$C_5H_4)CMe_2PHR\}_2ZrCl_2$] and [$\{(\eta^5$-$C_5H_4)CMe_2PHR\}_2TiCl$] (R = Ph, ^{t}Bu). The latter slowly decompose on recrystallisation from THF, Et_2O or toluene with formation of [$\{(\eta^5$-$C_5H_4)_2CMe_2\}MCl_2$] (M = Zr, Ti) and $(PR)_n$ (R = Ph, $n = 4$–6; R = ^{t}Bu, $n = 4$) and PH_2R [15].

We now report the synthesis of the first stable monosubstituted PH-functionalised phosphanylalkyl- and phosphanylsilylcyclopentadienyl complexes of Group 4 metals, namely, [$\{(\eta^5$-$C_5H_4)SiMe_2PHR\}ZrCl_3$] [R = Ph (**4**), Cy (**5**)] and [$\{(\eta^5$-$C_5H_4)CMe_2PH^tBu\}MCl_3$] [M = Ti (**6**), Zr (**7**)] and their activity in the polymerisation of ethene and propene. Recently, Erker et al. reported the synthesis and catalytic properties in the polymerisation of olefins of the constrained-geometry catalysts [$\{(\eta^5$-$C_5H_4)CMe_2PCy\}M(NR_2)_2$] (M = Ti, R = Me; M = Zr, R = Et) [16]. Hou et al. reported the synthesis of [$\{(\eta^5$-$C_5Me_4)SiMe_2PMes^*\}Ln(L)_n$] (Ln = Sm: L = THF, $n = 1$ or 3; L = $MeOCH_2CH_2OMe$, $n = 2$; L = $PO(NMe_2)_3$, $n = 2$; Ln = Yb, L = THF, $n = 3$) and the polymerisation of ethene, ε-caprolactone and 1,3-butadiene with the Sm^{II}–mono-THF complex [13].

2. Results and discussion

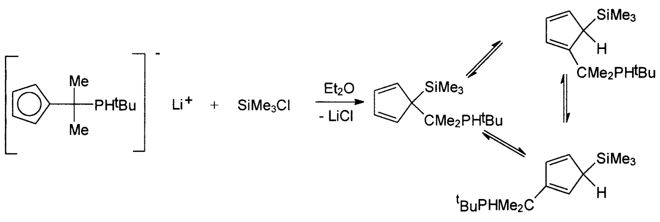
2.1. Synthesis

The general synthetic method for the preparation of a monocyclopentadienyl metal trichloride complex of Group 4 metals is the elimination of $SiMe_3Cl$ [17]. Occasionally, this method can also be employed for the synthesis of metallocene derivatives. We therefore prepared the silylated phosphanylsilyl- and phosphanylalkylcyclopentadienes 1- and 3-$SiMe_3$–1-$SiMe_2PHRC_5H_4$ [R = Ph (**1**), Cy (**2**)] and 1-, 2- and 3-CMe_2PH^tBu–1-$SiMe_3C_5H_4$ (**3**) from LiPHR and 1-$SiMe_3$–1-$SiMe_2ClC_5H_4$ [18] (Eq. (1)) and Li[1-$PH^tBuCMe_2C_5H_4$] and $SiMe_3Cl$ (Eq. (2)), respectively.



R = Ph (**1**), Cy (**2**)

(1)



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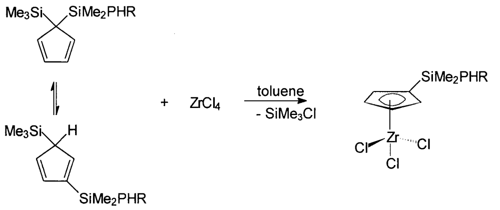
(2)

Work-up yielded **1**–**3** as colourless (**1**, **2**) or yellow (**3**) oil. The different constitutional isomers could not be separated by distillation [19]. Compounds **1**–**3** were characterised by NMR (^{1}H, ^{31}P) and IR spectroscopy and mass spectrometry. In the MS, molecular-ion peaks were observed, and the peak of 100% intensity was due to $m/z = M^+ - PHR$ (R = Ph, Cy, ^{t}Bu).

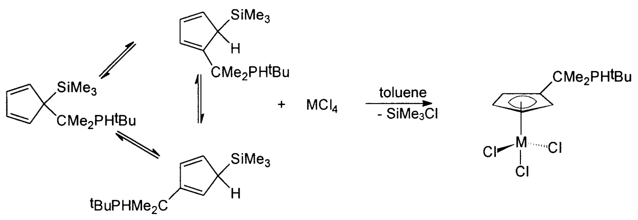
Compounds **1** and **2** react with $ZrCl_4$ in toluene to give [$\{(\eta^5$-$C_5H_4)SiMe_2PHR\}ZrCl_3$] [R = Ph (**4**), Cy (**5**); Eq. (3)], and **3** reacts with MCl_4 with formation of [$\{(\eta^5$-$C_5H_4)CMe_2PH^tBu\}MCl_3$] [M = Ti (**6**), Zr (**7**); Eq. (4)]. As $SiMe_3Cl$ is eliminated, the mixture of constitutional isomers (see Eqs. (1) and (2)) can be employed in these reactions. Compounds **4**–**7** can be recrystallised from dichloromethane or THF; the complexes are almost insoluble in non-coordinating and non-polar solvents, and this indicates association in the solid state (presumably by chloro bridges, cf. [$\{(\eta^5$-$C_5H_4)_2CH_2CH_2$-$PPh_2\}ZrCl_3$] [20]) and adduct formation in THF (cf. [$\{(\eta^5$-$C_5Me_4)_2CH_2CH_2PPh_2\}ZrCl_3(THF)$] [21]). Compounds **4**–**7** are obtained as yellow (**4**), white (**5**, **6**) or red (**7**) microcrystalline powders in good to moderate yields (45–80%). Compounds **4** and **5** are only moderately air sensitive, while **6** and **7** are more so, and all complexes decompose with formation of phosphine



1 (R = Ph)
2 (R = Cy)

4 (R = Ph)
5 (R = Cy)

(3)



3

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

(4)

(PH_2R).

Compounds **4**–**7** were characterised by NMR (^{1}H, ^{13}C, ^{31}P) and IR spectroscopy and mass spectrometry. Compounds **4**, **5** and **7** [**4**: -117.1 ($^1J_{P\text{–}H} = 200.9$ Hz); **5**: -121.6 ($^1J_{P\text{–}H} = 201.0$ Hz); **7**: 36.7 ppm ($^1J_{P\text{–}H} = 213.4$ Hz)] exhibit a doublet in the ^{31}P NMR spectrum (in [D$_8$]THF), which is shifted to low field by approximately 1–12 ppm relative to the starting materials **1**–**3** [**1**: -121.6 ($^1J_{P\text{–}H} = 201.0$ Hz) and -122.3 ppm ($^1J_{P\text{–}H} = 204.1$ Hz); **2**: -124.9 ($^1J_{P\text{–}H} = 191.2$ Hz) and -127.6 ppm ($^1J_{P\text{–}H} = 189.5$ Hz); **3**: 25.2 (d of dec, $^1J_{P\text{–}H} = 196.7$ Hz, $^3J_{P\text{–}H} = 12.1$ Hz), 19.2 (d, $^1J_{P\text{–}H} = 198.4$ Hz) and 13.1 ppm (d of dec, $^1J_{P\text{–}H} = 199.5$ Hz, $^3J_{P\text{–}H} = 12.2$ Hz)]. This indicates that there is no interaction between the phosphanyl group and the transition metal. In contrast, **6** [-6.8 ppm ($^1J_{P\text{–}H} = 282.5$ Hz)] exhibits a doublet in the ^{31}P NMR spectrum (in [D$_8$]THF) which is shifted to high field relative to the starting material **3**, and the coupling constant increased by approximately 85 Hz.

For **4**–**7**, only peaks for the monomeric complexes were observed in the mass spectra. While the formation of monomeric molecules is rather unlikely, this suggests that readily cleavable dimers are probably present rather than oligomers.

3. Polymerisation studies

The complexes **4**–**7** were studied in the catalytic polymerisation of ethene, propene and styrene with activation by MAO (1000-fold excess, in toluene) as cocatalyst. No reaction was observed with styrene, which was rather unexpected as related side-chain-functionalised monocyclopentadienyl complexes of Ti exhibit good catalytic properties [22]. Presumably, complexes **4**–**7** are destroyed by MAO (attack at the P–Si or P–C bond with concomitant decomposition of the complexes) at the elevated temperatures employed (60 °C). However, ethene and propene are readily polymerised with formation of high-density polyethylene and polypropylene (Table 1); the elastomeric properties of the latter indicate a P–M interaction during the polymerisation process. Similar behaviour was already observed for related constrained-geometry catalysts with *N*-functionalised side-chains [6e].

Table 1
Activity of **4**–**7** in the polymerisation of propene

Complex	Ratio MAO:cat.	Activity for polypropylene (g mol^{-1} h^{-1})
4	300	0.86×10^3
5	300	2.61×10^3
6	300	0.84×10^3
7	300	8.20×10^3

The activities of complexes **4** and **7** are slightly higher than those of the constrained-geometry complexes and on the same order of magnitude as those of the Cp/phosphanido Group 4 complexes [14]. Regarding propene, the activity attained by complexes **4**–**7** is far lower than that observed with metallocene complexes [2,6e].

4. Experimental

All experiments were carried out under purified dry Ar. Solvents were dried and freshly distilled under Ar. The NMR spectra were recorded at 25 °C in C_6D_6 or [D$_8$]THF with an AVANCE DRX 400 spectrometer (Bruker): ^{1}H NMR: internal standard solvent (C_6H_6 or THF), external standard SiMe$_4$; ^{13}C NMR: external standard SiMe$_4$, internal standard solvent; ^{31}P NMR: external standard 85% H_3PO_4. The IR spectra were recorded on a Perkin–Elmer System 2000 FT-IR spectrometer in the range 350–4000 cm^{-1}. The mass spectra were recorded with an MAT-212 (Finnigan), EI MS, 70 eV. The m.p. were determined in sealed capillaries under Ar and are uncorrected.

LiPHPh [23], LiPHCy [24], Li[1-PH^{t}BuCMe$_2$C$_5$H$_4$] [15], and 1-SiMe$_3$–1-SiMe$_2$ClC$_5$H$_4$ [18] were prepared according to literature procedures.

4.1. 1- and 3-SiMe$_3$–1-SiMe$_2$PHPhC$_5$H$_4$ (**1**)

LiPHPh (4.10 g, 35 mmol) was suspended in *n*-C$_6$H$_{14}$ (150 ml) and cooled to -20 °C. Then 1-SiMe$_3$–1-SiMe$_2$ClC$_5$H$_4$ (8.10 g, 35 mmol) was added, and the reaction mixture warmed to ambient temperature. The mixture was stirred for 1 day, filtered, the solvent evaporated in vacuo and the resulting yellow oil distilled under reduced pressure (65–75 °C, 2×10^{-2} Torr) to give 6.5 g (61%) of **1** as a colourless oil.

^{1}H NMR (C_6D_6): $\delta = -0.05$ (s, 18H, CH_3 in SiMe$_3$, 2 isomers), 0.01 (d, 6H, CH_3 in SiMe$_2$, $^3J_{P\text{–}H} = 2.4$, 2 isomers), 0.02 (d, 6H, CH_3 in SiMe$_2$, $^3J_{P\text{–}H} = 2.8$ Hz, 2 isomers), 3.10 (br s, 1H, CH in C$_5$H$_4$, 1 isomer), 3.20 (d, 2H, PH, $^1J_{P\text{–}H} = 192.6$ Hz, 2 isomers), 6.44 (m, 2H, CH in C$_5$H$_4$, 2 isomers), 6.48 (m, 1H, CH in C$_5$H$_4$, 1 isomer), 6.75 (m, 4H, CH in C$_5$H$_4$, 2 isomers), 7.01 (m, 6H, *o*- and *p*-CH in Ph, 2 isomers), 7.26 (t, 4H, *m*-CH in Ph, $^3J_{H\text{–}H} = 5.4$ Hz, 2 isomers).—^{31}P NMR (C_6D_6): $\delta = -121.6$, d, $^1J_{P\text{–}H} = 201$ Hz; -122.3, d, $^1J_{P\text{–}H} = 204$ Hz.—EI MS: *m/z* 304 (45%, [M^+]), 195 (100%, [$M^+ -$ PHPh]), 73 (65%, SiMe$_3$), and fragmentation products thereof.—IR (KBr): $\bar{\nu}$ (cm^{-1}): 2352 st (νPH), 1622 m, 1484 m (νC=C).—*Anal*. Calc. for C$_{16}$H$_{25}$PSi$_2$ (304.51): C 63.1, H 8.3, P 10.2; Found: C 56.8 (due to silicon carbide formation), H 8.1, P 9.3%.

*4.2. 1- and 3-SiMe$_3$–1-SiMe$_2$PHCy–C$_5$H$_4$ (**2**)*

LiPHCy (3.80 g, 31 mmol) was suspended in n-C$_6$H$_{14}$ (150 ml) and cooled to −50 °C. Then 1-SiMe$_3$–1-SiMe$_2$ClC$_5$H$_4$ (8.00 g, 34 mmol) was added, and the reaction mixture warmed to ambient temperature. The mixture was stirred for 1 day, filtered, the solvent evaporated in vacuo and the resulting yellow oil distilled under reduced pressure (50–55 °C, 1×10^{-2} Torr) to give 4.1 g (43%) of **2** as a colourless oil.

^{1}H NMR (C$_6$D$_6$): $\delta = -0.01$ (s, 18H, CH_3 in SiMe$_3$, 2 isomers), 0.03 (d, 6H, CH_3 in SiMe$_2$, $^3J_{\text{P–H}} = 3.0$ Hz, 2 isomers), 0.04 (d, 6H, CH_3 in SiMe$_2$, $^3J_{\text{P–H}} = 3.3$ Hz, 2 isomers), 1.2–2.1 (m, 22H, Cy, 2 isomers), 2.60 (d of d, 2H, PH, $^1J_{\text{P–H}} = 191.0$, $^3J_{\text{P–H}} = 6.4$ Hz, 2 isomers), 2.91 (br s, 1H, CH in C$_5$H$_4$, 1 isomer), 6.50 (m, 3H, CH in C$_5$H$_4$, 2 isomers), 6.62 (m, 4H, CH in C$_5$H$_4$, 2 isomers).—^{31}P NMR (C$_6$D$_6$): $\delta = -124.9$, d, $^1J_{\text{P–H}} =$ 191.2 Hz; −127.6, d, $^1J_{\text{P–H}} = 189.5$ Hz.—EI MS: *m/z* 360 (27%, [M^+]), 209 (100%, [M^+ −PHCy]), 73 (100%, SiMe$_3$) and fragmentation products thereof.—IR (KBr): $\bar{\nu}$ (cm^{-1}): 2327 st (νPH), 1635 m, 1625 m (νC=C).—*Anal*. Calc. for C$_{20}$H$_{33}$PSi$_2$ (360.62): C 61.9, H 10.1, P 10.0; Found: C 56.9 (due to silicon carbide formation), H 9.5, P 8.9%.

*4.3. 1-, 2- and 3-CMe$_2$PH^{t}Bu–1-SiMe$_3$C$_5$H$_4$ (**3**)*

Li[1-PH^{t}BuCMe$_2$C$_5$H$_4$] (1.00 g, 4.5 mmol) was dissolved in Et$_2$O (25 ml), SiMe$_3$Cl (0.6 ml, 5 mmol) was added and the reaction mixture stirred for 12 h. LiCl was filtered off, the solvent evaporated in vacuo and the resulting yellow oil distilled under reduced pressure (55 °C, 3×10^{-3} Torr) to give 1.1 g (91%) of **3** as a yellow oil.

^{1}H NMR (C$_6$D$_6$): $\delta = -0.09$ (br s, 27H, CH_3 in SiMe$_3$, 3 isomers), 0.98 (d, 9H, CH_3 in ^{t}Bu, $^3J_{\text{P–H}} = 8.5$ Hz, 1 isomer), 1.07 (d, 9H, CH_3 in ^{t}Bu, $^3J_{\text{P–H}} = 8.7$ Hz, 1 isomer), 1.10 (d, 9H, CH_3 in ^{t}Bu, $^3J_{\text{P–H}} = 13.2$ Hz, 1 isomer), 1.34 (d, 3H, CH_3 in CMe$_2$, $^3J_{\text{P–H}} = 16.6$ Hz, 1 isomer), 1.36 (d, 3H, CH_3 in CMe$_2$, $^3J_{\text{P–H}} = 16.6$ Hz, 1 isomer), 1.43 (d, 3H, CH_3 in CMe$_2$, $^3J_{\text{P–H}} = 13.6$ Hz, 1 isomer), 1.45 (d, 3H, CH_3 in CMe$_2$, $^3J_{\text{P–H}} = 10.1$ Hz, 1 isomer), 1.48 (d, 3H, CH_3 in CMe$_2$, $^3J_{\text{P–H}} = 12.3$ Hz, 1 isomer), 1.56 (d, 3H, CH_3 in CMe$_2$, $^3J_{\text{P–H}} = 7.6$ Hz, 1 isomer), 3.08 (br s, 2H, CH in C$_5$H$_4$, 2 isomers), 3.31 (d, 2H, PH, $^1J_{\text{P–H}} = 197.4$ Hz, 2 isomers), 3.49 (d, 1H, PH, $^1J_{\text{P–H}} = 199.5$ Hz, 1 isomer), 5.98 (s, 2H, CH in C$_5$H$_4$, 1 isomer), 6.05 (s, 1H, CH in C$_5$H$_4$, 1 isomer), 6.15 (s, 1H, CH in C$_5$H$_4$, 1 isomer), 6.36 (s, 2H, CH in C$_5$H$_4$, 1 isomer), 6.63 (s, 1H, CH in C$_5$H$_4$, 1 isomer), 6.65 (s, 1H, CH in C$_5$H$_4$, 1 isomer), 6.80 (s, 1H, CH in C$_5$H$_4$, 1 isomer), 6.81 (s, 1H, CH in C$_5$H$_4$, 1 isomer).—^{31}P NMR (C$_6$D$_6$): $\delta = 25.2$, d of dec, $^1J_{\text{P–H}} = 196.7$ Hz, $^3J_{\text{P–H}} = 12.1$ Hz; 19.2, d, $^1J_{\text{P–H}} = 198.4$ Hz; 13.1, d of dec, $^1J_{\text{P–H}} = 199.5$ Hz, $^3J_{\text{P–H}} = 12.2$ Hz.—EI MS: *m/z* 268 (25%, [M^+]), 179 (100%, [M^+ −PH^{t}Bu]), 73 (100%, SiMe$_3$), and fragmentation products thereof.—IR (KBr): $\bar{\nu}$ (cm^{-1}): 2345 m (νPH), 1625 m, 1503 m (νC=C).—*Anal*. Calc. for C$_{15}$H$_{29}$PSi (268.45): C 67.1, H 10.9, P 11.5; Found: C 65.9, H 9.9, P 10.9%.

*4.4. [{(η^5-C$_5$H$_4$)SiMe$_2$PHPh}ZrCl$_3$] (**4**)*

ZrCl$_4$ (1.33 g, 5.7 mmol) was suspended in C$_6$H$_5$CH$_3$ (30 ml), and a solution of **1** (1.75 g, 5.8 mmol) in C$_6$H$_5$CH$_3$ (20 ml) was added dropwise. The reaction mixture was stirred for 1 day, then the solvent was evaporated in vacuo and the resulting residue washed with n-C$_5$H$_{12}$ (30 ml) and extracted with THF to give 2.0 g (80%) of **4** as a yellow microcrystalline solid. M.p.: 150–155 °C. ^{1}H NMR ([D$_8$]THF): $\delta = 0.54$ (d, 3H, CH_3 in SiMe$_2$, $^3J_{\text{P–H}} = 4.9$ Hz), 0.55 (d, 3H, CH_3 in SiMe$_2$, $^3J_{\text{P–H}} = 3.9$ Hz), 2.62 (d, 1H, PH, $^1J_{\text{P–H}} = 200.9$ Hz), 6.52 (m, 1H, CH in C$_5$H$_4$), 6.55 (m, 1H, CH in C$_5$H$_4$), 6.58 (m, 1H, CH in C$_5$H$_4$), 6.61 (m, 1H, CH in C$_5$H$_4$), 7.10 (m, 3H, CH in Ph), 7.11 (m, 2H, CH in Ph).—^{13}C NMR ([D$_8$]THF): $\delta = -1.09$ (d, 1C, CH$_3$Si, $^2J_{\text{P–C}} = 2.9$ Hz), −1.00 (d, 1C, CH$_3$Si, $^2J_{\text{P–C}} = 5.5$), 119.34 (s, 2C, C in C$_5$H$_4$), 121.95 (d, 2C, C in C$_5$H$_4$, $^3J_{\text{P–C}} = 6.2$ Hz), 126.32 (d, 1C, *ipso*-C in Ph, $^1J_{\text{P–C}} =$ 22.0 Hz), 126.70 (d, 1C, C1 in C$_5$H$_4$, $^2J_{\text{P–C}} = 12.8$ Hz), 127.00 (s, 1C, p-C in Ph), 128.66 (d, 2C, m-C in Ph, $^3J_{\text{P–C}} = 5.8$ Hz), 134.45 (d, 2C, o-C in Ph, $^2J_{\text{P–C}} = 14.4$ Hz).—^{31}P NMR ([D$_8$]THF): $\delta = -117.1$, d, $^1J_{\text{P–H}} =$ 200.9 Hz.—EI MS: *m/z* 428 (2%, [M^+]), 319 (32%, [M^+ −PHPh]), 122 (100%, C$_5$H$_4$SiMe$_2$$^+$), 109 (52%, PHPh$^+$), and fragmentation products thereof.—IR (KBr): $\bar{\nu}$ (cm^{-1}): 2351 s (νPH).—*Anal*. Calc. for C$_{13}$H$_{16}$Cl$_3$PSiZr (428.9): C 36.4, H 3.8, P 7.2; Found: C 26.4 (due to silicon carbide formation), H 4.0, P 7.1%.

*4.5. [{(η^5-C$_5$H$_4$)SiMe$_2$PHCy}ZrCl$_3$] (**5**)*

ZrCl$_4$ (1.80 g, 7.7 mmol) was suspended in C$_6$H$_5$CH$_3$ (50 ml), and a solution of **2** (2.79 g, 7.8 mmol) in C$_6$H$_5$CH$_3$ (50 ml) was added dropwise. The reaction mixture was stirred for 1 day, then the solvent was evaporated in vacuo and the resulting residue washed with n-C$_5$H$_{12}$ (30 ml) and extracted with THF to give 2.0 g (58%) of **5** as white microcrystalline solid. M.p.: 145 °C. ^{1}H NMR ([D$_8$]THF): $\delta = 0.63$ (d, 3H, CH_3 in SiMe$_2$, $^3J_{\text{P–H}} = 4.3$ Hz), 0.64 (d, 3H, CH_3 in SiMe$_2$, $^3J_{\text{P–H}} = 6.1$ Hz), 1.18–1.85 (m, 11H, Cy), 2.59 (d, 1H, PH, $^1J_{\text{P–H}} = 191.1$ Hz), 6.57 (m, 2H, CH in C$_5$H$_4$), 6.64 (m, 2H, CH in C$_5$H$_4$).—^{31}P NMR ([D$_8$]THF): $\delta =$ −121.6, d, $^1J_{\text{P–H}} = 201.0$ Hz.—EI MS: *m/z* 434 (7%, [M^+]), 319 (45%, [M^+ −PHCy]), 122 (100%, C$_5$H$_4$SiMe$_2$$^+$), 115 (82%, PHCy$^+$), and fragmentation products thereof.—IR (KBr): $\bar{\nu}$ (cm^{-1}): 2403 m (νPH).—*Anal*. Calc. for C$_{13}$H$_{22}$Cl$_3$PSiZr (434.95): C

35.9, H 5.1, P 7.1; Found: C 27.3 (due to silicon carbide formation), H 4.9, P 6.5%.

4.6. *[{(η^5-C_5H_4)CMe_2PH^tBu}$ZrCl_3$]* (**6**)

$ZrCl_4$ (1.00 g, 4.3 mmol) was suspended in $C_6H_5CH_3$ (50 ml), and a solution of **3** (1.15 g, 4.3 mmol) in $C_6H_5CH_3$ (10 ml) was added dropwise. The reaction mixture was stirred for 12 h, then the solvent was evaporated in vacuo and the resulting residue washed with n-C_5H_{12} (30 ml) and extracted with THF to give 0.76 g (45%) of **6** as white microcrystalline solid. M.p.: 105 °C. ^1H NMR ([D_8]THF): $\delta = 1.03$ (d, 9H, CH_3 in ^{t}Bu, $^3J_{H-H} = 13.2$ Hz), 1.46 (d, 3H, CH_3C, $^3J_{P-H} = 8.1$ Hz), 1.54 (d, 3H, CH_3C, $^3J_{P-H} = 11.2$ Hz), 3.54 (d, 1H, PH, $^1J_{P-H} = 294.9$ Hz), 6.31 (m, 1H, CH in C_5H_4), 6.53 (m, 1H, CH in C_5H_4), 6.55 (m, 1H, CH in C_5H_4), 6.63 (m, 1H, CH in C_5H_4).—^{13}C NMR ([D_8]THF): $\delta =$ 30.04 (d, 3C, CH$_3$ in ^{t}Bu, $^2J_{P-C} = 5.5$ Hz), 33.02 (d, 1C, C(CH$_3$)$_2$, $^1J_{P-C} = 8.1$ Hz), 33.20 (d, 1C, C(CH$_3$)$_3$, $^1J_{P-C} = 11.9$ Hz), 33.64 (d, CH$_3$C, $^2J_{P-C} = 4.3$ Hz), 34.30 (d, CH$_3$C, $^2J_{P-C} = 5.8$ Hz), 115.39 (s, 1C, C in C_5H_4), 119.01 (s, 1C, C in C_5H_4), 119.78 (s, 1C, C in C_5H_4), 119.82 (s, 1C, C in C_5H_4), 129.71 (d, 1C, C1 in C_5H_4, $^2J_{P-C} = 10.2$ Hz).—^{31}P NMR (d_8-THF): $\delta = -6.8$, d, $^1J_{P-H} = 282.5$ Hz.—EI MS: m/z 392 (3%, [M^+]), 303 (11%, [$M^+ -$PH^{t}Bu]), 107 (80%, $C_5H_4CMe_2^+$), and fragmentation products thereof.—IR (KBr): $\tilde{\nu}$ (cm^{-1}): 2379 m (νPH).—*Anal*. Calc. for $C_{12}H_{20}Cl_3PZr$ (392.84): C 36.7, H 5.1, P 7.9; Found: C 34.3, H 4.9, P 7.5%.

4.7. *[{(η^5-C_5H_4)CMe_2PH^tBu}$TiCl_3$] (7)*

$TiCl_4$ (1.50 g, 7.9 mmol) was suspended in $C_6H_5CH_3$ (50 ml), and a solution of **3** (2.11 g, 7.9 mmol) in $C_6H_5CH_3$ (20 ml) was added dropwise. The reaction mixture was stirred for 12 h, then the solvent was evaporated in vacuo and the resulting residue washed with n-C_5H_{12} (30 ml) and extracted with $C_6H_5CH_3$ to give 1.85 g (67%) of **7** as a red microcrystalline solid. M.p.: 82–86 °C. ^1H NMR ([D_8]THF): $\delta = 0.92$ (d, 9H, CH_3 in ^{t}Bu, $^3J_{H-H} = 12.0$ Hz), 1.69 (m, 6H, CH_3C), 3.50 (d, 1H, PH, $^1J_{P-H} = 212.6$ Hz), 6.26 (m, 2H, CH in C_5H_4), 6.93 (m, 2H, CH in C_5H_4).—^{13}C NMR ([D_8]THF): $\delta = 31.07$ (d, 3C, CH$_3$ in ^{t}Bu, $^2J_{P-C} = 12.8$ Hz), 31.45 (d, 1C, C(CH$_3$)$_2$, $^1J_{P-C} = 19.2$ Hz), 33.12 (d, 1C, C(CH$_3$)$_3$, $^1J_{P-C} = 10.1$ Hz), 35.37 (s, CH$_3$C), 37.20 (s, CH$_3$C), 121.09 (s, 2C, C in C_5H_4), 122.64 (d, 1C, C1 in C_5H_4, $^2J_{P-C} = 27.7$ Hz), 130.88 (s, 2C, C in C_5H_4).—^{31}P NMR ([D_8]THF): $\delta = 36.7$, d, $^1J_{P-H} =$ 213.4 Hz.—EI MS: m/z 348 (5%, [M^+]), 224 (26%, [$M^+ -$Cl–PH^{t}Bu]), 107 (20%, $C_5H_4CMe_2^+$), and fragmentation products thereof.—IR (KBr): $\tilde{\nu}$ (cm^{-1}): 2324 m (νPH).—*Anal*. Calc. for $C_{12}H_{20}Cl_3PTi$ (349.5): C 41.2, H 5.8, P 8.9; Found: C 39.8, H 5.5, P 8.4%.

4.8. *Polymerisation experiments*

All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual-manifold Schlenk line, or interfaced to a high vacuum (10^{-5} Torr) line, or in a nitrogen-filled Vacuum Atmospheres glove box with a medium-capacity recirculator (1–2 ppm O_2). Argon, ethene, propene and nitrogen gases were purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular sieve column. Styrene (Spectrum) was freshly distilled under vacuum from CaO. All solvents for vacuum-line manipulations were stored in vacuo over Na/K alloy in resealable bulbs.

The polymerisation experiments were conducted in a 100 ml flamed heavy-wall glass round-bottom reaction flask attached to a high-vacuum line. In a typical experiment, 10 mg of **4**–**7** and the corresponding amount of MAO (MAO:cat. = 1:300) were charged to the flask containing a magnetic stir bar. The reaction vessel was connected to a high-vacuum line, pumped down and back-filled three times with Ar. Then the flask was re-evacuated, and a measured quantity of $C_6H_5CH_3$ (5 ml) was vacuum transferred into the reaction flask from Na/K. Then gaseous ethene or propene was condensed into the vessel through a gas-purification column. The flask was warmed to room temperature, and the pressure was continuously measured by means of a manometer. Rapid stirring of the solution was initiated, and after a measured time interval (2 h), the polymerisation was quenched by releasing the excess pressure of ethene or propene and immediately injecting a methanol/HCl mixture. The polymer product was collected by filtration, washed with C_6H_{14} and C_3H_6O and dried under vacuum for several hours.

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