Generation of Homogeneous (sp^3-C_1)-Bridged Cp/Amido and Cp/Phosphido Group 4 Metal Ziegler−Natta Catalyst Systems

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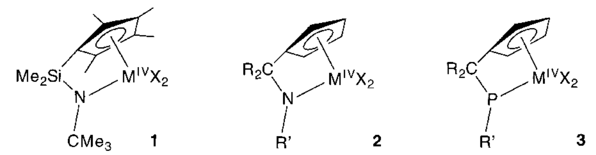
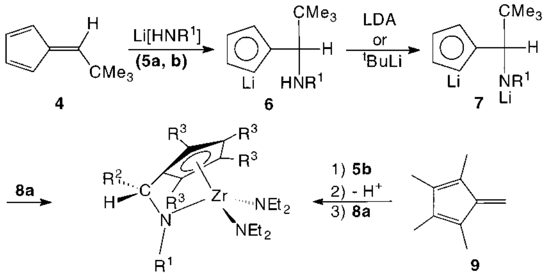
The silylene-bridged Cp/amido group 4 metal complexes have played an important role in the development of homogeneous Ziegler−Natta catalysis. Such "constrained geometry" catalysts, derived from e.g. **1** ($M^{IV}X_2$ = $ZrCl_2$ or $TiCl_2$) have been of great interest because of their polymerization and, especially, copolymerization behavior of α-olefins and other reactive alkenes.[1] Cp/amido ligands with larger bridging moieties have been described,[2] but it is remarkable that the corresponding chemistry of the methylene- and alkylidene-(sp^3-C_1)-bridged Cp/amido systems (**2**) appears not at all developed.[3] We here wish to disclose two rather simple and straightforward synthetic routes to such systems (**2**) and their Cp/phosphido relatives (**3**) and describe first examples of their use in homogeneous Ziegler−Natta catalysis (Chart 1).

Chart 1



The first route starts with a "non-enolizable" fulvene, such as 6-*tert*-butylfulvene (**4**).[4] Addition of, for example, lithium 4-methylanilide (**5a**) yields the functionalized lithium cyclopentadienide **6a**. Subsequent deprotonation (LDA) gave the dianionic sp^3-C_1-bridged "constrained geometry" ligand **7a**. Analogous treatment of the fulvene **4** with lithium *tert*-butylamide (**5b**) followed by deprotonation with *tert*-butyllithium gave **7b**. Transmetalation to zirconium employing the $[Cl_2Zr(NEt_2)_2(THF)_2]$ reagent (**8a**)[5a] proceeded without problems to yield the complexes **2a** (66%) and **2b** (71%), respectively. Due to the chiral bridge each of these complexes exhibits four diastereotopic ^{1}H NMR Cp methine resonances [**2a**: δ 6.38, 5.93 (α-C*H*), 6.10, 6.07 (β-C*H*)] and pairs of diastereotopic $-N(CH_2^{AB})-$ signals [**2a**: δ 3.31, 3.28, 3.19, 3.08].[6]

Scheme 1



2a [R^1 = p-tolyl, R^2 = $-CMe_3$, R^3 = H]
2b [R^1 = $-CMe_3$, R^2 = $-CMe_3$, R^3 = H]
2c [R^1 = $-CMe_3$, R^2 = H, R^3 = Me]
8a = $[Cl_2Zr(NEt_2)_2(THF)_2]$

The related sp^3-C_1-bridged Cp/amido metal complex analogue **2c** ("Cp*C_1N"ZrX_2) of the silylene-bridged ("Cp*Si_1N"ZrX_2) "constrained geometry" system **1** was obtained by treatment of tetramethylfulvene **9**[7] with $Li[HN(CMe_3)]$ (**5b**) followed by deprotonation with *tert*-butyllithium and transmetalation to Zr to give $[Cp^*-CH_2-N(CMe_3)]Zr(NEt_2)_2$ (**2c**) in 66% yield [^{1}H/^{13}C NMR: δ 4.34/68.6 (Cp*CH_2N)][6] (Scheme 1).

Our second route to "CpC_1N" systems starts with "non-enolizable" 6-aminofulvenes, such as **10**.[8a] Treatment of 6-dimethylaminofulvene (**10**) with lithium anilide **5c** results in an addition/elimination sequence to cleanly yield the formimino-substituted Cp-anion system **11** (isolated as a THF adduct in 91% yield).[8b] Addition of p-tolyllithium yields the "dianionic" ligand system isolated as the dilithio compound **12** (94%). Subsequent transmetalation by treatment with $[Cl_2Zr(NEt_2)_2(THF)_2]$ (**8a**) then gave the "CpC_1N"ZrX_2 system **2d** [75% isolated, ^{1}H NMR: δ 6.03 (μ-sp^3-CH), Cp signals at δ 6.14, 5.90 (α-C*H*), 6.00, 5.96 (β-C*H*), four diastereotopic $Zr-NCH_2^{AB}$ resonances at δ 3.38, 3.37, 3.28, and 3.16].

The reagent **11** adds 1 equiv of methyllithium to yield the "CpC_1N"Li_2 reagent **13** (96%), which was transmetalated by treatment with $[Cl_2Ti(NMe_2)_2]$ (**8b**)[5b] to give the "CpC_1N"$Ti(NMe_2)_2$ complex **2e** (69% isolated). Single crystals of **2e** that were suited for an X-ray crystal structure analysis[9] were obtained from dichloromethane at −20 °C during several days (Scheme 2).

In the crystal complex **2e** exhibits a close to tetrahedral coordination geometry of the central titanium atom. The fused cyclopentadienide ligand is η^5-coordinated, exhibiting a slightly unsymmetrical array of Ti−C bonds, with Ti−C1 (2.266(2) Å) being slightly shorter than the Ti−C2/C5 (2.314(2), 2.351(2) Å) and Ti−C3/C4 bonds (2.402(2), 2.424(2) Å). The C1−C6 vector (1.505(2) Å) forms an angle of 155.3° with the Cp-plane (Cp-

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[‡] X-ray crystal structure analysis.

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(6) Typical example: **2c**: 290 mg (66%) of **2c** isolated as a colorless oil. Anal. Calcd for $C_{22}H_{43}N_3Zr$ (440.8): C, 59.95; H, 9.83; N, 9.53. Found: C, 59.10; H, 10.54; N, 9.67. ^{1}H NMR (THF-d_8, 200 MHz): δ 4.34 (s, 2H, CH_2), 3.5−3.2 (m, 8H, NCH_2CH$_3$), 2.08, 2.06 (s, each 6H, CpCH_3), 1.15 (s, 9H, CMe$_3$), 0.97 (t, 12H, NCH$_2$CH_3). ^{13}C NMR (THF-d_8, 150 MHz): δ 119.5 (ipso-C), 68.6 (CH_2), 55.6/29.4 (CMe_3), 43.5/15.2 (NCH_2CH_3), 11.2/10.5 ($CpCH_3$).

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(9) For details, see the Supporting Information.

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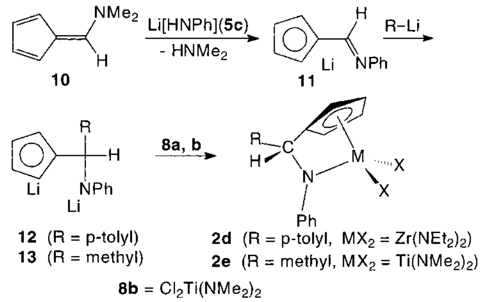
Scheme 2



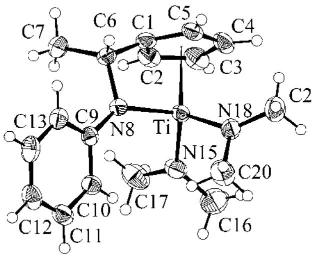
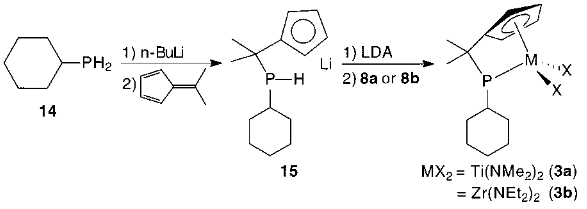


Figure 1. Molecular structure of **2e**. Selected bond lengths (Å) and angles (deg): C1−C2 1.413(2), C2−C3 1.394(3), C3−C4 1.400(3), C4−C5 1.399(3), C1−C5 1.407(2), C6−C7 1.517(2), N8−C9 1.387(2), N15−C16 1.449(3), N15−C17 1.449(3), N18−C19 1.445(2), N18−C20 1.452(2), C1−C6−N8 99.1(1), C1−C6−C7 112.8(1), C6−N8−Ti 104.3(1), C6−N8−C9 119.1(1), C9−N8−Ti 136.2(1), N8−Ti−N15 105.8(1), N8−Ti−N18 112.8(1), N15−Ti−N18 102.3(1).

Scheme 3



(centroid)−C1−C6). The C1−C6−N8 angle amounts to 99.1(1)°, and the adjacent C6−N8 bond length is 1.476(2) Å. The N8−Ti distance is found at 2.006(1) Å, which is markedly longer than the adjacent Ti−N15 (1.911(2) Å) and Ti−N18 (1.898(1) Å) bonds. The observed lengthening of the Ti−N8 bond may indicate some increased constraint of the "CpC$_1$N"Ti framework of **2e**, which is also reflected by the markedly reduced N8−Ti−Cp-(centroid) angle of 95.6° relative to that of the "CpSi$_1$N"M^{IV} frameworks of the otherwise closely related complexes [Cp*−SiMe$_2$−N(CMe$_3$)]Zr(NMe$_2$)$_2$ at 100.2° or [Cp−SiMe$_2$−N(CMe$_3$)]-Ti(NMe$_2$)$_2$ at 105.5°[10] (Figure 1).

The analogous alkylidene-bridged Cp/phosphido ("CpC$_1$P") constrained geometry Ti and Zr systems **3** were prepared starting by deprotonation of cyclohexylphosphine, followed by the addition to 6,6-dimethylfulvene to yield **15** (accompanied by ∼20% of the 2-propenyl-CpLi deprotonation product).[7b,11] Subsequent deprotonation of **15** with LDA followed by transmetalation using **8a** or **8b** gave good yields of the "CpC$_1$P"MX$_2$ complexes **3b** (Zr, 72%) and **3a** (Ti, 62%)[12] (Scheme 3).

The "CpC$_1$N"M^{IV}(NR$_2$)$_2$ and "CpC$_1$P"M^{IV}(NR$_2$)$_2$ complexes **2** and **3** gave active homogeneous Ziegler−Natta catalysts when treated with excess methylalumoxane. Ethene polymerization activities with the new catalyst systems depended on the specific NR/PR group, but were often found to be higher as compared to the conventional "Cp*Si$_1$N"Zr-derived catalysts under comparable laboratory conditions. Especially the new sp^3-C$_1$-bridged Cp/phosphidozirconium systems show increased polymerization activities (see Table 1). The new systems also form active catalysts for ethene/1-octene copolymerization. At 90 °C a considerable uptake of the linear 1-alkene was observed (up to ∼20% 1-octene found incorporated in the copolymer under the applied nonoptimized conditions; see Table 1) leading to long-chain-branched polymer structures.[1c,13] Again, the "CpC$_1$P"Zr-derived catalyst system is remarkably active also in ethene/1-octene copolymerization, relative to the conventional reference systems **1b** and **1a**/MAO under comparable conditions.

Table 1. Selected Alkene Polymerization Reactions That Were Carried Out with "CpC$_1$N"MX$_2$ and "CpC$_1$P"MX$_2$/MAO Ziegler−Natta Catalysts[a]

complex	M	mg[cat][b]	g polymer	ethene/octene[c]	act[d]
		ethene polymerization (60 °C):			
1a[e]	Zr	17.1	2.4	-	29
2a	Zr	20.0	1.1	-	13
1b[e]	Zr	20.0	4.9	-	53
2b	Zr	21.5	6.3[g]	-	101
3a	Ti	21.0	13.5	-	114
3b	Zr	21.0	21.0[h]	-	910
		ethene/1-octene copolymerization (90 °C):			
3a	Ti	16.0	0.5[f,i]	5:1	22
2b	Zr	20.0	3.3	4:1	37
2c	Zr	19.0	4.2	13:1	47
1a[e]	Zr	18.0	28.8[f,k]	4:1	660
1b[e]	Zr	20.0	10.3[f,i]	3:1	420
3b	Zr	21.0	51.5[f,i]	6:1	2240

[a] Ethene polymerizations carried out in toluene at 60 °C, copolymerizations in toluene/1-octene (1:1) at 90 °C/1 h, 2 bar ethene unless indicated; Al:Zr ≈ 700. [b] mg zirconium or titanium complex. [c] Component ratio in the obtained copolymer determined by ^{13}C NMR analysis. [d] In g polymer/mmol [Zr] or [Ti]•h•bar. [e] "Cp*Si$_1$N"ZrCl$_2$ (**1a**) and "Cp*Si$_1$N"Zr(NMe$_2$)$_2$ (**1b**) used for a comparison. [f] At 1 bar ethene pressure. [g] Reaction time: 40 min. [h] Reaction time: 15 min. [i] Reaction time: 30 min. [k] Reaction time: 45 min.

This study shows that the "CpC$_1$N"M^{IV}X$_2$ carbon relatives (**2**) and their "CpC$_1$P"M^{IV}X$_2$ analogues (**3**) of the well established "Cp*Si$_1$N"M^{IV}X$_2$ "constrained geometry" Cp/amido systems (**1**)[1c] are readily available in good yields by means of rather straightforward synthetic routes. These new complexes serve as suitable components for the generation of active new Ziegler−Natta catalyst systems that show an interesting potential in CC-bond forming catalysis. The application-profile of the new "CpC$_1$N" and "CpC$_1$P" metal catalysts is currently explored in our laboratory.

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Supporting Information Available: Spectroscopic data of the new compounds, including ^{13}C NMR spectra of the obtained copolymers, and details of the X-ray crystal structure analysis of complex **2e** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(12) **3b**: 312 mg (72%) isolated as a red oil. Anal. Calcd for C$_{22}$H$_{41}$N$_2$PZr (455.8): C, 57.98; H, 9.07. Found: C, 58.27; H, 8.61%. ^{1}H NMR (toluene-d_8, 600 MHz, 298 K): δ 5.92, 5.47 (m, each 2 H, β- and α-H of Cp), 3.26, 3.15 (m, each 8 H, NCH$_2$), 1.62 (d, $^3J_{PH}$ = 10 Hz, CMe$_2$), 1.99−1.23 (m, 11 H, C$_6$H$_{11}$), 0.93 (t, ^3J = 6.0 Hz, 12 H, NCH$_2$CH_3). ^{13}C NMR (toluene-d_8, 150 MHz, 298 K): δ 124.0 (ipso-C of Cp), 108.1 (β-CH of Cp), 106.4 ($^3J_{PC}$ = 3.6 Hz, α-CH of Cp), 42.5 ($^3J_{PC} \leq$ 2 Hz, NCH$_2$), 33.2 (CMe$_2$), 30.9 ($^2J_{PC}$ = 13 Hz, C(CH$_3$)$_2$), 35.6 ($^1J_{PC}$ = 38 Hz, CH of C$_6$H$_{11}$), 36.0 ($^2J_{PC}$ = 16 Hz), 27.6 ($^3J_{PC}$ = 11 Hz), 26.9 (CH$_2$ of C$_6$H$_{11}$), 16.1 (NCH$_2$CH$_3$). ^{31}P NMR (toluene-d_8, 81 MHz, 298 K): δ −11.5.

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