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Cluster Compounds

New Tetracobalt Cluster Compounds for Electrocatalytic Proton Reduction: Syntheses, Structures, and Reactivity

Ping Li, Riccardo Zaffaroni, Bas de Bruin, and Joost N. H. Reek^{*[a]}

Abstract: Reaction of $\text{Co}_2(\text{CO})_8$ and 1,3-propanedithiol in a 1:1 molar ratio in toluene affords a novel tetracobalt complex, $[(\mu_2\text{-pdt})_2(\mu_3\text{-S})\text{Co}_4(\text{CO})_6]$ ($\text{pdt} = \text{-SCH}_2\text{CH}_2\text{CH}_2\text{S-}$, **1**), which possesses some of the structural features of the active site of [FeFe]-hydrogenase. Carbonyl displacement reaction of complex **1** in the presence of mono- or diphosphine ligands leads to the formation of $[(\mu_2\text{-pdt})_2(\mu_3\text{-S})\text{Co}_4(\text{CO})_5(\text{PCy}_3)]$ (**2**) and $[(\mu_2\text{-pdt})_2(\mu_3\text{-S})\text{Co}_4(\text{CO})_4(\text{L})]$ [$\text{L} = \text{Ph}_2\text{PCH=CHPPh}_2$, **3**; $\text{Ph}_2\text{PCH}_2\text{N(Ph)CH}_2\text{PPh}_2$, **4**; $\text{Ph}_2\text{PCH}_2\text{N(iPr)CH}_2\text{PPh}_2$, **5**]. Complexes **1–5** have been fully characterized by spectroscopy

and single-crystal X-ray diffraction studies. Cyclic voltammetry has revealed that complexes **1–5** show a reversible first reduction wave and are active for electrocatalytic proton reduction in the presence of CF_3COOH . Protonation reactions have been monitored by ^{31}P and ^1H NMR and infrared spectroscopies, which revealed the formation of different protonated species. The mono-reduced species of **1–5** have been spectroscopically characterized by EPR and spectro-electro-infrared techniques.

Introduction

In the past decade, chemists have successfully explored several families of earth abundant transition metal-based monometallic complexes as homogeneous electrocatalysts for hydrogen evolution.^[1] The well-known examples include DuBois' nickel-phosphine complexes,^[2] cobalt oxime complexes,^[3] and molybdenum and cobalt complexes bearing polypyridyl ligands^[4] as well as other mononuclear cobalt^[5] and iron^[6] complexes. Some of the above complexes have also been recently developed as photodriven catalysts in hydrogen production systems.^[5c,7]

Besides the abovementioned monometallic complexes, two families of dimetallic complexes, Fe_2S_2 ^[8] and FeNiS_2 ^[9] have been synthesized as mimics of the active sites of [FeFe]- and [FeNi]-hydrogenases,^[10] respectively. More [FeFe]-hydrogenase model complexes have been reported compared to their [FeNi] counterparts, mainly due to two factors: 1) most Fe_2S_2 complexes are relatively air-stable compared to their FeNi analogues; 2) the synthetic routes leading to the hexacarbonyl diiron dithiolate precursors are easier than those leading to FeNi complexes. For example, the hexacarbonyl diiron dithiolate complex formulated as $[(\mu\text{-SR})_2\text{Fe}_2(\text{CO})_6]$ can be readily prepared by the straightforward reaction of $\text{Fe}_3(\text{CO})_{12}/\text{Fe}_2(\text{CO})_9$

with the corresponding thiol (RSH) or disulfide (RSSR) in organic solvents.^[11] The hexacarbonyl precursors are easily prepared in this way, and constitute starting materials for hundreds of derivatives through ligand substitution, acid–base, and redox reactions.^[8] Some of them have been investigated as electro- or photocatalysts for homogeneous proton reduction or hydrogen oxidation in the past decade.^[8f,g,12]

In 2004, Rauchfuss and co-workers reported an Ru_2S_2 complex, $[(\mu\text{-pdt})\text{Ru}_2(\text{CO})_4(\text{PCy}_3)_2]$, as a non-iron analogue of the active site of [FeFe]-hydrogenase, which proved to be active for dihydrogen activation.^[13] More recently, the same group reported the preparation of a series of heteronuclear FeMn and FeCo complexes by using ferrous carbonyl dithiolates as precursors, but the electrochemical properties of these complexes were not reported.^[14] On the other hand, Sun and co-workers reported a family of efficient electrocatalysts (MP_4N_2 ; $\text{M} = \text{Fe, Co}$) for hydrogen production when applied in neutral water at a low overpotential. With the same ligand, the corresponding P_4N_2 cobalt complex has a higher efficiency and lower overpotential than its iron analogue.^[15] Moreover, cobalt complexes bearing oxime or polypyridyl ligands also exhibit promising catalytic properties.^[3,4]

With these considerations in mind, we attempted to synthesize a cobalt analogue of the class of diiron dithiolate complexes as functional mimics of the active site of [FeFe]-hydrogenase, aiming for an efficient electrocatalytic hydrogen evolution reaction (HER). Although many Co-S-CO clusters have been studied previously,^[16,17] we are not aware of any literature report on the reaction of 1,3-propanedithiol with $\text{Co}_2(\text{CO})_8$. We thus decided to explore this straightforward reaction as a starting point. During the synthesis, we isolated an unexpected new tetracobalt cluster complex, $[(\mu_2\text{-pdt})_2(\mu_3\text{-S})\text{Co}_4(\text{CO})_6]$ (**1**), bearing two propane-1,3-dithiolate ligands, six carbon mon-

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Scheme 1. Synthesis of complex 1.

oxide ligands, and a tri-bridging sulfido atom (Scheme 1). Although more complex, this cluster features some of the characteristics of the Fe_2S_2 model. In analogy to the Fe_2S_2 hexacarbonyl complex, treatment of compound 1 with phosphine ligands readily afforded a series of mono- or disubstituted complexes, $[(\mu_2\text{-pdt})(\mu_3\text{-S})\text{Co}_4(\text{CO})_5(\text{PCy}_3)]$ (2) and $[(\mu_2\text{-pdt})(\mu_3\text{-S})\text{Co}_4(\text{CO})_4(\text{L})]$ [$\text{L} = \text{Ph}_2\text{PCH}=\text{CHPPh}_2$, 3; $\text{Ph}_2\text{PCH}_2\text{N}(\text{Ph})\text{CH}_2\text{PPh}_2$, 4; $\text{Ph}_2\text{PCH}_2\text{N}(\text{iPr})\text{CH}_2\text{PPh}_2$, 5]. In this contribution, we report the syntheses, structures, and protonation properties of this series of tetracobalt compounds. All of the tetracobalt compounds 1–5 have been demonstrated to be electrocatalysts for the HER.

Results and Discussion

Syntheses and spectroscopic characterization

Reaction of $\text{Co}_2(\text{CO})_8$ and 1,3-propanedithiol in toluene at 40 °C overnight resulted in a dark-brown suspension. After an insoluble black powder was removed by filtration, complex 1 was isolated by column chromatography in 31% yield based on cobalt (Scheme 1).

Phosphine-substituted analogues 2–5 were readily prepared in moderate to high yields (65–89%) by carbonyl displacement reactions of complex 1 in the presence of one equivalent of the corresponding mono- or diphosphine ligand, as shown in Scheme 2. All of these carbonyl substitution reactions were conducted in toluene or dichloromethane solution at room temperature and TLC analysis was used to monitor their progress.

All of the tetracobalt complexes 1–5 reported in this study have been spectroscopically characterized by IR, ^1H NMR, and $^{31}\text{P}\{^1\text{H}\}$ NMR, as well as by elemental analysis. Complex 1 displayed three $\nu(\text{CO})$ bands at $\tilde{\nu} = 2062$, 2020, and 1986 cm^{-1} in its IR spectrum recorded in CH_2Cl_2 (Figure S1). The PCy_3 -substituted complex 2 exhibited a more complicated IR pattern in the region $\tilde{\nu} = 2014\text{--}1913\text{ cm}^{-1}$, with a red shift of about 40 cm^{-1} in the average value of $\nu(\text{CO})$ compared to that for complex 1, indicative of enhanced π -back-donation to the CO ligands (i.e., enhanced electron density at the relevant cobalt atoms). Even larger red shifts of $\nu(\text{CO})$ of 46, 56, and 58 cm^{-1} were observed for the diphosphine-substituted complexes 3, 4, and 5, respectively. Broad $^{31}\text{P}\{^1\text{H}\}$ NMR signals were observed at $\delta = 53.6$, 65.2, 19.5, and 17.5 ppm for 2–5, respectively. These broad $^{31}\text{P}\{^1\text{H}\}$ NMR signals indicate exchange processes, as might be expected for a flexible coordination sphere about

Scheme 2. Syntheses of complexes 2–5.

the cobalt atom ligated by the phosphine ligand. The results of elemental analyses of complexes 1–5 were in good agreement with the compositions revealed by X-ray diffraction studies, showing incorporation of co-crystallized solvent molecules.

Molecular structures

ORTEP plots of the molecular structures of complexes 1–5 are presented in Figure 1. Selected bond lengths, angles, and dihedral angles are listed in Table 1.

The molecular structures of 1–5 each display a butterfly-like tetracobalt core assembled from two $\mu_2\text{-SCH}_2\text{CH}_2\text{CH}_2\text{S}^-$ groups and a μ_3 -sulfido atom. Each cobalt atom is ligated by at least one carbonyl group. The three carbonyl ligands coordinated to Co1, Co2, and Co3 lie in the plane defined by these three cobalt atoms. The geometry at Co1 is distorted square-pyramidal, made up of one CO and four sulfur ligands, while Co2 and Co3 reside in identical environments. The dihedral angles between the Co1-Co2-Co3 and Co2-Co3-Co4 planes range from $150.70(4)$ to $141.27(2)^\circ$ (Table 1). The six-membered Co4-P1-C-N1-C-P2 rings in complexes 4 and 5 each adopt a chair configuration.

As shown in Figure 1, a distorted tetrahedral geometry was found for Co4 in complexes 1–5, regardless of the metal–metal bonds. Carbonyl displacement reactions took place at Co4 in the presence of diphosphine ligands and the original geometry of Co4 was retained in the resulting disubstituted complexes 3–5. This phenomenon is consistent with the similar bond distances for Co4-C4 ($1.815(2)\text{ \AA}$) and Co4-C5 ($1.8268(19)\text{ \AA}$), which suggest significantly weaker bonds than Co4-C6 ($1.794(2)\text{ \AA}$) in complex 1. On the other hand, the geometry at Co4 in complex 2 became more symmetrical after one of the carbonyl ligands was displaced by PCy_3 . This rearrangement significantly affected the redox and protonation properties, as discussed below.

Figure 1. ORTEP plots of 1–5. All hydrogen atoms in 1–5, disordered cyclohexyl groups in 2, and the disordered phenyl group in 3 have been omitted for clarity. Thermal ellipsoids (296 K) are drawn at the 30% probability level.

Table 1. Selected bond lengths [Å], angles [°], and dihedral angles [°] for 1–5.							
	1	2	3 a ^[b]	3 ^[a] 3 b	4	5 a ^[b]	5 ^[a] 5 b
bond lengths							
Co1–Co2	2.5122(3)	2.5295(5)	2.5401(12)	2.5540(11)	2.5509(6)	2.5400(6)	2.5422(5)
Co1–Co3	2.5332(3)	2.5295(5)	2.5335(11)	2.5421(13)	2.5454(6)	2.5335(6)	2.5411(6)
Co2–Co3	2.6493(3)	2.6994(4)	2.6406(11)	2.6147(12)	2.6329(6)	2.6296(5)	2.6389(5)
Co2–Co4	2.5605(3)	2.5523(5)	2.5433(10)	2.5915(11)	2.5781(6)	2.5711(5)	2.5882(6)
Co3–Co4	2.5527(3)	2.5523(5)	2.6371(11)	2.5302(11)	2.6045(6)	2.6038(5)	2.5729(5)
Co1–C1	1.7761(18)	1.760(4)	1.773(8)	1.760(8)	1.767(4)	1.757(4)	1.756(3)
Co2–C2	1.7472(18)	1.747(3)	1.737(8)	1.747(7)	1.739(3)	1.731(4)	1.743(3)
Co3–C3	1.7488(18)	1.747(3)	1.753(7)	1.739(8)	1.733(4)	1.741(3)	1.737(3)
Co4–C4	1.815(2)	1.759(3)					
Co4–C5	1.8268(19)	1.759(3)					
Co4–C6	1.794(2)		1.759(7)	1.770(7)	1.771(3)	1.760(3)	1.767(3)
Co4–P1		2.2389(10)	2.2459(18)	2.2010(17)	2.2351(10)	2.2322(8)	2.2114(8)
Co4–P2			2.2096(16)	2.2163(19)	2.2342(9)	2.2107(8)	2.2258(9)
bond angles							
S5–Co4–C4	108.68(7)	126.03(9)					
S5–Co4–C5	100.99(7)	126.03(9)					
S5–Co4–C6	138.70(6)		139.7(2)	142.0(2)	143.49(11)	142.45(10)	142.45(10)
S5–Co4–P1		101.05(4)	103.47(7)	112.60(7)	107.10(3)	111.06(3)	90.35(3)
S5–Co4–P2			113.71(6)	105.16(7)	106.45(3)	107.41(3)	107.41(3)
C4–Co4–C5	101.13(9)	97.64(19)					
C4–Co4–C6	97.83(9)						
C5–Co4–C6	104.31(9)						
C4–Co4–P1		100.24(10)					
C5–Co4–P1		100.24(10)					
C6–Co4–P1			105.1(2)	95.2(2)	98.20(12)	97.08(9)	96.42(9)
C6–Co4–P2			95.8(2)	101.3(2)	96.59(11)	96.38(9)	95.64(10)
P1–Co4–P2			86.68(6)	87.71(7)	95.57(3)	90.35(3)	90.52(3)
dihedral angle							
Co1–Co2–Co3–Co4	148.74(1)	147.90(3)	150.70(4)	147.28(4)	145.90(2)	143.60(2)	141.27(2)

[a] Two independent molecules were found in one asymmetric unit. [b] The molecule shown Figure 1.

Electrochemistry

Cyclic voltammetry (CV) measurements on complexes **1–5** were carried out in THF under a nitrogen atmosphere. The cyclic voltammograms shown in Figure 2 were initiated by

Figure 2. Cyclic voltammograms of complexes **1–5** (1.0 mM) recorded in THF (0.1 M $n\text{Bu}_4\text{PF}_6$) at a scan rate of 100 mV s^{-1} .

scanning in the cathodic direction at a rate of 100 mV s^{-1} . The redox potentials were referenced against the Fc/Fc^+ couple (using ferrocene as an internal standard), and are summarized in Table 2.

Table 2. Redox potentials of complexes **1–5**.^[a]

	$E_{1/2}^{\text{red1}}$ [V]	$E_{\text{pa}}^{\text{red2}}$ [V]	$E_{\text{pa}}^{\text{oxi}}$ [V]
1	−1.17	−1.89	0.60, 0.73
2	−1.39	−2.13	0.26
3	−1.59	−2.23	0.01
4	−1.60	−2.21	0.00
5	−1.63	−2.25	−0.05

[a] Electrochemical potentials vs Fc/Fc^+ obtained from cyclic voltammetry in THF/0.1 M $n\text{Bu}_4\text{NPF}_6$ at 298 K. Scan rate: 100 mV s^{-1} .

All of the tetracobalt complexes showed a fully reversible one-electron reduction. When the window was increased to investigate further reduced species, each complex displayed a quasi-reversible first reduction wave and an irreversible second reduction wave in THF, as shown in Figure 2. The first reduction wave for each complex was confirmed to be a one-electron process by bulk electrolysis (Figures S2–S6 in the Supporting Information). By ligand substitution in complexes **1–5**, the potentials were tuned from −1.17 to −1.63 V. The donor strengths of the phosphine ligands used in our study decrease in the order $\text{PNP}^{\text{Pr}} > \text{PNP}^{\text{Ph}} > \text{dppv} > \text{PCy}_3$, which is in line with the results deduced from IR spectral analysis. The second

reduction for each complex is negatively shifted by 0.61 to 0.72 V compared to its first reduction.

Frontier orbitals

To gain more insight into the frontier orbitals relevant to the redox events, we optimized the geometries of complexes **1**, $[(\mu_2\text{-pdt})(\mu_3\text{-S})\text{Co}_4(\text{CO})_5(\text{PMe}_3)]$ (**2-PMe**₃), and **3** by DFT at the BP86/def2-TZVP level. The monosubstituted complex **2-PMe**₃ was utilized as an analogue of **2** because all attempts to optimize complex **2** converged to a structure with a bridging carbonyl ligand (Figure S7), which is inconsistent with the IR spectroscopic and X-ray diffraction results (all of the CO ligands are terminally bound). Complex **3** was chosen as a representative example of the diphosphine-substituted compounds, as complexes **3–5** have identical geometries and redox properties. The optimized geometries of **1**, **2-PMe**₃, and **3**, as well as their frontier orbitals, are shown in Figure 3.

Figure 3. Plots (isovalue = ± 0.06) of the HOMOs (left) and LUMOs (right) of complexes **1** (top), **2-PMe**₃ (middle), and **3** (bottom).

All of the HOMOs shown in Figure 3 (left) are mainly located on the d orbitals of the cobalt atoms, and scarcely on the organic ligands, suggesting that the oxidation events observed by cyclic voltammetry are metal-centered. The HOMO of complex **1** is delocalized over all of the cobalt atoms, with the

highest coefficients on Co2 and Co3 (labels correspond to those in Figure 1). This suggests a lower oxidation state for Co2 and Co3. Interestingly, the LUMOs shown in Figure 3 (right) are metal-centered, but are partially located on the two sulfur atoms of the pdt ligands. The corresponding reduction waves are quasi-reversible processes, as observed by cyclic voltammetry.

Spectro-electrochemistry

To investigate the electronic structure of the mono-reduced species for each compound, we investigated the changes in their IR spectra upon scanning over their first reduction waves by spectro-electrochemical measurements in THF in an OTTE cell.^[18] Spectral changes for complexes 1–3 are shown in Figure 4, and those for complexes 4 and 5 are displayed in Figures S8 and S9 in the Supporting Information.

As shown in Figure 4a, disappearance of the neutral complex 1 was accompanied by the appearance of new peaks at $\tilde{\nu} = 1994$ and 1950 cm^{-1} , attributable to formation of the radical anion $1^{\cdot-}$. An average red shift of around 50 cm^{-1} was found for the reduction of 1 to $1^{\cdot-}$, which is consistent with increased π back-donation from the reduced cobalt cluster

Figure 4. Infrared spectral changes occurring upon scanning over the first reduction waves of 1–3 (a–c, respectively). Measurements were made on 1.0 mM solutions in THF (0.1 M $n\text{Bu}_4\text{NPF}_6$) in an OTTE cell at 295 K. Negative peaks indicate disappearance of the starting compounds, positive peaks indicate appearance of the one-electron-reduced species.

atoms to the carbonyl ligands. A somewhat smaller red shift was found for the one-electron-reduced monosubstituted complex 2 ($\Delta\nu(\text{CO}) \approx 40\text{ cm}^{-1}$), but a larger red shift was seen for the disubstituted complex 3 ($\Delta\nu(\text{CO}) \approx 55\text{ cm}^{-1}$). Notably, no bridging CO band appeared upon one-electron reduction of any of the tetracobalt complexes 1–5.

EPR spectroscopy

The electronic structures of the anionic tetranuclear cobalt clusters $1^{\cdot-}$, $2^{\cdot-}$, and $3^{\cdot-}$ were further investigated by X-band EPR spectroscopy. Species $1^{\cdot-}$, $2^{\cdot-}$, and $3^{\cdot-}$ were generated in situ by reducing the corresponding neutral clusters with 0.9 equivalents of Cp^*Co in THF. To obtain a better glass, we added 0.1 M $n\text{Bu}_4\text{NPF}_6$ (TBAH) to the solutions before freezing. X-band EPR spectra (20 K) recorded from the thus obtained samples are shown in Figures 5 and 6, and are characteristic of low-spin $S = 1/2$ systems. The g -anisotropy in the spectra of $1^{\cdot-}$ and $2^{\cdot-}$ is not well resolved, leading to broad, nearly isotropic spectra without any resolved hyperfine couplings (Figure 5, top). Although the spectrum of $2^{\cdot-}$ shows hyperfine interactions (HFIs) with multiple cobalt nuclei (Figure 5, bottom),

Figure 5. Top: X-band EPR spectrum of tetranuclear cobalt cluster $1^{\cdot-}$ in frozen THF (TBAH added). Experimental conditions: temperature 20 K, microwave power 0.2 mW, field modulation amplitude 2 Gauss, microwave frequency 9.369488 GHz. Bottom: X-band EPR spectrum of tetranuclear cobalt cluster $2^{\cdot-}$ in frozen THF (TBAH added). Experimental conditions: temperature 20 K, microwave power 0.2 mW, field modulation amplitude 2 Gauss, microwave frequency 9.369488 GHz.

Figure 6. Experimental (black) and simulated (gray) X-band EPR spectra of tetranuclear cobalt cluster 3^+ in frozen THF (TBAH added). Experimental conditions: temperature 20 K, microwave power 2 mW, field modulation amplitude 4 Gauss, microwave frequency 9.369488 GHz. The simulated spectrum was obtained with the parameters shown in Table S1 (Supporting Information).

these are not well resolved and any attempts to simulate them would be futile (no unique fit). In contrast, the g -anisotropy of 3^+ is well resolved in the EPR spectrum (Figure 6). Some of its cobalt hyperfine interactions are also evident, but since the spectrum is still relatively broad and HFIs with four cobalt and two phosphorus nuclei overlap, these are not easily simulated. A reasonable simulation was obtained using resolved HFIs with only two of its cobalt nuclei, but this is unlikely to be a unique fit of the experimental spectrum. The DFT-calculated g -values match reasonably well with the experimental values. The calculated cobalt HFIs, on the other hand, seem to be larger than indicated by the simulated values (Table S1). This is likely to be due to non-coinciding hyperfine- and g -tensors (indeed, each of the DFT-calculated cobalt HFI tensors has large Euler rotation angles with respect to the g -tensor, with $\alpha = 0\text{--}37^\circ$, $\beta = 6\text{--}70^\circ$, and $\gamma = 16\text{--}84^\circ$).

Protonation reactions

To spectroscopically characterize the protonated species that might be involved in the possible electrocatalytic proton reduction, protonation reactions of **1–5** using $\text{HBF}_4\cdot\text{Et}_2\text{O}$ were carried out at room temperature and monitored by $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR as well as IR spectroscopy. In line with the electrocatalysis, no protonation reaction was observed for complex **1** upon the addition of $\text{HBF}_4\cdot\text{Et}_2\text{O}$ to a solution in dichloromethane.

Complete conversion of **2** to its protonated species $[\text{2H}_3]^+$ was observed, as indicated by the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (Figure 7). The broad signal at $\delta = 53.6$ ppm diminished and a new sharp peak at $\delta = 29.4$ ppm developed when 1.7 equiv of $\text{HBF}_4\cdot\text{Et}_2\text{O}$ was added to the solution. No hydride signal was detected by ^1H NMR, indicating that the protonation did not occur at one of the cobalt centers. Instead, a new peak was observed with a chemical shift of $\delta = 3.58$ ppm (labeled with an asterisk in Figure 7), which can most likely be ascribed to

Figure 7. $^{31}\text{P}\{^1\text{H}\}$ (left) and ^1H (middle) NMR spectra recorded for complex **2** in CD_2Cl_2 in the presence of a) 0, b) 0.8, and c) 1.7 equivalents of $\text{HBF}_4\cdot\text{Et}_2\text{O}$ at 295 K. Right: The proposed structure of $[\text{2H}_3]^+$.

protonation on the $\mu_3\text{-S}$ atom. This is in line with the computational frontier orbitals in Figure 3, which indicated delocalization of the HOMO over the $\mu_3\text{-S}$ atom in **2-PMe**. CF_3COOH was also used as a milder acid to protonate complex **2**. Again, no hydride signal was observed and a sharp $^{31}\text{P}\{^1\text{H}\}$ signal appeared ($\delta = 33.7$ ppm) at the expense of the broad peak at $\delta = 53.6$ ppm (Figure S10). The different chemical shift observed upon protonation with CF_3COOH (compared to $\text{HBF}_4\cdot\text{Et}_2\text{O}$) might be attributed to the formation of a hydrogen bond between CF_3COO^- and H^+ . The structure of $[\text{2H}_3]^+$ in the solid state could not be established as all attempts to crystallize it were unsuccessful.

Upon protonation of complex **3**, a hydride signal was observed at $\delta = -20.1$ ppm for $[\text{3Hy}]^+$ in the ^1H NMR spectra (Figure 8), indicating the formation of a cobalt-hydride species. The sharp singlet at $\delta = 86.3$ ppm in the $^{31}\text{P}\{^1\text{H}\}$ spectrum may also be ascribed to $[\text{3Hy}]^+$. The downfield shift of the $^{31}\text{P}\{^1\text{H}\}$ signal is consistent with protonation of the cobalt core, which decreases the electron density on the cobalt atoms. Protonation of the diphosphine-coordinated cobalt atom is unlikely, as no coupling was observed between the hydride and the phosphorus signals. As shown in Figure S11, complex **4** displayed similar protonation behavior as complex **3**.

Figure 8. $^{31}\text{P}\{^1\text{H}\}$ (left) and ^1H (middle) NMR spectra recorded for complex **3** in CD_2Cl_2 in the presence of a) 0 and b) 1.5 equivalents of $\text{HBF}_4\cdot\text{Et}_2\text{O}$ at 295 K. Right: The proposed structure of $[\text{3Hy}]^+$.

Figure 9. $^{31}\text{P}\{^1\text{H}\}$ (left) and ^1H (middle) NMR spectra recorded for complex **5** in CD_2Cl_2 in the presence of a) 0, b) 0.6, c) 1.2, d) 2.4, and e) 3.6 equivalents of $\text{HBF}_4\cdot\text{Et}_2\text{O}$ at 295 K. Right: Proposed structures of the protonated species $[\text{5H}_\text{N}]^+$, $[\text{5Hy}]^+$, and $[\text{5H}_\text{NHy}]^{2+}$.

The $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra obtained for complex **5** in CD_2Cl_2 upon addition of $\text{HBF}_4\cdot\text{Et}_2\text{O}$ are shown in Figure 9. A broad signal at $\delta = 17.6$ ppm was seen in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5** in the absence of acid. Upon the addition of 0.6 equiv $\text{HBF}_4\cdot\text{Et}_2\text{O}$ (Figure 9b), two new ^{31}P signals developed, a broad peak at $\delta = 23.5$ and a sharp one at $\delta = 28.1$ ppm. At the same time, a hydride signal at $\delta = -18.7$ ppm was observed in the ^1H NMR spectrum. The sharp ^{31}P signal at $\delta = 28.1$ ppm and the hydride signal at $\delta = -18.7$ ppm may be assigned to a cobalt-hydride species $[\text{5Hy}]^+$ formed upon protonation of one of the cobalt atoms. The broad ^{31}P peak at $\delta = 23.5$ ppm can be ascribed to protonation of the N atom of the diphosphine ligand, PNP^{Pr} , leading to the formation of $[\text{5H}_\text{N}]^+$, whereas the cobalt core was well preserved without formation of a hydride ligand. No starting material **5** was left following the addition of 1.2 equiv of $\text{HBF}_4\cdot\text{Et}_2\text{O}$ to the solution (Figure 9c). The ratio of $[\text{5Hy}]^+ / [\text{5H}_\text{N}]^+$ remained at around 1:7 when the acid concentration was increased from 0.6 to 1.2 equiv. Upon the addition of more equivalents of $\text{HBF}_4\cdot\text{Et}_2\text{O}$ (Figure 9d, e), all of the signals corresponding to the mono-protonated species $[\text{5Hy}]^+$ and $[\text{5H}_\text{N}]^+$ disappeared, and two singlet ^{31}P signals were observed at $\delta = 40.1$ and 34.2 ppm. Moreover, two hydride signals were

observed at $\delta = -18.9$ and -20.8 ppm, suggesting the formation of two hydrido species in a ratio of approximately 10:7. The final protonation products are proposed to be two isomers of a diprotonated species, $[\text{5H}_\text{NHy}]^{2+}$, as no coupling between the two hydride signals was detected in H-H COSY or NOESY experiments. The formation of a proton-hydride species rather than a hydride-hydride species is also supported by the IR spectrum shown in Figure 10. The fully protonated species of complex **5** displayed an identical IR pattern as $[\text{4Hy}]^+$, albeit with a small difference (ca. 5 cm^{-1}) in carbonyl stretching frequency (Table 3). The protonation process of complex **5** and the proposed structures of the protonated species $[\text{5Hy}]^+$, $[\text{5H}_\text{N}]^+$, and $[\text{5H}_\text{NHy}]^{2+}$ are shown in Figure S12. Importantly, the more complex protonation reactions are consistent with the more complex catalytic waves observed in the CV experiments.

The protonated species in this study were also characterized by IR spectroscopy, and the spectra together with those of their parent compounds are displayed in Figure 10. The $\mu_3\text{-S}$ -protonated species $[\text{2H}_\text{S}]^+$ displayed three $\nu(\text{C}=\text{O})$ bands at 2062, 2019, and 1982 cm^{-1} . As expected, the metal-protonated species $[\text{3Hy}]^+$ and $[\text{4Hy}]^+$ show a different pattern to that of $[\text{2H}_\text{S}]^+$. The IR patterns of $[\text{3Hy}]^+$ and $[\text{4Hy}]^+$ are nearly identical to one another, suggesting that the N atom in complex **4** is not involved in the protonation reaction, which is consistent

Table 3. Summary of spectroscopic data for **1–5** and their protonated species.^[a]

	$\nu(\text{CO})$ [cm^{-1}]	$^{31}\text{P}\{^1\text{H}\}$ [ppm]	^1H [ppm] ^[b]
1	2062 (s), 2020 (s), 1986 (m)		
2	2014 (m), 1994 (s), 1979 (s), 1946 (m), 1913 (w)	53.6	
$[\text{2H}_\text{S}]^+$	2062 (m), 2019 (s), 1982 (w)	29.4	
3	2004 (m), 1974 (m, sh), 1959 (s)	65.2	
$[\text{3Hy}]^+$	2045 (w, sh), 2030 (s), 1995 (w)	86.3	−20.1
4	2003 (m), 1963 (s), 1931 (s)	19.2	
$[\text{4Hy}]^+$	2043 (w, sh), 2030 (s), 1994 (vw)	29.2	−18.6
5	2001 (m), 1962 (s), 1928 (w)	17.6	
$[\text{5H}_\text{N}]^+$	2012 (m), 1970 (s), 1930 (w)	23.5	
$[\text{5Hy}]^+$		28.1	−18.7
$[\text{5H}_\text{NHy}]^{2+}$	2049 (w, sh), 2035 (s), 2001 (w)	40.1, 34.2	−18.9, −20.8

[a] Data measured in CD_2Cl_2 (NMR) or CH_2Cl_2 (IR). [b] Hydride signals.

with the NMR observations. The N-protonated species $[\text{5H}_\text{N}]^+$ displayed a blue shift in $\nu(\text{C}=\text{O})$ by about 10 cm^{-1} compared to its precursor **5**, although the IR pattern remained similar. The diprotonated species, $[\text{5H}_\text{NHy}]^{2+}$, exhibited a similar IR pattern in the carbonyl region as $[\text{4Hy}]^+$. All of the spectroscopic data for complexes **1–5** and their protonated species are summarized in Table 3.

Electrocatalytic proton reduction

All of the tetracobalt clusters reported in this study were investigated as electrocatalysts for proton reduction in THF. Cyclic voltammetric responses were recorded for complex **1** (1 mM) upon gradually increasing the concentration of CF_3COOH (0–

Figure 10. IR spectra of complexes **2–5** and their protonated species in CH_2Cl_2 .

Figure 11. Electrochemical response of 1.0 mM **1** to the addition of CF_3COOH (0–90 mM) recorded in THF (0.1 M $n\text{Bu}_4\text{NPF}_6$, scan rate 100 mV s^{-1}).

90 mM). The results are shown in Figure 11, from which it is evident that the one-electron-reduced complex $1^{\cdot-}$ was not active for proton reduction, whereas the further reduced species (probably 1^{2-}) showed significant current enhancement ($i_c/i_p=34$) at a scan rate of 100 mV s^{-1} when the concentration of CF_3COOH was gradually increased from 0 to 90 mM. The current enhancement indicated an electro-catalytic proton reduction process. Complex **2** displayed identical properties to those of complex **1** in terms of proton reduction, as shown in Figure S13. The onset potentials for current enhancements with complexes **3** and **4** were between the first and second reductions (Figures S14 and S15 in the Supporting Information). In contrast, the mono-reduced species $5^{\cdot-}$ was already active for electrocatalytic hydrogen evolution (Figure 12), which might be assisted by the N atom of the ligand as a proton relay.

In order to confirm the formation of molecular hydrogen, we conducted GC-coupled bulk electrolysis in the presence of CF_3COOH (160 μL) and the corresponding cobalt complex in THF using 0.15 M $n\text{Bu}_4\text{NPF}_6$ as the supporting electrolyte within a gas-tight set-up (see Figure S16 for a photograph of our set-up). The system was calibrated with nine data points measured

Figure 12. Electrochemical response of 1.0 mM **5** to the addition of CF_3COOH (0–90 mM) recorded in THF (0.1 M $n\text{Bu}_4\text{NPF}_6$, scan rate 100 mV s^{-1}).

Figure 13. Electrocatalytic H_2 formation profiles obtained by bulk electrolysis of **1** at -2.15 V , **3** and **5** at -2.45 V in the presence of CF_3COOH (160 μL) in THF (20 mL) with 0.15 M $n\text{Bu}_4\text{NPF}_6$ as supporting electrolyte. Amount of catalyst: **1**, 19.6 mg, 30 μmol ; **3**, 10.5 mg, 10.6 μmol ; **5**, 9.6 mg, 9.1 μmol ; **3_LF**, 9.0 mg, 9.1 μmol ; **1_LF**, 5.9 mg, 9.1 μmol . For the data series of **1_LF**, bulk electrolysis was conducted for 3000 s while the GC was run for 5000 s, showing that there was no H_2 leaking out nor O_2 leaking into the set-up. LF = leak-free reference electrode.

by injection of different amounts of H_2 into the set-up (Figure S17). In our experiments, up to 800 μL of H_2 was obtained during 5000 s (Figure 13).

Conclusions

We have reported herein the syntheses and full characterization of a new series of butterfly-like tetracobalt cluster complexes, which serve as molecular catalysts for electrocatalytic hydrogen evolution. The potential of the first quasi-reversible reduction of the Co_4S_5 clusters is tunable in the range from -1.17 to -1.63 V vs Fc/Fc^+ by phosphine substitution of one or two carbonyl ligands in the all-carbonyl parent complex. The mono-reduced radical anions, $1^{\cdot-}$, $2^{\cdot-}$, and $3^{\cdot-}$, have been characterized by EPR spectroscopy and IR spectro-electrochemistry. Different protonated species have been observed by NMR and IR, providing insights into the reactivity of the tetracobalt clusters pertinent to electrocatalytic proton reduction. Most importantly, this work shows for the first time that synthetic Co-S-CO-based clusters can partially mimic the active sites of [FeFe]-hydrogenases, although the onset potential for proton

reduction was observed in the range of around -1.5 to -2.0 V, which limits more practical applications of these catalysts.

Experimental Section

General considerations

All experiments and manipulations were carried out under a dry and oxygen-free atmosphere of nitrogen or argon using standard Schlenk techniques unless otherwise specified. Solvents were dried and distilled over an appropriate drying agent under a nitrogen atmosphere. All commercially available reagents were used as received. Bis(phosphinomethyl)amines, $(\text{Ph}_2\text{PCH}_2)_2\text{NPh}$ (PNP^{Ph}) and $(\text{Ph}_2\text{PCH}_2)_2\text{NCH}(\text{CH}_3)_2$ (PNP^{ipr}), were synthesized according to reported procedures.^[19] ^1H , ^{13}C , and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were collected on a Bruker AVANCE 400 spectrometer. Infrared spectra were recorded on a Nicolet Nexus FTIR spectrometer. Elemental analyses were performed with a Perkin-Elmer 2400 elemental analyzer.

Electrochemistry

Cyclic voltammetry (CV) measurements were made using an Autolab PGSTAT302N electrochemical workstation. All measurements were performed in anhydrous THF ($0.1\text{ M } n\text{Bu}_4\text{NPF}_6$) containing a 1.0 mM solution of the investigated complex. Cyclic voltammetry measurements were performed using glassy carbon (diameter 3 mm) as the working electrode, a leak-free Ag/AgCl electrode (eDAQ, ET069) as the reference, and a carbon rod as the counter electrode. All redox potentials reported in this work are referenced to the ferrocene/ferrocenium (Fc/Fc^+) couple as an internal standard.

Bulk electrolysis experiments were conducted in an argon-flushed cell using a carbon foam (80 PPI , pores per inch) working electrode, a Pt counter electrode with a P5 frit, and an Ag wire with a P3 frit as the reference. Alternatively, leak-free Ag/AgCl (eDAQ, ET069) was used as the reference electrode. The solvent was THF containing $0.15\text{ M } n\text{Bu}_4\text{NPF}_6$ as supporting electrolyte. GC-coupled bulk electrolysis was conducted with the same set-up. In this case, the cell was directly connected to a GC equipped with circulation pump to detect H_2 evolution over time. The amount of CF_3COOH ($160\text{ }\mu\text{L}$) was kept constant at the beginning of each experiment.

Spectro-electrochemistry

Spectro-electrochemistry was performed in an optically transparent thin-layer ($200\text{ }\mu\text{m}$) electrochemical (OTTLE) cell equipped with CaF_2 optical windows and a Pt minigrid working electrode, a Pt minigrid counter electrode, and an Ag wire as reference electrode. The temporal evolution of IR absorbance spectra was monitored on a Nicolet Nexus FTIR spectrometer in the course of thin-layer cyclic voltammetry scanning (scan rate 2 mVs^{-1} controlled by a PGSTAT 10 (Eco-Chemie) potentiostat).

EPR spectroscopy

Experimental X-band EPR spectra were recorded on a Bruker EMX spectrometer (Bruker BioSpin) equipped with an He temperature control cryostat system (Oxford Instruments). Simulations of the EPR spectra were performed by iteration of the anisotropic g -values and line widths using the EPR simulation program W95EPR developed by Prof. Dr. Frank Neese.

Syntheses

$[(\mu_2\text{-pdt})_2(\mu_3\text{-S})\text{Co}_4(\text{CO})_6]$ (1): A mixture of $\text{Co}_2(\text{CO})_8$ (700 mg , 2.05 mmol) and 1,3-propanedithiol (220 mg , 2.03 mmol) in toluene (20 mL) was heated at 40°C overnight. The precipitated black powder was removed by filtration and the brown filtrate was concentrated to dryness. The analytically pure product was isolated by column chromatography on silica gel ($60\text{--}200\text{ }\mu\text{m}$), eluting with petroleum ether/ CH_2Cl_2 ($5:1$, v/v). Yield of **1**: 206 mg (31% , based on Co). ^1H NMR (400 MHz , CDCl_3 , 25°C): $\delta = 2.72\text{--}2.36\text{ ppm}$ (br m, 12 H ; $\text{SCH}_2\text{CH}_2\text{CH}_2\text{S}$); ^{13}C NMR (101 MHz , CDCl_3 , 25°C): $\delta = 31.88\text{ (s)}$, 29.87 (s) , 26.41 (s) , 26.17 ppm (s) ; IR (CH_2Cl_2): $\tilde{\nu} = 2062\text{ (s)}$, 2020 (s) , $1986\text{ cm}^{-1}\text{ (m)}$ (C=O); elemental analysis calcd (%) for $\text{C}_{12}\text{H}_{12}\text{Co}_4\text{O}_6\text{S}_5 \cdot 0.5\text{C}_5\text{H}_{12}$: C 25.45 , H 2.65 ; found: C 25.51 , H 2.59 .

$[(\mu_2\text{-pdt})_2(\mu_3\text{-S})\text{Co}_4(\text{CO})_5\{\text{P}(\text{C}_6\text{H}_{11})_3\}]$ (2): A solution of $\text{P}(\text{C}_6\text{H}_{11})_3$ (PCy_3 ; 141 mg , 0.50 mmol) in toluene (10 mL) was added to a solution of **1** (327 mg , 0.50 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for 1 h . The resulting dark solution was then concentrated to dryness. The analytically pure product was obtained as microcrystals by diffusion of pentane into a concentrated solution of the crude product in CH_2Cl_2 . Yield of **2**: 400 mg (89%). ^1H NMR (400 MHz , CD_2Cl_2 , 25°C): $\delta = 2.79\text{--}2.35\text{ (m)}$, 12 H ; $\text{SCH}_2\text{CH}_2\text{CH}_2\text{S}$), $2.10\text{--}1.29\text{ ppm (m)}$, 33 H ; PCy_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz , CD_2Cl_2 , 25°C): $\delta = 53.55\text{ ppm (s)}$; ^{13}C NMR (101 MHz , CD_2Cl_2 , 25°C): $\delta = 37.78\text{ (s)}$, 37.61 (s) , 32.18 (s) , 30.24 (s) , 28.10 (s) , 28.00 (s) , 27.30 (s) , 26.71 (s) , 25.88 ppm (s) ; IR (CH_2Cl_2): $\tilde{\nu} = 2014\text{ (m)}$, 1994 (s) , 1979 (s) , $1946\text{ cm}^{-1}\text{ (m)}$ (C=O); elemental analysis calcd (%) for $\text{C}_{36}\text{H}_{34}\text{Co}_4\text{O}_4\text{P}_2\text{S}_5 \cdot 0.33\text{C}_5\text{H}_{12}$: C 39.83 , H 5.34 ; found: C 39.84 , H 5.45 .

$[(\mu_2\text{-pdt})_2(\mu_3\text{-S})\text{Co}_4(\text{CO})_4(\text{Ph}_2\text{PCH=CHPPh}_2)]$ (3): A solution of *cis*- $\text{Ph}_2\text{PCH=CHPPh}_2$ (dppv ; 110 mg , 0.28 mmol) in toluene (10 mL) was added to a solution of **1** (180 mg , 0.28 mmol) in toluene (10 mL). The reaction mixture was stirred at room temperature for 4 h . The resulting dark-red solution was then concentrated to dryness. The residue was redissolved in CH_2Cl_2 (2 mL) and then hexane (20 mL) was added to precipitate the crude product. The latter operation was repeated twice. The analytically pure product was obtained as black crystals by layering hexanes on a solution of the crude product in CH_2Cl_2 . Yield of **3**: 232 mg (84%). ^1H NMR (400 MHz , CDCl_3 , 25°C): $\delta = 7.89\text{ (s)}$, 4 H ; Ph), $7.54\text{--}7.36\text{ (m)}$, 16 H ; Ph), 7.22 (s) , 2 H ; PCH), $2.79\text{--}2.24\text{ ppm (m)}$, 12 H ; $\text{SCH}_2\text{CH}_2\text{CH}_2\text{S}$); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz , CDCl_3 , 25°C): $\delta = 65.20\text{ ppm (brs)}$; ^{13}C NMR (101 MHz , CDCl_3 , 25°C): $\delta = 149.02\text{ (t)}$, 134.49 (m) , 133.51 (t) , 133.02 (t) , 130.14 (d) , 128.49 (m) , 32.71 (s) , 26.47 (s) , 25.64 ppm (s) ; IR (CH_2Cl_2): $\tilde{\nu} = 2004\text{ (m)}$, 1974 (m, sh) , $1959\text{ cm}^{-1}\text{ (s)}$ (C=O); elemental analysis calcd (%) for $\text{C}_{36}\text{H}_{34}\text{Co}_4\text{O}_4\text{P}_2\text{S}_5 \cdot \text{CH}_2\text{Cl}_2$: C 41.39 , H 3.38 ; found: C 41.72 , H 3.43 .

$[(\mu_2\text{-pdt})_2(\mu_3\text{-S})\text{Co}_4(\text{CO})_4(\text{Ph}_2\text{PCH}_2)_2\text{NPh}]$ (4): The same procedure as described for **3** was followed, but using $(\text{Ph}_2\text{PCH}_2)_2\text{NPh}$ (46 mg , 0.09 mmol) and **1** (60 mg , 0.09 mmol). Yield of **4**: 85 mg (0.08 mmol , 85%). ^1H NMR (400 MHz , CD_2Cl_2 , 25°C): $\delta = 7.97\text{--}6.76\text{ (m)}$, 25 H ; Ph), 4.06 (m) , 2 H ; PCH_2), 3.55 (m) , 2 H ; PCH_2), $2.72\text{--}2.11\text{ ppm (m)}$, 12 H ; $\text{SCH}_2\text{CH}_2\text{CH}_2\text{S}$); $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz , CD_2Cl_2 , 25°C): $\delta = 19.24\text{ ppm (brs)}$; ^{13}C NMR (101 MHz , CD_2Cl_2 , 25°C): $\delta = 134.47\text{ (t)}$, 133.07 (t) , 130.30 (s) , 129.84 (s) , 129.65 (s) , 128.40 (t) , 128.15 (t) , 122.66 (s) , 119.62 (s) , 31.92 (s) , 26.60 (s) , 25.70 ppm (s) ; IR (CH_2Cl_2): $\tilde{\nu} = 2003\text{ (m)}$, 1963 (m, sh) , $1931\text{ cm}^{-1}\text{ (s)}$ (C=O); elemental analysis calcd (%) for $\text{C}_{42}\text{H}_{41}\text{Co}_4\text{NO}_4\text{P}_2\text{S}_5 \cdot 0.5\text{C}_5\text{H}_{12}$: C 47.81 , H 4.24 ; found: C 48.20 , H 4.11 .

$[(\mu_2\text{-pdt})_2(\mu_3\text{-S})\text{Co}_4(\text{CO})_4(\text{Ph}_2\text{PCH}_2)_2\text{NiPr}]$ (5): The same procedure as described for **3** was followed, but using $(\text{Ph}_2\text{PCH}_2)_2\text{NiPr}$ (78 mg , 0.17 mmol) and **1** (110 mg , 0.17 mmol). Yield of **5**: 116 mg (0.11 mmol , 65%). ^1H NMR (400 MHz , CD_2Cl_2 , 25°C): $\delta = 7.96\text{--}7.23$

Table 4. Crystallographic details of 1–5.

	1	2	3	4	5
formula	C ₁₂ H ₁₂ Co ₄ O ₆ S ₅	C ₂₉ H ₄₅ Co ₄ O ₅ P ₂ S ₅	C ₃₆ H ₃₄ Co ₄ O ₄ P ₂ S ₅ ·(CH ₂ Cl ₂)	C ₄₂ H ₄₁ Co ₄ NO ₄ P ₂ S ₅	C ₃₉ H ₄₃ Co ₄ NO ₄ P ₂ S ₅ ·0.5(CH ₂ Cl ₂)
<i>M_w</i> [g mol ^{−1}]	648.24	900.64 ^[a]	1073.52	1081.72 ^[a]	1090.17 ^[a]
crystal system	monoclinic	hexagonal	triclinic	triclinic	triclinic
space group	C2/c (no. 15)	P6 ₃ /m (no. 176)	P $\bar{1}$ (no. 2)	P $\bar{1}$ (no. 2)	P $\bar{1}$ (no. 2)
<i>T</i> [K]	296(2)	296(2)	296(2)	296(2)	296(2)
<i>a</i> [Å]	32.3770(7)	23.8758(4)	13.9618(10)	11.9462(13)	15.6937(7)
<i>b</i> [Å]	8.9993(2)	23.8758(4)	16.3711(13)	13.5437(15)	18.1137(8)
<i>c</i> [Å]	14.2237(3)	11.7662(5)	20.1739(17)	16.9442(19)	18.6237(9)
α [°]	90.00	90.00	106.961(2)	82.599(2)	71.8070(10)
β [°]	93.1660(10)	90.00	92.786(2)	70.867(2)	88.8740(10)
γ [°]	90.00	120.00	101.716(2)	71.792(2)	71.5290(10)
<i>V</i> [Å ³]	4138.04(16)	5808.7(3)	4290.0(6)	2459.3(5)	4751.9(4)
<i>Z</i>	8	6	4	2	4
ρ_{calcld} [g cm ^{−3}]	2.081	1.545 ^[a]	1.662	1.461 ^[a]	1.524 ^[a]
μ [mm ^{−1}]	3.681	2.028 ^[a]	2.000	1.641 ^[a]	1.753 ^[a]
$\lambda_{\text{MoK}\alpha}$ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
reflms measured/unique	5222/4678	5046/3708	15 002/11 382	12 042/8142	23 794/16 052
parameters/restraints	244/0	257/36	1004/108	523/12	1022/17
<i>R</i> _{int}	0.0197	0.0442	0.0407	0.0276	0.0257
<i>F</i> (000)	2560	2772	2168	1100	2220
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0197/0.466	0.0358/0.0816	0.0603/0.1572	0.0437/0.1055	0.0414/0.0911
<i>R</i> ₁ / <i>wR</i> ₂ [all refl.]	0.240/0.483	0.0583/0.0881	0.0807/0.1733	0.0761/0.1161	0.0753/0.1007
GOF	1.042	1.041	1.062	1.026	1.010
ρ (min/max) [e Å ^{−3}]	−0.235/0.238	−1.079/0.879	−0.976/1.256	−1.058/1.072	−0.670/0.829

[a] Derived values do not contain the contribution of the disordered solvent molecules.

(m, 20H; Ph), 3.44 (m, 2H; PCH₂), 2.94 (m, 2H; PCH₂), 2.84 (m, 1H; NCH), 2.70–2.02 ppm (SCH₂CH₂CH₂S); ³¹P{¹H} NMR (162 MHz, CD₂Cl₂, 25 °C): δ = 17.57 ppm (brs); ¹³C NMR (101 MHz, CD₂Cl₂, 25 °C): δ = 138.57 (s), 138.36 (s), 138.17 (s), 134.62 (t), 132.92 (t), 132.32 (s), 132.16 (s), 132.03 (s), 129.91 (s), 129.53 (s), 127.99 (m), 60.09 (t), 56.63 (t), 31.89 (s), 26.61 (s), 25.68 (s), 17.19 ppm (s); IR (CH₂Cl₂): $\tilde{\nu}$ = 2001 (m), 1962 (s), 1928 cm^{−1} (m) (C=O); elemental analysis calcd (%) for C₃₉H₄₃Co₄NO₄P₂S₅·CH₂Cl₂·0.5C₅H₁₂: C 43.67, H 4.40, N 1.20; found: C 43.93, H 4.01, N 1.20.

X-ray crystallography

Single crystals of 1–5 suitable for X-ray diffraction analysis were each obtained by carefully layering pentane onto their solutions in CH₂Cl₂. Crystallographic details for all of the compounds are given in Table 4. X-ray diffraction data were collected on a Bruker Apex Kappa-II CCD diffractometer at 296 K using graphite-monochromated MoK α radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXS-97)^[20] and refined by full-matrix least-squares procedures (SHELXL-97).^[20] Semiempirical absorption corrections were applied (SADABS).^[21] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in the refinement at calculated positions using a riding model. The crystal structures of 2, 4, and 5 contain large voids (551 Å³ in 2, 387 Å³ in 4, and 426 Å³ in 5/unit cell), which are occupied by severely disordered pentane molecules for 2 and 4, and pentane and CH₂Cl₂ molecules for 5. Their contribution to the structure factors was delineated by back-Fourier transformation with the SQUEEZE routine of the PLATON software,^[22] resulting in 96 electrons in 2, 71 electrons in 4, and 117 electrons in 5/unit cell. CCDC-997422 (1), 997423 (2), 997424 (3), 997425 (4), and 997426 (5) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

DFT geometry optimization and EPR property calculations

The gas-phase geometries of the anionic tetranuclear cobalt clusters 1[−] (full model), 2[−] (simplified PMe₃ model), and 3[−] (full model) were optimized with the Turbomole program package^[23] coupled to the PQS Baker optimizer^[24] via the BOpt package^[25] at the ri-DFT^[26]/BP86^[27] level. We used the def2-TZVP basis set^[28] for all atoms. The minima (no imaginary frequencies) were characterized by calculating the Hessian matrix. Complex 2 (simplified PMe₃ model) consistently converged to a structure containing a single bridging carbonyl (which was not indicated by the spectro-electrochemical measurements). This optimization problem did not occur for clusters 1 (full model) or 3 (full model).

EPR parameters were calculated with the ORCA^[29] program system, using the coordinates from the structures optimized in Turbomole as input. In the ORCA calculations we used the b3-lyp^[30] functional and def2-TZVP basis set.

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