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1′-(Diphenylphosphino)-1-cyanoferrocene: A Simple Ligand with Complicated Coordination Behavior toward Copper(I)

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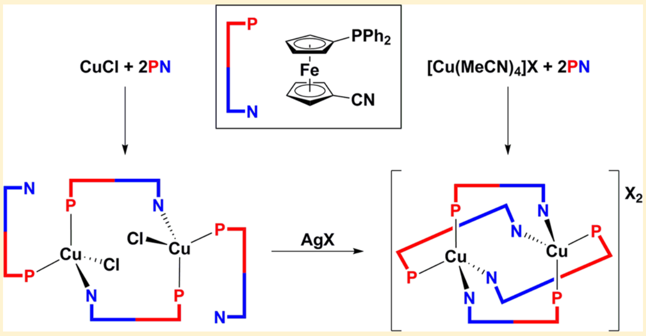
Ⓢ *Supporting Information*

ABSTRACT: 1′-(Diphenylphosphino)-1-cyanoferrocene (**3**), a new donor-asymmetric ferrocene ligand obtained in two steps from 1′-(diphenylphosphino)ferrocene-1-carboxaldehyde, reacts with CuCl at a Cu/**3** molar ratio of 1:1 to give the heterocubane complex $[Cu(\mu_3\text{-}Cl)(\mathbf{3}\text{-}\kappa P)]_4$ (**4**). When the Cu/**3** ratio is changed to 1:2 or 1:3, the reaction takes a different course, producing the P,N-bridged dimer $[CuCl(\mathbf{3}\text{-}\kappa P)(\mu(P,N)\text{-}\mathbf{3})]_2$ (**5**) after crystallization. Notably, CuBr and CuI behave differently, affording the corresponding 2D coordination polymers $[CuX(\mu(P,N)\text{-}\mathbf{3})]_n$ [X = I (**7**), and Br (**8**)], regardless of the Cu/**3** ratio. Reaction of **3** with sources of naked Cu^+, such as $[Cu(MeCN)_4]^+$ salts or their synthetic equivalents, provides the 1D coordination polymer $[Cu(MeCN\text{-}\kappa N)(\mu(P,N)\text{-}\mathbf{3})][BF_4]$ (**9**) or salts of a quadruply bridged dicopper(I) cation, $[Cu_2(\mu(P,N)\text{-}\mathbf{3})_4]X_2$ ($[\mathbf{10}]X_2$), depending on the Cu/**3** molar ratio (1:1 vs 1:2 and 1:3). Except for **4**, in which **3** binds as a simple P-monodentate ligand, the complexes reported here represent the first structurally characterized compounds in which a phosphinonitrile ligand coordinates through both of its soft donor moieties, thereby extending the coordination chemistry of these ligands.



INTRODUCTION

In the vast majority of coordination compounds containing simple (organic) phosphinonitrile donors, such as Ph_2PCH_2CN,[1] $(Ph_2P)_2CHCN$,[2] $Ph_2PCH(CN)_2$,[3] $Ph_{3-n}P(CH_2CH_2CN)_n$ (n = 1−3),[4,5] 2- and 4-$Ph_2PC_6H_4CN$,[6−8] and similar compounds,[9] in their native (neutral) form,[10] these compounds coordinate as simple P-donors, with their cyano groups acting as auxiliary substituents. Compounds in which *both* functional groups are coordinated to a metal center remain extremely rare and have not been definitively confirmed using methods of direct structural analysis.[1b,11]

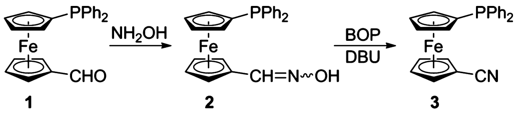
Given the numerous reports dealing with the multifaceted coordination chemistry of 1′-functionalized ferrocene phosphines,[12,13] we decided to prepare and study the new ferrocene-based mixed-donor ligand **3**, which combines the soft cyano and phosphine donor groups and formally represents a congener of the ubiquitous 1,1′-bis(diphenylphosphino)ferrocene (dppf).[14] Compounds of this type are not entirely unprecedented, even among ferrocene derivatives, being represented by 1-(diphenylphosphino)-2-(cyanomethyl)ferrocene[15] and its Cα-substituted derivatives,[16] 1-(diphenylphosphino)-2-cyano-3-ethylferrocene,[17] and 2-cyano-1-phosphaferrocene.[18] However, only the last of these compounds has been studied as a ligand in transition-metal complexes, coordinating as a P-monodentate donor.[18]

In this contribution, we report the synthesis and structural characterization of 1′-(diphenylphosphino)-1-cyanoferrocene (**3**) as a new ferrocene-based donor-asymmetric ligand and the copper(I) complexes resulting from its reactions with Cu(I) halides and $[Cu(MeCN)_4]^+$ salts or their synthetic equivalents. Because the stoichiometries of copper(I) complexes usually "give little clue to their structures, which can be very complicated",[19] we have focused mainly on the structural characterization of the prepared complexes and have thus identified both conventional and novel compound types.

RESULTS AND DISCUSSION

Synthesis of the Phosphinonitrile Ligand. 1′-(Diphenylphosphino)-1-cyanoferrocene (**3**) was prepared in a standard manner starting from phosphinoaldehyde **1**[20] (Scheme 1). In the first step, the aldehyde was converted into the corresponding oxime **2** by reaction with hydroxylamine in methanol.[21] The oxime was subsequently dehydrated with

Scheme 1. Preparation of Phosphinonitrile 3[a]



[a]BOP = (benzotriazol-1-yloxy)tris(dimethylamino)phosphonium hexafluorophosphate, DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

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BOP/DBU[22] to afford nitrile **3** as an orange, air-stable solid in a good overall yield (73% from **1**).[23]

The ^{1}H and ^{13}C NMR spectra of **2** and **3** show four signals typical for asymmetrically 1,1′-disubstituted ferrocene units and a characteristic multiplet of the PPh_2 substituents. The spectra of **2** also display additional signals of two nonequivalent CH═NOH moieties attributable to the (*E*) and (*Z*) double-bond isomers in a ca. 1:2 ratio. The ^{31}P NMR resonances of **2** and **3** are observed at approximately δ_P −17, close to that of the starting aldehyde.[20] In addition, compound **3** shows a characteristic C≡N stretching band at 2225 cm^{-1} in its IR spectrum, well within the range typical for conjugated nitriles.[24] A cyclic voltammetry study (Figure 1) showed that nitrile **3** becomes oxidized in a single irreversible step at $E_{pa} \approx 0.48$ V[25] versus the ferrocene/ferrocenium reference. This primary, presumably iron-centered (Fe^{II}/Fe^{III}) oxidation shows signs of electrochemical reversibility at higher scan rates and is associated with another irreversible oxidation at more positive potentials, which was tentatively attributed to a redox response of a decomposition product (EC mechanism, Figure 1).[26]

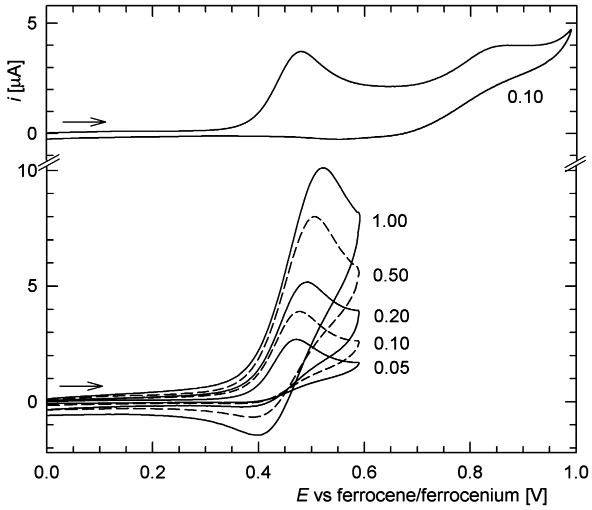
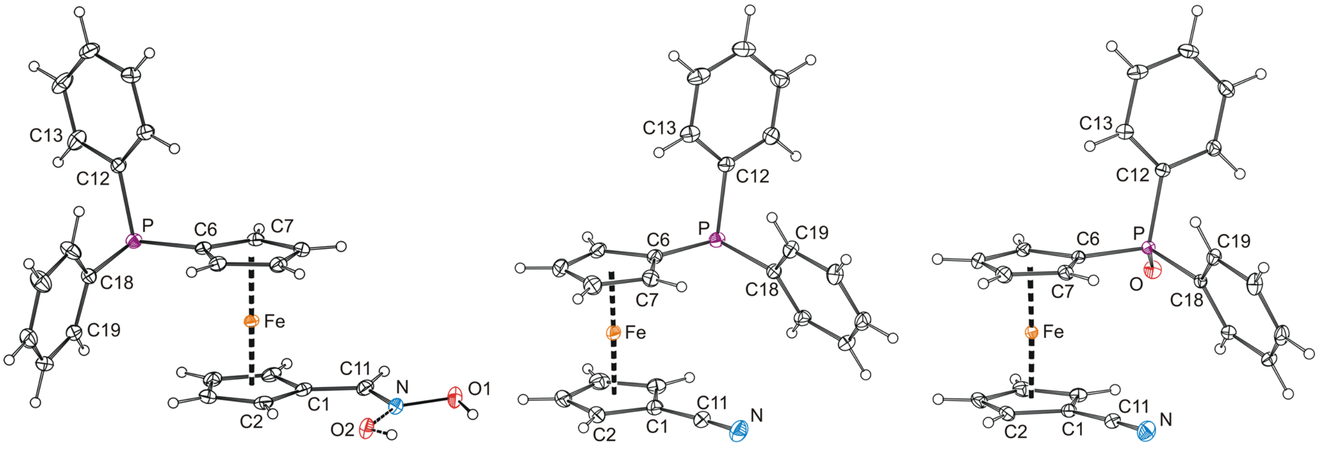


Figure 1. Cyclic voltammograms of **3**, as recorded on a Pt disk electrode in 1,2-dichloroethane (*c* = 0.5 mM). The scan direction (arrow) and scan rates (in V s^{-1}) are indicated in the figure.

The solid-state structures of compounds **2** and **3** and the corresponding phosphine oxide **3O**[27] were determined by X-ray diffraction analysis (Figure 2). The CH═NOH moiety in the structure of **2** was found to be disordered over the two positions corresponding to the (*E*) and (*Z*) isomers [the refined (*E*)/(*Z*) ratio was ca. 34:66], which corresponds with the solution observations. The individual conformers assemble through O−H···N hydrogen bonds, forming dimers around the crystallographic inversion centers (see the Supporting Information, Figure S1). A similar mode of assembly was observed with FcCH═NOH[28] (Fc = ferrocenyl). Notably, compounds **3** and **3O** are practically isostructural. From a formal viewpoint, they differ only in the occupancy of one of the four compartments within the tetrahedron around the phosphorus atom (oxygen vs lone electron pair[29]), which has a rather minor impact on the overall molecular structure. Oxidation of the phosphorus atom results in shortening of the P−C bonds by ca. 0.03 Å, presumably due to an electron density transfer from the aromatic rings toward the electron-withdrawing phosphoryl moiety.[30] The C−P−C angles in **3O** are increased (by ca. 4°) by the higher steric demands of the fourth substituent (oxygen) at the phosphorus atom.

The molecular parameters of **2**, **3**, and **3O** presented in Table 1 are generally comparable with the corresponding data reported for simple ferrocene derivatives such as fc(CH═NOH)$_2$[31] (fc = ferrocene-1,1′-diyl; note that oxime FcCH═NOH is heavily disordered[28]), FcCN,[32] and $FcPPh_2$.[33] The ferrocene moieties exhibit balanced Fe−C distances and, consequently, practically negligible tilting. The cyclopentadienyl rings in **3** and **3O** are eclipsed, and their substituents assume a synclinal orientation (see *τ* angle in Table 1). In contrast, the substituents in **2** adopt an anti configuration, halfway between the eclipsed anticlinal (*τ* = 144°) and the staggered antiperiplanar (*τ* = 180°) conformations.

Preparation of Complexes from Copper(I) Halides. The copper(I) ion is a typical soft acid according to Pearson's hard and soft acids and bases concept.[34] Nevertheless, its character can be partly influenced by the attached donors (e.g., halides),[35] and a previous study on Cu(I)/dppf/dppfO$_2$ complexes (dppfO$_2$ = 1,1′-bis(diphenylphosphinoyl)ferrocene)



2 **3** **3O**

Figure 2. PLATON plots of the molecular structures of **2**, **3**, and **3O** showing the atom labeling scheme and the displacement ellipsoids at the 30% probability level. For oxime **2**, both orientations of the disordered OH group are shown.

Table 1. Selected Distances (Å) and Angles (deg) for Compounds **2**, **3**, and **3O**

parameter[a]	**2**[b]	**3**	**3O**[c]
Fe−C (range)	2.034(1)−2.057(1)	2.024(2)−2.057(2)	2.025(1)−2.062(1)
Fe−Cg1	1.6507(6)	1.6456(8)	1.6469(6)
Fe−Cg2	1.6531(6)	1.6457(8)	1.6422(6)
∠Cp1, Cp2	1.08(8)	0.9(1)	0.38(8)
τ	162.13(9)	69.8(1)	69.0(1)
C1−C11	1.452(2)	1.430(2)	1.430(2)
C11−N	1.273(2)	1.144(2)	1.143(2)
C1−C11−N	125.4(1)	177.3(2)	177.5(2)
P−C6	1.817(1)	1.813(2)	1.786(1)
P−C12	1.835(1)	1.842(2)	1.809(1)
P−C18	1.836(1)	1.836(2)	1.806(1)

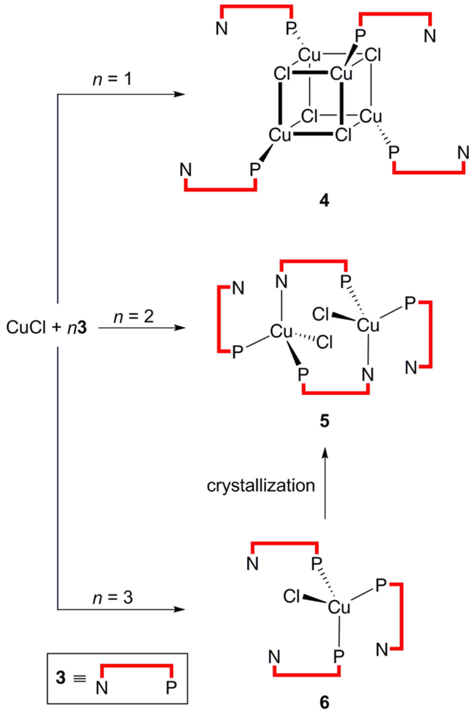
[a] Ring planes are defined as follows: Cp1 = C(1−5), C2 = C(6−10). Cg1 and Cg2 are the respective ring centroids. Parameter τ stands for the torsion angle C1−Cg1−Cg2−C6. [b] Further data: N−O1 = 1.424(2) Å, N−O2 = 1.436(3) Å. [c] Further data: P−O = 1.487(1) Å.

have suggested some borderline character for this metal ion.[36] Considering the nature of the donor groups available in **3** and the coordination variability of Cu(I)-complexes,[37] we decided to study the interactions of the newly prepared ligand **3** with Cu(I) by probing its reactivity toward copper(I) halides and precursors of the free Cu^+ ion.

Addition of ligand **3** (1, 2, or 3 molar equiv) to a suspension of CuCl in $CDCl_3$ led to complete dissolution of the solid copper(I) salt within hours. NMR analysis of the resulting solutions revealed that these reactions proceeded cleanly and afforded *three* different products at the three mentioned metal-to-ligand ratios (see the Supporting Information, Figure S2). An ESI mass spectrometric analysis performed in parallel was rather inconclusive. Regardless of the CuCl:**3** molar ratio, the mass spectra showed only fragments attributable to $[Cu_2Cl(\mathbf{3})_2]^+$ (m/z 951; the heaviest ionic species observed), $[Cu(\mathbf{3})_2]^+$ (m/z 853), $[Cu_2Cl(\mathbf{3})]^+$ (m/z 556), and $[Cu(\mathbf{3})]^+$ (m/z 458). However, the absence of higher molecular weight fragments is likely due to fragmentation during the ionization process and/or disintegration in the highly polar solvent used (methanol).

Subsequent evaporation and crystallization from an ethyl acetate/hexane mixture produced air-stable crystalline solids. The NMR spectra of the crystalline products isolated from the reactions performed at Cu/**3** ratios of 1:1 and 1:2 were identical with those recorded in situ. The compounds were characterized by X-ray diffraction analysis as a heterocubane comprising the ferrocene ligand as a P-monodentate donor, $[(\mu_3\text{-Cl})_4\{Cu(\mathbf{3}\text{-}\kappa P)\}_4]$ (**4**), and the ligand-bridged dimer $[(\mu(P,N)\text{-}\mathbf{3})\{CuCl(\mathbf{3}\text{-}\kappa P)\}]_2$ (**5**), respectively (Scheme 2). In contrast, the crystallization of the product obtained upon addition of 3 molar equiv of **3** to CuCl afforded exclusively the already mentioned dicopper(I) complex **5**. Because complexes of the type $[CuCl(PR_3)_3]$ are relatively common among Cu(I)-phosphine complexes,[38] we assume that the reaction of CuCl with 3 equiv of **3** indeed produced the tris-phosphine complex $[CuCl(\mathbf{3}\text{-}\kappa P)_3]$ (**6**) *in the solution* (perhaps in equilibrium with other species). However, upon crystallization, this species likely dissociated to give the less soluble dimer **5**, which then separated from the reaction mixture in pure crystalline form. The dissociative formation of **5** may be aided by steric destabilization of intermediate **6**, resulting from the presence of the bulky phosphinoferrocene ligand,[39] and the availability of another, much less sterically demanding soft donor group (nitrile).

Scheme 2. Reactions of **3** with CuCl[a]



[a] As formulated, compound **6** represents a plausible intermediate that was characterized in solution but could not be isolated as a defined solid substance.

The ^{31}P NMR spectra of **4**-**6** showed broad singlets near $\delta_P = -13$ ppm, suggesting coordination of the phosphine groups in all cases. The compounds were clearly distinguished by their ^1H NMR spectra, which showed the signals of the phosphinoferrocene ligand at different positions (Figure S2, Supporting Information). The observation of a single set of resonances in the ^1H NMR spectrum of **5** corroborates the fluxional nature of the Cu−**3** complexes. The IR spectra of crystalline complexes **4** and **5** differed mainly in the fingerprint region and provided limited diagnostic information. The spectrum of **5** showed a strong $\nu_{C\equiv N}$ band (2224 cm^{-1}) at a position identical to that observed for uncoordinated **3** (2225 cm^{-1}), whereas the $\nu_{C\equiv N}$ band in the spectrum of complex **4** (2241 cm^{-1}), which contains only uncoordinated C≡N moieties, was shifted to higher energies compared to free **3**.[40]

The crystal structures of **4** and **5** are presented in Figures 3 and 4 (for complete views, see the Supporting Information, Figures S3 and S4). As indicated above, complex **4** adopts a typical[37,41] heterocubane structure in which each copper(I) atom has a distorted Cl_3P tetrahedral coordination environment. The heterocubane unit in **4** has an exact C_2 symmetry, residing on the crystallographic symmetry element. The interatomic distances within the Cu_4Cl_4 cube in **4** are within the range observed for other $[CuCl(PR_3)]_4$ complexes,[42] while the P−Cu bond lengths compare well with those reported for the $[CuI(L)]_4$ complexes obtained from phosphinoferrocene donors.[43] The faces of the heterocubane moiety (see the Supporting Information, Figure S5) are distorted from the ideal square shape. The intraface Cu···Cu contacts (3.1950(5)-3.3332(5) Å) are shorter than the Cl···Cl distances (3.540(1)-3.6634(8) Å), and the associated Cl−Cu−Cl angles (93.31(3)-99.41(2)°) are less acute that the Cu−Cl−Cu angles (81.89(2)-86.70(3)°). The ferrocene moieties that decorate the cubane unit at its exterior maintain their regular geometry [tilt angles ca. 2°; Fe−Cg 1.648(1)−1.653(2) Å] but assume different conformations (τ = −162.5(2)° (Fe1) and −66.4(2)° (Fe2)), which direct their arm-like cyano pendants into structural voids and away from the Cu_4Cl_4 core.

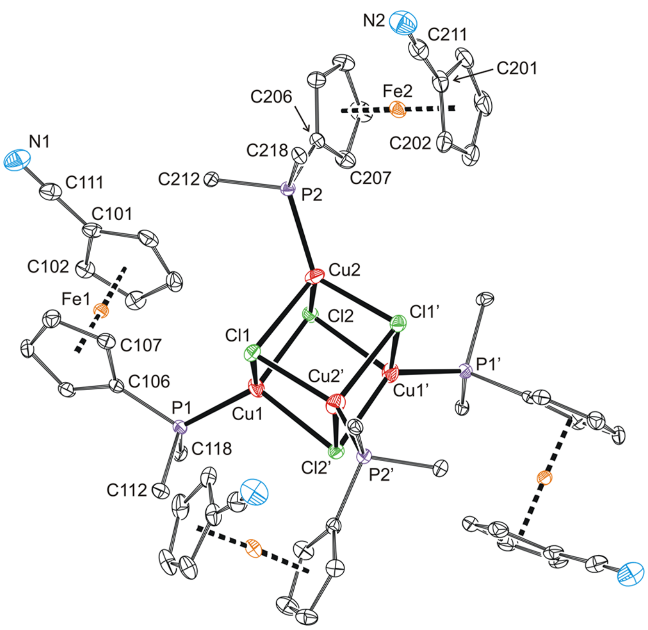


Figure 3. PLATON plot of the molecular structure of heterocubane **4** with 50% probability displacement ellipsoids. The phenyl ring carbons, except for those in ipso positions, and all hydrogens were omitted to simplify the figure. Atoms labeled with a prime are generated by the $(-x, y, {}^3/_2 - z)$ symmetry operation. Selected distances (Å) and angles (deg): Cu1−P1 2.1760(8), Cu1−Cl1 2.4431(7), Cu1−Cl2 2.3595(5), Cu1−Cl2′ 2.4558(9), Cu2−P2 2.1856(8), Cu2−Cl1 2.5229(7), Cu2−Cl2 2.4820(7), Cu2−Cl1′ 2.3412(9), Cl1−Cu1−Cl2 99.41(2), Cl1−Cu1−Cl2′ 93.57(3), Cl2−Cu1−Cl2′ 96.36(2), Cl1−Cu2−Cl2 94.10(2), Cl1−Cu2−Cl1′ 93.31(3), Cl2−Cu2−Cl1′ 95.46(3), Cl−Cu−P 115.30(3)−132.26(3).

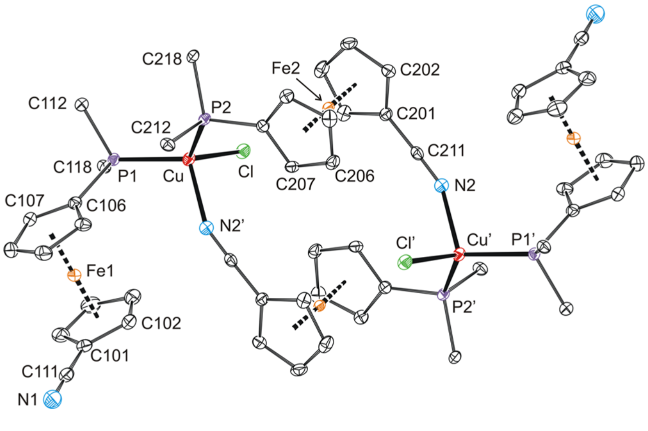


Figure 4. PLATON plot of the molecular structure of dimer **5** with 50% probability displacement ellipsoids. For clarity, the phenyl ring carbons, except for the ipso ones, and all hydrogens were omitted. The primed atoms are generated by crystallographic inversion. Selected distances (Å) and angles (deg): Cu−Cl 2.2877(4), Cu−P1 2.2558(5), Cu−P2 2.2673(4), Cu−N2′ 2.111(1), C111−N1 1.145(2), C211−N2 1.148(2), Cl−Cu−P1 113.38(1), Cl−Cu−P2 116.10(1), Cl−Cu−N2′ 98.16(4), P1−Cu−P2 117.62(2), P1−Cu−N2′ 108.16(4), P2−Cu−N2′ 99.97(4).

Complex **5**, obtained at CuCl:**3** ratios of 1:2 and 1:3 (after crystallization), is a dicopper(I) complex in which two phosphinoferrocene ligands coordinate as P-monodentate donors while the other two bridge the Cu(I) centers as P,N donors, thus resulting in identical $CuClP_2N$ centers (Figure 4). The symmetrical nature of the complex species is manifested in the crystal structure, in which the complex molecules reside on the crystallographic inversion centers.

The tetrahedral coordination environment of the Cu(I) ions in **5** is distorted, reflecting the dissimilar steric demands of the donor moieties attached to Cu(I) [cf. the interligand angles ranging from 98.16(4)° (Cl1−Cu−N2′) to 117.62(2)° (P1−Cu−P2)]. With respect to the Cu−donor distances, the coordination can be described as 3 + 1 because the rather similar Cu−Cl and Cu−P bonds are significantly longer that the remaining Cu−N bond (by ca. 0.15−0.18 Å). The ferrocene units are rotated into open intermediate conformations [τ = 159.0(1)° for Fe1, τ = −137.7(1)° for Fe2]. The bridging ligand shows a larger tilt and slightly shorter Fe−Cg distances [tilt 3.88(9)°, Fe−Cg 1.6475(7) and 1.6456(7) Å] than the P-coordinated one [tilt 1.8(1)°, Fe−Cg 1.6515(8) and 1.6559(8) Å].

As for the CuCl/**3** system, the NMR spectra of CuX−**3** (X = Br and I) mixtures obtained by mixing the appropriate copper(I) halide with **3** in $CDCl_3$ at metal-to-ligand ratios of 1:1, 1:2, or 1:3 suggested the formation of distinct species in each case. However, the subsequent crystallizations afforded only the insoluble polymeric complexes $[CuX(\mu(P,N)\text{-}\mathbf{3})]_n$ (**7** X = Br, **8** X = I) instead of the heterocubanes analogous to **4**. This confirms the dynamic nature of the $CuX(\mathbf{3})_n$ species in solution, which in turn enables the selective formation (upon crystallization) of the most stable and/or the least soluble product.

The crystal structures of **7** and **8** were determined by X-ray crystallography. In contrast to the other crystal structures reported in this paper, which were determined at 150 K, the diffraction data for **7** were recorded at 250 K because this compound undergoes a phase transition associated with a roughly 3-fold increase in the length of the monoclinic (b) axis. Differential scanning calorimetry (DSC) analysis demonstrated that the compound undergoes a reversible second-order phase transition at approximately −12 °C (see the Supporting Information). In addition, while compounds **7** and **8** have very similar structures, they are not isostructural (Figure S6, Supporting Information).[44]

The crystal structure of **8** is depicted in Figure 5, and the data for both polymeric complexes are given in the figure caption.

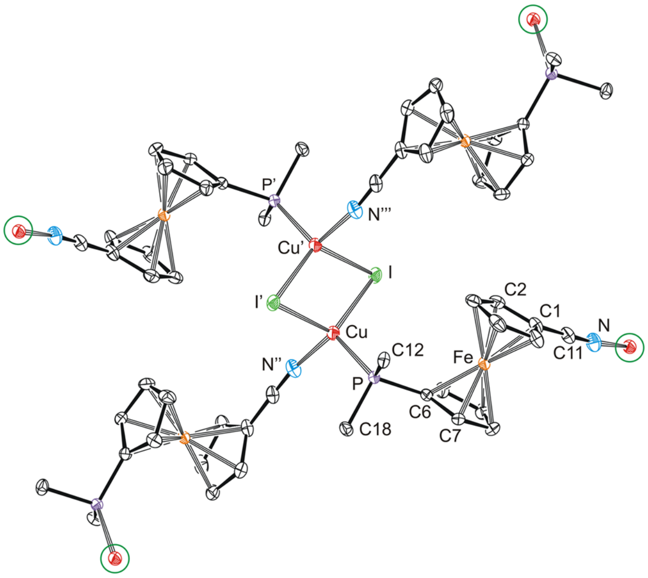


Figure 5. Section of the 2D polymeric structure of **8**, showing displacement ellipsoids at the 30% probability level. The circles indicate the atoms through which the propagation of the infinite assembly occurs. Selected distances (Å) and angles (deg) for **7** (X = Br) and [**8** (X = I)]: Cu−X 2.4494(5) [2.6027(3)], Cu−X′ 2.5224(5) [2.6857(3)], Cu−P 2.2169(9) [2.2394(6)], Cu−N″ 2.022(3) [2.016(2)], C11−N 1.137(4) [1.144(3)], X−Cu−X′ 109.96(2) [115.93(1)], X−Cu−P 118.25(2) [115.19(2)], X′−Cu−P 108.50(3) [105.21(2)], X−Cu−N″ 109.06(8) [112.34(6)], X′−Cu−N″ 99.96(8) [97.57(5)], Cu−X−Cu′ 70.04(1) [64.07(1)].

Each copper(I) ion in the structures of **7** and **8** is coordinated by two ligands (one through the phosphorus and one through its CN group), and the resulting Cu(**3**)$_2$ units are connected into a dimeric unit through asymmetric halide bridges[45] that complete the distorted tetrahedral coordination spheres around the Cu(I) ions. Because each ligand acts as a P,N bridge between two adjacent dicopper(I) units, the dimer units are interlinked into infinite corrugated layers (see the Supporting Information, Figure S7). The donor substituents in bridging **3** are rotated away from each other ($\tau = -158.9(2)°$ for **7** and $-157.9(1)°$ for **8**). Otherwise, the ferrocene units remain regular [**7**: Fe−Cg 1.644(2)/1.647(1) Å; **8**: 1.647(1)/1.6480(9) Å] and display negligible tilting (below 1°).

Reactions of 3 with Precursors of Bare Cu$^+$. Similar to the above experiments, reactions were performed at metal-to-ligand ratios of 1:1, 1:2, and 1:3 using [Cu(MeCN)$_4$]$^+$ salts as the common precursors of Cu(I) ions devoid of any firmly bound supporting ligands. The reaction of [Cu(MeCN)$_4$][BF$_4$] with 1 molar equiv of **3** in dichloromethane produced an orange precipitate, which redissolved upon addition of little acetonitrile. Layering with hexane and crystallization by liquid-phase diffusion afforded the *catena*-polymer [Cu(μ-**3**)(MeCN)]$_n$[BF$_4$]$_n$ (**9**).

This compound was insoluble in common deuterated, nondonor solvents and could therefore not be analyzed by NMR spectroscopy. Its IR spectrum featured several $\nu_{C\equiv N}$ bands: a strong band at 2249 cm^{-1} and two bands of medium intensity at 2314 and 2283 cm^{-1}. The crystal structure of **9** (Figure 6) confirmed the presence of different nitrile groups, indicating that **9** is a coordination polymer in which ligand **3** bridges the adjacent Cu(MeCN) units. The copper(I) centers are thus coordinated by two phosphinonitrile ligands and one acetonitrile, constituting an irregular trigonal N$_2$P donor set. Because the disubstituted ferrocene unit [tilt 4.4(1)°, Fe−Cg 1.6474(9)/1.6398(9) Å] assumes a conformation similar to synclinal eclipsed [$\tau = -63.8(1)°$, ideal value = 72°], the infinite chains are angular and, therefore, rather contracted (note that, owing to the overall symmetry, the Cu···Cu separation is exactly equal to the length of the crystallographic *a* axis). The BF$_4^-$ ions are located in between the chains and are fixed by the soft F···H−C interactions.[46]

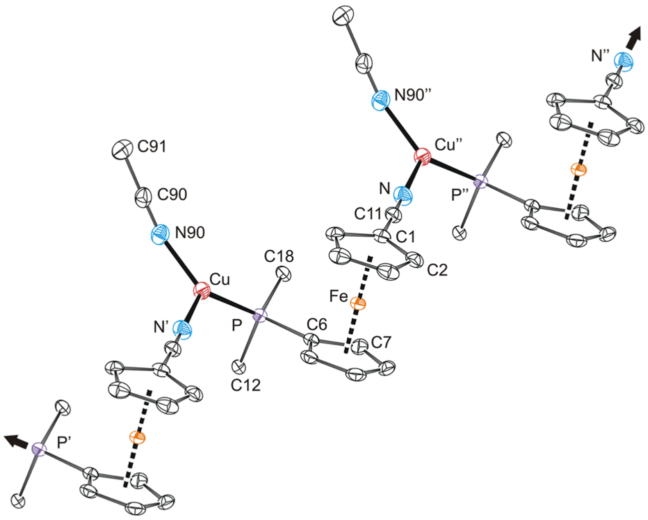
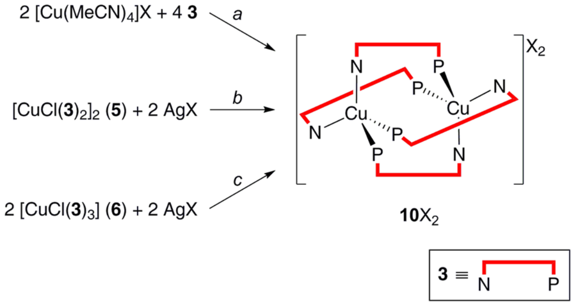


Figure 6. Section of the polymeric chain in the structure of **9**, in which the "monomer units" are related by elemental translation along the *a* axis. The counteranions (BF$_4^-$), phenyl ring carbons (except for those in ipso positions), and all hydrogens are omitted for clarity. Displacement ellipsoids are scaled to the 50% probability level. Selected distances (Å) and angles (deg): Cu−P 2.1985(5), Cu−N′ 1.954(2), Cu−N90 1.956(2), C11−N 1.141(3), C90−N90 1.136(3), P−Cu−N′ 120.19(5), P−Cu−N90 128.37(5), N′−Cu−N90 111.22(7).

Rather unexpectedly, increasing the Cu/**3** ratio to 1:2 and 1:3[47] in reactions of the phosphinonitrile with [Cu(MeCN)$_4$]X [X = BF$_4$, PF$_6$, CF$_3$SO$_3$, or B(C$_6$F$_5$)$_4$[48]] resulted in the selective formation of the respective quadruply ligand-bridged dicopper(I) complex salts **10**X$_2$ (Scheme 3, route *a*). These complexes, which were accessible equally well by the treatment of CuCl with 2 equiv of **3** and then by a silver(I) salt (i.e., from AgX and **5** formed in situ, Scheme 3, route *b*) or, similarly, by halogen removal from in situ generated **6** (Scheme 3, route *c*), represent an unprecedented structural type among Cu(I) complexes prepared from P,N donors. Previously structurally characterized compounds[49] in which a P,N donor bridges two discrete Cu(I) centers devoid of any supporting halide ligands include only asymmetric, triply bridged complexes of the type [(MeCN)Cu(μ-P−N)$_2$(μ-N−P)Cu]$^{2+}$, where N−P is 2-(diphenylphosphino)pyridine[50] or 2-(diphenylphosphino)-1-methylimidazole.[51,52] The former ligand also forms a doubly bridged dicopper(I) cation having two or four additional acetonitrile ligands, viz. [(MeCN)$_n$Cu(μ-P−N)(μ-N−P)Cu(MeCN)$_n$]$^{2+}$ (n = 1 or 2).[50,53] The different coordination

Scheme 3. Alternative Routes Leading to the Dicopper(I) Salts $10X_2$[a]



[a]Route a for X = BF_4^-, PF_6^-, $CF_3SO_3^-$, and $B(C_6F_5)_4^-$; route b for X = SbF_6^- and $(CF_3SO_2)_2N^-$; and route c for X = SbF_6^-.

behavior of **3** is very likely due to the presence of the rather small, rod-like CN donor unit, which cannot easily participate in the chelation of the P-bonded metal ion but can be directed to another metal center (through practically unrestricted rotation of the ferrocene cyclopentadienyls) and thus supplement the preferred tetrahedral coordination environment around the "other" Cu(I) ion.

Although the salts of the cation $\mathbf{10}^{2+}$ crystallize readily, their structural characterization proved difficult owing to the presence of extensively disordered counteranions and/or solvent molecules. Good-quality, disorder-free crystals were ultimately obtained for $\mathbf{10}[SbF_6]_2$. The structure of the complex cation in this salt is presented in Figure 7. A complete view and a projection of the cation along the (Cu2, Cu1) vector are available in the Supporting Information (Figures S8 and S9), which also presents the structure of the less symmetric solvate $\mathbf{10}[SbF_6]_2 \cdot 2Me_2CO$ for comparison.

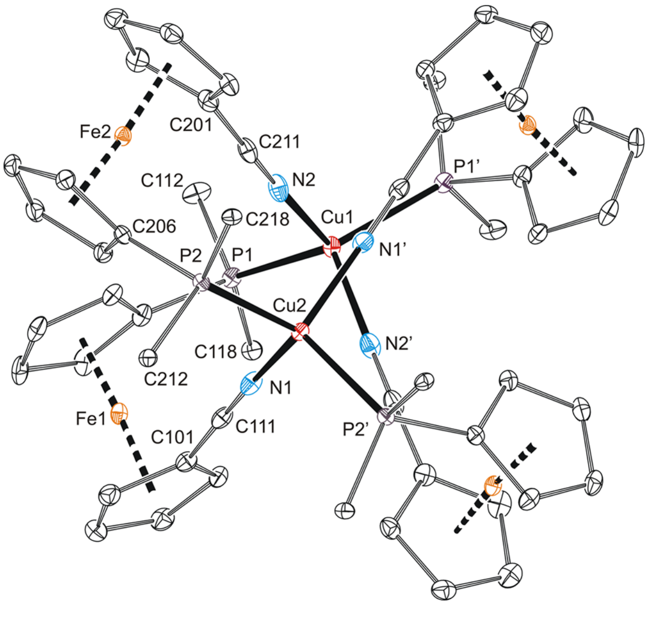


Figure 7. View of the complex cation in the structure of $\mathbf{10}[SbF_6]_2$, showing the displacement ellipsoids at the 30% probability level. The primed atoms are generated by the crystallographic 2-fold axis ($-x$, $2 - y$, z). Selected distances (Å) and angles (deg): Cu1−P1 2.3069(5), Cu1−N2 2.051(2), Cu2−P2 2.2807(5), Cu2−N1 2.016(2), C111−N1 1.143(3), C211−N2 1.144(3), P1−Cu1−P1′ 124.05(3), P1−Cu1−N2 104.52(5), P1−Cu1−N2′ 109.84(6), N2−Cu1−N2′ 102.05(8), P2−Cu2−P2′ 119.18(2), P2−Cu2−N1 107.10(5), P2−Cu2−N1′ 108.59(5), N1−Cu2−N1′ 105.49(7).

The structure of cation $\mathbf{10}^{2+}$ can be likened to a fragment of a quadruple helix consisting of pairs of chains with opposite polarity arranged around the central Cu1⋯Cu2 axis or, more figuratively, to a propeller with four blades (see Figure S9, Supporting Information). The compound crystallizes with the symmetry of the chiral orthorhombic space group *Aba*2 such that the copper atoms reside on the 2-fold axis. This "external" symmetry renders only one-half of the complex cation and one counterion (SbF_6^-) structurally independent.

The Cu1⋯Cu2 separation in $\mathbf{10}[SbF_6]_2$ is 5.4820(5) Å, which is considerably longer than the sum of covalent radii (2.64 Å[54]) or the Cu⋯Cu distances in heterocubane **4** [3.1950(5)−3.3332(4) Å] and much less than the Cu⋯Cu′ distances in **5** [8.2816(8) Å] and **9** [7.9595(5) Å]. Each copper(I) atom in $\mathbf{10}^{2+}$ forms two relatively shorter bonds to the nitrile groups and two longer bonds to the phosphine groups within a distorted tetrahedral coordination environment. The P−Cu−P angles are the largest, while the N−Cu−N angles are the most acute, reflecting the different steric properties of the donor moieties. The departure from the ideal tetrahedral angles is larger for Cu1 than for Cu2. The ferrocene units assume a synclinal eclipsed conformation [τ = 75.6(2)° for Fe1 and τ = 74.1(2)° for Fe2], which brings the donor moieties into positions suitable for bridging the two Cu(I) centers. However, this conformation of the donor units results in a mutual rotation of the CuN_2P_2 units (P1−Cu1⋯Cu2−N1 = 26.94(7)°, P2−Cu2⋯Cu1−N2 = 24.28(7)°) and, consequently, the helical character of the dicopper(I) cation.

The $\nu_{C\equiv N}$ bands in the IR spectrum of the $\mathbf{10}^{2+}$ salts appear shifted toward higher frequencies (2230 and 2237 cm^{-1} for $\mathbf{10}[BF_4]_2$ and $\mathbf{10}[SbF_6]_2$, respectively) compared with the free ligand (2225 cm^{-1}). Together with a marginal variation of the lengths of the C≡N bonds,[55] this shift is in line with the usual trend, reflecting changes in the electronic structure of the nitrile moiety upon coordination.[40]

■ CONCLUSIONS

The readily accessible phosphinonitrile **3** exhibits some unique properties, primarily due to the presence of the ferrocene moiety.[56] As a ligand, it can rotate along the axis of the ferrocene unit and thus undergo the rotational reorganization of the donor moieties, but it remains inflexible with respect to the tilting of the cyclopentadienyl rings. Furthermore, the entire molecule of **3** is conjugated and, because of strong electron-donating nature of the ferrocene unit, electron-rich. This results in unprecedented coordination behavior, which is exemplified herein for the soft Cu(I) ion.

In addition to conventional complexes in which the cyano groups remain uncoordinated and thus serve as spectators, albeit rather specific substituents, the structures determined for the Cu(I) complexes with ligand **3** reported in this Article demonstrate the ability of the phosphinonitrile donor to coordinate as a P,N bridge through both soft donor sites. The molecular structures of such complexes have been determined for the first time. Although limited to Cu(I) and a few coordination geometries (halide complexes PX_3 or NPX_2 tetrahedral donor sets, complexes without halide ligands PN_2 trigonal or P_2N_2 tetrahedral coordination environments), the results presented here demonstrate as yet undocumented coordination behavior of phosphinonitrile donors and stress the necessity of selecting the appropriate metal ions for evaluating the coordination potential of these donors.

EXPERIMENTAL SECTION

Materials and Methods. The syntheses of **2** and **3** were performed in an argon atmosphere using standard Schlenk techniques.[57] Complexes with ligand **3** were prepared in argon-flushed vessels and in the dark. Aldehyde **1** was prepared according to the literature.[20] Dichloromethane and tetrahydrofuran (THF) were dried with a Pure Solv MD-5 Solvent Purification System (Innovative Technology, Amesbury, MA). Other chemicals and solvents utilized for crystallizations and chromatography were used as received (Sigma-Aldrich; solvents from Lachner, Brno, Czech Republic).

NMR spectra were measured with a Varian UNITY Inova 400 spectrometer (^{1}H 399.95, ^{13}C 100.58, ^{31}P 161.90 MHz) at 25 °C unless noted otherwise. Chemical shifts (δ, ppm) are given relative to internal tetramethylsilane (^{1}H and ^{13}C) or external 85% aqueous H_3PO_4 (^{31}P). In addition to the usual notation for signal multiplicity, vt and vq are used to denote virtual triplets and quartets arising from the AA′BB′ and AA′BB′X spin systems of the cyano- and PPh_2-substituted cyclopentadienyl rings, respectively (fc = ferrocene-1,1′-diyl). IR spectra were recorded with an FTIR Nicolet 760 instrument in the range 400−4000 cm^{-1}. Conventional (low-resolution) electrospray ionization mass spectra (ESI MS) were recorded on a Bruker Esquire 3000 spectrometer. The samples were dissolved in HPLC-grade methanol. High-resolution (HR) ESI MS measurements were obtained with an LTQ Orbitrap XL mass spectrometer. Elemental analyses were determined by a conventional combustion method with a PE 2400 Series II CHNS/O Elemental Analyzer (Perkin-Elmer). Melting points were determined with a melting point B-540 apparatus (Büchi, Flawil, Switzerland).

1′-(Diphenylphosphino)ferrocene-1-carboxaldehyde Oxime (2). A solution of sodium ethoxide prepared separately by dissolving sodium metal (0.063 g, 2.7 mmol) in anhydrous ethanol (5 mL) was added to a solution of hydroxylamine hydrochloride (0.190 g, 2.7 mmol) in absolute ethanol (15 mL), whereupon a fine white precipitate (NaCl) separated. The mixture was stirred for 10 min and then filtered through a polytetrafluoroethylene (PTFE) syringe filter into a suspension of 1′-(diphenylphosphino)ferrocene-1-carboxaldehyde (**1**; 0.360 g, 0.90 mmol) in anhydrous ethanol (20 mL). The resulting mixture was stirred at 60 °C for 3 h, cooled to room temperature, and diluted with brine (20 mL) and dichloromethane (20 mL). The organic layer was separated, washed with brine, dried over $MgSO_4$, and evaporated with chromatographic silica gel. The preadsorbed crude product was transferred onto a silica gel column packed in a hexane/diethyl ether (3:1) mixture. The same mobile phase was used to remove nonpolar impurities. The red band that eluted when the eluent was changed to hexane/diethyl ether (1:1) was collected and evaporated to afford aldoxime **2** as an orange solid (yield: 0.306 g, 82%). The compound was a mixture of (*E*) and (*Z*) isomers in ca. 2:1 ratio. Crystals suitable for X-ray diffraction analysis were grown by liquid-phase diffusion from an ethyl acetate/hexane mixture.

^{1}H NMR ($CDCl_3$): major isomer δ 4.13 (m, 2H, fc), 4.23 (vt, J' = 1.9 Hz, 2H, fc), 4.43 (m, J' = 1.8 Hz, 4H, fc), 7.30−7.39 (m, 10H, Ph), 7.71 (s, 1H, C*H*NOH), 7.96 (br s, 1H, CHNO*H*); minor isomer δ 4.11 (m, 2H, fc), 4.25 (vt, J' = 1.9 Hz, 2H, fc), 4.41 (vt, J' = 1.8 Hz, 2H, fc), 4.70 (vt, J' = 1.9 Hz, 2H, fc), 6.96 (s, 1H, C*H*NOH), 7.30−7.39 (m, 10H, Ph), 7.96 (br s, 1H, CHNO*H*). ^{13}C{^{1}H} NMR ($CDCl_3$): major isomer δ 68.44 (CH of fc), 71.28 (CH of fc), 72.16 (d, J_{PC} = 4 Hz, CH of fc), 72.46 (d, J_{PC} = 4 Hz, CH of fc), 73.88 (d, $^{1}J_{PC}$ = 14 Hz, C−P of fc), 76.86 (C−CHN of fc), 128.20 (d, $^{2}J_{PC}$ = 7 Hz, CH$^{\text{ortho}}$ of Ph), 128.62 (CH$^{\text{para}}$ of Ph), 133.47 (d, $^{3}J_{PC}$ = 20 Hz, CH$^{\text{meta}}$ of Ph), 138.71 (d, $^{1}J_{PC}$ = 9 Hz, C$^{\text{ipso}}$ of Ph). ^{31}P{^{1}H} NMR ($CDCl_3$): −16.7 (major), −16.6 (minor). IR (Nujol): ν_{max} (cm^{-1}) 3280 br m, 3240 br m, 3160 br m, 3017 m, 1642 w, 1304 m, 1245 w, 1195 w, 1188 w, 1161 w, 1090 w, 1070 m, 1040 m, 997 w, 948 s, 897 m, 827 m, 783 m, 751 s, 703 m, 695 s, 636 w, 582 w, 569 w, 499 s, 453 w, 413 w. ESI+ MS: *m*/*z* 414 ([M + H]$^{+}$), 436 ([M + Na]$^{+}$). Anal. Calcd for $C_{23}H_{20}FeNOP\cdot 0.2CH_3CO_2Et$ (430.8): C 66.34, H 5.05, N 3.25%. Found: C 66.24, H 4.73, N 3.28%. The amount of clathrated solvent was verified by NMR spectroscopy.

1′-(Diphenylphosphino)-1-cyanoferrocene (3). Oxime **2** (0.293 g, 0.71 mmol) and (benzotriazol-1-yloxy)tris(dimethylamino)-phosphonium hexafluorophosphate (BOP; 0.628 g, 1.42 mmol) were mixed in dry THF (15 mL). After the mixture had been stirred at room temperature for 5 min, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 0.25 mL, 1.7 mmol) dissolved in 5 mL of THF was added, and the stirring was continued for another 2 h. The mixture was washed with water (2× 5 mL) and brine (5 mL), and the organic phase was dried over $MgSO_4$ and evaporated with silica gel. The preadsorbed product was transferred to the top of a chromatographic column (silica gel; hexane/diethyl ether 1:1). Elution with the same solvent mixture afforded a single red band, which was collected and evaporated to give nitrile **3** as an orange microcrystalline solid (yield: 0.250 g, 89%). Crystals suitable for X-ray diffraction analysis were grown from ethyl acetate/hexane.

Mp 163−164 °C (ethyl acetate/hexane). ^{1}H NMR ($CDCl_3$): δ 4.26 (vq, J' = 1.9 Hz, 2H, fc), 4.28 (vt, J' = 1.9 Hz, 2H, fc), 4.53 (vt, J' = 1.9 Hz, 2H, fc), 4.56 (vt, J' = 1.9 Hz, 2H, fc), 7.32−7.37 (m, 10H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 52.62 (C−CN of fc), 72.17 (d, J_{PC} = 1 Hz, CH of fc), 72.56 (CH of fc), 73.72 (d, J_{PC} = 4 Hz, CH of fc), 74.87 (d, J_{PC} = 14 Hz, CH of fc), 79.29 (d, $^{1}J_{PC}$ = 10 Hz, C−P of fc), 119.60 (C≡N), 128.35 (d, $^{2}J_{PC}$ = 7 Hz, CH$^{\text{ortho}}$ of Ph), 128.86 (CH$^{\text{para}}$ of Ph), 133.40 (d, ^{3}J = 20 Hz, CH$^{\text{meta}}$ of Ph), 138.03 (d, $^{1}J_{PC}$ = 10 Hz, C$^{\text{ipso}}$ of Ph). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −17.7. IR (Nujol): ν_{max} (cm^{-1}) 3114 w, 3100 w, 3082 w, 3055 w, 2225 m, 1232 w, 1194 w, 1160 m, 1090 w, 1232 w, 1032 m, 1027 m, 913 w, 848 w, 840 w, 823 m, 749 s, 699 s, 562 w, 555 w, 519 w, 510 m, 478 m, 495 m, 448 m, 450 m, 425 w. ESI+ MS: *m*/*z* 396 ([M + H]$^{+}$), 418 ([M + Na]$^{+}$), 434 ([M + K]$^{+}$). HR MS (ESI+): calcd for $C_{23}H_{19}FeNP$ ([M + H]$^{+}$) 396.0599, found 396.0599. Anal. Calcd for $C_{23}H_{18}FeNP$ (395.2): C 69.90, H 4.59, N 3.55%. Found: C 69.60, H 4.44, N 3.45%.

Reactions of Ligand 3 with CuCl. A solution of phosphine **3** in dichloromethane (1.5 mL) was added to a suspension of CuCl in the same solvent (0.5 mL). The resulting mixture was stirred at room temperature for 90 min, during which time all of the CuCl dissolved. Following evaporation under a vacuum, the solid products were analyzed by NMR spectroscopy and subsequently recrystallized by liquid-phase diffusion from ethyl acetate/hexane or chloroform/hexane.

Complex 4. Reaction between **3** (20 mg, 51 μmol) and CuCl (5.0 mg, 51 μmol) as described above gave **4** as a yellow microcrystalline solid (yield: 16 mg, 64%). ^{1}H NMR ($CDCl_3$): δ 4.36 (br vt, J' = 1.8 Hz, 2H, fc), 4.46 (vt, J' =1.9 Hz, 2H, fc), 4.50−4.53 (br m, 4H, fc), 7.25−7.31 (m, 4H, Ph), 7.33−7.39 (m, 2H, Ph), 7.56−7.65 (m, 2H, Ph). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −13.3 (br s). IR (Nujol): ν_{max} (cm^{-1}) 3109 w, 3065 w, 3039 w, 2241 m, 1232 w, 1194 w, 1160 w, 1090 w, 1032 m, 1027 m, 913 w, 848w, 839 w, 823 m, 749 s, 699 s, 562 w, 558 w, 519 w, 511 m, 495 m, 478 m, 450 m, 425 w. ESI+ MS: *m*/*z* 458 ([Cu(**3**)]$^{+}$), 516 ([CuCl(**3**) + Na]$^{+}$), 558 ([Cu$_2$Cl(**3**)]$^{+}$), 853 ([Cu(**3**)$_2$]$^{+}$), 911 ([CuCl(**3**)$_2$ + Na]$^{+}$), 953 ([Cu$_2$Cl(**3**)$_2$]$^{+}$). Anal. Calcd for $(C_{23}H_{18}ClCuFeNP)_4$ (1976.8): C 55.89, H 3.67, N 2.83%. Found: C 55.91, H 3.60, N 2.59%.

Complex 5. Reaction of **3** (15 mg, 38 μmol) and CuCl (1.9 mg, 19 μmol) as described above produced **5** as a red crystalline solid (yield: 11 mg, 66%). ^{1}H NMR ($CDCl_3$): δ 4.34 (br vt, 2H, fc), 4.46 (vt, J' = 2.0 Hz, 2H, fc), 4.51 (vt, J' = 2.0 Hz, 2H, fc), 4.54 (vt, J' = 1.9 Hz, 2H, fc), 7.27−7.33 (m, 4H, Ph), 7.36−7.41 (m, 2H, Ph), 7.43−7.51 (br m, 4H, Ph). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −13.1 (br s). IR (Nujol): ν_{max} (cm^{-1}) 3101 w, 3047 m, 2224 s, 1586 w, 1236 w, 1192 w, 1167 w, 1035 w, 1026 w, 846 w, 833 w, 755 m, 740 m, 696 s, 630 w, 595 w, 553 w, 530 m, 510 m, 476 m, 458 m, 425 w. ESI+ MS: *m*/*z* 458 ([Cu(**3**)]$^{+}$), 516 ([CuCl(**3**) + Na]$^{+}$), 558 ([Cu$_2$Cl(**3**)]$^{+}$), 853 ([Cu(**3**)$_2$]$^{+}$), 911 ([CuCl(**3**)$_2$ + Na]$^{+}$), 953 ([Cu$_2$Cl(**3**)$_2$]$^{+}$). Anal. Calcd for $C_{46}H_{36}ClCuFe_2N_2P_2$ (889.4): C 62.12, H 4.08, N 3.15%. Found: C 61.87, H 3.94, N 3.10%.

According to monitoring by NMR spectroscopy, when the reaction was performed similarly with 3 equiv of **3** (**3**: 15 mg, 38 μmol; CuCl

1.3 mg, 13 μmol), it produced a different product (formulated as [CuCl(**3**)$_3$] (**6**)), which was converted completely to complex **5** during the subsequent crystallization from ethyl acetate/hexane (yield of **5**: 11 mg, 95%). Data recorded for **6** in situ. ^{1}H NMR (CDCl$_3$): δ 4.31 (br vt, J' = 1.8 Hz, 2H, fc), 4.42 (br vt, J' = 1.8 Hz, 2H, fc), 4.50 (vt, J' = 1.9 Hz, 2H, fc), 4.56 (vt, J' = 1.9 Hz, 2H, fc), 7.28−7.43 (m, 10H, Ph). ^{31}P{^{1}H} NMR (CDCl$_3$): δ −15.0 (br s). ESI+ MS: *m/z* 458 ([Cu(**3**)]$^+$), 516 ([CuCl(**3**) + Na]$^+$), 558 ([Cu$_2$Cl(**3**)]$^+$), 853 ([Cu(**3**)$_2$]$^+$), 911 ([CuCl(**3**)$_2$ + Na]$^+$), 953 ([Cu$_2$Cl(**3**)$_2$]$^+$). The NMR and IR spectra of the crystallized samples were identical to those of **5**.

[CuBr(3)]$_n$ **(7)**. CuBr (7.3 mg, 51 μmol) and **3** (20 mg, 51 μmol) were reacted in dry chloroform (2 mL) for 1 h to afford a clear solution, which was partly evaporated under a vacuum (to ca. 1 mL) and filtered through a PTFE syringe filter. The filtrate was layered with chloroform (1 mL) and hexane (10 mL), and the mixture was allowed to crystallize by diffusion to produce **8** as an orange-red crystalline solid (yield: 19 mg, 70%). Note: Complete solvent removal produces a glassy solid, which can be dissolved in ethyl acetate. The solution, however, rapidly deposits **8** as an orange precipitate.

^{1}H NMR (in situ, CDCl$_3$): δ 4.38 (vt, J' = 1.9 Hz, 2H, fc), 4.40 (vt, J' =1.9 Hz, 2H, fc), 4.57 (vt, J' = 1.7 Hz, 2H, fc), 4.59 (br s, 2H, fc), 7.28−7.34 (m, 4H, Ph), 7.36−7.42 (m, 2H, Ph), 7.56−7.63 (m, 4H, Ph). ^{31}P{^{1}H} NMR (in situ, CDCl$_3$): δ −16.1 (br s). IR (Nujol): ν_{max} (cm^{-1}) 3112 w, 3103 w, 3061 w, 3040w, 2243 s, 1238 m, 1193 w, 1167 s, 1033 s, 914 s, 890 w, 753 s, 745 s, 697 s, 636 w, 535 s, 517 s, 509 m, 481 s, 457 m, 432 m. Anal. Calcd for C$_{23}$H$_{18}$BrCuFeNP (538.7): C 51.28, H 3.37, N 2.60%. Found: C 50.90, H 3.29, N 2.34%.

The NMR spectra recorded for the reaction mixtures obtained similarly at Cu/**3** molar ratios of 1:2 and 1:3 were different, but the subsequent crystallization always produced only complex **8**. **Cu/3 = 1:2.** ^{1}H NMR (in situ, CDCl$_3$): δ 4.39 (br vt, J' = 1.7 Hz, 2H, fc), 4.45 (vt, J' = 1.9 Hz, 2H, fc), 4.48 (vt, J' = 1.9 Hz, 2H, fc), 4.54 (vt, J' = 1.9 Hz, 2H, fc), 7.27−7.32 (m, 4H, Ph), 7.36−7.41 (m, 2H, Ph), 7.43−7.48 (m, 4H, Ph). ^{31}P{^{1}H} NMR (in situ, CDCl$_3$): δ −13.6 (br s). **Cu/3 = 1:3.** ^{1}H NMR (in situ, CDCl$_3$): δ 4.35 (br vt, J' = 1.8 Hz, 2H, fc), 4.42 (br vt, J' = 1.9 Hz, 2H, fc), 4.49 (vt, J' = 1.9 Hz, 2H, fc), 4.56 (vt, J' = 1.9 Hz, 2H, fc), 7.28−7.33 (m, 4H, Ph), 7.35−7.41 (m, 6H, Ph). ^{31}P{^{1}H} NMR (in situ, CDCl$_3$): δ −14.7 (br s).

[CuI(3)]$_n$ **(8)**. Ligand **3** (50 mg, 0.13 mmol) and CuI (24 mg, 0.13 mmol) were reacted in dry CHCl$_3$ as described above. After filtration, the clear, orange solution was layered with chloroform (2 mL) and hexane (20 mL) and set aside for crystallization to produce **8** in the form of orange-red crystals (yield: 65 mg, 87%).

^{1}H NMR (in situ, CDCl$_3$): δ 4.07 (br s, 2H, fc), 4.26 (br s, 2H, fc), 4.52−4.56 (m, 4H, fc), 7.39−7.45 (m, 4H, Ph), 7.47−7.60 (m, 6H, Ph). ^{31}P{^{1}H} NMR (in situ, CDCl$_3$): δ −27.9 (br s). IR (Nujol): ν_{max} (cm^{-1}) 3112 w, 3103 m, 3089 w, 3065 m, 3041 m, 2242 s, 1586 w, 1237 m, 1193 m, 1165 s, 1098 m, 1070 w, 1050 w, 1033 s, 999 w, 987 w, 914 m, 889 w, 865 w, 839 s, 832 s, 809 m, 952 s, 744 s, 697 s, 635 w, 577 w, 534 s, 516 s, 509 m, 478 s, 459 s, 432 m. Anal. Calcd for C$_{23}$H$_{18}$CuFeINP (585.7): C 47.17, H 3.10, N 2.39%. Found: C 46.90, H 3.03, N 2.20%.

Similar to the CuBr/**3** system, the reaction mixtures obtained at CuI/**3** ratios of 1:2 and 1:3 gave different NMR spectra but provided only complex **9** upon crystallization. **CuI/3 = 1:2.** ^{1}H NMR (in situ, CDCl$_3$): δ 4.41−4.46 (m, 6H, fc), 4.54 (vt, J' =1.9 Hz, 2H, fc), 7.26−7.31 (m, 4H, Ph), 7.35−7.43 (m, 6H, Ph). ^{31}P{^{1}H} NMR (in situ, CDCl$_3$): δ −14.8 (br s). **CuI/3 = 1:3.** ^{1}H NMR (in situ, CDCl$_3$): δ 4.39−4.42 (m, 4H, fc), 4.48 (vt, J' =1.9 Hz, 2H, fc), 4.48 (vt, J' =1.9 Hz, 2H, fc), 4.55 (vt, J' =1.9 Hz, 2H, fc), 7.27−7.32 (m, 4H, Ph), 7.34−7.40 (m, 6H, Ph). ^{31}P{^{1}H} NMR (in situ, CDCl$_3$): δ −14.9 (br s).

Preparation of [Cu(3)(MeCN)]$_x$[BF$_4$]$_x$ (9). A solution of **3** (20 mg, 51 μmol) in dichloromethane (2 mL) was added to a suspension of solid [Cu(MeCN)$_4$][BF$_4$] (16 mg, 51 μmol) in the same solvent (1 mL), and the resulting mixture was stirred for 1 h. The separated solid was dissolved by addition of acetonitrile (2 drops), and the solution was filtered through a syringe filter. The filtrate was layered with hexane (ca. 6 mL) and set aside for crystallization. The dark orange-red crystals, which separated over several days, were filtered off, washed with pentane, and dried under a vacuum to afford analytically pure **9** (yield: 25 mg, 84%).

IR (Nujol): ν_{max} (cm^{-1}) 3099 w, 3071 w, 3048 w, 2314 w, 2283 m, 2249 s, 1306 w, 1285 w, 1242 m, 1195 w, 1169 m, 1102 s, 1075 s, 1052 s, 1027 s, 997 m, 916 m, 845 m, 831 w, 749 s, 699 s, 538 s, 519 s, 488 s, 481 s, 464 m, 429 w. Anal. Calcd for C$_{25}$H$_{21}$N$_2$BF$_4$PFeCu (586.6) C 51.18, H 3.61, N 4.78%. Found: C 51.48, H 3.59, N 4.59%.

Complex ***10****[BF$_4$]$_2$ (Route a in Scheme 3).* A solution of **3** (15 mg, 38 μmol) in dry dichloromethane was added to a suspension of [Cu(MeCN)$_4$][BF$_4$] in the same solvent (6.0 mg, 19 μmol in 0.5 mL). The resulting mixture was stirred for 1 h and evaporated under a vacuum. The residue was taken up with acetone (5 mL) and filtered through a syringe filter. Evaporation of the filtrate under vacuum gave **10**[BF$_4$]$_2$ as a yellow solid (yield: 14 mg, 78%). IR (Nujol): ν_{max} (cm^{-1}) 2230 s, 1712 w, 1618 w, 1237 m, 1166 m, 1071 s, 1044 s, 999 m, 913 w, 741 m, 722 m, 696 w, 635 w, 532 w, 511 s, 490 s, 476 s, 463 s, 433 m. ESI+ MS: *m/z* 458 [Cu(**3**)$^+$]. Anal. Calcd for C$_{92}$H$_{72}$B$_2$Cu$_2$F$_8$Fe$_4$N$_4$P$_4$·H$_2$O (1899.6): C 58.17, H 3.93, N 2.95%. Found: C 57.85, H 4.00, N 2.95%. (Note: Salts with other anions were obtained similarly.)

Complex ***10****[SbF$_6$]$_2$ (Route c in Scheme 3).* A solution of ligand **3** (30 mg, 76 μmol) in dichloromethane (3 mL) was added to a suspension of CuCl (3.8 mg, 38 μmol) in the same solvent (1 mL). After being stirred for 60 min, the resulting solution was treated with a suspension of Ag[SbF$_6$] (13 mg, 38 μmmol) in dichloromethane (3 mL), and the reaction mixture was stirred for another 30 min and filtered through a PTFE syringe filter. The filtrate was evaporated under a vacuum, and the residue was taken up with acetone (1.5 mL) and filtered into a 5 mm NMR tube. The solution was carefully layered with acetone (0.5 mL) and hexane (ca. 2 mL), and the mixture was allowed to crystallize at room temperature. The separated crystalline solid was filtered off, washed with pentane, and dried under a vacuum. Yield of **10**[SbF$_6$]$_2$: 34 mg (82%), red crystalline solid. IR (Nujol): ν_{max} (cm^{-1}) 3122 w, 3055 w, 2237 s, 1587 w, 1481 m, 1435 s, 1238 m, 1196 w, 1099 m, 1041 m, 999 w, 912 w, 830 m, 741 m, 695 s, 659 s, 577 w, 531 w, 511 s, 487 s, 478 s, 466 m, 433 w. ESI+ MS: *m/z* 458 [Cu(**3**)$^+$]. Anal. Calcd for C$_{92}$H$_{72}$Cu$_2$F$_{12}$Fe$_4$P$_4$N$_4$Sb$_2$ (2179.4) C 50.70, H 3.33, N 2.57%. Found: C 50.43, H 3.33, N 2.36%.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional structural diagrams, NMR spectra of CuCl/**3** mixtures, results of DSC measurements for **7**, description of single-crystal X-ray diffraction analyses, and copies of NMR and IR spectra. Complete crystallographic data in standard CIF format (CCDC deposition numbers 966377−966386). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Braunstein, P.; Matt, D.; Mathey, F.; Thavard, D. *J. Chem. Res. Synop.* **1978**, 232−233. (b) Braunstein, P.; Matt, D.; Dusausoy, Y.; Fischer, J.; Mitschler, A.; Ricard, L. *J. Am. Chem. Soc.* **1981**, *103*, 5115−5125. (c) Klasen, C.; Lorenz, I. P.; Schmid, S.; Beuter, G. *J. Organomet. Chem.* **1992**, *428*, 363−378.

(2) (a) Braun, L.; Liptau, P.; Kehr, G.; Ugolotti, J.; Fröhlich, R.; Erker, G. *Dalton Trans.* **2007**, 1409−1415. (b) Sithole, S. V.; Staples, R. J.; van Zyl, W. E. *Acta Crystallogr. E: Struct. Rep. Online* **2011**, *67*, m64. (c) Sithole, S. V.; Staples, R. J.; van Zyl, W. E. *Inorg. Chem. Commun.* **2012**, *15*, 216−220.

(3) (a) Maraval, A.; Owsianik, K.; Arquier, D.; Igau, A.; Coppel, Y.; Donnadieu, B.; Zablocka, M.; Majoral, J.-P. *Eur. J. Inorg. Chem.* **2003**, 960−968. (b) Minko, Y. A.; Belina, N. V.; Sushev, V. V.; Fukin, G. K.; Bubnov, M. P.; Kornev, A. N. *J. Organomet. Chem.* **2007**, *692*, 4157−4160.

(4) Selected examples: (a) Meriwether, L. S.; Fiene, M. L. *J. Am. Chem. Soc.* **1959**, *81*, 4200−4208. (b) Meriwether, L. S.; Colthup, E. C.; Fiene, M. L.; Cotton, F. A. *J. Inorg. Nucl. Chem.* **1959**, *11*, 181−183. (c) Magee, T. A.; Matthews, C. N.; Wang, T. S.; Wotiz, J. H. *J. Am. Chem. Soc.* **1961**, *83*, 3200−3203. (d) Cotton, F. A.; Oldham, C.; Walton, R. A. *Inorg. Chem.* **1967**, *6*, 214−223. (e) Ross, E. P.; Dobson, G. R. *Inorg. Chem.* **1967**, *6*, 1256−1257. (f) Houk, L. W.; Dobson, G. R. *J. Chem. Soc. A* **1968**, 1846−1849. (g) Forbus, N. P.; Brown, T. L. *Inorg. Chem.* **1981**, *20*, 4343−4347. (h) Habib, M.; Trujillo, H.; Alexander, C. A.; Storhoff, B. N. *Inorg. Chem.* **1985**, *24*, 2344−2349. (i) Gutiérrez Alonso, A.; Ballester Reventós, L. *J. Organomet. Chem.* **1988**, *338*, 249−259. (j) Pringle, P. G.; Smith, M. B. *J. Chem. Soc., Chem. Commun.* **1990**, 1701−1702. (k) Khan, M. N. I.; King, C.; Fackler, J. P., Jr.; Winpenny, R. E. P. *Inorg. Chem.* **1993**, *32*, 2502−2505. (l) Liu, C. W.; Pan, H.; Fackler, J. P., Jr.; Wu, G.; Wasylishen, R. E.; Shang, M. *J. Chem. Soc., Dalton Trans.* **1995**, 3691−3697. (m) Rosi, L.; Bini, A.; Frediani, P.; Bianchi, M.; Salvini, A. *J. Mol. Catal. A: Chem.* **1996**, *112*, 367−383. (n) Hussain, M. S.; Al-Arfaj, A. R.; Akhtar, M. N.; Isab, A. A. *Polyhedron* **1996**, *15*, 2781−2785. (o) Orpen, A. G.; Pringle, P. G.; Smith, M. B.; Worboys, K. *J. Organomet. Chem.* **1998**, *550*, 255−266. (p) Pruchnik, F. P.; Smolenski, P.; Wajda-Hermanowicz, K. *J. Organomet. Chem.* **1998**, *570*, 63−69. (q) Blin, J.; Braunstein, P.; Fischer, J.; Kickelbick, G.; Knorr, M.; Morise, X.; Wirth, T. *J. Chem. Soc., Dalton Trans.* **1999**, 2159−2170. (r) Chantler, J.; Fanwick, P. E.; Walton, R. A. *Inorg. Chim. Acta* **2000**, *305*, 215−220. (s) Smolenski, P. *J. Organomet. Chem.* **2011**, *696*, 3867−3872. (t) Boschi, A.; Cazzola, E.; Uccelli, L.; Pasquali, M.; Ferretti, V.; Bertolasi, V.; Duatti, A. *Inorg. Chem.* **2012**, *51*, 3130−3137. (u) Kihara, K.; Suzuki, T.; Kita, M.; Sunatsuki, Y.; Kojima, M.; Takagi, H. D. *Bull. Chem. Soc. Jpn.* **2012**, *85*, 1160−1166.

(5) For examples of donors containing longer aliphatic spacers, $Ph_2P(CH_2)_nCN$ ($n \geq 3$), see: (a) Storhoff, B. N.; Harper, D. P.; Saval, I. H.; Worstell, J. H. *J. Organomet. Chem.* **1981**, *205*, 161−166. (b) Pitter, S.; Dinjus, E.; Jung, B.; Görls, H. *Z. Naturforsch. B, Chem. Sci.* **1996**, *51*, 934−946.

(6) (a) Payne, D. H.; Frye, H. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 73−77. (b) Hatano, M.; Asai, T.; Ishihara, K. *Chem. Lett.* **2006**, *35*, 172−173. (c) Kawatsura, M.; Yamamoto, M.; Namioka, J.; Kajita, K.; Hirakawa, T.; Itoh, T. *Org. Lett.* **2011**, *13*, 1001−1003 and refs 4h and 5a.

(7) For complexes featuring the analogous di- and trinitriles, $PhP(C_6H_4CN\text{-}2)_2$ and $P(C_6H_4CN\text{-}2)_3$, see: (a) Chapman, S.; Kane-Maguire, L. A. P. *J. Chem. Soc., Dalton Trans.* **1995**, 2021−2026. (b) Elliott, M. E.; Kimmerling, T. S.; Zhu, L.; Storhoff, B. N.; Huffman, J. C. *Polyhedron* **1999**, *18*, 1603−1608. (c) Klein, H.-F.; Beck, R.; Florke, U.; Haupt, H.-J. *Eur. J. Inorg. Chem.* **2003**, 853−862. (d) Szesni, N.; Weibert, B.; Fischer, H. *Inorg. Chim. Acta* **2004**, *357*, 1789−1798.

(8) 2-(Diphenylphosphino)benzonitrile has been used as a synthetic precursor in the preparation of various phosphinoheterocyclic donors: (a) Koch, G.; Lloyd-Jones, G. C.; Loiseleur, O.; Pfaltz, A.; Pretot, R.; Schaffner, S.; Schnider, P.; von Matt, P. *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 206−210; *Chem. Abstr.* **1995**, *123*, 198930. (b) Baltzer, N.; Macko, L.; Schaffner, S.; Zehnder, M. *Helv. Chim. Acta* **1996**, *79*, 803−812. (c) Cahill, J. P.; Bohnen, F. M.; Goddard, R.; Kruger, C.; Guiry, P. J. *Tetrahedron: Asymmetry* **1998**, *9*, 3831−3839. (d) Kündig, E. P.; Meier, P. *Helv. Chim. Acta* **1999**, *82*, 1360. (e) Lait, S. M.; Parvez, M.; Keay, B. A. *Tetrahedron: Asymmetry* **2004**, *15*, 155−158.

(9) 1-(Diphenylphosphino)cyclopropanecarbonitrile: (a) Vinogradova, N. M.; Odinets, I. L.; Lyssenko, K. A.; Pasechnik, M. P.; Petrovskii, P. V.; Mastryukova, T. A. *Mendeleev Commun.* **2001**, 219−221. (b) Odinets, I. L.; Vinogradova, N. M.; Matveeva, E. V.; Golovanov, D. D.; Lyssenko, K. A.; Keglevich, G.; Kollár, L.; Roëschenthaler, G.-V.; Mastryukova, T. A. *J. Organomet. Chem.* **2005**, *690*, 2559−2570. 1-Cyano-2-(diphenylphosphino)cyclopentane and -cyclohexane: (c) Blinn, D. A.; Button, R. S.; Farazi, V.; Neeb, M. K.; Tapley, C. L.; Trehearne, T. E.; West, S. D.; Kruger, T. L.; Storhoff, B. N. *J. Organomet. Chem.* **1990**, *393*, 143−152. (d) Fredericks, E. J.; Gindling, M. J.; Kroll, L. C.; Storhoff, B. N. *J. Organomet. Chem.* **1994**, *465*, 289−296. 1,3,5-Tricyano-1,3,5-tris(diphenylphosphino)cyclohexane: (e) Mayer, H. A.; Stössel, P.; Fawzi, R.; Steimann, M. *Chem. Ber.* **1995**, *128*, 719−723. (f) Stössel, P.; Heins, W.; Mayer, H. A.; Fawzi, R.; Steinman, M. *Organometallics* **1996**, *15*, 3393−3403. (g) Heins, W.; Stössel, P.; Mayer, H. A.; Steinmann. *J. Organomet. Chem.* **1999**, *587*, 258−266.

(10) Phosphinonitrile Ph_2PCH_2CN easily undergoes deprotonation at the methylene group. The resulting C anion can be used as a ligand in transition-metal complexes. For a review, see: Braunstein, P. *Chem. Rev.* **2006**, *106*, 134−159.

(11) Barratt, D. S.; Hosseiny, A.; McAuliffe, C. A.; Stacey, C. *J. Chem. Soc., Dalton Trans.* **1985**, 135−139.

(12) Štěpnička, P. In *Ferrocenes: Ligands, Materials and Biomolecules*; Štěpnička, P., Ed.; Wiley: Chichester, U.K., 2008; Chapter 5, pp 177−204.

(13) Selected recent examples of Ph_2PfcY-type donors: (a) Y = OH: Atkinson, R. C. J.; Gibson, V. C.; Long, N. J.; White, A. J. P. *Dalton Trans.* **2010**, *39*, 7540−7546. (b) Y = $B(2,4,6\text{-}Me_3C_6H_2)_2$: Bebbington, M. W. P.; Bontemps, S.; Bouhadir, G.; Hanton, M. J.; Tooze, R. P.; van Rensburg, H.; Bourissou, D. *New J. Chem.* **2010**, *34*, 1556−1559. (c) Y = CH_2(benzimidazolium): Gülcemal, S.; Labande, A.; Daran, J.-C.; Çetinkaya, B.; Poli, R. *Eur. J. Inorg. Chem.* **2009**, 1806−1815. (d) Y = 2-Py, 3-Py, and CH_2(2-Py) (Py = pyridyl): Štěpnička, P.; Schulz, J.; Klemann, T.; Siemeling, U.; Císařová, I. *Organometallics* **2010**, *29*, 3187−3200. (e) Siemeling, U.; Klemann, T.; Bruhn, C.; Schulz, J.; Štěpnička, P. *Dalton Trans.* **2011**, *40*, 4722−4740. (f) Y = CH_2NMe_2: Štěpnička, P.; Zábranský, M.; Císařová, I. *ChemistryOpen* **2012**, *1*, 71−79. (g) Y = $CH{=}NR'$: Teo, S.; Weng, Z.; Hor, T. S. A. *J. Organomet. Chem.* **2011**, *696*, 2928−2934. (h) Y = CH_2PPh_2: Štěpnička, P.; Císařová, I.; Schulz, J. *Organometallics* **2011**, *30*, 4393−4403. (i) Štěpnička, P.; Císařová, I. *J. Organomet. Chem.* **2012**, *716*, 110−119. (j) Y = CH_2OMe: Štěpnička, P.; Císařová, I. *Dalton Trans.* **2013**, *42*, 3373−3389. (k) Y = CONHR (R = H, Cy, Ph, NH_2): Štěpnička, P.; Solařová, H.; Lamač, M.; Císařová, I. *J. Organomet. Chem.* **2010**, *695*, 2423−2431. (l) Štěpnička, P.; Solařová, H.; Císařová, I. *J. Organomet. Chem.* **2011**, *696*, 3727−3740. (m) Y = $CONHCH(R)CO_2Me$ and related compounds: Tauchman, J.; Císařová, I.; Štepnička, P. *Organometallics* **2009**, *28*, 3288−3302. (n) Tauchman, J.; Císařová, I.; Štěpnička, P. *Eur. J. Org. Chem.* **2010**, 4276−4287. (o) Tauchman, J.; Císařová, I.; Štěpnička, P. *Dalton Trans.* **2011**, *40*, 11748−11757. (p) Tauchman, J.; Therrien, B.; Süss-Fink, G.; Štěpnička, P. *Organometallics* **2012**, *31*, 3985−3994. (q) Y = $CONHCH_{(3-n)}(CH_2OH)_n$ (n = 1−3) and analogues: Schulz, J.; Císařová, I.; Štěpnička, P. *J. Organomet. Chem.* **2009**, *694*, 2519. (r) Schulz, J.; Císařová, I.; Štěpnička, P. *Eur. J. Inorg. Chem.* **2012**, 5000−5010. (s) Y = $CONH(CH_2)_nSO_3[HNEt_3]$ (n = 1−3): Schulz, J.; Císařová, I.; Štěpnička, P. *Organometallics* **2012**, *31*, 729−738.

(14) (a) Chien, S. W.; Hor, T. S. A. In *Ferrocenes: Ligands, Materials and Biomolecules*; Štěpnička, P., Ed.; Wiley: Chichester, U.K., 2008; Chapter 2, pp 33−116. (b) Gan, K.-S.; Hor, T. S. A. In *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science*; Togni, A., Hayashi, T., Eds.; Wiley-VCH: Weinheim, Germany, 1995; Chapter 1, pp 3−104; (c) Young, D. J.; Chien, S. W.; Hor, T. S. A. *Dalton Trans.* **2012**, *41*, 12655. (d) Bandoli, G.; Dolmella, A. *Coord. Chem. Rev.* **2000**, *209*, 161.

(15) Štěpnička, P.; Císařová, I. *Organometallics* **2003**, *22*, 1728−1740.

(16) Lamač, M.; Štěpnička, P. *Inorg. Chem. Commun.* **2006**, *9*, 319−321.

(17) Zirakzadeh, A.; Schuecker, R.; Weissensteiner, W. *Tetrahedron: Asymmetry* **2010**, *21*, 1494−1502.

(18) Fassbender, J.; Frank, W.; Ganter, C. *Eur. J. Inorg. Chem.* **2012**, 4356−4364.

(19) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; Wiley: New York, 1999; Chapter 17-H, p 858.

(20) Štěpnička, P.; Baše, T. *Inorg. Chem. Commun.* **2001**, *4*, 682−687.

(21) This standard approach was also employed in the original preparations of FcCH═NOH: (a) Lindsay, J. K.; Hauser, C. R. *J. Org. Chem.* **1957**, *22*, 355−358. (b) Graham, P. J.; Lindsey, R. V.; Parshall, G. W.; Peterson, M. L.; Whitman, G. M. *J. Am. Chem. Soc.* **1957**, *79*, 3416−3420.

(22) Singh, M. K.; Lakshman, M. L. *J. Org. Chem.* **2009**, *74*, 3079−3084.

(23) A one-pot procedure based on the reaction of aldehydes with $NH_2OH \cdot HCl/KI/ZnO$ in hot acetonitrile, which was shown to work well with (unsubstituted) ferrocenecarboxaldehyde, gave disappointing results in the case of **1**. Using this procedure, nitrile **3** was not only isolated in a low yield but was also contaminated with the difficult-to-separate starting aldehyde. See: Kivrak, A.; Zora, M. *J. Organomet. Chem.* **2007**, *692*, 2346−2349.

(24) Kitson, R. E.; Griffith, N. E. *Anal. Chem.* **1952**, *24*, 334−337.

(25) E_{pa} is the anodic peak potential in cyclic voltammetry. The value was recorded at a scan rate of 0.1 V s^{-1} in 1,2-dichloromethane solution (c = 0.5 mM) containing 0.1 M $Bu_4N[PF_6]$ as the supporting electrolyte using a μAutolab III instrument (Eco Chemie, Utrecht, The Netherlands), a Pt disk working electrode, a Pt sheet auxiliary electrode, and a Ag/AgCl (3 M KCl) reference electrode.

(26) Electrochemical oxidations of phosphinoferrocenes to the respective ferrocenia are often associated with followup chemical reactions that render the redox response irreversible. For selected examples, see: (a) Ong, J. H. L.; Nataro, C.; Golen, J. A.; Rheingold, A. L. *Organometallics* **2003**, *22*, 5027−5032. (b) Zanello, P.; Opromolla, G.; Giorgi, G.; Sasso, G.; Togni, A. *J. Organomet. Chem.* **1996**, *506*, 61−65. (c) Pilloni, G.; Longato, B.; Corain, B. *J. Organomet. Chem.* **1991**, *420*, 57−65. (d) Podlaha, J.; Štěpnička, P.; Ludvík, J.; Císařová, I. *Organometallics* **1996**, *15*, 543−550.

(27) Crystals of **3O** were isolated accidentally from an attempted preparation of $[Cu_2(\mathbf{3})_4][BPh_4]_2$ by the metathesis of in situ formed $[Cu_2(\mathbf{3})_4][PF_6]_2$ with solid $Na[BPh_4]$ in dichloromethane during crystallization of the crude reaction mixture from ethyl acetate/hexane.

(28) Ferguson, G.; Bell, W.; Glidewell, C. *J. Organomet. Chem.* **1991**, *405*, 229−236.

(29) The electron density corresponding to the lone electron pair can be refined as a He atom (two electrons), although with a large displacement factor $[U_{iso}(He)/U_{eq}(P) \approx 10]$. The refinement leads to a reasonable geometry [P···He 1.25(2) Å, C—P···He angles ca. 115−118°] and markedly decreases the residual electron density (0.96 → 0.33 e $Å^{-3}$). However, the reliability factor (R) for the observed diffractions changes only marginally (from 2.72% to 2.63%).

(30) Compare the Hammett σ_p constants for PPh_2 and $P(O)Ph_2$, at 0.19 and 0.53, respectively. Data from: Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165−195.

(31) Ossola, F.; Tomasin, P.; Benetollo, F.; Foresti, E.; Vigato, P. A. *Inorg. Chim. Acta* **2003**, *353*, 292−300.

(32) Bell, W.; Ferguson, G.; Glidewell, C. *Acta Crystallogr. C: Cryst. Struct. Commun.* **1996**, *52*, 1928−1930.

(33) Adeleke, J. A.; Liu, L.-K. *Acta Crystallogr. C: Cryst. Struct. Commun.* **1993**, *49*, 680−682.

(34) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533−3539.

(35) Pearson, R. G. *Inorg. Chem.* **1988**, *27*, 734−740.

(36) Pilloni, G.; Corain, B.; Degano, M.; Longato, B.; Zanotti, G. *J. Chem. Soc., Dalton Trans.* **1993**, 1777−1778.

(37) Hathaway, B. J. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: New York, 1987; Vol. 5, Chapter 53, p 533−774.

(38) Representative early examples: (a) L = PPh_3: Lippard, S. J.; Ucko, D. A. *Inorg. Chem.* **1968**, *7*, 1051−1056 and references therein. (b) Gill, J. T.; Mayerle, J. J.; Welcker, P. S.; Lewis, D. F.; Ucko, D. A.; Barton, D. J.; Stowens, D.; Lippard, S. J. *Inorg. Chem.* **1976**, *15*, 1155−1168 (crystal structure determination). (c) L = PMe_3: Schmidbaur, H.; Adlkofer, J.; Schwirten, K. *Chem. Ber.* **1972**, *105*, 3382−3388.

(39) (a) Lippard, S. J.; Mayerle, J. J. *Inorg. Chem.* **1972**, *11*, 753−759. (b) Fife, D. J.; Moore, W. M.; Morse, K. W. *Inorg. Chem.* **1984**, *23*, 1684−1691.

(40) Coordination of a nitrile usually results in a shift of the C≡N stretching band toward higher energies because of the removal of electron density from a weakly antibonding molecular orbital (σ-donation of the lone pair at N). The associated π-back-donation, which has the opposite effect of increasing the population of antibonding π-orbitals, is relatively weak. See: (a) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds. Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry*, 5th ed.; Wiley: New York, 1997; Section III-15, p 105−115. (b) Kuznetsov, M. L. *Russ. Chem. Rev.* **2002**, *71*, 265−282.

(41) According to DFT calculations, the closed heterocubane structures represent global energy minima for the $[CuX(PH_3)]_4$ tetramers: Schwerdtfeger, P.; Krawczyk, R. P.; Hammerl, A.; Brown, R. *Inorg. Chem.* **2004**, *43*, 6707−6716.

(42) Vega, A.; Saillard, J.-Y. *Inorg. Chem.* **2004**, *43*, 4012−4018.

(43) (a) Štěpnička, P.; Gyepes, R.; Podlaha, J. *Collect. Czech. Chem. Commun.* **1998**, *63*, 64−74. (b) Štěpnička, P.; Císařová, I. *Collect. Czech. Chem. Commun.* **2006**, *71*, 215−236.

(44) The same set of symmetry elements is distributed differently in the crystal lattices of **7** and **8** (see Supporting Information, Figure S6).

(45) The halide bridges are asymmetrical, with slightly different distances to the two bridged Cu atoms [Δ(Cu−X) ≈ 0.08 Å].

(46) Mainly C15—H15···F3&(x − 1, y, z) with C15···F3 = 3.399(3) Å and C22—H22···F4&(1 − x, 2 − y, 1 − z) with C22···F4 = 3.333(3) Å.

(47) The reaction of $[Cu(MeCN)_4][BF_4]$ with 3 equiv of **3** in CH_2Cl_2 afforded a mixture of unreacted **3** and $[\mathbf{10}][BF_4]_2$, from which the latter compound separated upon crystallization.

(48) $[Cu(MeCN)_4][B(C_6F_5)_4]$ was prepared according to the literature: Liang, H.-C.; Kim, En.; Incarvito, C. D.; Rheingold, A. L.; Karlin, K. D. *Inorg. Chem.* **2002**, *41*, 2209−2212. Other $[Cu(MeCN)_4]^+$ salts were commercially available.

(49) According to a search in the Cambridge Structural Database, version 5.33, in Nov 2011 with updates from Nov 2011 and from Feb, May, and Aug 2012.

(50) Lastra, E.; Gamasa, M. P.; Gimeno, J.; Lanfranchi, M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1989**, 1499−1506.

(51) Abdul Jalil, M.; Yamada, T.; Fujinami, S.; Honjo, T.; Nishikawa, H. *Polyhedron* **2001**, *20*, 627−633.

(52) The reaction of $Cu[BF_4]_2$ with an excess of 2-(diphenylphosphino)-1-benzylimidazole yielded a similar complex containing one η^1-coordinated BF_4 anion per the metal center (Cu−F ≈ 2.7−2.8 Å): Bachechi, F.; Burini, A.; Fontani, M.; Galassi, R.; Machioni, A.; Pietroni, B. R.; Zanello, P.; Zuccaccia, C. *Inorg. Chim. Acta* **2001**, *323*, 45−54.

(53) Maekawa, M.; Munakata, M.; Kitagawa, S.; Yonezawa, T. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2286−2288.

(54) Cordero, B.; Gómez, V.; Platero-Prats, A. E.; Revés, M.; Echeverría, J.; Cremades, E.; Barragán, F.; Alvarez, S. *Dalton Trans.* **2008**, 2832.

(55) With the exception of the value determined for **7** [C≡N = 1.137(4) Å at 250 K], the length of the C≡N bond remained statistically constant in the *entire* series of structurally characterized compounds (ca. 1.144 Å at 150 K). The C—C≡N angle spanned the range from 176.6(2)° to 179.1(2)°.

(56) For an overview of the chemistry of ferrocene ligands, see: *Ferrocenes: Ligands, Materials and Biomolecules*; Štěpnička, P., Ed.; Wiley: Chichester, U.K., 2008.

(57) Shriver, D. F. *The Manipulation of Air-Sensitive Compounds*; McGraw-Hill: New York, 1969.