Supplementary Material

Supramolecular Assemblies of Polyphosphorus Ligands based on weak Tl–P and In–P Interactions

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Content

1 General information

All experiments were performed under an atmosphere of dry argon or nitrogen using standard Schlenk and drybox techniques. Commercially available reagents were used as received without further purification. Solvents were freshly distilled under nitrogen from CaH_2 (CH_2Cl_2, CD_2Cl_2), or Na/K-alloy (*n*-pentane). Solution NMR spectra were recorded on a Bruker Avance 400 spectrometer (^{1}H: 400.130 MHz, ^{31}P: 161.976 MHz, ^{13}C: 100.613 MHz). The chemical shifts δ are presented in parts per million ppm and coupling constants J in Hz. The following samples were used for external reference: TMS (^{1}H, ^{13}C), $CFCl_3$ (^{19}F), H_3PO_4 85 % (^{31}P). $^{31}P\{^1H\}$ MAS NMR spectra were recorded on a Bruker Avance 300 (^{31}P: 121.495 MHz, 13C: 75.468 MHz). The chemical shifts of the MAS NMR spectra are also presented in the δ scale using NaH_2PO_4 as an external standard. ESI-MS spectra were measured on a Finnigan Thermoquest TSQ 7000 mass-spectrometer. IR spectra were recorded on a VARIAN FTS-800 FT-IR spectrometer in CH_2Cl_2 solution or the solid substances were grinded together with dried KBr and pressed to pellets. All compounds involving the *cyclo*-P_3 complexes **B1** and **B2** cannot be grinded with KBr for very long since this changes the IR stretching frequencies of the CO ligands. We assume decomposition, but were unable to further analyze the outcome. VPO measurements were performed in CH_2Cl_2 on a Knauer K-7000 vapour pressure osmometer. The system was left for two hours the reach the equilibrium. The melting points were determined under an Argon atmosphere using a Büchi B-545 melting point apparatus. The synthesis and X-ray structures of the compounds **1**(CCDC-658370), **3** (CCDC-773847) and **4a** (CCDC-773849) were described earlier. [1, 2] The starting materials Tl[TEF],[3] In[TEF],[2] $[Cp_2Mo_2(CO)_4(\mu,\eta^2:\eta^2\text{-}P_2)]$ (**A1**) [4] $[Cp^*_2Mo_2(CO)_4(\mu,\eta^2:\eta^2\text{-}P_2)]$ (**A2**) [5] $[CpCr(CO)_2(\eta^3\text{-}P_3)]$ (**B1**) [6] and $[CpMo(CO)_2(\eta^3\text{-}P_3)]$ (**B2**) [4] were prepared according to the literature procedure.

2 Syntheses of described coordination compounds

2.1 Synthesis of $[Tl_2(A2)_4][TEF]_2$ (2)

23 mg (0.02 mmol, 1eq.) Tl[TEF] and 25 mg $[Cp^*_2Mo_2(CO)_4(\mu,\eta^2:\eta^2\text{-}P_2)]$ (**A2**, 0.04 mmol, 2eq.) are dissolved in 5 mL CH_2Cl_2 and stirred for 3 h at room temperature. The dark red solution is carefully layered below *n*-pentane (40 mL) by a teflon capillary. Compound **2** is obtained as dark red crystals in the course of two weeks. These are filtered off, washed with *n*-pentane (3 × 2 mL) and dried in vacuum.

Yield	34 mg (70 %)
^{1}H-NMR (CD_2Cl_2)	δ/ppm = 2.03 (s, Cp*)
$^{13}C\{^1H\}$-NMR (CD_2Cl_2)	δ/ppm = 11.6 (s; $C_5(\underline{C}H3)_5$), 77.7 (br m; $\underline{C}(CF_3)_3$), 103.0 (s; $\underline{C}_5(CH_3)_5$), 121.6 (q, $^1J_{F,C}$ = 292.5 Hz; CF_3), 231.6 (s; CO)
$^{19}F\{^1H\}$-NMR (CD_2Cl_2)	δ/ppm = −75.6 (s; CF_3)
$^{31}P\{^1H\}$-NMR (CD_2Cl_2)	δ/ppm = −33.9 (s)
ESI-MS (CH_2Cl_2)	cations: m/z (%) = 841.1 (13) $[Tl\{Cp^*_2Mo_2(CO)_4P_2\}]^+$, 637.0 (48) $[Cp^*_2Mo_2(CO)_4P_2H]^+$, 205.0 (100) $[Tl]^+$; anions: 967.0 (100) $[Al\{OC(CF_3)_3\}_4]^-$.

IR (KBr)	$\tilde{\nu}$/cm^{-1} = 2988 (w sh), 2964 (w), 2919 (w), 2853 (w), 2030 (w sh), 2017 (m sh), 2017 (m), 1991 (m), 1920 (s), 1852 (m), 1829 (m), 1479 (w), 1456 (vw), 1383 (m), 1353 (m), 1301 (s), 1278 (s), 1242 (s), 1220 (vs), 1165 (m), 1134 (vw), 1072 (vw), 1027 (w), 975 (vs), 829 (w), 728 (s), 571 (vw), 558 (vw), 538 (w), 525 (vw), 512 (vw), 466 (vw), 450 (m), 422 (vw)
IR (CH_2Cl_2)	$\tilde{\nu}$/cm^{-1} = 2985 (w), 2966 (w), 2914 (w), 2867 (w), 2024 (m), 1995 (s), 1978 (s), 1911 (s), 1853 (m), 1477 (w), 1458 (vw), 1426 (m), 1382 (m), 1352 (m), 1300 (s), 1274 (vs), 1242 (vs), 1224 (vs), 1167 (m), 1135 (vw), 1071 (vw), 1027 (w), 976 (vs), 832 (w), 561 (vw), 537 (w), 521 (vw), 481 (vw), 449 (m), 419 (vw)
melting point	> 200 °C, decomposition ≈ 160 °C

2.2 Synthesis of $[In(B2)_3]_n[TEF]_n$ (4b)

87 mg (0.08 mmol, 1eq.) In[TEF] and 74 mg $[CpMo(CO)_2(\eta^3\text{-}P_3)]$ (**B2**, 0.24 mmol, 3eq.) are dissolved in 10 mL CH_2Cl_2 and stirred for 1 h at room temperature. The yellow solution is filtered through a G4 frit plate and the amount of solvent is reduced under reduced pressure to about 5 mL. This solution is carefully layered with *n*-pentane by a Teflon capillary. Upon diffusion compound **4b** is obtained as yellow needles in the course of five days. The product is very sensitive to air, water and temperature. The crystals are filtered off, washed with *n*-pentane (3 × 2 mL) and dried in vacuum.

Yield	88 mg (55 %)
^{1}H-NMR (CD_2Cl_2)	δ/ppm = 5.40 (s; C_5H_5)
^{13}C{^{1}H}-NMR (CD_2Cl_2)	δ/ppm = 86.9 (q; $^2J_{P,C}$ = 0.9 Hz; C_5H_5), 121.7 (q, $^1J_{F,C}$ = 292.3 Hz; CF_3), 221.0 (q; $^2J_{P,C}$ = 2.4 Hz; CO)
^{31}P{^{1}H}-NMR (CD_2Cl_2)	δ/ppm = −347.5 (s)
ESI-MS (CH_2Cl_2)	cations: *m/z* (%) = 426.7 (51) $[In\{CpMo(CO)_2P_3\}]^+$, 311.8 (8) $[CpMo(CO)_2P_3H]^+$, 114.8 (100) $[In]^+$; anions: 967.0 (100) $[Al\{OC(CF_3)_3\}_4]^-$.
IR (KBr)	$\tilde{\nu}$/cm^{-1} = 3137 (w), 2966 (vw), 2919 (vw), 2851 (vw), 2026 (s), 1972 (s), 1424 (w), 1353 (m), 1303 (s), 1279 (vs), 1241 (vs), 1219 (vs), 1168 (m), 1065 (vw), 1012 (vw), 974 (vs), 830 (m), 755 (vw), 727 (s), 552 (w), 537 (w), 501 (m), 468 (m), 411 (m), 409 (w)
IR (CH_2Cl_2)	$\tilde{\nu}$/cm^{-1} = 3115 (w), 3057 (w), 2988 (w), 2907 (vw), 2004 (vs), 1945 (vs), 1394 (vw), 1352 (s), 1300 (vs), 1277 (vs), 1242 (vs), 1225 (vs), 1167 (m), 1135 (vw), 1074 (vw), 1028 (m), 1009 (w), 976 (vs), 867 (w), 825 (m), 561 (m), 537 (m), 517 (m), 481 (m), 460 (m), 447 (m), 417 (w)
Elemental analysis	calc. for $C_{37}H_{15}AlF_{36}InMo_3O_{10}P_9$ C: 22.09%, H: 0.75%; found C: 21.59%, H: 0.97%.

2.3 Synthesis of [Tl(B1)$_3$]$_n$[TEF]$_n$ (4c)

110 mg (0.09 mmol, 1eq.) Tl[TEF] and 75 mg [CpCr(CO)$_2$(η^3-P$_3$)] (**B1**, 0.28 mmol, 3eq.) are dissolved in 10 mL CH$_2$Cl$_2$ and stirred in the dark for 1 h at room temperature. The orange solution is filtered and careful layering with *n*-pentane affording compound **4c** as brown needles in the course of one day. These crystals are filtered off, washed with *n*-pentane (3 × 2 mL) and dried in vacuum. The solvent of the mother liquor is reduced to half the amount and addition of an excess of *n*-pentane precipitates another crop of compound **4c** as a light brown powder.

Yield	145 mg (78 %)
^{1}H-NMR (CD$_2$Cl$_2$, 300 K)	δ/ppm = 4.95 (s; C$_5$H$_5$).
^{1}H-NMR (CD$_2$Cl$_2$, 193 K)	δ/ppm = 4.98 (s; C$_5$H$_5$).
^{13}C{^{1}H}-NMR (CD$_2$Cl$_2$)	δ/ppm = 79.1 (br, $\underline{C}$(CF$_3$)$_3$), 86.0 (s; C$_5$H$_5$), 121.6 (q, $^1J_{F,C}$ = 298.5 Hz; CF$_3$), 233.4 (s, CO)
^{31}P{^{1}H}-NMR (CD$_2$Cl$_2$, 300 K)	δ/ppm = −287.6 (s)
^{31}P{^{1}H}-NMR (CD$_2$Cl$_2$, 193 K)	δ/ppm = −289.2 (s, br)
^{19}F{^{1}H}-NMR (CD$_2$Cl$_2$)	δ/ppm = −75.6 (s; CF$_3$)
ESI-MS (CH$_2$Cl$_2$)	cations: *m/z* (%) = 470.9 (3) [Tl{CpCr(CO)$_2$P$_3$}]$^+$, 205.1 (100) [Tl]$^+$; anions: 967.0 (100) [Al{OC(CF$_3$)$_3$}$_4$]$^-$.
IR (KBr)	$\tilde{\nu}$/cm^{-1} = 2964 (vw), 2925 (vw), 2851 (vw), 1979 (s), 1927 (s), 1626 (w), 1426 (vw), 1353 (m), 1303 (s), 1277 (s), 1245 (s), 1222 (s), 1170 (w), 974 (s), 821 (w), 728 (s), 607 (vw), 595 (vw), 569 (w), 537 (w), 494 (vw), 448 (w), 419 (w)
IR (CH$_2$Cl$_2$)	$\tilde{\nu}$/cm^{-1} = 3115 (vw), 3065 (vw), 2965 (vw), 1990 (s), 1937 (s), 1425 (vw), 1352 (m), 1301 (s), 1278 (s), 1241 (vs), 1224 (vs), 1168 (m), 1092 (w), 1013 (w), 967 (vs), 820 (w), 763 (m), 608 (vw), 570 (m), 537 (m), 494 (vw), 446 (w)
Elemental analysis	calc. for C$_{37}$H$_{15}$AlCr$_3$F$_{36}$O$_{10}$P$_9$Tl C: 22.56%, H: 0.77%; found C: 22.26%, H: 0.99%.
melting point	decomposition ≈ 155 °C

2.4 Synthesis of [Tl(B2)$_3$]$_n$[TEF]$_n$ (4d)

94 mg (0.08 mmol, 1eq.) Tl[TEF] and 74 mg [CpMo(CO)$_2$(η^3-P$_3$)] (**B2**, 0.024 mmol, 3eq.) are dissolved in 15 mL CH$_2$Cl$_2$ and stirred for 3 h at room temperature. The yellow solution is filtered and the amount of solvent is reduced under reduced pressure to about 5 mL. The yellow product can be obtained as precipitate by fast addition of about 30 mL of *n*-pentane to the solution. The yellow powder is washed with *n*-pentane (3 × 2 mL) and dried in vacuum (waterbath 40 °C).

Yield	149 mg (89 %)
^{1}H-NMR (CD$_2$Cl$_2$)	δ/ppm = 5.35 (s; C$_5$H$_5$).
^{13}C{^{1}H}-NMR (CD$_2$Cl$_2$)	δ/ppm = 86.7 (q, $^2J_{P,C}$ = 1.0 Hz; C$_5$H$_5$), 121.6 (q, $^1J_{F,C}$ = 292.0 Hz; CF$_3$), 221.6 (q, $^2J_{P,C}$ = 2.3 Hz; CO)
^{31}P{^{1}H}-NMR (CD$_2$Cl$_2$)	δ/ppm = −348.2 (s)
^{31}P{^{1}H}-MAS-NMR	δ/ppm = −344.3 (dd, $^1J_{Tl,P}$ = 984 Hz, 984 Hz)
^{19}F{^{1}H}-NMR (CD$_2$Cl$_2$)	δ/ppm = −75.6 (s; CF$_3$)

ESI-MS (CH_2Cl_2)	cations: *m/z* (%) = 514.8 (4) $[Tl\{CpMo(CO)_2P_3\}]^+$, 205.0 (100) $[Tl]^+$; anions: 967.0 (100) $[Al\{OC(CF_3)_3\}_4]^-$.
IR (KBr)	$\tilde{\nu}$/cm^{-1} = 3137 (w), 3082 (vw), 2966 (w), 2917 (vw), 2850 (vw), 2025 (s), 1989 (s), 1977 (s), 1951 (s), 1422 (w), 1353 (m), 1303 (vs), 1278 (vs), 1242 (vs), 1221 (vs), 1169 (m), 1133 (vw), 1099 (vw), 1084 (vw), 1064 (vw), 1013 (w sh), 1007 (w), 974 (vs), 862 (vw), 826 (m), 797 (w sh); 783 (vw sh), 728 (s), 713 (w sh), 578 (vw), 561 (w), 537 (w), 512 (w sh), 502 (w), 478 (vw sh), 468 (w sh), 446 (m), 415 (vw)
IR (CH_2Cl_2)	$\tilde{\nu}$/cm^{-1} = 3116 (vw), 3056 (vw), 2965 (vw), 2004 (s), 1945 (s), 1604 (vw), 1420 (w), 1352 (m), 1301 (s), 1270 (vs), 1241 (vs), 1224 (vs), 1167 (m), 1097 (w), 1009 (w), 976 (vs), 894 (vw), 824 (m), 668 (w), 562 (w), 537 (w)
Elemental analysis	calc. for $C_{37}H_{15}AlF_{36}Mo_3O_{10}P_9Tl$ C: 21.15%, H: 0.72%; found C: 21.06%, H: 1.13%.
melting point	> 200 °C, decomposition ≈ 160 °C

2.5 Synthesis of $[Tl(C)_2]_n[TEF]_n$ (5)

70 mg (0.06 mmol, 1eq.) Tl[TEF] and 74 mg $[Cp^*_2Mo_2(\mu,\eta^3{:}\eta^3\text{-}P_3)(\mu,\eta^2{:}\eta^2\text{-}PS)]$ (**C**, 0.12 mmol, 2eq.) are dissolved in 10 mL CH_2Cl_2 and stirred for 3 h at room temperature. The amount of solvent is reduced under reduced pressure to about 5 mL. The red to brown product can be obtained as microcristalline precipitate by fast addition of about 40 mL of *n*-pentane to the solution. Compound **5** always contains one CH_2Cl_2 solvent molecule per repeating unit. The obtained powder is washed with *n*-pentane (3 × 2 mL) and dried in vacuum (waterbath 40 °C). The elemental analysis shows, that the CH_2Cl_2 inside the crystal lattice is not removed.

Yield	138 mg (92 %)
^{1}H-NMR (CD_2Cl_2)	δ/ppm = 1.92 (s; Cp*)
^{13}C{^{1}H}-NMR (CD_2Cl_2)	δ/ppm = 13.7 (s; $C_5(\underline{C}H_3)_5$), 105.1 (s; $\underline{C}_5(CH_3)_5$), 121.7 (q, $^1J_{F,C}$ = 294.7 Hz; CF_3)
^{19}F{^{1}H}-NMR (CD_2Cl_2)	δ/ppm = −75.6 (s; CF_3)
^{31}P{^{1}H}-NMR (CD_2Cl_2)	δ/ppm = −357.6 (ddd, $^1J_{P,P}$ = 377 Hz, $^1J_{P,P}$ = 377 Hz, $^2J_{P,P}$ = 21 Hz; P_X), −126.7 (dd, $^1J_{P,P}$ = 65 Hz, $^2J_{P,P}$ = 20 Hz; P_M), 340.0 (d, $^1J_{P,P}$ = 378 Hz, $\omega_{½}$ = 26 Hz; P_B), 356.7 (ddd, $^1J_{P,P}$ = 377 Hz, $^1J_{P,P}$ = 65 Hz, $^2J_{P,P}$ = 8 Hz; P_A) see Figure 1

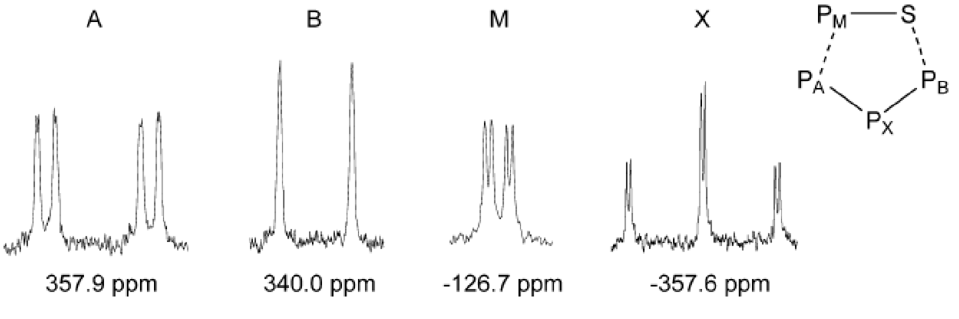

Figure 1. Excerpt of the ^{31}P{^{1}H} NMR spectrum of compound 5 in CD_2Cl_2 solution at room temperature. The chemical shifts are significantly different from the free ligand C (343.3, 320.6, –132.0 and –3.67.1 ppm)

^{31}P{^{1}H}-MAS-NMR	δ/ppm = −351.4 (br s, $\omega_{½}$ = 1746 Hz; P_X), −127.9 (br m; P_M), 350.4 (br m; P_A, P_B)
ESI-MS (CH_2Cl_2)	cations: *m/z* (%) = 1441.1 (9) $[Tl\{Cp^*_2Mo_2P_3(PS)\}_2]^+$, 822.8 (42) $[Tl\{Cp^*_2Mo_2P_3(PS)\}]^+$, 618.9 (46) $[Cp^*_2Mo_2P_3(PS)H]^+$, 205.0 (100) $[Tl]^+$; anions: 967.0 (100) $[Al\{OC(CF_3)_3\}_4]^-$.
IR (KBr)	$\tilde{\nu}$/cm^{-1} = 2970 (w), 2955 (w), 2913 (m), 2851 (w), 1541 (vw), 1481 (w), 1458 (w), 1448 (w), 1425 (w), 1377 (m), 1353 (m), 1302 (s), 1277 (vs), 1242 (vs), 1221 (vs), 1168 (m), 1134 (vw), 1074 (vw), 1026 (m), 975 (vs), 815 (m), 756 (vw), 728 (s), 669 (vw), 560 (w), 537 (w), 447 (m)
IR (CH_2Cl_2)	$\tilde{\nu}$/cm^{-1} = 2975 (w), 2960 (w), 2912 (m), 2854 (w), 1479 (w), 1462 (w), 1451 (w), 1427 (w), 1377 (m), 1352 (m), 1300 (s), 1275 (vs), 1242 (vs), 1224 (vs), 1167 (m), 1136 (vw), 1097 (vw), 1071 (vw), 1027 (m), 976 (vs), 896 (m), 832 (w), 561 (w), 537 (w), 446 (m)
Osmometric weigth determination (CH_2Cl_2)	Average molecular mass 1350 g mol^{-1} ± 80 g mol^{-1}
Elemental analysis	calc. for $C_{57}H_{62}AlCl_2F_{36}Mo_4O_4P_8S_2Tl$ C: 27.46%, H: 2.51%, S: 2.57%; found C: 27.77%, H: 2.36%, S: 2.35%.
melting point	> 200 °C, decomposition ≈ 165°C

3 X-ray structure determinations

3.1 General considerations

All crystal manipulations were performed under mineral oil or perfluorinated oil. The diffraction experiments were performed at 100 or 123 K on an Agilent Technologies Gemini R Ultra diffractometer with Cu-K_α or Mo-K_α radiation. Crystallographic data together with the details of the experiments are given in Table 1. The cell determination, data reduction and absorption correction for all compounds were performed with the help of the CrysAlis PRO software by Agilent Technologies Ltd. The structure solution was done by direct methods with SIR97. The full-matrix least-square refinement against F^2 was done with ShelXL. During the refinement several restraints and constraints had to be applied. For the description of the refinement strategy we list the commonly used syntax for the ShelXL program (DFIX, DANG, SADI, SIMU, ISOR, EADP). All atoms except hydrogen were refined anisotropically. The H atoms were calculated geometrically and a riding model was used during refinement process. Graphical material was created with the free software Schakal99 or Olex2. CCDC-658370 (**1**), CCDC-1017587 (**2**), CCDC-773847 (**3**), CCDC-773849 (**4a**), CCDC-1017588 (**4b**), CCDC-1017589 (**4c**), CCDC-1017590 (**4d**) and CCDC-1017591 (**5**) 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.

3.2 Special comments on the weakly coordinating anion [TEF]

Due to its weakly coordinating nature, the anion [TEF] tends to be disordered in a lot of its solid state structures. The CF_3- as well as whole $(CF_3)_3CO$-groups frequently exhibit rotational disorder by rotation of C–O or C–C bonds, respectively. In some cases even a positional disorder of the whole anion can be observed. To resolve these kinds of disorder which are still present at 100 K good data sets with high resolution are needed. In addition, most of the compounds containing the anion [TEF] show a rather weak diffraction at high angles which proves the X-ray crystallography of these compounds to be a very challenging task. During the refinement of these solid state structures it is common that a series of least-square restraints has to be applied to prevent the results to display an unrealistic geometry or displacement parameters. In rare cases, even good data sets do not enable the refinement of all disorders which usually results in large displacement parameters, especially of the fluorine atoms.

3.3 Crystallographic details

Table 1. Crystallographic data for the described compounds:

	2	**4b**	**4c**	**4d**	**5**
Empirical formula	$C_{64}H_{60}AlF_{36}Mo_4O_{12}P_4Tl$	$C_{37}H_{15}AlF_{36}InMo_3O_{10}P_9$	$C_{37}H_{15}AlCr_3F_{36}O_{10}P_9Tl$	$C_{37}H_{15}AlF_{36}Mo_3O_{10}P_9Tl$	$C_{57}H_{62}AlCl_2F_{36}Mo_4O_4P_8S_2Tl$
M [gmol^{-1}]	2444.11	2012.16	1969.57	2101.34	2492.99
Cryst. size [mm]	0.14 × 0.09 × 0.02	1.02 × 0.08 × 0.07	0.30 × 0.10 × 0.05	0.25 × 0.16 × 0.08	0.23 × 0.06 × 0.02
T [K]	100(1)	100(1)	123(1)	100(1)	100(1)
λ [Å]	1.54178	1.54178	0.71073	1.54178	1.54178
crystal system	triclinic	hexagonal	hexagonal	hexagonal	monoclinic
space group	$P\bar{1}$	$P6_3/m$	$P6_5$	$P6_3/m$	$C2/c$
a [Å]	14.5298(6)	18.59063(18)	18.304(3)	18.7735(11)	38.9470(7)
b [Å]	16.4844(5)	18.59063(18)	18.304(3)	18.7735(11)	14.3778(2)
c [Å]	18.4998(5)	10.20330(9)	30.849(6)	10.0369(8)	31.5972(5)
α [°]	75.820(3)	90	90	90	90
β [°]	84.986(3)	90	90	90	113.475(2)
γ [°]	88.705(3)	120.0	120	120	90
V [Å^3]	4279.5(3)	3053.93(4)	8951(4)	3063.5(4)	16229.1(5)
Z	2	2	6	2	8
ρ_{calc} [gcm^{-3}]	1.90	2.19	2.19	2.28	2.04
μ [mm^{-1}]	10.2	11.8	3.6	13.8	12.5
diffractometer	Agilent Gemini R Ultra	Agilent Gemini R Ultra	Agilent Gemini R Ultra	Agilent Gemini R Ultra	Agilent Gemini R Ultra
radiation	Cu K_α	Cu K_α	Mo K_α	Cu K_α	Cu K_α
θ range [°]	3.05 – 66.93	4.76 – 66.59	3.24 – 25.08	4.71 – 64.77	3.05 – 66.70
absorption correct.	gaussian	gaussian	multi-scan	multi-scan	multi-scan
T_{min} / T_{max}	0.510 / 0.860	0.025 / 0.775	0.90611 / 1.05652	0.197 / 0.352	0.545 / 0.810
reflns collect / unique	40547 / 14773	16953 / 1903	24526 / 8686	6499 / 1813	29513 / 13971
reflns obs [$I>2\sigma(I)$]	12262	1812	6438	1449	9850
R_{int}	0.0333	0.0307	0.0589	0.0317	0.0347
Flack parameter	—	—	0.680(4)*	—	—
parameters / restraints	1295 / 971	243 / 113	875 / 89	261 / 121	1045 / 128
GOF on F^2	1.054	1.164	0.909	1.063	1.043
R_1 / wR_2 [$I>2\ \sigma(I)$]	0.0656 / 0.1877	0.0907 / 0.2030	0.0365 / 0.0631	0.0395 / 0.1122	0.0548 / 0.1499
R_1 / wR_2 (all data)	0.0753 / 0.1964	0.0945 / 0.2045	0.0637 / 0.0672	0.0571 / 0.1185	0.0745 / 0.1608
max / min $\Delta\rho$[eÅ^{-3}]	2.04 / –0.92	1.27 / –1.27	1.22 / –0.66	1.01 / –1.27	1.83 / –1.40

*racemic twin with BASF 0.680(4)

3.4 X-ray structure refinement of $[Tl_2(A2)_4][TEF]_2$ (2)

Crystals suitable for X-ray diffraction analysis can be obtained by layering a CH_2Cl_2 solution of **2** with *n*-pentane. One of the P_2 complexes **A2** shows a disorder over three positions (see Figure 2) with partial superposition of the CO- and Cp* ligands of the different parts. The corresponding SOF parameters were refined to 0.71, 0.19 and 0.10, respectively. For the ligand with an SOF of 0.10, only the Mo_2P_2 core could be refined. Therefore, the total C, H and O atom count is too low in the final model. In Table 1 the actual formula and all affected parameters are listed.

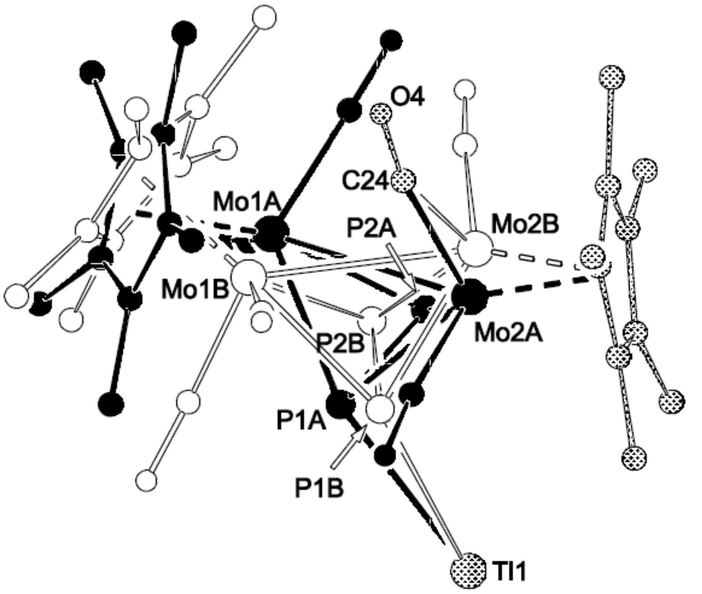

Figure 2. Representation of the disordered ligand A2 in the solid state structure of compound 2. The third orientation of the Mo_2P_2 tetrahedron as well as the H atoms are omitted for clarity.

The [TEF] anion is also disordered over two positions (see Figure 3). The SOF parameters of the two positions were refined to 0.53 and 0.47. The inherent disorder of individual parts of the anion by rotation around O–C and C–C bonds could not be further resolved. It is reflected in relatively large anisotropic displacement parameters of the atoms.

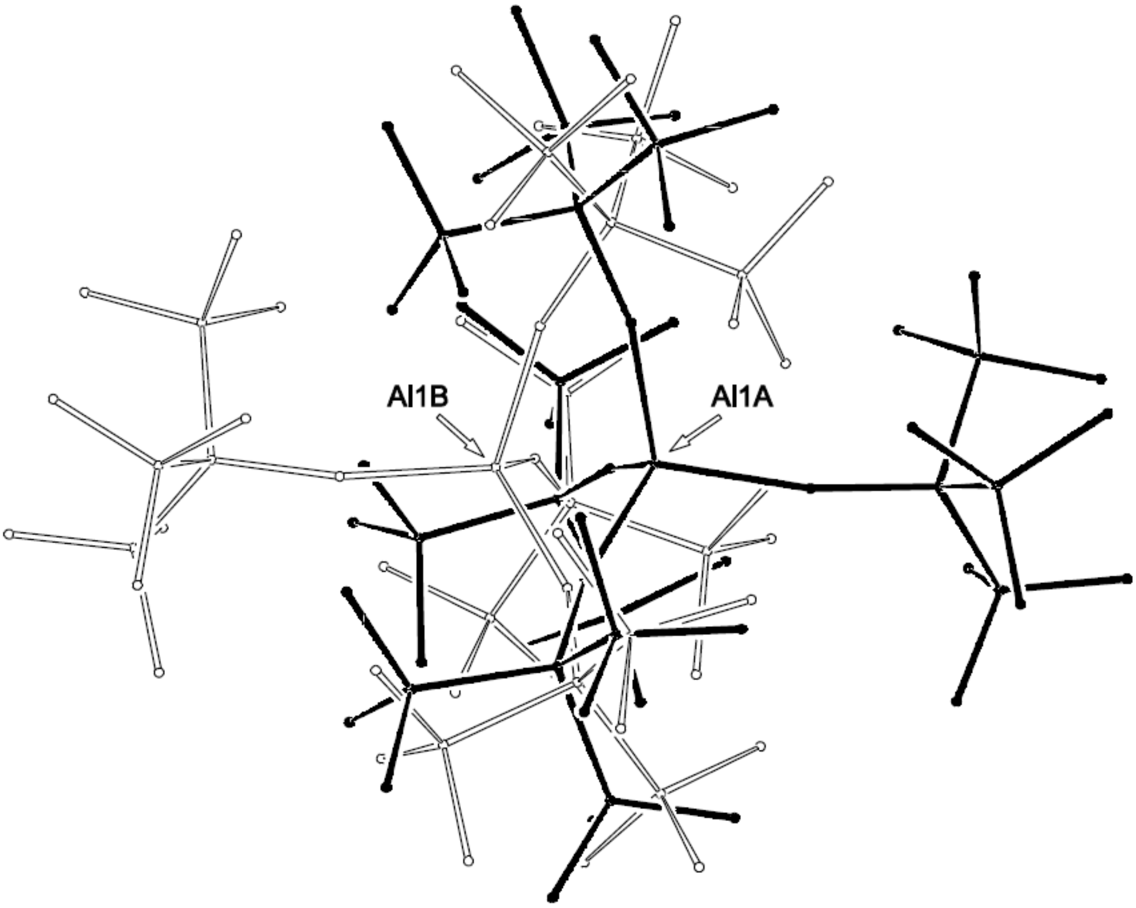

Figure 3. Representation of the disorder of the [TEF] anion in the solid state structure of compound 2.

During the refinement of the disordered parts of the solid state structure of compound **2** several DANG and ISOR restraints and also some EADP constraints were applied. The Cp* ligands of the disordered Mo_2P_2 complex **A2** were refined as rigid groups (AFIX 106).

3.5 X-ray structure refinement of $[In(B2)_3]_n[TEF]_n$ (4b)

Crystals suitable for X-ray diffraction analysis can be obtained by layering a concentrated CH_2Cl_2 solution of compound **4b** with *n*-pentane. The $[CpMo(CO)_2P_3]$ complexes of the one-dimensional coordination polymer are disordered across a mirror plane. The atoms Mo1, P1, P2, C5 and H5 are situated on the special positions of the mirror plane (see Figure 4 a).

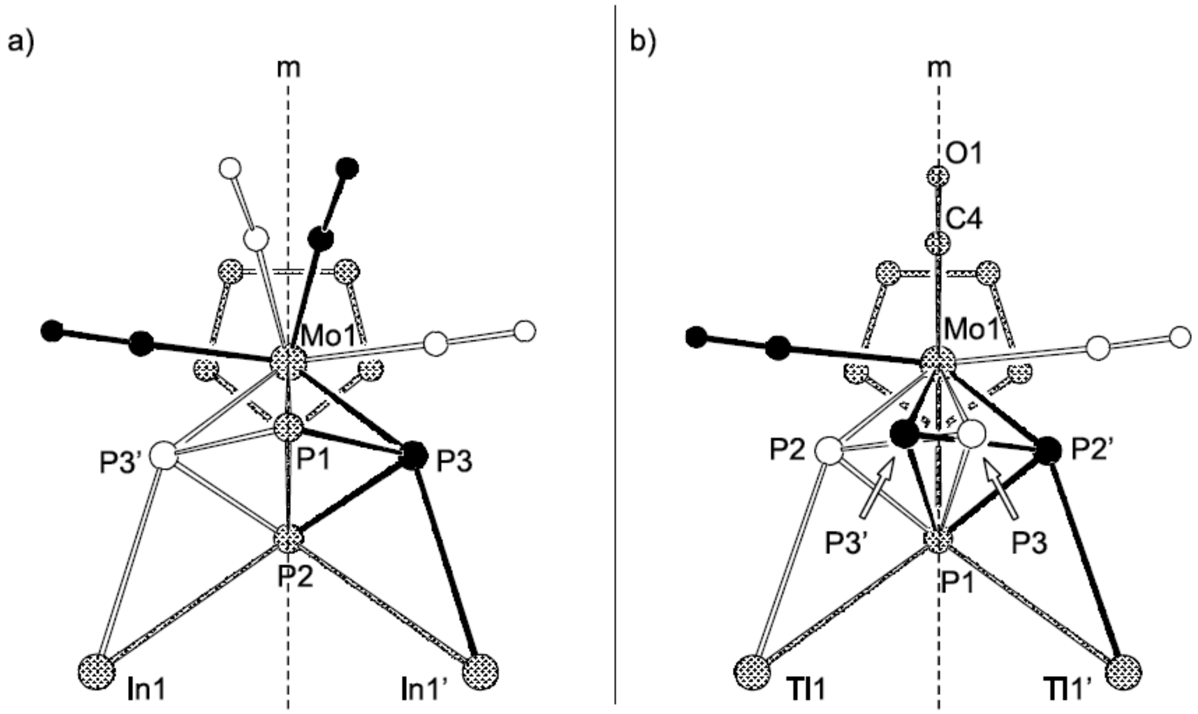

Figure 4. Comparison of the different disorder of the $[CpMo(CO)_2P_3]$ complex (B2) in the solid state structures of coordination compounds with In^+ (4b, a) and Tl^+ (4d, b). H atoms are omitted for clarity. One C atom of each Cp ring (C5 in a, C3 in b) is not visible in this representation.

The [TEF] anions exhibit a complicated disorder across a 6_3-screw axis as well as perpendicular mirror planes. This disorder is very similar to the disorder observed in **4d** (see Figure 5 b). In contrast to the Tl^+ compound **4d** the analogues In^+ complex **4b** shows no additional rotational disorder of the CF_3 groups of the anion. During the refinement of the disordered anions, several SADI, DFIX, DANG and ISOR restraints were applied.

3.6 X-ray structure refinement of $[Tl(B1)_3]_n[TEF]_n$ (4c)

Compound 4c crystallizes in the chiral hexagonal space group P65. The measured crystal was twinned by inversion with a BASF of 0.679(7). During the refinement some ISOR, SIMU and DELU restraints were applied to light atoms (C, O) to prevent unrealistic displacement parameters.

3.7 X-ray structure refinement of $[Tl(B2)_3]_n[TEF]_n$ (4d)

Crystals suitable for X-ray diffraction analysis can be obtained by storing a concentrated CH_2Cl_2 solution of compound **4d** at –28 °C for three weeks. The $[CpMo(CO)_2P_3]$ complexes **B2** of the one-dimensional coordination polymer are disordered across a mirror plane. The atoms Mo1, P1, C3, C4, O1 and H3 are situated on the special positions of the mirror plane (see Figure 5 a).

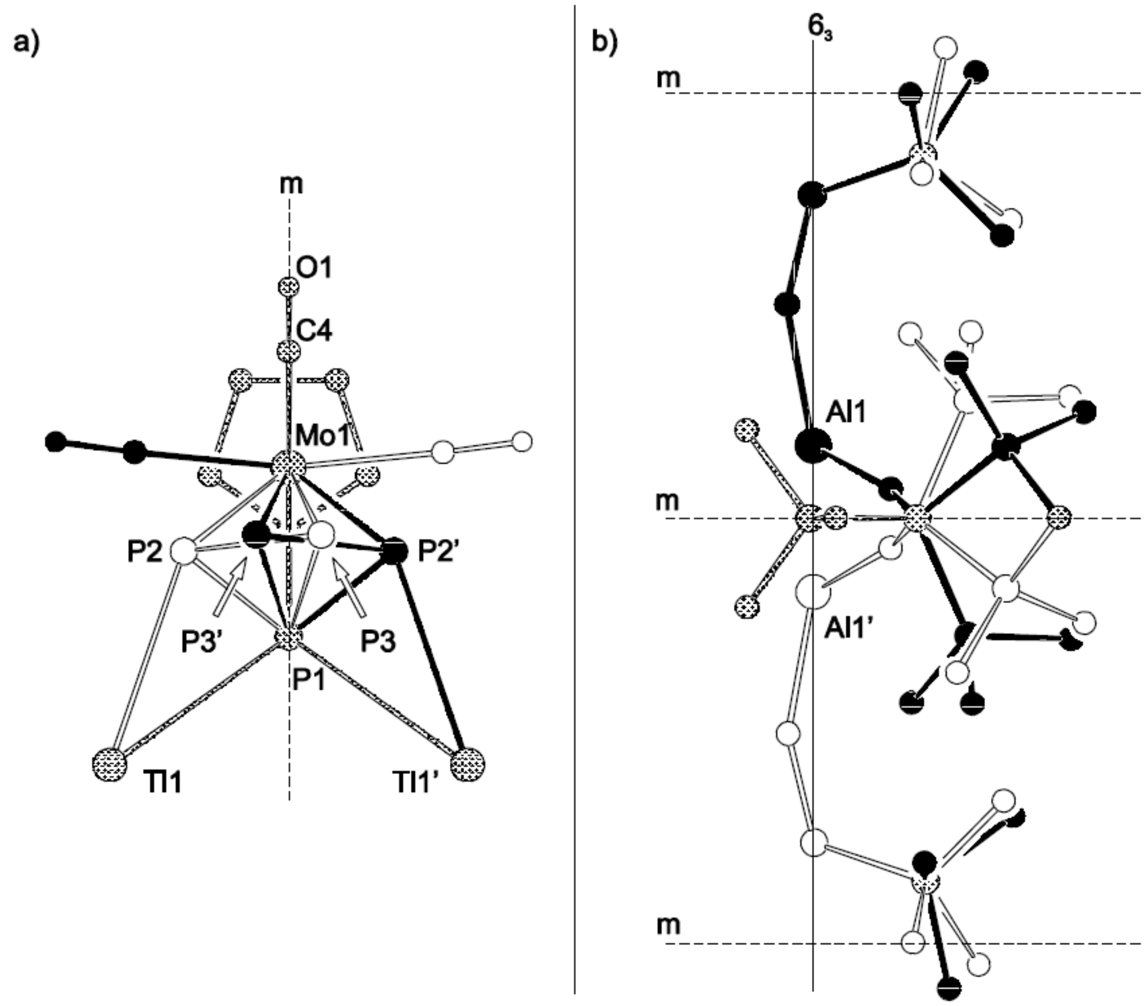

Figure 5. Illustration of the disordered molecules in the solid state structure of compound 4d. (a) Representation of the disordered P_3 complex B2 (H atoms omitted for clarity, C3 is not visible). (b) Representation of the disordered [TEF] anion in the solid state structure of compound 4d with viewing direction perpendicular to the crystallographic *c*-axis. Only one third of the [TEF] anion is shown here. The rest is symmetry generated by the 6_3-axis.

The [TEF] anions exhibit a complicated disorder across a 6_3-screw axis as well as perpendicular mirror planes (see Figure 5 b). In addition, the CF_3 groups show a rotational disorder and the correspondent SOF parameters were refined to 0.65 and 0.35. During the refinement of the disordered anions, several SADI, DFIX, DANG and ISOR restraints were applied.

3.8 Comparison of bond lengths for the one-dimensional polymers 4a-d

Table 1. List of selected bond lengths [Å] of the isostructural compounds 4 a-d; *d*(MP)σ shows the length of the σ-bonds, *d*(MP)π describes the distance between the group 13 metal cation and the center of the π-coordinating P–P bond, av. *d*(PP)free describes the P–P bond length of the non-coordinating and *d*(PP)π of the π-coordinating P–P bond.

	d(MP)σ	*d*(MP)π	av. *d*(PP)free	*d*(PP)π
4 a	3.251(2)	3.221(1)	2.134(2)	2.151(2)
4 b	3.393(5)	3.103(1)	2.067(10)	2.042(9)
4 c	3.326(2)	3.263(1)	2.136(4)	2.154(3)
4 d	3.430(3)	3.197(1)	2.164(6)	2.015(5)

Table 1 gives a summary of important bond lengths observed in the solid state to allow a better comparison. It has to be noted, that the defined atomic distances may have a more than usual uncertainty since the weakly coordinating anion [TEF] as well as parts of the coordination compound itself are heavily disordered in some cases. The Tl–P distances are generally longer than the analogues In–P distances. When looking closely at Table 1 it can be noted that the MoP_3 ligand **B2** (**4 b** and **d**) shows shorter π- and longer σ- coordination than the CrP_3 complex **B1** (**4 a** and **c**) for both In^+ and Tl^+. The π-coordinating P-P bond is elongated for **B1** while it is shortened for **B2**.

3.9 X-ray structure refinement of $[Tl(C)_2]_n[TEF]_n$ (5)

Crystals suitable for X-ray diffraction analysis can be obtained by storing a concentrated CH_2Cl_2 solution of compound **5** at –28 °C for one week. The asymmetric unit contains one Tl atom, one [TEF] anion, two $[Cp^*_2Mo_2(P_3)(PS)]$ complexes and one CH_2Cl_2 solvent molecule. The orientation of the P–S ligands in the coordinated $[Cp^*_2Mo_2(P_3)(PS)]$ triple-decker complexes could not be determined definitely by X-ray diffraction analysis since the difference of one electron (P to S) has only a low influence on the structure factors. It has to be emphasized that the presented example also contains heavier atoms (Mo) as well as the [TEF] anion with 57 light atoms. When a superposition of both orientations of the P–S bar with fixed SOF parameters of 50% was used instead of either one orientation during the refinement process, slightly better wR_2 values were reached (wR_2 all data 16.08 versus 16.14). Therefore, this model was applied for the final structure refinement. During the process SADI restraints and EADP constraints were used.

The geometry of two $(CF_3)CO$-groups of the [TEF] anion was restrained by SADI and DFIX commands during the structure refinement. In addition, several displacement parameters of the involved C and F atoms had to be restrained by ISOR and DELU commands to avoid unrealistic results.

4 DFT calculations

4.1 Computational details for ligand exchange in compound 4a

A detailed discussion about the dynamic coordination behavior of In^+ and the *cyclo*-P_3 ligand B1 in the coordination compound 4a and the equilibria involved in CH2Cl2 solution was previously described in the literature.[2]

4.2 Computational details for ligand exchange in compound 5

The optimized geometries of the species $[Tl(\mathbf{C})(CH_2Cl_2)]^+$ and $[Tl(\mathbf{C})_2]^+$ are depicted in Figure 6. Results from the DFT calculations are summarized in Table 2.

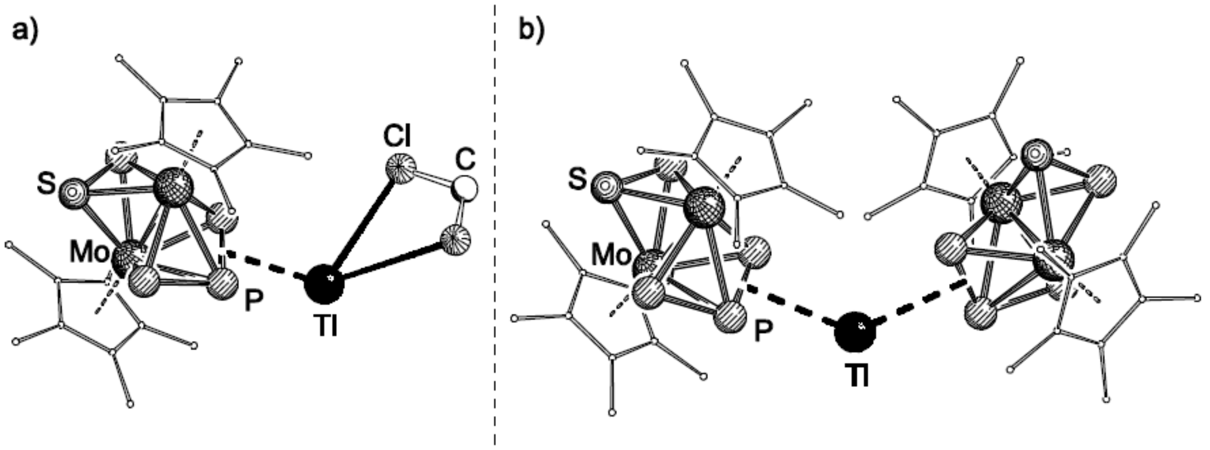

Figure 6. Representation of optimized geometries for the species $[Tl(C)(CH_2Cl_2)]^+$ (a) and $[Tl(C)_2]^+$ (b) in the gas phase. H atoms are omitted for clarity.

Table 2. Calculated Gibbs energies for ligand exchange reactions for the system Tl^+/(C)/CH_2Cl_2 of compound 5.

reaction	ΔG_0/ (kJ mol^{-1}) gas phase	ΔG_{300}/ (kJ mol^{-1}) gas phase	ΔG_0/ (kJ mol^{-1}) solution	ΔG_{300}/ (kJ mol^{-1}) solution
(I)	–80	17	–19	–3
(II)	–47	21	–17	4
(I) $[Tl(CH_2Cl_2)_2]^+ + \mathbf{C} \rightarrow [Tl(\mathbf{C})(CH_2Cl_2)]^+ + CH_2Cl_2$ (II) $[Tl(\mathbf{C})(CH_2Cl_2)]^+ + \mathbf{C} \rightarrow [Tl(\mathbf{C})_2]^+ + CH_2Cl_2$				

DFT calculations concerning the system Tl^+/**C**/CH_2Cl_2 of compound **5** were conducted using the TURBOMOLE program package.[7] The geometries were optimized using the RI-[8, 9]BP86[10, 11, 12] functional together with the TZVP[13] basis set. For the geometry optimizations the Multipole Accelerated Resolution of Identity (MARI-J)[8, 14] approximation was used. For Mo and Tl quasi relativistic pseudo potentials were used.[15, 16, 17] The species $[Tl(\mathbf{C})(CH_2Cl_2)]^+$ shows one imaginary frequency at –2.05 cm^{-1} (Tl-Cl pendulum motion) and the species $[Tl(\mathbf{C})_2]^+$ shows two imaginary frequencies at –8.48 cm^{-1} and at –4.77 cm^{-1} (Mo-C(Cp*) torsion). These motions were disregarded since several tries to eliminate them were unsuccessful and the concerned groups should not significantly affect the investigated reactions. As a result, ΔG values from these calculations will generally have a higher uncertainty. The Gibbs energies at room temperature were derived from a harmonic approximation using the calculated frequencies of the DFT computations (without the imaginary frequencies). Solvation energies were calculated using the COSMO [18] model.

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