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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 Co₃(CO)₉ and 1,3-propanedithiol in a 1:1 molar ratio in toluene affords a novel tetracobalt complex, [(μ₂-pdt)(μ₂-S)Co₄(CO)₉] (pdt = -SCH₂CH₂CH₂S-), 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 [(μ₂-pdt)(μ₂-S)Co₄(CO)₉(PCy₃)] (2) and [(μ₂-pdt)(μ₂-S)Co₄(CO)₉(L)] [L = Ph₂PCH₂CH₂PPh₂, 3; Ph₂PCH₂N(PPh₂)CH₂PPh₂, 4; Ph₂PCH₂NiPr(PPh₂), 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 CF₃COOH. Protonation reactions have been monitored by ³¹P 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. The well-known examples include DuBois’ nickel-phosphine complexes,[2] cobaltoxime 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.[6a-c] Besides the abovementioned monometallic complexes, two families of dimetallic complexes, Fe₂S₂,[8] and FeNiS₂,[9] have been synthesized as functional 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 Fe₂S₂ 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 Fe₅Ni complexes. For example, the hexacarbonyl diiron dithiolate complex formulated as [(μ₂-SR)Fe₂(CO)₆] can be readily prepared by the straightforward reaction of Fe₂(CO)₉/Fe₂(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.[12] Some of them have been investigated as electro- or photocatalysts for homogeneous proton reduction or hydrogen oxidation in the past decade.[10d,g,12] In 2004, Rauchfuss and co-workers reported an Ru₂S₂ complex, [(μ₂-pdt)Ru₂(CO)₆(PCy₃)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 (MP₄N₄; M = Fe, Co) for hydrogen production when applied in neutral water at a low overpotential. With the same ligand, the corresponding P₄N₄ 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 Co₃(CO)₉. We thus decided to explore this straightforward reaction as a starting point. During the synthesis, we isolated an unexpected new tetracobalt cluster complex, [(μ₂-pdt)(μ₂-S)Co₄(CO)₉] (1), bearing two propane-1,3-dithiolate ligands, six carbon mon-
oxides ligands, and a tri-bridging sulfido atom (Scheme 1). Although more complex, this cluster features some of the characteristics of the $\text{Fe}_2\text{S}_2$ model. In analogy to the $\text{Fe}_2\text{S}_2$ hexacarbonyl complex, treatment of compound 1 with phosphine ligands readily afforded a series of mono- or disubstituted complexes, $[(\mu_2-pdt)(\mu_2-S)\text{Co}_4(\text{CO})_6(\text{PCy}_3)]$ (2) and $[(\mu_2-pdt)(\mu_2-S)\text{Co}_4(\text{CO})_4(\text{L})]$ [L=Ph$_2$PCH$_2$CH$_2$PCl$_2$N$_3$; Ph$_2$PCH$_2$N(Ph)CH$_2$PPh$_2$, 3; Ph$_2$PCH$_2$N(Ph)CH$_2$PCl$_2$N$_3$; Ph$_2$PCH$_2$N(Ph)CH$_2$PPh$_2$, 4; Ph$_2$PCH$_2$N(Ph)CH$_2$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 Co$_2$(CO)$_8$ and 1,3-propanedithiol in toluene at 40 °C overnight resulted in an insoluble black powder. 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, $^1$H NMR, and $^{31}$P($^1$H) NMR, as well as by elemental analysis. Complex 1 displayed three ν(CO) bands at $\tilde{\nu}=2062,2020,$ and 1986 cm$^{-1}$ in its IR spectrum recorded in CH$_2$Cl$_2$ (Figure S1). The PCy$_3$-substituted complex 2 exhibited a more complicated IR pattern in the region $\tilde{\nu} = 2014–1913$ cm$^{-1}$, with a red shift of about 40 cm$^{-1}$ in the average value of ν(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 ν(CO) of 46, 56, and 58 cm$^{-1}$ were observed for the diphosphine-substituted complexes 3, 4, and 5, respectively. Broad $^{31}$P($^1$H) NMR signals were observed at $\delta = 53.6, 65.2, 19.5,$ and 17.5 ppm for 2–5, respectively. These broad $^{31}$P($^1$H) NMR signals indicate exchange processes, as might be expected for a flexible coordination sphere about 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 $\mu_3$-SCH$_2$CH$_2$CH$_2$S groups and a $\mu_3$-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)° (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 1–3, 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) Å) and Co4-C5 (1.8268(19) Å), which suggest significantly weaker bonds than Co4-C6 (1.794(2) Å) 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.

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<td>126.03(9)</td>
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<td>S5−Co4−P1</td>
<td>101.05(4)</td>
<td>103.47(7)</td>
<td>112.60(7)</td>
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<td>111.06(3)</td>
<td>90.35(3)</td>
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<td>105.16(7)</td>
<td>106.45(3)</td>
<td>107.41(3)</td>
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<td>C4−Co4−C5</td>
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<tr>
<td>C5−Co4−P1</td>
<td>100.24(10)</td>
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<tr>
<td>Co1−Co2−Co3−Co4</td>
<td>148.74(1)</td>
<td>147.90(3)</td>
<td>150.70(4)</td>
<td>147.28(4)</td>
<td>145.90(2)</td>
<td>143.60(2)</td>
<td>141.27(2)</td>
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[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 scanning in the cathodic direction at a rate of 100 mV s\(^{-1}\). The redox potentials were referenced against the Fc/Fc\(^{+}\) couple (using ferrocence as an internal standard), and are summarized in Table 2.

To gain more insight into the frontier orbitals relevant to the redox events, we optimized the geometries of complexes 1, [(μ_2-pdt)(μ_3-S)Co_4(CO)_10(PMe_3)_4] (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.

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 PNP\(^i\) > PNP\(^n\) > dpv > 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

Table 2. Redox potentials of complexes 1–5.\(^{[a]}\)

<table>
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<th>Complex</th>
<th>(E^{\text{red}}_{1/2}) [V]</th>
<th>(E^{\text{red}}_{pa}) [V]</th>
<th>(E^{\text{oxi}}_{pa}) [V]</th>
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<td>1</td>
<td>(-1.17)</td>
<td>(-1.89)</td>
<td>0.60, 0.73</td>
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<td>2</td>
<td>(-1.39)</td>
<td>(-2.13)</td>
<td>0.26</td>
</tr>
<tr>
<td>3</td>
<td>(-1.59)</td>
<td>(-2.23)</td>
<td>0.01</td>
</tr>
<tr>
<td>4</td>
<td>(-1.60)</td>
<td>(-2.21)</td>
<td>0.00</td>
</tr>
<tr>
<td>5</td>
<td>(-1.63)</td>
<td>(-2.25)</td>
<td>(-0.05)</td>
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\(^{[a]}\) Electrochemical potentials vs Fc/Fc\(^{+}\) obtained from cyclic voltammetry in THF/0.1 m nBu_{4}PF_6 at 298 K. Scan rate: 100 mV s\(^{-1}\).

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 second

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 OTTLE cell. 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 \( 1^- \). An average red shift of around 50 cm\(^{-1}\) was found for the reduction of \( 1 \) to \( 1^- \), which is consistent with increased \( \pi \) back-donation from the reduced cobalt cluster atoms to the carbonyl ligands. A somewhat smaller red shift was found for the one-electron-reduced monosubstituted complex 2 (\( \Delta \tilde{\nu}(\text{CO}) \approx 40 \) cm\(^{-1}\)), but a larger red shift was seen for the disubstituted complex 3 (\( \Delta \tilde{\nu}(\text{CO}) \approx 55 \) 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 tetrananuclear cobalt clusters \( 1^- \), \( 2^- \), and \( 3^- \) were further investigated by X-band EPR spectroscopy. Species \( 1^- \), \( 2^- \), and \( 3^- \) were generated in situ by reducing the corresponding neutral clusters with 0.9 equivalents of \( \text{Cp}^*2\text{Co} \) in THF. To obtain a better glass, we added 0.1 m \( \text{nBu}_4\text{NPF}_6 \) (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 \( S = \frac{1}{2} \) systems. The \( g \)-anisotropy in the spectra of \( 1^- \) and \( 2^- \) is not well resolved, leading to broad, nearly isotropic spectra without any resolved hyperfine couplings (Figure 5, top). Although the spectrum of \( 2^- \) shows hyperfine interactions (HFIs) with multiple cobalt nuclei (Figure 5, bottom),

![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 \( \text{nBu}_4\text{NPF}_6 \)) in an OTTLE cell at 295 K. Negative peaks indicate disappearance of the starting compounds, positive peaks indicate appearance of the one-electron-reduced species.](image)

![Figure 5. Top: X-band EPR spectrum of tetrananuclear cobalt cluster \( 1^- \) 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 tetrananuclear cobalt cluster \( 2^- \) 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.](image)
these are not well resolved and any attempts to simulate them would be futile (no unique fit). In contrast, the g-anisotropy of 3\textsubscript{C}/C\textsubscript{0} 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 $\alpha = 0$–37°, $\beta = 6$–70°, and $\gamma = 16$–84°).

Protonation reactions

To spectroscopically characterize the protonated species that might be involved in the possible electrocatalytic proton reduction, protonation reactions of 1–5 using HBF\textsubscript{4}·Et\textsubscript{2}O were carried out at room temperature and monitored by \textsuperscript{31}P(\textsuperscript{1}H) and \textsuperscript{1}H NMR as well as IR spectroscopy. In line with the electrocatalysis, no protonation was observed for complex 1 upon the addition of HBF\textsubscript{4}·Et\textsubscript{2}O to a solution in dichloromethane.

Complete conversion of 2 to its protonated species [2H\textsubscript{3}]\textsuperscript{+} was observed, as indicated by the \textsuperscript{31}P(\textsuperscript{1}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 HBF\textsubscript{4}·Et\textsubscript{2}O was added to the solution. No hydride signal was detected by \textsuperscript{1}H 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 protonation on the \mu\textsubscript{3}-S atom. This is in line with the computational frontier orbitals in Figure 3, which indicated delocalization of the HOMO over the \mu\textsubscript{3}-S atom in 2-PMe\textsubscript{3}CF\textsubscript{3}COOH was also used as a milder acid to protonate complex 2. Again, no hydride signal was observed and a sharp \textsuperscript{31}P(\textsuperscript{1}H) signal appeared at $\delta = 33.7$ ppm at the expense of the broad peak at $\delta = 53.6$ ppm (Figure S10). The different chemical shift observed upon protonation with CF\textsubscript{3}COOH (compared to HBF\textsubscript{4}·Et\textsubscript{2}O) might be attributed to the formation of a hydrogen bond between CF\textsubscript{3}COO\textsuperscript{-} and H\textsuperscript{+}. The structure of [2H\textsubscript{3}]\textsuperscript{+} 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 [3H\textsubscript{2}]\textsuperscript{+} in the \textsuperscript{1}H NMR spectra (Figure 8), indicating the formation of a cobalt-hydride species. The sharp singlet at $\delta = 86.3$ ppm in the \textsuperscript{31}P(\textsuperscript{1}H) spectrum may also be ascribed to [3H\textsubscript{2}]\textsuperscript{+}. The downfield shift of the \textsuperscript{31}P(\textsuperscript{1}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.
The $^{31}$P($^1$H) and $^1$H NMR spectra obtained for complex 5 in CD$_2$Cl$_2$ upon addition of HBF$_4$·Et$_2$O are shown in Figure 9. A broad signal at $\delta = 17.6$ ppm was seen in the $^{31}$P($^1$H) NMR spectrum of 5 in the absence of acid. Upon the addition of 0.6 equiv HBF$_4$·Et$_2$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 $^1$H 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 [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, leading to the formation of [5H$_{\text{NP}}$]⁺, 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 HBF$_4$·Et$_2$O to the solution (Figure 9c). The ratio of [5Hy]⁺/[5H$_{\text{NP}}$]⁺ 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 HBF$_4$·Et$_2$O (Figure 9d, e), all of the signals corresponding to the mono-protonated species [5Hy]⁺ and [5H$_{\text{NP}}$]⁺ 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, [5H$_2$Hy]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 [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 [5Hy]⁺, [5H$_{\text{NP}}$]⁺, and [5H$_2$Hy]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 µ₅-protonated species [2H$_{\text{NP}}$]⁺ displayed three ν(C=O) bands at 2062, 1902, and 1982 cm⁻¹. As expected, the metal-protonated species [3Hy]⁺ and [4Hy]⁺ show a different pattern to that of [2H$_{\text{NP}}$]⁺. The IR patterns of [3Hy]⁺ and [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 with the NMR observations. The N-protonated species [5H$_{\text{NP}}$]⁺ displayed a blue shift in ν(C=O) by about 10 cm⁻¹ compared to its precursor 5, although the IR pattern remained similar. The diprotonated species, [5H$_2$Hy]²⁺, exhibited a similar IR pattern in the carbonyl region as [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$_3$COOH (0–
The results are shown in Figure 11, from which it is evident that the one-electron-reduced complex \( 1' \) was not active for proton reduction, whereas the further reduced species (probably \( 1'' \)) showed significant current enhancement \((i/c/i_p = 34)\) at a scan rate of \(100 \text{ mV s}^{-1}\) when the concentration of \( \text{CF}_3\text{COOH} \) 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 \( 5' \) 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 \( \text{CF}_3\text{COOH} \) (160 mM) and the corresponding cobalt complex in THF using \( 0.15 \text{ m} \text{nBu}_4\text{NPF}_6 \) 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 by injection of different amounts of \( \text{H}_2 \) into the set-up (Figure S17). In our experiments, up to 800 \( \text{mL} \text{H}_2 \) 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 \( \text{Co}_4\text{S}_5 \) clusters is tunable in the range from \( 1.17 \) to \( 1.63 \text{ V vs Fc/Fc}^+ \) by phosphine substitution of one or two carbonyl ligands in the all-carbonyl parent complex. The mono-reduced radical anions, \( 1' \), \( 2' \), and \( 3' \), 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...
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. Bisphosphinomethyl)amines, (Ph₂PCH₂)₂NPh (PNPPh²) and (Ph₂PCH₂)₂NCH₂(CH₂)₆(PNP²), were synthesized according to reported procedures.[19] ¹H, ¹³C, and ⁴⁰P{¹H} 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 m Bu₄NPF₆) containing a 1.0 mM solution of the investigated complex. Cyclic voltammograms were measured using glassy carbon (diameter 3 mm) as the working electrode, a Pt wire as a counter electrode and Pt and Ag wire as the reference 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 batch 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 P₇ frit as the reference. Alternatively, leak-free Ag/AgCl (eDAQ, Australia) was used as the reference electrode. The solvent was THF containing 0.15 M Bu₄NPF₆ 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 a circulation pump to detect H₂ evolution over time. The amount of CF₃COOH produced was determined using IR

Spectro-electrochemistry

Spectro-electrochemistry was performed in an optically transparent thin-layer (200 μm) electrochemical OTTLE cell equipped with CaF₂ optical windows and a Pt mini grid working electrode, a Pt mini grid 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 mV s⁻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

[µμ-pdt]₂(µμ-S)Co₄(CO)₈ (1): A mixture of Co₂(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 (60–200 μm), eluting with petroleum ether/CH₂Cl₂ (5:1, v/v). Yield of 1: 206 mg (31 %, based on Co). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 2.72–2.36 ppm (brm, 12H; SCH₂CH₂CH₂S); ¹³C NMR (101 MHz, CDCl₃, 25 °C): δ = 31.88 (s), 29.87 (s), 26.41 (s), 26.17 ppm (s); IR (CH₂Cl₂): ν = 2062 (s), 2020 (s), 1986 cm⁻¹ (m) (C=C=O); elemental analysis calc (%) for C₁₅H₁₅Co₄O₄S₅: C 45.35, H 3.33; found: C 45.35, H 3.45.

[µμ-pdt]₂(µμ-S)Co₄(CO)₈[P(C₆H₅)₃] (2): A solution of P(CH₂C₅H₅)₃ (PC₅H₃; 141 mg, 0.50 mmol) in toluene (10 mL) was added to a solution of 1 (327 mg, 0.50 mmol) in CH₂Cl₂ (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 CH₂Cl₂. Yield of 2: 400 mg (89 %). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 2.79–2.35 (m, 12H; SCH₂CH₂CH₂S); ¹³C NMR (101 MHz, CDCl₃, 25 °C): δ = 37.88 (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 (CH₂Cl₂): ν = 2041 cm⁻¹ (m, 1994 (s), 1979 (s), 1946 cm⁻¹ (m) (C=C=O); elemental analysis calc (%) for C₁₅H₁₅Co₄O₄S₅·0.33CH₂Cl₂: C 38.93, H 5.34; found: C 39.84, H 5.45.

[µμ-pdt]₁(µμ-S)Co₄(CO)₈(P(C₆H₅)₃CH₂PPh₂) (3): A solution of cis-Ph,PCH₂-ChHPPh₂ (dpdpv; 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 CH₂Cl₂ (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 CH₂Cl₂. Yield of 3: 232 mg (84 %). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 7.89 (s, 4H; Ph), 7.54–7.36 (m, 16H; Ph), 7.22 (s, 2H; PCH₂); 2.79–2.24 ppm (m, 12H; SCH₂CH₂CH₂S); ¹³C NMR (162 MHz, CDCl₃, 25 °C): δ = 149.02 (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 (CH₂Cl₂): ν = 2004 cm⁻¹ (m, 1974 (m, sh), 1959 cm⁻¹ (m) (C=C=O); elemental analysis calc (%) for C₁₉H₁₇Co₄O₄P₂S₅·0.33CH₂Cl₂: C 43.19, H 3.38; found: C 41.72, H 3.43.

[µμ-pdt]₁(µμ-S)Co₄(CO)₈(P(C₆H₅)₃CH₂PPh₂) (4): The same procedure as described for 3 was followed, but using (Ph₂PCH₂)₂NPh (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, CDCl₃, 25 °C): δ = 7.97–6.76 (m, 25H; Ph), 4.06 (m, 2H; PCH₂), 3.55 (m, 2H; PCH₂), 2.72–2.11 ppm (m, 12H; SCH₂CH₂CH₂S); ¹³C NMR (162 MHz, CDCl₃, 25 °C): δ = 19.24 ppm (brs); ¹³C NMR (101 MHz, CDCl₃, 25 °C): δ = 134.47 (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 (CH₂Cl₂): ν = 2003 (m, 1963 (m, sh), 1931 cm⁻¹ (m) (C=C=O); elemental analysis calc (%) for C₁₅H₁₅Co₄O₄P₂S₅·0.33CH₂Cl₂: C 47.81, H 4.24; found: C 48.20, H 4.11.

[µμ-pdt]₁(µμ-S)Co₄(CO)₈(P(Ph₂PCH₂)₂NPh) (5): The same procedure as described for 3 was followed, but using (Ph₂PCH₂)₂NPh (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, CDCl₃, 25 °C): δ = 7.96–7.23.
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-monochromatized Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXS-97)[22] 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 refinements 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 1, 2, and 3 contain large voids (551 Å³ in 1, 387 Å³ in 2, 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 for free 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 tetracnuclear 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 BPopt package[25] at the ri-DFT[26]/BP86[27] level. We used the def2-TZVP basis set[26] for all the minima. 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 carbyl (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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