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The synthesis of the heterocubane cluster [{CpMn}$_4$(μ_3-P)$_4$] as a tetrahedral shaped starting material for the formation of polymeric coordination compounds†‡§

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Thermolysis of [CpMn(η^6-cht)] with P_4 in 1,3-diisopropylbenzene leads to the formation of the heterocubane [$Cp_4Mn_4P_4$] (1) in high yields, as a rare example of 'naked' phosphorus containing complexes of manganese. Compound 1 is characterized and studied by DFT calculations and reflection measurements. 1D coordination polymers [{(CpMn)$_4$(μ_3-P)$_4$}(CuX)]$_n$ (2-Cl: X = Cl; 2-Br: X = Br) are obtained in the reaction with CuX. Furthermore, it is shown that all four P atoms in 1 can be addressed for a coordination towards cymantrene resulting in [{(CpMn)$_4$(μ_3-P)$_4$}{CpMn(CO)$_2$}$_n$] (3a: *n* = 1; 3b: *n* = 2; 3c: *n* = 3; 3d: *n* = 4), and shows that 1 is a tetra-topic building block in coordination chemistry.

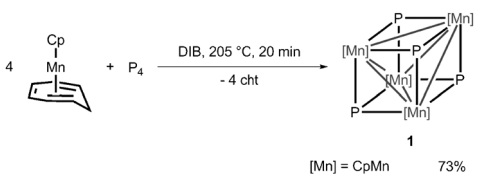
In the last few decades, the field of P_n ligand complexes[1] has been well established in chemistry.[2] Within this area, we demonstrated that P_n ligand complexes in combination with monovalent coinage metal salts are perfect starting materials to construct supramolecular assemblies. Especially, using the complexes [{CpMo(CO)$_2$}$_2$(μ,$\eta^{2:2}$-P_2)] and [Cp*Fe(η^5-P_5)] (Cp* = C_5Me_5) together with CuX (X = Cl, Br, I), a wide spectrum of *pseudo*-0D,[3] 1D[4] or 2D[4a,d] frameworks could be realized. For the formation of 3D architectures, ideally multitopic linkers with an appropriate symmetry (*e.g.* T_d, O_h) would be needed. All attempts to construct 3D scaffolds by using P_n ligand complexes have failed so far.[5]

The existence of a restricted number of clusters and complexes of manganese with substituent-free P atoms motivated us to prepare such compounds.[6] Very recently we reported on the synthesis of the two triple decker sandwich complexes [{Cp^{BIG}Mn}$_2$(μ,$\eta^{5:5}$-P_5)] and [{Cp^{BIG}Mn}$_2$(μ,$\eta^{2:2}$-P_2)$_2$] (Cp^{BIG} = C_5(4-*n*BuC_6H_4)$_5$) *via* the thermolysis of [Cp^{BIG}Mn(cht)] (cht = cycloheptatriene) with P_4.[6a] Substitution of the sterically demanding Cp^{BIG} ligand by the usual Cp ligand should alter the product outcome dramatically.

In general, Mn^{4+} ions are very promising candidates for future warm white LEDs due to their emission in the red range of the visible spectrum and large intensities in some host lattices, but their luminescence is mainly investigated by doping in oxidic or fluoridic solid state materials.[7] For the cluster presented in this communication the electronic situation is quite different, but the formal manganese oxidation state is also IV. Therefore we investigated the optical properties of **1**.

Herein we report on the synthesis and characterization of the heterocubane cluster [(CpMn)$_4$(μ_3-P)$_4$] (**1**) and the first coordination studies of **1** with CuX (X = Cl, Br) resulting in 1D coordination polymers. It is also shown that the coordination of all four P atoms in **1** towards metals can be generally achieved.

The co-thermolysis (20 min) of [CpMn(η^6-cht)] (cht = cycloheptatriene) and P_4 in 1,3-diisopropylbenzene (DIB) results in the formation of [$Cp_4Mn_4P_4$] (**1**) (eqn (1)). After solvent removal, extraction with CH_2Cl_2 and cooling to −35 °C, **1** is obtained as dark red to brown needle shaped crystals in yields of about 73%. Decomposition is observed at longer reaction times (metal mirror).



(1)

Heterocubanes of the formulae M_4E_4 (M = metal fragment; E = 'naked' element of the 15th or 16th group) have been well known in chemistry for decades. In particular, O, S and N atoms show a high tendency to form this structural motif.

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† Parts of the presented results are already part of the doctoral thesis of S. Heinl, University of Regensburg (Regensburg, Germany), 2014.

‡ Dedicated to Professor Todd Marder on the occasion of his 60th birthday.

§ Electronic supplementary information (ESI) available: Full crystallographic data, NMR spectra. CCDC 1404879–1404885. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc04800a

Therefore, hundreds of such compounds could be characterized until now. Additionally, a very large number of Se and Te containing heterocubanes have been published. However, only very few phosphorus derivatives are known. Structural characterization was possible for three similar cobalt compounds $[(Cp^RCo)_4(\mu_3\text{-}P)_4]$ (**A**: $Cp^R = C_5H_5$; **B**: $Cp^R = C_5H_4{}^tBu$; **C**: $Cp^R = C_5H_3{}^tBu_2$)[8] and the tungsten cluster $[\{W(CO)_3Cp^*W\}_2(\mu_3\text{-}P)_2\{\mu_3\text{-}PW(CO)_5\}_2]$ (**D**).[9] Schumann *et al.* also proposed a heterocubane structure for $(PhSnP)_4$.[10] Structural similarities can also be found for $[(CpFe)_4(P_2)_2]$,[11] $[(Cp^*Ni)_3(\mu_3\text{-}P)(P_4)]$,[12] $[(CpV)_4(P_2)_2]$[13] and $[(Cp^*Cr)_4(\mu_3\text{-}P)_4]$.[14] Heterocubane clusters with substituent-free As units are also known, but are very rare.[11,15]

Both the ^1H NMR and the $^{13}C\{^1H\}$ NMR spectra (CD_2Cl_2) of **1** show singlets at 4.58 ppm and 82.7 ppm, respectively, in the expected regions. In contrast, the $^{31}P\{^1H\}$ NMR spectrum of **1** shows an extremely low-field shifted singlet at 1079.8 ppm (slightly broadened, $\omega_{1/2}$ = 31.3 Hz). Astonishingly, the signal is about 230 ppm to 600 ppm low field shifted compared to **A–D**.

The NMR data indicate a highly symmetric molecule, which is confirmed by single crystal X-ray diffraction (Fig. 1). Compound **1** crystallizes with one solvent molecule CH_2Cl_2 from concentrated CH_2Cl_2 solutions in the monoclinic space group *C*2/*c*. The core of **1** can be described as a Mn_4 tetrahedron, wherein the faces are capped by P atoms, resulting in a heterocubane structure. In comparison, the central cores of the structures of **A**, **C** and **D** are much more distorted from a perfect cube structure than **1** is. The four Mn atoms in **1** are coordinatively saturated by Cp ligands. The Mn–Mn and Mn–P bond lengths vary from 2.6914(8) Å to 2.7320(6) Å and from 2.2249(9) Å to 2.2411(10) Å, respectively.

The number of valence electrons of the Mn atoms can be calculated classically to be 18 and the Mn centers have a formal oxidation state of +4, but **1** could be better described to contain a $[Mn_4P_4]^{4+}$ cluster. To gain more insight into the electronic structure of **1** DFT calculations have been performed (Fig. 2). The geometry of **1** has been optimized for different spin states. According to the calculations **1** has a singlet ground state (Table S5, ESI§). The triplet spin state is with 70.3 kJ mol^{-1} higher in energy. All other spin states are more than 100 kJ mol^{-1} higher in energy. Interestingly, the spin state of **1** has a strong influence on the geometry. In the singlet spin state the optimized geometry is very close to the observed experimental one. *E.g.* it possesses short Mn–Mn distances (2.705 Å) which are very similar to the experimentally determined distance of 2.713 Å (average). By stepwise increasing the spin multiplicity the elongation of one Mn–Mn distance is observed. For example in the triplet spin state there is one longer Mn–Mn distance of 3.189 Å and five shorter ones of 2.714 Å (average). In comparison with the experimentally found parameters it is indicative that **1** has a singlet spin state. The Wiberg bond index indicates a Mn–Mn bond order of 0.33, while the Mn–P bond order is close to unity (0.92). The molecular orbitals (MO) as well as the localized molecular orbitals (LMO) of **1** show the presence of Mn_2P_2 four centre bonds ($2e^-$) and the presence of lone pairs at the phosphorus atoms (Fig. 2 and Fig. S18 and S19, ESI§).

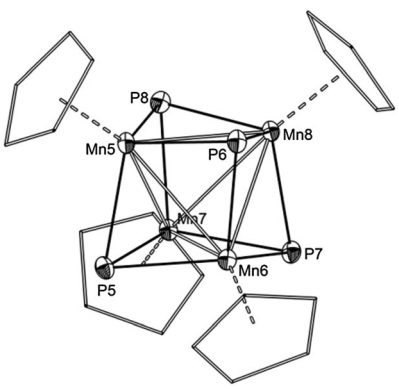

Fig. 1 Molecular structure of **1** in the crystal. For clarity only one molecule of the asymmetric unit is depicted, C atoms are shown in 'wireframe' model and H atoms and solvent molecules are omitted. Ellipsoids are drawn at the 50% probability level.

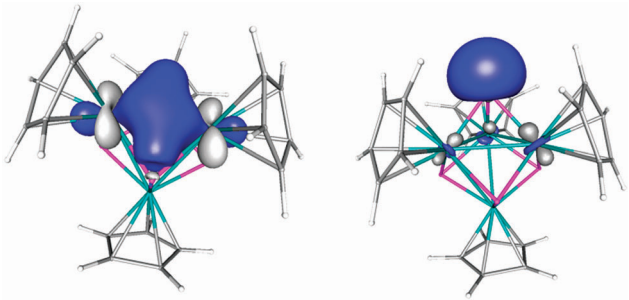

Fig. 2 Selected localized molecular orbitals representing the Mn–P bonding (left) and the lone pair of the phosphorus atoms (right) in $[(CpMn)_4(P)_4]$ (**1**) in singlet spin state. Calculated at the BP86/def2-TZVP level of theory.

The results of the optical measurements fit well to the findings of the theoretical calculations. No emission of compound **1** could be observed neither in the visible range nor in the IR range (down to 1600 nm) even at 10 K. This can be explained by the different spin multiplicities of the ground and excited states which causes low emission intensity due to the spin selection rule. On the other hand the large number of electronic states in relatively small energetic distances causes non-radiative transitions rather than emission of radiation.

The room temperature reflection spectrum of **1** is depicted in Fig. 3. Besides some vibrational transition in the IR range the electronic transitions of the basis of the DFT calculations described above can be detected in the reflection spectrum. In detail, the first singlet–triplet electronic transition at about 1700 nm and also the one of the next higher electronic state identified by the DFT calculations to be at about 930 nm could be detected (Fig. 3).

The four P atoms in **1** are pyramidal and bear a lone pair each. This should be a perfect building block for the formation of three-dimensional networks. By slow diffusion of CH_3CN solutions of CuX (X = Cl, Br) into CH_2Cl_2 solutions of **1**, some black needle-shaped crystals and plenty of off-white to brown voluminous, amorphous powder were obtained. The reaction with a 1 : 1 stoichiometry of **1** and CuX results in a still coloured

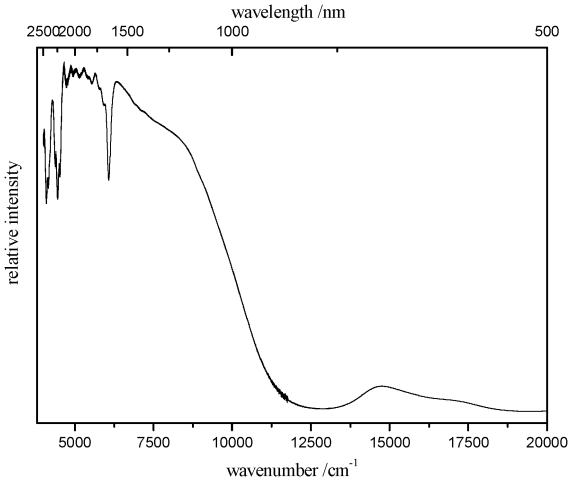

Fig. 3 Room temperature reflection spectrum of **1**. *Cf.* calculated electronic transitions: 1702 nm (5874 cm^{-1}) for singlet–triplet and 935 nm (10 693 cm^{-1}) for singlet–quintet (BP86/def2-TZVP level of theory).

mother liquor solution and a larger amount of crystals. In contrast, a 1 : 5 stoichiometry results in a colourless solution and more powder. The crystals as well as the powder are totally insoluble in all common solvents.

The crystals were characterized by single crystal X-ray diffraction. The crystal structures illustrate zigzag like 1D coordination polymers with the sum formulae $[\{(CpMn)_4(\mu_3\text{-}P)_4\}(CuX)]_n$ (**2-Cl:** X = Cl; **2-Br:** X = Br) (Fig. 4).[16] However, in the case of **2-Cl**, one molecule CH_2Cl_2 co-crystallizes per formula unit, which is not the case for **2-Br**. Two of the P atoms in **2-Cl** and **2-Br** coordinate to CuX units resulting in a trigonal planar coordination of the Cu atoms. In **2-Br** a disorder of the Br atom over two positions was observed. With angular sums around the Cu centres of 359.8° for **2-Cl** and 356.8° and 360.0°, respectively, for **2-Br** this is an indication for almost perfect planarity. The polymeric strands are orientated in parallel with respect to each other.

The off-white powder was found to be amorphous, as indicated by X-ray powder diffraction. Also $^{31}P\{^1H\}$ MAS NMR did not show any signals. To further analyse the amorphous powder, it was washed several times with CH_3CN and dried carefully in a vacuum. To get a hint of the composition, elemental analyses were carried out. With the assumption of complete removal of the solvent and excess of CuX, the result fits best for a **1** : CuX ratio of roughly 1 : 3. This might be a hint for the coordination of more than two of P atoms to CuX and the formation of a 3D structure.

For the formation of three-dimensional networks, the coordination of all four P atoms in **1** is necessary. To check whether this is possible at all, **1** was reacted with $[CpMn(CO)_2(thf)]$, and in fact, the coordination of up to four P atoms can be achieved, resulting in the formation of $[\{(CpMn)_4(\mu_3\text{-}P)_4\}\{CpMn(CO)_2\}_n]$ (**3a:** n = 1; **3b:** n = 2; **3c:** n = 3; **3d:** n = 4). In a 1 : 1 stoichiometry the mono- and di-coordination product is obtained and in a 1 : 4 stoichiometry the tri- and tetra-coordination derivative occurs. Compounds **3a–d** can be separated by column chromatography. However, complex **3a** elutes together with the unreacted cluster **1**.

All four compounds were crystallized as solvates from concentrated CH_2Cl_2 solutions. The molecular structures are depicted in Fig. 5. The average bond lengths between the P atoms and the $\{CpMn(CO)_2\}$ fragments increase with the degree of coordination (**3a:** 2.260 Å; **3b:** 2.262 Å; **3c:** 2.272 Å; **3d:** 2.287 Å). The steric parameters of the heterocubane cores are also affected by the coordination. While the average Mn–Mn and Mn–P bond lengths in **3a** are almost identical in comparison to **1**, they

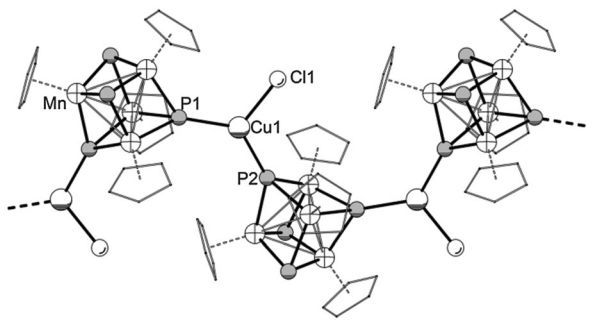

Fig. 4 Section of the 1D zigzag chain $[\{(CpMn)_4(\mu_3\text{-}P)_4\}(CuCl)]_n$ (**2-Cl**) in the crystal. View along crystallographic *c*-axis. For clarity reasons the C atoms are shown in 'wireframe' model and H atoms and solvent molecules are omitted. Because of the isostructural constitution of **2-Br**, its structure is not depicted. Selected bond lengths [Å] and angles [°] of **2-Cl**: P1–Cu1 2.248(1), P2–Cu1 2.252(1), Cu1–Cl1 2.245(2), P1–Cu1–P2 129.64(5), P1–Cu1–Cl1 117.26(5), P2–Cu1–Cl1 112.85(5), av. Mn–P 2.228, av. Mn–Mn 2.720. Selected bond lengths [Å] and angles [°] of **2-Br** (for labeling see the ESI§): P1–Cu1 2.248(3), P4–Cu1 2.252(3), Cu1–Br1 2.372(8), Cu1–Br2 2.324(5), P1–Cu1–P4 129.0(1), P1–Cu1–Br1 119.8(2), P1–Cu1–Br2 115.1(1), P4–Cu1–Br1 108.0(2), P4–Cu1–Br2 115.9(1), av. Mn–P 2.231, av. Mn–Mn 2.718.

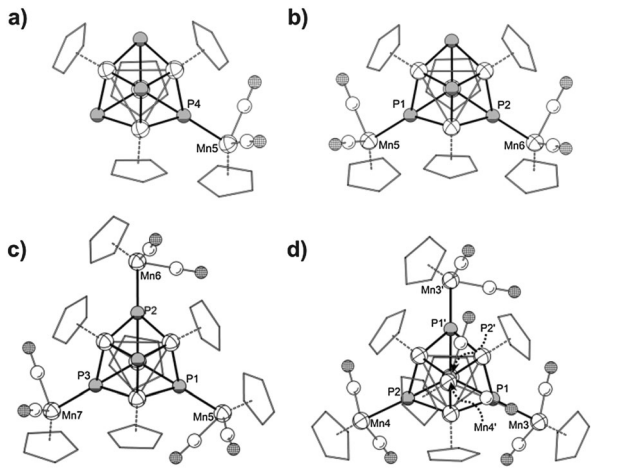

Fig. 5 Molecular structures in the crystals: (a) **3a**, (b) **3b**, (c) **3c**, (d) **3d**. For clarity the Cp carbon atoms are shown in 'wireframe' model and H atoms and solvent molecules are omitted. In the case of the disordered molecule **3b** only the main part is depicted. Selected Mn–P bond lengths [Å] in **3a**: Mn5–P4 2.2603(8), av. Mn–P 2.234, av. Mn–Mn 2.719; in **3b**: Mn5–P1 2.2576(10), Mn6–P2 2.2672(8), av. Mn–P 2.246, av. Mn–Mn 2.740; in **3c**: Mn5–P1 2.2779(8), Mn6–P2 2.2778(7), Mn7–P3 2.2616(9) av. Mn–P 2.245, av. Mn–Mn 2.748; in **3d**: Mn3–P1 2.2928(7), Mn4–P2 2.2818(11), av. Mn–P 2.258, av. Mn–Mn 2.757. Average values are calculated only from the heterocubane cores.

increase steadily from **3b** to **3d** (**1**: av. Mn–P 2.235 Å, av. Mn–Mn 2.713 Å; **3d**: av. Mn–P 2.258 Å, av. Mn–Mn 2.757 Å). The increase in the Mn–Mn and Mn–P bond lengths effectively results in an expansion of the heterocubane cages. The volumes of the Mn_4P_4 cages vary in the same way as the bond lengths. With just one coordination it remains almost unaffected, but starting from the second coordination in **3b** the volume increases constantly (V(**1**) = 9.159 Å^3; V(**3a**) = 9.151 Å^3; V(**3b**) = 9.333 Å^3; V(**3c**) = 9.372 Å^3; V(**3d**) = 9.490 Å^3).[17] The core overall expands by 3.5%. This observation might be explained by the electron withdrawing effect of the $\{CpMn(CO)_2\}$ fragments.

In conclusion, we have reported on the synthesis of the novel cluster $[Cp_4Mn_4P_4]$ (**1**) with a central heterocubane structure in good yields, which is a good building block for promoting higher-dimensional aggregation. Compound **1** was characterized by X-ray diffraction, spectroscopic measurements and DFT calculations. Reaction with CuX (X = Cl, Br) leads to the formation of 1D coordination polymers with the zigzag-like structural motif. As a proof of concept it was demonstrated that all four P atoms in **1** can be addressed for coordination, which was exemplified by the coordination of $\{CpMn(CO)_2\}$ moieties. An interesting cluster volume expansion is observed, correlating with the degree of coordination. The formation of 3D networks starting from **1** will be the focus of future work.

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