Chalcogenide-capped triiron clusters $[\text{Fe}_3(\text{CO})_9(\mu_3-E)_2]$, $[\text{Fe}_3(\text{CO})_7(\mu_3-\text{CO})(\mu_3-E)(\mu-\text{dppm})]$ and $[\text{Fe}_3(\text{CO})_7(\mu_3-E)_2(\mu-\text{dppm})]$ ($E = \text{S}, \text{Se}$) as proton-reduction catalysts

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ABSTRACT

Chalcogenide-capped triiron clusters $[\text{Fe}_3(\text{CO})_9(\mu_3-\text{CO})(\mu_3-E)(\mu-\text{dppm})]$ and $[\text{Fe}_3(\text{CO})_7(\mu_3-E)(\mu-\text{dppm})]$ ($E = \text{S}, \text{Se}$) have been examined as proton-reduction catalysts. Protonation studies show that $[\text{Fe}_3(\text{CO})_9(\mu_3-E)_2]$ are unaffected by strong acids. Mono-capped $[\text{Fe}_3(\text{CO})_7(\mu_3-\text{CO})(\mu_3-E)(\mu-\text{dppm})]$ react with $\text{HBF}_4\cdot\text{Et}_2\text{O}$ but changes in IR spectra are attributed to $\text{BF}_3$ binding to the face-capping carbonyl, while bicapped $[\text{Fe}_3(\text{CO})_7(\mu_3-E)_2(\mu-\text{dppm})]$ are protonated but in a process that is not catalytically important. DFT calculations are presented to support these protonation studies. Cyclic voltammetry shows that $[\text{Fe}_3(\text{CO})_7(\mu_3-\text{Se})_2]$ exhibits two reduction waves, and upon addition of strong acids, proton-reduction occurs at a range of potentials. Mono-chalcogenide clusters $[\text{Fe}_3(\text{CO})_7(\mu_3-\text{CO})(\mu_3-E)(\mu-\text{dppm})]$ ($E = \text{S}, \text{Se}$) exhibit proton-reduction at ca. $1.85$ ($E = \text{S}$) and $1.62$ $V$ (E = Se) in the presence of $p$-toluene sulfonic acid ($p$-TsOH). Bicapped $[\text{Fe}_3(\text{CO})_7(\mu_3-E)_2(\mu-\text{dppm})]$ undergo quasi-reversible reductions at $1.55$ ($E = \text{S}$) and $1.45$ $V$ (E = Se) and $p$-TsOH to hydrogen but protonated species do not appear to be catalytically important. Current uptake is seen at the first reduction potential in each case, showing that $[\text{Fe}_3(\text{CO})_7(\mu_3-E)_2(\mu-\text{dppm})]$ are catalytically active but a far greater response is seen at ca. $-1.9$ $V$ being tentatively associated with reduction of $[\text{H}_2\text{Fe}_3(\text{CO})_7(\mu_3-E)_2(\mu-\text{dppm})]$*. In general, selenide clusters are reduced at slightly lower potentials than sulfide analogues and show slightly higher current uptake under comparable conditions.

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1. Introduction

Hydrogen is a potentially clean and efficient energy-carrier [1–3]; however, its current synthesis is energy-intensive and uses fossil-fuel resources, while the direct utilization of solar energy for hydrogen production through photocatalytic [4] or photo-electrochemical [5,6] water-splitting is poorly developed. Algae can produce hydrogen and oxygen from water [7] and hydrogenases then act as catalysts for the reversible oxidation of hydrogen to protons and electrons. In the late 1990s, crystal structures of $[\text{FeFe}]$-hydrogenases revealed that the active site consists of a diiron sub-unit with a bridging dithiolate ligand and ancillary CO/CN-active site consists of a diiron sub-unit with a bridging dithiolate ligand and ancillary CO/CN ligands linked to an Fe4S4 ferredoxin subunit [8–11]. This generated enormous interest in the development of synthetic analogues of the active site with a wide range of diiron biomimetics being tested as proton-reduction catalysts [12]. Key

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features of (electro)catalysts for proton reduction include the abilities to bind a proton(s) and undergo facile reduction, both being well-established properties of low-valent transition metal clusters [13]. Hence, clusters with nuclearities of three or greater are promising candidates as catalysts for clean hydrogen formation via proton-reduction [14–27]. Two groups have independently studied proton-reduction by the sulfide cluster [Fe3(CO)9(μ3-S)2] (1S) [14,15]. In MeCN with acetic acid, H2 production takes place at the second reduction potential (−1.75 V), establishing the dianion [Fe3(CO)9(μ3- S)2]2− (1S−) as the catalyst [14]. In the presence of the strong acid HBFI-Br2O, both mono and diions are active proton-reduction catalysts at potentials of −1.03 V and −1.30 V, respectively [15]. Since [Fe3(CO)9(μ3-S)2] (1S) does not readily protonate even with strong acids, initial reduction is a prerequisite for proton-reduction. Sun, Åkermark and co-workers [16] have explored the proton-reduction activity of the diphosphine-substituted cluster [Fe3(CO)9(μ3-S)2(η6-dppm)2] [dppm = cis-1,2-bis(diphenylphosphino)ethylened] that, in contrast, is readily protonated by trifluoromethanesulfonic (triflic) acid and catalyses proton-reduction at −0.98 V in CH2Cl2, the first reduction potential of [μ-H]Fe3(CO)9(μ3-S)2 (x2-dppm)2]−. In seeking to extend and develop the proton-reduction chemistry of low-valent triiron clusters, we turned our attention to the chalcogenide-capped acid and catalyses proton-reduction at 0.98 V in CH2Cl2, the first reduction potential of [μ-H]Fe3(CO)9(μ3-S)2 (x2-dppm)2]−. In seeking to extend and develop the proton-reduction chemistry of low-valent triiron clusters, we turned our attention to the chalcogenide-capped cluster [Fe3(CO)9(μ3-CO)(η6-E-dppm)] (2S, 2Se) and [Fe3(CO)9(μ3-CO)(η6-μ2-dppm)] (3Se) with the expectation that introduction of the diphosphine bis(diphenylphosphine)methane (dppm) may serve to stabilise the relatively fragile triiron core, while also favouring protonation at the triiron centre. Further, the ability to vary the chalcogenide cap potentially allows redox-tuning. Herein we report the electrocatalytic proton-reduction properties of 2 and 3, as well as [Fe3(CO)9(μ3-Se)2] (1Se), the latter being studied in order to compare with previous studies of [Fe3(CO)9(μ3-S)2] (1S) [14,15].

2. Experimental

2.1. General procedures

Unless otherwise stated, purification of solvents, reactions, and manipulation of compounds were carried out under a nitrogen atmosphere using standard Schlenk techniques. Reagent grade solvents were dried by standard procedures and were freshly distilled prior to use. All chromatographic separations and ensuing workup were carried out in air. Thin layer chromatography was carried out on glass plates pre-coated with Merck 60 0.25 mm silica gel. Dppm was purchased from Acros Organics Chemicals Inc. and [Fe3(CO)12], [Fe3(CO)9], elemental sulfur and selenium were purchased from Sigma-Aldrich; [Fe3(CO)9(μ-μ-dppm)] [28] and [Fe3(CO)9(μ3-S)2] (1S) [29] were prepared as previously reported. Infrared spectra were recorded on Nicolet 6700 FT-IR or Nicolet Avatar 360 FT-IR-spectrometers in a solution cell fitted with CaF2 or NaCl plates, subtraction of the solvent absorptions being achieved by computation. Fast atom bombardment (FAB) mass spectra were obtained on a JEOL SX-102 spectrometer using 3-nitrobenzyl alcohol as matrix and CsI as calibrant. Proton and 31P({1H} NMR spectra were recorded on Varian Unity 500 MHz or Bruker AMX400 instruments. Chemical shifts were referenced to residual solvent or 85% H3PO4. Elemental analyses were performed at University College London.

2.2. Synthesis of [Fe3(CO)9(μ3-Se)2] (1Se) [30]

A benzene solution (20 mL) of [Fe3(CO)9(μ3-Se)2] (100 mg, 0.198 mmol) and selenium (31 mg, 0.398 mmol) was refluxed for 20 h. The solvent was removed under reduced pressure, and the residue extracted with hexane and filtered on Kieselguhr. The faster moving band gave [Fe3(CO)9(μ3-Se)2] (1Se) (20 mg, 17%) [30] (IR (ν(CO), n-hexane): 2071, 2056sv, 2037vs, 2017s, 2002br, 1982sh cm−1) as black crystals after recrystallization from hexane/CH2Cl2 at 4 °C.

2.3. Synthesis of [Fe3(CO)9(μ3-CO)(μ3-S)(μ-μ-dppm)] (2S) and [Fe3(CO)9(μ3-S)2(μ-μ-dppm)] (3S)

A number of routes were used to access these clusters. (i) A CH2Cl2 solution (20 mL) of [Fe3(CO)9(μ-μ-dppm)] (40 mg, 0.048 mmol) and sulfur (3.1 mg, 0.096 mmol) was refluxed for 10 h. The solvent was removed under reduced pressure, and the residue was chromatographed by TLC on silica gel. Elution with cyclohexane/CH2Cl2 (9:1 v/v) developed three bands. The faster moving band gave [Fe3(CO)9(μ3-S)2(μ-μ-dppm)] (3S) (6S, 15%), the second band was unreacted [Fe3(CO)9(μ3-S2)2(μ-μ-dppm)] (2S) (20 mg, 51%) as red crystals after recrystallization from hexane/CH2Cl2 at 4 °C. (ii) A benzene solution (20 mL) of [Fe3(CO)9(μ3-S)2] (1S) (18 mg, 0.037 mmol) and dppm (15 mg, 0.037 mmol) was refluxed for 30 min. Solvent was removed under reduced pressure, and the residue was chromatographed by TLC on silica gel. Elution with cyclohexane/CH2Cl2 (3:1 v/v) developed three bands. The faster moving band was unreacted [Fe3(CO)9(μ3-S)2(μ-μ-dppm)] (1S) (2.0 mg), the second band afforded [Fe3(CO)9(μ3-S)2(μ-μ-dppm)] (3S) (6.0 mg, 20%) and the third afforded [Fe3(CO)9(μ3-S)2(μ-μ-dppm)] (2S) (20 mg, 0.025 mmol) and sulfur (1.6 mg, 0.049 mmol) was refluxed for 1 day. The solvent was removed under reduced pressure, and the residue was chromatographed by TLC on silica gel. Elution with cyclohexane/CH2Cl2 (9:1 v/v) developed two bands. The faster moving band gave 3S (3.0 mg, 14%), the second band was unreacted 2S (10 mg). (iv) A benzene solution (20 mL) of 1S (18 mg, 0.037 mmol) and dppm (15 mg, 0.037 mmol) was refluxed for 30 min. The solvent was removed under reduced pressure, and the residue was chromatographed by TLC on silica gel. Elution with cyclohexane/CH2Cl2 (9:1 v/v) developed two bands. The faster moving band was unreacted 1S (2.0 mg) and the second band afforded 3S (8.0 mg, 34%). Characterising data: 2S. Anal. Calc. for C33H22Fe3O6S2P2: C, 49.97; H, 2.72 Found: C, 49.91; H, 2.78. IR (ν(CO), CH2Cl2): 2057s, 2005vs, 1966s, 1666w cm−1. 1H NMR (CDCl3): δ 7.6–7.1 (m, 20 H), 3.45 (m, br), 2H, CH2. 31P (1H) NMR (CDCl3): δ 55.4 (s), ESI-MS: m/z 808.10 found, m/z 807.85 cal for [M]+. 3S. Anal. Calc. for C33H22Fe3O6S2P2: C, 47.29; H, 2.70 Found: C, 47.50; H, 2.71. IR (ν(CO), CH2Cl2): 2045s, 2000vs, 1961w, 1930br cm−1. 1H NMR (CDCl3): δ 7.75–7.33 (m, 20H), 2.98 (t, 2H, J 10 Hz). 31P (1H) NMR (CDCl3): δ 75.3 (s).

2.4. Synthesis of [Fe3(CO)9(μ3-CO)(μ3-Se)(μ-μ-dppm)] (2Se) and [Fe3(CO)9(μ3-Se)(μ3-Se)(μ-μ-dppm)] (3Se)

A number of routes were used to access these clusters. (i) A CH2Cl2 solution (20 mL) of [Fe3(CO)9(μ-μ-dppm)] (30 mg, 0.036 mmol) and selenium (6.0 mg, 0.071 mmol) was refluxed for 10 h. The solvent was removed under reduced pressure, and the residue was chromatographed by TLC on silica gel. Elution with cyclohexane/CH2Cl2 (9:1 v/v) developed three bands. The faster moving band gave [Fe3(CO)9(μ3-Se)(μ-μ-dppm)] (2Se) (7.0 mg, 21%), the second band was unreacted [Fe3(CO)9(μ3-Se)(μ-μ-dppm)] (1mg) and the third afforded [Fe3(CO)9(μ3-Se)(μ3-Se)(μ-μ-dppm)] (3Se) (17 mg, 55%) as red crystals after recrystallization from hexane/CH2Cl2 at 4 °C. (ii) A CH2Cl2 solution (20 mL) of [Fe3(CO)9(μ3-CO)(μ3-Se)(μ-μ-dppm)] (2Se) (20 mg, 0.023 mmol) and selenium (4.0 mg, 0.047 mmol) was refluxed for 1 day. The solvent was removed under reduced pressure, and the residue was chromatographed by...
TLC on silica gel. Elution with cyclohexane/CH2Cl2 (9:1 v/v) developed two bands. The faster moving band gave [Fe3(CO)3[μ3-Se2]μ-dppm]) (3Se) (4.0 mg, 19%), the second band was unreacted [Fe3(CO)3[μ3-CO][μ3-Se][μ-dppm]) (2Se) (9.0 mg). (iii) A benzene solution (20 mL) of 1Se (25 mg, 0.0432 mmol) and dppm (18 mg, 0.0432 mmol) was refluxed for 2 h. The solvent was removed under reduced pressure, and the residue was chromatographed by TLC on silica gel. Elution with cyclohexane/CH2Cl2 (7:3 v/v) developed two bands. The faster moving band was unreacted 1Se (5.0 mg) and the second band afforded 3Se (6.0 mg, 19%). Characterising data. 2Se: Anal. Calcd for C32H22Fe3O7Se2P2: C, 42.38; H, 2.42 Found: C, 42.75; H, 2.60. IR (ν(CO), CH2Cl2): 2050s, 2003vs, 1957sh, 1659 cm⁻¹. 31P{1H} NMR (CDCl3): δ 7.89 (m, 1H), 7.76 (br, 2H), 7.65 (m, 4H), 7.52 (t, 2H, J 10 Hz), 7.38 – 7.33 (m, 11H), 4.02 (br, 2H, CH2, CHCl). 31P[¹H] NMR (CDCl3): δ 55.3 (s). ESI-MS: m/z 855.12 found, m/z 855.80 calc for [M⁺]. 3Se: Anal. Calcd for C32H22Fe3O7Se2P2: C, 42.38; H, 2.42 Found: C, 42.75; H, 2.55. IR (ν(CO), CH2Cl2): 2050s, 2040s, 1991vs, 1942w cm⁻¹. ¹H NMR (CDCl3): δ 7.89 (m, 1H), 7.76 (br, 2H), 7.65 (m, 4H), 7.52 (t, 2H, J 10 Hz), 7.38 – 7.33 (m, 11H), 4.02 (br, 2H, CH2, B), 3.16 (t, 2H, CH2, J 10 Hz, A), 3.01 (¹H) NMR (CDCl3): δ 78.7 (b, S), 53.0 (d, A), 42.6 (d, A) Jpp 56 Hz. Ratio A:B ca. 2:3 (see text).

2.5. Protonation experiments
To CH2Cl2 solutions (ca. 1 mL) of the triiron clusters (made by dissolving 1 × 10⁻³ mmol of each complex) were added 2 molar equivalents of HBF4·Et2O. The resultant acid-containing solution was immediately transferred to an IR cell and monitored over time.

2.6. X-ray structure determinations
Crystals of 25, 2Se, 35 and 3Se suitable for X-ray structure analysis were grown by slow diffusion of hexane into a saturated CH2Cl2 solution at 4 °C. Crystals were immersed in cryo-oil, mounted on a Nylon loop, and measured at a temperature of 120–170 K. The X-ray diffraction data were collected on a Bruker Kappa Apex II Duo or an Agilent Supernova diffractometer using Mo Kα radiation (λ = 0.71073 Å). The APEX2 [31] or CrysAlisPro [32] program packages were used for cell refinements and data reductions. Structures were solved by direct methods or by charge flipping using the SHELXS-97 [33] or SUPERFLIP [34] programs. A multi-scale, numerical, or Gaussian absorption correction (SADABS [35] or CrysAlisPro [32]) was applied to all data. Structural refinements were carried out using SHELXL-97 or SHELXL-2013 [33]. The hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with C–H = 0.95–0.99 Å and Uiso = 1.2 Ueq (parent atom). Crystallographic details are summarised in Table S1.

2.7. Electrochemistry
Electrochemistry was carried out under solvent-saturated nitrogen in deoxygenated MeCN and CH2Cl2 solutions with 0.1 M [NBu4][PF6] as the supporting electrolyte. The working electrode was a 3 mm diameter glassy carbon electrode that was polished with 0.3 μm alumina slurry as needed, the counter electrode was a platinum wire, and the reference electrode was either a silver wire or an Ag/AgCl electrode that was separated from the working electrode by a glass frit. Potentials are referenced versus the ferrocene/ferrocenium couple (Fc+/Fc). A Pine potentiostat (Pine WaveNow potentiostat) was used for all electrochemical measurements. Catalysis studies were carried out by adding equivalents of p-TsOH and HBF4·Et2O (Sigma-Aldrich).

2.8. Computational details and modelling
All DFT calculations were carried out with the Gaussian 09 package of programs [36] using the B3LYP hybrid functional. This functional is comprised of Becke's three-parameter hybrid exchange functional (B3) [37] and the correlation functional of Lee, Yang, and Parr (LYP) [38]. Each iron atom was described with the Stuttgart-Dresden effective core potential and SDD basis set [39] and the 6-31G(d,p) basis set [40] was employed for all remaining atoms. All reported geometries were fully optimized, and analytical second derivatives confirmed each structure as an energy minimum (no negative eigenvalues). Unscaled vibrational frequencies were used to make zero-point and thermal corrections to the electronic energies, and the resulting free energies are reported in kcal mol⁻¹ relative to the specified standard. The reported carbonyl stretching bands for species C (vide infra, Section 3.3) were obtained from the harmonic frequencies and have been scaled using a factor of 0.965. The Natural Population Analysis (NPA) and Viberg bond indices (WBI) were computed using Weinhold’s natural bond orbital (NBO) program, as executed by Gaussian 09 [41,42]. The geometry-optimized structures have been drawn with the Jmol2 molecular visualization and manipulation program [43].

3. Results and discussion
3.1. Synthesis and characterisation
For [Fe3(CO)3[μ3-CO][μ3-Se][μ-dppm]) (E = S, Se) two pathways were considered; (i) addition of dppm to [Fe3(CO)3[μ3-CO][μ3-E]) (1) [44,45] and (ii) addition of group 16 elements to [Fe3(CO)3[μ-dppm]) [28]. Sulfide-capped [Fe3(CO)3[μ3-CO][μ3-S]) has previously been reported [41] but yields were low and separation (from other sulfur-containing species) difficult. A brief report of [Fe3(CO)3[μ3-CO][μ3-Se]) has appeared; it was formed in low yield upon addition of BiCl3 to K2[Fe3(CO)3[μ3-Se]) [45]. In line with the established increase in stabilisation of the triruthenium centre in [Ru3(CO)10[μ-dppm]) [46] as compared to [Ru3(CO)12], it was expected that the triiron core of [Fe3(CO)3[μ3-E]) [28] will be less susceptible to fragmentation than that of [Fe3(CO)3]. This was found to be the case and the isostructural clusters, [Fe3(CO)3[μ3-E][μ-dppm]) (E = S, Se) (2), were prepared in moderate yields upon heating CH2Cl2 solutions of [Fe3(CO)3[μ-dppm]) with elemental sulfur or selenium. Minor products were known bis-(chalcogenide) clusters [Fe3(CO)3[μ3-E2][μ-dppm]) (3) [47,48] (Scheme 1), previously prepared by addition of dppmS2 [17] or...
dppmSe₂ [48] to [Fe₃(CO)₁₂]. In separate experiments 2S and 2Se reacted with excess chalcogenide over 10 h to afford 3S and 3Se, respectively, indicating that chalcogenide-capping takes place in a stepwise fashion. While 1Se is known [30], we have found that it may be prepared in a single step from elemental selenium and [Fe₃(CO)₁₂]. Reactions of 1S and 1Se with dppm in refluxing CH₂Cl₂ afford 3S and 3Se, respectively, in moderate yields.

3.2. Structural studies

Molecular structures of [Fe₃(CO)₇(μ₃-S)(μ-dppm)] (2S) and [Fe₃(CO)₇(μ₃-Se)(μ-dppm)] (2Se) are depicted in Fig. 1. Those of [Fe₃(CO)₇(μ₃-Se)₂(μ-dppm)] (3S) [17] and [Fe₃(CO)₇(μ₃-Se)₃(μ-dppm)] (3Se) [48] have been previously reported but for comparison we have also collected data (see ESI). Important metric parameters are summarised in Table S1 and selected bond lengths and angles in Table S2.

Spectroscopic data for 2 are consistent with the solid-state structure being maintained in solution. IR spectra contain an absorption between 1650 and 1670 cm⁻¹, confirming the presence of the triply-bridging carbonyl. Each displays well-resolved ¹H and ³¹P NMR spectra, the latter consisting of a singlet at 55.5 ppm ca. 20 ppm higher wavenumbers by ca. 20-30 cm⁻¹ (Scheme 2). Thus, absorptions at 2057, 2006, 1666 cm⁻¹ for 2S were replaced by new peaks at 2086, 2047, 2029 and 2008 cm⁻¹. The magnitude of this change suggests no significant change in electron-density at the triiron centre; metal-centred protonation is expected to result in a ~50-70 cm⁻¹ positive shift [49]. The relatively symmetric IR spectrum suggests a reaction site at one of the face-capping ligands, with the μ₃-CO group being implicated on the basis of the absence of the face-capping ν(CO) band. Monitoring reactions of 2 with HB₃Et₂O (in CDCl₃) by ¹H NMR spectroscopy revealed no evidence of hydride formation. Noting that HB₃Et₂O is a complex of BF₃ and HF, we added BF₃·Et₂O to CH₂Cl₂ solutions of both 2S and 2Se and observed IR spectra identical to those generated upon addition of HB₃Et₂O. Addition of piperidine led to regeneration of the starting clusters, indicating that the so-called “protonation reaction” simply reflects the reversible addition of BF₃ to the face-capping μ₃-CO ligand (Scheme 2).

We thus conclude that addition of both HB₃Et₂O to 2 leads to formation of [Fe₃(CO)₇(μ₃-COBF₃)(μ₃-E)(μ-dppm)] (2BBF₃). This was investigated by DFT calculations employing optimized structures of 2S (species A) and BF₃ (both of which are not shown) for the ensuing stability calculations. Interestingly, coordination of the chalcogenide in A by BF₃ does not afford a stable species, this adduct spontaneously liberating 2S and free BF₃. A stable BF₃ complex is, however, obtained when the oxygen atom of the μ₃-CO ligand functions as a Lewis base, and the geometry-optimized structure of this adduct (species B) is depicted in Fig. S1. Table S3 summarises the natural charges and Wiberg bond indices for A and B, and the data confirm that the coordinated BF₃ molecule in B does not adversely perturb the charges or bond orders within the Fe₃ core relative to the parent cluster A. Scaled frequencies of the major ν(CO) bands in B are 2074, 2041, 2028, and 1998 cm⁻¹, in good agreement with IR solution data. This led us to discard
HBF₄-Et₂O as a proton source for catalytic studies. Addition of two equivalents of p-TsOH to a CH₂Cl₂ solution of 2S did not lead to major changes in the IR spectrum; a small (~5%) new absorption appeared at 2085 cm⁻¹, the intensity of which did not change with time. We, therefore, elected to use this acid for electrocatalytic proton-reduction studies (vide infra).

We also probed reactions of 3 with two equivalents of HBF₄-Et₂O. For 3S, peaks at 2045s, 2000vs, 1961w, 1930br cm⁻¹ were very slowly (over 24 h) replaced by new absorptions at 2102 m, 2065sh, 2046s and 2004 m cm⁻¹ which we associate with [Fe₃(CO)₇(μ-H)₃(μ-S)(μ-dppm)][BF₄] (3SH⁻), while for 3Se the analogous species is associated with peaks at 2097 m, 2055w, 2039vs and 1996 m cm⁻¹, being generated at a similar rate (Scheme 3). Attempts to observe hydride species by NMR spectroscopy were unsuccessful in both cases. We also protonated 3S with 2 equivalents of p-TsOH and again there was some evidence of formation of small amounts of 3SH⁺ after 3 h (ca. 10% as estimated by band intensity). Kaiser and Knör have published details of a protonation study of 3S by CF₃CO₂H and provide evidence from differential IR spectroscopy of both mono- and di-protonated complexes of 3S [17]. The latter is apparently characterised by an absorption at 2144 cm⁻¹, but we have not been able to observe any absorption in this region. It seems likely that our results differ from those of Kaiser and Knör as a result of the different concentrations of acids added and the quality of IR equipment used. What is clear is that protonation of 3S and 3Se is slow (especially when compared to the time scale for the cyclic voltammetry experiments), and thus, while 3H⁺ are chemically accessible, we conclude that they are not catalytically relevant.

In order to better understand the reactivity of clusters 2S and 3S in the presence of strong acids, we carried out DFT calculations on the preferred sites of protonation. Optimized structures for [Fe₃(CO)₇(μ-S)(μ-dppm)] (A) and [Fe₃(CO)₇(μ-S)₂(μ-dppm)] (D) are in accord with reported solid-state structures. The DFT data indicate that the preferred site of protonation in A coincides with the dppm-substituted iron-iron vector to give 2S-H⁺ (species C1), as depicted in Scheme 2. The HOMO in A (not shown) is a metal-based orbital whose parentage is not unlike that computed earlier by Schilling and Hoffmann in related tetrahedral clusters [50], with the largest concentration of electron density located between the iron centres ligated by the dppm ligand. Fig. 2 shows the geometry-optimized structure of the thermodynamically favoured product C1. Protonation of the non-dppm ligated metal-metal bond in A affords C2, which is 3.8 kcal mol⁻¹ less stable than C1. Protonation of the oxygen and sulfur sites associated with the μ₃-CO and μ₃-S moieties furnishes species C3 and C4, respectively. In comparison with the C1 and C2 hydride species, these latter two species are not energetically favoured in the protonation of A. Protonation of the μ₃-S group is the least stable of the protonated species computed, lying 30.5 kcal mol⁻¹ above A.

The protonation of the iron-iron bond in C1 and C2 leads to slight changes in the charge at the iron centres but more significant are the structural changes in the face-capping carbonyl group. Protonation is accompanied by lengthening of two of the three Fe₃-CO bonds to afford a pseudo-terminal CO ligand. The slippage of the μ₃-CO ligand in both C1 and C2 is visually verified in the optimized structures, and this feature is reflected by the Wiberg bond indices that reveal a CO group that is asymmetrically bound to the three iron atoms. In the case of C1, the computed Wiberg bond indices for the original face-capping CO group are 0.33 (Fe₁-CO), 0.16 (Fe₂-CO), and 0.93 (Fe₃-CO). These indices suggest that this particular CO group is best viewed as a pseudo-terminal ligand at Fe₃ and that this particular CO exhibits semi-bridging interactions with the Fe₁ and Fe₂ centres. C2 displays similar behaviour for the face-capping CO upon protonation, and here the Fe₃ centre serves as the site of coordination for the pseudo-terminal CO ligand. The Wiberg bond indices of 0.46 and 0.19 for the Fe₂-CO and Fe₃-CO vectors in C2 underscore this assertion.

The site of protonation in 3S was also examined by DFT. Cluster 3S was optimized (species D, not shown) and subsequently employed in the protonation studies. Fig. 3 shows the optimized structures and energy ordering for E₁ and E₂, which correspond to the products from Fe-Fe bond and sulfur protonation, respectively. Protonation of the Fe-Fe bond in D is clearly favoured over protonation of one of the face-capping sulfide ligands. The computed HOMO in D (not shown) is best described as a metal-based bonding orbital where the electron density is localized about the two formal Fe-Fe bonds in the nido polyhedral core. Examination of the Wiberg bond indices for the Fe₁-Fe₂ (0.30) and Fe₂-Fe₃ (0.18) bonds in E₁ provides insight into the structural changes that occur upon protonation. The Wiberg bond index for the protonation of an Fe-Fe
3.4. Electrochemical studies

The sulfide cluster \([\text{Fe}_3(\text{CO})_9(\mu_3-\text{S})_2] (1\text{S})\) is reported to undergo two one-electron reduction processes at -0.94 V (reversible) and -1.75 V (irreversible) in MeCN and an irreversible oxidation was also observed at +0.80 V [14]. In MeCN, \([\text{Fe}_3(\text{CO})_9(\mu_3-\text{Se})_2] (1\text{Se})\) (Fig. 4) also shows three reduction waves; at \(E_{1/2} = -0.96\) V (reversible, \(\Delta E = 70\) mV), -1.70 V (quasi-reversible) and -2.5 V (irreversible) and an irreversible oxidation at \(E_{p} = +0.80\) V. Reversibility of the second reduction wave improves at higher scan rates (\(>0.025\) V s\(^{-1}\)), this quasi-reversibility being the main difference in the electrochemical behaviour of \(1\text{S}\) and \(1\text{Se}\).

Mono-capped \([\text{Fe}_3(\text{CO})_9(\mu_2-\text{CO})(\mu_3-\text{S})(\mu-\text{dppm})] (2\text{S})\) and \([\text{Fe}_3(\text{CO})_9(\mu_3-\text{CO})(\mu_3-\text{Se})(\mu-\text{dppm})] (2\text{Se})\) were also studied in MeCN (Fig. S3) and for comparison with \(1\) and in \(\text{CH}_2\text{Cl}_2\) (Fig. 5 and Fig. S2) as proton-reduction catalysis was carried out in this solvent (\textit{vide infra}). In \(\text{CH}_2\text{Cl}_2\), \(2\text{S}\) and \(2\text{Se}\) display similar reductive behaviour, showing a quasi-reversible reduction at \(E_{1/2} = -1.29\) V (\(\Delta E = 230\) mV) for \(2\text{S}\) and at \(E_{1/2} = -1.30\) V (\(\Delta E = 308\) mV) for \(2\text{Se}\). A second peak is seen for both on the return scan (\(E_p = -0.58\) for \(2\text{S}\) and -0.64 V for \(2\text{Se}\)), but this was not further investigated. The two clusters display somewhat different oxidation behaviour, but for both all oxidative processes are irreversible. For \(2\text{S}\) a single oxidation process is seen at +0.81 V, while for \(2\text{Se}\) two separate oxidation waves are seen at +0.55 and +1.00 V. As the first oxidation wave for \(2\text{S}\) occurs at more positive potential than for \(2\text{Se}\), we deem it likely that a second oxidation wave for \(2\text{S}\) is out of the solvent window. In MeCN, the first reduction of each cluster occurs at lower potentials than in \(\text{CH}_2\text{Cl}_2\) and becomes reversible; for \(2\text{S}\) \(E_{1/2} = -1.16\) V (\(\Delta E = 80\) mV) for \(2\text{Se}\) \(E_{1/2} = -1.15\) V (\(\Delta E = 90\) mV), and the small additional oxidation on the reverse scan remains. For \(2\text{Se}\) an irreversible oxidation feature is again observed (at +0.20 V). Oxidation of \(2\text{Se}\) is complicated, the main oxidation at +0.28 V being followed by poorly defined further oxidative features, all irreversible. The electrochemical behaviour of \(2\text{S}\) contrasts with that reported for \([\text{Fe}_3(\text{CO})_9(\mu_3-\text{CO})(\mu_3-\text{S})][51]\), where both reduction and oxidation (at -0.26 and +0.43 V respectively) are irreversible. Thus, coordination of the diphosphine stabilises the reduced product while shifting it more negative by ca. 1 V.

CVs of \([\text{Fe}_3(\text{CO})_9(\mu_3-\text{S})(\mu-\text{dppm})] (3\text{S})\) and \([\text{Fe}_3(\text{CO})_9(\mu_3-\text{Se})(\mu-\text{dppm})] (3\text{Se})\) were carried out in \(\text{CH}_2\text{Cl}_2\) (Fig. 6) and MeCN (Fig. S4). In \(\text{CH}_2\text{Cl}_2\), \(3\text{S}\) displays a quasi-reversible reduction \((E_{1/2} = -1.55\) V, \(\Delta E = 215\) mV) together with two oxidation waves at +0.36 and +0.57 V. The second is almost completely irreversible, but the first has a small degree of quasi-reversibility (\(\Delta E = 205\) mV). The selenium analogue \(3\text{Se}\) shows two reduction waves within the potential window of \(\text{CH}_2\text{Cl}_2\), the first reduction is reversible and appearing at ca. 0.1 V lower potential \((E_{1/2} = -1.45\) V, \(\Delta E = 81\) mV) and a second irreversible reduction appears at -2.13 V. The oxidative behaviour with \(3\text{Se}\) is very similar to that of \(3\text{S}\), showing two processes at +0.38 and +0.63 V, the second being completely irreversible, while the first has a hint of quasi-reversibility (\(\Delta E = 174\) mV). When the scan rate was varied between 0.01 and 0.50 V\(^{-1}\) for \(3\text{S}\) and 0.025-2.0 V\(^{-1}\) for \(3\text{Se}\), no additional features were observed (Fig. S4). In MeCN, slightly different behaviour is noted for both clusters (Fig. S5). Most notably a second reduction...
process is seen for 3S, and the second reduction of 3Se that appears at -1.94 V becomes quasi-reversible. Thus, it is clear that the cluster anions are stabilised in MeCN with respect to CH$_2$Cl$_2$. Both clusters now show a single irreversible oxidation wave at +0.36 and +0.45 V for 3Se and 3S, respectively. In summary, for all three cluster types oxidation occurs at relatively low potentials but is irreversible. The first reduction is reversible or quasi-reversible, suggesting that the radical anions have some stability, which bears well for their proposed proton-reduction chemistry. Redox potentials are not particularly sensitive to the nature of the chalcogenide and, as expected, the introduction of the diphosphine results in a shift of oxidation potentials to less positive and reduction potentials to more negative values.

3.5. Electrocatalytic studies

With weak acids [Fe$_3$(CO)$_9$(μ$_3$-$S$)$_2$] (1S) [14] is catalytically active only at the second reduction potential, but with strong acids, it is catalytic at both the first and second reduction potential [15]. We studied the catalytic proton-reduction behaviour of [Fe$_3$(CO)$_9$(μ$_3$-Se)$_2$] (1Se) in both CH$_2$Cl$_2$ (Fig. S6) and MeCN (Fig. 7) but only discuss the latter as it allows a direct comparison with 1S. IR studies (vide supra) showed that 1Se does not protonate upon addition of HBF$_4$ Et$_2$O and thus the first step in any catalytic proton-reduction is reduction. On addition of one to ten molar equivalent of HBF$_4$ Et$_2$O to 1Se, a series of complex CVs result with up to five successive peaks being observed in the reductive region. However, three of these peaks are quite prominent and well separated, their height increasing with sequential addition of acid, indicating that they originate due to sequential reduction and protonation of 1Se.

We assume that 1Se is somewhat unstable in the presence of HBF$_4$ Et$_2$O and that its partial degradation results in formation of redox-active species in solution, possibly accounting for the additional peaks seen in the CV of 1S in the presence of HBF$_4$ Et$_2$O. Overall, a relatively large total current results, ca. 800 μA after addition of 10 equivalents of acid. Given the complex nature of the spectra, it is difficult to fully interpret likely mechanistic steps but it is assumed that 1Se is first reduced at ca. -0.9 V followed by likely protonation to give [HFe$_3$(CO)$_9$(μ$_3$-Se)$_2$] (1SeH$^+$) and this binds a proton to yield [H$_2$Fe$_3$(CO)$_9$(μ$_3$-Se)$_2$] (1SeH$_2$), which regenerates 1Se after H$_2$ loss. The current at this second potential is ca. 350 μA but at ca. -2.3 V, further H$_2$ generation ensues possibly associated with reduction to [H$_2$Fe$_3$(CO)$_9$(μ$_3$-Se)$_2$] (1SeH$_2$) and either H$_2$ loss (to generate 1Se$^-$) or rapid protonation and H$_2$ loss to give 1SeH. However, direct reduction of HBF$_4$ Et$_2$O by the electrode becomes prominent at this potential that also contributes to the catalytic currents. Liu and co-workers [15] previously studied the proton-reduction ability of [Fe$_3$(CO)$_9$(μ$_3$-Se)$_2$] (1S) in CH$_2$Cl$_2$ finding that peak current of the first catalytic wave levels off upon addition of over three equivalents of acid, characteristic of a kinetically-controlled process; behaviour similar to that observed here.

We next considered the ability of 2S and 2Se to act as proton reduction catalysts (Fig. 8 and Fig S7) in CH$_2$Cl$_2$ using tosyl acid (p-TsOH) as the proton source. For 2S, until addition of ca. 20 equivalents of acid there is no current uptake at the first reduction potential and even with 50 equivalents there is barely any catalysis at this potential. This shows that [Fe$_3$(CO)$_9$(μ$_3$-S$_2$)(μ-dppm)] (2S$^-$) is not catalytically active. After addition of ca. 20 equivalents of acid a new reduction peak appears at ca. -1.85 V, which we attribute to reduction of [HFe$_3$(CO)$_9$(μ$_3$-S$_2$)(μ-dppm)] (2SH) formed in situ. The peak height increases upon addition of further acid, suggesting generation of [H$_2$Fe$_3$(CO)$_9$(μ$_3$-CO)(μ$_3$-S$_2$)(μ-dppm)] (2SH$_2$), formed upon reduction of 2SH followed by proton addition. At ca. 20 equivalents of acid, a third peak develops at ca. -2.10 V that continues to grow upon further addition of acid. We associate this with reduction to [H$_2$Fe$_3$(CO)$_9$(μ$_3$-CO)(μ$_3$-S$_2$)(μ-dppm)] (2SH$_2$) becoming competitive with H$_2$ loss. Thus, at higher acid concentrations the main H$_2$-generating pathway(s) is likely to occur from either [H$_2$Fe$_3$(CO)$_9$(μ$_3$-CO)(μ$_3$-S)(μ-dppm)] (2SH$^-$) or [H$_2$Fe$_3$(CO)$_9$(μ$_3$-CO)(μ$_3$-S$_2$)(μ-dppm)] (2SH$_2$), the latter being formed upon protonation of the anion. Behaviour of 2Se is similar to that of 2S. Even after addition of ca. 50 equivalents of acid there is virtually no electron uptake at the first reduction potential but after addition of ca. 20 equivalents, electron uptake begins at -1.85 V associated with reduction of [HFe$_3$(CO)$_9$(μ$_3$-Se)(μ-dppm)] (2SeH). Soon after this (ca. 15 equivalents of acid) a further reduction wave appears at ca. -2.0 V associated with the formation of [H$_2$Fe$_3$(CO)$_9$(μ$_3$-CO)(μ$_3$-Se)(μ-dppm)] (2SeH$_2$).

We next performed electrocatalytic studies of [Fe$_3$(CO)$_9$(μ$_3$-E)$_2$(μ-dppm)] (3) under the same conditions as the studies on 2.
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(9). Kaiser and Knör have previously reported the electrocatalytic behaviour of 3S in CH2Cl2 using CF3CO2H as the proton source [17]. Unlike 1 and 2, bicapped 3 protonated to some extent by strong acids in CH2Cl2 which means that a mixture of [Fe3(CO)7(µ3-E)2(µ-dppm)] (3) and [HFe3(CO)7(µ3-E)2(µ-dppm)]⁺ (3⁺) is present, the relative amounts of which depend on acid concentration, however except for at high acid concentrations the predominant species in solution is the neutral cluster, 3. As generation of [Fe3(CO)7(µ3-S)2(µ-dppm)]⁻ (3S⁻) leads to H2 formation, this suggests that it can react with two equivalents of acid to afford [H2Fe3(CO)7(µ3-S)2(µ-dppm)]²⁻ (3SH2) which also releases H2. After addition of ca. 10 equivalents of acid, a further new reduction peak appears at ca. -1.48 V, which we associate with reduction of [HFe3(CO)7(µ3-S)2(µ-dppm)]⁺ (3S⁺), formed as a result of protonation of 3S. After addition of ca. 20 acid equivalents, this peak does not change in size suggesting that H2 loss is rate-determining from this species, a conclusion also made by Kaiser and Knör [17]. After addition of ca. 6 equivalents of acid a new reduction peak appears at ca. -2.1 V, and this grows with increasing acid concentration. This is possibly associated with reduction or rate-limiting loss of hydrogen from [H2Fe3(CO)7(µ3-S)2(µ-dppm)] (3SH2) leading to competitive reduction to afford [H2Fe3(CO)7(µ3-S)2(µ-dppm)]⁻ (3SH⁻) that further protonates to give [H3Fe3(CO)7(µ3-S)2(µ-dppm)]⁺ (3SH3) and releases hydrogen to generate [HFe3(CO)7(µ3-S)2(µ-dppm)]²⁻ (3SH). Selenide-capped 3Se behaves differently to 3S. Even after addition of ca. 50 equivalents of acid no new reduction peaks are seen at less negative potentials than that for the formation of [Fe3(CO)7(µ3-Se)2(µ-dppm)]⁻ (3⁻), suggesting that a protonated species does not exist in solution. The peak current of the first reduction potential increases gradually with the concentration of acid from the beginning, and this grows steadily upon further acid addition until around ca. 30 acid equivalents when it reaches a steady state, being associated with rate-limiting H2 loss. After addition of ca. 10 equivalents of acid a new broad reduction peak appears at around -2.1 V and upon further acid addition, this grows and shifts to slightly more negative potentials but is always clearly positive of the direct reduction of acid by the electrode.

4. Summary and conclusions

We have reported comparative electrochemical and catalytic proton-reduction activity of three types of chalcogenide-capped clusters: [Fe3(CO)7(µ3-E)2] (1), [Fe3(CO)7(µ3-CO)(µ3-E)(µ-dppm)] (2) and [Fe3(CO)7(µ3-E)2(µ-dppm)] (3) (E = S, Se). In general, the nature of the chalcogenide has little effect on the triiron core and consequent proton-reduction ability. Sulphide-capped clusters appear to be slightly more electron-rich than their selenide analogues, protonating to a greater extent in the presence of strong acids but being reduced at more negative reduction potentials. As expected, substitution of two carbonyls for the dppm ligand in 3 leads to shifts of the reduction potential to more negative values, but this is not mitigated by cluster core protonation (which lowers the reduction potential). More strongly electron-donating diphasphine ligands will need to be introduced in order to achieve the desired effect, and the introduction of dialkyl-substituted

Fig. 9. CVs of complex (a) [Fe3(CO)7(µ3-S)2(µ-dppm)] (3S) and (b) [Fe3(CO)7(µ3-Se)2(µ-dppm)] (3Se) in CH2Cl2 in the absence and presence of up to 1–30 (3S) and up to 1–50 (3Se) molar equivalents of TsOH (1 mM solution, supporting electrolyte [NBu4][PF6], scan rate 0.25 V s⁻¹, glassy carbon electrode, potential vs. Fe⁺/Fe.)
diphosphines such as Cy3P(CH2)3Cy2 into this type of cluster is currently under investigation. However, introduction of the diphosphine does stabilise the triiron centre towards CO loss, which has been shown to lead to complicated proton–reduction catalysis by [Fe3(CO)10μ3-S2] (15) [15] and probably also accounts for the complex nature of the proton-reduction catalysis observed for 1Se in the present study. While mono-chalcogenide clusters 2 are reduced at relatively low potentials (as compared to bipapped 3), the corresponding 49-electron anions generated are not catalytically active, rendering 2 unattractive as proton–reduction catalysts. A further complication noted with these clusters was the Lewis basicity of the face-capping carbonyl, which ruled out using HBF4·Et2O as a proton source. DFT calculations support formation of BF3 adducts and also allow us to probe likely sites of protonation even when clusters do not protonate significantly with strong acids.

Thus, protonation of 3 is shown to occur across an iron–iron bonded vector and not across the open edge or at one of the capping sulfide ligands.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2018.10.018.

References


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