

# Supramolecular Assemblies of Polyphosphorus Ligands Based on Weak Tl–P and In–P Interactions

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*Dedicated to Professor Hubert Schmidbaur on the occasion of his 80<sup>th</sup> birthday*

A systematic investigation of the coordination behavior of  $P_n$  complexes towards the main group Lewis acids  $Tl^+$  and  $In^+$  is presented. While the reaction of the tetrahedral  $P_2$  complex  $[CpMo(CO)_2]_2(\mu, \eta^2: \eta^2-P_2)$  (**A1**) with  $Tl[TEF]$  ( $[TEF] = [Al\{OC(CF_3)_3\}_4]^-$ ) leads to the formation of the dicationic complex  $[Tl_2(\mathbf{A1})_6]^{2+}$  (**1**) with a central six-membered  $Tl_2P_4$  ring, the analogous reaction with  $In[TEF]$  leads instead to a tetranuclear  $[In_4(\mathbf{A1})_8]^{4+}$  complex (**3**) exhibiting a weak  $In^I-In^I$  interaction in the solid state. When the  $Cp^*$ -analogous  $P_2$  complex  $[Cp^*Mo(CO)_2]_2(\mu, \eta^2: \eta^2-P_2)$  (**A2**) is reacted with  $Tl[TEF]$  the dinuclear complex  $[Tl_2(\mathbf{A2})_4]^{2+}$  (**2**) is formed, containing only four  $P_2$  ligands but also featuring a six-membered  $Tl_2P_4$  ring motif. From the reactions of the *cyclo*- $P_3$  complexes  $[CpM'(CO)_2(\eta^3-P_3)]$  ( $M' = Cr$  (**B1**),  $Mo$  (**B2**)) with  $In[TEF]$  and  $Tl[TEF]$ , a series of four isostructural one-dimensional coordination polymers (**4a–d**) are obtained which exhibit a novel bridging coordination mode of the *cyclo*- $P_3$  ligands in the solid state. Additionally, the mixed  $P_mS_n$  ligand complex  $[(Cp^*Mo)_2(\mu, \eta^3: \eta^3-P_3)(\mu, \eta^2: \eta^2-PS)]$  (**C**) was reacted with  $Tl[TEF]$  to afford a novel one-dimensional coordination polymer (**5**), which shows an unprecedented bridging  $\sigma$ -1,3-coordination mode of ligand **C** towards  $Tl^+$ . The compounds were analyzed by single-crystal X-ray structure determination, elemental analysis, and mass spectrometry, as well as by multinuclear NMR and IR spectroscopy. All products are readily soluble in  $CH_2Cl_2$ , despite in many cases being polymeric in the solid state. Multinuclear NMR spectroscopy suggests a highly dynamic coordination behavior in solution, including fast equilibria between different monomeric species, which is also supported by DFT calculations. The one-dimensional polymers **4c** and **4d** reveal a triplet in the  $^31P\{^1H\}$  MAS NMR spectrum at room temperature, which could be explained by fast rotation of the  $P_3$  rings in the solid state.

**Key words:** Group 13 Metals, Weakly Coordinating Anion, Polyphosphorus Complexes, Supramolecular Chemistry, Weak Interactions

## Introduction

Supramolecular chemistry is mainly based on weak forces like hydrogen bonds, weak dative bonds, or van der Waals interactions instead of the strong covalent bonds found in traditional chemistry. A uniquely established field in this context is the coordination chemistry of mostly monovalent metal cations connected by a large variety of multidentate organic linkers to form capsules, spheres or metal-organic frameworks [1–8]

The distinctive feature of our group's contribution to this field during the last decade is the use of organometallic  $P_n$  complexes as multidentate linkers. This class of polyphosphorus ligands [9–12] contains substituent-free P atoms in a variety of geometrical environments, such as P–P dumbbells and planar  $P_3$ ,  $P_4$ ,  $P_5$  or even  $P_6$  rings, and exhibits a wide variety of unique bonding modes in their assemblies. While we were able to isolate fullerene-like supermolecules and polymers from reactions of these ligands with

Cu<sup>I</sup> halides [13–27] we have also studied the reactions of P<sub>n</sub> ligands with “naked” Ag<sup>+</sup> cations featuring the weakly coordinating anion [Al{OC(CF<sub>3</sub>)<sub>3</sub>}<sub>4</sub>]<sup>−</sup> ([TEF]) [28, 29]. In subsequent efforts, we sought to expand this chemistry to monocationic group 13 Lewis acids. Fortunately, suitable Tl<sup>+</sup> and Ga<sup>+</sup> precursors containing the [TEF] anion were previously prepared by Krossing *et al.* [30, 31]. The isolation of the analogous In<sup>+</sup> source was first described by our group [32] with a new synthetic strategy published recently [33]. The exceptional coordination chemistry of these main group cations is exemplified by the reaction of In<sup>+</sup> and Ga<sup>+</sup> with the bulky phosphane PrBu<sub>3</sub>, which affords carbene-analogous complexes of the form [M(PrBu<sub>3</sub>)<sub>2</sub>]<sup>+</sup> (M = Ga, In) [33]. Additionally, *N*-heterocyclic carbenes (NHC) exhibit an unusual tilted coordination to In<sup>I</sup> and Ga<sup>I</sup> in the complexes [M(NHC)<sub>2</sub>]<sup>+</sup> (M = Ga, In), which can be explained by a σ back donation of the lone pair of the group 13 metal (s orbital) into the empty p orbital of the NHC [34]. In the meantime we reported the first complexes of In<sup>+</sup> and Tl<sup>+</sup> with P<sub>n</sub> complexes, which also showed unusual coordination behavior [32, 35]. Recently, we were able to extend this chemistry to As<sub>n</sub> complexes, as well as to Ga<sup>+</sup> for the first time [36]. Several isostructural polymeric compounds have been isolated from reactions of the group 13 cations with the well-known *cyclo-E*<sub>5</sub> sandwich complexes [Cp\*Fe(η<sup>5</sup>-E<sub>5</sub>)] (E = P, As), all of which exhibit a hitherto unprecedented η<sup>5</sup>:η<sup>1</sup>-coordination mode of the E<sub>5</sub> ligands towards the group 13 metal in the solid state. In order to further investigate the ligative behavior of organometallic P<sub>n</sub> ligand complexes towards group 13 cations, we have now investigated the assembly of selected P<sub>n</sub> ligand complexes with the group 13 Lewis acids In<sup>+</sup> and Tl<sup>+</sup>. The results of these investigations are presented in this paper.

## Results and Discussion

### General syntheses

The syntheses of the compounds **1**, **3** and **4a** have been reported earlier [32, 35]. Here we describe a general procedure for the syntheses of these complexes. For the synthesis of the desired complexes the M[TEF] (M = In, Tl) salts are dissolved in CH<sub>2</sub>Cl<sub>2</sub> together with a stoichiometric amount of the corresponding P<sub>n</sub> complexes and stirred at

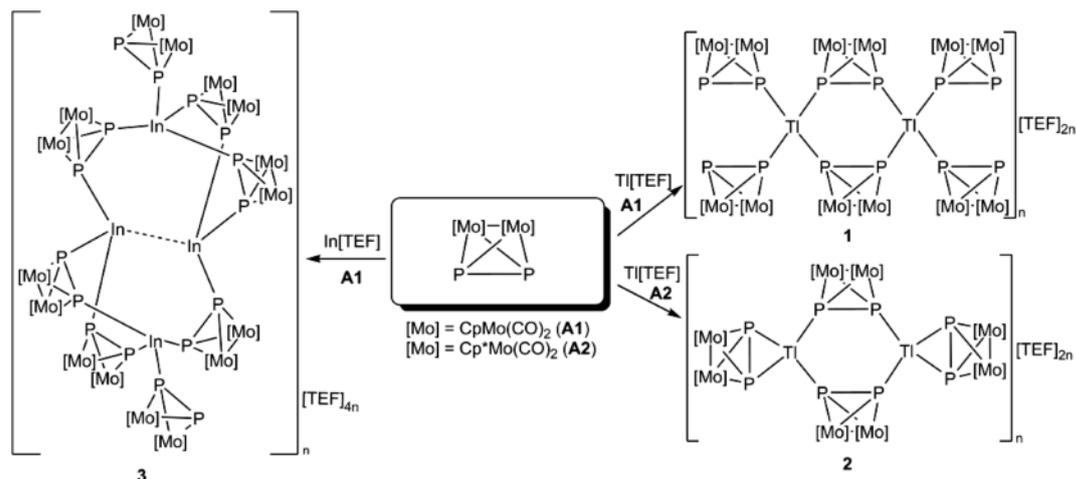
room temperature. The obtained solutions are filtered and either carefully layered with *n*-pentane for solvent diffusion, or the products are precipitated by fast addition of an excess of *n*-pentane to the stirred solution. Crystals suitable for X-ray crystallography are obtained by recrystallization of the pure products.

### Assemblies based on the P<sub>2</sub> ligands **A1** and **A2**

Earlier studies have clearly demonstrated that the coordination of the tetrahedral P<sub>2</sub> complex **A1** to coinage metal cations is a very fruitful area of research, affording a variety of homo- and heteroleptic complexes [20, 37]. The richness of this chemistry stems in large part from the variety of coordination modes of the P<sub>2</sub> unit observed in conjunction with the different metal centers. Among these complexes, a frequently observed structural element is a six-membered M<sub>2</sub>P<sub>4</sub> ring (M = Cu, Ag, Au). Within our attempts to transfer this chemistry to main group Lewis acids, the complex **A1** was reacted with the soluble Tl<sup>I</sup> source Tl[TEF] [35]. The obtained product (**1**, Scheme 1) contains a dinuclear [Tl<sub>2</sub>(**A1**)<sub>6</sub>]<sup>2+</sup> complex exhibiting a central Tl<sub>2</sub>P<sub>4</sub> six-membered ring, comparable to the coinage metal complexes of **A1**, with four terminal **A1** ligands which coordinate in an κ<sup>1</sup> fashion. The P–Tl distances are rather long and lie between 3.044(6) and 3.380(6) Å.

When the steric demand of the P<sub>2</sub> ligand is increased by using the Cp\*-analog of **A1** **A2**, compound **2** is obtained upon reaction with Tl[TEF] [38]. The solid state structure of **2** is depicted in Fig. 1. Although the dinuclear [Tl<sub>2</sub>(**A2**)<sub>4</sub>]<sup>2+</sup> complex found in **2** differs from that found in **1**, the central six-membered Tl<sub>2</sub>P<sub>4</sub> ring motif is again observed. The Tl–P distances of the bridging P<sub>2</sub> ligands are similar (Tl1–P3 3.092(3), Tl1–P4' 2.989(3) Å), while the terminal P<sub>2</sub> ligands coordinate in an asymmetric, side-on η<sup>2</sup>-mode with distinctly different Tl–P distances (Tl1–P1 2.963(3), Tl1–P2 3.557(4) Å) [39]. The central six-membered ring adopts a chair conformation with a folding angle of 44.0(1)°.

The exchange of the group 13 metal in this reaction has a dramatic effect. When the P<sub>2</sub> complex **A1** reacts with the soluble In<sup>I</sup> source In[TEF] in CH<sub>2</sub>Cl<sub>2</sub>, a red solution is formed [32]. Subsequent diffusion of *n*-pentane into this solution affords red crystals of **3**. The isolated compound consists of a hitherto



Scheme 1. Summary of the compounds which are obtained from the reactions of the  $\text{P}_2$  ligand complexes **A1** and **A2** with  $\text{Ti}^+$  and  $\text{In}^+$ .

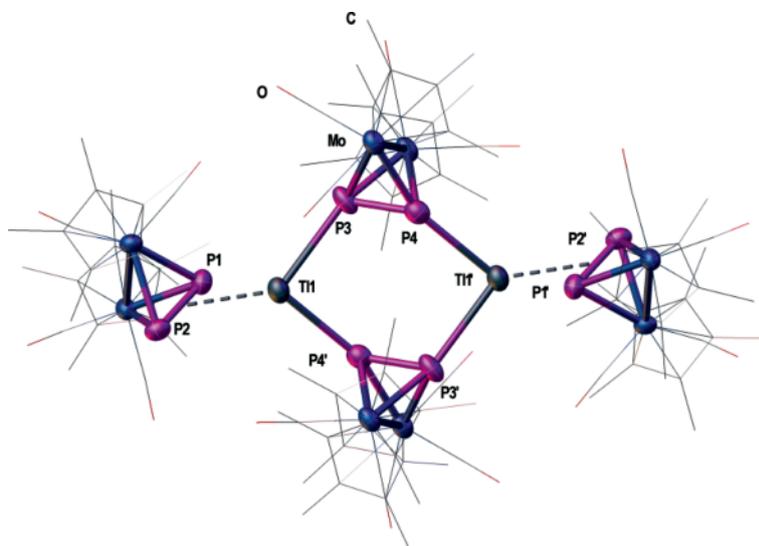


Fig. 1 (color online). Solid-state structure of the dicationic complex in compound **2**; H atoms are omitted, and the  $\text{Cp}^*$  and CO ligands are drawn with thin lines for clarity. Selected bond lengths ( $\text{\AA}$ ):  $\text{Ti1-P1}$  2.963(3),  $\text{Ti1-P2}$  3.557(4),  $\text{Ti1-P3}$  3.092(3),  $\text{Ti1-P4'}$  2.989(3),  $\text{P1-P2}$  2.086(5),  $\text{P3-P4}$  2.089(4).

unprecedented  $[\text{In}_4(\mathbf{A1})_8]^{4+}$  complex without a six-membered  $\text{M}_2\text{P}_4$  ring. The tetracation consists of four  $\text{In}^+$  cations that are bridged by six units of **A1** in a  $\mu, \eta^1: \eta^1$ -coordination mode (Scheme 1). Two additional  $\text{Mo}_2\text{P}_2$  ligands are coordinated in an end-on fashion to two of the  $\text{In}^+$  cations. The other two  $\text{In}^+$  cations, which are coordinated by only three P atoms, exhibit a close contact to each other (3.482(1)  $\text{\AA}$ ; sum of the vdW radii = 3.8  $\text{\AA}$ ), depicted by the dashed line

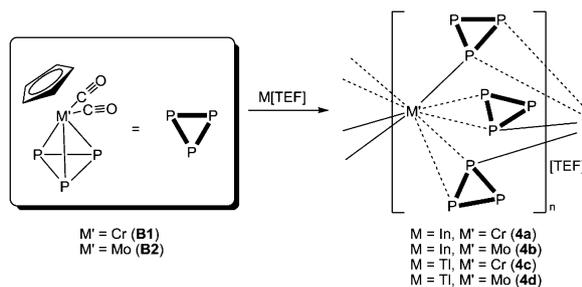
in Scheme 1. Theoretical calculations suggested the presence of a weak interaction between these In atoms but no bond critical point could be found [32].

Compounds **1**, **2** and **3** are insoluble in alkanes, but readily soluble in  $\text{CH}_2\text{Cl}_2$ . The  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{19}\text{F}\{^1\text{H}\}$  NMR spectra of these complexes in  $\text{CD}_2\text{Cl}_2$  show characteristic signals for the Cp (**1**, **3**),  $\text{Cp}^*$  (**2**) and CO ligands as well as for the anion  $[\text{TEF}]^-$ . The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of the  $\text{Ti}^+$  complexes both show

one singlet (**1**:  $-37.3$  ppm, **2**:  $-33.9$  ppm) which is shifted to lower field compared to that of the free ligands (**A1**:  $-43.2$  ppm, **A2**:  $-47.1$  ppm). No coupling to the Tl nuclei can be observed, even at low temperature [40]. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the  $\text{In}^{\text{I}}$  compound **3** reveals only one singlet at  $-47.1$  ppm, which is shifted by 3.9 ppm to higher field compared to that of the free ligand. The ESI mass spectra of the Tl complexes **1** and **2** from  $\text{CH}_2\text{Cl}_2$  solutions show peaks next to the free ligand assignable to  $[\text{Tl}(\text{A1})]^+$  (**1**) or  $[\text{Tl}(\text{A2})]^+$  (**2**), but no dication could be detected. In contrast, the ESI mass spectrum of the  $\text{In}^{\text{I}}$  complex **3** from  $\text{CH}_2\text{Cl}_2$  solution shows no assignable peaks for any cationic fragments. In MeCN solution, however,  $\text{In}^+$  and  $[\text{In}(\text{MeCN})]^+$  can be detected. The high solubility of the complexes **1–3**, the detection of only small fragments in the mass spectra, as well as the appearance of only one singlet in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra suggests a dynamic coordination behavior in solution, which is in good agreement with the weak  $\text{M}^{\text{I}}\text{–P}$  interactions present in the solid state.

#### Assemblies based on the *cyclo-P<sub>3</sub>* ligands **B1** and **B2**

When we investigated the coordination chemistry of  $\text{In}^{\text{I}}$  for the first time, we allowed  $\text{In}[\text{TEF}]$  to react with the *cyclo-P<sub>3</sub>* complex  $[\text{CpCr}(\text{CO})_2(\eta^3\text{-P}_3)]$  (**B1**) [41–43] in  $\text{CH}_2\text{Cl}_2$  in a 1 : 3 stoichiometry which afforded compound **4a** (see Scheme 2) [32]. The single-crystal structure determination revealed a one-



Scheme 2. Formation of the one-dimensional coordination polymers **4a–d** containing the *cyclo-P<sub>3</sub>* complexes **B1** and **B2** as linking units between the  $\text{In}^+$  or  $\text{Tl}^+$  cations. Dashed lines illustrate the  $\pi$ -coordination of a P–P bond.

dimensional coordination polymer, in which every  $\text{In}^+$  cation is connected to the next one by three bridging *cyclo-P<sub>3</sub>* ligands of **B1**.

In subsequent studies we systematically investigated the reaction outcome by first exchanging the complex **B1** for the Mo analog [37, 44] **B2**, followed by changing the central group 13 cation from  $\text{In}^+$  to  $\text{Tl}^+$ . To our surprise the resulting compounds **4a–d** (see Scheme 2) form a similar one-dimensional coordination polymer in the solid state [45]. As an example the structure of **4c** is shown in Fig. 2.

The special feature of compounds **4a–d** is the bridging bonding mode of the  $\text{P}_3$  ring of **B1** or **B2** towards the group 13 metals, which can be specified as a  $\mu\text{-}1\kappa\text{P}_A:1\kappa\text{P}_B:2\kappa\text{P}_B$  coordination. This describes a  $\sigma$ -

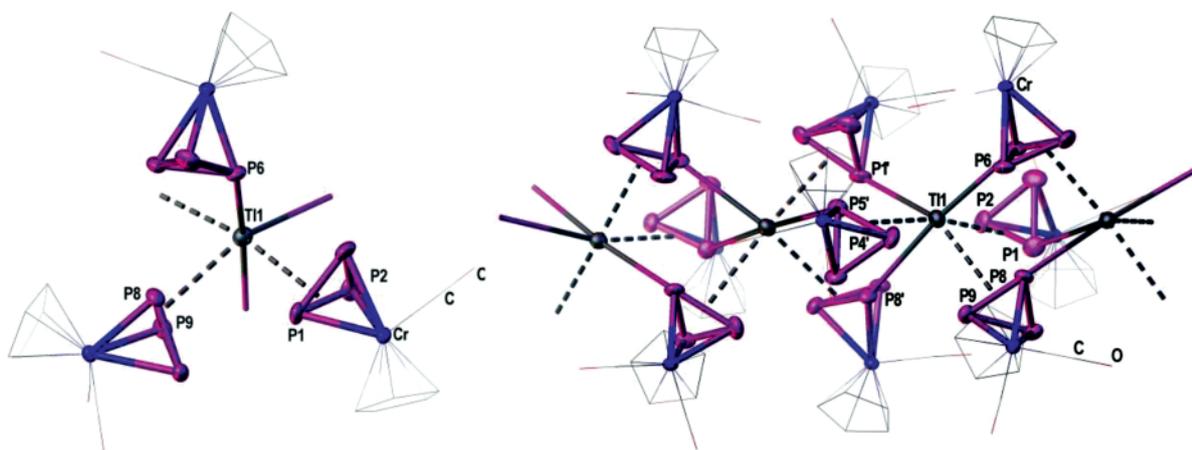


Fig. 2 (color online). Solid-state structure of **4c** as an example of the isostructural one-dimensional polymers **4a–d**; (left) view along the polymeric chain; (right) view perpendicular to the polymeric chain;  $\sigma$  bonds are shown as solid lines, while  $\pi$  bonds are represented by dashed lines from the metal to the center of the P–P edges. H atoms are omitted, and Cp and CO ligands are drawn with thin lines for clarity.

	$^{31}\text{P}\{^1\text{H}\}$ NMR $\delta$ ( $\text{CD}_2\text{Cl}_2$ , r. t.) (ppm)	$^{31}\text{P}\{^1\text{H}\}$ MAS NMR $\delta$ (ppm)	$\nu(\text{CO})$ ( $\text{CH}_2\text{Cl}_2$ ) ( $\text{cm}^{-1}$ )	$\nu(\text{CO})$ (KBr) ( $\text{cm}^{-1}$ )
<b>B1</b>	−288.3	–	1990, 1937	1964, 1910
<b>B2</b>	−351.9	–	2004, 1946	1977, 1925
<b>4 a</b> [32]	−287.9	−287.3 ( $\omega_{1/2}$ = 1229 Hz)	1990, 1936	2013, 1964
<b>4 b</b>	−347.5	–	2004, 1945	2026, 1972
<b>4 c</b>	−287.6	−288.0 (t, $^1J_{\text{TIP}}$ = 920 Hz)	1990, 1937	1979, 1927
<b>4 d</b>	−348.2	−344.3 (t, $^1J_{\text{TIP}}$ = 984 Hz)	2004, 1945	2025, 1972

Table 1. Spectroscopic data for **4a–4d**.

ordination of one P atom to one  $\text{M}^+$  cation ( $\text{M} = \text{In}$ ,  $\text{Tl}$ ) and a simultaneous  $\pi$  coordination of the adjacent P–P bond to the next cation in the sequence. Although it was shown previously [29] that  $\text{Ag}[\text{TEF}]$  also forms one-dimensional polymers with the *cyclo*- $\text{P}_3$  complex **B2**, the observed bonding mode of the *cyclo*- $\text{P}_3$  ligands **B1** and **B2** was unprecedented prior to the isolation of **4a–d**. The  $\text{Tl}$ –P distances are generally longer than the analogous  $\text{In}$ –P distances. Upon closer inspection of **4a–d** [46], it can be noted that the  $\text{MoP}_3$  ligand **B2** (**4b** and **d**) shows shorter  $\pi$  and longer  $\sigma$  coordination lengths than the  $\text{CrP}_3$  complex **B1** (**4a** and **4c**) for both  $\text{In}^+$  and  $\text{Tl}^+$ . The  $\pi$ -coordinating P–P bond is elongated for **B1** while it is shortened for **B2**.

Compounds **4a–d** are insoluble in alkanes, but readily soluble in  $\text{CH}_2\text{Cl}_2$  despite of their polymeric structure in the solid state. The  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{19}\text{F}\{^1\text{H}\}$  NMR spectra in  $\text{CD}_2\text{Cl}_2$  show characteristic signals assignable to the cyclopentadienyl and to the CO ligands as well as to the anion  $[\text{TEF}]^-$ . The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra at room temperature reveal only one singlet for the  $\text{M}'\text{P}_3$  complex in all cases, which is only slightly shifted to lower field ( $\text{M}' = \text{Cr} \sim 1$  ppm,  $\text{Mo} \sim 5$  ppm) compared to that of the free ligands (Table 1). No splitting of the signals or coupling to the  $\text{Tl}$  nuclei can be observed, even at low temperatures. The ESI mass spectra in  $\text{CH}_2\text{Cl}_2$  solution contain only signals corresponding to the monocations  $[\text{M}(\text{L})]^+$  ( $\text{M} = \text{In}$ ,  $\text{Tl}$ ;  $\text{L} = \text{B1}$ , **B2**). The IR spectra of **4a–d** in  $\text{CH}_2\text{Cl}_2$  solution show no change of the CO stretching frequencies compared to the free ligands. By contrast, the IR spectra recorded from solid samples in KBr [47] show a significant blue shift ( $\sim 15$ – $50$   $\text{cm}^{-1}$ , see Table 1) of the CO stretching frequencies compared to those of the free ligands **B1** and **B2**. This behavior is consistent with donation of electron density of the ligands

**B1** and **B2** to the group 13 metals in the solid state. All analytical data, especially the small changes in the chemical shift and lack of differentiation of the P atoms in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum suggest a dynamic coordination behavior in solution, which renders all P atoms equivalent on the NMR timescale. DFT calculations support this assumption and suggest fast ligand exchange of **B1** and **B2** for  $\text{CH}_2\text{Cl}_2$  molecules on the central  $\text{In}^+$  and  $\text{Tl}^+$  cations in solution [32]. The interactions between the P atoms and the group 13 metal cations in **4a–d** seem to be weak enough to allow dynamic behavior, even in the solid state at room temperature. While the  $^{31}\text{P}\{^1\text{H}\}$  MAS NMR spectrum of **4a** shows only a broad signal ( $\omega_{1/2} = 1229$  Hz) at a similar chemical shift ( $-287.3$  ppm) as in solution, the spectra of the  $\text{Tl}$  compounds **4c** and **4d** both show a pseudo-triplet, which can also be found at a similar chemical shift as the singlet in their solution NMR spectra (**4c**:  $-288.0$  ppm, **4d**:  $-344.3$  ppm). A similar phenomenon has previously been observed for the related one-dimensional polymer  $[\text{Tl}\{(\mu, \eta^5: \eta^1\text{-P}_5)\text{FeCp}^*\}_3]_n[\text{TEF}]_n$  [35, 36]. A logical explanation for the pseudo-triplet would be a fast rotation of the *cyclo*- $\text{P}_3$  ligand and coupling to two neighboring  $\text{Tl}$  nuclei ( $I = 1/2$ ) with coupling constants of similar magnitude [40]. The observed  $^1J_{\text{TIP}}$  coupling constants of **4c** and **4d** are about three times larger than that found for  $[\text{Tl}\{(\mu, \eta^5: \eta^1\text{-P}_5)\text{FeCp}^*\}_3]_n[\text{TEF}]_n$  (305 Hz), but distinctly smaller than coupling constants of  $\text{Tl}^{\text{I}}$  phosphine adducts (*e. g.*  $^1J_{\text{TIP}} = 5204$  Hz for  $[\text{Tl}^{\text{I}}(\text{PPh}_2\text{CH}_2)_3\text{BPh}])$  [48].

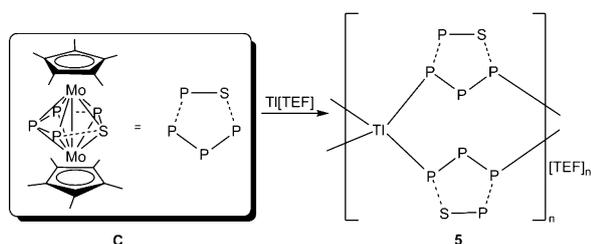
All the analytical data are in agreement with very weak  $\text{M}$ – $\text{P}$  ( $\text{M} = \text{In}$ ,  $\text{Tl}$ ) interactions in **4a–d**. We suppose a rotation of the *cyclo*- $\text{P}_3$  ligands in the solid state at room temperature that is frozen at the temperature of the X-ray diffraction analysis (100 K). Upon dissolving the compounds in  $\text{CH}_2\text{Cl}_2$ , a depolymerization

occurs, leading to fast equilibria of different smaller molecular aggregates in solution.

*Reaction of [(Cp\*Mo)<sub>2</sub>(μ,η<sup>3</sup>:η<sup>3</sup>-P<sub>3</sub>)(μ,η<sup>2</sup>:η<sup>2</sup>-PS)] with Tl[TEF]*

Previous investigations have shown that mixed P<sub>m</sub>S<sub>n</sub> complexes possess the same potential as P<sub>n</sub> complexes to act as bridging multidentate ligands towards coinage metals in supramolecular chemistry [49]. Since the group 13 metal cations in most cases exhibit a different reactivity than the coinage metals, it seemed worthwhile to also investigate the reactivity of the well-known complex [(Cp\*Mo)<sub>2</sub>(μ,η<sup>3</sup>:η<sup>3</sup>-P<sub>3</sub>)(μ,η<sup>2</sup>:η<sup>2</sup>-PS)] (C) towards group 13 metal cations [50, 51]. The triple-decker complex C presents an interesting building block for supramolecular chemistry, exhibiting a bent P<sub>3</sub> chain and a diatomic P–S dumbbell forming a distorted five-membered ring as a middle-deck between two [MoCp\*] fragments. The reaction of C and Tl[TEF] in CH<sub>2</sub>Cl<sub>2</sub> in a 2 : 1 stoichiometry leads to a clear solution. From this reaction mixture, purple crystals of the one-dimensional coordination polymer **5** (Scheme 3) are obtained upon storage of a concentrated solution at low temperature.

The solid-state structure of **5** is shown in Fig. 3 and reveals that each unit of C engages the Tl<sup>+</sup> cations in a μ,η<sup>1</sup>:η<sup>1</sup>-coordination mode *via* the 1,3-positions of the P<sub>3</sub> chain. This is a particularly interesting result, since it reveals an unprecedented bonding mode for the ligand C. All previously reported complexes of C involved coordination *via* the atom P1 or a simultaneous coordination *via* the P1 and P2 atoms of the P<sub>3</sub> chain. The P–S dumbbell is not involved in the coordination to Tl<sup>+</sup>. It must be noted that the location of the P and S atoms in the dumbbells cannot be exactly determined by X-ray crystallography, and we assume a statistical



Scheme 3. Synthesis of the one-dimensional coordination polymer **5** formed by the reaction of Tl[TEF] with the mixed P<sub>m</sub>S<sub>n</sub> ligand C.

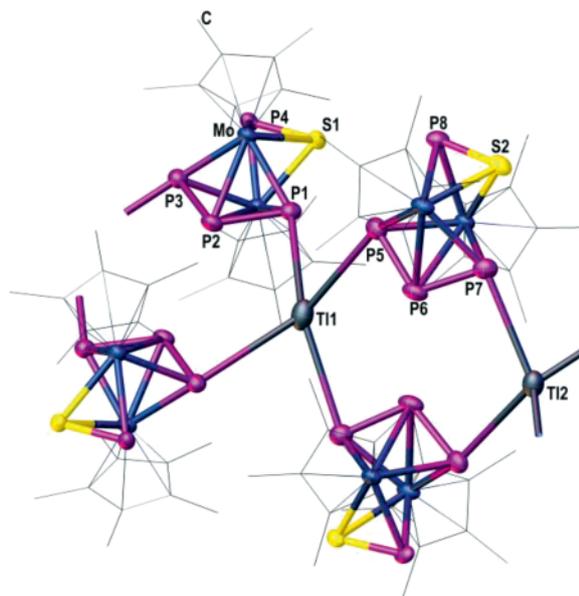


Fig. 3 (color online). Section of the solid-state structure of the one-dimensional polymer **5**. H atoms, the [TEF] anion and CH<sub>2</sub>Cl<sub>2</sub> solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Tl1–P1 3.442(2), Tl1–P5 3.433(2), Tl2–P3 3.389(2), Tl2–P7 3.391(2), P1–P2 2.155(3), P2–P3 2.152(3), P5–P6 2.165(3), P6–P7 2.158(3); P1–Tl1–P5 74.9(1), P3–Tl2–P7 79.4(1), P1–P2–P3 109.0(1), P5–P6–P7 109.2(1).

distribution of both possibilities [46]. The positions of P and S in the dumbbells shown in Scheme 3 and Fig. 3 are therefore arbitrary. The polymeric chain consists of two orientations of almost planar Tl<sub>2</sub>P<sub>6</sub> 8-membered rings (largest deviations ~0.35 Å), which are twisted with an angle of 44.0(2)° against each other.

The coordination polymer **5** is insoluble in alkanes, but readily soluble in CH<sub>2</sub>Cl<sub>2</sub>. The <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>19</sup>F{<sup>1</sup>H} NMR spectra in CD<sub>2</sub>Cl<sub>2</sub> solution show characteristic signals for the Cp\* ligands and the anion [TEF]. The <sup>31</sup>P{<sup>1</sup>H} NMR solution spectrum shows a ABMX spin system (with signals centered at 357.9, 340.0, –126.7, and –357.6 ppm) [52], which differs from that of the free ligand (signals centered at 343.3, 320.6, –132.0, and –367.1 ppm). The <sup>31</sup>P{<sup>1</sup>H} MAS NMR spectrum of **5** at room temperature reveals broad, partially overlapping signals at similar chemical shifts. The ESI mass spectrum from a CH<sub>2</sub>Cl<sub>2</sub> solution of **5** shows peaks assignable to [Tl(C)]<sup>+</sup> and [Tl(C)<sub>2</sub>]<sup>+</sup>. The experimental data are in agreement with a depolymerization of **5** in CH<sub>2</sub>Cl<sub>2</sub> solution, with all ligands C

being equivalent on the NMR timescale. To elucidate the species present in solution, DFT calculations were performed for the system  $\text{Tl}^+/\text{C}/\text{CH}_2\text{Cl}_2$ . The results show that the  $[\text{Tl}(\text{C})_2]^+$  complex is the most stable species in the gas phase as well as in solution [46]. However, the determined energy barriers for ligand substitution by one or even two  $\text{CH}_2\text{Cl}_2$  molecules are very small. This suggests a fast equilibrium between different monomeric species in solution.

## Conclusion

The main group coordination compounds presented are based on very weak In–P or Tl–P interactions and display fast equilibria in solution as revealed by NMR spectroscopy. Since all of the investigated compounds are readily soluble in  $\text{CH}_2\text{Cl}_2$  and exhibit very limited aggregation in solution, the primary characterization and comparison of the products was done by single-crystal X-ray structure analysis. The preparation of the supramolecular assemblies can easily be achieved by the coordination of polyphosphorus ligands to the main group Lewis acids  $\text{Tl}^+$  and  $\text{In}^+$ . A systematical variation of the metal centers and of the ligands allows direct comparisons between series of analogous products. The complexes containing the  $\text{P}_2$  ligand **A1**  $[\text{Tl}_2(\text{A1})_6]^{2+}$  (**1**) and  $[\text{In}_4(\text{A1})_8]^{4+}$  (**3**), which have been described earlier [32, 35], show distinctively different assemblies in the solid state. With  $\text{Tl}^+$  a  $[\text{Tl}_2(\text{A1})_6]^{2+}$  dication with a central  $\text{Tl}_2\text{P}_4$  six-membered ring is formed, whereas  $\text{In}^+$  leads to a unique  $[\text{In}_4(\text{A1})_8]^{4+}$  tetra-cationic complex featuring a very weak  $\text{In}^{\text{I}}\text{--}\text{In}^{\text{I}}$  interaction. The increased steric demand of the  $\text{P}_2$  ligand **A2** results in the formation of the dication  $[\text{Tl}_2(\text{A2})_4]^{2+}$ , exhibiting a similar central  $\text{Tl}_2\text{P}_4$  six-membered ring but with only one additional ligand **A2** coordinating to each Tl atom. The reactions of  $\text{In}[\text{TEF}]$  and  $\text{Tl}[\text{TEF}]$  with the *cyclo*- $\text{P}_3$  ligands **B1** and **B2** lead to the formation of the four isostructural, one-dimensional polymers **4a–d** with an unprecedented  $\sigma, \pi$ -bridging bonding mode for the *cyclo*- $\text{P}_3$  ligands. MAS-NMR characterization reveals that the  $\text{P}_3$  rings are rotating even at low temperature. All polymers **4a–d** are readily soluble in

$\text{CH}_2\text{Cl}_2$  and exhibit a dynamic coordination behavior, including a fast ligand exchange of **B1** or **B2** by  $\text{CH}_2\text{Cl}_2$  molecules. Finally the mixed  $\text{P}_m\text{S}_n$  ligand  $[(\text{Cp}^*\text{Mo})_2(\mu, \eta^3: \eta^3\text{-P}_3)(\mu, \eta^2: \eta^2\text{-PS})]$  (**C**) was reacted with  $\text{Tl}[\text{TEF}]$  to yield the novel, one-dimensional polymeric compound **5**. The solid-state structure of **5** revealed a new bonding mode of the ligand **C** and shows the potential of mixed  $\text{P}_m\text{S}_n$  complexes to act as linking units in conjunction with main group Lewis acids.

In summary, the presented results demonstrate the numerous diverse coordination modes of different ligand and main group metal combinations under the conditions of weak coordination. Although the substitution of the main group metals or the ligands may not significantly change in the case of the polymers **4a–d**, it is clear that the reaction outcome certainly cannot be predicted or even derived from analogous complexes in light of the  $\text{In}^{\text{I}}$  and  $\text{Tl}^{\text{I}}$  complexes **1** and **3**. Therefore, the investigation of weakly interacting main group coordination compounds represents a desirable research goal as well as an ongoing challenge.

## Crystal structure determinations

Details of the crystal structure determinations are given in the Supporting Information available online (*vide infra*).

CCDC 1017587–1017591 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](http://www.ccdc.cam.ac.uk/data_request/cif).

## Supporting information

The Experimental Part of this paper is available online as electronic Supporting Information (14 pages, DOI: 10.5560/ZNB.2014-4177). It contains the detailed syntheses of the compounds **2**, **4b–d** and **5** and their spectroscopic and analytical characterization. Details including commands used, comments on the X-ray structure refinements, and some figures to describe the encountered disorders in some of the X-ray structures are also presented. Additionally, the performed DFT calculations are discussed in greater detail.

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