Supporting Information

*cyclo*-P$_4$ Building Blocks: Achieving Non-Classical Fullerene Topology and Beyond

Fabian Dielmann, Eugenia V. Peresypkina, Barbara Krämer, Florian Hastreiter, Brian P. Johnson, Manfred Zabel, Claudia Heindl, and Manfred Scheer*

anie_201606074_sm_miscellaneous_information.pdf
Supplementary information

CONTENTS

1. Experimental Part .............................................................................................................................. 3
   1.1 Synthesis of [{Cp'''Ta(CO)}2(μ3-I)(η4-P4)] (1b) ........................................................................... 3
   1.2 Synthesis of [{Cp'''Ta(CO)}2(μ5-η4:η1:η1:η1:η1-P3)]6{CuBr}7.6 (2b) ............................................. 3
   1.3 Synthesis of [{Cp'''Ta(CO)}2(μ5-η4:η1:η1:η1:η1-P3)]6{CuCl}7.4 (2c) ............................................. 4
   1.4 Synthesis of [{Cp'''Ta(CO)}2(μ5-η4:η1:η1:η1:η1-P3)]6{CuBr}7.7 (2d) ............................................. 4
   1.5 Synthesis of [{Cp'''Ta(CO)}2(μ5-η4:η1:η1:η1:η1-P3)]6{Cp''Ta(CO)}2(μ4-η4:η1:η1:η1:η1-P3)]4{CuI10(μ-I)2(μ3-I)2} (3) and [{Cp'''Ta(CO)}2(μ5-η4:η1:η1:η1:η1-P3)]6{Cp''Ta(CO)}2(μ5-η4:η1:η1:η1:η1-P3)]6{CuBr}7.7 (2d) ............................................. 5
   1.6 Selective synthesis of [{Cp'''Ta(CO)}2(μ5-η4:η1:η1:η1:η1-P3)]6{CuI10(μ-I)8(μ4-I)(MeCN)5} (4) .......... 6
   1.7 Synthesis of [{Cp'''Ta(CO)}2(μ5-η4:η1:η1:η1:η1-P3)]6{Cu4(μ3-I)4}6 (5) ............................................. 7

2. X-ray Structure Analysis ................................................................................................................. 8
   2.1 General remarks .......................................................................................................................... 8
   2.2 Crystal structure of 1b ............................................................................................................... 13
   2.3 Crystal structure of 2b .............................................................................................................. 14
   2.4 Preliminary data on the crystal structure of 2c ......................................................................... 17
   2.5 Crystal structure of 2d ............................................................................................................ 19
   2.6 A comparison of the supramolecules in 2b and 2d .................................................................... 22
   2.7 Crystal structure of 3 ............................................................................................................... 23
   2.8 Topological interrelation between inorganic scaffolds of the supramolecules 2 and 3 ............... 26
   2.9 Crystal structures and isomerism in compound 4 ..................................................................... 27
   2.10 Crystal structure of 5 ............................................................................................................. 30

3. Size Estimation from DOSY Experiments .................................................................................... 32
   3.1 Spectroscopic Details ............................................................................................................... 32
   3.2 Size Estimation ........................................................................................................................ 32

4. Additional Figures .......................................................................................................................... 33
1. Experimental Part

All reactions were performed under an inert atmosphere of dry nitrogen or argon with standard vacuum, Schlenk, and glove-box techniques. Solvents were purified, dried and degassed prior to use by standard procedures. \([\text{Cp''''Ta(CO)}_2(\eta^4-P_4)]\)\(^1\) and \([\text{Cp*Fe(\eta^3-P_3)}]\)\(^2\) was synthesized following reported procedures. Commercially available chemicals were used without further purification. Solution NMR spectra were recorded on either Bruker Avance 300 or 400 spectrometer. The corresponding ESI-MS spectra were acquired on a ThermoQuest Finnigan MAT TSQ 7000 mass spectrometer, while elemental analyses were performed on a Vario EL III apparatus. IR spectra were recorded on a VARIAN FTS-800 FT-IR spectrometer in the form of KBr discs.

1.1 Synthesis of \([\text{Cp''''Ta(CO)}_2(\eta^4-P_4)]\) (1b)

A solution of \([\text{Cp''''Ta(CO)}_4]\) (0.961 g, 1.83 mmol) and \(P_4\) (739 mg, 5.96 mmol) in 40 mL toluene are irradiated for 8 hours, while a color change from red to brown can be observed. Afterwards the solvent is removed in vacuo, the residue pre-absorbed on silica and separated by column chromatography (hexane, \(34 \times 3.8 \text{ cm}\)). 1b is eluted as a yellow band using a hexane/toluene mixture (15:1). The solvent is removed in vacuo to give pure 1b as a yellow solid. Single crystals of 1b can be obtained by cooling of a saturated solution of 1b in hexane.

Analytical data of 1b:

**Yield:** 785 mg (1.32 mmol, 73%)

\(^1\)H NMR (CD\(_6\)) \(\delta \text{ [ppm]} =\)

- 0.87 (s, \(^t\)Bu, 9 H),
- 1.33 (s, \(^t\)Bu, 18 H),
- 6.16 (s, \(-\text{CH=},\ 2 \text{ H})\)

\(^{31}\)P\({\{^1}\text{H}\}}\) NMR (CD\(_6\)) \(\delta \text{ [ppm]} =\)

- 50.6 (t, \(^1J_{PP} = 297 \text{ Hz, 1 P}),
- 21.0 (t, \(^1J_{PP} = 242 \text{ Hz, 1 P}),
- 1.2 (dd, \(^1J_{PP} = 297 \text{ Hz, }\ 2 \text{ P}),
- \IR \text{ (KBr) } \nu_{CO} [\text{cm}^{-1}] = 1982 \text{ (vs), 1939 (vs).}
- \FDI-MS \ (\text{CH}_2\text{Cl}_2) \ m/z = 594.4 \ [\text{Cp''''Ta(CO)}_2P_4]^+\)

1.2 Synthesis of \([\{\text{Cp''Ta(CO)}_2(\mu_5-\eta^4:\eta^1:\eta^1:\eta^1-P_4)\}_6(\text{CuBr})_{7.6}\] (2b)

A thin Schlenk tube was charged with a solution of 1a (52 mg, 0.095 mmol) in 2 mL CH\(_2\)Cl\(_2\). Onto this solution was carefully layered a mixture of 4 mL CH\(_2\)Cl\(_2\) and 2 mL CH\(_3\)CN, followed by a solution of CuBr (18 mg, 0.13 mmol) in CH\(_3\)CN/CH\(_2\)Cl\(_2\) (1 mL / 1 mL). The doubly layered system was allowed to stand in an undisturbed area and orange crystals of 2b formed within 24 hours. The mixture was allowed to stand a total of 5 days to ensure thorough diffusion, and the mother liquor was decanted away. The crystals were washed once with 2 mL CH\(_3\)CN and twice with 2 mL CH\(_2\)Cl\(_2\) and dried under vacuum.
Analytical data for 2b:

**Yield**: 34 mg (49% based on 1a)

**IR (KBr)**: $\tilde{\nu}_{\text{CO}}$ [cm$^{-1}$] = 2042 (vs, br), 1972 (sh)

**Elemental analysis**: Calculated (%) for C$_{90}$H$_{126}$Br$_7$Cu$_{6}$O$_{12}$P$_{24}$Ta$_6$: 0.5(CH$_2$Cl)$_2$-(CH$_3$CN)$_2$ (4429.1 g/mol): C 24.92, H 2.94, N 0.13; found: C 25.22, H 3.00; N 0.12.

1.3 Synthesis of [{Cp'''Ta(CO)$_2$(μ$_5$-η$_4$:η$_1$:η$_1$:η$_1$:η$_1$-P$_4$)}$_6${CuCl}]$_{7.4}$ (2c)

A mixture of CuCl (6.7 mg, 0.067 mmol) and 1b (30 mg, 0.051 mmol) in CH$_2$Cl$_2$ (2.5 mL) was stirred for 5 hours at room temperature. The resulting red solution was transferred into a thin Schlenk tube and carefully layered with Et$_2$O (2.5 mL). The mixture was stored at room temperature in the dark. Within two weeks tiny red prisms deposited in the vessel. The microcrystalline material was isolated, washed with CH$_2$Cl$_2$ (1 mL) and Et$_2$O (3 × 2 mL) and dried under vacuum at room temperature to yield 26 mg (71 %) of 2c.

Single crystals suitable for an X-ray structure analysis were obtained by the following procedure: A solution of CuCl (7 mg, 0.071 mmol) in CH$_3$CN (1 mL) was added to a stirred solution of 1b (30 mg, 0.051 mmol) in toluene (2 mL) at room temperature. After stirring the resulting orange solution over 10 minutes it was transferred into a thin Schlenk tube and carefully layered with Et$_2$O (1.5 mL). The mixture was left at room temperature in the dark. Within one month red prisms of 2c were formed. The crystalline material was isolated, washed with toluene (1 mL) and Et$_2$O (2 × 2 mL) and dried under vacuum at room temperature to yield 19 mg (52 %) of 2c.

Analytical data of [{Cp'''Ta(CO)$_2$(μ$_5$-η$_4$:η$_1$:η$_1$:η$_1$:η$_1$-P$_4$)}$_6${CuCl}]$_{7.4}$ (2c):

**Yield**: 26 mg (71 %, based on 1b)

$^1$H NMR (CD$_2$Cl$_2$, 400.13 MHz, 300 K): δ [ppm] = 7.46 (s {br}; C$_H$), 6.39 (s {br}; C$_H$), 1.81 (s {br}; tBu), 1.53 (s {br}; tBu), 1.19 (s {br}; tBu), 1.15 (s {br}; tBu), 1.05 (s {br}; tBu), 1.01 (s {br}; tBu)

$^{31}$P($^1$H) NMR (CD$_2$Cl$_2$, 161.98 MHz, 300 K): δ [ppm] = −50.6 (s {br}), −81.0 (s {br})

**ESI-MS** (CD$_2$Cl$_2$/CH$_3$CN): $m/z$ (%) = 1944.6 (3) [{Cp''''Ta(CO)$_2$P$_4$$_2$CuCl}]$, 1845.6 (60) [{Cp''''Ta(CO)$_2$P$_4$$_2$Cu}]$, 1251.2 (100) [{Cp''''Ta(CO)$_2$$_2$Cu}]$, 657.0 (9) [{Cp''''Ta(CO)$_2$P$_4$}Cu$^+$

**IR (KBr)**: $\tilde{\nu}$ [cm$^{-1}$] = 3095 (vw; CH), 3021 (vw; CH), 2962 (m; CH), 2922 (w; CH), 2869 (w; CH), 2019 (vs, CO), 1979 (s; CO), 1486 (w), 1463 (m), 1405 (w), 1367 (m), 1242 (m), 1168 (m), 508 (w), 464 (w)

**Elemental analysis**: Calculated (%) for (C$_{90}$H$_{126}$O$_{12}$P$_{24}$Ta$_6$·0.5(CH$_2$Cl)$_2$·(CH$_3$CN)$_2$) (4429.1 g/mol): C 31.89, H 4.08, N 0.0; found: C 32.32, H 4.38, N 0.0

1.4 Synthesis of [{Cp'''Ta(CO)$_2$(μ$_5$-η$_4$:η$_1$:η$_1$:η$_1$:η$_1$-P$_4$)}$_6${CuBr}]$_{7.7}$ (2d)
A mixture of CuBr (18 mg, 0.126 mmol) and 1b (25 mg, 0.042 mmol) in CH₂Cl₂ (3 mL) was stirred for 5 hours at room temperature. The resulting red solution was transferred into a thin Schlenk tube and carefully layered with Et₂O (4 mL). The mixture was left at room temperature in the dark. Within two weeks a red, microcrystalline material was formed. It was isolated, washed with CH₂Cl₂ (1 mL) and Et₂O (3 × 2 mL) and dried under vacuum at room temperature to yield 5 mg (25%) of 2d.

Single crystals suitable for an X-ray structure analysis were obtained by the following procedure: A solution of CuBr (7 mg, 0.049 mmol) in CH₃CN (0.4 mL) was added to a stirred solution of 1b (15 mg, 0.025 mmol) in benzene (0.8 mL) at room temperature. After stirring the resulting orange solution over 10 minutes the mixture was left at room temperature in the dark. Within three weeks red prisms of 2d were formed. The crystalline material was isolated, washed with toluene (1 mL) and Et₂O (2 × 2 mL) and dried under vacuum at room temperature to yield 5 mg (25%) of 2d.

Analytical data of [{Cp'''Ta(CO)₂(μ₅-η⁵:η¹:η¹:η¹:η¹-P₄)}₆{CuBr}_7] (2d):

**Yield:** 23 mg (70%, based on 1b)

1H NMR (CD₂Cl₂, 400.13 MHz, 300 K): δ [ppm] = 7.39 (s {br}; CH), 6.37 (s {br}; CH), 1.79 (s {br}; tBu), 1.523 (s {br}; tBu), 1.21 (s {br}; tBu), 1.17 (s {br}; tBu), 1.08 (s {br}; tBu), 1.03 (s {br}; tBu), 31P{[¹H]} NMR (CD₂Cl₂, 161.98 MHz, 300 K): δ [ppm] = −60.7 (s {br}), −79.7 (s {br}), −91.0 (s {br})

ESI-MS (CH₂Cl₂): m/z (%) = 1251.2 [{Cp'''Ta(CO)₂P₄]Cu}⁺

IR (KBr): ν [cm⁻¹] = 3095 (vw; CH), 3021 (vw; CH), 2963 (m; CH), 2922 (w; CH), 2869 (w; CH), 2695 (m; CH), 2486 (w; CH), 1973 (s; CO), 1479 (w), 1463 (w), 1404 (w), 1367 (w), 1241 (w), 1168 (w), 512 (w), 465 (w)

1.5 Synthesis of [{Cp'''Ta(CO)₂(μ₅-η⁵:η¹:η¹:η¹:η¹-P₄)}₆{Cp''''Ta(CO)₂(μ₄-η⁴:η¹:η¹:η¹-P₄)}₄{Cu₁₄I₁₀(μ-I)₂(μ₅-I)₂} (3) and [{Cp'''Ta(CO)₂(μ₅-η⁵:η¹:η¹:η¹:η¹-P₄)}₃{Cu₁₂I₃(μ-I)₈(μ-I)(MeCN)₅}] (4)

A solution of CuI (26 mg, 0.134 mmol) in CH₃CN (3 mL) was carefully layered over a solution of 1a (30 mg, 0.0557 mmol) and in toluene (3 mL) at room temperature. The mixture was left at room temperature in the dark. Within three days orange crystals of 3 were formed at the phase boundary. After 10 days also yellow crystals of 4 formed. The mother liquor was decanted and the crystals were washed with Diethylether (3 × 4 mL) and dried for 5 hours under vacuum at room temperature. Thereby, the orange crystals completely decomposed to give a bright orange powder, due to loss of solvent molecules included in the crystal lattice. The yellow crystals were separated manually.

Analytical data of [{Cp'''Ta(CO)₂(μ₅-η⁵:η¹:η¹:η¹:η¹-P₄)}₆{Cp''''Ta(CO)₂(μ₄-η⁴:η¹:η¹:η¹-P₄)}₄{Cu₁₄I₁₀(μ-I)₂(μ₅-I)₂}] (3):

**Yield:** 13 mg (29% based on 1a)
Elementary Analysis: Calculated (%) for (C₁₃H₂₃O₂TaP₄)₁₀(CuI)₁₀(C₇H₈)₁₀ (8324.4 g/mol): C 24.67, H 3.02, N 0.0; found: C 24.55, H 3.02, N 0.0

IR (KBr): $\tilde{\nu} [\text{cm}^{-1}] = 3078$ (w; CH), 2960 (m; CH), 2865 (w; CH), 2011 (vs; CO), 1969 (vs; CO), 1486 (m), 1463 (m), 1445 (w), 1396 (w), 1364 (m), 1249 (m), 1164 (m), 1057 (w), 1024 (w), 919 (w), 871 (w), 858 (w), 512 (w), 463 (m)

Analytical data of $\{\text{Cp''Ta(CO)}₂(\mu_5-\eta^4:\eta^1:\eta^1:\eta^1:P₄)\}_5\{\text{CuI}_2(\mu-I)_8(\mu_4-I)(\text{MeCN})_8\}$ (4)

Yield: 25 mg (44 % based on 1a)

Elementary Analysis: Calculated (%) for (C₁₃H₂₃O₂TaP₄)₅(CuI)₁₂(C₇H₈) (5068.4 g/mol): C 19.43, H 2.25, N 0.0; found: C 19.84, H 2.28, N 0.0

IR (KBr): $\tilde{\nu} [\text{cm}^{-1}] = 2961$ (w; CH), 2927 (w; CH), 2017 (s; CO), 1976 (s; CO)

1.6 Selective synthesis of $\{\text{Cp''Ta(CO)}₂(\mu_5-\eta^4:\eta^1:\eta^1:\eta^1:P₄)\}_5\{\text{CuI}_2(\mu-I)_8(\mu_4-I)(\text{MeCN})_8\}$ (4)

A solution of CuI (81 mg, 0.423 mmol) in CH₃CN (5 mL) was carefully layered over a solution of 1a (30 mg, 0.056 mmol) and [Cp*Fe(η⁵-P₅)] (58 mg, 0.168 mmol) in toluene (8 mL) at room temperature. The mixture was left at room temperature in the dark. Within one month brown needles of a 2D coordination polymer containing [Cp*Fe(η⁵-P₅)] and CuI in a 1:1 stoichiometry and yellow blocks of the spherical cluster 4 were deposited in the vessel. The crystalline material was isolated, washed with CH₂Cl₂ (3 × 2 mL) and Et₂O (4 mL) and dried under vacuum at room temperature. Crystals of 4 were separated mechanically.

Analytical data of $\{\text{Cp''Ta(CO)}₂(\mu_5-\eta^4:\eta^1:\eta^1:\eta^1:P₄)\}_5\{\text{CuI}_2(\mu-I)_8(\mu_4-I)(\text{MeCN})_8\}$ (4):

Yield: 10 mg (15 % based on 1a)

IR (KBr): $\tilde{\nu} [\text{cm}^{-1}] = 2961$ (w; CH), 2927 (w; CH), 2017 (s; CO), 1976 (s; CO)
1.7 Synthesis of \( \{[\text{Cp}'''\text{Ta}({\text{CO}})_2(\mu_5-\eta^1:\eta^1:\eta^1:\eta^1-\text{P}_4)]\}_{n}(5) \)

A solution of CuI (15 mg, 0.079 mmol) in CH\(_3\)CN (4 mL) was added to a stirred solution of 1b (35 mg, 0.059 mmol) in toluene (10 mL) at room temperature. After stirring the resulting orange solution over 10 minutes it was transferred into a thin Schlenk tube and carefully layered with Et\(_2\)O (18 mL). The mixture was left at room temperature in the dark. Within three weeks yellow plates of 5 were formed, which were isolated, washed with toluene (1 mL) and Et\(_2\)O (2 × 2 mL) and dried under vacuum at room temperature.

Analytical data of the reaction mixture obtained by stirring 1b and CuI in a ratio of 2:1 in CH\(_2\)Cl\(_2\)/MeCN mixtures over 4 hours:

- **\( ^1H \text{ NMR} \)** (CD\(_2\)Cl\(_2\), 400.13 MHz, 300 K): \( \delta \) [ppm] = 7.30−7.00 (m {br}; C\(_2\)H), 6.44−6.06 (m {br}; C\(_2\)H), 1.72 (s {br}; tBu), 1.51 (m {br}; tBu), 1.33 (s {br}; tBu), 1.29 (s {br}; tBu), 1.25 (s {br}; tBu), 1.18 (s {br}; tBu), 1.15 (s {br}; tBu), 1.11 (s {br}; tBu),

- **\( ^{31}P\{^1H\} \text{ NMR} \)** (C\(_6\)D\(_6\), 161.98 MHz, 300 K): \( \delta \) [ppm] = broad signals between −27 and −92 ppm

**Positive ion ESI-MS** (CH\(_2\)Cl\(_2\)): \( m/z \) (%) = 1441.2 (20) [(Cp'''Ta(CO)\(_2\)P\(_4\))\(_2\)CuI], 1251.2 (100) [(Cp'''Ta(CO)\(_2\)P\(_4\))\(_2\)Cu], 698.1 (35) [(Cp'''Ta(CO)\(_2\)P\(_4\))Cu(CH\(_3\)CN)]

**Negative ion ESI-MS** (CH\(_2\)Cl\(_2\)): \( m/z \) (%) = 888.5 (0.5) [Cu\(_4\)I\(_5\)]\(^−\), 698.7 (1) [Cu\(_3\)I\(_4\)]\(^−\), 506.8 (3) [Cu\(_2\)I\(_3\)]\(^−\), 316.8 (100) [CuI\(_2\)]\(^−\), 127.1 (31) [I\(^−\)]

**IR** (KBr): \( \tilde{\nu} \) [cm\(^−1\)] = 2961 (m), 2920 (w), 2868 (w), 2013 (s; CO), 1971 (s; CO), 1485 (w), 1460 (m), 1404 (w), 1366 (m), 1261 (m), 1240 (m), 1167 (m), 1097 (m {br}), 1023 (m {br}), 803 (w), 465 (m)

Analytical data of \( \{[\text{Cp}'''\text{Ta}({\text{CO}})_2(\mu_5-\eta^1:\eta^1:\eta^1:\eta^1-\text{P}_4)]\}_{n}(5) \):

- **Yield**: 12 mg (45 % based on CuI)
- **IR** (KBr): \( \tilde{\nu} \) [cm\(^−1\)] = 2961 (m), 2920 (w), 2868 (w), 2013 (s; CO), 1973 (s; CO), 1485 (w), 1460 (m), 1404 (w), 1366 (m), 1262 (m), 1240 (m), 1167 (m), 1101 (m {br}), 1024 (m {br}), 803 (w), 511 (w), 465 (m)

**Elemental analysis**: Calculated (%) for (C\(_{19}\)H\(_{29}\)TaO\(_7\)P\(_4\))(CuI\(_6\))(CH\(_3\)CN)\(_2\)(C\(_7\)H\(_8\))\(_3\) (5782.9 g/mol): C 20.98, H 2.55, N 0.48; found: C 21.01, H 2.79, N 0.37.
2. X-ray Structure Analysis

2.1 General remarks

Crystals of were taken from a Schlenk flask under a stream of argon and immediately covered with mineral oil or perfluorinated Fomblin® mineral oil to prevent both decomposition and a loss of solvent. The quickly chosen single crystals covered by a drop of the oil were taken to the pre-centered goniometer head with CryoMount® and directly placed on diffractometer into a stream of cold nitrogen. X-ray diffraction studies faced many challenges, since the crystals have relatively small size and decompose rapidly losing solvent molecules. The data for 1b, 2d, 4a and 5 were collected on an Agilent Technologies Gemini R-Ultra diffractometer equipped with Ruby CCD detector and an Enhanced Ultra CuKα sealed tube (λ = 1.54178 Å) using 1° ω scans. The data for 2b were collected on a STOE IPDS equipped with STOE image plate detector and MoKα sealed tube (λ = 0.71073 Å) using 0.5° φ scans. The data for 3 and 4b were collected on a Rigaku SuperNova diffractometer equipped with Titan2 CCD detector and a SuperNova CuKα microfocus source using 0.5° ω scans. All measurements were performed at 150 (1b) or 123 K (the rest). Preliminary data were collected for 2c (see Sect. 2.4 for detail)

The following composition was established for structurally investigated compounds (see corresponding sections):

|   |   |
|---|---|
| 1b: | [Cp''''Ta(CO)₂(η⁷-P₄)] |
| 2b: | [{Cp''''Ta(CO)₂(μ-η⁷:η⁷:η⁷:η⁷:η⁷-P₄)}₆{CuBr₁₇₆}·0.5(CH₂Cl₂) |
| 2c: | [{Cp''''Ta(CO)₂(μ-η⁷:η⁷:η⁷:η⁷:η⁷-P₄)}₆{CuCl₁₇₆}·nC₃H₆·mMeCN, n and m are unidentified (see Sect. 2.4) |
| 2d: | [{Cp''''Ta(CO)₂(μ-η⁷:η⁷:η⁷:η⁷:η⁷-P₄)}₆{CuBr₁₇₆}·3C₄H₆ |
| 3: | [{Cp''''Ta(CO)₂(μ-η⁷:η⁷:η⁷:η⁷:η⁷-P₄)}₆{Cp'Ta(CO)₂(μ-η⁷:η⁷:η⁷:η⁷:η⁷-P₄)}₆{CuI₀(μ-I)₂(μ-I)₂}·2.3C₃H₈·4.9MeCN |
| 4a, |
| 4b: for 4a: n=4.3, m=2.4, for 4b: n=2.35, m=3.5 |
| 5: | [{Cp''''Ta(CO)₂(μ-η⁷:η⁷:η⁷:η⁷:η⁷-P₄)}₆{Cu₄(μ₄-I)₄}·nC₃H₆·N |

The structures of 1b-5 were solved by either charge flipping or direct methods with SUPERFLIP, SIR97, or SHELX97. The structures were refined by full-matrix least-squares method against |F|² in anisotropic approximation using SHELXL97 or the multiprocessor and variable memory version SHELXL2013. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were set in calculated positions and refined riding on pivot atoms. Compound 2b is isostructural to previously reported 2a. In the crystal structures of 2b-2d, partly vacant positions of one CuX unit in the scaffold are indicated by high displacement parameters. In addition, one CuX unit appears inside the cavity of the supramolecules. The displacement parameters of these heavy atoms were set equal to Uiso = 0.03 Å², and the occupancy factors
were refined. Their resulting values were fixed, and the refinement of the displacement parameters was performed. The solvent molecules in 2b-4 are disordered.

X-ray structure analysis of the compound 3 has proven to be a complicated task. The crystals of 3 are very unstable towards loss of the solvent and show quick amorphization out of mother solution even being protected by Fomblin® oil. The crystals slowly decay when irradiated. The unit cell determined from very quickly mounted crystal is monoclinic C-centered with $a=32.91$, $b=26.31$, $c=34.63$ Å, $\beta=103.4^\circ$, $V=29171$ Å$^3$, while crystals that were kept longer demonstrate twice smaller monoclinic C-centered unit cell $a=20.94$, $b=26.32$, $c=26.51$ Å, $\beta=93.0^\circ$, $V=14588$ Å$^3$. Both unit cells are related as structure-superstructure (Fig. S1a). Our experiments show that the intensity of superstructural reflections fades in the series of consequent structural determinations performed from the same single crystal (Fig. S1b-d). Depending on the crystal size, these reflections disappear within 1 or 2 days of irradiation that together with small crystal size means that diffraction data of only a limited quality can be collected. In addition, the quality of the crystals is also limited by strong tendency to twinning, which is not systematic as follows from the five diffraction experiments from different crystals. The structural models in bigger unit cell (space group $C2/c$) feature high residual density (up to 8 e·Å$^{-3}$) at heavy atoms, which can be assigned as the second position (~15%) of the entire supramolecule, which lie in an inversion center 1 (site symmetry $C_i$). Together with systematically observed higher intensity of the observed reflections compared to calculated ones, the structure 3 demonstrates typical signs of allotwinning. When this electron density is described as the second position (refined portion 0.14), the quality factors ($R_1$, $wR_2$ and weighting scheme) decrease from $R_1 = 0.155$ to 0.069, $wR_2 = 0.355$ to 0.212, etc.

**Figure S1.** (a) Unit cells determined from fresh and aged crystal of 3 related as structure-superstructure. The unit cell relation is $a'=1/2a+1/2c$, $b'=-b$, $c'=1/2a-1/2c$, where $a$, $b$, $c$ and $a'$, $b'$, $c'$ are primitive vectors in

9
super- and substructural cells, respectively. (b-d) The decrease of intensity of superstructural reflections in the series of consequent structural determinations performed from the same single crystal.

When weak superstructural reflections are ignored, the structure solution in smaller unit cell and C2/m space group gives the supramolecule lying in 2/m position (C2h site symmetry). In contrast, this model does not demonstrate significant electron density peaks at heavy atoms, and the displacement parameters of all the heavy atoms are significantly larger giving an impression of a structure averaged by symmetry. If this model is refined over the data collected from the crystal that showed no superstructural effect, it shows the a.d.p. ellipsoids systematically elongated in the direction perpendicular to the m plane. For this reason the model in larger unit cell is preferred.

For 4, two structures had been obtained, 4a as a bulk product of the reaction in presence of Cp*FeP3, and 4b as a 2nd phase in a fractional crystallization in the synthesis of 3. The crystals of 4b showed radiolysis that complicated the structure determination. Initially yellow crystals turned brown after several attempts to determine their crystal structure (Fig. S2) accompanied by gradual weakening of the diffraction pattern.

**Figure S2.** The crystal of 4b before (left) and after irradiation with X-rays (right). The color change takes place after about 1 day irradiation. In case of 4a the degradation of the crystal was not observed most probably due to its large size (Table S2) that allowed relatively fast X-ray diffraction experiment.

CIF files with comprehensive information on the details of the diffraction experiments and full tables of bond lengths and angles for 1b-5 are deposited in Cambridge Crystallographic Data Centre under the deposition codes CCDC-1482592 - CCDC-1482598, respectively. Crystallographic data and details of the diffraction experiments are given in Tables S1 and S2. The figures are generated with Olex" and ToposPro."
Table S1. Experimental details for 1b-3

|       | 1b             | 2b             | 2d             | 3               |
|-------|----------------|----------------|----------------|-----------------|
| CCDC Code | 1482592        | 1482593        | 1482594        | 1482595         |
| Crystal data |                |                |                |                 |
| Chemical formula | C₁₀H₂₉O₃P₂Ta     | C₂₆H₅₂Br₇.₆₆Cu₇.₆₆O₁₂ | C₁₀H₂₉Br₇.₆₆Cu₇.₆₆O₁₂ | C₁₇₅.₆₈H₄₃.₃₄Cu₁₄.₃₄N₁₉.₃₄O₂₈ |
| Mᵣ      | 594.25         | 4361.56        | 4904.39        | 8460.70         |
| Crystal system, space group | Monoclinic, P₂₁/n | Trigonal, R₃₂/H | Monoclinic, P₂₁/n | Monoclinic, C₂/c |
| Temperature (K) | 150            | 123            | 123            | 123             |
| a, b, c (Å) | 16.3097(4), 8.4189(1), 18.4362(4) | 23.1232(15), 22.5841(18) | 17.3683(4), 18.9520(3), 26.5452(4) | 32.9105(7), 26.3272(5), 34.6595(8) |
| β (°)    | 114.727(3)     | 90             | 97.595(2)      | 103.477(2)      |
| V (Å³)   | 2299.36(10)    | 10457.5(16)    | 8661.1(3)      | 29203.5(11)     |
| Z        | 4              | 3              | 2              | 4               |
| F(000)   | 1168           | 6202           | 4742           | 15883           |
| Dm (Mg m⁻³) | 1.717          | 2.078          | 1.881          | 1.924           |
| Radiation type | Cu Kα         | Mo Kα          | Cu Kα          | Cu Kα           |
| μ (mm⁻¹) | 11.54          | 8.34           | 12.29          | 21.84           |
| Crystal habit and colour | yellow plate | red prism       | brown plate     | orange prism    |
| Crystal size (mm) | 0.25 × 0.09 × 0.02 | 0.09 × 0.08 × 0.06 | 0.13 × 0.08 × 0.02 | 0.09 × 0.08 × 0.05 |
| Data collection |                |                |                |                 |
| Diffractometer | Xcalibur, Ruby, Gemini ultra | STOE-IPDS diffractometer | Xcalibur, Ruby, Gemini ultra | SuperNova, TitanS2 |
| Absorption correction | Multi-scan | Numerical       | Gaussian        | Gaussian         |
| Tmin, Tmax | 0.317, 1.419   | 0.474, 0.664   | 0.361, 0.801   | 0.314, 0.538    |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 47006, 3686, 2802 | 27008, 4989, 4172 | 28998, 13244, 9306 | 49327, 27041, 17500 |
| Rint | 0.058          | 0.081          | 0.050          | 0.051           |
| (sin θ/λ)max (Å⁻¹) | 0.578         | 0.636          | 0.572          | 0.623           |
| Range of h, k, l | h = -18→18, k = -9→9, l = -20→21 | h = -25→29, k = -29→27, l = -28→28 | h = -19→19, k = -21→20, l = -20→30 | h = -34→40, k = -20→32, l = -41→43 |
| Refinement |                |                |                |                 |
| R(F² > 2σ(F²)), wR(F²), S | 0.024, 0.058, 0.95 | 0.028, 0.064, 0.96 | 0.042, 0.117, 0.95 | 0.070, 0.212, 1.04 |
| No. of reflections | 3686          | 4989           | 13244          | 27041           |
| No. of parameters | 244           | 245            | 1004           | 1478            |
| No. of restraints | 0            | 0              | 55             | 16              |
| H-atom treatment | H-atom parameters constrained | H-atom parameters constrained | H-atom parameters constrained | H-atom parameters constrained |
| Δ(Δmax, Δmin) (e Å⁻³) | 1.43, -0.58   | 1.63, -0.65    | 1.81, -2.01    | 4.27, -2.72     |

Computer programs: CrysAlis CCD, Oxford Diffraction, CrysAlis RED, SIR97 (Altomare, 1993), SHELXL97 (Sheldrick, 1997), PLATON (Spek, 2003), STOE (1998), SHELXL2013 (Sheldrick, 2013), PLATON (Spek, 2003), SUPERFLIP (Palatinus, 2007).
Table S2. Experimental details for 4-5

|                | 4a                  | 4b                  | 5                   |
|----------------|---------------------|---------------------|---------------------|
| CCDC Code      | 1482596             | 1482597             | 1482598             |
| Crystal data   |                     |                     |                     |
| Chemical formula | C₈₆H₁₁₆.66Cu₁₂I₁₂N₇.₄₇O₁₀P₂₀Ta₅ | C₁₀₆.₄₅H₁₄₆.₃₈Cu₁₂I₁₂N₇.₅₀O₁₀P₂₀Ta₅ | C₂₁H₂₃NCu₁₂O₂₃P₃Ta |
| Mᵣ             | 5675.99             | 5500.43             | 1397.06             |
| Crystal system, space group | Orthorhombic, Pbcₐ   | Monoclinic, P2₁/n   | Monoclinic, P2₁/c   |
| Temperature (K) | 123                 | 123                 | 123                 |
| a, b, c (Å)    | 31.1708(4), 31.9398(5), 35.6999(5) | 20.9613 (5), 32.1655 (6), 30.1770 (6) | 17.6897(4), 14.1142(4), 14.2011(3) |
| β (°)          | 90                  | 108.513 (2)         | 94.870 (2)          |
| V (Å³)         | 35542.4 (9)         | 19293.4 (7)         | 3532.87 (15)        |
| Z              | 8                   | 4                   | 4                   |
| F(000)         | 21294               | 10266               | 2568                |
| Dᵣ (Mg m⁻³)   | 2.121               | 1.894               | 2.627               |
| Radiation type | Cu Kα               | Cu Kα               | Cu Kα               |
| μ (mm⁻¹)       | 25.41               | 23.40               | 37.67               |
| Crystal habit and colour | yellow prism         | yellow prism         | yellow plate        |
| Crystal size (mm) | 0.32 × 0.30 × 0.23 | 0.09 × 0.07 × 0.04  | 0.25 × 0.13 × 0.01  |
| Data collection |                     |                     |                     |
| Diffractometer | Xcalibur, Ruby, Gemini ultra | Rugaku SuperNova, Titan⁴² | Xcalibur, Ruby, Gemini ultra |
| Absorption correction | For a sphere         | Gaussian            | Gaussian            |
| Tₘᵢₙ, Tₘₐₓ | 0.014, 0.077       | 0.239, 0.527        | 0.057, 0.827        |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 69945, 27585, 23733 | 70458, 37049, 21383 | 12538, 5449, 4072 |
| Rₚₛₜ | 0.058               | 0.054               | 0.051               |
| (sin 0λ)max (Å⁻¹) | 0.574               | 0.623               | 0.573               |
| Range of h, k, l | h = -35→34, k = -35→36, l = -40→37 | h = -25→21, k = -29→38, l = -36→36 | h = -12→20, k = -15→16, l = -15→16 |
| Refined |                     |                     |                     |
| R(F² > 2σ(F²)), wR(F²), S | 0.050, 0.131, 1.03 | 0.053, 0.138, 0.88 | 0.043, 0.104, 0.93 |
| No. of reflections | 27585               | 37049               | 5449                |
| No. of parameters | 1748               | 1638               | 344                 |
| No. of restraints | 12                 | 22                 | 0                   |
| H-atom treatment | H-atom parameters constrained | H-atom parameters constrained | H-atom parameters constrained |
| Δₘᵢₙ, Δₘᵢₙ (e Å⁻³) | 2.37, -1.43         | 4.92, -2.90         | 2.43, -1.14         |

Computer programs: CrysAlis PRO 1.171.38.41 (Rigaku OD, 2015), SIR97 (Altomare, 1999), SHELXL97 (Sheldrick, 1997), SHELXL2013 (Sheldrick, 2013), SUPERFLIP (Palatinus, 2007).
2.2 Crystal structure of 1b

Compound 1b crystallizes as yellow plates from hexane solution.

Figure S3. Molecular structure of 1b in (a) ball-and-stick and (b) a.d.p. ellipsoid (50%) representation. Hydrogen atoms are omitted for clarity.

Table S3. Selected geometric parameters (Å, º) for 1b

| Bond             | Distance (Å) | Bond             | Distance (Å) |
|------------------|--------------|------------------|--------------|
| Ta1—P1           | 2.6410 (12)  | Ta1—C6           | 2.406 (3)    |
| Ta1—P2           | 2.6495 (10)  | Ta1—C7           | 2.386 (3)    |
| Ta1—P3           | 2.6385 (10)  | P1—P2            | 2.1729 (17)  |
| Ta1—P4           | 2.6200 (11)  | P1—P4            | 2.1555 (15)  |
| Ta1—C1           | 2.078 (4)    | P2—P3            | 2.1800 (15)  |
| Ta1—C2           | 2.082 (5)    | P3—P4            | 2.1624 (17)  |
| Ta1—C3           | 2.415 (3)    | O1—C1            | 1.138 (5)    |
| Ta1—C4           | 2.464 (3)    | O2—C2            | 1.134 (6)    |
| Ta1—C5           | 2.414 (3)    |                  |              |
| P2—P1—P4         | 88.64 (6)    | P1—P4—P3         | 92.00 (6)    |
| P1—P2—P3         | 91.06 (6)    | Ta1—C1—O1        | 178.7 (3)    |
| P2—P3—P4         | 88.28 (6)    | Ta1—C2—O2        | 177.8 (4)    |
2.3 Crystal structure of 2b

Compound [(Cp"Ta(CO)₂P₄)(CuBr)₇.6]·0.5(CH₂Cl₂) (2b) crystallizes as orange blocks from CH₂Cl₂/CH₃CN/dmf-d₇ mixtures. 2b crystallizes with half of the molecule CH₂Cl₂ per formula unit. The electron density at the center of the core of 2b was assigned as minor position of bromide, which is coordinated to η²-coordinated to cyclo-P₄ Cu(I) ion.

Figure S4. The independent part of supramolecule 2b: (a) the disorder and (b) the enumeration scheme (cf. Table S4).

The inorganic scaffold of 2b contains partly occupied Cu and Br positions, (Cu(1), Br(1) with occupancies 0.75; Cu(1i), Br(1i) with occupancies 0.1). They always have complimentary occupancies, so that the CuBr unit is present or absent as a whole. These partial occupancies give rise to a disorder in the inorganic core similar to those in 2b. The disorder can be only interpreted as a number of co-crystallizing supramolecules of similar but different inorganic scaffolds. Some of the co-crystallizing species are depicted in Fig. S5.
Moiety 1: max 0.75
[(Cp'''Ta(CO)2P4)6(CuBr)6]]

Moiety 2: max 0.875
[(Cp'''Ta(CO)2P4)6(CuBr)7]]

Moiety 3: max 1
[(Cp'''Ta(CO)2P4)6(CuBr)6]]

Moiety 4: max 0.1 probability
[(Cp'''Ta(CO)2P4)5(CuBr)8(CuBr)]]

Moiety 5: max 0.1 probability
[(Cp'''Ta(CO)2P4)5(CuBr)7(CuBr)]]

Moiety 6: max 0.1 probability
[(Cp'''Ta(CO)2P4)5(CuBr)6(CuBr)]]

Figure S5. Some co-crystallizing supramolecules of 2b of similar but different inorganic scaffolds.
Table S4. Selected geometric parameters (Å, °) for 2b.

|                  |                |                  |                  |
|------------------|----------------|------------------|------------------|
| Br—I—CuI        | 2.25 (5)       | Ta—I—P4         | 2.6177 (10)      |
| Br—I—CuIii      | 2.25 (5)       | Ta—I—P3         | 2.6385 (10)      |
| Br—I—CuIii      | 2.25 (5)       | Ta—I—P1         | 2.6405 (11)      |
| Br—I—CuIiv      | 2.25 (5)       | P1—P4           | 2.1595 (15)      |
| Br—I—CuI        | 2.25 (5)       | P1—P2           | 2.1828 (15)      |
| Cu—I—P4         | 2.23 (6)       | P2—P3           | 2.1840 (15)      |
| Cu—I—P1         | 2.34 (6)       | Cu—I—Br1       | 2.3281 (14)      |
| Cu—I—P2         | 2.47 (6)       | Cu—I—Br2       | 2.3635 (7)       |
| Cu—I—P3         | 2.3072 (12)    | P1—I—CuI       | 2.28 (6)         |
| Cu—I—P1         | 2.3073 (12)    | P2—I—CuI       | 2.47 (6)         |
| Cu—I—P4         | 2.3074 (12)    | P3—I—Cu2       | 2.3113 (11)      |
| Cu—I—P5         | 2.3113 (11)    | P4—I—Cu2       | 2.3152 (12)      |
| Cu—I—P6         | 2.3152 (12)    | C—I—O         | 1.141 (6)        |
| Cu—I—P7         | 2.3312 (12)    | C—I—O         | 1.137 (6)        |
| Cu—I—P8         | 180 (3)        | P3—I—Cu2—I—P4  | 98.77 (4)        |
| Cu—I—P9         | 124 (2)        | P3—I—Cu2—I—P2  | 101.27 (4)       |
| P1—I—P4         | 97 (2)         | P4—I—Cu2—I—P2  | 98.84 (4)        |
| P1—I—P5         | 126 (2)        | P3—I—Cu2—I—Br1 | 114.72 (4)       |
| P1—I—P6         | 99.71 (4)      | P4—I—Cu2—I—Br2 | 118.18 (3)       |
| P1—I—P7         | 99.71 (4)      | P2—I—Cu2—I—Br2 | 121.29 (3)       |
| P1—I—P8         | 99.71 (4)      | P4—I—P1—I—P2   | 88.18 (5)        |
| P1—I—P9         | 118.04 (3)     | P1—I—P2—I—P3   | 91.09 (6)        |
| P1—I—P10        | 118.04 (3)     | P4—I—P3—I—P2   | 88.22 (5)        |
| P1—I—P11        | 118.04 (3)     | P3—I—P4—I—P1   | 92.46 (6)        |

Symmetry code(s): (i) x-y, x, -z; (ii) -x+y, -x, z; (iii) -x, -y, -z; (iv) -y, x-y, z; (v) y, -x+y, -z.
2.4 Preliminary data on the crystal structure of 2c

Compound 2c crystallizes as very small orange blocks from toluene/MeCN mixtures. The dataset was collected on a synchrotron from a small and twinned crystal. The data were collected only up to the minimal resolution of 1 Å. The limited quality of the resulting dataset and lack of data allowed however to establish the major features of the crystal structure, but did not allow its proper refinement. The compound is not isostructural to 2d probably because of the differences in a solvate portion.

Table S5. Preliminary data for X-ray diffraction experiment for 2c

| Empirical formula | C₁₁₄H₁₇₄Cl₇₄Cu₇₄O₁₂P₂₄Ta₆ · n C₇H₈ · m CH₃CN |
|-------------------|-----------------------------------------------|
| Measurement device type | STOE IPDS 2 |
| Wavelength | synchrotron (\(\lambda = 0.80000\) Å) |
| Temperature | 100 K |
| Crystal system | monoclinic |
| Space group | \(P2₁/n\) |
| Unit cell dimensions | \(a = 18.358(4)\) Å |
| | \(b = 18.145(4)\) Å |
| | \(c = 29.282(6)\) Å |
| | \(\beta = 107.31(3)°\) |
| | \(V = 9312(4)\) \(\text{Å}^3\) |
| Formula units per unit cell | 2 |
| Crystal size [mm] | \(0.05 \times 0.05 \times 0.02\) |
| \(R_{\text{int}}\) | 0.1162 |

The scaffold of the supramolecule 2c is constituted similarly to 2b and 2d. The CuCl vacancy in the inorganic core is also proved, and the disorder revealing CuCl group pointing inside the inner cavity of the supramolecule is confirmed in analogy to the crystal structures of 2b and 2d. Nevertheless, the weight of two copper positions that was localized in the cavity do not suffice to compensate the occupancy of the central Cl atom. Therefore, charge balance cannot be achieved for this structure. The \((\text{CuCl})_{7.4}\) composition was determined according to the chloride content solely can be criticized. Three positions of a toluene and one position of a MeCN solvate molecules were also localized. The resulting quality factors are \(R_1 = 0.0780, wR_2 = 0.2274, \text{GooF} = 1.049\) that is high for low-resolution dataset. The largest difference peak and hole are 2.17 and -1.64 \(\text{e}\cdot\text{Å}^{-3}\), while r.m.s. of the electron density is very high (0.29 \(\text{e}\cdot\text{Å}^{-3}\)) and does not allow to recognize the missing low-occupied positions of Cu and solvent molecules. Even if 150 peaks of electron density are constructed in the difference Fourier map. For this reason the refinement of 2c crystal structure cannot be accomplished. For the same reason the bond distances and other details are not further discussed.
Figure S6. The supramolecule 2c: (a) the independent part (ellipsoids of 50% probability). The occupancies of partly occupied Cu and Cl atoms are depicted; (b) ball-and-stick representation.
2.5 Crystal structure of 2d

Compound \([(\text{Cp''Ta(CO)}_2\text{P}_4\text{Br})_{2.6}\text{CuBr}_{0.1}]\cdot3\text{C}_6\text{H}_6\) (2d) crystallizes as orange blocks from benzene/MeCN mixtures. The asymmetric unit (Fig. S7) contains half a molecule of 2d and two benzene solvent molecules. The terminal bromide group, tBu groups of the Cp'' ligands, one entire Cp'' groups, and one benzene molecule are disordered over two positions.

The inorganic scaffold of 2d contains partly occupied Cu and Br positions, \((\text{Cu(2v)}, \text{Br(2a)}+\text{Br(2b)})\) with occupancies 0.8; \((\text{Cu(1i)}, \text{Br(1i)})\) with occupancies 0.1. They always have complimentary occupancies, so that the CuBr unit is present or absent as a whole. These partial occupancies give rise to a disorder in the inorganic core similar to those in 2b. The disorder can be only interpreted as a number of co-crystallizing supramolecules of similar but different inorganic scaffolds. Some of the isomers are depicted in Fig. S8.

![Figure S7](image_url)

**Figure S7.** The independent part of supramolecule 2d: (a) the disorder and (b) the enumeration scheme (cf. Table S6).
| Bond                        | Distance (Å) | Symmetry Code(s) |
|-----------------------------|--------------|------------------|
| Br1—Cu2I                    | 2.26 (6)     |                  |
| Br1—Cu2I′                   | 2.26 (6)     |                  |
| Br1—Cu1I                    | 2.33 (4)     |                  |
| Br1—Cu1I′                   | 2.33 (4)     |                  |
| Cu1I—P1                     | 2.23 (4)     |                  |
| Cu1I—P6                     | 2.31 (4)     |                  |
| Cu1I—P5                     | 2.33 (5)     |                  |
| Cu1I—P2                     | 2.42 (5)     |                  |
| Cu1I—Cu1                    | 2.81 (4)     |                  |
| Cu1I—Cu2V                   | 2.83 (4)     |                  |
| Cu2I—P9                     | 2.21 (6)     |                  |
| Cu2I—P12                    | 2.33 (6)     |                  |
| Cu2I—P7                     | 2.36 (7)     |                  |
| Cu2I—P6                     | 2.41 (7)     |                  |
| Cu2I—Cu2V                   | 2.77 (6)     |                  |
| Cu2I—Cu4                    | 2.26 (5)     |                  |
| Cu2V—Cu2V                   | 2.338 (7)    |                  |
| Cu2V—P9                     | 2.307 (3)    |                  |
| Cu2V—P2                     | 2.325 (2)    |                  |
| Cu2V—P6                     | 2.326 (3)    |                  |
| Cu1—P1                      | 2.314 (2)    |                  |
| Cu1—P11′                    | 2.316 (2)    |                  |
| Cu1—P5                      | 2.326 (2)    |                  |
| Cu3—P8′                     | 2.301 (3)    |                  |
| Cu3—P10                     | 2.319 (2)    |                  |
| Cu3—P3                      | 2.322 (2)    |                  |
| Cu4—P12                     | 2.298 (2)    |                  |
| Cu4—P7                      | 2.306 (2)    |                  |
| Cu4—P4′                     | 2.312 (2)    |                  |
| Cu1—Br1                     | 2.3406 (15)  |                  |

Symmetry code(s): (i) -x+1, -y, -z.
**Figure S8.** Some supramolecules co-crystallizing in 2d possessing similar but different inorganic scaffolds.
2.6 A comparison of the supramolecules in 2b and 2d

**Figure S9.** Steric hindrance of Cp‴ ligand at 1b when coordinating CuX to form supramolecule 2. View along the threefold axis of the major isomer in 2b and 2d. The disordered tBu groups (in 0.6/0.4 ratio), which positions cause isomerism are marked in yellow.

**Figure S10.** The geometry of the disordered fragments in (left) 2b and (right) 2d.
2.7  **Crystal structure of 3**

Compound 3 crystallizes as orange blocks from toluene/MeCN mixtures. The solvent molecules occupy the vacancy between the clusters 3 and are strongly positionally disordered. The inorganic scaffold of 3 contains no vacant or disordered positions (Fig. S11). The solvent toluene and MeCN molecule occupy their positions with low probability. To refine them, a number of restraints was applied.

![Image](image1)

**Figure S11.** (a) The supramolecule in 3 (a.d.p. ellipsoids at 50% probability). Hydrogen atoms are not shown for clarity. (b) The μ-I ions blocking the cavity in the scaffold of the supramolecule 3 are shown as van der Waals spheres. (c) allotwinning in 3 described in the structural model a s second component of the inorganic core, which refined portion is about 14%.
Figure S12. (a,b) The enumeration scheme in the inorganic scaffold of the supramolecule 4a (independent part is shown of the scaffold only).
Table S7. Selected geometric parameters (Å, °) for 3 and enumerating scheme.

|         | Major part | Minor part* | Major part | Minor part* |
|---------|------------|-------------|------------|-------------|
| Cu1—I1  | 2.532 (2)  | 2.51 (2)    | Ta1—P12   | 2.605 (3)   | 2.619 (18) |
| Cu2—I2  | 2.540 (2)  | 2.53 (3)    | Ta1—P11   | 2.631 (4)   | 2.61 (3)   |
| Cu3—I3  | 2.519 (3)  | 2.558 (17)  | Ta1—P13   | 2.638 (4)   | 2.68 (2)   |
| Cu4—I4  | 2.532 (2)  | 2.514 (17)  | Ta1—P14   | 2.696 (4)   | 2.70 (3)   |
| Cu5—I5  | 2.515 (2)  | 2.490 (17)  | Ta2—P23   | 2.590 (4)   | 2.60 (3)   |
| Cu5—I6  | 2.704 (2)  | 2.731 (16)  | Ta2—P24   | 2.634 (5)   | 2.66 (4)   |
| Cu6—I6  | 2.682 (2)  | 2.71 (2)    | Ta2—P21   | 2.656 (4)   | 2.60 (2)   |
| Cu6—I7  | 2.596 (2)  | 2.698 (17)  | Ta2—P22   | 2.683 (4)   | 2.62 (3)   |
| Cu7—I7  | 2.600 (3)  | 2.592 (17)  | Ta3—P31   | 2.599 (4)   | 2.63 (3)   |
| Cu7—I6  | 2.675 (3)  | 2.61 (2)    | Ta3—P33   | 2.639 (4)   | 2.71 (2)   |
| Cu1—I41 | 2.286 (4)  | 2.30 (3)    | Ta3—P34   | 2.654 (5)   | 2.58 (3)   |
| Cu1—I21 | 2.307 (4)  | 2.30 (3)    | Ta3—P32   | 2.674 (4)   | 2.71 (3)   |
| Cu1—I11 | 2.310 (4)  | 2.32 (3)    | Ta4—P41   | 2.590 (4)   | 2.55 (3)   |
| Cu2—I44 | 2.335 (4)  | 2.18 (4)    | Ta4—P43   | 2.657 (4)   | 2.67 (3)   |
| Cu2—I52 | 2.367 (5)  | 2.60 (4)    | Ta4—P44   | 2.667 (4)   | 2.66 (2)   |
| Cu2—I14 | 2.373 (4)  | 2.38 (5)    | Ta4—P42   | 2.672 (4)   | 2.72 (3)   |
| Cu3—I51 | 2.279 (4)  | 2.27 (3)    | Ta5—P51   | 2.596 (4)   | 2.59 (3)   |
| Cu3—I33 | 2.308 (4)  | 2.28 (3)    | Ta5—P53   | 2.669 (4)   | 2.63 (3)   |
| Cu3—I13 | 2.309 (5)  | 2.30 (2)    | Ta5—P54   | 2.673 (4)   | 2.68 (3)   |
| Cu4—I12 | 2.301 (4)  | 2.28 (2)    | Ta5—P52   | 2.681 (4)   | 2.65 (3)   |
| Cu4—I34 | 2.339 (5)  | 2.45 (3)    | P11—P12   | 2.140 (5)   | 2.12 (3)   |
| Cu4—I24 | 2.347 (5)  | 2.28 (5)    | P11—P14   | 2.157 (6)   | 2.21 (4)   |
| Cu5—I31 | 2.278 (4)  | 2.25 (3)    | P12—P13   | 2.144 (6)   | 2.18 (3)   |
| Cu5—I23 | 2.283 (4)  | 2.26 (3)    | P13—P14   | 2.190 (6)   | 2.11 (4)   |
| Cu6—I34 | 2.251 (4)  | 2.30 (4)    | P21—P24   | 2.165 (6)   | 2.19 (5)   |
| Cu6—I22 | 2.444 (4)  | 2.46 (3)    | P21—P22   | 2.191 (5)   | 2.12 (3)   |
| Cu7—I53 | 2.255 (4)  | 2.28 (3)    | P22—P23   | 2.167 (6)   | 2.17 (3)   |
| Cu7—I32 | 2.433 (5)  | 2.43 (3)    | P23—P24   | 2.138 (5)   | 2.23 (5)   |
| P53—Cu7 | 2.255 (4)  | 2.28 (3)    | P31—P32   | 2.149 (6)   | 2.20 (3)   |
|         |             |             | P31—P34   | 2.155 (5)   | 2.17 (4)   |
| C11C—O11C | 1.135 (17) | -           | P32—P33   | 2.163 (5)   | 2.24 (3)   |
| C12C—O12C | 1.100 (17) | -           | P33—P34   | 2.167 (6)   | 2.15 (4)   |
| C21C—O21C | 1.134 (17) | -           | P41—P44   | 2.150 (5)   | 2.16 (4)   |
| C22C—O22C | 1.098 (15) | -           | P41—P42   | 2.154 (5)   | 2.12 (4)   |
| C31C—O31C | 1.123 (16) | -           | P42—P43   | 2.164 (6)   | 2.15 (5)   |
| C32C—O32C | 1.153 (18) | -           | P43—P44   | 2.169 (5)   | 2.21 (3)   |
| C41C—O41C | 1.081 (16) | -           | P51—P52   | 2.144 (6)   | 2.22 (4)   |
| C42C—O42C | 1.159 (15) | -           | P51—P54   | 2.159 (5)   | 2.18 (4)   |
| C51C—O51C | 1.147 (17) | -           | P52—P53   | 2.183 (5)   | 2.07 (3)   |
| C52C—O52C | 1.142 (15) | -           | P53—P54   | 2.174 (6)   | 2.19 (4)   |

* the second position of the disordered inorganic scaffold has the same atom names with a suffix A.
Topological interrelation between inorganic scaffolds of the supramolecules 2 and 3

The supramolecules 2 and 3 contain similar fragments with topology of a truncated octahedron also known as non-classical fullerene topology.

**Supramolecule 2d**

![Supramolecule 2d](image)

**Supramolecule 3**

![Supramolecule 3](image)

**Figure S13.** The interrelation of the fragments with non-classical fullerene-like topology (a and c, yellow highlighted) in supramolecules 2 and 3. (b) The fragment \((\text{cyclo-P}_4)(\text{CuX})_4\) to be removed from 2d structure of fullerene-like topology to afford construction of supramolecule 3. (d) The fragment CuI3 that in combination with fragment (c) gives the nanocapsule 3.
2.9 Crystal structures and isomerism in compound 4

Compound 4 crystallizes as yellow blocks from toluene/MeCN mixtures as two crystalline phases. In 4a the asymmetric unit contains one supramolecule in general position next to five and four positions of toluene and acetonitrile solvent molecules, respectively. In 4b the asymmetric unit also contains one supramolecule in general position and another portion of the same solvent molecules. In both cases the inorganic scaffold of 4 contains no vacant positions (Fig. S12). Essential that in 4a and 4b the inorganic scaffold is isomeric. The isomerism between these scaffolds is traced back to only two different positions occupied either by iodide or MeCN molecule (Fig. S14).

Figure S14. (a) The supramolecule 4a (a.d.p. ellipsoids at 50% probability). Hydrogen atoms are not shown for clarity. (b, c) \{Cu$_4$I$_5$\} capping fragment in the scaffold (d). The \(\mu_4\)-I ion belonging to the \{Cu$_4$I$_5$\}⁻ unit and occupying the cavity is shown in van der Waals spheres.
Figure S15. (a,b) The enumeration scheme in the inorganic scaffold of the supramolecule 4a. Carbon and hydrogen atoms are not shown. Structurally isomeric supramolecules 4a (b) and 4b (c). Atom I(3) coordinated to Cu(5) in 4b (not to Cu(3) as in 4a) is highlighted in orange.
Table S8. Bond lengths in the inorganic scaffold (Å, °) for 4a and 4b. The enumeration scheme is the same except for the isomeric part (orange highlight).

|      | 4a     | 4b     | 4a     | 4b     |
|------|--------|--------|--------|--------|
| Ta1—P1 | 2.6414 (19) | 2.661 (3) | Cu6—I5 | 2.6651 (13) | 2.6330 (17) |
| Ta1—P2 | 2.6289 (19) | 2.639 (3) | Cu6—I6 | 2.5593 (13) | 2.5433 (17) |
| Ta1—P3 | 2.6480 (19) | 2.633 (3) | Cu7—I7 | 2.6443 (13) | 2.6379 (19) |
| Ta1—P4 | 2.6677 (19) | 2.640 (3) | Cu8—I7 | 2.6290 (13) | 2.641 (2) |
| Ta2—P5 | 2.668 (2) | 2.653 (4) | Cu9—I8 | 2.8066 (15) | 2.758 (2) |
| Ta2—P6 | 2.612 (2) | 2.623 (3) | Cu9—I9 | 2.6089 (15) | 2.597 (2) |
| Ta2—P7 | 2.620 (2) | 2.609 (3) | Cu9—I12 | 2.5643 (14) | 2.553 (2) |
| Ta2—P8 | 2.644 (2) | 2.632 (4) | Cu10—I8 | 2.7253 (14) | 2.781 (2) |
| Ta3—P9 | 2.654 (2) | 2.656 (3) | Cu10—I9 | 2.5917 (14) | 2.602 (2) |
| Ta3—P10 | 2.637 (2) | 2.635 (3) | Cu10—I10 | 2.5676 (13) | 2.57 (2) |
| Ta3—P11 | 2.641 (2) | 2.632 (3) | Cu11—I8 | 2.7780 (14) | 2.754 (2) |
| Ta4—P12 | 2.616 (2) | 2.619 (3) | Cu11—I10 | 2.5722 (13) | 2.556 (2) |
| Ta4—P13 | 2.643 (2) | 2.663 (3) | Cu11—I11 | 2.6047 (13) | 2.6083 (19) |
| Ta4—P14 | 2.627 (2) | 2.607 (3) | Cu12—I8 | 2.7551 (14) | 2.7754 (19) |
| Ta4—P15 | 2.632 (2) | 2.638 (3) | Cu12—I11 | 2.6065 (14) | 2.6151 (19) |
| Ta5—P16 | 2.644 (2) | 2.648 (3) | Cu12—I12 | 2.5664 (14) | 2.5689 (19) |
| Ta5—P17 | 2.629 (2) | 2.657 (3) | P1—I4 | 2.159 (3) | 2.156 (4) |
| Ta5—P18 | 2.637 (2) | 2.628 (3) | P1—I2 | 2.161 (3) | 2.161 (4) |
| Ta5—P19 | 2.647 (2) | 2.626 (3) | P2—I3 | 2.151 (3) | 2.152 (4) |
| Ta5—P20 | 2.629 (2) | 2.618 (3) | P3—I4 | 2.162 (3) | 2.147 (4) |
| Cu1—P1 | 2.284 (2) | 2.284 (3) | P5—I6 | 2.129 (3) | 2.128 (4) |
| Cu1—P5 | 2.296 (2) | 2.286 (4) | P5—I8 | 2.142 (3) | 2.145 (5) |
| Cu2—P12 | 2.268 (2) | 2.287 (3) | P6—I7 | 2.160 (3) | 2.160 (5) |
| Cu2—P6 | 2.302 (2) | 2.283 (4) | P7—I8 | 2.148 (3) | 2.158 (5) |
| Cu3—P2 | 2.299 (2) | 2.284 (3) | P9—I10 | 2.148 (3) | 2.140 (4) |
| Cu3—P9 | 2.303 (2) | 2.300 (3) | P9—I12 | 2.149 (3) | 2.132 (4) |
| Cu4—P10 | 2.239 (2) | 2.274 (3) | P10—I11 | 2.158 (3) | 2.153 (4) |
| Cu4—P16 | 2.257 (2) | 2.254 (3) | P11—I12 | 2.159 (3) | 2.161 (4) |
| Cu5—P3 | 2.266 (2) | 2.310 (3) | P13—I14 | 2.138 (3) | 2.141 (4) |
| Cu5—P13 | 2.285 (2) | 2.339 (3) | P13—I16 | 2.142 (3) | 2.166 (4) |
| Cu6—P14 | 2.298 (2) | 2.281 (3) | P14—I15 | 2.162 (3) | 2.148 (4) |
| Cu6—P20 | 2.292 (2) | 2.289 (3) | P15—I16 | 2.160 (3) | 2.155 (4) |
| Cu7—P4 | 2.297 (2) | 2.302 (3) | P17—I20 | 2.145 (3) | 2.135 (4) |
| Cu7—P17 | 2.261 (2) | 2.310 (3) | P17—I18 | 2.146 (3) | 2.146 (4) |
| Cu8—P8 | 2.253 (2) | 2.239 (4) | P18—I19 | 2.168 (3) | 2.151 (4) |
| Cu8—P18 | 2.262 (2) | 2.259 (4) | P19—I20 | 2.157 (3) | 2.159 (4) |
| Cu9—P19 | 2.306 (2) | 2.299 (3) | C11C—I11 | 1.144 (10) | 1.144 (15) |
| Cu10—P7 | 2.293 (2) | 2.304 (4) | C12C—I12 | 1.151 (11) | 1.128 (15) |
| Cu11—P11 | 2.301 (2) | 2.313 (3) | C21C—I21 | 1.132 (12) | 1.13 (2) |
| Cu12—P15 | 2.309 (2) | 2.288 (3) | C22C—I22 | 1.169 (12) | 1.132 (16) |
|                  | Cu1—I1         | Cu2—I1         | Cu2—I2         | Cu3—I3*        | Cu3—I4         | Cu4—I4         | Cu5—I5         |
|------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
|                  | 2.6033 (13)    | 2.629 (2)      | 2.649 (2)      | 2.5390 (13)    | 2.6873 (13)    | 2.6144 (12)   | 2.6209 (13)    |
|                  | 2.629 (2)      | 2.649 (2)      | 2.573 (6)      | 2.5553 (18)    | 2.635 (2)      | 2.5964 (18)   | 2.6612 (18)    |
|                  | C31C—O31       | C32C—O32       | C41C—O41       | C42C—O42       | C51C—O51       | C52C—O52       |                |
|                  | 1.152 (11)     | 1.131 (10)     | 1.165 (11)     | 1.146 (11)     | 1.130 (11)     | 1.117 (11)     |                |
|                  |                |                |                | 1.116 (16)     |                |                |                |
|                  |                |                |                | (for Cu3—I5)   |                |                |                |
|                  |                |                |                |                |                |                |                |
|                  |                |                |                |                |                |                |                |

* The difference between structural isomers in 4a and 4b.

2.10 Crystal structure of 5

Compound 5 crystallizes as yellow plates from toluene/CH$_2$CN/Et$_2$O mixtures. The asymmetric unit contains one unit of 1b bound to a Cu$_4$I$_4$ unit and an acetonitrile solvent molecule.

![Diagram](image1)

**Figure S16.** The enumeration scheme (up left) and the structure of a layer (up right) in 5. The side view of the layer (bottom).
### Table S9. Selected geometric parameters (Å, °) for 5

|       | Distance (Å) |       | Distance (Å) |
|-------|--------------|-------|--------------|
| Ta1—P2 | 2.639 (2)    | Cu4—P4<sup>iii</sup> | 2.260 (3)    |
| Ta1—P3 | 2.641 (2)    | P4—Cu4<sup>iii</sup> | 2.260 (3)    |
| Ta1—P4 | 2.644 (2)    | Cu2—I1       | 2.6273 (14)  |
| Ta1—P1 | 2.665 (2)    | Cu2—I4       | 2.6439 (17)  |
| Cu1—P1 | 2.254 (3)    | Cu2—I2       | 2.7130 (14)  |
| Cu1—I1 | 2.6373 (17)  | Cu3—I3       | 2.6289 (17)  |
| Cu1—I4 | 2.6470 (15)  | Cu3—I2       | 2.6340 (14)  |
| Cu1—I3 | 2.7169 (15)  | Cu3—I1       | 2.7106 (14)  |
| Cu1—Cu2| 2.837 (2)    | Cu4—I2       | 2.6279 (16)  |
| Cu1—Cu4| 2.8666 (18)  | Cu4—I3       | 2.6425 (15)  |
| Cu2—Cu3| 2.926 (2)    | Cu4—I4       | 2.6963 (15)  |
| Cu2—Cu4| 2.814 (2)    | P1—P4        | 2.153 (4)    |
| Cu2—Cu3| 2.858 (2)    | P1—P2        | 2.157 (3)    |
| Cu3—Cu4| 2.927 (2)    | P2—P3        | 2.146 (4)    |
| P2—Cu2<sup>iv</sup>| 2.261 (3) | P3—P4        | 2.145 (3)    |
| P3—Cu3<sup>v</sup>| 2.277 (3) | O1—C1        | 1.129 (11)   |
| Cu2—P2<sup>i</sup>| 2.261 (3) | O2—C2        | 1.129 (14)   |
| Cu3—P3<sup>iii</sup>| 2.278 (3) |

|       | Angle (°)    |       | Angle (°)    |
|-------|--------------|-------|--------------|
| I1—I4—Cu1 | 108.38 (6) | Cu2—I1—I3—Cu3 | 64.73 (4) |
| I1—I4—Cu1 | 109.42 (5) | I1—I1—Cu3—Cu4 | 66.31 (5) |
| I1—I4—Cu1 | 110.96 (5) | Cu4—I2—Cu3 | 67.58 (5) |
| I1—I4—Cu1 | 111.50 (5) | Cu4—I2—Cu2 | 63.56 (5) |
| I1—I4—Cu1 | 108.59 (5) | Cu3—I2—Cu2 | 64.61 (4) |
| I4—I4—Cu1 | 111.61 (5) | Cu3—I3—Cu4 | 67.45 (5) |
| I3—I4—Cu1 | 106.03 (5) | Cu3—I3—Cu1 | 66.34 (5) |
| I2—I4—Cu1 | 105.81 (5) | Cu4—I3—Cu1 | 64.65 (4) |
| I3—I4—Cu1 | 111.55 (5) | Cu1—I4—Cu2 | 64.94 (5) |
| P4—I4—P1 | 90.93 (12) | Cu1—I4—Cu4 | 64.97 (4) |
| P3—I4—P1 | 88.70 (12) | Cu2—I4—Cu4 | 63.58 (5) |
| P4—I4—P1 | 91.47 (13) |                 |             |
| P3—I4—P1 | 88.82 (12) |                 |             |

Symmetry code(s): (i) x, -y+1/2, z+1/2; (ii) -x+1, y+1/2, -z+1/2; (iii) -x+1, -y, -z+1; (iv) x, -y+1/2, z-1/2; (v) x+1, y-1/2, -z+1/2.
3. Size Estimation from DOSY Experiments

3.1 Spectroscopic Details

The DOSY spectra were recorded on an Avance III HD 600 (600.25 MHz) spectrometer equipped with a z gradient (53.5 Gauss/cm), 5 mm TCI cryo probe and BVT 3000 unit at 298 K. The NMR data was processed with the Bruker program TopSpin® 3.2 and the diffusion coefficient was calculated with the Bruker software T1/T2 relaxation package. For the calibration of the 1H chemical shifts and for the temperature- and viscosity-correction of the diffusion coefficients, TMS (tetramethylsilane) was added. The 1H-diffusion measurement was performed with the convection suppressing DSTE (double stimulated echo) pulse sequence, developed by Mueller and Jerschow\(^9a\) in a pseudo 2D mode. 120 dummy scans and 16 scans were used with a relaxation delay of 2 s. Sinusoidal shapes were used for the gradient and a linear gradient ramp with 20 or 5 increments between 5 and 95 % of the maximum gradient strength was applied for the diffusion relevant gradients. For the homospoil gradients, -13.7, 20 and 17.13 G cm\(^{-1}\) were applied. The length of the gradient pulse \(\delta\) was adjusted for every species in the sample to achieve appropriate signal attenuation curves, giving values for \(\delta\) of 2.0 ms for TMS and 3.4 or 3.6 ms for the supramolecules. A diffusion time \(\Delta\) of 45 ms was used.

3.2 Size Estimation

From crystallographic data the diameter of the two clusters were estimated to be \(d = 25.0\) Å (2c), 25.4 Å (2d) from the maximum H-H distance plus twice the Van-der-Waals radius of a proton. From diffusion-ordered spectroscopy (DOSY) experiments\(^9b-c\) the translational self-diffusion coefficient \(D\) of molecules in solution can be calculated according to the Stejskal-Tanner equation.\(^9\) With the diffusion coefficients \(D\) of the analyte and of TMS (acting as viscosity reference), the hydrodynamic radius \(r_H\) of the analyte can be estimated following the Stokes-Einstein equation\(^10\) to be \(r_H = 10.73\) Å (2c), 9.45 Å (2d). These are in good agreement with the crystal-derived radii of 12.5 Å (2c) and 12.7 Å (2d) in the solid state. Therefore, these results indicate the presence of the intact spherical supramolecules in solution. For the reaction of \(\{\text{Cp}^+\text{Ta(CO)}_2(\mu_5-\eta^4:\eta^1:\eta^1:\eta^1:\eta^1-\text{P}_4)\}\) with 2 eq. CuI a hydrodynamic radius of the species in solutions of \(r_H = 7.32\) Å could be derived from the DOSY experiment, which is smaller than those obtained in the case of the CuCl and CuBr constructed spheres.
4. Additional Figures

Figure S17. Polyhedra built by Ta (green), Cu (blue) and P (pink) in a) 2a-d; b) 3; c) 4.

References

[1] O. J. Scherer, R. Winter, G. Wolmershäuser, Z. Anorg. Allg. Chem. 1993, 619, 827-835.
[2] O. J. Scherer, T. Brück, Angew. Chem. 1987, 99, 59-59.
[3] J. Bai, A. V. Virovets, M. Scheer, Angew. Chem., Int. Ed. 2002, 41, 1737-1740.
[4] L. Palatinus, G. Chapuis J. Appl. Cryst. 2007, 40, 786-790.
[5] G. Scheldrick, Acta Cryst. ser. A., 2008, 64, 112-122.
[6] 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.
[7] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. Appl. Cryst. 2009, 42, 339-341.
[8] V. A. Blatov, A. P. Shevchenko, D. M. Proserpio. Cryst. Growth Des. 2014, 14, 3576–3586.
[9] a) A. Jerschow, N. Müller, J. Magn. Reson. 1997, 125, 372-375. b) C. S. Johnson, Prog. Nucl. Magn. Reson. Spectrosc. 1999, 34, 203-256; c) W. S. Price, Concepts Magn. Reson. 1998, 10, 197-237; d) E. O. Stejskal, J. E. Tanner, The Journal of Chemical Physics 1965, 42, 288-292.
[10] A. Macchioni, G. Ciancaleoni, C. Zuccaccia, D. Zuccaccia, Chem. Soc. Rev. 2008, 37, 479-489.