The Diphosphorus Complex $[Cp_2Cr_2(CO)_4(\eta^2\text{-}P_2)]$ as a Building Block in the Coordination Chemistry of Silver

Mehdi Elsayed Moussa,[a] Stephan Welsch,[a] Laurence J. Gregoriades,[a] Gábor Balázs,[a] Michael Seidl[a] and Manfred Scheer*[a]

Dedicated to Professor Wolfgang Bensch on the occasion of his 65th birthday

Abstract: *The reaction of the tetrahedral diphosphorus complex* $[Cp_2Cr_2(CO)_4(\eta^2\text{-}P_2)]$ *(Cp = C_5H_5) (**2**) with* $Ag[Al\{OC(CF_3)_3\}_4]$ *(AgTEF) (**3**) leads to the formation of the Ag^I dimer* $[Ag_2(\eta^2\text{-}\mathbf{2})(\eta^1\text{-}\mathbf{2})(\eta^1{:}\eta^1\text{-}\mathbf{2})_2][TEF]_2$ *(**5**). This dimer can be used as a suitable precursor for the synthesis of the unprecedented 1D organometallic-organic hybrid polymer* $[Ag_2(\eta^1\text{-}\mathbf{2})_2(\eta^1{:}\eta^1\text{-}\mathbf{2})_2\{\mu,\eta^1{:}\eta^1\text{-}(C_8H_4N_2)\}]_n[TEF]_{2n}$ *(**8**) upon its reaction with 1,4-dicyanobenzene (**7**). The driving force for this supramolecular assembly reaction is supported by DFT calculations.*

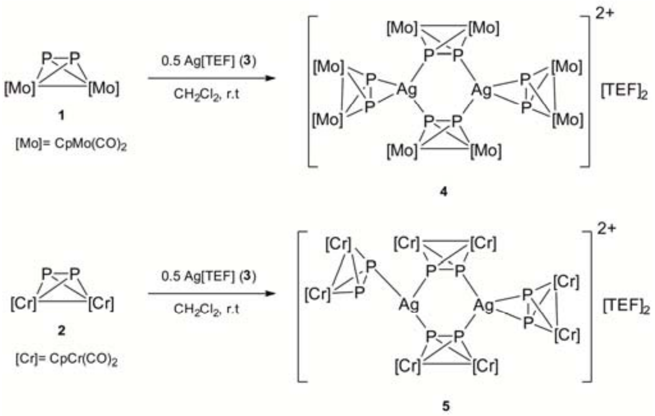
Introduction

The design and construction of discrete and polymeric supramolecular architectures through metal-directed self-assembly have attracted great attention in the past few decades.[1] Commonly, a large variety of metal centers are connected by suitable N-, O- and/or S-donor-containing organic molecules as linkers.[2] In our group, however, an alternative approach was developed by using polyphosphorus(P_n) and polyarsenic(As_n)-donating organometallic ligand complexes with flexible coordination modes as linkers between metal ions.[3] This novel method allows the synthesis of 1D, 2D or even 3D coordination polymers (CPs),[4] giant fullerene-like inorganic spherical aggregates[5] and organometallic nanosized capsules.[6] Recently, an additional interest in these organometallic ligand complexes emerged, as, for example, the tetrahedrane complex $[Cp_2Mo_2(CO)_4(\eta^2\text{-}P_2)]$ (Cp = C_5H_5) (**1**) was used in a mixed-ligand reaction together with Ag^I or Cu^I salts and ditopic pyridine-based linkers to form unprecedented organometallic-organic hybrid CPs.[7] Our interest in investigating the possibility to design a new class of hybrid CPs was therefore sparked. One way to do so is to change the nature of the P_2 ligand complex used (e.g. $[Cp_2Cr_2(CO)_4(\eta^2\text{-}P_2)]$ instead of $[Cp_2Mo_2(CO)_4(\eta^2\text{-}P_2)]$). Another possibility is to change the kind of organic linker involved (cyano-based linkers instead of pyridine-based linkers). However, $[Cp_2Cr_2(CO)_4(\eta^2\text{-}P_2)]$ (**2**) is less stable than its molybdenum analogue (**1**) and readily undergoes fragmentation reactions.[8] For that reason, its coordination chemistry has so far only been studied to a very limited extent compared to its molybdenum analogue (**1**).[9] On the other hand, cyano-based linkers are weaker donors than pyridine-based linkers. Nevertheless, we focused on both these challenges and targeted the design of a new class of hybrid CPs based on the chromium-containing ligand complex **2** and cyano-based organic linkers. We report herein the synthesis of the first coordination complex of **2** towards Ag^I with the formula $[Ag_2(\eta^2\text{-}\mathbf{2})(\eta^1\text{-}\mathbf{2})(\eta^1{:}\eta^1\text{-}\mathbf{2})_2][TEF]_2$ (**5**), which according to DFT calculations reveals an unprecedented different coordination geometry at the two Ag atoms. Independent of its limited stability in solution, the dimer **5** can be used as a suitable precursor for the synthesis of the unique organometallic-organic hybrid CP $[Ag_2(\eta^1\text{-}\mathbf{2})_2(\eta^1{:}\eta^1\text{-}\mathbf{2})_2\{\mu,\eta^1{:}\eta^1\text{-}(C_8H_4N_2)\}]_n[TEF]_{2n}$ (**8**) upon its reaction with 1,4-dicyanobenzene. To the best of our knowledge, no other organometallic-organic hybrid polymer based on unsubstituted P_n complexes and nitrile linkers have yet been reported. Moreover, the gas phase structure of **5** and the driving force for the formation of the supramolecular aggregate **8** are studied by DFT calculations.

Results and Discussion

The P_2 ligand complex **2** was reacted with $Ag[Al\{OC(CF_3)_3\}_4]$ (AgTEF) (**3**), since the use of this well soluble anion generally offers the advantage of the solubility of the reaction compounds in common organic solvents.[10] This reaction, carried out in CH_2Cl_2 at room temperature with a 2:1 stoichiometric ratio, leads to the isolation of the complex **5** as dark wine red powder in good yields (82%, Scheme 1). Interestingly, compound **5** is the only isolated product from similar reactions using **2** and **3** in different stoichiometric ratios or in the presence of an excess of **2**.

Complex **5** is light- and air-sensitive and is soluble in CH_2Cl_2, THF and CH_3CN. Solutions of this compound slowly decompose, even at low temperatures (-28 °C), and the more stable solid



Scheme 1. Reactions of **1** and **2** with $Ag[Al\{OC(CF_3)_3\}_4]$ (**3**) leading to the dimers **4** and **5**.

---

[a] Dr. M. E. Moussa, Dr. S. Welsch, Dr. L. J. Gregoriades, Dr. G. Balázs, Dr. M. Seidl, Prof. Dr. M. Scheer
Institut für Anorganische Chemie der Universität Regensburg,
93040 Regensburg (Germany)
E-mail: manfred.scheer@chemie.uni-regensburg.de

Supporting information for this article is given via a link at the end of the document.

samples should be stored under an inert atmosphere below room temperature, preferably in a freezer (below -30°C). Probably due to this instability and despite several attempts, we were not successful in obtaining single crystals of **5** under various crystallization conditions. The elemental analysis of **5** confirms a 2:1 stoichiometry of **2** and the Ag^{I} salt. This information in addition to the fact that **2** was shown to react with CuX (X = Cl, Br, I) in an identical manner to that of its molybdenum analogue **1**[9] suggest that the structure of **5** is similar to that of **4** (Scheme 1). Based on this information, DFT calculations have been performed at the RI-B3LYP/def2-TZVP level of theory in the gas phase. Surprisingly, these calculations show that the stable geometry of the dimer **5** (Figure 1) is different from that already reported for its molybdenum analogue **4**. In contrast to **4**, the two terminal ligands $[Cp_2Cr_2(CO)_4(\eta^2\text{-}P_2)]$ (**2**) in the dimer **5** possess different coordination modes: one revealing an η^2-coordination mode while the other one shows an η^1-coordination.

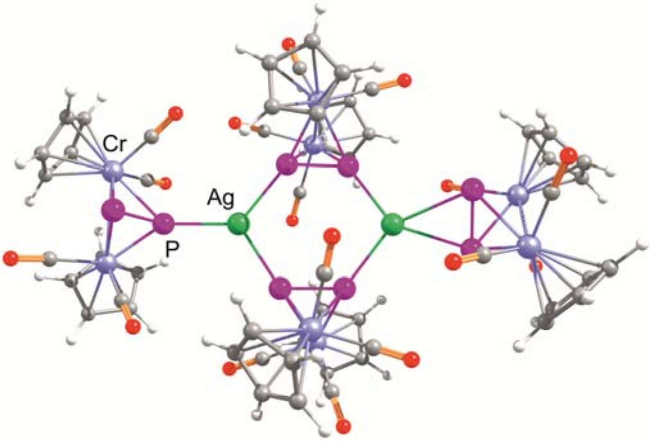
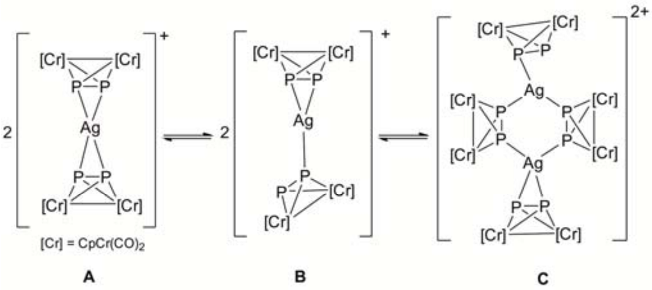


Figure 1. Gas-phase optimized geometry of **5** at the RI-B3LYP/def2-TZVP level of theory.

In the positive ion ESI-MS spectra of **5**, the most abundant fragment detected is attributable to the cation $[Ag\{Cp_2Cr_2(CO)_4P_2\}_2]^+$, regardless of whether the measurements are made in CH_2Cl_2 or CH_3CN. A fragment of low abundance, assigned to the cation $[Ag_2\{Cp_2Cr_2(CO)_4P_2\}\{Cp_2Cr_2(CO)_3P_2\}]^{2+}$, is also detected. These two fragments suggest the existence of an equilibrium similar to that proposed for **4**[11] in solution (Scheme 2), involving the dimer **5** and the monomer $[Ag\{Cp_2Cr_2(CO)_4P_2\}_2][Al\{OC(CF_3)_3\}_4]$ (**6**).



Scheme 2. Proposed cation equilibria in solutions of **5** (**C**).

Variable temperature ^{31}P NMR spectroscopic measurements in CD_2Cl_2 of **5** (Figure 2) give results similar to those found for **4**, which support the dynamic behavior in solution and therefore the existence of a monomer-dimer equilibrium. At room temperature, a singlet without any detectable coupling to the $^{107/109}Ag$ nuclei is observed at 43.3 ppm, which is shifted upfield by about 70 ppm relative to the uncoordinated ligand complex **2**.[12] As the temperature is reduced, the signal becomes broader and, at -40 °C, it splits into two signals, one at 62.2 ppm and one centered at approximately 20 ppm. The high-field shifted signal is particularly broad and the integration ratio of the two signals is about 2:1.

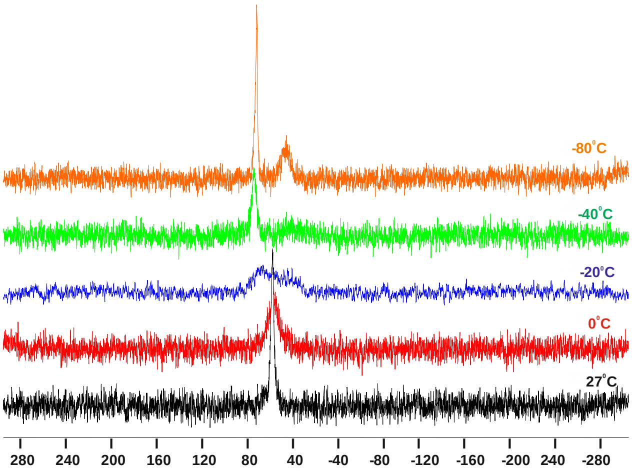


Figure 2. Variable temperature ^{31}P NMR spectra of **5** in CD_2Cl_2.

Vapor pressure osmometric (VPO) measurements on **5** in CH_2Cl_2 at 28 °C reveal an average molecular mass of 3060±153 g mol^{-1} for the species in solution (expected: **5**: 3784 g mol^{-1}; **6**: 1892 g mol^{-1}) and therefore suggest a monomer to dimer ratio of approximately 1:2. It is interesting to note that the presence of a monomer in solutions of the molybdenum derivative **4** is almost exclusive.[11]

Considering the ESI-MS, ^{31}P NMR and VPO data as well as the previous discussion of the solution behaviour of **5**, it is not unlikely that the equilibria illustrated in Scheme 2 (which was proposed and proved for the molybdenum analogue) also exist in solutions of **5**, involving the monocations **A** and **B** and the

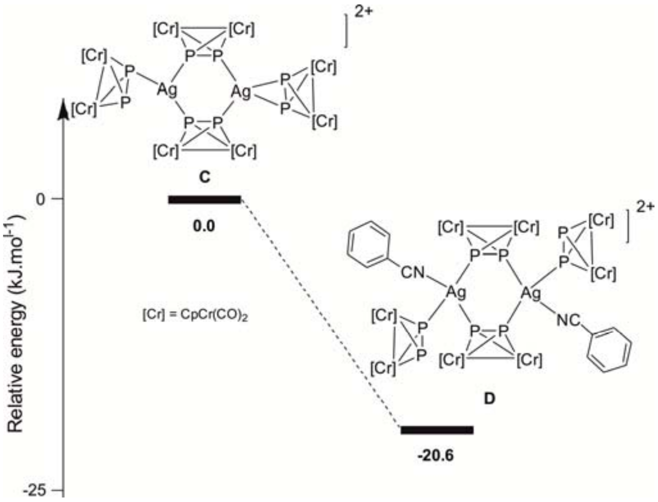


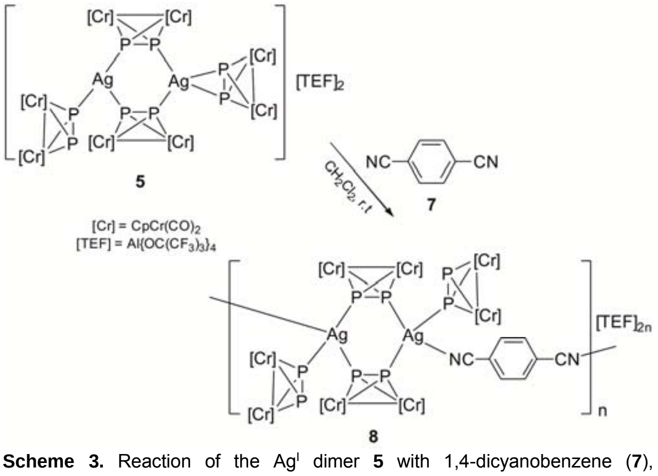
Figure 3. Energy diagram of the reaction of **C** with benzonitrile.

dication **C**.[11]

In order to study the potential of the dimeric compound **5** as a suitable precursor for the synthesis of new organometallic-organic hybrid polymers, DFT calculations were performed at the RI-B3LYP/def2-TZVP level of theory. Accordingly, the substitution of the terminal ligands **2** in the preformed dimeric complex **C** by benzonitrile as a model ligand, leading to **D**, is exothermic (-20.6 kJ mol^{-1}) in solution (Figure 2). Thus, theoretically, it is suggested that it should be possible to synthesize organometallic-organic hybrid polymers from the reaction of **C** with cyano-based multitopic linkers.

The dimer **5** was synthesized and reacted *in situ* with 1,4-dicyanobenzene (**7**) using a 1:1 stoichiometry in CH_2Cl_2 at room temperature. This reaction afforded compound **8** as a violet crystalline solid in a good isolated yield (69%, Scheme 3, Figure 3). Compound **8** can also be obtained in a one-pot three-component reaction of the components **2**, **3** and **7**, suggesting that **8** is probably thermodynamically stable over other possible intermediates in solution.

The crystal structure analysis of **8** reveals an unprecedented 1D organometallic-organic hybrid polymer consisting of the organometallic units $[Ag_2(\mathbf{2})_4]$, linked to polycationic chains by the connectors **7** (Scheme 3, Figure 3). At the Ag^I ions within the organometallic nodes of **8**, two P_2 ligands of **2** are coordinated by a bridging η^1:η^1-coordination mode and two other moieties of **2** each possessing an η^1-coordination mode. In addition, two molecules of **7** are also coordinated to these silver ions, each by one N atom. The P-P bond lengths in **8** (2.061(4)-2.069(2) Å) are slightly elongated compared to that of the non-coordinated ligand **2** (2.060(1) Å).[11] The Ag-P bond lengths are in the range between 2.470(9) and 2.480(5) Å. The Ag···Ag distance is long (4.872(0) Å) revealing no argentophilic interactions.[13] The Ag_2P_4 six-membered motifs in **8** are nearly planar (folding angle 9.38°).



Scheme 3. Reaction of the Ag^I dimer **5** with 1,4-dicyanobenzene (**7**), Synthesis of the 1D organometallic-organic hybrid CP **8**.

In the $^{31}P\{^1H\}$ NMR spectrum of **8** in CD_2Cl_2 at room temperature, a very broad singlet at 42.9 ppm is detected, which indicates a dynamic behaviour in solution. This signal is comparable to the one of the dimer **5** herein reported at room temperature (43.3 ppm in CD_2Cl_2) and highly upfield shifted compared to that of the free P_2 ligand complex **2** (110.8 ppm in C_6D_6).[11] The room temperature ^1H and $^{13}C\{^1H\}$ NMR spectra of **5** and **8** are similar revealing the expected signals corresponding to the Cp and CO ligands (for **5** and **8**) and the linker **7** (for **8**). The room temperature $^{19}F\{^1H\}$ NMR spectra of **5** and **8** show singlets at ≈ -75.0 ppm for the TEF anions. The solution and solid state IR spectra of both **5** and **8** exhibit strong bands between 1927 and 1977 cm^{-1}, which can be attributed to the carbonyl groups of **2**. The similarity of the spectroscopic data between **8** and the starting material **5** suggests the dissociation of the polymer **8** to the starting materials in CD_2Cl_2 solution. However, compound **8** can be again recrystallized from this solution at room temperature.

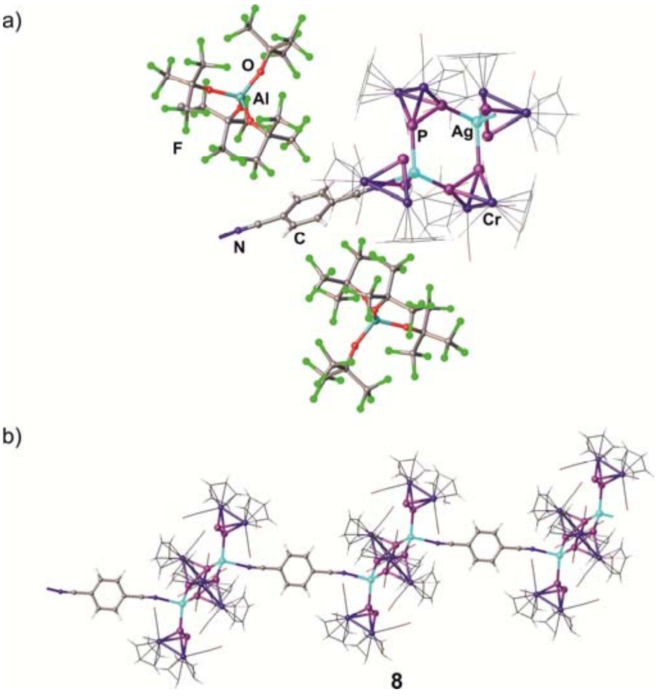


Figure 4. a) Molecular structure of the repeating unit of **8** in the solid state. b) Section of the 1D CP **8**, counterions have been omitted for clarity.

It is worth to note that the Ag^I dimer **5** was also reacted with a variety of ditopic pyridine-based linker. However, in each case decomposition of the dimeric structure was observed. This was concluded by recording the room temperature ^{31}P NMR spectra of the crude reaction mixtures in C_6D_6, where in each case, only one signal at ca. 111 ppm was observed corresponding to the free complex **2**.[12]

Conclusions

In conclusion, we have shown that the P_2 ligand complex $[Cp_2Cr_2(CO)_4(\eta^2\text{-}P_2)]$ (**2**) can be used as a suitable organometallic linker in the coordination chemistry of silver, whether in a two- or a three-component reaction approach. Parallel to our previous well-developed method involving *bipyridyl linker* together with metal salts and iron- or molybdenum-based P_n ligand complexes, the use of *1,4-dicyanobenzene* together with Ag^I and a chromium-based P_2 ligand complex allows the access to an unprecedented 1D organometallic-organic hybrid CP and opens a new chapter in this field of supramolecular chemistry by now using *nitrile linker*. These new results, in addition to the large variety of assemblies based on the ligand **1**,[7] show the advantage of our approach using P-donating ligand complexes in metal-directed self-assembly, which will lead to a very rich and original library of supramolecular compounds. Current investigations involve reactions based on the phosphorus-rich P_n ligand complexes (n = 3, 4, 5) to study the possibility of utilizing these rarely used ligands in similar three-component reactions leading to valuable phosphorus-rich organometallic-organic hybrid materials.

Experimental Section.

General: The experiments were performed under an atmosphere of dry argon using standard Schlenk techniques. 1,4-dicyanobenzene (**7**) was purchased from Sigma-Aldrich and used as received without further purification. The compounds $[CpCr_2(CO)_4(\eta^2\text{-}P_2)]$ (**2**)[11] and $Ag[Al\{OC(CF_3)_3\}]_4$ (**3**)[10] were synthesized according to literature procedures. Solvents were freshly distilled under argon from CaH_2 (CH_2Cl_2) and from Na/K alloy (n-pentane). IR spectra were recorded on a Varian FTS-800 spectrometer. The ^1H, ^{13}C, ^{31}P and ^{19}F NMR spectra were recorded on a Bruker Avance 300 or 400 spectrometers. ^1H and ^{13}C NMR chemical shifts were reported in parts per million (ppm) relative to Me_4Si as an external standard. ^{31}P NMR chemical shifts were expressed in ppm relative to external 85% H_3PO_4 and were decoupled from the protons. ^{19}F NMR chemical shifts were reported relative to $CFCl_3$. For the ESI-MS, a Finnignan Thermoquest TSQ 7000 mass spectrometer was used. Elemental analyses were performed by the microanalytical laboratory of the Universität Regensburg. Molecular mass determinations were performed under the supervision of Dr. Roland Neueder (Institute of Physical Chemistry, University of Regensburg) using a Knauer K-7000 vapour pressure osmometer, at 28 °C. The osmometer was calibrated using 0.01, 0.03, 0.05 and 0.1 M solutions of benzil in CH_2Cl_2.

$[Ag_2\{Cp_2Cr_2(CO)_4(\mu_3,\eta^2:\eta^2:\eta^2\text{-}P_2)\}\{Cp_2Cr_2(CO)_4(\mu_3,\eta^2:\eta^2:\eta^1\text{-}P_2)\}\{Cp_2Cr_2(CO)_4(\mu_4,\eta^2:\eta^2:\eta^1:\eta^1\text{-}P_2)\}_2][\langle Al\{OC(CF_3)_3\}_4\rangle_2]$ (5):
To a stirred solution of $[Cp_2Cr_2(CO)_4(\eta^2\text{-}P_2)]$ (**2**) (100mg, 0.25 mmol, 2 eq.) in 5 ml CH_2Cl_2, $Ag[Al\{OC(CF_3)_3\}_4]\bullet(CH_2Cl_2)$ (**3**) (142 mg, 0.125 mmol, 1 eq.) in 5 ml of CH_2Cl_2, was slowly added. The crude reaction mixture was stirred in the absence of light for 4 h at room temperature. The solution was filtrated over diatomaceous earth, which was subsequently washed with CH_2Cl_2 (2 × 2 ml). The addition of pentane (10 ml) to the combined filtrate and washings led to the isolation of **5** as a microcrystalline wine red powder, which was filtered, washed with hexane (2 × 3 ml) and dried under vacuum at room temperature. Yield: 205 mg (82%).
^1H NMR (400.13 MHz, CD_2Cl_2, 27°C): δ = 5.05 ppm (s, C_5H_5), $^{13}C\{^1H\}$ NMR (100.63 MHz, CD_2Cl_2, 27°C): δ = 88.86 (s, C_5H_5), 121.68 (q, $^1J_{FC}$ = 291 Hz; CF_3), 234.31 ppm (C_{CO}). ^{27}Al NMR (104.26 MHz, CD_2Cl_2, 27°C): δ = 33.66 ppm (s, $[Al\{OC(CF_3)_3\}_4]$). $^{19}F\{^1H\}$ NMR (376.47 MHz, CD_2Cl_2, 25 °C): δ = -75.60 ppm (s, CF_3). $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2, 27 °C): δ = 43.3 (s) ppm. $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2, -80 °C): δ = 59.0 (bs), 29.7 (bs) ppm. Positive ion ESI-MS (CH_2Cl_2, RT): m/z (%) = 1004.1 (12) $[Ag_2\{Cp_2Cr_2(CO)_4P_2\}\{Cp_2Cr_2(CO)_3P_2\}]^{2+}$, 924.9 (100) $[Ag\{Cp_2Cr_2(CO)_4P_2\}_2]^+$, 868.9 (30) $[Ag\{Cp_2Cr_2(CO)_3P_2\}_2]^+$, 812.8 (17) $[Ag\{Cp_2Cr_2(CO)_2P_2\}_2]^+$, 756.8 (5) $[Ag\{Cp_2Cr_2(CO)P_2\}_2]^+$, Negative ion ESI-MS ($CH_2Cl_2$, RT): m/z (%) = 967.1 (100) $[Al\{OC(CF_3)_3\}_4]^-$. IR (CH_2Cl_2): $\tilde{\upsilon}$ = 3114 (s), 1977 (s; CO), 1928 (s; CO), 1426 (w; CO), 1352 (m), 1300 (s), 1278 (s), 1264 (s), 1241 (s), 1224 (s), 1167 (w), 843 (w), 976 (s), 561 (w), 537 (w), 489 (w), 447 (w) cm^{-1}. IR (KBr): $\tilde{\nu}$ = 3131 (w), 1976 (vs; CO), 1942 (vs; CO), 1429 (w; CO), 1353 (m), 1302 (vs), 1278 (vs), 1243 (vs), 1220 (vs), 1169 (m), 1067 (w), 1017 (w), 975 (vs), 846 (m), 756 (w), 728 (vs), 595 (m), 558 (s), 536 (m), 485 (m), 447 (m) cm^{-1}. Molecular mass: Theoretical for $C_{88}H_{40}Ag_2Al_2Cr_8F_{72}O_{24}P_8$ = 3782.61 $g.mol^{-1}$; found (osmometric, CH_2Cl_2, 28 °C) = 3060 ± 153 $g.mol^{-1}$. Elemental analysis: calculated (%) for $C_{88}H_{40}Ag_2Al_2Cr_8F_{72}O_{24}P_8$ (3782.61): C 27.94, H 1.07; found: C 27.59, H 1.28. Melting point: 158 °C (decomposition).

$[Ag_2\{Cp_2Cr_2(CO)_4(\mu_4,\eta^2:\eta^2:\eta^1:\eta^1\text{-}P_2)\}_2\{Cp_2Cr_2(CO)_4(\mu_3,\eta^2:\eta^2:\eta^1\text{-}P_2)\}_2\{\mu,\eta^1:\eta^1\text{-}(C_8H_4N_2)\}]_n\ [\langle Al\{OC(CF_3)_3\}_4\rangle]_{2n}$ (8):
$[Cp_2Cr_2(CO)_4(\eta^2\text{-}P_2)]$ (**2**) (105mg, 0.26 mmol, 2 eq.) was dissolved in 5 ml of CH_2Cl_2. $AgAl\{OC(CF_3)_3\}_4]\bullet(CH_2Cl_2)[$ (**3**) (149 mg, 0.13 mmol, 1 eq.) was dissolved in 5 ml of CH_2Cl_2 and slowly added to the stirred solution of **2**. The crude reaction mixture was stirred in the absence of light for 20 minutes at room temperature, after which 1,4-dicyanobenzene (**7**) (8 mg, 0.065 mmol, 1/2 eq.) in 1 ml of CH_2Cl_2 was added and the whole mixture was stirred for further 3 h. The dark red-violet solution was filtrated over diatomaceous earth to remove any suspended particles. Compound **8** was formed as dark-violet blocks within two days at -28 °C. The crystals were washed with pentane (3 × 2 ml), dried under vacuum and isolated as a dark-violet solid.
Yield: 121 mg (69%).
^1H NMR (300.13 MHz, CD_2Cl_2, 22°C): δ = 5.05 (s, C_5H_5), 7.74 (s, CH) ppm, $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2, 22°C): δ = 88.88 (s, C_5H_5), 121.68 (q, $^1J_{FC}$ = 291 Hz; CF_3), 117.2 ($C_{benzonitrile}$), 121.9 (C_{CN}), 133.7 ($CH_{benzonitrile}$), 233.37 (C_{CO}) ppm. $^{31}P\{^1H\}$ NMR (121.29 MHz, CD_2Cl_2, 22 °C): δ = 42.9 (bs) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3114 (vw), 3056(w), 2989 (vw), 2361 (vw), 2300 (vw), 2238 (vw), 1978 (s; CO), 1958 (s; CO), 1925 (s; CO), 1422 (w), 1352 (w), 1301 (m), 1272 (vs), 1241 (vs), 1224 (vs), 1168 (w), 976 (vs), 896 (w), 843 (w), 833 (w), 609 (w), 561 (m), 537 (w), 490 (w) cm^{-1}. IR (KBr): 2360 (w), 2342 (w), 2243 (vw), 1974 (vs), 1939 (vs), 1429 (w), 1358 (m), 1302 (vs), 1278 (vs), 1242 (vs), 1220 (vs), 1166 (m), 1068 (vw), 1018 (vw), 974 (vs), 846 (m), 728 (s), 596 (w), 560 (m), 536 (m), 487 (w), 446 (w) cm^{-1}. Elemental analysis: Calculated (%) for $C_{99}H_{50}Ag_2Cl_6Al_2Cr_8F_{72}N_2O_{24}P_8$ (4165.54 g/mol): C 28.55, H 1.21, N 0.67; found: C 29.37, H 1.20, N 0.68. Melting point: > 200 °C

CCDC 1589784 for **8** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center.

Supporting Information (see footnote on the first page of this article): crystal structure refinement data for compound **8** and details about DFT calculations.

Acknowledgements

This work was supported by the European Research Council via the Grant ERC-2013-AdG 339072. The COST action CM 1302 (SIPS) is gratefully acknowledged.

Keywords: dicyanobenzene • hybrid polymer • diphosphorus complex • chromium • silver salt

[1] Recent reviews: a) M. L. Saha, X. Yan, P. Stang, *Acc. Chem. Res.* **2016**, *49*, 2527-2539; b) T. R. Cook, P. Stang, *Chem. Rev.* **2015**, *115*, 7001-7045; c) C. Rest, R. Kandanelli, G. Fernandez, *Chem. Soc. Rev.* **2015**, *44*, 2543-2572; d) L. Xu, Y. -X. Wang, L. -J. Chen, H. -B. Yang, *Chem. Soc. Rev.* **2015**, *44*, 2148-2167; e) L. Xu, L. -J. Chen, H. -B. Yang, *Chem. Commun.* **2014**, *50*, 5156-5170; f) M. Han, D. M. Engelhard, G. H. Clever, *Chem. Soc. Rev.* **2014**, *43*, 1848-1860; g) K. Harris, D. Fujita, M. Fujita, *Chem. Commun.* **2013**, *49*, 6703-6712; h) M. M. J. Smulders, I. A. Riddell, C. Browne, J. R. Nitschke, *Chem. Soc. Rev.* **2013**, *42*, 1728-1754.

[2] Recent reviews: a) T. R. Cook, Y.-R. Zheng, P. J. Stang, *Chem. Rev.* **2013**, *113*, 734-777; b) S Park, S. Y. Lee, K.-M. Park, S. S. Lee, *Acc. Chem. Res.* **2012**, *3*, 391-403; c) M.-X. Li, H. Wang, S.-W. Liang, M. Shao, X. He, Z.-X. Wang, S.-R. Zhu, *Cryst. Growth Des.* **2009**, *9*, 4626-4633.

[3] M. Scheer, *Dalton Trans.* **2008**, *33*, 4372-4386.

[4] Recent papers: a) M. E. Moussa, M. Fleischmann, E. V. Peresypkina, L. Dütsch, M. Seidl, G. Balázs, M. Scheer, *Eur. J. Inorg. Chem.* **2017**, *25*, 3222-3226; b) C. Heindl, A. Kuntz, E. V. Peresypkina, A. V. Virovets, M. Zabel, D. Lüdeker, G. Brunklaus, M. Scheer, *Dalton Trans.*, **2015**, *44*, 6502-6509; c) C. Heindl, E. V. Peresypkina, A. V. Virovets, V. Y. Komarov, M. Scheer, *Dalton Trans.* **2015**, *44*, 10245-10252; d) M. Fleishmann, S. Welsch, E. V. Peresypkina, A. V. Virovets, M. Scheer, *Chem. Eur. J.* **2015**, *21*, 14332-14336; e) F. Dielmann, C. Heindl, F. Hastreiter, E. V. Peresypkina, A. V. Virovets, R. M. Gschwind, M. Scheer, *Angew. Chem. Int. Ed.* **2014**, *53*, 13605-13608; f) E.-M. Rummel, M. Eckhardt, M. Bodensteiner, E. V. Peresypkina, W. Kremer, C. Gröger, M. Scheer, *Eur. J. Inorg. Chem.* **2014**, *10*, 1625-1637; g) H. Krauss, G. Balázs, M. Bodensteiner, M. Scheer, *Chem. Sci.* **2010**, *1*, 337-342.

[5] a) E. V. Peresypkina, C. Heindl, A. V. Virovets, M. Scheer, *Structure and Bonding,* **2016**, *174*, 321-373. b) C. Heindl, E. V. Peresypkina, D. Lüdeker, G. Brunklaus, A. V. Virovets, M. Scheer, *Chem. Eur. J.* **2016**, *22*, 2599-2604; c) C. Heindl, E. V. Peresypkina, A. V. Virovets, W. Kremer, M. Scheer, *J. Am. Chem. Soc.* **2015**, *137*, 10938-10941; d) M. Fleischmann, S. Welsch, H. Krauss, M. Schmidt, M. Bodensteiner, E. V. Peresypkina, M. Sierka, C. Gröger, M. Scheer, *Chem. Eur. J.* **2014**, *20*, 3759-3768; e) F. Dielmann, C. Heindl, F. Hastreiter, E. V. Peresypkina, A. V. Virovets, R. M. Gschwind, M. Scheer, *Angew. Chem. Int. Ed.* **2014**, *53*, 13605-13608; f) M. Scheer, A. Schindler, R. Merkle, B. P. Johnson, M. Linseis, R. Winter, C. E. Anson, A. V. Virovets, *J. Am. Chem. Soc.* **2007**, *129*, 13386-13387; g) J. Bai, A. V. Virovets, M. Scheer, *Science* **2003**, *300*, 781-783; h) C. Heindl, E. Peresypkina, A. V. Virovets, I. S. Bushmarinov, M. G. Medvedev, B. Krämer, B. Dittrich, M. Scheer, *Angew. Chem. Int. Ed.* **2017**, 43, 13237-13243.

[6] S. Welsch, C. Groeger, M. Sierka, M. Scheer, *Angew. Chem. Int. Ed.* **2011**, *50*, 1435-1438.

[7] a) M. E. Moussa, B. Attenberger, E. V. Peresypkina, M. Scheer, *Dalton Trans.,* **2018**, *47*, 1014-1017; b) M. E. Moussa, B. Attenberger, M. Seidl, A. Schreiner, M. Scheer, *Eur. J. Inorg. Chem.* **2017**, *47*, 5616-5620; c) M. E. Moussa, M. Seidl, G. Balázs, M. Zabel, A. V. Virovets, B. Attenberger, A. Schreiner, M. Scheer, *Chem. Eur. J.* **2017**, *23*, 16199-16203; b) M. E. Moussa, B. Attenberger, M. Fleischmann, A. Schreiner, M. Scheer, *Eur. J. Inorg. Chem.* **2016**, *28*, 4538-4541; c) M. Elsayed Moussa, B. Attenberger, E. V. Peresypkina, M. Fleischmann, G. Balázs, M. Scheer, *Chem. Commun.* **2016**, *52*, 10004-10007; d) B. Attenberger, E. V. Peresypkina, M. Scheer, *Inorg. Chem.* **2015**, *54*, 7021-7029; e) B. Attenberger, S. Welsch, M. Zabel, E. Peresypkina, M. Scheer, *Angew. Chem. Int. Ed.* **2011**, *50*, 11516-11519.

[8] a) P. Sekar, M. Scheer, A. Voigt, R. Kirmse, *Organometallics* **1999**, *18*, 2833-2837; b) P. Sekar, S. Umbarkar, M. Scheer, A. Voigt, R. Kirmse, *Eur. J. Inorg. Chem.* **2000**, *12*, 2585-2589.

[9] M. Scheer, L. J. Gregoriades, M. Zabel, M. Sierka, L. Zhang, H. Eckert, *Eur. J. Inorg. Chem.* **2007**, *18*, 2775-2782.

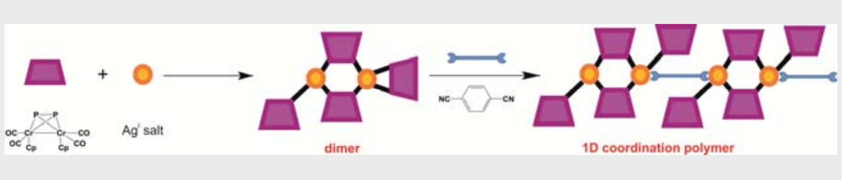
[10] I. Krossing, *Chem. Eur. J.* **2001**, *7*, 490-502.

[11] M. Scheer, L. J. Gregoriades, M. Zabel, J. Bai, I. Krossing, G. Brunklaus, H. Eckert. *Chem. Eur. J.*, **2008**, *14*, 282-295.

[12] a) L. Y. Goh, C. K. Chu, R. C. S. Wong, T. W. Hambley, *J. Chem. Soc. Dalton Trans.* **1989**, 1951-1956; b) L. Y. Goh, R. C. S. Wong, *Inorg. Synth.* **1992**, *29*, 247-250.

[13] H. Schmidbaur, A. Schier, *Angew. Chem. Int. Ed.,* **2015**, *54*, 746-784.

SHORT COMMUNICATION



The reaction of the diphosphorus complex [$Cp_2Cr_2(CO)_4(\eta^2-P_2)$] (Cp = C_5H_5) with Ag[Al{$OC(CF_3)_3$}$_4$] results in an Ag^I dimer, which is used as a suitable precursor for the synthesis of an unprecedented 1D organometallic-organic hybrid coordination polymer upon its reaction with 1,4-dicyanobenzene.

Self-assembly

*M. Elsayed Moussa, S. Welsch, L. J. Gregoriades, G. Balázs, M. Seidl and M. Scheer**

Page No. – Page No.

The Diphosphorus Complex [$Cp_2Cr_2(CO)_4(\eta^2-P_2)$] as a Building Block in the Coordination Chemistry of Silver