Tuning low-coordinate metal environments: high spin d⁵–d⁷ complexes supported by bis(phosphinimino)methyl ligation

David J. Evans,[a] Michael S. Hill *[b] and Peter B. Hitchcock[c]

[a] *Department of Biological Chemistry, John Innes Centre, Norwich Research Park, Colney, Norwich, UK NR4 7UH*
[b] *Department of Chemistry, Imperial College of Science, Technology and Medicine, Exhibition Road, South Kensington, London, UK SW7 2AY. E-mail: mike.hill@ic.ac.uk*
[c] *School of Chemistry, Physics and Environmental Science, University of Sussex, Falmer, Brighton, UK BN1 9QJ*

Treatment of $FeCl_2$ with the lithium derivative of $[CH_2(Ph_2P=NC_6H_2Me_3-2,4,6)_2]$ in THF and crystallisation from Et_2O gave the 'ate' complex $[\{CH(Ph_2PNC_6H_2Me_3-2,4,6)_2\}Fe(\mu-Cl)_2Li(THF)(OEt_2)]$ in which the iron is four-coordinate and the chlorides bridge to lithium. Treatment of $[M\{N(SiMe_3)_2\}_2]$ (M = Mn, Fe, Co) with $[CH_2(Ph_2P=NC_6H_2Me_3-2,4,6)_2]$ in toluene afforded the complexes $[\{CH(Ph_2PNC_6H_2Me_3-2,4,6)_2\}MN(SiMe_3)_2]$ which all feature essentially planar N(1)–N(2)–N(3)–M coordination. The carbanionic character of the bis(phosphinimino)methyl ligand results in close C(1)–M contacts in both the Mn and Co complexes effectively raising the coordination number to four. The analogous iron compound is strictly three-coordinate as demonstrated by X-ray crystallography and ^{57}Fe Mössbauer. However protonolysis of this compound with Ph_3COH yields the iron alkoxide $[\{CH(Ph_2PNC_6H_2Me_3-2,4,6)_2\}FeOCPh_3]$ that features a close C(1)–Fe contact of 2.375 Å. Although the iron centre in this complex is only marginally pyramidalised by this contact, its ^{57}Fe Mössbauer spectrum indicates a significant perturbation to the local electronic environment at the metal.

Introduction

The presence of a low-coordinate or coordinatively unsaturated transition metal centre is fundamental to a great number of industrial and biocatalytic processes.[1] The desire to model and better understand the fundamental chemistry of these systems has prompted a general interest in the development of ligands that are capable of supporting a range of low-coordinate metal centres. For example, several recent reports describe the use of bulky aryl-substituted β-diketiminate ligands such as **I** and **II**, to support three coordinate iron(II) complexes.[2] The primary importance of these compounds derives from their ability to promote reduction of dinitrogen in a stepwise manner and thus their relationship to the iron centres of the iron–molybdenum cofactor (FeMoco), **III**, of the nitrogenase enzyme.[2b,c] The recognition that six of the seven iron sites of FeMoco possess trigonal geometry was based upon X-ray crystallographic data with a resolution greater than 1.55 Å.[3] A recent higher resolution (to 1.16 Å) crystallographic study has revealed that this assignment of coordination geometry is erroneous and that a light atom (most plausibly nitrogen, as depicted in **III**, although refinement for carbon and oxygen also yielded acceptable temperature factors) resides in a central location of the cofactor.[4] This additional ligand interaction effectively raises the coordination number of these iron sites to four and indicates that future model compounds must also include contacts to similar light atom donors in order to accommodate the presence of this previously undetected interstitial atom. The realisation of this goal therefore dictates an increasingly refined supporting ligand design and ever greater control over the resultant metal coordination geometry.

With such considerations in mind, we have recently embarked upon a program of study that aims to assemble a suite of sterically demanding ligands that allow control of both coordination geometry and compound symmetry in low-coordinate systems.[5] We now wish to report the synthesis of divalent Mn, Fe and Co complexes supported by the mesityl-substituted bis(phosphinimino)methyl ligand **IV**,[6] and present preliminary evidence that both the denticity of the ligand and

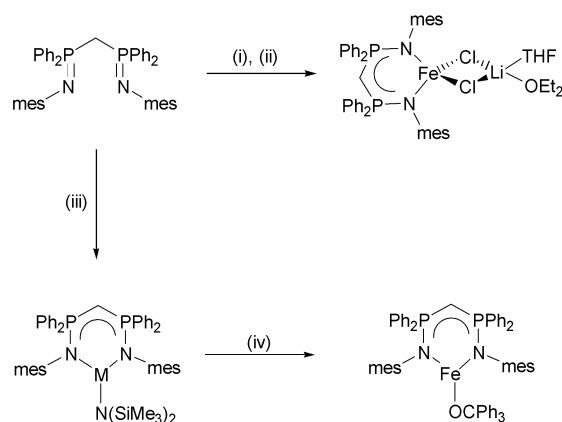**I**; R = Me: **II**; R = ᵗBu   **IV**

III
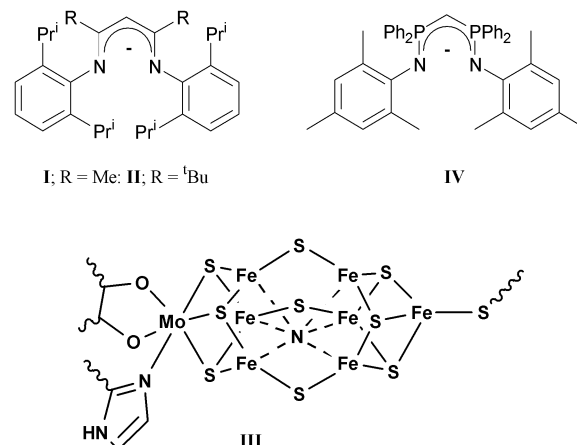
the coordination geometry adopted in these compounds can be determined by the both the metal and co-ligand identity.

Results and discussion

Reaction of the lithium derivative of $[CH_2(Ph_2P=NC_6H_2Me_3-2,4,6)_2]$, **[IV]Li**, and $FeCl_2$ in THF (Scheme 1), followed by crystallisation from diethyl ether at −30 °C allowed the isolation of an air-sensitive colourless crystalline compound. Although this was only sparingly soluble in hydrocarbon solvents, its solubility in THF-d_8 allowed the determination of a solution magnetic moment (Evans' method, 298 K) of 5.0 μ_B. This is typical for tetrahedral d^6 high spin iron(II)[7a] as are the ^{57}Fe Mössbauer parameters in the solid state (isomer shift (i.s.) = 0.93 mm s⁻¹, quadrupole splitting (q.s.) = 3.54 mm s⁻¹).[7a] An X-ray diffraction study revealed this product to be the 'ate' complex, $[\{CH(Ph_2PNC_6H_2Me_3-2,4,6)_2\}Fe(\mu-Cl)_2Li(THF)(OEt_2)]$ **1** (Fig. 1). Details of the crystallographic analysis are given in Table 1 and selected bond lengths and angles are listed in Table 2. The iron coordination sphere of **1** is similar that of the recently reported β-diketiminate derivative $[\textbf{I}]Fe(\mu-Cl)_2Li(THF)_2$,[2a] in

Table 1 Selected crystallographic and data collection parameters for compounds **1**–**5**

	1	2	3	4	5
Chemical formula	$C_{51}H_{61}N_2P_2Cl_2O_2FeLi$	$C_{49}H_{61}N_3P_2Si_2Mn$	$C_{49}H_{61}N_3P_2Si_2Fe$	$C_{49}H_{61}N_3P_2Si_2Co$	$C_{62}H_{58}N_2P_2OFe$
Formula weight	929.65	865.07	865.98	869.06	964.89
T/K)	173(2)	173(2)	173(2)	173(2)	173(2)
Crystal size/mm³)	$0.2 \times 0.15 \times 0.05$	$0.30 \times 0.30 \times 0.25$	$0.15 \times 0.15 \times 0.05$	$0.3 \times 0.3 \times 0.2$	$0.4 \times 0.4 \times 0.2$
Crystal system	Triclinic	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$Pna2_1$ (no. 33)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	12.8140(12)	23.9011(4)	11.9774(3)	12.2503(6)	10.4976(2)
b/Å	13.1172(7)	15.5577(3)	18.4685(4)	19.5120(9)	12.7168(2)
c/Å	16.2526(16)	12.6739(2)	21.5940(7)	19.5346(10)	19.7847(4)
α/°	91.262(6)	90	90	90	92.801(1)
β/°	101.066(4)	90	94.420(1)	94.046(2)	92.638(1)
γ/°	117.249(5)	90	90	90	107.006(1)
Z	2	4	4	4	2
V/Å³	2364.5(3)	4712.74(14)	4762.5	4657.7(4)	2517.63(8)
D_c/Mg m^{-3}	1.31	1.22	1.21	1.24	1.27
μ/mm^{-1}	0.54	0.44	0.47	0.53	0.41
θ range/°	3.70 to 21.95	3.77 to 24.69	3.72 to 23.04	3.71 to 22.99	3.77 to 27.50
$R1$; $wR2$ [$I > 2\sigma(I)$]	0.048, 0.093	0.035, 0.065	0.049, 0.100	0.051, 0.116	0.052, 0.105
$R1$; $wR2$ all data	0.080, 0.105	0.046, 0.069	0.074, 0.112	0.080, 0.131	0.090, 0.119
Measured/indep. rflns./R(int)	12078/5716/0.065	30367/7304/0.058	24917/6580/0.078	20510/6409/0.093	24791/11383/0.056
Rflns. with $I > 2\sigma(I)$	4151	6402	5041	4662	7910

Scheme 1 Reagents and conditions for the synthesis of **1**–**5**. **1**: (i) *n*-BuLi, THF; (ii) FeCl₂. **2**–**4**: (iii) [M{N(SiMe₃)₂}₂], toluene; **2**, M = Mn; **3**, M = Fe; **4**, M = Co. **5**: (iv) Ph₃COH, toluene.
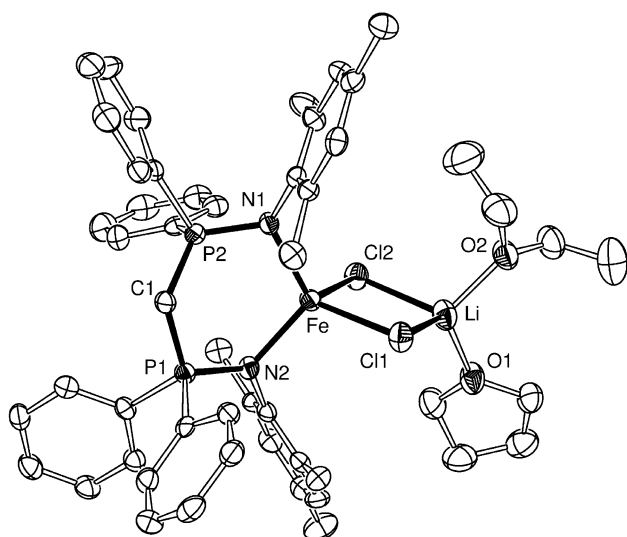
Fig. 1 Molecular structure of **1**. Hydrogen atoms omitted for clarity, thermal ellipsoids at 50% probability.

that coordination to the distorted tetrahedral iron centre is provided by two nitrogen atoms of the chelated ligand and two chlorides which bridge to lithium. There is a significant widening of the N(1)–Fe–N(2) angle in **1** [110.11(13) *vs.* 93.21(14)°] that results, most likely, from the differing steric demands of the

I and **IV** ligands and the flattened twist boat conformation that is enforced upon the bis(phosphinimino)methyl group by the pseudo-tetrahedral P(v) centres. That the bidentate ligands **I** and **IV** provide similar donation of charge however may be gauged from the similarity of the Fe–N bond lengths that are only marginally longer in **1** [2.025(3), 2.046(3) Å *vs.* 2.006(3), 2.021(4) Å].

Several three-coordinate Mn(II), Fe(II) and Co(II) derivatives have been synthesised by reaction of bulky β-diketimine ligands and the appropriate metal silylamide [M{N(SiMe₃)₂}₂] (M = Mn, Fe and Co).[8–10] In the same manner, reaction of [CH₂(Ph₂P=NC₆H₂Me₃-2,4,6)₂] and [M{N(SiMe₃)₂}₂] in toluene afforded the formally 11-, 12- and 13-electron amido derivatives [{CH(Ph₂PNC₆H₂Me₃-2,4,6)₂}MN(SiMe₃)₂], compounds **2** (M = Mn), **3** (M = Fe) and **4** (M = Co) (Scheme 1). The three compounds were isolated as colourless (compounds **2** and **3**) and green (compound **4**) crystalline solids from toluene solutions. Their solution magnetic moments (Evans' method, 298 K) were determined in C₆D₆ and afforded values consistent with high spin d⁵ (**2**, μ_B = 5.80), d⁶ (**3**, μ_B = 5.25) and d⁷ (**4**, μ_B = 4.90) electron configurations with five, four and three unpaired electrons, respectively. These values are similar to those reported for the closely related β-diketiminate derivatives, [**IM**]N(SiMe₃)₂.[2e] Recrystallisation from concentrated toluene solution provided crystals of **2**–**4** suitable for single crystal X-ray diffraction analysis. The molecular structures are illustrated in Figs. 2–4, while details of the X-ray analyses and selected bond lengths and angles are listed in Tables 1 and 2, respectively.

In all three compounds **2**–**4** the metal is bound to one bis(phosphinimino)methyl and a single N(SiMe₃)₂ ligand. The N(1)–N(2)–N(3)–M coordination planes reveal in each case a very minor pyramidalisation of the metal centre (Σ_{angles} = **2**: 356.16°; **3**: 359.45°; **4**: 358.93°). Compound **3** is unambiguously three-coordinate. The lower coordination number of the iron atom causes the Fe–N(1) and Fe–N(2) bond lengths in **3** [1.992(3), 1.997(3) Å] to decrease in comparison to **1**. Although there is a slight decrease of ligand bite angle in **3** [106.99(11)°] compared to that of **1** this value, as are the N(1)–M–M(2) bond angles in the analogous Mn and Co derivatives [**2**: 109.16(9)°; **4**: 110.87(12)°], is some 10–15° wider than the corresponding bite angles of three coordinate β-diketiminate derivatives containing the same metal and coligand.[2e] The remaining inter-ligand angles around the metal centres are, as a consequence, more acute and show less overall variation. Although the M–N(3) distances [**2**: 2.012(2); **3**: 1.932(3); **4**: 1.934(3) Å] are within the range previously observed in three-coordinate

Table 2 Selected bond lengths (Å) and angles (°) for compounds **1**–**5**

	1	**2**	**3**	**4**	**5**
M–N(1)	2.025(3)	2.110(2)	1.992(3)	1.996(3)	2.083(2)
M–N(2)	2.046(3)	2.124(2)	1.997(3)	1.997(3)	2.1096(19)
M–Cl/N(3)/O	2.371(1)^a 2.368(1)^b	2.012(2)	1.932(3)	1.934(3)	1.8558(16)
P(1)–N(1)	1.632(3)^c	1.618(2)	1.632(3)	1.616(3)	1.614(2)
P(2)–N(2)	1.636(3)^d	1.609(2)	1.620(3)	1.618(3)	1.603(2)
P(1)–C(1)	1.706(4)	1.735(3)	1.710(4)	1.729(4)	1.739(3)
P(2)–C(1)	1.722(4)	1.717(3)	1.706(4)	1.735(4)	1.737(2)
N(1)–M–N(3)	119.23(10)^e 108.05(10)^f	120.27(9)	125.37(12)	126.00(13)	132.17(8)^j
N(2)–M–N(3)	110.41(10)^g 112.69(10)^h	126.76(9)	127.09(12)	122.06(13)	123.32(8)^k
N(1)–M–N(2)	110.11(13) 95.61(4)^i	109.16(9)	106.99(11)	110.87(12)	103.25(8)
M–N(1)–P(1)	123.06(18)	104.62(11)	117.02(15)	101.73(16)	95.48(9)
M–N(2)–P(2)	108.66(16)	104.99(11)	117.54(15)	102.97(16)	96.57(9)
N(1)–P(1)–C(1)	109.63(19)	107.10(14)	111.40(16)	106.65(17)	106.77(11)
N(2)–P(2)–C(1)	117.72(19)	106.12(14)	109.46(16)	105.34(18)	103.90(11)
P(1)–C(1)–P(2)	125.2(3)	130.73(18)	136.2(2)	133.5(2)	128.23(15)

^{a} Fe–Cl(1). ^{b} Fe–Cl(2). ^{c} P(2)–N(1). ^{d} P(1)–N(2). ^{e} N(1)–Fe–Cl(1). ^{f} N(1)–Fe–Cl(2). ^{g} N(2)–Fe–Cl(1). ^{h} N(2)–Fe–Cl(2). ^{i} C(1)–Fe–Cl(2). ^{j} N(1)–Fe–O. ^{k} N(2)–Fe–O.
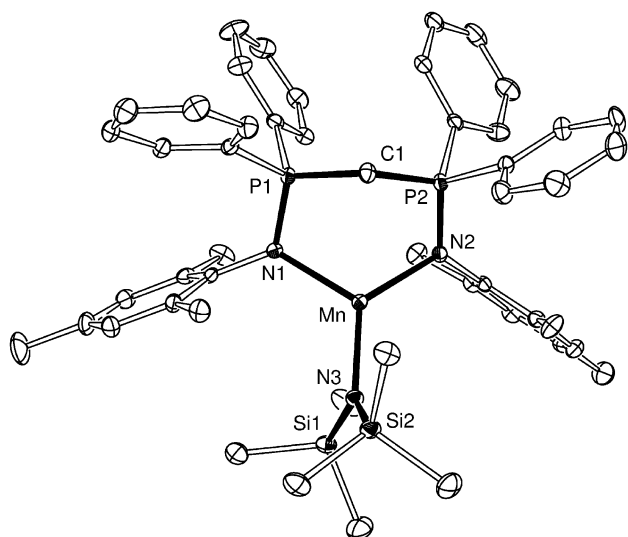
Fig. 2 Molecular structure of **2**. Hydrogen atoms omitted for clarity, thermal ellipsoids at 25% probability.
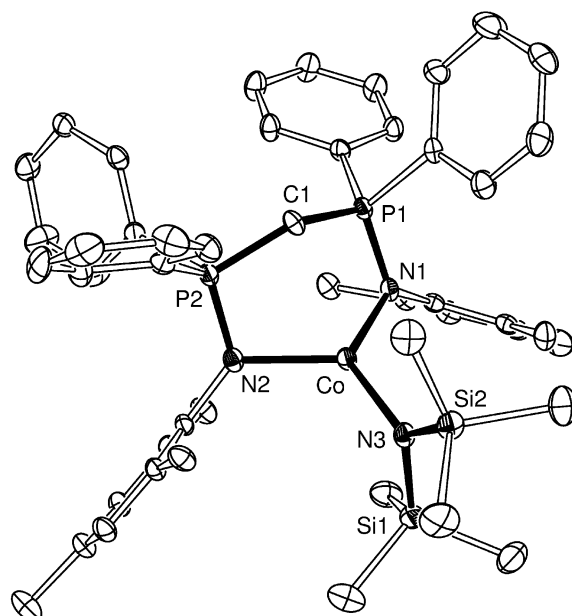
Fig. 4 Molecular structure of **4**. Hydrogen atoms omitted for clarity, thermal ellipsoids at 25% probability.
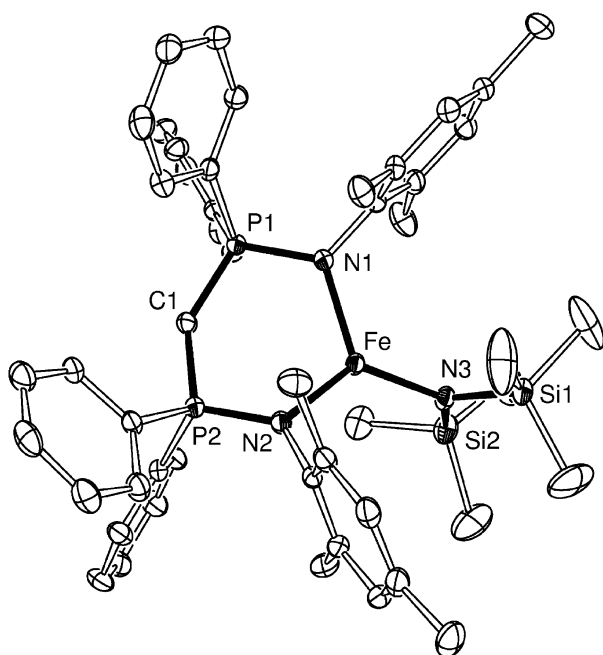
Fig. 3 Molecular structure of **3**. Hydrogen atoms omitted for clarity, thermal ellipsoids at 25% probability.

divalent manganese, iron and cobalt derivatives that are terminally bonded to the N(SiMe$_3$)$_2$ ligand,[11–13] they do not show the expected sequence Mn–N > Fe–N > Co–N that would be consistent with the decreasing size of the M^{2+} ions.[14] The observation that the Co–N(3) bond length of **4** is effectively identical to that of the Fe–N(3) bond length of **3** may be related to the more pronounced boat conformation of the chelating bis(phosphinimino)methyl ligand adopted in the cobalt complex (Fig. 5). This results in a significantly closer approach of the C(1) methanide carbon to the cobalt centre in **4** [2.570 Å] in comparison to the C(1)–Fe distance [3.177 Å] observed in **3** and effectively increases the cobalt coordination number to four. That this occurs without significant pyramidalisation at the cobalt centre is surprising and may be related to the crowded environment provided by the bulky bis(phosphinimino)methyl and hexamethyldisilazide ligands. A shortening of the C(1)–M distance also occurs in the manganese analogue **2** [2.689 Å]. We have recently observed such ligand distortions in a series of three-coordinate zinc compounds of **IV**,[15] while Cavell and coworkers have reported several structurally similar zinc and aluminium derivatives of a bis(phosphinimino)methyl ligand bearing trimethylsilyl substituents.[16] At present we
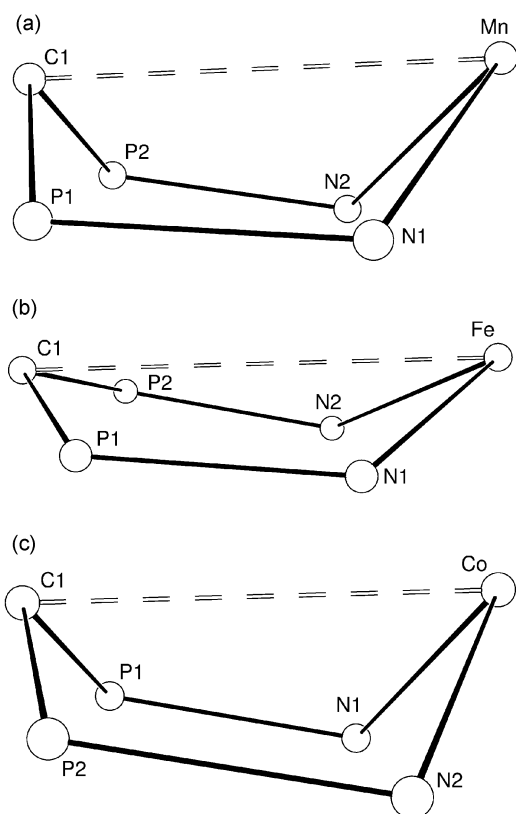
Fig. 5 The N–P–C–P–N–M chelate cores of (a) **2**, (b) **3** and (c) **4** emphasising the M–C(1) contact of compounds **2** and **4**. For **2**, **3** and **4** the respective angles defined by the P(1)–C(1)–P(2) and N(1)–M–N(2) least square planes and the P(1)–N(1)–P(2)–N(2) plane are; **2**: 61.25, 54.36°; **3**: 24.01, 37.87°; **4**: 51.47, 64.89°.

believe that this structural feature is most straightforwardly rationalised as a consequence of the substantial carbanionic character of the methanide centre C(1). The ligand frameworks of **2**, **3** and **4** nevertheless provide evidence for considerable delocalisation of charge *via* the P–N linkages. The P–C(1) (Table 2) bonds are shortened in comparison to typical P–C σ bonds while the P–N bond (Table 2) distances are elongated compared to the corresponding values of structurally characterised bis(phosphinimino)methanes [*e.g.* for [H$_2$C(Ph$_2$P=NSiMe$_3$)$_2$] P–C(1) = 1.825(1); P–N = 1.536(2) Å].[17]

We have previously observed that Zn(II) analogues of compounds **2**–**4** may be reacted with sterically demanding phenols and alcohols to form three-coordinate aryloxy- and alkoxy-zinc derivatives supported by the bidentate ligand **IV**.[15] Such compounds are of interest as potential catalysts for the living ring opening polymerisation of cyclic esters such as *rac*-lactide.[18] As catalysts based upon ferric alkoxides have also been reported to mediate polymer formation in a controlled manner, we have begun to explore whether a similar protolytic strategy will enable the synthesis of comparable systems based on iron(II). Consequently, reaction of **3** with triphenylmethanol in toluene affected clean elimination of (Me$_3$Si)$_2$NH and the formation of [{CH(Ph$_2$PNC$_6$H$_2$Me$_3$-2,4,6)$_2$}FeOCPh$_3$], compound **5** (μ_{eff} = 5.10 μ_B, 298 K, C$_6$D$_6$), in high yield. Crystallisation from toluene gave **5** as analytically pure yellow crystals suitable for an X-ray analysis. The molecular structure is illustrated in Fig. 6, while details of the X-ray analysis and selected bond lengths and angles are listed in Tables 1 and 2, respectively.

The most notable feature of **5** is the pronounced boat conformation adopted by the bis(phosphinimino)methyl ligand, which allows a close Fe–C(1) contact of 2.375 Å and the adoption of an unusual trigonal pyramidal geometry. As was noted for the manganese and cobalt derivatives, **2** and **4**, this interaction causes little disruption to the planarity of the ON$_2$M
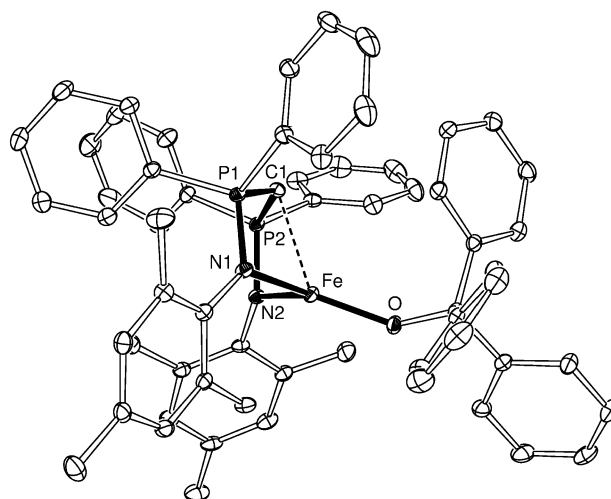

Fig. 6 The molecular structure of **5**. Hydrogen atoms omitted for clarity, thermal ellipsoids at 25% probability.

coordination plane in **5** (Σ_{angles} = 359.24°). It is accompanied however by a lengthening of the Fe–N bonds [2.083(2), 2.191(2) Å] from the corresponding distances in the three-coordinate compound **3**. A number of structurally characterised bis(phosphinimino)methyl complexes have been shown to contain direct metal to methanide carbon bonds including the closely related complex [NiBr{HC(Ph$_2$PNC$_6$H$_3^i$Pr$_2$-2,6)$_2$}].[6] In this latter case, the bromine atom is sufficiently small to allow the nickel coordination geometry to adjust to square planar with a direct Ni–C bond of 2.008(2) Å. In compound **5**, the bulk of the triphenylmethoxy substituent is apparently sufficient to prevent such a dramatic structural distortion and the formation of an iron to carbon bond that would be more typical of four-coordinate iron(II) alkyls (<2.15 Å).[19]

Although the lack of any appreciable pyramidalisation at iron in **5** mitigates against the formulation of this Fe–C(1) contact as being directly coordinative, one of us (D. J. E.) has demonstrated previously that longer range (<2.5 Å) interactions in low-coordinate iron complexes are important in assigning coordination number and geometry. Such long range interactions can have a significant effect on the electron density and electric field gradient experienced by the iron nucleus and may be examined by ^{57}Fe Mössbauer spectroscopy.[20] The observed i.s. and q.s. parameters for compound **3** of 0.57 mm s^{-1} and 0.89 mm s^{-1} respectively fall within the established range for truly three-coordinate iron (*e.g.* for [Fe{N(SiMe$_3$)$_2$}$_2$]$_2$, i.s. = 0.58 mm s^{-1}, q.s. = 1.02 mm s^{-1}).[19] On the other hand the parameters for compound **5** (i.s. = 0.96 mm s^{-1}, q.s. = 2.02 mm s^{-1}) are significantly larger, consistent with an increased coordination number and asymmetry at the iron nucleus.

In conclusion, we have demonstrated that the coordination environment provided by **IV** is suitable for the support of low coordinate d^5–d^7 first row transition metal centres. The ligand framework allows considerable conformational adjustment with variation of co-ligand identity and a transition from bidentate to effectively tridentate coordination. Compound **5** includes a direct contact from iron to the methanide carbon of the ligand, which results in significant perturbation to the electronic environment of the iron centre *without* significant pyramidalisation of the otherwise planar geometry.

The prospect of being able to fine tune the coordination geometry of low coordinate centres in this manner offers great potential for the subtle adjustment of the local metal environment. We are continuing to study the chemistry of these and related systems to determine whether these observations are essentially electronic or steric in origin and are exploring the possibility of tuning the strength of the weak

axial interaction provided by the methanide carbon centre of bulky bis(phosphinimino)methyl ligands.

Experimental

All reactions were conducted under an atmosphere of dry argon and manipulated either on a double manifold vacuum line or in a dinitrogen-filled drybox operating at less than 1 ppm of O_2. Toluene was purified by distillation from molten sodium and diethyl ether from sodium/benzophenone ketyl. $[M\{N(SiMe_3)_2\}_2]$ (M = Mn, Fe, Co),[8–10] mesityl azide[21] and **IV**[6] were synthesised by literature procedures. Mass spectra were obtained at 70 eV. Mössbauer spectra, recorded at 77 K, in zero magnetic field, on an ES-Technology MS-105 spectrometer with a 75 MBq [57]Co source in a rhodium matrix at ambient temperature, were referenced to a 25 μm iron foil at 298 K and spectral parameters obtained by fitting of Lorentzian curves. Solid samples were prepared by grinding with boron nitride under an atmosphere of dinitrogen. Elemental analyses were performed by SACS at the University of North London.

[{CH(Ph₂PNC₆H₂Me₃-2,4,6)₂}Fe(μ-Cl)₂Li(OEt₂)(THF)] 1

A solution of **IVLi**, prepared in THF (25 mL) from **IV** (0.75 g, 1.15 mmol) and *n*-BuLi (1.15 mmol), was added at −78 °C to a stirred suspension of $FeCl_2$ (0.15 g, 1.18 mmol) in THF (25 mL). This was allowed to warm to room temperature to give a light brown solution. Filtration to remove a small amount of suspended solid, followed by removal of solvent and crystallisation from Et₂O (30 mL) at −30 °C produced **1** as large colourless crystals. (Yield 59%). Anal. Calc. for $C_{51}H_{61}Cl_2N_2P_2O_2$-LiFe: C 65.83, H 6.56, N 3.01; Found: C 65.59, H 6.45, N 2.86%. MS (*m/z*): 740 [L³FeCl₂⁺]. [57]Fe Mössbauer; i.s. = 0.93 mm s⁻¹, q.s. = 3.54 mm s⁻¹, $\Gamma_{1/2}$ = 0.12 mm s⁻¹.

[{CH(Ph₂PNC₆H₂Me₃-2,4,6)₂}MN(SiMe₃)₂] (M = Mn 2, Fe 3, Co 4)

These compounds were prepared by the same general method. A solution of $[CH_2(Ph_2P=NC_6H_2Me_3-2,4,6)_2]$ (1.00 g, 1.54 mmol) in toluene (20 mL) was added at room temperature to an equimolar solution of the appropriate silylamide, $[M\{N(SiMe_3)_2\}_2]$ in toluene (20 mL). In the case of the iron derivative this produced an immediate darkening of the solution and a colour change from green to red/brown. The solutions were stirred for 14 h at which point they were concentrated to incipient crystallisation (ca. 5 mL). **2**, **3** and **4** were crystallised by slow cooling of this solution from 60 °C and isolated as large colourless (**2**, **3**) or green (**4**) crystals in *ca.* 60–70% yields. **2**: Anal. Calc. for $C_{49}H_{61}N_3P_2Si_2Mn$: C 68.03, H 7.12, N 4.86; Found: C 68.02, H 7.23, N 4.71%. MS (*m/z*): 864 [M⁺], 849, 793, 740, 703 [L³Mn⁺], 440. **3**: Anal. Calc. for $C_{49}H_{61}N_3P_2Si_2Fe$: C 67.96, H 7.11, N 4.85; Found: C 68.06, H 7.06, N 4.80%. MS (*m/z*): 865 [M⁺], 704 [L³Fe⁺]. [57]Fe Mössbauer; i.s. = 0.57 mm s⁻¹, q.s. = 0.89 mm s⁻¹, $\Gamma_{1/2}$ = 0.12 mm s⁻¹. **4**: Anal. Calc. for $C_{49}H_{61}N_3P_2Si_2Fe$: C 67.72, H 7.09, N 4.84; Found: C 67.68, H 6.98, N 4.84%. MS (*m/z*): 869 [M⁺], 707 [L³Co⁺], 574, 522, 440.

[{CH(Ph₂PNC₆H₂Me₃-2,4,6)₂}FeOCPh₃] 5

A solution of Ph₃COH (0.12 g, 0.46 mmol) in toluene (15 mL) was added at room temperature to a stirred solution of **3** in toluene (15 mL). This produced a colour change from colourless to pale yellow. After stirring had been continued for 13 h, the solution was concentrated to incipient crystallisation and **3** was isolated as large pale yellow crystals by slow cooling from 60 °C. (Yield 75%). Anal. Calc. for $C_{62}H_{58}N_2P_2OFe$: C 77.17, H 6.07, N 2.90; Found: C 76.88, H 5.94, N 2.86%. MS (*m/z*): 965 [M⁺], 705 [L³Fe]. [57]Fe Mössbauer; i.s. = 0.96 mm s⁻¹, q.s. = 2.02 mm s⁻¹, $\Gamma_{1/2}$ = 0.12 mm s⁻¹.

Crystal structure determinations

Data were collected at 173 K on a Nonius Kappa CCD diffractometer, λ(Mo-Kα) = 0.71073 Å; details are given in Table 1. The structures were solved by direct methods (SHELXS-97)[22] and refined by full matrix least squares (SHELXL-97)[23] with non-H atoms anisotropic and H atoms included in riding mode.

CCDC reference numbers 191080–191082 and 198768–198769.

See http://www.rsc.org/suppdata/dt/b2/b210467a/ for crystallographic data in CIF or other electronic format.

Acknowledgements

References

1 See, for example: (*a*) G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**, 428; (*b*) *Biomimetic Oxidations Catalyzed by Transition Metal Complexes*, ed. B. Meunier, Imperial College Press, London, 2000.

2 (*a*) J. M. Smith, R. J. Lachiotte and P. L. Holland, *Chem. Commun.*, 2000, 1542; (*b*) J. M. Smith, R. J. Lachiotte, K. A. Pittard, T. R. Cundari, G. Lukat-Rodgers, K. R. Rogers and P. L. Holland, *J. Am. Chem. Soc.*, 2001, **123**, 9222; (*c*) H. Andres, E. L. Bominaar, J. M. Smith, N. A. Eckert, P. L. Holland and E. Münck, *J. Am. Chem. Soc.*, 2002, **124**, 3012; (*d*) T. J. J. Sciarone, A. Meetsma, B. Hessen and J. H. Teuben, *Chem. Commun.*, 2002, 1580; (*e*) A. Panda, M. Stender, R. J. Wright, M. M. Olmstead, P. Klavins and P. P. Power, *Inorg. Chem.*, 2002, **41**, 3909.

3 M. K. Chan, J. Kim and D. C. Rees, *Science*, 1993, **260**, 792.

4 O. Einsle, F. A. Tezcan, S. L. A. Andrade, B. Schmid, M. Yoshida, J. B. Howard and D. C. Rees, *Science*, 2002, **297**, 1696.

5 See, for example: (*a*) M. S. Hill and P. B. Hitchcock, *Angew. Chem., Int. Ed.*, 2001, **40**, 4089; (*b*) M. S. Hill and P. B. Hitchcock, *Organometallics*, 2002, **21**, 220; (*c*) M. S. Hill and P. B. Hitchcock, *Organometallics*, 2002, **21**, 3258.

6 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.

7 See for example: (*a*) S. L. Stokes, W. M. Davies, A. L. Odom and C. C. Cummins, *Organometallics*, 1996, **15**, 4521; (*b*) C. D. Burbridge and D. M. L. Goodgame, *J. Chem. Soc. A*, 1967, 694.

8 H. Bürger and U. Wannagat, *Monatsh. Chem.*, 1963, **94**, 1007.

9 H. Bürger and U. Wannagat, *Monatsh. Chem.*, 1964, **95**, 1099.

10 R. A. Andersen, K. Faegri, J. C. Green, A. Haarland, M. F. Lappert, W.-P. Leung and K. Rypdal, *Inorg. Chem.*, 1988, **27**, 1782.

11 D. C. Bradley, M. B. Hursthouse, K. M. A. Malik and R. Moseler, *Transition Met. Chem.*, 1978, **3**, 353.

12 (*a*) P. P. Power and B. D. Murray, *Inorg. Chem.*, 1984, **23**, 4584; (*b*) U. Siemeling, U. Vorfeld, B. Neumann and H.-G. Stammler, *Inorg. Chem.*, 2000, **39**, 5159 and references therein.

13 M. M. Olmstead, P. P. Power and S. C. Shoner, *Inorg. Chem.*, 1991, **30**, 2547.

14 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.

15 M. S. Hill and P. B. Hitchcock, *J. Chem. Soc., Dalton Trans.*, 2002, 4694.

16 (*a*) A. Kasani, R. McDonald and R. G. Cavell, *Organometallics*, 1999, **18**, 3775; (*b*) K. Aparna, R. McDonald, M. Ferguson and R. G. Cavell, *Organometallics*, 1999, **18**, 4241; for a general review of iminophosphorane coordination chemistry, see: (*c*) A. Steiner, S. Zacchini and P. I. Richards, *Coord. Chem. Rev.*, 2002, **227**, 193.

17 A. Müller, M. Möhlen, B. Neumüller, N. Faza, W. Massa and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1999, **625**, 1748.

18 General review of catalyst types in lactide polymerisation: B. J. O'Keefe, M. A. Hillmyer and W. B. Tolman, *J. Chem. Soc., Dalton Trans.*, 2001, 2215.

19 See for example: H. K. Lee, B.-S. Luo, T. C. W. Mak and W.-P. Leung, *J. Organomet. Chem.*, 1995, **489**, C71.

20 D. J. Evans, D. L. Hughes and J. Silver, *Inorg. Chem.*, 1997, **36**, 747.

21 I. Ugi, H. Perlinger and L. Behringer, *Chem. Ber.*, 1958, **91**, 2324.

22 G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, Göttingen, 1997.

23 G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, Göttingen, 1997.