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FULL PAPER

Titanium and zirconium complexes with sterically hindered aryl-substituted iminophosphoranato ligands

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The benzyliminophosphorane $4\text{-Bu}^tC_6H_4CH_2P(Ph)_2{=}NC_6H_2Me_3\text{-}2,4,6$ reacted with $TiCl_4$ or $ZrCl_4$ to give the N-donor adducts, $MCl_4\{4\text{-Bu}^tC_6H_4CH_2P(Ph)_2{=}NC_6H_2Me_3\text{-}2,4,6\}$. Whereas the zirconium compound proved unreactive, solutions of the titanium analogue at 10–20 °C slowly underwent C–H activation to give the phosphoranato complex $TiCl_3\{4\text{-Bu}^tC_6H_4CHP(Ph)_2{=}NC_6H_2Me_3\text{-}2,4,6\}$. The trichloro complexes $MCl_3\{4\text{-Bu}^tC_6H_4CHP(Ph)_2{=}NC_6H_2Me_3\text{-}2,4,6\}$ were also accessible from $Li[4\text{-Bu}^tC_6H_4CHP(Ph)_2{=}NC_6H_2Me_3\text{-}2,4,6]$ and MCl_4 (M = Ti or Zr). The reaction of $4\text{-Bu}^tC_6H_4CH_2P(Ph)_2{=}NC_6H_2Me_3\text{-}2,4,6$ with $Zr(NMe_2)_4$ in refluxing toluene led to $Zr(NMe_2)_3\{4\text{-Bu}^tC_6H_4CHP(Ph)_2{=}NC_6H_2Me_3\text{-}2,4,6\}$. The compound is fluxional in solution. Treatment with an excess of Me_3SiCl led to silylation of the ligand to give $ZrCl_4\{4\text{-Bu}^tC_6H_4CH(SiMe_3)P(Ph)_2{=}NC_6H_2Me_3\text{-}2,4,6\}$. The structures of $4\text{-Bu}^tC_6H_4CH_2P(Ph)_2{=}NC_6H_2Me_3\text{-}2,4,6$ and $Zr(NMe_2)_3\{4\text{-Bu}^tC_6H_4CHP(Ph)_2{=}NC_6H_2Me_3\text{-}2,4,6\}$ were determined by X-ray diffraction.

Introduction

Sterically hindered phosphinimine and phosphiniminato complexes have increasingly attracted attention in recent years,[1] not least because of their potential as olefin polymerisation catalysts.[2,3] A number of bulky phosphiniminato complexes are known in which the ligand acts as an N–N chelate (Chart 1, structures **A** and **B**),[4,5] while the dimetallation of bis(iminophosphorano)methanes may lead to N–C chelate complexes (**C**, **D**).[6,7] We have recently reported a number of early and late transition metal bi- and tri-dentate iminophosphine and bis(iminophosphorano)methyl complexes (*e.g.*, type **E**)[8] and found that C–N chelates can easily arise as the consequence of C–H activation (for example, to give **F**).[9] As a consequence we have become interested in alternative and more direct routes to C–N bidentate compounds of type **G**, in the expectation that the substitution of an N-donor in **A** by carbon would result in stronger donor properties of the ligand and different reactivity patterns. A number of C–N chelating iminophosphoranato complexes of main group elements are known.[10] We have reported recently the reactions of *N*-trimethylsilyliminophosphoranes with titanium and zirconium halides where dehalosilylation was a prominent reaction pathway.[11] Here we describe the reactivity of titanium and zirconium complexes towards *N*-aryliminophosphoranes $Ar^1{=}NPPh_2{-}CH_2Ar^2$ where dehalosilylation is not possible ($Ar^1 = 2,4,6\text{-}Me_3C_6H_2$; $Ar^2 = 4\text{-Bu}^tC_6H_4$).

Results and discussion

The new benzylic iminophosphorane $4\text{-Bu}^tC_6H_4CH_2P(Ph)_2{=}NC_6H_2Me_3\text{-}2,4,6$ **1**, prepared in good yield by oxidising $4\text{-Bu}^tC_6H_4CH_2PPh_2$ with mesityl azide, was chosen to explore the propensity of benzylic C–H bonds towards activation by titanium and zirconium complexes. Addition of $TiCl_4$ to a toluene solution of **1** at temperatures up to 25 °C leads to a dark-red precipitate which exhibits a single peak in the ^{31}P NMR spectrum, at δ 48.4 (see Table 1), indicative of the formation of an N-donor adduct. The spectroscopic and analytic parameters of the product are in agreement with the formulation $TiCl_4\{4\text{-Bu}^tC_6H_4CH_2P(Ph)_2{=}NC_6H_2Me_3\text{-}2,4,6\}$ **2** (Scheme 1). Variable-temperature NMR studies show that **2** is stable in toluene-d_8 for at least 30 min at temperatures up to 0 °C. However, on warming to 30 °C, additional signals are observed in the ^{31}P NMR spectrum, at δ 30.7 and 40.8.

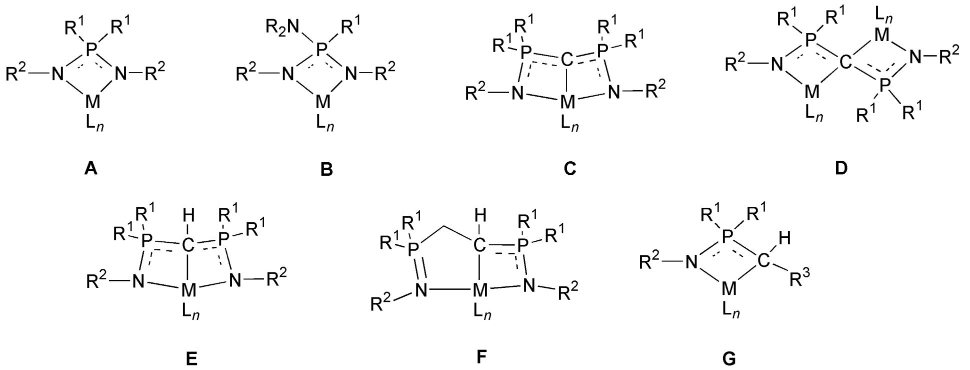


Chart 1

Table 1 NMR spectroscopic data for iminophosphorane compounds

Compound	NMR data
4-Bu^{t}C$_6$H$_4$CH$_2$P(Ph)$_2$=NC$_6$H$_2$Me$_3$-2,4,6 **1** (CDCl$_3$, 20 °C)	^{1}H NMR (300.13 MHz): δ 1.67 (s, 9H, CMe$_3$), 2.13 (s, 6H, 2CH$_3$), 2.33 (s, 3H, CH$_3$), 3.55 (d, J_{HP} = 12.96 Hz, 2H, CH$_2$), 6.80–7.75 (m, 16H, Ph). ^{13}C{^{1}H} NMR (75.46 MHz): δ 20.76 (s, *p*-CH$_3$), 21.85 (s, *o*-CH$_3$), 31.15 (s, C*Me*$_3$), 34.10 (s, *C*Me$_3$), 38.28 (d, J_{CP} = 60.37 Hz, 1C, CH$_2$), 124.93–149.05 (m, Ph). ^{31}P NMR (121.49 MHz): δ −10.12.
TiCl$_4${4-Bu^{t}C$_6$H$_4$CH$_2$P(Ph)$_2$=NC$_6$H$_2$Me$_3$-2,4,6} **2** (C$_6$D$_6$, 20 °C)	^{1}H NMR (300.13 MHz): δ 1.06 (s, 9H, CMe$_3$), 1.94 (s, 3H, CH$_3$), 2.50 (s, 6H, 2CH$_3$), 5.02 (d, J_{HP} = 17.32 Hz, 2H, CH$_2$), 6.39–7.41 (m, 16H, Ph). ^{13}C{^{1}H} NMR (C$_7$D$_8$, 20 °C, 75.46 MHz): δ 20.78 (s, *p*-CH$_3$), 22.30 (s, *o*-CH$_3$), 31.15 (s, C*Me*$_3$), 34.30 (s, *C*Me$_3$), 39.34 (br, CH$_3$), 124.52–150.29 (Ph). ^{31}P NMR (121.49 MHz): δ 48.44.
TiCl$_3${4-Bu^{t}C$_6$H$_4$CHP(Ph)$_2$=NC$_6$H$_2$Me$_3$-2,4,6} **3** (CD$_2$Cl$_2$, 20 °C)	^{1}H NMR (300.13 MHz): δ 1.14 (s, 9H, CMe$_3$), 1.96 (s, 3H, CH$_3$), 2.11 (s, 3H, CH$_3$), 2.47 (s, 3H, CH$_3$), 4.37 (d, J_{HP} = 11.4 Hz, H, CH), 6.48–8.13 (m, 16H, Ph). ^{13}C{^{1}H} NMR (75.46 MHz): δ 20.91 (s, CH$_3$), 21.74 (s, CH$_3$), 22.90 (s, CH$_3$), 31.33 (s, C*Me*$_3$), 34.39 (s, *C*Me$_3$), 125.68–149.42 (Ph). ^{31}P NMR (121.49 MHz): δ 30.29.[a]
Li[4-Bu^{t}C$_6$H$_4$CHP(Ph)$_2$=NC$_6$H$_2$Me$_3$-2,4,6] **4** (C$_6$D$_6$, 20 °C)	^{1}H NMR (300.13 MHz): δ 1.24 (s, 9H, CMe$_3$), 1.85 (s, 6H, 2CH$_3$), 2.22 (s, 3H, CH$_3$), 3.04 (d, J_{HP} = 13.87 Hz, 1H, CH), 6.79–7.79 (m, 16H, Ph). ^{13}C{^{1}H} NMR (75.46 MHz): δ 20.59 (s, CH$_3$), 21.42 (s, CH$_3$), 31.17 (s, C*Me*$_3$), 33.65 (s, *C*Me$_3$), 36.96 (d, J_{CP} = 138.1 Hz, CH), 119.81–138.36 (Ph). ^{31}P NMR (CDCl$_3$, 20 °C, 121.49 MHz): δ 11.66.
[4-Bu^{t}C$_6$H$_4$CH$_2$P(Ph)$_2$NHC$_6$H$_2$Me$_3$-2,4,6]$^+$Cl$^-$ **5** (C$_6$D$_6$, 20 °C)	^{1}H NMR (300.13 MHz): δ 1.09 (s, 9H, CMe$_3$), 1.93 (s, 3H, *p*-CH$_3$), 2.32 (s, 6H, *o*-CH$_3$), 5.63 (d, J_{HP} = 17.72 Hz, 2H, CH$_2$), 6.47–8.12 (m, 16H, Ph). ^{13}C{^{1}H} NMR (75.46 MHz): δ 20.87 (s, *p*-CH$_3$), 21.16 (s, *o*-CH$_3$), 31.46 (s, C*Me*$_3$), 34.45 (s, *C*Me$_3$), 122.06–150.18 (Ph).[a] ^{31}P NMR (121.49 MHz): δ 41.45 ppm.
ZrCl$_4${4-Bu^{t}C$_6$H$_4$CH$_2$P(Ph)$_2$=NC$_6$H$_2$Me$_3$-2,4,6} **6** (CD$_2$Cl$_2$, 20 °C)	^{1}H NMR (300.13 MHz): δ 1.18 (s, 9H, CMe$_3$), 2.13 (s, 3H, CH$_3$), 2.13 (s, 6H, 2CH$_3$), 5.02 (br, 2H, CH$_2$), 6.56–7.60 (m, 16H, Ph). ^{31}P NMR (121.49 MHz): δ 46.47.
ZrCl$_3${4-Bu^{t}C$_6$H$_4$CHP(Ph)$_2$=NC$_6$H$_2$Me$_3$-2,4,6} **7** (CDCl$_3$, 20 °C)	^{1}H NMR (300.13 MHz): δ 1.20 (s, 9H, CMe$_3$), 2.11 (s, 3H, CH$_3$), 2.12 (s, 3H, CH$_3$), 2.42 (s, 3H, CH$_3$), 3.92 (br, H, CH), 6.71–7.41 (m, 16H, Ph). ^{13}C{^{1}H} NMR (75.46 MHz): δ 21.33 (s, CH$_3$), 21.93 (s, CH$_3$), 22.95 (s, CH$_3$), 31.64 (s, C*Me*$_3$), 34.77 (s, *C*Me$_3$), 125.84–135.43 (Ph).[a] ^{31}P NMR (121.49 MHz): δ 21.28.
Zr(NMe$_2$)$_3${4-Bu^{t}C$_6$H$_4$CHP(Ph)$_2$=NC$_6$H$_2$Me$_3$-2,4,6} **8** (C$_6$D$_6$, 20 °C)	^{1}H NMR (300.13 MHz): δ 1.19 (s, 9H, CMe$_3$), 2.13 (br, 9H, CH$_3$), 3.07 (s, 18H, NMe$_2$), 3.15 (d, J_{HP} = 7.11 Hz, 1H, CH), 6.75–7.64 (m, 16H, Ph). ^{13}C{^{1}H} NMR (75.46 MHz): δ 20.59 (s, *p*-CH$_3$), 21.01 (br, *o*-CH$_3$), 31.34 (s, C*Me*$_3$), 33.80 (s, *C*Me$_3$), 39.34 (d, J_{CP} = 83.75 Hz, CH), 42.80 (s, NMe$_2$), 124.45–143.55 (Ph). ^{31}P NMR (121.49 MHz): δ 24.68.
ZrCl$_4${4-Bu^{t}C$_6$H$_4$CH(SiMe$_3$)P(Ph)$_2$=NC$_6$H$_2$Me$_3$-2,4,6} **9** (CD$_2$Cl$_2$, 20 °C)	^{1}H NMR (300.13 MHz): δ 0.19 (s, 9H, SiMe$_3$), 1.17 (s, 9H, CMe$_3$), 2.24 (s, 6H, *o*-CH$_3$), 2.28 (s, 3H, *p*-CH$_3$), 4.04 (d, J_{HP} = 15.63 Hz, 1H, CH), 6.4–7.83 (m, 16H, Ph). ^{13}C{^{1}H} NMR (75.46 MHz): δ 5.01 (s, SiMe$_3$), 22.77 (s, *p*-CH$_3$), 23.54 (s, *o*-CH$_3$), 33.28 (s, C*Me*$_3$), 35.74 (d, J_{CP} = 60.74 Hz, CH), 36.64 (s, *C*Me$_3$), 121.98–154.03 (Ph). ^{31}P NMR (121.49 MHz): δ 45.47.
4-Bu^{t}C$_6$H$_4$CH(SiMe$_3$)P(Ph)$_2$=NC$_6$H$_2$Me$_3$-2,4,6 **10** (C$_6$D$_6$, 20 °C)	^{1}H NMR (300.13 MHz): δ 0.09 (s, 9H, SiMe$_3$), 1.19 (s, 9H, CMe$_3$), 2.31 (s, 3H, CH$_3$), 2.38 (s, 6H, 2CH$_3$), 3.3 (d, J_{HP} = 13.90 Hz, 1H, CH), 6.80–7.90 (m, 16H, Ph). ^{13}C{^{1}H} NMR (75.46 MHz): δ 0.24 (s, SiMe$_3$), 20.61 (s, *p*-CH$_3$), 22.46 (s, *o*-CH$_3$), 31.22 (s, C*Me*$_3$), 34.10 (s, *C*Me$_3$), 42.24 (d, J_{CP} = 80.78 Hz, CH), 124.90–148.52 (Ph). ^{31}P NMR (121.49 MHz): δ −5.21.

[a] The P–*C*H ^{13}C NMR signal could not be located.

The latter is typical of an aminophosphonium cation, [4-Bu^{t}C$_6$H$_4$CH$_2$P(Ph)$_2$–NHC$_6$H$_2$Me$_3$-2,4,6]$^+$, formed by protonation of the ligand. This implies that during the reaction HCl must have been produced. Since care was taken to exclude trace hydrolysis, a source of protons is C–H activation of **2** to give HCl and TiCl$_3${4-Bu^{t}C$_6$H$_4$CHP(Ph)$_2$=NC$_6$H$_2$Me$_3$-2,4,6} **3**. A phosphorus chemical shift of *ca.* δ 30 would be in agreement with that formulation. Interestingly, the addition of triethylamine or proton sponge to a solution of **2** before the reaction mixture is allowed to warm to room temperature prevented the formation of **3** or of phosphonium cations and instead led to simple displacement of the iminophosphine ligand to give TiCl$_4$(NEt$_3$)$_2$.

The formation of **3** was confirmed by the independent synthesis of this compound from Li[4-Bu^{t}C$_6$H$_4$CHP(Ph)$_2$=NC$_6$H$_2$Me$_3$-2,4,6] **4** and TiCl$_4$. The product was isolated as a yellow microcrystalline solid which showed the expected ^{31}P NMR signal at δ 30.3. The identity of the second by-product was confirmed by passing HCl through a solution of **1**, which resulted in the precipitation of [4-Bu^{t}C$_6$H$_4$CH$_2$P(Ph)$_2$NHC$_6$H$_2$Me$_3$-2,4,6]Cl **5**. The compound exhibits a ^{31}P NMR signal at δ 41.5. Efforts to prepare alkyl derivatives of **3** by alkylation with MeMgCl or PhCH$_2$MgCl were unsuccessful. Monitoring these reactions by means of ^{31}P NMR spectroscopy showed that complex product mixtures were formed.

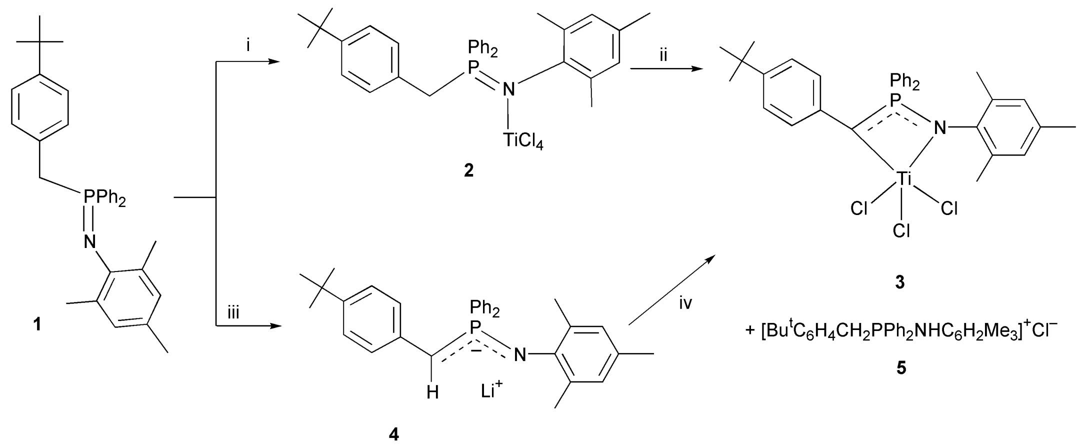
The reaction of **1** with ZrCl$_4$ in toluene affords ZrCl$_4${4-Bu^{t}C$_6$H$_4$CH$_2$P(Ph)$_2$=NC$_6$H$_2$Me$_3$-2,4,6} **6** in high yield (Scheme 2), characterised by a ^{31}P NMR signal at δ 46.5. In contrast to **2**, compound **6** is thermally stable and shows no sign of further reaction on heating to 110 °C in toluene for 15 h. The compound is presumably polymeric and poorly soluble in dichloromethane, while in thf the iminophosphine ligand is displaced to give $ZrCl_4(thf)_2$. This and the reaction of **2** with NEt_3 indicate that neutral monodentate iminophosphines are comparatively weak ligands towards early transition metals.

The failure to observe C–H activation to give a zirconium analogue of **3** is, however, not due to thermodynamic instability since the product of such a reaction, $ZrCl_3\{4\text{-}Bu^tC_6H_4CHP(Ph)_2{=}NC_6H_2Me_3\text{-}2,4,6\}$ **7**, is readily accessible in 75% yield by heating **4** and $ZrCl_4$ in toluene at 90 °C. Compound **7** is obtained as a colourless microcrystalline solid and is characterised by a ^{31}P NMR signal at δ 21.3. Although this product is thermally stable, attempts to use it as starting material for zirconium alkyl complexes were not successful. For example, the reaction with methylmagnesium chloride in diethyl ether gave a large number of unidentifiable products.

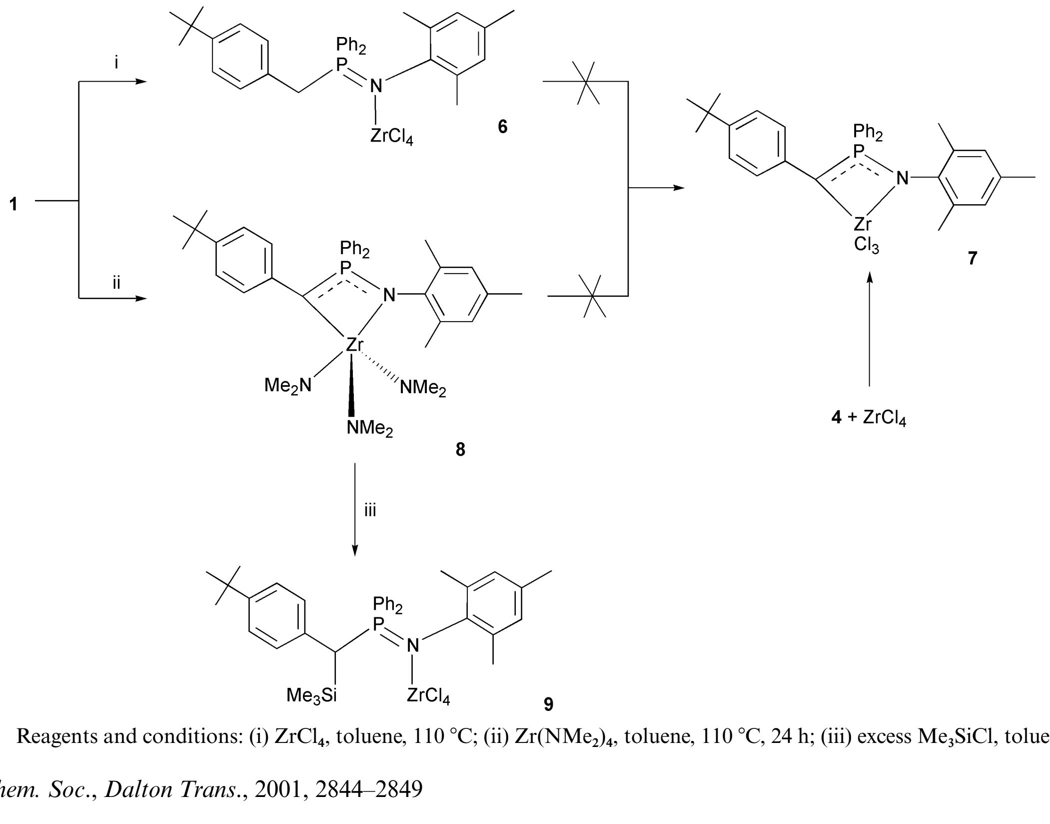
In contrast to the reaction between **1** and $ZrCl_4$, direct metallation of **1** is achieved by heating **1** with $Zr(NMe_2)_4$ in refluxing toluene for 24 h to give $Zr(NMe_2)_3\{4\text{-}Bu^tC_6H_4CHP(Ph)_2{=}NC_6H_2Me_3\text{-}2,4,6\}$ **8** as colourless crystals. Remarkably, the similar reaction between $Zr(NMe_2)_4$ and $4\text{-}Bu^tC_6H_4CH_2P(Ph)_2{=}NSiMe_3$ does not show any signs of reactivity, even after prolonged heating. Treatment of **8** with an excess of Me_3SiCl did not lead to the formation of **7** but instead proceeded with C-silylation of the ligand, to give a new iminophosphine adduct, $ZrCl_4\{4\text{-}Bu^tC_6H_4CH(SiMe_3)P(Ph)_2{=}NC_6H_2Me_3\text{-}2,4,6\}$ **9**. To confirm the identity of the product, the iminophosphine $\{4\text{-}Bu^tC_6H_4CH(SiMe_3)P(Ph)_2{=}NC_6H_2Me_3\text{-}2,4,6\}$ **10** was independently prepared from Me_3SiCl and **4** as colourless crystals in good yield. Typically, the ^{31}P NMR signal of **9** is down-field shifted by *ca.* 50 ppm with respect to that of uncoordinated **10** (*cf.* Table 1).

Ethene polymerisation tests were conducted with **3**, **7**, **8** and **9** activated with methylaluminoxane (Al : Zr = 1000 : 1) in toluene under 1 bar ethene pressure at room temperature, with 5 min reaction time. The compounds displayed modest polymerisation activity, *ca.* 0.9–1.6 × 10^4 g PE (mol catalyst)$^{-1}$ h^{-1} bar^{-1}.

The molecular structures of **1** and **8** were confirmed by X-ray diffraction. Selected bond lengths and angles are collected in Table 2. Compound **1** (Fig. 1) shows the expected geometry with tetrahedral phosphorus, a P=N double bond length of 1.5620(13) Å and sp^2-hybridised nitrogen, with a P(1)–N(1)–C(1) angle of 127.14(10)°. Complex **8** (Fig. 2) is based on a



Scheme 1 Reagents and conditions: (i) $TiCl_4$, toluene, −78 to 0 °C; (ii) toluene, >10 °C; (iii) Bu^nLi, toluene, −78 °C to r.t.; (iv) $TiCl_4$, toluene, 25 °C.



Scheme 2 Reagents and conditions: (i) $ZrCl_4$, toluene, 110 °C; (ii) $Zr(NMe_2)_4$, toluene, 110 °C, 24 h; (iii) excess Me_3SiCl, toluene reflux.

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

$4\text{-Bu}^tC_6H_4CH_2P(Ph)_2{=}NC_6H_2Me_3\text{-}2,4,6$ **1**			
P(1)–N(1)	1.5620(13)	P(1)–C(22)	1.815(2)
P(1)–C(10)	1.809(2)	P(1)–C(16)	1.825(2)
N(1)–C(1)	1.409(2)	C(22)–C(23)	1.509(2)
N(1)–P(1)–C(22)	110.62(7)	P(1)–N(1)–C(1)	127.14(10)
N(1)–P(1)–C(10)	115.24(7)	N(1)–P(1)–C(16)	113.87(7)
C(10)–P(1)–C(16)	105.26(7)	C(10)–P(1)–C(22)	105.77(7)
$Zr(NMe_2)_3\{4\text{-Bu}^tC_6H_4CHP(Ph)_2{=}NC_6H_2Me_3\text{-}2,4,6\}$ **8**			
Zr–N(1)	2.262(3)	Zr–N(2)	2.048(3)
Zr–N(3)	2.049(3)	Zr–N(2)	2.064(3)
Zr–C(1)	2.560(3)	N(1)–P(1)	1.631(3)
C(1)–P(1)	1.735(3)	C(1)–C(131)	1.487(4)
N(1)–C(11)	1.436(4)	P(1)–C(121)	1.811(3)
N(2)–C(21)	1.456(5)	N(2)–C(22)	1.457(5)
N(1)–Zr–C(1)	63.93(9)	N(1)–P(1)–C(1)	99.27(14)
Zr–N(1)–C(11)	129.7(2)	Zr–C(1)–C(131)	127.9(2)
N(4)–Zr–C(1)	148.37(11)	N(2)–Zr–C(1)	106.05(11)
N(3)–Zr–C(1)	88.67(11)	N(1)–Zr–N(2)	118.54(11)
N(1)–Zr–N(3)	130.27(11)	N(1)–Zr–N(4)	89.26(10)
N(2)–Zr–N(3)	108.27(12)	N(2)–Zr–N(4)	101.37(12)
N(3)–Zr–N(4)	97.53(12)	Zr–N(2)–C(21)	133.1(2)
Zr–N(2)–C(22)	116.1(2)	Zr–N(3)–C(31)	124.4(3)
Zr–N(3)–C(32)	124.5(3)	Zr–N(4)–C(41)	119.8(2)
Zr–N(4)–C(42)	128.5(2)	C(21)–N(2)–C(22)	110.0(3)

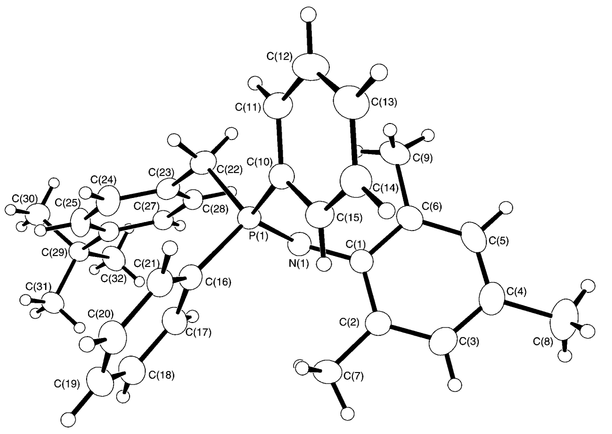


Fig. 1 Molecular structure of $4\text{-Bu}^tC_6H_4CH_2P(Ph)_2{=}NC_6H_2Me_3\text{-}2,4,6$ **1**, showing the atomic numbering scheme. Ellipsoids are drawn at 40% probability.

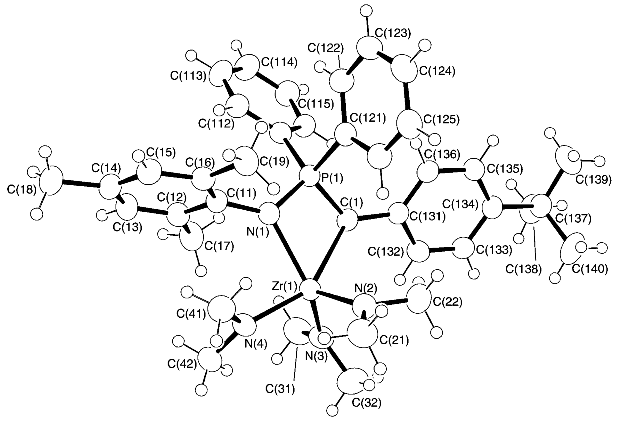


Fig. 2 Molecular structure of $Zr(NMe_2)_3\{4\text{-Bu}^tC_6H_4CHP(Ph)_2{=}NC_6H_2Me_3\text{-}2,4,6\}$ **8**, showing the atomic numbering scheme. Ellipsoids are drawn at 40% probability.

strongly distorted trigonal bipyramid, with C(1) and the amido-nitrogen N(4) in roughly axial positions [C(1)–Zr–N(4) = 148.37(11)°]. The distortion is caused by the narrow bite angle of the iminophosphoranyl ligand, N(1)–Zr–C(1) = 63.93(9)°. As a consequence of this geometry, the Zr–N(4)Me_2 bond approximately *trans* to C(1) is longer than the Zr–N bonds to the other two dimethylamido ligands, 2.064(3) Å *versus* 2.049(3) Å. All the nitrogen atoms in **8** are trigonal-planar. The P(1)–N(1)–C(11) angle in **8** [126.5(2)°] differs only marginally from the corresponding angle in **1** [127.14(10)°], while the P–C–C angle around the benzylic carbon atom changes from close to tetrahedral in **1** [P(1)–C(22)–C(23) = 114.80(11)°] towards trigonal-planar in **8** [P(1)–C(1)–C(131) = 127.9(2)°]. The P–N bond in **8** of 1.631(3) Å is significantly longer than that in **1** [1.5620(13) Å]. The N–P–C angle in **1** of 110.62(7)° is reduced in **8** to 99.27(14)°. The C–N–C angles of the NMe_2 ligands are close to 111° in all cases. However, the Zr–N–Me angles are subject to considerable variation; for example, the Zr–N–C angles for N(2) range from 116.1(2)° to 133.1(2)°. This angular distortion is even more pronounced than in the related sterically hindered bis(imino)pyrrolato complex $Zr(NMe_2)_3\{C_4H_2N(CH{=}NC_6H_3Pr^i{}_2\text{-}2,6)_2\}$.[12] Variable Zr–N–Me angles have been found previously, *e.g.* in the case of $Zr(NMe_2)_6Li_2(thf)_2$.[13]

Conclusion

Aryliminophosphoranes, $Ar^1{=}NPPh_2{-}CH_2Ar^2$, act as relatively weak donor ligands towards titanium and zirconium tetrachloride but on metallation form stable C–N chelates. C–H activation of the benzylic CH_2 group is possible and facile for $TiCl_4$. There is no such C–H activation with $ZrCl_4$ but it is possible with $Zr(NMe_2)_4$ under forcing conditions. The resulting five-coordinate complexes contain a new type of sterically hindered C–N chelate ligands and show modest ethene polymerisation activity.

Experimental

All manipulations were performed under a dinitrogen atmosphere unless specified using Schlenk techniques. Solvents were distilled under N_2 over sodium–benzophenone (thf, diethyl ether), sodium (toluene), sodium–potassium alloy (light petroleum, bp 40–60 °C), or CaH_2 (dichloromethane). NMR solvents were dried over activated molecular sieves and degassed by several freeze–thaw cycles. NMR spectra were recorded on Bruker DPX300 or DRX500 spectrometers. Chemical shifts are reported in ppm and referenced to residual solvent resonances (^{1}H, ^{13}C). ^{31}P NMR chemical shifts are relative to external 85% H_3PO_4. $ZrCl_4$ was freshly sublimed under nitrogen before use (400–450 °C, 1 atm). Mesityl azide[14] and $Zr(NMe_2)_4$[15] were prepared according to literature procedures; 4-Bu^t$C_6H_4CH_2PPh_2$ was prepared following the procedure for $PhCH_2PPh_2$.[16]

Preparations

4-Bu^t$C_6H_4CH_2P(Ph)_2$=$NC_6H_2Me_3$-2,4,6 1. To a 250 mL round bottom flask charged with freshly distilled 4-Bu^t-$C_6H_4CH_2PPh_2$ (11.20 g, 33.73 mmol) and 100 mL of light petroleum, at 0 °C was added dropwise 2,4,6-trimethylaniline azide (6.00 g, 37.3 mmol) over a period of 15 min. A light precipitate started to form. The mixture was allowed to warm slowly to room temperature and stirred for 3 h. The precipitate was collected and washed with light petroleum (50 mL) to yield analytically pure **1** (12.30 g, 78%). Further purification was achieved by recrystallisation from toluene–light petroleum (1 : 10) to yield colourless crystals, yield 9.70 g (60%). Found (calcd.): C, 82.3 (82.6); H, 7.9 (7.8); N, 2.7 (3.0)%.

$TiCl_4${4-Bu^t$C_6H_4CH_2P(Ph)_2$=$NC_6H_2Me_3$-2,4,6} 2. To a solution of **1** (2.13 g, 4.58 mmol) in toluene (50 mL) at −78 °C was added dropwise $TiCl_4$ (0.87 g, 4.58 mmol) in toluene (3.5 mL) over a period of 15 min. A dark red precipitate formed after 30 min which was collected at low temperature and dried under vacuum before being allowed to warm to ambient temperature, to give **2** (1.90 g, 63%). The solid was stable under an inert atmosphere but there were signs of dissociation in solution. Found (calcd.): C, 58.9 (58.7); H, 5.8 (5.5); N, 1.9 (2.1); Cl, 21.4 (21.6)%.

$TiCl_3${4-Bu^t$C_6H_4CHP(Ph)_2$=$NC_6H_2Me_3$-2,4,6} 3. To a solution of 4-Bu^t$C_6H_4CH_2P(Ph)_2$=$NC_6H_2Me_3$-2,4,6 (1.50 g, 3.22 mmol) in toluene (40 mL) was added dropwise Bu^{n}Li (2.01 mL, 3.22 mmol) at ambient temperature. After stirring for 2 h, a solution of $TiCl_4$ (0.61 g, 3.22 mmol) in toluene (20 mL) was added dropwise at −78 °C. The mixture was allowed to warm to room temperature, stirred for 12 h and filtered. Concentrating to *ca.* 10 mL and adding light petroleum (30 mL) gave **3** as a yellow solid, yield 0.9 g (45%). Found (calcd.): C, 63.7 (62.9); H, 6.3 (5.7); N, 2.4 (2.3)%.

Li[4-Bu^t$C_6H_4CHP(Ph)_2$=$NC_6H_2Me_3$-2,4,6] 4. Bu^{n}Li (17 mL, 27.2 mmol) was added dropwise to a suspension of compound **1** in light petroleum at −78 °C. The mixture was allowed to warm slowly to ambient temperature and stirred for 3 h. The light yellow precipitate was filtered and washed twice with light petroleum (2 × 20 mL) to remove excess Bu^{n}Li, yield 9.50 g (84%). Found (calcd.): C, 80.6 (81.5); H, 7.6 (7.5); N, 3.1 (3.0)%.

[4-Bu^t$C_6H_4CH_2P(Ph)_2NHC_6H_2Me_3$-2,4,6]$^+$$Cl^-$ 5. Dried hydrogen chloride was slowly passed through a solution of **1** (0.54 g, 1.16 mmol) in toluene for 15 min. The volume was reduced to 5 mL, and light petroleum (5 mL) was added. A colourless solid formed after 12 h which was filtered off and washed with warm light petroleum (2 × 10 mL), yield 0.43 g (74%). Found (calcd.): C, 75.5 (76.6); H, 7.1 (7.4); N, 2.7 (2.8); Cl, 7.1 (8.9)%.

$ZrCl_4${4-Bu^t$C_6H_4CH_2P(Ph)_2$=$NC_6H_2Me_3$-2,4,6} 6. A mixture of **1** (1.50 g, 33.23 mmol) and $ZrCl_4$ (0.75 g, 3.23 mmol) in toluene (50 mL) was heated to 110 °C for 15 h to give an insoluble white powder which was collected, washed with warm toluene and dried under reduced pressure for 12 h, yield 1.90 g (84%). Found (calcd.): C, 54.0 (55.0); H, 5.5 (5.2); N, 1.8 (2.0)%.

$ZrCl_3${4-Bu^t$C_6H_4CHP(Ph)_2$=$NC_6H_2Me_3$-2,4,6} 7. To a solution of **1** (1.50 g, 3.22 mmol) in toluene (40 mL) was added dropwise Bu^{n}Li (2.01 mL, 3.22 mmol). After stirring for 2 h, $ZrCl_4$ (0.75 g, 3.22 mmol) was added at room temperature. The mixture was heated to 90 °C, stirred for 12 h and filtered. The solvent was removed and dichloromethane (20 mL) was added followed by light petroleum (30 mL) to give **7**·0.5CH_2Cl_2, yield 1.6 g (75%). Found (calcd.): C, 53.1 (55.3); H, 5.5 (5.3); N, 1.7 (1.6); Cl, 19.8 (20.1)%.

$Zr(NMe_2)_3${4-Bu^t$C_6H_4CHP(Ph)_2$=$NC_6H_2Me_3$-2,4,6} 8. In an inert atmosphere drybox compound **1** (1.00 g, 2.15 mmol) and $Zr(NMe_2)_4$ (0.56 g, 2.15 mmol) were weighed into a 50 mL Schlenk flask and dissolved in toluene (20 mL). The mixture was heated at 110 °C for 24 h. After filtration, toluene was reduced to half the volume and kept at *ca.* 4 °C for 2 d to give a colourless crystalline product, yield 1.10 g (74%). Found (calcd.): C, 65.4 (66.3); H, 7.3 (7.7); N, 6.4 (8.1)%.

Reaction of $Zr(NMe_2)_3${4-Bu^t$C_6H_4CHP(Ph)_2$=$NC_6H_2Me_3$-2,4,6} 8 with Me_3SiCl. To a solution of **8** (0.25 g, 0.36 mmol) in toluene (20 mL) was added Me_3SiCl (3 mL) *via* syringe. The mixture was stirred and heated to reflux for 12 h. Removal of volatiles yielded an oily material which, according to the ^{1}H and ^{13}P NMR spectra, consisted mainly of **9**.

4-Bu^t$C_6H_4CH(SiMe_3)P(Ph)_2$=$NC_6H_2Me_3$-2,4,6 10. In an inert atmosphere drybox compound **4** (3.30 g, 7.00 mmol) was weighed into a 100 mL Schlenk flask and dissolved in toluene (50 mL). An excess of trimethylchlorosilane (1.52 g, 13.99 mmol) was added. The mixture was heated at 70 °C for 2 h and filtered. After removal of volatiles, the product was recrystallised from light petroleum, yield 2.5 g (66%). Found (calcd.): C, 78.0 (78.2); H, 8.2 (8.3); N, 2.3 (2.6)%.

$ZrCl_4${4-Bu^t$C_6H_4CH(SiMe_3)P(Ph)_2$=$NC_6H_2Me_3$-2,4,6} 9. To a solution of **10** (1.98 g, 3.68 mmol) in toluene (50 mL) was added solid $ZrCl_4$ (0.86 g, 3.68 mmol) in one portion. The mixture was heated to 90 °C overnight. Cooling to −78 °C for 10 min gave a white solid which was filtered, washed with light petroleum (20 mL) and dried at room temperature, yield 1.7 g (60%).

X-Ray crystallography

Suitable crystals of **1** and **8** were coated in an inert perfluoropolyether oil and mounted in a nitrogen stream at 150 K on a Nonius Kappa CCD area-detector diffractometer. Data collection was performed using Mo-Kα radiation ($\lambda = 0.71073$ Å) with the CCD detector placed 30 mm from the sample *via* a mixture of 1° φ and ω scans at different θ and κ settings using the program COLLECT.[17] The raw data were processed to produce conventional data using the program DENZO-SMN.[18] The datasets were corrected for absorption using the program SORTAV.[19] The structures were solved by heavy-atom methods using SHELXS-97[20] and were refined by full-matrix least squares refinement (on F^2) using SHELXL-97.[21] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained to idealised positions. Crystal data are collected in Table 3.

CCDC reference numbers 165391 and 165392.

See http://www.rsc.org/suppdata/dt/b1/b105038a/ for crystallographic data in CIF or other electronic format.

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Table 3 Crystal data for iminophosphorane complexes

	1	**8**
Formula	$C_{32}H_{36}NP$	$C_{38}H_{52}N_4PZr$
Formula weight	465.59	687.03
Crystal system	Orthorhombic	Triclinic
Space group	*Pbca*	$P\bar{1}$
a/Å	20.5350(3)	10.6664(6)
b/Å	10.3459(2)	13.6098(5)
c/Å	24.7566(6)	14.1992(8)
α/°	90	92.661(3)
β/°	90	111.753(3)
γ/°	90	104.507(3)
V/Å^3	5259.6(2)	1831.08(16)
D_c/g cm^{-3}	1.176	1.246
Z	8	2
μ/mm^{-1}	0.125	0.374
Independent/observed reflections	5093/4379	7079/6024
R_{int} [a]	0.0599	0.0658
R_1 $[I > 2\sigma(I)]$ [b]	0.0434	0.0528
wR_2 (all data) [c]	0.1197	0.1502

[a] $\Sigma|F_o^2 - F_o^2 \text{(mean)}|/\Sigma F_o^2$. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = [2F_c^2 + \max(F_o^2, 0)]/3$.

References

1 Reviews: K. Dehnicke, M. Krieger and W. Massa, *Coord. Chem. Rev.*, 1999, **182**, 19; K. Dehnicke and F. Weller, *Coord. Chem. Rev.*, 1997, **158**, 103.

2 M. Grün, F. Weller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1997, **623**, 224; D. W. Stephan, J. C. Steward, F. Guérin, R. E. v. H. Spence, W. Xu and D. G. Harrison, *Organometallics*, 1999, **18**, 1116; D. W. Stephan, F. Guérin, R. E. v. H. Spence, L. Koch, X. Gao, S. J. Brown, J. W. Swabey, Q. Wang, W. Xu, P. Zoricak and D. G. Harrison, *Organometallics*, 1999, **18**, 2046; C. A. Carraz and D. W. Stephan, *Organometallics*, 2000, **19**, 3791; C. M. Ong, P. McKarns and D. W. Stephan, *Organometallics*, 1999, **18**, 4197.

3 W. Keim, R. Appel, A. Storeck, C. Krüger and R. Goddard, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 116; R. Vollmershaus, P. Shao, N. J. Taylor and S. Collins, *Organometallics*, 1999, **18**, 2731.

4 M. Witt, H. W. Roesky, D. Stalke, F. Pauer, T. Henkel and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1989, 2173; M. Witt, D. Stalke, H. W. Roesky and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1991, 663.

5 V. D. Romanenko, V. F. Shul'gin, A. I. Brusilovets, V. V. Skopenko and L. N. Markovskii, *Zh. Obshch. Khim.*, 1982, **52**, 2648; V. D. Romanenko, V. F. Shul'gin, A. I. Brusilovets, V. V. Skopenko and L. N. Markovskii, *Chem. Abstr.*, 1982, **98**, 107410j; V. D. Romanenko, V. F. Shul'gin, A. I. Brusilovets, V. V. Skopenko and L. N. Markovskii, *Zh. Obshch. Khim.*, 1983, **53**, 1428; V. D. Romanenko, V. F. Shul'gin, A. I. Brusilovets, V. V. Skopenko and L. N. Markovskii, *Chem. Abstr.*, 1983, **99**, 175897; V. D. Romanenko, V. F. Shul'gin, V. V. Skopenko and L. N. Markovskii, *Zh. Obshch. Khim.*, 1984, **54**, 2791; V. D. Romanenko, V. F. Shul'gin, V. V. Skopenko and L. N. Markovskii, *Zh. Obshch. Khim.*, 1985, **55**, 538; V. D. Romanenko, V. F. Shul'gin, V. V. Skopenko and L. N. Markovskii, *Chem. Abstr.*, 1985, **103**, 142085a; L. M. Markovskii, V. D. Romanenko, V. F. Shul'gin, A. V. Ruban, A. N. Chernega, M. Y. Antipin and Y. T. Struchkov, *Zh. Obshch. Khim.*, 1985, **55**, 1752; L. M. Markovskii, V. D. Romanenko, V. F. Shul'gin, A. V. Ruban, A. N. Chernega, M. Y. Antipin and Y. T. Struchkov, *Chem. Abstr.*, 1986, **105**, 70457q.

6 C. M. Ong and D. W. Stephan, *J. Am. Chem. Soc.*, 1999, **121**, 2939; A. Kasani, R. P. Kamalesh Babu, R. McDonald and R. G. Cavell, *Angew. Chem., Int. Ed.*, 1999, **38**, 1483; R. G. Cavell, R. P. Kamalesh Babu, A. Kasani and R. McDonald, *J. Am. Chem. Soc.*, 1999, **121**, 5805; A. Kasani, R. McDonald and R. G. Cavell, *Chem. Commun.*, 1999, 1993; K. Aparna, R. McDonald, M. Ferguson and R. G. Cavell, *Organometallics*, 1999, **18**, 4241; K. Aparna, M. Ferguson and R. G. Cavell, *J. Am. Chem. Soc.*, 2000, **122**, 726; R. P. Kamalesh Babu, R. McDonald and R. G. Cavell, *Chem. Commun.*, 2000, 481.

7 Review: R. G. Cavell, R. P. Kamalesh Babu and K. Aparna, *J. Organomet. Chem.*, 2001, **617–618**, 158.

8 S. Al-Benna, M. J. Sarsfield, M. Thornton-Pett, D. L. Ormsby, P. J. Maddox, P. Brès and M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 2000, 4247.

9 M. J. Sarsfield, M. Thornton-Pett and M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 1999, 3329.

10 H. Schmidbaur and G. Jonas, *Chem. Ber.*, 1967, **100**, 1120; A. Müller, B. Neumüller and K. Dehnicke, *Chem. Ber.*, 1996, **129**, 253; A. Müller, B. Neumüller and K. Dehnicke, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2350; F. López-Ortiz, E. Peláez-Arango, B. Tejerina, E. Pérez-Carreno and S. García-Granda, *J. Am. Chem. Soc.*, 1995, **117**, 9972; A. Steiner and D. Stalke, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1752; S. Wingerter, H. Gornitzka, G. Bertrand and D. Stalke, *Eur. J. Inorg. Chem.*, 1999, 173; P. B. Hitchcock, M. F. Lappert, P. G. H. Uiterweerd and Z. X. Wang, *J. Chem. Soc., Dalton Trans.*, 1999, 3413.

11 M. J. Sarsfield, M. Said, M. Thornton-Pett, L. A. Gerrard and M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 2001, 822.

12 D. M. Dawson, D. A. Walker, M. Thornton-Pett and M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 2000, 459.

13 M. H. Chisholm, C. E. Hammond and J. C. Huffman, *Polyhedron*, 1988, **7**, 2515.

14 I. Ugi, H. Perlinger and L. Behringer, *Chem. Ber.*, 1958, **91**, 2330.

15 D. C. Bradley and I. M. Thomas, *Proc. Chem. Soc., London*, 1956, 225; D. C. Bradley and I. M. Thomas, *Proc. Chem. Soc., London*, 1960, 3857.

16 V. D. Bianco and S. Doronzo, *Inorg. Synth.*, 1976, **16**, 159.

17 COLLECT, Data collection software, Nonius B.V., Delft, 1999.

18 Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1996, **276**, 307.

19 R. H. Blessing, *Acta Crystollogr., Sect. A*, 1995, **51**, 33.

20 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

21 G. M. Sheldrick, SHELXL-97, Program for crystal structure refinement, University of Göttingen, 1997.