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PAPER

Complexation of 1,1'-bis(diphenylphosphino)ferrocene dioxide (dppfO₂) with 3d metals and revisit of its coordination to Pd(II)[†]

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Complexation of $dppfO_2$ with 3d metals has been examined and its coordination towards Pd(II) re-visited. Adduct formation is complicated by ligand exchanges followed by formation of coordination metal salts, and oxidation.

Introduction

Pd(II) complexes are almost invariably square planar, although there are exceptions, such as the trigonal pyramidal tris(phosphino)silyl Pd(II) cation.¹ A decade ago one of us reported the formation of $[PdCl_2(dppfO_2)]$ (dppfO₂ = bis(diphenylphosphino)ferrocene dioxide-O,O') (1) with an unusual tetrahedral Pd(II) structure from the reaction of dppfO₂ with PdCl₂(MeCN)₂ in CH₂Cl₂.² Fey and Orpen *et al.* subsequently performed DFT calculation which suggested that the energy content of the paramagnetic triplet configuration is probably too high, and that the metal is more likely to be Ni(II).³ Personal correspondence with Orpen, Koch and a few others⁴ suggested that this work required substantiation and that the substance in question is probably a Ni(II) species.

The nature of the metal remains a mystery today. Confusion with NiCl₂(dppfO₂) obtained in poor yield from NiCl₂· $6H_2O$ and $dppfO_2^2$ is suspected but could not be verified. We have since repeated this Ni(II) reaction but no crystals suitable for X-ray analysis could be obtained (see below). Repeated refinement of the crystal structure using the original experimental diffraction data but with the metal fitted as Ni (instead of Pd) indeed gave improved results in terms of significantly lower R factor (R =0.0388 (Ni) vs. 0.0713 (Pd) based on 4010 unique reflections), and more reasonable thermal motion of the metal ion compared to its four bonded atoms. The latter also leads to the absence of two Hirshfeld rigid-bond test alert for the M-O bonds in the CheckCIF/Platon⁵ report which in many cases are caused by mis-assigned atom types (ESI).6-9 However, structural refinement without other experimental or supporting characterisation data would not be sufficient as several 3d metals such as Co(II), Cu(II)

and Zn(II) could also give similar or even better R factors with reasonable bond data (ESI). In principle, dppfO₂ should complex with a range of 3d metals and give tetrahedral complexes such as $MX_2(dppfO_2)$ (X = halides or pseudohalides; M = Fe(II), Co(II), Ni(II), Cu(II), Zn(II), etc), but surprisingly very few of these are known in the literature.¹⁰⁻¹³ This adds to the mystery of the identity of 1 and precludes a comprehensive structural comparison with related complexes. Accepting that the nature of the metal in 1 is questionable and as there is no concrete data in our laboratory or the literature to pinpoint an alternative, we have re-investigated and expanded the coordination chemistry of dppfO2 with PdCl2 and $PdCl_2(MeCN)_2$ as well as a range of 3d metals from Cr(III) to Zn(II). Reported herein is a series of single-crystal X-ray crystallographic diffraction and supplementary characterisation analyses of the products. It also highlights some unexpected structural features thus unveiled.

Results and discussion

Stoichiometric reaction of $PdCl_2(MeCN)_2$ with $dppfO_2$ (1:1) in CH₂Cl₂ at r.t. for 8 h leads to a deep-red solution accompanied by a small amount of brown precipitate which was filtered off. Saturated slowly by Et₂O vapour, the solution gave rise to a deep red solid (A). Upon isolation, it (A) is stable in air and partly soluble in CH₂Cl₂, but quickly decomposes in DMF and DMSO to give free dppfO₂. Solid A was extracted into CH_2Cl_2 to give a suspension, which led to the isolation of **B** (from the filtrate), and brown residue C in a roughly 2:1 mass ratio. Subsequent elemental analysis and infrared analysis suggested that B and C are chemically indistinguishable. Comparison of the carbon and hydrogen content of **B** and **C** with those of **A** suggests that in the isolation process, A has transformed to **B** and **C** that have significantly lower carbon and hydrogen content. B and C may also be obtained in a similar mass ratio from the filtrate of the reaction mixture through direct precipitation upon addition of Et₂O followed by phase separation using CH₂Cl₂. Recrystallizations of both **B** and **C** in different solvents have insofar failed to yield any crystals suitable for X-ray crystallographic analysis.

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[†] Bond distances and angles for 2–12. Ortep diagrams of 3–5, 8, 10–12. Field dependence of the magnetization for **B** and **C** at 100 K and 193 K. ¹H V.T. NMR for the *in situ* mixture of $PdCl_2(MeCN)_2$ and $dppfO_2$ in CD_2Cl_2 . XRD spectra. CheckCIF/Platon report for **1** and the metal fitted as Co, Ni, Cu and Zn using the same diffraction data. CCDC reference numbers 823889–823899. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10920k

The powder X-ray diffraction (XRD) patterns shows that **B** is amorphous in nature. **C** exhibits some crystallinity but its diffraction pattern is inconsistent with that simulated from the crystallographic data set of 1 (ESI \dagger). Vibrating Sample Magnetometric (VSM) measurements of **B** and **C** at both 100 K and 193 K suggested that they are diamagnetic (ESI \dagger), thus ruling out tetrahedral Pd(II).

V.T. ³¹P{¹H} NMR analysis have been carried out on the *in situ* reaction mixture of PdCl₂(MeCN)₂ and dppfO₂ in CD₂Cl₂. The r.t. spectrum shows a broad peak at δ 34.0 and a minor resonance at δ 47.2 ppm (Fig. 1), which is in agreement with that reported.² The major peak (δ 34.0 ppm) gradually sharpens as the temperature is lowered to 233 K, but broadens at 193 K with the formation of a shoulder peak. The V.T. ¹H NMR spectra do not give any additional information (ESI[†]). These are indicative of a dynamic system of interchanging species with similar ligand environment but statistically varied dispositions.¹⁴⁻¹⁷



Fig. 1 V.T. ³¹P{¹H} NMR spectra (193 K to 298 K) of the *in situ* reaction mixture of $[PdCl_2(MeCN)_2]$ and $dppfO_2$ in CD_2Cl_2 .

Mixing of PdCl₂ and dppfO₂ (1:1) in CH₂Cl₂, CHCl₃, CH₂Cl₂/CHCl₃, MeOH/CH₂Cl₂, MeOH/CHCl₃ and many other solvent systems led to incomplete reactions. Attempts to isolate the products therein through Et₂O vapour diffusion invariably yielded single crystals of dppfO₂. Oxidation of [PdCl₂(dppf)]^{18,19} with excess t-BuOOH (5–6 M in decane) or H₂O₂ (30%) in CH₂Cl₂ for one day at r.t. also failed to give any product apart from nearquantitative recovery of [PdCl₂(dppf)].

Similar reactions of $PtCl_2(MeCN)_2$ or $PtCl_2$ with $dppfO_2$ under various solvent conditions were carried out for comparisons. There is no evidence of addition reaction between $PtCl_2(MeCN)_2$ and $dppfO_2$ in CH_2Cl_2 or $CHCl_3$ but formation of uncharacterisable white inorganic salt. There is no apparent reaction between $PtCl_2$ and $dppfO_2$ in CH_2Cl_2 and $CHCl_3$ upon mixing for 2 days.

These results suggest that the reported reaction leading to **1** is irreproducible and that the exact identity of the product remains elusive. Since the tetrahedral metal is suspected to be Ni, we proceeded to investigate similar preparations using Ni(II) substrates. Treatment of NiCl₂·6H₂O and dppfO₂ in CHCl₃/MeOH (2:1, v/v) followed by slow diffusion with Et₂O did not yield the anticipated tetrahedral complex NiCl₂(dppfO₂). Instead, it gave rise to a poor yield (*ca* 5%) of a mix-valent Ni complex salt [Ni^{IV}Cl₂(dppfO₂)₂][Ni^{II}Cl₄] (**2**) (Fig. 2a). The identity of the bulk of the product remains unknown whilst all optimisation experiments aiming to improve the yield of **2** have been futile. During the crystal



Fig. 2 Ortep diagrams of **2** (a), **6** (b), **7** (c) and **9** (d) with 50% thermal ellipsoids. All solvent molecules, hydrogen atoms and one disordered component of $[NiCl_4]^{2-}$ in **2** are omitted for clarity purpose. Symmetry code for **6**: A: 1 - x, *y*, 0.5 - z; **7**: A: 1 - x, *y*, 1.5 - z.

growing process, the solution turned from orange-red to deep red, possibly due to aerial oxidation. When the freshly prepared reaction mixture was treated with Et_2O and the orange crystalline precipitate was subjected to XRD analysis, it gives a diffraction pattern that partly resembles that simulated from the original Xray data set of 1 (ESI⁺). This suggests that if Ni is indeed the metal in 1, the tetrahedral complex is just one of the products in this deceptively simple addition reaction.

To examine the possibility that the metal in question could be other 3d metals, we have carried out additional experiments. Reactions of dppfO₂ with CrCl₃·6H₂O in 1:1 stoichiometric ratio gives [Cr(dppfO₂)₂Cl₂][CrCl₄]·MeOH (3) (22%), as revealed by Xray single-crystal diffraction. Similar reaction with FeCl₃·6H₂O gives $[Fe(dppfO_2)_2Cl_2][FeCl_4] \cdot 3CH_2Cl_2$ (4) (77%). Both 3 and 4 are isostructural to 2 except that their lattice solvent are different. Together with 2, formation of these products suggested that for metals that are amenable to tetrahedral and octahedral geometries, there is a tendency for halide migratory reaction leading to cationic octahedral dppfO₂ complexes with anionic tetrachlorometallates. The steric bulk of $dppfO_2$ possibly forces the two $dppfO_2$ chelates to be mutually *trans* on the same coordination plane thus fixing the chloride above and below the plane. Other reactions on the $Fe(ClO_4)_2/2Et_4NX/dppfO_2$ (X = Cl; I) mixtures failed to give the complex $FeX_2(dppfO_2)$. Instead, these preparations led to the isolation of oxidised octahedral [FeCl2(dppfO2)2][ClO4].0.5CH2Cl2 (5) (8%) and square pyramidal [FeI(dppfO₂)₂][I₃][Cl] \cdot Et₂O \cdot H₂O (6) (trace) (Fig. 2b). The absence of $FeX_2(dppfO_2)$ in these reactions is noteworthy, suggesting also that the metal in 1 is unlikely to be iron. The experimental conditions used favored facile aerial oxidation of Fe(II). Similar reaction of dppfO₂ with CuCl₂·2H₂O gives $[CuCl_2(dppfO_2)_2] \cdot 2CH_2Cl_2 \cdot 3H_2O$ (7), which is the only primary neutral and octahedral adduct isolated in this series (Fig. 2c).

Reactions of MnCl₂·4H₂O, CoCl₂·6H₂O, Co(BF₄)₂/2NaBr, CoI₂ and ZnCl₂·4H₂O with dppfO₂ successfully result in the 1:1 adduct of neutral tetrahedral complexes in [MnCl₂(dppfO₂)] (8), $[CoX_2(dppfO_2)]$ (X = Cl (9); Br (10); I (11)) (Fig. 2d) and $[ZnCl_2(dppfO_2)] \cdot 0.25H_2O(12)$ respectively, which are isostructural to 1. Their facile formation and ease of crystallisation is a sharp contrast to those of Ni(II) and Pd(II), adding further mystery to the nature of the metal in 1. Their space groups and M-X (X = Cl, Br, I) bond lengths are listed in Table 1. Only 10 and 11 crystallize in the same space group as "PdCl₂(dppfO₂)" (1). But they are unlikely to be the same materials as their respective Co-Br (av. 2.373 Å) and Co-I (av. 2.567 Å) lengths are significantly longer than those of 1 (av. 2.213 Å). A CSD search of the M-Cl bond distances for the tetrahedral MCl₂(R₃PO)₂ complexes gives Mn–Cl (2.29–2.34 Å), Fe-Cl (2.19-2.29 Å), Co-Cl (2.20-2.26 Å), Ni-Cl (2.20-2.22 Å), Cu-Cl (2.13-2.20 Å) and Zn-Cl (2.20-2.27 Å), suggesting that the M-Cl lengths in 1 are much closer to that of a 3d metal although its exact identity remains uncertain.

This study suggested that formation of the deceptively straightforward $MX_2(dppfO_2)$ is complicated by facile ligand (halide and dppfO₂) dissociation, migration and interchanges, and hence generating coordination salts $[MX_2(dppfO_2)_2][MX_4]$ as secondary

Table 1 A list of tetrahedral $MX_2(dppfO_2)$ complexes prepared in this study for comparison with "PdCl₂(dppfO₂)" (1)

Complex	Space Group	M-X(1) (Å)	M-X(2) (Å)
"PdCl ₂ (dppfO ₂)" (1)	Сс	2.204(3)	2,222(4)
$MnCl_2(dppfO_2)(8)$	$P2_1/c$	2.3341(9)	2.3052(11)
$CoCl_2(dppfO_2)(9)$	$P2_1/n$	2.2370(8)	2.2489(8)
$CoBr_2(dppfO_2)$ (10)	ĊĊ	2.3695(8)	2.3770(8)
$CoI_2(dppfO_2)(11)$	Сс	2.5624(8)	2.5722(8)
$ZnCl_2(dppfO_2)$ (12)	Pbca	2.2122(14)	2.2005(16)

or alternative products such as in Ni(II)Ni(IV) (2), Cr(III) (3) and Fe(III) (4). Other cationic complexes such as $[FeX_2(dppfO_2)_2]X'$ or $[FeX(dppfO_2)_2]X'X''$ (5 & 6) are accordingly formed. Those that give neutral adducts tend to be divalent metals with predominantly tetrahedral structures MX₂(dppfO₂), such as Mn (8), Co (9-11) and Zn (12), but octahedral $MX_2(dppfO_2)_2$ (Cu(II) in 7) is also possible. These adduct formation reactions are complicated by oxidation, as witnessed in the formation of Ni(IV) from Ni(II) (in 2) and Fe(III) from Fe(II) (in 5 & 6). The d⁸ complexes of interest NiCl₂(dppfO₂) and PdCl₂(dppfO₂) are unstable with respect to ligand exchanges (and oxidation, in Ni(II)) under the formation conditions and hence their exact identity remains elusive. Reproduction of the Pd(II) preparation yielded a diamagnetic product that could give exchange products which can be tentatively assigned as [Pd₂(µ-Cl)₂(dppfO₂)₂][PdCl₄] in solution. Although Mn(II), Co(II) and Zn(II) form MX₂(dppfO₂) easily, they are unlikely to be the metal in the questionable " $MCl_2(dppfO_2)$ " (1) based on the differences in the space groups and XRD patterns. Ni(II) remains the more likely option but further study is needed since $NiCl_2(dppfO_2)$ appears to be susceptible to oxidation and we are still unable to obtain suitable stable single-crystals for X-ray crystallographic analysis. Worthy of mention is that dppfO₂ can support octahedral complexes in a mutually trans bis-chelating fashion. It therefore poses an intriguing question on why the sq. planar [M(dppfO₂)₂] core remains elusive. Current activities in our laboratories are targeting at such structural motif apart from addressing the mysterious puzzle on tetrahedral Pd(II).

Experimental

General remarks

1,1'-Bis(diphenylphosphino)ferrocene dioxide (dppfO₂) was synthesized following the literature method.²⁰ All synthetic procedures were carried out at ambient conditions in air. Elemental analyses were performed on a Perkin–Elmer PE 2400 CHNS Elemental Analyzer. The ¹H and ³¹P NMR spectra were recorded on Bruker AMX 500-MHz spectrometer and their chemical shifts were referenced to Me₄Si (TMS). IR spectra were recorded on a Bruker IFS 48 FTIR spectrometer using KBr as pellets. MS-FAB spectra were obtained with a Finnigan MAT95XL mass spectrometer. Peaks were assigned from the m/z values and the isotope distribution patterns. Powder X-ray diffraction spectra were recorded on a Siemens D5005 X-ray diffractometer. Magnetic measurement was carried out on a Lakeshove 7400 vibrating sample magnetometer.

Reaction of PdCl₂(MeCN)₂ with dppfO₂. PdCl₂(MeCN)₂ (0.26 g, 1.0 mmol) was dissolved in CH₂Cl₂ (40 mL) and dppfO₂ (0.58 g, 1.0 mmol) added. The mixture was stirred at r.t. for 8 h. A small amount of brown powder formed which was filtered off. The deep red filtrate was slowly saturated using Et₂O vapor to yield a small amount of deep red solid (A). This solid was redissolved in CH₂Cl₂ and stirred for 24 h to yield the red solution and a brown powder (C). Solid C was separated from the mother liquor which was then concentrated and Et₂O added to precipitate the red solid **B**. Solid **B** and **C** may be prepared alternatively by dropwise addition of Et₂O to the original reaction mixture to precipitate a brown solid (0.57 g) which was then separated using CH₂Cl₂ similar to that describe for **A**. Yield: **B** (0.30 g), **C**

(0.15 g). Characterization data of A: ¹H NMR (500 MHz, CD₂Cl₂): δ 7.43–7.58 (m, 20H), 4.55 (s, 4H), 4.29 (s, 4H), 1.96 (s, 3H) ppm. ³¹P NMR (202 MHz, CDCl₃): 33.8 ppm. Anal. calcd. (%) for C₃₄H₂₈Cl₁₂FeO₂P₂Pd: C 53.47, H 3.70; found: C 47.53, H 3.28 corresponding to $[Pd_2(\mu-Cl)_2(dppfO_2)_2][PdCl_4]$. IR (KBr pellet): 3054 (w), 1971 (w), 1902 (w), 1821 (w), 1588 (w), 1483 (m), 1435 (s), 1388 (w), 1310 (w), 1253 (w), 1186 (s), 1121 (s), 1066 (w), 1033 (m), 997 (w), 931 (w), 912 (m), 832 (m), 752 (s), 727 (s), 692 (s), 629 (m), 569 (s), 529 (s), 492 (s) cm⁻¹. Characterization data of **B**: FAB-MS (-): 212.6 m/z, [PdCl₃]⁻. Anal. calcd. (%) for C₃₄H₂₈Cl₁₂FeO₂P₂Pd: C 53.47, H 3.70; found: C 45.57, H 3.40 corresponding to [Pd₂(µ-Cl)₂(dppfO₂)₂][PdCl₄][PdCl₂]_{0.5}. IR (KBr pellet): 3079 (w), 3055 (w), 1970 (w), 1899 (w), 1822 (w), 1618 (w), 1589 (m), 1483 (m), 1435 (s), 1388 (w), 1311 (m), 1252 (w), 1186 (s), 1121 (s), 1068 (w), 1032 (w), 997 (w), 930 (w), 911 (w), 832 (m), 752 (s), 727 (s), 693 (s), 629 (m), 569 (s), 530 (s), 494 (s), 448 (w) cm⁻¹. Characterization data of C: FAB-MS (-): 212.6 m/z, [PdCl₃]⁻. Anal. calcd. (%) for C₃₄H₂₈Cl₁₂FeO₂P₂Pd: C 53.47, H 3.70; found: C 45.39, H 3.37 corresponding to [Pd2(µ-Cl)2(dppfO2)2][PdCl4][PdCl2]0.5. IR (KBr pellet): 3108 (w), 3054 (w), 1987 (w), 1901 (w), 1822 (w), 1588 (m), 1484 (w), 1436 (s), 1389 (w), 1311 (m), 1251 (w), 1208 (m), 1186 (s), 1122 (s), 1069 (w), 1035 (m), 998 (w), 931 (m), 912 (m), 887 (w), 833 (m), 752 (m), 729 (s), 692 (s), 631 (m), 568 (s), 525 (s), 493 $(s), 447 (m) \text{ cm}^{-1}.$

Synthesis of $[Ni^{IV}Cl_2(dppfO_2)_2][Ni^{II}Cl_4]$ (2). $NiCl_2 \cdot 6H_2O$ (0.24 g, 1.0 mmol) and dppfO₂ (0.58 g, 1.0 mmol) were mixed in a CH₂Cl₂/MeOH solvent mixture (15 mL, 2:1 v/v). The solution was stirred at r.t. for 24 h and then filtered. Diffusion with an atmosphere of Et₂O vapor yielded a few red block crystals of 2 deposited on the outside surface of the inner glass tube and the surface of the host tube (see the figure below). The crystals were collected, washed with Et₂O and dried under vacuum. Yield 0.04 g, 5% based on dppfO₂. FAB-MS (+): 711.8 m/z [NiCl(dppfO₂)(CH₃OH)]⁺; 1298.1 m/z [NiCl(dppfO₂)₂(CH₃OH)]⁺. FAB-MS (-): 197.5 m/z $[NiCl_3(CH_3OH)]^-$. Anal. calcd. (%) for $C_{68}H_{56}Cl_6Fe_2Ni_2O_4P_4$: C 54.34, H 3.76; found: C 54.23, H 3.98. IR (KBr pellet): 2861 (w), 1632 (br, m), 1590 (w), 1484 (w), 1436 (s), 1388 (w), 1363 (w), 1311 (w), 1191 (s), 1153 (s), 1120 (s), 1099 (s), 1070 (w), 1032 (m), 997 (w), 830 (m), 751 (m), 726 (s), 701 (s), 636 (w), 570 (s), 529 (s), 497 (s), 447 (m) cm⁻¹.



Synthesis of [CrCl_2(dppfO_2)_2][CrCl_4]·MeOH (3). Compound **3** was prepared as brown-red block crystals similarly as **2** using $CrCl_3 \cdot 6H_2O$ (0.27 g, 1.0 mmol) and $dppfO_2$ (0.58 g, 1.0 mmol) as starting material and $CH_2Cl_2/MeOH$ (24 mL, 2 : 1 v/v) as solvent. Yield 0.17 g, 22%. FAB-MS (+): 1294.0 *m/z* [$CrCl_2(dppfO_2)_2$]⁺. Anal. calcd. (%) for $C_{69}H_{60}Cl_6Cr_2Fe_2O_5P_4$: C 54.47, H 3.97; found: C 54.46, H 3.82. IR (KBr pellet): 3096 (w), 3053 (w), 2022(w), 1915 (w), 1897 (w), 1617 (w), 1591 (w), 1485 (w), 1438 (s), 1389

(w), 1313 (m), 1192 (s), 1170 (s), 1122 (s), 1104 (m), 1037 (m), 998 (w), 856 (w), 829 (w), 749 (m), 728 (s), 706 (s), 691 (s), 641 (w), 571 (s), 528 (s), 501 (s), 485 (w), 408 (w) cm⁻¹.

Synthesis of [FeCl₂(dppfO₂)₂][FeCl₄]-3CH₂Cl₂ (4). Compound 4 was prepared as black platelet crystals similarly as 2 using FeCl₃·6H₂O (0.27 g, 1.0 mmol) and dppfO₂ (0.58 g, 1.0 mmol) as starting materials and CH₂Cl₂ (15 mL) as solvent. Yield 0.67 g, 77%. FAB-MS (+): 1300.0 m/z [FeCl₂(dppfO₂)₂]⁺. Anal. calcd. (%) for C₇₁H₆₂Cl₁₂Fe₄O₄P₄: C 48.67, H 3.57; found: C 53.83, H 3.72 corresponding to [FeCl₂(dppf)₂)[FeCl₄]. IR (KBr pellet): 3145 (w), 3101 (w), 3056 (w), 1589 (w), 1484 (w), 1436 (s), 1389 (w), 1361 (w), 1310 (w), 1191 (s), 1151 (s), 1120 (s), 1098 (s), 1032 (m), 997 (w), 845 (w), 829 (m), 751 (s), 726 (s), 702 (s), 636 (w), 618 (w), 570 (s), 528 (s), 498 (s), 449 (w) cm⁻¹.

Synthesis of [FeCl₂(dppfO₂)₂][ClO₄]-0.5CH₂Cl₂ (5). Compound **5** was prepared as black block crystals using the method as described for **2** using Fe(ClO₄)₂·*x*H₂O (0.26 g, 1.0 mmol), dppfO₂ (0.58 g, 1.0 mmol) and Et₄NCl (0.33 g, 2.0 mmol) as starting materials and CH₂Cl₂ (20 mL) as solvent. Yield 0.057 g, 8%. FAB-MS (+): 1300.0 *m*/*z* [FeCl₂(dppfO₂)₂]⁺. Anal. calcd. (%) for C_{68.5}H₅₇Cl₄Fe₃O₈P₄: C 57.08, H 3.99; found: C 57.17, H 3.62. IR (KBr pellet): 3101 (w), 3055 (w), 1628 (w), 1589 (m), 1484 (m), 1437 (s), 1389 (m), 1362 (w), 1312 (m), 1190 (s), 1147 (br, s), 1094 (br, s), 1032 (s), 998 (m), 929 (w), 900 (w), 880 (w), 841 (m), 827 (m), 754 (s), 727 (s), 704 (s), 636 (m), 622 (m), 570 (s), 529 (s), 498 (s), 448 (w) cm⁻¹.

Synthesis of [FeI(dppfO₂)₂]**I**₃]**[Cl]·Et**₂**O·H**₂**O** (6). Compound **6** was prepared as black block crystals using the method as described for **2** using Fe(ClO₄)₂·*x*H₂O (0.25 g, 1.0 mmol) and dppfO₂ (0.58 g, 1.0 mmol) and Et₄NI (0.51 g, 2.0 mmol) as starting materials and CH₂Cl₂ (20 mL) as solvent. Yield: trace amount. FAB-MS (+): 676.8 *m*/*z* [FeI(dppfO₂)₂]²⁺. Anal. calcd. (%) for C₇₂H₆₈ClFe₃I₄O₆P₄: C 46.40, H 3.68; found: C 45.96, H 3.26. IR (KBr pellet): 3083 (w), 3052 (w), 2970 (w), 2865 (w), 2477 (w), 1588 (m), 1574 (w), 1483 (m), 1435 (s), 1388 (w), 1366 (w), 1311 (w), 1224 (m), 1188 (s), 1151 (s), 1120 (s), 1098 (s), 1071 (m), 1036 (s), 997 (m), 924 (w), 902 (w), 874 (w), 843 (m), 823 (m), 749 (s), 726 (s), 700 (s), 638 (m), 568 (s), 529 (s), 496 (s), 444 (m) cm⁻¹.

Synthesis of [CuCl₂(dppfO₂)₂]-2CH₂Cl₂·3H₂O (7). Compound 7 was prepared as orange block crystals using the method as described for **2** using CuCl₂·2H₂O (0.17 g, 1.0 mmol) and dppfO₂ (0.58 g, 1.0 mmol) as substrates in a mixture of CH₂Cl₂/MeOH (16 mL, 1:1 v/v) solvent. Yield 0.13 g, 17%. Anal. calcd. (%) for C₇₀H₆₆Cl₆CuFe₂O₇P₄: C 54.91, H 4.34; found: C 50.41, H 3.46 corresponding to [CuCl₂(dppfO₂)₂]·3CH₂Cl₂·H₂O. IR (KBr pellet): 3098 (w), 3054 (w), 2986 (w), 1589 (w), 1484 (w), 1437 (s), 1388 (w), 1362 (w), 1312 (w), 1190 (s), 1147 (s), 1121 (s), 1095 (s), 1072 (w), 1032 (m), 997 (w), 899 (w), 851 (w), 821 (m), 753 (s), 726 (s), 702 (s), 695 (s), 640 (w), 619 (w), 569 (s), 530 (s), 498 (s), 484 (m), 449 (m) cm⁻¹.

Synthesis of $[MnCl_2(dppfO_2)_2]$ (8). Compound 8 was prepared as orange block crystals using the method as described for 2 using $MnCl_2 \cdot 4H_2O$ (0.20 g, 1.0 mmol) and $dppfO_2$ (0.58 g, 1.0 mmol) as starting material and $CH_2Cl_2/MeOH$ (24 mL, 1 : 1 v/v) as solvent. Yield 0.11 g, 15%. FAB-MS (+): 675.8 *m*/*z* [MnCl(dppfO_2)]⁺. Anal. calcd. (%) for $C_{34}H_{28}Cl_2FeMnO_2P_2$: C 57.34, H 3.96; found: Published on 21 September 2011. Downloaded by University of California - Santa Cruz on 31/10/2014 05:55:18.

	2	3	4	5	6	7	8	6	10	11	12
Formula	C ₆₈ H ₅₆ Cl ₆ Fe ₂ -	C69H60Cl6Cr2-	$C_{71}H_{62}Cl_{12}Fe_4$ -	C _{68.50} H ₅₇ Cl ₄ Fe ₃ -	C ₂₂ H ₆₆ ClFe ₃ I ₄ -	$C_{71}H_{57}Cl_6Cu$ -	C ₃₄ H ₂₈ Cl ₂ Fe-	C ₃₄ H ₂₈ Cl ₂ Co-	$C_{34}H_{28}Br_2Co$ -	C ₃₄ H ₂₈ CoFeI ₂ -	C ₃₄ H _{28.5} Cl ₂ Fe-
	$Ni_2O_4P_4$	$\mathrm{Fe}_{2}\mathrm{O}_{5}\mathrm{P}_{4}$	O_4P_4	O_8P_4	O_6P_4	$\mathrm{Fe}_2\mathrm{O_7P_4}$	MnO_2P_2	FeO_2P_2	FeO_2P_2	$\mathbf{O}_2\mathbf{P}_2$	$O_{225}P_2Zn$
fw	1502.83	1521.45	1751.89	1441.37	1861.73	1533.99	712.19	716.18	805.10	899.08	727.13
cryst. sys.	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$P\overline{1}$	$P\bar{l}$	C2/c	C2/c	$P2_1/c$	$P2_1/n$	C_{C}	C_c	Pbca
a/Å	10.5328(4)	11.1220(4)	13.7506(5)	18.3426(11)	30.6672(16)	18.9691(9)	10.066(4)	11.6658(6)	10.1369(6)	10.3600(7)	11.3093(4)
$b/\text{\AA}$	33.6751(15)	15.5622(5)	18.2129(10)	19.6446(12)	14.5893(7)	13.3154(6)	16.609(7)	14.1127(7)	19.6944(12)	20.4629(13)	18.4373(7)
$c/\text{\AA}$	18.5393(7)	39.1918(13)	32.9846(18)	20.0689(12)	18.7987(9)	27.6655(13)	18.436(8)	19.1893(9)	16.1275(10)	16.0513(10)	31.0211(10)
α (°)	90.00	90.00	74.7150(10)	74.9240(10)	90.00	90.00	90.00	90.00	90.00	90.00	90.00
β (°)	97.6450(10)	92.4650(10)	84.3700(10)	87.5210(10)	121.3280(10)	92.9990(10)	96.426(9)	92.5930(10)	91.4830(10)	92.800(2)	90.00
$\chi^{(0)}$	90.00	90.00	78.4280(10)	65.0060(10)	90.00	90.00	90.00	90.00	90.00	90.00	90.00
$V/Å^3$	6517.3(5)	6777.1(4)	7560.4(7)	(6310.3(7))	7184.5(6)	6978.2(6)	3063(2)	3156.0(3)	3218.6(3)	3398.7(4)	6468.3(4)
T/K	223(2)	223(2)	223(2)	223(2)	223(2)	223(2)	100(2)	223(2)	223(2)	223(2)	223(2)
Z	4	4	4	4	4	4	4	4	4	4	8
$D_{ m c}/{ m g~cm^{-3}}$	1.532	1.491	1.539	1.517	1.721	1.460	1.545	1.507	1.661	1.757	1.493
μ/mm^{-1}	1.398	1.112	1.308	1.008	2.493	1.086	1.196	1.286	3.578	2.854	1.485
F_{000}	3064	3104	3552	2952	3652	3128	1452	1460	1604	1748	2964
collected refins	45546	47443	99083	81628	20457	19719	21442	21869	11144	11844	43884
uniq. refins	14762	15537	34647	28928	6314	6144	7015	7227	6649	6255	7423
$R_{ m int}$	0.0887	0.0526	0.0659	0.0564	0.0335	0.0377	0.0423	0.0386	0.0351	0.0342	0.1108
Parameters	794	815	1799	1576	418	407	379	379	425	425	394
$R^a(I > 2\sigma(I))$	0.0827	0.0637	0.0824	0.0702	0.0712	0.1046	0.0408	0.0434	0.0442	0.0427	0.0699
wRb	0.1810	0.1496	0.1997	0.1615	0.2056	0.2893	0.1004	0.1004	0.1031	0.1047	0.1472
GOF^c	1.048	1.057	1.091	1.073	1.045	1.143	1.042	1.042	1.050	1.041	1.051
$\Delta ho_{\max} / \Delta ho_{\min} / \sigma_{\Delta}$	0.928/-1.095	1.399/-0.770	1.535/-1.048	1.138/-1.075	4.176/-2.682	1.735/-2.642	0.571/-0.304	0.779/-0.351	0.809/-0.645	1.374/-0.568	2.550/-0.683

C 57.75, H 4.08. IR (KBr pellet): 3097 (w), 3054 (w), 1633 (w), 1589 (w), 1483 (w), 1436 (s), 1389 (m), 1363 (w), 1311 (m), 1198 (br, s), 1119 (s), 1101 (s), 1071 (m), 1037 (s), 997 (m), 845 (s), 829 (m), 753 (s), 726 (s), 700 (s), 635 (m), 570 (s), 535 (s), 497 (s), 448 (m) cm⁻¹.

Synthesis of [CoCl₂(dppfO₂)] (9). Compound **9** was prepared as green platelet crystals using the method as described for **2** using CoCl₂·6H₂O (0.24 g, 1.0 mmol) and dppfO₂ (0.58 g, 1.0 mmol) as starting materials and CH₂Cl₂ (20 mL) as solvent. Yield 0.52 g, 73%. FAB-MS (+): 679.8.9 *m*/*z* [CoCl(dppfO₂)]⁺. Anal. calcd. (%) for C₃₄H₂₈Cl₂CoFeO₂P₂: C 57.02, H 3.94; found: C 56.94, H 3.99. IR (KBr pellet): 3092 (w), 3055 (w), 1589 (w), 1483 (w), 1437 (s), 1389 (w), 1368 (w), 1312 (w), 1203 (s), 1159 (s), 1119 (s), 1100 (m), 1072 (w), 1038 (m), 997 (m), 828 (m), 755 (m), 725 (s), 700 (s), 630 (m), 568 (s), 536 (m), 528 (m), 497 (s), 447 (m) cm⁻¹.

Synthesis of [CoBr₂(dppfO₂)] (10). Compound **10** was prepared as green platelet crystals using the method as described for **2** using Co(BF₄)₂·*x*H₂O (0.32 g, 1.0 mmol), dppfO₂ (0.58 g, 1.0 mmol) and NaBr (0.21 g, 2.0 mmol) as starting materials and CH₂Cl₂ (20 mL) as solvent. Yield 0.72 g, 90%. FAB-MS (+): 723.8 m/z [CoBr(dppfO₂)]⁺. Anal. calcd. (%) for C₃₄H₂₈Br₂CoFeO₂P₂: C 50.72, H 3.51; found: C 50.68, H 3.53. IR (KBr pellet): 3089 (w), 3053 (w), 1590 (w), 1483 (w), 1437 (s), 1389 (w), 1363 (w), 1311 (w), 1193 (s), 1161 (m), 1142 (s), 1121 (s), 1096 (m), 1069 (w), 1036 (s), 996 (w), 835 (m), 753 (m), 728 (s), 704 (s), 693 (s), 635 (m), 572 (s), 531 (s), 493 (s), 449 (m) cm⁻¹.

Synthesis of [Col₂(dppfO₂)] (11). Compound **11** was prepared as green platelet crystals using the method as described for **2** using Col₂ (0.31 g, 1.0 mmol), dppfO₂ (0.58 g, 1.0 mmol) as starting materials and CH₂Cl₂ (20 mL) as solvent. Yield 0.55 g, 61%. FAB-MS (+): 771.8 m/z [CoI(dppfO₂)]⁺. Anal. calcd. (%) for C₃₄H₂₈CoFeI₂O₂P₂: C 45.42, H 3.14; found: C 45.14, H 3.22. IR (KBr pellet): 3088 (w), 3052 (w), 1590 (w), 1483 (w), 1436 (s), 1389 (w), 1363 (w), 1310 (w), 1191 (s), 1161 (s), 1139 (s), 1121 (s), 1093 (m), 1068 (w), 1036 (m), 997 (w), 835 (m), 751 (m), 728 (s), 704 (s), 692 (s), 635 (w), 617 (w), 571 (s), 531 (s), 493 (s), 448 (m) cm⁻¹.

Synthesis of [ZnCl₂(dppfO₂)]-0.25H₂O (12). Compound 12 was prepared as light orange block crystals using the method as described for **2** by reacting ZnCl₂·4H₂O (0.21 g, 1.0 mmol) and dppfO₂ (0.58 g, 1.0 mmol) in a mixture of CH₂Cl₂/MeOH (15 mL, 2:1 v/v) solvent. Yield 0.39 g, 54%. ¹H NMR (400 MHz, CD₂Cl₂): δ 7.28–7.80 (m, 20H), 4.84 (s, 4H), 4.27 (s, 4H) ppm. ³¹P NMR (162 MHz, CDCl₃): 48.4 ppm. FAB-MS (+): 684.9 *m*/*z* [ZnCl(dppfO₂)]⁺. Anal. calcd. (%) for C₃₄H_{28.5}Cl₂FeO_{2.25}P₂Zn: C 56.16, H 3.95; found: C 56.21, H 3.81 corresponding to ZnCl₂(dppfO₂). IR (KBr pellet): 3099 (w), 3055 (w), 1624 (w), 1589 (w), 1484 (m), 1436 (s), 1390 (w), 1361 (w), 1311 (w), 1205 (s), 1166 (s), 1153 (s), 1121 (s), 1100 (m), 1072 (w), 1037 (s), 997 (w), 875 (w), 841 (m), 825 (w), 753 (s), 726 (s), 700 (s), 695 (s), 631 (w), 568 (s), 537 (s), 526 (m), 497 (s), 447 (w), 431 (w) cm⁻¹.

X-ray Crystallography

Crystallographic measurements were made on a Bruker AXS APEX diffractometer by using graphite-monochromated Mo-K α ($\lambda = 0.71073$ Å). The data were corrected for Lorentz and polarization effects with the SMART suite of programs and for absorption effects with SADABS.²¹ All crystal structures were solved by direct methods and refined on F^2 by full-matrix leastsquares techniques with SHELXTL-97 program.²² A summary of the key crystallographic data for **2–12** are listed in Table 2.

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