# Chemical Science



## **EDGE ARTICLE**

View Article Online
View Journal | View Issue



Cite this: Chem. Sci., 2020, 11, 6745

dll publication charges for this article have been paid for by the Royal Society of Chemistry

Received 25th March 2020 Accepted 23rd May 2020

DOI: 10.1039/d0sc01740i

rsc.li/chemical-science

# Transformations of the cyclo- $P_4$ ligand in $[Cp'''Co(\eta^4-P_4)]^{\dagger}$

Martin Piesch, Michael Seidl and Manfred Scheer \*\*D\*\*

The reactivity of the *cyclo*-P<sub>4</sub> ligand complex  $[Cp'''Co(\eta^4-P_4)]$  (1) (Cp'''=1,2,4-tri-tert-butyl-cyclopentadienyl) towards reduction and main group nucleophiles was investigated. By using  $K[CpFe(CO)_2]$ , a selective reduction to the dianionic complex  $[(Cp'''Co)_2(\mu,\eta^3:\eta^3-P_8)]^{2-}$  (2) was achieved. The reaction of 1 with  $^tBuLi$  and  $LiCH_2SiMe_3$  as carbon-based nucleophiles yielded  $[Cp'''Co(\eta^3-P_4R)]^-$  ( $R=^tBu$  (4),  $CH_2SiMe_3$  (7)), which, depending on the reaction conditions, undergo subsequent reactions with another equivalent of 1 to form  $[(Cp'''Co)_2(\mu,\eta^3:\eta^3-P_8R)]^-$  ( $R=^tBu$  (5),  $CH_2SiMe_3$  (8)). In the case of 4, a different pathway was observed, namely a dimerisation followed by a fragmentation into  $[Cp'''Co(\eta^3-P_5{}^tBu_2)]^-$  (6) and  $[Cp'''Co(\eta^3-P_3)]^-$  (3). With  $OH^-$  as an oxygen-based nucleophile, the synthesis of  $[Cp'''Co(\eta^3-P_4(O)H)]^-$  (9) was achieved. All compounds were characterized by X-ray crystal structure analysis, NMR spectroscopy and mass spectrometry. Their electronic structures and reaction behavior were elucidated by DFT calculations.

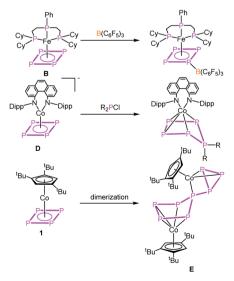
#### Introduction

The parent organic carbon aromates  $C_nH_n$  have been widely used as ligands in organometallic chemistry in sandwich, halfsandwich or multi-decker sandwich complexes. While the majority of compounds include Cp (C<sub>5</sub>H<sub>5</sub>) and benzene (C<sub>6</sub>H<sub>6</sub>) as ligands, examples for complexes with C<sub>3</sub>H<sub>3</sub> and C<sub>4</sub>H<sub>4</sub> ligands are rather limited. Due to the isolobal analogy of the CH unit and P, a large variety of ligands have been described where CH units were replaced partially by P atoms as in e.g. phospholes (C<sub>4</sub>H<sub>4</sub>P, C<sub>2</sub>H<sub>2</sub>P<sub>3</sub>)<sup>2</sup> or phosphinines (C<sub>5</sub>H<sub>5</sub>P)<sup>3</sup> or completely resulting in aromatic  $cyclo-P_n$  ligands. While complexes with cyclo-P<sub>3</sub> (e.g.  $[Cp*Ni(\eta^3-P_3)]$ ,  $[(Cp'''Ni)_2(\mu,\eta^3:\eta^3-P_3)]^5)$ , cyclo-P<sub>5</sub> (e.g.  $[Cp*M(\eta^5-P_5)]$  (M = Fe, Ru<sup>7</sup>)  $[(Cp^RM)_2(\mu, \eta^5: \eta^5-P_5)]$  (M =  $(Cr, {}^{8}Mn^{9})$ ) and cyclo- $P_{6}[(Cp^{R}M)_{2}(\mu, \eta^{6}; \eta^{6}-P_{6})](M = Ti, {}^{10}V, {}^{11}Nb, {}^{12})$ Mo, 13 W11) ligands have been known for decades, the cyclo-P4 Co complex in this row was unknown for a long time. Recently, we succeeded in the synthesis of  $[Cp'''Co(\eta^4-P_4)]$  (1). <sup>14</sup> This inspired the synthesis of other complexes containing cyclo-P4 ligands a few of which were recently reported as e.g. being based on rare earth metals like [{(DippForm)<sub>2</sub>Sm}<sub>2</sub>( $\mu$ , $\eta$ <sup>4</sup>-P<sub>4</sub>)],<sup>15</sup> group five metals,  $[Cp^RM(CO)_2(\eta^4-P_4)]$  (M = V, Nb, Ta (A)), <sup>16</sup> on chromium,  $[L_2Cr_2(\eta^2:\eta^2:\eta^1:\eta^1-P_4)]$  (L = (2,6-diisopropylphenyl)-{6-(2,6dimethylphenyl)-pyridin-2-yl}-amide)),<sup>17</sup> on iron, [PhPP<sub>2</sub>CyFe(η<sup>4</sup>- $P_4$ ] (B), <sup>18</sup> on molybdenum, [(Ar<sup>Dipp</sup>CN)<sub>2</sub>Mo(CO)<sub>2</sub>( $\eta^4$ -P<sub>4</sub>)] (C)<sup>19</sup>

Institut für Anorganische Chemie, Universität Regensburg, 93040 Regensburg, Germany. E-mail: Manfred.Scheer@ur.de; Web: https://www.uni-regensburg.de/chemie-pharmazie/anorganische-chemie-scheer/

† Electronic supplementary information (ESI) available. CCDC 1984450-1984455. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0sc01740j

and on the anionic iron complex  $[Cp^{Ar}Fe(\eta^4-P_4)]^-$  (ref. 20) as well as on the anionic cobalt complex  $[(PHDI)Co(\eta^4-P_4)]^-$  (**D**).<sup>21</sup> The reactivity of these complexes was only little investigated by the coordination chemistry of **A** and **B** towards coinage metal salts<sup>18,22</sup> and the reactivity of **B** towards Lewis acids as for instance  $B(C_6F_5)_3$  (Scheme 1).<sup>18</sup> The anionic compound **D** was quenched with phosphorus-based electrophiles ( $R_2PCl$ ) leading to neutral complexes with substituted *cyclo-P*<sub>5</sub> $R_2$  ligands (Scheme 1).<sup>21</sup> Ring expansion reactions were also reported for **1** using the pnictogenidene complexes  $[Cp^*E\{W(CO)_5\}_2]$  (E = P, As), leading to neutral cobalt complexes with organo-



Scheme 1 Reactivity of selected cyclo-P<sub>4</sub> ligand complexes.

substituted cyclo-P<sub>5</sub> and cyclo-P<sub>4</sub>As ligands, 23a with the latter showing that reactions with electrophiles were investigated (other examples cf. ref. 23b and c), though not yet the reactivity towards nucleophiles or reduction reactions in general. As for the former chemistry, however, it was studied for  $[Cp*Fe(\eta^5-P_5)]$ and [Cp\*Ni(n<sup>3</sup>-P<sub>3</sub>)],<sup>5,24</sup> for which organo-substituted anionic complexes of the types  $[Cp*Fe(\eta^4-P_5R)]^-$  and  $[Cp'''Ni(\eta^2-P_3R)]^-$ 

**Chemical Science** 

were obtained.

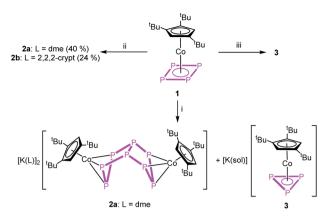
With this state of the art in mind, questions arose as to how 1 would respond to redox reactions or to a nucleophilic attack. Would a dimerisation by a P-P bond formation or a simple substitution occur, as known from the reactions of other cyclo- $P_n$  ligand complexes? Would a structural rearrangement be possible, including a reorganisation process? Moreover, controlling the reactivity of 1 is a challenging task since it has a high intrinsic tendency to dimerising irreversibly in solution to give a connected five- and three-membered P8 ligand in  $[(Cp'''Co)_2(\mu,\eta^4:\eta^3-P_8)]$  (E, Scheme 1).<sup>14</sup> Furthermore, there are only few examples known of four-membered heterocycles to undergo ring expansion reactions, e.g. by nucleophiles being added to phosphetanes<sup>25</sup> or by oxidizing the diphosphete complex  $[Cp'''Co(\eta^4-P_2(C^tBu)_2)]$  to give the five- and the threemembered ring products,  $\left[\operatorname{Cp'''}\operatorname{Co}(\eta^{5}-\operatorname{P}_{3}(\operatorname{C}^{t}\operatorname{Bu})_{2})\right]^{+}$  $[Cp'''Co(\eta^3-P(C^tBu)_2)]^+$ , respectively.<sup>26</sup>

Herein we report the unprecedented transformations of the cyclo-P<sub>4</sub> ligand complex 1 upon reduction and the reactions with main-group nucleophiles to give novel P-rich ligand complexes.

#### Results and discussion

To obtain a first insight into the reactivity of 1, the frontier molecular orbitals (cf. Fig. S32†) were computed by DFT calculations. They reveal that both HOMO and LUMO are mainly located on the cyclo-P4 ligand and, hence, 1 should react with both electrophiles and nucleophiles. The reactivity of 1 towards electrophiles has been shown by reactions with  $[Cp*E\{W(CO)_5\}_2]$  (E = P, As).<sup>23</sup> On the other hand, the cyclic voltammogram (cf. Fig. S18†) of 1 in dme reveals a weak irreversible oxidation process at +275 mV and a strong irreversible reduction process at -2081 mV against [Cp<sub>2</sub>Fe]/[Cp<sub>2</sub>Fe]<sup>+</sup>, indicating the potential ligand-centred redox activity of 1 (for details *cf.* ESI†).

Due to the low reduction potential of 1, we used potassium, potassium graphite and potassium hydride for the chemical reduction. In all cases, the formation of a mixture of  $[(Cp'''Co)_2(\mu,\eta^3:\eta^3-P_8)]^{2-}$  (2) and  $[Cp'''Co(\eta^3-P_3)]^{-}$  (3)<sup>27</sup> in an approximate ratio of 1:1 (Scheme 2) is observed (cf. Fig. S1†). When the reaction is conducted in the presence of 18-c-6 or 2,2,2-cryptand, only 3 can be detected in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum. The selective synthesis of 2 can be achieved by using  $K[CpFe(CO)_2]$  at low temperatures. Interestingly,  $K[CpFe(CO)_2]$ should not be able to reduce 1 (its reduction potential of -1800 mV in thf against [Cp<sub>2</sub>Fe]/[Cp<sub>2</sub>Fe]<sup>+</sup> is higher than that of 1 (*vide supra*)). After workup,  $[K(dme)]_2[(Cp'''Co)_2(\mu, \eta^3: \eta^3-P_8)]$ (2a) can be obtained as a dark green solid in crystalline yields of 40% (Scheme 2). Although well-diffracting single crystals of 2a could be obtained, a satisfactory refinement of the X-ray data



Scheme 2 Reaction of 1 with (i) K, KH or KC<sub>8</sub> in thf at r.t., (ii) K[CpFe(CO)<sub>2</sub>] in thf at -80 °C and (iii) with K, KH or KC<sub>8</sub> in thf at r.t. in the presence of 18-c-6 or 2,2,2-cryptand.

was not possible since the potassium counterions and dme molecules are severely disordered over several positions with side occupancies partially below 8% (cf. ESI†). The addition of 2,2,2-cryptand to a crude reaction mixture of 2a and the recrystallization from a dme/acetonitrile mixture at -30 °C yielded single crystals of  $[K(2,2,2\text{-cryptand})]_2[(Cp'''Co)_2(\mu,\eta^3:\eta^3-\mu^3)]_2$ P<sub>8</sub>] (2b) suitable for X-ray diffractions in 24% yield. Both 2a and 2b can be isolated as dark green solids that are extremely air- and moisture-sensitive. The structure in the solid state (Fig. 1) shows a dianionic dinuclear complex with a P<sub>8</sub> ligand consisting of a cis-bicyclo[3.3.0] octane core that coordinates to two {Cp"Co} fragments. Compound 2 displays the first compound possessing such a ligand. The structural motif is similar to the realgar-like P<sub>8</sub> cages (tricyclo[3.3.0.0] =  $nacnacGa_{29}^{29}$   $nacnacFe_{30}^{30}$   $NN^{fc}Sc_{31}^{31}$   $Cp_{2}^{*}Sm^{32}$ ),  $[(Cp^{Me}Fe(CO)_2)_2(Cp^{Me}Fe(CO))_2(\mu_4,\eta^1:\eta^1:\eta^1:\eta^1:\eta^1:\eta^1-P_8)]^{33}$  $[(Cp*Ir(CO))_2(\mu_5,\eta^1:\eta^1:\eta^1:\eta^1:\eta^1:\eta^1:\eta^1-P_8)\{Cr(CO)_5\}_3]^{34}$  $[(Cp'''Ni)_2(\mu,\eta^2:\eta^2-P_8)]^{2-}$ , with the difference that in **2b** one P-P bond is cleaved (P1-P5, Fig. 1). In all mentioned complexes, the  $P_8$  ligands coordinate either in an  $\eta^1:\eta^1$  (Ga, Fe, Sc, Sm, Ir) or  $\eta^2$  (Ni) fashion to the metal fragments, while in 2b two allylic P3 subunits (P1-P2 2.1554(6), P1-P8

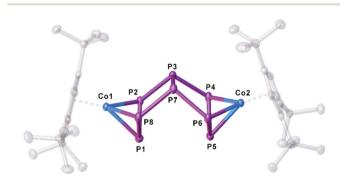


Fig. 1 Structure of the dianion in 2b in the solid state. Thermal ellipsoids are shown at 50% probability level. Hydrogen atoms, cations and solvent molecules are omitted for clarity.

Edge Article Chemical Science

2.1577(6), P4–P5 2.1519(6), P5–P6 2.1580(6) Å) coordinate to two {Cp‴Co} fragments in an  $\eta^3$  fashion. These P–P bond lengths are between single³⁵ and double³⁶ bond lengths, in line with the calculated Wiberg Bond Indices (WBIs) of 1.11 and 1.12, respectively.

All other P–P distances are in the range of single bonds (2.1947(6)–2.2247(6) Å), which is underlined by WBIs between 0.93 and 0.96. The  $^1H$  NMR spectrum of 2a in thf-d $_8$  shows three singlets centred at  $\delta=3.96,\,1.31$  and 1.22 ppm with an integral ratio of 4:36:18 indicating two equivalent freely rotating Cp $^{\prime\prime\prime}$  ligands. The  $^{31}$ P{ $^1H$ } NMR spectrum in thf-d $_8$  shows three multiplets centred at  $\delta=96.2,\,83.1$  and -124.2 ppm with an integral ratio of 2:4:2 of an AA'MM'M"M"XX' spin system.

Instead of adding electrons to the system by reduction, nucleophiles can also serve as electron donors. We selected  $^tBuLi$  as a strong carbon-based nucleophile with a higher steric demand to avoid side reactions. The reaction with 1 in thf at  $-80~^{\circ}C$  proceeds instantly during the addition of  $^tBuLi$  indicated by an immediate colour change from red to brown. After warming to room temperature, the  $^1H$  and  $^{31}P\{^1H\}$  NMR spectra reveal the selective formation of  $[Cp'''Co(\eta^3-P_4{}^tBu)]^-$  (4) (Scheme 3). Pure 4 can be precipitated from the reaction mixture in a yield of 48% after addition of 2,2,2-cryptand.

Regardless of numerous attempts to obtain single crystals of 4 suitable for X-ray diffractions, we were only able to receive poorly diffracting ones (resolution < 1.20 Å). The atom connectivity can be determined unambiguously, a discussion of the bond lengths and angles, however, would not be appropriate. The solid-state structure (cf. Fig. S22†) reveals a folded cyclo-P<sub>4</sub> ligand with one P atom deviating from the former planar P<sub>4</sub> unit, to which the <sup>t</sup>Bu substituent is bonded in an axial position (isomer 4a). Theoretically, a second isomer with the  $^{t}$ Bu substituent in an equatorial position (4b) would be possible, it could, however, not be detected by NMR spectroscopy ( $vide\ infra;\ cf.$  Fig. S4†). According to DFT calculations, the energy difference between the axial and equatorial isomers of 4 (i.e. 4a and 4b) is 11.91 kJ mol<sup>-1</sup>, with 4a being favoured. During

**Scheme 3** Reaction of **1** with <sup>t</sup>BuLi and subsequent reaction.

the optimization of the crystallization conditions, we noticed that 4 is not stable in solution over time (especially in the absence of 2,2,2-cryptand) and is converted to  $[(Cp'''Co)_2(-\mu,\eta^3:\eta^3-P_8{}^tBu)]^-$  (5) or  $[Cp'''Co(\eta^3-P_3)]^-$  (3) and  $[Cp'''Co(\eta^3-P_5{}^tBu_2)]^-$  (6) (Scheme 3). This process was monitored by  $^{31}P\{^1H\}$  NMR spectroscopy and the products 5 and 6 could be isolated and characterized spectroscopically and by single crystal X-ray diffractions.

For compound 5, few single crystals suitable for X-ray diffractions could be obtained, while the quality of the crystals of 6 gave only very poor data indicating, however, the atom connectivity in 6 (cf. ESI†). The molecular structure of 5 (Fig. 2) shows a binuclear complex with a substituted  $P_8{}^tBu$  ligand coordinating to two {Cp‴Co} fragments, each in an  $\eta^3$  fashion similar to 2. All P-P distances are comparable to those in 2. The identity of 3, 5 and 6 was further proven by simulation of the related  ${}^{31}P\{{}^{1}H\}$  NMR spectra. Performing the reaction of 1 with  ${}^{t}BuLi$  at room temperature, the  ${}^{31}P\{{}^{1}H\}$  NMR spectrum of the reaction mixture in thf-d $_8$  reveals a mixture of all four compounds 3, 4, 5 and 6 beside traces of unknown compounds (Fig. 3). The  ${}^{31}P\{{}^{1}H\}$  NMR spectra of 4, 5 and 6 were simulated independent of this spectrum, since 3, 5 and 6 could not be separated preparatively from each other.

The formation of 5 can be explained by the reaction of 4 with another equivalent of 1, which is energetically favoured by 52.48 kJ mol<sup>-1</sup> (Fig. 4) and probably driven by the decrease of the ring strain. An alternative pathway to the release of ring strain would be the dimerisation of two equivalents of 4 followed by a subsequent fragmentation to form 6 (containing an unprecedented, disubstituted *cyclo*-P<sub>5</sub> ligand) and 3 (containing a *cyclo*-P<sub>3</sub> ligand). This reaction is exothermic by 161.09 kJ mol<sup>-1</sup>. Interestingly, these subsequent reactions can be avoided or at least slowed down when the lithium counter ion is completely separated from the anion in 4 by *i.e.* the addition of 2,2,2-cryptand.

Since the nucleophile <sup>t</sup>BuLi seems to be too strong and induces subsequent reactions, we employed LiCH<sub>2</sub>SiMe<sub>3</sub> as a weaker and sterically less demanding carbon-based nucleophile in the reaction with 1.

The reaction of 1 with LiCH<sub>2</sub>SiMe<sub>3</sub> in thf at -80 °C leads to the formation of  $[Cp'''Co(\eta^3-P_3CH_2SiMe_3)]^-$  (7) and, after

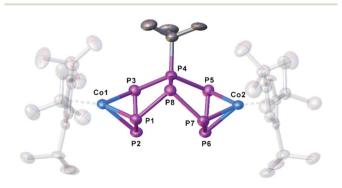


Fig. 2 Molecular structure of the anion of 5 in the solid state. Thermal ellipsoids are shown at 50% probability level. Hydrogen atoms, cations and solvent molecules are omitted for clarity.

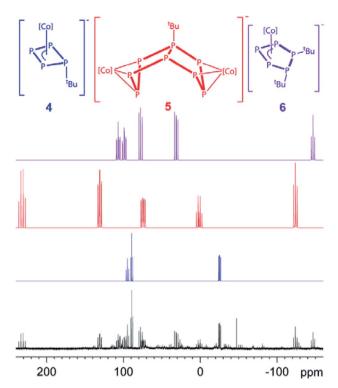


Fig. 3  $^{31}$ P{ $^{1}$ H} NMR spectrum of the reaction of 1 with  $^{t}$ BuLi at r.t. in thf-d<sub>8</sub> and the simulated NMR spectra of 4, 5 and 6 ([Co] = Cp'''Co).

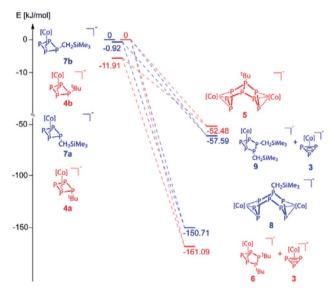


Fig. 4 Energetic diagram of the isomers 4a,b and 7a,b and their subsequent reactions. 4b and 7b were each used as reference for the related calculations (0 kJ mol $^{-1}$ , [Co] = Cp $^{\prime\prime\prime}$ Co).

warming to room temperature, of [Li(dme)<sub>3</sub>][(Cp'''Co)<sub>2</sub>( $\mu$ , $\eta^3$ : $\eta^3$ -P<sub>8</sub>CH<sub>2</sub>SiMe<sub>3</sub>)] (8), which can be isolated in crystalline yields of 33% after workup (Scheme 4). The formation of 7 and 8 becomes manifest by color changes from red (1) to brown (7) to green (8). The outcome of the reaction is independent of whether 0.5 or 1 equivalents of LiCH<sub>2</sub>SiMe<sub>3</sub> are used.

$$\begin{array}{c} ^{t}\text{Bu} \\ \text{$\downarrow$} \\ \text{$$

Scheme 4 Reaction of 1 with LiCH<sub>2</sub>SiMe<sub>3</sub> ([Co] = Cp"'Co)

The reaction can be stopped partially and the formation of 8 be reduced when 12-c-4 or 2,2,2-cryptand is added directly after the addition of LiCH<sub>2</sub>SiMe<sub>3</sub> at -80 °C. The crude  $^{31}P\{^{1}H\}$  NMR spectra of these reactions reveal two isomers of 7 in a ratio of 1: 0.25 (2,2,2-crypt) and 1: 1.33 (12-c-4), respectively, which can be assigned to complexes where the CH2SiMe3 substituent is located in an axial position (7a) or in an equatorial position (7b). The <sup>31</sup>P{<sup>1</sup>H} NMR spectra reveal also the formation of 8 and 3 beside minor amounts of unknown side products, while the reaction in the presence of 2,2,2-cryptand seems to be much more selective to giving 3, 7a, 7b and 8 (cf. Fig. S10 and S11†). According to DFT calculations, the energy of the isomers 7a and 7b differs only by 0.92 kJ mol<sup>-1</sup>, with 7a being favoured (Fig. 4). Few crystals of the isomer 7a were obtained from a concentrated solution of the mixture of isomers in thf layered with *n*-hexane at -30 °C. The molecular structure (Fig. 5, left) shows a folded cyclo-P4 ligand with one P atom bent out of the plane bearing the CH<sub>2</sub>SiMe<sub>3</sub> substituent. The P1-P2 (2.2283(16) Å) and P1-P4 (2.2229(19) Å) distances are longer than the P2–P3 (2.1877(17) Å) and P3-P4 (2.1895(16) Å) bonds. All P-P bond lengths are elongated compared to 1.14 The 31P{1H} NMR spectrum of 7 in thf-d<sub>8</sub> shows three multiplets of an AMXX' spin system (7a) centred at  $\delta = 52.6$ , 46.0 and 18.8 ppm with an integral ratio of 1:1:2 and three multiplets of an AMM'X spin system (7b) centred at  $\delta = 39.5$ , 3.94 and -78.0 ppm with an integral ratio of

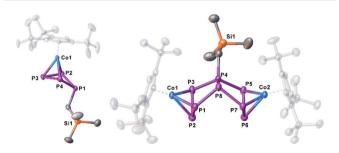


Fig. 5 Molecular structure of the anions 7a and 8 in the solid state. Thermal ellipsoids are shown at 50% probability level. Hydrogen atoms, cations and solvent molecules are omitted for clarity.

1:2:1. The  $J_{\rm PP}$  coupling constants obtained from the simulation (*cf.* ESI†) correlate nicely with the bond distances obtained from the X-ray structure determination.

When the reaction is conducted without the use of 12-c-4 or 2,2,2-cryptand, a colour change from initial red to brown (7) to dark green (8) is observed. Crystals of 8 suitable for single crystal X-ray diffraction were obtained from a concentrated solution in a mixture of *n*-hexane and dme stored at -30 °C. The structure of 8 (Fig. 5, right) shows a dinuclear anionic complex with a substituted P<sub>8</sub> ligand. The P<sub>8</sub> structural motif is similar to that observed in the reduced complex 2 and analogous to that found in 5. The P8 ligand consists of two condensed fivemembered rings (bicyclo[3.3.0]octane) coordinating to the {Cp"Co} fragments via the allylic P3 subunits (P1-P2-P3 and P5-P6-P7). The bond distances (P1-P2 2.1643(11), P2-P3 2.1574(11), P5-P6 2.1494(11), P6-P7 2.1575(11) Å) are in the range between single and double bonds, indicated by the WBIs between 1.09 and 1.11. All other P-P distances are in the range of single bonds. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of 8 in thf-d<sub>8</sub> shows five multiplets centred at  $\delta = 187.9$ , 102.8, 74.4, 40.6 and -118.8 ppm with an integral ratio of 1:2:2:1:2 indicating an AM<sub>2</sub>N<sub>2</sub>OX<sub>2</sub> spin system. The simulation of the spectrum at 193 K was conducted to determine the coupling constants and chemical shifts (cf. Fig. S13†). The formation of 8 can be explained by the reaction of 7 with another equivalent of 1, energetically favoured by -150.71 kJ mol<sup>-1</sup>. Alternatively, as also might be true for the formation of 5, a formal intermolecular nucleophilic attack of 7 at another molecule 7 under release of LiCH2SiMe3 to 8 (SN2 type), which is supported by the VT <sup>31</sup>P{<sup>1</sup>H} NMR of the reaction between 1 and LiCH<sub>2</sub>SiMe<sub>3</sub> (cf. Fig. S14-S16†). At 193 K, the reaction is already complete (absence of signals of 1). The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows six broad multiplets that can be assigned to 7a,b. Upon warming, these signals broaden and only two broad triplets remain (at 233 and 253 K). The formation of 8 is detected for the first time at 253 K. At room temperature, 3, 7a,b, 8 and a second set of signals quite similar to those of 8 are observed. The latter might represent an isomer of 8 (starting either from 7a or 7b). After 24 hours at room temperature, the signals of 7a,b disappeared completely. Interestingly, whereas the formation of 6 as an

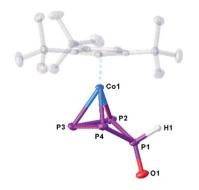


Fig. 6 Molecular structure of the anion in 10 in the solid state. Thermal ellipsoids are shown at 50% probability level. Hydrogen atoms, cations and solvent molecules are omitted for clarity.

additional product of the reaction between 1 and  $^tBuLi$  was found, the corresponding product  $[Cp'''Co(\eta^3-P_5(CH_2SiMe_3)_2)]^-$  (9) for the reaction of 1 with LiCH<sub>2</sub>SiMe<sub>3</sub> could never be detected by NMR, since the dimerisation and subsequent fragmentation of 7 to 9 and 3 would be energetically less favoured ( $-57.59 \text{ kJ mol}^{-1}$ ; Fig. 4). Beside the relative thermodynamic stability of the intermediates 4 and 7, the kinetic effects of the transformation processes play an important role, which is indicated by the outcome of these reactions, as well as their conversion rates.

The reaction of the oxygen-based nucleophile NaOH with 1 at room temperature yields  $[Na(dme)_3][Cp'''Co(\eta^3-P_4(O)H)]$  (10) in crystalline yields of 55% after workup (eqn (1)). In the first step, OH<sup>-</sup> binds to one phosphorus atom of the *cyclo-P*<sub>4</sub> ligand in 1, followed by a proposed tautomeric rearrangement with the formation of a P=O double and P-H single bond.

The structure of **10** (Fig. 6) reveals a folded *cyclo*-P<sub>4</sub> ligand in which one P atom is bent out of the plane (P1). The hydrogen atom bonded to phosphorus (H1) was found on the electron density map and was freely refined. The P-P distances are in the range of single or slightly shortened single bonds (P1-P2 2.1659(7), P1-P4 2.1676(7), P2-P3 2.1984(8), P3-P4 2.1938(8) Å; WBIs 0.94-1.07). The P1-O1 bond (1.5200(15) Å) is in the range between a single and a double bond (WBI of 1.08).

The  $^{31}P\{^{1}H\}$  NMR spectrum of **10** in thf-d<sub>8</sub> shows three multiplets centred at  $\delta = 74.5$ , 29.0 and -21.8 ppm with an integral ratio of 2:1:1 indicating an A<sub>2</sub>MX spin system. In the  $^{31}P$  NMR spectrum, a coupling between H1 and all P atoms can be observed. In the  $^{1}H$  NMR spectrum, a doublet of triplet of doublets at 7.78 ppm with the coupling constants of  $^{1}J_{\rm PH} = 356.8$ ,  $^{2}J_{\rm PH} = 20.6$  and  $^{3}J_{\rm PH} = 5.1$  Hz could be detected among the characteristic signals for the Cp‴ ligand. A similar reaction was reported by Peruzzini and co-workers for the reaction of [Ir(dppm)(Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>PPPP)]<sup>+</sup> with water under basic conditions.<sup>37</sup>

#### Conclusions

In summary, we were able to show that the irreversible dimerisation reaction of 1 can be overcome by carrying out the reactions at room temperature or lower. That way, in reactions with main group nucleophiles and upon reduction, 1 displays a unique tendency to release the ring strain of the *cyclo-P*<sub>4</sub> ligand. Here, unprecedented aggregation and rearrangement processes occur. The reduction of 1 with  $K[CpFe(CO)_2]$  yields selectively the dinuclear dianionic complex  $[(Cp'''Co)_2(\mu,\eta^3:\eta^3-P_8)]^{2-}$  (2), comprising an unprecedented open realgar-like  $P_8$  cage that reveals a double  $\eta^3$ -coordinated  $P_8$  ligand for the first

time. Compound 1 was functionalised with the main group nucleophiles <sup>t</sup>BuLi and LiCH<sub>2</sub>SiMe<sub>3</sub>, respectively, and  $[Cp'''Co(\eta^3-P_4R)]^-$  (R =  ${}^tBu$  (4), CH<sub>2</sub>SiMe<sub>3</sub> (7)) could be isolated as the first reaction products. Both compounds are metastable and show further rearrangement processes such as dimerisation and/or fragmentation. In comparison to other nucleophilesubstituted polyphosphorus complexes starting from a fourmembered ring in 1, here the first-formed product is highly reactive. Thus, compounds 4 and 7 can act as nucleophiles and react with another equivalent of 1 to the dinuclear complexes  $[(Cp'''Co)_2(\mu,\eta^3:\eta^3-P_8R)]^-(R={}^tBu(5), CH_2SiMe_3(8))$  comprising novel organo-substituted open realgar-like P8R ligands. For 4, an additional reaction pathway was observed. The formal dimerisation of 4 followed by an unprecedented fragmentation gives  $[Cp'''Co(\eta^3-P_5^tBu_2)]^-$  (6) with a new diorgano-substituted cyclo- $P_5$  ligand and  $[Cp'''Co(\eta^3-P_3)]^-$  (3).

#### Conflicts of interest

There are no conflicts to declare.

### Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft within the project Sche 384/38-1 and Sche 384/33-2. M. P. is grateful to the Fonds der Chemischen Industrie for a PhD fellowship.

#### Notes and references

- 1 Examples for complexes with a C<sub>4</sub>H<sub>4</sub> ligand: (a) P. D. Harvey, W. P. Schaefer, H. B. Gray, D. F. R. Gilson and I. S. Butler, *Inorg. Chem.*, 1988, 27, 57; (b) L. M. Cirjak, J.-S. Huang, Z.-H. Zhu and L. F. Dahl, *J. Am. Chem. Soc.*, 1980, 102, 6623; (c) P. E. Riley and R. E. Davis, *J. Organomet. Chem.*, 1977, 137, 91; (d) R. E. Davis and P. E. Riley, *Inorg. Chem.*, 1980, 19, 674; (e) P. E. Riley and R. E. Davis, *J. Organomet. Chem.*, 1976, 113, 157. For C<sub>3</sub>H<sub>3</sub> no examples were found in the CSD data bank. For more stable substituted derivatives with C<sub>3</sub>R<sub>3</sub> (R = alkyl, aryl, *e.g.* R. M. Tuggle and D. L. Weaver, *Inorg. Chem.* 1971, 10, 1504) and C<sub>4</sub>R<sub>4</sub> ligands (R = alkyl, aryl, *e.g.* A. R. Kudinov, E. V. Mutseneck and D. A. Luginov, *Coord.* Chem. Rev. 2004, 248, 571) are known and studied.
- (a) R. S. P. Turbervill, A. R. Jupp, P. S. B. McCullough, D. Ergöçmen and J. M. Goicoechea, *Organometallics*, 2013, 32, 2234; (b) F. Nief and L. Ricard, *Organometallics*, 2001, 20, 3884; (c) S. Du, Z. Chai, J. Hu, W.-X. Zhang and Z. Xi, *Chin. J. Org. Chem.*, 2019, 39, 2338; (d) S. Du, J. Yin, Y. Chi, L. Xu and W.-X. Zhang, *Angew. Chem., Int. Ed.*, 2017, 56, 15886; (e) S. Du, J. Yang, J. Hu, Z. Chai, G. Luo, Y. Luo, W.-X. Zhang and Z. Xi, *J. Am. Chem. Soc.*, 2019, 141, 6843.
- 3 C. Elschenbroich, M. Nowotny, B. Metz, W. Massa, J. Graulich, K. Biehler and W. Sauer, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 547.
- 4 O. J. Scherer, J. Braun and G. Wolmershäuser, *Chem. Ber.*, 1990, **123**, 471.

- 5 E. Mädl, G. Balázs, E. V. Peresypkina and M. Scheer, *Angew. Chem., Int. Ed.*, 2016, 55, 7702.
- 6 O. J. Scherer and T. Brück, Angew. Chem., Int. Ed. Engl., 1987, 26, 59.
- 7 O. J. Scherer, T. Brück and G. Wolmershäuser, *Chem. Ber.*, 1988, **121**, 935.
- 8 (a) L. Y. Goh, R. C. S. Wong, C. K. Chu and T. W. Hambley, *J. Chem. Soc., Dalton Trans.*, 1990, **6**, 977; (b) O. J. Scherer, J. Schwalb, G. Wolmershäuser, W. Kaim and R. Gross, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 363.
- 9 S. Heinl, G. Balázs, M. Bodensteiner and M. Scheer, *Dalton Trans.*, 2016, 45, 1962.
- 10 O. J. Scherer, H. Swarowsky, G. Wolmershäuser, W. Kaim and S. Kohlmann, Angew. Chem., Int. Ed. Engl., 1987, 26, 1153
- 11 O. J. Scherer, J. Schwalb, H. Swarowsky, G. Wolmershäuser, W. Kaim and R. Gross, *Chem. Ber.*, 1988, 121, 443.
- 12 O. J. Scherer, J. Vondung and G. Wolmershäuser, *Angew. Chem., Int. Ed. Engl.*, 1989, 28, 1355.
- 13 (a) M. Fleischmann, C. Heindl, M. Seidl, G. Balázs, A. V. Virovets, E. V. Peresypkina, M. Tsunoda, F. P. Gabbaï and M. Scheer, Angew. Chem., Int. Ed., 2012, 51, 9918; (b) M. Fleischmann, F. Dielmann, G. Balázs and M. Scheer, Chem.–Eur. J., 2016, 22, 15248; (c) O. J. Scherer, H. Sitzmann and G. Wolmershäuser, Angew. Chem., Int. Ed. Engl., 1985, 24, 351.
- 14 F. Dielmann, A. Timoshkin, M. Piesch, G. Balázs and M. Scheer, *Angew. Chem., Int. Ed.*, 2017, **56**, 1671.
- (a) C. Schoo, S. Bestgen, M. Schmidt, S. N. Konchenko,
   M. Scheer and P. W. Roesky, *Chem. Commun.*, 2018, 54,
   4770; (b) L. Qiao, C. Zhang, X.-W. Zhang, Z.-C. Wang,
   H. Yin and Z.-M. Sun, *Chin. J. Chem.*, 2020, 38, 295.
- 16 (a) O. J. Scherer, R. Winter and G. Wolmershäuser, Z. Anorg. Allg. Chem., 1993, 619, 827; (b) M. Herberhold, G. Frohmader and W. Milius, J. Organomet. Chem., 1996, 522, 185.
- 17 C. Schwarzmaier, A. Noor, G. Glatz, M. Zabel, A. Y. Timoshkin, B. M. Cossairt, C. C. Cummins, R. Kempe and M. Scheer, *Angew. Chem., Int. Ed.*, 2011, 50, 7283.
- 18 A. Cavaillé, N. Saffon-Merceron, N. Nebra, M. Fustier-Boutignon and N. Mézailles, *Angew. Chem., Int. Ed.*, 2018, 57, 1874.
- 19 K. A. Mandla, C. E. Moore, A. L. Rheingold and J. S. Figueroa, *Angew. Chem., Int. Ed.*, 2018, **57**, 6853.
- 20 U. Chakraborty, J. Leitl, B. Mühldorf, M. Bodensteiner, S. Pelties and R. Wolf, *Dalton Trans.*, 2018, 47, 3693.
- 21 C. M. Hoidn, T. M. Maier, K. Trabitsch, J. J. Weigand and R. Wolf, *Angew. Chem., Int. Ed.*, 2019, **58**, 18931.
- 22 F. Dielmann, E. V. Peresypkina, B. Krämer, F. Hastreiter, B. P. Johnson, M. Zabel, C. Heindl and M. Scheer, *Angew. Chem.*, *Int. Ed.*, 2016, 55, 14833.
- 23 (a) M. Piesch, M. Seidl, M. Stubenhofer and M. Scheer, Chem.-Eur. J., 2019, 25, 6311; (b) G. Capozzi, L. Chiti, M. Di Vaira, M. Peruzzini and P. Stoppioni, J. Chem. Soc., Chem. Commun., 1986, 1799; (c) P. Barbaro, A. Ienco, C. Mealli, M. Peruzzini, O. Scherer, G. Schmitt, F. Vizza and G. Wolmershäuser, Chem.-Eur. J., 2003, 9, 5195.

24 E. Mädl, M. V. Butovskii, G. Balázs, E. V. Peresypkina, A. V. Virovets, M. Seidl and M. Scheer, *Angew. Chem., Int. Ed.*, 2014, 53, 7643.

**Edge Article** 

- 25 J. R. Corfield, M. J. P. Harger, J. R. Shutt and S. Trippett, *J. Chem. Soc. C*, 1970, 1855.
- 26 E.-M. Rummel, G. Balázs, V. Heinl and M. Scheer, *Angew. Chem., Int. Ed.*, 2017, **56**, 9592.
- 27 [Cp"Co(η³-P₃)] was obtained by the reaction of 1 with MeNHC (1,3,4,5-tetramethyl-imidazol-2-ylidene): M. Piesch, S. Reichl, M. Seidl, G. Balázs and M. Scheer, Angew. Chem., Int. Ed., 2019, 58, 16563.
- 28 N. G. Connelly and W. E. Geiger, Chem. Rev., 1996, 96, 877.
- 29 F. Hennersdorf, J. Frötschel and J. J. Weigand, *J. Am. Chem. Soc.*, 2017, **139**, 14592.

- 30 F. Spitzer, C. Graßl, G. Balázs, E. M. Zolnhofer, K. Meyer and M. Scheer, *Angew. Chem., Int. Ed.*, 2016, 55, 4340.
- 31 W. Huang and P. L. Diaconescu, Chem. Commun., 2012, 48, 2216.
- 32 S. N. Konchenko, N. A. Pushkarevsky, M. T. Gamer, R. Köppe, H. Schnöckel and P. W. Roesky, *J. Am. Chem. Soc.*, 2009, **131**, 5740.
- 33 M. E. Barr, B. R. Adams, R. R. Weller and L. F. Dahl, *J. Am. Chem. Soc.*, 1991, **113**, 3052.
- 34 M. Scheer, U. Becker and E. Matern, *Chem. Ber.*, 1996, **129**, 721.
- 35 P. Pyykkö and M. Atsumi, Chem.-Eur. J., 2009, 15, 186.
- 36 P. Pyykkö and M. Atsumi, Chem.-Eur. J., 2009, 15, 12770.
- 37 V. Mirabello, M. Corpali, L. Gonsalvi, G. Manca, A. Ienco and M. Peruzzini, *Chem.–Asian J.*, 2013, **8**, 3177.