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# SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF $[Fe_2(CO)_5(\mu\text{-}PBu^t_2)(\mu\text{-}PCy_2)(dppm\text{-}P)]$: A COMPLEX CONTAINING dppm [dppm = BIS(DIPHENYLPHOSPHINO) METHANE] IN THE RARE MONODENTATE COORDINATION

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**Abstract**—The coordinatively unsaturated complex $[Fe_2(CO)_5(\mu\text{-}PBu^t_2)(\mu\text{-}PCy_2)]$ (Fe=Fe) (1) adds spontaneously dppm [dppm = bis(diphenylphosphino)methane] and yields the saturated compound $[Fe_2(CO)_5(\mu\text{-}PBu^t_2)(\mu\text{-}PCy_2)(dppm\text{-}P)]$ (2). Compounds **1** and **2** exist in a reversible thermal equilibrium; heating **2** in toluene produces **1** together with the free ligand dppm, whereas by cooling to room temperature **2** is recovered. A conversion of **2** into the known complex $[Fe_2(CO)_3(\mu\text{-}PBu^t_2)(\mu\text{-}PCy_2)(\mu\text{-}dppm)]$ (3) is only possible by photochemical means. Compound **3** is readily transformed back into **2** by carbon monoxide under normal conditions. The molecular structure of **2** determined by X-ray analysis is described.

Recently, we reported the synthesis of the unprecedented triply-bridged electron-poor complex $[Fe_2(CO)_3(\mu\text{-}PBu^t_2)(\mu\text{-}PCy_2)(\mu\text{-}dppm)]$ (3) by addition of dppm to the coordinatively unsaturated compound $[Fe_2(CO)_5(\mu\text{-}PBu^t_2)(\mu\text{-}PCy_2)]$ (Fe=Fe) (1) under UV irradiation.[1] Hogarth and Lavender[2] described the closely related, but sterically less demanding, complexes $[Fe_2(CO)_4(\mu\text{-}PPh_2)(\mu\text{-}PR_2)(\mu\text{-}dppm)]$ (R = Ph, Cy) and therefore we were faced with the question about the existence of the compound $[Fe_2(CO)_4(\mu\text{-}PBu^t_2)(\mu\text{-}PCy_2)(\mu\text{-}dppm)]$. We found that **1** reacts in a first step spontaneously with dppm to form $[Fe_2(CO)_5(\mu\text{-}PBu^t_2)(\mu\text{-}PCy_2)(dppm\text{-}P)]$ (2) as a complex with dppm in monodentate coordination, which is relatively rare in such binuclear systems. The results of the X-ray crystal structure determination of **2**, as well as some reactions with this compound, are described in this paper.

## EXPERIMENTAL

All reactions were performed under oxygen-free argon using conventional Schlenk techniques. Solvents were dried over molecular sieves or over sodium benzophenone ketyl and distilled under argon prior to use. Starting materials were either commercially available or were prepared as described elsewhere: $[Fe_2(CO)_5(\mu\text{-}PBu^t_2)(\mu\text{-}PCy_2)]$ and $[Fe_2(CO)_3(\mu\text{-}PBu^t_2)(\mu\text{-}PCy_2)(\mu\text{-}dppm)]$.[1]

### *Preparation of* $[Fe_2(CO)_5(\mu\text{-}PBu^t_2)(\mu\text{-}PCy_2)(dppm\text{-}P)]$ (2)

To a solution of **1** (594 mg, 1 mmol) in 40 $cm^3$ THF, dppm was added (384 mg, 1 mmol) and the mixture stirred at room temperature for 2 h. The colour of the solution changes quickly from deep green to violet–brown. The THF was removed *in vacuo* and the residue extracted three times with 15 $cm^3$ pentane. The combined extracts were filtered, concentrated *in vacuo* to *ca* 15 $cm^3$ and crystallized at −30°C. Yield 970 mg **2** (~100%), violet–brown

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needles, m.p. 143–144°C (decomp.). Found: C, 61.2; H, 6.5; P, 12.5. Calc. for $C_{50}H_{62}Fe_2O_5P_4$: C, 61.4; H, 6.3; P, 12.7%. IR (KBr): 1987 (s), 1950 (s), 1901 (vs, br, sh); ($CH_2Cl_2$): 1990 (s), 1952 (s), 1900 (vs). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 330.3 (d, $^2J_{PP}$ = 52 Hz, $\mu$-$PBu^t_2$), 233.9 (dd, $^2J_{PP}$ = 52 Hz, $^2J_{PP}$ = 12 Hz, $\mu$-$PCy_2$), 62.7 (dd, $^2J_{PP}$ = 46 Hz, $^2J_{PP}$ = 12 Hz, dppm-P), −25.4 (d, $^2J_{PP}$ = 46 Hz, dppm-P); a coupling $^2J_{PP}$ between $\mu$-$PBu^t_2$ and dppm-P was practically not observed. $^1H$ NMR: for discussion see text.

### *Thermal equilibrium between* **2** *and* **1**

Compound **2** (489 mg, 0.5 mmol) was refluxed in toluene (20 $cm^3$) for 30 min. During the heating to the b.p., the solution became immediately deep green. The reaction is reversible; during cooling to room temperature the colour of the solution became violet–brown; **2** was detectable by spectroscopic means.

### *Reaction of* **2** *with carbon monoxide*

Compound **2** (489 mg, 0.5 mmol) was dissolved in THF (20 $cm^3$) and a stream of CO was bubbled through the solution at room temperature for 3 h. The solvent was removed *in vacuo* and the residue extracted with pentane. Cooling at −30°C overnight yielded unchanged **2**, characterized by IR and NMR measurements.

### *Reaction of* **2** *with carbon monoxide under pressure*

Compound **2** (489 mg, 0.5 mmol) was dissolved in THF (20 $cm^3$) and transferred into a 200-ml steel autoclave. The solution was pressurized with 20 bar CO and stirred at room temperature for 2 h. After venting, the resulting deep violet solution was evaporated to dryness. The residue was extracted with pentane; a colourless solid remained which was identified as dppm. Compound **4** crystallized from the deep violet solution at −78°C in nearly quantitative yield, characterized by the known spectroscopic data.[3]

### *Reaction of* **3** *with carbon monoxide*

Compound **3** (461 mg, 0.5 mmol) was dissolved in THF (20 $cm^3$) and a stream of CO was bubbled through the solution at room temperature for 1 h. A noticeable colour change from red–brown to violet–brown after 30 min was observed. The solvent was removed *in vacuo* and the residue extracted with pentane. By cooling at −30°C overnight, **2** was obtained in nearly quantitative yield.

### *Crystal structure determination for complex* **2**

Single crystals of **2** were obtained by slow diffusion of hexane into a concentrated THF solution of the compound. A summary of crystal data and details of the structure determination are given in Table 1.

The intensity data were collected on a Stoe STADI-4 diffractometer at room temperature, using graphite-monochromated Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å) and the $\omega$–$\theta$ scan measuring technique. Lattice constants were obtained by a least-squares treatment of the setting angles of 64 reflections. Lorentz and polarization corrections were applied during data reduction. Additionally, an empirical absorption correction ($\psi$-scan method, transmission factors in the range of 0.762–0.849) was performed. The structure was solved by direct methods[4] and refined by full-matrix least-squares on $F^2$ [5] with anisotropic displacement parameters for the non-hydrogen atoms of the complex molecule. The hydrogen atoms were placed at their geometrically calculated positions and the methyl groups were treated as rigid groups. A difference Fourier map reveals several additional peaks outside the complex, with heights of 0.8–1.1 e Å$^{-3}$, which pointed to the presence of THF. The subsequent refinement applying geometrical restraints indicated a disorder phenomenon: two THF molecules differentiated from each other by their orientation occupy alternatively the same site in the crystal lattice. Each THF molecule was included in the final refinement with a site occupation factor of 0.25 and isotropic displacement parameters for the non-hydrogen atoms.

Tables of atomic coordinates and displacement parameters, lists of observed and calculated structure factors and complete lists of bond lengths and angles have been deposited with the Editor; atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre.

## RESULTS AND DISCUSSION

### *Synthesis and reactions*

Two linked metal centres are preferably bridged by the ligand dppm in a bidentate coordination mode.[6] The monodentate coordination is relatively rare, as discussed by Puddephatt,[7] and we have shown that dppm is even able to bridge strongly sterically demanding systems with metal–metal bonds.[1] The existence of $[Fe_2(CO)_4(\mu\text{-}PPh_2)(\mu\text{-}PR_2)(\mu\text{-dppm})]$ (R = Ph, Cy)[2] prompted us to search for a synthetic way to the analogous complex $[Fe_2(CO)_4(\mu\text{-}PBu^t_2)(\mu\text{-}PCy_2)(\mu\text{-dppm})]$. If the

Table 1. Crystal data and details of X-ray structure analysis of **2**·0.5THF

| | | | |
|---|---|---|---|
| Empirical formula | $C_{50}H_{62}Fe_2O_5P_4 \cdot 0.5(C_4H_8O)$ | Crystal size (mm) | $0.46 \times 0.28 \times 0.28$ |
| | | Check reflections | 3, no significant intensity variation |
| Molecular weight (g mol$^{-1}$) | 1014.6 | | |
| Crystal system | monoclinic | Range of measurement (°) | $3 \leqslant 2\theta \leqslant 48$ |
| Space group | $P2_1/n$ | Min. $h, k, l$/max. $h, k, l$ | $-13, 0, 0/13, 26, 23$ |
| Lattice parameters | | Independent reflections | 8373 |
| $a$ (Å) | 11.803(2) | Reflections used in refinement | 8352 |
| $b$ (Å) | 22.930(4) | Reflections/parameter | 14.0 |
| $c$ (Å) | 20.447(4) | Weighting scheme | $w = 1/[\sigma^2(F_0^2)+(0.0649P)^2 + 4.5624P], P = (F_0^2+2F_c^2)/3$ |
| $\beta$ (°) | 104.77(1) | | |
| $V$ (Å$^3$) | 5351(2) | | |
| $Z$ | 4 | Max. shift/$\sigma$ (last least-squares cycle) | 0.005 |
| $F(000)$ | 2136 | Min./max. heights in the final $\Delta\rho$ map (e Å$^{-3}$) | $-0.37/0.63$ |
| $D_{calc}$ (g cm$^{-3}$) | 1.259 | $R(F)/wR(F^2)/S(F^2)$ (all data) | 0.072/0.141/1.10 |
| $\mu$(Mo-$K_\alpha$) (cm$^{-1}$) | 7.06 | | |

reaction of **1** with dppm in THF is carried out without UV irradiation and without passing a stream of argon through the solution we can obtain the binuclear compound **2** with dppm in monodentate coordination, as outlined in eq. (1).

$$\underset{\mathbf{1}}{[Fe_2(CO)_5(\mu\text{-}PBu^t_2)(\mu\text{-}PCy_2)]} \xrightarrow{\text{dppm}} \underset{\mathbf{2}}{[Fe_2(CO)_5(\mu\text{-}PBu^t_2)(\mu\text{-}PCy_2)(\text{dppm-P})]} \quad (1)$$

The new complex **2** was characterized by microanalysis, IR and $^{31}P$ NMR spectra (see Experimental). Surprisingly, no coupling between the phosphorus of the $\mu$-$PBu^t_2$ bridge and the coordinated phosphorus of dppm could be observed. $^1H$ NMR measurements are complicated since already at room temperature in solution a slow separation of the dppm occurs and a mixture of **1**, **2** and the free dppm can be identified (also by $^{31}P$ NMR). Therefore, we were especially interested in an X-ray crystal structure determination of **2**.

Following the aim to obtain a coordinatively saturated triply bridged tetracarbonyl species, we studied a thermal reaction with **2** in toluene. Some reactions are known in which a change from the monodentate to the bidendate coordination mode of dppm is realized, for instance $[Cr(CO)_5(\text{dppm-P})]$ yields, on heating under loss of CO, the complex $[Cr(CO)_4(\eta^2\text{-dppm})]$.[8] If a solution of **2** is heated, a colour change from violet–brown to deep green is observed, indicating the formation of **1**. The process is reversible, cooling yielding a colour change back to violet–brown, and by spectroscopic means **2** can be detected:

$$\mathbf{2} \underset{\text{cooling}}{\overset{\text{heating}}{\rightleftharpoons}} \mathbf{1} + \text{dppm}. \quad (2)$$

Consequently, by this thermal reaction pathway a possible tetracarbonyl species is not obtainable and we tested a reaction under photochemical conditions in THF, but without the argon stream. In this case we could detect by spectroscopic means only a mixture of **2** and **3**. If a stream of argon is bubbled through the solution during irradiation, a clean conversion of **2** into **3** takes place. A conversion of **3** back into **2** is also possible by passing a stream of CO through a solution of **3** in THF at room temperature:

$$\mathbf{2} \underset{+CO}{\overset{h\nu,\,-CO}{\rightleftharpoons}} \mathbf{3}. \quad (3)$$

The reaction occurs relatively rapidly and, therefore, also by this way no tetracarbonyl species was detectable. A change from the bridging bidentate to the monodentate coordination of dppm is not surprising; some examples are known. For instance, the CO-based equilibrium

$$[Ni_2(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})_2](\text{Ni-Ni}) \underset{-CO}{\overset{+CO}{\rightleftharpoons}}$$

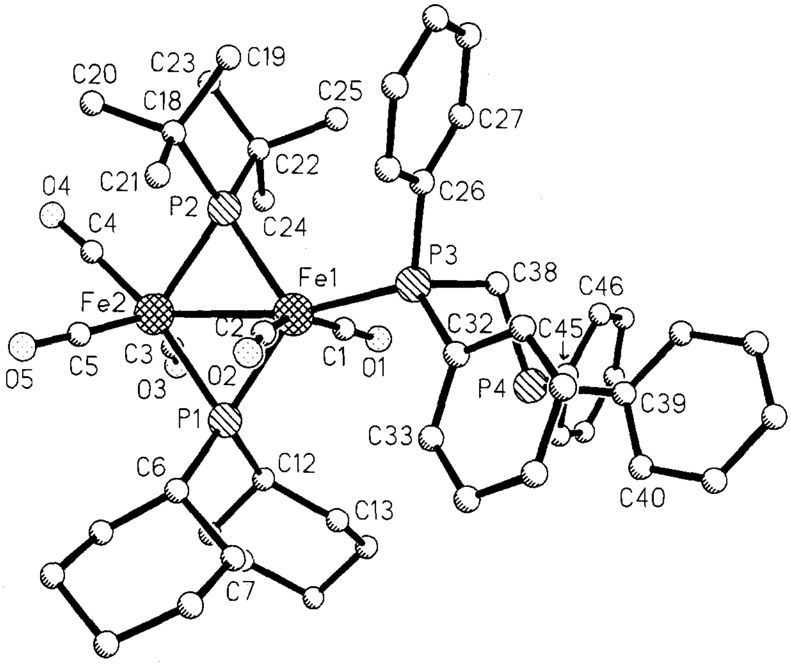

Fig. 1. Molecular structure of $[Fe_2(CO)_5(\mu\text{-}PBu^t_2)(\mu\text{-}PCy_2)(dppm\text{-}P)]$ (**2**).

$$[Ni_2(CO)_4(\mu\text{-dppm})_2] \underset{-2CO}{\overset{+2CO}{\rightleftharpoons}} 2[Ni(CO)_3(dppm\text{-}P)]$$

was described as fully reversible in solution.[9] However, in our case probably a break of the Fe═Fe bond in **3** and **2** is prevented by the presence of both phosphido groups. Furthermore, we studied whether a reaction of **2** with CO is possible yielding the coordinatively saturated compound $[Fe_2(CO)_6(\mu\text{-}PBu^t_2)(\mu\text{-}PCy_2)]$ (**4**)[3] and the free ligand dppm. By passing a stream of CO through a solution of **2** we could not observe any reaction (IR, NMR). Although the dppm seems to be only weakly bound (deduced from the thermal instability of **2**), under normal conditions the CO is not capable of displacing the phosphine ligand. However, assuming that this should be possible under increased CO pressure, we tried a reaction of **2** with 20 bar CO (2 h, THF, room temperature) and this treatment indeed resulted in the formation of **4** and dppm (see Experimental).

### *Crystal structure of* $[Fe_2(CO)_5(\mu\text{-}PBu^t_2)(\mu\text{-}PCy_2)(dppm\text{-}P)]$ (**2**)

Compound **2** crystallizes as the solvated species **2**·0.5 THF, which was the subject of investigation. As a result, the THF molecules are located in voids between the complex molecules within the crystal lattice. The observed intermolecular contact distances give no indication of special interactions between solvent and complex molecules and, thus, for a noticeable influence of the former on the molecular structure of the latter. Therefore, in the following only the molecular structure of **2** will be discussed.

The results of the X-ray analysis confirmed the assumed structure of **2** as a doubly-bridged di-iron complex with two non-equivalent metal atoms and the dppm ligand in monodentate coordination. The molecular structure of **2** is illustrated by Fig. 1; relevant geometric parameters are given in Table 2.

The $Fe_2P_2$ core in **2** shows nearly exact planarity. The dihedral angle Θ between the two $Fe_2P$ planes describing the fold of the core with respect to the P···P line amounts to 178.5°. The phosphine donor atom P(3) deviates only very slightly by 0.044(1) Å from the $Fe_2P_2$ best plane. The Fe—Fe distance of 2.719(1) Å indicates clearly a single bond between the two iron atoms. Ignoring the Fe—Fe bond, the coordination spheres of the iron atoms can be interpreted as strongly distorted tetragonal pyramids with P(2) located in both apical positions and P(1)···P(2) as a common edge. The different coordination spheres of the two iron atoms is reflected in their distances to the bridging phosphorus atoms (*cf* Table 2): the Fe(1)—P bond lengths are about 0.05 Å shorter than those in which Fe(2) is involved.

The molecular structure of **2** is strongly related to that of the parent complex $[Fe_2(CO)_6(\mu\text{-}PBu^t_2)(\mu\text{-}PCy_2)]$,[3] as well as to those of the analogous phosphine complexes $[Fe_2(CO)_5(\mu\text{-}PBu^t_2)(\mu\text{-}PCy_2)(PR'_2R'')]$ with R′ = R″ = Bu$^n$ and R′ = Ph, R″ = H, respectively.[1] An agreement to a very

Table 2. Relevant bond lengths (Å) and angles (°) for **2**

| | | | |
|---|---|---|---|
| Fe(1)—Fe(2) | 2.719(1) | Fe(2)—P(1) | 2.288(1) |
| Fe(1)—P(1) | 2.231(1) | Fe(2)—P(2) | 2.268(1) |
| Fe(1)—P(2) | 2.230(1) | Fe(2)—C(3) | 1.783(5) |
| Fe(1)—P(3) | 2.242(1) | Fe(2)—C(4) | 1.755(5) |
| Fe(1)—C(1) | 1.779(4) | Fe(2)—C(5) | 1.770(5) |
| Fe(1)—C(2) | 1.773(4) | | |
| Fe(1)—P(1)—Fe(2) | 73.95(3) | Fe(1)—P(2)—Fe(2) | 74.36(4) |
| P(1)—Fe(1)—P(2) | 107.45(4) | P(1)—Fe(2)—P(2) | 104.23(4) |
| P(1)—Fe(1)—P(3) | 138.98(4) | P(1)—Fe(2)—C(3) | 85.5(1) |
| P(1)—Fe(1)—C(1) | 87.8(1) | P(1)—Fe(2)—C(4) | 165.8(2) |
| P(1)—Fe(1)—C(2) | 86.3(1) | P(1)—Fe(2)—C(5) | 90.9(2) |
| P(2)—Fe(1)—P(3) | 113.57(4) | P(2)—Fe(2)—C(3) | 116.2(2) |
| P(2)—Fe(1)—C(1) | 99.9(1) | P(2)—Fe(2)—C(4) | 89.3(2) |
| P(2)—Fe(1)—C(2) | 103.2(1) | P(2)—Fe(2)—C(5) | 109.6(2) |
| P(3)—Fe(1)—C(1) | 85.1(1) | C(3)—Fe(2)—C(4) | 84.4(2) |
| P(3)—Fe(1)—C(2) | 84.6(1) | C(3)—Fe(2)—C(5) | 133.4(2) |
| C(1)—Fe(1)—C(2) | 156.8(2) | C(4)—Fe(2)—C(5) | 88.8(2) |

large extent can be noticed for all relevant details of molecular geometry of the four complexes. Thus, the Fe—Fe distances are in the close range of 2.686(2)–2.719(1) Å.

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