ROYAL SOCIETY OF CHEMISTRY

PAPER

CrossMark
click for updates

Tris(pyrazolyl)phosphines with copper(I): from monomers to polymers†

Cornelis G. J. Tazelaar,[a] Emmanuel Nicolas,[a] Tom van Dijk,[a] Daniël L. J. Broere,[a] Mitchel Cardol,[a] Martin Lutz,[b] Dietrich Gudat,[c] J. Chris Slootweg*[a] and Koop Lammertsma*[a,d]

The parent tris(pyrazolyl)phosphine and its 3,5-Me$_2$, 3-Ph, and 3-*t*-Bu derivatives have been prepared by a simple procedure and show modest Lewis basicity of the phosphorus apex as was established by the magnitude of the $^1J_{P,Se}$ coupling constant of the phosphine selenides. Because of the chelating properties of both the N- and P-sites, neutral phosphorus-centered scorpion ligands allow coordination modes that are unavailable to the abundantly used anionic tris(pyrazolyl)borate scorpionates as we established for Cu(I)-complexation. The substituted P-scorpion ligands only allow for N-coordination, as the P-apex is presumably less accessible. Two X-ray crystal structures were obtained for the Cu-complex of tris(3,5-dimethylpyrazolyl)-phosphine with acetonitrile and triphenylphosphine in the fourth coordination site. The parent P-scorpion ligand can chelate with both its pyrazolyl groups and its P-apex with the product depending on the ratio in which it is mixed with the Cu(I) complex. Reacting two equivalents of the ligand with [Cu(MeCN)$_4$][PF$_6$] resulted in a complex in which Cu is coordinated to the three pyrazolyl groups of one ligand and to the P-apex of the other ligand as confirmed by an X-ray crystal structure determination and a DFT computational analysis. Reacting the ligand and the Cu(I) complex in an equimolar ratio resulted in a remarkable one-dimensional P-scorpion coordination polymer for which a single crystal X-ray structure could be determined. A detailed analysis of the structural features is presented.

Introduction

Tris(pyrazolyl)borates (**A**, Fig. 1) were first introduced by Trofimenko[1] in 1966 and became one of the most widely applied polydentate anionic ligands in coordination chemistry and catalysis because of their versatility and stability.[2–5] Neutral ligands result from changing the boron apex to a carbon one as in tris(pyrazolyl)methane (**B**)[6] for which ample syntheses have been reported.[7] The neutral phosphorus-centered analogues **C** and their oxides **OC** were introduced in the mid-1970s, but hardly used.[8–10] Tolman's group explored
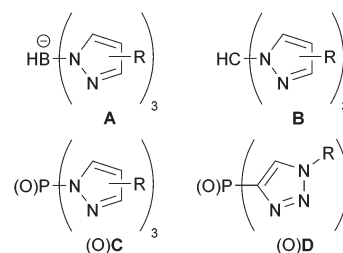

Fig. 1 Scorpion-type ligands.

chiral versions of **OC** ligands for asymmetric catalysis,[11–14] while Weigand's group applied tris(3,5-dimethylpyrazolyl)-phosphine (**C^{Me2}**) as a synthon for cationic phosphorus compounds.[15–19] Recently, we reported a simple method to synthesize the PO-centered **OC** ligands and studied their coordination chemistry.[20]

Tris(pyrazolyl)phosphines have multiple coordination sites, making them well suited for ligation with more than one metallic complex. Recently, Hazari and coworkers showed **C** coordinating to Mg in a κ³ fashion, leaving the phosphorus apex available for additional coordination.[21] We were able to use this coordinating ability in a study on the related tris-

[a]Department of Chemistry and Pharmaceutical Sciences, Vrije Universiteit Amsterdam, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands. E-mail: j.c.slootweg@vu.nl, k.lammertsma@vu.nl

[b]Bijvoet Center for Biomolecular Research, Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands

[c]Institute for Inorganic Chemistry, Universität Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany

[d]Department of Chemistry, University of Johannesburg, Auckland Park, Johannesburg, 2006 South Africa
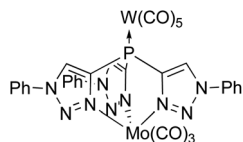
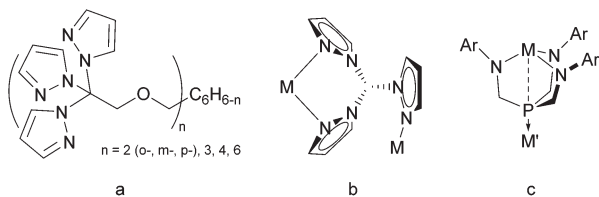**Fig. 2** A bimetallic complex supported by ligand **D**.

Fig. 3 (a) Multitopic tris(pyrazolyl)methane ligands, (b) the κ^2–κ^1 bonding mode, and (c) a bimetallic Janus-type complex.

(triazolyl)phosphine **D** to form the bimetallic complex $(OC)_5WDMo(CO)_3$ (Fig. 2).[22] We also showed that the two oxidized ligands **OC** and **OD** influence the coordinated metal similarly,[23] but **OC** has more substitution options because of the position of the carbon atoms in its heterocyclic rings.

Besides multimetallic complexes, scorpion ligands **B** also enable access to coordination macrocycles and polymers as shown in the seminal work of Reger,[24] who used tethered, multitopic tris(pyrazolyl) moieties (Fig. 3a) with silver(I) complexes to generate an abundance of well-identified supramolecular structures,[25–29] including argentachains with κ^2–κ^1 coordination modes (Fig. 3b).[26,28–33] One-dimensional coordination polymers are also accessible by the embedded use of cyano-substituted pyrazoles as has been demonstrated for the coordination of $A^{(t\text{-Bu}/Ph,4\text{-CN})}$ with Cu(I).[34] Similarly, S_2N-coordination polymers result when Ir complexes react with heteroscorpionates akin to **B**, but with methimazolyl instead of pyrazolyl groups.[35] A 'metallic tape' forms on reacting a thallium salt with tris(mercaptothiadiazolyl)borate[36,37] that can be viewed as a Janus scorpionate ligand because of the combined soft and hard binding sites.[38] Janus-type ligands like tris(amidomethyl)phosphines with N- and P-coordination sites (Fig. 3c) have been deployed to form bimetallic complexes[39,40] and coordination polymers[41] with the Co–Y, Co–Gd, and Rh–Ti transition metal pairs.

Herein we present the synthesis of tris(pyrazolyl)phosphines **C**, their coordination with copper(I), and their Janus property to generate a one-dimensional coordination polymer.

## Results and discussion

Ligand synthesis

The known tris(pyrazolyl)phosphine $\mathbf{C^H}$ and tris(dimethyl-pyrazolyl)phosphine $\mathbf{C^{Me2}}$,[8,9] and the new, more congested tris(3-phenylpyrazolyl)phosphine $\mathbf{C^{Ph}}$ and tris(3-tert-butylpyr-
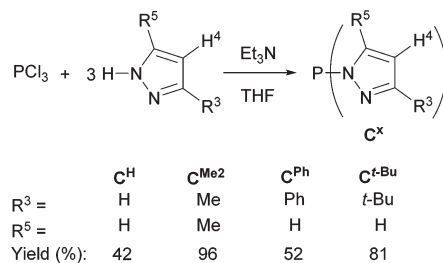
Scheme 1 Synthesis of tris(pyrazolyl)phosphines $\mathbf{C^H}$–$\mathbf{C^{t\text{-Bu}}}$.

azolyl)phosphine $\mathbf{C^{t\text{-Bu}}}$ were synthesized in modest to excellent yields using our recently reported protocol (Scheme 1).[20] The products were obtained by slow addition of phosphorus trichloride to a mixture of three equivalents of the appropriate pyrazole and a slight excess of triethylamine in THF cooled to 0 °C, followed by prolonged stirring, either at room temperature for $\mathbf{C^H}$ and $\mathbf{C^{Me2}}$ or under reflux for the bulkier $\mathbf{C^{Ph}}$ and $\mathbf{C^{t\text{-Bu}}}$. The reaction progress was monitored by ^{31}P NMR spectroscopy using the characteristic singlet for the phosphorus apex of the products (δ 61.1 ($\mathbf{C^H}$), 72.0 ($\mathbf{C^{Me2}}$), 60.2 ($\mathbf{C^{Ph}}$), and 58.2 ($\mathbf{C^{t\text{-Bu}}}$)). After filtering off by-products and removal of the volatiles, colorless to yellow solids were obtained for which additional purification was only needed for $\mathbf{C^H}$ (recrystallization) and $\mathbf{C^{Ph}}$ (washings), reducing their isolated yields significantly. The ^1H and ^{13}C NMR spectra revealed simple signal patterns, reflecting the expected equivalence of the three pyrazolyl groups; the $^{13}C\{^1H\}$ NMR spectra showed the characteristic doublets ($J_{C,P} \sim 10$ Hz) for the C^3 and C^5 carbons.

Relative Lewis basicities of P-centered systems, and thus their ligating ability, can be examined by means of their phosphine selenides since the magnitude of the $^1J_{P,Se}$ coupling constant is inversely related to the σ donating character of the free phosphine.[42–44] To examine the P-donor capacity of compounds $\mathbf{C^x}$, we have investigated selenides $\mathbf{SeC^H}$ and $\mathbf{SeC^{Me2}}$ (Scheme 2). Both selenides were obtained as yellow powders after reaction of the parent compounds with an excess of selenium for two to three days in refluxing toluene, followed by filtration over silica, evaporation of the volatiles, and washing with pentane. Unsubstituted $\mathbf{SeC^H}$ (~24%) showed a resonance at $\delta(^{31}P)$ 37.7 ppm with a $^1J_{P,Se}$ coupling constant of 1014 Hz with the corresponding values for $\mathbf{SeC^{Me2}}$ (~88%) of 40.7 ppm and 872 Hz (see ESI p. S-17 and S-19† respectively). The latter $^1J_{P,Se}$ coupling is at the high end of those reported
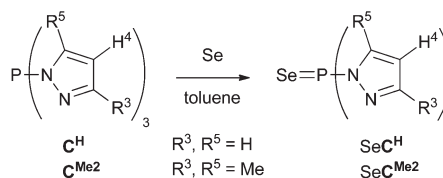
Scheme 2 Synthesis of tris(pyrazolyl)phosphine selenides $\mathbf{SeC^H}$ and $\mathbf{SeC^{Me2}}$.

for selenophosphoramides, indicating **C**[Me2] to be a weaker donor than, *e.g.*, P(NMe$_2$)$_3$ (*cf.*, $^1J_{P,Se}$ = 784 Hz for the corresponding selenide).[45] Unsubstituted **C**[H] turns out to be a still weaker donor that compares better with weakly donating phosphonates (*cf.*, $^1J_{P,Se}$ = 1025 Hz for SeP(OPh)$_3$).[46] The weak σ donating nature of the P apices of **C**[H] and **C**[Me2] is also reflected by the harsh conditions required for the formation of their selenides.

Complexation to copper(ɪ)

For tris(pyrazolyl)phosphines (**C**) to be suitable Janus-type ligands for generating one-dimensional coordination polymers they must be able to ligate in a head-to-tail fashion with Cu(ɪ). Hence, their N- and P-donor sites must have complementary affinities for the copper complex. Earlier, it has been shown that the three pyrazolyl groups of carbon-centered **B**[t-Bu] and phosphine oxide-centered **OC**[Ph,Me] and **OC**[t-Bu] coordinate with Cu(ɪ) with acetonitrile completing the coordination sphere.[20,47] For **OC**[Me2] we have shown that the coordination can also be completed with a phosphorus ligand such as triphenylphosphine.[20] However, the donor ability of PPh$_3$ differs significantly from that of **C** (*e.g.*, $^1J_{P,Se}$ = 735 Hz for SeP(Ph)$_3$[48]). Ideally, a head-to-tail Cu(ɪ)-complex with **C** would result from simply treating a Cu(ɪ) complex with two equivalents of **C**, one providing the three coordinating pyrazolyl groups and the other the phosphorus apex. However, this approach did not give the desired result when [Cu(NCMe)$_4$][PF$_6$] was treated overnight in THF with the dimethyl substituted ligand **C**[Me2].

A colorless solid precipitated, yielding crystals suitable for X-ray diffraction upon recrystallization (CH$_2$Cl$_2$/pentane). The determined molecular structure reveals [**C**[Me2]Cu(NCMe)][PF$_6$] (Fig. 4, left), which must have been formed by replacing three acetonitrile ligands of [Cu(NCMe)$_4$][PF$_6$] for one **C**[Me2]. Apparently, the phosphorus apex of the second **C**[Me2] is unable to replace the remaining acetonitrile. Reacting **C**[Me2] and the Cu-complex in an equimolar ratio gave the same product in 67.7% isolated yield. In the crystal, the metal complex is located at a general position and has only a very approximate non-crystallographic C_{3v} symmetry. The molecular structure shows the **C**[Me2] ligand to be bound in a tridentate fashion *via* its pyrazolyl rings with Cu–N bond lengths ranging from 2.071(3) to 2.080(3) Å and N–Cu–N angles ranging from 88.49(11) to 94.52(10)°. The acetonitrile is linearly coordinated to copper with a Cu–N14 bond length of 1.888(3) Å that is typical for tris(pyrazolyl)-acetonitrile Cu(ɪ)-complexes.[49] The ^{1}H and ^{13}C NMR data are also similar to those of the comparable acetonitrile containing Cu-complexes of **B**[t-Bu], **OC**[Ph,Me] and **OC**[t-Bu], but the acetonitrile ligand could not be observed due to a rapid exchange with the CD$_3$CN solvent; the solid material was poorly soluble in common NMR solvents. It is interesting to note that, while the ^{13}C chemical shifts are hardly effected by coordination of Cu, the $J_{C,P}$ coupling constants show typical changes, suggesting an altered electron density in the Pz rings. For [**C**[Me2]Cu-(NCMe)][PF$_6$], $\Delta J_{C3,P}$ = −8.5, $\Delta J_{C4,P}$ = 4.3, and $\Delta J_{C5,P}$ = 20.4 Hz. Similar changes are observed for all complexes reported here (see the Experimental section). The observed ^{31}P NMR chemi-
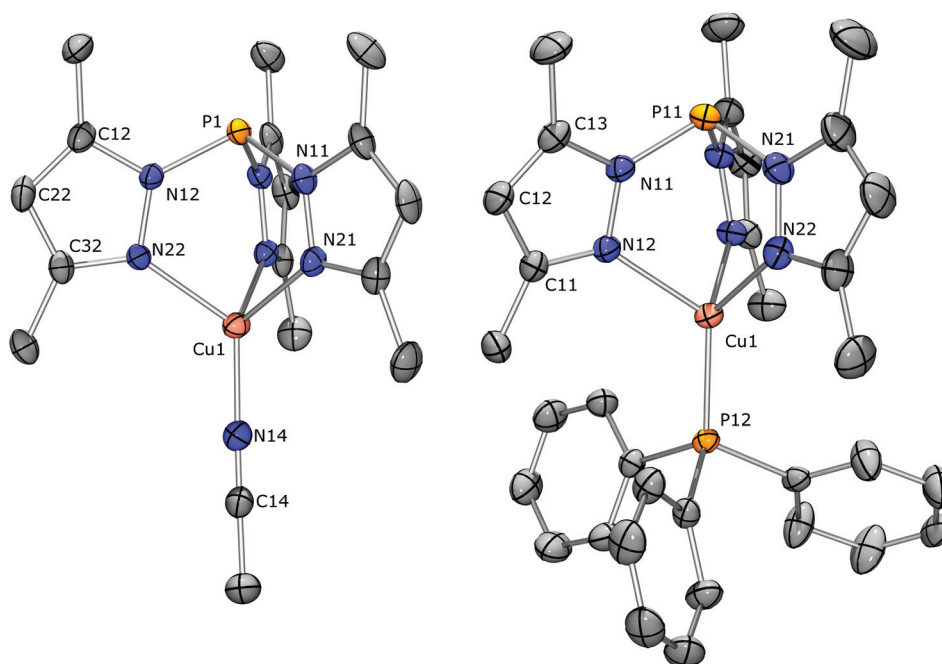
Fig. 4 Displacement ellipsoid plot of [**C**[Me2]Cu(NCMe)][PF$_6$] (left) and [**C**[Me2]Cu(PPh$_3$)][PF$_6$] (right) drawn at the 50% probability level. The PF$_6$ anions and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°] for [**C**[Me2]Cu(NCMe)][PF$_6$]: Cu1–N21 2.077(3), Cu1–N14 1.888(3), P1–N11 1.713(3), P1···Cu1 3.3176(12), N21–Cu1–N22 94.52(10), N14–Cu1–N21 120.02(12), N11–P1–N12 101.63(13), Cu1–N14–C14 176.4(3). Only one of the two independent cations is displayed for [**C**[Me2]Cu(PPh$_3$)][PF$_6$], without PF$_6$ anions and CH$_2$Cl$_2$ solvent molecules: Cu1–N12 2.110(2), Cu1–P12 2.1819(8), P11–N11 1.713(3), P11···Cu1 3.3479(9), N12–Cu1–N22 89.54(9), P12–Cu1–N12 123.57(7), N11–P11–N21 100.04(12).

cal shift at 23.3 ppm is substantially shielded compared to 72.0 ppm for the uncomplexed **C^Me2** ligand, reflecting the significant influence of Cu-complexation, even though the P1–Cu distance of 3.3176(12) Å is well outside the range of a direct interaction between the two atoms. To ascertain the presence of the acetonitrile ligand, a better soluble complex could be obtained by either anion or ligand exchange. For example, treating [**C^Me2**Cu(NCMe)][PF$_6$] with Na[BArF$_{24}$] in CH$_2$Cl$_2$ gave in 57% isolated yield colorless [**C^Me2**Cu(NCMe)][BArF$_{24}$] that readily dissolves in solvents less polar than acetonitrile.

Its ^{31}P NMR chemical shift at 20.0 ppm (CDCl$_3$) compares with the complex having PF$_6^-$ as the counterion (23.3 ppm; CD$_3$CN), while the ^{1}H NMR chemical shift at 2.23 ppm confirms the presence of the acetonitrile ligand.

The loosely bound acetonitrile of [**C^Me2**Cu(NCMe)][PF$_6$] could be exchanged for PPh$_3$ upon stirring an equimolar mixture in CH$_2$Cl$_2$ for one hour. Following workup, the product (81%) showed NMR spectra with features similar to its precursor, but with additional signals in the aromatic region of both ^{1}H and ^{13}C NMR spectra. The ^{31}P NMR spectrum showed in addition to the resonance for the **C^Me2** apex at δ 21.4 ppm one at δ 6.5 ppm for the new PPh$_3$ ligand. Crystals obtained from CH$_2$Cl$_2$/pentane were suitable for a crystal structure determination by X-ray diffraction. The asymmetric unit showed two independent complexes with two CH$_2$Cl$_2$ molecules. Fig. 4 (right) displays one [**C^Me2**Cu(PPh$_3$)][PF$_6$] complex. Its molecular structure confirms **C^Me2** as a tridentate ligand with PPh$_3$ completing the distorted tetrahedral coordination around copper. The Cu–N bond lengths range from 2.079(2) to 2.110(2) Å (2.056(2) to 2.103(2) Å in the second independent molecule) with the Cu(1)–P(12) bond being 2.1819(8) Å (2.1692(8) Å in the second independent molecule). A comparison with the molecular structure of [O**C^Me2**Cu(PPh$_3$)][PF$_6$][20] reveals the structural effect of the phosphorus apex. While the two geometries are very similar, the differences are more pronounced around the apex with [**C^Me2**Cu(PPh$_3$)][PF$_6$] having longer P–N bonds (1.710(3)–1.714(3) Å) than its oxidized form (1.673(2)–1.681(2) Å) and a longer P1···Cu separation of 3.3479(9) Å (*versus* 3.2301(5) Å) due to the *circa* 4° more acute P–N angles.

As for **C^Me2**, treating the more congested ligands **C^Ph** and **C^t-Bu** with [Cu(NCMe)$_4$][PF$_6$] in either a uni- or a bimolecular ratio gives only the acetonitrile adducts [**C^Ph**Cu(NCMe)][PF$_6$] and [**C^t-Bu**Cu(NCMe)][PF$_6$] in 56 and 43% isolated yields, respectively. Their ^{1}H and ^{13}C NMR spectra confirmed a 1 : 1 ratio of acetonitrile and the scorpion ligand. For both complexes the ^{31}P NMR resonance of the P-apex is shielded by about 15 ppm compared to the free ligands [**C^Ph**Cu(NCMe)]-[PF$_6$] δ 46.4, **C^Ph** δ 60.2 ppm; [**C^t-Bu**Cu(NCMe)][PF$_6$] δ 43.3, **C^t-Bu** δ 58.2 ppm) which is much less than 49 ppm observed for the dimethyl derivative **C^Me2**. This difference is likely due to the methyl groups at the 5-position of **C^Me2**, which shield the P-apex upon κ^3-N$_3$ complexation (Fig. 4).

Next, we turned to tris(pyrazolyl)phosphine **C^H**, because its substituted derivatives are apparently too congested around the phosphorus apex for Cu(I) complexation. Reacting **C^H** and [Cu(NCMe)$_4$][PF$_6$] in a 2 : 1 ratio in CH$_2$Cl$_2$ also gave a colorless

solid, isolated in 88% yield, but its spectroscopic properties showed it to differ substantially from the Cu-complexes of the other **C** ligands. Whereas the ^{1}H and ^{31}P NMR spectra recorded in CD$_2$Cl$_2$ at ambient temperature gave only very broad signals that could not be interpreted, ^{1}H and ^{13}C NMR spectra at 201 K both showed two sets of signals for the pyrazolyl groups in a 1 : 1 ratio (see ESI p. S-30 and 31†). The ^{31}P NMR spectrum at the same temperature demonstrated the different effects Cu coordination has on both sides of the **C^H** ligand. It displayed two singlets for the complex, and a septet at δ −144.7 ppm ($^1J_{P,F}$ = 712 Hz) for the PF$_6^-$ anion. The phosphorus at δ 39.0 is shielded compared to the apex of the free ligand (δ 61.1 ppm) due to adoption of the paddlewheel conformation required for κ^3-N$_3$ coordination. The other phosphorus, at δ 62.0 ppm, is deshielded, as is common for coordinating phosphines. The small change in the chemical shift reflects the modest interaction of this weakly donating phosphorus with the Cu(I) center. The connectivity for this dimeric Cu-complex [(**C^H**)$_2$Cu][PF$_6$] could be confirmed by a single crystal X-ray structure determination at 110 K. The crystal structure contains two independent metal complex molecules. One metal complex is located at an exact, crystallographic threefold axis, the other molecule is located at a general position with an approximate, non-crystallographic C_3 symmetry (r.m.s. deviation 0.149 Å, see Fig. 5). Its molecular structure confirms κ^3-coordination of the three pyrazolyl groups of one **C^H** ligand to Cu(I), forming Cu–N bonds and N–Cu–N angles that range from 2.035(3) to 2.051(3) Å and 91.25(14) to 92.96(13)°, respectively, and κ^1-coordination of the phosphorus apex of the other **C^H** ligand with a Cu–P bond
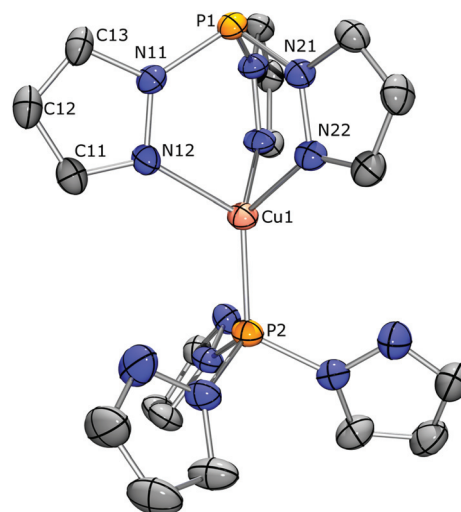

Fig. 5 Displacement ellipsoid plot of [(**C^H**)$_2$Cu][PF$_6$] drawn at the 50% probability level. One of the two independent cations is displayed, PF$_6$ anions, disordered solvent molecules, and all hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu1–N12 2.038(3), Cu1–P2 2.0938(11), P1–N11 1.715(4), P1···Cu1 3.3201(12), N12–Cu1–N22 91.25(14), P2–Cu1–N12 123.55(10), N11–P1–N21 99.20(17).
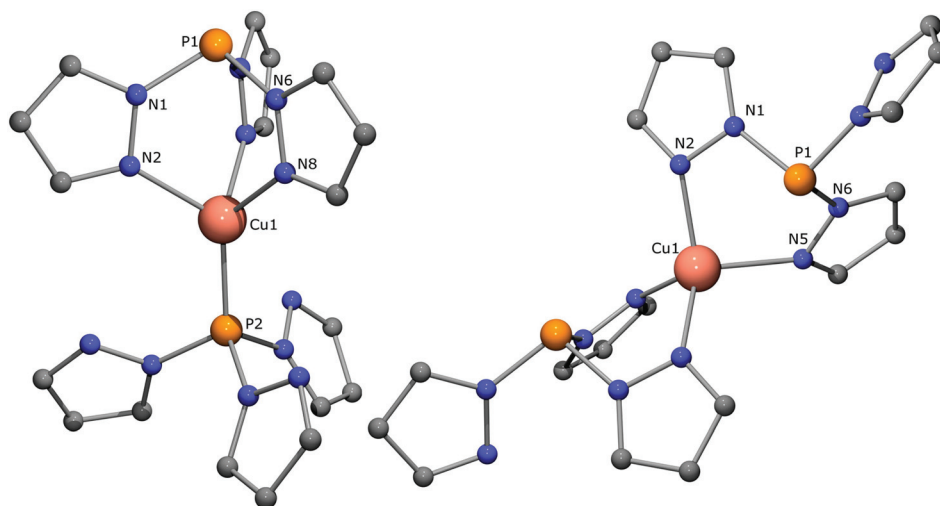
Fig. 6 Optimized structures for the κ^3,κ^1-N_3P (left) and κ^2,κ^2-N_4 (right) bound isomers of $[(C^H)_2Cu]^+$ as calculated at the B3PW91/6-31G(d) (LANL2DZ for Cu) level of theory. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°] for κ^3,κ^1-N_3P: Cu1–N2 2.115, Cu1–P2 2.204, P1–N1 1.735, P1–Cu1 3.365, N2–Cu1–N8 90.09, P2–Cu1–N2 125.20, N1–P1–N6 100.67. Selected bond lengths [Å] and angles [°] for κ^2,κ^2-N_4: Cu1–N2 2.091, Cu1–N5 2.141, P1–N1 1.756, P1–Cu1 3.053, N2–Cu1–N5 96.80, N1–P1–N6 99.00.

length of 2.0938(11) Å. Interestingly, the pyrazolyl rings of this second ligand are all oriented with their nitrogens toward the metal, with non-bonding Cu⋯N distances in the range 3.403(6) to 3.499(4) Å. All distances around copper are shorter than those for $[C^{Me2}Cu(PPh_3)][PF_6]$, reflecting reduced steric crowding, while the non-bonding Cu1⋯P1 distance of 3.3201(12) Å is only marginally shorter. Surprisingly, while the solution NMR data are in harmony with the determined crystal structure of $[(C^H)_2Cu][PF_6]$, repetitively recorded solid state ^{13}C and ^{31}P NMR data at 297 K are not. Only one singlet is observed at δ 40.3 ppm for the two phosphorus apices and the ^{13}C NMR spectrum suggests the presence of two sets of signals for the pyrazolyl rings in a 2:1 ratio. This may suggest that both C^H ligands are bound to Cu(ɪ) with two pyrazolyl groups, leaving the third one uncoordinated. Density functional calculations at B3PW91/6-31G(d) (LANL2DZ for Cu) showed the C_2 symmetric form of the $[(C^H)_2Cu]$ cation to be only 2.8 kcal mol^{-1} less stable than the C_3 isomer (Fig. 6).[50] This energy difference may even be less as the C_2 form can be stabilized by π–π stacking in the solid state as has been demonstrated for Ag(ɪ) complexes of tris(pyrazolyl)methane ligands **B**.[25,26] Since both isomers are so close in energy, it may well be that isomerisation has occurred due to the large difference in the measurement temperature (187 K) or due to loss of the co-crystallized solvent during solid state NMR sample preparation. The geometry of the calculated κ^3,κ^1-N_3P isomer corresponds reasonably well with the structures found in the X-ray crystal structure, but the gas phase calculations overestimate all bond lengths around the Cu center; the calculated Cu–N and Cu–P bonds are 2.115 Å and 2.204 Å, respectively, whereas in the crystal structure Cu–N bonds of 2.035(3)–2.051(3) Å and Cu–P bonds of 2.074(2)–2.0938(11) Å are found. It seems fair to conclude that the Cu–P interaction is readily disturbed, which

concurs with the low P-donor ability of C^H and its inability to form the substituted analogues $[(C^x)_2Cu][PF_6]$ (x = Me$_2$, Ph, t-Bu).

Coordination polymer

With the promising $[(C^H)_2Cu][PF_6]$ result in hand, we were eager to learn whether a one-dimensional coordination polymer $([C^HCu][PF_6])_n$ could be formed. The logical step was to attempt equimolar mixing of C^H and $[Cu(NCMe)_4][PF_6]$. In CH$_2$Cl$_2$, this gave a beige suspension from which a solid material was isolated that was insoluble in common NMR solvents like CD$_2$Cl$_2$ and CDCl$_3$. Solid state NMR was employed to identify its nature. ^{31}P MAS NMR spectroscopy revealed a slightly asymmetric (due to residual dipolar interactions) quartet at δ 42.0 ppm ($^1J_{P,Cu}$ = 2250 Hz) and a septet for the PF$_6^-$ anion at δ −145.4 ppm ($^1J_{P,F}$ = 713 Hz) (see ESI p. S-33†). The quartet, due to coupling with the two Cu isotopes (I = 3/2), clearly indicates P–Cu coordination. The chemical shift at δ 42.0 ppm suggests a tridentate N-coordinated C^H ligand, as found for $[(C^H)_2Cu][PF_6]$ in solution (δ 39.0 ppm) and for $[C^HCu(PPh_3)][PF_6]$ in both solution and the solid state (δ 42.4 and 40.6 ppm, respectively; *vide infra*). These NMR data are supportive of the formation of a polymeric complex $([C^HCu]-[PF_6])_n$ with alternating ligands and Cu(ɪ) centers in which each C^H acts on one side as a tridentate N-ligand and on the other side as a monodentate P-ligand. Elemental analysis of the solid matches the proposed stoichiometry (see the Experimental section).

The crystal structure determination of $([C^HCu][PF_6])_n$ turned out to be rather difficult. A needle-shaped crystal obtained from dichloromethane was cracked into two fragments. There is severe disorder in the PF$_6$ anions and co-crystallized solvent molecules. More importantly, we detected "whole molecule"
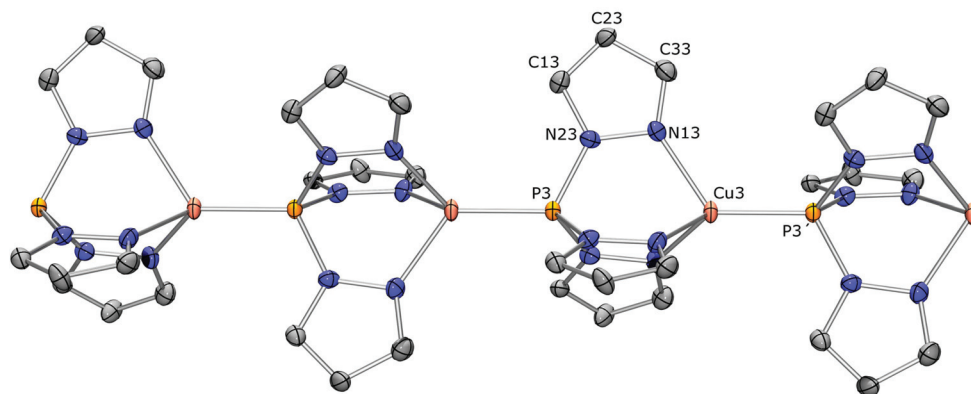
Fig. 7 One-dimensional Cu coordination chain in the crystallographic *c*-direction of ([C^HCu][PF_6])$_n$. Only one of the two independent polymers is shown. Location in the unit cell at (0, 0, *z*), Wyckoff position *a*. A slight disorder in this chain has been ignored in the structure refinement. In the drawing, hydrogen atoms, PF_6 anions and $C_2H_4Cl_2$ solvent molecules have been omitted for clarity. Symmetry codes: (i) *y*, *x*, *z* − 1/2; (ii) *y*, *x*, *z* + 1/2; (iii) *x*, *y*, *z* + 1. Selected bond lengths [Å] and angles [°]: Cu3−N13 2.034(5), Cu3−P3′ 2.081(2), P3−N23 1.700(4), P3···Cu3 3.227(2), N13−Cu3−N13 93.22(17), P3′−Cu3−N13 122.95(12), N23−P3−N23′ 101.8(2).
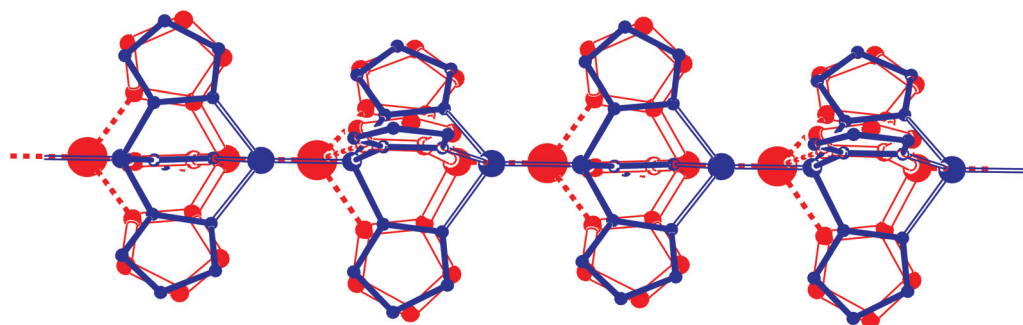
Fig. 8 Disorder in the one-dimensional Cu coordination chain of ([C^HCu][PF_6])$_n$. Location in the unit cell at (2/3, 1/3, *z*), Wyckoff position *b*. The major disorder component is drawn in red, the minor component in blue. The estimated ratio between the two components is 65 : 35%.

disorder in the one-dimensional Cu coordination polymer. It appears that a chain running in the *uvw* = [1, −1, 1] direction has very similar packing properties as a chain running in the opposite direction. Least-squares refinement of this crystal structure in the triclinic space group *P*1 (no. 1) could only be handled by introducing a large number of geometry restraints. Details are given in the ESI.†

A first crystal obtained from 1,2-dichloroethane had a trigonal symmetry and was merohedrally twinned (see the ESI†). Fortunately we were able to obtain a non-twinned crystal with the same unit cell parameters. The crystal structure contains two independent polymeric Cu coordination chains which are located on threefold axes, respectively. Both polymers show the "whole molecule" disorder described above. In one of the chains this disorder could be ignored because of rather low residual electron densities (Fig. 7). In the other chain, a disorder model could be found and refined (Fig. 8). Because of the disorder, it was not possible to obtain reliable bond distances and angles, but the coordination mode could be proofed unambiguously. The two independent one-dimen-

sional coordination polymers are oriented in the direction of the crystallographic *c*-axis. Both chains have two monomeric units in the crystallographic unit cell, respectively. Consequently, the axis length of *c* = 10.6155(4) Å leads to an average Cu···Cu distance of *c*/2 = 5.3078(2) Å. The polymeric nature of the structure is also reflected in the shape of the crystal. The *c*-direction corresponds to the long dimension of the needle shaped crystal (Fig. S4 in the ESI†).

The fact that tris(pyrazolyl)phosphine C^H but not C^{Me2} gives access to a Cu(I)-coordination polymer highlights that even modest steric factors can be inhibiting. A similar observation was made by Dougherty *et al.* who were unable to obtain a polymetallic species from tris-[2-(1-methylimidazolyl)-phosphine] and Cu(ClO$_4$)$_2$·6H$_2$O.[51] Apparently, methyl groups at 3- and/or 5-positions of the imidazolyl and pyrazolyl groups hamper sufficiently the weak ligation of the copper center to the P-donor site.

Formation of the coordination polymer ([C^HCu][PF_6])$_n$ was further supported by ligand exchange experiments to trap monomeric units (Scheme 3). For example, reaction of the
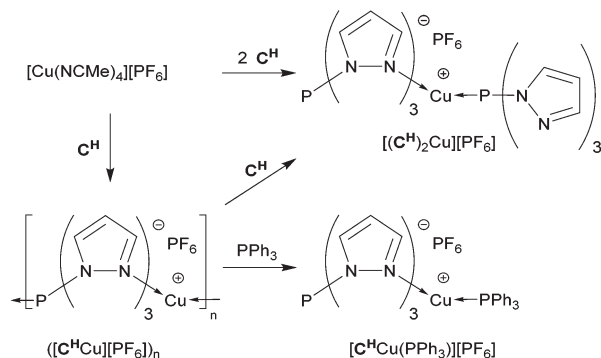
Scheme 3 Formation and reactivity of Cu complexes of tris(pyrazolyl)-phosphine C^H.

polymer with one equivalent of C^H in CH_2Cl_2 gave a clear solution from which a yellow powder was isolated. This was identified by NMR spectroscopy to be identical to the separately synthesized $[(C^H)_2Cu][PF_6]$ (*vide supra*), now with an isolated yield of 81%. Likewise, cleaving the polymeric chain with one equivalent of PPh_3 in CH_2Cl_2 gave a 97% isolated yield of $[C^HCu(PPh_3)][PF_6]$. The ^{31}P NMR spectrum resembles that of $[C^{Me2}Cu(PPh_3)][PF_6]$ (*vide supra*) and showed a broad singlet at δ 7.8 ppm for PPh_3 bound to Cu(I) and a sharp singlet at δ 42.4 ppm for the P-apex of C^H. The ^1H NMR spectrum showed a 1:1 stoichiometric ratio for the set of signals for C^H and a multiplet for the phenyl hydrogens of PPh_3. The ^{31}P MAS NMR spectrum resembled that recorded in solution, but the Cu(I)-coordinated PPh_3 appeared as a quartet at δ 14.2 ppm ($^1J_{P,63Cu}$ = 1862 Hz), while the P-apex of the C^H ligand gives a singlet at δ 40.6 ppm that resembles its chemical shift of δ 42.0 ppm found for the polymer.

Conclusions

We have demonstrated the different binding modes of tris(pyrazolyl)phosphine **C**. It can bind metals as a tridentate nitrogen donor and as a monodentate phosphine donor. Both binding modes of this Janus-type ligand can be combined when choosing the appropriate steric requirements, making it a suitable building block for coordination polymers. The fact that ligands **C** are readily available and that a great variety of substituted pyrazoles is already known[3,4] make tris(pyrazolyl)phosphines very promising candidates for further studies.

Experimental section

General procedures

All experiments were performed under an atmosphere of dry nitrogen. Solvents were purified, dried, and degassed by standard techniques. 3-Phenyl-1*H*-pyrazole,[52] 3-*tert*-butyl-1*H*-pyrazole,[52] [Cu(NCMe)$_4$][PF$_6$],[53] and [Na][BArF$_{24}$][54] were pre-

pared according to literature procedures. Triethyl amine was dried over sodium, and phosphorus trichloride was distilled under nitrogen before use. Other reagents were obtained commercially and used as received.

NMR spectra were recorded at 298 K with a Bruker Avance 250, a Bruker Avance 400, or a Bruker Ultrashield 500 spectrometer. ^1H and ^{13}C NMR spectra were referenced internally to residual solvent resonances (CDCl$_3$: ^1H: 7.26 ppm (CHCl$_3$), $^{13}C\{^1H\}$: 77.16 ppm; CD$_2$Cl$_2$: ^1H: 5.32 ppm (CDHCl$_2$), $^{13}C\{^1H\}$: 53.84 ppm; CD$_3$CN: ^1H: 1.94 ppm (CD$_2$HCN), $^{13}C\{^1H\}$: 1.32 ppm). Other nuclei were referenced to external standards: ^{19}F: BF$_3$·Et$_2$O (0.0 ppm) and ^{31}P: 85% H$_3$PO$_4$ (0.0 ppm). Most coupling constants in the ^1H NMR spectra were determined after applying line narrowing. Solid-state CP-MAS NMR spectra were recorded on a Bruker Avance 400 spectrometer (^{31}P: 161.9 MHz) equipped with a 4 mm MAS probe. Solid samples were prepared in standard ZrO$_2$ rotors. MAS experiments were carried out using spinning speeds between 6 and 15 kHz at 297 K. Cross polarization was applied using a ramp-shaped contact pulse and a mixing time between 3 and 5 ms. ^{31}P chemical shifts were referenced to 85% H$_3$PO$_4$ as the external standard ($\varXi$ = 40.480747 MHz). The given values for ^1J(P,Cu) refer to the averaged value of couplings to the two isotopes ^{63}Cu and ^{65}Cu if not specified otherwise. High-resolution electrospray ionization mass spectrometry (HR ESI-MS) was performed using a Bruker MicroTOFQ, with ESI in positive mode (capillary voltage 4.5 kV). Melting points were determined on a Stuart Scientific SMP3 melting point apparatus using sealed capillaries. Elemental analyses were performed at the Microanalytical Laboratory of the Laboratorium für Organische Chemie, ETH Zürich, Switzerland.

Tris(pyrazolyl)phosphine (C^H).[8,9] A solution of phosphorus trichloride (5.65 g, 41.1 mmol) in THF (40 mL) was added dropwise over 50 min to a stirred solution of pyrazole (8.4 g, 123 mmol) and triethyl amine (17.5 mL, 126 mmol) in THF (200 mL) cooled to 0 °C. Immediately a colorless solid (Et$_3$N·HCl) started to precipitate. After the addition was complete, the reaction mixture was allowed to attain room temperature while stirring was continued for 24 h. The colorless solids were removed from the reaction mixture by filtration over a cannula fitted with a glass wool filter and the residue was washed twice with THF (20 mL). After concentrating the combined light yellow filtrates to about half the volume, they were cannula filtered again. Taking the resulting filtrates to dryness yielded a light yellow solid (8.17 g, 85.6%). According to ^1H NMR spectroscopy (CDCl$_3$) this solid contained some impurities (less than 2 mol%). Therefore, the solid was recrystallized from CH$_2$Cl$_2$ (19 mL) at −20 °C. After removal of the mother liquor, the light yellow crystals were dried *in vacuo* yielding C^H (4.03 g, 17.4 mmol, 42.2%). Mp: 105.5–107.6 °C (lit.[8] 104 °C). ^1H NMR (500.2 MHz, CDCl$_3$): δ 6.46 (dd, $^3J_{H,H}$ = 2.6 Hz, $^3J_{H,H}$ = 1.6 Hz, 3H; Pz*H*-4), 7.86 (ddd, $^3J_{H,H}$ = 1.6 Hz, $^4J_{H,H}$ = 0.5 Hz, $^4J_{H,P}$ = 0.4 Hz, 3H; Pz*H*-3), 8.00 (ddd, $^3J_{H,H}$ = 2.6 Hz, $^3J_{H,P}$ = 1.7 Hz, $^4J_{H,H}$ = 0.5 Hz, 3H; Pz*H*-5). $^{13}C\{^1H\}$ NMR (62.9 MHz, CDCl$_3$): δ 108.9 (d, $^3J_{C,P}$ = 1.8 Hz; Pz*C*-4), 135.7 (d, $^2J_{C,P}$ = 12.1 Hz; Pz*C*-5), 145.6 (d, $^3J_{C,P}$ = 10.3 Hz; Pz*C*-3). $^{31}P\{^1H\}$

NMR (101.3 MHz, CDCl$_3$): δ 61.1 (s). ^{31}P{^{1}H} MAS NMR (162.0 MHz): δ 60.3 (s).

Tris(3,5-dimethylpyrazolyl)phosphine (C^{Me2}).[8,9] In a similar procedure as reported for tris(pyrazolyl)phosphine (C^H), phosphorus trichloride (0.9 mL, 10.7 mmol), 3,5-dimethyl pyrazole (3.08 g, 32 mmol) and triethylamine (4.6 mL, 33 mmol) were reacted in a total of 50 mL of THF. The time to complete the reaction was 1 h at room temperature. All volatiles were evaporated from the obtained THF extracts to yield a colorless oil. To remove the residual solvent, pentane (10 mL) was added, which was then removed *in vacuo* to co-evaporate the last traces of THF. This was done twice to afford C^{Me2} as a pale yellow solid (3.26 g, 10.3 mmol, 96.3%). Mp: 91.5–92.0 °C. ^{1}H NMR (250.1 MHz, CDCl$_3$): δ 2.13 (s, 9H; 5-CH_3), 2.21 (s, 9H; 3-CH_3), 5.93 (s, 3H; PzH-4). ^{13}C{^{1}H} NMR (62.9 MHz, CDCl$_3$): δ 11.6 (d, $^3J_{C,P}$ = 8.8 Hz; 5-CH_3), 13.8 (s; 3-CH_3), 109.7 (s; PzC-4), 147.3 (d, $^2J_{C,P}$ = 10.8 Hz; PzC-5), 153.4 (d, $^3J_{C,P}$ = 10.1 Hz; PzC-3). ^{31}P NMR (101.3 MHz, CDCl$_3$): δ 72.0.

Tris(3-phenylpyrazol-1-yl)phosphine (C^{Ph}). In a similar procedure as reported for tris(pyrazolyl)phosphine (C^H), phosphorus trichloride (1.6 g, 11.7 mmol), 3-phenyl-1H-pyrazole (5.05 g, 35.0 mmol) and triethylamine (4.9 mL, 35.3 mmol) were reacted in a total of 50 mL of THF. The time to complete the reaction was 16 h at reflux temperature. All volatiles were evaporated from the obtained THF extracts and the resulting solid was treated with pentane (10 mL) to co-evaporate any remaining THF. ^{1}H-NMR spectroscopy showed that some 3-phenyl-1H-pyrazole was still present, therefore the solid was washed with diethyl ether. After all volatiles were removed, C^{Ph} (2.82 g, 6.12 mmol, 52%) was isolated as a colorless solid. Mp: 205.5–206.5 °C. ^{1}H-NMR (500.2 MHz, CDCl$_3$): δ 6.78 (br.s, 3H; PzH-4), 7.37 (m, 3H; p-PhH), 7.42 (m, 6H; m-PhH), 7.87 (m, 6H; o-PhH), 8.14 (br.s, 3H, PzH-5). ^{13}C-NMR (125.8 MHz, CDCl$_3$): δ 106.7 (s; PzC-4), 126.4 (s; o-PhC), 128.8 (s; m-PhC), 128.9 (s; p-PhC), 132.3 (s; $ipso$-PhC), 137.0 (d, $^2J_{C,P}$ = 10.1 Hz; PzC-5), 157.2 (d, $^3J_{C,P}$ = 10.7 Hz; PzC-3). ^{31}P-NMR (162.0 MHz, CDCl$_3$): δ 60.2.

Tris(3-*tert*-butylpyrazol-1-yl)phosphine (C$^{t\text{-}Bu}$). In a similar procedure as reported for tris(pyrazolyl)phosphine (C^H), phosphorus trichloride (1.46 g, 10.6 mmol), 3-*tert*-butyl-1H-pyrazole (3.96 g, 31.9 mmol) and triethylamine (4.6 mL, 33 mmol) were reacted in a total of 50 mL of THF. The time to complete the reaction was 16 h at room temperature and 2 h at reflux temperature. All volatiles were evaporated from the obtained THF extracts and the resulting solid was treated with pentane (10 mL) to co-evaporate any remaining THF. C$^{t\text{-}Bu}$ (3.48 g, 8.68 mmol, 81%) was isolated as a white-yellow solid. Mp: 104–106 °C. ^{1}H-NMR (500.2 MHz, CDCl$_3$): δ 1.29 (s, 27H; C(CH_3)$_3$), 6.26 (d, 3H; PzH-4), 7.88 (br.s, 3H; PzH-5). ^{13}C-NMR (125.8 MHz, CDCl$_3$): δ 30.4 (s; C(CH$_3$)$_3$), 32.6 (s; C(CH$_3$)$_3$), 105.7 (d, $^3J_{C,P}$ = 1.7 Hz, PzC-4), 135.8 (d, $^2J_{C,P}$ = 9.5 Hz; PzC-5), 167.1 (d, $^3J_{C,P}$ = 10.3 Hz; PzC-3). ^{31}P-NMR (162.0 MHz, CDCl$_3$): δ 58.2.

Tris(pyrazolyl)phosphine selenide (SeC^H). C^H (231 mg, 0.995 mmol) and elemental selenium (232 mg, 2.94 mmol) were stirred in toluene (7 mL) for 38 h at 120 °C in a closed Schlenk tube. After cooling down, the reaction mixture was

filtered by cannula filtration. All volatiles were removed from the filtrate, yielding 96.5 mg of a brown solid. This solid was a mixture of mainly SeC^H and C^H (1 : 0.3) according to ^{1}H NMR spectroscopy. Further purification of SeC^H was not successful.

^{1}H NMR (400.1 MHz, CDCl$_3$): δ 6.51 (ddd, $^4J_{H,P}$ = 2.8 Hz, $^3J_{H,H}$ = 2.8 Hz, $^3J_{H,H}$ = 1.5 Hz, 3H; PzH-4), 7.96 (ddd, $^4J_{H,P}$ = 2.1 Hz, $^3J_{H,H}$ = 1.5 Hz, $^4J_{H,H}$ = 0.5 Hz, 3H; PzH-3), 8.04 (ddd, $^3J_{H,H}$ = 2.8 Hz, $^3J_{H,P}$ = 1.4 Hz, $^4J_{H,H}$ = 0.5 Hz, 3H; PzH-5). ^{13}C{^{1}H} NMR (125.8 MHz, CDCl$_3$): δ 109.7 (d, $^3J_{C,P}$ = 6.9 Hz; PzC-4), 136.6 (d, $^2J_{C,P}$ = 13.9 Hz; PzC-5), 147.4 (d, $^3J_{C,P}$ = 14.9 Hz; PzC-3). ^{31}P{^{1}H} NMR (101.3 MHz, CDCl$_3$): δ 37.7 (s, $^1J_{P,Se}$ = 1014 Hz).

Tris(3,5-dimethylpyrazolyl)phosphine selenide (SeC^{Me2}). C^{Me2} (400 mg, 1.26 mmol) and elemental selenium (2 g, 25 mmol) were stirred in toluene (20 mL) for 3 days at 120 °C in a closed Schlenk tube. After cooling down, the reaction mixture was filtered over silica and the residue was washed with toluene until the washings were colorless. After evaporation of the volatiles, the remaining powder was washed with pentane (50 mL) and dried *in vacuo* to yield 440 mg of a yellow powder, which was not pure according to ^{31}P NMR analysis (small unassigned signals between δ 5–15 and 35–45). Further purification of SeC^{Me2} was not successful. ^{1}H NMR (500.2 MHz, CDCl$_3$): δ 2.11 (s, 9H; 3-CH_3) 2.36 (s, 9H; 5-CH_3) 6.04 (s, 3H; PzH-4). ^{13}C NMR (125.8 MHz, CDCl$_3$): δ 13.1 (s; 3-CH_3), 14.3 (s; 5-CH_3), 111.7 (d, $^3J_{C,P}$ = 4.7 Hz; PzC-4), 147.2 (d, $^2J_{C,P}$ = 11.4 Hz; PzC-5), 152.4 (d, $^3J_{C,P}$ = 13.6 Hz; PzC-3). ^{31}P{^{1}H} NMR (162.0 MHz, CDCl$_3$): δ 40.7 (s, $^1J_{P,Se}$ = 872 Hz).

Attempted preparation of bis(tris(3,5-dimethylpyrazolyl)-phosphine) copper(ı) hexafluorophosphate ([(C^{Me2})$_2$Cu]-[PF$_6$]). [Cu(MeCN)$_4$][PF$_6$] (100 mg, 0.268 mmol) and C^{Me2} (170 mg, 0.537 mmol) were dissolved in THF (15 mL) at room temperature. After stirring overnight, a large amount of solid had precipitated, which was collected by filtration and was washed with pentane. No ^{31}P NMR signal was observed in the supernatant. Further drying led to the isolation of a colorless powder (171 mg). Vapor diffusion of pentane in a saturated solution of the title compound in CH$_2$Cl$_2$ afforded crystals suitable for an X-ray structure determination, which showed the crystals to be those of [C^{Me2}Cu(NCMe)][PF$_6$].

Acetonitrile tris(3,5-dimethylpyrazolyl)phosphine copper(ı) hexafluorophosphate ([C^{Me2}Cu(NCMe)][PF$_6$]). C^{Me2} (505 mg, 1.60 mmol) in CH$_2$Cl$_2$ (10 mL) was added to a Schlenk vessel containing [Cu(NCMe)$_4$][PF$_6$] (596 mg, 1.60 mmol). The resulting turbid colorless mixture was stirred overnight followed by cannula filtration. The residue was washed with CH$_2$Cl$_2$ (2 × 3 mL), yielding a colorless solid. All remaining volatiles were removed *in vacuo* and [C^{Me2}Cu(NCMe)][PF$_6$] (612 mg, 1.08 mmol, 67.7%) remained. Mp: 240.0–241.1 °C (dec). ^{1}H NMR (500.2 MHz, CD$_3$CN): δ 2.31 (s, 9H; 5-CH_3), 2.53 (dd, $^3J_{H,P}$ = 1.5 Hz, $^3J_{H,H}$ = 1.0 Hz, 9H; 3-CH_3), 6.09 (d, $^4J_{H,P}$ = 5.2 Hz, 3H; PzH-4); signals of the coordinated MeCN ligand were not observed due to exchange with the solvent. ^{13}C NMR (125.8 MHz, CD$_3$CN): δ 12.5 (d, $^3J_{C,P}$ = 19.1 Hz; 5-CH_3), 13.9 (s; 3-CH_3) 109.0 (d, $^3J_{C,P}$ = 4.3 Hz; PzC-4), 150.5 (d, $^2J_{C,P}$ = 31.2 Hz; PzC-5), 156.4 (d, $^3J_{C,P}$ = 1.6 Hz; PzC-3); signals of the

coordinated MeCN ligand were not observed due to exchange with the solvent. ^{19}F NMR (235.3 MHz, CD$_3$CN): δ −73.0 (d, $^1J_{F,P}$ = 706.0 Hz; PF$_6$). ^{31}P NMR (162.0 MHz, CD$_3$CN): δ −144.6 (sept, $^1J_{P,F}$ = 706.3 Hz; PF$_6$), 23.3 (s; P(Pz)). ^{31}P{^{1}H} CP/MAS NMR (162.0 MHz): δ −144.1 (sept, $^1J_{P,F}$ = 710 Hz; PF$_6$), 21.4 (s; P(Pz)).

Acetonitrile tris(3,5-dimethylpyrazolyl)phosphine copper(ɪ) tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate ([C^{Me2}Cu-(NCMe)][BArF$_{24}$]). [C^{Me2}Cu(NCMe)][PF$_6$] (48 mg, 0.085 mmol), [Na][BArF$_{24}$] (75 mg, 0.085 mmol) and CH$_2$Cl$_2$ (5 mL) were mixed in a Schlenk flask. The reaction mixture was stirred for 3.5 h during which the pale brown suspension became slightly clearer. The solids were removed by cannula filtration, yielding a pale yellow filtrate. Removal of all volatiles from this filtrate afforded [C^{Me2}Cu(NCMe)][BArF$_{24}$] as a colorless solid (62 mg, 0.048 mmol, 57%). Mp: 151.7–152.6 °C. ^{1}H NMR (250.1 MHz, CDCl$_3$): δ 2.23 (s, 3H; NCCH$_3$), 2.25 (s, 9H; 3-CH$_3$), 2.51 (s, 9H; 5-CH$_3$), 5.93 (d, $^4J_{H,P}$ = 5.3 Hz, 3H; PzH-4), 7.51 (s, 4H; p-ArH), 7.71 (s, 8H; o-ArH). ^{13}C{^{1}H} NMR (62.9 MHz, CDCl$_3$): δ 2.7 (s; NCCH$_3$), 12.1 (d, $^3J_{C,P}$ = 19.6 Hz; 5-CH$_3$), 13.8 (s; 3-CH$_3$), 108.8 (d, $^3J_{C,P}$ = 4.5 Hz; PzC-4), 115.3 (s; NCCH$_3$), 117.6 (m, $^3J_{C,F}$ = 3.8 Hz; p-ArC), 124.7 (q, $^1J_{C,F}$ = 272.5 Hz; CF$_3$), 129.1 (q, $^2J_{C,F}$ = 32 Hz; m-ArC), 135.0 (s; o-ArC), 147.9 (d, $^2J_{C,P}$ = 31.4 Hz; PzC-5), 155.7 (d, $^3J_{C,P}$ = 1.9 Hz; PzC-3), 161.9 (q, $^1J_{C,B}$ = 49.9 Hz; ipso-ArC). ^{19}F NMR (235.3 MHz, CDCl$_3$): δ −62.5 (s). ^{31}P NMR (101.3 MHz, CDCl$_3$): δ 20.0 (s). HR-ESI-MS: calcd for C$_{15}$H$_{21}$CuN$_6$P (M−MeCN−B(C$_6$H$_3$(CF$_3$)$_2$)$_4$) 379.0856, found 379.0815.

Tris(3,5-dimethylpyrazolyl)phosphine triphenylphosphine copper(ɪ) hexafluorophosphate ([C^{Me2}Cu(PPh$_3$)][PF$_6$]). A Schlenk vessel was charged with [C^{Me2}Cu(NCMe)][PF$_6$] (95.9 mg, 0.169 mmol) and triphenylphosphine (44.3 mg, 0.169 mmol). CH$_2$Cl$_2$ (5 mL) was added to give a clear solution, which was stirred for 1 h. Then all volatiles were removed from the colorless solution to yield colorless [C^{Me2}Cu(PPh$_3$)][PF$_6$] (107 mg, 0.136 mmol, 80.5%) which was pure according to NMR spectroscopy. Crystals suitable for single crystal X-ray diffraction were obtained by applying a layer of pentane onto a concentrated solution of [C^{Me2}Cu(PPh$_3$)][PF$_6$] in CH$_2$Cl$_2$. After allowing slow diffusion of the pentane for four days, colorless crystals had formed. Mp: 281.6 °C (dec). ^{1}H NMR (250.1 MHz, CDCl$_3$): δ 1.76 (s, 9H; 3-CH$_3$), 2.63 (s, 9H; 5-CH$_3$), 6.05 (d, $^4J_{H,P}$ = 5.4 Hz, 3H; PzH-4), 7.36–7.60 (m, 15H; PhH). ^{13}C{^{1}H} NMR (62.9 MHz, CDCl$_3$): δ 12.4 (d, $^3J_{C,P}$ = 20.5 Hz; 5-CH$_3$), 14.3 (s; 3-CH$_3$), 109.5 (d, $^3J_{C,P}$ = 4.4 Hz; PzC-4), 129.3 (d, $^3J_{C,P}$ = 10.0 Hz; m-PhC), 130.9 (d, $^4J_{C,P}$ = 1.7 Hz; p-PhC), 132.8 (d, $^1J_{C,P}$ = 36.8 Hz; ipso-PhC), 134.0 (d, $^2J_{C,P}$ = 15.5 Hz; o-PhC), 149.2 (d, $^2J_{C,P}$ = 32.3 Hz; PzC-5), 156.7 (d, $^3J_{C,P}$ = 1.3 Hz; PzC-3). ^{19}F NMR (235.3 MHz, CDCl$_3$): δ −73.7 (d, $^1J_{F,P}$ = 712 Hz; PF$_6$). ^{31}P NMR (101.3 MHz, CDCl$_3$): δ −144.3 (sept, $^1J_{P,F}$ = 712 Hz; PF$_6$), 6.5 (br. s; P(Ph)$_3$), 21.4 (s; P(Pz)$_3$). HR-ESI-MS: calcd for C$_{33}$H$_{36}$CuN$_6$P$_2$ (M−PF$_6$) 641.1767, found 641.1698.

Acetonitrile tris(3-phenylpyrazolyl)phosphine copper(ɪ) hexafluorophosphate ([C^{Ph}Cu(NCMe)][PF$_6$]). C^{Ph} (0.50 g, 1.1 mmol) and [Cu(NCMe)$_4$][PF$_6$] (0.40 g, 1.1 mmol) were stirred in THF (10 mL) at room temperature. After 16 h, a large amount of

solid had precipitated, which was collected via Schlenk filtration and was washed with THF (3 × 10 mL). After drying in vacuo, [C^{Ph}Cu(NCMe)][PF$_6$] (0.43 g, 0.55 mmol, 51%) was collected as a pale yellow powder, retaining 1 eq. of THF according to ^{1}H NMR spectroscopy. Mp: 225–226 °C (dec). ^{1}H NMR (500.2 MHz, CDCl$_3$ + CD$_3$CN): δ 6.73 (br. s, 3H; PzH-4), 7.34 (m, 3H; p-PhH), 7.41 (m, 6H; m-PhH), 7.74 (m, 6H; o-PhH), 8.19 (br. s, 3H; PzH-5); signals of the coordinated MeCN ligand were not observed due to exchange with the solvent. ^{13}C{^{1}H} NMR (125.8 MHz, CDCl$_3$ + CD$_3$CN): δ 107.4 (d, $^3J_{C,P}$ = 8.1 Hz; PzC-4), 127.3 (s; o-PhC), 128.2 (s; m-PhC), 129.6 (s; p-PhC), 130.2 (s; ipso-PhC), 138.8 (d, $^2J_{C,P}$ = 26.8 Hz; PzC-5), 158.2 (br.s.; PzC-3); signals of the coordinated MeCN ligand were not observed due to exchange with the solvent. ^{19}F-NMR (235.4 MHz, CDCl$_3$ + CD$_3$CN): δ −72.9 (d, $^1J_{F,P}$ = 710 Hz; PF$_6$). ^{31}P-NMR (162.0 MHz, CDCl$_3$ + CD$_3$CN): δ −144.5 (sept, $^1J_{P,F}$ = 711 Hz; PF$_6$), 46.4 (s; P(Pz)). HR-ESI-MS: calcd for C$_{27}$H$_{21}$CuN$_6$P (M−MeCN−PF$_6$) 523.0856, found 523.0835.

Acetonitrile tris(3-tert-butylpyrazolyl)phosphine copper(ɪ) hexafluorophosphate ([C^{t-Bu}Cu(NCMe)][PF$_6$]). C^{t-Bu} (0.50 g, 1.3 mmol) and [Cu(NCMe)$_4$][PF$_6$] (0.47 g, 1.3 mmol) were stirred in THF (10 mL) at room temperature. After 16 h, a large amount of solid had precipitated, which was collected via Schlenk filtration and was washed with THF (3 × 10 mL). After drying in vacuo, [C^{t-Bu}Cu(NCMe)][PF$_6$] (0.35 g, 0.48 mmol, 39%) was collected as a pale yellow powder, retaining 1 eq. of THF according to ^{1}H NMR spectroscopy. Mp: 165–167 °C (dec). ^{1}H-NMR (500.2 MHz, CDCl$_3$ + CD$_3$CN): δ 1.35 (s, 27H; C(CH$_3$)$_3$), 6.31 (d, 3H; PzH-4), 7.95 (br.s, 3H; PzH-5); signals of the coordinated MeCN ligand were not observed due to exchange with the solvent. ^{13}C-NMR (125.8 MHz, CDCl$_3$ + CD$_3$CN): δ 29.6 (s; C(CH$_3$)$_3$), 32.3 (s; C(CH$_3$)$_3$), 106.1 (d, $^3J_{C,P}$ = 10.0 Hz; PzC-4), 138.2 (d, $^2J_{C,P}$ = 40.3 Hz; PzC-5), 168.9 (s; PzC-3); signals of the coordinated MeCN ligand were not observed due to exchange with the solvent. ^{19}F-NMR (235.4 MHz, CDCl$_3$ + CD$_3$CN): δ −73.0 (d, $^1J_{F,P}$ = 711 Hz; PF$_6$). ^{31}P-NMR (162.0 MHz, CDCl$_3$ + CD$_3$CN): δ −144.5 (sept, $^1J_{P,F}$ = 711 Hz; PF$_6$), 43.3 (s; P(Pz)). HR-ESI-MS: calcd for C$_{21}$H$_{33}$CuN$_6$P (M−MeCN−PF$_6$) 463.1795, found 463.1784.

Bis(tris(pyrazolyl)phosphine)copper(ɪ) hexafluorophosphate ([(C^H)$_2$Cu][PF$_6$]). *Procedure A starting with [Cu(NCMe)$_4$][PF$_6$]*: CH$_2$Cl$_2$ (30 mL) was added to a mixture of [Cu(NCMe)$_4$][PF$_6$] (185 mg, 0.496 mmol) and C^H (240 mg, 1.03 mmol) while stirring. The resulting reaction mixture was initially turbid, but after stirring for 24 h most solids had (re)dissolved. The solution was filtered over a cannula fitted with a glass wool filter and the filtrate was evaporated to dryness. The remaining colorless solid was washed with Et$_2$O (10 mL) and dried in vacuo to yield [(C^H)$_2$Cu][PF$_6$] (0.294 mg, 0.437 mmol, 88.0%). *Procedure B starting with ([C^{H}Cu][PF$_6$])$_n$*: CH$_2$Cl$_2$ (10 mL) was added to a mixture of ([C^{H}Cu][PF$_6$])$_n$ (217 mg, 0.492 mmol) and C^H (111 mg, 0.478 mmol) while stirring. Within a minute a clear solution was formed which was stirred for 6 h at room temperature. After cannula filtration, the solution was evaporated to dryness, yielding [(C^H)$_2$Cu][PF$_6$] (0.26 g, 0.386 mmol, 80.8%). 0.14 g of this material was dissolved in CH$_2$Cl$_2$

(10 mL). The resulting pale solution was filtered and concentrated to one third of its volume. Storing this solution at −20 °C resulted in a small amount of crystals, suitable for an X-ray diffraction study. Mp: 199.8–201.4 °C (dec). ^{1}H NMR (400.1 MHz, 201 K, CD_2Cl_2): δ 6.54 (ddd, $^4J_{H,P}$ = 3.4 Hz, $^3J_{H,H}$ = 2.8 Hz, $^3J_{H,H}$ = 1.9 Hz, 3H; Pz$_{\kappa3N}$H-4), 6.63 (dd, $^3J_{H,H}$ = 2.8 Hz, $^3J_{H,H}$ = 1.6 Hz, 3H; Pz$_{\kappa1P}$H-4), 7.64 (d, $^3J_{H,H}$ = 2.8 Hz, 3H; Pz$_{\kappa1P}$H-5), 8.05 (m, $^3J_{H,H}$ = 1.5 Hz, 3H; Pz$_{\kappa1P}$H-3), 8.28 (dd, $^3J_{H,P}$ = 4.8 Hz, $^3J_{H,H}$ = 2.8 Hz, 3H; Pz$_{\kappa3N}$H-5) 8.41 (ddd, $^3J_{H,H}$ = 1.9 Hz, $^4J_{H,P}$ = 1.3 Hz, $^4J_{H,H}$ = 0.5 Hz, 3H; Pz$_{\kappa3N}$H-3). ^{13}C{^{1}H} NMR (100.6 MHz, 201 K, CD_2Cl_2): δ 108.4 (d, $^3J_{C,P}$ = 8.7 Hz; Pz$_{\kappa3N}$C-4), 110.2 (s, Pz$_{\kappa1P}$C-4), 134.4 (d, $^2J_{C,P}$ = 6.7 Hz; Pz$_{\kappa1P}$C-5), 138.8 (d, $^2J_{C,P}$ = 38.0 Hz; Pz$_{\kappa3N}$C-5), 146.7 (d, $^3J_{C,P}$ = 14.5 Hz; Pz$_{\kappa1P}$C-3), 148.0 (s; Pz$_{\kappa3N}$C-3). ^{19}F NMR (235.3 MHz, $CDCl_3$): δ −71.8 (d, $^1J_{P,F}$ = 713 Hz; PF_6). ^{31}P{^{1}H} NMR (162.0 MHz, 201 K, CD_2Cl_2): δ −144.7 (sept, $^1J_{P,F}$ = 712 Hz; PF_6), 39.0 (s; P(Pz$_{\kappa3N}$)), 62.0 (br.s; P(Pz$_{\kappa1P}$)). ^{31}P{^{1}H} CP/MAS NMR (162.0 MHz): δ −143.4 (sept, $^1J_{P,F}$ = 713 Hz; PF_6), 40.3 (s; P(Pz)). HR-ESI-MS: calcd for $C_{18}H_{18}CuN_{12}P_2$ ((C^H)$_2$Cu$^+$) 527.0543, found 527.0530 m/z (%) 295 (100) [M–P(Pz)$_3$]$^+$, 330 (21.4), 362 (3.6), 476 (20.5), 492 (9.5), 527 (22.6) [M]$^+$.

Tris(pyrazolyl)phosphine copper(ι) hexafluorophosphate (([C^{H}Cu][PF$_6$])$_n$). CH_2Cl_2 (50 mL) was added to a mixture of [Cu(NCMe)$_4$][PF$_6$] (1.86 g, 5.00 mmol) and C^H (1.18 g, 5.07 mmol) while stirring. The resulting yellow suspension was stirred for 15 h, during which the color changed to beige. After stirring for three more days, the reaction mixture was transferred onto a Schlenk frit and filtered. The beige residue was washed with CH_2Cl_2 (4 × 10 mL) and subsequently dried *in vacuo* affording ([C^{H}Cu][PF$_6$])$_n$ (2.00 g, 4.53 mmol, 91%). Mp: 196.0–197.4 °C (dec). ^{31}P{^{1}H} MAS NMR (162.0 MHz): δ −145.4 (sept, $^1J_{P,F}$ = 713 Hz; PF_6), 42.0 (q, ^1J(P,Cu) = 2250 Hz; P(Pz)). Anal. Calcd for $C_9H_9CuF_6N_6P_2$: C, 24.53; H, 2.06; N, 19.07; found: C, 24.42; H, 2.10; N, 18.99. Addition of CD_3CN to solid ([C^{H}Cu][PF$_6$])$_n$ resulted in a clear colorless solution, which allowed the following NMR spectra to be recorded. ^{1}H NMR (400.1 MHz, CD_3CN): δ 6.61 (ddd, $^3J_{H,H}$ = 2.8 Hz, $^4J_{H,P}$ = 2.2 Hz, $^3J_{H,H}$ = 1.7 Hz, 3H; PzH-4), 8.15 (d, $^3J_{H,H}$ = 1.7 Hz, 3H; PzH-3), 8.18 (dd, $^3J_{H,P}$ = 3.7 Hz, $^3J_{H,H}$ = 2.8 Hz, 3H; PzH-5). ^{13}C{^{1}H} NMR (125.8 MHz, CD_3CN): δ 110.1 (d, $^3J_{C,P}$ = 6.2 Hz; PzC-4), 139.3 (d, $^2J_{C,P}$ = 24.2 Hz; PzC-5), 148.6 (d, $^3J_{C,P}$ = 5.2 Hz; PzC-3). ^{19}F NMR (235.3 MHz, CD_3CN): δ −72.8 (d, $^1J_{P,F}$ = 713 Hz; PF_6). ^{31}P{^{1}H} NMR (101.3 MHz, CD_3CN): δ −144.6 (sept, $^1J_{P,F}$ = 707 Hz; PF_6), 47.4 (br.s; P(Pz)). Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of a solution of 31 mg (0.13 mmol) of C^H in 1 mL of dichloroethane in a solution of 50 mg (0.13 mmol) of [Cu(MeCN)$_4$][PF$_6$] in dichloroethane; the crystals grew at the interface between the two layers as fine needles.

Triphenylphosphine tris(pyrazolyl)phosphine copper(ι) hexafluorophosphate ([C^{H}Cu(PPh$_3$)][PF$_6$]). CH_2Cl_2 (20 mL) was added to a mixture of ([C^{H}Cu][PF$_6$])$_n$ (441 mg, 1.00 mmol) and PPh$_3$ (257 mg, 0.980 mmol) while stirring. Instantly, a clear solution was formed which was stirred for 6 h at room temperature. After cannula filtration, the filtrate was taken to dryness, yielding [C^{H}Cu(PPh$_3$)][PF$_6$] (0.67 g, 0.953 mmol,

97.3%). 0.59 g of this material was dissolved in CH_2Cl_2 (11 mL). This solution was filtered, concentrated to one sixth of its volume, carefully layered with pentane (5 mL) and allowed to diffuse at room temperature. The resulting crystalline solid was filtered off and dried to give 0.44 g of [C^{H}Cu(PPh$_3$)][PF$_6$]. Mp: 205.6–208.8 °C (dec). ^{1}H NMR (500.2 MHz, $CDCl_3$): δ 6.44 (ddd, $^4J_{H,P}$ = 3.2 Hz, $^3J_{H,H}$ = 2.8 Hz, $^3J_{H,H}$ = 1.9 Hz, 3H; PzH-4), 7.44 (ddd, $^3J_{H,H}$ = 1.9 Hz, $^4J_{H,P}$ = 1.4 Hz, $^4J_{H,H}$ = 0.5 Hz overlapping; PzH-5), 7.42–7.55 (m, overlapping, 15H; PhH), 8.37 (ddd, $^3J_{H,P}$ = 5.2 Hz, $^3J_{H,H}$ = 2.8 Hz, $^4J_{H,H}$ = 0.5 Hz, 3H; PzH-3). ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$): δ 108.7 (d, $^3J_{C,P}$ = 8.9 Hz; PzC-4), 129.4 (d, $^3J_{C,P}$ = 10.1 Hz; m-PhC), 130.9 (s; p-PhC), 132.6 (d, $^1J_{C,P}$ = 38.0 Hz; $ipso$-PhC), 133.6 (d, $^2J_{C,P}$ = 16.0 Hz; o-PhC), 139.3 (d, $^2J_{C,P}$ = 39.2 Hz; PzC-5), 146.9 (s; PzC-3). ^{19}F NMR (235.3 MHz, $CDCl_3$): δ −72.0 (d, $^1J_{P,F}$ = 713 Hz; PF_6). ^{31}P{^{1}H} NMR (101.3 MHz, $CDCl_3$): δ −144.1 (sept, $^1J_{P,F}$ = 713 Hz; PF_6), 7.8 (s; P(Ph)), 42.4 (s; P(Pz)). ^{31}P{^{1}H} CP/MAS NMR (162.0 MHz): δ −143.4 (sept, $^1J_{P,F}$ = 712 Hz; PF_6), 14.2 (q, ^1J(P,^{63}Cu) = 1862 Hz; P(Ph)), 40.6 (s; P(Pz)). HR-ESI-MS: calcd for $C_{27}H_{24}CuN_6P_2$ (C^{H}Cu(PPh$_3$)$^+$) 557.0828, found 557.0839; m/z (%) 366 (75) [Ph$_3$PCuNCMe]$^+$, 557 (61) [M]$^+$, 587 (100) [(Ph$_3$P)$_2$Cu]$^+$.

X-ray crystal structure determination

A table containing the experimental details of the crystal structure determination is included in the ESI (ESI p. S-6†).

[C^{Me2}Cu(NCMe)][PF$_6$]. [$C_{17}H_{24}CuN_7P$](PF$_6$), F_w = 565.91, colorless needle, 0.41 × 0.14 × 0.06 mm^3, monoclinic, $C2/c$ (no. 15), a = 26.0651(16), b = 7.7824(3), c = 25.9327(13) Å, β = 116.124(3)°, V = 4723.0(4) Å^3, Z = 8, D_x = 1.592 g cm^{-3}, μ = 1.13 mm^{-1}. 33686 reflections were measured on a Bruker Kappa ApexII diffractometer with a sealed tube and a Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of (sin θ/λ)$_{max}$ = 0.65 Å^{-1}. The crystal appeared to be cracked into two fragments. Consequently, two orientation matrices were used for the integration of the intensity data with the Eval15 software.[55] Multiscan absorption correction and scaling were performed with TWINABS[56] (correction range 0.57–0.75). 5582 reflections were unique (R_{int} = 0.057), of which 4261 were observed [$I > 2\sigma(I)$]. The structure was solved with direct methods using the program SHELXS-97.[57] Least-squares refinement was performed with SHELXL-2014[58] against F^2 of all reflections based on a HKLF-5 file.[59] Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were introduced in calculated positions and refined with a riding model. 306 parameters were refined with no restraints. R_1/wR_2 [$I > 2\sigma(I)$]: 0.0484/0.1198. R_1/wR_2 [all refl.]: 0.0704/0.1328. S = 1.023. Residual electron density between −0.87 and 1.24 e Å^{-3}. Batch scale factor for the second crystal fragment BASF = 0.518(2). Geometry calculations and checking for higher symmetry were performed with the PLATON program.[60]

[C^{Me2}Cu(PPh$_3$)][PF$_6$]. [$C_{33}H_{36}CuN_6P_2$](PF$_6$)·CH_2Cl_2, F_w = 872.05, colorless block, 0.51 × 0.36 × 0.12 mm^3, monoclinic, $P2_1/n$ (no. 14), a = 14.3558(1), b = 31.5939(2), c = 16.7621(1) Å, β = 90.6316(2)°, V = 7602.08(8) Å^3, Z = 8, D_x = 1.524 g cm^{-3}, μ =

0.91 mm^{-1}. 102481 reflections were measured on a Nonius KappaCCD diffractometer with a rotating anode and a graphite monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1}. X-ray intensities were integrated with the Denzo software.[61] Multiscan absorption correction and scaling were performed with SADABS[56] (correction range 0.54–0.89). 17382 reflections were unique (R_{int} = 0.067), of which 12960 were observed [$I > 2\sigma(I)$]. The structure was solved with automated Patterson methods using the program DIRDIF-08.[62] Least-squares refinement was performed with SHELXL-2014[58] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were introduced in calculated positions and refined with a riding model. The PF$_6$ anions and CH$_2$Cl$_2$ solvent molecules were refined with disorder models. 1014 parameters were refined with 934 restraints (distances, angles and displacement parameters of the disordered groups). R_1/wR_2 [$I > 2\sigma(I)$]: 0.0481/0.1134. R_1/wR_2 [all refl.]: 0.0729/0.1250. S = 1.026. Residual electron density between −1.31 and 1.39 e Å^{-3}. Geometry calculations and checking for higher symmetry were performed with the PLATON program.[60]

[(C^H)$_2$Cu][PF$_6$]. [C$_{18}$H$_{18}$CuN$_{12}$P$_2$](PF$_6$) + disordered solvent, F_w = 672.89,[63] colorless needle, 0.41 × 0.17 × 0.15 mm^3, trigonal, $P31c$ (no. 159), a = b = 19.5288(14), c = 18.0311(14) Å, V = 5955.3(10) Å^3, Z = 8, D_x = 1.501 g cm^{-3},[63] μ = 0.96 mm^{-1}.[63] 83 529 reflections were measured on a Bruker Kappa ApexII diffractometer with a sealed tube and a Triumph monochromator (λ = 0.71073 Å) at a temperature of 110(2) K up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1}. X-ray intensities were integrated with the Saint software.[64] Multiscan absorption correction and scaling were performed with SADABS[56] (correction range 0.67–0.75). 9095 reflections were unique (R_{int} = 0.027), of which 8301 were observed [$I > 2\sigma(I)$]. The structure was solved with direct methods using the program SHELXS-97.[57] Least-squares refinement was performed with SHELXL-2014[58] against F^2 of all reflections. The crystal structure contains large voids (930 Å^3 per unit cell) filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation with the Squeeze routine[65] resulting in 338 electrons per unit cell. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were introduced in calculated positions and refined with a riding model. 481 parameters were refined with 1 restraint (floating origin). R_1/wR_2 [$I > 2\sigma(I)$]: 0.0317/0.0799. R_1/wR_2 [all refl.]: 0.0377/0.0830. S = 1.050. Flack parameter[66] x = 0.003(3). Residual electron density between −1.04 and 0.99 e Å^{-3}. Geometry calculations and checking for higher symmetry were performed with the PLATON program.[60]

([C^{H}Cu][PF$_6$])$_n$·3C$_2$H$_4$Cl$_2$. [C$_9$H$_9$CuN$_6$P](PF$_6$)·3C$_2$H$_4$Cl$_2$, F_w = 737.56, colorless needle, 0.40 × 0.13 × 0.06 mm^3, trigonal, $P31c$ (no. 159), a = b = 21.2337(5), c = 10.6155(4) Å, V = 4145.0(3) Å^3, Z = 6, D_x = 1.773 g cm^{-3}, μ = 1.55 mm^{-1}. 46288 reflections were measured on a Bruker Kappa ApexII diffractometer with a sealed tube and a Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max}$ =

0.65 Å^{-1}. X-ray intensities were integrated with the Eval15 software.[55] Numerical absorption correction and scaling were performed with SADABS[56] (correction range 0.61–0.94). 6330 reflections were unique (R_{int} = 0.048), of which 5148 were observed [$I>2\sigma(I)$]. The structure was solved with Patterson superposition methods using the program SHELXT.[67] Least-squares refinement was performed with SHELXL-2014[58] against F^2 of all reflections. One polymeric coordination chain was refined with a disorder model [see the text]. A slight disorder in the other coordination chain has been ignored. Also, the carbon atoms of one dichloroethane solvent molecule were refined with a disorder model. Non-hydrogen atoms were refined freely with anisotropic displacement parameters with the exception of the minor disorder component of the Cu chain which was refined isotropically. All hydrogen atoms were introduced in calculated positions and refined with a riding model. 394 parameters were refined with 208 restraints (floating origin, distances and angles of the disordered groups, displacement parameters of the disordered dichloroethane). R_1/wR_2 [$I > 2\sigma(I)$]: 0.0462/0.1100. R_1/wR_2 [all refl.]: 0.0627/0.1176. S = 1.030. Refinement as a two-component inversion twin resulted in a Flack parameter[66] x = 0.03(2). Residual electron density between −0.57 and 2.36 e Å^{-3} (non-modeled disorder). Geometry calculations and checking for higher symmetry were performed with the PLATON program.[60]

Acknowledgements

Notes and references

1 S. Trofimenko, *J. Am. Chem. Soc.*, 1966, **88**, 1842–1844.
2 S. Trofimenko, *Chem. Rev.*, 1993, **93**, 943–980.
3 S. Trofimenko, *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, 1999.
4 C. Pettinari, *Scorpionates II: Chelating Borate Ligands*, Imperial College Press, London, 2008.
5 V. Gandin, F. Tisato, A. Dolmella, M. Pellei, C. Santini, M. Giorgetti, C. Marzano and M. Porchia, *J. Med. Chem.*, 2014, **57**, 4745–4760.
6 H. R. Bigmore, S. C. Lawrence, P. Mountford and C. S. Tredget, *Dalton Trans.*, 2005, 635–651.
7 D. L. Reger, T. C. Grattan, K. J. Brown, C. A. Little, J. J. S. Lamba, A. L. Rheingold and R. D. Sommer, *J. Organomet. Chem.*, 2000, **607**, 120–128.
8 S. Fischer, L. K. Peterson and J. F. Nixon, *Can. J. Chem.*, 1974, **52**, 3981–3985.

9 S. Fischer, J. Hoyano and L. K. Peterson, *Can. J. Chem.*, 1976, **54**, 2710–2714.

10 H. B. Davis, J. K. Hoyano, P. Y. Leung, L. K. Peterson and B. Wolstenholme, *Can. J. Chem.*, 1980, **58**, 151–158.

11 C. J. Tokar, P. B. Kettler and W. B. Tolman, *Organometallics*, 1992, **11**, 2737–2739.

12 D. D. Lecloux and W. B. Tolman, *J. Am. Chem. Soc.*, 1993, **115**, 1153–1154.

13 D. D. Lecloux, C. J. Tokar, M. Osawa, R. P. Houser, M. C. Keyes and W. B. Tolman, *Organometallics*, 1994, **13**, 2855–2866.

14 M. C. Keyes, B. M. Chamberlain, S. A. Caltagirone, J. A. Halfen and W. B. Tolman, *Organometallics*, 1998, **17**, 1984–1992.

15 J. J. Weigand, K. O. Feldmann, A. K. C. Echterhoff, A. W. Ehlers and K. Lammertsma, *Angew. Chem., Int. Ed.*, 2010, **49**, 6178–6181.

16 K. O. Feldmann, S. Schulz, F. Klotter and J. J. Weigand, *ChemSusChem*, 2011, **4**, 1805–1812.

17 K. O. Feldmann and J. J. Weigand, *Angew. Chem., Int. Ed.*, 2012, **51**, 7545–7549.

18 K. O. Feldmann, R. Frohlich and J. J. Weigand, *Chem. Commun.*, 2012, **48**, 4296–4298.

19 K. O. Feldmann and J. J. Weigand, *J. Am. Chem. Soc.*, 2012, **134**, 15443–15456.

20 C. G. J. Tazelaar, V. Lyaskovskyy, T. van Dijk, D. L. J. Broere, L. A. Kolfschoten, R. O. H. Khiar, M. Lutz, J. C. Slootweg and K. Lammertsma, *Organometallics*, 2012, **31**, 3308–3315.

21 A. K. Bartholomew, L. M. Guard, N. Hazari and E. D. Luzik, *Aust. J. Chem.*, 2013, **66**, 1455–1458.

22 S. G. A. van Assema, C. G. J. Tazelaar, G. B. de Jong, J. H. van Maarseveen, M. Schakel, M. Lutz, A. L. Spek, J. C. Slootweg and K. Lammertsma, *Organometallics*, 2008, **27**, 3210–3215.

23 C. G. J. Tazelaar, V. Lyaskovskyy, I. M. van Doorn, X. Schaapkens, M. Lutz, A. W. Ehlers, J. C. Slootweg and K. Lammertsma, *Eur. J. Inorg. Chem.*, 2014, **2014**, 1836–1842.

24 D. L. Reger, T. D. Wright, R. F. Semeniuc, T. C. Grattan and M. D. Smith, *Inorg. Chem.*, 2001, **40**, 6212–6219.

25 D. L. Reger, R. F. Semeniuc and M. D. Smith, *Inorg. Chem.*, 2001, **40**, 6545–6546.

26 D. L. Reger, R. F. Semeniuc, I. Silaghi-Dumitrescu and M. D. Smith, *Inorg. Chem.*, 2003, **42**, 3751–3764.

27 D. L. Reger, R. F. Semeniuc and M. D. Smith, *Inorg. Chem.*, 2003, **42**, 8137–8139.

28 D. L. Reger, R. F. Semeniuc, V. Rassolov and M. D. Smith, *Inorg. Chem.*, 2004, **43**, 537–554.

29 D. L. Reger, E. A. Foley, R. F. Semenluc and M. D. Smith, *Inorg. Chem.*, 2007, **46**, 11345–11355.

30 D. L. Reger, R. F. Semeniuc and M. D. Smith, *Eur. J. Inorg. Chem.*, 2002, 543–546.

31 D. L. Reger, R. F. Semeniuc and M. D. Smith, *Dalton Trans.*, 2003, 285–286.

32 D. L. Reger, R. F. Semeniuc and M. D. Smith, *Eur. J. Inorg. Chem.*, 2003, 3480–3494.

33 D. L. Reger, R. F. Semeniuc, C. A. Little and M. D. Smith, *Inorg. Chem.*, 2006, **45**, 7758–7769.

34 N. F. Zhao, J. C. Bullinger, M. J. Van Stipdonk, C. L. Stern and D. M. Eichhorn, *Inorg. Chem.*, 2008, **47**, 5945–5950.

35 M. J. Lopez-Gomez, N. G. Connelly, M. F. Haddow, A. Hamilton, M. Lusi, U. Baisch and A. G. Orpen, *Dalton Trans.*, 2011, **40**, 4647–4659.

36 R. M. Silva, C. Gwengo, S. V. Lindeman, M. D. Smith and J. R. Gardinier, *Inorg. Chem.*, 2006, **45**, 10998–11007.

37 J. R. Gardinier, R. M. Silva, C. Gwengo and S. V. Lindeman, *Chem. Commun.*, 2007, 1524–1526.

38 For a review on the chemistry of tripodal Janus ligands see: I. Kuzu, I. Krummenacher, J. Meyer, F. Armbruster and F. Breher, *Dalton Trans.*, 2008, 5836–5865.

39 H. Han, M. Elsmaili and S. A. Johnson, *Inorg. Chem.*, 2006, **45**, 7435–7445.

40 R. Raturi, J. Lefebvre, D. B. Leznoff, B. R. McGarvey and S. A. Johnson, *Chem. – Eur. J.*, 2008, **14**, 721–730.

41 H. Han and S. A. Johnson, *Eur. J. Inorg. Chem.*, 2008, 471–482.

42 D. W. Allen and B. F. Taylor, *J. Chem. Soc., Dalton Trans.*, 1982, 51–54.

43 T. S. Barnard and M. R. Mason, *Organometallics*, 2001, **20**, 206–214.

44 P. W. Dyer, J. Fawcett, M. J. Hanton, R. D. W. Kemmitt, R. Padda and N. Singh, *Dalton Trans.*, 2003, 104–113.

45 R. D. Kroshefsky, R. Weiss and J. G. Verkade, *Inorg. Chem.*, 1979, **18**, 469–472.

46 S. M. Socol and J. G. Verkade, *Inorg. Chem.*, 1984, **23**, 3487–3493.

47 D. L. Reger, J. E. Collins, A. L. Rheingold and L. M. Liable-Sands, *Organometallics*, 1996, **15**, 2029–2032.

48 R. P. Pinnell, C. A. Megerle, S. L. Manatt and P. A. Kroon, *J. Am. Chem. Soc.*, 1973, **95**, 977–978.

49 Search result (30-03-2015) in the Cambridge Structural Database V5.36: 22 structures identified displaying an average Cu–N distance of 1.881 Å.

50 Calculations at the BP86/6-311G(dp) (SDD for Cu) and B3PW91/6-311G(dp)D3 (SDD for Cu) levels of theory result in lower relative stabilities of the κ^2,κ^2-N_4 isomer of 5.0 and 11.0 kcal mol^{-1} respectively.

51 W. G. Dougherty and W. S. Kassel, *Inorg. Chim. Acta*, 2010, **364**, 120–124.

52 S. Trofimenko, J. C. Calabrese and J. S. Thompson, *Inorg. Chem.*, 1987, **26**, 1507–1514.

53 G. J. Kubas, *Inorg. Synth.*, 1990, **28**, 68–70.

54 N. A. Yakelis and R. G. Bergman, *Organometallics*, 2005, **24**, 3579–3581.

55 A. M. M. Schreurs, X. Y. Xian and L. M. J. Kroon-Batenburg, *J. Appl. Crystallogr.*, 2010, **43**, 70–82.

56 G. M. Sheldrick, *SADABS and TWINABS: Area-Detector Absorption Correction*, Universität Göttingen, Göttingen, 1999.

57 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **64**, 112–122.

58 G. M. Sheldrick, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2015, **71**, 3–8.

59 R. Herbst-Irmer and G. M. Sheldrick, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1998, **54**, 443–449.

60 A. L. Spek, *Acta Crystallogr., Sect. D: Biol. Crystallogr.*, 2009, **65**, 148–155.

61 Z. Otwinowski and W. Minor, in *Methods in Enzymology*, ed. J. C. W. Carter and R. M. Sweet, Academic Press, New York, 1997, vol. 276, pp. 307–326.

62 P. T. Beurskens, G. Beurskens, R. d. Gelder, S. Garcia-Granda, R. O. Gould and J. M. M. Smits, *The DIRDIF2008 program system, Crystallography Laboratory*, University of Nijmegen, Nijmegen, 2008.

63 Derived values do not contain the contribution of the disordered solvent molecules.

64 *SAINT-Plus*, Bruker AXS Inc., Madison, WI, 2001.

65 A. L. Spek, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2015, **71**, 9–18.

66 S. Parsons, H. D. Flack and T. Wagner, *Acta Crystallogr., Sect. B: Struct. Sci.*, 2013, **69**, 249–259.

67 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2015, **71**, 3–8.