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Alkyldiphenylphosphine substituted diiron ethanedithiolate or toluenedithiolate complexes

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ABSTRACT

A series of diiron complexes has been prepared and structurally characterized. Treatment of the complex (μ-SCH_2CH_2S-μ)$Fe_2(CO)_6$ (**1**) or [μ-$SC_6H_3(CH_3)S$-μ]$Fe_2(CO)_6$ (**2**) with a monophosphine ligand, Ph_2PR [R = CH_3, $CH(CH_3)_2$, $CH_2CH{=}CH_2$] in the presence of $Me_3NO{\cdot}2H_2O$ afforded the complexes (μ-SCH_2CH_2S-μ)$Fe_2(CO)_5(Ph_2PR)$ [R = CH_3, **3**; $CH(CH_3)_2$, **4**; $CH_2CH{=}CH_2$, **5**] and [μ-$SC_6H_3(CH_3)S$-μ]$Fe_2(CO)_5(Ph_2PR)$ [R = CH_3, **6**; $CH(CH_3)_2$, **7**; $CH_2CH{=}CH_2$, **8**] in 66–92% yields. The complexes **3**–**8** were characterized by elemental analysis, spectroscopy and single crystal X-ray diffraction analysis.

1. Introduction

In recent years, research on dithiolate-bridged diiron complexes has received special attention due to their structural relevance to the active site of [FeFe]-hydrogenases [1–10]. [FeFe]-hydrogenases are a class of natural enzymes that can catalyze the reversible reactions of protons and hydrogen [11–13]. X-ray crystallographic studies revealed that the active site of [FeFe]-hydrogenases, the so-called H cluster, as shown in Fig. 1 (**A**), features a diiron unit ligated by a bridging dithiolate ligand, three terminal carbonyls, a bridging carbonyl, two cyanides and a cysteinyl ligand [14,15]. The bridging dithiolate ligand was regarded as propanedithiolate [16–18] or azadithiolate [19–21]. Consequently, the diiron propanedithiolate complex (μ-$SCH_2CH_2CH_2S$-μ)$Fe_2(CO)_6$ (Fig. 1, **B**) [22] and the diiron azadithiolate complex (μ-SCH_2NHCH_2S-μ)$Fe_2(CO)_6$ (Fig. 1, **C**) [23] were prepared in order to mimic the active site of [FeFe]-hydrogenases. In addition, a large number of diiron analogs with various ligands, such as monophosphine PMe_3, PMe_2Ph, PPh_3 or $P(OEt)_3$ [24], intermolecular bridging diphosphine [25], intramolecular bridging diphosphine [26], chelating diphosphine [27], cyanide [28], N-heterocyclic carbene [29], pyridine [30], were reported in order to increase the basicity on the diiron unit.

The diiron ethanedithiolate complex (μ-SCH_2CH_2S-μ)$Fe_2(CO)_6$ (Fig. 1, **1**) [31] and diiron toluenedithiolate complex [μ-$SC_6H_3(CH_3)S$-μ]$Fe_2(CO)_6$ (Fig. 1, **2**) [32] were reported many years ago. However, research on the reactions of **1** or **2** was only intensively studied since the discovery of the active site of [FeFe]-hydrogenases [33–35] because they can be regarded as model compounds. With respect to **1**, **2** has a large steric hindrance group, possibly giving different results in the spectral or structural studies.

Inspired by the published work, we paid our attention to carbonyl substitution of the hexacarbonyl complex with a monophosphine ligand, alkyldiphenylphosphine, due to these complexes having structural novelty. As a result, six diiron complexes were obtained from the corresponding reactions and were structurally characterized by spectroscopy and X-ray diffraction analysis. In this paper, we herein report the synthesis, spectroscopy and X-ray crystal structures of diiron complexes containing the monophosphine ligands methyldiphenylphosphine, isopropyldiphenylphosphine and allyldiphenylphosphine.

2. Experimental

2.1. Materials and methods

Methyldiphenylphosphine, isopropyldiphenylphosphine, allyldiphenylphosphine and $Me_3NO{\cdot}2H_2O$ were available commercially and used as received. Complexes **1** [31] and **2** [32] were prepared according to literature procedures. IR spectra were recorded on a Nicolet MAGNA 560 FTIR spectrometer. NMR spectra were obtained on a Bruker 500 MHz spectrometer. Elemental analyses were performed using a Perkin-Elmer 240C analyzer.

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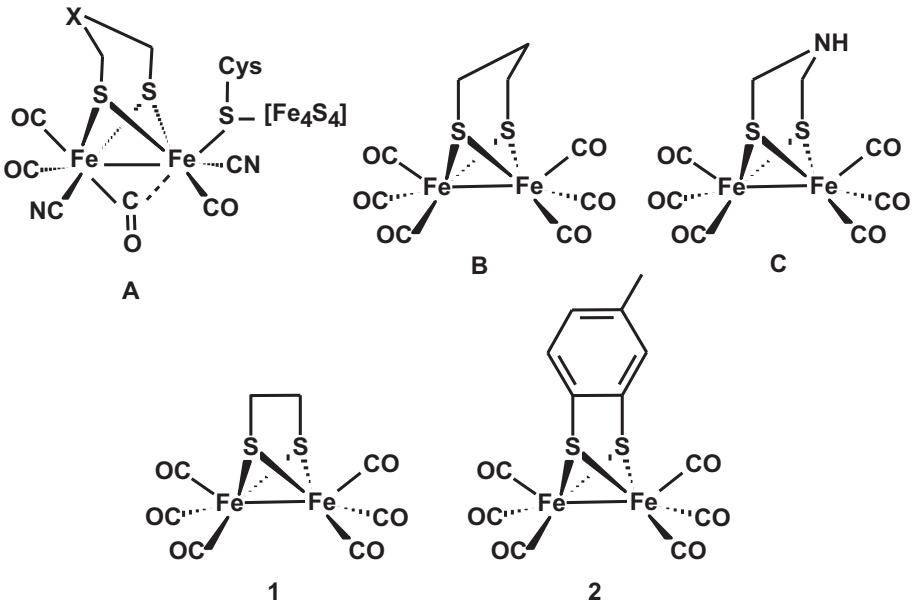

Fig. 1. The active site of [FeFe]-hydrogenases (**A**) and synthetic model complexes **B**, **C**, **1** and **2**.

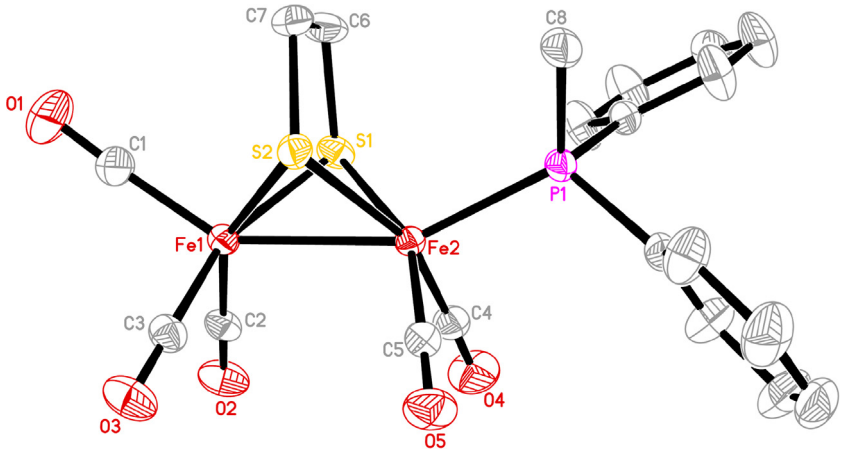

Fig. 2. ORTEP view of **3** with 30% probability level ellipsoids.

2.2. Synthesis of (μ-SCH_2CH_2S-μ)$Fe_2(CO)_5(Ph_2PCH_3)$ (**3**)

To a solution of (μ-SCH_2CH_2S-μ)$Fe_2(CO)_6$ (0.075 g, 0.2 mmol) and methyldiphenylphosphine (0.040 g, 0.2 mmol) in CH_2Cl_2 (10 mL) was added a solution of $Me_3NO{\cdot}2H_2O$ (0.022 g, 0.2 mmol) in MeCN (5 mL). The mixture was stirred at room temperature for 1 h and then the solvent was reduced on a rotary evaporator. The residue was subjected to TLC separation using CH_2Cl_2/petroleum ether = 1:4 (v/v) as eluent. From the main red band, 0.100 g (92%) of complex **3** was obtained as a red solid. IR (CH_2Cl_2, cm^{-1}): $\nu_{C\equiv O}$ 2045 (vs), 1984 (vs), 1933 (m). ^1H NMR (500 MHz, $CDCl_3$) δ, ppm: 7.60 (s, 4H, Ph*H*), 7.43 (s, 6H, Ph*H*), 2.12 (d, J = 7.5 Hz, 3H, CH_3), 1.98 (d, J = 7.5 Hz, 2H, CH_2), 1.55 (s, 2H, CH_2). $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$, 85% H_3PO_4) δ, ppm: 44.33 (s). Anal. Calcd. for $C_{20}H_{17}Fe_2O_5PS_2$: C, 44.15; H, 3.15. Found: C, 44.32; H, 3.21%.

2.3. Synthesis of (μ-SCH_2CH_2S-μ)$Fe_2(CO)_5[Ph_2PCH(CH_3)_2]$ (**4**)

The procedure was similar to that of **3**, except isopropyldiphenylphosphine (0.046 g, 0.2 mmol) was used instead of methyldiphenylphosphine; 0.078 g (68%) of complex **4** was obtained as a red solid. IR (CH_2Cl_2, cm^{-1}): $\nu_{C\equiv O}$ 2046 (vs), 1982 (vs), 1928 (m). ^1H NMR (500 MHz, $CDCl_3$) δ, ppm: 7.63 (s, 4H, Ph*H*), 7.44 (s, 6H, Ph*H*), 2.67 (s, 1H, C*H*), 1.85 (d, J = 7.5 Hz, 2H, CH_2), 1.28 (d, J = 7.5 Hz, 2H, CH_2), 1.18 (d, J = 9.5 Hz, 6H, $2CH_3$). $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$, 85% H_3PO_4) δ, ppm: 67.33 (s). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ, ppm: 216.10 (d, $J_{P\text{-}C}$ = 8.5 Hz, PFe*C*O), 210.20 (*C*O), 134.62 (d, $J_{P\text{-}C}$ = 34 Hz, *i*-Ph*C*), 133.04 (d, $J_{P\text{-}C}$ = 9.6 Hz, *o*-Ph*C*), 130.07 (s, *p*-Ph*C*), 128.28 (d, $J_{P\text{-}C}$ = 8.7 Hz, *m*-Ph*C*), 34.94 (s, CH_2), 30.90 (d, $J_{P\text{-}C}$ = 23.7 Hz, *C*H), 18.80 (s, CH_3). Anal. Calcd. for $C_{22}H_{21}Fe_2O_5PS_2$: C, 46.18; H, 3.70. Found: C, 45.88; H, 3.76%.

2.4. Synthesis of (μ-SCH_2CH_2S-μ)$Fe_2(CO)_5(Ph_2PCH_2CH{=}CH_2)$ (**5**)

The procedure was similar to that of **3**, except allyldiphenylphosphine (0.045 g, 0.2 mmol) was used instead of methyldiphenylphosphine; 0.087 g (76%) of complex **5** was obtained as a red solid. IR (CH_2Cl_2, cm^{-1}): $\nu_{C\equiv O}$ 2047 (vs), 1985 (vs), 1933 (m). ^1H NMR (500 MHz, $CDCl_3$) δ, ppm: 7.61 (s, 4H, Ph*H*), 7.43 (s, 6H, Ph*H*), 5.66 (s, 1H, *C*H), 5.12–5.06 (m, 2H,