Journal of Inorganic and General Chemistry
ZAAC
Zeitschrift für anorganische und allgemeine Chemie
www.zaac.wiley-vch.de
RESEARCH ARTICLE

DOI: 10.1002/zaac.202300242

One-dimensional Polymers derived from a Sterically Demanding 1,3-Diphosphete Complex

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Dedicated to Professor Rhett Kempe on the occasion of his 60th birthday

The 1,3-disphosphete complex [$Cp^{Bn}Co(\eta^4\text{-}P_2C_2tBu_2)$] (**1**) is prepared from the reaction of the sterically demanding [$Cp^{Bn}Co]_n$ ($Cp^{Bn} = C_5(CH_2C_6H_5)_5$) with tert-butyl phosphaalkyne ($tBu{-}C{\equiv}P$). The reaction of **1** with copper halides CuX (X = Cl, Br, I) leads to the formation of one-dimensional coordination polymers of the general formula [$\{(Cp^{Bn}Co)(\mu_3,\eta^{4:1:1}\text{-}(PCtBu)_2)\}\{Cu(\mu\text{-}X)\}_2(MeCN)]_n$ (X = Cl (**2**), Br (**3**), I (**4**)). All compounds are studied in solution by multinuclear NMR spectroscopy and mass spectrometry and in the solid state, by single crystal X-ray diffraction and $^{31}P\{^1H\}$ MAS NMR.

Introduction

Diphosphabutadiene (diphosphete) metal complexes are captivating molecules that are commonly assembled from phosphaalkynes $R{-}C{\equiv}P$.[1] This process can generally lead to both 1,2- and 1,3-diphosphete complexes with the latter being the most common products although the 1,2-diphosphetes are energetically favored.[2] The first diphosphete complexes date back to the year 1986 when the groups of Regitz[3] and Nixon[4] discovered the 1,3-diphosphete complexes [$Cp^RCo(\eta^4\text{-}P_2C_2tBu_2)$] (R = H, Me) concurrently. Ever since, numerous heteroleptic, and to a lesser extent, homoleptic diphosphete complexes have been synthesized.[5] The majority of these compounds contain relatively small Cp ligands which could be introduced by using the analogous bis-ethylene complexes in the reaction with phosphaalkynes. To this field, our group contributed by developing a new synthetic pathway to 1,3-diphosphetes starting from the triple decker complex [$(Cp'''Co)_2(\eta^4{:}\eta^4\text{-}C_7H_8)$] ($Cp''' = 1,2,4\text{-}C_5H_2(tBu)_3$), which dissociates in solution to 14 VE $Cp'''Co$ moieties.[6] These fragments react nearly quantitatively with different phosphaalkynes leading to targeted 1,3-diphosphete derivatves.[7] Bulkier substituents on the Cp moiety, however, have not yet been used in the synthesis of these species. Following one of the major research directions of our group regarding the coordination chemistry of complexes bearing unsubstituted pnictogen donor atoms,[8] we were interested in studying the coordination behavior of 1,3-diphosphete compounds towards transition metal ions. In the reaction of [$Cp'''Co(\eta^4\text{-}P_2C_2tBu_2)$] (**A**) with copper halides, we showed that depending on the Cu(I):**A** ratio used, different reaction products could be obtained. Accordingly, dimeric complexes were isolated as well as one- and two-dimensional polymers (Figure 1).[7] Based on these results, we targeted the synthesis of 1,3-diphosphete complexes bearing even bigger, sterically more demanding Cp^R ligands and sought to explore their coordination behaviour towards Lewis acidic metal centers. Herein, we present the synthesis of a 1,3-diphosphete complex possessing the pentabenzylcyclopentadienyl ligand (Cp^{Bn}). The reaction of this complex with copper halides leads to the isolation of new one-dimensional coordination polymers.

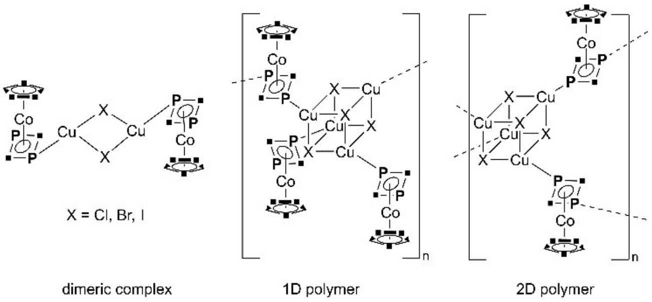

Figure 1. Dimeric complexes [$(Cp'''Co)(\mu,\eta^{4:1}\text{-}\{PCtBu\}_2)Cu(\mu\text{-}X)]_2$; 1D polymers [$(Cp'''Co)(\mu_3,\eta^{4:1:1}\text{-}\{PCtBu\}_2)(\{Cp'''Co\}\{\mu,\eta^{4:1}\text{-}(PCtBu)_2\})(Cu\{\mu_3\text{-}X\})_4]_n$ and 2D polymers [$(\{Cp'''Co\}\{\mu_3,\eta^{4:1:1}\text{-}(PCtBu)_2\})_2(Cu\{\mu_3\text{-}X\})_4]_n$ (X = Cl, Br, I).

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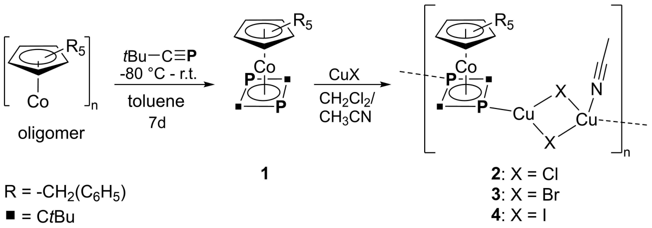
[+] Parts of this work are part of the dissertation of M. Parzefall: M. Eckhardt, PhD. thesis, University of Regensburg, 2015.

Supporting information for this article is available on the WWW under https://doi.org/10.1002/zaac.202300242

Results and Discussion

Tert-butyl phosphaalkyne (tBu–C≡P) was reacted with $[\mathrm{Cp^{Bn}Co}]_n$[9] (an oligomer in the solid state, existing in solution as a 14 VE species) using a 2:1 ratio in toluene at −80 °C. This reaction, left to reach room temperature and stirred for one week followed by column chromatographic workup, led to the 1,3-diphosphete complex $[\mathrm{Cp^{Bn}Co}(\eta^4\text{-}\mathrm{P_2C_2}t\mathrm{Bu_2})]$ (**1**, Scheme 1). Single crystals of **1** could be obtained as orange bars in yields of 26% when stored in $\mathrm{Et_2O}$ at −30 °C (Figure 2). The molecular structure of **1** represents a heteroleptic complex similar to the reported Cp′′′-derivatives $[\mathrm{Cp'''Co}(\eta^4\text{-}\mathrm{P_2C_2}t\mathrm{Bu_2})]$ (**A**) and $[\mathrm{Cp'''Co}(\eta^4\text{-}\mathrm{P_2C_2}i\mathrm{Pr_2})]$ (**B**)[7] and features η^4-coordinated diphosphacyclobutadiene and η^5-coordinated $\mathrm{Cp^{Bn}}$ ligands. The 1,3-diphosphete moiety in **1** is essentially planar with a torsion angle P1-C1-P2-C2 of 3.14(8)°; the C–P bond lengths correspond to a delocalized π-electron system.

Compound **1** is soluble in all common organic solvents. Its room temperature $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR in $\mathrm{C_6D_6}$ shows a singlet at $\delta = 35.3$ ppm, which is in accord with common rotational dynamics of $\mathrm{Cp^R}$-complexes. A similar situation could be observed for the reported complex **B** ($\delta = 41.3$ ppm) in solution. However, in the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ MAS NMR spectrum of **1**, two singlets at $\delta = 28.7$ and 39.5 ppm are found for the two different phosphorus atoms in the solid state. In the EI mass spectrum, the molecular ion peak is found at m/z = 774.3 Da and elemental analysis agrees well with the correct composition for **1** established from the X-ray data.



Scheme 1. Synthesis of the 1,3-diphosphete complex **1** and its subsequent reaction with Cu(I)X (X = Cl, Br, I) leading to the 1D coordination polymers **2–4**.

When a solution of **1** in $\mathrm{CH_2Cl_2}$ is mixed with $\mathrm{CH_3CN}$ solutions of CuX (X = Cl, Br, I), an instant precipitation of the compounds **2–4** occurs. These products are obtained selectively, as in each case, according to their $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra, only one signal is detected (17.0 ppm (**2**), 18.6 (**3**), and 13.3 ppm (**4**)), upfield shifted as compared to that of **1**. Single crystals of **2–4** were obtained within three weeks when a solution of **1** in $\mathrm{CH_2Cl_2}$ was layered with $\mathrm{CH_3CN}$ solutions of CuX, however in a rather low crystalline yield (4–17%). Their molecular structures reveal one-dimensional (1D) coordination polymers with the general formula $[\{(\mathrm{Cp^{Bn}Co})(\mu^3,\eta^{4:1:1}\text{-}(\mathrm{PC}t\mathrm{Bu})_2)\}\{\mathrm{Cu}(\mu\text{-X})\}_2(\mathrm{MeCN})]_n$ (X = Cl (**2**), Br (**3**), I (**4**)). In contrast to what was observed for the reactions of **A** and **B** with CuX,[7] the polymers **2–4** are the only isolated solid-state products regardless of the stoichiometry of the reactants and the solvent used. Crystalline products are obtained as orange prisms or needles (Figure 3, for further information see ESI). The 1D polymeric chains of **2–4** are based on the coordination of copper atoms of the $\mathrm{Cu_2X_2}$ dimers by the phosphorus atoms of the 1,3-diphosphete ligands. Additionally, one copper atom in the $\mathrm{Cu_2X_2}$ dimer is coordinated by a $\mathrm{CH_3CN}$ solvent molecule, giving rise to the distorted tetrahedral coordination sphere of Cu1 connected to two halides, one P atom and one N atom of

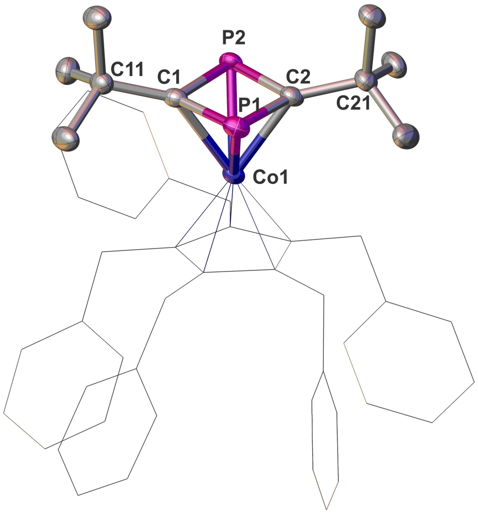


Figure 2. Molecular structure of **1** in the solid state. H atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C1 1.7886(16), P1–C2 1.7935(15), P2–C1 1.7939(15), P2–C2 1.7894(16), C1–C11 1.511(2), C2–C21 1.512(2), $[\mathrm{Cp^{Bn}}]_{\mathrm{Cent}}$–Co1 1.6844(3), $[\mathrm{C_2P_2}]_{\mathrm{Cent}}$–Co1 1.7659(3); C1–P1–C2 80.93(7), C1–P2–C2 80.90(7).

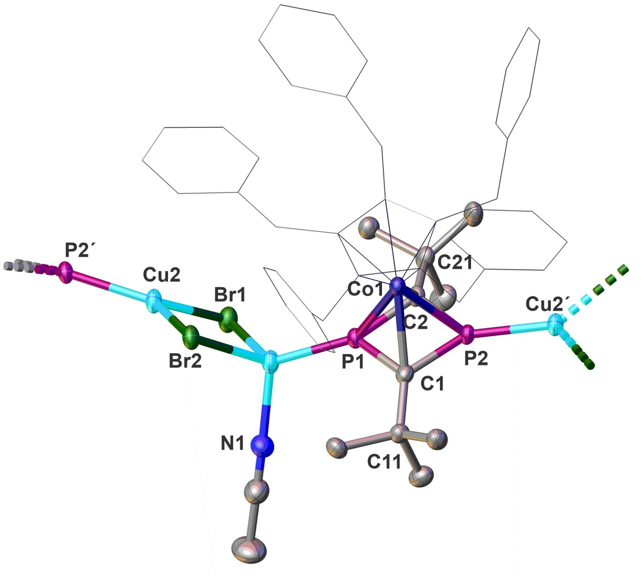


Figure 3. Section of the polymeric structure of **3** (**2** and **4** have similar (isotypic) structures) in the solid state. H atoms and solvent molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1–C1 1.768(6), P2–C1 1.789(6), P1–Cu1 2.196(2), P2–Cu2′ 2.172(2), Cu1–Br1 2.5431(11), $[\mathrm{Cp^{Bn}}]_{\mathrm{Cent}}$–Co1 1.677(1), $[\mathrm{C_2P_2}]_{\mathrm{Cent}}$–Co1 1.771(1); C2–P1–C1 83.3(3), P1–C1–P2 96.9(3).

the acetonitrile ligand and a distorted trigonal planar coordination sphere of Cu2, consisting of two halides and one P atom. The P–C bond lengths (1.768(6)-1.788(4) Å) in the P_2C_2 four-membered rings in **2**–**4** vary very little compared to those in the free complex **1** (1.789(2)-1.794(2) Å). Thus, the coordination of **1** to Lewis acidic copper atoms does not considerably affect the delocalised π-system of the diphosphete moiety. In the coordination product of **A** and CuX, a one-dimensional structural motif also occurs in [μ$_2$-**A**,μ-**A**(Cu{μ$_3$-X})$_4$]$_n$ (**C**, X = Cl, Br, I). However, in contrast to **2**–**4**, the Cu and X atoms in **C** do not form a Cu_2X_2 dimer, but a Cu_4X_4 cubane fragment with 1,3-diphosphete complexes at Cu vertices.

Crystals of the polymeric compounds **2**–**4** are soluble in CH_3CN or in a mixture of CH_2Cl_2 and CH_3CN. Their ^{31}P{^{1}H} NMR spectra show the same signals as those recorded for their crude reaction mixtures. The ^{31}P{^{1}H} MAS NMR spectra do not show separated singlets for the different phosphorus atoms in **2**–**4** similar to those observed for **1**, but only broad signals (**2**: δ −18.2 ppm, $\omega_{1/2}$ = 5280 Hz, **3**: δ 6.1 ppm, $\omega_{1/2}$ = 6486 Hz, **4**: δ −3.0 ppm, $\omega_{1/2}$ = 2745 Hz). The ESI mass spectra of the polymeric compounds show different fragments and ratios of **1** and Cu and the corresponding halide X up to masses of m/z = 3755.9 Da for **2** (attributed to [(**1**)$_4$Cu$_7$Cl$_6$]$^+$), 3103.7 Da for **3** (attributed to [(**1**)$_3$Cu$_6$Br$_5$]$^+$) and 3337.6 Da for **4** (attributed to [(**1**)$_3$Cu$_6$I$_5$]$^+$). This leads to the conclusion that a fragmentation, but not a complete degradation, of the polymeric structures takes place for all products **2**–**4**. However, the 1D polymers can be recrystallized from solutions (if CH_3CN is present) and the thus formed crystals exhibit the same unit cell constants as the initial compounds. A similar behavior was also found for other polymeric coordination compounds derived from 1,3-diphosphete complexes and Cu(I) halides.[7]

Conclusion

The reaction of [Cp^{Bn}Co]$_n$ with *tert*-butyl phosphaalkyne lead to the straightforward formation of the heteroleptic 1,3-diphosphete complex [Cp^{Bn}Co(η^4-P$_2$C$_2$*t*Bu$_2$)] (**1**) which is a rare example of a diphosphete complex bearing such a sterically demanding Cp^R ligand. The subsequent reaction of **1** with Lewis acidic Cu(I) halides leads to the formation of the one-dimensional coordination polymers [{(Cp^{Bn}Co)(μ$_3$,η$^{4:1:1}$-(PC*t*Bu)$_2$)}{Cu(μ-X)}$_2$(MeCN)]$_n$ (X = Cl (**2**), Br (**3**), I (**4**)). NMR spectroscopy studies of the crude reaction mixtures show that selective reactions occur, however, products **2**–**4** could only be isolated as crystalline material in low yields what might be caused by the high solubility of the oligomers present in solution. In addition, mass spectrometry data show that a fragmentation of the polymeric structures takes place in solution. They can, however, be re-crystallized from those solutions to form the isostructural products they were dissolved from.

Experimental Section

All manipulations were performed by using standard Schlenk techniques under the atmosphere of N_2 with the rigorous exclusion of oxygen and moisture. All solvents were dried by using standard procedures and distilled freshly before use. Compounds [Cp^{Bn}Co]$_n$[9] and *t*BuC≡P[10] were synthesized according to known procedures. Commercial Cu(I) halides were stored under argon and used as received. Deuterated solvents were dried and distilled prior to use. NMR spectra were recorded with a Bruker Avance 400 spectrometer (^{1}H: 400.130 MHz, ^{31}P: 161.976 MHz, ^{13}C: 100.613 MHz) at ambient temperature. The chemical shifts are reported in ppm relative to tetramethylsilane or phosphoric acid. Elemental analyses (CHN) were determined by using a Vario EL III instrument. FD mass spectra were measured with a Finnigan MAT95 spectrometer. ^{31}P{^{1}H} MAS NMR spectra were recorded with a Bruker Advance 300 spectrometer equipped with a double resonance 2.5 mm MAS probe. The ^{31}P{^{1}H} resonance was 121.495 MHz. The spectra were obtained at MAS rotation frequencies of 30 and 34 kHz, a 90° pulse length of 2.3 μs, and with relaxation delays between 120 and 450 s.

[Cp^{Bn}Co(η^4-P$_2$C$_2$*t*Bu$_2$)] (1): A solution of 0.8 mmol *t*BuC≡P (0.1 mL) in 20 mL toluene is cooled to −80 °C. A solution of 0.4 mmol [Cp^{Bn}Co]$_n$ (230 mg) in 60 mL toluene is added and the reaction mixture is left to reach room temperature and subsequently stirred for a week. After that, the reaction mixture is filtered over silica and the solvent is removed in vacuo. A few mL of Et_2O are added to the residue and the mixture is left to crystallize at −30 °C. **1** crystallizes as orange bars. Yield: 80 mg (26 %). ^{1}H NMR (C_6D_6): δ [ppm] = 1.22 (s, 18 H, C$_2$*t*Bu$_2$P$_2$)), 4.18 (s, 10 H, CH_2), 6.73–6.86 (m, 25 H, C_6H_5); ^{31}P{^{1}H} NMR (C_6D_6): δ [ppm] = 35.3 (s); ^{31}P{^{1}H} MAS NMR: δ [ppm] = 28.7 (s), 39.5 (s); EI MS (70 eV, n-hexane): m/z (%) = 774.3 (98.5) [Cp^{Bn}Co-(η^4-P$_2$C$_2$*t*Bu$_2$)]$^+$, 574.3 (100) [Cp^{Bn}Co]$^+$, 483.3 (37.0) [$C_5(CH_2C_6H_5)_4Co$]$^+$, 392.3 (3.3) [$C_5(CH_2C_6H_5)_3Co$]$^+$; Elemental analysis calculated for $C_{50}H_{53}CoP_2$ (774.84 g mol^{-1}): C 77.50 H 6.89, found: C 77.21 H 6.78.

[{(Cp^{Bn}Co)(μ$_3$,η$^{4:1:1}$-(PC*t*Bu)$_2$)}$_2$Cu(μ-X)(MeCN)]$_n$ (X = Cl (2), Br (3), I (4)): A solution of 0.32 mmol **1** (248 mg) in 6 mL CH_2Cl_2 is layered with a solution of 0.64 mmol CuX (CuCl: 64 mg, CuBr: 103 mg, CuI: 122 mg) in 8 mL CH_3CN. After one day, a dark yellow ring of microcrystalline powder is formed at the phase boundary. To obtain single crystals of **2**–**4**, the microcrystalline powder of **2**–**4** is taken up in a hot mixture of 10 mL CH_2Cl_2 and 10 mL CH_3CN and filtered subsequently. The solutions are stored at room temperature with **2**–**4** crystallizing as orange prisms or needles. Crystalline yields: **2**: 12 mg (4 %); **3**: 58 mg (17 %); **4**: 15 mg (4 %). Compounds **2**–**4** are obtained quantitatively from the direct mixing of **1** in CH_2Cl_2 and the copper halides in CH_3CN.

[{(Cp^{Bn}Co)(μ$_3$,η$^{4:1:1}$-(PC*t*Bu)$_2$)}$_2$Cu(μ-Cl)(MeCN)]$_n$ (2): ^{1}H NMR (CD_2Cl_2/CD_3CN): δ [ppm] = 1.07 (s, 18 H, C$_2$*t*Bu$_2$P$_2$)), 4.01 (s, 10 H, CH_2), 6.62–6.60 (m, 10 H, C_6H_5), 6.90–6.81 (m, 15 H, C_6H_5); ^{31}P{^{1}H} NMR (CD_2Cl_2/CD_3CN): δ [ppm] = 17.0 (s); ^{31}P{^{1}H} MAS NMR: δ [ppm] = −18.2 (bs, $\omega_{1/2}$ = 5280 Hz); ESI MS (CH_3CN, L = **1**): m/z (%) = 3755.9 (10.8) [$L_4Cu_7Cl_6$]$^+$, 3654.8 (28.8) [$L_4Cu_6Cl_5$]$^+$, 3555.2 (29.4) [$L_4Cu_5Cl_4$]$^+$, 3459.2 (44.1) [$L_4Cu_4Cl_3$]$^+$, 2782.4 (6) [$L_3Cu_5Cl_4$]$^+$, 2684.7 (9) [$L_3Cu_4Cl_3$]$^+$, 2584.4 (3.5) [$L_3Cu_3Cl_2$]$^+$, 2485.0 (1.1) [L_3Cu_2Cl]$^+$, 1811.2 (5.9) [$L_2Cu_3Cl_2$]$^+$, 1711.4 (1.4) [L_2Cu_2Cl]$^+$, 1612.5 (1.3) [L_2Cu]$^+$, 937.1 (6.8) [LCu_2Cl]$^+$, 837.2 (100) [LCu]$^+$; Elemental analysis calculated for $C_{50}H_{53}CoCu_2Cl_2P_2$ (972.83 g mol^{-1}): C 61.73 H 5.49; found: C 61.97 H 5.78.

[{(Cp^{Bn}Co)(μ$_3$,η$^{4:1:1}$-(PC*t*Bu)$_2$)}$_2$Cu(μ-Br)(MeCN)]$_n$ (3): ^{1}H NMR (CD_2Cl_2/CD_3CN): δ [ppm] = 1.15 (s, 18 H, C$_2$*t*Bu$_2$P$_2$)), 4.11 (s, 10 H, CH_2), 6.67 (m, 10 H, C_6H_5), 6.96–6.86 (m, 15 H, C_6H_5); ^{31}P{^{1}H} NMR (CD_2Cl_2/CD_3CN): δ [ppm] = 18.6 (s); ^{31}P{^{1}H} MAS NMR: δ [ppm] = 6.1 (bs, $\omega_{1/2}$ = 6486 Hz); ESI MS (CH_3CN, L = **1**): m/z (%) = 3103.7 (22.8) [$L_3Cu_6Br_5$]$^+$, 2961.3 (94.2) [$L_3Cu_5Br_4$]$^+$, 2817.4 (100) [$L_3Cu_4Br_3$]$^+$, 2674.7 (79.2) $[L_3Cu_3Br_2]^+$, 2042.9 (1.0) $[L_2Cu_4Br_3]^+$, 1900.1 (7.9) $[L_2Cu_3Br_2]^+$, 1755.6 (1.2) $[L_2Cu_2Br]^+$, 1612.7 (0.1) $[L_2Cu]^+$, 1124.9 (4.6) $[L_3Br_2]^+$, 1022.2 (23.4) $[LCu_2Br+CH_3CN]^+$, 981.1 (6.5) $[LCu_2Br]^+$, 837.3 (100) $[LCu]^+$.

$[\{(Cp^{Bn}Co)(\mu_3,\eta^{4:1:1}\text{-}(PC\mathit{t}Bu)_2)\}_2Cu(\mu\text{-}I)(MeCN)]_n$ (4): ^1H NMR (CD_2Cl_2/CD_3CN): δ [ppm] = 1.12 (s, 18 H, $C_2\mathit{t}Bu_2P_2$)), 4.06 (s, 10 H, CH_2), 6.62–6.60 (m, 10 H, C_6H_5), 6.90–6.80 (m, 15 H, C_6H_5); $^{31}P\{^1H\}$ NMR (CD_2Cl_2/CD_3CN): δ [ppm] = 13.3 (s); $^{31}P\{^1H\}$ MAS NMR: δ [ppm] = −3.0 (bs, $\omega_{1/2}$ = 2745 Hz); ESI MS (CH_3CN, L = **1**): m/z (%) = 3337.6 (7.7) $[L_3Cu_6I_5]^+$, 3148.0 (7.7) $[(Cp^{bn}Co(\eta^4\text{-}P_2C_2\mathit{t}Bu_2))_3Cu_5I_4]^+$, 2958.0 (5.4) $[(Cp^{Bn}Co(\eta^4\text{-}P_2C_2\mathit{t}Bu_2))_3Cu_4I_3]^+$, 2766.5 (3.4) $[(Cp^{Bn}Co(\eta^4\text{-}P_2C_2\mathit{t}Bu_2))_3Cu_3I_2]^+$, 1992.8 (10.3) $[(Cp^{bn}Co(\eta^4\text{-}P_2C_2\mathit{t}Bu_2))_2Cu_3I_2]^+$, 1804.1 (1.5) $[(Cp^{bn}Co(\eta^4\text{-}P_2C_2\mathit{t}Bu_2))_2Cu_2I]^+$, 1612.2 (1.3) $[(Cp^{Bn}Co(\eta^4\text{-}P_2C_2\mathit{t}Bu_2))_2Cu]^+$, 1216.9 (4.1) $[(Cp^{Bn}Co(\eta^4\text{-}P_2C_2\mathit{t}Bu_2))Cu_3I_2]^+$, 1070.1 (14) $[(Cp^{Bn}Co(\eta^4\text{-}P_2C_2\mathit{t}Bu_2))Cu_2I]^+$, 837.3 (100) $[(Cp^{Bn}Co(\eta^4\text{-}P_2C_2\mathit{t}Bu_2))Cu]^+$; Elemental analysis calculated for $C_{50}H_{53}CoCu_2I_2P_2$ (1155.74 $g\,mol^{-1}$): C 51.96 H 4.62; found: C 51.54 H 4.79.

Crystallographic data. Deposition numbers CCDC-2239365 (**1**), CCDC-2239368 (**2**), CCDC-2239366 (**3**), CCDC-2239367 (**4**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft within the project Sche 384/25-2. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: 1,3-diphosphete · coordination polymer · copper · cobalt · phosphaalkynes

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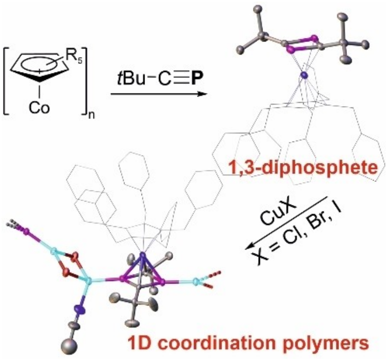
Manuscript received: December 11, 2023
Revised manuscript received: January 2, 2024
Accepted manuscript online: January 5, 2024



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One-dimensional Polymers derived from a Sterically Demanding 1,3-Diphosphete Complex