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Tris(pentafluoroethyl)difluorophosphorane for fluoride abstraction and ligand exchange reactions of N-heterocyclic carbene and cyclic alkyl(amino) carbene copper(I) fluorides†

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The synthesis and structural characterization of a variety of N-heterocyclic carbene (NHC)- and cyclic (alkyl)(amino)carbene (cAAC)-ligated cationic copper(I) complexes, featuring the weakly coordinating tris(pentafluoroethyl)trifluorophosphate counteranion (**FAP**$^-$ anion, $[(C_2F_5)_3PF_3]^-$) are reported. Starting with the complex [(IDipp)Cu(C_6Me_6)]$^+$**FAP**$^-$ (**IIa**) reported previously, (S. A. Föhrenbacher, M. J. Krahfuss, L. Zapf, A. Friedrich, N. V. Ignat'ev, M. Finze and U. Radius, *Chem. – Eur. J.*, 2021, **27**, 3504-3516) a series of mononuclear complexes [(IDipp)Cu(LB)]$^+$**FAP**$^-$ (IDipp = 1,3-bis(2,6-di-*iso*-propylphenyl)-imidazolin-2-ylidene) were obtained *via* ligand exchange of C_6Me_6 with neutral two valence electron (2 VE) donor molecules (LB = NH_3, **1**; $C_6H_{12}N_2$ = DABCO, **2**; $C_7H_{10}N_2$ = DMAP, **3**; $C_4H_4N_2$ = pyrazine, **4**; $C_{13}H_9N$ = acridine, **5**; η^1-O═$C_{13}H_9N$ = acridone, **6**; $C_4H_{10}S$ = SEt_2, **7**; C_4H_8S = THT, **8**; PCy_3, **9**), alongside the dinuclear species [{(IDipp)Cu}$_2$($C_2N_3H_3$)$_2$]$^{2+}$2**FAP**$^-$ (**10**) with 1,2,4-triazole. In a parallel strategy, [(cAAC^{Me})Cu(C_6Me_6)]$^+$**FAP**$^-$ (**IIb**) was employed as precursor for Cu(I) complex formation, leading to [(cAAC^{Me})Cu(LB)]$^+$**FAP**$^-$ (LB = $C_7H_{10}N_2$, **13**; $C_4H_{10}S$, **14**) and the dinuclear complexes [{(cAAC^{Me})Cu}$_2$($C_6H_{12}N_2$)]$^{2+}$**2FAP**$^-$ (**11**) and [{(cAAC^{Me})Cu}$_2$($C_4H_4N_2$)]$^{2+}$2**FAP**$^-$ (**12**). Additionally, the reaction of [(carbene)CuF] with $(C_2F_5)_3PF_2$ in the presence of different 2 VE donor ligands induced fluoride replacement with a 2 VE donor ligand (LB). This strategy facilitated the isolation of a broad range of complexes of the type [(carbene)Cu(LB)]$^+$**FAP**$^-$, including [(IDipp)Cu(LB)]$^+$**FAP**$^-$ (LB = (N≡CMe)$_2$, **16**; N≡CPh, **17**; NH_2Ph, **18**; $NHPh_2$, **21**; NC_5H_5, **22**; $NC_5H_3F_2$, **24**; $NC_5H_2F_3$, **25**; η^1-O═CPh_2, **27**), [(SIDipp)Cu(NH_2Ph)]$^+$**FAP**$^-$ (**19**) (SIDipp = 1,3-bis(2,6-di-*iso*-propylphenyl)-imidazolidin-2-ylidene) and [(cAAC^{Me})Cu(LB)]$^+$**FAP**$^-$ (cAAC^{Me} = 1-(2,6-di-*iso*-propylphenyl)-3,3,5,5-tetramethyl-pyrrolidin-2-ylidene; LB = N≡CMe, **15**; NH_2Ph, **20**; NC_5H_5, **23**; THF, **28**). Additionally, the dinuclear complex [{(IDipp)Cu(μ-ONC_5H_5)}$_2$]$^{2+}$2**FAP**$^-$ (**26**) was obtained upon reaction with pyridine-*N*-oxide. In all cases the carbene ligand stayed intact and the formation of Lewis acid/base pairs of the 2 VE ligand and $(C_2F_5)_3PF_2$ was never observed. As a result, mixtures of [(carbene)CuF] and $(C_2F_5)_3PF_2$ may serve as synthons for [(carbene)Cu]$^+$, as demonstrated in this work.

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Introduction

Lewis acids (LAs) were originally defined by Gilbert N. Lewis as electron pair acceptors that exhibit a strong propensity to form bonds with electronegative electron pair donors, known as Lewis bases (LBs).[2] The combination of a LA and a LB with both low to moderate steric demand typically results in the formation of classical Lewis acid/base adducts, characterized by stable covalent bonding interactions. However, when sterically more hindered LA/LB entities are combined, such as PPh_3 with $B(C_6F_5)_3$, intramolecular interactions are reduced, leading to the formation of weakly bound adducts. These systems often exhibit elongated bond distances, equilibria between the free acid and base, or structural rearrangement, as exemplified

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by the zwitterionic species $Ph_3PH–C_6F_4–BF(C_6F_5)_2$.[3] Such systems are classified as Frustrated Lewis Pairs (FLPs), where steric constraints prevent complete Lewis acid/base adduct formation, resulting in highly reactive centers with unique chemical properties. This phenomenon enables the activation of otherwise inert small molecules, including H_2,[4] CO,[5] CO_2,[6,7] N_2O,[7,8] or SO_2.[9] To further rationalize the formation of Lewis acid/base adducts while accounting for steric effects, we recently developed a novel and, to date, the first generalizable and experimentally accessible approach.[10] The Lewis Acid/Base Repulsion (LAB-Rep) model utilizes the percent buried volume ($\%V_{bur}$) as a quantitative measure of steric hindrance and relies on readily available structural data, such as crystallographic information or computationally derived structures. This model enables the estimation of steric constraints that may impede Lewis acid/base interactions, providing valuable insights, particularly in the context of FLP chemistry.

The chemistry of Lewis acid/base combinations involving *N*-heterocyclic carbenes (NHCs) has been extensively studied, particularly in the context of classical adduct-type complexes with p-block elements. To date, numerous well-characterized examples exist, most of them with group 13 and 15 Lewis acids, such as BF_3, $AlCl_3$, PF_5, AsF_5, and SbF_5. However, Lewis acid/base adducts of phosphoranes (PR_5) with NHCs remain comparatively rare, and only a limited number exhibit FLP behavior.[11] In 2021, we expanded the scope of such systems by isolating a series of NHC-phosphorane adducts $(C_2F_5)_3PF_2·NHC$ *via* the straightforward reaction of free (small) NHCs with the readily available and highly Lewis-acidic tris(pentafluoroethyl) difluorophosphorane, $(C_2F_5)_3PF_2$, in Et_2O. Furthermore, mixtures of $(C_2F_5)_3PF_2$ with sterically demanding NHCs, such as I*t*Bu (I*t*Bu = 1,3-di-*tert*-butylimidazolin-2-ylidene), IDipp, and SIDipp, exhibited FLP reactivity, facilitating the deprotonation of acetonitrile and other C–H acidic compounds (*e.g.*, acetone, ethyl acetate) to form the corresponding imidazolium salts and $[(C_2F_5)_3PF_2(R)]^-$ (R = CH_2CN, $OC({=}CH_2)CH_3$, CH_2CO_2Et).[12]

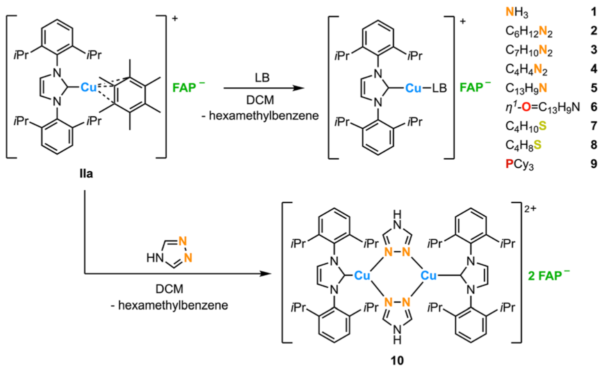
Recently, we reported on the reaction of $(C_2F_5)_3PF_2$ with the copper fluoride complexes [(IDipp)CuF] (**Ia**), [(SIDipp)CuF] (**Ib**) and $[(cAAC^{Me})CuF]$ (**Ic**) in the presence of various carbon-based ligands LB, such as alkynes and benzenes.[13] This reaction facilitated fluoride transfer, yielding the corresponding tris(pentafluoroethyl)trifluorophosphate (**FAP**$^-$, $[(C_2F_5)_3PF_3]^-$) salts of the copper complex cations $[(carbene)Cu(LB)]^+$. Due to the relatively weak interaction between the neutral carbon co-ligand and the metal center, these complexes serve as isolable synthons for cationic $[(carbene)Cu]^+$. Furthermore, the hexamethylbenzene complexes $[(IDipp)Cu(C_6Me_6)]^+$**FAP**$^-$ (**IIa**) and $[(cAAC^{Me})Cu(C_6Me_6)]^+$**FAP**$^-$ (**IIb**) were evaluated for their catalytic performance and demonstrated high efficacy as copper(I) catalysts in the cycloaddition reaction of benzyl azide and various terminal alkynes, yielding 1,4-disubstituted 1,2,3-triazoles.[13] These findings indicate that the phosphorane $(C_2F_5)_3PF_2$ exhibits sufficient Lewis acidity to abstract fluoride from transition metal complexes, thereby serving as a viable precursor for the synthesis of cationic transition metal species incorporating the **FAP**$^-$ counteranion.[1] Herein, we report the reactivity of **IIa** and **IIb** with selected different Lewis bases, focusing on the synthesis and characterization of *N*-heterocyclic carbene (NHC)- and cyclic (Alkyl)(amino) carbene (cAAC)-ligated copper cations featuring the weakly coordinating **FAP**$^-$ counteranion.

Results and discussion

The use of $[(carbene)Cu(C_6Me_6)]^+$ as synthon for $[(carbene)Cu]^+$

As our recent investigations already revealed that the hexamethylbenzene ligand of $[(IDipp)Cu(C_6Me_6)]^+$**FAP**$^-$ (**IIa**) can be exchanged easily by other 2 VE (valence electron) donors, such as THF,[1] we became interested in studying this behavior in more detail. Thus, we reacted **IIa** with selected nitrogen, oxygen, sulfur as well as phosphorus 2 VE donor ligands to probe their ability to replace C_6Me_6. Using this strategy, we isolated and fully characterized the copper **FAP**$^-$ salts $[(IDipp)Cu(LB)]^+$**FAP**$^-$ (LB = NH_3, **1**; $C_6H_{12}N_2$ = DABCO, **2**; $C_7H_{10}N_2$ = DMAP, **3**; $C_4H_4N_2$ = pyrazine, **4**; $C_{13}H_9N$ = acridine, **5**; η^1-$O{=}C_{13}H_9N$ = acridone, **6**; $C_4H_{10}S$ = SEt_2, **7**; C_4H_8S = THT, **8**; PCy_3, **9**) as well as the dinuclear complex $[\{(IDipp)Cu\}_2(C_2N_3H_3)_2]^{2+}2$**FAP**$^-$ (**10**) ($C_2N_3H_3$ = 1,2,4-triazole). All reactions occur at room temperature in dichloromethane or chloroform in yields of 40–87% (Scheme 1).

The most straight forward probe to confirm the formation of the complexes presented in Scheme 1 is a shift of the methyl resonances of the coordinated hexamethylbenzene in the ^1H NMR spectra of the reaction mixtures. After work-up, the ^1H NMR signal of hexamethylbenzene is absent. In the ^1H NMR spectrum of $[(IDipp)Cu(NH_3)]^+$**FAP**$^-$ (**1**) the four *i*Pr methyl groups of the Dipp ligand gave rise to two doublets at 1.24 and 1.25 ppm in $CDCl_3$ and the corresponding methine protons were observed as a septet at 2.49 ppm. The signals of both phenyl groups were split into doublets (CH_{meta}) and triplets (CH_{para}) and were detected at 7.34 and 7.56 ppm, respectively. Additionally,



Scheme 1 Synthesis of $[(IDipp)Cu(LB)]^+$**FAP**$^-$ (LB = NH_3, **1**; $C_6H_{12}N_2$ = DABCO, **2**; $C_7H_{10}N_2$ = DMAP, **3**; $C_4H_4N_2$ = pyrazine, **4**; $C_{13}H_9N$ = acridine, **5**; η^1-$O{=}C_{13}H_9N$ = acridone, **6**; $C_4H_{10}S$ = SEt_2, **7**; C_4H_8S = THT, **8**; PCy_3, **9**) (top) and $[\{(IDipp)Cu\}_2(C_2N_3H_3)_2]^{2+}2$**FAP**$^-$ (**10**, bottom, $C_2N_3H_3$ = 1,2,4, triazole) *via* substitution of hexamethylbenzene of $[(IDipp)Cu(C_6Me_6)]^+$**FAP**$^-$ (**IIa**).

the signals of the olefinic protons of the backbone were observed at 7.24 ppm. Besides the typical signals of the NHC ligand, the three protons of the ammine ligand in **1** gave rise to a broad resonance at 2.05 ppm in CDCl$_3$, which is similar to δ(^{1}H) of [(IDipp)Cu(NH$_3$)][BF$_4$] with 2.26 ppm.[14] There are neither significant differences in the ^{19}F and ^{31}P NMR spectra of the *mer*-**FAP$^-$** anion nor in the ^{1}H and ^{13}C{^{1}H} NMR spectra of the IDipp ligand in any of these compounds. Likewise, there is no mentionable variation in the chemical shifts in dependence of whether nitrogen, sulfur or phosphorous binds towards the copper center. Table 1 summarizes selected chemical shifts of the ^{1}H and ^{13}C{^{1}H} NMR spectra of the carbene ligand in the complex cations of [(IDipp)Cu(LB)]$^+$**FAP$^-$**.

In addition to multinuclear NMR spectroscopy, the NHC copper **FAP$^-$** salts were characterized by using IR spectroscopy, HRMS, as well as elemental analysis (see ESI†). Furthermore, single crystals of **1**, **3**, **5**, **6**, **7**, and **10** suitable for X-ray diffraction (XRD) were obtained (Fig. 1, 2 and Table 2). The central copper atom in the complexes **1**, **3**, **5**, and **7** is linearly coordinated by the IDipp ligand and the nitrogen or sulfur atom of the neutral donor ligand with C1–Cu–N1 angles of 177.19(15)° (**1**), 175.45(9)° (**3**), and 179.62(7)° (**5**) and a C1–Cu–S angle of 176.49(8)° (**7**). Interestingly, the acridone ligand in **6** coordinates *via* the oxygen atom. The C1–Cu–O angle of 169.58(9)° is slightly distorted from a linear arrangement and the Cu–O distance amounts to 1.8313(16) Å. In **1**, **3**, **5**, **6**, and **7** the distances between the carbenic carbon atom and the copper atom are very close (<3σ) (**1:** 1.882(3) Å, **3:** 1.875(2) Å, **5:** 1.8789(18) Å, **6:** 1.863(2) Å, **7:** 1.887(3) Å) and similar to d(Cu–C) in other copper NHC complexes reported by Nolan *et al.* (1.884(2)–1.956(10) Å).[15] The Cu–N1 bond distances in **1** (1.908(3) Å) and **5** (1.9038(15) Å) are slightly longer than d(Cu–N1) found in **3** (1.8785(19) Å), but within the standard range of precedent Cu–N bonds in NHC complexes.[16,17]

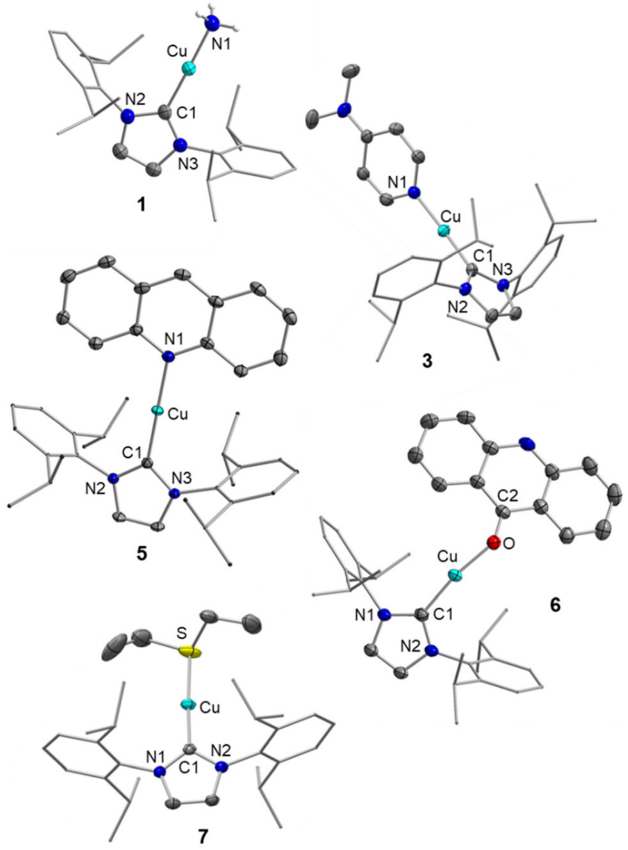


Fig. 1 Molecular structures of the complex cations of [(IDipp)Cu(NH$_3$)]$^+$**FAP$^-$** (**1**, top left), [(IDipp)Cu(C$_7$H$_{10}$N$_2$)]$^+$**FAP$^-$** (**3**, top right), [(IDipp)Cu(C$_{13}$H$_9$N)]$^+$**FAP$^-$** (**5**, middle left), [(IDipp)Cu(η^1-O═C$_{13}$H$_9$N)]$^+$**FAP$^-$** (**6**, middle right) and [(IDipp)Cu(C$_4$H$_{10}$S)]$^+$**FAP$^-$** (**7**, bottom) in the solid state (ellipsoids set at the 50% probability level; Dipp substituents are shown as wire-and-stick models). Hydrogen atoms (except the ones of NH$_3$ in **1**) and co-crystallized solvent molecules in the crystal structures of **1**, **3**, and **6** are omitted for clarity. Only one of two independent molecules in the asymmetric unit of **1** and **3** are shown. Selected bond length and angles are given in Table 2 and Fig. S1–S5 in the ESI.†

The Cu–S bond distance of the central copper atom to sulfur in **7** of 2.1705(8) Å is similar to values observed for [(IMes)Cu(SSi(iPr)$_3$)] (2.1336(4) Å) or [(IMes)Cu(SC(O)CH$_3$)] (2.1483(9) Å).[18] The dinuclear complex **10** crystallizes in the monoclinic space group $P2_1/m$ with one dinuclear dicationic complex [{(IDipp)Cu}$_2$(C$_2$N$_3$H$_3$)$_2$]$^{2+}$, two *mer*-isomer **FAP$^-$** counteranions, and three solvent molecules in the unit cell. Thus, a crystallographically imposed mirror plane is located perpendicular through the atoms N5 and N6. The Cu–C1 distance of 1.937(6) Å is slightly longer than the distances observed in the related mononuclear compounds discussed before (Table 2). Both [(IDipp)Cu]$^+$ moieties are bridged by two 1,2,4-triazole ligands with angles of C1–Cu1–N3 128.50(19)° and C1–Cu1–N4 132.12(19)°, respectively, and bond distances of 2.038(5) and

Table 1 Selected ^{1}H and ^{13}C{^{1}H} NMR chemical shifts [ppm] of the IDipp ligands of **1**–**10** in CDCl$_3$

	δ (^{13}C{^{1}H}) N–*C*–N	δ (^{1}H) aryl-C*H$_{para}$*	δ (^{1}H) aryl-C*H$_{meta}$*	δ (^{1}H) N–C*H*–C*H*–N	δ (^{1}H) iPr–C*H*	δ (^{1}H) iPr–C*H$_3$*
1	177.5	7.56	7.34	7.24	2.49	1.24/1.25
2	176.6	7.56	7.34	7.28	2.44	1.21/1.26
3	178.3	7.57	7.36	7.29	2.55	1.24/1.27
4	177.2	7.60	7.35	7.29	2.51	1.07/1.25
5	177.5	7.57	7.54	7.50	2.67	1.17/1.33
6	177.9	7.59	7.38	7.31	2.62	1.26/1.28
7	176.2	7.56	7.35	7.32	2.50	1.22/1.27
8	176.3	7.58	7.36	7.32	2.49	1.21/1.27
9	178.0	7.53	7.34	7.32	2.54	1.24/1.26
10	181.8	7.65	7.35	7.23	2.52	0.94–1.06/1.22

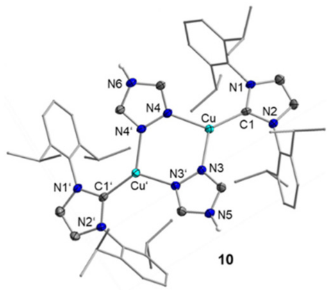
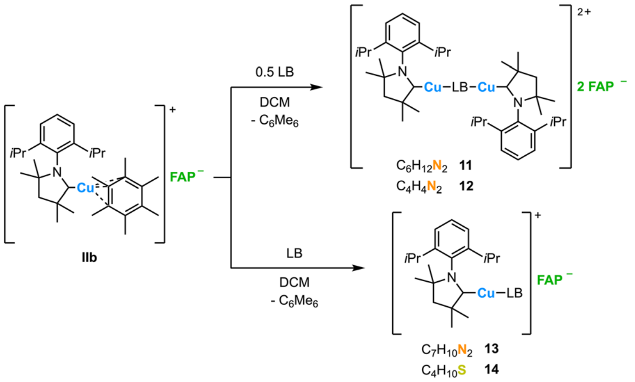


Fig. 2 Molecular structure of the complex cation of [{(IDipp)Cu}$_2$(C$_2$N$_3$H$_3$)$_2$]$^{2+}$2**FAP**$^-$ (**10**) in the solid state (ellipsoids set at the 50% probability level; Dipp substituents are shown as wire-and-stick models). Hydrogen atoms except for the ones bound to N5 and N6 and a co-crystallized solvent molecule are omitted for clarity. Selected bond length and angles are collected in Table 2 and Fig. S6 in the ESI.†

Table 2 Selected bond lengths [Å] and angles [°] of the copper carbene-complexes **1**, **3**, **5**, **6**, **7**, **10**, **11**, and **12**

	Cu–C1	Cu–N/O/S	C1–Cu–N/O/S
1	1.882(3)	1.908(3)	177.19(15)
3	1.875(2)	1.8785(19)	175.45(9)
5	1.8789(18)	1.9038(15)	179.62(7)
6	1.863(2)	1.8313(16)	169.58(9)
7	1.887(3)	2.1705(8)	176.49(8)
10	1.937(6)	2.038(5)	128.50(19)
		2.035(4)	132.12(19)
11	1.900(4)	1.927(3)	176.68(15)
12	1.890(3)	1.906(2)	170.45(12)



Scheme 2 Synthesis of [{(cAAC^{Me})Cu}$_2$(C$_6$H$_{12}$N$_2$)]$^{2+}$2**FAP**$^-$ (**11**), [{(cAAC^{Me})Cu}$_2$(C$_4$H$_4$N$_2$)]$^{2+}$2**FAP**$^-$ (**12**), [(cAAC^{Me})Cu(C$_7$H$_{10}$N$_2$)]$^+$**FAP**$^-$ (**13**), and [(cAAC^{Me})Cu(C$_4$H$_{10}$S)]$^+$**FAP**$^-$ (**14**) *via* hexamethylbenzene substitution of [(cAAC^{Me})Cu(C$_6$Me$_6$)]$^+$**FAP**$^-$ (**IIb**).

2.035(4) Å between Cu and N3 or N4. These distances are longer compared to *d*(Cu–N) in **1**, **3**, and **5** (1.88–1.91 Å) due to the higher steric demand and the increased coordination number at copper in **10**.

As the hexamethylbenzene ligand in the IDipp complex **IIa** is easily replaced by various 2 VE donor ligands, we expanded our study to the related cAAC-ligated complex [(cAAC^{Me})Cu(C$_6$Me$_6$)]$^+$**FAP**$^-$ (**IIb**). The reaction of **IIb** with DABCO or pyrazine resulted in the formation of dinuclear complexes [{(cAAC^{Me})Cu}$_2$(C$_6$H$_{12}$N$_2$)]$^{2+}$2**FAP**$^-$ (**11**) and [{(cAAC^{Me})Cu}$_2$(C$_4$H$_4$N$_2$)]$^{2+}$2**FAP**$^-$ (**12**) in 62% (**11**) and 68% (**12**) yield, respectively. The reaction of **IIb** with DMAP or SEt$_2$ afforded the mononuclear complexes [(cAAC^{Me})Cu(C$_7$H$_{10}$N$_2$)]$^+$**FAP**$^-$ (**13**) and [(cAAC^{Me})Cu(C$_4$H$_{10}$S)]$^+$**FAP**$^-$ (**14**) in 57% (**13**) and 74% (**14**) yield (Scheme 2).

The complexes **11–14** were characterized by multinuclear NMR spectroscopy, elemental analysis, IR spectroscopy, and HRMS (**13**, **14**). In analogy to the IDipp copper complexes **1–10** introduced above, the ^{19}F and ^{31}P NMR chemical shifts of *mer*-**FAP**$^-$ and the ^{1}H and ^{13}C{^{1}H} chemical shifts of the cAAC^{Me} ligand of these compounds did not reveal significant differences. In case of **11** and **12**, the signals for the carbene ligand were observed with a relative intensity of 2 with respect to the signals of DABCO or pyrazine. These findings match the results of the elemental analysis and X-ray diffraction, which are in accordance with dinuclear structures in solution and in the solid state. Single crystals of **11** and **12** suitable for XRD were obtained by diffusion of *n*-hexane into solutions of **11** or **12** in dichloromethane (Fig. 3 and Table 2). Both complexes **11** and **12** crystallize in the monoclinic space group *P*2$_1$/*n* and are located on an inversion center. Besides the coordination of the carbene ligand, the copper atom is coordinated to the nitrogen atom N1 of the DABCO or pyrazine ligand, respectively, with almost linear C1–Cu–N1 angles of 176.68(15)° (**11**) and 170.45(12)° (**12**). A comparison of both closely related structures shows that the Cu–C1 bond lengths (**11**: 1.900(4) Å; **12**: 1.890(3) Å) and the Cu–N1 distances (**11**: 1.927(3) Å; **12**: 1.906(2) Å) differ only marginally.

Fluoride abstraction in the presence of neutral N- and O-donor ligands

Previous studies demonstrated that the percent buried volume model (%*V$_{Bur}$*), developed by Cavallo and colleagues, serves as a powerful descriptor for evaluating the steric properties of

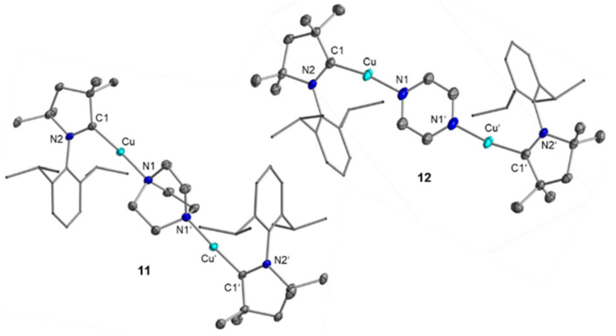
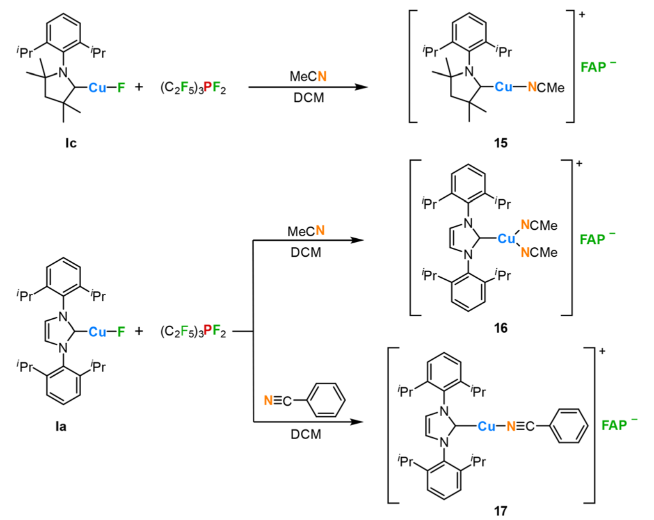


Fig. 3 Molecular structures of the complex cations of [{(cAAC^{Me})Cu}$_2${C$_6$H$_{12}$N$_2$}]$^{2+}$2**FAP**$^-$ (**11**; left) and [{(cAAC^{Me})Cu}$_2${C$_4$H$_4$N$_2$}]$^{2+}$2**FAP**$^-$ (**12**; right) in the solid state (ellipsoids set at the 50% probability level; Dipp ligands are shown as wire-and-stick models). Hydrogen atoms are omitted for clarity. Selected bond length and angles are collected in Table 2 and Fig. S7, S8 in the ESI.†

N-heterocyclic carbenes, phosphines, and related ligands in transition metal chemistry.[19] Building on this approach, we introduced the LAB-Rep model, designed to assess steric repulsion between specific Lewis acid and base pairs.[10] According to this model, the favored *mer-trans* isomer of $(C_2F_5)_3PF_2$–LB, with a percent buried volume of 67.7%V_{bur}, is considered to be very bulky, rendering the formation of LA/LB adducts with sterically hindered Lewis bases unlikely. Building on our previous studies,[1] we employed the phosphorane $(C_2F_5)_3PF_2$ for the fluoride abstraction from fluoride complexes [(carbene)CuF], featuring IDipp, SIDipp, and cAAC^{Me} as carbene ligands, in the presence of a nucleophile. In the following we explore the question whether $(C_2F_5)_3PF_2$ can assist fluoride exchange reactions in complexes [(carbene)CuF] with 2 VE ligands, or if (i) a replacement of the neutral carbene ligand with the 2 VE ligand or (ii) the formation of Lewis acid/base pair of the 2 VE ligand and $(C_2F_5)_3PF_2$ prevails.

The reaction of [(cAAC^{Me})CuF] (**Ic**) with $(C_2F_5)_3PF_2$ in a solvent mixture of acetonitrile and dichloromethane afforded the acetonitrile adduct [(cAAC^{Me})Cu(N≡CMe)]$^+$**FAP**$^-$ (**15**), whereas the reaction of [(IDipp)CuF] (**Ia**) under similar conditions led to the three-coordinated complex [(IDipp)Cu(N≡CMe)$_2$]$^+$**FAP**$^-$ (**16**) (Scheme 3). This observation may seem contradictory to the assumption of the LAB-Rep model, as acetonitrile is considered a sterically non-demanding LB, and the formation of a phosphorane-acetonitrile adduct would be expected. However, the pronounced fluoride ion affinity of the phosphorane (405.5 kJ mol^{-1})[1] seemingly favors fluoride abstraction over adduct formation, thus leading to the generation of [(IDipp)Cu(N≡CMe)$_2$]$^+$ and the weakly coordinating **FAP**$^-$ anion.

The sterically more demanding benzonitrile yielded the dicoordinated copper(I) complex [(IDipp)Cu(N≡CPh)]$^+$**FAP**$^-$ (**17**). All reactions proceeded in good yields of 69% (**15**), 81% (**16**) and 82% (**17**), respectively (Scheme 3). Compounds **15–17** were fully characterized by ^{1}H, ^{13}C{^{1}H}, ^{19}F, and ^{31}P NMR spectroscopy, IR spectroscopy, HRMS, and elemental analysis. The ^{19}F and ^{31}P NMR spectra confirm the formation of the *mer*-isomer of the **FAP**$^-$ anion, consistent with other previously reported **FAP**$^-$ complex salts.[1,20]



Scheme 3 Synthesis of [(carbene)Cu(LB)]$^+$**FAP**$^-$ complexes **15–17** *via* fluoride ion abstraction from [(carbene)CuF] using $(C_2F_5)_3PF_2$ in the presence of N-donor ligands.

The IR spectrum of **17** displays a characteristic band at 2275 cm^{-1} for the N≡C stretching vibration, which is shifted 40 cm^{-1} to higher wavenumbers compared to non-coordinated benzonitrile (2234 cm^{-1}).[21] This shift can be rationalized by coordination to a Lewis-acidic center in conjunction with negligible π-back-bonding from copper to benzonitrile. Significant π-back-bonding would lead to a decrease in $\tilde{\nu}$(C≡N). Higher wavenumbers for the C≡N stretch have been reported for other *end-on* coordinated Cu(I) complexes, previously.[22] We discussed these phenomena for other cationic copper complexes previously. For example, the related complex [(IDipp)Cu(PhC≡CPh)]$^+$**FAP**$^-$ shows a lack of π-back-bonding from the cationic [(IDipp)Cu]$^+$ complex fragment to the alkyne, which was evident from very similar δ(^{13}C) shifts of the C≡C unit of the free and coordinated alkyne ($\Delta\delta_{alkyne}$ ~0.5 ppm), which indicates a rather weak copper–alkyne interaction.[13]

Single crystals suitable for XRD were obtained for compounds **16** and **17**, and selected bonding parameters of the molecular structures (Fig. 4) are summarized in Table 3. The cationic complex [(IDipp)Cu(N≡CMe)$_2$]$^+$ in **16** exhibits a distorted trigonal-planar geometry at the metal atom with angels of 121.11(9)° (C1–Cu–N1), 131.08(10)° (C1–Cu–N2), and 107.71(9)° (N1–Cu–N2). In contrast, the copper atom in **17** adopts a linear environment with a C1–Cu–N1 angle of 178.03(7)°. Due to the reduced coordination number of copper in **17**, the Cu–N1 distance of 1.8453(14) Å is significantly shorter than those observed in the tri-coordinated complex **16** (1.967(2) and 1.938(2) Å). The Cu–C1 bond length, however, is less sensitive to the coordination number, with 1.909(2) and 1.8848(15) Å in **16** and **17**, respectively.

Additionally, we explored the reaction of fluoride complexes **Ia** with $(C_2F_5)_3PF_2$ in the presence of aniline, and for **Ic**, with $(C_2F_5)_3PF_2$ in the presence of diphenylamine and the cationic copper complexes [(carbene)Cu(NH$_2$Ph)]$^+$**FAP**$^-$ (carbene =

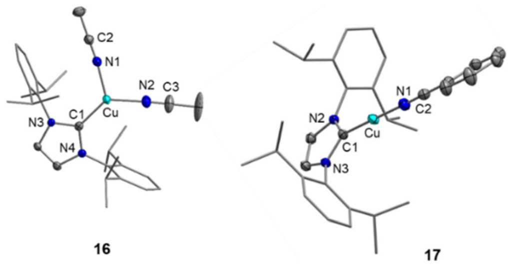


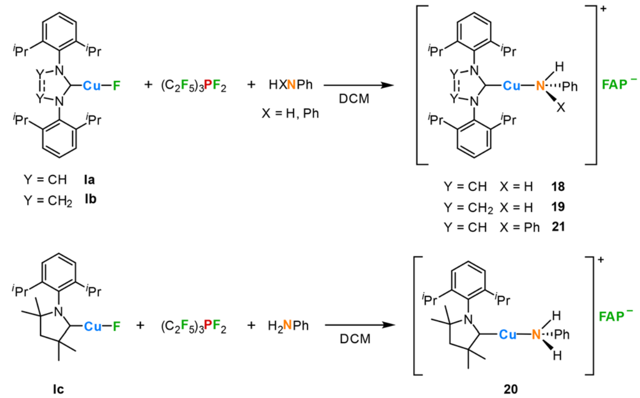
Fig. 4 Molecular structures of the complex cations of [(IDipp)Cu(N≡CMe)$_2$]$^+$**FAP**$^-$ (**16**; left) and [(IDipp)Cu(N≡CPh)]$^+$**FAP**$^-$ (**17**; right) in the solid state (ellipsoids set at the 50% probability level; Dipp substituents are shown as wire-and-stick models). Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are collected in Table 3 and Fig. S9, S10 in the ESI.†

Table 3 Selected bond lengths [Å] and angles [°] of the copper carbene-complexes **16**, **17**, **19–21**, **23**, **24**, **26**, and **27**

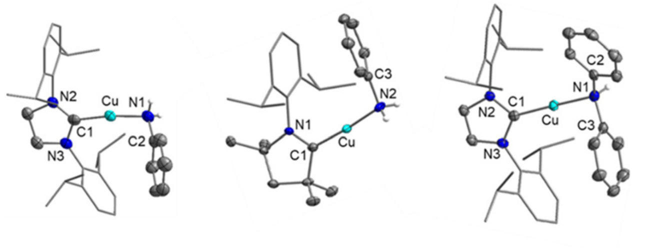
	Cu–C1	N/O	C1–Cu–N/O
16	1.909(2)	1.967(2)	121.11(9)
		1.938(2)	131.08(10)
17	1.8848(15)	1.8453(14)	178.03(7)
19	1.893(3)	1.935(3)	171.88(13)
20	1.882(3)	1.942(3)	175.47(12)
21	1.8716(17)	1.9492(15)	175.97(7)
23	1.8853(17)	1.9038(15)	174.25(6)
24	1.878(2)	1.916(2)	172.2(1)
26	1.873(3)	2.054(2)	142.16(11)
	1.876(3)	2.027(2)	145.85(11)
			144.71(12)
			143.59(11)
27	1.866(3)	1.8624(19)	167.61(9)

IDipp, **18**; SIDipp, **19**; cAAC^{Me}, **20**) and [(IDipp)Cu(NHPh$_2$)]$^+$**FAP**$^-$ (**21**) were isolated in moderate to good yields (Scheme 4). The ^{1}H NMR spectra of complexes **18–21** show characteristic broad singlets for the N*H* protons (**18:** 4.74 ppm, **19:** 4.24 ppm, **20:** 4.58 ppm, **21:** 6.36 ppm), compared to free aniline (3.69 ppm)[23] and diphenylamine (5.69 ppm).[24] Further characterization was carried out using NMR and IR spectroscopy, HRMS and elemental analysis. SC-XRD confirmed the molecular structures of **19–21** (Fig. 5 and Table 3). The complex cations adopt linear structures in which copper is coordinated by both the carbene and the amino ligand, with C1–Cu–N1 angles of 171.88(13)° (**19**), 175.47(12)° (**20**), and 175.97(7)° (**21**). In **19** and **20**, the Cu–N1 bond length (**19:** 1.935(3) Å; **20:** 1.942(3) Å) is significantly shorter than *d*(Cu–N) reported for related aniline complexes [(dtbpe)Cu(NH$_2$Ph)]$^+$[BF$_4$]$^-$ (2.010(2) Å; dtbpe = 1,2-bis(di-*tert*butyl-phosphino)ethane)[25] and [(JohnPhos)Cu (NH$_2$Ph)][PF$_6$] (1.964(2) Å; JohnPhos = 2-(di-*tert*-butyl-phosphino)-1,1′-biphenyle).[26]

This difference may be attributed to the lower coordination number of copper in **19** and **20**. The Cu–C1 distances in **19** (1.893(3) Å) and **20** (1.882(3) Å) are nearly identical within experimental error. Compound **21** displays slightly different bond lengths (Cu–N1: 1.9492(15) Å, Cu–C1: 1.8716(17) Å).



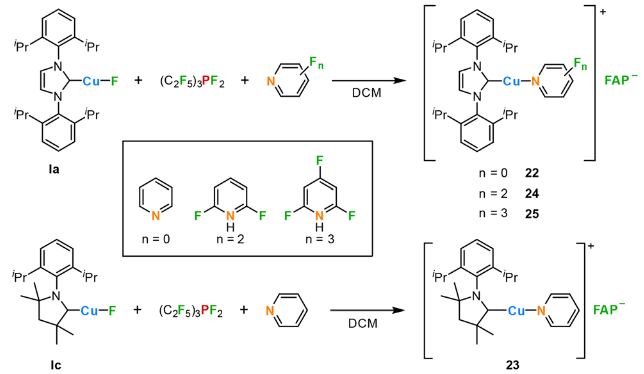
Scheme 4 Synthesis of [(carbene)Cu(LB)]$^+$**FAP**$^-$ complexes **18–20** *via* fluoride ion abstraction from [(carbene)CuF] using (C$_2$F$_5$)$_3$PF$_2$ in the presence of amines.



19 20 21

Fig. 5 Molecular structures of the complex cations of [(SIDipp)Cu(NH$_2$Ph)]$^+$**FAP**$^-$ (**19**, left), [(cAAC^{Me})Cu(NH$_2$Ph)]$^+$**FAP**$^-$ (**20**, middle) and [(IDipp)Cu(NHPh$_2$)]$^+$**FAP**$^-$ (**21**, right) in the solid state (ellipsoids set at the 50% probability level; Dipp substituents are shown as wire-and-stick models). Hydrogen atoms except for those of the N atom of the aniline and diphenylamine ligands and a solvent molecule in the crystal structure of **19** are omitted for clarity. Only one of two independent cations in the asymmetric unit of **19** is shown. Selected bond lengths and angles are collected in Table 2 and Fig. S11–S13 in the ESI.†

Moreover, the reactivity of the fluoride complexes [(IDipp)CuF] (**Ia**) and [(cAAC^{Me})CuF] (**Ic**) towards (C$_2$F$_5$)$_3$PF$_2$ in the presence of one equivalent of pyridine or fluorinated pyridine derivates was investigated. Fluoride abstraction followed by pyridine coordination led to isolation and full characterization of the cationic complexes [(IDipp)Cu(NC$_5$H$_5$)]$^+$**FAP**$^-$ (**22**), [(cAAC^{Me})Cu(NC$_5$H$_5$)]$^+$**FAP**$^-$ (**23**), [(IDipp)Cu(NC$_5$H$_3$F$_2$)]$^+$**FAP**$^-$ (**24**), and [(IDipp)Cu(NC$_5$H$_2$F$_3$)]$^+$ **FAP**$^-$ (**25**) in yields of 68–80% (Scheme 5). The reaction of the highly fluorinated 2,3,5,6-tetrafluoropyridine with **Ia** in the presence of (C$_2$F$_5$)$_3$PF$_2$ did not result in [(IDipp)Cu(NC$_5$HF$_4$)]$^+$**FAP**$^-$ but [{(IDipp)Cu}$_2$]$^{2+}$2**FAP**$^-$ was obtained. The low basicity and thus poor coordination ability of tetrafluoropyridine favors the coordination of the IDipp substituent of the carbene ligand, resulting in the dimeric dicationic complex [{(IDipp)Cu}$_2$]$^{2+}$.[1] The formation of **22–25** was confirmed by ^{1}H, ^{13}C{^{1}H}, ^{19}F, and ^{31}P NMR spectroscopy. A decreasing resonance frequency of the hydrogen and carbon nuclei in *meta*-position of pyridine with an increasing number of fluorine substituents was observed (*δ*(^{1}H): **22:** 7.77/7.50 ppm, **24:** 7.03 ppm; **25:** 6.75 ppm; *δ*(^{13}C): **22:** 147.5/



Scheme 5 Synthesis of [(carbene)Cu(LB)]$^+$**FAP**$^-$ complexes **22–25** *via* fluoride ion abstraction from [(carbene)CuF] using (C$_2$F$_5$)$_3$PF$_2$ in the presence of (partially fluorinated) pyridine.

126.8 ppm; **24**: 108.3 ppm; **25**: 98.1 ppm). In addition, single crystals of **23** and **24** suitable for XRD studies were obtained (Fig. 6).

The solid-state structures of **23** and **24** confirm the coordination of pyridine and the linear geometry at copper, with C1–Cu–N1 angles of 174.25(6)° (**23**) and 172.2(1)° (**24**). The Cu–C1 distances in **23** (1.8853(17) Å) and **24** (1.878(2) Å) are within the typical range compared to related complexes.[13,27] In contrast, the Cu–N1 bond in **23** (1.9038(15) Å) is slightly shorter than in **24** (1.916(2) Å), which mirrors the reduced basicity of 2,6-difluoropyridine relative to pyridine. The Cu–C1 and Cu–N1 bond lengths in **23** are slightly longer than those reported by Steffen *et al.* for the related pyridine complex [(IDipp)Cu(NC$_5$H$_5$)][BF$_4$] (Cu–C1: 1.872(2) Å; Cu–N1: 1.8900(18) Å).[27]

The stabilization of the carbene copper cations [(IDipp)Cu]$^+$ by oxygen donor ligands is demonstrated by the formation of [{(IDipp)Cu(μ-ONC$_5$H$_5$)}$_2$]$^{2+}$2**FAP**$^-$ (26), [(IDipp)Cu(η^{1}O=CPh$_2$)]$^+$ **FAP**$^-$ (27), and [(cAAC^{Me})Cu(THF)]$^+$**FAP**$^-$ (28) depicted in Scheme 6. Fluoride abstraction from [(IDipp)CuF] (**Ia**) with (C$_2$F$_5$)$_3$PF$_2$ in the presence of pyridine-*N*-oxide yielded the dinuclear pyridine-*N*-oxide-bridged complex **26** in 81% yield. The reaction of **Ia** with (C$_2$F$_5$)$_3$PF$_2$ in the presence of benzophenone afforded the mononuclear complex **27** in 79% yield and the reaction of [(cAAC^{Me})CuF] (**Ic**) with the phosphorane in Et$_2$O/THF afforded **28** in 68% yield. The ^{1}H NMR analysis of **26** revealed broadening of the pyridine-*N*-oxide resonances at room temperature. However, at −36.5 °C, three well resolved resonances were observed at 7.71 (pyridine-aryl-C$_{para}$*H*), 7.47 (pyridine-aryl-C$_{ortho}$*H*), and 7.38 ppm (pyridine-aryl-C$_{meta}$*H*) (see Fig. S118 in the ESI†). SC-XRD confirmed the dinuclear structure of **26** in the solid state, revealing a central Cu$_2$O$_2$ core, in which two [(IDipp)Cu]$^+$ cations are bridged by two pyridine-*N*-oxide ligands (Fig. 7). These extended bond distances indicate the absence of significant Cu⋯Cu bonding interactions. The Cu–O–Cu angles in **26** are 108.47(11)° and 107.84(10)°, respectively. The benzophenone ligand in [(IDipp)Cu(η^1-O=CPh$_2$)]$^+$**FAP**$^-$ (27) adopts an *end-on* η^1-coordination mode in the solid state and in solution. Such a shift in δ(^{13}C) is a hallmark of benzophenone ligands coordinated *via* the oxygen atom in an *end-on* η^1-fashion.[28]

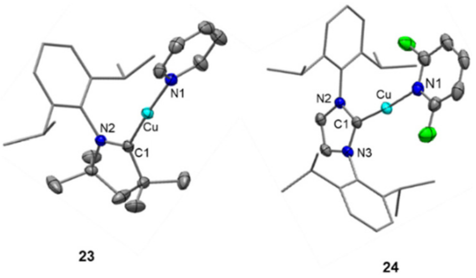
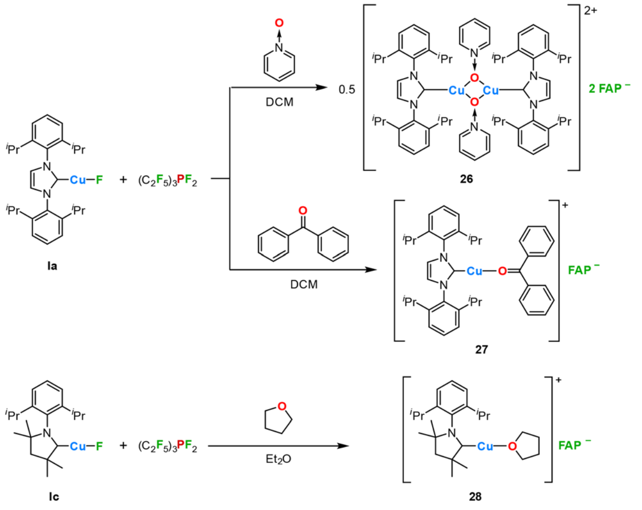


Fig. 6 Molecular structures of the complex cations of [(cAAC^{Me})Cu(NC$_5$H$_5$)]$^+$**FAP**$^-$ (**23**; left) and [(IDipp)Cu(NC$_5$H$_3$F$_2$)]$^+$**FAP**$^-$ (**24**; right) in the solid state (ellipsoids set at the 50% probability level; Dipp substituents are shown as wire-and-stick models). Hydrogen atoms are omitted for clarity. Selected bond lengths and angles are collected in Table 3 and Fig. S14, S15 in the ESI.†



Scheme 6 Synthesis of complexes **26–28** *via* fluoride ion abstraction from [(carbene)CuF] using (C$_2$F$_5$)$_3$PF$_2$ in the presence of *O*-donor ligands.

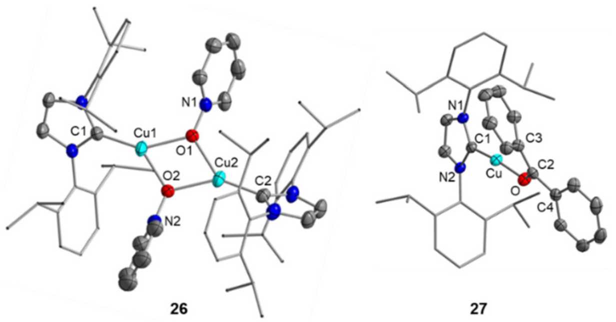


Fig. 7 Molecular structures of the complex cations of [{(IDipp)Cu(μ-ONC$_5$H$_5$)}$_2$]$^{2+}$2**FAP**$^-$ (**26**; left) and [(IDipp)Cu(η^1-O=CPh$_2$)]$^+$**FAP**$^-$ (**27**; right) in the solid state (ellipsoids set at the 50% probability level; Dipp substituents are shown as wire-and-stick models). Hydrogen atoms and two co-crystallized solvent molecules in the crystal structure of **26** are omitted for clarity. Selected bond lengths and angles are collected in Table 3 and Fig. S16, S17 in the ESI.†

In contrast, a *side-on* η^2-coordination of the O=C moiety would induce a shift to lower resonance frequency,[29,30] as previously observed for the nickel complexes [(NHC)$_2$Ni(η^2-O=CPh$_2$)] (NHC = I*i*Pr, IMes) which we have reported earlier.[30] In these nickel complexes, the [(NHC)$_2$Ni] unit exhibits strong π-back-donation, favoring *side-on* coordination. SC-XRD experiments of **27** further confirm the *end-on* η^1-coordination mode in the solid state (Fig. 7). The η^1-hapticity of the oxygen atom suggests minimal or no *π*-back-donation from the [(IDipp)Cu]$^+$ cation, which is consistent with the contracted and energetically low-lying d-orbitals characteristic for the closed-shell copper(I) center. The O–C2 bond length in **27** (1.246(3) Å) remains nearly unchanged compared to free benzophenone (*cf.* distances of benzophenone: 1.23(1) Å),[31] indicating negligible electron density donation from copper to the carbonyl moiety. The Cu–O bond distance of 1.8624(19) Å is slightly longer than those observed in the alkoxide complexes [(IDipp)Cu(OX)] (X = Et: 1.799(3) Å;[16] *t*Bu: 1.8104(13) Å;[32] CH(Me)Ph: 1.794(3) Å (ref. 33)) or carboxylato complexes [(IDipp)Cu(OX)] (X = C(═O)H: 1.848(2) Å;[34] C(═O)Me:1.850(3) Å (ref. 35)), as expected for a ketone ligand. The Cu–O–C2 bond angle of 133.48(18)° is consistent with oxygen lone-pair coordination to the $[(\text{IDipp})\text{Cu}]^+$ center.

Conclusions

Ligand exchange reactions of $[(\text{IDipp})\text{Cu}(\text{C}_6\text{Me}_6)]^+$**FAP**$^-$ (**IIa**) were studied in some detail leading to the copper **FAP**$^-$ salts $[(\text{IDipp})\text{Cu}(\text{LB})]^+$**FAP**$^-$ (LB = NH_3, **1**; $C_6H_{12}N_2$ = DABCO, **2**; $C_7H_{10}N_2$ = DMAP, **3**; $C_4H_4N_2$ = pyrazine, **4**; $C_{13}H_9N$ = acridine, **5**; η^1-O═$C_{13}H_9N$ = acridone, **6**; $C_4H_{10}S$ = SEt_2, **7**; C_4H_8S = THT, **8**; PCy_3, **9**) as well as the dinuclear 1,2,4-triazole complex $[\{(\text{IDipp})\text{Cu}\}_2(\text{C}_2\text{N}_3\text{H}_3)_2]^{2+}2$**FAP**$^-$ (**10**). Similarly, $[(\text{cAAC}^{\text{Me}})\text{Cu}(\text{C}_6\text{Me}_6)]^+$**FAP**$^-$ (**IIb**) was used for the synthesis of $[(\text{cAAC}^{\text{Me}})\text{Cu}(\text{LB})]^+$**FAP**$^-$ (LB = $C_7H_{10}N_2$, **13**; $C_4H_{10}S$, **14**) *via* replacement of the C_6Me_6 ligand. The reactions of DABCO or pyrazine with **IIa** afforded $[\{(\text{cAAC}^{\text{Me}})\text{Cu}\}_2(\text{C}_6\text{H}_{12}\text{N}_2)]^{2+}2$**FAP**$^-$ (**11**) and $[\{(\text{cAAC}^{\text{Me}})\text{Cu}\}_2(\text{C}_4\text{H}_4\text{N}_2)]^{2+}2$**FAP**$^-$ (**12**). In all cases the cationic copper(I) complexes $[(\text{carbene})\text{Cu}(\text{LB})]^+$ were stabilized by the weakly coordinating tris(pentafluoroethyl)trifluorophosphate anion (**FAP**$^-$ anion, $[(\text{C}_2\text{F}_5)_3\text{PF}_3]^-$). Furthermore, we extended the use of the readily available Lewis acid tris(pentafluoroethyl)difluorophosphorane $(C_2F_5)_3PF_2$ as fluoride abstraction reagent for the generation of cationic copper(I) complexes. The reactions of $(C_2F_5)_3PF_2$ with [(IDipp)CuF] (**Ia**), [(SIDipp)CuF] (**Ib**), or $[(\text{cAAC}^{\text{Me}})\text{CuF}]$ (**Ic**) in the presence of different Lewis bases (LB), *i.e.* nitriles, amines, fluorinated and non-fluorinated pyridines, and oxygen donor ligands, were studied. The complex salts $[(\text{IDipp})\text{Cu}(\text{LB})]^+$**FAP**$^-$ (LB = (N≡CMe)$_2$, **16**; N≡CPh, **17**; NH_2Ph, **18**; $NHPh_2$, **21**; NC_5H_5, **22**; $NC_5H_3F_2$, **24**; $NC_5H_2F_3$, **25**; η^1-O═CPh_2, **27**), $[(\text{SIDipp})\text{ Cu}(\text{NH}_2\text{Ph})]^+$**FAP**$^-$ (**19**), and $[(\text{cAAC}^{\text{Me}})\text{Cu}(\text{LB})]^+$**FAP**$^-$ (LB = N≡CMe, **15**; NH_2Ph, **20**; NC_5H_5, **23**; THF, **28**) were isolated and characterized. In addition, the dinuclear complex $[\{(\text{IDipp})\text{Cu}(\mu\text{-ONC}_5\text{H}_5)\}_2]^{2+}2$**FAP**$^-$ (**26**) was isolated. This approach was investigated for different 2 VE nitrogen and oxygen donor ligands. In none of these cases the carbene ligand was replaced with the 2 VE ligand employed, the formation of Lewis acid/base pair of the 2 VE ligand and $(C_2F_5)_3PF_2$ was never observed in the presence of the copper fluoride, and the **FAP**$^-$ anion coordinated in none of these cases to the copper cations. Hence, mixtures of [(carbene)CuF] and $(C_2F_5)_3PF_2$ serve as synthon for $[(\text{carbene})\text{Cu}]^+$.

Experimental

General considerations

All reactions and subsequent manipulations involving organometallic reagents were carried out under an argon atmosphere by using standard Schlenk techniques or in a Glovebox (Innovative Technology Inc., and MBraun Uni Lab).[36] All reactions were performed in oven-dried glassware. Elemental analyses were performed in the microanalytical laboratory of the Institute of Inorganic Chemistry of the University Würzburg with an Elementar vario micro cube. High-resolution mass spectroscopy (HRMS) was performed on a Thermo Scientific Exactive Plus mass spectrometer, equipped with an Orbitrap Mass Analyzer. NMR spectra were recorded on a Bruker Avance 400 (^{1}H, 400.1 MHz; ^{13}C, 100.6 MHz; ^{19}F, 376.8 MHz; ^{31}P, 162.0 MHz), a Bruker Avance 500 (^{1}H, 500.1 MHz; ^{13}C, 125.8 MHz; ^{19}F, 470.5 MHz; ^{31}P, 202.4 MHz) and a Bruker Avance 600 (^{1}H, 600.2 MHz; ^{13}C, 150.9 MHz; ^{19}F, 564.7 MHz; ^{31}P, 242.9 MHz) spectrometer using CD_2Cl_2 or $CDCl_3$ as solvent. Assignment of the ^{1}H NMR and ^{13}C{^{1}H} NMR data was supported by ^{1}H, ^{1}H and ^{13}C{^{1}H},^{1}H correlation experiments. ^{13}C NMR spectra were recorded broad-band proton-decoupled (^{13}C{^{1}H}) at 298 K, if not otherwise noted. Chemical shifts are listed in parts per million (ppm), reported relative to TMS and were calibrated against residual solvent signals ($\delta(^1\text{H})$: CD*H*Cl_2 5.32, C*H*Cl_3 7.26; $\delta(^{13}\text{C})$: CD_2Cl_2 53.84, $CDCl_3$ 77.16)[37] or external $CFCl_3$ ($\delta(^{19}\text{F})$: 0) and 85% H_3PO_4 ($\delta(^{31}\text{P})$: 0). If not otherwise noted ^{19}F and ^{31}P NMR spectra were not proton decoupled. Coupling constants are quoted in Hertz. Infrared spectra were recorded under an argon atmosphere on solid samples on a Bruker Alpha FT-IR spectrometer by using an ATR unit at room temperature. Values are given in cm^{-1}. All solvents for synthetic reactions were HPLC grade, further treated to remove traces of water using an Innovative Technology Inc. Pure-Solv Solvent Purification System. CD_2Cl_2 and $CDCl_3$ were purchased from Sigma-Aldrich and stored over molecular sieve. The compounds [(IDipp)CuF] (**Ia**),[38] [(SIDipp)CuF] (**Ib**),[13] $[(\text{cAAC}^{\text{Me}})\text{CuF}]$ (**Ic**),[13] $[(\text{IDipp})\text{Cu}(\text{C}_6\text{Me}_6)]^+$**FAP**$^-$ (**IIa**)[1] and $[(\text{cAAC}^{\text{Me}})\text{Cu}(\text{C}_6\text{Me}_6)]^+$**FAP**$^-$ (**IIb**)[13] were prepared according to literature procedures. Commercially available $(C_2F_5)_3PF_2$ was used or the phosphorane was synthesized *via* electrochemical fluorination (ECF) starting from triethyl phosphine as reported in the literature.[39] All other starting materials were purchased from commercial sources and used without further purification.

Preparation of compounds

$[(\text{IDipp})\text{Cu}(\text{NH}_3)]^+FAP^-$ (1). At room temperature and under atmospheric pressure anhydrous gaseous NH_3 was passed through a solution of **IIa** (100 mg, 94.4 μmol) in $CHCl_3$ (15 mL) over a period of 1 h. The reaction mixture was stirred for another 2 h at room temperature. All volatiles were removed under reduced pressure and the remaining solid was suspended in *n*-hexane (10 mL) and the product was filtered off. The product was washed with *n*-hexane (2 × 10 mL) and dried *in vacuo* to yield **1** (50 mg, 54.7 μmol, 58%) as a colorless solid. Single crystals of **1** suitable for X-ray diffraction were obtained by diffusion of *n*-hexane into a solution of **1** in chloroform. **^{1}H NMR** (500.1 MHz, $CDCl_3$, 298 K): δ [ppm] = 1.24 (d, 12 H, $^3J_{\text{HH}}$ = 7.0 Hz, *i*Pr–C*H*$_3$), 1.25 (d, 12 H, $^3J_{\text{HH}}$ = 7.0 Hz, *i*Pr–C*H*$_3$), 2.05 (s$_{\text{br}}$, 3 H, N*H*$_3$), 2.49 (sept, 4 H, $^3J_{\text{HH}}$ = 6.9 Hz, *i*Pr–C*H*), 7.24 (s, 2 H, N–C*H*–C*H*–N), 7.34 (d, 4 H, $^3J_{\text{HH}}$ = 7.8 Hz, IDipp-aryl-C$_{meta}$*H*), 7.56 (t, 2 H, $^3J_{\text{HH}}$ = 7.8 Hz, IDipp-aryl-C$_{para}$*H*); **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 298 K): δ [ppm] =

24.0 (iPr–CH_3), 25.0 (*i*Pr–CH_3), 28.9 (*i*Pr–CH), 124.1 (N–CH–CH–N), 124.7 (IDipp-aryl-C_{meta}), 131.4 (IDipp-aryl-C_{para}), 133.8 (IDipp-aryl-C_{ipso}), 145.5 (IDipp-aryl-C_{ortho}), 177.5 (N–C–N); **^{19}F NMR** (470.5 MHz, $CDCl_3$, 298 K): δ [ppm] = −44.9 (dm, 1 F, $^1J_{PF}$ = 888 Hz, P*F*), −80.3 (m, 3 F, CF_3), −81.9 (m, 6 F, CF_3), −88.8 (dm, 2 F, $^1J_{PF}$ = 903 Hz, PF_2), −115.8 (dm, 2 F, $^2J_{PF}$ = 85 Hz, CF_2), −116.2 (dm, 4 F, $^2J_{PF}$ = 98 Hz, CF_2); **^{31}P NMR** (202.4 MHz, $CDCl_3$, 298 K): δ [ppm] = −146.6 (tdm, $^1J_{PF}$ = 903 Hz, $^1J_{PF}$ = 888 Hz); **IR** ([cm^{-1}]): 3370 (w), 3300 (w), 3174 (vw), 3074 (vw), 2967 (s), 2929 (m), 2875 (m), 1666 (w), 1594 (w), 1551 (w), 1469 (m), 1413 (w), 1388 (w), 1366 (w), 1295 (m), 1271 (m), 1212 (s), 1183 (s), 1140 (s), 1126 (s), 1099 (s), 1060 (m), 963 (m), 936 (w), 875 (vw), 862 (vw), 804 (m), 759 (m), 724 (m), 706 (m), 673 (m), 618 (vs), 581 (m), 533 (m), 504 (w), 494 (m), 466 (w), 439 (m), 430 (m); **HRMS** (ESI) *m*/*z* [*M*]$^+$ calcd for $C_{27}H_{39}CuN_3$: 468.2440, found: 468.2427; *m*/*z* **FAP$^-$** calcd for $C_6F_{18}P$: 444.9450, found: 444.9447; **elemental analysis** calcd (%) for $C_{33}H_{39}CuF_{18}N_3P$: C 43.36, H 4.30, N 4.60; found: C 43.35, H 4.01, N 4.73.

[(IDipp)Cu($C_6H_{12}N_2$)]$^+$FAP$^-$ (2). A solution of **IIa** (100 mg, 94.4 μmol) and DABCO (10.6 mg, 94.4 μmol) in dichloro methane (5 mL) was stirred for 6 h at room temperature. All volatiles were removed under reduced pressure and the remaining solid was suspended in *n*-hexane (7 mL) and product was filtered off. The product was washed with *n*-hexane (2 × 5 mL) and dried *in vacuo* to yield **2** (62.0 mg, 61.4 μmol, 65%) as a colorless solid. **^{1}H NMR** (400.1 MHz, $CDCl_3$, 298 K): δ [ppm] = 1.21 (d, 12 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr–CH_3), 1.26 (d, 12 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr–CH_3), 2.44 (sept, 4 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr–C*H*), 2.66 (s, 12 H, DABCO–CH_2), 7.28 (s, 2 H, N–C*H*–C*H*–N), 7.34 (d, 4 H, $^3J_{HH}$ = 7.8 Hz, IDipp-aryl-C$_{meta}$*H*), 7.56 (t, 2 H, $^3J_{HH}$ = 7.8 Hz, IDipp-aryl-C$_{para}$*H*); **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$, 298 K): δ [ppm] = 23.7 (*i*Pr–CH_3), 25.3 (*i*Pr–CH_3), 28.9 (*i*Pr–CH), 124.3 (N–CH–CH–N), 124.7 (IDipp-aryl-C_{meta}), 131.5 (IDipp-aryl-C_{para}), 133.7 (IDipp-aryl-C_{ipso}), 145.6 (IDipp-aryl-C_{ortho}), 176.6 (N–C–N); the signal for the DABCO–CH_2-group was not detected; **^{19}F NMR** (470.5 MHz, $CDCl_3$, 298 K): δ [ppm] = −45.3 (dm, 1 F, $^1J_{PF}$ = 891 Hz, P*F*), −80.2 (m, 3 F, CF_3), −81.8 (m, 6 F, CF_3), −88.5 (dm, 2 F, $^1J_{PF}$ = 903 Hz, PF_2), −115.9 (dm, 2 F, $^2J_{PF}$ = 83 Hz, CF_2), −116.4 (dm, 4 F, $^2J_{PF}$ = 98 Hz, CF_2); **^{31}P NMR** (202.4 MHz, $CDCl_3$, 298 K): δ [ppm] = −147.3 (tdm, $^1J_{PF}$ = 903 Hz, $^1J_{PF}$ = 891 Hz); **IR** ([cm^{-1}]): 3172 (vw), 3144 (vw), 3073 (vw), 2957 (m), 2928 (w), 2875 (w), 1593 (vw), 1568 (vw), 1552 (vw), 1463 (m), 1415 (w), 1387 (w), 1367 (w), 1350 (vw), 1311 (m), 1295 (m), 1273 (vw), 1258 (vw), 1211 (vs), 1179 (s), 1140 (s), 1125 (s), 1099 (s), 1058 (m), 1015 (w), 973 (m), 962 (m), 937 (w), 905 (vw), 809 (s), 761 (m), 746 (w), 723 (m), 700 (w), 636 (w), 618 (s), 581 (w), 533 (w), 505 (vw), 495 (w), 439 (w), 429 (w); **HRMS** (ESI) *m*/*z* [*M*]$^+$ calcd for $C_{33}H_{48}CuN_4$: 563.3175, found: 563.3159; *m*/*z* **FAP$^-$** calcd for $C_6F_{18}P$: 444.9450, found: 444.9446; **elemental analysis** calcd (%) for $C_{39}H_{48}CuF_{18}N_4P$: C 46.41, H 4.79, N 5.55; found: C 46.05, H 4.31, N 5.40.

[(IDipp)Cu($C_7H_{10}N_2$)]$^+$FAP$^-$ (3). A solution of **IIa** (150 mg, 142 μmol) and DMAP (17.3 mg, 142 μmol) in dichloro methane (5 mL) was stirred for 3 h at room temperature. All volatiles were removed under reduced pressure and the remaining solid was suspended in *n*-hexane (10 mL) and the product was filtered off. The product was washed with *n*-hexane (2 × 5 mL) and dried *in vacuo* to yield **3** (106 mg, 104 μmol, 73%) as a colorless solid. Single crystals of **3** suitable for X-ray diffraction were obtained by diffusion of *n*-hexane into a solution of **3** in chloroform. **^{1}H NMR** (400.1 MHz, $CDCl_3$, 298 K): δ [ppm] = 1.24 (d, 12 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr–CH_3), 1.27 (d, 12 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr–CH_3), 2.55 (sept, 4 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr–C*H*), 2.93 (s$_{br}$, 6 H, DMAP–CH_3), 6.36 (s$_{br}$, 2 H, DMAP-aryl-C$_{meta}$*H*), 7.17 (s$_{br}$, 2 H, DMAP-aryl-C$_{ortho}$*H*), 7.29 (s, 2 H, N–C*H*–C*H*–N), 7.36 (d, 4 H, $^3J_{HH}$ = 7.9 Hz, IDipp-aryl-C$_{meta}$*H*), 7.57 (t, 2 H, $^3J_{HH}$ = 7.9 Hz, IDipp-aryl-C$_{para}$*H*); **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$, 298 K): δ [ppm] = 23.8 (*i*Pr–CH_3), 25.1 (*i*Pr–CH_3), 28.9 (*i*Pr–CH), 39.4 (DMAP–CH_3), 124.2 (N–CH–CH–N), 124.6 (IDipp-aryl-C_{meta}), 131.3 (IDipp-aryl-C_{para}), 134.1 (IDipp-aryl-C_{ipso}), 145.8 (IDipp-aryl-C_{ortho}), 178.3 (N–C–N); the signals for the DMAP-aryl-C_{ortho}, DMAP-aryl-C_{meta} and DMAP-aryl-C_{ipso} carbon atoms were not detected; **^{19}F NMR** (470.5 MHz, $CDCl_3$, 298 K): δ [ppm] = −45.3 (dm, 1 F, $^1J_{PF}$ = 893 Hz, P*F*), −80.2 (m, 3 F, CF_3), −81.8 (m, 6 F, CF_3), −88.6 (dm, 2 F, $^1J_{PF}$ = 903 Hz, PF_2), −115.9 (dm, 2 F, $^2J_{PF}$ = 81 Hz, CF_2), −116.5 (dm, 4 F, $^2J_{PF}$ = 94 Hz, CF_2); **^{31}P NMR** (202.4 MHz, $CDCl_3$, 298 K): δ [ppm] = −147.3 (tdm, $^1J_{PF}$ = 903 Hz, $^1J_{PF}$ = 893 Hz); **IR** ([cm^{-1}]): 3172 (vw), 3146 (vw), 3076 (vw), 2963 (m), 2952 (m), 2924 (w), 2876 (w), 2865 (w), 1715 (vw), 1623 (s), 1549 (m), 1464 (m), 1447 (m), 1410 (w), 1397 (w), 1365 (w), 1347 (w), 1313 (w), 1296 (m), 1256 (vw), 1213 (vs), 1178 (vs), 1125 (s), 1098 (s), 1075 (m), 1029 (m), 971 (m), 949 (w), 936 (w), 885 (vw), 832 (vw), 805 (s), 761 (m), 740 (w), 728 (m), 699 (w), 661 (vw), 637 (w), 618 (s), 581 (m), 549 (w), 530 (m), 505 (w), 494 (m), 438 (m), 429 (m); **HRMS** (ESI) *m*/*z* [*M*]$^+$ calcd for $C_{34}H_{46}CuN_4$: 573.3019, found: 573.3002; *m*/*z* **FAP$^-$** calcd for $C_6F_{18}P$: 444.9450, found: 444.9437; **elemental analysis** calcd (%) for $C_{40}H_{46}CuF_{18}N_4P$: C 47.13, H 4.55, N 5.50; found: C 47.64, H 4.12, N 5.83.

[(IDipp)Cu($C_4H_4N_2$)]$^+$FAP$^-$ (4). A solution of **IIa** (150 mg, 142 μmol) and pyrazine (11.3 mg, 142 μmol) in dichloro methane (5 mL) was stirred for 2 h at room temperature. All volatiles were removed under reduced pressure and the remaining solid was suspended in *n*-hexane (10 mL) and the product was filtered off. The product was washed with *n*-hexane (2 × 5 mL) and dried *in vacuo* to yield **4** (108 mg, 110 μmol, 78%) as a yellow solid. **^{1}H NMR** (400.1 MHz, $CDCl_3$, 298 K): δ [ppm] = 1.07 (d, 12 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr–CH_3), 1.25 (d, 12 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr–CH_3), 2.51 (sept, 4 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr–C*H*), 7.29 (s, 2 H, N–C*H*–C*H*–N), 7.35 (d, 4 H, $^3J_{HH}$ = 7.8 Hz, IDipp-aryl-C$_{meta}$*H*), 7.60 (t, 2 H, $^3J_{HH}$ = 7.8 Hz, IDipp-aryl-C$_{para}$*H*), 7.93 (s, 4 H, pyrazine-aryl-C*H*); **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$, 298 K): δ [ppm] = 23.8 (*i*Pr–CH_3), 24.8 (*i*Pr–CH_3), 28.9 (*i*Pr–CH), 124.1 (N–CH–CH–N), 124.8 (IDipp-aryl-C_{meta}), 131.3 (IDipp-aryl-C_{para}), 134.6 (IDipp-aryl-C_{ipso}), 145.3 (IDipp-aryl-C_{ortho}), 145.9 (pyrazine-aryl-CH), 177.2 (N–C–N); **^{19}F NMR** (470.5 MHz, $CDCl_3$, 298 K): δ [ppm] = −44.9 (dm, 1 F, $^1J_{PF}$ = 889 Hz, P*F*), −80.2 (m, 3 F, CF_3), −81.9 (m, 6 F, CF_3), −88.6 (dm, 2 F, $^1J_{PF}$ = 903 Hz, PF_2), −115.8 (dm, 2 F, $^2J_{PF}$ = 80

Hz, CF_2), −116.3 (dm, 4 F, $^{2}J_{\mathrm{PF}}$ = 98 Hz, CF_2); **^{31}P NMR** (202.4 MHz, $CDCl_3$, 298 K): δ [ppm] = −147.2 (tdm, $^{1}J_{\mathrm{PF}}$ = 904 Hz, $^{1}J_{\mathrm{PF}}$ = 890 Hz); **IR** ([cm^{-1}]): 3166 (vw), 3139 (vw), 3082 (vw), 2967 (m), 2929 (w), 2874 (w), 1591 (vw), 1554 (vw), 1468 (m), 1419 (m), 1388 (w), 1366 (w), 1294 (m), 1212 (vs), 1180 (s), 1136 (s), 1124 (s), 1098 (s), 1070 (m), 1060 (m), 1042 (w), 961 (m), 936 (w), 864 (vw), 805 (s), 759 (s), 721 (s), 637 (w), 618 (s), 580 (m), 549 (w), 533 (m), 505 (w), 494 (m), 458 (m), 437 (w), 429 (w); **HRMS** (ESI) *m*/*z* [*M*]$^+$ calcd for $C_{31}H_{40}CuN_4$: 531.2549, found: 531.2533; *m*/*z* **FAP$^-$** calcd for $C_6F_{18}P$: 444.9450, found: 444.9445; **elemental analysis** calcd (%) for $C_{37}H_{40}CuF_{18}N_4P$: C 45.48, H 4.13, N 5.73; found: C 46.08, H 4.23, N 5.47.

[(IDipp)Cu($C_{13}H_9N$)]$^+$FAP$^-$ (5). A solution of **IIa** (100 mg, 94.4 μmol) and acridine (16.9 mg, 94.4 μmol) in dichloro methane (5 mL) was stirred for 4 h at room temperature. All volatiles were removed under reduced pressure and the remaining solid was suspended in *n*-hexane (10 mL) and the product was filtered off. The product was washed with *n*-hexane (2 × 5 mL) and dried *in vacuo* to yield **5** (84 mg, 78.0 μmol, 83%) as a yellow solid. Single crystals of **5** suitable for X-ray diffraction were obtained by diffusion of *n*-hexane into a solution of **5** in chloroform. **^{1}H NMR** (500.1 MHz, $CDCl_3$, 298 K): δ [ppm] = 1.17 (d, 12 H, $^{3}J_{\mathrm{HH}}$ = 6.7 Hz, *i*Pr–C*H*$_3$), 1.33 (d, 12 H, $^{3}J_{\mathrm{HH}}$ = 6.7 Hz, *i*Pr–C*H*$_3$), 2.67 (sept, 4 H, $^{3}J_{\mathrm{HH}}$ = 6.1 Hz, *i*Pr–C*H*), 6.77 (d$_{\mathrm{br}}$, 2 H, acridine–C*H*), 7.46 (t, 2 H, $^{3}J_{\mathrm{HH}}$ = 7.4 Hz, acridine–C*H*), 7.50 (s, 2 H, N–C*H*–C*H*–N), 7.54 (d, 4 H, $^{3}J_{\mathrm{HH}}$ = 7.9 Hz, IDipp-aryl-C$_{meta}$*H*), 7.57 (t, 2 H, $^{3}J_{\mathrm{HH}}$ = 7.7 Hz, IDipp-aryl-C$_{para}$*H*), 7.83 (t, 2 H, $^{3}J_{\mathrm{HH}}$ = 7.8 Hz, acridine–C*H*), 8.06 (d, 2 H, $^{3}J_{\mathrm{HH}}$ = 8.3 Hz, acridine–C*H*), 9.05 (s, 1 H, acridine–C*H*); **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 298 K): δ [ppm] = 24.0 (*i*Pr–*C*H$_3$), 25.3 (*i*Pr–*C*H$_3$), 29.1 (*i*Pr–*C*H), 124.5 (N–*C*H–*C*H–N), 124.9 (IDipp-aryl-*C*$_{meta}$), 127.15 (acridine–*C*), 127.21 (IDipp-aryl-*C*$_{para}$), 129.6 (acridine–*C*H), 131.4 (acridine–*C*H), 134.27 (IDipp-aryl-*C*$_{ipso}$), 134.32 (acridine–*C*H), 142.3 (acridine–*C*H), 146.7 (IDipp-aryl-*C*$_{ortho}$), 148.0 (acridine–*C*), 177.5 (N–*C*–N); **^{19}F NMR** (470.5 MHz, $CDCl_3$, 298 K): δ [ppm] = −45.2 (dm, 1 F, $^{1}J_{\mathrm{PF}}$ = 890 Hz, P*F*), −80.2 (m, 3 F, C*F*$_3$), −81.8 (m, 6 F, C*F*$_3$), −88.6 (dm, 2 F, $^{1}J_{\mathrm{PF}}$ = 904 Hz, P*F*$_2$), −115.9 (dm, 2 F, $^{2}J_{\mathrm{PF}}$ = 81 Hz, C*F*$_2$), −116.3 (dm, 4 F, $^{2}J_{\mathrm{PF}}$ = 96 Hz, C*F*$_2$); **^{31}P NMR** (202.4 MHz, $CDCl_3$, 298 K): δ [ppm] = −147.2 (tdm, $^{1}J_{\mathrm{PF}}$ = 905 Hz, $^{1}J_{\mathrm{PF}}$ = 891 Hz); **IR** ([cm^{-1}]): 3173 (vw), 3147 (vw), 3076 (vw), 2963 (m), 2927 (w), 2873 (vw), 1671 (vw), 1620 (w), 1591 (vw), 1577 (w), 1546 (vw), 1521 (w), 1464 (w), 1414 (m), 1399 (w), 1388 (vw), 1365 (vw), 1349 (vw), 1313 (m), 1258 (vw), 1212 (vs), 1182 (s), 1130 (s), 1115 (w), 1099 (s), 1070 (m), 1010 (vw), 998 (vw), 963 (m), 935 (w), 851 (vw), 803 (s), 784 (w), 759 (m), 738 (m), 719 (m), 703 (m), 671 (w), 636 (w), 619 (s), 581 (w), 535 (m), 504 (w), 494 (w), 486 (w), 443 (w), 430 (w), 421 (w), 407 (w); **HRMS** (ESI) *m*/*z* [*M*]$^+$ calcd for $C_{40}H_{45}CuN_3$: 630.2910, found: 630.2896; *m*/*z* **FAP$^-$** calcd for $C_6F_{18}P$: 444.9450, found: 444.9457; **elemental analysis** calcd (%) for $C_{46}H_{45}CuF_{18}N_3P$: C 51.33, H 4.21, N 3.90; found: C 51.09, H 4.21, N 3.92.

[(IDipp)Cu(η^1-O═$C_{13}H_9N$)]$^+$FAP$^-$ (6). A solution of **IIa** (120 mg, 113 μmol) and acridone (22.1 mg, 113 μmol) in dichloro methane (5 mL) was stirred for 4 h at room temperature. All volatiles were removed under reduced pressure and the remaining solid was suspended in *n*-hexane (10 mL) and the product was filtered off. The product was washed with *n*-hexane (2 × 5 mL) and dried *in vacuo* to yield **6** (108 mg, 98.9 μmol, 87%) as a green solid. Single crystals of **6** suitable for X-ray diffraction were obtained by diffusion of *n*-hexane into a solution of **6** in chloroform. **^{1}H NMR** (400.1 MHz, $CDCl_3$, 298 K): δ [ppm] = 1.26 (d, 12 H, $^{3}J_{\mathrm{HH}}$ = 7.7 Hz, *i*Pr–C*H*$_3$), 1.28 (d, 12 H, $^{3}J_{\mathrm{HH}}$ = 7.7 Hz, *i*Pr–C*H*$_3$), 2.62 (sept, 4 H, $^{3}J_{\mathrm{HH}}$ = 6.2 Hz, *i*Pr–C*H*), 7.13 (t, 2 H, $^{3}J_{\mathrm{HH}}$ = 6.5 Hz, acridone–C*H*), 7.32 (s, 2 H, N–C*H*–C*H*–N), 7.38 (d, 4 H, $^{3}J_{\mathrm{HH}}$ = 7.8 Hz, IDipp-aryl-C$_{meta}$*H*), 7.59 (t, 2 H, $^{3}J_{\mathrm{HH}}$ = 7.6 Hz, IDipp-aryl-C$_{para}$*H*), 7.67 (d, 2 H, acridone–C*H*), 7.76 (t, 3 H, acridone–C*H*), 8.00 (d, 2 H, $^{3}J_{\mathrm{HH}}$ = 6.2 Hz, acridone–C*H*), 9.71 (s, 1 H, acridone–N*H*); **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 298 K): δ [ppm] = 24.0 (*i*Pr–*C*H$_3$), 25.0 (*i*Pr–*C*H$_3$), 29.0 (*i*Pr–*C*H), 118.9 (acridone–*C*H), 123.5 (acridone–*C*H), 124.3 (N–*C*H–*C*H–N), 124.7 (IDipp-aryl-C$_{meta}$), 131.3 (IDipp-aryl-C$_{para}$), 134.2 (IDipp-aryl-*C*$_{ipso}$), 135.5 (acridone–*C*H), 140.9 (acridone–*C*), 145.8 (IDipp-aryl-*C*$_{ortho}$), 177.9 (N–*C*–N); one out of four signals for the acridone–*C*H-groups, one out of two signals for the quaternary carbon atoms as well as the signal for the carbonyl carbon atom were not detected; **^{19}F NMR** (376.8 MHz, $CDCl_3$, 298 K): δ [ppm] = −43.5 (dm, 1 F, $^{1}J_{\mathrm{PF}}$ = 889 Hz, P*F*), −80.1 (m, 3 F, C*F*$_3$), −81.8 (m, 6 F, C*F*$_3$), −87.9 (dm, 2 F, $^{1}J_{\mathrm{PF}}$ = 902 Hz, P*F*$_2$), −115.6 (dm, 2 F, $^{2}J_{\mathrm{PF}}$ = 78 Hz, C*F*$_2$), −115.8 (dm, 4 F, $^{2}J_{\mathrm{PF}}$ = 98 Hz, C*F*$_2$); **^{31}P NMR** (202.4 MHz, $CDCl_3$, 298 K): δ [ppm] = −145.8 (tdm, $^{1}J_{\mathrm{PF}}$ = 902 Hz, $^{1}J_{\mathrm{PF}}$ = 889 Hz); **IR** ([cm^{-1}]): 3390 (w), 3179 (vw), 3076 (vw), 2965 (w), 2929 (w), 2872 (vw), 1629 (m), 1593 (w), 1531 (m), 1468 (m), 1414 (w), 1386 (vw), 1365 (vw), 1351 (w), 1311 (m), 1297 (m), 1261 (w), 1216 (vs), 1184 (s), 1162 (s), 1137 (s), 1098 (s), 1087 (s), 1062 (m), 1027 (vw), 968 (m), 937 (w), 862 (vw), 812 (s), 801 (s), 757 (m), 744 (m), 719 (m), 670 (w), 660 (w), 636 (m), 617 (s), 580 (m), 549 (m), 535 (m), 505 (w), 493 (w), 440 (w), 429 (w), 421 (vw); **HRMS** (ESI) *m*/*z* [*M*]$^+$ calcd for $C_{40}H_{45}CuN_3O$: 646.2859, found: 646.2843; *m*/*z* **FAP$^-$** calcd for $C_6F_{18}P$: 444.9450, found: 444.9451; **elemental analysis** calcd (%) for $C_{46}H_{45}CuF_{18}N_3OP$: C 50.58, H 4.15, N 3.85; found: C 50.13, H 4.38, N 3.29.

[(IDipp)Cu($C_4H_{10}S$)]$^+$FAP$^-$ (7). SEt_2 (10.1 μL, 94.4 μmol) was added to a solution of **IIa** (100 mg, 94.4 μmol) in dichloro methane (8 mL). The reaction mixture was stirred for 4 h at room temperature. All volatiles were removed under reduced pressure and the remaining solid was suspended in *n*-hexane (10 mL) and the product was filtered off. The product was washed with *n*-hexane (2 × 5 mL) and dried *in vacuo* to yield **7** (69.0 mg, 69.9 μmol, 74%) as a colorless solid. Single crystals of **7** suitable for X-ray diffraction were obtained by diffusion of *n*-hexane into a solution of **7** in chloroform. **^{1}H NMR** (600.2 MHz, $CDCl_3$, 298 K): δ [ppm] = 0.83 (t, 6 H, S–CH$_2$–C*H*$_3$, $^{3}J_{\mathrm{HH}}$ = 7.4 Hz), 1.22 (d, 12 H, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, *i*Pr–C*H*$_3$), 1.27 (12 H, d, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, *i*Pr–C*H*$_3$), 2.50 (sept, 4 H, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, *i*Pr–C*H*), overlap with 2.46–2.53 (m, 4 H, S–C*H*$_2$–CH$_3$), 7.32 (s, 2 H, N–C*H*–C*H*–N), 7.35 (d, 4 H, $^{3}J_{\mathrm{HH}}$ = 7.8 Hz, IDipp-aryl-C$_{meta}$*H*), 7.56 (t, 2 H, $^{3}J_{\mathrm{HH}}$ = 7.8 Hz, IDipp-aryl-C$_{para}$*H*); **^{13}C{^{1}H} NMR** (150.9 MHz, $CDCl_3$, 298 K): δ [ppm] = 14.1 (S–CH$_2$–*C*H$_3$), 23.8 (*i*Pr–*C*H$_3$), 25.4 (*i*Pr–*C*H$_3$), 28.5 (S–*C*H$_2$–CH$_3$), 28.9 (*i*Pr–

*C*H), 124.5 (N–*C*H–*C*H–N), 124.7 (IDipp-aryl-C_{meta}), 131.5 (IDipp-aryl-C_{para}), 133.7 (IDipp-aryl-C_{ipso}), 145.8 (IDipp-aryl-C_{ortho}) 176.3 (N–*C*–N); **^{19}F NMR** (470.5, CDCl$_3$, 298 K): δ [ppm] = −45.3 (dm, 1 F, $^{1}J_{\mathrm{PF}}$ = 891 Hz, P*F*), −80.2 (m, 3 F, C*F*$_3$), −81.9 (m, 6 F, C*F*$_3$), −88.6 (dm, 2 F, $^{1}J_{\mathrm{PF}}$ = 904 Hz, P*F*$_2$), −115.9 (dm, 2 F, $^{2}J_{\mathrm{PF}}$ = 82 Hz, CF$_2$), −116.4 (dm, 4 F, $^{2}J_{\mathrm{PF}}$ = 97 Hz, C*F*$_2$); **^{31}P NMR** (202.4 MHz, CDCl$_3$, 298 K): δ [ppm] = −147.2 (tdm, $^{1}J_{\mathrm{PF}}$ = 904 Hz, $^{1}J_{\mathrm{PF}}$ = 891 Hz); **IR** ([cm^{-1}]): 3166 (vw), 3142 (vw), 3075 (vw), 2959 (w), 2929 (w), 2876 (vw), 1665 (vw), 1593 (vw), 1548 (vw), 1462 (m), 1415 (w), 1387 (w), 1366 (w), 1310 (m), 1295 (m), 1257 (w), 1212 (vs), 1179 (s), 1135 (s), 1125 (s), 1097 (s), 1061 (m), 972 (m), 962 (m), 936 (w), 806 (s), 783 (vw), 762 (m), 743 (m), 723 (m), 700 (s), 676 (vw), 637 (m), 618 (s), 580 (m), 534 (w), 505 (vw), 493 (w), 465 (vw), 439 (w), 429 (w), 422(w); **HRMS** (ESI) *m*/*z* [*M*]$^+$ calcd for C$_{31}$H$_{46}$CuN$_2$S: 541.2678, found: 541.26665; *m*/*z* **FAP$^-$** calcd for C$_6$F$_{18}$P: 444.9450, found: 444.9462; **elemental analysis** calcd (%) for C$_{37}$H$_{46}$CuF$_{18}$N$_2$PS: C 45.01, H 4.70, N 2.84, S 3.25; found: C 46.17, H 4.77, H 2.83, S 2.95.

[(IDipp)Cu(C$_4$H$_8$S)]$^+$FAP$^-$ (8). THT (12.5 µL, 142 µmol) was added to a solution of **IIa** (150 mg, 142 µmol) in dichloro methane (5 mL). The reaction mixture was stirred for 4 h at room temperature. All volatiles were removed under reduced pressure and the remaining solid was suspended in *n*-hexane (7 mL) and the product was filtered off. The product was washed with *n*-hexane (2 × 5 mL) and dried *in vacuo* to yield **8** (106 mg, 108 µmol, 76%) as a colorless solid. **^{1}H NMR** (500.1 MHz, CDCl$_3$, 298 K): δ [ppm] = 1.21 (d, 12 H, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, *i*Pr–C*H*$_3$), 1.27 (d, 12 H, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, *i*Pr–C*H*$_3$), 1.72–1.76 (m, 4 H, S–CH$_2$–C*H*$_2$), 2.49 (sept, 4 H, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, *i*Pr–C*H*), 2.62–2.66 (m, 4 H, S–C*H*$_2$–CH$_2$) 7.32 (s, 2 H, N–C*H*–C*H*–N), 7.36 (d, 4 H, $^{3}J_{\mathrm{HH}}$ = 7.8 Hz, IDipp-aryl-C$_{meta}$*H*), 7.58 (t, 2 H, $^{3}J_{\mathrm{HH}}$ = 7.8 Hz, IDipp-aryl-C$_{para}$*H*); **^{13}C{^{1}H} NMR** (100.6 MHz, CDCl$_3$, 298 K): δ [ppm] = 23.7 (*i*Pr–*C*H$_3$), 25.4 (*i*Pr–*C*H$_3$), 28.9 (*i*Pr–*C*H), 30.9 (S–CH$_2$–*C*H$_2$), 35.4 (S–*C*H$_2$–CH$_2$), 124.6 (N–*C*H–*C*H–N), 124.8 (IDipp-aryl-C_{meta}), 131.5 (IDipp-aryl-C_{para}), 133.8 (IDipp-aryl-C_{ipso}), 145.7 (IDipp-aryl-C_{ortho}), 176.3 (N–*C*–N); **^{19}F NMR** (470.5 MHz, CDCl$_3$, 298 K): δ [ppm] = −45.3 (dm, 1 F, $^{1}J_{\mathrm{PF}}$ = 891 Hz, P*F*), −80.2 (m, 3 F, C*F*$_3$), −81.8 (m, 6 F, C*F*$_3$), −88.6 (dm, 2 F, $^{1}J_{\mathrm{PF}}$ = 904 Hz, P*F*$_2$), −115.9 (dm, 2 F, $^{2}J_{\mathrm{PF}}$ = 82 Hz, C*F*$_2$), −116.4 (dm, 4 F, $^{2}J_{\mathrm{PF}}$ = 98 Hz, C*F*$_2$); **^{31}P NMR** (202.4 MHz, CDCl$_3$, 298 K): δ [ppm] = −147.3 (tdm, $^{1}J_{\mathrm{PF}}$ = 904 Hz, $^{1}J_{\mathrm{PF}}$ = 890 Hz); **IR** ([cm^{-1}]): 3167 (vw), 3142 (vw), 3076 (vw), 2967 (w), 2931 (w), 2874 (vw), 1721 (vw), 1593 (vw), 1575 (vw), 1548 (vw), 1468 (w), 1412 (w), 1388 (vw), 1364 (vw), 1295 (m), 1258 (vw), 1212 (vs), 1179 (s), 1144 (s), 1134 (s), 1125 (s), 1097 (s), 1060 (m), 972 (m), 962 (m), 936 (w), 883 (vw), 807 (s), 782 (m), 762 (s), 741 (m), 724 (m), 699 (m), 637 (vw), 618 (vs), 580 (m), 533 (m), 505 (m), 495 (m), 438 (m), 429 (m); **HRMS** (ESI) *m*/*z* [*M*]$^+$ calcd for C$_{31}$H$_{44}$CuN$_2$S: 539.2521, found: 539.2505; *m*/*z* **FAP$^-$** calcd for: 444.9450, found: 444.9438; **elemental analysis** calcd (%) for C$_{37}$H$_{44}$CuF$_{18}$N$_2$PS: C 45.10, H 4.50, N 2.84, S 3.25; found: C 46.63, H 4.58, N 2.77, S 2.25.

[(IDipp)Cu(PCy$_3$)]$^+$FAP$^-$ (9). A solution of **IIa** (150 mg, 142 µmol) and PCy$_3$ (39.7 mg, 142 µmol) in dichloro methane (7 mL) was stirred for 5 h at room temperature. All volatiles were removed under reduced pressure and the remaining solid was suspended in *n*-hexane (10 mL) and the product was filtered off. The product was washed with *n*-hexane (2 × 10 mL) and dried *in vacuo* to yield **9** (142 mg, 121 µmol, 85%) as a colorless solid. **^{1}H NMR** (500.1 MHz, CDCl$_3$, 298 K): δ [ppm] = 0.79–1.66 (m, 33 H, PCy$_3$), 1.24 (d, 12 H, $^{3}J_{\mathrm{HH}}$ = 7.3 Hz, *i*Pr–C*H*$_3$), 1.26 (d, 12 H, $^{3}J_{\mathrm{HH}}$ = 7.3 Hz, *i*Pr–C*H*$_3$), 2.54 (sept, 4 H, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, *i*Pr–C*H*), 7.32 (s, 2 H, N–C*H*–C*H*–N), 7.34 (d, 4 H, $^{3}J_{\mathrm{HH}}$ = 7.8 Hz, IDipp-aryl-C$_{meta}$*H*), 7.53 (t, 2 H, $^{3}J_{\mathrm{HH}}$ = 7.8 Hz, IDipp-aryl-C$_{para}$*H*); **^{13}C{^{1}H} NMR** (125.8 MHz, CDCl$_3$, 298 K): δ [ppm] = 24.1 (*i*Pr–*C*H$_3$), 24.9 (*i*Pr–*C*H$_3$), 25.58 (PCy$_3$), 25.59 (PCy$_3$), 26.9 (PCy$_3$), 27.0 (PCy$_3$), 29.0 (*i*Pr–*C*H), 30.85 (PCy$_3$), 30.86 (PCy$_3$), 31.2 (PCy$_3$), 31.3 (PCy$_3$), 124.3 (N–*C*H–*C*H–N), 124.4 (IDipp-aryl-C_{meta}), 131.1 (IDipp-aryl-C_{para}), 134.0 (IDipp-aryl-C_{ipso}), 145.8 (IDipp-aryl-C_{ortho}), 178.0 (N–*C*–N); **^{19}F NMR** (470.5 MHz, CDCl$_3$, 298 K): δ [ppm] = −45.3 (dm, 1 F, $^{1}J_{\mathrm{PF}}$ = 891 Hz, P*F*), −80.2 (m, 3 F, C*F*$_3$), −81.8 (m, 6 F, C*F*$_3$), −88.5 (dm, 2 F, $^{1}J_{\mathrm{PF}}$ = 903 Hz, P*F*$_2$), −115.9 (dm, 2 F, $^{2}J_{\mathrm{PF}}$ = 83 Hz, C*F*$_2$), −116.4 (dm, 4 F, $^{2}J_{\mathrm{PF}}$ = 98 Hz, C*F*$_2$); **^{31}P NMR** (202.4 MHz, CDCl$_3$, 298 K): δ [ppm] = −147.3 (tdm, $^{1}J_{\mathrm{PF}}$ = 904 Hz, $^{1}J_{\mathrm{PF}}$ = 891 Hz), 27.2 (PCy$_3$); **IR** ([cm^{-1}]): 3171 (vw), 3144 (vw), 3078 (vw), 2931 (m), 2854 (m), 1717 (vw), 1592 (vw), 1549 (vw), 1464 (vw), 1448 (m), 1411 (m), 1387 (w), 1364 (w), 1294 (m), 1272 (vw), 1213 (vs), 1175 (s), 1135 (s), 1124 (s), 1098 (s), 1070 (m), 1061 (w), 1004 (vw), 970 (m), 959 (w), 937 (w), 920 (w), 890 (w), 851 (vw), 816 (s), 784 (vw), 762 (m), 742 (m), 725 (m), 700 (w), 636 (w), 618 (vs), 580 (m), 533 (w), 516 (w), 505 (m), 493 (m), 475 (w), 466 (w), 438 (m), 430 (w); **HRMS** (ESI) *m*/*z* [*M*]$^+$ calcd for C$_{45}$H$_{69}$CuN$_2$P: 731.4494, found: 731.4475; *m*/*z* **FAP$^-$** calcd for C$_6$F$_{18}$P: 444.9450, found: 444.9443; **elemental analysis** calcd (%) for C$_{51}$H$_{69}$CuF$_{18}$N$_2$P$_2$: C 52.02, H 5.91, N 2.38; found: C 52.31, H 5.70, N 2.67.

[{(IDipp)Cu}$_2$(C$_2$N$_3$H$_3$)$_2$]$^{2+}$2FAP$^-$ (10). A solution of **IIa** (150 mg, 142 µmol) and 1,2,4-triazole (9.78 mg, 142 µmol) in dichloro methane (7 mL) was stirred for 4 h at room temperature. All volatiles were removed under reduced pressure and the remaining solid was suspended in *n*-hexane (10 mL) and the product was filtered off. The product was washed with *n*-hexane (2 × 5 mL) and dried *in vacuo* to yield **10** (109 mg, 56.4 µmol, 40%) as a colorless solid. Single crystals of **10** suitable for X-ray diffraction were obtained by diffusion of *n*-hexane into a solution of **10** in chloroform. **^{1}H NMR** (400.1 MHz, CDCl$_3$, 298 K): δ [ppm] = 0.94–1.06 (m, 24 H, *i*Pr–C*H*$_3$), 1.22 (d, 24 H, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, *i*Pr–C*H*$_3$), 2.52 (sept, 8 H, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, *i*Pr–C*H*), 5.88 (s$_{\mathrm{br}}$, 4 H, triazole-C*H*), 7.23 (s, 4 H, N–C*H*–C*H*–N), 7.35 (d, 8 H, $^{3}J_{\mathrm{HH}}$ = 7.8 Hz, IDipp-aryl-C$_{meta}$*H*), 7.65 (t, 4 H, $^{3}J_{\mathrm{HH}}$ = 7.8 Hz, IDipp-aryl-C$_{para}$*H*), 10.65 (s$_{\mathrm{br}}$, 2 H, triazole–N*H*); **^{13}C{^{1}H} NMR** (125.8 MHz, CDCl$_3$, 298 K): δ [ppm] = 23.8 (*i*Pr–*C*H$_3$), 24.6 (*i*Pr–*C*H$_3$), 28.8 (*i*Pr–*C*H), 123.8 (N–*C*H–*C*H–N), 125.0 (IDipp-aryl-C_{meta}), 131.9 (IDipp-aryl-C_{para}), 135.3 (IDipp-aryl-C_{ipso}), 146.0 (IDipp-aryl-C_{ortho}), 182.0 (N–*C*–N); the signal for the triazol–*C*H-groups were not detected; **^{19}F NMR** (470.5 MHz, CDCl$_3$, 298 K): δ [ppm] = −43.8 (dm, 1 F, $^{1}J_{\mathrm{PF}}$ = 881 Hz, P*F*), −80.1 (m, 3 F, C*F*$_3$), −81.7 (m, 6 F, C*F*$_3$), −88.5 (dm, 2 F, $^{1}J_{\mathrm{PF}}$ = 902 Hz, P*F*$_2$), −115.5 (dm, 2 F, $^{2}J_{\mathrm{PF}}$ = 80 Hz, C*F*$_2$), −115.6 (dm, 4 F, $^{2}J_{\mathrm{PF}}$ = 98 Hz, C*F*$_2$); **^{31}P NMR**

(202.4 MHz, $CDCl_3$, 298 K): δ [ppm] = −145.0 (tdm, $^{1}J_{PF}$ = 899 Hz, $^{1}J_{PF}$ = 881 Hz); **IR** ([cm^{-1}]): 3386 (vw), 3147 (w), 3075 (vw), 2968 (w), 2933 (w), 2875 (vw), 1723 (vw), 1592 (vw), 1544 (vw), 1504 (vw), 1463 (w), 1419 (w), 1405 (vw), 1390 (vw), 1370 (vw), 1352 (vw), 1296 (m), 1258 (vw), 1212 (vs), 1185 (s), 1137 (s), 1125 (s), 1098 (s), 1061 (m), 964 (m), 937 (w), 863 (vw), 805 (m), 758 (vw), 743 (m), 720 (m), 679 (w), 667 (w), 637 (w), 618 (vs), 581 (w), 551 (vw), 534 (w), 505 (vw), 494 (w), 465 (vw), 438 (w), 430 (w); **HRMS** (ESI) *m*/*z* $[M]^+$ calcd for 520.2502, found: 520.2484; *m*/*z* **FAP⁻** calcd for $C_6F_{18}P$: 444.9450, found: 444.9445; **elemental analysis** calcd (%) for $C_{70}H_{78}Cu_2F_{36}N_{10}P_2$: C 43.51, H 4.07, N 7.25; found: C 43.99, H 4.35, N 7.20.

[{(cAAC^{Me})Cu}$_2${$C_6H_{12}N_2$}]$^{2+}$2FAP$^-$ (11). A suspension of **IIb** (100 mg, 105 μmol) and DABCO (11.7 mg, 105 μmol) in dichloro methane (5 mL) was stirred for 6 h at room temperature and the suspension was filtered over a plug of Celite. All volatiles of the filtrate were removed under reduced pressure and the remaining solid was suspended in *n*-hexane (10 mL) and the product was filtered off. The product was washed with *n*-hexane (2 × 5 mL) and dried *in vacuo* to yield **11** (55.0 mg, 53.2 μmol, 62%) as a colorless solid. Single crystals of **11** suitable for X-ray diffraction were obtained by diffusion of *n*-hexane into a solution of **11** in dichloro methane. **^{1}H NMR** (500.1 MHz, CD_2Cl_2, 298 K): δ [ppm] = 1.18 (d, 12 H, $^{3}J_{HH}$ = 6.7 Hz, *i*Pr–C*H*$_3$), 1.33 (d, 12 H, $^{3}J_{HH}$ = 6.7 Hz, *i*Pr–C*H*$_3$), 1.37 (s, 12 H, Cu–C–C(C*H*$_3$)$_2$), 1.41 (s, 12 H, N–C(C*H*$_3$)$_2$), 2.12 (s, 4 H, C*H*$_2$), 2.78 (sept, 4 H, $^{3}J_{HH}$ = 6.8 Hz, *i*Pr–C*H*), 2.86 (s$_{br}$, 12 H, DABCO–C*H*$_2$), 7.33 (d, 4 H, $^{3}J_{HH}$ = 7.8 Hz, cAAC^{Me}-aryl-C$_{meta}$*H*), 7.48 (t, 2 H, $^{3}J_{HH}$ = 7.8 Hz, cAAC^{Me}-aryl-C$_{para}$*H*); **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 298 K): δ [ppm] = 22.3 (*i*Pr–*C*H$_3$), 27.4 (*i*Pr–*C*H$_3$), 28.1 (Cu–C–C(*C*H$_3$)$_2$), 29.41 (N–C(*C*H$_3$)$_2$/*i*Pr–*C*H), 29.47 (N–C(*C*H$_3$)$_2$/*i*Pr–*C*H), 47.8 (DABCO–*C*H$_2$), 49.4 (*C*H$_2$), 54.1 (Cu–C–*C*(CH$_3$)$_2$), 83.7 (N–*C*(CH$_3$)$_2$), 125.7 (cAAC^{Me}-aryl-*C*$_{meta}$), 131.2 (cAAC^{Me}-aryl-*C*$_{para}$), 134.7 (cAAC^{Me}-aryl-*C*$_{ipso}$), 145.1 (cAAC^{Me}-aryl-*C*$_{ortho}$) 246.1 (N–*C*–Cu); **^{19}F NMR** (470.5 MHz, CD_2Cl_2, 298 K): δ [ppm] = −45.2 (dm, 1 F, $^{1}J_{PF}$ = 890 Hz, P*F*), −80.5 (m, 3 F, C*F*$_3$), −82.1 (m, 6 F, C*F*$_3$), −88.6 (dm, 2 F, $^{1}J_{PF}$ = 903 Hz, P*F*$_2$), −115.9 (dm, 2 F, $^{2}J_{PF}$ = 84 Hz, C*F*$_2$), −116.4 (dm, 4 F, $^{2}J_{PF}$ = 98 Hz, C*F*$_2$); **^{31}P NMR** (202.4 MHz, CD_2Cl_2, 298 K): δ [ppm] = −147.3 (tdm, $^{1}J_{PF}$ = 902 Hz, $^{1}J_{PF}$ = 890 Hz); **IR** ([cm^{-1}]): 2965 (m), 2942 (m), 2875 (w), 1588 (vw), 1530 (m), 1461 (m), 1387 (vw), 1374 (vw), 1364 (vw), 1312 (w), 1293 (w), 1207 (m), 1184 (m), 1136 (m), 1125 (m), 1100 (m), 1069 (m), 1054 (m), 1023 (w), 974 (m), 959 (m), 898 (vw), 814 (m), 779 (w), 759 (w), 720 (m), 637 (w), 618 (m), 580 (w), 532 (w), 496 (m), 467 (w), 439 (w); **elemental analysis** calcd (%) for $C_{58}H_{74}Cu_2F_{36}N_4P_2$: C 40.97, H 4.39, N 3.30; found: C 41.38, H 4.36, N 3.61.

[{(cAAC^{Me})Cu}$_2${$C_4H_4N_2$}]$^{2+}$2FAP$^-$ (12). A suspension **IIb** (100 mg, 105 μmol) and pyrazine (8.34 mg, 105 μmol) in dichloro methane (5 mL) was stirred for 3 h at room temperature and the suspension was filtered over a plug of Celite. All volatiles of the filtrate were removed under reduced pressure and the remaining solid was suspended in *n*-hexane (10 mL) and the product was filtered off. The product was washed with *n*-hexane (2 × 5 mL) and dried *in vacuo* to yield **12** (59.0 mg, 35.4 μmol, 68%) as an off-white solid. Single crystals of **12** suitable for X-ray diffraction were obtained by diffusion of *n*-hexane into a solution of **12** in dichloro methane. **^{1}H NMR** (500.1 MHz, $CDCl_3$, 298 K): δ [ppm] = 1.16 (d, 12 H, $^{3}J_{HH}$ = 6.8 Hz, *i*Pr–C*H*$_3$), 1.36 (d, 12 H, $^{3}J_{HH}$ = 6.8 Hz, *i*Pr–C*H*$_3$), 1.44 (s, 12 H, N–C(C*H*$_3$)$_2$), 1.47 (s, 12 H, Cu–C–C(C*H*$_3$)$_2$), 2.18 (s, 4 H, C*H*$_2$), 2.84 (sept, 4 H, $^{3}J_{HH}$ = 6.8 Hz, *i*Pr–C*H*), 7.37 (d, 4 H, $^{3}J_{HH}$ = 7.8 Hz, cAAC^{Me}-aryl-C$_{meta}$*H*), 7.53 (t, 2 H, $^{3}J_{HH}$ = 7.8 Hz, cAAC^{Me}-aryl-C$_{para}$*H*), 8.27 (s$_{br}$, 4 H, pyrazine-aryl-C*H*); **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 298 K): δ [ppm] = 22.3 (*i*Pr–*C*H$_3$), 27.6 (*i*Pr–*C*H$_3$), 28.1 (Cu–C–C(*C*H$_3$)$_2$), 29.45 (N–C(*C*H$_3$)$_2$/*i*Pr–*C*H), 29.47 (N–C(*C*H$_3$)$_2$/*i*Pr–*C*H), 49.5 (*C*H$_2$), 54.3 (Cu–C–*C*(CH$_3$)$_2$), 83.8 (N–*C*(CH$_3$)$_2$), 125.8 (cAAC^{Me}-aryl-*C*$_{meta}$), 131.3 (cAAC^{Me}-aryl-*C*$_{para}$), 134.6 (cAAC^{Me}-aryl-*C*$_{ipso}$), 145.4 (cAAC^{Me}-aryl-*C*$_{ortho}$), 147.0 (pyrazine-aryl-*C*H), 245.5 (N–*C*–Cu); **^{19}F NMR** (470.5 MHz, CD_2Cl_2, 298 K): δ [ppm] = −45.0 (dm, 1 F, $^{1}J_{PF}$ = 890 Hz, P*F*), −80.5 (m, 3 F, C*F*$_3$), −82.1 (m, 6 F, C*F*$_3$), −88.6 (dm, 2 F, $^{1}J_{PF}$ = 902 Hz, P*F*$_2$), −115.9 (dm, 2 F, $^{2}J_{PF}$ = 88 Hz, C*F*$_2$), −116.4 (dm, 4 F, $^{2}J_{PF}$ = 98 Hz, C*F*$_2$); **^{31}P NMR** (202.4 MHz, CD_2Cl_2, 298 K): δ [ppm] = −147.2 (tdm, $^{1}J_{PF}$ = 902 Hz, $^{1}J_{PF}$ = 888 Hz); **IR** ([cm^{-1}]): 3146 (vw), 3112 (vw), 3079 (vw), 3061 (vw), 2969 (m), 2945 (m), 2875 (m), 1587 (vw), 1534 (m), 1460 (m), 1432 (m), 1388 (w), 1373 (w), 1365 (w), 1295 (m), 1268 (vw), 1205 (s), 1183 (s), 1137 (s), 1124 (m), 1101 (m), 1070 (m), 1053 (w), 1023 (vw), 975 (m), 932 (w), 899 (vw), 833 (vw), 805 (s), 781 (m), 766 (m), 757 (m), 715 (s), 637 (m), 618 (vs), 600 (m), 580 (m), 553 (w), 532 (m), 494 (m), 468 (w), 437 (m), 428 (m); **elemental analysis** calcd (%) for $C_{56}H_{66}Cu_2F_{36}N_4P_2$: C 40.32, H 3.99, N 3.36; found: C 39.72, H 3.47, N 4.12.

[(cAAC^{Me})Cu($C_7H_{10}N_2$)]$^+$FAP$^-$ (13). A suspension of **IIb** (100 mg, 105 μmol) and DMAP (11.7 mg, 105 μmol) in dichloro methane (5 mL) was stirred for 4 h at room temperature and the suspension was filtered over a plug of Celite. All volatiles of the filtrate were removed under reduced pressure and the remaining solid was suspended in *n*-hexane (10 mL) and the product was filtered off. The product was washed with *n*-hexane (2 × 5 mL) and dried *in vacuo* to yield **27** (55.0 mg, 60.0 μmol, 57%) as a colorless solid. **^{1}H NMR** (500.1 MHz, $CDCl_3$, 298 K): δ [ppm] = 1.20 (d, 6 H, $^{3}J_{HH}$ = 6.8 Hz, *i*Pr–C*H*$_3$), 1.35 (d, 6 H, $^{3}J_{HH}$ = 6.8 Hz, *i*Pr–C*H*$_3$), 1.43 (s, 6 H, N–C(C*H*$_3$)$_2$), 1.49 (s, 6 H, Cu–C–C(C*H*$_3$)$_2$), 2.15 (s, 2 H, C*H*$_2$), 2.84 (sept, 2 H, $^{3}J_{HH}$ = 6.8 Hz, *i*Pr–C*H*), 3.02 (s, 6 H, DMAP–C*H*$_3$), 6.43 (d, 2 H, DMAP–C$_{meta}$*H*), 7.31–7.39 (m, 2 H, DMAP–C$_{ortho}$*H*) 7.34 (d, 2 H, $^{3}J_{HH}$ = 7.8 Hz, cAAC^{Me}-aryl-C$_{meta}$*H*), 7.51 (t, 1 H, $^{3}J_{HH}$ = 7.8 Hz, cAAC^{Me}-aryl-C$_{para}$*H*); **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 298 K): δ [ppm] = 22.4 (*i*Pr–*C*H$_3$), 26.9 (*i*Pr–*C*H$_3$), 28.2 (Cu–C–C(*C*H$_3$)$_2$), 29.10 (*i*Pr–*C*H, N–C(*C*H$_3$)$_2$), 29.15 (*i*Pr–*C*H, N–C(*C*H$_3$)$_2$), 39.1 (DMAP–*C*H$_3$), 49.3 (*C*H$_2$), 82.5 (N–*C*(CH$_3$)$_2$), 107.4 (DMAP–C$_{meta}$*H*), 125.2 (cAAC^{Me}-aryl-*C*$_{meta}$), 130.5 (cAAC^{Me}-aryl-*C*$_{para}$), 134.3 (cAAC^{Me}-aryl-*C*$_{ipso}$), 145.0 (cAAC^{Me}-aryl-*C*$_{ortho}$), 147.9 (DMAP–C$_{ortho}$*H*), 155.5 (DMAP–C$_{para}$), 247.7 (N–*C*–Cu); **^{19}F NMR** (470.5 MHz, $CDCl_3$, 298 K): δ [ppm] = −45.3 (dm, 1 F, $^{1}J_{PF}$ = 889 Hz, P*F*), −80.2 (m, 3 F, C*F*$_3$), −81.8 (m, 6 F, C*F*$_3$), −88.9 (dm, 2 F, $^{1}J_{PF}$ = 904 Hz, P*F*$_2$), −115.8 (dm, 2 F, $^{2}J_{PF}$ = 84 Hz, C*F*$_2$), −116.3 (dm, 4 F, $^{2}J_{PF}$ = 98 Hz, C*F*$_2$); **^{31}P NMR** (202.4 MHz, $CDCl_3$, 298 K): δ [ppm] = −147.0 (tdm, $^{1}J_{PF}$ = 904 Hz, $^{1}J_{PF}$ = 889 Hz); **IR** ([cm^{-1}]): 3395 (vw), 2969 (m), 2953 (m), 2926 (m), 2875 (m), 2863 (m), 1791 (vw), 1619 (s), 1590 (w), 1549 (m), 1529 (m), 1458 (w), 1447 (w), 1397 (m), 1374 (w), 1346 (vw), 1312 (m), 1295 (m), 1206 (s), 1178 (s), 1136 (s), 1123 (s), 1097 (m), 1070 (m), 1027 (m), 960 (m), 897 (vw), 810 (vs), 782 (m), 761 (m), 722 (s), 637 (m), 617 (s), 580 (m), 556 (w), 529 (m), 505 (w), 494 (m), 467 (w), 438 (m), 428 (m); **HRMS** (ESI) *m*/*z* [*M*]$^+$ calcd for C$_{27}$H$_{41}$CuN$_3$: 470.2597, found: 470.2579; *m*/*z* **FAP$^-$** calcd for C$_6$F$_{18}$P: 444.9450, found: 444.9441; **elemental analysis** calcd (%) for C$_{33}$H$_{41}$CuF$_{18}$N$_3$P: C 43.26, H 4.51, N 4.59; found: C 43.06, H 4.00, N 5.39.

[(cAAC^{Me})Cu(C$_4$H$_{10}$S)]$^+$FAP$^-$ (14). SEt$_2$ (11.2 µL, 105 µmol) was added to a suspension of **IIb** (100 mg, 105 µmol) in dichloro methane (5 mL). The reaction mixture was stirred for 2 h at room temperature and the suspension was filtered over a plug of Celite. All volatiles of the filtrate were removed under reduced pressure and the remaining solid was suspended in *n*-hexane (10 mL) and the product was filtered off. The product was washed with *n*-hexane (2 × 5 mL) and dried *in vacuo* to yield **14** (178 mg, 201 µmol, 74%) as a black solid. **^{1}H NMR** (400.1 MHz, CDCl$_3$, 298 K): *δ* [ppm] = 1.07–1.18 (m, 6 H, S–CH$_2$–C*H*$_3$), 1.20 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr–C*H*$_3$), 1.35 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr–C*H*$_3$), 1.43 (s, 6 H, N–C(C*H*$_3$)$_2$), 1.44 (s, 6 H, Cu–C–C(C*H*$_3$)$_2$), 2.15 (s, 2 H, C*H*$_2$), 2.63–2.77 (m, 4 H, S–C*H*$_2$–CH$_3$), 2.81 (sept, 2 H, $^3J_{HH}$ = 6.3 Hz, *i*Pr–C*H*), 7.33 (d, 2 H, $^3J_{HH}$ = 7.8 Hz, cAAC^{Me}-aryl-C$_{meta}$*H*), 7.48 (t, 1 H, $^3J_{HH}$ = 7.8 Hz, cAAC^{Me}-aryl-C$_{para}$*H*); **^{13}C{^{1}H} NMR** (100.6 MHz, CDCl$_3$, 298 K): *δ* [ppm] = 14.5 (S–CH$_2$–*C*H$_3$), 22.3 (*i*Pr–*C*H$_3$), 27.4 (*i*Pr–*C*H$_3$), 28.1 (Cu–C–C(*C*H$_3$)$_2$), 28.4 (S–*C*H$_2$–CH$_3$), 29.23 (*i*Pr–*C*H, N–C (*C*H$_3$)$_2$), 29.25 (*i*Pr–*C*H, N–C(*C*H$_3$)$_2$), 49.2 (*C*H$_2$), 54.2 (Cu–C–*C*(CH$_3$)$_2$), 83.4 (N–*C*(CH$_3$)$_2$), 125.5 (cAAC^{Me}-aryl-*C*$_{meta}$), 130.9 (cAAC^{Me}-aryl-*C*$_{para}$), 134.2 (cAAC^{Me}-aryl-*C*$_{ipso}$), 145.1 (cAAC^{Me}-aryl-*C*$_{ortho}$) 245.3 (N–*C*–Cu); **^{19}F NMR** (470.5 MHz, CDCl$_3$, 298 K): *δ* [ppm] = −45.2 (dm, 1 F, $^1J_{PF}$ = 891 Hz, P*F*), −80.1 (m, 3 F, C*F*$_3$), −81.8 (m, 6 F, C*F*$_3$), −88.5 (dm, 2 F, $^1J_{PF}$ = 904 Hz, P*F*$_2$), −115.8 (dm, 2 F, $^2J_{PF}$ = 84 Hz, C*F*$_2$), −116.3 (dm, 4 F, $^2J_{PF}$ = 98 Hz, C*F*$_2$); **^{31}P NMR** (202.4 MHz, CDCl$_3$, 298 K): *δ* [ppm] = −147.2 (tdm, $^1J_{PF}$ = 904 Hz, $^1J_{PF}$ = 890 Hz); **IR** ([cm^{-1}]): 3066 (vw), 2969 (m), 2948 (m), 2873 (m), 1721(vw), 1588 (vw), 1542 (m), 1459 (m), 1388 (w), 1373 (w), 1366 (w), 1344 (vw), 1310 (m), 1296 (m), 1267 (w), 1211 (s), 1178 (vs), 1126 (s), 1090 (s), 1068 (m), 1013 (vw), 972 (m), 963 (m), 933 (vw), 914 (vw), 896 (vw), 885 (vw), 809 (s), 779 (m), 761 (m), 742 (w), 721 (s), 675 (vw), 636 (m), 616 (vs), 580 (m), 552 (vw), 533 (m), 506 (w), 495 (m), 467 (vw), 439 (w), 428 (w); **HRMS** (ESI) *m*/*z* [*M*]$^+$ calcd for C$_{24}$H$_{41}$CuNS: 438.2256, found: 438.2240; *m*/*z* **FAP$^-$** calcd for C$_6$F$_{18}$P: 444.9450, found: 444.9435; **elemental analysis** calcd (%) for C$_{30}$H$_{41}$CuF$_{18}$NPS: C 40.75, H 4.67, N 1.58, S 3.63; found: C 40.60, H 4.62, N 1.67, S 3.16.

[(cAAC^{Me})Cu(N≡CMe)]$^+$FAP$^-$ (15). The phosphorane (C$_2$F$_5$)$_3$PF$_2$ (77.0 µL, 327 µmol) was added at room temperature to a solution of **Ic** (120 mg, 326 µmol) in acetonitrile (5 mL). The reaction mixture was stirred for 2 h at room temperature. All volatiles were removed under reduced pressure and the remaining solid was suspended in *n*-hexane (5 mL) and the product was filtered off. The product was washed with *n*-hexane (5 mL) and dried *in vacuo* to yield **15** (188 mg, 225 µmol, 69%) as a colorless solid. **^{1}H NMR** (500.1 MHz, CDCl$_3$, 298 K): *δ* [ppm] = 1.19 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr–C*H*$_3$), 1.34 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr–C*H*$_3$), 1.38 (s, 6 H, N–C(C*H*$_3$)$_2$), 1.42 (s, 6 H, Cu–C–C(C*H*$_3$)$_2$), 2.10 (s, 2 H, C*H*$_2$), 2.22 (s, 3 H, N≡C–C*H*$_3$), 2.75 (sept, 2 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr–C*H*), 7.31 (d, 2 H, $^3J_{HH}$ = 7.8 Hz, cAAC^{Me}-aryl-C$_{meta}$*H*), 7.48 (t, 1 H, $^3J_{HH}$ = 7.8 Hz, cAAC^{Me}-aryl-C$_{para}$*H*); **^{13}C{^{1}H}-NMR** (125.8 MHz, CDCl$_3$, 298 K): *δ* [ppm] = 2.1 (N≡C–*C*H$_3$), 22.3 (*i*Pr–*C*H$_3$), 27.3 (*i*Pr–*C*H$_3$), 28.0 (Cu–C–C(*C*H$_3$)$_2$), 29.18 (*i*Pr–*C*H/N–C(*C*H$_3$)$_2$), 29.20 (*i*Pr–*C*H/N–C(*C*H$_3$)$_2$), 49.2 (*C*H$_2$), 54.2 (Cu–*C*–C(CH$_3$)$_2$), 83.1 (N–*C*(CH$_3$)$_2$), 118.2 (N≡C), 125.2 (cAAC^{Me}-aryl-*C*$_{meta}$), 130.7 (cAAC^{Me}-aryl-*C*$_{para}$), 133.7 (cAAC^{Me}-aryl-*C*$_{ipso}$), 145.0 (cAAC^{Me}-aryl-*C*$_{ortho}$), 245.5 (N–*C*–Cu); **^{19}F-NMR** (470.5 MHz, CDCl$_3$, 298 K): *δ* [ppm] = −45.0 (dm, 1 F, $^1J_{PF}$ = 892 Hz, P*F*), −80.1 (m, 3 F, C*F*$_3$), −81.8 (m, 6 F, C*F*$_3$), −88.4 (dm, 2 F, $^1J_{PF}$ = 903 Hz, P*F*$_2$), −115.8 (dm, 2 F, $^2J_{PF}$ = 83 Hz, C*F*$_2$), −116.3 (dm, 4 F, $^2J_{PF}$ = 98 Hz, C*F*$_2$); **^{31}P-NMR** (202.4 MHz, CDCl$_3$, 298 K): *δ* [ppm] = −147.3 (tdm, $^1J_{PF}$ = 903 Hz, $^1J_{PF}$ = 892 Hz); **IR** (ATR [cm^{-1}]): 2975 (w), 2948 (w), 2873 (vw), 2323 (vw), 2297 (vw), 1588 (vw), 1524 (vw), 1460 (w), 1388 (vw), 1372 (vw), 1364 (vw), 1309 (w), 1296 (w), 1210 (s), 1180 (s), 1135 (s), 1124 (s), 1097 (m), 1068 (m), 962 (m), 932 (vw), 808 (s), 762 (m), 722 (s), 618 (vs), 580 (m), 533 (m), 494 (w), 467 (vw), 438 (vw), 428 (w); **HRMS** (ESI) *m*/*z* [*M*]$^+$ calcd for C$_{22}$H$_{34}$CuN$_2$: 389.2018, found: 389.2002; *m*/*z* **FAP$^-$** calcd for C$_6$F$_{18}$P: 444.9450, found: 444.9444; **elemental analysis** calcd (%) for C$_{28}$H$_{34}$CuF$_{18}$N$_2$P: (gefunden): C 40.27, H 4.10, N 3.35; found: C 40.81, H 4.26, N 3.51.

[(IDipp)Cu(N≡CMe)$_2$]$^+$FAP$^-$ (16). The phosphorane (C$_2$F$_5$)$_3$PF$_2$ (46.5 µL, 197 µmol) was added at room temperature to a solution of **Ia** (93.0 mg, 197 µmol) in acetonitrile (3 mL). The reaction mixture was stirred for 1.5 h at room temperature. All volatiles were removed under reduced pressure and the product was dried *in vacuo* to yield **16** (157 mg, 160 µmol, 81%) as a colorless solid. Single crystals of **16** suitable for X-ray diffraction were obtained by vapor diffusion of *n*-pentane into a solution of **16** in toluene. **^{1}H NMR** (500.1 MHz, CDCl$_3$, 298 K): *δ* [ppm] = 1.23 (d, 12 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr–C*H*$_3$) overlap with 1.25 (d, 12 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr–C*H*$_3$), 1.99 (s, 6 H, N≡C–C*H*$_3$), 2.51 (sept, 4 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr–C*H*), 7.27 (s, 2 H, N–C*H*–C*H*–N), 7.36 (d, 4 H, $^3J_{HH}$ = 7.8 Hz, IDipp-aryl-C$_{meta}$*H*), 7.55 (t, 2 H, $^3J_{HH}$ = 7.8 Hz, IDipp-aryl-C$_{para}$*H*); **^{13}C{^{1}H} NMR** (125.8 MHz, CD$_2$Cl$_2$, 298 K): *δ* [ppm] = 2.3 (N≡C–*C*H$_3$), 24.0 (*i*Pr–*C*H$_3$), 24.9 (*i*Pr–*C*H$_3$), 29.1 (*i*Pr–*C*H), 117.3 (N≡*C*), 124.4 (N–*C*H–*C*H–N), 124.6 (IDipp-aryl-*C*$_{meta}$), 131.1 (IDipp-aryl-*C*$_{para}$), 134.6 (IDipp-aryl-*C*$_{ipso}$), 146.2 (IDipp-aryl-*C*$_{ortho}$), 178.3 (N–*C*–N); **^{19}F NMR** (470.5 MHz, CD$_2$Cl$_2$, 298 K): *δ* [ppm] = −45.1 (dm, 1 F, $^1J_{PF}$ = 889 Hz, P*F*), −80.6 (m, 3 F, C*F*$_3$), −82.3 (m, 6 F, C*F*$_3$), −88.6 (dm, 2 F, $^1J_{PF}$ = 902 Hz, P*F*$_2$), −116.1 (dm, 2 F, $^2J_{PF}$ = 83 Hz, C*F*$_2$), −116.7 (dm, 4 F, $^2J_{PF}$ = 98 Hz, C*F*$_2$); **^{31}P NMR** (202.4 MHz, CD$_2$Cl$_2$, 298 K): *δ* [ppm] = −147.7 (tdm, $^1J_{PF}$ = 902 Hz, $^1J_{PF}$ = 889 Hz); **IR** ([cm^{-1}]): 3186 (vw), 3151 (vw), 2967 (m), 2931 (w), 2871 (w), 2314 (vw), 1681 (vw), 1580 (vw), 1552 (vw), 1471 (m), 1408 (w), 1385 (w), 1365 (w), 1329 (w), 1310 (m), 1258 (vw), 1213 (vs), 1189 (vs), 1138 (s), 1127 (s), 1088 (s), 1061 (m), 967 (m), 949 (w), 937 (w), 806 (s), 763 (s), 742 (m), 724 (vs), 695 (w), 636 (m), 617 (vs), 602 (m), 580 (m), 560 (vw), 534 (w), 506 (w), 495 (w), 443 (w), 429 (w), 422 (w); **HRMS** (ESI) *m*/*z* [M − CH_3CN]$^+$ calcd for. $C_{29}H_{39}CuN_3$: 492.2440, found: 492.2427; *m*/*z* **FAP**$^-$ calcd for $C_6F_{18}P$: 444.9450, found: 444.9458; **elemental analysis** calcd (%) for $C_{37}H_{42}CuF_{18}N_4P$: C 45.38, H 4.32, N 5.72; found: C 45.75, H 4.38, N 5.12.

[(IDipp)Cu(N≡CPh)]$^+$FAP$^-$ (17). The phosphorane $(C_2F_5)_3PF_2$ (75.0 µL, 319 µmol) was added at room temperature to a solution of **Ia** (150 mg, 318 µmol) and benzonitrile (32.6 µL, 319 µmol) in dichloro methane (5 mL). The reaction mixture was stirred for 3 h at room temperature. All volatiles were removed under reduced pressure and the remaining solid was suspended in *n*-hexane (5 mL) and the product was filtered off. The product was washed with *n*-hexane (2 × 5 mL) and dried *in vacuo* to yield **17** (235 mg, 262 µmol, 82%) as a colorless solid. Single crystals of **17** suitable for X-ray diffraction were obtained by vapor diffusion of *n*-pentane into a saturated solution of **17** in toluene. **^{1}H NMR** (500.1 MHz, $CDCl_3$, 298 K): δ [ppm] = 1.26 (d, 12 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr–C*H*$_3$), 1.27 (d, 12 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr–C*H*$_3$), 2.51 (sept, 4 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr–C*H*), 7.30 (s, N–C*H*–C*H*–N), 7.37 (d, 4 H, $^3J_{HH}$ = 7.8 Hz, IDipp-aryl-C$_{meta}$*H*), 7.54 (t$_{br}$, 2 H, $^3J_{HH}$ = 7.6 Hz, benzonitrile-aryl-C$_{meta}$*H*), 7.58 (t, 2 H, $^3J_{HH}$ = 7.8 Hz, IDipp-aryl-C$_{para}$*H*), 7.65 (d$_{br}$, 2 H, $^3J_{HH}$ = 7.6 Hz, benzonitrile-aryl-C$_{ortho}$*H*), 7.77 (t$_{br}$, 1 H, $^3J_{HH}$ = 7.6 Hz, benzonitrile-aryl-C$_{para}$*H*); **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 298 K): δ [ppm] = 23.8 (*i*Pr–*C*H$_3$), 25.2 (*i*Pr–*C*H$_3$), 28.9 (*i*Pr–*C*H), 106.9 (benzonitrile-aryl-*C*$_{ipso}$), 118.3 (N≡*C*), 124.71 (N–*C*H–*C*H–N), 124.74 (IDipp-aryl-*C*$_{meta}$), 130.0 (benzonitrile-aryl-*C*$_{meta}$), 131.4 (IDipp-aryl-*C*$_{para}$), 133.6 (benzonitrile-aryl-*C*$_{ortho}$), 133.7 (IDipp-aryl-*C*$_{ipso}$), 136.3 (benzonitrile-aryl-*C*$_{para}$), 145.7 (IDipp-aryl-*C*$_{ortho}$), 175.5 (N–*C*–N); **^{19}F NMR** (470.5 MHz, $CDCl_3$, 298 K): δ [ppm] = −45.3 (dm, 1 F, $^1J_{PF}$ = 892 Hz, P*F*), −80.2 (m, 3 F, C*F*$_3$), −81.8 (m, 6 F, C*F*$_3$), −88.6 (dm, 2 F, $^1J_{PF}$ = 903 Hz, P*F*$_2$), −115.9 (dm, 2 F, $^2J_{PF}$ = 82 Hz, C*F*$_2$), −116.4 (dm, 4 F, $^2J_{PF}$ = 98 Hz, C*F*$_2$); **^{31}P NMR** (202.4 MHz, $CDCl_3$, 298 K): δ [ppm] = −147.3 (tdm, $^1J_{PF}$ = 903 Hz, $^1J_{PF}$ = 892 Hz); **IR** ([cm^{-1}]): 3186 (vw), 3134 (vw), 2967 (w), 2927 (w), 2874 (w), 2275 (w), 1597 (w), 1547 (vw), 1468 (w), 1414 (w), 1389 (vw), 1367 (vw), 1312 (m), 1215 (vs), 1184 (s), 1138 (s), 1125 (m), 1111 (w), 1089 (m), 1061 (w), 963 (m), 934 (w), 805 (s), 758 (s), 743 (m), 716 (vs), 702 (w), 681 (w), 636 (w), 618 (vs), 601 (w), 581 (w), 551 (w), 534 (w), 505 (w), 494 (vw), 441 (w), 429 (w), 420 (w); **HRMS** (ESI) *m*/*z* [*M*]$^+$ calcd for $C_{34}H_{41}CuN_3$: 554.2597, found: 554.2583; *m*/*z* **FAP**$^-$ calcd for $C_6F_{18}P$: 444.9450, found: 444.9426; **elemental analysis** calcd (%) for $C_{40}H_{41}CuF_{18}N_3P$: C 48.03, H 4.13, N 4.20; found: C 48.23, H 4.07, N 4.42.

[(IDipp)Cu(NH$_2$Ph)]$^+$FAP$^-$ (18). The phosphorane $(C_2F_5)_3PF_2$ (75.0 µL, 319 µmol) was added at room temperature to a solution of **Ia** (150 mg, 318 µmol) and aniline (29.2 µL, 320 µmol) in dichloro methane (5 mL). The reaction mixture was stirred for 1.5 h at room temperature. All volatiles were removed under reduced pressure and the remaining solid was suspended in *n*-hexane (5 mL) and the product was filtered off. The product was washed with *n*-hexane (2 × 5 mL) and dried *in vacuo* to yield **18** (197 mg, 199 µmol, 62%) as a colorless solid. **^{1}H NMR** (500.1 MHz, CD_2Cl_2, 298 K): δ [ppm] = 1.11 (d, 12 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr–C*H*$_3$), 1.22 (d, 12 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr–C*H*$_3$), 2.45 (sept, 4 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr–C*H*), 4.74 (s, 2 H, N*H*$_2$), 6.51 (m, 2 H, aniline-aryl-C$_{ortho}$*H*), 7.16 (m, 3 H, overlap of aniline-aryl-C$_{meta}$*H* and aniline-aryl-C$_{para}$*H*), 7.28 (s, 2 H, N–C*H*–C*H*–N), 7.33 (d, 4 H, $^3J_{HH}$ = 7.8 Hz, IDipp-aryl-C$_{meta}$*H*), 7.57 (t, 2 H, $^3J_{HH}$ = 7.8 Hz, IDipp-aryl-C$_{para}$*H*); **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 298 K): δ [ppm] = 23.9 (*i*Pr–*C*H$_3$), 25.0 (*i*Pr–*C*H$_3$), 29.1 (*i*Pr–*C*H), 120.5 (aniline-aryl-*C*$_{ortho}$), 124.7 (N–*C*H–*C*H–N), 124.9 (IDipp-aryl-*C*$_{meta}$), 126.5 (aniline-aryl-*C*$_{para}$), 130.6 (aniline-aryl-*C*$_{meta}$), 131.4 (IDipp-aryl-*C*$_{para}$), 134.3 (IDipp-aryl-*C*$_{ipso}$), 136.3 (aniline-aryl-*C*$_{ipso}$), 146.0 (IDipp-aryl-*C*$_{ortho}$), 176.9 (N–*C*–N); **^{19}F NMR** (470.5 MHz, CD_2Cl_2, 298 K): δ [ppm] = −45.0 (dm, 1 F, $^1J_{PF}$ = 889 Hz, P*F*), −80.6 (m, 3 F, C*F*$_3$), −82.2 (m, 6 F, C*F*$_3$), −88.6 (dm, 2 F, $^1J_{PF}$ = 904 Hz, P*F*$_2$), −116.0 (dm, 2 F, $^2J_{PF}$ = 84 Hz, C*F*$_2$), −116.5 (dm, 4 F, $^2J_{PF}$ = 99 Hz, C*F*$_2$); **^{31}P NMR** (202.4 MHz, CD_2Cl_2, 298 K): δ [ppm] = −147.1 (tdm, $^1J_{PF}$ = 904 Hz, $^1J_{PF}$ = 889 Hz); **IR** ([cm^{-1}]): 3325 (w), 3264 (w), 2967 (w), 2874 (w), 1597 (w), 1577 (w), 1550 (vw), 1494 (w), 1462 (w), 1414 (w), 1387 (vw), 1367 (vw), 1295 (m), 1211 (vs), 1186 (s), 1137 (m), 1125 (s), 1098 (m), 971 (m), 937 (vw), 807 (s), 759 (s), 722 (s), 693 (m), 637 (w), 617 (vs), 580 (w), 532 (m), 495 (w), 467 (vw), 438 (w), 429 (w); **HRMS** (ESI) *m*/*z* [*M*]$^+$ calcd for $C_{33}H_{43}CuN_3$: 544.2753, found: 544.2734; *m*/*z* **FAP**$^-$ calcd for $C_6F_{18}P$: 444.9450, found: 444.9431; **elemental analysis** calcd (%) for $C_{39}H_{43}CuF_{18}N_3P$: C 47.30, H 4.38, N 4.24; found: C 46.99, H 4.31, N 4.39.

[(SIDipp)Cu(NH$_2$Ph)]$^+$FAP$^-$ (19). The phosphorane $(C_2F_5)_3PF_2$ (27.1 µL, 297 µmol) was added at room temperature to a solution of **Ib** (140 mg, 296 µmol) and aniline (70.0 µL, 297 µmol) in dichloro methane (5 mL). The reaction mixture was stirred for 2 h at room temperature. All volatiles were removed under reduced pressure and the remaining solid was suspended in *n*-hexane (5 mL) and the product was filtered off. The product was washed with *n*-hexane (2 × 5 mL) and dried *in vacuo* to yield **19** (222 mg, 224 µmol, 76%) as a colorless solid. Single crystals of **19** suitable for X-ray diffraction were obtained by diffusion of *n*-hexane into a solution of **19** in toluene. **^{1}H NMR** (500.1 MHz, CD_2Cl_2, 298 K): δ [ppm] = 1.16 (d, 12 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr–C*H*$_3$), 1.33 (d, 12 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr–C*H*$_3$), 2.98 (sept, 4 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr–C*H*), 4.10 (s, 4 H, N–C*H*$_2$–C*H*$_2$–N), 4.24 (br, 2 H, N*H*$_2$), 6.35 (m, 2 H, aniline-aryl-C$_{ortho}$*H*), 7.08 (m, 3 H, overlap of aniline-aryl-C$_{meta}$*H* and aniline-aryl-C$_{para}$*H*), 7.27 (d, 4 H, $^3J_{HH}$ = 7.8 Hz, SIDipp-aryl-C$_{meta}$*H*), 7.48 (t, 2 H, $^3J_{HH}$ = 7.8 Hz, SIDipp-aryl-C$_{para}$*H*); **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 298 K): δ [ppm] = 23.9 (*i*Pr–*C*H$_3$), 25.7 (*i*Pr–*C*H$_3$), 29.2 (*i*Pr–*C*H), 54.4 (N–*C*H$_2$–*C*H$_2$–N), 119.9 (aniline-aryl-*C*$_{ortho}$), 125.2 (SIDipp-aryl-*C*$_{meta}$), 125.7 (aniline-aryl-*C*$_{para}$), 130.5 (aniline-aryl-*C*$_{meta}$), 130.7 (SIDipp-aryl-*C*$_{para}$), 134.1 (SIDipp-aryl-*C*$_{ipso}$), 137.5 (aniline-aryl-*C*$_{ipso}$), 147.1 (SIDipp-aryl-*C*$_{ortho}$), 200.4 (N–*C*–N); **^{19}F NMR** (470.5 MHz, CD_2Cl_2, 298 K): δ [ppm] = −45.1 (dm, 1 F, $^1J_{PF}$ = 891 Hz, P*F*), −80.6 (m, 3 F, C*F*$_3$), −82.3 (m, 6 F, C*F*$_3$), −88.6 (dm, 2 F, $^1J_{PF}$ = 902 Hz, P*F*$_2$), −116.1 (dm, 2 F, $^2J_{PF}$ = 83 Hz, C*F*$_2$), −116.6 (dm, 4 F, $^2J_{PF}$ = 98 Hz, C*F*$_2$); **^{31}P NMR** (202.4 MHz, CD_2Cl_2, 298 K): δ [ppm] = −147.4 (tdm, $^1J_{PF}$ = 902 Hz, $^1J_{PF}$ = 891 Hz); **IR** ([cm^{-1}]): 3324 (vw), 3267 (w), 2964 (w), 2926 (w), 2875 (w), 1601 (w), 1579 (w), 1493 (m), 1464 (m), 1388 (vw), 1367 (vw), 1310 (m), 1296 (m), 1276 (m), 1212 (vs), 1179 (s), 1137 (m), 1126 (m), 1100 (m), 1057 (w), 1016 (vw), 972 (w), 935 (vw), 806 (m), 760 (m), 724 (m), 692 (w), 637 (w), 618 (vs), 581 (w), 548 (vw), 532 (w), 505 (vw), 495 (vw), 439 (w); **HRMS** (ESI) *m*/*z* [*M*]$^+$ calcd for $C_{33}H_{45}CuN_3$: 546.2910, found: 546.2893; *m*/*z* **FAP**$^-$ calcd for $C_6F_{18}P$: 444.9450, found: 444.9429; elemental analysis calcd (%) for $C_{39}H_{45}CuF_{18}N_3P$: C 47.21, H 4.57, N 4.23; found: C 47.36, H 4.72, N 4.34.

[(cAAC^{Me})Cu(NH$_2$Ph)]$^+$FAP$^-$ (20). The phosphorane $(C_2F_5)_3PF_2$ (24.8 μL, 272 μmol) was added at room temperature to a solution of **Ic** (100 mg, 272 μmol) and aniline (64.0 μL, 272 μmol) in dichloro methane (5 mL). The reaction mixture was stirred for 2 h at room temperature. All volatiles were removed under reduced pressure and the remaining solid was suspended in *n*-hexane (5 mL) and the product was filtered off. The product was washed with *n*-hexane (2 × 5 mL) and dried *in vacuo* to yield **20** (110 mg, 124 μmol, 46%) as a colorless solid. Single crystals of **20** suitable for X-ray diffraction were obtained by diffusion of *n*-hexane into a solution of **20** in toluene. **^{1}H NMR** (500.1 MHz, CD_2Cl_2, 298 K): δ [ppm] = 0.99 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr–C*H*$_3$), 1.29 (d, 6 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr–C*H*$_3$), 1.39 (s, 6 H, N–C(C*H*$_3$)$_2$), 1.41 (s, 6 H, Cu–C–C(C*H*$_3$)$_2$), 2.11 (s, 2 H, C*H*$_2$), 2.75 (sept, 2 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr–C*H*), 4.58 (br, 2 H, N*H*$_2$), 6.56 (br, 2 H, aniline-aryl-C$_{ortho}$*H*), 7.16 (m, 3 H, overlap of aniline-aryl-C$_{meta}$*H* and aniline-aryl-C$_{para}$*H*), 7.26 (d, 2 H, $^3J_{HH}$ = 7.8 Hz, cAAC^{Me}-aryl-C$_{meta}$*H*), 7.48 (t, 1 H, $^3J_{HH}$ = 7.8 Hz, cACC^{Me}-aryl-C$_{para}$*H*); **^{13}C{^{1}H} NMR** (125.8 MHz, CD_2Cl_2, 298 K): δ [ppm] = 22.5 (*i*Pr–*C*H$_3$), 27.1 (*i*Pr–*C*H$_3$), 28.1 (Cu–C–C(*C*H$_3$)$_2$), 29.35 (*i*Pr–*C*H), 29.41 (N–C(*C*H$_3$)$_2$), 49.6 (*C*H$_2$), 54.3 (Cu–C–*C*(CH$_3$)$_2$), 83.3 (N–*C*(CH$_3$)$_2$), 120.9 (aniline-aryl-*C*$_{ortho}$), 125.7 (cAAC^{Me}-aryl-*C*$_{meta}$), 126.5 (aniline-aryl-*C*$_{para}$), 130.4 (aniline-aryl-*C*$_{meta}$), 130.7 (cAAC^{Me}-aryl-*C*$_{para}$), 134.9 (cAAC^{Me}-aryl-*C*$_{ipso}$), 137.2 (aniline-aryl-*C*$_{ipso}$), 145.2 (cAAC^{Me}-aryl-*C*$_{ortho}$), 246.7 (N–*C*–Cu); **^{19}F NMR** (470.5 MHz, CD_2Cl_2, 298 K): δ [ppm] = −44.8 (dm, 1 F, $^1J_{PF}$ = 889 Hz, P*F*), −80.5 (m, 3 F, C*F*$_3$), −82.1 (m, 6 F, C*F*$_3$), −88.5 (dm, 2 F, $^1J_{PF}$ = 901 Hz, P*F*$_2$), −115.9 (dm, 2 F, $^2J_{PF}$ = 84 Hz, C*F*$_2$), −116.3 (dm, 4 F, $^2J_{PF}$ = 98 Hz, C*F*$_2$); **^{31}P NMR** (202.4 MHz, CD_2Cl_2, 298 K): δ [ppm] = −147.1 (tdm, $^1J_{PF}$ = 901 Hz, $^1J_{PF}$ = 889 Hz); **IR** ([cm^{-1}]): 3347 (w), 3296 (w), 2963 (w), 2874 (vw), 1605 (w), 1580 (w), 1535 (vw), 1497 (w), 1463 (w), 1391 (vw), 1373 (vw), 1366 (vw), 1311 (m), 1298 (m), 1214 (vs), 1182 (vs), 1123 (s), 1099 (s), 1085 (w), 1017 (vw), 967 (m), 933 (w), 897 (w), 810 (s), 780 (w), 750 (m), 714 (s), 690 (m), 636 (w), 617 (vs), 580 (m), 532 (m), 505 (w), 494 (w), 466 (vw), 439 (vw), 428 (w), 422 (w); **HRMS** (ESI) *m*/*z* [*M*]$^+$ calcd for $C_{26}H_{38}CuN_2$: 441.2331, found: 441.2316; *m*/*z* **FAP**$^-$ calcd for $C_6F_{18}P$: 444.9450, found: 444.9425; **elemental analysis** calcd (%) for $C_{32}H_{38}CuF_{18}N_2P$: C 43.32, H 4.32, N 3.16; found: C 43.22, H 4.43, N 3.20.

[(IDipp)Cu(NHPh$_2$)]$^+$FAP$^-$ (21). The phosphorane $(C_2F_5)_3PF_2$ (75.0 μL, 319 μmol) was added at room temperature to a solution of **Ia** (150 mg, 318 μmol) and diphenylamine (53.8 mg, 318 μmol) in dichloro methane (5 mL). The reaction mixture was stirred for 2 h at room temperature. All volatiles were removed under reduced pressure and the remaining solid was suspended in *n*-hexane (5 mL) and the product was filtered off. The product was washed with *n*-hexane (2 × 5 mL) and dried *in vacuo* to yield **21** (289 mg, 271 μmol, 85%) as a colorless solid. Single crystals of **21** suitable for X-ray diffraction were obtained by diffusion of *n*-hexane into a solution of **21** in chloroform. **^{1}H NMR** (500.1 MHz, $CDCl_3$, 298 K): δ [ppm] = 1.02 (d, 12 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr–C*H*$_3$), 1.20 (d, 12 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr–C*H*$_3$), 2.42 (sept, 4 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr–C*H*), 6.36 (br, 1 H, N*H*), 6.74 (br, 4 H, diphenylamine-aryl-C$_{ortho}$*H*), 7.10 (t, 2 H, $^3J_{HH}$ = 7.6 Hz, diphenylamine-aryl-C$_{para}$*H*), 7.18 (t, 4 H, $^3J_{HH}$ = 7.6 Hz, diphenylamine-aryl-C$_{meta}$*H*), 7.27 (s, 2 H, N–C*H*–C*H*–N), 7.33 (d, 4 H, $^3J_{HH}$ = 7.8 Hz, IDipp-aryl-C$_{meta}$*H*), 7.60 (t, 2 H, $^3J_{HH}$ = 7.8 Hz, IDipp-aryl-C$_{para}$*H*); **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 298 K): δ [ppm] = 24.0 (*i*Pr–*C*H$_3$), 24.7 (*i*Pr–*C*H$_3$), 28.9 (*i*Pr–*C*H), 121.1 (diphenylamine-aryl-*C*$_{ortho}$), 124.4 (N–*C*H–*C*H–N), 124.6 (IDipp-aryl-*C*$_{meta}$), 125.4 (diphenylamine-aryl-*C*$_{para}$), 130.0 (diphenylamine-aryl-*C*$_{meta}$), 131.3 (IDipp-aryl-*C*$_{para}$), 134.0 (IDipp-aryl-*C*$_{ipso}$), 141.8 (diphenylamine-aryl-*C*$_{ipso}$), 145.7 (IDipp-aryl-*C*$_{ortho}$), 176.8 (N–*C*–N); **^{19}F NMR** (470.5 MHz, $CDCl_3$, 298 K): δ [ppm] = −44.9 (dm, 1 F, $^1J_{PF}$ = 891 Hz, P*F*), −80.2 (m, 3 F, C*F*$_3$), −81.8 (m, 6 F, C*F*$_3$), −88.5 (dm, 2 F, $^1J_{PF}$ = 904 Hz, P*F*$_2$), −115.7 (dm, 2 F, $^2J_{PF}$ = 82 Hz, C*F*$_2$), −116.1 (dm, 4 F, $^2J_{PF}$ = 98 Hz, C*F*$_2$); **^{31}P NMR** (202.4 MHz, $CDCl_3$, 298 K): δ [ppm] = −146.8 (tdm, $^1J_{PF}$ = 904 Hz, $^1J_{PF}$ = 891 Hz); **IR** ([cm^{-1}]): 3270 (vw), 3202 (vw), 3141 (vw), 2964 (w), 2927 (vw), 2874 (w), 1592 (w), 1510 (w), 1491 (w), 1469 (w), 1414 (w), 1387 (vw), 1366 (vw), 1310 (m), 1295 (m), 1212 (vs), 1182 (s), 1136 (m), 1124 (m), 1095 (m), 1069 (vw), 1060 (vw), 1026 (vw), 1005 (vw), 973 (m), 936 (w), 805 (m), 751 (m), 724 (m), 690 (m), 637 (w), 618 (vs), 580 (w), 533 (w), 495 (w), 483 (vw), 466 (vw), 438 (w), 429 (w); **HRMS** (ESI) *m*/*z* [*M*]$^+$ calcd for $C_{39}H_{47}CuN_3$: 620.3066, found: 620.3049; *m*/*z* **FAP**$^-$ calcd for $C_6F_{18}P$: 444.9450, found: 444.9433; elemental analysis calcd (%) for $C_{45}H_{47}CuF_{18}N_3P$: C 50.68, H 4.44, N 3.94; found: C 51.61, H 4.49, N 4.26.

[(IDipp)Cu(NC$_5$H$_5$)]$^+$FAP$^-$ (22). The phosphorane $(C_2F_5)_3PF_2$ (75.0 μL, 319 μmol) was added at room temperature to a solution of **Ia** (150 mg, 318 μmol) and pyridine (26.0 μL, 322 μmol) in dichloro methane (5 mL). The reaction mixture was stirred for 2 h at room temperature. All volatiles were removed under reduced pressure and the remaining solid was suspended in *n*-hexane (5 mL) and the product was filtered off. The product was washed with *n*-hexane (5 mL) and dried *in vacuo* to yield **22** (215 mg, 216 μmol, 68%) as a colorless solid. **^{1}H NMR** (500.1 MHz, $CDCl_3$, 298 K): δ [ppm] = 1.22 (d, 12 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr–C*H*$_3$), 1.28 (d, 12 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr–C*H*$_3$), 2.56 (sept, 4 H, $^3J_{HH}$ = 6.9 Hz, *i*Pr–C*H*), 7.32 (s, 2 H, N–C*H*–C*H*–N), 7.37 (d, 4 H, $^3J_{HH}$ = 7.8 Hz, IDipp-aryl-C$_{meta}$*H*), 7.59 (t, 2 H, $^3J_{HH}$ = 7.8 Hz, IDipp-aryl-C$_{para}$*H*), 7.50 (br, 2 H, pyridine-aryl-C$_{ortho/meta}$*H*), 7.77 (br, 2 H, pyridine-aryl-C$_{ortho/meta}$*H*), 8.02 (br, 1 H, pyridine-aryl-C$_{para}$*H*); **^{13}C{^{1}H} NMR** (125.8 MHz, $CDCl_3$, 298 K): δ [ppm] = 23.8 (*i*Pr–*C*H$_3$), 25.2 (*i*Pr–*C*H$_3$), 28.9 (*i*Pr–*C*H), 124.4 (N–*C*H–*C*H–N), 124.7 (IDipp-aryl-*C*$_{meta}$), 126.8 (pyridine-aryl-*C*$_{ortho/meta}$), 131.3 (IDipp-aryl-*C*$_{para}$), 134.1 (IDipp-aryl-*C*$_{ipso}$), 142.1 (pyridine-aryl-*C*$_{para}$), 145.8 (IDipp-aryl-*C*$_{ortho}$), 147.5 (pyridine-aryl-*C*$_{ortho/meta}$), 177.6 (N–*C*–N); **^{19}F NMR** (470.5 MHz, $CDCl_3$, 298 K): δ [ppm] = −45.1 (dm, 1 F, $^1J_{PF}$ = 890 Hz, P*F*), −80.2 (m, 3 F, C*F*$_3$), −81.8 (m, 6 F, C*F*$_3$), −88.6 (dm, 2 F, $^1J_{PF}$ = 905 Hz, P*F*$_2$), −115.8 (dm, 2 F, $^2J_{PF}$ = 84 Hz, C*F*$_2$), −116.3 (dm, 4

F, $^{2}J_{\mathrm{PF}}$ = 98 Hz, CF_2); **^{31}P NMR** (202.4 MHz, CDCl$_3$, 298 K): δ [ppm] = −146.9 (tdm, $^{1}J_{\mathrm{PF}}$ = 905 Hz, $^{1}J_{\mathrm{PF}}$ = 890 Hz); **IR** ([cm^{-1}]): 2963 (w), 2928 (w), 2874 (w), 1640 (vw), 1611 (w), 1600 (w), 1544 (w), 1491 (w), 1469 (w), 1450 (w), 1414 (w), 1388 (vw), 1366 (vw), 1294 (m), 1209 (vs), 1182 (vs), 1136 (s), 1124 (s), 1098 (s), 1070 (m), 972 (m), 961 (m), 936 (vw), 810 (s), 758 (m), 741 (vw), 720 (s), 699 (m), 674 (w), 637 (w), 617 (vs), 581 (m), 532 (w), 495 (w), 467 (vw), 438 (w), 428 (w); **HRMS** (ESI) *m*/*z* $[M]^+$ calcd for $\mathrm{C_{32}H_{41}CuN_3}$: 530.2597, found: 530.2577; *m*/*z* **FAP$^-$** calcd for $\mathrm{C_6F_{18}P}$: 444.9450, found: 444.9424; **elemental analysis** calcd (%) for $\mathrm{C_{38}H_{41}CuF_{18}N_3P}$: C 46.75, H 4.23, N 4.30; found: C 45.03, H 3.38, N 4.57.

$[(\mathrm{cAAC^{Me}})\mathrm{Cu(NC_5H_5)}]^+\mathrm{FAP}^-$ (23). The phosphorane $\mathrm{(C_2F_5)_3PF_2}$ (84.6 µL, 359 µmol) was added at room temperature to a solution of **Ic** (132 mg, 359 µmol) and pyridine (29.0 µL, 359 µmol) in dichloro methane (5 mL). The reaction mixture was stirred for 2 h at room temperature. All volatiles were removed under reduced pressure and the remaining solid was suspended in *n*-hexane (5 mL) and the product was filtered off. The product was washed with *n*-hexane (2 × 5 mL) and dried *in vacuo* to yield **23** (233 mg, 267 µmol, 74%) as a colourless solid. Single crystals of **23** suitable for X-ray diffraction were obtained by diffusion of *n*-hexane into a solution of **23** in 1,2-difluorbenzene. **^{1}H NMR** (500.1 MHz, CDCl$_3$, 298 K): δ [ppm] = 1.20 (d, 12 H, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, *i*Pr–CH_3), 1.36 (d, 12 H, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, *i*Pr–CH_3), 1.45 (s, 6 H, N–C(CH_3)$_2$), 1.50 (s, 6 H, Cu–C–C(CH_3)$_2$), 2.17 (s, 2 H, CH_2), 2.86 (sept, 2 H, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, *i*Pr–C*H*), 7.36 (d, 2 H, $^{3}J_{\mathrm{HH}}$ = 7.6 Hz, cAAC$^{\mathrm{Me}}$-aryl-C$_{meta}H$), 7.50 (br, 2 H, pyridine-aryl-C$_{ortho/meta}H$), 7.53 (t, 1 H, $^{3}J_{\mathrm{HH}}$ = 7.6 Hz, cAAC$^{\mathrm{Me}}$-aryl-C$_{para}H$), 7.97 (br, 3 H, overlap of pyridine-aryl-C$_{para}H$ and pyridine-aryl-C$_{ortho/meta}H$); **^{13}C{^{1}H} NMR** (125.8 MHz, CDCl$_3$, 298 K): δ = 22.4 (*i*Pr–CH$_3$), 27.2 (*i*Pr–CH$_3$), 28.2 (Cu–C–C(CH$_3$)$_2$), 29.26 (*i*Pr–CH), 29.30 (N–C(CH$_3$)$_2$), 49.4 (CH$_2$), 54.1 (Cu–C–C(CH$_3$)$_2$), 83.1 (N–C(CH$_3$)$_2$), 125.5 (cAAC$^{\mathrm{Me}}$-aryl-C_{meta}), 126.7 (pyridine-aryl-$C_{ortho/meta}$), 130.8 (cAAC$^{\mathrm{Me}}$-aryl-C_{para}), 134.5 (cAAC$^{\mathrm{Me}}$-aryl-C_{ipso}), 141.4 (pyridine-aryl-C_{para}), 145.2 (cAAC$^{\mathrm{Me}}$-aryl-C_{ortho}), 149.3 (pyridine-aryl-$C_{ortho/meta}$), 247.1 (N–C–Cu); **^{19}F NMR** (470.5 MHz, CDCl$_3$, 298 K): δ [ppm] = −45.1 (dm, 1 F, $^{1}J_{\mathrm{PF}}$ = 891 Hz, PF), −80.1 (m, 3 F, CF_3), −81.8 (m, 6 F, CF_3), −88.5 (dm, 2 F, $^{1}J_{\mathrm{PF}}$ = 903 Hz, PF_2), −115.8 (dm, 2 F, $^{2}J_{\mathrm{PF}}$ = 83 Hz, CF_2), −116.3 (dm, 4 F, $^{2}J_{\mathrm{PF}}$ = 98 Hz, CF_2); **^{31}P NMR** (202.4 MHz, CDCl$_3$, 298 K): δ [ppm] = −147.4 (tdm, $^{1}J_{\mathrm{PF}}$ = 903 Hz, $^{1}J_{\mathrm{PF}}$ = 891 Hz); **IR** ([cm^{-1}]): 2969 (w), 2937 (w), 2875 (w), 1610 (w), 1585 (vw), 1524 (w), 1491 (vw), 1451 (m), 1389 (vw), 1373 (vw), 1311 (m), 1262 (vw), 1201 (vs), 1178 (vs), 1133 (vs), 1098 (s), 1071 (m), 1052 (vw), 1018 (vw), 964 (s), 930 (w), 897 (vw), 883 (vw), 806 (vs), 781 (m), 755 (m), 717 (vs), 698 (s), 636 (w), 617 (vs), 579 (m), 533 (m), 504 (w), 473 (vw), 443 (vw), 421 (m); **HRMS** (ESI) *m*/*z* $[M]^+$ calcd for $\mathrm{C_{25}H_{36}CuN_2}$: 427.2175, found: 427.2161; *m*/*z* **FAP$^-$** calcd for $\mathrm{C_6F_{18}P}$: 444.9450, found: 444.9427; elemental analysis calcd (%) for $\mathrm{C_{31}H_{36}CuF_{18}N_2P}$: C 42.64, H 4.16, N 3.21; found: C 43.04, H 4.16, N 3.40.

$[(\mathrm{IDipp})\mathrm{Cu(NC_5H_3F_2)}]^+\mathrm{FAP}^-$ (24). The phosphorane $\mathrm{(C_2F_5)_3PF_2}$ (74.0 µL, 314 µmol) was added at room temperature to a solution of **Ia** (148 mg, 314 µmol) and 2,6-difluoropyridine (28.6 µL, 315 µmol) in dichloro methane (5 mL). The reaction mixture was stirred for 2 h at room temperature and the suspension was filtered over a plug of Celite. All volatiles of the filtrate were removed under reduced pressure and the remaining solid was suspended in *n*-hexane (5 mL) and the product was filtered off. The product was washed with *n*-hexane (3 × 5 mL) and dried *in vacuo* to yield **24** (255 mg, 252 µmol, 80%) as a colorless solid. Single crystals of **24** suitable for X-ray diffraction were obtained by diffusion of *n*-hexane into a solution of **24** in chloroform. **^{1}H NMR** (500.1 MHz, CDCl$_3$, 298 K): δ [ppm] = 1.22 (d, 12 H, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, *i*Pr–CH_3), 1.27 (d, 12 H, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, *i*Pr–CH_3), 2.54 (sept, 4 H, $^{3}J_{\mathrm{HH}}$ = 6.9 Hz, *i*Pr–C*H*), 7.03 (d, 2 H, $^{3}J_{\mathrm{HH}}$ = 8.2 Hz, pyridine-aryl-C$_{meta}H$), 7.32 (s, 2 H, N–C*H*–C*H*–N), 7.34 (d, 4 H, $^{3}J_{\mathrm{HH}}$ = 7.8 Hz, IDipp-aryl-C$_{meta}H$), 7.55 (t, 2 H, $^{3}J_{\mathrm{HH}}$ = 7.8 Hz, IDipp-aryl-C$_{para}H$), 8.20 (tt, 1 H, $^{3}J_{\mathrm{HH}}$ = 8.2 Hz, $^{4}J_{\mathrm{FH}}$ = 7.5 Hz, pyridine-aryl-C$_{para}H$); **^{13}C{^{1}H} NMR** (125.8 MHz, CDCl$_3$, 298 K): δ [ppm] = 24.0 (*i*Pr–CH$_3$), 24.9 (*i*Pr–CH$_3$), 29.0 (*i*Pr–CH), 108.3 (m, pyridine-aryl-C_{meta}), 124.56 (N–CH–CH–N/IDipp-aryl-C_{meta}), 124.60 (N–CH–CH–N/IDipp-aryl-C_{meta}), 131.4 (IDipp-aryl-C_{para}), 133.8 (IDipp-aryl-C_{ipso}), 145.7 (IDipp-aryl-C_{ortho}), 150.9 (t, $^{3}J_{\mathrm{FC}}$ = 9.3 Hz, pyridine-aryl-C_{para}), 160.5 (dd, $^{1}J_{\mathrm{FC}}$ = 262 Hz, $^{3}J_{\mathrm{FC}}$ = 7.1 Hz, pyridine-aryl-C_{ortho}), 176.3 (N–C–N); **^{19}F NMR** (470.5 MHz, CDCl$_3$, 298 K): δ [ppm] = −45.3 (dm, 1 F, $^{1}J_{\mathrm{PF}}$ = 890 Hz, PF), −64.5 (d, 2 F, $^{4}J_{\mathrm{FH}}$ = 7.5 Hz, pyridine-aryl-C$_{ortho}F$), −80.3 (m, 3 F, CF_3), −81.9 (m, 6 F, CF_3), −88.6 (dm, 2 F, $^{1}J_{\mathrm{PF}}$ = 903 Hz, PF_2), −115.9 (dm, 2 F, $^{2}J_{\mathrm{PF}}$ = 83 Hz, CF_2), −116.5 (dm, 4 F, $^{2}J_{\mathrm{PF}}$ = 98 Hz, CF_2); **^{31}P NMR** (202.4 MHz, CDCl$_3$, 298 K): δ [ppm] = −147.3 (tdm, $^{1}J_{\mathrm{PF}}$ = 903 Hz, $^{1}J_{\mathrm{PF}}$ = 890 Hz); **IR** ([cm^{-1}]): 3178 (vw), 2962 (w), 2929 (w), 2875 (w), 1637 (m), 1621 (vw), 1591 (vw), 1571 (vw), 1548 (vw), 1473 (m), 1415 (w), 1388 (vw), 1367 (vw), 1326 (vw), 1319 (w), 1295 (w), 1272 (w), 1258 (w), 1213 (s), 1180 (s), 1137 (m), 1124 (m), 1098 (m), 1060 (w), 1010 (m), 974 (m), 960 (m), 936 (w), 852 (vw), 809 (m), 800 (m), 761 (m), 722 (s), 703 (vw), 637 (w), 618 (vs), 580 (w), 533 (w), 496 (w), 438 (w), 429 (w); **HRMS** (ESI) *m*/*z* $[M]^+$ calcd for $\mathrm{C_{32}H_{39}CuF_2N_3}$: 566.2408, found: 566.2390; *m*/*z* **FAP$^-$** calcd for $\mathrm{C_6F_{18}P}$: 444.9450, found: 444.9434; **elemental analysis** calcd (%) for $\mathrm{C_{38}H_{39}CuF_{20}N_3P}$: C 45.09, H 3.88, N 4.15; found: C 45.49, H 3.85, N 4.20.

$[(\mathrm{IDipp})\mathrm{Cu(NC_5H_2F_3)}]^+\mathrm{FAP}^-$ (25). The phosphorane $\mathrm{(C_2F_5)_3PF_2}$ (75.0 µL, 319 µmol) was added at room temperature to a solution of **Ia** (150 mg, 318 µmol) and 2,4,6-trifluoropyridine (30.8 µL, 320 µmol) in dichloro methane (5 mL). The reaction mixture was stirred for 3 h at room temperature. All volatiles were removed under reduced pressure and the remaining solid was suspended in *n*-hexane (5 mL) and the product was filtered off. The product was washed with *n*-hexane (2 × 5 mL) and dried *in vacuo* to yield **25** (232 mg, 225 µmol, 71%) as a colorless solid. **^{1}H NMR** (500.1 MHz, CDCl$_3$, 298 K): δ [ppm] = 1.21 (d, 12 H, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, *i*Pr–CH_3), 1.26 (d, 12 H, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, *i*Pr–CH_3), 2.52 (sept, 4 H, $^{3}J_{\mathrm{HH}}$ = 6.8 Hz, *i*Pr–C*H*), 6.75 (d, 2 H, $^{3}J_{\mathrm{FH}}$ = 6.8 Hz, pyridine-aryl-C$_{meta}H$), 7.32 (s, 2 H, N–C*H*–C*H*–N), 7.33 (d, 4 H, $^{3}J_{\mathrm{HH}}$ = 7.9 Hz, IDipp-aryl-C$_{meta}H$), 7.55 (t, 2 H, $^{3}J_{\mathrm{HH}}$ = 7.9 Hz, IDipp-aryl-C$_{para}H$); **^{13}C{^{1}H} NMR** (125.8 MHz, CDCl$_3$, 298 K): δ [ppm] = 24.0 (*i*Pr–CH$_3$), 24.9 (*i*Pr–CH$_3$), 29.0 (*i*Pr–CH), 98.1 (m, pyridine-aryl-C_{meta}), 124.5 (N–CH–CH–N/IDipp-aryl-C_{meta}), 124.6 (N–CH–CH–N/IDipp-aryl-C_{meta}), 131.4

(IDipp-aryl-*C*$_{para}$), 133.7 (IDipp-aryl-*C*$_{ipso}$), 145.6 (IDipp-aryl-*C*$_{ortho}$), 162.0 (pyridine-aryl-*C*$_{ortho}$), 175.9 (pyridine-aryl-*C*$_{para}$), 176.2 (N–*C*–N); **^{19}F NMR** (470.5 MHz, CDCl$_3$, 298 K): δ [ppm] = −45.4 (dm, 1 F, $^1J_{\text{PF}}$ = 891 Hz, P*F*), −61.0 (d, 2 F, $^4J_{\text{FF}}$ = 22.6 Hz, pyridine-aryl-C$_{ortho}$*F*), −76.0 (tt, 1 F, $^4J_{\text{FF}}$ = 22.6 Hz, $^3J_{\text{FH}}$ = 6.8 Hz, pyridine-aryl-C$_{para}$*F*), −80.3 (m, 3 F, C*F*$_3$), −82.0 (m, 6 F, C*F*$_3$), −88.7 (dm, 2 F, $^1J_{\text{PF}}$ = 904 Hz, P*F*$_2$), −116.1 (dm, 2 F, $^2J_{\text{PF}}$ = 83 Hz, C*F*$_2$), −116.6 (dm, 4 F, $^2J_{\text{PF}}$ = 98 Hz, C*F*$_2$); **^{31}P NMR** (202.4 MHz, CDCl$_3$, 298 K): δ [ppm] = −147.5 (tdm, $^1J_{\text{PF}}$ = 904 Hz, $^1J_{\text{PF}}$ = 891 Hz); **IR** ([cm^{-1}]): 3085 (vw), 2965 (w), 2930 (w), 2874 (w), 1674 (vw), 1650 (m), 1593 (m), 1552 (vw), 1523 (vw), 1462 (m), 1413 (w), 1388 (vw), 1367 (vw), 1294 (w), 1213 (vs), 1179 (vs), 1148 (s), 1138 (m), 1125 (s), 1101 (m), 1071 (w), 1060 (w), 1043 (w), 1005 (w), 973 (m), 959 (m), 936 (vw), 854 (w), 815 (m), 807 (m), 761 (m), 726 (s), 702 (vw), 638 (w), 618 (vs), 580 (w), 560 (vw), 533 (w), 517 (w), 495 (w), 465 (vw), 438 (w), 429 (w); **HRMS** (ESI) *m*/*z* [*M*]$^+$ calcd for $C_{32}H_{38}CuF_3N_3$: 584.2314, found: 584.2299; *m*/*z* **FAP**$^-$ calcd for $C_6F_{18}P$: 444.9450, found: 444.9423; **elemental analysis** calcd (%) for $C_{38}H_{38}CuF_{21}N_3P$: C 44.30, H 3.72, N 4.08; found: C 44.81, H 3.80, H 4.15.

[{(IDipp)Cu(μ-ONC$_5$H$_5$)}$_2$]$^{2+}$2FAP$^-$ (26). The phosphorane $(C_2F_5)_3PF_2$ (71.6 µL, 304 µmol) was added at room temperature to a solution of **Ia** (150 mg, 318 µmol) and pyridine-*N*-oxide (29.0 mg, 305 µmol) in dichloro methane (5 mL). The reaction mixture was stirred for 2 h at room temperature. All volatiles were removed under reduced pressure and the remaining solid was suspended in *n*-hexane (5 mL) and the product was filtered off. The product was washed with *n*-hexane (2 × 5 mL) and dried *in vacuo* to yield **26** (243 mg, 122 µmol, 81%) as a colorless solid. Single crystals of **26** suitable for X-ray diffraction were obtained by diffusion of *n*-hexane into a solution of **26** in 1,2-difluorobenzene. **^{1}H NMR** (400.1 MHz, CDCl$_3$, 236.5 K): δ [ppm] = 1.18 (d, 24 H, $^3J_{\text{HH}}$ = 6.9 Hz, *i*Pr–C*H*$_3$), 1.25 (d, 24 H, $^3J_{\text{HH}}$ = 6.9 Hz, *i*Pr–C*H*$_3$), 2.46 (sept, 8 H, $^3J_{\text{HH}}$ = 6.9 Hz, *i*Pr–C*H*), 7.32 (s, 4 H, N–C*H*–C*H*–N), overlap with 7.37 (d, 8 H, $^3J_{\text{HH}}$ = 7.8 Hz, IDipp-aryl-C$_{meta}$*H*), 7.38 (br, 4 H, pyridine-aryl-C$_{meta}$*H*), 7.47 (br, 4 H, pyridine-aryl-C$_{ortho}$*H*), 7.62 (t, 4 H, $^3J_{\text{HH}}$ = 7.8 Hz, IDipp-aryl-C$_{para}$*H*), 7.71 (t, 2 H, $^3J_{\text{HH}}$ = 7.2 Hz, pyridine-aryl-C$_{para}$*H*); **^{13}C{^{1}H} NMR** (100.6 MHz, CDCl$_3$, 236.5 K): δ [ppm] = 23.5 (*i*Pr–*C*H$_3$), 25.4 (*i*Pr–*C*H$_3$), 28.7 (*i*Pr–*C*H), 124.0 (N–*C*H–*C*H–N), 124.6 (IDipp-aryl-*C*$_{meta}$), 127.7(pyridine-aryl-*C*$_{meta}$), 131.1 (IDipp-aryl-*C*$_{para}$), 133.9 (IDipp-aryl-*C*$_{ipso}$), 134.3 (pyridine-aryl-*C*$_{para}$), 138.3 (pyridine-aryl-*C*$_{ortho}$), 145.8 (IDipp-aryl-*C*$_{ortho}$), 176.3 (N–*C*–N); **^{19}F NMR** (470.5 MHz, CD$_2$Cl$_2$, 298 K): δ [ppm] = −45.1 (dm, 1 F, $^1J_{\text{PF}}$ = 890 Hz, P*F*), −80.6 (m, 3 F, C*F*$_3$), −82.3 (m, 6 F, C*F*$_3$), −88.5 (dm, 2 F, $^1J_{\text{PF}}$ = 903 Hz, P*F*$_2$), −116.1 (dm, 2 F, $^2J_{\text{PF}}$ = 83 Hz, C*F*$_2$), −116.9 (dm, 4 F, $^2J_{\text{PF}}$ = 98 Hz, C*F*$_2$); **^{31}P NMR** (202.4 MHz, CD$_2$Cl$_2$, 298 K): δ [ppm] = −147.5 (tdm, $^1J_{\text{PF}}$ = 903 Hz, $^1J_{\text{PF}}$ = 890 Hz); **IR** ([cm^{-1}]): 3191 (vw), 3124 (vw), 2962 (w), 2926 (w), 2872 (w), 1593 (vw), 1556 (vw), 1469 (m), 1413 (w), 1387 (w), 1365 (w), 1293 (m), 1258 (vw), 1207 (vs), 1181 (vs), 1135 (s), 1124 (s), 1100 (s), 1070 (m), 1027 (w), 975 (m), 961 (m), 937 (w), 835 (w), 814 (s), 806 (s), 761 (s), 744 (m), 715 (s), 668 (m), 637 (w), 617 (vs), 581 (m), 549 (vw), 532 (m), 496 (w), 467 (vw), 452 (vw), 438 (w), 429 (w); **HRMS** (ESI) *m*/*z* [*M*]$_n$$^{n+}$ calcd for $[C_{32}H_{41}CuN_3O]_n$: 546.2546, found: 546.2533; *m*/*z* **FAP**$^-$ calcd for $C_6F_{18}P$: 444.9450, found: 444.9429; **elemental analysis** calcd (%) for $C_{76}H_{82}Cu_2F_{36}N_6O_2P_2$: C 46.00, H 4.17, N 4.23; found: C 46.14, H 4.13, N 4.52.

[(IDipp)Cu(η^1-O═CPh$_2$)]$^+$FAP$^-$ (27). The phosphorane $(C_2F_5)_3PF_2$ (75.0 µL, 319 µmol) was added at room temperature to a solution of **Ia** (150 mg, 318 µmol) and benzophenone (58.0 mg, 318 µmol) in dichloro methane (5 mL). The reaction mixture was stirred for 2 h at room temperature. All volatiles were removed under reduced pressure and the remaining solid was suspended in *n*-hexane (5 mL) and the product was filtered off. The product was washed with *n*-hexane (2 × 5 mL) and dried *in vacuo* to yield **27** (272 mg, 252 µmol, 79%) as an off-white solid. Single crystals of **27** suitable for X-ray diffraction were obtained by diffusion of *n*-hexane into a solution of **27** in 1,2-difluorobenzene. **^{1}H NMR** (500.1 MHz, CDCl$_3$, 298 K): δ [ppm] = 1.13 (d, 12 H, $^3J_{\text{HH}}$ = 6.8 Hz, *i*Pr–C*H*$_3$), 1.24 (d, 12 H, $^3J_{\text{HH}}$ = 6.8 Hz, *i*Pr–C*H*$_3$), 2.50 (sept, 4 H, $^3J_{\text{HH}}$ = 6.8 Hz, *i*Pr–C*H*), 7.28 (s, 2 H, N–C*H*–C*H*–N), 7.34 (d, 4 H, $^3J_{\text{HH}}$ = 7.8 Hz, IDipp-aryl-C$_{meta}$*H*), 7.39 (m, 4 H, benzophenone-aryl-C$_{meta}$*H*), 7.52 (dd, 4 H, $^3J_{\text{HH}}$ = 8.4 Hz, $^4J_{\text{HH}}$ = 1.2 Hz, benzophenone-aryl-C$_{ortho}$*H*), 7.59 (t, 2 H, $^3J_{\text{HH}}$ = 7.8 Hz, IDipp-aryl-C$_{para}$*H*), 7.70 (tt, 2 H, $^3J_{\text{HH}}$ = 7.5 Hz, $^4J_{\text{HH}}$ = 1.2 Hz, benzophenone-aryl-C$_{para}$*H*); **^{13}C{^{1}H} NMR** (125.8 MHz, CDCl$_3$, 298 K): δ [ppm] = 23.8 (*i*Pr–*C*H$_3$), 25.0 (*i*Pr–*C*H$_3$), 28.9 (*i*Pr–*C*H), 124.7 (N–*C*H–*C*H–N/IDipp-aryl-*C*$_{meta}$), 124.8 (N–*C*H–*C*H–N/IDipp-aryl-*C*$_{meta}$), 129.4 (benzophenone-aryl-*C*$_{meta}$), 131.1 (benzophenone-aryl-*C*$_{ortho}$), 131.3 (IDipp-aryl-*C*$_{para}$), 134.0 (IDipp-aryl-*C*$_{ipso}$), 135.6 (benzophenone-aryl-*C*$_{ipso}$), 136.0 (benzophenone-aryl-*C*$_{para}$), 145.7 (IDipp-aryl-*C*$_{ortho}$), 175.7 (N–*C*–N), 206.3 (O═*C*); **^{19}F NMR** (470.5 MHz, CDCl$_3$, 298 K): δ [ppm] = −45.3 (dm, 1 F, $^1J_{\text{PF}}$ = 891 Hz, P*F*), −80.2 (m, 3 F, C*F*$_3$), −81.8 (m, 6 F, C*F*$_3$), −88.7 (dm, 2 F, $^1J_{\text{PF}}$ = 903 Hz, P*F*$_2$), −115.9 (dm, 2 F, $^2J_{\text{PF}}$ = 83 Hz, C*F*$_2$), −116.4 (dm, 4 F, $^2J_{\text{PF}}$ = 98 Hz, C*F*$_2$); **^{31}P NMR** (202.4 MHz, CDCl$_3$, 298 K): δ [ppm] = −147.2 (tdm, $^1J_{\text{PF}}$ = 903 Hz, $^1J_{\text{PF}}$ = 891 Hz); **IR** ([cm^{-1}]): 3137 (vw), 2964 (w), 2927 (w), 2872 (w), 1591 (w), 1558 (m), 1493 (vw), 1461 (w), 1451 (w), 1416 (w), 1388 (vw), 1366 (vw), 1333 (m), 1293 (m), 1212 (vs), 1177 (vs), 1142 (s), 1126 (s), 1098 (s), 1061 (m), 1026 (vw), 999 (vw), 972 (m), 958 (m), 926 (w), 850 (vw), 817 (s), 810 (s), 761 (s), 746 (m), 721 (s), 706 (s), 681 (w), 651 (w), 637 (w), 617 (vs), 580 (m), 532 (w), 496 (w), 438 (w), 429 (w), 411 (vw); **HRMS** (ESI) *m*/*z* [*M*]$^+$ calcd for $C_{40}H_{46}CuN_2O$: 633.2906, found: 633.2888; *m*/*z* **FAP**$^-$ calcd for $C_6F_{18}P$: 444.9450, found: 444.9430; **elemental analysis** calcd (%) for $C_{46}H_{46}CuF_{18}N_2OP$: C 51.19, H 4.30, N 2.60; found: C 51.79, H 4.30, N 2.88.

[(cAAC$^{\text{Me}}$)Cu(THF)]$^+$FAP$^-$ (28). The phosphorane $(C_2F_5)_3PF_2$ (77.0 µL, 327 µmol) was added at room temperature to a solution of **Ic** (120 mg, 326 µmol) in Et$_2$O (3 mL) and THF (3 mL). The reaction mixture was stirred for 2 h at room temperature. All volatiles were removed under reduced pressure and the remaining solid was suspended in *n*-hexane (5 mL) and the product was filtered off. The product was washed with *n*-hexane (5 mL) and dried *in vacuo* to yield **28** (192 mg, 222 µmol, 68%) as an off-white solid. **^{1}H NMR** (500.1 MHz, CDCl$_3$, 298 K): δ [ppm] = 1.21 (d, 6 H, $^3J_{\text{HH}}$ = 6.8 Hz, *i*Pr–C*H*$_3$), 1.35 (d, 6 H, $^3J_{\text{HH}}$ = 6.8 Hz, *i*Pr–C*H*$_3$), 1.42 (s, 6 H, N–C(C*H*$_3$)$_2$), 1.43 (s, 6 H, Cu–C–C(CH_3)$_2$), 1.90 (m, 4 H, THF–$C_{3,4}H_2$), 2.14 (s, 2 H, CH_2), 2.80 (sept, 2 H, $^3J_{HH}$ = 6.8 Hz, *i*Pr–C*H*), 3.72 (m, 4 H, THF-$C_{2,5}H_2$), 7.34 (d, 2 H, $^3J_{HH}$ = 7.8 Hz, cAAC^{Me}-aryl-$C_{meta}H$), 7.50 (t, 1 H, $^3J_{HH}$ = 7.8 Hz, cAAC^{Me}-aryl-$C_{para}H$); **^{13}C {^{1}H} NMR** (125.8 MHz, CDCl$_3$, 298 K): δ [ppm] = 22.4 (*i*Pr–*C*H$_3$), 24.8 (THF-$C_{3,4}$), 27.0 (*i*Pr–*C*H$_3$), 28.1 (Cu–C–C(*C*H$_3$)$_2$), 29.20 (*i*Pr–*C*H), 29.24 (N–C(*C*H$_3$)$_2$), 49.3 (*C*H$_2$), 53.9 (Cu–*C*–C(CH$_3$)$_2$), 73.5 (THF-$C_{2,5}$), 83.1 (N–*C*(CH$_3$)$_2$), 125.4 (cAAC^{Me}-aryl-C_{meta}), 130.9 (cAAC^{Me}-aryl-C_{para}), 134.5 (cAAC^{Me}-aryl-C_{ipso}), 145.1 (cAAC^{Me}-aryl-C_{ortho}), 245.6 (N–*C*–Cu); **^{19}F NMR** (470.5 MHz, CDCl$_3$, 298 K): δ [ppm] = −45.3 (dm, 1 F, $^1J_{PF}$ = 891 Hz, P*F*), −80.1 (m, 3 F, CF_3), −81.8 (m, 6 F, CF_3), −88.6 (dm, 2 F, $^1J_{PF}$ = 904 Hz, PF_2), −115.9 (dm, 2 F, $^2J_{PF}$ = 83 Hz, CF_2), −116.4 (dm, 4 F, $^2J_{PF}$ = 98 Hz, CF_2); **^{31}P NMR** (202.4 MHz, CDCl$_3$, 298 K): δ [ppm] = −147.4 (tdm, $^1J_{PF}$ = 904 Hz, $^1J_{PF}$ = 891 Hz); **IR** ([cm^{-1}]): 2973 (w), 2942 (w), 1589 (vw), 1532 (w), 1388 (vw), 1373 (vw), 1310 (w), 1294 (w), 1265 (vw), 1208 (vs), 1179 (vs), 1134 (s), 1125 (s), 1098 (s), 1069 (m), 1010 (w), 960 (m), 869 (w), 815 (s), 777 (w), 760 (m), 719 (vs), 636 (w), 617 (vs), 580 (m), 532 (m), 495 (w), 468 (vw), 438 (vw), 428 (w); **HRMS** (ESI) *m*/*z* $[M]^+$ calcd for $C_{24}H_{39}CuNO$: 420.2328, found: 420.2313; *m*/*z* **FAP$^-$** calcd for $C_6F_{18}P$: 444.9450, found: 444.9443; **elemental analysis** calcd (%) for $C_{30}H_{39}CuF_{18}NOP$: C 41.60, H 4.54, N 1.62; found: C 41.89, H 4.51, N 1.77.

Crystallographic details

Crystal data were collected on a Bruker X8 Apex-2 diffractometer with a CCD area detector and graphite monochromated Mo-Kα radiation or a Rigaku XtaLAB Synergy-DW diffractometer with an Hy-Pix-6000HE detector and monochromated Cu-Kα radiation equipped with an Oxford Cryo 800 cooling unit. Crystals were immersed in a film of perfluoropolyether oil on a glass fiber MicroMount™ (MiTeGen) and data were collected at 100 K. Images were processed with Bruker or CrySalis software packages and equivalent reflections were merged. Corrections for Lorentz-polarization effects and absorption were performed if necessary and the structures were solved by direct methods. Subsequent difference Fourier syntheses revealed the positions of all other non-hydrogen atoms. Structures were solved by using the ShelXTL software package.[40] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were assigned to idealized geometric positions and were included in structure factors calculations.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 2444352 (**1**), 2444336 (**3**), 2444351 (**5**), 2444348 (**6**), 2444349 (**7**), 2444343 (**10**), 2444350 (**11**), 2444347 (**12**), 2444346 (**16**), 2444340 (**17**), 2444345 (**19**), 2444342 (**20**), 2444338 (**21**), 2444341 (**23**), 2444344 (**24**), 2444339 (**26**), 2444337 (**27**).

Data availability

The data supporting this article have been included as part of the manuscript and the ESI.† Crystallographic data are also deposited in the form of CIF files at the Cambridge Crystallographic Data Centre with reference number CCDC 2444352 (**1**), 2444336 (**3**), 2444351 (**5**), 2444348 (**6**), 2444349 (**7**), 2444343 (**10**), 2444350 (**11**), 2444347 (**12**), 2444346 (**16**), 2444340 (**17**), 2444345 (**19**), 2444342 (**20**), 2444338 (**21**), 2444341 (**23**), 2444344 (**24**), 2444339 (**26**), 2444337 (**27**).

Conflicts of interest

The authors declare no conflict to declare.

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