

Copper(I) complexes containing 1,1'-bis(diphenylphosphino)ferrocene (dppf) as a chelate ligand. X-ray crystal structures of $[\text{Cu}_2(\mu\text{-Cl})_2(\kappa^2\text{-}P,P\text{-dppf})_2]$ and $[\text{Cu}(\text{CN}^t\text{Bu})_2(\kappa^2\text{-}P,P\text{-dppf})][\text{BF}_4]$

Josefina Díez ^a, M. Pilar Gamasa ^a, José Gimeno ^{a,*}, Maurizio Lanfranchi ^b, Antonio Tiripicchio ^{b,*}

^a *Departamento de Química Orgánica e Inorgánica, Facultad de Química, Instituto de Química Organometálica 'Enrique Moles' (Unidad Asociada al CSIC), Universidad de Oviedo, 33071 Oviedo, Spain*

^b *Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma, Centro di Studio per la Strutturistica Diffattometrica del CNR, Parco Area delle Scienze 17A, 43100 Parma, Italy*

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Abstract

Copper(I) complexes $[\text{Cu}(\text{CNR})_2(\kappa^2\text{-}P,P\text{-dppf})][\text{BF}_4]$ (R = ^tBu (**1**), 2,6-Me₂C₆H₃ (**2**), Cy (**3**), Bz (**4**)) containing the chelating dppf ligand (dppf = 1,1'-bis(diphenylphosphino)ferrocene) have been prepared by reaction of the complex $[\text{Cu}_2(\mu\text{-Cl})_2(\kappa^2\text{-}P,P\text{-dppf})_2]$ with the corresponding isocyanide C≡NR (molar ratio 1:1). Alternatively, complexes **1–4** can also be obtained by the reaction of the acetonitrile complexes $[\text{Cu}(\text{MeCN})_2(\kappa^2\text{-}P,P\text{-dppf})][\text{BF}_4]$ with 2.5 equivalents of C≡NR in refluxing dichloromethane. The crystal structures of $[\text{Cu}_2(\mu\text{-Cl})_2(\kappa^2\text{-}P,P\text{-dppf})_2]$ and $[\text{Cu}(\text{CN}^t\text{Bu})_2(\kappa^2\text{-}P,P\text{-dppf})][\text{BF}_4]$, determined by X-ray diffraction, are also reported. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Copper(I) complexes; dppf; Isocyanide complexes

1. Introduction

It is well known that the bidentate ligand 1,1'-bis(diphenylphosphino)ferrocene (dppf) shows a versatile coordination mode adapting its steric bite angle to the geometric requirement of the metal through appropriate ring twisting or tilting [1,2]. Although dppf usually shows a chelating ability, its bridging behavior in homo- and heteronuclear complexes is also well documented [3].

We have recently reported the synthesis of a series of trinuclear copper(I) complexes of the type $[\text{Cu}_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CR})_n(\mu\text{-dppm})_3][\text{BF}_4]_{3-n}$ (**A**) ($n = 1, 2$) [4,5] and $[\text{Cu}_3(\mu_3\text{-}\eta^1\text{-C}\equiv\text{CR})(\mu\text{-CNR})(\mu\text{-dppm})_3][\text{BF}_4]_2$ (**B**) [6]. Moreover, we have shown that dppf can also act as a bridging ligand giving rise to the formation of binuclear copper(I) complexes of the type $[\text{Cu}_2(\mu_2\text{-}\eta^1\text{-C}\equiv\text{CR})_2(\mu\text{-}$

$\text{dppf})_2]$ (**C**) (R = C₆H₄CH₃-4, Ph, CH₂OCH₃, CH₂CH₂-CH₃, ($\eta^5\text{-C}_5\text{H}_4$)Fe($\eta^5\text{-C}_5\text{H}_5$)) [7]. Given that these complexes have been obtained from the reaction of the chelate dppf complex $[\text{Cu}_2(\mu\text{-Cl})_2(\kappa^2\text{-}P,P\text{-dppf})_2]$ (**D**) with LiC≡CR, the capability of dppf to act as a bridging ligand forming the $[\text{Cu}_2(\mu\text{-dppf})_2]$ framework can also be observed (Chart 1).

Following our interest in preparing novel polynuclear copper(I) complexes of type **C** we have tried to synthesize novel $\mu\text{-CNR}$ derivatives containing the $[\text{Cu}_2(\mu\text{-dppf})_2]$ framework starting from the precursor complex $[\text{Cu}_2(\mu\text{-Cl})_2(\kappa^2\text{-}P,P\text{-dppf})_2]$ (**D**).

The reactions of **D** with C≡NR, in the presence of a chloride abstractor, however, led to mononuclear cationic copper(I) complexes $[\text{Cu}(\text{CNR})_2(\kappa^2\text{-}P,P\text{-dppf})][\text{BF}_4]$ (R = ^tBu (**1**), 2,6-Me₂C₆H₃ (**2**), Cy (**3**), Bz (**4**)) in which dppf behaves as a chelating ligand. Here we report the synthesis and characterization of these complexes along with the X-ray crystal structures of complex **1** and of its precursor derivative $[\text{Cu}_2(\mu\text{-Cl})_2(\kappa^2\text{-}P,P\text{-dppf})_2]$ (**D**).

* Corresponding authors. Tel.: +34-985-103-461; fax: +34-985-103-446 (J.G.).

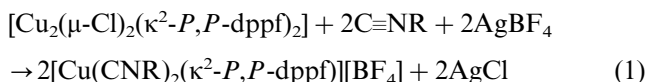
E-mail addresses: jgh@sauron.quimica.uniovi.es (J. Gimeno), tiri@uniipr.it (A. Tiripicchio).

2. Results and discussion

2.1. Synthesis and characterization of

$[\text{Cu}(\text{CNR})_2(\kappa^2\text{-P,P-dppf})][\text{BF}_4]$ ($\text{R} = \text{}^t\text{Bu}$ (**1**),
2,6- $\text{Me}_2\text{C}_6\text{H}_3$ (**2**), Cy (**3**), Bz (**4**))

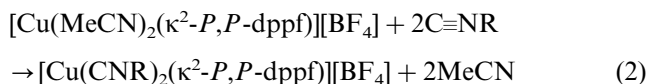
The reactions of $[\text{Cu}_2(\mu\text{-Cl})_2(\kappa^2\text{-P,P-dppf})_2]$ (**D**) with the corresponding isocyanide $\text{C}\equiv\text{NR}$ (molar ratio 1:1) in CH_2Cl_2 and in the presence of AgBF_4 at room temperature, lead to the formation of complexes **1–4** which are isolated from the reaction mixture as yellow insoluble tetrafluoroborate salts in good yields (Eq. (1))



where

$\text{R} = \text{}^t\text{Bu}$ (**1**), 2,6- $\text{Me}_2\text{C}_6\text{H}_3$ (**2**), Cy (**3**), or Bz (**4**).

Alternatively, complexes **1–4** can also be obtained by the reaction of the acetonitrile complexes $[\text{Cu}(\text{MeCN})_2(\kappa^2\text{-P,P-dppf})][\text{BF}_4]$ with 2.5 equivalents of $\text{C}\equiv\text{NR}$ in refluxing dichloromethane. (Eq. (2))



All the complexes are air stable in the solid state and soluble in chlorinated solvents. They have been characterized by elemental analyses, conductance measurements and IR and NMR (^1H and $^{31}\text{P}\{^1\text{H}\}$) spectroscopies. Selected spectroscopic data are given in

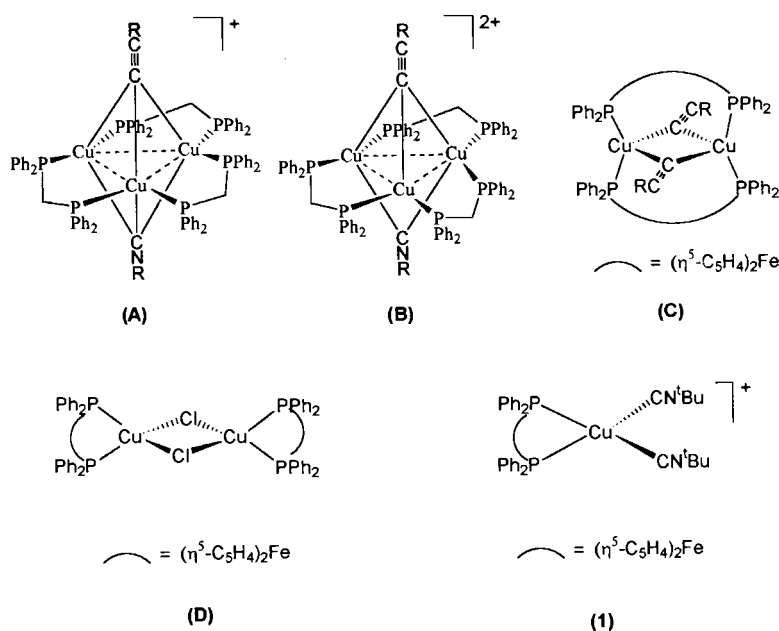


Chart 1.

Table 1
IR, $^{31}\text{P}\{^1\text{H}\}$, and ^1H -NMR data for complexes **1–4**

Complexes	IR ($\nu(\text{NC})$ or $\nu(\text{BF})$)	NMR	
		$^{31}\text{P}\{^1\text{H}\}$	^1H
$[\text{Cu}(\text{CN}^t\text{Bu})_2(\kappa^2\text{-P,P-dppf})][\text{BF}_4]$ (1)	2175 w, 1086 br	-5.17	1.3 (s, 18H, $(\text{Me}_3)\text{C}$), 4.12 (s, 4H, C_5H_4), 4.43 (s, 4H, C_5H_4), 7.3–7.6 (m, 20H, Ph)
$[\text{Cu}(\text{CN}2,6\text{-Me}_2\text{C}_6\text{H}_3)_2(\kappa^2\text{-P,P-dppf})][\text{BF}_4]$ (2)	2153 w, 1065 br	-3.6	2.1 (s, 12H, Me), 4.15 (s, 4H, C_5H_4), 4.4 (s, 4H, C_5H_4), 7–7.7 (m, 23H, Ph)
$[\text{Cu}(\text{CNCy})_2(\kappa^2\text{-P,P-dppf})][\text{BF}_4]$ (3)	2178 w, 1052 br	-5.02	1.25–2.1 (m, 22H, C_6H_{11}), 4.1 (s, 4H, C_5H_4), 4.45 (s, 4H, C_5H_4), 7.1–7.7 (m, 20H, Ph)
$[\text{Cu}(\text{CNBz})_2(\kappa^2\text{-P,P-dppf})][\text{BF}_4]$ (4)	2198 w, 1053 br	-5.25	4.1 (s, 4H, PhCH_2), 4.4 (s, 4H, C_5H_4), 4.8 (s, 4H, C_5H_4), 7–7.5 (m, 24H, Ph)

Spectra recorded in CDCl_3 ; δ in ppm.

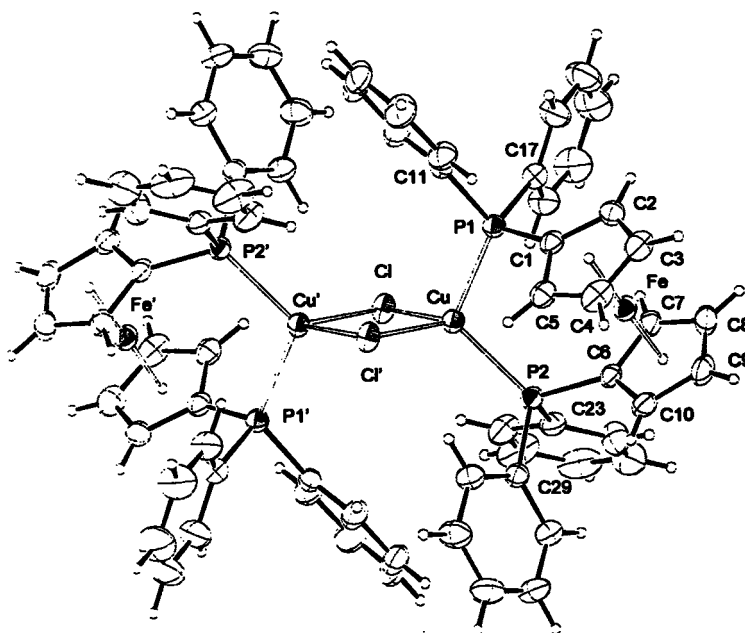


Fig. 1. View of the dimeric centrosymmetrical complex **D** with the atomic numbering system. The ellipsoids are drawn at 30% probability level.

Table 1. Elemental analyses are consistent with the proposed formulations and the conductivity data (in Me_2CO) show that complexes **1–4** are 1:1 electrolytes. The IR spectra (KBr) exhibit the expected absorptions for the BF_4^- anion as well as those characteristic for the dppf and the rest of the ligands. In particular, the presence of the coordinated terminal CNR ligands is evidenced by the appearance of one weak $\nu(\text{CN})$ absorption band in the range of $2153\text{--}2198\text{ cm}^{-1}$. IR spectra of other copper(I) complexes with terminal isocyanide ligands show comparable $\nu(\text{CN})$ absorptions [6].

^1H NMR spectra of complexes **1–4** at room temperature show the expected signals due to aromatic and cyclopentadienyl protons, along with those assigned to the isocyanide ligands. The resonance of the $\eta^5\text{-C}_5\text{H}_4$ protons appears as two unresolved multiplets of the A_2B_2 spin system at δ ca. 4.1–4.8 in accord with the proposed formulations. $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra of complexes **1–4** (Table 1) at room temperature show a single resonance at δ ca. -5 indicating that all phosphorus atoms in each complex are chemically equivalent. These chemical shifts are in the range of those found in copper(I) complexes containing chelating dppf ligands [7,8]. In order to confirm these features the structure of complex **1** as well as that of the precursor complex $[\text{Cu}_2(\mu\text{-Cl})_2(\kappa^2\text{-P,P-dppf})_2]$ (**D**) have been determined by an X-ray diffraction study (see below).

In summary, although the bridging coordination mode of dppf is well documented, only few examples have been previously described for copper(I) complexes and its coordination behavior is strongly dependent on the accompanying ligands. In this work it is shown the

coordinate preference of dppf to act as a chelating ligand in the presence of isocyanides. The reactions performed to obtain bridging isocyanide–dppf copper(I) complexes, analogous to **C**, afforded only the chelate dppf complexes **1–4**.

2.2. Description of the structures of $[\text{Cu}(\text{CN}^t\text{Bu})_2(\kappa^2\text{-P,P-dppf})][\text{BF}_4]\cdot\text{CH}_2\text{Cl}_2$ (**1** $\cdot\text{CH}_2\text{Cl}_2$), and of its precursor derivative $[\text{Cu}_2(\mu\text{-Cl})_2(\kappa^2\text{-P,P-dppf})_2]\cdot\text{CH}_2\text{Cl}_2$ (**D** $\cdot\text{CH}_2\text{Cl}_2$)

A view of the molecular structure of **D** is shown in Fig. 1 together with the atomic numbering system. Selected bond distances and angles are given in Table 2.

In the crystals of **D** $\cdot\text{CH}_2\text{Cl}_2$ molecules of solvation are also present. The complex consists of centrosymmetrical dimeric units with the two chlorine atoms bridging the two copper atoms. The tetrahedral coordination of the copper atoms is achieved by two P atoms of the chelating dppf ligand [Cu–P bond lengths = 2.275(1) and 2.270(1) Å]. The P1–Cu–P2 bite angle, $111.26(4)^\circ$, of the chelating dppf is very close to the expected value for this coordination. The other coordination bond angles are rather distorted [(P2–Cu–Cl = $115.95(4)$, P2–Cu–Cl' = $118.74(4)$, P1–Cu–Cl = $113.52(4)$, P1–Cu–Cl' = $99.65(4)$, Cl–Cu–Cl' = $96.00(3)^\circ$], because of the four-membered Cu_2Cl_2 ring and of the steric hindrance of the dppf ligand. The two Cu–Cl bond lengths are asymmetrical, 2.358(1) and 2.434(1) Å. The two substituted Cp rings in the dppf ligand adopt the usual staggered conformation, which determines the conformational chirality of the Cp_2Fe fragment. The structure of **D** is strictly comparable to

that of the iodine derivative $[\text{Cu}_2(\mu\text{-I})_2(\kappa^2\text{-}P,P\text{-dppf})_2]$ [9].

A view of the molecular structure of **1** is shown in Fig. 2 together with the atomic numbering system. Selected bond distances and angles are given in Table 3.

In the crystals of **1** cationic $[\text{Cu}(\text{CN}'\text{Bu})_2(\kappa^2\text{-}P,P\text{-dppf})]$ complexes, BF_4^- anions and CH_2Cl_2 molecules

Table 2
Selected bond lengths (Å) and bond angles (°) for **D**- CH_2Cl_2

Bond lengths			
Cu–P(1)	2.275(1)	Cu–P(2)	2.270(1)
Cu–Cl	2.358(1)	Cu–Cl'	2.434(1)
Fe–C(1)	2.036(3)	Fe–C(6)	2.045(3)
Fe–C(2)	2.048(4)	Fe–C(7)	2.032(4)
Fe–C(3)	2.058(4)	Fe–C(8)	2.043(4)
Fe–C(4)	2.055(4)	Fe–C(9)	2.048(4)
Fe–C(5)	2.028(4)	Fe–C(10)	2.047(4)
P(1)–C(1)	1.799(4)	P(2)–C(6)	1.819(4)
P(1)–C(11)	1.829(4)	P(2)–C(23)	1.829(4)
P(1)–C(17)	1.825(4)	P(2)–C(29)	1.834(4)

Bond angles			
P(2)–Cu–P(1)	111.26(4)	P(2)–Cu–Cl'	118.74(4)
P(2)–Cu–Cl	115.95(4)	P(1)–Cu–Cl'	99.65(4)
P(1)–Cu–Cl	113.52(4)	Cl–Cu–Cl'	96.00(3)
C(1)–Fe–C(9)	176.0(2)	C(4)–Fe–C(7)	177.8(2)
C(2)–Fe–C(10)	175.4(2)	C(5)–Fe–C(8)	177.5(2)
C(3)–Fe–C(6)	176.5(2)		

Symmetry transformations used to generate equivalent atoms: $-x+1/2$, $-y+1/2$, $-z+1$.

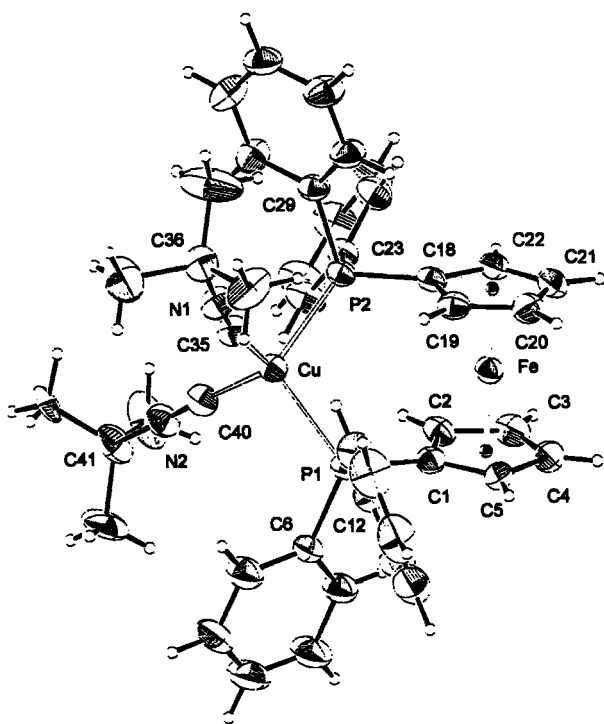


Fig. 2. View of the cationic complex of **1** with the atomic numbering system. The ellipsoids are drawn at 30% probability level.

Table 3
Selected bond lengths (Å) and bond angles (°) for **1**- CH_2Cl_2

Bond lengths			
Cu–P(1)	2.309(2)	Cu–P(2)	2.328(2)
Cu–C(35)	1.957(5)	Cu–C(40)	1.956(6)
Fe–C(1)	2.023(5)	Fe–C(18)	2.031(5)
Fe–C(2)	2.009(5)	Fe–C(19)	2.028(5)
Fe–C(3)	2.054(5)	Fe–C(20)	2.053(6)
Fe–C(4)	2.047(6)	Fe–C(21)	2.050(5)
Fe–C(5)	2.045(5)	Fe–C(22)	2.027(5)
P(1)–C(1)	1.817(5)	P(2)–C(18)	1.786(5)
P(1)–C(6)	1.822(5)	P(2)–C(23)	1.832(5)
P(1)–C(12)	1.837(5)	P(2)–C(29)	1.826(5)
N(1)–C(35)	1.134(6)	N(2)–C(40)	1.135(7)
N(1)–C(36)	1.482(6)	N(2)–C(41)	1.462(8)

Bond angles			
P(1)–Cu–P(2)	108.96(5)	C(40)–Cu–C(35)	114.3(2)
C(35)–Cu–P(1)	114.0(2)	C(35)–Cu–P(2)	102.2(2)
C(40)–Cu–P(1)	103.8(2)	C(40)–Cu–P(2)	113.8(2)
C(1)–Fe–C(21)	173.1(2)	C(4)–Fe–C(18)	170.6(3)
C(2)–Fe–C(20)	172.9(2)	C(5)–Fe–C(22)	171.7(2)
C(3)–Fe–C(19)	171.9(3)		

of solvation are present. The cation adopts a pseudo C_2 symmetry, with the two-fold axis passing through the metal atoms. The tetrahedral coordination around Cu involves two C atoms from $\text{CN}'\text{Bu}$ ligands [Cu–C bonds = 1.956(6) and 1.957(5) Å] and two P atoms from the chelating dppf. The Cu–P bond lengths, 2.309(2) and 2.328(2) Å, are significantly longer than those found in **D**. The P1–Cu–P2 bite angle, 108.96(5)°, of the chelating dppf is very similar to that found in **D**. The values of other angles involved in the tetrahedral coordination are in the range 102.2(2)–114.3(2)°. As in **D** the Cp_2Fe fragment shows a conformational chirality in the crystals, however, both enantiomers are present.

3. Experimental

The reactions were carried out under dry N_2 using Schlenk techniques. All solvents were dried by standard methods and distilled under N_2 before use. IR spectra were recorded (4000–400 cm^{-1}) on a Perkin–Elmer 1720-X FT spectrometer using KBr pellets. The C, N and H analyses were carried out with a Perkin–Elmer 240-B microanalyzer. Conductivities of Me_2CO solutions in ca. 5×10^{-4} mol dm^{-3} were measured with a Jenway PCM_3 conductimeter. NMR spectra were recorded on Bruker AC300 at 300 MHz (^1H) and 121.5 MHz (^{31}P) using Me_4Si or 85% H_3PO_4 as standards. The complexes $[\text{Cu}_2(\mu\text{-Cl})_2(\kappa^2\text{-}P,P\text{-dppf})_2]$ and $[\text{Cu}(\text{MeCN})_2(\kappa^2\text{-}P,P\text{-dppf})][\text{BF}_4]$ were prepared as described in the literature [7]. IR and NMR spectroscopic data for all the new complexes are collected in Table 1.

3.1. $[\text{Cu}(\text{CNR})_2(\kappa^2\text{-P,P-dppf})][\text{BF}_4]$ ($R = \textit{t}\text{-Bu}$ (**1**),
2,6- $\text{Me}_2\text{C}_6\text{H}_3$ (**2**), Cy (**3**), Bz (**4**))

3.1.1. Procedure A

A mixture of the corresponding isocyanide (0.30 mmol), $[\text{Cu}_2(\mu\text{-Cl})_2(\kappa^2\text{-P,P-dppf})_2]$ (0.1 g, 0.15 mmol) and AgBF_4 (0.059 g, 0.30 mmol) in CH_2Cl_2 (20 ml) was stirred at room temperature (r.t.) for 4 h. The resulting solution after filtration was concentrated under vacuum. The addition of Et_2O (20 ml) to the concentrated solution led to the precipitation of yellow solids, which were recrystallized from $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$. Yields: 50–65%. A_M ($\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$) **1** = 114, **2** = 111, **3** = 120, and **4** = 116. Anal. Found: C, 59.06; H, 5.28; N, 3.08. Calc. for $\text{C}_{44}\text{H}_{46}\text{N}_2\text{BCuF}_4\text{P}_2\text{Fe}$ (**1**): C, 60.67; H, 5.32;

N, 3.21%. Anal. Found: C, 63.99; H, 4.73; N, 2.79. Calc. for $\text{C}_{52}\text{H}_{46}\text{N}_2\text{BCuF}_4\text{P}_2\text{Fe}$ (**2**): C, 64.58; H, 4.79; N, 2.89%. Anal. Found: C, 62.69; H, 5.38; N, 2.98. Calc. for $\text{C}_{48}\text{H}_{50}\text{N}_2\text{BCuF}_4\text{P}_2\text{Fe}$ (**3**): C, 62.46; H, 5.46; N, 3.03%. Anal. Found: C, 63.93; H, 4.51; N, 2.91. Calc. for $\text{C}_{50}\text{H}_{40}\text{N}_2\text{BCuF}_4\text{P}_2\text{Fe}$ (**4**): C, 63.95; H, 4.51; N, 2.98%.

3.1.2. Procedure B

The corresponding isocyanide (0.625 mmol.) was added to a solution of $[\text{Cu}(\text{MeCN})_2(\kappa^2\text{-P,P-dppf})][\text{BF}_4]$ (0.23 g, 0.25 mmol) in CH_2Cl_2 (20 ml) and the mixture was stirred and heated to reflux for 4 h. The addition of Et_2O (20 ml) to the concentrated solution led to the precipitation of yellow solids, which were washed with Et_2O (3×10 ml) and vacuum-dried. Analytically pure samples were obtained by recrystallization from $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$. Yields: 60–75%.

Table 4

Crystal data and structure refinement parameters for $[\text{Cu}_2(\mu\text{-Cl})_2(\kappa^2\text{-P,P-dppf})_2]\cdot\text{CH}_2\text{Cl}_2$ and $[\text{Cu}(\text{CN}\textit{t}\text{-Bu})_2(\kappa^2\text{-P,P-dppf})][\text{BF}_4]\cdot\text{CH}_2\text{Cl}_2$

	$[\text{Cu}_2(\mu\text{-Cl})_2(\kappa^2\text{-P,P-dppf})_2]\cdot\text{CH}_2\text{Cl}_2$	$[\text{Cu}(\text{CN}\textit{t}\text{-Bu})_2(\kappa^2\text{-P,P-dppf})][\text{BF}_4]\cdot\text{CH}_2\text{Cl}_2$
Empirical formula	$\text{C}_{69}\text{H}_{58}\text{Cl}_4\text{Cu}_2\text{Fe}_2\text{P}_4$	$\text{C}_{45}\text{H}_{48}\text{BCl}_2\text{CuF}_4\text{FeN}_2\text{P}_2$
Formula weight	1391.61	955.89
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/n$
Unit cell dimensions		
<i>a</i> (Å)	24.801(5)	18.280(6)
<i>b</i> (Å)	13.393(3)	15.221(5)
<i>c</i> (Å)	18.751(4)	18.498(6)
β (°)	93.130(10)	115.65(2)
<i>V</i> (Å ³)	6219(2)	4640(3)
<i>Z</i>	4	4
D_{calc} (Mg m^{-3})	1.486	1.368
Absorption coefficient (mm^{-1})	1.449	1.004
<i>F</i> (000)	2840	1968
Crystal size (mm)	0.12 × 0.15 × 0.25	0.16 × 0.21 × 0.34
θ range for data collection (°)	3.04–28.03	3.32–25.00
Index ranges	–32 ≤ <i>h</i> ≤ 32, –6 ≤ <i>k</i> ≤ 17, –24 ≤ <i>l</i> ≤ 23	–21 ≤ <i>h</i> ≤ 21, –18 ≤ <i>k</i> ≤ 17, –13 ≤ <i>l</i> ≤ 21
Reflections collected/unique	7721	8384
Unique reflections	7507 [$R_{\text{int}} = 0.0477$]	8127 [$R_{\text{int}} = 0.0322$]
Data/restraints/parameters	7507/0/417	8127/24/579
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0403$, $wR_2 = 0.0869$	$R_1 = 0.0696$, $wR_2 = 0.1983$
<i>R</i> indices (all data)	$R_1 = 0.0928$, $wR_2 = 0.1224$	$R_1 = 0.1030$, $wR_2 = 0.2251$
Goodness-of-fit on F^2	1.087	1.096
Largest difference peak and hole (e Å^{-3})	0.405 and –0.443	1.285 and –0.647

$\text{GOF} = [\sum[w(F_o^2 - F_c^2)]/(n-p)]^{1/2}$, $R_1 = \sum|F_o| - |F_c| / \sum|F_o|$, $wR_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_c^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_c^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

3.2. X-ray crystal structure determination of $\text{D}\cdot\text{CH}_2\text{Cl}_2$ and $\text{1}\cdot\text{CH}_2\text{Cl}_2$

Diffraction data were recorded at 293(2) K with the θ – 2θ technique on a Siemens AED diffractometer for both compounds. The structures were solved by direct methods (SIR92) [10] and refined by full-matrix least-squares methods based on F^2 using the SHELXL-97 [11] program. All the non-hydrogen atoms were refined anisotropically. The chlorine atoms of CH_2Cl_2 in $\text{D}\cdot\text{CH}_2\text{Cl}_2$ were found disordered as well as the methyl carbon atoms of the $\textit{t}\text{-Bu}$ groups in $\text{1}\cdot\text{CH}_2\text{Cl}_2$. Crystal data and some details of the structure determination are listed in Table 4. All calculations were carried out on the DIGITAL AlphaStation 255 of the ‘Centro di Studio per la Strutturistica Diffraattometrica’ del CNR, Parma.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 158660 and 158661 for compounds $\text{D}\cdot\text{CH}_2\text{Cl}_2$ and $\text{1}\cdot\text{CH}_2\text{Cl}_2$, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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