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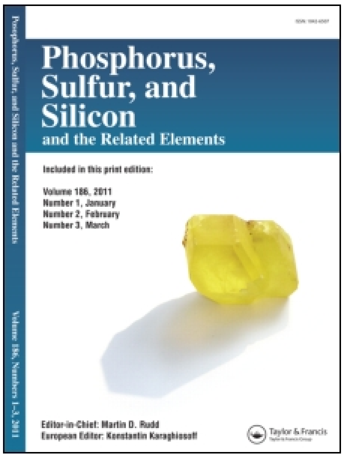

Phosphorus, Sulfur, and Silicon and the Related Elements

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Phosphoraneiminato Complexes of Manganese, Iron, and Cobalt with Heterocubane Structures

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PHOSPHORANEIMINATO COMPLEXES OF MANGANESE, IRON, AND COBALT WITH HETEROCUBANE STRUCTURES

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The phosphoraneiminato complexes $[MnBr(NPEt_3)]_4$ 3, $[FeCl(NPEt_3)]_4$ 4 and $[CoBr(NPEt_3)]_4$ 5 were built from the element halides MX_2 and excess trimethylsilyltriethylphosphoraneimine in the presence of potassium fluoride. They form shiny orange (M = Mn), dark brown (M = Fe), and dark green (M = Co) crystals. According to single crystal structure determinations these compounds form M_4N_4 heterocubane frameworks with μ_3-N-bridges and M–N bond lengths of 213.4 pm (M = Mn), 205.7 pm (M = Fe), and 204.4 pm (M = Co) which lead to intermetallic distances of 295.7 pm (M = Mn), 272.9 pm (M = Fe), and 279.0 pm (M = Co).

Keywords: Phosphoraneiminato complexes; heterocubanes; manganese compounds; iron compounds; cobalt compounds

INTRODUCTION

There are three known modes of coordination of the phosphoraneiminato ligand $[R_3PN]^-$ to transition metals shown in figure 1. Experience has shown that the ligand often coordinates terminally to transition metal centres in high oxidation states (type A) as in $[Ru(NPEt_2Ph)Cl_3(PEt_2Ph)_2]$ [1], while transition metals in low oxidation states prefer coordination type B with μ_2-N- and type C with μ_3-N-bridges. Especially substituents R with +I-effect at the phosphorus atom favour type C.

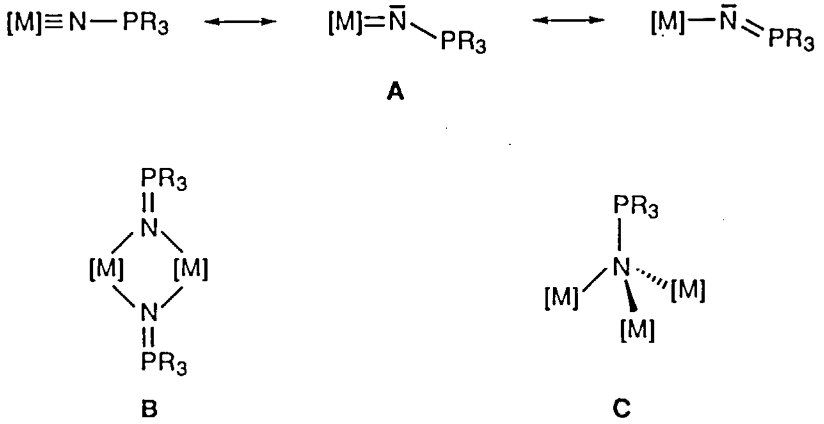

FIGURE 1 Coordination modes of the phosphoraneiminato ligand $[R_3PN]^-$

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RESULTS AND DISCUSSION

Stable Donor Acceptor Complexes

Phosphoraneiminato complexes are available from a number of reactions [2]. A successful method for the preparation is the reaction of anhydrous element halides with trimethylsilylsubstituted phosphoraneimines. If the applied element halides show Lewis acidic properties the formation of donor acceptor complexes as a primary step can be assumed. In some cases these donor acceptor complexes were isolated and characterized by single crystal structure determinations. Figure 2 shows the structures of the donor acceptor complexes $MnI_2(Me_3SiNPEt_3)_2$ **1** and $[MnCl_2(Me_3SiNPEt_3)]_2$ **2** [3]. In both compounds the P–N and Si–N bonds are shortened by

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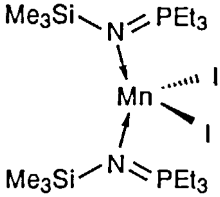
approximately 3 pm in comparison with the free phosphoraneimine. This observation correlates with the high thermal stabilities of **1** and **2** and gives an explanation for the decreased readiness to eliminate trimethylsilylhalide.



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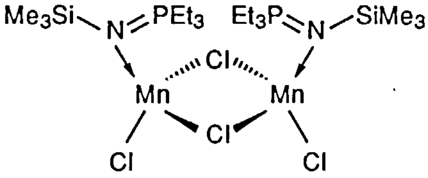

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FIGURE 2 Structures of the donor acceptor complexes $MnI_2(Me_3SiNPEt_3)_2$ **1** and $[MnCl_2(Me_3SiNPEt_3)]_2$ **2**

Tetrameric Phosphoraneiminato Complexes of Manganese, Iron, and Cobalt

Synthesis of 3-5

We obtained the tetrameric phosphoraneiminato complex $[MnBr(NPEt_3)]_4$ **3** as described [4] as a shiny orange powder. The dark green cobalt derivative $[CoBr(NPEt_3)]_4$ **4** and the dark brown iron derivative $[FeCl(NPEt_3)]_4$ **5** were synthesized by analogous reaction of MX_2 with excess trimethylsilyltriethylphosphoraneimine in the presence of potassium fluoride and heating of the reaction mixtures for several hours at $t > 160$ °C (see figure 3).

$$MX_2 \xrightarrow[\substack{Me_3SiPNEt_3 \\ t > 160^\circ C}]{KF} \tfrac{1}{4}[MX(NPEt_3)]_4 + FSiMe_3 + KX$$

M = Mn, Fe, Co; X = Cl, Br

FIGURE 3 Synthesis of **3-5**

All compounds are air- and moisture-sensitive. The tetrameric units show the molecular mass ions with high relative intensities under electron impact conditions. Vapour pressure osmometry measurements of solutions of **3** and **5** in tetrahydrofuran at 0 °C have shown aggregation states of $n = 2$ for both compounds [5]. According to these results we assume the formation of tetrahydrofuran adducts with an average aggregation state of $n = 2$. IR spectra of **3-5** show broad strong absorption bands for the P–N stretching vibrations at 1050 cm^{-1} which are clearly shifted to lower frequencies in comparison with the free trimethylsilyltriethylphosphoraneimine (1310 cm^{-1}) [6]. This frequency area correlates with the results of single crystal structure determinations which show P–N distances of 159 pm.

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Crystal Structure Determinations

The tetrameric units **3** and **5** form nearly perfect M_4N_4 heterocubane frameworks (see figure 4) with Mn–N bond lengths of 213.4 pm and Co–N bond lengths of 204.4 pm, respectively, which lead to intermetallic Mn···Mn contacts of 295.7 pm and Co···Co contacts of 279.0 pm on average. Each metal centre in the tetrameric units is coordinated in a distorted tetrahedral fashion by a terminally bonded bromo atom and three nitrogen atoms of the phosphoraneiminato ligands. The maximum deviation of the angles inside the heterocubane frameworks from the rectangle amount to 3.4° for the manganese compound and 4.4° for the cobalt compound. The M–N bond lengths of **3** and **5** can be classified as M–N single bonds. These distances as well as the observed short P–N bond lengths are identical with those in $[MnX(NPEt_3)]_4$ (X = Cl, I) [4,7] and $[CoCl(NPEt_3)]_4$ [7].

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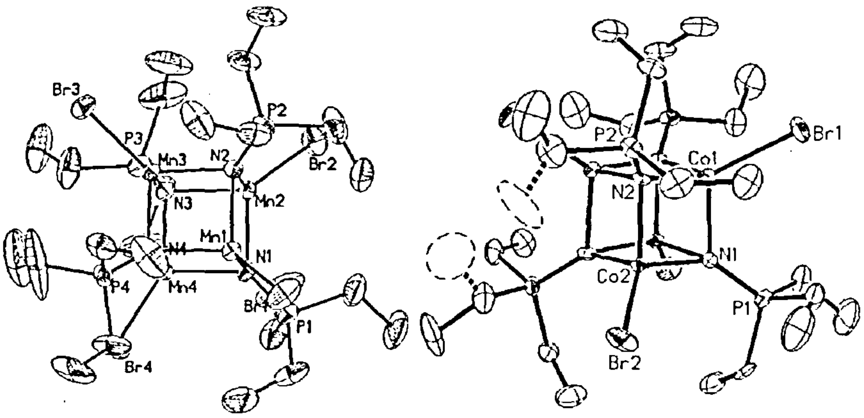

3 5

FIGURE 4 Crystal structures of $[MnBr(NPEt_3)]_4$ 3 and $[CoBr(NPEt_3)]_4$ 5, selected average bond lengths [pm] and bond angles [°] with standard deviations in brackets; 3: Mn···Mn 295.7(1), Mn-Br 244.8(1), Mn–N 213.4(6), P–N 159.4(6), Mn–N–Mn 87.8(2), N–Mn–N 92.1(2), Br–Mn–N 123.7(2), Mn–N–P 126.8(3); 5: Co···Co 279.0(2), Co-Br 237.0(1), Co–N 204.4(6), P–N 159.2(6), Co–N–Co 86.0(2), N–Co–N 93.9(2), Br–Co–N 122.4(2), Co–N–P 128.0(4). Two of the ethyl groups of the tetrameric unit 5 are disordered.

In comparison with the tetrameric units 3 and 5 the isotypic iron derivative $[FeCl(NPEt_3)]_4$ 4 forms a more distorted heterocubane framework with Fe–N–Fe angles of 83.1° and N–Fe–N angles of 96.5°on average, which leads to unexpected short intermetallic distances of 272.9 pm on average (see figure 5). This is the shortest observed intermetallic distance in first row transition metal phosphoraneiminato complexes with M_4N_4 heterocubane frameworks so far [4,7,8]. The average Fe–N bond lengths of 205.7 pm are lenghtened about 2 pm in comparison with the cobalt derivatives $[MnX(NPEt_3)]_4$ (X = Cl, Br, I) and shortened about 8 pm in comparison with the manganese derivatives $[CoX(NPEt_3)]_4$ (X = Cl, Br). This observation correlates with the decrease of the ionic radii of M^{2+} in the row Mn>Fe>Co. The P–N bond lengths are identical with those of 3 and 5. The magnetic properties of 3-5 are currently under investigation.

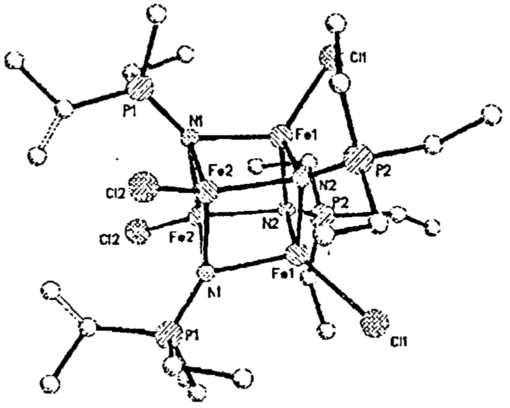

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FIGURE 5 Crystal structure of $[FeCl(NPEt_3)]_4$ 4, selected average bond lengths [pm] and bond angles [°] with standard deviations in brackets: Fe···Fe 272.9(1), Fe–Cl 226.6(6), Fe–N 205.7(2), P–N 158.9(2), Fe–N–Fe 83.1(1), N–Fe–N 96.5(1), Cl–Fe–N 120.5(1), Fe–N–P 130.0(1). Two of the ethyl groups of the tetrameric unit 4 are disordered.

Reactivity of 3-5 towards Organolithium Reagents

The compounds 3-5 react with organolithium reagents LiR to form thermally stable tetrameric organomanganese phosphoraneiminato complexes with R = alkyl, alkynyl [9] and organoiron phosphoraneiminato complexes as well as organocobalt phosphoraneiminato complexes with R = alkynyl in solid state. According to single crystal structure determinations and IR investigations the organic substituents are bonded terminally in all cases.

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Conclusions

The phosphoraneiminato complexes $[MnBr(NPEt_3)]_4$ **3**, $[FeCl(NPEt_3)]_4$ **4**, and $[CoBr(NPEt_3)]_4$ **5** as well as their organometallic derivatives form stable tetrameric units in solid state. Further experiments to connect the tetramers via conjugated hydrocarbons are within the scope of our investigations.

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