

Three-coordinate bis(phosphinimino)methanide derivatives of ‘open shell’ [M(II)] (M = Mn, Fe, Co) transition metals

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Received 8 June 2004; accepted 25 June 2004

Available online 14 August 2004

Abstract

An alternative two-step synthesis of the previously reported bis(diphenylphosphinimino)methane [$\text{CH}_2(\text{Ph}_2\text{P}=\text{NC}_6\text{H}_3^i\text{Pr}_{2-2,6})_2$] involving bromine oxidation of dppm and metathesis with 2,6-diisopropylaniline is described. [$\text{CH}_2(\text{Ph}_2\text{P}=\text{NC}_6\text{H}_3^i\text{Pr}_{2-2,6})_2$] is readily deprotonated by the transition metal silylamides [$\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2$] (M = Mn, Fe and Co) to provide a series of exclusively three-coordinate derivatives [$\{\text{CH}(\text{Ph}_2\text{PNC}_6\text{H}_3^i\text{Pr}_{2-2,6})_2\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2$] which have been characterised by elemental analysis, magnetic measurements and, in the case of the Fe derivative, X-ray structural analysis. Reactivity studies have shown that even such sterically demanding bis(phosphinimino)methanide ligands are prone to protonolysis and reductive [P(V) to P(III)] degradation which limits their utility as stable platforms for further M(II) derivitisation.

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Keywords: Three-coordinate; Manganese; Iron; Cobalt; Amides

1. Introduction

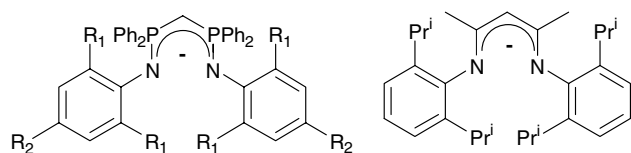
We have recently reported synthetic and preliminary reactivity studies of a variety of s-, p-, d- and f-block derivatives supported by the sterically demanding bis(phosphinimino)methanide anion (**I**) [1–4]. In these compounds, a level of kinetic stability is attained due to the steric demands of the *N*-mesityl substituents and the Ph_2P -ligand ‘backbone’. Our original interest in this class of ligand arose from the topological similarity of **I** to *N*-aryl substituted β -diketiminato anions exemplified by the 2,6-diisopropylphenyl (Dipp)-substituted derivative, **II**. β -diketiminates have attained recent prominence as stable and robust supporting ligands for an enormous variety of metal fragments [5]. Use of the anion **II**, for example, has enabled the synthesis of several electroni-

cally and coordinatively unsaturated ‘open shell’ (i.e. <10 d electrons) derivatives of the divalent first row transition elements Mn, Fe and Co, some of which have demonstrated a spectacular reaction chemistry [6–9]. The common entry point for much of this chemistry has been the synthesis of low-coordinate halide and amido complexes. Our initial attempts to synthesise analogous derivatives stabilised by **I** indeed resulted in the isolation of three- and four-coordinate compounds with similar stability and electronic properties. Furthermore, we reasoned that studies of the reaction chemistry of three-coordinate amides, such as the amido-derivatives **III** would be equally fruitful [3b]. We have noted that many of our compounds feature a pronounced folding of the ligand at the two four-coordinate geminal phosphorus(V) atoms [1–4]. This ligand non-planarity is in marked contrast to the vast majority of β -diketiminato compounds where planarity is effectively maintained through charge delocalisation over the exclusively sp^2 -hybridised atoms of the N–C–C–N chelate. This

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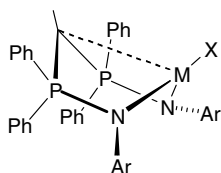
E-mail address: mike.hill@imperial.ac.uk (M.S. Hill).

feature of bis(phosphinimino)methanide coordination chemistry results in a degree of interaction between the central P–C–P methanide carbon and the metal centre that is apparently subtly dependent upon both the overall metal coordination number and co-ligand identity [3,10]. This carbanionic character indicates that anions such as **I** are perhaps more realistically compared to other heteroatom substituted methyl ligands, $(X)_nH_{3-n}C^-$ (e.g. $X = R_3Si$, $n = 1-3$; $X = R_2P(III)$, $R_2P(V)$; $n = 1, 2$), resulting in a chelating ligand with enhanced basicity and reactivity. We hoped however that the steric demands of the N- and P-bound substituents would provide sufficient kinetic stabilisation to enable the synthesis of a range of low-coordinate derivatives in which the chelated ligand would behave as an inert spectator in subsequent reactions. This was indeed the case in reaction with relatively bulky acids where, for example, protonolysis of the Fe(II) amide (**IIIb**), with Ph_3COH provided the triphenylmethoxy-derivative **IV** [b]. All attempts to react **IIIa–c** with less sterically demanding O- and N-acids were frustrated by competitive protonolysis of the bis(phosphinimino)methanide ligand **I** or, in reactions with reducing agents, reductive degradation of the ligand P(V) centres [11]. We have made similar observations with regard to the reactivity of closely related three-coordinate zinc derivatives [3a]. In an attempt to enhance the kinetic stability of the complexes, we turned our attention to the bulkier Dipp *N*-substituted analogue of **I**, the anion **V**, which may be obtained by deprotonation of the neutral bis(phosphinimino)methane, $[CH_2(Ph_2P=NDipp)_2]$ (**VI**).



I: $R_1 = R_2 = CMe_3$
V: $R_1 = iPr$; $R_2 = H$

II



Ar = 2,4,6-Me₃C₆H₂
III: M = a, Mn; b, Fe; c, Co.; X = N(SiMe₃)₂
IV: M = Fe; X = OCPH₃

2. Results and discussion

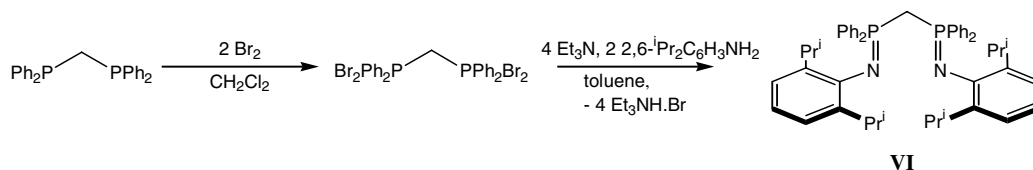
The synthesis of compound **VI** has previously been reported by Bochmann and coworkers via the oxidation of bis(diphenylphosphino)methane (dppm) with two

equivalents of 2,6-diisopropylphenyl azide [12]. As the purification of this azide entails a potentially hazardous distillation, this compound was used as a crude red oil. In our hands, this protocol resulted in only poor yields of the target bis(phosphinimino)methane. We sought therefore an alternative route to **VI** (Scheme 1). Reaction of two molar equivalents of molecular bromine with dppm in CH_2Cl_2 produced a pale yellow solution and, after removal of volatiles, a colourless solid that was assumed to be $[CH_2(Ph_2PBr)_2]$. This was employed without characterisation or further purification in reaction with two equivalents of DippNH₂ and four equivalents of Et₃N in toluene. Heating of this mixture to reflux gave a colourless suspension from which crude **VI** was isolated by filtration and removal of volatiles. Crystallisation from diethyl ether produced a monosolvated form of **VI** as large colourless crystals.

Addition of one equivalent of **VI** to a toluene solution of $[M\{N(SiMe_3)_2\}_2]$ at room temperature produced, after removal of volatiles, the monoamides $[CH(Ph_2PNDipp)_2MN(SiMe_3)_2]$ as colourless (**1**, M = Mn; **2**, M = Fe) and green (**3**, M = Co) solids. Recrystallisation from toluene at room temperature provided the analytically pure crystalline compounds containing a single toluene molecule of crystallisation. In the case of the Fe(II) derivative, **2**, these were suitable for analysis by a single crystal X-ray study. Although crystals of **1** and **3** appeared to be equally well-formed, our attempts to obtain X-ray structural data were hampered by weak diffraction at high angle. Solution magnetic measurements (Evans' method) in C_6D_6 , however, gave $\mu_{eff}(C_6D_6)$ values for all three compounds that were consistent with high spin d^5 (**1**, $\mu_B = 5.90$, $S = 5/2$), d^6 (**2**, $\mu_B = 5.15$, $S = 2$) and d^7 (**3**, $\mu_B = 4.80$, $S = 3/2$) electronic configurations with five, four and three unpaired electrons, respectively. Solid-state magnetic studies of the crystalline sample employed in the X-ray study of the iron derivative **2** were also carried out. A plot of $1/\chi(m)$ versus temperature in the range 5–300 K (Fig. 1) displayed simple Curie behaviour and gave a μ_{eff} of $5.16 \mu_B$. The similarity of this value to that of the solution measurement provides evidence that a similar three-coordinate structure to that determined by the X-ray study (vide infra) also persists in non-coordinating solvents, while the close correspondence of the values obtained here to those of amide derivatives supported by the less sterically demanding ligand **I** and closely related β -diketiminato derivatives indicates that all three compounds are, most likely, exclusively three-coordinate in both solid and solution states [3b,6,7].

The molecular structure of **2** is illustrated in Fig. 2 while selected bond lengths and angles are listed in the figure caption. The complex crystallises as the monomer along with a disordered molecule of toluene solvent.

The iron is bound to one bis(phosphinimino)methanide and a single $N(SiMe_3)_2$ ligand. As was the case in



Scheme 1.

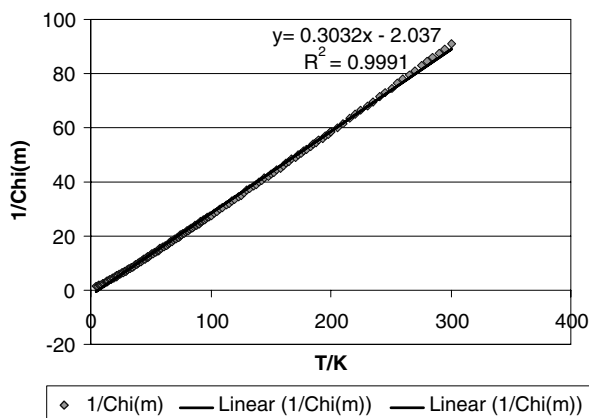
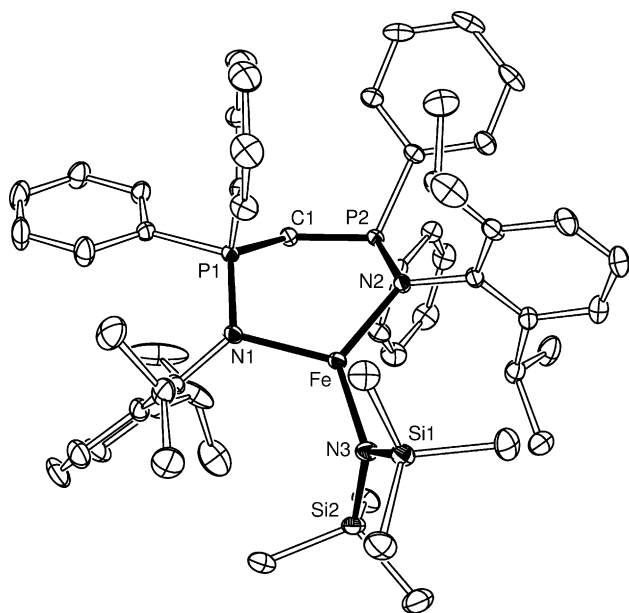
Fig. 1. $\chi(m)$ vs. T in the range 5–300 K for compound **2**.

Fig. 2. The molecular structure of **2** (30% probability ellipsoids). H atoms removed for clarity. Selected bond lengths (Å) and angles (°): Fe–N(1) 2.035(3); Fe–N(2) 2.034(3); Fe–N(3) 1.931(3); P(1)–N(1) 1.639(3); 1.640(3); P(1)–C(1) 1.714(4); N(1)–Fe–N(2) 112.33(13); N(2)–Fe–N(3) 125.74(14); N(1)–Fe–N(3) 121.86(14); Fe–N(1)–P(1) 108.36(17); Fe–N(1)–P(1) 117.89(17); N(1)–P(1)–C(1) 114.31(18); N(2)–P(2)–C(1) 110.47(18); P(1)–C(1)–P(2) 126.6(2).

the previously reported Fe(II) derivative (**IIIb**), there is no contact between the methanide carbon centre and the metal [Fe–C(1), 3.279 Å] which is unambiguously

three-coordinate. The N(1)–N(2)–N(3)–Fe coordination plane reveals no significant pyramidalisation at iron ($\sum \text{angles} = 359.93^\circ$). The Fe–N(1) and Fe–N(2) bond lengths in **2** [2.035(3), 2.034(3) Å], although slightly elongated in comparison to those of **IIIb** [1.992(3), 1.997(3) Å], are shorter than in the closely related four-coordinate ‘ate’ complex $\{[\text{CH}(\text{Ph}_2\text{PNC}_6\text{H}_2\text{Me}_3\text{-}2,4,6)_2]\text{Fe}(\alpha\text{-Cl})_2\text{-Li}(\text{THF})(\text{OEt}_2)\}$ [**3b**]. There is a slight increase of ligand bite angle in **2** [112.3(13)°] compared to that of **IIIb** [110.87(12)°]. Although possibly a result of the increased steric demands of the Dipp substituents, this value is some 10–15° wider than the corresponding bite angles of three-coordinate b-diketiminato derivatives containing the same metal and coligand [6–9]. It is more likely therefore that this bite angle is influenced more directly by the chemical constitution, and hence conformation of the N–P–C–P–N chelate (vide infra). Consequently, the remaining interligand angles around the iron centre are more acute than those of **IIIb** [**b**]. The M–N(3) distance to the silylamido substituent [1.931(3) Å] is essentially identical to that of **IIIb** [1.932(3) Å] and is within the range previously observed in three-coordinate iron derivatives that are terminally bonded to the N(SiMe₃)₂ ligand [13–15]. As we have noted previously [1–4], the ligand framework of **2** provides evidence for considerable delocalisation of charge via the P–N linkages. The P–C(1) bond lengths are shortened in comparison to typical P–C σ bonds while the P–N bond distances are elongated compared to the corresponding values of structurally characterised bis(phosphinimino)methanes [e.g. for $[\text{H}_2\text{C}(\text{Ph}_2\text{P}=\text{NSiMe}_3)_2]$ P–C(1) = 1.825(1); P–N = 1.536(2) Å] [16]. The most notable feature of the Fe–N–P–C–P–N metallacycle of **2** is the irregular ‘flattened chair’ conformation adopted. This results in a transoid relationship of the N-bonded 2,6-diisopropylphenyl substituents (Fig. 3) and contrasts to the pronounced boat conformation observed in the structure of **IIIb**. In this latter case, the less sterically demanding mesityl groups adopt a cisoid configuration that is more typical of derivatives of this ligand.

As outlined above, β -diketiminato derivatives of the first row transition elements have given rise to a great variety of unusual and striking reaction chemistry [5–9]. The heteroleptic compounds **1–3** are rare examples of stable of open shell (i.e. <10 d electrons) three-coordinate transition metal complexes. Such low coordinate centres are often implicated as transients in a wide vari-

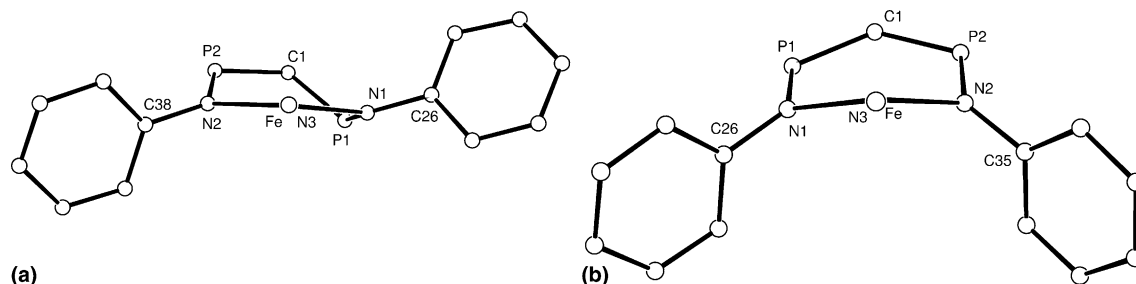


Fig. 3. The N–P–C–P–N–M cores of (a) **2**, (b) **IIIb** [b] viewed along the Fe–N(3) bond, emphasising the chelate conformations and the respective orientations of the *N*-aryl substituents. For **2** the angles defined by the P(1)–C(1)–P(2) and N(1)–Fe–N(2) least square planes and the P(1)–N(1)–P(2)–N(2) plane are; 36.74° and 14.27°.

ety of transition metal-catalysed processes such as olefin polymerisation, C–H activation and the activation of otherwise inert small molecules [17]. Based upon the recent precedent provided by known β -diketiminato chemistry, we were hopeful that reactions of compounds **1–3** would provide a route to novel chemistry. Accordingly we have attempted reactions with a variety of protic and reducible substrates. Addition of 1,2-diphenylhydrazine to solutions of **1**, **2** or **3** produced indiscriminate protonolysis of both the bis(phosphinimino)methyl and hexamethyldisilazido ligand, while reactions with azobenzene gave no reaction at room temperature and apparent decomposition, evidenced from ^{31}P NMR monitoring of the reaction in C_6D_6 , upon heating to 60 °C in toluene.

In summary, we have prepared an isoleptic series of three-coordinate and divalent Mn, Fe and Co amides supported by a highly sterically demanding bis(diphenylphosphinimino)methanide. Despite steric bulk which is comparable to a variety of β -diketiminato derivatives, the ‘carbanionic’ nature and presence of reducible P(V) centres appears to limit the potential of this class of ligand in subsequent reactivity studies.

3. Experimental

3.1. General considerations

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 1 ppm of O_2 . Toluene was purified by distillation from molten sodium. $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2]$ ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}$) [18–20], were synthesised by the literature procedures. Elemental analyses were performed by SACS at the London Metropolitan University. Solid-state magnetic measurements were performed on a Quantum Design MPMS5 SQUID magnetometer.

3.2. $[\text{CH}_2(\text{Ph}_2\text{PNC}_6\text{H}_2^i\text{Pr}_{2-2,6})_2]$ (**VI**)

A solution of Br_2 (2.50 g, 15.6 mmol) in CH_2Cl_2 (30 ml) was added dropwise at 0 °C to a stirred solution of

dppm (3.0 g, 7.81 mmol) in CH_2Cl_2 (60 ml). Over the course of 1 h the initial brown colouration faded to give a pale yellow solution. Removal of volatiles gave a cream-coloured solid which was then suspended in toluene (80 ml). Triethylamine (3.40 g, 33.7 mmol) and 2,6-diisopropylphenylaniline were added via syringe and the resulting suspension heated to reflux for 14 h. After filtration, removal of volatiles produced a yellow glass. This was crystallised from diethyl ether to produce large colourless blocks of **VI** as an ether solvate (4.36 g, 69%) with ^1H NMR data identical to those quoted in the literature [12].

3.3. $[\{\text{CH}(\text{Ph}_2\text{PNC}_6\text{H}_2^i\text{Pr}_{2-2,6})_2\}\text{MN}(\text{SiMe}_3)_2]$ **1**, ($\text{M} = \text{Mn}$); **2**, ($\text{M} = \text{Fe}$); **3** ($\text{M} = \text{Co}$)

These compounds were prepared by the same general method. A solution of **VI** in toluene was added at room temperature to an equimolar solution of the appropriate silylamide, $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2]$ in toluene. In the case of the iron derivative this produced an immediate darkening of the solution and a colour change from green to brown. The solutions were stirred for 12 h at which point they were concentrated to incipient crystallisation. **1**, **2** and **3** were crystallised as mono-toluene solvates by slow cooling of this solution from 60 °C and isolated as large colourless (**1**, **2**) or green (**3**) crystals in ca. 60–70% yields. **1**: Anal. Calc. for $\text{C}_{62}\text{H}_{81}\text{N}_3\text{P}_2\text{Si}_2\text{Mn}$: C, 71.50; H, 7.78; N, 4.04. Found: C, 71.10; H, 7.21; N, 3.85%. **2**: Anal. Calc. for $\text{C}_{62}\text{H}_{81}\text{N}_3\text{P}_2\text{Si}_2\text{Fe}$: C, 71.44; H, 7.85; N, 4.03. Found: C, 71.45; H, 7.74; N, 3.95%. **3**: Anal. Calc. for $\text{C}_{62}\text{H}_{81}\text{N}_3\text{P}_2\text{Si}_2\text{Co}$: C, 71.23; H, 7.82; N, 4.02. Found: C, 71.10; H, 7.69; N, 3.91%. All analyses calculated as mono-toluene solvate.

3.4. Crystallography

Data for **2** were recorded on a Kappa CCD diffractometer by use of Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods (SHELXS-97) [21] and refined by full-matrix least-squares on all data (SHELXL-97) [22]. Non-H atoms were anisotropic and H atoms were included in riding mode. The toluene

solvent molecule was disordered. Chemical formula $C_{55}H_{73}FeN_3P_2 \cdot (C_7H_8)$. Formula weight 1042.27; T (K) 173(2); triclinic, $P\bar{1}$ (No. 2); $a = 12.2460(2)$ Å, $b = 13.3237(2)$ Å, $c = 18.9399(3)$ Å; $\alpha = 71.032(1)^\circ$, $\beta = 86.286(1)^\circ$, $\gamma = 84.644(1)^\circ$; $Z = 2$; $V = 2907.77(8)$ Å³; $D_{\text{calc}} = 1.19$ Mg m⁻³; $\mu = 0.40$ mm⁻¹; θ range = 3.75–25.08°; R_1 ; wR_2 [$I > 2\sigma(I)$] = 0.059; 0.150; R_1 ; wR_2 all data = 0.082; 0.164; measured/independent reflections/ R_{int} = 30984/10101/0.052; reflections with $I > 2\sigma(I) = 7714$.

Acknowledgements

We thank the Royal Society for a University Research Fellowship (M.S.H.) and Mr. Kieran Brigatti for assistance with the SQUID measurement.

Appendix A. Supplementary material

Crystallographic data for the structural analysis of **2** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 240802. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2004.06.050.

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