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The reactivity of trimethylsilyliminophosphines towards titanium and zirconium halides

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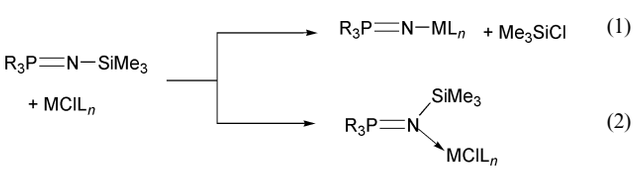
Zirconium tetrachloride reacted with $C_2H_4(Ph_2P{=}NSiMe_3)_2$-1,2 **1** under C–H activation to give the NCN chelate complex $ZrCl_3\{\kappa^3\text{-}N,C,N'\text{-}C_2H_3(Ph_2P{=}NSiMe_3)_2\}$, while the reaction with $C_5H_3N(Ph_2P{=}NSiMe_3)_2$-2,6 gave an *N*-donor adduct. Cp^*TiCl_3 reacts with trimethylsilyliminophosphines under dehalosilylation in all cases. In contrast to **1**, the potentially C–N chelating benzylphosphinimine $(4\text{-}Bu^tC_6H_4CH_2)Ph_2P{=}NSiMe_3$ undergoes dehalosilylation with $TiCl_4$ in preference to C–H activation, while prolonged reflux with $ZrCl_4$ affords the salt $[4\text{-}Bu^tC_6H_4CH_2P(Ph)_2NHSiMe_3]_2[Zr_2Cl_{10}]$. The molecular structures of the latter, $ZrCl_3\{C_2H_3(Ph_2PNSiMe_3)_2\}$, $C_5H_3N(Ph_2P{=}NTiCl_2Cp^*)_2$-2,6, and $TiCl_2Cp^*\{N{=}PPh_2CH_2C_6H_4Bu^t\text{-}4\}$ have been determined by X-ray diffraction.

Introduction

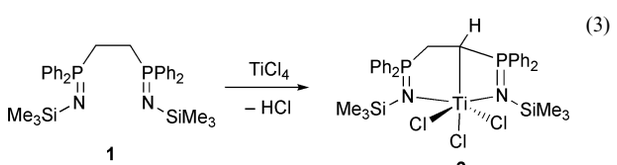
Trimethylsilyl substituted phosphinimines $R_3P{=}NSiMe_3$ are known to react with Lewis acidic metal halides to give phosphinimido complexes *via* a dehalosilylation reaction (eqn. 1).[1]



(1)

(2)

Titanium tris(*t*-butyl)phosphinimido complexes formed in this way have proved to be highly active ethene polymerisation catalysts.[2] Alternatively, silyl phosphinimines may simply form *N*-donor adducts (eqn. 2), some of which have proved to be thermally surprisingly stable.[1,3] As part of an exploration of the coordination chemistry of oligodentate P=N ligands and possible applications to catalysis,[4] we recently reported that 1,2-bis[diphenyl(trimethylsilylimino)phosphoranyl]ethane **1** reacts with $TiCl_4$ not under dehalosilylation and formation of titanium imido complexes as expected, but undergoes C–H activation and HCl elimination to give the red-purple complex **2** (eqn. 3).[5] We report here on the reaction of **1** and related

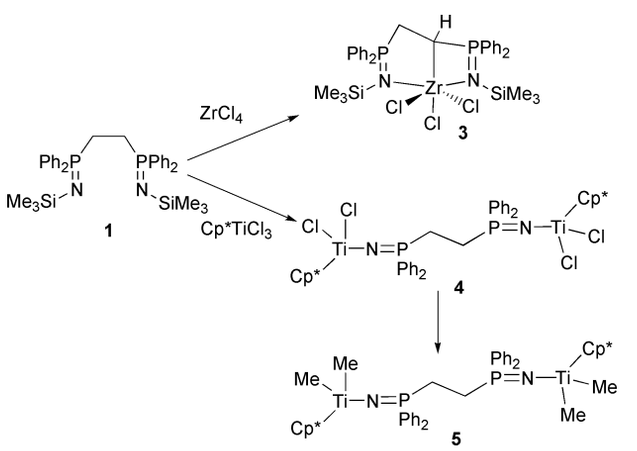


(3)

trimethylsilyliminophosphine ligands with $TiCl_4$, $ZrCl_4$ and Cp^*TiCl_3 ($Cp^* = \eta\text{-}C_5Me_5$).

Results and discussion

The reaction of 1,2-bis[diphenyl(trimethylsilylimino)phosphoranyl]ethane **1** with $ZrCl_4$ in dichloromethane at room temperature leads to the formation of a poorly soluble white precipitate. Comparison of the NMR data of this product with those of **2** suggested that the analogous zirconium complex **3** had been formed (Scheme 1). The CH_2CH bridge gives rise to a



Scheme 1

characteristic set of three multiplets in the ^1H NMR spectrum, at δ 1.07 (CH), 2.63 and 2.96, which each show coupling to two protons and two phosphorus atoms. As is typical for phosphinimine *N*-donor adducts, the ^{31}P NMR chemical shifts are found at comparatively positive values, at δ 28.5 and 39.1, similar to those of aminophosphonium salts (*e.g.* compound **13** below: δ 40.4).

Compound **3** retains variable amounts of dichloromethane of crystallisation. The bulk material analysed for $\mathbf{3}\cdot CH_2Cl_2$, while after some attempts of slow recrystallisation from dichloromethane crystals of $\mathbf{3}\cdot 2CH_2Cl_2$ were obtained which proved suitable for X-ray diffraction. The crystal structure (Fig. 1) confirmed the NMR assignments. Selected bond distances and angles are collected in Table 1. Unfortunately the crystal suffered from solvent loss during data collection, in addition to disorder problems (see Experimental section) and did not give high quality diffraction data. Zirconium is in a distorted octahedral environment containing a four- and a five-membered C–N chelate ring. The Zr–Cl(1) bond *trans* to the zirconium–carbon bond is slightly longer [2.477(2) Å] than

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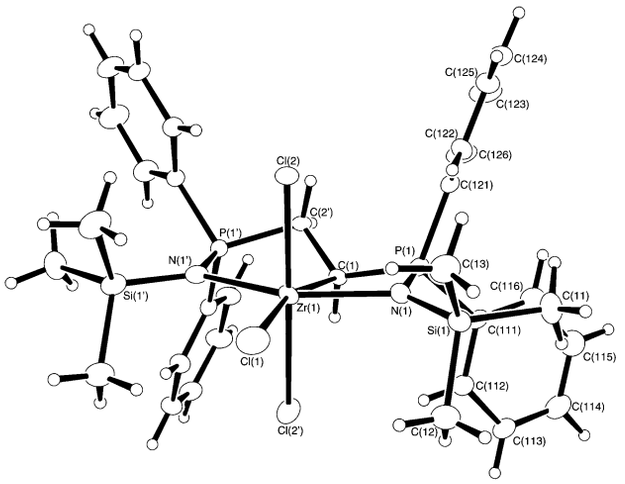


Fig. 1 Molecular structure of $ZrCl_3\{Me_3SiNP(Ph_2)CHCH_2P(Ph_2)$-$NSiMe_3\}$ **3**, showing the atomic numbering scheme. Ellipsoids are drawn at 40% probability. Note that the $CHCH_2$ backbone is disordered 50 : 50 over two positions, one of which is shown.

the other two Zr–Cl distances [2.4580(13) Å]. By comparison, the Zr–C(1) distance is long, 2.407(11) Å. As a consequence of disorder only average Zr–N bond distances can be given, 2.201(4) Å. Both nitrogen atoms in **3** are trigonal planar.

Initial ethene polymerisation attempts with compound **3** in toluene activated with methylaluminoxane (MAO), $(MeAlO)_n$ (nominal Al : Zr ratio 1000 : 1), showed encouraging activity (50 °C, 1 bar). However, recrystallised **3** proved to be inactive, and we ascribe the observed catalytic activity to an impurity which could not be identified.

By contrast to the C–H activation leading to compound **3**, the reaction of **1** with Cp^*TiCl_3 proceeds cleanly with dechlorosilylation, to give the titanium phosphinimido complex C_2H_4-$\{Ph_2P{=}NTiCl_2Cp^*\}_2$-1,2 **4** as orange-red crystals. The symmetric structure is evident from the observation in the ^1H NMR spectrum of a simple doublet for the C_2H_4 bridge (δ 2.87, J_{HP} = 2.4 Hz). The linear transoid geometry was confirmed by X-ray diffraction which allowed the identification of all heavy atoms, although the data were of insufficient quality to be discussed here further.

Alkylation of compound **4** with MeMgCl in diethyl ether leads cleanly to $C_2H_4\{Ph_2P{=}NTiMe_2Cp^*\}_2$-1,2 **5**. Mixtures of **4** activated with methylaluminoxane (MAO, Al : Ti = 1000 : 1) in toluene at 60 °C under 1 bar ethene show modest polymerisation activity [*ca.* 5×10^3 g polyethylene (PE) (mol Ti)$^{-1}$ h^{-1} bar^{-1}], while equimolar mixtures of **5** and $B(C_6F_5)_3$ only gave traces of polymer.

Dehalosilylation is also observed on exposure of the potentially tridentate[4] bis(iminophosphino)pyridine C_5H_3N-$(Ph_2P{=}NSiMe_3)_2$-2,6 **6** to Cp^*TiCl_3 in dichloromethane at room temperature, to give orange crystalline $C_5H_3N\{Ph_2P{=}$ $NTiCl_2Cp^*\}_2$-2,6·CH_2Cl_2 **7**·CH_2Cl_2 (Scheme 2). The molecular structure of **7** is shown in Fig. 2. The molecule contains near-linear Ti–N–P moieties, with an average Ti–N–P angle of 160.5(2)°. The Ti–N and P=N distances of, on average, 1.793(2) and 1.578(2) Å, respectively, correspond closely to those found in the parent complex, $CpCl_2TiN{=}PPh_3$.[6] There is no coordination to the pyridine N atom.

By contrast, the reaction of compound **6** with $ZrCl_4$ under similar conditions leads to a product analysing for C_5H_3N-$\{Ph_2P{=}N(SiMe_3)ZrCl_4\}_2$-2,6·$2CH_2Cl_2$ **8**·$2CH_2Cl_2$. Although crystals suitable for X-ray diffraction could not be grown, the composition of **8** is confirmed by the NMR spectra, *e.g.* the ^{31}P NMR chemical shift of δ 39.5. Heating **8**·$2CH_2Cl_2$ to 180 °C for 3 h failed to induce dehalosilylation but allowed the recovery of solvate-free **8**.

In an attempt to probe the extent of C–H activation of alkyl-

Table 1 Selected bond length (Å) and angles (°)

$ZrCl_3\{C_2H_3(Ph_2{=}NSiMe_3)_2\}$ **3**

Zr(1)–N(1)	2.201(4)	Zr(1)–Cl(2′)[a]	2.4580(13)
Zr(1)–C(1)	2.407(11)	N(1)–P(1)	1.618(5)
Zr(1)–Cl(2)	2.4580(13)	Si(1)–C(13)	1.863(6)
Zr(1)–Cl(1)	2.477(2)	P(1)–C(2)	1.825(10)
N(1)–Si(1)	1.754(5)	P(1)–C(121)	1.806(5)
P(1)–C(1)	1.771(9)	C(1)–C(2)[a]	1.527(12)
P(1)–C(11)	1.809(5)		
N(1)[a]–Zr(1)–N(1)	145.5(3)	N(1)[a]–Zr(1)–C(1)	82.9(3)
N(1)–Zr(1)–Cl(2)	90.59(11)	N(1)–Zr(1)–C(1)	63.2(3)
Cl(2)–Zr(1)–Cl(2)[a]	177.15(10)	C(1)–Zr(1)–Cl(2)	101.4(2)
C(1)[a]–Zr(1)–Cl(2)	81.4(2)	N(1)–Zr(1)–Cl(2)[a]	90.25(11)
C(1)–Zr(1)–Cl(1)	165.9(2)	N(1)–Zr(1)–Cl(1)	107.26(14)
P(1)–N(1)–Si(1)	126.8(3)	Cl(2)–Zr(1)–Cl(1)	88.57(5)
Si(1)–N(1)–Zr(1)	124.7(3)	P(1)–N(1)–Zr(1)	108.4(2)
C(1)–P(1)–C(111)	115.9(4)	N(1)–P(1)–C(1)	91.0(4)

$C_5H_3N(Ph_2PNTiCl_2Cp^*)_2$-2,6 **7**

Ti(1)–N(1)	1.794(2)	Ti(1)–Cl(1)	2.2849(8)
Ti(1)–Cl(2)	2.3091(8)	Ti(1)–C(2)	2.334(3)
Ti(1)–C(3)	2.345(3)	Ti(1)–C(4)	2.377(3)
Ti(1)–C(1)	2.412(3)	Ti(1)–C(5)	2.421(3)
N(1)–P(1)	1.578(2)	P(1)–C(121)	1.800(3)
P(1)–C(111)	1.804(3)	P(1)–C(11)	1.823(3)
C(11)–N(12)	1.340(3)	Ti(2)–N(2)	1.791(2)
C(13)–P(2)	1.824(2)	Ti(2)–Cl(3)	2.3116(8)
Ti(2)–Cl(4)	2.3044(9)	N(2)–P(2)	1.578(2)
Cl(1)–Ti(1)–Cl(2)	102.99(3)	N(1)–Ti(1)–Cl(1)	102.40(8)
P(1)–N(1)–Ti(1)	155.4(2)	N(1)–Ti(1)–Cl(2)	101.81(8)
N(1)–P(1)–C(111)	112.14(11)	N(1)–P(1)–C(121)	113.08(12)
N(1)–P(1)–C(11)	111.69(12)	C(16)–C(11)–P(1)	123.0(2)
N(12)–C(11)–P(1)	114.1(2)	C(11)–N(12)–C(13)	117.7(2)

$TiCl_2Cp^*\{N{=}PPh_2CH_2C_6H_4Bu^t\text{-}4\}$ **12**

Ti(1)–N(1)	1.7737(16)	Ti(1)–Cl(1)	2.3085(5)
Ti(1)–Cl(2)	2.3158(5)	P(1)–C(11)	1.8018(19)
N(1)–P(1)	1.5841(16)	P(1)–C(31)	1.8170(18)
P(1)–C(21)	1.8066(18)		
N(1)–Ti(1)–Cl(1)	104.39(5)	N(1)–Ti(1)–Cl(2)	101.21(5)
Cl(1)–Ti(1)–Cl(2)	101.38(2)	N(1)–P(1)–C(11)	111.10(9)
P(1)–N(1)–Ti(1)	165.69(11)	C(11)–P(1)–C(21)	108.59(8)
N(1)–P(1)–C(21)	111.69(8)	C(11)–P(1)–C(31)	105.75(9)
N(1)–P(1)–C(31)	112.74(9)		

$[4\text{-}Bu^tC_6H_4CH_2P(Ph)_2NHSiMe_3]_2[Zr_2Cl_{10}]$ **13**

Zr(1)–Cl(5)	2.371(2)	Zr(1)–Cl(2)	2.388(2)
Zr(1)–Cl(4)	2.407(2)	Zr(1)–Cl(1)	2.431(2)
Zr(1)–Cl(3)	2.615(2)	Zr(1)–Cl(3)*	2.640(2)
Cl(3)–Zr(1)*	2.640(2)	P(1)–N(1)	1.635(5)
P(1)–C(18)	1.790(6)	P(1)–C(12)	1.792(6)
P(1)–C(1)	1.823(6)	Si(1)–N(1)	1.772(5)
Cl(5)–Zr(1)–Cl(2)	100.51(8)	Cl(5)–Zr(1)–Cl(4)	93.68(8)
Cl(2)–Zr(1)–Cl(4)	92.09(7)	Cl(5)–Zr(1)–Cl(1)	92.54(8)
Cl(2)–Zr(1)–Cl(1)	89.28(7)	Cl(4)–Zr(1)–Cl(3)	173.28(7)
Cl(5)–Zr(1)–Cl(3)	89.62(6)	Cl(2)–Zr(1)–Cl(3)	169.56(6)
Cl(4)–Zr(1)–Cl(3)	89.74(6)	Cl(1)–Zr(1)–Cl(3)	87.75(6)
Cl(5)–Zr(1)–Cl(3)*	166.74(6)	Cl(2)–Zr(1)–Cl(3)*	92.71(6)
Cl(4)–Zr(1)–Cl(3)*	86.76(7)	Cl(1)–Zr(1)–Cl(3)*	86.60(6)
Cl(3)–Zr(1)–Cl(3)*	77.12(5)	Zr(1)–Cl(3)–Zr(1)*	102.88(5)
N(1)–P(1)–C(18)	108.8(3)	N(1)–P(1)–C(12)	111.7(3)
C(18)–P(1)–C(12)	110.3(3)	N(1)–P(1)–C(1)	110.5(3)
C(18)–P(1)–C(1)	108.1(3)	C(12)–P(1)–C(1)	107.3(3)

[a] Symmetry relation: $1 - x, +y, \frac{1}{2} - z$.

phosphinimines with formation of CPN chelate structures analogous to those of **2** and **3**, the reaction of the benzyl phosphinimine $4\text{-}Bu^tC_6H_4CH_2P(Ph)_2{=}NSiMe_3$ **9** with titanium and zirconium halides was explored (Scheme 3). Unlike **1**, the reaction of **9** with $TiCl_4$ failed to give a chelate complex of type **10** but led instead to dehalosilylation with formation of **11** as a poorly soluble orange microcrystalline solid in high yield.

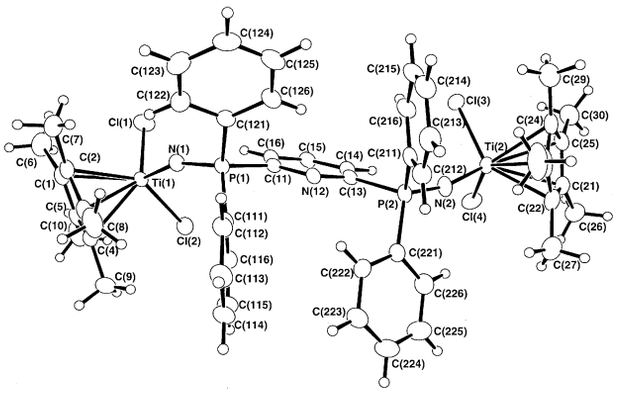


Fig. 2 Molecular structure of $C_5H_3N\{Ph_2P{=}NTiCl_2Cp^*\}_2$-2,6, **7**.

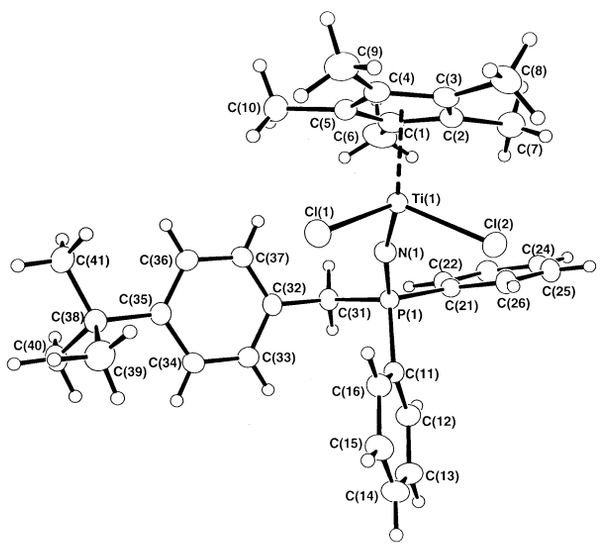
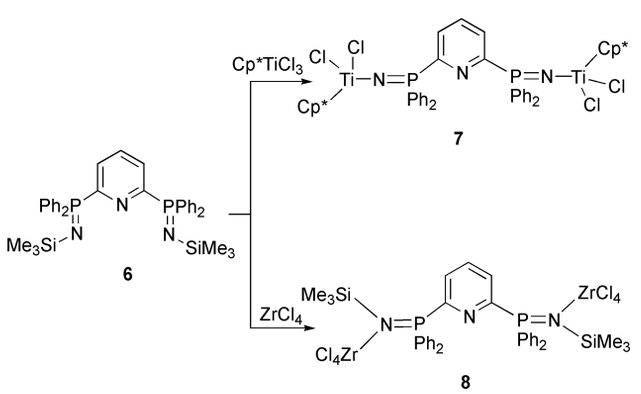


Fig. 3 Molecular structure of $TiCl_2Cp^*\{N{=}PPh_2CH_2C_6H_4Bu^t\text{-}4\}\cdot C_6H_5Me$ **12**·C_6H_5Me).



Scheme 2

Similarly, the reaction of **9** with Cp^*TiCl_3 affords orange $TiCl_2Cp^*\{N{=}PPh_2CH_2C_6H_4Bu^t\text{-}4\}$ **12**. The structure of **12** (Fig. 3) shows a Ti–N bond of 1.7737(16) Å and a near-linear Ti–N–P arrangement, with an angle of 165.69(11)°.

A different course of reaction was followed when compound **9** was treated with $ZrCl_4$. A product derived from dehalosilylation was not observed. Refluxing the mixture in dichloromethane for 5 h followed by crystallisation led to the isolation of a colourless material which was identified as a salt of the decachlorodizirconate dianion, $[4\text{-}Bu^tC_6H_4CH_2P(Ph)_2NHSiMe_3]_2[Zr_2Cl_{10}]$ **13**, in moderate yield. The compound shows a ^{31}P NMR signal at δ 40.4, as expected of a phosphonium cation. The structure of **13** was confirmed by X-ray diffraction (Fig. 4). The $[Zr_2Cl_{10}]^{2-}$ anion is rare and appears

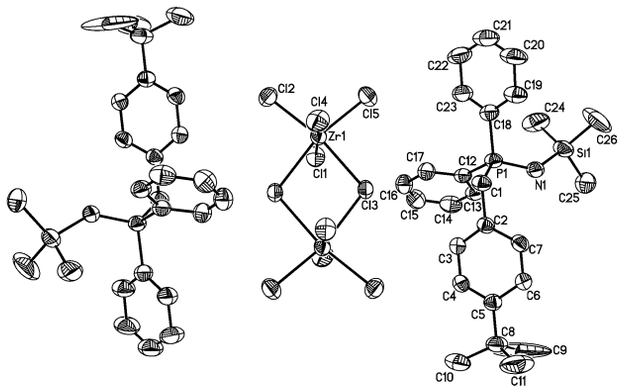
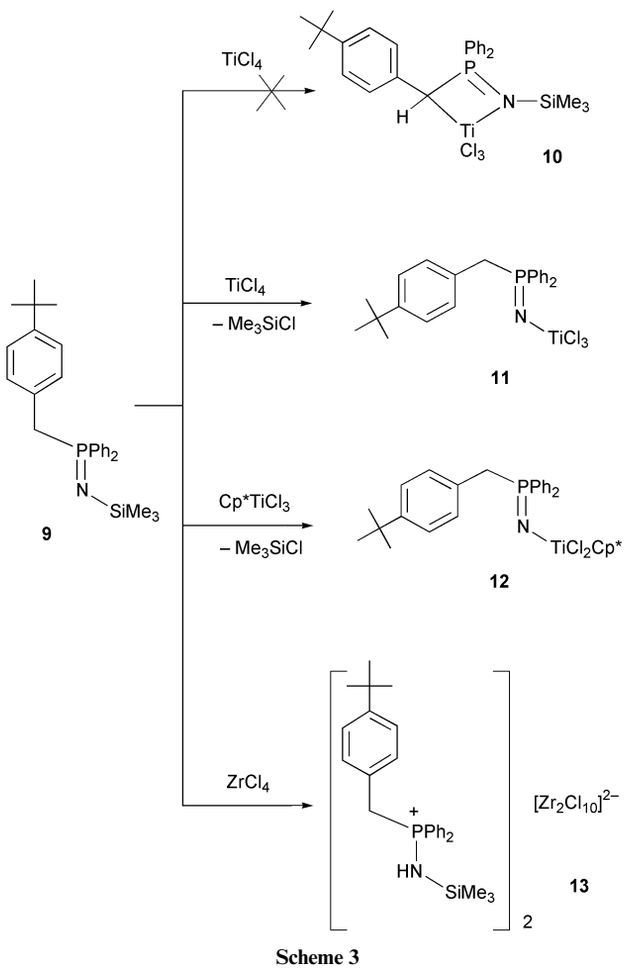


Fig. 4 Crystal structure of $[4\text{-}Bu^tC_6H_4CH_2P(Ph)_2NHSiMe_3]_2[Zr_2Cl_{10}]$ **13**.

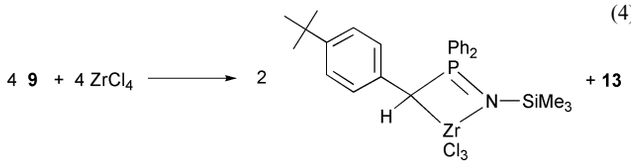


Scheme 3

to have been crystallographically characterised in only a few cases.[7] Typically, the Zr–Cl distances to the bridging chlorine atoms are *ca*. 0.2 Å longer than the terminal Zr–Cl bonds. The bridge is slightly unsymmetric, with Zr–Cl(3) and Zr–Cl(3*) bond lengths of 2.615(2) Å and 2.640(2) Å, respectively. There is no indication for hydrogen bonding between cations and anion.

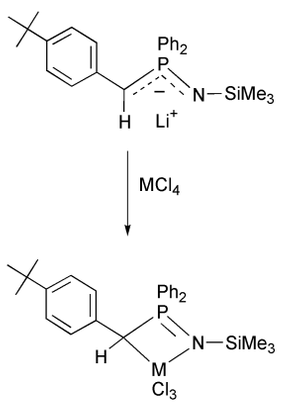
There was evidence for a second species in solution, with a ^{31}P NMR shift of δ 31.45, which was suspected to be the metallated compound $ZrCl_3\{4\text{-}Bu^tC_6H_4CHP(Ph)_2NSiMe_3\}$ **14**. The formation of such a product would provide the HCl required for the generation of **13** according to eqn. (4), although in view of the almost 40% yield of **13** hydrolysis by traces of moisture could not be ruled out. However, the reaction of $Li[4\text{-}Bu^t\text{-}C_6H_4CHP(Ph)_2NSiMe_3]$ with $ZrCl_4$ (eqn. 5) affords a product with a very similar ^{31}P NMR chemical shift (δ 31.92). Although

(4)



an analytically pure sample of **14** could not be obtained, the spectroscopic data are in agreement with the suggested structure. Similarly, the reaction of Li[4-Bu^{t}C$_6$H$_4$CHP(Ph)$_2$NSiMe$_3$] with TiCl$_4$ gives TiCl$_3${4-Bu^{t}C$_6$H$_4$CHP(Ph)$_2$NSiMe$_3$} **10** mentioned earlier; the compound was isolated as a light yellow powder.

(5)



10, M = Ti
14, M = Zr

Conclusion

Chelating bis(trimethylsilylimino)phosphines undergo C–H activation in preference to dehalosilylation with both titanium and zirconium tetrachloride, to give products containing [C–N]$^-$ chelate rings. In all other cases ZrCl$_4$ forms *N*-donor adducts or salts. The (phosphinimine)ZrCl$_4$ complexes are thermally stable and cannot be converted into dehalosilylation products. By contrast, TiCl$_4$ shows a preference for dehalosilylation to give phosphinimido complexes, a reaction pathway that is exclusively followed by the less Lewis acidic Cp*TiCl$_3$. The potentially tridentate ligand C$_2$H$_4$(Ph$_2$P=NSiMe$_3$)$_2$-1,2 **1** has a significantly greater tendency towards C–H activation than monoiminophosphines; the latter require lithiation to give [C–N]$^-$ chelate complexes.

Experimental

All manipulations were performed under a dinitrogen atmosphere unless specified using Schlenk techniques. Solvents were distilled under N_2 over sodium–benzophenone (thf), sodium (toluene), sodium–potassium alloy [diethyl ether, light petroleum (bp 40–60 °C)], or CaH_2 (dichloromethane). NMR solvents were dried over activated molecular sieves and degassed through 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) or to external 85% H_3PO_4 (^{31}P). Bis(diphenylphosphino)methane (dppm), azidotrimethylsilane and 2,6-difluoropyridine were used as purchased, ZrCl$_4$ was freshly sublimed under nitrogen before use (400–450 °C, 1 atm), Cp*TiCl$_3$,[8] C$_2$H$_4$(Ph$_2$P=NSiMe$_3$)$_2$-1,2 **1**[9] and C$_5$H$_3$N-(Ph$_2$P=NSiMe$_3$)$_2$-2,6 **6**[4] were prepared according to literature procedures.

Preparations

ZrCl$_3${CHCH$_2$(Ph$_2$PNSiMe$_3$)$_2$} 3. A mixture of compound **1** (2.50 g, 4.36 mmol), ZrCl$_4$ (1.00 g, 4.29 mmol) and dichloromethane (40 cm^3) was stirred at room temperature for 17 h. A milky white precipitate developed which was allowed to settle for 1 h and filtered off. The white residue was washed with dichloromethane (40 cm^3) and dried *in vacuo* to give **3**·CH$_2$Cl$_2$, yield 2.20 g (2.58 mmol, 60%). Crystals suitable for X-ray diffraction were obtained from warm dichloromethane. ^{1}H NMR (CD$_2$Cl$_2$, 20 °C): δ 0.13 (s, 9H, SiMe$_3$), 0.14 (s, 9H, SiMe$_3$), 1.07 (d,d,d,d, 1H, CH, J_{HH} = 14.2, 4.7, J_{HP} = 6.1, 3.5), 2.63 (d,d,d,d, 1H, CH$_2$, J_{HH} = 14.2, 4.7, J_{HP} = 6.0, 1.7), 2.96 (d,d,d,d, 1H, CH$_2$, J_{HH} = 14.2, 14.2, J_{HP} = 17.4, 10.5 Hz) and 7.93–7.35 (m, 20H, Ph). ^{13}C-{^{1}H} NMR (CD$_2$Cl$_2$, 20 °C): δ 2.9 (d, SiMe$_3$, J_{CP} = 3.3), 3.9 (d, SiMe$_3$, J_{CP} = 3.6), 20.8 (d,d CH, J_{CP} = 71.8, 9.9), 36.0 (d, CH$_2$, J_{CP} = 77.9), 124.7 (d, *ipso*-*C* of Ph$_2$, J_{CP} = 86.9), 125.6 (d, *ipso*-*C* of Ph, J_{CP} = 90.3), 129.0 (d, *m*-C of Ph, J_{CP} = 12.4), 129.1 (d, *m*-C of Ph, J_{CP} = 11.5), 129.2 (d, *m*-C of Ph, J_{CP} = 12.7), 129.3 (d, *m*-C of Ph, J_{CP} = 12.7), 131.0 (d, *o*-C of Ph, J_{CP} = 10.4), 132.1 (d, *p*-C of Ph, J_{CP} = 3.0), 132.8 (d, *p*-C of Ph, J_{CP} = 3.0), 133.3 (d, *p*-C of Ph, J_{CP} = 2.0), 133.4 (d, *p*-C of Ph, J_{CP} = 2.2), 133.4 (d, *o*-C of Ph, J_{CP} = 10.4), 133.7 (d, *o*-C of Ph, J_{CP} = 10.6), 134.0 (d, *o*-C of Ph, J_{CP} = 9.8) and 136.2 (d,d, *ipso*-C of Ph, J_{CP} = 80.1, 1.8 Hz). ^{31}P NMR (CD$_2$Cl$_2$, 20 °C): δ 28.5 (d, J_{PP} = 81.9) and 39.1 (d, J_{PP} = 81.9 Hz). Calc. for C$_{32}$H$_{41}$Cl$_3$N$_2$P$_2$Si$_2$Zr·CH$_2$Cl$_2$: C, 46.4; H, 5.1; N, 3.3%. Found: C, 47.0; H, 5.3; N, 3.8%.

C$_2$H$_4${Ph$_2$P=NTiCl$_2$Cp*}$_2$-1,2 4. A solution of compound **1** (0.50 g, 1.73 mmol) and Cp*TiCl$_3$ (1.00 g, 3.45 mmol) in dichloromethane (30 cm^3) was stirred at room temperature for 16 h. The solution was filtered, reduced in volume (*ca*. 20 cm^3) and placed in the freezer overnight. Bright orange-red crystals of C$_2$H$_4${Ph$_2$P=NTiCl$_2$Cp*}$_2$-1,2 **4** were isolated, yield 1.45 g (1.55 mmol, 90%). ^{1}H NMR (CD$_2$Cl$_2$, 20 °C): δ 1.98 (s, 30 H, Cp*), 2.87 (d, 4H, CH$_2$, J_{HP} = 2.4 Hz), 7.50 (m, 8H, *o*-H of Ph), 7.58 (m, 4H, *p*-H of Ph) and 7.78 (m, 8H, *m*-H of Ph). ^{13}C NMR (CD$_2$Cl$_2$, 20 °C): δ 12.1 (s, C$_5$*Me*$_5$), 22.7 (vt, 2CH$_2$, J_{CP} = 31.7), 127.2 (s, *C*$_5$Me$_5$), 129.0 (t, *o*-C of Ph, J_{CP} = 6.4), 129.8 (d, *ipso*-C of Ph, J_{CP} = 97.9), 132.9 (d, *m*-C of Ph, J_{CP} = 5.3 Hz) and 132.4 (s, *p*-C of Ph). ^{31}P NMR (CD$_2$Cl$_2$, 20 °C): δ 6.6. Calc. for C$_{23}$H$_{27}$Cl$_2$NPTi: C, 59.1; H, 5.8; Cl, 15.2; N, 3.0%. Found: C, 58.8; H, 5.8; Cl, 15.0; N, 3.2%.

C$_2$H$_4${Ph$_2$P=NTiMe$_2$Cp*}$_2$-1,2 5. This compound was prepared from **1** (0.50 g, 1.73 mmol) and Cp*TiCl$_3$ (1.00 g, 3.45 mmol) in a one-pot procedure. A dichloromethane solution of **4** was prepared as described above and the solvent replaced by thf (30 cm^3). The solution was cooled to −78 °C and treated with MeMgCl (2.6 cm^3, 6.9 mmol, 3 M solution in thf). The orange suspension slowly turned pale yellow on warming to room temperature. After 3 h the solvent was removed and the product extracted into 50 : 50 toluene–light petroleum (2 × 30 cm^3). The combined extracts were cooled to −20 °C overnight to afford **5** as a crystalline material (0.35 g, 24%). ^{1}H NMR (C$_6$D$_6$, 20 °C): δ 0.63 (s, 12H, TiMe), 1.95 (s, 30 H, Cp*), 3.01 (d, 4H, 2CH$_2$, J = 2.0 Hz), 7.02 (m, 12H, *o*,*p*-H of Ph) and 7.85 (m, 8H, *m*-H of Ph). ^{13}C NMR (C$_6$D$_6$, 20 °C): δ 12.0 (s, C$_5$*Me*$_5$), 24.5 ("t", 2CH$_2$, J_{CP} = 32.1), 43.2 (TiMe), 119.3 (s, *C*$_5$Me$_5$), 129.0 (t, *o*-C of Ph, J_{CP} = 5.7), 131.5 (d, *m*-C of Ph, J_{CP} = 4.5), 131.7 (s, *p*-C of Ph) and 134.0 (d, *ipso*-C of Ph, J_{CP} = 95.0 Hz). ^{31}P NMR (C$_6$D$_6$, 20 °C): δ −6.6. Calc. for C$_{25}$H$_{33}$NP$_2$Ti: C, 70.4; H, 7.8; N, 3.3%. Found: C, 70.3; H, 8.0; N, 3.0%.

C$_5$H$_3$N{Ph$_2$P=NTiCl$_2$Cp*}$_2$-2,6 7. A solution of C$_5$H$_3$-N(Ph$_2$P=NSiMe$_3$)$_2$-2,6 **6**[4] (1.07 g, 1.73 mmol) and Cp*TiCl$_3$ (1.00 g, 3.45 mmol) in dichloromethane (30 cm^3) was stirred at room temperature for 16 h. The solution was filtered, reduced in volume to *ca*. 20 cm^3 and placed in a freezer overnight. Bright orange crystals of C$_5$H$_3$N{Ph$_2$P=NTiCl$_2$Cp*}$_2$-2,6·CH$_2$Cl$_2$ **7**·CH$_2$Cl$_2$ were isolated, yield 1.49 g (1.40 mmol, 81%). ^{1}H NMR (CD$_2$Cl$_2$, 20 °C): δ 1.97 (s, 30 H, C$_5$*Me*$_5$), 7.33 (m, 8H, *o*-H of Ph), 7.53 (m, 12H, *m*,*p*-H of Ph), 8.17 (m, 1H, *p*-H of

Table 2 Crystal data of iminophosphorane complexes

	3·2CH_2Cl_2	**7**	**12**	**13**
Formula	$C_{32}H_{41}Cl_3N_2P_2Si_2Zr·2CH_2Cl_2$	$C_{50}H_{55}Cl_6N_3P_2Ti_2$	$C_{40}H_{48}Cl_2NPTi$	$C_{52}H_{70}Cl_{10}N_2P_2Si_2Zr_2$
M	939.21	1068.41	692.56	1374.13
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	*C*2/*c*	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a/Å	22.6760(10)	12.0929(2)	19.5778(5)	16.729(3)
b/Å	9.5021(5)	13.4161(4)	10.3318(3)	11.509(2)
c/Å	21.3807(7)	16.3861(4)	19.8983(4)	17.448(4)
α/°		84.4990(14)		
β/°	113.031(3)	80.911(2)	112.136(2)	98.13(3)
γ/°		81.787(2)		
U/Å^3	4239.7(3)	2590.85(11)	3728.24(16)	3325.5(11)
Z	4	2	4	2
μ/mm^{-1}	0.86	0.716	0.444	0.832
Independent/ observed reflections	4113/3582	10152/8694	7286/6403	5572/3623
R_{int} [a]	0.0491	0.0595	0.0627	0.0422
*R*1 [$I > 2\sigma(I)$]	0.0661	0.0484	0.0427	0.0544
*wR*2 (all data)	0.1472	0.1314	0.1193	0.2193

[a] $\Sigma|F_o^2 - F_o^2\,(\text{mean})|/\Sigma F_o^2$.

py) and 8.79 (m, 2H, *m*-H of py). ^{13}C NMR (CD_2Cl_2, 20 °C): *δ* 13.0 (s, C_5Me_5), 127.9 (s, C_5Me_5), 128.8 (d, *o*-C of Ph, J_{CP} = 13.6), 130.3 (d, *ipso*-C of Ph, J_{CP} = 101.1), 131.4 (d,d, *m*-C of py, J_{CP} = 21.9, 3.0), 132.6 (s, *p*-C of Ph), 132.9 (d, *m*-C of Ph, J_{CP} = 10.6), 137.8 (t, *p*-C of py, J_{CP} = 8.7) and 156.2 (d,d, *ipso*-C of py, J_{CP} = 128.3, 18.1 Hz). ^{31}P NMR (CD_2Cl_2, 20 °C): *δ* −5.2. Calc. for $C_{49}H_{53}Cl_4N_3P_2Ti_2·CH_2Cl_2$: C, 56.2; H, 5.2; N, 3.9%. Found: C, 56.0; H, 5.2; N, 3.4%.

$C_5H_3N\{Ph_2P{=}N(SiMe_3)ZrCl_4\}_2$-2,6 8. A mixture of $ZrCl_4$ (0.376 g, 1.607 mmol) and compound **6** (0.500 g, 0.834 mmol) in dichloromethane (20 cm^3) was heated at 40 °C for 30 min and left to stir at room temperature for 16 h. Some solid precipitate was removed by filtration. The filtrate was concentrated to provide $C_5H_3N\{Ph_2P{=}N(SiMe_3)ZrCl_4\}_2$-2,6·2$CH_2Cl_2$ **8**·2CH_2Cl_2, yield 0.65 g (0.6 mmol, 72%). Heating this compound at 180 °C for 3 h gave unsolvated **8** only. ^{1}H NMR (CD_2Cl_2, 20 °C): *δ* 0.40 (s, 18 H, $SiMe_3$), 7.70 (m, 12H, *o*- and *p*-H of Ph), 7.95 (m, 2H, *m*-H of py), 8.12 (m, 8H, *m*-H of Ph) and 8.61 (m, 1H, *p*-H of py). ^{13}C NMR (CD_2Cl_2, 20 °C): *δ* 4.8 ($SiMe_3$), 124.1 (d, *ipso*-C of Ph, J_{CP} = 96.6), 130.4 (d, *o*-C of Ph, J_{CP} = 13.6), 133.1 (d,d, *m*-C of py, J_{CP} = 21.1, 2.3), 134.1 (d, *m*-C of Ph, J_{CP} = 12.1), 135.5 (d, *p*-C of Ph, J_{CP} = 3.0), 145.2 (t, *p*-C of py, J_{CP} = 9.1) and 158.1 (d,d, *ipso*-C of py, J_{CP} = 122.3, 11.3 Hz). ^{31}P NMR (CD_2Cl_2, 20 °C): *δ* 39.5. **8**·2CH_2Cl_2. Calc. for $C_{35}H_{41}Cl_8N_3P_2Si_2Zr_2·2CH_2Cl_2$: C, 36.9; H, 3.7; Cl, 30.2; N, 3.6%. Found: C, 37.0; H, 3.6; Cl, 30.4; N, 3.4%. **8**. Calc. for $C_{35}H_{41}Cl_8N_3P_2Si_2Zr_2$: C, 38.6; H, 3.8; Cl, 26.1; N, 3.9%. Found: C, 38.0; H, 3.8; Cl, 26.6; N, 4.1%.

4-Bu^{t}C$_6$H$_4$CH$_2$P(Ph)$_2$=NSiMe$_3$ 9. To a solution of freshly distilled 4-Bu^{t}C$_6$H$_4$CH$_2$PPh$_2$ (3.20 g, 9.64 mmol) in toluene (50 cm^3) was added trimethylsilyl azide (2.78 g, 24.10 mmol) at room temperature. The mixture was heated to reflux for 18 h, the volatiles were removed, and light petroleum was added (*ca.* 30 cm^3). Crystals were grown at −25 °C over a period of two days, yield 2.5 g (6.0 mmol, 62%). ^{1}H NMR (C_6D_6, 20 °C, 300.13 MHz): *δ* 0.43 (s, 9H, $SiMe_3$), 1.23 (s, 9H, CMe_3), 3.46 (d, J_{HP} = 13.1 Hz, 2H, CH_2) and 7.11–7.71 (m, 14H, Ph). ^{13}C-{^{1}H} NMR (C_6D_6, 20 °C, 75.46 MHz): *δ* 4.34 (s, 3C, $SiMe_3$), 31.16 (s, 3C, CMe_3), 34.13 (s, *C*Me$_3$), 39.04 (d, J_{CP} = 68.7 Hz, CH_2) and 124.98–149.09 (aryl). ^{31}P NMR (C_6D_6, 20 °C, 121.49 MHz): *δ* −0.8. Calc. for $C_{26}H_{34}NPSi$: C, 74.4; H, 8.2; N, 3.3%. Found: C, 74.5; H, 8.4; N, 3.3%.

TiCl$_3${4-Bu^{t}C$_6$H$_4$CHP(Ph)$_2$=NSiMe$_3$} 10. In a one-pot procedure, to a solution of compound **9** (0.43 g, 1.02 mmol) in toluene (20 cm^3) was added dropwise at −78 °C Bu^{n}Li (0.64 cm^3, 1.02 mmol) over a period of 10 min. The solution was warmed to ambient temperature, stirred for 2 h, and added dropwise to a cold (−70 °C) solution of $TiCl_4$ (0.19 g, 1.02 mmol) in toluene (20 cm^3). After warming to room temperature and stirring for 2 h the mixture was filtered. The filtrate was concentrated to 10 cm^3 and 10 cm^3 of light petroleum were added to give a light yellow powdery solid, yield 0.28 g (0.49 mmol, 48%). ^{1}H NMR (CD_2Cl_2, 20 °C): *δ* 0.29 (s, 9H, $SiMe_3$), 1.06(s, 9H, CMe_3), 3.65 (br, H, CH) and 6.91–7.70 (m, 14H, Ph). ^{31}P NMR (CD_2Cl_2, 20 °C): *δ* 5.14.

TiCl$_3${4-Bu^{t}C$_6$H$_4$CH$_2$P(Ph)$_2$=N} 11. To a solution of compound **9** (1.10 g, 2.62 mmol) in toluene (30 cm^3) at −78 °C was added dropwise a solution of $TiCl_4$ (0.50 g, 2.62 mmol) in toluene (3.5 cm^3) over a period of 10 min. The resulting light orange solution was allowed to warm to ambient temperature and stirred for 3 h. Solvent was reduced to 5 cm^3 and light petroleum (30 cm^3) added to yield an orange precipitate which was collected and dried overnight under vacuum, yield 1.90 g (3.8 mmol, 84%). ^{1}H NMR (C_6D_6, 20 °C): *δ* 1.14 (s, 9H, CMe_3), 3.16 (d, J_{HP} = 13.21 Hz, 2H, CH_2) and 6.93–7.53 (m, 14H, Ph). ^{13}C-{^{1}H} NMR (C_6D_6, 20 °C): *δ* 31.01 (s, CMe_3), 34.28 (s, *C*Me$_3$), 36.11 (d, J_{CP} = 60.4 Hz, CH_2) and 124.83–151.11 (aryl). ^{31}P NMR (C_6D_6, 20 °C, 121.49 MHz): *δ* 11.6. Calc. for $C_{23}H_{25}Cl_3NPTi$: C, 55.2; H, 5.0; N, 2.8%. Found: C, 54.5; H, 5.3; N, 2.9%.

TiCl$_2$Cp*{N=PPh$_2$CH$_2$C$_6$H$_4$Bu^t-4}·C$_6$H$_5$Me 12·C$_6$H$_5$Me. A solution of compound **9** (1.45 g, 3.46 mmol) and Cp*$TiCl_3$ (1.0 g, 3.46 mmol) in toluene (20 cm^3) was heated at 110 °C overnight. The mixture was concentrated to 5 cm^3 and light petroleum added to yield an orange precipitate which was purified by recrystallisation from hot toluene (1 g cm^{-3}) to yield crystals of **12**·C_6H_5Me after 3 h, yield 1.7 g (2.45 mmol, 71%). ^{1}H NMR (C_6D_6, 20 °C): *δ* 1.13(s, 9H, CMe_3), 2.07(s, 15H, C_5Me_5), 2.13(s, 3H, Me of toluene), 3.16 (d, J_{HP} = 14.2 Hz, 2H, CH_2) and 6.99–7.90 (m, 19H, aryl). ^{13}C-{^{1}H} NMR (C_6D_6, 20 °C): *δ* 12.85 (s, 5C, C_5Me_5), 21.17 (s, 1C, Me of toluene), 31.06 (s, 3C, CMe_3), 34.14 (s, 1C, *C*Me$_3$), 37.04 (d, J_{CP} = 64.1 Hz, CH_2) and 125.39–149.70 (aryl). ^{31}P NMR (C_6D_6, 20 °C): *δ* 2.5. Calc. for $C_{33}H_{38}Cl_2NPTi·C_7H_8$: C, 69.4; H, 7.0; Cl, 10.2; N, 2.0%. Found: C, 69.5; H, 7.0; Cl, 10.3; N, 1.3%.

[4-Bu^{t}C$_6$H$_4$CH$_2$P(Ph)$_2$NHSiMe$_3$]$_2$[Zr$_2$Cl$_{10}$] 13. A mixture of compound **9** (1.00 g, 2.38 mmol) and $ZrCl_4$ (0.55 g, 2.38 mmol) in 30 cm^3 of dichloromethane was heated to reflux for 5 h. After reducing the solvent volume to 5 cm^3 the solution was cooled to 4 °C for three days to give colourless crystals of **13**, yield 0.65 g

(0.47 mmol, 39%). ^{1}H NMR (thf-d_8, 20 °C): δ 0.06 (s, 9H, $SiMe_3$), 1.25 (s, 9H, CMe_3), 4.04 (br, 2H, CH_2), 4.99 (br, 1H, NH) and 6.97–7.84 (m, 14H, aryl). ^{13}C-{^{1}H} NMR (thf-d_8, 20 °C): δ 2.55 (s, 3C, $SiMe_3$), 31.00 (s, CMe_3), 32.92 (d, J_{CP} = 60.1 Hz, CH_2), 36.64 (s, *C*Me_3) and 121.82–151.14 (aryl). ^{31}P NMR (thf-d_8, 20 °C): δ 40.4. Calc. for $C_{26}H_{35}Cl_5NPSiZr$: C, 45.3; H, 5.2; Cl, 25.0; N, 20%. Found: C, 45.2; H, 5.2; Cl, 26.2; N, 1.9%. The mother liquor showed an additional peak in the ^{31}P NMR spectrum at δ 31.45 (see text).

$ZrCl_3${4-Bu^tC_6H_4CHP(Ph)$_2$=NSiMe_3} **14.** Following the procedure described for **10**, the compound was prepared from **9** (1.5 g, 3.57 mmol) Bu^{n}Li (2.23 cm^3, 3.57 mmol), and $ZrCl_4$ (0.83 g, 3.57 mmol). ^{1}H NMR (CD_2Cl_2, 20 °C): δ 0.38 (s, 9H, $SiMe_3$), 1.31(s, 9H, CMe_3), 3.39 (d, J_{HP} = 13.3 Hz, 1H, CH) and 6.92–7.65 (m, 14H, Ph). Major ^{31}P NMR (CD_2Cl_2, 20 °C, 121.49 MHz): δ 31.92. Unidentified by-products were also apparent in the spectra which could not be removed.

X-Ray crystallography

In each case a suitable crystal was 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 (λ = 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.[10] The raw data were processed to produce conventional data using the program DENZO-SMN.[11] The datasets were corrected for absorption using the program SORTAV.[12] All structures were solved by heavy-atom methods using SHELXS 97[13] and refined by full-matrix least squares (on F^2) using SHELXL 97.[14] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were constrained to idealised positions. Crystallographic data for compounds **3**, **7**, **12** and **13** are summarised in Table 2. Crystals of **3**, which also contain a molecule of CH_2Cl_2 solvent per asymmetric unit, proved to be highly efflorescent and were therefore of limited quality. In addition, molecular C_2 crystallographic symmetry introduces a 50 : 50 disorder into the CH_2CH backbone of the ligand of this structure. Only one of the two positions is shown in Fig. 1. Rigid-bond restraints were applied to the thermal parameters of the carbon atoms involved in the disorder.

CCDC reference numbers 154069–154072.

See http://www.rsc.org/suppdata/dt/b0/b009082o/ for crystallographic data in CIF or other electronic format.

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