

Controlled aggregation of a 1,3-diphosphacyclobutadiene complex in the coordination sphere of Ag(I) and Au(I) ions

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ABSTRACT

Reactions of the 1,3-diphosphete complex $[\text{Cp}^{\text{R}}\text{Co}(\eta^4\text{-P}_2\text{C}_2\text{tBu}_2)]$ ($\text{Cp}^{\text{R}} = \text{Cp}(\text{tBu})_3$, **1**) with $\text{Ag}[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ ($\text{Ag}[\text{TEF}]$) and $[\text{LAu}][\text{TEF}]$ ($\text{L} = (\text{THT})_2, (\text{THT})\text{PPh}_3$) were studied under various reaction conditions. Depending on the stoichiometry of the reactants, reaction time and temperature involved, a selective formation of the monomers, $[(\text{Et}_2\text{O})\text{Ag}\{\text{Cp}^{\text{R}}\text{Co}(\mu, \eta^4: \eta^1: \eta^1\text{-P}_2\text{C}_2\text{tBu}_2)\}][\text{TEF}]$ (**4**) and $[\text{Au}\{\text{Cp}^{\text{R}}\text{Co}(\eta^4: \eta^1: \eta^1\text{-P}_2\text{C}_2\text{tBu}_2)\}_2][\text{TEF}]$ (**6**), the dimer $[(\text{Et}_2\text{O})\text{Ag}\}_2\{\text{Cp}^{\text{R}}\text{Co}(\mu, \eta^4: \eta^1: \eta^1\text{-P}_2\text{C}_2\text{tBu}_2)\}_2][2[\text{TEF}]$ (**3**), the trimers $[\text{Au}_3\{\text{Cp}^{\text{R}}\text{Co}(\eta^4: \eta^1: \eta^1\text{-P}_2\text{C}_2\text{tBu}_2)\}_4][3[\text{TEF}]$ (**7**) and $[(\eta^1\text{-PPh}_3)_2\text{Au}_3\{\text{Cp}^{\text{R}}\text{Co}(\eta^4: \eta^1: \eta^1\text{-P}_2\text{C}_2\text{tBu}_2)\}_2][3[\text{TEF}]$ (**8**), and the one-dimensional polymer $[\text{Ag}\{\text{Cp}^{\text{R}}\text{Co}(\eta^4: \eta^1: \eta^1\text{-P}_2\text{C}_2\text{tBu}_2)\}_n][\text{TEF}]_n$ (**2**) was realized. DFT calculations provided additional insight into the formation of the polymeric species during the assembling process of **2**, **3** and **4**. All compounds were characterized in the solid state by X-ray crystallography and in solution by multinuclear NMR spectroscopy and mass spectrometry.

1. Introduction

Phosphaalkynes ($\text{RC}\equiv\text{P}$, R = alkyl, aryl) are captivating molecules owing to their potential as building blocks in the synthesis of heterocyclic and cage-like compounds **1** as well as their unusual reactivity **2**. The first kinetically stable phosphaalkyne $\text{tBuC}\equiv\text{P}$ was isolated by Becker and coworkers in 1981 **3**. A few years later, the groups of Regitz **4** and Nixon **5** achieved its cyclodimerization in the coordination sphere of the metal complexes $\text{Cp}^{\text{R}}\text{M}(\text{C}_2\text{H}_4)_2$ (M = Co, Rh, Ir; R = H, Me) allowing for the synthesis of the first diphosphabutadiene (diphosphete) metal complexes $[\text{Cp}^{\text{R}}\text{M}(\eta^4\text{-P}_2\text{C}_2\text{R}_2)]$ (type A, **Scheme 1a**). Since then, a number of heteroleptic **6** and, to a lesser extent, homoleptic **7** diphosphete metal compounds were assembled from cyclodimerization of phosphaalkynes. This process generally leads to both 1,2- and 1,3-diphosphetes with the latter being the most common one although it is energetically less favoured **8**. One very interesting feature of diphosphete complexes is the possibility to use them as metalloligands. Those species were found to coordinate further metal cations through the P atoms, to give homo- and heterodinuclear complexes as well as oligomeric aggregates and coordination polymers. For example, the reaction of the type A diphosphete complex $[\text{CpCo}(\eta^4\text{-P}_2\text{C}_2\text{tBu}_2)]$ with

one or two equivalents of $[\text{CpCo}(\text{C}_2\text{H}_4)_2]$ allows for the synthesis of di- and tricobalt complexes of the type **D** (**Scheme 1**) **9**. A similar reaction of $[\text{CpRh}(\eta^4\text{-P}_2\text{C}_2\text{tBu}_2)]$ with $[\text{Rh}\{\text{Cl}(\text{C}_2\text{H}_4)_2\}_2]$ gives the hexarhodium complex $[\text{RhCl}_2\{\text{Rh}(\text{Cp})(\text{P}_2\text{C}_2\text{tBu}_2)\}_4]$ **10** (type **E**, **Scheme 1**). More recently, Wolf *et al.* prepared homoleptic anionic diphosphete complexes $[\text{M}(\text{P}_2\text{C}_2\text{R}_2)_2]^-$ (M = Fe, Co, R = *tert*-butyl (tBu), *tert*-pentyl (tPent), adamantyl (Ad); type **B**, **Scheme 1**) **7a**, and demonstrated their potential to form Cobalt, Nickel and coinage metal complexes via the coordination of one or two phosphorus atoms towards the various metal centers **11**. A remarkable outcome of this approach is the formation of the molecular square $[\text{Au}\{\text{Co}(\text{P}_2\text{C}_2\text{tBu}_2)_2\}_4]$ (**F**, **Scheme 1**) involving four $[\text{Co}(\text{P}_2\text{C}_2\text{tBu}_2)_2]^-$ moieties connected by four Au(I) ions **12**. One of our contributions to this field was the synthesis of 1,3-diphosphete complexes $[\text{Cp}^{\text{R}}\text{Co}(\eta^4\text{-P}_2\text{C}_2\text{R}_2)]$ ($\text{Cp}^{\text{R}} = \text{Cp}(\text{tBu})_3$, R = tBu, iPr) of the type **C** (**Scheme 1**) **13**. In their reactions with Lewis acids such as $[\text{W}(\text{CO})_4(\text{nbd})]$ CuX (X = Cl, Br, I), depending on the stoichiometry, a variety of products including molecular complexes (**Scheme 1**, type **G**) as well as 1D and 2D supramolecular assemblies were obtained. Based on these results, we became further interested in understanding the aggregation pathways and controlling a selective formation of the targeted products. Herein, we report one of our efforts in this direction in which

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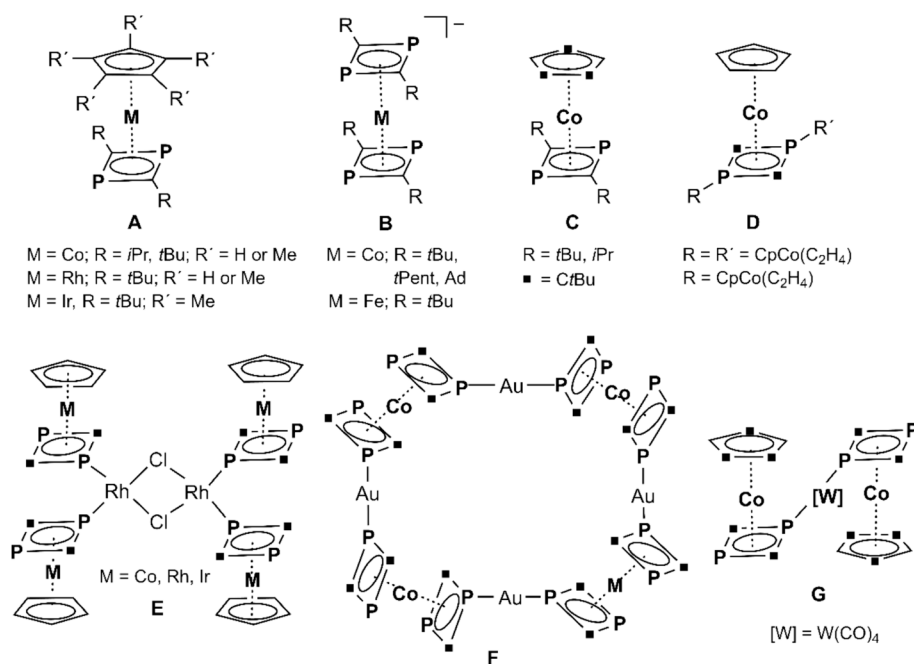
the effect of the reaction temperature and the ratio of the reactants on the aggregation processes obtained from the reaction of the diphosphete complex $[\text{Cp}^{\text{***}}\text{Co}(\eta^4\text{-P}_2\text{C}_2\text{tBu}_2)]$ (**1**) with Ag(I) and Au(I) salts, respectively, are studied. Accordingly, a controlled synthesis can be achieved to a large extent allowing the isolation of six supramolecular coordination complexes (SCCs) and one 1D polymer based on the complex **1** and Ag(I) or Au(I) ions as building blocks. To the best of our knowledge, this study is the first and only of its type in the field of diphosphete chemistry.

2. Results and discussions

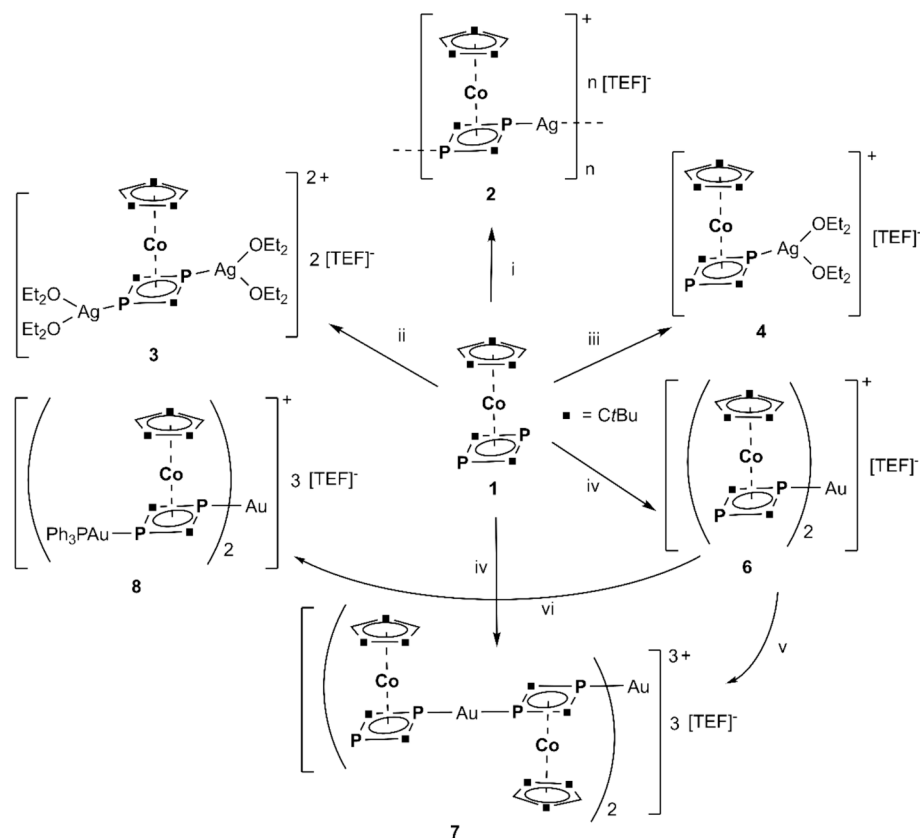
In a first approach, the diphosphete complex **1** was prepared [13] and treated with $\text{Ag}[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$ ($\text{Ag}[\text{TEF}]$) due to the high solubility of the $[\text{TEF}]^-$ anion [14]. This reaction was carried out in CH_2Cl_2 or in a 4:1 mixture of $\text{Et}_2\text{O}:\text{CH}_2\text{Cl}_2$ using a 1:1 ratio of **1**: $\text{Ag}(\text{TEF})$ (Scheme 2). The starting materials were mixed at -80°C and the reaction mixture was slowly warmed to room temperature and stirred overnight. From this reaction, compound **2** was obtained (Scheme 2) as orange crystals in 72 % yield upon layering the crude reaction mixture with *n*-hexane at room temperature or $+5^\circ\text{C}$. Although crystals of **2** only show weak diffraction ($d_{\text{min}} \sim 1 \text{ \AA}$), its 1D polymeric structure with the general formula $[\text{Ag}\{\text{Cp}^{\text{***}}\text{Co}(\eta^4:\eta^1:\eta^1\text{-P}_2\text{C}_2\text{tBu}_2)\}_n \cdot n[\text{TEF}]$ (Fig. 1) could be unambiguously identified. The preliminary structural model in the monoclinic space group $P2_1/c$ reveals a repeating unit which contains four (**1**)Ag fragments and four highly disordered TEF anions which complicate further structural refinement. The group of Wolf reported the neutral polymeric compound $[\text{Ag}\{\text{Co}(\text{P}_2\text{C}_2\text{Ad}_2)_2\}_n]$ from the reaction of $[\text{K}(\text{THF})_4][\text{Co}(\eta^4\text{-P}_2\text{C}_2\text{Ad}_2)_2]$ with $\text{Ag}[\text{SbF}_6]$ [11c]. Therein, however, it was neither possible to crystallize it nor to characterize it in solution due to its lack of solubility. In contrast, polymer **2** is well soluble in common organic solvents such as CH_2Cl_2 . Accordingly, **2** was further characterized in solution by multinuclear NMR spectroscopy and mass spectrometry. The ^{31}P and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **2** at room temperature reveal in each case one broad signal centered at ca. -0.3 ppm which is upfield shifted compared to those of the free diphosphete ligand complex **1** (23.4 and 41.3 ppm) [13]. The ^1H NMR spectrum shows typical signals for the $\text{Cp}(\text{tBu})_3$ group stabilizing the Co-diphosphete moiety and

the $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum shows one signal at -75.5 ppm attributed to the $[\text{TEF}]^-$ anion. In the electrospray ionization mass spectrometry (ESI-MS) spectrum of **2** in CH_2Cl_2 , the most abundant peak is attributed to the $[\text{Ag}(\text{1})]^+$ fragment. Additionally, the peak corresponding to $[\text{Ag}(\text{1})_2]^+$ could also be detected. Finally, the composition of the crystals could be revealed by elemental analysis which fits well with the structure extracted from the X-ray data analysis. A number of 1D polymers are found in literature which are based on diphosphete molecules connected by Ag(I) ions [15]. In all those cases however, the Ag centers possess trigonal or tetrahedral environments due to their interaction with the counteranions.

As the process towards the formation of polymer **2** seems to be the sequential aggregation of units of **1** with Ag^+ cations, we subsequently attempted to stop this process at earlier stages in the search of oligomeric compounds instead of the 1D polymer. Accordingly, two equivalents of $\text{Ag}[\text{TEF}]$ were added to **1** at -80°C and the reaction mixture was allowed to reach 0°C and stirred only for one hour. The follow-up layering of the crude reaction mixture with *n*-hexane was also performed at -30°C instead of room temperature. Under these reaction conditions, the dicationic complex $[\{(\text{Et}_2\text{O})_2\text{Ag}\}_2\{\text{Cp}^{\text{***}}\text{Co}(\mu,\eta^4:\eta^1:\eta^1\text{-P}_2\text{C}_2\text{tBu}_2)\}_2 \cdot 2[\text{TEF}]$ (**3**, Scheme 2) was obtained within two days as orange crystals. An analogous reaction using a 1:1 ratio of **1**: $\text{Ag}[\text{TEF}]$, stirred for one hour at -60°C allowed for the formation of the monocationic complex $[(\text{Et}_2\text{O})_2\text{Ag}\{\text{Cp}^{\text{***}}\text{Co}(\eta^4:\eta^1\text{-P}_2\text{C}_2\text{tBu}_2)\}][\text{TEF}]$ (**4**, Scheme 2). Interestingly, both **3** and **4** were isolated selectively from the corresponding layered solutions in good yields (58 % and 50 %, respectively) with no traces of the 1D polymer **2**. The X-ray structure analysis performed on single crystals of **3** and **4**, respectively, shows one unit of **1** coordinated to two and one Ag(I) ions via two and one P atoms of the diphosphete unit (Fig. 2a and 2b). Moreover, on each Ag(I) ion, two additional ether (Et_2O) molecules are coordinated, thus the Ag(I) ions in both compounds each possess a trigonal planar coordination mode with two O atoms and one P atom. The bond lengths and angles within the 1,3-diphosphete moieties of **3** and **4** are similar to those of the starting material **1** [13]. Remarkably, compound **2** can be neither transformed to **3** nor to **4** upon adding a large excess of Et_2O to its CH_2Cl_2 solution. However, compound **4** transforms to **2** when dissolved in CH_2Cl_2 , stirred overnight at room temperature and layered with *n*-



Scheme 1. Selected examples of three types of 1,3-diphosphete complexes A-C and coordination aggregates (types D-G) obtained from their coordination reactions as metalloligands towards Au, Rh, Ir, Co and W metal ions and complexes.



Scheme 2. Scheme of the reactions of $[\text{Cp}^*\text{Co}(\eta^4\text{-P}_2\text{C}_2\text{tBu}_2)]$ (**1**) with $\text{Ag}[\text{TEF}]$ and $(\text{THT})_2\text{Au}[\text{TEF}]$ salts: i) 1 eq. of $\text{Ag}[\text{TEF}]$ in $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ mixture, $-80^\circ\text{C} \rightarrow \text{r.t.}$, overnight; ii) 2 eq. of $\text{Ag}[\text{TEF}]$ in $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ mixture, $-80^\circ\text{C} \rightarrow 0^\circ\text{C}$, 1 h; iii) 1 eq. of $\text{Ag}[\text{TEF}]$ in $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ mixture, $-80^\circ\text{C} \rightarrow -60^\circ\text{C}$, 1 h; iv) 0.5 eq. of $(\text{THT})_2\text{Au}[\text{TEF}]$ in CH_2Cl_2 , $-80^\circ\text{C} \rightarrow \text{r.t.}$ Reaction of 1 eq. of **6** with: v) 0.5 eq. of $(\text{THT})_2\text{Au}[\text{TEF}]$ in CH_2Cl_2 at r.t. and vi) 2 eq. of $[(\text{THT})\text{Au}(\text{PPh}_3)][\text{TEF}]$ in CH_2Cl_2 at r.t.

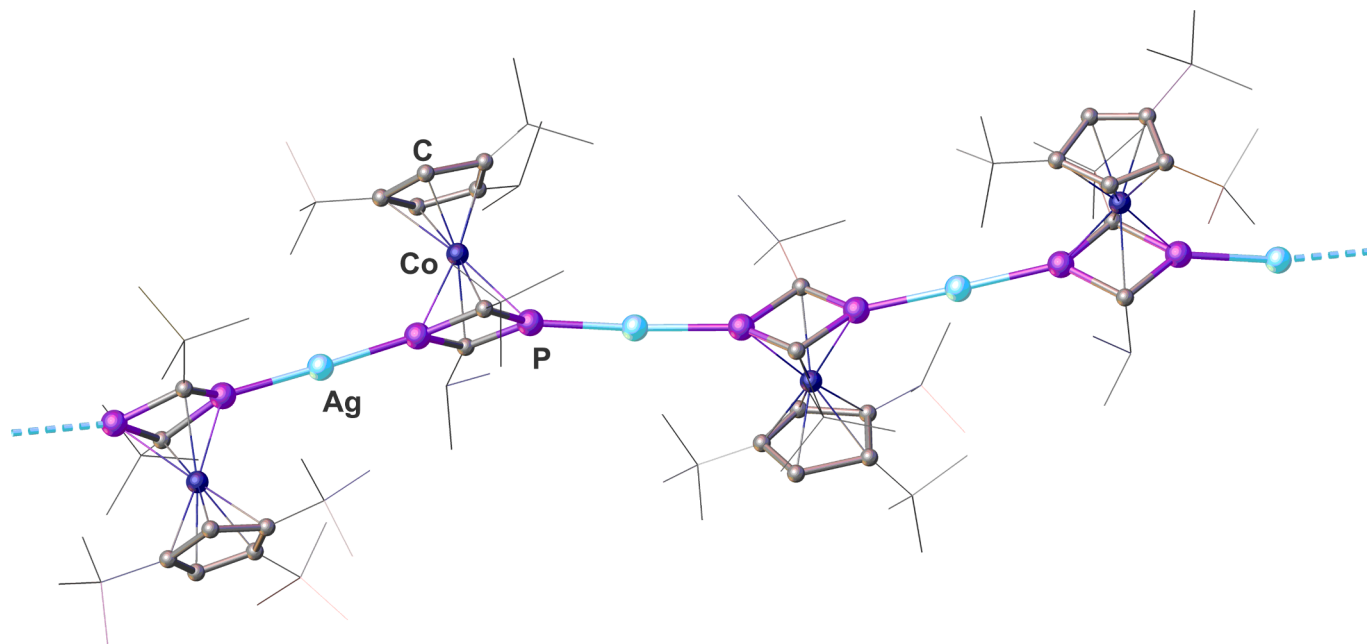


Fig. 1. Ball and stick model of the cationic repeating unit of **2**. tBu substituents are depicted in a wireframe model. Hydrogen atoms and anions (due to their high disorder) are omitted for clarity.

hexane. Finally, it is also worth mentioning that we repeated the reaction of **1** with $\text{Ag}[\text{TEF}]$ using a large variety of experimental conditions. On the basis of these experimental attempts we came to the conclusion

that compounds **2–4** are only accessible in a selective manner when the exact aforementioned reaction conditions are used.

Computational data ($\omega\text{B97X-D4}$ [16]/def2tzvpp [17], Table 1 and

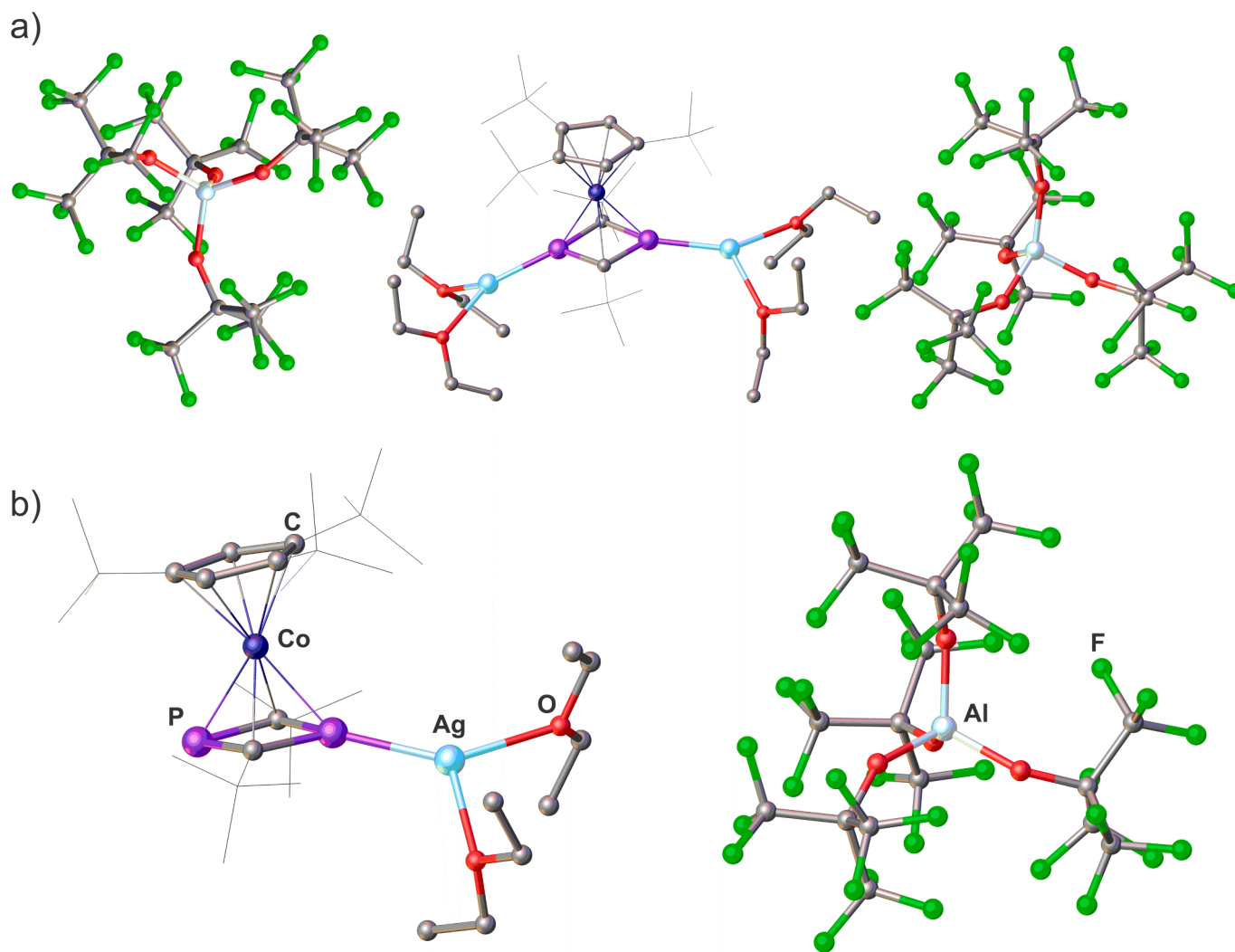


Fig. 2. Molecular structure of a) **3** and b) **4** in the solid state. *t*Bu substituents are depicted in a wireframe model. Hydrogen atoms are omitted for clarity.

Table 1

Calculated Gibbs free energies for the stepwise aggregation of oligomeric species in the reaction mixture of **1** and Ag(I) ions; energies were obtained with the ORCA 5.0 [18] software suite at the ω B97X-D4/def2tzvpp level of theory using implicit solvent correction for CH_2Cl_2 [19]; the $[\text{Ag}(\text{OEt}_2)_3]^+$ is presumed to be the most stable solvate under the given reaction conditions prior to coordination to **1**.

| Reaction | ΔG [kJ/mol] |
|--|---------------------|
| $\mathbf{1} + [\text{Ag}(\text{OEt}_2)_3]^+ \rightarrow \mathbf{4}^+ + \text{Et}_2\text{O}$ | -60.3 |
| $\mathbf{1} + 2 \cdot [\text{Ag}(\text{OEt}_2)_3]^+ \rightarrow \mathbf{3}^+ + 2 \text{Et}_2\text{O}$ | -80.1 |
| $\mathbf{2} \cdot \mathbf{1} + [\text{Ag}(\text{OEt}_2)_3]^+ \rightarrow [\mathbf{1}_2\text{Ag}]^+ + 3 \text{Et}_2\text{O}$ | -82.8 |
| $\mathbf{2} \cdot \mathbf{1} + 2 \cdot [\text{Ag}(\text{OEt}_2)_3]^+ \rightarrow [\mathbf{1}_2\text{Ag}_2]^{2+} + 4 \text{Et}_2\text{O}$ | -113.3 |
| $\mathbf{3} \cdot \mathbf{1} + 2 \cdot [\text{Ag}(\text{OEt}_2)_3]^+ \rightarrow [\mathbf{1}_3\text{Ag}_2]^{2+} + 6 \text{Et}_2\text{O}$ | -88.4 |

Scheme S1 in the ESI show that the stepwise aggregation of **1** and Ag(I) ions to form oligomeric compounds in solution is exergonic. However, the initial binding of one Ag(I) cation to one unit of **1** is by far the most favorable step, explaining the possible selective isolation of **4** at low temperatures. Furthermore, the isolation of **3** can be stoichiometrically controlled, although the addition of a second Ag(I) cation to **4** is exergonic by only -19.8 kJ/mol. The sequential chain elongation towards an oligomer consisting of two units of **1** and two Ag(I) ions is energetically favorable in each step. However, the addition of another unit of **1** to this species in solution is endergonic by 24.9 kJ/mol. Thus, further polymerization is primarily driven by crystal packing effects and the

resulting lattice energy, providing an additional explanation for the experimentally inaccessible interconversion of **2** to **3** and **4**.

In a second step, **1** was reacted with the Ag(I) salt of the more coordinating anion $[\text{BF}_4]^-$ under reaction conditions similar to those used for the formation of the polymer **2**. After layering the crude reaction mixture with *n*-hexane, only a red precipitate was obtained. The crude $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum reveals one broad signal centered at ca. 0 ppm, which is comparable to that of **2**. Unfortunately, all attempts using a variety of solvent mixtures failed to provide any crystalline material. During multiple crystallization workups, traces of moisture apparently entered the Schlenk flask leading to the formation of red crystals of the 1D polymer $[\text{Ag}_2\{\text{Cp}^*\text{Co}(\eta^4\text{-}\eta^1\text{-P}_2\text{C}_2\text{tBu}_2)\}_2(\text{H}_2\text{O})]_n \cdot 2n[\text{BF}_4]$ (**5**) in low yields (10 %) at the solvent boundary. In contrast to polymer **2** in which the $[\text{TEF}]^-$ anions are well separated from the cationic polymeric aggregate, each of the $[\text{BF}_4]^-$ anions in **5** interact with one Ag(I) ion from the polymeric strand via one F atom with Ag-F distances of 2.554 (2) and 2.579(2) Å, respectively. The repeating unit in **5** is composed of two diphosphate units of **1**, two interacting $\text{Ag}[\text{BF}_4]$ and one H_2O molecule coordinated to Ag_2 (2.452(3) Å; Fig. 3). Accordingly, two different coordination geometries for the Ag(I) ions are realized; Ag1: possessing a trigonal planar coordination sphere with two P atoms and one F atom, and Ag2: showing a distorted tetrahedral coordination with two P atoms, one Ag(I) ion and one O atom. The difference in the chemical environments of the Ag(I) ions results in a twisted polymeric strand in **5** with the diphosphate complexes rotating slightly around the

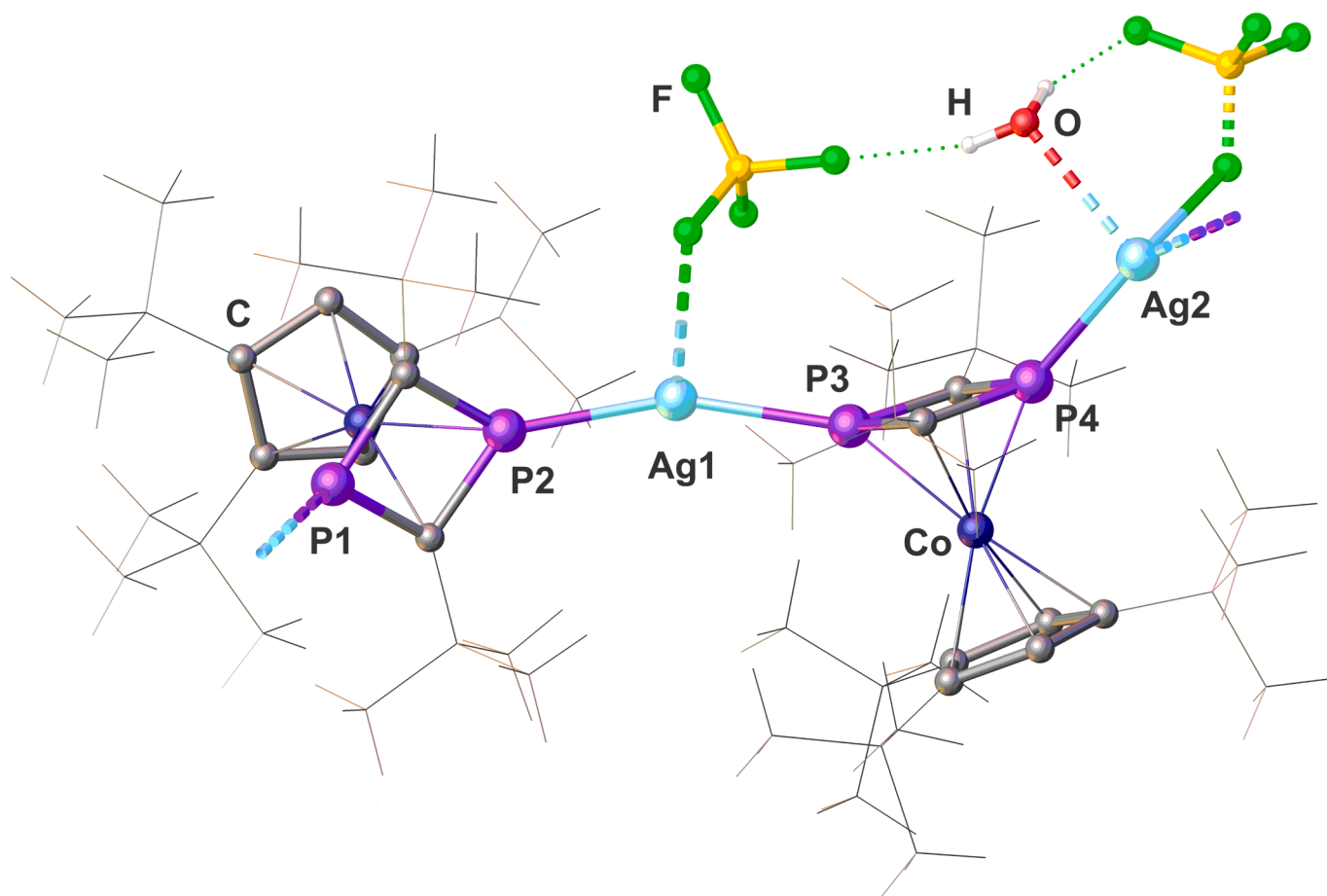


Fig. 3. Molecular structures of **5** in the solid state. *t*Bu substituents are depicted in a wireframe model. Hydrogen atoms on diphosphite ligands are omitted for clarity.

axis containing Ag1 (P2-Ag1-P3 angle of $158.46(5)^\circ$) and largely around the axis containing Ag2 (P1-Ag2-P4 angle of $147.35(5)^\circ$).

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** at room temperature in CH_2Cl_2 reveals one broad singlet at 4.5 ppm which does not reflect the different environments of the P atoms found in the solid state and reveals a up-field shift as compared to those found in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the free diphosphite **1** (23.4 and 41.3 ppm) [13]. This implies an only partial degradation of the polymeric framework of **5** in CH_2Cl_2 . The ^1H NMR spectrum shows signals for the protons of the *t*Bu group of the Cp^{'''} ligand as well as of the coordinated water molecule. Similar to **2**, the ESI-MS spectrum of **5** in CH_2Cl_2 shows peaks for the cationic fragments $[\text{Ag}(\text{I})]^+$ and $[\text{Ag}(\text{I})_2]^+$. Finally, elemental analysis confirms the constitution of **5** in the solid state.

Furthermore, compound **1** was reacted with $\text{Ag}[\text{BF}_4]$ under reaction conditions similar to those that resulted in the isolation of compounds **3** and **4**. However, in all cases, no crystals could be isolated. Notably, in the reaction of **1** with both $\text{Ag}[\text{TEF}]$ and $\text{Ag}[\text{BF}_4]$, a competition between the oxidation of **1** by the Ag(I) salts and the desired coordination reactions was noticed. When the ratio of **1** to Ag(I) is > 1 , no (or little) oxidation is observed. When the ratio of **1** to Ag(I) is ≤ 1 , a black precipitate is formed if the reactions are performed at room or higher temperature, with an apparent oxidation of **1** due to the formation of a layer of Ag(0) on the walls of the reaction vessel. While no structurally characterized compounds similar to **4** and **5** with any diphosphine ligand and Ag(I) salts are found in literature, the group of Morris reported a compound similar to **3** in which one 1,2-bis(diethylphosphino) ethane ligand is coordinated to two $\text{Ag}(\text{OTf})_2$ fragments [20].

The reaction of **1** with $[(\text{THT})_2\text{Au}][\text{TEF}]$ using a 1:1 ratio in CH_2Cl_2 at room temperature followed by layering with *n*-hexane at -30°C

allowed for the formation of a mixture of two types of coordination compounds $[\text{Au}\{\text{Cp}'''\text{Co}(\eta^4:\eta^1\text{-P}_2\text{C}_2\text{tBu}_2)\}_2][\text{TEF}]$ (**6**) and $[\text{Au}_3\{\text{Cp}'''\text{Co}(\eta^4:\eta^1:\eta^1\text{-P}_2\text{C}_2\text{tBu}_2)\}_4]\cdot 3n[\text{TEF}]$ (**7**) (Scheme 2). However, crystals of both compounds could be obtained in pure form from their fractional crystallization because they crystallize at different time intervals. Compound **6** is the first to crystallize, while the mother liquor almost exclusively contains **7**. A mixture of both compounds is also obtained when a ratio of 2:1 of 1: $[(\text{THT})_2\text{Au}][\text{TEF}]$ is used under similar reaction conditions. Compound **6** is a monocationic supramolecular coordination complex (SCC) which is composed of two diphosphite ligands **1** coordinated to a Au(I) ion in an η^1 fashion (Fig. 4a). The two diphosphite moieties are found in a *trans*-configuration towards each other over the linearly coordinated Au(I) center. This structure is related to the previously reported tungsten complex $[(\text{CO})_4\text{W}\{\text{Cp}'''\text{Co}(\eta^4:\eta^1\text{-P}_2\text{C}_2\text{iPr}_2)\}_2]$ (type **G**, Scheme 1) [13]. Compound **7** is an Au(I) trimer stabilized by four ligands **1** with two of them (terminal ones) coordinated through one P atom and two (central ones) via both P atoms in an η^1 -coordination mode (Fig. 4b). The trimer **7** can alternatively be described as composed of two molecules of **6** which are connected to one another via one Au(I) ion and thus assumably could have been aggregated from the latter. To prove the accuracy of this assumption, two equivalents of **6** were reacted with one equivalent of $[(\text{THT})_2\text{Au}][\text{TEF}]$ under reaction conditions similar to those used to obtain the mixture of **6** and **7**. Interestingly, from this reaction, a selective formation of compound **7** with no traces of **6** was realized. The bond lengths in the P_2C_2 four-membered ring in both products resemble those in the starting compound **1**. The Au(I) ions all possess a linear coordination sphere with P-Au-P angles ranging between $175.04(10)^\circ$ and $178.03(11)^\circ$. As compounds **6** and **7** were initially isolated as a mixture, NMR shifts for both compounds can be

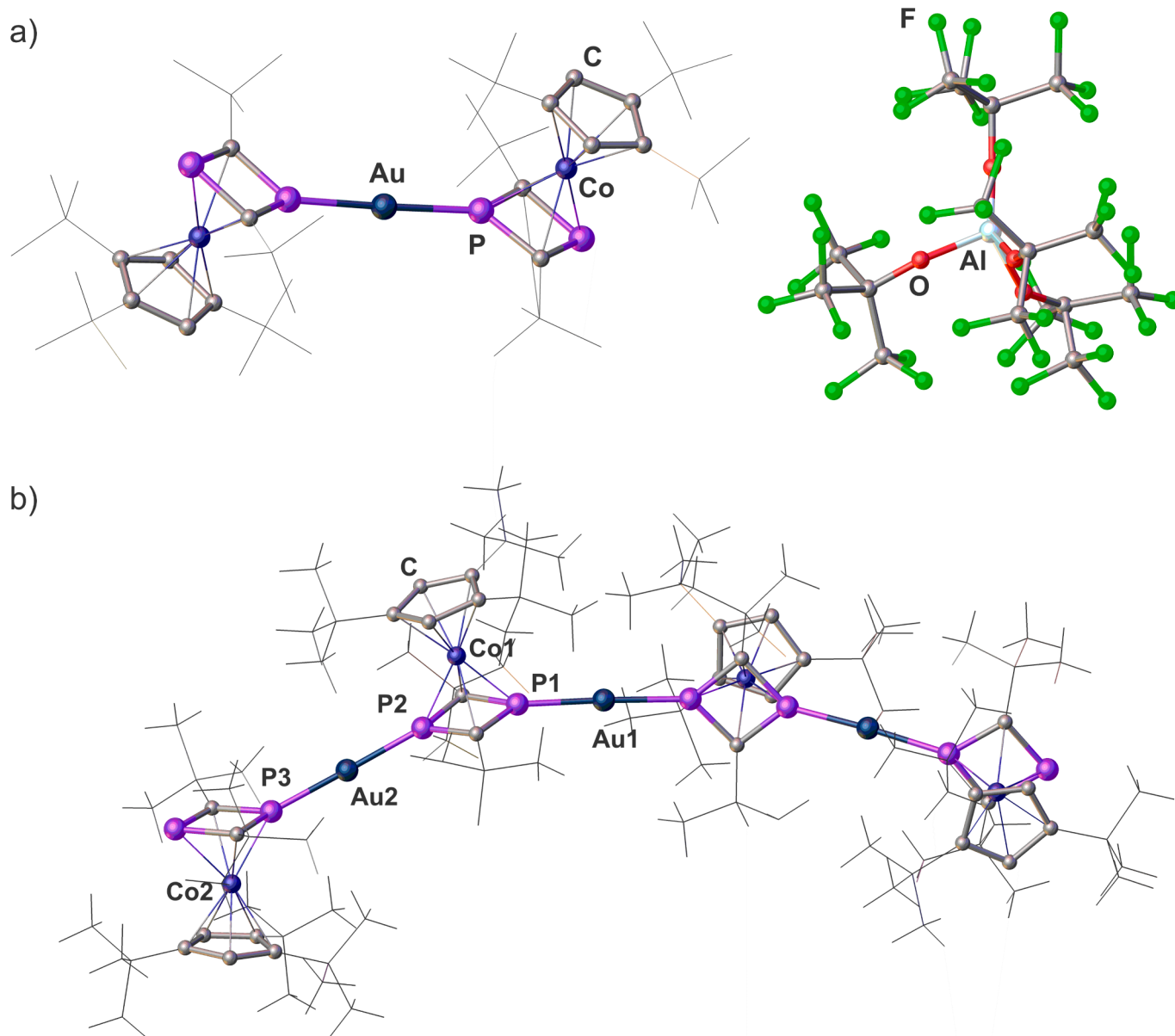


Fig. 4. Molecular structure of a) **6** and b) **7** in the solid state. *t*Bu substituents are depicted in a wireframe model. Hydrogen atoms in **6** and **7** and anions in **7** are omitted for clarity.

found in the crude ^{31}P NMR spectrum of the reaction mixture. The spectrum of pure **6** shows a broad peak at about 0 ppm while that of pure **7** reveals two signals at $\delta = 48.4$ and -15.0 ppm.

The formation of **7** from **6** shows that the latter can be used as a metalloligand to be further employed in a postsupramolecular synthesis. Accordingly, a reaction of **6** with two equivalents of $[(\text{THT})\text{Au}(\text{PPh}_3)]$ [TEF] was performed. As expected, this reaction allowed for the exclusive isolation of the Au(I) trimer $[(\eta^1\text{-PPh}_3)_2\text{Au}_3\{\text{Cp}^*\text{Co}(\eta^4:\eta^1:\eta^1\text{-P}_2\text{C}_2\text{tBu}_2)\}_2]\cdot 3[\text{TEF}]$ (**8**) (Scheme 1, Fig. 5). Single crystal X-ray analysis of **8** shows a Au(I) trimer stabilized by two terminal PPh_3 ligands and two central diphosphite ligands **1** in addition to three non-coordinating $[\text{TEF}]^-$ anions. Thus, two different Au(I) ions exist in **8**. Au1 with a coordination sphere surrounded by one PPh_3 ligand and one complex **1** and Au2 surrounded by two molecules of **1**. The cationic part of **8** could have formed from a simple substitution of two THT ligands from two $[(\text{THT})\text{Au}(\text{PPh}_3)]^+$ moieties with two P atoms from one equivalent of the cationic fragment in **6**. To the best of our knowledge, no compounds similar to **7** and **8** based on any phosphine ligand are known. In contrary,

many examples are found in which two monophosphine ligands are bridged by a Au(I) center [21] and only one phosphine containing compound, similar to **6** is reported [12].

3. Conclusions

In summary, we have demonstrated the potential of the diphosphite complex $[\text{Cp}^*\text{Co}(\eta^4\text{-P}_2\text{C}_2\text{tBu}_2)]$ (**1**) as a metalloligand in its coordination chemistry with $\text{Ag}[\text{TEF}]$ and $[(\text{THT})_2\text{Au}][\text{TEF}]$, respectively. The first reaction showed a high dependence on the temperature at which the reaction is stopped and the products crystallized. When the reaction is allowed to reach room temperature, the 1D polymer $[\text{Ag}\{\text{Cp}^*\text{Co}(\eta^4:\eta^1:\eta^1\text{-P}_2\text{C}_2\text{tBu}_2)\}_n[\text{TEF}]_n$ (**2**) is obtained. However when it is stopped at 0°C or -60°C , the SCCs $[(\text{Et}_2\text{O})_4\text{Ag}_2\{\text{Cp}^*\text{Co}(\mu,\eta^4:\eta^1:\eta^1\text{-P}_2\text{C}_2\text{tBu}_2)\}_2]\cdot 2[\text{TEF}]$ (**3**) and $[(\text{Et}_2\text{O})_4\text{Ag}\{\text{Cp}^*\text{Co}(\mu,\eta^4:\eta^1:\eta^1\text{-P}_2\text{C}_2\text{tBu}_2)\}]\cdot [\text{TEF}]$ (**4**), respectively, could be selectively isolated. DFT calculations gave additional insight into the thermodynamics of this stepwise aggregation process in solution. The coordination of **1** towards the Au(I)

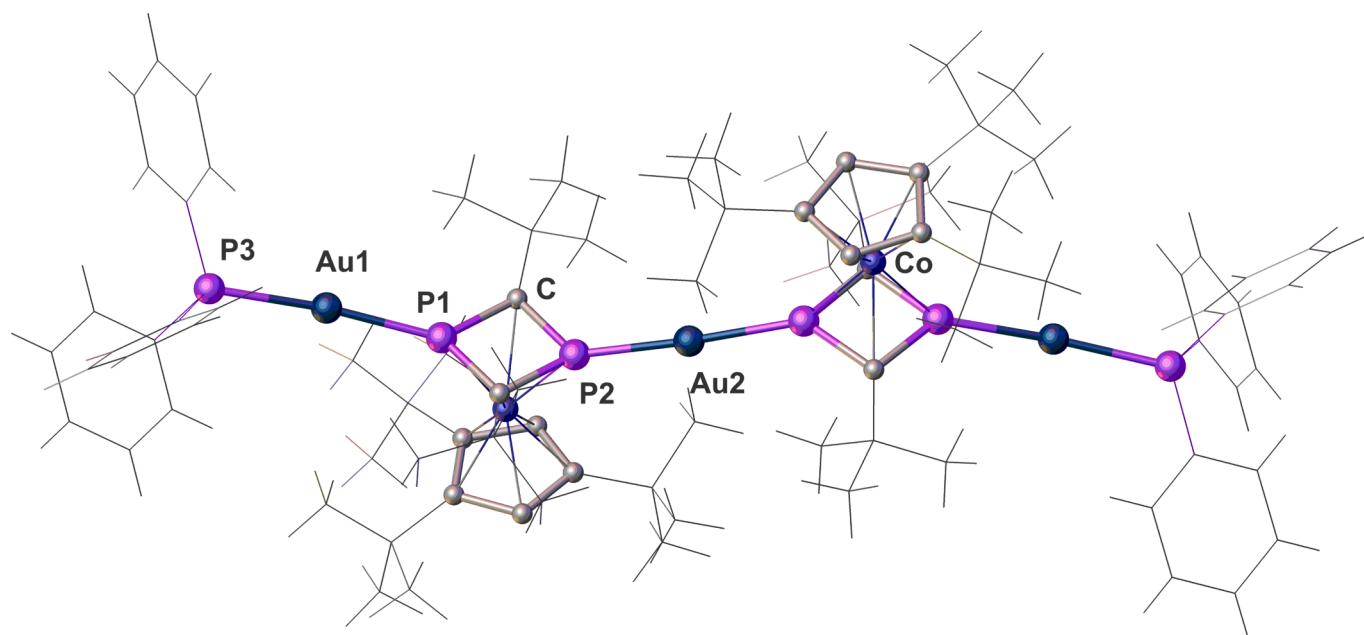


Fig. 5. Molecular structure of complex **8** in the solid state. *t*Bu substituents are depicted in the wireframe model. Hydrogen atoms and anions are omitted for clarity.

salt results in the SCC $[\text{Au}\{\text{Cp}^*\text{Co}(\eta^4\text{-}\eta^1\text{-P}_2\text{C}_2\text{tBu}_2)\}_2][\text{TEF}]$ (**6**). This compound can be further used as a larger metalloligand to react with $[(\text{THT})_2\text{Au}][\text{TEF}]$ or $[(\text{THT})(\text{PPh}_3)\text{Au}][\text{TEF}]$ allowing for the synthesis of the Au(I) trimers $[\text{Au}\{\text{Cp}^*\text{Co}(\eta^4\text{-}\eta^1\text{-P}_2\text{C}_2\text{tBu}_2)\}_4\cdot 3n][\text{TEF}]$ (**7**) and $[(\eta^1\text{-PPh}_3)_2\text{Au}_3\{\text{Cp}^*\text{Co}(\eta^4\text{-}\eta^1\text{-P}_2\text{C}_2\text{tBu}_2)\}_2]\cdot 3[\text{TEF}]$ (**8**), respectively. All the aforementioned compounds are well soluble and thus were thoroughly characterized in solution.

CRediT authorship contribution statement

Mehdi Elsayed Moussa: Investigation. **Eva-Maria Rummel:** Investigation. **Veronika Heini:** Investigation. **Christoph Riesinger:** Data curation. **Manfred Scheer:** Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request and are partially given in the Supporting Informations.

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Appendix A. Supplementary data

CCDC-2367680 (**3**), CCDC-2367681 (**4**), CCDC-2367682 (**5**), CCDC-2367683 (**6**), CCDC-2367684 (**7**) and CCDC-2367685 (**8**) contain the supplementary crystallographic data. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge

CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data to this article can be found online at <https://doi.org/10.1016/j.poly.2024.117227>.

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