

**Synthesis and Molecular Structure of  
[Fe<sub>2</sub>Cl<sub>2</sub>(μ-S-*t*Bu)<sub>2</sub>(η<sup>1</sup>-η<sup>1</sup>-μ-dppe)]  
(dppe = Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>)**

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The red title compound was synthesized by the metathesis reaction of [FeCl<sub>2</sub>(dppe)] (dppe = Ph<sub>2</sub>PCH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>) and NaS-*t*Bu in THF. The X-ray structure analysis revealed a dinuclear complex with two iron(II) centers coordinated in a distorted tetrahedral fashion by two bridging thiolates, one bridging dppe molecule and one terminal chloro ligand.

**Key words:** Dinuclear Complexes, Iron, Thiolates

## Introduction

In our search for model compounds for the Fe(μ-S)<sub>2</sub>Fe ferredoxine [1] we explored the reactivity of [Fe(Cl)<sub>2</sub>(dppe)] towards thiolates. Expecting that the reaction with simple alkylthiolato salts NaSR would lead to complexes of the type [Fe(SR)<sub>2</sub>(dppe)]. Next it was planned to substitute the dppe ligand by a functionalized bidentate benzenedithiolato ligand [2] or a bridging bis(benzenedithiolato) ligand [3]. However, the reaction of [Fe(Cl)<sub>2</sub>(dppe)] with NaS-*t*Bu does not proceed with substitution of both chloro ligands but instead yields the novel dinuclear complex [Fe<sub>2</sub>Cl<sub>2</sub>(μ-S-*t*Bu)<sub>2</sub>(η<sup>1</sup>-η<sup>1</sup>-μ-dppe)].

## Experimental Section

All manipulations were performed in an atmosphere of dry argon by standard Schlenk techniques. Solvents were dried by standard methods and freshly distilled prior to use. [Fe(Cl)<sub>2</sub>(dppe)] was prepared according to a literature procedure [4].

[Fe<sub>2</sub>Cl<sub>2</sub>(μ-S-*t*Bu)<sub>2</sub>(η<sup>1</sup>-η<sup>1</sup>-μ-dppe)]: A suspension of 526 mg (1 mmol) of [Fe(Cl)<sub>2</sub>(dppe)] in 50 ml THF was treated with a mixture of 225 μl (2 mmol) of *tert*-butylthiol und 48 mg (2 mmol) of NaH in 10 ml of THF. The brown reaction mixture was stirred for 2 h at ambient temperature. Subsequently the solvent was stripped *in vacuo*. The solid residue was suspended in toluene (60 ml) and filtered through celite. The filtrate was concentrated to 30 ml and *n*-hexane (30 ml) was added. A red precipitate formed immediately which was isolated by filtration and washed with *n*-hexane. Red crystals suitable for an X-ray diffraction analysis were obtained from a concentrated toluene/*n*-hexane solution (3:1, v:v) at –20 °C. Yield: 410 mg (0.54 mmol, 54 %). – C<sub>34</sub>H<sub>42</sub>Cl<sub>2</sub>Fe<sub>2</sub>P<sub>2</sub>S<sub>2</sub> (759.34); calcd. C 53.78, H 5.57; found C 53.99, H 5.38.

**X-ray structure determination:** Formula C<sub>34</sub>H<sub>42</sub>Cl<sub>2</sub>Fe<sub>2</sub>P<sub>2</sub>S<sub>2</sub>, *M* = 759.34, red crystal 0.30 × 0.25 × 0.25 mm<sup>3</sup>, *a* = 9.785(1), *b* = 21.733(1), *c* = 17.428(1) Å, β = 96.06(1)°, *V* = 3685.5(5) Å<sup>3</sup>, ρ<sub>calcd</sub> = 1.369 g cm<sup>–3</sup>, μ = 11.54 cm<sup>–1</sup>, empirical absorption correction (0.723 ≤ θ ≤ 0.761), *Z* = 4, monoclinic, space group *P*2<sub>1</sub>/*n* (No. 14), λ = 0.71073 Å, *T* = 198 K, ω and φ scans, 33670 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.71 Å<sup>–1</sup>, 10923 independent (*R*<sub>int</sub> = 0.037) and 8771 observed reflections [*I* ≥ 2 σ(*I*)], 385 refined parameters, *R* = 0.042, w*R*<sub>2</sub> = 0.100, max. residual electron density 1.07 (–0.64) e Å<sup>–3</sup>, hydrogens calculated and refined as riding atoms. The data set was collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator Nonius FR591. Programs used: data collection COLLECT [5], data reduction Denzo-SMN [6], absorption correction SORTAV [7], structure solution SHELXS-97 [8], structure refinement SHELXL-97 [9], graphics SCHAKAL [10]. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-201201. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk].

## Results and Discussion

The reaction of  $[\text{FeCl}_2(\text{dppe})]$  with two equivalents of  $\text{NaS-}t\text{Bu}$  yields the title compound  $[\text{Fe}_2\text{Cl}_2(\mu\text{-S-}t\text{Bu})_2(\eta^1\text{-}\eta^1\text{-}\mu\text{-dppe})]$  as a red solid. The complex is air sensitive and turns to a black solid upon decomposition. Crystals suitable for an X-ray structure determination were obtained from a concentrated toluene/*n*-hexane solution at  $-20^\circ\text{C}$ .

The X-ray structure analysis reveals a dinuclear complex (Fig. 1). The iron(II) centers are coordinated in a distorted tetrahedral fashion by two bridging thiolato sulfur atoms, a terminal chloro ligand and a phosphorus atom from a bridging dppe ligand. The dppe ligand forms together with the two iron(II) centers and one  $\mu\text{-S}$  atom a seven-membered ring next to a four-membered  $\text{Fe}(\mu\text{-S})_2\text{Fe}$  ring. Both *t*Bu substituents are located on

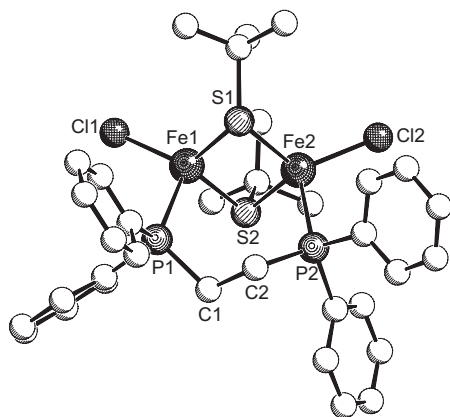


Fig. 1. Molecular structure of  $[\text{Fe}_2\text{Cl}_2(\mu\text{-S-}t\text{Bu})_2(\eta^1\text{-}\eta^1\text{-}\mu\text{-dppe})]$ . Hydrogen atoms have been omitted. Selected bond lengths [Å] and angles [ $^\circ$ ]: Fe1–Cl1 2.2096(7), Fe1–S1 2.3197(6), Fe1–S2 2.3341(6), Fe1–P1 2.4355(6), Fe2–Cl2 2.2133(6), Fe2–S1 2.3426(6), Fe2–S2 2.3206(6), Fe2–P2 2.4345(6); Cl1–Fe1–S1 124.70(3), Cl1–Fe1–S2 117.14(3), Cl1–Fe1–P1 106.21(3), S1–Fe1–S2 106.11(2), S1–Fe1–P1 98.66(2), S2–Fe1–P1 99.22(2), Cl2–Fe2–S1 120.30(2), Cl2–Fe2–S2 121.94(2), Cl2–Fe2–P2 106.17(2), S1–Fe2–S2 105.81(2), S1–Fe2–P2 100.54(2), S2–Fe2–P2 97.30(2), Fe1–S1–Fe2 73.94(2), Fe1–S2–Fe2 74.08(2).

the same side of the roughly planar  $\text{Fe}(\mu\text{-S})_2\text{Fe}$  ring. Steric interactions between these alkyl groups lead to almost identical small Fe–S–Fe angles (Fe1–S1–Fe2  $73.94(2)^\circ$ , Fe1–S2–Fe2  $74.08(2)^\circ$ ) and larger S–Fe–S angles (S1–Fe1–S2  $106.11(2)^\circ$ , S1–Fe2–S2  $105.81(2)^\circ$ ). The other angles around the iron centers deviate strongly from the value expected for tetrahedral coordination. Due to steric requirements of the bridging dppe ligand the S–Fe–P angles are smaller than expected for tetrahedral coordination (range  $97.30(2)^\circ$ – $100.54(2)^\circ$ ) while the Cl–Fe–S angles are larger (range  $117.14(3)^\circ$ – $124.70(3)^\circ$ ).

The Fe–S bond distances (range  $2.3197(6)$  Å– $2.3426(6)$  Å) are comparable to equivalent distances observed in the  $\text{Fe}^{\text{II}}$  phosphine-thiolato complexes  $[\text{Fe}_2(\text{SR})_4(\text{dppe})_2]$ ,  $[\text{Fe}(\text{SR})_2(\text{dppp})]$  and  $[\text{Fe}(\text{SR})_2(\text{PMePh}_2)]$  [11] and in the thiourea-thiolato complex  $[\text{Fe}_2(\text{SR})_2(\text{SC}(\text{NMe}_2)_2)_2]$  [12]. They even fall in the range found for homoleptic  $\text{Fe}^{\text{II}}$  tetrathiolates  $[\text{Fe}(\text{SR})_4]^{2-}$  [13].

Substitution of a chloro ligand in  $[\text{FeCl}_2(\text{dppe})]$  by a thiolato ligand and the subsequent rearrangement to the dinuclear  $[\text{Fe}_2\text{Cl}_2(\mu\text{-S-}t\text{Bu})_2(\eta^1\text{-}\eta^1\text{-}\mu\text{-dppe})]$  leaves the Fe–Cl and Fe–P distances virtually unchanged as can be seen by comparison to the molecular structure of  $[\text{FeCl}_2(\text{dppe})]$  [14].

Surprisingly, the reaction of  $[\text{FeCl}_2(\text{dppe})]$  with  $\text{NaS-}t\text{Bu}$  leads to the substitution of only one chloro ligand and a rearrangement to the dinuclear  $[\text{Fe}_2\text{Cl}_2(\mu\text{-S-}t\text{Bu})_2(\eta^1\text{-}\eta^1\text{-}\mu\text{-dppe})]$ . The steric bulk of the *tert*-butylthiolato ligand together with that of the phosphine ligand are apparently sufficient to prevent the substitution of the second chloro ligand. The mononuclear complex  $[\text{Fe}(\text{SR})_2(\text{dppp})]$  (dppp =  $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$ ) is known [11]. However, in this complex the thiolato ligand is sterically less demanding and the bidentate phosphane ligand forms with the iron(II) center a six-membered ring. Complexes of the type  $[\text{X}_2\text{Fe}(\eta^1\text{-}\eta^1\text{-}\mu\text{-dppe})_2\text{FeX}_2]$  ( $\text{X} = \text{I}^-$ ,  $\text{RS}^-$ ) have also been described [11]. However, the coordination of only one bridging dppe ligand and two bridging thiolato ligands together with a terminal chloro ligand has not been observed in  $\text{Fe}^{\text{II}}$  coordination chemistry so far.

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