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Synthesis and catalytic properties of oxalic amidinato complexes

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The oxalic amidine compounds $C_6H_5N{=}C(NH^tBu){-}C(NH^tBu){=}NC_6H_5$ **1** and $C_6H_5N{=}C\{N(^tBu)(SiMe_3)\}{-}C\{N(^tBu)(SiMe_3)\}{=}NC_6H_5$ **2** are described. The compound $[(C_6H_5N)C(NH^tBu){-}C(NH^tBu)(NHC_6H_5)][Br]$ **3*** has been isolated from the reaction between **1** and $[NiBr_2(DME)]$. Treatment of **1** with $M(NMe_2)_4$ (M = Zr or Ti), $[Ta(NEt_2)_2Cl_3(py)]$ or $[Zr\{N(SiMe_3)_2\}_3Cl]$ gives the bimetallic complexes $[M(NMe_2)_3(C_6H_5N)C(N^tBu){-}]_2$ (M = Zr (**4**) or M = Ti (**5**)) and the mono-amidinato complexes $[Ta(NEt_2)Cl_3\{(C_6H_5N)C(N^tBu)C(HN^tBu)(NC_6H_5)\}]$ **6*** and $[Zr\{N(SiMe_3)_2\}_2Cl\{(C_6H_5N)C(N^tBu)C(HN^tBu)(NC_6H_5)\}]$ **7*** respectively: * indicates the crystal structure has been determined. The activity toward ethylene polymerisation has been investigated for compounds **4**, **5** and **7**.

Introduction

Owing to the success of metallocenes containing one or more cyclopentadienyl ligands as pre-catalysts for the polymerisation of α-olefins, there is considerable interest in the development of new 'non-metallocene' catalysts.[1] The amidinato ligands of general formula $[R^1C(NR^2)(NR^3)]^-$ have been the focus of attention because they can often be used in place of cyclopentadienyl ligands to provide new metal complexes. The steric and electronic properties of amidinato ligands are programmable by variation of the substituents R^1, R^2 and R^3.[2] Indeed, over the past thirty years, a large diversity of metal–amidinato compounds has been synthesized and these have been reviewed recently by Barker and Kilner (on amidine)[3] and Edelmann (on benzamidine).[4] However, to date there are only a few new examples of amidinato ligands with bulky substitutents,[5–7] asymmetrical substituents ($R^2 \neq P^3$),[8–10] and of pendant[11,12] or bridged amidinato ligands.[13–15]

Oxalic amidines were first described in the 1900s.[16,17] They have been employed in the organic syntheses of heterocyclic[18–21] and macrocyclic[22] compounds. Recently, they have attracted renewed interest, mainly driven by the discovery that the late transition metal diimine complexes display efficient activity as catalysts for olefin polymerisation reaction.[1,23] Since the oxalic amidines can be deprotonated, they also have the potential to act as diamide or diamidinate ligands. The steric and electronic effects of these versatile ligands are programmable through variation of the substituents on the nitrogen atoms.[24] However, to date only a few examples of diimine,[25–27] imine–amide[26,28,29] and diimine–diamide[30] complexes have been developed.

Here we report the preparation and structural properties of early transition metal complexes containing oxalic amidinato ligands. Their ability to act as pre-catalysts toward olefin polymerisation has also been investigated.

Results and discussion

Treatment of the bis-phenylimidoyl chloride with an excess of $^tBuNH_2$ (6 equivalents) in toluene gives a white powder which the data show to be a bis-amidine, tethered *via* the carbon–carbon single bond, namely $C_6H_5N{=}C(NH^tBu){-}C(NH^tBu){=}NC_6H_5$ **1**. No tautomer was observed in the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra. Treatment of one equivalent of **1** with two equivalents of n-BuLi followed by refluxing in THF with an excess of Me_3SiCl gives the silyl amidine compound $C_6H_5N{=}C\{N(^tBu)(SiMe_3)\}{-}C\{N(^tBu)(SiMe_3)\}{=}NC_6H_5$ **2**, in high yield.

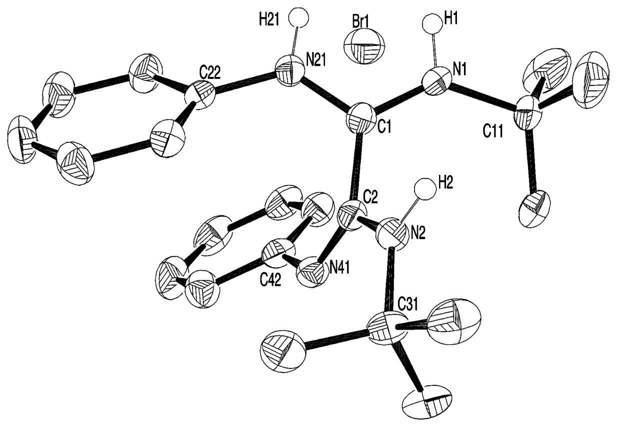

Fig. 1 Molecular structure of $[(C_6H_5N)C(NH^tBu)C(NH^tBu)(NHC_6H_5)][Br]$ **3**. Hydrogen atoms on carbon atoms omitted for clarity.

The analytical and spectroscopic data characterising **1** and **2** and the other new compounds described in this paper are collected in Table 1. A summary of syntheses and proposed structures is shown in Scheme 1.

In view of the diimine property of compound **1**, it was decided to attempt to prepare a Brookhart type nickel catalyst.[23] Treatment of **1** with one equivalent of $NiBr_2(DME)$ in CH_2Cl_2 at room temperature affords a pale green solid, which was purified by diffusion of concentrated CH_2Cl_2 solution into toluene to give a green crystalline solid. The analytical data were consistent with the salt product $[(C_6H_5N)C(NH^tBu)C(NH^tBu)(NHC_6H_5)][Br]$ **3** and no nickel adduct was formed. A possible explanation of the formation of compound **3** is the occurrence of hydrogen migration from the ligand or solvent followed by reduction of $[NiBr_2(DME)]$ to form **3** in low yield (23%).

The crystal structure of $[(C_6H_5N)C(NH^tBu)C(NH^tBu)(NHC_6H_5)][Br]$ **3** has been determined and the molecular structure is shown in Fig. 1. The interatomic distances and angles are listed in Table 2. The structure displays the proposed diimine–diamine structure with one proton attaching to one of the diimine nitrogens to form a cation. The three $C_{CNN}{-}N(H)$ bond distances, 1.309(4), 1.356(4) and 1.324(4) Å, are between those of the C–N single bond, 1.504(4), 1.480(4) Å, and C=N double bond, 1.271(4) Å, in the same structure. The partial double bond property shows the delocalisation around the CNN unit. Bond angles around the bridged carbon, 123.5(3), 117.4(3), 119.1(3), 123.8(3), 112.0(2) and 124.2(3)°, display the sp^2

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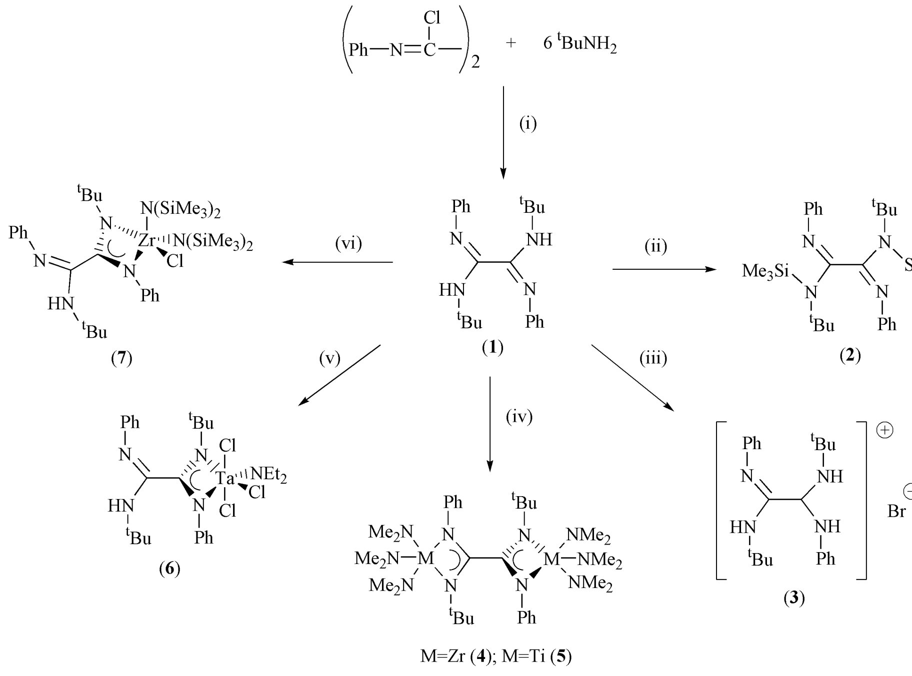
Table 1 Analytical and spectroscopic data

Compound and analysis[a]	Spectroscopic data[b]
1 White C, 75.1 (75.4) H, 9.0 (8.6) N, 15.9 (16.0)	^{1}H: 1.07 (s, 18H, $NC(C\mathit{H}_3)_3$), 3.96 (s, 2H, $N\mathit{H}$), 6.90 (m, 2H, $p\text{-}C_6\mathit{H}_5$), 7.02 (m, 4H, $o\text{-}C_6\mathit{H}_5$), 7.11 (m, 4H, $m\text{-}C_6\mathit{H}_5$) $^{13}C\text{-}\{^{1}H\}$: 27.9 (s, $NC(\mathit{C}H_3)_3$), 51.8 (s, $N\mathit{C}(CH_3)_3$), 121.8 (s, $o\text{-}\mathit{C}_6H_5$), 122.5 (s, $p\text{-}\mathit{C}_6H_5$), 129.2 (s, $m\text{-}\mathit{C}_6H_5$), 149.3 (s, C_{ipso}-Ph), 150.2 (s, *C*NN) IR: 3390m (NH), 1636s, 1590s, 1506s, 1454m, 1362m, 1324m, 1250m, 1206s, 1158m, 902m, 780m, 754s, 696s, 558m, 436m
2 White C, 68.0 (68.0) H, 8.6 (9.4) N, 11.6 (11.3)	^{1}H: 0.27 (s, 18H, $Si(C\mathit{H}_3)_3$), 1.06 (s, 18H, $NC(C\mathit{H}_3)_3$), 6.96 (m, 2H, $p\text{-}C_6\mathit{H}_5$), 7.09 (m, 4H, $m\text{-}C_6\mathit{H}_5$), 7.48 (br, 4H, $o\text{-}C_6\mathit{H}_5$) $^{13}C\text{-}\{^{1}H\}$: 2.8 (s, $Si(\mathit{C}H_3)_3$), 30.3 (s, $NC(\mathit{C}H_3)_3$), 54.9 (s, $N\mathit{C}(CH_3)_3$), 125.5 (s, $p\text{-}\mathit{C}_6H_5$), 128.6 (s, $m\text{-}\mathit{C}_6H_5$), 130.0 (s, $o\text{-}\mathit{C}_6H_5$), 143.4 (s, C_{ipso}-Ph), 149.9 (s, *C*NN) IR: 2970s, 1646s, 1620s, 1594s, 1492s, 1358m, 1292s, 1248s, 1208s, 1146s, 848s, 750s, 702s, 680m, 622m, 586m, 556m, 420m
3 Yellowish green C, 60.3 (61.3) H, 6.7 (7.2) N, 12.7 (13.0) Br, 18.3 (18.5)	^{1}H: 1.11 (s, 18H, $NC(C\mathit{H}_3)_3$), 3.98 (br, 2H, $N\mathit{H}$), 6.91 (br, 2H, $p\text{-}C_6\mathit{H}_5$), 7.08 (br, 4H, $m\text{-}C_6\mathit{H}_5$), 7.14 (br, 4H, $o\text{-}C_6\mathit{H}_5$) $^{13}C\text{-}\{^{1}H\}$:[c] 28.1, 30.0 (2s, $NC(\mathit{C}H_3)_3$), 54.3, 58.8 (2s, $N\mathit{C}(CH_3)_3$), 121.6, 124.0, 124.3, 127.7, 129.0, 129.3 (6s, $o,m,p\text{-}\mathit{C}_6H_5$), 134.5, 140.2, 146.5, 157.5 (4s, 2C_{ipso}-Ph + 2*C*NN) IR: 3244m (NH), 1638s, 1592s, 1536m, 1484m, 1372m, 1186m, 762m, 694m
4 Off-white C, 51.4 (51.3) H, 8.7 (8.1) N, 17.0 (17.6)	^{1}H: 1.00 (s, 18H, $NC(CH_3)_3$), 3.03 (s, 36H, $N(CH_3)_2$), 6.93 (m, 2H, *p*-Ph), 7.27 (m, 4H, *m*-Ph), 7.57 (m, 4H, *o*-Ph) $^{13}C\text{-}\{^{1}H\}$: 30.8 (s, $N(C(\mathit{C}H_3)_3)$, 42.5 (s, $N(\mathit{C}H_3)_2$), 55.2 (s, $N(\mathit{C}(CH_3)_3)$, 123.0 (s, $p\text{-}\mathit{C}_6H_5$), 123.3 (s, $o\text{-}\mathit{C}_6H_5$), 129.4 (s, $m\text{-}\mathit{C}_6H_5$), 147.1 (s, C_{ipso}-Ph), 167.6 (s, *C*NN) IR: 2822s, 2766s, 1618m, 1592s, 1496s, 1450s, 1390m, 1360m, 1242s, 1202s, 1146m, 986m, 938s, 792m, 754s, 696s, 536s, 478m
5 Orange C, 57.0 (57.6) H, 9.0 (9.1) N, 19.2 (19.8)	^{1}H: 1.08 (s, 18H, $NC(CH_3)_3$), 3.23 (s, 36H, $N(CH_3)_2$), 6.95 (m, 2H, *p*-Ph), 7.29 (m, 4H, *m*-Ph), 7.57 (m, 4H, *o*-Ph) $^{13}C\text{-}\{^{1}H\}$:[c] 31.4 (s, $N(C(\mathit{C}H_3)_3)$, 46.5 (s, $N(\mathit{C}H_3)_2$), 55.5 (s, $N(\mathit{C}(CH_3)_3)$, 122.5 (s, $p\text{-}\mathit{C}_6H_5$), 123.5 (s, $o\text{-}\mathit{C}_6H_5$), 129.1 (s, $m\text{-}\mathit{C}_6H_5$), 148.0 (s, C_{ipso}-Ph), 167.6 (s, *C*NN) IR: 2846s, 2762s, 1618m, 1592s, 1496s, 1440s, 1394m, 1358m, 1242s, 1198s, 1150m, 946s, 794m, 752m, 696m, 588m, 560m, 482m
6 Red C, 43.8 (44.1) H, 5.5 (5.5) N, 9.8 (9.9) Cl, 14.3 (15.0)	^{1}H: 0.59 (t, 6H, $J = 6.9$, $N(CH_2C\mathit{H}_3)_2$), 1.16 (s, 9H, $NC(C\mathit{H}_3)_3$), 1.67 (s, 9H, $NC(C\mathit{H}_3)_3$), 4.12 (q, 4H, $J = 6.9$, $N(C\mathit{H}_2CH_3)_2$), 4.24 (s, 1H, $N\mathit{H}C(CH_3)_3$), 6.78–7.00 (overlapping, 6H, Ph), 7.22–7.31 (overlapping, 4H, Ph) $^{13}C\text{-}\{^{1}H\}$:[c] 11.7 (s, $N(CH_2\mathit{C}H_3)_2$), 28.2 (s, $NC(\mathit{C}H_3)_3$), 30.2 (s, $NC(\mathit{C}H_3)_3$), 44.8 (s, $N(\mathit{C}H_2CH_3)_2$), 53.0 (s, $N\mathit{C}(CH_3)_3$), 58.3 (s, $N\mathit{C}(CH_3)_3$), 122.5 (s, *o*-Ph), 123.5 (s, *p*-Ph), 124.8 (s, *o*-Ph), 126.2 (s, *p*-Ph), 128.1 (s, *m*-Ph), 128.8 (s, *m*-Ph), 143.2, 145.1, 146.7 (3s, 2 C_{ipso}-Ph + 1*C*NN), 166.0 (s, *C*NN) IR: 3416m (NH), 2974s, 1632s, 1592m, 1532s, 1492s, 1452m, 1370s, 1246m, 1222m, 1202m, 1164m, 1040m, 992m, 928m, 788m, 768m, 740m, 698m
7 Off-white C, 50.9 (51.2) H, 8.4 (8.2) N, 10.5 (10.6) Cl, 4.0 (4.5)	^{1}H: 0.18 (s, 18H, $N[Si(C\mathit{H}_3)_3]_2$), 0.40 (s, 18H, $N[Si(C\mathit{H}_3)_3]_2$), 1.32 (s, 9H, $NC(C\mathit{H}_3)_3$), 1.62 (s, 9H, $NC(C\mathit{H}_3)_3$), 4.72 (s, 1H, $N\mathit{H}C(CH_3)_3$), 6.33 (d, $J = 7.5$, 2H, *o*-Ph), 6.83–7.01 (overlapping, 8H, Ph) $^{13}C\text{-}\{^{1}H\}$:[c] 5.4 (s, $N[Si(\mathit{C}H_3)_3]_2$), 5.7 (s, $N[Si(\mathit{C}H_3)_3]_2$), 28.1 (s, $NC(\mathit{C}H_3)_3$), 31.4 (s, $NC(\mathit{C}H_3)_3$), 53.0 (s, $N\mathit{C}(CH_3)_3$), 56.3 (s, $N\mathit{C}(CH_3)_3$), 121.5 (s, Ph), 122.5 (s, Ph), 125.1 (s, Ph), 125.3 (s, Ph), 129.0 (s, Ph), 129.3 (s, Ph), 143.7, 147.3, 147.7 (3s, 2 C_{ipso}-Ph + 1*C*NN), 168.8 (s, *C*NN) IR: 3450w, 3412m (NH), 2966s, 1618s, 1590s, 1488s, 1454s, 1398s, 1362m, 1252s, 1218m, 1162m, 852s, 784m, 762m, 696s, 668m, 426m

[a] Analytical data given as: found (required)%. [b] All the data were taken in benzene-d_6 at room temperature unless otherwise stated. Chemical shifts are quoted in ppm, *J* in Hz. [c] In chloroform-*d*.



Scheme 1 *Reagents and conditions*: (i) in toluene, r.t., 48 h; (ii) 2 n-BuLi, Et_2O, 3 h; followed by excess Me_3SiCl, THF, 75 °C, 8 h; (iii) $[NiBr_2(DME)]$, CH_2Cl_2, r.t., 72 h; (iv) $M(NMe_2)_4$ (two equivalents), toluene, 85 °C, 3 h; (v) $[Ta(NEt_2)_2Cl_3(py)]$ (two equivalents), toluene, 110 °C, 7.5 h; (vi) $[Zr\{N(SiMe_3)_2\}_3Cl]$, toluene, 105 °C, 4 h.

Table 2 Selected bond lengths (Å) and angles (°) for **3**

N(1)–C(1)	1.309(4)	N(2)–C(2)	1.356(4)
N(1)–C(11)	1.504(4)	N(2)–C(31)	1.480(4)
C(1)–N(21)	1.324(4)	C(2)–N(41)	1.271(4)
N(21)–C(22)	1.424(4)	N(41)–C(42)	1.406(4)
C(1)–C(2)	1.523(4)		
C(1)–N(1)–C(11)	135.1(2)	C(2)–N(2)–C(31)	125.2(3)
N(1)–C(1)–N(21)	117.4(3)	N(2)–C(2)–N(41)	123.8(3)
C(1)–N(21)–C(22)	128.1(3)	C(2)–N(41)–C(42)	124.7(3)
N(1)–C(1)–C(2)	123.5(3)	C(2)–C(1)–N(21)	119.1(3)
C(1)–C(2)–N(2)	112.0(2)	C(1)–C(2)–N(41)	124.2(3)

character. This structure also confirms the proposed structure of the neutral ligand.

Amine elimination reactions have been employed in the synthesis of metal amide complexes for many years,[31–33] and the synthesis of mixed amide complexes was attempted *via* this route. Therefore, the reactions of the diimine–diamine ligand with $M(NMe_2)_4$ (M = Zr or Ti) were investigated. Treatment of compound **1** with one equivalent of $Zr(NMe_2)_4$ in toluene at 85 °C affords an off-white compound in low yield. The ^{1}H NMR spectrum shows two methyl resonances assigned to the *tert*-butyl and NMe_2 groups with the intensity of one to two. This indicates three NMe_2 groups remain co-ordinated to the metal centre. No N–H stretch was observed in the infrared spectrum. The elemental analysis data are consistent with the bimetallic amidinate compound, $[Zr(NMe_2)_3(C_6H_5N)C(N\text{-}^tBu)\text{-}]_2$ **4**. The compound **4** was subsequently prepared in good yield (82%) from the reaction of **1** with two equivalents of $Zr(NMe_2)_4$ in toluene at 85 °C, followed by recrystallisation from a concentrated toluene solution. The same route was employed in preparing the analogous titanium compound (**5**) in good yield (75%). Attempts to make metal halide complexes by treatment of compounds **4** or **5** with Me_3SiCl or $Me_2NH{\cdot}HCl$[34–36] have been performed. However, these reactions only result in formation of intractable mixtures. Reactions of compound **2** with $[ZrCl_4(THF)_2]$ either in CH_2Cl_2 at room temperature or in refluxing toluene also failed to yield characterisable metal halide complexes.

The successful synthesis of the mixed amidinate–amide complexes *via* amine elimination led us to explore the synthesis of related metal complexes by an analogous method. Treatment of compound **1** with $[Ta(NEt_2)_2Cl_3(py)]$ in the 1 : 2 molar ratio in refluxing toluene gave a red compound (**6**), but it was not the expected bimetallic amidinate complex. The ^{1}H NMR spectrum of **6** showed two peaks with the same intensity corresponding to the *tert*-butyl groups. Irradiation of one (δ 1.16) of those two resonances resulted in an NOE enhancement of the signal for the N–H resonance (δ 4.24). This indicates that one amidine function remains intact. A sharp single peak in the infrared spectrum is observed at 3416 cm^{-1} indicative of an N–H stretch. The elemental analysis data of compound **6** are consistent with the mono-amidinate compound, $[Ta(NEt_2)Cl_3\{(C_6H_5N)C(N\text{-}^tBu)C(HN^tBu)(NC_6H_5)\}]$. Variation of the stoichiometry of the reaction of $[Ta(NEt_2)_2Cl_3(py)]$ and compound **1** did not yield the bimetallic amidinate or bis-amidinate compound. Instead a mixture of starting material and **6** was obtained.

Table 3 Selected bond lengths (Å) and angles (°) for **6**

Ta(1)–Cl(1)	2.367(4)	N(4)–C(3)	1.367(17)
Ta(1)–Cl(2)	2.385(3)	N(4)–C(41)	1.382(16)
Ta(1)–Cl(3)	2.345(3)	C(3)–C(5)	1.519(19)
Ta(1)–N(1)	1.960(10)	N(6)–C(5)	1.349(17)
Ta(1)–N(2)	2.249(8)	N(6)–C(61)	1.492(16)
Ta(1)–N(4)	2.090(10)	N(7)–C(5)	1.285(16)
N(2)–C(3)	1.220(20)	N(7)–C(71)	1.414(17)
N(2)–C(21)	1.547(18)		
Cl(1)–Ta(1)–Cl(2)	88.42(14)	Cl(1)–Ta(1)–Cl(3)	89.38(14)
Cl(2)–Ta(1)–Cl(3)	170.11(13)	Cl(1)–Ta(1)–N(1)	104.4(3)
Cl(2)–Ta(1)–N(1)	89.8(3)	Cl(3)–Ta(1)–N(1)	100.1(3)
Cl(3)–Ta(1)–N(2)	88.9(3)	N(2)–Ta(1)–N(4)	58.4(5)
Ta(1)–N(2)–C(3)	94.2(9)	Ta(1)–N(2)–C(21)	133.3(10)
C(3)–N(2)–C(21)	132.3(12)	Ta(1)–N(4)–C(3)	96.9(8)
Ta(1)–N(4)–C(41)	137.9(8)	C(3)–N(4)–C(41)	123.2(11)
N(2)–C(3)–N(4)	110.3(12)	N(6)–C(5)–N(7)	121.1(13)
C(5)–N(7)–C(71)	122.1(12)	C(5)–N(6)–C(61)	126.0(11)

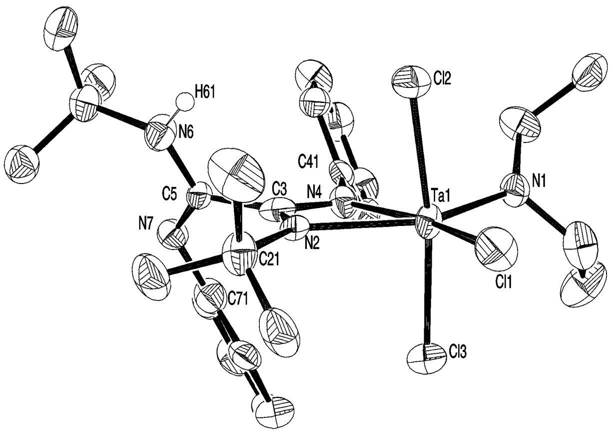


Fig. 2 Molecular structure of $[Ta(NEt_2)Cl_3\{(C_6H_5N)C(N^tBu)C(HN\text{-}^tBu)(NC_6H_5)\}]$ **6**. Details as in Fig. 1.

The crystal structure of compound **6** has been determined and the molecular structure is shown in Fig. 2. Selected bond lengths and angles are listed in Table 3. The amidinato ligand, occupying one edge of the octahedron, co-ordinates to the metal centre with one end free to form a pseudo-octahedral geometry. The NEt_2 group and one chloride are *trans* to the amidinato ligand with the other two chlorides occupying the axial positions of the octahedron. The Ta–N_{CNN} bond distances, 2.090(10) and 2.249(8) Å, are asymmetric, which leads to the observation of inequivalent C–N bonds, 1.367(17) and 1.220(20) Å. These asymmetric bond lengths may result from the differing *trans* influences of amide and chloride ligands. The Ta–Cl bond distances, 2.345(3), 2.367(4) and 2.385(3) Å, are in the range expected for Ta–Cl bond lengths. The small bite angle N(2)–Ta(1)–N(4), 58.4(5)°, compared with those found in mono-[37–39] or bis-[40–42] amidinato compounds, may be attributed to the steric congestion around the metal centre. The dihedral angle indicates two CNN planes are intersecting with an angle of 115.59°. Attempts to prepare a heterobimetallic compound by the reaction between compound **6** and $Ti(NMe_2)_4$ proved unsuccessful.

Treatment of one equivalent of compound **1** with one equivalent of $[Zr\{N(SiMe_3)_2\}_3Cl]$ in refluxing toluene yielded a pale yellow solution. Purification from a concentrated pentane solution afforded an off-white solid in good yield. Two peaks at δ 0.18 and 0.40 were observed in the ^{1}H NMR spectrum in the regions of the $SiMe_3$ group with the same intensity and two peaks corresponding to the methyl groups (δ 1.32 and 1.62) on the *tert*-butyl groups. This indicates two $N(SiMe_3)_2$ groups and two *tert*-butyl groups should have different environments in solution. The ^{1}H NMR (δ 4.72) and infrared (3450 cm^{-1}) data also indicate one non-co-ordinated N–H group on the amidinato ligand. The elemental analysis data are consistent with the mono-amidinate compound, $[Zr\{N(SiMe_3)_2\}_2Cl\{(C_6H_5N)\text{-}C(N^tBu)C(HN^tBu)(NC_6H_5)\}]$ **7**. Attempts to make the bimetallic complex by treating compound **7** with $Zr(NMe_2)_4$ in 1 : 1 ratio yielded a mixture of **4** and **7**. Compound **7** rearranged into **4** completely on addition of an excess of $Zr(NMe_2)_4$, indicating not only the amine elimination but also the substitution reaction proceeded in solution.

The crystal structure of compound **7** has been determined and the molecular structure is shown in Fig. 3. Similar to the structure of compound **6**, the amidinato ligand is bound to the metal centre with one end to form square pyramidal geometry

Table 4 Selected bond lengths (Å) and angles (°) for **7**

Zr(1)–Cl(1)	2.4366(5)	N(2)–C(1)	1.318(3)
Zr(1)–N(1)	2.2351(16)	N(3)–C(2)	1.271(3)
Zr(1)–N(2)	2.2907(17)	N(3)–C(9)	1.410(3)
Zr(1)–N(5)	2.0459(18)	N(4)–C(2)	1.357(3)
Zr(1)–N(6)	2.0760(17)	N(4)–C(19)	1.481(3)
N(1)–C(1)	1.353(3)	C(1)–C(2)	1.538(3)
N(1)–Zr(1)–N(2)	58.60(6)	N(1)–C(1)–N(2)	112.09(17)
Cl(1)–Zr(1)–N(5)	99.79(5)	N(3)–C(2)–N(4)	122.09(19)
N(1)–Zr(1)–N(5)	112.19(7)	C(2)–N(3)–C(9)	125.72(19)
N(2)–Zr(1)–N(5)	112.69(7)	C(2)–N(4)–C(19)	126.55(18)
N(5)–Zr(1)–N(6)	114.39(7)		

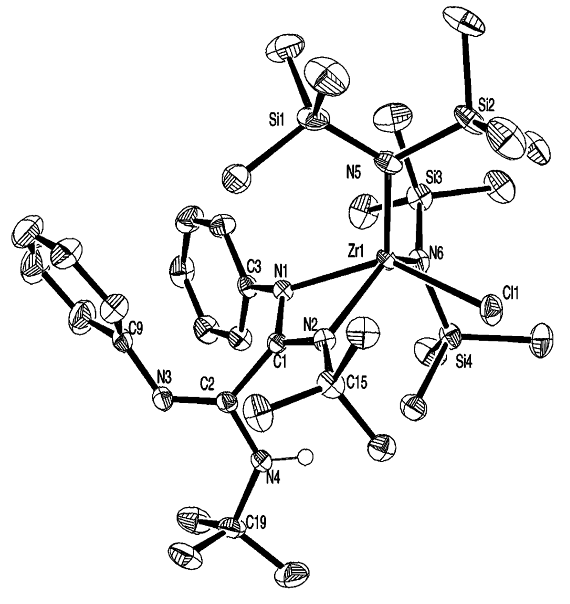


Fig. 3 Molecular structure of $[Zr\{N(SiMe_3)_2\}_2Cl\{(C_6H_5N)C(N^tBu)C(HN^tBu)(NC_6H_5)\}]$ **7**. Details as in Fig. 1.

with the amidinato ligand occupying one edge, and one $N(SiMe_3)_2$ and one chloride the other corners of the square base. The other $N(SiMe_3)_2$ group occupies the apex of the pyramid. The structure exhibits two $N(SiMe_3)_2$ groups in different environments, consistent with two $SiMe_3$ peaks in the ^1H NMR spectrum. Selected bond lengths and angles are listed in Table 4. The Zr–Cl bond distance, 2.4366(5) Å, is slightly longer than that (2.394(2) Å) in the starting material, $Zr\{N(SiMe_3)_2\}_3Cl$.[43] The $Zr–NSiMe_3$ bond distances, 2.0459(18) and 2.0760(17) Å, are close to those (2.070(3) Å) in $Zr\{N(SiMe_3)_2\}_3Cl$. Similar to compound **6**, the $Zr–N_{CNN}$ bond distances, 2.2351(16) and 2.2907(17) Å, are asymmetric, which leads to the observation of inequivalent C–N bonds, 1.353(3) and 1.318(3) Å. The small bite angle N(2)–Zr(1)–N(1), 58.60(6)°, compared with those found in mixed cyclopentadienyl amidinato[44,45] or bis-amidinato[46,47] compounds, may be attributed to the steric repulsion around the metal centre. The steric hindrance also reflects on the puckered angle between the CNN and ZrNN planes, 164.03°. Two CNN planes are intersecting with a 117.02° dihedral angle, which is close to that found in compound **6**.

Polymerisation studies

One aim of this research was to find interesting catalysts for olefin polymerisation. Ethylene polymerisation studies were performed in toluene at room temperature with a monomer pressure of 2 bar. Methylaluminoxane $(MeAlO)_n$ (MAO) was initially tested using a known pre-catalyst, $[Zr(\eta-C_5H_5)_2Cl_2]$, and gave an activity of 1.41×10^6 g PE mol M^{-1} h^{-1}, which is close to the reported activity of 3.57×10^6 g PE mol M^{-1} h^{-1}.[48] The new amidinato complexes used as pre-catalysts were **4**, **5**, **6** and **7**. Compound **6** did not exhibit any reactivity in ethylene polymerisation.

It has been reported that an excess of MAO can activate some metal amide complexes for polymerisation.[49,50] Others have reported that the catalytic activity of metal amide complexes can be enhanced by pre-alkylation with AlR_3 (R = Me or ^iBu).[51–54] Therefore, the catalytic activity of **4**, **5** and **7** was tested using similar conditions to those reported by Kim and coworkers.[52–54] The ethylene polymerisation results are given in Table 5. Compound **4** in the presence of MAO as activator shows low activity as an ethene polymerisation catalyst. The activity is enhanced about twelve times after pre-activation with $AlMe_3$. No further studies were made using compound **4** due to the low reactivity. Compound **5** shows moderate catalytic activity as an ethene polymerisation catalyst using the same conditions as for **4**. The activity increases after pre-alkylation treatment with $AlMe_3$ or $Al(^iBu)_3$. A similar enhancement in activity is also found for compound **7**. The lower activity observed for the non-alkylated system may reflect insufficient alkylation by MAO.[52] The alkylated compound **5**, without the addition of MAO, also shows a low activity in the polymerisation reaction (entry 7). It may be inferred that the pre-alkylated system creates an electron-deficient centre. We assumed the pre-alkylation of compound **5** gave an alkyl product and therefore should be expected as a catalytic system of the addition to the alkylated compound with the Lewis acid $B(C_6F_5)_3$. This has been shown primarily to act as an alkyl abstraction when combined with metal alkyl, *e.g.* $[Zr(\eta-C_5H_5)_2(CH_3)_2]$.[55] Indeed, moderate activity was found when $B(C_6F_5)_3$ was used as the co-catalyst and the activity becomes even higher when $[Ph_3C][B(C_6F_5)_4]$ is used as co-catalyst with the pre-alkylated system.

The polyethylenes produced by the mixed amidinato–amide complexes show melting points (T_m) in the range 130–140 °C, indicating that they are highly linear and highly crystalline.[56] The molecular weights are too high to be measured by GPC analysis.

In conclusion, the oxalic amidinato ligand prefers to form early transition metal amidinato complexes. Some of the new amidinato complexes exhibit moderate to high activity towards ethylene polymerisation.

Experimental

All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk-line or dry-box techniques. Solvents were pre-dried over molecular sieves, refluxed over the appropriate drying agent and distilled prior to use. NMR solvents were dried over calcium hydride or molten potassium, distilled under vacuum and stored under dinitrogen in Young's ampoules.

^1H and $^{13}C-\{^1H\}$ NMR spectra were recorded either on Varian Unity 500 or Mercury 300 spectrometers and referenced internally to the residual solvent peak relative to tetramethylsilane, infrared spectra on a Perkin-Elmer 1600 Series FT-IR instrument in the range 4000–400 cm^{-1} as caesium iodide pellets. Elemental analyses were performed by the Microanalytical Department of the Inorganic Chemistry Laboratory in Oxford. The differential scanning calorimetry (DSC) data of the polymers were obtained from the laboratories of the Chisso Petrochemical Corporation (Japan). The melting point (T_m) of the polymer was determined with a Seiko SSC-5500 system at a heating rate of 20 °C min^{-1}. In order to obtain reproducible values, the polymer was first melted and cooled before the actual measurement.

$[NiBr_2(DME)]$ (Aldrich), $Ti(NMe_2)_4$ (Strem), the oxanilide $C_6H_5N{=}C(Cl){-}C(Cl){=}NC_6H_5$ (Acros), PCl_5 (Lancaster) and methylaluminoxane (10 wt% in toluene, Witco) were used as supplied. $^tBuNH_2$ was dried over CaH_2 and distilled before use. Bis-phenylimidoyl chloride,[24] $Zr(NMe_2)_4$,[36] [Zr{N(Si-

Table 5 Activity toward ethylene polymerisation[a]

Run	Catalyst	Catalyst/ mol × 10^6	AlR_3 (mol × 10^4)	Co-catalyst (equiv.)	Time/ min	Yield/g	Activity[b]/kg mol M^{-1} h^{-1} bar^{-1}	T_m/°C
1	**4**	6.25	None	MAO (1220)	120	0.03	0.7	—
2	**4**	6.25	$AlMe_3$ (1.94)	MAO (1220)	120	0.49	9.7	134.5
3	**5**	6.25	None	MAO (1220)	120	0.85	17.0	137.1
4	**5**	6.25	$AlMe_3$ (1.94)	MAO (1220)	60	2.80	112.0	136.7
5	**5**	12.5	$AlMe_3$ (3.88)	$B(C_6F_5)_3$ (2)	65	2.18	40.2	135.3
6	**5**	12.5	$AlMe_3$ (3.88)	$[Ph_3C][B(C_6F_5)_4]$ (2)	60	1.74	34.8	137.2
7	**5**	14.1	$AlMe_3$ (4.2)	None	60	0.17	3.1	139.0
8	**5**	6.25	$Al(^iBu)_3$ (1.88)	MAO (1220)	60	3.37	134.8	136.3
9	**5**	12.5	$Al(^iBu)_3$ (3.75)	$B(C_6F_5)_3$ (2)	40	1.77	53.2	135.1
10	**5**	12.5	$Al(^iBu)_3$ (3.75)	$[Ph_3C][B(C_6F_5)_4]$ (2)	15	1.30	104.0	137.1
11	**7**	6.25	None	MAO (2450)	120	0.10	4.1	139.2
12	**7**	6.25	$AlMe_3$ (1.94)	MAO (2450)	120	0.34	13.7	130.1
13	**7**	25	$AlMe_3$ (1.94)	$B(C_6F_5)_3$ (2)	60	0.03	0.5	—

[a] Conditions: 2 bar absolute monomer pressure, room temperature, toluene *ca.* 220 cm^3. [b] mol M = Total amount of metal used.

$Me_3)_2\}_3Cl]$,[43] $[Ta(NEt_2)_2Cl_3(py)]$,[57] $B(C_6F_5)_3$,[58] and $[Ph_3C][B(C_6F_5)_4]$[59] were prepared by the literature methods.

Preparations

$C_6H_5N{=}C(NH^tBu){-}C(NH^tBu){=}NC_6H_5$ 1. A yellow solution of $C_6H_5N{=}C(Cl){-}C(Cl){=}NC_6H_5$ (2.7 g, 9.6 mmol) in toluene (50 ml) was treated with 6.1 ml $^tBuNH_2$ (4.2 g, 57.8 mmol) at room temperature while stirring. After 48 h the resulting precipitate was removed by filtration. The filtrate was dried *in vacuo* to give a white solid. Yield 3.1 g, 92%.

$C_6H_5N{=}C\{N(^tBu)(SiMe_3)\}{-}C\{N(^tBu)(SiMe_3)\}{=}NC_6H_5$ 2. A pale yellow solution of $C_6H_5N{=}C(NH^tBu){-}C(NH^tBu){=}NC_6H_5$ (2.0 g, 5.7 mmol) in diethyl ether (80 ml) was treated with 8 ml n-BuLi (1.6 M, 12.8 mmol) at 0 °C in a dropwise manner. The reaction mixture was stirred in an ice-bath for 1 h, then allowed to warm to room temperature and react for 2 h. The volatiles were removed under reduced pressure to afford a yellow solid. To this 50 ml THF were added, followed by 2 ml Me_3SiCl (1.7 g, 15.8 mmol). Then the orange solution was heated to 75 °C for 8 h gradually becoming yellow. After cooling, the volatiles were removed under reduced pressure and the residue was extracted into pentane (30 ml). Recrystallisation from concentrated pentane afforded a white crystalline solid. Yield 2.3 g, 80%.

$[(C_6H_5N)C(NH^tBu)C(NH^tBu)(NHC_6H_5)][Br]$ 3. A mixture of $C_6H_5N{=}C(NH^tBu){-}C(NH^tBu){=}NC_6H_5$ (0.35 g, 1 mmol) and $[NiBr_2(DME)]$ (0.31 g, 1 mmol) was treated with CH_2Cl_2 (30 ml) at room temperature. The mixture was stirred at room temperature for 3 days. The volatiles were removed under reduced pressure to afford a pale green solid. This was extracted with CH_2Cl_2 (5 ml) and diffused into toluene to afford a yellowish green solid. Yield 0.10 g, 23%.

$[Zr(NMe_2)_3(C_6H_5N)C(N^tBu){-}]_2$ 4. A pale yellow solution of $Zr(NMe_2)_4$ (2.1 g, 8 mmol) in toluene (20 ml) was treated with a pale yellow solution of $C_6H_5N{=}C(NH^tBu){-}C(NH^tBu){=}NC_6H_5$ (1.4 g, 4 mmol) in toluene (20 ml) at room temperature. The reaction mixture was then heated to 85 °C for 3 h. The resulting pale yellow solution was filtered and the volatiles were removed *in vacuo* to afford a pale yellow solid, which was washed with pentane (5 ml) to afford an off-white solid. Yield 2.5 g, 82%.

$[Ti(NMe_2)_3(C_6H_5N)C(N^tBu){-}]_2$ 5. A yellow solution of $Ti(NMe_2)_4$ (1.5 g, 6.8 mmol) in toluene (15 ml) was treated with a pale yellow solution of $C_6H_5N{=}C(NH^tBu){-}C(NH^tBu){=}NC_6H_5$ (1.2 g, 3.4 mmol) in toluene (20 ml) at room temperature. The reaction mixture was then heated to 85 °C for 3.5 h. The solution was filtered and the filtrate concentrated until a precipitate appeared. The concentrated solution was kept at −25 °C overnight to yield an orange solid. Yield 1.8 g, 75%.

$[Ta(NEt_2)Cl_3\{(C_6H_5N)C(N^tBu)C(HN^tBu)(NC_6H_5)\}]$ 6. A red solution of $[Ta(NEt_2)_2Cl_3(py)]$ (2.5 g, 4.9 mmol) in toluene (10 ml) was treated with a pale yellow solution of $C_6H_5N{=}C(NH^tBu){-}C(NH^tBu){=}NC_6H_5$ (0.86 g, 2.4 mmol) in toluene (30 ml) at room temperature. The reaction mixture was then heated to 110 °C for 7.5 h. The red solution was filtered and the volatiles were removed from the filtrate *in vacuo* to afford a red solid, which was washed with pentane (5 ml) to give a red solid. Yield 0.49 g, 28%.

$[Zr\{N(SiMe_3)_2\}_2Cl\{(C_6H_5N)C(N^tBu)C(HN^tBu)(NC_6H_5)\}]$ 7. A white suspension of $[Zr\{N(SiMe_3)_2\}_3Cl]$ (0.96 g, 1.58 mmol) in toluene (15 ml) was treated with a pale yellow solution of $C_6H_5N{=}C(NH^tBu){-}C(NH^tBu){=}NC_6H_5$ (0.50 g, 1.43 mmol) in toluene (10 ml) at room temperature. The reaction mixture was then heated to 105 °C for 4 h. The pale yellow solution was filtered and the volatiles were removed from the filtrate *in vacuo* to afford an off-white solid that was extracted with pentane (20 ml) to give an off-white solid. Yield 1.0 g, 88%.

Polymerisation studies

Ethylene was purified by passage through 4 Å molecular sieves. Polymerisation reactions were carried out in a Fischer–Porter reactor equipped with a magnetic stirrer using conditions similar to those employed by Kim and co-workers.[53,54,60] Toluene (*ca.* 200 ml) was added to the Fischer–Porter bottle, which was connected to the ethylene supply *via* a gas supply system and filled with ethylene. The vessel was depressurised before the co-catalyst or the precursor complex solution was syringed.

For the catalyst–MAO system. Methylaluminoxane (10 ml) was then syringed, the ethylene pressure increased to 2 bar (absolute pressure) and the mixture stirred at room temperature until saturated with ethylene. Precursor complex (6.25×10^{-6} mol) in toluene (10 ml) was then added quickly to the reactor by syringe.

For the pre-alkylated catalyst–MAO system. Methylaluminoxane (10 ml) was then syringed, the ethylene pressure increased to 2 bar (absolute pressure) and the mixture stirred at room temperature until saturated with ethylene. Meanwhile, precursor complex (6.25×10^{-6} mol) in toluene (10 ml) was added to the prescribed amount of AlR_3 and stirred for 15 min pre-alkylation. The pre-alkylated mixture was then added quickly to the reactor by syringe.

For the pre-alkylated catalyst–$B(C_6F_5)_3$ or –$[Ph_3C][B(C_6F_5)_4]$ system. The precursor complex (6.25×10^{-6} mol) in toluene (10

Table 6 Summary of crystal data for compounds **3**, **6**, and **7**

	3	**6**	**7**
Formula	$C_{22}H_{32}BrN_4$	$C_{26}H_{39}Cl_3N_5Ta$	$C_{34}H_{65}ClN_6Si_4Zr$
M	432.43	708.94	796.95
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1$	$P2_1/c$
a/Å	14.0530(6)	11.2870(7)	11.623(1)
b/Å	10.0580(6)	10.705(1)	12.225(1)
c/Å	17.5050(10)	12.5560(11)	30.868(1)
β/°	113.913(3)	96.282(6)	93.925(2)
V/Å^3	2261.9(2)	1508.0(5)	4375.8
Z	4	2	4
T/K	150	150	150
μ(Mo-Kα)/ mm^{-1}	1.831	3.93	0.45
Total no. of data	4450	24613	15217
No. of unique data	4450	3245	7155
No. of observed data	3373	2603	6779
R	0.0429	0.0463	0.0529
R_w	0.0932	0.0382	0.0378

ml) was added to the prescribed amount of AlR_3 and stirred for 15 min pre-alkylation. The pre-alkylated mixture was then added quickly to the reactor by syringe followed by the prescribed equivalent of $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ in toluene (10 ml).

Each reaction mixture for those three systems was stirred vigorously at room temperature under 2 bar pressure of ethylene for the prescribed time. The reaction was quenched by venting the ethylene and adding a small amount of ethanol. The contents of the reactor were then transferred to a conical flask and 250 ml of conc. HCl in ethanol were added (20% by volume) and the mixture was stirred overnight. The polymer was then separated by filtration, washed with water and ethanol then dried *in vacuo* at 60 °C.

Crystal structure data

Crystals were grown from diffusion of concentrated CH_2Cl_2 solution into toluene (**3**), concentrated ether solution (**6**) or concentrated pentane solution (**7**), and isolated by filtration. A specimen was chosen under an inert atmosphere, covered with paratone-N oil, and mounted on the end of a glass fibre. Data were collected on an Enraf-Nonius DIP2000 image plate diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) as summarised in Table 6. The images were processed with the DENZO and SCALEPACK programs.[61] Corrections for Lorentz and polarisation effects were performed.

Solution, refinement, and graphical calculations were performed using the CRYSTALS[62] software package. The structures were solved by direct methods using the SIR 92 program[63] and refined by full-matrix least squares minimisation on *F*. All non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon-bound hydrogen atoms were placed in geometrically calculated positions and allowed to ride on their corresponding carbon atoms with fixed thermal parameters.

CCDC reference numbers 155032–155034.

See http://www.rsc.org/suppdata/dt/b0/b010017j/ for crystallographic data in CIF or other electronic format.

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