Synthesis of group 4 complexes that contain the tridentate diamido ligands $[(ArNCH_2CH_2)_2O]^{2-}$ (Ar = C_6H_3-Me_2-2,6 or $C_6H_3Pr^i_2$-2,6)

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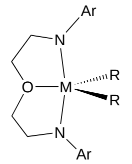
Complexes of Zr and Hf of the type $[(2,6\text{-}R_2C_6H_3NCH_2CH_2)_2O]ZrMe_2$ (R = Me or Pr^i) can be activated by $[PhNMe_2H][B(C_6F_5)_4]$ or $[Ph_3C][B(C_6F_5)_4]$ in chlorobenzene or bromobenzene to yield catalysts for the polymerization of hex-1-ene, but analogous titanium catalysts are relatively poorly behaved.

Significant advances have been made in the synthesis of ‘well defined’ alkene polymerization catalysts of the early metals (largely group 4) in the last 15 years, the vast majority of which contain two cyclopentadienyl-like rings.[1–3] (See, however, ref. 4, and references therein.) Recently group 4 complexes that contain chelating diamido ligand systems have received increased attention as potential alkene polymerization catalysts.[5–13] The most successful so far appear to be dialkyl complexes of Ti that contain diamido ligands such as $[ArNCH_2CH_2CH_2NAr]^{2-}$ (Ar = $C_6H_3Pr^i_2$-2,6),[5,6] and dialkyl complexes of Zr that contain the ‘diamido/donor’ ligand, $[(o\text{-}[^2H_6]Bu^tNC_6H_4)_2O]^{2-}$ ($[NON]^{2-}$).[10] Both types can be activated to yield (presumably) cationic catalysts for the living polymerization of hex-1-ene. We report here Ti, Zr and Hf complexes that contain potentially interesting ‘diamido/donor’ variations of the $[NON]^{2-}$ ligand, $[(2,6\text{-}R_2C_6H_3NCH_2CH_2)_2O]^{2-}$ (R = Me, Pr^i), and preliminary experiments concerning their use as catalysts for the polymerization of hex-1-ene.

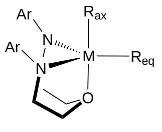
The diamines, $(2,6\text{-}Me_2C_6H_3NHCH_2CH_2)_2O$ (H_2L^{1a}) and $(2,6\text{-}Pr^i_2C_6H_3NHCH_2CH_2)_2O$ (H_2L^{1b}), can be prepared readily from $(TsOCH_2CH_2)_2O$ (TsO = tosylate) and 2 equiv. of $LiNH(C_6H_3Me_2\text{-}2,6)$ or $LiNH(C_6H_3Pr^i_2\text{-}2,6)$, respectively, in thf.† Compound H_2L^{1a} can be obtained in 60% yield as colorless crystals upon crystallization from pentane.‡,§ Compound H_2L^{1b} is obtained in 80% yield as an oil that has crystallized in some instances upon standing for several days, and that can be crystallized from pentane in low yield at −30 °C.†,‡ Crude H_2L^{1b} can be used in subsequent reactions.

The reaction between H_2L^{1a} or H_2L^{1b} and $Zr(NMe_2)_4$ in pentane at room temp. yields crystalline $ZrL^{1a}(NMe_2)_2$‡ or $ZrL^{1b}(NMe_2)_2$‡ readily. The dimethylamido compounds react with excess $SiMe_3Cl$ in ether overnight at room temp. to yield $ZrL^{1a}Cl_2$‡ and $ZrL^{1b}Cl_2$‡ as colorless, relatively insoluble crystals. NMR spectra of $ZrL^{1b}(NMe_2)_2$ and $ZrL^{1b}Cl_2$ show two sets of isopropyl methyl groups, but only one methine resonance, consistent with restricted rotation of the aryl ring about the N–C*ipso* bond, a phenomenon that was also noted by McConville and co-workers[5–8,14] in complexes containing the $[ArNCH_2CH_2CH_2NAr]^{2-}$ and related ligands. Only a single amido methyl resonance is observed in all dimethylamido compounds at room temp. in C_6D_6.

Alkylation of $ZrL^{1a}Cl_2$ with MeMgBr in ether gives $ZrL^{1a}Me_2$ **1a**‡ in good yield, while alkylation of $ZrL^{1b}Cl_2$ with Me or Bu^i Grignard reagents in ether yields $ZrL^{1b}Me_2$ **1b**‡ or $ZrL^{1b}(CH_2CHMe_2)_2$ **2b**,‡ respectively, in good yields as colorless cubes. NMR spectra are again consistent with slow rotation around the N–C*ipso* bond on the NMR timescale. In all dialkyl compounds the alkyl groups are equivalent, consistent either with a pseudotrigonal bipyramidal structure of type **A** or a pseudotrigonal bipyramid of type **B** in which the alkyl groups become equivalent on the NMR timescale *via* a rapid ‘flipping’ of the ligand backbone through an intermediate with structure **A**.



A



B

An X-ray study of $ZrL^{1a}Me_2$ (Fig. 1)¶ showed it to have structure **A** with ‘axial’ Zr–N bond distances of 2.084(3) Å and a Zr–O(2) bond length of 2.336(3) Å. The compound has a crystallographic mirror plane defined by Zr, O(2), C(5) and C(6). The planes of the aryl rings are perpendicular to the ZrO(2)N(3)N(4) pseudo-plane. The structure is closely related to that of $[(2,6\text{-}Et_2C_6H_3NCH_2)_2NC_5H_3]ZrMe_2$ [N–Zr–N 139.6(2)° and C–Zr–C 102.4(3)°][8] and contrasts markedly with that of $\{[(o\text{-}[^2H_6]Bu^tNC_6H_4)_2O]ZrMe\}\{MeB(C_6F_5)_3\}$,[10] in which $B(C_6F_5)_3$ has partially removed Me_{ax}. The two Me groups are technically inequivalent in the solid state structure of $ZrL^{1a}Me_2$ [C(8)–O(2)–C(18) 113.7(4)°] as a consequence of C(18) and C(8) not lying in the ZrN_2 plane.

Reactions similar to those employed to prepare Zr compounds can be employed to prepare $HfL^{1a}(NMe_2)_2$,‡ $HfL^{1a}Cl_2$,‡ and $HfL^{1a}Me_2$ **3a**.‡ The Hf compounds are virtually identical to the Zr compounds in physical properties and NMR characteristics.

Addition of Li_2L^{1a} to $TiCl_4(thf)_2$ in diethyl ether at −30 °C led to formation of a deep red precipitate, which could be recrystallized from CH_2Cl_2 to yield $TiL^{1a}Cl_2$ in 57% yield. Alkylation of $TiL^{1a}Cl_2$ in ether with MeMgCl in thf at −30 °C gave $TiL^{1a}Me_2$ **4a** in 53% yield as a yellow powder from pentane. Red, crystalline $TiL^{1a}(CH_2Ph)_2$ **5a** was prepared in low yield (*ca.* 15%) *via* the reaction between $Ti(CH_2Ph)_4$ (2 mmol)

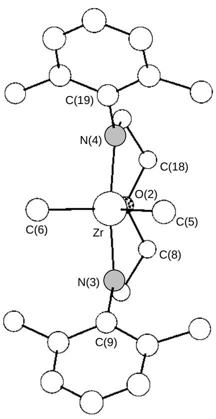


Fig. 1 A view of the structure of $ZrL^{1a}Me_2$ nearly opposite the Zr–O bond in the ZrC_2 plane. Bond lengths (Å) and angles (°): Zr–C(5) 2.253(6); N(4)–Zr–N(3) 139.1(2), C(8)–O(2)–C(18) 113.7(4), Zr–N(3)–C(9) 120.2(2), C(5)–Zr–C(6) 100.0(2)°.

Table 1 GPC and yield data for poly(hex-1-ene)[a]

Complex	Activator	M_n(theory)	M_n[b]	M_w[b]	M_w/M_n[b]	Yield (%)
$ZrL^{1b}Me_2$	$[NHMe_2Ph]^+$	13 440	2 670	3 560	1.33	96
$ZrL^{1b}Me_2$	$[CPh_3]^+$	16 800	2 460	4 220	1.72	96
$ZrL^{1b}(CH_2CHMe_2)_2$	$[NHMe_2Ph]^+$	16 800	2 650	8 550	3.23	94
$ZrL^{1b}Me_2$	$[CPh_3]^+$	16 800	11 700	18 000	1.55	100

[a] Dialkyl complex (44 μmol), activator (40 μmol), 200 equiv. hex-1-ene (except first entry = 160 equiv.), 10 ml chlorobenzene. [b] Determined by GPC coupled with on-line light scattering (Wyatt Technology).

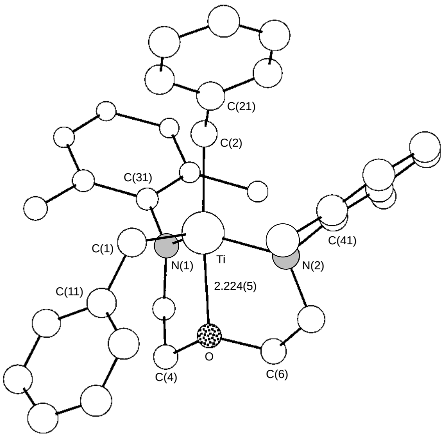


Fig. 2 A view of the structure of $TiL^{1a}(CH_2Ph)_2$. Bond lengths (Å) and angles (°): Ti–C(1) 2.129(10), Ti–N(1) 1.962(6), C(2)–Ti–O 169.3(3).

and H_2L^{1a} (2 mmol) in pentane (*ca.* 15 ml) in 40 h. In **4a** and **5a** the alkyl groups are equivalent on the NMR timescale at room temp., although several proton and carbon resonances in **5a** are broad at 22 °C. The structure of $TiL^{1a}(CH_2Ph)_2$ (Fig. 2)¶ is best described as type **B** in which O and C(2) are in the apical position and N(1), N(2), and C(1) are in the equatorial positions of a pseudotrigonal bipyramid. Surprisingly, the benzyl groups are bound only in an η^1 fashion; if two Ti–N π bonds can form, the metal should be viewed as having a 14 electron count, an electron deficiency that has led in many situations to η^2 or η^3 binding of benzyl ligands.[15]

Activation of alkyl complexes **1a**,**b**, **2b** and **3a** by either $[PhNMe_2H][B(C_6F_5)_4]$ or $[Ph_3C][B(C_6F_5)_4]$ yields initiators for the polymerization of hex-1-ene in chlorobenzene at 0 °C.‖ Polymerization yields are high, but the molecular masses of the polymers were found to be significantly smaller than expected when $ZrL^{1b}Me_2$ and $ZrL^{1b}(CH_2CHMe_2)_2$ were employed (Table 1). These results suggest that chain termination competes with propagation, but that the catalyst remains active thereafter and polymerization of a new chain is initiated. The $[PhNMe_2H]^+$ and $[Ph_3C]^+$ activators seem to be equally efficient. The number average molecular mass of poly(hex-1-ene) prepared using $ZrL^{1a}Me_2$ is approximately that expected if no significant chain termination is taking place. In all cases polymerization activity ceases when 2,4-dimethylpyridine is added to the catalyst mixture, consistent with competitive binding of the nitrogen base to a cationic metal center. Analogous experiments employing $HfL^{1a}Me_2$ yielded results similar to those employing $ZrL^{1a}Me_2$, but use of $TiL^{1a}Me_2$ (activated by $[PhNMe_2H][B(C_6F_5)_4]$ in [$^2H_5$]bromobenzene) led to only *ca.* 75% consumption of 25 equiv. of hex-1-ene to give poly(hex-1-ene).

We conclude that $[(2,6\text{-}R_2C_6H_3NCH_2CH_2)_2O]^{2-}$ ligands produce stable five-coordinate dialkyl complexes of Ti, Zr and Hf, and that 'cations' formed by protonation or oxidative cleavage of an alkyl group from Zr or Hf are initiators for the polymerization of hex-1-ene. These results should be contrasted with results obtained by McConville and co-workers[5,6] where Ti is the most successful when the diamido ligand does not contain an additional donor.

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Footnotes and References

† Solid $(TsOCH_2CH_2)_2O$ (5 g, 12.0 mmol) was added to a chilled (−30 °C) solution of $2,6\text{-}Pr^i_2C_6H_3NHLi$ (4.53 g, 24.8 mmol) in thf (30 ml). After 24 h all solvents were removed *in vacuo* and the residue was extracted with pentane. The pentane was removed *in vacuo* to yield an orange oil (4.2 g, 82%). An analytically pure sample was obtained by recrystallization from a concentrated pentane solution at −30 °C: ^1H NMR (C_6D_6) δ 7.18–7.14 (m, 6, H_{aryl}), 3.60 (t, 2, NH), 3.48 (spt, 4, C*H*Me$_2$), 3.35 (t, 4, OCH_2), 3.07 (q, 4, CH_2N), 1.06 (d, 24, CH*Me*$_2$); ($CDCl_3$) δ 7.18–7.05 (m, 6, H_{aryl}), 3.70 (t, 4, OCH_2), 3.57 (br, 2, NH), 3.36 (spt, 4, C*H*Me$_2$), 3.14 (br t, 4, CH_2N), 1.27 (d, 24, CH*Me*$_2$).

‡ Satisfactory elemental analyses have been obtained (C, H, N).

§ ^1H NMR (C_6D_6) δ 3.15 (t, 4, OCH_2), 2.95 (dt, 4, CH_2N), 2.24 (s, 12, Ar*Me*).

¶ *Crystallographic data*: $ZrL^{1a}Me_2$: Siemens SMART/CCD, orthorhombic, space group *Pnma*, a = 12.741(3), b = 22.663(5), c = 7.518(2) Å, U = 2170.9(8) Å^3, Z = 4, D_c = 1.321 g cm^{-3}, R = 0.0368, R_w = 0.1009, GOF = 1.179. For $TiL^{1a}(CH_2Ph)_2$: Siemens SMART/CCD, orthorhombic, space group *Fdd*2, a = 32.803(8), b = 42.342(13), c = 8.547(4) Å, U = 11872(7) Å^3, Z = 16, D_c = 1.210 g cm^{-3}, R = 0.0609, R_w = 0.1269, GOF = 1.095. CCDC 182/679.

‖ In a typical experiment a chilled (−30 °C) solution of **1b** (19 mg, 44 μmol) in chlorobenzene (3 ml) was added to a suspension of $[PhNMe_2H][B(C_6F_5)_4]$ (32 mg, 40 μmol) in chlorobenzene (6 ml) at −30 °C. The reaction mixture was allowed to warm to room temp. and was stirred for 15 min. The reaction mixture was cooled to 0 °C and hex-1-ene (1.0 ml, 8.0 mmol) was added all at once. After stirring for 1 h at 0 °C the reaction was quenched with HCl (1.0 M in ether, 4 ml). In a typical experiment employing $[Ph_3C][B(C_6F_5)_4]$ the reaction mixture was stirred for 2 min at −30 °C and allowed to equilibrate at 0 °C before hex-1-ene (1.0 ml, 8.0 mmol) was added all at once.

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