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Niobium- and tantalum-benzamidinato complexes with trimethylphosphine, imido, or η-cyclopentadienyl derivatives

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The mononuclear benzamidinato compounds, $[M\{(2,4,6\text{-tri-}^i\text{Pr})C_6H_2C(NSiMe_3)_2\}Cl_4]$ (M = Nb (**1**) or Ta (**2***)), $[Nb\{(2,4,6\text{-tri-}^i\text{Pr})C_6H_2C(NSiMe_3)_2\}Cl_4(PMe_3)]$ (**4***), $[M\{(2,4,6\text{-tri-}^i\text{Pr})C_6H_2C(NSiMe_3)_2\}(N^t\text{Bu})(H_2N^t\text{Bu})Cl_2]$ (M = Nb (**5**), M = Ta (**6**)), $[Nb\{(2,4,6\text{-tri-}^i\text{Pr})C_6H_2C(NSiMe_3)_2\}(N^t\text{Bu})(L)Cl_2]$ (L = THF (**7**), L = pyridine (**8**)), and $[M\{(2,4,6\text{-tri-}^i\text{Pr})C_6H_2C(NSiMe_3)_2\}(\eta\text{-}C_5H_5)Cl_3]$ (M = Nb (**9**), M = Ta (**10***), and a nitrile tantalum complex, $[Ta\{(2,4,6\text{-tri-}^i\text{Pr})C_6H_2CN\}Cl_5]$ (**3***), obtained in a side-reaction have been prepared:* indicates the crystal structures have been determined. Variable temperature NMR studies show there is hindered rotation of the aryl group around C_{ipso}–C bonds for compounds **5** and **6**; $\Delta G^‡ = 55.2$ kJ mol^{-1} at 268 K for **5**. Hindered rotation about the N–Si bonds for compounds **9** and **10** occurs with the $\Delta G^‡ = 51.0$ kJ mol^{-1} at 273 K and 40.6 kJ mol^{-1} at 213 K for **10**. The compounds **1**, **5** and **9** are very poor pre-catalysts for ethene polymerisation.

Introduction

Metallocenes containing one or more cyclopentadienyl ligands are exceptionally active and selective pre-catalysts for homogeneous catalysis for the iso-specific polymerisation of α-olefins.[1] This has stimulated research into ligands with properties similar to the cyclopentadienyl group.[2–7] The benzamidinato ligand $R'C(NR)_2$ has been a focus of much attention because it can readily be used in place of cyclopentadienyl ligands whilst the steric demands are considered to lie between those of the cyclopentadienyl and pentamethylcyclopentadienyl ligands.[8,9] Benzamidinato ligands are hard four-electron donors[8] which are expected to generate an electron-deficient metal centre, allowing the isolation of Lewis acidic compounds or providing sufficient electronic unsaturation for further reactivity to occur.[10,11] Some benzamidinato compounds have already been shown to provide active catalysts for olefin polymerisation.[11–17]

Benzamidinato ligands of the general formula $R'C(NR)_2$ (where R = alkyl, silyl; R′ = Ph, substituted Ph) have been extensively studied.[18] They can be synthesised readily and variation of the substituents R and R′ is facile providing the opportunity of tailoring these ligands to achieve specific properties, such as bite or cone angles. However, to date only *para*-substituted, 2,4,6-trimethyl-substituted, and 2,4,6-tris(trifluoromethyl)-substituted benzamidinato ligands[19] have been used as ancillary ligands, whilst studies of bulkier complexes have not been made. Many examples of bis-benzamidinato transition metal complexes are known, however, there are few mono-benzamidinato complexes, especially of the Group 5 metals.

In this paper we report the preparation and structural properties of a series of niobium and tantalum complexes containing a bulky benzamidinato ligand, and a brief study of their ability to act as pre-catalysts towards olefin polymerisation.

Results and discussion

Treatment of the carbodiimide $Me_3SiN{=}C{=}NSiMe_3$ with $Li[(2,4,6\text{-tri-}^i\text{Pr})C_6H_2]$ gives a white powder which the data show to be the lithium salt of the highly sterically demanding 2,4,6-triisopropyl-substituted benzamidinato anion, namely $[Li\{(2,4,6\text{-tri-}^i\text{Pr})C_6H_2C(NSiMe_3)_2\}]$.

Treatment of the pentachlorides MCl_5 (M = Nb, Ta) with one equivalent of $[Li\{(2,4,6\text{-tri-}^i\text{Pr})C_6H_2C(NSiMe_3)_2\}]$ in toluene affords the compounds, $[M\{(2,4,6\text{-tri-}^i\text{Pr})C_6H_2C(NSiMe_3)_2\}Cl_4]$; where M = Nb (**1**) and Ta (**2**), in good yields. Reaction of MCl_5 with two equivalents of the lithium salt does not yield the expected bis-benzamidinato compounds. Instead a complex mixture of products is formed from which compounds **1** and **2** were isolated, in low yield. Thus, the bulky isopropyl substituents on the aryl groups of the benzamidinato ligands prevent the formation of the bis-benzamidinato metal compounds which are commonly formed with unsubstituted aryl benzamidinato ligands. Further, the mono-benzamidinato compounds **1** and **2** show no tendency towards ligand redistribution.

The analytical and spectroscopic data characterising compounds **1** and **2**, and all the other new compounds described below, are given in Table 1. A summary of the syntheses and proposed structures is shown in Scheme 1.

The crystal structure of $[Ta\{(2,4,6\text{-tri-}^i\text{Pr})C_6H_2C(NSiMe_3)_2\}Cl_4]$ (**2**) has been determined and the molecular structure is shown in Fig. 1 and selected interatomic distances and angles are listed in Table 2. The asymmetric unit of **2** contains two independent molecules. Compound **2** displays a pseudo-octahedral geometry with the benzamidinato ligand occupying one edge of the octahedron. The two Ta–N bond lengths, 2.093(5) and 2.109(4); 2.108(4) and 2.130(4) Å, are shorter than those normally found in the literature for which typical values are in the range 2.15(1) to 2.29(1) Å for compounds of the type $[Ta\{p\text{-}CH_3\text{-}C_6H_4C(NSiMe_3)_2\}_2X_3]$[20] (X = Me) and 2.133(2) and 2.199(2) Å for compound **10**. These shortened bond lengths may be attributed to the lack of severe steric repulsion, which is usually observed in bis-benzamidinato and cyclopentadienyl benzamidinato compounds.[20,21] Likewise the Ta–Cl bonds distances, 2.3505(14) and 2.3580(15), 2.3739(15) and 2.3456(15); 2.3125(14) and 2.3200(16), 2.3287(16) and 2.3287(16) Å, are all towards the shorter end of the range expected for Ta–Cl bond lengths[20–23] (*vide infra*).

During the synthesis of compound **2**, pale-brown crystals of another compound (**3**) were obtained, in 5% yield, for which only resonances corresponding to the tris-isopropyl phenyl

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Table 1 Analytical and spectroscopic data

Compound and analysis[a]	Spectroscopic data[b]
1 Red C, 42.3 (42.3) H, 6.6 (6.6) N, 4.5 (4.5) Cl, 22.9 (22.7)	$^{1}\mathrm{H}$: 0.27 (s, 18H, $\mathrm{Si(C}H_3)_3$), 1.07 (d, 6H, $J = 7.0$, 4-$\mathrm{CH(C}H_3)_2$), 1.15 (d, 12H, $J = 7.0$, 2,6-$\mathrm{CH(C}H_3)_2$), 2.63 (m, 1H, 4-$\mathrm{C}H\mathrm{(CH_3)_2}$), 3.01 (m, 2H, 2,6-$\mathrm{C}H\mathrm{(CH_3)_2}$), 6.89 (s, 2H, 3,5-$\mathrm{C_6}H_2\mathrm{\{CH(CH_3)_2\}_3}$) $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$: 0.9 (s, $\mathrm{Si(}C\mathrm{H_3)_3}$), 24.1 (s, 4-$\mathrm{CH(}C\mathrm{H_3)_2}$), 24.5 (s, 2,6-$\mathrm{CH(}C\mathrm{H_3)_2}$), 31.4 (s, 2,6-$C\mathrm{H(CH_3)_2}$), 34.7 (s, 4-$C\mathrm{H(CH_3)_2}$), 121.6 (s, 3,5-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 133.2 (s, C_{ipso}-Ph), 145.2 (s, 2,6-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 153.4 (s, 4-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 188.4 (s, $C\mathrm{\{NSi(CH_3)_3\}_2}$) IR: 2965s, 2903m, 1343s, 1256s, 847vs, 665s
2 Yellow C, 36.9 (37.1) H, 5.6 (5.8) N, 3.9 (3.9) Cl, 20.0 (19.9)	$^{1}\mathrm{H}$: 0.23 (s, 18H, $\mathrm{Si(C}H_3)_3$), 1.07 (d, 6H, $J = 6.5$, 4-$\mathrm{CH(C}H_3)_2$), 1.17 (d, 12H, $J = 6.5$, 2,6-$\mathrm{CH(C}H_3)_2$), 2.63 (m, 1H, 4-$\mathrm{C}H\mathrm{(CH_3)_2}$), 3.05 (m, 2H, 2,6-$\mathrm{C}H\mathrm{(CH_3)_2}$), 6.89 (s, 2H, 3,5-$\mathrm{C_6}H_2\mathrm{\{CH(CH_3)_2\}_3}$) $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$: 0.9 (s, $\mathrm{Si(}C\mathrm{H_3)_3}$), 24.1 (s, 4-$\mathrm{CH(}C\mathrm{H_3)_2}$), 24.5 (s, 2,6-$\mathrm{CH(}C\mathrm{H_3)_2}$), 31.1 (s, 2,6-$C\mathrm{H(CH_3)_2}$), 34.7 (s, 4-$C\mathrm{H(CH_3)_2}$), 121.6 (s, 3,5-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 133.7 (s, C_{ipso}-Ph), 145.3 (s, 2,6-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 153.2 (s, 4-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 188.0 (s, $C\mathrm{\{NSi(CH_3)_3\}_2}$) IR: 2965s, 2934m, 2907m, 2874m, 1607m, 1487m, 1462m, 1422m, 1350s, 1256m, 995s, 951s, 835s, 766m
3 Pale-brown C, 33.0 (32.7) H, 4.3 (4.0) N, 2.4 (2.4)	$^{1}\mathrm{H}$: 0.92 (d, 6H, $J = 7$, 4-$\mathrm{CH(C}H_3)_2$), 1.04 (d, 12H, $J = 6.8$, 2,6-$\mathrm{CH(C}H_3)_2$), 2.43 (m, 1H, 4-$\mathrm{C}H\mathrm{(CH_3)_2}$), 3.12 (m, 2H, 2,6-$\mathrm{C}H\mathrm{(CH_3)_2}$), 6.75 (s, 2H, 3,5-$\mathrm{C_6}H_2\mathrm{\{CH(CH_3)_2\}_3}$) $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$: 23.1 (s, 2,6-$\mathrm{CH(}C\mathrm{H_3)_2}$), 23.2 (s, 4-$\mathrm{CH(}C\mathrm{H_3)_2}$), 33.4 (s, 2,6-$C\mathrm{H(CH_3)_2}$), 35.2 (s, 4-$C\mathrm{H(CH_3)_2}$), 103.0 (s, C_{ipso}-Ph), 122.3 (s, 3,5-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 125.0 (s, N$C$-), 156.9 (s, 2,6-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 159.2 (s, 4-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$) IR: 2967s, 2253s, 1601s, 1464m, 883s, 719m
4 Red C, 42.8 (43.0) H, 6.9 (7.2) N, 4.0 (4.0) Cl, 19.8 (20.2)	$^{1}\mathrm{H}$: 0.43 (br, 18H, $\mathrm{Si(C}H_3)_3$), 1.13 (d, 6H, $J = 7$, 4-$\mathrm{CH(C}H_3)_2$), 1.33 (d, 12H, $J = 7$, 2,6-$\mathrm{CH(C}H_3)_2$), 1.39 (d, 9H, $^{2}J_{\mathrm{PH}} = 12$, $\mathrm{P(C}H_3)_3$), 2.68 (m, 1H, 4-$\mathrm{C}H\mathrm{(CH_3)_2}$), 3.57 (m, 2H, 2,6-$\mathrm{C}H\mathrm{(CH_3)_2}$), 6.96 (s, 2H, 3,5-$\mathrm{C_6}H_2\mathrm{\{CH(CH_3)_2\}_3}$) $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$: 2.9 (s, $\mathrm{Si(}C\mathrm{H_3)_3}$), 16.2 (d, $^{1}J_{\mathrm{PC}} = 30$, $\mathrm{P(}C\mathrm{H_3)_3}$), 24.1 (s, 4-$\mathrm{CH(}C\mathrm{H_3)_2}$), 24.8 (s, 2,6-$\mathrm{CH(}C\mathrm{H_3)_2}$), 30.3 (s, 2,6-$C\mathrm{H(CH_3)_2}$), 34.7 (s, 4-$C\mathrm{H(CH_3)_2}$), 121.4 (s, 3,5-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 135.8 (s, C_{ipso}-Ph), 145.7 (s, 2,6-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 152.1 (s, 4-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 188.8 (s, $C\mathrm{\{NSi(CH_3)_3\}_2}$) $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$: 47.1 ($P\mathrm{Me_3}$) IR: 2963s, 2901m, 1667m, 1607m, 1462s, 1381s, 1302m, 1252s, 984s, 955s, 839s, 780s, 683s
5 Yellow C, 51.7 (51.6) H, 8.5 (8.8) N, 7.8 (8.0) Cl, 10.1 (10.2)	$^{1}\mathrm{H}$: 0.14 (s, 18H, $\mathrm{Si(C}H_3)_3$), 1.16 (d, 6H, $J = 7$, 4-$\mathrm{CH(C}H_3)_2$), 1.26 (d, 12H, $J = 7$, 2,6-$\mathrm{CH(C}H_3)_2$), 1.37 (s, 9H, $\mathrm{H_2NC(C}H_3)_3$), 1.50 (s, 9H, $\mathrm{NC(C}H_3)_3$), 2.50 (s, 2H, $H_2\mathrm{NC(CH_3)_3}$), 2.72 (m, 1H, 4-$\mathrm{C}H\mathrm{(CH_3)_2}$), 3.12 (m, 2H, 2,6-$\mathrm{C}H\mathrm{(CH_3)_2}$), 6.94 (s, 2H, 3,5-$\mathrm{C_6}H_2\mathrm{\{CH(CH_3)_2\}_3}$) $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$:[c] 2.2 (s, $\mathrm{Si(}C\mathrm{H_3)_3}$), 24.2 (s, 4-$\mathrm{CH(}C\mathrm{H_3)_2}$), 24.9 (s, 2,6-$\mathrm{CH(}C\mathrm{H_3)_2}$), 30.4 (s, $\mathrm{NC(}C\mathrm{H_3)_3}$), 31.1 (s, 2,6-$C\mathrm{H(CH_3)_2}$), 32.1 (s, $\mathrm{H_2NC(}C\mathrm{H_3)_3}$), 34.7 (s, 4-$C\mathrm{H(CH_3)_2}$), 51.7 (s, $\mathrm{H_2N}C(C\mathrm{H_3)_3}$), 69.2 (s, $\mathrm{N}C(C\mathrm{H_3)_3}$), 121.4 (s, 3,5-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 136.2 (s, C_{ipso}-Ph), 143.9 (s, $C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 151.1 (s, 4-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 178.2 (s, 2,6-$C\mathrm{\{NSi(CH_3)_3\}}$) IR: 2971s, 2905m, 1462m, 1422s, 1246s, 1215m, 1086m, 988s, 905m, 806vs, 762s, 714s
6 Pale-green C, 45.9 (45.9) H, 7.9 (7.8) N, 7.0 (7.1) Cl, 9.0 (9.0)	$^{1}\mathrm{H}$: 0.10 (s, 18H, $\mathrm{Si(C}H_3)_3$), 1.15 (d, 6H, $J = 6.8$, 4-$\mathrm{CH(C}H_3)_2$), 1.26 (d, 12H, $J = 6.8$, 2,6-$\mathrm{CH(C}H_3)_2$), 1.32 (s, 9H, $\mathrm{H_2NC(C}H_3)_3$), 1.51 (s, 9H, $\mathrm{NC(C}H_3)_3$), 2.55 (s, 2H, $H_2\mathrm{NC(CH_3)_3}$), 2.71 (m, 1H, 4-$\mathrm{C}H\mathrm{(CH_3)_2}$), 3.07 (br, 2H, 2,6-$\mathrm{C}H\mathrm{(CH_3)_2}$), 6.93 (s, 2H, 3,5-$\mathrm{C_6}H_2\mathrm{\{CH(CH_3)_2\}_3}$) $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$: 2.1 (s, $\mathrm{Si(}C\mathrm{H_3)_3}$), 24.1 (s, 4-$\mathrm{CH(}C\mathrm{H_3)_2}$), 24.9 (s, 2,6-$\mathrm{CH(}C\mathrm{H_3)_2}$), 31.0 (s, $\mathrm{NC(}C\mathrm{H_3)_3}$), 32.1 (s, 2,6-$C\mathrm{H(CH_3)_2}$), 32.6 (s, $\mathrm{H_2NC(}C\mathrm{H_3)_3}$), 34.6 (s, 4-$C\mathrm{H(CH_3)_2}$), 52.0 (s, $\mathrm{H_2N}C\mathrm{(CH_3)_3}$), 65.5 (s, $\mathrm{N}C\mathrm{(CH_3)_3}$), 121.5 (s, 3,5-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 136.0 (s, C_{ipso}-Ph), 144.0 (br, 2,6-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 151.2 (s, 4-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 176.4 (s, $C\mathrm{\{NSi(CH_3)_3\}_2}$) IR: 2959s, 2930m, 2899m, 1462m, 1404s, 1275m, 1250m, 1094m, 995m, 847s, 766m, 718m
7 Yellow C, 51.3 (51.7) H, 8.6 (8.4) N, 6.0 (6.0) Cl, 9.4 (10.2)	$^{1}\mathrm{H}$: 0.14 (s, 18H, $\mathrm{Si(C}H_3)_3$), 1.16 (d, 6H, $J = 6.9$, 4-$\mathrm{CH(C}H_3)_2$), 1.26 (d, 12H, $J = 6.9$, 2,6-$\mathrm{CH(C}H_3)_2$), 1.45 (m, 4H, THF), 1.51 (s, 9H, $\mathrm{NC(C}H_3)_3$), 2.73 (m, 1H, 4-$\mathrm{C}H\mathrm{(CH_3)_2}$), 3.18 (m, 2H, 2,6-$\mathrm{C}H\mathrm{(CH_3)_2}$), 4.08 (m, 4H, THF), 6.96 (s, 2H, 3,5-$\mathrm{C_6}H_2\mathrm{\{CH(CH_3)_2\}_3}$) $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$:[d] 2.3 (s, $\mathrm{Si(}C\mathrm{H_3)_3}$), 24.1 (s, 4-$\mathrm{CH(}C\mathrm{H_3)_2}$), 25.0 (s, 2,6-$\mathrm{CH(}C\mathrm{H_3)_2}$), 25.2 (s, $C_4\mathrm{H_8O}$), 30.4 (s, $\mathrm{NC(}C\mathrm{H_3)_3}$), 30.8 (s, 2,6-$C\mathrm{H(CH_3)_2}$), 34.6 (s, 4-$C\mathrm{H(CH_3)_2}$), 70.5 (s, $C_4\mathrm{H_8O}$), 121.5 (s, 3,5-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 136.2 (s, C_{ipso}-Ph), 144.1 (s, 2,6-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 150.9 (s, 4-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 178.9 (s, $C\mathrm{\{NSi(CH_3)_3\}_2}$) IR: 2969s, 2895m, 1462m, 1424s, 1250s, 990s, 880m, 837vs, 764m, 714m
8 Yellow C, 52.9 (52.9) H, 8.1 (7.9) N, 7.9 (8.0) Cl, 9.8 (10.1)	$^{1}\mathrm{H}$: 0.16 (s, 18H, $\mathrm{Si(C}H_3)_3$), 1.15 (m, 18H, 2,4,6-$\mathrm{CH(C}H_3)_2$), 1.61 (s, 9H, $\mathrm{NC(C}H_3)_3$), 2.71 (m, 1H, 4-$\mathrm{C}H\mathrm{(CH_3)_2}$), 2.85 (br, 2H, 2,6-$\mathrm{C}H\mathrm{(CH_3)_2}$), 6.69 (m, 2H, m-$\mathrm{NC_5}H_5$), 6.91 (s, 2H, 3,5-$\mathrm{C_6}H_2\mathrm{\{CH(CH_3)_2\}_3}$), 6.94 (m, 1H, p-$\mathrm{NC_5}H_5$), 9.45 (d, 2H, $J = 5.4$, o-$\mathrm{NC_5}H_5$) $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$: 2.5 (s, $\mathrm{Si(}C\mathrm{H_3)_3}$), 24.1 (s, 2,6-$\mathrm{CH(}C\mathrm{H_3)_2}$), 25.0 (s, 4-$\mathrm{CH(}C\mathrm{H_3)_2}$), 30.3 (s, $\mathrm{NC(}C\mathrm{H_3)_3}$), 30.6 (s, 2,6-$C\mathrm{H(CH_3)_2}$), 34.6 (s, 4-$C\mathrm{H(CH_3)_2}$), 69.3 (s, $\mathrm{N}C\mathrm{(CH_3)_3}$), 121.4 (s, 3,5-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 123.2 (s, m-$\mathrm{N}C_5\mathrm{H_5}$), 136.3 (s, C_{ipso}-Ph), 137.5 (s, p-$\mathrm{N}C_5\mathrm{H_5}$), 144.3 (s, 2,6-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 150.9 (s, 4-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 151.2 (s, o-$\mathrm{N}C_5\mathrm{H_5}$), 178.8 (s, $C\mathrm{\{NSi(CH_3)_3\}_2}$) IR: 2961s, 2928m, 2872m, 1603m, 1460m, 1404s, 1360m, 1250s, 990s, 839s, 770m, 712m
9 Dark-red C, 48.9 (49.5) H, 6.8 (7.1) N, 4.1 (4.3) Cl, 16.4 (16.3)	$^{1}\mathrm{H}$: −0.01 (s, 9H, $\mathrm{Si(C}H_3)_3$ (close to Cp)), 0.65 (br, 9H, $\mathrm{Si(C}H_3)_3$ (close to Cl)), 1.12 (d, 6H, $J = 7.0$, 4-$\mathrm{CH(C}H_3)_2$), 1.23 (d, 6H, $J = 7.0$, 2,6-$\mathrm{CH(C}H_3)_2$ (Cp side)), 1.38 (d, 6H, $J = 7.0$, 2,6-$\mathrm{CH(C}H_3)_2$ (Cl side)), 2.67 (m, 1H, 4-$\mathrm{C}H\mathrm{(CH_3)_2}$), 3.60 (m, 2H, 2,6-$\mathrm{C}H\mathrm{(CH_3)_2}$), 6.60 (s, 5H, $\mathrm{C_5}H_5$), 6.89 (s, 2H, 3,5-$\mathrm{C_6}H_2\mathrm{\{CH(CH_3)_2\}_3}$) $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$:[c] 1.9 (br, $\mathrm{Si(}C\mathrm{H_3)_3}$), 3.1 (s, $\mathrm{Si(}C\mathrm{H_3)_3}$), 24.1 (s, 4-$\mathrm{CH(}C\mathrm{H_3)_2}$), 24.7 (s, 2,6-$\mathrm{CH(}C\mathrm{H_3)_2}$ (Cp side)), 25.1 (s, 2,6-$\mathrm{CH(}C\mathrm{H_3)_2}$ (Cl side)), 29.6 (s, 2,6-$C\mathrm{H(CH_3)_2}$), 34.7 (s, 4-$C\mathrm{H(CH_3)_2}$), 121.4 (s, 3,5-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 124.5 (s, $C_5\mathrm{H_5}$), 135.8 (s, C_{ipso}-Ph), 146.5 (s, 2,6-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 152.0 (s, 4-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 184.8 (s, $C\mathrm{\{NSi(CH_3)_3\}_2}$) IR: 2963s, 2905m, 1447m, 982s, 839s, 766m, 700m, 662m
10 Yellow C, 43.7 (43.7) H, 6.5 (6.3) N, 3.7 (3.8) Cl, 14.2 (14.3)	$^{1}\mathrm{H}$: 0.00 (s, 9H, $\mathrm{Si(C}H_3)_3$ (close to Cp)), 0.55 (br, 9H, $\mathrm{Si(C}H_3)_3$ (close to Cl)), 1.12 (d, 6H, $J = 6.9$, 4-$\mathrm{CH(C}H_3)_2$), 1.24 (d, 6H, $J = 6.8$, 2,6-$\mathrm{CH(C}H_3)_2$ (Cp side)), 1.37 (d, 6H, $J = 6.7$, 2,6-$\mathrm{CH(C}H_3)_2$ (Cl side)), 2.68 (m, 1H, 4-$\mathrm{C}H\mathrm{(CH_3)_2}$), 3.57 (m, 2H, 2,6-$\mathrm{C}H\mathrm{(CH_3)_2}$), 6.41 (s, 5H, $\mathrm{C_5}H_5$), 6.94 (s, 2H, 3,5-$\mathrm{C_6}H_2\mathrm{\{CH(CH_3)_2\}_3}$) $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$:[c] 2.0 (br, $\mathrm{Si(}C\mathrm{H_3)_3}$), 3.3 (s, $\mathrm{Si(}C\mathrm{H_3)_3}$), 24.1 (s, 4-$\mathrm{CH(}C\mathrm{H_3)_2}$), 24.7 (s, 2,6-$\mathrm{CH(}C\mathrm{H_3)_2}$ (Cp side)), 25.0 (s, 2,6-$\mathrm{CH(}C\mathrm{H_3)_2}$ (Cl side)), 29.6 (s, 2,6-$C\mathrm{H(CH_3)_2}$), 34.7 (s, 4-$C\mathrm{H(CH_3)_2}$), 121.35 (s, $C_5\mathrm{H_5}$), 121.42 (s, 3,5-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 136.2 (s, C_{ipso}-Ph), 146.5 (s, 2,6-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 152.0 (s, 4-$C_6\mathrm{H_2\{CH(CH_3)_2\}_3}$), 183.9 (s, $C\mathrm{\{NSi(CH_3)_3\}_2}$) IR: 2965m, 1472m, 1348s, 1337s, 991s, 845s

[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 and coupling constants in Hz. IR data/cm^{-1}. [c] In toluene-d_8. [d] The quaternary carbon cannot be observed.

group could be detected by $^{1}\mathrm{H}$ and $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR spectroscopy. An X-ray structure determination identified the crystals as the compound $[\mathrm{Ta\{(2,4,6\text{-}tri\text{-}^{i}Pr)C_6H_2CN\}Cl_5}]$ (**3**) and the molecular structure is shown in Fig. 2. Compound **3** adopts a pseudo-octahedral geometry, with the nitrile binding end on with an almost linear Ta–N(1)–C(1) angle of 172.4(2)° which is typical for other nitrile compounds such as the cluster $[\mathrm{Ta_6Cl_{12}(PrCN)_6}][(\mathrm{Ta_6Cl_{12}})\mathrm{Cl_6}]\cdot 2\mathrm{PrCN}$ (175(7)° and 170(7)°).[24]

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

Ta(1)–Cl(1)	2.3505(14)	Ta(2)–Cl(8)	2.3287(16)
Ta(1)–Cl(2)	2.3739(15)	Ta(2)–N(3)	2.108(4)
Ta(1)–Cl(3)	2.3125(14)	Ta(2)–N(4)	2.130(4)
Ta(1)–Cl(4)	2.3287(16)	N(1)–Si(2)	1.790(5)
Ta(1)–N(1)	2.093(5)	N(2)–Si(1)	1.787(5)
Ta(1)–N(2)	2.109(4)	N(1)–C(10)	1.363(7)
Ta(2)–Cl(5)	2.3580(15)	N(2)–C(10)	1.345(7)
Ta(2)–Cl(6)	2.3456(15)	C(10)–C(11)	1.481(7)
Ta(2)–Cl(7)	2.3200(16)		
Cl(1)–Ta(1)–Cl(2)	178.40(6)	N(1)–C(10)–N(2)	110.1(5)
Cl(3)–Ta(1)–Cl(4)	108.21(6)	Ta(1)–N(1)–Si(2)	134.1(2)
Cl(1)–Ta(1)–Cl(3)	90.23(5)	Ta(1)–N(2)–Si(1)	134.5(2)
N(1)–Ta(1)–N(2)	63.75(17)	C(10)–N(1)–Si(2)	132.6(4)
Ta(1)–N(1)–C(10)	93.2(3)	C(10)–N(2)–Si(1)	132.5(4)
Ta(1)–N(2)–C(10)	93.0(3)		

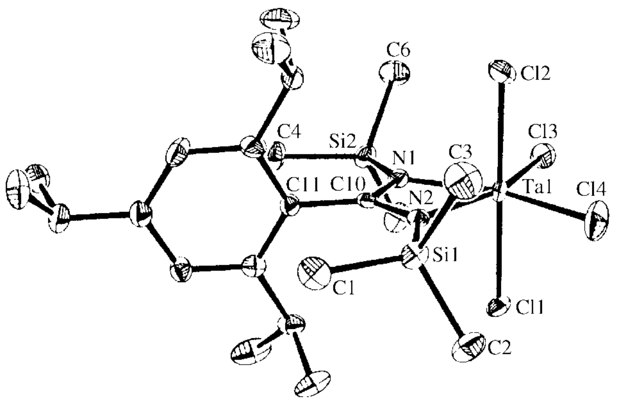
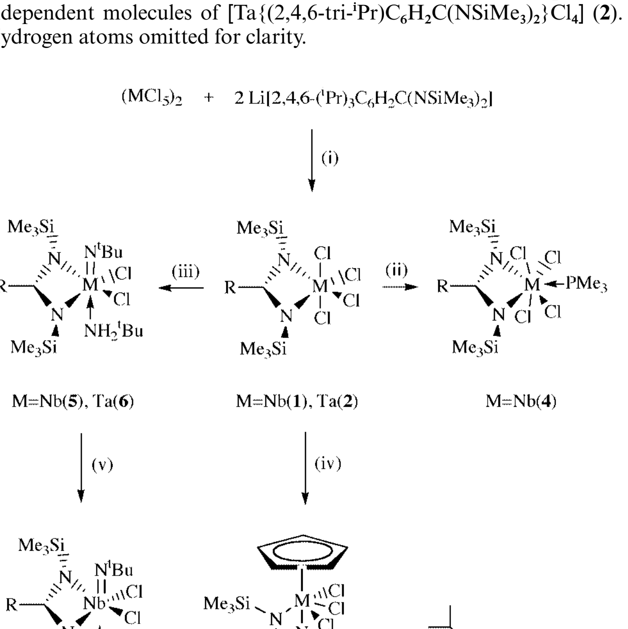


Fig. 1 Molecular structure of one of the two crystallographically independent molecules of [Ta{(2,4,6-tri-^{i}Pr)$C_6H_2C(NSiMe_3)_2$}Cl_4] (**2**). Hydrogen atoms omitted for clarity.



Scheme 1 *Reagents and conditions*: (*i*) in toluene, −78 °C to rt, 18 h; (*ii*) neat PMe_3, rt 2.5 h; (*iii*) ^{t}BuNH$_2$ (four equivalents) in CH_2Cl_2, −78 °C to rt, 16 h or LiNH^{t}Bu (two equivalents) in pentane, rt, 13 h; (*iv*) Cp_2Mg (half an equivalent) in toluene, −78 °C to rt, 16 h; (*v*) in thf, rt, 1 h for **7**; excess pyridine, in toluene, rt, 16 h for **8**.

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

Ta(1)–Cl(1)	2.2668(6)	Ta(1)–Cl(5)	2.3315(6)
Ta(1)–Cl(2)	2.3196(6)	Ta(1)–N(1)	2.207(2)
Ta(1)–Cl(3)	2.3348(6)	N(1)–C(1)	1.147(3)
Ta(1)–Cl(4)	2.3393(6)	C(1)–C(11)	1.422(3)
Cl(1)–Ta(1)–Cl(2)	95.69(2)	Cl(2)–Ta(1)–N(1)	82.21(6)
Cl(2)–Ta(1)–Cl(3)	90.32(2)	Ta(1)–N(1)–C(1)	172.4(2)
Cl(3)–Ta(1)–Cl(4)	88.54(2)	N(1)–C(1)–C(11)	177.3(3)
Cl(1)–Ta(1)–N(1)	177.74(6)		

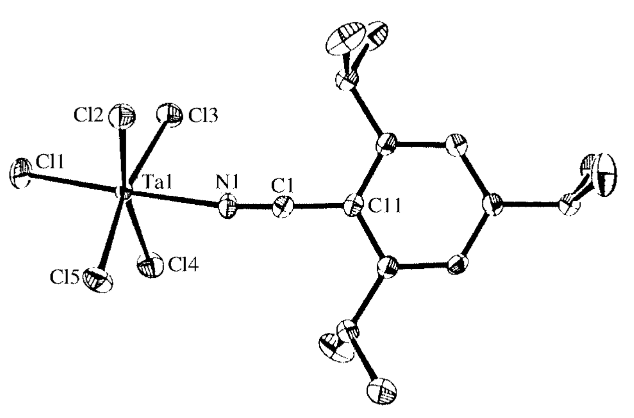


Fig. 2 Molecular structure of [Ta{(2,4,6-tri-^{i}Pr)C_6H_2CN}Cl_5] (**3**). Hydrogen atoms omitted for clarity.

Selected bond lengths and angles are listed in Table 3. The length of the Ta–Cl bond *trans* to the nitrile ligand is 2.2668(6) Å and this is shorter than the others, 2.3196(6)–2.3393(6) Å. This may be associated with greater π-bonding in the tantalum chloride bond due to the greater σ-donor ability of the *trans*-nitrile ligand when compared to the other chloride ligands. The N(1)–C(1) 1.147(3) Å bond length is consistent with a C–N triple-bond character. The infrared spectrum for **3** shows a strong band at $\nu_{CN} = 2253$ cm^{-1}, some 34 cm^{-1} higher than for the free nitrile (2,4,6-tri-^{i}Pr)C_6H_2CN where $\nu_{CN} = 2219$ cm^{-1}.[25]

A possible explanation for the formation of compound **3** is the formation of (2,4,6-tri-^{i}Pr)C_6H_2CN by elimination of $LiN(SiMe_3)_2$ from the lithium salt of the benzamidinato ligand to leave the nitrile. This would require the migration of one trimethylsilyl group to the other nitrogen to form lithium bis(trimethylsilyl)amide with the subsequent elimination of a molecule of (2,4,6-tri-^{i}Pr)C_6H_2CN.[26] In order to test this hypothesis, the lithium salt of the benzamidinato ligand was heated up to 85 °C in benzene-d_6 in a sealed NMR tube. Upon heating, a new set of resonances gradually appeared besides those corresponding to [Li{(2,4,6-tri-^{i}Pr)$C_6H_2C(NSiMe_3)_2$}]. After 160 hours of heating, the lithium salt had been completely converted into (2,4,6-tri-^{i}Pr)C_6H_2CN as identified by ^{1}H and ^{13}C{^{1}H} NMR spectra in comparison with literature values.[25]

In view of the low formal electron count of 14 for compounds **1** and **2**, the reaction with Lewis bases was explored. Compound **1** was treated with neat PMe_3 to give red crystals for the compound [Nb{(2,4,6-tri-^{i}Pr)$C_6H_2C(NSiMe_3)_2$}$Cl_4(PMe_3)$] (**4**). The crystal structure of **4** was determined and the molecular structure is shown in Fig. 3. Selected bond lengths and angles are listed in Table 4. The structure can be described as a distorted pentagonal biprism with the PMe_3 and benzamidinato ligands both occupying equatorial sites, in accord with their larger cone angles in comparison to chloride. The two chlorides which are eclipsed by the two N–$SiMe_3$ groups are moved towards the phosphine such that the Cl(3)–Nb(1)–Cl(4) angle is 132.43(4)° instead of the 144° expected. However, it appears that in order to relieve the strain created by these chlorides, the phosphine lies below the equatorial plane by 27° with the result that it approaches Cl(1) (moving it towards the nitrogen ligand) resulting in the angle Cl(1)–Nb–Cl(2) = 169.72(4)°. Such steric demands could also account for the Nb–Cl(1) bond length, 2.4509(8) Å, being slightly longer than the other Nb–Cl bonds, 2.361(1), 2.3875(9) and 2.3984(8) Å. Not surprisingly, the Nb–P bond length, 2.6711(9) Å, is considerably longer than

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

Nb(1)–Cl(1)	2.4509(8)	P(1)–C(31)	1.809(4)
Nb(1)–Cl(2)	2.361(1)	N(1)–Si(1)	1.781(3)
Nb(1)–Cl(3)	2.3875(9)	N(2)–Si(2)	1.783(3)
Nb(1)–Cl(4)	2.3984(8)	N(1)–C(1)	1.333(4)
Nb(1)–P(1)	2.6711(9)	N(2)–C(1)	1.329(4)
Nb(1)–N(1)	2.183(2)	C(1)–C(11)	1.498(4)
Nb(1)–N(2)	2.155(2)		
Cl(1)–Nb(1)–Cl(2)	169.72(4)	P(1)–Nb(1)–N(1)	142.21(7)
Cl(1)–Nb(1)–Cl(3)	101.28(4)	P(1)–Nb(1)–N(2)	138.45(7)
Cl(2)–Nb(1)–Cl(3)	84.75(5)	N(1)–Nb(1)–N(2)	61.40(9)
Cl(1)–Nb(1)–Cl(4)	95.99(4)	Nb(1)–N(1)–C(1)	92.30(18)
Cl(2)–Nb(1)–Cl(4)	85.76(4)	Nb(1)–N(2)–C(1)	93.65(17)
Cl(3)–Nb(1)–Cl(4)	132.43(4)	N(1)–C(1)–N(2)	112.6(2)
Cl(1)–Nb(1)–P(1)	72.60(3)	Nb(1)–N(1)–Si(1)	135.55(13)
Cl(2)–Nb(1)–P(1)	117.46(4)	C(1)–N(1)–Si(1)	132.0(2)
Cl(3)–Nb(1)–P(1)	71.50(3)	Nb(1)–N(2)–Si(2)	134.37(13)
Cl(4)–Nb(1)–P(1)	72.13(3)	C(1)–N(2)–Si(2)	131.8(2)
Cl(1)–Nb(1)–N(1)	83.07(7)	Cl(1)–Nb(1)–N(2)	81.33(7)
Cl(2)–Nb(1)–N(1)	87.12(7)	Cl(2)–Nb(1)–N(2)	91.26(7)
Cl(3)–Nb(1)–N(1)	143.17(7)	Cl(3)–Nb(1)–N(2)	82.91(7)
Cl(4)–Nb(1)–N(1)	82.44(7)	Cl(4)–Nb(1)–N(2)	143.84(7)

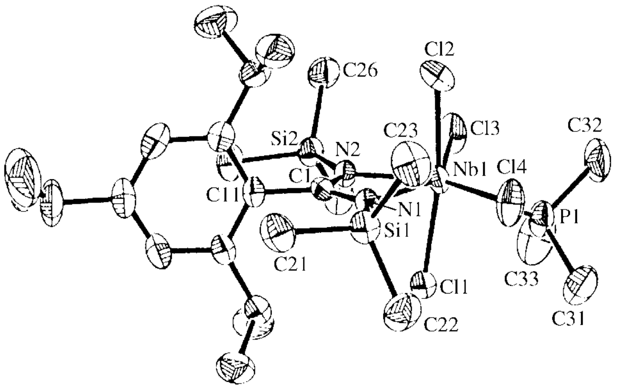


Fig. 3 Molecular structure of $[Nb\{(2,4,6\text{-tri-}^iPr)C_6H_2C(NSiMe_3)_2\}Cl_4(PMe_3)]$ (**4**). Hydrogen atoms omitted for clarity.

the Nb–P bond length, 2.5462(12) Å, in $[Nb(\eta\text{-}C_5H_5)(2\text{-}^tBu\text{-}C_6H_4N)(PhCCPh)(PMe_3)]$[27] and those, 2.601(1) and 2.604(2) Å, in the compound $[Nb(\eta\text{-}C_5H_5)(NMe)Cl_2(PMe_3)]$.[28]

Evidence of steric crowding in the solid state structure of **4** is also reflected in the spectra. Thus the ^1H NMR spectrum of **4** at 25 °C shows that the $SiMe_3$ resonance occurs as a broad peak, 10.8 Hz (fwhh), which may be attributed to a hindered rotation of the $SiMe_3$ group. Attempts to prepare the metal–imido compounds $[M\{(2,4,6\text{-tri-}^iPr)C_6H_2C(NSiMe_3)_2\}(N^tBu)Cl_2]$ (M = Nb, Ta) by treatment of **1** and **2** with three equivalents of $^tBuNH_2$ proved unsuccessful, and these reactions gave the $^tBuNH_2$ adducts $[M\{(2,4,6\text{-tri-}^iPr)C_6H_2C(NSiMe_3)_2\}(N^tBu)(NH_2{}^tBu)Cl_2]$ (M = Nb (**5**), Ta (**6**)) in low yields. The compounds **5** and **6** have been subsequently prepared in good yield (50–60%) from the reaction of compounds **1** or **2** with four equivalents of $^tBuNH_2$, followed by crystallisation from pentane. Alternatively, treatment of compound **1** with two equivalents of $LiNH^tBu$ also afforded compound **5**, however in lower yield (32%). Formation of mixed amino–imido complexes such as **5** and **6** is well-known, however, the mechanism of formation is unsure. Possible pathways include both intramolecular reactions (bis-amido-compound formation, followed by α-abstraction of a NH proton by one of the amido groups) and intermolecular reactions, the former having been postulated in the formation of metal multiple bonds in related complexes.[29,30]

The ^1H NMR spectra of the compounds **5** and **6** exhibit two methyl resonances for the *tert*-butyl groups with equal intensity. The $^{13}C\{^1H\}$ NMR spectra also show two methyl carbon resonances corresponding to *tert*-butyl imido and amino groups (δ 30.4 and 32.1 in **5**; δ 31.0 and 32.6 in **6**) along with two quaternary carbon resonances for each compound (δ 51.7 and 69.2 for **5**; δ 52.0 and 65.5 for **6**). Those resonances are in the range reported for other M–amino and M–imido compounds (δ 51–52 for $M\text{–}NH_2{}^tBu$ and δ 64–70 for $M = N^tBu$).[31–34] The ^1H NOESY spectra of **5** and **6** show the two NH protons correlate only to one of the *tert*-butyl resonances, confirming that the compounds comprise one imido and one amine ligand. A variable temperature NMR study showed that the resonances corresponding to the proton on 2,6-^iPr-*Me*, 2,6-*H*CMe_2 and 3,5-Ph decoalesce as the temperature of the sample is reduced. No splitting of the other resonances was observed. The NMR data show the barrier to rotation of the aryl ring around the C_{ipso}–C bond is 55.2 kJ mol^{-1} at 268 K in **5**.

Crystals of compound **5** were grown by the slow evaporation of a pentane solution. Severe disorder is present in the crystals as a result of an averaging of the positions of the imido and amino ligands. Consequently, the thermal ellipsoid of the niobium atom is elongated in the axis defined between the two nitrogens because of the difference in Nb–N bond lengths. This prevented a satisfactory refinement from being achieved. Compound **6** was also crystallised in a similar manner, however refinement of the structure was also problematic due to the same type of disorder and an adequate model proved unattainable.

The *tert*-butyl amino ligand of compound **5** was found to be substitutionally labile, since the THF adduct $[Nb\{(2,4,6\text{-tri-}^iPr)C_6H_2C(NSiMe_3)_2\}(N^tBu)(THF)Cl_2]$ (**7**) could be prepared by stirring compound **5** in THF for one hour followed by recrystallisation from pentane. The ^1H NMR spectrum of **7** in benzene-d_6 showed two multiplets at 1.45 ppm (4H) and 4.08 ppm (4H) corresponding to the coordinated THF, the latter peak being shifted downfield by 0.4 ppm relative to the free solvent. No resonance corresponding to the coordinated $^tBuNH_2$ group was observed. This preference for the oxygen of THF over the nitrogen of the amine, is consistent with the 'hard' character of the electron deficient metal centre. The pyridine adduct $[Nb\{(2,4,6\text{-tri-}^iPr)C_6H_2C(NSiMe_3)_2\}(N^tBu)(py)Cl_2]$ (**8**) could also be prepared by the reaction of compound **5** with an excess of pyridine.

Treatment of compounds **1** or **2** with half an equivalent of Cp_2Mg in toluene at −78 °C forms the compounds $[Nb\{(2,4,6\text{-tri-}^iPr)C_6H_2C(NSiMe_3)_2\}(\eta\text{-}C_5H_5)Cl_3]$ (**9**) and $[Ta\{(2,4,6\text{-tri-}^iPr)C_6H_2C(NSiMe_3)_2\}(\eta\text{-}C_5H_5)Cl_3]$ (**10**). The ^1H NMR spectra of compounds **9** and **10** both show one sharp and one broad resonance (δ −0.01 and 0.65 in **9**; δ 0.00 and 0.55 in **10**) corresponding to dissimilar $SiMe_3$ groups. They also show three doublet resonances (δ 1.12, 1.23 and 1.38 in **9**; δ 1.12, 1.24 and 1.37 in **10**) corresponding to the methyl groups of the iso-propyl groups of the benzamidinato ligand, but only two septets with an intensity ratio of two to one for the isopropyl C–H(methine) groups. The $^{13}C\{^1H\}$ NMR spectra closely reflect the ^1H NMR spectra. Thus there are two resonances for the $SiMe_3$ groups and three resonances for the methyl carbons on the isopropyl groups but only two resonances corresponding to C–H(methine) carbon on the isopropyl groups. These observations are readily reconciled by considering the structure of compound **10** shown in Fig. 4 (*vide infra*). Based on this structure, we can define a plane in which the phenyl ring, C11 and C1 all lie. The two $SiMe_3$ groups are located on opposite sides of this plane: hence, two $SiMe_3$ resonances are observed. This plane also bisects the isopropyl groups, and provided that the aryl ring is slow to rotate on the NMR timescale, the two methyl groups on the *same* isopropyl group (2,6-positions) are then in different environments. This leads to two doublet signals. The two methyl groups of the isopropyl group in the 4 position then constitute the third doublet (assuming that this substituent *is* free to rotate). However, the two C–H(methine) carbons (C2 and C5) of these groups (in the 2 and 6 positions) are located in this plane, and are thus equivalent. This leads to

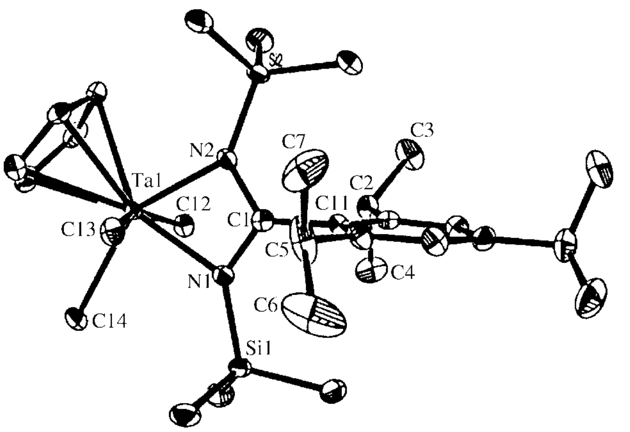


Fig. 4 Molecular structure of [Ta{(2,4,6-tri-^{i}Pr)$C_6H_2C(NSiMe_3)_2$}-(η-C_5H_5)Cl_3] (**10**). Hydrogen atoms omitted for clarity.

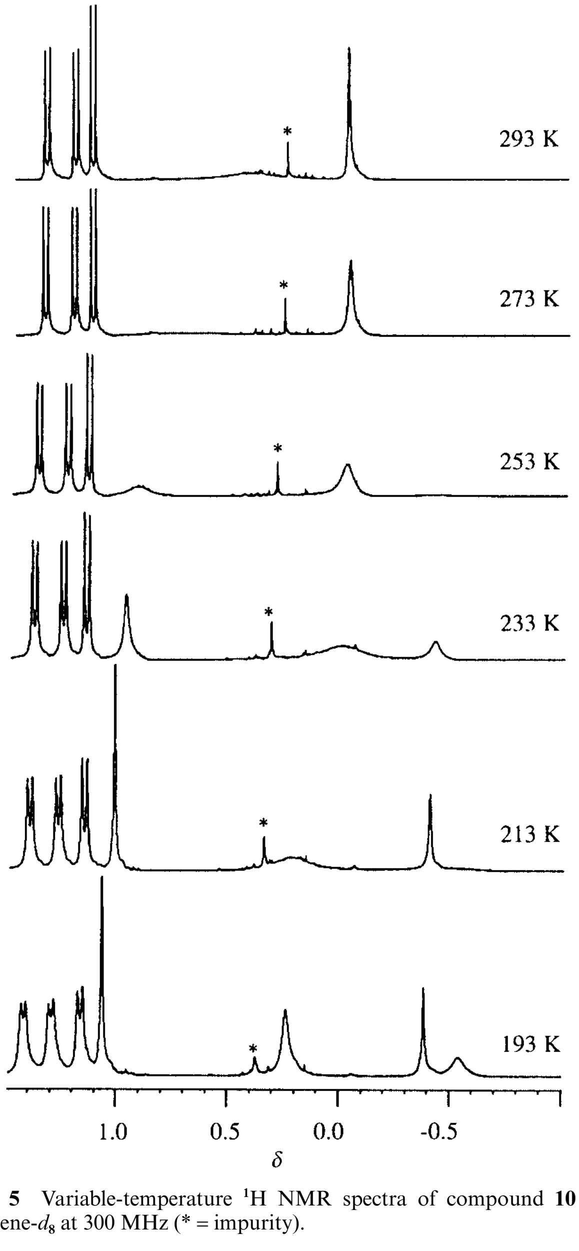


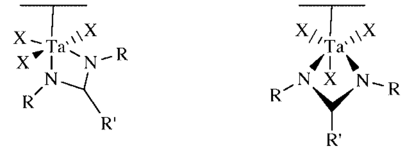
Fig. 5 Variable-temperature ^{1}H NMR spectra of compound **10** in toluene-d_8 at 300 MHz (* = impurity).

only two resonances corresponding to these C–H(methine) protons being observed at room temperature.

The variable temperature ^{1}H NMR spectra of compound **10** in toluene-d_8 between 293 and 193 K are shown in Fig. 5. Each $SiMe_3$ signal decoalesces into two singlets of relative ratio 2:1, but at different coalescence temperatures (273 K and 213 K). This is consistent with two different methyl environments for each $SiMe_3$ group at low temperature. The barriers to rotation of the $SiMe_3$ groups around the N–Si bonds in solution have been determined: 51.0 kJ mol^{-1} (for the $SiMe_3$ group close to Cl, T_c = 273 K) and 40.6 kJ mol^{-1} (for the $SiMe_3$ group close to Cp, T_c = 213 K).[35]

Table 5 Selected bond lengths (Å) and angles (°) for **10**

Ta(1)–Cl(2)	2.4408(7)	N(1)–C(1)	1.318(4)
Ta(1)–Cl(3)	2.4530(7)	N(2)–C(1)	1.359(4)
Ta(1)–Cl(4)	2.4151(7)	C(1)–C(11)	1.504(4)
Ta(1)–N(1)	2.199(2)	N(1)–Si(1)	1.778(2)
Ta(1)–N(2)	2.133(2)	N(2)–Si(2)	1.778(2)
Ta(1)–Cp(ctr.)	2.147		
N(1)–Ta(1)–N(2)	61.68(8)	C(1)–N(2)–Si(2)	128.5(2)
Ta(1)–N(1)–C(1)	92.20(17)	Cp–Ta(1)–Cl(2)	102.32
Ta(1)–N(2)–C(1)	93.96(17)	Cp–Ta(1)–Cl(3)	101.04
N(1)–C(1)–N(2)	112.2(2)	Cp–Ta(1)–Cl(4)	102.61
Ta(1)–N(1)–Si(1)	134.60(13)	Cp–Ta(1)–N(1)	172.89
C(1)–N(1)–Si(1)	133.2(2)	Cp–Ta(1)–N(2)	111.21
Ta(1)–N(2)–Si(2)	137.58(13)		



(a) (b)

Fig. 6 The two structure types observed for compounds of the general formula [Ta{R′C(NR)$_2$}Cp′X_3] (Cp′ = Cp* or Cp, R′ = Me, *p*-MeO-C_6H_4 or 2,4,6-(^{i}Pr)$_3$-C_6H_2; R = ^{i}Pr or $SiMe_3$; X = F, Cl or Me).

The crystal structure of compound **10** [Ta{(2,4,6-tri-^{i}Pr)-$C_6H_2C(NSiMe_3)_2$}(η-C_5H_5)Cl_3] has been determined and the molecular structure is shown in Fig. 4. Selected bond lengths and angles are listed in Table 5. The cyclopentadienyl group is bound in a η^5-manner and the benzamidinato ligand lies on the opposite side of the metal to form a "bent sandwich" structure. One $SiMe_3$ group lies in close proximity to the cyclopentadienyl group and the other $SiMe_3$ group is situated on the other side of the metal centre, *trans* to the C_5 ring and close to Cl(4). This results in a strong steric interaction between the cyclopentadienyl ring and the proximate silyl group, producing a Ta–N(2)–Si(2) angle of 137.6°, which is 3° larger than the corresponding Ta–N(1)–Si(1) angle; this being reflected in the rotational energy barriers observed in the ^{1}H NMR spectra. The Ta–N(benzamidinato) bond lengths, 2.199(2) and 2.133(2) Å, are typical of those found in the literature,[22] but again are unsymmetrical due to the orientation of the prolate benzamidinato ligand relative to the Cp group.

Previous reports of the structures of η-cyclopentadienyl–amidinato complexes fall into two structure types (a and b), as shown in Fig. 6. The compound [Ta{ArC(NSiMe$_3$)$_2$}(η-C_5Me_5)-F_3], has a structure type b in which a mirror plane exists through the metal and the cyclopentadienyl and benzamidinato ligands: the $SiMe_3$ groups are symmetrical and therefore only one $SiMe_3$ resonance is observed in the ^{1}H NMR spectrum.[21] However, compound **10** has structure type a and is isostructural to [Ta{MeC(N^{i}Pr)$_2$}(η-C_5Me_5)Cl_3] and [Ta{MeC(N^{i}Pr)$_2$}-(η-C_5Me_5)$(CH_3)_3$].[22] The factors determining the two structure types are unclear.

The compounds presented in this paper were designed to yield a highly electron deficient metal centre through use of the bulky benzamidinato ligand. The activity of compounds **1**, **5** and **9** as ethene polymerisation catalysts was tested, using MAO (methylaluminoxane) as a co-catalyst. Ethene polymerisations were performed in toluene at room temperature with a monomer pressure of 2 bar, in accordance with the procedures used

Table 6 Activity toward ethylene polymerisation

Compound	Time/min	Yield/mg	Activity/g PE (mol M)$^{-1}$ h^{-1}
1	120	22	1.76×10^3
5	120	42	3.36×10^3
9	120	44	3.52×10^3

At 2 bar absolute monomer pressure, rt, 220 cm^3 toluene, 10 ml 10% MAO, Al/M = 2448. mol M: total amount of metal used (6.25×10^{-6} mol for each run).

by Kaminsky and co-workers.[36] The activity data are given in Table 6. All three compounds (**1**, **5** and **9**) show extremely low activity as ethene polymerisation catalysts, similar to that reported for the zirconium systems.[11,37] Owing to the poor reactivity of these catalyst precursors, further studies were discontinued.

In conclusion, the presence of bulky 2,4,6-tri-isopropyl substituents on the aryl rings of the benzamidinato ligand favours the formation of mono-benzamidinato–metal compounds. However, these compounds are not active pre-catalysts for olefin polymerisation.

Experimental

All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk-line or drybox techniques. Solvents were pre-dried over molecular sieves and 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.

^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded either on Varian Unity 500 or Varian Mercury 300 spectrometers and referenced internally to the residual solvent peak relative to tetramethylsilane. ^{31}P{^{1}H} NMR spectra were referenced externally to H_3PO_4. Variable temperature ^{1}H NMR experiments were recorded on a Varian-VXR-300S spectrometer. Infrared spectra were recorded on a 6020 Galaxy 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.

$NbCl_5$, $TaCl_5$, 1,3-bis(trimethylsilyl)carbodiimide, ^{t}Bu-NH_2, pyridine (Aldrich), 2-bromo-1,3,5-triisopropylbenzene (Lancaster) and methylaluminoxane (Witco) were used as supplied. Cp_2Mg,[38] PMe_3,[39] LiNH^{t}Bu,[40] and 2,4,6-triisopropylphenyllithium[41] were prepared by the literature methods.

Preparations

Lithium *N*,*N*′-bis(trimethylsilyl)-2,4,6-triisopropylbenzamidinate. This compound was prepared as a white powder from the reaction between ($Me_3SiN{=}C{=}NSiMe_3$) and [Li(2,4,6-tri-^{i}PrC$_6$H$_2$)] in ether at room temperature followed by crystallisation from ether according to the procedure given for the 2,4,6-trimethylphenyl analogue.[42] It was characterised from the ^{1}H NMR spectrum and elemental analysis.

[Nb{(2,4,6-tri-^{i}Pr)C$_6$H$_2$C(NSiMe$_3$)$_2$}Cl$_4$] (1). A white suspension of lithium *N*,*N*′-bis(trimethylsilyl)-2,4,6-triisopropylbenzamidinate (2.61 g, 6.6 mmol) in 20 ml toluene at room temperature was added to a stirred suspension of $NbCl_5$ (1.78 g, 6.6 mmol) in 20 ml toluene cooled to −78 °C. The resulting red suspension was allowed to warm slowly to room temperature and stirred for a further 19 h. The suspension was filtered and the volatiles were removed under reduced pressure to afford a red solid. Extraction with pentane, filtering and slow cooling to −25 °C afforded the product as a red powder. Yield, 1.81 g, 44%.

[Ta{(2,4,6-tri-^{i}Pr)C$_6$H$_2$C(NSiMe$_3$)$_2$}Cl$_4$] (2). A white suspension of lithium *N*,*N*′-bis(trimethylsilyl)-2,4,6-triisopropylbenzamidinate (1.19 g, 3.0 mmol) in 30 ml toluene at room temperature was added, with stirring, to a suspension of $TaCl_5$ (1.08 g, 3.0 mmol) in 20 ml toluene cooled to −78 °C. The resulting white suspension was allowed to warm to room temperature and stirred for a further 18 h to give a yellow suspension. The mixture was filtered and the volatiles were removed under reduced pressure to afford a yellow solid. Extraction with 20 ml pentane, filtering and cooling to −25 °C afforded the product as yellow crystals. Yield, 1.16 g, 54%.

[Ta{(2,4,6-tri-^{i}Pr)C$_6$H$_2$CN}Cl$_5$] (3). $TaCl_5$ (3.58 g, 10.0 mmol) in toluene was reacted with lithium *N*,*N*′-bis(trimethylsilyl)-2,4,6-triisopropylbenzamidinate (3.97 g, 10.0 mmol) as described for the synthesis of compound **2**. The pentane extract was concentrated until some solid precipitated, then cooled to −25 °C for two days. Decantation of the yellow solution allowed isolation of a mixture of pale-brown crystals and a yellow solid. The mixture was washed with 20 ml pentane and the residue was dried *in vacuo* to afford pale-brown crystals (**3**). Yield, 0.29 g, 5%. Evaporation of the supernatant to dryness, yielded further yellow solid (compound **2**), which was washed with 10 ml cold pentane and dried. Yield, 2.56 g, 36%.

[Nb{(2,4,6-tri-^{i}Pr)C$_6$H$_2$C(NSiMe$_3$)$_2$}Cl$_4$(PMe$_3$)] (4). Trimethylphosphine (*ca.* 3 ml) was condensed into an ampoule charged with [(2,4,6-tri-Pr^i)C$_6$H$_2$C(NSiMe$_3$)$_2$]NbCl$_4$ (0.97 g, 1.6 mmol). The reaction mixture was warmed to room temperature and stirred for a further 2.5 h. After this time, the excess PMe_3 was removed *in vacuo* and the residue was extracted with 40 ml pentane. The extract was concentrated until some solid precipitated, then cooled to −25 °C to afford a red solid. Yield, 0.54 g, 50%.

[Nb{(2,4,6-tri-^{i}Pr)C$_6$H$_2$C(NSiMe$_3$)$_2$}(NH$_2$^{t}Bu)(N^{t}Bu)Cl$_2$] (5). *(1) By amine hydrochloride elimination.* To a red solution of (2,4,6-tri-^{i}Pr)C$_6$H$_2$C(NSiMe$_3$)$_2$NbCl$_4$ (0.89 g, 1.4 mmol) in 20 ml CH_2Cl_2, stirred at −78 °C, was added a solution of *tert*-butylamine (0.6 ml, 5.7 mmol) in 20 ml CH_2Cl_2. The reaction mixture was allowed to warm to the room temperature and stirred for 16 hours. The yellow mixture was filtered and the volatiles were removed *in vacuo* to afford a yellow solid. Yield, 0.58 g, 59%.

(2) By lithium chloride elimination. A colourless solution of LiNH^{t}Bu (0.16 g, 2.0 mmol) in 15 ml pentane was added dropwise, at room temperature, to a red solution of (2,4,6-tri-^{i}Pr)C$_6$H$_2$C(NSiMe$_3$)$_2$NbCl$_4$ (0.62 g, 1.0 mmol) in 20 ml pentane. After stirring for 13 h, the yellow mixture was filtered and the volatiles were removed *in vacuo* to afford a yellow solid that was purified by crystallisation from pentane at −25 °C. Yield, 0.22 g, 32%.

[Ta{(2,4,6-tri-^{i}Pr)C$_6$H$_2$C(NSiMe$_3$)$_2$}(NH$_2$^{t}Bu)(N^{t}Bu)Cl$_2$] (6). To a yellow solution of (2,4,6-tri-^{i}Pr)C$_6$H$_2$C(NSiMe$_3$)$_2$TaCl$_4$ (0.82 g, 1.2 mmol) in 20 ml CH_2Cl_2, stirred at −78 °C, was added a colourless solution of *tert*-butylamine (0.49 ml, 4.8 mmol) in 20 ml CH_2Cl_2. The yellow solution was allowed to warm to the room temperature and react overnight. After 19 hours of stirring, the pale-green mixture was filtered and the volatiles were removed *in vacuo* to afford a pale-green solid that was purified by crystallisation from pentane. Yield, 0.48 g, 53%.

[Nb{(2,4,6-tri-^{i}Pr)C$_6$H$_2$C(NSiMe$_3$)$_2$}(THF)(N^{t}Bu)Cl$_2$] (7). A sample of compound **5** (0.40 g, 0.6 mmol) was dissolved in 10 ml THF and stirred at room temperature for 1 hour. The solvent was removed *in vacuo* to afford a yellow solid that was recrystallised from pentane to form a yellow crystalline solid. Yield, 0.21 g, 52%.

Table 7 Summary of crystal data for compounds **2**, **3**, **4**, and **10**

	2	**3**	**4**	**10**
Formula	$C_{22}H_{41}Cl_4N_2Si_2Ta$	$C_{16}H_{23}Cl_5NTa$	$C_{25}H_{50}Cl_4N_2NbPSi_2$	$C_{27}H_{46}Cl_3N_2Si_2Ta$
FW	712.52	587.58	700.55	742.16
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$Pca2_1$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a/Å	19.289(4)	12.722(4)	18.388(4)	16.852(5)
b/Å	15.548(2)	10.598(2)	10.256(2)	15.111(4)
c/Å	20.389(4)	15.931(4)	18.799(7)	13.049(2)
β/°		97.829(6)	96.701(6)	75.653(5)
V/Å^3	6114.8(5)	2127.9(6)	3521.0(5)	3219.3(3)
Z	8	4	4	4
ρ_{calc}/g cm^{-3}	1.55	1.83	1.32	1.53
T/K	150	125	270	125
μ(Mo-Kα)/mm^{-1}	4.00	5.74	0.78	3.72
Total no. of data	27302	11112	16427	16990
No. of unique data	6889	4606	7484	6635
No. of observed data	5903	4066	5739	5902
R^a	0.0243	0.0237	0.0523	0.0290
Rw^a	0.0281	0.0257	0.0537	0.0316

[a] $R = [\Sigma(|F_o| - |F_c|)/\Sigma|F_o|]$; $Rw = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

[Nb{(2,4,6-tri-^{i}Pr)$C_6H_2C(NSiMe_3)_2$}(py)(N^{t}Bu)Cl_2] (8). To a yellow solution of compound **5** (0.70 g, 1.0 mmol) in 20 ml toluene, a colourless solution of pyridine (0.168 g, 2.1 mmol) in 10 ml toluene was added at room temperature. After 16 hours of stirring, the volatiles were removed *in vacuo* to afford a yellow solid that was recrystallised from pentane to form a yellow crystalline solid. Yield, 0.26 g, 37%.

[Nb{(2,4,6-tri-^{i}Pr)$C_6H_2C(NSiMe_3)_2$}(η-C_5H_5)Cl_3] (9). A solution of Cp_2Mg (0.20 g, 1.3 mmol) in 20 ml of toluene was added to a red solution of (2,4,6-tri-^{i}Pr)$C_6H_2C(NSiMe_3)_2NbCl_4$ (1.65 g, 2.6 mmol) in 20 ml toluene at −78 °C. The reaction mixture was allowed to warm to the room temperature and was stirred for a further 17 hours. The dark-red suspension was filtered and the solvent was evaporated under reduced pressure to form a dark red solid. This was washed with 5 ml pentane to afford a dark-red powder. Yield, 0.82 g, 48%.

[Ta{(2,4,6-tri-^{i}Pr)$C_6H_2C(NSiMe_3)_2$}(η-C_5H_5)Cl_3] (10). To a yellow solution of (2,4,6-tri-^{i}Pr)$C_6H_2C(NSiMe_3)_2TaCl_4$ (1.42 g, 2.0 mmol) in 20 ml toluene was added a solution of Cp_2Mg (0.15 g, 1.0 mmol) in 10 ml toluene at −78 °C. The reaction mixture was allowed to warm to room temperature and was stirred for a further 16 hours. The dark-brown mixture was filtered and the volatiles were removed *in vacuo* to afford a dark-brown solid that was washed with 5 ml pentane forming a yellow powder. Yield, 0.28 g, 19%.

Polymerisation studies

Ethylene was purified by passage through 4 Å molecular sieves and then over finely divided potassium metal supported on glass wool. Polymerisation reactions were carried out in a Fischer-Porter reactor equipped with a magnetic stirrer using conditions similar to those employed by Kaminsky *et al.*[36] Methylaluminoxane(MAO) (9.4 ml) was syringed into the Fischer-Porter bottle, which was connected to the ethylene supply *via* a gas supply system and filled with ethylene. Toluene (200 cm^3) was then added, the ethylene pressure increased to 2 bar (absolute pressure) and the mixture was stirred at room temperature until saturated with ethylene. Meanwhile, 0.6 ml of MAO was added to a solution of the benzamidinato catalyst precursor complex (6.25×10^{-6} mol) in 10 cm^3 of toluene and stirred for 15 min pre-activation. The catalyst–MAO mixture was then added quickly to the reactor by syringe. The reaction mixture was stirred vigorously at room temperature under 2 bar pressure of ethylene for 2 hours. The reaction was quenched by venting the ethylene and adding a small amount of ethanol. The contents of the reactor were then transferred into a conical flask and 250 cm^3 of conc. HCl in ethanol was added (20% by volume) and the mixture was stirred overnight. The polymer was then separated by filtration and washed with water and ethanol then dried *in vacuo* at 60 °C.

Crystal structure data

Crystals were grown from a saturated pentane solution (**2**, **3**, **4**) or dichloromethane–pentane solution (**10**) at 248 K, and isolated by filtration. Specimens were mounted on the end of a glass fibre, and data were collected on an Enraf-Nonius DIP2000 image plate diffractometer. The images were processed with the DENZO and SCALEPACK programs.[43] Corrections for Lorentz and polarisation effects were performed.

Solution, refinement, and graphical calculations were performed using the CRYSTALS[44] and CAMERON[45] software packages. The structures were solved by direct methods using the SIR92 program.[46] Crystallographic information is summarised in Table 7.

CCDC reference number 186/1825.

See http://www.rsc.org/suppdata/dt/a9/a909333h/ for crystallographic files in .cif format.

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References

1 H. Sinn and W. Kaminsky, *Adv. Organomet. Chem.*, 1980, **18**, 99.
2 M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 1996, 255.
3 H. H. Brintzinger, D. Fischer, R. Mulhaupt, B. Reiger and R. M. Waymouth, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1143.
4 G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**, 428.
5 W. Kaminsky, *J. Chem. Soc., Dalton Trans.*, 1998, 1413.
6 A. L. McKnight and R. M. Waymouth, *Chem. Rev.*, 1998, **98**, 2587.
7 P. C. Mohring and N. J. Coville, *J. Organomet. Chem.*, 1994, **479**, 1.

8 R. Duchateau, C. T. v. Wee, A. Meetsma, P. T. v. Duijnen and J. H. Teuben, *Organometallics*, 1996, **15**, 2279.
9 M. Wedler, F. Knosel, F. T. Edelmann and U. Behrens, *Chem. Ber.*, 1992, **125**, 1313.
10 R. Duchateau, A. Meetsma and J. H. Teuben, *Organometallics*, 1996, **15**, 1656.
11 R. Gomez, R. Duchateau, A. N. Chernega, J. H. Teuben, F. T. Edelmann and M. L. H. Green, *J. Organomet. Chem.*, 1995, **491**, 153.
12 A. N. Chernega, R. Gomes and M. L. H. Green, *J. Chem. Soc., Chem. Commun.*, 1993, 1415.
13 R. Duchateau, C. T. v. Wee and J. H. Teuben, *Organometallics*, 1996, **15**, 2291.
14 J. C. Flores, J. C. W. Chien and M. D. Rausch, *Organometallics*, 1995, **14**, 1827.
15 J. C. Flores, J. C. W. Chien and M. D. Rausch, *Organometallics*, 1995, **14**, 2106.
16 R. Gomez, J. L. Haggitt and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1996, 939.
17 J. R. Hagadorn and J. Arnold, *J. Chem. Soc., Dalton Trans.*, 1997, 3087.
18 F. T. Edelmann, *Coord. Chem. Rev.*, 1994, **137**, 403.
19 M. Wedler, F. Knosel, M. Noltemeyer and F. T. Edelmann, *J. Organomet. Chem.*, 1990, **388**, 21.
20 D. Y. Dawson and J. Arnold, *Organometallics*, 1997, **16**, 1111.
21 F. Schrumpf, H. W. Roesky, T. Subrahmanyan and M. Noltemeyer, *Z. Anorg. Allg. Chem.*, 1990, **583**, 124.
22 J. M. Decker, S. J. Geib and T. Y. Meyer, *Organometallics*, 1999, **18**, 4417.
23 M. G. B. Drew and J. D. Wilkins, *J. Chem. Soc., Dalton Trans.*, 1974, 1579.
24 N. Brnicevic, S. Sirac, I. Basic, Z. Zhang, R. E. McCarley and I. A. Guzei, *Inorg. Chem.*, 1999, **38**, 4159.
25 E. T. K. Haupt and D. Leibfritz, *Spectrochim. Acta*, 1989, **45A**, 119.
26 M. P. Coles, D. C. Swenson and R. F. Jordan, *Organometallics*, 1997, **16**, 5183.
27 M. C. W. Chan, J. M. Cole, V. C. Gibson, J. A. K. Howard, C. Lehmann, A. D. Poole and U. Siemeling, *J. Chem. Soc., Dalton Trans.*, 1998, 103.
28 D. N. Williams, J. P. Mitchell, A. D. Poole, U. Siemeling, W. Clegg, D. C. R. Hockless, P. A. O'Neil and V. C. Gibson, *J. Chem. Soc., Dalton Trans.*, 1992, 739.
29 C. G. Ortiz, K. A. Abboud and J. M. Boncella, *Organometallics*, 1999, **18**, 4253.
30 D. M.-T. Chan, W. C. Fultz, W. A. Nugent, D. C. Roe and T. H. Tulip, *J. Am. Chem. Soc.*, 1985, **107**, 251.
31 M. I. Alcalde, M. P. Gomez-Sal and P. Royo, *Organometallics*, 1999, **18**, 546.
32 P. A. Bates, A. J. Nielson and J. M. Waters, *Polyhedron*, 1985, **4**, 1391.
33 S. Schmidt and J. Sundermeyer, *J. Organomet. Chem.*, 1994, **472**, 127.
34 K. C. Jayaratne, G. P. A. Yap, B. S. Haggerty, A. L. Rheingold and C. H. Winter, *Inorg. Chem.*, 1996, **35**, 4910.
35 J. Sandstrom, *Dynamic NMR Spectroscopy*, Academic Press, New York, 1982.
36 W. Kaminsky, R. Engehausen, K. Zoumis, W. Spaleck and J. Rohrmann, *Makromol. Chem.*, 1992, **193**, 1643.
37 D. Herskovics-Korine and M. S. Eisen, *J. Organomet. Chem.*, 1995, **503**, 307.
38 A. W. Duff, P. B. Hitchcock, M. F. Lappert, R. G. Taylor and J. A. Segal, *J. Organomet. Chem.*, 1985, **293**, 271.
39 J. M. L. Luetkens, A. P. Sattelberger, H. H. Murray, J. D. Basil and J. J. P. Fackler, *Inorg. Synth.*, 1990, **28**, 305.
40 M. I. Alcalde, M. P. Gomes-Sal and P. Royo, *Organometallics*, 1999, **18**, 546.
41 B. H. Lipshutz and T. Gross, *J. Org. Chem.*, 1995, **60**, 3572.
42 F. T. Edelmann, M. Noltemeyer, M. Wedler and F. Knosel, *J. Organomet. Chem.*, 1990, **388**, 21.
43 Z. Otwinowski and W. Minor, *Processing of X-Ray Diffraction Data Collected in Oscillation Mode*, Academic Press, New York, 1996, p. 276.
44 D. J. Watkin, C. K. Prout, J. R. Carruthers and P. W. Bettridge, CRYSTALS, Oxford, 1996.
45 D. J. Watkin, C. K. Prout and L. J. Pearce, CAMERON, Oxford, 1996.
46 A. Altomare, G. Cascarano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1994, **27**, 435.

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