

Supporting Information for:

Synthesis of the heterocubane cluster [$\{\text{CpMn}\}_4(\mu_3\text{-P})_4$] as a tetrahedral shaped starting material for the formation of polymeric coordination compounds

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1) Experimental Part

All experiments were carried out under an atmosphere of dry argon or nitrogen using glovebox and schlenk techniques. Solvents were purified, dried and degassed prior to use. P₄, CuCl and CuBr were available, [CpMn(cht)]^[1] and [CpMn(CO)₂(thf)]^[2] were prepared according to literature procedures. The NMR spectra were measured on a Bruker Avance 300, 400 or 600 spectrometer. EI-MS spectra were measured on a Finnigan MAT SSQ 710A mass spectrometer and FD-MS spectra on a Finnigan MAT 95 mass spectrometer. The elemental analyses were determined on a Vario EL III apparatus. Photoluminescence emission and excitation measurements were performed using a Fluorolog3 spectrofluorometer (Jobin Yvon). Emission was detected starting from 400 nm down to 1600 nm. A liquid helium closed-cycle cryostat was used for measurements at 10 K. Reflection spectra at room temperature were recorded with the aid of a Cary 5000 (Varian) from 200 to 2500 nm.

Synthesis of [Cp₄Mn₄P₄] (1):

[CpMn(cht)] (0.93 g, 4.4 mmol) and P₄ (1.8 g, 14.5 mmol) are dissolved 50 mL 1,3-diisopropylbenzene and refluxed for 20 min. The solution becomes dark brown and sometimes a metal mirror is observed. The solvent and unreacted P₄ are removed in vacuum at 60 °C. The residue is triturated with 25 mL CH₂Cl₂ and filtered through Celite. This is repeated with a further portion of 10 mL CH₂Cl₂. The collected filtrates are condensed to 15 mL and cooled to -35 °C. The obtained crystals are decanted and dried in vacuum. Another portion of crystals is obtained from the mother liquor (485 mg, 73%).

1: [C₂₀H₂₀Mn₄P₄] calc.: C, 39.77; H, 3.34. found: C, 39.48; H, 3.49. ESI-MS (CH₂Cl₂): *m/z* (%) = 603.9 (51%, [M]⁺), 422.0 (78%, [Cp₃Mn₃P₂]⁺), 185.1 (48%, [Cp₂Mn]⁺), 66.1 (100%, [CpH]⁺). ¹H NMR (CD₂Cl₂): δ [ppm] = 4.58 (s, C₅H₅). ³¹P{¹H} NMR (CD₂Cl₂): δ [ppm] = 1079.8 (s, ω_{1/2} = 31 Hz, P). ¹³C{¹H} NMR (CD₂Cl₂): δ [ppm] = 82.7 (C₅H₅).

Synthesis of [{Cp₄Mn₄P₄}{CuX}]_n (2-Cl: X = Cl; 2-Br: X = Br):

A solution of CuX (83 μmol) in 10 mL CH₃CN is layered over a solution of [Cp₄Mn₄P₄] (50 mg, 83 μmol) in 10 mL CH₂Cl₂. After complete diffusion, black crystals of **2-Cl** and **2-Br**, respectively, and an off-white powder is obtained. The heterogeneous mixture is shaken carefully, the crystals are allowed to settle down and the mother liquor suspension is decanted via cannula. The crystals are washed twice with 15 mL CH₃CN in the same manner as before and dried in vacuum. The collected liquids are filtrated, washed with 15 mL CH₃CN three-times and dried in vacuum.

2-Cl: Crystalline yield of **2-Cl**: 42 mg (72%); Yield (Powder): 5 mg.

[C₂₀H₂₀Mn₄P₄CuCl] calc.: C, 34.17; H, 2.87. found: C, 39.94; H, 2.92. Powder found: C, 24.64; H, 2.55; N, 2.25.

2-Br: Crystalline yield of **2-Br**: 11 mg (18%); Yield (Powder): 5 mg.

[C₂₀H₂₀Mn₄P₄CuBr] calc.: C, 32.14; H, 2.70. found: C, 31.86; H, 2.79. Powder found: C, 26.21; H, 2.77; N, traces.

Synthesis of $\{[(\text{CpMn})_4(\mu_3\text{-P})_4]\{\text{CpMn}(\text{CO})_2\}_n\}$ (3a**: $n = 1$; **3b**: $n = 2$):**

A solution of $[\text{CpMn}(\text{CO})_3]$ (2.04 g, 10 mmol) and cycloheptatriene (3.0 g, 3.4 mL, 32.6 mmol) in 150 mL 1,3-diisopropylbenzene is irradiated for 20 h (CO bands are not completely vanished). After P_4 (3.72 g, 30 mmol) was added, the reaction mixture is refluxed for 60 min. The solvent and unreacted P_4 are removed in vacuum at 60 °C. The residue is triturated with 25 mL CH_2Cl_2 and filtered through Celite. This is repeated with a further portion of 10 mL CH_2Cl_2 . A column chromatography (silica, 20x4 cm, CH_2Cl_2) affords a small brown fraction of **3b**. With THF another brown band is collected which is composed of a 3:1 mixture of **3a** and **1**, as indicated by NMR spectroscopy and elemental analysis. An analytically pure sample of **3b** can be obtained from concentrated CH_2Cl_2 solution. A crystalline mixture of **3a** and **1** is also obtained from concentrated CH_2Cl_2 solution.

3a (as 3:1 mixture with **1**): Yield: 215 mg \rightarrow 180 mg pure **3a** (9%).

$3[\text{C}_{27}\text{H}_{25}\text{Mn}_5\text{O}_2\text{P}_4] \cdot \mathbf{1}$ calc.: C, 40.79; H, 3.28. found: C, 41.22; H, 3.32. ESI-MS (CH_2Cl_2): m/z (%) = 779.7 (12%, $[\text{M}]^+$), 723.7 (9%, $[\text{Cp}_5\text{Mn}_5\text{P}_4]^+$), 603.7 (61%, $[\text{Cp}_4\text{Mn}_4\text{P}_4]^+$), 510.8 (30%, $[\text{Cp}_4\text{Mn}_4\text{P}]^+$), 421.9 (100%, $[\text{Cp}_3\text{Mn}_3\text{P}_2]^+$), 301.9 (16%, $[\text{Cp}_2\text{Mn}_2\text{P}_2]^+$), 185.0 (91%, $[\text{Cp}_2\text{Mn}]^+$), 120.0 (65%, $[\text{CpMn}]^+$). IR (CH_2Cl_2): ν_{CO} [cm^{-1}] = 1917 (s), 1858 (s). ^1H NMR (CD_2Cl_2): δ [ppm] = 4.59 (s-br, $\omega_{1/2}$ = 10 Hz, 5H, C_5H_5), 4.62 (s-br, $\omega_{1/2}$ = 5 Hz, 15H, C_5H_5), 4.68 (d, $^3J_{\text{PH}}$ = 1.3 Hz, 5H, C_5H_5); 4.53 (s, 6.8H, C_5H_5 from **1**). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ [ppm] = 915.0 (s, 1P), 1091.8 (s-br, $\omega_{1/2}$ = 107 Hz, 3P); 1079.7 (s, 1P from **1**). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ [ppm] = 82.6 (s, C_5H_5 , superimposed with signal of **1**) 83.1 (q, $^3J_{\text{PC}}$ = 4 Hz, C_5H_5), 85.3 (m, C_5H_5), 234.8 (d, $^2J_{\text{PC}}$ = 19 Hz, CO).

3b: Yield: 13 mg (<1%).

ESI-MS (CH_2Cl_2): m/z (%) = 955.5 (10%, $[\text{M}]^+$), 899.6 (2%, $[\text{Cp}_6\text{Mn}_6\text{P}_4(\text{CO})_2]^+$), 779.6 (17%, $[\text{Cp}_5\text{Mn}_5\text{P}_4(\text{CO})_2]^+$), 723.6 (5%, $[\text{Cp}_5\text{Mn}_5\text{P}_4]^+$), 658.6 (10%, $[\text{Cp}_4\text{Mn}_5\text{P}_4]^+$), 603.7 (33%, $[\text{Cp}_4\text{Mn}_4\text{P}_4]^+$), 510.8 (71%, $[\text{Cp}_4\text{Mn}_4\text{P}]^+$), 421.9 (16%, $[\text{Cp}_3\text{Mn}_3\text{P}_2]^+$), 325.9 (21%, $[\text{Cp}_2\text{Mn}_3\text{P}]^+$), 301.9 (19%, $[\text{Cp}_2\text{Mn}_2\text{P}_2]^+$), 207.0 (44%, $[\text{CpMn}(\text{CO})_2\text{P}]^+$), 185.0 (77%, $[\text{Cp}_2\text{Mn}]^+$), 181.1 (48%, $[\text{CpMnP}_2]^+$), 119.9 (83%, $[\text{CpMn}]^+$). IR (CH_2Cl_2): ν_{CO} [cm^{-1}] = 1917 (s), 1858 (s). ^1H NMR (CD_2Cl_2): δ [ppm] = 4.77 (d, $^3J_{\text{PH}}$ = 1.1 Hz, 10H, C_5H_5), 4.81 (s-br, $\omega_{1/2}$ = 11 Hz, 20H, C_5H_5). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ [ppm] = 922 (s-br, $\omega_{1/2}$ \approx 310 Hz, 1P), δ 925 (s-br, $\omega_{1/2}$ \approx 730 Hz, 1P), 1100 (s-br, $\omega_{1/2}$ \approx 560 Hz, 1P), 1105 (s-br, $\omega_{1/2}$ \approx 420 Hz, 1P). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ [ppm] = 82.9 (C_5H_5), 85.9 (C_5H_5), 88.9 (C_5H_5); CO signal is not observed. As expected, the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra show only one set of signals. However, the $^{31}\text{P}\{^1\text{H}\}$ NMR show two sets of signals. This may likely be explained by two different rotamers.

Synthesis of $\{[(\text{CpMn})_4(\mu_3\text{-P})_4]\{\text{CpMn}(\text{CO})_2\}_n\}$ (3c**: $n = 3$; **3d**: $n = 4$):**

According to literature procedure a solution of $[\text{CpMn}(\text{CO})_2(\text{thf})]$ in 50 mL is prepared from $[\text{CpMn}(\text{CO})_3]$ (200 mg, 0.99 μmol). The solution is added to a solution of $[\text{Cp}_4\text{Mn}_4\text{P}_4]$ (100 mg, 0.16 μmol) in 10 mL THF. The mixture is dried under vacuum, the residue is dissolved in 15 mL toluene and refluxed for 3 h. The solvent is removed again and the residue is washed with hexane. A column

chromatography (silica, 15x4 cm, CH₂Cl₂) first affords a brown fraction of **3d** followed by another brown band of **3c**. Analytically pure samples can be obtained from concentrated CH₂Cl₂ solutions.

3c: Yield: 51 mg (28%).

[C₄₁H₃₅Mn₇O₆P₄] * 1.5 CH₂Cl₂ calc.: C, 40.53; H, 3.04. found: C, 41.08; H, 3.38. ESI-MS (CH₂Cl₂): *m/z* (%) = 1131.4 (< 1%, [M]⁺), 955.5 (4%, [Cp₆Mn₆P₄(CO)₄]⁺), 723.6 (5%, [Cp₅Mn₅P₄]⁺), 421.8 (16%, [Cp₃Mn₃P₂]⁺), 207.0 (100%, [CpMn(CO)₂P]⁺), 185.0 (42%, [Cp₂Mn]⁺), 119.9 (57%, [CpMn]⁺). IR (CH₂Cl₂): *v*_{CO} [cm⁻¹] = 1918 (s), 1860 (s). ¹H NMR (CD₂Cl₂): δ [ppm] = 4.75 (d, ³*J*_{PH} = 1.2 Hz, 15H, C₅H₅), 4.86 (q, ³*J*_{PH} = 1.6 Hz, 5H, C₅H₅), 4.91 (s-br, ω_{1/2} = 9 Hz, 15H, C₅H₅). ³¹P{¹H} NMR (CD₂Cl₂): δ [ppm] = 932.1 (s-br, ω_{1/2} = 288 Hz, 3P), 1103.5 (s-br, ω_{1/2} = 348 Hz, 1P). ¹³C{¹H} NMR (CD₂Cl₂): δ [ppm] = 81.8 (C₅H₅); CO signal is not observed.

3d: Yield: 39 mg (19%).

[C₄₈H₄₀Mn₈O₈P₄] calc.: C, 44.07; H, 3.08. found: C, 43.68; H, 3.38. ESI-MS (CH₂Cl₂): *m/z* (%) = 1308.3 (< 1%, [M]⁺), 1131.4 (< 1%, [M]⁺), 955.5 (2%, [Cp₆Mn₆P₄(CO)₄]⁺), 421.8 (8%, [Cp₃Mn₃P₂]⁺), 207.0 (37%, [CpMn(CO)₂P]⁺), 185.0 (86%, [Cp₂Mn]⁺), 119.9 (100%, [CpMn]⁺). IR (CH₂Cl₂): *v*_{CO} [cm⁻¹] = 1921 (s), 1862 (s). ¹H NMR (CD₂Cl₂): δ [ppm] = 4.77 (d, ³*J*_{PH} = 1.1 Hz, 20H, C₅H₅), 5.0 (s-br, ω_{1/2} = 13 Hz, 20H, C₅H₅). ³¹P{¹H} NMR (CD₂Cl₂): δ [ppm] = 940 (very broad, ω_{1/2} ≈ 2000 Hz). ¹³C{¹H} NMR (CD₂Cl₂): δ [ppm] = 81.9 (C₅H₅), 82.2 (C₅H₅); CO signal is not observed.

2) NMR Investigations:

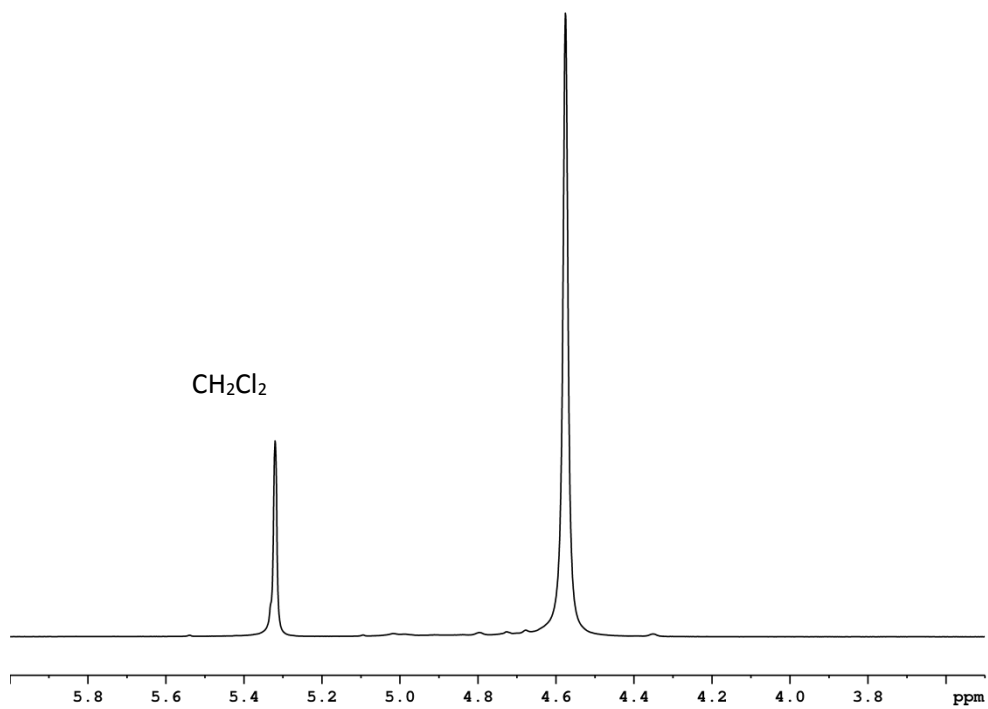


Figure S1: ^1H NMR spectrum of **1** in CD_2Cl_2 at 298 K.

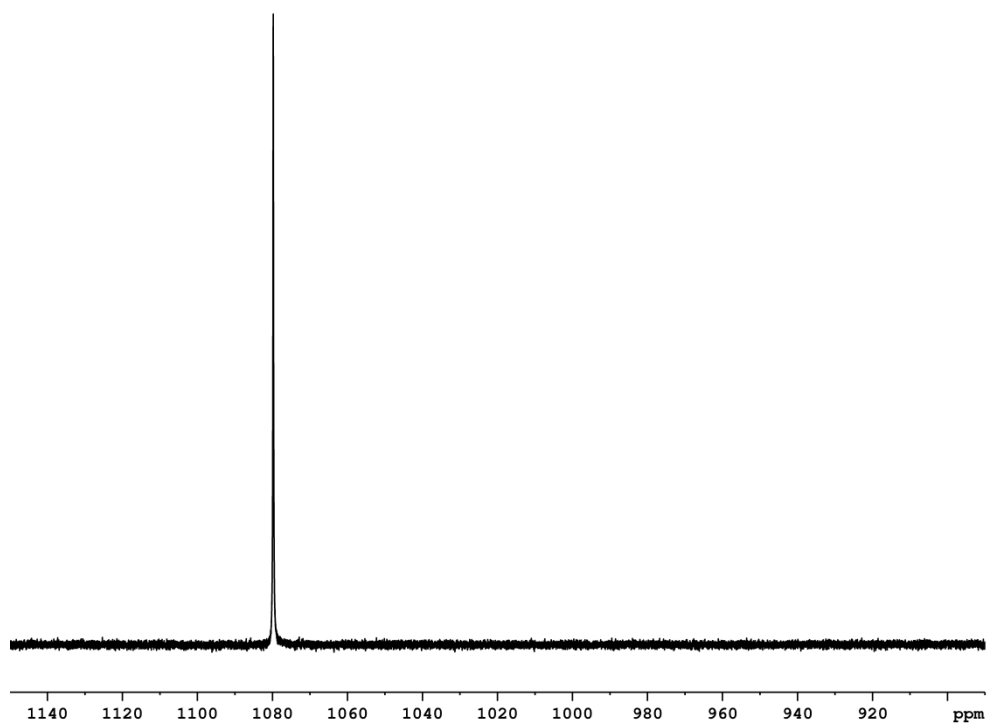


Figure S2: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** in CD_2Cl_2 at 298 K.

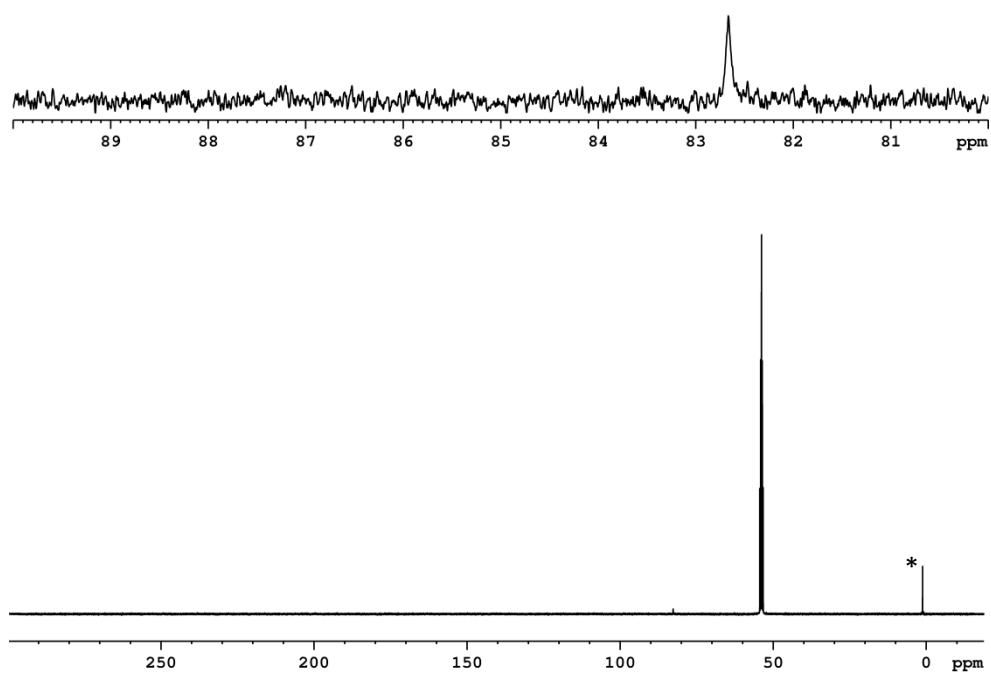


Figure S3: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1** in CD_2Cl_2 at 298 K. Signal marked with an asterisk arises from silicon grease.

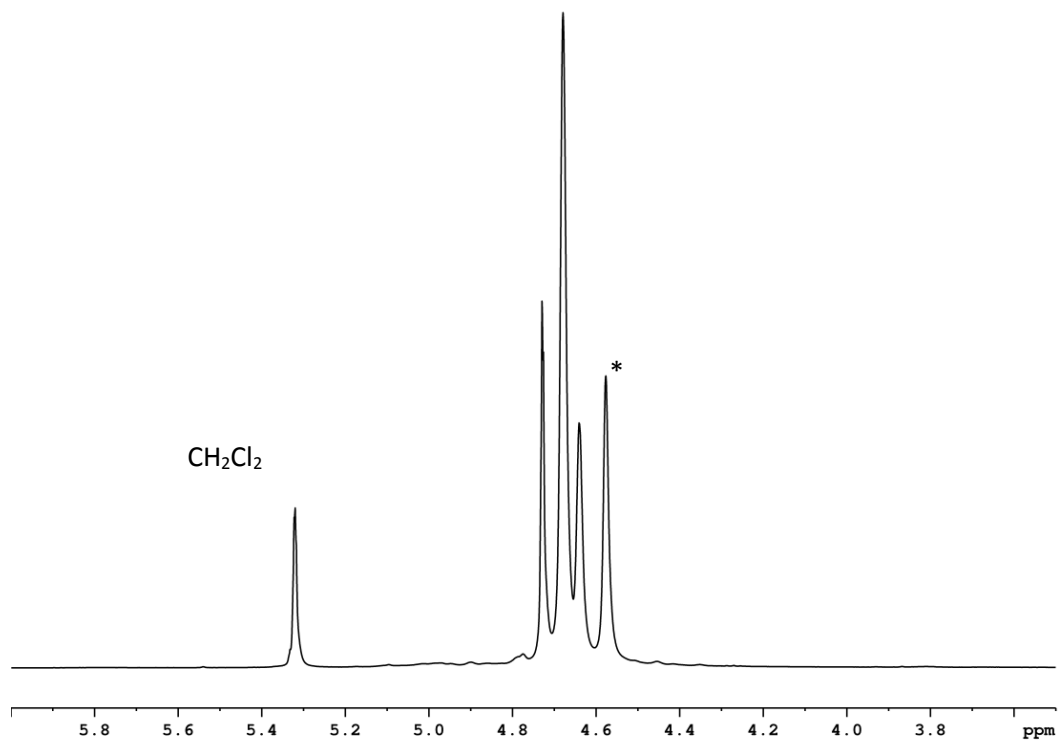


Figure S4: ^1H NMR spectrum of **3a** in CD_2Cl_2 at 298 K. Signal marked with an asterisk arises from impurities of **1**.

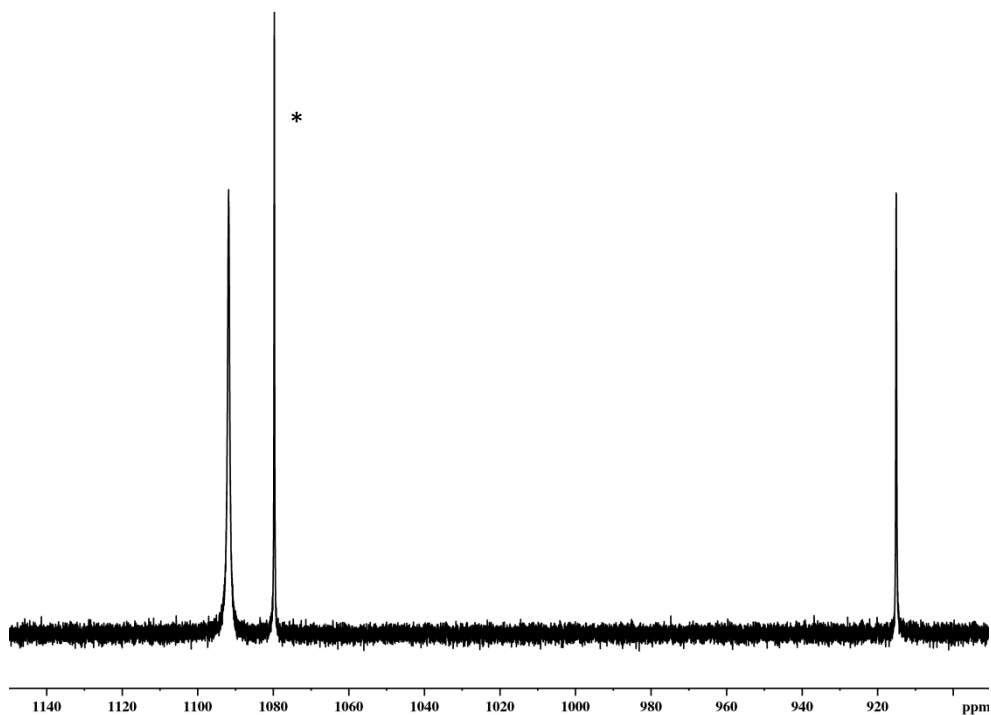


Figure S5: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3a** in CD_2Cl_2 at 298 K. Signal marked with an asterisk arises from impurities of **1**.

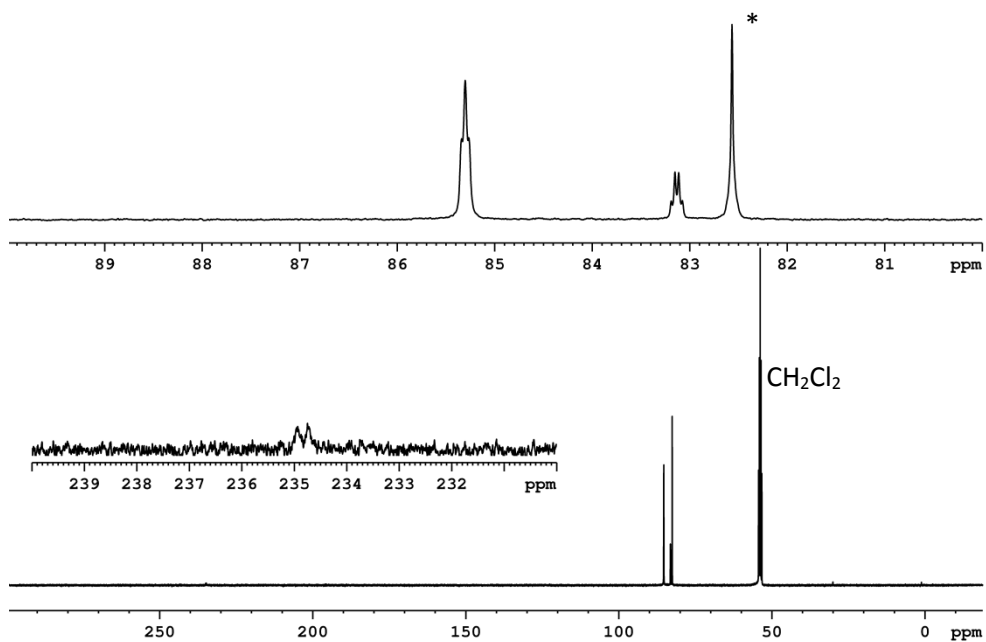


Figure S6: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3a** in CD_2Cl_2 at 298 K. Signal marked with an asterisk is superimposed with signal of **1**.

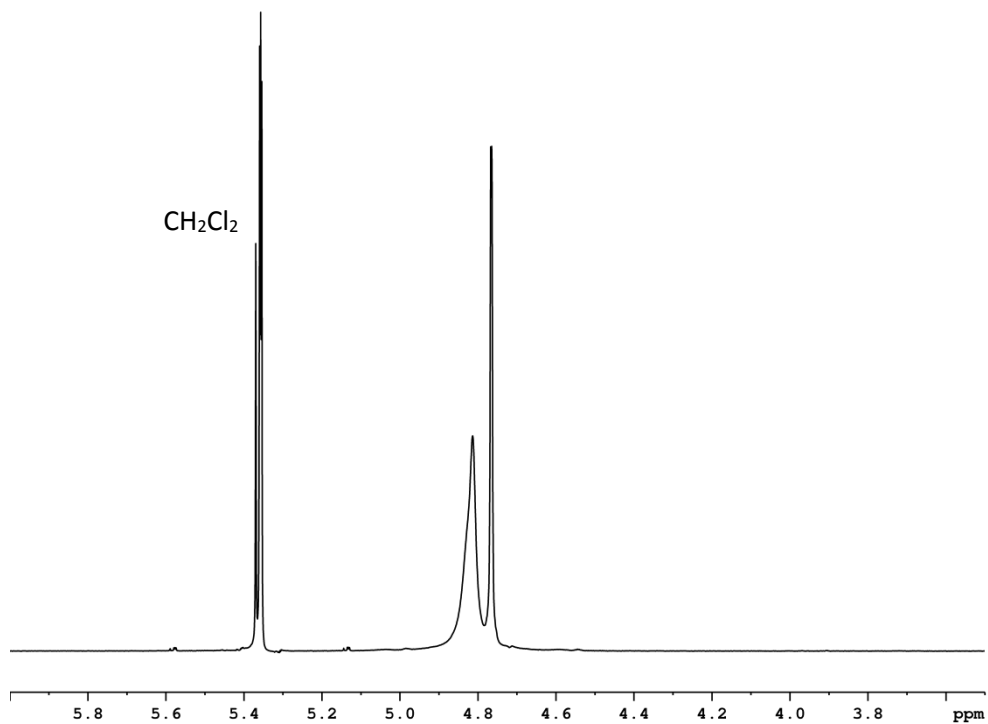


Figure S7: ^1H NMR spectrum of **3b** in CD_2Cl_2 at 298 K.

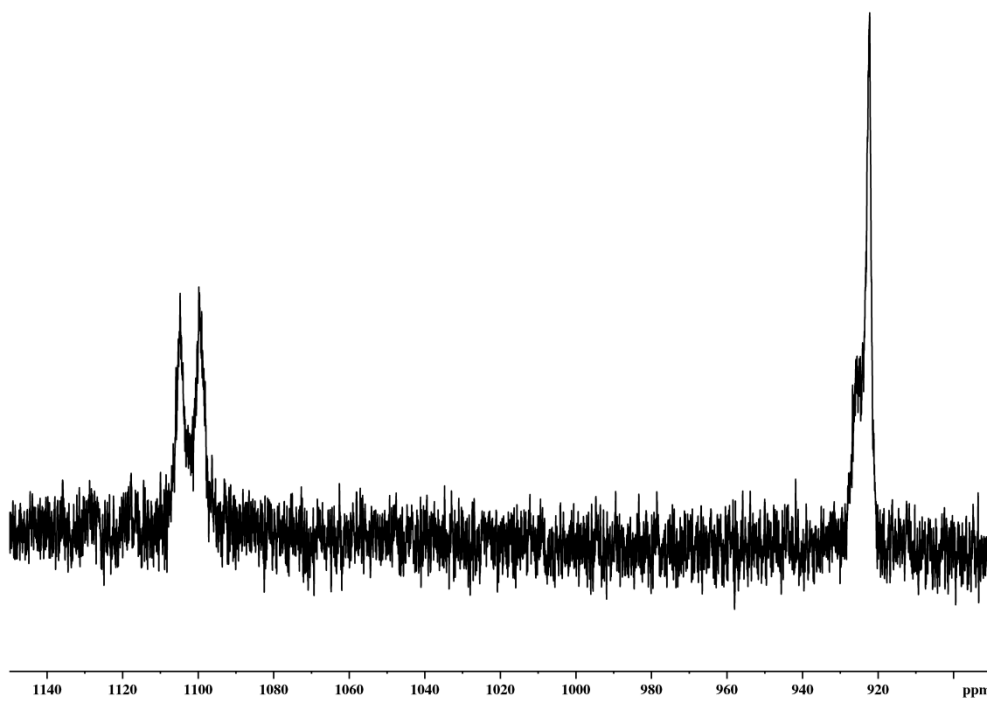


Figure S8: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3b** in CD_2Cl_2 at 298 K.

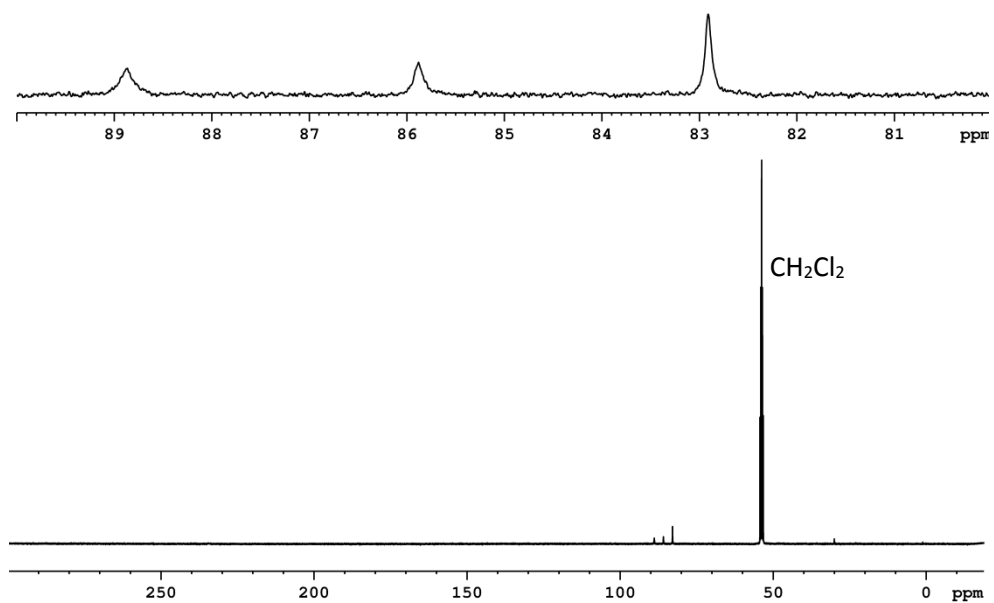


Figure S9: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3b** in CD_2Cl_2 at 298 K.

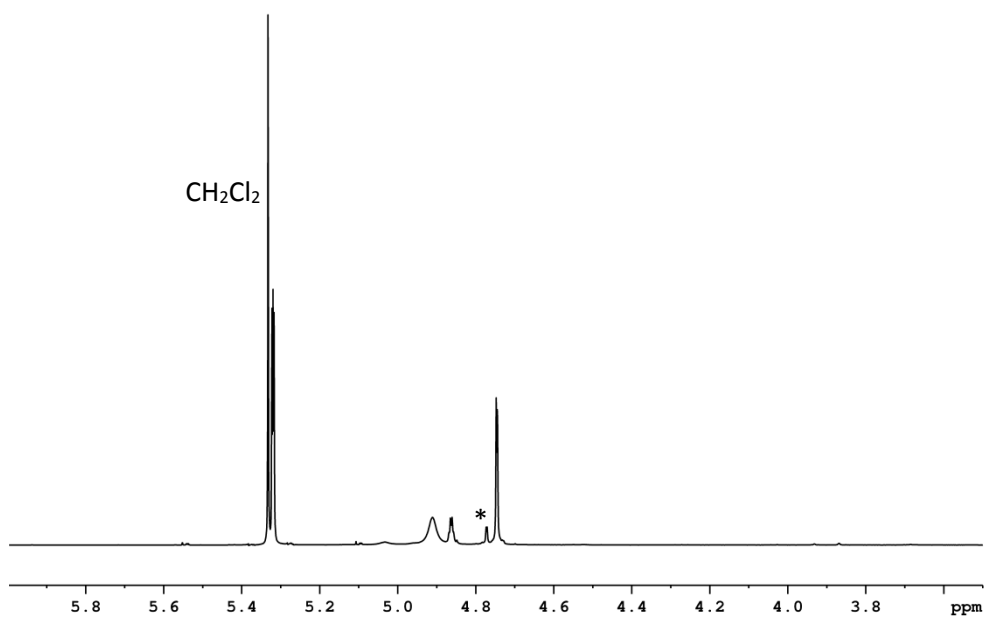


Figure S10: ^1H NMR spectrum of **3c** in CD_2Cl_2 at 298 K. Signal marked with an asterisk arises from impurities.

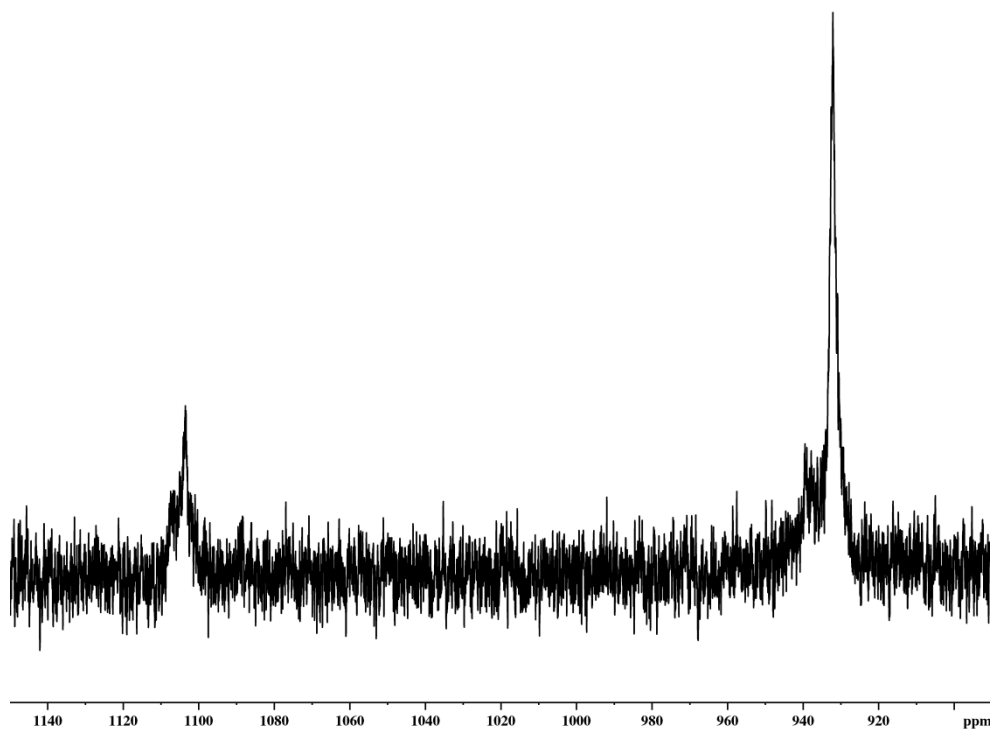


Figure S11: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3c** in CD_2Cl_2 at 298 K.

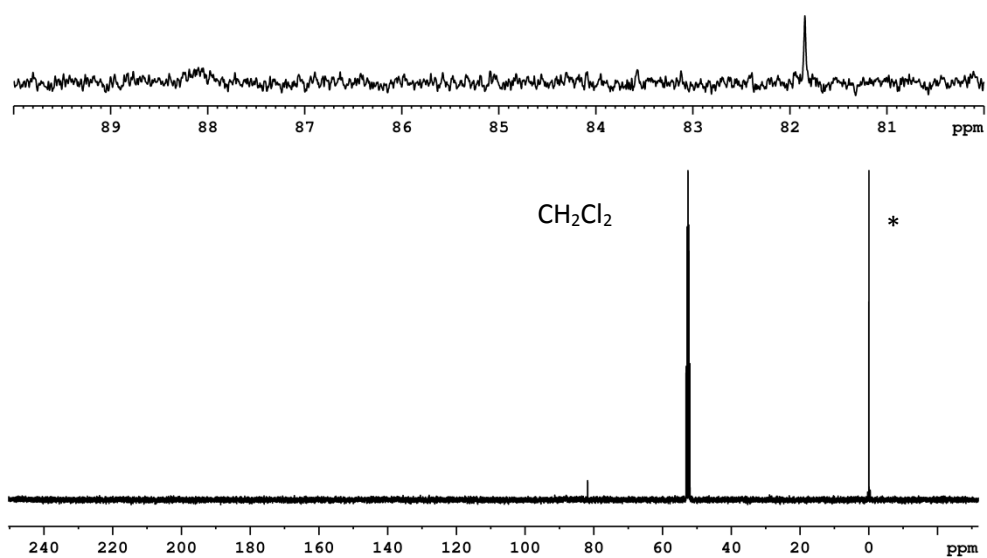


Figure S12: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3c** in CD_2Cl_2 at 298 K. Signal marked with an asterisk arises from silicon grease.

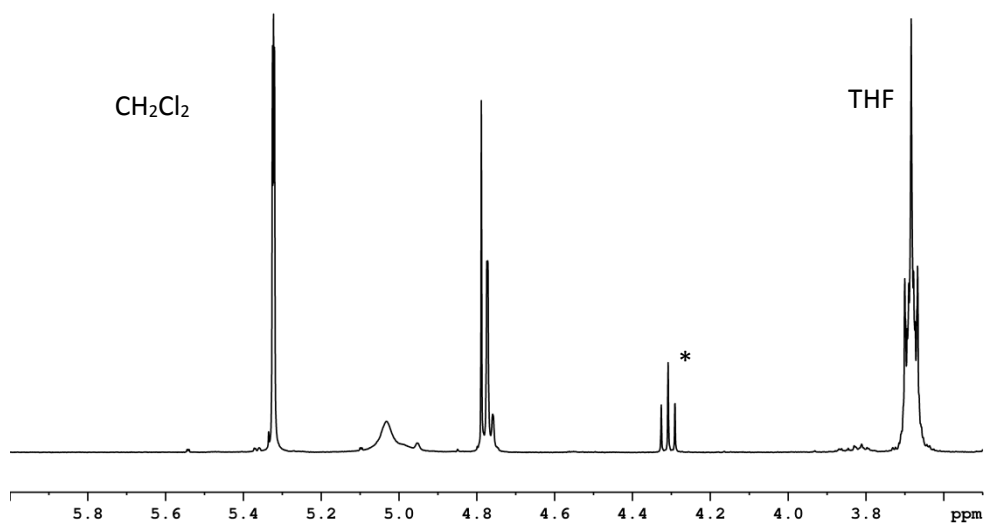


Figure S13: ^1H NMR spectrum of **3d** in CD_2Cl_2 at 298 K. Signal marked with an asterisk arises from impurities.

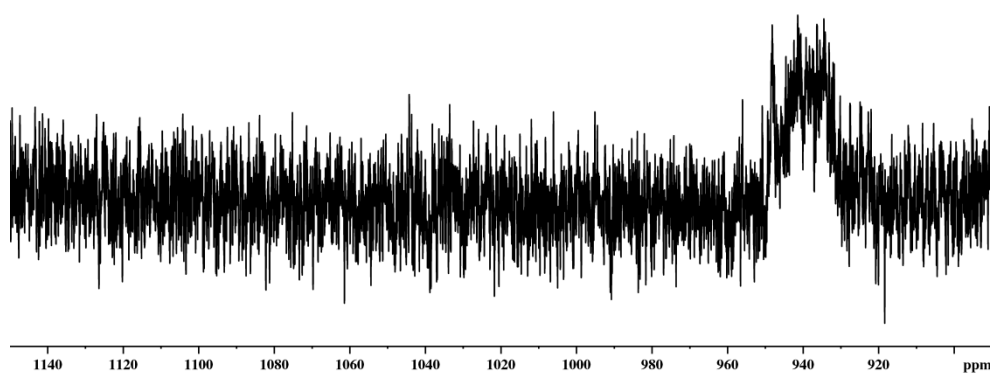


Figure S14: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **3d** in CD_2Cl_2 at 298 K.

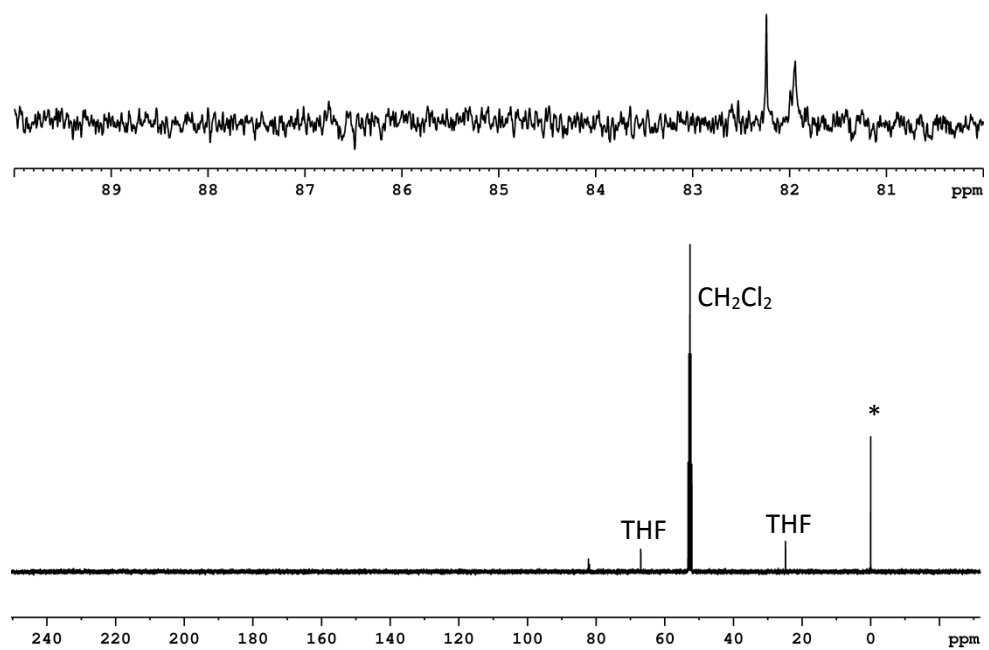


Figure S15: $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3d** in CD_2Cl_2 at 298 K. Signal marked with an asterisk arises from silicon grease.

3) Crystallographic Details:

The crystal structure analyses were performed on an Oxford Diffraction Gemini R Ultra CCD diffractometer (**1**, **2-Cl**, **2-Br**, **3a**) or an Oxford Diffraction SuperNova diffractometer (**3b**, **3c**, **3d**). For all compounds an analytical absorption correction was carried out.^[3] The structures were solved by direct methods of the program SIR-92^[4] and refined with least the square method on F^2 employing SHELXL-97^[5] with anisotropic displacements for non-H atoms. Hydrogen atoms were located in idealized positions and refined isotropically according to the riding model.

CCDC-10404879-1404885 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

	Crystal Data for 1 *CH ₂ Cl ₂	Crystal Data for 2-Cl *2CH ₂ Cl ₂
Empirical Formula	C ₂₁ H ₂₂ Cl ₂ Mn ₄ P ₄	C ₂₂ H ₂₄ Cl ₅ CuMn ₄ P ₄
Formula Weight	688.93	872.85
Temperature [K]	123.0(6)	123.0(4)
Crystal System	monoclinic	monoclinic
Space Group	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> [Å]	40.9164(6)	23.8316(6)
<i>b</i> [Å]	9.3302(1)	12.8659(3)
<i>c</i> [Å]	27.2353(4)	18.4127(4)
α [°]	90	90
β [°]	116.922(2)	93.404(2)
γ [°]	90	90
Volume [Å ³]	9270.5(3)	5635.7(2)
<i>Z</i>	16	8
ρ_{calc} [mg/mm ³]	1.974	2.057
μ [mm ⁻¹]	22.144	21.660
F(000)	5472.0	3440.0
Crystal Size [mm ³]	0.5337 × 0.1091 × 0.0262	0.2249 × 0.0817 × 0.0446
Radiation	Cu-K α (λ = 1.54178)	Cu-K α (λ = 1.54178)

2θ Range	7.28 to 133.08°	7.44 to 133.38°
Index Ranges	-39 ≤ h ≤ 48 -9 ≤ k ≤ 10 -32 ≤ l ≤ 31	-26 ≤ h ≤ 28 -14 ≤ k ≤ 15 -21 ≤ l ≤ 16
Reflections Collected	25380	18021
Independent Reflections	8019 [$R_{\text{int}} = 0.0490$, $R_{\text{sigma}} = 0.0385$]	4948 [$R_{\text{int}} = 0.0260$, $R_{\text{sigma}} = 0.0234$]
Data/Restraints/Parameters	8019/24/559	4948/0/325
Goodness-of-Fit on F^2	0.975	1.096
Final R Indexes [$I > 2\sigma(I)$]	$R_I = 0.0390$, $wR_2 = 0.1010$	$R_I = 0.0414$, $wR_2 = 0.1276$
Final R Indexes [All Data]	$R_I = 0.0425$, $wR_2 = 0.1021$	$R_I = 0.0451$, $wR_2 = 0.1294$
Largest Diff. Peak/Hole [$e \cdot \text{\AA}^{-3}$]	0.96/-1.00	2.21/-1.54
Flack Parameter	-	-

	Crystal Data for 2-Br	Crystal Data for 3a *CH ₂ Cl ₂
Empirical Formula	C ₂₀ H ₂₀ BrCuMn ₄ P ₄	C ₂₈ H ₂₇ Cl ₂ Mn ₅ O ₂ P ₄
Formula Weight	747.45	864.98
Temperature [K]	123.0(2)	123.10(10)
Crystal System	monoclinic	monoclinic
Space Group	<i>Cc</i>	<i>P2₁/n</i>
a [Å]	14.1032(6)	11.9099(1)
b [Å]	12.6047(5)	14.8210(1)
c [Å]	12.7139(4)	17.9552(2)
α [°]	90	90
β [°]	101.172(3)	106.097(1)
γ [°]	90	90
Volume [Å ³]	2217.28(15)	3045.13(5)
Z	4	4

ρ_{calc} [mg/mm ³]	2.239	1.887
μ [mm ⁻¹]	23.994	20.248
F(000)	1456.0	1720.0
Crystal Size [mm ³]	0.078 × 0.0436 × 0.0287	0.1889 × 0.1035 × 0.1005
Radiation	Cu-K α (λ = 1.54178)	Cu-K α (λ = 1.54178)
2 θ Range	9.5 to 132.96°	7.86 to 133.1258°
Index Ranges	-16 ≤ h ≤ 16 -10 ≤ k ≤ 14 -14 ≤ l ≤ 15	-13 ≤ h ≤ 13 -17 ≤ k ≤ 16 -21 ≤ l ≤ 14
Reflections Collected	3838	13200
Independent Reflections	2437 [R_{int} = 0.0229, R_{sigma} = 0.0264]	5258 [R_{int} = 0.0311, R_{sigma} = 0.0419]
Data/Restraints/Parameters	2437/8/280	5258/0/370
Goodness-of-Fit on F^2	1.071	0.867
Final R Indexes [$I > 2\sigma(I)$]	R_I = 0.0402, wR_2 = 0.1244	R_I = 0.0255, wR_2 = 0.0561
Final R Indexes [All Data]	R_I = 0.0409, wR_2 = 0.1248	R_I = 0.0329, wR_2 = 0.0572
Largest Diff. Peak/Hole [e·Å ⁻³]	1.35/-1.12	0.48/-0.30
Flack Parameter	0.013(7)	-

	Crystal Data for 3b *2CH ₂ Cl ₂	Crystal Data for 3c *3CH ₂ Cl ₂
Empirical Formula	C ₃₆ H ₃₄ Cl ₄ Mn ₆ O ₄ P ₄	C ₈₅ H ₇₆ Cl ₆ Mn ₁₄ O ₁₂ P ₈
Formula Weight	1125.95	2519.08
Temperature [K]	123.00(10)	123.00(10)
Crystal System	triclinic	triclinic
Space Group	$P\bar{1}$	$P\bar{1}$
a [Å]	10.5319(4)	10.3548(2)
b [Å]	10.8158(6)	10.5563(1)
c [Å]	18.0191(8)	20.4728(3)

α [°]	77.832(4)	79.072(1)
β [°]	80.265(4)	82.668(1)
γ [°]	85.858(4)	83.529(1)
Volume [Å ³]	1976.14(16)	2170.28(6)
Z	2	1
ρ_{calc} [mg/mm ³]	1.892	1.927
μ [mm ⁻¹]	19.488	19.547
F(000)	1120.0	1254.0
Crystal Size [mm ³]	0.1852 × 0.1225 × 0.0656	0.3779 × 0.0484 × 0.0379
Radiation	Cu-K α (λ = 1.54178)	Cu-K α (λ = 1.54178)
2 θ Range	8.36 to 147.0416°	8.56 to 147.0034°
Index Ranges	-10 ≤ h ≤ 13 -12 ≤ k ≤ 13 -19 ≤ l ≤ 22	-12 ≤ h ≤ 12 -11 ≤ k ≤ 12 -25 ≤ l ≤ 25
Reflections Collected	14154	26928
Independent Reflections	7594 [R_{int} = 0.0351, R_{sigma} = 0.0436]	8389 [R_{int} = 0.0413, R_{sigma} = 0.0290]
Data/Restraints/Parameters	7594/132/706	8389/0/568
Goodness-of-Fit on F^2	0.948	1.077
Final R Indexes [$I > 2\sigma(I)$]	R_I = 0.0364, wR_2 = 0.0886	R_I = 0.0363, wR_2 = 0.1004
Final R Indexes [All Data]	R_I = 0.0448, wR_2 = 0.0907	R_I = 0.0398, wR_2 = 0.1019
Largest Diff. Peak/Hole [e·Å ⁻³]	0.97/-0.62	0.90/-1.02
Flack Parameter	-	-

Crystal Data for **3d***2CH₂Cl₂

Empirical Formula	C ₅₀ H ₄₄ Cl ₄ Mn ₈ O ₈ P ₄
Formula Weight	1478.05
Temperature [K]	123.00(10)

Crystal System	monoclinic
Space Group	<i>C2/c</i>
<i>a</i> [Å]	29.4777(8)
<i>b</i> [Å]	11.0635(3)
<i>c</i> [Å]	21.2608(6)
α [°]	90
β [°]	132.060(4)
γ [°]	90
Volume [Å ³]	5147.9(4)
<i>Z</i>	4
ρ_{calc} [mg/mm ³]	1.907
μ [mm ⁻¹]	18.978
F(000)	2944.0
Crystal Size [mm ³]	0.067 × 0.0411 × 0.0365
Radiation	Cu-K α ($\lambda = 1.54178$)
2 θ Range	8.08 to 147.1652°
Index Ranges	-36 ≤ <i>h</i> ≤ 35 -12 ≤ <i>k</i> ≤ 13 -23 ≤ <i>l</i> ≤ 26
Reflections Collected	13730
Independent Reflections	4948 [$R_{\text{int}} = 0.0269$, $R_{\text{sigma}} = 0.0312$]
Data/Restraints/Parameters	4948/0/334
Goodness-of-Fit on F^2	0.988
Final <i>R</i> Indexes [<i>I</i> > 2 σ (<i>I</i>)]	$R_1 = 0.0267$, $wR_2 = 0.0652$
Final <i>R</i> Indexes [All Data]	$R_1 = 0.0343$, $wR_2 = 0.0667$
Largest Diff. Peak/Hole [e·Å ⁻³]	1.17/-1.07
Flack Parameter	-

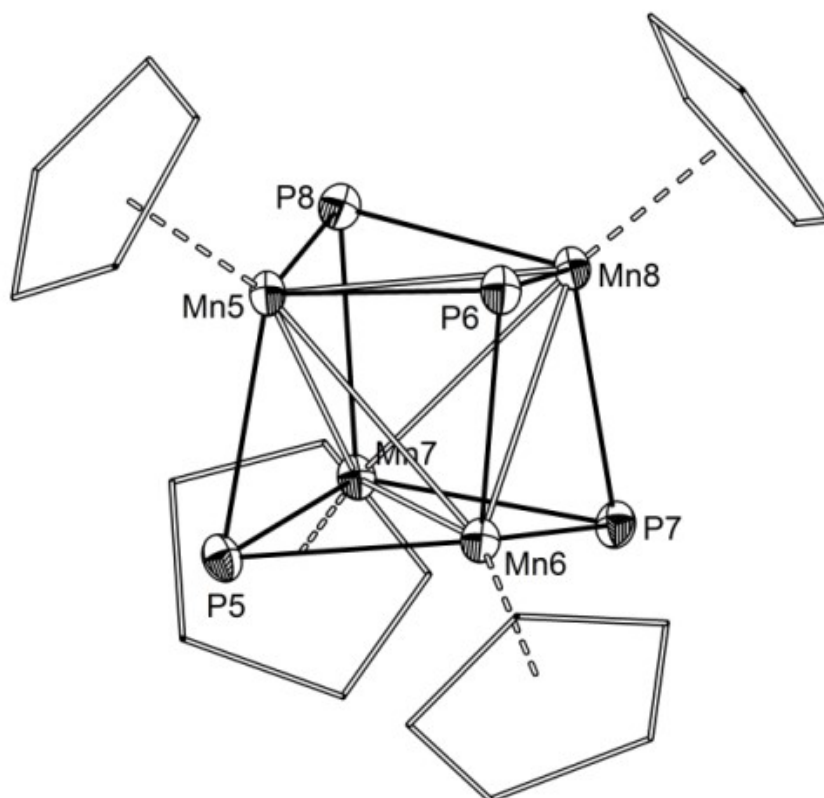


Figure S16. Molecular structure of **1** in the crystal. For clarity only one molecule of the asymmetric unit is depicted, C atoms are shown in ‘wire-or-stick’ model and H atoms and solvent molecules are omitted. Ellipsoids are drawn at 50% probability level. Selected bond lengths [Å] and angles [°]: Mn1-P1 2.2381(8), Mn1-P2 2.2251(9), Mn1-P3 2.2628(10), Mn2-P1 2.2365(9), Mn2-P2 2.2284(9), Mn2-P4 2.2374(10), Mn3-P1 2.2411(10), Mn3-P3 2.2353(9), Mn3-P4 2.2249(9), Mn4-P2 2.2398(10), Mn4-P3 2.2337(9), Mn4-P4 2.2299(9), Mn5-P5 2.2373(9), Mn5-P6 2.2392(8), Mn5-P8 2.2336(10), Mn6-P5 2.2311(8), Mn6-P6 2.2299(9), Mn6-P7 2.2352(10), Mn7-P5 2.2377(10), Mn7-P7 2.2367(9), Mn7-P8 2.2395(9), Mn8-P6 2.2336(10), Mn8-P7 2.2285(9), Mn8-P8 2.2343(9), Mn1-Mn2 2.7320(6), Mn1-Mn3 2.6992(5), Mn1-Mn4 2.6948(8), Mn2-Mn3 2.6997(6), Mn2-Mn4 2.6914(8), Mn3-Mn4 2.7227(7), Mn5-Mn6 2.7095(6), Mn5-Mn7 2.7282(7), Mn5-Mn8 2.7170(5), Mn6-Mn7 2.7182(8), Mn6-Mn8 2.7150(6), Mn7-Mn8 2.7273(8), av. Mn-P 2.235, av. Mn-Mn 2.713.

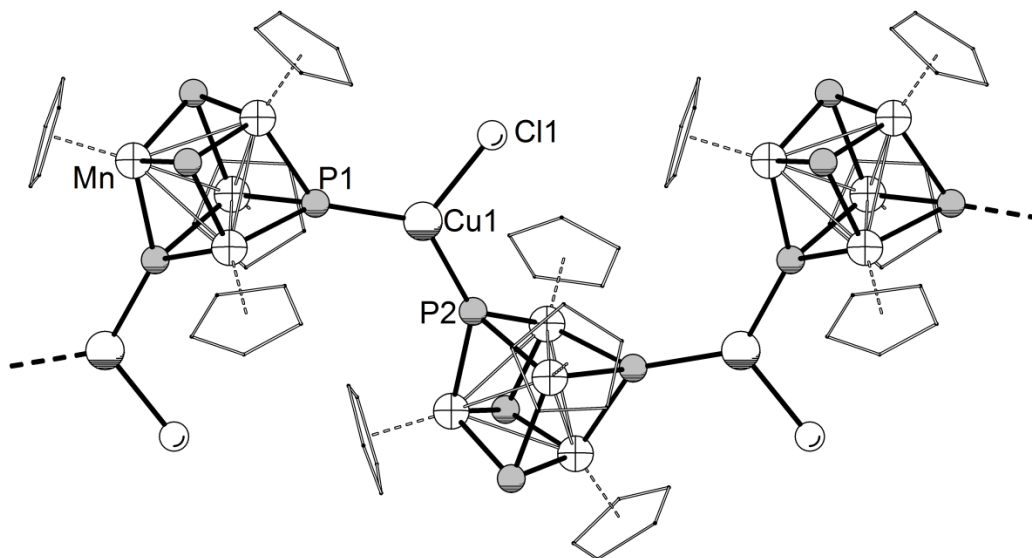


Figure S17: Section of the 1D zigzag chain $[\{(CpMn)_4(\mu^3-P)_4\}(CuCl)]_n$ (**2-Cl**) in the crystal. View along crystallographic *c*-axis. For clarity reasons the C atoms are shown in ‘wire-or-stick’ model and H atoms and solvent molecules are omitted. Because of the isostructural constitution of **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 Supporting Information): 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.

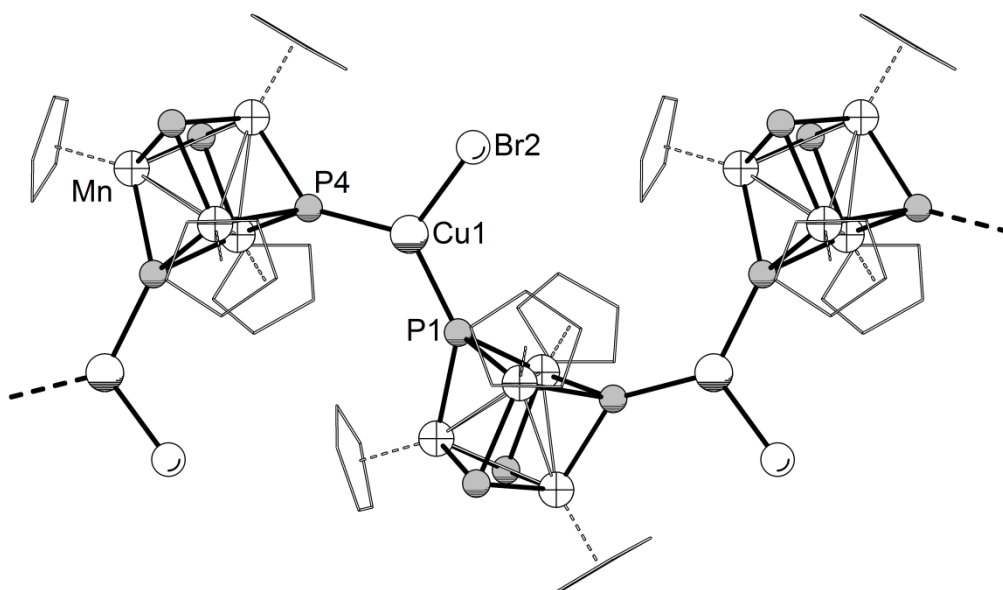


Figure S18: Section of 1D zigzag chain $[\{(\text{CpMn})_4(\mu_3\text{-P})_4\}(\text{CuBr})]_n$ (**2-Br**) in the crystal. View along crystallographic *a*-axis. For clarity reasons the C atoms are shown in ‘wire-or-stick’ model and H atoms and solvent molecules are omitted. Br atom is disordered over two positions with occupancies of 0.57 and 0.43, only main part is shown. Selected bond lengths [Å] and angles [°]: 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.

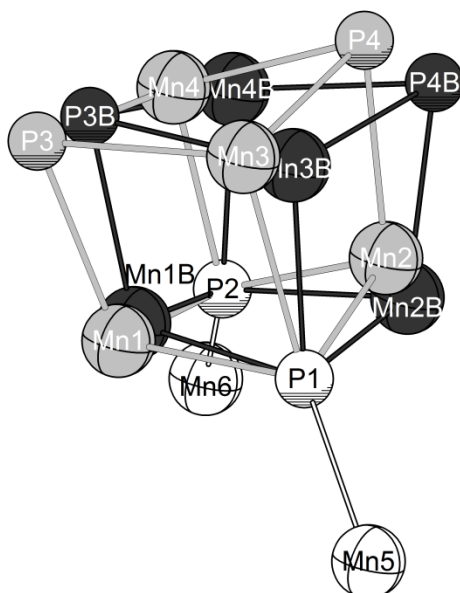


Figure S19: Disordered core of compound **3b**. Cp and CO ligands as well as Mn–Mn bonds are omitted for clarity. Parts 1 and 2 are colored differently. White colored atoms belong to both parts and therefore are not disordered.

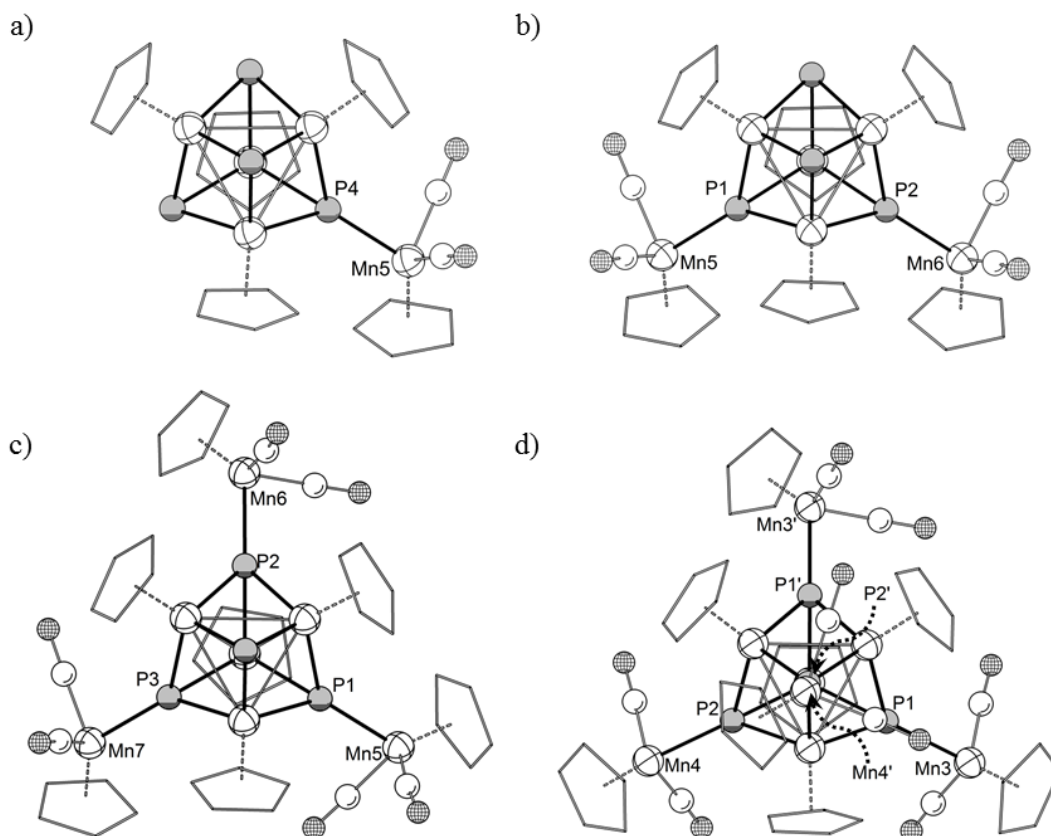


Figure S20: Molecular structures in the crystals: a) **3a**, b) **3b**, c) **3c**, d) **3d**. For clarity the Cp carbon atoms are shown in ‘wireframe’ model and H atoms and solvent molecules are omitted. In case of the disordered molecule **3b** only the main part is depicted. Selected Mn–P bond lengths [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.

4) DFT Calculations:

All calculations were carried out using the TURBOMOLE program package.^[6] The geometries were optimized using the RI-^[7]BP86^[8] functional together with the def2-TZVP^[9] basis set for all atoms. The Multipole Accelerated Resolution of Identity (MARI-J)^[10] approximation was used in the geometry optimizations. The final energy of the molecules has been determined by single point calculations without using the RI formalism. The relative energies were calculated by using the SCF energies.

Table S1: Relative energies of [(CpMn)₄(P)₄] (**1**) in different spin states. Calculated at the BP86/def2-TZVP level of theory.

Multiplicity	1	3	5	7	9	11	13
Rel. Energy (kJ mol ⁻¹)	0	70.27	127.92	163.67	214.09	n.c.	n.c.

n.c. = SCF not converged

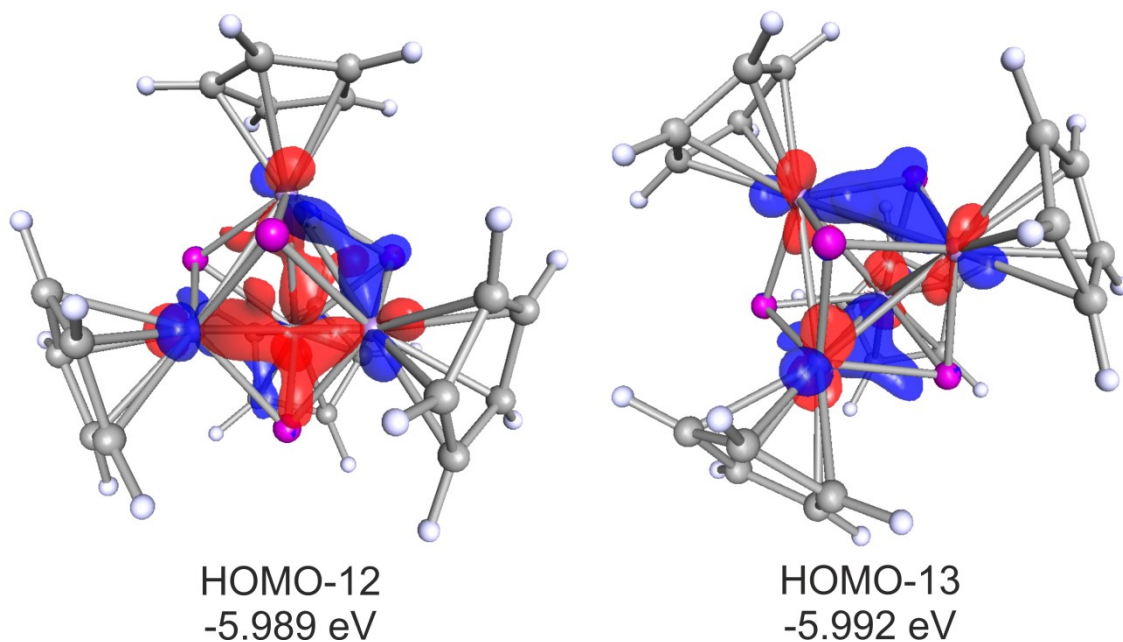


Figure S21: Selected molecular orbitals representing the Mn–P bonding in [(CpMn)₄(P)₄] (**1**) in singlet spin state. Calculated at the BP86/def2-TZVP level of theory.

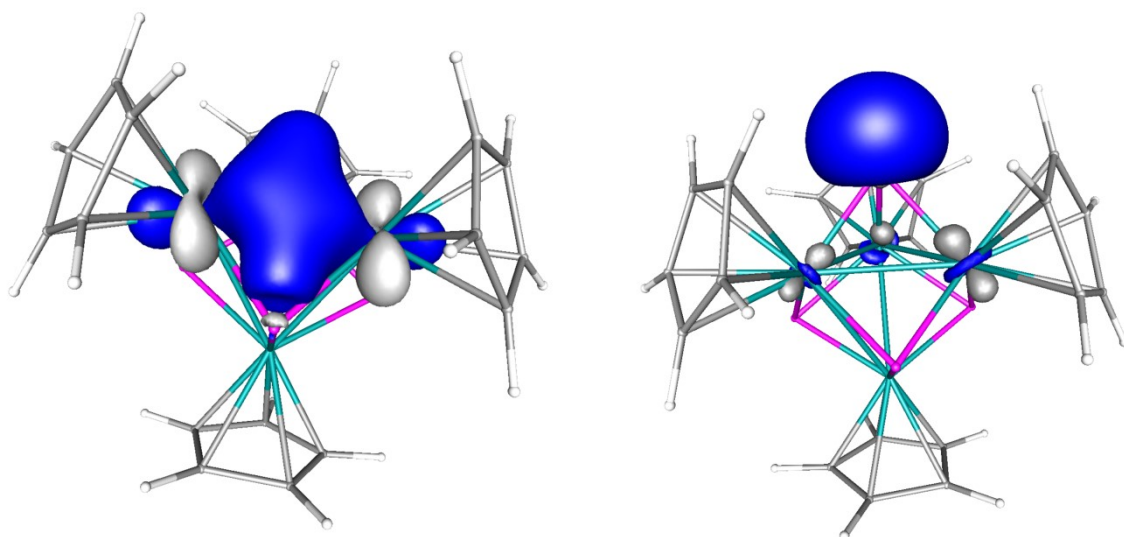


Figure S22: Selected localized molecular orbitals representing the Mn–P bonding (left) and the lone pair of the phosphorus atoms (right) in $[(\text{CpMn})_4(\text{P})_4]$ (**1**) in singlet spin state. Calculated at the BP86/def2-TZVP level of theory.

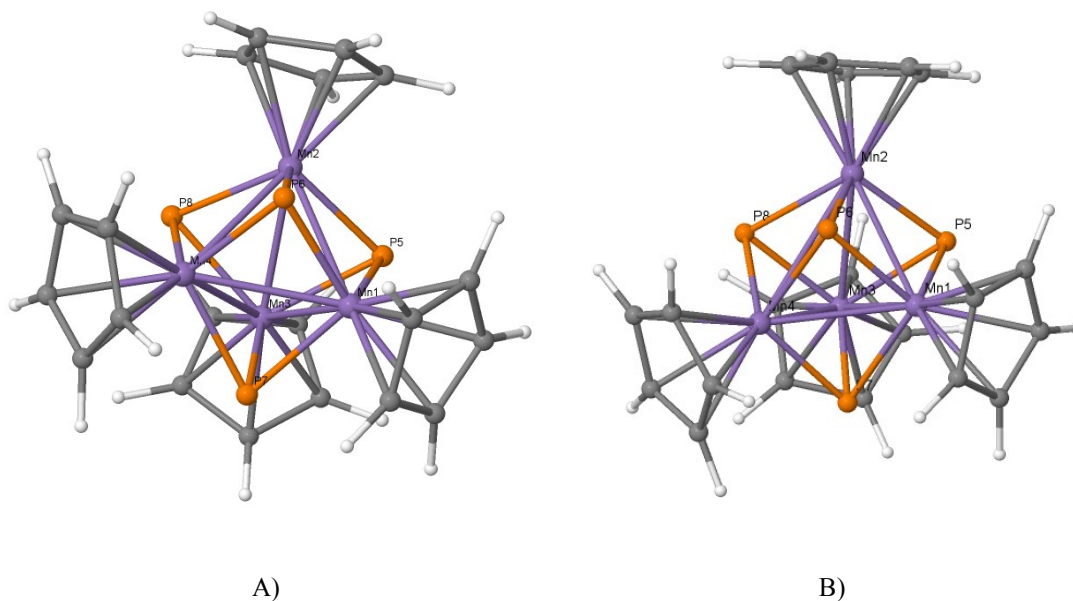


Figure S3: Optimized geometry of $[(\text{CpMn})_4(\text{P})_4]$ (**1**) **A)** in singlet spin state **B)** in the triplet spin state. Selected bond lengths (Å): **A)** P8–Mn2 2.226, Mn2–P6 2.220, Mn2–P6 2.220, Mn2–P5 2.220, P5–Mn1 2.226, P5–Mn3 2.219, Mn2–Mn1 2.705, P6–Mn1 2.222, Mn1–P7 2.218, Mn1–Mn3 2.705, Mn1–Mn4 2.705, Mn3–Mn4 2.706, P7–Mn4 2.223, P7–Mn3 2.225, Mn3–Mn2 2.705, P6–Mn4 2.225, Mn2–Mn4 2.705, Mn4–P8 2.218, P8–Mn3 2.222. **B)** Mn2–P8 2.254, Mn2–P6 2.254, Mn2–P5 2.206, Mn2–Mn4 3.189, Mn2–Mn3 2.717, Mn2–Mn1 2.717, P5–Mn1 2.238, P5–Mn3 2.238, Mn1–P6 2.240, Mn1–P7 2.238, Mn1–Mn4 2.716, Mn1–Mn3 2.702, Mn2–P6 2.254, P7–Mn3 2.238, P7–Mn4 2.206, Mn3–P8 2.240, Mn4–P8 2.255, Mn3–Mn4 2.717, P6–Mn4 2.254.

Table S2: Cartesian coordinates of the optimized geometry of $[(\text{CpMn})_4(\text{P})_4]$ (**1**; singlet) at the BP86/def2-SVP level of theory.

Atom	x	z	y	Atom	x	z	y
Mn	5.5725756	-3.0634705	16.7212452	C	3.07046	-1.23439	19.78121
Mn	4.4295672	-0.780238	15.828574	C	1.901976	-0.96697	19.01673
Mn	3.2767684	-3.1683163	15.295251	C	1.269736	-2.21751	18.72319
Mn	3.2587448	-2.1899478	17.817917	C	2.050283	-3.25219	19.30629
P	5.2565477	-2.4400967	14.6078313	H	8.273309	-1.95713	16.58867
P	5.2413819	-1.1816545	17.8549663	H	7.665807	-3.90772	14.81939
P	3.7592589	-4.2584852	17.1741544	H	6.303916	-5.83436	16.14081
P	2.2793741	-1.3224908	16.0272746	H	6.146716	-5.11517	18.73696
C	7.7470084	-2.8801391	16.8106809	H	7.381371	-2.72568	19.01929
C	7.4122899	-3.9027522	15.874507	H	6.588404	1.072342	16.56285
C	6.7074606	-4.9235299	16.5717124	H	4.059358	1.78271	17.18297
C	6.6204181	-4.5396379	17.9480624	H	2.503126	1.307666	15.0236
C	7.2646951	-3.2823474	18.0950039	H	4.057655	0.209622	13.10423
C	5.7262542	0.9805842	15.9099766	H	6.588414	0.100508	14.03894
C	4.3872114	1.3649001	16.2363589	H	0.548504	-4.19416	15.49668
C	3.5651945	1.0999081	15.1035968	H	1.009164	-2.29246	13.63404
C	4.3868254	0.5352782	14.0858768	H	3.323527	-2.903	12.37527
C	5.7261218	0.4699881	14.5847377	H	4.271524	-5.19567	13.43602
C	1.3922883	-4.1618776	14.8146396	H	2.530091	-6.02344	15.33232
C	1.6426191	-3.1500011	13.8366192	H	3.964267	-3.17233	20.47732
C	2.8554954	-3.4731431	13.1714595	H	3.758438	-0.49521	20.17857
C	3.3565688	-4.6917494	13.7311885	H	1.546295	0.010662	18.70727
C	2.4466874	-5.1196405	14.7374808	H	0.353671	-2.3456	18.15533
C	3.1721966	-2.6482725	19.9517225	H	1.829074	-4.3143	19.27877

Table S3: Cartesian coordinates of the optimized geometry of $[(\text{CpMn})_4(\text{P})_4]$ (**1**; triplet) at the BP86/def2-SVP level of theory.

Atom	x	z	y	Atom	x	z	y
Mn	5.5157269	-3.0253051	16.8091735	C	2.6371031	-1.395784	19.804361
Mn	4.6290623	-0.7375794	15.6422317	C	1.4622202	-1.451054	19.003502
Mn	3.2850243	-3.0710769	15.2843875	C	1.1352834	-2.828424	18.797743
Mn	3.1144965	-2.3912554	17.9093481	C	2.1013928	-3.622035	19.479391
P	5.3609971	-2.5546379	14.6271973	H	8.221419	-2.144034	16.168051
P	4.9693622	-1.1122162	17.8389117	H	7.4377784	-4.51897	15.148126
P	3.7244339	-4.3403551	17.0746532	H	6.1664419	-5.88693	17.100366
P	2.4699369	-1.1639139	16.1310632	H	6.1604838	-4.354261	19.324663
C	7.688959	-2.9212022	16.7066911	H	7.4817765	-2.062344	18.767655
C	7.2657471	-4.1767718	16.1634721	H	7.2479494	0.5993296	15.664201
C	6.5971343	-4.8947894	17.1886465	H	5.2349254	1.7705852	17.033457
C	6.6027146	-4.0867333	18.3704189	H	3.0243399	1.7107792	15.475774
C	7.2898679	-2.8742142	18.0733341	H	3.679824	0.5034717	13.149146

C	6.2348005	0.7467601	15.3026008	H	6.3045822	-0.12682	13.239383
C	5.1654026	1.3523838	16.0350373	H	0.765221	-4.499854	15.629865
C	4.0025491	1.3208852	15.2155214	H	0.7012471	-2.222958	14.172974
C	4.354388	0.6955719	13.9779611	H	2.8444657	-2.23456	12.524838
C	5.7349226	0.3505554	14.029896	H	4.1759716	-4.554792	12.897694
C	1.4765993	-4.2106578	14.8631472	H	2.890335	-5.955322	14.817297
C	1.4493911	-3.0060621	14.1027787	H	3.9077634	-3.033255	20.667805
C	2.572732	-3.0165659	13.2264806	H	3.1381329	-0.496574	20.146576
C	3.2838163	-4.2424378	13.43079	H	0.9048766	-0.601365	18.624005
C	2.6085927	-4.9779438	14.4390396	H	0.3030187	-3.202737	18.209424
C	3.0342743	-2.7394491	20.0935529	H	2.121101	-4.705952	19.524689

Table S4: Cartesian coordinates of the optimized geometry of $[(\text{CpMn})_4(\text{P})_4]$ (**1**; quintet) at the BP86/def2-SVP level of theory.

Atom	x	z	y	Atom	x	z	y
Mn	5.7403328	-3.0005743	16.6385054	C	2.5867844	-1.5294436	19.9850084
Mn	4.5859699	-0.7715821	15.6566187	C	1.5111141	-1.0356547	19.1867783
Mn	3.3523784	-3.1741039	15.353298	C	0.739567	-2.1560303	18.754885
Mn	2.9004949	-2.2698718	17.9255581	C	1.3396494	-3.3323808	19.2690535
P	5.3410689	-2.513508	14.5144913	H	8.3905361	-1.7390826	16.4169772
P	4.9636355	-1.2527083	17.8209838	H	7.9416687	-3.8585699	14.8046727
P	3.9169676	-4.1706045	17.2851866	H	6.6838986	-5.754322	16.2606482
P	2.3997669	-1.2426354	15.9891152	H	6.4540538	-4.8522473	18.7970171
C	7.9253858	-2.6749156	16.7100631	H	7.5096662	-2.3644581	18.8945906
C	7.6797382	-3.7905877	15.8553527	H	7.222645	0.520436	15.4726204
C	7.0352308	-4.7944454	16.6266916	H	5.4120121	1.6150137	17.1538293
C	6.8937829	-4.3093069	17.967207	H	3.034971	1.708532	15.8674639
C	7.4502886	-3.0016838	18.0185331	H	3.3842289	0.6688642	13.3980417
C	6.1770969	0.7063007	15.2484478	H	5.9865764	-0.0013484	13.1284542
C	5.2167401	1.2758045	16.1420783	H	0.7034084	-4.3150159	15.7486653
C	3.9663645	1.3232674	15.4664864	H	0.9497907	-2.4289564	13.8298699
C	4.1577062	0.7914971	14.1500629	H	3.2038933	-2.9532632	12.4329868
C	5.5224988	0.4211039	14.0135019	H	4.3225678	-5.1880628	13.4589765
C	1.4969344	-4.2570219	15.0108279	H	2.756977	-6.0517244	15.4868409
C	1.6339913	-3.2536448	14.002895	H	3.1581095	-3.6284162	20.5494962
C	2.8161707	-3.5316448	13.2655087	H	3.3458061	-0.9281791	20.4746162
C	3.40908	-4.7181097	13.8092662	H	1.3040661	0.0056531	18.9609868
C	2.5892687	-5.1679541	14.8794384	H	-0.1337362	-2.1104894	18.1106452
C	2.4895458	-2.9532558	20.0248108	H	1.0099471	-4.3515684	19.0894866

Table S5: Cartesian coordinates of the optimized geometry of $[(\text{CpMn})_4(\text{P})_4]$ (**1**; septet) at the BP86/def2-SVP level of theory.

Atom	x	z	y	Atom	x	z	y
Mn	5.7553035	-3.2130165	16.7876934	C	2.6729504	-1.5049534	19.9393966
Mn	4.4017806	-0.5935081	15.6338052	C	1.5810929	-1.0134058	19.1627546
Mn	3.403398	-3.1782646	15.2826075	C	0.7840769	-2.1326567	18.7723004

Mn	2.914955	-2.2873878	17.8766625	C	1.3866983	-3.3061161	19.2871445
P	5.4306488	-2.378698	14.7183527	H	8.5137625	-2.3377435	16.1255933
P	4.9750405	-1.2800627	17.7450771	H	7.7885509	-4.7317523	15.1157365
P	3.8041297	-4.2521186	17.2224667	H	6.5601923	-6.129596	17.0692072
P	2.2935184	-1.3287525	15.9338926	H	6.5183554	-4.6028	19.2934518
C	7.9979606	-3.1254254	16.6654403	H	7.7373628	-2.2561588	18.7174893
C	7.6313785	-4.4018625	16.1382912	H	6.9799204	0.6487621	14.8445545
C	6.987068	-5.1356428	17.1637887	H	5.7022731	1.6339352	17.0176628
C	6.9459161	-4.3211156	18.3364029	H	3.0954324	1.9646396	16.3695672
C	7.5884374	-3.0834328	18.0314008	H	2.7739167	1.2014317	13.8014946
C	5.9246483	0.8935912	14.9113504	H	5.1691	0.3899674	12.8617069
C	5.2502446	1.4129494	16.0563931	H	0.7684698	-4.4306239	15.3877916
C	3.8753093	1.5880227	15.7154285	H	1.1108377	-2.4487835	13.5838834
C	3.7112971	1.2031411	14.3495797	H	3.501937	-2.8235335	12.3787797
C	4.9681687	0.7762582	13.856503	H	4.6095721	-5.0643368	13.399781
C	1.6202983	-4.311209	14.7259005	H	2.9021974	-6.0805798	15.2330305
C	1.808856	-3.2559032	13.7825504	H	3.2406886	-3.6000726	20.5179359
C	3.0621525	-3.4574151	13.1421822	H	3.4501812	-0.9038765	20.3996621
C	3.649	-4.6457273	13.6827646	H	1.3790375	0.0263202	18.9258124
C	2.7549862	-5.1742198	14.6543568	H	-0.107077	-2.0884379	18.1532671
C	2.5633764	-2.9265588	20.0025441	H	1.0412385	-4.3241706	19.1341013

Table S6: Cartesian coordinates of the optimized geometry of [(CpMn)₄(P)₄] (**1**; nonet) at the BP86/def2-SVP level of theory.

Atom	x	z	y	Atom	x	z	y
Mn	5.8004432	-3.0323588	16.2536918	C	2.0540377	-0.898801	19.8474125
Mn	4.8824877	-0.525285	15.996755	C	1.3279096	-0.3511964	18.7576281
Mn	3.3919833	-3.8070325	15.3718385	C	0.5445291	-1.3988551	18.1761412
Mn	2.7363979	-1.9433513	17.8791211	C	0.7830631	-2.588644	18.9225037
P	4.7121362	-2.1988415	14.4887504	H	8.3409934	-1.6670871	15.812135
P	5.0645228	-1.6686014	17.9256618	H	7.4816609	-3.3537843	13.8803423
P	4.0766289	-3.8313151	17.5162959	H	6.5579306	-5.5945002	15.0795994
P	2.7234509	-1.5109147	15.603213	H	6.8579634	-5.2972345	17.7512656
C	7.9225941	-2.6557894	15.9699113	H	7.9606995	-2.8719846	18.2035199
C	7.4573419	-3.5418673	14.949191	H	7.2713668	0.912841	17.0458645
C	6.9800321	-4.7307977	15.582924	H	4.8572608	1.573297	18.0537441
C	7.1383128	-4.5743996	16.9920598	H	3.1226311	1.7944579	15.9770588
C	7.7216322	-3.2907799	17.2314395	H	4.4874666	1.2938034	13.6996625
C	6.3702173	1.0903383	16.466679	H	7.048025	0.7637951	14.3566026
C	5.0880909	1.431524	17.0028216	H	1.6360072	-5.7648103	16.6785982
C	4.1782271	1.5502276	15.9112834	H	0.5108381	-3.9715714	14.9779047
C	4.9032602	1.2976217	14.7023521	H	2.0294914	-3.8829332	12.7444888
C	6.2548575	1.0283485	15.0504342	H	4.0797144	-5.6034988	13.0555164
C	2.0029154	-5.490608	15.694844	H	3.8521064	-6.7474143	15.4937333
C	1.4097582	-4.5530559	14.7986574	H	2.1417246	-2.9871149	20.6609788
C	2.205574	-4.5155703	13.6089165	H	2.7591111	-0.3670409	20.4798206
C	3.2807359	-5.4301936	13.7711635	H	1.3598623	0.6797343	18.4166162
C	3.1725937	-6.0192463	15.0611078	H	-0.1313125	-1.2926697	17.3329821

C	1.7307814	-2.2851918	19.9411377	H	0.3405838	-3.562548	18.7331704
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5) Calculation of Core Volumes:

Table S7: Volumes V of cluster cores of **1** and **3a-d**. The heterocubane scaffold is broken up into one Mn_4 pyramid and four Mn_3P pyramids for the volume calculations (Heron's formula and $V = 1/3*b*h$). ΔV and the percentage increases are calculated compared to compound **1**.

		$V [\text{\AA}^3]$	$\Delta V [\text{\AA}^3]$	percentage
1	unsubstituted	9.159		
3a	mono-coordinated	9.151	-0.008	-0.1%
3b	di-coordinated	9.333	0.173	1.9%
3c	tri-coordinated	9.372	0.213	2.3%
3d	tetra-coordinated	9.490	0.331	3.5%

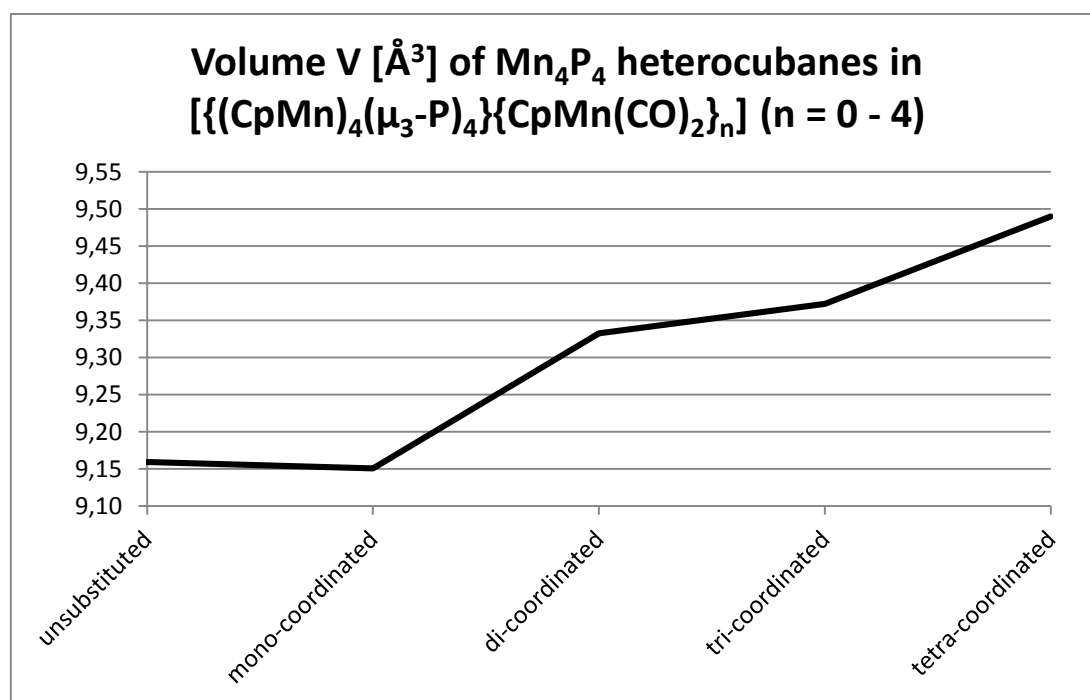


Figure S23: Graphical display of volumes $V [\text{\AA}^3]$ of cluster cores of **1** and **3a-d**.

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- [1] a) P. L. Pauson, J. A. Segal, *J. Organomet. Chem.* 1973, **63**, C13-C14. b) P. L. Pauson, J. A. Segal, *J. Chem. Soc., Dalton Trans.* 1975, 2387-2392.
- [2] W. A. Herrmann, R. Serrano, J. Weichmann, *J. Organomet. Chem.* 1983, **246**, c57-c60.
- [3] R. C. Clark, J. S. Reid, *Acta Cryst.* 1995, **A51**, 887-897.
- [4] A. Altomare, M. C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.* 1999, **32**, 115-119.
- [5] G. M. Sheldrick, *Acta Cryst.* 2008, **A64**, 112-122.
- [6] a) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* 1989, **162**, 165-169; b) O. Treutler, R. Ahlrichs, *J. Chem. Phys.* 1995, **102**, 346-354.
- [7] a) K. Eichkorn, O. Treutler, H. Oehm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* 1995, **242**, 652-660; b) K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* 1997, **97**, 119.
- [8] a) P. A. M. Dirac, *Proc. Royal Soc. A*, 1929, **123**, 714-733. b) J. C. Slater, *Phys. Rev.* 1951, **81**, 385-390. c) S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* 1980, **58**, 1200-1211. d) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098. e) J. P. Perdew, *Phys. Rev. B* 1986, **33**, 8822-8824.
- [9] a) F. Weigend, M. Häser, H. Patzelt, R. Ahlrichs, *Chem. Phys. Letters* 1998, **294**, 143; b) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* 2005, **7**, 3297; c) F. Weigend, *Phys. Chem. Chem. Phys.* 2006, **8**, 1057.
- [10] M. Sierka, A. Hogekamp, R. Ahlrichs, *J. Chem. Phys.* 2003, **118**, 9136.