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FULL PAPER

Synthesis of new adducts and co-ordination complexes of zirconium and titanium containing β-aminoketone ligands. Crystal structures of isostructural adducts MCl_4·2Pr^{i}HNCMe=CHCMe=O (M = Ti or Zr) and the complex [Zr(PhNCMe=CHCMe=O)$_2$Cl$_2$]

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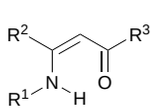
The reaction of MCl_4 (M = Zr or Ti) with β-aminoketones HL (R^{1}HNCR^2=CHCR^3=O; R^2 = R^3 = Me; R^2 = Me, R^3 = CF_3) yielded the bis(ligand) adducts MCl_4·2HL (M = Zr, R^1 = Pr^i or Ph; R^2 = R^3 = Me; or R^1 = Pr^i, R^2 = Me, R^3 = CF_3; M = Ti, R^1 = Pr^i or $CH_2CH{=}CH_2$, R^2 = R^3 = Me). Reaction of MCl_4 with the alkali-metal salts of the β-aminoketone ligands yielded the bis(ligand) complexes [M(R^{1}NCMe=CHCMe=O)$_2$Cl$_2$] (M = Zr, R^1 = Ph, *p*-ClC_6H_4, *p*-$MeOC_6H_4$ or Pr^i; M = Ti, R^1 = Ph or *p*-$MeOC_6H_4$). Crystal structure determinations of the isostructural compounds $ZrCl_4$·2Pr^{i}HNCMe=CHCMe=O and $TiCl_4$·2Pr^{i}HNCMe=CHCMe=O indicated an octahedral co-ordination environment around the metal with the *trans* monodentate N–O ligands bound through the oxygen only. Strong intramolecular hydrogen bonding of the hydrogen on the nitrogen with the ligand oxygen is consistent with a ligand immonium enolate structure. An X-ray study of the octahedral complex [Zr(PhNCMe=CHCMe=O)$_2$Cl$_2$] indicated that the oxygens of the chelating N–O ligands are *trans* to each other and the chloride ligands are in a *cis* arrangement. The plane of one N–O chelate is in the equatorial plane of the complex and the plane of the second N–O ligand is at right angles to the first. The ligand forms a predominantly delocalised chelate ring but some ene–imine structure is apparent.

Although the chemistry of organo-titanium, -zirconium and -hafnium complexes has been extensively studied, particularly in relation to their application as polymerisation catalysts, the co-ordination chemistry of these oxophilic metals has concentrated on the use of oxygen donors.[1] A relatively small number of articles have reported complexes with ligands containing nitrogen, phosphorus and sulfur donors.[1] Several reports have appeared describing Group 4 metal complexes containing mixed donor chelating ligand systems, *e.g.* complexes of monothio-β-diketonates and N–O Schiff bases; tetradentate *o*-phenylenebis(salicylideneiminate) (salphen) complexes of zirconium[1–9] have been reported and a single bis(ligand) ZrL_2Cl_2 complex (L = msal = *N*-methylsalicylideneiminate) has been described.[2] These mixed donor ligand systems offer opportunities for synthesizing complexes with potentially valuable reaction chemistry. Ligands of the type O–Y (where Y is for example N or S) are particularly interesting; the oxygen provides a site for strong co-ordination whereas the donor, Y, is likely to be less strongly bound and hence may lead to ligand hemilability and subsequently to interesting catalytic behaviour.

We have found that efficient catalyst systems for the conversion of ethylene into linear α-olefins are generated by *in situ* reaction of $ZrCl_4$ with an appropriate alkylaluminium cocatalyst in the presence of β-aminoketones.[10,11] To gain a better understanding of the nature of the catalyst system and to investigate factors which affect Group 4 metal-catalysed 1-olefin oligomerisation/polymerisation it was desirable to synthesize possible catalyst precursors formed from the reaction of β-aminoketones with the metal halide. Furthermore, complexes of the type ML_2Cl_2 (where M = Zr or Ti, and L = mixed donor, chelate ligand) are of interest; mixed-ligand complexes have been shown to be very effective catalysts in, for example, nickel-based systems.[12–14] In particular, β-aminoketones are an interesting class of bidentate ligand for Group 4 elements as amine/imine nitrogens co-ordinate relatively weakly to these metals. Although extensively studied for the late transition metals,[15–17] very few Group 4 metal complexes containing such ligands have been reported.[18] Several complexes containing analogous tetradentate β-aminoketones have been reported.[2–7] None of the published complexes has the form ML_2Cl_2.

We describe here the reaction of a variety of free β-aminoketones and β-aminoketonate anions with MCl_4 (M = Zr or Ti) to produce a number of unusual bis(β-aminoketone) adducts MCl_4·2HL (HL = R^{1}HNCR^2=CHCR^3=O or R^{1}MeNCR^2=CHCR^3=O) (M = Zr, R^1 = Pr^i or Ph, R^2 = R^3 = Me; or R^1 = Pr^i, R^2 = Me, R^3 = CF_3; M = Ti, R^1 = Pr^i or $CH_2CH{=}CH_2$, R^2 = R^3 = Me) and complexes of the type [ML_2Cl_2] (L = R^{1}HNCMe=CHCMe=O) (M = Zr, R^1 = Ph, *p*-ClC_6H_4, *p*-$MeOC_6H_4$ or Pr^i; M = Ti, R^1 = Ph or *p*-$MeOC_6H_4$). An X-ray crystallographic study of the isomorphous compounds MCl_4·2Pr^{i}HNCMe=CHCMe=O (M = Zr or Ti) and the complex [$ZrCl_2$(PhNCMe=CHCMe=O)$_2$] has provided detailed structural information.



Experimental

All reactions were carried out under purified nitrogen using normal Schlenk techniques. Solvents were dried and purified

using standard techniques. The ligands were prepared by known methods either in the presence of a drying agent,[17] in refluxing toluene using a Dean–Stark apparatus,[19] or where reaction rates were slow or the β-diketone acidity was too high (leading to formation of the β-diketonate ammonium salt) by reaction with the trimethylsilyl ether of the appropriate β-diketone.[20] Infrared spectra were recorded on a Hitachi 270-30 spectrometer, ^{1}H and ^{13}C NMR spectra with a Varian EM390, Bruker CXP 200 or Bruker AM300 spectrometer. The highly moisture-sensitive potassium or sodium alkyl- or aryl-β-aminoketonates have been isolated for the first time by a modified literature reaction.[16]

Synthesis of R^1KNCMe=CHCMe=O (R^1 = *p*-ClC_6H_4, *p*-$MeOC_6H_4$, Ph or Pr^i)

A typical procedure for the formation of these salts is described using *p*-$MeOC_6H_4$KNCMe=CHCMe=O as an example. In a Schlenk flask (250 cm^3), KOBu^t (1.6 g, 14.25 mmol) was suspended in a mix of toluene (20 cm^3) and tetrahydrofuran (50 cm^3). A solution of (*p*-MeOPh)HNCMe=CHCMe=O [3.22 g, 15.68 mmol (10% excess)] in thf (20 cm^3) was added and the flask heated to 60 °C with stirring for 4 h. The solution went yellow-orange as the KOBu^t reacted. After 4 h the solution was cooled to room temperature and the thf was removed under vacuum (a voluminous precipitate formed). Enough toluene (20–30 cm^3) was added to slurry the precipitate and the product was filtered off. Excess of aminoketone and impurities were removed by washing with toluene (2 × 20 cm^3) then with hexane (2 × 20 cm^3). The product was dried under vacuum and did not need recrystallising. Sodium salts of the ligands could also be isolated following the above procedure using sodium hydride instead of KOBu^t. In CD_3OD the salts appear to be partially deuteriated.† In non-protic solvents (*i.e.* [$^2H_8$]toluene) the ^{1}H NMR spectrum is 'normal' showing a ketoenamine structure.

p-$MeOC_6H_4$KNCMe=CHCMe=O: yield 86.0%; δ_H(CD_3OD, 300 MHz) 2.14 (m, 2 H, CH_2), 2.227 (s, 3 H, Me), 3.982 (s, 3 H, OMe), 5.301 (s, 2 H, CH_2), 7.127 (d, 2 H, J_{HH} 8.3, *m*-H of Ph) and 7.262 (d, 2 H, J_{HH} 8.3 Hz, *o*-H of Ph).

PhKNCMe=CHCMe=O: yield 92.0%; δ_H(CD_3OD, 300 MHz) 2.085 (m, 2 H, CH_2), 2.101 (s, 3 H, Me), 4.974 (s, 2 H, CH_2), 7.284 (m, 1 H, *p*-H of Ph), 7.365 (m, 2 H, J_{HH} 8.4, *o*-H of Ph) and 7.414 (t, 2 H, J_{HH} 8.1 Hz, *m*-H of Ph). An identical spectrum is obtained when NaOMe is added to the aminoketone in CD_3OD in a 1:1 ratio. In both cases when water is added the spectrum of the free aminoketone is seen.

PhNaNCMe=CHCMe=O: yield 96.0%; δ_H([$^2H_8$]toluene, 300 MHz) 1.507 (br s, 3 H, Me), 1.975 (br s, 3 H, Me), 4.575 (br s, 1 H, CH), 6.369 (br s, 2 H, *m*-H of Ph), 6.759 (m, 1 H, *p*-H of Ph) and 6.994 (m, 2 H, *o*-H of Ph).

p-ClC_6H_4KNCMe=CHCMe=O: yield 92.7%; δ_H(CD_3OD, 300 MHz) 2.08 (m, 2 H, CH_2), 2.099 (s, 3 H, Me), 5.054 (s, 2 H, CH_2), 7.204 (d, 2 H, J_{HH} 6.6, C_6H_4Cl) and 7.421 (d, 2 H, J_{HH} 6.6 Hz, C_6H_4Cl). Other salts were synthesized and used as required without characterisation.

Synthesis of the adducts MCl_4·2R^1HNCR^2=CHCR^3=O (M = Zr or Ti, R^1 = Pr^i, Ph, R^2 = R^3 = Me; M = Zr; R^1 = *p*-$MeOC_6H_4$, R^2 = Me, R^3 = CF_3) and MCl_4·2$R^1R^{1'}$NCMe=CHCMe=O (M = Zr, R^1 = $R^{1'}$ = Et or Ph; M = Ti, R^1 = *p*-$MeOC_6H_4$, $R^{1'}$ = Me)

A similar method to that reported for the preparation of the thf adduct of $ZrCl_4$ was used.[21] A typical synthesis is described for the adduct $ZrCl_4$·2Pr^iHNCMe=CHCMe=O. In a Schlenk flask (250 cm^3), $ZrCl_4$ (11.83 g, 50.8 mmol) was suspended in CH_2Cl_2 (150 cm^3) at 0 °C. To this was added a solution of Pr^iHNCMe=CHCMe=O [16 g, 115 mmol (10% excess)] in CH_2Cl_2 (20 cm^3). The solution initially went clear before a white solid precipitated. The slurry was stirred for 60 min at room temperature and the solids filtered off, washed twice with CH_2Cl_2 (20 cm^3) and dried under vacuum. The product could be purified by continuous extraction with refluxing CH_2Cl_2. Crystals suitable for structure determination were obtained by slow cooling of a saturated CH_2Cl_2 solution. For the zirconium complexes the synthesis can be performed in the presence of an excess of ligand, or in the presence of Et_3N as base; in each case only the adduct is formed.

$ZrCl_4$·2Pr^iHNCMe=CHCMe=O **1**: white crystalline solid (yield 74.8%) (Found: C, 37.21; H, 5.90; N, 5.46. $C_{16}H_{30}Cl_4N_2O_2Zr$ requires C, 37.28; H, 5.87; N, 5.43%); δ_H($CDCl_3$, 300 MHz) 1.43 [d, 6 H, J_{HH} 6.5, CH(CH_3)$_2$], 2.10 (s, 3 H, Me), 2.44 (s, 3 H, Me), 3.90 [d of spt, 1 H, $^2J_{HH}$ 9.2, J_{HH} 6.5 Hz, CH(CH_3)$_2$], 5.07 (s, 1 H, CH) and 10.50 (br s, 1 H, NH).

$ZrCl_4$·2PhHNCMe=CHCMe=O **2**: pale yellow crystalline solid (yield 76.2%) (Found: C, 44.98; H, 4.61; N, 4.79. $C_{22}H_{26}Cl_4N_2O_2Zr$ requires C, 45.29; H, 4.49; N, 4.80%); δ_H($CDCl_3$, 300 MHz) 2.136 (s, 3 H, Me), 2.537 (s, 3 H, Me), 5.397 (s, 1 H, CH), 7.3–7.4 (br m, 5 H, Ph) and 12.1 (s, 1 H, NH).

$ZrCl_4$·2(*p*-$MeOC_6H_4$)HNCMe=CHCCF_3=O **3**: pale yellow crystalline solid (yield 86.4%) (Found: C, 37.93; H, 3.25; N, 3.60. $C_{24}H_{24}Cl_4F_6N_2O_4Zr$ requires C, 38.36; H, 3.22; N, 3.73%); insoluble in CD_2Cl_2, $CDCl_3$ and ligand is displaced by C_4D_8O solvent.

$ZrCl_4$·2Ph_2NCMe=CHCMe=O **4**: yellow crystalline solid (yield 60.6%) (Found: C, 55.42; H, 4.91; N, 3.84. $C_{34}H_{34}Cl_4N_2O_2Zr$ requires C, 55.51; H, 4.66; N, 3.81%); δ_H($CDCl_3$, 300 MHz) 2.464 (s, 3 H, Me), 2.983 (s, 3 H, Me), 5.335 (s, 1 H, CH) and 7.1–7.5 (br m, 10 H, Ph).

$ZrCl_4$·2Et_2NCMe=CHCMe=O **5**: yellow crystalline solid (yield 82.3%) (Found: C, 39.55; H, 6.09; N, 5.04. $C_{18}H_{34}Cl_4N_2O_2Zr$ requires C, 39.78; H, 6.31; N, 5.15%); δ_H($CDCl_3$, 300 MHz) 1.27 (t, 3 H, J_{HH} 7.2, CH_2CH_3), 1.30 (t, 3 H, J_{HH} 7.2, CH_2CH_3), 2.539 (s, 3 H, Me), 2.983 (s, 3 H, Me), 3.532 (q, 2 H, J_{HH} 7.2, CH_2CH_3), 3.540 (q, 2 H, J_{HH} 7.2 Hz, CH_2CH_3) and 5.309 (s, 1 H, CH).

$TiCl_4$·2Pr^iHNCMe=CHCMe=O **6**: dark red crystalline solid (yield 96.0%) (Found: C, 40.67; H, 6.49; N, 6.14. $C_{16}H_{30}Cl_4N_2O_2Ti$ requires C, 40.70; H, 6.40; N, 5.93%); δ_H($CDCl_3$, 300 MHz) 11.02 (br s, 1 H, NH), 5.122 (s, 1 H, CH), 3.972 [d of spt, 1 H, $^2J_{HH}$ 9.3, J_{HH} 6.6, NCH(CH_3)$_2$], 2.678 (s, 3 H, Me), 2.173 (s, 3 H, Me) and 1.486 [d, 6 H, J_{HH} 6.6 Hz, NCH(CH_3)$_2$]; δ_C($CDCl_3$, 75.5 MHz) 189.1 (CO), 168.9 (CN), 98.0 (CH), 49.1 [NCH(CH_3)$_2$], 25.9 and 20.1 (Me) and 21.8 [NCH(CH_3)$_2$].

$TiCl_4$·2(*p*-$MeOC_6H_4$)MeNCMe=CHCMe=O **7**: dark maroon crystalline solid (yield 75.1%) (Found: C, 49.77; H, 5.52; N, 4.39. $C_{26}H_{34}Cl_4N_2O_4Ti$ requires C, 49.71; H, 5.45; N, 4.46%); two ligand environments, δ_H(CD_2Cl_2, 300 MHz) 5.623 (s, 1 H, CH), 5.040 (s, 1 H, CH), 3.839 (m, 6 H, *p*-*Me*OC_6H_4), 3.550 [s, 6 H, N*Me*(*p*-$MeOC_6H_4$)], 3.226 (narrow m, 2 H, part Me), 2.990 (s, 1 H, part Me), 2.820 (s, 3 H, Me), 2.768 (s, 3 H, Me), 2.635 (s, 1 H, part Me), 2.466 (s, 2 H, part Me) and 6.92–7.19 (m, 8 H, *p*-$MeOC_6H_4$); δ_C(CD_2Cl_2, 75.5 MHz, referenced to CD_2Cl_2 at δ 53.80) 193.8 and 191.9 (CO), 176.5 and 175.1 (CN), 160.2 (*p*-C of Ph), 136.9 (*i*-C of Ph), 126.9, 126.6 and 124.2 (*m*-C of Ph), 115.8, 115.7, 115.5 and 115.3 (*o*-C of Ph), 98.61 and 96.87 (CH), 55.9 (MeO), 44.2 and 43.6 (NMe), 28.26, 27.87, 22.96 and 20.63 (Me).

$TiCl_4$·2(CH_2=$CHCH_2$)HNCMe=CHCMe=O **8**: maroon microcrystalline solid (yield 97%) (Found: C, 40.97; H, 5.57; N, 5.95. $C_{16}H_{26}Cl_4N_2O_4Ti$ requires C, 41.05; H, 5.60; N, 5.98%); δ_H($CDCl_3$, 300 MHz) 11.58 (br s, 1 H, NH), 5.937 (ddt, 1 H, J_{XH} 5.5, J_{AX} 17.2, J_{BX} 10.3 Hz, =CH), 5.34–5.24 [br m(ddt's), 2

† The splitting pattern tends to indicate partial deuteriation. However, extensive exchange of the methyl and methine protons is not observed. Rapid quenching with water followed by hexane extraction led to isolation of the fully protonated free aminoketone. In non-protic solvents metal chelate formation is observed with the expected methine signal.

H, CH_2=], 5.234 (s, 1 H, CH), 4.170 [br m(dddd, 2 H, CH_2], 2.644 (s, 3 H, Me) and 2.160 (s, 3 H, Me); resolution inadequate to determine finer coupling constants; δ_C(CD_2Cl_2, 58.9 MHz) 186.9 (CO), 172.7 (CN), 131.1 (=CH), 118.7 (CH_2=), 98.9 (CH), 48.5 (CH_2), 25.5 and 20.3 (Me).

Synthesis of the complexes [Zr(R^1NCR^2=$CHCR^3$=O)$_2Cl_2$] (R^1 = Pr^i, Ph, *p*-C_6H_4 or *p*-$MeOC_6H_4$, R^2 = R^3 = Me)

The bis(ligand) complexes can be synthesized by the reaction of $ZrCl_4$ with the isolated ligand salt, by *in situ* generation of the ligand salt, or from the bis(ligand) adduct and LiBu^n. Typical procedures are described below.

Method A. In a Schlenk flask (100 cm^3), $ZrCl_4$ (1.26 g, 5.39 mmol) was suspended at −20 °C in CH_2Cl_2 (20 cm^3). To this was slowly added a cold (−20 °C) solution of *p*-ClC_6H_4-KNCMe=CHCMe=O (2.67 g, 10.8 mmol) in CH_2Cl_2 (20 cm^3). The solution, which went pale yellow with some suspended solids, was stirred for 1 h and then filtered, keeping the solution below 0 °C. Hexane (30 cm^3) was added to the filtrate and the volume reduced under vacuum to approximately 40 cm^3. The flask was placed in a freezer overnight yielding a crop of pale yellow crystals. The complex was recrystallised from CH_2Cl_2 and hexane at 0 °C.

[Zr(*p*-ClC_6H_4NCMe=CHCMe=O)$_2Cl_2$]·CH_2Cl_2 **9**: yield 56.1% [Found: C, 40.99; H, 3.68; N, 4.11. Calc. for $C_{23}H_{24}Cl_6N_2O_2Zr$: C, 41.58; H, 3.64; N, 4.22% (non-stoichiometric solvent ratio of approximately 1:1)]; δ_H(CD_2Cl_2, 200 MHz, −20 °C) 1.327 (s, 3 H, Me), 1.690 (s, 3 H, Me), 5.300 (s, ≈2 H, CH_2Cl_2), 5.341 (s, 1 H, CH), 6.566 (dd, 1 H, J_{HH} 8.4, 2.4, *o*-H of Ph), 7.260 (dd, 1 H, J_{HH} 8.4, 2.4, *o*-H of Ph), 7.157 (dd, 1 H, J_{HH} 8.4, 2.4, *m*-H of Ph) and 7.348 (dd, 1 H, J_{HH} 8.4, 2.4 Hz, *m*-H of Ph); see Discussion for interpretation; δ_C(CD_2Cl_2, 75.5 MHz, −20 °C) 175.2 or 174.6 (CO), 175.2 or 174.6 (CN), 147.0 (*i*-C of Ph), 131.6 (*p*-C of Ph), 127.3 and 125.0 (*o*-C of Ph), 129.4 (*m*-C of Ph), 107.2 (CH), 25.3 and 23.1 (Me).

[Zr(*p*-MeC_6H_4NCMe=CHCMe=O)$_2Cl_2$] **10**: yield 57.2% (Found: C, 50.56; H, 5.07; N, 4.87. Calc. for $C_{24}H_{28}Cl_2N_2O_4Zr$: C, 50.52; H, 4.95; N, 4.91%); δ_H(CD_2Cl_2, 200 MHz, −20 °C) 1.359 (s, 3 H, Me), 1.687 (s, 3 H, Me), 3.755 (s, 3 H, C_6H_4OMe), 5.305 (s, 1 H, CH), 6.566 (d, 1 H, J_{HH} 8.5, *o*-H of Ph), 6.796 (d, 1 H, J_{HH} 8.5, *m*-H of Ph), 6.876 (d, 1 H, J_{HH} 8.5, *m*-H of Ph) and 7.098 (d, 1 H, J_{HH} 8.5 Hz, *o*-H of Ph); see the Discussion section for interpretation; δ_C(CD_2Cl_2, 75.5 MHz, −20 °C) 174.7 (CO), 174.7 (CN), 157.6 (*p*-C of Ph), 140.9 (*i*-C of Ph), 126.4 and 124.5 (*o*-C of Ph), 114.7 and 113.5 (*m*-C of Ph), 107.2 (CH), 55.8 (C_6H_4OMe), 25.0 and 23.2 (Me); δ_H($CDCl_3$, 200 MHz, 20 °C), 1.433 (s, 3 H, Me), 1.721 (s, 3 H, Me), 3.811 (s, 3 H, C_6H_4OMe), 5.271 (s, 1 H, CH) and 6.5–7.3 (br m, 4 H, C_6H_4OMe); see Discussion for interpretation.

Method B. To a Schlenk flask (100 cm^3) containing NaH (1 g, 80% in mineral oil, 15% excess) suspended in thf (20 cm^3) at 0 °C was slowly added a solution of PhHNCMe=CHCMe=O (5.00 g, 28.5 mmol) in thf (20 cm^3). A vigorous reaction occurred. The solution was stirred at room temperature for 1 h and then filtered through dry Celite. The solution volume was reduced by about 10 cm^3 under vacuum to ensure all hydrogen was removed. This thf solution of PhNaNCMe=CHCMe=O was slowly added to a suspension of $ZrCl_4$ (3.30 g, 14.16 mmol) in toluene (30 cm^3) at 0 °C (the initial addition must be very slow). The $ZrCl_4$ dissolved during the addition and the solution went a cloudy pale yellow. It was stirred for 1 h at room temperature, filtered through dry Celite to remove the NaCl and the volume reduced to about half. The product precipitated on adding hexane (40 cm^3). It was recrystallised from CH_2Cl_2 with hexane (the complex can also be recrystallised from thf with hexane at 0 °C). Crystals of [Zr(PhNCMe=CHCMe=O)$_2Cl_2$] suitable for structure determination were obtained by slow cooling of a saturated toluene–CH_2Cl_2 solution.

[Zr(PhNCMe=CHCMe=O)$_2Cl_2$] **11**: yield 65.6% (Found: C, 51.56; H, 4.72; N, 5.30. Calc. for $C_{22}H_{24}Cl_2N_2O_2Zr$: C, 51.75; H, 4.74; N, 5.49%); δ_H($CDCl_3$, 200 MHz, 20 °C), 1.327 (s, 3 H, Me), 1.701 (s, 3 H, Me), 5.247 (s, 1 H, CH) and 6.5–7.4 (br m, 5 H, *o*-, *m*-, *p*-H of Ph); see Discussion for interpretation; δ_H(CD_2Cl_2, 200 MHz, −20 °C) 1.248 (s, 3 H, Me), 1.681 (s, 3 H, Me), 5.309 (s, 1 H, CH), 6.662 (d, 1 H, J_{HH} 7.6, *o*-H of Ph), 7.189 (t, 1 H, J_{HH} 6.33, *p*-H of Ph overlapping with *o*-H), 7.201 (d, 1 H, J_{HH} 7.6, *o*-H of Ph), 7.295 (t, 1 H, J_{HH} 7.0, *m*-H of Ph) and 7.373 (d, 1 H, J_{HH} 7.0 Hz, *m*-H of Ph); see Discussion for interpretation; δ_C(CD_2Cl_2, 75.5 MHz, −20 °C) 174.6 or 174.0 (CO), 174.6 or 174.0 (CN), 148.3 (*i*-C of Ph), 129.3 and 129.1 (*m*-C of Ph), 126.1 and 123.3 (*o*-C of Ph), 125.2 (*p*-C of Ph), 107.1 (CH), 25.1 and 22.9 (Me).

[Zr(*p*-$MeOC_6H_4NCMe$=$CHCCF_3$=O)$_2Cl_2$] **12**: yield 3.2% (microanalytical data for the fluorine-containing complexes were unreliable, consistently falling outside the accepted range, hence the data are not reported); δ_H($CDCl_3$, 200 MHz, 20 °C) 1.912 (s, 3 H, Me), 3.788 (s, 3 H, OMe), 5.807 (s, 1 H, CH) and 6.9 (br m, 4 H, *o*-, *m*-H of Ph); see Discussion for interpretation; δ_C(CD_2Cl_2, 75.5 MHz, 20 °C) 177.8 (CN), 159.6 (*p*-C of Ph), 156.1 (q, J_{CF} 34.7, CO), 138.7 (*i*-C of Ph), 125 (br s, *o*-C of Ph), 119.3 (q, J_{CF} 281 Hz, CF_3), 115.7 (*m*-C of Ph), 105.2 (CH) and 25.5 (Me).

Method C. In a Schlenk flask (250 cm^3) the adduct $ZrCl_4$·2Pr^{i}HNCMe=CHCMe=O (1.21 g, 2.33 mmol) was suspended in thf (30 cm^3) at −70 °C. To this was slowly added LiBu^n (6.98 cm^3, 0.671 M, 4.668 mmol) in pentane (20 cm^3) leaving a pale yellow solution with some suspended solids. The solution was stirred and allowed to warm to 0 °C. It was then filtered and the volume reduced to 30 cm^3. Pentane (40 cm^3) was added to precipitate a pale yellow solid. The complex may be recrystallised from thf and hexane.

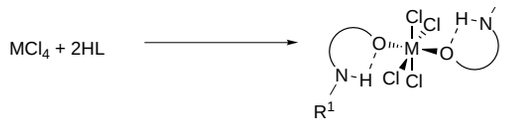
[Zr(Pr^{i}NCMe=CHCMe=O)$_2Cl_2$] **13**: yield 65.6% (Found: C, 43.61; H, 6.44; N, 6.28. Calc. for $C_{16}H_{28}Cl_2N_2O_2Zr$: C, 43.43; H, 6.38; N, 6.33%); δ_H($CDCl_3$, 300 MHz) 1.450 [d, 6 H, J_{HH} 6.8, $CH(CH_3)_2$], 1.918 (s, 3 H, Me), 2.159 (s, 3 H, Me), 4.539 [spt, 1 H, J_{HH} 6.8 Hz, $CH(CH_3)_2$] and 5.382 (s, 1 H, CH); δ_H(CD_2Cl_2, 300 MHz, 0 °C), 1.392 [d, 6 H, J_{HH} 6.8, $CH(CH_3)_2$], 1.909 (s, 3 H, Me), 2.154 (s, 3 H, Me), 4.497 [spt, 1 H, J_{HH} 6.8 Hz, $CH(CH_3)_2$] and 5.398 (s, 1 H, CH); δ_C(75.5 MHz, CD_2Cl_2, 0 °C) 173.9 and 172.6 (CO and CN), 109.0 (CH), 52.6 [$CH(CH_3)_2$], 25.0 and 24.1 (Me), 22.2 [$CH(CH_3)_2$].

Synthesis of the complexes [Ti(R^1NCR^2=$CHCR^3$=O)$_2Cl_2$] (R^1 = *p*-$MeOC_6H_4$, Ph or allyl, R^2 = R^3 = Me)

The bis(ligand) complexes can be synthesized by the reaction of $TiCl_4$ with the isolated ligand salt (Method A, above), also by reaction of $TiCl_4$·2L with an excess of triethylamine (Method D, below).

[Ti(*p*-$MeOC_6H_4NCMe$=CHCMe=O)$_2Cl_2$] **14**: very dark red-black crystals (yield 75.0%) (Found: C, 54.76; H, 5.29; N, 5.22. $C_{24}H_{28}Cl_2N_2O_4Ti$ requires C, 54.67; H, 5.35; N, 5.31%); δ_H(CD_2Cl_2, 300 MHz) 1.407 (s, 3 H, Me), 1.694 (s, 3 H, Me), 3.801 (s, 3 H, MeO), 5.412 (s, 1 H, CH), 6.582 (dd, 1 H, J_{HH} 2.4, 8.7, *o*-H of Ph), 6.826 (dd, 1 H, J_{HH} 3.0, 8.7, *o*-H of Ph), 6.945 (dd, 1 H, J_{HH} 2.7, 9.0, *m*-H of Ph) and 7.181 (dd, 1 H, J_{HH} 2.4, 8.7 Hz, *m*-H of Ph); δ_C(CD_2Cl_2, 75.5 MHz) 175.5 (CO), 170.9 (CN), 157.7 (*p*-C of Ph), 144.75 (*i*-C of Ph), 126.8 and 123.5 (*o*-C of Ph), 113.9 (*m*-C of Ph), 110.0 (CH), 55.8 (MeO), 24.6 and 22.3 (Me).

[Ti(PhNCMe=CHCMe=O)$_2Cl_2$] **15**: dark maroon leaflet crystals (yield 47.5%) (Found: C, 56.32; H, 5.11; N, 5.90. $C_{22}H_{24}Cl_2N_2O_2Ti$ requires C, 56.55; H, 5.18; N, 5.99%); δ_H($CDCl_3$, 300 MHz) 1.328 (s, 3 H, Me), 1.694 (s, 3 H, Me), 5.364 (s, 1 H, CH), 6.667 (dd, 1 H, J_{HH} 1.6, 8.2, *o*-H of Ph), 7.186 (dt, 1 H, J_{HH} 1.2, 7.1 Hz, *p*-H of Ph) and 7.26–7.38 (m, 3 H, *m*-, *o*-H of Ph); δ_C($CDCl_3$, 75.5 MHz) 175.5 (CO), 169.7



M = Zr or Ti
L = $R^1NCM{=}CHCMe{=}O$

$MCl_4{\cdot}2Pr^iHNCMe{=}CHCMe{=}O$ M = Zr **1**; Ti **6**
$ZrCl_4{\cdot}2PhHNCMe{=}CHCMe{=}O$ **2**
$ZrCl_4{\cdot}2(p\text{-}MeOC_6H_4)NCMe{=}CHCMe{=}O$ **3**
$ZrCl_4{\cdot}2Ph_2NCMe{=}CHCMe{=}O$ **4**
$ZrCl_4{\cdot}2Et_2NCMe{=}CHCMe{=}O$ **5**
$TiCl_4{\cdot}2(p\text{-}MeOC_6H_4)MeNCMe{=}CHCMe{=}O$ **7**
$TiCl_4{\cdot}2(CH_2{=}CHCH_2)HNCMe{=}CHCMe{=}O$ **8**

Scheme 1

(CN), 151.2 (*i*-C of Ph), 128.7 and 128.2 (*m*-C of Ph), 125.8 and 125.6 (*p*-, *o*-C of Ph), 122.0 (*o*-C of Ph), 109.5 (CH), 24.4 and 22.0 (Me).

Method D. To a stirred suspension of $TiCl_4{\cdot}2(CH_2{=}CHCH_2)HNCMe{=}CHCMe{=}O$ (0.53 g, 1.13 mmol) in CH_2Cl_2 (12 cm^3) at 0 °C was added NEt_3 (0.80 g, 7.90 mmol) dropwise, giving a dark solution. Stirring was continued for 1.5 h at 0 °C before concentrating the solution under vacuum (to 4 cm^3). Hexane (30 cm^3) was added, precipitating an impure solid. This was collected and vacuum dried before extracting with toluene (4 × 25 cm^3) and filtering through Celite to give a dark solution. Removal of toluene followed by redissolution in CH_2Cl_2 (4 cm^3), then layering with hexane (30 cm^3) and storage in a freezer overnight gave a crop of very dark red block-shaped crystals.

$[Ti\{(CH_2{=}CHCH_2)NCMe{=}CHCMe{=}O\}_2Cl_2]$ **16**: yield 58% (Found: C, 48.57; H, 6.32; N, 7.08. $C_{16}H_{24}Cl_2N_2O_4Ti$ requires C, 48.63; H, 6.12; N, 7.09%); two ligand environments with labile N-alkyl substituents labelled $NCH_AH_BCHCH_2$ and NCH_2CHCH_2; $\delta_H(CDCl_3$, 300 MHz) 5.771 (s, 1 H, CH), 1.954, 2.030, 2.041, 2.136 (s, 12 H, Me), 4.427 (br m, 1 H, CH_B), 4.601 (br m, 3 H, CH_2 overlapping CH_A), 5.098 (br m, 4 H, $CH_2{=}$), 5.615 (s, 1 H, CH) and 5.771 (s, 1 H, CH); $\delta_H(C_6D_5CD_3$, 200 MHz) 1.416 and 1.511 (s, 6 H, MeCN), 1.730 (s, 6 H, MeCO), 4.2–4.4 (vbr s, *ca.* 0.5 H, CH_2N), 4.511 (br s, *ca.* 3.5 H, CH_2N) and 5.146 (s, 2 H, CH); $\delta_C(CDCl_3$, 75.5 MHz) 177.8, 174.8, 173.4 and 173.0 (CO, CN), 133.5 and 133.29 (=CH), 116.4 and 116.1 ($CH_2{=}$), 111.4 and 110.9 (CH), 57.2 and 55.3 (CH_2), 23.5, 23.1, 22.2 and 21.5 (Me); $\delta_C(CD_2Cl_2$, 75.5 MHz) 174.9 (both CO), 173.5 and 173.1(CN), 134.2 and 133.9 (=CH), 116.6 and 116.4 ($CH_2{=}$), 111.5 and 111.1 (CH), 57.3 and 55.7 (CH_2), 23.5, 23.2, 22.5 and 21.8 (Me).

Crystallography

Unique room-temperature diffractometer data sets (2θ–θ scan mode; monochromatic Mo-Kα radiation, λ = 0.710 73 Å; $T \approx 295$ K) were measured yielding N independent reflections, N_o with $I > 3\sigma(I)$ being considered 'observed' [$I > \sigma(I)$ for compound **1**] and used in the full-matrix least-squares refinement after absorption correction. Anisotropic displacement parameters were refined for the non-hydrogen atoms; $(x,y,z, U_{iso})_H$ were included constrained at estimated values for **11** and refined for **1** and **6**. Conventional residuals R, R' on $|F|$ are quoted (statistical weights). Neutral atom complex scattering factors were employed. Pertinent results are given in the figures and tables.

Crystal/refinement data. $ZrCl_4{\cdot}2Pr^iHNCMe{=}CHCMe{=}O$ **1**, $C_{16}H_{30}Cl_4N_2O_2Zr$, M = 515.5, triclinic, space group $P\bar{1}$ (no. 2), a = 8.636(4), b = 9.090(6), c = 9.117(6) Å, α = 119.58(4), β = 91.07(5), γ = 107.25(5)°, U = 582.6 $Å^3$, $D_c(Z = 1)$ = 1.469 g cm^{-3}, $F(000)$ = 264, μ_{Mo} = 9.4 cm^{-1}, specimen 0.20 × 0.20 × 0.20 mm, $A^*_{min,max}$ = 0.9721, 0.999, $2\theta_{max}$ = 70°, N = 5112, N_0 = 4010, R = 0.053, R' = 0.058.

$TiCl_4{\cdot}2Pr^iHNCMe{=}CHCMe{=}O$ **6**, $C_{16}H_{30}Cl_4N_2O_2Ti$, M = 472.14, triclinic, space group $P\bar{1}$, a = 8.834(4), b = 8.974(4), c = 9.028(4) Å, α = 120.18(3), β = 90.10(3), γ = 107.62(3)°, U = 579.3 $Å^3$, $D_c(Z = 1)$ = 1.353 g cm^{-3}, $F(000)$ = 246, μ_{Mo} = 8.6 cm^{-1}, specimen 0.20 × 0.16 × 0.60 mm, $A^*_{min,max}$ = 1.13, 1.35, $2\theta_{max}$ = 50°, N = 3297, N_0 = 2624, R = 0.037, R' = 0.044.

$[Zr(PhNCMe{=}CHCMe{=}O)_2Cl_2]$ **11**, $C_{22}H_{24}Cl_2N_2O_2Zr$, M = 510.6, orthorhombic, space group *Pbca* (no. 61), a = 17.221(3), b = 16.448(12), c = 16.584(4) Å, U = 4697 $Å^3$, $D_c(Z = 8)$ = 1.449 g cm^{-3}, $F(000)$ = 2080, μ_{Mo} = 7.1 cm^{-1}, specimen 0.28 × 0.65 × 0.36 mm, $A^*_{min,max}$ = 1.20, 1.27, $2\theta_{max}$ = 50°, N = 4141, N_0 = 2619, R = 0.037, R' = 0.037.

CCDC reference number 186/784.

See http://www.rsc.org/suppdata/dt/1998/255/ for crystallographic files in .cif format.

Results and Discussion

In situ addition of a Lewis acid cocatalyst to a solution of MCl_4 and a β-aminoketonate gives rise to active catalyst systems for the oligomerisation and polymerisation of ethylene.[11] To study the nature of the catalyst and hence selectively moderate catalyst behaviour it was considered important to investigate possible compounds formed from the treatment of Group 4 metal salts with N–O ligand species. The reaction of β-aminoketonate ligands with MCl_4 (M = Zr or Ti) under various reaction conditions generated several isolable complex types (adducts and complexes) which may be formed in the *in situ* catalysis. Consistent with the concept that these new compounds may be the catalyst precursors, treatment of bis(ligand) adducts and complexes with an alkylaluminium cocatalyst generated active ethylene oligomerisation catalysts, even under very mild conditions. Furthermore, the adducts gave rise to catalysts with very similar catalytic behaviour to that observed for the *in situ* generated catalyst systems. Owing to complicated ligand–cocatalyst interactions the complexes and adducts have significantly different activities and product distributions.[11]

On reaction of ⩾2 equivalents of free β-aminoketone with MCl_4 in CH_2Cl_2 the low acidity of the ligand leads to formation of the bis(ligand) adducts (Scheme 1). In the case of the zirconium adducts there is no further reaction (deprotonation of the ligand) even in the presence of triethylamine or under forcing conditions, such as refluxing toluene. It has been previously observed that the more acidic salicylaldimines often deprotonate in refluxing toluene.[1] Interestingly, unlike the analogous zirconium compounds, the titanium adduct **8** smoothly deprotonates in the presence of triethylamine to give the relevant complex (TiL_2Cl_2) in reasonable yield and high purity. In fact this approach proved to be the best method for the synthesis of **16**. Synthesis of **16** *via* the sodium salt of the ligand resulted in the production of a large quantity of unidentified solid, giving a much lower yield for the desired complex. The ease with which the titanium adduct **8** was deprotonated possibly indicates an interaction in solution between the nitrogen of the bound ligand and the more Lewis-acidic and smaller titanium centre, leading to labilisation of the nitrogen proton. The treatment with triethylamine may be a general and very effective method for conversion of titanium adducts into complexes, and work is continuing in this area.

The bis(ligand) adducts show limited solubility in most non-protic polar solvents of lower donor ability than that of the ligand. They can be purified by extraction with CH_2Cl_2 which also allows spectroscopic characterisation by proton NMR spectroscopy. Ligand peaks for the adducts **1**, **6** and **2** are shifted slightly downfield compared to those of the free aminoketone, Table 1, and are somewhat broadened. For **1** and

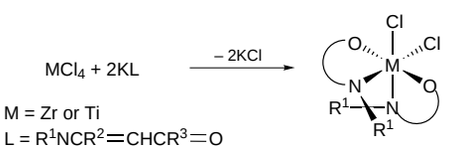
Table 1 Selected NMR data for the ligands $R^1HNCMe{=}CHCMe{=}O$ (R = Ph or Pr^i), and bis(ligand) adducts **1**, **6** and **2**

Compound	$R^2 = R^3 = Me$	Methine	NH	R^1
$Pr^iHNCMe{=}CHCMe{=}O$	1.96, 1.92	4.88	10.80	1.20 (d, 6 H, Me), 3.68 (m, 1 H, CH)
1	2.44, 2.10	5.07	10.50	1.43 (d, 6 H, Me), 3.90 (m, 1 H, CH)
6	2.68, 2.17	5.12	11.02	1.49 (d, 6 H, Me), 3.97 (m, 1 H, CH)
PhHNCMe=CHCMe=O	2.05, 1.98	5.19	12.50	7.14 (m, 2 H), 7.17 (m, 1 H), 7.33 (m, 2 H)
2	2.54, 2.14	5.40	12.10	7.32–7.42 (m, 5 H)

Table 2 Selected ^1H and ^{13}C NMR data for the ligand PhHNCMe=CHCMe=O and complexes **11** and **15**

		Ligand backbone				Amine substituent (C, H of Ph)			
		Me	CH	CO	CN	*i*	*o*	*m*	*p*
δ_H	PhHNCMe=CHCMe=O	1.978, 2.050	5.191				7.135	7.335	7.174
	11	1.698, 1.322	5.294				6.689, 7.114	7.336	7.192
	15	1.690, 1.335	5.354				6.65, 7.26	7.32	7.160
δ_C	PhHNCMe=CHCMe=O	20.35, 29.62	98.19	196.5	160.6	139.6	125.2	129.8	126.0
	11	23.38, 25.17	107.2	175.5	174.3	149.3	121.3, 126.6	129.6	126.6
	15	22.0, 24.5	109.5	175.6	169.7	151.2	125.9, 122.0	128.8, 128.2	125.6

Shifts (ppm) in CD_2Cl_2 at room temperature.



[Zr(*p*-$MeOC_6H_4NCMe{=}CHCMe{=}O)_2Cl_2$] **9**
[M(*p*-$MeOC_6H_4NCMe{=}CHCMe{=}O)_2Cl_2$ M = Zr **10**; Ti **14**
[M(PhNCMe=CHCMe=O)$_2Cl_2$ M = Zr **11**; Ti **15**
[Zr(Pr^iNCMe=CHCMe=O)$_2Cl_2$] **13**
[Zr(*p*-$MeOC_6H_4NCMe{=}CHCCF_3{=}O)_2Cl_2$] **12**
[Ti{$(CH_2{=}CHCH_2)CMe{=}CHCMe{=}O\}_2Cl_2$] **16**

Scheme 2

6 the isopropyl α-proton signal is split indicating coupling with a proton on the amine nitrogen, providing evidence that the ligand is still protonated with the proton on the nitrogen. The IR spectra of the free aminoketones show a strong band at approximately 1620 cm^{-1} [ν(C=O)] which shifts to lower wavenumbers [to overlap with a strong band at 1560 cm^{-1} (C=C stretch)] for the adduct **1**. The appearance of a sharp peak at 3280 cm^{-1} on adduct formation has been assigned to an N–H stretching band with diminution of strong hydrogen bonding.[18] These data clearly demonstrate that co-ordination of the N–O ligand to the metal is *via* the ligand oxygen. A subsequent X-ray study (see later) indicates that the solid-state structure is consistent with these proposals.

Reaction of $ZrCl_4$ with either a potassium β-aminoketonate (isolated by reaction of the free aminoketone with $KOBu^t$ in thf–toluene) or a sodium β-aminoketonate (formed *in situ*) in a 1:2 ratio or greater leads to the formation of the bis(ligand) complexes [Zr($R^1NCR^2{=}CHCR^3{=}O)_2Cl_2$] (Scheme 2). The pale yellow, moisture-sensitive zirconium complexes **9**–**13** are generally stable at room temperature or below and soluble in polar, non-protic organic solvents. N-Alkyl-substituted complexes are significantly less stable in solution than the N-aryl-substituted complexes with 10–15% decomposition of **13** in CD_2Cl_2 at room temperature in 24 h. No change was seen for a solution of **11** over a similar time-frame. Variable-temperature ^1H and ^{13}C NMR studies indicate that the β-aminoketonate ligands in bis(ligand) complexes are bonded through nitrogen and oxygen with no line broadening apparent for the backbone methyl groups up to 40 °C in CD_2Cl_2, indicating no observable ligand hemilability at these temperatures (Table 2). The complexes contain a delocalised chelate ring as indicated by the similar shifts of the amino and carbonyl carbons (δ_C 175.5 and 174.3), which are widely separated for the free aminoketones. The aminophenyl group in **11** displays restricted movement, with

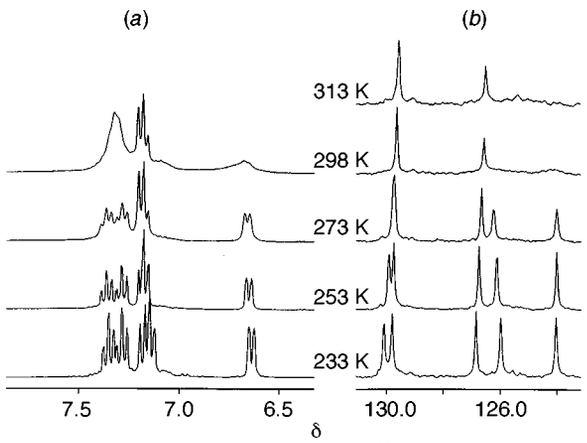


Fig. 1 Variable-temperature ^1H (*a*) and ^{13}C (*b*) NMR spectra of complex **11**

a broad resonance for the *m*-proton (δ_H 7.34) and split broad resonances for the *o*-protons (δ_H 6.66 and 7.20). The peaks resolve and sharpen with decreasing temperature [Fig. 1(*a*)]. The variable-temperature ^{13}C NMR spectra show similar changes [Fig. 1(*b*)]. All bis(ligand) complexes isolated to date show similar restricted movement of the aminohydrocarbyl unit. The NMR spectra display temperature-dependent splitting of phenyl resonances or separate environments for alkyl-substituted β-aminoketones. The underlying cause of the NMR splitting is thought to be due to the preferred *cis*-nitrogen/*trans*-oxygen configuration of the complexes as will be discussed in the next section.

The dark red, moisture-sensitive bis(ligand) titanium complexes **14**–**16** are in general less stable than their zirconium analogues. The Pr^i-substituted complex could not be isolated. Although these titanium complexes also show temperature-dependent NMR spectra the variation is significantly less than for the analogous zirconium complexes **9**–**13** with little evidence for peak coalescence on warming to room temperature. This can be explained by the smaller titanium atom effectively limiting the free rotation of the ligand substituents, even at higher temperatures. The NMR data indicate that the titanium complexes have similar structures to those of the zirconium complexes.

Solid-state structures of $ZrCl_4{\cdot}2Pr^iHNCMe{=}CHCMe{=}O$, $TiCl_4{\cdot}2Pr^iHNCMe{=}CHCMe{=}O$ and [Zr(PhNCMe=CHCMe=O)$_2Cl_2$]

The unusual nature of the adducts formed from the direct

Table 3 Selected ligand bond lengths for **1**, **6** and **11** and related complexes

Complex	O–C(1)	C(1)–C(2)	C(2)–C(3)	C(3)–N
1	1.303(2)	1.363(3)	1.418(3)	1.310(3)
6	1.318(3)	1.357(3)	1.449(3)	1.323(3)
11	1.323(6), 1.320(6)	1.337(7), 1.348(7)	1.430(7), 1.412(7)	1.321(5), 1.331(6)
$[Zr(acen)Cl_2]$	1.318(5), 1.329(6)	1.359(7), 1.334(9)	1.429(7), 1.421(8)	1.319(6), 1.317(7)
$[Zr(msal)_2Cl_2]$	1.349(8)	1.38(1)	1.468(10)	1.305(9)
$[Ti(\eta\text{-}C_5H_5)_3L]^{+}$ [a]	1.266(13)	1.342(17)	1.431(18)	1.271(15)
$[Pd(\eta\text{-}C_3H_4Me)\text{-}(PhCH_2CH_2NCMe{=}CHCMe{=}O)]_2$ [b]	1.34(2)	1.38(2)	1.51(3)	1.28(3)

[a] L = 2,4,6-$Me_3C_6H_2$NCMe=CHCMe=O.[18] [b] Ref. 22.

Table 4 Selected geometries (distances in Å, angles in °) for complexes **1** and **6**. The two values in each entry are for M = Zr, Ti respectively

M–Cl(1)	2.468(1), 2.3726(9)	Cl(1)–M–Cl(2)	90.20(2), 91.10(4)
M–Cl(2)	2.464(1), 2.378(1)	Cl(1)–M–O	87.98(4), 88.77(6)
M–O	2.052(1), 1.916(2)	Cl(2)–M–O	92.02(5), 90.87(6)
O–C(1)	1.303(2), 1.318(3)	M–O–C(1)	154.72(13), 153.4(1)
C(1)–C(2)	1.363(3), 1.357(3)	O–C(1)–C(2)	122.2(2), 120.9(2)
C(2)–C(3)	1.418(3), 1.449(3)	C(1)–C(2)–C(3)	126.8(2), 127.0(2)
C(3)–N	1.310(3), 1.323(3)	C(2)–C(3)–N	122.9(2), 123.5(2)
N–H	0.84(3), 0.77(3)	C(3)–N–H	111(2), 117(2)
H · · · O	2.05(4), 2.19(2)	N–H · · · O	141(3), 133(3)

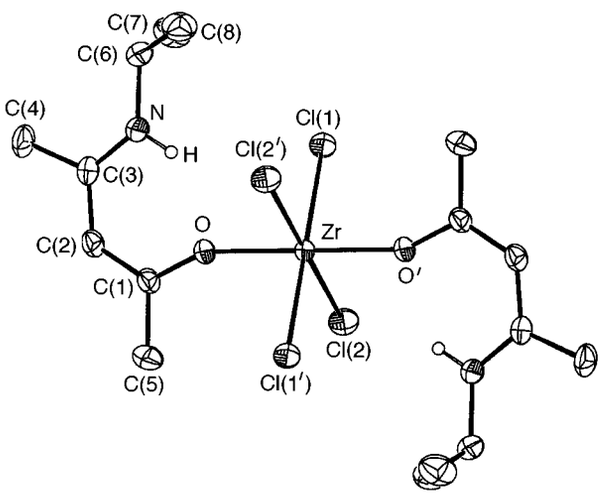


Fig. 2 A PLATON plot[23] of complex **1** with 30% probability ellipsoids; the carbon-bonded hydrogens have been omitted for clarity. Primed atoms are related to unprimed ones by the symmetry operation $-x, -y, -z$

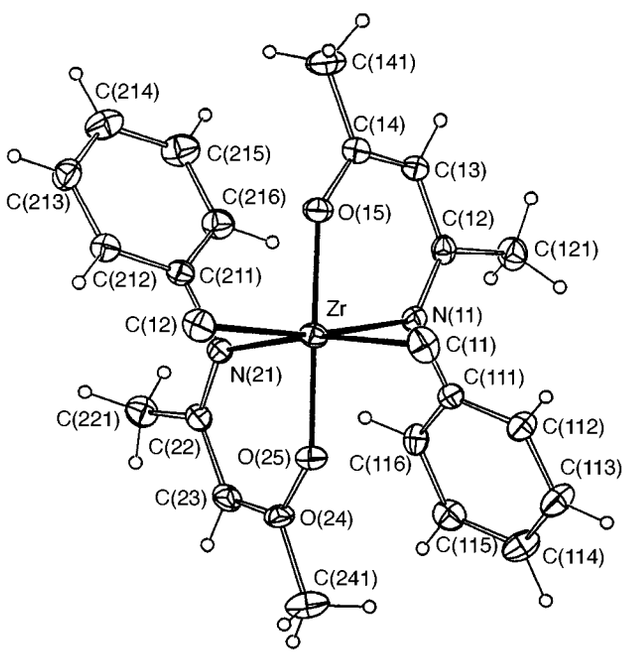


Fig. 3 Projection of a molecule of complex **11**; 20% thermal ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å

reaction of MCl_4 (M = Zr or Ti) with β-aminoketones led us to investigate in detail the structures of these compounds. Crystals of the isostructural complexes **1** and **6** suitable for structure determination were grown by slow cooling of a saturated CH_2Cl_2 solution or from a CH_2Cl_2 solution layered with hexane, respectively. Selected bond distances and angles are presented in Tables 3 and 4 and the structure of the zirconium complex **1** is shown in Fig. 2. The structure shows the oxygen donors of the N–O ligands co-ordinated in *trans* positions. A significant rearrangement of electron density in the ligand is apparent to give what could be called an immonium enolate structure in the solid state. The N–C(3) bond lengths in **1** and **6** (Table 4) approach that of a C–N double bond (*ca.* 1.30 Å). The C(1)–C(2) bonds are notably shorter than a normal C–C single bond (*ca.* 1.53 Å) and therefore can be considered to have appreciable olefinic character, whereas the O–C(1) bonds are considerably longer than expected for a C–O double bond (*ca.* 1.19 Å). The ligand amine hydrogens for **1** and **6** have been refined isotropically and are clearly associated with the nitrogen atom. They form intramolecular hydrogen bonds to the ligand oxygens with the following geometries: **1**, N–H 0.84(3), O · · · H 2.05(4) Å, N–H · · · O 141(3)°; **6**, N–H 0.77(3), O · · · H 2.19(2) Å, N–H · · · O 133(3)°. A less intimate association is found with Cl(1). This structure is maintained in solution as indicated by the splitting pattern of the NPr^i methine in the ^{1}H NMR spectrum (doublet of septets). The strength of the N–H · · · O intramolecular hydrogen bond and hence the ease or difficulty of deprotonation in adducts of type **1** appears to be an important feature of the catalytic behaviour of these compounds. It is apparent that the catalyst species formed during activation (and hence the product distribution obtained) depends on whether deprotonation occurs or not. The behaviour of catalyst systems generated from these compounds will be discussed in detail in a later publication.

Crystals of complex **11**, suitable for structural analysis, were obtained by slow cooling of a saturated toluene–CH_2Cl_2 solution. The structure is shown in Fig. 3 with relevant crystallographic data collected in Tables 3 and 5. The monomeric complex contains zirconium in a slightly distorted octahedral

Table 5 Selected bond lengths (Å) and angles (°) for complex **11**. Where two entries are given they are for segments $n = 1, 2$ respectively. Primed atoms lie in the alternate segment

Zr–Cl(*n*)	2.432(2), 2.421(2)	O(*n*1)–C(*n*1)	1.323(6), 1.320(6)
Zr–N(*n*)	2.312(3), 2.299(3)	C(*n*1)–C(*n*2)	1.337(7), 1.348(6)
Zr–O(*n*)	2.007(3), 2.012(3)	C(*n*2)–C(*n*3)	1.430(7), 1.412(7)
		C(*n*3)–N(*n*)	1.321(5), 1.331(6)
N(1)–Zr–N(2)	86.0(1)	Cl(*n*)–Zr–O(*n*′)	92.34(9), 92.6(1)
O(1)–Zr–O(2)	165.1(1)	N(*n*)–Zr–O(*n*′)	91.7(1), 91.6(1)
Cl(1)–Zr–Cl(2)	95.58(6)	Zr–O(*n*)–C(*n*1)	142.3(3), 141.6(3)
Cl(*n*)–Zr–N(*n*)	89.6(1), 90.5(1)	O(*n*)–C(*n*1)–C(*n*2)	122.4(4), 122.3(4)
Cl(*n*)–Zr–O(*n*)	97.41(9), 97.64(9)	C(*n*1)–C(*n*2)–C(*n*3)	125.2(4), 125.5(4)
N(*n*)–Zr–O(*n*)	77.1(1), 77.6(1)	C(*n*2)–C(*n*3)–N(*n*)	123.1(4), 123.3(4)
Cl(*n*)–Zr–N(*n*′)	168.87(9), 169.04(9)	C(*n*3)–N(*n*)–Zr	129.8(3), 129.4(3)

Table 6 Interplanar dihedral angles (°) for complex **11** where L1, P1 and L2, P2 are the planes formed by the ligand chelate ring and phenyl ring for ligands 1 and 2 respectively

	L1	L2	P1
L2	83.0(1)		
P1	88.3(2)	24.3(1)	
P2	27.6(2)	88.6(2)	85.8(2)

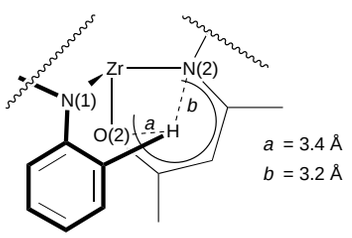


Fig. 4 Positioning of the *o*-proton of the phenyl ring attached to the nitrogen of one β-aminoketone ligand in relation to the plane of the second ligand

environment in which the oxygen atoms are *trans* to each other while the nitrogen atoms are *cis*, presumably due to unfavourable steric interactions between the amino-substituent and the carbonyl methyl of the second ligand if the nitrogen atoms were *trans*. In this orientation the aminophenyl substituent can align approximately parallel with the chelate ring formed by the second ligand, but being offset (interplanar dihedral angles are shown in Table 6), thereby bringing one *o*-carbon in line with the centre of the chelate ring (H · · · chelate plane distance ≈2.8, H · · · O ≈3.4 and H · · · N ≈3.2 Å; see Fig. 4) while the other approaches one of the chlorides leading to significantly different environments for the two *ortho* protons. The variable-temperature NMR data indicate that this structure is maintained in solution although the degree of association is unknown.

Deprotonation of the β-aminoketone in adducts of type **1** to form the ligand chelate in complexes such as **11** is accompanied by an electronic redistribution. The C–N and C–O bond lengths increase slightly for **11** compared with **1** and the C(1)–C(2) carbon double bond is shortened but an ene–imine structure is assigned (Table 3). As expected the M–Cl and M–O distances are shorter in **11** than in **1**. In the similar cationic titanium complex the C–O and C–N distances are considerably shorter, presumably due to the higher Lewis acidity of the cationic titanium centre. This may be compared with the palladium complex [Pd(η-C_3H_4Me)($PhCH_2CH_2$-NCMe=CHCMe=O)] in which an ene–imine structure is an appropriate description.[22]

Related acen ($^-$OCMe=CHCMe=NCH_2CH_2N=CMeCH=CMeO$^-$) zirconium complexes have shorter M–N bond lengths than those of **11** (presumably due to constraints imposed by the acen ligand) while the M–O distances are roughly equivalent (Table 4), and the M–Cl bonds are even longer than those in **1**. The M–N and M–O bond lengths in **11** are closer to those for $[Zr(msal)_2Cl_2]$ indicating a closer affinity with the ene–imine structure in the solid state.[2]

Conclusion

In situ mixtures of Group 4 metal chlorides ($TiCl_4$ and $ZrCl_4$), β-aminoketones and an alkylaluminium cocatalyst generate exciting new catalysts for the oligomerisation of ethylene. To furnish information about the possible nature of the active species we have synthesized likely catalyst precursers formed by the addition of β-aminoketones to MCl_4. The adduct compounds formed initially (**1**–**8**) are unusual species involving monodentate co-ordination through the ligand oxygen atom with the oxygens in *trans* positions. Reaction of MCl_4 with the β-aminoketonate anion leads to formation of bis(ligand) complexes $[M(N–O)_2Cl_2$ **9**–**16**] in which the β-aminoketonate is now chelating through the oxygen and nitrogen atoms. Deprotonation of β-aminoketones may be achieved with strong bases, or in some instances under catalytic conditions at higher temperatures. In the complexes the (N–O)$^-$ ligands are so arranged that the remaining chloride ligands on the metal centre are in *cis* positions, ideally placed for activation of the complexes for catalysis. It has been found that the bis(ligand) complexes give rise to very active oligomerisation catalysts on treatment with suitable cocatalysts. Details of the catalytic behaviour of the various systems will be reported in a forthcoming publication.

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